Supporting Information

Versatile Cp*Co(III)(LX) Catalyst System for Selective Intramolecular C−H Amidation Reactions

Jia Lee,[†,‡,§] Jeonghyo Lee,[†,‡,§] Hoimin Jung,[†,‡] Dongwook Kim,[‡,†] Juhyeon Park,[†,‡] and Sukbok Chang*[,‡,†]

† Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, South Korea

‡ Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 34141, South Korea

[§] *These authors contributed equally.*

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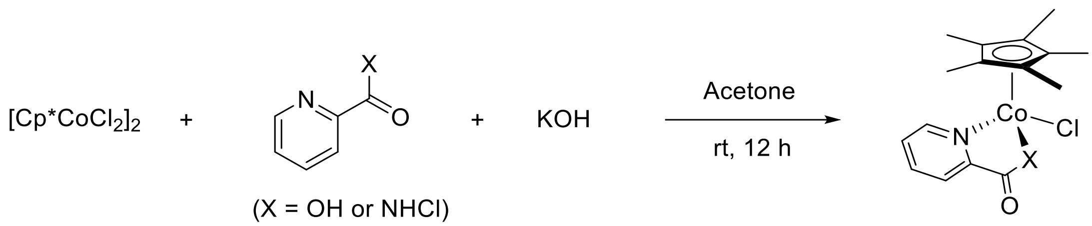
Crystallographic Data

I. General Methods

Unless otherwise stated, all commercial reagents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by UV light (254 nm). Silica-gel chromatography was performed using a Combi*Flash*® R_f^+ system with Redi*Sep*® R_f Silica columns (230 - 400 mesh) using a proper eluent. ^{1}H NMR spectra were recorded on Agilent Technologies DD2 (600 MHz) or Bruker AVHD-400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak. The following abbreviations were used to describe peak splitting patterns when appropriate: s (singlet), d (doublet), t (triplet), m (multiplet). Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR spectra were obtained on Agilent Technologies DD2 (150 MHz) or Bruker AVHD-400 (400 MHz) or Bruker DRX800 (200 MHz) at the Korea Basic Science Institute in Ochang and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the appropriate solvent peak. ^{19}F NMR was recorded on Agilent Technologies Bruker AVHD-400 (376 MHz). Infrared (IR) spectra were recorded on Bruker Alpha FT-IR Spectrometer. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were obtained from KAIST Research Analysis Center (KARA, Daejeon) by using the ESI method and the Korea Basic Science Institute (Daegu) by using EI or FAB method. Melting point was measured with Buchi Melting Point M-565. X-ray diffraction data was collected on a Bruker D8 QUEST APEX III coated with Paraton-*N* oil under a stream of N_2 (g) at 173 K.

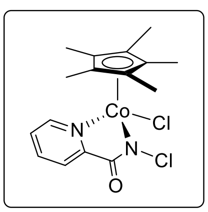
II. Procedures for the Preparation of Cp*Metal(III) Complexes

II - 1. Preparation of Cp*Co(III) Complexes (Co1 and Co9)



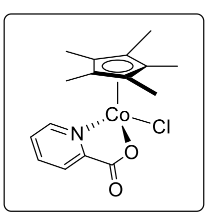
$[Cp^*CoCl_2]_2$ was prepared according to the literature procedure.[1] To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added $[Cp^*CoCl_2]_2$ (0.50 mmol, 0.50 equiv), ligand (1.0 mmol), potassium hydroxide (2.0 mmol, 2.0 equiv), and acetone (20 mL) under atmospheric conditions. The reaction mixture was stirred for 12 h at r.t., and then filtered through a pad of celite with dichloromethane (15 mL x 3). The solvent was removed under the reduced pressure and the residual solid was washed with hexane (15 mL x 3) and filtered by membrane filter. Residue was collected and dried under reduced pressure to afford desired Cp*Co(III) complexes.

_N_-Chloro-picolinamide bound Cp*Co(III) complex (**Co1**)



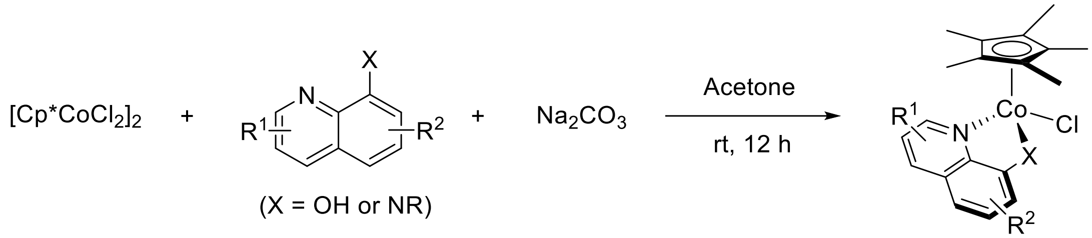
The corresponding ligand (*N*-chloro-picolinamide) was prepared according to the literature procedure.[2] Dichloromethane was used as solvent. Black solid (0.29 g, 76 %); **IR** (cm^{-1}) 1627, 1596, 1562, 1466, 1431, 1375, 1326, 1281, 1094, 1015, 802, 760, 672; **High Resolution MS** (ESI): Calculated for $NaC_{16}H_{19}Cl_2CoN_2O$ $[M+Na]^+$: 407.0104, found: 407.0097.

2-Picolinic acid bound Cp*Co(III) complex (**Co9**)



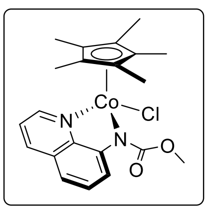
Dark blue solid (0.15 g, 43 %); **IR** (cm^{-1}) 1654, 1599, 1467, 1440, 1340, 1249, 1160, 1024, 848, 833, 782, 694; **High Resolution MS** (ESI): Calculated for $NaC_{16}H_{19}ClCoNO_2$ $[M+Na]^+$: 374.0334, found: 374.0328; **X-ray crystal structure** is available in the *Appendix II.*

II - 2. Preparation of Cp*Co(III) Complexes (Co2 to Co8)



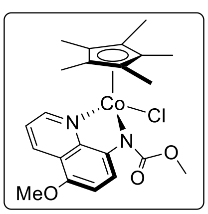
$[Cp^*CoCl_2]_2$ was prepared according to the literature procedure.[1] To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added $[Cp^*CoCl_2]_2$ (0.25 mmol, 0.50 equiv), ligand (0.50 mmol), sodium carbonate (2.0 mmol, 4.0 equiv), and acetone (10 mL) under atmospheric conditions. The reaction mixture was stirred for 12 h at r.t., and then filtered through a pad of celite with dichloromethane (15 mL x 3). The solvent was removed under the reduced pressure and the residual solid was washed with hexane (15 mL x 3) and filtered by membrane filter. Residue was collected and dried under reduced pressure to afford desired Cp*Co(III) complexes.

8-{*N*-(Methyloxycarbonyl)amino}quinoline bound Cp*Co(III) complex (**Co2**)



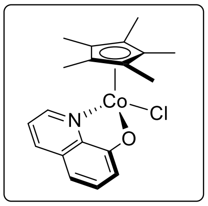
The corresponding ligand [8-{*N*-(methyloxycarbonyl)amino}quinoline] was prepared from quinoline *N*-oxide according to the literature procedure.[3] Dark green solid (82 mg, 38 %); **IR** (cm^{-1}) 2920, 2851, 1736, 1647, 1530, 1436, 1378, 1325, 827; **High Resolution MS** (FAB): Calculated for $C_{21}H_{24}CoN_2O_2$ [M-Cl]$^+$: 395.1170, Found: 395.1169; **X-ray crystal structure** is available in the *Appendix II*.

5-Methoxy-8-{*N*-(methyloxycarbonyl)amino}quinoline bound Cp*Co(III) complex (**Co3**)



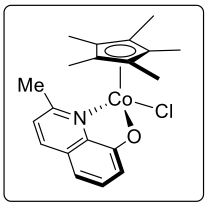
The corresponding ligand [5-methoxy-8-{*N*-(methyloxycarbonyl)amino}quinoline] was prepared from quinoline *N*-oxide according to the literature procedure.[3] Black solid (0.11 g, 49 %); **IR** (cm^{-1}) 1723, 1638, 1528, 1426, 1325, 1220, 1087, 878, 834, 777, 701; **High Resolution MS** (ESI): Calculated for $NaC_{22}H_{26}ClCoN_2O_3$ [M+Na]$^+$: 483.0862, found: 483.0860; **X-ray crystal structure** is available in the *Appendix II*.

8-Quinolinol bound Cp*Co(III) complex (Co4)



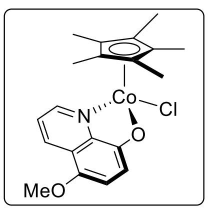
Dark green solid (0.11 g, 57%); **IR** (cm^{-1}) 1567, 1494, 1459, 1368, 1319, 1284, 1269, 1107, 821, 783, 748, 737; **High Resolution MS** (FAB): Calculated for $C_{19}H_{21}CoNO$ $[M-Cl]^+$: 338.0955, Found: 338.0957.

2-Methyl-8-quinolinol bound Cp*Co(III) complex (Co5)



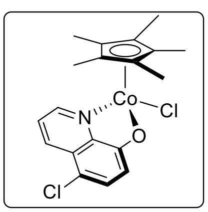
Dark green solid (97 mg, 50 %); **IR** (cm^{-1}) 1558, 1499, 1459, 1421, 1370, 1328, 1282, 1107, 1014, 861, 840, 755; **High Resolution MS** (FAB): Calculated for $C_{20}H_{23}CoNO$ $[M-Cl]^+$: 352.1112, Found: 352.1110; **X-ray crystal structure** is available in the *Appendix II*.

5-Methoxy-8-quinolinol bound Cp*Co(III) complex (Co6)



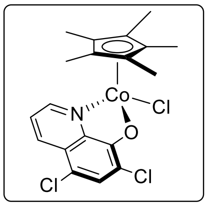
5-Methoxyquinolin-8-ol was prepared from 3-amino-4-methoxyphenol according to the literature procedure.[4] Black solid (0.11 g, 54 %); **IR** (cm^{-1}) 1570, 1528, 1460, 1403, 1372, 1318, 1268, 1213, 1144, 1103, 813, 777, 747; **High Resolution MS** (FAB): Calculated for $C_{20}H_{23}CoNO_2$ $[M-Cl]^+$: 368.1061, Found: 368.1064.

5-Chloro-8-quinolinol bound Cp*Co(III) complex (Co7)



Dark green solid (0.13 g, 66 %); **IR** (cm^{-1}) 1563, 1493, 1454, 1359, 1321, 1085, 1044, 1015, 965, 820, 780, 743, 673, 543; **High Resolution MS** (FAB): Calculated for $C_{19}H_{20}ClCoNO$ $[M-Cl]^+$: 372.0565, Found: 372.0567; **X-ray crystal structure** is available in the *Appendix II*.

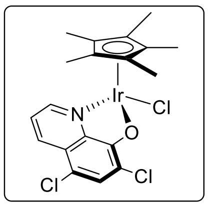
5,7-Dichloro-8-quinolinol bound Cp*Co(III) complex (Co8)



Dark green solid (0.12 g, 55 %); **IR** (cm^{-1}) 1553, 1486, 1446, 1361, 1247, 1219, 1203, 1013, 970, 887, 825, 745, 657; **High Resolution MS** (FAB): Calculated for $C_{19}H_{19}Cl_2CoNO$ $[M-Cl]^+$: 406.0176, Found: 406.0173; **X-ray crystal structure** is available in the *Appendix II*.

II - 3. Preparation of Cp*Ir(III) Complex

5,7-Dichloro-8-quinolinol bound Cp*Ir(III) complex (Ir1)



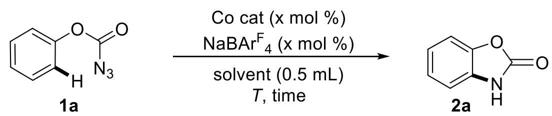
Ir1 was Prepared according to the literature procedure and ^1H, ^{13}C NMR spectral data are matched with the reported ones.[5] **X-ray crystal structure** is available in the *Appendix II*.

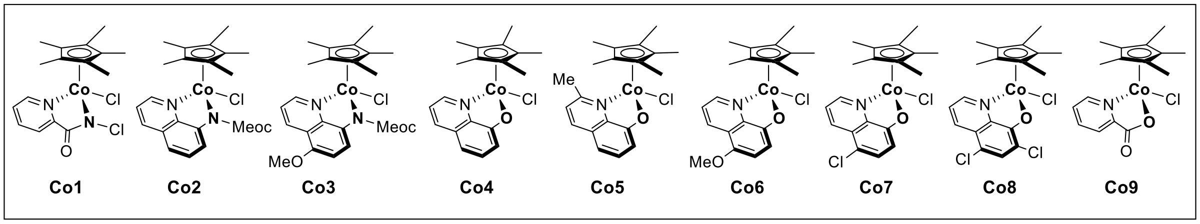
III. Procedures for the Optimization Study

III – 1. Procedures for the Optimization of Co-Catalyzed C(sp^2)−H Amidation of Azidoformate

To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added the indicated amount of Co catalyst (**Co1** to **Co9**), sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (NaBAr$^F_4$), solvent and the reaction mixture was stirred for 1 min at r.t. To the reaction mixture was added phenyl azidoformate (**1a**) and then sealed. The reaction mixture was vigorously stirred in a pre-heated heating block at the indicated temperature for the indicated time, filtered through a pad of silica with EtOAc (10 mL × 5) and concentrated under reduced pressure to afford crude product **2a**.

Table S1. Optimization for Cp*Co(III)(LX)-catalyzed C(sp^2)−H amidation of phenyl azidoformate[a]





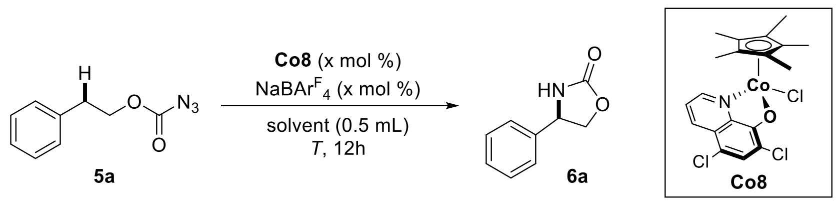
Entry	Catalyst (x mol %)	solvent	*T* (°C)	time (h)	yield (%)
1	$[Cp^*CoCl_2]_2$ (2.5)	HFIP	40	12	< 5
2	Co1 (5)	HFIP	40	12	< 5
3	Co2 (5)	HFIP	40	12	< 5
4	Co3 (5)	HFIP	40	12	< 5
5	Co4 (5)	HFIP	40	12	6
6	Co5 (5)	HFIP	40	12	< 5
7	Co6 (5)	HFIP	40	12	< 5
8	Co7 (5)	HFIP	40	12	17
9	**Co8 (5)**	**HFIP**	**40**	**12**	**99 (93)**
10	Co9 (5)	HFIP	40	12	11
11	Co8 (5)	CHCl3	40	12	54
12	Co8 (5)	1,2-DCE	40	12	73
13	Co8 (5)	DCM	40	12	76
14	Co8 (5)	acetone	40	12	< 5
15	Co8 (5)	EtOAc	40	12	< 5
16	Co8 (5)	TFE	40	12	65
17	Co8 (2)	HFIP	40	12	74
18	Co8 (5)	HFIP	25	12	57
19[b]	Co8 (2)	HFIP	60	48	87
20[c]	Co8 (0.1)	HFIP	60	84	12

[a]**1a** (0.1 mmol), Co catalyst (x mol %), and NaBAr$^F_4$ (x mol %) in solvent (0.5 mL) at *T* (°C) for time (h). Yields were determined by ^{1}H NMR analysis of the crude reaction mixture (internal standard: 1,1,2,2-tetrachloroethane). Isolated yields are presented in the parenthesis. [b]Large scale reaction: **1a** (5 mmol), **Co8** (2 mol %), and NaBAr$^F_4$ (2 mol %) in HFIP (5 mL) at 60 °C for 48 h. [c]Reaction for measuring a catalytic turnover number of **Co8**: **1a** (1 mmol), **Co8** (0.1 mol %), and NaBAr$^F_4$ (0.1 mol %) in HFIP (2 mL) at 60 °C for 84 h.

III – 2. Procedures for the Optimization of Co-Catalyzed C(sp^3)−H Amidation of Azidoformate

To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added the indicated amount of Co catalyst (**Co8**), $NaBAr^F{}_4$, solvent and the reaction mixture was stirred for 1 min at r.t. To the reaction mixture was added phenethyl azidoformate (**5a**) and then sealed. The reaction mixture was vigorously stirred in a pre-heated heating block at the indicated temperature for the indicated time, filtered through a pad of silica with EtOAc (10 mL × 5) and concentrated under reduced pressure to afford crude product **6a**.

Table S2. Optimization for **Co8**-catalyzed C(sp^3)−H amidation of phenethyl azidoformate[a]

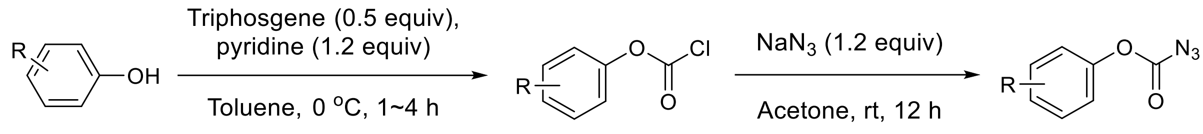


Entry	Co8 (x mol %)	solvent	*T* (°C)	Conversion (%)	yield (%)
1	5	1,2-DCE	60	70	59
2	5	$CHCl_3$	60	59	56
3	5	DCM	60	65	50
4	5	acetone	60	1	N.D.
5	5	EtOAc	60	1	N.D.
6	5	TFE	60	93	93
7	5	HFIP	60	>99	99 (96)
8	**2**	**HFIP**	**60**	**97**	**97 (96)**
9	1	HFIP	60	70	70
10	**5**	**HFIP**	**40**	**95**	**95**
11	2	HFIP	40	75	72
12	1	HFIP	40	40	40
13[b]	2	HFIP	60	40	90

[a]Reaction conditions: **5a** (0.1 mmol), **Co8** (x mol %), and $NaBAr^F{}_4$ (x mol %) in HFIP (0.5 mL) at *T* (°C) for 12 h. Yields were determined by ^1H NMR analysis of the crude reaction mixture (internal stand ard: 1,1,2,2-tetrachloroethane). Isolated yields are presented in the parenthesis. [b]Large scale reaction: **5a** (5 mmol), **Co8** (2 mol %), and $NaBAr^F{}_4$ (2 mol %) in HFIP (5 mL) at 60 °C for 48 h.

IV. Procedures for the Preparation of Starting Materials

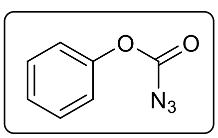
IV – 1. Preparation of Phenyl Azidoformates



1

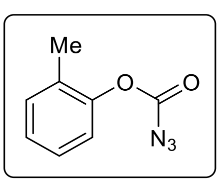
To a solution of triphosgene (5 mmol, 0.5 equiv) in toluene (50 mL) was added pyridine (12 mmol, 1.2 equiv) dropwise at 0 °C. Then, phenol (10 mmol) was added at 0 °C in a dropwise fashion. The reaction was allowed to stir at r.t. until reaction completion (1 to 4 h). The reaction mixture was washed with water (50 mL x 2), extracted with EtOAc (50 mL x 2), dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude chloroformate products. To a solution of unpurified chloroformate, sodium azide (12 mmol, 1.2 equiv) was added in acetone (50 mL). After stirring for 12 h at r.t., the reaction mixture was filtered through a pad of celite with dichloromethane (50 mL), concentrated under reduced pressure and purified by flash column chromatography to yield phenyl azidoformate **1** (eluent: *n*-hexane/EtOAc = 4:1 to 3:1).

Phenyl azidoformate (1a)[6]



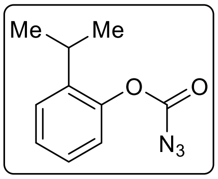
Prepared from 4 mmol of commercially available phenyl chloroformate. Colorless oil (0.51 g, 78 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 1H), 7.22 – 7.16 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.5, 150.8, 129.8, 126.8, 121.0; **High Resolution MS** (EI): Calculated for $C_7H_5N_3O_2$ $[M]^+$: 163.0382, Found: 163.0382.

***o*-Tolyl azidoformate (1b)**[6]



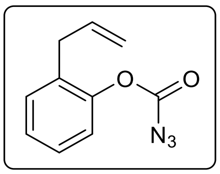
Colorless oil (1.2 g, 71 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 3H), 7.11 (d, *J* = 7.9, 1H), 2.25 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.3, 149.4, 131.5, 130.0, 127.3, 127.0, 121.4, 16.0; **High Resolution MS** (EI): Calculated for $C_8H_7N_3O_2$ $[M]^+$: 177.0538, Found: 177.0536.

2-Isopropylphenyl azidoformate (1c)[6]



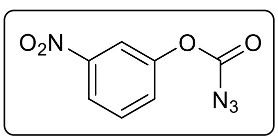
Colorless oil (0.94 g, 46 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.32 – 7.20 (m, 2H), 7.10 (m, 1H), 3.09 (hept, *J* = 7.0, 6.1 Hz, 1H), 1.24 (s, 3H), 1.23 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) 156.7, 148.2, 140.1, 127.3, 127.2, 127.0, 121.7, 27.5, 23.1; **High Resolution MS** (EI): Calculated for $C_{10}H_{11}N_3O_2$ $[M]^+$: 205.0851, Found: 205.0851.

2-Allylphenyl azidoformate (1d)[6]



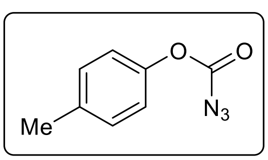
Colorless oil (0.51 g, 25 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 3H), 7.23 – 7.11 (m, 1H), 5.94 (ddt, *J* = 16.8, 10.3, 6.6 Hz, 1H), 5.14 (m, 1H), 5.12 (dq, *J* = 11.1, 1.6 Hz, 1H), 3.39 (dt, *J* = 6.5, 1.6 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) 156.3, 149.0, 135.5, 131.9, 130.8, 127.8, 127.1, 121.9, 116.7, 34.5; **High Resolution MS** (EI): Calculated for $C_{10}H_9N_3O_2$ $[M]^+$: 203.0695, Found: 203.0692.

3-Nitrophenyl azidoformate (1e)



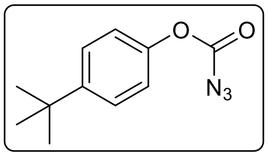
White solid (0.29 g, 28 %, 5 mmol scale); **m.p.** 99 – 101 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.18 (ddd, *J* = 8.2, 2.1, 1.1 Hz, 1H), 8.11 (t, *J* = 2.2 Hz, 1H), 7.61 (t, *J* = 8.2 Hz, 1H), 7.56 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.1, 150.8, 149.0, 130.5, 127.4, 121.7, 117.0; **IR** (cm^{-1}) 3105, 2212, 2175, 1742, 1727, 1529, 1347, 1272, 1221, 1096, 956, 883, 820, 802, 738, 725, 681, 660; **High Resolution MS** (EI): Calculated for $C_7H_4N_4O_4$ $[M]^+$: 208.0233, found: 208.0235.

***p*-Tolyl azidoformate (1f)**[6]



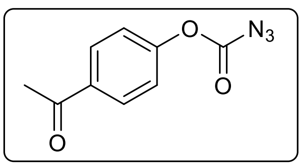
Colorless oil (1.5 g, 87 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2H), 7.13 – 6.98 (m, 2H), 2.36 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) 156.6, 148.6, 136.5, 130.3, 120.7, 21.0; **High Resolution MS** (EI): Calculated for $C_8H_7N_3O_2$ $[M]^+$: 177.0538, Found: 177.0540.

4-(*tert*-Butyl)phenyl azidoformate (1g)[6]



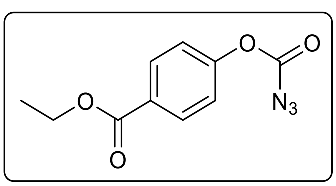
Colorless oil (0.91 g, 75 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 7.16 – 7.06 (m, 2H), 1.35 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.5, 149.6, 148.4, 126.6, 120.3, 34.6, 31.4; **IR** (cm^{-1}) 2962, 2950, 2942, 2157, 1737, 1508, 1196, 1105, 1101, 954, 838, 737; **High Resolution MS** (EI): Calculated for $NaC_{11}H_{13}N_3O_2$ $[M+Na]^+$: 242.0905, Found: 242.0905.

4-Acetylphenyl azidoformate (1h)



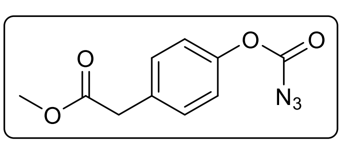
White solid (0.10 g, 10 %, 5 mmol scale); **m.p.** 79 – 81 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 2.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 156.1, 154.1, 135.5, 130.3, 121.2, 26.8; **IR** (cm^{-1}) 3068, 2921, 2160, 1750, 1735, 1679, 1590, 1503, 1360, 1250, 1211, 1134, 1101, 1010, 959, 932, 889, 868, 818, 731, 659, 586; **High Resolution MS** (ESI): Calculated for $NaC_9H_7N_3O_3$ $[M+Na]^+$: 228.0385, found: 228.0385.

Ethyl 4-{(azidocarbonyl)oxy}benzoate (1i)



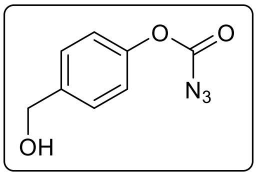
Colorless solid (0.16 g, 14 %, 5 mmol scale); **m.p.** 23 – 25 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 – 8.09 (m, 2H), 7.40 – 7.32 (m, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 156.0, 154.0, 131.4, 129.0, 121.0, 61.4, 14.4; **IR** (cm^{-1}) 2983, 2198, 2159, 1715, 1603, 1504, 1191, 1094, 1016, 948, 857, 748, 735; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_9N_3O_4$ $[M+Na]^+$: 258.0491, Found: 258.0486.

Methyl 2-[4-{(azidocarbonyl)oxy}phenyl]acetate (1j)



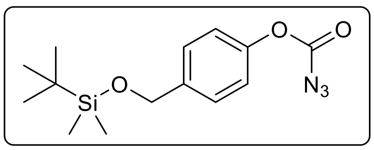
Colorless oil (1.4 g, 61 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.7 Hz, 2H), 3.70 (d, J = 1.0 Hz, 3H), 3.63 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.7, 156.4, 149.8, 132.6, 130.6, 121.1, 52.3, 40.6; **IR** (cm^{-1}) 2954, 2158, 1730, 1507, 1206, 1187, 1142, 1017, 736; **High Resolution MS** (EI): Calculated for $C_{10}H_9N_3O_4$ $[M]^+$: 235.0593, Found: 235.0591.

4-(Hydroxymethyl)phenyl azidoformate (1k)



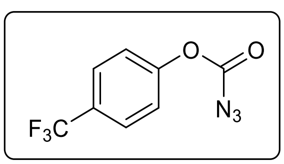
1k was prepared from deprotection of TBS group from **1l**.[7] Colorless oil (0.10 g, 95 %, 0.5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.67 (s, 2H), 1.94 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.5, 150.0, 139.5, 128.3, 121.1, 64.6; **IR** (cm^{-1}) 3437, 3303, 2928, 2904, 2170, 2157, 1737, 1506, 1212, 1190, 1014, 880; **High Resolution MS** (ESI): Calculated for $NaC_8H_7N_3O_3$ $[M+Na]^+$: 216.0385, found: 216.0378.

4-[{(*tert*-Butyldimethylsilyl)oxy}methyl]phenyl azidoformate (1l)



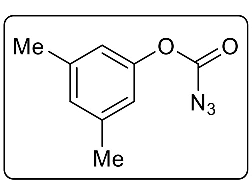
The corresponding alcohol(4-[{(*tert*-butyldimethylsilyl)oxy}methyl] phenol) was prepared from 4-hydroxybenzyl alcohol according to the literature procedure.[8] Colorless oil (0.61 g, 39 %, 4.7 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 4.75 (s, 2H), 0.97 (s, 9H), 0.12 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) 156.4, 149.5, 140.0, 127.1, 120.6, 64.3, 25.9, 18.4, -5.3; **IR** (cm^{-1}) 2929, 2910, 2169, 2153, 1751, 1743, 1505, 1213, 1088, 836,776; **High Resolution MS** (ESI): Calculated for $NaC_{14}H_{21}N_3O_3Si$ $[M+Na]^+$: 330.1250, found: 330.1246.

4-(Trifluoromethyl)phenyl azidoformate (1m)



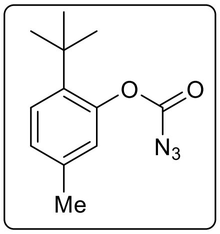
White solid (0.27 g, 23 %, 5 mmol scale); **m.p.** 63 – 65 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.8, 2.4 Hz, 2H), 7.43 (dd, *J* = 8.9, 2.3 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.2, 151.1, 129.0 (q, *J* = 32.9 Hz), 127.3 (q, *J* = 3.9 Hz), 123.8 (d, *J* = 270.5 Hz), 121.5; **^{19}F NMR** (376MHz, $CDCl_3$) δ -62.4; **IR** (cm^{-1}) 2952, 2910, 2175, 2163, 1744, 1613, 1324, 1216, 1164, 1125, 1064, 1017, 837; **High Resolution MS** (EI): Calculated for $C_8H_4F_3N_3O_2$ $[M]^+$: 231.0256, Found: 231.0257.

3,5-Dimethylphenyl azidoformate (1n)[6]



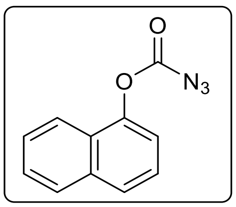
Colorless oil (1.0 g, 53 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.79 (s, 2H), 2.32 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.6, 150.7, 139.7, 128.4, 118.5, 21.3; **High Resolution MS** (EI): Calculated for $C_9H_9N_3O_2$ $[M]^+$: 191.0695, Found: 191.0696.

2-(*tert*-Butyl)-5-methylphenyl azidoformate (1o)[6]



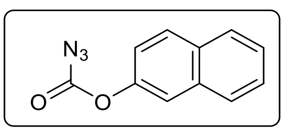
Colorless oil (0.58 g, 45 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 2.33 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.7, 149.2, 138.1, 137.4, 127.5, 127.3, 123.8, 34.4, 30.4, 20.7; **High Resolution MS** (ESI): Calculated for $NaC_{12}H_{15}N_3O_2$ $[M+Na]^+$: 256.1062, found: 256.1050.

Naphthalen-1-yl azidoformate (1p)



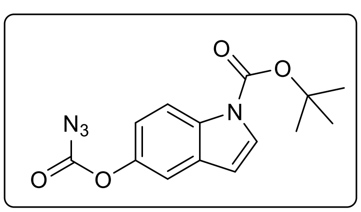
White solid (0.31 g, 29 %, 5 mmol scale); **m.p.** 29 – 31 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (ddt, *J* = 8.2, 2.4, 1.2 Hz, 1H), 7.91 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.58 (m, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.40 (dt, *J* = 7.9, 1.6 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.6, 146.5, 134.7, 128.1, 127.0, 126.9, 126.8, 126.3, 125.3, 120.8, 117.6; **IR** (cm^{-1}) 3063, 2192, 2167, 2130, 1736, 1572, 1506, 1390, 1209, 950, 774, 761, 734; **High Resolution MS** (EI): Calculated for $C_{11}H_7N_3O_2$ $[M]^+$: 213.0538, Found: 213.0538.

Naphthalen-2-yl azidoformate (1q)



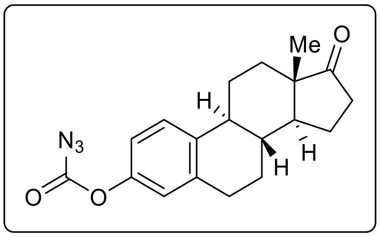
White solid (0.51 g, 48 %, 5 mmol scale); **m.p.** 39 – 41 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.83 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.32 (dd, *J* = 8.9, 2.4 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.6, 148.3, 133.6, 131.8, 129.9, 127.9, 127.9, 127.0, 126.3, 120.1, 118.2; **IR** (cm^{-1}) 3060, 2167, 2147, 1733, 1510, 1202, 1104, 964, 951, 855, 729; **High Resolution MS** (EI): Calculated for $C_{11}H_7N_3O_2$ $[M]^+$: 213.0538, Found: 213.0535.

***tert*-Butyl 5-{(azidocarbonyl)oxy}-1*H*-indole-1-carboxylate (1r)**



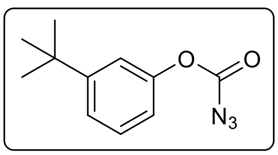
The corresponding alcohol (*tert*-butyl 5-hydroxy-1*H*-indole-1-carboxylate) was prepared according to the reported procedure[9] from 20 mmol scale of resorcinol. White solid (2.8 g, 47 %, 2 steps yield); **m.p.** 53 – 55 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 3.7 Hz, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.11 (dt, *J* = 8.9, 2.2 Hz, 1H), 6.56 (d, *J* = 3.7 Hz, 1H), 1.68 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.8, 149.5, 146.4, 133.4, 131.2, 127.6, 117.2, 116.0, 112.8, 107.2, 84.2, 28.2; **IR** (cm^{-1}) 2925, 2865, 2195, 2166, 2128, 1724, 1491, 1240, 1205, 1180; **High Resolution MS** (EI): Calculated for $C_{14}H_{14}N_4O_4$ $[M]^+$: 302.1015, Found: 302.1016.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl azidoformate (1s)[6]



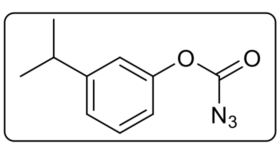
1s was prepared according to the literature procedure.[6] White solid (1.5 g, 44 %, 10 mmol scale); **m.p.** 139 – 141 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.90 (d, *J* = 2.6 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.50 (dd, *J* = 19.1, 8.9 Hz, 1H), 2.40 (ddd, *J* = 12.4, 5.9, 3.8 Hz, 1H), 2.28 (td, *J* = 10.9, 4.2 Hz, 1H), 2.14 (dt, *J* = 18.7, 8.9 Hz, 1H), 2.09 – 2.00 (m, 2H), 1.97 (dt, *J* = 12.7, 2.8 Hz, 1H), 1.69 – 1.39 (m, 6H), 0.91 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 220.6, 156.6, 148.7, 138.5, 138.4, 126.7, 121.0, 118.1, 50.5, 48.0, 44.2, 38.0, 35.9, 31.6, 29.5, 26.3, 25.8, 21.7, 13.9; **High Resolution MS** (EI): Calculated for $C_{19}H_{21}N_3O_3$ $[M]^+$: 339.1583, Found: 339.1586.

3-(*tert*-Butyl)phenyl azidoformate (1t)[6]



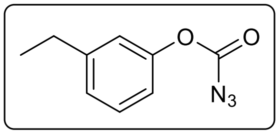
Colorless oil (0.52 g, 47 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.8 Hz, 1H), 7.30 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.16 (t, *J* = 2.0 Hz, 1H), 7.00 (ddd, *J* = 7.7, 2.4, 1.4 Hz, 1H), 1.32 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) 156.6, 153.6, 150.7, 129.2, 123.8, 118.1, 118.0, 35.0, 31.3; **High Resolution MS** (EI): Calculated for $C_{11}H_{13}N_3O_2$ $[M]^+$: 219.1008, Found: 219.1010.

3-Isopropylphenyl azidoformate (1u)



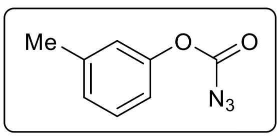
Colorless oil (0.36 g, 35 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.07 (s, 1H), 7.03 (ddd, *J* = 8.1, 2.5, 1.0 Hz, 1H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) 156.4, 151.0, 150.8, 129.4, 124.8, 118.8, 118.2, 34.0, 23.8; **IR** (cm^{-1}) 2962, 2958, 2942, 2161, 2142, 1738, 1487, 1320, 1196, 1079, 1002, 957, 739; **High Resolution MS** (EI): Calculated for $C_{10}H_{11}N_3O_2$ $[M]^+$: 205.0851, Found: 205.0852.

3-Ethylphenyl azidoformate (1v)



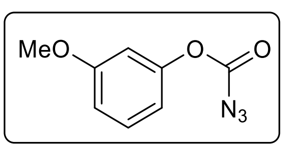
Colorless oil (0.57 g, 30 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 (t, J = 7.8 Hz, 1H), 7.12 (dtd, J = 7.5, 1.5, 0.7 Hz, 1H), 7.03 – 6.96 (m, 2H), 2.68 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.5, 150.8, 146.4, 129.5, 126.3, 120.3, 118.1, 28.7, 15.3; **IR** (cm^{-1}) 2967, 2934, 2171, 2135, 1737, 1613, 1585, 1487, 1448, 1199, 1151, 1132, 1003, 985, 902, 875, 798, 759, 735, 688; **High Resolution MS** (EI): Calculated for $C_9H_9N_3O_2$ $[M]^+$: 191.0695, Found: 191.0693.

***m*-Tolyl azidoformate (1w)**[6]



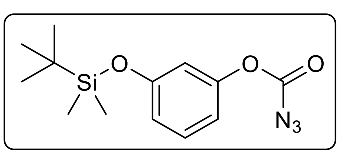
Colorless oil (0.95 g, 27 %, 20 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (t, J = 7.8 Hz, 1H), 7.09 (d, J = 7.7 Hz, 1H), 7.01 – 6.95 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.5, 150.7, 140.1, 129.5, 127.5, 121.6, 117.9, 21.4; **High Resolution MS** (EI): Calculated for $C_8H_7N_3O_2$ $[M]^+$: 177.0538, Found: 177.0536.

3-Methoxyphenyl azidoformate (1x)



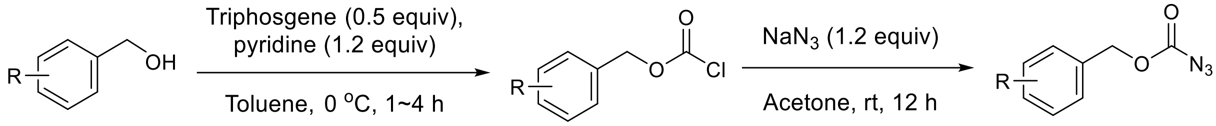
Colorless oil (1.4 g, 36 %, 20 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (t, J = 8.2 Hz, 1H), 6.87 – 6.80 (m, 1H), 6.80 – 6.76 (m, 1H), 6.73 (s, 1H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 156.4, 151.6, 130.2, 113.1, 112.6, 107.1, 55.6; **IR** (cm^{-1}) 2944, 2838, 2189, 2148, 1737, 1610, 1590, 1490, 1190, 1126, 1035, 957, 843, 758, 734, 681; **High Resolution MS** (EI): Calculated for $C_8H_7N_3O_3$ $[M]^+$: 193.0487, Found: 193.0489.

3-{(*tert*-Butyldimethylsilyl)oxy}phenyl azidoformate (1y)



The corresponding alcohol (3-((*tert*-butyldimethylsilyl)oxy)phenol) was prepared according to the literature procedure[10] from 10 mmol scale of resorcinol. Colorless oil (0.62 g, 21 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 (t, J = 8.2 Hz, 1H), 6.77 (m, 2H), 6.68 (t, J = 2.3 Hz, 1H), 0.98 (s, 9H), 0.21 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.8, 156.3, 151.4, 130.0, 118.5, 113.8, 113.2, 25.7, 18.3, -4.3; **IR** (cm^{-1}) 2955, 2931, 2887, 2859, 2182, 2137, 1741, 1605, 1484, 1219, 1192, 1127, 1004, 979, 837, 779, 683; **High Resolution MS** (EI): Calculated for $C_{13}H_{19}N_3O_3Si$ $[M]^+$: 293.1196, Found: 293.1194.

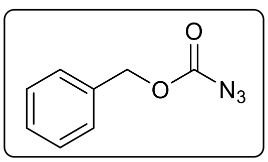
IV – 2. Preparation of Benzyl Azidoformates (3a and 3b)



3

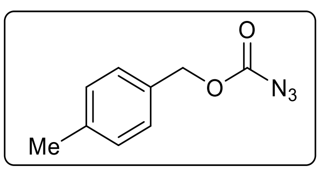
To a solution of triphosgene (5 mmol, 0.5 equiv) in toluene (50 mL) was added pyridine (12 mmol, 1.2 equiv) dropwise at 0 °C. Then, benzyl alcohol (10 mmol) was added at 0 °C in a dropwise fashion. The reaction was allowed to stir at r.t. until reaction completion (1 to 4 h). The reaction mixture was washed with water (50 mL x 2), extracted with EtOAc (50 mL x 2), dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude chloroformate products. To a solution of unpurified chloroformate, sodium azide (12 mmol, 1.2 equiv) was added in acetone (50 mL). After stirring for 12 h at r.t., the reaction mixture was filtered through a pad of celite with dichloromethane (50 mL), concentrated under reduced pressure and purified by flash column chromatography to yield benzyl azidoformate **3** (eluent: *n*-hexane/EtOAc = 4:1 to 3:1).

Benzyl azidoformate (3a)[11]



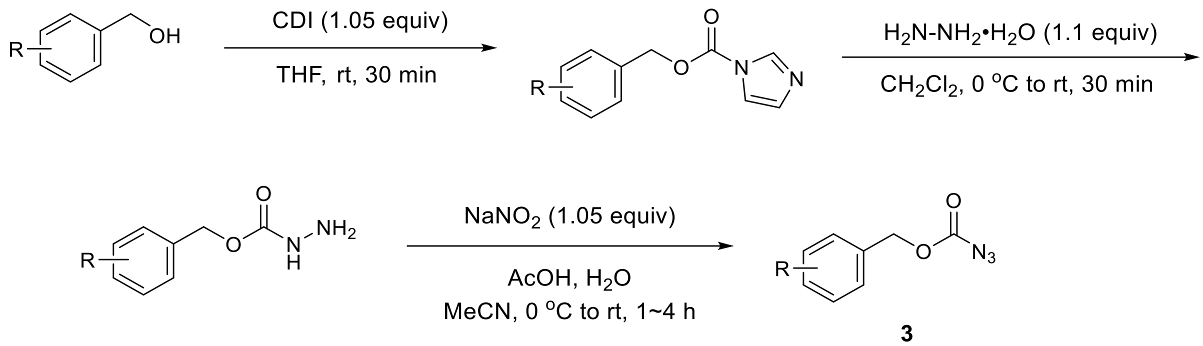
Colorless oil (0.50 g, 28 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 5H), 5.23 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) 157.5, 134.5, 128.9, 128.8, 128.6, 70.1; **High Resolution MS** (EI): Calculated for $C_8H_7N_3O_2$ $[M]^+$: 177.0538, Found: 177.0537.

4-Methylbenzyl azidoformate (3b)



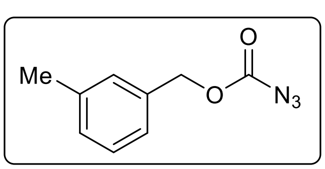
Colorless oil (0.63 g, 33 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 5.19 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.6, 139.0, 131.5, 129.5, 128.9, 70.3, 21.4; **IR** (cm^{-1}) 3029, 2960, 2924, 2137, 1726, 1374, 1217, 957, 805, 752; **High Resolution MS** (EI): Calculated for $C_9H_9N_3O_2$ $[M]^+$: 191.0695, Found: 191.0695.

IV - 3. Preparation of Benzyl Azidoformates (3c, 3d and 3e)[12-13]



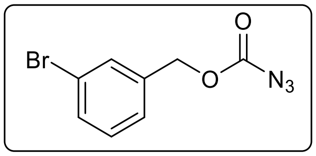
Benzyl alcohol (10 mmol) was added to a solution of 1,1'-carbonyldiimidazole (CDI, 10.5 mmol, 1.05 equiv) in anhydrous THF (20 mL) and the resulting mixture was stirred at room temperature for 30 min. The mixture was quenched with water (20 mL) and extracted with EtOAc (50 mL x 3). The combined organic layer was dried over $MgSO_4$, filtered through filter paper with dichloromethane (50 mL) and concentrated under reduce pressure. The product obtained was dissolved in dichloromethane (20 mL). Hydrazine hydrate (11 mmol, 1.1 equiv) and the resulting mixture was stirred at r.t. for 2 h. After the completion of reaction (based on TLC), the solvent was removed under reduced pressure, and the crude product obtained was used without any further purification in the next step. The afforded hydrazine carboxylate was dissolved in a mixture of acetic acid (8 mL) and water (5 mL) in MeCN (20 mL). The solution was cooled to 0 ºC, stirred and treated dropwise with $NaNO_2$ (10.5 mmol, 1.05 equiv). After the addition, mixture was stirred at 0 ºC for 15 min and at r.t. for an hour. After the completion of reaction, mixture was poured in water (20 mL) followed by extraction with ether (50 mL x 2). The combined organic layers were washed with brine (20 mL) and $NaHCO_3$ (20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash column chromatography to yield benzyl azidoformate **3** (eluent: n-hexane/EtOAc = 4:1).

3-Methylbenzyl azidoformate (3c)



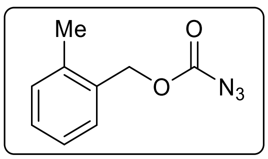
Colorless oil (0.61 g, 64 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.16 (m, 3H), 5.20 (s, 2H), 2.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.6, 138.6, 134.4, 129.8, 129.4, 128.7, 125.7, 70.3, 21.4; **IR** (cm^{-1}) 3029, 2961, 2923, 2141, 1724, 1491, 1454, 1373, 1217, 1160, 958, 773; **High Resolution MS** (EI): Calculated for $C_9H_9N_3O_2$ $[M]^+$: 191.0695, Found: 191.0697

3-Bromobenzyl azidoformate (3d)



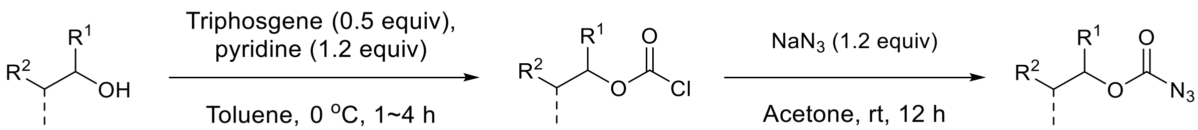
Colorless oil (1.4 g, 55 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.28 – 7.23 (m, 1H), 5.18 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.6, 136.7, 132.1, 131.5, 130.4, 127.1, 122.9, 69.1; **IR** (cm^{-1}) 2962, 2164, 2139, 1722, 1572, 1475, 1429, 1372, 1209, 1159, 1071, 963, 772, 748, 689, 667; **High Resolution MS** (EI): Calculated for $C_8H_6BrN_3O_2$ $[M]^+$: 254.9643, Found: 254.9645.

2-Methylbenzyl azidoformate (3e)



Colorless oil (0.96 g, 50%, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (d, J = 7.2 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.25 – 7.18 (m, 2H), 5.26 (s, 2H), 2.38 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.6, 137.4, 132.5, 130.7, 129.9, 129.3, 126.3, 68.7, 19.0; **IR** (cm^{-1}) 3026, 2963, 2162, 2137, 1723, 1495, 1462, 1373, 1216, 1159, 956, 745; **High Resolution MS** (EI): Calculated for $C_9H_9N_3O_2$ $[M]^+$: 191.0695, Found: 191.0694.

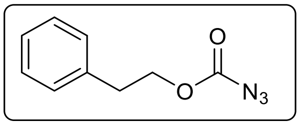
IV – 4. Preparation of Azidoformates



5, 7

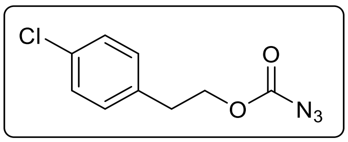
To a solution of triphosgene (5 mmol, 0.5 equiv) in toluene (50 mL) was added pyridine (12 mmol, 1.2 equiv) dropwise at 0 °C. Then, alcohol (10 mmol) was added at 0 °C in a dropwise fashion. The reaction was allowed to stir at r.t. until reaction completion (1-4 h). The reaction mixture was washed with water (50 mL x 2), extracted with EtOAc (50 mL x 2), dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude chloroformate products. To a solution of unpurified chloroformate, sodium azide (12 mmol, 1.2 equiv) was added in acetone (50 mL). After stirring for 12 h at r.t., the reaction mixture was filtered through a pad of celite with dichloromethane (50 mL), concentrated under reduced pressure and purified by flash column chromatography to yield azidoformate **5** and **7** (eluent: *n*-hexane/EtOAc = 4:1 to 3:1).

Phenethyl azidoformate (5a)[14]



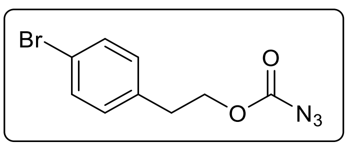
Colorless oil (2.6 g, 92 %, 15 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.28 – 7.22 (m, 2H), 4.44 (td, *J* = 7.1, 0.9 Hz, 2H), 3.02 (t, *J* = 7.1 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.5, 136.9, 129.0, 128.8, 127.0, 69.0, 35.1; **High Resolution MS** (EI): Calculated for $C_9H_9N_3O_2$ $[M]^+$: 191.0695, Found: 191.0696.

4-Chlorophenethyl azidoformate (5b)



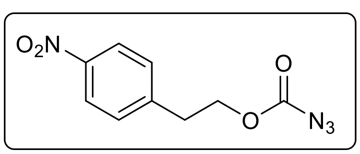
Colorless oil (1.1 g, 97 %, 5 mmol); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.39 (td, *J* = 6.9, 0.8 Hz, 2H), 2.96 (t, *J* = 6.9 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.5, 135.4, 132.9, 130.4, 128.9, 68.6, 34.4; **IR** (cm^{-1}) 2963, 2175, 2134, 1724, 1493, 1382, 1222, 1166, 1092, 1015, 984, 813, 748; **High Resolution MS** (EI): Calculated for $C_9H_8ClN_3O_2$ $[M]^+$: 225.0305, Found: 225.0308.

4-Bromophenethyl azidoformate (5c)



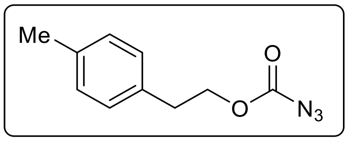
Colorless oil (1.3 g, 93 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 4.39 (t, *J* = 6.9 Hz, 2H), 2.95 (t, *J* = 6.9 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.5, 135.9, 131.9, 130.8, 121.0, 68.5, 34.5; **IR** (cm^{-1}) 2962, 2176, 2133, 1723, 1488, 1382, 1221, 1165, 1071, 1010, 984, 944, 927, 809, 748; **High Resolution MS** (EI): Calculated for $C_9H_8BrN_3O_2$ $[M]^+$: 268.9800, Found: 268.9801.

4-Nitrophenethyl azidoformate (5d)



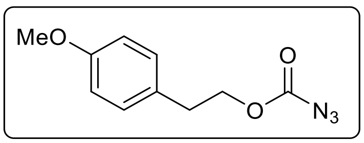
White solid (0. 91 g, 77 %, 5 mmol scale); **m.p.** 65 – 67 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 4.46 (t, *J* = 6.7 Hz, 2H), 3.11 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.4, 147.0, 144.8, 129.8, 123.8, 67.7, 34.7; **IR** (cm^{-1}) 2194, 2144, 1720, 1600, 1512, 1342, 1240, 1219, 1196, 1104, 1068, 1013, 950, 868, 845, 824, 743, 695; **High Resolution MS** (EI): Calculated for $C_9H_8N_4O_4$ $[M]^+$: 236.0546, Found: 236.0544.

4-Methylphenethyl azidoformate (**5e**)



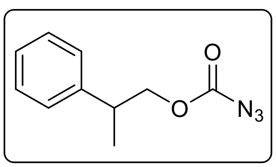
Colorless oil (1.0 g, 97 %, 5 mmol); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.11 (m, 4H), 4.39 (t, J = 7.1 Hz, 2H), 2.96 (t, J = 7.1 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.5, 136.6, 133.8, 129.5, 128.9, 69.2, 34.6, 21.2; **IR** (cm^{-1}) 3021, 2961, 2923, 2176, 2133, 1752, 1725, 1516, 1460, 1383, 1223, 1166, 1114, 980, 808, 749; **High Resolution MS** (EI): Calculated for $C_{10}H_{11}N_3O_2$ $[M]^+$: 205.0851, Found: 205.0848.

4-Methoxyphenethyl azidoformate (**5f**)



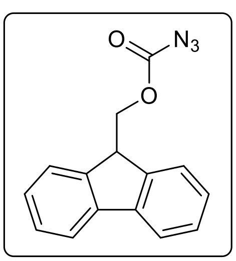
Colorless oil (1.0 g, 91 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.13 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 4.37 (t, J = 7.1 Hz, 2H), 3.80 (s, 3H), 2.94 (t, J = 7.1 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.7, 157.5, 130.0, 128.9, 114.2, 69.2, 55.4, 34.2; **IR** (cm^{-1}) 2959, 2938, 2177, 2134, 1724, 1612, 1512, 1463, 1385, 1221, 1175, 1112, 1031, 980, 823, 811, 748; **High Resolution MS** (EI): Calculated for $C_{10}H_{11}N_3O_3$ $[M]^+$: 221.0800, Found: 221.0798.

2-Phenylpropyl azidoformate (**7a**)



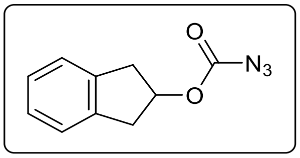
Colorless oil (2.0 g, 99 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (t, J = 7.6 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.25 – 7.20 (m, 2H), 4.33 (dd, J = 10.6, 6.8 Hz, 1H), 4.25 (dd, J = 10.6, 7.4 Hz, 1H), 3.15 (h, J = 7.0 Hz, 1H), 1.33 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.5, 142.3, 128.8, 127.4, 127.2, 73.3, 39.0, 17.9; **IR** (cm^{-1}) 3030, 2970, 2139, 1723, 1495, 1453, 1389, 1372, 1220, 1169, 983, 946, 749, 698; **High Resolution MS** (EI): Calculated for $C_{10}H_{11}N_3O_2$ $[M]^+$: 205.0851, Found: 205.0854.

(9*H*-Fluoren-9-yl)methyl azidoformate (**7b**)[11]



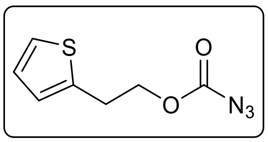
White solid (2.5 g, 93 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.39 – 7.29 (m, 2H), 4.49 (d, J = 7.4 Hz, 2H), 4.28 (t, J = 7.4 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.7, 143.1, 141.4, 128.2, 127.4, 125.2, 120.3, 70.4, 46.6; **High Resolution MS** (EI): Calculated for $C_{15}H_{11}N_3O_2$ $[M]^+$: 265.0851, Found: 265.0852.

2,3-Dihydro-1*H*-inden-2-yl azidoformate (7c)



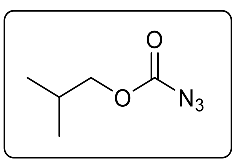
Colorless oil (1.5 g, 72 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 4H), 5.54 (tt, *J* = 6.3, 3.0 Hz, 1H), 3.36 (dd, *J* = 17.0, 6.4 Hz, 2H), 3.12 (dd, *J* = 17.1, 3.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 139.7, 127.1, 124.8, 80.1, 39.4; **IR** (cm^{-1}) 3072, 3025, 2956, 2906, 2152, 2131, 1718, 1483, 1434, 1357, 1231, 1205, 1184, 1005, 972, 922, 739; **High Resolution MS** (EI): Calculated for $C_{10}H_9N_3O_2$ [M]$^+$: 203.0695, Found: 203.0693.

2-(Thiophen-2-yl)ethyl azidoformate (7d)



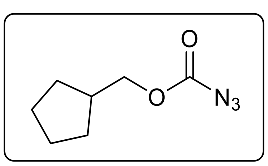
Colorless oil (1.4 g, 72%, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.93 – 6.86 (m, 1H), 4.43 (t, *J* = 6.8 Hz, 2H), 3.22 (td, *J* = 6.8, 0.9 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.4, 138.8, 127.1, 126.0, 124.5, 68.6, 29.2; **IR** (cm^{-1}) 3109, 2963, 2170, 2133, 1723, 1464, 1383, 1218, 1166, 983, 849, 827, 748, 695; **High Resolution MS** (EI): Calculated for $C_7H_7N_3O_2S$ [M]$^+$: 197.0259, Found: 197.0257.

Isobutyl azidoformate (7e)[15]



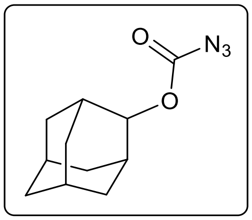
Colorless oil (0.39 g, 55 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.00 (d, *J* = 6.7 Hz, 2H), 1.99 (dh, *J* = 13.5, 6.8 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.7, 74.7, 27.8, 18.9; **High Resolution MS** (EI): Calculated for $C_5H_9N_3O_2$ [M]$^+$: 143.0695, Found: 143.0696.

Cyclopentylmethyl azidoformate (7f)



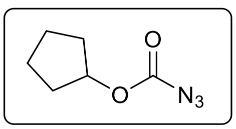
Colorless oil (1.0 g, 62 %, 10 mmol); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.10 (d, *J* = 7.2 Hz, 2H), 2.25 (hept, *J* = 7.6 Hz, 1H), 1.84 – 1.71 (m, 2H), 1.69 – 1.47 (m, 4H), 1.25 (ddt, *J* = 15.1, 8.0, 4.3 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.8, 72.6, 38.5, 29.3, 25.4; **IR** (cm^{-1}) 2955, 2870, 2186, 2134, 1757, 1725, 1453, 1218, 973, 750; **High Resolution MS** (EI): Calculated for $C_7H_{11}N_3O_2$ [M]$^+$: 169.0851, Found: 169.0853.

(1*r*,3*r*,5*r*,7*r*)-Adamantan-2-yl azidoformate (7g)



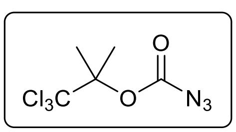
White solid (1.9 g, 85 %, 10 mmol); **m.p.** 55 – 57 ºC; **^{1}H NMR** (400MHz, $CDCl_3$) δ 4.92 (t, *J* = 3.6 Hz, 1H), 2.09 (s, 2H), 2.06 – 2.00 (m, 1H), 2.00 – 1.95 (m, 1H), 1.93 – 1.80 (m, 4H), 1.76 (dd, *J* = 13.2, 3.2 Hz, 4H), 1.59 (q, *J* = 1.6 Hz, 1H), 1.56 (d, *J* = 2.3 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.9, 82.3, 37.3, 36.4 (2C), 31.9, 31.6 (2C), 27.1, 26.9; **IR** (cm^{-1}) 2910, 2854, 2178, 2134, 1719, 1449, 1338, 1234, 1213, 1098, 1040, 976, 921, 752; **High Resolution MS** (EI): Calculated for $C_{11}H_{15}N_3O_2$ $[M]^+$: 221.1164, Found: 221.1160

Cyclopentyl azidoformate (7h)



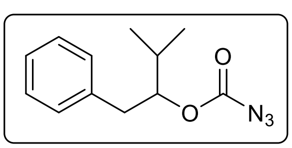
Colorless oil (0.65 g, 42 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.18 (tt, *J* = 5.9, 2.7 Hz, 1H), 1.98 – 1.83 (m, 2H), 1.83 – 1.66 (m, 4H), 1.66 – 1.54 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.3, 82.2, 32.7, 23.6; **IR** (cm^{-1}) 2965, 2876, 2190, 2147, 2131, 1751, 1720, 1438, 1361, 1320, 1223, 1159, 1033, 956, 921, 752; **High Resolution MS** (EI): Calculated for C6H9N3O2 $[M]^+$: 155.0695, Found: 276.1839. **High Resolution MS** (ESI): Calculated for $NaC_6H_9N_3O_2$ $[M+Na]^+$: 178.0592, found: 178.0596.

1,1,1-Trichloro-2-methylpropan-2-yl azidoformate (7i)[16]



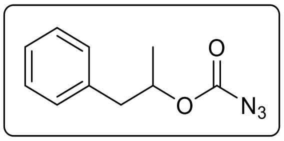
White solid (1.1 g, 89 %, 5 mmol scale); **m.p.** 53 – 55 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 1.96 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.6, 105.1, 91.6, 21.3 (2C); **High Resolution MS** (ESI): Calculated for $NaC_5H_6Cl_3N_3O_2$ $[M+Na]^+$: 267.9423, found: 267.9415.

3-Methyl-1-phenylbutan-2-yl azidoformate (7j)



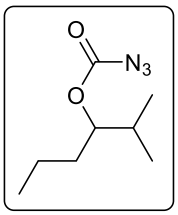
Colorless oil (2.1 g, 90 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.22 (m, 1H), 7.22 – 7.18 (m, 2H), 4.91 (dt, *J* = 8.3, 5.1 Hz, 1H), 2.98 – 2.79 (m, 2H), 1.92 (pd, *J* = 6.8, 5.0 Hz, 1H), 1.00 (dd, *J* = 6.8, 4.7 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.3, 137.3, 129.4, 128.6, 126.8, 84.6, 37.6, 31.1, 18.8, 17.3; **IR** (cm^{-1}) 2966, 2177, 2130, 1722, 1496, 1455, 1356, 1226, 1175, 987, 743, 698; **High Resolution MS** (EI): Calculated for $C_{12}H_{15}N_3O_2$ $[M]^+$: 233.1164, found. 233.1166.

1-Phenylpropan-2-yl azidoformate (7k)



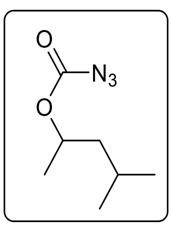
Colorless oil (1.9 g, 93 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.27 – 7.23 (m, 1H), 7.21 – 7.18 (m, 2H), 5.09 (h, J = 6.4 Hz, 1H), 3.00 (dd, J = 13.8, 6.8 Hz, 1H), 2.82 (dd, J = 13.8, 6.4 Hz, 1H), 1.31 (d, J = 6.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.0, 136.8, 129.5, 128.7, 126.9, 76.9, 42.2, 19.4; **IR** (cm^{-1}) 2982, 2186, 2133, 1719, 1497, 1454, 1383, 1352, 1230, 1176, 1128, 1074, 1047, 1030, 956, 744, 698; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_{11}N_3O_2$ $[M+Na]^+$: 228.0749, found: 228.0741.

2-Methylhexan-3-yl azidoformate (7l)



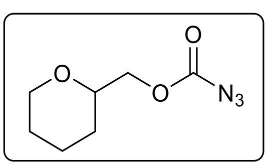
Colorless oil (0.48 g, 26 %, 10 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.70 (ddd, J = 9.1, 5.4, 4.0 Hz, 1H), 2.01 – 1.80 (m, 1H), 1.70 – 1.45 (m, 2H), 1.45 – 1.19 (m, 2H), 0.92 (m, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.7, 84.2, 33.2, 31.6, 18.8, 18.5, 17.5, 14.0; **IR** (cm^{-1}) 2963, 2938, 2876, 2189, 2165, 2131, 1753, 1723, 1466, 1370, 1224, 1178, 1122, 968, 938, 749; **High Resolution MS** (ESI): Calculated for $NaC_8H_{15}N_3O_2$ $[M+Na]^+$: 208.1062, found: 208.1061.

4-Methylpentan-2-yl azidoformate (7m)



Colorless oil (1.1 g, 44 %, 15 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.03 – 4.89 (m, 1H), 1.79 – 1.52 (m, 2H), 1.38 – 1.31 (m, 1H), 1.29 (d, J = 6.2 Hz, 3H), 0.91 (dd, J = 6.5, 2.5 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.3, 75.2, 44.9, 24.8, 22.9, 22.4, 20.4; **IR** (cm^{-1}) 2960, 2937, 2185, 2134, 1753, 1723, 1469, 1369, 1227, 1119, 1006, 909, 752; **High Resolution MS** (EI): Calculated for $C_7H_{13}N_3O_2$ $[M]^+$: 171.1008, found: 171.1009.

(Tetrahydro-2*H*-pyran-2-yl)methyl azidoformate (7n)

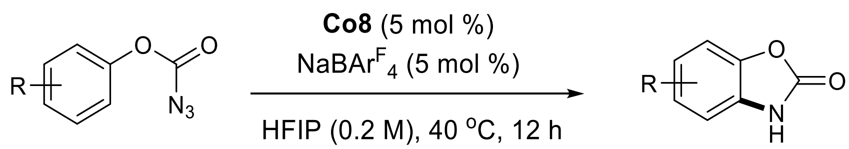


Colorless oil (0.82 g, 89 %, 5 mmol scale); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.21 – 4.09 (m, 2H), 3.99 (ddt, J = 11.7, 4.0, 1.7 Hz, 1H), 3.56 (dddd, J = 10.8, 6.3, 3.9, 2.1 Hz, 1H), 3.42 (td, J = 11.7, 2.4 Hz, 1H), 1.87 (ddp, J = 12.6, 5.3, 2.4 Hz, 1H), 1.62 – 1.44 (m, 4H), 1.39 – 1.25 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.8, 75.0, 71.2, 68.5, 27.7, 25.77, 23.0; **IR** (cm^{-1}) 2940, 2850, 2164, 2136, 1725, 1451, 1223, 1204, 1178, 1094, 1077, 1048, 997, 749; **High Resolution MS** (EI): Calculated for $C_7H_{11}N_3O_3$ $[M]^+$: 185.0800, Found: 185.0802.

V. Procedures for the Co-Catalyzed C−H Amidation of Azidoformate

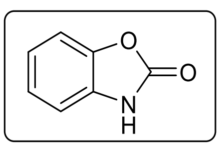
V-1. Procedures for the Co-Catalyzed C(sp^2)−H Amidatoin of Phenyl Azidoformate

To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added **Co8** (2.2 mg, 5.0 mol %), sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (4.4 mg, 5.0 mol %), hexafluoro-2-propanol (0.5 mL) and the reaction mixture was stirred at r.t. for 1 min. To the vial was added phenyl azidoformate **1** (x mg, 0.1 mmol) and then sealed with Teflon cap. The reaction mixture was vigorously stirred in a pre-heated heating block at 40 °C for 12 h, filtered through a pad of silica with EtOAc (10 mL × 5) and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to yield benzoxazolone **2** (*n*-hexane/EtOAc, 2:1 to 1:2).



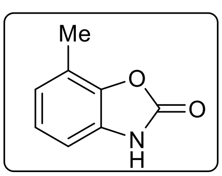
1 **2**

Benzo[*d*]oxazol-2(3*H*)-one (2a)[6]



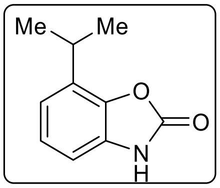
White solid (13 mg, 93 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.23 (m, 1H), 7.17 (td, J = 7.6, 1.3 Hz, 1H), 7.13 (td, J = 7.8, 1.5 Hz, 1H), 7.11 – 7.07 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) 156.5, 144.0, 129.6, 124.4, 122.9, 110.4, 110.3; **High Resolution MS** (ESI): Calculated for $NaC_7H_5NO_2$ [M+Na]$^+$: 158.0218, found: 158.0213.

7-Methylbenzo[*d*]oxazol-2(3*H*)-one (2b)[6]



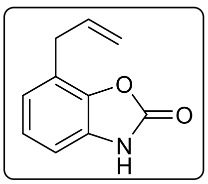
White solid (9.4 mg, 63 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.06 (t, J = 7.8 Hz, 1H), 6.94 (dt, J = 7.8, 1.0 Hz, 1H), 6.91 (dt, J = 7.6, 0.8 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.0, 143.4, 129.0, 124.4, 124.0, 121.0, 106.2, 14.7; **High Resolution MS** (ESI): Calculated for $NaC_8H_7NO_2$ [M+Na]$^+$: 172.0374, found: 172.0377.

7-Isopropylbenzo[*d*]oxazol-2(3*H*)-one (2c)[6]



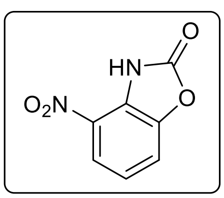
White solid (15 mg, 85 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.98 (m, 2H), 3.23 (h, *J* = 7.0 Hz, 1H), 1.33 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) 156.6, 141.7, 131.8, 129.3, 124.3, 120.5, 107.8, 28.8, 22.4; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_{11}NO_2$ $[M+Na]^+$: 200.0687, found: 200.0678.

7-Allylbenzo[*d*]oxazol-2(3*H*)-one (2d)[17]



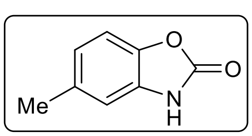
White solid (14 mg, 78 %); **^{1}H NMR** (800 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.01 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.20 – 5.12 (m, 2H), 3.53 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (200 MHz, $CDCl_3$) δ 154.8, 142.3, 135.0, 128.9, 124.1, 123.6, 123.3, 117.0, 107.7, 33.4; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_9NO_2$ $[M+Na]^+$: 198.0531, found: 198.0591.

4-Nitrobenzo[*d*]oxazol-2(3*H*)-one (2e)



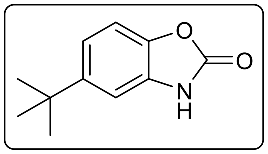
Only the major product of reioisomers is reported. White solid (12 mg, 65%, C2/C6, 5:1); **^{1}H NMR** (600 MHz, Acetone-*d*$_6$) δ 11.34 (s, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 8.3 Hz, 1H); **^{13}C NMR** (175 MHz, Acetone-*d*$_6$) δ 154.2, 146.3, 132.4, 128.5, 122.5, 119.2, 116.1; **IR** (cm^{-1}) 3168, 3103, 2922, 2851, 1809, 1787, 1615, 1524, 1478, 1320, 1252, 1209, 1146, 1053, 984, 959, 832, 804, 732, 714, 642, 572; **High Resolution MS** (EI): Calculated for $C_7H_4N_2O_4$ $[M]^+$: 180.0171, found: 180.0170.

5-Methylbenzo[*d*]oxazol-2(3*H*)-one (2f)[6]



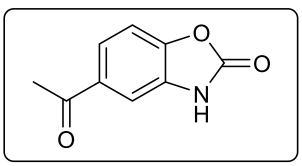
Whit solid (13 mg, 87 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.94 – 6.89 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.5, 142.1, 134.3, 129.5, 123.3, 110.8, 109.8, 21.6; **IR** (cm^{-1}) 3337, 3303, 2963, 2928, 2904, 2867, 1655, 1592, 1531, 1518, 1505, 1480, 1448, 1397, 1364, 1292, 1272, 1262, 1219, 1172, 943, 917; **High Resolution MS** (ESI): Calculated for $NaC_8H_7NO_2$ $[M+Na]^+$: 172.0374, found: 172.0360.

5-(*tert*-Butyl)benzo[*d*]oxazol-2(3*H*)-one (2g)[6]



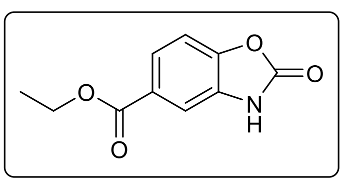
White solid (17 mg, 88 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.19 – 7.09 (m, 3H), 1.33 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.8, 148.1, 142.0, 129.3, 119.8, 109.5, 107.6, 35.1, 31.7; **IR** (cm^{-1}) 3337, 3303, 2963, 2928, 2904, 2867, 1655, 1592, 1531, 1518, 1505, 1480, 1448, 1397, 1364, 1292, 1272, 1262, 1219, 1172, 943, 917; **High Resolution MS** (ESI): Calculated for $NaC_{11}H_{13}NO_2$ $[M+Na]^+$: 214.0844, found: 214.0838.

5-Acetylbenzo[*d*]oxazol-2(3*H*)-one (2h)



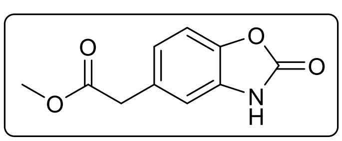
White solid (12 mg, 68 %); **m.p.** 209 – 211 ºC; **^{1}H NMR** (600 MHz, Acetone-*d_6*) δ 10.58 (s, 1H), 7.85 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 2.59 (s, 3H); **^{13}C NMR** (150 MHz, Acetone-*d_6*) δ 196.7, 154.9, 148.2, 134.5, 131.7, 124.7, 110.1, 110.0, 26.7; **IR** (cm^{-1}) 3230, 1798, 1768, 1656, 1616, 1459, 1357, 1264, 1151, 924, 893, 880, 825, 742, 704, 640, 587; **High Resolution MS** (ESI): Calculated for $NaC_9H_7NO_3$ $[M+Na]^+$: 200.0324, found: 200.0315.

Ethyl 2-oxo-2,3-dihydrobenzo[*d*]oxazole-5-carboxylate (2i)[18]



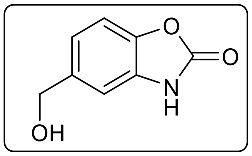
White solid (8.9 mg, 43 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H), 7.42 – 7.03 (m, 1H), 4.40 (qd, *J* = 7.1, 1.9 Hz, 2H), 1.41 (td, *J* = 7.2, 1.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 155.6, 147.2, 129.5, 127.0, 125.4, 111.5, 110.0, 61.6, 14.4; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_9NO_4$ $[M+Na]^+$: 230.0429, found: 230.0428.

Methyl 2-(2-oxo-2,3-dihydrobenzo[*d*]oxazol-5-yl)acetate (2j)



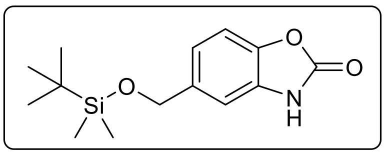
White solid (21 mg, 99 %); **m.p.** 117 – 119 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 7.03 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 3.72 (s, 3H), 3.65 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.3, 155.9, 143.2, 130.2, 129.9, 123.8, 111.1, 110.2, 52.4, 41.0; **IR** (cm^{-1}) 3308, 2956, 1772, 1730, 1624, 1463, 1300, 1257, 1170, 1134, 1100, 1007, 925, 798, 709; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_9NO_4$ $[M+Na]^+$: 230.0429, found: 230.0427.

5-(Hydroxymethyl)benzo[*d*]oxazol-2(3*H*)-one (2k)



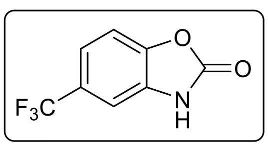
White solid (8.6 mg, 52 %); **m.p.** 140 – 142 ºC; **^{1}H NMR** (600 MHz, CD_3OD) δ 7.16 (d, *J* = 8.2 Hz, 1H), 7.12 – 7.05 (m, 3H), 4.60 (s, 2H) (*OH peak is unseen.*); **^{13}C NMR** (100 MHz, CD_3OD) δ 157.4, 144.6, 139.3, 131.7, 122.0, 110.3, 109.6, 64.9; **IR** (cm^{-1}) 3264, 2959, 2886, 1753, 1499, 1465, 1307, 1263, 1170, 957, 929, 816; **High Resolution MS** (ESI): Calculated for $NaC_8H_7NO_3$ [M+Na]$^+$: 188.0324, found: 188.0310.

5-[{(*tert*-Butyldimethylsilyl)oxy}methyl]benzo[*d*]oxazol-2(3*H*)-one (2l)



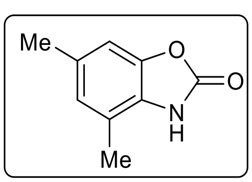
White solid (20 mg, 72 %); **m.p.** 94 – 96 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.11 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 4.74 (s, 2H), 0.94 (s, 9H), 0.11 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 143.0, 138.2, 129.4, 120.5, 109.9, 108.1, 64.8, 26.1, 18.6, -5.1; **IR** (cm^{-1}) 3227, 2954, 2928, 2884, 2856, 1770, 1560, 1465, 1258, 1135, 837; **High Resolution MS** (ESI): Calculated for $NaC_{14}H_{21}NO_3Si$ [M+Na]$^+$: 302.1188, found: 302.1184.

5-(Trifluoromethyl)benzo[*d*]oxazol-2(3*H*)-one (2m)



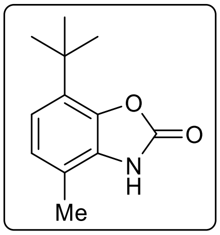
White solid (9.7 mg, 48 %); **m.p.** 160 – 162 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.37 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.8, 146.0, 129.6, 127.1 (q, *J* = 33.0 Hz), 123.9 (q, *J* = 270.5 Hz), 120.7 (q, *J* = 4.1 Hz), 110.6, 107.4 (q, *J* = 3.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.7; **IR** (cm^{-1}) 3259, 2950, 2860, 1791, 1756, 1468, 1323, 1293, 1146, 1119, 939, 915, 881; **High Resolution MS** (ESI): Calculated for $NaC_8H_4F_3NO_2$ [M+Na]$^+$: 226.0092, found: 226.0082; **X-ray crystal structure** is available in the *Appendix II*.

4,6-Dimethylbenzo[*d*]oxazol-2(3*H*)-one (2n)[6]



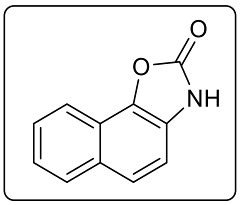
White solid (14 mg, 84 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 6.87 (s, 1H), 6.79 (s, 1H), 2.35 (s, 3H), 2.34(s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.0, 143.9, 132.7, 126.3, 126.1, 120.0, 108.3, 21.5, 16.2; **High Resolution MS** (ESI): Calculated for $NaC_9H_9NO_2$ [M+Na]$^+$: 186.0531, found: 186.0519.

7-(*tert*-Butyl)-4-methylbenzo[*d*]oxazol-2(3*H*)-one (2o)[6]



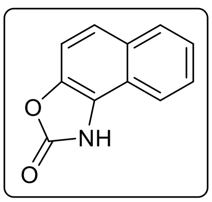
White solid (16 mg, 78 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.00 – 6.88 (m, 2H), 2.35 (s, 3H), 1.42 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 141.6, 131.9, 128.7, 125.1, 119.8, 118.0, 34.0, 29.8, 15.9; **High Resolution MS** (ESI): Calculated for $NaC_{12}H_{15}NO_2$ $[M+Na]^+$: 228.1000, found: 228.0987.

Naphtho[2,1-*d*]oxazol-2(3*H*)-one (2p)[18]



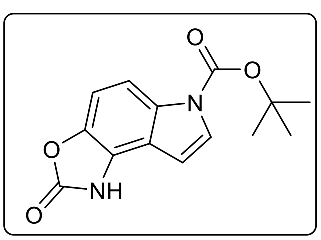
White solid (9.6 mg, 52 %); **^{1}H NMR** (600 MHz, Acetone-d_6) δ 10.47 (s, 1H), 7.97 (m, 2H), 7.77 (d, J = 8.6 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.52 – 7.39 (m, 2H); **^{13}C NMR** (150 MHz, Acetone-d_6) δ 155.4, 138.5, 130.7, 129.6, 128.1, 127.1, 125.3, 125.0, 120.2, 119.6, 111.3; **High Resolution MS** (ESI): Calculated for $NaC_{11}H_7NO_2$ $[M+Na]^+$: 208.0374, found: 208.0363.

Naphtho[1,2-*d*]oxazol-2(1*H*)-one (2q)



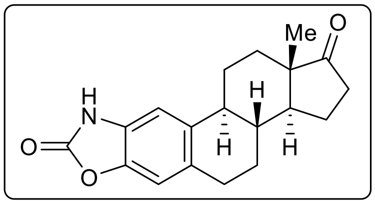
Only the major product of reioisomers is reported. White solid (17 mg, 90 %, **2q**/**2q'**, 5.6:1); **m.p.** 203 – 205 °C; **^{1}H NMR** (600 MHz, Acetone-d_6) δ 11.09 (s, 1H), 8.06 (dd, J = 8.4, 1.1 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.59 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.51 (d, J = 8.8 Hz, 1H), 7.49 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H); **^{13}C NMR** (150 MHz, Acetone-d_6) δ 155.6, 140.9, 131.5, 129.8, 127.6, 125.8, 125.5, 123.2, 121.6, 120.3, 111.3; **IR** (cm^{-1}) 3166, 2961, 2925, 1741, 1459, 1305, 1270, 938, 792, 734, 671, 656; **High Resolution MS** (ESI): Calculated for $NaC_{11}H_7NO_2$ $[M+Na]^+$: 208.0374, found: 208.0370.

***tert*-Butyl 2-oxo-1,2-dihydro-6*H*-oxazolo[4,5-*e*]indole-6-carboxylate (2r)**



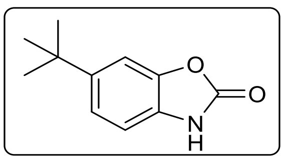
Only the major product of reioisomers is reported. White solid (15 mg, 55 %, **2r**/**2r'**, 1.9:1); **m.p.** 176 – 178 °C; **^{1}H NMR** (400 MHz, Acetone-d_6) δ 10.70 (s, 1H), 7.96 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 3.9 Hz, 1H), 7.23 (d, J = 9.0 Hz, 1H), 6.71 (d, J = 3.8 Hz, 1H), 1.68 (s, 9H); **^{13}C NMR** (150 MHz, Acetone-d_6) δ 155.6, 150.3, 140.1, 133.6, 128.3, 122.9, 115.8, 109.3, 106.9, 103.8, 84.9, 28.2; **IR** (cm^{-1}) 3201, 3152, 3504, 2921, 1736, 1656, 1396, 1335, 1275, 1141, 1116, 978, 950, 801, 753, 710; **High Resolution MS** (ESI): Calculated for $NaC_{14}H_{14}N_2O_4$ $[M+Na]^+$: 297.0851, found: 297.0847.

(3a*S*,3b*R*,10b*S*,12a*S*)-12a-methyl-3,3a,3b,4,5,9,10b,11,12,12a-decahydro-1*H*-cyclopenta[7,8]phenanthro[3,2-*d*]oxazole-1,8(2*H*)-dione (2s)[17]



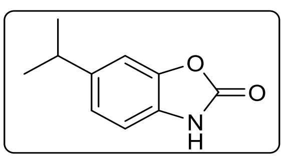
Only the major product of reioisomers is reported. White solid (26 mg, 82 %, **2s**/**2s'**, 3.6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.00 (s, 1H), 6.93 (s, 1H), 3.02 – 2.90 (m, 2H), 2.52 (dd, *J* = 18.9, 8.6 Hz, 1H), 2.40 – 2.26 (m, 2H), 2.23 – 1.94 (m, 4H), 1.71 – 1.39 (m, 6H), 0.92 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 220.8, 155.8, 142.5, 136.1, 131.6, 127.5, 110.3, 106.9, 50.6, 48.1, 44.5, 38.2, 36.0, 31.7, 29.7, 26.5, 26.4, 21.7, 14.0; **High Resolution MS** (ESI): Calculated for $NaC_{19}H_{21}NO_3$ $[M+Na]^+$: 334.1419, found: 334.1411.

6-(*tert*-Butyl)benzo[*d*]oxazol-2(3*H*)-one (2t)[6]



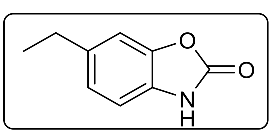
White solid (18 mg, 94 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.26 (s, 1H), 7.20 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 1.33 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.8, 146.9, 144.2, 127.0, 121.1, 109.6, 107.6, 35.0, 31.7; **High Resolution MS** (ESI): Calculated for $NaC_{11}H_{13}NO_2$ $[M+Na]^+$: 214.0844, found: 214.0830.

6-Isopropylbenzo[*d*]oxazol-2(3*H*)-one (2u)



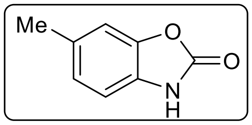
White solid (17 mg, 96 %); **m.p.** 99 – 101 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.10 (s, 1H), 7.03 (m, 2H), 2.94 (hept, *J* = 7.0 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8, 144.5, 144.2, 127.3, 122.4, 109.9, 108.3, 34.3, 24.4; **IR** (cm^{-1}) 3260, 2952, 2878, 1736, 1505, 1490, 1449, 1254, 94, 887, 855; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_{11}NO_2$ $[M+Na]^+$: 200.0687, found: 200.0687.

6-Ethylbenzo[*d*]oxazol-2(3*H*)-one (2v)



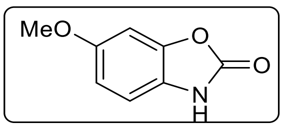
Only the major product of regioisomers is reported. White solid (16 mg, 97 %, C6/C2, 11:1); **m.p.** 107 – 109 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.06 (s, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 7.9, 1.5 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.7, 144.2, 139.6, 127.3, 123.7, 109.9, 109.7, 29.0, 16.0; **IR** (cm^{-1}) 3251, 2960, 2925, 2854, 1733, 1500, 1449, 1399, 1300, 1261, 1177, 1102, 934, 853, 821, 707, 682; **High Resolution MS** (ESI): Calculated for $NaC_9H_9NO_2$ $[M+Na]^+$: 186.0531, found: 186.0519.

6-Methylbenzo[*d*]oxazol-2(3*H*)-one (2w)[6]



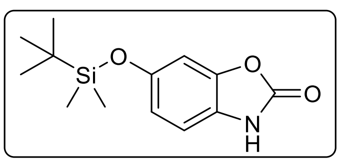
Only the major product of reioisomers is reported. White solid (11 mg, 76 %, C6/C2, 7.5:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.04 (s, 1H), 7.01 – 6.93 (m, 2H), 2.39 (s, 3H); **^{13}C NMR** (200 MHz, $CDCl_3$) δ 156.3, 144.2, 133.0, 127.0, 124.7, 110.9, 109.7, 21.6; **IR** (cm^{-1}) 3337, 3303, 2963, 2928, 2904, 2867, 1655, 1592, 1531, 1518, 1505, 1480, 1448, 1397, 1364, 1292, 1272, 1262, 1219, 1172, 943, 917; **High Resolution MS** (EI): **High Resolution MS** (ESI): Calculated for $NaC_8H_7NO_2$ $[M+Na]^+$: 172.0374, found: 172.0362.

6-Methoxybenzo[*d*]oxazol-2(3*H*)-one (2x)[19]



Only the major product of reioisomers is reported. White solid (15 mg, 90 %, C6/C2, 5.6:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.77 (s, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.4, 156.0, 144.8, 122.8, 110.1, 109.8, 97.7, 56.1; **High Resolution MS** (ESI): Calculated for $NaC_8H_7NO_3$ $[M+Na]^+$: 188.0324, found: 188.0319.

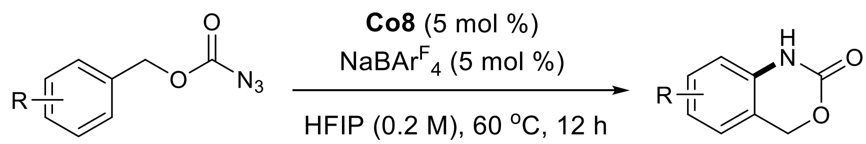
6-{(*tert*-Butyldimethylsilyl)oxy}benzo[*d*]oxazol-2(3*H*)-one (2y)



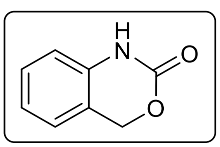
Only the major product of reioisomers is reported. White solid (18 mg, 67 %, C6/C2, 13:1); **m.p.** 139 – 141 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 6.65 (dd, *J* = 8.4, 2.3 Hz, 1H), 0.98 (s, 9H), 0.19 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 151.9, 144.5, 123.5, 115.8, 110.2, 103.4, 25.8, 18.3, -4.4; **IR** (cm^{-1}) 3247, 2929, 2858, 1773, 1736, 1635, 1492, 1471, 1309, 1252, 1181, 1136, 1096, 964, 935; **High Resolution MS** (ESI): Calculated for $NaC_{13}H_{19}NO_3Si$ $[M+Na]^+$: 288.1032, found: 288.1029.

V-2. Procedures for the Co-Catalyzed C(sp^2)−H Amidation of Benzyl Azidoformate

To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added **Co8** (2.2 mg, 5 mol %), sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (4.4 mg, 5 mol %), hexafluoro-2-propanol (0.5 mL) and the reaction mixture was stirred at r.t. for 1 min. To the vial was added azidoformate **3** (x mg, 0.1 mmol) and then sealed with Teflon cap. The reaction mixture was vigorously stirred in a pre-heated heating block at 60 ºC for 12 h, filtered through a pad of silica with EtOAc (10 mL × 5) and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to yield dihydrobenzoxazinone **4** (*n*-hexane/EtOAc, 2:1 to 1:2).

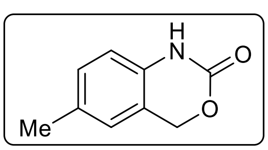


1,4-Dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4a)[20]



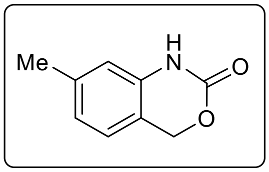
White solid (12 mg, 81 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.27 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.8, 135.7, 129.4, 124.3, 123.5, 118.0, 114.3, 68.8; **High Resolution MS** (ESI): Calculated for $NaC_8H_7NO_2$ [M+Na]$^+$: 172.0374, found: 172.0362.

6-Methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4b)



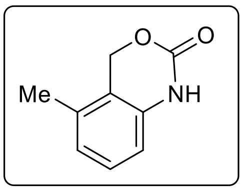
White solid (9.8 mg, 60 %); **m.p.** 139 – 141 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.29 (s, 2H), 2.30 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.1, 133.2, 133.1, 129.8, 124.7, 117.8, 114.3, 68.9, 20.9; **IR** (cm^{-1}) 3099, 2924, 1699, 1511, 1463, 1391, 1296, 1267, 1236; **High Resolution MS** (ESI): Calculated for $NaC_9H_9NO_2$ [M+Na]$^+$: 186.0531, found: 186.0529; **X-ray crystal structure** is available in the *Appendix II*.

7-Methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4c)



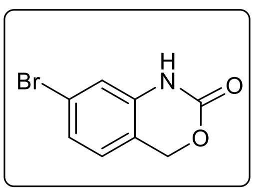
White solid (7.6mg, 47 %); **m.p.** 119 – 121 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.65 (s, 1H), 5.29 (s, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 139.7, 135.6, 124.2 (2C), 115.2, 114.7, 68.8, 21.4; **IR** (cm^{-1}) 3262, 1719, 1630, 1601, 1521, 1486, 1462, 1380, 1287, 1216, 1166, 1052, 886, 768; **High Resolution MS** (ESI): Calculated for $NaC_9H_9NO_2$ $[M+Na]^+$: 186.0531, found: 186.0529.

5-methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4c')



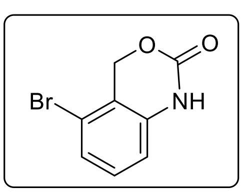
White solid (5.4 mg, 33 %); **m.p.** 148 – 150 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.34 (s, 2H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 135.4, 134.0, 129.0, 125.3, 116.5, 111.8, 67.0, 18.1; **IR** (cm^{-1}) 3093, 1702, 1599, 1464, 1419, 1381, 1283, 1210, 1062, 884, 777; **High Resolution MS** (ESI): Calculated for $NaC_9H_9NO_2$ $[M+Na]^+$: 186.0531, found: 186.0532.

7-Bromo-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4d)



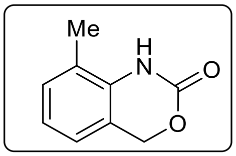
White solid (4.6 mg, 20 %); **m.p.** 156 – 158 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.19 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.03 (d, *J* = 1.8 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.28 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 137.0, 126.5, 125.8, 122.9, 117.3, 117.0, 68.5; **IR** (cm^{-1}) 3151, 3090, 3062, 2983, 2929, 1705, 1584, 1476, 1451, 1404, 1289, 1195, 1063, 947, 778, 751, 734, 694, 655, 576; **High Resolution MS** (ESI): Calculated for $NaC_8H_6BrNO_2$ $[M+Na]^+$: 249.9480, found: 249.9478.

5-bromo-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4d')



White solid (4.1 mg, 18 %); **m.p.** 189 – 191 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.24 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.13 (tt, *J* = 8.0, 0.7 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.0 Hz, 1H), 5.40 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 136.7, 130.5, 127.3, 119.8, 117.8, 113.3, 69.2; **IR** (cm^{-1}) 3141, 3075, 1710, 1596, 1493, 1457, 1429, 1374, 1304, 1243, 1212, 1059, 888, 853, 818, 760, 728, 603; **High Resolution MS** (ESI): Calculated for $NaC_8H_6BrNO_2$ $[M+Na]^+$: 249.9480, found: 249.9477.

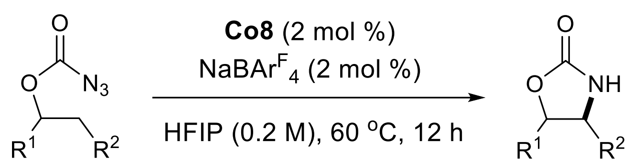
8-Methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4e)[21]



White solid (4.7 mg, 29 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.12 (t, *J* = 4.5 Hz, 1H), 6.97 (m, 2H), 5.29 (s, 2H), 2.27 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.1, 134.1, 130.7, 123.1, 122.2, 122.1, 118.0, 68.8, 16.2; **High Resolution MS** (ESI): Calculated for $NaC_9H_9NO_2$ $[M+Na]^+$: 186.0531, found: 186.0525.

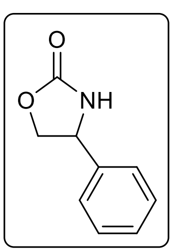
V-3. Procedures for the Co-Catalyzed C(sp^3)−H Amidation of Azidoformate

To an oven-dried screwed vial equipped with a spinvane triangular-shaped Teflon stirbar were added **Co8** (0.9 mg, 2.0 mol %), sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (1.8 mg, 2.0 mol %), hexafluoro-2-propanol (0.5 mL) and the reaction mixture was stirred at r.t. for 1 min. To the vial was added azidoformate **5** and **7** (x mg, 0.1 mmol), then sealed with Teflon cap. The reaction mixture was vigorously stirred in a pre-heated heating block at 60 ºC for 12 h, filtered through a pad of silica with EtOAc (10 mL × 5) and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to yield oxazolidinone **6** and **8** (*n*-hexane/EtOAc, 2:1 to 1:2).



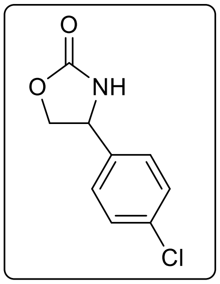
5, **7** → **6**, **8**

4-Phenyloxazolidin-2-one (6a)[22]



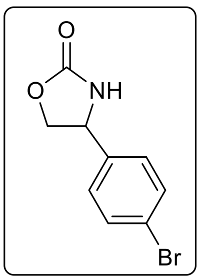
White solid (15 mg, 90 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.28 (m, 3H), 6.53 (s, 1H), 4.95 (t, *J* = 7.9 Hz, 1H), 4.71 (t, *J* = 8.7 Hz, 1H), 4.15 (dd, *J* = 8.6, 7.0 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.1, 139.7, 129.3, 128.8, 126.1, 72.6, 56.5; **High Resolution MS** (ESI): Calculated for $NaC_9H_9NO_2$ $[M+Na]^+$: 186.0531, found: 186.0526; **X-ray crystal structure** is available in the *Appendix II*.

4-(4-Chlorophenyl)oxazolidin-2-one (6b)[23]



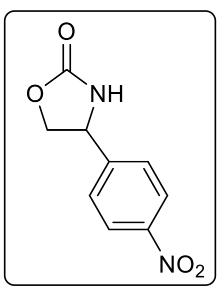
White solid (19 mg, 95 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.25 (s, 1H), 4.94 (t, *J* = 7.8 Hz, 1H), 4.72 (t, *J* = 8.7 Hz, 1H), 4.13 (dd, *J* = 8.7, 6.8 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.9, 138.1, 134.9, 129.6, 127.5, 72.5, 55.9; **High Resolution MS** (ESI): Calculated for $NaC_9H_8ClNO_2$ $[M+Na]^+$: 220.0141, found: 220.0137.

4-(4-Bromophenyl)oxazolidin-2-one (6c)



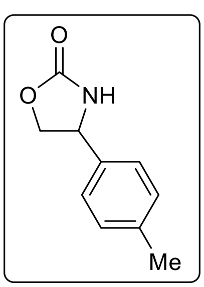
White solid (15 mg, 63 %); **m.p.** 102 – 104 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 6.18 (s, 1H), 4.93 (t, *J* = 7.9 Hz, 1H), 4.72 (t, *J* = 8.7 Hz, 1H), 4.13 (t, *J* = 7.7 Hz, 1H); **^{13}C NMR** δ 159.8, 138.7, 132.5, 127.9, 123.0, 72.4, 56.0; **IR** (cm^{-1}) 3230, 3134, 2969, 2911, 1773, 1743, 1708, 1487, 1472, 1420, 1399, 1238, 1097, 1035, 1008, 964, 923, 822; **High Resolution MS** (ESI): Calculated for $NaC_9H_8BrNO_2$ $[M+Na]^+$: 263.9636, found: 263.9639.

4-(4-Nitrophenyl)oxazolidin-2-one (6d)



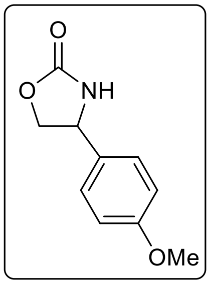
White solid (15 mg, 74 %); **m.p.** 104 – 106 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 5.87 (s, 1H), 5.10 (t, *J* = 7.8 Hz, 1H), 4.82 (t, *J* = 8.8 Hz, 1H), 4.18 (dd, *J* = 8.8, 6.7 Hz, 1H); **^{13}C NMR** (175 MHz, $CDCl_3$) δ 159.0, 148.3, 146.4, 127.0, 124.6, 71.8, 55.7; **IR** (cm^{-1}) 3279, 2918, 2851, 1748, 1601, 1519, 1346, 1236, 1097, 1037, 960, 924, 857;**High Resolution MS** (ESI): Calculated for $NaC_9H_8N_2O_4$ $[M+Na]^+$: 231.0382, found: 231.0368.

4-(*p*-Tolyl)oxazolidin-2-one (6e)[23]



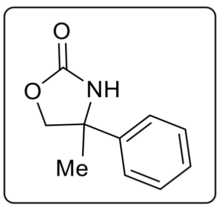
White solid (14 mg, 81 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 5.97 (s, 1H), 5.01 – 4.84 (m, 1H), 4.71 (t, *J* = 8.6 Hz, 1H), 4.16 (dd, *J* = 8.6, 7.0 Hz, 1H), 2.35 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.9, 138.9, 136.6, 130.0, 126.1, 72.8, 56.3, 21.2; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_{11}NO_2$ $[M+Na]^+$: 200.0687, found: 200.0690.

4-(4-Methoxyphenyl)oxazolidin-2-one (6f)[23]



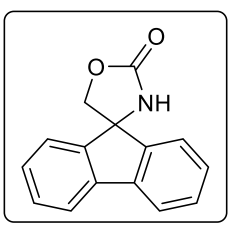
White solid (17 mg, 89 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 2H), 7.00 – 6.80 (m, 2H), 5.95 (s, 1H), 4.90 (t, *J* = 7.8 Hz, 1H), 4.69 (t, *J* = 8.6 Hz, 1H), 4.15 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 159.8, 131.5, 127.5, 114.6, 72.9, 56.1, 55.5; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_{11}NO_3$ $[M+Na]^+$: 216.0637, found: 216.0632.

4-Methyl-4-phenyloxazolidin-2-one (8a)[13]



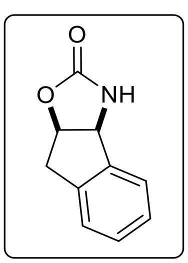
White solid (16 mg, 91 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.34 – 7.29 (m, 1H), 6.57 (s, 1H), 4.39 (d, *J* = 8.4 Hz, 1H), 4.35 (d, *J* = 8.4 Hz, 1H), 1.75 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.52, 143.67, 129.11, 128.03, 124.71, 78.20, 77.48, 77.16, 76.84, 60.64, 28.00; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_{11}NO_2$ $[M+Na]^+$: 200.0687, found: 200.0673.

Spiro[fluorene-9,4'-oxazolidin]-2'-one (8b)[24]



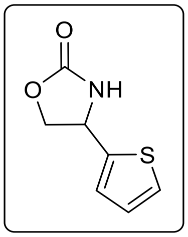
White solid (23 mg, 99 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 5.14 (s, 1H), 4.63 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) 159.3, 145.3, 139.7, 130.2, 128.9, 123.9, 120.5, 75.7, 67.0; **High Resolution MS** (ESI): Calculated for $NaC_{15}H_{11}NO_2$ $[M+Na]^+$: 260.0687, found: 260.0680.

(3a*S,8a*R**)-3,3a,8,8a-Tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one (8c)**[23]



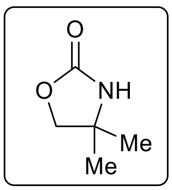
White solid (11 mg, 60 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 4H), 6.73 (s, 1H), 5.40 (td, *J* = 6.8, 1.8 Hz, 1H), 5.16 (d, *J* = 7.2 Hz, 1H), 3.41 (dd, *J* = 17.9, 6.4 Hz, 1H), 3.34 (d, *J* = 18.0, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.9, 140.4, 139.8, 129.5, 128.0, 125.7, 125.0, 80.7, 61.4, 39.0; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_9NO_2$ $[M+Na]^+$: 198.0531, found: 198.0522.

4-(Thiophen-2-yl)oxazolidin-2-one (8d)[23]



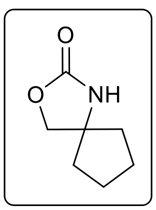
White solid (8.8 mg, 52 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.06 (dt, *J* = 3.3, 1.1 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.66 (s, 1H), 5.27 – 5.21 (m, 1H), 4.73 (t, *J* = 8.6 Hz, 1H), 4.30 (dd, *J* = 8.7, 6.8 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.8, 143.0, 127.4, 126.3, 125.6, 72.7, 52.4; **High Resolution MS** (ESI): Calculated for $NaC_7H_7NO_2S$ $[M+Na]^+$: 192.0095, found: 192.0083.

4,4-Dimethyloxazolidin-2-one (8e)[24]



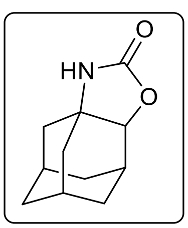
Colorless oil (5.0 mg, 43 %); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.86 (s, 1H), 4.08 (s, 2H), 1.36 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.2, 77.1, 55.3, 27.7; **High Resolution MS** (ESI): Calculated for $NaC_5H_9NO_2$ $[M+Na]^+$: 138.0531, found: 138.0534.

3-Oxa-1-azaspiro[4.4]nonan-2-one (8f)



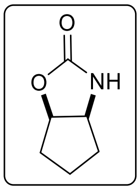
White solid (12 mg, 86 %); **m.p.** 43 – 45 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.31 (s, 1H), 4.22 (s, 2H), 1.85 (ddtd, *J* = 13.0, 11.3, 4.1, 2.2 Hz, 2H), 1.79 – 1.69 (m, 4H), 1.65 (dtd, *J* = 11.4, 7.8, 7.2, 5.2 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5, 76.3, 65.4, 38.6, 23.4; **IR** (cm^{-1}) 3203, 3129, 2957, 2898, 2875, 1736, 1381, 1272, 1224, 1207, 1047, 943, 918, 771, 677; **High Resolution MS** (ESI): Calculated for $NaC_7H_{11}NO_2$ $[M+Na]^+$: 164.0687, found: 164.0676.

(3a*s*,5*R*,7*S*,9*s*)-hexahydro-4*H*-3a,7:5,9-dimethanocycloocta[*d*]oxazol-2(3*H*)-one (8g)



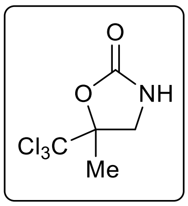
White solid (16 mg, 82 %); **m.p.** 113 – 115 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.07 (s, 1H), 4.15 (s, 1H), 2.43 (q, *J* = 3.3 Hz, 1H), 2.16 (p, *J* = 3.3 Hz, 1H), 2.11 – 2.01 (m, 1H), 1.97 – 1.82 (m, 5H), 1.80 – 1.56 (m, 5H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.9, 82.3, 37.3, 36.4, 31.9, 31.6, 27.1, 26.9; **IR** (cm^{-1}) 3299, 2923, 2858, 1754, 1730, 1278, 1243, 1218, 1036, 925, 906, 801, 777, 663; **High Resolution MS** (ESI): Calculated for $NaC_{11}H_{15}NO_2$ $[M+Na]^+$: 216.1000, found: 216.0994.

(3a*S,6a*R**)-Hexahydro-2*H*-cyclopenta[*d*]oxazol-2-one (8h)**[23]



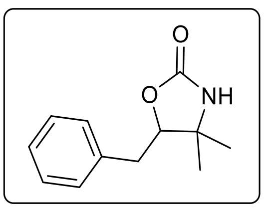
Colorless oil (5.1 mg, 40 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.31 (s, 1H), 5.07 (t, *J* = 6.5 Hz, 1H), 4.27 (t, *J* = 6.7 Hz, 1H), 2.17 – 2.05 (m, 1H), 1.87 – 1.70 (m, 3H), 1.69 – 1.59 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.8, 82.5, 56.7, 34.8, 34.0, 22.2; **High Resolution MS** (ESI): Calculated for $NaC_6H_9NO_2$ $[M+Na]^+$: 150.0531, found: 150.0526.

5-Methyl-5-(trichloromethyl)oxazolidin-2-one (8i)



White solid (13 mg, 60 %); **m.p.** 154 – 156 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.15 (s, 1H), 4.01 (d, *J* = 9.7 Hz, 1H), 3.54 (d, *J* = 10.2 Hz, 1H), 1.89 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.6, 103.2, 88.7, 49.3, 23.4; **IR** (cm^{-1}) 3226, 3161, 2917, 1749, 1488, 1370, 1284, 1186, 1127, 1096; **High Resolution MS** (ESI): Calculated for $NaC_5H_6Cl_3NO_2$ $[M+Na]^+$: 239.9362, found: 239.9360.

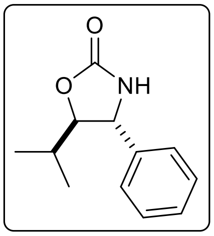
5-Benzyl-4,4-dimethyloxazolidin-2-one (8j)



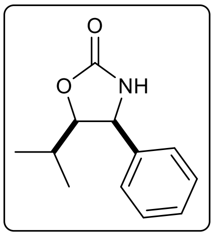
White solid (7.2 mg, 35 %); **m.p.** 123 – 125 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.24 (d, *J* = 7.2 Hz, 1H), 5.65 (s, 1H), 4.41 (dd, *J* = 9.4, 4.3 Hz, 1H), 3.04 (dd, *J* = 14.5, 9.4 Hz, 1H), 2.81 (dd, *J* = 14.5, 4.3 Hz, 1H), 1.31 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.6, 136.8, 129.3, 128.8, 127.0, 86.6, 58.2, 35.6, 27.2, 23.1; **IR** (cm^{-1}) 3274, 1740, 1709, 1371, 1304, 1208, 1100, 1072, 1012, 986, 697; **High Resolution MS** (ESI): Calculated for $NaC_{12}H_{15}NO_2$ $[M+Na]^+$: 228.1000, found: 228.1004.

5-Isopropyl-4-phenyloxazolidin-2-one (8j')

White solid (6.6 mg, 32 %, *anti*/*syn*, 1.4:1); **m.p.** 113 – 115 ºC; **IR** (cm^{-1}) 3232, 3129, 2963, 1728, 1456, 1388, 1230, 1072, 1020, 1007, 960, 753, 732, 696; **High Resolution MS** (ESI): Calculated for $NaC_{12}H_{15}NO_2$ $[M+Na]^+$: 228.1000, found: 228.1001; Diastereoselectivity was determined by the ^{1}H NMR analysis from crude mixture of isomers. Diastereomers were confirmed by vicinal coupling constant and ^{1}H spectral data is matched with the reported one.



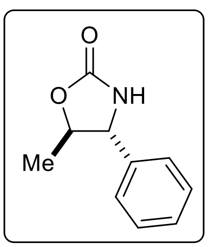
major isomer (***anti*-5-Isopropyl-4-phenyloxazolidin-2-one**)[25]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.23 (m, 5H), 6.36 (s, 1H), 4.58 (d, *J* = 5.9 Hz, 1H), 4.16 (t, *J* = 5.8 Hz, 1H), 1.99 (dq, *J* = 13.6, 6.6 Hz, 1H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H).



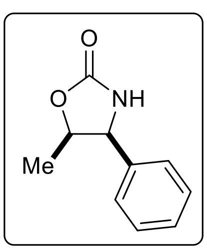
minor isomer (***syn*-5-Isopropyl-4-phenyloxazolidin-2-one**)[25-26]: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.23 (m, 5H), 6.19 (s, 1H), 4.74 (d, *J* = 7.2 Hz, 1H), 4.37 (dd, *J* = 10.1, 7.2 Hz, 1H), 1.52 (dp, *J* = 10.1, 6.5 Hz, 1H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.66 (d, *J* = 6.5 Hz, 3H).

5-Methyl-4-phenyloxazolidin-2-one (8k)

White solid (15 mg, 86 %, *anti*/*syn*, 2.3:1); Diastereoselectivity was determined by the ^{1}H NMR analysis from crude mixture of both isomers. Diastereomers were confirmed by the reported ^{1}H, ^{13}C NMR spectral data.

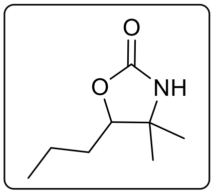


major isomer (*anti*-5-Methyl-4-phenyloxazolidin-2-one)[23]: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.33 (m, 3H), 6.47 (s, 1H), 4.45 (d, *J* = 7.1 Hz, 1H), 4.40 (q, *J* = 6.4 Hz, 1H), 1.48 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.4, 138.8, 129.1, 128.7, 126.2, 81.7, 64.0, 19.3; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_{11}NO_2$ $[M+Na]^+$: 200.0687, found: 200.0679; **X-ray crystal structure** is available in the *Appendix II*.



minor isomer (*syn*-5-Methyl-4-phenyloxazolidin-2-one)[27]: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 3H), 7.22 (d, *J* = 7.3 Hz, 2H), 6.19 (s, 1H), 5.00 (t, *J* = 7.1 Hz, 1H), 4.92 (d, *J* = 8.1 Hz, 1H), 0.91 (dd, *J* = 6.6, 2.3 Hz, 3H); **^{13}C NMR** (200 MHz, $CDCl_3$) δ 159.9, 136.7, 128.9, 128.8, 127.0, 77.3, 60.0, 16.7; **High Resolution MS** (ESI): Calculated for $NaC_{10}H_{11}NO_2$ $[M+Na]^+$: 200.0687, found: 200.0691.

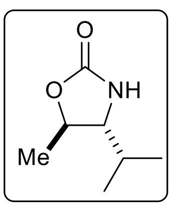
4,4-Dimethyl-5-propyloxazolidin-2-one (8l)



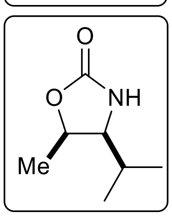
Colorless oil (9.4 mg, 60 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.76 (s, 1H), 4.14 (dd, J = 10.1, 3.1 Hz, 1H), 1.69 – 1.56 (m, 2H), 1.49 – 1.36 (m, 2H), 1.30 (s, 3H), 1.18 (s, 3H), 0.97 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.0, 86.1, 57.9, 31.3, 27.3, 22.9, 19.7, 14.0; **IR** (cm^{-1}) 3272, 2962, 2936, 2875, 1740, 1466, 1372, 1296, 1212, 1074, 985, 774; **High Resolution MS** (ESI): Calculated for $NaC_8H_{15}NO_2$ [M+Na]$^+$: 180.1000, found: 180.0999.

