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Cascade Aryne Insertion/Vinylogous Aldol Reaction of Vinyl-substituted *β*-Keto/enol Carbonyls

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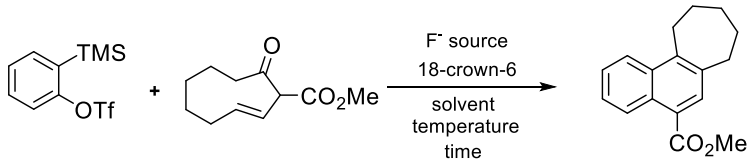
I. General Information:

All reactions were carried out in oven- or flame-dried glassware under nitrogen atmosphere using standard gas-tight syringes, cannulae and septa. Stirring was achieved with oven dried magnetic stir bars. THF was dried in the presence of sodium metal using benzophenone as indicator and distilled prior to use. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), iodine treatment or using p-anisaldehyde stain. Column chromatography was carried out using silica gel (100-200 mesh) packed in glass columns. Deuterated solvents were purchased from Sigma-Aldrich Company. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise mentioned) at 300, 400, 500 MHz and 75, 101, 126 MHz respectively and calibrated to the residual solvent peak (^{1}H: $\delta = 7.26$ and ^{13}C: $\delta = 77.16$ ppm). High-resolution mass spectrometry (HRMS) was recorded using EI or ESI-TOF techniques.

II. Table S1. Optimization of reaction conditions.[a,b,c]



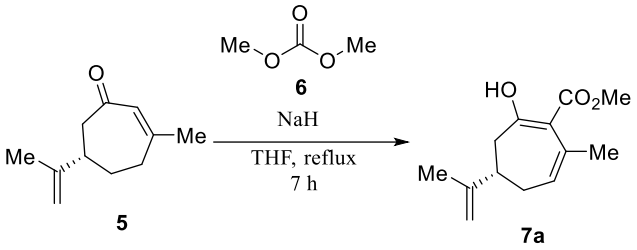
3b **7b** **14b**

Entry	Fluoride source	Solvent	Temperture (ºC)	Time (h)	Yield (%)[b]
1[c]	CsF	CH_3CN	80	6	30
2	CsF	CH_3CN	rt	10	44
3	CsF	CH_3CN	60	10	45
4	CsF	THF	rt	10	65
5	CsF	THF	60	6	76
6[c]	TBAF	CH_3CN	rt	2	38
7	KF	CH_3CN	rt	10	26
8	KF	THF	60	8	16
9	CsF	1,4-dioxane	60	6	51
10	CsF	DME	60	6	58
11	CsF	toluene	100	6	17

[a] Standard reaction conditions: **3b** (1.2 equiv), **7b** (1.0 equiv) and fluoride source (3.0 equiv), 18-crown-6 (3.0 equiv) in solvent (0.1 M) for 6 h; [b] Isolated yields after column chromatography; [c] Without 18-crown-6.

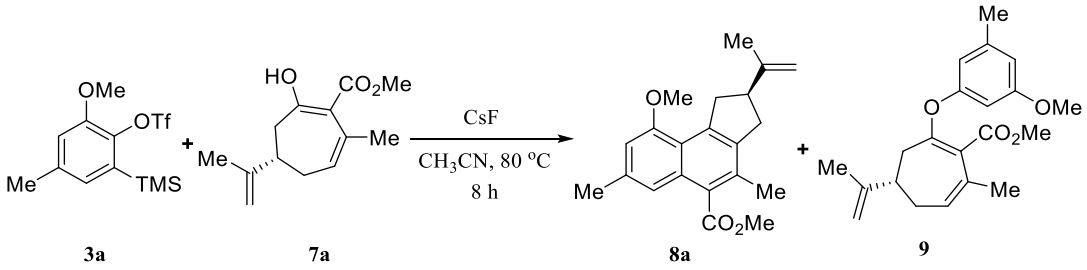
III. Experimental procedure:

Methyl (*S*)-2-hydroxy-7-methyl-4-(prop-1-en-2-yl)cyclohepta-1,6-diene-1-carboxylate (**7a**):



Enantiopure cycloheptenone derivative (**5**) was prepared from (*S*)-(+)-carvone.[1] To sodium hydride (60% oil dispersion, 0.49 g) was added a solution of dimethyl carbonate (1.3 mL, 15.3 mmol) in dry THF (10 mL). The mixture was stirred at reflux temperature, and then, a solution of cycloheptenone compound **6** (1.0 g, 6.1 mmol) in dry THF (3 mL) was added slowly to the reaction mixture over a period of 1.5 h with the help of a syringe pump. The mixture was refluxed and stirred for an additional 5 h, after complete addition of **6**. Then the reaction mixture was cooled to room temperature and acidified with 10% acetic acid. The mixture was poured into brine solution and extracted with EtOAc (20 mL X 3). Combined organic layers were dried over Na_2SO_4 and filtered. The filtrate was evaporated in *vacuo* to give a thick yellow liquid. The target product was purified by column chromatography (1% EtOAc in hexane) to give compound **7a** (0.79 g, 58% yield) as a colourless liquid: $\mathbf{R_f}$ = 0.8 (5% EtOAc in hexane); $\mathbf{[\alpha]_D}^{20}$ = -4.33 (c = 0.3, $CHCl_3$); **IR (neat):** υ_{max} 3021, 2966, 1721, 1441, 1216, 1085, 751 cm^{-1}**; ^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.80 (s, 1H), 5.83 (ddd, *J* = 8.8, 5.8, 1.5 Hz, 1H), 4.83 – 4.79 (m, 1H), 4.71 – 4.68 (m, 1H), 3.77 (s, 3H), 3.03 (p, *J* = 7.0 Hz, 1H), 2.41 – 2.25 (m, 2H), 2.10 (dd, *J* = 13.4, 6.7 Hz, 1H), 2.00 – 1.93 (m, 1H), 1.92 – 1.89 (m, 3H), 1.73 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.1, 172.4, 148.4, 134.2, 126.8, 109.9, 102.3, 54.3, 51.5, 37.2, 30.3, 22.2, 21.1; **HRMS** (ESI) m/z: calcd for $C_{13}H_{19}O_3$ $[M + H]^+$ 223.1329; found 223.1325.

Methyl (*S*)-9-methoxy-4,7-dimethyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8a) and methyl (*S*)-2-(3-methoxy-5-methylphenoxy)-7-methyl-4-(prop-1-en-2-yl)cyclohepta-1,6-diene-1-carboxylate (9):



A flame-dried two-neck round bottom flask with a magnetic stir bar was charged with acetonitrile (3 mL) at room temperature under N_2 atmosphere. Compound **7a** (100 mg, 0.4 mmol, 1.0 equiv), aryne precursor **3a** (185 mg, 0.58 mmol, 1.3 equiv), CsF (205 mg, 1.4 mmol, 3.0 equiv) and 18-crown-6 (357 mg, 1.4 mmol) were sequentially added to the flask. The reaction mixture was then heated at 80 °C for 8 h. When compound **7a** was consumed by TLC analysis, the mixture was cooled to room temperature. Then the mixture was poured in to brine (5 mL) and extracted with EtOAc (10 mL X 2). The organic layers were combined and dried over Na_2SO_4. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by silica gel column chromatography, which afforded compound **8a** (45 mg, 32% yield, R_f = 0.5, 5% EtOAc in hexane) as a colourless solid and compound **9** (38 mg, 25% yield, R_f = 0.3, 5% EtOAc in hexane) as a pale-yellow liquid.

Compound 8a:

R_f = 0.5 (5% EtOAc in hexane); **m.p** = 97.0 – 99.0 °C; **$[\alpha]_D^{20}$** = +14.0 (c = 0.1, $CHCl_3$); **IR (neat)**: υ_{max} 2928, 2848, 1725, 1580, 1445, 1258, 1179, 1034, 796 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.57 (s, 1H), 4.86 (d, *J* = 0.8 Hz, 1H), 4.77 (d, *J* = 1.4 Hz, 1H), 4.02 (s, 3H), 3.89 (s, 3H), 3.88 – 3.82 (m, 1H), 3.41 (dd, *J* = 17.7, 8.0 Hz, 1H), 3.23 – 3.06 (m, 2H), 2.83 (dd, *J* = 15.2, 7.9 Hz, 1H), 2.44 (s, 3H), 2.33 (s, 3H), 1.80 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.4, 156.8, 148.7, 139.3, 139.2, 135.9, 131.8, 130.4, 128.6, 120.2, 116.5, 109.5, 106.7, 55.3, 52.3, 46.0, 41.1, 36.7, 22.4, 20.6, 17.5; **HRMS** (ESI) m/z: calcd for $C_{21}H_{25}O_3$ $[M+H]^+$ 325.1798; found 325.1787.

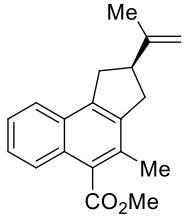
Compound 9:

R_f = 0.3 (5% EtOAc in hexane); **$[\alpha]_D^{20}$** = -3.0 (c = 0.1, $CHCl_3$); **IR (neat)**: υ_{max} 2930, 2854, 1725, 1596, 1440, 1260, 1157, 1057, 801 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.45 – 6.43 (m, 1H), 6.42 – 6.40 (m, 1H), 6.38 (t, *J* = 2.1 Hz, 1H), 5.99 (td, *J* = 6.9, 1.5 Hz, 1H), 4.73 – 4.70 (m, 1H), 4.66 – 4.63 (m, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 3.03 (p, *J* = 6.9 Hz, 1H), 2.36 – 2.27 (m, 6H), 2.19 – 2.10 (m, 1H), 1.86 (d, *J* = 1.1 Hz, 3H), 1.66 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 160.7, 160.1, 156.6, 148.1, 140.5, 133.5, 129.2, 120.8, 111.4, 109.9, 109.7, 101.7, 56.0, 55.4, 51.8, 34.7, 31.4, 21.8, 21.5, 21.1; **HRMS** (ESI) m/z: calcd for $C_{21}H_{27}O_4$ $[M+H]^+$ 343.1903; found 343.1887.

A. General procedure for the synthesis of cyclic naphthalene derivatives:

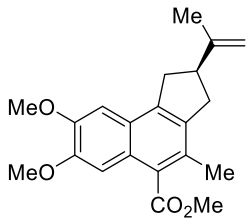
A screw-cap vial equipped with magnetic stir bar was charged with unsaturated enoldiene (1.0 equiv), aryne precursor (1.2 equiv), CsF (3.0 equiv) and 18-crown-6 (3.0 equiv) in dry THF (0.1 M) as solvent under nitrogen atmosphere. The reaction mixture was stirred at 60 ºC for 6 h. After completion of the reaction (monitored by TLC), diluted with ethyl acetate (5 mL) and water (5 mL) was added. The aqueous layer was extracted with ethyl acetate (2 X 5 mL), the combined organic layers were dried over Na_2SO_4 and the volatiles were evaporated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (EtOAc/hexane) to get desired compounds.

Methyl (*S*)-4-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8b):



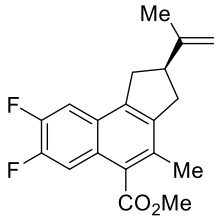
Following the general procedure **A,** compound **7a** (100 mg, 0.4 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (161 mg, 0.5 mmol), CsF (205 mg, 1.4 mmol) and 18-crown-6 (357 mg, 1.4 mmol) in 5 mL of THF afforded compound **8b** with 68% (86 mg) yield as colourless oil: **R_f** = 0.6 (5% EtOAc in hexane); **$[\alpha]_D^{20}$** = +6.0 (c = 0.05, $CHCl_3$); **IR (neat)**: υ_{max} 2926, 2860, 1727, 1445, 1252, 1215, 1162, 1040, 805 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.47 – 7.43 (m, 2H), 4.90 – 4.87 (m, 1H), 4.82 – 4.79 (m, 1H), 4.04 (s, 3H), 3.51 (dd, *J* = 15.9, 8.3 Hz, 1H), 3.35 – 3.14 (m, 3H), 2.97 (dd, *J* = 15.6, 7.8 Hz, 1H), 2.40 (s, 3H), 1.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 148.0, 140.4, 139.9, 130.6, 129.8, 129.3, 128.7, 126.1, 125.6, 125.2, 124.6, 109.8, 52.4, 45.9, 37.7, 36.6, 20.8, 17.6; **HRMS** (ESI) m/z: calcd for $C_{19}H_{21}O_2$ $[M+H]^+$ 281.1536; found 281.1523.

Methyl (*S*)-7,8-dimethoxy-4-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8c):



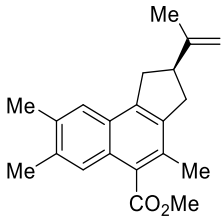
Following the general procedure **A,** compound **7a** (100 mg, 0.4 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3c** (194 mg, 0.5 mmol), CsF (205 mg, 1.4 mmol) and 18-crown-6 (357 mg, 1.4 mmol) in 5 mL of THF afforded compound **8c** with 38% (58 mg) yield as white solid: $\mathbf{R_f}$ = 0.2 (10% EtOAc in hexane); **m.p** = 114-116 °C; $\mathbf{[\alpha]_D}^{\mathbf{20}}$ = +14.67 (c = 0.3, $CHCl_3$); **IR (neat)**: υ_{max} 2939, 2842, 1720, 1501, 1474, 1438, 1248, 1202, 1159, 1032, 756 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 (s, 1H), 6.98 (s, 1H), 4.90 – 4.86 (m, 1H), 4.82 – 4.78 (m, 1H), 4.02 (d, *J* = 2.1 Hz, 3H), 4.00 (s, 3H), 3.97 (s, 3H), 3.45 – 3.36 (m, 1H), 3.29 – 3.18 (m, 2H), 3.16 – 3.07 (m, 1H), 2.99 – 2.87 (m, 1H), 2.36 (s, 3H), 1.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.0, 149.5, 149.2, 148.1, 139.2, 138.2, 128.9, 127.7, 125.5, 124.5, 109.8, 104.3, 103.2, 55.9, 55.9, 52.2, 45.9, 37.6, 36.9, 20.8, 17.6; **HRMS** (ESI) m/z: calcd for $C_{21}H_{25}O_4$ $[M+H]^+$ 341.1747; found 341.1731.

Methyl (*S*)-7,8-difluoro-4-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8d):



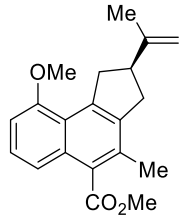
Following the general procedure **A,** compound **7a** (100 mg, 0.4 mmol), 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3d** (178 mg, 0.5 mmol), CsF (205 mg, 1.4 mmol) and 18-crown-6 (357 mg, 1.4 mmol) in 5 mL of THF afforded compound **8d** with 44% (63 mg) yield as white solid: $\mathbf{R_f}$ = 0.6 (5% EtOAc in hexane); **m.p** = 77-79 °C; $\mathbf{[\alpha]_D}^{\mathbf{20}}$ = +3.0 (c = 0.1, $CHCl_3$); **IR (neat)**: υ_{max} 2960, 2927, 2859, 1723, 1525, 1451, 1255, 1031, 801 cm^{-1}, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 12.3, 8.0 Hz, 1H), 7.46 (dd, *J* = 11.1, 8.2 Hz, 1H), 4.88 – 4.86 (m, 1H), 4.82 – 4.80 (m, 1H), 4.03 (s, 3H), 3.41 (dd, *J* = 15.9, 8.1 Hz, 1H), 3.31 – 3.20 (m, 2H), 3.12 (dd, *J* = 15.9, 7.5 Hz, 1H), 2.96 (dd, *J* = 15.5, 7.4 Hz, 1H), 2.39 (s, 3H), 1.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 151.0 (dd, $J_{C\text{-}F}$ = 251.0, 18.3 Hz), 148.5 (dd, $J_{C\text{-}F}$ = 258.7, 22.3 Hz), 147.4, 140.5 (d, $J_{C\text{-}F}$ = 1.9 Hz), 134.0 (d, $J_{C\text{-}F}$ = 4.0 Hz), 131.6 (d, $J_{C\text{-}F}$ = 1.9 Hz), 128.5 (d, $J_{C\text{-}F}$ = 3.2 Hz), 126.7 (d, $J_{C\text{-}F}$ = 6.9 Hz), 125.6 (d, $J_{C\text{-}F}$ = 7.0 Hz), 111.9 (d, $J_{C\text{-}F}$ = 18.4 Hz), 110.5 (d, $J_{C\text{-}F}$ = 16.4 Hz), 110.0, 52.4, 45.6, 37.7, 36.7, 20.7, 17.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -136.81 (d, *J* = 21.1 Hz), -137.09 (d, *J* = 21.1 Hz); **HRMS** (ESI) m/z: calcd for $C_{19}H_{19}F_2O_2$ $[M+H]^+$ 317.1353; found 317.1346.

Methyl (*S*)-4,7,8-trimethyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8e):



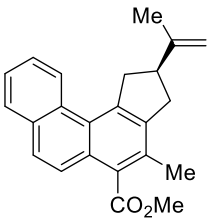
Following the general procedure **A,** compound **7a** (100 mg, 0.4 mmol), 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3e** (176 mg, 0.5 mmol), CsF (205 mg, 1.4 mmol) and 18-crown-6 (357 mg, 1.4 mmol) in 5 mL of THF afforded compound **8e** with 45% (62 mg) yield as white solid: $\mathbf{R_f}$ = 0.6 (5% EtOAc in hexane); **m.p** = 82-84 °C; $\mathbf{[\alpha]_D}^{\mathbf{20}}$ = +15.67 (c = 0.3, $CHCl_3$); **IR (neat)**: υ_{max} 3085, 2960, 2927, 1723, 1525, 1451, 1255, 1156, 1031, 801 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (s, 2H), 4.87 (s, 1H), 4.78 (s, 1H), 4.03 (s, 3H), 3.46 (dd, *J* = 15.9, 8.3 Hz, 1H), 3.31 – 3.11 (m, 3H), 2.93 (dd, *J* = 15.5, 7.8 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H), 1.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 148.2, 139.4, 138.9, 135.7, 135.3, 129.4, 128.7, 128.4, 127.6, 124.7, 124.2, 109.7, 52.2, 45.9, 37.7, 36.6, 20.8, 20.6, 20.4, 17.5; **HRMS** (ESI) m/z: calcd for $C_{21}H_{25}O_2$ $[M+H]^+$ 309.1849; found 309.1836.

Methyl (*S*)-9-methoxy-4-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8f):



Following the general procedure **A,** compound **7a** (100 mg, 0.4 mmol), 2-methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **3f** (169 mg, 0.5 mmol), CsF (205 mg, 1.4 mmol) and 18-crown-6 (357 mg, 1.4 mmol) in 5 mL of THF afforded compound **8f** with 68% (95 mg) yield as yellow oil: $\mathbf{R_f}$ = 0.4 (5% EtOAc in hexane); $\mathbf{[\alpha]_D}^{\mathbf{20}}$ = +14.0 (c = 0.1, $CHCl_3$); **IR (neat)**: υ_{max} 2939, 2853, 1721, 1522, 1451, 1249, 1155, 1038, 880, 760 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.31 – 7.27 (m, 1H), 7.27 – 7.24 (m, 1H), 6.73 (dd, *J* = 7.2, 1.3 Hz, 1H), 4.88 – 4.85 (m, 1H), 4.79 – 4.75 (m, 1H), 4.01 (s, 3H), 3.92 – 3.85 (m, 4H), 3.49 – 3.39 (m, 1H), 3.21 – 3.08 (m, 2H), 2.85 (dd, *J* = 14.9, 7.5 Hz, 1H), 2.35 (s, 3H), 1.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 171.2, 157.0, 148.6, 140.2, 139.5, 131.7, 130.5, 129.2, 126.1, 121.9, 117.4, 109.6, 104.4, 55.4, 52.3, 45.9, 41.2, 36.8, 20.6, 17.6; **HRMS** (ESI) m/z: calcd for $C_{20}H_{23}O_3$ $[M+H]^+$ 311.1642; found 311.1636.

