Supporting information

Regioselectivity of the Intermolecular Pauson-Khand Reactions of Disymmetric Fluorinated Alkynes

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General procedures: All reactions were run under N_2 in solvents dried using a Solvent Purification System (SPS). Dry toluene was purchased from Aldrich. All experiments were monitored by analytical thin layer chromatography (TLC) performed on aluminum silica-gel TLC sheets (Merck 60 F_{254}). Chromatographic purifications were performed under flash conditions on 400-630 mesh silica gel and using mixtures of hexane/EtOAc. NMR spectra were recorded at room temperature on a Varian Mercury 400, Varian Unity 300 or Bruker 250 apparatus. ^{1}H-NMR and ^{13}C-NMR spectra were referenced to residual solvent peaks; ^{31}P-NMR spectra were referenced with phosphoric acid; and ^{19}F-NMR spectra were referenced by the spectrometer, without any external reference. Signal multiplicities in the ^{13}C spectra were assigned according to DEPT and HSQC experiments. High-resolution mass spectra were recorded using an electrospray ionization spectrometer. IR spectra were recorded in an FT-IR apparatus. Compounds **1-4** were prepared following previously described procedures.[1],[2]

[1] a) Fustero, S.; Fernández, B.; Bello, P.; del Pozo, C.; Arimitsu, S.; Hammond, G. B. *Org. Lett.* **2007**, *9*, 4251-4253 and literature cited therein. b) Arimitsu, S.; Fernández, B.; del Pozo, C.; Fustero, S.; Hammond, G. B. *J. Org. Chem.* **2008**, *73*, 2656-2661. See, also: c) Fustero, S.; Bello, P.; Fernández, B.; del Pozo, C.; Hammond, G. B. *J. Org. Chem.* **2009**, *74*, 7690-7696.

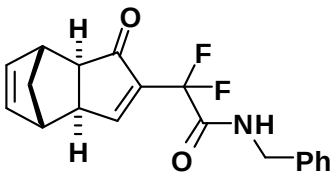
[2] a) Hamper, B. C. *J. Org. Chem.* **1988**, *53*, 5558. b) Hamper, B. C. *Org. Synth.* **1992**, *70*, 246.

General procedure for the stoichiometric intermolecular Pauson-Khand reactions

To a solution of the alkyne (1 equiv.) in toluene was added a solution of $Co_2(CO)_8$ (1.1 equiv.) in toluene (10mL/mmol alkyne) under N_2. The mixture was stirred at room temperature for 1 hour, until the alkyne had been totally consumed (as determined by TLC). The solvent was removed under vacuum, and the crude alkyne-cobalt complex was either chromatographed on silica gel or directly used without purification.

The alkyne-cobalt complex was placed in a Schlenk tube and dissolved in toluene (10mL/mmol complex). Norbornadiene (10 equiv.) was added, and the reaction mixture was heated at the temperature and for the time indicated below for each compound. The reaction mixture was filtered through silica to remove cobalt impurities, and the solvent was removed under vacuum. The residue was purified by silica gel chromatography.

***N*-Benzyl-2,2-difluoro-2-(1-oxo-3a,4,7,7a-tetrahydro-1H-4,7-methano-inden-2-yl)-acetamide (7).** The general procedure was followed starting from alkyne **1** (63 mg, 0.3 mmol). The intermediate cobalt complex was not purified. Reaction temperature and time: 75 °C for 4.3 h. After chromatography, **7** was isolated in 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.27 (d, J = 10 Hz, 1H), 1.43 (d, J = 10 Hz, 1H), 2.43 (d, J = 5 Hz, 1H), 2.83 (br s, 1H), 2.91 (br s, 1H), 2.95 (br s, 1H), 4.49 (dd, J = 15 and 6 Hz, 1H), 4.58 (dd, J = 15.0, 6.0 Hz, 1H), 6.23 (dd, J = 6 and 3 Hz, 1H), 6.33 (dd, J = 6 and 3 Hz, 1H), 7.12 (br s, 1H), 7.25-7.40 (m, 5H), 7.92 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 41.4 (CH_2), 43.2 (CH), 43.8 (CH_2), 44.3 (CH), 48.4 (CH), 53.7 (CH), 111.7 (t, C, J_F = 251 Hz), 127.8, 127.9, 128.9 (5CH), 136.9 (C), 137.4 (CH), 138.8 (CH), 142.3 (t, C, J_F = 25 Hz), 162.7 (t, C, J_F = 29 Hz), 166.2 (t, CH, J_F = 5 Hz), 204.8 (t,C, J_F = 2 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -106.40 (d, J_{FF} = 268 Hz), -107.14 (d, J_{FF} = 268 Hz) ppm; IR (film) ν = 3334, 1707 cm^{-1}; HRMS (ESI) $C_{19}H_{18}F_2NO_2$: calculated 330.1306, found 330.1310.



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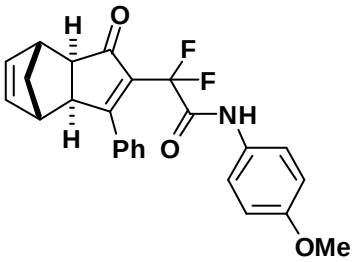
2,2-Difluoro-*N*-(4-methoxy-phenyl)-2-(1-oxo-3a,4,7,7a-tetrahydro-1H-4,7-methano-inden-2-yl)-acetamide (8). The general procedure was followed starting from alkyne **2** (70 mg, 0.23 mmol). The intermediate cobalt complex was not purified. Reaction temperature and time: 70 °C for 24 h. The PKR adduct **8** was isolated as a white solid (47 mg, 48% yield). mp 161ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.35 (d, J = 9 Hz, 1H), 1.42 (d, J = 9 Hz, 1H), 2.50 (br s, 1H), 2.59 (d, J = 6 Hz, 1H), 3.04 (br s, 1H), 3.27 (br s, 1H), 3.80 (s, 3H), 6.26 (m, 2H), 6.89 (d, J = 9 Hz, 2H), 7.46 (m, 3H), 7.51 (d, J = 9 Hz, 2H), 7.57 (m, 2H), 8.64 (br s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 41.9 (CH_2), 43.5 (CH), 44.4 (CH), 53.3 (CH), 53.7 (CH), 55.6 (CH_3), 112.9 (t, C, J_F = 253 Hz), 114.4, 122.2, 128.5, 130.5 (7CH), 127.8 (t, 2CH, J_F = 2 Hz), 129.6 (C), 134.1 (C), 135.8 (t, C, J_F = 24 Hz), 137.9 (CH), 138.6 (CH), 157.3 (C), 161.1 (t, C, J_F = 29 Hz), 179.6 (t, C, J_F = 2 Hz), 205.7 (t, C, J_F = 3 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -103.72 (d, J_{FF} = 266 Hz), -102.99 (d, J_{FF} = 265 Hz) ppm; IR (film) $\nu_{màx.}$ = 3321, 1700 cm^{-1}; HRMS (ESI) $C_{25}H_{22}F_2NO_3$: calculated 422.1568, found 422.1578



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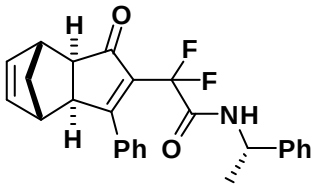
2,2-Difluoro-2-(1-oxo-3a,4,7,7a-tetrahydro-1H-4,7-methano-inden-2-yl)-N-(1-phenyl-ethyl)-acetamide (**9).** The general procedure was followed starting from alkyne **3** (50 mg, 0.17 mmol). The intermediate cobalt complex was not purified. Reaction temperature and time: 75 ºC for 9 h. The PKR adduct **9** was isolated as a colorless oil (44 mg; 62% yield; 1:1 mixture of diastereoisomers). ^{1}H NMR(400 MHz, $CDCl_3$) δ = 1.07-1.31 (m, 2H), 1.41 (AB, J = 10 Hz, 2H*), 1.55 (d, J = 7 Hz, 3H), 1.59 (d, J = 7 Hz, 3H*), 2.41 (s, 1H), 2.49 (s, 1H*), 2.54 (d, J = 6 Hz, 1H), 2.56 (d, J = 6 Hz, 1H*), 2.96 (s, 1H), 3.05 (s, 1H*), 3.23 (br s, 1H and 1H*), 5.12 (quint., J = 7 Hz, 1H), 5.13 (quint., J = 7 Hz, 1H*), 6.19-6.29 (m, 2H and 2H*), 7.10-7.60 (m, 11H and 11H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6 (CH_3), 21.8 (CH_3*), 41.7 (CH_2), 41.8 (CH_2*), 43.4 (CH), 43.5 (CH*), 44.4 (CH and



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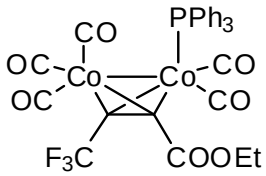
CH*), 49.6 (CH), 49.6 (CH*), 53.2 (CH and CH*), 53.5 (CH), 53.6 (CH*), 112.9 (t, C, J_F = 253 Hz), 113.0 (t, C*, J_F = 253 Hz), 126.2 (2CH), 126.3 (2CH*), 127.6 (CH), 127.7 (t, CH, J_F = 2 Hz), 127.8 (CH*), 127.8 (t, CH*, J_F = 2 Hz), 128.4 (4CH and 4CH*), 128.8 (CH), 128.9 (CH*), 130.3 (CH), 130.4 (CH*), 134.1 (C), 134.3 (C*), 135.6 (t, C, J_F = 25 Hz), 135.9 (t, C*, J_F = 25 Hz), 137.9 (CH), 138.0 (CH*), 138.6 (CH), 138.6 (CH*), 142.0 (C), 142.4 (C*), 162.5 (t, C, J_F = 29 Hz), 162.6 (t, C*, J_F = 29 Hz), 179.0 (t, C, J_F = 3 Hz), 179.2 (d, C*, J_F = 2 Hz), 205.2 (t, C, J_F = 3 Hz), 205.3 (m, C*) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.28 (AB, $J_{F\text{-}F}$ = 263 Hz), -104.02* (s) ppm; IR (film) ν = 3321, 2975, 1707, 1624 cm^{-1}; HRMS (ESI) $C_{26}H_{24}F_2NO_2$ calculated 420.1775, found 420.1778. The signals marked with an asterisk correspond to one of the diastereomers.