4-Isopropyl-5-methyloxazolidin-2-one (8m)

Colorless oil (3.7 mg, 26 %, *anti*/*syn*, 4.2:1); **IR** (cm^{-1}) 3268, 2965, 1743, 1385, 1240, 1049, 772; **High Resolution MS** (ESI): Calculated for $NaC_7H_{13}NO_2$ [M+Na]$^+$: 166.0844, found: 166.0832.
Diastereoselectivity was determined by the ^{1}H NMR analysis from crude mixture of isomers.
Diastereomers were confirmed by vicinal coupling constant[28] and ^{1}H NMR spectral data is matched with the reported one.

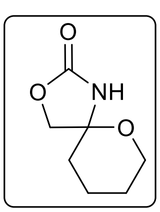


major isomer (*anti*-4-Isopropyl-5-methyloxazolidin-2-one)[25]: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.52 (s, 1H), 4.39 (p, J = 6.1 Hz, 1H), 3.13 (dd, J = 6.6, 5.3 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.41 (d, J = 6.4 Hz, 3H), 0.94 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (200 MHz, $CDCl_3$) δ 159.6, 76.8, 65.3, 32.3, 21.5, 17.9, 17.9.



minor isomer (*syn*-4-Isopropyl-5-methyloxazolidin-2-one)[25]: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.37 (s, 1H), 4.73 (p, J = 6.8 Hz, 1H), 3.53 (t, J = 7.7 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.36 (d, J = 6.5 Hz, 3H), 0.99 (d, J = 6.5 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (200 MHz, $CDCl_3$) δ 160.3, 76.4, 62.2, 27.7, 19.7, 19.2, 14.5.

3,6-Dioxa-1-azaspiro[4.5]decan-2-one (8n)[23]



White solid (9.7 mg, 62 %); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 4.31 (d, J = 9.4 Hz, 1H), 4.10 (d, J = 9.3 Hz, 1H), 3.75 (tdd, J = 12.2, 7.8, 5.1 Hz, 2H), 1.85 – 1.69 (m, 4H), 1.59 (h, J = 4.2, 3.4 Hz, 2H);**^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.6, 87.2, 76.2, 63.2, 33.7, 24.7, 20.2; **High Resolution MS** (ESI): Calculated for $NaC_7H_{11}NO_3$ [M+Na]$^+$: 180.0637, found: 180.0633; **X-ray crystal structure** is available in the *Appendix II*.

VI. Computational Data

VI - 1. General Details

Computations were performed using density functional theory[29] (DFT) implemented in Jaguar 9.1 suite of program.[30] Geometry optimizations were performed with B3LYP[31-32] levels of theory with Grimme D3 correction[33] and 6-31G** basis set.[34] For the Co metal center, Los Alamos LACVP**[35-37] basis set which includes effective core potentials was applied. After the geometry optimizations, , the single point energies were re-evaluated using triple-ζ quality of basis set, cc-pVTZ(-f)[38], where Co center was evaluated with LACV3P** basis set. Vibrational frequencies were calculated at the same level as the geometry optimizations to derive zero-point energies and entropy correction terms. Solvation correction energies were evaluated from the self-consistent reaction field (SCRF) approximations,[39-41] which is the solution for the linearized Poisson-Boltzmann equations with the proper dielectric constants (ε=17.8 for hexafluoro-2-propanol). Using energy components collected above, the solution phase Gibbs free energies were computed as follows:

$$G(Sol) = G(gas) + G^{solv} \quad (1)$$

$$G(gas) = H(gas) - TS(gas) \quad (2)$$

$$H(Gas) = E(SCF) + ZPE \quad (3)$$

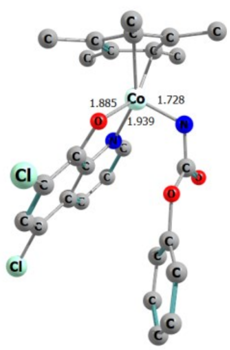
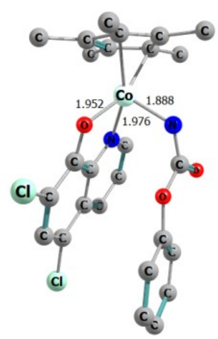
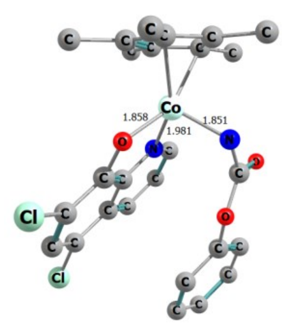
$$\Delta G(Sol) = \Sigma G(Sol) \text{ for products} - \Sigma G(Sol) \text{ for reactants} \quad (4)$$

G(Sol) is the solvation corrected Gibbs free energy; G(gas) is the gas phase free energy; H(gas) is the enthalpy in the gas phase; T is the temperature (313.15 K); S(gas) is the entropy in the gas phase; E(SCF) is the electronic energy converged from the self-consistent field method; ZPE is the vibrational zero-point energy; and S for the vibrational entropy correction. Note that here entropy refers specifically to the vibrational/rotational/translational entropy of the solute(s). The solvent entropies are implicitly included in the continuum model.

VI – 2. Spin States of Co-Nitrenoid Species

The calculations were conducted using the optimized Cp*Co(III)(LX) catalyst **Co8** and **1a** as a model substrate. Since the first-row transition metal complexes are capable to have multiple spin states, we considered three representative spin states for the presumed cobalt-nitrenoid species, which are singlet, triplet and open-shell singlet configurations. Structures of Co-nitrenoid species (**Co-1a**) with three different spin states and their relative Gibbs free energies are enumerated in **Table S3**. Based on the Gibbs energy calculations, it was found that the ground state of **Co-1a** is the triplet state, and therefore, we followed the triplet energy surface for further computational studies.

Table S3. Three representative spin states of **Co8**-nitrenoid species **Co-1a**. All hydrogens are omitted for clarity. Bond lengths in Å.

^{1}**Co-1a**	^{3}**Co-1a**	^{OS}**Co-1a**
(6.92 kcal/mol)	(0.00 kcal/mol)	(1.18 kcal/mol)
		

VI – 3. Gibbs energy profiles with *meta*-substituted phenyl azidoformates

Energy diagrams for the C(sp^2)−H amidation reactions with *meta*-substituted phenyl azidoformates are shown in **Figure S1**. After the generation of cobalt-nitrenoid species, subsequent C−N formation step takes place with low barriers. For substrate **1t** carrying a *tert*-butyl group, the transition state of C6-amidation process was located at 11.5 kcal/mol, which was around 2.1 kcal/mol lower than that of C2-amidation (13.6 kcal/mol). For **1w** bearing a methyl group at the *meta* position, the transition state of C6-amidation process was calculated to be 7.4 kcal/mol, which was around 1.2 kcal/mol more stable than that of C2-amidation (8.6 kcal/mol). For all cases, the overall process is highly exergonic to form zwitterionic intermediates, thus an irreversible path was suggested in the current C(sp^2)−H amidation reactions.

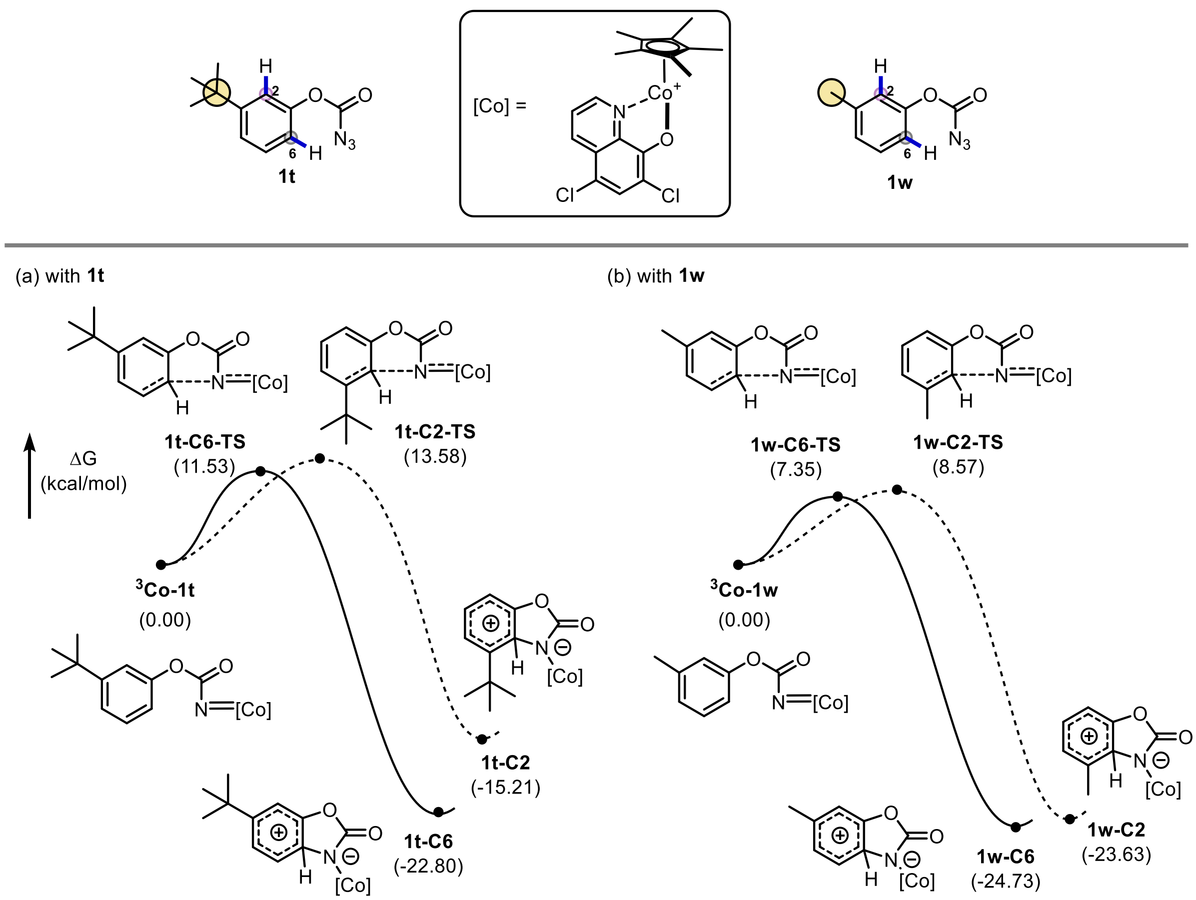


Figure S1. Energy diagrams for the **Co8**-catalyzed amidation of *meta*-substituted phenyl azidoformates

VI – 4. Energies, Coordinates, and Vibrational Frequencies of Optimized Structures

Table S4. Computed energies of the optimized geometries

	E(SCF)/(eV)	ZPE/(kcal/mol)	S(gas)/(cal/mol·K)	G(solv)/(kcal/mol)
	cc-pVTZ(-f)/LACV3P**	6-31G**/LACVP**	6-31G**/LACVP**	6-31G**/LACVP**
^{1}Co-1a	-65477.090	278.96	209.45	-44.01
^{3}Co-1a	-65477.336	278.23	209.67	-43.28
^{OS}Co-1a	-65477.441	278.19	205.64	-43.26
^{3}Co-1t	-69758.352	348.22	237.30	-44.68
1t-C6-TS	-69758.008	347.33	234.32	-41.13
1t-C6	-69759.500	348.80	235.33	-42.20
1t-C2-TS	-69758.008	347.76	229.57	-41.00
1t-C2	-69759.336	349.10	224.49	-42.09
^{3}Co-1w	-66547.539	295.12	222.53	-45.62
1w-C6-TS	-66547.383	293.56	215.97	-42.36
1w-C6	-66548.773	295.29	218.89	-43.20
1w-C2-TS	-66547.328	293.56	217.56	-41.91
1w-C2	-66548.828	296.65	215.68	-43.20

Table S5. Cartesian coordinates of the optimized geometries

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^{1}Co-1a

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Co	2.256763697	-0.703122497	-0.031859979
C	3.681333303	-0.594080269	-1.609551430
C	4.279972076	-1.369369507	-0.555850387
C	4.300984383	-0.552411616	0.610058844
C	3.856121302	0.791672528	0.237008572
C	3.490342617	0.767015874	-1.122814894
C	3.487975121	-1.071552157	-3.011671782
H	4.442047119	-1.024315000	-3.552034378
H	2.776655674	-0.452369869	-3.561198711
H	3.142517567	-2.107546091	-3.031123877
C	4.674796581	-2.800026178	-0.676313341
H	5.316391468	-2.942990065	-1.551207423
H	3.779538631	-3.420037270	-0.803321481
H	5.210594654	-3.147650242	0.207760468
C	4.715451241	-0.927297711	1.991433382
H	3.918488979	-0.663142562	2.693860531
H	5.615625381	-0.371840239	2.279648542
H	4.918721676	-1.994726777	2.082449436
C	3.787484646	1.934097409	1.191290498
H	4.797128677	2.235490799	1.492922783
H	3.244761229	1.629842997	2.091299534
H	3.288492203	2.802091599	0.757838070
C	2.990446091	1.913073301	-1.940173984
H	3.822233438	2.359091997	-2.497984886
H	2.547349930	2.690928221	-1.316152334
H	2.242532730	1.595149159	-2.669624090
C	0.527729273	0.369738996	1.704561234
C	-0.126112193	0.540847957	0.460153341
N	0.585632443	0.086069293	-0.619361639
C	0.052040100	0.115512602	-1.834417939
C	-1.222997546	0.668500900	-2.056713820
C	-1.958508015	1.150664806	-0.990476191
C	-1.433200717	1.083426952	0.321665287
H	0.631414652	-0.327263355	-2.634923697
H	-1.619375467	0.691775441	-3.065340281

O	-0.141779974	-2.562265635	1.160645485
C	0.375763834	-2.622950554	-0.066414267
O	-0.182522148	-2.875321865	-1.123929381
N	1.722378731	-2.344075680	-0.115917958
C	-1.453171849	1.342708349	2.741705656
H	-1.961459517	1.648448110	3.648945093
O	1.718326211	-0.204737082	1.704856277
C	-0.155673087	0.794801354	2.841697693
Cl	0.587540686	0.613151252	4.400207520
C	-2.083764791	1.484112859	1.520999193
Cl	-3.694944143	2.152763844	1.455718637
H	-2.949168205	1.564778090	-1.145481467
C	-1.519051671	-2.755858421	1.402227640
C	-2.504192829	-2.270236969	0.543270469
C	-1.822021961	-3.363662481	2.614801168
C	-3.838864565	-2.412729502	0.926478446
C	-3.160926342	-3.497242451	2.979499102
C	-4.170413971	-3.023137093	2.137196541
H	-2.239185810	-1.800166845	-0.393877387
H	-1.017685652	-3.711203575	3.254334927
H	-4.620970726	-2.042222500	0.270950437
H	-3.413353205	-3.968546629	3.924149275
H	-5.211605072	-3.127700567	2.425749779

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^{3}Co-1a

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Co	2.281734228	-0.645896256	0.113064915
C	3.386627674	-0.629951119	-1.700895190
C	4.214530945	-1.299757719	-0.724973500
C	4.401212692	-0.401204139	0.365349084
C	3.824292660	0.884235024	-0.001229265
C	3.213942766	0.745350480	-1.274597764
C	2.917641640	-1.242977858	-2.981454134
H	3.776383638	-1.567595720	-3.580024004
H	2.346712828	-0.534336448	-3.583766937
H	2.290627956	-2.118309736	-2.784050465
C	4.660757065	-2.714361191	-0.820775092
H	4.966327667	-2.950705767	-1.843870282
H	3.823290110	-3.374387503	-0.555980206
H	5.492048740	-2.922173262	-0.145575300
C	5.066013336	-0.673545778	1.671943903
H	4.396482468	-0.386399120	2.489439011
H	5.984015465	-0.081731103	1.765242934
H	5.316483021	-1.728716731	1.786877155
C	3.855183363	2.090590715	0.874884307
H	4.887014866	2.436498880	1.003452539
H	3.462160826	1.839621544	1.865046024
H	3.269468546	2.913241148	0.462409288
C	2.523739576	1.824280024	-2.044708967
H	3.251653194	2.343802929	-2.679259062
H	2.067498446	2.563127279	-1.383251786
H	1.745644093	1.426476359	-2.698048592
C	0.716397583	0.344281912	2.038686752
C	-0.132518142	0.416101247	0.900354266
N	0.444073439	-0.009746558	-0.264561564
C	-0.272400886	-0.029396290	-1.384754181
C	-1.606354833	0.416658998	-1.412864923
C	-2.206985712	0.862623155	-0.251759827
C	-1.474626422	0.867451727	0.958389819
H	0.206745058	-0.442876309	-2.262969732
H	-2.154257298	0.382070661	-2.347309589

O	-0.299535662	-2.831104279	0.759651184
C	0.546193480	-2.751812220	-0.282564282
O	0.288408548	-2.922927618	-1.467512012
N	1.822523355	-2.439296722	0.120774619
C	-1.144126892	1.211892366	3.354710579
H	-1.529261351	1.517877102	4.320487499
O	1.942067504	-0.108398974	1.858750463
C	0.191133186	0.761649013	3.263148069
Cl	1.182928562	0.714974999	4.682056427
C	-1.959709048	1.262102246	2.241248846
Cl	-3.606252670	1.801823139	2.413445234
H	-3.240775108	1.189352632	-0.252883881
C	-1.695632577	-2.744997978	0.641760290
C	-2.422519207	-3.120264769	-0.489598066
C	-2.319956541	-2.223830938	1.775556684
C	-3.806394815	-2.925025463	-0.476756006
C	-3.701274633	-2.042347193	1.769576907
C	-4.447422981	-2.382686377	0.637977600
H	-1.925223231	-3.546025038	-1.348885179
H	-1.714767814	-1.957252264	2.635474682
H	-4.385192871	-3.209863901	-1.350455880
H	-4.191795349	-1.630698800	2.646160841
H	-5.523437500	-2.238037348	0.630947351

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^{OS}Co-1a

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Co	2.414805412	-0.416619539	-0.033876460
C	3.696665049	-0.522038877	-1.668464780
C	4.309198380	-1.289961100	-0.614043891
C	4.443474293	-0.439585805	0.517820776
C	4.053422928	0.905502617	0.122503720
C	3.630616665	0.856622458	-1.233151674
C	3.373633862	-1.062420011	-3.026602745
H	4.293347359	-1.223120451	-3.601464033
H	2.748617172	-0.377111584	-3.603784323
H	2.853202581	-2.020165205	-2.946119547
C	4.610577106	-2.746027708	-0.696141481
H	5.129666328	-2.970237017	-1.632988811
H	3.673350573	-3.313819885	-0.673204005
H	5.233260155	-3.076657534	0.136074334
C	4.913902283	-0.812664211	1.886849642
H	4.216551781	-0.437445283	2.641131878
H	5.898081303	-0.373757213	2.087142706
H	4.987096310	-1.894507051	2.004784584
C	4.111391068	2.098860025	1.022464037
H	5.149740219	2.428711653	1.144958377
H	3.720629692	1.853079915	2.013041973
H	3.538336754	2.938778639	0.624786496
C	3.175444126	2.016282797	-2.060240269
H	4.030027866	2.434714079	-2.604906797
H	2.749664783	2.811606646	-1.445467472
H	2.432209492	1.723126173	-2.804596186
C	0.574722588	0.334472835	1.797311544
C	-0.120388672	0.512025893	0.538727999
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C	0.089375503	0.373117089	-1.766723275
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C	-2.068768978	0.891298115	-0.825419307
C	-1.502357602	0.778251767	0.463130236
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H	-1.676771045	0.753485858	-2.936416626

O	-0.272821635	-2.381992102	1.073803425
C	0.397576779	-2.405686617	-0.139470175
O	-0.126848131	-2.610365868	-1.224263906
N	1.721469998	-2.171396255	0.038780291
C	-1.557738662	0.741817176	2.933694601
H	-2.128743887	0.812341690	3.851795197
O	1.805947065	0.013826639	1.769670963
C	-0.188322082	0.495095879	2.995454073
Cl	0.593234360	0.287282348	4.513738155
C	-2.213309526	0.866223216	1.709071755
Cl	-3.919797421	1.105240226	1.708348751
H	-3.126474857	1.102836967	-0.934607625
C	-1.643880844	-2.517938852	1.234454036
C	-2.596931934	-2.457686424	0.209075734
C	-2.034618139	-2.649969101	2.574644089
C	-3.947927713	-2.527229071	0.552417815
C	-3.386112213	-2.715482950	2.895220518
C	-4.350856304	-2.649313688	1.884340286
H	-2.283877373	-2.380579472	-0.820920765
H	-1.265199065	-2.696681738	3.338409185
H	-4.693331242	-2.485704184	-0.236286819
H	-3.687560320	-2.820814610	3.932886362
H	-5.406141758	-2.702041864	2.132893801

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^{3}Co-1t

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Co	2.336053133	-0.892724752	0.075748809
C	3.624179602	-0.908998370	-1.820752025
C	4.319440365	-1.503809214	-0.641781390
C	4.511508942	-0.484440088	0.322387516
C	3.857586384	0.690294743	-0.177204177
C	3.384033918	0.436620981	-1.536028862
C	3.321295738	-1.678122520	-3.062566996
H	4.253756523	-1.981429696	-3.554190874
H	2.742278576	-1.088417292	-3.776355743
H	2.771125078	-2.595348358	-2.824032068
C	4.820922375	-2.908657074	-0.611439884
H	5.721751690	-2.986791611	-1.234585881
H	4.070508003	-3.595611572	-1.009601712
H	5.081771374	-3.223511219	0.400390983
C	5.164591312	-0.603948057	1.667846084
H	4.471340179	-0.312966585	2.462749720
H	6.045793056	0.043413844	1.732262969
H	5.486095428	-1.628283858	1.864781499
C	3.790988922	2.004732847	0.529392838
H	4.677107334	2.606896639	0.290209562
H	3.766637564	1.866628289	1.612683296
H	2.912666798	2.582194090	0.229269505
C	2.766851425	1.475953698	-2.418441534
H	3.525937080	2.195072412	-2.748032570
H	1.992884159	2.044909477	-1.893844366
H	2.321354866	1.035784125	-3.313034773
C	0.791771650	0.216475546	2.209110975
C	-0.046045128	0.477034122	1.034597635
N	0.507149816	0.135813177	-0.145500481
C	-0.192056552	0.313503891	-1.266867399
C	-1.472742677	0.884010136	-1.261976242
C	-2.047003269	1.254562020	-0.057743326
C	-1.336493611	1.039424300	1.140591025
H	0.285665154	-0.010589706	-2.185131073
H	-2.007012844	1.015694261	-2.196117163
O	-0.226333842	-3.791461945	-0.469859064
C	1.099810362	-3.485483170	-0.630568206
O	1.745744586	-4.093154907	-1.475002885
N	1.628376603	-2.536526680	0.168739140
C	-1.053025007	1.095602632	3.600172997
H	-1.455495119	1.333102345	4.578267097
O	1.946697116	-0.251446307	2.060883045
C	0.218657047	0.539115489	3.497236013
Cl	1.146778584	0.218250409	4.904119968
C	-1.820462108	1.342482805	2.462942600
Cl	-3.387667179	2.036256790	2.664587498
H	-3.038247347	1.692049026	-0.027744122
C	-1.041641235	-3.123157024	0.441638440
C	-0.681884170	-2.908893824	1.776390672
C	-2.302249908	-2.771510363	-0.030074628
C	-1.619980931	-2.309002638	2.616740465
C	-3.259623766	-2.186995506	0.815133035
C	-2.884989023	-1.946978331	2.147853136
H	0.284444660	-3.228036642	2.146332264
H	-2.529894352	-3.004426956	-1.064154983
H	-1.367340922	-2.145180225	3.660767555
H	-3.589735270	-1.504777431	2.841703653
C	-4.682968140	-1.925189257	0.292598903
C	-4.649339199	-1.239173055	-1.091196418
H	-4.171100616	-0.256378859	-1.033447742
H	-4.116557598	-1.831499577	-1.840451479
H	-5.669585228	-1.092396498	-1.458930850
C	-5.400616646	-3.290428400	0.157347843
H	-4.884222984	-3.944296837	-0.552047789
H	-5.441984653	-3.806607246	1.121541023
H	-6.426659584	-3.146330118	-0.197968617
C	-5.497438908	-1.029574394	1.245162606
H	-6.479428768	-0.824328363	0.808859229
H	-5.668944836	-1.506901264	2.214504004
H	-5.001909733	-0.068156891	1.419337630

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1t-C6-TS

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Co	2.044601202	-1.130732298	0.217573792
C	3.646096230	-0.691071093	-1.468731642
C	4.154399395	-1.510715723	-0.331261158
C	4.121427059	-0.717154562	0.842831731
C	3.515617132	0.532639027	0.481397718
C	3.295332909	0.558301330	-0.967489839
C	3.602306366	-1.183389664	-2.877137899
H	4.618426800	-1.374024630	-3.244161129
H	3.136403084	-0.457756221	-3.547166586
H	3.055465937	-2.129818201	-2.937910795
C	4.738616467	-2.873497486	-0.498890281
H	5.747253895	-2.785189629	-0.924416304
H	4.135332584	-3.475394249	-1.181672335
H	4.821206093	-3.398615837	0.454277962
C	4.543292522	-1.101779103	2.229971886
H	3.724726677	-0.938916802	2.937119484
H	5.402590752	-0.505799949	2.555853128
H	4.828616619	-2.154152393	2.280961514
C	3.268198967	1.682489991	1.398049951
H	4.078079224	2.417591333	1.303788066
H	3.218922377	1.359283924	2.438683033
H	2.335058928	2.197229385	1.148882270
C	2.789306879	1.750228167	-1.715018392

H	3.571434975	2.515621424	-1.785820842
H	1.933043003	2.209273338	-1.212103367
H	2.487909555	1.491148710	-2.731659412
C	0.350072950	0.139973700	2.077503204
C	-0.226824641	0.561865807	0.816016018
N	0.343650907	0.010208471	-0.283481658
C	-0.143974021	0.284663975	-1.488120914
C	-1.217832923	1.174995422	-1.669557571
C	-1.776084661	1.795765758	-0.567576051
C	-1.292265296	1.496029615	0.728286803
H	0.345793813	-0.199499458	-2.327710390
H	-1.584762692	1.378214478	-2.669656515
O	-0.084107593	-4.250615597	-1.009446383
C	1.169153094	-3.647729158	-1.088593483
O	1.898825288	-3.860564232	-2.037925243
N	1.452148914	-2.842458010	-0.036230668
C	-1.271452904	1.635661960	3.172921419
H	-1.678003430	2.046576977	4.089897633
O	1.306030154	-0.712715387	2.080993176
C	-0.220570445	0.710621417	3.244697571
Cl	0.397366881	0.228290215	4.789274216
C	-1.798341393	2.028327942	1.952241778
Cl	-3.117701292	3.161794901	1.928050637
H	-2.589947701	2.503324032	-0.683970213
C	-0.766858041	-3.723350048	0.065390669
C	-0.098529361	-3.672050714	1.316605449
C	-2.028779745	-3.180914164	-0.123253867
C	-0.711342752	-2.941887617	2.357015371
C	-2.670420647	-2.526326180	0.937265694
C	-1.956104755	-2.375510216	2.161510229
H	0.721081793	-4.346509457	1.528043985
H	-2.479913950	-3.272629499	-1.102687478
H	-0.217206284	-2.866756439	3.318793297
H	-2.428357124	-1.856599569	2.987855911
C	-4.111294746	-2.018048048	0.834625781
C	-4.714329243	-2.234828472	-0.565106511
H	-4.149582863	-1.702205420	-1.338408709
H	-4.755606651	-3.295307636	-0.833025336
H	-5.738848209	-1.852221370	-0.584761083
C	-4.963461876	-2.802889585	1.867121339
H	-4.925457954	-3.878950357	1.671970367
H	-4.626167297	-2.630566597	2.893142700
H	-6.007419586	-2.480531931	1.799438953
C	-4.172648907	-0.508595288	1.161177397
H	-5.215040684	-0.176057950	1.179634213
H	-3.732022762	-0.265754104	2.132334471
H	-3.647954941	0.070364691	0.397689611

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1t-C6

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Co	2.081482649	-1.249055266	0.451213092
C	3.775713682	-0.664225161	-1.162936926
C	4.264826298	-1.561964631	-0.074774548
C	4.168070793	-0.866093397	1.135455728
C	3.583041191	0.440603524	0.833453715
C	3.371390581	0.548277617	-0.589839458
C	3.826334953	-1.021899939	-2.607832909
H	4.869124889	-1.173403382	-2.914947510
H	3.400850296	-0.238554850	-3.237232924
H	3.300327778	-1.960920930	-2.801225662
C	4.834892750	-2.920230627	-0.326250374
H	5.822312832	-2.833131790	-0.796843231
H	4.194549561	-3.490787029	-1.004153848
H	4.952733994	-3.484265089	0.600707889
C	4.526952744	-1.311209917	2.520236731
H	3.663301468	-1.201528072	3.184679031
H	5.341241360	-0.701827109	2.927980661
H	4.846425056	-2.354700804	2.536942244
C	3.350420952	1.524516463	1.824389458
H	4.247314453	2.155961037	1.890619397
H	3.139622211	1.120516896	2.815211058
H	2.519593239	2.168808222	1.525778890
C	2.800118685	1.753644466	-1.272175789
H	3.506597519	2.591216803	-1.249683738
H	1.881193519	2.087087631	-0.779157579
H	2.560096979	1.547793627	-2.316688061
C	0.337684989	0.237782076	1.999753237
C	-0.229102015	0.458314002	0.697476745
N	0.329202324	-0.273392618	-0.310427457
C	-0.138978824	-0.163521215	-1.546267033
C	-1.203937531	0.701741219	-1.866747141
C	-1.770804167	1.471977830	-0.871308088
C	-1.296209812	1.374144316	0.460693151
H	0.345598280	-0.773283422	-2.304036140
H	-1.557160020	0.762219906	-2.890268564
O	-0.359118164	-3.649739027	-1.546581149
C	1.213024259	-3.437736034	-1.195207238
O	1.944319844	-3.541639328	-2.131572962
N	1.275516629	-3.140076637	0.096613303
C	-1.254325032	1.909712553	2.833711386
H	-1.639101028	2.471126795	3.677511930
O	1.296760559	-0.644056439	2.146298170
C	-0.203379691	0.992041111	3.044085026
Cl	0.434841663	0.782110751	4.653578281
C	-1.793800592	2.099251032	1.577903986
Cl	-3.110824585	3.235100269	1.371215701
H	-2.580149889	2.158483267	-1.096225023
C	-0.976756632	-3.453684092	-0.436516076
C	-0.013411856	-3.453841686	0.701045871
C	-2.340942860	-3.204629421	-0.268189937
C	-0.502248049	-2.790365219	1.935334921
C	-2.761511803	-2.685778618	0.952654600
C	-1.816437602	-2.493204355	2.041732788
H	0.003238987	-4.525710583	1.012781858
H	-3.001836777	-3.292874813	-1.119154930
H	0.192486197	-2.641719103	2.751825333
H	-2.183162451	-2.077922821	2.972407579
C	-4.202922821	-2.242701769	1.180666208
C	-5.110015869	-2.515714884	-0.032061536
H	-4.784217358	-1.963005781	-0.919295430
H	-5.153777599	-3.581715345	-0.277272105
H	-6.128316402	-2.190037727	0.196838304
C	-4.774493694	-3.002537251	2.407191038
H	-5.811062336	-2.691291094	2.566020250
H	-4.766805649	-4.083935261	2.240520239
H	-4.222971439	-2.792652845	3.327148676
C	-4.199106216	-0.715450406	1.463891506
H	-5.225033760	-0.381850630	1.646489263
H	-3.600829601	-0.446281612	2.338218451
H	-3.808945179	-0.160488978	0.605821073

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1t-C2-TS

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Co	2.443884611	-1.186597943	0.068739988
C	4.286354542	-1.155045986	-1.461941957
C	4.597131729	-1.651179671	-0.090716548
C	4.435129166	-0.584932089	0.820175886
C	3.890900135	0.517362654	0.068473764
C	3.880867481	0.171643600	-1.354033351
C	4.457246304	-1.985195041	-2.688942432
H	5.486120224	-2.359617472	-2.749988317
H	4.248788357	-1.415124416	-3.595989466
H	3.781596899	-2.845155239	-2.671244860
C	5.093976498	-3.031741858	0.176359400
H	6.098487854	-3.160030127	-0.245665088
H	4.436338425	-3.766434431	-0.298348188
H	5.140568256	-3.248630762	1.244550228
C	4.705546856	-0.563444734	2.295255423
H	3.817596197	-0.244488060	2.848818541
H	5.518332005	0.134720832	2.524671078
H	4.997894764	-1.548265815	2.662872553
C	3.533801317	1.852952957	0.626916766
H	4.389369011	2.535668135	0.537835777
H	3.268119335	1.783731937	1.683241129
H	2.700452566	2.306054592	0.082819268
C	3.514505386	1.120142698	-2.451316357
H	4.333086491	1.826253891	-2.636432409
H	2.631097317	1.712112188	-2.195026636
H	3.310566425	0.596154392	-3.387273073
C	0.567645907	0.316994309	1.520240426
C	0.127243027	0.544451654	0.157041401
N	0.827854037	-0.126977399	-0.788159609
C	0.461305857	-0.049235653	-2.066090822
C	-0.629208267	0.738338470	-2.473923683
C	-1.329503536	1.469884992	-1.532083988
C	-0.964270592	1.388635635	-0.167747006
H	1.041770220	-0.638056517	-2.768568039
H	-0.903480291	0.769895673	-3.522555113
O	-0.358171314	-3.355876207	-1.193862438
C	0.998509169	-3.129592180	-1.409429431
O	1.426729679	-3.094516277	-2.551465750
N	1.765375853	-2.944061041	-0.305938572
C	-1.205361962	1.879955530	2.222262859
H	-1.712323189	2.404477835	3.023922443
O	1.547935605	-0.475061715	1.744322062
C	-0.141985655	1.019480228	2.531950951
Cl	0.357607245	0.837068141	4.178584576
C	-1.617116332	2.063416719	0.912138224
Cl	-2.959772110	3.119286060	0.592531323
H	-2.162261963	2.098937273	-1.827632308
C	-0.667704880	-3.059853077	0.116269782
C	0.180437937	-3.593045712	1.115902543
C	-1.683559299	-2.174183607	0.414690882
C	0.071152709	-3.139392376	2.464178562
C	-1.832167864	-1.789540291	1.753346324
C	-0.961264729	-2.252981424	2.754664660
H	0.719563067	-4.507439613	0.905911803
H	-2.305011988	-1.771096230	-0.376857370
H	-2.623465538	-1.095640421	2.020828724
H	-1.104104280	-1.895974874	3.766326427
C	1.035239577	-3.704032183	3.507939100
C	2.484786272	-3.527853489	2.995657921
H	3.191869736	-3.904866219	3.741803885
H	2.662327766	-4.064576149	2.059850454
H	2.690487146	-2.468271017	2.823066473
C	0.730340004	-5.210485458	3.707378149
H	0.855948985	-5.782495975	2.782553911
H	1.414173365	-5.631208897	4.451640606
H	-0.293953061	-5.360345364	4.062637329
C	0.904785395	-2.984947205	4.861156464
H	1.640046716	-3.388777971	5.563066006
H	1.088627100	-1.911507368	4.758910656
H	-0.083840452	-3.128963232	5.308978558

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Co	1.999644637	-1.330792308	0.543473065
C	3.730111361	-0.881673813	-1.099608421
C	4.192627430	-1.618143439	0.112565592
C	4.046741962	-0.769040704	1.219132185
C	3.409665346	0.452000976	0.736134291
C	3.263968229	0.375458181	-0.701462209
C	3.870272636	-1.415413141	-2.482973099
H	4.934128284	-1.545518637	-2.721098423
H	3.440238953	-0.740829468	-3.225703955
H	3.390749454	-2.392525911	-2.579308033
C	4.784081459	-2.989238262	0.058995038
H	5.773374081	-2.961242676	-0.414260060
H	4.150989056	-3.655553579	-0.534283459
H	4.896393299	-3.418172359	1.056411862
C	4.450728893	-0.981553674	2.646550894
H	3.603304625	-0.806294203	3.316999912
H	5.246234417	-0.280826390	2.925730467
H	4.822663307	-1.993538499	2.815482378
C	3.075883389	1.633265376	1.577281475
H	3.935819626	2.316508532	1.612149358
H	2.832138062	1.337006927	2.598612547
H	2.231470585	2.192152023	1.165984631
C	2.701578140	1.470870137	-1.554641008
H	3.405812263	2.307668686	-1.631288528
H	1.771485686	1.864002466	-1.132014751
H	2.485937357	1.123283029	-2.566850901
C	0.121698402	0.181571960	1.913980961
C	-0.383469254	0.308115751	0.573394179
N	0.267062664	-0.437677294	-0.365613014
C	-0.123572893	-0.395580590	-1.633418679
C	-1.203283548	0.403206676	-2.055679321
C	-1.867303729	1.182943583	-1.130695701
C	-1.469690561	1.164440155	0.228893965
H	0.429808110	-1.018135190	-2.330175400
H	-1.493223190	0.404357046	-3.100662947
O	-0.619067132	-3.444186687	-1.133358717
C	0.938832879	-3.426704645	-0.987321138
O	1.550619364	-3.482695580	-2.014748335
N	1.229984760	-3.267145157	0.308701962
C	-1.553137660	1.861644387	2.556740999
H	-1.984793901	2.473276138	3.340803862
O	1.099069118	-0.660511851	2.159156799
C	-0.476689488	1.004741669	2.872728586
Cl	0.134076148	1.012237072	4.507335186
C	-2.050689220	1.936276436	1.273688912
Cl	-3.391791105	3.007962227	0.934851944
H	-2.691563368	1.820207357	-1.433065772

C	-1.079943061	-3.273186922	0.068077892
C	0.002732673	-3.535859346	1.064968944
C	-2.346091270	-2.839355469	0.426807255
C	-0.226121277	-3.081451893	2.481195927
C	-2.490724802	-2.460753441	1.759644508
C	-1.481026530	-2.582853794	2.749468803
H	-0.074555650	-4.640982151	1.208576798
H	-3.127230406	-2.694815874	-0.309836864
H	-3.446082830	-2.043150902	2.069864988
H	-1.737994194	-2.297435284	3.762751341
C	0.710667849	-3.544025898	3.594549656
C	2.137356520	-3.841272116	3.099028826
H	2.744786501	-4.181572914	3.942961931
H	2.166747332	-4.614470005	2.327271700
H	2.602674723	-2.943319798	2.691153288
C	0.092571281	-4.863323212	4.147790432
H	0.012750751	-5.633077621	3.371425390
H	0.736412287	-5.256339073	4.941074371
H	-0.903127551	-4.691916466	4.566863537
C	0.793563604	-2.512364388	4.739243031
H	1.431852698	-2.911912203	5.533413887
H	1.216023326	-1.576781988	4.375219822
H	-0.180501163	-2.297827005	5.186748028

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[3]Co-1w

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Co	2.382194281	-0.922678411	0.276700288
C	3.815116644	-0.591339648	-1.604379654
C	4.447595119	-1.259903431	-0.430787086
C	4.492751598	-0.328101486	0.643492222
C	3.805517435	0.847792447	0.200128183
C	3.449476957	0.694930732	-1.213117003
C	3.649096012	-1.259245992	-2.927377701
H	4.628343582	-1.518011928	-3.347911835
H	3.134171247	-0.618086696	-3.646089077
H	3.089983940	-2.196679115	-2.818574190
C	5.030498981	-2.631374836	-0.491296411
H	5.972126484	-2.607558489	-1.055642962
H	4.345749855	-3.313468695	-1.001713991
H	5.240883827	-3.027283430	0.503535390
C	5.060902119	-0.535787046	2.017613649
H	4.310225487	-0.324310094	2.785010099
H	5.917444229	0.124917507	2.189842224
H	5.398643970	-1.564187050	2.157251835
C	3.588111877	2.085551739	1.006617427
H	4.412060738	2.792340279	0.841469646
H	3.551016808	1.861234188	2.074658632
H	2.663008451	2.594709635	0.722161055
C	2.800009012	1.767491937	-2.029430151
H	3.486599445	2.609744549	-2.174576521
H	1.906988382	2.164000750	-1.534417272
H	2.508903503	1.404965878	-3.017444134
C	0.474217594	-0.007338420	2.197826624
C	-0.234995976	0.199679837	0.932305694
N	0.483970791	-0.070093706	-0.176275030
C	-0.076125823	0.085229762	-1.374659777
C	-1.387569189	0.561057866	-1.523924828
C	-2.134708166	0.856806755	-0.397599816
C	-1.566205263	0.666203439	0.879828691
H	0.541057885	-0.172582760	-2.228873491
H	-1.804247737	0.684090912	-2.517277718
O	-0.087466933	-3.510373592	-0.888442874
C	1.280872822	-3.353654146	-0.841658056
O	1.948114634	-3.830276489	-1.752020717
N	1.825029969	-2.702647448	0.203594252
C	-1.585193753	0.714106739	3.354707241
H	-2.119145155	0.908332944	4.277780056
O	1.673182607	-0.391295671	2.194413185
C	-0.267962605	0.268264949	3.405067205
Cl	0.510165572	0.022109021	4.915750504
C	-2.231011629	0.904731572	2.134009123
Cl	-3.866239786	1.460396409	2.148356199
H	-3.153203964	1.216848612	-0.487125754
C	-0.942501128	-3.103883505	0.124335252
C	-0.651924491	-3.216928959	1.491236567
C	-2.181689262	-2.633536577	-0.307042778
C	-1.628647923	-2.830070734	2.411566257
C	-3.161978722	-2.255108833	0.615557849
C	-2.867061138	-2.350378990	1.985583901
H	0.303100497	-3.607487679	1.819309235
H	-2.370919466	-2.584161997	-1.374753118
H	-1.417804956	-2.919415474	3.473435402
H	-3.618758202	-2.063574553	2.715931654
C	-4.511623383	-1.772300243	0.145560697
H	-4.458770275	-1.340278864	-0.858690441
H	-5.226891994	-2.602479219	0.103918314
H	-4.927102566	-1.021476150	0.824776351

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1w-C6-TS

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Co	2.094933748	-1.146613002	0.319794893
C	3.661225319	-0.559664905	-1.367771149
C	4.220648766	-1.355657578	-0.239245474
C	4.127127171	-0.580092072	0.945637941
C	3.437405586	0.628371179	0.595909417
C	3.213417053	0.652256787	-0.852340877
C	3.661793232	-1.031558275	-2.783554554
H	4.691303730	-1.166300058	-3.137358189
H	3.171176672	-0.318663776	-3.449504137
H	3.164371252	-2.002950907	-2.869220495
C	4.893216133	-2.674645185	-0.423226982
H	5.893034935	-2.517030954	-0.849291086
H	4.327445030	-3.305336714	-1.112529039
H	5.010024548	-3.205626488	0.522882223
C	4.571650982	-0.948941946	2.330488205
H	3.747595310	-0.833450258	3.041180372
H	5.397676468	-0.308810651	2.659603119
H	4.913316250	-1.984698296	2.375631094
C	3.108585119	1.746325850	1.525437832
H	3.892618179	2.513491154	1.477114320
H	3.033515453	1.397538185	2.556225777
H	2.165877819	2.229475021	1.251898408
C	2.599382639	1.803377390	-1.583479524
H	3.301036358	2.644466877	-1.632934093
H	1.697707176	2.163329840	-1.078531981
H	2.329125643	1.536195040	-2.606906414
C	0.195307031	0.046301439	2.001643419
C	-0.371750444	0.315840572	0.694454789
N	0.317621082	-0.216774940	-0.343905240
C	-0.143973544	-0.083052143	-1.581900835
C	-1.321519256	0.634165287	-1.861606240
C	-2.011452198	1.233827233	-0.824552238

C	-1.547651410	1.090076804	0.504802406
H	0.444845319	-0.545130849	-2.368871212
H	-1.665998459	0.723042071	-2.885960102
O	0.000511448	-4.048110008	-1.089955926
C	1.314747810	-3.574074507	-1.060609221
O	2.050373316	-3.743509293	-2.011738300
N	1.636402249	-2.931059122	0.095734738
C	-1.643585920	1.395362020	2.931844711
H	-2.132679939	1.814976692	3.803579092
O	1.242832541	-0.685887039	2.100396872
C	-0.491786718	0.614050627	3.105103254
Cl	0.110641643	0.311166853	4.700181484
C	-2.166160107	1.635511994	1.669912100
Cl	-3.604959249	2.605508566	1.521348715
H	-2.908601284	1.811993361	-1.017808437
C	-0.642593622	-3.603634596	0.042391472
C	0.022882609	-3.798840761	1.285176396
C	-1.823159218	-2.888310671	-0.056359142
C	-0.513015985	-3.172660351	2.433915615
C	-2.374237776	-2.318399906	1.099911332
C	-1.688118935	-2.453305006	2.336835384
H	0.744931936	-4.598601341	1.390345216
H	-2.282935619	-2.751997232	-1.029208064
H	-0.022556948	-3.302936077	3.391675949
H	-2.119683027	-2.001698256	3.224942923
C	-3.672130585	-1.566299319	1.051329494
H	-3.964423180	-1.314161420	0.029715206
H	-4.472992420	-2.173936367	1.491562247
H	-3.615771770	-0.645513356	1.640571117

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1w-C6

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Co	2.122997284	-1.207296729	0.432551652
C	3.786434174	-0.570875525	-1.217313886
C	4.304574490	-1.419758320	-0.103646986
C	4.175817966	-0.697401702	1.091953874
C	3.522115231	0.562831223	0.758836567
C	3.323278666	0.630706787	-0.675998151
C	3.851940155	-0.972629964	-2.650195599
H	4.898806572	-1.102422953	-2.952779293
H	3.403209925	-0.223608330	-3.304923534
H	3.352334976	-1.932101369	-2.813074827
C	4.925396919	-2.760909319	-0.320883036
H	5.902074337	-2.649651051	-0.808571041
H	4.298232555	-3.375483751	-0.972900152
H	5.076465607	-3.292593718	0.619960308
C	4.556434155	-1.097886920	2.484891653
H	3.697283030	-0.996291339	3.156032085
H	5.359251499	-0.458742291	2.868164539
H	4.903412342	-2.132002115	2.523514986
C	3.208628178	1.651099324	1.723239422
H	4.057110786	2.347047091	1.779631734
H	3.021507025	1.255051255	2.722061634
H	2.334896088	2.226391077	1.406437874
C	2.700855732	1.792761922	-1.386456966
H	3.365625858	2.664157867	-1.371394157
H	1.761703014	2.089796543	-0.908558846
H	2.483026266	1.557597756	-2.430047512
C	0.210249960	0.115577400	1.946475506
C	-0.341090173	0.289750636	0.631406009
N	0.337622941	-0.340585679	-0.370628834
C	-0.106851377	-0.271345139	-1.618413806
C	-1.271415234	0.445253611	-1.956607819
C	-1.974558949	1.097658277	-0.964124918
C	-1.529148221	1.036664248	0.379885614
H	0.471208841	-0.804025412	-2.368265867
H	-1.600609422	0.477370232	-2.989328384
O	-0.330734134	-3.518962383	-1.380506992
C	1.265052557	-3.399337292	-1.116041303
O	1.937424898	-3.478414297	-2.097936869
N	1.420080781	-3.165879250	0.184244245
C	-1.647900581	1.492564917	2.767899990
H	-2.143065214	1.957738757	3.612622738
O	1.262817264	-0.647045374	2.110485554
C	-0.476922154	0.738553822	2.990961552
Cl	0.107314751	0.533925831	4.620983601
C	-2.170106411	1.638156176	1.498490810
Cl	-3.637187958	2.568984270	1.275293231
H	-2.872148037	1.659464717	-1.200033307
C	-0.870749056	-3.345889568	-0.224388704
C	0.159270093	-3.480698109	0.850207627
C	-2.193764210	-3.000186443	0.047988802
C	-0.207633421	-2.905689001	2.169512510
C	-2.487752676	-2.558785200	1.335777879
C	-1.494757891	-2.545094490	2.387963533
H	0.152110919	-4.574678898	1.070960402
H	-2.923237085	-2.946709156	-0.751979828
H	0.540448129	-2.883595943	2.950999260
H	-1.797697306	-2.185365200	3.366161108
C	-3.839013577	-2.002953053	1.658099890
H	-4.550057888	-2.121857166	0.839154899
H	-4.245681286	-2.475352526	2.559474468
H	-3.736057520	-0.932564378	1.885514021

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1w-C2-TS

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Co	2.090867043	-1.156063795	0.327831030
C	3.658751488	-0.552163780	-1.360006571
C	4.218901157	-1.351433635	-0.234708264
C	4.117735863	-0.582796752	0.954101622
C	3.426111937	0.626638651	0.608271718
C	3.201884508	0.654460073	-0.839257479
C	3.668000221	-1.014841080	-2.778641939
H	4.700042725	-1.142341018	-3.128004789
H	3.177472115	-0.299945354	-3.442429543
H	3.176020622	-1.988155007	-2.872859478
C	4.901714325	-2.664298534	-0.424820006
H	5.900478840	-2.496736288	-0.849676132
H	4.341084480	-3.295748711	-1.117606878
H	5.022575378	-3.199293852	0.518563330
C	4.562053204	-0.957110941	2.337451696
H	3.739990711	-0.836417735	3.049511671
H	5.393401146	-0.324070126	2.666953087
H	4.896187305	-1.995503664	2.379827261
C	3.094758749	1.741554618	1.540360928
H	3.868529081	2.518340588	1.481134295
H	3.035144091	1.394544482	2.572642088
H	2.143179655	2.213068485	1.276647210
C	2.578470707	1.803595185	-1.565697312
H	3.272343159	2.651330233	-1.611072659
H	1.673158169	2.152796268	-1.059580803
H	2.311099768	1.538504481	-2.590428114

C	0.200093433	0.055644430	2.009537458
C	-0.380650073	0.298156023	0.703028202
N	0.307455420	-0.239284381	-0.332765311
C	-0.164777830	-0.126140967	-1.569830298
C	-1.355908871	0.567273617	-1.848985076
C	-2.048614740	1.167794585	-0.813439131
C	-1.569893241	1.052449226	0.513280809
H	0.425679505	-0.588211417	-2.355681896
H	-1.709460855	0.637931824	-2.871725798
O	0.007811951	-4.041310310	-1.115041137
C	1.322219968	-3.572435617	-1.062758803
O	2.069219828	-3.728499174	-2.007367611
N	1.634909034	-2.945537329	0.106657848
C	-1.628762603	1.420414686	2.932872295
H	-2.106959820	1.859944940	3.800722837
O	1.245848060	-0.680795610	2.109408379
C	-0.464955002	0.658009529	3.107553482
Cl	0.176747724	0.423969805	4.699966908
C	-2.177901983	1.616093993	1.674735308
Cl	-3.633403301	2.558176041	1.526960254
H	-2.956649065	1.728494048	-1.007796526
C	-0.648592293	-3.605961084	0.013732327
C	0.010594252	-3.812772036	1.257118583
C	-1.826424122	-2.883930445	-0.082625151
C	-0.494095117	-3.198119640	2.434793234
C	-2.334499598	-2.322911263	1.090928435
C	-1.669417620	-2.464280844	2.325809002
H	0.717193007	-4.629343510	1.350572467
H	-2.294750690	-2.734164000	-1.048391819
H	-3.250963211	-1.741762757	1.047503591
H	-2.099866390	-2.010349989	3.213071585
C	0.228199914	-3.374973536	3.741124630
H	-0.419420600	-3.152411699	4.592337608
H	0.610246003	-4.394799709	3.852174044
H	1.080783486	-2.688990355	3.777418613

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1w-C2

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Co	2.057521343	-1.026653290	0.275706947
C	4.016963482	-1.006635904	-1.020384789
C	4.346554279	-1.519551635	0.336464763
C	4.086526871	-0.508776486	1.252368927
C	3.530294657	0.634942114	0.495593637
C	3.568033934	0.328468174	-0.905395031
C	4.228432178	-1.799286246	-2.263408899
H	5.304744720	-1.937803030	-2.432161093
H	3.798869133	-1.316020370	-3.140621662
H	3.780910015	-2.792517185	-2.171008825
C	4.869742870	-2.898195744	0.584447682
H	5.844170094	-3.036405325	0.102762818
H	4.188537598	-3.647070646	0.166018039
H	4.989399433	-3.099354506	1.650789022
C	4.230256081	-0.516506612	2.740458012
H	3.244854927	-0.416526675	3.207935095
H	4.850057125	0.322286785	3.075620890
H	4.691178322	-1.439849734	3.096280336
C	3.110277891	1.920786500	1.120167732
H	3.990110159	2.548289061	1.317415833
H	2.612100840	1.740145326	2.076162815
H	2.436785460	2.484509945	0.471472383
C	3.193158150	1.261991620	-2.016891956
H	4.013868809	1.954313397	-2.236253262
H	2.318972588	1.863064766	-1.753509045
H	2.962077141	0.717471540	-2.935010672
C	0.066976018	-0.025682518	1.946620464
C	-0.451620311	0.418551922	0.685162604
N	0.297508687	0.083955236	-0.407575786
C	-0.119210839	0.437462837	-1.617197156
C	-1.310011029	1.164082170	-1.818351865
C	-2.079774618	1.518157125	-0.730493844
C	-1.672165394	1.145355821	0.573992729
H	0.493799865	0.114623971	-2.451365232
H	-1.609301567	1.430490613	-2.825915337
O	-0.833438993	-2.869469166	-1.454538107
C	0.729706466	-2.668242216	-1.570431113
O	1.129459977	-2.337771654	-2.645622253
N	1.253331900	-2.862205505	-0.354513556
C	-1.891697049	1.008793354	2.996363640
H	-2.436746120	1.234123111	3.905747414
O	1.186445236	-0.713350296	1.977703094
C	-0.684075654	0.284055054	3.079183340
Cl	-0.114900075	-0.243674263	4.645033836
C	-2.378384590	1.429699183	1.777481079
Cl	-3.884039164	2.320778847	1.722083092
H	-3.000296116	2.077205181	-0.859970033
C	-1.063002229	-3.099834919	-0.203708693
C	0.215975180	-3.413813591	0.500726998
C	-2.281078815	-3.044476032	0.467521846
C	0.230703890	-3.262317419	1.990257382
C	-2.200995922	-3.043267727	1.856240988
C	-0.989971340	-3.141956091	2.601096392
H	0.248087987	-4.529563904	0.423739374
H	-3.213344574	-2.888508081	-0.061439212
H	-3.124883652	-2.931718349	2.418723822
H	-1.042785883	-3.095428705	3.683514357
C	1.505999565	-3.486483335	2.736492634
H	1.453296065	-3.027043581	3.724714279
H	1.678584218	-4.564229012	2.861804247
H	2.361701727	-3.073280096	2.200466633

Table S6. Vibrational frequencies of all optimized geometries

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[1]Co-1a

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14.61	18.52	28.37	32.00	42.85	49.09
83.55	85.70	96.87	100.36	103.85	110.26
126.97	130.48	138.21	144.10	149.81	157.77
164.88	174.34	178.34	194.06	202.20	205.57
226.46	230.91	246.70	261.94	268.50	279.36
285.47	295.73	307.78	319.24	323.52	358.73
365.05	369.69	396.08	405.82	420.30	421.78

427.22	443.37	470.29	500.95	504.32	510.76
513.87	527.83	534.73	545.11	573.60	583.60
585.10	598.48	608.82	617.48	621.91	625.16
669.94	684.85	696.06	709.02	764.76	769.06
772.84	782.61	812.35	816.60	821.89	824.04
826.10	840.08	907.35	913.50	924.06	955.50
967.13	971.60	973.14	998.44	1005.87	1007.92
1014.50	1018.53	1029.59	1038.94	1044.29	1047.62
1053.86	1055.17	1090.24	1094.40	1106.58	1115.59
1130.44	1147.30	1173.74	1180.33	1185.62	1187.48
1200.64	1215.56	1241.98	1260.47	1283.15	1290.42
1335.79	1347.84	1365.43	1379.46	1387.11	1397.47
1411.84	1418.87	1423.27	1424.03	1433.64	1439.05
1440.53	1446.02	1461.07	1470.94	1477.54	1483.16
1487.10	1490.37	1492.89	1496.52	1499.71	1500.20
1505.04	1510.57	1531.00	1532.44	1534.65	1560.71
1608.40	1621.68	1634.04	1640.48	1656.00	1700.21
3047.05	3048.25	3050.19	3053.39	3056.75	3114.63
3115.32	3118.42	3120.13	3126.15	3154.72	3157.01
3158.79	3160.41	3164.86	3194.90	3204.09	3214.38
3218.44	3222.81	3229.85	3230.33	3244.84	3251.66

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^{3}Co-1a

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13.18	26.44	29.19	29.51	49.42	60.89
76.96	86.07	94.35	106.98	109.94	111.83
116.94	131.04	135.53	139.66	144.95	152.15
156.16	174.08	181.20	188.86	198.26	204.16
217.77	232.16	241.20	260.18	265.04	273.04
286.63	294.78	305.44	314.48	326.09	354.64
364.49	368.58	385.84	391.82	403.35	416.75
418.49	423.32	445.88	467.62	508.31	511.55
514.18	520.36	526.71	541.26	554.64	572.11
573.30	583.31	595.98	617.11	620.50	623.49
672.40	685.61	692.78	710.67	761.64	771.29
774.54	781.34	786.46	813.20	816.66	822.41
825.26	846.39	904.52	914.21	928.27	958.78
967.55	970.85	977.62	995.27	1005.32	1007.23
1010.25	1017.46	1029.45	1038.58	1044.42	1049.03
1054.54	1056.94	1090.58	1095.48	1106.61	1114.32
1131.47	1144.19	1171.17	1176.40	1183.19	1195.26
1200.40	1209.53	1228.40	1257.25	1269.57	1285.65
1338.36	1344.15	1361.55	1369.13	1384.74	1387.75
1410.01	1416.32	1422.33	1424.32	1431.46	1439.07
1440.53	1445.40	1450.61	1461.45	1468.51	1479.18
1483.64	1487.09	1492.56	1494.01	1498.61	1499.88
1506.00	1515.26	1517.61	1527.01	1529.39	1544.60
1590.16	1617.54	1635.00	1639.84	1653.06	1687.24
3027.95	3049.34	3049.76	3053.32	3056.41	3110.30
3112.95	3115.24	3116.20	3128.20	3150.00	3157.08
3157.41	3161.73	3163.28	3191.50	3200.93	3211.25
3220.15	3223.59	3230.95	3235.25	3250.31	3269.29

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2.58	20.55	36.90	43.06	48.91	54.25
68.51	76.64	86.92	94.23	103.54	109.87
116.68	120.50	123.46	131.39	145.50	149.51
156.53	162.90	176.01	184.26	195.71	206.68
215.51	233.20	238.86	257.05	259.29	268.59
281.27	290.93	307.84	317.99	332.67	347.14
359.24	386.20	389.97	397.93	415.70	418.91
425.90	428.80	447.91	460.90	467.94	502.73
509.49	514.75	532.51	541.81	569.53	570.92
588.78	589.68	600.66	612.47	616.33	620.35
675.54	684.32	691.91	706.27	761.94	774.67
777.15	787.45	791.46	800.33	815.93	823.23
824.52	845.85	901.38	913.26	929.92	961.56
965.89	968.74	973.47	980.13	1001.69	1003.89
1013.50	1015.23	1036.80	1042.09	1047.21	1051.78
1052.59	1058.22	1094.00	1097.41	1104.55	1114.87
1130.81	1140.13	1154.13	1178.20	1180.04	1187.70
1197.08	1213.54	1228.51	1260.41	1264.80	1324.44
1331.51	1340.89	1364.85	1376.57	1391.51	1394.20
1414.22	1422.67	1426.87	1436.48	1437.88	1442.10
1447.14	1457.79	1460.46	1468.81	1482.84	1487.41
1487.99	1492.37	1494.67	1497.48	1498.24	1503.61
1505.85	1514.17	1516.11	1522.28	1528.81	1540.55
1546.24	1616.47	1622.79	1628.95	1641.57	1706.16
3048.10	3049.74	3052.03	3053.61	3055.74	3115.33
3117.13	3119.75	3121.11	3123.12	3144.38	3149.62
3154.53	3155.84	3161.55	3191.99	3199.62	3211.29
3218.57	3223.26	3234.86	3235.00	3253.67	3278.47

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15.26	22.26	28.88	36.99	42.61	44.75
67.00	76.39	80.01	86.71	93.86	102.12
105.50	111.94	117.84	122.15	126.08	133.76
148.09	152.42	158.01	163.16	177.30	181.83
187.63	190.18	197.16	206.20	208.78	213.81
230.77	236.37	242.09	253.54	272.33	284.62
294.81	298.67	308.65	312.07	317.13	318.36
326.93	329.69	348.98	352.53	364.92	373.05
375.42	390.84	402.55	402.57	411.97	421.98
449.48	468.12	478.51	490.81	495.08	500.42
512.31	539.32	550.82	568.20	582.10	587.70
599.31	605.36	606.47	608.17	636.79	664.97
673.98	691.59	712.55	729.45	742.19	751.35
772.25	798.97	803.78	813.09	816.99	829.87
834.61	901.71	904.64	906.35	907.27	918.20
921.17	939.96	951.76	967.88	975.20	979.32
979.81	996.81	1014.65	1016.97	1025.23	1028.47
1044.06	1046.19	1054.60	1055.49	1058.94	1064.05
1093.78	1096.09	1100.63	1117.71	1128.55	1133.73
1143.75	1145.28	1174.85	1184.17	1205.22	1219.50
1231.99	1233.13	1240.47	1261.79	1269.76	1305.90
1322.82	1323.89	1325.59	1347.28	1360.12	1361.24
1366.20	1407.57	1419.45	1420.59	1426.87	1430.93
1433.03	1433.71	1435.67	1440.10	1443.29	1453.20
1463.43	1471.28	1477.03	1479.36	1489.84	1492.33
1495.46	1495.86	1499.58	1501.17	1506.28	1506.47
1508.18	1511.17	1512.12	1516.31	1519.45	1521.46
1531.66	1537.01	1539.69	1576.84	1581.01	1613.69
1617.37	1634.82	1649.29	1681.63	3036.14	3039.07
3042.12	3043.09	3046.94	3047.18	3054.31	3054.71
3096.71	3103.51	3110.70	3117.60	3118.28	3118.68
3121.51	3121.69	3125.92	3127.31	3128.48	3138.42
3143.74	3146.69	3150.30	3161.26	3186.37	3217.28
3217.97	3224.65	3227.68	3229.84	3234.51	3237.17

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-303.33	15.92	21.84	30.63	32.26	44.34
46.76	64.39	72.97	85.38	89.79	101.66
105.13	118.74	119.49	121.02	129.50	139.51
147.92	154.14	157.71	158.99	168.89	173.62
184.92	193.35	198.32	201.56	203.05	208.48
232.53	241.02	246.95	250.42	253.09	277.70
284.91	293.14	299.67	300.03	307.22	311.68
328.13	339.64	345.68	354.90	358.43	359.59
370.74	382.85	398.13	404.08	412.24	423.78
453.63	474.68	477.31	482.00	493.98	499.52
503.09	539.35	545.25	568.85	580.78	584.40
595.99	600.20	603.09	615.96	617.77	656.11
687.11	690.16	715.29	723.90	742.33	748.40
749.48	798.25	809.18	813.30	815.92	830.58
832.07	886.18	892.78	899.03	902.02	908.36
923.25	941.22	949.10	954.66	967.95	972.41
977.07	978.52	983.71	1004.72	1016.19	1023.48
1041.07	1044.48	1052.14	1055.01	1055.46	1062.75
1078.71	1095.89	1100.22	1113.77	1119.25	1125.52
1132.97	1139.08	1151.76	1176.78	1178.07	1212.48
1217.42	1224.73	1236.98	1255.06	1266.44	1309.63
1314.64	1316.24	1322.35	1339.01	1356.00	1373.60
1384.92	1400.52	1419.83	1422.30	1425.20	1428.21
1429.79	1431.66	1432.84	1438.53	1439.42	1454.02
1457.32	1463.65	1475.97	1480.11	1480.96	1488.15
1491.27	1494.28	1496.93	1498.90	1500.62	1501.19
1503.62	1507.92	1510.03	1511.97	1514.61	1522.70
1527.12	1535.85	1539.71	1552.50	1566.36	1589.29
1603.77	1630.78	1637.18	1748.17	3038.03	3039.98
3041.36	3042.19	3047.65	3049.33	3053.68	3057.95
3101.88	3104.39	3106.93	3114.34	3118.90	3122.57
3123.50	3124.83	3129.96	3131.44	3142.30	3144.54
3147.92	3149.18	3158.46	3163.17	3203.02	3213.02
3218.39	3227.16	3228.45	3230.53	3238.84	3243.67

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14.54	26.28	30.31	34.58	40.77	49.88
64.78	72.08	78.25	82.71	87.70	97.80
108.98	118.34	122.52	124.53	129.94	144.67
156.71	159.87	166.20	170.58	178.91	184.34
187.77	198.54	203.39	208.48	226.00	227.41
234.26	237.95	256.60	263.54	267.17	274.91
286.45	299.35	303.83	309.06	312.58	320.59
340.45	351.22	355.56	356.61	376.97	383.87
389.17	393.83	408.60	426.86	429.39	439.44
453.22	475.27	480.06	482.40	504.43	509.31
520.37	540.22	561.94	568.40	584.28	585.49
595.05	603.75	607.60	617.20	665.73	668.08
681.44	688.53	697.80	721.11	751.14	752.50
786.47	797.68	812.55	814.31	816.52	827.25
828.89	851.17	856.72	897.69	900.80	907.54
939.31	944.76	953.38	963.88	967.37	977.70
980.72	999.78	1013.44	1016.02	1037.29	1046.74
1046.97	1050.55	1055.20	1061.71	1077.26	1082.84
1093.15	1094.24	1096.08	1107.31	1114.22	1131.53
1137.33	1170.40	1177.03	1181.81	1218.76	1226.16
1230.98	1237.02	1240.56	1259.01	1278.08	1294.78
1296.56	1322.61	1326.33	1355.09	1359.52	1396.55
1399.18	1420.62	1422.81	1423.69	1424.79	1426.98
1429.55	1431.68	1433.30	1434.41	1438.26	1456.73
1463.31	1463.72	1474.63	1482.52	1486.40	1488.48
1489.97	1492.89	1497.00	1497.72	1498.28	1501.20
1503.24	1506.25	1512.80	1518.36	1521.32	1527.61
1529.99	1539.20	1551.99	1569.68	1581.29	1604.04
1615.45	1637.51	1677.91	1960.20	2861.26	3033.88
3042.26	3045.02	3046.92	3047.99	3048.89	3054.91
3057.73	3105.66	3108.71	3111.30	3113.49	3117.61
3120.40	3128.75	3131.84	3135.34	3136.91	3138.96
3146.33	3148.62	3154.96	3156.77	3164.73	3192.82
3215.26	3226.22	3228.30	3228.57	3255.06	3257.09

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-411.08	26.83	31.80	32.47	42.52	59.50
63.24	75.52	79.14	87.47	91.22	95.02
109.14	115.35	118.20	122.48	133.51	137.10
141.29	145.68	152.34	159.44	172.21	178.43
182.23	189.63	194.64	202.78	206.89	223.75
235.26	246.70	250.38	259.01	260.90	278.24
292.77	294.15	302.42	306.46	307.46	316.24
323.55	334.87	350.10	358.55	371.81	381.09
385.76	393.20	395.64	403.10	424.69	433.88
439.08	452.15	474.06	478.61	500.88	505.78
507.87	538.12	542.60	556.74	571.46	585.96
593.59	602.43	605.53	617.87	626.02	665.40
670.64	686.60	705.07	742.74	752.61	760.09
768.33	795.22	807.67	814.11	816.23	834.64
837.49	861.14	897.14	902.43	905.06	905.89
918.80	941.32	951.88	963.02	964.46	984.20
985.94	986.17	990.78	1005.29	1019.76	1020.17
1037.97	1042.61	1055.24	1056.22	1061.76	1063.82
1090.05	1093.96	1094.39	1098.10	1120.93	1131.25
1142.83	1145.61	1156.43	1175.18	1180.85	1201.81
1224.67	1230.76	1241.06	1261.07	1274.28	1313.05
1314.53	1329.41	1330.94	1340.81	1353.44	1371.59
1381.57	1398.53	1415.17	1419.74	1423.27	1423.49
1430.03	1432.18	1432.38	1434.34	1436.75	1446.74
1452.40	1464.33	1474.70	1476.01	1481.49	1485.24
1488.76	1490.83	1497.26	1499.88	1500.65	1501.90
1504.91	1508.38	1511.89	1513.47	1523.08	1527.17
1535.13	1539.90	1543.44	1551.54	1580.02	1583.33
1609.27	1629.56	1639.26	1725.58	3038.71	3043.99
3045.11	3046.30	3048.23	3049.93	3052.21	3055.31
3105.99	3108.83	3109.91	3116.30	3119.12	3119.21
3120.31	3126.03	3127.69	3135.76	3144.27	3146.53
3152.49	3153.38	3154.62	3158.08	3200.56	3216.24
3223.85	3226.05	3229.25	3229.57	3233.86	3241.31

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3.05	18.88	27.06	47.37	59.54	65.05
68.49	82.63	88.27	92.89	94.74	98.66
111.97	116.53	119.05	131.37	141.68	144.24
147.76	160.11	169.18	172.52	181.47	193.43
195.57	203.51	204.72	212.08	215.47	232.24
244.00	255.28	264.69	270.39	281.93	285.96
296.82	305.78	308.05	308.88	324.00	331.19
351.81	354.59	357.25	359.66	377.98	382.09
389.43	402.49	411.32	424.00	430.06	444.41
452.47	460.94	481.90	499.54	507.80	512.49
523.23	538.80	567.84	572.89	585.07	586.02
592.69	604.97	609.77	616.02	618.26	666.91
675.12	686.45	722.41	748.29	754.59	762.73
794.43	797.55	813.13	814.01	814.11	832.97
842.78	853.46	862.10	900.81	906.42	907.89
937.08	959.49	965.14	972.81	982.51	983.95
985.45	1016.06	1017.15	1034.34	1037.68	1043.93
1047.49	1053.36	1054.39	1059.47	1078.70	1088.02
1088.53	1094.88	1095.38	1107.91	1124.10	1130.23
1139.23	1170.61	1175.63	1183.13	1203.40	1209.37
1220.05	1235.10	1240.69	1257.94	1264.42	1292.17
1305.94	1325.84	1328.70	1354.51	1379.15	1393.63
1398.48	1399.91	1416.34	1420.27	1422.63	1424.37
1424.65	1428.06	1428.82	1431.40	1434.63	1436.79
1453.73	1463.17	1474.32	1481.33	1485.16	1486.92
1487.89	1490.81	1493.97	1496.84	1497.29	1500.08
1501.67	1504.00	1505.30	1513.47	1522.52	1529.66
1533.07	1539.60	1551.03	1576.91	1581.33	1600.62
1618.34	1639.80	1656.69	1924.82	2852.72	3033.54
3039.43	3040.14	3044.58	3046.75	3047.31	3062.06
3067.09	3105.21	3107.98	3111.30	3113.00	3113.08
3117.47	3125.24	3131.76	3134.34	3143.74	3148.65
3152.76	3156.75	3160.53	3168.00	3185.52	3189.81
3202.65	3216.48	3225.37	3226.71	3229.28	3237.01

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14.53	24.14	35.40	39.65	50.99	64.37
73.79	78.95	80.94	90.66	97.00	101.07
106.21	108.24	110.39	117.70	131.10	144.18
150.41	155.92	162.65	166.81	173.08	180.97
186.18	193.06	200.90	203.50	222.54	229.67
235.58	250.47	268.38	282.86	289.24	296.12
305.45	308.88	348.08	358.76	370.39	381.63
383.44	390.84	407.33	416.98	442.31	456.86
463.47	491.03	496.36	498.96	527.12	536.55
544.50	571.13	576.94	585.45	593.25	599.20
604.78	606.38	659.70	663.43	689.77	695.74
723.76	744.25	771.38	777.54	800.34	802.44
812.57	816.06	829.99	888.92	896.86	904.48
906.04	915.38	917.97	925.50	964.63	976.86
983.11	999.31	1005.79	1013.73	1016.00	1037.94
1045.10	1048.15	1055.39	1057.56	1057.92	1090.89
1094.17	1098.81	1113.30	1126.59	1128.05	1134.76
1163.91	1169.83	1181.63	1192.18	1207.41	1226.52
1235.99	1265.78	1295.44	1324.36	1324.85	1328.17
1345.46	1363.34	1370.03	1377.06	1408.24	1426.83
1428.67	1430.87	1432.59	1433.55	1435.18	1439.65
1444.20	1469.91	1471.51	1477.39	1487.65	1490.48
1492.73	1499.45	1502.09	1502.46	1507.68	1508.74
1509.85	1511.15	1514.19	1523.47	1525.47	1560.78
1573.04	1603.31	1617.06	1628.39	1640.37	1648.01
1670.95	3032.24	3038.62	3038.97	3042.10	3044.67
3053.37	3091.55	3098.84	3103.66	3106.42	3115.96
3118.12	3124.88	3136.75	3143.34	3148.00	3150.29
3159.27	3183.04	3199.64	3204.16	3215.53	3226.37
3230.34	3236.69	3236.83			

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-333.85	22.22	30.87	37.61	43.21	53.26
74.48	79.25	83.14	92.86	101.64	115.18
115.98	121.90	128.22	129.13	135.13	142.57
153.24	158.31	161.41	163.31	171.89	186.15
195.19	199.20	200.42	208.04	225.88	233.14
240.43	253.84	257.02	284.77	300.42	302.21
306.12	310.09	312.55	344.06	346.63	357.14
374.63	384.75	398.53	427.28	431.10	452.18
454.17	474.05	480.58	491.60	503.04	503.83
536.44	558.47	569.12	582.28	591.13	597.14
599.77	604.75	615.43	650.43	660.19	689.00
724.04	728.47	746.68	748.99	777.41	796.60
805.25	812.77	815.35	831.09	873.26	879.78
897.55	901.06	908.77	916.15	945.10	966.82
971.74	973.44	979.54	994.09	1016.18	1022.27
1030.93	1040.08	1043.95	1048.69	1055.11	1061.24

1081.94	1095.47	1099.85	1118.99	1124.39	1129.73
1132.79	1138.92	1173.56	1176.38	1195.75	1209.44
1218.13	1255.48	1302.08	1309.18	1317.09	1320.93
1337.73	1357.09	1376.83	1389.32	1400.48	1419.24
1424.64	1427.80	1429.14	1431.13	1432.22	1437.72
1440.08	1459.57	1462.31	1471.67	1474.75	1480.37
1487.41	1487.95	1490.23	1493.06	1497.17	1500.05
1502.37	1509.52	1510.32	1513.40	1516.46	1533.89
1553.60	1569.69	1589.69	1604.02	1632.19	1640.45
1759.59	3038.80	3039.43	3042.34	3042.41	3047.68
3051.35	3103.50	3104.09	3104.59	3106.78	3115.22
3122.54	3142.06	3146.41	3147.20	3148.28	3159.17
3162.71	3201.62	3201.74	3217.63	3218.78	3225.71
3227.57	3231.29	3236.89			

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1w-C6

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14.65	27.80	29.77	38.47	47.08	69.45
76.79	85.19	86.41	91.15	97.45	106.89
124.14	125.49	128.25	138.30	141.05	152.50
157.24	158.05	162.75	169.93	184.31	187.03
198.69	201.33	207.59	228.52	233.17	237.09
255.88	267.32	277.71	291.53	299.86	304.43
310.09	341.72	353.63	358.50	361.25	379.18
391.13	399.96	408.15	439.15	452.28	463.41
475.17	495.51	505.97	509.81	535.45	540.48
556.50	569.85	572.22	587.21	597.55	606.47
608.13	615.63	634.72	667.92	681.01	687.75
723.56	736.87	753.37	760.85	772.71	797.60
807.59	813.77	815.47	830.66	843.58	859.42
887.49	903.51	906.51	945.37	966.81	971.34
985.32	988.21	1014.91	1020.36	1034.26	1039.01
1046.29	1051.01	1054.84	1061.90	1075.76	1085.74
1094.50	1095.56	1105.56	1110.42	1131.03	1142.37
1165.36	1177.61	1183.98	1193.70	1217.48	1231.53
1239.84	1263.00	1291.28	1297.04	1324.75	1327.89
1355.92	1365.86	1399.40	1400.64	1410.12	1423.50
1424.12	1426.11	1426.82	1429.11	1431.79	1436.44
1438.04	1462.31	1466.11	1474.80	1476.06	1485.38
1487.15	1487.75	1488.41	1489.06	1493.08	1496.13
1500.41	1505.12	1511.72	1528.40	1531.94	1556.27
1572.93	1578.76	1604.53	1616.62	1639.69	1675.39
1954.75	2864.18	3031.68	3034.22	3041.91	3044.32
3047.69	3049.96	3095.47	3105.11	3109.56	3111.28
3113.01	3114.27	3143.58	3148.06	3153.25	3156.41
3158.15	3163.88	3197.21	3208.17	3216.05	3226.29
3226.91	3229.34	3257.86			

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1w-C2-TS

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-354.86	15.42	31.77	33.14	45.99	53.75
75.30	79.24	81.52	95.89	97.23	102.60
116.15	118.18	122.22	128.34	132.80	139.67
144.84	155.56	161.34	164.16	170.34	181.85
187.26	197.47	200.10	203.82	216.93	233.66
239.77	252.56	254.64	285.04	299.45	302.42
308.14	309.14	311.87	346.07	347.95	360.63
374.18	384.96	397.95	430.68	432.50	452.11
453.72	474.85	480.38	496.42	503.57	515.82
536.06	557.55	569.28	582.22	589.69	597.02
601.38	604.23	615.71	658.46	661.37	687.01
708.05	738.40	751.56	752.75	769.57	794.40
810.25	813.18	815.19	831.35	869.10	893.53
900.57	902.47	909.13	917.25	958.03	966.25
972.01	984.42	986.66	995.19	1016.00	1022.19
1037.72	1039.77	1043.75	1054.78	1060.52	1066.85
1083.68	1095.33	1098.61	1099.84	1118.43	1132.64
1137.58	1142.84	1173.18	1176.22	1196.82	1211.89
1217.02	1257.30	1300.12	1309.27	1322.62	1330.29
1336.95	1356.68	1369.15	1384.85	1400.35	1416.88
1424.64	1426.83	1427.37	1430.58	1431.41	1432.02
1437.51	1441.80	1460.07	1464.48	1474.58	1479.77
1487.13	1489.87	1492.68	1496.29	1499.63	1501.30
1503.07	1509.49	1509.85	1515.68	1530.03	1533.52
1553.22	1583.86	1588.90	1604.94	1630.98	1639.25
1759.76	3038.44	3038.97	3042.32	3047.58	3051.23
3052.72	3102.80	3104.73	3106.07	3114.89	3119.38
3122.15	3141.82	3142.41	3147.49	3147.69	3159.82
3162.31	3196.02	3201.22	3209.91	3215.00	3218.59
3228.70	3231.01	3231.61			

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1w-C2

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13.23	26.25	33.17	46.87	55.46	72.61
82.89	84.43	91.84	96.20	102.08	112.21
119.21	129.73	131.56	138.96	147.09	148.05
158.37	165.62	167.91	173.34	182.40	197.59
204.70	206.82	224.44	226.43	241.57	248.27
256.88	278.03	284.07	292.48	300.31	308.91
334.06	345.35	353.27	359.34	372.99	386.55
393.16	419.57	442.82	446.15	453.76	479.87
495.18	503.10	512.64	532.83	536.32	547.97
560.17	566.08	586.67	588.09	594.98	601.18
616.16	649.66	660.22	675.02	687.10	728.26
741.73	761.82	772.84	788.28	801.10	809.32
813.90	820.35	831.69	835.23	840.99	885.84
903.73	908.11	948.28	971.76	979.87	982.21
1012.94	1017.11	1018.95	1028.08	1033.70	1036.47
1049.72	1054.02	1062.35	1063.14	1083.55	1084.98
1095.09	1101.26	1105.58	1118.80	1129.84	1156.05
1170.85	1180.74	1190.75	1203.90	1208.52	1226.07
1237.88	1263.21	1292.48	1294.40	1324.53	1326.06
1370.86	1379.24	1398.28	1403.27	1406.04	1419.99
1422.12	1422.53	1425.72	1428.32	1430.97	1432.98
1433.84	1460.90	1465.96	1472.63	1479.19	1485.50
1486.26	1489.10	1492.42	1493.09	1499.33	1501.85
1502.24	1506.61	1510.81	1518.98	1534.57	1543.61
1583.97	1604.07	1614.73	1620.44	1644.09	1668.36
1943.32	2838.54	3035.63	3035.91	3038.26	3046.44
3048.59	3052.02	3104.31	3110.75	3112.09	3115.01
3115.91	3126.42	3143.47	3144.15	3149.20	3152.58
3170.18	3170.59	3195.44	3214.60	3218.57	3224.26
3228.50	3233.44	3240.20			

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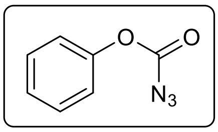
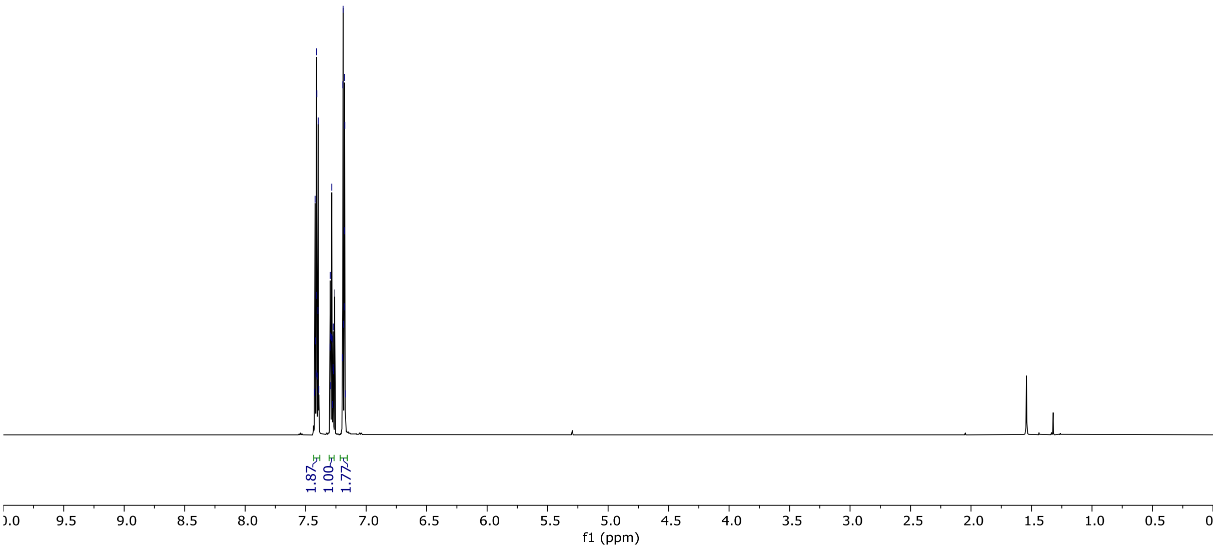
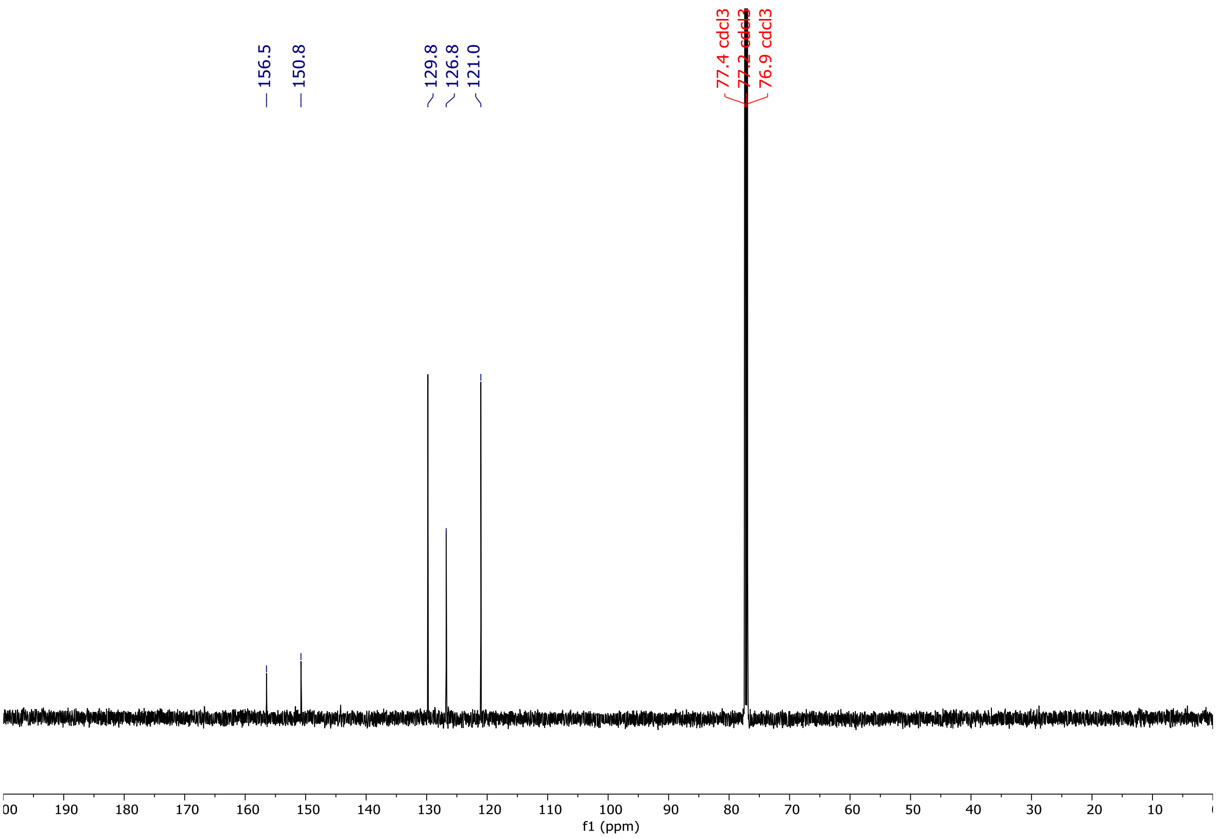
Appendix I

Spectral Copies of ^{1}H, ^{13}C and ^{19}F NMR of Compounds Obtained in this Study

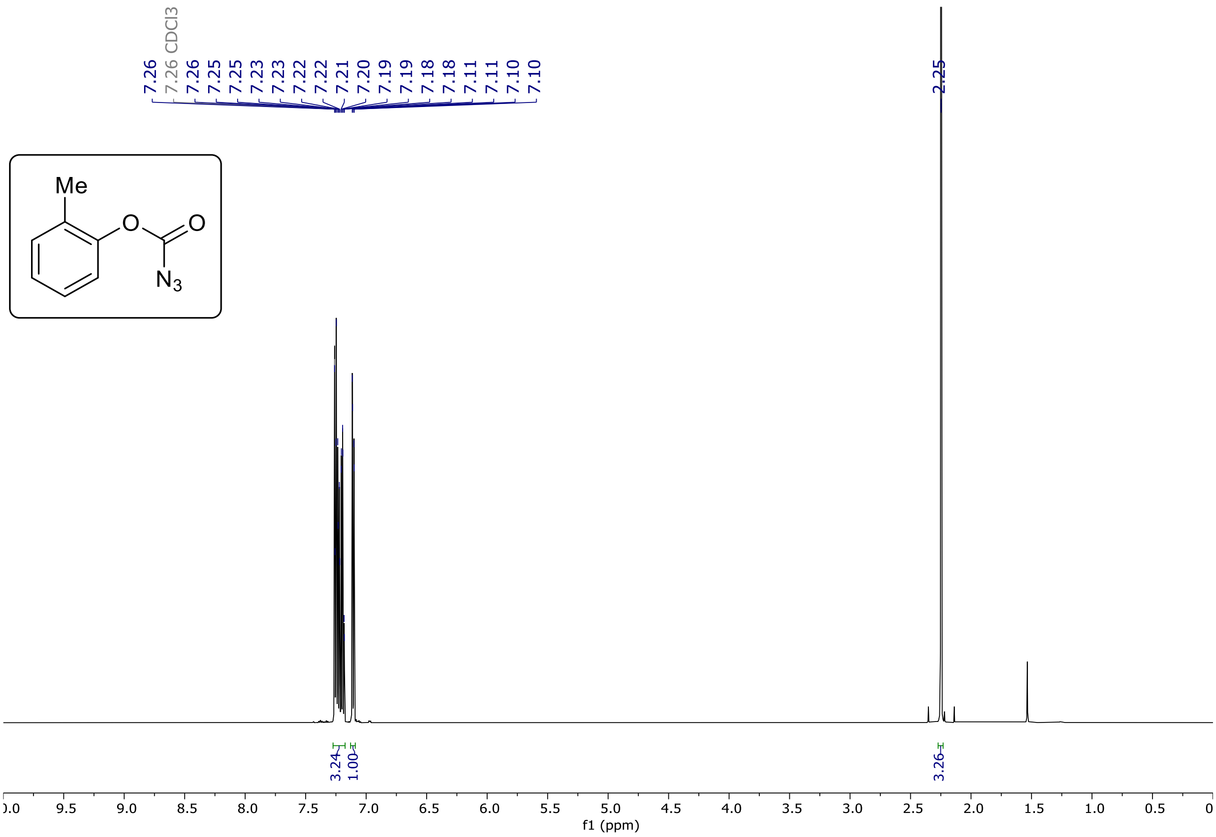
Phenyl azidoformate (1a)

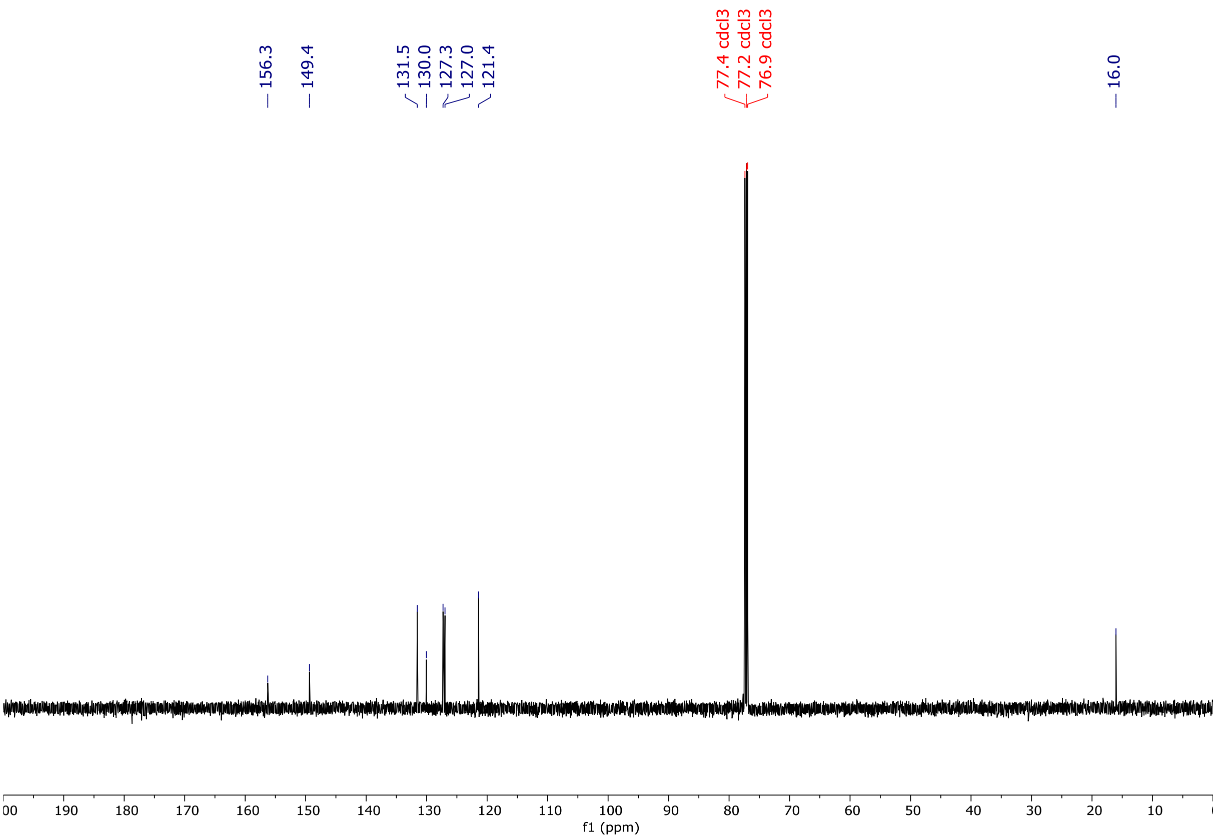




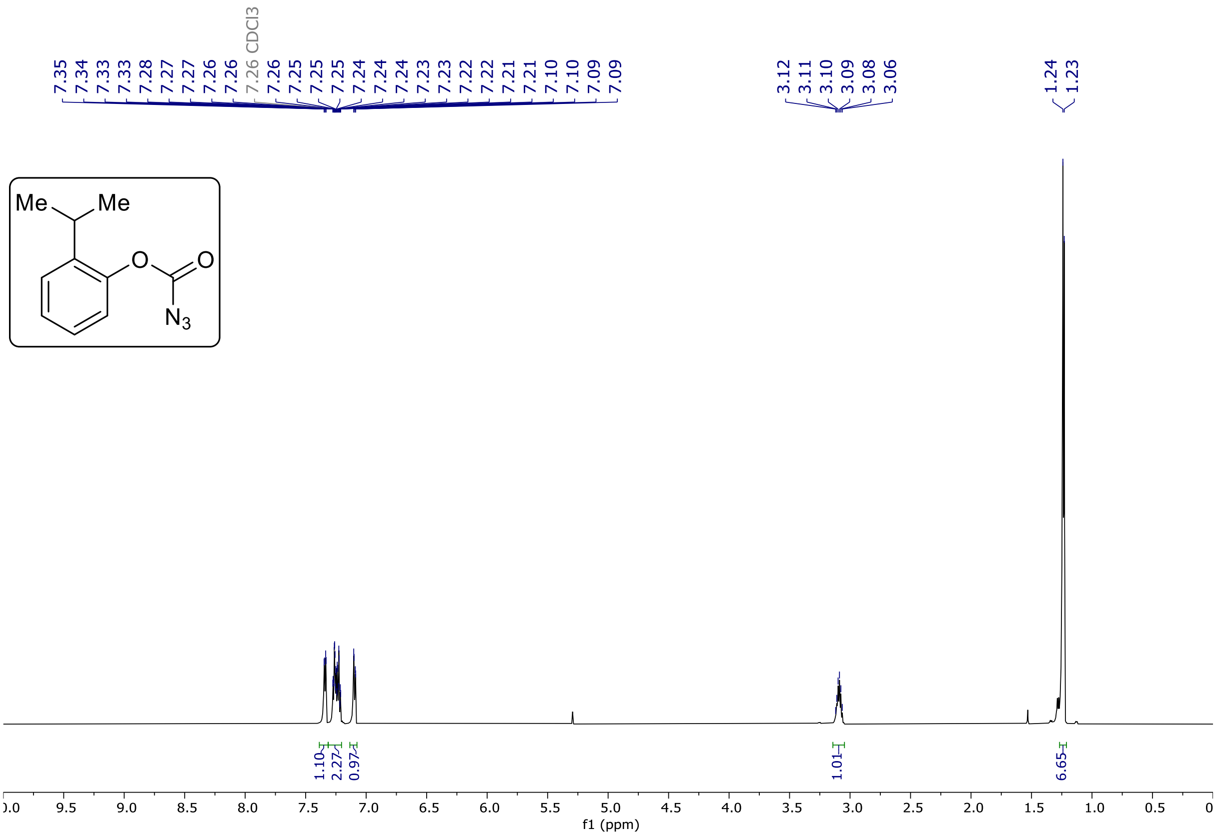


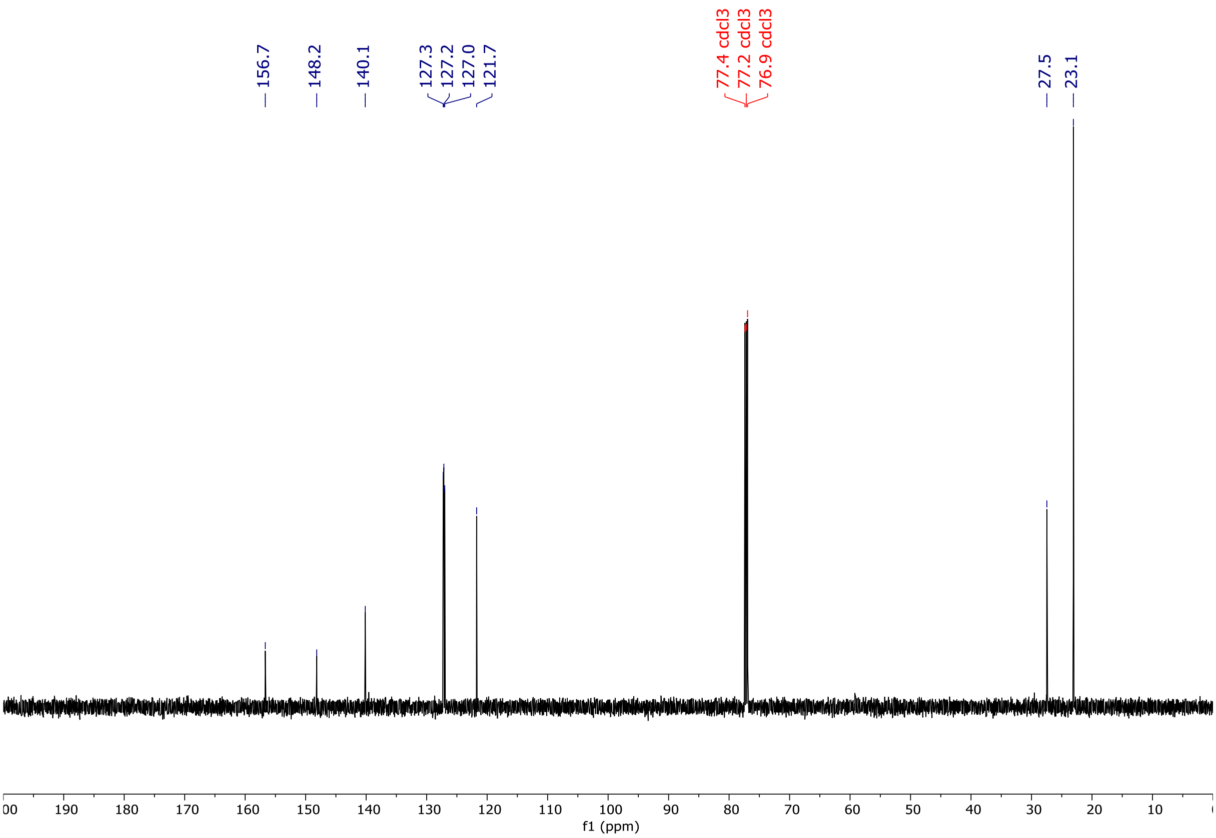
o-Tolyl azidoformate (1b)



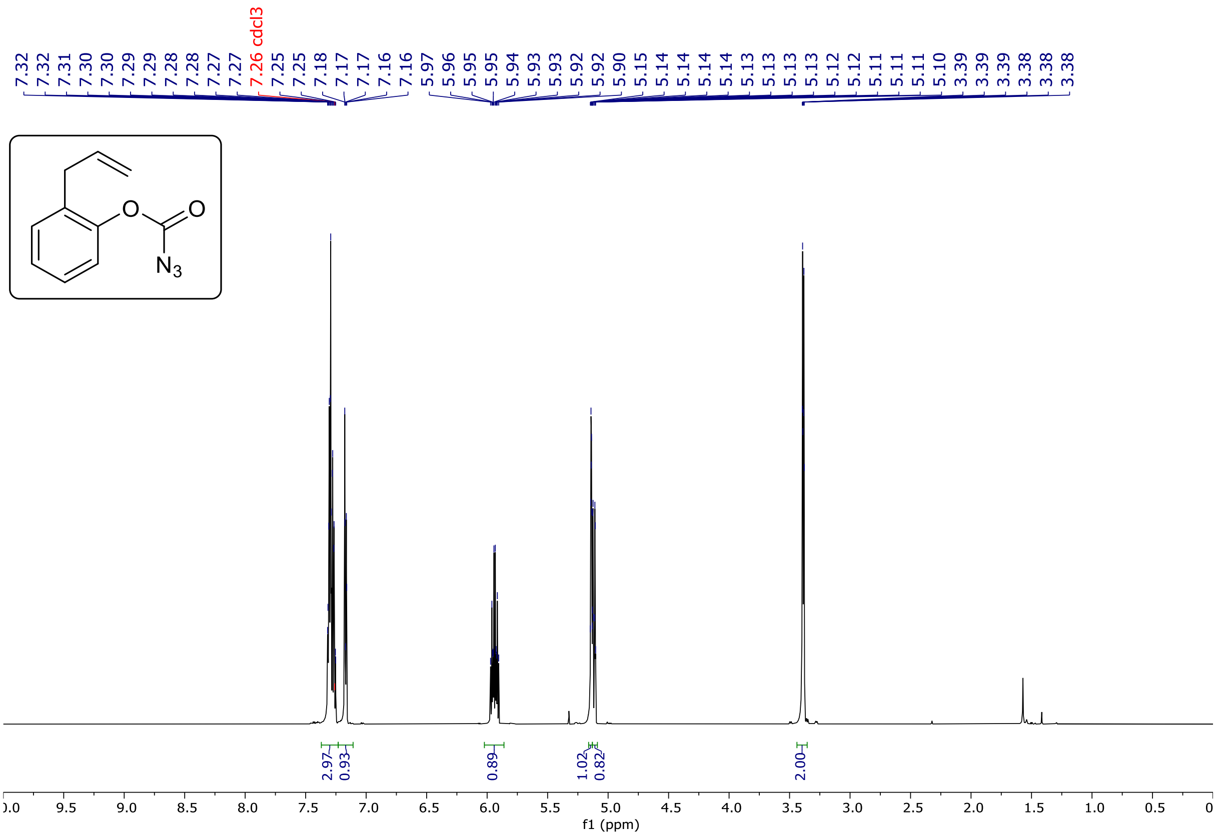


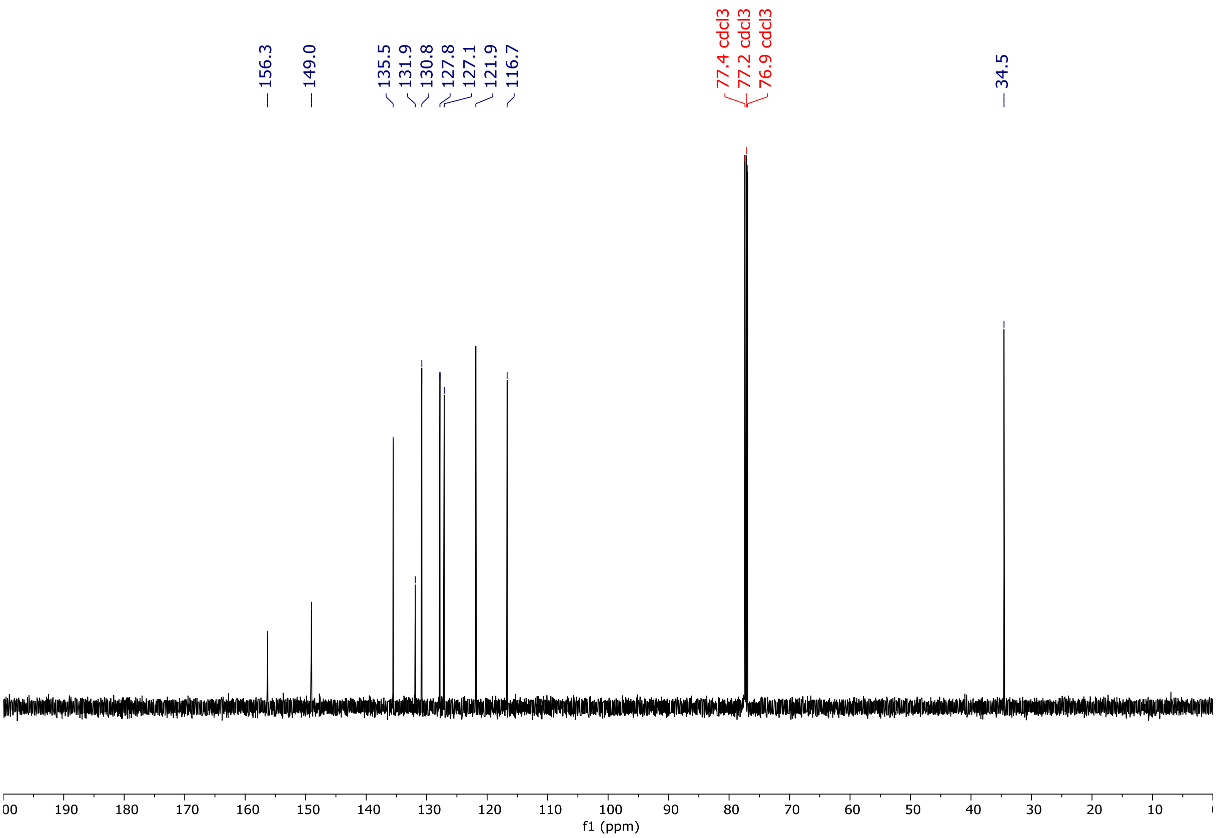
2-Isopropylphenyl azidoformate (1c)



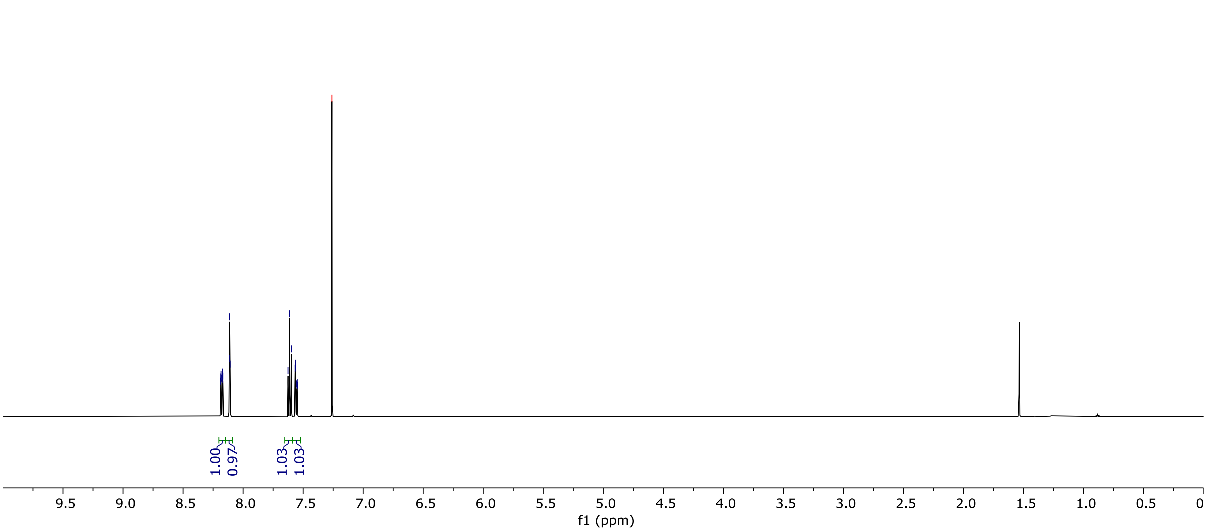


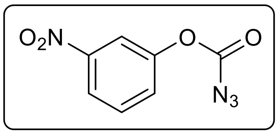
2-Allylphenyl azidoformate (1d)

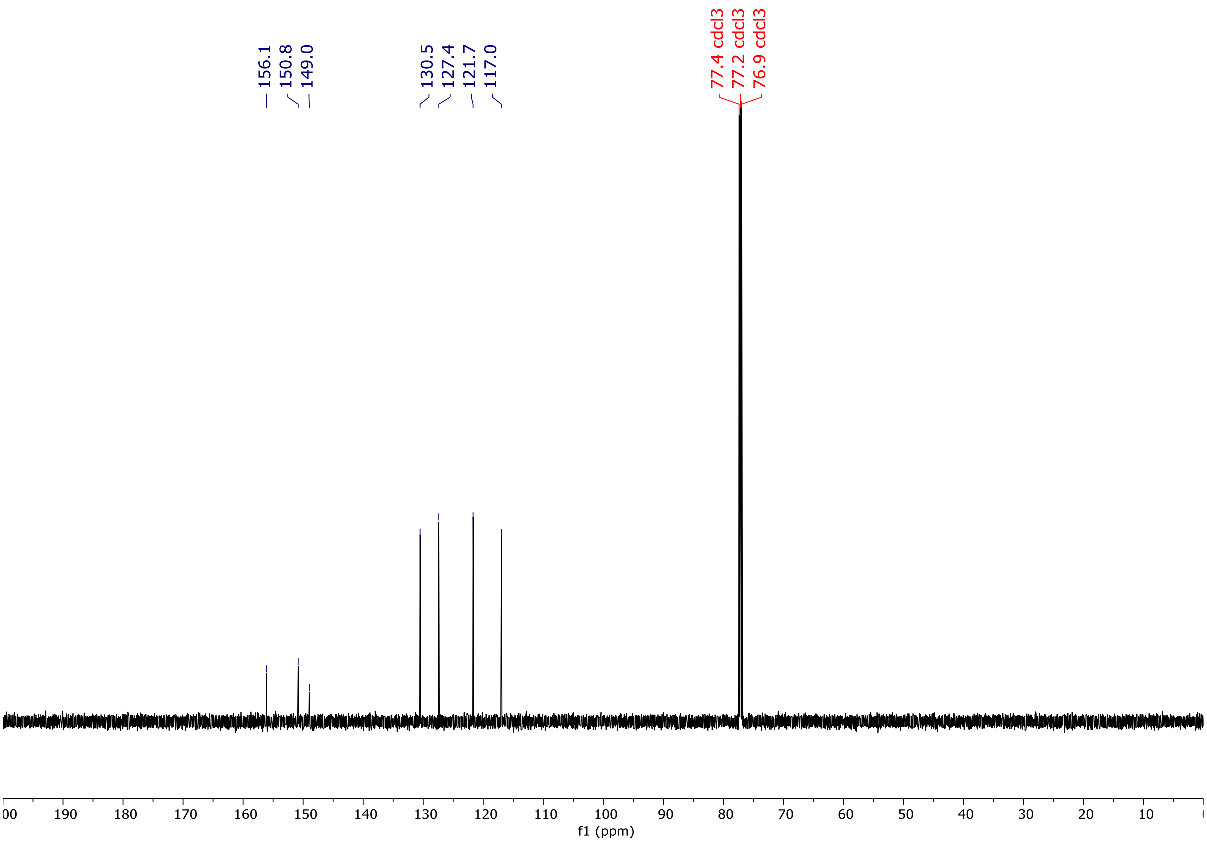




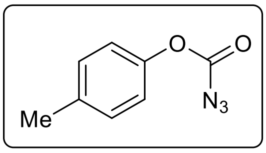
3-Nitrophenyl azidoformate (1e)

