

Supporting Information

**Domino C–H Activation/Directing Group
Migration/Alkyne Annulation: Unique
Selectivity by d⁶-Cobalt(III) Catalysts**

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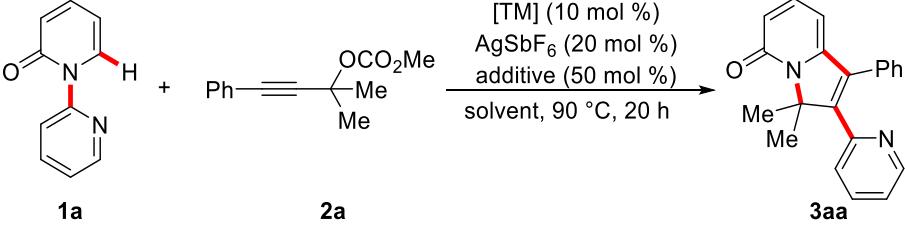
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General Remarks

Catalytic reactions were carried out in Schlenk flasks under a nitrogen atmosphere using pre-dried glassware. The cobalt catalyst,^[1] pyridones **1**,^[2] and propargylic carbonates **2**^[3] were synthesized according to previously described methods. Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ¹H-NMR and GC analysis. Chromatography: Merck silica gel 60 (40–63 µm). NMR: Spectra were recorded on Varian Mercury 300, Varian Inova 500, Bruker Avance III 300, Bruker Avance III HD 400 and Bruker Avance III HD 500 in the solvent indicated; chemical shifts (δ) are provided in ppm relative to the residual solvent peak. All IR spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS was recorded on Jeol AccuTOF at 70 eV and ESI-MS was recorded on Bruker micrOTOF and maXis. X-ray structure was measured on Bruker APEX-II CCD diffractometer. M.p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected.

Optimization of the Reaction Conditions

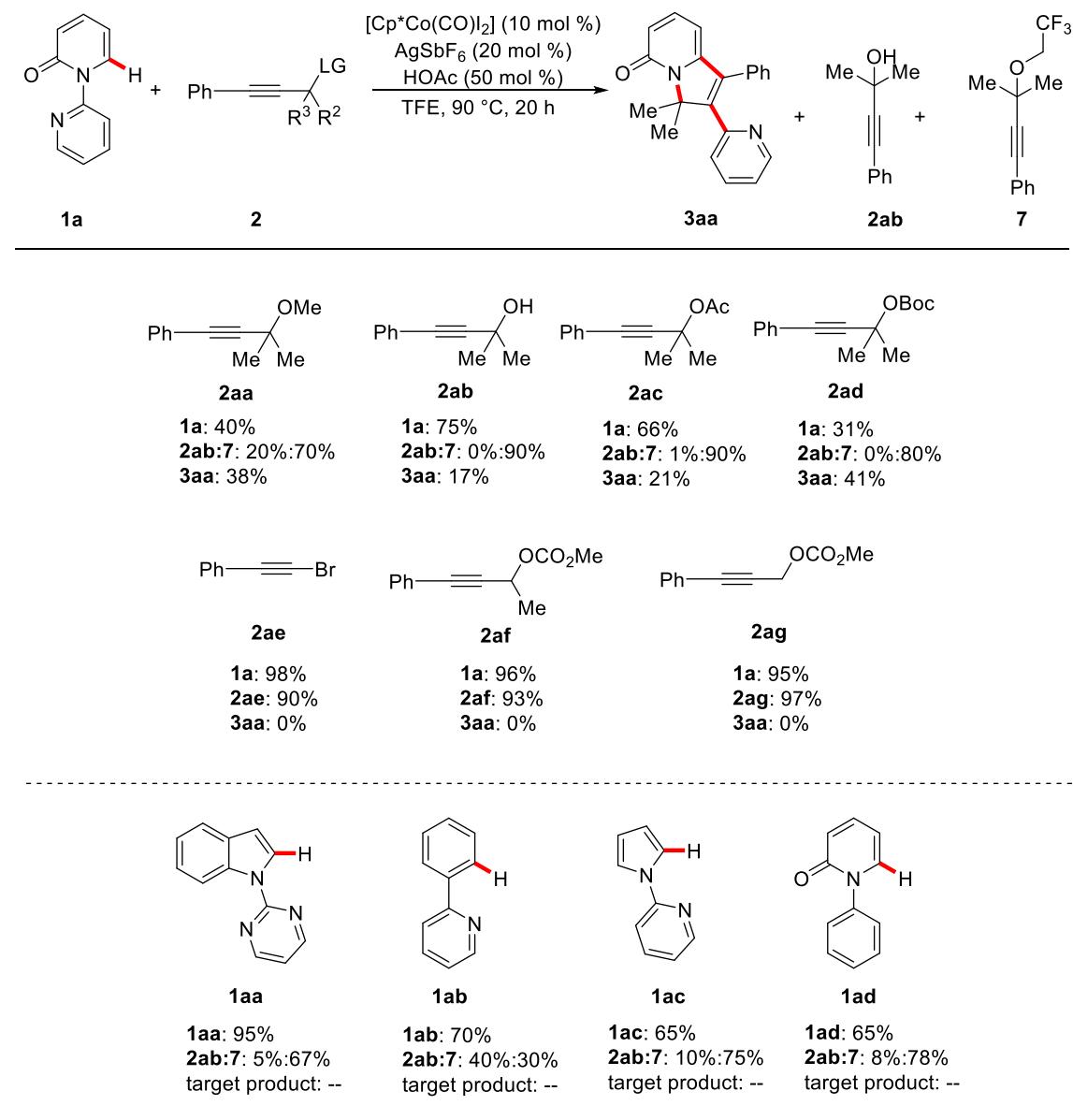
Table S1: Optimization of the cobalt(III)-catalyzed annulation.^[a]

|  | | $\xrightarrow[\text{solvent, } 90^\circ\text{C, 20 h}]{\begin{array}{l} [\text{TM}] \text{ (10 mol \%)} \\ \text{AgSbF}_6 \text{ (20 mol \%)} \\ \text{additive (50 mol \%)} \end{array}}$ | | | |
|--|---|--|-----------------------------------|--------------------|--|
| Entry | [TM] | Additive | Solvent | Yield (%) | |
| 1 | --- | NaOAc | HFIP | --- | |
| 2 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | NaOAc | HFIP | 46 | |
| 3 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | NaOPiv | HFIP | 14 | |
| 4 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | NaOAc | HFIP | --- ^[b] | |
| 5 | $[\text{Cp}^*\text{RhCl}_2]_2$ | NaOAc | HFIP | 17 | |
| 6 | $[\text{RuCl}_2(\text{p-cymene})]_2$ | NaOAc | HFIP | --- | |
| 7 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | NaOAc | DCE | --- | |
| 8 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | NaOAc | $\text{C}_6\text{H}_5\text{CF}_3$ | --- | |
| 9 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | NaOAc | TFE | 52 | |
| 10 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | AgOAc | TFE | 56 | |
| 11 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | HOAc | TFE | 81 | |
| 12 | $[\text{Cp}^*\text{RhCl}_2]_2$ | HOAc | TFE | --- | |
| 13 | $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ | HOAc | TFE | 76 ^[c] | |
| 14 | $[\text{Cp}^*\text{Co}(\text{MeCN})_3][\text{SbF}_6]_2$ | HOAc | TFE | 6 ^[c] | |

| | | | | |
|----|----------------------------|-----|-----|------------------|
| 15 | [Cp*Co(CO)I ₂] | --- | TFE | 42 |
| 16 | [Cp*Co(CO)I ₂] | --- | TFE | 8 ^[c] |

^[a] Reaction conditions: **1a** (0.50 mmol), **2a** (1.50 mmol), [TM] (10 mol %), AgSbF₆ (20 mol %), additive (50 mol %), solvent (2.0 mL), 90 °C, 20 h. Yields of isolated products. ^[b] At 50 °C. ^[c] Without AgSbF₆. HFIP = 1,1,1,3,3,3-Hexafluoro-2-propanol, TFE = 2,2,2-Trifluoroethanol.

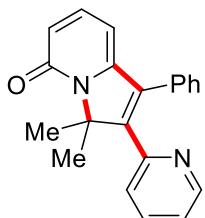
Scheme S1. Effect of Leaving and Directing Groups



General Procedure for Domino C–H Activation/Directing Group Migration/Alkyne Annulation

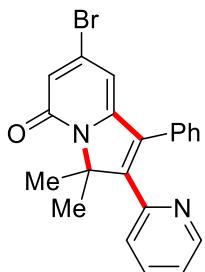
Pyridones **1** (0.50 mmol, 1.0 equiv), propargylic carbonates **2** (1.50 mmol, 3.0 equiv), $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ (24.0 mg, 10 mol %), AgSbF_6 (34.4 mg, 20 mol %), HOAc (15.0 mg, 50 mol %), and TFE (2.0 mL) were placed in a 25 mL Schlenk pressure tube and stirred at 90 °C for 20 h. After cooling to ambient temperature, the mixture was transferred into a round bottom flask with CH_2Cl_2 (20 mL) and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1 → 1/1) afforded the desired products **3**.

Characterization Data of Products **3**

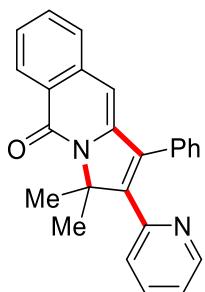


3,3-Dimethyl-1-phenyl-2-(pyridin-2-yl)indolin-5(3H)-one (3aa): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3aa** (128 mg, 81%) as a white solid. **M.p.:** 123–124 °C. **¹H-NMR** (400 MHz, CDCl_3) δ = 8.61 (dd, J = 4.8, 1.8 Hz, 1H), 7.39–7.27 (m, 4H), 7.27–7.19 (m, 3H), 7.08 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 6.83 (ddd, J = 8.0, 1.2, 1.2 Hz, 1H), 6.33 (dd, J = 9.0, 1.2 Hz, 1H), 6.04 (dd, J = 6.9, 1.2 Hz, 1H), 2.03 (s, 6H). **¹³C-NMR** (100 MHz, CDCl_3) δ = 162.2 (C_q), 152.5 (C_q), 150.7 (C_q), 150.4 (C_q), 149.3 (CH), 138.9 (CH), 135.6 (CH), 133.2 (C_q), 131.8 (C_q), 129.3 (CH), 128.9 (CH), 128.6 (CH), 125.7 (CH), 122.5 (CH),

118.9 (CH), 100.0 (CH), 75.1 (C_q), 21.1 (CH₃). **IR** (ATR): 1654, 1577, 1529, 1462, 1443, 1154, 793, 701, 617, 498 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 651 (7) [2M+Na]⁺, 315 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₁H₁₉N₂O [M+H]⁺ 315.1492, found 315.1495. The structure of compound **3aa** was unambiguously verified by X-ray crystallographic diffraction analysis (*vide infra*).

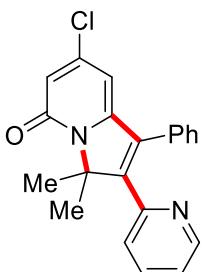


7-Bromo-3,3-dimethyl-1-phenyl-2-(pyridin-2-yl)indolin-5(3H)-one (3ba): The general procedure was followed using 4-bromo-2*H*-[1,2'-bipyridin]-2-one (**1b**) (126 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ba** (132 mg, 67%) as a white solid. **M.p.:** 200–201 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.63 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.39–7.34 (m, 4H), 7.23 (ddd, *J* = 5.6, 2.7, 1.4 Hz, 2H), 7.12 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.58 (d, *J* = 1.9 Hz, 1H), 6.18 (d, *J* = 1.9 Hz, 1H), 2.03 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 160.6 (C_q), 152.5 (C_q), 151.8 (C_q), 150.6 (C_q), 149.3 (CH), 135.7 (CH), 135.2 (C_q), 132.4 (C_q), 131.1 (C_q), 129.2 (CH), 129.1 (CH), 128.9 (CH), 125.7 (CH), 122.8 (CH), 120.5 (CH), 104.0 (CH), 75.3 (C_q), 21.1 (CH₃). **IR** (ATR): 1652, 1583, 1518, 1462, 887, 790, 702 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 393 (100) [M+H]⁺ (79Br). **HR-MS** (ESI) *m/z* calcd for C₂₁H₁₈N₂O⁷⁹Br [M+H]⁺ 393.0597, found 393.0602.



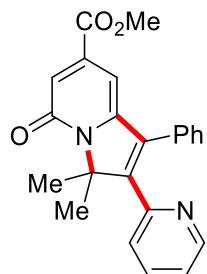
3,3-Dimethyl-1-phenyl-2-(pyridin-2-yl)pyrrolo[1,2-b]isoquinolin-5(3H)-one (3ca):

The general procedure was followed using 2-(pyridin-2-yl)isoquinolin-1(2*H*)-one (**1c**) (111 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ca** (100 mg, 55%) as a white solid. **M.p.**: 208–209 °C. **1H-NMR** (300 MHz, CDCl₃) δ = 8.69 (ddd, *J* = 5.0, 1.9, 0.9 Hz, 1H), 8.47 (dd, *J* = 8.1, 1.50 Hz, 1H), 7.65–7.54 (m, 1H), 7.51–7.31 (m, 8H), 7.16 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.94 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.43 (s, 1H), 2.15 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 160.6 (C_q), 144.1 (C_q), 143.0 (C_q), 139.5 (CH), 138.3 (C_q), 136.4 (C_q), 133.1 (C_q), 132.3 (C_q), 132.0 (CH), 130.7 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 126.4 (CH), 125.8 (CH), 123.9 (C_q), 120.0 (CH), 111.0 (CH), 99.4 (CH), 38.4 (C_q), 28.8 (CH₃). **IR** (ATR): 1652, 1621, 1600, 1583, 1563, 1462, 1431, 1353, 1334, 701 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 751 (15) [2M+Na]⁺, 365 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₅H₂₁N₂O [M+H]⁺ 365.1648, found 365.1649. The structure of compound **3ca** was also unambiguously verified by X-ray crystallographic diffraction analysis (*vide infra*).

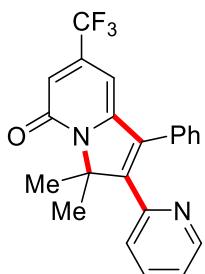


7-Chloro-3,3-dimethyl-1-phenyl-2-(pyridin-2-yl)indolizin-5(3H)-one (3da): The general procedure was followed using 4-chloro-2*H*-[1,2'-bipyridin]-2-one (**1d**) (103 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3da** (95.9 mg, 55%) as a white solid. **M.p.**: 192–193 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.60 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.46–7.30 (m, 4H), 7.27–7.20 (m, 2H), 7.13 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 6.87 (dd, *J* = 7.9, 1.0 Hz, 1H), 5.88 (d, *J* = 7.6 Hz, 1H), 2.06 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 158.7

(C_q), 152.2 (C_q), 151.4 (C_q), 150.8 (C_q), 149.4 (CH), 147.9 (CH), 135.7 (CH), 133.0 (C_q), 131.5 (C_q), 129.3 (CH), 129.1 (CH), 128.8 (CH), 125.8 (CH), 122.7 (CH), 101.3 (CH), 91.4 (C_q), 76.5 (C_q), 21.1 (CH₃). **IR** (ATR): 1727, 1691, 1610, 1547, 1484, 1399, 1131, 1037, 881, 726 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 349 (100) [M+H]⁺ (³⁵Cl). **HR-MS** (ESI) *m/z* calcd for C₂₁H₁₈N₂O³⁵Cl [M+H]⁺ 349.1102, found 349.1104.

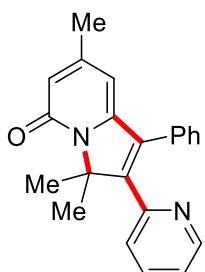


Methyl 3,3-dimethyl-5-oxo-1-phenyl-2-(pyridin-2-yl)-3,5-dihydroindolizine-7-carboxylate (3ea): The general procedure was followed using methyl 2-oxo-2*H*-[1,2'-bipyridine]-4-carboxylate (**1e**) (115 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ea** (96.8 mg, 52%) as a white solid. **M.p.:** 165–166 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.66 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.42–7.34 (m, 4H), 7.31–7.23 (m, 2H), 7.14 (ddd, *J* = 7.6, 4.9, 1.0 Hz, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 6.87 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.55 (d, *J* = 1.6 Hz, 1H), 3.86 (s, 3H), 2.07 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 165.7 (C_q), 161.7 (C_q), 152.2 (C_q), 151.7 (C_q), 151.1 (C_q), 149.4 (CH), 140.4 (CH), 135.7 (C_q), 133.2 (C_q), 131.5 (C_q), 129.4 (CH), 129.1 (CH), 128.8 (CH), 125.8 (CH), 122.8 (CH), 120.6 (CH), 98.6 (CH), 75.5 (C_q), 52.7 (CH₃), 21.0 (CH₃). **IR** (ATR): 1730, 1661, 1593, 1531, 1463, 1442, 1251, 1086, 775, 703 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 767 (43) [2M+Na]⁺, 395 (100) [M+Na]⁺, 373 (78) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₃H₂₁N₂O₃ [M+H]⁺ 373.1547, found 373.1546.



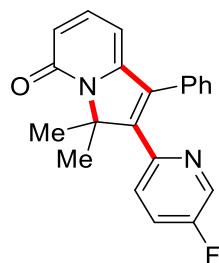
3,3-Dimethyl-1-phenyl-2-(pyridin-2-yl)-7-(trifluoromethyl)indolin-5(3H)-one (3fa):

(3fa): The general procedure was followed using methyl 2-oxo-2*H*-[1,2'-bipyridine]-4-carboxylate (**1f**) (120 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3fa** (99.4 mg, 52%) as a white solid. **M.p.:** 151–153 °C. **¹H-NMR** (400 MHz, CDCl_3) δ = 8.66 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.43–7.37 (m, 4H), 7.29–7.23 (m, 2H), 7.15 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H), 6.87 (dd, J = 8.0, 1.1 Hz, 1H), 6.64 (dd, J = 1.8, 0.9 Hz, 1H), 6.16 (d, J = 1.8 Hz, 1H), 2.07 (s, 6H). **¹³C-NMR** (100 MHz, CDCl_3) δ = 160.8 (C_q), 152.7 (C_q), 152.1 (C_q), 151.9 (C_q), 149.4 (CH), 141.1 (q, $^2J_{\text{C}-\text{F}}$ = 33.3 Hz, C_q), 135.8 (CH), 132.8 (C_q), 131.2 (C_q), 129.2 (CH), 129.1 (CH), 129.0 (CH), 125.8 (CH), 122.9 (CH), 122.6 (q, $^1J_{\text{C}-\text{F}}$ = 274.1 Hz, C_q), 116.1 (q, $^3J_{\text{C}-\text{F}}$ = 4.2 Hz, CH), 95.0 (q, $^3J_{\text{C}-\text{F}}$ = 3.0 Hz, CH), 75.8 (C_q), 21.0 (CH₃). **¹⁹F-NMR** (376 MHz, CDCl_3) δ = -66.1 (s). **IR** (ATR): 2050, 1672, 1603, 1538, 1466, 1281, 1175, 1138, 751, 702 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 787 (20) [2M+Na]⁺, 405 (18) [2M+Na]⁺, 383 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{OF}_3$ [M+H]⁺ 383.1367, found 383.1366.



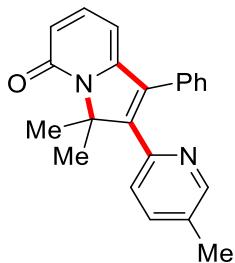
3,3,7-Trimethyl-1-phenyl-2-(pyridin-2-yl)indolin-5(3H)-one (3ga): The general procedure was followed using 4-methyl-2*H*-[1,2'-bipyridin]-2-one (**1g**) (93.1 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50

mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ga** (123 mg, 75%) as a white solid. **M.p.**: 126–127 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.63 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.40–7.31 (m, 4H), 7.24 (dd, *J* = 6.2, 3.1 Hz, 2H), 7.10 (dd, *J* = 7.8, 4.6 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.12 (s, 1H), 5.82 (s, 1H), 2.10 (s, 3H), 2.06 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 160.5 (C_q), 152.5 (C_q), 150.9 (C_q), 150.0 (C_q), 149.7 (C_q), 149.2 (CH), 135.6 (CH), 135.5 (CH), 133.2 (C_q), 131.9 (C_q), 129.3 (CH), 128.9 (CH), 128.5 (CH), 125.6 (CH), 122.4 (CH), 102.7 (CH), 74.5 (C_q), 21.5 (CH₃), 21.3 (CH₃). **IR** (ATR): 1655, 1584, 1531, 1462, 1433, 1349, 1156, 791, 734, 701 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 329 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₂H₂₁N₂O [M+H]⁺ 329.1648, found 329.1653. The structure of compound **3ga** was also unambiguously verified by X-ray crystallographic diffraction analysis (*vide infra*).

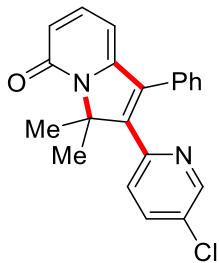


2-(5-Fluoropyridin-2-yl)-3,3-dimethyl-1-phenylindolin-5(3*H*)-one (3ha): The general procedure was followed using 5'-fluoro-2*H*-[1,2'-bipyridin]-2-one (**1h**) (95.1 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ha** (105 mg, 63%) as a white solid. **M.p.**: 177–178 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.49 (dd, *J* = 3.0, 0.6 Hz, 1H), 7.42–7.33 (m, 3H), 7.30–7.19 (m, 3H), 7.09 (ddd, *J* = 8.8, 8.1, 3.0 Hz, 1H), 6.87 (ddd, *J* = 8.8, 4.4, 0.6 Hz, 1H), 6.36 (dd, *J* = 9.1, 1.1 Hz, 1H), 6.04 (dd, *J* = 6.9, 1.1 Hz, 1H), 2.05 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 162.1 (C_q), 158.3 (d, ¹J_{C-F} = 259.5 Hz, C_q), 150.3 (C_q), 149.5 (C_q), 148.5 (d, ⁴J_{C-F} = 4.5 Hz, C_q), 138.9 (CH), 137.6 (d, ²J_{C-F} = 23.5 Hz, CH), 133.3 (C_q), 131.8 (C_q), 129.3 (CH), 129.1 (CH), 128.8 (CH), 126.8 (d, ³J_{C-F} = 4.3 Hz, CH), 122.6 (d, ²J_{C-F} = 18.5 Hz, CH), 119.1 (CH), 100.1 (CH), 75.1 (C_q), 21.1 (CH₃). **19F-NMR** (376 MHz,

CDCl_3) $\delta = -126.5$ (dd, $J = 8.1, 4.5$ Hz). **IR** (ATR): 1654, 1584, 1531, 1473, 1229, 1177, 798, 736, 700, 420 cm^{-1} . **MS** (ESI) m/z (relative intensity): 329 (100) $[\text{M}+\text{H}]^+$. **HR-MS** (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 329.1648, found 329.1648.

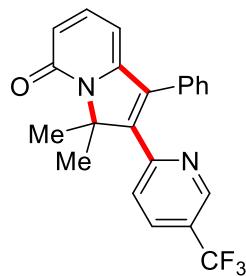


3,3-Dimethyl-2-(5-methylpyridin-2-yl)-1-phenylindolin-5(3H)-one (3ia): The general procedure was followed using 5'-methyl-2*H*-[1,2'-bipyridin]-2-one (**1i**) (93.1 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ia** (100 mg, 61%) as a white solid. **M.p.:** 190–191 °C. **¹H-NMR** (400 MHz, CDCl_3) $\delta = 8.46$ (d, $J = 2.0$ Hz, 1H), 7.36–7.31 (m, 4H), 7.29–7.21 (m, 2H), 7.18 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.30 (s, 1H), 5.97 (s, 1H), 2.26 (s, 3H), 2.06 (s, 6H). **¹³C-NMR** (100 MHz, CDCl_3) $\delta = 162.2$ (C_q), 150.8 (C_q), 150.7 (C_q), 149.7 (CH), 149.5 (C_q), 138.5 (CH), 136.1 (CH), 132.7 (C_q), 132.2 (C_q), 132.1 (C_q), 129.3 (CH), 128.8 (CH), 128.4 (CH), 125.1 (CH), 104.9 (CH), 100.1 (CH), 74.9 (C_q), 21.2 (CH_3), 18.2 (CH_3). **IR** (ATR): 1652, 1583, 1530, 1475, 1445, 1347, 1176, 797, 734, 700 cm^{-1} . **MS** (ESI) m/z (relative intensity): 329 (100) $[\text{M}+\text{H}]^+$. **HR-MS** (ESI) m/z calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 329.1648, found 329.1648.



2-(5-Chloropyridin-2-yl)-3,3-dimethyl-1-phenylindolin-5(3H)-one (3ja): The general procedure was followed using 5'-chloro-2*H*-[1,2'-bipyridin]-2-one (**1j**) (103.3

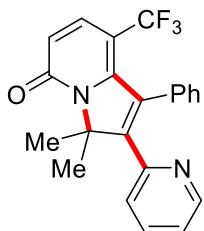
mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ja** (126 mg, 72%) as a white solid. **M.p.**: 163–164 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.59 (d, *J* = 2.3 Hz, 1H), 7.42–7.36 (m, 3H), 7.34 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.31–7.20 (m, 3H), 6.80 (dd, *J* = 8.5, 0.7 Hz, 1H), 6.36 (s, 1H), 6.02 (d, *J* = 6.7 Hz, 1H), 2.06 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 162.2 (C_q), 150.4 (C_q), 150.3 (C_q), 149.3 (C_q), 148.2 (CH), 138.7 (CH), 135.4 (CH), 133.9 (C_q), 131.7 (C_q), 131.1 (C_q), 129.2 (CH), 129.2 (CH), 128.9 (CH), 126.3 (CH), 119.5 (CH), 100.4 (CH), 75.1 (C_q), 21.2 (CH₃). **IR** (ATR): 1652, 1582, 1528, 1458, 1445, 1155, 1110, 858, 799, 703 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 349 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₁H₁₈N₂OCl [M+H]⁺ 349.1102, found 349.1102.



3,3-Dimethyl-1-phenyl-2-(5-(trifluoromethyl)pyridin-2-yl)indolin-5(3H)-one

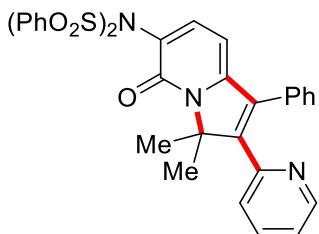
(3ka): The general procedure was followed using 5'-(trifluoromethyl)-2H-[1,2'-bipyridin]-2-one (**1k**) (103 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ja** (115 mg, 60%) as a white solid. **M.p.**: 155–156 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.91 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.59 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 7.41 (ddd, *J* = 5.7, 4.0, 2.1 Hz, 3H), 7.34–7.24 (m, 3H), 6.98 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.39 (s, 1H), 6.05 (d, *J* = 6.8 Hz, 1H), 2.10 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 156.0 (C_q), 155.9 (C_q), 150.1 (C_q), 148.9 (C_q), 146.1 (q, ³J_{C-F} = 4.0 Hz, CH), 138.7 (CH), 135.4 (C_q), 132.7 (q, ³J_{C-F} = 3.5 Hz, CH), 131.5 (C_q), 129.3 (CH), 129.2 (CH), 129.1 (CH), 125.2 (CH), 124.9 (q, ²J_{C-F} = 33.2 Hz, C_q), 123.3 (q, ¹J_{C-F} = 272.4 Hz, C_q), 119.9 (CH), 100.9 (CH), 75.3 (C_q), 21.2 (CH₃). **IR** (ATR): 1655, 1588, 1531, 1327, 1166, 1131, 1081, 852, 799, 702 cm⁻¹. **MS** (ESI) *m/z* (relative

intensity): 383 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₂H₁₈N₂OF₃ [M+H]⁺ 383.1366, found 383.1367.



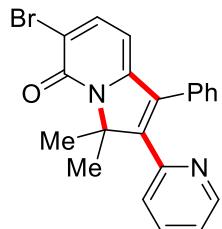
3,3-Dimethyl-1-phenyl-2-(pyridin-2-yl)-8-(trifluoromethyl)indolin-5(3H)-one

(3la): The general procedure was followed using 5-(trifluoromethyl)-2*H*-[1,2'-bipyridin]-2-one (**1l**) (120 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3la** (122 mg, 64%) as a white solid. **M.p.:** 112–113 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.66 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.69 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.47–7.33 (m, 4H), 7.25 (ddd, *J* = 5.4, 3.0, 1.1 Hz, 2H), 7.16 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.89 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.12 (dd, *J* = 7.5, 0.7 Hz, 1H), 2.09 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 162.0 (C_q), 157.9 (C_q), 154.1 (C_q), 151.8 (C_q), 149.4 (CH), 138.6 (q, ³J_{C-F} = 5.0 Hz, CH), 135.8 (CH), 132.7 (C_q), 131.1 (C_q), 129.3 (CH), 129.2 (CH), 129.0 (CH), 125.8 (CH), 123.4 (q, ¹J_{C-F} = 271.2 Hz, C_q), 123.0 (CH), 117.6 (q, ²J_{C-F} = 30.1 Hz, C_q), 98.0 (CH), 76.4 (C_q), 21.2 (CH₃). **¹⁹F-NMR** (376 MHz, CDCl₃) δ = -4.46 (s). **IR** (ATR): 1666, 1553, 1463, 1314, 1153, 1128, 1062, 787, 732, 702 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 383 (15) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₂H₁₈N₂OF₃ [M+H]⁺ 383.1366, found 383.1365.



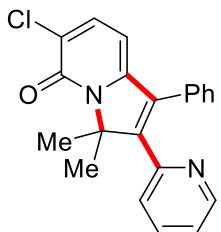
N-(3,3-Dimethyl-5-oxo-1-phenyl-2-(pyridin-2-yl)-3,5-dihydroindolin-6-yl)-N-(phenylsulfonyl)benzenesulfonamide (3ma): The general procedure was followed

using *N*-(2-oxo-2*H*-[1,2'-bipyridin]-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (**1m**) (234 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ma** (171 mg, 56%) as a white solid. **M.p.**: 154–155 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.64 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.11–7.89 (m, 4H), 7.67–7.54 (m, 2H), 7.52–7.46 (m, 4H), 7.44–7.35 (m, 5H), 7.29–7.24 (m, 2H), 7.14 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.05 (d, *J* = 7.6 Hz, 1H), 1.91 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 158.3 (C_q), 153.5 (C_q), 153.0 (C_q), 152.0 (C_q), 149.4 (CH), 143.7 (CH), 139.5 (C_q), 135.8 (CH), 133.7 (CH), 132.8 (C_q), 131.3 (C_q), 129.3 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 125.7 (CH), 122.9 (CH), 121.8 (C_q), 98.5 (CH), 76.0 (C_q), 20.9 (CH₃). **IR** (ATR): 1661, 1599, 1537, 1448, 1375, 1354, 1170, 1084, 891, 551 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 610 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₃₃H₂₈N₃O₅S₂ [M+H]⁺ 610.1465, found 610.1475.

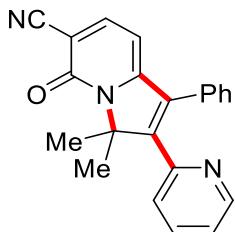


6-Bromo-3,3-dimethyl-1-phenyl-2-(pyridin-2-yl)indolin-5(3*H*)-one (3na**):** The general procedure was followed using 3-bromo-2*H*-[1,2'-bipyridin]-2-one (**1n**) (126 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3na** (130 mg, 66%) as a white solid. **M.p.**: 206–207 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.63 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.46–7.30 (m, 4H), 7.26–7.20 (m, 2H), 7.12 (ddd, *J* = 7.6, 4.9, 1.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.97 (d, *J* = 7.6 Hz, 1H), 2.06 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 157.8 (C_q), 152.1 (C_q), 150.9 (C_q), 150.2 (C_q), 149.3 (CH), 140.9 (CH), 135.7 (CH), 132.9 (C_q), 131.4 (C_q), 129.2 (CH), 129.0 (CH), 128.8 (CH), 125.7 (CH), 122.7 (CH), 114.7

(C_q), 99.9 (CH), 76.3 (C_q), 21.0 (CH₃). **IR** (ATR): 1642, 1586, 1563, 1518, 1337, 1075, 1060, 796, 739, 698 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 415 (10) [M+Na]⁺, 393 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₁H₁₈N₂OBr [M+H]⁺ 393.0597, found 393.0604.

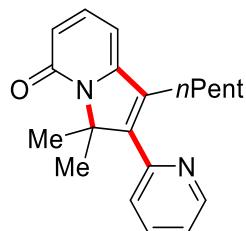


6-Chloro-3,3-dimethyl-1-phenyl-2-(pyridin-2-yl)indolin-5(3H)-one (3oa): The general procedure was followed using 3-chloro-2*H*-[1,2'-bipyridin]-2-one (**1o**) (103 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3oa** (122 mg, 70%) as a white solid. **M.p.:** 208–209 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.62 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.41–7.32 (m, 4H), 7.26–7.21 (m, 2H), 7.11 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.86 (dt, *J* = 8.0, 1.0 Hz, 1H), 6.02 (d, *J* = 7.6 Hz, 1H), 2.06 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 157.7 (C_q), 152.1 (C_q), 150.9 (C_q), 149.3 (CH), 149.2 (C_q), 137.1 (CH), 135.6 (CH), 132.8 (C_q), 131.4 (C_q), 129.2 (CH), 129.0 (CH), 128.8 (CH), 125.7 (CH), 124.1 (C_q), 122.7 (CH), 99.0 (CH), 76.1 (C_q), 21.0 (CH₃). **IR** (ATR): 1647, 1588, 1564, 1524, 1339, 1173, 1089, 789, 764, 699 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 719 (6) [2M+Na]⁺, 371 (25) [M+Na]⁺, 349 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₁H₁₈N₂OCl [M+H]⁺ 349.1102, found 349.1109.



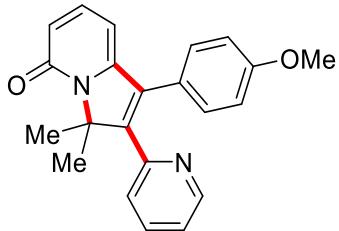
3,3-Dimethyl-5-oxo-1-phenyl-2-(pyridin-2-yl)-3,5-dihydroindolizine-6-

carbonitrile (3pa): The general procedure was followed using 3-chloro-2*H*-[1,2'-bipyridin]-2-one (**1p**) (98.6 mg, 0.50 mmol) and methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3oa** (127 mg, 75%) as a white solid. **M.p.:** 219–220 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.64 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.14–7.96 (m, 4H), 7.64–7.56 (m, 2H), 7.53–7.46 (m, 4H), 7.44–7.34 (m, 5H), 7.31–7.24 (m, 2H), 7.14 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.86 (ddd, *J* = 8.0, 1.1, 1.1 Hz, 1H), 6.05 (d, *J* = 7.6 Hz, 1H), 1.91 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 159.0 (C_q), 155.2 (C_q), 155.2 (C_q), 151.3 (C_q), 149.5 (CH), 146.4 (CH), 135.9 (CH), 132.8 (C_q), 130.8 (C_q), 129.3 (CH), 129.2 (CH), 129.1 (CH), 125.8 (CH), 123.3 (CH), 116.5 (C_q), 102.3 (C_q), 99.8 (CH), 76.8 (C_q), 21.0 (CH₃). **IR** (ATR): 2219, 1650, 1583, 1536, 1460, 1432, 1179, 776, 728, 699 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 340 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₂H₁₈N₃O [M+H]⁺ 340.1444, found 340.1453.

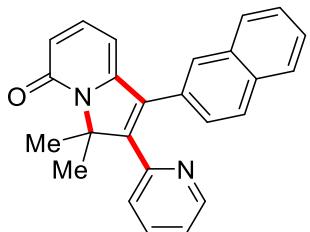


3,3-Dimethyl-1-*n*-pentyl-2-(pyridin-2-yl)indolin-5(3*H*)-one (3ab): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.5 mmol) and methyl (2-methylnon-3-yn-2-yl) carbonate (**2b**) (318.5 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ab** (123 mg, 80%) as an orange oil. **1H-NMR** (400 MHz, CDCl₃) δ = 8.71 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.36–7.24 (m, 3H), 6.34 (d, *J* = 9.2 Hz, 1H), 6.18 (d, *J* = 6.9 Hz, 1H), 2.39–2.26 (m, 2H), 1.86 (s, 6H), 1.52–1.45 (m, 2H), 1.22 (ddd, *J* = 7.2, 4.2, 3.1 Hz, 4H), 0.84–0.77 (m, 3H). **13C-NMR** (100 MHz, CDCl₃) δ = 162.4 (C_q), 153.0 (C_q), 150.8 (C_q), 150.7 (C_q), 149.9 (CH), 139.0 (CH), 136.2 (CH), 132.6 (C_q), 124.7 (CH), 122.8 (CH), 118.6 (CH), 98.4 (CH), 74.3 (C_q), 31.6 (CH₂), 28.4 (CH₂), 24.6 (CH₂), 22.2 (CH₂), 21.0 (CH₃), 13.9 (CH₃). **IR** (ATR): 1655, 1583, 1533, 1465,

1432, 1166, 1141, 794, 749 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 331 (15) [M+Na]⁺, 309 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₀H₂₅N₂O [M+H]⁺ 309.1691, found 309.1964.

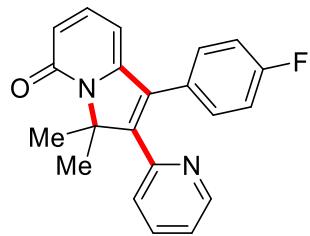


1-(4-Methoxyphenyl)-3,3-dimethyl-2-(pyridin-2-yl)indolin-5(3H)-one (3ac): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50 mmol) and 4-(4-methoxyphenyl)-2-methylbut-3-yn-2-yl methyl carbonate (**2c**) (373 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ac** (115 mg, 67%) as a white solid. **M.p.:** 161–162 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.64 (ddd, *J* = 4.8, 1.8, 0.8 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.31 (d, *J* = 6.5 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.12 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 6.92–6.84 (m, 3H), 6.33 (s, 1H), 6.04 (d, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 2.05 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 162.0 (C_q), 159.7 (C_q), 152.8 (C_q), 150.8 (C_q), 150.2 (C_q), 149.3 (CH), 138.7 (CH), 135.6 (CH), 132.9 (C_q), 130.6 (CH), 125.7 (CH), 123.9 (C_q), 122.4 (CH), 119.2 (CH), 114.3 (CH), 100.2 (CH), 75.0 (C_q), 55.2 (CH₃), 21.2 (CH₃). **IR** (ATR): 1654, 1583, 1532, 1511, 1463, 1251, 1177, 1029, 845, 793 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 345 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₂H₂₁N₂O₂ [M+H]⁺ 345.1598, found 345.1600.



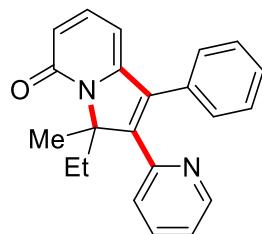
3,3-Dimethyl-1-(naphthalen-2-yl)-2-(pyridin-2-yl)indolin-5(3H)-one (3ad): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50

mmol) and methyl (2-methyl-4-(naphthalen-2-yl)but-3-yn-2-yl) carbonate (**2d**) (403 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ad** (106 mg, 58%) as a white solid. **M.p.**: 185–186 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.66 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 7.92–7.70 (m, 4H), 7.58–7.43 (m, 2H), 7.35–7.26 (m, 3H), 7.10 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.89 (ddd, *J* = 7.9, 1.1, 1.1 Hz, 1H), 6.40 (dd, *J* = 9.0, 1.1 Hz, 1H), 6.13 (dd, *J* = 6.9, 1.1 Hz, 1H), 2.12 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 162.3 (C_q), 152.5 (C_q), 151.1 (C_q), 150.6 (C_q), 149.3 (CH), 138.9 (CH), 135.7 (CH), 133.3 (C_q), 133.2 (C_q), 133.0 (C_q), 129.4 (C_q), 128.8 (CH), 128.7 (CH), 128.0 (CH), 127.8 (CH), 126.9 (CH), 126.7 (CH), 126.5 (CH), 125.8 (CH), 122.6 (CH), 119.0 (CH), 100.2 (CH), 75.3 (C_q), 21.2 (CH₃). **IR** (ATR): 1653, 1582, 1531, 1460, 1433, 1153, 787, 746, 479 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 365 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₅H₂₁N₂O [M+H]⁺ 365.1648, found 365.1658.

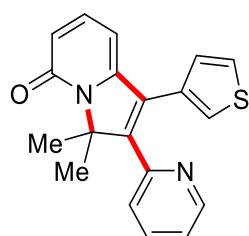


1-(4-Fluorophenyl)-3,3-dimethyl-2-(pyridin-2-yl)indolin-5(3H)-one (3ae): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50 mmol) and 4-(4-fluorophenyl)-2-methylbut-3-yn-2-yl methyl carbonate (**2e**) (354 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ae** (140 mg, 84%) as a white solid. **M.p.**: 148–149 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.63 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.28 (dd, *J* = 9.0, 7.0 Hz, 1H), 7.25–7.18 (m, 2H), 7.13 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.06–6.97 (m, 2H), 6.85 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.36 (dd, *J* = 9.0, 1.1 Hz, 1H), 6.06 (dd, *J* = 7.0, 1.1 Hz, 1H), 2.02 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 162.65 (d, ¹J_{C-F} = 249.0 Hz, C_q), 162.3 (C_q), 152.2 (C_q), 151.2 (C_q), 150.2 (C_q), 149.4 (CH), 139.0 (CH), 135.8 (CH), 132.1 (C_q), 131.1 (d, ³J_{C-F} = 8.1 Hz, CH), 127.6 (d, ⁴J_{C-F} = 3.5 Hz, C_q), 125.6 (CH), 122.7 (CH), 118.9 (CH), 116.0 (d, ²J_{C-F} = 21.6 Hz, CH), 100.1 (CH),

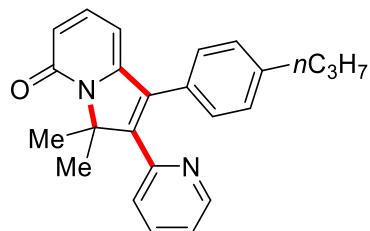
75.2 (C_q), 21.0 (CH₃). **¹⁹F-NMR** (376 MHz, CDCl₃) δ = -112.01 (s). **IR** (ATR): 1651, 1581, 1531, 1508, 1462, 1433, 1348, 1224, 1157, 851, 796 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 687 (32) [2M+Na]⁺, 355 (10) [M+Na]⁺, 333 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₁H₁₈N₂OF [M+H]⁺ 333.1398, found 333.1399.



3-Ethyl-3-methyl-1-phenyl-2-(pyridin-2-yl)indolin-5(3H)-one (3af): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50 mmol) and methyl (3-methyl-1-phenylpent-1-yn-3-yl) carbonate (**2f**) (349 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3af** (136 mg, 83%) as a white solid. **M.p.:** 117–118 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.64 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.40–7.33 (m, 4H), 7.30 (dd, *J* = 9.0, 6.9 Hz, 1H), 7.27–7.22 (m, 2H), 7.11 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.85 (dt, *J* = 7.9, 1.1 Hz, 1H), 6.38 (dd, *J* = 9.0, 1.1 Hz, 1H), 6.07 (dd, *J* = 6.9, 1.1 Hz, 1H), 3.18 (dq, *J* = 14.6, 7.4 Hz, 1H), 2.34 (dq, *J* = 13.8, 7.4 Hz, 1H), 2.05 (s, 3H), 0.61 (t, *J* = 7.4 Hz, 3H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 162.2 (C_q), 152.6 (C_q), 151.4 (C_q), 149.4 (CH), 148.6 (C_q), 139.0 (CH), 135.6 (CH), 134.9 (C_q), 132.0 (C_q), 129.4 (CH), 128.9 (CH), 128.6 (CH), 125.6 (CH), 122.5 (CH), 118.8 (CH), 99.8 (CH), 79.0 (C_q), 25.5 (CH₂), 21.0 (CH₃), 8.0 (CH₃). **IR** (ATR): 1653, 1582, 1530, 1463, 1445, 1433, 1352, 1155, 795, 701 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 351 (8) [M+Na]⁺, 329 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₂H₂₁N₂O [M+H]⁺ 329.1648, found 329.1655.

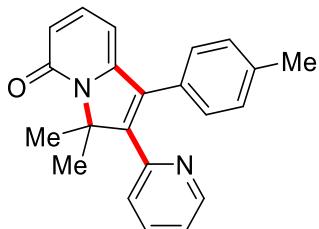


3,3-Dimethyl-2-(pyridin-2-yl)-1-(thiophen-3-yl)indolin-5(3H)-one (3ag): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50 mmol) and methyl (2-methyl-4-(thiophen-2-yl)but-3-yn-2-yl) carbonate (**2g**) (337 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ag** (106 mg, 62%) as a white solid. **M.p.:** 142–143 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.65 (d, *J* = 4.3 Hz, 1H), 7.57–7.11 (m, 5H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 4.3 Hz, 1H), 6.32 (s, 1H), 6.21–6.03 (m, 1H), 2.02 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 162.5 (C_q), 152.5 (C_q), 150.7 (C_q), 150.1 (C_q), 149.3 (CH), 138.6 (CH), 135.7 (CH), 131.5 (C_q), 128.1 (C_q), 127.9 (CH), 126.3 (CH), 125.3 (CH), 125.1 (CH), 122.6 (CH), 119.4 (CH), 100.0 (CH), 74.7 (C_q), 21.1 (CH₃). **IR** (ATR): 1650, 1578, 1461, 1433, 1151, 842, 792, 735, 672 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 663 (10) [2M+Na]⁺, 321 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₁₉H₁₇N₂OS [M+H]⁺ 321.1056, found 321.1057.

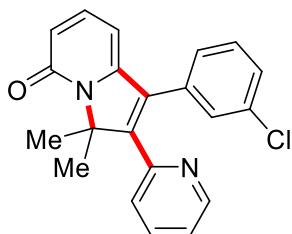


3,3-Dimethyl-1-(4-*n*-propylphenyl)-2-(pyridin-2-yl)indolin-5(3H)-one (3ah): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50 mmol) and methyl (2-methyl-4-(4-propylphenyl)but-3-yn-2-yl) carbonate (**2h**) (391 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ag** (102 mg, 57%) as a white solid. **M.p.:** 137–138 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.62 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.36 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.25 (dd, *J* = 9.0, 6.9 Hz, 1H), 7.13 (s, 4H), 7.09 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.34 (dd, *J* = 9.0, 1.1 Hz, 1H), 6.08 (dd, *J* = 6.9, 1.1 Hz, 1H), 2.66–2.41 (m, 2H), 2.04 (s, 6H), 1.70–1.50 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **13C-NMR** (100 MHz, CDCl₃) δ = 162.2 (C_q), 152.6 (C_q), 150.6 (C_q), 150.4 (C_q), 149.2 (CH), 143.2 (C_q), 138.8 (CH), 135.5 (CH), 133.2 (C_q), 129.1 (CH), 129.0 (C_q), 128.9 (CH), 125.7

(CH), 122.4 (CH), 118.7 (CH), 100.1 (CH), 75.0 (C_q), 37.7 (CH₂), 24.2 (CH₂), 21.1 (CH₃), 13.7 (CH₃). **IR** (ATR): 1656, 1585, 1531, 1463, 1154, 795, 744, 640 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 379 (12) [M+Na]⁺, 357 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₄H₂₄N₂O [M+H]⁺ 357.1961, found 357.1964.

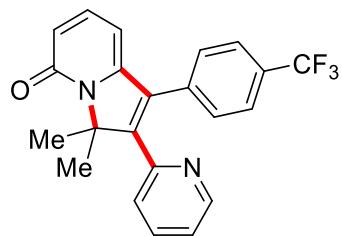


3,3-Dimethyl-2-(pyridin-2-yl)-1-(p-tolyl)indolin-5(3H)-one (3al): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50 mmol) and 2,2- Dimethyl-4-p-tolylbut-3-yn-2-yl carbonate (**2l**) (349 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3al** (100 mg, 61%) as a white solid. **M.p.:** 156–158 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.65 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.40 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.28 (s, 1H), 7.18–7.08 (m, 5H), 6.89 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.36 (d, *J* = 9.0 Hz, 1H), 6.08 (d, *J* = 6.9 Hz, 1H), 2.35 (s, 3H), 2.06 (s, 6H). **¹³C-NMR** (100 MHz, CDCl₃) δ = 162.3 (C_q), 152.7 (C_q), 150.7 (C_q), 150.5 (C_q), 149.3 (CH), 138.9 (CH), 138.5 (C_q), 135.7 (CH), 133.3 (C_q), 129.7 (CH), 129.2 (CH), 128.9 (C_q), 125.8 (CH), 122.5 (CH), 118.9 (CH), 100.1 (CH), 75.1 (C_q), 21.3 (CH₃), 21.2 (CH₃). **IR** (ATR): 1653, 1584, 1531, 1462, 1348, 840, 1177, 1154, 795, 743 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 679 (35) [2M+Na]⁺, 329 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₂H₂₀N₂O [M+H]⁺ 329.1648, found 329.1652.



1-(3-Chlorophenyl)-3,3-dimethyl-2-(pyridin-2-yl)indolin-5(3H)-one (3aj): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50

mmol) and 4-(3-chlorophenyl)-2-methylbut-3-yn-2-yl methyl carbonate (**2j**) (379 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ag** (96 mg, 55%) as a white solid. **M.p.**: 126–127 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.63 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.32–7.20 (m, 4H), 7.15–7.06 (m, 2H), 6.86 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.35 (dd, *J* = 9.0, 1.1 Hz, 1H), 6.02 (dd, *J* = 6.9, 1.1 Hz, 1H), 2.02 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 162.1 (C_q), 152.0 (C_q), 151.6 (C_q), 149.8 (C_q), 149.5 (CH), 138.9 (CH), 135.8 (CH), 134.8 (C_q), 133.6 (C_q), 131.8 (C_q), 130.2 (CH), 129.2 (CH), 128.8 (CH), 127.6 (CH), 125.6 (CH), 122.8 (CH), 119.2 (CH), 99.9 (CH), 75.2 (C_q), 21.0 (CH₃). **IR** (ATR): 1711, 1651, 1582, 1529, 1461, 1432, 1347, 1178, 1155, 793 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 719 (15) [2M+Na]⁺, 371 (12) [M+Na]⁺, 349 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₁H₁₈N₂OCl [M+H]⁺ 349.1102, found 349.1103.

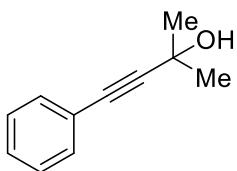


3,3-Dimethyl-2-(pyridin-2-yl)-1-(4-(trifluoromethyl)phenyl)indolin-5(3H)-one

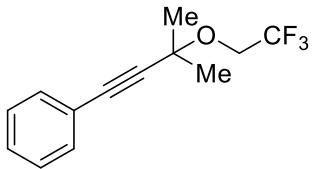
(3ak): The general procedure was followed using 2*H*-[1,2'-bipyridin]-2-one (**1a**) (86.1 mg, 0.50 mmol) and methyl (2-methyl-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl) carbonate (**2k**) (430 mg, 1.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3ak** (105 mg, 55%) as a white solid. **M.p.**: 138–139 °C. **1H-NMR** (400 MHz, CDCl₃) δ = 8.7 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.65–7.59 (m, 2H), 7.47 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.41 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.31 (dd, *J* = 9.1, 6.9 Hz, 1H), 7.19 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 6.86 (dt, *J* = 7.8, 1.0 Hz, 1H), 6.41 (dd, *J* = 9.1, 1.1 Hz, 1H), 6.05 (dd, *J* = 6.9, 1.1 Hz, 1H), 2.07 (s, 6H). **13C-NMR** (100 MHz, CDCl₃) δ = 162.2 (C_q), 152.2 (C_q), 152.0 (C_q), 149.7 (C_q), 149.6 (CH), 138.9 (CH), 136.0 (CH), 135.7 (C_q), 131.9 (C_q), 130.7 (q, ²J_{C-F} = 32.7 Hz, C_q), 129.8 (CH), 125.9 (q, ³J_{C-F} = 3.8 Hz, CH), 125.5 (CH), 123.8 (q, ¹J_{C-F} = 272.2 Hz, C_q), 122.9 (CH),

119.4 (CH), 99.8 (CH), 75.3 (C_q), 21.1 (CH₃). **¹⁹F-NMR** (376 MHz, CDCl₃) δ = -62.74 (s). **IR** (ATR): 1655, 1584, 1531, 1463, 1321, 1164, 1123, 1068, 1018 cm⁻¹. **MS** (ESI) *m/z* (relative intensity): 787 (45) [2M+Na]⁺, 383 (100) [M+H]⁺. **HR-MS** (ESI) *m/z* calcd for C₂₂H₁₇N₂OF₃ [M+H]⁺ 383.1366, found 383.1367.