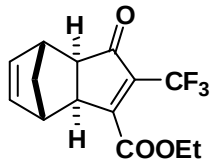
Ethyl 4,4,4- Trifluoroproynoate triphenylphosphine pentacarbonyldicobalt (14). To a solution of alkyne **4** (1.5 g, 9.06 mmol) in hexanes (15 mL) was added $Co_2(CO)_8$ (3.1 g, 9.06 mmol). The reaction was monitored by TLC. After 2 h of stirring at room temperature, the reaction mixture was concentrated and chromatographed. The cobalt complex **11** was isolated as a red oil (3.40 g, 83% yield).



14

To a solution of the cobalt complex **11** (1.6 g, 3.5 mmol, 1equiv.) in toluene (15 mL) was added triphenylphosphine (2.2 g, 8.4 mmol, 2.2 equiv.). The mixture was stirred for 72 h at room temperature. The solvent was partially removed under vacuum and the residue was directly purified by silica gel chromatography. Complex **14** was isolated as a viscous red oil (2.03 g, 84% yield). ^{1}H NMR (400MHz, C_6D_6): 0.86 (t, J = 6.8 Hz, 3H), 3.75-3.84 (m, 2H), 6.93-6.99 (m, 9H), 7.44-7.50 (m, 6H) ppm; ^{19}F NMR (376.3 MHz): -49.8 ppm; ^{31}P NMR (121.4 MHz): +46.7 ppm; HRMS: $C_{29}H_{20}O_7F_3PCo_2Na$ found 708.9467; calculated 708.9460.

3-Oxo-2-trifluoromethyl-3a,4,7,7a-tetrahydro-3H-4,7-methano-indene-1-carboxylic acid ethyl ester (10): <u>*Stoichiometric PKR:*</u> The general procedure was followed starting from alkyne **4** (500 mg, 3.01 mmol). The intermediate cobalt complex **11** was not purified. Reaction temperature and time: 70 °C for 4 h. After chromatography, **10** was isolated as a yellow oil in 92% yield.



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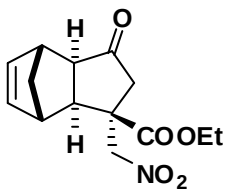
<u>*Catalytic PKR:*</u> Alkyne **4** (232 mg, 1.4 mmol, 1 equiv.), mono-phosphine complex **14** (98 mg, 0.14 mmol, 10 mol%) and norbornadiene (1.43 mL, 14 mmol, 10 equiv.) were dissolved in toluene (6 mL). The vessel was placed in a pressure reactor under CO (2 bars) and heated at 70 ºC for 24 h. After chromatography, compound **10** was obtained as a yellow oil (291 mg; 73% yield);^{1}H NMR (400MHz, $CDCl_3$): 1.38 (t, *J* = 7.2 Hz, 3H), 1.57 (s, 1H), 2.53 (d, *J* = 5.2 Hz, 1H), 2.99 (s, 1H), 3.10 (m, 2H), 4.40 (q, *J* = 6.8 Hz, 2H), 6.28 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.33 (dd, *J* = 5.6, 3.2 Hz, 1H) ppm;^{13}C NMR (100MHz, $CDCl_3$): 13.9, 41.4, 43.0, 44.6, 49.5, 53.0, 62.6, 119.6 (q, J_{CF} = 273 Hz), 137.7, 138.2, 164.3, 166.9 (q, J_{CF} = 3 Hz), 200.8 ppm; ^{19}F NMR (376.3 MHz): -63.3 ppm; IR: 3067, 2981, 2876, 1728, 1659, 1461, 1352, 1269, 1190, 1014, 723, 687 cm^{-1}; HRMS: $C_{14}H_{13}O_3F_3Na$ found 309.0717; calculated 309.0714

1-Nitromethyl-3-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-methano-indene-1-carboxylic acid ethyl ester (12a):

<u>a) Using TBAF·3H$_2$O:</u> The PK adduct **10** (90 mg, 0.31 mmol, 1 equiv.) was dissolved in nitromethane (5 mL), and TBAF·3H$_2$O (100 mg, 0.31 mmol, 1 equiv.) was added in one portion at room temperature. The reaction mixture was stirred at 90 ºC for 3 h. The volume was partially reduced under vacuum and the residue was purified by chromatography. The product was isolated as a white solid (87 mg, 99% yield).



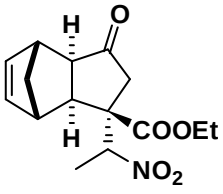
12a

b) *Using DBU (1 equiv.) and water:* The PK adduct **10** (100 mg, 0.34 mmol, 1 equiv) was dissolved in nitromethane (5 mL), and DBU (0.05 mL, 0.34 mmol, 1 equiv) and water (0.1 mL, 5.56 mmol, 16 equiv) were added. The reaction mixture was stirred at 90ºC for 1.5 h. The solvent was removed under vacuum and the residue was purified by silica gel chromatography, affording the desired product as a pale yellow oil that solidified on standing (55 mg, 56% yield).

c) *Using DBU (0.2 equiv):* The PK adduct **10** (100 mg, 0.34 mmol, 1 equiv) was dissolved in nitromethane (10 mL), and DBU (0.01 mL, 0.07 mmol, 0.2 equiv) was added. The reaction mixture was stirred at 80ºC for 18 h. The reaction was monitored by ^{19}F-NMR, allowing us to follow the disappearance of the starting material and the appearance of a new peak at aprox 155 ppm (no internal reference was used) that we identified as HF-DBU. To assign this peak, HF-DBU was prepared from aqueous HF and DBU. When no starting material could be observed by TLC, the solvent was removed under vacuum and the residue was purified by chromatography, affording the desired product as a pale yellow oil that solidified on standing (35 mg, 36% yield).

The reaction was also performed in D_3C-NO_2 and monitored by ^{19}F NMR. Two main new peaks were found: xxx ppm assigned to free HF and xxx asssigned to HF-DBU.

mp 102ºC. ^{1}H (400MHz, $CDCl_3$): 1.35 (t, *J* = 7.2 Hz, 3H), 2.08 (d, *J* = 8 Hz, 1H), 1.44-1.47 (m, 2H), 2.42 (dt, *J* = 8 Hz, *J* = 1.2 Hz, 1H), 2.53 (dd, *J* = 20.4 Hz, *J* = 1.2 Hz, 1H), 2.75-2.79 (m, 1H), 3.16-3.21 (d, *J* = 1.2 Hz, 1H), 3.59 (d, *J* = 20.4 Hz, 1H), 4.30 (dq, *J* = 10.8 Hz, *J* = 7.2 Hz, 1H), 4.38 (dq, *J* = 10.8 Hz, *J* = 7.2 Hz, 1H), 4.41 (d, *J* = 14.8 Hz, 1H), 5.07 (dd, *J* = 14.8 Hz, *J* = 1.6 Hz, 1H), 6.21-6.27 (m, 2H); ^{13}C (100MHz, $CDCl_3$): 14.1, 29.7, 44.4, 46.2, 47.4, 47.8, 49.8, 49.9, 54.5, 62.3, 80.8, 138.9, 139.0, 170.6, 214.9; IR: 2986, 2962, 2890, 1723, 1555, 1372, 1225, 1196, 1182, 1011, 683; HRMS: $C_{14}H_{18}NO_5$ [MH^+] found 280.1185; calculated 280.1185.