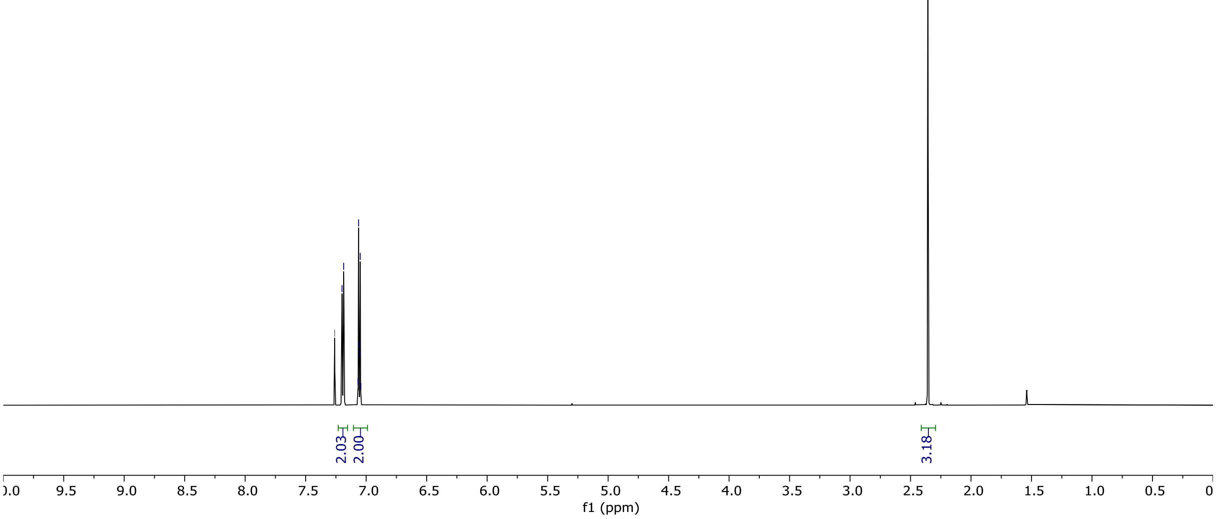


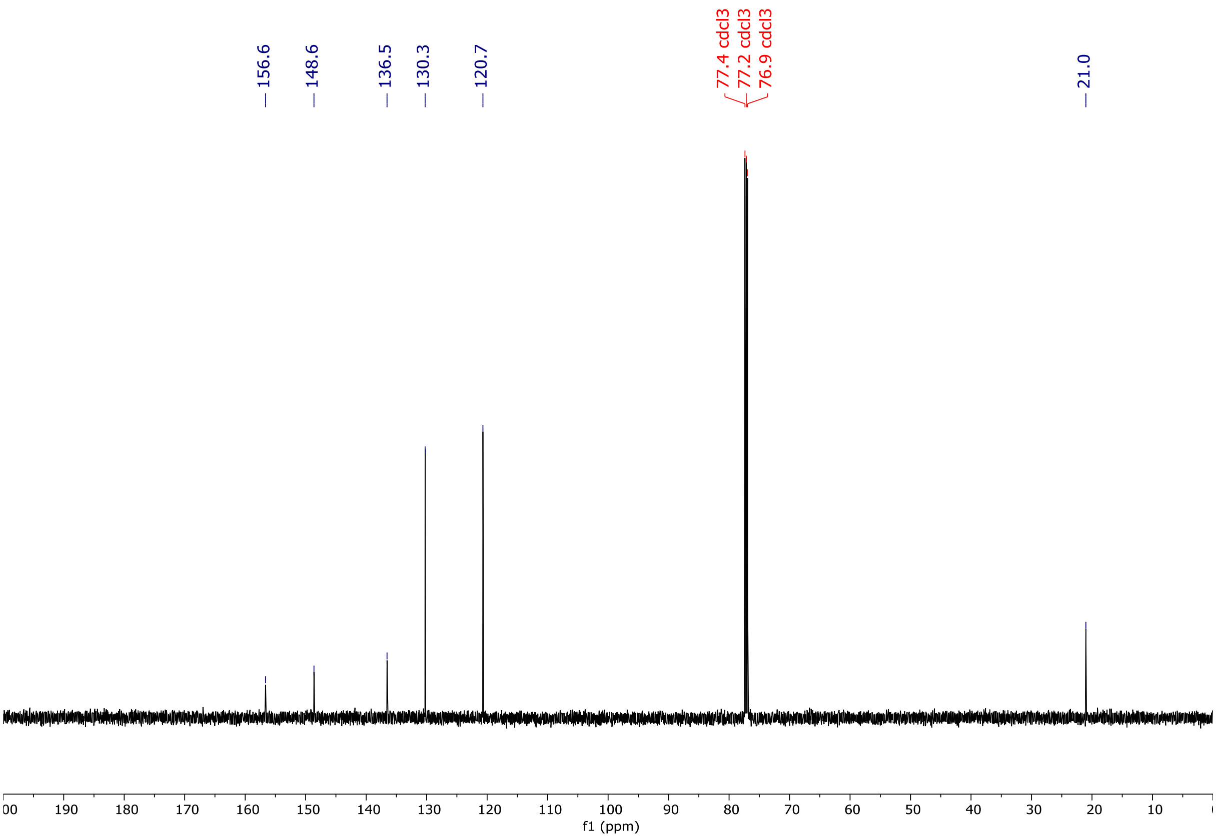




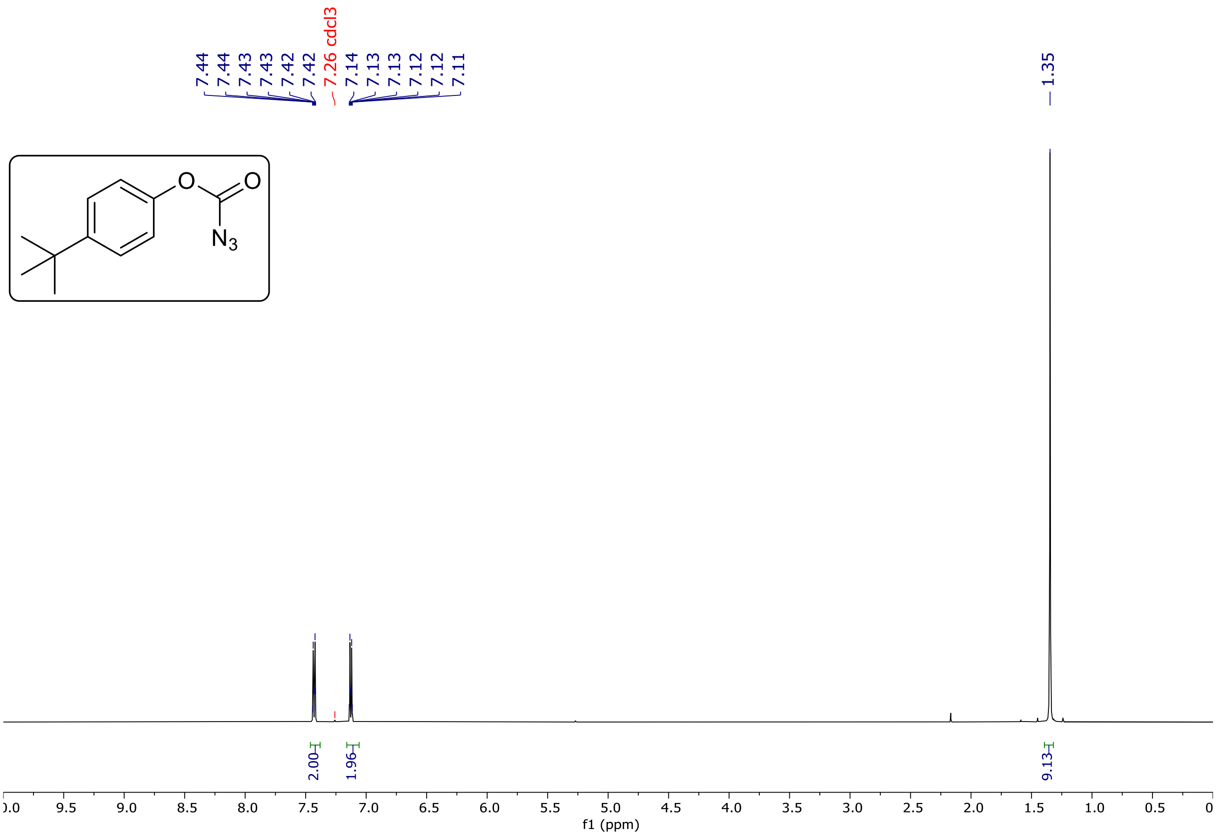
_p_-Tolyl azidoformate (1f)

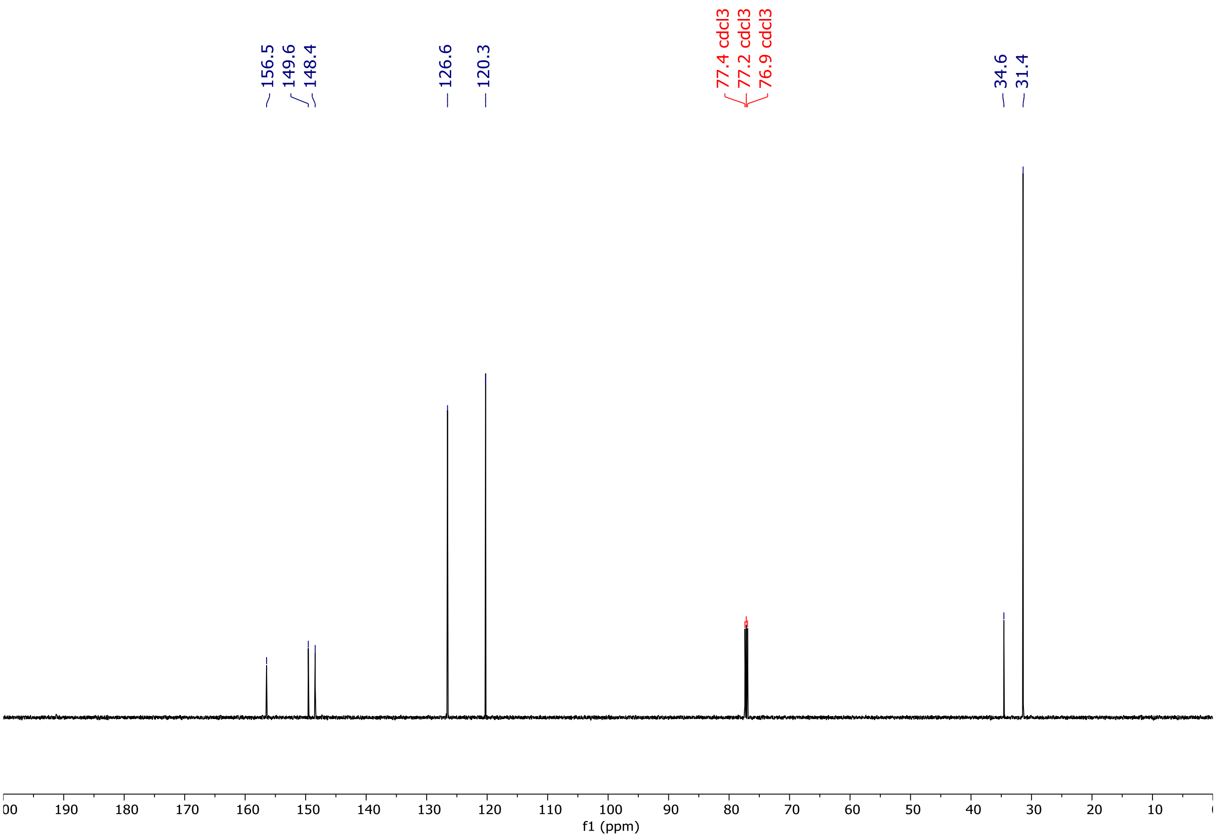




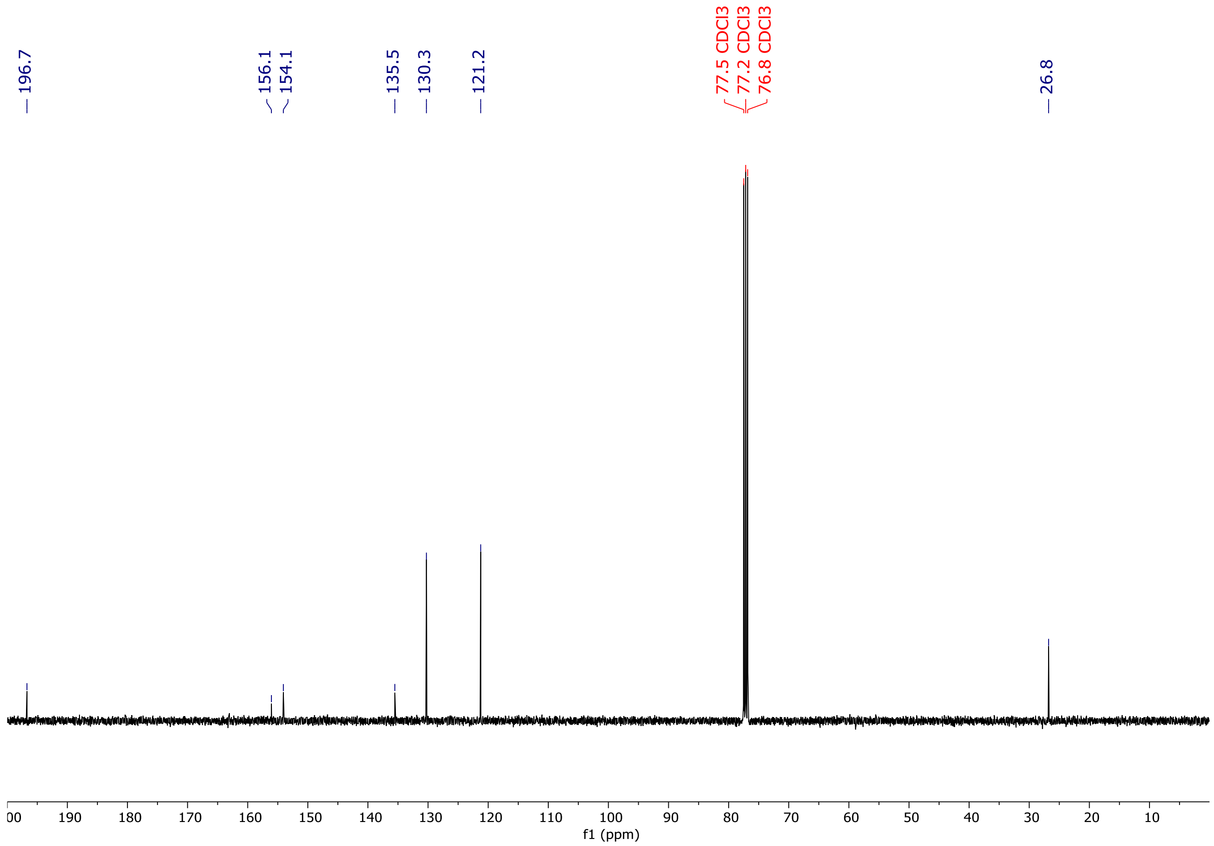


4-(*tert*-Butyl)phenyl azidoformate (1g)

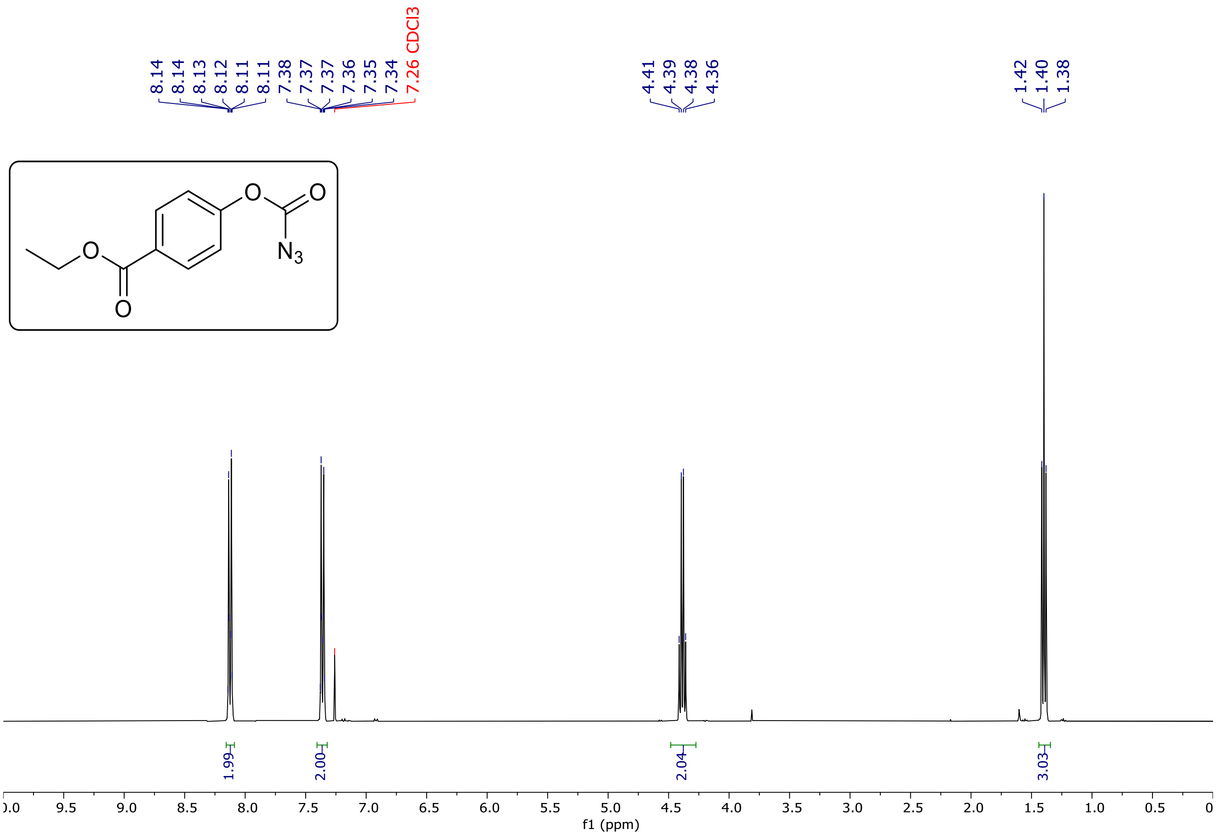


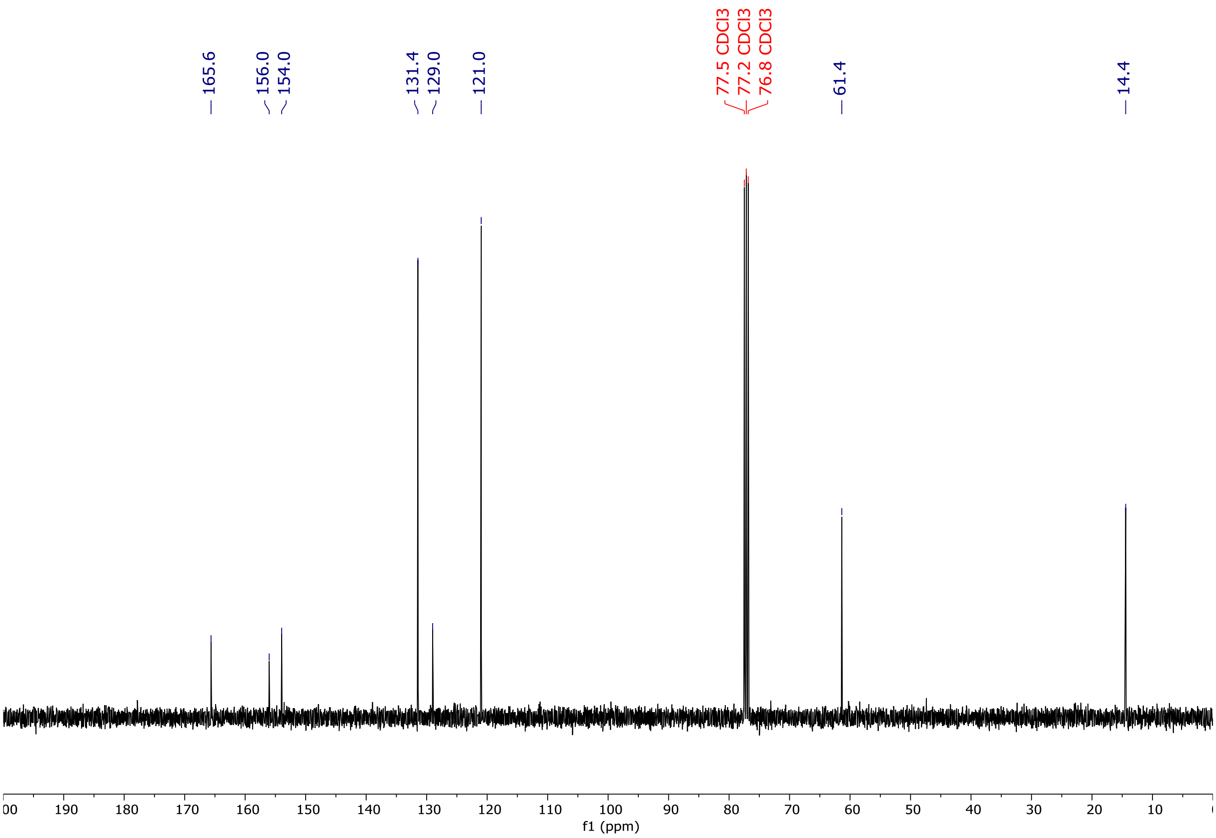


4-Acetylphenyl azidoformate (1h)

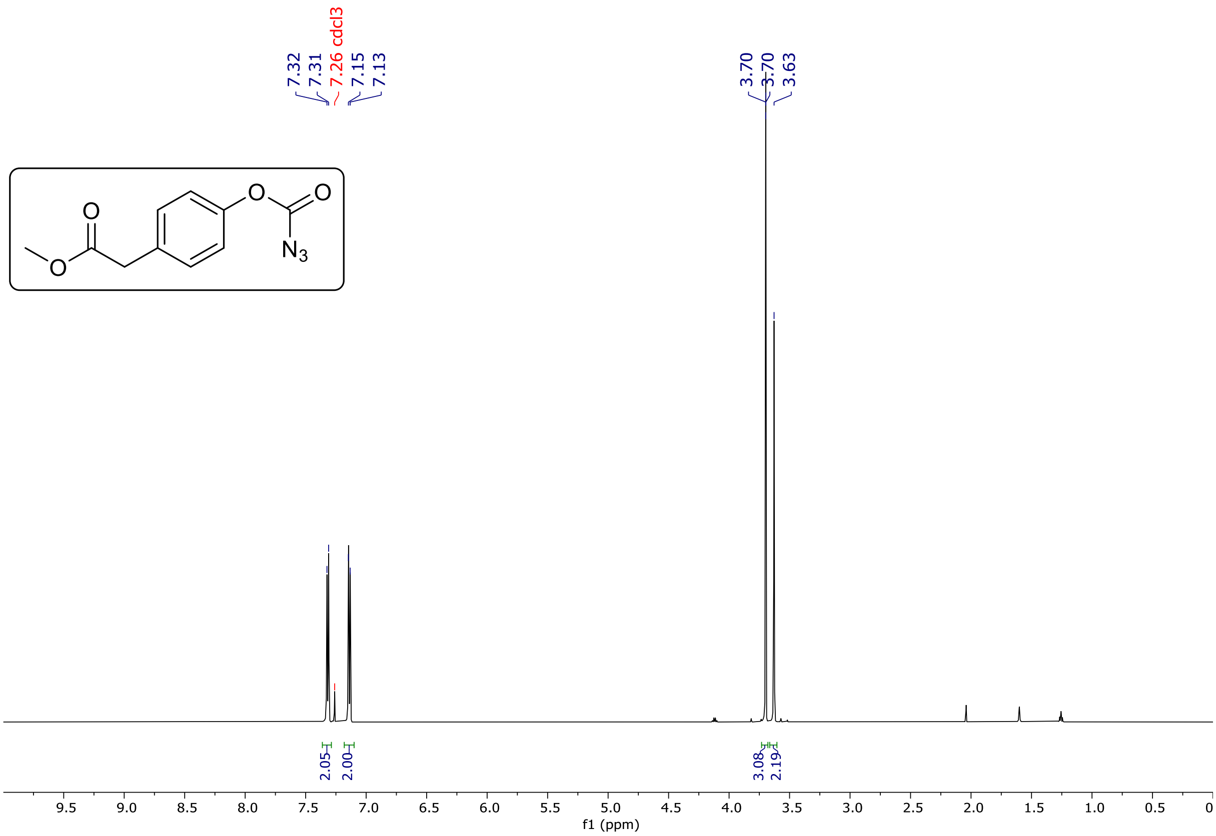


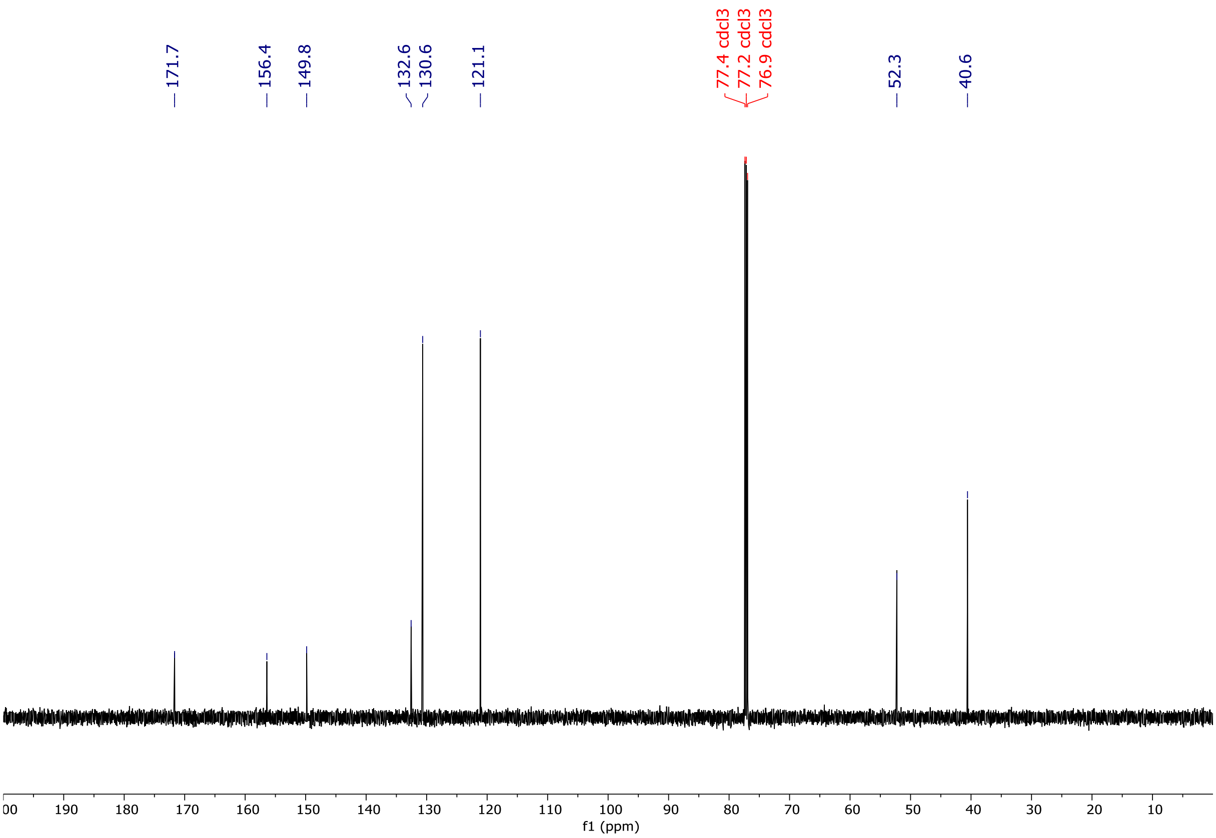
Ethyl 4-{(azidocarbonyl)oxy}benzoate (1i)



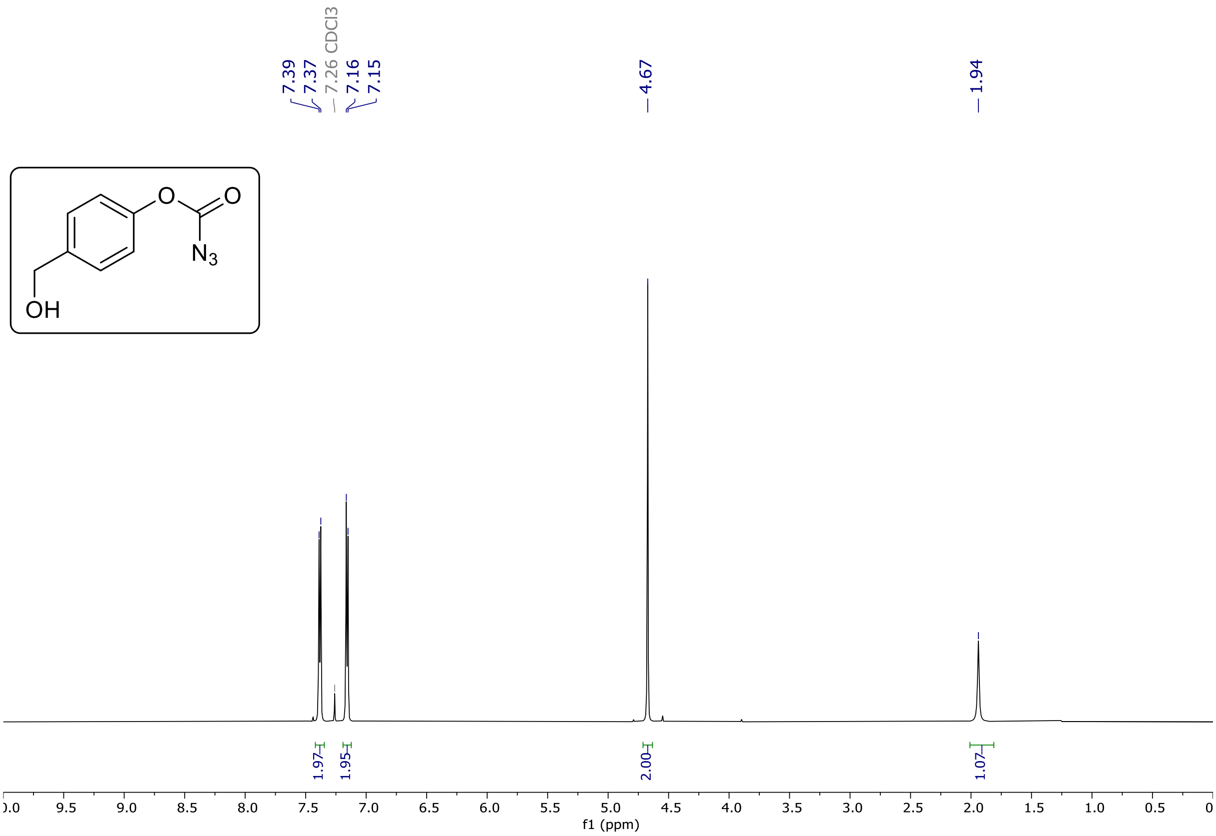


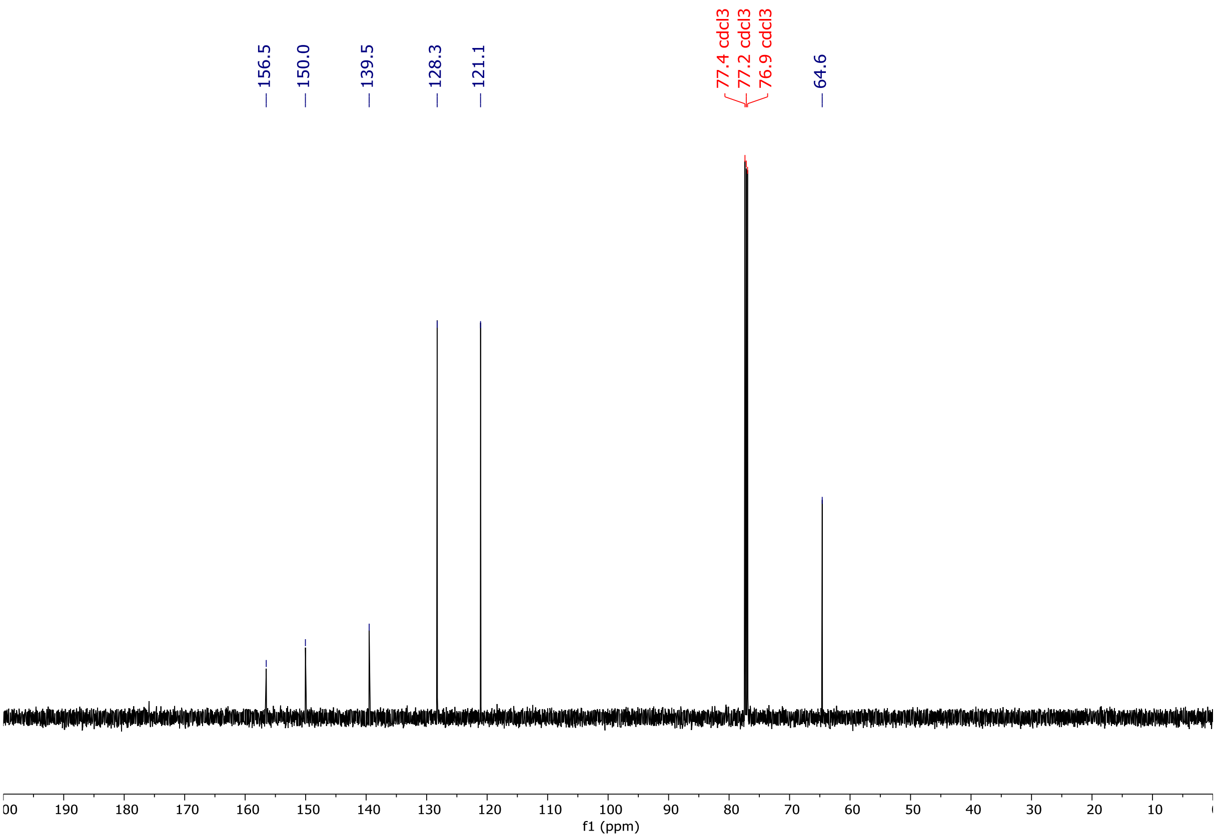
Methyl 2-[4-{(azidocarbonyl)oxy}phenyl]acetate (1j)



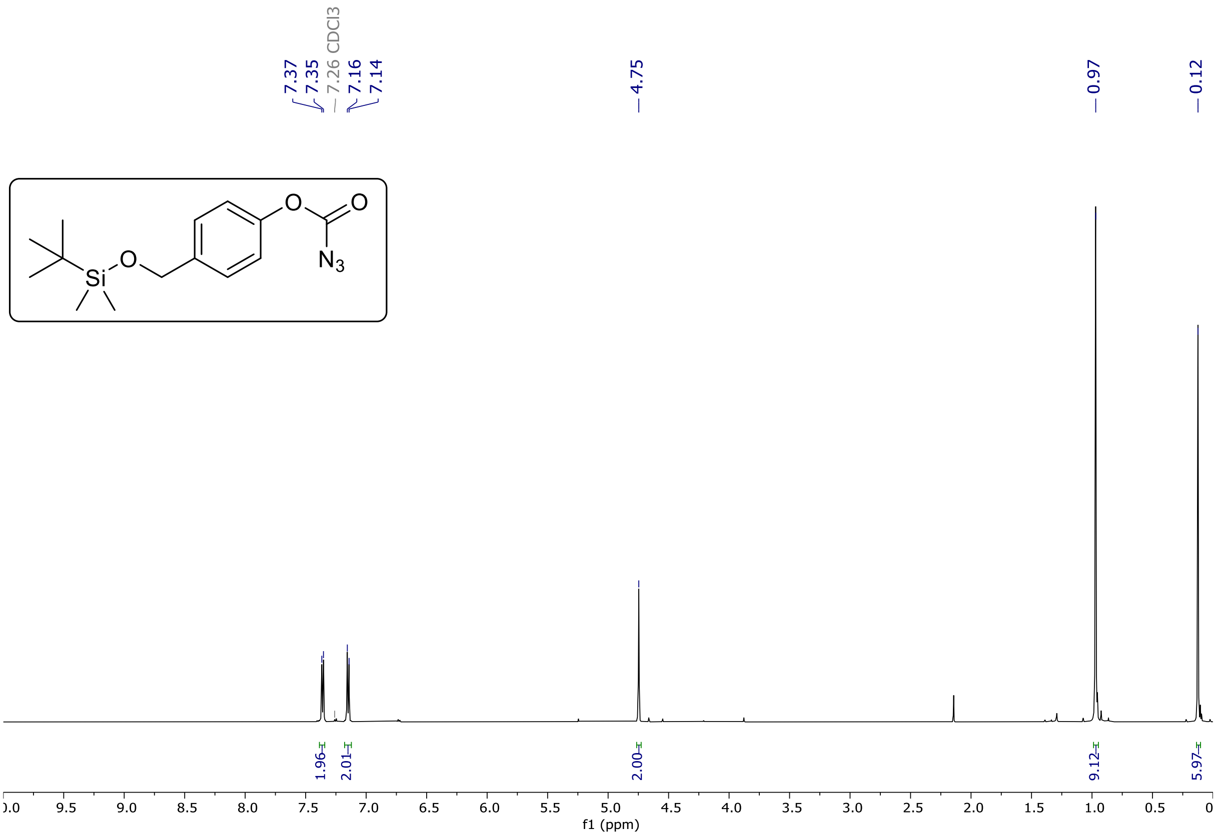


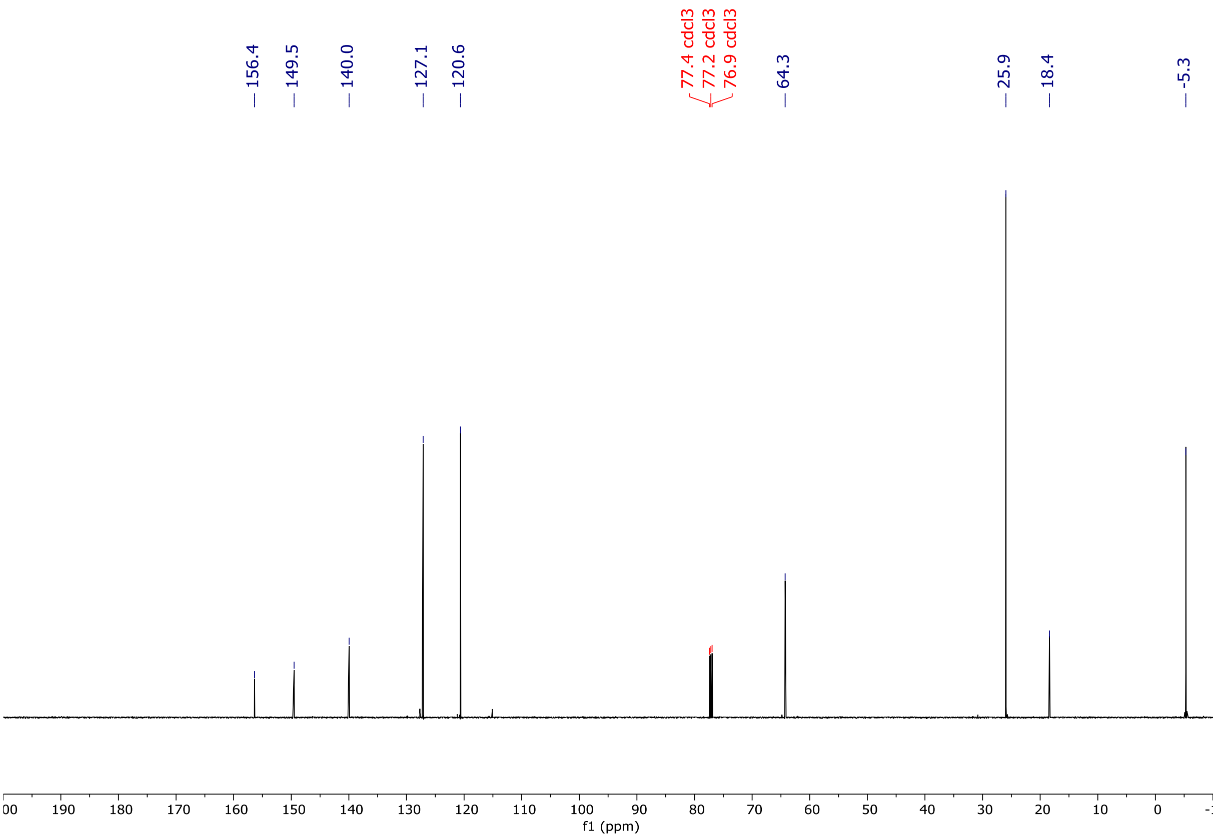
4-(Hydroxymethyl)phenyl azidoformate (1k)



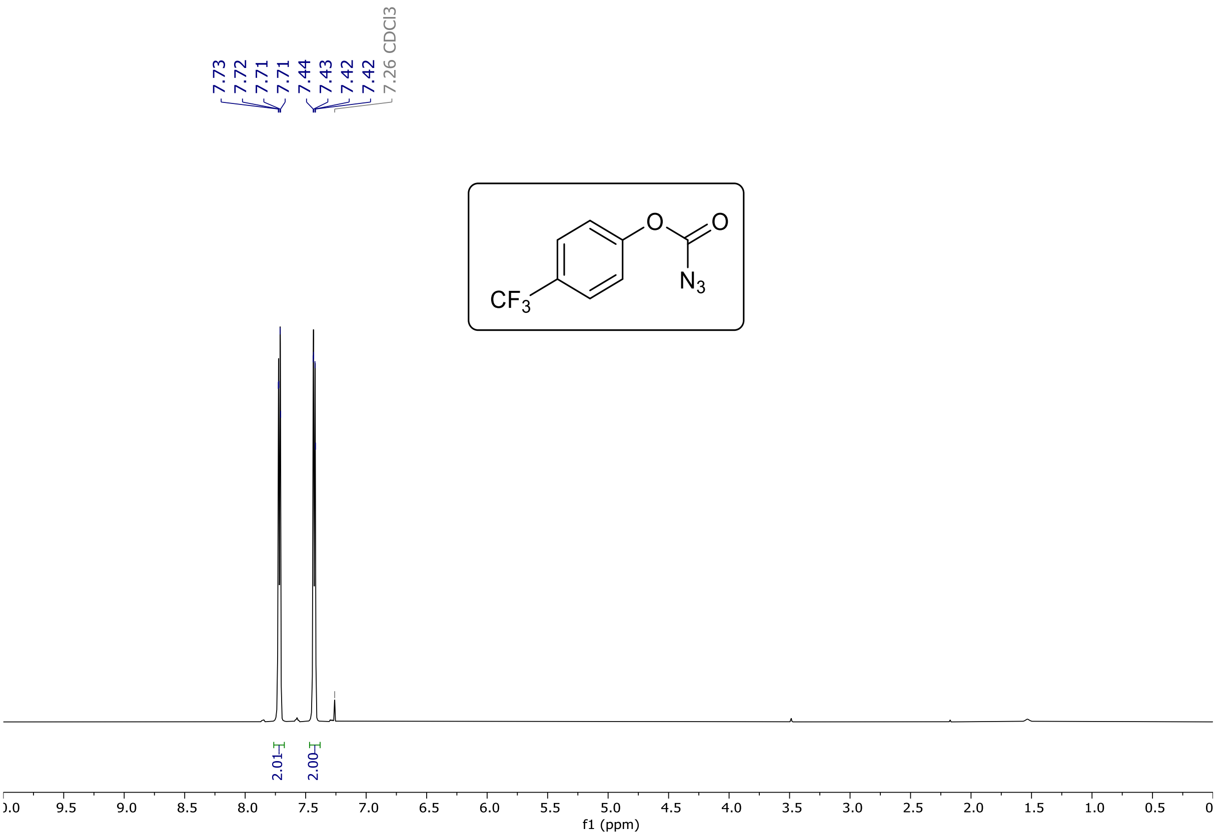


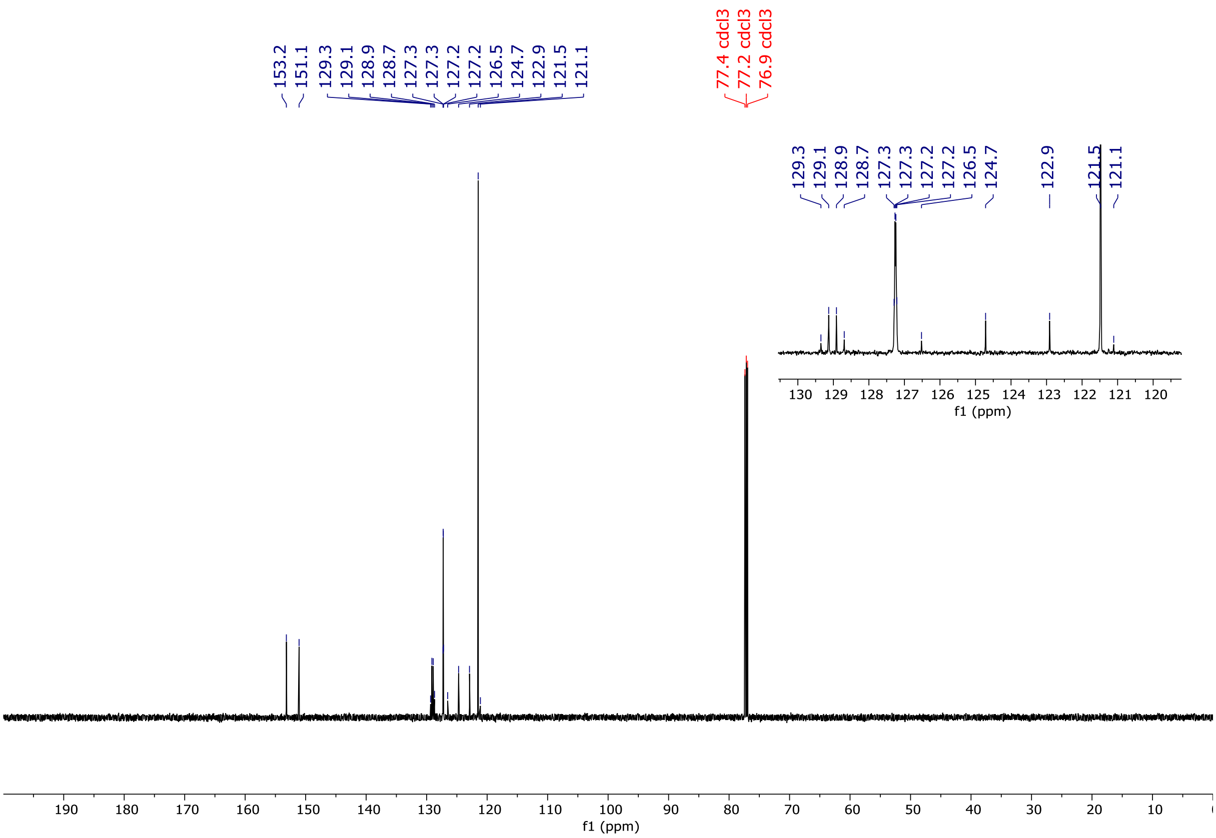
4-[{(*tert*-Butyldimethylsilyl)oxy}methyl]phenyl azidoformate (1l)

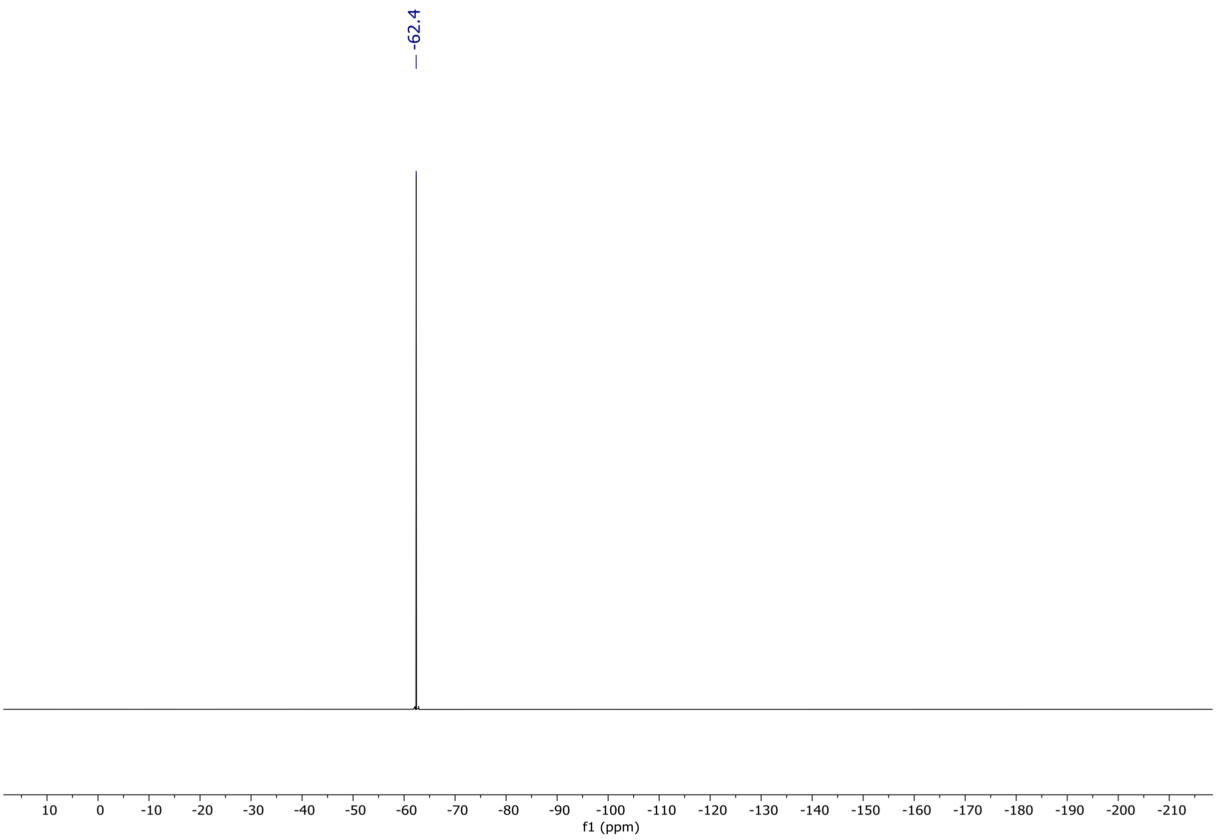




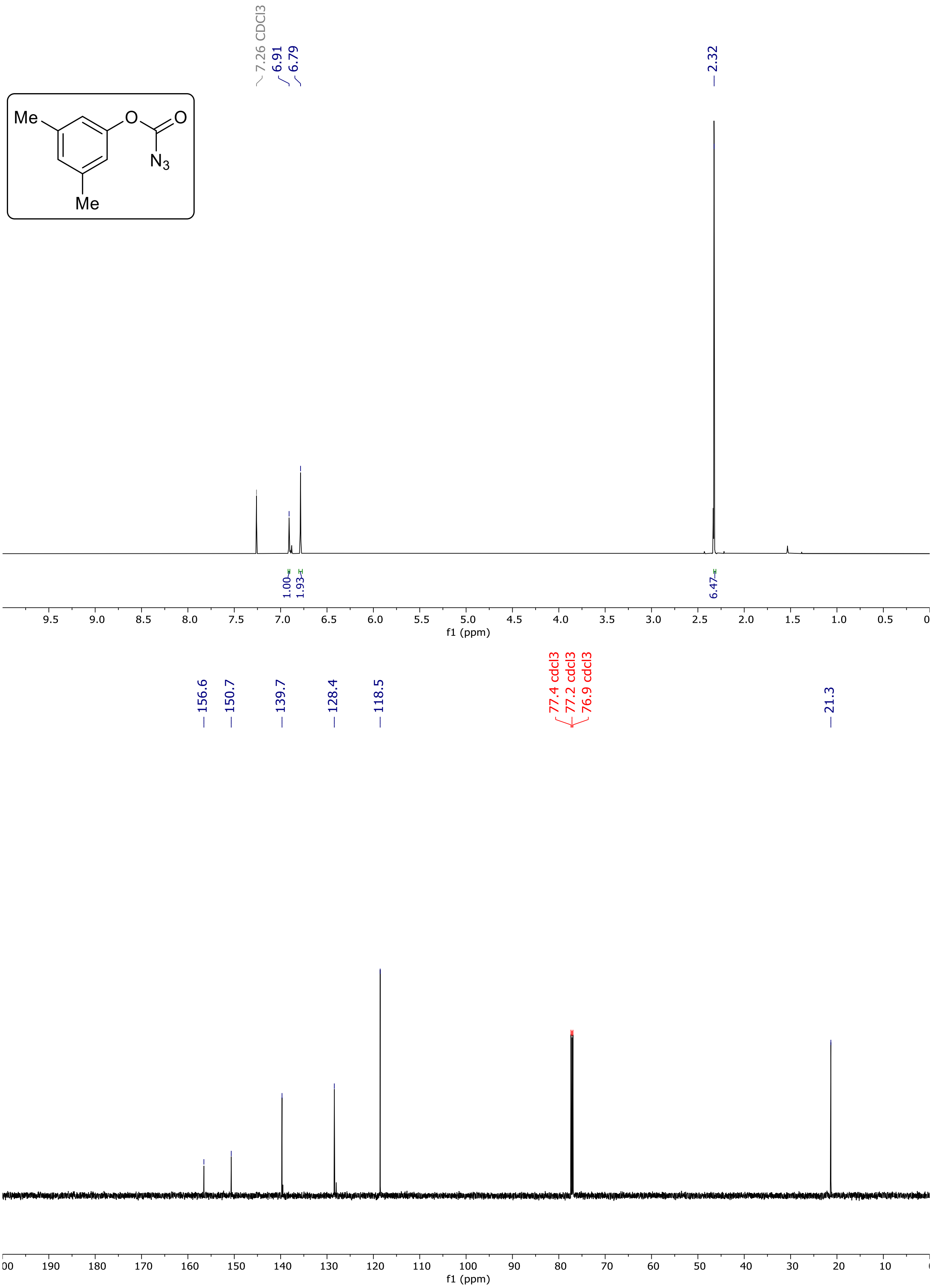
4-(Trifluoromethyl)phenyl azidoformate (1m)



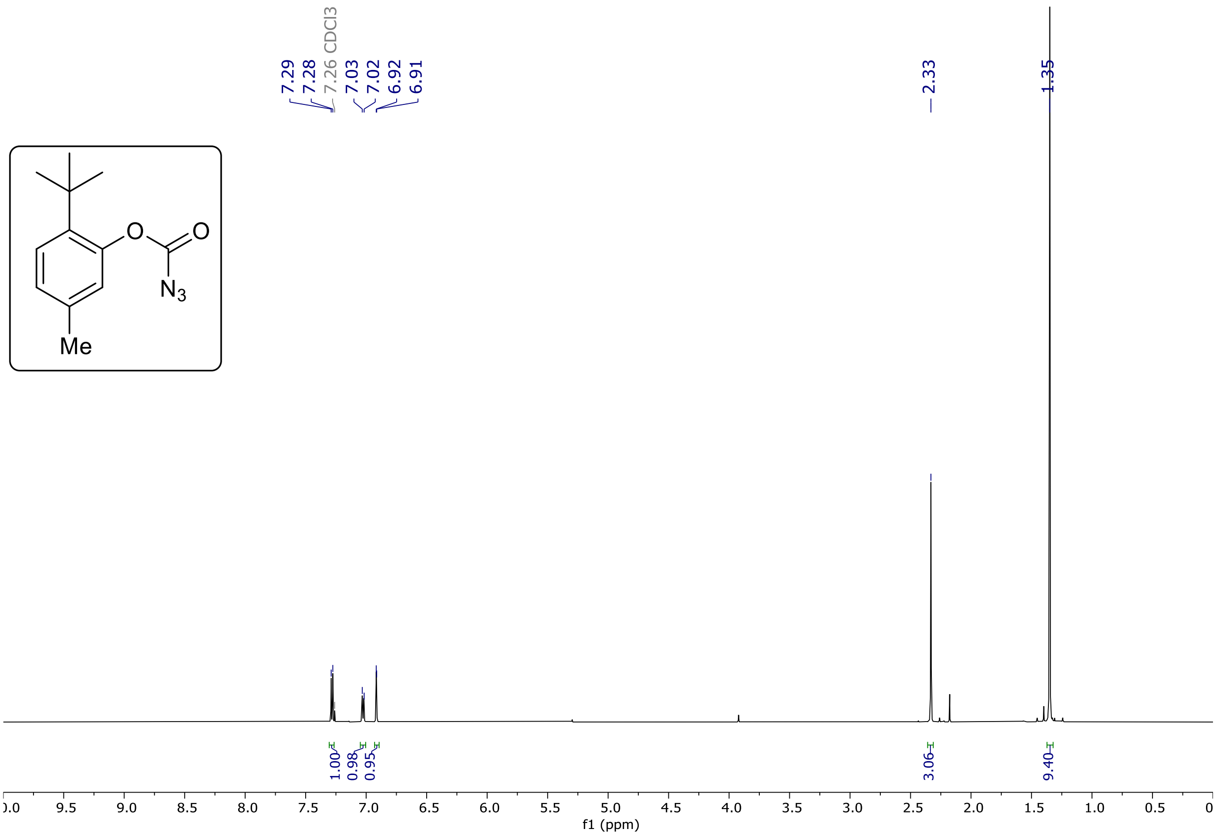


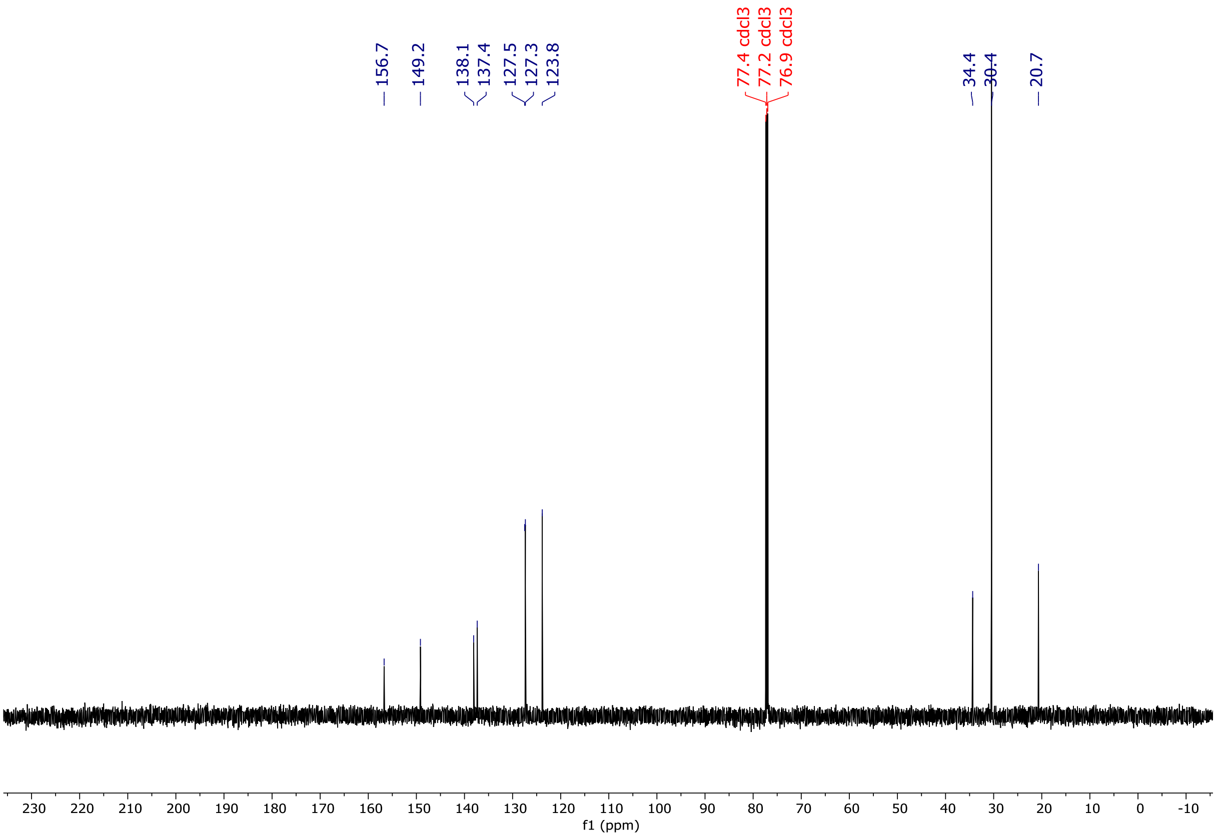

-62.4
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

3,5-Dimethylphenyl azidoformate (1n)

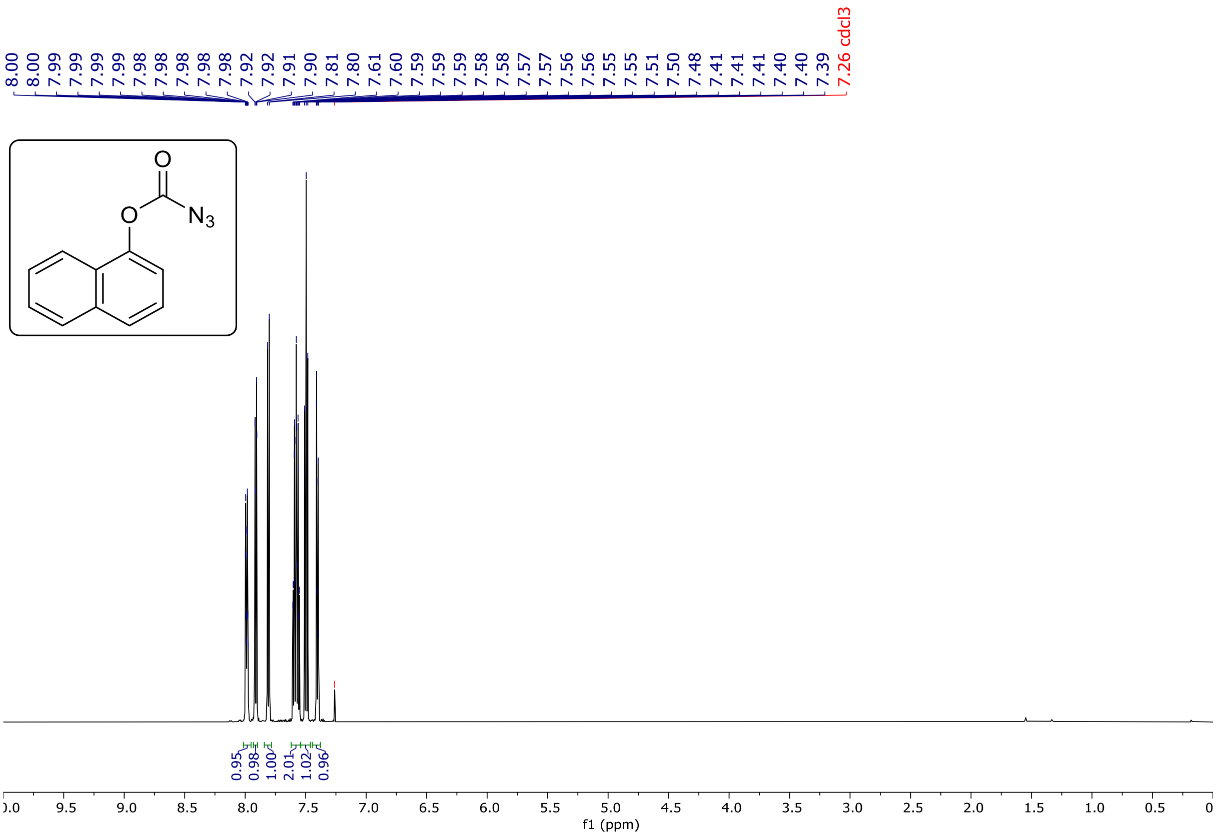


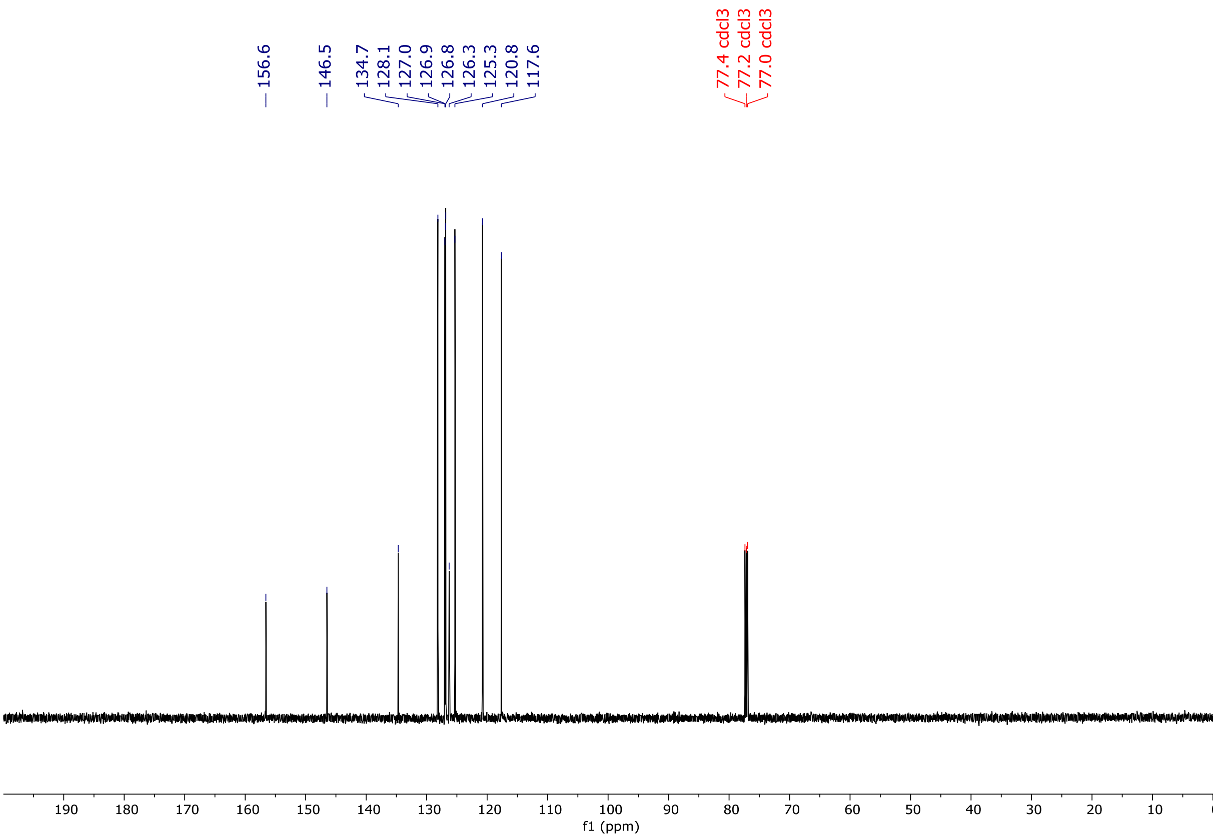
2-(*tert*-Butyl)-5-methylphenyl azidoformate (1o)



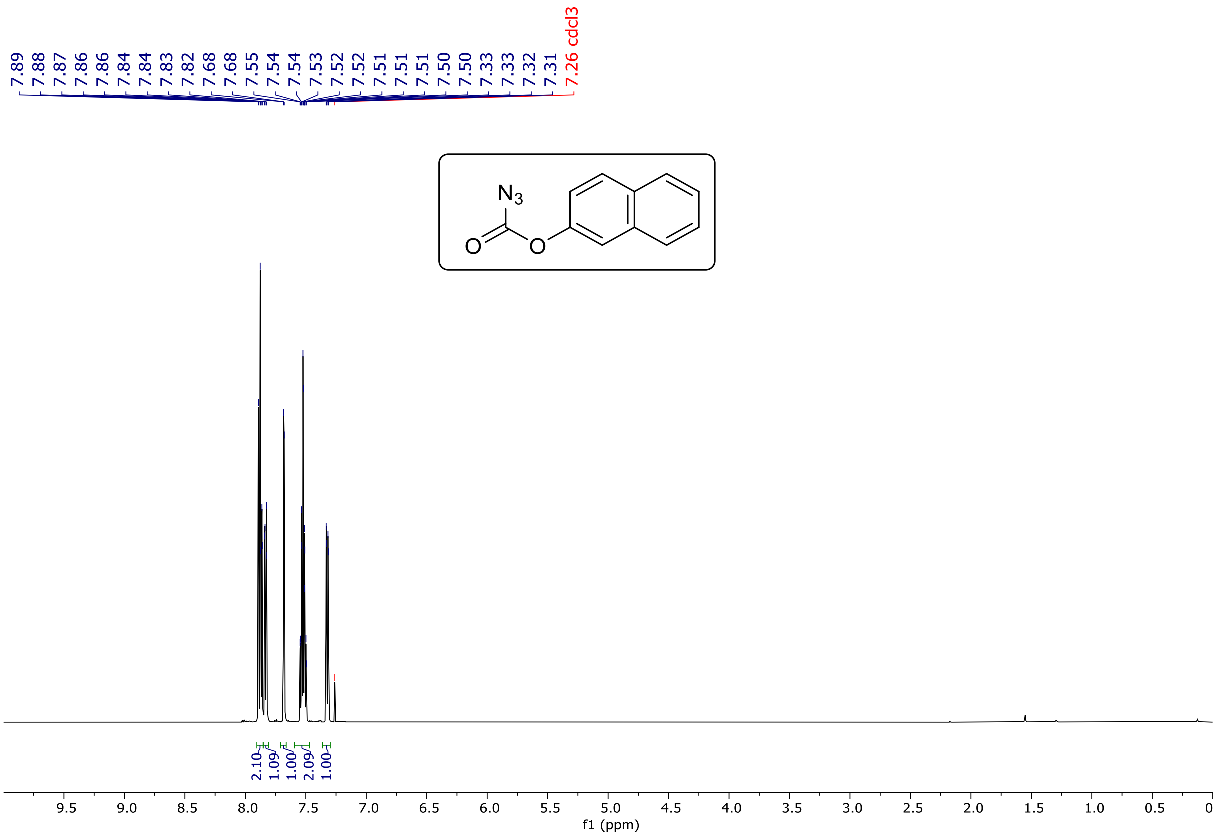


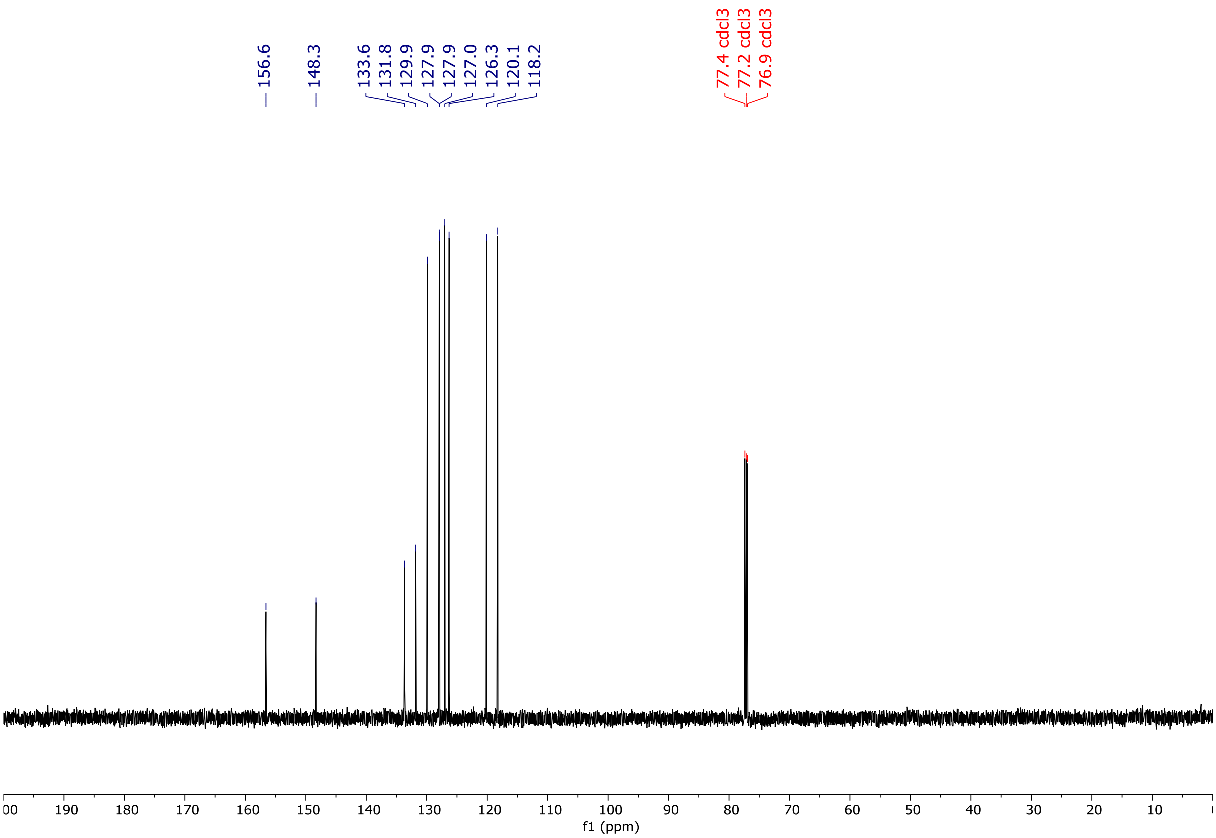
Naphthalen-1-yl azidoformate (1p)



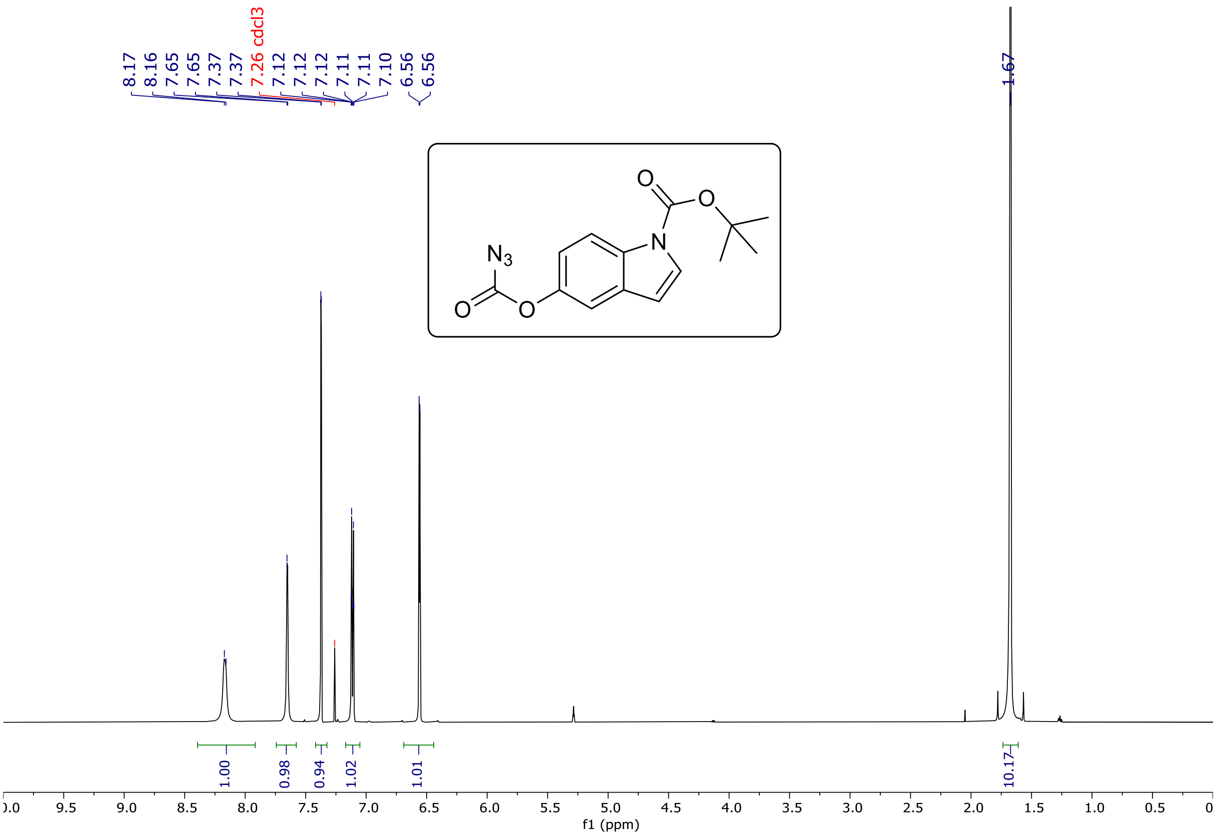


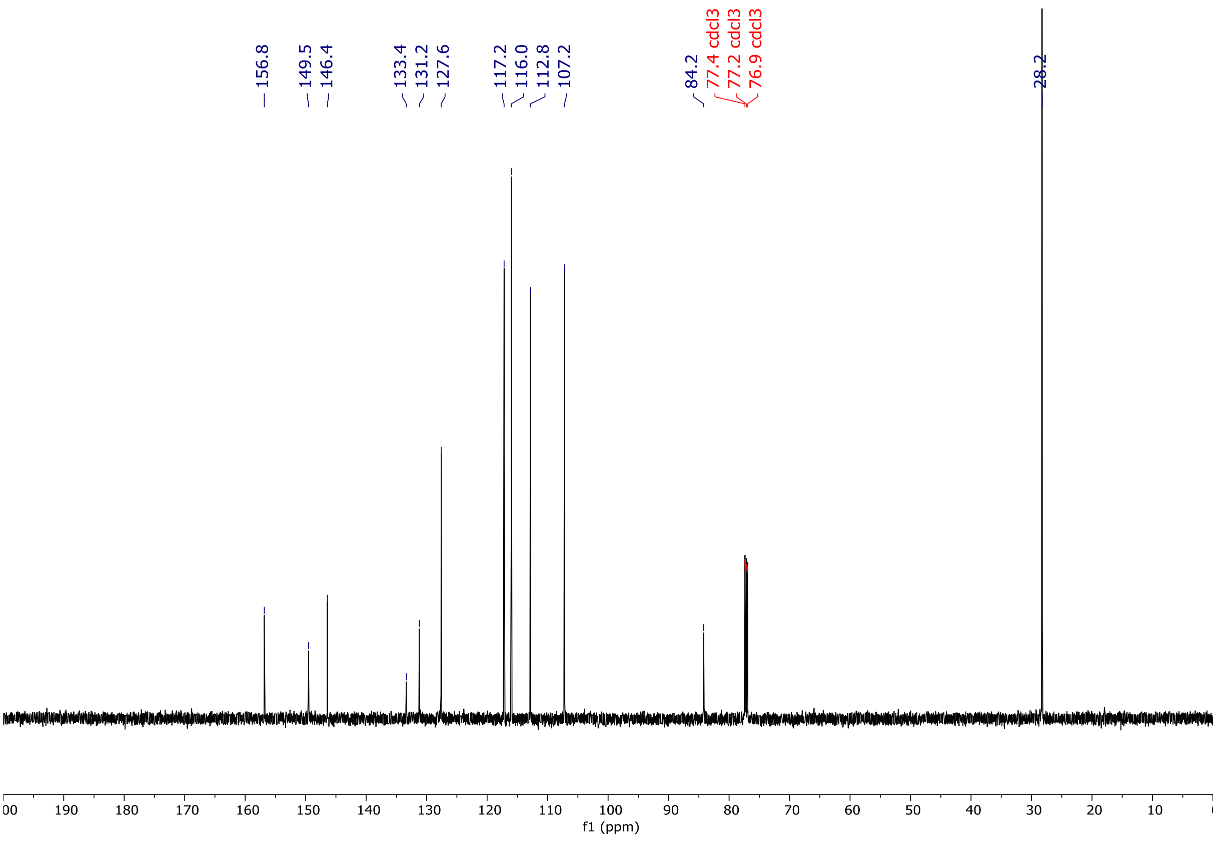
Naphthalen-2-yl azidoformate (1q)



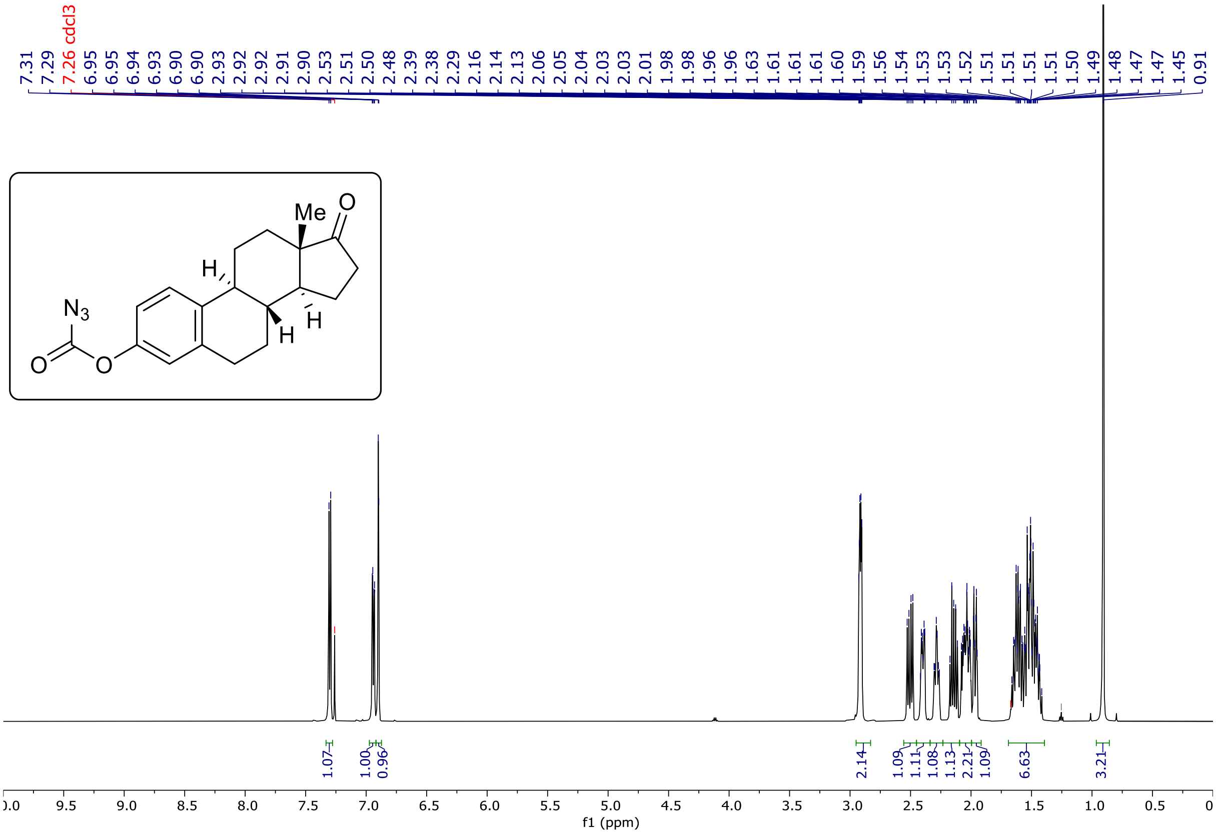


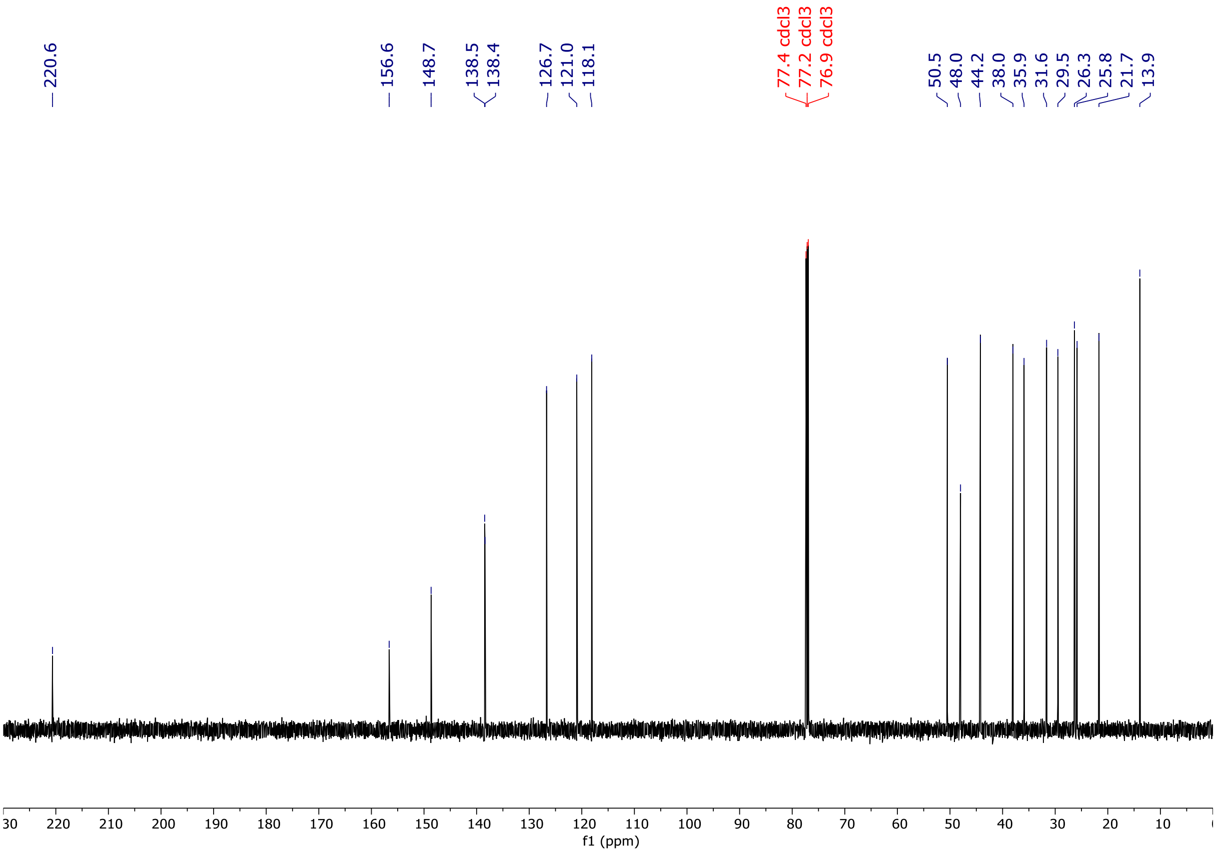
***tert*-Butyl 5-{(azidocarbonyl)oxy}-1*H*-indole-1-carboxylate (1r)**



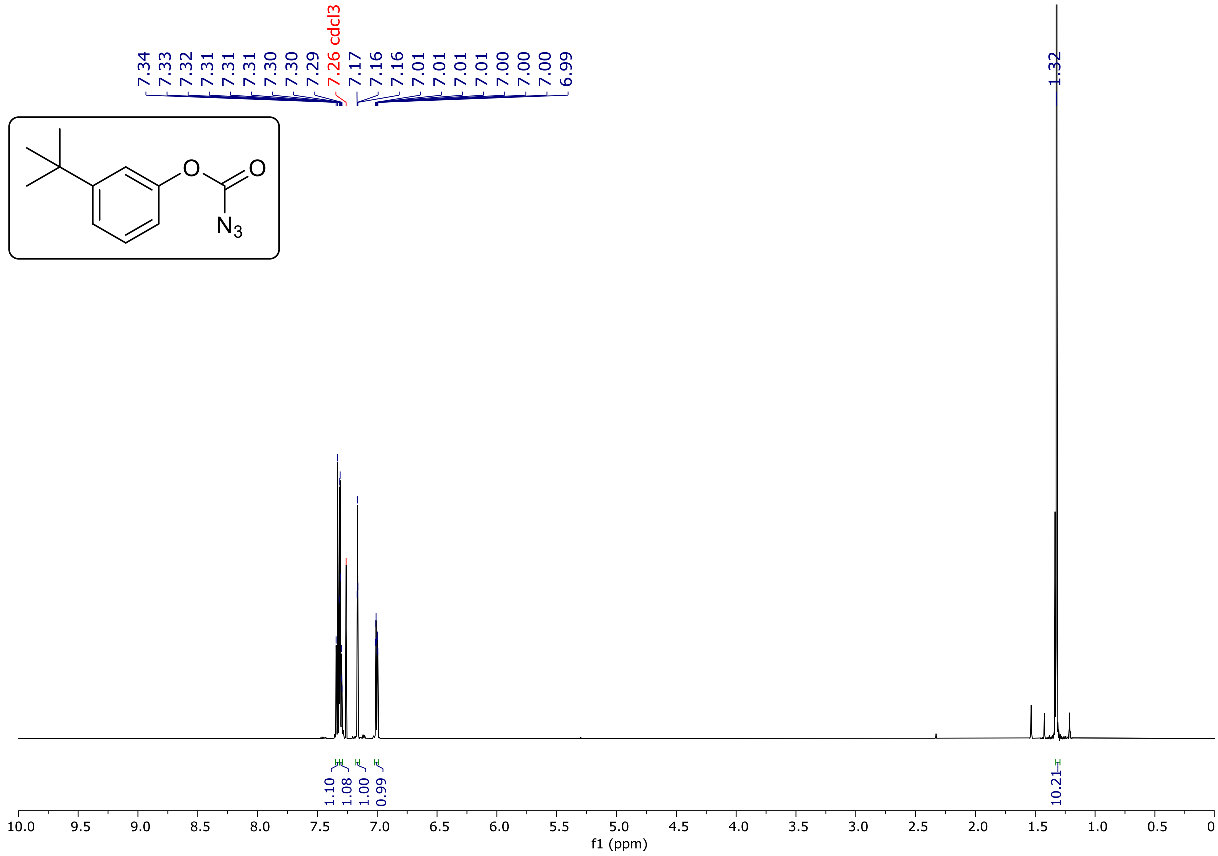


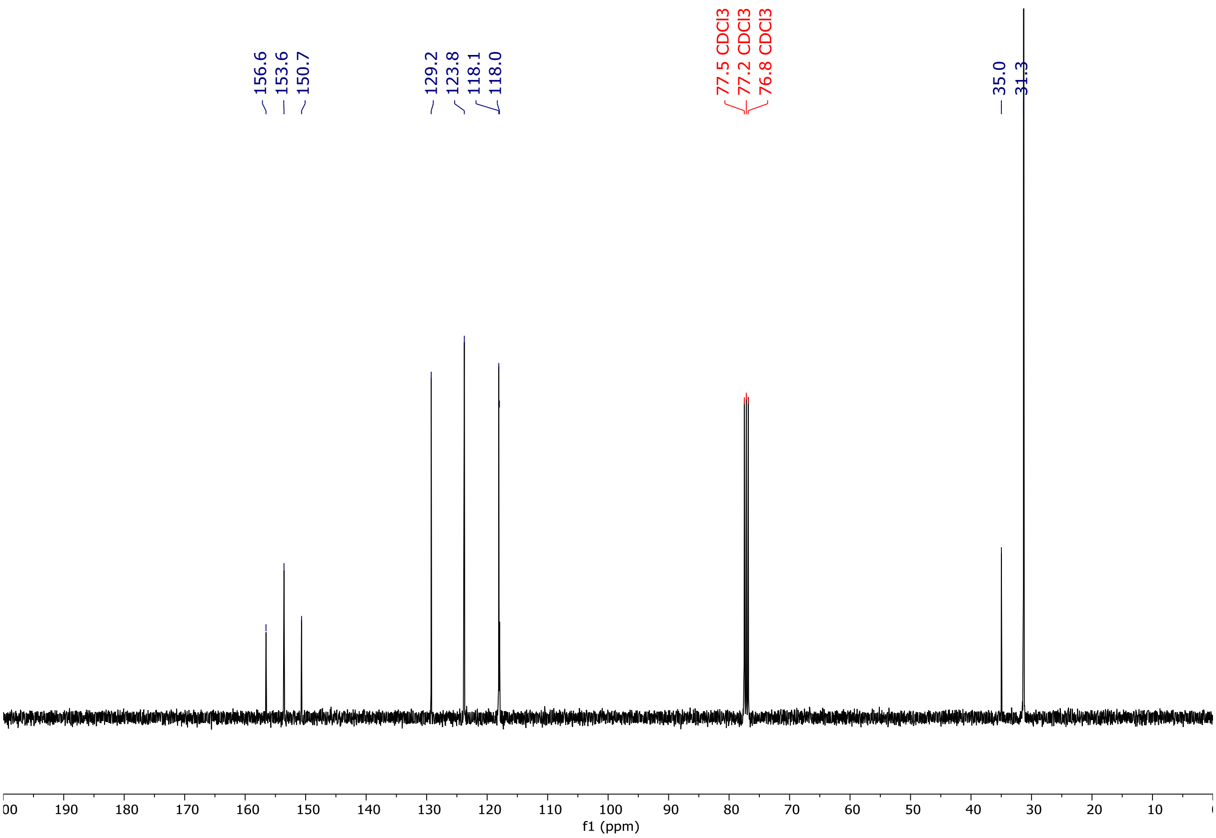
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl azidoformate (1s)



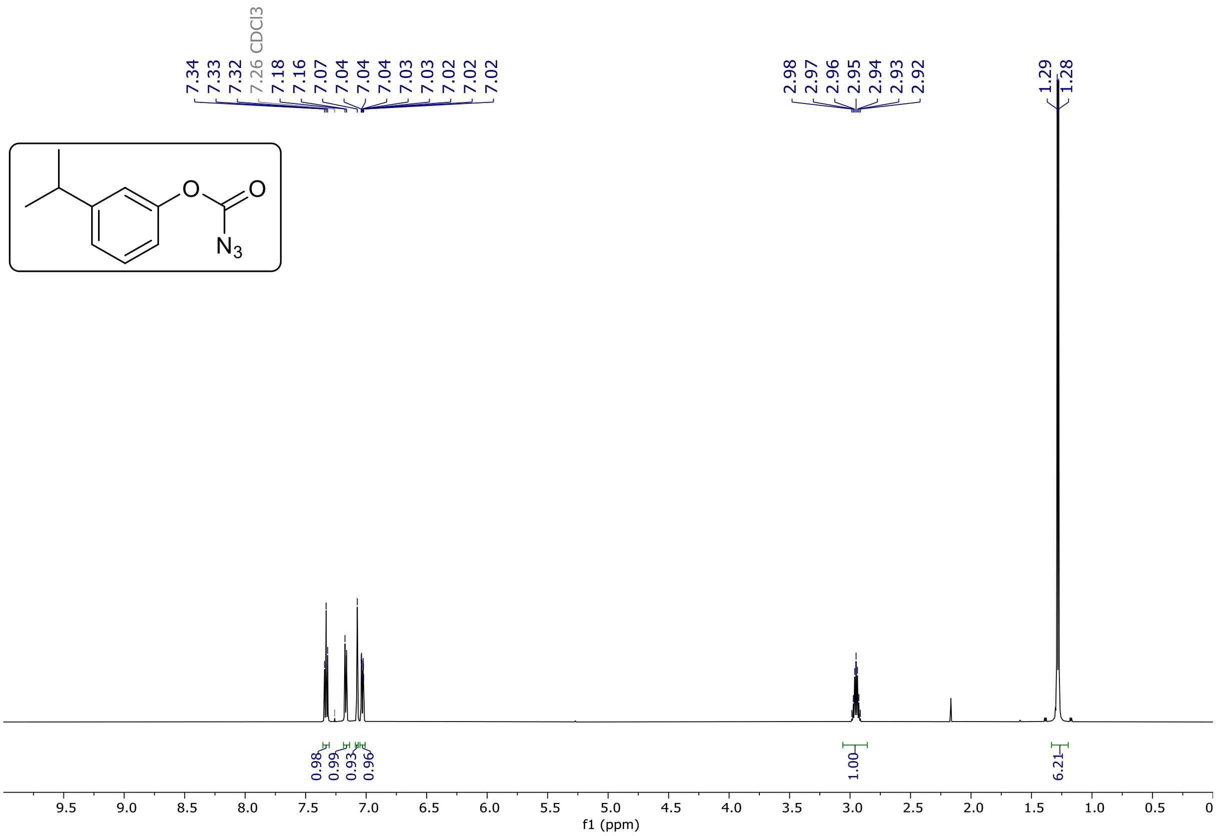


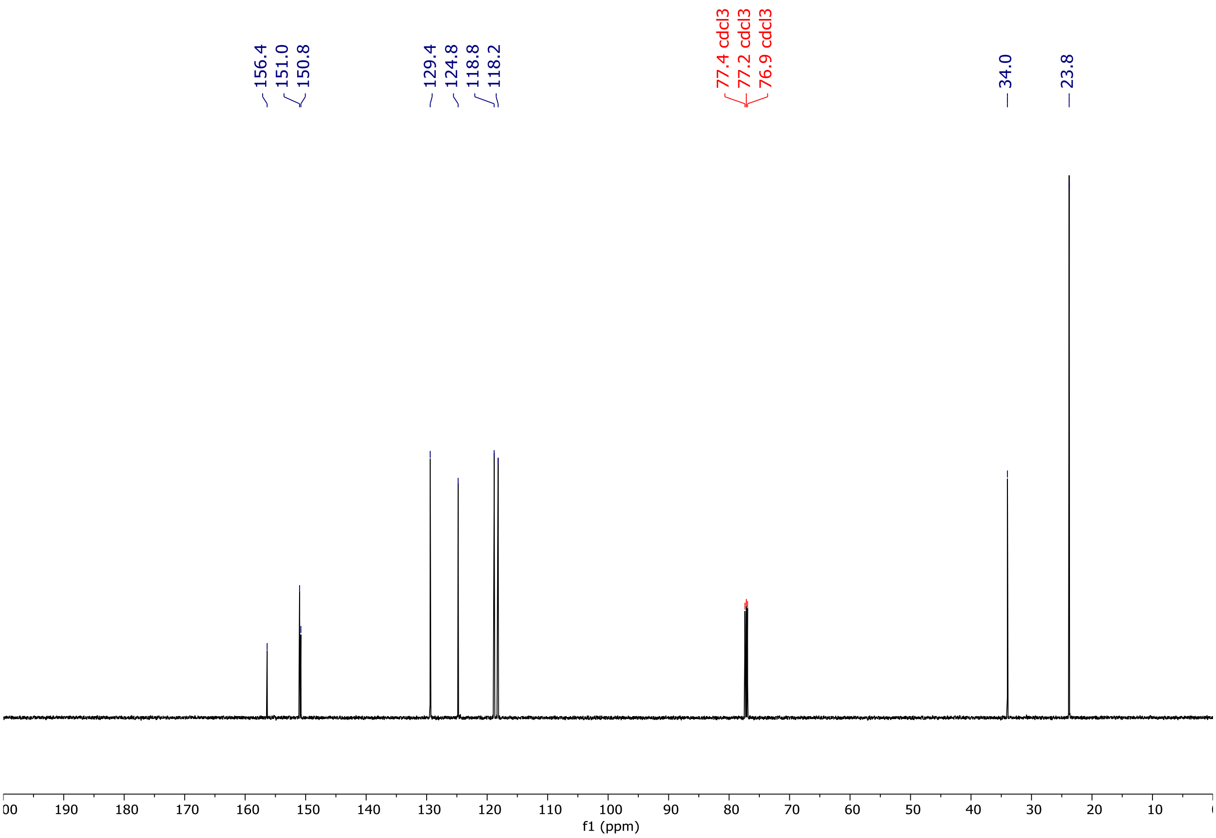
3-(*tert*-Butyl)phenyl azidoformate (1t)



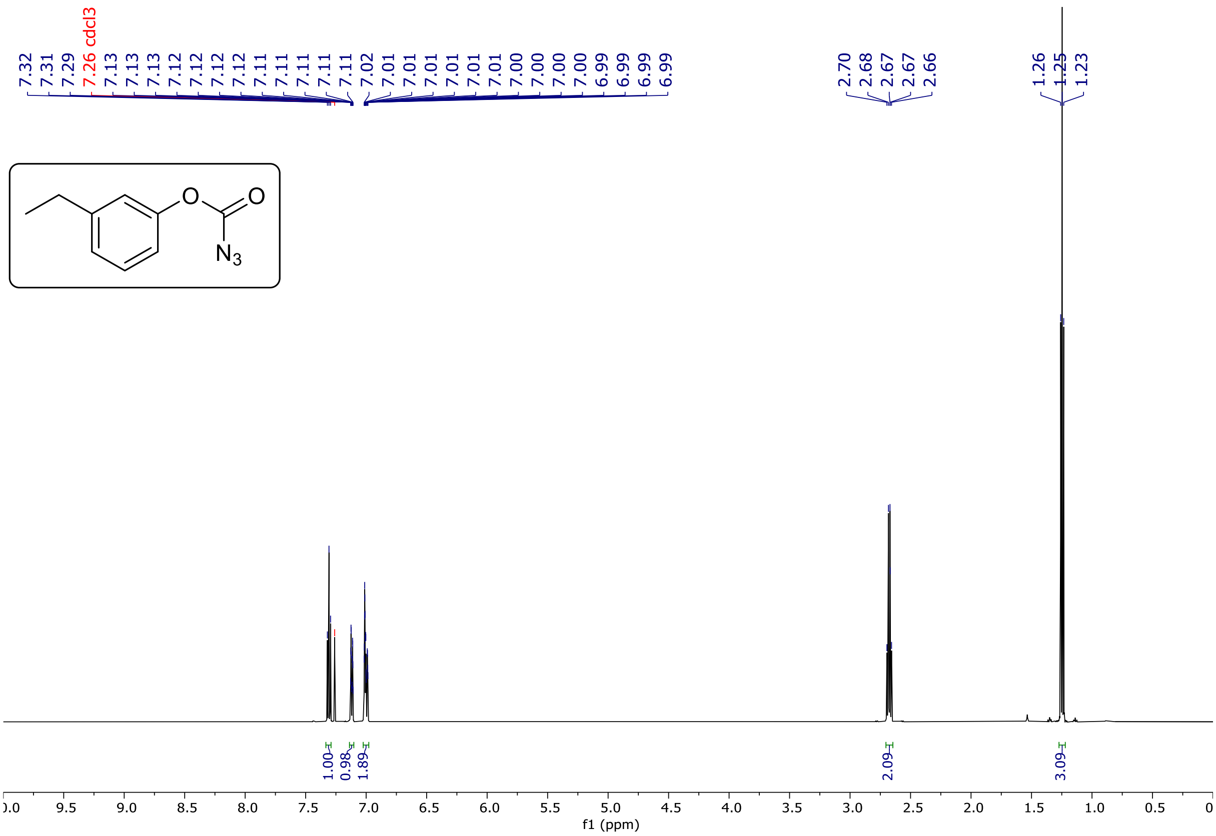


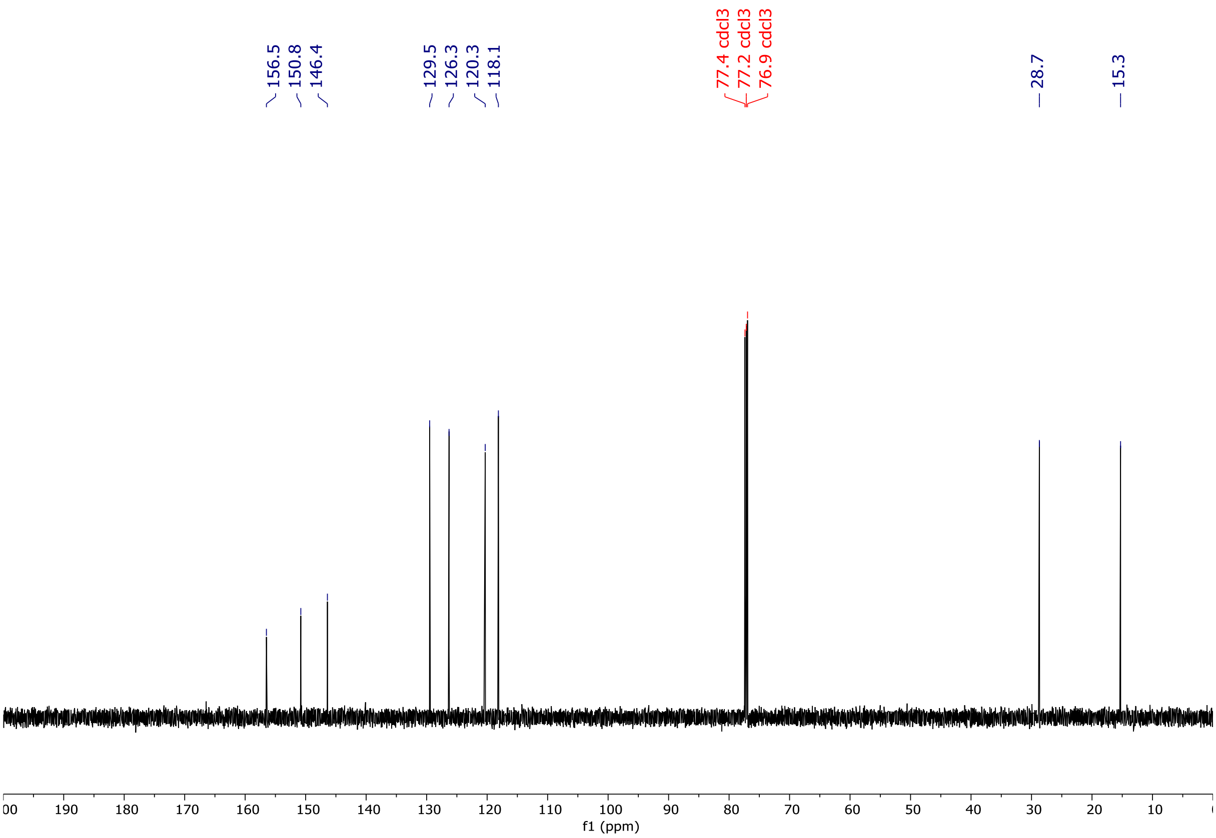
3-Isopropylphenyl azidoformate (1u)



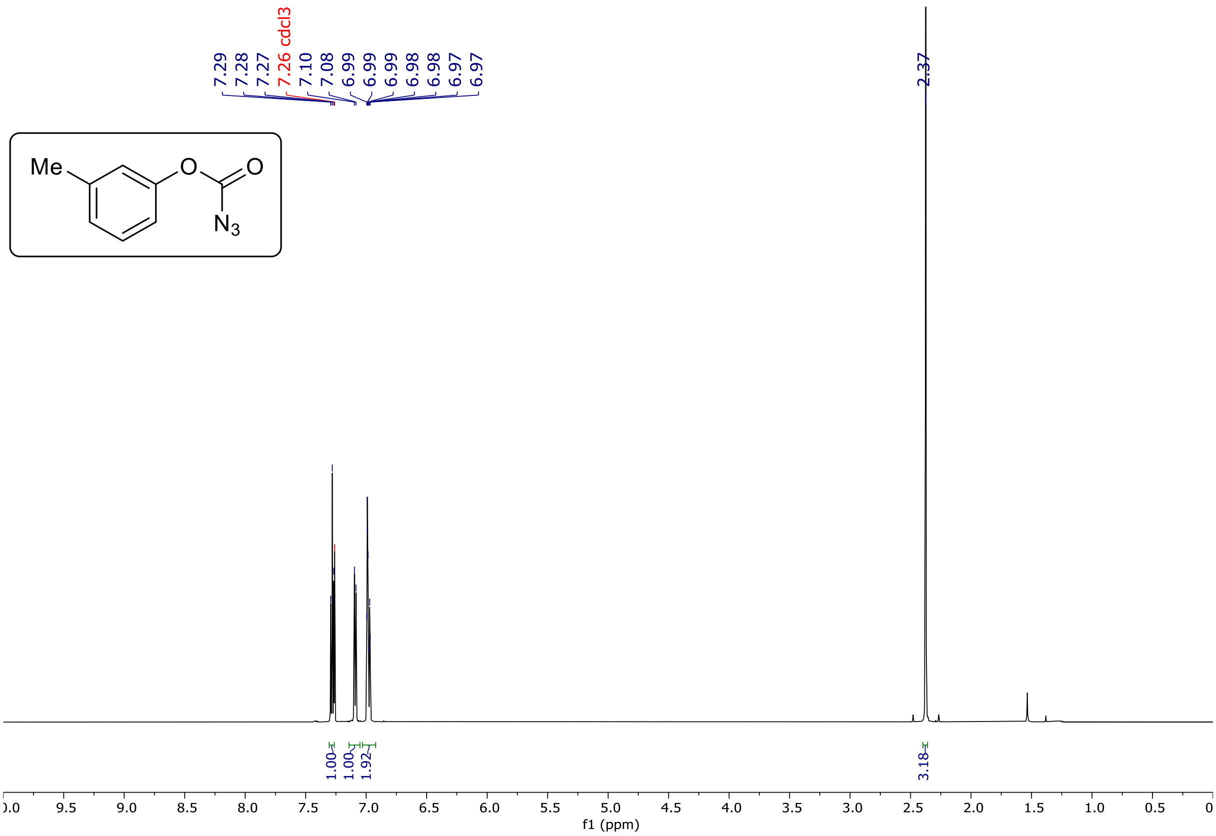


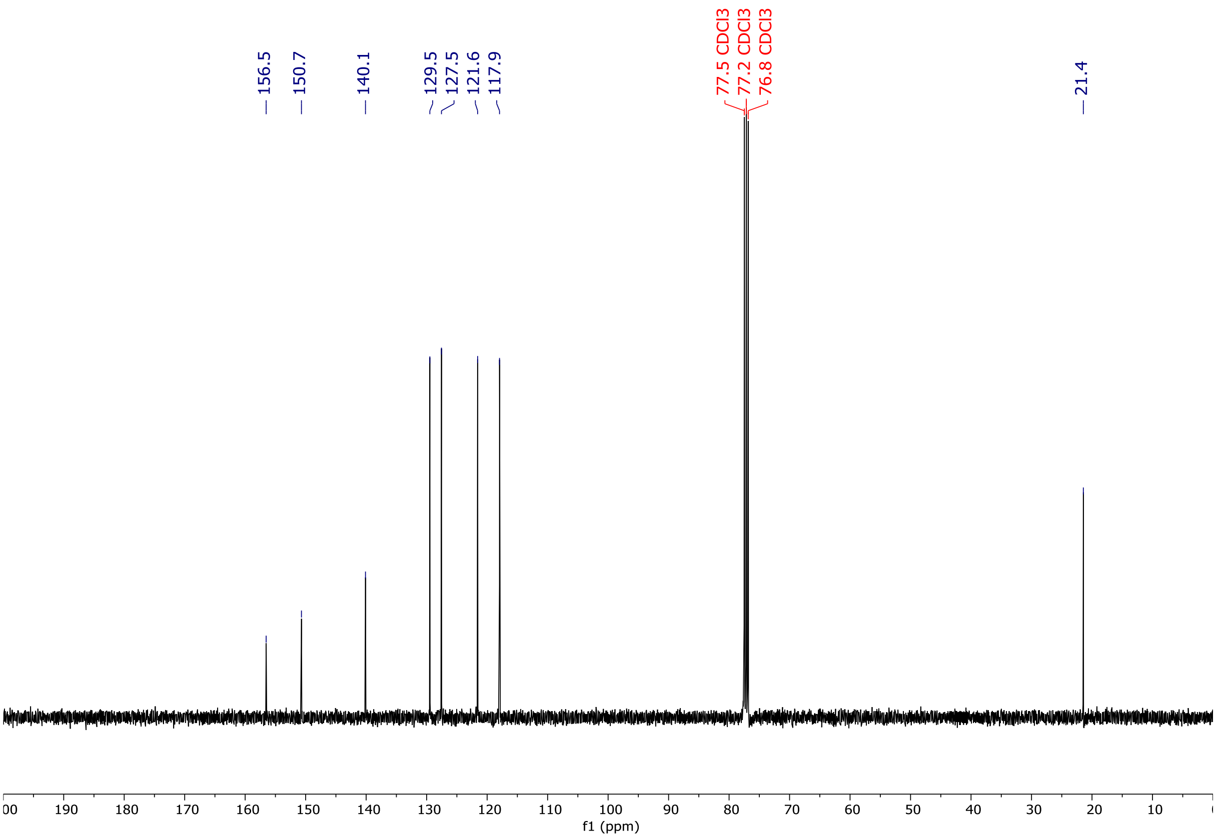
3-Ethylphenyl azidoformate (1v)