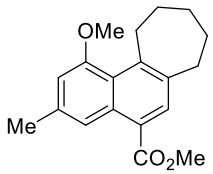
Methyl (*S*)-12-methyl-16-(prop-1-en-2-yl)-16,17-dihydro-15*H*-cyclopenta[*c*]phenanthrene-11-carboxylate (8g):



Following the general procedure **A,** compound **7a** (100 mg, 0.4 mmol), 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate **3g** (188 mg, 0.5 mmol), CsF (205 mg, 1.4 mmol) and 18-crown-6 (357 mg, 1.4 mmol) in 5 mL of THF afforded compound **8g** with 50% (75 mg) yield as white solid: $\mathbf{R_f}$ = 0.7 (5% EtOAc in hexane); **m.p** = 103-105 °C; $\mathbf{[\alpha]_D}^{\mathbf{20}}$ = +12.0 (c = 0.3, $CHCl_3$); **IR (neat)**: υ_{max} 3075, 2943, 2857, 1728, 1443,

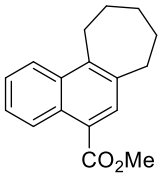
1221, 1039, 754 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 4.96 – 4.92 (m, 1H), 4.86 – 4.84 (m, 1H), 4.08 – 4.05 (m, 3H), 3.97 (dd, *J* = 14.9, 7.8 Hz, 1H), 3.73 – 3.66 (m, 1H), 3.29 – 3.21 (m, 2H), 3.03 (dd, *J* = 18.1, 11.6 Hz, 1H), 2.43 (s, 3H), 1.87 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 147.7, 142.7, 140.1, 132.7, 131.2, 131.1, 129.6, 128.9, 128.6, 127.4, 126.6 (2C), 126.2, 126.2, 124.0, 110.2, 52.5, 46.7, 43.1, 36.7, 20.8, 17.5; **HRMS** (ESI) m/z: calcd for $C_{23}H_{23}O_2$ $[M+H]^+$ 331.1693; found 331.1679.

Methyl 1-methoxy-3-methyl-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11a):



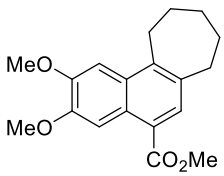
Following the general procedure **A,** compound **7b**[2] (100 mg, 0.5 mmol), 2-methoxy-4-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **3a** (209 mg, 0.6 mmol), CsF (232 mg, 1.5 mmol) and 18-crown-6 (404 mg, 1.5 mmol) in 5 mL of THF afforded compound **11a** with 74% (106 mg) yield as white solid: **R_f =** 0.4 (5% EtOAc in hexane); **m.p** = 100-102 ºC; **IR (neat)**: υ_{max} 2923, 2853, 1716, 1624, 1566, 1451, 1259, 1171, 1043 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 1.4, 1.0 Hz, 1H), 7.85 (s, 1H), 6.70 (d, *J* = 1.4 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 3.55 – 3.48 (m, 2H), 3.03 – 2.98 (m, 2H), 2.49 (d, *J* = 0.7 Hz, 3H), 1.90 – 1.76 (m, 4H), 1.72 – 1.67 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9, 157.6, 145.5, 140.1, 136.3, 133.0, 132.3, 124.0, 123.9, 117.5, 108.4, 55.7, 52.1, 36.1, 32.4, 31.7, 27.8, 26.5, 22.4; **HRMS** (ESI) m/z: calcd for $C_{19}H_{23}O_3$ $[M + H]^+$ 299.1642; found 299.1644.

Methyl 8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11b):



Following the general procedure **A,** compound **7b** (110 mg, 0.6 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (201 mg, 0.7 mmol), CsF (255 mg, 1.7 mmol) and 18-crown-6 (444 mg, 1.7 mmol) in 5 mL of THF afforded compound **11b** with 76% (109 mg) yield as colourless oil: **R_f** = 0.7 (5% EtOAc in hexane); **IR (neat)**: υ_{max} 2921, 2852, 1712, 1573, 1514, 1441, 1280, 1245, 1196, 1150, 1028, 782 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.96 – 8.92 (m, 1H), 8.22 – 8.16 (m, 1H), 8.02 (s, 1H), 7.58 – 7.50 (m, 2H), 4.00 (s, 3H), 3.34 – 3.24 (m, 2H), 3.08 – 2.99 (m, 2H), 1.95 – 1.89 (m, 2H), 1.75 – 1.66 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 144.8, 139.8, 132.5, 132.2, 130.6, 126.3, 126.1, 124.7, 123.8, 52.1, 36.5, 32.3, 28.7, 27.5, 26.6; **HRMS** (ESI) m/z: calcd for $C_{17}H_{19}O_2$ $[M + H]^+$ 255.1380; found 255.1379.

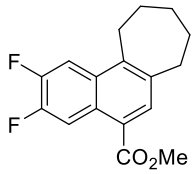
Methyl 2,3-dimethoxy-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11c):



Following the general procedure **A,** compound **7b** (100 mg, 0.5 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3c** (219 mg, 0.6 mmol), CsF (232 mg, 1.5 mmol) and 18-

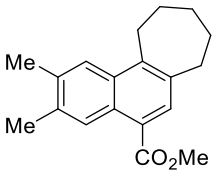
crown-6 (404 mg, 1.5 mmol) in 5 mL of THF afforded compound **11c** with 85% (122 mg) yield as white solid: $\mathbf{R_f}$ = 0.2 (10% EtOAc in hexane); **m.p** = 120-122 °C; **IR (neat)**: υ_{max} 2921, 2848, 1706, 1512, 1434, 1242, 1191, 1151, 1030, 869, 756 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.95 (s, 1H), 7.40 (s, 1H), 4.05 (s, 3H), 4.03 (s, 3H), 3.96 (s, 3H), 3.25 – 3.18 (m, 2H), 3.02 – 2.95 (m, 2H), 1.90 (dt, *J* = 11.8, 6.0 Hz, 2H), 1.75 – 1.64 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 149.9, 149.3, 143.7, 138.2, 131.0, 128.3, 127.4, 122.1, 105.3, 102.8, 55.9, 55.8, 52.0, 36.5, 32.2, 29.3, 27.8, 26.7; **HRMS** (ESI) m/z: calcd for $C_{19}H_{23}O_4$ $[M + H]^+$ 315.1591; found 315.1592.

Methyl 2,3-difluoro-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11d):



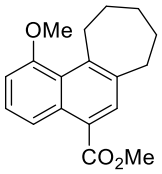
Following the general procedure **A,** compound **7b** (100 mg, 0.5 mmol), 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3d** (204 mg, 0.6 mmol), CsF (232 mg, 1.5 mmol) and 18-crown-6 (404 mg, 1.5 mmol) in 5 mL of THF afforded compound **11d** with 60% (86 mg) yield as white solid: $\mathbf{R_f}$ = 0.6 (5% EtOAc in hexane); **m.p** = 90-92 °C; **IR (neat)**: υ_{max} 2931, 2856, 1716, 1582, 1529, 1474, 1241, 1143, 892, 813 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 13.4, 8.9 Hz, 1H), 8.05 (s, 1H), 7.88 (dd, *J* = 13.1, 8.4 Hz, 1H), 3.98 (s, 3H), 3.21 – 3.16 (m, 2H), 3.03 – 2.99 (m, 2H), 1.95 – 1.89 (m, 2H), 1.73 – 1.65 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 150.3 (dd, $J_{C\text{-}F}$ = 251.5, 17.4 Hz), 150.1 (dd, $J_{C\text{-}F}$ = 251.5, 17.4 Hz), 144.6 (d, $J_{C\text{-}F}$ = 3.5 Hz), 140.3, 133.2, 129.8 (d, $J_{C\text{-}F}$= 5.9 Hz), 128.1 (d, $J_{C\text{-}F}$= 8.2 Hz), 123.7 (d, $J_{C\text{-}F}$ = 3.8 Hz), 113.1 (d, $J_{C\text{-}F}$ = 19.0 Hz), 110.3 (d, $J_{C\text{-}F}$ = 17.7 Hz), 52.3, 36.5, 32.1, 29.5, 27.4, 26.5; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -136.55 (d, *J* = 22.2 Hz), -136.75 (d, *J* = 22.2 Hz); **HRMS** (ESI) m/z: calcd for $C_{17}H_{17}F_2O_2$ $[M + H]^+$ 291.1191; found 291.1186.

Methyl 2,3-dimethyl-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (14e):



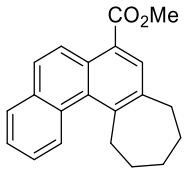
Following the general procedure **A,** compound **7b** (100 mg, 0.5 mmol), 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3e** (200 mg, 0.6 mmol), CsF (232 mg, 1.5 mmol) and 18-crown-6 (404 mg, 1.5 mmol) in 5 mL of THF afforded compound **14e** with 81% (116 mg) yield as white solid: $\mathbf{R_f}$ = 0.7 (5% EtOAc in hexane); **m.p** = 69-71 °C; **IR (neat)**: υ_{max} 2920, 2852, 1712, 1566, 1502, 1447, 1363, 1238, 1179, 1135, 1030, 762 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.92 (d, *J* = 2.6 Hz, 2H), 3.98 (s, 3H), 3.29 – 3.24 (m, 2H), 3.03 – 2.97 (m, 2H), 2.46 (s, 6H), 1.94-1.88 (m, 2H), 1.75 – 1.64 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 144.0, 138.8, 136.2, 135.6, 131.7, 131.1, 129.6, 125.8, 123.6, 123.5, 52.0, 36.5, 32.3, 28.7, 27.7, 26.8, 20.7, 20.5; **HRMS** (ESI) m/z: calcd for $C_{19}H_{23}O_2$ $[M + H]^+$ 283.1693; found 283.1694.

Methyl 1-methoxy-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11f):



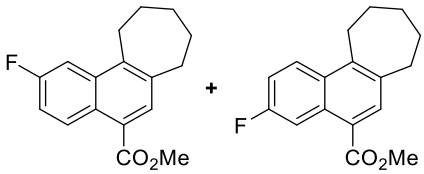
Following the general procedure **A,** compound **7b** (100 mg, 0.5 mmol), 2-methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **3f** (201 mg, 0.6 mmol), CsF (232 mg, 1.5 mmol) and 18-crown-6 (404 mg, 1.5 mmol) in 5 mL of THF afforded compound **11f** with 72% (103 mg) yield as pale yellow oil: $\mathbf{R}_f$ = 0.5 (5% EtOAc in hexane); **IR (neat)**: υ_{max} 2925, 2853, 1716, 1566, 1446, 1252, 1195, 1139, 1031, 769 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.7, 1.0 Hz, 1H), 7.89 (s, 1H), 7.39 (dd, *J* = 8.6, 7.7 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 3.70 (s, 3H), 3.93 (s, 3H), 3.55 – 3.49 (m, 2H), 3.07 – 3.00 (m, 2H), 1.90 – 1.77 (m, 4H), 1.71 (dt, *J* = 8.1, 6.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 157.8, 145.6, 141.1, 132.8, 132.3, 126.3, 125.7, 124.6, 118.5, 106.1, 55.7, 52.2, 36.2, 32.6, 31.7, 27.8, 26.4; **HRMS** (ESI) m/z: calcd for $C_{18}H_{21}O_3$ $[M + H]^+$ 285.1485; found 285.1487.

Methyl 10,11,12,13-tetrahydro-9*H*-cyclohepta[*c*]phenanthrene-7-carboxylate (11g):



Following the general procedure **A,** compound **7b** (100 mg, 0.5 mmol), 2-(trimethylsilyl)naphthalen-1-yl trifluoromethanesulfonate **3g** (213 mg, 0.6 mmol), CsF (232 mg, 1.5 mmol) and 18-crown-6 (404 mg, 1.5 mmol) in 5 mL of THF afforded compound **11g** with 70% (108 mg) yield (two regioisomers with 99:1 ratio) as white solid: $\mathbf{R}_f$ = 0.5 (5% EtOAc in hexane); **m.p** = 93-95 °C; **IR (neat)**: υ_{max} 2922, 2852, 1715, 1440, 1301, 1245, 1197, 1145, 1048, 828, 755 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 – 8.63 (d, *J* = 9.2 Hz, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 7.97 (s, 1H), 7.88 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.60 – 7.50 (m, 2H), 4.00 (s, 3H), 3.49 – 3.48 (m, 2H), 3.13 – 3.07 (m, 2H), 2.11 – 2.00 (m, 4H), 1.91 – 1.82 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 145.5, 142.6, 133.1, 131.6, 131.0, 130.5, 130.3, 128.4, 128.1, 127.7, 126.5, 125.0, 123.8, 52.3, 37.1, 34.2, 32.4, 28.1, 27.4; **HRMS** (ESI) m/z: calcd for $C_{21}H_{21}O_2$ $[M + H]^+$ 305.1536; found 305.1537.

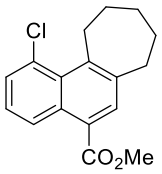
Methyl 2-fluoro-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11h) and Methyl 2-fluoro-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11h'):



Following the general procedure **A,** compound **7b** (100 mg, 0.5 mmol), 5-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3h** (193 mg, 0.6 mmol), CsF (232 mg, 1.5 mmol) and 18-crown-6 (404 mg, 1.5 mmol) in 5 mL of THF afforded compound **11h** with 75% yield (two regioisomers **11h** and **11h'** with 3:2 ratio respectively) as pale yellow oil: $\mathbf{R}_f$ = 0.6 (5% EtOAc in hexane); **IR (neat)**: υ_{max} 2924, 2854, 1712, 1625, 1519, 1439, 1248,1199, 1144, 1029, 832, 775 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 9.5, 6.2 Hz, 0.95H, major), 8.71 (dd, *J* = 12.1, 2.7 Hz, 0.61H, minor), 8.16 (dd, *J* = 9.5, 5.9 Hz, 0.71H, minor), 8.08 (s, 0.66H, minor), 7.97 (s, 1H, major), 7.77 (dd, *J* = 12.0, 2.6 Hz, 1H, major), 7.34 – 7.27 (m, 1.67H, major + minor), 3.99 (s, 5.30H, major + minor), 3.29 – 3.24 (m, 1.47H, minor), 3.22 – 3.17 (m, 2.19H, major), 3.02 (dd, *J* = 7.9, 3.1 Hz, 3.61H, major + minor), 1.91 (qd, *J* = 8.1, 4.5 Hz, 3.74H, major + minor), 1.69 (tt, *J* = 11.4, 5.9 Hz, 7.24H, major + minor); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1 (major), 167.9 (minor), 161.3 (d, $J_{C\text{-}F}$ = 245.5 Hz, minor), 161.1 (d, $J_{C\text{-}F}$ = 245.5 Hz, major), 145.4 (minor), 144.1 (d, $J_{C\text{-}F}$ = 5.5 Hz, major), 140.9 (major), 139.1 (minor), 133.9 (major), 133.6 (d, $J_{C\text{-}F}$ = 8.0 Hz, major), 132.0 (major), 131.8 (major),

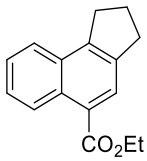
129.4 (minor), 129.1 (d, J_{C-F} = 8.8 Hz, major), 127.6 (minor), 126.4 (d, J_{C-F} = 9.0 Hz, minor), 124.8 (minor), 123.7 (d, J_{C-F} = 5.5 Hz, minor), 116.4(d, J_{C-F} = 24.7 Hz, major), 116.2 (d, J_{C-F} = 25.0 Hz, minor), 110.2 (d, J_{C-F} = 23.5 Hz, minor), 107.5 (d, J_{C-F} = 21.64 Hz, major), 52.2 (major), 52.2 (minor), 36.5 (major), 36.4 (minor), 32.2 (major), 32.2 (minor), 29.1 (major + minor), 27.5 (minor), 27.4 (major), 26.6 (minor), 26.5 (major). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -114.04 (s, minor), -114.37 (s, major); **HRMS** (ESI) m/z: calcd for $C_{17}H_{18}FO_2$ $[M + H]^+$ 273.1285; found 273.1280.

Methyl 1-chloro-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11i):



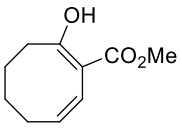
Following the general procedure **A,** compound **7b** (100 mg, 0.5 mmol), 2-chloro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **3i** (203 mg, 0.6 mmol), CsF (232 mg, 1.5 mmol) and 18-crown-6 (404 mg, 1.5 mmol) in 5 mL of THF afforded compound **11i** with 64% (94 mg) yield as white solid: $\mathbf{R_f}$ = 0.7 (5% EtOAc in hexane); **IR (neat)**: υ_{max} 2930, 2857, 1721, 1446, 1263, 1205, 1156 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.93 (s, 1H), 7.58 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.35 (dd, *J* = 8.6, 7.4 Hz, 1H), 3.98 (s, 3H), 3.56 – 3.46 (m, 2H), 3.09 – 3.03 (m, 2H), 1.97 – 1.90 (m, 4H), 1.79 – 1.72 (m, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 145.0, 143.2, 133.0, 132.6, 131.3, 131.2, 129.8, 125.8, 125.5, 125.3, 52.4, 36.6, 32.6, 31.9, 27.7, 26.7; **HRMS** (ESI) m/z: calcd for $C_{17}H_{17}ClO_2$ $[M]^+$ 288.0917; found 285.0897.

Ethyl 2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (11j):



Following the general procedure **A,** compound **7c**[2] (100 mg, 0.6 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (197 mg, 0.7 mmol), CsF (250 mg, 1.6 mmol) and 18-crown-6 (435 mg, 1.6mmol) in 5 mL of THF afforded compound **11j** with 78% (103 mg) yield as colourless liquid: $\mathbf{R_f}$ = 0.8 (3% EtOAc in hexanes); **IR (neat)**: υ_{max} 3066, 2952, 2836, 1730, 1442, 1209, 1025, 769 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.96 – 8.87 (m, 1H), 8.11 (s, 1H), 7.87 – 7.80 (m, 1H), 7.57 – 7.50 (m, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.13 (t, *J* = 7.4 Hz, 2H), 2.31 – 2.22 (m, 2H), 1.45 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 145.6, 139.8, 130.8, 130.7, 127.6, 126.6, 126.5, 126.2, 124.9, 61.0, 33.7, 31.9, 24.5, 14.6; **HRMS** (ESI) m/z: calcd for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1223; found 241.1211.

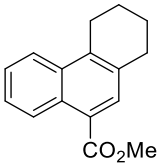
Methyl (1*Z*,7*Z*)-2-hydroxycycloocta-1,7-diene-1-carboxylate (7d):



A suspension of methyl (*Z*)-8-oxocyclooct-2-ene-1-carboxylate[3] (2.0 g, 11.0 mmol) and ion-exchange resin (300 mg; DOWEX 50WX8, hydrogen form) was stirred in MeOH (5 mL) for about 5 days at rt. After removal of all volatile materials in *vacuo*, chromatography on silica gel yielded two fractions, the first containing

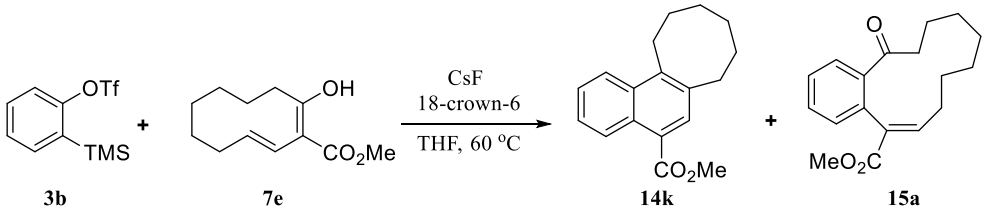
dienol **7d** (190 mg, 1.0 mmol, 9.5%; $\mathbf{R_f}$ = 0.8 (10% EtOAc in hexane) as colourless liquid and the second containing the starting material (1.78 g, 9.8 mmol, 89%; $\mathbf{R_f}$ = 0.3 (10% EtOAc in hexane) as colourless oil: **IR (neat)**: υ_{max} 2930, 2859, 1650, 1605, 1445, 1357, 1321, 1264, 1230, 1069, 970, 841, 725; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.58 (t, *J* = 1.3 Hz, 1H), 6.08 (dt, *J* = 10.8, 1.1 Hz, 1H), 5.70 (dt, *J* = 10.8, 7.4 Hz, 1H), 3.77 (s, 3H), 2.39 – 2.32 (m, 2H), 2.08 (bs, 2H), 1.63 (bs, 2H), 1.49 (bs, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 173.0, 131.2, 122.7, 99.3, 51.8, 33.0, 28.5, 23.8, 23.8: **HRMS** (EI) m/z: calcd for $C_{10}H_{14}O_3$ $[M]^+$ 183.0943; found 183.0940.