Characterization Data of 2ab and 7



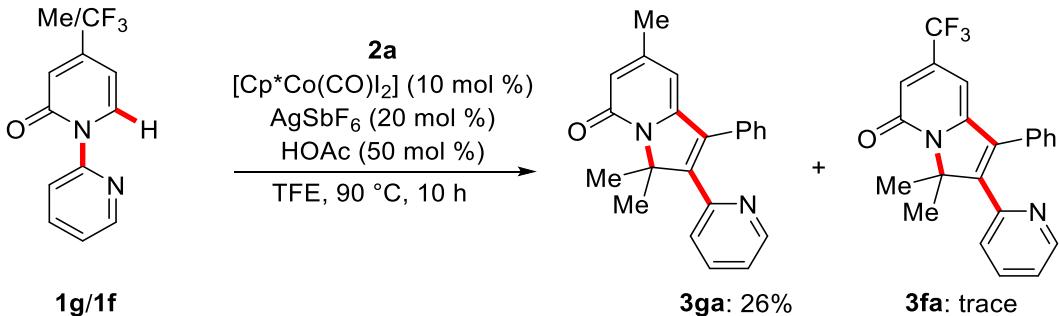
2-Methyl-4-phenylbut-3-yn-2-ol (2ab): Following the general reaction procedure, **2ab** was isolated as a yellow oil in 0 – 40% yields in the control experiments after column chromatography on silica gel (*n*-hexane/EtOAc). **¹H NMR** (400 MHz, CDCl₃) δ = 7.47–7.41 (m, 3H), 7.35–7.24 (m, 2H), 1.65 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ = 131.6 (CH), 128.2 (CH), 128.1 (CH), 122.8 (C_q), 94.1 (C_q), 82.5 (C_q), 65.5 (C_q), 31.5 (CH₃). **IR** (ATR): 3335, 2980, 1597, 1489, 1443, 1362, 1271, 1160, 961, 755 cm⁻¹. ^[4]



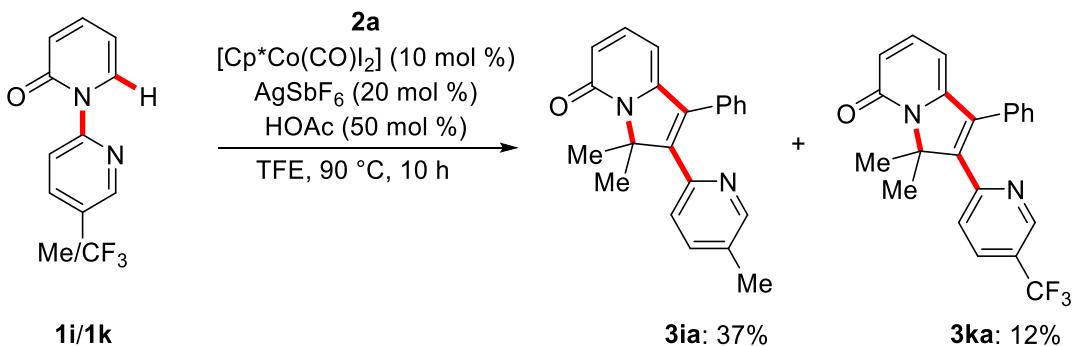
1-[3-(2,2,2-Trifluoroethoxy)-3-methylbut-1-ynyl] benzene (7): Following the general procedure **7** was isolated as a yellow oil in 40 – 90% yields in the control experiments after column chromatography on silica gel (*n*-hexane/EtOAc). **¹H NMR** (400 MHz, CDCl₃) δ = 7.49–7.43 (m, 2H), 7.36 (dd, *J* = 5.3, 2.0 Hz, 3H), 4.05 (q, *J* = 8.8 Hz, 2H), 1.63 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ = 131.7 (CH), 128.6 (CH), 128.3 (CH), 122.2 (q, ¹J_{C-F} = 277.1 Hz, C_q), 89.3 (C_q), 85.5 (C_q), 72.4 (C_q), 66 (q, ²J_{C-F} = 34.6 Hz, CH₂), 28.57 (CH₃). **¹⁹F NMR** (376 MHz, CDCl₃) δ = -74.16 (t, *J* = 8.7 Hz). **IR** (ATR): 2987, 2932, 1490, 1444, 1364, 1275, 1149, 1107, 968, 756 cm⁻¹. **MS** (EI)

m/z calcd for C₁₃H₁₄F₃O [M+H]⁺ 242.0918, found 242.0914. The analytical data are in accordance to those reported in the literature.^[5]

Intermolecular Competition Experiments

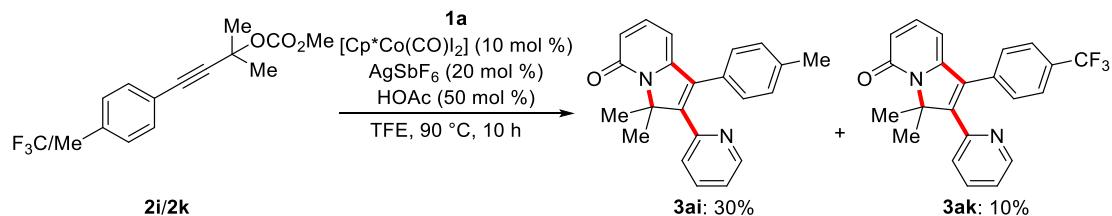


4-Methyl-2*H*-[1,2'-bipyridin]-2-one (**1g**) (93.1 mg, 0.50 mmol), 4-(trifluoromethyl)-2*H*-[1,2'-bipyridin]-2-one (**1f**) (120 mg, 0.50 mmol), methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol), $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ (24.0 mg, 10 mol %), AgSbF_6 (34.4 mg, 20 mol %), HOAc (15.0 mg, 50 mol %), and TFE (2.0 mL) were placed in a 25 mL Schlenk pressure tube and stirred at 90 °C for 10 h. After cooling to ambient temperature, the mixture was transferred into a round bottom flask with CH_2Cl_2 (20 mL) and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1 → 1/1) afforded **3ga** (42.7 mg, 26%) as a white solid and trace of **3fa**.



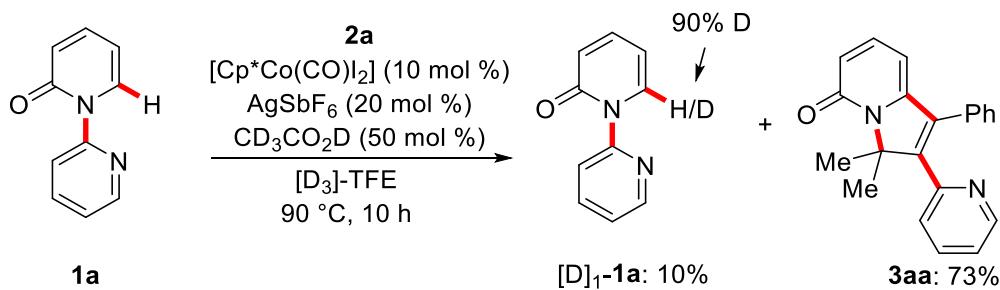
5'-Methyl-2*H*-[1,2'-bipyridin]-2-one (**1i**) (93.1 mg, 0.50 mmol), 5'-(trifluoromethyl)-2*H*-[1,2'-bipyridin]-2-one (**1k**) (103 mg, 0.50 mmol), methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol), $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ (24.0 mg, 10 mol %), AgSbF_6 (34.4 mg, 20 mol %), HOAc (15.0 mg, 50 mol %), and TFE (2.0 mL) were placed in a 25 mL Schlenk pressure tube and stirred at 90 °C for 10 h. After cooling to

ambient temperature, the mixture was transferred into a round bottom flask with CH₂Cl₂ (20 mL) and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1 → 1/1) afforded **3ia** (60.8 mg, 37%) as a white solid and **3ka** (22.9 mg, 12%) as a white solid.



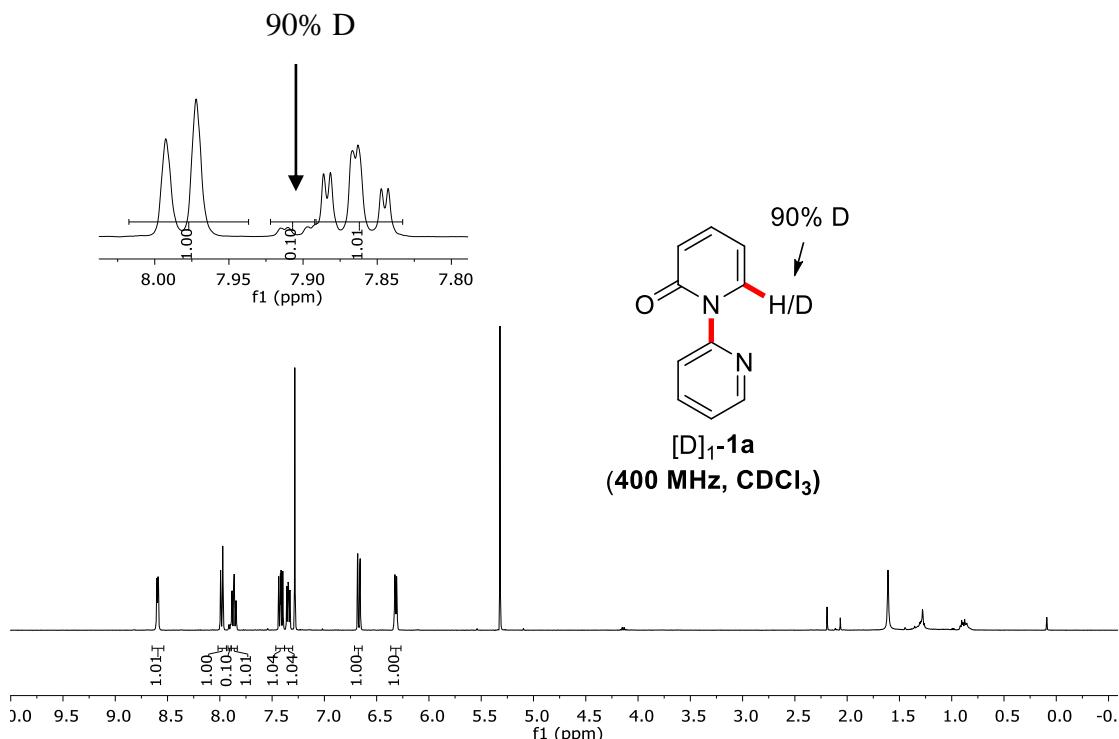
2H-[1,2'-Bipyridin]-2-one (1a**)** (86.1 mg, 0.50 mmol), methyl (2-methyl-4-(p-tolyl)but-3-yn-2-yl) carbonate (**2i**), methyl (2-methyl-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl) carbonate (**2k**) (430 mg, 1.50 mmol), [Cp^{*}Co(CO)I₂] (24.0 mg, 10 mol %), AgSbF₆ (34.4 mg, 20 mol %), HOAc (15.0 mg, 50 mol %), and TFE (2.0 mL) were placed in a 25 mL Schlenk pressure tube and stirred at 90 °C for 10 h. After cooling to ambient temperature, the mixture was transferred into a round bottom flask with CH₂Cl₂ (20 mL) and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 6/1 → 1/1) afforded **3ai** (49.3 mg, 30%) as a white solid and **3ak** (19.1 mg, 10%) as a white solid.

H/D Exchange Experiments

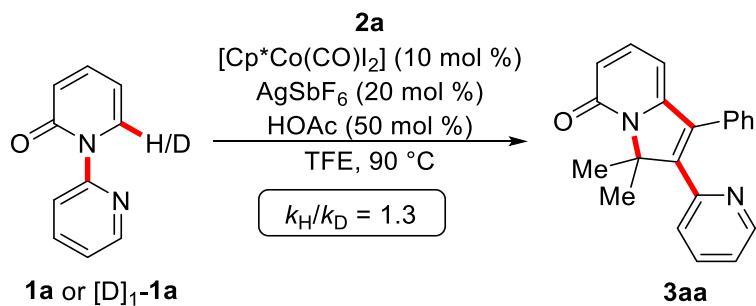


2H-[1,2'-Bipyridin]-2-one (1a**)** (86.1 mg, 0.50 mmol), methyl (2-methyl-4-phenylbut-3-yn-2-yl)carbonate (**2a**) (328 mg, 1.50 mmol), [Cp^{*}Co(CO)I₂] (24.0 mg, 10 mol %), AgSbF₆ (34.4 mg, 20 mol %), CD₃CO₂D (16.0 mg, 50 mol %), and [D₃]-TFE (2.0 mL)

were placed in a 25 mL Schlenk pressure tube under N₂ atmosphere, and stirred at 90 °C for 10 h. After cooling to ambient temperature, the mixture was transferred into a round bottom flask with CH₂Cl₂ (20 mL) and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1 → 1/1) afforded [D]₁-**1a** (8.7 mg, 10%) as a white solid and **3aa** (115 mg, 73%) as a white solid. The D incorporation was determined by ¹H-NMR spectroscopy.



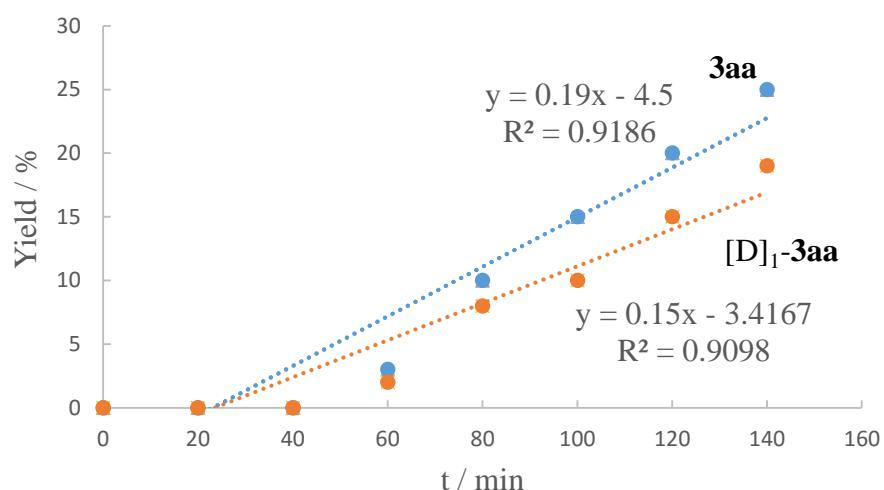
Kinetic Isotope Effect Study



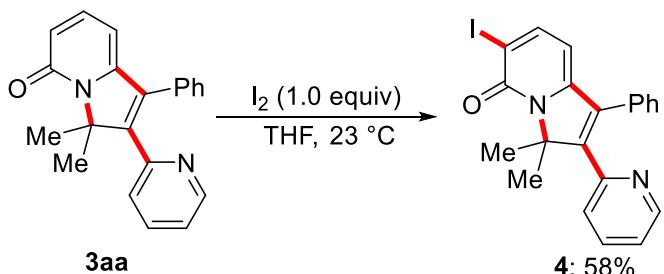
Five independent reactions of **1a** or [D]₁-**1a** with **2a** were performed to determine the

KIE. **1a** (86.2 mg, 0.50 mmol) or [D]₁-**1a** (86.6 mg, 0.50 mmol), **2a** (328 mg, 1.50 mmol), [Cp*Co(CO)L₂] (24.0 mg, 10 mol %), AgSbF₆ (34.4 mg, 20 mol %), HOAc (15.0 mg, 50 mol %), and TFE (2.0 mL) were placed in a 25 mL Schlenk pressure tube and stirred at 90 °C. After cooling to ambient temperature, the mixture was transferred into a round bottom flask with CH₂Cl₂ (20 mL) and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) yielded **3aa** or [D]₁-**3aa**.

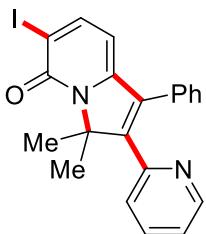
| <i>t</i> (min) | 0 | 20 | 40 | 60 | 80 | 100 | 120 | 140 |
|-----------------------------------|---|----|----|----|----|-----|-----|-----|
| 3aa (%) | 0 | 0 | 0 | 3 | 10 | 15 | 20 | 25 |
| [D] ₁ - 3aa (%) | 0 | 0 | 0 | 2 | 8 | 10 | 15 | 19 |



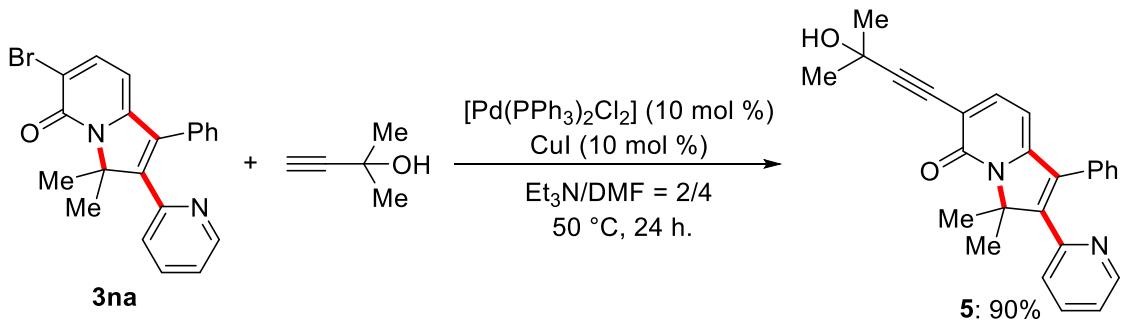
Late-Stage Modifications



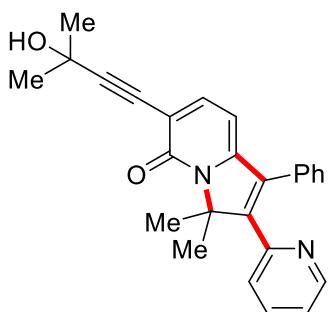
3aa (57.4 mg, 0.20 mmol) and I₂ (50.8 mg, 0.20 mmol) were dissolved in THF (1.0 mL). The resulting solution was stirred for 24 h at 23 °C. The mixture was transferred into a round bottom flask with CH₂Cl₂ (20 mL) and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 1/1) afforded the desired product **4** (51.1 mg, 58%).



6-Iodo-3,3-dimethyl-1-phenyl-2-(pyridin-2-yl)indolin-5(3H)-one (4): White solid.
M.p.: 212–213 °C. **¹H-NMR** (400 MHz, CDCl₃) δ = 8.64 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.43–7.33 (m, 4H), 7.27–7.21 (m, 2H), 7.13 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1H), 6.87 (dd, *J* = 7.9, 1.0 Hz, 1H), 5.88 (d, *J* = 7.5 Hz, 1H), 2.06 (s, 6H).
¹³C-NMR (100 MHz, CDCl₃) δ = 158.7 (C_q), 152.2 (C_q), 151.4 (C_q), 150.8 (C_q), 149.4 (CH), 147.9 (CH), 135.7 (CH), 133.0 (C_q), 131.5 (C_q), 129.3 (CH), 129.1 (CH), 128.8 (CH), 125.8 (CH), 122.7 (CH), 101.3 (CH), 91.4 (C_q), 76.5 (C_q), 21.1 (CH₃). **IR (ATR):** 1645, 1591, 1510, 1462, 1337, 1076, 1053, 791, 701 cm⁻¹. **MS (ESI)** *m/z* (relative intensity): 903 (5) [2M+Na]⁺, 463 (10) [M+Na]⁺, 441 (100) [M+H]⁺. **HR-MS (ESI)** *m/z* calcd for C₂₁H₁₈N₂OI [M+H]⁺ 441.0458, found 441.0462.

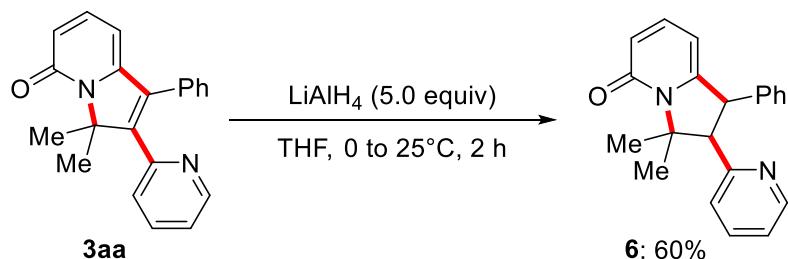


3na (78.7 mg, 0.20 mmol), 2-methylbut-3-yn-2-ol (33.6 mg, 0.40 mmol), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (14.0 mg, 10 mol %), CuI (3.8 mg, 10 mol %), Et_3N (0.4 mL) and DMF (0.8 mL) were placed in a 25 mL Schlenk pressure tube and stirred at 50 °C for 24 h. After cooling to ambient temperature, the mixture was transferred into a round bottom flask with CH_2Cl_2 (20 mL) and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 3/1 → 1/1) afforded **5** (71.4 mg, 90%) as a white solid.

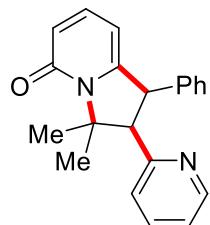


6-(3-Hydroxy-3-methylbut-1-yn-1-yl)-3,3-dimethyl-1-phenyl-2-(pyridin-2-yl)indolin-5(3H)-one (5): M.p.: 162–163 °C. **1H-NMR** (400 MHz, CDCl_3) δ = 8.63 (ddd, J = 4.8, 1.9, 1.0 Hz, 1H), 7.48 (d, J = 7.4 Hz, 1H), 7.42–7.32 (m, 4H), 7.27–7.19 (m, 2H), 7.12 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H), 6.86 (dd, J = 8.0, 1.1 Hz, 1H), 6.07 (d, J = 7.4 Hz, 1H), 2.06 (s, 6H), 1.61 (s, 6H). **13C-NMR** (100 MHz, CDCl_3) δ = 161.2 (C_q), 152.2 (C_q), 151.8 (C_q), 150.3 (C_q), 149.3 (CH), 142.2 (CH), 135.7 (CH), 133.1 (C_q), 131.5 (C_q), 129.3 (CH), 129.0 (CH), 128.8 (CH), 125.7 (CH), 122.7 (CH), 113.3 (C_q), 100.1 (CH), 99.8 (C_q), 78.3 (C_q), 75.9 (C_q), 65.4 (C_q), 31.4 (CH_3), 21.2 (CH_3). **IR (ATR):** 2979, 1637, 1583, 1539, 1463, 1339, 1270, 1166, 780, 702 cm^{-1} . **MS (ESI) *m/z* (relative intensity):** 815 (12) $[2\text{M}+\text{Na}]^+$, 419 (100) $[\text{M}+\text{Na}]^+$, 397 (65) $[\text{M}+\text{H}]^+$. **HR-MS (ESI)**

m/z calcd for C₂₆H₂₅N₂O₂ [M+H]⁺ 397.1911, found 397.1917.



To a solution of **3aa** (62.8 mg, 0.20 mmol) in anhydrous THF (1.0 mL) under N₂ atmosphere was added LiAlH₄ (38.0 mg, 1.00 mmol) at 0 °C. The solution was warmed to ambient temperature and stirred for 2h. Then, the solution was cooled to 0 °C and water (1.0 mL) was added. The solution extracted with EtOAc (3 × 15 mL) followed by drying with Na₂SO₄ and evaporation of the solvents under reduced pressure. Purification by column chromatography on silica gel (EtOAc, 100%) yielded **6** (38.0 mg, 60%) as a white solid.



2,3-Dihydro-3,3-dimethyl-1-phenyl-2-(pyridin-2-yl)indolin-5(1H)-one (6):

M.p.: 209–211 °C. **¹H NMR** (400 MHz, CDCl₃) δ = 8.65 (d, *J* = 4.7 Hz, 1H), 7.59 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.34–7.06 (m, 8H), 6.42 (d, *J* = 9.2 Hz, 1H), 5.72 (d, *J* = 6.8 Hz, 1H), 5.29 (d, *J* = 12.0 Hz, 1H), 3.59 (d, *J* = 12.0 Hz, 1H), 2.02 (s, 3H), 1.28 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃) δ = 162.6 (C_q), 154.9 (C_q), 153.4 (C_q), 149.4 (CH), 139.3 (CH), 139.0 (C_q), 136.2 (CH), 128.9 (CH), 128.6 (CH), 127.4 (CH), 125.1 (CH), 122.6 (CH), 119.8 (CH), 101.9 (CH), 69.9 (C_q), 64.0 (CH), 50.0 (CH), 26.6 (CH₃), 20.2 (CH₃).

IR (ATR): 2925, 1660, 1588, 1541, 1436, 1143, 1382, 1097, 778, 743 cm⁻¹. **MS** (EI) *m/z* calcd for C₂₁H₂₁N₂O [M+H]⁺ 316.1576, found 316.1571.

X-Ray Crystallographic Analysis

The crystal was kept at 99.93 K during data collection. Using Olex2,^[6] the structure was solved with the XT^[7] structure solution program using Intrinsic Phasing and refined with the XL^[8] refinement package using Least Squares minimisation.

Table S2. Crystal data and structure refinement **3aa**.

| Compound | 3aa |
|--------------------------------------|--|
| Empirical formula | C ₂₁ H ₁₈ N ₂ O |
| CCDC deposition No. | 1963220 |
| Formula weight | 314.37 |
| Temperature/K | 99.93 |
| Crystal system | monoclinic |
| Space group | P2 ₁ /c |
| a/Å | 10.2077(4) |
| b/Å | 19.7705(7) |
| c/Å | 8.1575(3) |
| α/° | 90 |
| β/° | 97.3950(10) |
| γ/° | 90 |
| Volume/Å ³ | 1632.58(11) |
| Z | 4 |
| ρ _{calcd} g/cm ³ | 1.279 |
| μ/mm ⁻¹ | 0.079 |
| F(000) | 664.0 |
| Crystal size/mm ³ | 0.475 × 0.36 × 0.242 |
| Radiation | MoKα ($\lambda = 0.71073$) |
| 2Θ range for data collection/° | 5.76 to 59.326 |

| | |
|---|--|
| Index ranges | $-14 \leq h \leq 14, 0 \leq k \leq 27, 0 \leq l \leq 11$ |
| Reflections collected | 4532 |
| Independent reflections | 4532 [$R_{\text{int}} = ?, R_{\text{sigma}} = 0.0160$] |
| Data/restraints/parameters | 4532/0/220 |
| Goodness-of-fit on F^2 | 1.071 |
| Final R indexes [$I >= 2\sigma(I)$] | $R_1 = 0.0364, wR_2 = 0.0939$ |
| Final R indexes [all data] | $R_1 = 0.0380, wR_2 = 0.0953$ |
| Largest diff. peak/hole / e Å ⁻³ | 0.35/-0.21 |

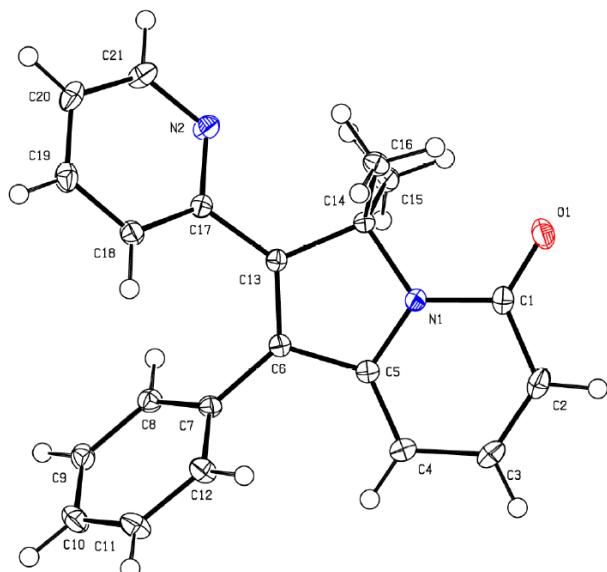


Figure S1. Molecular structure of **3aa** with thermal ellipoids at 50% probability level.

The hydrogen atoms are omitted for clarity.

Crystal Data for C₂₁H₁₈N₂O ($M = 314.37$ g/mol): monoclinic, space group P2₁/c (no. 14), $a = 10.2077(4)$ Å, $b = 19.7705(7)$ Å, $c = 8.1575(3)$ Å, $\beta = 97.3950(10)^\circ$, $V = 1632.58(11)$ Å³, $Z = 4$, $T = 99.93$ K, $\mu(\text{MoK}\alpha) = 0.079$ mm⁻¹, $D_{\text{calc}} = 1.279$ g/cm³, 4532 reflections measured ($5.76^\circ \leq 2\Theta \leq 59.326^\circ$), 4532 unique ($R_{\text{int}} = ?, R_{\text{sigma}} = 0.0160$) which were used in all calculations. The final R_1 was 0.0364 ($I > 2\sigma(I)$) and wR_2 was 0.0953 (all data).

Table S3. Bond Lengths [Å] for **3aa**.

| Atom | Atom | Length/Å |
|------|------|------------|
| O1 | C1 | 1.2373(12) |
| N1 | C1 | 1.3934(11) |
| N1 | C5 | 1.3734(11) |
| N1 | C14 | 1.4892(11) |
| N2 | C17 | 1.3504(12) |
| N2 | C21 | 1.3377(12) |
| C1 | C2 | 1.4426(14) |
| C2 | C3 | 1.3595(15) |
| C3 | C4 | 1.4182(14) |
| C4 | C5 | 1.3674(13) |
| C5 | C6 | 1.4609(12) |
| C6 | C7 | 1.4775(12) |
| C6 | C13 | 1.3554(12) |
| C7 | C8 | 1.3980(12) |
| C7 | C12 | 1.3969(13) |
| C8 | C9 | 1.3903(13) |
| C9 | C10 | 1.3889(15) |
| C10 | C11 | 1.3891(15) |
| C11 | C12 | 1.3922(13) |
| C13 | C14 | 1.5253(12) |
| C13 | C17 | 1.4775(12) |
| C14 | C15 | 1.5377(12) |
| C14 | C16 | 1.5318(12) |
| C17 | C18 | 1.3995(12) |
| C18 | C19 | 1.3896(13) |
| C19 | C20 | 1.3857(15) |

| | | |
|-----|-----|------------|
| C20 | C21 | 1.3881(14) |
|-----|-----|------------|

Table S4. Bond angles [°] for **3aa**

| Atom | Atom | Atom | Angle/° |
|------|------|------|-----------|
| C1 | N1 | C14 | 124.13(8) |
| C5 | N1 | C1 | 124.01(8) |
| C5 | N1 | C14 | 111.80(7) |
| C21 | N2 | C17 | 117.57(9) |
| O1 | C1 | N1 | 121.11(9) |
| O1 | C1 | C2 | 125.04(9) |
| N1 | C1 | C2 | 113.84(8) |
| C3 | C2 | C1 | 122.27(9) |
| C2 | C3 | C4 | 121.15(9) |
| C5 | C4 | C3 | 117.38(9) |
| N1 | C5 | C6 | 107.74(7) |
| C4 | C5 | N1 | 121.30(8) |
| C4 | C5 | C6 | 130.93(8) |
| C5 | C6 | C5 | 122.42(8) |
| C13 | C6 | C5 | 108.82(8) |
| C13 | C6 | C7 | 128.75(8) |
| C8 | C7 | C6 | 120.16(8) |
| C12 | C7 | C6 | 120.72(8) |
| C12 | C7 | C8 | 119.12(8) |
| C9 | C8 | C7 | 120.43(9) |
| C10 | C9 | C8 | 120.16(9) |
| C9 | C10 | C11 | 119.77(9) |
| C10 | C11 | C12 | 120.34(9) |
| C11 | C12 | C7 | 120.17(9) |

| | | | |
|-----|-----|-----|-----------|
| C6 | C13 | C14 | 110.84(8) |
| C6 | C13 | C17 | 127.92(8) |
| C17 | C13 | C14 | 120.76(8) |
| N1 | C14 | C13 | 100.45(7) |
| N1 | C14 | C15 | 109.05(7) |
| N1 | C14 | C16 | 110.85(7) |
| C13 | C14 | C15 | 112.40(7) |
| C13 | C14 | C16 | 111.10(7) |
| C16 | C14 | C15 | 112.37(7) |
| N2 | C17 | C13 | 116.92(8) |
| N2 | C17 | C18 | 121.84(8) |
| C18 | C17 | C13 | 120.98(8) |
| C19 | C18 | C17 | 119.38(9) |
| C20 | C19 | C18 | 118.93(9) |
| C19 | C20 | C21 | 117.92(9) |
| N1 | C21 | C20 | 124.36(9) |

Table S5. Crystal data and structure refinement **3ca**.

| | |
|---------------------|--|
| Compound | 3ca |
| Empirical formula | C ₂₅ H ₂₀ N ₂ O |
| CCDC deposition No. | 1963222 |
| Formula weight | 364.43 |
| Temperature/K | 100.01 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 8.7963(9) |
| b/Å | 10.3540(12) |
| c/Å | 11.5419(14) |

| | |
|---|--|
| $\alpha/^\circ$ | 110.430(3) |
| $\beta/^\circ$ | 100.373(3) |
| $\gamma/^\circ$ | 101.270(4) |
| Volume/ \AA^3 | 930.16(18) |
| Z | 2 |
| $\rho_{\text{calcd}}/\text{cm}^3$ | 1.301 |
| μ/mm^{-1} | 0.080 |
| F(000) | 384.0 |
| Crystal size/mm ³ | 0.348 \times 0.281 \times 0.191 |
| Radiation | MoK α ($\lambda = 0.71073$) |
| 2 Θ range for data collection/° | 4.904 to 59.224 |
| Index ranges | -12 \leq h \leq 11, -14 \leq k \leq 14, -15 \leq l \leq 15 |
| Reflections collected | 17309 |
| Independent reflections | 5094 [$R_{\text{int}} = 0.0229$, $R_{\text{sigma}} = 0.0231$] |
| Data/restraints/parameters | 5094/0/255 |
| Goodness-of-fit on F ² | 1.048 |
| Final R indexes [I \geq 2 σ (I)] | $R_1 = 0.0410$, wR ₂ = 0.1026 |
| Final R indexes [all data] | $R_1 = 0.0469$, wR ₂ = 0.1081 |
| Largest diff. peak/hole / e \AA^{-3} | 0.38/-0.21 |

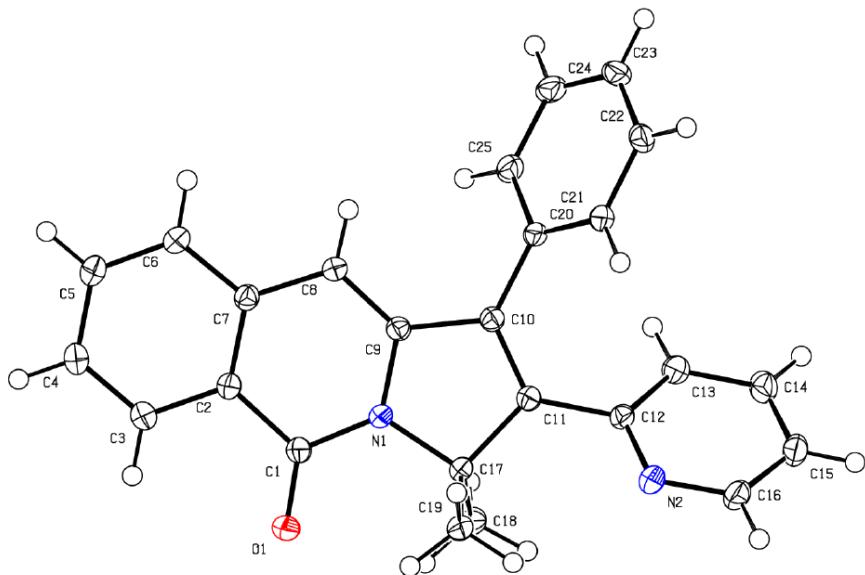


Figure S2. Molecular structure of **3ca** with thermal ellipoids at 50% probablitiy level. The hydrogen atoms are omitted for clarity.

Crystal Data for $C_{25}H_{20}N_2O$ ($M = 364.43$ g/mol): triclinic, space group P-1 (no. 2), $a = 8.7963(9)$ Å, $b = 10.3540(12)$ Å, $c = 11.5419(14)$ Å, $\alpha = 110.430(3)^\circ$, $\beta = 100.373(3)^\circ$, $\gamma = 101.270(4)^\circ$, $V = 930.16(18)$ Å³, $Z = 2$, $T = 100.01$ K, $\mu(\text{MoK}\alpha) = 0.080$ mm⁻¹, $D_{\text{calc}} = 1.301$ g/cm³, 17309 reflections measured ($4.904^\circ \leq 2\Theta \leq 59.224^\circ$), 5094 unique ($R_{\text{int}} = 0.0229$, $R_{\text{sigma}} = 0.0231$) which were used in all calculations. The final R_1 was 0.0410 ($I > 2\sigma(I)$) and wR_2 was 0.1081 (all data).

Table S6. Bond Lengths [Å] for **3ca**.

| Atom | Atom | Length/Å |
|------|------|------------|
| O1 | C1 | 1.2327(13) |
| N1 | C1 | 1.3789(13) |
| N1 | C9 | 1.3903(13) |
| N1 | C17 | 1.4948(12) |
| N2 | C12 | 1.3460(13) |
| N2 | C16 | 1.3422(14) |
| C1 | C2 | 1.4741(14) |

| | | |
|-----|-----|------------|
| C2 | C3 | 1.4044(14) |
| C2 | C7 | 1.4116(14) |
| C3 | C4 | 1.3780(15) |
| C4 | C5 | 1.4032(16) |
| C5 | C6 | 1.3816(15) |
| C6 | C7 | 1.4129(14) |
| C7 | C8 | 1.4351(14) |
| C8 | C9 | 1.3572(14) |
| C9 | C10 | 1.4625(14) |
| C10 | C11 | 1.3541(14) |
| C10 | C20 | 1.4775(14) |
| C11 | C12 | 1.4793(14) |
| C11 | C17 | 1.5207(14) |
| C12 | C13 | 1.4000(15) |
| C13 | C14 | 1.3855(15) |
| C14 | C15 | 1.3883(18) |
| C15 | C16 | 1.3849(18) |
| C17 | C18 | 1.5314(15) |
| C17 | C19 | 1.5339(14) |
| C20 | C21 | 1.3983(14) |
| C20 | C25 | 1.3986(14) |
| C21 | C22 | 1.3909(15) |
| C22 | C23 | 1.3912(17) |
| C23 | C24 | 1.3882(18) |
| C24 | C25 | 1.3882(16) |

Table S7. Bond angles [°] for **3ca**

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| | | | |

| | | | |
|-----|-----|-----|------------|
| C1 | N1 | C9 | 124.06(9) |
| C1 | N1 | C17 | 124.06(8) |
| C9 | N1 | C17 | 111.77(8) |
| C16 | N2 | C12 | 117.36(10) |
| O1 | C1 | N1 | 122.02(9) |
| O1 | C1 | C2 | 123.40(9) |
| N1 | C1 | C2 | 114.58(9) |
| C3 | C2 | C1 | 117.99(9) |
| C2 | C3 | C4 | 120.53(9) |
| C3 | C2 | C7 | 121.46(9) |
| C7 | C2 | C1 | 120.15(10) |
| C4 | C3 | C2 | 119.85(10) |
| C3 | C4 | C5 | 120.76(10) |
| C6 | C5 | C4 | 120.38(10) |
| C5 | C6 | C7 | 118.32(9) |
| C2 | C7 | C6 | 119.16(9) |
| C6 | C7 | C8 | 122.50(9) |
| C9 | C8 | C7 | 118.80(9) |
| N1 | C9 | C10 | 107.24(8) |
| C8 | C9 | N1 | 121.92(9) |
| C8 | C9 | C10 | 130.82(9) |
| C9 | C10 | C20 | 122.63(9) |
| C11 | C10 | C9 | 108.94(9) |
| C11 | C10 | C20 | 128.43(9) |
| C10 | C11 | C12 | 125.89(9) |
| C10 | C11 | C17 | 111.62(9) |
| C12 | C11 | C17 | 122.34(9) |
| N2 | C12 | C11 | 117.10(9) |

| | | | |
|-----|-----|-----|------------|
| N2 | C12 | C13 | 122.52(9) |
| C13 | C12 | C11 | 120.38(9) |
| C14 | C13 | C12 | 118.93(10) |
| C13 | C14 | C15 | 118.85(11) |
| C16 | C15 | C14 | 118.41(10) |
| N2 | C16 | C15 | 123.86(11) |
| N1 | C17 | C11 | 100.31(8) |
| N1 | C17 | C18 | 110.87(8) |
| N1 | C17 | C19 | 109.89(8) |
| C11 | C17 | C18 | 110.49(9) |
| C11 | C17 | C19 | 113.37(8) |
| C18 | C17 | C19 | 111.42(9) |
| C21 | C20 | C10 | 121.26(9) |
| C21 | C20 | C25 | 118.79(9) |
| C25 | C20 | C10 | 119.95(9) |
| C22 | C21 | C20 | 120.51(10) |
| C21 | C22 | C23 | 120.28(10) |
| C24 | C23 | C22 | 119.43(10) |
| C25 | C24 | C23 | 120.58(10) |
| C24 | C25 | C20 | 120.40(10) |

Table S8. Crystal data and structure refinement **3ga**.

| | |
|---------------------|--|
| Compound | 3ga |
| Empirical formula | C ₂₂ H ₂₀ N ₂ O |
| CCDC deposition No. | 1963221 |
| Formula weight | 328.40 |
| Temperature/K | 100.0 |
| Crystal system | triclinic |

| | |
|---|--|
| Space group | P-1 |
| a/Å | 9.0581(12) |
| b/Å | 9.9273(12) |
| c/Å | 10.2645(12) |
| $\alpha/^\circ$ | 105.947(4) |
| $\beta/^\circ$ | 96.819(4) |
| $\gamma/^\circ$ | 97.151(4) |
| Volume/Å ³ | 869.20(19) |
| Z | 2 |
| $\rho_{\text{calcg}}/\text{cm}^3$ | 1.255 |
| μ/mm^{-1} | 0.078 |
| F(000) | 348.0 |
| Crystal size/mm ³ | 0.346 × 0.235 × 0.178 |
| Radiation | MoKα ($\lambda = 0.71073$) |
| 2Θ range for data collection/° | 4.592 to 57.512 |
| Index ranges | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13 |
| Reflections collected | 24237 |
| Independent reflections | 4505 [$R_{\text{int}} = 0.0217$, $R_{\text{sigma}} = 0.0172$] |
| Data/restraints/parameters | 4505/0/229 |
| Goodness-of-fit on F ² | 1.036 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0409$, $wR_2 = 0.1051$ |
| Final R indexes [all data] | $R_1 = 0.0437$, $wR_2 = 0.1077$ |
| Largest diff. peak/hole / e Å ⁻³ | 0.43/-0.19 |

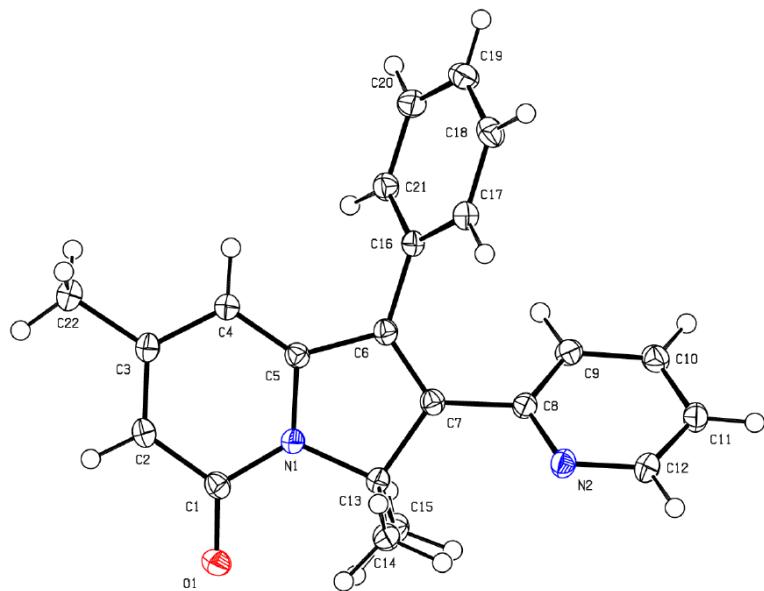


Figure S3. Molecular structure of **3ga** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity.

Crystal Data for $C_{22}H_{20}N_2O$ ($M = 328.40$ g/mol): triclinic, space group P-1 (no. 2), $a = 9.0581(12)$ Å, $b = 9.9273(12)$ Å, $c = 10.2645(12)$ Å, $\alpha = 105.947(4)^\circ$, $\beta = 96.819(4)^\circ$, $\gamma = 97.151(4)^\circ$, $V = 869.20(19)$ Å³, $Z = 2$, $T = 100.0$ K, $\mu(\text{MoK}\alpha) = 0.078$ mm⁻¹, $D_{\text{calc}} = 1.255$ g/cm³, 24237 reflections measured ($4.592^\circ \leq 2\Theta \leq 57.512^\circ$), 4505 unique ($R_{\text{int}} = 0.0217$, $R_{\text{sigma}} = 0.0172$) which were used in all calculations. The final R_1 was 0.0409 ($I > 2\sigma(I)$) and wR_2 was 0.1077 (all data).

Table S9. Bond Lengths [Å] for **3ga**.

| Atom | Atom | Length/Å |
|------|------|------------|
| O1 | C1 | 1.2364(12) |
| N1 | C1 | 1.3934(13) |
| N1 | C5 | 1.3747(12) |
| N1 | C13 | 1.4938(12) |
| N2 | C8 | 1.3432(13) |
| N2 | C12 | 1.3407(13) |
| C1 | C2 | 1.4437(14) |

| | | |
|-----|-----|------------|
| C2 | C3 | 1.3664(14) |
| C3 | C4 | 1.4228(14) |
| C3 | C22 | 1.5027(14) |
| C4 | C5 | 1.3620(14) |
| C5 | C6 | 1.4607(13) |
| C6 | C7 | 1.3470(14) |
| C6 | C16 | 1.4776(13) |
| C7 | C8 | 1.4773(13) |
| C7 | C13 | 1.5227(14) |
| C8 | C9 | 1.3990(14) |
| C9 | C10 | 1.3833(15) |
| C10 | C11 | 1.3886(15) |
| C11 | C12 | 1.3839(15) |
| C13 | C14 | 1.5329(14) |
| C13 | C15 | 1.5330(14) |
| C16 | C17 | 1.3959(14) |
| C16 | C21 | 1.3951(14) |
| C17 | C18 | 1.3890(14) |
| C18 | C19 | 1.3874(15) |
| C19 | C20 | 1.3913(16) |
| C20 | C21 | 1.3895(14) |

Table S10. Bond angles [°] for **3ga**

| Atom | Atom | Atom | Angle/° |
|------|------|------|-----------|
| C1 | N1 | C9 | 125.09(8) |
| C5 | N1 | C17 | 123.29(9) |
| C5 | N1 | C17 | 111.60(8) |
| C12 | N2 | C12 | 117.65(9) |

| | | | |
|-----|-----|-----|------------|
| O1 | C1 | N1 | 121.33(9) |
| O1 | C1 | C2 | 124.71(9) |
| N1 | C1 | C2 | 113.95(9) |
| C3 | C2 | C1 | 123.28(9) |
| C2 | C3 | C4 | 119.32(9) |
| C2 | C3 | C7 | 121.47(9) |
| C4 | C3 | C1 | 119.20(9) |
| C5 | C4 | C2 | 118.40(9) |
| N1 | C5 | C5 | 107.79(8) |
| C4 | C5 | C4 | 121.72(9) |
| C4 | C5 | C7 | 130.49(9) |
| C5 | C6 | C6 | 122.11(9) |
| C7 | C6 | C8 | 108.88(9) |
| C7 | C6 | C7 | 129.01(9) |
| C6 | C7 | C10 | 126.08(9) |
| C6 | C7 | N1 | 111.32(9) |
| C8 | C7 | C10 | 122.38(8) |
| N2 | C8 | C20 | 116.91(9) |
| N2 | C8 | C9 | 122.27(9) |
| C9 | C8 | C20 | 120.81(9) |
| C10 | C9 | C12 | 119.18(9) |
| C9 | C10 | C17 | 118.74(10) |
| C12 | C11 | C17 | 118.41(10) |
| N2 | C12 | C11 | 123.75(10) |
| N1 | C13 | C13 | 100.37(7) |
| N1 | C13 | C11 | 109.92(8) |
| N1 | C13 | C12 | 110.88(8) |
| C7 | C13 | C15 | 113.59(8) |

| | | | |
|-----|-----|-----|------------|
| C7 | C13 | C14 | 110.30(8) |
| C14 | C13 | C15 | 111.31(8) |
| C17 | C16 | C11 | 120.90(9) |
| C21 | C16 | C18 | 119.84(9) |
| C21 | C16 | C19 | 119.25(9) |
| C18 | C17 | C18 | 120.13(9) |
| C19 | C18 | C19 | 120.30(10) |
| C18 | C19 | C19 | 119.98(10) |
| C21 | C20 | C19 | 119.79(10) |
| C20 | C21 | C16 | 120.55(10) |

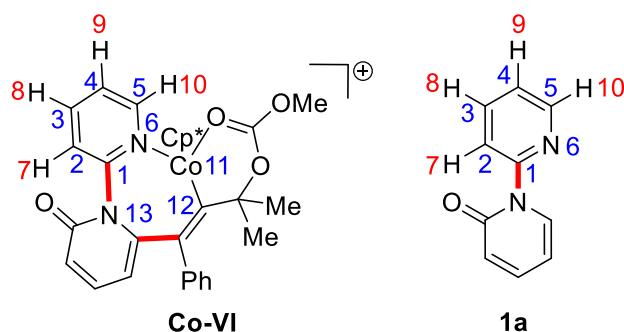
Computational Data

All calculations were carried out using Density Functional Theory with Orca software version 3.0.3.^[9] Geometry optimizations were carried out at the TPSS^[10] level of theory including D3(BJ)^[11] dispersion corrections. All atoms were described with a def2-TZVP basis set.^[12] All stationary points were fully characterized by numerical frequency calculations as either a minimum or a transition state (only one imaginary frequency) at the same level of theory. Solvent effects were taken into consideration in the single point calculations through the use of the Conductor-like Screening Model (COSMO) with a dielectric constant of $\epsilon = 26.726$, which corresponds to 2,2,2-trifluoroethanol (TFE) for cobalt system and with a dielectric constant of $\epsilon = 7.2$, which corresponds to 1,2-dimethoxyethane (DME) for manganese system.^[13] Single point calculations were performed at the PW6B95^[14] and PBE0^[15] level of theory including D3(BJ) dispersion corrections with a def2-TZVP basis set for all atoms. RIJCOSX approximation was used in all calculations together with a def2-TZVP/J auxiliary basis sets.^[16] Unless otherwise stated, all reported energies are Gibbs free energies in kcal mol⁻¹, which were calculated by adding the gas-phase thermal and non-thermal corrections and entropy contribution at 298 K to the single-point energies.

Bond order analysis was performed with NBO 6.0 software using Wiberg bond orders in NAO basis.^[17] This was carried out with Gaussian 16, Revision A.03 package^[18] using PW6B95 level of theory including D3(BJ) dispersion corrections with a def2-TZVP basis set for all the atoms. Solvent effects were implicitly included for these analysis through the use of the SMD^[19] model with a dielectric constant of $\epsilon = 26.726$, which corresponds to 2,2,2-trifluoroethanol (TFE) for cobalt system.

Table S11. Wiberg bond order analysis for C–H cobaltation

| Structure | Co–C bond order | C–H bond order |
|----------------|-----------------|----------------|
| Co-I | 0.0021 | 0.8953 |
| Co-II | 0.5412 | 0.0339 |
| TS(2-3) | 0.1670 | 0.6949 |
| Co-III | 0.2616 | 0.5072 |

Table S12. NBO charges for the intermediate Co-VI and substrate 1a

| Atom Number | Co-VI | 1a |
|-------------|----------|----------|
| 1 | 0.40465 | 0.34668 |
| 2 | -0.21960 | -0.24935 |
| 3 | -0.13556 | -0.16211 |
| 4 | -0.23048 | -0.25931 |
| 5 | 0.04030 | 0.03308 |
| 6 | -0.42298 | -0.46410 |
| 7 | 0.25781 | 0.26036 |
| 8 | 0.25140 | 0.24048 |
| 9 | 0.25438 | 0.24250 |
| 10 | 0.24047 | 0.21418 |
| 11 | 0.78568 | --- |
| 12 | -0.08185 | --- |
| 13 | -0.42986 | --- |

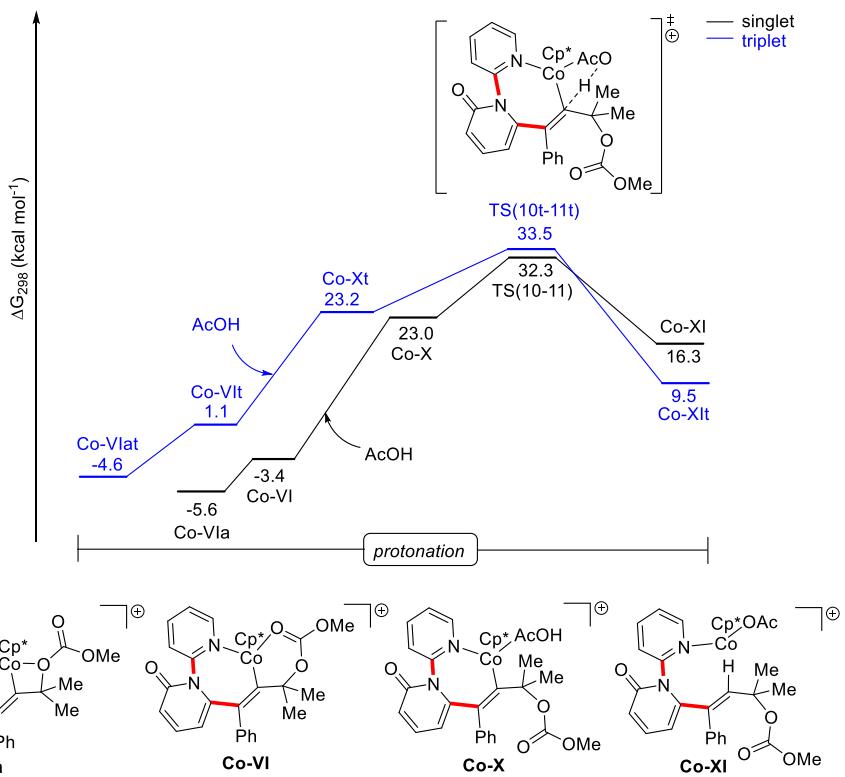


Figure S4. Gibbs free energy profile in kcal mol⁻¹ for the protonation step from intermediate **Co-VIa** at the PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)//TPSS-D3(BJ)/ def2-TZVP level of theory.

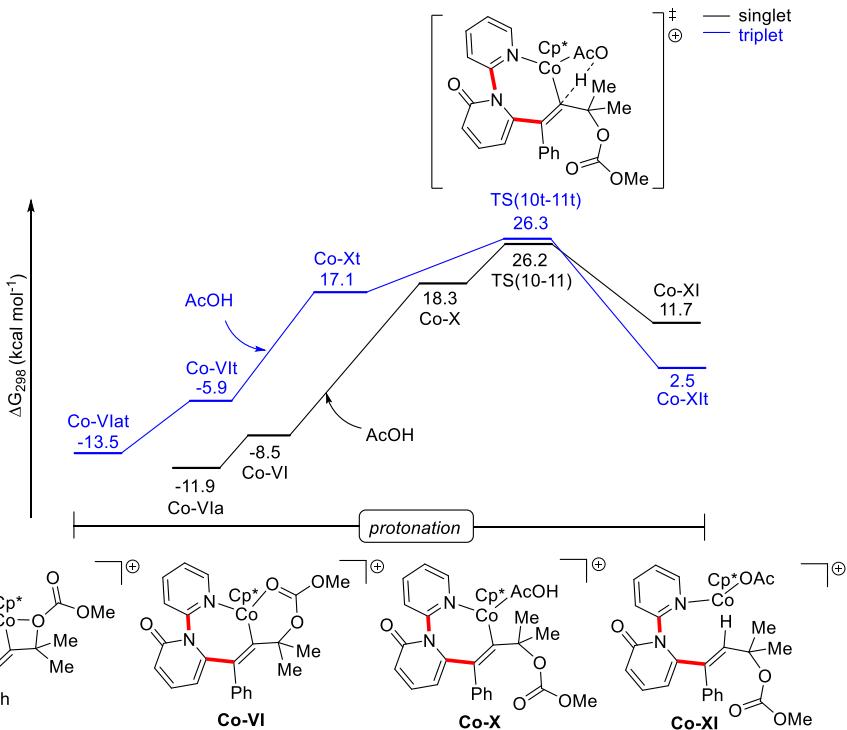


Figure S5. Gibbs free energy profile in kcal mol⁻¹ for the protonation step from intermediate **Co-VIa** at the PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)//TPSS-D3(BJ)/ def2-TZVP level of theory.

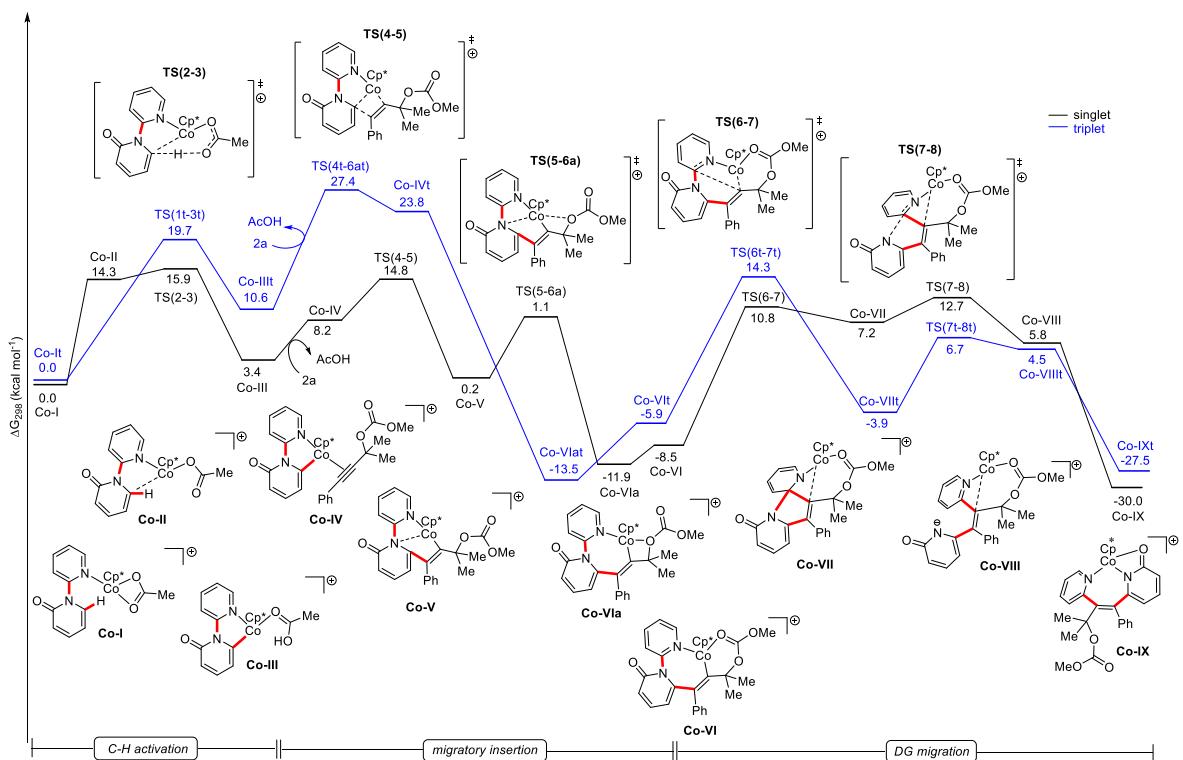


Figure S6. Gibbs free energy profile in kcal mol⁻¹ for the cobalt(III)-catalyzed Domino C–H activation at the PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)//TPSS-D3(BJ)/def2-TZVP level of theory.