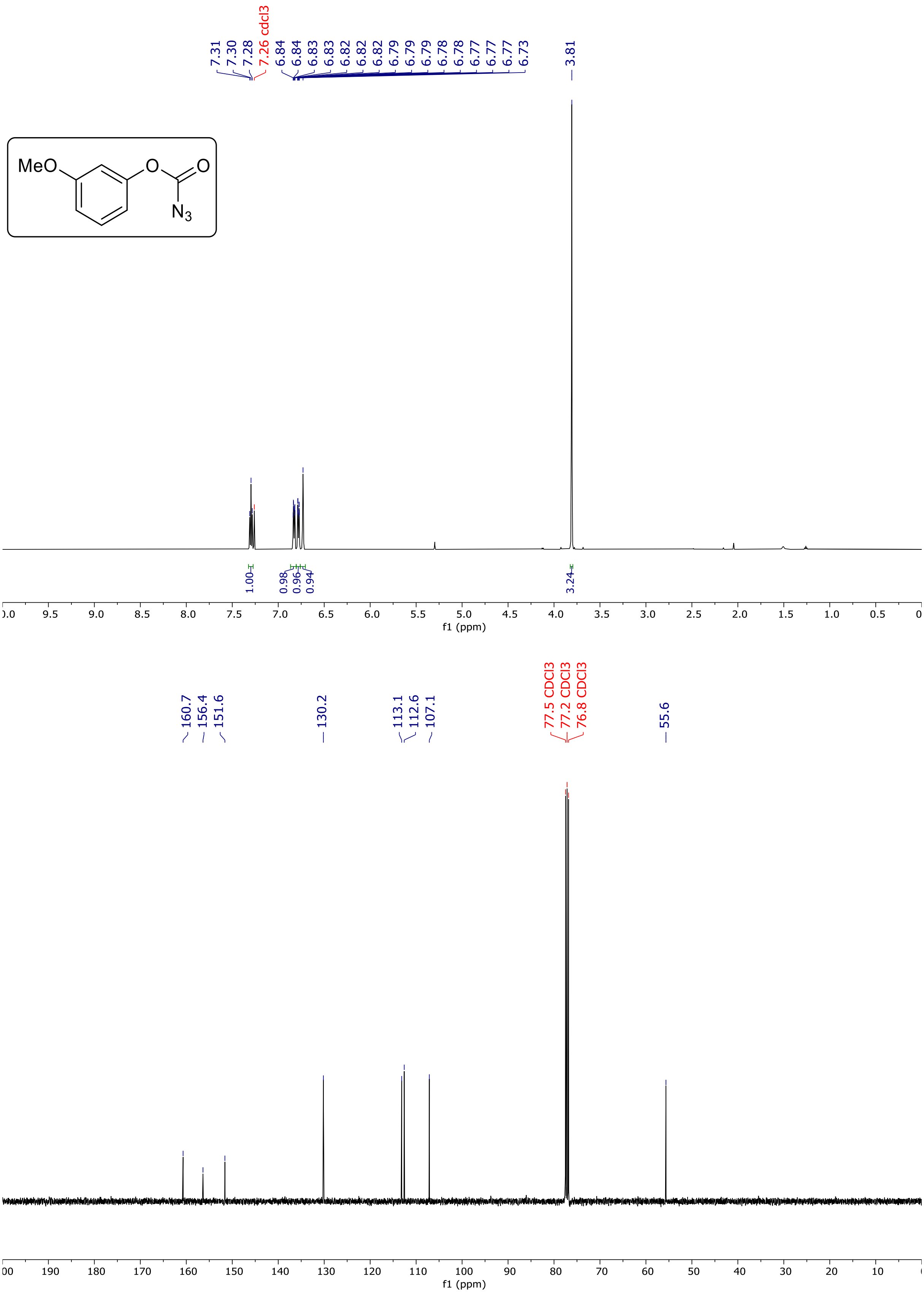


***m*-Tolyl azidoformate (1w)**

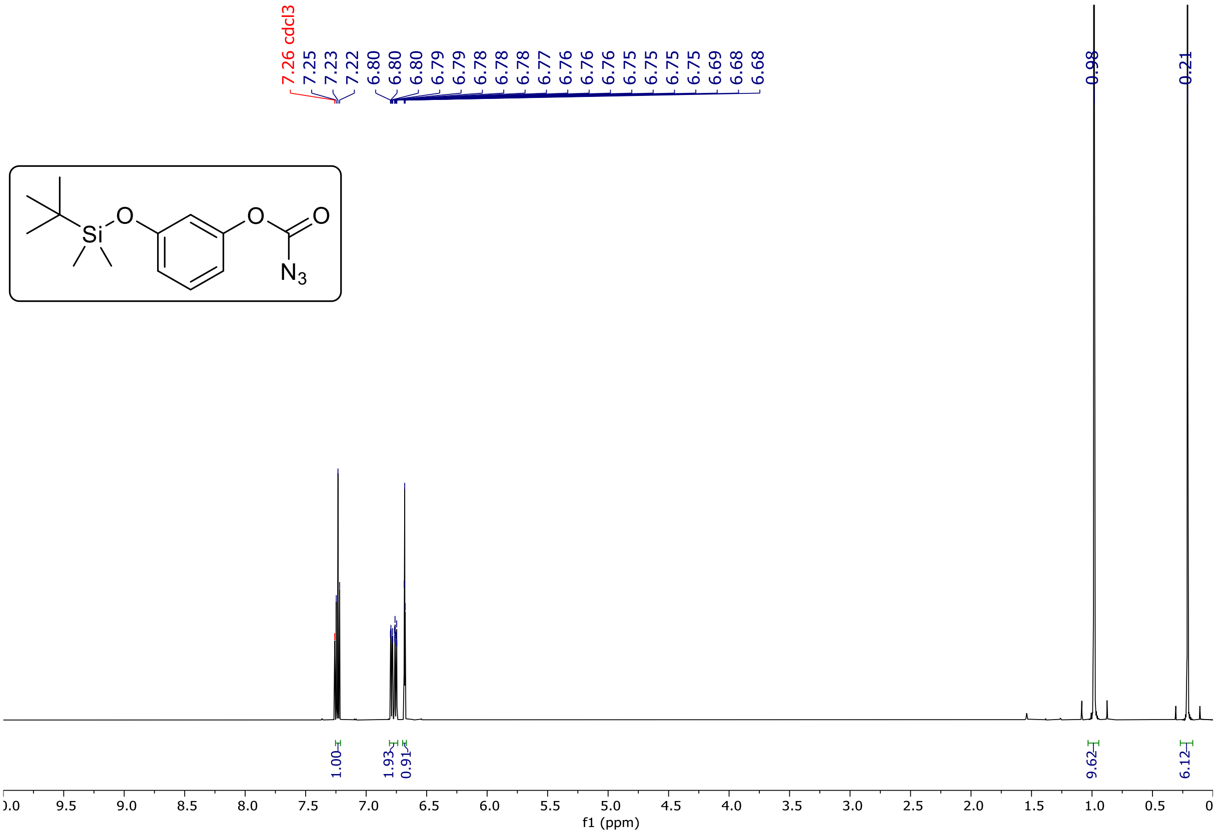


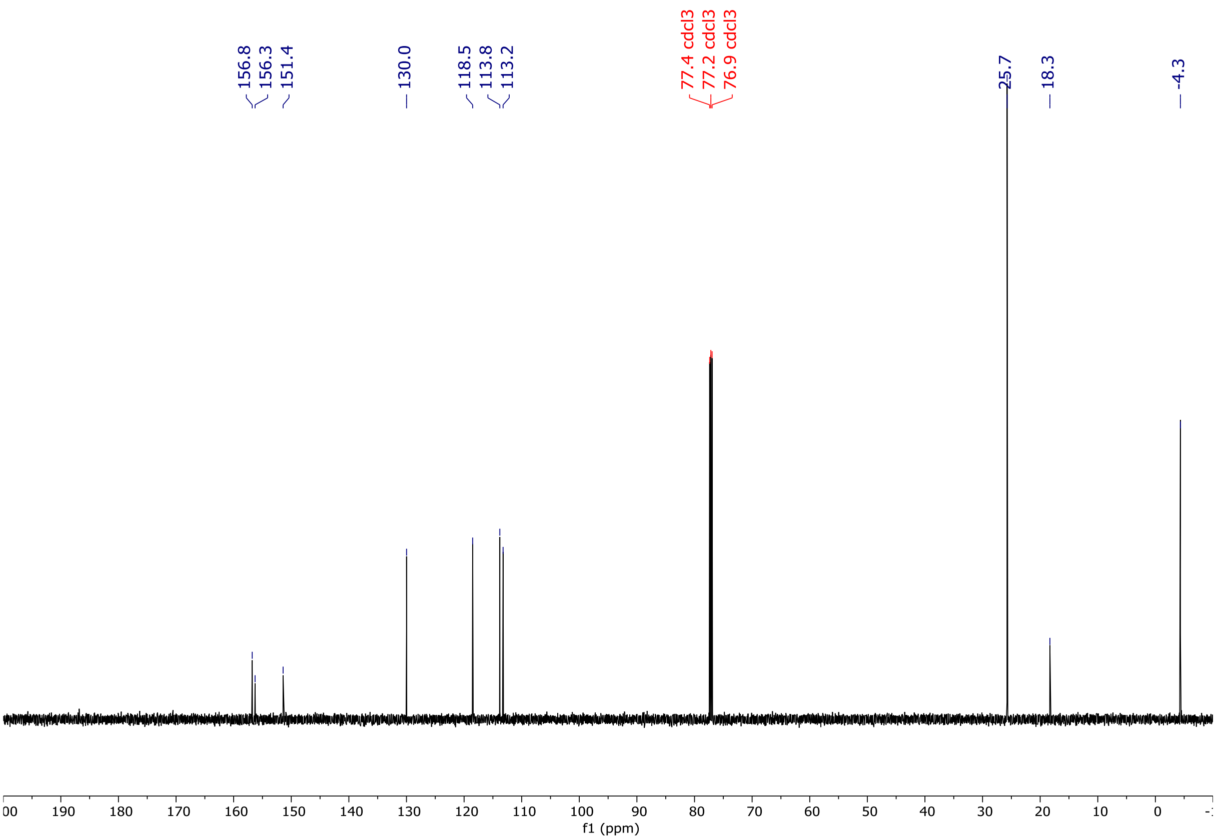


3-Methoxyphenyl azidoformate (1x)

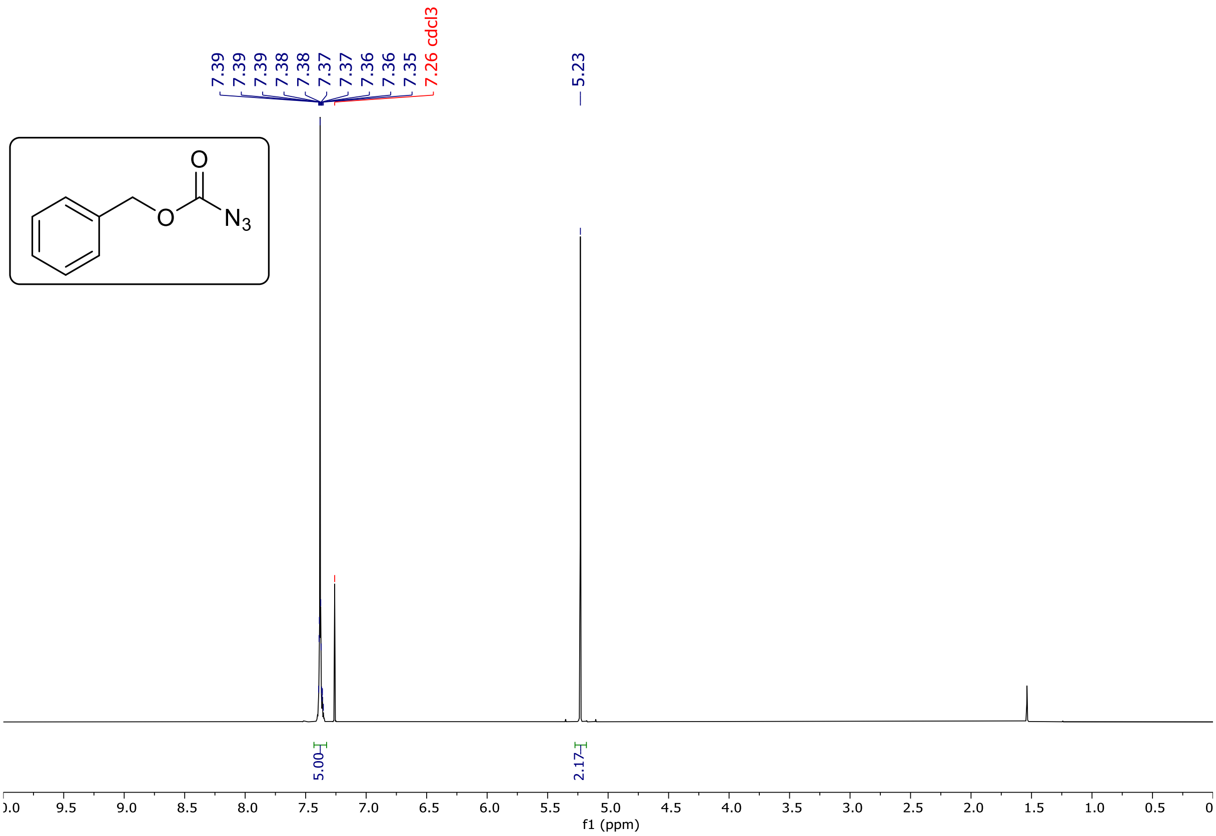


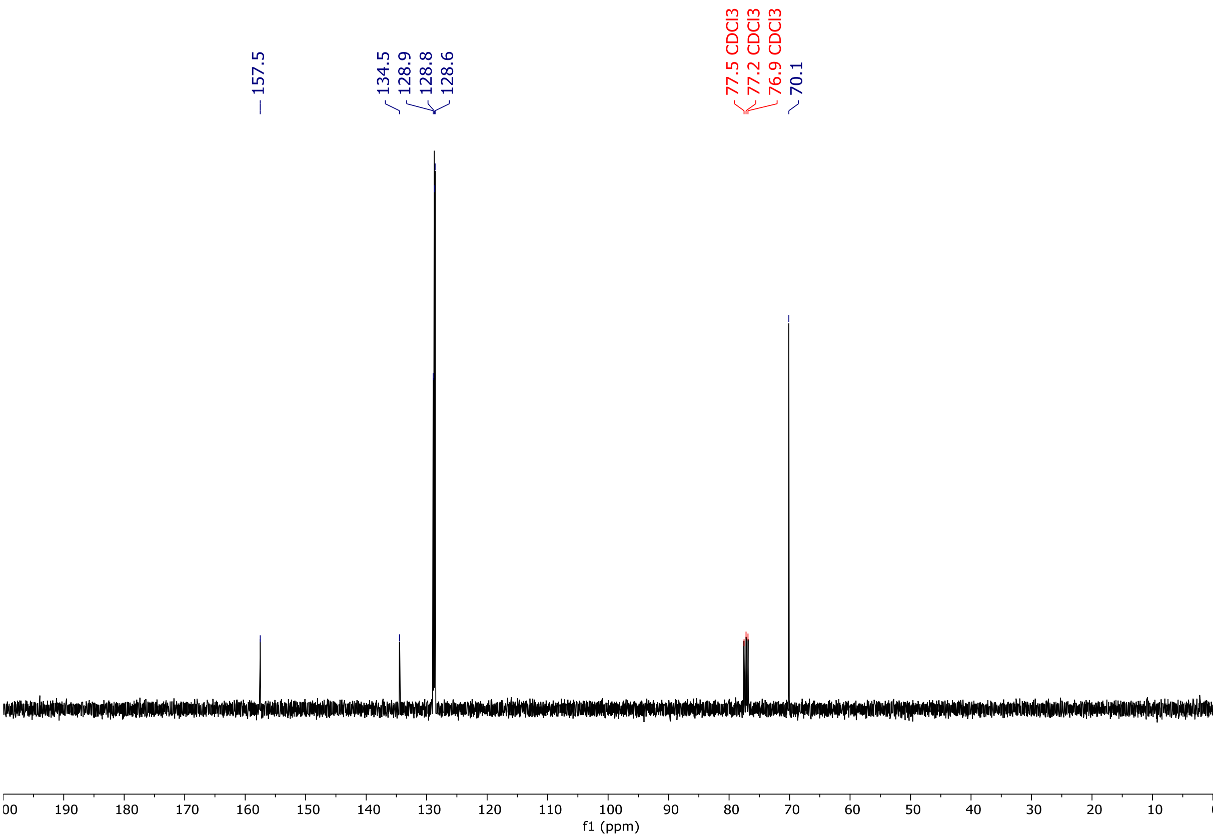
3-{(*tert*-Butyldimethylsilyl)oxy}phenyl azidoformate (1y)



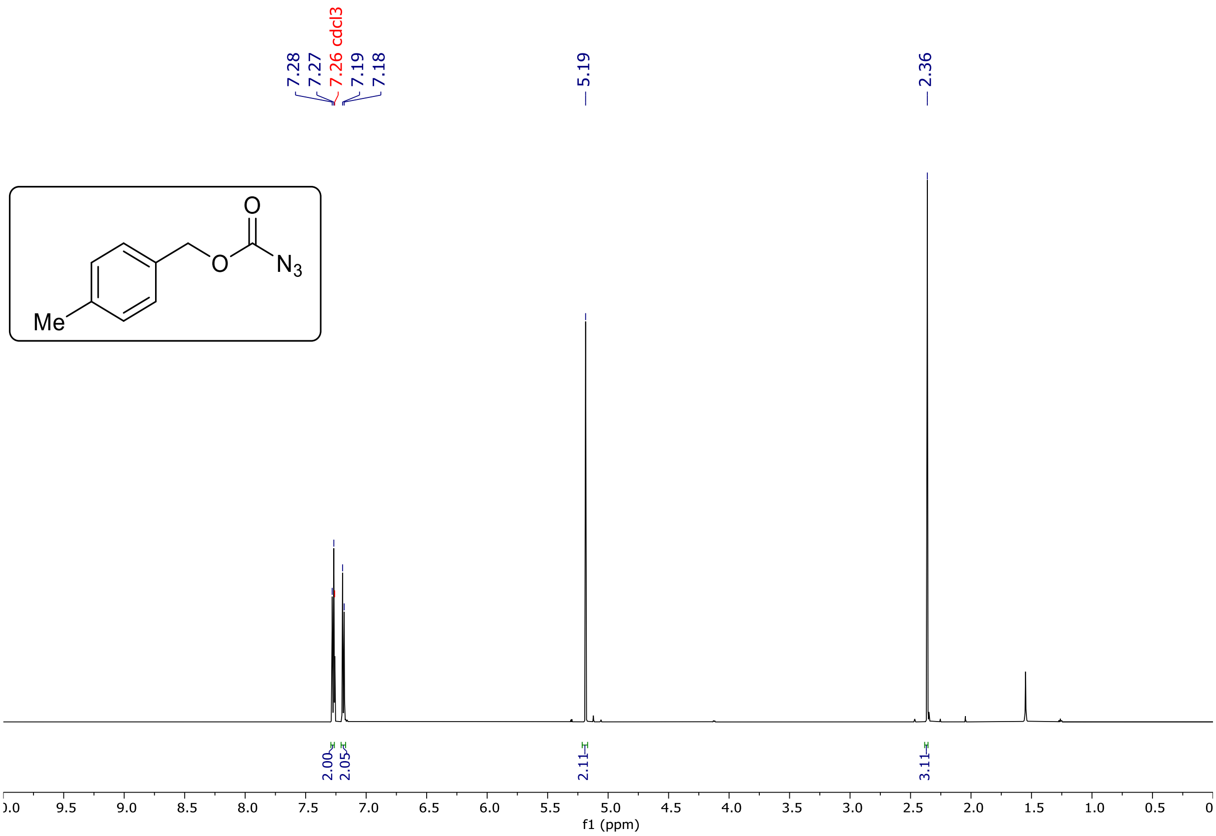


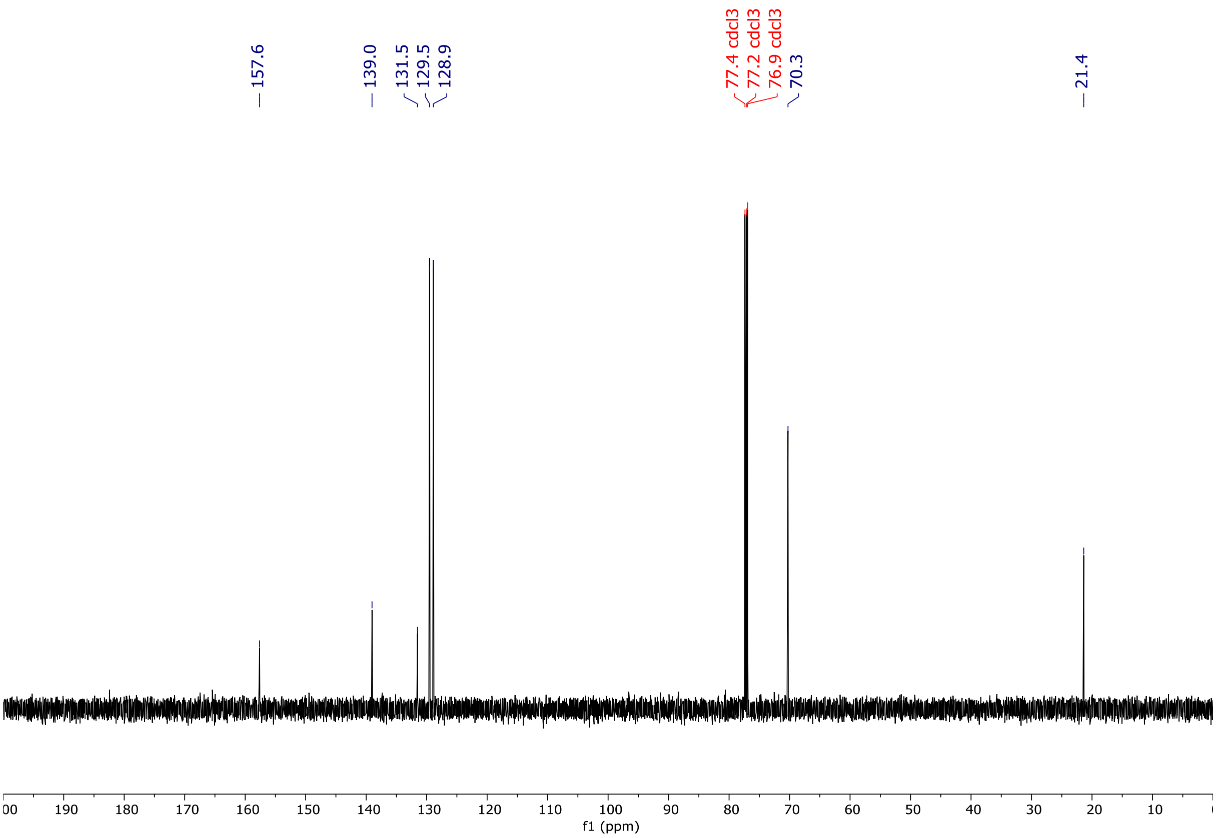
Benzyl azidoformate (3a)



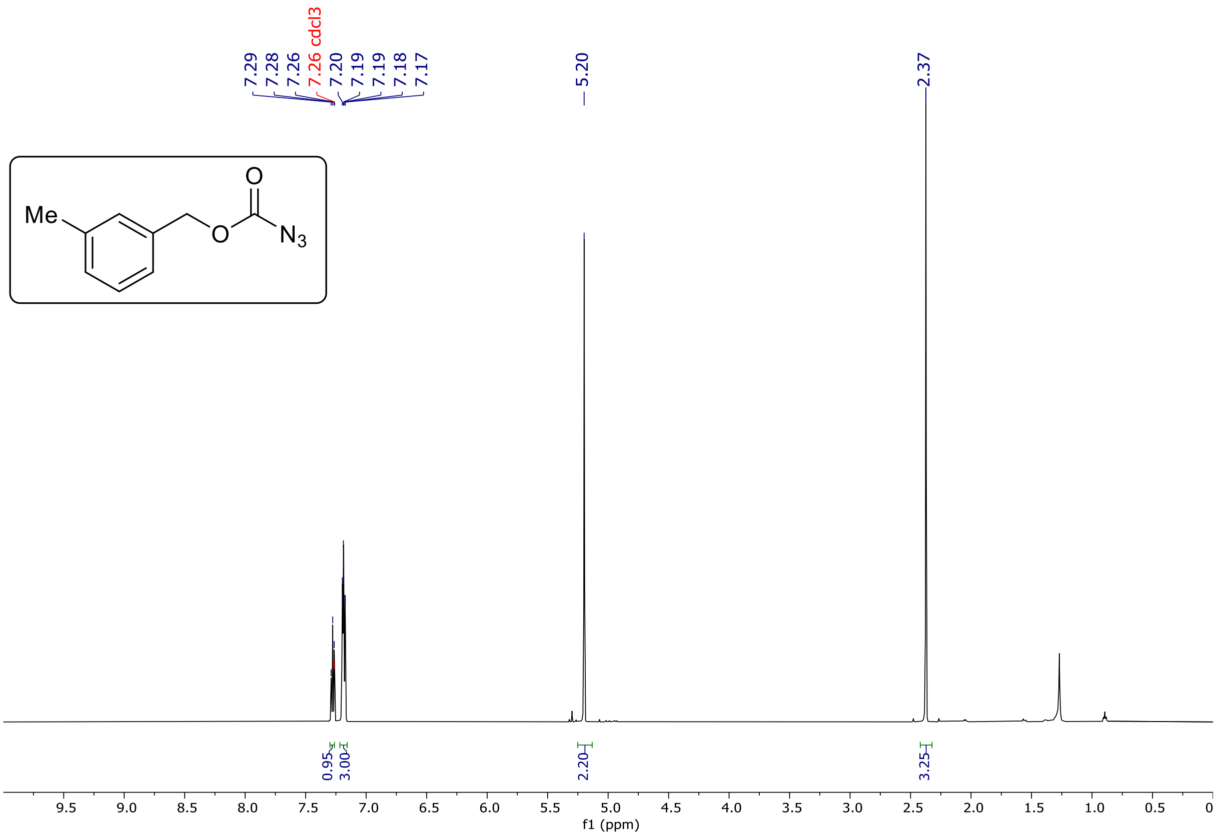


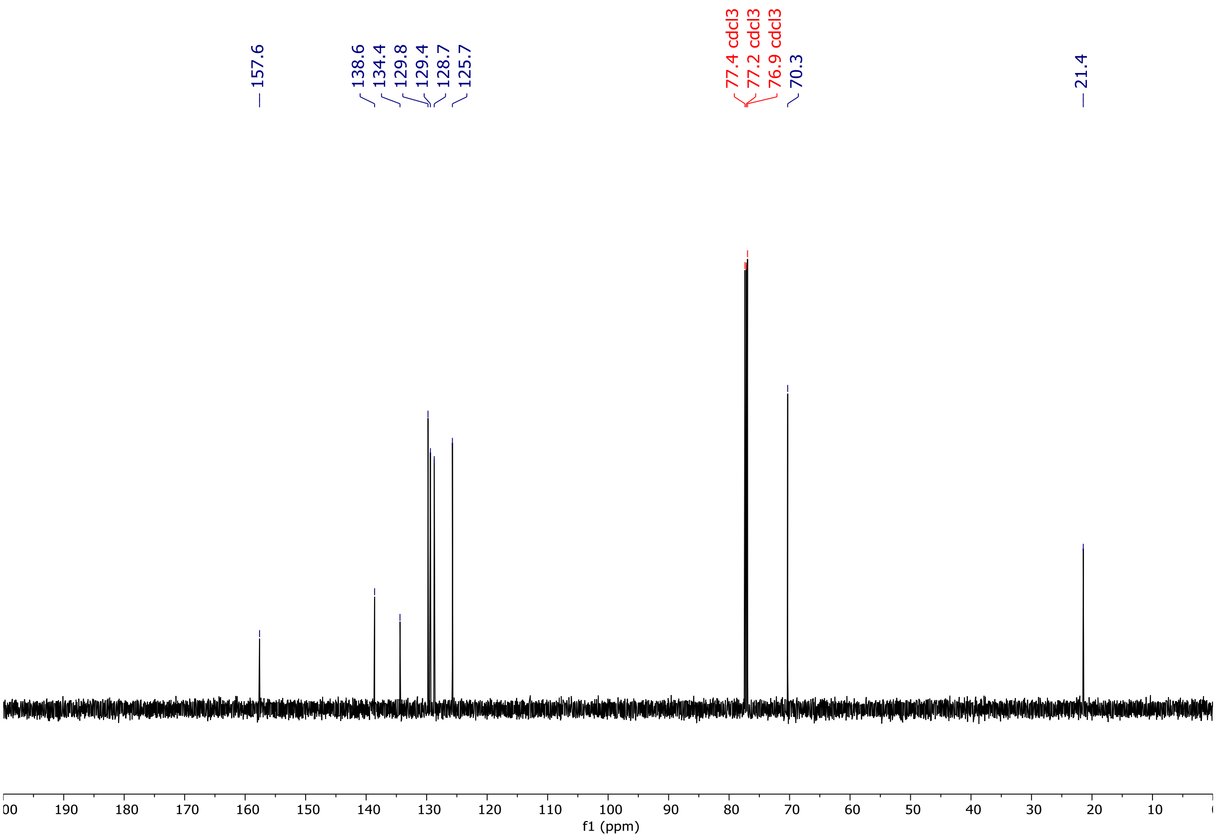
4-Methylbenzyl azidoformate (3b)



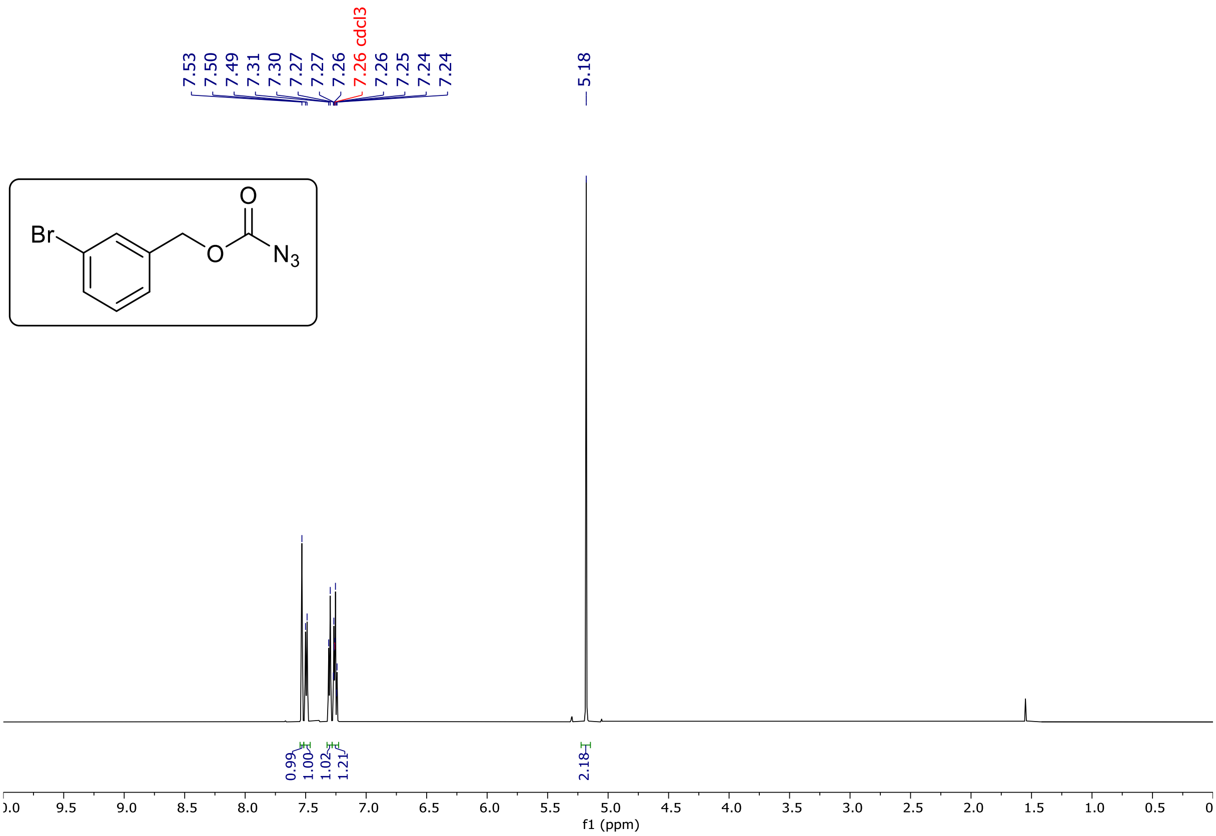


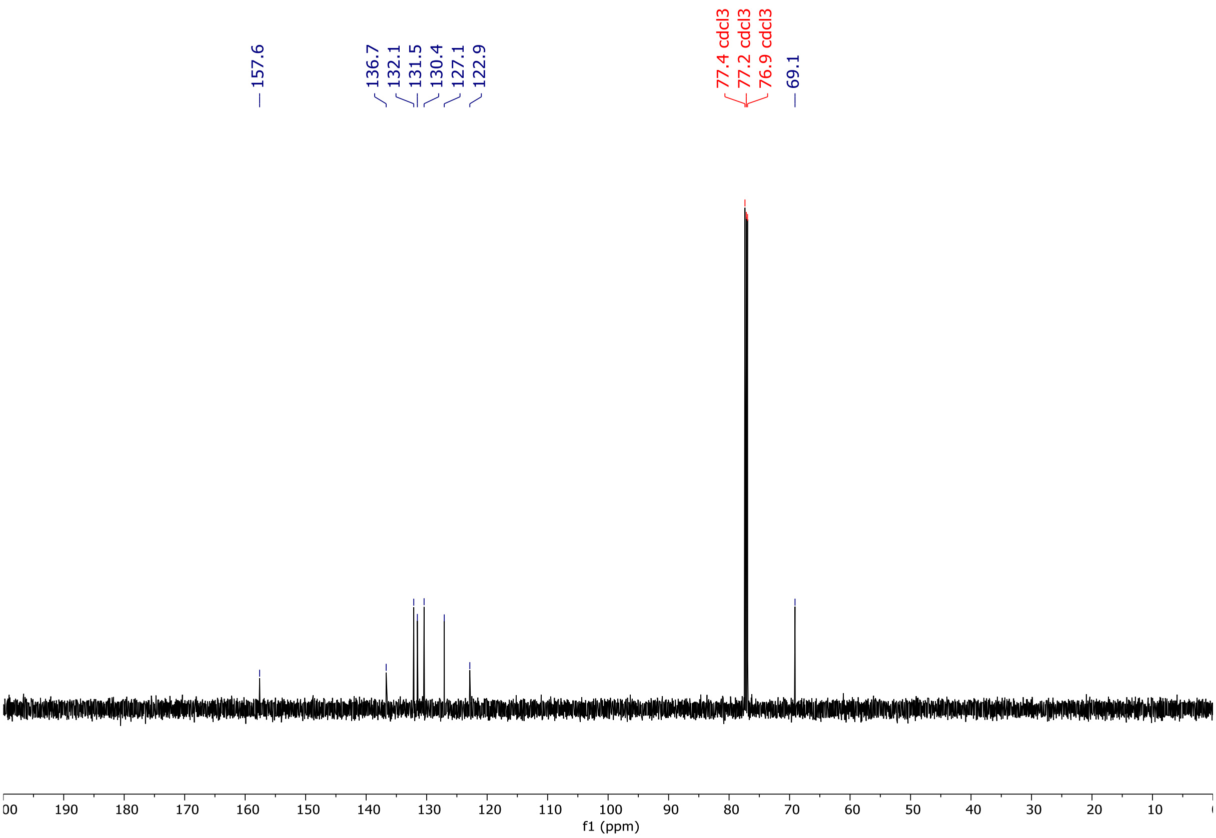
3-Methylbenzyl azidoformate (3c)



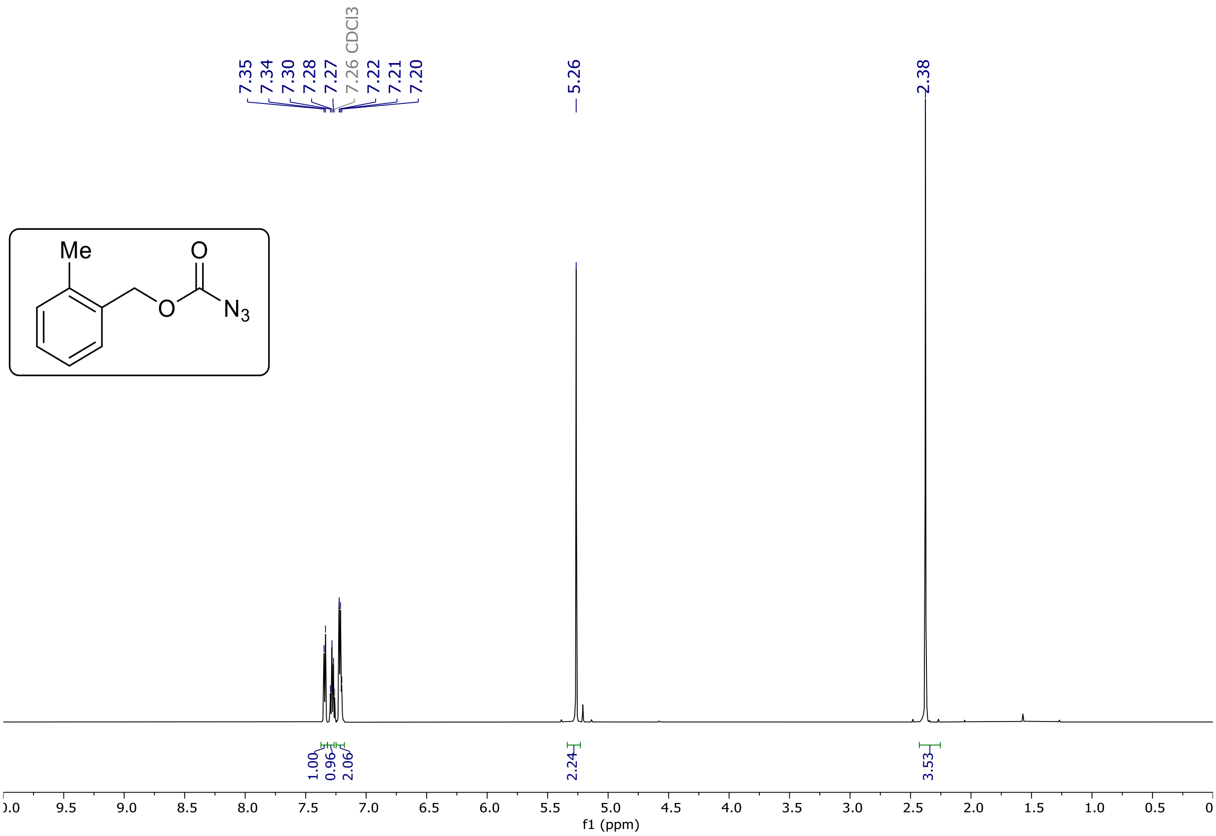


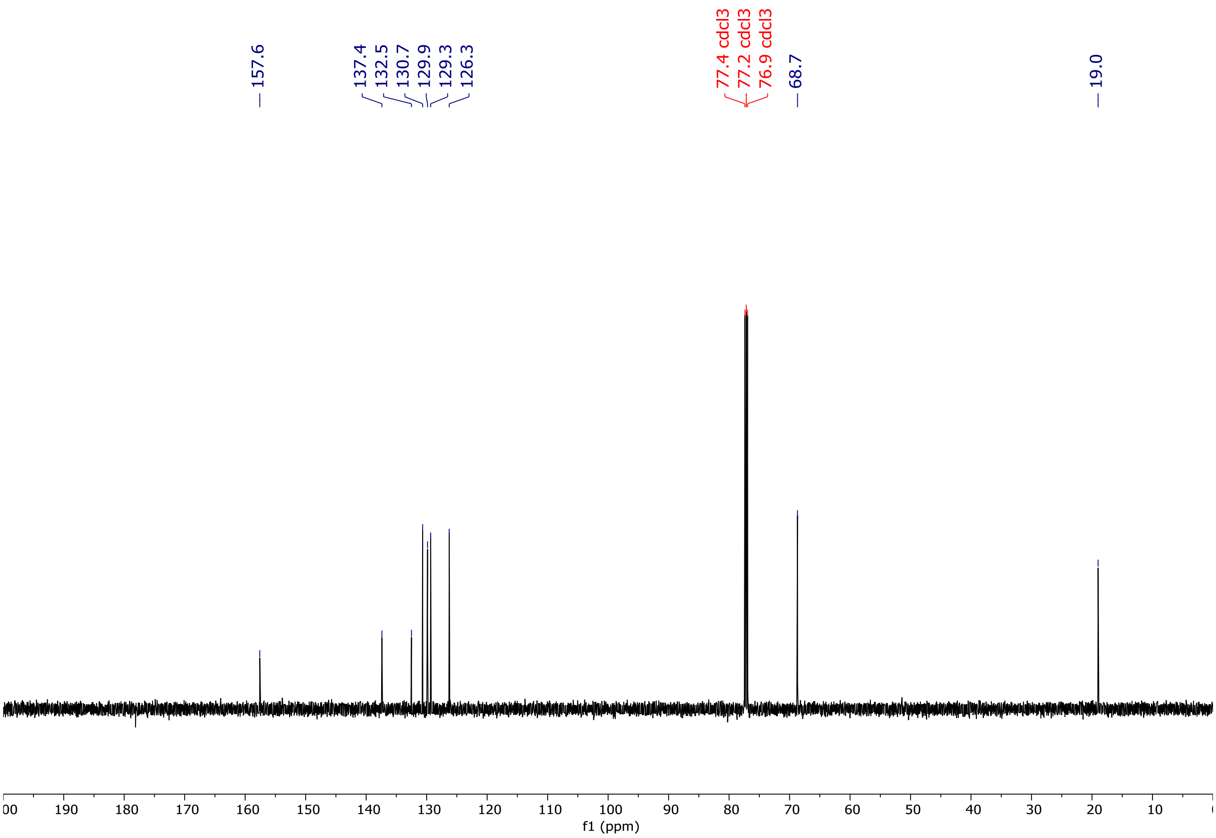
3-Bromobenzyl azidoformate (3d)



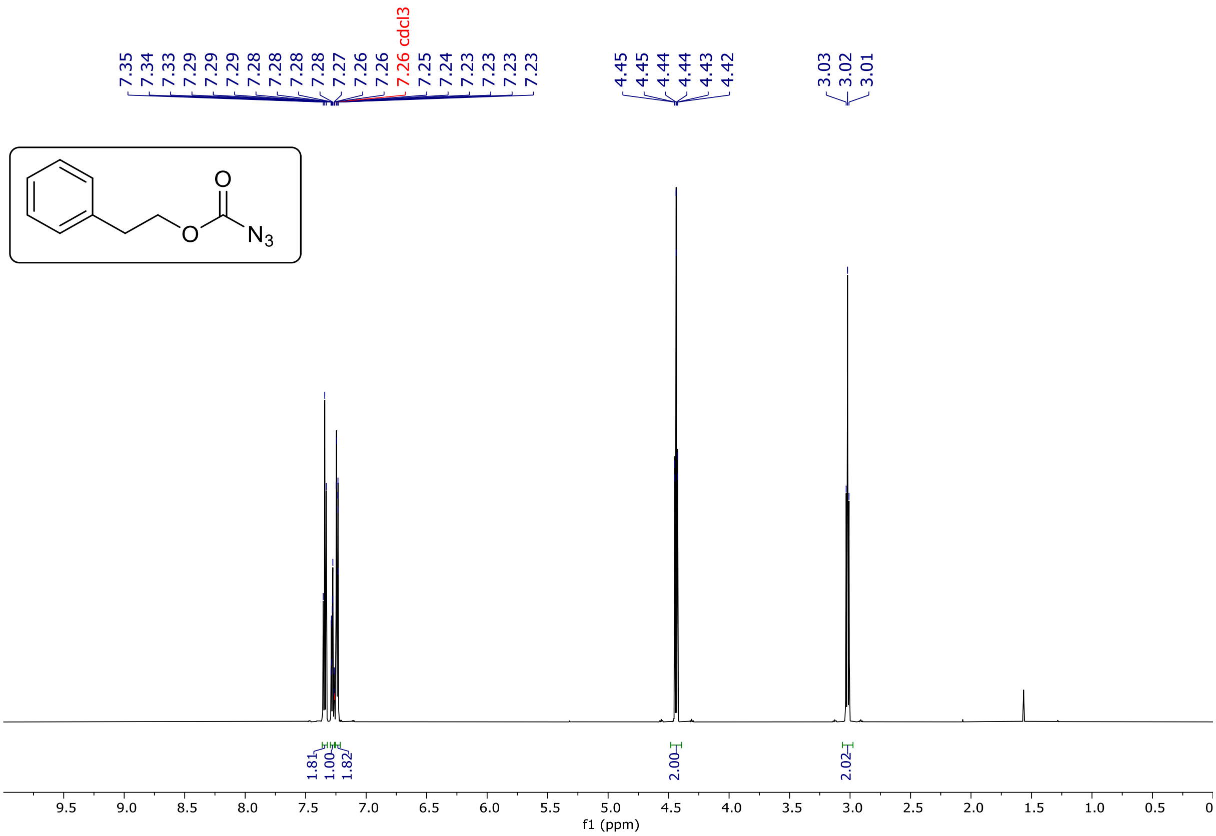


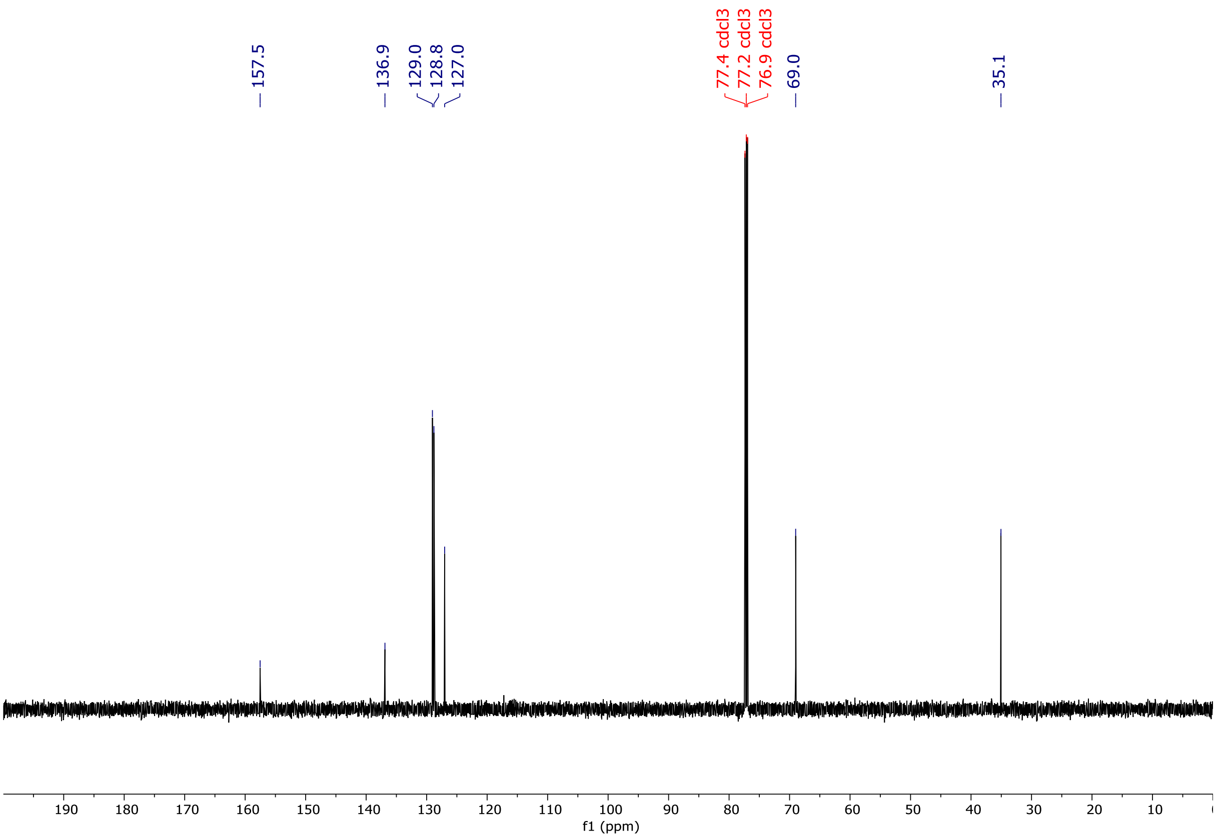
2-Methylbenzyl azidoformate (3e)



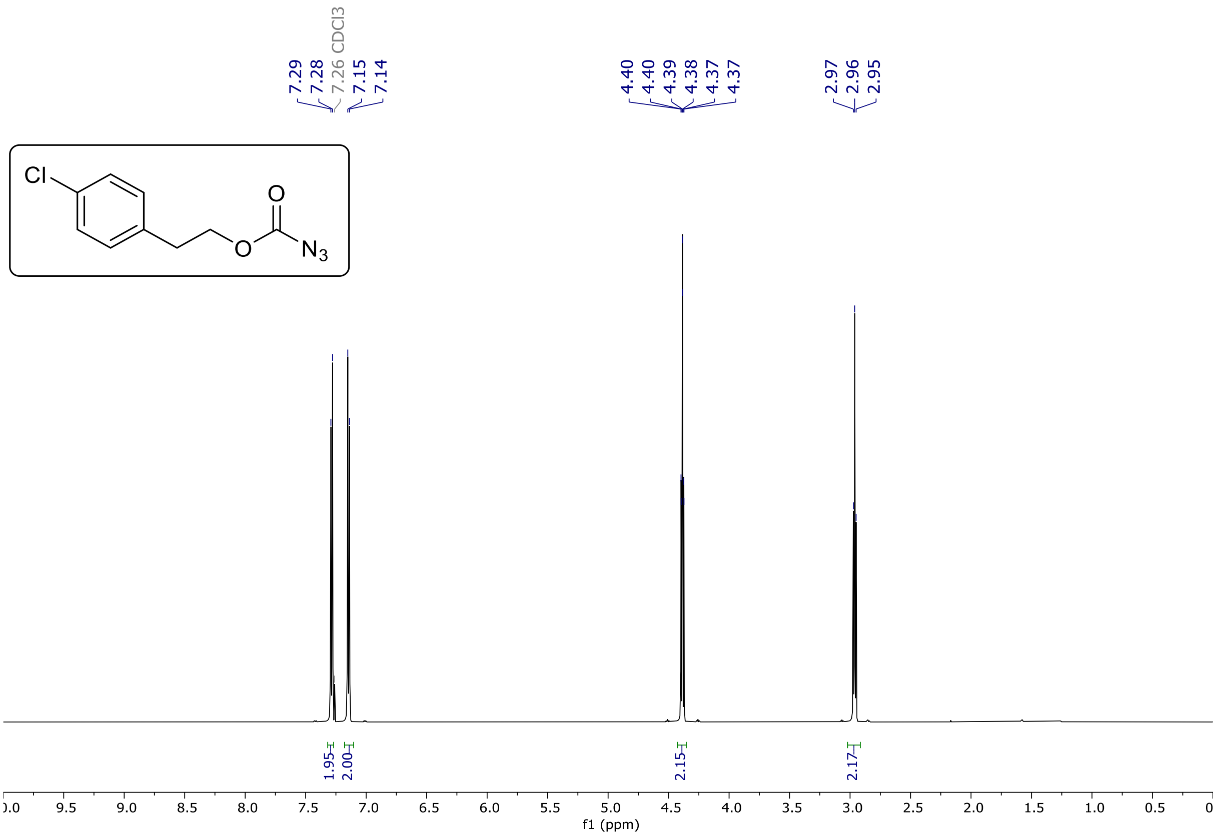


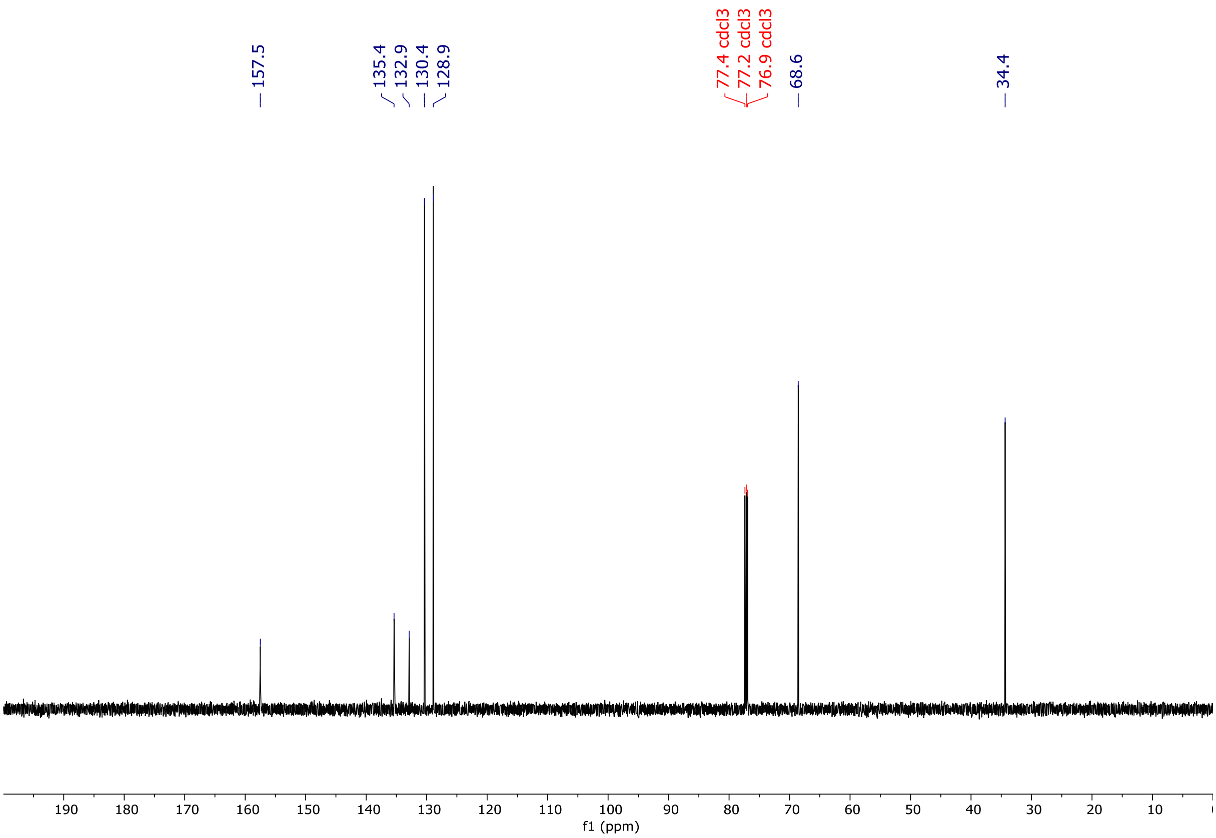
Phenethyl azidoformate (5a)



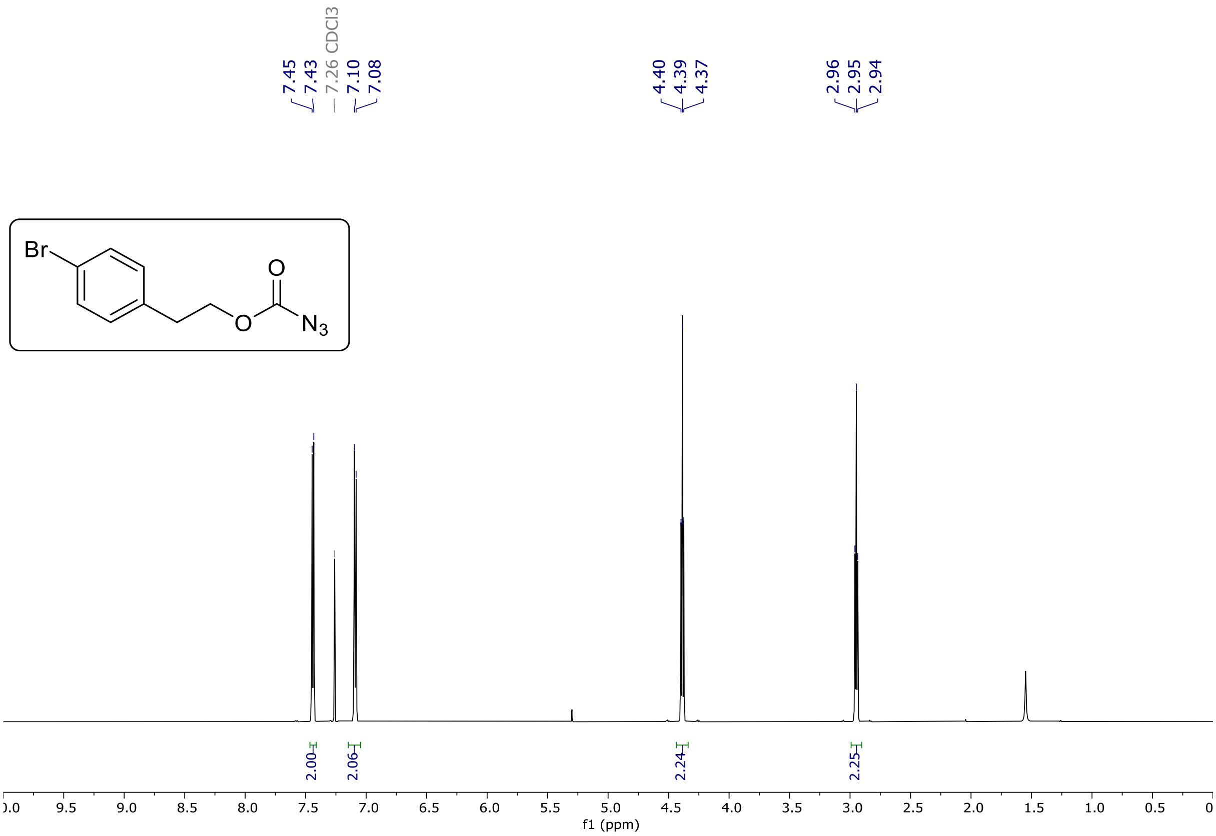


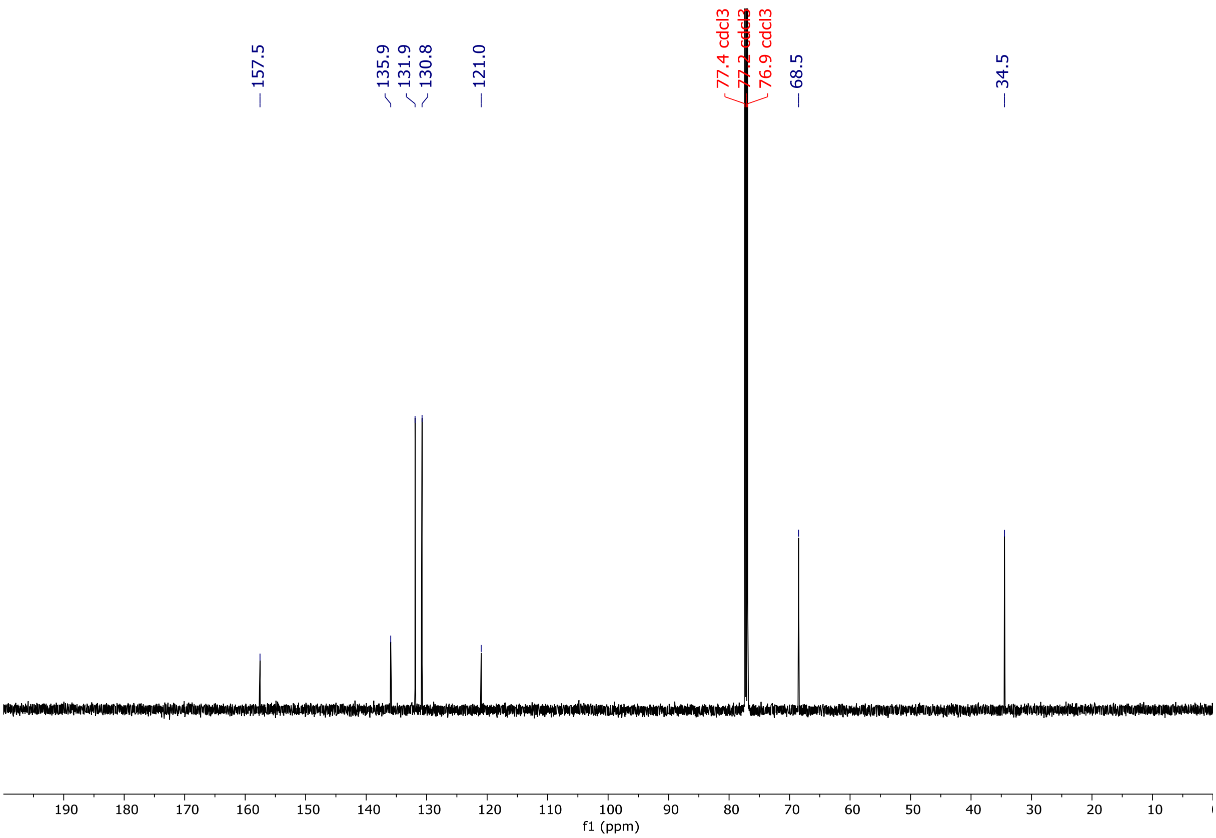
4-Chlorophenethyl azidoformate (5b)



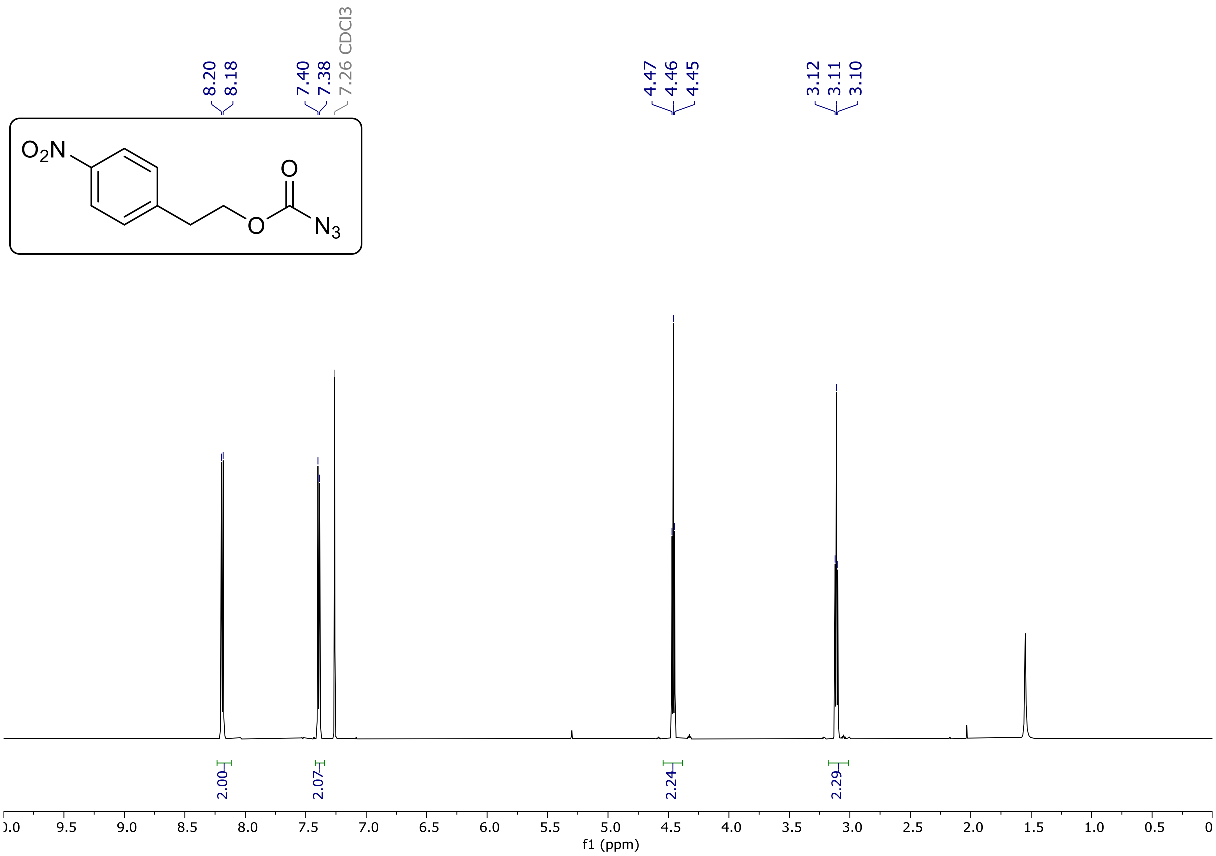


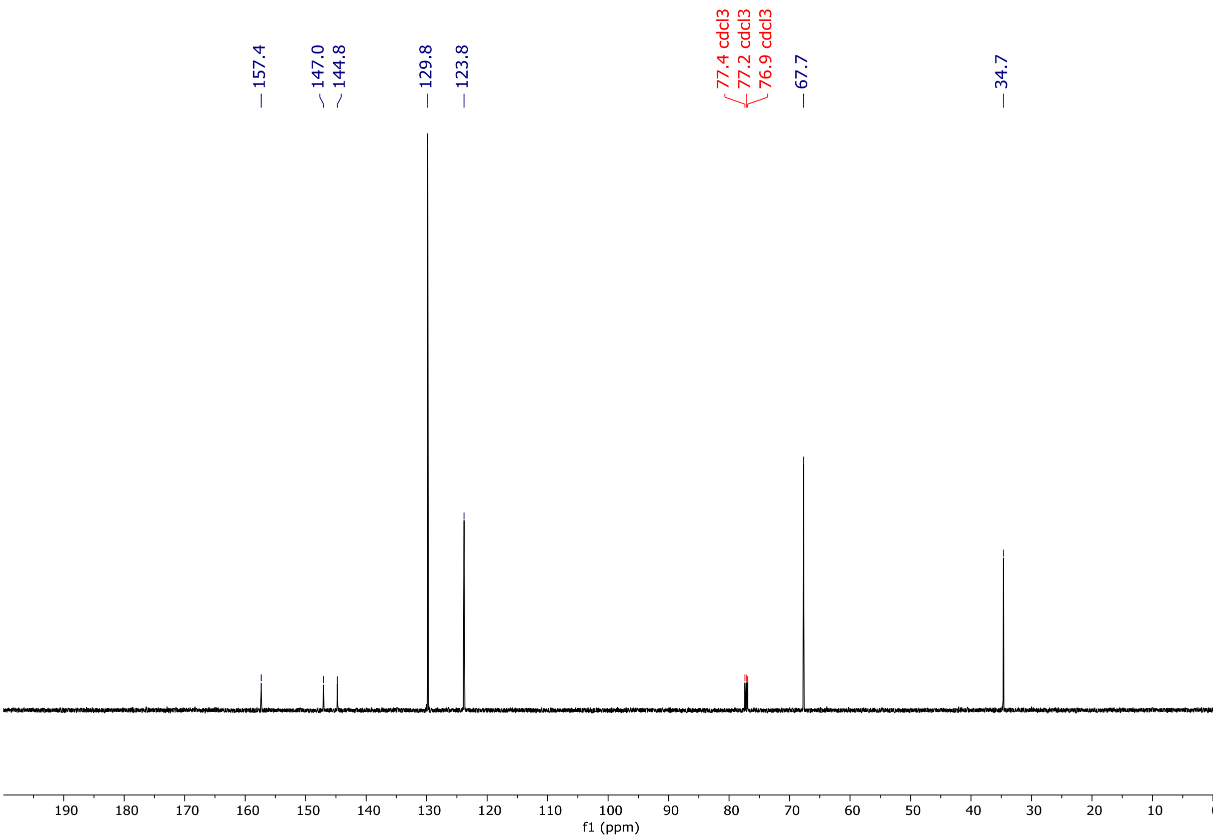
4-Bromophenethyl azidoformate (5c)



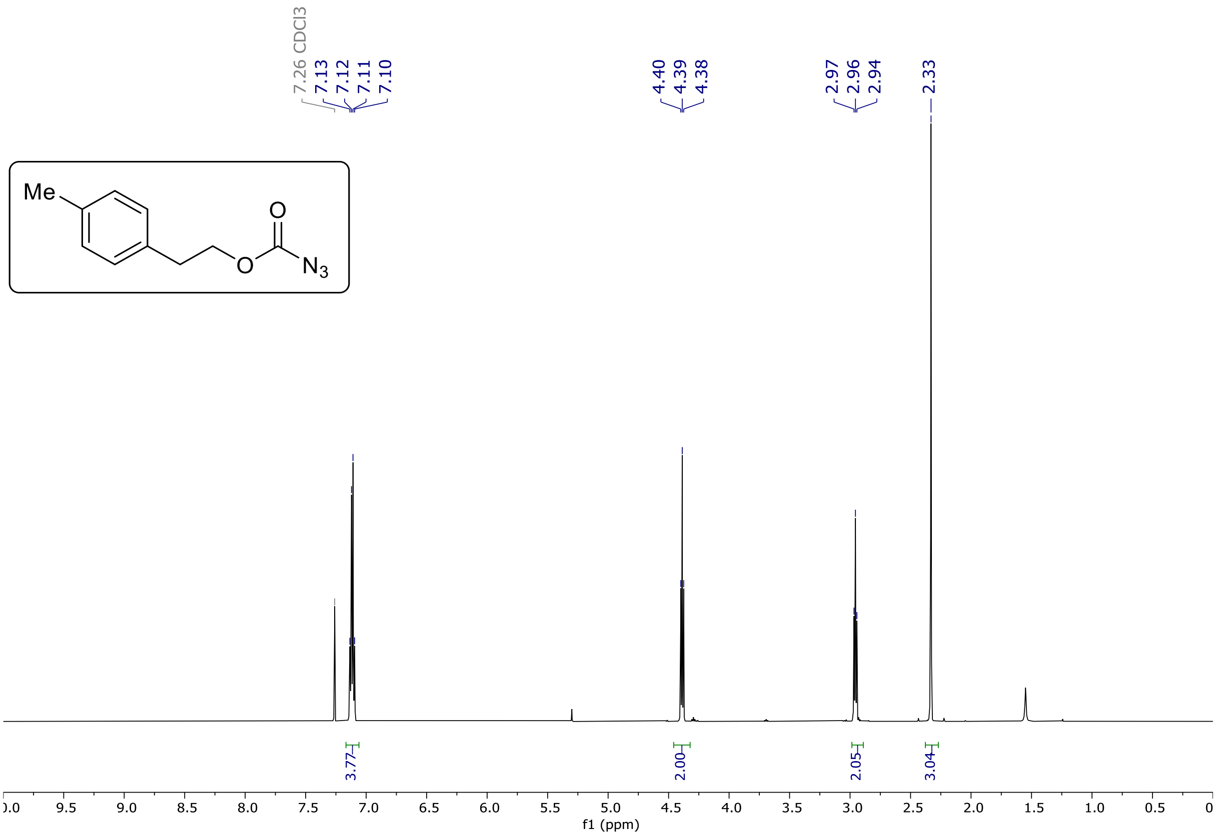


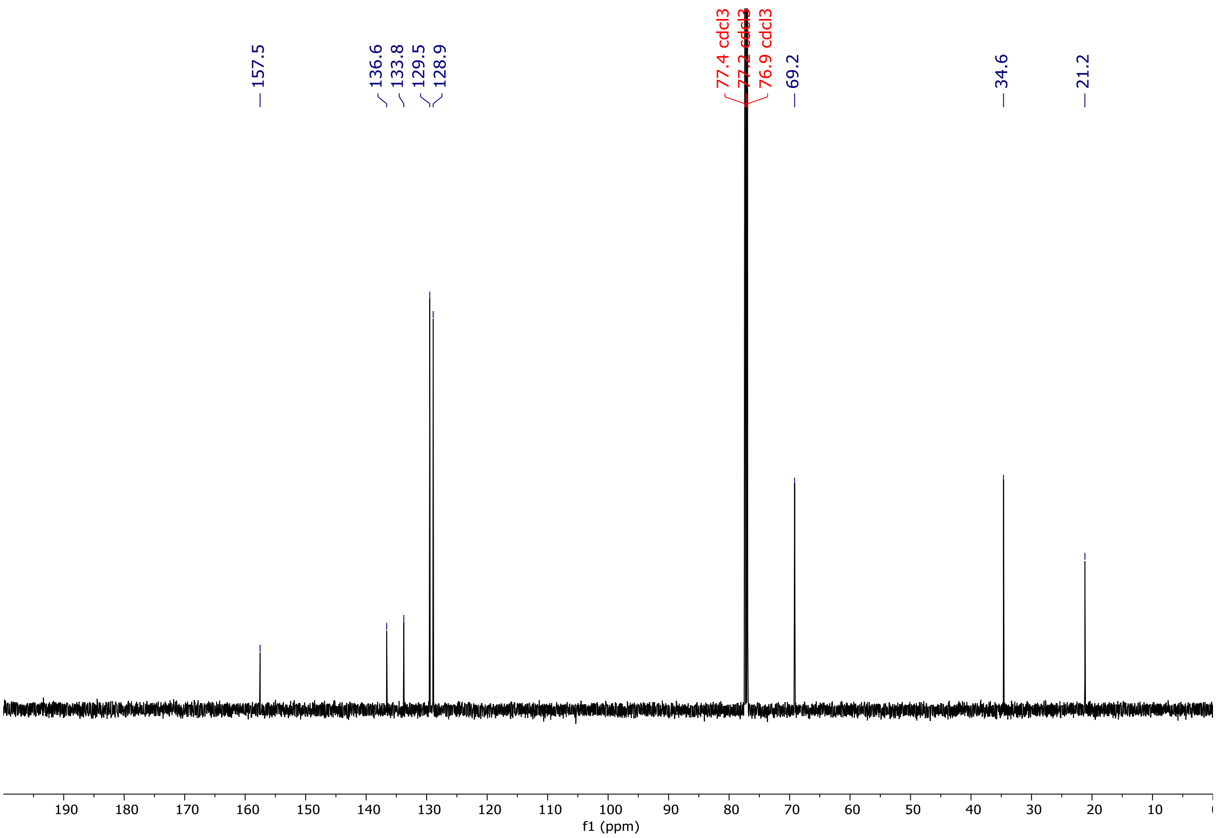
4-Nitrophenethyl azidoformate (5d)



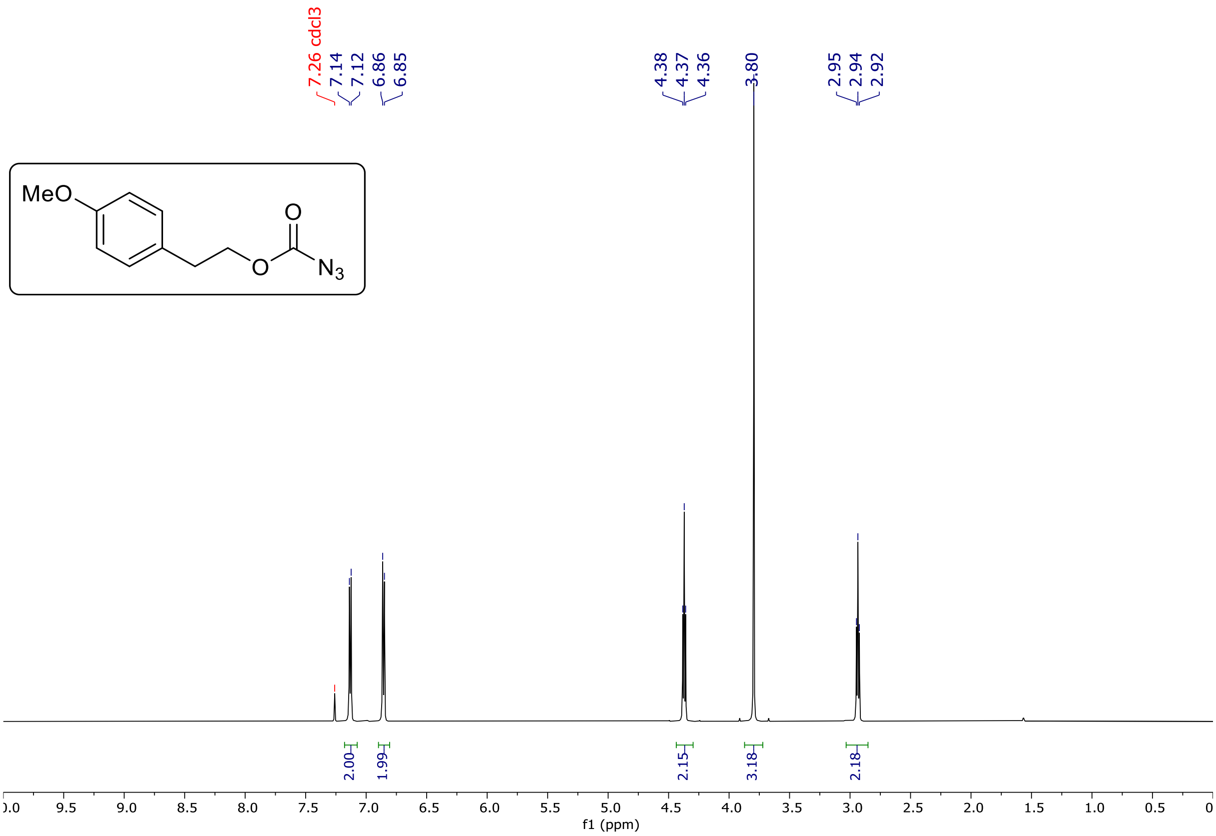


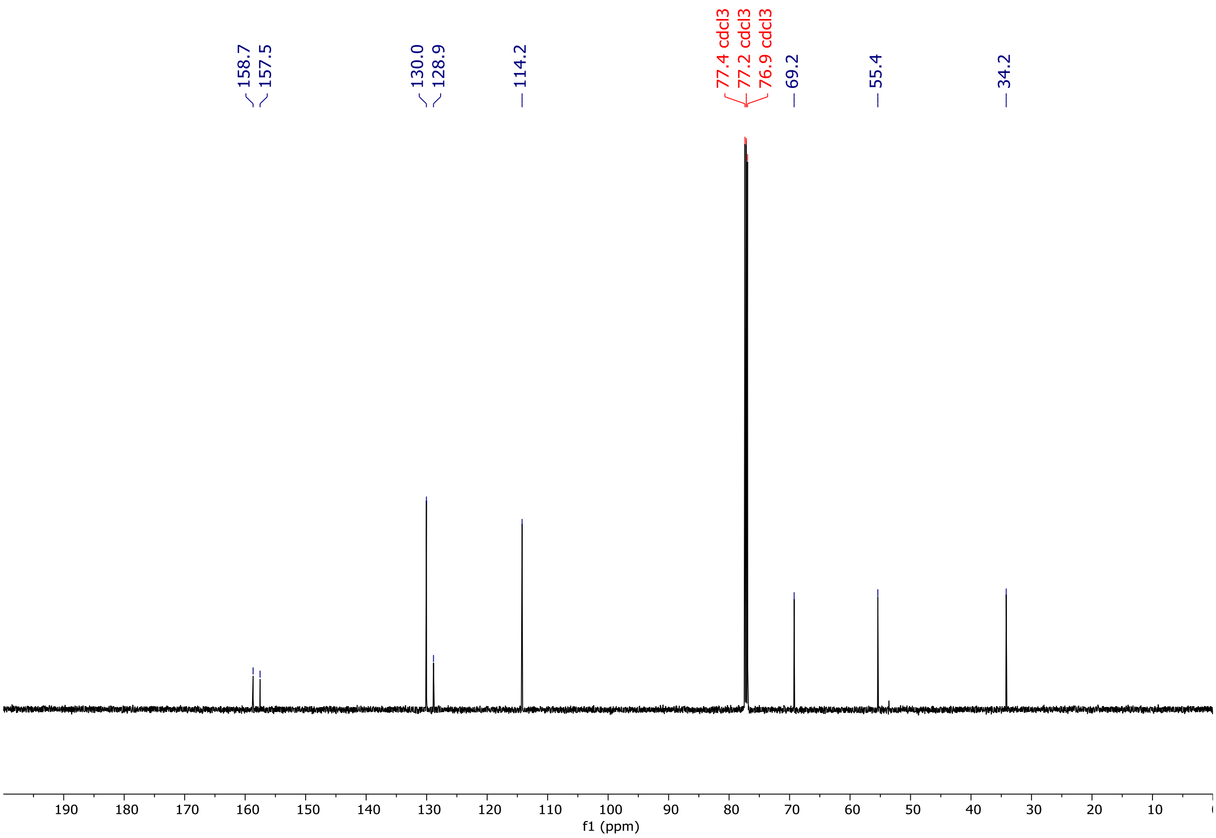
4-Methylphenethyl azidoformate (5e)



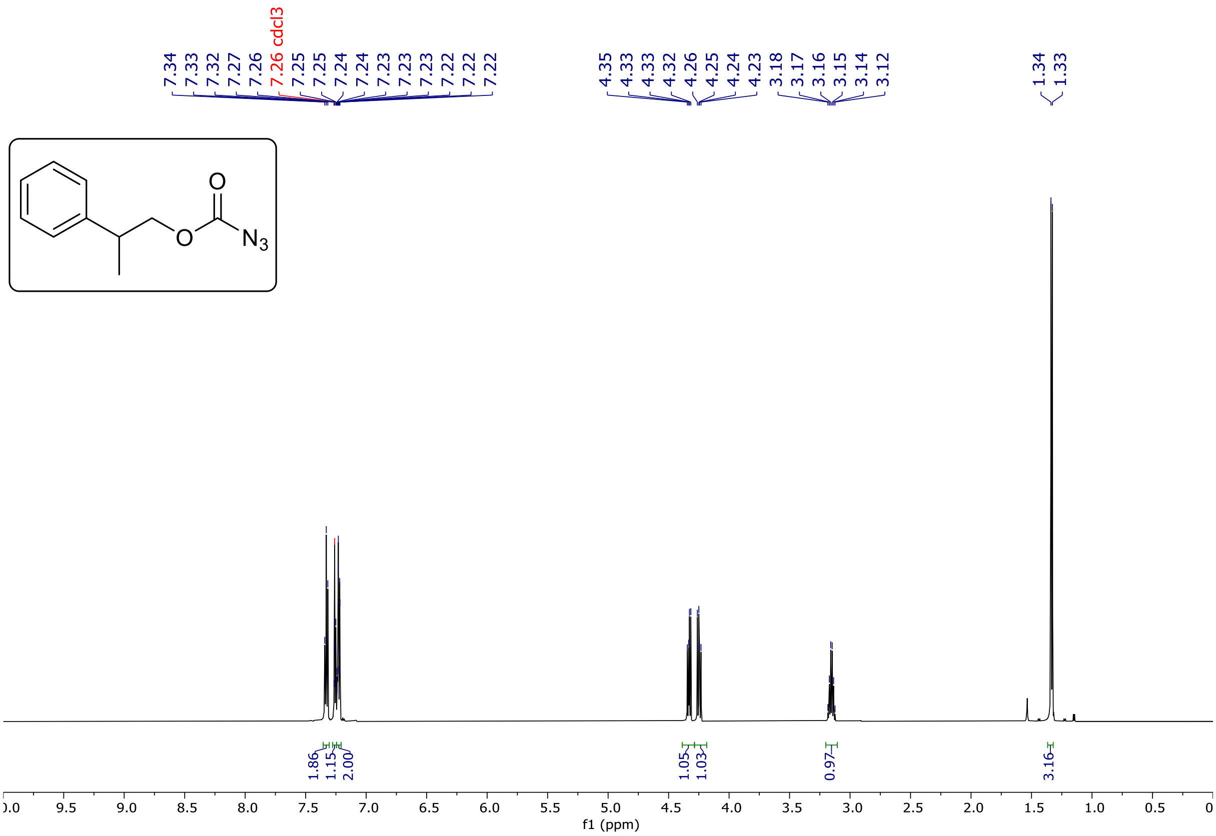


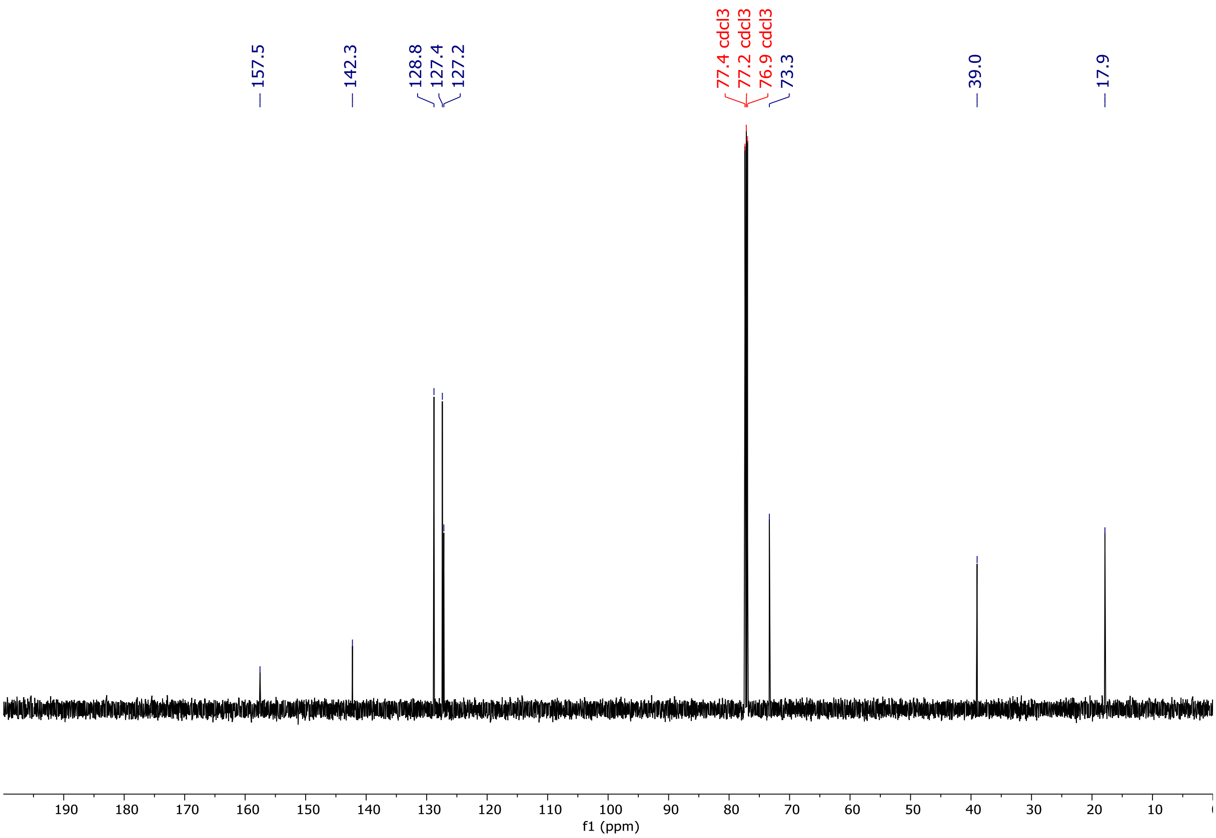
4-Methoxyphenethyl azidoformate (5f)



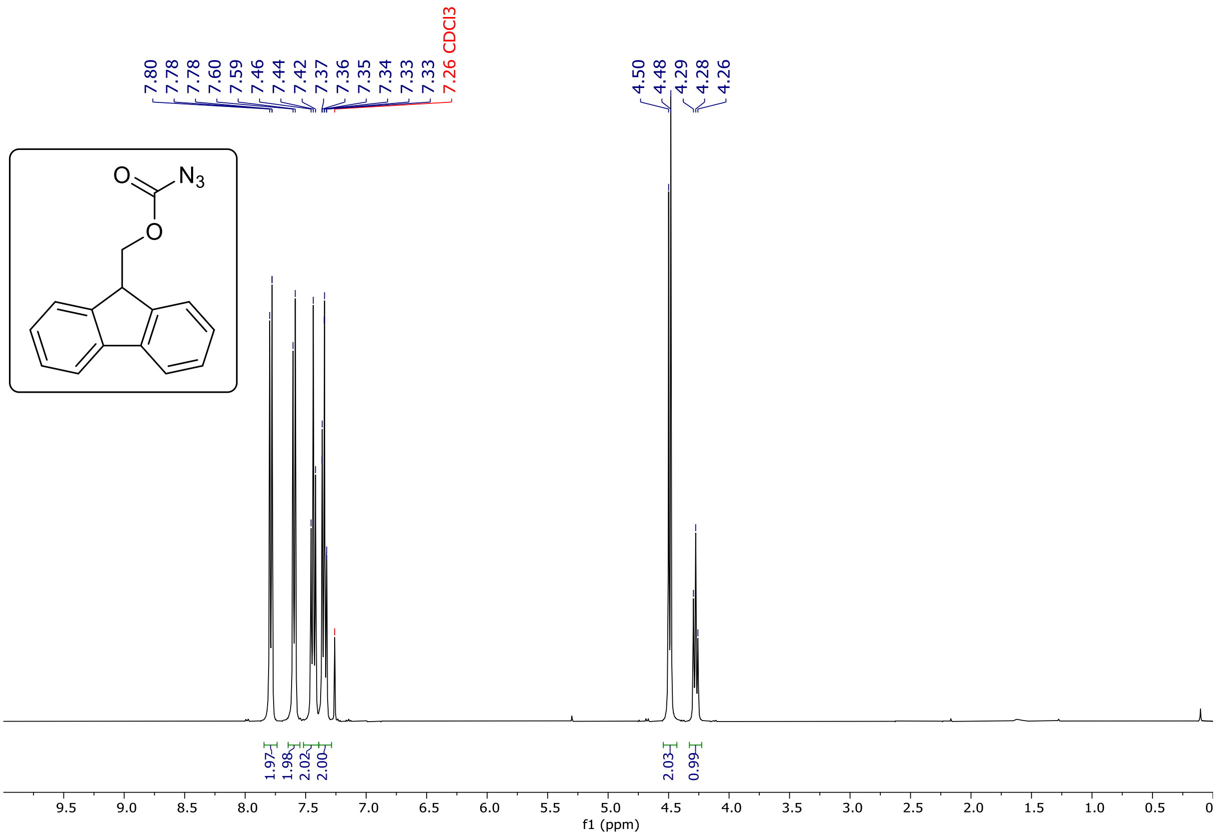


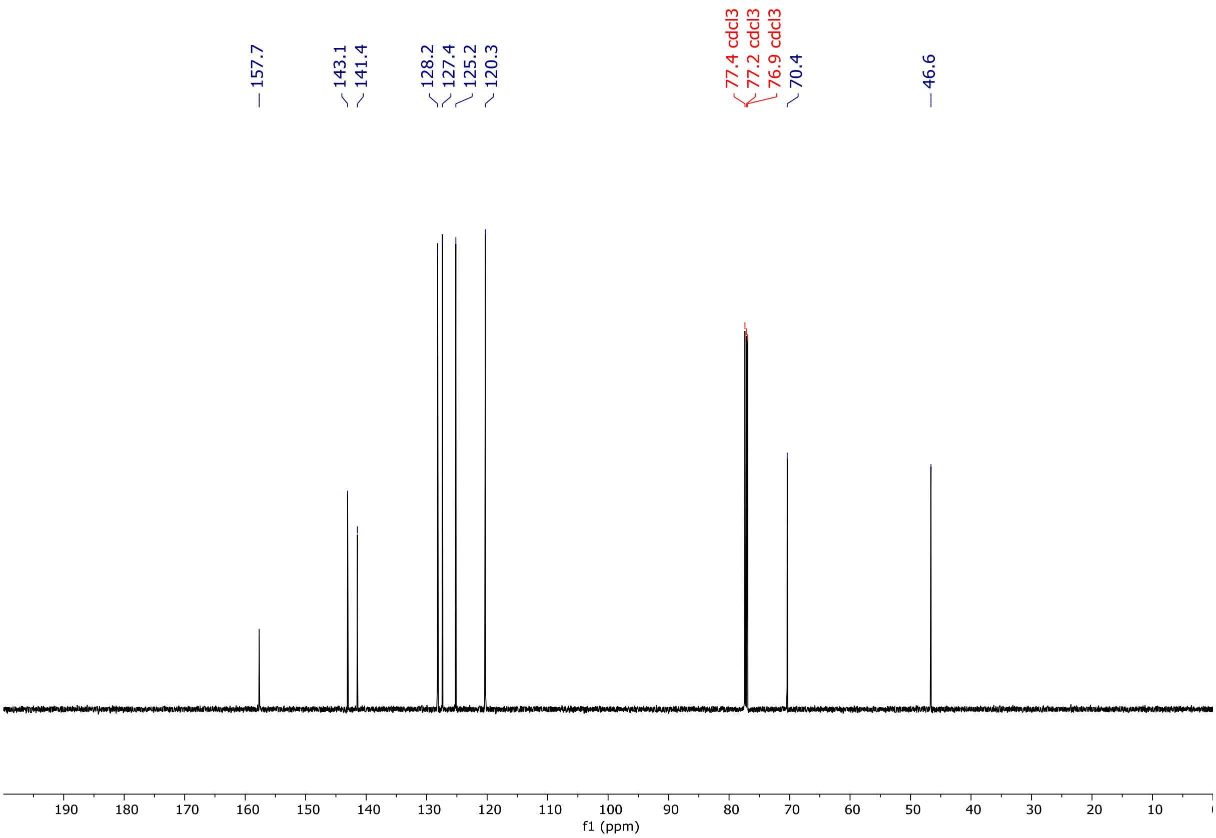
2-Phenylpropyl azidoformate (7a)



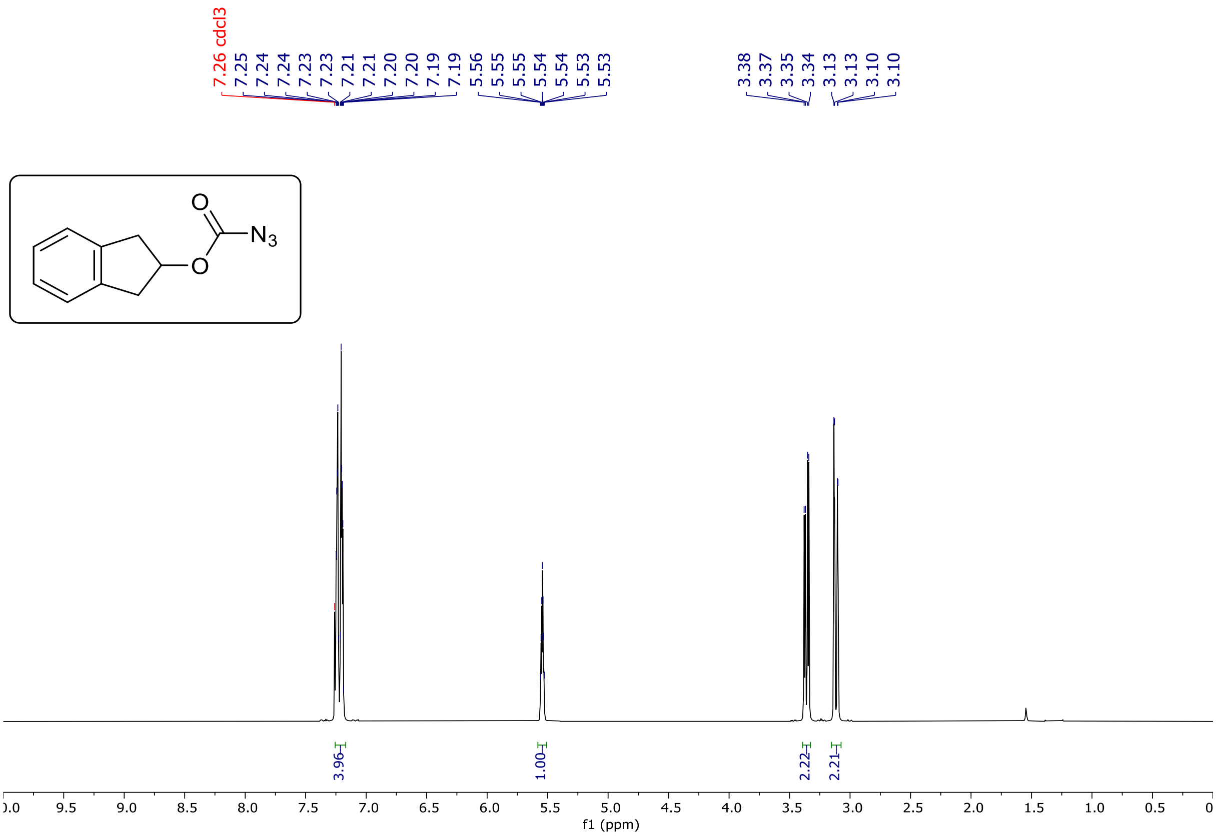


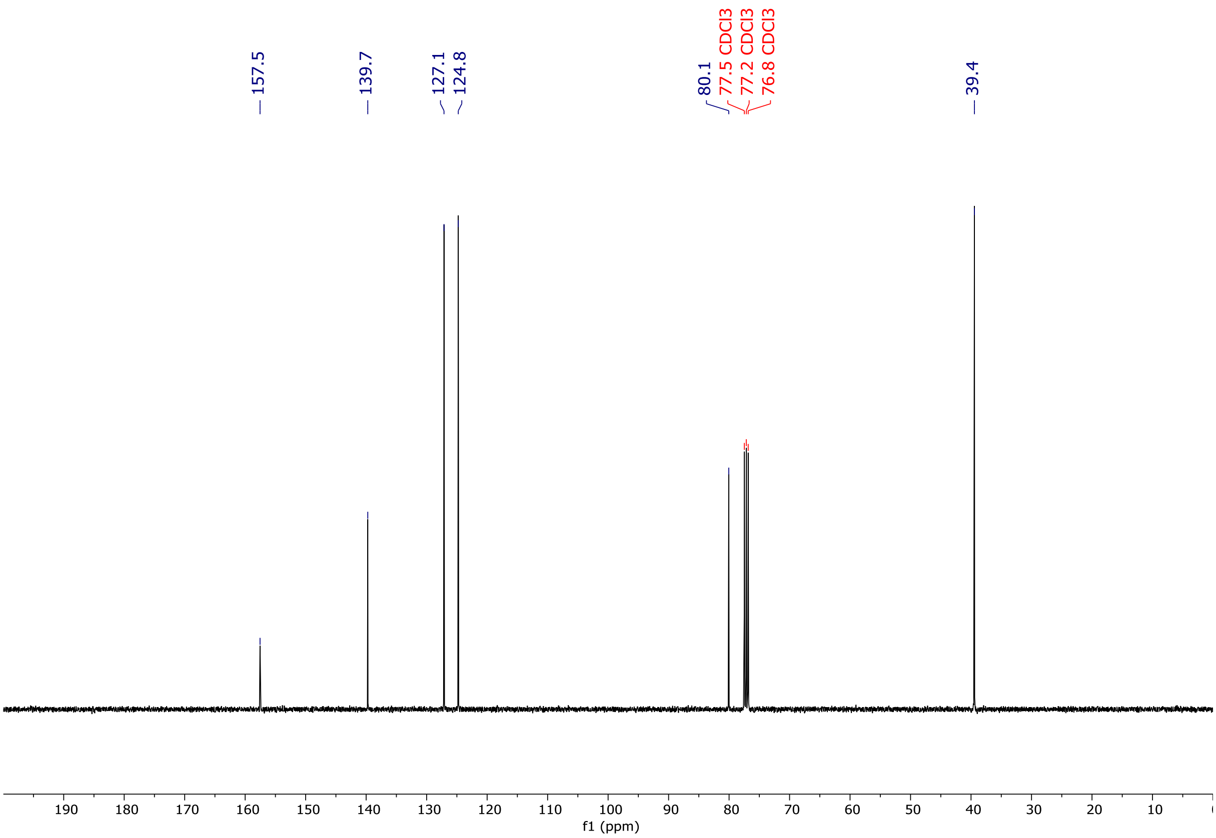
(9*H*-Fluoren-9-yl)methyl azidoformate (7b)



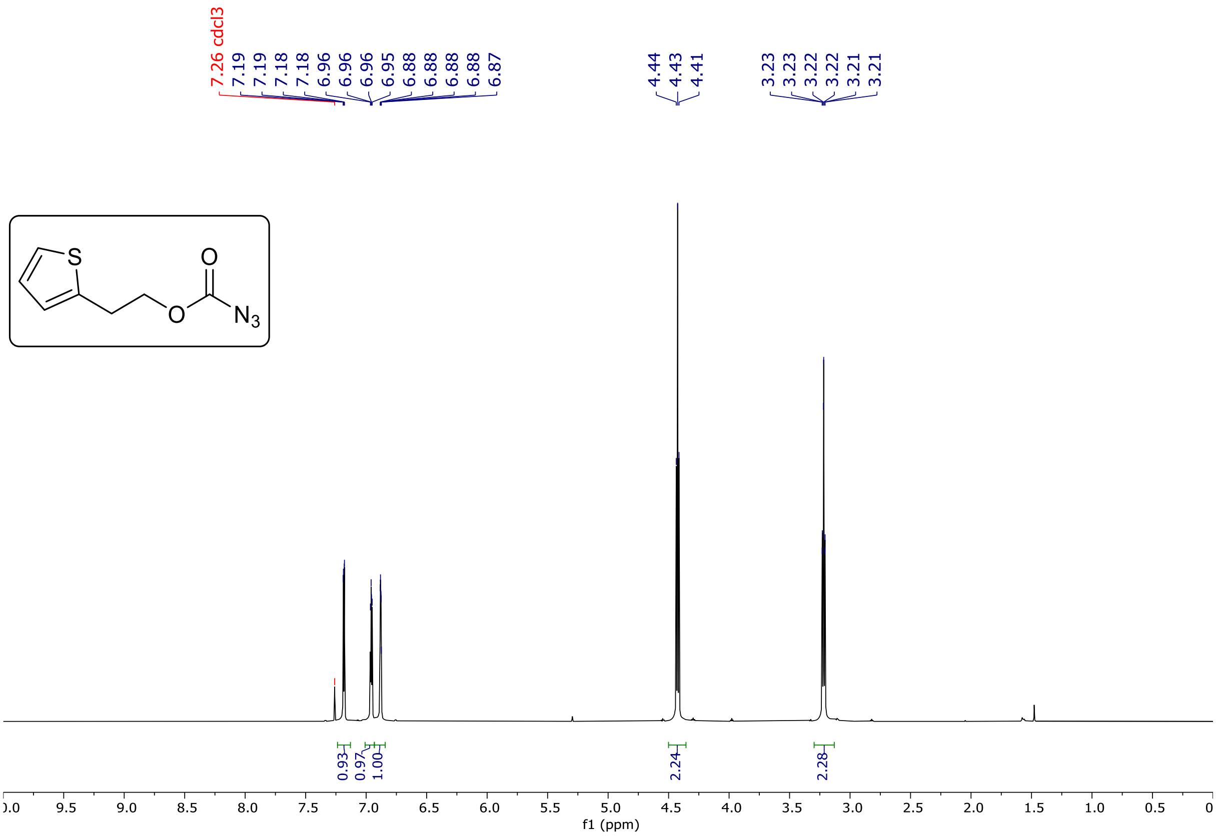


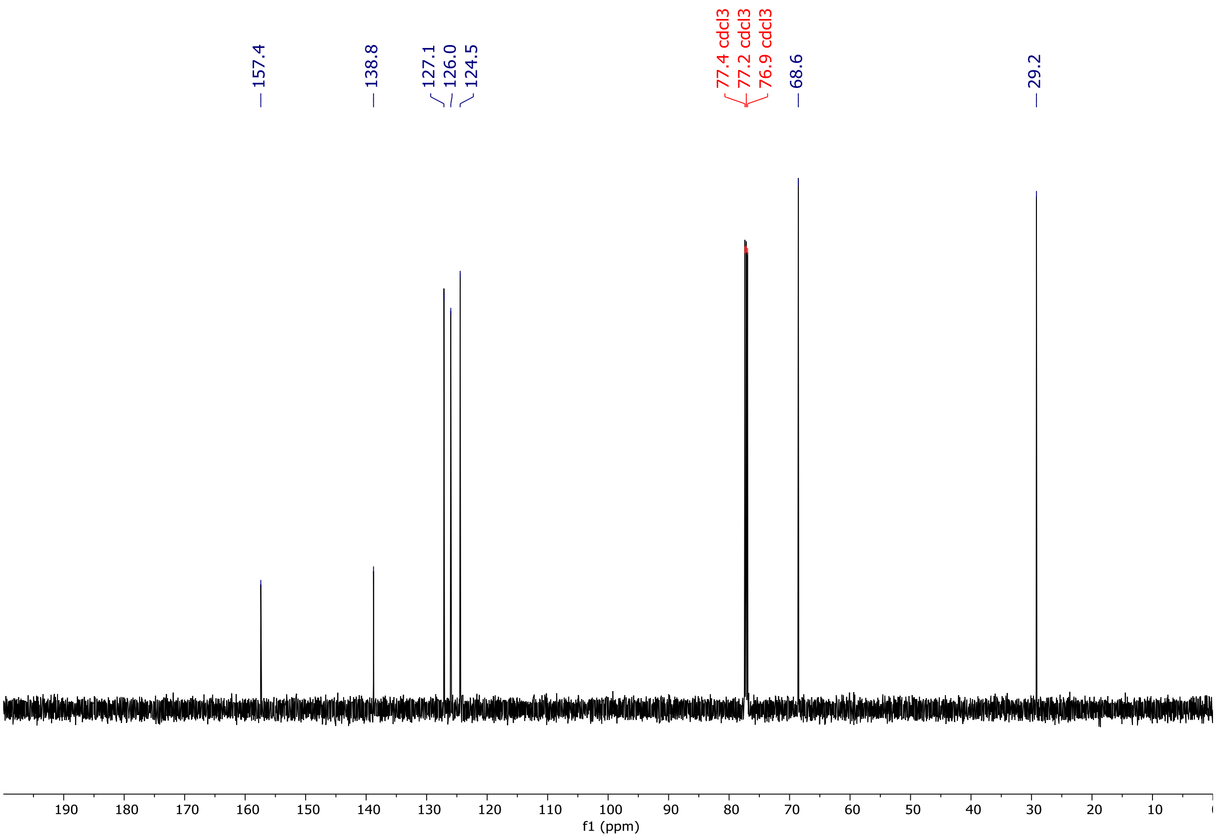
2,3-Dihydro-1*H*-inden-2-yl azidoformate (7c)



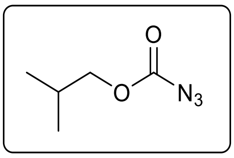


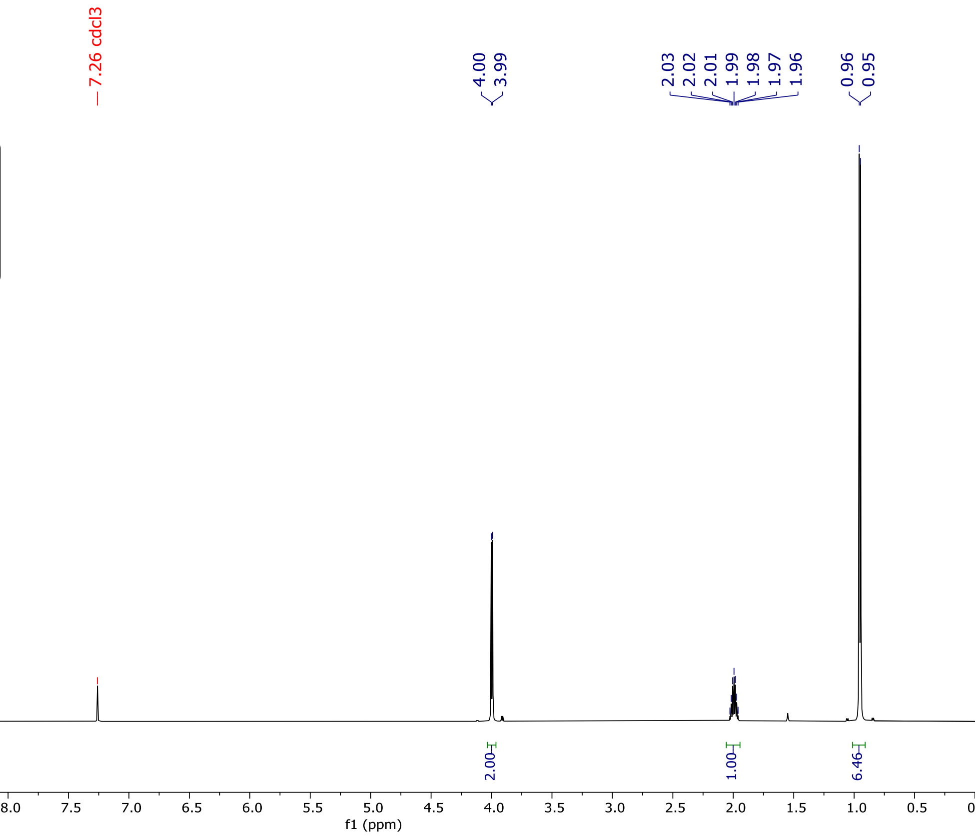
2-(Thiophen-2-yl)ethyl azidoformate (7d)

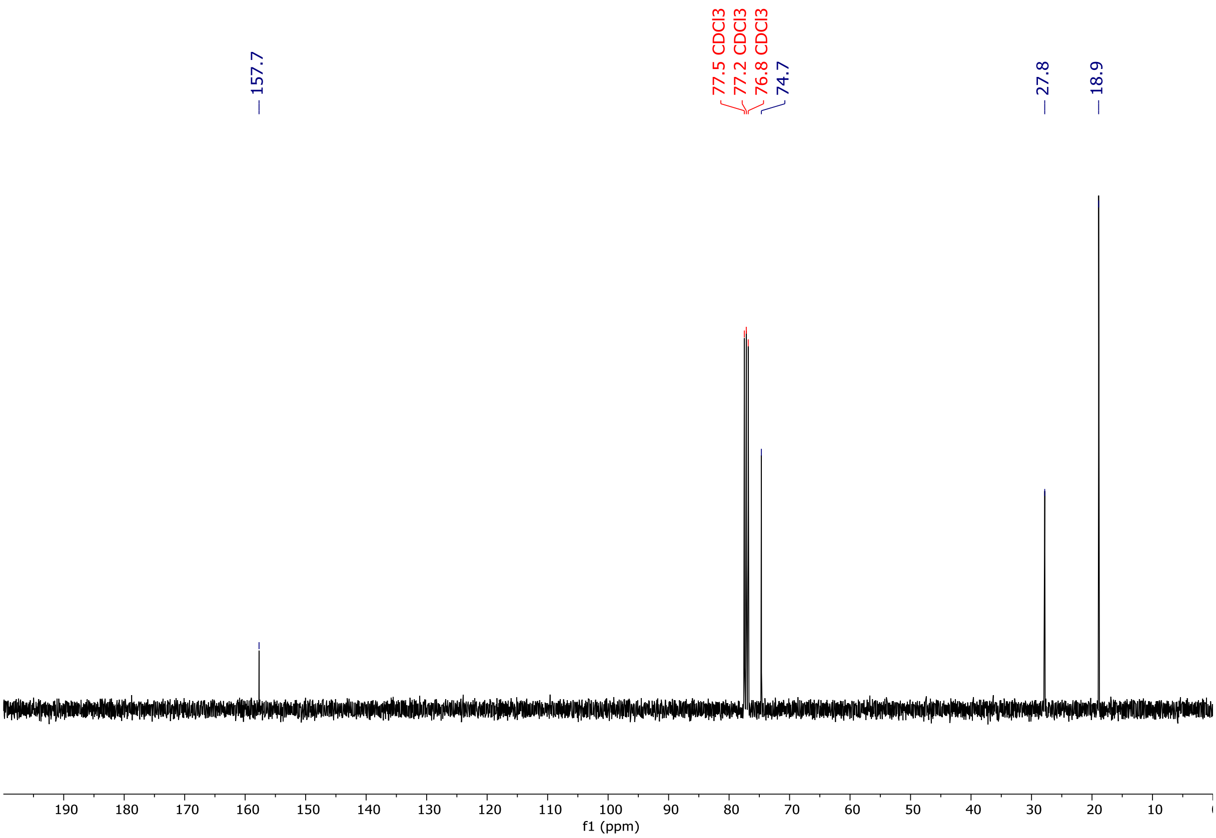




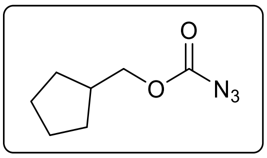
Isobutyl azidoformate (7e)