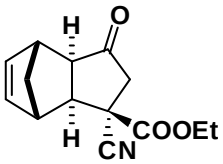


12b

1-(1'-Nitroethyl)-3-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-methano-indene-1-carboxylic acid ethyl ester(12b). The PK adduct **10** (100 mg, 0.35 mmol, 1

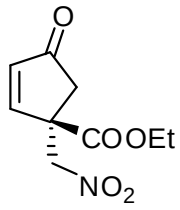
equiv.) was dissolved in nitroethane (10 mL), and TBAF (1M in THF, 0.15 mL, 0.14 mmol, 0.4 equiv.) was added. The reaction mixture was heated at 65ºC for 1.5 h. The solvent was partially eliminated under vacuum and the residue was purified by silica gel chromatography. The compound **12b** was isolated as a yellow oil that solidified on standing (58 mg, 57% yield; 2:1 mixture of diastereomers). mp 99ºC. ^{1}H-NMR (400MHz, $CDCl_3$): 1.32 (t, *J=7 Hz*, 3H), 1.38 (t, *J=7 Hz*, 3H*), 1.40-1.52 (m, 2H+5H*), 1.53 (d, *J=7 Hz*, 3H), 2.10 (d, *J=8 Hz*, 1H), 2.29 (m, 1H*), 2.41 (m, 1H), 2.48 (d, *J=8 Hz*, 1H*), 2.73 (m, 2H), 2.78 (m, 2H*), 3.98-3.19 (m, 1H+1H*), 3.42 (d, *J=20 Hz*, 1H*), 3.63 (d, *J=20 Hz*, 1H), 4.21-4.40 (m, 2H+2H*), 5.20 (q, *J=7 Hz*, 1H), 5.30 (q, *J=7 Hz*, 1H*), 6.19-6.29 (m, 2H+2H*). ^{13}C-NMR (100MHz, $CDCl_3$): 14.2 (CH_3), 14.4 (CH_3*),14.8 (CH_3), 16.6 (CH_3*), 44.2 (CH*), 44.5 (CH_2*), 44.7 (CH), 45.6 (CH_2), 46.8 (CH_2*), 47.1 (CH_2), 47.4 (CH*), 47.7 (CH), 51.1 (CH), 51.4 (CH*), 53.7 (C), 53.7 (C*), 55.2 (CH*), 55.6 (CH), 62.4 (CH_2), 62.6 (CH_2*), 85.5 (CH*), 87.6 (CH), 139.0 (CH*), 139.2 (CH), 139.2 (CH*),139.4 (CH), 170.5 (C*),171.3 (C), 215.3 (C*), 216.4 (C) ppm. IR: 2981, 1732, 1546, 1233 cm^{-1}. HRMS: $C_{14}H_{20}NO_3$ $[M+H]^+$ calculated: 294.13360, found: 294.13360

1-Cyano-3-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-methano-indene-1-carboxylic acid ethyl ester(12c). Alkyne **10** (75 mg, 0.26 mmol, 1 eq) and KCN (170 mg, 2.60 mmol, 10 equiv) were dissolved in acetonitrile (10 mL). The mixture was heated at 90ºC for 2 h. The solvent was then removed under vacuum, and the crude was purified by silica gel chromatography to afford **12c** as a pale yellow oil (32 mg, 50% yield).^{1}H-NMR (400MHz, $CDCl_3$): 1.26 (s, 2H), 1.42 (t, *J=7 Hz*, 3H), 1.57 (d, *J=10 Hz*, 2H), 2.71 (br s, 1H), 2.78 (d, *J=7 Hz*, 1H), 2.96 (d, *J=7 Hz*, 1H), 3.12 (br s, 1H), 4.41 (dq, *J=7 and 2 Hz*, 2H), 6.16-6.26 (m, 2H). ^{13}C-NMR (100MHz, $CDCl_3$): 14.3 (CH_3), 29.9 (CH_2), 42.9 (CH_2), 43.9 (CH), 45.7 (CH), 50.3 (CH), 51.9 (CH), 52.1 (C), 63.8 (CH_2), 137.9 (CH), 138.9 (CH), 165.1 (C), 177.0 (C) ppm. IR: 2917, 2847, 2206, 1745, 1655 cm^{-1}.



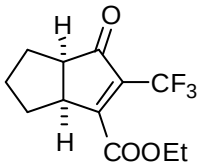
12c

1-Nitromethyl-4-oxo-cyclopent-2-enecarboxylic acid ethyl ester (13a): Compound **12a** (63 mg, 0.20 mmol, 1 equiv.) was dissolved in dichloroethane (5 mL). Maleic anhydride (97 mg, 1.0 mmol, 5 equiv.) and $MeAlCl_2$ (0.22 mL, 0.22 mmol, 1 equiv., 1M in hexane) were successively added at room temperature. The reaction mixture was heated at 55 ºC for 4 h. The solution was diluted in Et_2O (20 mL) and treated with HCl 1M. The organic layer was extracted with Et_2O (3 x 10 mL), and dried over $MgSO_4$. After filtration and evaporation of the solvents, the residue was purified by silica gel chromatography to give ester **13a** as a yellow oil (23 mg, 60% yield); ^1H (400 MHz, $CDCl_3$): 1.29 (t, *J* = 7.2 Hz, 3H), 2.44 (d, *J* = 18.8 Hz, 1H), 3.10 (d, *J* = 18.8 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.73 (d, *J* = 14.4 Hz, 1H), 4.88 (d, *J* = 14.4 Hz, 1H), 6.39 (d, *J* = 6 Hz, 1H), 7.56 (d, *J* = 6 Hz, 1H); ^{13}C (100MHz, $CDCl_3$): 13.9, 42.3, 54.2, 63.0, 78.5, 136.7, 158.8, 169.7, 204.4; ^{19}F (376.3 MHz): -63.14; IR: 2956, 2920, 2851, 1732, 1557, 1464, 1376, 1258, 1080.



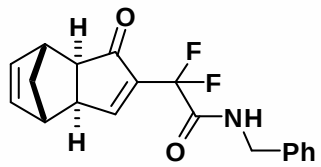
13a

3-Oxo-2-trifluoromethyl-3,3a,4,5,6,6a-hexahydro-pentalene-1-carboxylic acid ethyl ester (15): Ethyl 4,4,4-trifluorobutynoate (300 mg, 1.8 mmol, 1 equiv.) was dissolved in toluene with Co_2CO_8 (615 mg, 1.8 mmol, 1 equiv.) and the mixture was stirred at room temperature for 2 h. The intermediate cobalt complex was not purified. Cyclopentene (1.6 mL, 18 mmol, 10 equiv.) was added, and the resulting mixture was stirred at 65 ºC for 24 h. After chromatography the PK adduct **15** was isolated as a yellow oil (170 mg, 36% yield); ^1H NMR (400MHz, $CDCl_3$): 1.34-1.42 (m, 1H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.69-1.86 (m, 3H), 1.88-1.95 (m, 1H), 2.00-2.08 (m, 1H), 2.93-3.00 (m, 1H), 3.56-3.63 (m, 1H), 4.39 (q, *J* = 7.2 Hz, 2H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): 13.9, 24.0, 28.5, 30.0, 46.1, 50.7 (q, *J* = 1.2 Hz), 62.5, 119.8 (q, *J* = 271 Hz), 131.6 (q, *J* = 32.9 Hz), 164.5, 168.2 (q, *J* = 3.2 Hz), 203.9 ppm; ^{19}F NMR (376.3 MHz): - 63.2 ppm; IR: 2964, 2944, 2873, 1731, 1664, 1450, 1354, 1271, 1200, 945, 710. cm^{-1}; HRMS: $C_{12}H_{14}O_3F_3$ [MH^+] found 263.0895; calculated 263.0895.



15

^{1}H-NMR (400MHz, $CDCl_3$)