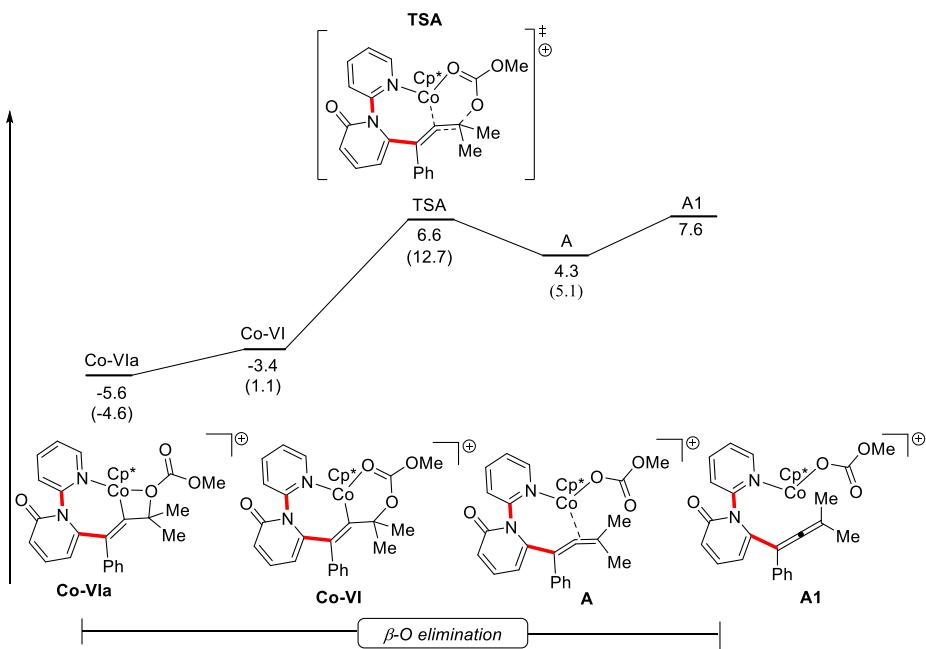


Figure S7. Gibbs free energy profile in kcal mol⁻¹ for the β -O elimination step from intermediate **Co-VIa** at the PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)//TPSS-D3(BJ)/def2-TZVP level of theory. Values in parenthesis are for the corresponding triplet.

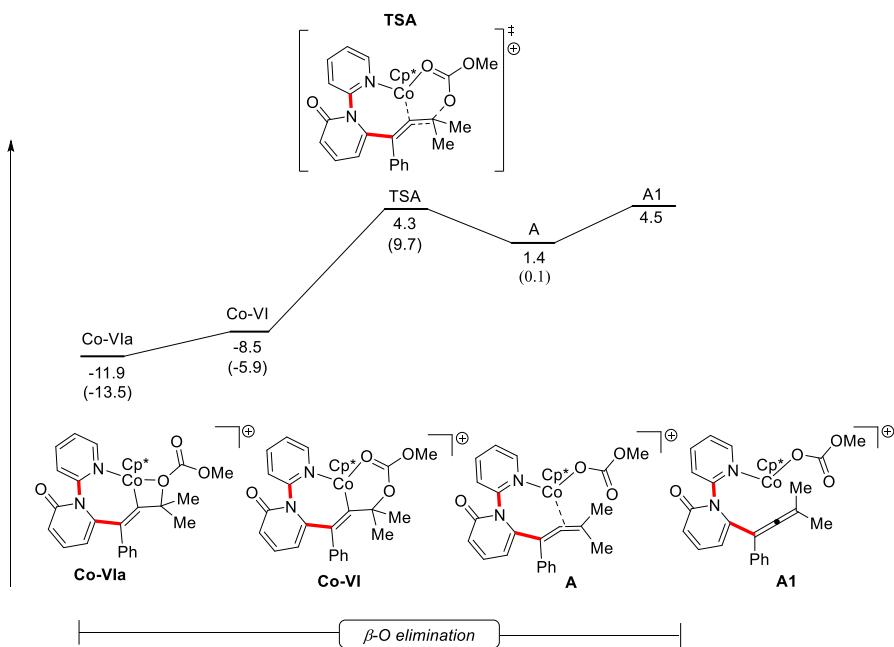


Figure S8. Gibbs free energy profile in kcal mol⁻¹ for the β -O elimination step from intermediate **Co-VIa** at the PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)//TPSS-D3(BJ)/def2-TZVP level of theory. Values in parenthesis are for the corresponding triplet.

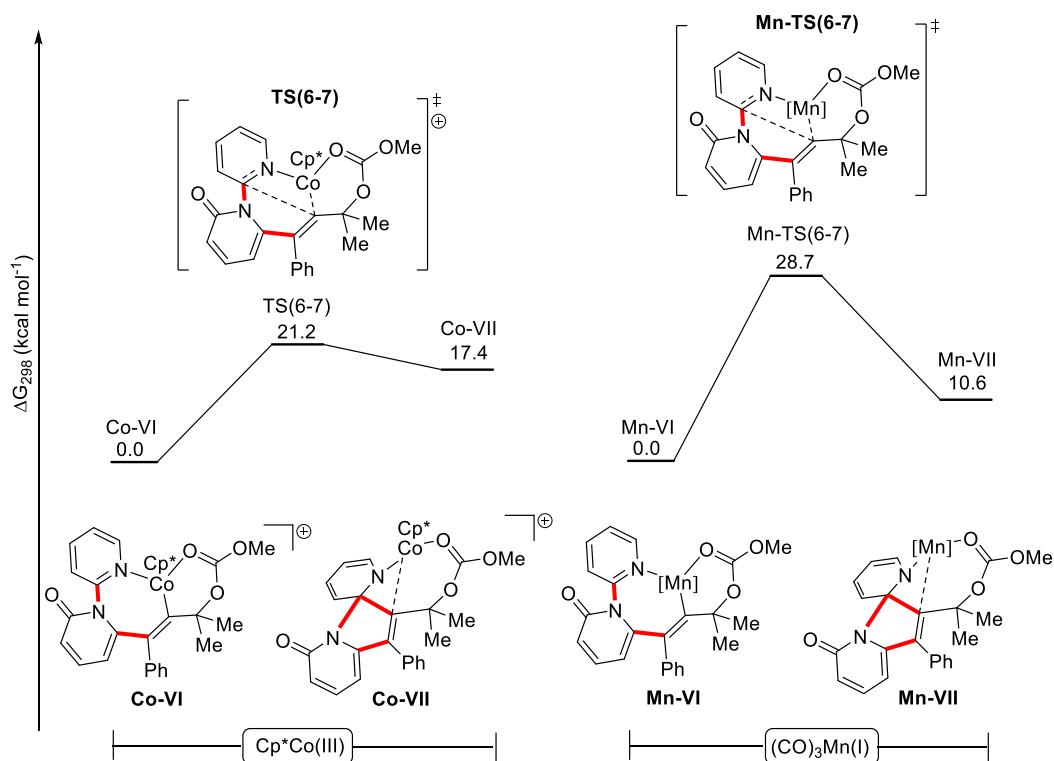


Figure S9. Gibbs free energy profile in kcal mol⁻¹ for the nucleophilic attack from intermediate **Co-VI** versus **Mn-VI** at the PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)//TPSS-D3(BJ)/def2-TZVP level of theory for cobalt complex and at the PW6B95-D3(BJ)/def2-TZVP+COSMO(DME)//TPSS-D3(BJ)/def2-TZVP for the manganese complex. [Mn] = MnCO₃, DME = 1,2-dimethoxyethane, TFE = 2,2,2-trifluoroethanol.

Cartesian Coordinates and Energies

Acetic Acid

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -229.461356 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -228.945310 E_h

$\Delta\Delta H(298)$ = 0.065121 E_h

S(298) = 0.032926 E_h

Lowest frequency: 64.07 cm⁻¹

Charge = 0, Multiplicity = 1

| | | | |
|---|-----------|-----------|-----------|
| C | -2.658792 | 0.579267 | 0.004988 |
| C | -3.220475 | -0.133015 | 1.207787 |
| O | -3.914318 | 0.353119 | 2.073882 |
| O | -2.847350 | -1.449400 | 1.218990 |
| H | -3.247872 | -1.836941 | 2.021430 |
| H | -3.016111 | 0.097495 | -0.910590 |
| H | -2.967017 | 1.623748 | 0.024625 |
| H | -1.566660 | 0.507361 | 0.008102 |

1a

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -571.572290 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -570.193786 E_h

$\Delta\Delta H(298)$ = 0.168948 E_h

S(298) = 0.046617 E_h

Lowest frequency: 58.73 cm⁻¹

Charge = 0, Multiplicity = 1

| | | | |
|---|-----------|-----------|----------|
| N | -0.120180 | 0.796402 | 1.202363 |
| C | 0.980567 | 1.498311 | 1.481551 |
| C | -0.958183 | 0.515492 | 2.208751 |
| C | -0.739953 | 0.926098 | 3.520444 |
| C | 0.420623 | 1.648998 | 3.794725 |
| H | -1.842635 | -0.057870 | 1.939363 |
| H | 0.640735 | 1.979430 | 4.805580 |
| H | -1.454662 | 0.684025 | 4.300447 |
| N | 1.845766 | 1.731980 | 0.356815 |

| | | | |
|---|----------|-----------|-----------|
| C | 1.842638 | 0.792137 | -0.649310 |
| C | 1.308299 | 1.946068 | 2.765976 |
| H | 2.212950 | 2.510137 | 2.938717 |
| C | 2.629186 | 2.941335 | 0.272348 |
| C | 3.417559 | 3.046309 | -0.932525 |
| H | 4.014970 | 3.947440 | -1.013955 |
| C | 3.408287 | 2.092436 | -1.908651 |
| C | 2.601789 | 0.932602 | -1.770591 |
| H | 4.019920 | 2.221047 | -2.798071 |
| H | 2.581446 | 0.160028 | -2.529440 |
| O | 2.591277 | 3.790419 | 1.163119 |
| H | 1.185315 | -0.048340 | -0.470030 |

2a

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -730.657486 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -728.911823 E_h

$\Delta\Delta H(298) = 0.251941 \text{ E}_h$

S(298) = 0.057597 E_h

Lowest frequency: 13.87 cm⁻¹

Charge = 0, Multiplicity = 1

| | | | |
|---|-----------|-----------|-----------|
| C | -2.945514 | -5.730718 | -2.816866 |
| C | -4.061885 | -5.707234 | -3.288379 |
| C | -1.631473 | -5.673156 | -2.274517 |
| C | -0.955146 | -4.438975 | -2.212387 |
| C | -0.990158 | -6.829323 | -1.792266 |
| C | 0.327403 | -4.369684 | -1.678460 |
| H | -1.452990 | -3.549370 | -2.584940 |
| C | 0.295079 | -6.750070 | -1.264873 |
| H | -1.510690 | -7.780787 | -1.838068 |
| C | 0.957345 | -5.522494 | -1.204685 |
| H | 0.839050 | -3.412457 | -1.633313 |
| H | 0.781411 | -7.649112 | -0.897126 |
| H | 1.959666 | -5.464377 | -0.790320 |
| C | -5.409054 | -5.714827 | -3.848903 |
| O | -6.263108 | -4.726777 | -3.130784 |
| C | -5.843685 | -3.447737 | -3.084911 |
| O | -4.867246 | -2.964966 | -3.617840 |
| C | -5.415063 | -5.402596 | -5.351087 |
| H | -4.925367 | -4.448771 | -5.546470 |

| | | | |
|---|-----------|-----------|-----------|
| H | -4.880198 | -6.195136 | -5.882217 |
| H | -6.449273 | -5.371255 | -5.708084 |
| C | -6.113501 | -7.043336 | -3.550179 |
| H | -6.141498 | -7.221064 | -2.473111 |
| H | -7.135533 | -7.011170 | -3.938289 |
| H | -5.568691 | -7.858673 | -4.032786 |
| O | -6.732336 | -2.777089 | -2.319757 |
| C | -6.428945 | -1.369268 | -2.174468 |
| H | -6.425515 | -0.880775 | -3.151784 |
| H | -7.225746 | -0.975727 | -1.544006 |
| H | -5.454063 | -1.241927 | -1.698025 |

Intermediate **Co-I**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2574.672937 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2570.816968 E_h

$\Delta\Delta H(298) = 0.461560 \text{ E}_h$

S(298) = 0.086205 E_h

Lowest frequency: 26.11 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | 1.312965 | -0.072035 | -0.185041 |
| C | 1.317692 | -0.937436 | 1.692809 |
| C | 2.631319 | -0.537857 | 1.281850 |
| C | 0.797726 | -1.852952 | 0.711038 |
| C | 2.952167 | -1.253035 | 0.058263 |
| C | 1.822257 | -2.053153 | -0.286872 |
| C | 0.601335 | -0.472959 | 2.916240 |
| H | -0.481629 | -0.419922 | 2.772053 |
| H | 0.959610 | 0.505997 | 3.243179 |
| H | 0.795631 | -1.184339 | 3.729333 |
| C | 3.541146 | 0.416785 | 1.982345 |
| H | 2.994201 | 1.060822 | 2.674142 |
| H | 4.286728 | -0.139120 | 2.564981 |
| H | 4.083089 | 1.043948 | 1.268640 |
| C | -0.486584 | -2.610699 | 0.780076 |
| H | -1.119849 | -2.250856 | 1.590958 |
| H | -0.270408 | -3.669946 | 0.968948 |
| H | -1.043432 | -2.554378 | -0.159292 |
| C | 4.235960 | -1.140274 | -0.694147 |
| H | 4.126695 | -1.470967 | -1.729049 |

| | | | |
|---|-----------|-----------|-----------|
| H | 4.994757 | -1.774038 | -0.217952 |
| H | 4.607010 | -0.112944 | -0.694567 |
| C | 1.673329 | -2.920300 | -1.491436 |
| H | 0.654426 | -2.876133 | -1.883374 |
| H | 1.883589 | -3.962105 | -1.217260 |
| H | 2.364622 | -2.634557 | -2.286087 |
| O | 2.355024 | 1.275700 | -1.228140 |
| C | 1.671850 | 0.985934 | -2.272918 |
| O | 0.795450 | 0.065147 | -2.121494 |
| C | 1.865431 | 1.699893 | -3.571469 |
| C | -1.240503 | 1.365417 | 0.605748 |
| N | 0.095031 | 1.388610 | 0.414068 |
| C | -1.920527 | 2.399183 | 1.249680 |
| C | -1.214841 | 3.502846 | 1.702175 |
| H | -2.991828 | 2.315638 | 1.381357 |
| H | -1.729738 | 4.315474 | 2.203853 |
| C | 0.161920 | 3.549977 | 1.481021 |
| C | 0.772350 | 2.491209 | 0.834323 |
| H | 0.761025 | 4.395365 | 1.800497 |
| H | 1.833117 | 2.490431 | 0.622659 |
| H | 2.899602 | 2.035570 | -3.668019 |
| H | 1.587639 | 1.052671 | -4.405240 |
| H | 1.216286 | 2.583414 | -3.588557 |
| C | -2.032784 | -0.021141 | -1.224533 |
| C | -2.848361 | -0.408289 | 1.084421 |
| C | -2.885130 | -0.957400 | -1.724323 |
| H | -1.344208 | 0.544025 | -1.836658 |
| C | -3.763772 | -1.352232 | 0.502116 |
| H | -2.890964 | -1.157573 | -2.788470 |
| H | -4.433525 | -1.848118 | 1.195497 |
| N | -2.004824 | 0.260465 | 0.124224 |
| C | -3.777602 | -1.619340 | -0.838326 |
| H | -4.481372 | -2.345775 | -1.234863 |
| O | -2.716850 | -0.151916 | 2.283299 |

Intermediate **Co-II**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2574.647513 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2570.794000 E_h

$\Delta\Delta H(298) = 0.458495$ E_h

S(298) = 0.083336 E_h

Lowest frequency: 12.58 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -1.610948 | -0.662024 | -0.884240 |
| C | -1.113454 | -0.163126 | -2.847145 |
| C | -2.130878 | 0.703962 | -2.351647 |
| C | -1.622821 | -1.523493 | -2.792387 |
| C | -3.252846 | -0.106245 | -1.939047 |
| C | -2.937777 | -1.482328 | -2.254561 |
| N | -1.201774 | 0.761457 | 0.378672 |
| C | 0.102066 | 1.085678 | 0.530895 |
| C | -2.139723 | 1.415867 | 1.090636 |
| C | -1.812834 | 2.462120 | 1.936980 |
| C | -0.470641 | 2.826826 | 2.062691 |
| H | -3.156045 | 1.064779 | 0.959810 |
| H | -2.594197 | 2.974324 | 2.486688 |
| H | -0.180749 | 3.639140 | 2.721095 |
| N | 0.976275 | 0.228481 | -0.163527 |
| C | 0.469190 | -1.052015 | -0.426917 |
| O | -2.609217 | -1.585720 | 0.471170 |
| C | -2.068438 | -2.005551 | 1.585570 |
| O | -0.859047 | -1.908552 | 1.854635 |
| C | -3.035758 | -2.624123 | 2.571828 |
| H | -0.252834 | -1.439301 | 0.389457 |
| C | 0.506994 | 2.130543 | 1.362083 |
| H | 1.557109 | 2.370319 | 1.446997 |
| C | -2.045889 | 2.191956 | -2.269439 |
| H | -1.018460 | 2.531694 | -2.120309 |
| H | -2.406581 | 2.624059 | -3.211285 |
| H | -2.665774 | 2.591027 | -1.463741 |
| C | -4.552944 | 0.367602 | -1.379440 |
| H | -4.491565 | 1.398907 | -1.025498 |
| H | -5.326655 | 0.331666 | -2.156950 |
| H | -4.881098 | -0.274453 | -0.556964 |
| C | -3.845046 | -2.641409 | -2.022181 |
| H | -3.312152 | -3.591282 | -2.091674 |
| H | -4.313495 | -2.573792 | -1.037302 |
| H | -4.639520 | -2.639259 | -2.779090 |
| C | -0.945699 | -2.740957 | -3.334797 |
| H | -1.088133 | -3.610130 | -2.687335 |
| H | -1.382156 | -2.985317 | -4.311665 |
| H | 0.123357 | -2.578994 | -3.476215 |
| C | 0.182789 | 0.268978 | -3.448915 |
| H | 0.047156 | 0.429700 | -4.525979 |

| | | | |
|---|-----------|-----------|-----------|
| H | 0.536006 | 1.208671 | -3.018660 |
| H | 0.960632 | -0.485115 | -3.321257 |
| H | -3.171007 | -1.925785 | 3.404838 |
| H | -4.002418 | -2.827608 | 2.110860 |
| H | -2.600912 | -3.540321 | 2.977454 |
| C | 2.272418 | 0.671911 | -0.605043 |
| C | 3.063449 | -0.370731 | -1.227401 |
| H | 4.061691 | -0.073595 | -1.528909 |
| C | 2.591821 | -1.637184 | -1.428892 |
| C | 1.275362 | -1.983563 | -1.034015 |
| H | 3.230633 | -2.387987 | -1.885527 |
| H | 0.907711 | -2.996088 | -1.143494 |
| O | 2.623963 | 1.836320 | -0.459030 |

Transition state **TS(2-3)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2574.642341 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2570.791517 E_h

$\Delta\Delta H(298) = 0.455334 \text{ E}_h$

S(298) = 0.080149 E_h

Lowest frequency: -429.55 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -1.504647 | -0.087992 | -0.571538 |
| C | -2.071090 | 0.986057 | -2.255384 |
| C | -3.199940 | 0.706256 | -1.409321 |
| C | -1.473052 | -0.257631 | -2.635990 |
| C | -3.333536 | -0.730962 | -1.325193 |
| C | -2.278898 | -1.325135 | -2.072817 |
| N | -0.399393 | 1.378115 | 0.052265 |
| C | 0.934430 | 1.246524 | -0.138077 |
| C | -0.886228 | 2.482758 | 0.651197 |
| C | -0.062432 | 3.527755 | 1.033054 |
| C | 1.310127 | 3.413559 | 0.800562 |
| H | -1.956969 | 2.492942 | 0.815363 |
| H | -0.488560 | 4.406530 | 1.503340 |
| H | 1.984812 | 4.212571 | 1.090263 |
| N | 1.296925 | -0.013392 | -0.641755 |
| C | 0.336131 | -1.027356 | -0.436986 |
| O | -2.287142 | -0.242583 | 1.194666 |
| C | -1.588998 | -0.634374 | 2.204774 |

| | | | |
|---|-----------|-----------|-----------|
| O | -0.381512 | -0.985189 | 2.117734 |
| C | -2.277190 | -0.672315 | 3.545853 |
| H | -0.147824 | -0.990419 | 0.732549 |
| C | 1.825108 | 2.262708 | 0.216679 |
| H | 2.881892 | 2.132651 | 0.034497 |
| C | -4.133609 | 1.692407 | -0.786723 |
| H | -3.728326 | 2.706370 | -0.812354 |
| H | -5.084874 | 1.704770 | -1.333197 |
| H | -4.352631 | 1.423398 | 0.250849 |
| C | -4.399864 | -1.448387 | -0.569383 |
| H | -4.591022 | -0.964176 | 0.391022 |
| H | -5.331393 | -1.430578 | -1.149404 |
| H | -4.134472 | -2.491842 | -0.389429 |
| C | -2.131366 | -2.786244 | -2.353547 |
| H | -1.140165 | -3.025624 | -2.739868 |
| H | -2.320812 | -3.396129 | -1.466241 |
| H | -2.868173 | -3.077111 | -3.113166 |
| C | -0.316320 | -0.422505 | -3.566785 |
| H | 0.246439 | -1.332676 | -3.351648 |
| H | -0.682017 | -0.490401 | -4.599037 |
| H | 0.368191 | 0.427183 | -3.515031 |
| C | -1.592064 | 2.339114 | -2.665688 |
| H | -2.060441 | 2.609512 | -3.620331 |
| H | -1.860922 | 3.106042 | -1.936262 |
| H | -0.509523 | 2.359128 | -2.810469 |
| H | -1.689549 | -0.095647 | 4.265567 |
| H | -3.290144 | -0.276288 | 3.478483 |
| H | -2.303548 | -1.707460 | 3.899871 |
| C | 2.545133 | -0.217466 | -1.331475 |
| C | 2.803510 | -1.600136 | -1.673617 |
| H | 3.757713 | -1.786895 | -2.153371 |
| C | 1.911601 | -2.600928 | -1.413846 |
| C | 0.664133 | -2.311913 | -0.806360 |
| H | 2.157132 | -3.627604 | -1.671627 |
| H | -0.028121 | -3.110355 | -0.569557 |
| O | 3.284451 | 0.724155 | -1.594181 |

Intermediate **Co-III**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2574.661839 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2570.812605 E_h

$\Delta\Delta H(298) = 0.460097 \text{ E}_h$

S(298) = 0.083639 E_h

Lowest frequency: 9.23 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -1.460918 | -0.106595 | -0.692351 |
| C | -1.894005 | 0.810899 | -2.458443 |
| C | -3.064161 | 0.954009 | -1.607663 |
| C | -1.689892 | -0.592180 | -2.701749 |
| C | -3.498674 | -0.341220 | -1.256473 |
| C | -2.623502 | -1.314510 | -1.894494 |
| N | -0.602728 | 1.409745 | 0.139169 |
| C | 0.737267 | 1.505899 | -0.059064 |
| C | -1.244160 | 2.356136 | 0.852842 |
| C | -0.592762 | 3.471635 | 1.350086 |
| C | 0.772900 | 3.606117 | 1.094035 |
| H | -2.300864 | 2.184204 | 1.014140 |
| H | -1.144675 | 4.212258 | 1.917412 |
| H | 1.317320 | 4.472962 | 1.454669 |
| N | 1.275295 | 0.357420 | -0.662791 |
| C | 0.357179 | -0.696523 | -0.826556 |
| O | -1.969829 | -0.815762 | 1.089244 |
| C | -1.344130 | -1.425077 | 1.978904 |
| O | -0.110603 | -1.865964 | 1.838807 |
| C | -1.960662 | -1.715010 | 3.311310 |
| H | 0.205223 | -1.675508 | 0.907155 |
| C | 1.454256 | 2.620915 | 0.389663 |
| H | 2.512782 | 2.683719 | 0.185648 |
| C | -3.720229 | 2.250492 | -1.255118 |
| H | -2.996337 | 3.064954 | -1.173957 |
| H | -4.429930 | 2.524517 | -2.045804 |
| H | -4.283265 | 2.185629 | -0.320412 |
| C | -4.643648 | -0.688946 | -0.364714 |
| H | -4.950784 | 0.159355 | 0.250264 |
| H | -5.504248 | -0.995302 | -0.972430 |
| H | -4.391581 | -1.521938 | 0.296006 |
| C | -2.797986 | -2.798682 | -1.830215 |
| H | -1.890928 | -3.324323 | -2.136956 |
| H | -3.063480 | -3.126295 | -0.821267 |
| H | -3.605745 | -3.115533 | -2.501998 |
| C | -0.736234 | -1.157982 | -3.702055 |
| H | -0.505769 | -2.205416 | -3.504949 |
| H | -1.203081 | -1.096248 | -4.693544 |
| H | 0.200847 | -0.598525 | -3.738815 |

| | | | |
|---|-----------|-----------|-----------|
| C | -1.127486 | 1.929087 | -3.087675 |
| H | -1.597542 | 2.219908 | -4.035714 |
| H | -1.106526 | 2.812314 | -2.444498 |
| H | -0.097555 | 1.635741 | -3.304356 |
| H | -1.335450 | -1.284298 | 4.099770 |
| H | -2.967340 | -1.303270 | 3.359157 |
| H | -1.984264 | -2.797512 | 3.472290 |
| C | 2.695552 | 0.250068 | -0.978256 |
| C | 3.127048 | -1.094670 | -1.267104 |
| H | 4.189621 | -1.213915 | -1.444198 |
| C | 2.255368 | -2.139419 | -1.322306 |
| C | 0.857610 | -1.937987 | -1.129905 |
| H | 2.620643 | -3.140191 | -1.537878 |
| H | 0.172695 | -2.769127 | -1.253707 |
| O | 3.415998 | 1.240874 | -0.973422 |

Intermediate **Co-IV**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.853137 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.776195 E_h

$\Delta\Delta H(298) = 0.648638$ E_h

S(298) = 0.105377 E_h

Lowest frequency: 15.97 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.390133 | -4.553923 | -6.538273 |
| C | -1.068100 | -4.212202 | -8.166159 |
| C | -2.434951 | -4.123650 | -8.582240 |
| C | -0.861719 | -5.520216 | -7.617855 |
| C | -3.052229 | -5.416488 | -8.389877 |
| C | -2.087230 | -6.266535 | -7.786446 |
| N | -3.959311 | -3.461507 | -6.217764 |
| C | -3.742199 | -2.197303 | -5.769354 |
| C | -5.217415 | -3.864228 | -6.493966 |
| C | -6.309314 | -3.025722 | -6.362876 |
| C | -6.092231 | -1.722972 | -5.914345 |
| H | -5.318737 | -4.895316 | -6.797522 |
| H | -6.921270 | -1.032752 | -5.794942 |
| H | -7.300488 | -3.396614 | -6.598153 |
| N | -2.393101 | -1.939492 | -5.501033 |
| C | -1.529119 | -3.019152 | -5.725588 |

| | | | |
|---|-----------|-----------|------------|
| C | -1.874183 | -5.445059 | -4.638820 |
| C | -3.002340 | -5.809788 | -5.054142 |
| C | -4.806858 | -1.299292 | -5.607459 |
| H | -4.594927 | -0.302741 | -5.251438 |
| C | -4.387655 | -5.829539 | -8.919553 |
| H | -4.884924 | -6.557086 | -8.276021 |
| H | -5.049058 | -4.972608 | -9.063900 |
| H | -4.242997 | -6.294919 | -9.903438 |
| C | -2.260170 | -7.713620 | -7.467572 |
| H | -1.732870 | -7.982916 | -6.549111 |
| H | -3.313442 | -7.972049 | -7.355428 |
| H | -1.838756 | -8.316958 | -8.281778 |
| C | 0.447854 | -6.091677 | -7.181198 |
| H | 0.310367 | -7.023105 | -6.631182 |
| H | 1.061474 | -6.314230 | -8.063383 |
| H | 1.016171 | -5.402686 | -6.552099 |
| C | -0.019589 | -3.184353 | -8.436092 |
| H | 0.289834 | -3.283391 | -9.485257 |
| H | -0.390144 | -2.167925 | -8.290018 |
| H | 0.862107 | -3.324378 | -7.810671 |
| C | -3.069960 | -2.929608 | -9.217537 |
| H | -2.638293 | -2.000229 | -8.838088 |
| H | -2.906057 | -2.954287 | -10.302235 |
| H | -4.148607 | -2.907486 | -9.046090 |
| C | -1.942950 | -0.636052 | -4.988426 |
| C | -0.540906 | -0.581311 | -4.690878 |
| H | -0.186359 | 0.365088 | -4.299948 |
| C | 0.284042 | -1.648548 | -4.890099 |
| C | -0.209159 | -2.870074 | -5.411098 |
| H | 1.340277 | -1.569122 | -4.645407 |
| H | 0.465150 | -3.706008 | -5.536488 |
| O | -2.733791 | 0.290281 | -4.842810 |
| C | -0.771868 | -5.363439 | -3.730568 |
| C | -0.689185 | -4.303005 | -2.806541 |
| C | 0.201647 | -6.379082 | -3.699008 |
| C | 0.342228 | -4.266492 | -1.876437 |
| H | -1.441415 | -3.522143 | -2.824454 |
| C | 1.235225 | -6.330675 | -2.768597 |
| H | 0.126535 | -7.211534 | -4.389871 |
| C | 1.310715 | -5.273533 | -1.860135 |
| H | 0.392409 | -3.450765 | -1.161945 |
| H | 1.977817 | -7.122253 | -2.747116 |
| H | 2.117520 | -5.238739 | -1.134609 |
| C | -4.198943 | -6.572501 | -4.575941 |

| | | | |
|---|-----------|-----------|-----------|
| O | -4.991595 | -6.877365 | -5.788509 |
| C | -6.144603 | -7.579866 | -5.656523 |
| O | -6.626273 | -8.030927 | -4.643827 |
| C | -3.713670 | -7.873100 | -3.919761 |
| H | -3.205043 | -8.502822 | -4.653044 |
| H | -3.008611 | -7.624832 | -3.122214 |
| H | -4.560987 | -8.414053 | -3.496426 |
| C | -5.006380 | -5.707517 | -3.598350 |
| H | -5.858395 | -6.273407 | -3.218945 |
| H | -4.357663 | -5.431483 | -2.763154 |
| H | -5.357821 | -4.794027 | -4.081399 |
| O | -6.662592 | -7.679410 | -6.896361 |
| C | -7.910350 | -8.430500 | -6.959450 |
| H | -8.666397 | -7.943514 | -6.341182 |
| H | -8.189735 | -8.414177 | -8.011476 |
| H | -7.744255 | -9.451134 | -6.610825 |

Transition state TS(4-5)

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.840811 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.765221 E_h

ΔΔH(298) = 0.646859 E_h

S(298) = 0.104055 E_h

Lowest frequency: -315.36 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.411136 | -4.586567 | -6.803965 |
| C | -1.131957 | -4.181108 | -8.443555 |
| C | -2.492567 | -4.164455 | -8.849234 |
| C | -0.861633 | -5.480595 | -7.871618 |
| C | -3.068600 | -5.471432 | -8.580341 |
| C | -2.052672 | -6.276386 | -7.985748 |
| N | -3.922342 | -3.447736 | -6.338455 |
| C | -3.655721 | -2.382861 | -5.541149 |
| C | -5.203691 | -3.744688 | -6.641668 |
| C | -6.264420 | -2.977238 | -6.194965 |
| C | -5.996013 | -1.895259 | -5.355980 |
| H | -5.351435 | -4.638888 | -7.228340 |
| H | -6.804156 | -1.289749 | -4.958608 |
| H | -7.275747 | -3.243174 | -6.480845 |
| N | -2.287876 | -2.195660 | -5.310144 |

| | | | |
|---|-----------|-----------|------------|
| C | -1.466178 | -3.297538 | -5.620453 |
| C | -1.937634 | -4.884733 | -4.674390 |
| C | -2.925416 | -5.543961 | -5.194683 |
| C | -4.685425 | -1.597356 | -5.007839 |
| H | -4.437841 | -0.773491 | -4.356972 |
| C | -4.397795 | -5.955027 | -9.065346 |
| H | -4.893148 | -6.606787 | -8.343543 |
| H | -5.064489 | -5.126059 | -9.314234 |
| H | -4.246516 | -6.530672 | -9.988144 |
| C | -2.161995 | -7.726493 | -7.644153 |
| H | -1.504084 | -7.992356 | -6.813222 |
| H | -3.186672 | -7.997566 | -7.387001 |
| H | -1.855941 | -8.327220 | -8.510382 |
| C | 0.460162 | -5.993760 | -7.391832 |
| H | 0.385693 | -6.447772 | -6.399406 |
| H | 0.825460 | -6.766990 | -8.078612 |
| H | 1.211774 | -5.203539 | -7.355360 |
| C | -0.152126 | -3.073952 | -8.659931 |
| H | 0.182708 | -3.088111 | -9.704535 |
| H | -0.596907 | -2.094850 | -8.464907 |
| H | 0.728037 | -3.177873 | -8.024471 |
| C | -3.201070 | -3.019864 | -9.497437 |
| H | -2.755092 | -2.062908 | -9.217069 |
| H | -3.136186 | -3.113315 | -10.588804 |
| H | -4.261069 | -2.998430 | -9.231615 |
| C | -1.768319 | -0.891862 | -4.895575 |
| C | -0.334705 | -0.811715 | -4.874722 |
| H | 0.072251 | 0.151972 | -4.592003 |
| C | 0.460394 | -1.881152 | -5.186007 |
| C | -0.097941 | -3.124477 | -5.534293 |
| H | 1.541708 | -1.779740 | -5.146310 |
| H | 0.539364 | -3.987391 | -5.668741 |
| O | -2.533554 | 0.026569 | -4.623675 |
| C | -1.017364 | -5.003871 | -3.544637 |
| C | -0.896140 | -3.968507 | -2.602262 |
| C | -0.278747 | -6.184948 | -3.368553 |
| C | -0.066026 | -4.123673 | -1.498519 |
| H | -1.463834 | -3.052952 | -2.734274 |
| C | 0.562582 | -6.328875 | -2.266742 |
| H | -0.367346 | -6.982586 | -4.099265 |
| C | 0.668751 | -5.301174 | -1.330324 |
| H | 0.009207 | -3.326370 | -0.765642 |
| H | 1.133314 | -7.243875 | -2.140614 |
| H | 1.321550 | -5.415180 | -0.470523 |

| | | | |
|---|-----------|-----------|-----------|
| C | -3.983861 | -6.457613 | -4.660842 |
| O | -4.839272 | -6.762860 | -5.832796 |
| C | -5.951080 | -7.514321 | -5.650865 |
| O | -6.341015 | -8.032694 | -4.629928 |
| C | -3.380594 | -7.748661 | -4.093631 |
| H | -2.821588 | -8.286504 | -4.861897 |
| H | -2.702055 | -7.493422 | -3.276417 |
| H | -4.178576 | -8.385575 | -3.708578 |
| C | -4.786897 | -5.689310 | -3.598463 |
| H | -5.563376 | -6.330025 | -3.179019 |
| H | -4.103182 | -5.380116 | -2.803688 |
| H | -5.241574 | -4.796580 | -4.034605 |
| O | -6.559101 | -7.581053 | -6.852815 |
| C | -7.776005 | -8.382458 | -6.857813 |
| H | -8.503048 | -7.954871 | -6.165237 |
| H | -8.134110 | -8.335181 | -7.884865 |
| H | -7.544043 | -9.408571 | -6.567628 |

Intermediate Co-V

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.866275 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.788686 E_h

$\Delta\Delta H(298) = 0.649516 \text{ E}_h$

S(298) = 0.106509 E_h

Lowest frequency: 19.12 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.654997 | -4.519216 | -7.059696 |
| C | -1.174517 | -4.350637 | -8.524518 |
| C | -2.450646 | -4.049163 | -9.111053 |
| C | -1.213013 | -5.666865 | -7.951947 |
| C | -3.280960 | -5.195072 | -8.905512 |
| C | -2.514813 | -6.214978 | -8.229081 |
| N | -4.226221 | -3.626531 | -6.360000 |
| C | -3.586982 | -2.704753 | -5.631158 |
| C | -5.556147 | -3.759566 | -6.252411 |
| C | -6.275964 | -2.926899 | -5.398605 |
| C | -5.603518 | -1.974466 | -4.634208 |
| H | -6.017510 | -4.547875 | -6.833859 |
| H | -6.151459 | -1.326841 | -3.957833 |
| H | -7.352285 | -3.037641 | -5.328734 |

| | | | |
|---|-----------|-----------|------------|
| N | -2.161548 | -2.695377 | -5.951248 |
| C | -1.240565 | -3.297644 | -5.025173 |
| C | -1.688034 | -4.565160 | -4.464601 |
| C | -2.535382 | -5.292557 | -5.248878 |
| C | -4.214850 | -1.852986 | -4.746747 |
| H | -3.649652 | -1.117635 | -4.185577 |
| C | -4.697522 | -5.343383 | -9.350134 |
| H | -5.257868 | -5.997708 | -8.677896 |
| H | -5.198228 | -4.374310 | -9.416018 |
| H | -4.720715 | -5.793520 | -10.351463 |
| C | -2.917265 | -7.646106 | -8.111921 |
| H | -2.471141 | -8.138791 | -7.248689 |
| H | -3.999519 | -7.762250 | -8.065044 |
| H | -2.559407 | -8.166847 | -9.011348 |
| C | -0.061184 | -6.368448 | -7.306408 |
| H | -0.403740 | -7.185195 | -6.668146 |
| H | 0.605628 | -6.791196 | -8.068172 |
| H | 0.526415 | -5.680846 | -6.691662 |
| C | 0.028110 | -3.467695 | -8.522257 |
| H | 0.735177 | -3.836310 | -9.276933 |
| H | -0.218728 | -2.435279 | -8.771287 |
| H | 0.544786 | -3.488686 | -7.558707 |
| C | -2.828309 | -2.816667 | -9.869266 |
| H | -2.203331 | -1.964350 | -9.602579 |
| H | -2.721090 | -2.998238 | -10.946271 |
| H | -3.865889 | -2.532599 | -9.677953 |
| C | -1.825384 | -1.429368 | -6.672069 |
| C | -0.536055 | -0.882733 | -6.366781 |
| H | -0.283738 | 0.045209 | -6.867094 |
| C | 0.290674 | -1.464629 | -5.446630 |
| C | -0.046130 | -2.677681 | -4.789469 |
| H | 1.245596 | -0.998279 | -5.219759 |
| H | 0.651121 | -3.151116 | -4.108268 |
| O | -2.681837 | -0.949619 | -7.398041 |
| C | -1.165563 | -4.883113 | -3.102379 |
| C | -1.514385 | -4.084930 | -2.002119 |
| C | -0.261317 | -5.936073 | -2.912710 |
| C | -1.003917 | -4.359790 | -0.736303 |
| H | -2.203535 | -3.255990 | -2.142052 |
| C | 0.257153 | -6.207044 | -1.645837 |
| H | 0.045768 | -6.533409 | -3.766089 |
| C | -0.119077 | -5.425220 | -0.554586 |
| H | -1.294875 | -3.744028 | 0.109502 |
| H | 0.957519 | -7.026328 | -1.513826 |

| | | | |
|---|-----------|-----------|-----------|
| H | 0.280116 | -5.638608 | 0.432140 |
| C | -3.405129 | -6.418115 | -4.717743 |
| O | -4.409046 | -6.605146 | -5.812604 |
| C | -5.418691 | -7.479552 | -5.661436 |
| O | -5.620114 | -8.263224 | -4.761232 |
| C | -2.651256 | -7.727068 | -4.460904 |
| H | -1.999237 | -7.984930 | -5.297228 |
| H | -2.033034 | -7.602069 | -3.570443 |
| H | -3.360184 | -8.537146 | -4.283580 |
| C | -4.169381 | -5.958698 | -3.467433 |
| H | -4.864187 | -6.737736 | -3.149491 |
| H | -3.461862 | -5.765103 | -2.660261 |
| H | -4.719946 | -5.037539 | -3.677249 |
| O | -6.212175 | -7.329146 | -6.753586 |
| C | -7.353288 | -8.233243 | -6.780299 |
| H | -7.988672 | -8.054716 | -5.911079 |
| H | -7.875786 | -7.994549 | -7.705556 |
| H | -7.007163 | -9.268277 | -6.779383 |

Transition state **TS(5-6a)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.862610 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.788357 E_h

$\Delta\Delta H(298) = 0.649091$ E_h

S(298) = 0.105011 E_h

Lowest frequency: -104.63 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.718552 | -4.695670 | -7.075659 |
| C | -1.286542 | -4.383212 | -8.506939 |
| C | -2.573713 | -4.103719 | -9.086972 |
| C | -1.255700 | -5.744417 | -8.025685 |
| C | -3.355914 | -5.279943 | -8.934077 |
| C | -2.532480 | -6.313728 | -8.310294 |
| N | -4.090681 | -3.548909 | -6.332982 |
| C | -3.502277 | -2.550043 | -5.658411 |
| C | -5.428374 | -3.697541 | -6.271497 |
| C | -6.216250 | -2.810145 | -5.551189 |
| C | -5.606744 | -1.763858 | -4.859337 |
| H | -5.839126 | -4.552438 | -6.793463 |
| H | -6.200576 | -1.061119 | -4.284368 |

| | | | |
|---|-----------|-----------|------------|
| H | -7.291609 | -2.946705 | -5.530227 |
| N | -2.068700 | -2.456573 | -5.788861 |
| C | -1.204484 | -3.249325 | -5.006281 |
| C | -1.709246 | -4.522418 | -4.463607 |
| C | -2.517018 | -5.305518 | -5.227087 |
| C | -4.221027 | -1.630055 | -4.912016 |
| H | -3.702194 | -0.827390 | -4.401247 |
| C | -4.775843 | -5.472082 | -9.344417 |
| H | -5.312578 | -6.101353 | -8.629229 |
| H | -5.296905 | -4.517964 | -9.449463 |
| H | -4.808763 | -5.977487 | -10.319066 |
| C | -2.924699 | -7.745034 | -8.188896 |
| H | -2.414233 | -8.248440 | -7.367758 |
| H | -4.001081 | -7.862226 | -8.064787 |
| H | -2.635446 | -8.252466 | -9.120376 |
| C | -0.066977 | -6.420524 | -7.421472 |
| H | -0.357908 | -7.319644 | -6.875283 |
| H | 0.643670 | -6.714477 | -8.203674 |
| H | 0.453849 | -5.754082 | -6.728115 |
| C | -0.145094 | -3.432743 | -8.427123 |
| H | 0.606928 | -3.726703 | -9.172470 |
| H | -0.450728 | -2.408462 | -8.641227 |
| H | 0.343999 | -3.469208 | -7.449156 |
| C | -2.999901 | -2.798728 | -9.681249 |
| H | -2.737384 | -1.952416 | -9.038685 |
| H | -2.513896 | -2.652360 | -10.653371 |
| H | -4.079733 | -2.774612 | -9.842228 |
| C | -1.649830 | -1.223444 | -6.443542 |
| C | -0.304539 | -0.817463 | -6.157423 |
| H | 0.017201 | 0.117719 | -6.600995 |
| C | 0.506499 | -1.562729 | -5.346613 |
| C | 0.069944 | -2.788972 | -4.788370 |
| H | 1.516815 | -1.221625 | -5.137833 |
| H | 0.734905 | -3.393540 | -4.183711 |
| O | -2.469156 | -0.632977 | -7.146402 |
| C | -1.202320 | -4.828723 | -3.088894 |
| C | -1.571597 | -4.023614 | -2.000690 |
| C | -0.298413 | -5.877272 | -2.877024 |
| C | -1.083157 | -4.289735 | -0.724599 |
| H | -2.259026 | -3.196342 | -2.157609 |
| C | 0.198910 | -6.139014 | -1.599299 |
| H | 0.028012 | -6.476068 | -3.722165 |
| C | -0.199083 | -5.351983 | -0.519962 |
| H | -1.389965 | -3.668736 | 0.111749 |

| | | | |
|---|-----------|-----------|-----------|
| H | 0.900421 | -6.954455 | -1.450151 |
| H | 0.183389 | -5.557739 | 0.474970 |
| C | -3.349749 | -6.455876 | -4.689959 |
| O | -4.366940 | -6.631007 | -5.791257 |
| C | -5.363315 | -7.524418 | -5.652457 |
| O | -5.539289 | -8.336317 | -4.773082 |
| C | -2.570555 | -7.758539 | -4.498323 |
| H | -1.931847 | -7.968163 | -5.358467 |
| H | -1.936372 | -7.656252 | -3.616192 |
| H | -3.259523 | -8.589296 | -4.338695 |
| C | -4.113641 | -6.050707 | -3.425074 |
| H | -4.787870 | -6.852611 | -3.120589 |
| H | -3.404261 | -5.861419 | -2.618582 |
| H | -4.685377 | -5.136242 | -3.607024 |
| O | -6.174567 | -7.356268 | -6.729268 |
| C | -7.306062 | -8.273308 | -6.761971 |
| H | -7.931234 | -8.121108 | -5.880594 |
| H | -7.843645 | -8.019410 | -7.674440 |
| H | -6.948120 | -9.303926 | -6.788968 |

Intermediate Co-VIa

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.885113 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.809576 E_h

$\Delta\Delta H(298) = 0.650077 \text{ E}_h$

S(298) = 0.105441 E_h

Lowest frequency: 25.12 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -3.031121 | -4.998214 | -6.986693 |
| C | -2.494326 | -4.207854 | -8.857033 |
| C | -3.430852 | -5.248646 | -9.053027 |
| C | -1.356111 | -4.745307 | -8.132739 |
| C | -2.872401 | -6.455312 | -8.462310 |
| C | -1.591856 | -6.150750 | -7.915752 |
| N | -3.642288 | -3.302870 | -6.289420 |
| C | -2.862113 | -2.452613 | -5.595626 |
| C | -4.970746 | -3.045421 | -6.374904 |
| C | -5.556909 | -1.946841 | -5.771728 |
| C | -4.753910 | -1.077691 | -5.032932 |
| H | -5.548091 | -3.767972 | -6.938717 |

| | | | |
|---|-----------|-----------|------------|
| H | -5.178228 | -0.212250 | -4.534879 |
| H | -6.623524 | -1.783606 | -5.878000 |
| N | -1.440714 | -2.627123 | -5.552172 |
| C | -0.820830 | -3.627064 | -4.803222 |
| C | -1.603165 | -4.789033 | -4.357410 |
| C | -2.512911 | -5.371226 | -5.167616 |
| C | -3.393419 | -1.334984 | -4.953486 |
| H | -2.723584 | -0.677785 | -4.412200 |
| C | -3.526921 | -7.797068 | -8.497317 |
| H | -3.137594 | -8.465157 | -7.727510 |
| H | -4.610850 | -7.722146 | -8.381889 |
| H | -3.335989 | -8.264177 | -9.472117 |
| C | -0.599852 | -7.095811 | -7.316620 |
| H | -0.142997 | -6.669575 | -6.419388 |
| H | -1.054938 | -8.052862 | -7.053826 |
| H | 0.200825 | -7.296682 | -8.039110 |
| C | -0.041014 | -4.064292 | -7.958607 |
| H | 0.420876 | -4.289817 | -6.995094 |
| H | 0.640432 | -4.426399 | -8.740691 |
| H | -0.125427 | -2.984162 | -8.074886 |
| C | -2.631743 | -2.789866 | -9.304136 |
| H | -2.097086 | -2.656606 | -10.253449 |
| H | -3.678041 | -2.524836 | -9.474264 |
| H | -2.205733 | -2.085993 | -8.582731 |
| C | -4.711973 | -5.153691 | -9.820878 |
| H | -5.189722 | -4.179135 | -9.687791 |
| H | -4.513465 | -5.277746 | -10.892941 |
| H | -5.419026 | -5.926705 | -9.518694 |
| C | -0.724510 | -1.503436 | -6.122604 |
| C | 0.653177 | -1.408815 | -5.736228 |
| H | 1.195956 | -0.550042 | -6.113992 |
| C | 1.235486 | -2.350695 | -4.933057 |
| C | 0.506872 | -3.473568 | -4.479540 |
| H | 2.280816 | -2.250801 | -4.654324 |
| H | 0.979605 | -4.242506 | -3.881063 |
| O | -1.335594 | -0.730732 | -6.864964 |
| C | -1.283863 | -5.265036 | -2.977889 |
| C | -1.468221 | -4.418628 | -1.873718 |
| C | -0.766891 | -6.549434 | -2.765414 |
| C | -1.183662 | -4.863487 | -0.585919 |
| H | -1.850436 | -3.413213 | -2.029567 |
| C | -0.472905 | -6.993033 | -1.475179 |
| H | -0.571826 | -7.190394 | -3.620219 |
| C | -0.689666 | -6.154769 | -0.382706 |

| | | | |
|---|-----------|-----------|-----------|
| H | -1.344669 | -4.203752 | 0.261473 |
| H | -0.066647 | -7.989049 | -1.325928 |
| H | -0.464368 | -6.499307 | 0.621815 |
| C | -3.618164 | -6.306758 | -4.730317 |
| O | -4.510256 | -6.035278 | -5.983254 |
| C | -5.767196 | -6.547108 | -6.084131 |
| O | -6.262682 | -7.350663 | -5.334898 |
| C | -3.289166 | -7.789959 | -4.693088 |
| H | -2.700095 | -8.081761 | -5.563577 |
| H | -2.698470 | -7.979894 | -3.794383 |
| H | -4.202603 | -8.384781 | -4.642603 |
| C | -4.384479 | -5.827032 | -3.505419 |
| H | -5.270812 | -6.440144 | -3.335362 |
| H | -3.725789 | -5.911101 | -2.638300 |
| H | -4.669655 | -4.777657 | -3.617772 |
| O | -6.346956 | -5.992408 | -7.163138 |
| C | -7.712017 | -6.457312 | -7.404011 |
| H | -8.339794 | -6.204680 | -6.548503 |
| H | -8.029733 | -5.926682 | -8.299725 |
| H | -7.709400 | -7.536840 | -7.561416 |

Intermediate Co-VI

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.884586 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.807175 E_h

$\Delta\Delta H(298) = 0.650478 \text{ E}_h$

S(298) = 0.102796 E_h

Lowest frequency: 24.08 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.734294 | -4.998779 | -7.272058 |
| C | -1.859268 | -4.265231 | -9.057364 |
| C | -2.643880 | -5.398064 | -9.351780 |
| C | -0.842859 | -4.655898 | -8.098394 |
| C | -2.126530 | -6.515654 | -8.574500 |
| C | -1.016467 | -6.053621 | -7.812064 |
| N | -3.482488 | -3.259820 | -6.798200 |
| C | -2.869013 | -2.404670 | -5.959253 |
| C | -4.750944 | -2.972046 | -7.179695 |
| C | -5.458162 | -1.886646 | -6.695065 |
| C | -4.849360 | -1.054172 | -5.756693 |

| | | | |
|---|-----------|-----------|------------|
| H | -5.183920 | -3.658784 | -7.893927 |
| H | -5.378194 | -0.208153 | -5.330822 |
| H | -6.468640 | -1.707064 | -7.044841 |
| N | -1.467175 | -2.515360 | -5.709482 |
| C | -0.892438 | -3.510749 | -4.926965 |
| C | -1.664726 | -4.697846 | -4.526758 |
| C | -2.585488 | -5.320935 | -5.316853 |
| C | -3.533858 | -1.312075 | -5.404235 |
| H | -2.992600 | -0.666355 | -4.723158 |
| C | -2.620114 | -7.919138 | -8.706619 |
| H | -2.151968 | -8.589409 | -7.983798 |
| H | -3.707268 | -7.978097 | -8.595438 |
| H | -2.376435 | -8.289570 | -9.710493 |
| C | -0.103288 | -6.868092 | -6.955946 |
| H | 0.263774 | -6.279796 | -6.111790 |
| H | -0.599702 | -7.760661 | -6.569516 |
| H | 0.765164 | -7.192644 | -7.542761 |
| C | 0.395730 | -3.871868 | -7.824452 |
| H | 0.792356 | -4.045718 | -6.823940 |
| H | 1.163309 | -4.193277 | -8.542254 |
| H | 0.243208 | -2.803282 | -7.973157 |
| C | -2.009712 | -2.890236 | -9.623088 |
| H | -1.306425 | -2.758302 | -10.455016 |
| H | -3.017018 | -2.724685 | -10.013071 |
| H | -1.793381 | -2.117082 | -8.879910 |
| C | -3.797702 | -5.480414 | -10.297021 |
| H | -4.198257 | -4.490491 | -10.528647 |
| H | -3.478462 | -5.937625 | -11.241812 |
| H | -4.601089 | -6.097011 | -9.885790 |
| C | -0.739517 | -1.351921 | -6.190453 |
| C | 0.574195 | -1.194088 | -5.640024 |
| H | 1.110172 | -0.298581 | -5.932431 |
| C | 1.110450 | -2.136541 | -4.807246 |
| C | 0.394190 | -3.305969 | -4.471829 |
| H | 2.112640 | -2.000581 | -4.410339 |
| H | 0.844687 | -4.065903 | -3.847622 |
| O | -1.290833 | -0.605884 | -7.001987 |
| C | -1.230844 | -5.197892 | -3.181156 |
| C | -1.389826 | -4.416290 | -2.028658 |
| C | -0.594381 | -6.440498 | -3.071819 |
| C | -0.971658 | -4.890655 | -0.788857 |
| H | -1.860822 | -3.439932 | -2.106392 |
| C | -0.160213 | -6.911754 | -1.832440 |
| H | -0.438670 | -7.036327 | -3.966300 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.358428 | -6.142302 | -0.686591 |
| H | -1.120283 | -4.284670 | 0.099918 |
| H | 0.333373 | -7.876638 | -1.762965 |
| H | -0.028033 | -6.509008 | 0.280338 |
| C | -3.562414 | -6.334528 | -4.721461 |
| O | -4.992488 | -5.911460 | -5.146725 |
| C | -5.322133 | -5.924421 | -6.401632 |
| O | -4.550104 | -5.808706 | -7.376174 |
| C | -3.363867 | -7.754755 | -5.233123 |
| H | -3.304224 | -7.781763 | -6.319977 |
| H | -2.425661 | -8.138166 | -4.823009 |
| H | -4.177941 | -8.401084 | -4.891708 |
| C | -3.820363 | -6.343366 | -3.210138 |
| H | -4.755889 | -6.882864 | -3.041130 |
| H | -3.023414 | -6.854707 | -2.675044 |
| H | -3.921767 | -5.330440 | -2.818986 |
| O | -6.633078 | -6.066785 | -6.555069 |
| C | -7.142336 | -6.059337 | -7.918184 |
| H | -6.749130 | -6.919711 | -8.462650 |
| H | -8.221975 | -6.130886 | -7.805233 |
| H | -6.863749 | -5.131999 | -8.422255 |