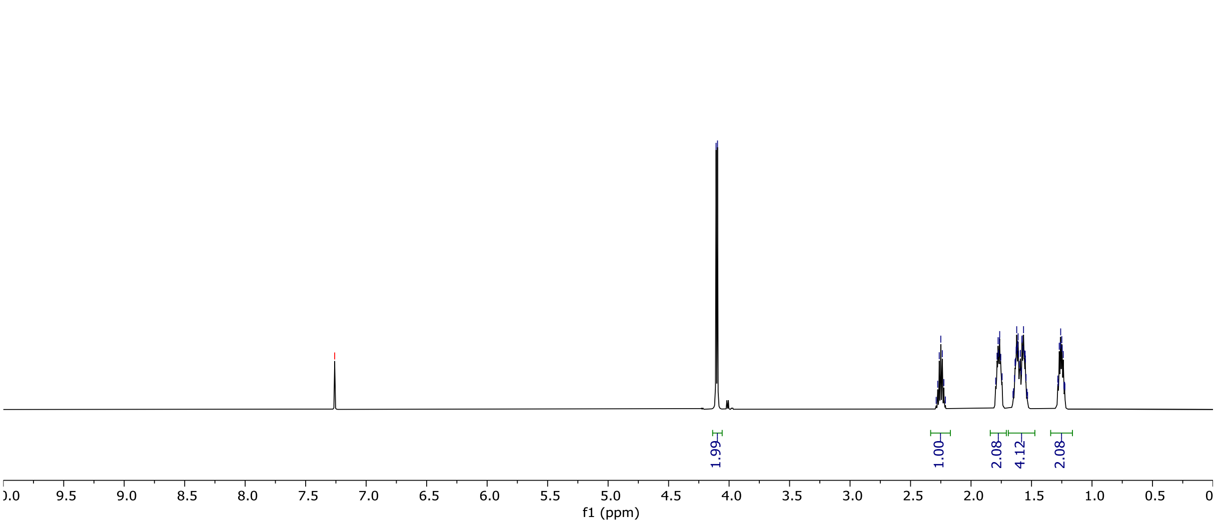


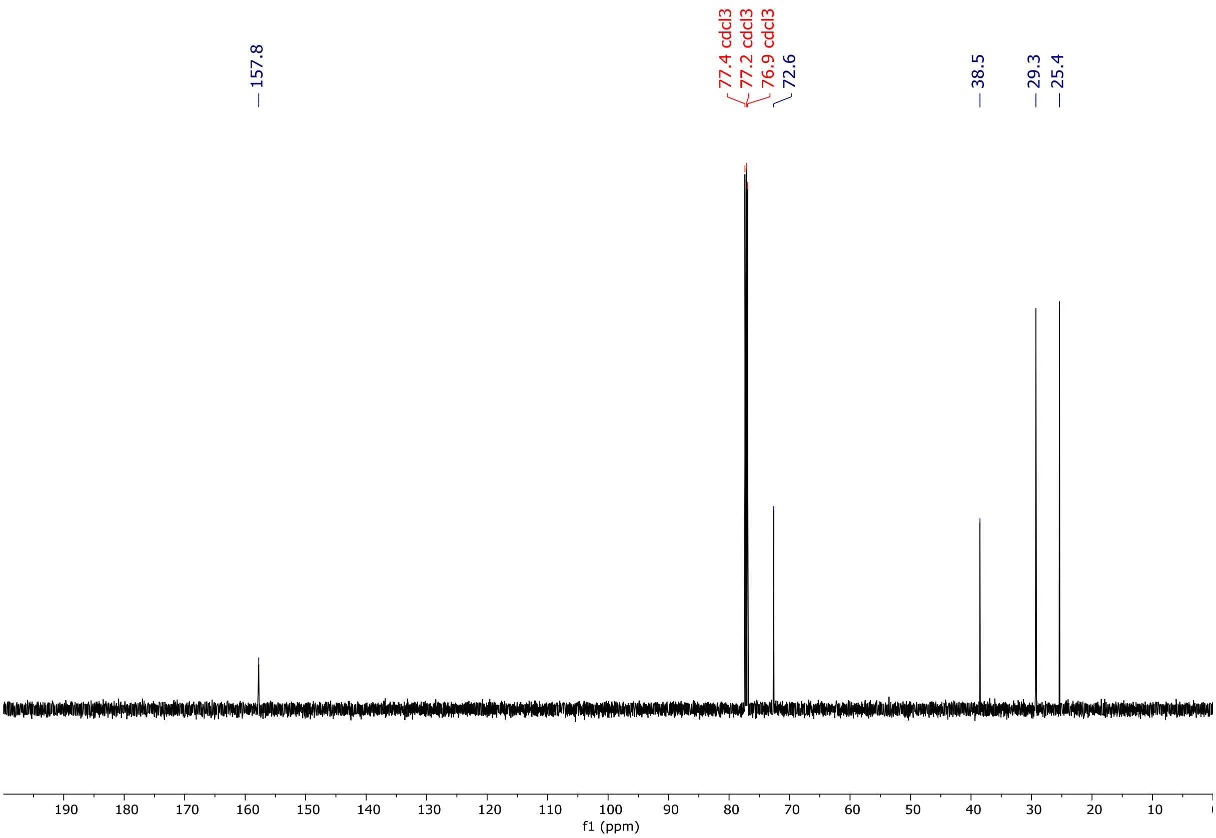




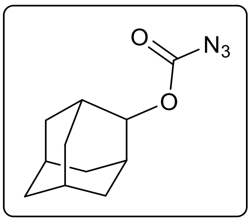
Cyclopentylmethyl azidoformate (7f)

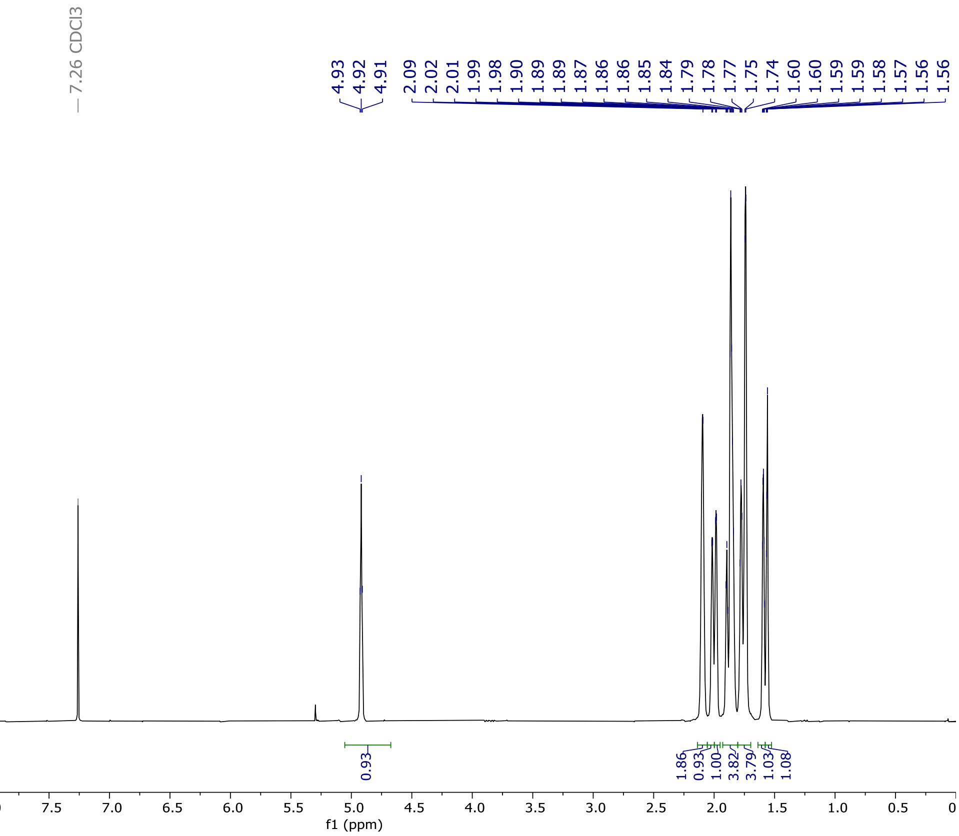


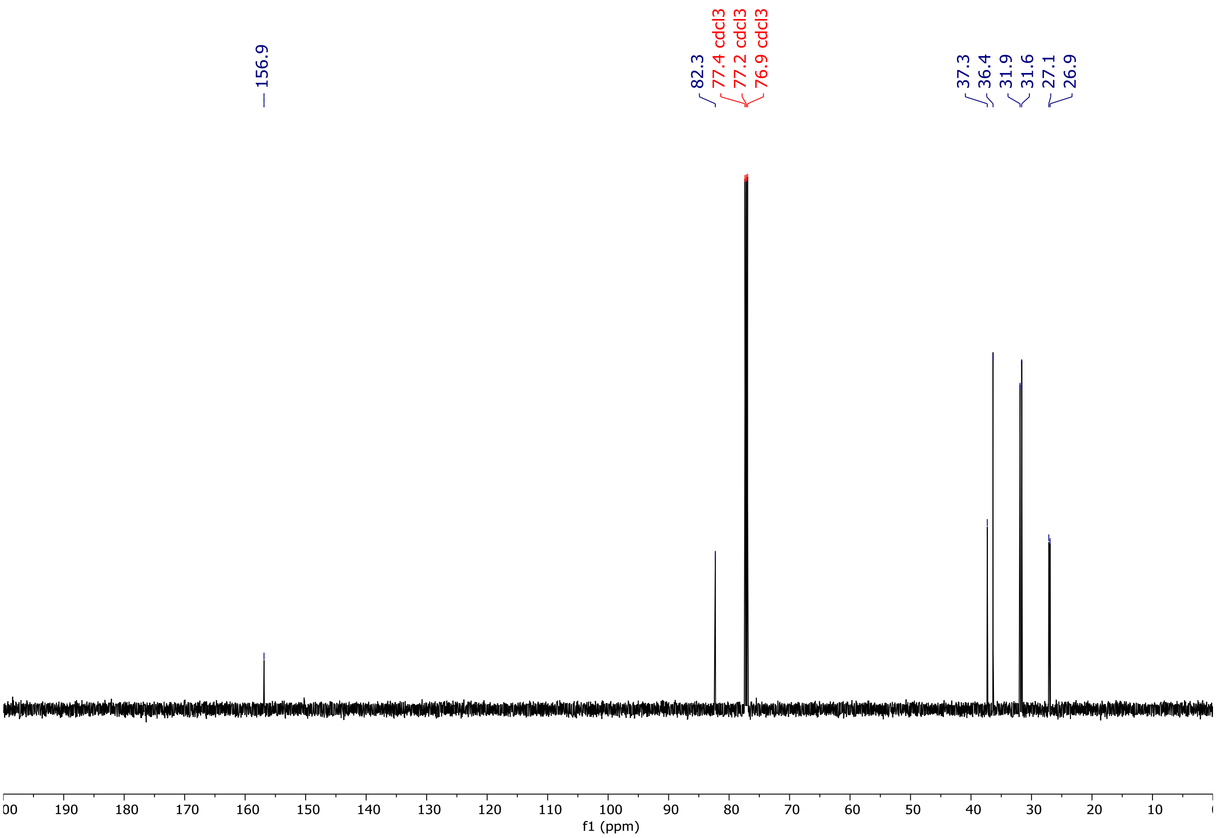




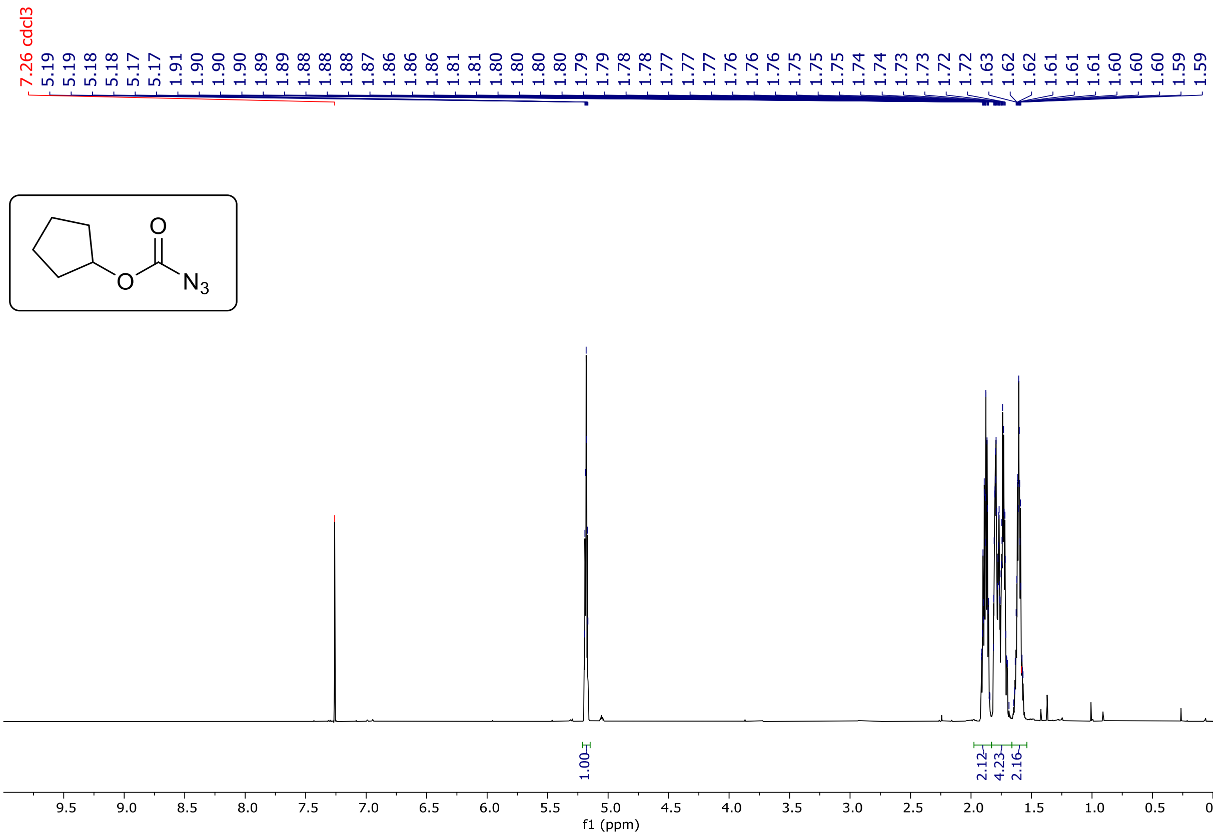
(1*r*,3*r*,5*r*,7*r*)-Adamantan-2-yl azidoformate (7g)

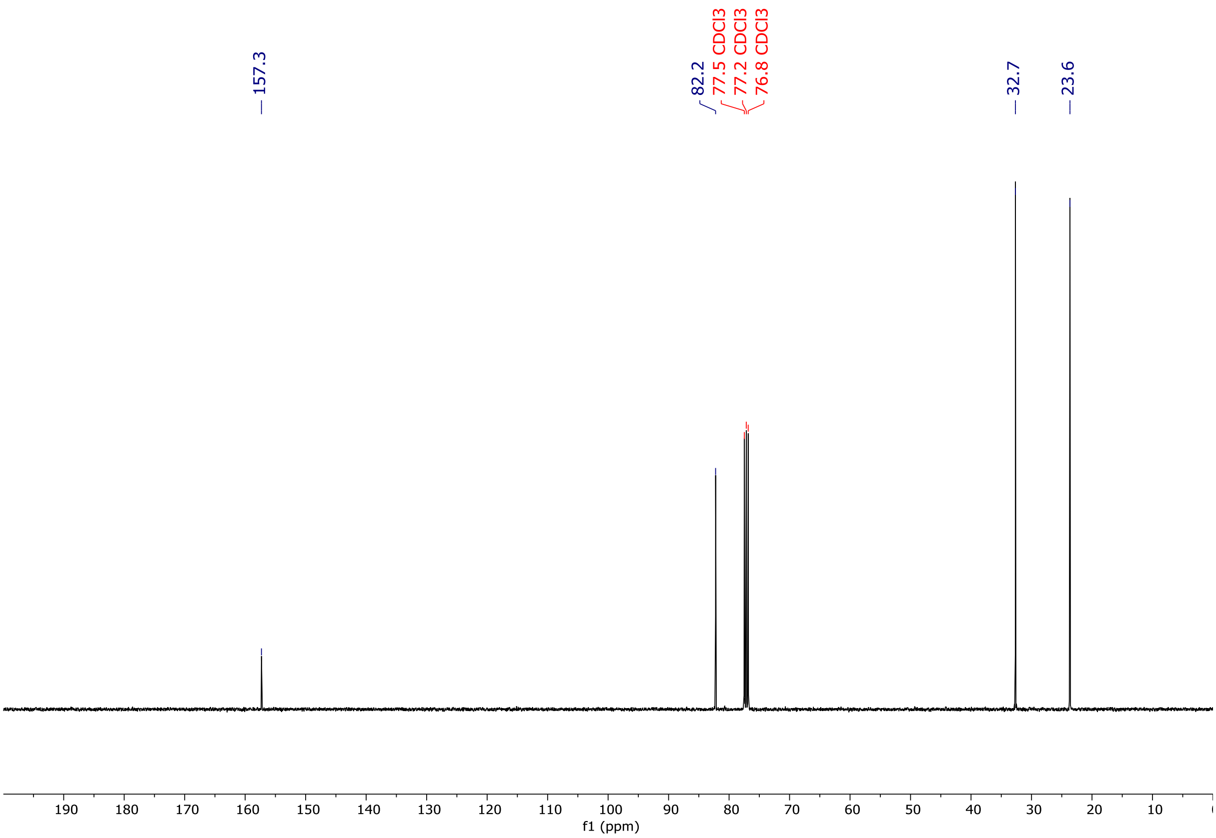




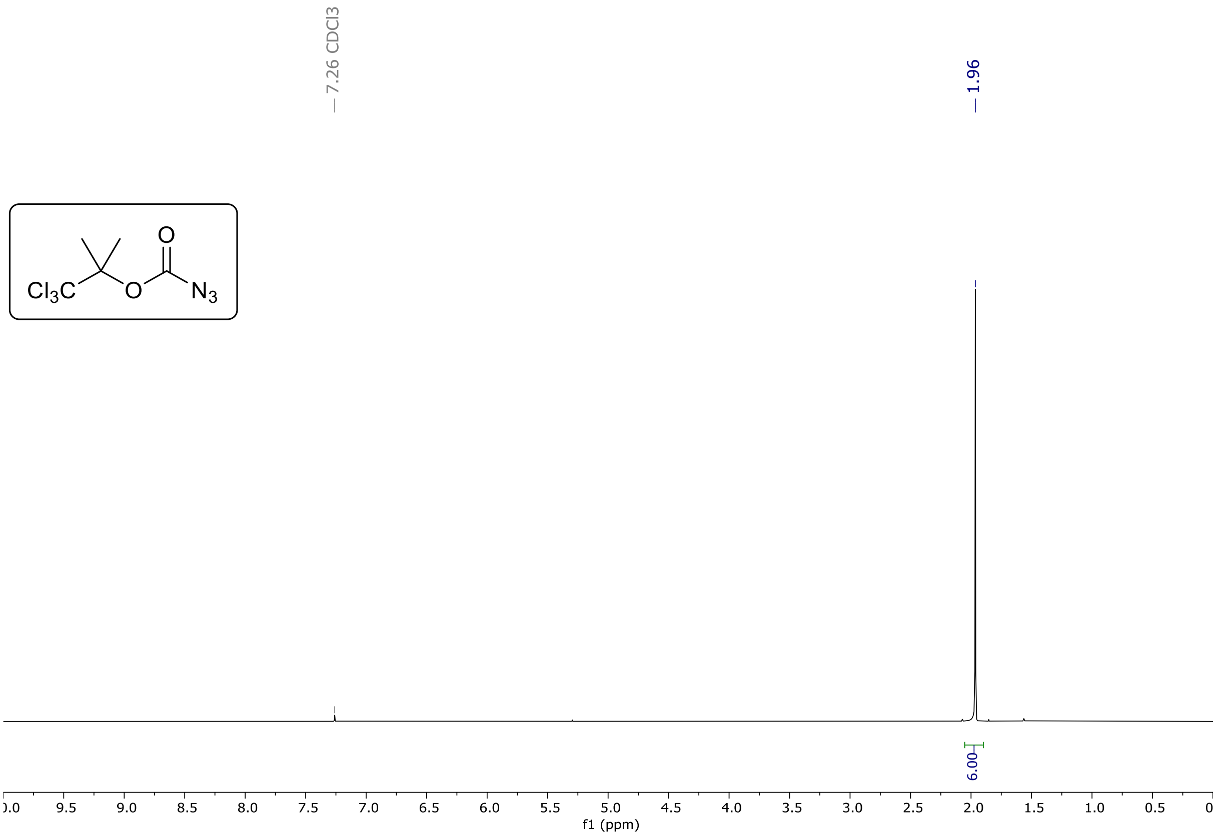


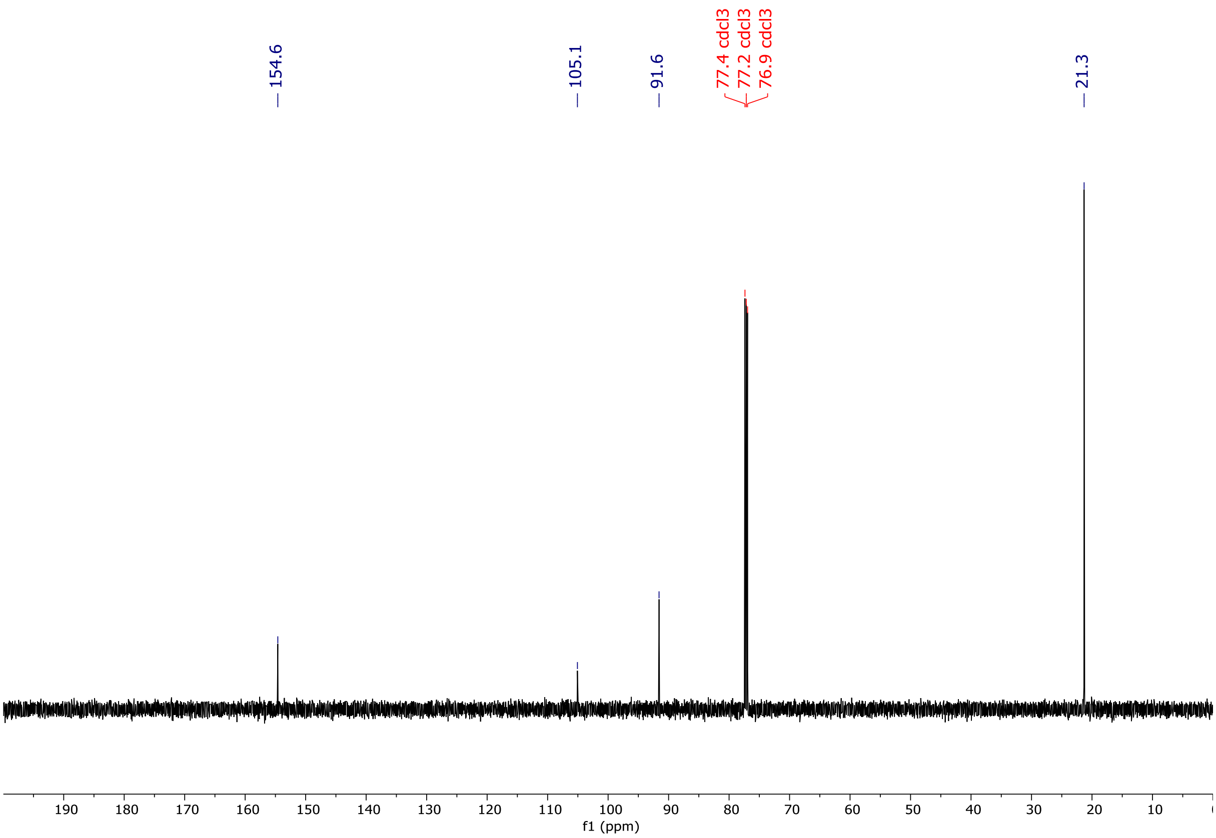
Cyclopentyl azidoformate (7h)



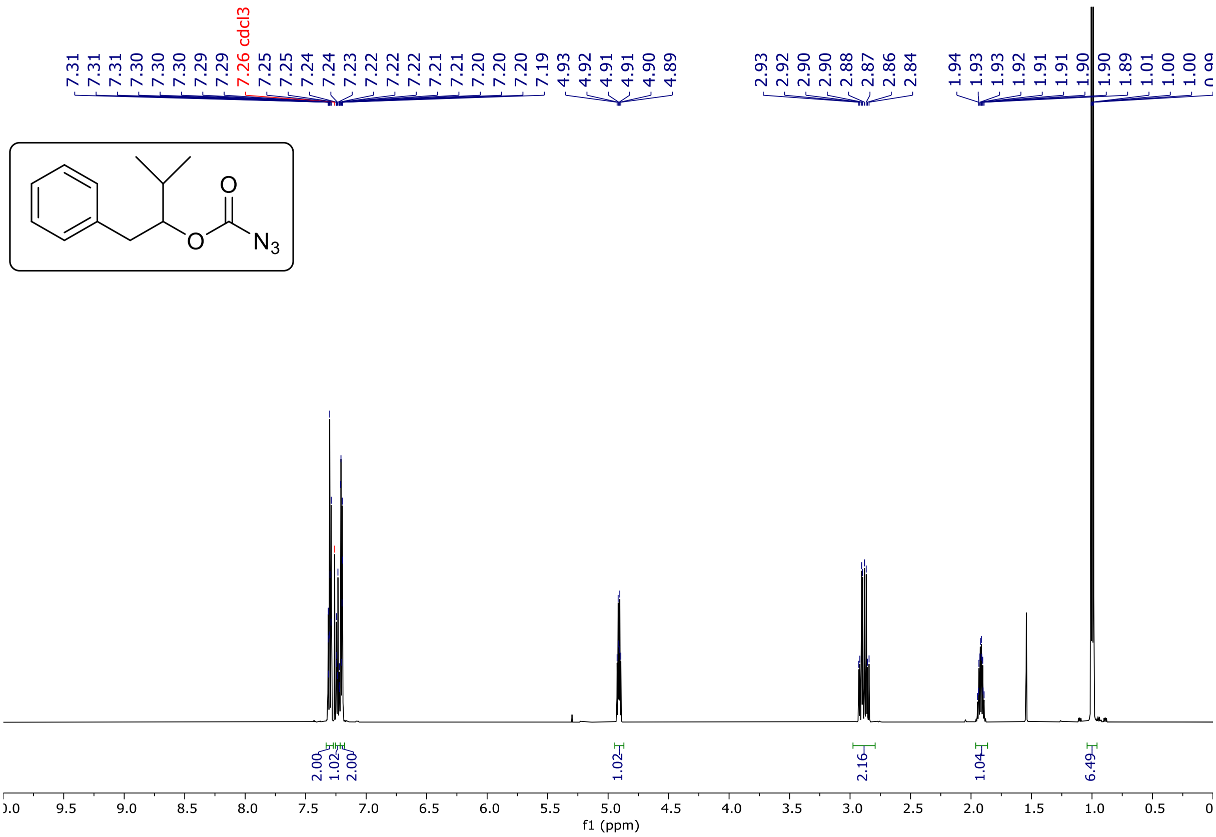


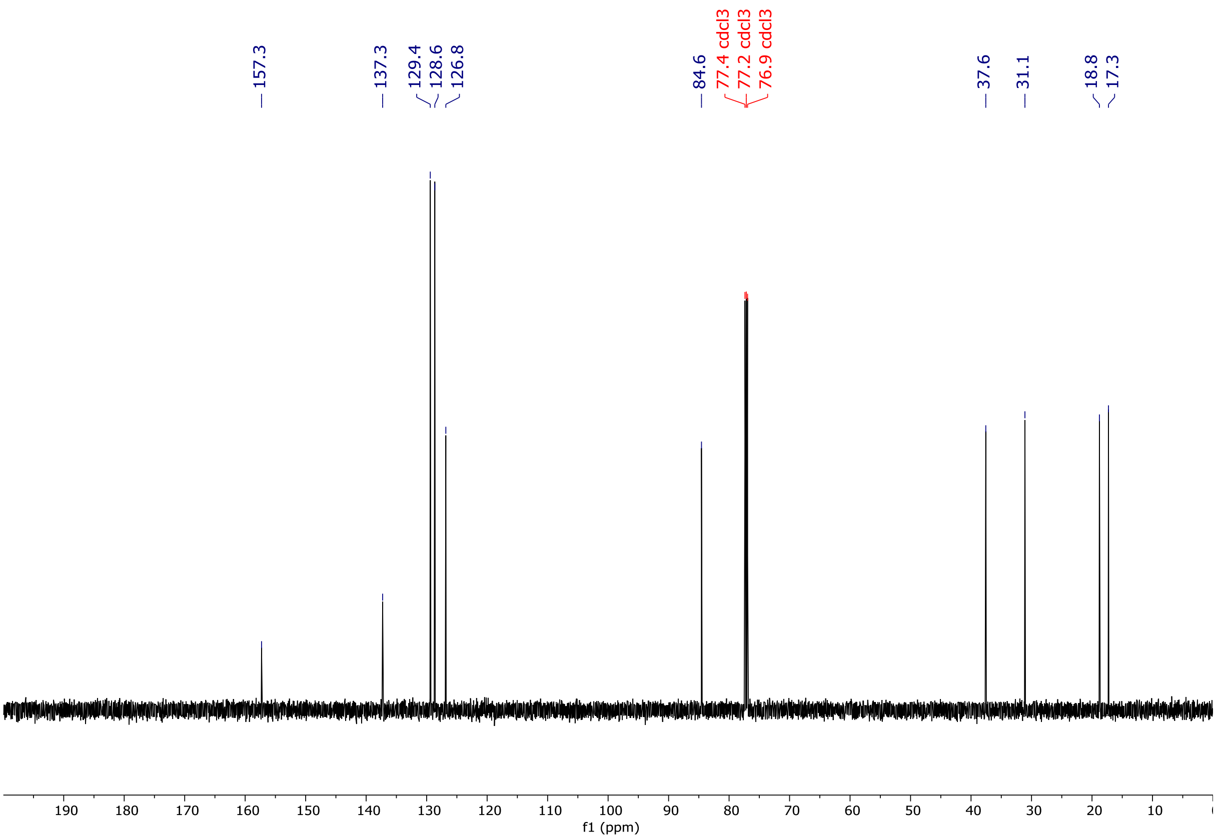
1,1,1-Trichloro-2-methylpropan-2-yl azidoformate (7i)



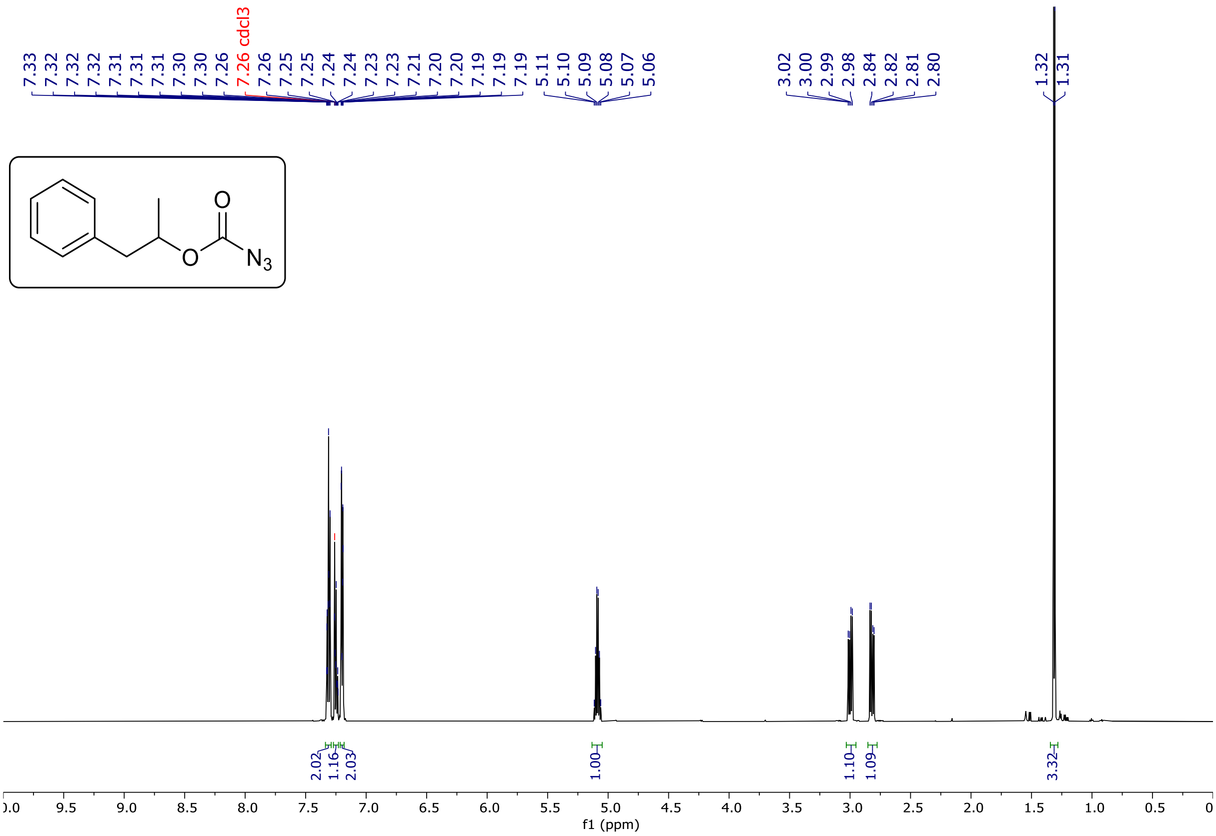


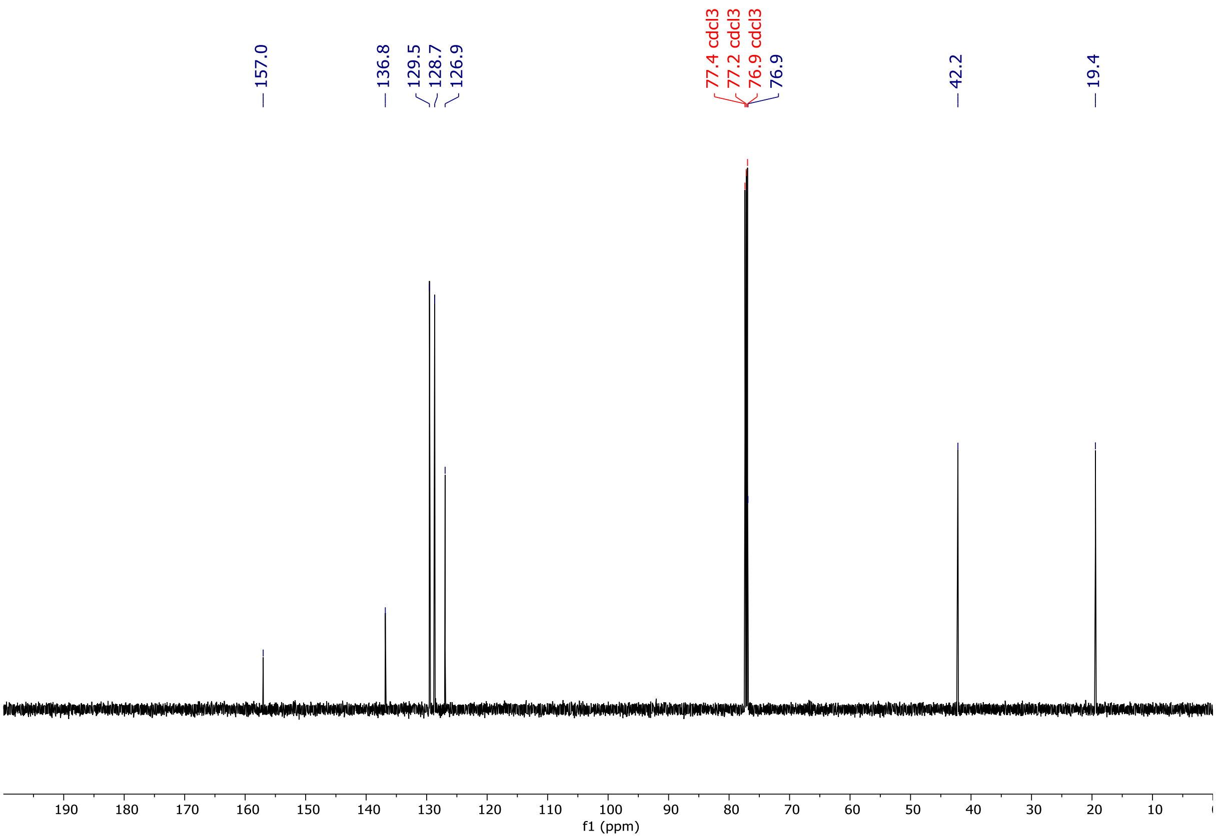
3-Methyl-1-phenylbutan-2-yl azidoformate (7j)



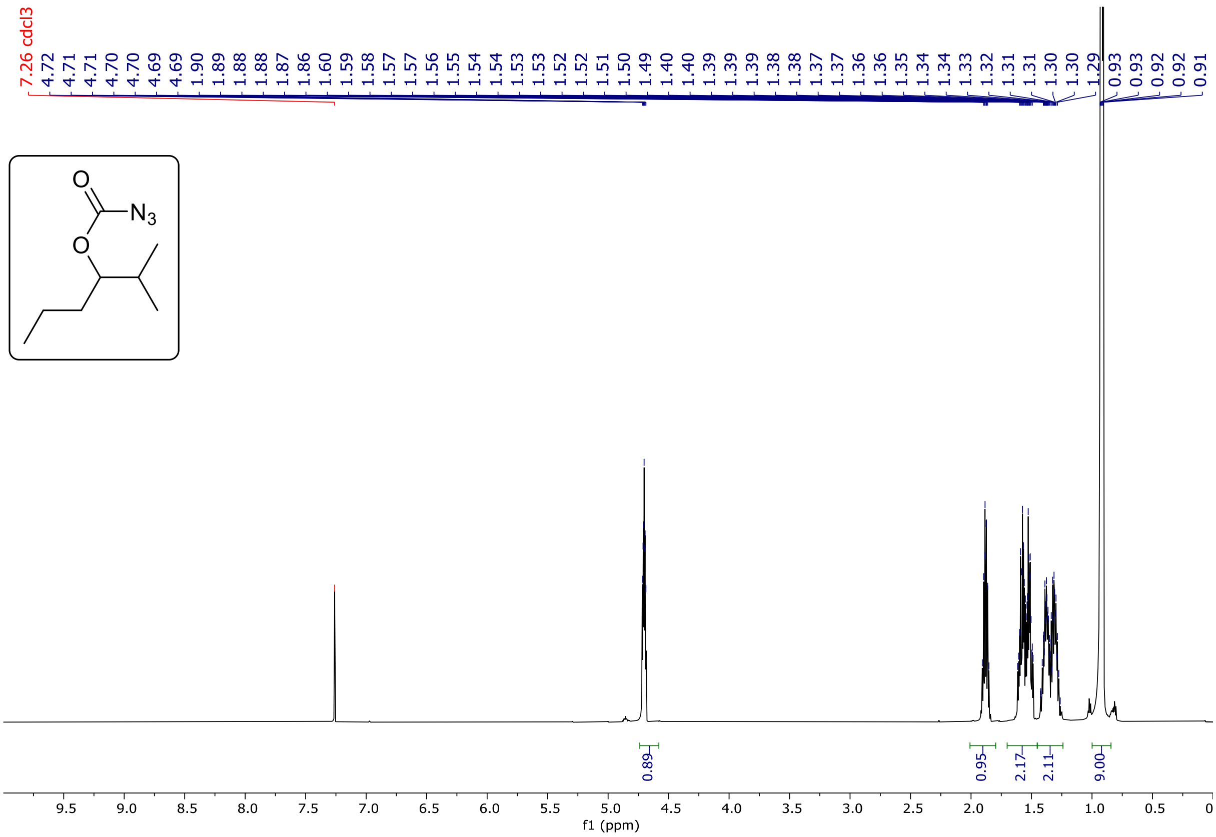


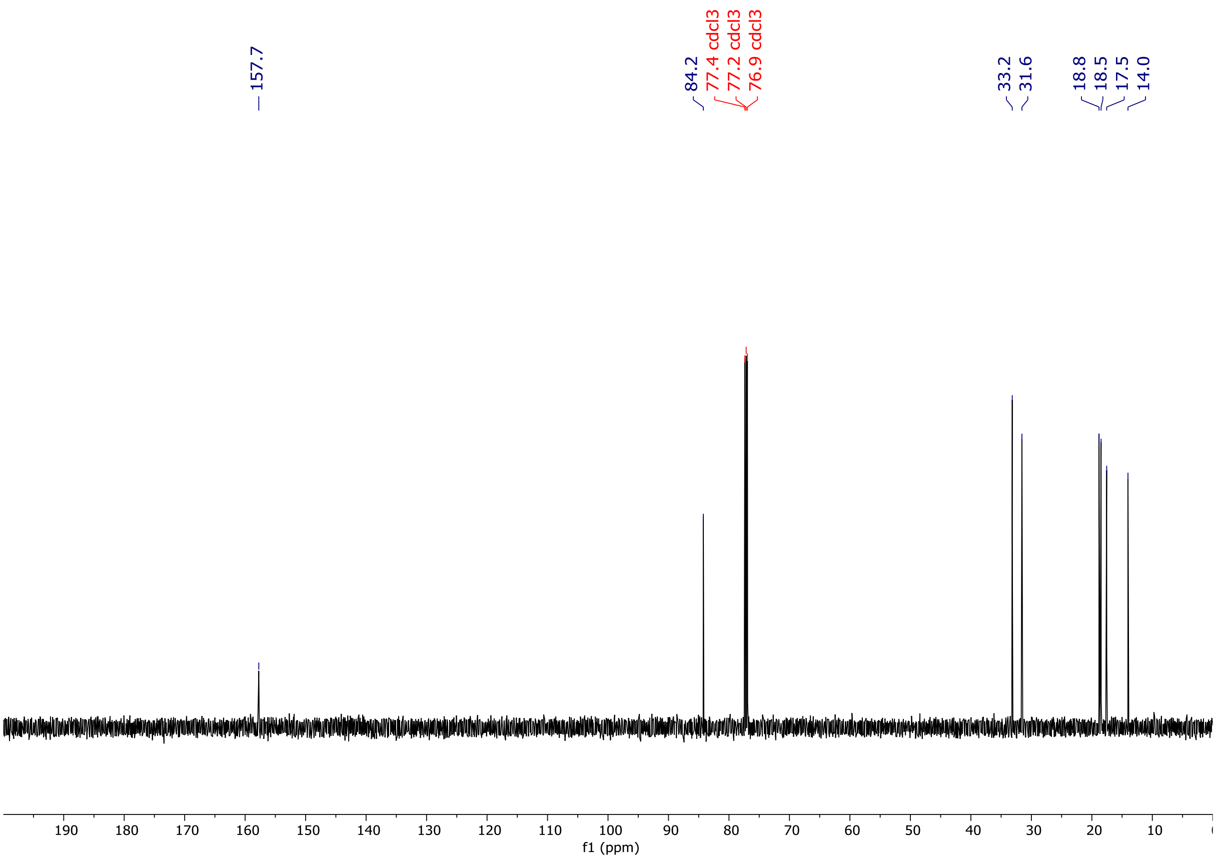
1-Phenylpropan-2-yl azidoformate (7k)



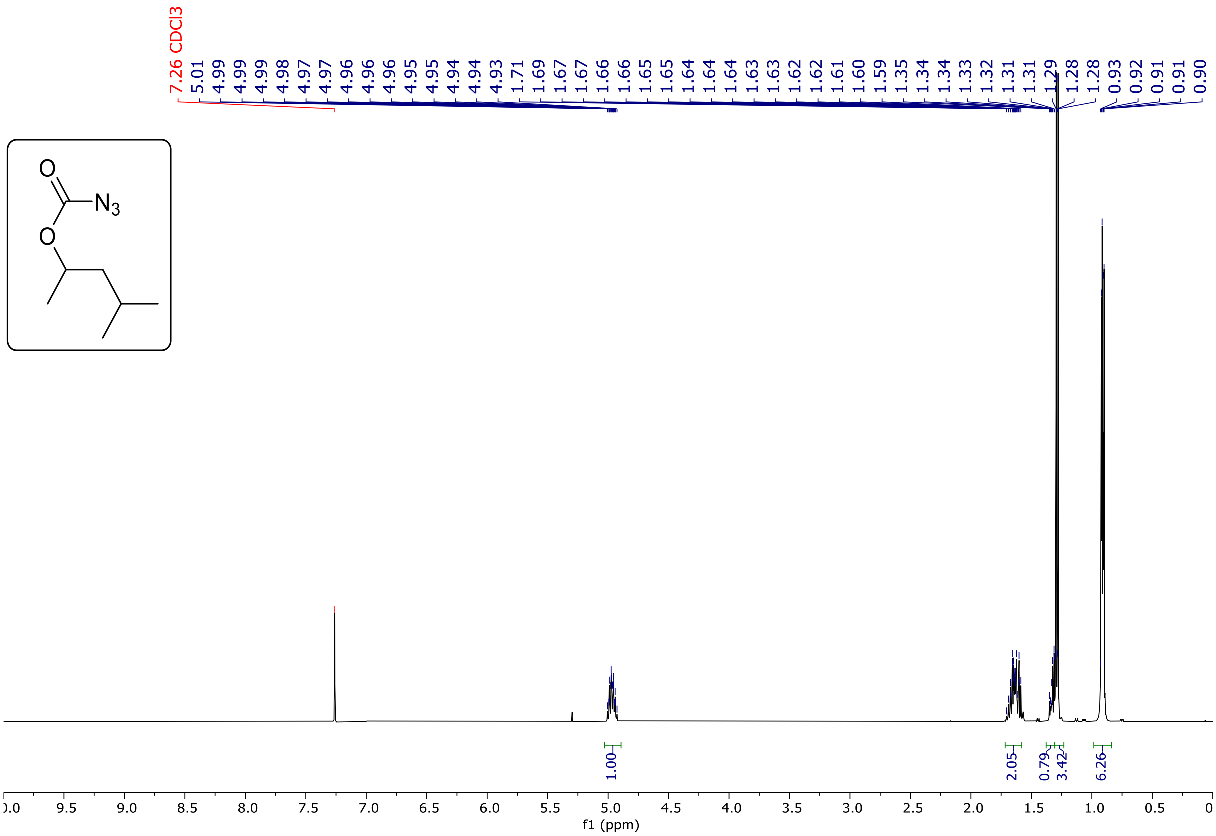


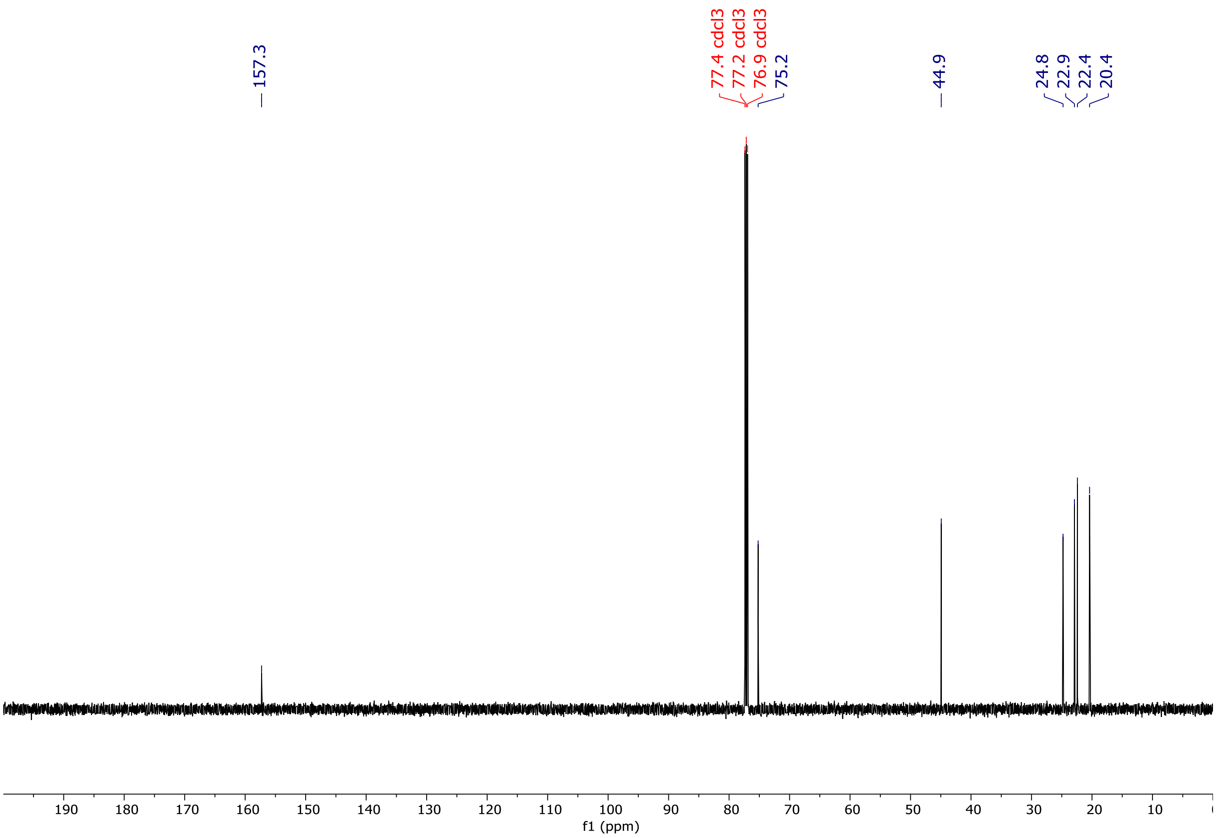
2-Methylhexan-3-yl azidoformate (7l)



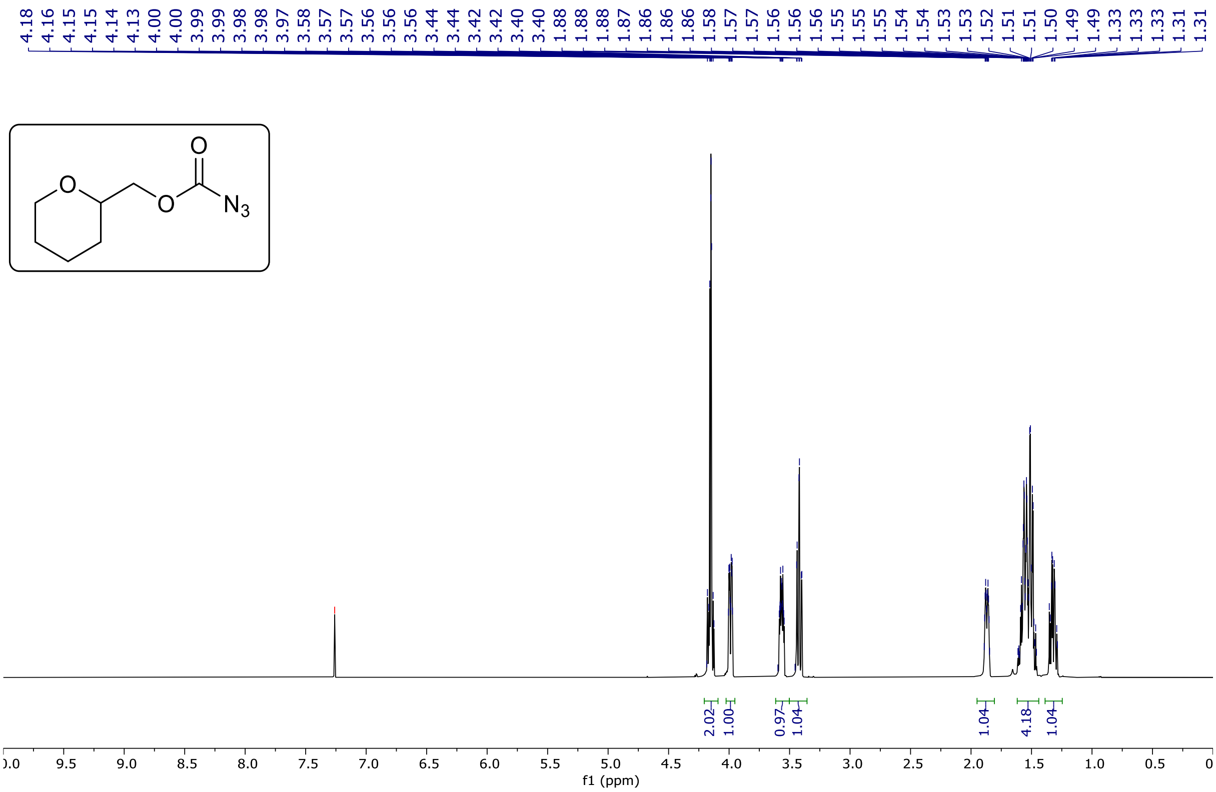


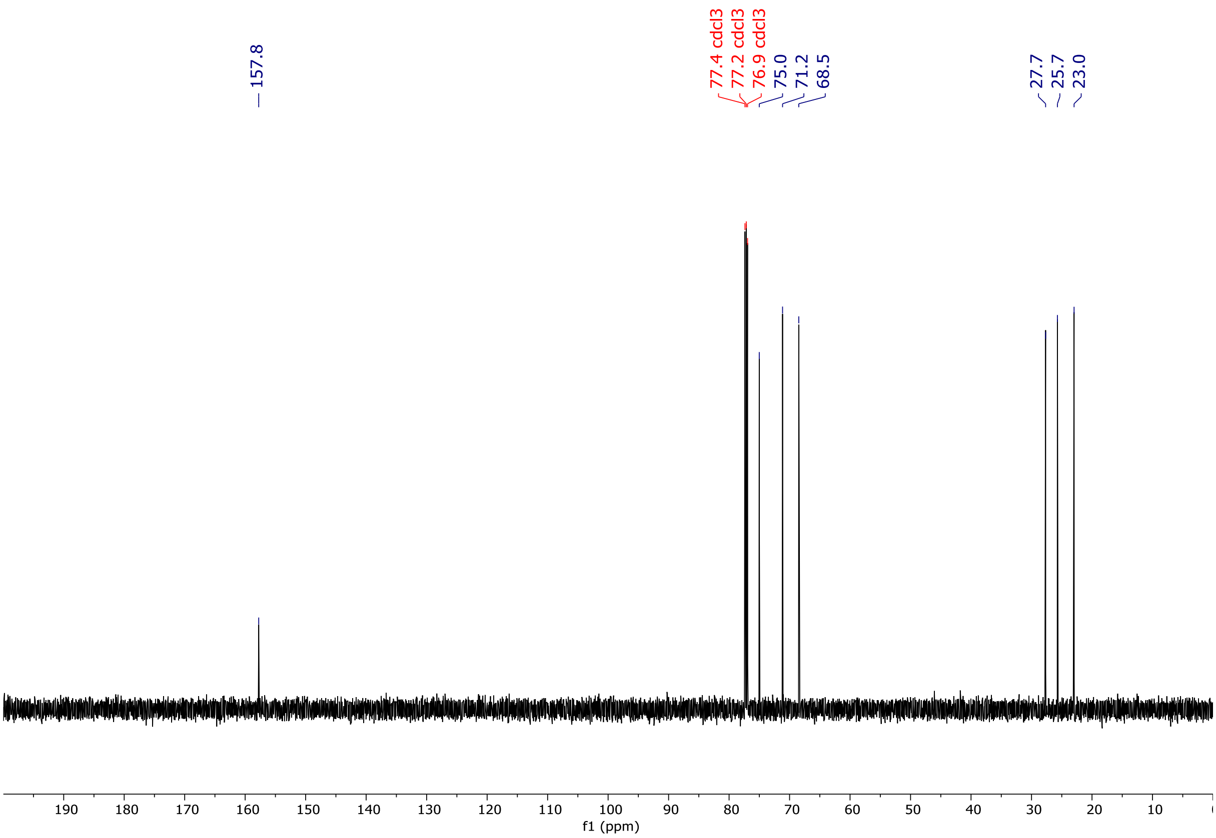
4-Methylpentan-2-yl azidoformate (7m)



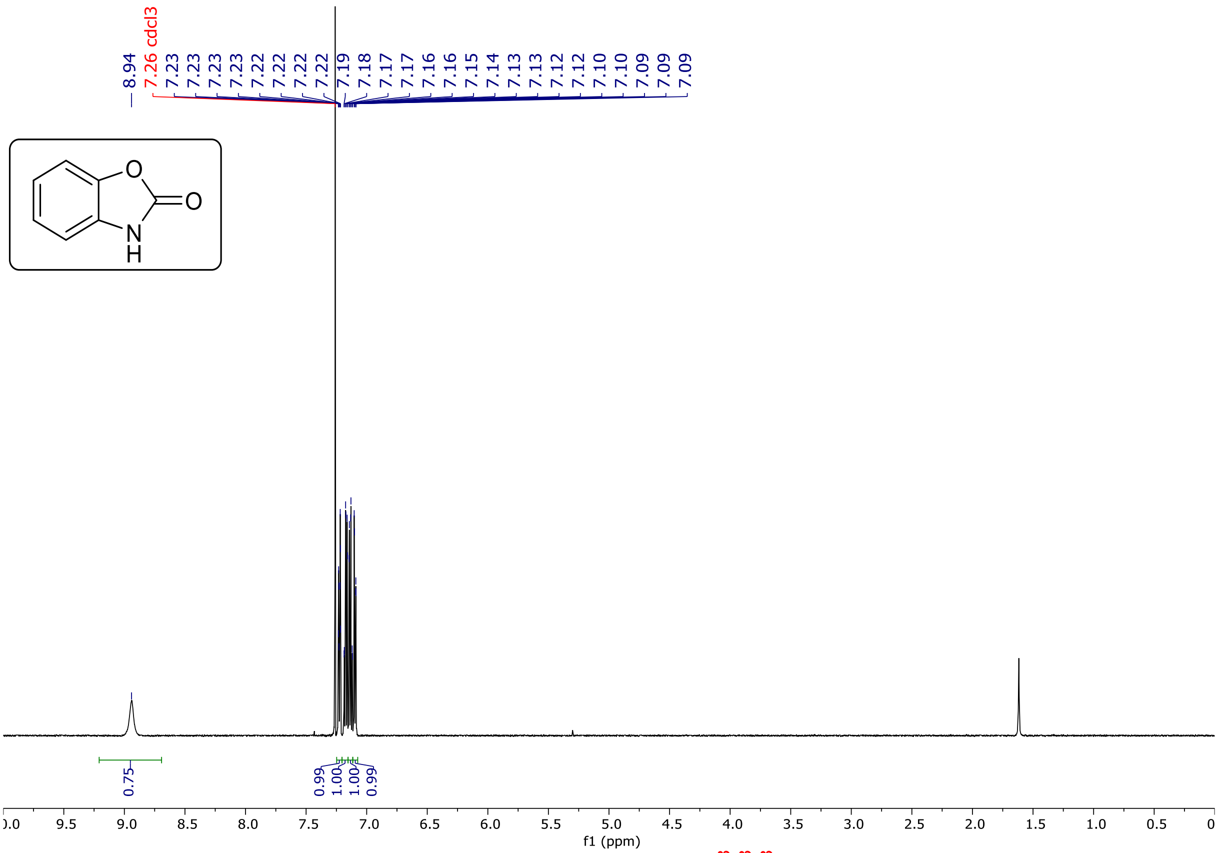


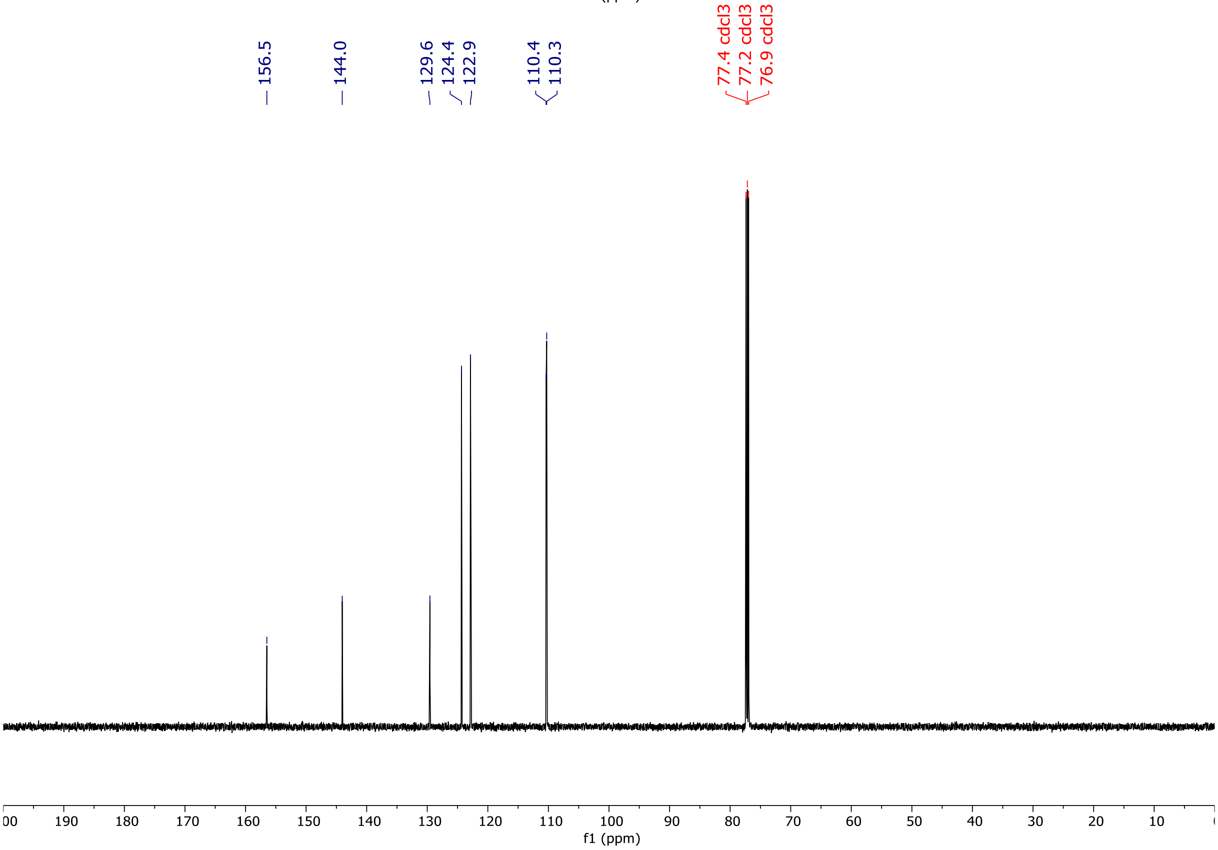
(Tetrahydro-2*H*-pyran-2-yl)methyl azidoformate (7n)



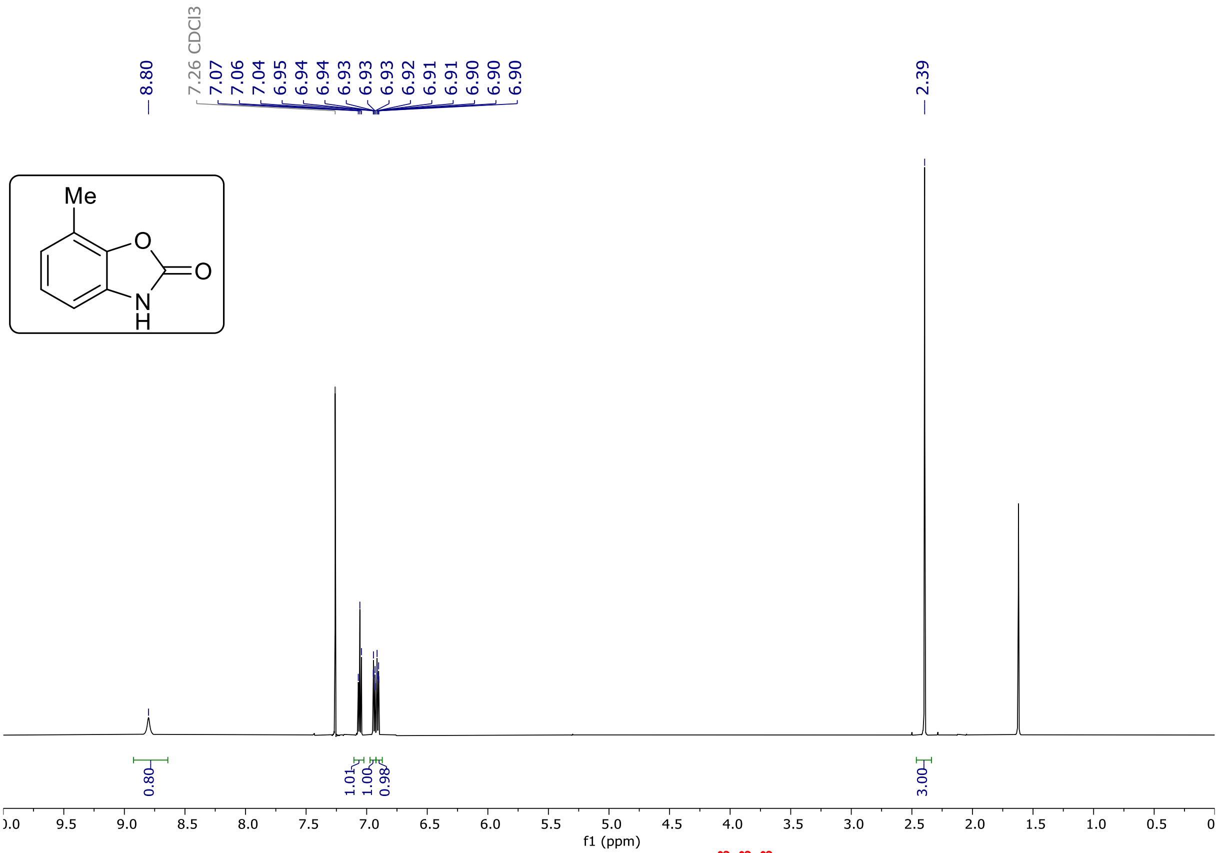


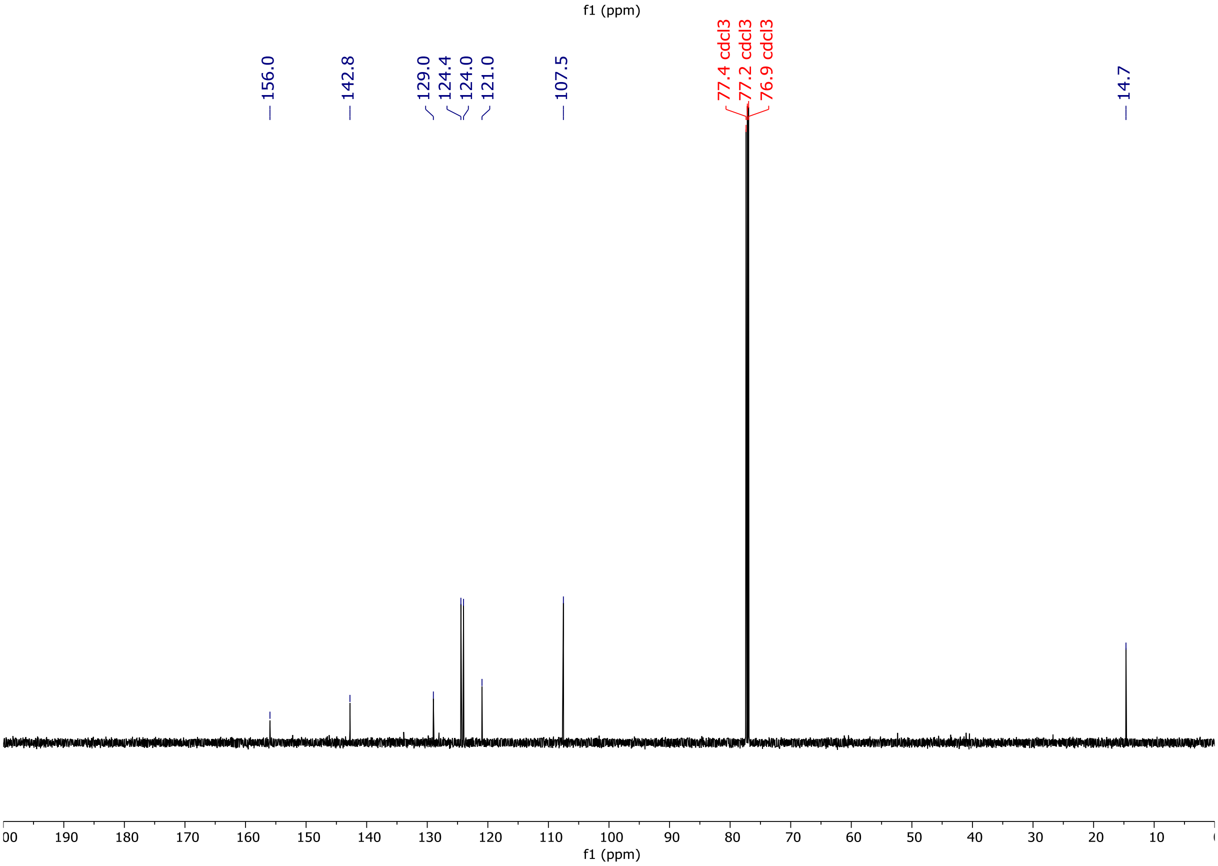
Benzo[*d*]oxazol-2(3*H*)-one (2a)



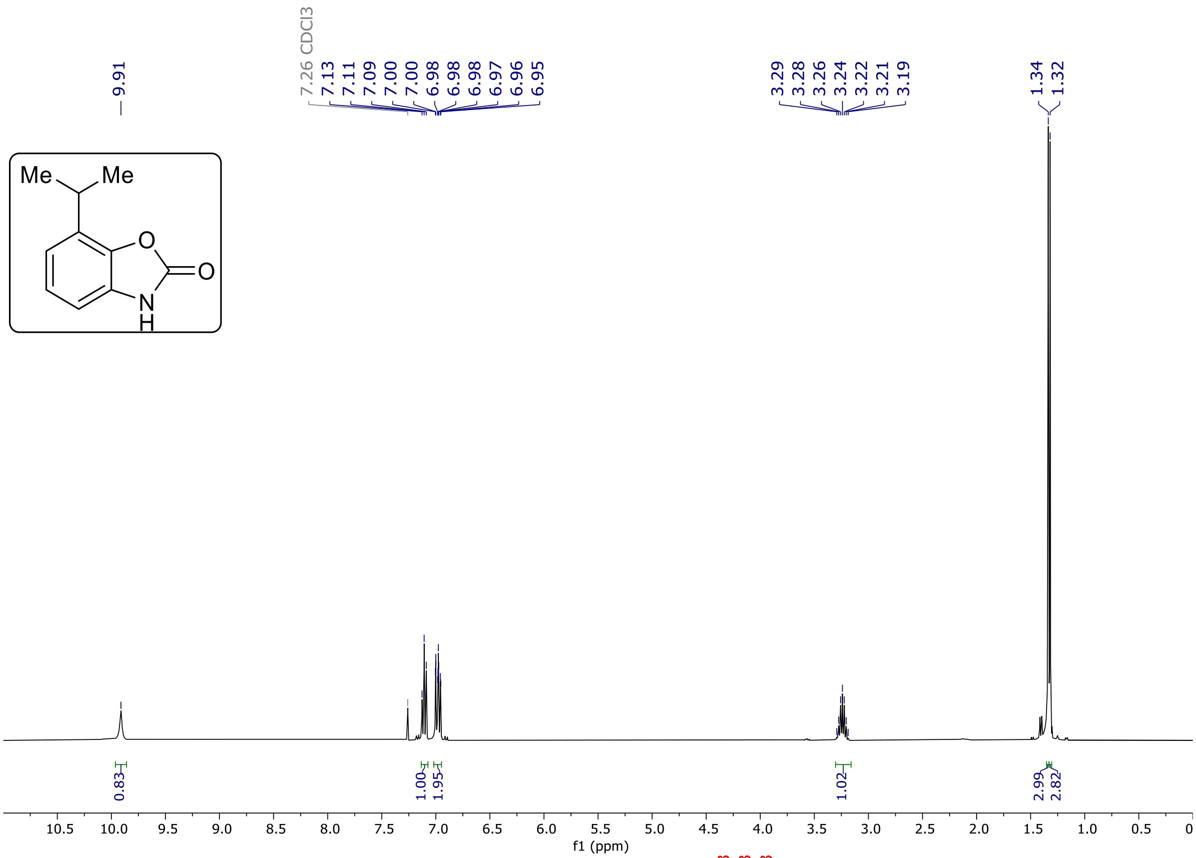


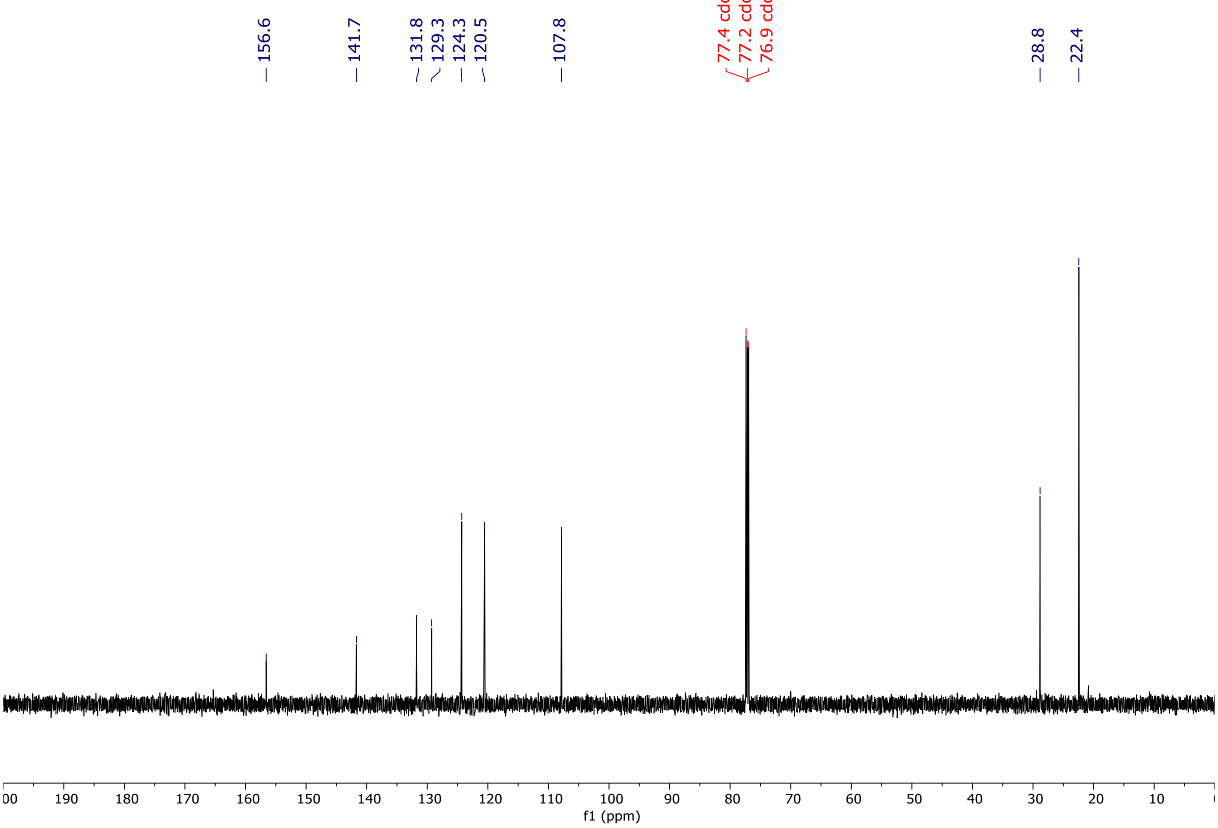
7-Methylbenzo[*d*]oxazol-2(3*H*)-one (2b)



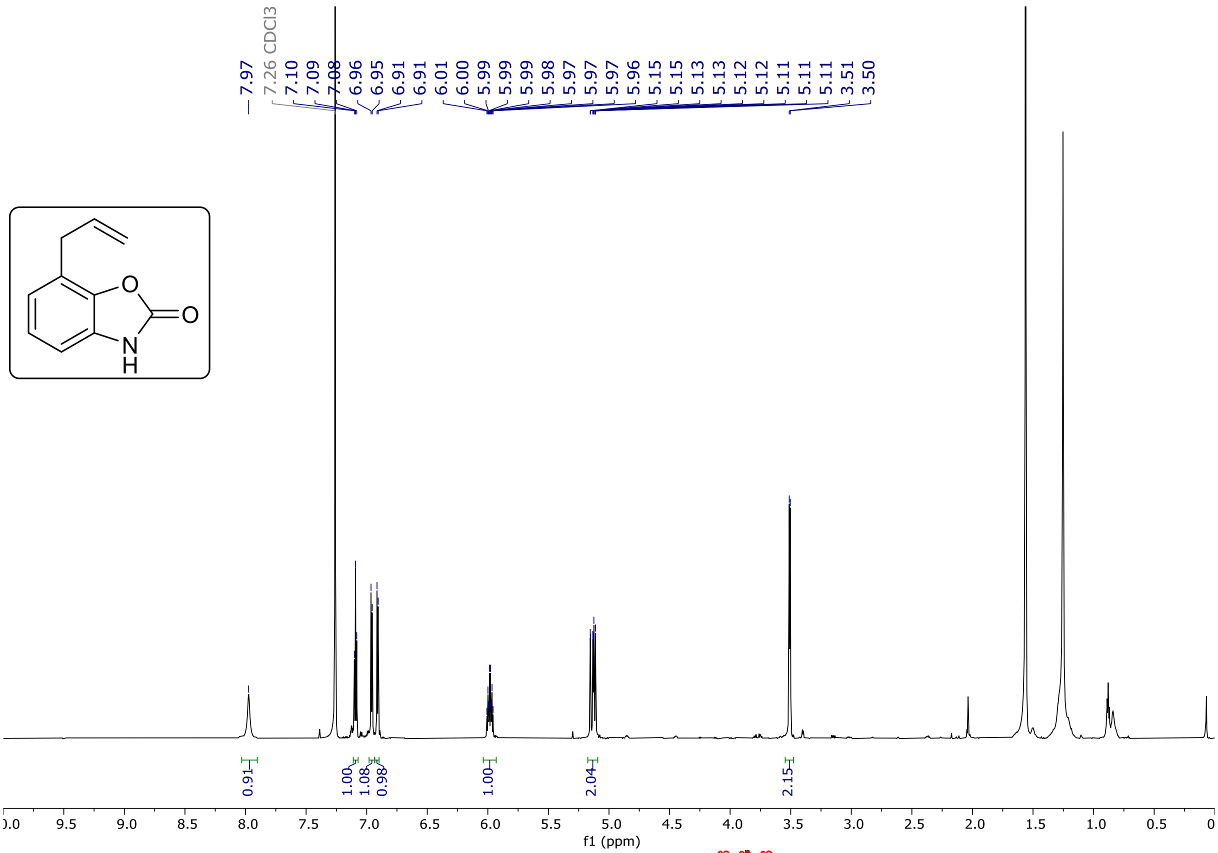


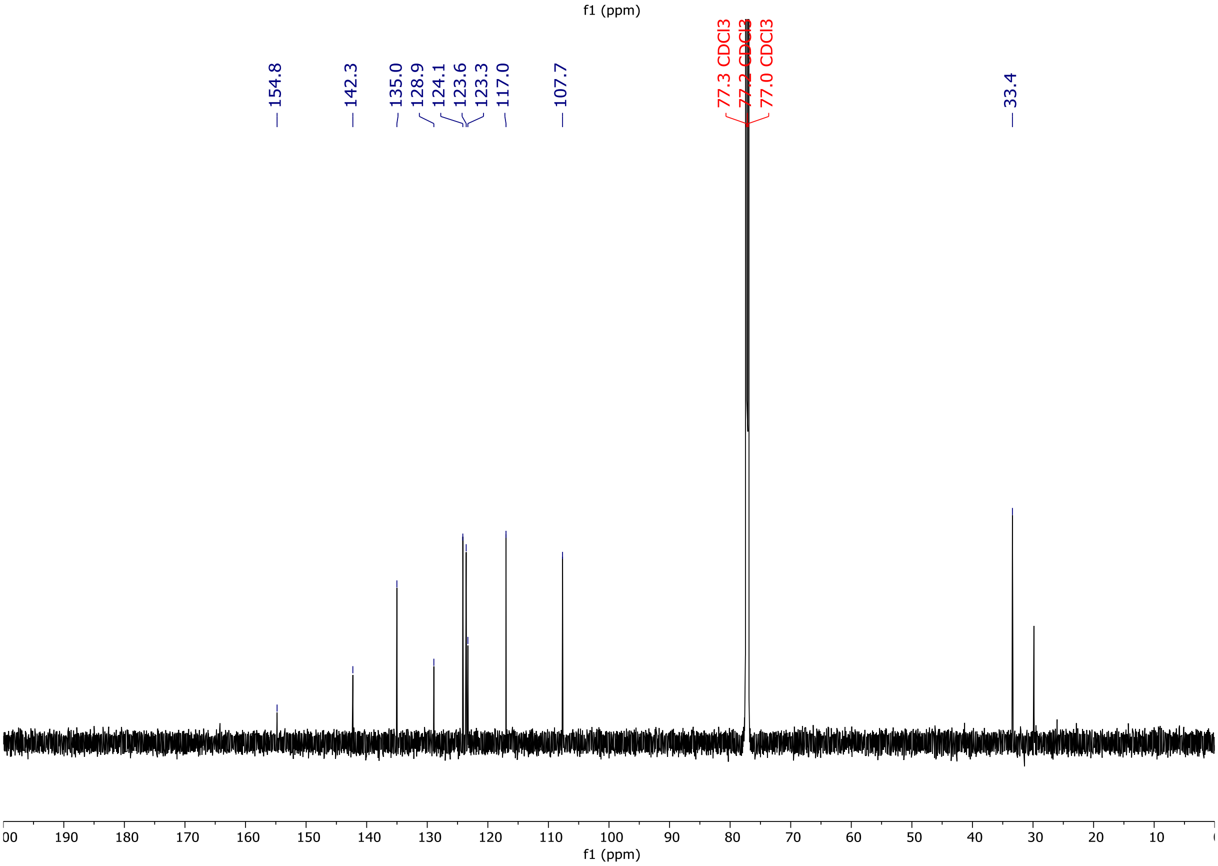
7-Isopropylbenzo[*d*]oxazol-2(3*H*)-one (2c)



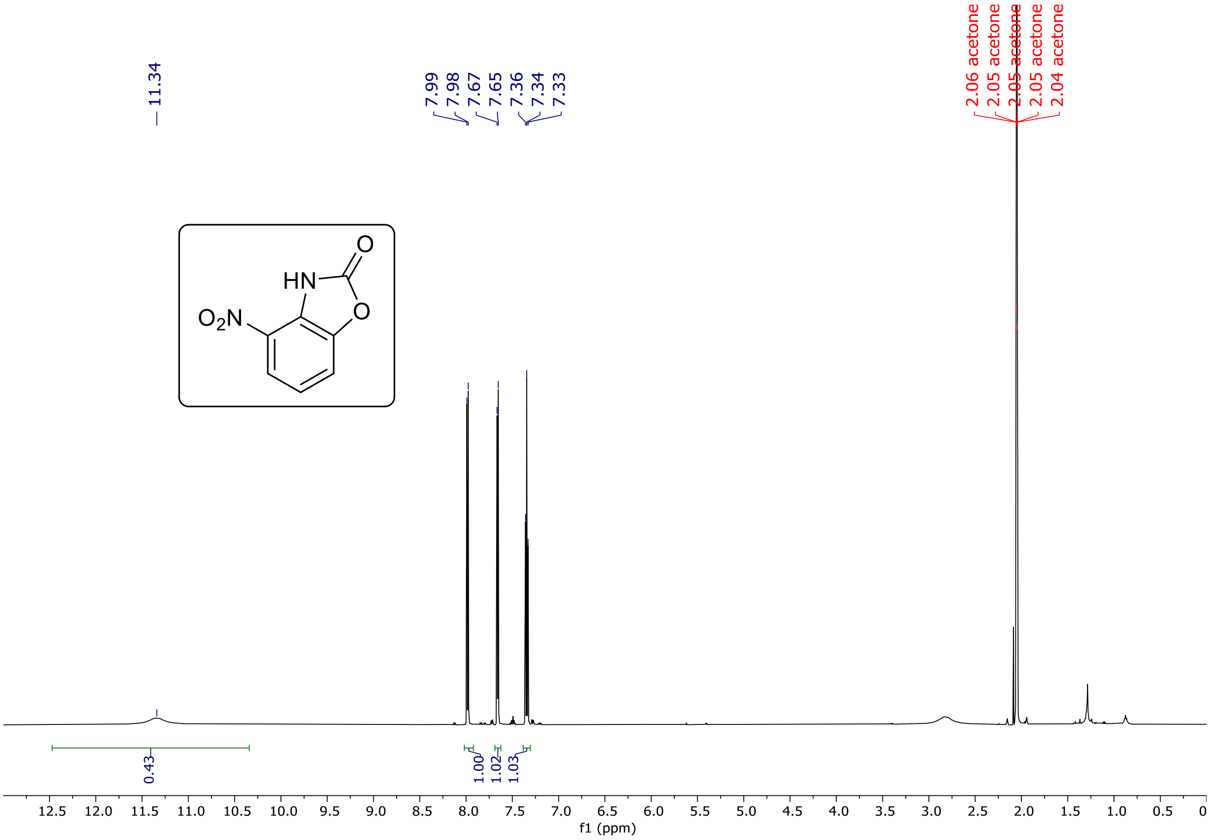


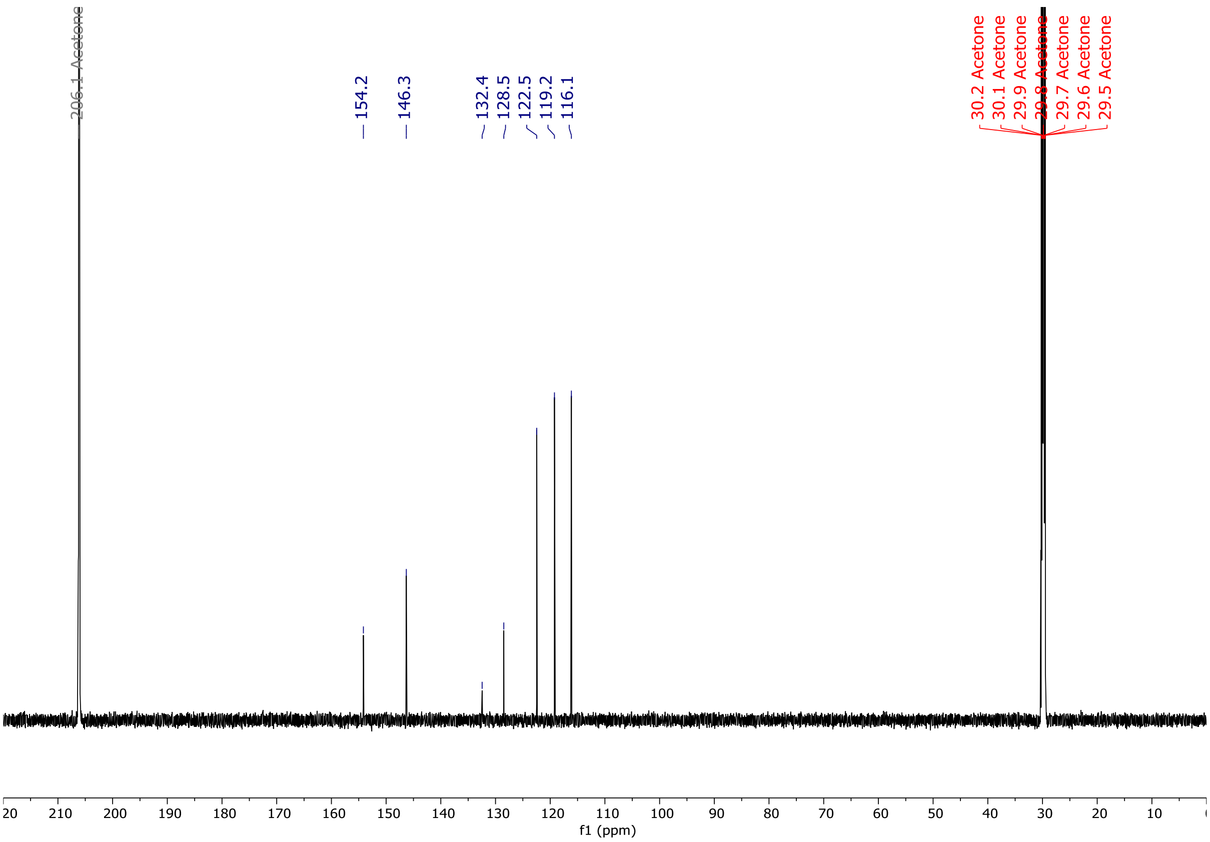
7-Allylbenzo[*d*]oxazol-2(3*H*)-one (2d)



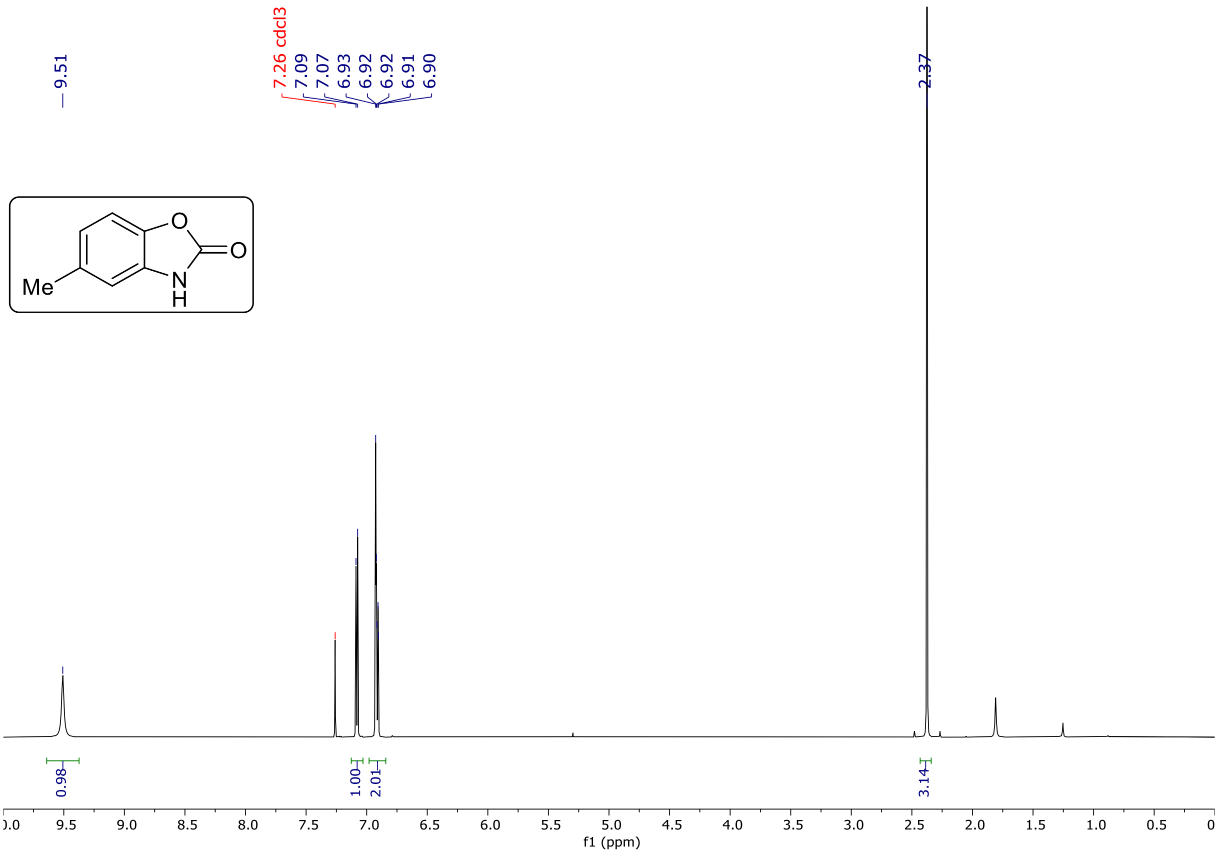


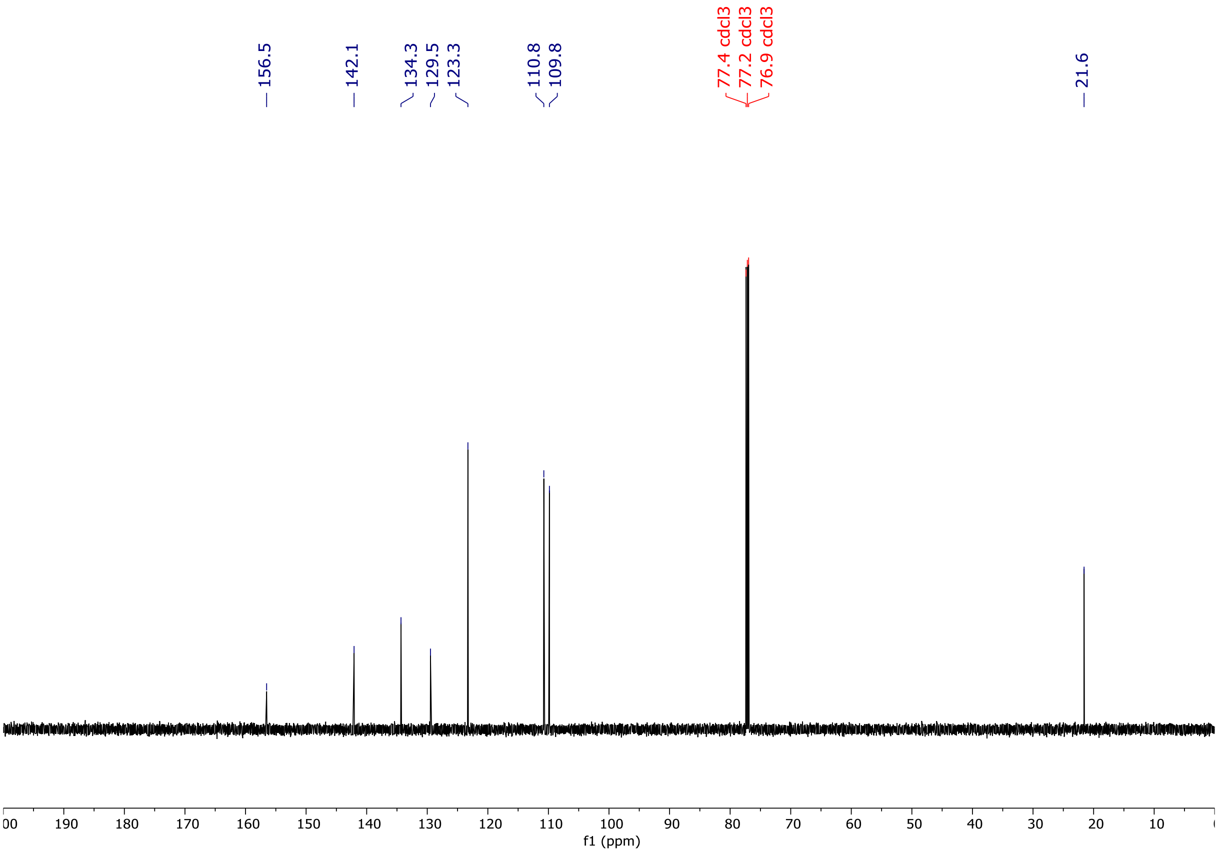
4-Nitrobenzo[*d*]oxazol-2(3*H*)-one (2e)



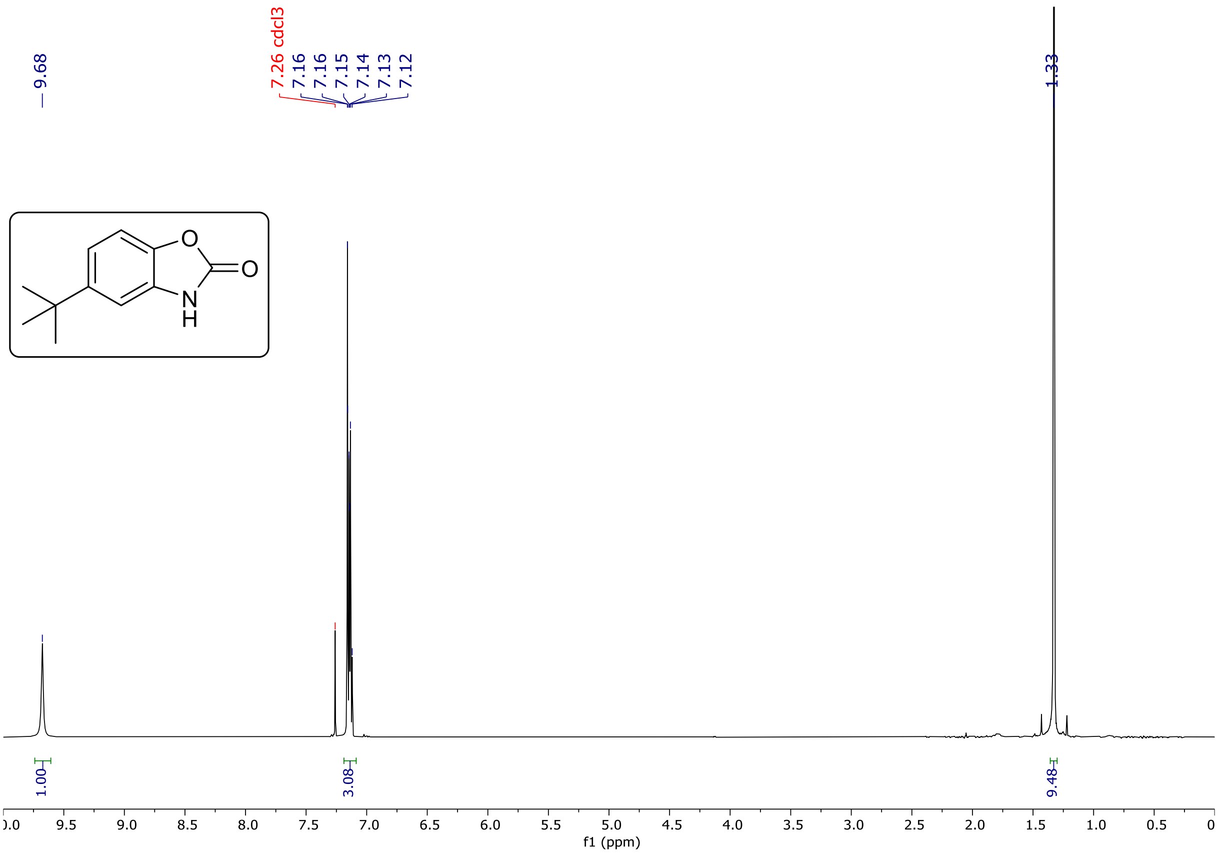


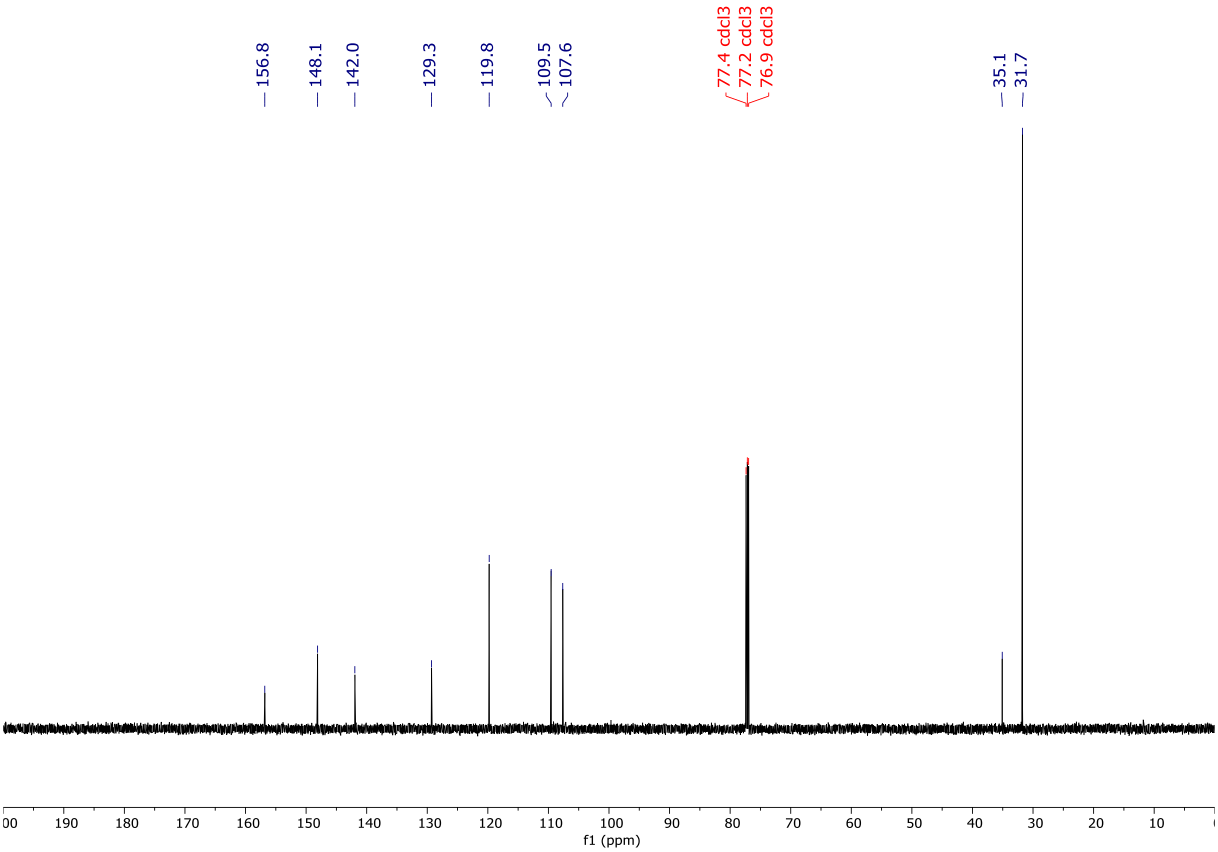
5-Methylbenzo[*d*]oxazol-2(3*H*)-one (2f)



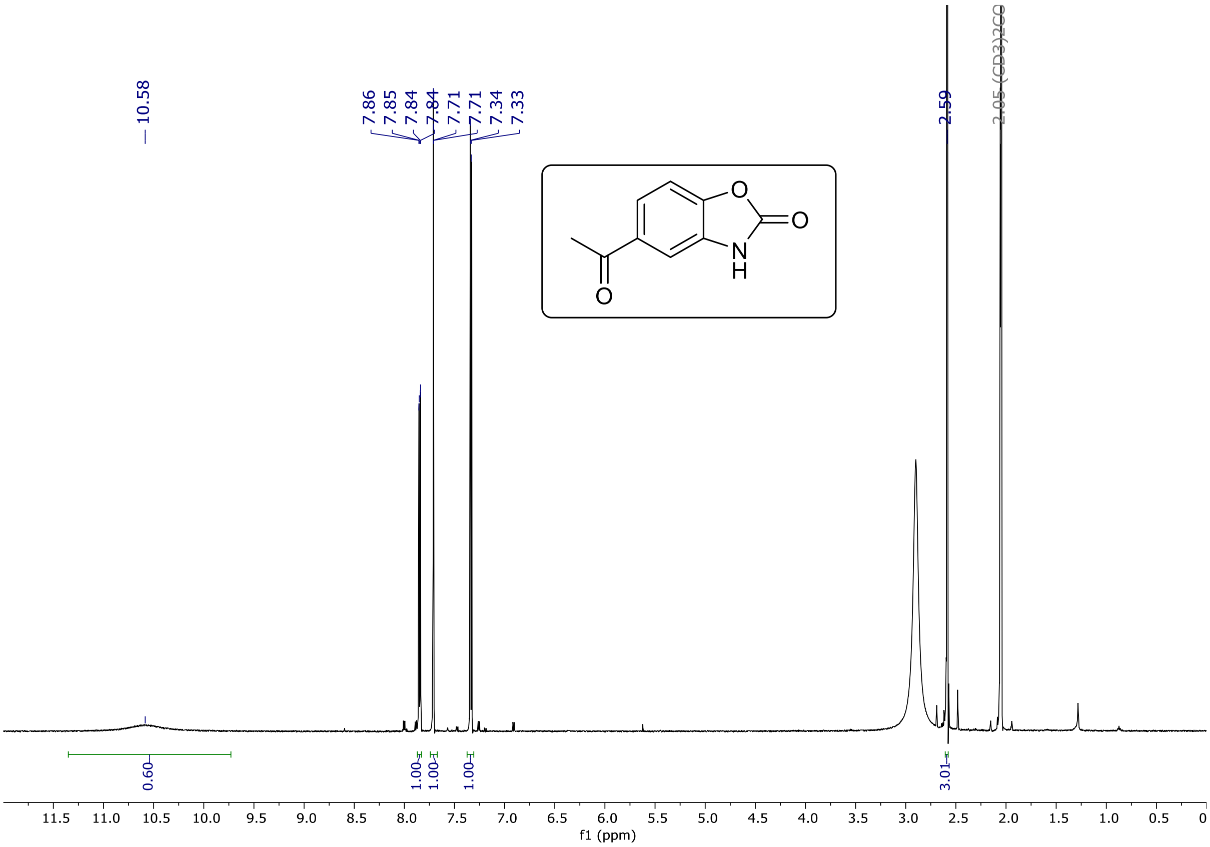


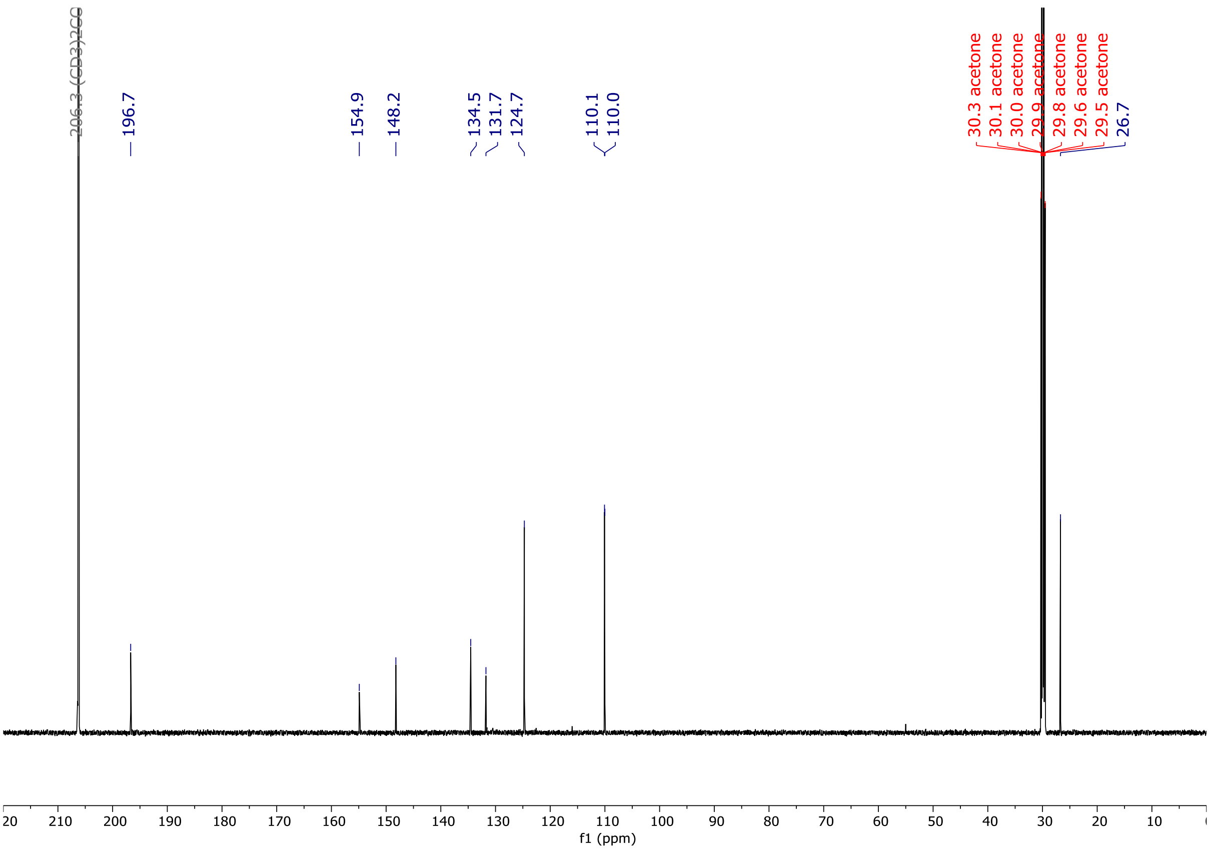
5-(*tert*-Butyl)benzo[*d*]oxazol-2(3*H*)-one (2g)