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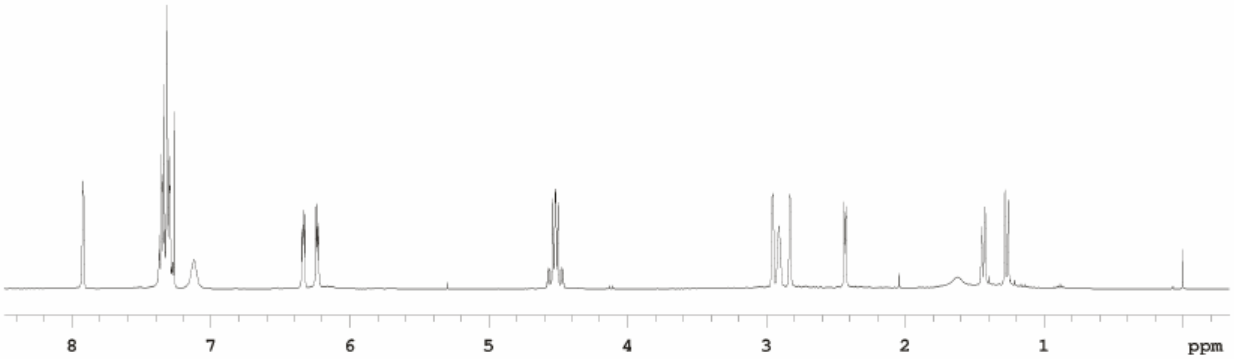
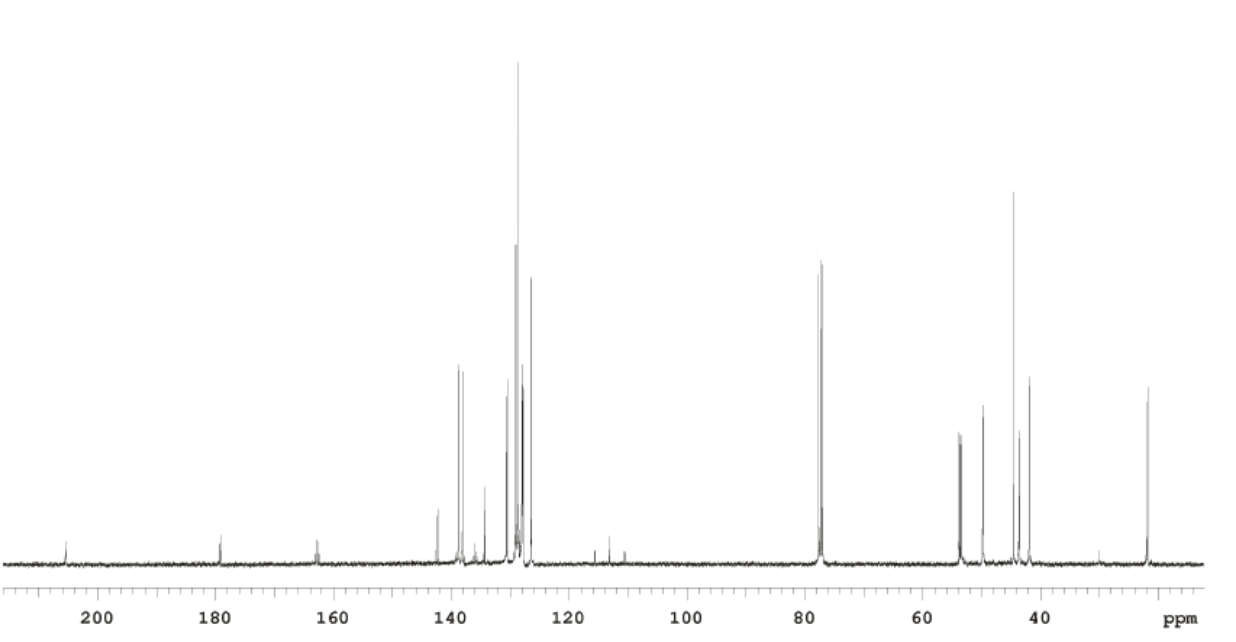
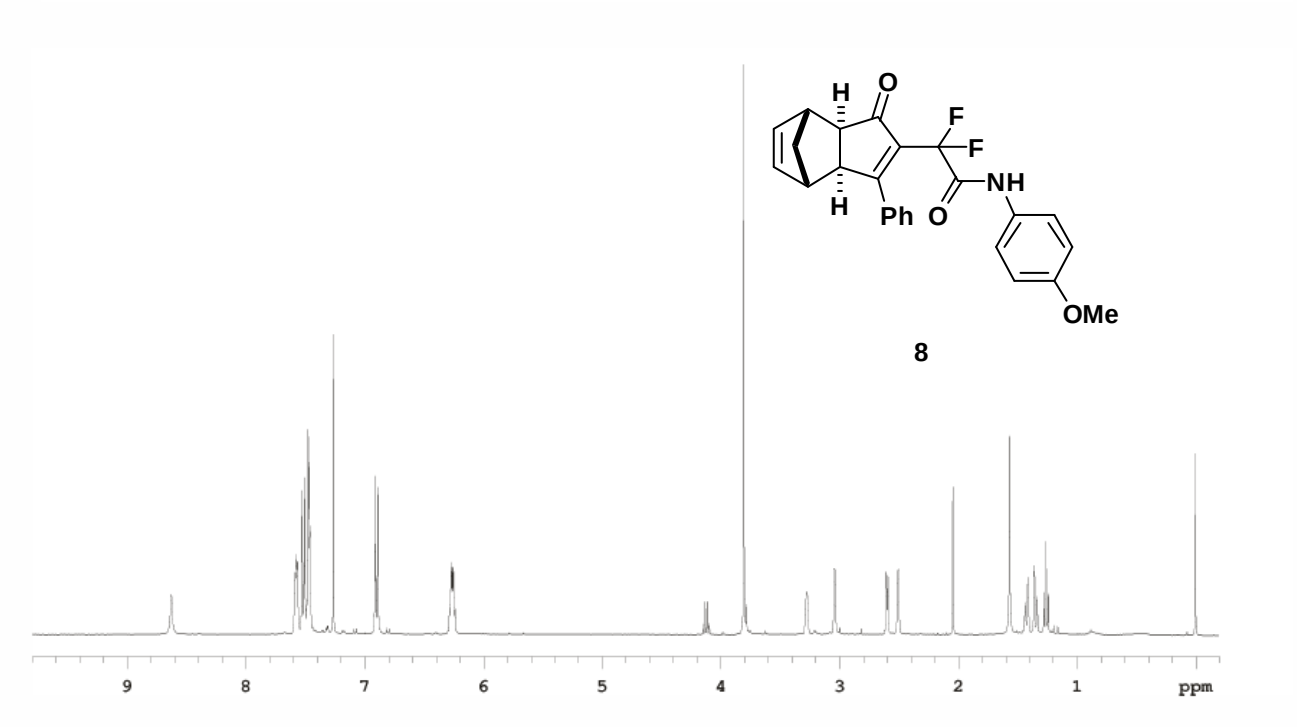


^{13}C-NMR (100MHz, $CDCl_3$)



^{1}H-NMR (400MHz, $CDCl_3$)



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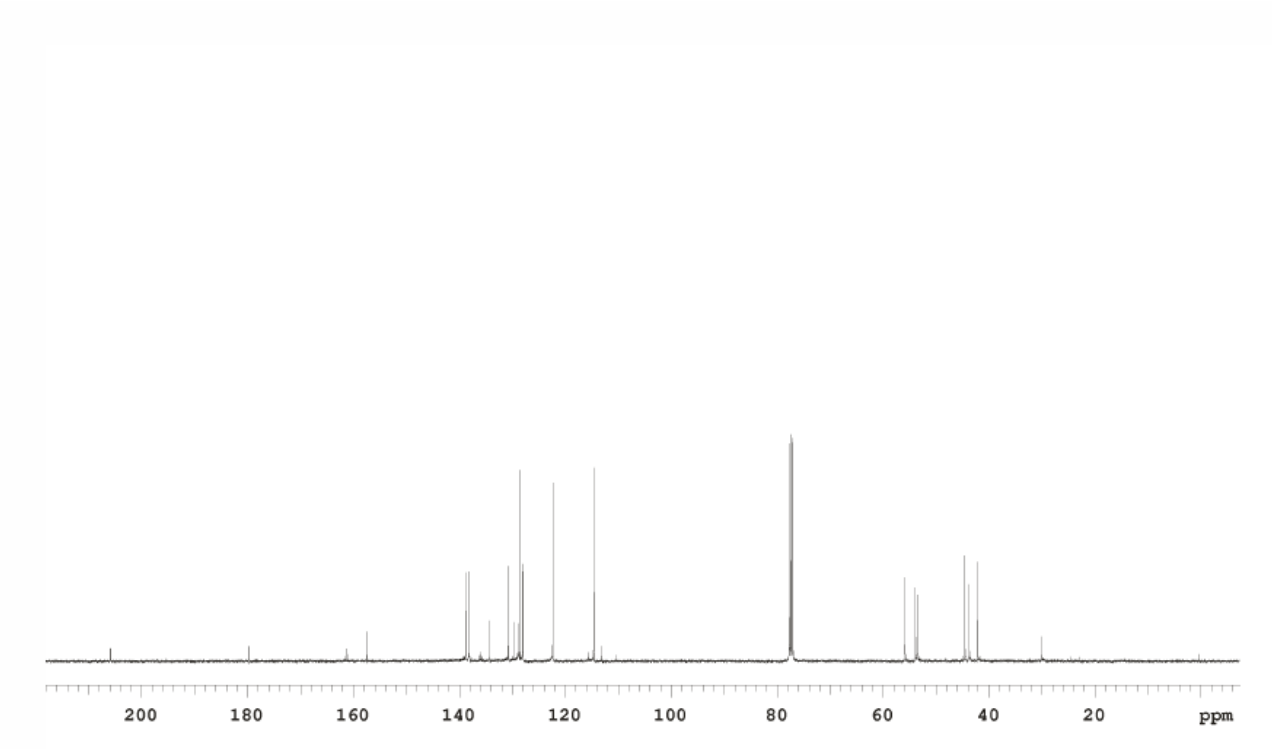