Transition state **TS(6-7)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.848156 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.773735 E_h

$\Delta\Delta H(298) = 0.648798 \text{ E}_h$

S(298) = 0.103768 E_h

Lowest frequency: -296.85 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.766402 | -4.952601 | -7.423700 |
| C | -1.857700 | -4.430918 | -9.228359 |
| C | -2.563219 | -5.646760 | -9.386886 |
| C | -0.884276 | -4.617379 | -8.175685 |
| C | -2.024616 | -6.614858 | -8.436012 |
| C | -0.967907 | -5.986328 | -7.727291 |
| N | -3.493677 | -3.219584 | -7.091758 |
| C | -3.199828 | -3.103081 | -5.733446 |
| C | -4.609373 | -2.678043 | -7.609098 |
| C | -5.507121 | -1.958761 | -6.846660 |

| | | | |
|---|-----------|-----------|------------|
| C | -5.275803 | -1.855470 | -5.455907 |
| H | -4.756759 | -2.834887 | -8.673409 |
| H | -5.976746 | -1.310695 | -4.830779 |
| H | -6.359532 | -1.480391 | -7.313377 |
| N | -1.799724 | -2.719333 | -5.489498 |
| C | -1.043096 | -3.599760 | -4.757137 |
| C | -1.775741 | -4.819896 | -4.496002 |
| C | -2.918266 | -4.931267 | -5.289593 |
| C | -4.156273 | -2.406308 | -4.896051 |
| H | -3.942386 | -2.315655 | -3.836836 |
| C | -2.463660 | -8.040177 | -8.341991 |
| H | -2.085151 | -8.522220 | -7.438105 |
| H | -3.554677 | -8.121901 | -8.350172 |
| H | -2.086388 | -8.604795 | -9.204015 |
| C | -0.027901 | -6.619917 | -6.758577 |
| H | 0.171725 | -5.968976 | -5.903742 |
| H | -0.405155 | -7.575983 | -6.392355 |
| H | 0.930261 | -6.810584 | -7.258171 |
| C | 0.193269 | -3.645455 | -7.836307 |
| H | 0.543294 | -3.760018 | -6.809148 |
| H | 1.052198 | -3.826816 | -8.497266 |
| H | -0.130523 | -2.615512 | -7.991706 |
| C | -2.059589 | -3.153790 | -9.976489 |
| H | -1.245507 | -3.016284 | -10.698743 |
| H | -2.998874 | -3.154778 | -10.534016 |
| H | -2.054402 | -2.295592 | -9.298506 |
| C | -3.655943 | -5.929794 | -10.362472 |
| H | -4.134888 | -5.011546 | -10.710198 |
| H | -3.242467 | -6.442997 | -11.239998 |
| H | -4.417769 | -6.578351 | -9.925293 |
| C | -1.367192 | -1.429240 | -5.910174 |
| C | -0.049509 | -1.084776 | -5.411871 |
| H | 0.293561 | -0.082373 | -5.642408 |
| C | 0.698071 | -1.950717 | -4.659341 |
| C | 0.223176 | -3.247314 | -4.342397 |
| H | 1.678578 | -1.645683 | -4.304453 |
| H | 0.827389 | -3.957730 | -3.792465 |
| O | -2.094587 | -0.717788 | -6.598557 |
| C | -1.345770 | -5.657942 | -3.361073 |
| C | -1.054656 | -5.056194 | -2.120555 |
| C | -1.196859 | -7.049793 | -3.477924 |
| C | -0.661232 | -5.826846 | -1.031494 |
| H | -1.171188 | -3.982569 | -2.010709 |
| C | -0.786376 | -7.817634 | -2.391500 |

| | | | |
|---|-----------|-----------|-----------|
| H | -1.372497 | -7.523368 | -4.435604 |
| C | -0.525778 | -7.210556 | -1.162611 |
| H | -0.462038 | -5.348140 | -0.077615 |
| H | -0.663005 | -8.890358 | -2.506049 |
| H | -0.213142 | -7.810583 | -0.313713 |
| C | -4.139225 | -5.707893 | -4.784014 |
| O | -5.379080 | -5.168469 | -5.458364 |
| C | -5.541876 | -5.412689 | -6.733590 |
| O | -4.635351 | -5.668572 | -7.549255 |
| C | -4.100785 | -7.213864 | -5.052121 |
| H | -3.691351 | -7.440889 | -6.036106 |
| H | -3.489200 | -7.696472 | -4.289439 |
| H | -5.114825 | -7.618833 | -4.973656 |
| C | -4.488204 | -5.431769 | -3.320053 |
| H | -5.427922 | -5.933364 | -3.074733 |
| H | -3.702969 | -5.815504 | -2.669061 |
| H | -4.606105 | -4.360744 | -3.148941 |
| O | -6.821659 | -5.370224 | -7.065401 |
| C | -7.128263 | -5.479556 | -8.484528 |
| H | -6.856747 | -6.473448 | -8.844145 |
| H | -8.203262 | -5.323928 | -8.543497 |
| H | -6.587314 | -4.710482 | -9.038073 |

Intermediate Co-VII

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.854709 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.779973 E_h

$\Delta\Delta H(298) = 0.650115 \text{ E}_h$

S(298) = 0.104692 E_h

Lowest frequency: 16.95 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.755427 | -4.970440 | -7.386717 |
| C | -1.947660 | -4.570642 | -9.252802 |
| C | -2.536334 | -5.864036 | -9.257413 |
| C | -0.943883 | -4.552574 | -8.214800 |
| C | -1.888368 | -6.671296 | -8.234784 |
| C | -0.872242 | -5.875422 | -7.641324 |
| N | -3.442901 | -3.242114 | -7.043559 |
| C | -3.247460 | -3.180931 | -5.627021 |
| C | -4.406689 | -2.532445 | -7.650468 |

| | | | |
|---|-----------|-----------|------------|
| C | -5.282520 | -1.717755 | -6.964008 |
| C | -5.201020 | -1.675196 | -5.547427 |
| H | -4.457431 | -2.635020 | -8.730019 |
| H | -5.904759 | -1.065680 | -4.988284 |
| H | -6.007303 | -1.121965 | -7.504655 |
| N | -1.858484 | -2.678019 | -5.342660 |
| C | -1.097291 | -3.572423 | -4.638519 |
| C | -1.851533 | -4.789993 | -4.438968 |
| C | -3.049360 | -4.729340 | -5.163153 |
| C | -4.255964 | -2.387847 | -4.880177 |
| H | -4.184686 | -2.372548 | -3.798700 |
| C | -2.172783 | -8.117919 | -7.980621 |
| H | -1.786772 | -8.440873 | -7.010727 |
| H | -3.246370 | -8.325185 | -8.009870 |
| H | -1.697528 | -8.739445 | -8.750090 |
| C | 0.181782 | -6.314377 | -6.681516 |
| H | 0.308003 | -5.608455 | -5.856723 |
| H | -0.018526 | -7.303688 | -6.270643 |
| H | 1.139859 | -6.362913 | -7.214721 |
| C | -0.004731 | -3.426612 | -7.941148 |
| H | 0.398076 | -3.475441 | -6.927581 |
| H | 0.843456 | -3.484419 | -8.636821 |
| H | -0.488724 | -2.458607 | -8.083653 |
| C | -2.260415 | -3.425777 | -10.158520 |
| H | -1.519755 | -3.385226 | -10.967329 |
| H | -3.245110 | -3.527564 | -10.621019 |
| H | -2.215822 | -2.473799 | -9.623423 |
| C | -3.621150 | -6.342178 | -10.161685 |
| H | -4.209409 | -5.512887 | -10.560351 |
| H | -3.177852 | -6.877258 | -11.011523 |
| H | -4.292640 | -7.031897 | -9.646480 |
| C | -1.428867 | -1.395736 | -5.757782 |
| C | -0.105383 | -1.060728 | -5.257006 |
| H | 0.238425 | -0.054966 | -5.471920 |
| C | 0.658049 | -1.947330 | -4.543942 |
| C | 0.185463 | -3.250146 | -4.247519 |
| H | 1.647615 | -1.653771 | -4.204917 |
| H | 0.799443 | -3.979298 | -3.733938 |
| O | -2.143183 | -0.678184 | -6.452396 |
| C | -1.380694 | -5.789916 | -3.471198 |
| C | -0.967771 | -5.362869 | -2.192700 |
| C | -1.303748 | -7.159550 | -3.774000 |
| C | -0.519752 | -6.280627 | -1.247756 |
| H | -1.032946 | -4.309797 | -1.937800 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.837050 | -8.072844 | -2.833894 |
| H | -1.585013 | -7.498594 | -4.762793 |
| C | -0.449991 | -7.638035 | -1.565466 |
| H | -0.225784 | -5.935761 | -0.261270 |
| H | -0.770394 | -9.125350 | -3.092510 |
| H | -0.092631 | -8.352343 | -0.830354 |
| C | -4.284345 | -5.528891 | -4.722610 |
| O | -5.484548 | -5.006132 | -5.451226 |
| C | -5.586725 | -5.283359 | -6.730236 |
| O | -4.655361 | -5.637268 | -7.476864 |
| C | -4.225809 | -7.041439 | -4.955186 |
| H | -3.729370 | -7.297489 | -5.890540 |
| H | -3.700235 | -7.513628 | -4.125200 |
| H | -5.248135 | -7.432040 | -4.965866 |
| C | -4.665114 | -5.253986 | -3.264193 |
| H | -5.548623 | -5.842831 | -3.003651 |
| H | -3.839409 | -5.548190 | -2.613305 |
| H | -4.890091 | -4.198708 | -3.111744 |
| O | -6.837733 | -5.155718 | -7.137058 |
| C | -7.062902 | -5.259277 | -8.571889 |
| H | -6.806926 | -6.262648 | -8.915385 |
| H | -8.125564 | -5.062271 | -8.695058 |
| H | -6.461161 | -4.509606 | -9.088583 |

Transition state TS(7-8)

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.844799 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.770223 E_h

$\Delta\Delta H(298) = 0.647795 \text{ E}_h$

S(298) = 0.103306 E_h

Lowest frequency: -176.03 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.820681 | -4.996994 | -7.435740 |
| C | -2.142874 | -4.635284 | -9.332663 |
| C | -2.548706 | -6.003094 | -9.221665 |
| C | -1.101867 | -4.404973 | -8.358733 |
| C | -1.770885 | -6.630079 | -8.183723 |
| C | -0.842761 | -5.655348 | -7.694274 |
| N | -3.618244 | -3.324884 | -6.994063 |
| C | -3.495010 | -3.257397 | -5.628344 |

| | | | |
|---|-----------|-----------|------------|
| C | -4.249850 | -2.349648 | -7.684407 |
| C | -4.920194 | -1.331727 | -7.047552 |
| C | -4.974146 | -1.343805 | -5.636373 |
| H | -4.232481 | -2.434757 | -8.763555 |
| H | -5.548440 | -0.586471 | -5.111540 |
| H | -5.415955 | -0.562639 | -7.626736 |
| N | -1.685208 | -2.627974 | -5.293038 |
| C | -1.096440 | -3.570665 | -4.547854 |
| C | -1.939583 | -4.754059 | -4.403353 |
| C | -3.164554 | -4.653295 | -5.056931 |
| C | -4.318564 | -2.313361 | -4.925427 |
| H | -4.335605 | -2.331314 | -3.842487 |
| C | -1.846598 | -8.079605 | -7.819059 |
| H | -1.351836 | -8.286210 | -6.868055 |
| H | -2.882794 | -8.422870 | -7.751191 |
| H | -1.349571 | -8.686670 | -8.586151 |
| C | 0.280204 | -5.881837 | -6.743262 |
| H | 0.340952 | -5.099997 | -5.979816 |
| H | 0.219282 | -6.851642 | -6.250276 |
| H | 1.221354 | -5.848636 | -7.307194 |
| C | -0.321507 | -3.142163 | -8.209531 |
| H | 0.309679 | -3.167951 | -7.320096 |
| H | 0.330730 | -3.016154 | -9.083718 |
| H | -0.968867 | -2.263406 | -8.142075 |
| C | -2.610814 | -3.650593 | -10.351820 |
| H | -2.050426 | -3.806295 | -11.283200 |
| H | -3.671455 | -3.772250 | -10.588906 |
| H | -2.430439 | -2.623631 | -10.028573 |
| C | -3.596752 | -6.676438 | -10.040105 |
| H | -4.300619 | -5.957596 | -10.464205 |
| H | -3.117855 | -7.206715 | -10.873782 |
| H | -4.153000 | -7.409886 | -9.452830 |
| C | -1.101303 | -1.411858 | -5.619977 |
| C | 0.196499 | -1.191796 | -4.984004 |
| H | 0.647638 | -0.215013 | -5.128809 |
| C | 0.818588 | -2.169164 | -4.245370 |
| C | 0.189185 | -3.415472 | -4.030355 |
| H | 1.800630 | -1.985323 | -3.817979 |
| H | 0.678834 | -4.218312 | -3.492909 |
| O | -1.644747 | -0.608439 | -6.389514 |
| C | -1.479208 | -5.837358 | -3.511666 |
| C | -1.189905 | -5.527576 | -2.169164 |
| C | -1.278159 | -7.153215 | -3.951594 |
| C | -0.737004 | -6.513483 | -1.295773 |

| | | | |
|---|-----------|-----------|-----------|
| H | -1.342987 | -4.513718 | -1.812408 |
| C | -0.805348 | -8.132799 | -3.083367 |
| H | -1.489926 | -7.399555 | -4.984402 |
| C | -0.538291 | -7.817354 | -1.750430 |
| H | -0.536071 | -6.260407 | -0.259408 |
| H | -0.644663 | -9.143295 | -3.447161 |
| H | -0.175448 | -8.582584 | -1.071458 |
| C | -4.371574 | -5.515550 | -4.641832 |
| O | -5.569286 | -5.079087 | -5.431728 |
| C | -5.625259 | -5.389037 | -6.705320 |
| O | -4.677840 | -5.773930 | -7.417592 |
| C | -4.241266 | -7.030979 | -4.805191 |
| H | -3.748863 | -7.307557 | -5.737109 |
| H | -3.678366 | -7.440506 | -3.967061 |
| H | -5.244741 | -7.466851 | -4.780021 |
| C | -4.812638 | -5.191354 | -3.209962 |
| H | -5.681415 | -5.801992 | -2.950242 |
| H | -3.995430 | -5.424448 | -2.524038 |
| H | -5.081932 | -4.139650 | -3.112233 |
| O | -6.858847 | -5.248939 | -7.156997 |
| C | -7.043610 | -5.401448 | -8.593752 |
| H | -6.794955 | -6.420914 | -8.892221 |
| H | -8.098725 | -5.191923 | -8.754935 |
| H | -6.415175 | -4.680330 | -9.119368 |

Intermediate Co-VIII

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.857066 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.780400 E_h

$\Delta\Delta H(298) = 0.649531$ E_h

S(298) = 0.105840 E_h

Lowest frequency: 27.46 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.872490 | -4.935385 | -7.517773 |
| C | -2.465790 | -4.728954 | -9.505669 |
| C | -2.511586 | -6.125549 | -9.172967 |
| C | -1.412964 | -4.123631 | -8.716775 |
| C | -1.533579 | -6.387647 | -8.167692 |
| C | -0.834170 | -5.153054 | -7.900498 |
| N | -3.648581 | -3.267926 | -6.945965 |

| | | | |
|---|-----------|-----------|------------|
| C | -3.630120 | -3.273516 | -5.597321 |
| C | -4.019422 | -2.158677 | -7.613737 |
| C | -4.434978 | -1.019940 | -6.947130 |
| C | -4.482799 | -1.033929 | -5.549677 |
| H | -3.976016 | -2.206343 | -8.694110 |
| H | -4.808062 | -0.154154 | -5.003985 |
| H | -4.718824 | -0.140091 | -7.512599 |
| N | -1.230211 | -2.741967 | -5.401746 |
| C | -0.987136 | -3.709843 | -4.513287 |
| C | -2.011329 | -4.755255 | -4.388102 |
| C | -3.248004 | -4.603577 | -5.000398 |
| C | -4.094255 | -2.175647 | -4.866894 |
| H | -4.077927 | -2.207372 | -3.783880 |
| C | -1.187129 | -7.748197 | -7.644041 |
| H | -0.360918 | -7.699658 | -6.932722 |
| H | -2.036715 | -8.239294 | -7.159744 |
| H | -0.870277 | -8.391701 | -8.473603 |
| C | 0.370833 | -5.015123 | -7.036663 |
| H | 0.674433 | -3.973362 | -6.940106 |
| H | 0.218276 | -5.416257 | -6.029689 |
| H | 1.194370 | -5.583719 | -7.489077 |
| C | -0.952404 | -2.708939 | -8.794666 |
| H | 0.116949 | -2.686560 | -9.034798 |
| H | -1.479280 | -2.163420 | -9.580553 |
| H | -1.079181 | -2.160677 | -7.850897 |
| C | -3.283996 | -4.072430 | -10.569816 |
| H | -2.934715 | -4.395950 | -11.558658 |
| H | -4.341594 | -4.342543 | -10.494924 |
| H | -3.198083 | -2.984885 | -10.535630 |
| C | -3.433168 | -7.136384 | -9.766787 |
| H | -4.339832 | -6.673229 | -10.159978 |
| H | -2.926022 | -7.639538 | -10.600625 |
| H | -3.714848 | -7.900264 | -9.038520 |
| C | -0.378114 | -1.659631 | -5.512284 |
| C | 0.796956 | -1.634819 | -4.648417 |
| H | 1.456488 | -0.776561 | -4.732476 |
| C | 1.060040 | -2.669305 | -3.781996 |
| C | 0.164132 | -3.749585 | -3.702721 |
| H | 1.947918 | -2.655279 | -3.155663 |
| H | 0.342458 | -4.573168 | -3.023032 |
| O | -0.600652 | -0.754163 | -6.345621 |
| C | -1.679275 | -5.908941 | -3.500244 |
| C | -1.813677 | -5.781122 | -2.109786 |
| C | -1.162071 | -7.100374 | -4.018048 |

| | | | |
|---|-----------|-----------|-----------|
| C | -1.468968 | -6.835649 | -1.264936 |
| H | -2.172147 | -4.845683 | -1.689944 |
| C | -0.814650 | -8.154121 | -3.174925 |
| H | -1.046963 | -7.202772 | -5.089573 |
| C | -0.973414 | -8.027086 | -1.794927 |
| H | -1.581009 | -6.721038 | -0.191092 |
| H | -0.417368 | -9.072897 | -3.596130 |
| H | -0.703802 | -8.846563 | -1.136189 |
| C | -4.458363 | -5.478420 | -4.609986 |
| O | -5.631209 | -5.095070 | -5.481523 |
| C | -5.646673 | -5.457141 | -6.740989 |
| O | -4.667494 | -5.786066 | -7.437942 |
| C | -4.285469 | -6.992944 | -4.715687 |
| H | -3.749215 | -7.281881 | -5.620294 |
| H | -3.737855 | -7.363148 | -3.849923 |
| H | -5.276978 | -7.456211 | -4.712235 |
| C | -5.009596 | -5.093991 | -3.233779 |
| H | -5.913995 | -5.673800 | -3.031332 |
| H | -4.263724 | -5.320260 | -2.471336 |
| H | -5.260645 | -4.032590 | -3.197864 |
| O | -6.883784 | -5.437547 | -7.207734 |
| C | -7.047052 | -5.694967 | -8.632251 |
| H | -6.711673 | -6.706961 | -8.863705 |
| H | -8.115159 | -5.586062 | -8.806760 |
| H | -6.479443 | -4.959128 | -9.204607 |

Intermediate Co-IX

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.915802 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.839394 E_h

$\Delta\Delta H(298) = 0.651489$ E_h

S(298) = 0.105935 E_h

Lowest frequency: 4.00 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.079828 | -4.003791 | -7.604090 |
| C | -1.795781 | -4.229510 | -9.629031 |
| C | -2.997724 | -4.881530 | -9.231577 |
| C | -0.699420 | -4.791898 | -8.864330 |
| C | -2.655666 | -5.894753 | -8.254475 |
| C | -1.242308 | -5.835875 | -8.041165 |

| | | | |
|---|-----------|-----------|------------|
| N | -3.621130 | -3.343099 | -6.587511 |
| C | -3.799043 | -3.590979 | -5.260024 |
| C | -4.280170 | -2.318916 | -7.170301 |
| C | -5.137258 | -1.478138 | -6.479249 |
| C | -5.276278 | -1.669036 | -5.108654 |
| H | -4.066695 | -2.167230 | -8.221282 |
| H | -5.891468 | -1.003344 | -4.511470 |
| H | -5.643786 | -0.675060 | -7.002372 |
| N | -1.116113 | -3.467996 | -6.008789 |
| C | -1.003377 | -3.711592 | -4.688257 |
| C | -1.888399 | -4.750920 | -4.125841 |
| C | -3.191049 | -4.760008 | -4.521456 |
| C | -4.601389 | -2.725291 | -4.507844 |
| H | -4.674410 | -2.879880 | -3.439307 |
| C | -3.592060 | -6.937579 | -7.749153 |
| H | -3.271082 | -7.346996 | -6.791590 |
| H | -4.605724 | -6.553300 | -7.639833 |
| H | -3.616646 | -7.763745 | -8.473133 |
| C | -0.464547 | -6.706857 | -7.113241 |
| H | 0.395088 | -6.176045 | -6.697145 |
| H | -1.088190 | -7.068622 | -6.293391 |
| H | -0.085527 | -7.580449 | -7.658541 |
| C | 0.731936 | -4.375910 | -8.962149 |
| H | 1.276356 | -4.602162 | -8.042012 |
| H | 1.227604 | -4.907129 | -9.784316 |
| H | 0.812309 | -3.303595 | -9.155466 |
| C | -1.660512 | -3.101228 | -10.594531 |
| H | -1.145220 | -3.453980 | -11.496445 |
| H | -2.632257 | -2.703792 | -10.894014 |
| H | -1.067203 | -2.291369 | -10.160608 |
| C | -4.377249 | -4.632171 | -9.751335 |
| H | -4.465676 | -3.646056 | -10.213240 |
| H | -4.625322 | -5.377881 | -10.516994 |
| H | -5.122351 | -4.715373 | -8.955388 |
| C | -0.725666 | -2.292117 | -6.563110 |
| C | 0.095998 | -1.407306 | -5.842304 |
| H | 0.450617 | -0.489734 | -6.297105 |
| C | 0.384145 | -1.748703 | -4.526653 |
| C | -0.181942 | -2.885003 | -3.924805 |
| H | 1.014244 | -1.093575 | -3.932289 |
| H | -0.038835 | -3.095028 | -2.871388 |
| O | -1.256700 | -2.175201 | -7.751960 |
| C | -1.281628 | -5.586894 | -3.053357 |
| C | -1.688187 | -5.425306 | -1.721601 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.224781 | -6.463659 | -3.333562 |
| C | -1.088737 | -6.161876 | -0.700884 |
| H | -2.459053 | -4.699731 | -1.483344 |
| C | 0.363054 | -7.211788 | -2.316968 |
| H | 0.128188 | -6.569054 | -4.353659 |
| C | -0.072191 | -7.068631 | -0.998224 |
| H | -1.413655 | -6.022633 | 0.325747 |
| H | 1.166781 | -7.902868 | -2.552395 |
| H | 0.389817 | -7.648949 | -0.205688 |
| C | -4.231844 | -5.824210 | -4.099892 |
| O | -5.123639 | -5.796667 | -5.293353 |
| C | -6.251766 | -6.537189 | -5.315243 |
| O | -6.664900 | -7.295533 | -4.466766 |
| C | -3.636183 | -7.226741 | -3.953930 |
| H | -2.912956 | -7.439519 | -4.743467 |
| H | -3.130734 | -7.322957 | -2.992788 |
| H | -4.448368 | -7.954713 | -3.987352 |
| C | -5.050818 | -5.458942 | -2.850813 |
| H | -5.644711 | -6.318699 | -2.540216 |
| H | -4.377349 | -5.181336 | -2.038863 |
| H | -5.731767 | -4.630062 | -3.052471 |
| O | -6.847646 | -6.278079 | -6.498554 |
| C | -8.092516 | -7.005192 | -6.701182 |
| H | -8.810711 | -6.733140 | -5.925713 |
| H | -8.439404 | -6.691868 | -7.684620 |
| H | -7.904548 | -8.080066 | -6.672399 |

Intermediate **Co-It**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2574.668848 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2570.814135 E_h

$\Delta\Delta H(298) = 0.459560$ E_h

S(298) = 0.087065 E_h

Lowest frequency: 26.20 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|----------|-----------|-----------|
| Co | 1.058525 | -0.015273 | -0.268082 |
| C | 1.249571 | -0.928914 | 1.672174 |
| C | 2.556081 | -0.530243 | 1.185433 |
| C | 0.717384 | -1.945196 | 0.803345 |
| C | 2.773934 | -1.213128 | -0.036188 |

| | | | |
|---|-----------|-----------|-----------|
| C | 1.609906 | -2.069429 | -0.290229 |
| C | 0.609905 | -0.452815 | 2.934386 |
| H | -0.481865 | -0.446979 | 2.869017 |
| H | 0.950005 | 0.549689 | 3.203771 |
| H | 0.889508 | -1.126862 | 3.754857 |
| C | 3.484547 | 0.442359 | 1.838570 |
| H | 2.946523 | 1.131810 | 2.493902 |
| H | 4.218904 | -0.089215 | 2.456364 |
| H | 4.031650 | 1.025690 | 1.093440 |
| C | -0.529924 | -2.736158 | 1.026183 |
| H | -1.167391 | -2.279049 | 1.784394 |
| H | -0.266317 | -3.741066 | 1.380117 |
| H | -1.107526 | -2.855181 | 0.106203 |
| C | 3.985641 | -1.147222 | -0.904180 |
| H | 3.722474 | -1.233244 | -1.961944 |
| H | 4.654479 | -1.984370 | -0.665308 |
| H | 4.536306 | -0.217536 | -0.753019 |
| C | 1.457587 | -2.969420 | -1.470615 |
| H | 0.429792 | -3.324332 | -1.569926 |
| H | 2.111282 | -3.844121 | -1.360558 |
| H | 1.739670 | -2.456161 | -2.393920 |
| O | 2.411115 | 1.555645 | -1.187835 |
| C | 1.937990 | 1.125151 | -2.272188 |
| O | 1.075285 | 0.155429 | -2.209804 |
| C | 2.317537 | 1.685422 | -3.610225 |
| C | -1.325235 | 1.441567 | 0.688649 |
| N | 0.003184 | 1.507847 | 0.458631 |
| C | -2.015174 | 2.437163 | 1.376047 |
| C | -1.313494 | 3.543923 | 1.832563 |
| H | -3.079497 | 2.329205 | 1.538086 |
| H | -1.830614 | 4.332984 | 2.368488 |
| C | 0.055693 | 3.631900 | 1.574649 |
| C | 0.676591 | 2.607354 | 0.882794 |
| H | 0.640248 | 4.484778 | 1.900645 |
| H | 1.729312 | 2.627994 | 0.636201 |
| H | 3.258288 | 2.232151 | -3.536235 |
| H | 2.388792 | 0.887857 | -4.353074 |
| H | 1.533239 | 2.377668 | -3.937629 |
| C | -1.842345 | -0.038641 | -1.151543 |
| C | -2.929254 | -0.383368 | 1.056199 |
| C | -2.558056 | -1.054394 | -1.707975 |
| H | -1.140916 | 0.566365 | -1.712979 |
| C | -3.714450 | -1.396297 | 0.397788 |
| H | -2.406675 | -1.301352 | -2.751316 |

| | | | |
|---|-----------|-----------|-----------|
| H | -4.442479 | -1.903451 | 1.020791 |
| N | -2.022787 | 0.315558 | 0.171843 |
| C | -3.530147 | -1.724516 | -0.915871 |
| H | -4.134689 | -2.507589 | -1.364812 |
| O | -2.949869 | -0.097255 | 2.251629 |

Transition state **TS(1t-3t)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2574.623911 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2570.776237 E_h

$\Delta\Delta H(298) = 0.453932 \text{ E}_h$

S(298) = 0.087942 E_h

Lowest frequency: -467.00 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -1.431410 | -0.508537 | -0.608557 |
| C | -1.508668 | 0.266704 | -2.622760 |
| C | -2.529372 | 1.022827 | -1.935494 |
| C | -1.870701 | -1.135281 | -2.599726 |
| C | -3.416798 | 0.093522 | -1.355554 |
| C | -3.024309 | -1.251648 | -1.780484 |
| N | -0.866395 | 1.182336 | 0.501945 |
| C | 0.413187 | 1.572924 | 0.347695 |
| C | -1.666155 | 1.846190 | 1.355777 |
| C | -1.227887 | 2.949278 | 2.069678 |
| C | 0.093046 | 3.368261 | 1.892071 |
| H | -2.677617 | 1.464491 | 1.446496 |
| H | -1.901690 | 3.465485 | 2.744183 |
| H | 0.475124 | 4.225767 | 2.436655 |
| N | 1.163571 | 0.721394 | -0.494971 |
| C | 0.650910 | -0.579130 | -0.643264 |
| O | -1.989659 | -1.464493 | 0.967448 |
| C | -1.133943 | -1.760619 | 1.881558 |
| O | 0.112081 | -1.552741 | 1.758366 |
| C | -1.650603 | -2.366181 | 3.155651 |
| H | 0.289692 | -1.096018 | 0.581111 |
| C | 0.933912 | 2.679538 | 1.026119 |
| H | 1.960920 | 2.975519 | 0.871229 |
| C | -2.566224 | 2.511989 | -1.828100 |
| H | -1.569688 | 2.929958 | -1.658459 |
| H | -2.945201 | 2.945155 | -2.762199 |

| | | | |
|---|-----------|-----------|-----------|
| H | -3.220103 | 2.844703 | -1.019282 |
| C | -4.606818 | 0.378120 | -0.498509 |
| H | -4.632790 | 1.419817 | -0.172255 |
| H | -5.528933 | 0.181604 | -1.060023 |
| H | -4.622408 | -0.271228 | 0.382783 |
| C | -3.782082 | -2.497116 | -1.454719 |
| H | -3.190856 | -3.392147 | -1.659532 |
| H | -4.084302 | -2.512742 | -0.404079 |
| H | -4.693309 | -2.549649 | -2.064286 |
| C | -1.203139 | -2.224838 | -3.376501 |
| H | -1.269087 | -3.189805 | -2.866704 |
| H | -1.689925 | -2.333985 | -4.353876 |
| H | -0.150308 | -1.998066 | -3.557788 |
| C | -0.389537 | 0.862297 | -3.410731 |
| H | -0.738442 | 1.072182 | -4.430619 |
| H | -0.048281 | 1.807227 | -2.981977 |
| H | 0.461282 | 0.182109 | -3.485593 |
| H | -0.862052 | -2.923963 | 3.660572 |
| H | -1.977392 | -1.550007 | 3.810998 |
| H | -2.514241 | -3.000402 | 2.949145 |
| C | 2.349145 | 1.197635 | -1.162142 |
| C | 3.075597 | 0.166171 | -1.870416 |
| H | 4.000133 | 0.488538 | -2.336177 |
| C | 2.625295 | -1.120608 | -1.960602 |
| C | 1.390408 | -1.487650 | -1.370405 |
| H | 3.210439 | -1.865925 | -2.492720 |
| H | 1.031827 | -2.508324 | -1.444520 |
| O | 2.670386 | 2.380290 | -1.116718 |

Intermediate **Co-III**t

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2574.645384 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2570.796917 E_h

$\Delta\Delta H(298) = 0.458060$ E_h

S(298) = 0.085902 E_h

Lowest frequency: 22.16 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -1.341609 | -0.275951 | -0.742452 |
| C | -1.692031 | 0.399690 | -2.809527 |
| C | -2.625127 | 1.093911 | -2.013971 |

| | | | |
|---|-----------|-----------|-----------|
| C | -1.923327 | -1.034180 | -2.621378 |
| C | -3.414930 | 0.111102 | -1.298419 |
| C | -3.027387 | -1.195345 | -1.727129 |
| N | -0.809038 | 1.250222 | 0.412272 |
| C | 0.472604 | 1.669075 | 0.270468 |
| C | -1.645885 | 1.918253 | 1.229228 |
| C | -1.255860 | 3.055189 | 1.916352 |
| C | 0.048590 | 3.516609 | 1.734978 |
| H | -2.642279 | 1.501912 | 1.320383 |
| H | -1.957585 | 3.563005 | 2.568130 |
| H | 0.390764 | 4.412532 | 2.243104 |
| N | 1.245024 | 0.787321 | -0.509207 |
| C | 0.559633 | -0.347184 | -0.972534 |
| O | -1.893561 | -1.303503 | 1.082245 |
| C | -1.127677 | -1.921119 | 1.835855 |
| O | 0.164288 | -2.092228 | 1.574597 |
| C | -1.570835 | -2.551058 | 3.119549 |
| H | 0.382428 | -1.667537 | 0.702594 |
| C | 0.929266 | 2.827617 | 0.908797 |
| H | 1.947956 | 3.150371 | 0.753821 |
| C | -2.762069 | 2.577827 | -1.901631 |
| H | -1.817723 | 3.085146 | -2.114503 |
| H | -3.505439 | 2.944339 | -2.620465 |
| H | -3.096217 | 2.882224 | -0.906194 |
| C | -4.538561 | 0.402438 | -0.354144 |
| H | -4.538206 | 1.445204 | -0.028659 |
| H | -5.499502 | 0.217601 | -0.850554 |
| H | -4.497979 | -0.245795 | 0.526783 |
| C | -3.672278 | -2.484233 | -1.322362 |
| H | -2.981201 | -3.325984 | -1.415622 |
| H | -4.025279 | -2.443449 | -0.288852 |
| H | -4.537779 | -2.695473 | -1.962917 |
| C | -1.300836 | -2.114446 | -3.445919 |
| H | -1.224844 | -3.058965 | -2.899634 |
| H | -1.930603 | -2.298617 | -4.326179 |
| H | -0.310411 | -1.832283 | -3.808049 |
| C | -0.683155 | 0.994676 | -3.738417 |
| H | -1.105716 | 1.084367 | -4.747173 |
| H | -0.381671 | 1.994692 | -3.416673 |
| H | 0.212322 | 0.371972 | -3.807348 |
| H | -0.958680 | -2.171805 | 3.943447 |
| H | -2.623662 | -2.338047 | 3.296692 |
| H | -1.408070 | -3.632454 | 3.067196 |
| C | 2.669927 | 0.998189 | -0.721019 |

| | | | |
|---|----------|-----------|-----------|
| C | 3.359970 | -0.151621 | -1.256051 |
| H | 4.433792 | -0.040446 | -1.354068 |
| C | 2.706350 | -1.287967 | -1.626227 |
| C | 1.288827 | -1.369012 | -1.531900 |
| H | 3.262506 | -2.132902 | -2.023466 |
| H | 0.776251 | -2.247408 | -1.902899 |
| O | 3.203146 | 2.064457 | -0.441215 |

Intermediate **Co-IVt**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.822675 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.747282 E_h

$\Delta\Delta H(298) = 0.645880$ E_h

S(298) = 0.106652 E_h

Lowest frequency: 15.04 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.370182 | -4.810068 | -6.478810 |
| C | -1.662461 | -4.060937 | -8.462666 |
| C | -3.078273 | -3.905194 | -8.585016 |
| C | -1.374610 | -5.471187 | -8.272715 |
| C | -3.673722 | -5.173752 | -8.341104 |
| C | -2.615439 | -6.158451 | -8.207368 |
| N | -3.313219 | -3.050651 | -5.889613 |
| C | -2.482678 | -2.071518 | -5.477343 |
| C | -4.643911 | -2.890307 | -5.815271 |
| C | -5.221168 | -1.718242 | -5.356213 |
| C | -4.368743 | -0.682200 | -4.969132 |
| H | -5.235771 | -3.741086 | -6.136355 |
| H | -4.775302 | 0.258841 | -4.612104 |
| H | -6.299956 | -1.620357 | -5.310013 |
| N | -1.121441 | -2.446803 | -5.504529 |
| C | -0.855430 | -3.772220 | -5.837250 |
| C | -2.425430 | -5.226057 | -4.408379 |
| C | -3.051709 | -6.095579 | -5.079849 |
| C | -2.990134 | -0.844872 | -5.023296 |
| H | -2.307281 | -0.066904 | -4.718758 |
| C | -5.130880 | -5.487940 | -8.443572 |
| H | -5.421183 | -6.293751 | -7.769662 |
| H | -5.748988 | -4.608568 | -8.244532 |
| H | -5.357897 | -5.813204 | -9.468096 |

| | | | |
|---|-----------|-----------|-----------|
| C | -2.774101 | -7.641282 | -8.321282 |
| H | -2.040537 | -8.179896 | -7.716563 |
| H | -3.773353 | -7.967642 | -8.041491 |
| H | -2.600957 | -7.928313 | -9.367562 |
| C | -0.029348 | -6.114227 | -8.383844 |
| H | 0.078763 | -6.959555 | -7.697503 |
| H | 0.102693 | -6.504246 | -9.401945 |
| H | 0.776654 | -5.403335 | -8.196539 |
| C | -0.655491 | -2.994561 | -8.747335 |
| H | -0.490716 | -2.938290 | -9.831473 |
| H | -1.002921 | -2.012167 | -8.417931 |
| H | 0.303561 | -3.203053 | -8.270321 |
| C | -3.778102 | -2.625660 | -8.905489 |
| H | -3.312188 | -1.770532 | -8.407041 |
| H | -3.730888 | -2.435928 | -9.985733 |
| H | -4.832878 | -2.656189 | -8.624539 |
| C | -0.064178 | -1.506631 | -5.111159 |
| C | 1.236898 | -2.102854 | -4.993356 |
| H | 2.025257 | -1.432176 | -4.672708 |
| C | 1.464610 | -3.416521 | -5.277993 |
| C | 0.413348 | -4.261662 | -5.718890 |
| H | 2.466157 | -3.827199 | -5.175957 |
| H | 0.608430 | -5.301793 | -5.944531 |
| O | -0.319888 | -0.323759 | -4.915118 |
| C | -2.007414 | -4.458601 | -3.276365 |
| C | -2.910279 | -3.550704 | -2.688903 |
| C | -0.717924 | -4.605914 | -2.731722 |
| C | -2.518789 | -2.795325 | -1.589434 |
| H | -3.908503 | -3.447770 | -3.101329 |
| C | -0.342173 | -3.851314 | -1.627461 |
| H | -0.026744 | -5.308906 | -3.181205 |
| C | -1.234721 | -2.937972 | -1.061107 |
| H | -3.217327 | -2.094199 | -1.143640 |
| H | 0.652026 | -3.971277 | -1.208879 |
| H | -0.930683 | -2.342039 | -0.206389 |
| C | -3.792882 | -7.364203 | -4.772085 |
| O | -4.706962 | -7.579865 | -5.904073 |
| C | -5.505011 | -8.676621 | -5.897651 |
| O | -5.590345 | -9.526638 | -5.041352 |
| C | -2.790281 | -8.517676 | -4.633399 |
| H | -2.238901 | -8.663501 | -5.564351 |
| H | -2.079434 | -8.271631 | -3.840420 |
| H | -3.316497 | -9.436284 | -4.371470 |
| C | -4.605053 | -7.139414 | -3.487460 |

| | | | |
|---|-----------|------------|-----------|
| H | -5.140196 | -8.053669 | -3.227059 |
| H | -3.926505 | -6.872741 | -2.673141 |
| H | -5.319201 | -6.324316 | -3.631227 |
| O | -6.194154 | -8.640532 | -7.053435 |
| C | -7.124816 | -9.748703 | -7.225231 |
| H | -7.865548 | -9.735698 | -6.423900 |
| H | -7.589105 | -9.571543 | -8.193771 |
| H | -6.579616 | -10.694006 | -7.214654 |

Transition state **TS(4t-6at)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.817111 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.741586 E_h

$\Delta\Delta H(298) = 0.645606 \text{ E}_h$

S(298) = 0.106254 E_h

Lowest frequency: -187.44 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.486484 | -4.785456 | -6.608028 |
| C | -1.727393 | -4.050472 | -8.535632 |
| C | -3.145982 | -3.839795 | -8.668834 |
| C | -1.491200 | -5.458395 | -8.376074 |
| C | -3.791716 | -5.076048 | -8.430787 |
| C | -2.767712 | -6.097769 | -8.289457 |
| N | -3.203892 | -2.912349 | -5.965541 |
| C | -2.257003 | -2.106798 | -5.445399 |
| C | -4.498229 | -2.561870 | -5.883470 |
| C | -4.904332 | -1.371137 | -5.303888 |
| C | -3.922231 | -0.521532 | -4.790324 |
| H | -5.203701 | -3.271717 | -6.302523 |
| H | -4.198351 | 0.419751 | -4.325863 |
| H | -5.957437 | -1.117055 | -5.259391 |
| N | -0.961600 | -2.669518 | -5.486261 |
| C | -0.906480 | -4.044020 | -5.699554 |
| C | -2.260196 | -5.059504 | -4.528516 |
| C | -2.826015 | -6.030652 | -5.174060 |
| C | -2.581740 | -0.880911 | -4.852725 |
| H | -1.800347 | -0.250675 | -4.456593 |
| C | -5.261252 | -5.352800 | -8.478053 |
| H | -5.547257 | -6.107305 | -7.741914 |
| H | -5.848847 | -4.446815 | -8.307025 |

| | | | |
|---|-----------|-----------|------------|
| H | -5.538693 | -5.735947 | -9.469030 |
| C | -3.001665 | -7.566444 | -8.445292 |
| H | -2.255916 | -8.164938 | -7.919267 |
| H | -3.994645 | -7.861382 | -8.112437 |
| H | -2.914911 | -7.808220 | -9.513813 |
| C | -0.170139 | -6.150973 | -8.469021 |
| H | -0.138109 | -7.050938 | -7.848591 |
| H | 0.009451 | -6.460704 | -9.506985 |
| H | 0.651235 | -5.495218 | -8.173631 |
| C | -0.677241 | -3.002619 | -8.724999 |
| H | -0.452476 | -2.890235 | -9.793380 |
| H | -1.006564 | -2.027616 | -8.356598 |
| H | 0.252393 | -3.269307 | -8.216809 |
| C | -3.784968 | -2.529839 | -8.991844 |
| H | -3.305489 | -1.699785 | -8.465050 |
| H | -3.686003 | -2.329461 | -10.066693 |
| H | -4.850893 | -2.523779 | -8.754610 |
| C | 0.230831 | -1.852371 | -5.289660 |
| C | 1.457690 | -2.605546 | -5.251946 |
| H | 2.356253 | -2.019985 | -5.097080 |
| C | 1.488807 | -3.964635 | -5.399185 |
| C | 0.297304 | -4.702356 | -5.602055 |
| H | 2.437648 | -4.492773 | -5.352830 |
| H | 0.313008 | -5.781418 | -5.684069 |
| O | 0.139941 | -0.634644 | -5.192286 |
| C | -2.223933 | -4.305670 | -3.289131 |
| C | -3.443839 | -3.855174 | -2.749666 |
| C | -1.023335 | -4.005665 | -2.624957 |
| C | -3.456419 | -3.127563 | -1.564709 |
| H | -4.368854 | -4.072943 | -3.272334 |
| C | -1.046843 | -3.285444 | -1.436024 |
| H | -0.082449 | -4.343557 | -3.045362 |
| C | -2.260048 | -2.840704 | -0.905626 |
| H | -4.401420 | -2.782388 | -1.156636 |
| H | -0.115558 | -3.065591 | -0.923624 |
| H | -2.271922 | -2.270702 | 0.018132 |
| C | -3.444773 | -7.340896 | -4.789745 |
| O | -4.508391 | -7.543074 | -5.788669 |
| C | -5.253244 | -8.673037 | -5.732514 |
| O | -5.167614 | -9.579512 | -4.935413 |
| C | -2.375856 | -8.441358 | -4.862912 |
| H | -1.943573 | -8.496389 | -5.863531 |
| H | -1.580382 | -8.202545 | -4.151637 |
| H | -2.814982 | -9.403991 | -4.598302 |

| | | | |
|---|-----------|------------|-----------|
| C | -4.064435 | -7.245337 | -3.388578 |
| H | -4.464908 | -8.218957 | -3.102387 |
| H | -3.299342 | -6.944701 | -2.668486 |
| H | -4.868466 | -6.505705 | -3.377902 |
| O | -6.121065 | -8.597828 | -6.759521 |
| C | -7.022760 | -9.737853 | -6.858839 |
| H | -7.625105 | -9.811838 | -5.951762 |
| H | -7.643611 | -9.524103 | -7.727155 |
| H | -6.446919 | -10.654129 | -7.000032 |

Intermediate **Co-VIat**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.878007 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.806607 E_h

$\Delta\Delta H(298) = 0.649138 \text{ E}_h$

S(298) = 0.110063 E_h

Lowest frequency: 22.50 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.830143 | -4.780899 | -6.981613 |
| C | -2.286554 | -4.116303 | -8.985633 |
| C | -3.317628 | -5.129253 | -9.042008 |
| C | -1.121854 | -4.697501 | -8.407199 |
| C | -2.792232 | -6.325477 | -8.467629 |
| C | -1.452649 | -6.037397 | -8.004500 |
| N | -3.707247 | -3.216183 | -6.293250 |
| C | -2.900544 | -2.434993 | -5.554161 |
| C | -5.037132 | -2.980716 | -6.310436 |
| C | -5.593647 | -1.931460 | -5.596744 |
| C | -4.759981 | -1.115516 | -4.830457 |
| H | -5.632090 | -3.669630 | -6.898369 |
| H | -5.168858 | -0.290040 | -4.257210 |
| H | -6.663591 | -1.762083 | -5.640039 |
| N | -1.485191 | -2.693034 | -5.594442 |
| C | -0.882386 | -3.710640 | -4.836262 |
| C | -1.700100 | -4.839468 | -4.353421 |
| C | -2.607603 | -5.421763 | -5.172845 |
| C | -3.393035 | -1.370485 | -4.810237 |
| H | -2.705610 | -0.755456 | -4.241607 |
| C | -3.462412 | -7.660953 | -8.461927 |
| H | -3.142793 | -8.280053 | -7.622383 |

| | | | |
|---|-----------|-----------|------------|
| H | -4.549291 | -7.563449 | -8.427679 |
| H | -3.206159 | -8.198796 | -9.384098 |
| C | -0.488672 | -7.008586 | -7.400081 |
| H | 0.127785 | -6.530104 | -6.634205 |
| H | -1.001976 | -7.858676 | -6.947186 |
| H | 0.183596 | -7.397928 | -8.175119 |
| C | 0.214906 | -4.051872 | -8.255914 |
| H | 0.666053 | -4.271311 | -7.284467 |
| H | 0.897469 | -4.437717 | -9.024873 |
| H | 0.155772 | -2.969746 | -8.381522 |
| C | -2.406595 | -2.720358 | -9.510696 |
| H | -1.995495 | -2.668382 | -10.526803 |
| H | -3.451315 | -2.404863 | -9.563263 |
| H | -1.867517 | -2.000834 | -8.888892 |
| C | -4.660438 | -4.967257 | -9.682243 |
| H | -5.017275 | -3.936146 | -9.609294 |
| H | -4.601133 | -5.214460 | -10.749953 |
| H | -5.401985 | -5.623148 | -9.222837 |
| C | -0.741788 | -1.586799 | -6.177808 |
| C | 0.651027 | -1.553508 | -5.836152 |
| H | 1.217418 | -0.715517 | -6.226009 |
| C | 1.216463 | -2.514720 | -5.044062 |
| C | 0.457873 | -3.605075 | -4.557695 |
| H | 2.272446 | -2.454865 | -4.795627 |
| H | 0.918702 | -4.385270 | -3.964188 |
| O | -1.352900 | -0.779816 | -6.877836 |
| C | -1.402320 | -5.257674 | -2.951558 |
| C | -1.596290 | -4.362239 | -1.888602 |
| C | -0.882912 | -6.530129 | -2.679899 |
| C | -1.317961 | -4.747288 | -0.580559 |
| H | -1.983665 | -3.367279 | -2.091866 |
| C | -0.593693 | -6.912234 | -1.369522 |
| H | -0.681855 | -7.208509 | -3.503385 |
| C | -0.820055 | -6.026075 | -0.317204 |
| H | -1.487096 | -4.051187 | 0.235509 |
| H | -0.185326 | -7.899044 | -1.172912 |
| H | -0.600233 | -6.324576 | 0.703108 |
| C | -3.725038 | -6.359871 | -4.764482 |
| O | -4.651542 | -6.128660 | -5.950896 |
| C | -5.872200 | -6.708264 | -5.988319 |
| O | -6.318966 | -7.540605 | -5.234910 |
| C | -3.333580 | -7.833982 | -4.701307 |
| H | -2.722545 | -8.115345 | -5.560497 |
| H | -2.749876 | -7.995582 | -3.793159 |

| | | | |
|---|-----------|-----------|-----------|
| H | -4.225070 | -8.461378 | -4.659424 |
| C | -4.457105 | -5.892911 | -3.506221 |
| H | -5.336696 | -6.513793 | -3.328826 |
| H | -3.786778 | -5.979438 | -2.649688 |
| H | -4.756445 | -4.845896 | -3.606882 |
| O | -6.520087 | -6.179775 | -7.051234 |
| C | -7.856601 | -6.727194 | -7.255538 |
| H | -8.476801 | -6.521494 | -6.381727 |
| H | -8.235006 | -6.213283 | -8.137783 |
| H | -7.793894 | -7.803828 | -7.422071 |

Intermediate **Co-VIt**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.871775 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.797346 E_h

$\Delta\Delta H(298) = 0.649182$ E_h

S(298) = 0.107162 E_h

Lowest frequency: 24.97 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.766186 | -4.886816 | -7.257985 |
| C | -1.778518 | -4.198279 | -9.115256 |
| C | -2.658064 | -5.302748 | -9.409919 |
| C | -0.745539 | -4.673070 | -8.262288 |
| C | -2.191278 | -6.445740 | -8.700491 |
| C | -1.062490 | -6.031972 | -7.903706 |
| N | -3.725406 | -3.233352 | -6.822815 |
| C | -3.093314 | -2.461221 | -5.922602 |
| C | -5.000260 | -2.933773 | -7.152433 |
| C | -5.688767 | -1.884476 | -6.566798 |
| C | -5.050449 | -1.120771 | -5.589769 |
| H | -5.448267 | -3.571029 | -7.903082 |
| H | -5.566704 | -0.303946 | -5.096565 |
| H | -6.708856 | -1.677026 | -6.869800 |
| N | -1.686599 | -2.664015 | -5.709130 |
| C | -1.164952 | -3.664936 | -4.882810 |
| C | -1.986978 | -4.829102 | -4.503414 |
| C | -2.861744 | -5.429906 | -5.358902 |
| C | -3.728075 | -1.407274 | -5.275348 |
| H | -3.171631 | -0.816209 | -4.557433 |
| C | -2.701653 | -7.839642 | -8.876475 |

| | | | |
|---|-----------|-----------|------------|
| H | -2.272845 | -8.527055 | -8.144977 |
| H | -3.792280 | -7.885244 | -8.808305 |
| H | -2.419880 | -8.203699 | -9.872725 |
| C | -0.207594 | -6.908545 | -7.044876 |
| H | 0.190566 | -6.351868 | -6.192082 |
| H | -0.767298 | -7.766076 | -6.665796 |
| H | 0.644604 | -7.290340 | -7.621400 |
| C | 0.495505 | -3.940536 | -7.884586 |
| H | 0.781622 | -4.117616 | -6.845672 |
| H | 1.323933 | -4.295732 | -8.513141 |
| H | 0.398593 | -2.866890 | -8.050711 |
| C | -1.883825 | -2.823730 | -9.697100 |
| H | -1.251257 | -2.746821 | -10.590643 |
| H | -2.909377 | -2.602639 | -10.003399 |
| H | -1.566810 | -2.053075 | -8.989673 |
| C | -3.798022 | -5.269682 | -10.375951 |
| H | -4.328846 | -4.313630 | -10.340478 |
| H | -3.426642 | -5.394408 | -11.401420 |
| H | -4.511003 | -6.070088 | -10.173217 |
| C | -0.911278 | -1.518112 | -6.165861 |
| C | 0.395549 | -1.405341 | -5.586794 |
| H | 0.966282 | -0.526717 | -5.864678 |
| C | 0.877013 | -2.355174 | -4.729415 |
| C | 0.114071 | -3.497621 | -4.399214 |
| H | 1.871414 | -2.246205 | -4.305544 |
| H | 0.521894 | -4.264551 | -3.753960 |
| O | -1.431520 | -0.743943 | -6.968552 |
| C | -1.640933 | -5.328158 | -3.134201 |
| C | -1.868105 | -4.547454 | -1.993468 |
| C | -1.006216 | -6.568934 | -2.992885 |
| C | -1.510541 | -5.018992 | -0.733249 |
| H | -2.341416 | -3.574520 | -2.096122 |
| C | -0.633489 | -7.035830 | -1.732576 |
| H | -0.801570 | -7.163038 | -3.879117 |
| C | -0.894180 | -6.265687 | -0.599312 |
| H | -1.708605 | -4.413907 | 0.146397 |
| H | -0.138994 | -7.997908 | -1.636540 |
| H | -0.610727 | -6.629437 | 0.383478 |
| C | -3.896424 | -6.449960 | -4.899654 |
| O | -5.273987 | -5.979615 | -5.380816 |
| C | -5.562058 | -5.937015 | -6.658192 |
| O | -4.764643 | -5.865843 | -7.601548 |
| C | -3.660605 | -7.841771 | -5.472214 |
| H | -3.542326 | -7.810379 | -6.553220 |

| | | | |
|---|-----------|-----------|-----------|
| H | -2.746359 | -8.247270 | -5.029981 |
| H | -4.491848 | -8.503592 | -5.211458 |
| C | -4.226116 | -6.537918 | -3.405048 |
| H | -5.163319 | -7.091894 | -3.308946 |
| H | -3.448751 | -7.068629 | -2.859509 |
| H | -4.356237 | -5.546885 | -2.968170 |
| O | -6.886520 | -5.953563 | -6.821354 |
| C | -7.358610 | -5.912718 | -8.195710 |
| H | -7.017434 | -6.801123 | -8.730176 |
| H | -8.443426 | -5.900118 | -8.112446 |
| H | -6.995964 | -5.013184 | -8.697902 |

Transition state **TS(6t-7t)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.836884 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.764414 E_h