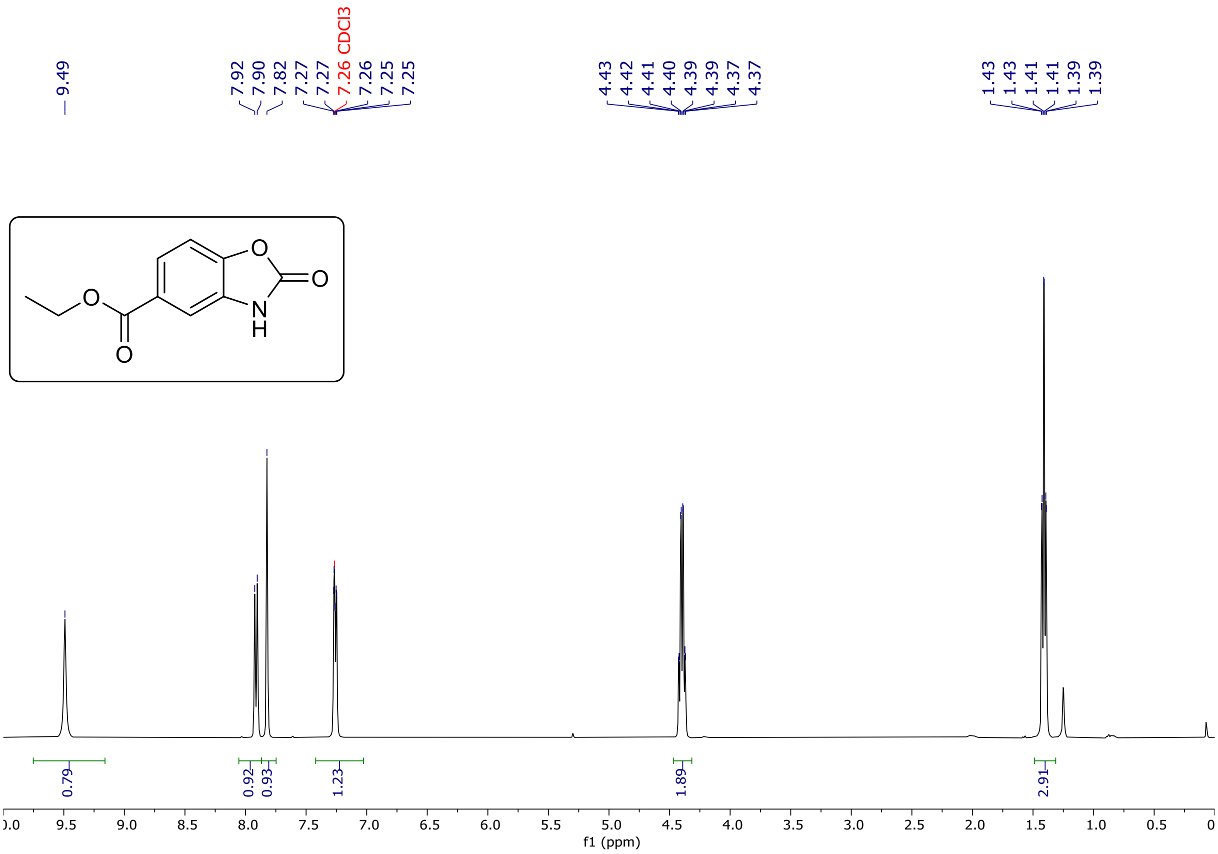


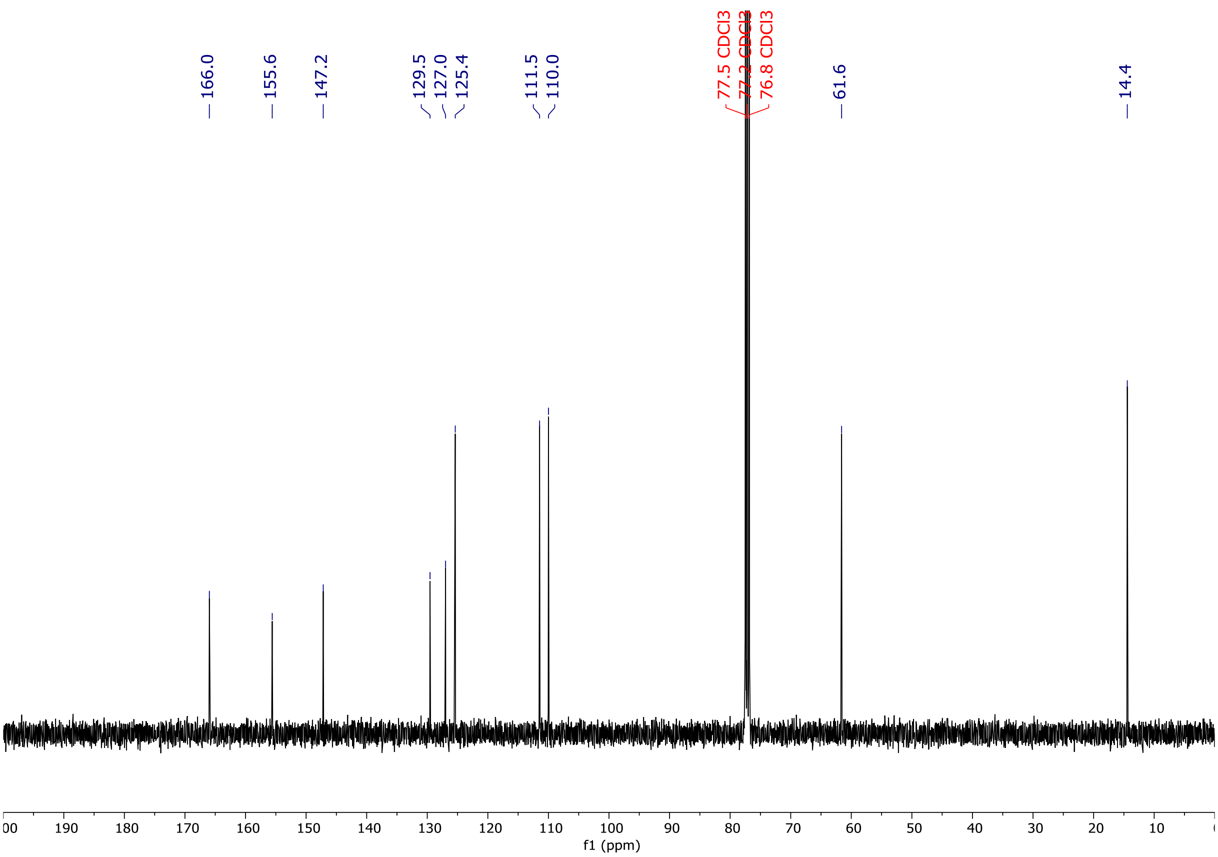
5-Acetylbenzo[*d*]oxazol-2(3*H*)-one (2h)



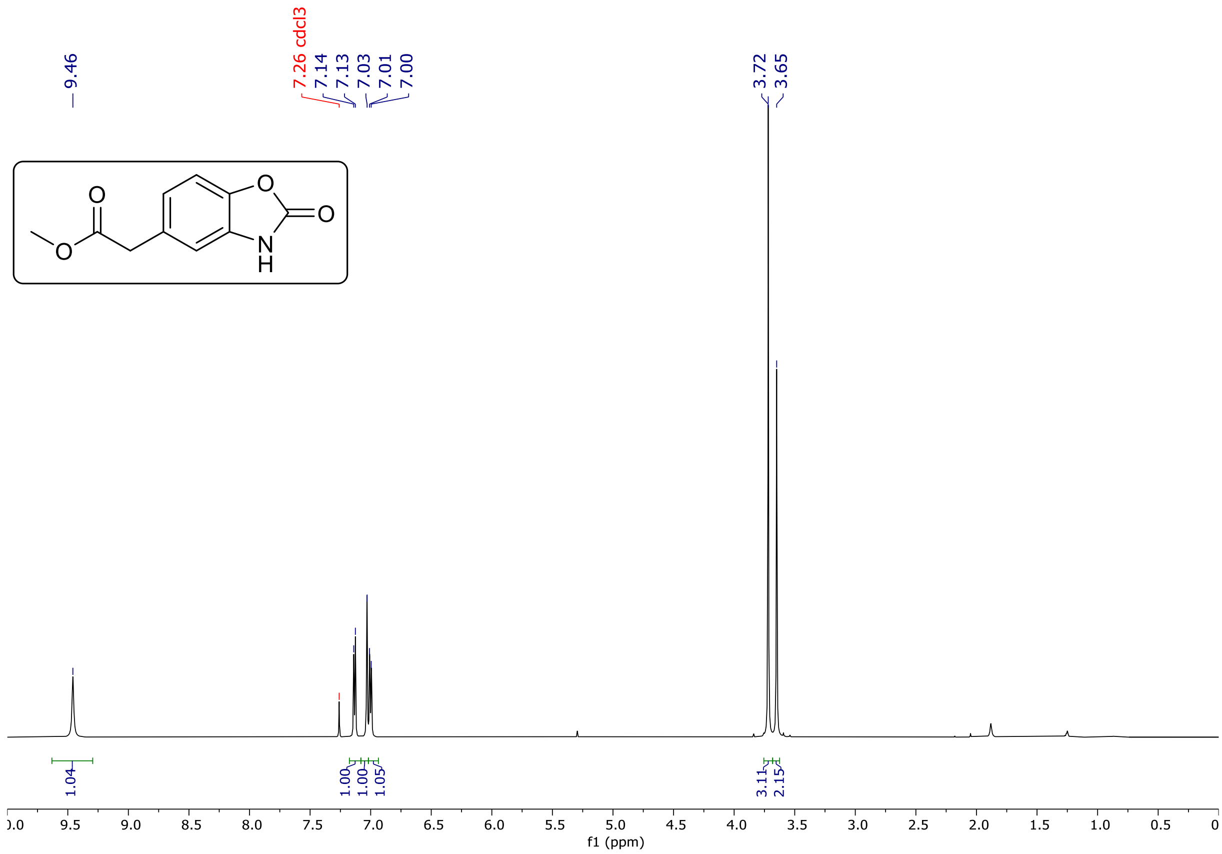


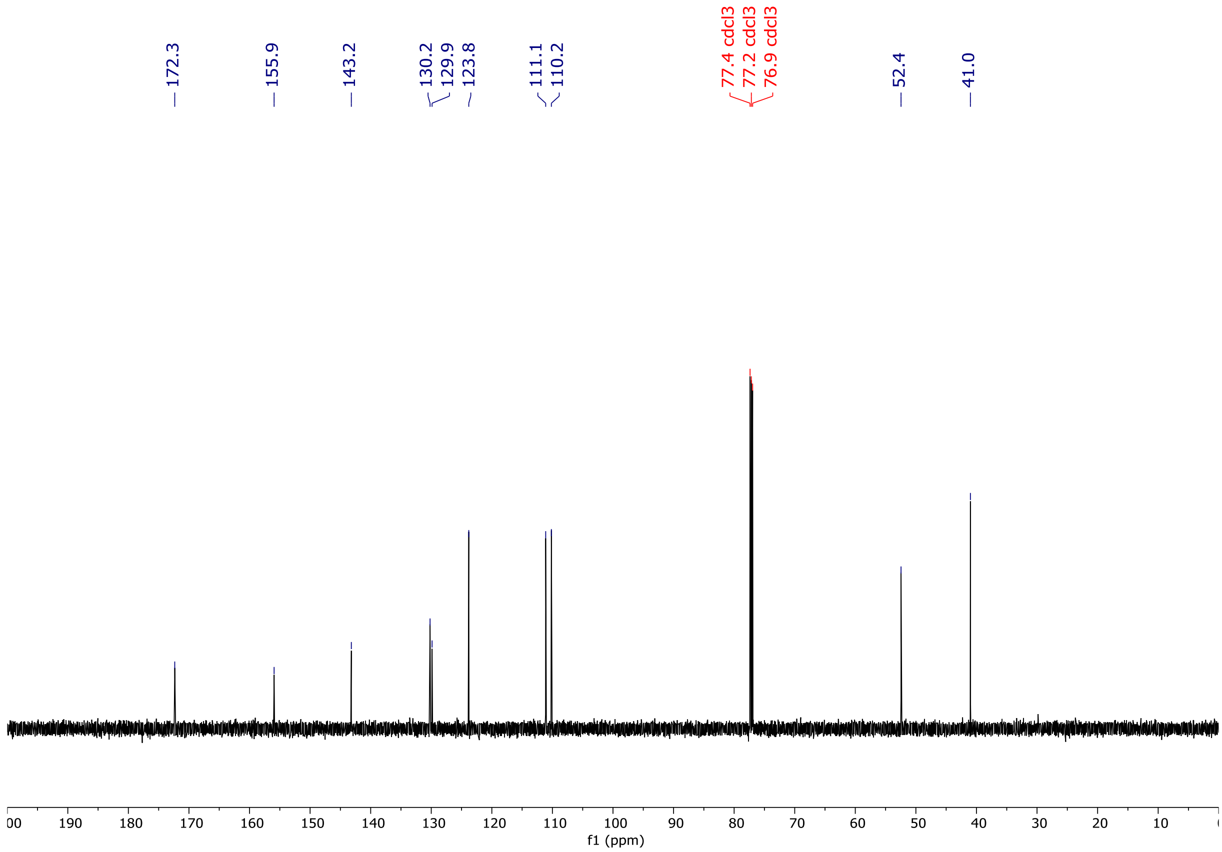
Ethyl 2-oxo-2,3-dihydrobenzo[*d*]oxazole-5-carboxylate (2i)



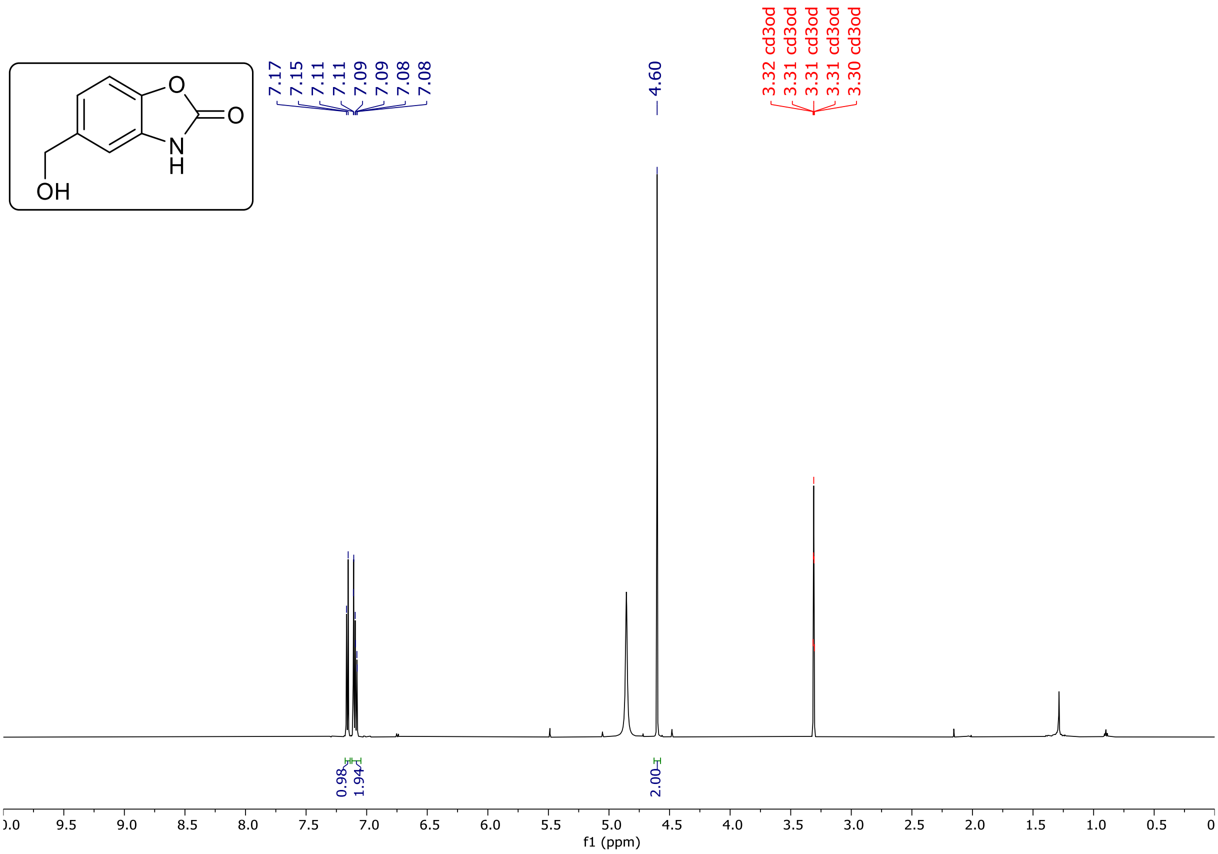


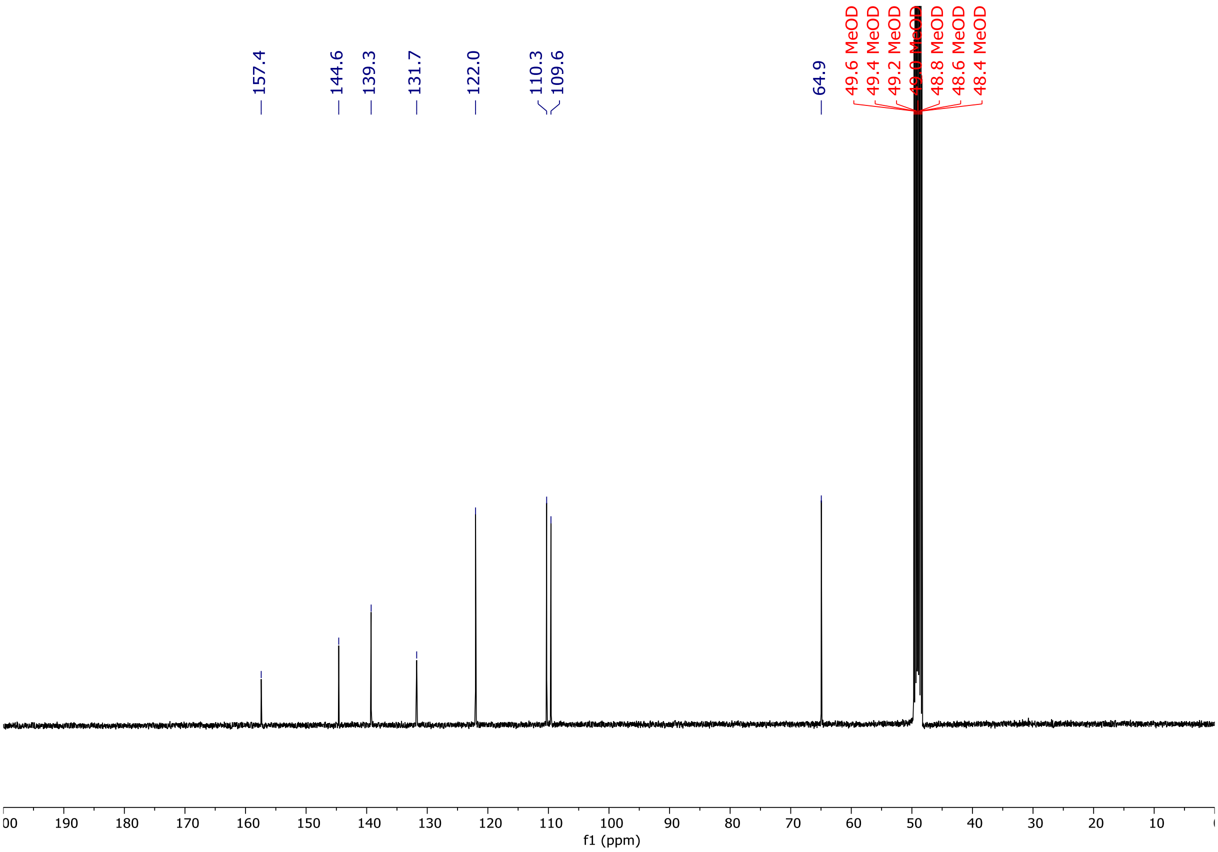
Methyl 2-(2-oxo-2,3-dihydrobenzo[*d*]oxazol-5-yl)acetate (2j)



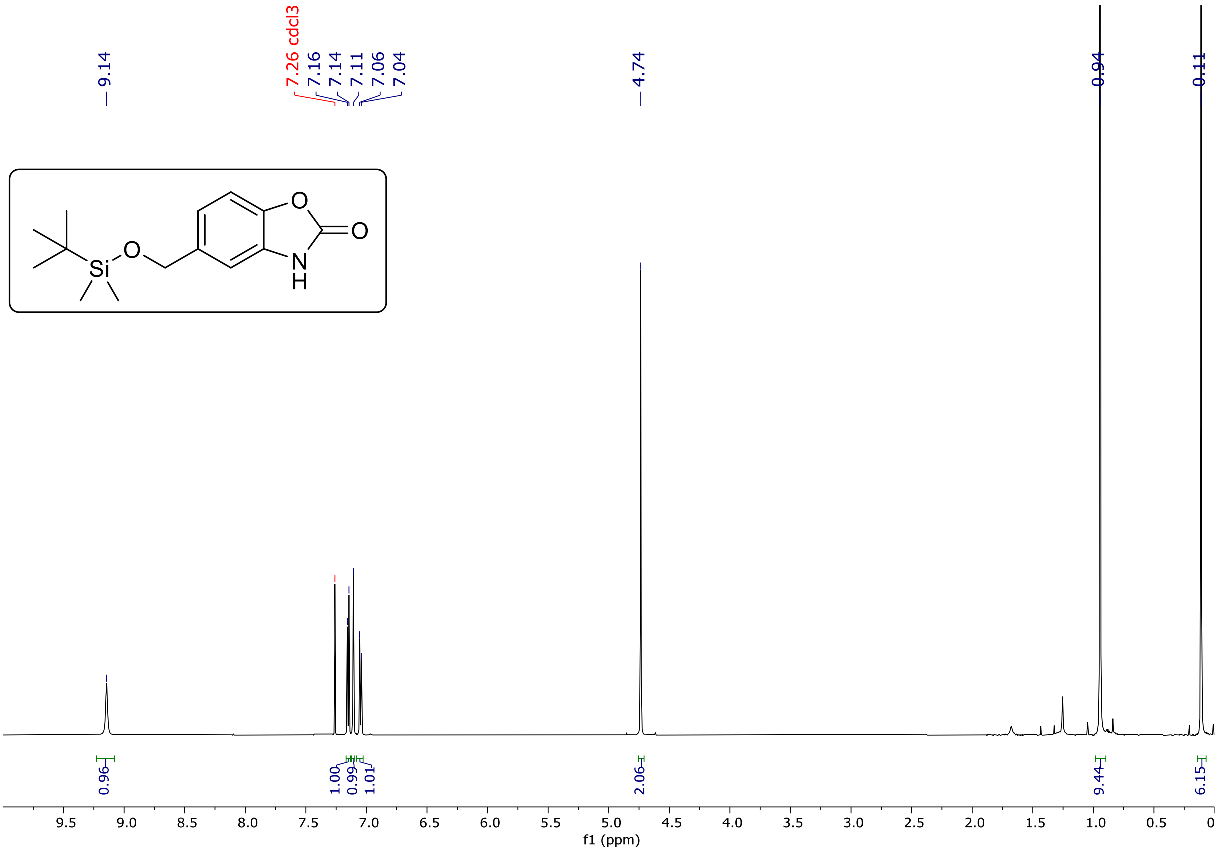


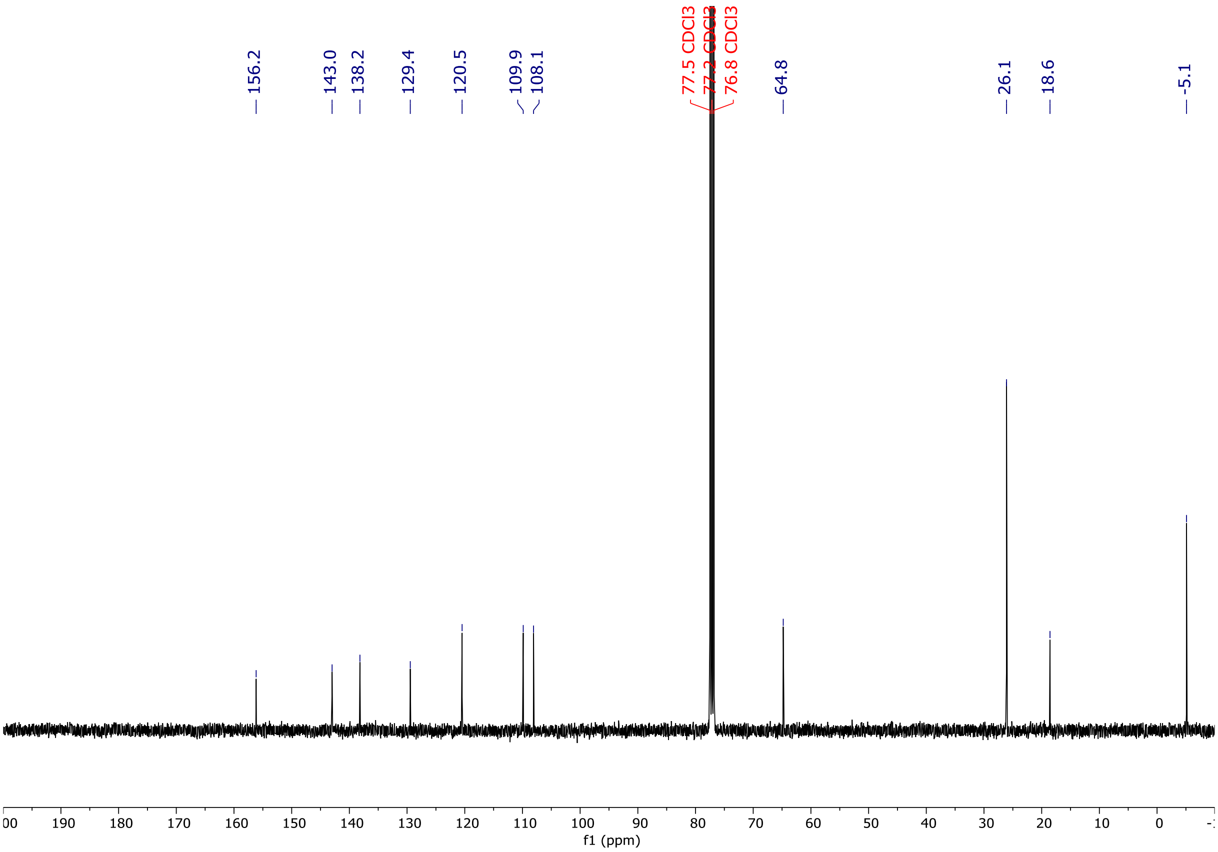
5-(Hydroxymethyl)benzo[*d*]oxazol-2(3*H*)-one (2k)



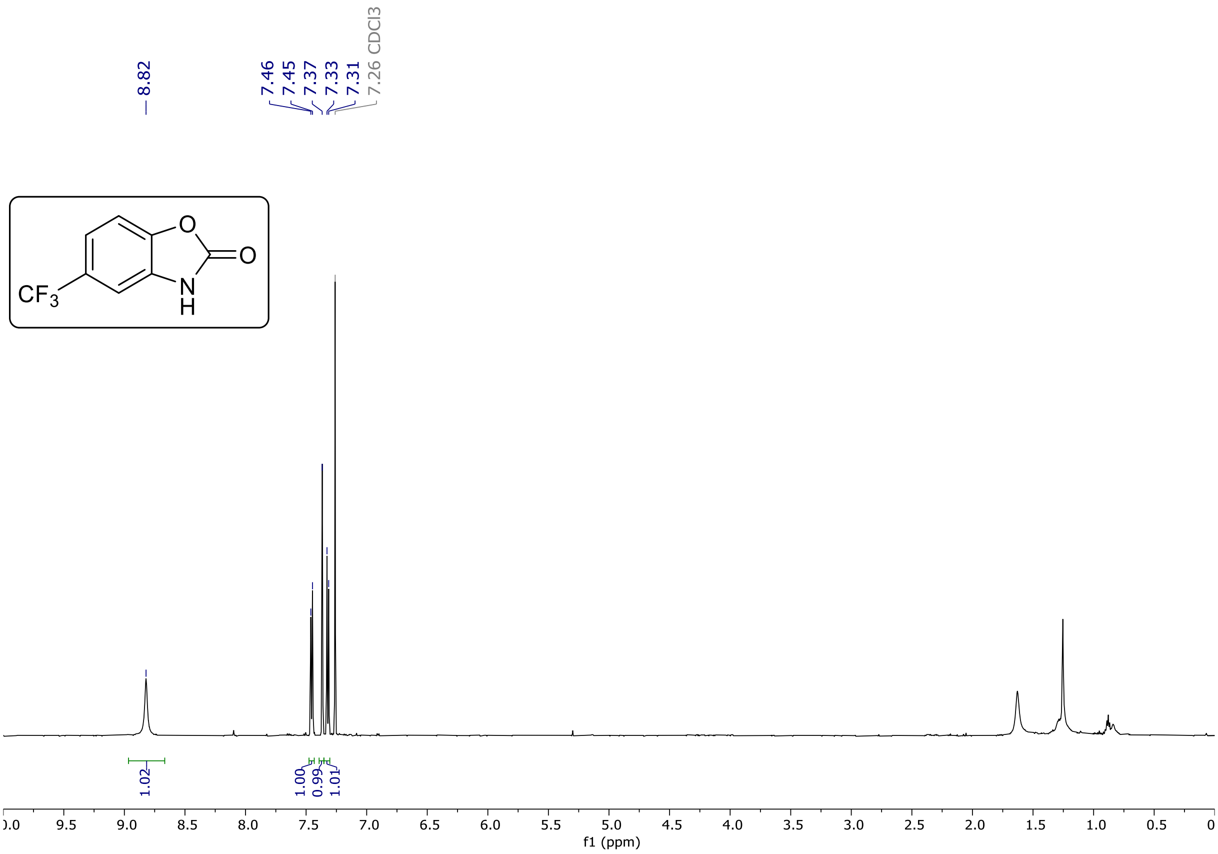


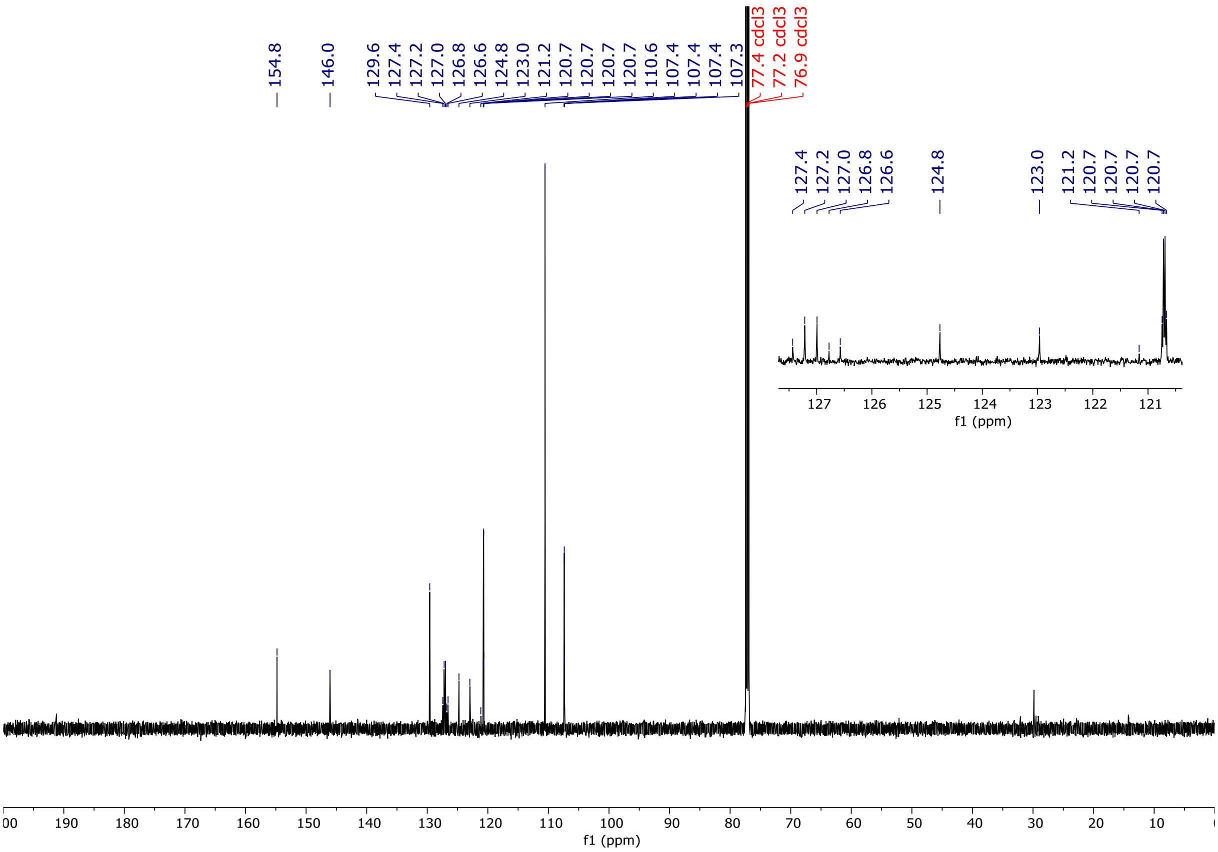
5-[{(*tert*-Butyldimethylsilyl)oxy}methyl]benzo[*d*]oxazol-2(3*H*)-one (2l)

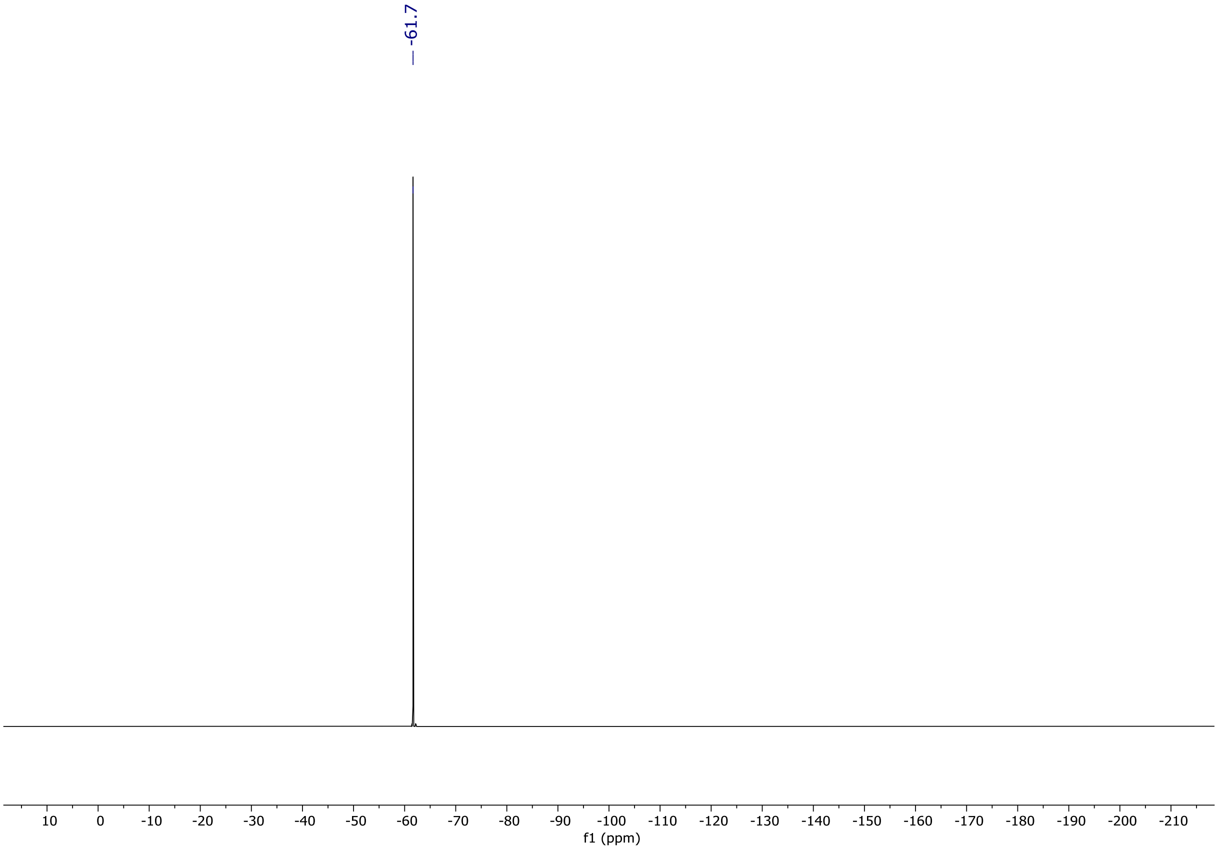




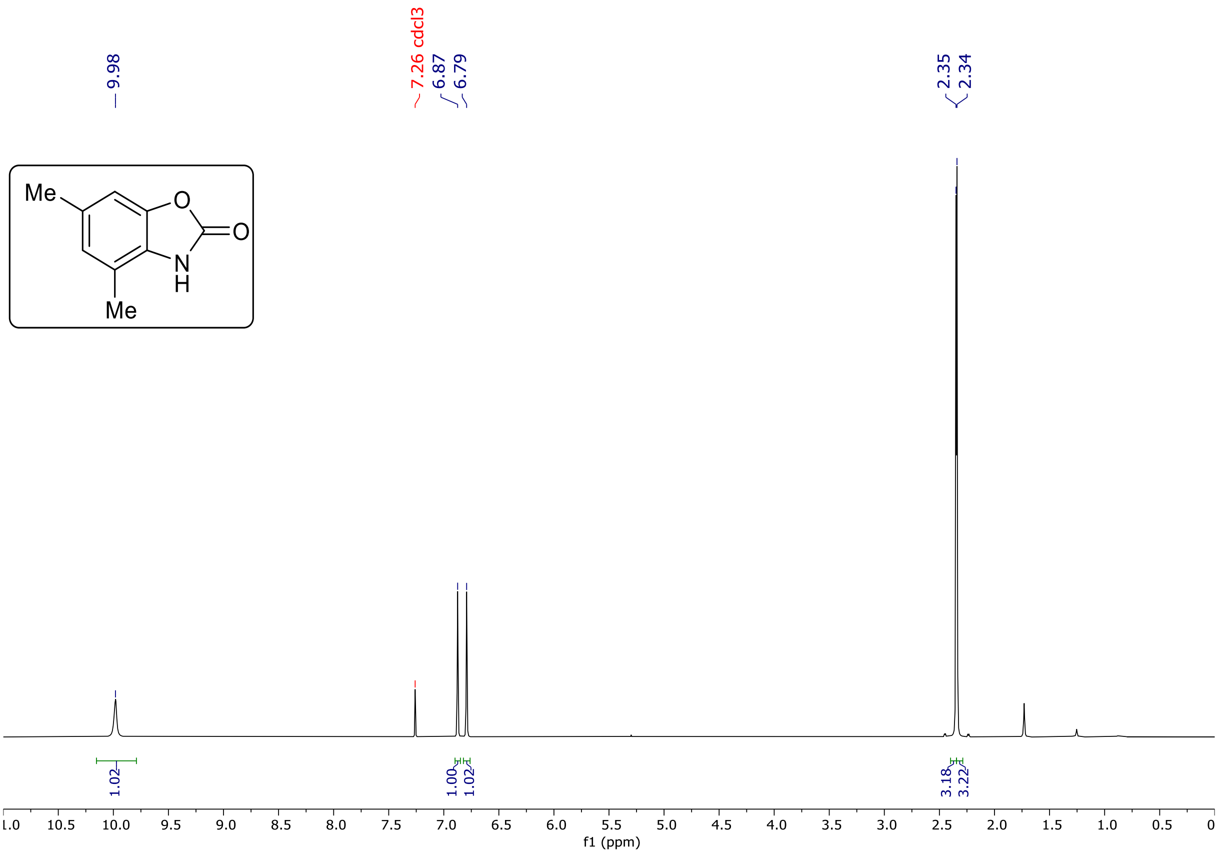
5-(Trifluoromethyl)benzo[*d*]oxazol-2(3*H*)-one (2m)

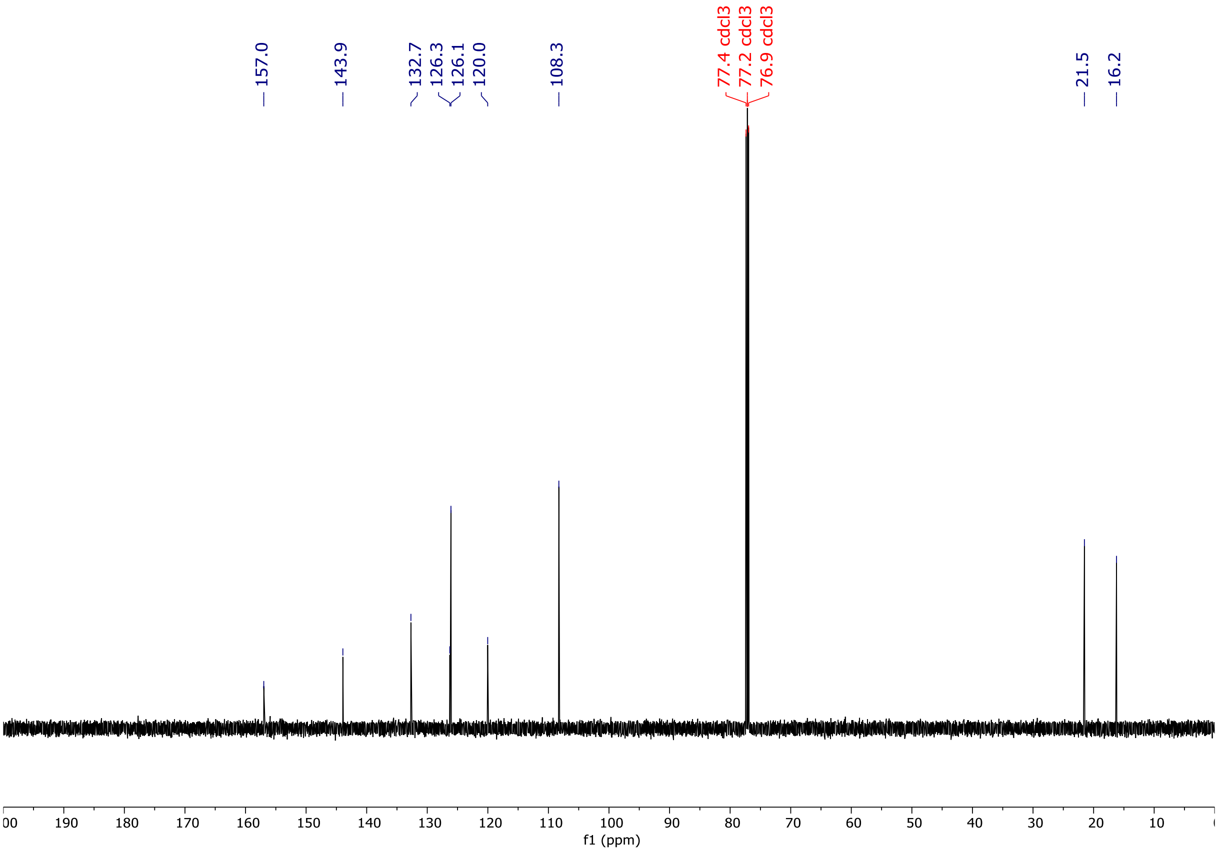




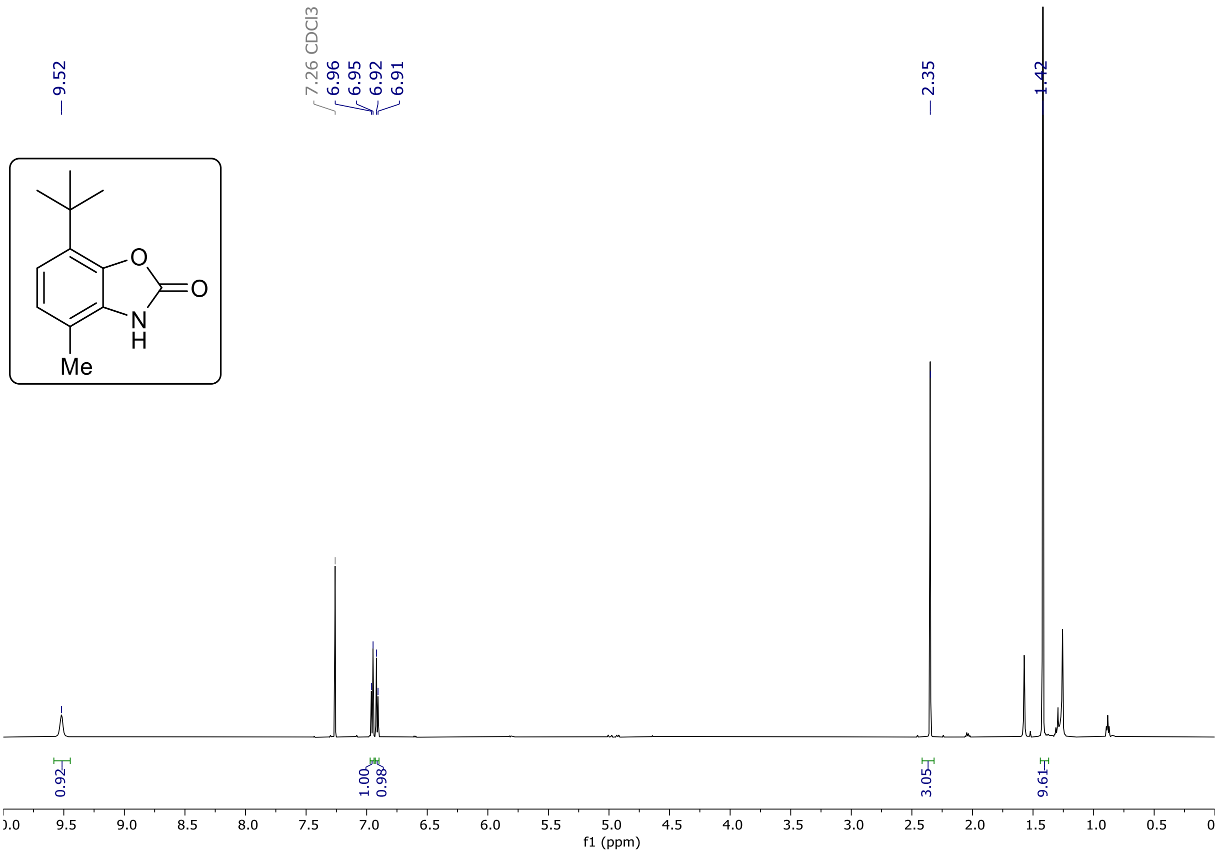

-61.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

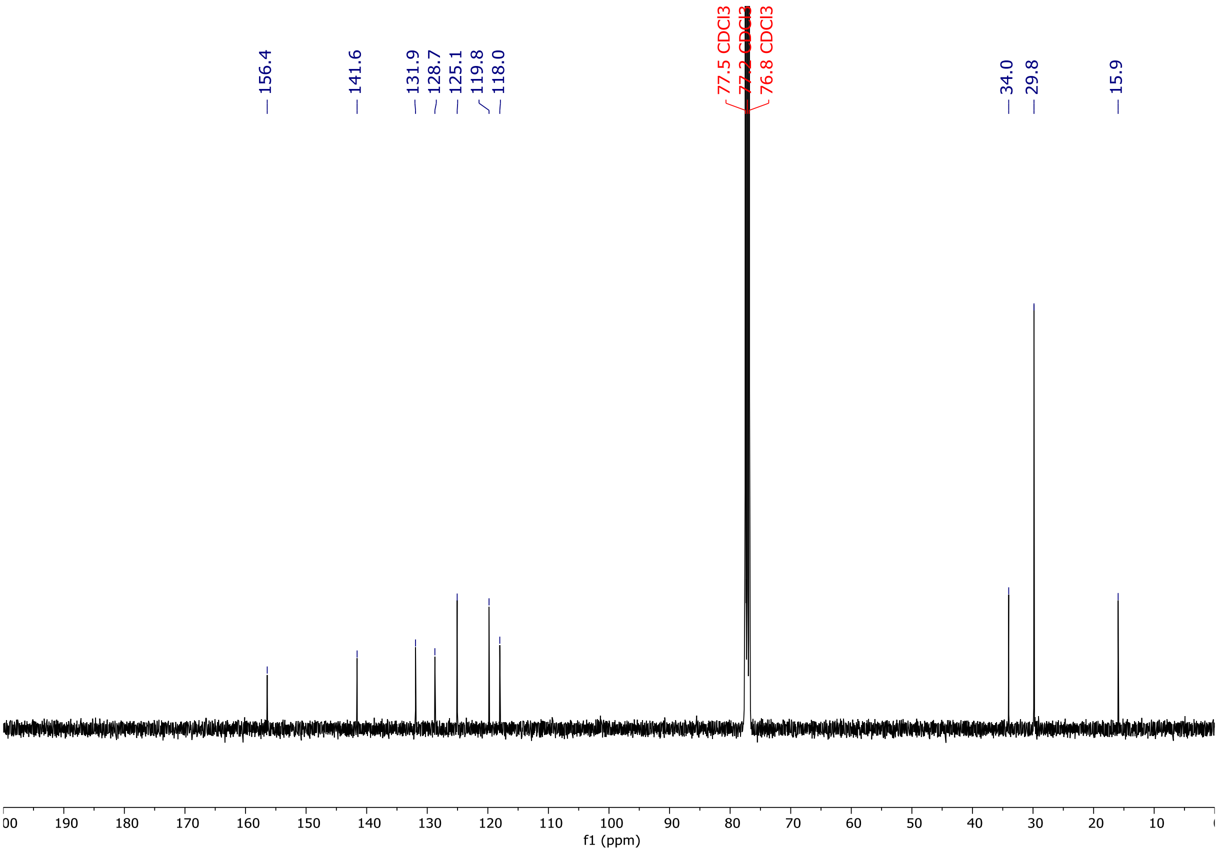
4,6-Dimethylbenzo[*d*]oxazol-2(3*H*)-one (2n)



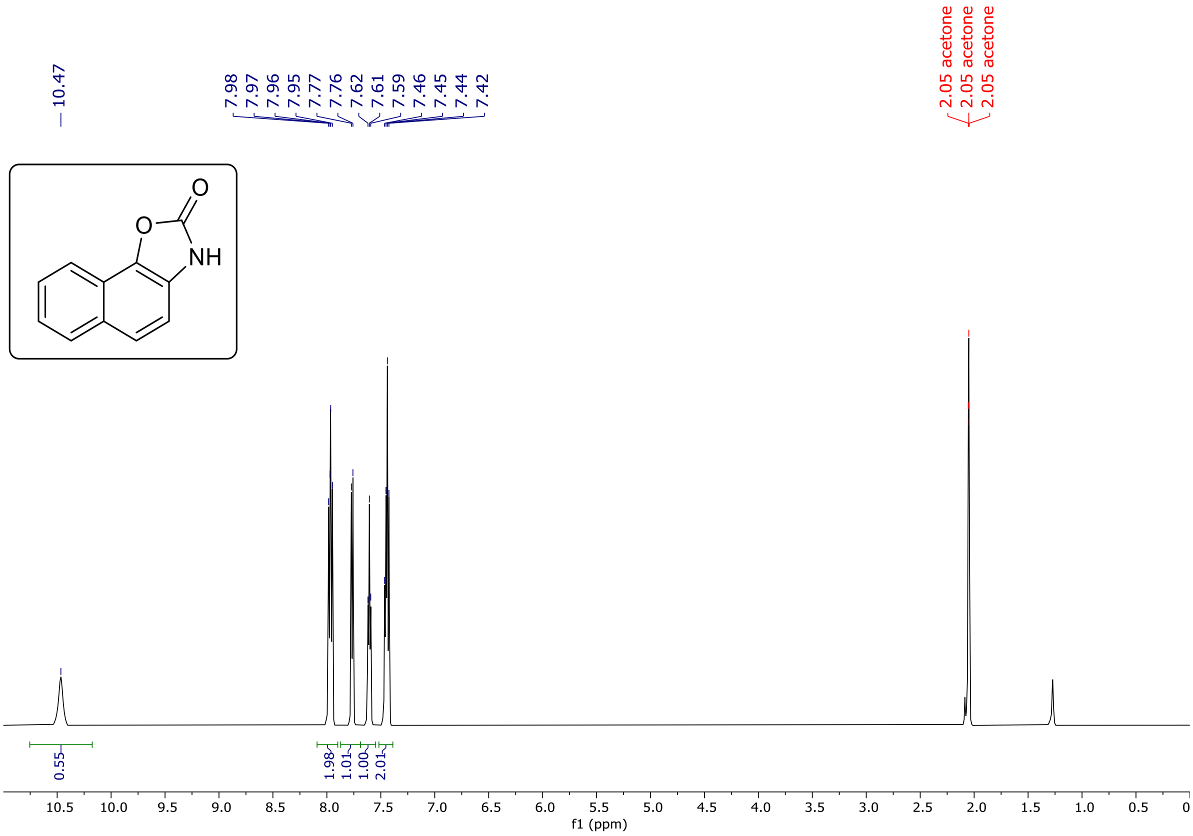


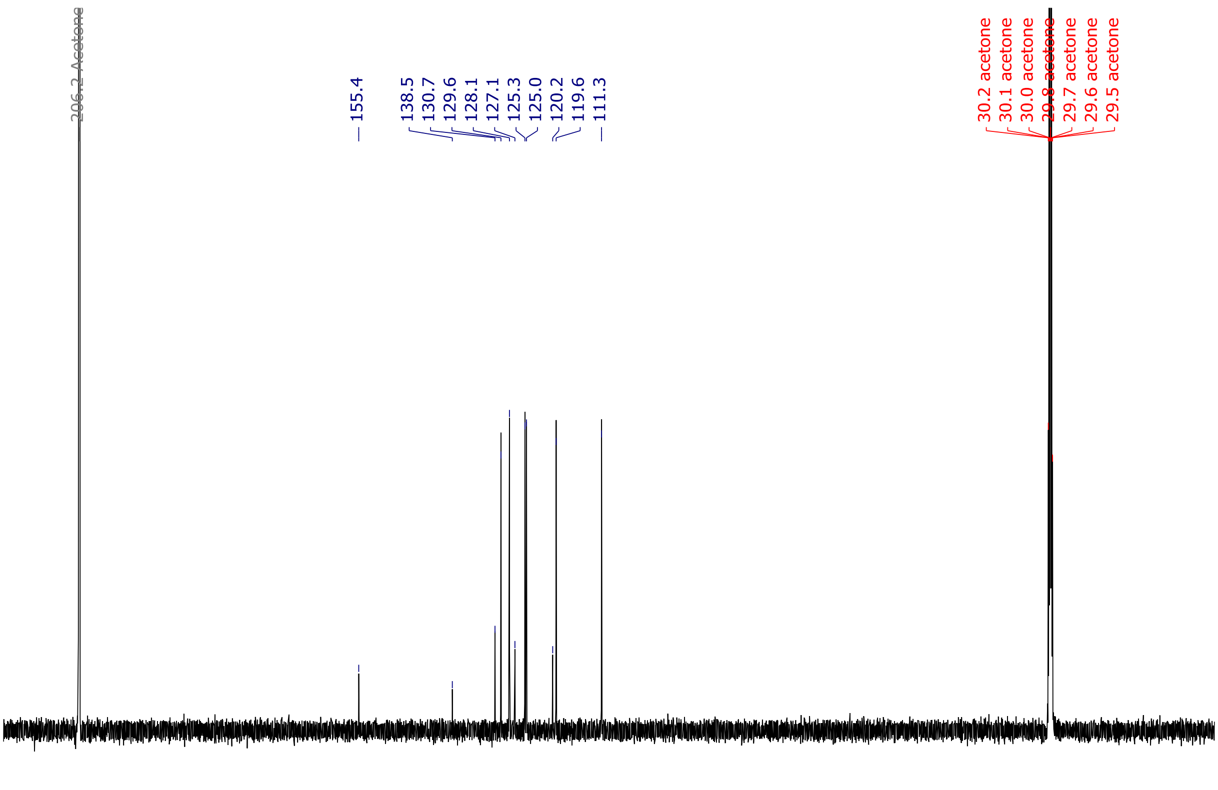
7-(*tert*-Butyl)-4-methylbenzo[*d*]oxazol-2(3*H*)-one (2o)



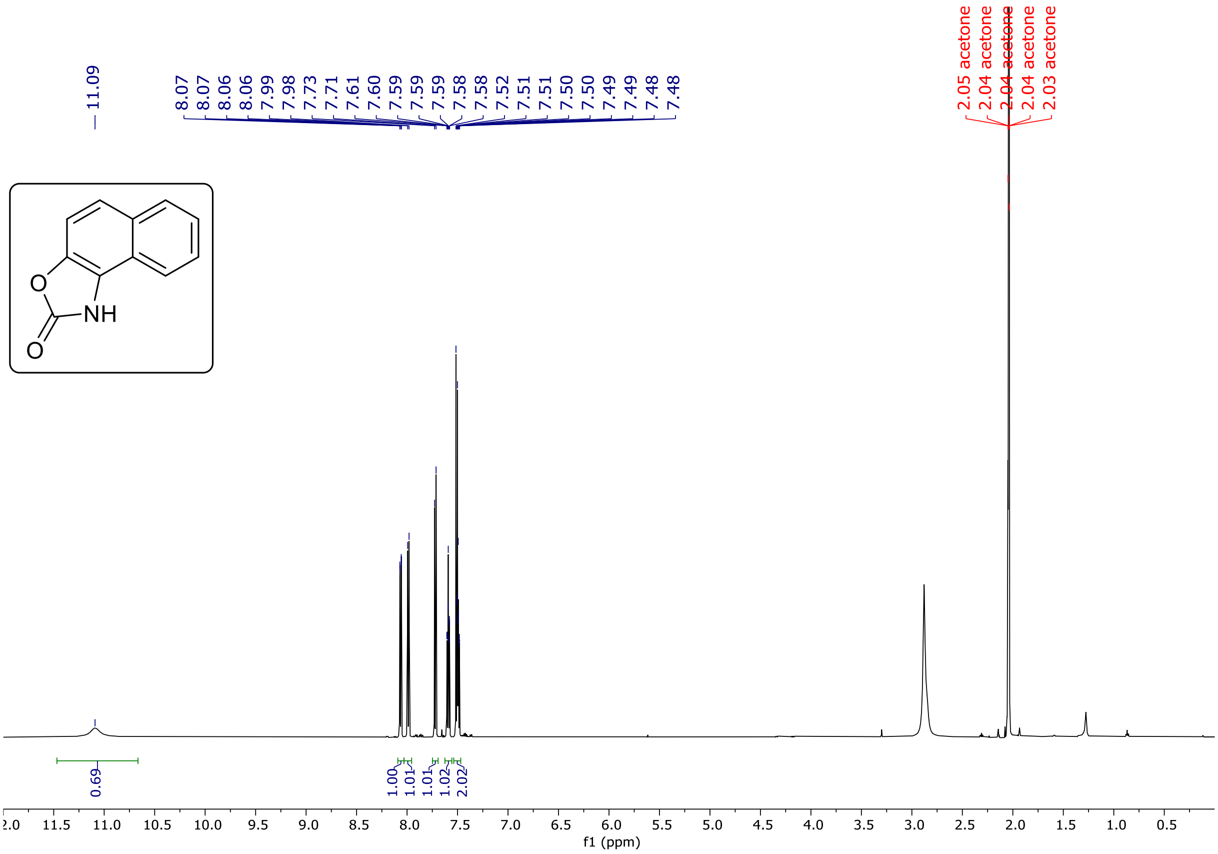


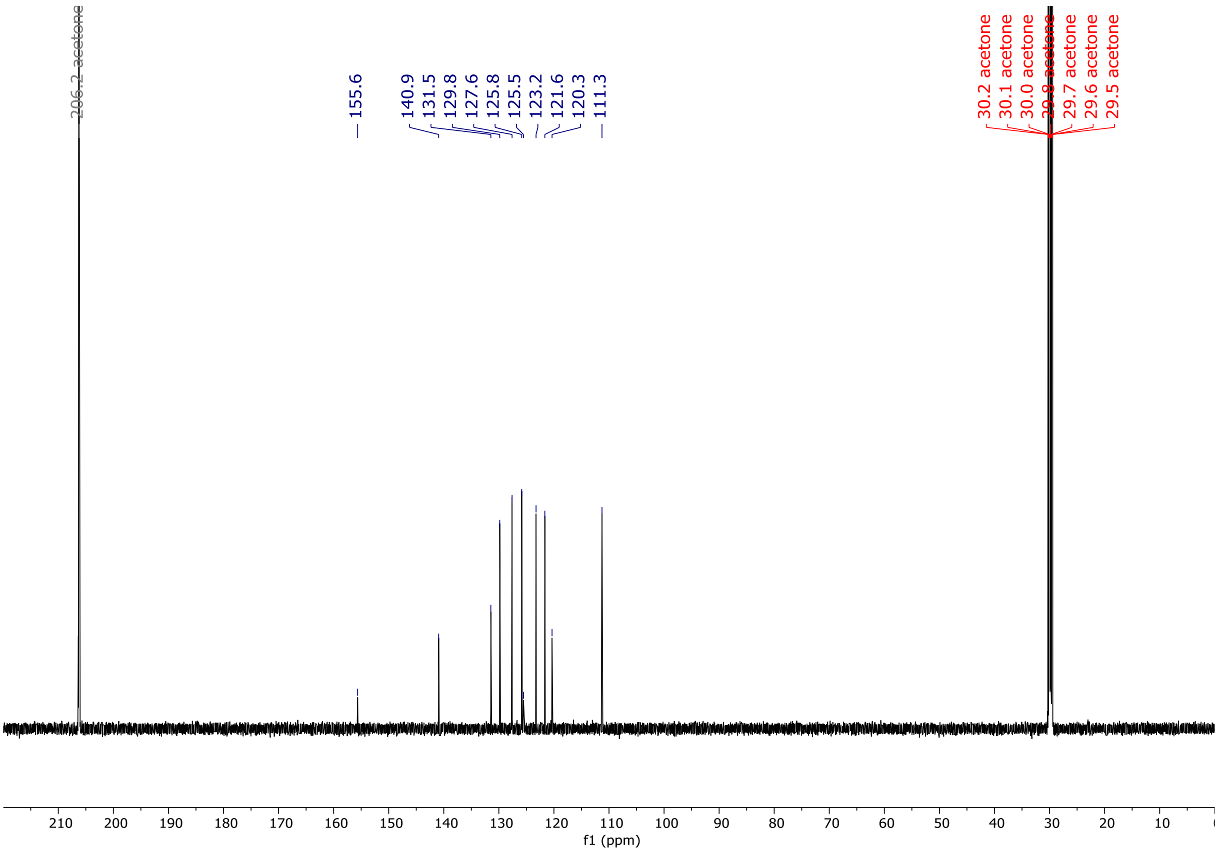
Naphtho[2,1-*d*]oxazol-2(3*H*)-one (2p)



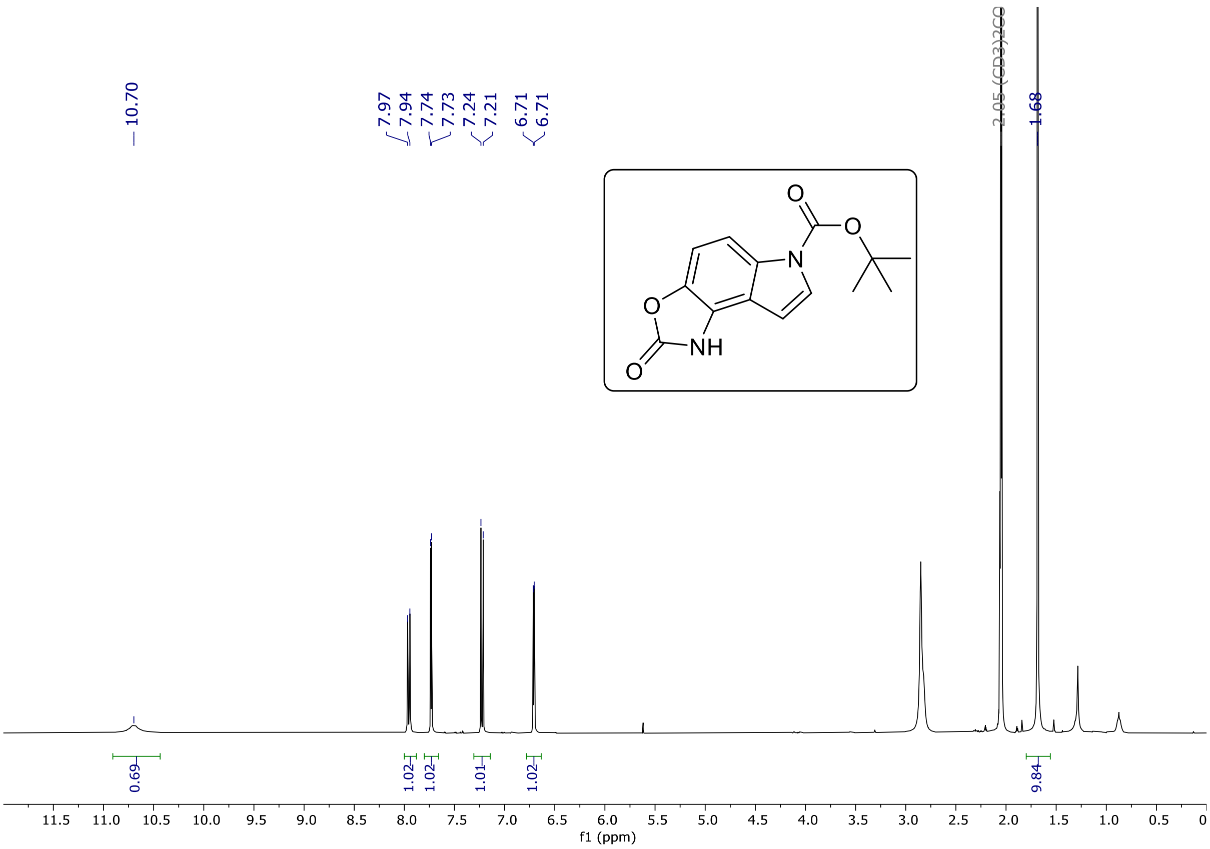


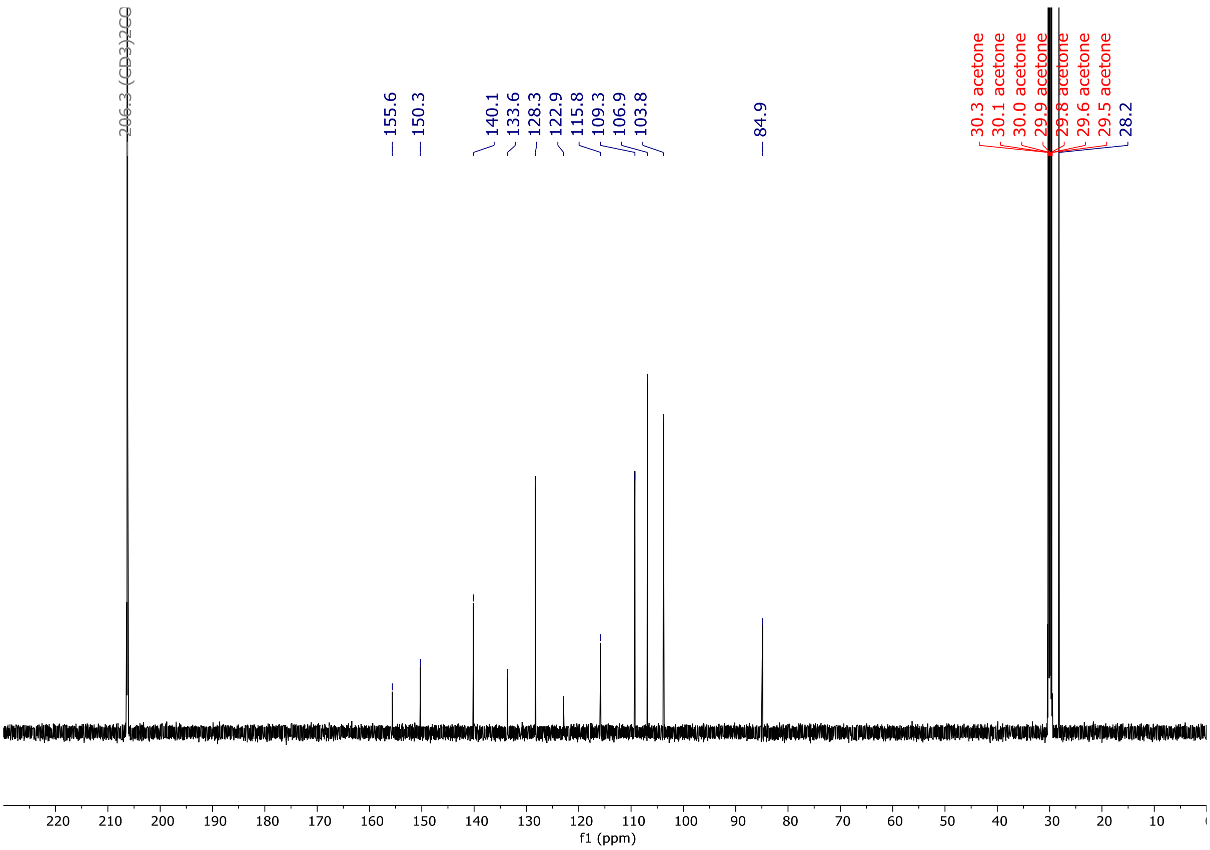
Naphtho[1,2-*d*]oxazol-2(1*H*)-one (2q)



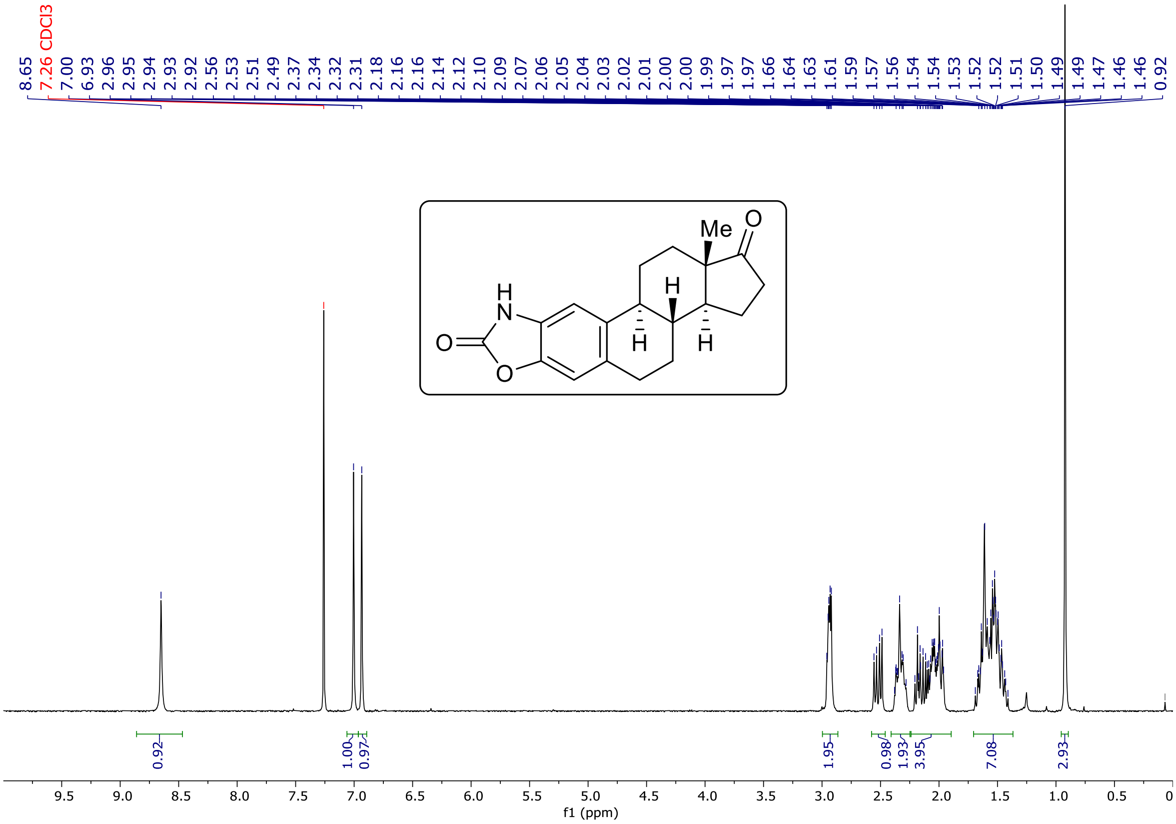


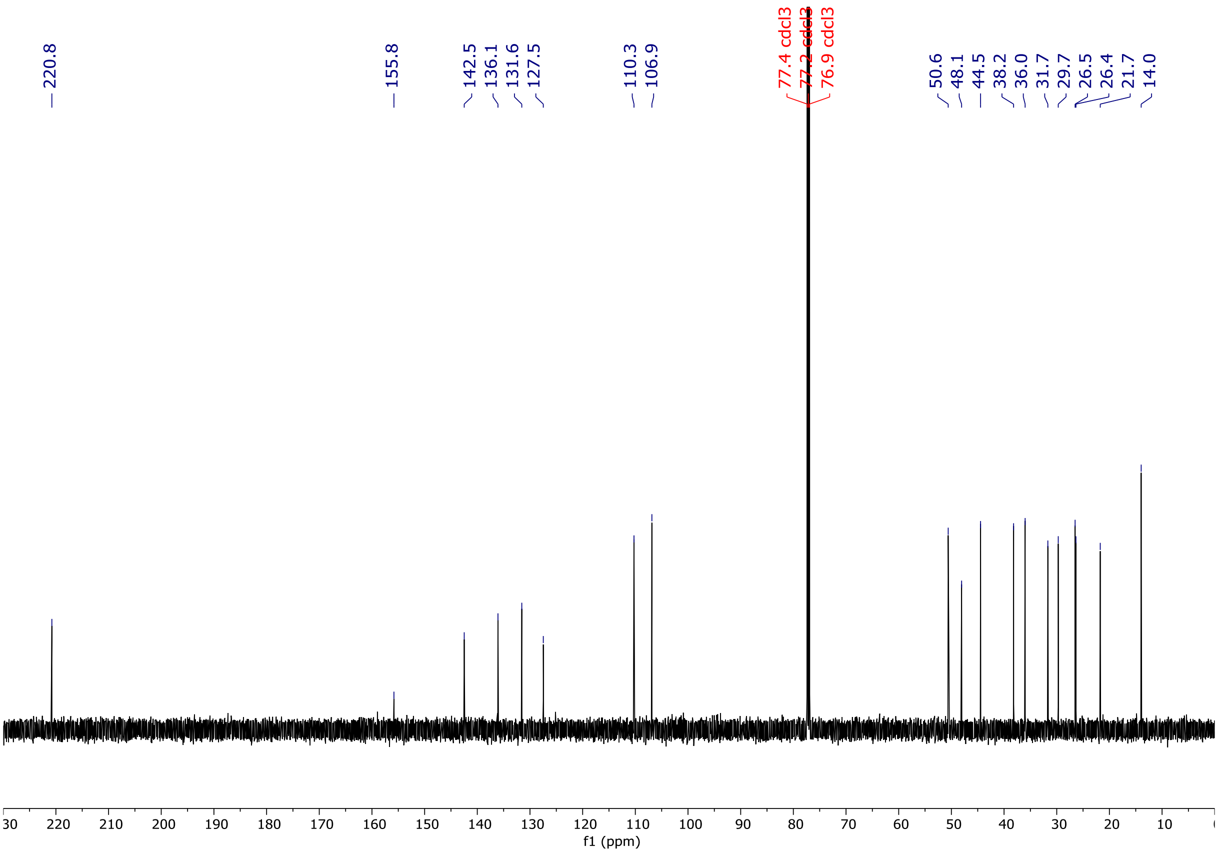
***tert*-Butyl 2-oxo-1,2-dihydro-6*H*-oxazolo[4,5-*e*]indole-6-carboxylate (2r)**



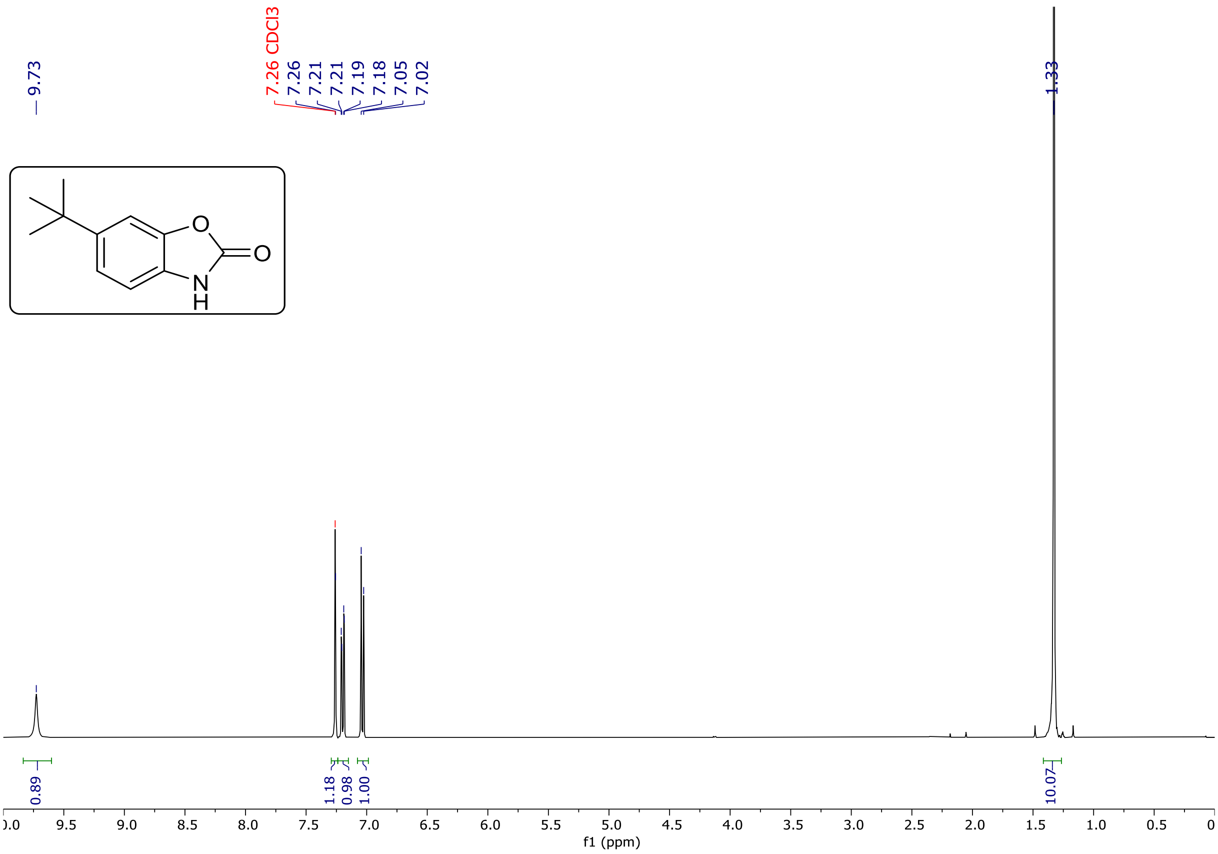


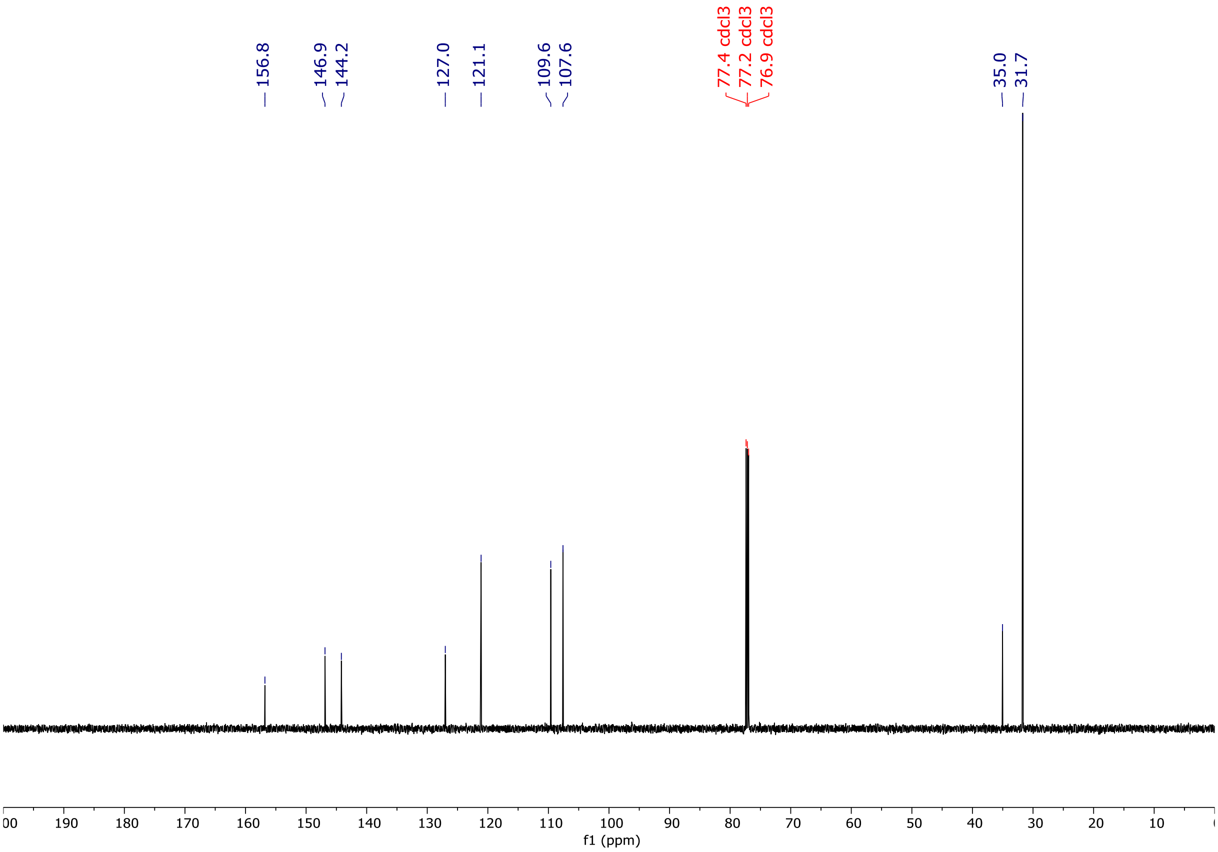
(3a*S*,3b*R*,10b*S*,12a*S*)-12a-methyl-3,3a,3b,4,5,9,10b,11,12,12a-decahydro-1*H*-cyclopenta[7,8]phenanthro[3,2-*d*]oxazole-1,8(2*H*)-dione (2s)



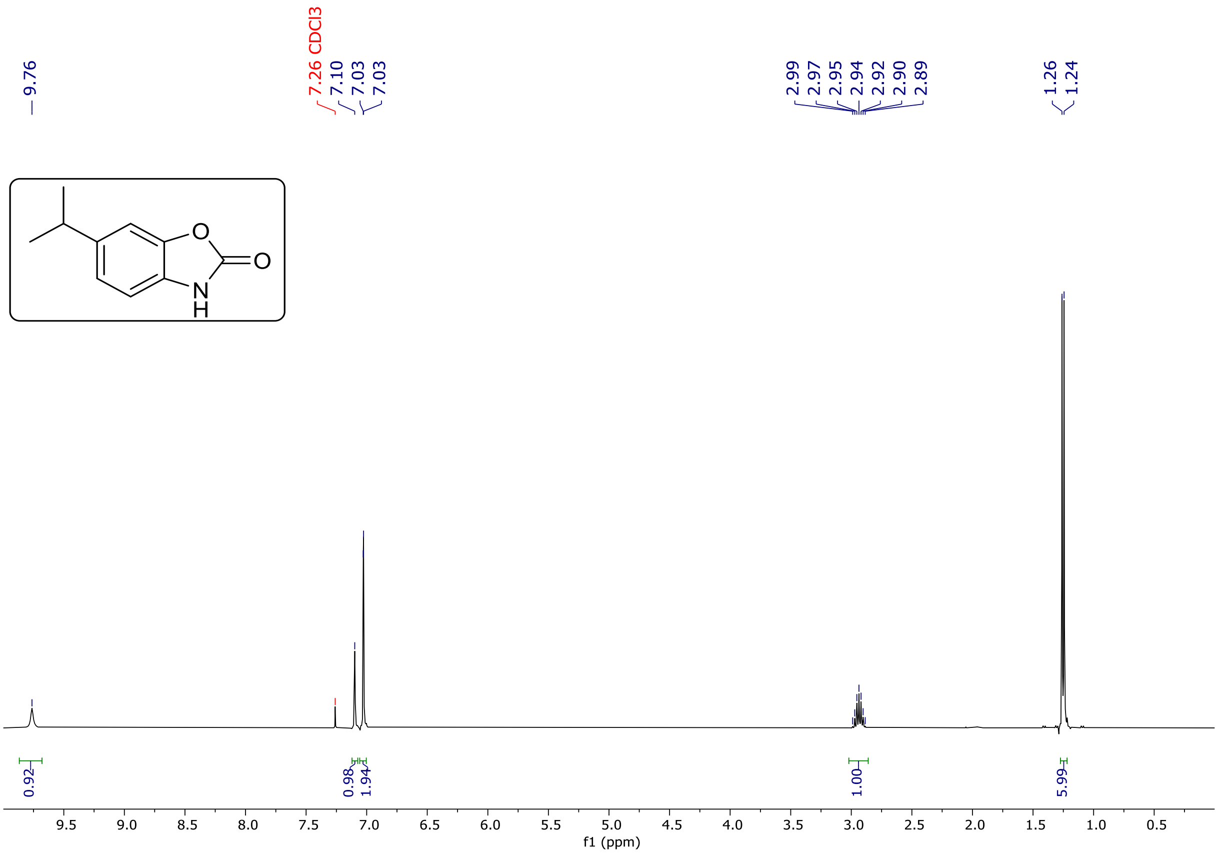


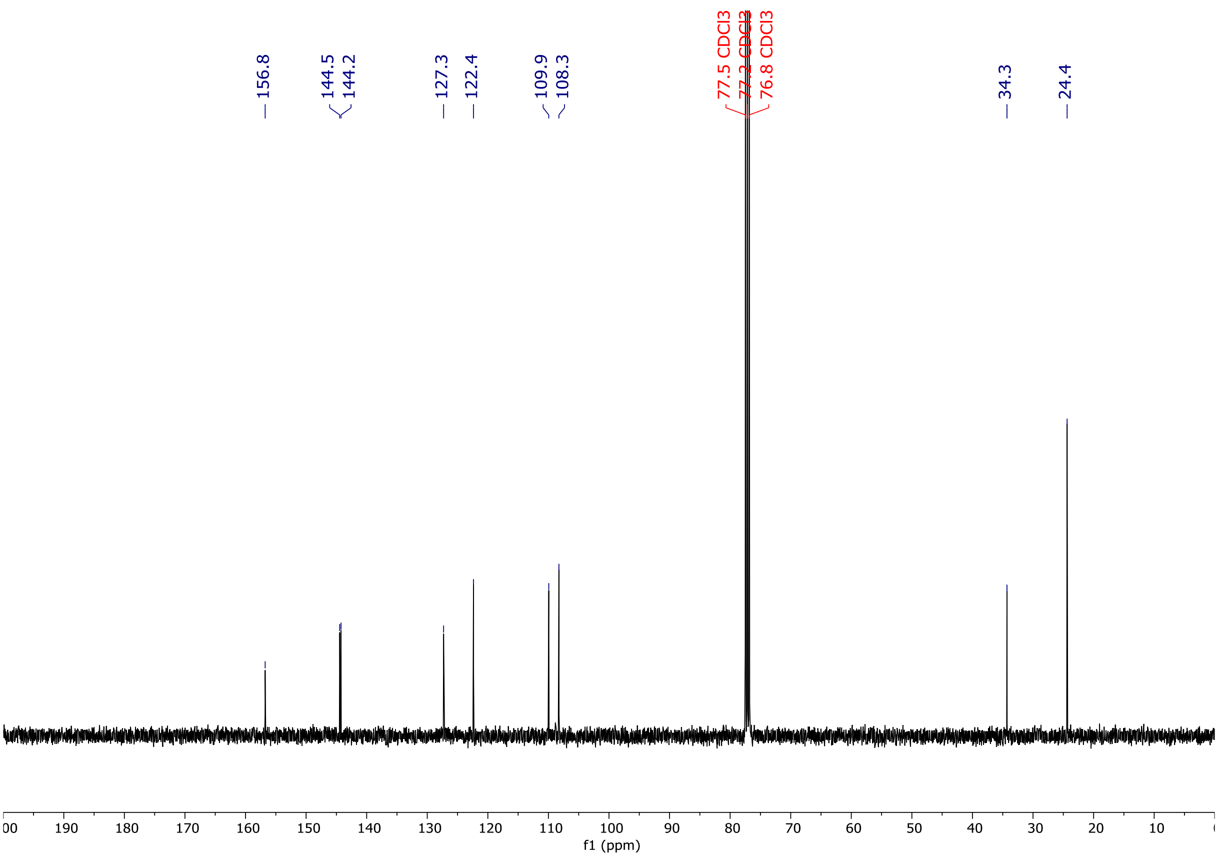
6-(*tert*-Butyl)benzo[*d*]oxazol-2(3*H*)-one (2t)



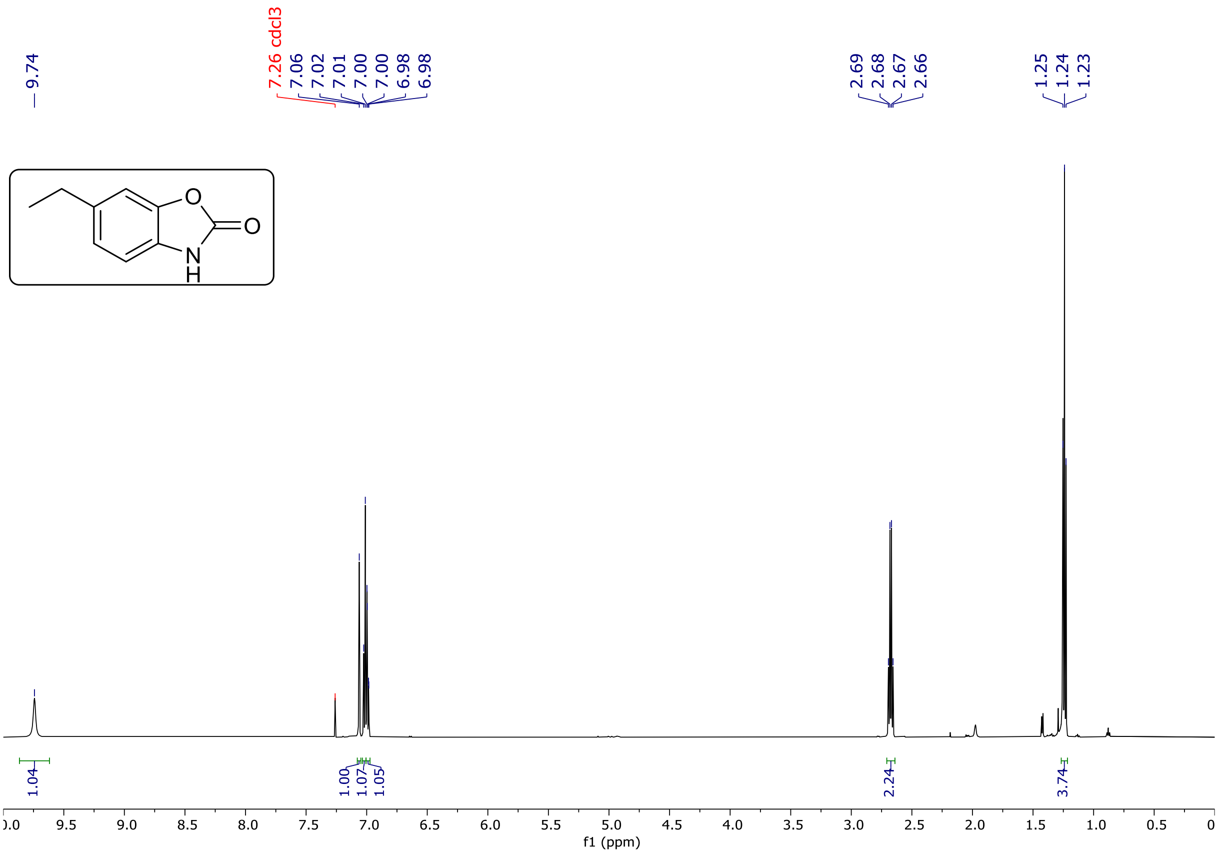


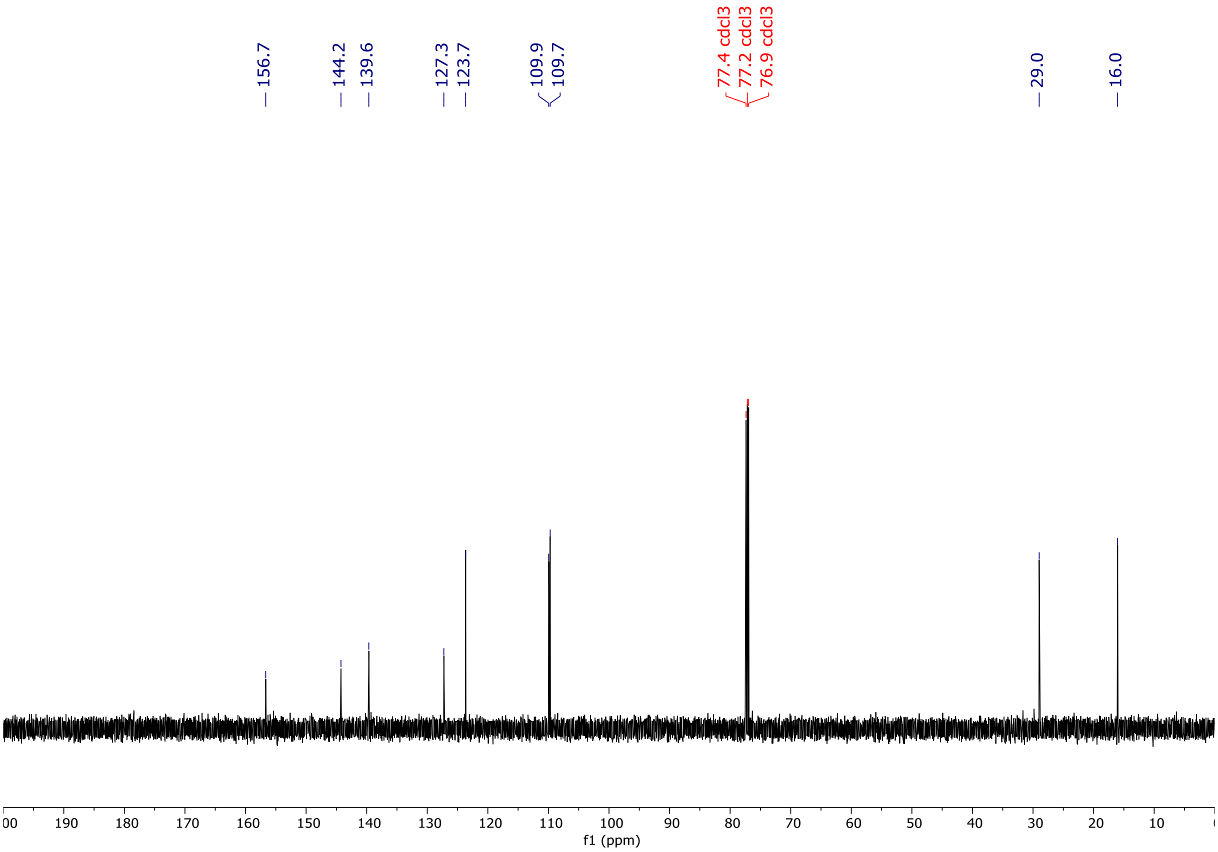
6-Isopropylbenzo[*d*]oxazol-2(3*H*)-one (2u)



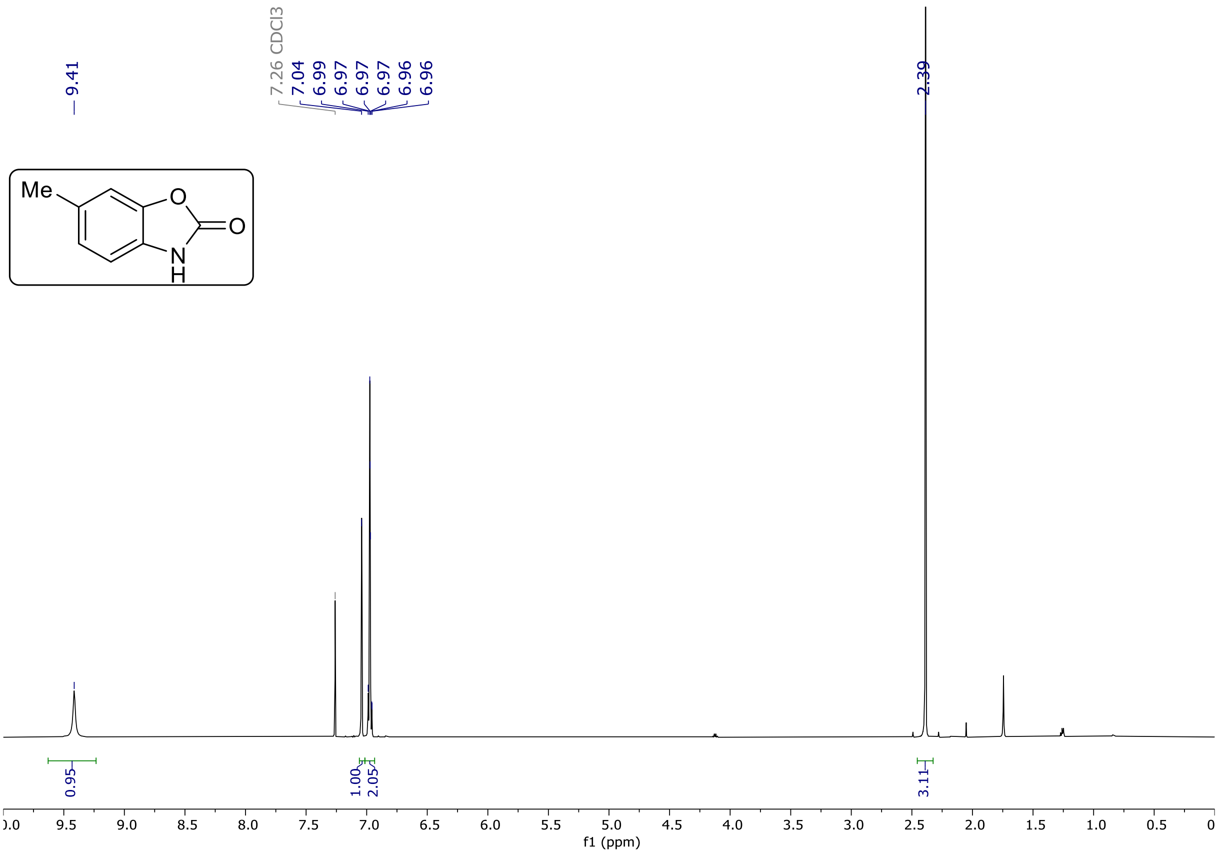


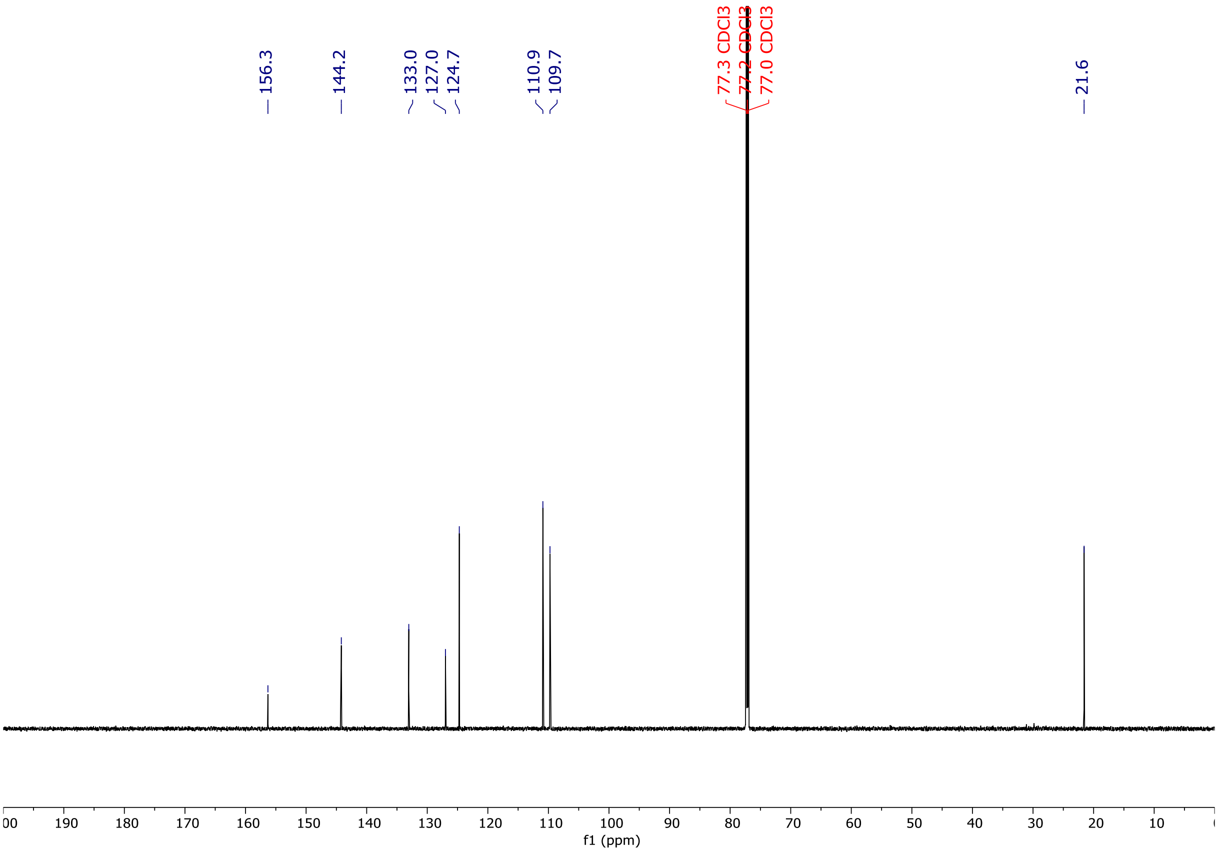
6-Ethylbenzo[*d*]oxazol-2(3*H*)-one (2v)



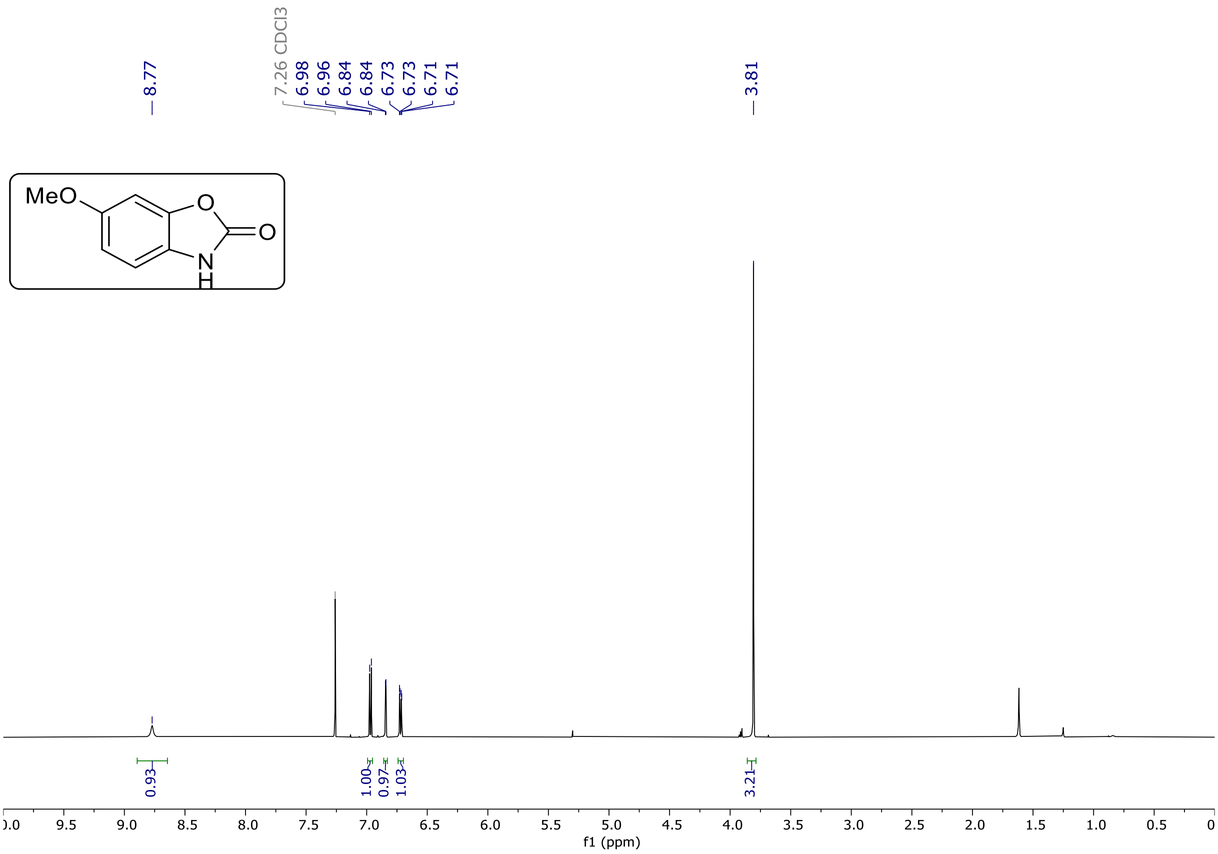


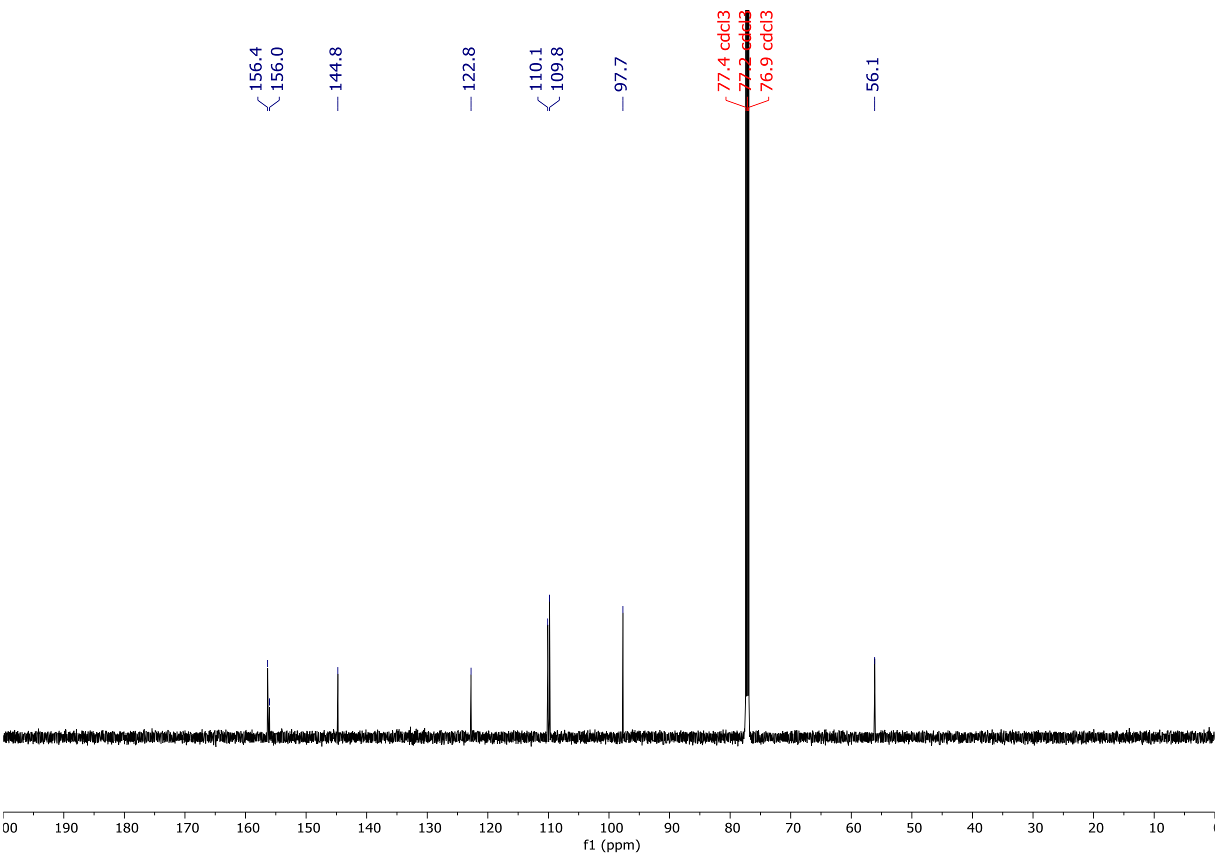
6-Methylbenzo[*d*]oxazol-2(3*H*)-one (2w)



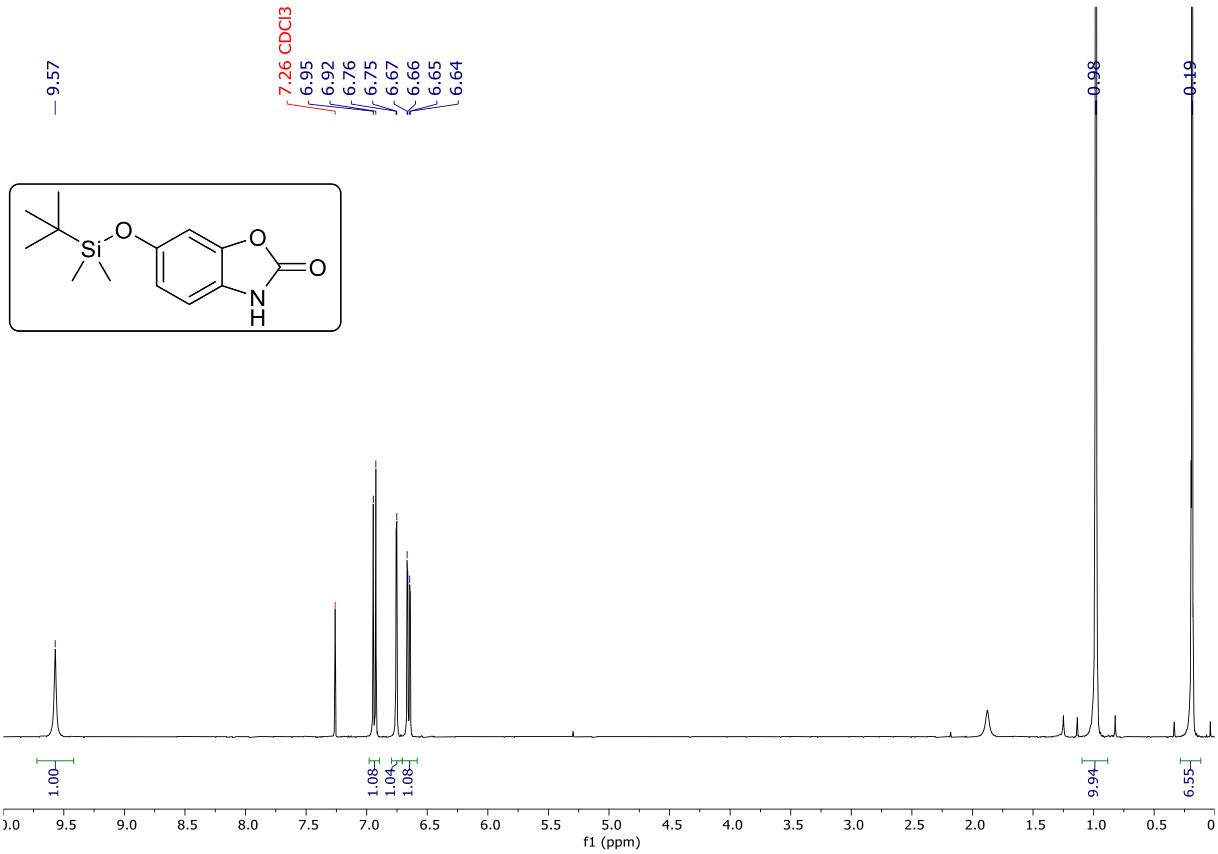


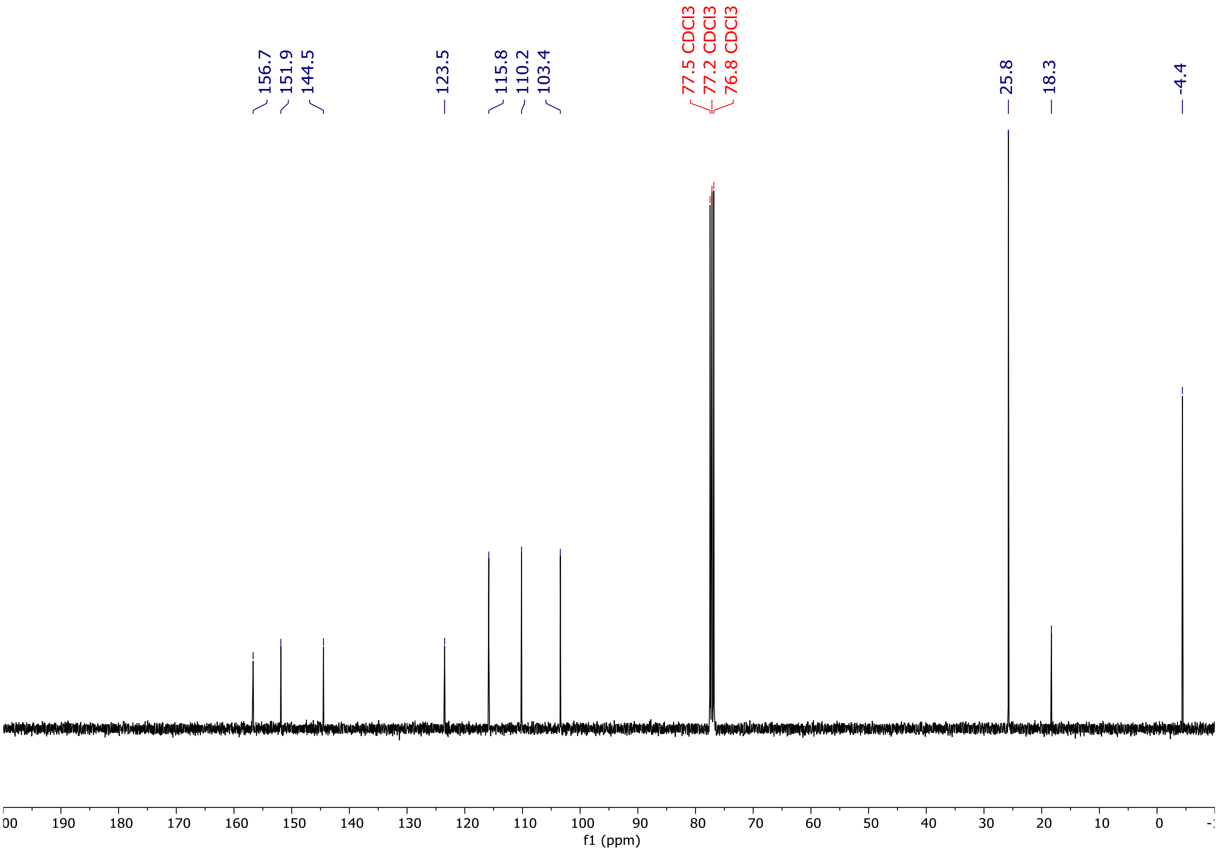
6-Methoxybenzo[*d*]oxazol-2(3*H*)-one (2x)