Methyl 1,2,3,4-tetrahydrophenanthrene-9-carboxylate (11k):



Following the general procedure **A,** compound **7d** (100 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (197 mg, 0.6 mmol), CsF (250 mg, 1.6 mmol) and 18-crown-6 (435 mg, 1.6 mmol) in 5 mL of THF afforded compound **11k** with 61% (80) yield as colourless liquid: R_f = 0.6 (10% EtOAc in hexane); **IR (neat)**: υ_{max} 2940, 2867, 1718, 1583, 1514, 1441, 1284, 1245, 1199, 1154, 1033, 792, 765; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 – 8.85 (m, 1H), 8.06 – 7.98 (m, 1H), 7.92 (s, 1H), 7.59 – 7.50 (m, 2H), 3.99 (s, 3H), 3.15 (t, *J* = 6.3 Hz, 2H), 2.93 (t, *J* = 6.1 Hz, 2H), 2.02 – 1.93 (m, 2H), 1.88 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 137.6, 133.4, 133.1, 132.8, 129.9, 126.5, 126.3, 126.2, 124.8, 123.2, 52.1, 30.4, 26.4, 23.1, 22.8; **HRMS** (EI) m/z: calcd for $C_{16}H_{16}O_2$ $[M]^+$ 240.1150; found 241.1140.

Methyl (*E*)-14-oxo-7,8,9,10,11,12,13,14-octahydrobenzo[12]annulene-5-carboxylate(11l) and Methyl 7,8,9,10,11,12-hexahydrocycloocta[*a*]naphthalene-5-carboxylate (12a):



3b **7e** **14k** **15a**

Following the general procedure **A,** compound **7e**[2] (150 mg, 0.7 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (255 mg, 0.9 mmol), CsF (325 mg, 2.1 mmol) and 18-crown-6 (565 mg, 2.1 mmol) in 10 mL of THF afforded compound **11l** with 24% (45 mg) yield as colourless liquid and compound **12a** with 52% (110 mg) yield as white solid.

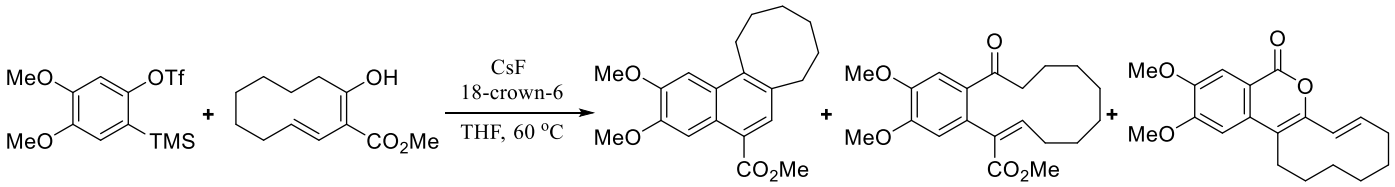
Compound 11l:

$\mathbf{R_f}$ = 0.6 (5% EtOAc in hexane); **IR (neat)**: υ_{max} 2922, 2853, 1714, 1577, 1513, 1443, 1248, 1196, 1154, 1030, 788, 757 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.94 – 8.89 (m, 1H), 8.16 – 8.11 (m, 1H), 7.99 (s, 1H), 7.56 – 7.51 (m, 2H), 4.00 (s, 3H), 3.34 – 3.29 (m, 2H), 3.01 – 2.96 (m, 2H), 1.85 (dt, *J* = 12.5, 6.3 Hz, 2H), 1.81 – 1.75 (m, 2H), 1.51 – 1.45 (m, 2H), 1.29 – 1.24 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 141.6, 138.0, 132.7, 132.3, 130.7, 126.4, 126.3, 126.1, 125.3, 124.4, 52.1, 34.3, 32.6, 30.4, 27.1, 26.6, 25.9; **HRMS** (ESI) m/z: calcd for $C_{18}H_{21}O_2$ $[M + H]^+$ 269.1536; found 269.1523.

Compound 12a:

R_f = 0.1 (5% EtOAc in hexane); **m.p** = 109-111 °C; **IR (neat)**: υ_{max} 2927, 2859, 1724, 1685, 1453, 1262, 1214, 769 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.49 (td, *J* = 7.6, 1.5 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.79 (dd, *J* = 12.1, 3.7 Hz, 1H), 3.71 (s, 3H), 3.08 (ddd, *J* = 14.2, 10.1, 1.5 Hz, 1H), 2.57 (ddd, *J* = 14.1, 9.3, 1.9 Hz, 1H), 2.18 – 1.97 (m, 2H), 1.84 – 1.60 (m, 2H), 1.46 – 1.29 (m, 2H), 1.17 (qdd, *J* = 13.4, 4.7, 2.7 Hz, 1H), 1.03 – 0.84 (m, 3H), 0.80 – 0.67 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.3, 167.7, 141.3, 138.1, 136.8, 135.7, 131.9, 131.7, 128.8, 127.9, 52.1, 39.3, 29.9, 27.5, 27.0, 25.6, 25.0, 23.6; **HRMS** (ESI) m/z: calcd for $C_{18}H_{23}O_3$ $[M + H]^+$ 287.1641; found 287.1628.

Methyl 2,3-dimethoxy-7,8,9,10,11,12-hexahydrocycloocta[*a*]naphthalene-5-carboxylate (11m), Methyl (*Z*)-2,3-dimethoxy-14-oxo-7,8,9,10,11,12,13,14-octahydrobenzo[12]annulene-5-carboxylate (12b) and (*E*)-2,3-Dimethoxy-9,10,11,12,13,14-hexahydro-5H-cyclodeca[*c*]isochromen-5-one (13):



3c **7e** **11l (12%)** **12b (34%)** **13 (38%)**

Following the general procedure **A,** compound **7e** (210 mg, 1.0 mmol), 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3c** (430 mg, 1.2 mmol), CsF (455 mg, 3.0 mmol) and 18-crown-6 (792 mg, 3.0 mmol) in 10 mL of THF afforded compound **11m** with 12% (39 mg) yield as white solid, compound **12b** with 34% (118 mg) yield as white solid and compound **13** with 38% (120 mg) yield as white solid.

Compound 11m:

R_f = 0.6 (20% EtOAc in hexane); **m.p** = 155-157 °C; **IR (neat)**: υ_{max} 2923, 2851, 1710, 1515, 1482, 1438, 1251, 1196, 1156 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.94 (s, 1H), 7.36 (s, 1H), 4.05 (s, 3H), 4.02 (s, 3H), 3.97 (s, 3H), 3.30 – 3.22 (m, 2H), 2.98 – 2.91 (m, 2H), 1.89 – 1.82 (m, 2H), 1.79 –1.73 (m, 2H), 1.52 – 1.46 (m, 2H), 1.29 – 1.23 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 149.9, 149.3, 140.4, 136.5, 131.3, 128.4, 127.3, 122.9, 105.5, 103.3, 55.9, 55.8, 52.0, 34.4, 32.8, 29.9, 27.2, 27.0, 25.9; **HRMS** (EI) m/z: calcd for $C_{20}H_{24}O_4$ $[M]^+$ 328.1675; found 328.1662.

Compound 12b:

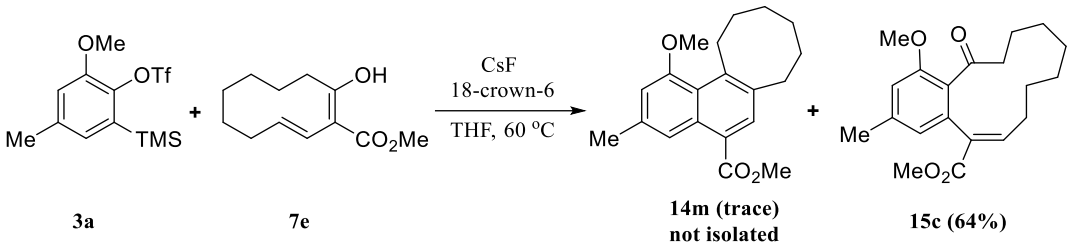
R_f = 0.2 (20% EtOAc in hexane); **m.p** = 107-109 °C; **IR (neat)**: υ_{max} 2934, 2856, 1718, 1671, 1565, 1517, 1453, 1359, 1263, 1205, 1140, 759 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.76 (dd, *J* = 12.2, 3.8 Hz, 1H), 6.61 (s, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.74 – 3.71 (s, 3H), 2.96 (ddd, *J* = 13.9, 10.0, 1.6 Hz, 1H), 2.52 (ddd, *J* = 14.0, 9.1, 1.9 Hz, 1H), 2.15 – 1.95 (m, 2H), 1.87 – 1.68 (m, 2H), 1.68 – 1.56 (m, 1H), 1.47 – 1.28 (m, 3H), 1.15 (qdd, *J* = 12.9, 4.7, 2.4 Hz, 1H), 1.00 – 0.70 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 167.7, 151.6, 147.9, 141.6, 135.7, 131.0, 130.8, 114.3, 111.8, 56.3, 56.2, 52.1, 39.2, 29.8, 27.6, 27.0, 25.7, 25.0, 23.5; **HRMS** (EI) m/z: calcd for $C_{20}H_{26}O_5$ $[M]^+$ 346.1780; found 346.1791.

Compound 13:

R_f = 0.4 (20% EtOAc in hexane); **m.p** = 134-136 °C; **IR (neat)**: υ_{max} 3012, 2927, 2856, 1710, 1608, 1509, 1457, 1393, 1261, 1215, 1170, 1041, 879, 755 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.00 (s, 1H), 6.15 (d, *J* = 16.2 Hz, 1H), 5.75 – 5.64 (m, 1H), 3.97 (d, *J* = 2.6 Hz, 6H), 2.66 (bs, 2H), 2.32 (bs, 2H), 1.70 (bs, 2H), 1.48 – 1.41 (m, 4H), 1.32 (bs, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 155.1, 153.4, 149.2, 141.5,

133.5, 122.4, 114.9, 113.6, 109.7, 105.1, 56.4, 56.4, 35.1, 28.4, 27.5, 26.7, 26.6, 23.0; **HRMS** (EI) m/z: calcd for $C_{19}H_{22}O_4$ $[M]^+$ 314.1518; found 314.1533.

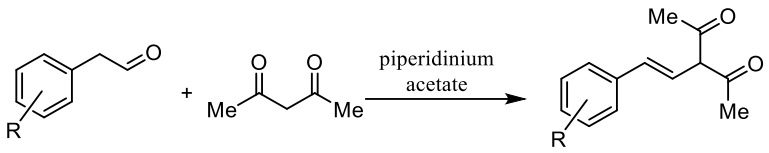
Methyl (*Z*)-1-methoxy-3-methyl-14-oxo-7,8,9,10,11,12,13,14-octahydrobenzo[12]annulene-5-carboxylate (12c):



3a **7e** **14m (trace) not isolated** **15c (64%)**

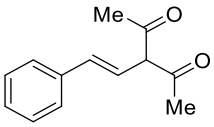
Following the general procedure **A,** compound **7e** (200 mg, 0.9 mmol), 2-methoxy-4-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **3a** (391 mg, 1.1 mmol), CsF (433 mg, 2.8 mmol) and 18-crown-6 (754 mg, 2.8 mmol) in 10 mL of THF afforded compound **12c** with 64% (202 mg) yield as white solid: $\mathbf{R_f}$ = 0.3 (20% EtOAc in hexane); **m.p** = 166-168 °C; **IR (neat)**: υ_{max} 2923, 2854, 1720, 1665, 1598, 1453, 1243, 1082, 1038, 761 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.77 (s, 1H), 6.70 – 6.63 (m, 1H), 6.51 (d, *J* = 0.7 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 2.89 (ddd, *J* = 16.2, 9.8, 1.4 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.37 (s, 3H), 2.09 – 1.97 (m, 2H), 1.97 – 1.84 (m, 1H), 1.67- 1.56 (m, 2H), 1.42 – 1.23 (m, 3H), 1.22 – 1.10 (m, 1H), 1.04 – 0.93 (m, 1H), 0.92 – 0.77 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.2, 168.0, 159.1, 142.3, 140.9, 137.7, 135.6, 126.0, 124.7, 112.0, 55.5, 52.0, 43.7, 29.9, 27.3, 27.0, 25.2, 25.0, 22.2, 21.9; **HRMS** (ESI) m/z: calcd for $C_{20}H_{27}O_4$ $[M + H]^+$ 331.1909; found 331.1886.

B. General procedure for Knoevenagel reaction of substituted Phenyl acetaldehydes with Acetyl Acetone:[4a]



In a 10 mL round-bottom flask, substituted phenyl acetaldehyde (1.0 equiv), acetyl acetone (1.0 equiv) and piperidinium acetate (0.2 equiv) were mixed, and the reaction mixture was shaken under solvent-free conditions. After the formation of the aldehyde−acetyl acetone adduct (monitored by TLC), the reaction mixture was diluted with ethyl acetate (10 mL) and water (10 mL). The aqueous layer was extracted with ethyl acetate (3 X 10 mL) and the combined organic layers were dried over Na_2SO_4 and the residue was purified by silica-gel column chromatography using EtOAc in hexane as eluent to give corresponding adducts.

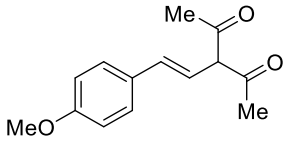
(*E*)-3-Styrylpentane-2,4-dione (14a):



Following the general procedure **B**, phenyl acetaldehyde (300 mg, 2.5 mmol), acetyl acetone (250 mg, 2.5 mmol) and piperidinium acetate (72 mg, 0.5 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14a** with 85% yield (430 mg) as a pale yellow oil: $\mathbf{R_f}$ = 0.5 (5% EtOAc in hexane); **IR (neat)**: υ_{max} 3024, 1708, 1590, 1493, 1411, 1255, 971, 919, 749, 696 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (tt, *J* = 7.2, 1.3 Hz, 1H),

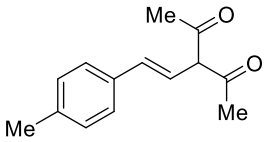
6.76 (d, *J* = 16.1 Hz, 1H), 6.43 (d, *J* = 16.1 Hz, 1H), 2.21 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.3, 137.2, 134.3, 128.8, 127.8, 126.2, 122.9, 111.5, 24.4; **HRMS** (ESI) m/z: calcd for $C_{13}H_{15}O_2$ $[M + H]^+$ 203.1067; found 203.1061.

(*E*)-3-(4-Methoxystyryl)pentane-2,4-dione (14b):



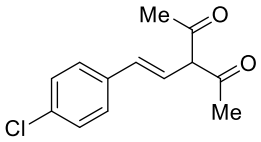
Following the general procedure **B**, 2-(4-methoxyphenyl)acetaldehyde (200 mg, 1.3 mmol), acetyl acetone (133 mg, 1.3 mmol) and piperidinium acetate (38 mg, 0.3 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14b** with 76% yield (235 mg) as yellow liquid: $\mathbf{R_f}$ = 0.8 (20% EtOAc in hexane); **IR (neat)**: υ_{max} 3008, 2942, 2838, 1699, 1599, 1509, 1415, 1248, 1173, 1029, 974, 823 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 6.92 – 6.87 (m, 2H), 6.59 (d, *J* = 16.1 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 3.83 (s, 3H), 2.20 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.2, 159.4, 134.0, 130.0, 127.4, 120.7, 114.2, 111.6, 55.4, 24.3; **HRMS** (ESI) m/z: calcd for $C_{14}H_{17}O_3$ $[M + H]^+$ 233.1172; found 233.1159.

(*E*)-3-(4-Methylstyryl)pentane-2,4-dione (14c):



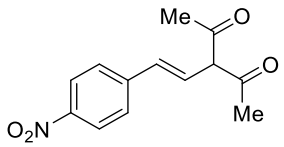
Following the general procedure **B**, 2-(*p*-tolyl)acetaldehyde (200 mg, 1.5 mmol), acetyl acetone (149 mg, 1.5 mmol)and piperidinium acetate (43 mg, 0.3 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14c** with 70% yield (225 mg) as pale yellow oil: $\mathbf{R_f}$ = 0.8 (20% EtOAc in hexane); **IR (neat)**: υ_{max} 3432, 3017, 2923, 2861, 1710, 1601, 1512, 1417, 1356, 1186, 1140, 979, 798 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 16.1 Hz, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 2.37 (s, 3H), 2.22 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.2, 180.7, 137.7, 134.4, 134.3, 129.5, 126.1, 121.9, 111.6, 24.4, 21.3; **HRMS** (ESI) m/z: calcd for $C_{14}H_{17}O_2$ $[M + H]^+$ 217.1223; found 217.1216.

(*E*)-3-(4-Chlorostyryl)pentane-2,4-dione (14d):



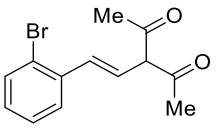
Following the general procedure **B**, 2-(4-chlorophenyl)acetaldehyde (200 mg, 1.3 mmol), acetyl acetone (130 mg, 1.3 mmol) and piperidinium acetate (38 mg, 0.3 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14d** with 85% yield (260 mg) as yellow solid: $\mathbf{R_f}$ = 0.8 (20% EtOAc in hexane); **m.p** = 67-69 ºC; **IR (neat)**: υ_{max} 3079, 2928, 2856, 1704, 1510, 1414, 1194, 998 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 16.76 (s, 1H), 7.36 – 7.29 (m, 4H), 6.72 (d, *J* = 16.1 Hz, 1H), 6.36 (d, *J* = 16.1 Hz, 1H), 2.21 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.3, 135.7, 133.5, 133.0, 129.0, 127.4, 123.6, 111.3, 24.4; **HRMS** (ESI) m/z: calcd for $C_{13}H_{14}ClO_2$ $[M - H]^+$ 235.0520; found 235.0528.

(*E*)-3-(4-Nitrostyryl)pentane-2,4-dione (14e):



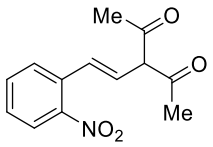
Following the general procedure **B**, 2-(4-nitrophenyl)acetaldehyde (200 mg, 1.2 mmol), acetyl acetone (121 mg, 1.2 mmol) and piperidinium acetate (35 mg, 0.2 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14e** with 85% yield (254 mg) as yellow coloured crystals: $\mathbf{R_f}$ = 0.4 (10% EtOAc in hexane); **m.p** = 148-150 ^{o}C; **IR (neat)**: υ_{max} 1579, 1501, 1418, 1328, 1105, 1016, 973, 861, 754 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 16.93 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 16.1 Hz, 1H), 6.47 (d, *J* = 16.1 Hz, 1H), 2.26 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.8, 146.9, 143.7, 131.1, 127.8, 126.6, 124.3, 111.1, 24.6; **HRMS** (ESI) m/z: calcd for $C_{13}H_{14}NO_4$ $[M + H]^+$ 248.0917; found 248.0916.

(*E*)-3-(2-Bromostyryl)pentane-2,4-dione (14f):



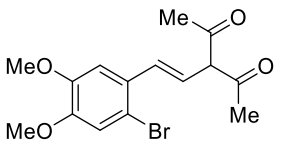
Following the general procedure **B**, 2-(2-bromophenyl)acetaldehyde (200 mg, 1.0 mmol), acetyl acetone (100 mg, 1.0 mmol) and piperidinium acetate (29 mg, 0.2 mmol) were shaken under solvent free conditions followed by column chromatography afforded compound **14f** with 78% yield (220 mg) as semisolid: $\mathbf{R_f}$ = 0.8 (20% EtOAc in hexane); **IR (neat)**: υ_{max} 3006, 1706, 1587, 1466, 1424, 1256, 1025, 972, 755 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.34 – 7.29 (m, 1H), 7.16 – 7.10 (m, 1H), 6.78 (d, *J* = 16.1 Hz, 1H), 6.67 (d, *J* = 16.1 Hz, 1H), 2.27 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.5, 137.3, 133.1, 132.8, 129.0, 127.7, 126.7, 125.9, 123.8, 111.3, 24.6; **HRMS** (ESI) m/z: calcd for $C_{13}H_{14}BrO_2$ $[M + H]^+$ 281.0172; found 281.0161.