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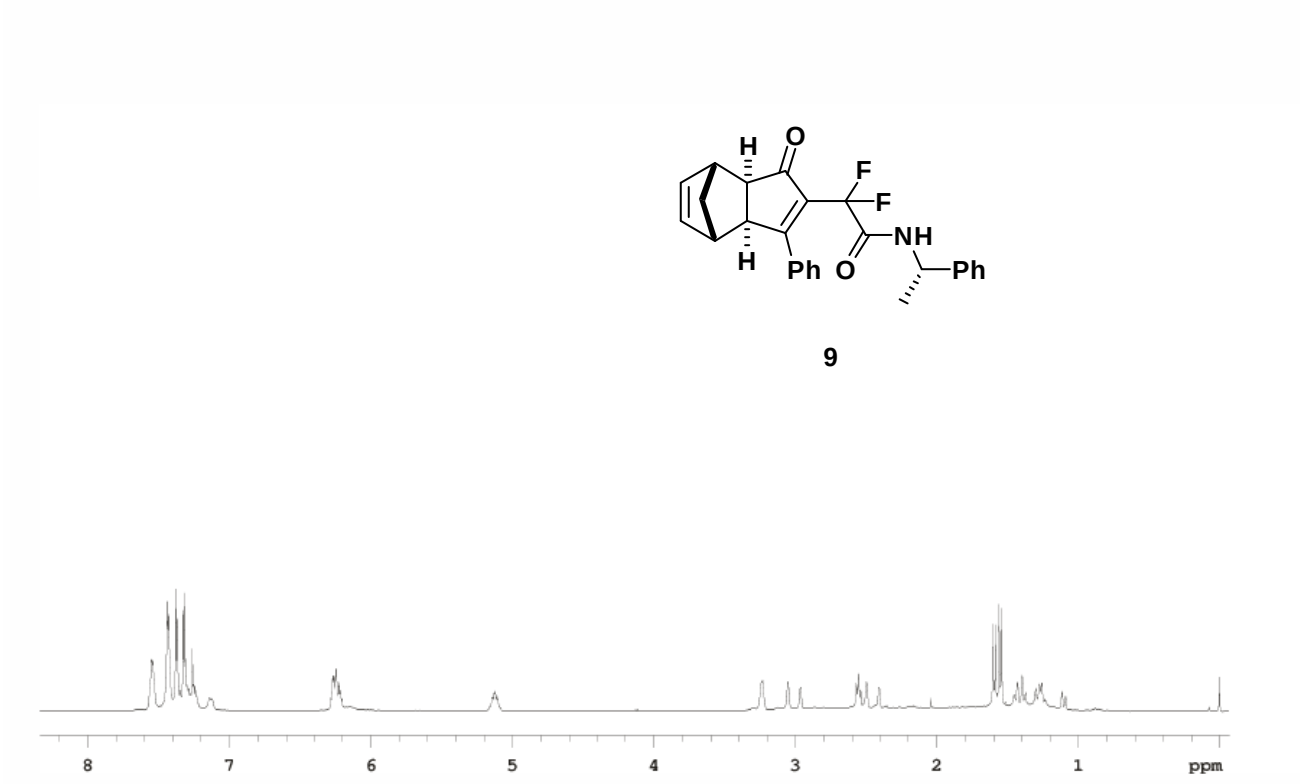
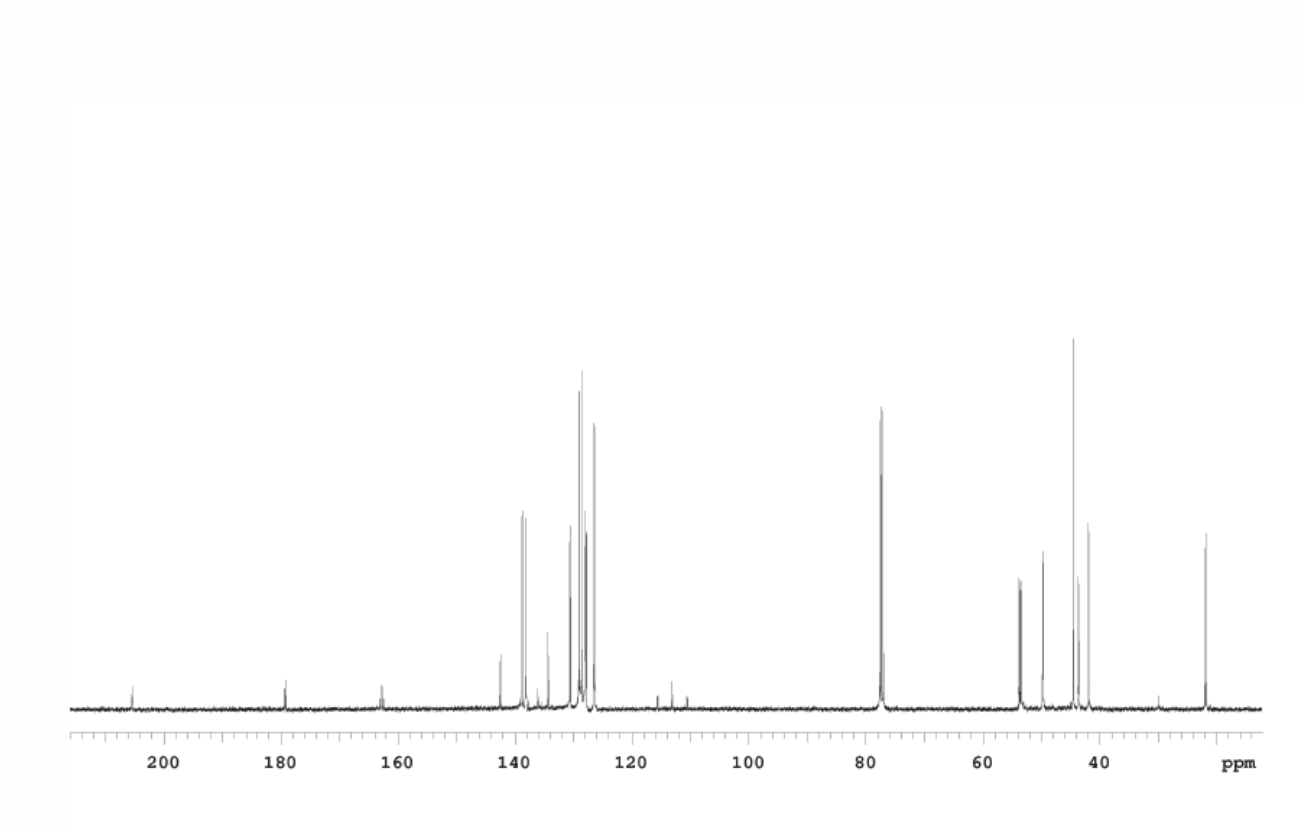


9

^{13}C-NMR (100MHz, $CDCl_3$)



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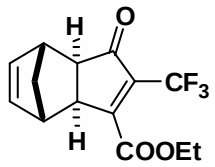

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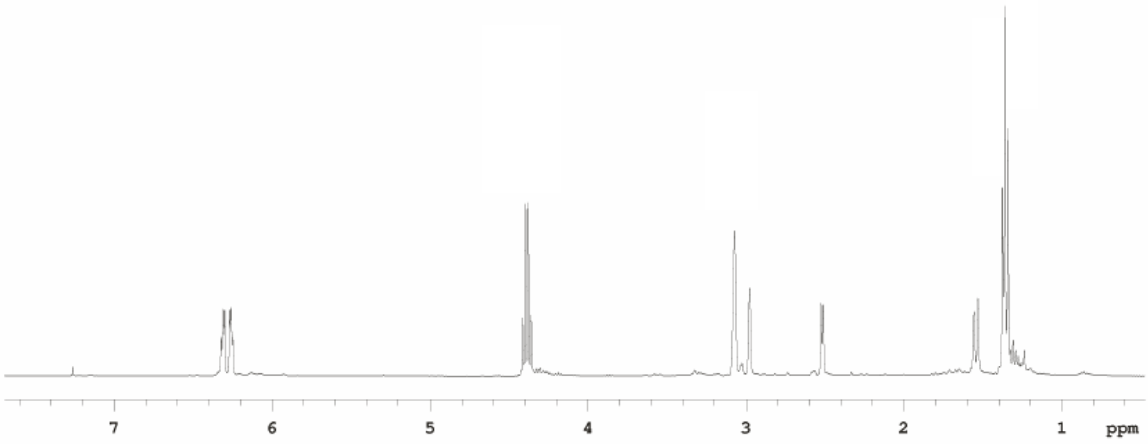