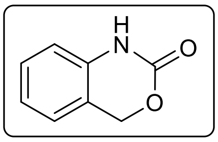


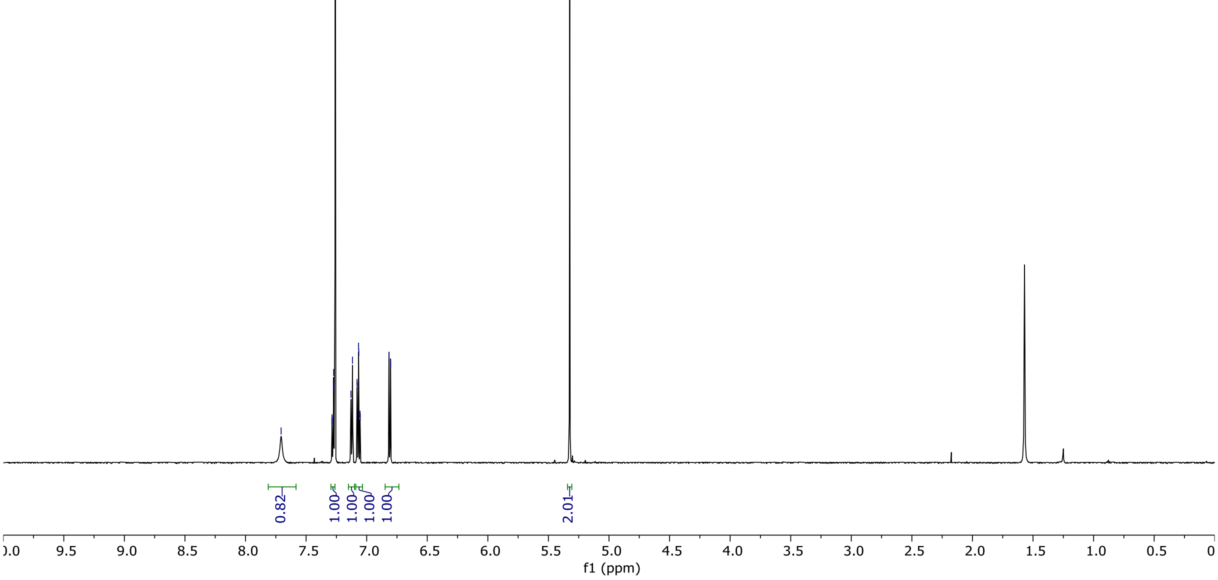
6-{(*tert*-Butyldimethylsilyl)oxy}benzo[*d*]oxazol-2(3*H*)-one (2y)

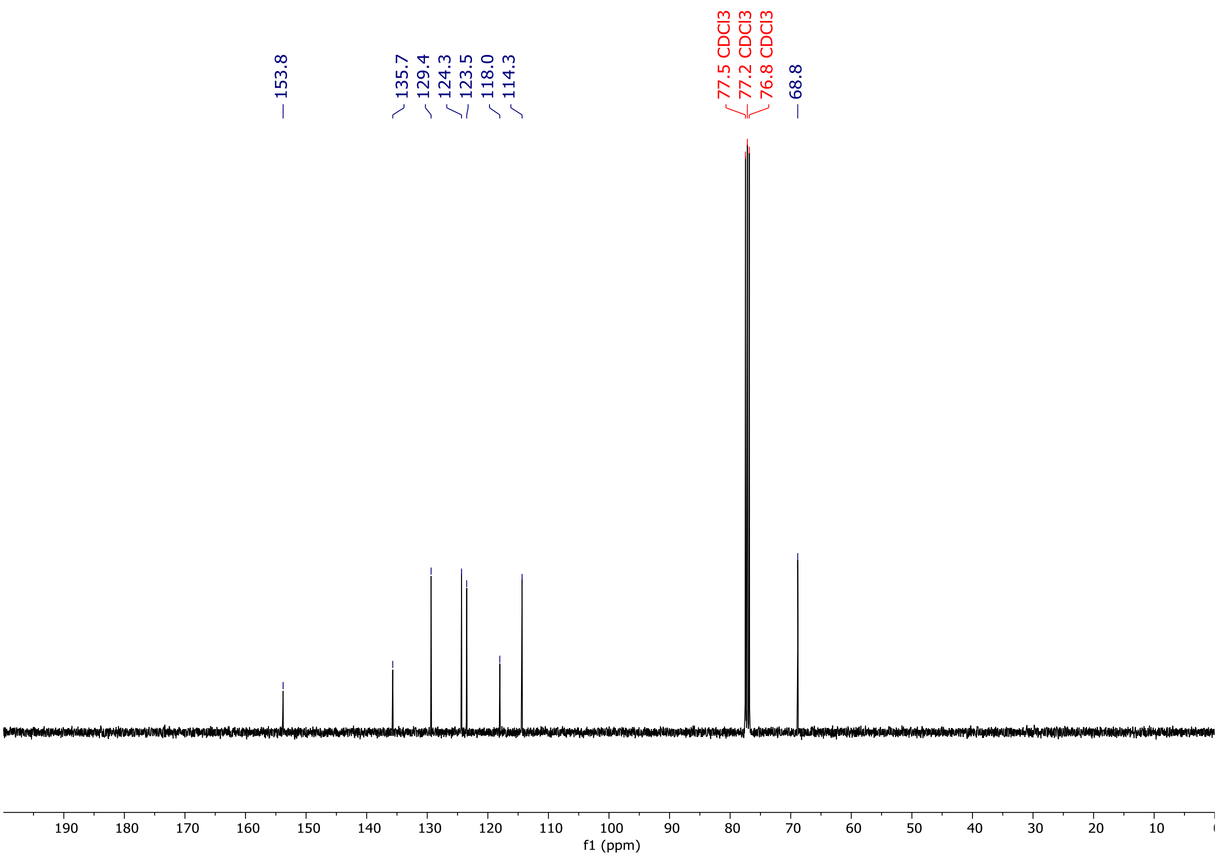




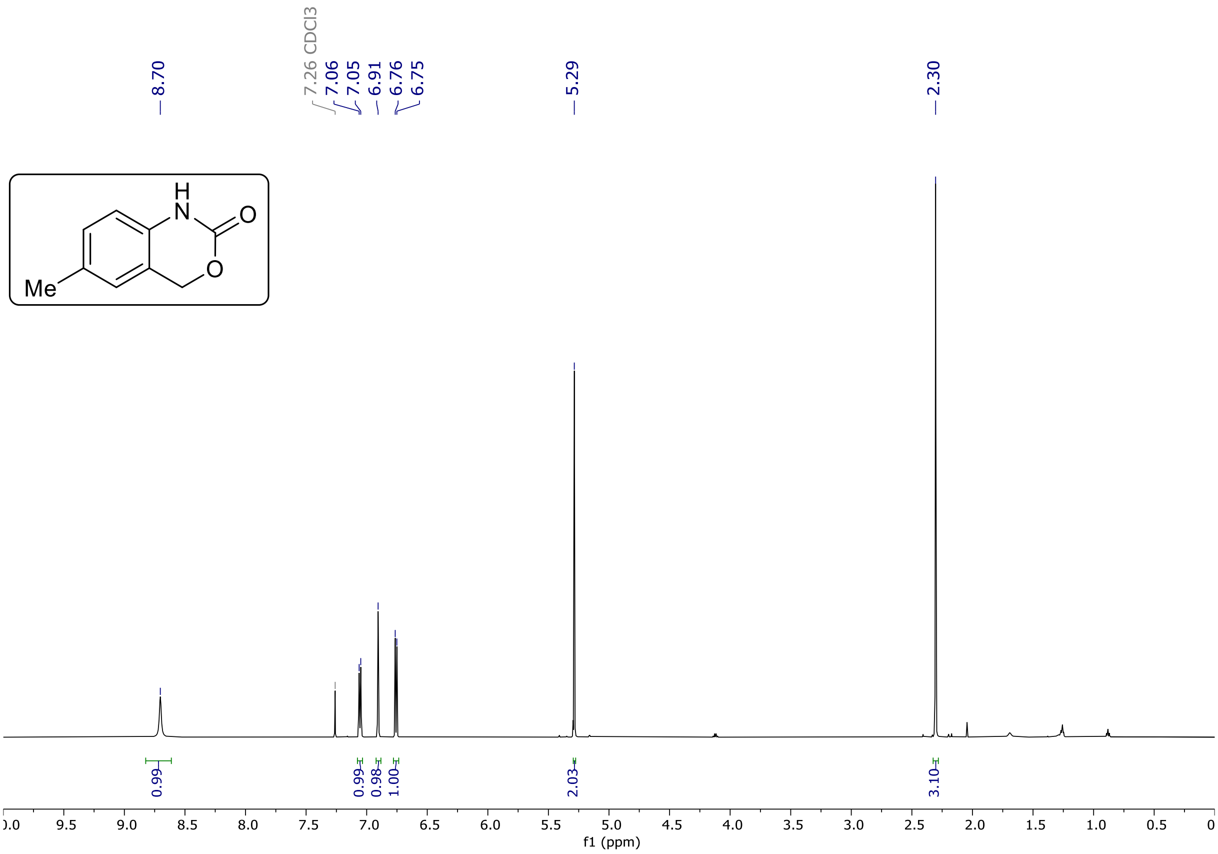
1,4-Dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4a)

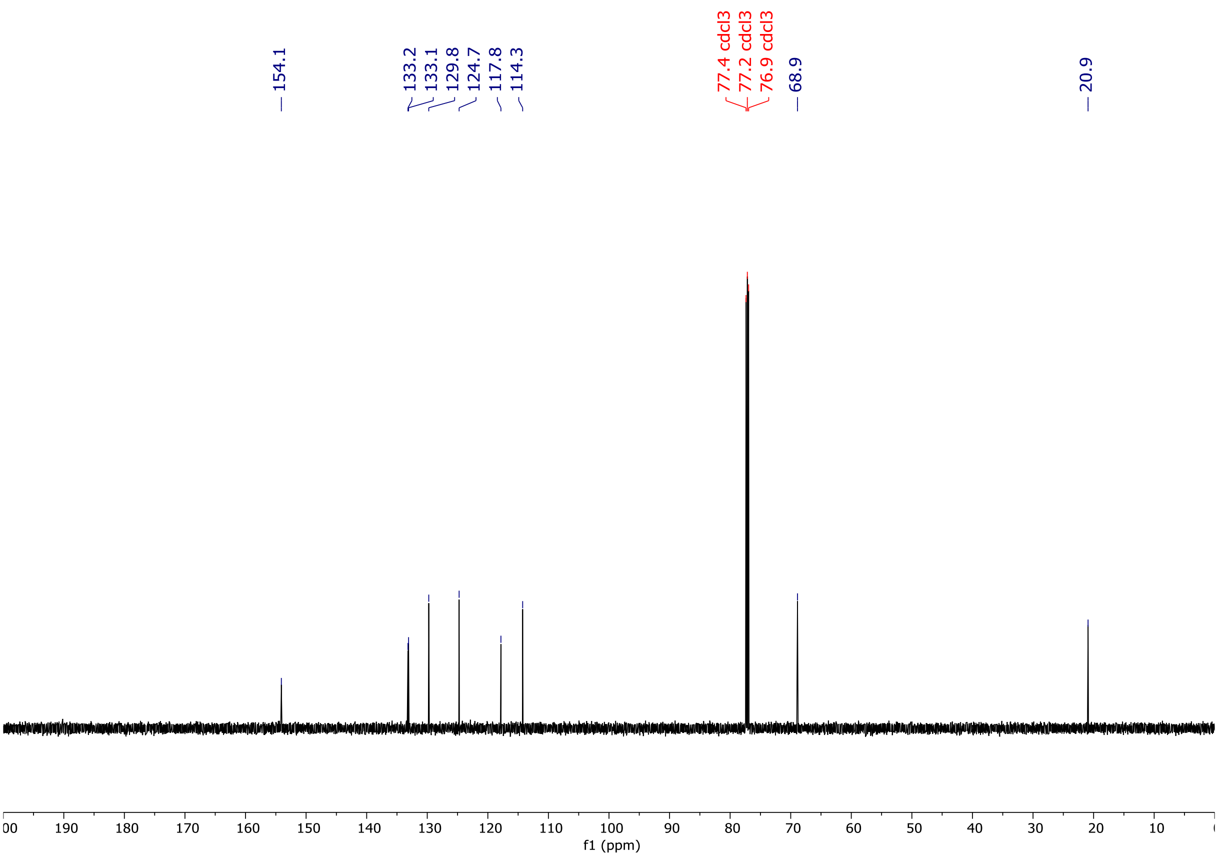




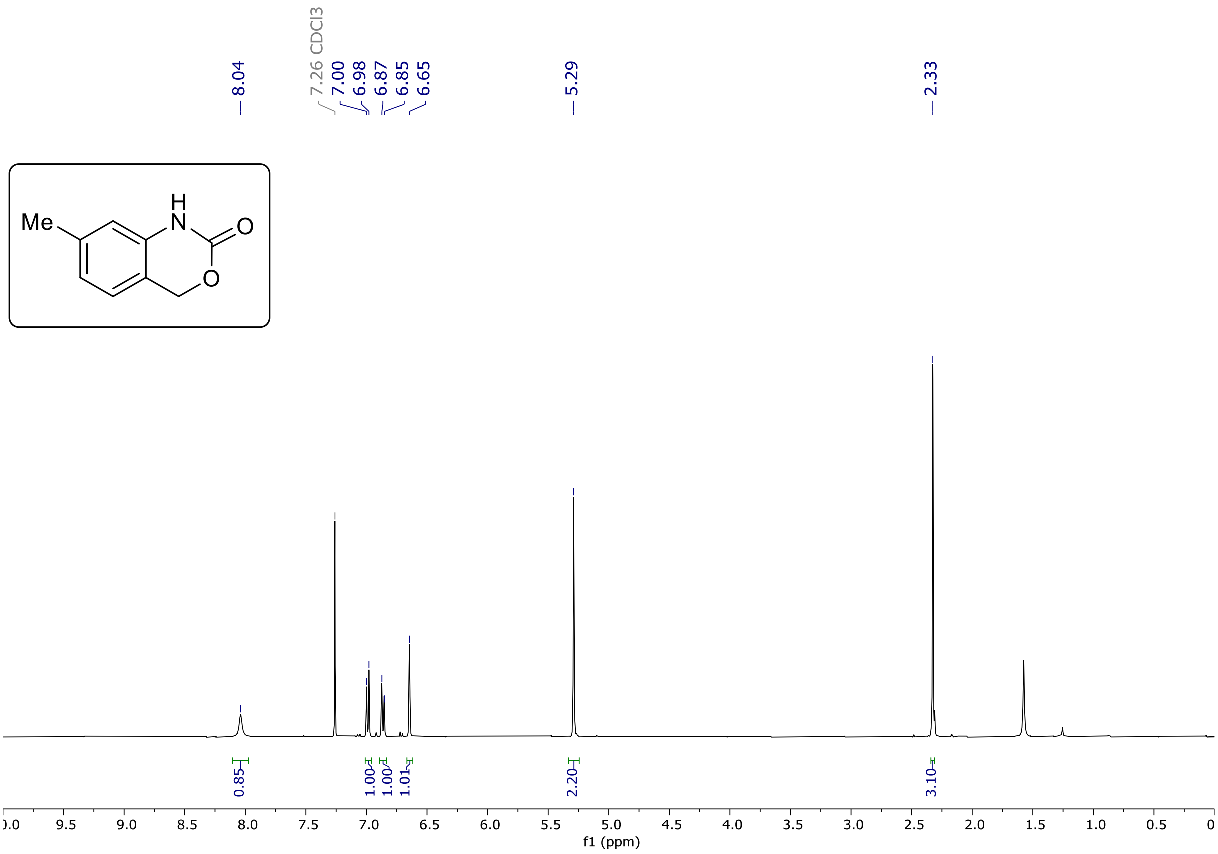


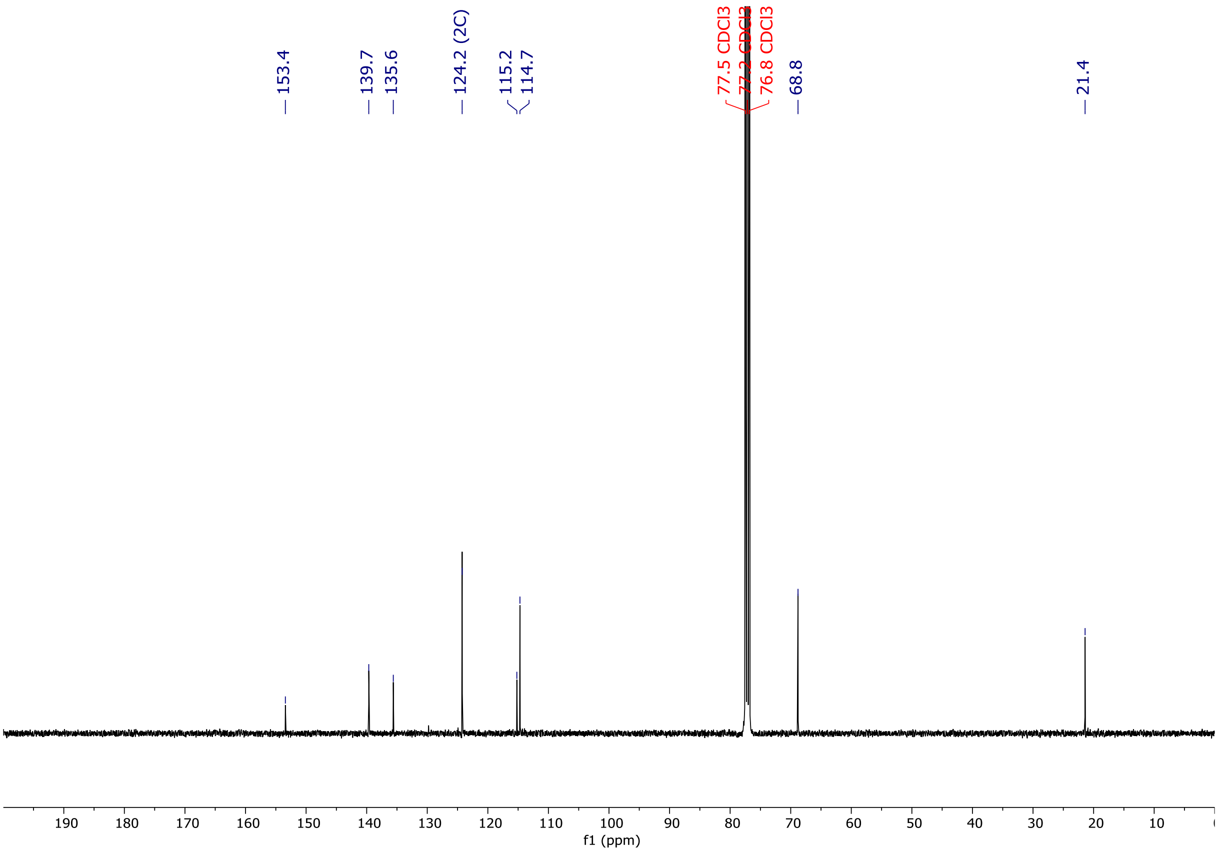
6-Methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4b)



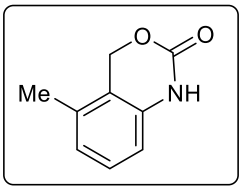


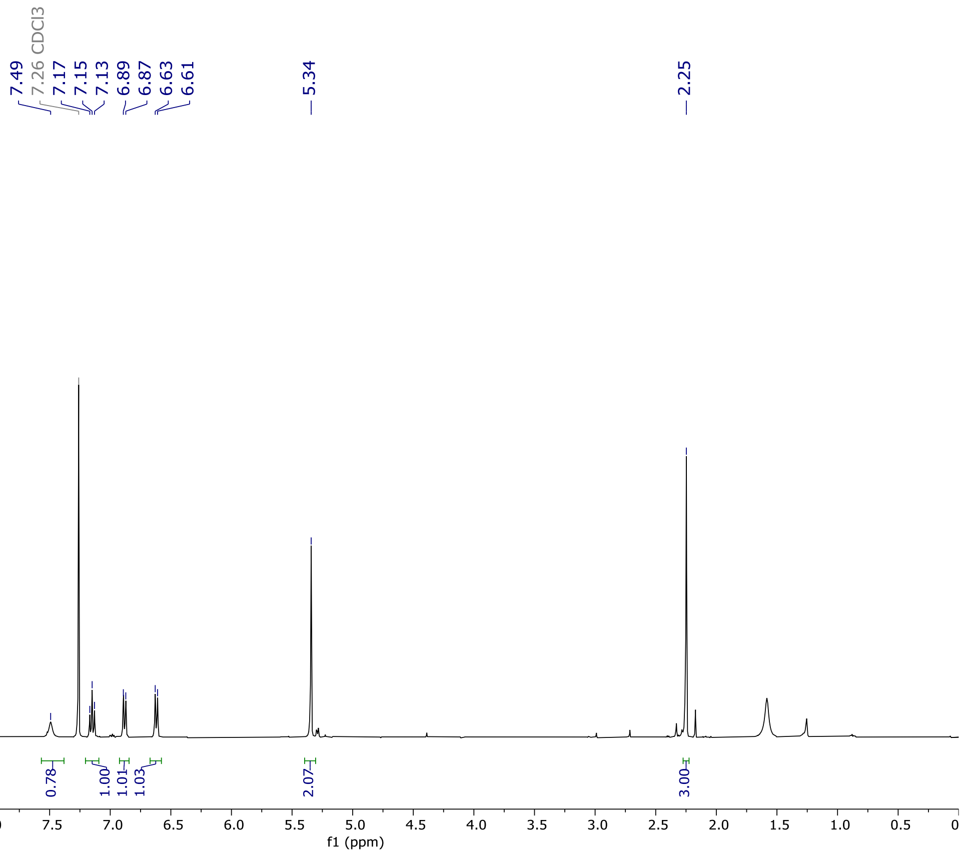
7-Methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4c)

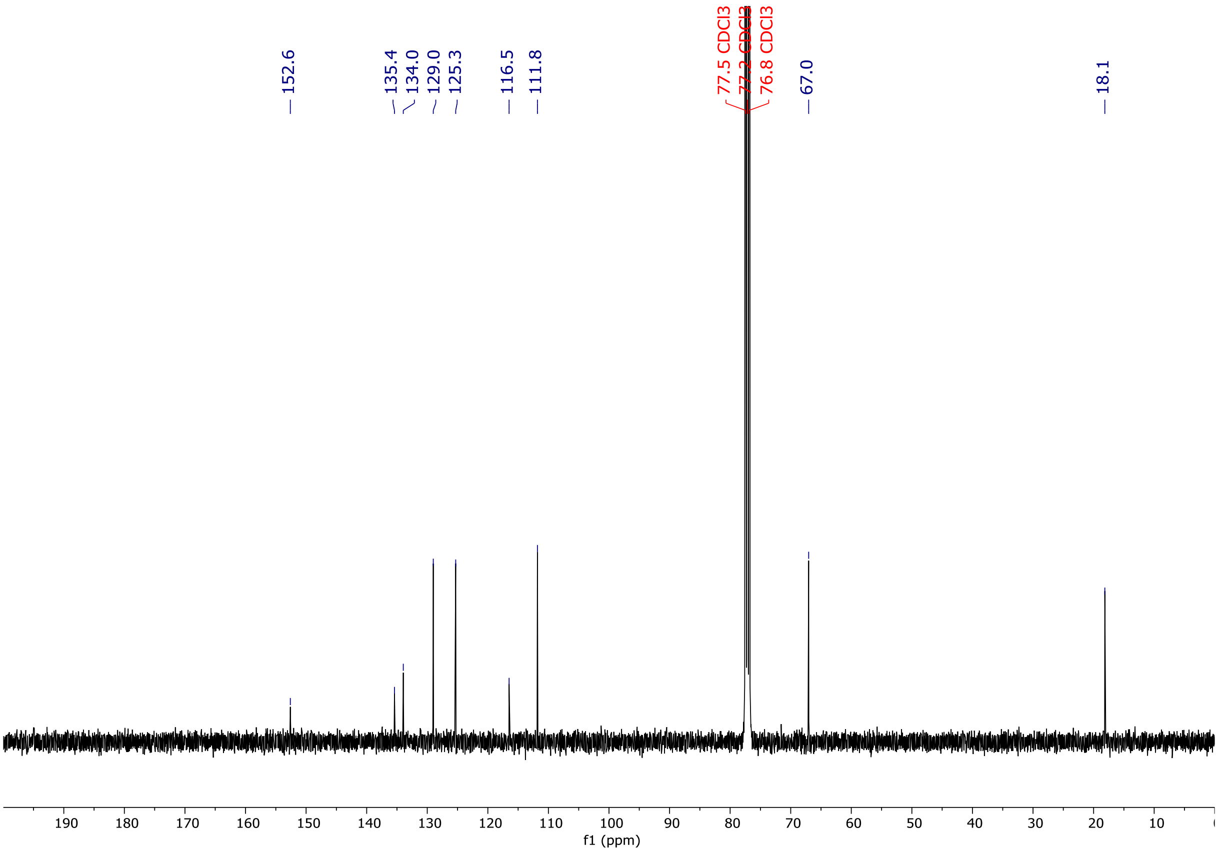




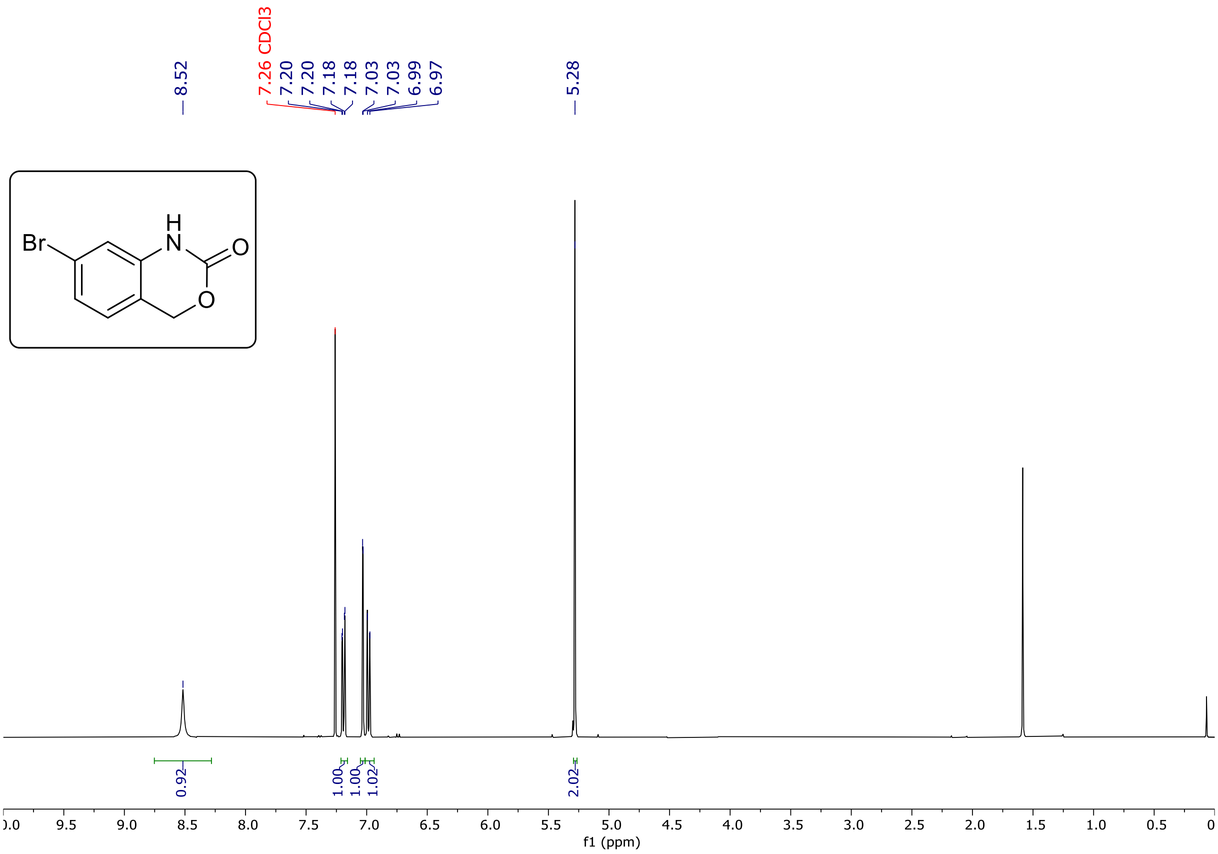
5-methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4c’)

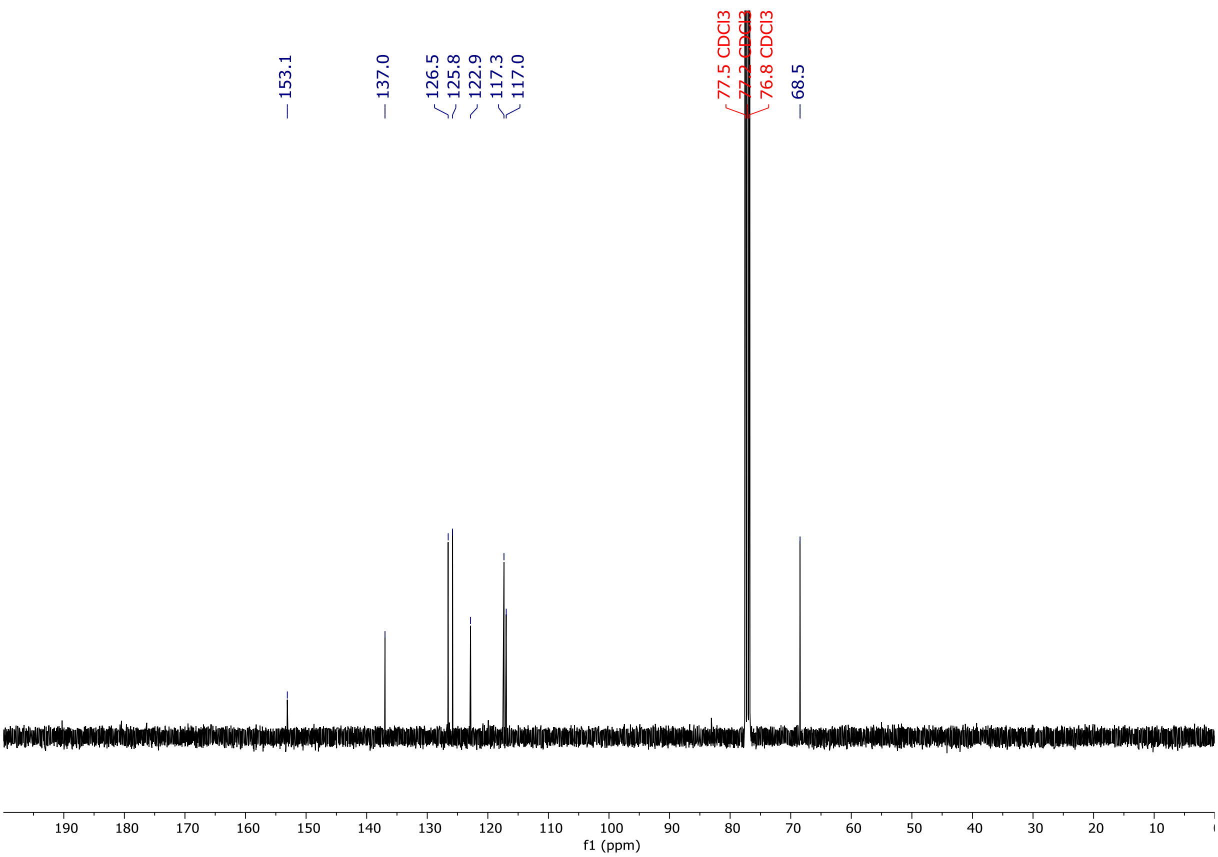






7-Bromo-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4d)





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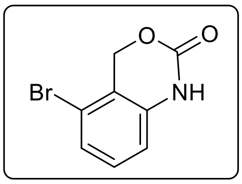
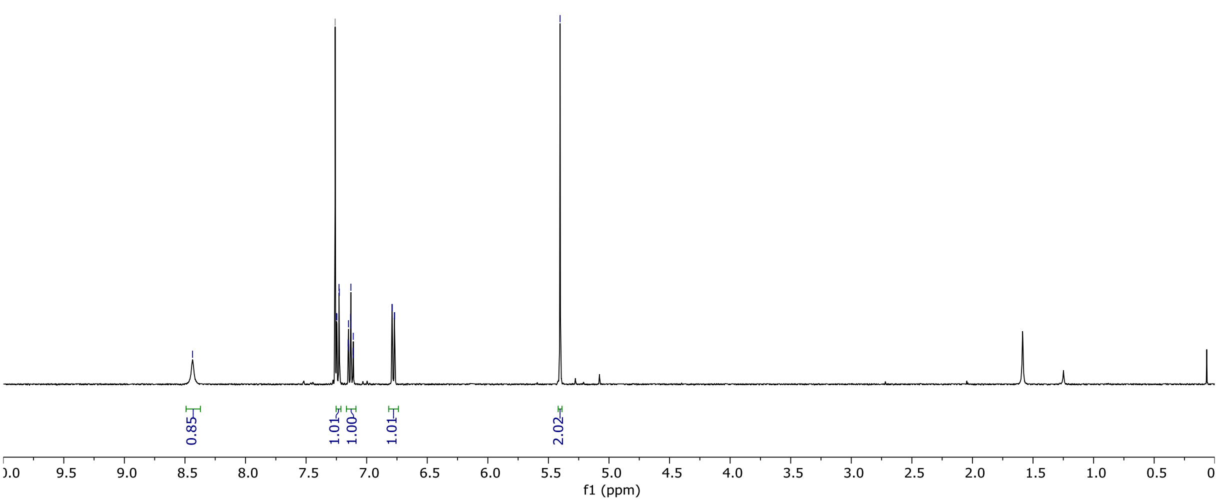
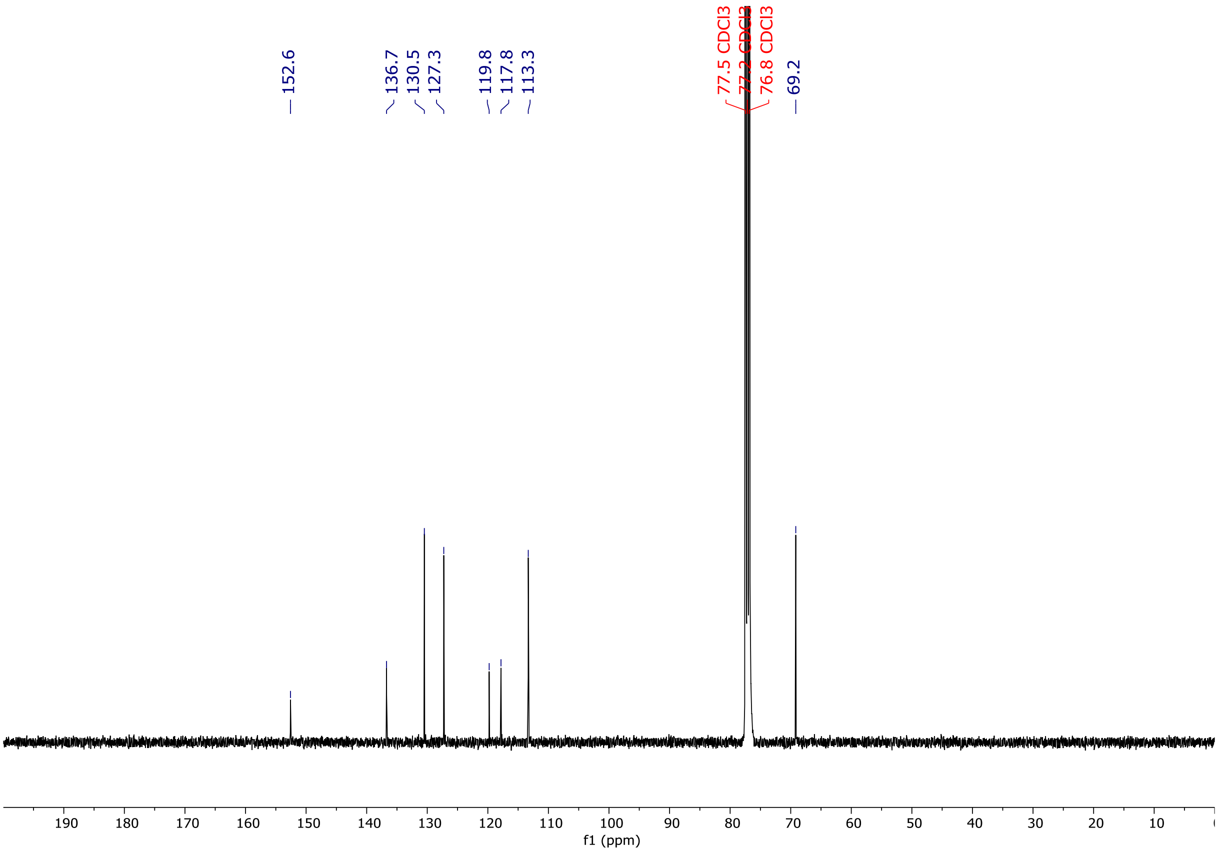
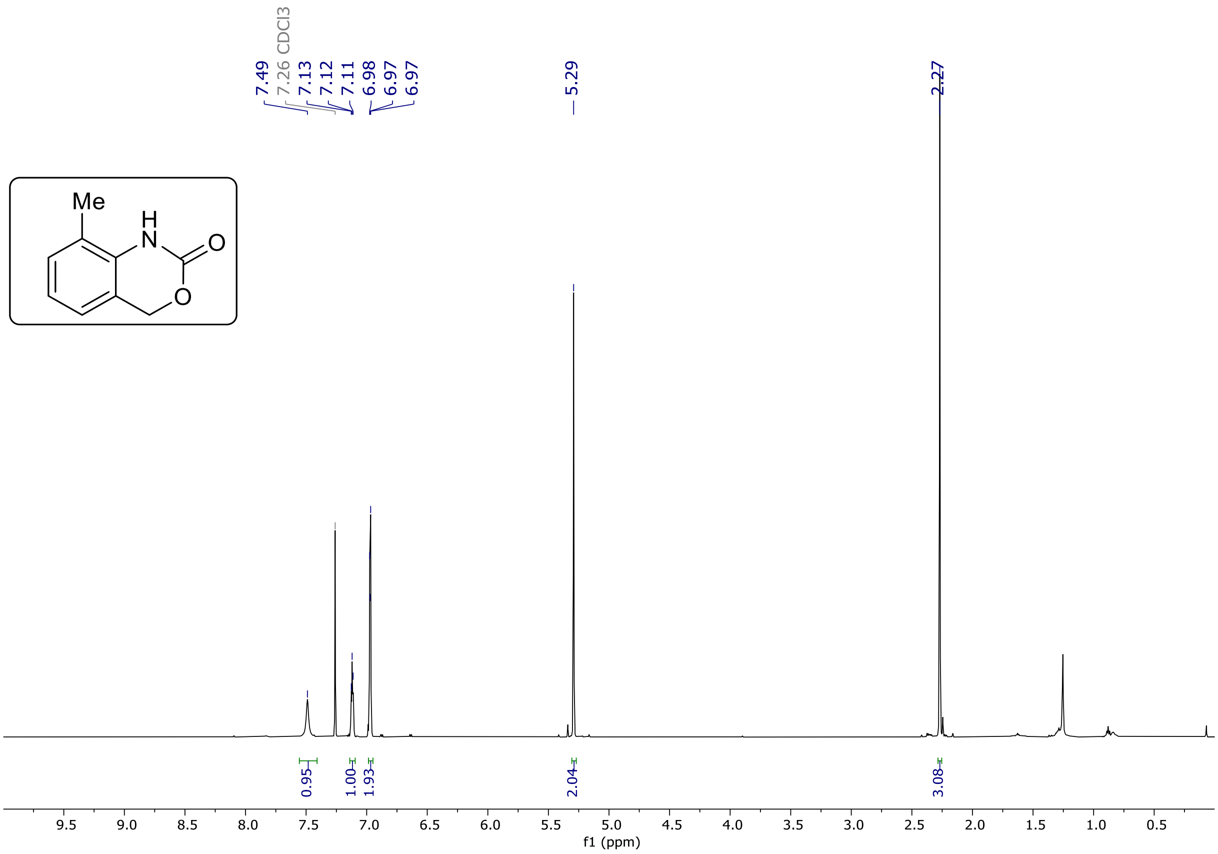
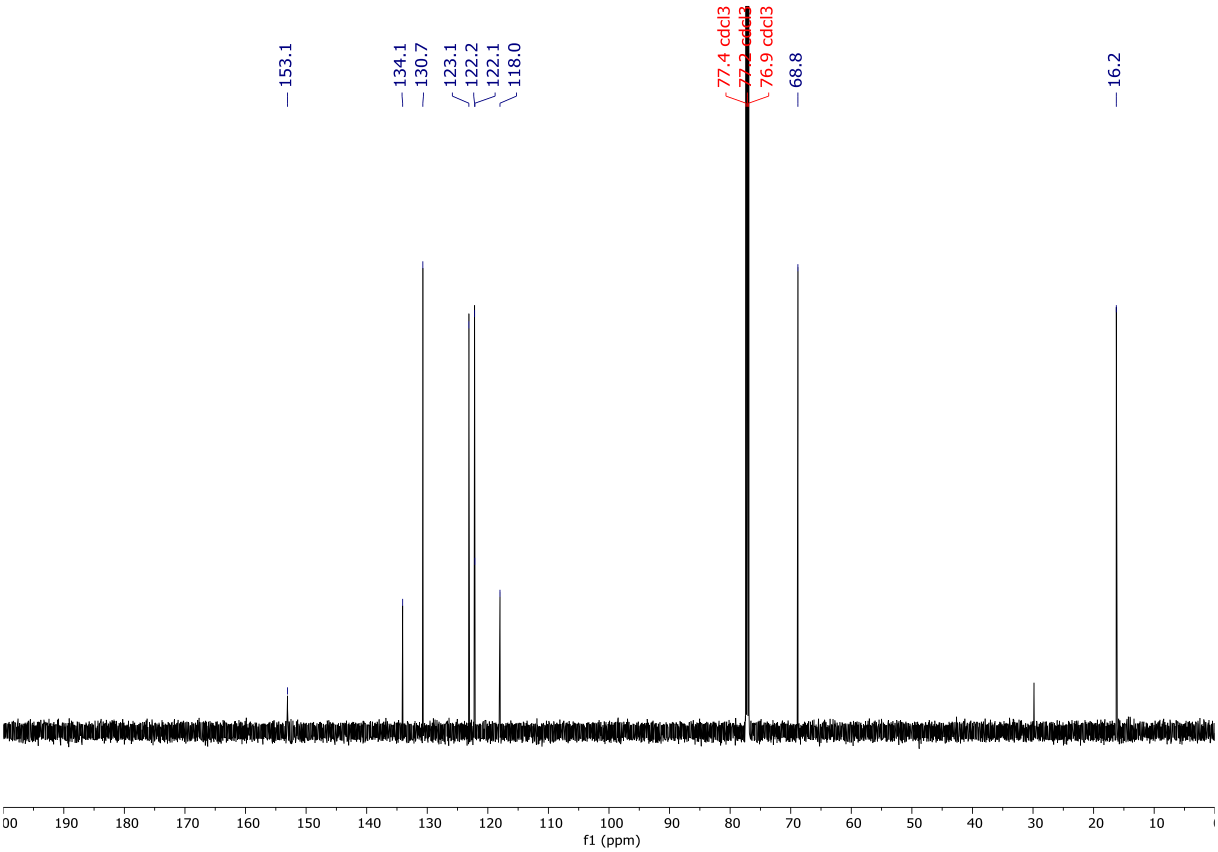




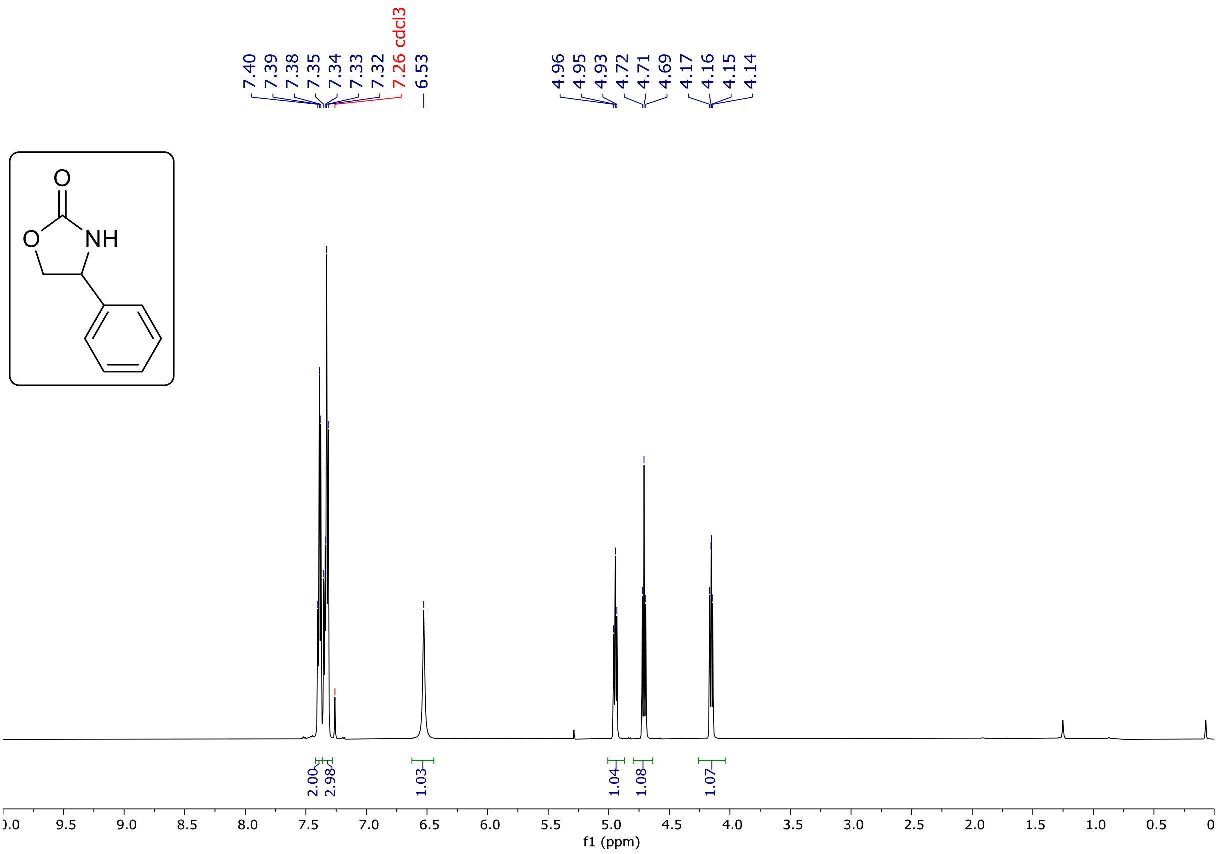


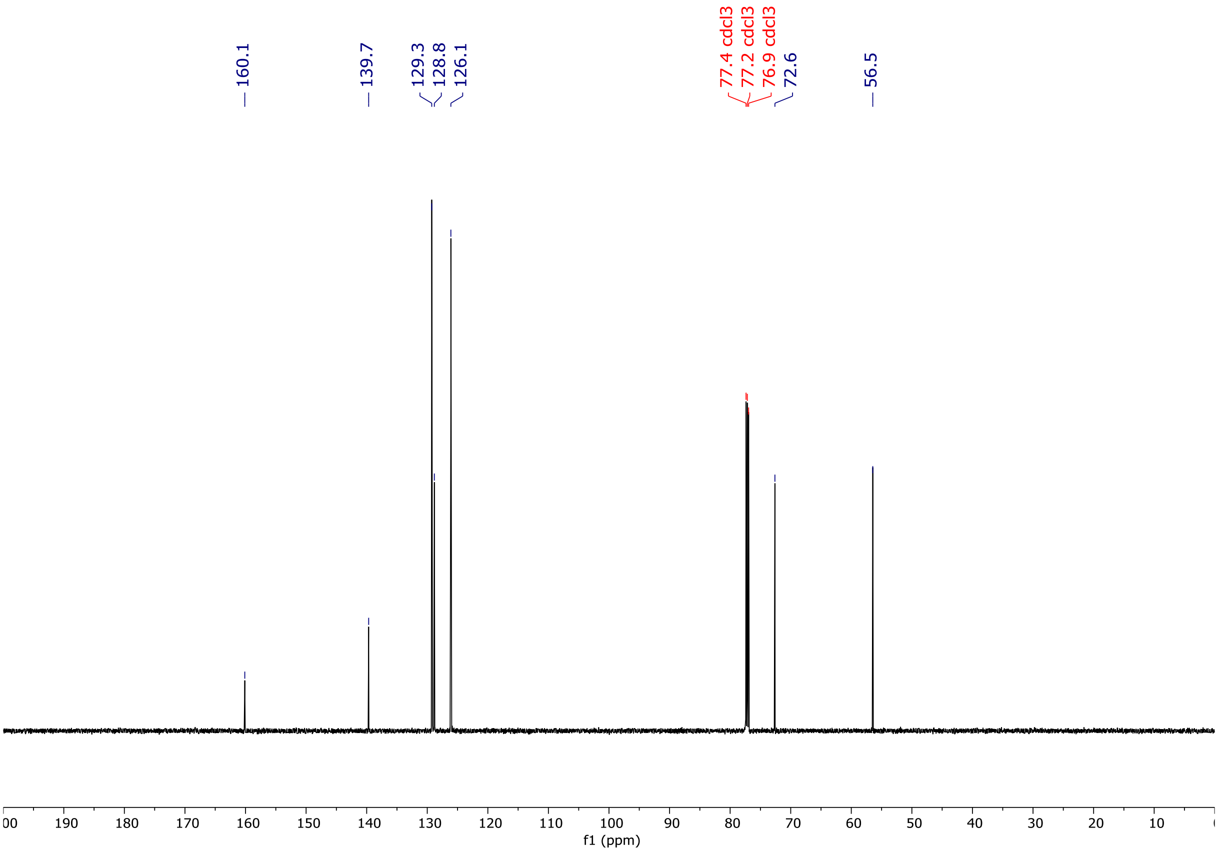
8-Methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (4e)



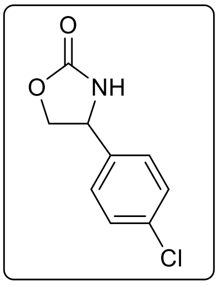


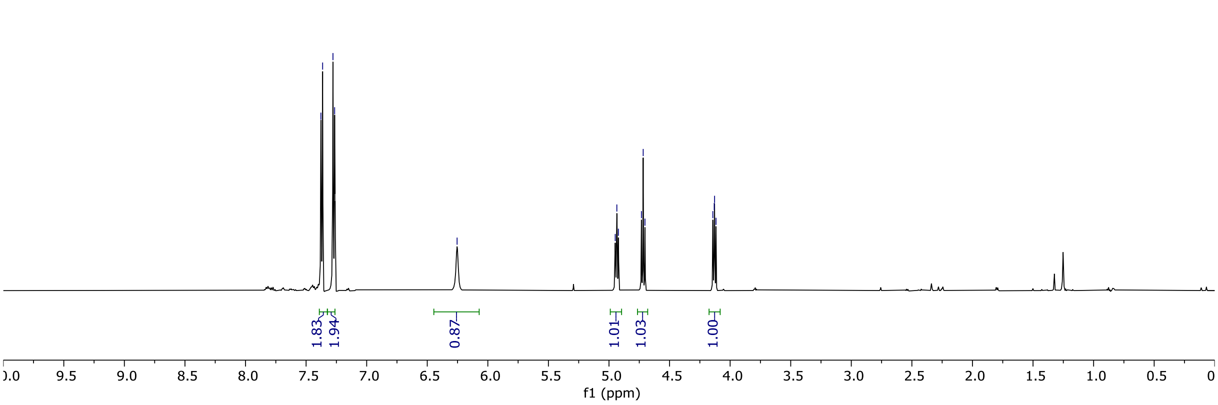
4-Phenyloxazolidin-2-one (6a)

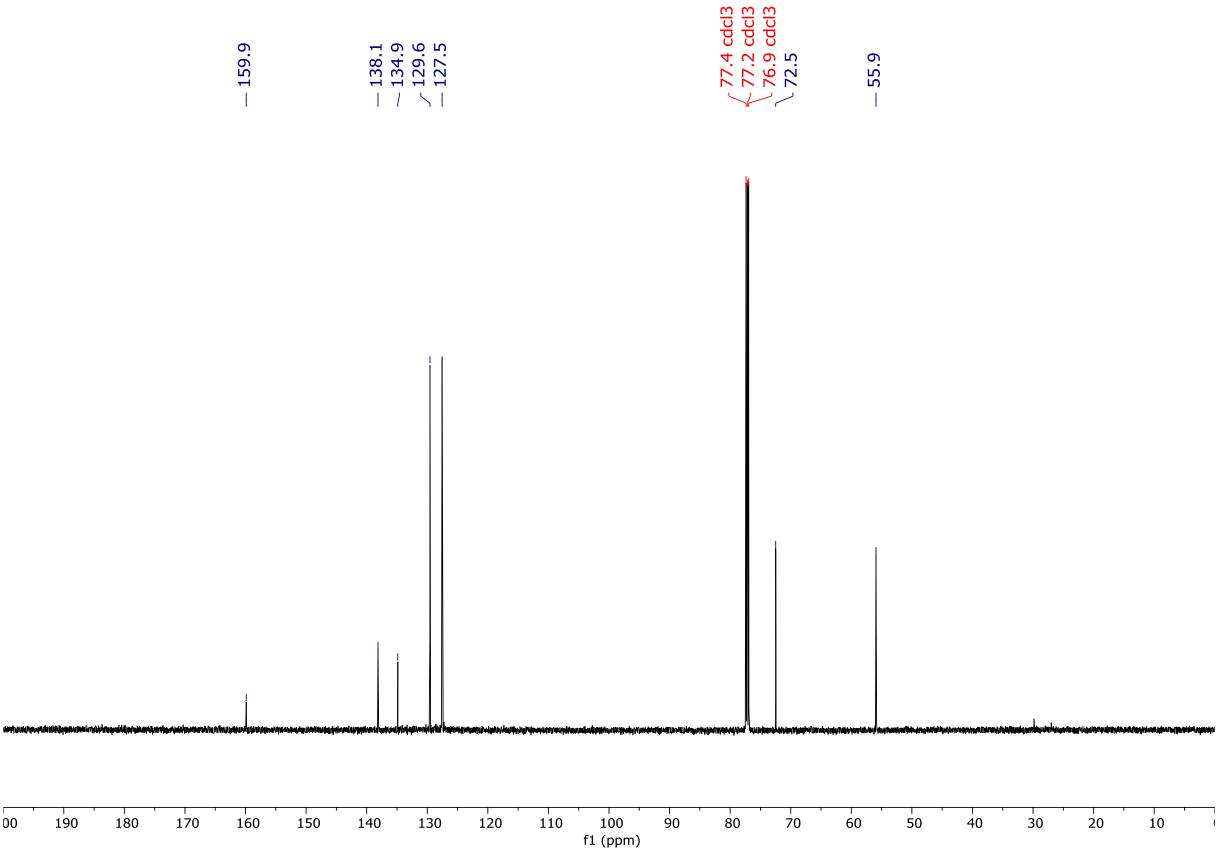




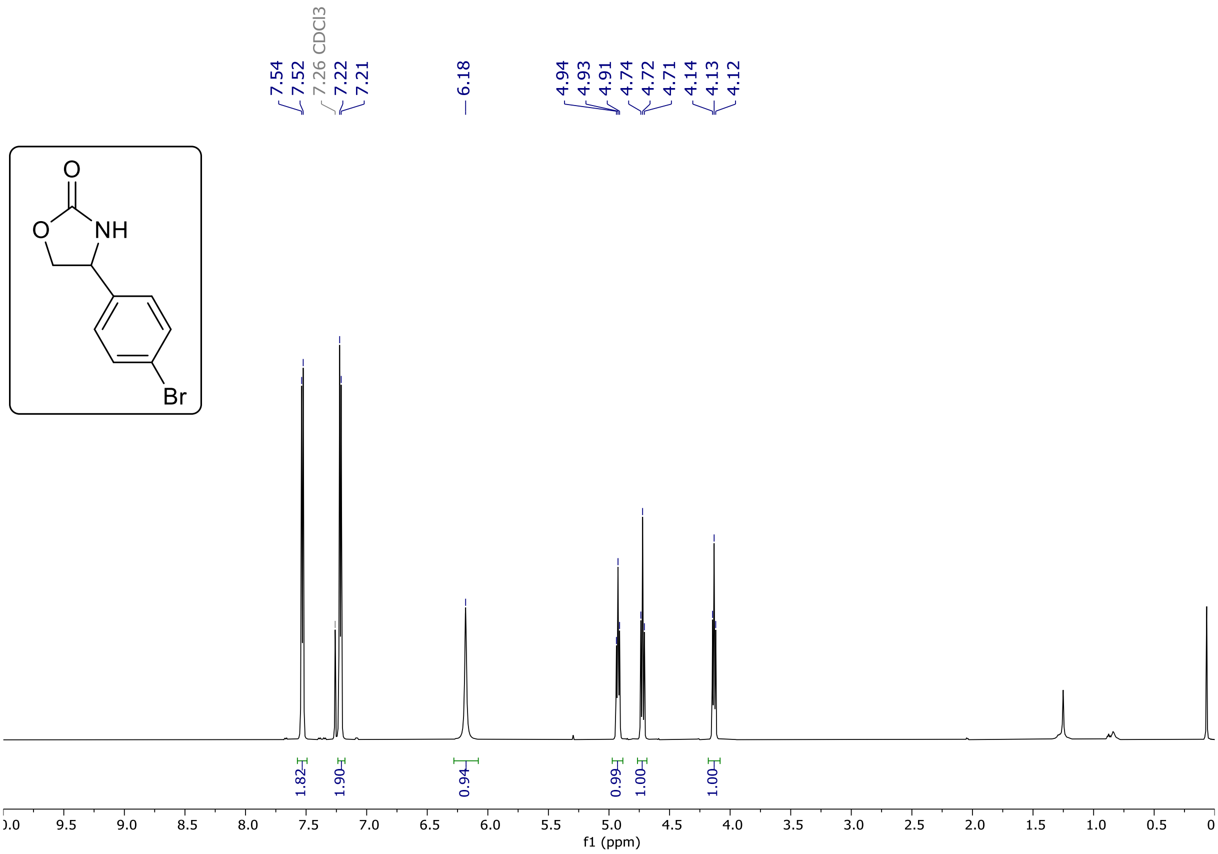
4-(4-Chlorophenyl)oxazolidin-2-one (6b)

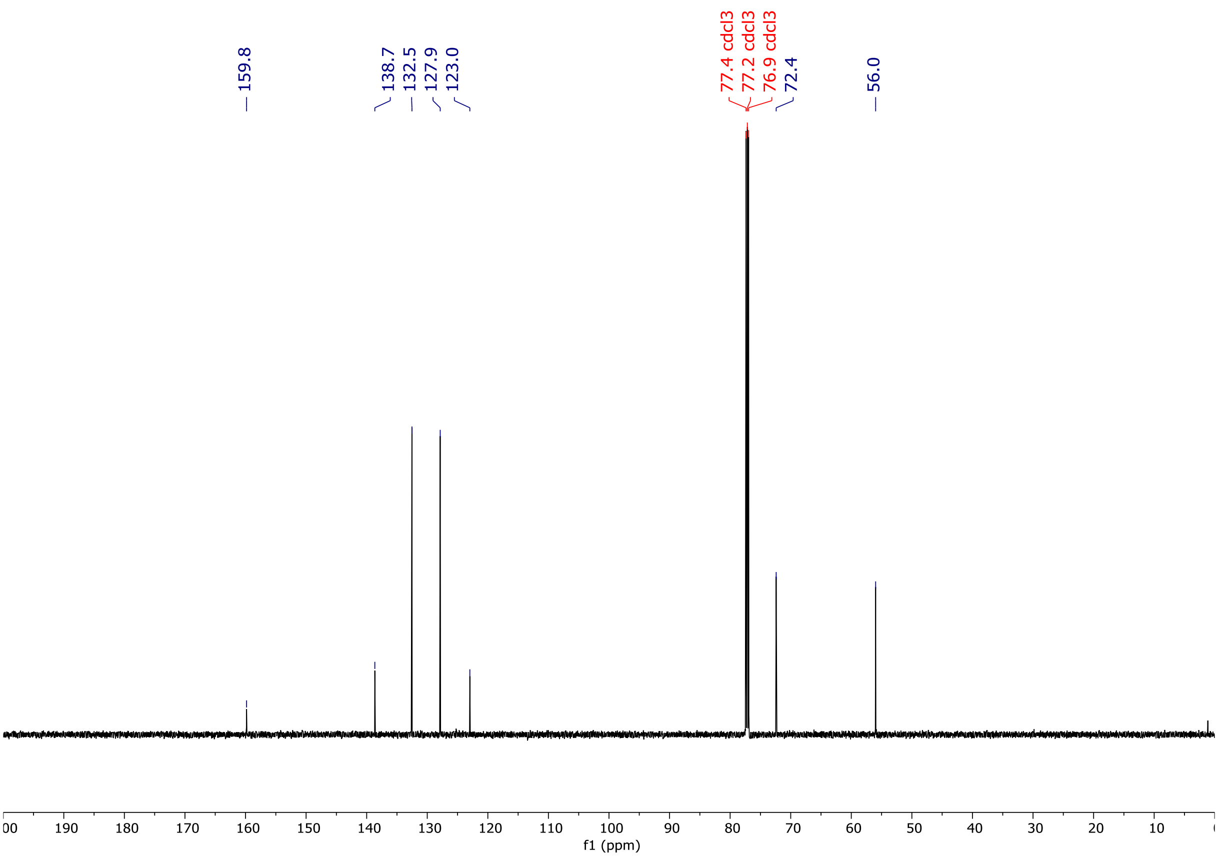




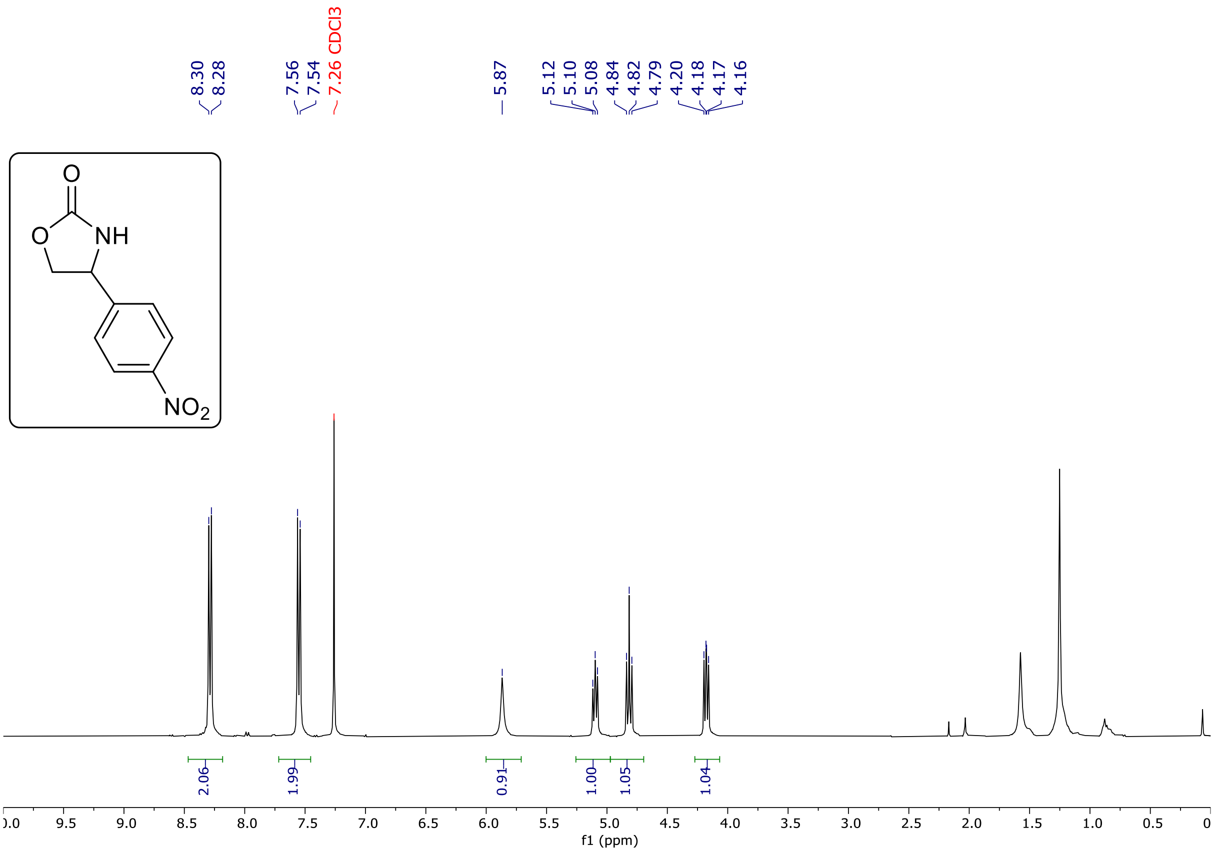


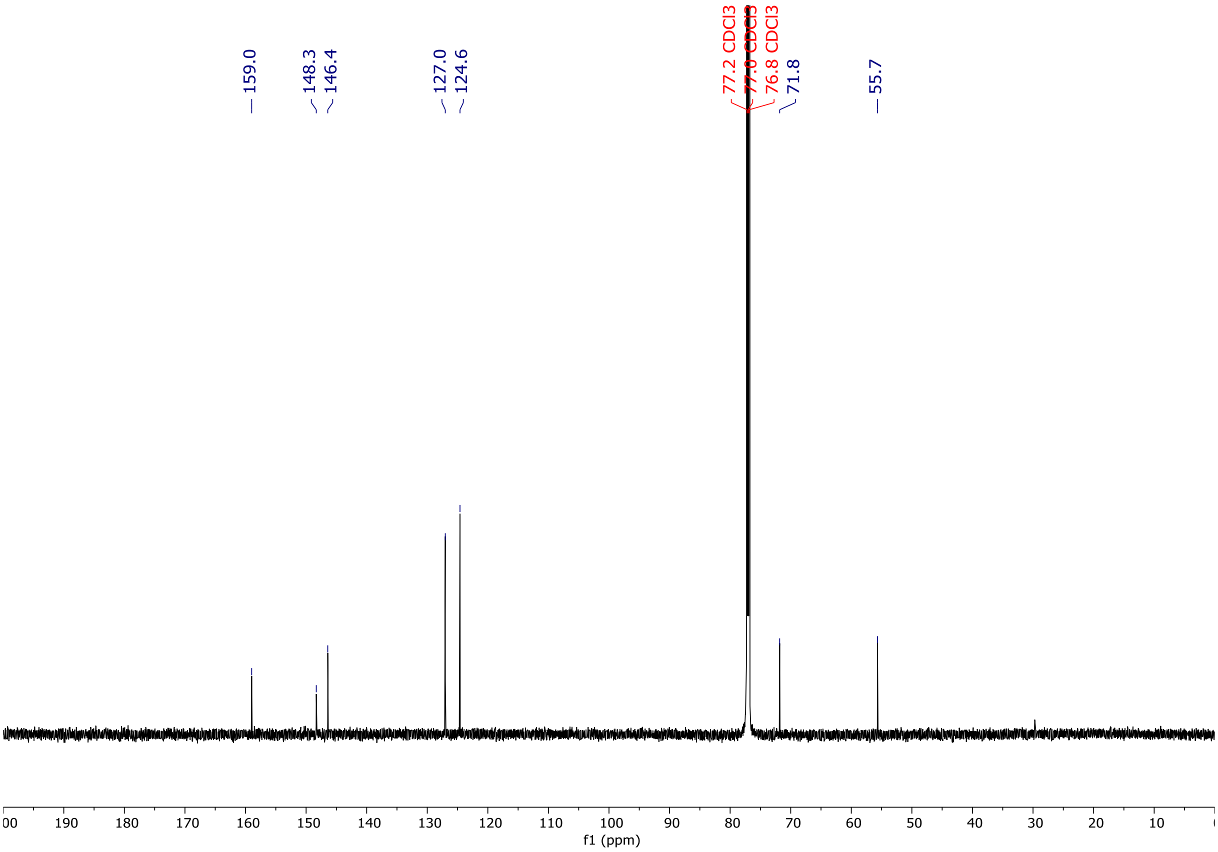
4-(4-Bromophenyl)oxazolidin-2-one (6c)



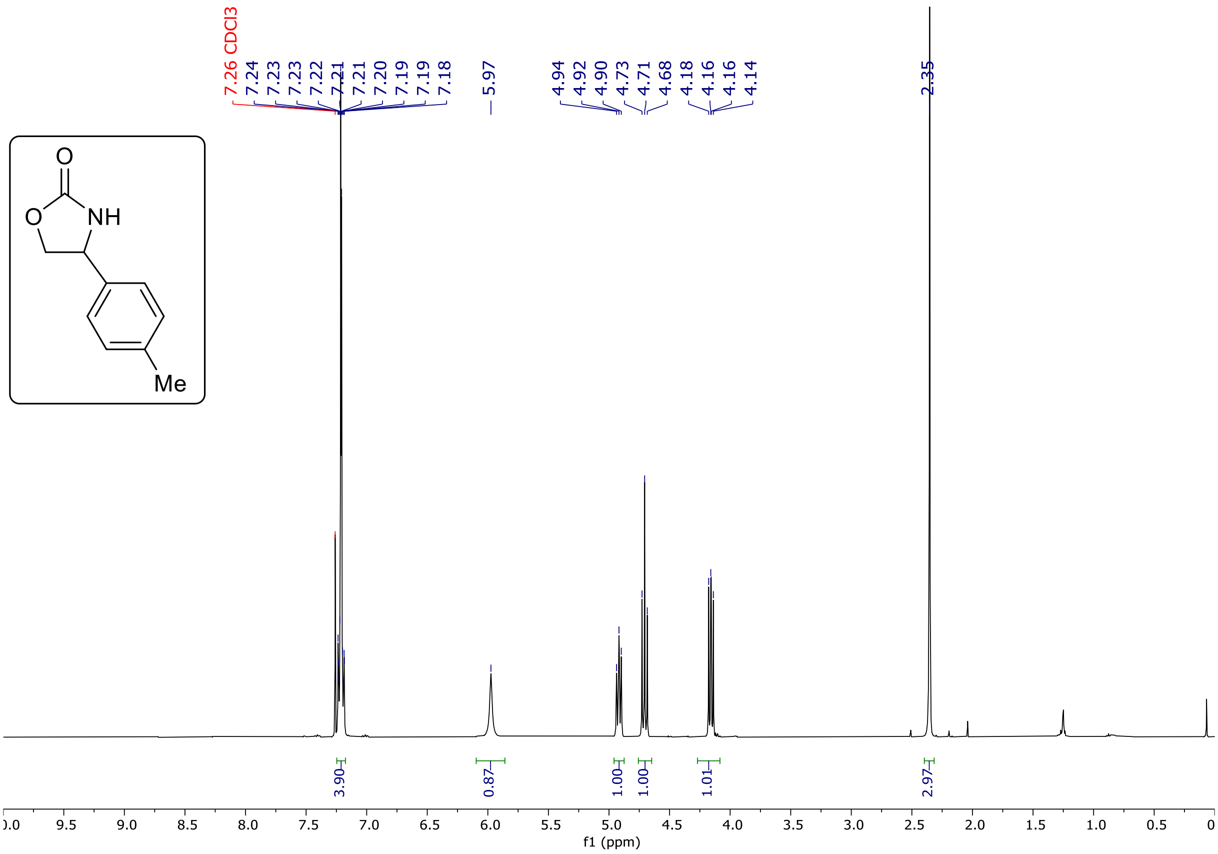


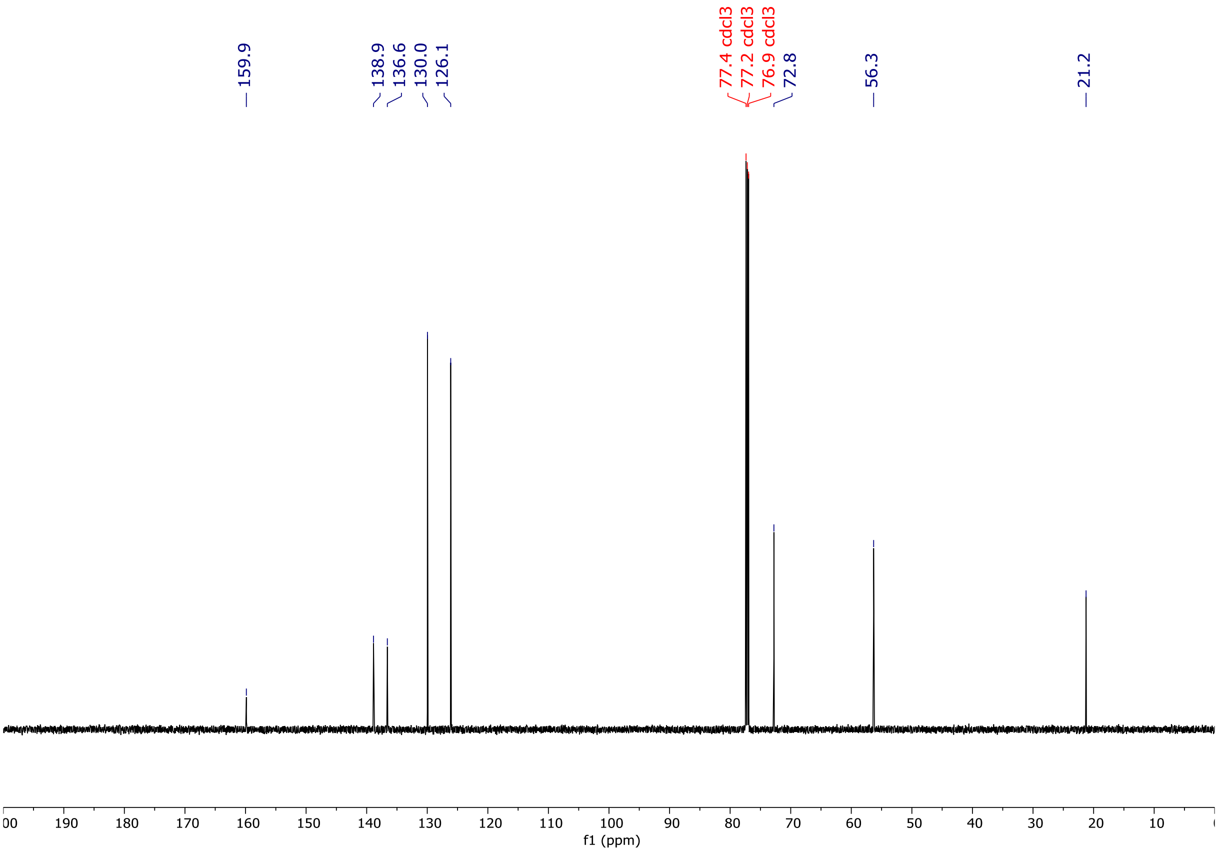
4-(4-Nitrophenyl)oxazolidin-2-one (6d)



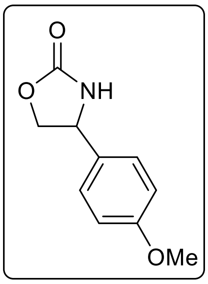


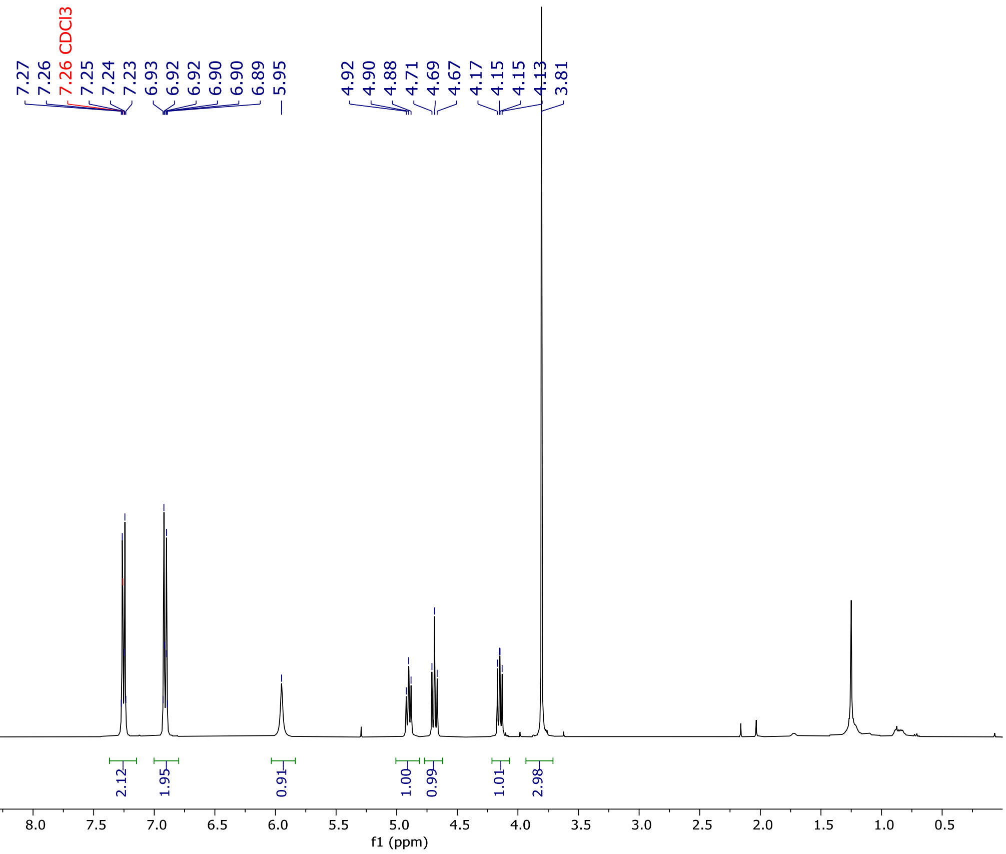
4-(*p*-Tolyl)oxazolidin-2-one (6e)

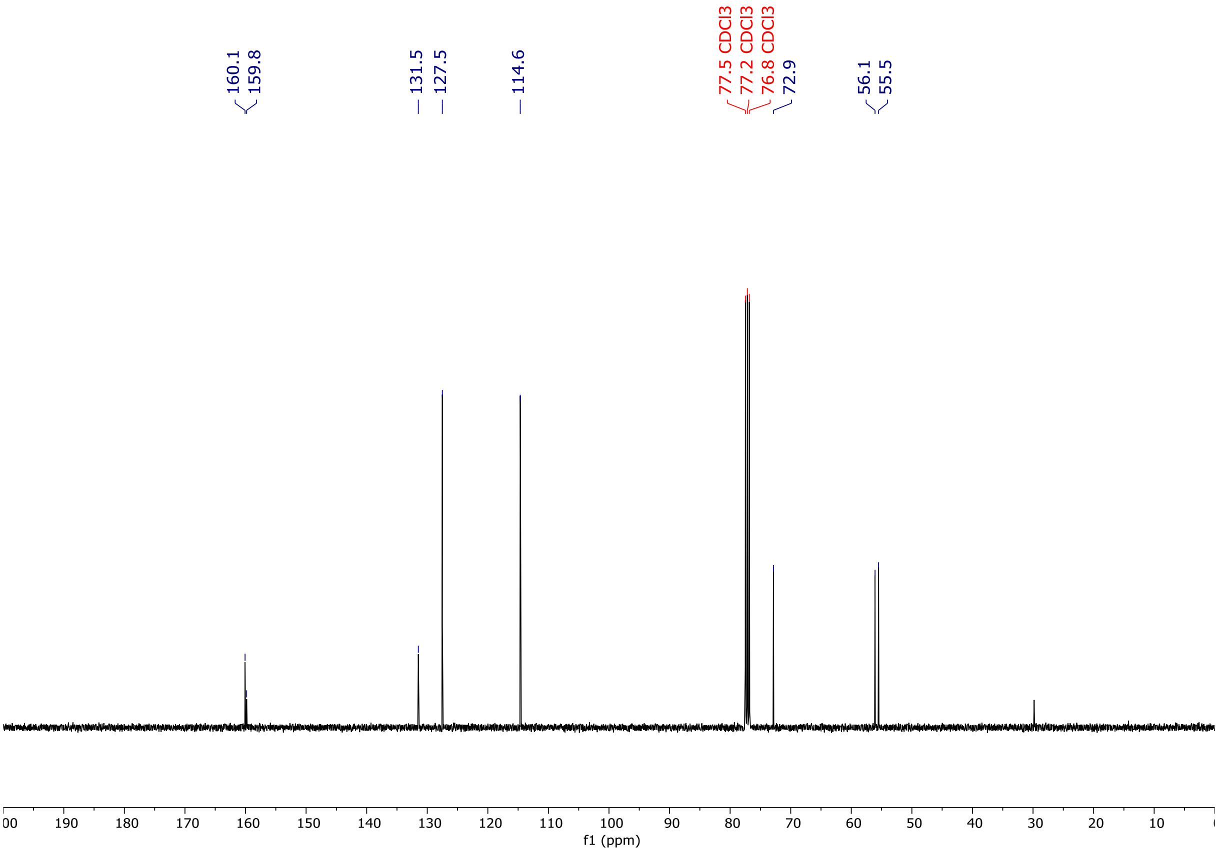




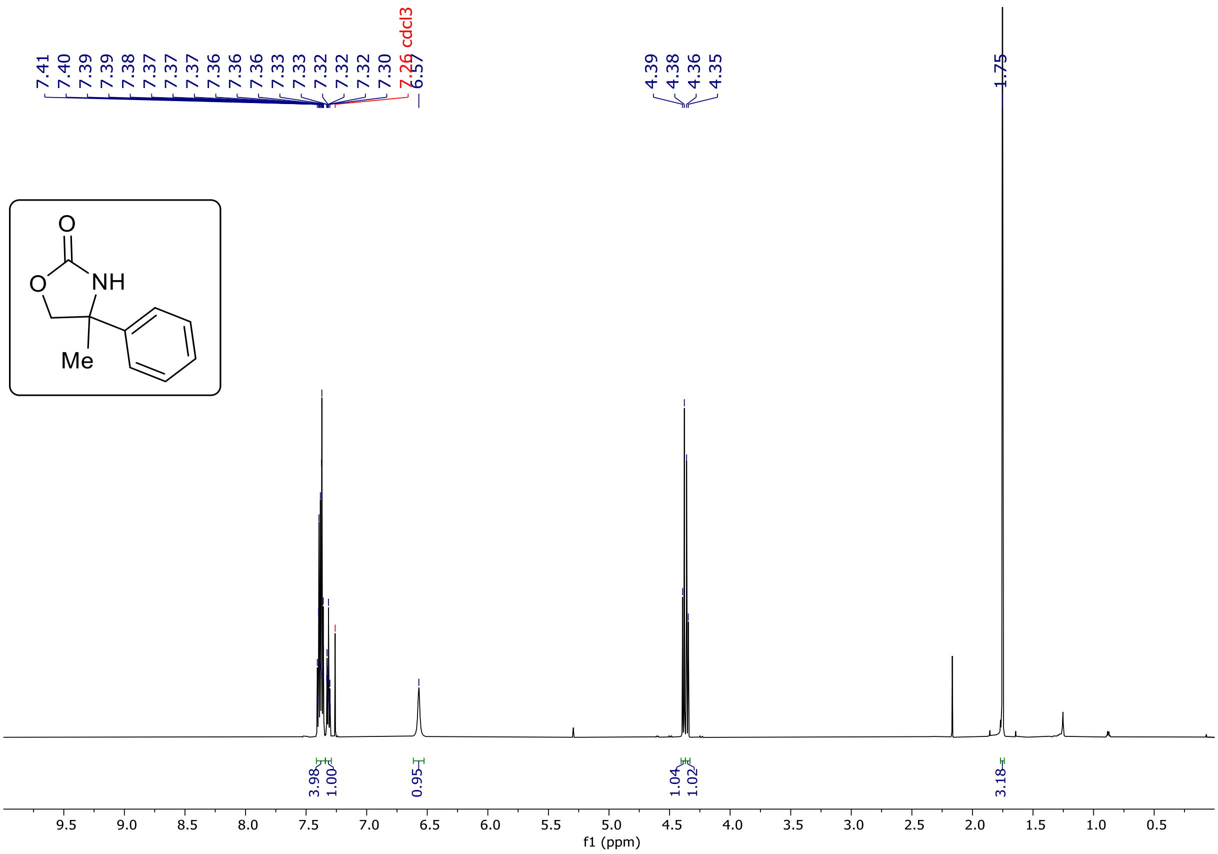
4-(4-Methoxyphenyl)oxazolidin-2-one (6f)

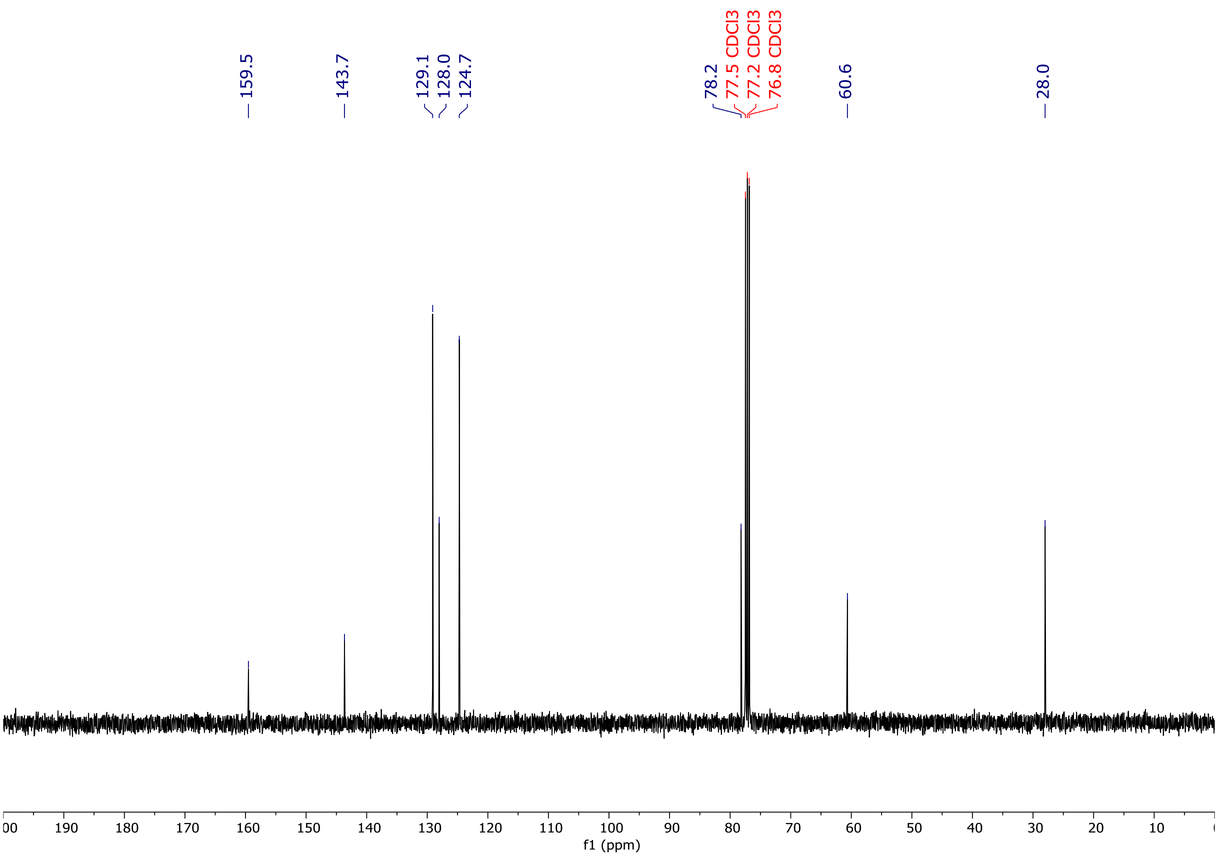




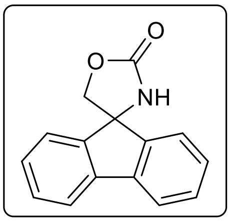


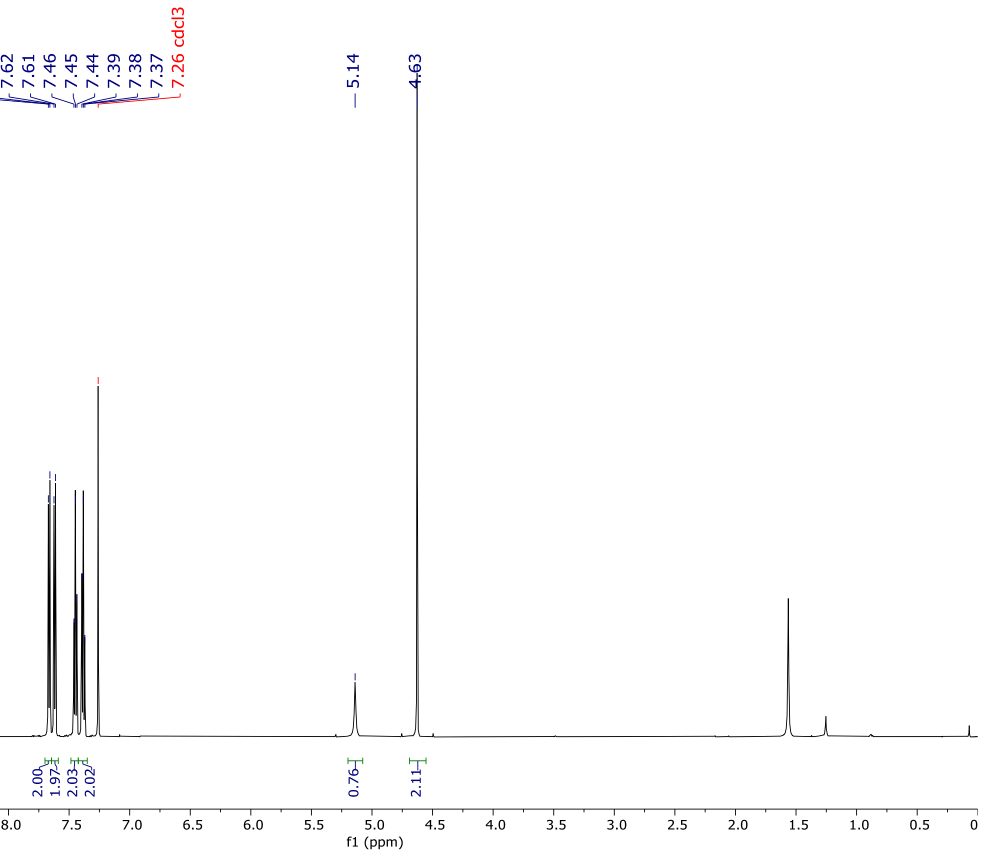
4-Methyl-4-phenyloxazolidin-2-one (8a)

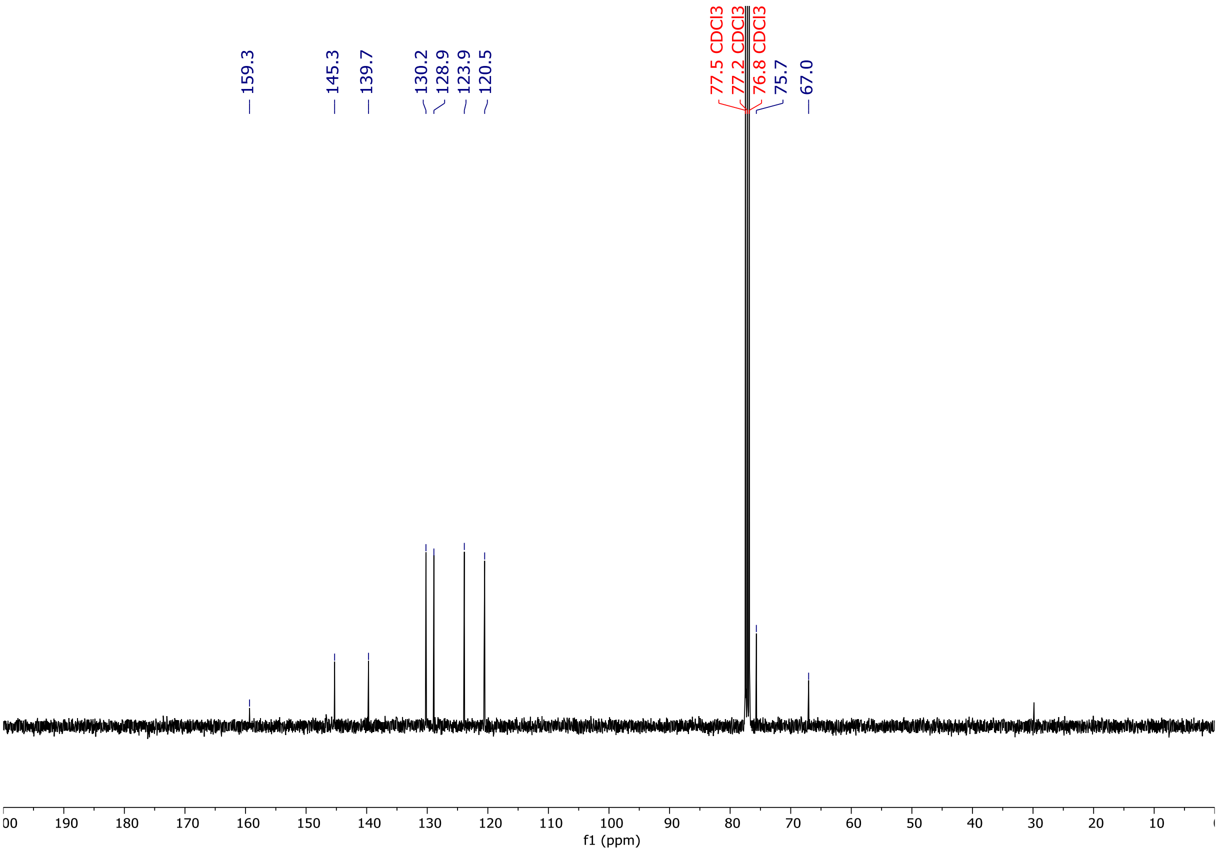




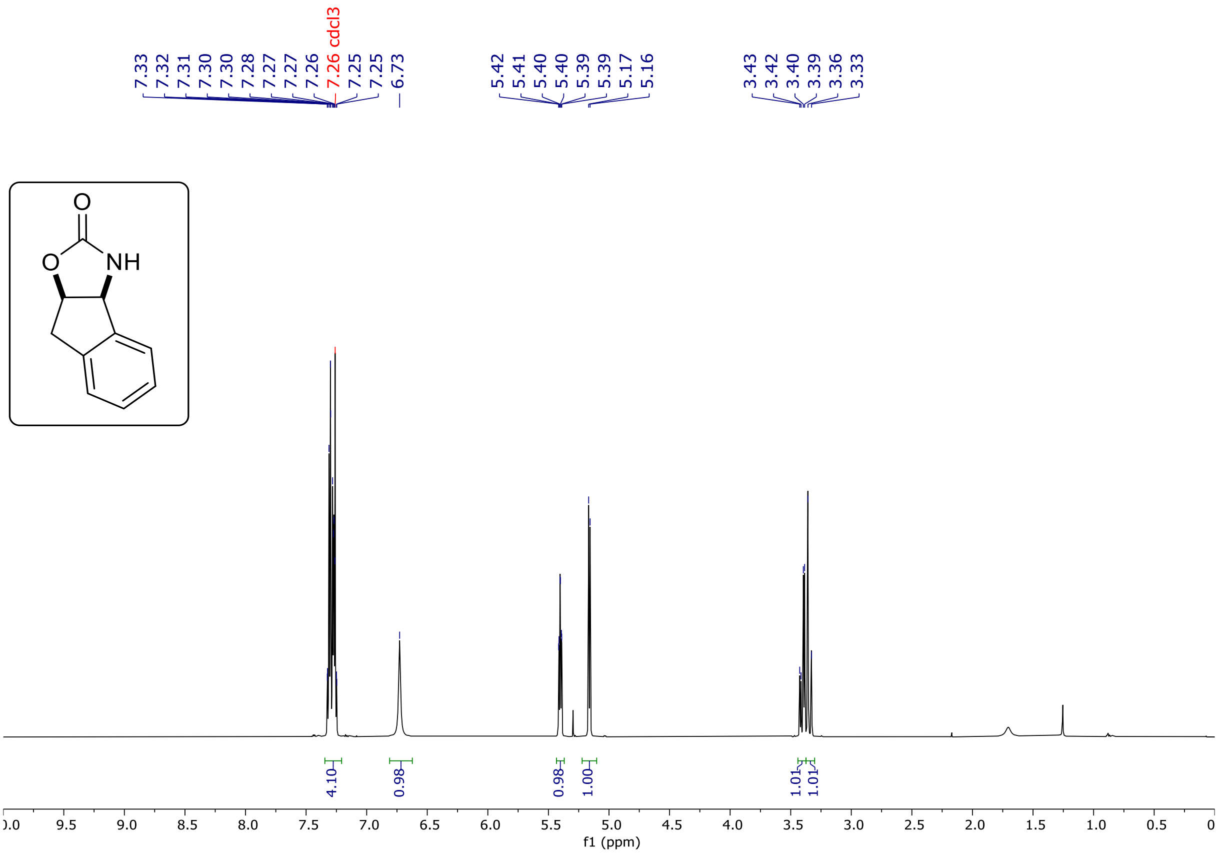
Spiro[fluorene-9,4'-oxazolidin]-2'-one (8b)

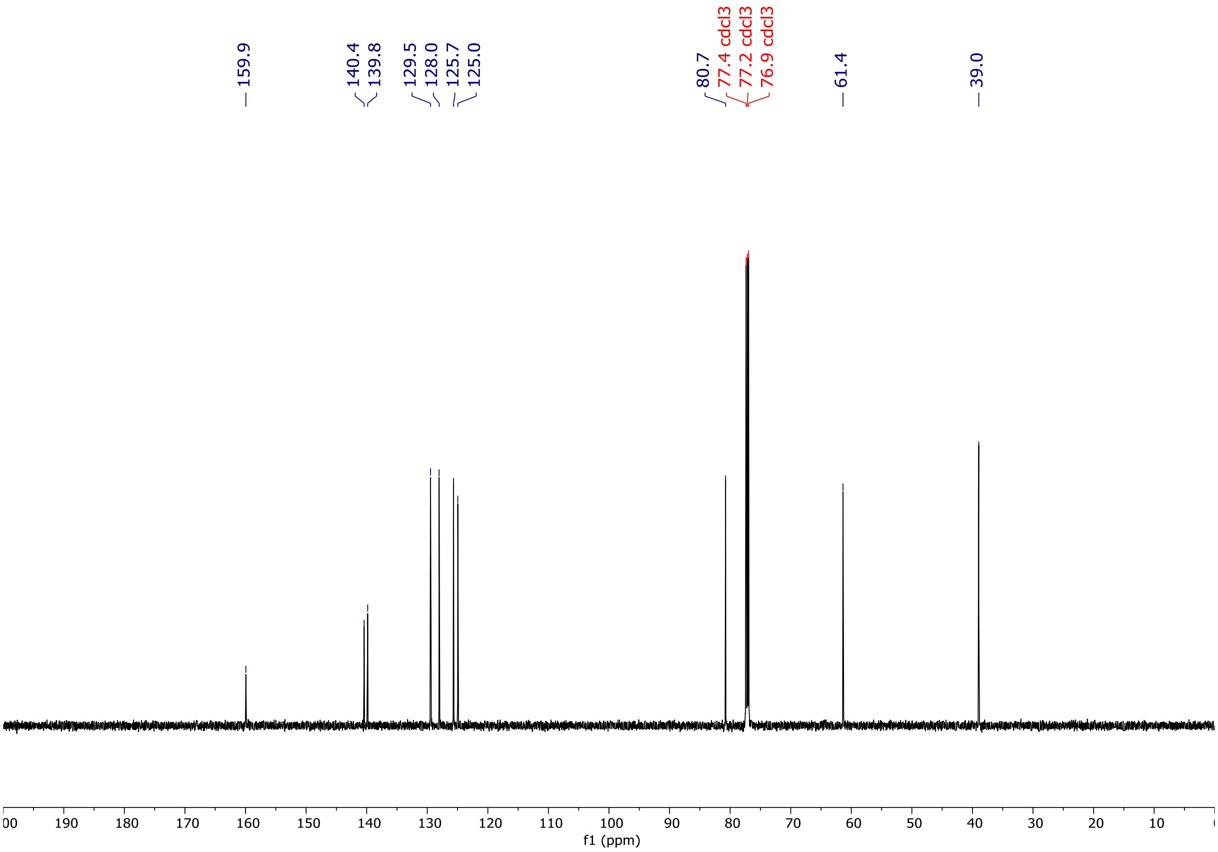




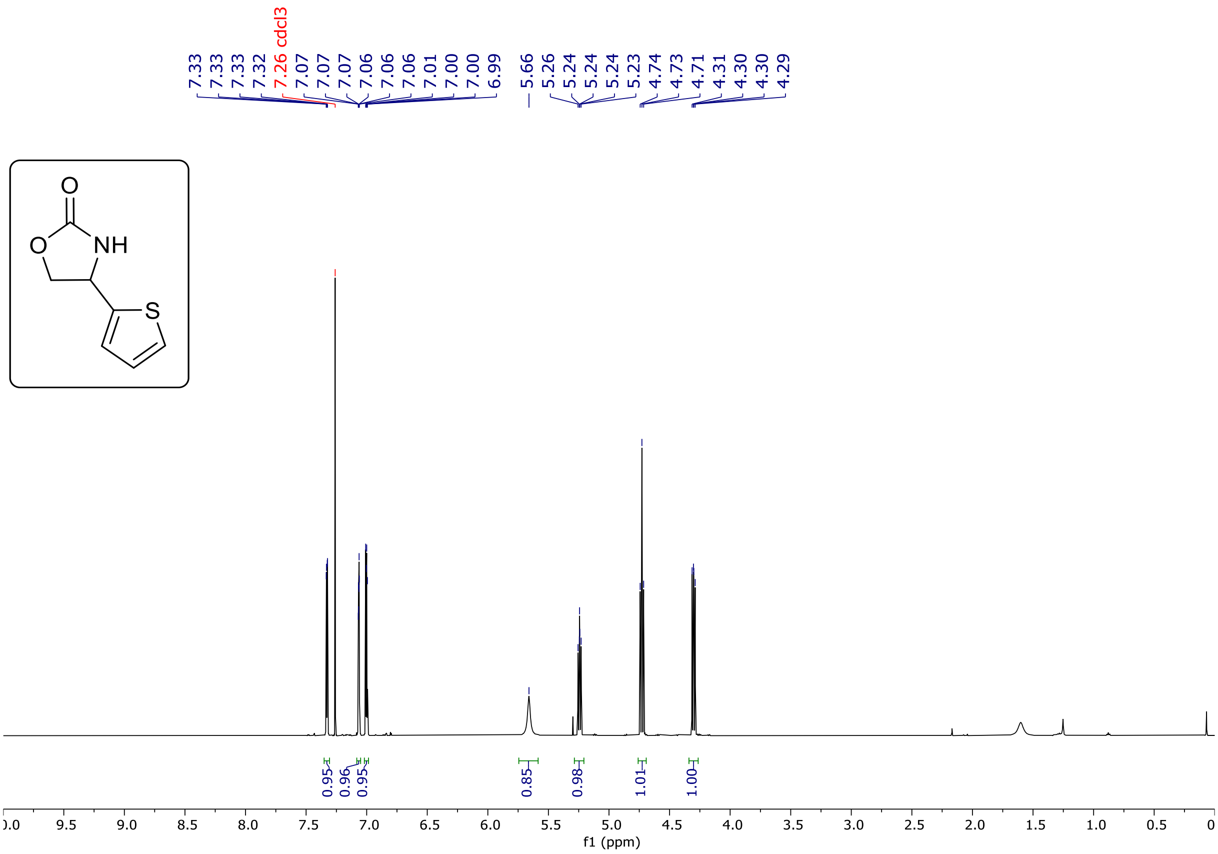


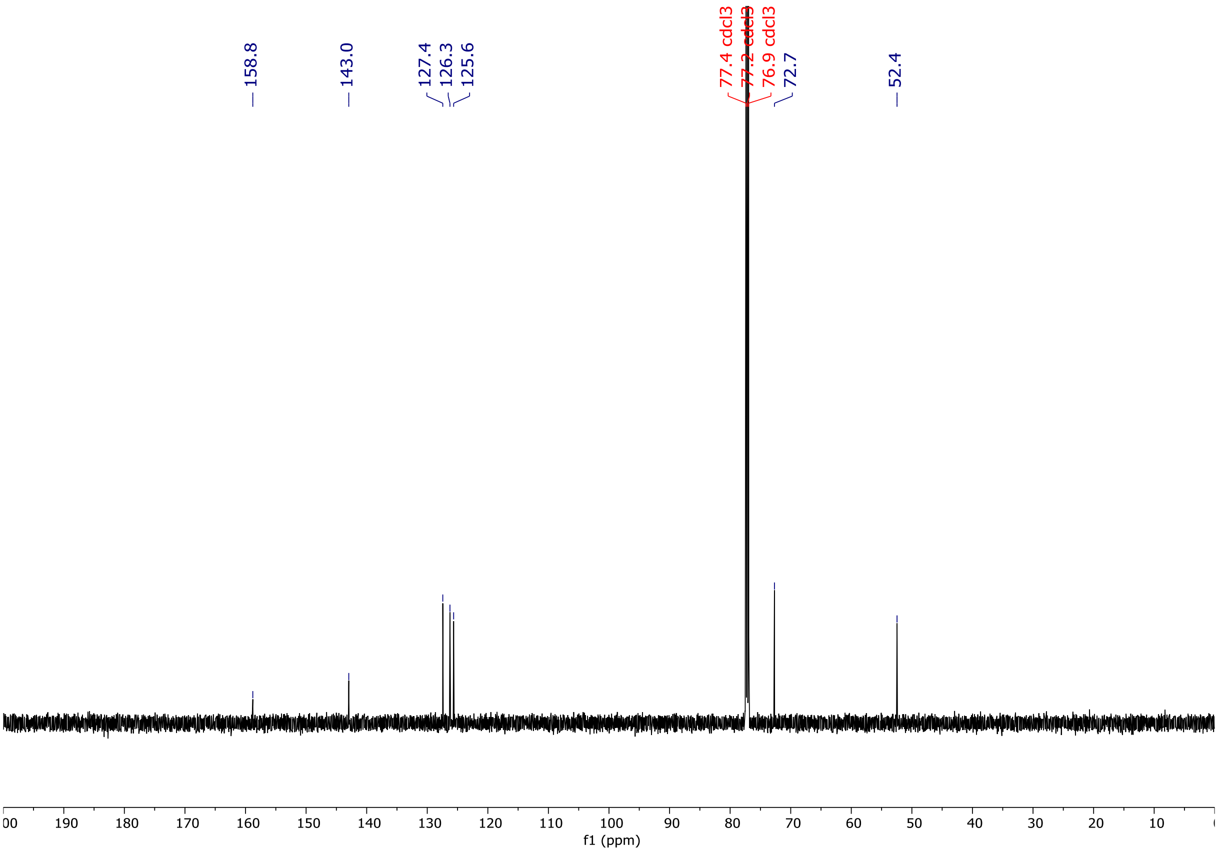
(3a*S,8a*R**)-3,3a,8,8a-Tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one (8c)**