$\Delta\Delta H(298) = 0.646560$ E_h

S(298) = 0.105329 E_h

Lowest frequency: -358.35 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.672686 | -4.830591 | -7.296918 |
| C | -1.982530 | -4.607743 | -9.345016 |
| C | -2.440326 | -5.958189 | -9.258502 |
| C | -0.871766 | -4.434662 | -8.432900 |
| C | -1.726731 | -6.581704 | -8.199883 |
| C | -0.727260 | -5.642946 | -7.702914 |
| N | -3.469115 | -3.088166 | -7.031677 |
| C | -3.205842 | -3.010239 | -5.660801 |
| C | -4.582648 | -2.535178 | -7.541633 |
| C | -5.481927 | -1.824628 | -6.771363 |
| C | -5.254779 | -1.731208 | -5.380699 |
| H | -4.719068 | -2.659501 | -8.611171 |
| H | -5.949362 | -1.180014 | -4.754408 |
| H | -6.325824 | -1.330634 | -7.237461 |
| N | -1.787237 | -2.737197 | -5.379016 |
| C | -1.081750 | -3.691782 | -4.681741 |
| C | -1.875159 | -4.880592 | -4.445400 |
| C | -3.023253 | -4.904394 | -5.233318 |
| C | -4.141826 | -2.299526 | -4.822677 |
| H | -3.928694 | -2.223664 | -3.762177 |

| | | | |
|---|-----------|-----------|------------|
| C | -1.833196 | -8.016548 | -7.792234 |
| H | -1.537813 | -8.164455 | -6.750413 |
| H | -2.847036 | -8.402522 | -7.927367 |
| H | -1.164641 | -8.632080 | -8.408873 |
| C | 0.373560 | -5.994821 | -6.754106 |
| H | 0.924760 | -5.108070 | -6.437570 |
| H | 0.003427 | -6.500328 | -5.858353 |
| H | 1.081223 | -6.675370 | -7.244364 |
| C | -0.037952 | -3.199729 | -8.325697 |
| H | 0.558995 | -3.196644 | -7.411628 |
| H | 0.651872 | -3.134445 | -9.176919 |
| H | -0.655869 | -2.297059 | -8.334514 |
| C | -2.468402 | -3.560545 | -10.294476 |
| H | -1.830526 | -3.536632 | -11.187522 |
| H | -3.489842 | -3.760512 | -10.628406 |
| H | -2.431939 | -2.566597 | -9.840299 |
| C | -3.507362 | -6.585754 | -10.094853 |
| H | -4.231631 | -5.845243 | -10.442184 |
| H | -3.062623 | -7.056482 | -10.981045 |
| H | -4.048146 | -7.356965 | -9.541831 |
| C | -1.277438 | -1.455351 | -5.742067 |
| C | 0.081299 | -1.234896 | -5.285476 |
| H | 0.497271 | -0.256953 | -5.500852 |
| C | 0.783700 | -2.181872 | -4.587424 |
| C | 0.214432 | -3.441695 | -4.284737 |
| H | 1.797424 | -1.967134 | -4.260967 |
| H | 0.772508 | -4.209103 | -3.763859 |
| O | -1.976151 | -0.658499 | -6.360178 |
| C | -1.457382 | -5.808870 | -3.380069 |
| C | -1.120766 | -5.310949 | -2.106674 |
| C | -1.353824 | -7.190776 | -3.609695 |
| C | -0.726463 | -6.175706 | -1.090310 |
| H | -1.199385 | -4.245473 | -1.913793 |
| C | -0.939784 | -8.051475 | -2.597309 |
| H | -1.567596 | -7.582184 | -4.598010 |
| C | -0.634126 | -7.547718 | -1.332124 |
| H | -0.490021 | -5.778726 | -0.107933 |
| H | -0.849065 | -9.114762 | -2.797290 |
| H | -0.318629 | -8.220072 | -0.540481 |
| C | -4.300325 | -5.628176 | -4.804671 |
| O | -5.479838 | -5.034533 | -5.518482 |
| C | -5.615025 | -5.250062 | -6.813677 |
| O | -4.712894 | -5.559551 | -7.601423 |
| C | -4.310171 | -7.134631 | -5.079273 |

| | | | |
|---|-----------|-----------|-----------|
| H | -3.919853 | -7.371364 | -6.068719 |
| H | -3.710243 | -7.642794 | -4.323865 |
| H | -5.338362 | -7.500265 | -4.994836 |
| C | -4.672784 | -5.348767 | -3.346793 |
| H | -5.621359 | -5.839353 | -3.114139 |
| H | -3.898644 | -5.741646 | -2.685925 |
| H | -4.780319 | -4.276028 | -3.179148 |
| O | -6.882775 | -5.083861 | -7.168068 |
| C | -7.157094 | -5.181027 | -8.594502 |
| H | -6.907954 | -6.181476 | -8.951507 |
| H | -8.223946 | -4.986771 | -8.681505 |
| H | -6.576056 | -4.430105 | -9.133017 |

Intermediate **Co-VIIt**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.867001 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.796221 E_h

$\Delta\Delta H(298) = 0.647955$ E_h

S(298) = 0.103879 E_h

Lowest frequency: 9.64 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.800288 | -5.000800 | -7.652154 |
| C | -1.985950 | -4.453171 | -9.498963 |
| C | -2.534676 | -5.747379 | -9.613556 |
| C | -0.967291 | -4.498075 | -8.446293 |
| C | -1.888311 | -6.594560 | -8.619562 |
| C | -0.870827 | -5.837327 | -7.962401 |
| N | -3.467916 | -3.408864 | -6.892387 |
| C | -3.204273 | -3.212806 | -5.457722 |
| C | -4.339255 | -2.610987 | -7.517870 |
| C | -5.132096 | -1.662091 | -6.886298 |
| C | -5.018710 | -1.488405 | -5.485416 |
| H | -4.438932 | -2.787682 | -8.584849 |
| H | -5.637734 | -0.756705 | -4.975858 |
| H | -5.827678 | -1.074399 | -7.472866 |
| N | -1.797156 | -2.747086 | -5.264189 |
| C | -1.078969 | -3.611394 | -4.474451 |
| C | -1.930454 | -4.752503 | -4.151875 |
| C | -3.150318 | -4.576736 | -4.731067 |
| C | -4.114718 | -2.218671 | -4.786255 |

| | | | |
|---|-----------|-----------|------------|
| H | -3.947511 | -2.071297 | -3.724327 |
| C | -2.210454 | -8.038846 | -8.396208 |
| H | -1.845126 | -8.387132 | -7.426836 |
| H | -3.288766 | -8.216521 | -8.439987 |
| H | -1.741962 | -8.658386 | -9.171269 |
| C | 0.140633 | -6.334331 | -6.978205 |
| H | 0.257133 | -5.651885 | -6.131604 |
| H | -0.124619 | -7.321024 | -6.593454 |
| H | 1.120555 | -6.426001 | -7.463506 |
| C | -0.051477 | -3.372894 | -8.098008 |
| H | 0.370669 | -3.492107 | -7.098138 |
| H | 0.784386 | -3.355990 | -8.810766 |
| H | -0.554645 | -2.405754 | -8.156309 |
| C | -2.303129 | -3.244053 | -10.319423 |
| H | -1.564552 | -3.129592 | -11.123201 |
| H | -3.288055 | -3.318452 | -10.788906 |
| H | -2.270110 | -2.331638 | -9.717100 |
| C | -3.609278 | -6.196688 | -10.551090 |
| H | -4.173461 | -5.350212 | -10.951532 |
| H | -3.173035 | -6.735482 | -11.401558 |
| H | -4.307149 | -6.878565 | -10.057141 |
| C | -1.322451 | -1.511193 | -5.761239 |
| C | 0.025960 | -1.215238 | -5.320799 |
| H | 0.434994 | -0.268072 | -5.653889 |
| C | 0.747309 | -2.077366 | -4.538245 |
| C | 0.206258 | -3.316768 | -4.102005 |
| H | 1.757384 | -1.810144 | -4.240252 |
| H | 0.763904 | -4.002175 | -3.476045 |
| O | -2.028470 | -0.819012 | -6.494195 |
| C | -1.446424 | -5.801201 | -3.224113 |
| C | -1.245910 | -5.463943 | -1.876269 |
| C | -1.135162 | -7.097579 | -3.652416 |
| C | -0.768237 | -6.413365 | -0.974654 |
| H | -1.471028 | -4.456549 | -1.537296 |
| C | -0.649109 | -8.042552 | -2.751194 |
| H | -1.276126 | -7.362097 | -4.693946 |
| C | -0.468125 | -7.704338 | -1.409975 |
| H | -0.628397 | -6.142379 | 0.067305 |
| H | -0.410063 | -9.043440 | -3.097825 |
| H | -0.091424 | -8.441954 | -0.708297 |
| C | -4.400554 | -5.382114 | -4.456516 |
| O | -5.480810 | -4.999592 | -5.430666 |
| C | -5.495333 | -5.497999 | -6.650010 |
| O | -4.527321 | -5.923878 | -7.308635 |

| | | | |
|---|-----------|-----------|-----------|
| C | -4.229092 | -6.900208 | -4.495929 |
| H | -3.691415 | -7.232532 | -5.384001 |
| H | -3.679631 | -7.221094 | -3.610436 |
| H | -5.219292 | -7.365171 | -4.469528 |
| C | -5.026580 | -4.959502 | -3.120972 |
| H | -5.926663 | -5.550861 | -2.933386 |
| H | -4.303580 | -5.138173 | -2.321165 |
| H | -5.293587 | -3.901521 | -3.138334 |
| O | -6.731890 | -5.488793 | -7.117705 |
| C | -6.900553 | -5.865262 | -8.516187 |
| H | -6.622988 | -6.911973 | -8.648541 |
| H | -7.959662 | -5.712633 | -8.711616 |
| H | -6.284418 | -5.222367 | -9.146082 |

Transition state **TS(7t-8t)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.845669 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.776060 E_h

$\Delta\Delta H(298) = 0.645757$ E_h

S(298) = 0.105043 E_h

Lowest frequency: -267.94 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.926548 | -4.983797 | -7.663840 |
| C | -2.193289 | -4.541028 | -9.600780 |
| C | -2.589633 | -5.894537 | -9.533566 |
| C | -1.172084 | -4.337455 | -8.581078 |
| C | -1.808874 | -6.543196 | -8.484434 |
| C | -0.882877 | -5.597299 | -7.960254 |
| N | -3.579496 | -3.372536 | -6.877847 |
| C | -3.491149 | -3.268332 | -5.502345 |
| C | -4.131835 | -2.354178 | -7.587409 |
| C | -4.765089 | -1.289114 | -6.991494 |
| C | -4.838568 | -1.246515 | -5.583712 |
| H | -4.098185 | -2.463671 | -8.664315 |
| H | -5.363641 | -0.436796 | -5.087482 |
| H | -5.214326 | -0.517518 | -7.604969 |
| N | -1.585361 | -2.639190 | -5.171714 |
| C | -1.037865 | -3.618093 | -4.447407 |

| | | | |
|---|-----------|-----------|------------|
| C | -1.978476 | -4.719578 | -4.194161 |
| C | -3.204048 | -4.565950 | -4.771246 |
| C | -4.230740 | -2.227029 | -4.846532 |
| H | -4.219438 | -2.197615 | -3.763193 |
| C | -1.931395 | -7.986543 | -8.108381 |
| H | -1.491093 | -8.186695 | -7.128694 |
| H | -2.977969 | -8.303735 | -8.086012 |
| H | -1.412922 | -8.615950 | -8.842655 |
| C | 0.227228 | -5.849655 | -6.991308 |
| H | 0.219056 | -5.146301 | -6.153947 |
| H | 0.185267 | -6.863990 | -6.591225 |
| H | 1.192179 | -5.738023 | -7.501128 |
| C | -0.433334 | -3.061378 | -8.353925 |
| H | 0.184130 | -3.115045 | -7.456187 |
| H | 0.228765 | -2.871757 | -9.209230 |
| H | -1.102546 | -2.202570 | -8.254835 |
| C | -2.645789 | -3.509410 | -10.585925 |
| H | -2.057525 | -3.593290 | -11.508754 |
| H | -3.698124 | -3.632496 | -10.859480 |
| H | -2.497531 | -2.496781 | -10.202726 |
| C | -3.618946 | -6.574680 | -10.377333 |
| H | -4.276432 | -5.852306 | -10.867367 |
| H | -3.132663 | -7.167244 | -11.162393 |
| H | -4.231581 | -7.258554 | -9.783369 |
| C | -0.949452 | -1.456675 | -5.528884 |
| C | 0.418218 | -1.364193 | -5.029602 |
| H | 0.973955 | -0.478371 | -5.319297 |
| C | 0.991697 | -2.372035 | -4.289754 |
| C | 0.269548 | -3.540359 | -3.972274 |
| H | 2.014439 | -2.263401 | -3.938451 |
| H | 0.678886 | -4.323576 | -3.345668 |
| O | -1.490190 | -0.599046 | -6.242094 |
| C | -1.540645 | -5.813327 | -3.287137 |
| C | -1.546880 | -5.591370 | -1.902154 |
| C | -1.058935 | -7.034120 | -3.773937 |
| C | -1.107908 | -6.582242 | -1.025049 |
| H | -1.891632 | -4.636495 | -1.514918 |
| C | -0.615178 | -8.022386 | -2.897392 |
| H | -1.045886 | -7.210323 | -4.843460 |
| C | -0.642531 | -7.800587 | -1.520375 |
| H | -1.124965 | -6.398985 | 0.044927 |
| H | -0.247408 | -8.965654 | -3.290129 |
| H | -0.297695 | -8.570536 | -0.837305 |
| C | -4.402516 | -5.459716 | -4.453836 |

| | | | |
|---|-----------|-----------|-----------|
| O | -5.540804 | -5.117205 | -5.385344 |
| C | -5.561719 | -5.561104 | -6.618654 |
| O | -4.593885 | -5.966173 | -7.297435 |
| C | -4.170111 | -6.968567 | -4.527016 |
| H | -3.607732 | -7.259735 | -5.413893 |
| H | -3.623572 | -7.292568 | -3.641755 |
| H | -5.142626 | -7.470560 | -4.526871 |
| C | -5.011286 | -5.084678 | -3.098390 |
| H | -5.883822 | -5.713172 | -2.900899 |
| H | -4.264275 | -5.251935 | -2.319395 |
| H | -5.320190 | -4.038262 | -3.087534 |
| O | -6.795939 | -5.533804 | -7.087329 |
| C | -6.965830 | -5.856792 | -8.499499 |
| H | -6.687473 | -6.897043 | -8.672992 |
| H | -8.025213 | -5.696907 | -8.687067 |
| H | -6.351688 | -5.187805 | -9.104141 |

Intermediate Co-VIIIIt

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.855444 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.779019 E_h

$\Delta\Delta H(298) = 0.647481 \text{ E}_h$

S(298) = 0.107338 E_h

Lowest frequency: 26.71 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.988475 | -4.950162 | -7.765095 |
| C | -2.480665 | -4.727643 | -9.799247 |
| C | -2.570295 | -6.102175 | -9.440157 |
| C | -1.495338 | -4.129689 | -8.930815 |
| C | -1.595481 | -6.373604 | -8.397290 |
| C | -0.909466 | -5.166916 | -8.105845 |
| N | -3.620475 | -3.344396 | -6.865840 |
| C | -3.645540 | -3.308914 | -5.511785 |
| C | -3.985229 | -2.239710 | -7.554413 |
| C | -4.405425 | -1.076804 | -6.933848 |
| C | -4.472303 | -1.047262 | -5.540566 |
| H | -3.927967 | -2.318659 | -8.632956 |
| H | -4.801441 | -0.153398 | -5.020653 |
| H | -4.676651 | -0.215789 | -7.533793 |
| N | -1.170536 | -2.727552 | -5.270020 |

| | | | |
|---|-----------|-----------|------------|
| C | -0.984589 | -3.671081 | -4.357792 |
| C | -2.047583 | -4.700323 | -4.196159 |
| C | -3.274636 | -4.558049 | -4.771869 |
| C | -4.099513 | -2.177751 | -4.829197 |
| H | -4.106471 | -2.185389 | -3.745290 |
| C | -1.325993 | -7.725322 | -7.813951 |
| H | -0.697527 | -7.655646 | -6.923842 |
| H | -2.250167 | -8.247625 | -7.547921 |
| H | -0.797215 | -8.352448 | -8.543089 |
| C | 0.276697 | -5.003432 | -7.209059 |
| H | 0.482132 | -3.950047 | -7.018809 |
| H | 0.143396 | -5.500887 | -6.244456 |
| H | 1.162952 | -5.442047 | -7.685470 |
| C | -1.043732 | -2.706536 | -8.961552 |
| H | -0.026405 | -2.657556 | -9.370470 |
| H | -1.681184 | -2.095157 | -9.604276 |
| H | -1.020385 | -2.251760 | -7.966872 |
| C | -3.242371 | -4.039626 | -10.889800 |
| H | -2.708572 | -4.127497 | -11.844661 |
| H | -4.235303 | -4.476837 | -11.029620 |
| H | -3.364884 | -2.971321 | -10.690776 |
| C | -3.478007 | -7.126606 | -10.041983 |
| H | -4.314562 | -6.662708 | -10.569999 |
| H | -2.926251 | -7.737412 | -10.767606 |
| H | -3.878890 | -7.801798 | -9.280856 |
| C | -0.241720 | -1.705381 | -5.409255 |
| C | 0.932092 | -1.693184 | -4.556737 |
| H | 1.639069 | -0.880392 | -4.685804 |
| C | 1.129328 | -2.707847 | -3.643507 |
| C | 0.171498 | -3.720624 | -3.529841 |
| H | 2.012385 | -2.723322 | -3.011130 |
| H | 0.297994 | -4.522435 | -2.812849 |
| O | -0.421833 | -0.826157 | -6.284073 |
| C | -1.691670 | -5.852949 | -3.312871 |
| C | -1.920064 | -5.790514 | -1.931750 |
| C | -1.054645 | -6.982015 | -3.840192 |
| C | -1.558002 | -6.854020 | -1.104574 |
| H | -2.367214 | -4.898807 | -1.501376 |
| C | -0.693738 | -8.045958 | -3.015905 |
| H | -0.860332 | -7.031043 | -4.906234 |
| C | -0.951595 | -7.987765 | -1.645737 |
| H | -1.745686 | -6.792989 | -0.036875 |
| H | -0.210767 | -8.919746 | -3.443015 |
| H | -0.672395 | -8.816181 | -1.002273 |

| | | | |
|---|-----------|-----------|-----------|
| C | -4.464559 | -5.482563 | -4.452439 |
| O | -5.600057 | -5.149412 | -5.392039 |
| C | -5.578334 | -5.535160 | -6.644780 |
| O | -4.595810 | -5.967935 | -7.280694 |
| C | -4.223451 | -6.990865 | -4.519414 |
| H | -3.620296 | -7.275600 | -5.380601 |
| H | -3.720879 | -7.321630 | -3.611029 |
| H | -5.194965 | -7.492558 | -4.568627 |
| C | -5.105052 | -5.094835 | -3.115464 |
| H | -6.006806 | -5.693030 | -2.959205 |
| H | -4.399434 | -5.294842 | -2.308907 |
| H | -5.379810 | -4.038115 | -3.107766 |
| O | -6.782990 | -5.418272 | -7.174402 |
| C | -6.889905 | -5.705802 | -8.600803 |
| H | -6.627120 | -6.747989 | -8.785330 |
| H | -7.933949 | -5.513234 | -8.837275 |
| H | -6.228925 | -5.038826 | -9.157182 |

Intermediate **Co-IXt**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.903734 Eh

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.830677 Eh

$\Delta\Delta H(298) = 0.649851$ Eh

S(298) = 0.108995 Eh

Lowest frequency: 22.83 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -2.238423 | -4.206055 | -7.323243 |
| C | -1.946234 | -4.314124 | -9.522430 |
| C | -3.084555 | -5.077443 | -9.110999 |
| C | -0.820607 | -4.801849 | -8.783949 |
| C | -2.640750 | -6.136827 | -8.235317 |
| C | -1.252103 | -5.942506 | -7.994682 |
| N | -3.701172 | -3.268487 | -6.472550 |
| C | -3.812817 | -3.451548 | -5.130876 |
| C | -4.296039 | -2.219960 | -7.071755 |
| C | -5.045580 | -1.293487 | -6.361994 |
| C | -5.136194 | -1.433860 | -4.980816 |
| H | -4.125526 | -2.125532 | -8.137029 |
| H | -5.676273 | -0.705642 | -4.384014 |
| H | -5.514613 | -0.467080 | -6.883633 |

| | | | |
|---|-----------|-----------|------------|
| N | -1.129715 | -3.421307 | -5.967409 |
| C | -1.003743 | -3.632939 | -4.638862 |
| C | -1.902047 | -4.660095 | -4.063890 |
| C | -3.212499 | -4.657810 | -4.450877 |
| C | -4.512072 | -2.517339 | -4.366337 |
| H | -4.547539 | -2.637957 | -3.290536 |
| C | -3.482736 | -7.276224 | -7.766370 |
| H | -3.122685 | -7.691765 | -6.823920 |
| H | -4.525870 | -6.982657 | -7.646751 |
| H | -3.443888 | -8.078361 | -8.516226 |
| C | -0.353473 | -6.813228 | -7.176865 |
| H | 0.473308 | -6.237895 | -6.752994 |
| H | -0.895142 | -7.300581 | -6.362780 |
| H | 0.081994 | -7.600068 | -7.805965 |
| C | 0.584360 | -4.307959 | -8.883120 |
| H | 1.081820 | -4.319343 | -7.909108 |
| H | 1.158483 | -4.960753 | -9.553717 |
| H | 0.616324 | -3.291162 | -9.274827 |
| C | -1.930325 | -3.177348 | -10.489443 |
| H | -1.516486 | -3.510463 | -11.449797 |
| H | -2.937361 | -2.798835 | -10.681053 |
| H | -1.314465 | -2.356854 | -10.115045 |
| C | -4.492531 | -4.903534 | -9.584502 |
| H | -4.673538 | -3.888951 | -9.947431 |
| H | -4.690887 | -5.589004 | -10.418538 |
| H | -5.209459 | -5.127497 | -8.790186 |
| C | -0.692391 | -2.281326 | -6.586608 |
| C | 0.207967 | -1.445494 | -5.873220 |
| H | 0.624512 | -0.572043 | -6.361901 |
| C | 0.476407 | -1.745651 | -4.549209 |
| C | -0.147025 | -2.828691 | -3.899577 |
| H | 1.144726 | -1.103084 | -3.983031 |
| H | -0.008773 | -3.012494 | -2.840871 |
| O | -1.193209 | -2.117863 | -7.753708 |
| C | -1.279887 | -5.537877 | -3.043113 |
| C | -1.768798 | -5.570140 | -1.729250 |
| C | -0.122902 | -6.268895 | -3.350822 |
| C | -1.145032 | -6.350872 | -0.758621 |
| H | -2.624242 | -4.958268 | -1.463524 |
| C | 0.487766 | -7.066467 | -2.387435 |
| H | 0.289971 | -6.217128 | -4.353057 |
| C | -0.024896 | -7.113659 | -1.089426 |
| H | -1.530453 | -6.358638 | 0.256357 |
| H | 1.370303 | -7.644057 | -2.645056 |

| | | | |
|---|-----------|-----------|-----------|
| H | 0.457207 | -7.728300 | -0.335640 |
| C | -4.260318 | -5.739963 | -4.118277 |
| O | -5.049448 | -5.711621 | -5.388636 |
| C | -6.181411 | -6.438691 | -5.496370 |
| O | -6.664699 | -7.196245 | -4.685765 |
| C | -3.677868 | -7.142194 | -3.942777 |
| H | -2.895450 | -7.338845 | -4.678386 |
| H | -3.249432 | -7.258303 | -2.947526 |
| H | -4.484536 | -7.868652 | -4.053262 |
| C | -5.179741 | -5.361700 | -2.947881 |
| H | -5.836565 | -6.197523 | -2.707118 |
| H | -4.575348 | -5.121726 | -2.071110 |
| H | -5.797484 | -4.496892 | -3.199633 |
| O | -6.687502 | -6.169733 | -6.720215 |
| C | -7.924563 | -6.880447 | -7.013442 |
| H | -8.693817 | -6.595741 | -6.293666 |
| H | -8.193439 | -6.564796 | -8.020317 |
| H | -7.754529 | -7.957705 | -6.968796 |

Transition state **TSA**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.866294 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.784409 E_h

$\Delta\Delta H(298) = 0.646668$ E_h

S(298) = 0.101361 E_h

Lowest frequency: -64.79 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|---|-----------|-----------|-----------|
| N | -0.371967 | 1.418046 | 1.035670 |
| C | 0.922702 | 1.786050 | 1.123651 |
| C | -1.171030 | 1.701989 | 2.096195 |
| C | -0.708872 | 2.289054 | 3.261376 |
| C | 0.647065 | 2.582871 | 3.378241 |
| H | -2.202740 | 1.405734 | 1.985914 |
| H | 1.056004 | 3.013894 | 4.286062 |
| H | -1.408701 | 2.496203 | 4.063434 |
| N | 1.793439 | 1.720126 | -0.011705 |
| C | 2.312461 | 0.517403 | -0.470363 |
| C | 1.690656 | -0.759704 | -0.096704 |
| C | 0.364974 | -1.020302 | -0.071766 |
| C | 1.462361 | 2.337684 | 2.284900 |

| | | | |
|----|-----------|-----------|-----------|
| H | 2.514692 | 2.593172 | 2.296061 |
| C | 2.364232 | 3.016066 | -0.362038 |
| C | 3.470511 | 2.956439 | -1.272118 |
| H | 3.894047 | 3.910344 | -1.564470 |
| C | 3.996251 | 1.762881 | -1.684298 |
| C | 3.428371 | 0.537399 | -1.273197 |
| H | 4.861426 | 1.751188 | -2.341369 |
| H | 3.838551 | -0.406270 | -1.609153 |
| O | 1.880064 | 4.034361 | 0.129616 |
| C | 2.673192 | -1.843316 | 0.242553 |
| C | 3.311418 | -1.836590 | 1.490494 |
| C | 2.975898 | -2.862328 | -0.669633 |
| C | 4.216404 | -2.841790 | 1.827033 |
| H | 3.092292 | -1.041601 | 2.198824 |
| C | 3.890077 | -3.862834 | -0.336186 |
| H | 2.501643 | -2.863007 | -1.647239 |
| C | 4.507366 | -3.857180 | 0.914195 |
| H | 4.697605 | -2.830919 | 2.800432 |
| H | 4.120313 | -4.644208 | -1.054338 |
| H | 5.216375 | -4.636782 | 1.174846 |
| C | -0.203746 | -2.238385 | 0.336294 |
| O | -2.727557 | -2.380182 | 0.059152 |
| C | -3.008027 | -1.483653 | 0.857072 |
| O | -2.431383 | -0.321981 | 0.939364 |
| C | -0.259189 | -3.440307 | -0.538710 |
| H | -0.185444 | -3.197506 | -1.595815 |
| H | 0.638036 | -4.021346 | -0.266919 |
| H | -1.138488 | -4.052176 | -0.338769 |
| C | -0.426474 | -2.449094 | 1.797709 |
| H | -1.161414 | -3.228848 | 2.002267 |
| H | 0.552823 | -2.780184 | 2.182759 |
| H | -0.679225 | -1.522256 | 2.313190 |
| O | -3.991319 | -1.714046 | 1.761262 |
| C | -4.306252 | -0.665992 | 2.704822 |
| H | -4.627196 | 0.239941 | 2.182664 |
| H | -5.122667 | -1.065039 | 3.305702 |
| H | -3.441234 | -0.446092 | 3.336504 |
| Co | -1.173834 | 0.283665 | -0.415982 |
| C | -0.660788 | 0.624691 | -2.423545 |
| C | -1.765536 | -0.308021 | -2.333365 |
| C | -2.850360 | 0.363795 | -1.693342 |
| C | -1.076736 | 1.854787 | -1.834146 |
| C | -2.407886 | 1.673744 | -1.310411 |
| C | 0.595077 | 0.380320 | -3.191731 |

| | | | |
|---|-----------|-----------|-----------|
| H | 1.035648 | -0.588169 | -2.943015 |
| H | 0.364167 | 0.378451 | -4.264650 |
| H | 1.340307 | 1.154122 | -3.007123 |
| C | -1.842183 | -1.647421 | -2.985658 |
| H | -2.417020 | -1.563310 | -3.917175 |
| H | -0.849844 | -2.019786 | -3.247608 |
| H | -2.343763 | -2.370763 | -2.339433 |
| C | -4.231258 | -0.165146 | -1.511939 |
| H | -4.853792 | 0.222391 | -2.329645 |
| H | -4.259921 | -1.254035 | -1.544775 |
| H | -4.677720 | 0.178298 | -0.575511 |
| C | -3.223209 | 2.714698 | -0.615985 |
| H | -3.823420 | 3.276423 | -1.343415 |
| H | -3.913783 | 2.262233 | 0.100741 |
| H | -2.588058 | 3.430454 | -0.088438 |
| C | -0.363851 | 3.161610 | -1.854001 |
| H | 0.621057 | 3.081621 | -2.313632 |
| H | -0.959086 | 3.864641 | -2.450458 |
| H | -0.243024 | 3.602296 | -0.861054 |

Intermediate A

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.868565 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.787527 E_h

$\Delta\Delta H(298) = 0.649092$ E_h

S(298) = 0.105298 E_h

Lowest frequency: 25.84 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|---|-----------|-----------|-----------|
| N | -0.453686 | 1.215439 | 1.147414 |
| C | 0.808196 | 1.659612 | 1.346000 |
| C | -1.331879 | 1.403167 | 2.163449 |
| C | -0.982754 | 1.936170 | 3.393174 |
| C | 0.345702 | 2.273514 | 3.629341 |
| H | -2.336219 | 1.065719 | 1.965249 |
| H | 0.672199 | 2.655892 | 4.590717 |
| H | -1.748552 | 2.062580 | 4.150379 |
| N | 1.737520 | 1.801021 | 0.267350 |
| C | 2.362820 | 0.732909 | -0.348478 |
| C | 1.890460 | -0.631949 | -0.088643 |
| C | 0.601697 | -0.996753 | -0.094776 |

| | | | |
|----|-----------|-----------|-----------|
| C | 1.239461 | 2.148515 | 2.577636 |
| H | 2.271418 | 2.464277 | 2.672128 |
| C | 2.124359 | 3.189387 | 0.041026 |
| C | 3.267469 | 3.356337 | -0.809943 |
| H | 3.595147 | 4.377681 | -0.965984 |
| C | 3.894297 | 2.289221 | -1.391375 |
| C | 3.436768 | 0.969191 | -1.173445 |
| H | 4.753158 | 2.452256 | -2.036363 |
| H | 3.929209 | 0.121002 | -1.632635 |
| O | 1.462387 | 4.083886 | 0.564307 |
| C | 2.948725 | -1.653465 | 0.164818 |
| C | 3.966834 | -1.385106 | 1.092648 |
| C | 2.941986 | -2.888194 | -0.496618 |
| C | 4.938724 | -2.342573 | 1.369946 |
| H | 3.989513 | -0.425967 | 1.602911 |
| C | 3.919842 | -3.843454 | -0.223452 |
| H | 2.185629 | -3.085939 | -1.248567 |
| C | 4.916457 | -3.575619 | 0.714821 |
| H | 5.715021 | -2.127100 | 2.097889 |
| H | 3.910070 | -4.791819 | -0.752321 |
| H | 5.678531 | -4.318851 | 0.927513 |
| C | -0.153959 | -2.102960 | 0.218978 |
| O | -3.331957 | -2.487658 | -0.037951 |
| C | -3.231343 | -1.660804 | 0.855894 |
| O | -2.444690 | -0.612653 | 0.913540 |
| C | -0.468998 | -3.203486 | -0.748911 |
| H | -0.146870 | -2.970446 | -1.762359 |
| H | 0.088302 | -4.084876 | -0.400051 |
| H | -1.530779 | -3.453997 | -0.730987 |
| C | -0.385871 | -2.419324 | 1.672759 |
| H | -1.309602 | -2.981487 | 1.828381 |
| H | 0.452491 | -3.066239 | 1.972951 |
| H | -0.370438 | -1.528829 | 2.299839 |
| O | -4.024773 | -1.812473 | 1.955225 |
| C | -3.924376 | -0.868284 | 3.037386 |
| H | -4.238549 | 0.129180 | 2.711912 |
| H | -4.608821 | -1.239282 | 3.800059 |
| H | -2.904218 | -0.831397 | 3.429712 |
| Co | -1.125016 | 0.022234 | -0.386619 |
| C | -0.695677 | 0.128451 | -2.445205 |
| C | -1.968615 | -0.520759 | -2.258027 |
| C | -2.839557 | 0.419939 | -1.603077 |
| C | -0.784161 | 1.450265 | -1.911787 |
| C | -2.100280 | 1.608177 | -1.334395 |

| | | | |
|---|-----------|-----------|-----------|
| C | 0.456553 | -0.408292 | -3.227276 |
| H | 0.522597 | -1.495604 | -3.163753 |
| H | 0.320026 | -0.144731 | -4.284363 |
| H | 1.402046 | 0.020364 | -2.890838 |
| C | -2.416307 | -1.793726 | -2.894868 |
| H | -3.087788 | -1.541250 | -3.726390 |
| H | -1.580125 | -2.358586 | -3.307981 |
| H | -2.967887 | -2.415658 | -2.188191 |
| C | -4.287260 | 0.221723 | -1.317388 |
| H | -4.863915 | 0.730810 | -2.101788 |
| H | -4.559043 | -0.833223 | -1.315025 |
| H | -4.573279 | 0.669501 | -0.362459 |
| C | -2.623106 | 2.850976 | -0.692535 |
| H | -3.077271 | 3.497177 | -1.454888 |
| H | -3.396154 | 2.623666 | 0.045608 |
| H | -1.825619 | 3.417915 | -0.207094 |
| C | 0.163140 | 2.565677 | -2.182230 |
| H | 1.187949 | 2.218156 | -2.318204 |
| H | -0.150648 | 3.035206 | -3.125572 |
| H | 0.132702 | 3.336545 | -1.411769 |

Transition state **TSAt**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.849035 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.768230 E_h

$\Delta\Delta H(298) = 0.644745$ E_h

S(298) = 0.107099 E_h

Lowest frequency: -41.78 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|---|-----------|-----------|-----------|
| N | -0.353677 | 1.425064 | 1.121395 |
| C | 0.943095 | 1.771729 | 1.214797 |
| C | -1.147182 | 1.644713 | 2.198335 |
| C | -0.666233 | 2.171132 | 3.385700 |
| C | 0.690947 | 2.464993 | 3.498405 |
| H | -2.178601 | 1.348942 | 2.075078 |
| H | 1.106468 | 2.856061 | 4.421283 |
| H | -1.352727 | 2.335760 | 4.208831 |
| N | 1.779833 | 1.724418 | 0.050866 |
| C | 2.320607 | 0.536453 | -0.426101 |
| C | 1.760278 | -0.767313 | -0.029286 |

| | | | |
|----|-----------|-----------|-----------|
| C | 0.451721 | -1.099171 | -0.015863 |
| C | 1.500325 | 2.270767 | 2.388591 |
| H | 2.553169 | 2.525720 | 2.399955 |
| C | 2.288949 | 3.039469 | -0.319410 |
| C | 3.372790 | 3.017712 | -1.258456 |
| H | 3.759904 | 3.984596 | -1.558654 |
| C | 3.913430 | 1.841792 | -1.699806 |
| C | 3.395949 | 0.595514 | -1.278669 |
| H | 4.754261 | 1.858656 | -2.387627 |
| H | 3.821543 | -0.333624 | -1.636015 |
| O | 1.773236 | 4.035014 | 0.184999 |
| C | 2.788612 | -1.803960 | 0.315612 |
| C | 3.494168 | -1.707961 | 1.522753 |
| C | 3.060644 | -2.870657 | -0.550252 |
| C | 4.436268 | -2.675235 | 1.867211 |
| H | 3.295254 | -0.877317 | 2.195100 |
| C | 4.012001 | -3.832799 | -0.208908 |
| H | 2.537771 | -2.934874 | -1.500134 |
| C | 4.696587 | -3.739943 | 1.002349 |
| H | 4.969096 | -2.597645 | 2.810184 |
| H | 4.220115 | -4.651333 | -0.891530 |
| H | 5.434378 | -4.490079 | 1.269458 |
| C | -0.125928 | -2.312099 | 0.351435 |
| O | -2.720628 | -2.349242 | 0.033262 |
| C | -3.029095 | -1.442376 | 0.813534 |
| O | -2.486629 | -0.271158 | 0.870240 |
| C | -0.226866 | -3.465117 | -0.584579 |
| H | -0.090482 | -3.173349 | -1.624512 |
| H | 0.601134 | -4.138841 | -0.309116 |
| H | -1.164793 | -4.006432 | -0.454027 |
| C | -0.408823 | -2.562368 | 1.796775 |
| H | -1.179508 | -3.321017 | 1.940517 |
| H | 0.537166 | -2.935602 | 2.223623 |
| H | -0.664545 | -1.643876 | 2.327042 |
| O | -4.020626 | -1.694993 | 1.708848 |
| C | -4.384970 | -0.639317 | 2.623129 |
| H | -4.694277 | 0.257033 | 2.077975 |
| H | -5.219416 | -1.038355 | 3.199080 |
| H | -3.548825 | -0.400830 | 3.287039 |
| Co | -1.010870 | 0.317568 | -0.422691 |
| C | -0.763576 | 0.548584 | -2.532385 |
| C | -1.920864 | -0.301276 | -2.366330 |
| C | -2.974743 | 0.465998 | -1.757663 |
| C | -1.075217 | 1.804694 | -1.942614 |

| | | | |
|---|-----------|-----------|-----------|
| C | -2.432192 | 1.719116 | -1.404863 |
| C | 0.463852 | 0.195510 | -3.311598 |
| H | 0.839682 | -0.795598 | -3.043312 |
| H | 0.235973 | 0.187985 | -4.384819 |
| H | 1.264662 | 0.916279 | -3.141330 |
| C | -2.083898 | -1.660611 | -2.954246 |
| H | -2.741512 | -1.588626 | -3.831322 |
| H | -1.130154 | -2.070858 | -3.290675 |
| H | -2.546426 | -2.344339 | -2.239585 |
| C | -4.371239 | 0.003243 | -1.518942 |
| H | -5.016268 | 0.345653 | -2.339345 |
| H | -4.432912 | -1.085257 | -1.473901 |
| H | -4.776612 | 0.419281 | -0.592868 |
| C | -3.136106 | 2.826937 | -0.694392 |
| H | -2.433457 | 3.462631 | -0.149667 |
| H | -3.665429 | 3.464670 | -1.414663 |
| H | -3.878271 | 2.436219 | 0.006714 |
| C | -0.308960 | 3.076972 | -2.057278 |
| H | 0.696790 | 2.910150 | -2.444762 |
| H | -0.833851 | 3.737659 | -2.760127 |
| H | -0.228103 | 3.612753 | -1.109433 |

Intermediate At

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.859347 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.781643 E_h

$\Delta\Delta H(298) = 0.647139$ E_h

S(298) = 0.111258 E_h

Lowest frequency: 19.53 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|---|-----------|----------|-----------|
| N | -0.491011 | 1.247985 | 1.184278 |
| C | 0.772478 | 1.656771 | 1.409145 |
| C | -1.377823 | 1.393345 | 2.199664 |
| C | -1.032327 | 1.872700 | 3.451455 |
| C | 0.297606 | 2.199980 | 3.703106 |
| H | -2.386056 | 1.080151 | 1.977458 |
| H | 0.617169 | 2.551013 | 4.678664 |
| H | -1.798077 | 1.972630 | 4.212631 |
| N | 1.698698 | 1.789272 | 0.328185 |
| C | 2.301485 | 0.714952 | -0.297999 |

| | | | |
|----|-----------|-----------|-----------|
| C | 1.867400 | -0.662592 | -0.014582 |
| C | 0.597724 | -1.106035 | 0.005324 |
| C | 1.202142 | 2.103533 | 2.656803 |
| H | 2.236241 | 2.405570 | 2.771481 |
| C | 2.084424 | 3.174558 | 0.093988 |
| C | 3.211933 | 3.338627 | -0.779104 |
| H | 3.543127 | 4.358249 | -0.939012 |
| C | 3.814682 | 2.268751 | -1.379878 |
| C | 3.352892 | 0.951710 | -1.153718 |
| H | 4.658563 | 2.426195 | -2.045656 |
| H | 3.831717 | 0.103570 | -1.626617 |
| O | 1.435844 | 4.068863 | 0.633427 |
| C | 2.977696 | -1.638478 | 0.202235 |
| C | 4.068849 | -1.284758 | 1.012407 |
| C | 2.938142 | -2.925491 | -0.351805 |
| C | 5.075623 | -2.207035 | 1.284908 |
| H | 4.119149 | -0.288160 | 1.441893 |
| C | 3.952214 | -3.843607 | -0.088763 |
| H | 2.123168 | -3.195662 | -1.015272 |
| C | 5.020689 | -3.489601 | 0.736126 |
| H | 5.904026 | -1.924912 | 1.927674 |
| H | 3.915055 | -4.831459 | -0.538069 |
| H | 5.810858 | -4.204802 | 0.942234 |
| C | 0.009756 | -2.287377 | 0.361619 |
| O | -3.533926 | -2.462243 | -0.119962 |
| C | -3.293606 | -1.716880 | 0.819859 |
| O | -2.327641 | -0.826018 | 0.903406 |
| C | -0.562608 | -3.244439 | -0.628949 |
| H | -0.225406 | -3.032709 | -1.644237 |
| H | -0.265238 | -4.261482 | -0.345800 |
| H | -1.661083 | -3.212038 | -0.596953 |
| C | -0.093811 | -2.660691 | 1.813170 |
| H | -1.052909 | -3.138339 | 2.034478 |
| H | 0.695633 | -3.399324 | 2.015663 |
| H | 0.060128 | -1.803944 | 2.469294 |
| O | -4.062803 | -1.831931 | 1.933038 |
| C | -3.813724 | -0.978018 | 3.066797 |
| H | -4.105909 | 0.052611 | 2.839666 |
| H | -4.449758 | -1.370634 | 3.859799 |
| H | -2.762895 | -1.017002 | 3.363257 |
| Co | -1.248000 | 0.134885 | -0.357769 |
| C | -0.751685 | 0.167163 | -2.565302 |
| C | -2.026703 | -0.416838 | -2.372767 |
| C | -2.888628 | 0.564091 | -1.703786 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.796780 | 1.486314 | -2.002070 |
| C | -2.131818 | 1.733970 | -1.484993 |
| C | 0.405706 | -0.419813 | -3.306994 |
| H | 0.372504 | -1.511305 | -3.305182 |
| H | 0.388840 | -0.089081 | -4.353433 |
| H | 1.356538 | -0.103759 | -2.872192 |
| C | -2.515625 | -1.696678 | -2.957932 |
| H | -3.147004 | -1.455164 | -3.824689 |
| H | -1.695111 | -2.322442 | -3.311976 |
| H | -3.123720 | -2.255649 | -2.245117 |
| C | -4.343931 | 0.378096 | -1.427913 |
| H | -4.919964 | 0.723427 | -2.296843 |
| H | -4.591036 | -0.670782 | -1.257931 |
| H | -4.670270 | 0.967314 | -0.566850 |
| C | -2.597347 | 3.024367 | -0.887754 |
| H | -2.887658 | 3.726443 | -1.679561 |
| H | -3.469620 | 2.875172 | -0.246212 |
| H | -1.808522 | 3.500938 | -0.299178 |
| C | 0.209836 | 2.554285 | -2.244844 |
| H | 1.224331 | 2.161302 | -2.319321 |
| H | -0.032031 | 3.014060 | -3.214337 |
| H | 0.168565 | 3.345233 | -1.495438 |

Intermediate A1

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3075.859706 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3070.779017 E_h

$\Delta\Delta H(298) = 0.646721$ E_h

S(298) = 0.106509 E_h

Lowest frequency: 13.75 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|---|-----------|----------|-----------|
| N | -0.488445 | 1.234926 | 0.979370 |
| C | 0.846802 | 1.111077 | 1.139286 |
| C | -1.222223 | 1.490126 | 2.091546 |
| C | -0.678879 | 1.571014 | 3.362117 |
| C | 0.684249 | 1.336560 | 3.526087 |
| H | -2.284888 | 1.606506 | 1.933846 |
| H | 1.144124 | 1.359269 | 4.508685 |
| H | -1.322874 | 1.798942 | 4.203973 |
| N | 1.698900 | 1.172548 | -0.013545 |

| | | | |
|----|-----------|-----------|-----------|
| C | 2.496497 | 0.109117 | -0.417916 |
| C | 2.303609 | -1.232244 | 0.165021 |
| C | 1.116806 | -1.757582 | 0.433615 |
| C | 1.452950 | 1.118287 | 2.392345 |
| H | 2.527840 | 0.991630 | 2.448649 |
| C | 1.998610 | 2.555817 | -0.349518 |
| C | 2.984253 | 2.717480 | -1.378798 |
| H | 3.190209 | 3.735454 | -1.689888 |
| C | 3.700190 | 1.648065 | -1.848109 |
| C | 3.477419 | 0.344502 | -1.353711 |
| H | 4.474459 | 1.803589 | -2.594399 |
| H | 4.082627 | -0.489155 | -1.685617 |
| O | 1.415303 | 3.447141 | 0.266180 |
| C | 3.533389 | -2.038279 | 0.441303 |
| C | 4.698866 | -1.427996 | 0.929191 |
| C | 3.521582 | -3.428647 | 0.263677 |
| C | 5.822873 | -2.192595 | 1.234618 |
| H | 4.726683 | -0.351356 | 1.072131 |
| C | 4.646969 | -4.190739 | 0.564807 |
| H | 2.624864 | -3.906732 | -0.119210 |
| C | 5.801387 | -3.575638 | 1.052314 |
| H | 6.715389 | -1.707297 | 1.618218 |
| H | 4.626057 | -5.265670 | 0.412097 |
| H | 6.679464 | -4.170007 | 1.285314 |
| C | 0.122529 | -2.544207 | 0.764562 |
| O | -3.437877 | -2.115179 | -0.409683 |
| C | -3.341872 | -1.369600 | 0.548607 |
| O | -2.495215 | -0.360380 | 0.694245 |
| C | -0.451312 | -3.543400 | -0.216610 |
| H | 0.080704 | -3.519048 | -1.170317 |
| H | -0.358914 | -4.550502 | 0.209052 |
| H | -1.514725 | -3.351641 | -0.388746 |
| C | -0.447718 | -2.553790 | 2.165136 |
| H | -1.541159 | -2.550733 | 2.139329 |
| H | -0.138953 | -3.479362 | 2.666852 |
| H | -0.094840 | -1.705128 | 2.753076 |
| O | -4.129183 | -1.586009 | 1.633091 |
| C | -4.027997 | -0.694457 | 2.764708 |
| H | -4.305344 | 0.324280 | 2.477751 |
| H | -4.739737 | -1.084220 | 3.491870 |
| H | -3.015668 | -0.705853 | 3.175698 |
| Co | -1.652879 | 0.683993 | -0.585230 |
| C | -0.944788 | 0.993885 | -2.496787 |
| C | -2.084589 | 0.086565 | -2.498560 |

| | | | |
|---|-----------|-----------|-----------|
| C | -3.194626 | 0.771231 | -1.929310 |
| C | -1.360773 | 2.239668 | -1.950210 |
| C | -2.726691 | 2.080525 | -1.514470 |
| C | 0.390019 | 0.652822 | -3.061128 |
| H | 0.738123 | -0.320270 | -2.703859 |
| H | 0.311081 | 0.587316 | -4.154508 |
| H | 1.140284 | 1.404043 | -2.815072 |
| C | -2.060021 | -1.295068 | -3.052806 |
| H | -2.190779 | -1.238755 | -4.142594 |
| H | -1.097853 | -1.778060 | -2.864174 |
| H | -2.849373 | -1.910401 | -2.624918 |
| C | -4.599775 | 0.289661 | -1.803846 |
| H | -5.200377 | 0.778540 | -2.582428 |
| H | -4.672604 | -0.789523 | -1.925769 |
| H | -5.037668 | 0.561201 | -0.838905 |
| C | -3.537024 | 3.124745 | -0.826329 |
| H | -4.019013 | 3.764529 | -1.579016 |
| H | -4.328692 | 2.685200 | -0.215243 |
| H | -2.911375 | 3.768345 | -0.202893 |
| C | -0.610871 | 3.526689 | -1.906478 |
| H | 0.403301 | 3.413819 | -2.289208 |
| H | -1.138655 | 4.248649 | -2.542509 |
| H | -0.542797 | 3.942697 | -0.899674 |

Intermediate Co-X

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3305.325727 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3299.731555 E_h

$\Delta\Delta H(298) = 0.718229$ E_h

S(298) = 0.115625 E_h

Lowest frequency: 21.1 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -3.246101 | -4.868643 | -7.068934 |
| C | -2.220408 | -4.198077 | -8.793304 |
| C | -3.383630 | -4.914354 | -9.177076 |
| C | -1.404990 | -5.065399 | -7.969354 |
| C | -3.262816 | -6.259068 | -8.660375 |
| C | -2.042526 | -6.359393 | -7.930224 |
| N | -3.553337 | -2.958982 | -6.608504 |
| C | -2.797124 | -2.214687 | -5.781580 |

| | | | |
|---|-----------|-----------|------------|
| C | -4.696309 | -2.394669 | -7.081246 |
| C | -5.154198 | -1.154800 | -6.676815 |
| C | -4.431499 | -0.451781 | -5.713151 |
| H | -5.246129 | -2.990138 | -7.796420 |
| H | -4.776678 | 0.506077 | -5.338953 |
| H | -6.068913 | -0.759161 | -7.104156 |
| N | -1.449300 | -2.590042 | -5.526703 |
| C | -1.085908 | -3.673683 | -4.747909 |
| C | -2.030337 | -4.742051 | -4.324520 |
| C | -2.886459 | -5.425473 | -5.144199 |
| C | -3.227768 | -0.985062 | -5.282201 |
| H | -2.583661 | -0.451068 | -4.594171 |
| C | -4.241735 | -7.345754 | -8.961127 |
| H | -3.960678 | -8.294428 | -8.502018 |
| H | -5.249669 | -7.076310 | -8.629884 |
| H | -4.283002 | -7.494228 | -10.047360 |
| C | -1.406004 | -7.606373 | -7.411271 |
| H | -0.829854 | -7.420423 | -6.505494 |
| H | -2.138540 | -8.384044 | -7.191467 |
| H | -0.725434 | -7.992632 | -8.181864 |
| C | -0.001058 | -4.801994 | -7.541125 |
| H | 0.244902 | -5.334862 | -6.621900 |
| H | 0.681320 | -5.156008 | -8.326015 |
| H | 0.194025 | -3.738761 | -7.395675 |
| C | -1.876798 | -2.803826 | -9.195341 |
| H | -1.193693 | -2.846879 | -10.053713 |
| H | -2.760941 | -2.242271 | -9.505312 |
| H | -1.377541 | -2.240021 | -8.405359 |
| C | -4.514200 | -4.431838 | -10.029091 |
| H | -4.513722 | -3.343596 | -10.124483 |
| H | -4.433679 | -4.849398 | -11.040353 |
| H | -5.478897 | -4.751064 | -9.621542 |
| C | -0.503067 | -1.590606 | -6.024905 |
| C | 0.843053 | -1.768370 | -5.581009 |
| H | 1.558789 | -1.028138 | -5.919045 |
| C | 1.186033 | -2.809999 | -4.763345 |
| C | 0.231066 | -3.758964 | -4.347627 |
| H | 2.214282 | -2.919812 | -4.430195 |
| H | 0.524725 | -4.581960 | -3.712101 |
| O | -0.922568 | -0.700194 | -6.766765 |
| C | -1.802948 | -5.026887 | -2.859532 |
| C | -2.420381 | -4.171454 | -1.937232 |
| C | -0.957826 | -6.037773 | -2.384047 |
| C | -2.242835 | -4.352907 | -0.567433 |

| | | | |
|---|-----------|------------|-----------|
| H | -3.061818 | -3.370239 | -2.297285 |
| C | -0.770880 | -6.210084 | -1.013120 |
| H | -0.460273 | -6.698596 | -3.083823 |
| C | -1.419934 | -5.378180 | -0.100537 |
| H | -2.745191 | -3.693528 | 0.134037 |
| H | -0.116682 | -7.001369 | -0.658641 |
| H | -1.279416 | -5.522440 | 0.966208 |
| C | -3.480572 | -6.765335 | -4.567786 |
| O | -2.232507 | -7.582813 | -4.469404 |
| C | -2.268111 | -8.788581 | -3.866393 |
| O | -3.227956 | -9.368571 | -3.406794 |
| C | -4.175685 | -6.662820 | -3.187340 |
| H | -3.465030 | -6.732637 | -2.367785 |
| H | -4.707984 | -5.715094 | -3.091291 |
| H | -4.892161 | -7.479358 | -3.086494 |
| C | -4.416579 | -7.521410 | -5.507417 |
| H | -4.472638 | -8.558287 | -5.172039 |
| H | -5.428547 | -7.117406 | -5.453234 |
| H | -4.077092 | -7.477108 | -6.537468 |
| O | -0.998695 | -9.248584 | -3.870000 |
| C | -0.844907 | -10.555000 | -3.250359 |
| H | -1.447382 | -11.293683 | -3.782591 |
| H | 0.217179 | -10.779440 | -3.336003 |
| H | -1.155361 | -10.509130 | -2.204682 |
| O | -5.224710 | -5.125091 | -6.925901 |
| C | -5.974523 | -4.787177 | -5.988965 |
| O | -5.522239 | -4.302430 | -4.847419 |
| C | -7.461349 | -4.908322 | -6.073193 |
| H | -7.797283 | -5.666542 | -5.357041 |
| H | -7.926551 | -3.961250 | -5.784605 |
| H | -7.760972 | -5.194122 | -7.080229 |
| H | -4.518821 | -4.373845 | -4.858196 |

Intermediate **Co-XI**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3305.332362 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3299.738113 E_h