(*E*)-3-(2-Nitrostyryl)pentane-2,4-dione (14g):



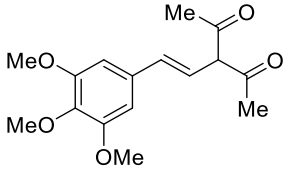
Following the general procedure **B**, 2-(2-nitrophenyl)acetaldehyde (200 mg, 1.2 mmol), acetyl acetone (121 mg, 1.2 mmol) and piperidinium acetate (35 mg, 0.2 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14g** with 80% yield (239 mg) as yellow solid: $\mathbf{R_f}$ = 0.2 (10% EtOAc in hexane); **m.p** = 136-138 ^{o}C; **IR (neat)**: υ_{max} 1568, 1519, 1475, 1411, 1348, 1301, 1257, 974, 787, 741 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.42 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 2.28 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.7, 147.7, 133.4, 133.3, 128.9, 128.4, 128.2, 128.1, 125.0, 111.1, 24.6; **HRMS** (ESI) m/z: calcd for $C_{13}H_{14}NO_4$ $[M + H]^+$ 248.0917; found 248.0915.

(*E*)-3-(2-Bromo-4,5-dimethoxystyryl)pentane-2,4-dione (14h):



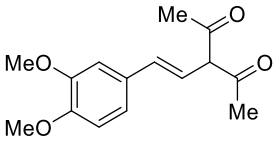
Following the general procedure **B**, 2-(2-bromo-4,5-dimethoxyphenyl)acetaldehyde (200 mg, 0.8 mmol), acetyl acetone (77 mg, 0.8 mmol) and piperidinium acetate (22 mg, 0.2 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14h** with 80% yield (210 mg) as yellow oil: $\mathbf{R_f}$ = 0.5 (20% EtOAc in hexane); **IR (neat)**: υ_{max} 2927, 2851, 1598, 1503, 1440, 1262, 1207, 1165, 1029, 976, 816 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.03 (s, 2H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 2.25 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.4, 149.5, 148.8, 132.9, 129.3, 123.9, 115.6, 114.5, 111.4, 108.9, 56.4, 56.3, 24.6; **HRMS** (ESI) m/z: calcd for $C_{15}H_{18}BrO_4$ $[M + H]^+$ 341.0383; found 341.0360.

(*E*)-3-(3,4,5-Trimethoxystyryl)pentane-2,4-dione (14i):



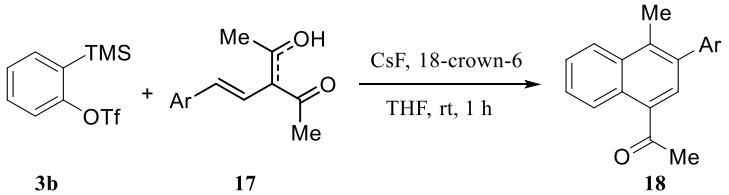
Following the general procedure **B**, 2-(3,4,5-trimethoxyphenyl)acetaldehyde (200 mg, 1.0 mmol), acetyl acetone (95 mg, 1.0 mmol) and piperidinium acetate (28 mg, 0.2 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14i** with 76% (211 mg) yield as white solid: $\mathbf{R_f}$ = 0.4 (20% EtOAc in hexane); **m.p** = 88-90 ^oC, **IR (neat)**: υ_{max} 2941, 2836, 1579, 1503, 1414, 1239, 1121, 994, 759 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.66 – 6.62 (m, 3H), 6.36 – 6.30 (d, *J* = 16.0 Hz, 1H), 3.90 (s, 6H), 3.85 (s, 3H), 2.21 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.3, 153.6, 138.1, 134.4, 132.9, 122.4, 111.3, 103.3, 61.1, 56.2, 24.4; **HRMS** (ESI) m/z: calcd for $C_{16}H_{21}O_5$ $[(M - CH_3CO) + H]^+$ 251.1278; found 251.1272.

(*E*)-3-(3,4-Dimethoxystyryl)pentane-2,4-dione (14j):



Following the general procedure **B**, 2-(3,4-dimethoxyphenyl)acetaldehyde (200 mg, 1.1 mmol), acetyl acetone (111 mg, 1.1 mmol) and piperidinium acetate (32 mg, 0.2 mmol) were shaken under solvent free conditions followed by column chromatography which afforded compound **14j** with 75% yield (218 mg) as yellow oil: $\mathbf{R_f}$ = 0.3 (20% EtOAc in hexane); **IR (neat)**: υ_{max} 3004, 2928, 2838, 1591, 1510, 1413, 1255, 1142, 1023, 969, 801 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.97 – 6.95 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.59 (d, *J* = 16.1 Hz, 1H), 6.34 (d, *J* = 16.1 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 2.20 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.2, 149.3, 149.1, 134.3, 130.3, 121.0, 119.3, 111.5, 111.4, 108.8, 56.1, 56.0, 24.4; **HRMS** (ESI) m/z: calcd for $C_{15}H_{19}O_4$ $[M + H]^+$ 263.1278; found 263.1279.

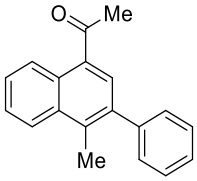
C. General procedure for the synthesis of naphthalene derivatives from unsaturated diketones:



3b **17** **18**

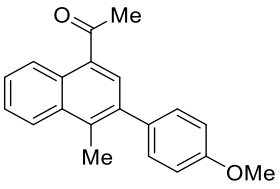
A screw-cap vial equipped with magnetic stir bar was charged with unsaturated diketone (1.0 equiv), aryne precursor (1.2 equiv), CsF (3.0 equiv) in dry THF (0.1 M) as solvent under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction (monitored by TLC), it was diluted with ethyl acetate (5 mL) and water (10 mL). The aqueous layer was extracted with ethyl acetate (2 X 10 mL), the combined organic layers were dried over Na_2SO_4 and the volatiles were evaporated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using EtOAc in hexane as eluent to get desired compounds.

1-(4-Methyl-3-phenylnaphthalen-1-yl)ethan-1-one (15a):



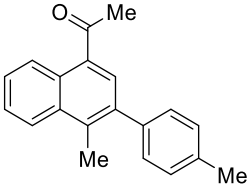
Following the general procedure **C**, compound **14a** (102 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15a** with 74% yield (110 mg) as pale yellow liquid: $\mathbf{R_f}$ **=** 0.4 (5% EtOAc in hexane); **IR (neat)**: υ_{max} 3061, 1676, 1573, 1504, 1447, 1360, 1245, 1185, 1001, 902, 764, 705 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 – 8.83 (m, 1H), 8.19 – 8.14 (m, 1H), 7.88 (s, 1H), 7.67 – 7.60 (m, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.39 (m, 3H), 2.74 (s, 3H), 2.66 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.8, 141.9, 137.9, 136.7, 133.6, 133.5, 131.3, 129.8, 129.5, 128.5, 127.6, 127.4, 126.8, 126.6, 124.9, 30.1, 17.1; **HRMS** (ESI) m/z: calcd for $C_{19}H_{17}O$ $[M + H]^+$ 261.1274; found 261.1276.

1-(3-(4-Methoxyphenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15b):



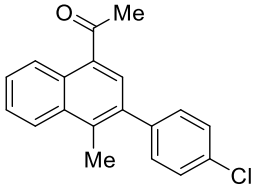
Following the general procedure **C**, compound **14b** (117 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15b** with 83% yield (123 mg) as white solid: $\mathbf{R_f}$ = 0.6 (20% EtOAc in hexane); **m.p** = 114-116 ^oC; **IR (neat)**: υ_{max} 3001, 2954, 1677, 1513, 1248, 1182, 1086, 839, 762 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 – 8.80 (m, 1H), 8.17 – 8.12 (m, 1H), 7.86 (s, 1H), 7.64 – 7.58 (m, 2H), 7.34 – 7.30 (m, 2H), 7.06 – 7.01 (m, 2H), 3.90 (s, 3H), 2.73 (s, 3H), 2.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 159.0, 137.5, 136.8, 134.2, 133.7, 133.4, 131.6, 130.9, 129.4, 127.4, 126.8, 126.6, 124.9, 113.9, 55.5, 30.1, 17.2; **HRMS** (ESI) m/z: calcd for $C_{20}H_{19}O_2$ $[M + H]^+$ 291.1380; found 291.1382.

1-(4-Methyl-3-(p-tolyl)naphthalen-1-yl)ethan-1-one (15c):



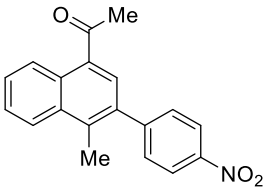
Following the general procedure **C**, compound **14c** (109 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15c** with with 68% yield (94 mg) as colourless liquid: $\mathbf{R_f}$ = 0.5 (5% EtOAc in hexane); **IR (neat)**: υ_{max} 3018, 2923, 1676, 1510, 1243, 1184, 824, 760 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 – 8.80 (m, 1H), 8.15 – 8.11 (m, 1H), 7.85 (s, 1H), 7.61 – 7.58 (m, 2H), 7.29-7.27 (m, 4H), 2.71 (s, 3H), 2.63 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.8, 138.9, 137.8, 137.1, 136.7, 133.6, 133.4, 131.5, 129.7, 129.1, 127.5, 126.8, 126.6, 124.8, 30.0, 21.3, 17.1; **HRMS** (ESI) m/z: calcd for $C_{20}H_{19}O$ $[M + H]^+$ 275.1430; found 275.1432.

1-(3-(4-Chlorophenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15d):



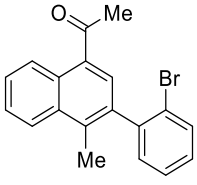
Following the general procedure **C**, compound **14d** (119 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15d** with 73% yield (108 mg) as yellow oil: $\mathbf{R_f}$ = 0.8 (20% EtOAc in hexane); **IR (neat)**: υ_{max} 2924, 1676, 1569, 1496, 1359, 1245, 1185, 1092, 1008, 836, 761 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.83 – 8.79 (m, 1H), 8.16 – 8.13 (m, 1H), 7.80 (s, 1H), 7.66 – 7.60 (m, 2H), 7.49 – 7.46 (m, 2H), 7.35 – 7.31 (m, 2H), 2.73 (s, 3H), 2.63 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.7, 140.3, 136.7, 136.6, 133.8, 133.6, 131.1, 130.8, 129.6, 128.7, 127.7, 127.0, 126.6, 124.9, 30.1, 17.1; **HRMS** (ESI) m/z: calcd for $C_{19}H_{16}ClO$ $[M + H]^+$ 295.0884; found 295.0887.

1-(4-Methyl-3-(4-nitrophenyl)naphthalen-1-yl)ethan-1-one (15e):



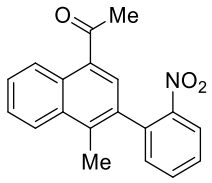
Following the general procedure **C**, compound **14e** (124 mg, 0.4 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15e** with 73% yield (108 mg) as yellow solid: $\mathbf{R_f}$ = 0.3 (10% EtOAc in hexane); **m.p** = 162-164 ^oC; **IR (neat)**: υ_{max} 1678, 1597, 1516, 1349, 1248, 1185, 860, 763, 703 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 – 8.76 (m, 1H), 8.36 (d, *J* = 8.4 Hz, 2H), 8.19 – 8.15 (m, 1H), 7.77 (s, 1H), 7.66 (dd, *J* = 6.8, 2.8 Hz, 2H), 7.59 – 7.56 (m, 2H), 2.74 (s, 3H), 2.64 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 148.6, 147.3, 136.7, 135.6, 134.3, 133.5, 130.8, 129.8, 129.7, 128.2, 127.3, 126.7, 124.9, 123.8, 30.1, 17.2; **HRMS** (ESI) m/z: calcd for $C_{19}H_{16}NO_3$ $[M + H]^+$ 306.1125; found 306.1126.

1-(3-(2-Bromophenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15f):



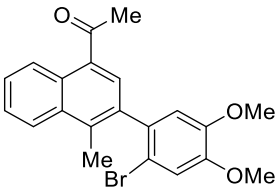
Following the general procedure **C**, compound **14f** (141 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15f** with 75% yield (111 mg) as pale yellow oil: $\mathbf{R_f}$ = 0.8 (20% EtOAc in hexane); **IR (neat)**: υ_{max} 3063, 3002, 2925, 1676, 1571, 1507, 1468, 1429, 1359, 1243, 1185, 1122, 1025, 901, 758 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (p, *J* = 6.7 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 2H), 2.71 (s, 3H), 2.50 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.6, 142.3, 137.7, 136.9, 133.4, 133.3, 132.9, 131.4, 130.9, 129.9, 129.4, 127.9, 127.5, 126.8, 126.8, 124.8, 124.2, 30.0, 16.9; **HRMS** (ESI) m/z: calcd for $C_{19}H_{16}BrO$ $[M + H]^+$ 339.0379; found 339.0383.

1-(4-Methyl-3-(2-nitrophenyl)naphthalen-1-yl)ethan-1-one (15g):



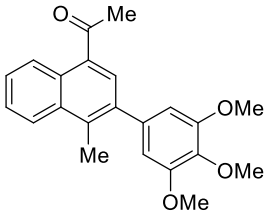
Following the general procedure **C**, compound **14g** (124 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15g** with with 75% yield (111 mg) as yellow oil: $\mathbf{R_f}$ = 0.2 (10% EtOAc in hexane); **IR (neat)**: υ_{max} 1667, 1608, 1521, 1354, 1260, 940, 760 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 – 8.81 (m, 1H), 8.13 – 8.08 (m, 2H), 7.72 (s, 1H), 7.70 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.67 – 7.59 (m, 3H), 7.40 (dd, *J* = 7.6, 1.3 Hz, 1H), 2.70 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 149.2, 137.2, 136.3, 133.7, 133.4, 133.2, 133.0, 132.7, 129.9, 129.5, 129.0, 128.0, 127.1, 126.7, 124.8, 124.5, 30.1, 17.0; **HRMS** (ESI) m/z: calcd for $C_{19}H_{16}NO_3$ $[M + H]^+$ 306.1125; found 306.1128.

1-(3-(2-Bromo-4,5-dimethoxyphenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15h):



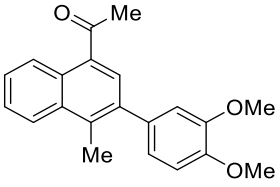
Following the general procedure **C**, compound **14h** (172 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15h** with 85% yield (125 mg) as white solid: $\mathbf{R_f}$ = 0.4 (20% EtOAc in hexane); **m.p** = 150-152 ºC; **IR (neat)**: υ_{max} 3007, 2958, 1678, 1506, 1250, 1213, 762 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.86 – 8.84 (m, 1H), 8.17 – 8.13 (m, 1H), 7.76 (s, 1H), 7.63 (pd, *J* = 6.8, 1.4 Hz, 2H), 7.18 (s, 1H), 6.79 (s, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 2.73 (s, 3H), 2.53 (s, 3H); **^{13}C NMR (**101 MHz, $CDCl_3$) δ 201.7, 149.3, 148.5, 138.0, 136.8, 134.3, 133.4, 131.1, 129.8, 127.8, 126.8, 126.7, 124.9, 115.4, 114.1, 113.8, 56.4, 56.3, 30.1, 16.9; **HRMS** (ESI) m/z: calcd for $C_{21}H_{20}BrO_3$ $[M + H]^+$ 399.0590; found 399.0591.

1-(4-Methyl-3-(3,4,5-trimethoxyphenyl)naphthalen-1-yl)ethan-1-one (15i):



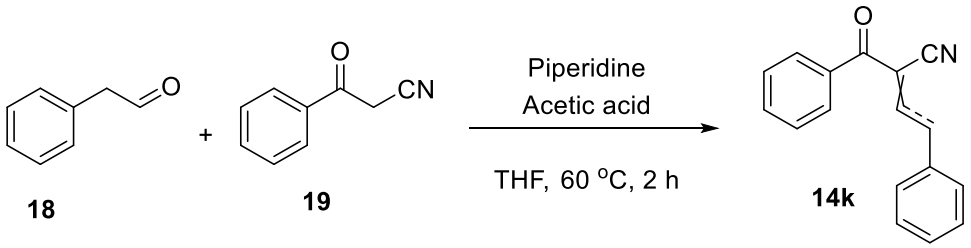
Following the general procedure **C**, compound **14i** (147 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15i** with 85% yield (126 mg) as white solid: $\mathbf{R_f}$ = 0.4 (20% EtOAc in hexane); **m.p** = 151-153 °C; **IR (neat)**: υ_{max} 3000, 2935, 2839, 1677, 1583, 1506, 1458, 1240, 1126, 1008, 763 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.81 – 8.76 (m, 1H), 8.17 – 8.12 (m, 1H), 7.85 (s, 1H), 7.64 – 7.60 (m, 2H), 6.57 (s, 2H), 3.94 (s, 3H), 3.90 (s, 6H), 2.73 (s, 3H), 2.66 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 153.2, 138.0, 137.6, 137.4, 136.7, 133.6, 130.8, 129.5, 127.6, 126.9, 126.6, 124.9, 107.0, 61.1, 56.4, 30.2, 17.2; **HRMS** (ESI) m/z: calcd for $C_{22}H_{23}O_4$ $[M + H]^+$ 351.1591; found 351.1590.

1-(3-(3,4-Dimethoxyphenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15j):



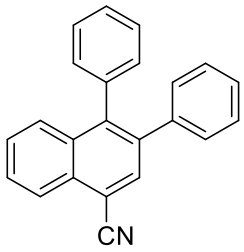
Following the general procedure **C**, compound **14j** (132 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol) and CsF (229 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15j** with 80% yield (118 mg) as white solid: $\mathbf{R_f}$ = 0.4 (20% EtOAc in hexane); **m.p** = 135-137 °C; **IR (neat)**: υ_{max} 3006, 2945, 1675, 1512, 1455, 1247, 1147, 1027, 758, 661 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 – 8.78 (m, 1H), 8.17 – 8.12 (m, 1H), 7.86 (s, 1H), 7.64 – 7.59 (m, 2H), 7.01 – 6.97 (m, 1H), 6.95 – 6.88 (m, 2H), 3.97 (s, 3H), 3.92 (s, 3H), 2.73 (s, 3H), 2.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.9, 148.8, 148.5, 137.7, 136.8, 134.6, 133.6, 133.5, 131.3, 129.4, 127.5, 126.8, 126.6, 124.9, 122.1, 113.1, 111.2, 56.1, 30.1, 17.2; **HRMS** (ESI) m/z: calcd for $C_{21}H_{21}O_3$ $[M + H]^+$ 321.1485; found 321.1486.

3,4-Diphenyl-1-naphthonitrile (15k):



To a mixture of phenyl acetaldehyde (200 mg, 1.6 mmol, 1.0 equiv), 2-phenylacetonitrile (241 mg, 1.6 mmol, 1.0 equiv) dissolved in dry THF was added piperidinium acetate (50 mg, 0.33 mmol 0.2 equiv) at room temperature. Then the reaction mixture was heated to 60 °C and stirred for 2 h. After monitoring with TLC,

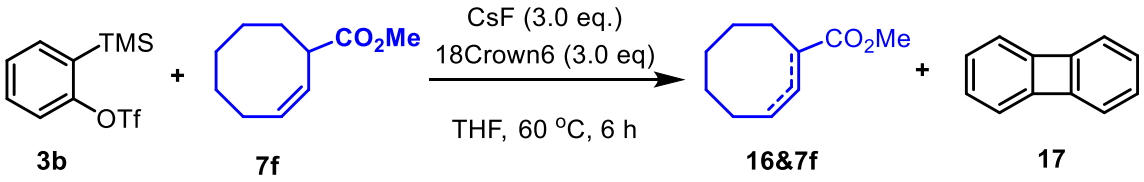
the reaction mixture was cooled to room temperature and quenched with saturated NH_4Cl solution. Then the reaction mixture was diluted with water (5 mL). The aqueous layer was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The crude material was dissolved in dichloromethane and added to a well-stirred hexane to separate the solids. After filtration, without further purification the crude pale-yellow solid of **14k** was utilised in the next step. (*The attempts to isolate the desired compound from the crude material were unsuccessful).



15k

Following the general procedure **C**, **14k** (123 mg, 0.5 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (180 mg, 0.6 mmol), CsF (229 mg, 1.5 mmol) and 18-crown-6 (396 mg, 1.5 mmol) were stirred in THF at room temperature and purified by column chromatography which afforded compound **15k** with 32% yield (51 mg) as white solid: $\mathbf{R_f}$ = 0.3 (5% EtOAc in hexane); **m.p** = 169-171 °C; **IR (neat)**: υ_{max} 3063, 2224, 1498, 1446, 1376, 909 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.3 Hz, 1H), 8.02 (s, 1H), 7.77 – 7.67 (m, 2H), 7.57 – 7.50 (m, 1H), 7.33 (m, 3H), 7.20 (m, 3H), 7.16 (m, 2H), 7.11 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.34, 140.01, 138.18, 137.60, 134.89, 132.79, 131.83, 131.00, 130.00, 128.32, 128.22, 128.10, 127.90, 127.87, 127.71, 127.17, 125.32, 118.03, 109.95; **HRMS** (ESI) m/z: calcd for $C_{23}H_{15}N$ $[M + H]^+$ 306.1282; found 306.1275.