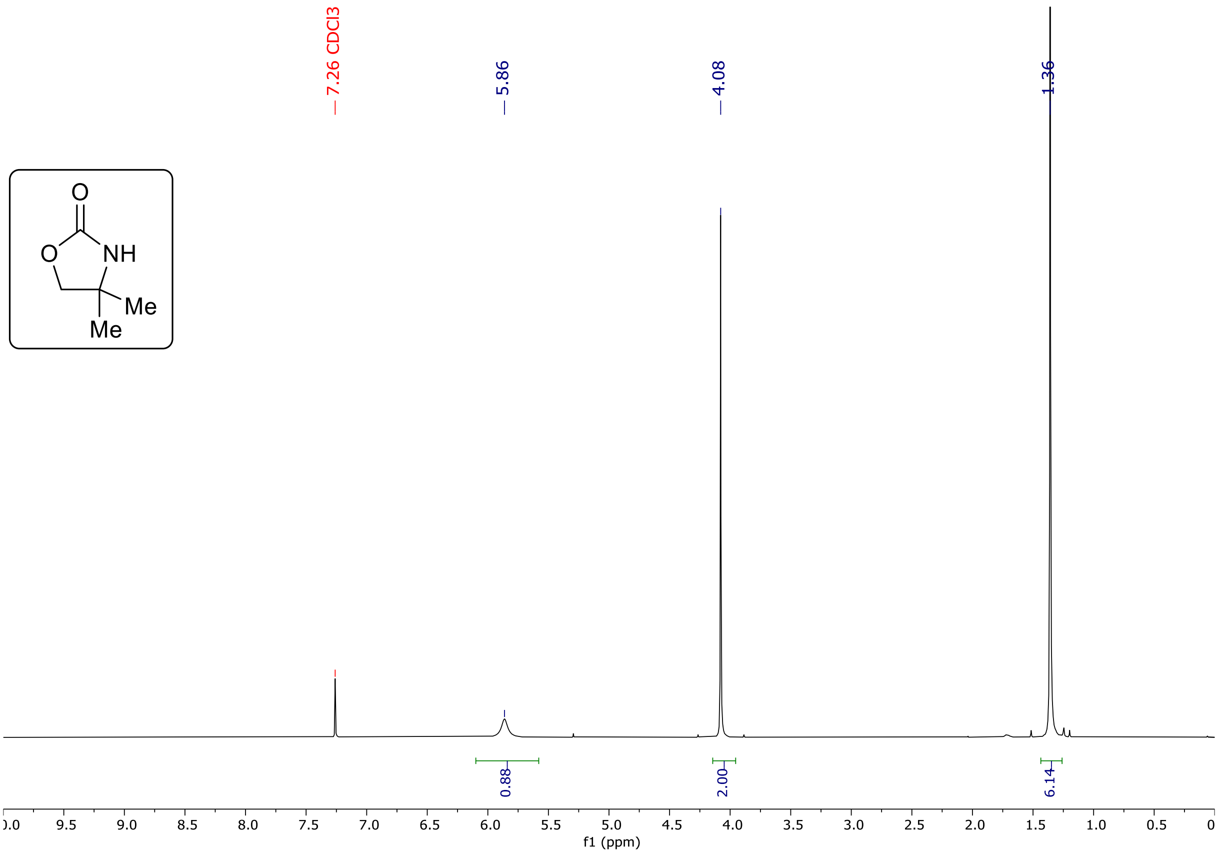


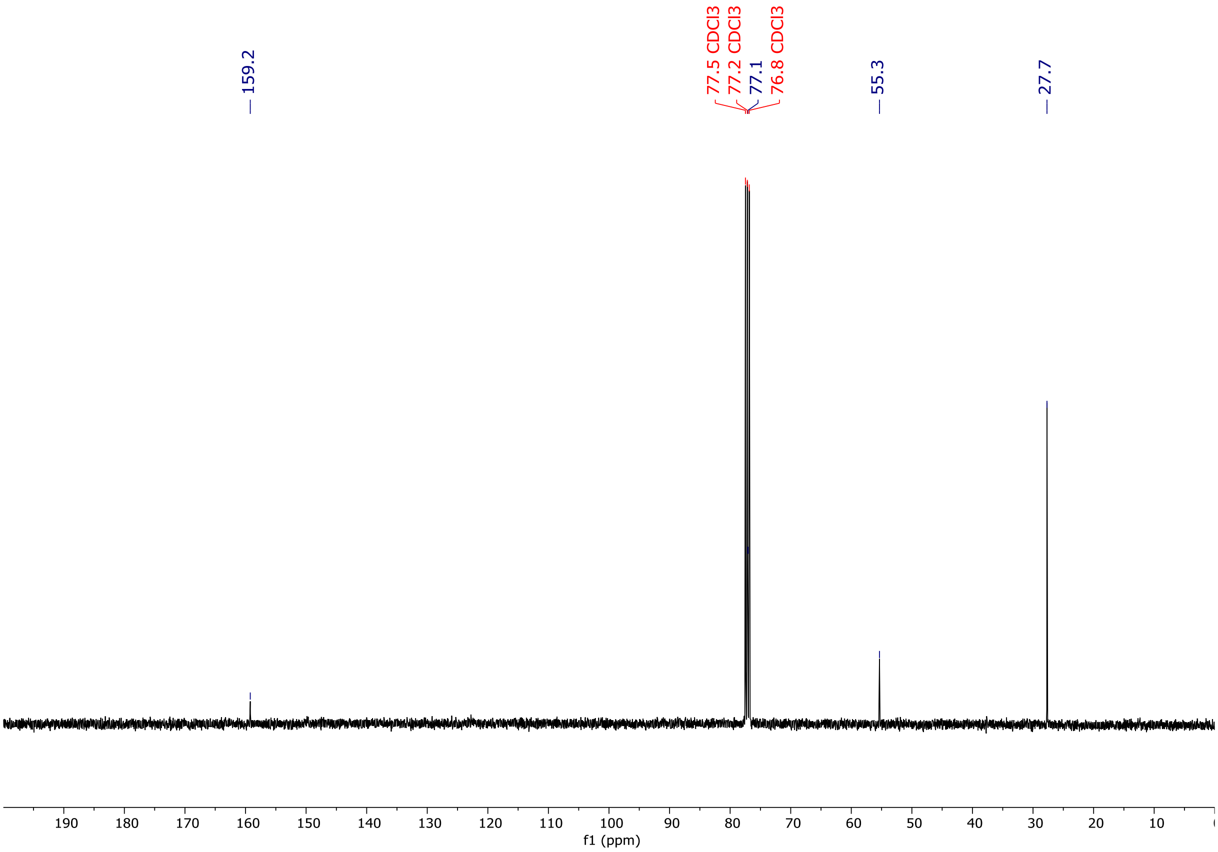
4-(Thiophen-2-yl)oxazolidin-2-one (8d)



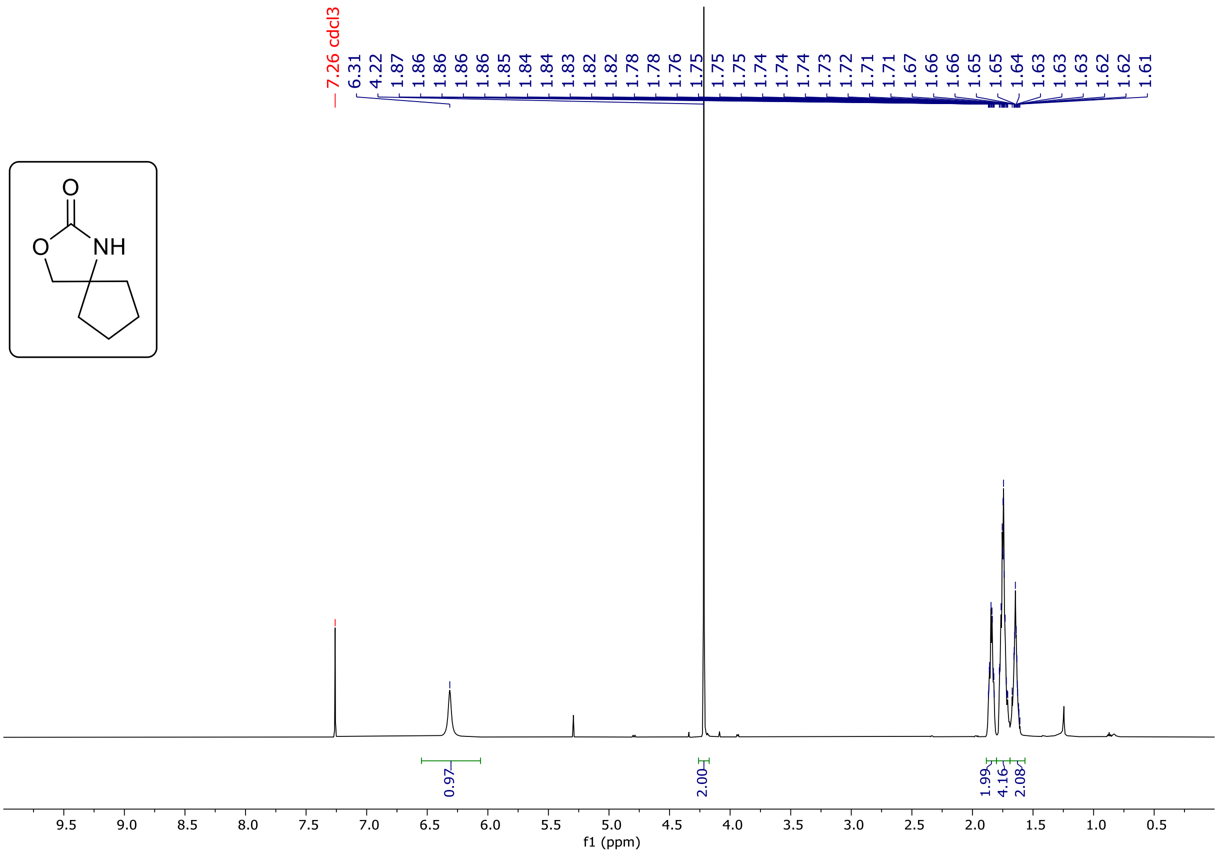


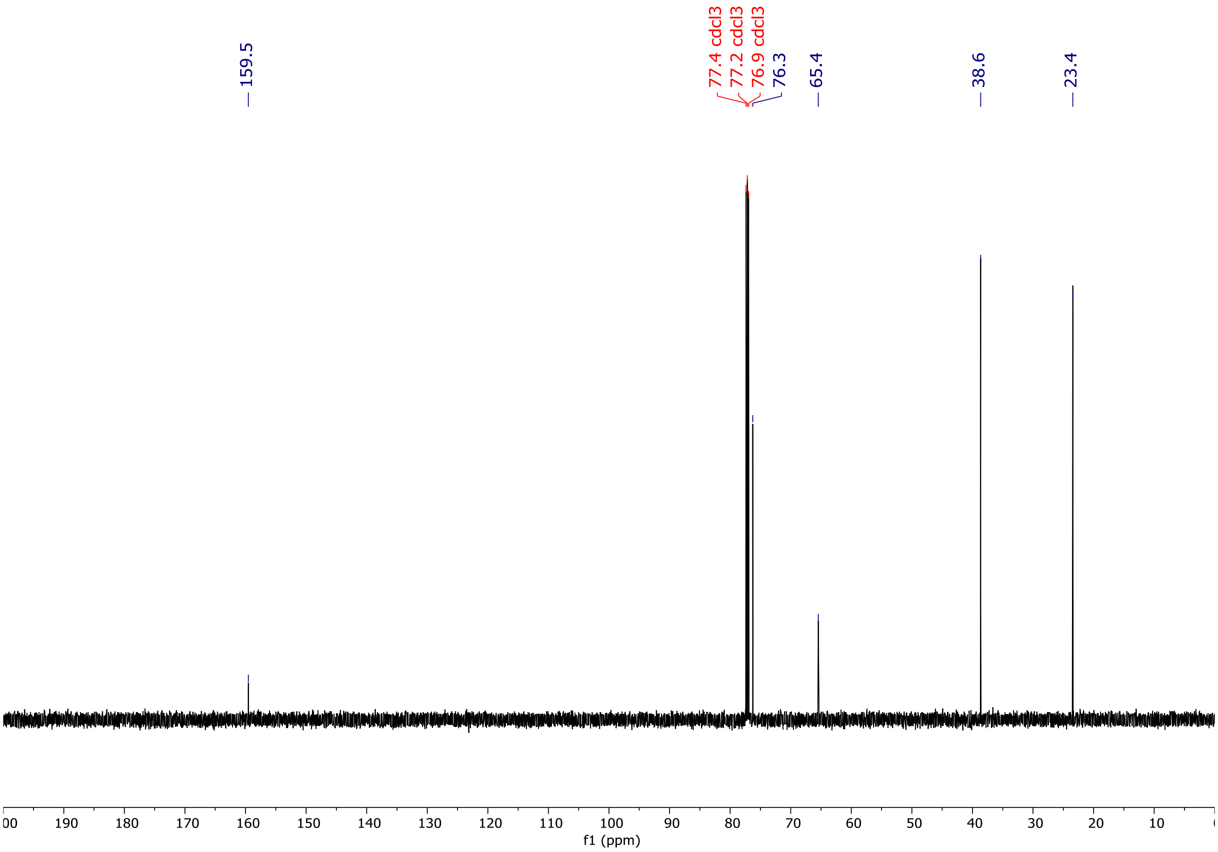
4,4-Dimethyloxazolidin-2-one (8e)



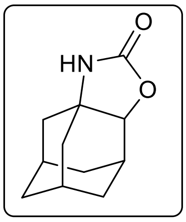


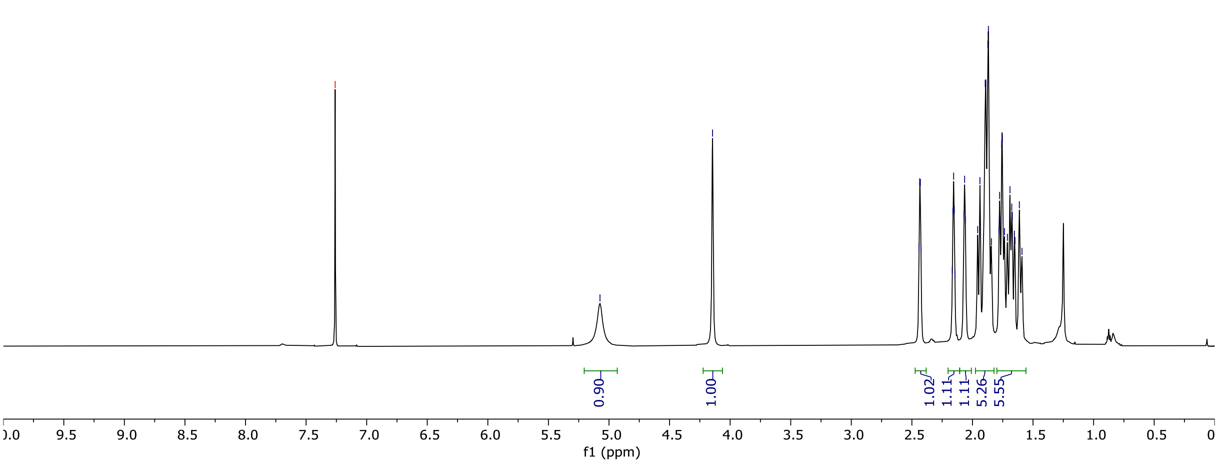
3-Oxa-1-azaspiro[4.4]nonan-2-one (8f)

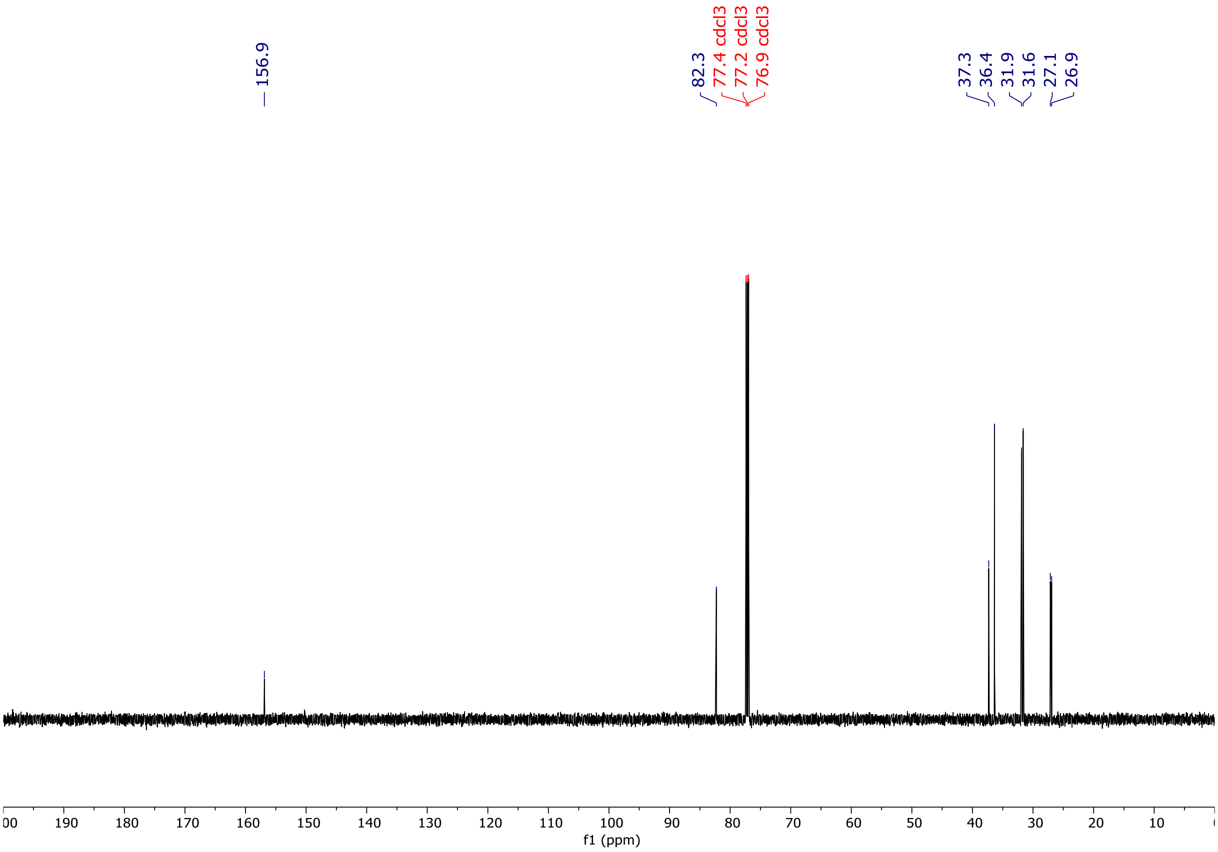




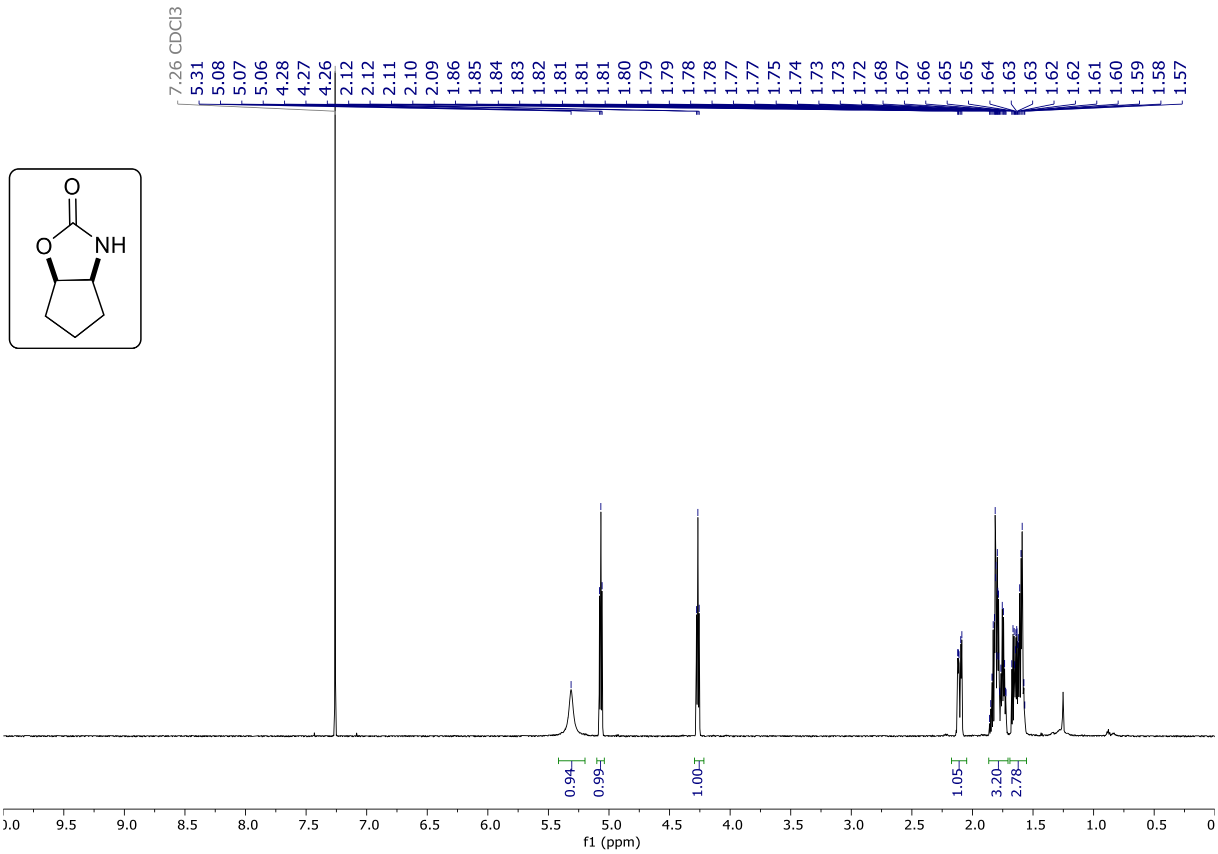
(3a*s*,5*R*,7*S*,9*s*)-hexahydro-4*H*-3a,7:5,9-dimethanocycloocta[*d*]oxazol-2(3*H*)-one (8g)

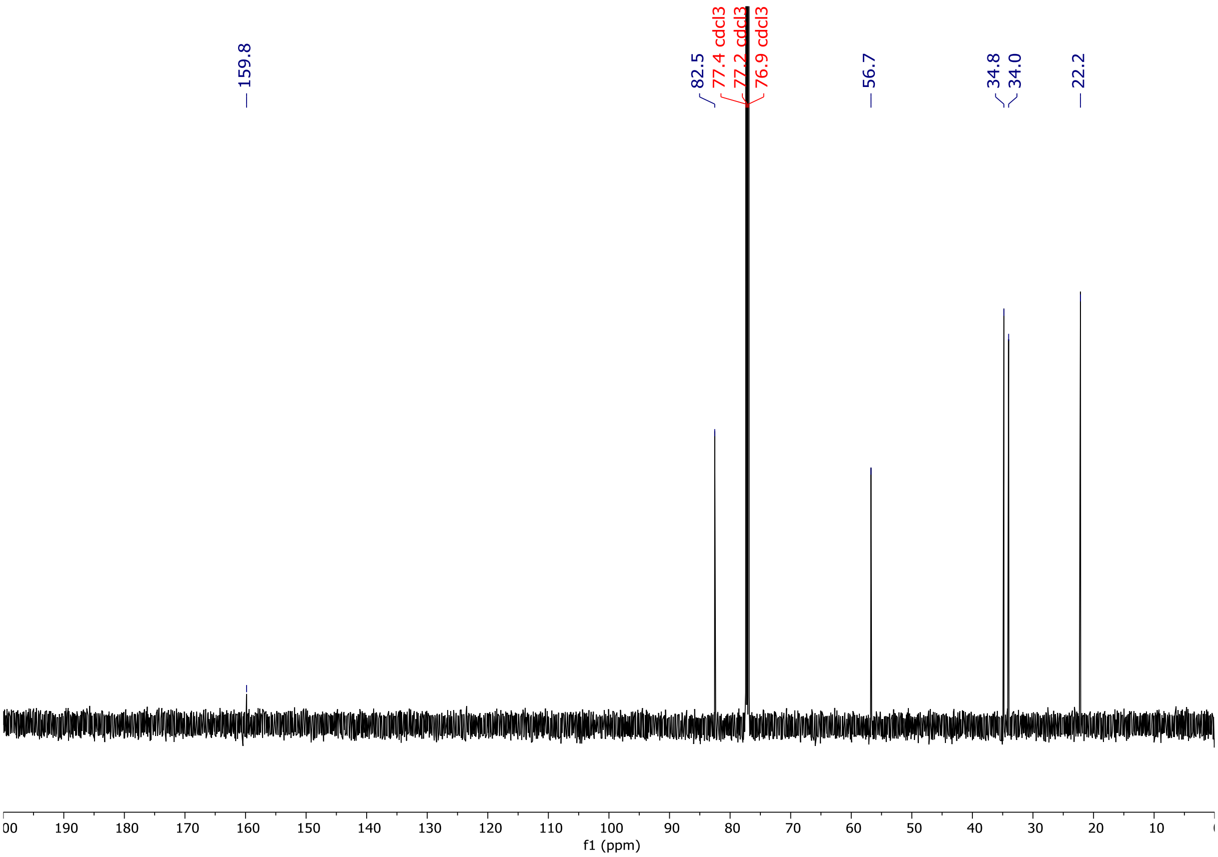




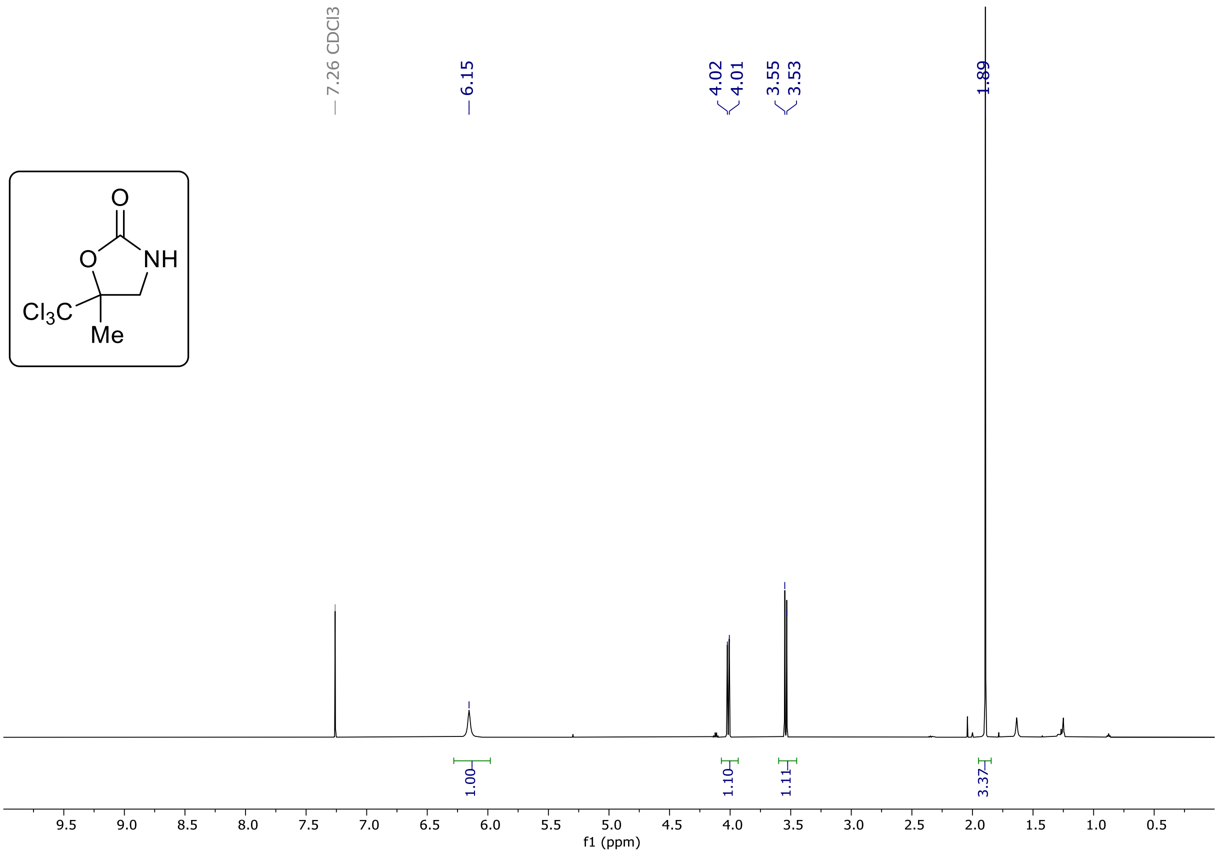


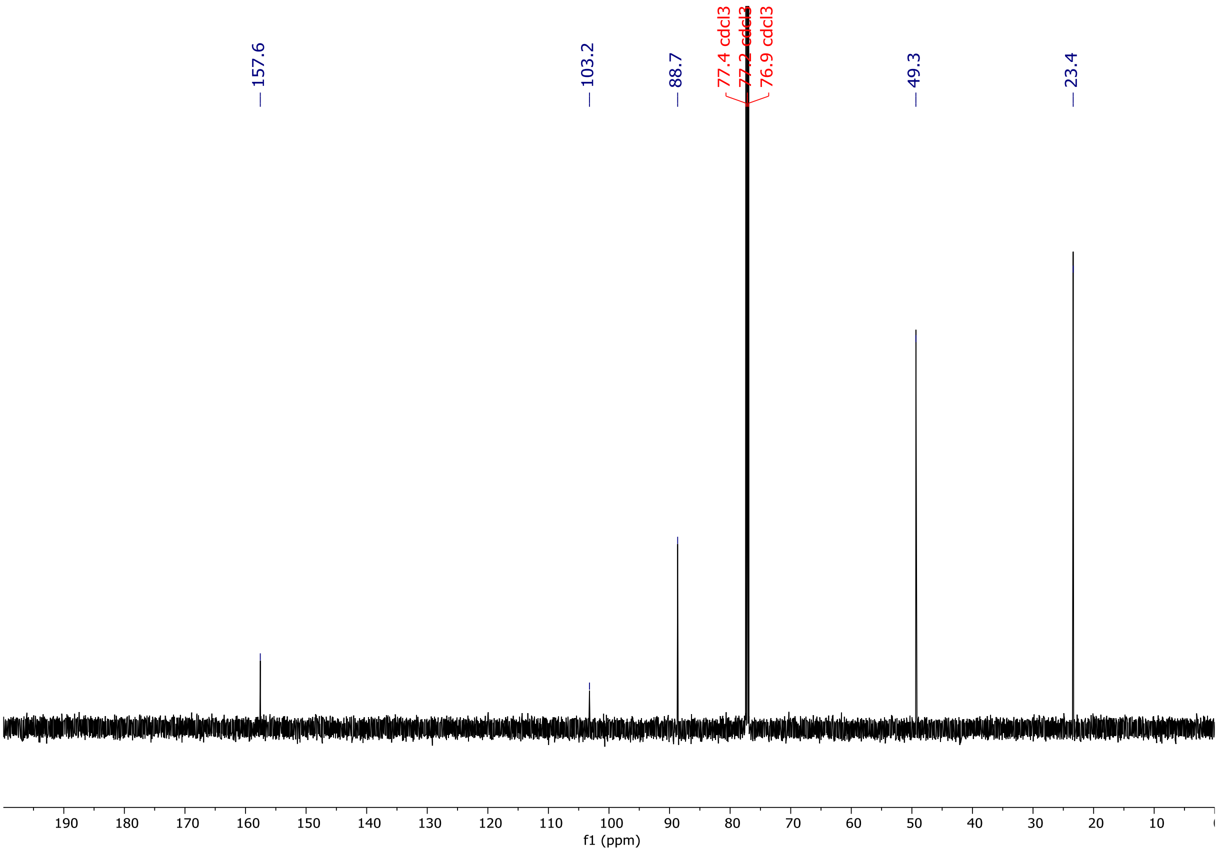
(3a*S,6a*R**)-Hexahydro-2*H*-cyclopenta[*d*]oxazol-2-one (8h)**



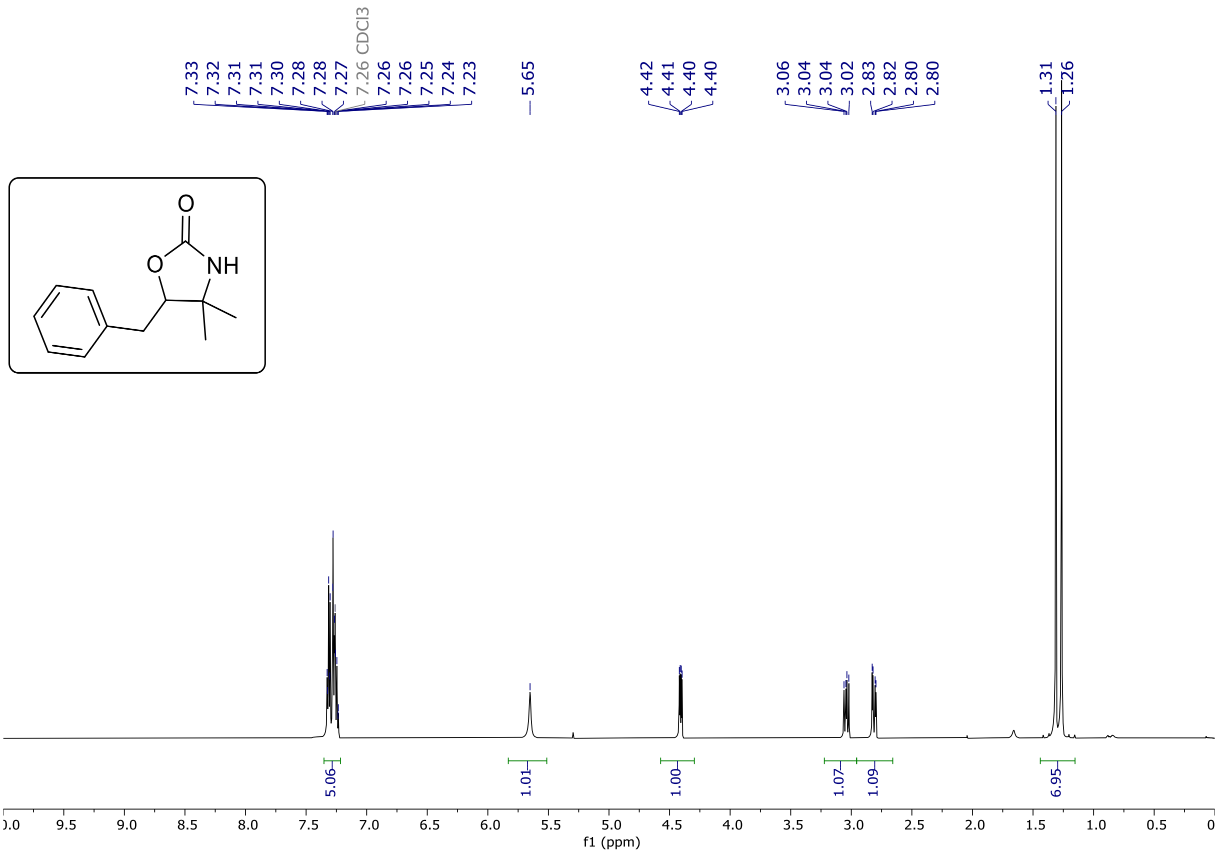


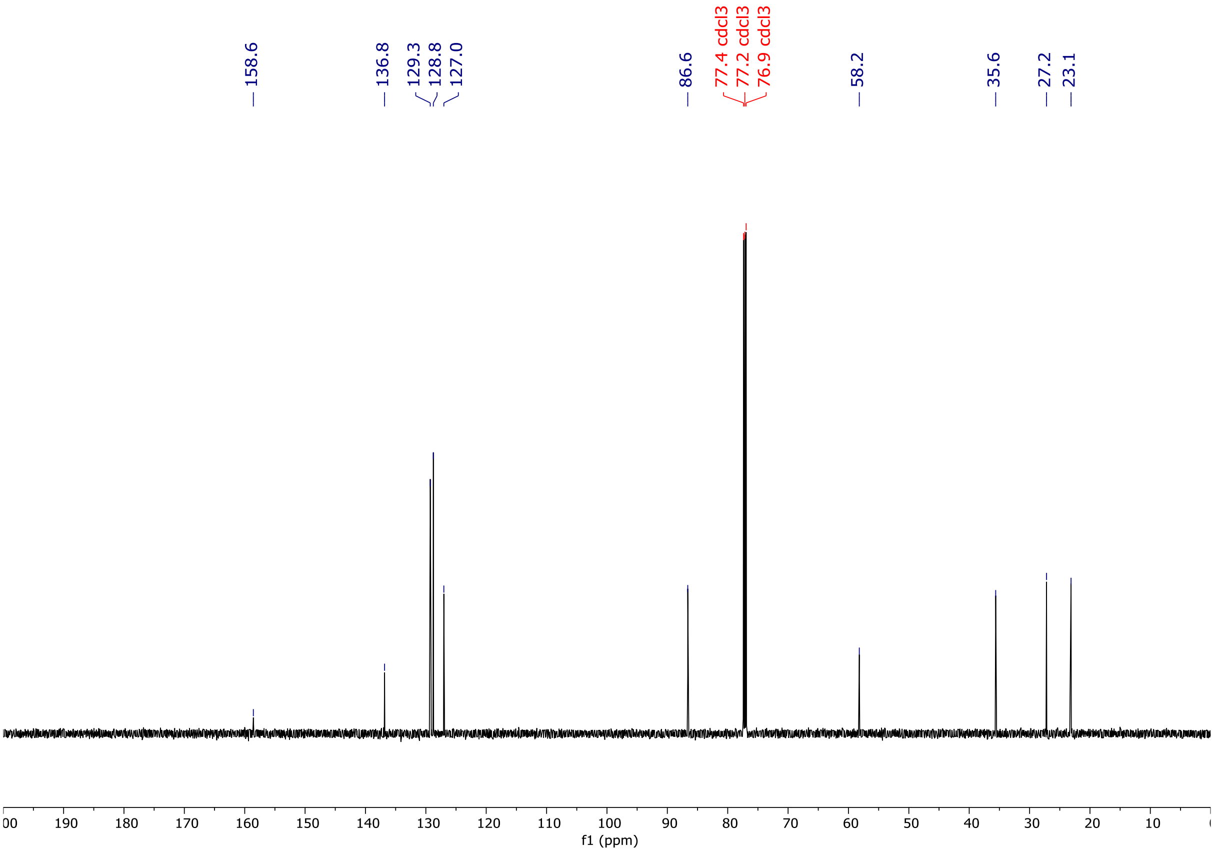
5-Methyl-5-(trichloromethyl)oxazolidin-2-one (8i)



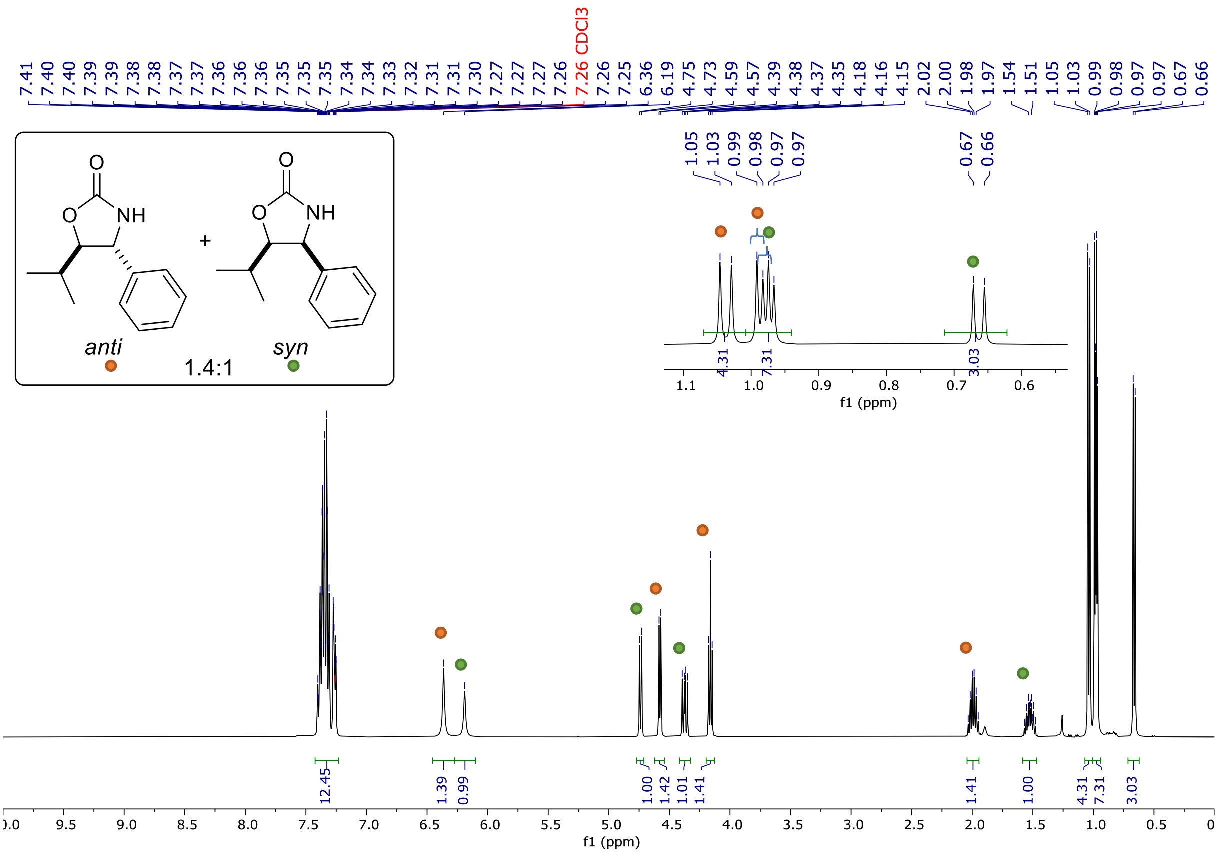


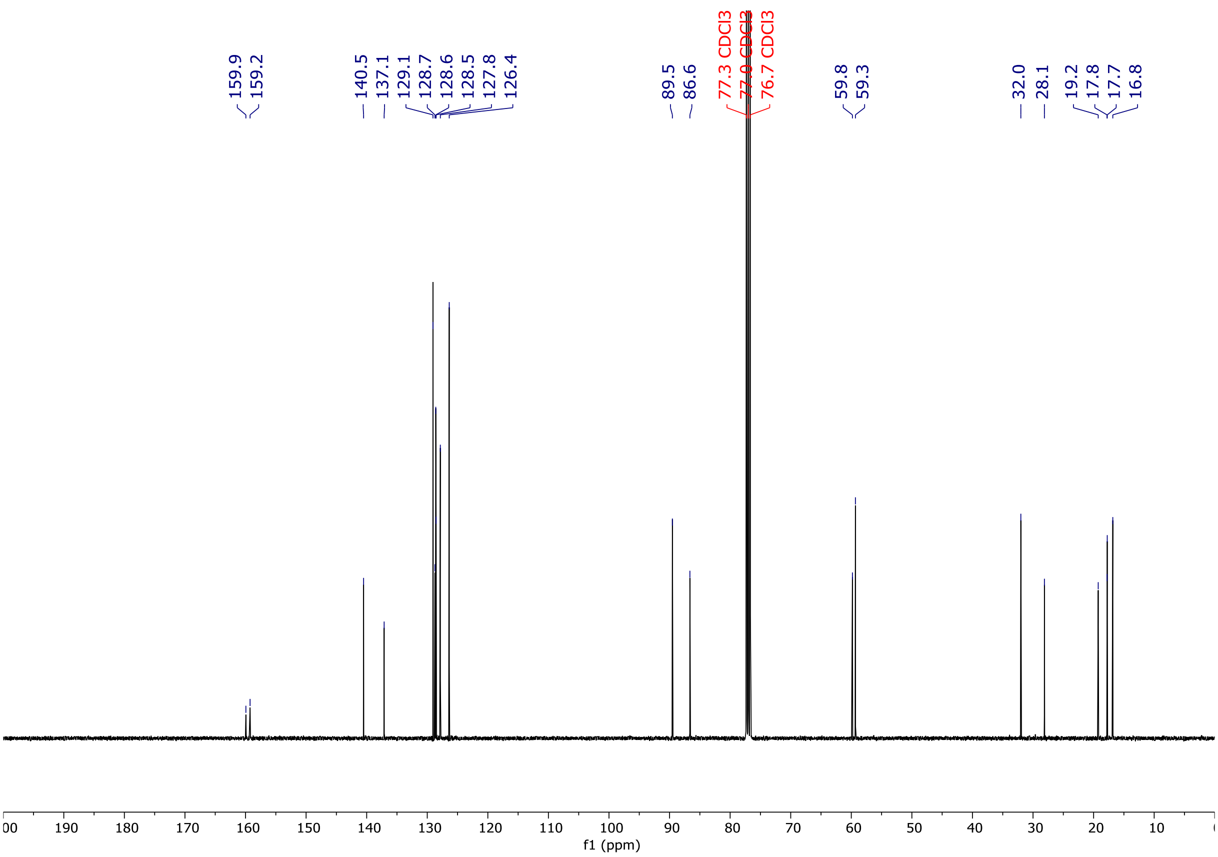
5-Benzyl-4,4-dimethyloxazolidin-2-one (8j)



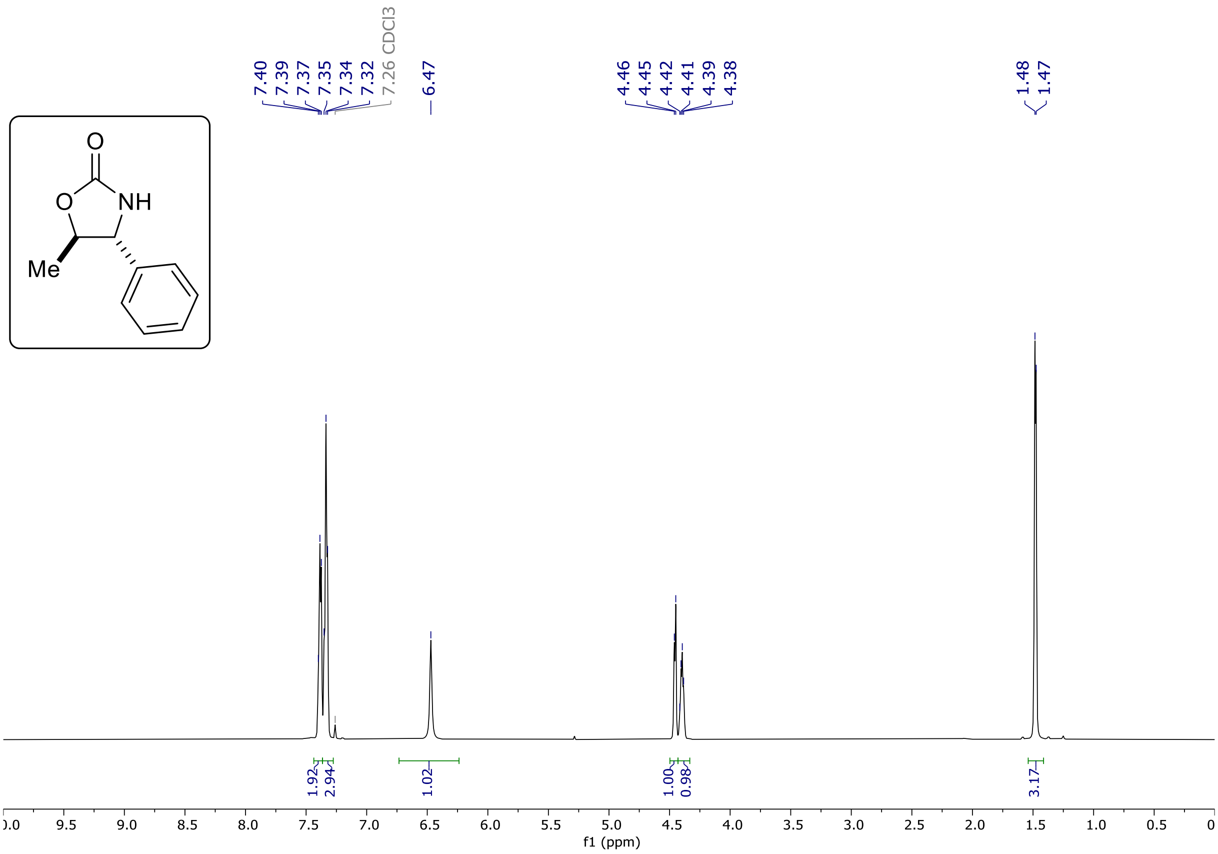


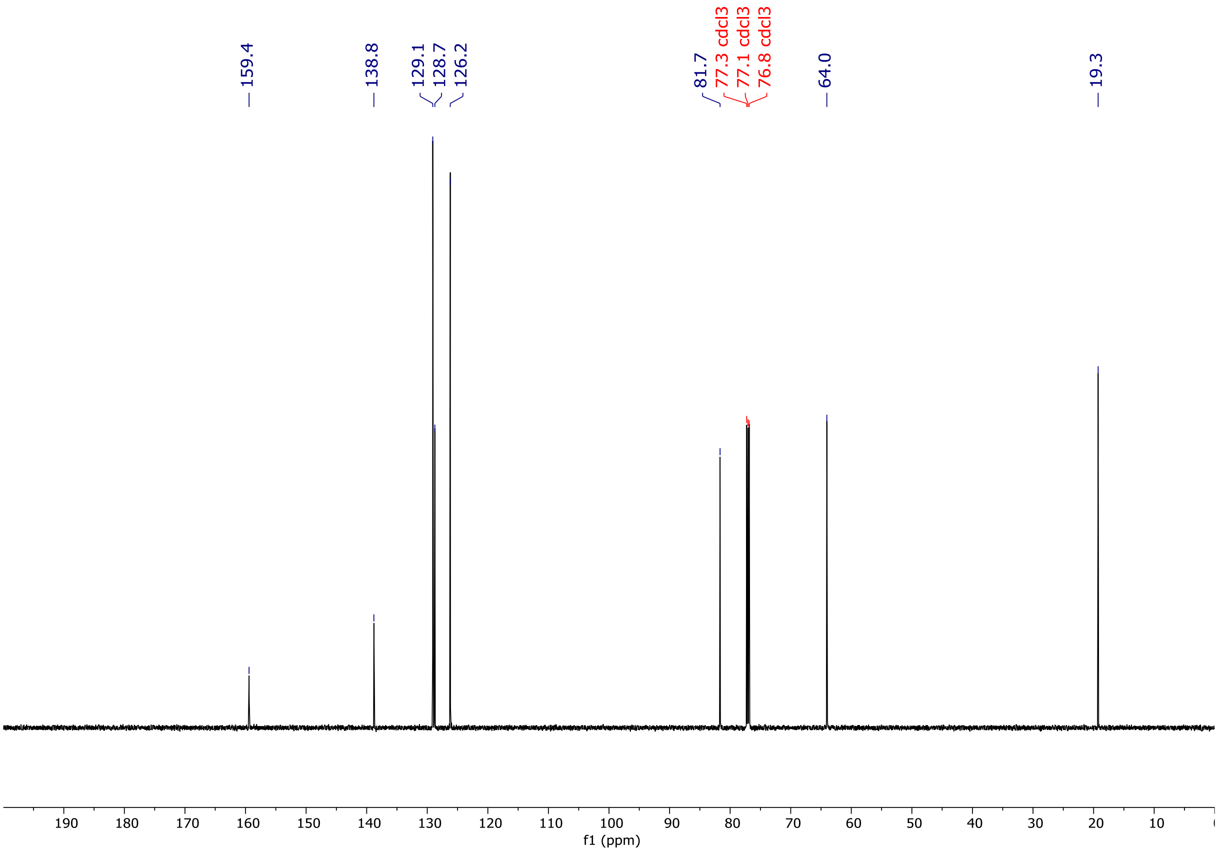
5-Isopropyl-4-phenyloxazolidin-2-one (8j')



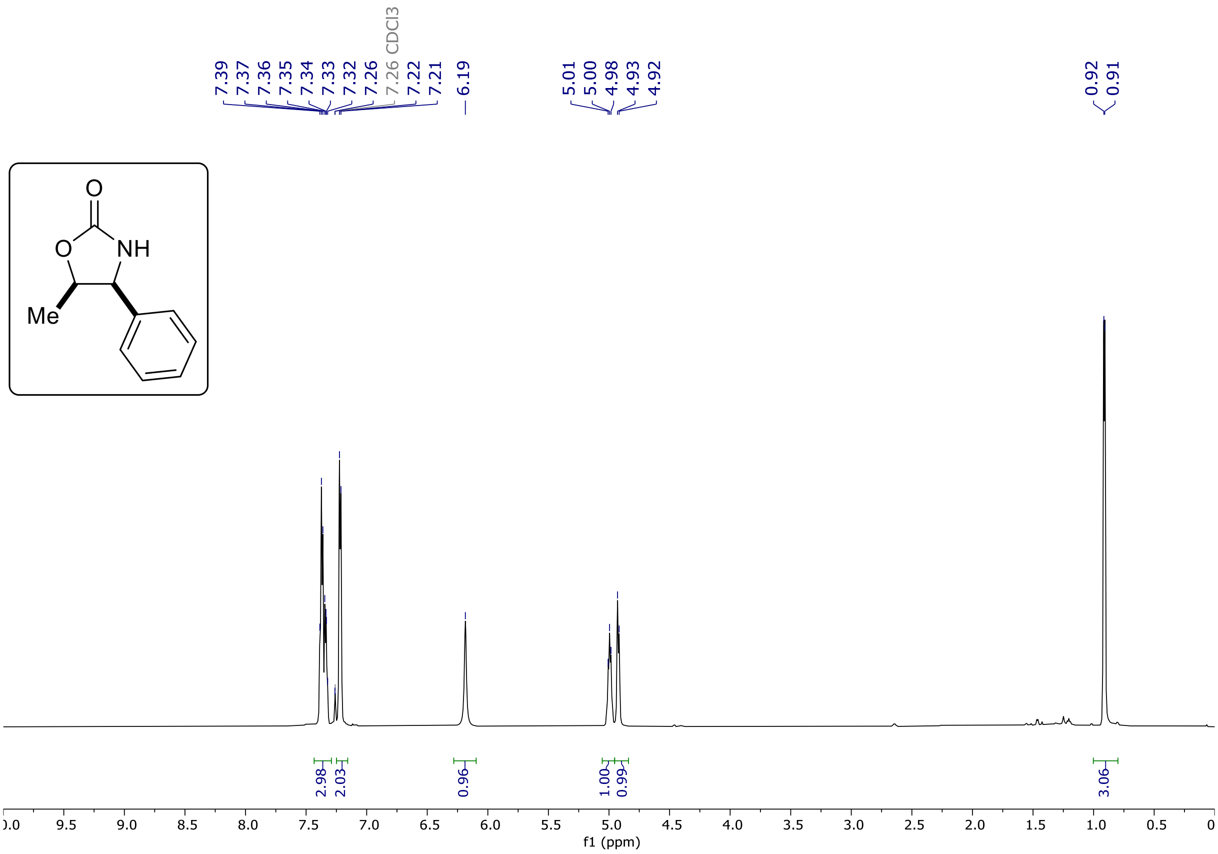


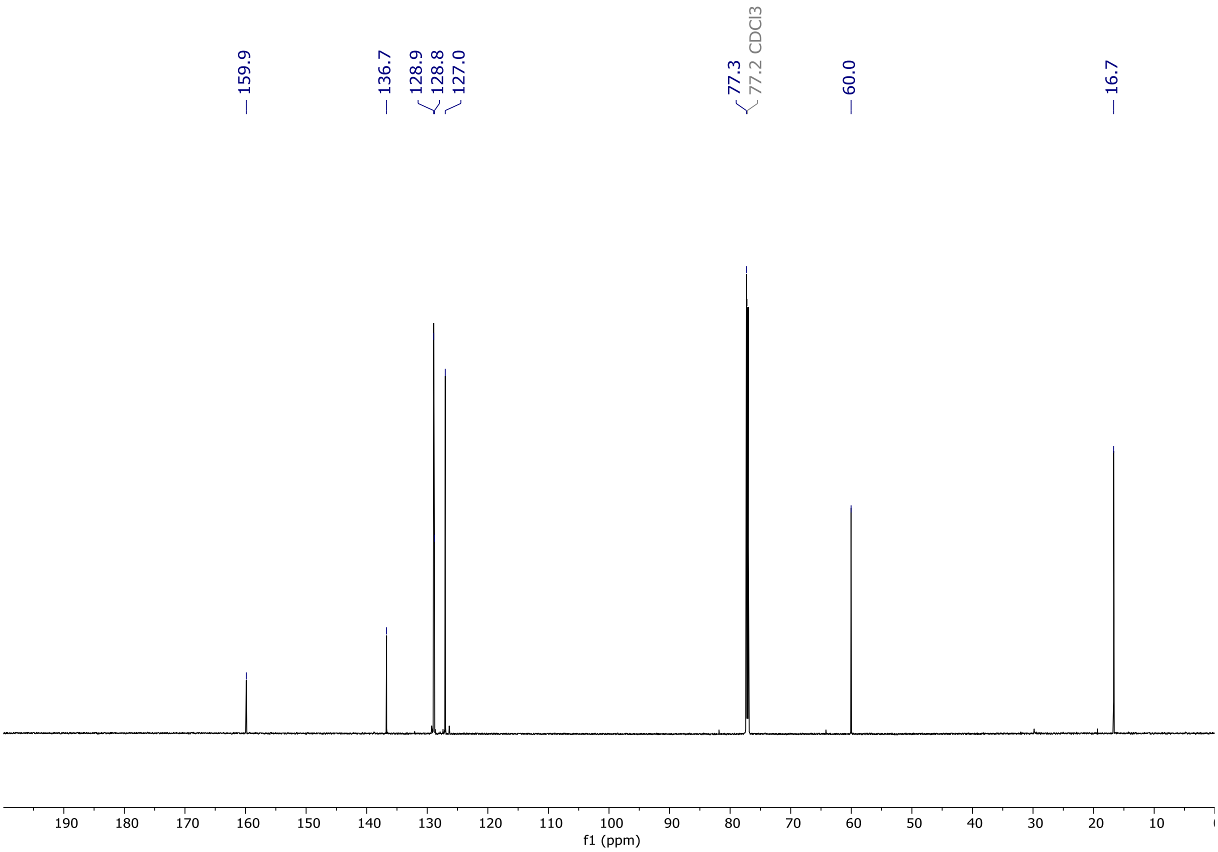
***anti*-5-Methyl-4-phenyloxazolidin-2-one (*anti*-8k)**



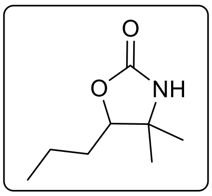


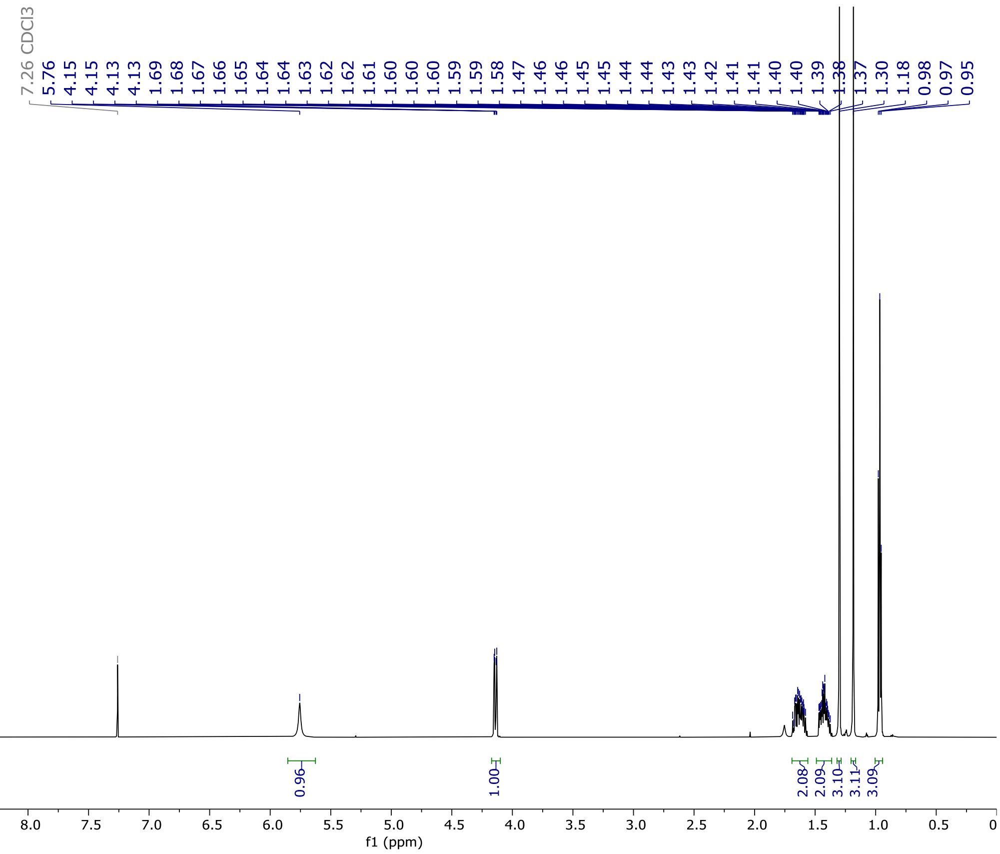
***syn*-5-Methyl-4-phenyloxazolidin-2-one (*syn*-8k)**

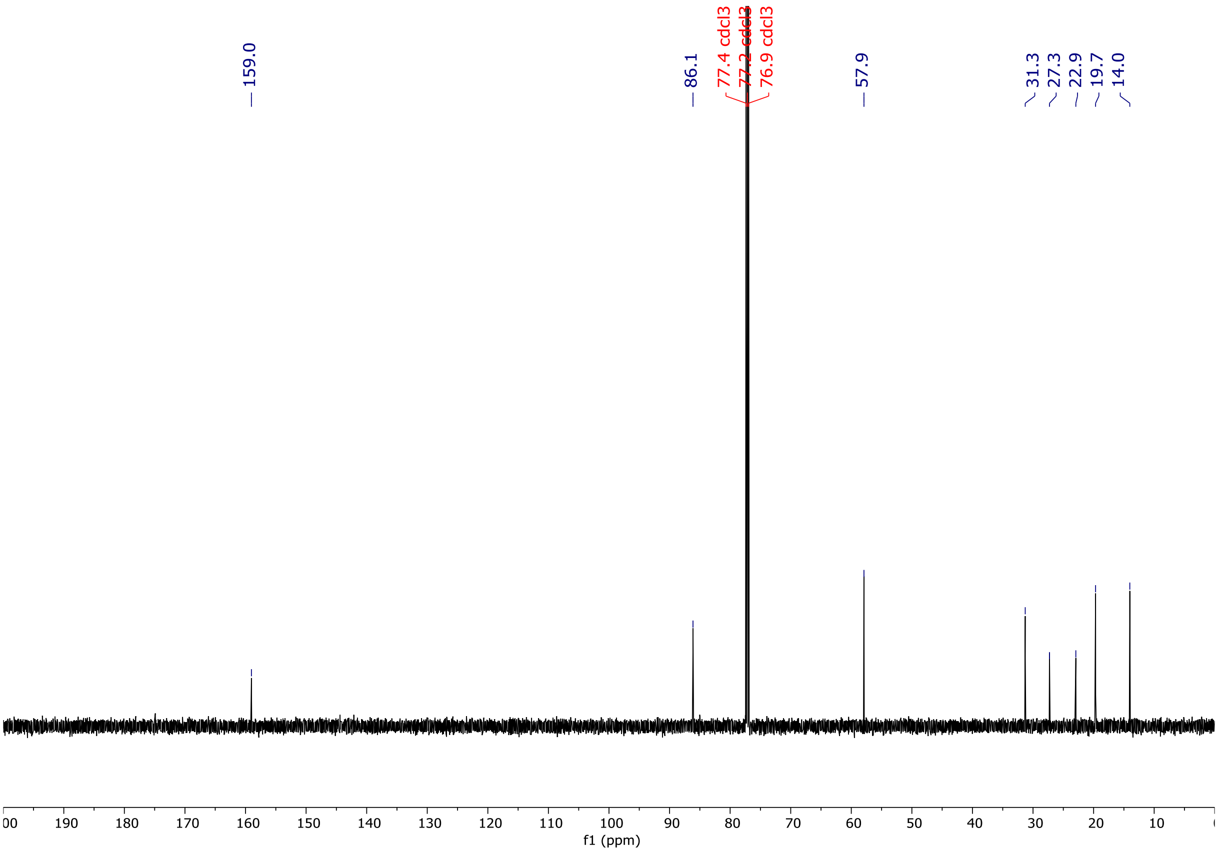




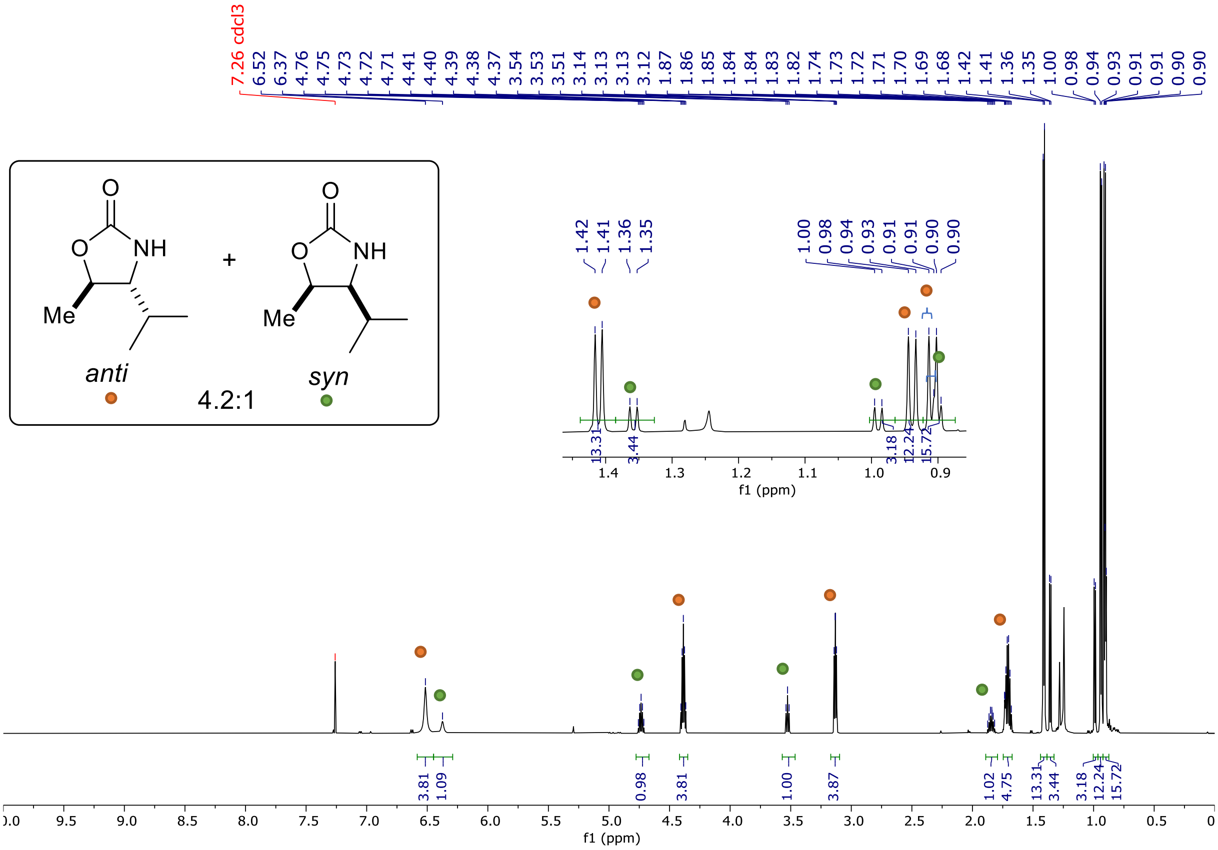
4,4-Dimethyl-5-propyloxazolidin-2-one (8l)

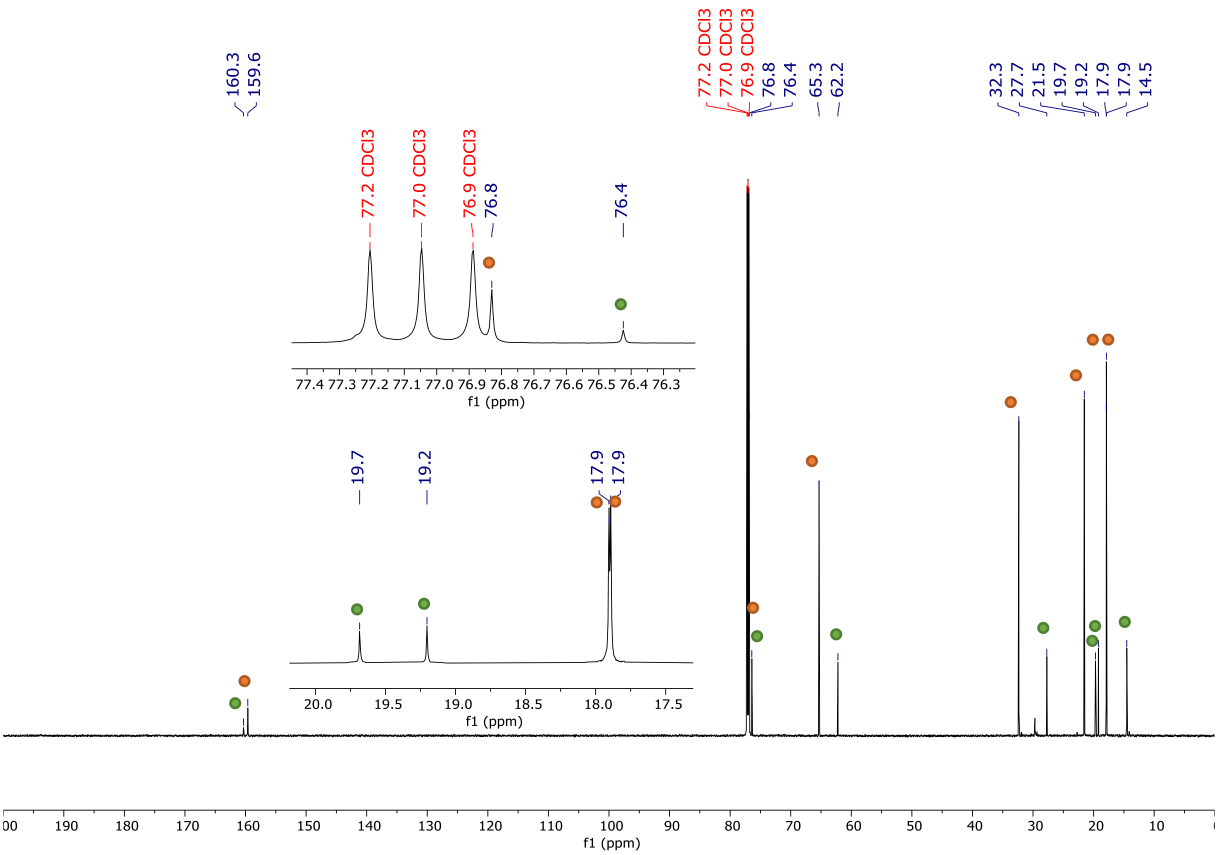




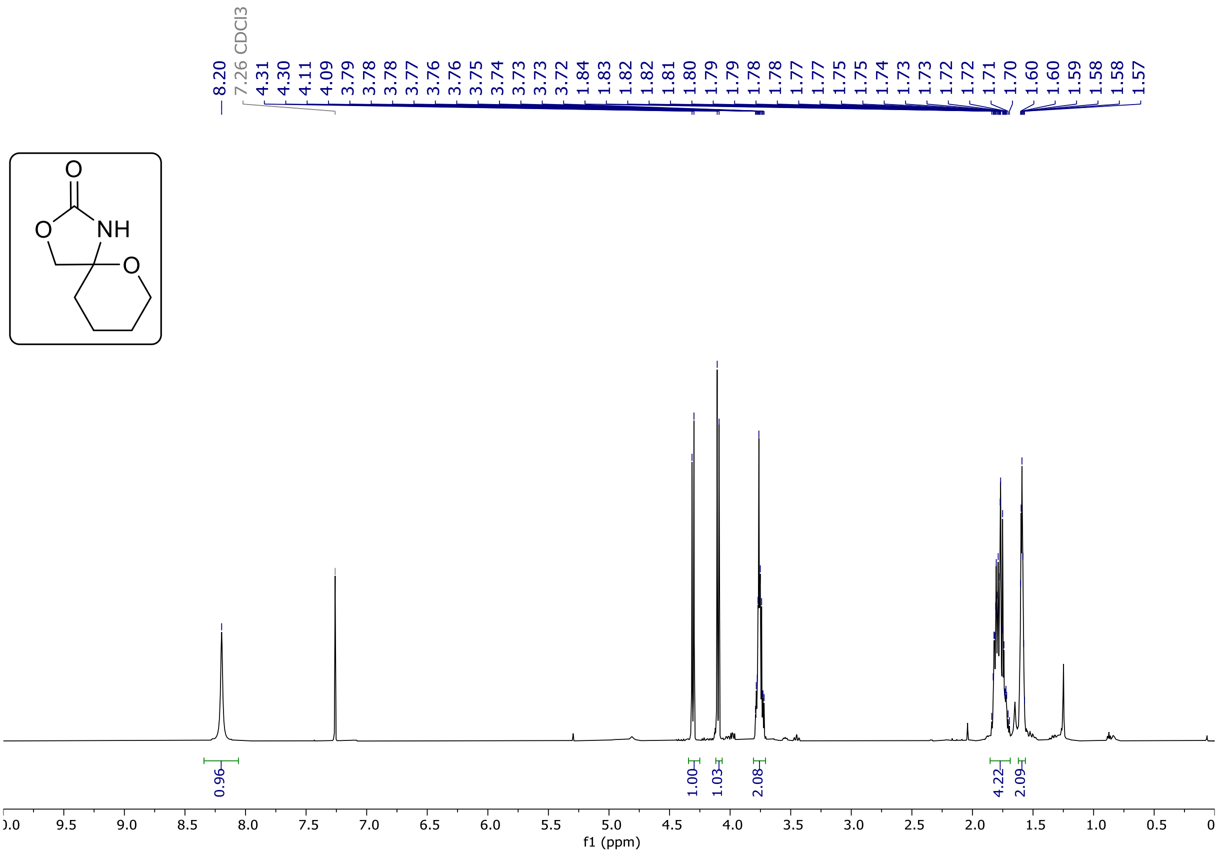


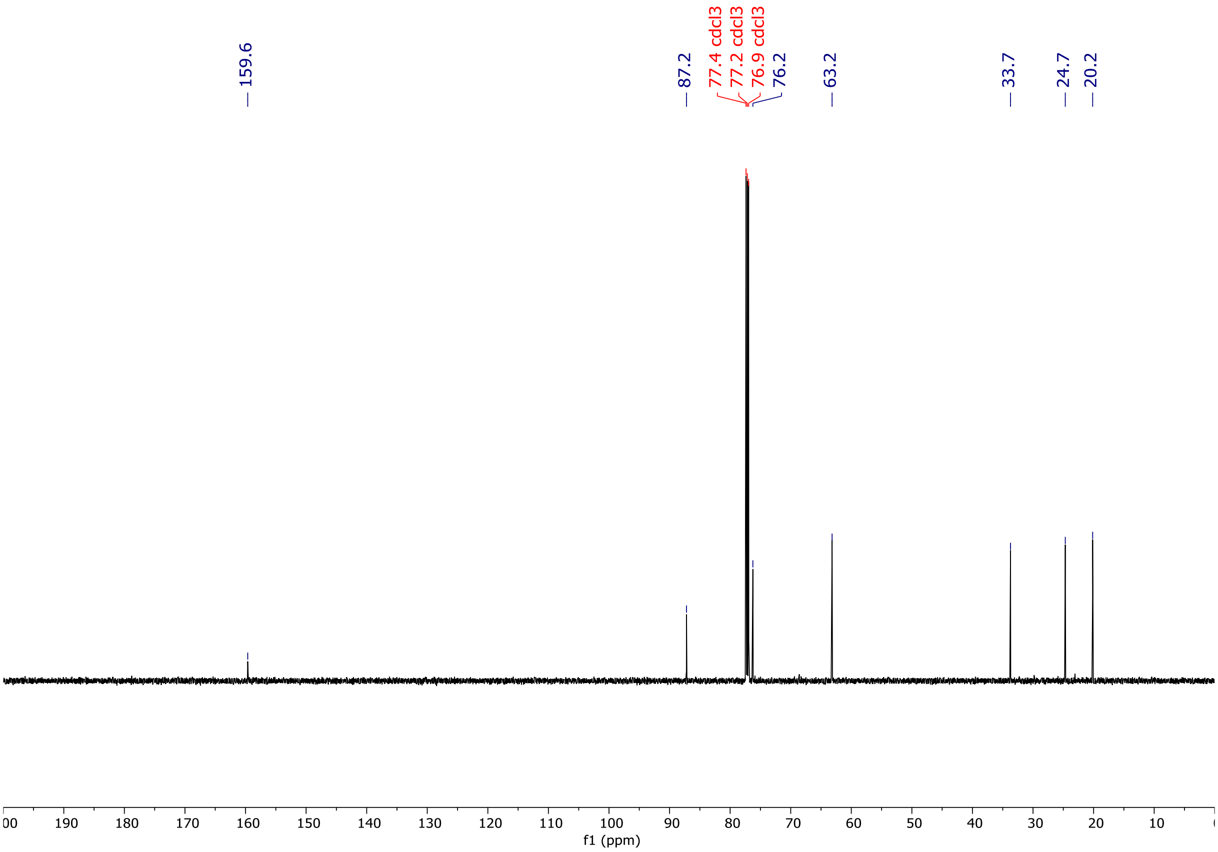
4-Isopropyl-5-methyloxazolidin-2-one (8m)





3,6-Dioxa-1-azaspiro[4.5]decan-2-one (8n)

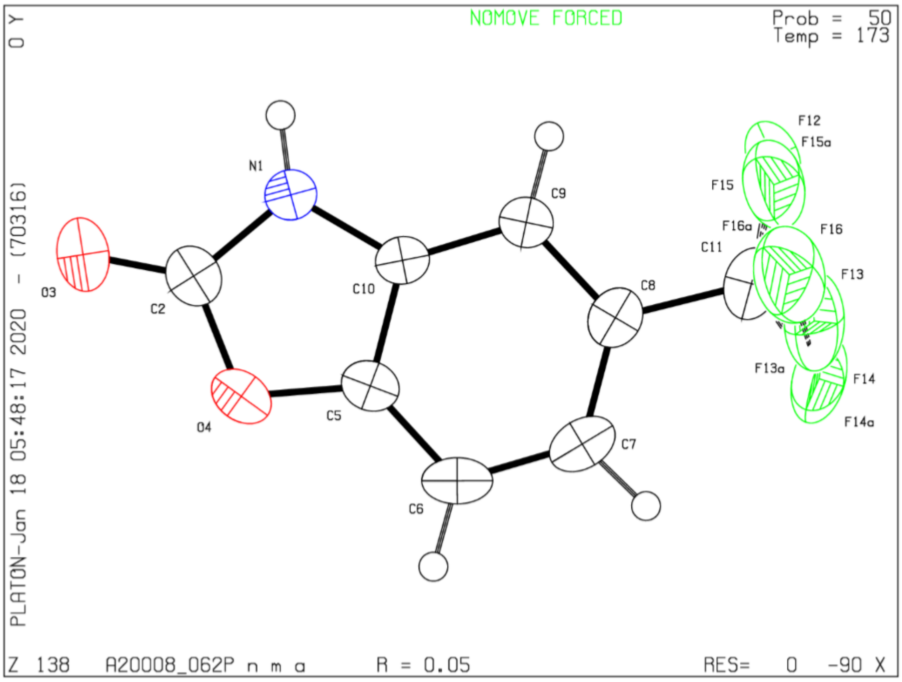




Appendix II

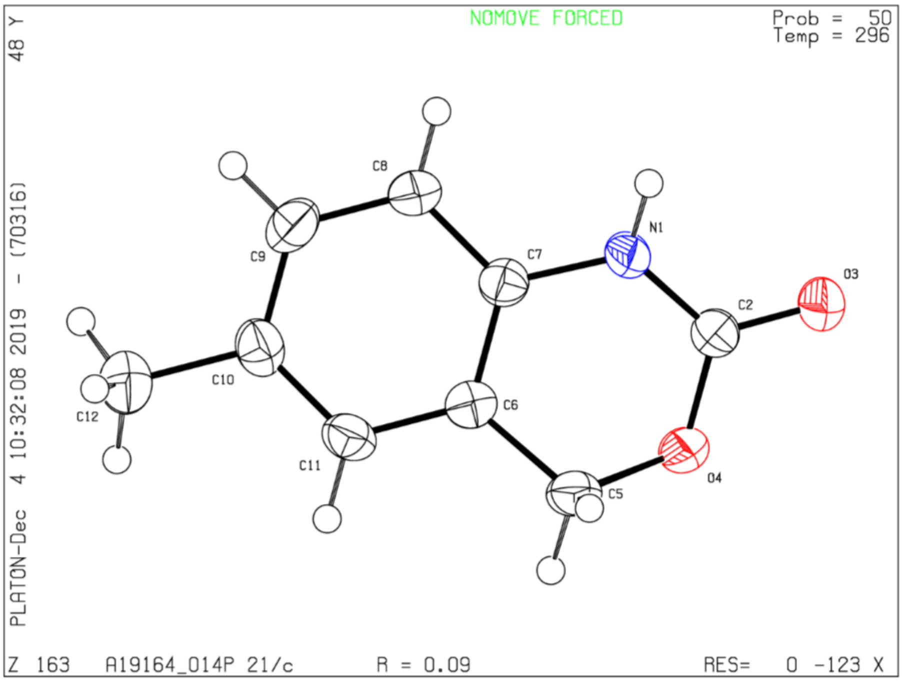
Crystallographic Data

Crystallographic data of 2m



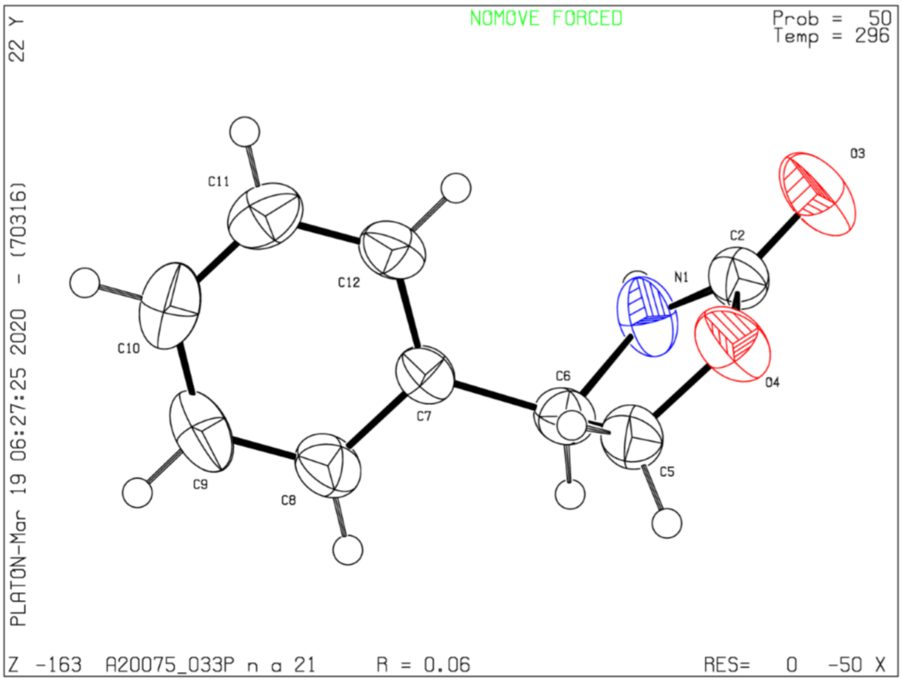
Empirical formula	$C_8H_4NO_2F_3$	
Formula weight	203.12	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pnma*	
Unit cell dimensions	a = 8.4183(3) Å	α = 90°
	b = 6.6594(3) Å	β = 90°
	c = 14.5280(8) Å	γ = 90°
Volume	814.44(7) Å^3	
Z	4	
Density (calculated)	1.657 Mg/m^3	
Absorption coefficient	0.164 mm^{-1}	
F(000)	408	
Crystal size	0.321 x 0.145 x 0.087 mm^3	
Theta range for data collection	3.365 to 28.342°.	
Index ranges	-11<=h<=11, -8<=k<=8, -19<=l<=19	
Reflections collected	63417	
Independent reflections	1082 [R(int) = 0.0392]	
Completeness to theta = 25.242°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7274	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1082 / 54 / 114	
Goodness-of-fit on F^2	1.176	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1270	
R indices (all data)	R1 = 0.0519, wR2 = 0.1323	
Largest diff. peak and hole	0.233 and -0.285 e.Å^{-3}	

Crystallographic data of 4b



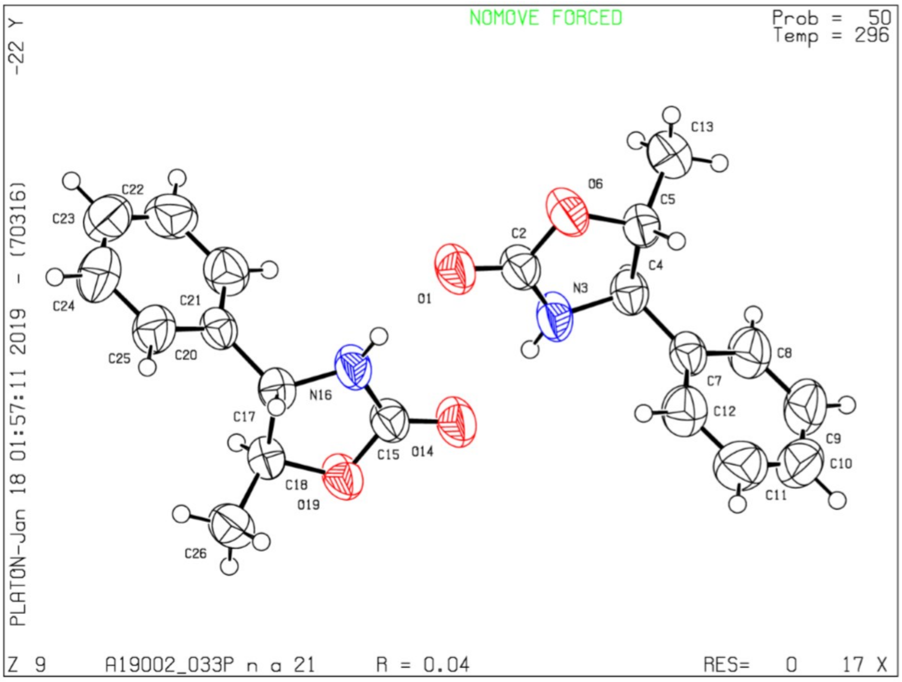
Empirical formula	$C_9H_9NO_2$	
Formula weight	163.17	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 4.8788(15) Å	α = 90°
	b = 11.048(3) Å	β = 96.277(11)°
	c = 15.069(5) Å	γ = 90°
Volume	807.4(4) $Å^3$	
Z	4	
Density (calculated)	1.342 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	344	
Crystal size	0.341 x 0.102 x 0.095 mm^3	
Theta range for data collection	3.286 to 25.994°.	
Index ranges	–6<=h<=6, –13<=k<=13, –18<=l<=18	
Reflections collected	14889	
Independent reflections	1549 [R(int) = 0.0851]	
Completeness to theta = 25.242°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6462	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1549 / 0 / 99	
Goodness-of-fit on F^2	1.110	
Final R indices [I>2sigma(I)]	R1 = 0.0943, wR2 = 0.1969	
R indices (all data)	R1 = 0.1056, wR2 = 0.2042	
Largest diff. peak and hole	0.254 and –0.233 e·$Å^{-3}$	

Crystallographic data of 6a



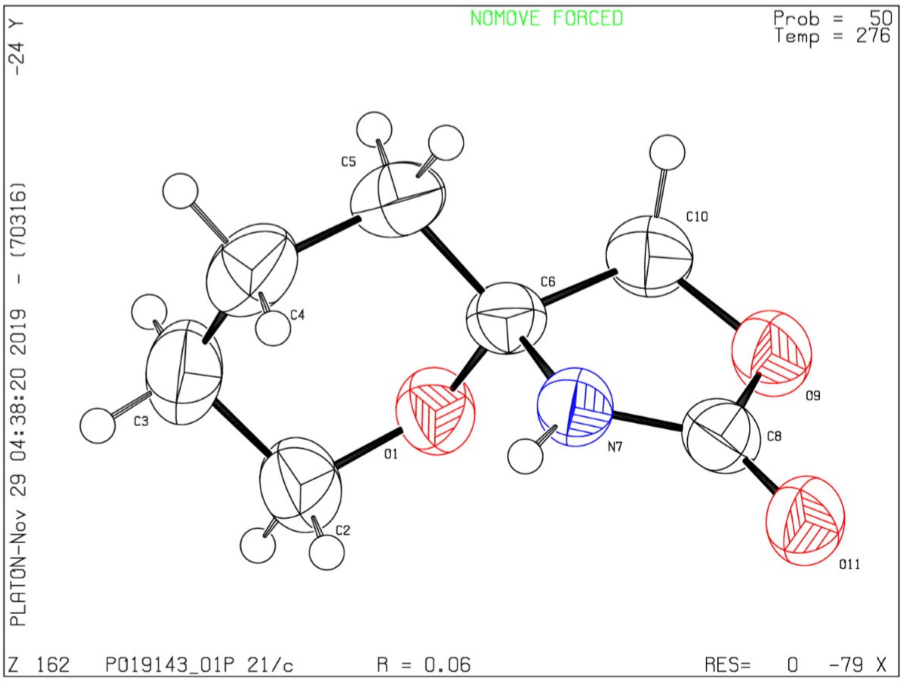
Empirical formula	$C_9H_9NO_2$	
Formula weight	163.17	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 8.175(3) Å	α = 90°
	b = 17.079(6) Å	β = 90°
	c = 5.881(2) Å	γ = 90.
Volume	821.1(5) $Å^3$	
Z	4	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	344	
Crystal size	0.345 x 0.082 x 0.078 mm^3	
Theta range for data collection	2.762 to 27.898°.	
Index ranges	–10<=h<=10, –22<=k<=22, –7<=l<=7	
Reflections collected	23084	
Independent reflections	1946 [R(int) = 0.0488]	
Completeness to theta = 25.242°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6954	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1946 / 1 / 109	
Goodness-of-fit on F^2	1.200	
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1457	
R indices (all data)	R1 = 0.0626, wR2 = 0.1476	
Absolute structure parameter	0.2(4)	
Largest diff. peak and hole	0.258 and –0.194 e·$Å^{-3}$	

Crystallographic data of 8k



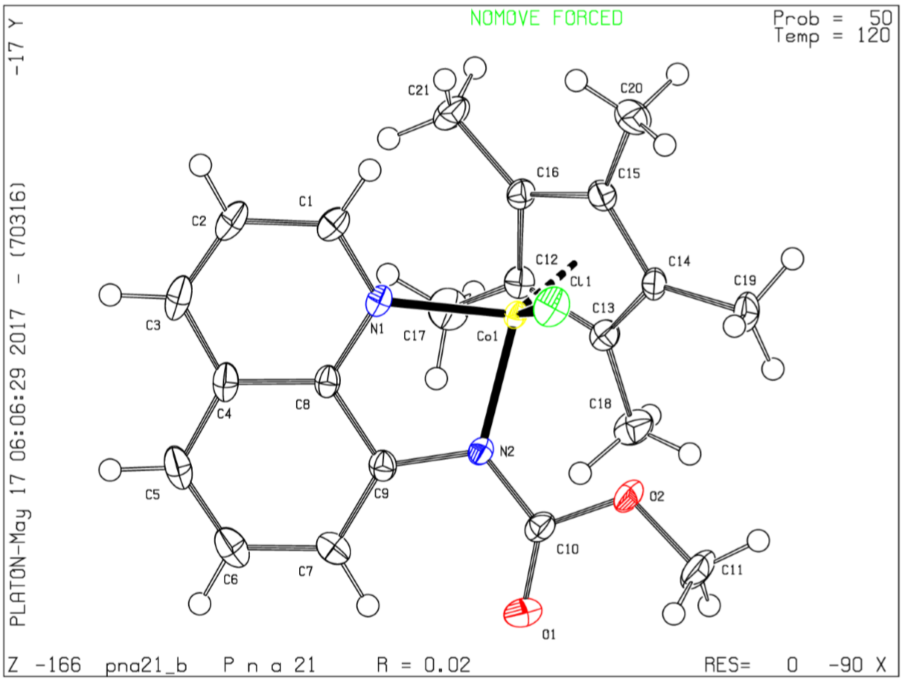
Empirical formula	$C_{10}H_{11}NO_2$	
Formula weight	177.20	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pna*2$_1$	
Unit cell dimensions	a = 14.2275(10) Å	α = 90°
	b = 8.9171(7) Å	β = 90°
	c = 14.9738(11) Å	γ = 90°
Volume	1899.7(2) Å^3	
Z	8	
Density (calculated)	1.239 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	752	
Crystal size	0.320 x 0.310 x 0.254 mm^3	
Theta range for data collection	2.863 to 28.335°.	
Index ranges	–18<=h<=19, –11<=k<=11, –19<=l<=19	
Reflections collected	32889	
Independent reflections	4562 [R(int) = 0.0403]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7023	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4562 / 1 / 243	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0912	
R indices (all data)	R1 = 0.0678, wR2 = 0.1029	
Largest diff. peak and hole	0.107 and –0.117 e·Å^{-3}	

Crystallographic data of 8n



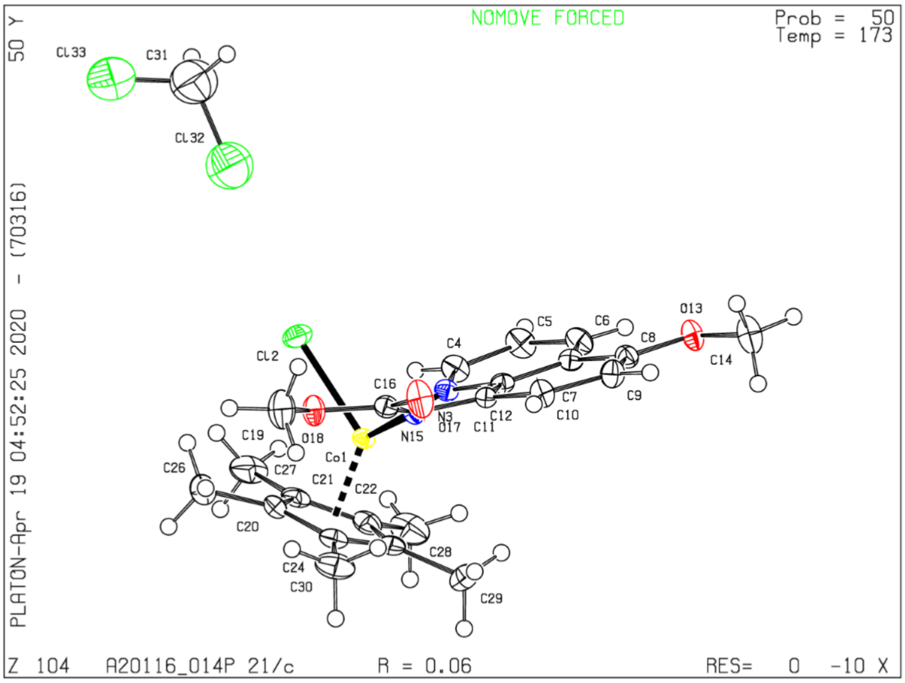
Empirical formula	$C_7H_{11}NO_3$	
Formula weight	157.17	
Temperature	276(2) K	
Wavelength	0.730 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.5210(15) Å	α = 90°
	b = 9.3830(19) Å	β = 94.99(3)°
	c = 10.932(2) Å	γ = 90°
Volume	768.5(3) Å^3	
Z	4	
Density (calculated)	1.358 Mg/m^3	
Absorption coefficient	0.112 mm^{-1}	
F(000)	336	
Crystal size	0.035 x 0.032 x 0.014 mm^3	
Theta range for data collection	2.792 to 29.981°.	
Index ranges	–10<=h<=10, –12<=k<=12, –14<=l<=14	
Reflections collected	5971	
Independent reflections	1883 [R(int) = 0.0709]	
Completeness to theta = 25.976°	99.3 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.895	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1883 / 0 / 103	
Goodness-of-fit on F^2	0.988	
Final R indices [I>2sigma(I)]	R1 = 0.0627, wR2 = 0.1596	
R indices (all data)	R1 = 0.1250, wR2 = 0.1860	
Largest diff. peak and hole	0.233 and –0.288 e·Å^{-3}	

Crystallographic data of Co2



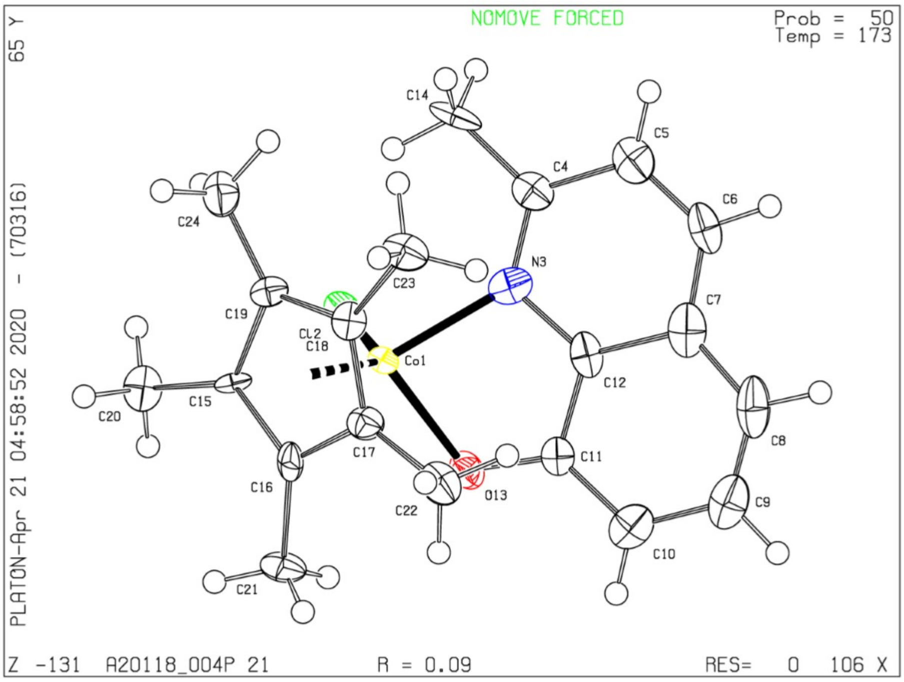
Empirical formula	$C_{21}H_{24}ClCoN_2O_2$	
Formula weight	430.80	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 17.0689(18) Å	a= 90°.
	b = 8.0006(8) Å	b= 90°.
	c = 14.0523(15) Å	g = 90°.
Volume	1919.0(3) $Å^3$	
Z	4	
Density (calculated)	1.491 Mg/m^3	
Absorption coefficient	1.052 mm^{-1}	
F(000)	896	
Crystal size	0.28 x 0.26 x 0.21 mm^3	
Theta range for data collection	2.81 to 33.22°.	
Index ranges	-26<=h<=26, -12<=k<=12, -21<=l<=21	
Reflections collected	115947	
Independent reflections	7342 [R(int) = 0.0297]	
Completeness to theta = 33.22°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6804 and 0.6188	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7342 / 1 / 250	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0209, wR2 = 0.0526	
R indices (all data)	R1 = 0.0225, wR2 = 0.0538	
Absolute structure parameter	0.013(6)	
Largest diff. peak and hole	0.294 and -0.402 e.$Å^{-3}$	

Crystallographic data of Co3



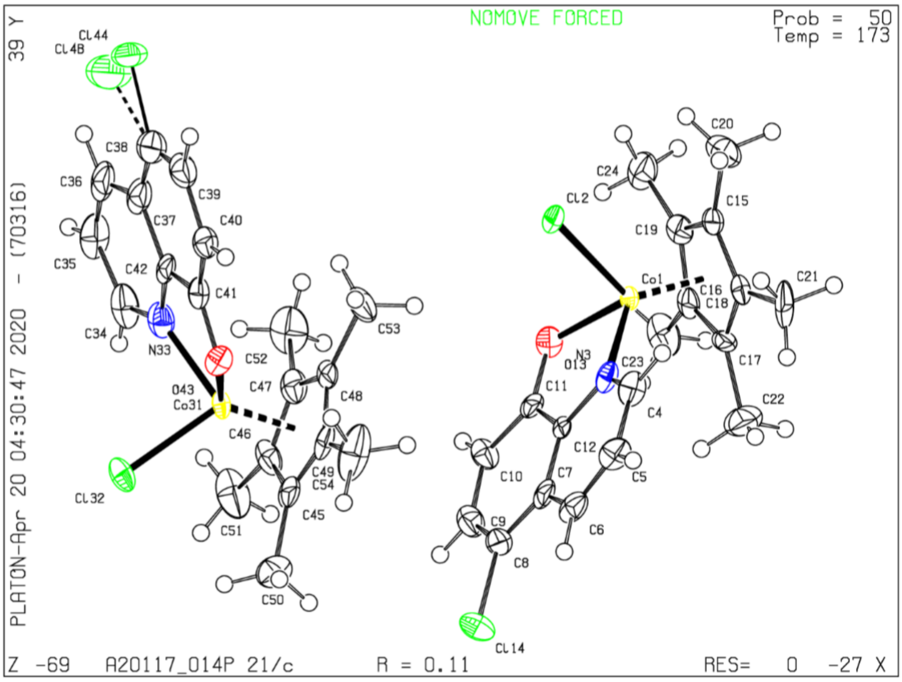
Empirical formula	$C_{23}H_{28}N_2O_3Cl_3Co$	
Formula weight	545.75	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.0736(10) Å	α = 90°
	b = 13.4634(9) Å	β = 106.827(3)°
	c = 14.0135(11) Å	γ = 90°
Volume	2361.0(3) $Å^3$	
Z	4	
Density (calculated)	1.535 Mg/m^3	
Absorption coefficient	1.095 mm^{-1}	
F(000)	1128	
Crystal size	0.321 x 0.122 x 0.042 mm^3	
Theta range for data collection	2.946 to 27.508°.	
Index ranges	–16<=h<=16, –16<=k<=17, –18<=l<=18	
Reflections collected	73018	
Independent reflections	5417 [R(int) = 0.0728]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6456	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5417 / 0 / 296	
Goodness-of-fit on F^2	1.116	
Final R indices [I>2sigma(I)]	R1 = 0.0629, wR2 = 0.1631	
R indices (all data)	R1 = 0.0788, wR2 = 0.1748	
Largest diff. peak and hole	1.060 and –1.386 e·$Å^{-3}$	

Crystallographic data of Co5



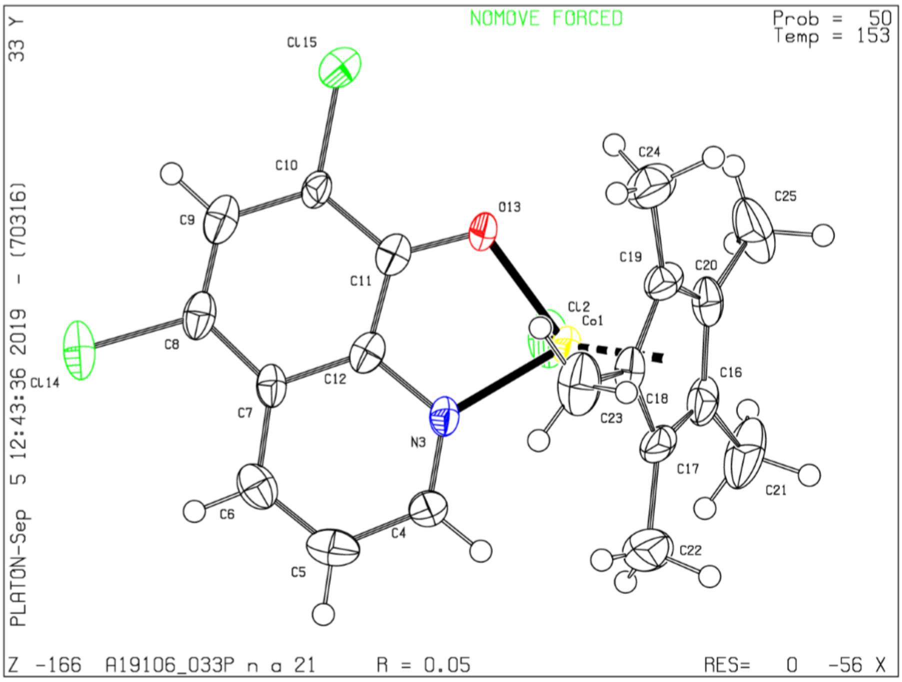
Empirical formula	$C_{20}H_{23}NOClCo$	
Formula weight	387.77	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 7.3569(8) Å	α = 90°
	b = 14.8206(17) Å	β = 112.145(4)°
	c = 8.4407(9) Å	γ = 90°
Volume	852.43(16) $Å^3$	
Z	2	
Density (calculated)	1.511 Mg/m^3	
Absorption coefficient	1.169 mm^{-1}	
F(000)	404	
Crystal size	0.112 x 0.072 x 0.019 mm^3	
Theta range for data collection	2.605 to 25.995°.	
Index ranges	–8<=h<=9, –18<=k<=18, –10<=l<=10	
Reflections collected	11672	
Independent reflections	3208 [R(int) = 0.0879]	
Completeness to theta = 25.242°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5759	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3208 / 145 / 224	
Goodness-of-fit on F^2	1.232	
Final R indices [I>2sigma(I)]	R1 = 0.0879, wR2 = 0.1590	
R indices (all data)	R1 = 0.1043, wR2 = 0.1646	
Absolute structure parameter	0.47(6)	
Largest diff. peak and hole	0.889 and –1.326 e·$Å^{-3}$	

Crystallographic data of Co7



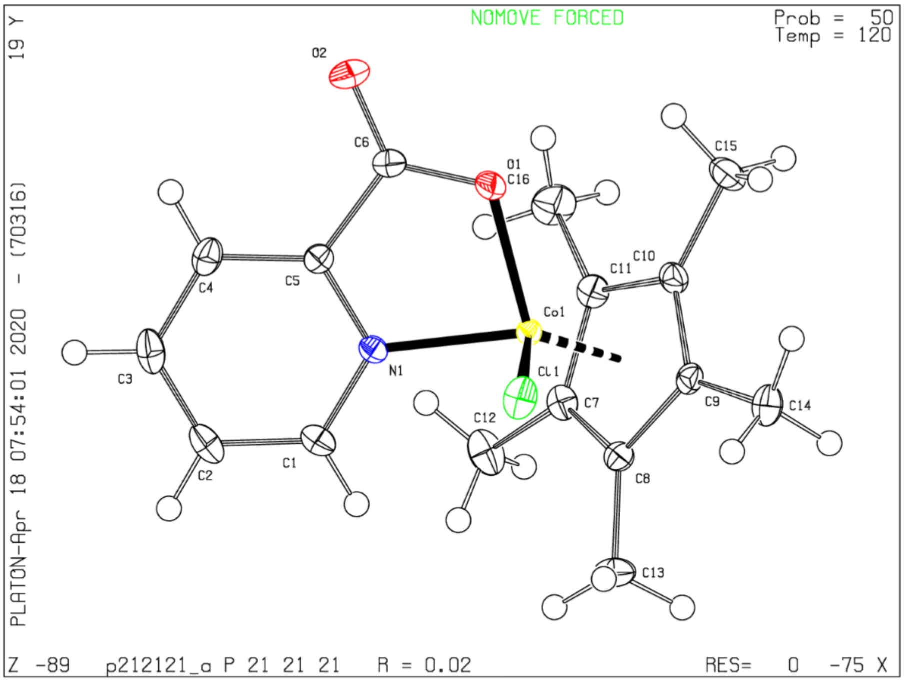
Empirical formula	$C_{19}H_{20}NOCl_2Co$	
Formula weight	408.19	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.8053(12) Å	α = 90°
	b = 13.5431(9) Å	β = 91.284(2)°
	c = 15.8434(11) Å	γ = 90°
Volume	3605.0(4) $Å^3$	
Z	8	
Density (calculated)	1.504 Mg/m^3	
Absorption coefficient	1.254 mm^{-1}	
F(000)	1680	
Crystal size	0.155 x 0.082 x 0.041 mm^3	
Theta range for data collection	2.853 to 25.498°.	
Index ranges	–20<=h<=20, –16<=k<=16, –19<=l<=18	
Reflections collected	68718	
Independent reflections	6701 [R(int) = 0.1367]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6363	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6701 / 13 / 453	
Goodness-of-fit on F^2	1.311	
Final R indices [I>2sigma(I)]	R1 = 0.1149, wR2 = 0.1793	
R indices (all data)	R1 = 0.1461, wR2 = 0.1896	
Largest diff. peak and hole	0.712 and –0.815 e·$Å^{-3}$	

Crystallographic data of Co8



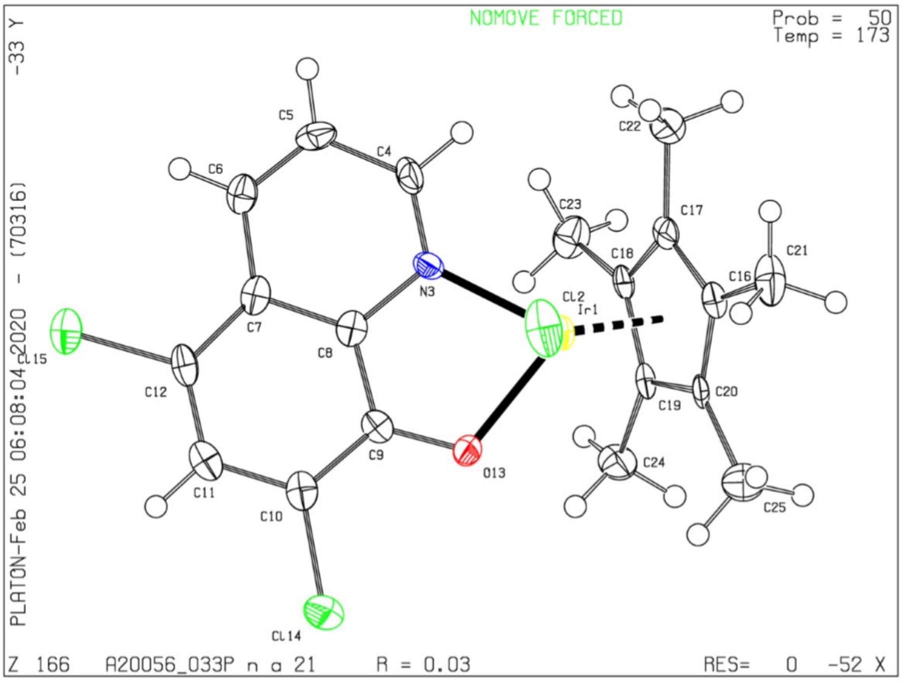
Empirical formula	$C_{19}H_{19}NOCl_3Co$	
Formula weight	442.63	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 16.361(9) Å	α = 90°
	b = 9.761(7) Å	β = 90°
	c = 11.670(7) Å	γ = 90°
Volume	1864(2) $Å^3$	
Z	4	
Density (calculated)	1.578 Mg/m^3	
Absorption coefficient	1.358 mm^{-1}	
F(000)	904	
Crystal size	0.378 x 0.038 x 0.031 mm^3	
Theta range for data collection	3.492 to 25.997°.	
Index ranges	–20<=h<=20, –11<=k<=12, –14<=l<=14	
Reflections collected	14569	
Independent reflections	3395 [R(int) = 0.0778]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.5797	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3395 / 31 / 232	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1126	
R indices (all data)	R1 = 0.0632, wR2 = 0.1193	
Absolute structure parameter	0.07(4)	
Largest diff. peak and hole	0.808 and –0.684 e·$Å^{-3}$	

Crystallographic data of Co9



Empirical formula	$C_{16}H_{19}NO_2ClCo$	
Formula weight	351.70	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.7804(9) Å	α = 90°
	b = 9.0745(11) Å	β = 90°
	c = 21.289(3) Å	γ = 90°
Volume	1503.1(3) $Å^3$	
Z	4	
Density (calculated)	1.554 Mg/m^3	
Absorption coefficient	1.322 mm^{-1}	
F(000)	728	
Crystal size	0.210 x 0.160 x 0.140 mm^3	
Theta range for data collection	3.243 to 33.236°.	
Index ranges	–11<=h<=11, –13<=k<=13, –32<=l<=32	
Reflections collected	103563	
Independent reflections	5738 [R(int) = 0.0493]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6646	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5738 / 0 / 196	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0239, wR2 = 0.0511	
R indices (all data)	R1 = 0.0292, wR2 = 0.0533	
Absolute structure parameter	0.016(11)	
Largest diff. peak and hole	0.322 and –0.464 e·$Å^{-3}$	

Crystallographic data of Ir1



Empirical formula	$C_{19}H_{19}NOCl_3Ir$	
Formula weight	575.90	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pna*2$_1$	
Unit cell dimensions	a = 16.7683(8) Å	α = 90°
	b = 10.3801(5) Å	β = 90°
	c = 10.5034(5) Å	γ = 90°
Volume	1828.19(15) Å^3	
Z	4	
Density (calculated)	2.092 Mg/m^3	
Absorption coefficient	7.749 mm^{-1}	
F(000)	1104	
Crystal size	0.128 x 0.043 x 0.021 mm^3	
Theta range for data collection	3.123 to 24.414°.	
Index ranges	–19<=h<=19, –12<=k<=11, –12<=l<=12	
Reflections collected	53644	
Independent reflections	2980 [R(int) = 0.0693]	
Completeness to theta = 24.414°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7451 and 0.5849	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2980 / 73 / 232	
Goodness-of-fit on F^2	1.161	
Final R indices [I>2sigma(I)]	R1 = 0.0286, wR2 = 0.0551	
R indices (all data)	R1 = 0.0312, wR2 = 0.0559	
Absolute structure parameter	0.042(15)	
Largest diff. peak and hole	0.917 and –2.185 e·Å^{-3}	