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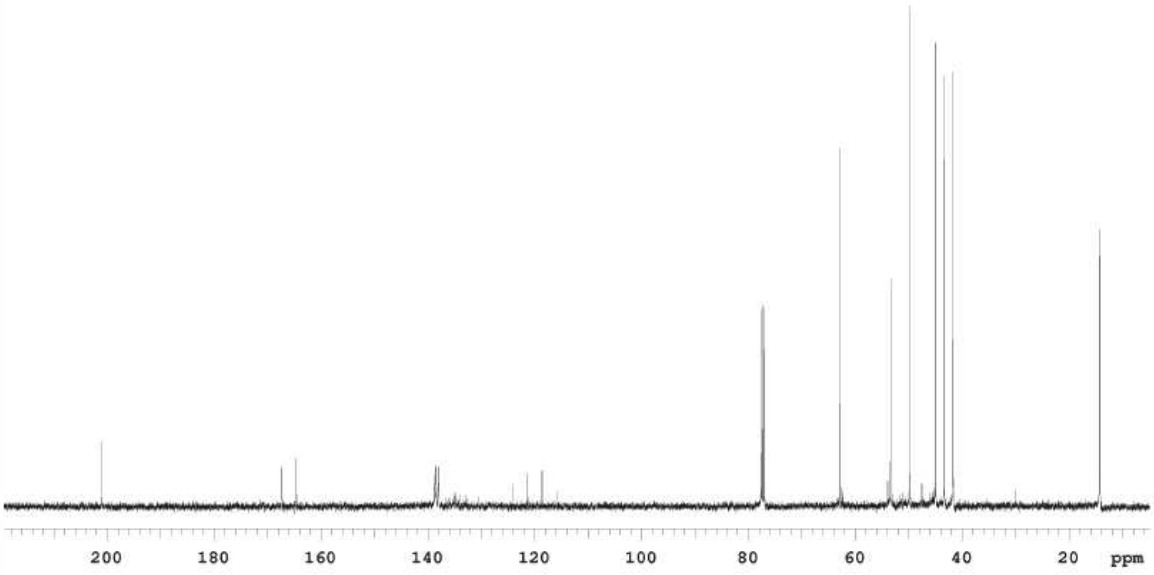
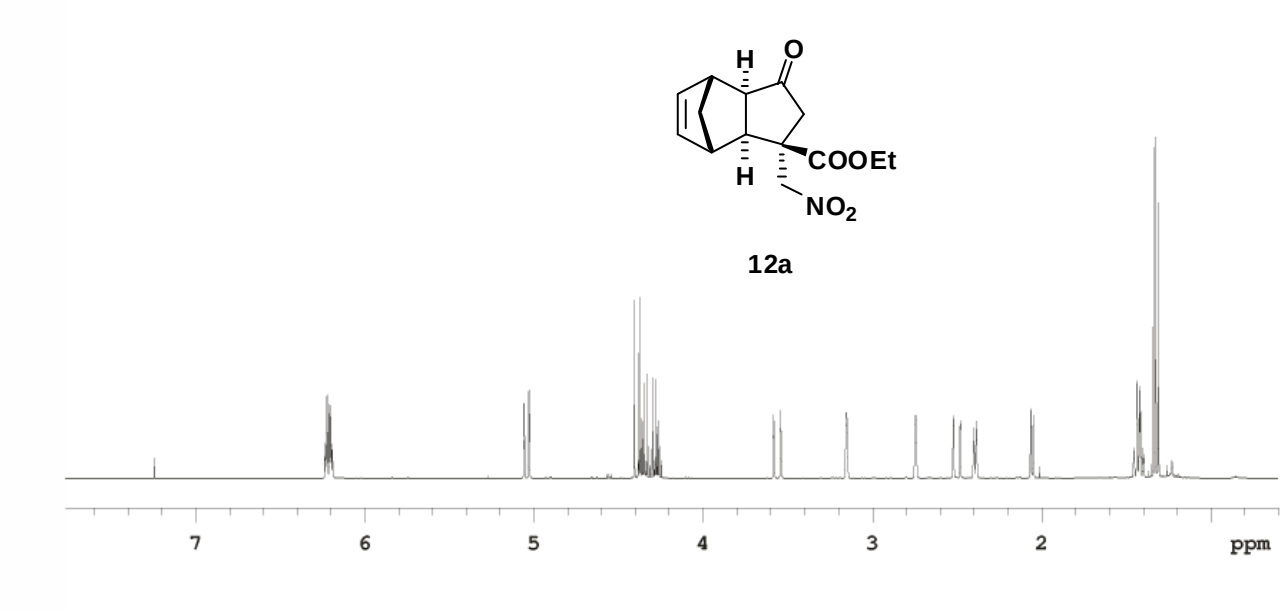


^{1}H-NMR (400MHz, $CDCl_3$)



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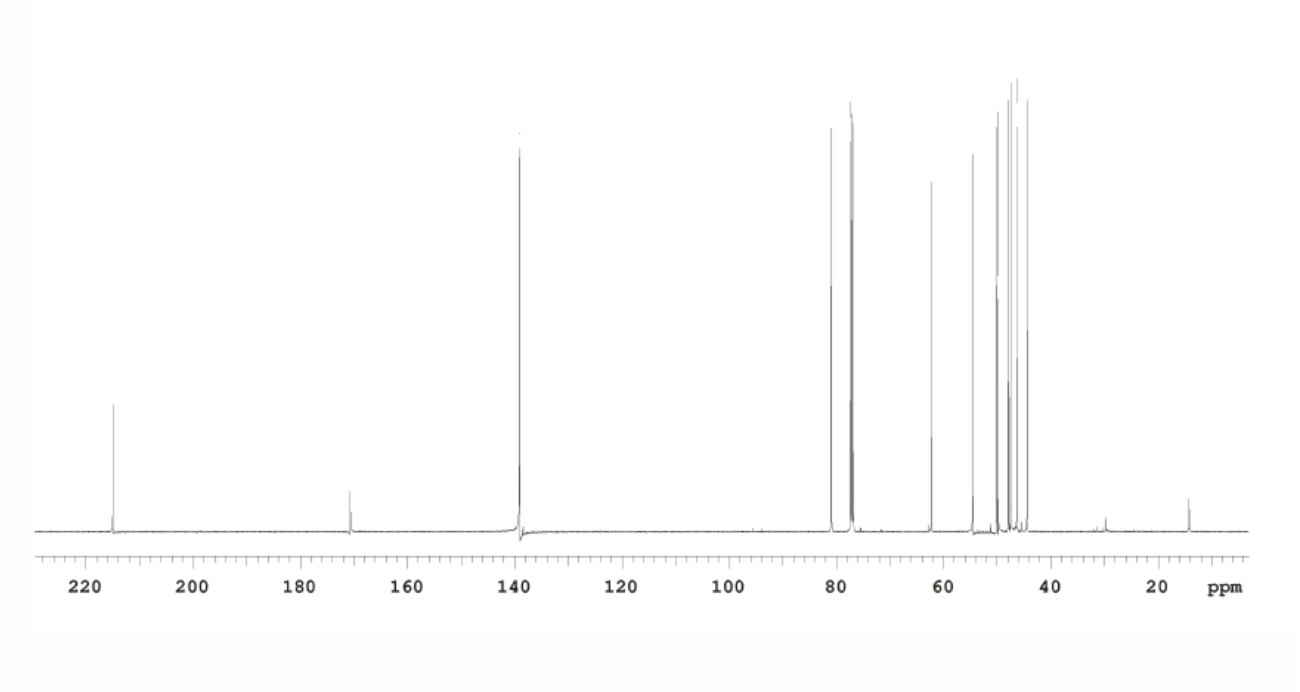
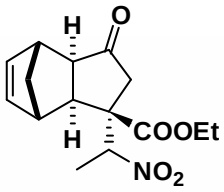
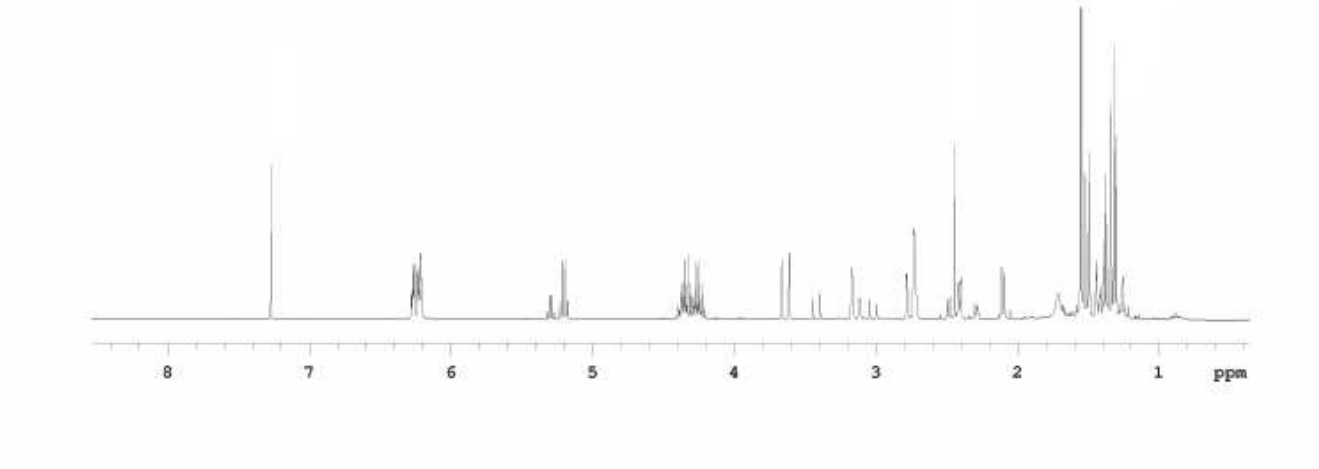


^{1}H-NMR (400MHz, $CDCl_3$)