Methyl (<u>Z</u>)-cyclooct-2-ene-1-carboxylate (16) and Biphenylene (17):



3b **7f** **16&7f** **17**

When the reaction was performed with carbonyl free analogue of 7d *i.e.*, methyl (Z)-cyclooct-2-ene-1-carboxylate 7f, with benzyne precursor 3b, we observed the isomerisation of double bond to give compound 16 and 7f in 3:1 ratio along with the formation of [2+2] cycloaddition product 17. This clearly shows that the enolisable carbonyl is indispensable for achieving the cascade transformation.

Compound **7f** was prepared according to literature.[4b] Following the general procedure **A,** compound **7f** (100 mg, 0.6 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (212 mg, 0.7 mmol), CsF (270 mg, 1.8 mmol) and 18-crown-6 (471 mg, 1.8 mmol) in 5 mL of THF afforded mixture of compounds **16** in 67% yield (90 mg, 0.5 mmol) as colourless liquid and **17** (26 mg) as pale-yellow solid:

16: **IR (neat)**: υ_{max} 2931, 2859, 1721, 1450, 1288, 1208, 788 cm^{-1}.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 (t, *J* = 8.5 Hz, 1H), 3.72 (s, 3H), 2.45 (dd, *J* = 7.3, 5.2 Hz, 2H), 2.29 – 2.23 (m, 2H), 1.59 – 1.53 (m, 4H), 1.48 – 1.41 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.29, 142.70, 133.25, 51.69, 29.21, 29.10, 27.29, 26.62, 26.03, 24.84. **HRMS** (ESI) m/z: calcd for $C_{10}H_{17}O_2$ $[M + H]^+$ 169.1223; found 169.1218.

17: **IR (neat)**: υ_{max} 3075, 1423, 1255, 1142, 960, 734 cm^{-1}.; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.74 (dd, J = 4.9, 2.9 Hz, 1H), 6.63 (dd, J = 4.8, 2.9 Hz, 1H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.51, 128.35, 117.49.; **HRMS** (ESI) m/z: calcd for $C_{12}H_8$ $[M]^+$ 152.0621; found 152.0626.

IV. a) X-ray Crystallography data for compound 8a:

X-ray data for the compound **8a** was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[5] The structure was solved using intrinsic phasing method[6] and further refined with the SHELXL[6] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for other H atoms].

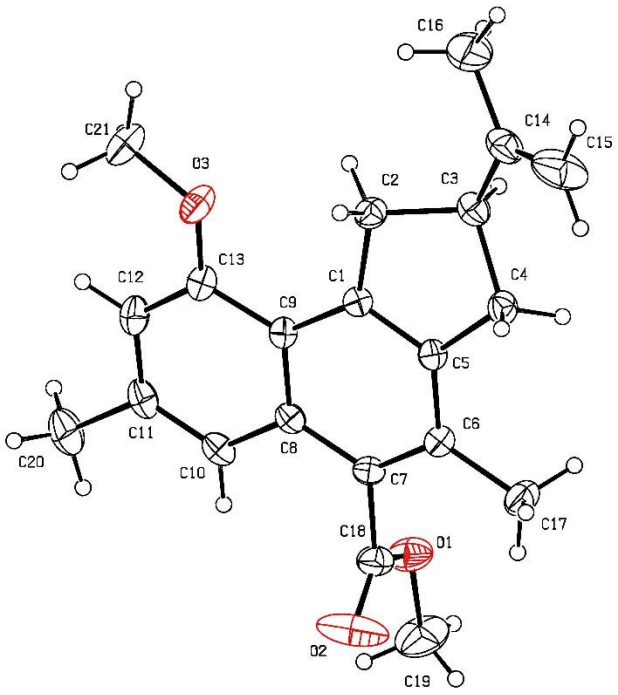


Figure 1: A view of **8a**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Crystal structure determination of 8a:

Crystal Data for $C_{21}H_{24}O_3$ (*M* =324.40 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 6.549(3) Å, *b* = 12.882(5) Å, *c* = 10.906(5) Å, *β* = 94.723(12)°, *V* = 916.9(7) Å^3, *Z* = 2, *T* = 295.15 K, μ(MoKα) = 0.077 mm^{-1}, *Dcalc* = 1.175 g/cm^3, 33298 reflections measured (4.904° ≤ 2Θ ≤ 61.082°), 5572 unique (R_{int} = 0.0612, R_{sigma} = 0.0445) which were used in all calculations. The final R_1 was 0.0518 (I > 2σ(I)) and wR_2 was 0.1401 (all data). CCDC 2052967 contains supplementary Crystallographic data for the structure.

b) X-ray crystallographic data for compound 12a:

X-ray data for the compound 12a was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo micro source (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[5] The structure was solved using intrinsic phasing method[6] and further refined with the SHELXL[6] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for other H atoms].

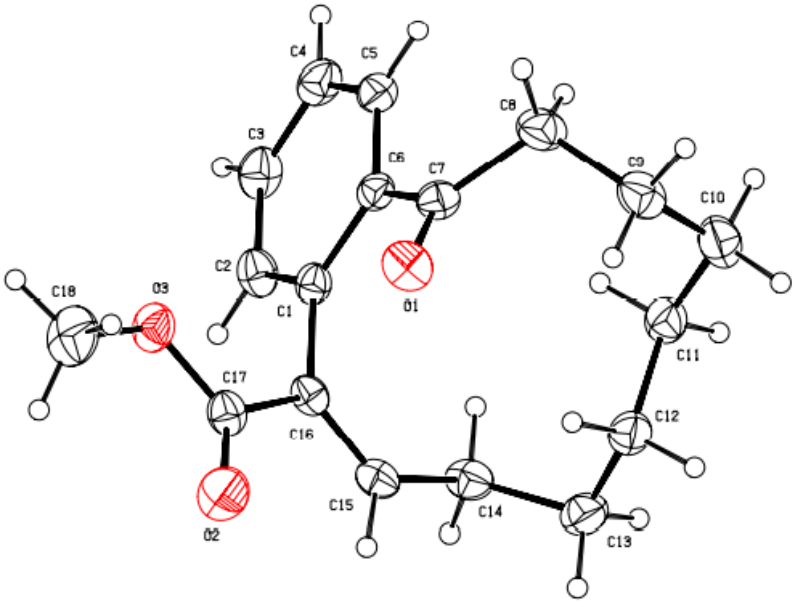


Figure 2: A view of Compound 12a, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Crystal structure determination of 12a:

Crystal Data for compound**:** $C_{18}H_{22}O_3$ (*M* =286.35 g/mol): triclinic, space group P-1 (no. 2), a = 8.4785(4) Å, b = 9.2084(4) Å, c = 10.5687(5) Å, α = 95.956(2)°, β = 104.157(2)°, γ = 100.451(2)°, V = 777.25(6) Å3, Z = 2, T = 294.15 K, μ(MoKα) = 0.082 mm-1, Dcalc = 1.224 g/cm3, 15804 reflections measured (5.072° ≤ 2Θ ≤ 54.996°), 3555 unique (Rint = 0.0595, Rsigma = 0.0606) which were used in all calculations. The final R1 was 0.0493 (I > 2σ(I)) and wR2 was 0.1164 (all data). CCDC 2085118 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

V. Computational Details:

Quantum chemical computations were carried out with (U)M06-2X[7,8] functional in conjunction with the 6-31G(d,p) basis set.[9] We employed a series of functionals starting with traditional B3LYP,[10] ωB97XD[11] and

M06-L,[8] along with 6-31G(d) and 6-31G(d,p) basis sets. However, we could not locate few transition states. Calculations with M06-2X functional yielded all the transition states successfully. It is well known that, the accuracy in reproducing the free energies of cycloadditions is better in the case of M06-2X functional when compared to other it also accounts for the non-covalent interactions.[12-14] Standard convergence criteria and an ultrafine integration grid were used. All the thermodynamic data was computed at 298.15 K and 1 atm. All the optimized geometries were verified as minima or first order saddle points by the harmonic vibrational frequency analysis. Both thermal and zero-point energy (ZPE) corrections were also included. As in the standard practice, the presence of one imaginary frequency criteria was used for the characterization of transition states (TS). Further, intrinsic reaction coordinate (IRC) calculations confirmed the nature of the transition states and provided the information that, they were connected to the respective minima (reactant and product). All the calculations were performed using G16 RevA.03 suite of program.[14]

DFT calculations have been performed to understand the selectivity between [2+2] and [4+2] cycloaddition reactions between **3a** and **7a**. The complete reaction energy profile is depicted in Figure 3. which reveals that, [2+2] cycloaddition occurs *via* stepwise mechanism where first step involves formation of new C-C bond between aryne and **7a** through the transition state of an activation barrier 6.21 kcal/mol, followed by the second step, formation of four membered ring *via* TS of activation energy 7.80 kcal/mol. This TS involves rotation of aryl group to form intermediate **B**, whereas [4+2] cycloaddition is a concerted reaction occurring through an activation energy of 9.20 kcal/mol. From these results, it is clear that [2+2] cycloaddition is more feasible than [4+2] cycloaddition.

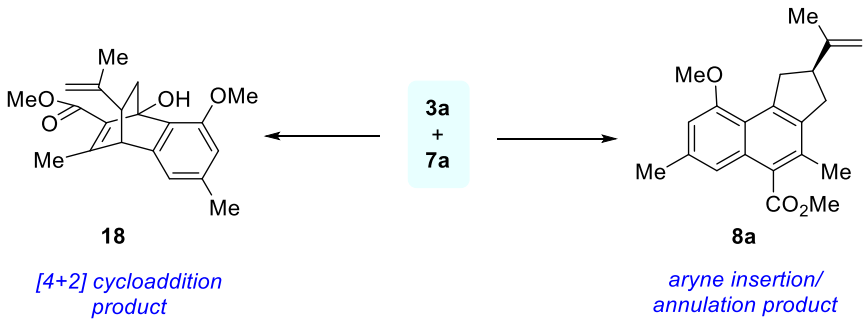


Figure 3. [4+2] addition product and [2+2] addition product.

Conversion of intermediate **B** to **C** involves opening of four membered ring *via* TS of activation barrier 29.28 kcal/mol. However, it is interesting to note that, in anionic form (in the presence of base) the four membered ring cleaves spontaneously and the ring-opening step is barrier less (Figure 4). This is observed during the geometry optimization of intermediate **B** by removing hydroxyl proton to form $\mathbf{[I_{BC}]^-}$. Proceeding from $\mathbf{[I_{BC}]^-}$, the structural rearrangement leads to $\mathbf{[C]^-}$. From this intermediate, the possibility of vinylogous aldol addition (AA) and Michael addition (MA) mechanisms have been investigated. These results are presented in Figure 5. It is evident that aldol addition mechanism is dominating the Michael addition as the former is proceeding through less activation barrier (4.46 kcal/mol) when compared to latter (23.81 kcal/mol). These DFT results are concomitant with the observed experimental results and confirm the formation of **8a** through aldol addition followed by protonation and dehydration.

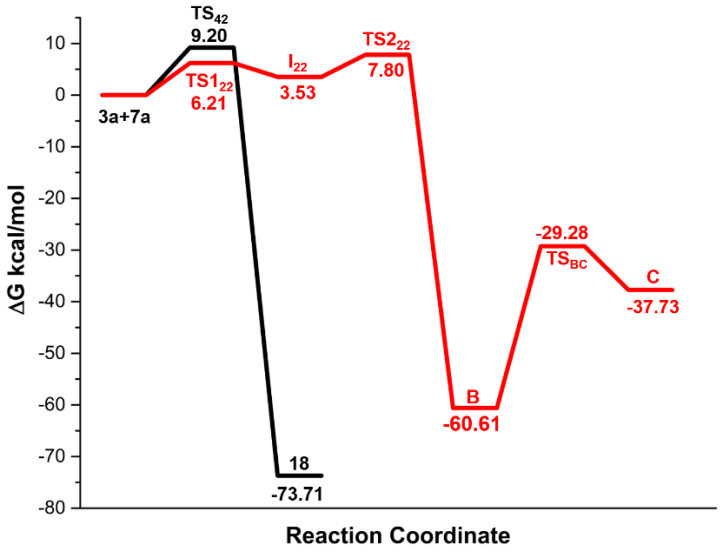


Figure 4. Gibbs free energy profile for cycloaddition of **3a** and **7a** calculated at UM06-2X/6-31G(d,p) level of theory.

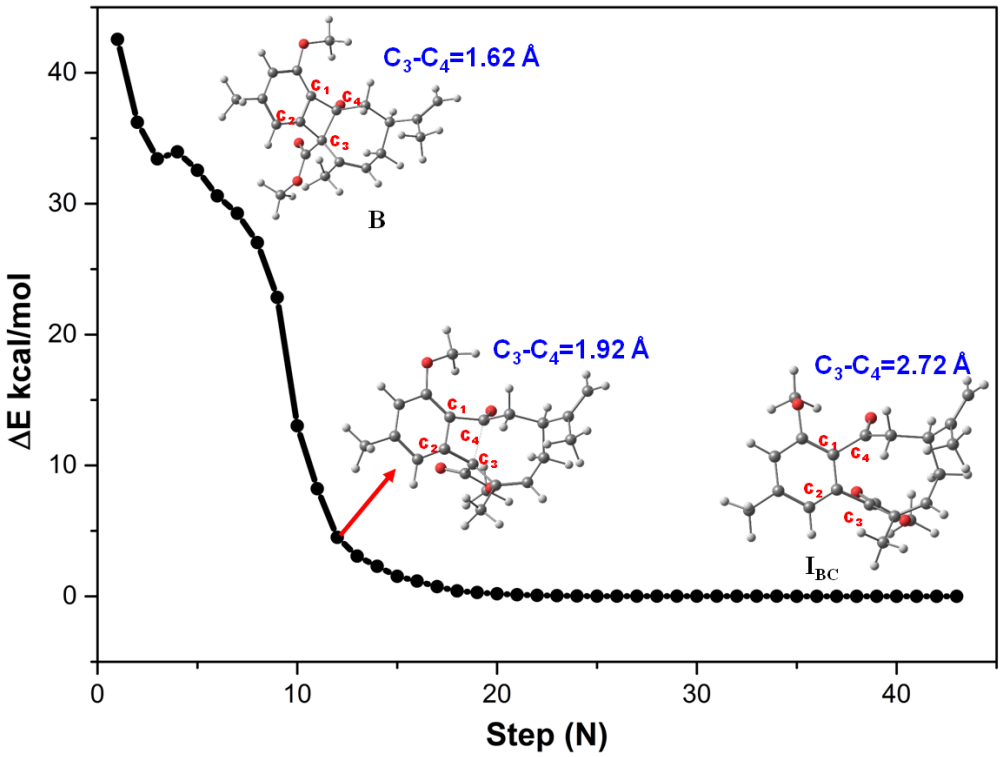


Figure 5. Potential energy surface for spontaneous opening of four membered ring in the presence of base (in anioinc form) calculated at UM06-2X/6-31G(d,p) level of theory.

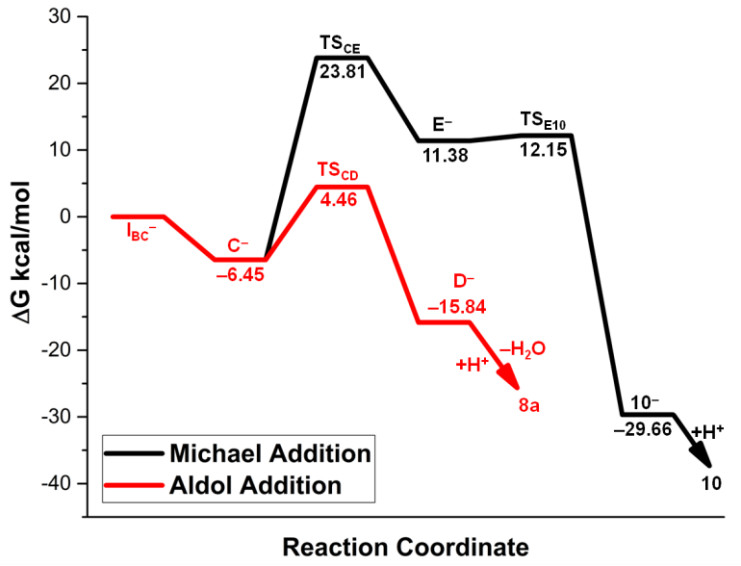


Figure 6. Gibbs free energy profile diagram for selectivity between aldol addition and Michael addition reactions calculated at UM06-2X/6-31G(d,p) level of theory.

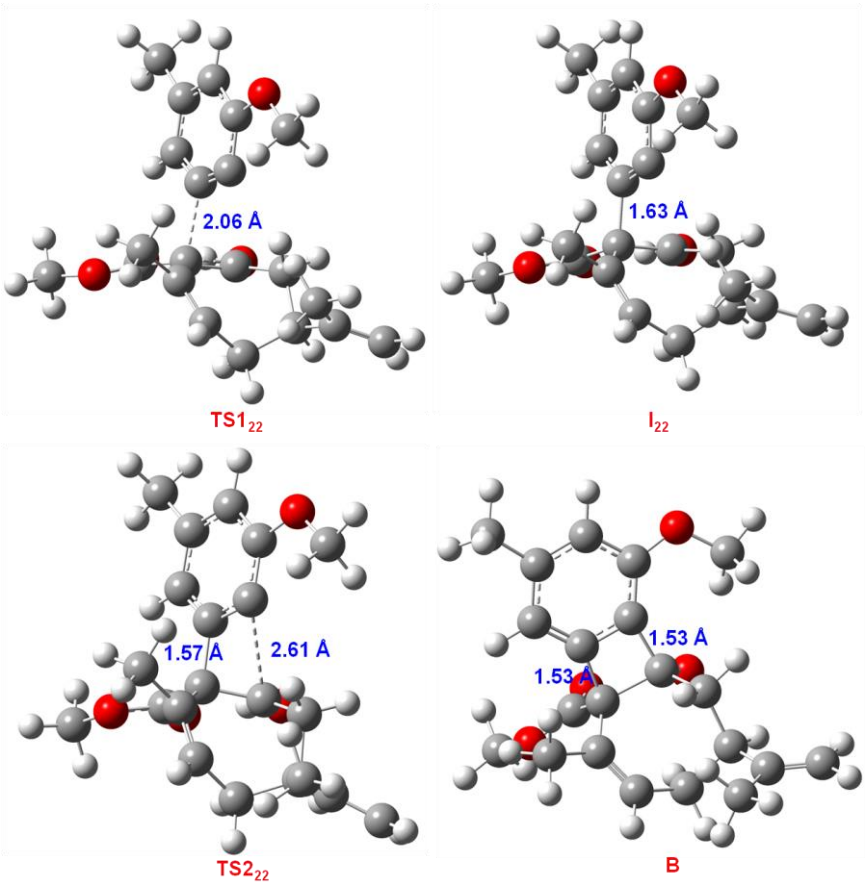


Figure 7. Optimized geometries of transition states and intermediates involved in [2+2] cycloaddition between **3a** and **7a** calculated at UM06-2X/6-31G(d,p) level of theory.