$\Delta\Delta H(298) = 0.714908 \text{ E}_h$

S(298) = 0.116295 E_h

Lowest frequency: 9.79 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|------------|
| Co | -3.176844 | -4.587748 | -7.561083 |
| C | -2.151796 | -4.170422 | -9.278131 |
| C | -3.341979 | -4.973457 | -9.506874 |
| C | -1.291799 | -4.908884 | -8.412731 |
| C | -3.183873 | -6.227730 | -8.806179 |
| C | -1.935999 | -6.170525 | -8.118565 |
| N | -3.332775 | -2.753390 | -6.872283 |
| C | -2.609522 | -2.273087 | -5.845059 |
| C | -4.432657 | -2.064391 | -7.251415 |
| C | -4.873743 | -0.931569 | -6.589850 |
| C | -4.186466 | -0.507657 | -5.456044 |
| H | -4.981113 | -2.481456 | -8.086624 |
| H | -4.524360 | 0.351527 | -4.886169 |
| H | -5.758078 | -0.415253 | -6.945332 |
| N | -1.273664 | -2.758842 | -5.630813 |
| C | -0.911719 | -3.563738 | -4.558155 |
| C | -1.877835 | -4.446229 | -3.858200 |
| C | -2.704794 | -5.280685 | -4.512511 |
| C | -3.027675 | -1.182125 | -5.093529 |
| H | -2.408613 | -0.849542 | -4.268078 |
| C | -4.185545 | -7.332642 | -8.802473 |
| H | -3.894941 | -8.140335 | -8.128946 |
| H | -5.163927 | -6.953499 | -8.491726 |
| H | -4.283646 | -7.748203 | -9.812136 |
| C | -1.330756 | -7.228037 | -7.257288 |
| H | -0.913955 | -6.814300 | -6.334975 |
| H | -2.043353 | -8.011027 | -6.997810 |
| H | -0.502107 | -7.691424 | -7.809733 |
| C | 0.104993 | -4.560585 | -8.021214 |
| H | 0.297367 | -4.747223 | -6.961372 |
| H | 0.798223 | -5.190866 | -8.593961 |
| H | 0.333696 | -3.520061 | -8.248210 |
| C | -1.886075 | -2.822236 | -9.852909 |
| H | -1.265552 | -2.937009 | -10.751860 |
| H | -2.811473 | -2.326117 | -10.154117 |
| H | -1.357367 | -2.179376 | -9.143915 |
| C | -4.519578 | -4.604901 | -10.340022 |
| H | -4.598719 | -3.524400 | -10.478207 |
| H | -4.414214 | -5.058135 | -11.335132 |
| H | -5.443105 | -4.980118 | -9.893529 |
| C | -0.322473 | -1.941359 | -6.367438 |
| C | 1.031090 | -2.022356 | -5.909684 |

| | | | |
|---|-----------|------------|-----------|
| H | 1.749425 | -1.402411 | -6.433962 |
| C | 1.375045 | -2.808073 | -4.844783 |
| C | 0.407925 | -3.583775 | -4.168826 |
| H | 2.407050 | -2.841131 | -4.506912 |
| H | 0.687671 | -4.213270 | -3.334286 |
| O | -0.744331 | -1.240912 | -7.291173 |
| C | -1.725170 | -4.412724 | -2.368874 |
| C | -2.266689 | -3.326536 | -1.668514 |
| C | -1.020602 | -5.398894 | -1.668388 |
| C | -2.132215 | -3.242367 | -0.284873 |
| H | -2.822361 | -2.564712 | -2.208306 |
| C | -0.877354 | -5.304127 | -0.284156 |
| H | -0.603823 | -6.244228 | -2.203561 |
| C | -1.435544 | -4.231638 | 0.410837 |
| H | -2.572548 | -2.406286 | 0.250204 |
| H | -0.331848 | -6.075619 | 0.251061 |
| H | -1.328858 | -4.165666 | 1.489202 |
| C | -3.520565 | -6.422319 | -3.911670 |
| O | -2.418799 | -7.341511 | -3.481513 |
| C | -2.722074 | -8.458786 | -2.785218 |
| O | -3.820344 | -8.896624 | -2.518379 |
| C | -4.397030 | -5.992919 | -2.730906 |
| H | -3.793606 | -5.705267 | -1.870485 |
| H | -4.994969 | -5.135472 | -3.048726 |
| H | -5.055511 | -6.814082 | -2.446177 |
| C | -4.349265 | -7.156961 | -4.962372 |
| H | -4.664293 | -8.119893 | -4.559033 |
| H | -5.240562 | -6.580212 | -5.202408 |
| H | -3.776686 | -7.312179 | -5.879350 |
| O | -1.545662 | -9.017981 | -2.437031 |
| C | -1.682608 | -10.251167 | -1.679390 |
| H | -2.217064 | -10.996071 | -2.272224 |
| H | -0.660361 | -10.568787 | -1.479557 |
| H | -2.224440 | -10.059270 | -0.751300 |
| O | -5.009812 | -4.861444 | -7.227427 |
| C | -5.708638 | -4.461200 | -6.167629 |
| O | -5.230989 | -3.962383 | -5.154327 |
| C | -7.194178 | -4.723462 | -6.333483 |
| H | -7.371600 | -5.802656 | -6.393921 |
| H | -7.737920 | -4.312113 | -5.483136 |
| H | -7.556814 | -4.282184 | -7.266775 |
| H | -2.692868 | -5.254333 | -5.618490 |

Intermediate **Co-Xt**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3305.320112 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3299.728260 E_h

$\Delta\Delta H(298) = 0.715997 \text{ E}_h$

S(298) = 0.118669 E_h

Lowest frequency: 22.18 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|------------|
| Co | -3.290500 | -5.003662 | -6.973078 |
| C | -1.948603 | -4.283232 | -8.763371 |
| C | -3.214251 | -4.869617 | -9.168786 |
| C | -1.272662 | -5.231109 | -7.979041 |
| C | -3.252979 | -6.228493 | -8.746403 |
| C | -2.080865 | -6.450095 | -7.946040 |
| N | -3.659789 | -2.966449 | -6.662379 |
| C | -2.935387 | -2.239731 | -5.795595 |
| C | -4.818213 | -2.423289 | -7.110936 |
| C | -5.323700 | -1.223080 | -6.641765 |
| C | -4.632289 | -0.550162 | -5.635170 |
| H | -5.346259 | -3.000407 | -7.856526 |
| H | -5.015105 | 0.372608 | -5.212054 |
| H | -6.249517 | -0.835250 | -7.052176 |
| N | -1.564099 | -2.573882 | -5.582756 |
| C | -1.137235 | -3.584774 | -4.740564 |
| C | -2.026387 | -4.672070 | -4.259211 |
| C | -2.881602 | -5.389747 | -5.044352 |
| C | -3.408275 | -1.058881 | -5.226632 |
| H | -2.783669 | -0.535536 | -4.512382 |
| C | -4.300515 | -7.230710 | -9.122126 |
| H | -4.201953 | -8.152515 | -8.544660 |
| H | -5.308061 | -6.834648 | -8.965892 |
| H | -4.204665 | -7.493526 | -10.182727 |
| C | -1.566268 | -7.769112 | -7.469479 |
| H | -0.990147 | -7.674544 | -6.549149 |
| H | -2.368369 | -8.489772 | -7.300744 |
| H | -0.907055 | -8.181985 | -8.245576 |
| C | 0.101401 | -5.130034 | -7.406219 |
| H | 0.166097 | -5.632866 | -6.438990 |
| H | 0.818716 | -5.617179 | -8.080262 |
| H | 0.413783 | -4.092073 | -7.280509 |

| | | | |
|---|-----------|------------|------------|
| C | -1.482295 | -2.921820 | -9.156315 |
| H | -1.424015 | -2.854009 | -10.249584 |
| H | -2.157774 | -2.131529 | -8.814988 |
| H | -0.493653 | -2.703904 | -8.751433 |
| C | -4.227146 | -4.203824 | -10.044166 |
| H | -4.180128 | -3.114965 | -9.961492 |
| H | -4.034825 | -4.457285 | -11.095133 |
| H | -5.241532 | -4.540805 | -9.810618 |
| C | -0.682864 | -1.550398 | -6.141572 |
| C | 0.690455 | -1.673776 | -5.757224 |
| H | 1.368129 | -0.931555 | -6.162987 |
| C | 1.096690 | -2.644157 | -4.883002 |
| C | 0.189311 | -3.591705 | -4.365368 |
| H | 2.139124 | -2.697308 | -4.581359 |
| H | 0.530835 | -4.359873 | -3.686098 |
| O | -1.171561 | -0.682216 | -6.863615 |
| C | -1.748925 | -4.949525 | -2.804868 |
| C | -2.343687 | -4.107881 | -1.855646 |
| C | -0.877384 | -5.956199 | -2.369663 |
| C | -2.112531 | -4.297142 | -0.494969 |
| H | -3.007739 | -3.313061 | -2.186759 |
| C | -0.636876 | -6.135141 | -1.007797 |
| H | -0.400593 | -6.605981 | -3.093926 |
| C | -1.260278 | -5.315646 | -0.066657 |
| H | -2.595651 | -3.648836 | 0.229904 |
| H | 0.038891 | -6.921000 | -0.683097 |
| H | -1.077941 | -5.464575 | 0.993114 |
| C | -3.448879 | -6.737767 | -4.492828 |
| O | -2.201446 | -7.552493 | -4.426441 |
| C | -2.238126 | -8.784922 | -3.876016 |
| O | -3.202279 | -9.384841 | -3.452417 |
| C | -4.128970 | -6.656174 | -3.108507 |
| H | -3.403197 | -6.653287 | -2.298947 |
| H | -4.725951 | -5.744609 | -3.034882 |
| H | -4.785364 | -7.518599 | -2.982086 |
| C | -4.406997 | -7.450512 | -5.451215 |
| H | -4.449475 | -8.507179 | -5.182065 |
| H | -5.416448 | -7.052800 | -5.341515 |
| H | -4.104526 | -7.351114 | -6.495140 |
| O | -0.969060 | -9.240463 | -3.889233 |
| C | -0.816042 | -10.574202 | -3.328713 |
| H | -1.411409 | -11.288941 | -3.900099 |
| H | 0.247488 | -10.790812 | -3.415243 |
| H | -1.135751 | -10.576745 | -2.284936 |

| | | | |
|---|-----------|-----------|-----------|
| O | -5.479092 | -5.120196 | -6.984558 |
| C | -6.195754 | -4.816699 | -6.019668 |
| O | -5.701898 | -4.376614 | -4.868649 |
| C | -7.687968 | -4.919559 | -6.040825 |
| H | -7.994101 | -5.740218 | -5.382038 |
| H | -8.132173 | -4.002472 | -5.644500 |
| H | -8.036463 | -5.115446 | -7.053688 |
| H | -4.703370 | -4.424100 | -4.914138 |

Intermediate **Co-XIt**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3305.340272 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3299.749862 E_h

$\Delta\Delta H(298) = 0.714800$ E_h

S(298) = 0.119179 E_h

Lowest frequency: 9.74 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -3.329322 | -4.371903 | -7.791147 |
| C | -2.233515 | -4.078637 | -9.598577 |
| C | -3.310263 | -4.961271 | -9.845819 |
| C | -1.353632 | -4.723038 | -8.620628 |
| C | -3.128575 | -6.129563 | -8.991025 |
| C | -1.897823 | -5.991941 | -8.277180 |
| N | -3.317950 | -2.669771 | -6.818159 |
| C | -2.645601 | -2.387282 | -5.684325 |
| C | -4.417831 | -1.934406 | -7.110056 |
| C | -4.926201 | -0.975128 | -6.253603 |
| C | -4.298679 | -0.776155 | -5.025977 |
| H | -4.903462 | -2.166519 | -8.051357 |
| H | -4.685229 | -0.055045 | -4.313347 |
| H | -5.808284 | -0.414328 | -6.540059 |
| N | -1.294648 | -2.842088 | -5.557249 |
| C | -0.853082 | -3.608700 | -4.479227 |
| C | -1.757414 | -4.524449 | -3.739482 |
| C | -2.654212 | -5.301234 | -4.376327 |
| C | -3.129730 | -1.475574 | -4.754118 |
| H | -2.548180 | -1.287023 | -3.859078 |
| C | -4.063441 | -7.287863 | -8.949059 |
| H | -3.885190 | -7.924548 | -8.081159 |
| H | -5.101263 | -6.945148 | -8.928514 |

| | | | |
|---|-----------|-----------|------------|
| H | -3.928522 | -7.895141 | -9.853839 |
| C | -1.240134 | -7.003460 | -7.392446 |
| H | -0.817157 | -6.543908 | -6.494879 |
| H | -1.936501 | -7.783972 | -7.083388 |
| H | -0.417452 | -7.486941 | -7.934672 |
| C | 0.025794 | -4.274064 | -8.281493 |
| H | 0.301058 | -4.521046 | -7.253758 |
| H | 0.723244 | -4.810786 | -8.940220 |
| H | 0.160334 | -3.206780 | -8.450091 |
| C | -1.971876 | -2.743899 | -10.217990 |
| H | -1.198028 | -2.836854 | -10.990815 |
| H | -2.868647 | -2.340784 | -10.694108 |
| H | -1.614367 | -2.029796 | -9.469853 |
| C | -4.476372 | -4.759547 | -10.757432 |
| H | -4.505427 | -3.741393 | -11.150711 |
| H | -4.413906 | -5.448454 | -11.608589 |
| H | -5.416435 | -4.963291 | -10.235165 |
| C | -0.408379 | -1.980455 | -6.339651 |
| C | 0.963618 | -1.998864 | -5.931110 |
| H | 1.632591 | -1.353266 | -6.488588 |
| C | 1.382725 | -2.751757 | -4.870336 |
| C | 0.479769 | -3.560246 | -4.144815 |
| H | 2.427378 | -2.731762 | -4.572591 |
| H | 0.822861 | -4.164334 | -3.315155 |
| O | -0.891133 | -1.303590 | -7.248279 |
| C | -1.491392 | -4.561394 | -2.265455 |
| C | -1.994202 | -3.525269 | -1.466907 |
| C | -0.706666 | -5.557343 | -1.672211 |
| C | -1.739442 | -3.496636 | -0.097515 |
| H | -2.611279 | -2.752606 | -1.917435 |
| C | -0.442589 | -5.520625 | -0.303771 |
| H | -0.322173 | -6.369222 | -2.278076 |
| C | -0.959252 | -4.494718 | 0.487172 |
| H | -2.150103 | -2.696913 | 0.511507 |
| H | 0.162714 | -6.302809 | 0.144459 |
| H | -0.756867 | -4.472956 | 1.553635 |
| C | -3.522405 | -6.394623 | -3.768869 |
| O | -2.536324 | -7.269115 | -3.082676 |
| C | -2.975872 | -8.335363 | -2.381437 |
| O | -4.114489 | -8.737624 | -2.270906 |
| C | -4.531839 | -5.816535 | -2.771256 |
| H | -4.009116 | -5.336382 | -1.941675 |
| H | -5.140440 | -5.071094 | -3.287943 |
| H | -5.172606 | -6.610759 | -2.386263 |

| | | | |
|---|-----------|------------|-----------|
| C | -4.192382 | -7.219405 | -4.868868 |
| H | -4.845456 | -7.973102 | -4.428847 |
| H | -4.778143 | -6.565412 | -5.514930 |
| H | -3.429009 | -7.720194 | -5.471284 |
| O | -1.886548 | -8.893775 | -1.817877 |
| C | -2.176847 | -10.071656 | -1.018300 |
| H | -2.639114 | -10.840981 | -1.640118 |
| H | -1.207701 | -10.399337 | -0.645027 |
| H | -2.846315 | -9.808423 | -0.196994 |
| O | -5.135394 | -4.801836 | -7.570172 |
| C | -5.847599 | -4.562304 | -6.463605 |
| O | -5.372068 | -4.125998 | -5.423819 |
| C | -7.311273 | -4.907676 | -6.634667 |
| H | -7.415264 | -5.997793 | -6.675027 |
| H | -7.881381 | -4.523273 | -5.788930 |
| H | -7.697737 | -4.506454 | -7.575266 |
| H | -2.772538 | -5.175446 | -5.455722 |

Transition state **TS(10-11)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3305.305098 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3299.713213 E_h

$\Delta\Delta H(298) = 0.712471$ E_h

S(298) = 0.115657 E_h

Lowest frequency: -1408.3499 cm⁻¹

Charge = 1, Multiplicity = 1

| | | | |
|----|-----------|-----------|-----------|
| Co | -3.177972 | -4.734935 | -7.037406 |
| C | -1.946708 | -4.424100 | -8.695882 |
| C | -3.120103 | -5.156395 | -9.057070 |
| C | -1.250921 | -5.164599 | -7.677358 |
| C | -3.109680 | -6.397847 | -8.317599 |
| C | -1.959588 | -6.408142 | -7.478370 |
| N | -3.469872 | -2.779165 | -6.913249 |
| C | -2.836918 | -2.002737 | -6.018668 |
| C | -4.553710 | -2.262271 | -7.538893 |
| C | -5.084078 | -1.023518 | -7.221413 |
| C | -4.511811 | -0.293000 | -6.182024 |
| H | -5.011682 | -2.899940 | -8.282318 |
| H | -4.928024 | 0.659103 | -5.870364 |
| H | -5.946073 | -0.656615 | -7.767293 |

| | | | |
|---|-----------|-----------|------------|
| N | -1.494073 | -2.321027 | -5.648491 |
| C | -1.125379 | -3.234404 | -4.672364 |
| C | -1.995416 | -4.316911 | -4.157640 |
| C | -3.000542 | -4.976959 | -4.840479 |
| C | -3.357055 | -0.785187 | -5.590754 |
| H | -2.814792 | -0.219960 | -4.841650 |
| C | -4.122374 | -7.479296 | -8.494942 |
| H | -3.942042 | -8.324387 | -7.829159 |
| H | -5.134202 | -7.099442 | -8.321417 |
| H | -4.078984 | -7.845490 | -9.528149 |
| C | -1.441182 | -7.568000 | -6.697597 |
| H | -0.902657 | -7.253606 | -5.805076 |
| H | -2.235350 | -8.249202 | -6.391528 |
| H | -0.746914 | -8.125481 | -7.341360 |
| C | 0.110272 | -4.867859 | -7.144276 |
| H | 0.232613 | -5.240041 | -6.126179 |
| H | 0.859051 | -5.367675 | -7.773434 |
| H | 0.332024 | -3.799695 | -7.158150 |
| C | -1.507545 | -3.136416 | -9.305320 |
| H | -0.836847 | -3.362297 | -10.144910 |
| H | -2.350015 | -2.564950 | -9.700501 |
| H | -0.968749 | -2.498360 | -8.605610 |
| C | -4.145318 | -4.783974 | -10.077903 |
| H | -4.078631 | -3.729356 | -10.354504 |
| H | -3.995602 | -5.372688 | -10.991708 |
| H | -5.154730 | -4.994733 | -9.712145 |
| C | -0.568456 | -1.381634 | -6.271224 |
| C | 0.766145 | -1.404251 | -5.749251 |
| H | 1.461071 | -0.696280 | -6.185975 |
| C | 1.111877 | -2.259979 | -4.743696 |
| C | 0.176126 | -3.169519 | -4.208020 |
| H | 2.123825 | -2.256659 | -4.348748 |
| H | 0.484171 | -3.860124 | -3.437371 |
| O | -0.984873 | -0.649162 | -7.167885 |
| C | -1.618685 | -4.605690 | -2.725975 |
| C | -2.070070 | -3.685946 | -1.767589 |
| C | -0.789728 | -5.656992 | -2.318436 |
| C | -1.750988 | -3.847813 | -0.421882 |
| H | -2.697576 | -2.854979 | -2.079093 |
| C | -0.456418 | -5.806149 | -0.972545 |
| H | -0.406011 | -6.358777 | -3.047695 |
| C | -0.944329 | -4.912828 | -0.019206 |
| H | -2.129280 | -3.140619 | 0.309989 |
| H | 0.188164 | -6.626786 | -0.671712 |

| | | | |
|---|-----------|------------|-----------|
| H | -0.690821 | -5.039612 | 1.028713 |
| C | -3.653077 | -6.221721 | -4.144854 |
| O | -2.495047 | -7.126634 | -3.928120 |
| C | -2.643049 | -8.249422 | -3.196971 |
| O | -3.647096 | -8.675708 | -2.670155 |
| C | -4.356487 | -5.867694 | -2.817470 |
| H | -3.646502 | -5.744323 | -2.002889 |
| H | -4.911161 | -4.935192 | -2.945206 |
| H | -5.052819 | -6.663740 | -2.552040 |
| C | -4.635725 | -6.993182 | -5.023564 |
| H | -4.793511 | -7.975125 | -4.574331 |
| H | -5.605046 | -6.494969 | -5.047485 |
| H | -4.267726 | -7.100898 | -6.040831 |
| O | -1.427598 | -8.838425 | -3.164491 |
| C | -1.393641 | -10.072294 | -2.396164 |
| H | -2.084611 | -10.799512 | -2.826846 |
| H | -0.363546 | -10.417560 | -2.470633 |
| H | -1.668125 | -9.871148 | -1.358821 |
| O | -5.137932 | -4.906253 | -7.053125 |
| C | -5.852059 | -4.390807 | -6.129060 |
| O | -5.347999 | -3.845691 | -5.092863 |
| C | -7.349141 | -4.436543 | -6.261181 |
| H | -7.748315 | -5.127337 | -5.510599 |
| H | -7.765036 | -3.448187 | -6.048358 |
| H | -7.641314 | -4.771554 | -7.256198 |
| H | -4.093609 | -4.231789 | -5.127516 |

Transition state **TS(10t-11t)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3305.298256 E_h

E(PBE0-D3(BJ)/def2-TZVP+COSMO(TFE)) = -3299.708110 E_h

$\Delta\Delta H(298) = 0.710984$ E_h

S(298) = 0.119131 E_h

Lowest frequency: -1112.5699 cm⁻¹

Charge = 1, Multiplicity = 3

| | | | |
|----|-----------|-----------|-----------|
| Co | -3.278598 | -4.954266 | -6.898474 |
| C | -1.714339 | -4.581930 | -8.563347 |
| C | -2.947238 | -5.135665 | -9.031617 |
| C | -1.218375 | -5.459099 | -7.562477 |
| C | -3.133257 | -6.442653 | -8.432448 |

| | | | |
|---|-----------|-----------|------------|
| C | -2.065415 | -6.647555 | -7.524116 |
| N | -3.540168 | -2.705625 | -7.028898 |
| C | -2.985359 | -1.997850 | -6.040521 |
| C | -4.675936 | -2.223371 | -7.574600 |
| C | -5.314246 | -1.085036 | -7.103673 |
| C | -4.792401 | -0.436958 | -5.985148 |
| H | -5.086465 | -2.797758 | -8.394999 |
| H | -5.286796 | 0.431578 | -5.562519 |
| H | -6.212547 | -0.728228 | -7.595641 |
| N | -1.612381 | -2.274288 | -5.723955 |
| C | -1.192633 | -3.128108 | -4.719962 |
| C | -2.018829 | -4.212183 | -4.149293 |
| C | -3.014828 | -4.920469 | -4.802025 |
| C | -3.592809 | -0.893483 | -5.452848 |
| H | -3.096192 | -0.379952 | -4.637296 |
| C | -4.236919 | -7.392101 | -8.772802 |
| H | -4.269179 | -8.234011 | -8.077686 |
| H | -5.208594 | -6.889851 | -8.752601 |
| H | -4.090021 | -7.796618 | -9.781916 |
| C | -1.705400 | -7.922131 | -6.833635 |
| H | -1.173256 | -7.745951 | -5.899585 |
| H | -2.582288 | -8.536793 | -6.619231 |
| H | -1.049046 | -8.503105 | -7.496051 |
| C | 0.076703 | -5.337728 | -6.832961 |
| H | 0.003848 | -5.740738 | -5.820583 |
| H | 0.845956 | -5.914530 | -7.364200 |
| H | 0.416361 | -4.302713 | -6.776811 |
| C | -1.092533 | -3.315695 | -9.048942 |
| H | -0.853810 | -3.408191 | -10.115341 |
| H | -1.753878 | -2.453589 | -8.928396 |
| H | -0.164043 | -3.099293 | -8.518303 |
| C | -3.825613 | -4.551482 | -10.087836 |
| H | -3.657085 | -3.478538 | -10.202782 |
| H | -3.606203 | -5.026025 | -11.053638 |
| H | -4.882693 | -4.733673 | -9.872391 |
| C | -0.746831 | -1.322368 | -6.397810 |
| C | 0.622234 | -1.335631 | -5.960387 |
| H | 1.289349 | -0.641518 | -6.458750 |
| C | 1.026004 | -2.141946 | -4.935463 |
| C | 0.123705 | -3.026563 | -4.304736 |
| H | 2.057280 | -2.115423 | -4.594967 |
| H | 0.471138 | -3.677902 | -3.516451 |
| O | -1.231164 | -0.582313 | -7.249895 |
| C | -1.614620 | -4.461478 | -2.721467 |

| | | | |
|---|-----------|------------|-----------|
| C | -2.073160 | -3.535873 | -1.771930 |
| C | -0.762221 | -5.492613 | -2.308933 |
| C | -1.736491 | -3.673190 | -0.427732 |
| H | -2.719227 | -2.721328 | -2.088522 |
| C | -0.410255 | -5.614649 | -0.965236 |
| H | -0.374078 | -6.197217 | -3.033199 |
| C | -0.905146 | -4.716913 | -0.019504 |
| H | -2.119457 | -2.962728 | 0.298460 |
| H | 0.254376 | -6.417314 | -0.659635 |
| H | -0.637356 | -4.823427 | 1.027103 |
| C | -3.602050 | -6.190745 | -4.110194 |
| O | -2.406086 | -7.053805 | -3.947999 |
| C | -2.500454 | -8.212576 | -3.262502 |
| O | -3.484411 | -8.703815 | -2.755253 |
| C | -4.286380 | -5.892886 | -2.763033 |
| H | -3.563081 | -5.711827 | -1.970880 |
| H | -4.914287 | -5.005478 | -2.875886 |
| H | -4.911989 | -6.739786 | -2.478159 |
| C | -4.587152 | -6.960744 | -4.994686 |
| H | -4.726972 | -7.955744 | -4.568612 |
| H | -5.558967 | -6.467707 | -5.003323 |
| H | -4.232548 | -7.060671 | -6.024510 |
| O | -1.259882 | -8.744190 | -3.254052 |
| C | -1.166416 | -10.010841 | -2.544232 |
| H | -1.821630 | -10.748613 | -3.011110 |
| H | -0.120892 | -10.301763 | -2.632617 |
| H | -1.450395 | -9.871583 | -1.499460 |
| O | -5.249679 | -4.883416 | -7.044861 |
| C | -5.926830 | -4.329062 | -6.112050 |
| O | -5.398676 | -3.833539 | -5.064549 |
| C | -7.424597 | -4.287819 | -6.244173 |
| H | -7.839923 | -5.150085 | -5.709058 |
| H | -7.818401 | -3.382809 | -5.778841 |
| H | -7.720480 | -4.354531 | -7.291516 |
| H | -4.133000 | -4.210977 | -5.080365 |

Intermediate **Mn-VI**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2793.935360 E_h

$\Delta\Delta H(298) = 0.449860$ E_h

S(298) = 0.094094 E_h

Lowest frequency: 17.20 cm⁻¹

Charge = 0, Multiplicity = 1

| | | | |
|---|-----------|-----------|-----------|
| N | -3.595988 | -2.976120 | -6.201941 |
| C | -2.731146 | -2.360439 | -5.375037 |
| C | -4.877090 | -2.536787 | -6.199587 |
| C | -5.328175 | -1.519477 | -5.374975 |
| C | -4.430332 | -0.909960 | -4.499847 |
| H | -5.543403 | -3.044478 | -6.883017 |
| H | -4.746782 | -0.111323 | -3.836558 |
| H | -6.367245 | -1.212758 | -5.427712 |
| N | -1.348600 | -2.705301 | -5.435062 |
| C | -0.893985 | -3.954440 | -5.040057 |
| C | -1.860800 | -4.979493 | -4.551313 |
| C | -2.800877 | -5.509531 | -5.372187 |
| C | -3.110060 | -1.333413 | -4.513126 |
| H | -2.355589 | -0.877076 | -3.884589 |
| C | -0.487414 | -1.625315 | -5.881982 |
| C | 0.908271 | -1.955279 | -5.879002 |
| H | 1.580915 | -1.177187 | -6.220695 |
| C | 1.355205 | -3.180696 | -5.468526 |
| C | 0.459239 | -4.182350 | -5.035557 |
| H | 2.420688 | -3.395876 | -5.481032 |
| H | 0.821014 | -5.148442 | -4.708721 |
| O | -0.991647 | -0.551697 | -6.213794 |
| C | -1.593579 | -5.255157 | -3.094116 |
| C | -2.147968 | -4.405514 | -2.124652 |
| C | -0.716478 | -6.262607 | -2.666512 |
| C | -1.860874 | -4.574654 | -0.770567 |
| H | -2.812839 | -3.606614 | -2.443066 |
| C | -0.424085 | -6.431761 | -1.313775 |
| H | -0.264461 | -6.921024 | -3.402808 |
| C | -0.998173 | -5.590862 | -0.359787 |
| H | -2.308572 | -3.909709 | -0.036949 |
| H | 0.254529 | -7.222211 | -1.005019 |
| H | -0.770720 | -5.723549 | 0.693927 |
| C | -3.747044 | -6.568585 | -4.816359 |
| O | -4.644110 | -7.202667 | -5.886984 |
| C | -5.417506 | -6.447542 | -6.620172 |
| O | -5.259271 | -5.244654 | -6.877346 |
| C | -3.061385 | -7.837952 | -4.313821 |
| H | -2.351205 | -8.204935 | -5.058855 |
| H | -2.531792 | -7.629614 | -3.385488 |
| H | -3.814224 | -8.609163 | -4.127288 |

| | | | |
|----|-----------|-----------|-----------|
| C | -4.727351 | -5.990195 | -3.793610 |
| H | -5.470183 | -6.744774 | -3.515180 |
| H | -4.176743 | -5.691257 | -2.899923 |
| H | -5.231663 | -5.108735 | -4.198836 |
| O | -6.440782 | -7.154358 | -7.103633 |
| C | -7.266150 | -6.454735 | -8.075455 |
| H | -6.644750 | -6.079216 | -8.890344 |
| H | -7.969031 | -7.206912 | -8.429633 |
| H | -7.789491 | -5.627988 | -7.590819 |
| Mn | -3.144347 | -4.732270 | -7.287959 |
| O | -4.107766 | -3.664897 | -9.906330 |
| O | -2.496432 | -7.378605 | -8.436806 |
| O | -0.434073 | -4.067202 | -8.221599 |
| C | -1.482662 | -4.301546 | -7.780153 |
| C | -3.730351 | -4.052047 | -8.880809 |
| C | -2.786269 | -6.347962 | -7.988390 |

Transition state **Mn-TS(6-7)**

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2793.888113 E_h

ΔΔH(298) = 0.448305 E_h

S(298) = 0.094062 E_h

Lowest frequency: -235.61 cm⁻¹

Charge = 0, Multiplicity = 1

| | | | |
|---|-----------|-----------|-----------|
| N | -3.631693 | -2.883440 | -6.651674 |
| C | -3.167020 | -2.761300 | -5.344091 |
| C | -4.710083 | -2.208403 | -7.064441 |
| C | -5.410995 | -1.335231 | -6.248352 |
| C | -4.985209 | -1.199386 | -4.912684 |
| H | -5.013166 | -2.398977 | -8.090068 |
| H | -5.509397 | -0.523547 | -4.241981 |
| H | -6.250747 | -0.774577 | -6.640043 |
| N | -1.697654 | -2.591587 | -5.242883 |
| C | -0.967147 | -3.589019 | -4.644056 |
| C | -1.798619 | -4.714626 | -4.241945 |
| C | -3.058545 | -4.669174 | -4.797740 |
| C | -3.896258 | -1.894320 | -4.451293 |
| H | -3.538781 | -1.790040 | -3.431813 |
| C | -1.137069 | -1.382532 | -5.752893 |
| C | 0.296260 | -1.287755 | -5.553642 |
| H | 0.756295 | -0.368734 | -5.899410 |

| | | | |
|----|-----------|-----------|------------|
| C | 1.020139 | -2.279570 | -4.953079 |
| C | 0.394743 | -3.464411 | -4.495048 |
| H | 2.094470 | -2.166956 | -4.832355 |
| H | 0.962908 | -4.278190 | -4.063518 |
| O | -1.844630 | -0.529271 | -6.281793 |
| C | -1.217059 | -5.719037 | -3.329868 |
| C | -0.579502 | -5.340320 | -2.137406 |
| C | -1.262434 | -7.080504 | -3.672331 |
| C | -0.026725 | -6.302197 | -1.295014 |
| H | -0.538746 | -4.289444 | -1.866498 |
| C | -0.691988 | -8.037608 | -2.838049 |
| H | -1.741062 | -7.378726 | -4.598853 |
| C | -0.078693 | -7.652571 | -1.644331 |
| H | 0.446237 | -5.997775 | -0.365685 |
| H | -0.725226 | -9.085598 | -3.121221 |
| H | 0.360683 | -8.401044 | -0.991249 |
| C | -4.294623 | -5.341257 | -4.200131 |
| O | -4.646239 | -6.610451 | -4.963728 |
| C | -5.128033 | -6.452026 | -6.178753 |
| O | -5.033964 | -5.438748 | -6.885638 |
| C | -4.159268 | -5.882156 | -2.772550 |
| H | -3.505166 | -6.749815 | -2.719371 |
| H | -3.757690 | -5.099190 | -2.124145 |
| H | -5.150759 | -6.167197 | -2.408335 |
| C | -5.540774 | -4.444891 | -4.237070 |
| H | -6.417314 | -5.076197 | -4.055658 |
| H | -5.473955 | -3.715913 | -3.427966 |
| H | -5.664970 | -3.908634 | -5.175432 |
| O | -5.751466 | -7.559759 | -6.575057 |
| C | -6.186818 | -7.551338 | -7.965421 |
| H | -5.328519 | -7.391908 | -8.620162 |
| H | -6.622352 | -8.536870 | -8.119906 |
| H | -6.926310 | -6.763364 | -8.116726 |
| Mn | -2.984222 | -4.725672 | -7.132279 |
| O | -3.559653 | -4.705635 | -10.037902 |
| O | -1.978600 | -7.516730 | -7.263780 |
| O | -0.229540 | -3.949600 | -7.810057 |
| C | -1.313488 | -4.225590 | -7.503669 |
| C | -3.333608 | -4.700544 | -8.901420 |
| C | -2.396676 | -6.433810 | -7.200755 |

Intermediate Mn-VII

E(PW6B95-D3(BJ)/def2-TZVP+COSMO(TFE)) = -2793.914749 E_h

$\Delta\Delta H(298) = 0.448184 \text{ E}_h$

$S(298) = 0.096197 \text{ E}_h$

Lowest frequency: 25.44 cm⁻¹

| | | | |
|---|-----------|-----------|-----------|
| N | -3.719053 | -3.025305 | -6.480647 |
| C | -3.298494 | -2.838203 | -5.117075 |
| C | -4.516313 | -2.115505 | -7.086995 |
| C | -5.117700 | -1.079234 | -6.420927 |
| C | -4.904442 | -0.971135 | -5.016174 |
| H | -4.697199 | -2.294850 | -8.143520 |
| H | -5.423788 | -0.197752 | -4.455461 |
| H | -5.753352 | -0.382823 | -6.952746 |
| N | -1.786871 | -2.475024 | -5.048490 |
| C | -1.026072 | -3.538103 | -4.649752 |
| C | -1.911313 | -4.683292 | -4.381705 |
| C | -3.218542 | -4.290767 | -4.563574 |
| C | -4.087314 | -1.829052 | -4.356287 |
| H | -3.919802 | -1.765588 | -3.284894 |
| C | -1.253932 | -1.241802 | -5.492352 |
| C | 0.186819 | -1.151999 | -5.304164 |
| H | 0.636857 | -0.204202 | -5.579134 |
| C | 0.940386 | -2.209533 | -4.877736 |
| C | 0.339445 | -3.456191 | -4.557415 |
| H | 2.019585 | -2.106828 | -4.797560 |
| H | 0.925163 | -4.317683 | -4.263646 |
| O | -1.962489 | -0.369886 | -5.987757 |
| C | -1.384187 | -5.907437 | -3.737839 |
| C | -0.603732 | -5.754720 | -2.576285 |
| C | -1.646235 | -7.203461 | -4.197780 |
| C | -0.116348 | -6.867031 | -1.895310 |
| H | -0.402820 | -4.756981 | -2.199168 |
| C | -1.147241 | -8.314126 | -3.522947 |
| H | -2.230548 | -7.345885 | -5.095859 |
| C | -0.383050 | -8.152234 | -2.367764 |
| H | 0.473238 | -6.727150 | -0.993892 |
| H | -1.355187 | -9.308593 | -3.906327 |
| H | 0.003604 | -9.019841 | -1.841320 |
| C | -4.467682 | -4.953230 | -4.002157 |
| O | -4.557526 | -6.397388 | -4.412580 |
| C | -4.809694 | -6.634588 | -5.687508 |
| O | -4.714372 | -5.830962 | -6.619064 |
| C | -4.341691 | -5.060043 | -2.478852 |

| | | | |
|----|-----------|-----------|-----------|
| H | -3.472028 | -5.657172 | -2.199811 |
| H | -4.234980 | -4.054779 | -2.062535 |
| H | -5.244708 | -5.520317 | -2.068135 |
| C | -5.799585 | -4.295210 | -4.374159 |
| H | -6.599698 | -4.992955 | -4.105925 |
| H | -5.925503 | -3.378060 | -3.799023 |
| H | -5.864035 | -4.040942 | -5.430485 |
| O | -5.179385 | -7.905239 | -5.842838 |
| C | -5.376715 | -8.322145 | -7.225775 |
| H | -4.439405 | -8.230169 | -7.776621 |
| H | -5.688185 | -9.362536 | -7.152978 |
| H | -6.149916 | -7.708154 | -7.689906 |
| Mn | -2.868111 | -4.726068 | -7.031822 |
| O | -3.708718 | -4.608437 | -9.849175 |
| O | -1.584976 | -7.339705 | -7.653222 |
| O | -0.352182 | -3.464377 | -7.874676 |
| C | -1.336831 | -3.946443 | -7.505751 |
| C | -3.381459 | -4.654789 | -8.740377 |
| C | -2.092398 | -6.337238 | -7.355334 |

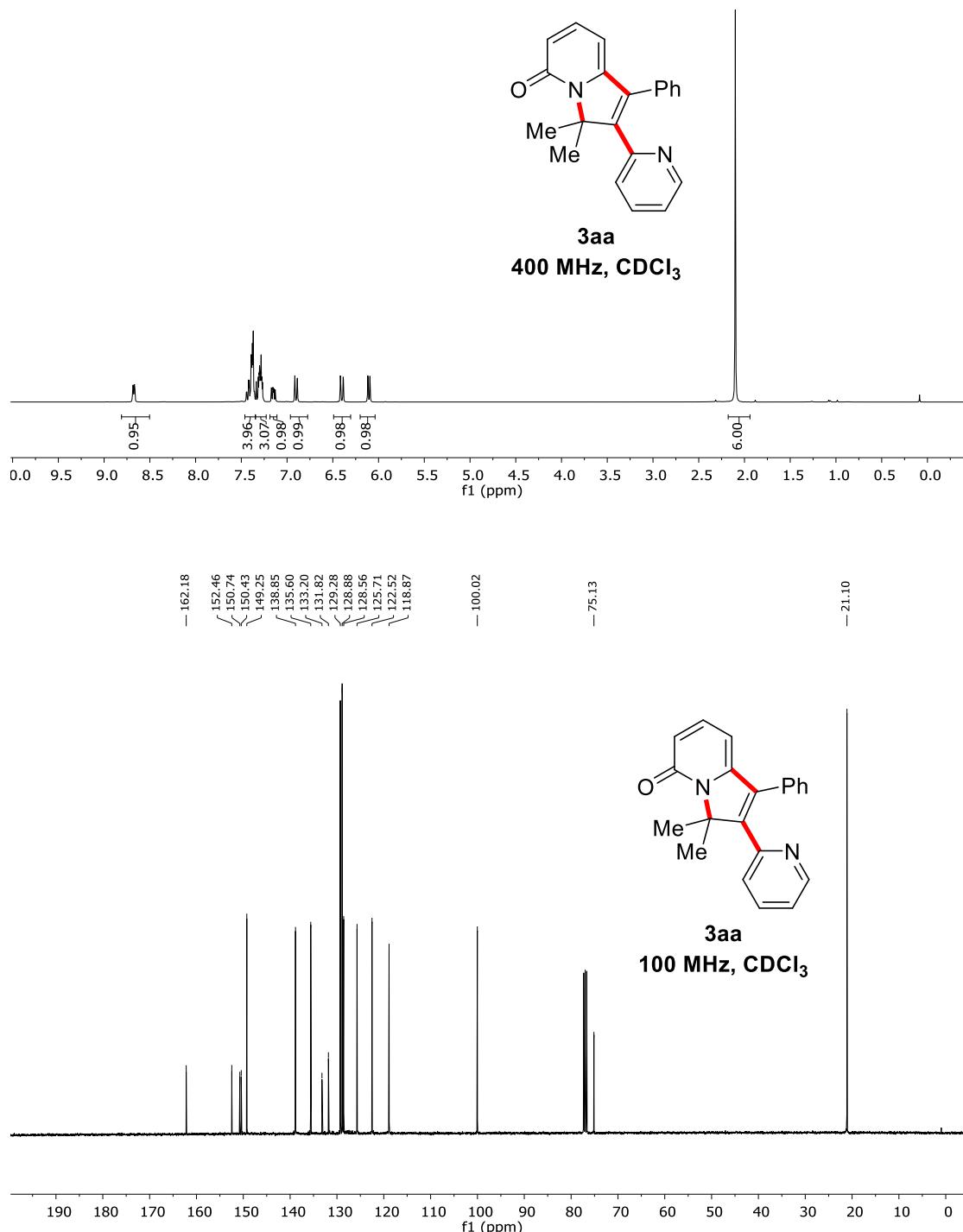
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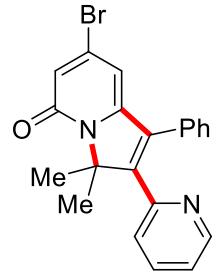
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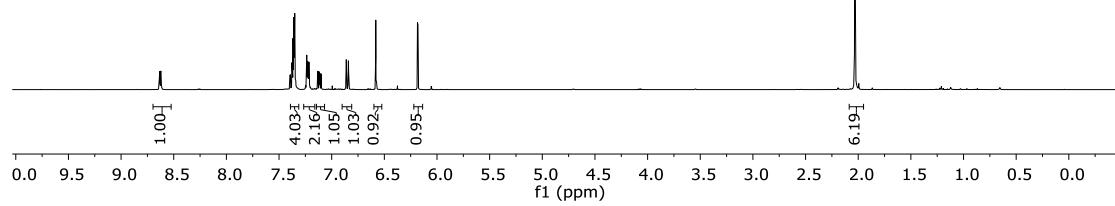
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¹H, ¹³C, and ¹⁹F-NMR Data

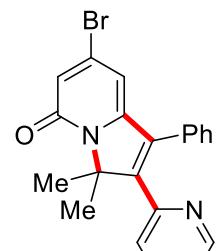




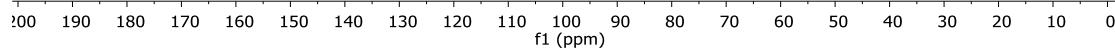
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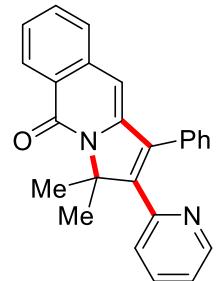


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-152.49
-151.84
-150.60
-149.28
-135.66
-135.23
-132.39
-131.14
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-129.09
-128.85
-125.70
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-75.31
-21.11



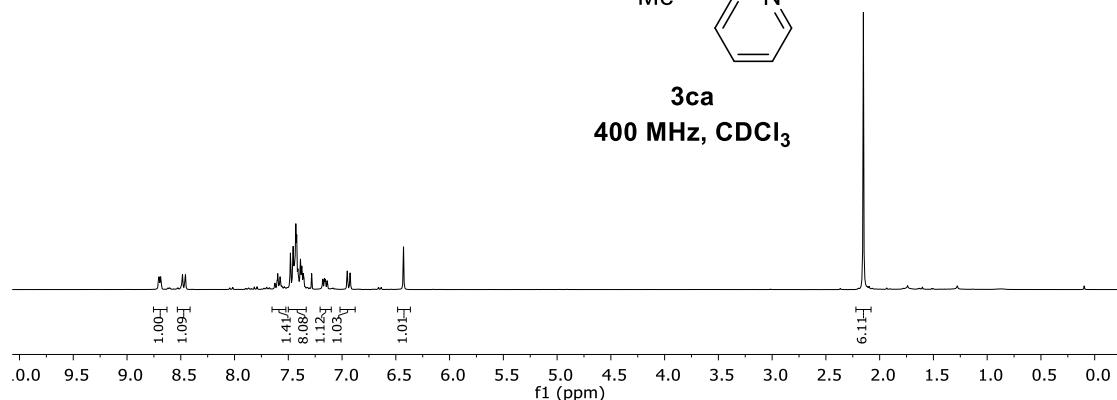
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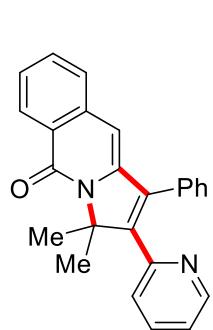


3ca

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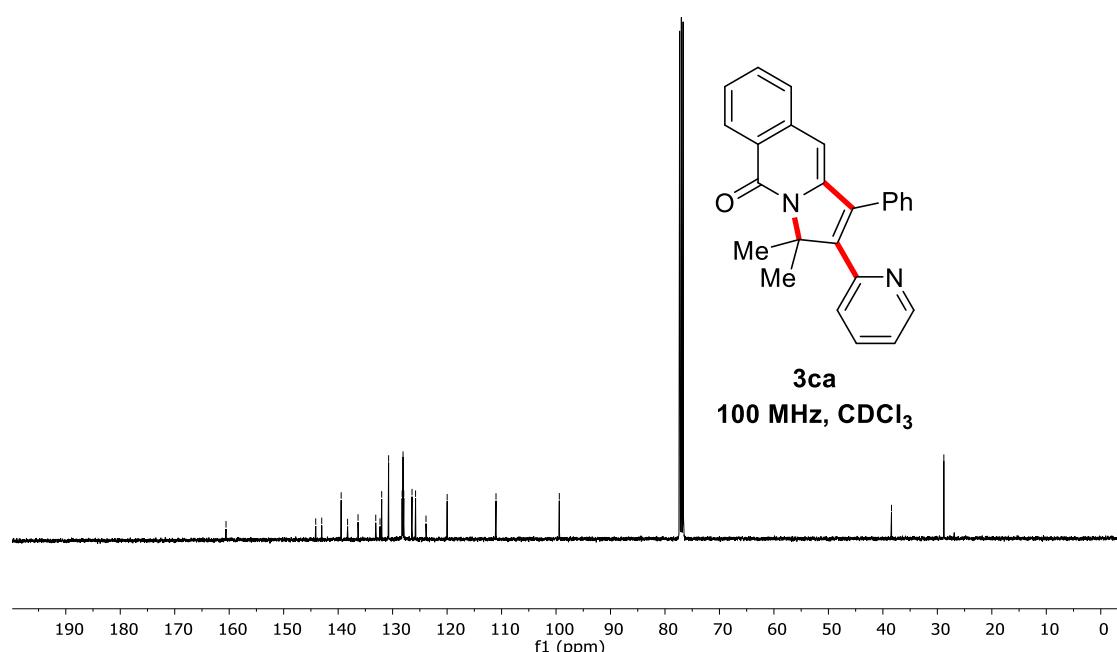


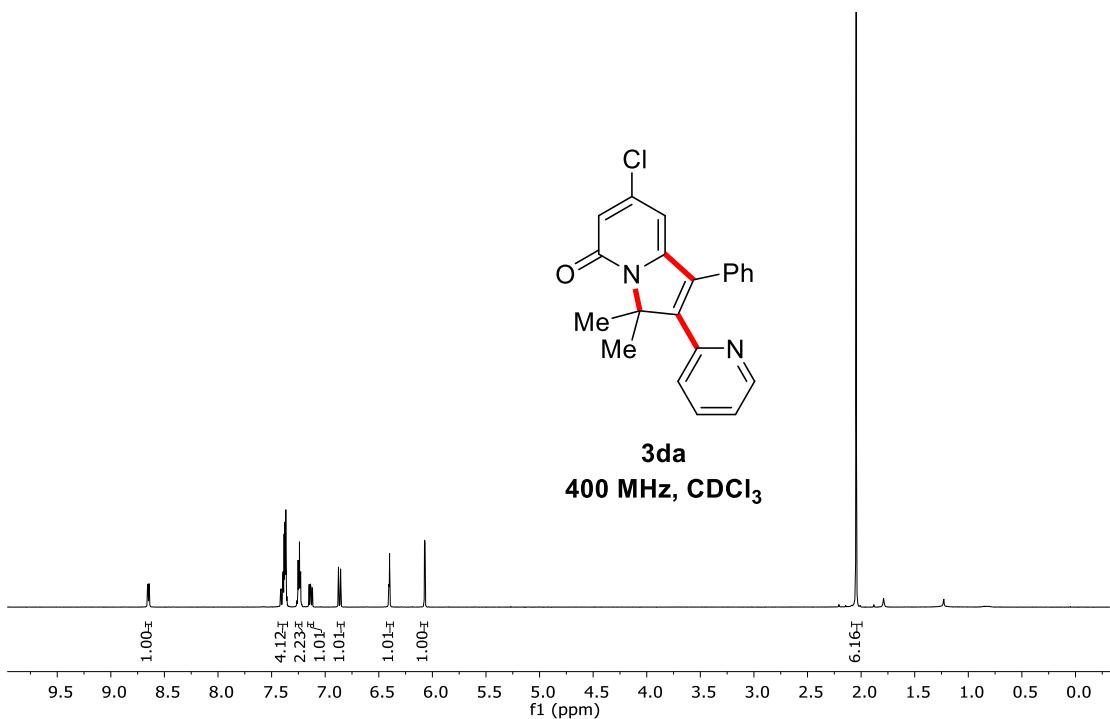
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139.45
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133.10
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126.44
125.79
123.87
119.99
— 111.02
— 99.40
— 38.42
— 28.81



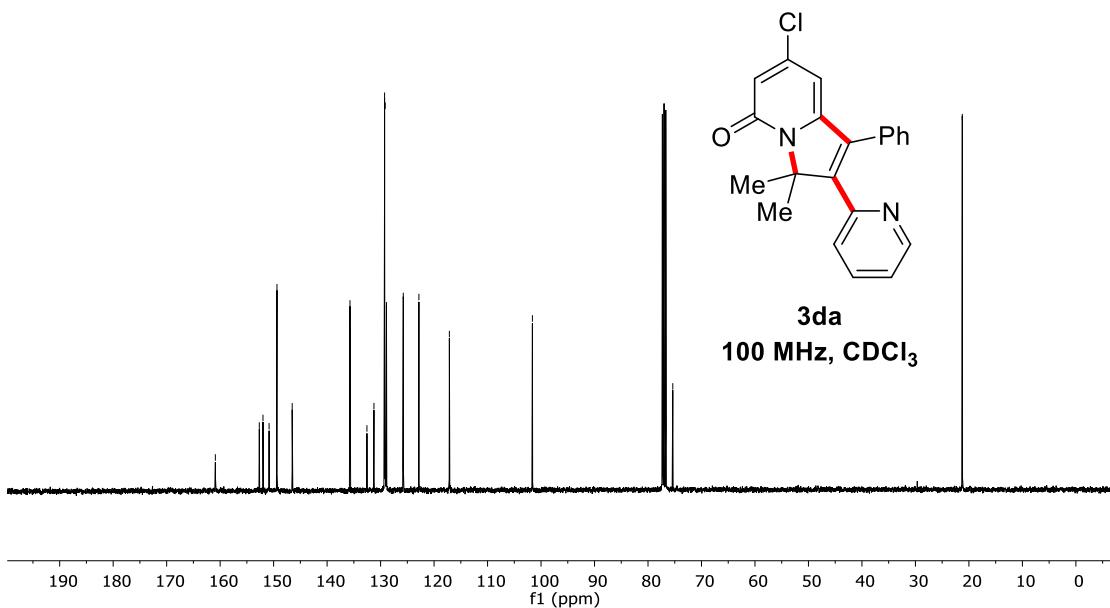
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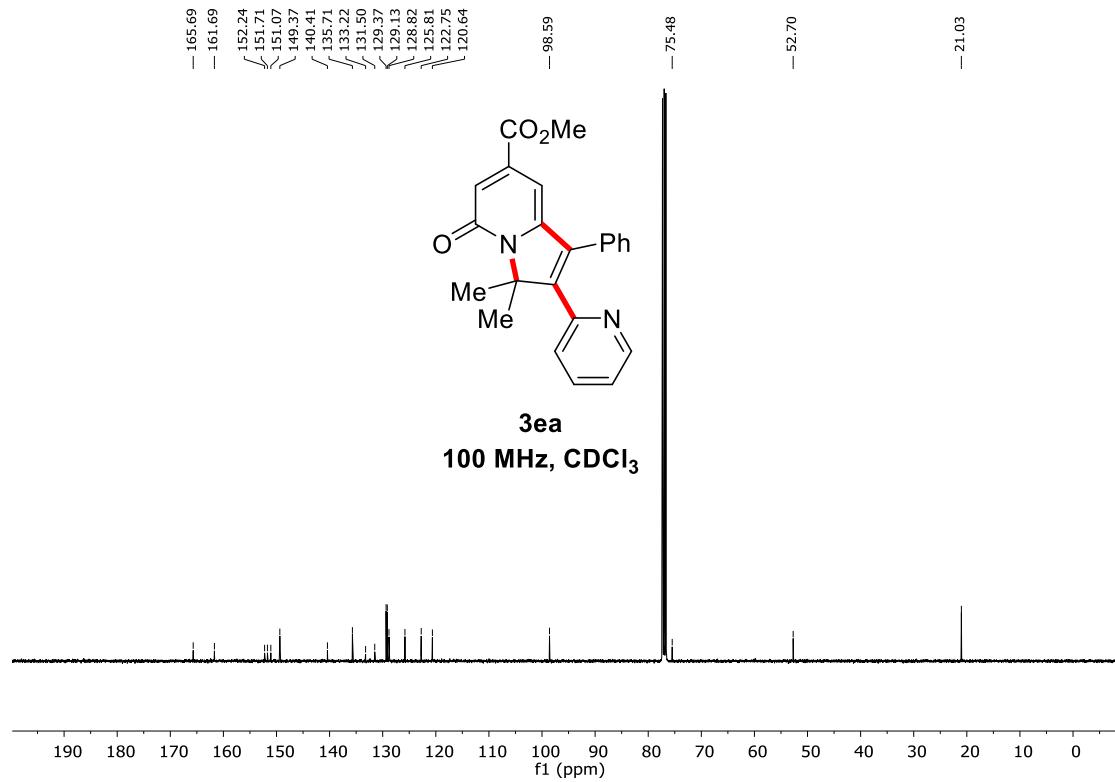
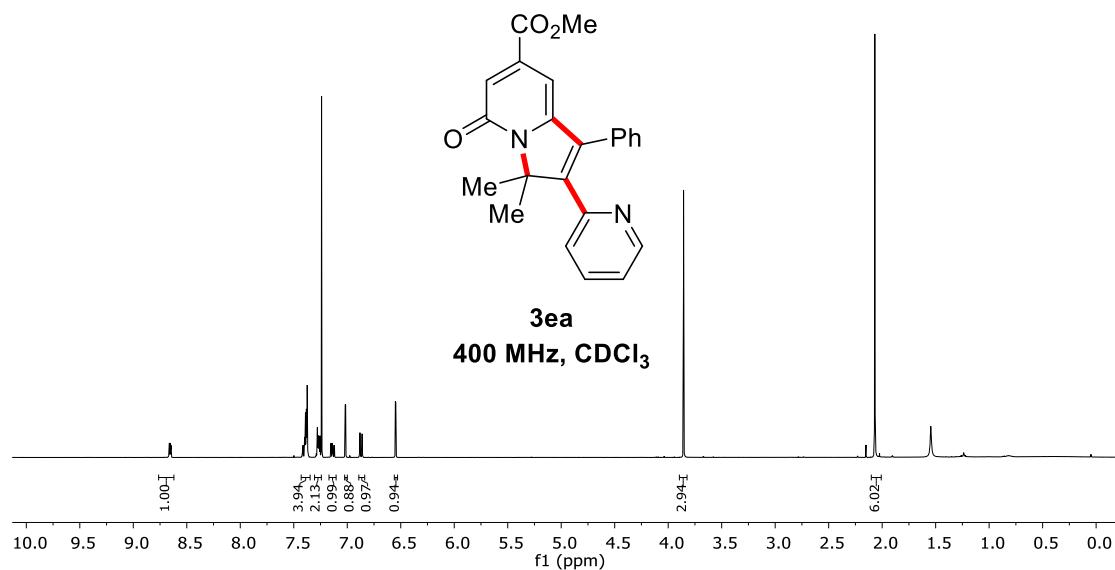
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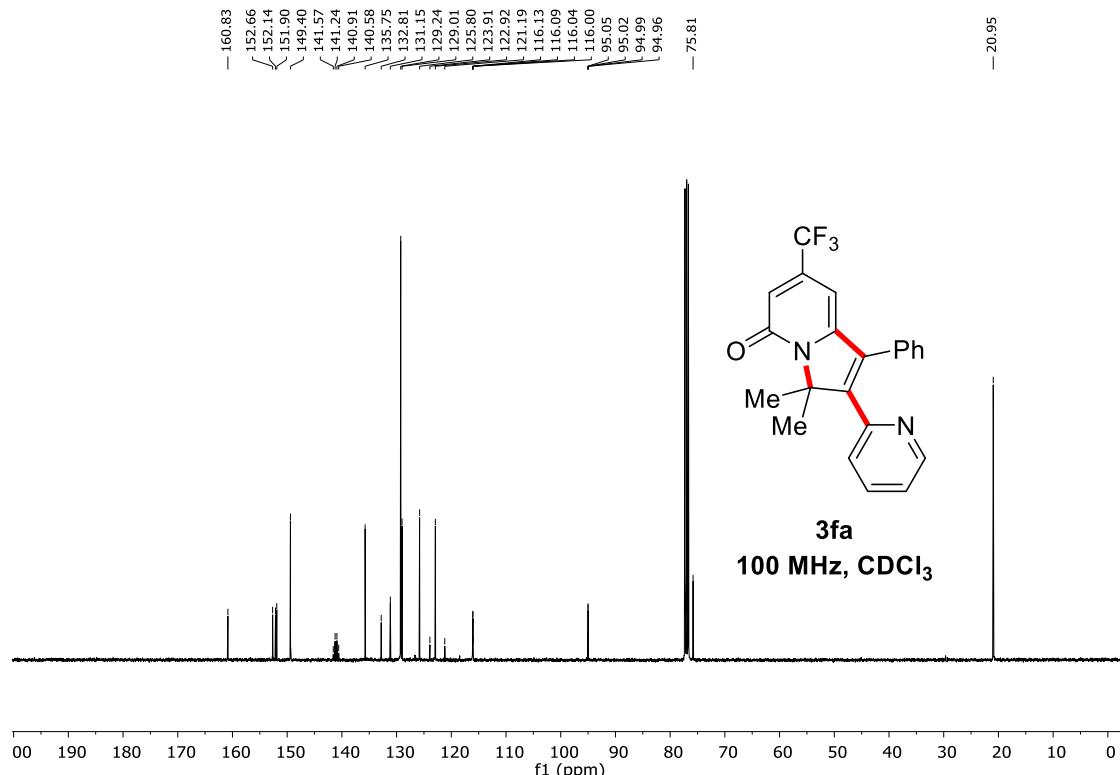
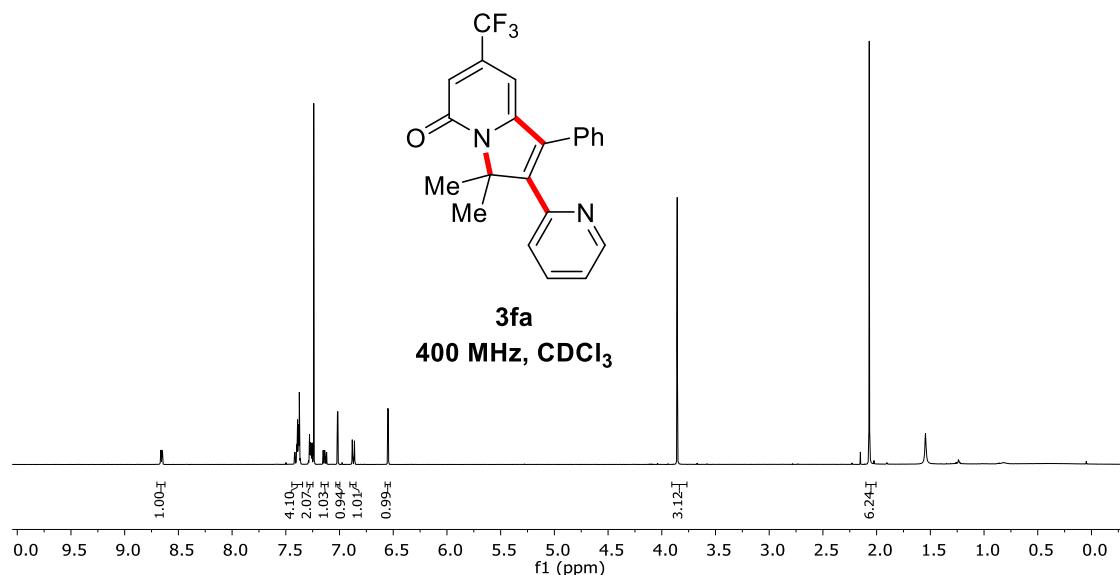