12b



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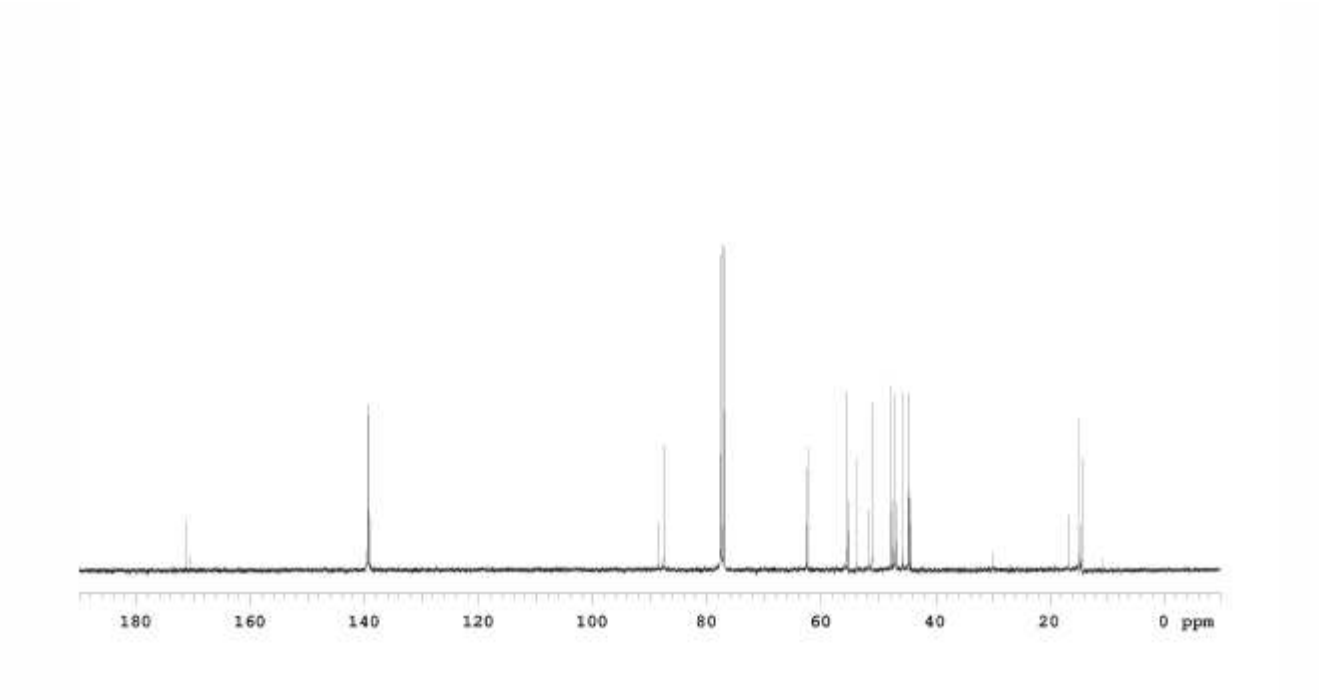

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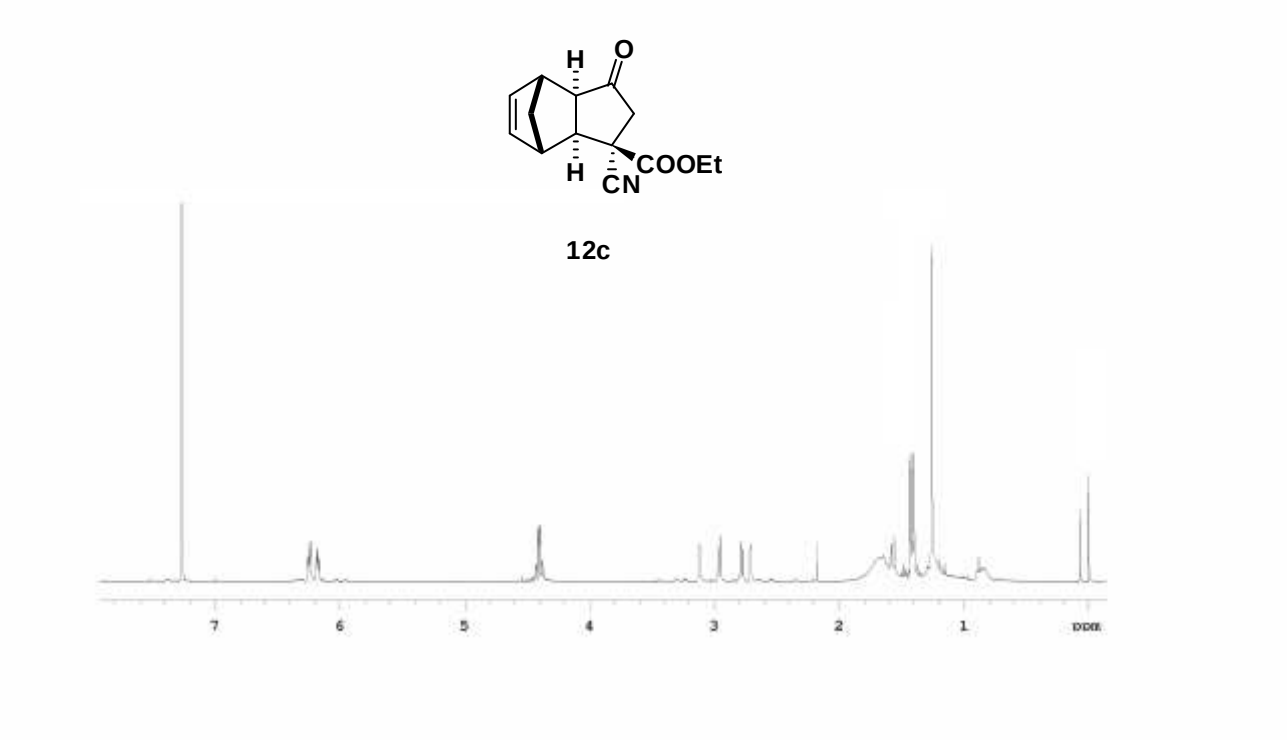

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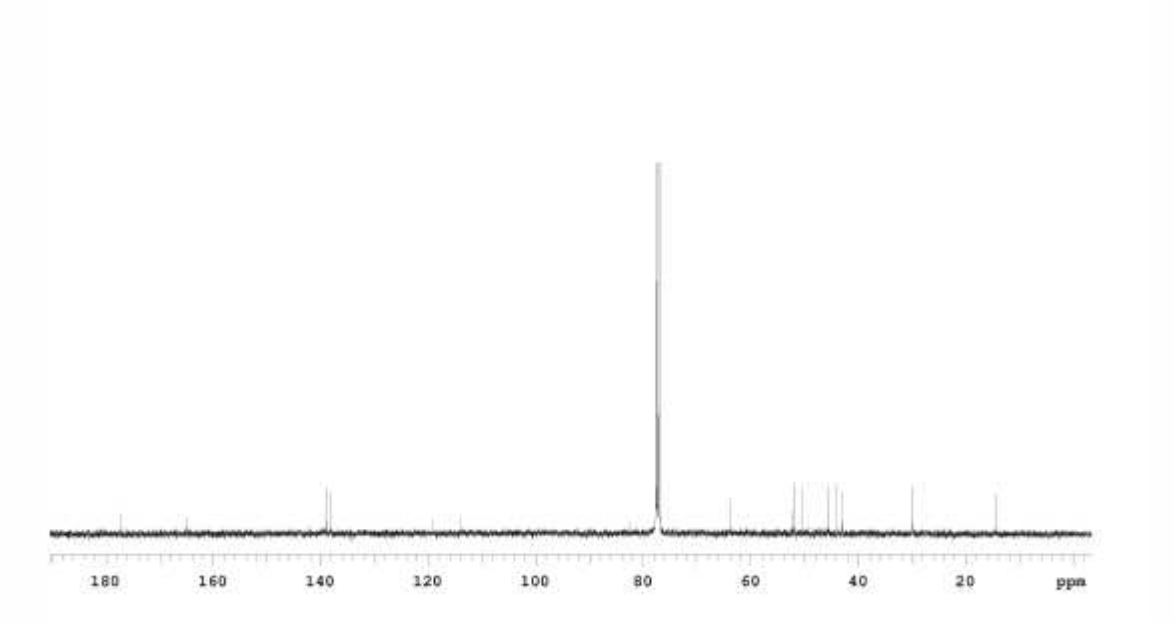
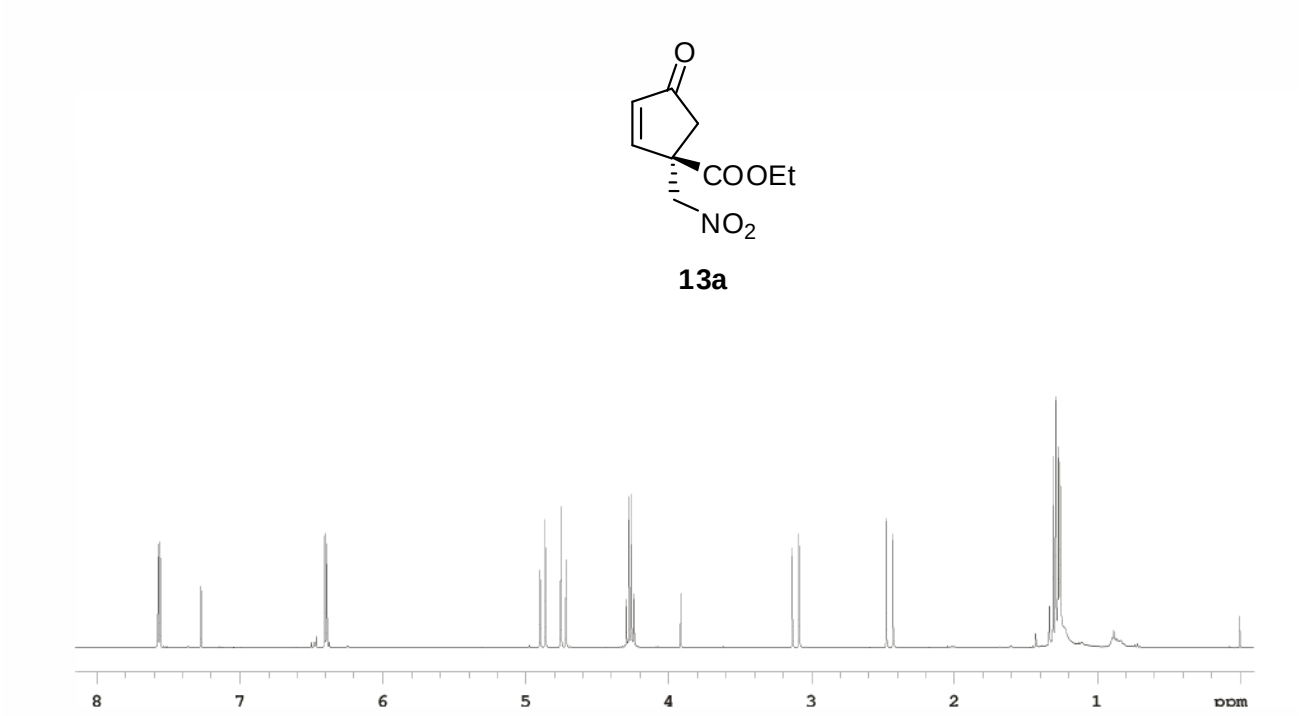