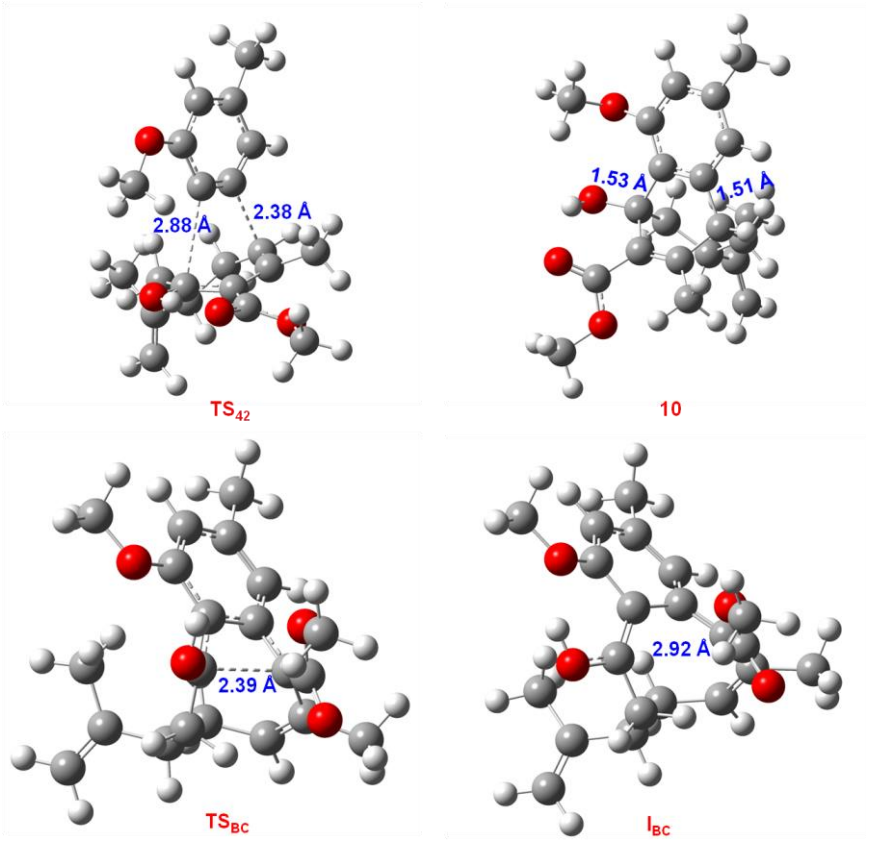


Figure 8. Optimized geometries of transition states and intermediates involved in [4+2] cycloaddition and four membered ring opening step calculated at UM06-2X/6-31G(d,p) level of theory.

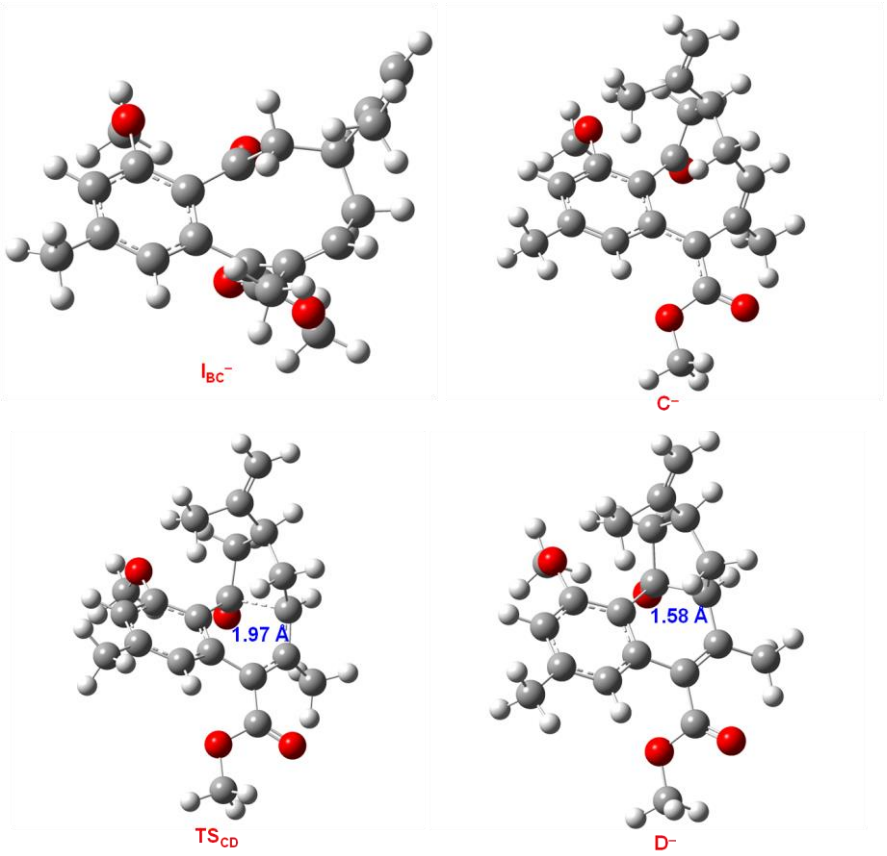


Figure 9. Optimized geometries of transition states and intermediates involved in Aldol addition mechanism calculated at UM06-2X/6-31G(d,p) level of theory.

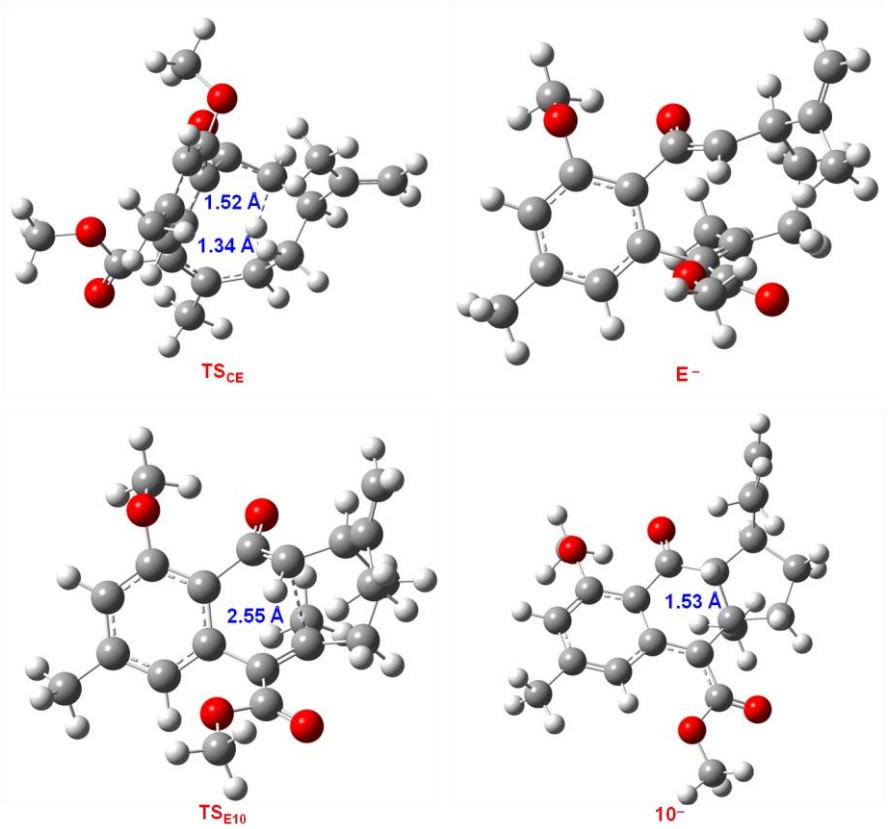


Figure 10. Optimized geometries of transition states and intermediates involved in Michael addition mechanism calculated at UM06-2X/6-31G(d,p) level of theory.

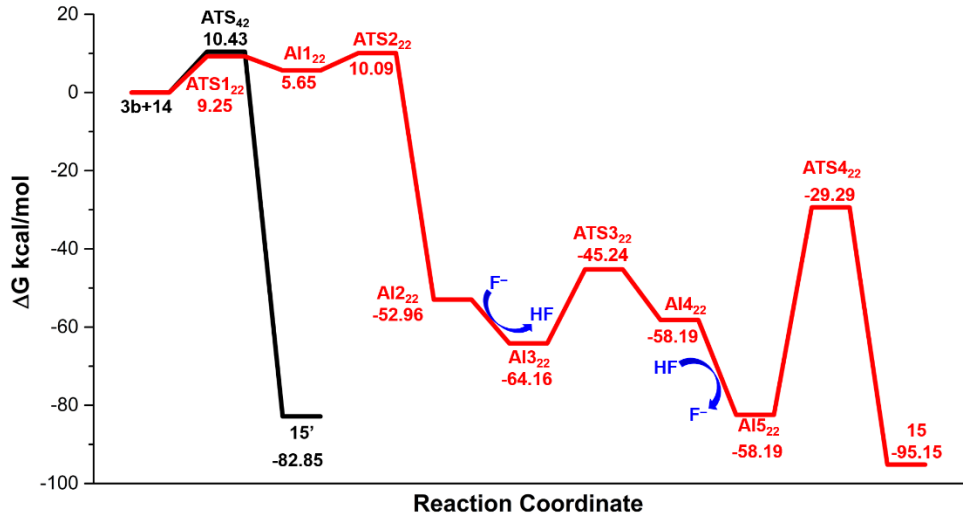


Figure 11. Gibbs free energy profile for cycloaddition of **3b** and **14a** and calculated at UM06-2X/6-31G(d,p) level of theory.

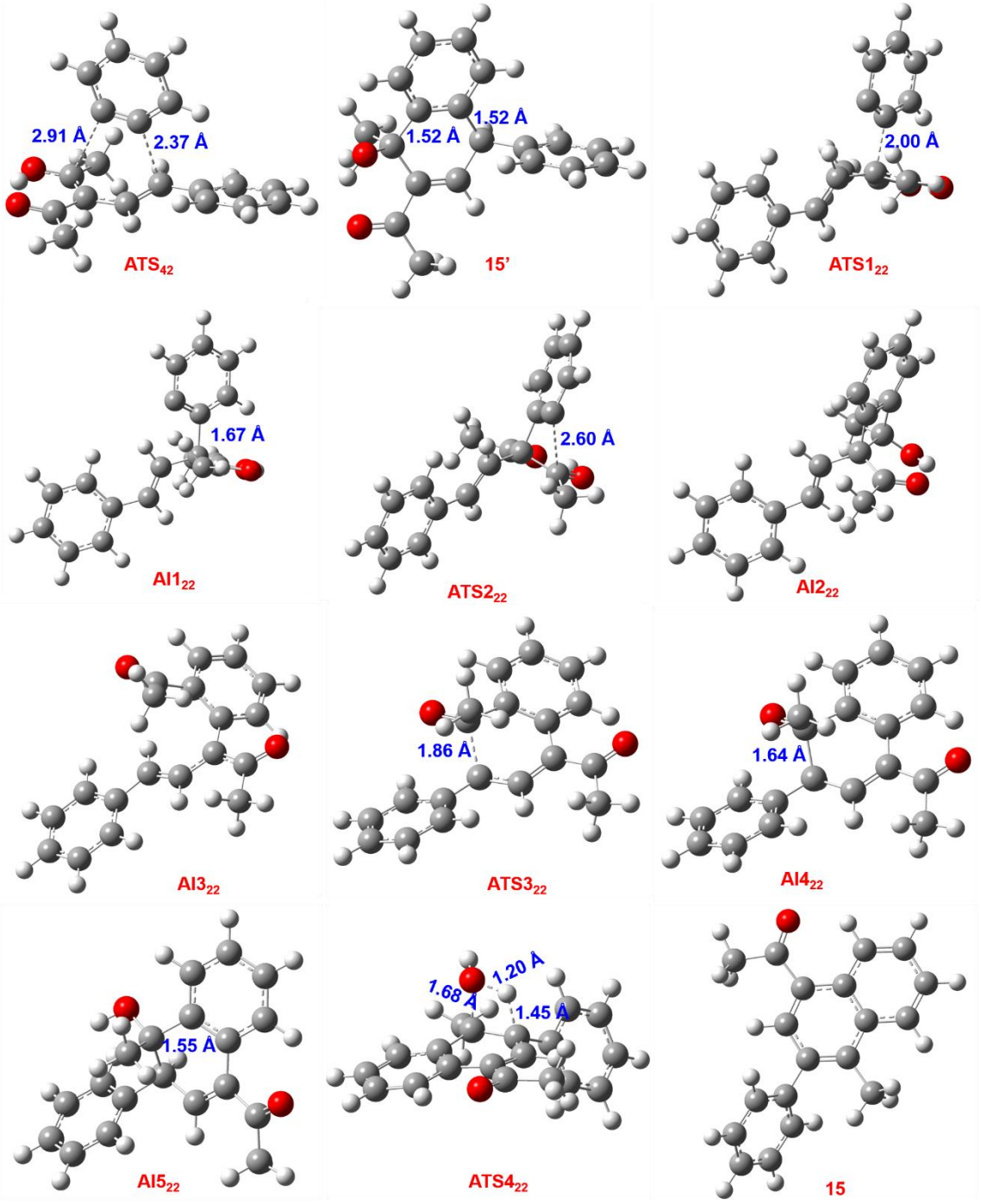


Figure 12. Optimized geometries of transition states and intermediates involved in cycloaddition of benzyn with open chain *β*-keto carbonyls calculated at UM06-2X/6-31G(d,p) level of theory.

VI. Cartesian coordinates of the intermediates computed at UM06-2X/6-31G(d,p) level of theory.

	3a		
C	-1.62310900	-0.19705800	-0.00015000
C	-1.69743800	1.21621400	-0.00013800
C	-0.41809200	1.70869400	0.00003400
C	0.72789100	1.21532300	0.00007300
C	0.84381200	-0.17569900	0.00003500
C	-0.38602200	-0.86078900	-0.00008900
H	-2.63345500	1.75831600	-0.00025900
H	-0.35894700	-1.94649800	-0.00019400
O	1.98767200	-0.88711600	0.00004400
C	3.17522300	-0.11632700	-0.00000200
H	4.00295100	-0.82427100	0.00003000
H	3.22512000	0.51909800	-0.89064000
H	3.22512800	0.51918700	0.89057300
C	-2.90091700	-1.00391900	0.00012900
H	-2.95463200	-1.65025500	-0.88024200
H	-2.95810300	-1.64400000	0.88486900
H	-3.77752100	-0.35328400	-0.00384900

	7a		
C	-0.78110900	1.44618300	-0.25737300
C	-1.03257000	-0.01674100	-0.32034700
C	-0.06967400	-0.91236800	-0.72359400
C	0.37998100	2.02060900	0.09653500
C	1.35801600	-0.53138200	-0.95435200
C	1.69184900	1.45828600	0.57683400
C	1.96967400	-0.04198800	0.38003100
H	0.40008800	3.10780500	0.02433900
H	1.87487400	-1.42029700	-1.32228300
H	2.47581000	2.02302300	0.05473100
H	1.48723700	-0.60041200	1.18948900
C	3.45878500	-0.31822400	0.46278100
C	3.98646600	-0.89476500	1.54167000
H	3.36658400	-1.20327700	2.37841000
H	5.05354400	-1.07858800	1.62307400
C	4.30754200	0.09244700	-0.71291800
H	5.36546100	-0.08718200	-0.51291100
H	4.03245300	-0.47033400	-1.61164800
H	4.18327700	1.15326500	-0.95490100
O	-0.28205200	-2.21132600	-0.84993400
H	-1.24401800	-2.36775700	-0.62530000
C	-2.32555100	-0.59433800	0.03422700
O	-2.62607600	-1.78343700	-0.11401100
O	-3.19656400	0.25294100	0.59070300
C	-4.45464200	-0.31441700	0.95554700
H	-4.31574100	-1.10337900	1.69685800
H	-5.03603700	0.50650000	1.37104500
H	-4.95206000	-0.73699200	0.08065000
C	-1.90817300	2.35479500	-0.71581600
H	-2.42659000	1.92768800	-1.57966700
H	-2.65389500	2.50046900	0.06745700
H	-1.51144000	3.33082100	-1.00236600
H	1.42615900	0.26120500	-1.70859900
H	1.82825500	1.70341900	1.63821400

	$TS1_{22}$		
C	0.66454100	-1.04745300	1.33421600
C	-0.08822100	-1.23922200	0.04896800
C	0.51043500	-0.89541500	-1.19006000
C	1.98895200	-1.23849900	1.37815300
C	1.64803300	0.05252900	-1.25290200
C	2.85567000	-1.64604800	0.21551500
C	3.01610000	-0.57383600	-0.88611800
H	2.48123300	-1.08485300	2.33634900
H	1.69072800	0.48049700	-2.25657600
H	3.84744600	-1.94096600	0.57017900
H	3.40064800	-1.08492500	-1.77587200
C	3.99363900	0.52841100	-0.53292100
C	4.97646200	0.85192600	-1.37274500
H	5.11701000	0.32501500	-2.31208900
H	5.67195500	1.65523000	-1.14890100
C	3.80398200	1.24261700	0.78131300
H	4.44333700	2.12613200	0.83713700
H	2.76330700	1.54947500	0.93608100
H	4.06287100	0.58456300	1.61861100
O	0.04463000	-1.31050400	-2.33691000
H	-0.71931100	-1.92937000	-2.14886900
C	-1.07258900	-2.34245800	-0.02026200
O	-1.58515100	-2.73678300	-1.06893200
O	-1.37269100	-2.89809100	1.14446700
C	-2.34589800	-3.94695200	1.09708900
H	-1.99228100	-4.76116900	0.46285200

	$TS2_{22}$		
C	0.67637800	-0.84786200	1.38845600
C	-0.10579600	-0.85077200	0.07971500
C	0.60793500	-0.19502600	-1.06351700
C	1.98900600	-1.10166200	1.38221200
C	1.74521900	0.73779400	-0.86638200
C	2.80286800	-1.36743100	0.13670500
C	3.03834100	-0.12370600	-0.76428600
H	2.51216800	-1.09802100	2.33572900
H	1.80970700	1.41475300	-1.72025100
H	3.77183300	-1.80027300	0.40056300
H	3.27866900	-0.48819800	-1.76919700
C	4.18264600	0.75176800	-0.29992500
C	5.11997800	1.14594100	-1.16113200
H	5.10067000	0.83762900	-2.20237400
H	5.93654900	1.79145000	-0.85246800
C	4.20939000	1.15693400	1.15029200
H	4.98500300	1.90349700	1.33087400
H	3.24797100	1.56759300	1.47557800
H	4.41663700	0.29234600	1.79104900
O	0.36966500	-0.55691500	-2.26821600
H	-0.23695000	-1.37502900	-2.23815800
C	-0.59443400	-2.22996500	-0.29867900
O	-0.77618800	-2.59589600	-1.45698700
O	-0.88383100	-2.99275900	0.73324500
C	-1.47302800	-4.26455800	0.42470900
H	-0.78727100	-4.85705300	-0.18211700

H	-2.46432600	-4.27889500	2.12591200
H	-3.28873300	-3.56672200	0.70015900
C	-0.09152800	-0.61706100	2.56786300
H	-0.24753100	0.46398400	2.54378700
H	-1.07216500	-1.09052400	2.62780100
H	0.47683700	-0.87616800	3.46376900
H	1.38420700	0.85165900	-0.53839000
H	2.41674500	-2.53451600	-0.25823900
C	-3.26902500	1.38639600	-0.64970400
C	-2.47580600	0.22933100	-0.61420900
C	-1.21271900	0.47699200	-0.10826700
C	-0.59574100	1.55477000	0.29606900
C	-1.41762000	2.68723900	0.25681100
C	-2.73376400	2.60392900	-0.21713400
H	-2.85950400	-0.72634300	-0.95067700
H	-3.33573400	3.50793300	-0.25444300
O	-1.00495100	3.92675300	0.64744500
C	0.32891200	4.01928200	1.09660000
H	0.48101100	5.06079500	1.38230700
H	0.50588700	3.36306300	1.95625200
H	1.03466500	3.73955000	0.30625900
C	-4.69330300	1.31571300	-1.14440900
H	-4.87734600	2.06594900	-1.91844200
H	-4.91730700	0.33287500	-1.56530100
H	-5.40141300	1.50359200	-0.33141600

H	-1.65431100	-4.73960700	1.38547400
H	-2.40635800	-4.11808600	-0.12168200
C	-0.10352900	-0.56811600	2.63833000
H	-0.46777100	0.46214900	2.61379400
H	-0.97659100	-1.22499300	2.70269500
H	0.52041900	-0.71844800	3.52162200
H	1.54672000	1.30947000	0.03779500
H	2.29404500	-2.12718500	-0.47434500
C	-3.64546400	0.62427000	-0.25602300
C	-2.61659700	-0.30847800	-0.21032100
C	-1.31674700	0.16144900	0.04871500
C	-0.91557700	1.49025500	0.20651800
C	-2.00852900	2.37475200	0.10432700
C	-3.32923000	1.97905400	-0.09581600
H	-2.85435700	-1.36271300	-0.34236100
H	-4.11402900	2.73174700	-0.13279400
O	-1.83835600	3.73199200	0.20318000
C	-0.51719000	4.18503500	0.39524600
H	-0.58318400	5.27207700	0.47351100
H	-0.07507500	3.76207100	1.30297800
H	0.12906800	3.90726800	-0.44498600
C	-5.07846300	0.19885000	-0.45185600
H	-5.66448900	0.35356400	0.45995100
H	-5.55594800	0.78047000	-1.24595900
H	-5.14650200	-0.85900400	-0.71841000