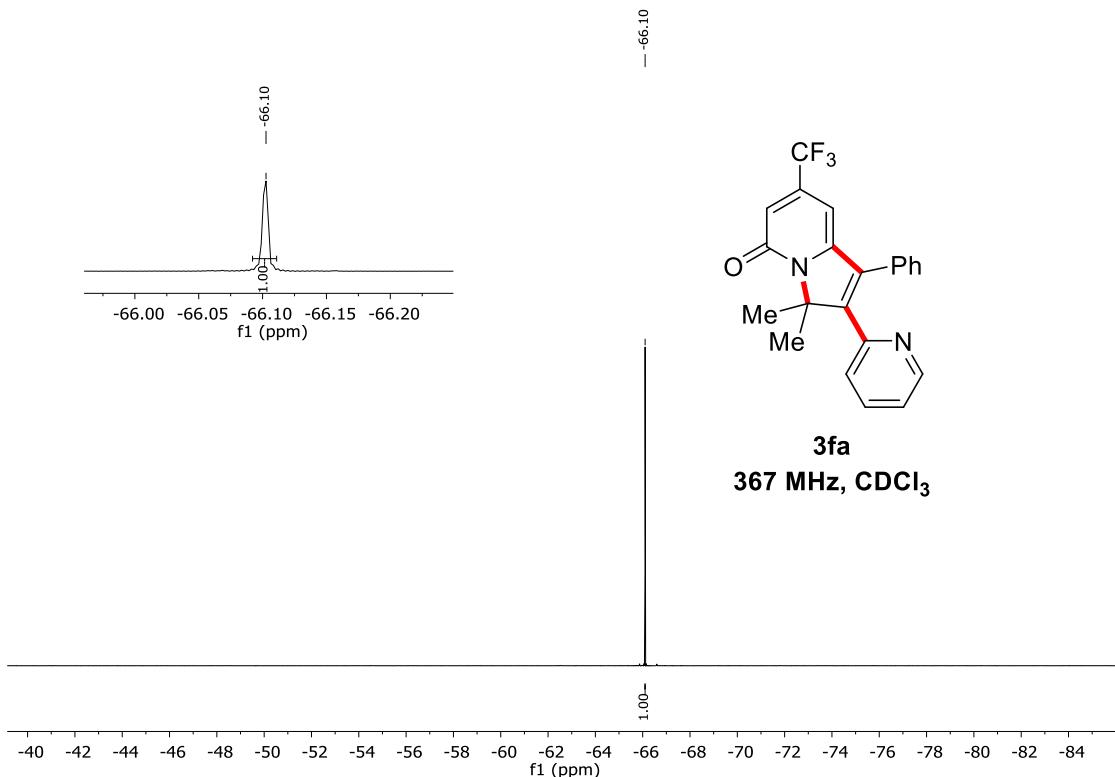


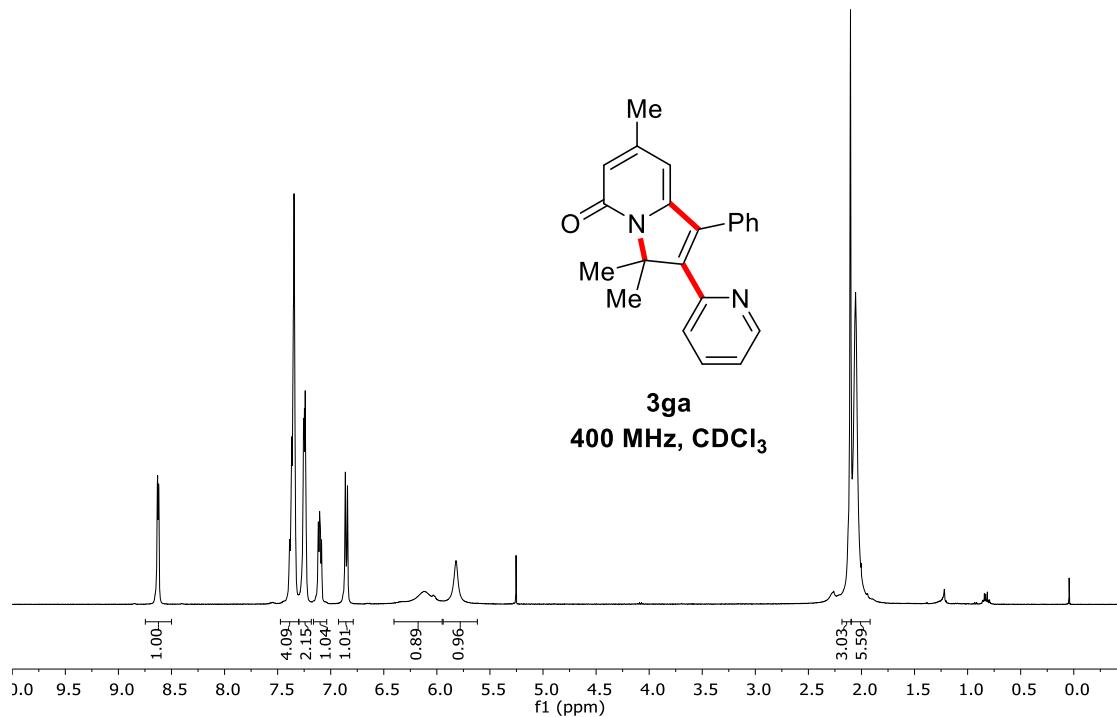
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 $-\quad 152.68$
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 $\diagdown\quad 146.53$
 $\diagup\quad 135.72$
 $\diagdown\quad 132.55$
 $\diagup\quad 131.24$
 $\diagdown\quad 129.25$
 $\diagup\quad 129.18$
 $\diagdown\quad 129.14$
 $\diagup\quad 128.90$
 $\diagdown\quad 125.76$
 $\diagup\quad 122.84$
 $\diagdown\quad 117.14$
 -101.61
 -75.37
 -21.23



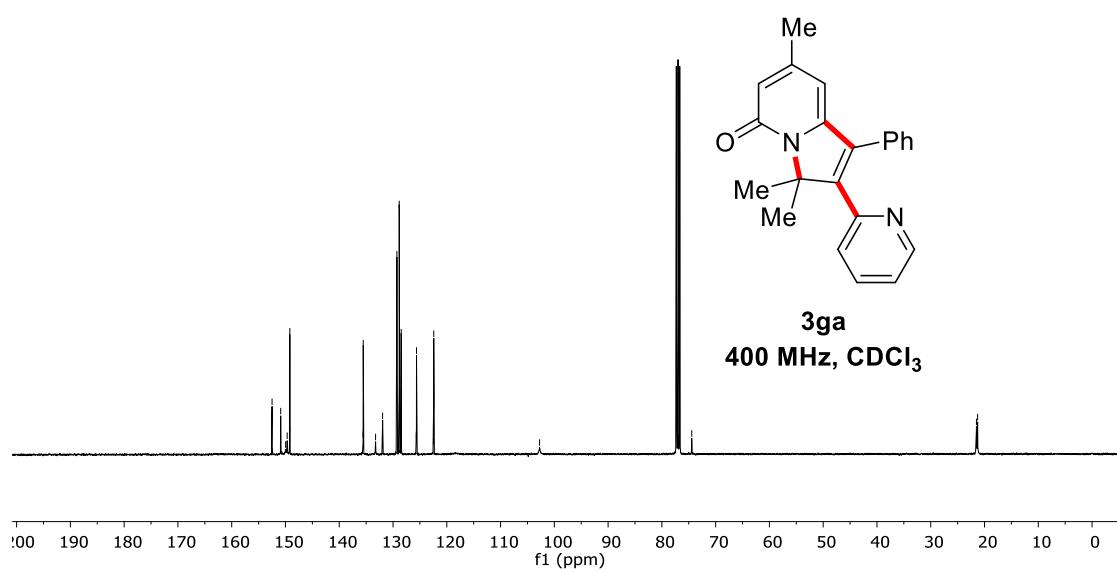


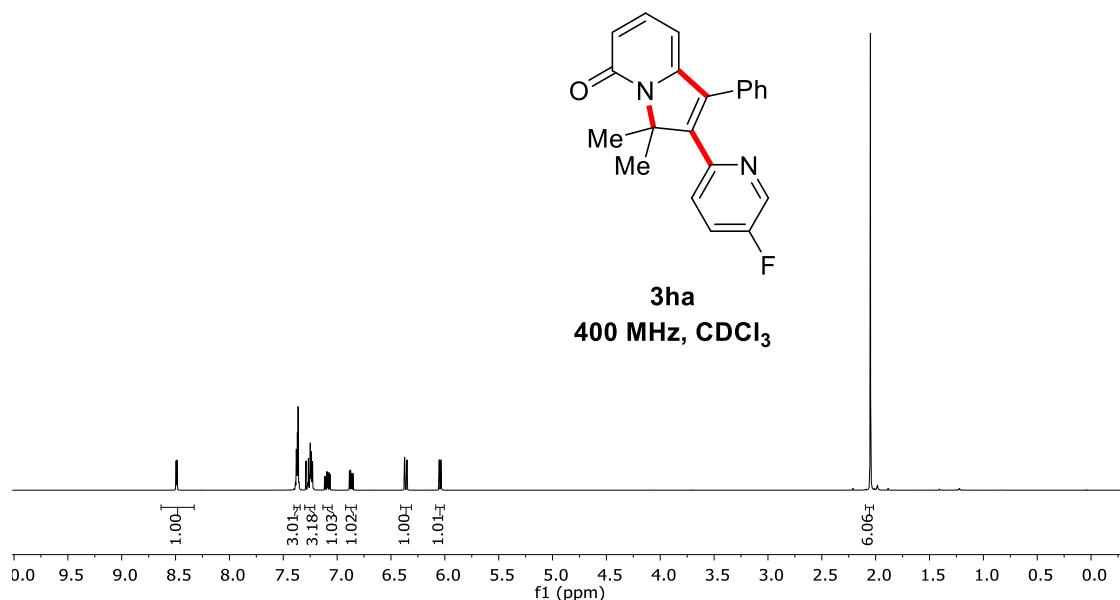




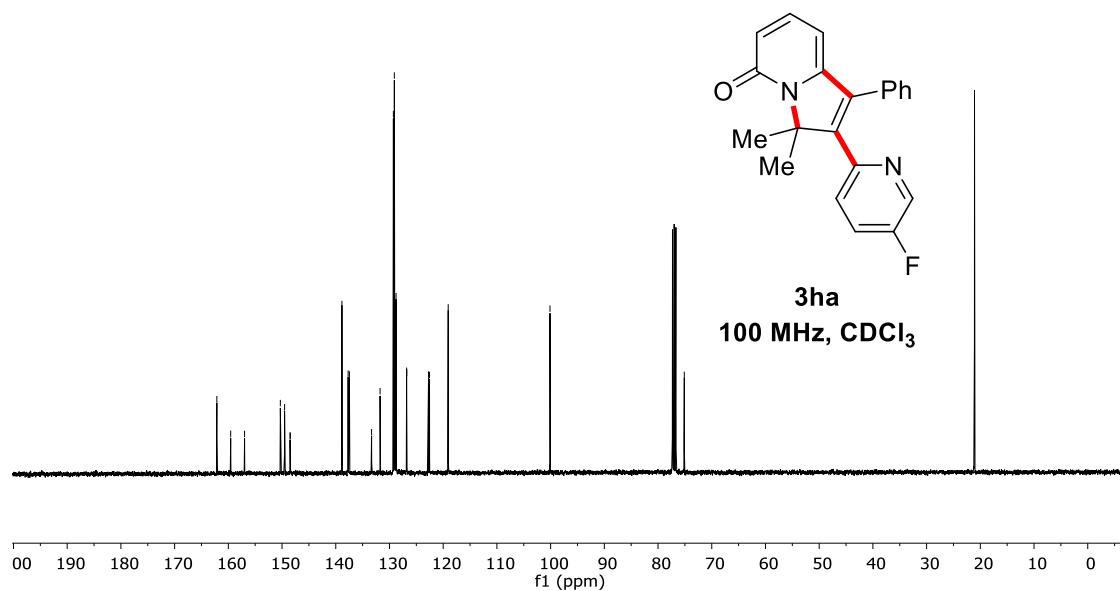


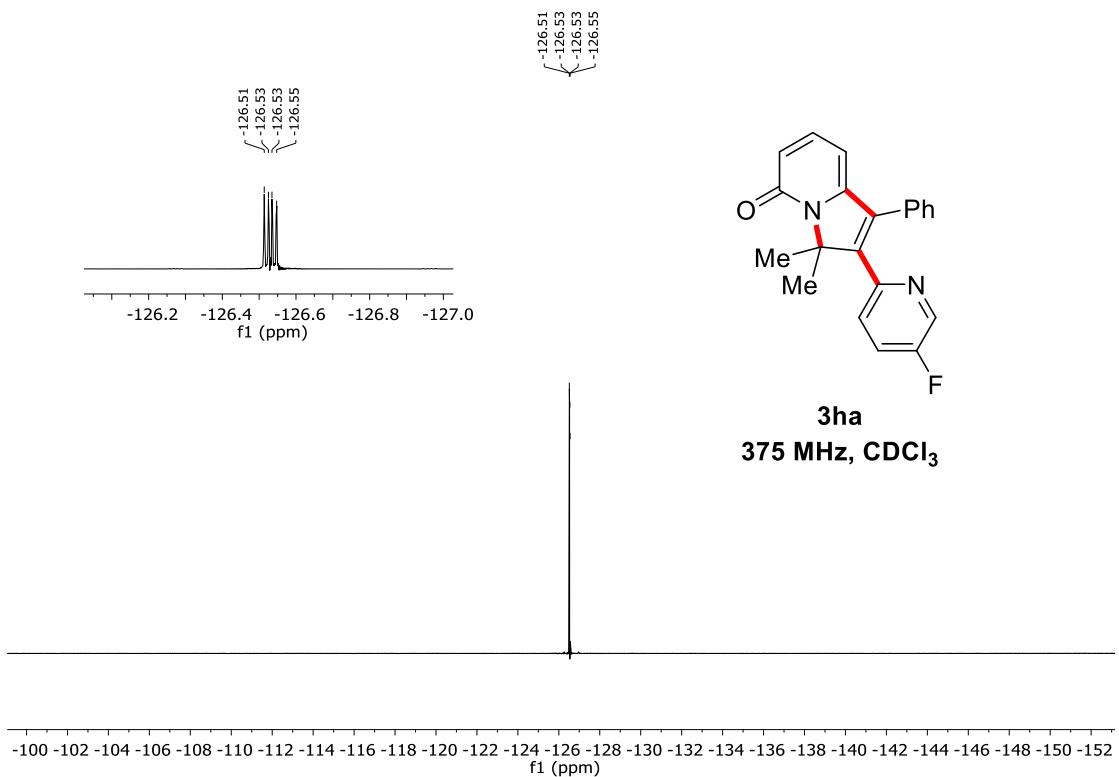
152.50
 150.89
 149.97
 149.68
 149.21
 149.19
 149.19
 135.57
 135.54
 133.24
 131.83
 129.28
 128.85
 128.53
 128.48
 125.66
 125.63
 122.48
 122.42
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 -74.45
 <21.50
 <21.28

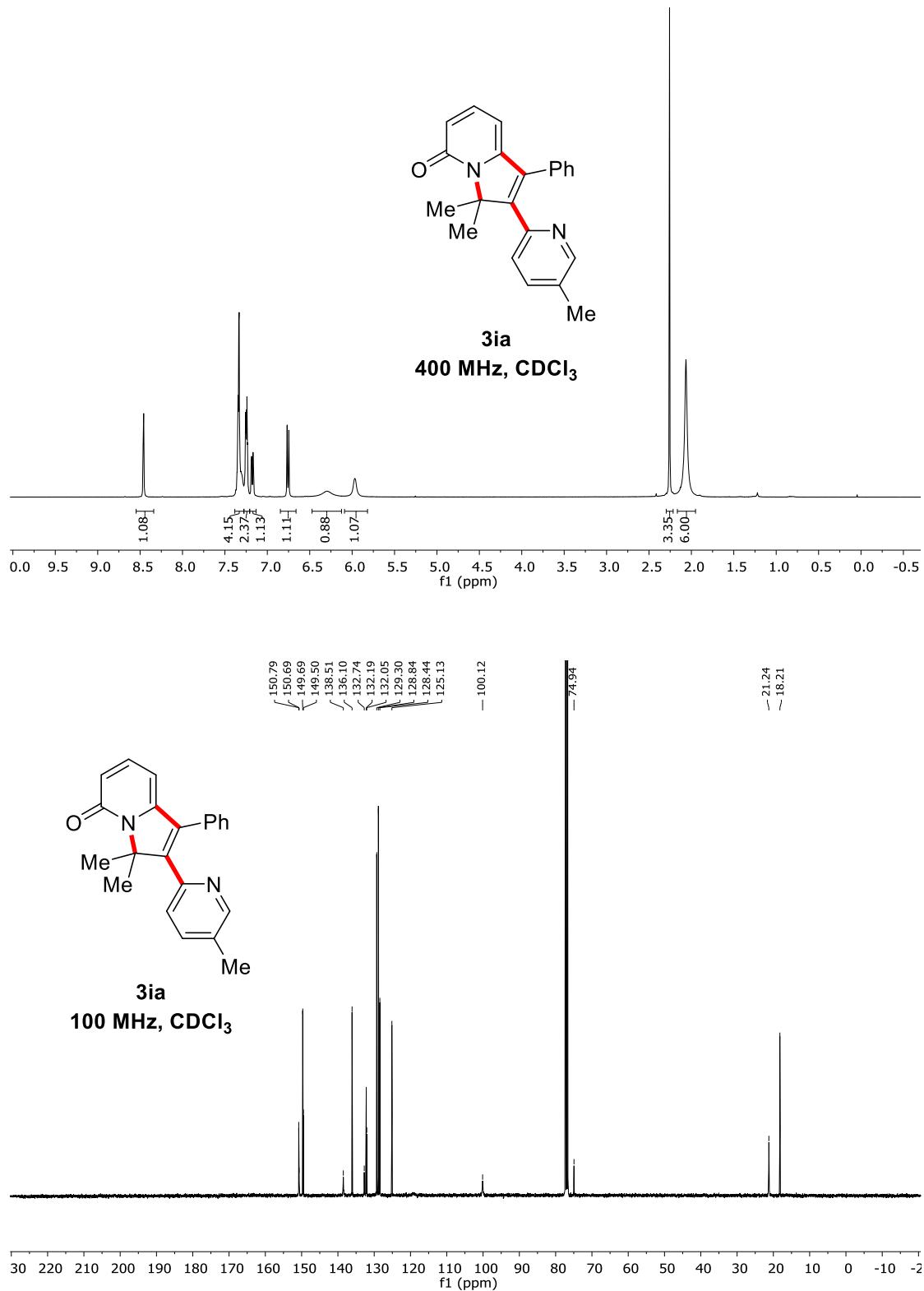


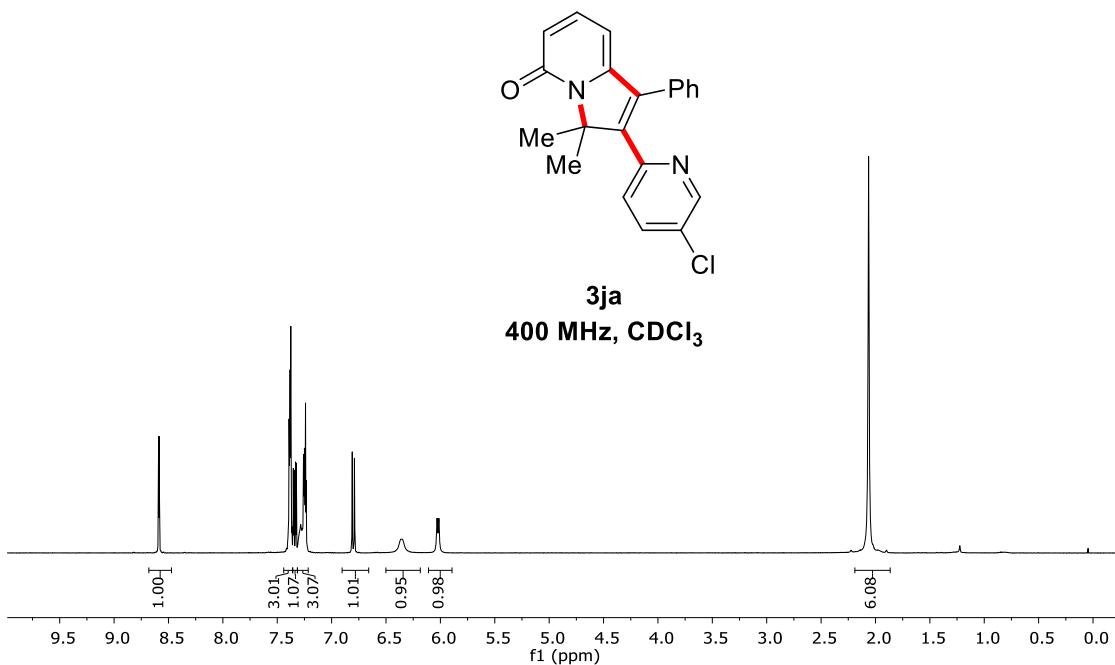


162.14
 159.56
 156.98
 150.32
 149.53
 148.51
 148.46
 138.85
 138.85
 137.69
 137.46
 133.33
 131.75
 129.27
 129.09
 128.77
 126.81
 126.77
 122.73
 122.55
 119.07
 -100.12
 -75.11
 -21.08

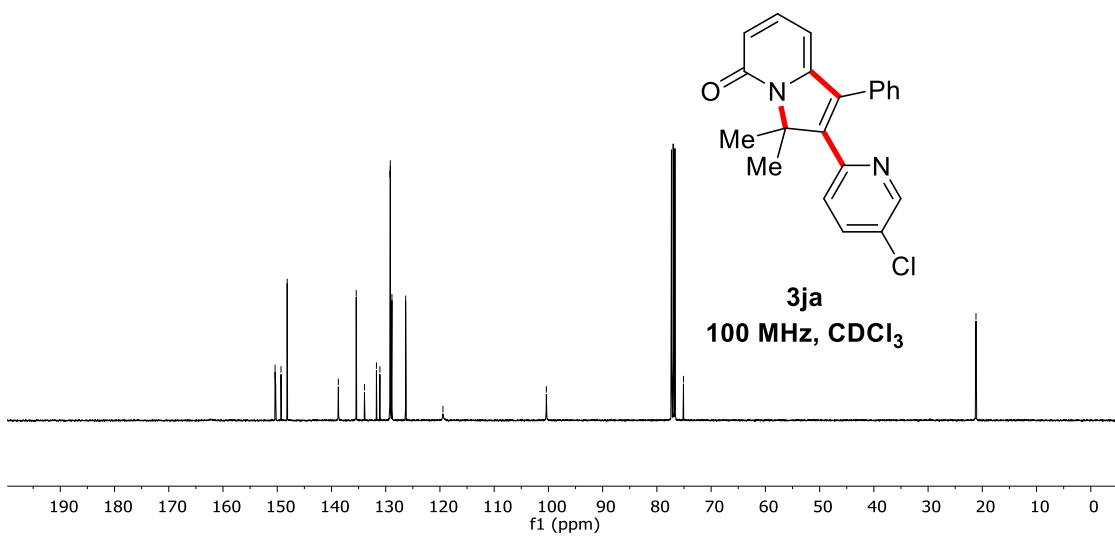


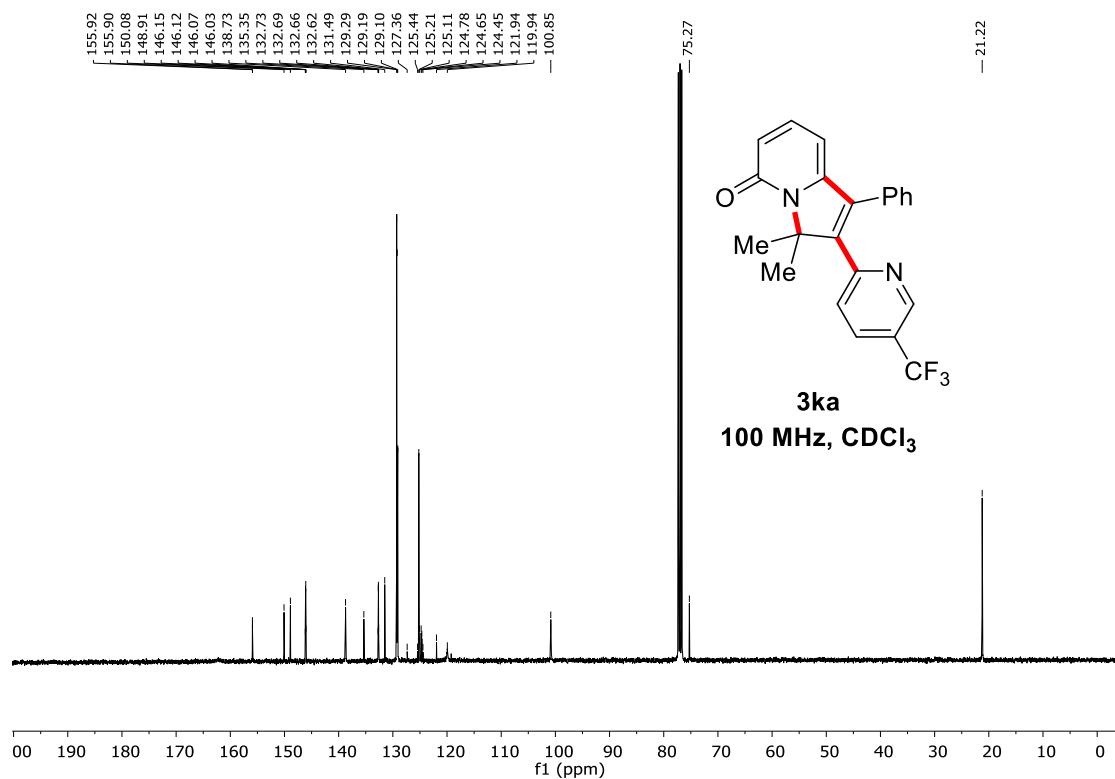
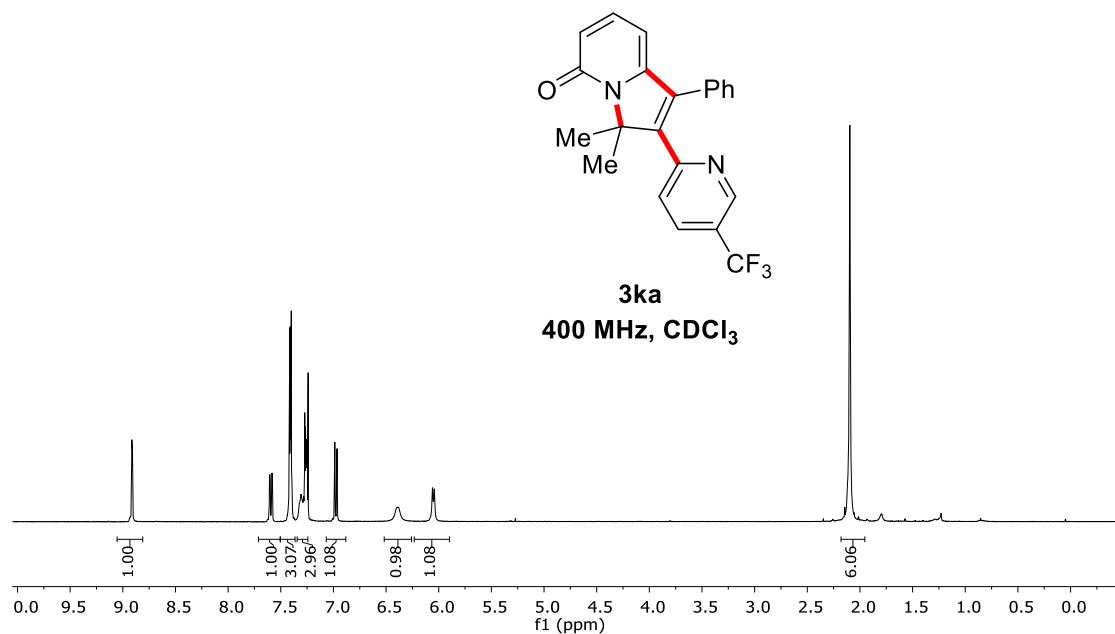


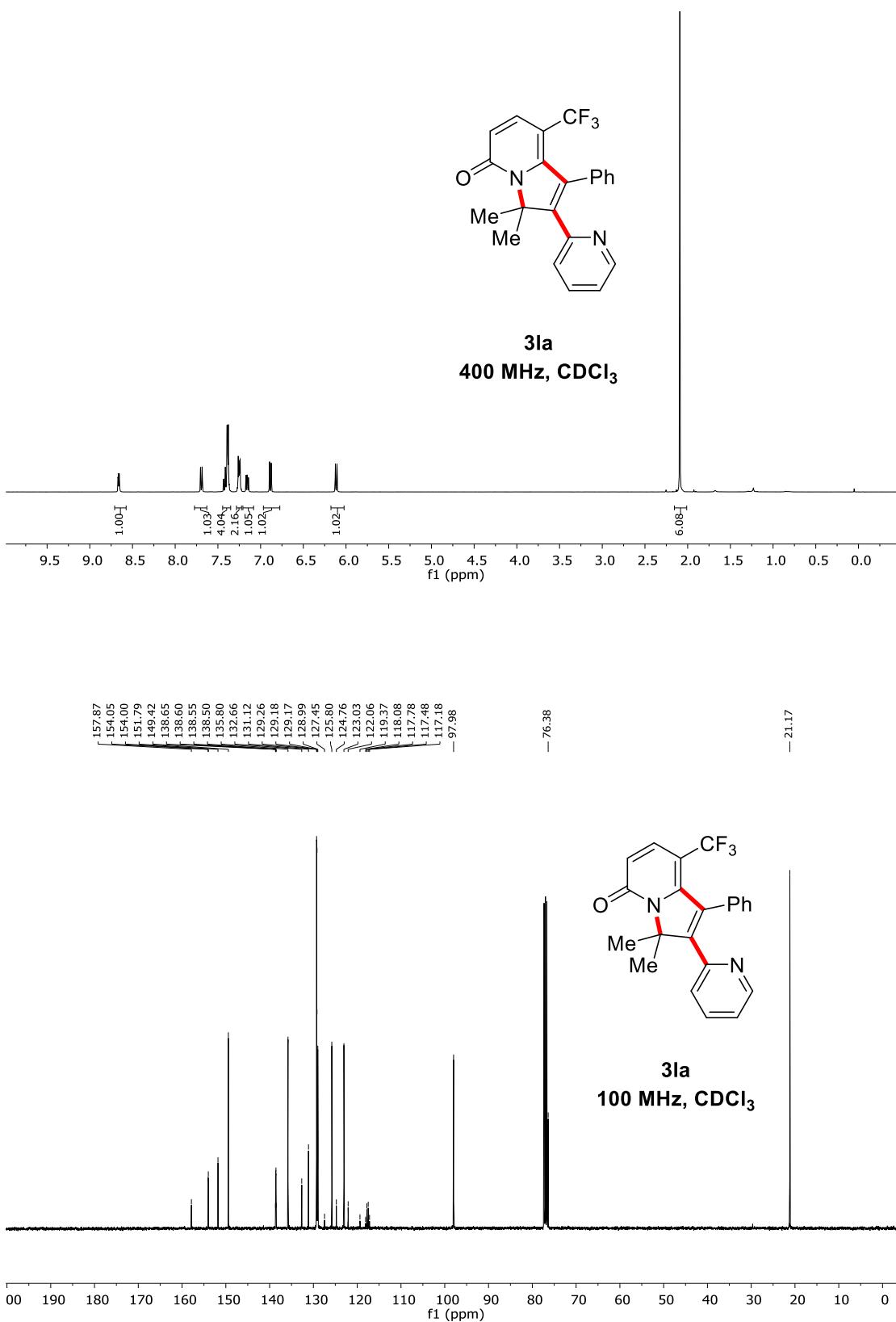


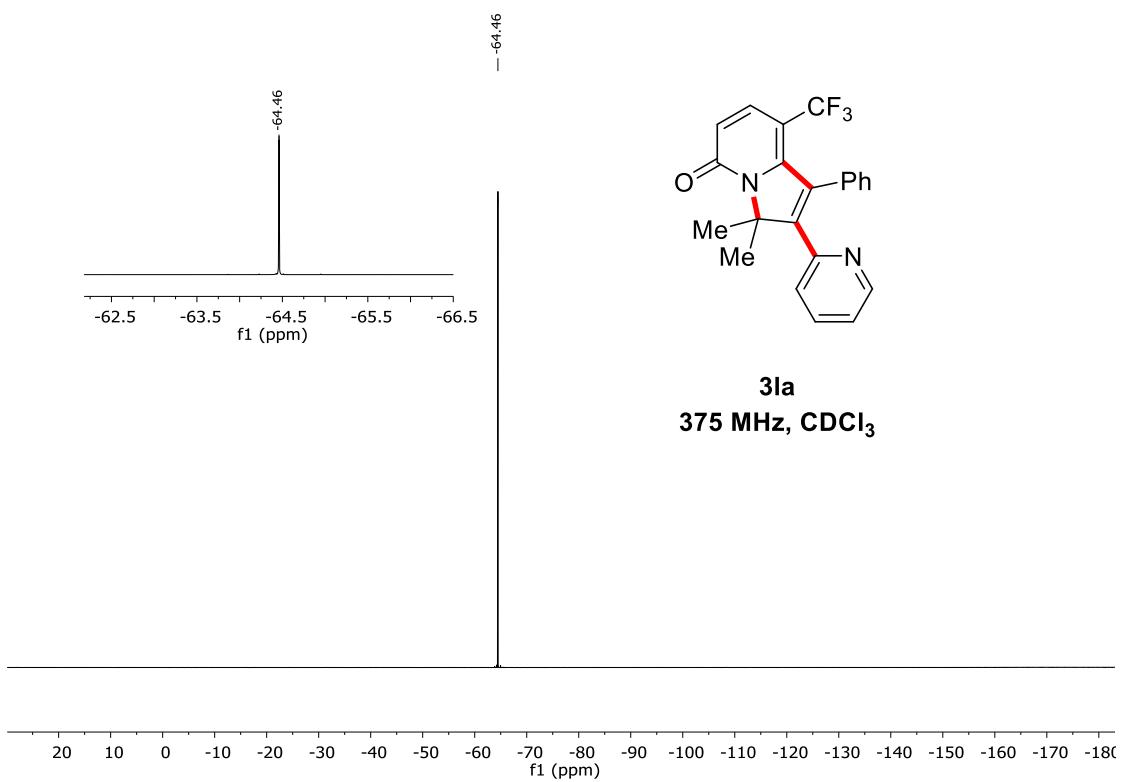


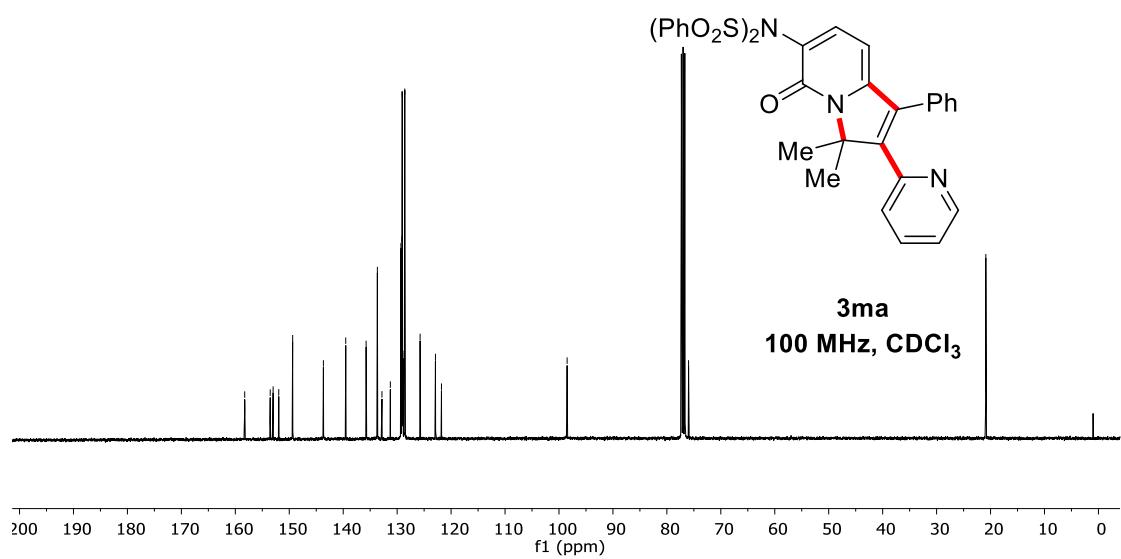
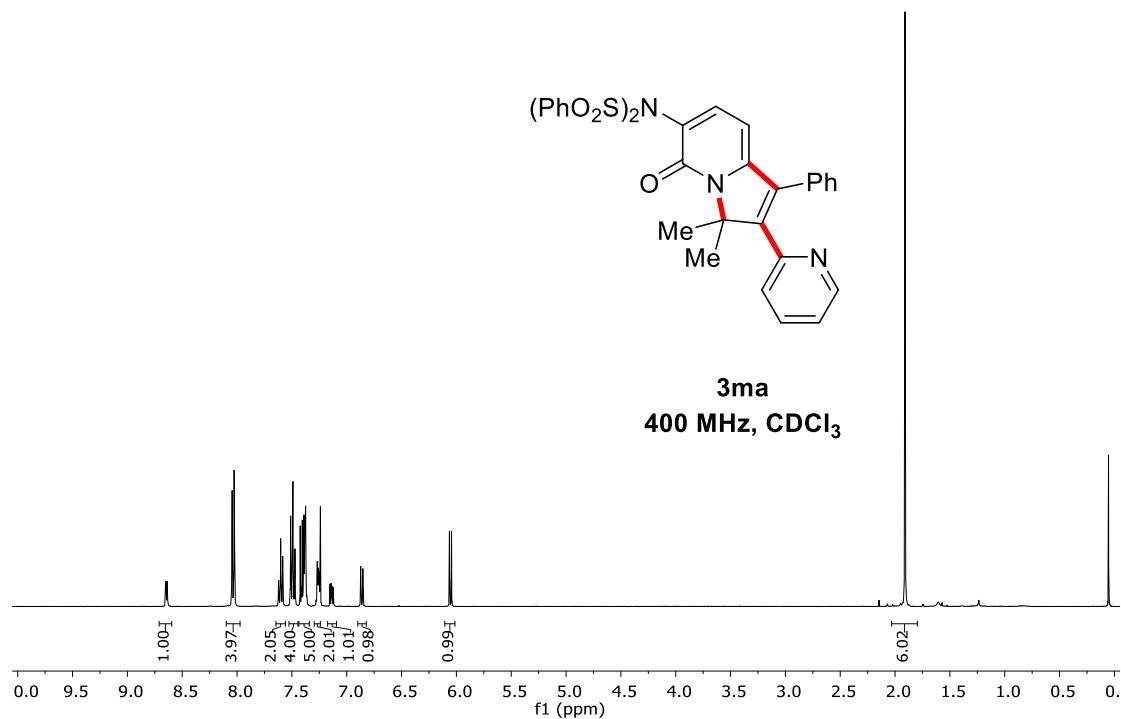
150.40 150.29 149.30 148.16 138.73 135.44 133.92 131.71 131.07 129.23 129.15 128.85 126.32 119.45
 -100.38 -75.10 -21.17

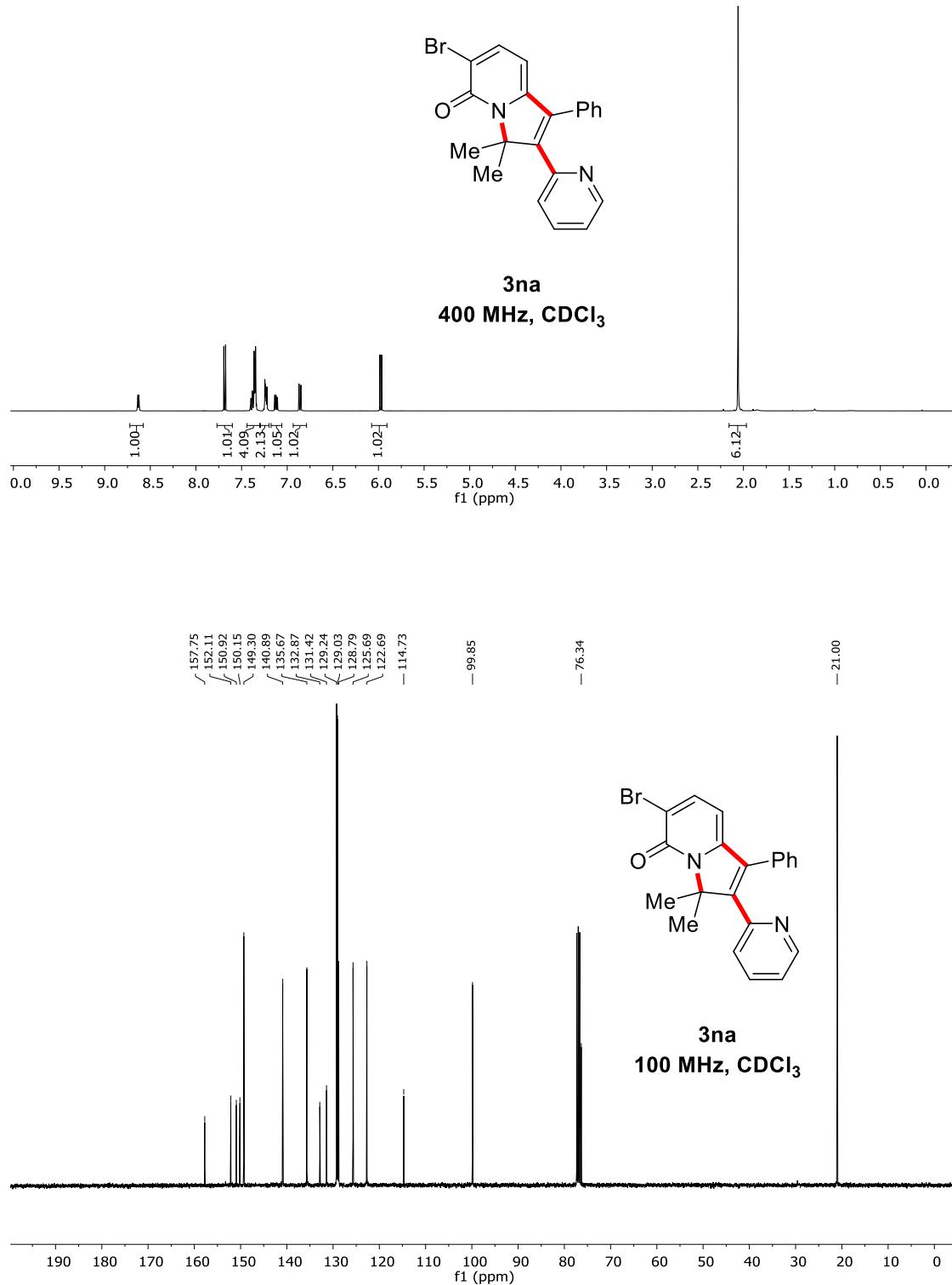


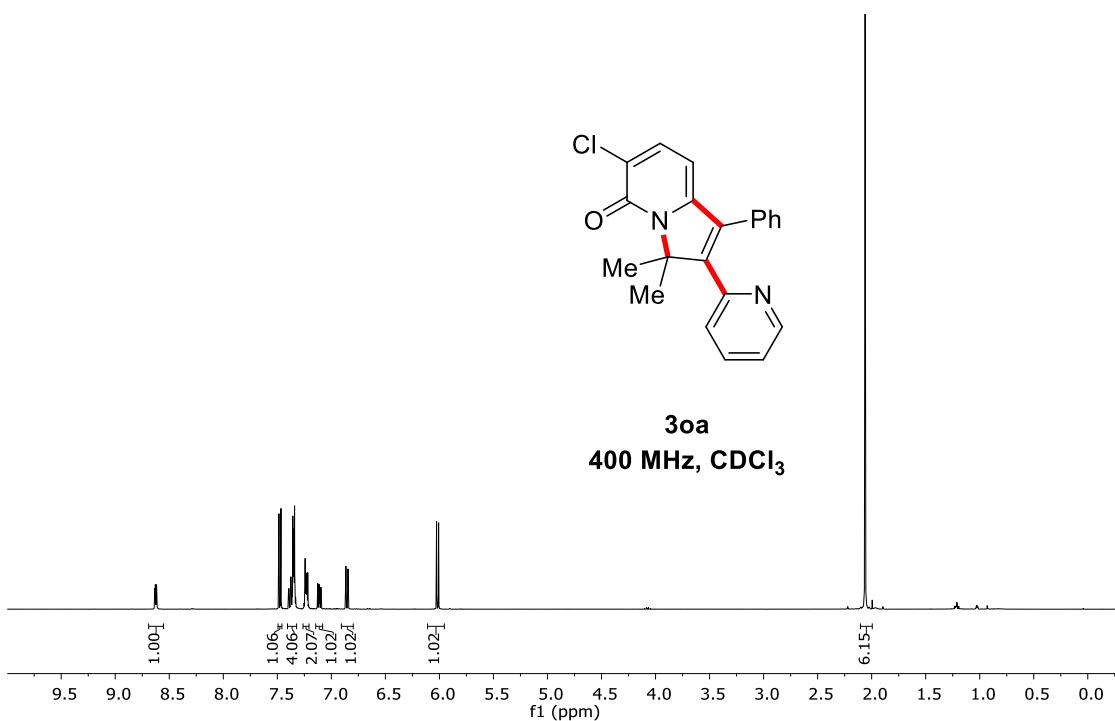




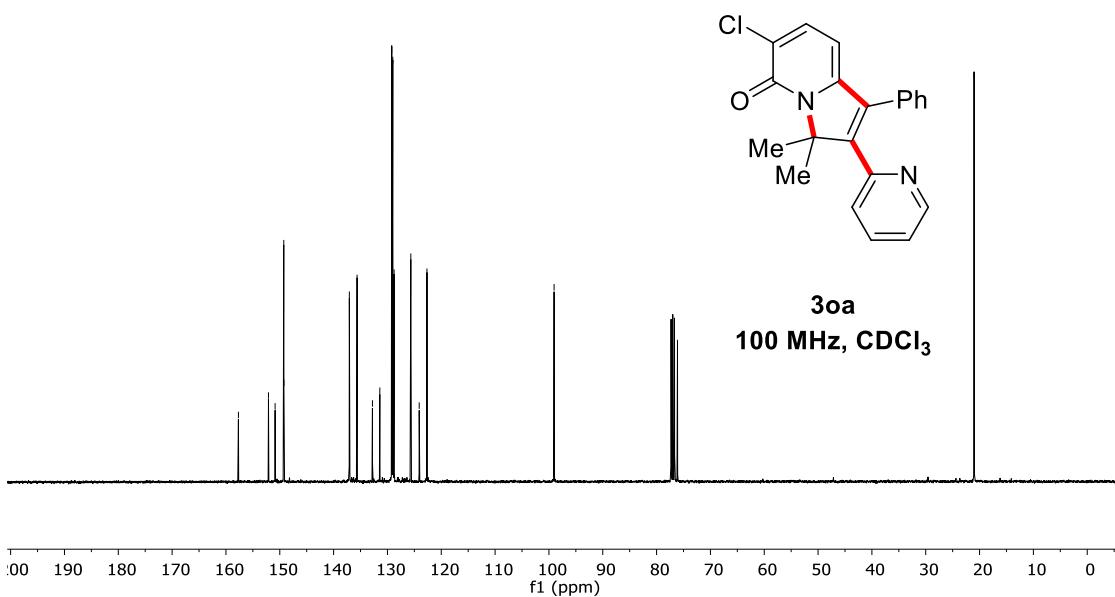


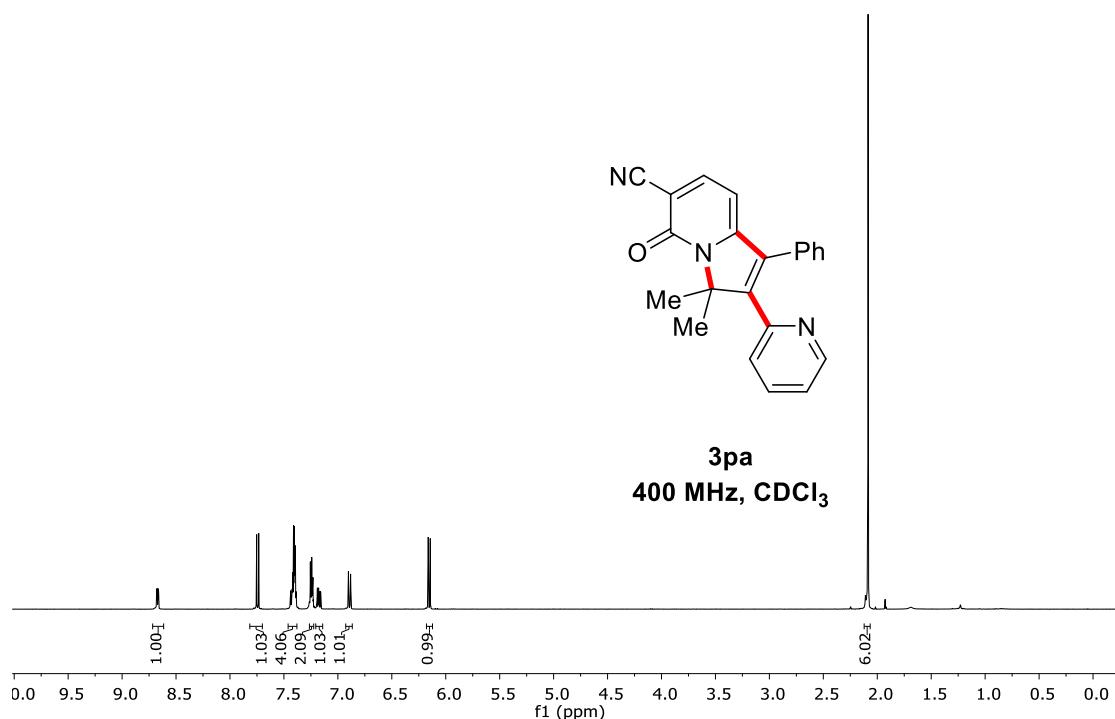




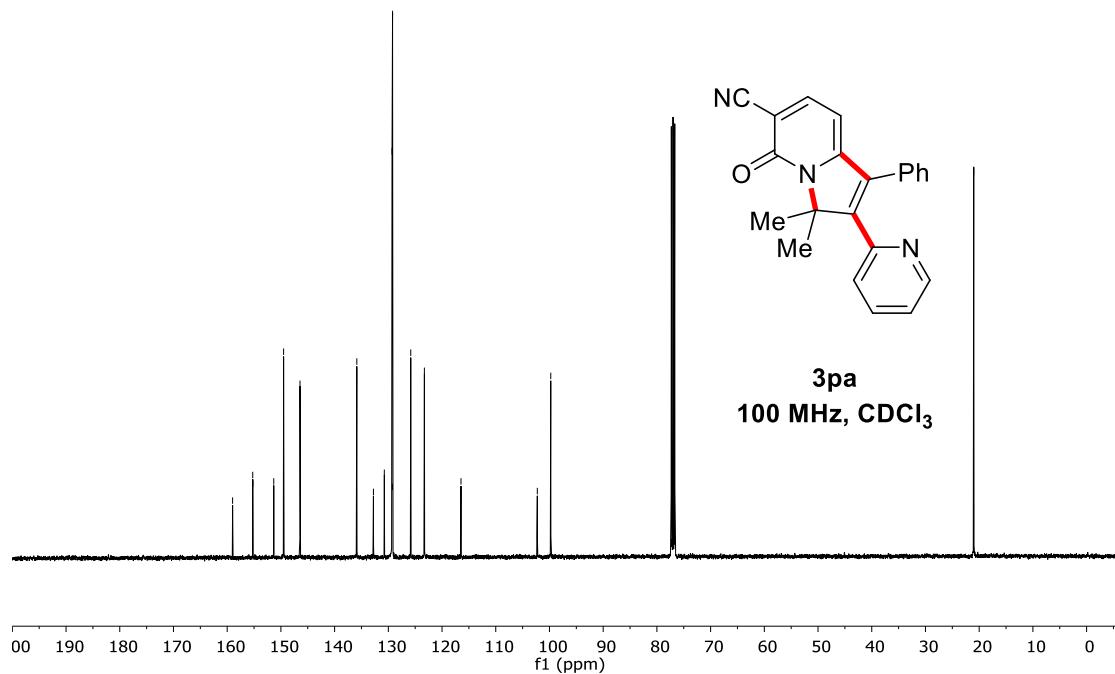


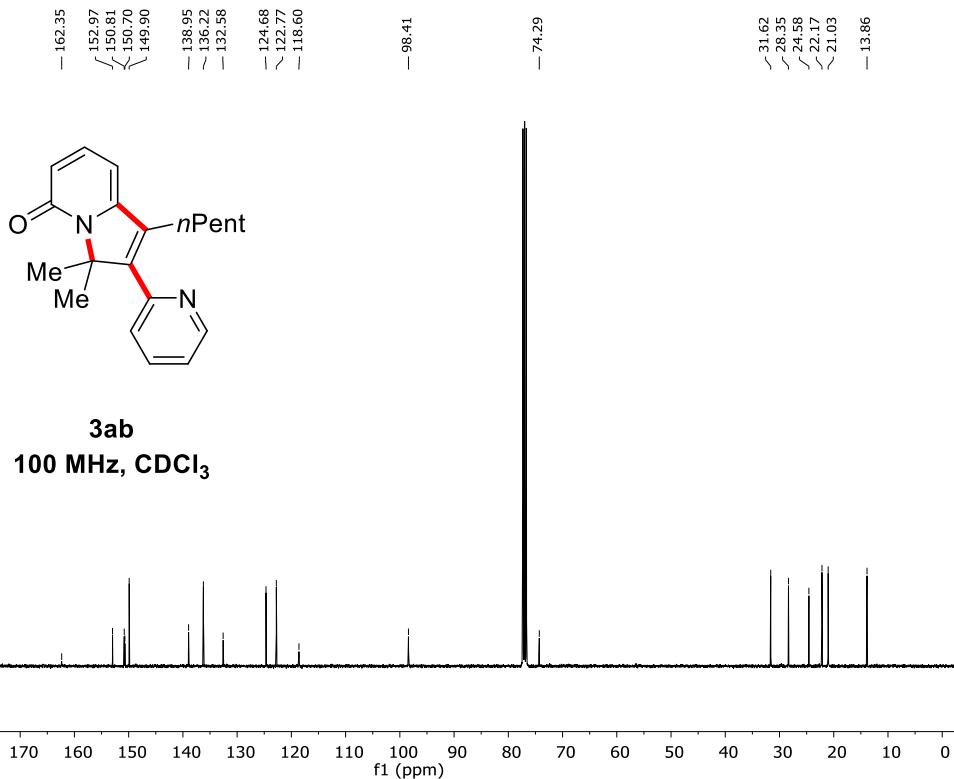
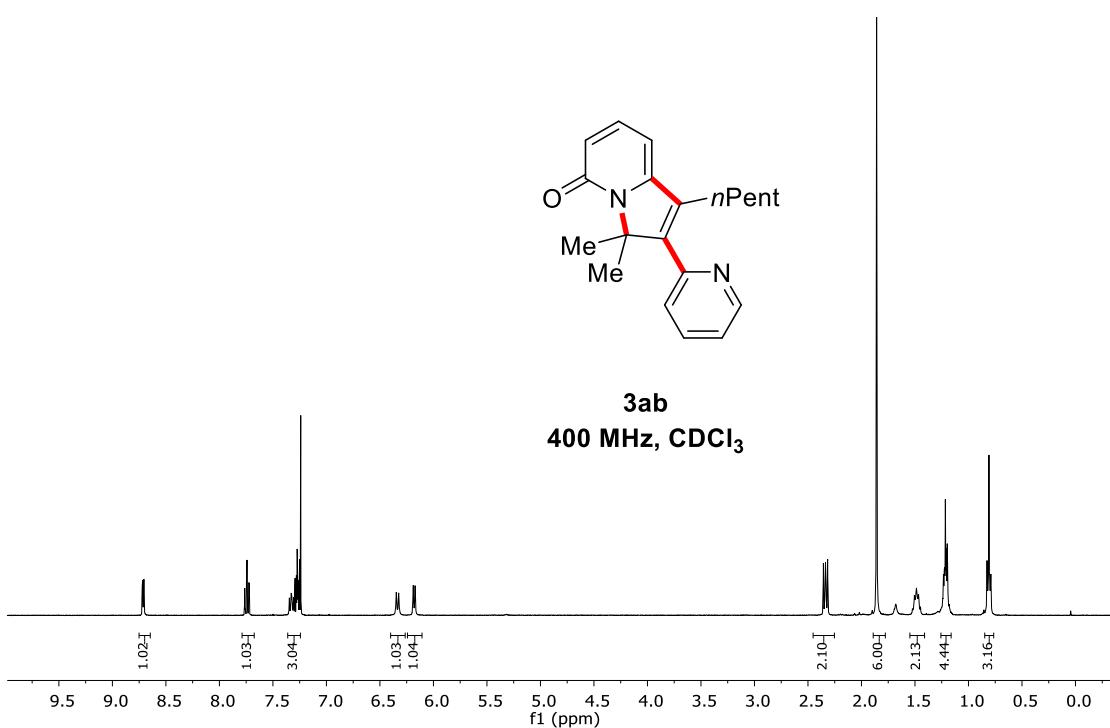
¹H chemical shifts (δ, ppm): 157.68, 152.10, 150.87, 149.26, 149.23, 137.08, 135.64, 132.79, 131.41, 129.20, 129.01, 128.76, 125.66, 124.10, 122.66, 99.04, 76.12, 21.02.