^{1}H-NMR (400MHz, $CDCl_3$)



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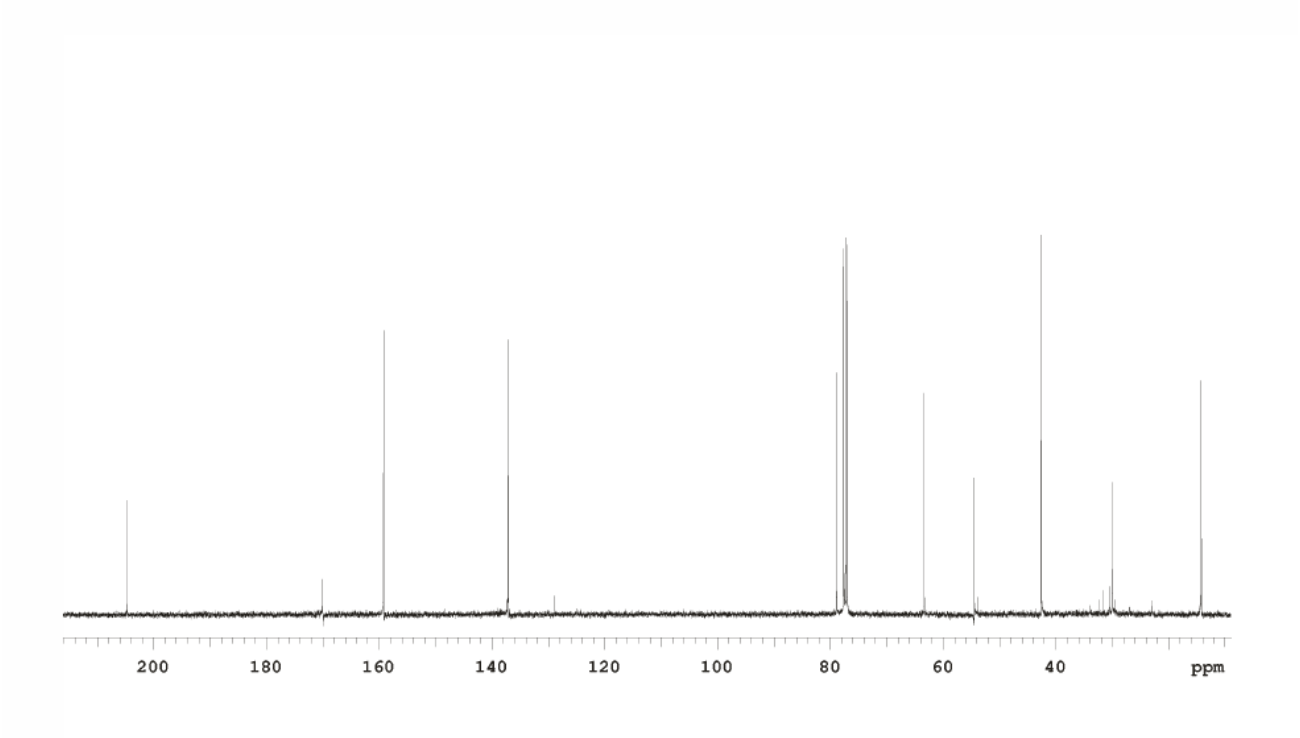

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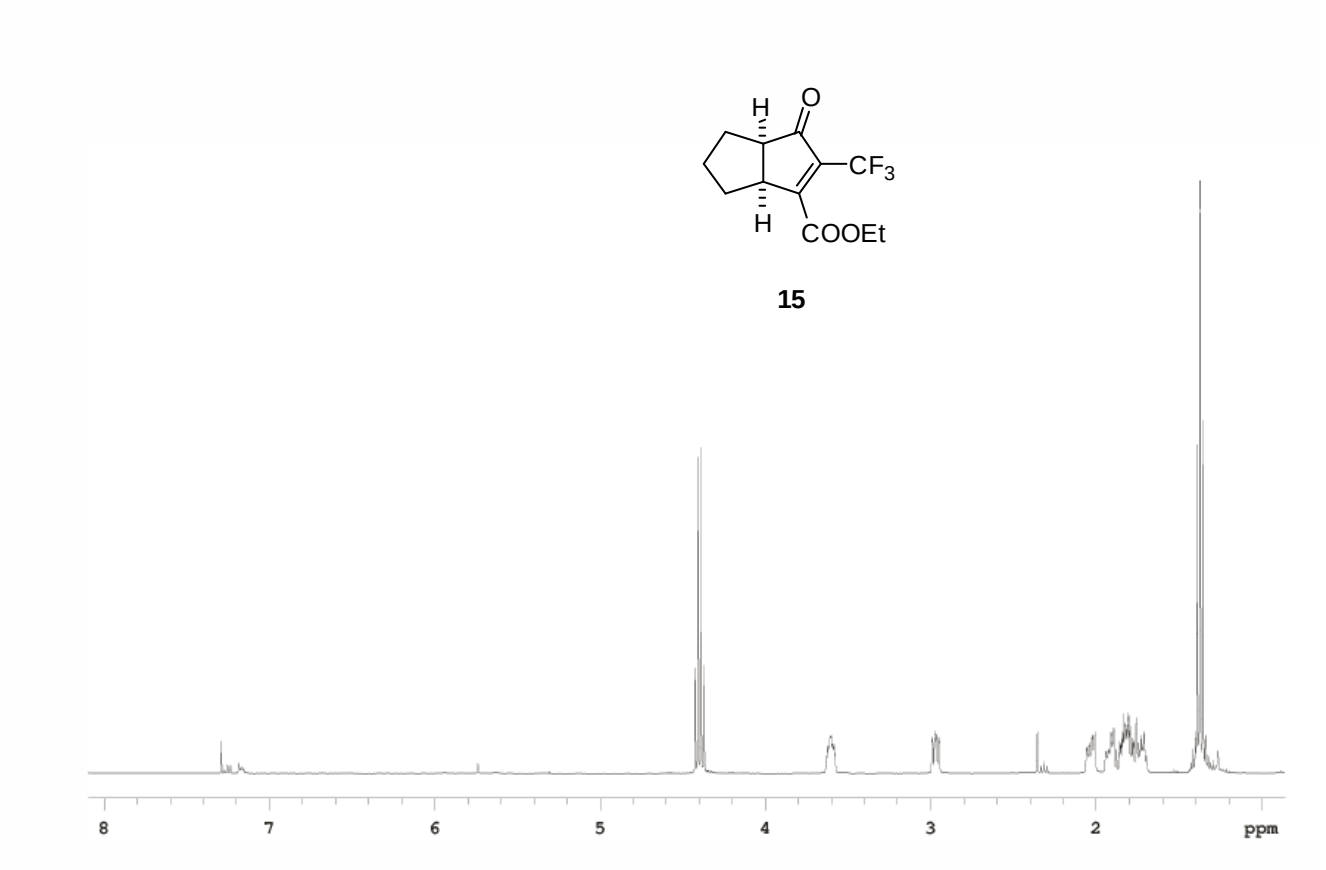

^{13}C-NMR (100MHz, $CDCl_3$)