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C	0.64814400	-0.96518600	1.33052900
C	-0.20867400	-1.01663900	0.07154600
C	0.47276600	-0.76731000	-1.20967000
C	1.93734100	-1.31505200	1.30163500
C	1.61876000	0.15579500	-1.27814600
C	2.72814900	-1.70980900	0.08045200
C	2.95277300	-0.56595200	-0.93674100
H	2.47881700	-1.27073600	2.24393900
H	1.67347600	0.58481100	-2.28077900
H	3.70140000	-2.10916500	0.37868100
H	3.32146700	-1.03207500	-1.85733600
C	3.97497400	0.46182600	-0.49815500
C	5.00890700	0.75350700	-1.28714800
H	5.15706900	0.25221800	-2.23924000
H	5.74059600	1.50501700	-1.00631500
C	3.77033100	1.14381000	0.83140800
H	4.42815200	2.01067100	0.92281100
H	2.73314100	1.46921200	0.97385200
H	4.00073800	0.45956700	1.65564000
O	0.06117100	-1.29649600	-2.31048300
H	-0.66070100	-1.96915000	-2.08039400
C	-1.08800900	-2.24647100	0.02034500
O	-1.43712600	-2.79101500	-1.02466000
O	-1.48245400	-2.68637700	1.19481200
C	-2.38082700	-3.80516700	1.17559200
H	-1.90505100	-4.65899400	0.69177200
H	-2.59746000	-4.01804800	2.21934600
H	-3.28993500	-3.54016000	0.63358500
C	-0.00745400	-0.50155400	2.60467400
H	-0.12605800	0.58375600	2.56728000
H	-0.99730100	-0.94160000	2.73698200
H	0.61540700	-0.77033800	3.46052200
H	1.37746800	0.94848700	-0.54366500
H	2.21384900	-2.52546000	-0.44801900
C	-3.22296200	1.30590300	-0.69211500
C	-2.42390100	0.17180300	-0.60093500
C	-1.13009600	0.33050700	-0.07178000
C	-0.52850400	1.50753800	0.31533800
C	-1.39469500	2.60672700	0.23142100
C	-2.69301400	2.53153400	-0.27526700
H	-2.83275900	-0.78614300	-0.91313400
H	-3.28507100	3.44066100	-0.35577700
O	-1.01010200	3.86699600	0.61190300

B

C	-0.69430600	1.60790200	1.00257400
C	0.16635300	0.91562400	-0.04000400
C	-0.33192800	-0.49787800	-0.66396100
C	-2.01283700	1.71460200	0.81896700
C	-1.52784900	-1.07703400	0.08837100
C	-2.73669300	1.12650900	-0.36408600
C	-2.85762500	-0.41850000	-0.32171400
H	-2.59757100	2.22597300	1.58131100
H	-1.59258200	-2.14672200	-0.13149500
H	-3.73571800	1.56261500	-0.45912500
H	-3.06694200	-0.74188200	-1.34575500
C	-3.98404900	-0.91718000	0.56021200
C	-4.83934600	-1.83677800	0.11318300
H	-4.77157700	-2.22735700	-0.89810500
H	-5.63346000	-2.22858400	0.74207700
C	-4.09494000	-0.35483800	1.95394400
H	-4.83312400	-0.90494100	2.54130900
H	-3.13572200	-0.38465700	2.48142600
H	-4.40310800	0.69652000	1.92320900
O	-0.65202300	-0.53585700	-2.02234800
H	0.01341100	-0.00390800	-2.49050500
C	0.65732700	1.88426900	-1.10742400
O	0.91329700	1.59789800	-2.25919000
O	0.86484000	3.10963100	-0.61844800
C	1.41046400	4.04972400	-1.54769600
H	0.73507100	4.17851900	-2.39513800
H	1.51838400	4.98086200	-0.99531100
H	2.37734400	3.70046700	-1.91473000
C	0.00445300	2.15965800	2.21337000
H	0.48644600	1.35853300	2.78398900
H	0.78555200	2.86876600	1.91979000
H	-0.70256400	2.67412300	2.86783400
H	-1.34802200	-0.97858700	1.16296400
H	-2.19491500	1.37291800	-1.28550000
C	3.43857200	-0.78539000	1.16471400
C	2.56754900	0.31739000	1.12601900
C	1.39016800	0.13042700	0.43035600
C	1.02761900	-1.04591100	-0.21450300
C	1.90040200	-2.13460400	-0.20478000
C	3.10142900	-1.96744300	0.50632300
H	2.83102800	1.25575100	1.60482700
H	3.78507500	-2.81104100	0.52468000
O	1.73907600	-3.32210800	-0.82574800

C	0.30849200	4.00307800	1.09052400
H	0.42054700	5.05447800	1.36188000
H	0.48853800	3.36658200	1.96388100
H	1.04446700	3.73138900	0.32561200
C	-4.63303700	1.22736100	-1.22117900
H	-4.78074100	1.92355500	-2.05221900
H	-4.86718700	0.22144300	-1.57856700
H	-5.36157000	1.48765700	-0.44686900

C	0.48552600	-3.56460200	-1.44181400
H	0.61893300	-4.44682000	-2.06758900
H	-0.27660100	-3.77593000	-0.68334900
H	0.16498600	-2.71540700	-2.05302600
C	4.73646200	-0.69136100	1.92761100
H	4.56218700	-0.79367400	3.00358100
H	5.43328600	-1.47589200	1.62589500
H	5.21819000	0.27633900	1.76463200

I_{BC}

C	2.50608800	-0.03432600	1.34583700
C	1.57894600	-0.81879200	0.50509700
C	-0.38003100	0.37786900	-1.31257500
C	2.20336300	1.24928100	1.62533100
C	0.80198200	1.33006300	-1.31630600
C	0.95443000	2.01757600	1.24566200
C	0.80177800	2.45193300	-0.23243500
H	1.77069300	0.83619200	-1.29446900
H	0.05416700	1.48232900	1.55638900
H	1.69270000	3.04005300	-0.48595400
C	-0.39916100	3.37212200	-0.39493200
C	-0.28028800	4.52075400	-1.06047400
H	0.66947300	4.83448400	-1.48461200
H	-1.12875000	5.18221000	-1.20881200
C	-1.71447200	2.95576500	0.21489100
H	-2.50724200	3.64978300	-0.07256400
H	-2.00980300	1.94774900	-0.09421100
H	-1.65401000	2.94325200	1.30841900
C	3.81398700	-0.64759200	1.77292200
H	4.42807100	0.07008000	2.32178400
H	3.63685200	-1.51692400	2.41496800
H	4.37158800	-0.98980800	0.89751300
H	0.73383700	1.84605000	-2.27761600
H	0.95237300	2.94894900	1.82444300
C	-1.69367600	-1.12470300	2.20226200
C	-0.36562000	-0.87025800	2.04847900
C	0.21856600	-0.81085300	0.73567500
C	-0.70497900	-0.58544000	-0.37248400
C	-2.07205300	-1.05582800	-0.19748200
C	-2.55121300	-1.29626800	1.05030600
H	0.29455600	-0.82946000	2.91061900
H	-3.57426100	-1.61368200	1.21392100
O	-2.81246300	-1.16001200	-1.34346500
C	-4.17767300	-1.51869500	-1.21328200
H	-4.71435900	-0.78792400	-0.59927600
H	-4.58733100	-1.53214400	-2.22200300
H	-4.26816300	-2.51221500	-0.76376900
C	-2.31062400	-1.31523600	3.56038300
H	-2.73189000	-2.32144600	3.65837300
H	-1.57565000	-1.17239800	4.35425400
H	-3.13000700	-0.60568700	3.71670400
O	-1.21564600	0.69657900	-2.30852200
C	2.14272800	-1.38428600	-0.73202900
O	3.19697200	-1.03682500	-1.23362200
O	1.40743900	-2.39220500	-1.25471100
C	1.90244600	-2.90399700	-2.48513300
H	2.91302900	-3.29928800	-2.36170600
H	1.21420900	-3.69594300	-2.77747100
H	1.92915900	-2.12043300	-3.24736500
H	2.94023000	1.81157800	2.19869600
H	-1.97702500	0.08979100	-2.30196100

TS_{BC}

C	2.34652700	0.64200900	1.34369900
C	1.60323500	-0.37754000	0.58249200
C	0.15364300	0.13641300	-1.24519600
C	1.75199700	1.81047500	1.65705800
C	0.67385700	1.55645900	-1.26553700
C	0.36402400	2.25848200	1.26237400
C	0.20474300	2.61001800	-0.23672300
H	1.77132100	1.51019400	-1.25483900
H	-0.39258500	1.52777400	1.55754300
H	0.88087400	3.45479900	-0.42029600
C	-1.19885800	3.11919900	-0.51862700
C	-1.41014500	4.41893600	-0.72729600
H	-0.59352900	5.13525700	-0.72034800
H	-2.40675800	4.80984100	-0.91040300
C	-2.33484900	2.13011800	-0.54532100
H	-3.29035100	2.64566900	-0.66763500
H	-2.22462500	1.41915900	-1.37370200
H	-2.37667200	1.53506800	0.37419800
C	3.77739000	0.37356600	1.74361300
H	4.17975200	1.20423000	2.32824600
H	3.84039700	-0.53766900	2.34763100
H	4.39739200	0.22347000	0.85828400
H	0.40299000	1.93408700	-2.26047700
H	0.12394100	3.17443200	1.81139300
C	-1.66184500	-1.50312900	2.14229600
C	-0.34674200	-1.07684200	2.14966000
C	0.24306500	-0.71344800	0.92384900
C	-0.54685000	-0.59884000	-0.21849600
C	-1.84586000	-1.15284700	-0.26454800
C	-2.40146600	-1.57288500	0.92849400
H	0.23549500	-1.07865200	3.06625600
H	-3.42035700	-1.94258800	0.96665200
O	-2.46280000	-1.14825900	-1.47578500
C	-2.33726300	-1.95778700	3.41073700
H	-1.68085100	-1.83415700	4.27381000
H	-3.25227000	-1.38541600	3.59223000
H	-2.62024100	-3.01315100	3.34647200
O	0.13775800	-0.35773000	-2.48287000
C	2.29568800	-1.04331200	-0.51133300
O	3.32308800	-0.62768500	-1.02642900
O	1.71841700	-2.20794700	-0.94658800
C	2.39387700	-2.80032500	-2.04982900
H	3.41707100	-3.07100500	-1.78097400
H	1.82243300	-3.69376900	-2.30345000
H	2.43266400	-2.11193000	-2.89835100
H	2.34020200	2.53096900	2.22425200
H	-0.16956400	-1.27649300	-2.44684900
C	-3.82702900	-1.52264300	-1.50597700
H	-4.42385800	-0.86359400	-0.86536500
H	-4.14903700	-1.41912400	-2.54114900
H	-3.95837500	-2.56089500	-1.18207100

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C	-0.85285600	-0.44552300	-1.51146300
C	-1.44104100	-0.81774500	-0.22720700
C	-1.32408100	-0.05989600	0.94229800
C	-0.36369800	0.78329000	-1.85045300
C	-1.06900500	1.41930200	1.03660800
C	-0.66104100	2.16045800	-1.32507300
C	-1.61984000	2.23335800	-0.14072600

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C	1.09706300	-0.18537000	1.59119300
C	1.21584400	-0.80614400	0.40879500
C	0.23693300	-0.44917900	-0.72975000
C	-0.02450100	0.82691100	1.70449500
C	0.60569000	0.94524500	-1.31391000
C	0.36585800	2.15228000	0.98490900
C	1.17268400	1.97345800	-0.31882500

H	0.16084200	0.81219000	-2.80390700
H	-1.54864200	1.72803300	1.97059100
H	0.28803200	2.64888000	-1.06860500
H	-2.57725800	1.79471400	-0.44650900
C	-1.88035800	3.67090500	0.26553500
C	-3.08780000	4.21376600	0.11607900
H	-3.91774200	3.64582000	-0.29385500
H	-3.28551200	5.24330500	0.39899600
C	-0.72606200	4.44981100	0.84121700
H	-1.03396400	5.46232700	1.10874400
H	-0.33032500	3.96599000	1.74083000
H	0.10364300	4.52489800	0.13056700
O	-1.59748200	-0.56011000	2.12884100
H	-1.80284100	-1.53716700	2.00163900
C	-2.03052100	-2.14758500	-0.02586500
O	-2.16311600	-2.69976500	1.07167700
O	-2.51364300	-2.73242600	-1.12208600
C	-3.09892800	-4.02119200	-0.92638800
H	-3.95886600	-3.94925800	-0.25847500
H	-3.40519900	-4.35479200	-1.91586700
H	-2.37091700	-4.70931600	-0.49319000
C	-0.47369100	-1.57188200	-2.45721800
H	-0.05729600	-2.42046100	-1.90687200
H	-1.33446000	-1.93159000	-3.02266500
H	0.28463400	-1.22047200	-3.15859900
H	0.00611600	1.58413100	1.15211300
H	-1.08399200	2.74275600	-2.15446400
C	3.88960000	0.12125200	-0.85220800
C	2.67481500	0.42425700	-1.49983400
C	1.60505100	0.09207000	-0.69950700
C	1.49413100	-0.42180700	0.46028700
C	2.69118400	-0.71339200	1.11544600
C	3.88793600	-0.44100200	0.43244400
H	2.64094300	0.86495600	-2.48983800
H	4.82909000	-0.67891600	0.92043700
O	2.77620700	-1.24838500	2.35757600
C	1.53339100	-1.49605500	2.98739500
H	1.76420300	-1.94333000	3.95414600
H	0.96757400	-0.56810300	3.12610700
H	0.91840200	-2.18000900	2.39080200
C	5.20167900	0.39941000	-1.54712400
H	5.82064800	1.08259900	-0.95852100
H	5.77334200	-0.52247400	-1.68822500
H	5.04064100	0.84998500	-2.52890200
H	-0.20605400	1.05687200	2.75998900
H	1.36074400	0.76776500	-2.08658400
H	-0.55746600	2.71260200	0.79953400
H	2.16175700	1.60787500	-0.02049000
C	1.38511000	3.32624500	-0.97493100
C	2.55143000	3.96069700	-0.85882500
H	3.38734300	3.51482200	-0.32724700
H	2.70996100	4.94355700	-1.29273200
C	0.23261500	3.92989300	-1.73623800
H	0.42092800	4.98150000	-1.96136200
H	0.07307000	3.40500500	-2.68403400
H	-0.70515000	3.85922900	-1.17499200
O	0.34133700	-1.34581200	-1.80736900
H	0.54892700	-2.22493700	-1.45835300
C	2.23328500	-1.85595700	0.14031600
O	1.98444800	-2.93071300	-0.36937000
O	3.47540400	-1.51090400	0.50685000
C	4.46890200	-2.51327800	0.27601200
H	4.52058100	-2.75451700	-0.78709100
H	5.40706200	-2.08346400	0.62121100
H	4.23034300	-3.42211700	0.83203300
C	1.94918200	-0.37364500	2.81046400
H	2.71974500	-1.13137300	2.68607500
H	2.43789900	0.57472300	3.06422200
H	1.31369400	-0.63968900	3.66190400
H	-0.28986100	1.32518000	-1.81627700
H	0.97842200	2.76230300	1.65809100
C	-3.69871200	0.00291100	1.09730200
C	-2.52459100	0.43788400	1.71688500
C	-1.29202300	0.26608200	1.10014500
C	-1.17749200	-0.35911500	-0.14517200
C	-2.35783400	-0.73460300	-0.79560400
C	-3.59408000	-0.57076400	-0.16499700
H	-2.57497000	0.92649000	2.68777200
H	-4.48233200	-0.87903500	-0.71032300
O	-2.36248000	-1.20639900	-2.08315300
C	-2.40535100	-2.61634100	-2.17891800
H	-3.32573300	-3.01572300	-1.73329100
H	-2.37813100	-2.86186000	-3.24095000
H	-1.54260500	-3.07101600	-1.68038900
C	-5.03493600	0.15008800	1.77823000
H	-5.84825100	0.18612300	1.04991100
H	-5.22656900	-0.69484500	2.44783400
H	-5.07347600	1.06136000	2.38042000

$\mathbf{I_{BC^-}}$			$\mathbf{C^-}$		
C	2.30317800	0.17649800	1.53715000	C	1.17241700	-2.01590700	0.42323400
C	1.80116200	-0.62589300	0.41865200	C	1.69068900	-0.68010700	0.03406600
C	-0.13723600	0.52167400	-1.41237800	C	-1.09063300	-0.64552500	1.39515300
C	1.54509700	1.09989000	2.17215400	C	0.11685800	-2.61216400	-0.15866000
C	0.53755900	1.77864600	-0.82608100	C	-2.28020600	-1.35189300	0.73853000
C	0.15013000	1.55181000	1.80057600	C	-0.73803500	-2.03216600	-1.24011800
C	0.05984100	2.41034400	0.50805900	C	-2.19173400	-1.85479000	-0.73049300
H	1.61363600	1.59680900	-0.74658300	H	-2.51024200	-2.18944500	1.40243100
H	-0.55321200	0.71542400	1.74074700	H	-0.31586500	-1.08215000	-1.57578500
H	0.75491200	3.24584000	0.66751400	H	-2.62794500	-2.86191100	-0.71636400
C	-1.32334600	3.02600700	0.38425300	C	-3.01625100	-1.05510400	-1.72044000
C	-1.51323300	4.33105400	0.58822400	C	-3.89792400	-1.66421200	-2.51609900
H	-0.68488600	4.99208000	0.82826200	H	-4.07477000	-2.73457600	-2.45049000
H	-2.50089200	4.78026800	0.51903700	H	-4.46639200	-1.11422900	-3.26140700
C	-2.47282800	2.11921800	0.03269800	C	-2.78244500	0.42953000	-1.80235000
H	-3.42303100	2.66036100	0.06909600	H	-3.33206900	0.86304300	-2.64221900
H	-2.35165900	1.70096000	-0.97274900	H	-3.10940900	0.92686000	-0.88251200
H	-2.52852700	1.26478000	0.71746500	H	-1.71876400	0.66679800	-1.91231200
C	3.73708600	-0.02704500	1.97237200	C	1.80858500	-2.68063200	1.62087000
H	4.02463700	0.67489300	2.76205300	H	1.49371600	-3.72466400	1.72039300
H	3.88049700	-1.05053800	2.33863600	H	2.89592800	-2.63793300	1.55140700
H	4.39426400	0.10598300	1.11016100	H	1.48732800	-2.13484400	2.51724800
H	0.39952900	2.53020700	-1.61225700	H	-3.10695300	-0.63647700	0.83457100
H	-0.22427200	2.19947200	2.60363100	H	-0.78299400	-2.69153000	-2.11724000

C	-1.37250500	-2.34969200	1.51480400
C	-0.05993600	-1.91663900	1.47661300
C	0.41333300	-1.07676400	0.44664400
C	-0.50938500	-0.61728900	-0.51231600
C	-1.82541700	-1.11919400	-0.51892000
C	-2.26164400	-1.96653500	0.49541600
H	0.64453300	-2.23209200	2.24240900
H	-3.28064600	-2.33743900	0.51666900
O	-2.65720500	-0.66503600	-1.50627600
C	-4.03146700	-0.89519900	-1.34961000
H	-4.39722200	-0.51414300	-0.38614900
H	-4.52535800	-0.36099500	-2.16286700
H	-4.27960500	-1.96262300	-1.42135800
C	-1.86214800	-3.26235100	2.61208700
H	-2.17375200	-4.23346800	2.21138500
H	-1.07918300	-3.43893000	3.35326400
H	-2.72773900	-2.83239600	3.12781200
O	-0.40110900	0.51502100	-2.60193900
C	2.55025200	-0.65886700	-0.78099000
O	3.59572700	-0.05075900	-1.04345300
O	1.98736300	-1.47052200	-1.75974800
C	2.45951600	-1.21360200	-3.06255400
H	3.54150300	-1.35846600	-3.13426400
H	1.93772300	-1.91387200	-3.71856800
H	2.22463800	-0.18856100	-3.37138300
H	1.98785300	1.61037400	3.02823800
C	0.40249200	2.83543400	-0.63921500
C	1.17775000	1.68960000	-0.66166700
C	0.83688400	0.48031600	0.02125400
C	-0.44428000	0.50286500	0.65607400
C	-1.19127400	1.68017600	0.69679300
C	-0.80357000	2.85356100	0.07292300
H	2.09919400	1.70918700	-1.22565700
H	-1.44038000	3.73171300	0.12423300
O	-2.40889700	1.66503300	1.37705800
C	-2.26376800	2.03537800	2.73778900
H	-1.88952800	3.06411400	2.82132100
H	-3.25521800	1.97246900	3.19313500
H	-1.57618700	1.35573500	3.25267100
C	0.84857000	4.07140100	-1.38251900
H	1.05155900	4.89602000	-0.68984000
H	1.76038000	3.87972400	-1.95312700
H	0.07552800	4.41734000	-2.07738700
O	-0.83117000	-0.87897400	2.56176800
C	3.09205300	-0.68080700	-0.23525400
O	3.82357400	-1.67170200	-0.30764600
O	3.68472200	0.56657000	-0.39704800
C	5.07229900	0.51331900	-0.63445000
H	5.30723300	-0.07952400	-1.52384600
H	5.39569200	1.54782400	-0.77489200
H	5.60716800	0.06586000	0.20936800
H	-0.22370200	-3.56645500	0.25071500