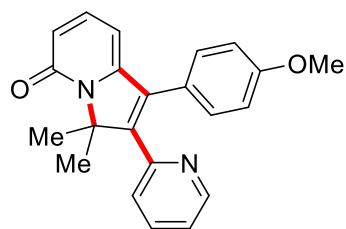




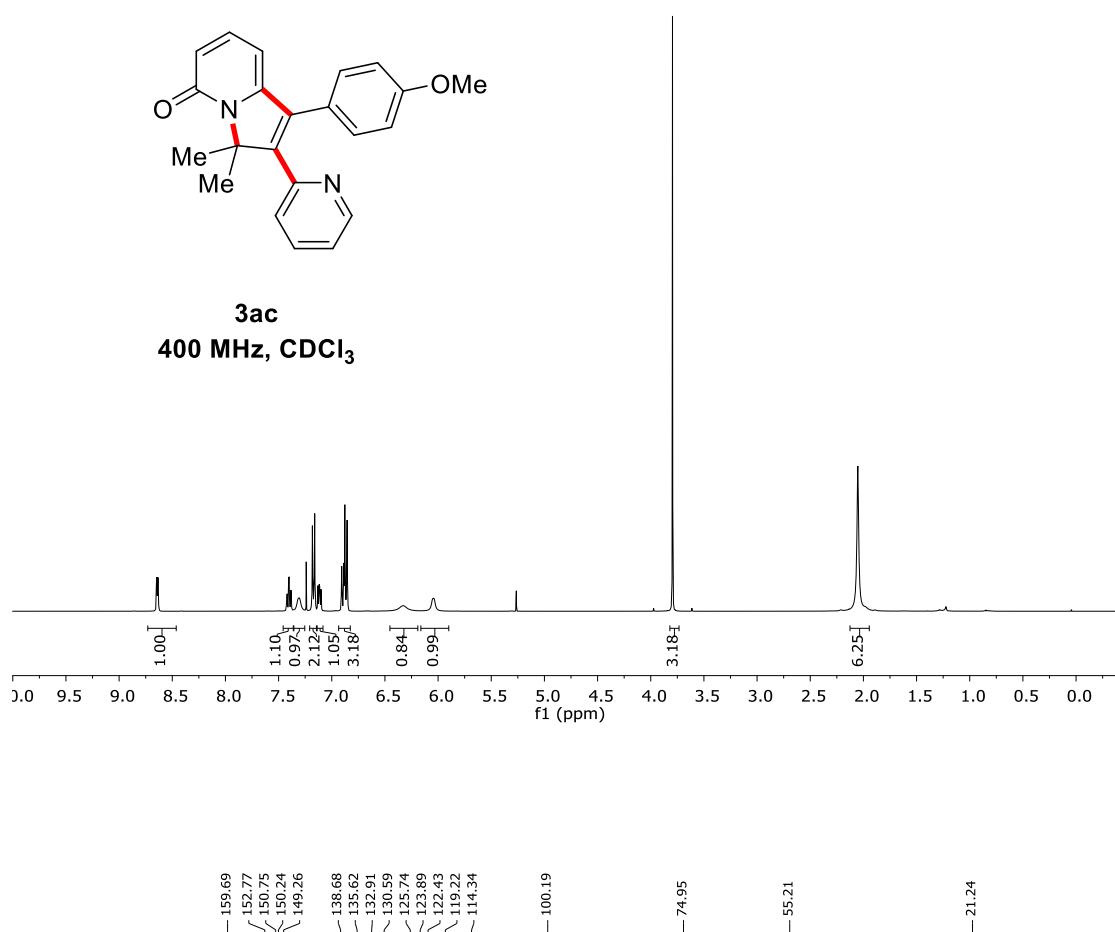
158.99
 155.24
 155.21
 151.33
 ~149.50
 ~146.44
 ~135.87
 132.77
 130.75
 129.31
 129.24
 129.21
 125.82
 123.29
 ~116.47
 -102.26
 -99.76
 -21.01



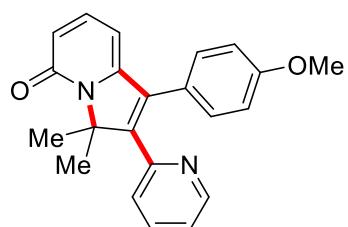




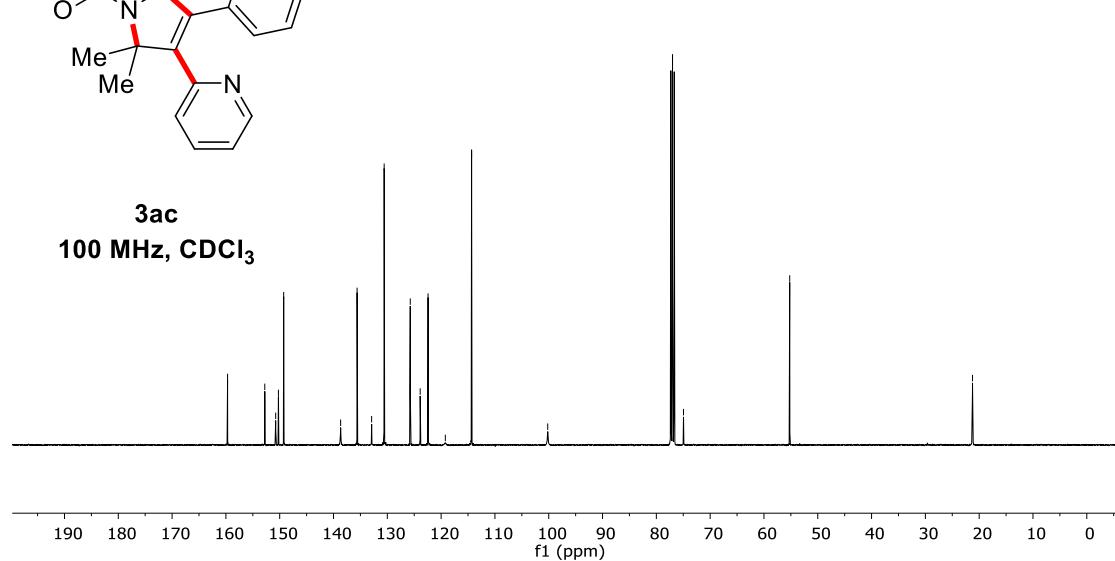
3ac
400 MHz, CDCl_3

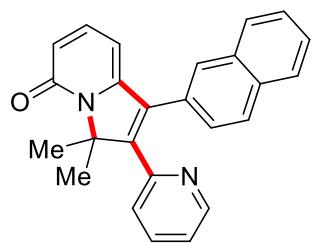


Chemical shifts (δ) for ^{13}C NMR (ppm):
 159.69, 152.77, 150.75, 150.24, 149.26, 138.68, 135.62, 132.91, 130.59, 125.74, 123.89, 122.43, 119.22, 114.34, 100.19, 74.95, 55.21, 21.24

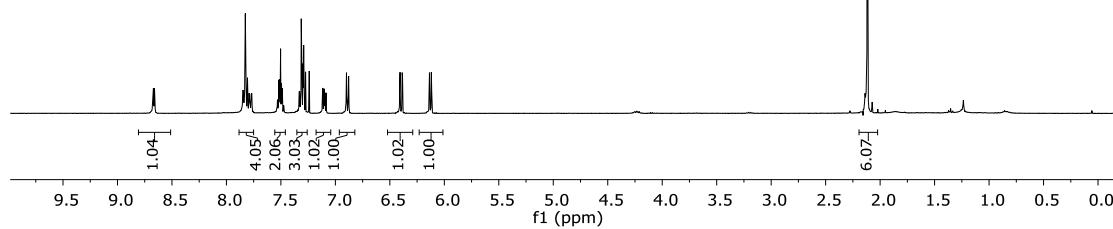


3ac
100 MHz, CDCl_3

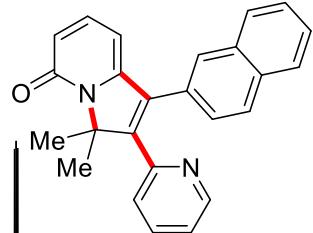




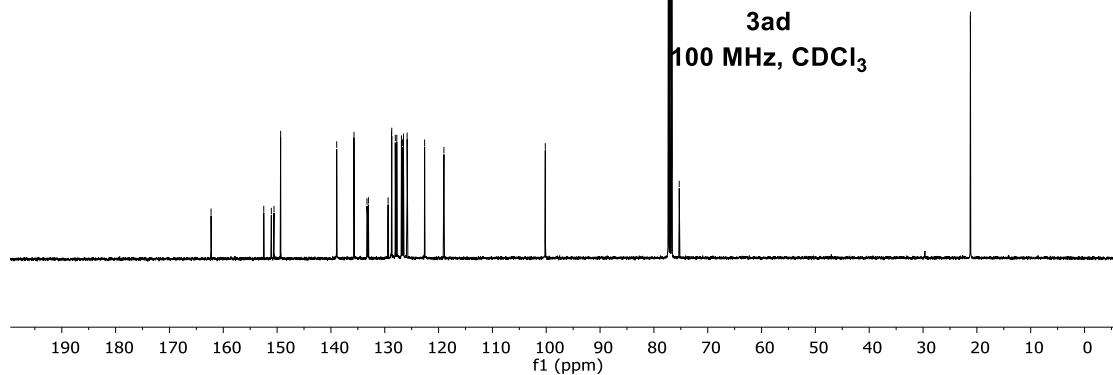
3ad
400 MHz, CDCl₃

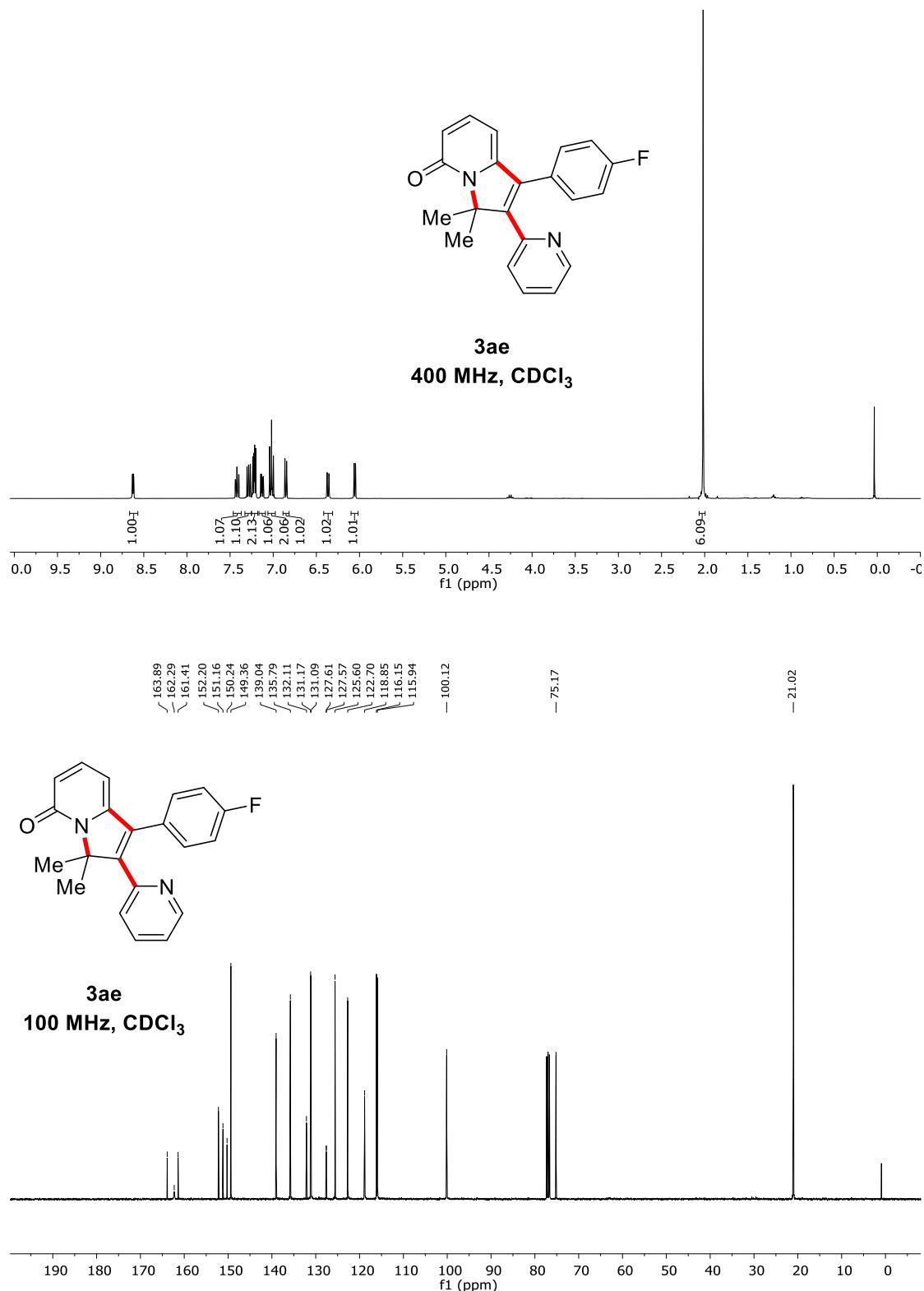


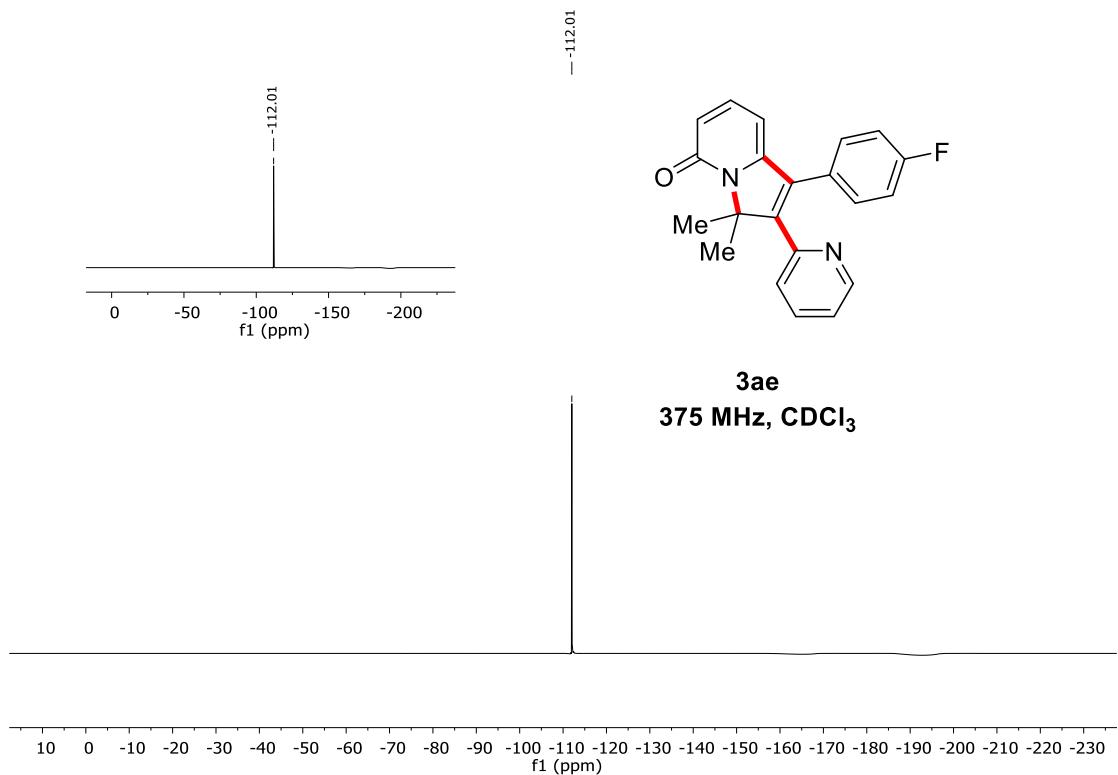
— 162.27
 — 152.48
 — 151.07
 — 150.58
 — 149.34
 — 138.93
 — 135.72
 — 133.31
 — 133.19
 — 133.04
 — 129.38
 — 128.74
 — 128.70
 — 128.04
 — 127.76
 — 126.90
 — 126.73
 — 126.53
 — 125.84
 — 122.60
 — 119.00
 — 100.18
 — 75.30
 — 21.20

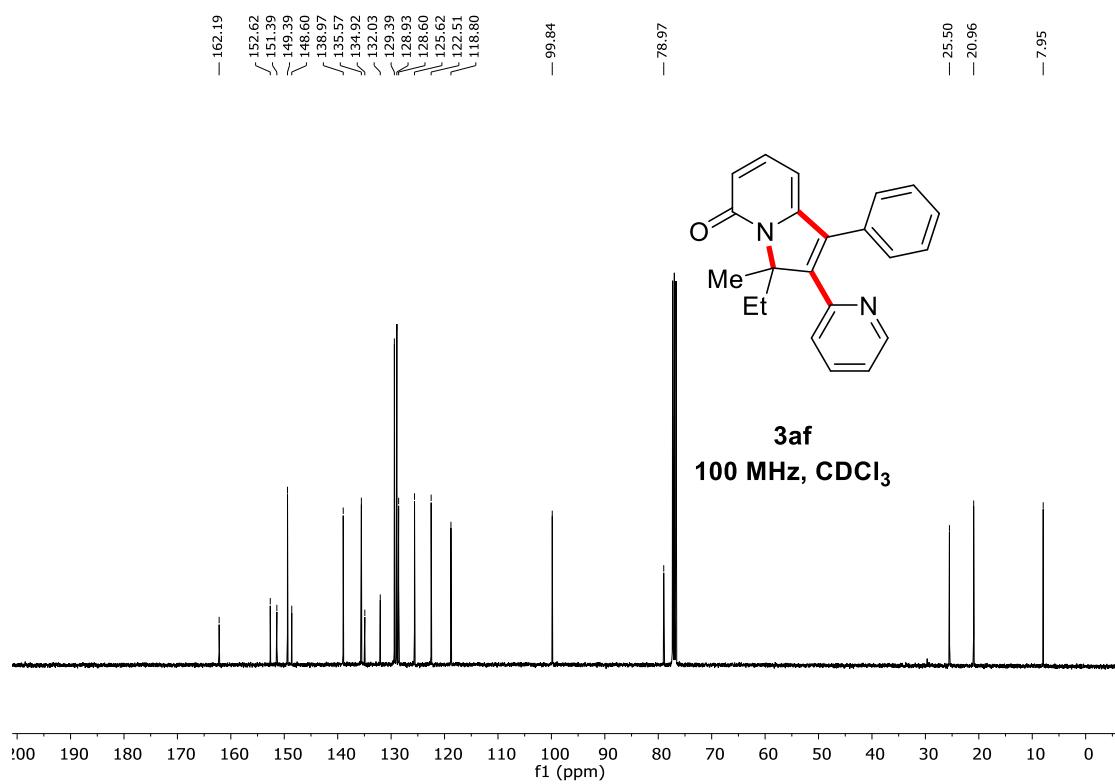
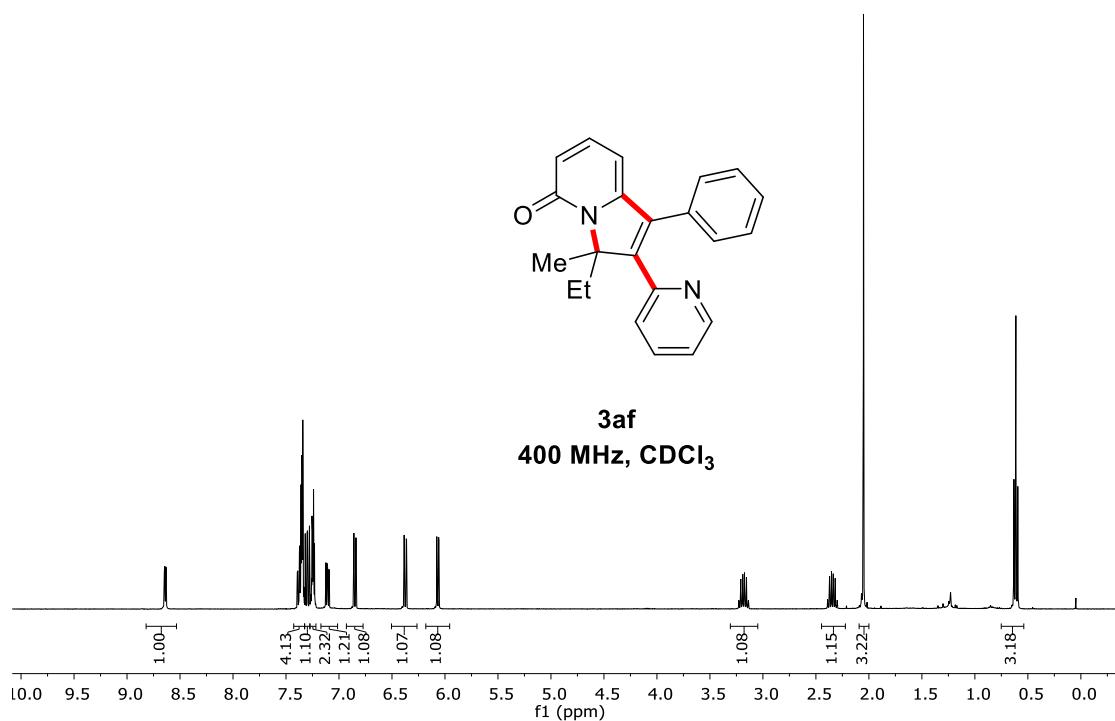


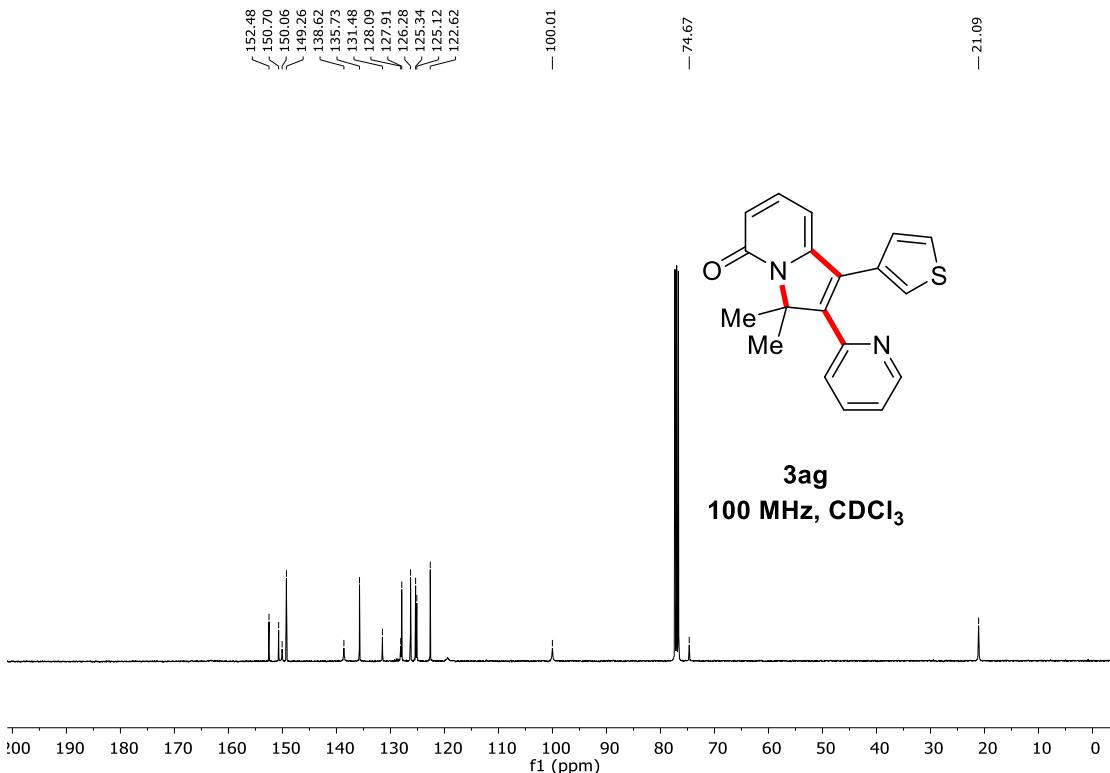
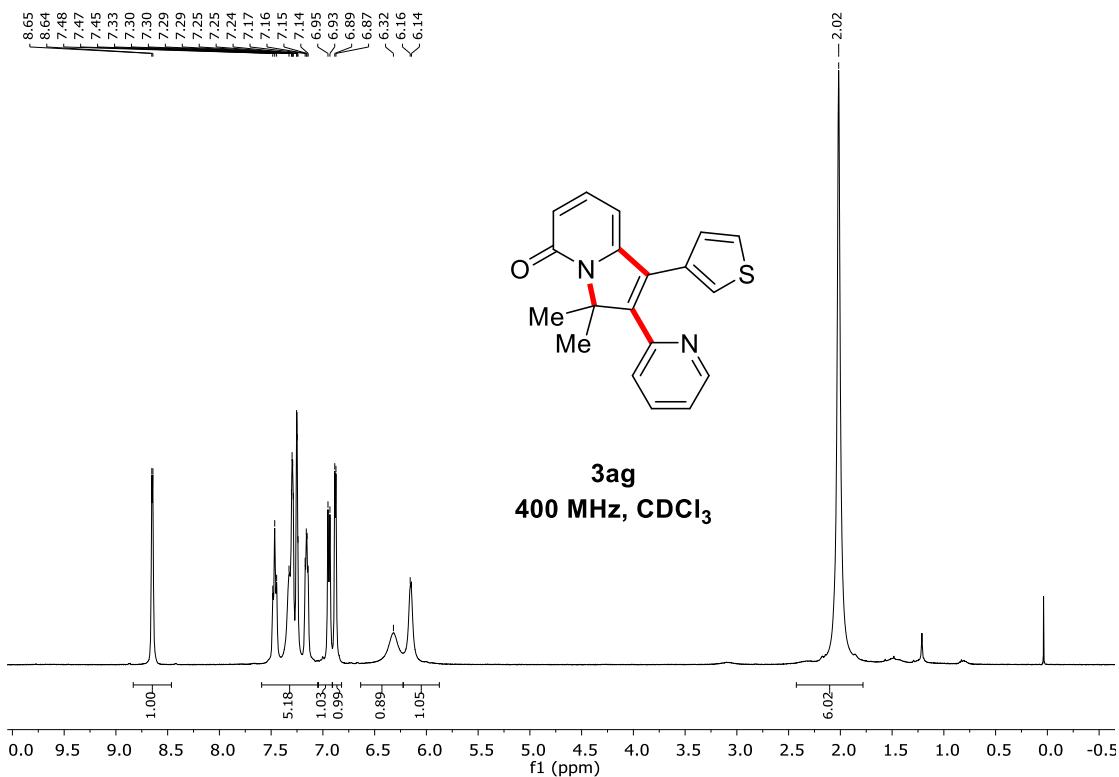
3ad
100 MHz, CDCl₃

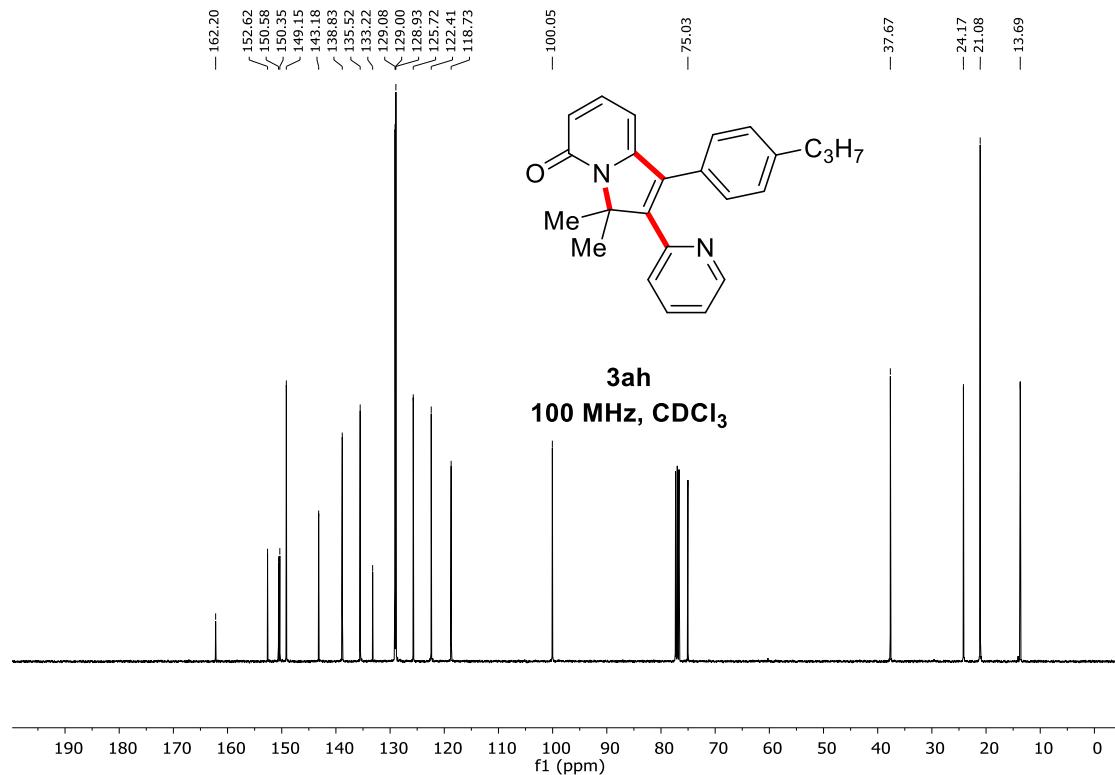
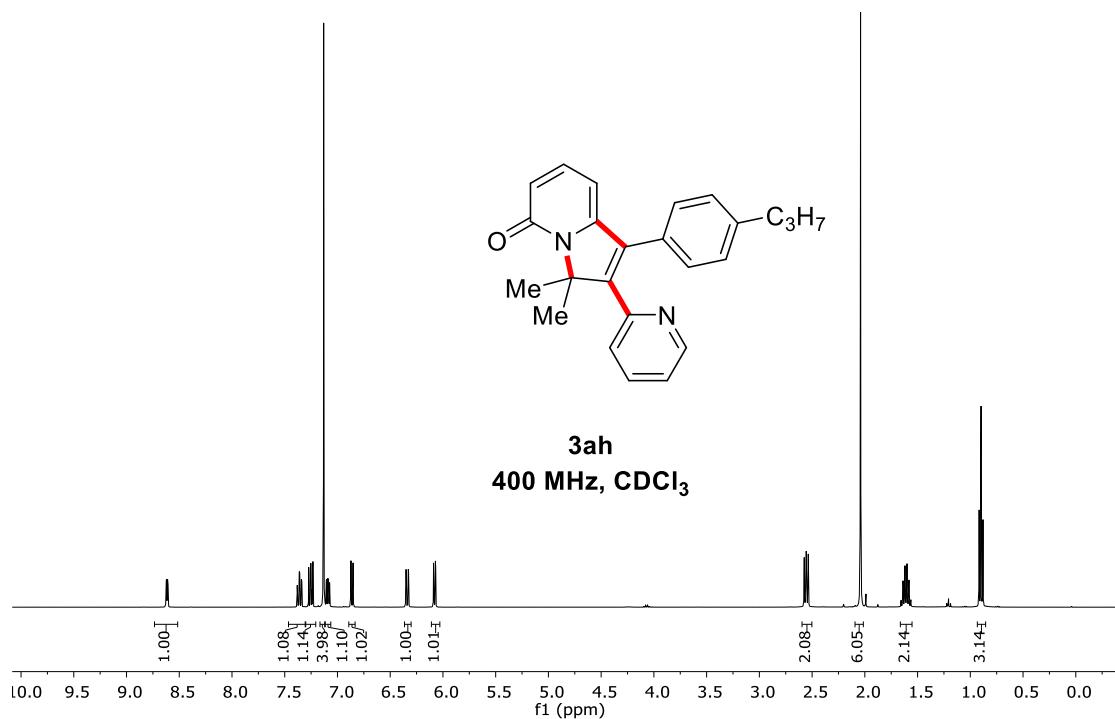


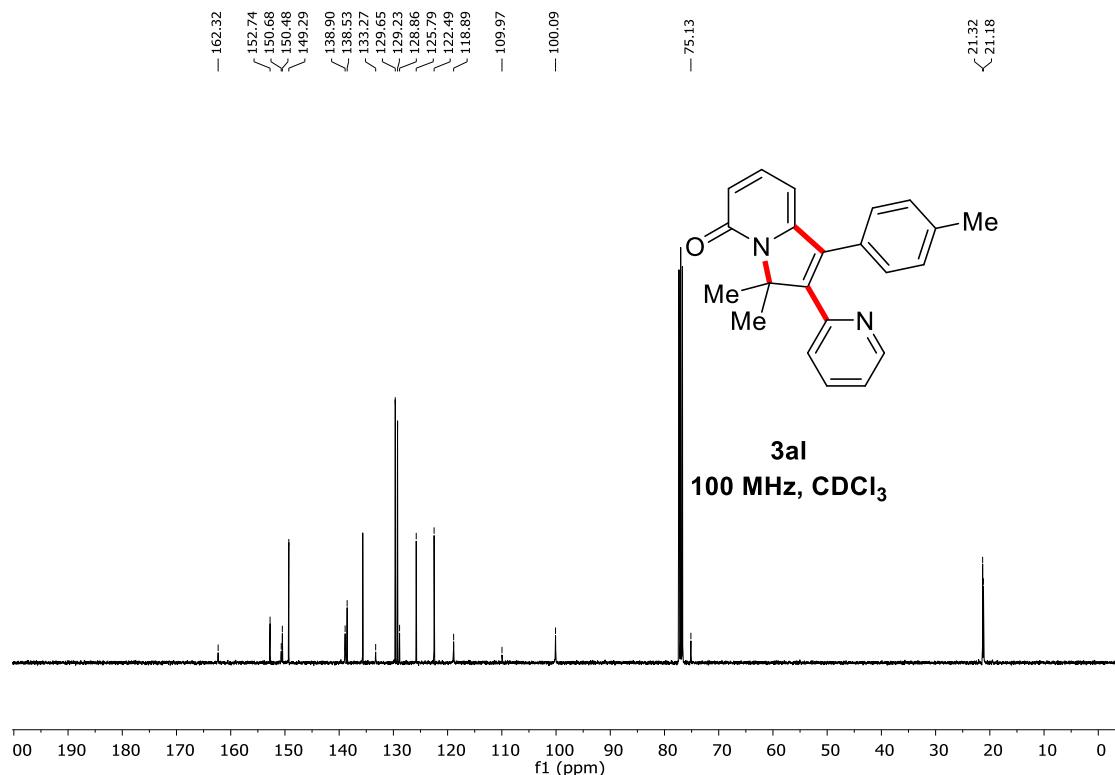
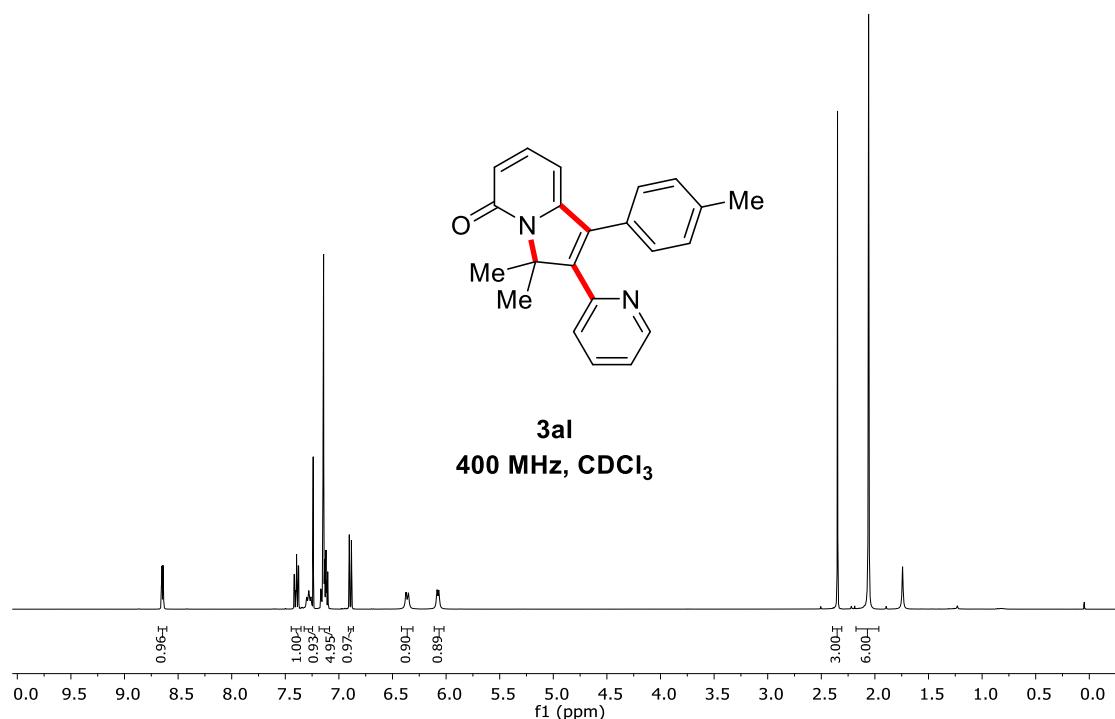


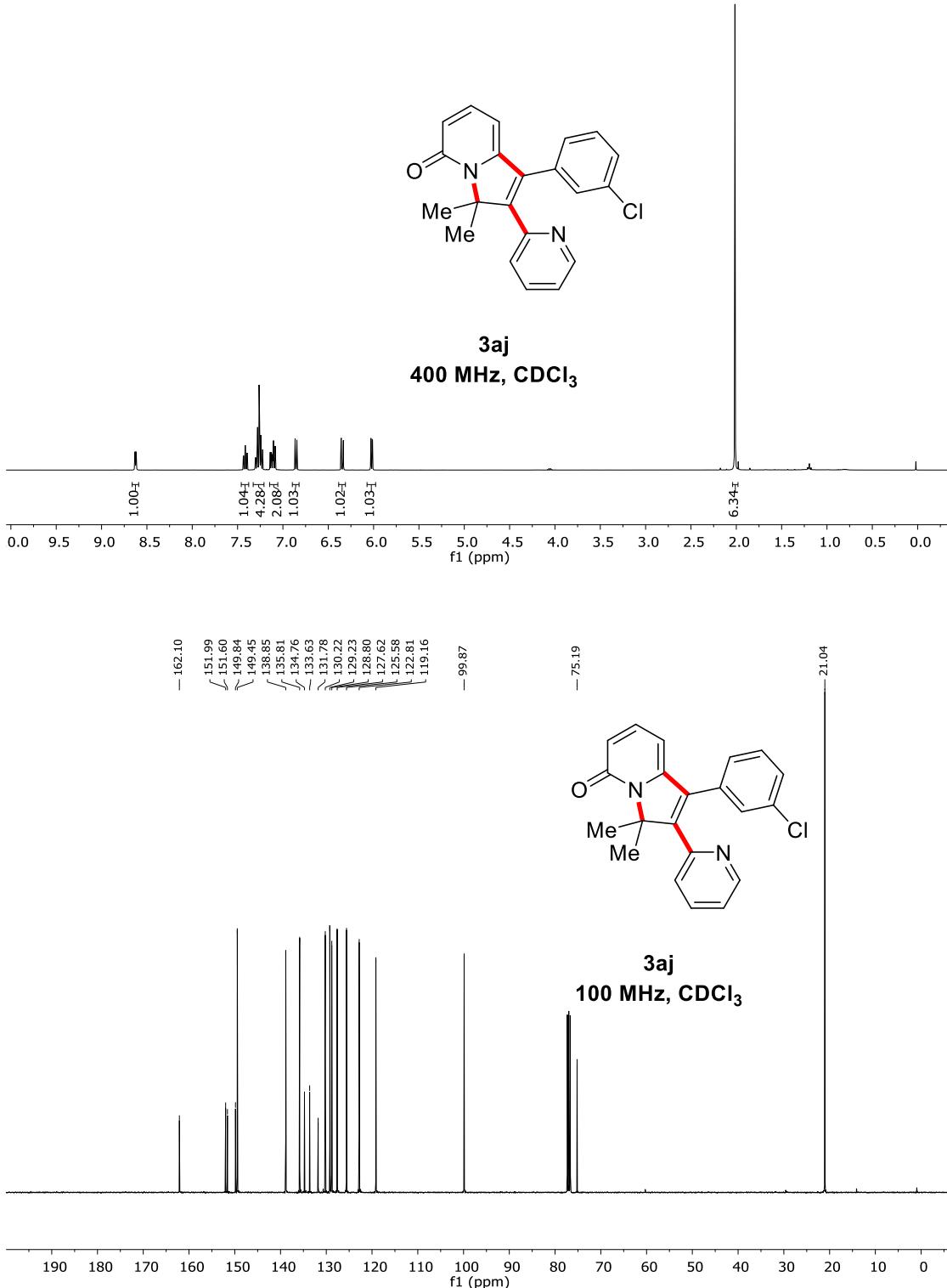


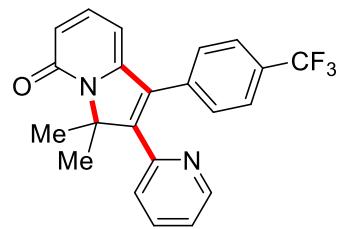




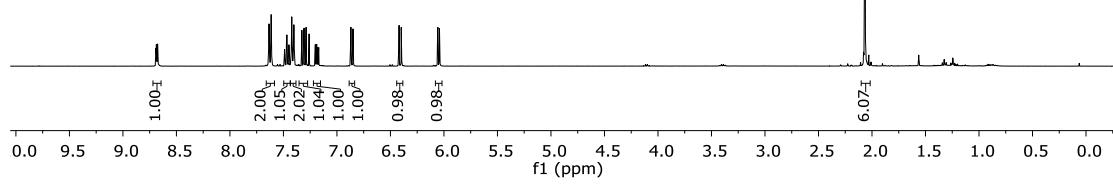




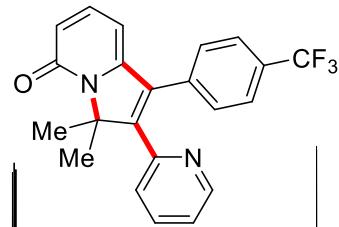




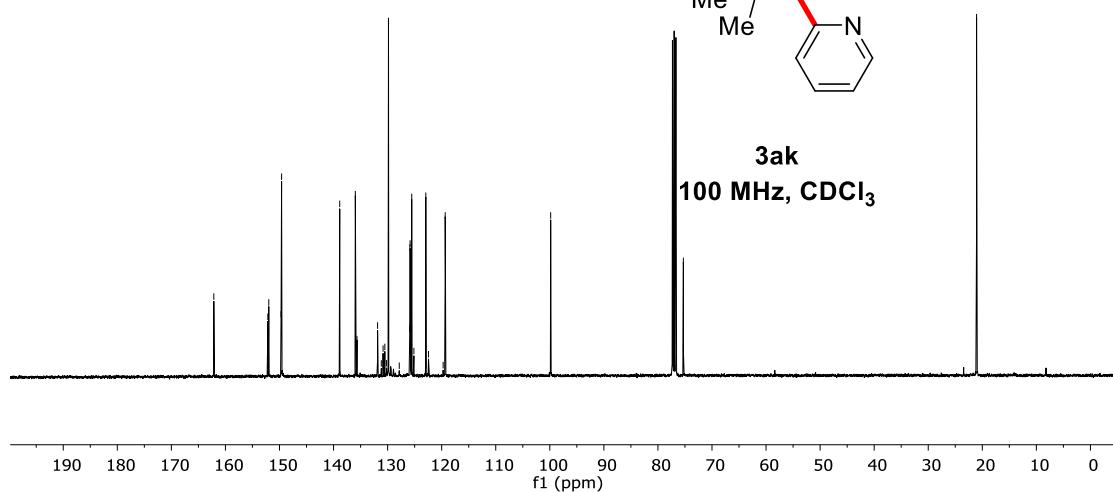
3ak
400 MHz, CDCl₃

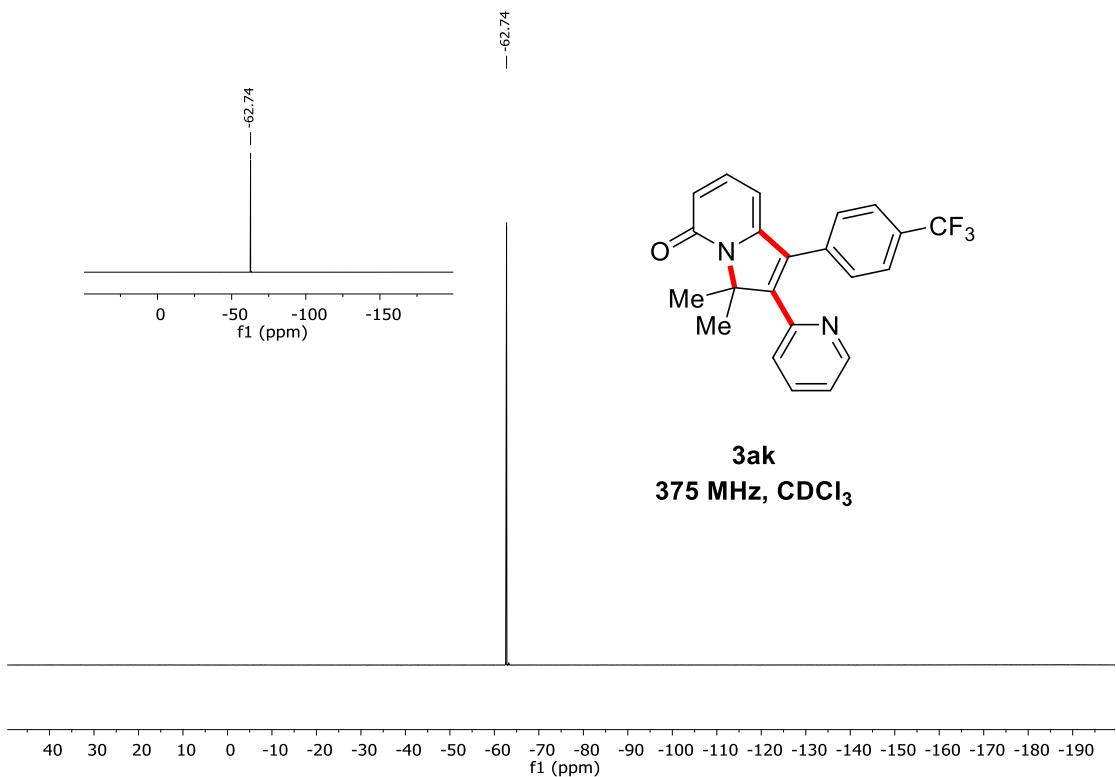


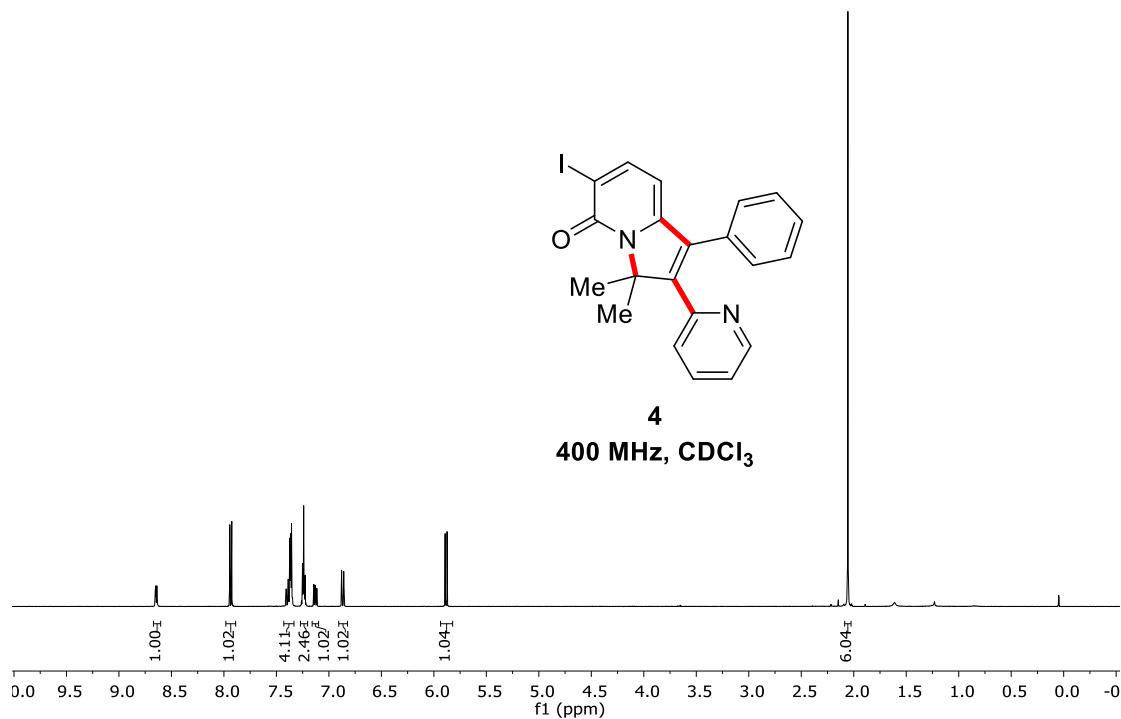
— 162.15 — 152.16 — 151.98 — 149.71
 — 149.61 — 138.86 — 135.67
 — 135.97 — 131.86 — 131.17
 — 130.84 — 130.52 — 130.19
 — 129.84 — 125.91 — 125.88
 — 125.84 — 125.80 — 125.54
 — 125.14 — 122.93 — 122.43
 — 122.43 — 119.73 — 119.35
 — 119.35 — 99.84 — 75.29
 — 21.06



3ak
100 MHz, CDCl₃







-158.66
 -152.16
 -151.40
 -150.82
 -149.35
 -147.87
 -135.69
 -133.00
 -131.53
 -129.29
 -129.06
 -128.81
 -125.76
 -122.72

 -101.27
 -91.37
 -76.48

 -21.05