TS_{CD}			
C	1.10334400	-2.07145400	0.03031600
C	1.68951400	-0.83547300	-0.28109500
C	-0.92937600	-0.93588300	1.21936200
C	-0.28409800	-2.25966500	-0.09510400
C	-2.40364400	-1.18869100	0.78157800
C	-1.12297700	-1.79987900	-1.25890300
C	-2.55511900	-1.57169800	-0.70795500
H	-2.72978900	-2.01483400	1.42051600
H	-0.71592000	-0.88439000	-1.69499000
H	-3.07155000	-2.53856500	-0.75535000
C	-3.35726000	-0.61369900	-1.56038500
C	-4.35134200	-1.05263300	-2.33611700
H	-4.63256600	-2.10224000	-2.35414600
H	-4.91428800	-0.37904700	-2.97706800
C	-2.98041200	0.84404000	-1.52795600
H	-3.56832900	1.41490400	-2.25198000
H	-3.14807700	1.26686300	-0.53133100
H	-1.91609900	0.99191400	-1.74290300
C	1.79797100	-3.10003600	0.88044100
H	1.64940300	-4.11461600	0.49755100
H	2.86003800	-2.91190400	1.00973800
H	1.28450500	-3.02808400	1.85327400
H	-3.00272600	-0.31541200	1.05422300
H	-1.15383000	-2.54489600	-2.06386300
C	0.50809600	2.76530300	-0.61392900
C	1.18750000	1.57303400	-0.84485300
C	0.84296500	0.36940800	-0.20387300
C	-0.32743900	0.34678300	0.60410100
C	-0.93455800	1.57024200	0.89708400
C	-0.54514800	2.76540500	0.29514800
H	2.03533300	1.57697300	-1.52082200
H	-1.10658900	3.66765900	0.52323500
O	-2.02909900	1.64101800	1.74460400
C	-1.66713800	1.62302100	3.12076100
H	-1.07093900	2.51276100	3.36776700
H	-2.60162900	1.65100500	3.68714300
H	-1.10925300	0.71205700	3.35485300
C	0.93821600	4.03875400	-1.29964200
H	1.70190800	4.56555500	-0.71601900
H	1.36665600	3.83003900	-2.28399300
H	0.09495200	4.72315300	-1.43157100
O	-0.62110200	-1.20642400	2.41078700

D^-			
C	1.02113100	-2.04125000	0.20633400
C	1.64330100	-0.88362200	-0.11121200
C	-0.94762200	-0.74201500	1.25752800
C	-0.44856500	-2.00591600	0.43651800
C	-2.49523400	-0.88131800	0.95297700
C	-1.26491200	-1.99049100	-0.85926700
C	-2.69713400	-1.58957500	-0.40999500
H	-2.84683000	-1.52374500	1.76699400
H	-0.84460200	-1.23960800	-1.53839100
H	-3.26919600	-2.51316900	-0.25782500
C	-3.42802600	-0.78883600	-1.46360500
C	-4.44663000	-1.31194100	-2.15066300
H	-4.79660200	-2.32292900	-1.95946400
H	-4.96480600	-0.74690900	-2.92140000
C	-2.95960900	0.62059300	-1.71788100
H	-3.50147000	1.06809400	-2.55577900
H	-3.10647900	1.24342600	-0.82890900
H	-1.88637100	0.65520300	-1.93512800
C	1.68852000	-3.36968900	0.41427200
H	1.22890900	-4.11640500	-0.24488400
H	2.76142700	-3.36164800	0.23380100
H	1.48516300	-3.69205900	1.44227000
H	-3.03306700	0.06442900	1.02565400
H	-1.26153500	-2.94597600	-1.39595200
C	0.82610500	2.74491200	-0.80510100
C	1.44541600	1.50412800	-0.81126100
C	0.90418000	0.40276400	-0.12714600
C	-0.33833300	0.50328200	0.53612600
C	-0.89680900	1.79526100	0.61109900
C	-0.34385800	2.88153000	-0.05869800
H	2.37858100	1.38791700	-1.35669700
H	-0.86162200	3.83527100	0.01037700
O	-2.07071500	2.06238200	1.28322500
C	-1.96957100	1.93027100	2.70576900
H	-1.36705600	2.75901700	3.10565000
H	-2.99027700	2.01757600	3.08890000
H	-1.52007200	0.95993500	2.97040000
C	1.40570500	3.91961900	-1.55266600
H	1.70074700	4.72272200	-0.86828300
H	2.29122500	3.62442300	-2.12203500
H	0.67961300	4.34406300	-2.25431200
O	-0.62569300	-0.75325000	2.53864100

C	3.13421700	-0.76578700	-0.39213800
O	3.89719800	-1.70162000	-0.59676200
O	3.66047600	0.49639700	-0.25290700
C	5.06547900	0.55456000	-0.37674400
H	5.39748100	0.16115100	-1.34215400
H	5.33310300	1.60879100	-0.28436200
H	5.55735500	-0.02889900	0.40733400
H	-0.65169000	-3.18880100	0.34854200

C	3.11091300	-0.88481300	-0.34732600
O	3.74179500	-1.70132100	-0.98737200
O	3.73941600	0.14480100	0.27075500
C	5.14089100	0.18794200	0.06730500
H	5.37923700	0.26647000	-0.99731500
H	5.49487700	1.06846100	0.60307500
H	5.61947000	-0.71450100	0.45701300
H	-0.74684700	-2.86597000	1.05161100

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C	1.02436000	-2.03013900	0.28016200
C	1.65439700	-0.89023500	-0.05890500
C	-0.96949700	-0.66599300	1.18116100
C	-0.45190400	-1.96659500	0.53133900
C	-2.49803700	-0.81437800	0.96457500
C	-1.28346600	-2.07433500	-0.75701900
C	-2.70813000	-1.62609700	-0.34172600
H	-2.87712600	-1.39734500	1.81359800
H	-0.86301900	-1.39379100	-1.50525000
H	-3.29476100	-2.52078800	-0.10967300
C	-3.43177900	-0.88815100	-1.44729500
C	-4.45666400	-1.45593500	-2.08327600
H	-4.81539700	-2.44450900	-1.81128300
H	-4.97077800	-0.95122900	-2.89561800
C	-2.94527400	0.49206500	-1.80650000
H	-3.47310600	0.87211800	-2.68362500
H	-3.10509900	1.19351200	-0.97983100
H	-1.87029300	0.50408200	-2.01994300
C	1.64598300	-3.38885800	0.41094300
H	1.13835200	-4.08641700	-0.26585200
H	2.70794700	-3.40288200	0.18001000
H	1.48357600	-3.76452600	1.42766400
H	-3.02201300	0.13788100	0.97496000
H	-1.27352100	-3.07873000	-1.18699000
C	0.84803300	2.71641500	-0.88542200
C	1.47430400	1.47582200	-0.83256200
C	0.92350800	0.39773800	-0.12897800
C	-0.32923000	0.53860000	0.50302100
C	-0.90599400	1.81642200	0.51548400
C	-0.33947500	2.88069500	-0.17716300
H	2.42277500	1.34846500	-1.34436200
H	-0.85560300	3.83640200	-0.15320500
O	-2.08337300	2.07012400	1.18277700
C	-1.89360000	2.39835700	2.55690900
H	-1.29222600	3.31052400	2.65103400
H	-2.88695700	2.57525300	2.97174400
H	-1.40210700	1.57530200	3.08303300
C	1.43213100	3.85162600	-1.68531800
H	1.33974400	4.79979500	-1.14952000
H	2.48905100	3.68060500	-1.90057400
H	0.90973500	3.96218300	-2.64095500
O	-0.61917300	-0.56760800	2.55555200
C	3.12600900	-0.90923800	-0.32935200
O	3.71146000	-1.73441100	-0.99188600
O	3.76410500	0.10111800	0.28872300
C	5.17422200	0.13213100	0.08019000
H	5.40264900	0.22169000	-0.98432000
H	5.53604900	1.00104700	0.62670300
H	5.63645400	-0.78183400	0.45889100
H	-0.74101000	-2.79063000	1.20173200
H	-1.04685100	-1.29948000	3.01872100

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C	0.12434400	-1.85838100	0.41458300
C	1.25760300	-1.12972000	0.09524800
C	-1.17877100	0.21339600	0.45804900
C	-1.09169000	-1.15329900	0.58343000
C	-2.60656000	0.67413600	0.65997400
C	-2.43514800	-1.76219300	0.90470500
C	-3.44247100	-0.63130000	0.57215300
H	-2.72275900	1.14083700	1.64660100
H	-2.64159600	-2.67377900	0.33311000
H	-4.25929700	-0.61508100	1.29862400
C	-4.04641600	-0.81227000	-0.80454300
C	-5.36498000	-0.92074500	-0.96468300
H	-6.04409900	-0.88298000	-0.11795300
H	-5.80793100	-1.04985100	-1.94768800
C	-3.09810200	-0.86273600	-1.97448800
H	-3.64211700	-0.99226100	-2.91222300
H	-2.50283900	0.05458700	-2.04345100
H	-2.38355200	-1.68759300	-1.87303500
C	0.10472800	-3.35658500	0.58451100
H	-0.25324000	-3.83596000	-0.33311200
H	1.08840900	-3.77130200	0.79691200
H	-0.57905900	-3.63337800	1.39101100
H	-2.91963800	1.41889500	-0.07429600
H	-2.48942400	-2.03599500	1.96660300
C	2.29955500	2.41054800	-0.63673900
C	2.35195500	1.04947000	-0.46729300
C	1.21507000	0.29539900	-0.06085400
C	-0.02140500	0.97814100	0.14953400
C	-0.03340800	2.39775100	0.00354800
C	1.08351200	3.08885300	-0.37924700
H	3.28807600	0.53636200	-0.64915100
H	1.01583000	4.16771800	-0.49100400
O	-1.19947200	3.08705300	0.24625400
C	-1.27621600	3.59087400	1.56994000
H	-0.49511000	4.33902700	1.75019700
H	-2.25844400	4.05327700	1.67698800
H	-1.16766800	2.78374300	2.30532100
C	3.50320900	3.19659300	-1.08409300
H	3.76891000	3.95970300	-0.34587000
H	4.36865600	2.54710000	-1.22886000
H	3.30249600	3.71345700	-2.02767600
C	2.53021300	-1.88788300	-0.11718700
O	2.63577500	-2.87820500	-0.80148600
O	3.56416600	-1.38203800	0.58193600
C	4.79493500	-2.08495200	0.41468700
H	5.09585400	-2.08677000	-0.63522700
H	5.52438100	-1.55547300	1.02478600
H	4.69066500	-3.11934900	0.74834500

TS_{CE}

C	1.17909400	-2.32016300	-0.41557300
C	1.60451800	-1.01108300	-0.24461500
C	-0.85359000	-0.29542000	1.55227500
C	-0.18521500	-2.72650500	-0.58696000
C	-1.64676200	-1.44455200	1.21622000
C	-1.31649300	-1.92719200	-1.21844000
C	-2.37825900	-1.77363200	-0.08548900

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C	0.72075400	0.48894100	1.83170800
C	-0.01376700	1.21862200	0.95013000
C	0.04469700	-1.49578300	-0.12216300
C	2.22887800	0.42419700	1.86852100
C	1.18767600	-0.93832500	-0.62765500
C	2.71720500	-0.98233600	1.40561000
C	2.53126800	-1.37576500	-0.10114100

H	-0.59748300	-2.38829800	0.64802600
H	-0.99016700	-0.95532100	-1.59111800
H	-2.73794800	-2.80065700	0.08023600
C	-3.60341300	-0.99174000	-0.50434900
C	-4.77288700	-1.61272600	-0.68443300
H	-4.88210200	-2.67846400	-0.50124300
H	-5.65936900	-1.07441400	-1.01056900
C	-3.47390300	0.48550100	-0.73776200
H	-4.39570100	0.89938000	-1.15706800
H	-3.25341500	0.99897800	0.20181000
H	-2.64768300	0.71093000	-1.42123900
C	2.13964700	-3.47498400	-0.20443900
H	1.60489000	-4.42346900	-0.28856200
H	2.94817100	-3.44918500	-0.93836800
H	2.62765800	-3.41754800	0.77026400
H	-2.08761000	-1.88135300	2.11105900
H	-1.75805800	-2.46426600	-2.06590700
C	0.53626600	2.34083400	-1.63835800
C	1.12201200	1.09284600	-1.46300500
C	0.75564700	0.21939900	-0.42728700
C	-0.28578400	0.59208900	0.43802700
C	-0.81708600	1.88387700	0.30390100
C	-0.42944800	2.74289800	-0.71596700
H	1.92335200	0.78158900	-2.12981800
H	-0.90276000	3.72004600	-0.77742100
O	-1.78886000	2.33155100	1.17803600
C	-1.24290800	2.92014900	2.35191100
H	-0.66094000	3.81630100	2.09383400
H	-2.09172800	3.21080300	2.97529900
H	-0.61982900	2.19323600	2.87878300
C	0.93488900	3.24257300	-2.77974700
H	1.84373000	2.88022800	-3.26681100
H	0.14689200	3.29428700	-3.53931800
H	1.11909000	4.26451400	-2.43339800
O	-0.56825200	0.01449100	2.72088100
C	2.98969600	-0.74124700	0.13231900
O	3.93024700	-1.52104800	0.19879300
O	3.19770700	0.57590700	0.45085500
C	4.51697000	0.87600700	0.85264700
H	5.23704200	0.64157700	0.06253600
H	4.52881900	1.94498000	1.07045000
H	4.79902900	0.30585000	1.74258400
H	-0.29857100	-3.79851800	-0.74781300
H	3.77697600	-1.08057200	1.68384700
H	2.55944300	-2.47325500	-0.10726800
C	3.67670500	-0.89233000	-0.96749100
C	4.40210600	-1.73443700	-1.70571400
H	4.20047400	-2.80160400	-1.70198000
H	5.20403800	-1.38198600	-2.35080600
C	3.98323200	0.58426200	-0.96798600
H	4.68073500	0.84564300	-1.76904500
H	3.07495200	1.18618400	-1.07620400
H	4.43559600	0.88402000	-0.01514000
C	0.02774500	-0.48559700	2.74920900
H	-0.04205300	-1.47969400	2.28361800
H	0.59459800	-0.57220800	3.68345000
H	-0.98597700	-0.14681300	2.97457400
H	2.16932800	-1.73790900	1.97797700
C	-3.67832500	0.81331200	-0.02194000
C	-2.50184500	1.32978700	0.51115700
C	-1.29497200	0.62735400	0.44320500
C	-1.23358500	-0.64789300	-0.17410800
C	-2.42941100	-1.14906300	-0.71051900
C	-3.62322000	-0.43720100	-0.63827400
H	-2.50976700	2.30905500	0.98566600
H	-4.51050100	-0.87993900	-1.08663300
O	-2.45361200	-2.35393500	-1.37564200
C	-2.67176900	-3.46392600	-0.51169600
H	-3.66226400	-3.38942700	-0.03706300
H	-2.64925700	-4.35478500	-1.14467900
H	-1.87565000	-3.50355200	0.23733100
C	-4.97382900	1.58414400	0.03747100
H	-5.28518900	1.91740500	-0.95877400
H	-5.78562600	0.97034300	0.44144200
H	-4.87454300	2.47089400	0.66910400
O	-0.02812500	-2.57907600	0.56380600
C	0.60289500	2.28551100	0.14875200
O	1.59095500	2.94378500	0.42497100
O	-0.08230600	2.52592400	-1.00023500
C	0.47599800	3.53870300	-1.81649900
H	1.48420200	3.26559100	-2.14097100
H	-0.18620100	3.62893500	-2.67759500
H	0.53743900	4.48836900	-1.27754300
H	2.57161300	0.56066700	2.90378700
H	1.12229100	0.00917500	-1.15573800
H	2.66944400	1.21881500	1.27197500

	TS_{E10}		
C	0.80739900	0.60798000	1.59455600
C	-0.12771700	1.30268400	0.85305600
C	0.20840400	-1.52654000	-0.00451300
C	2.30205100	0.83105600	1.58648600
C	1.32866900	-0.84852500	-0.44056700
C	3.04322400	-0.50927900	1.37702200
C	2.71631100	-1.20976900	0.00993500
H	4.12531500	-0.34648500	1.48358800
H	2.73711700	-2.29099100	0.18712200
C	3.76316100	-0.88388800	-1.03712100
C	4.44958400	-1.83763300	-1.66839300
H	4.28131300	-2.88823100	-1.45098200
H	5.18306300	-1.59929000	-2.43529900
C	4.01185700	0.57334100	-1.33490200
H	4.69673900	0.69572300	-2.17857100
H	3.07903800	1.10088800	-1.56005400
H	4.44865500	1.07754700	-0.46486000
C	0.34023800	-0.38822200	2.62729700
H	0.50070300	-1.43018400	2.32259500
H	0.89769500	-0.20492600	3.55507800
H	-0.72575100	-0.26503900	2.82730400
H	2.75881800	-1.19887900	2.17849900
C	-3.71841900	0.40652600	-0.06181100
C	-2.60730900	1.08168700	0.43615400
C	-1.32552500	0.52375000	0.41082700

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C	0.74767100	1.27889000	0.54448500
C	-0.69304300	1.25700900	0.06029100
C	0.90936000	-1.19528300	0.30599900
C	1.64632500	2.44998100	0.09781300
C	1.49913700	0.11890800	-0.13025100
C	3.08875000	1.90817400	0.21924900
C	2.98619100	0.35028800	0.14277200
H	3.74141800	2.30573800	-0.56590800
H	3.22329200	-0.09458300	1.11457200
C	3.92937400	-0.25080000	-0.87193000
C	4.98057600	-0.98283200	-0.50370400
H	5.16002200	-1.22042100	0.54024900
H	5.67593400	-1.38885900	-1.23394100
C	3.64707400	0.03200600	-2.32589500
H	4.50796500	-0.21452200	-2.95257800
H	2.79373600	-0.55990000	-2.67324900
H	3.38710200	1.08478500	-2.48602000
C	0.77936000	1.17091000	2.08266000
H	1.79858600	1.14575600	2.48896100
H	0.26354200	2.04536700	2.48876600
H	0.25748000	0.26848800	2.41836400
H	3.54370100	2.20119500	1.17116600
C	-3.24430700	-1.44182000	-0.69165800
C	-2.65096800	-0.20684400	-0.56795100
C	-1.28894200	-0.02619400	-0.15471900

C	-1.13409400	-0.78689100	-0.10788800
C	-2.26049600	-1.44512900	-0.61599100
C	-3.52772600	-0.86612400	-0.59446200
H	-2.72505300	2.08403700	0.84107400
H	-4.35866000	-1.43149700	-1.01144700
O	-2.14159400	-2.68691300	-1.20189000
C	-2.36732400	-3.75441700	-0.29254400
H	-3.39617900	-3.71885400	0.09710400
H	-2.23600100	-4.67861500	-0.86119200
H	-1.63769500	-3.70224900	0.51908000
C	-5.08356900	1.04880000	-0.06389800
H	-5.29162400	1.53703500	-1.02287300
H	-5.87204500	0.30877200	0.10334500
H	-5.16102400	1.81156900	0.71582200
O	0.20908600	-2.61704600	0.64900800
C	0.24197000	2.50418000	0.12660000
O	1.21595500	3.22164600	0.31604600
O	-0.66755600	2.84568400	-0.84010300
C	-0.35509600	4.03340900	-1.53775500
H	0.60183200	3.94434500	-2.06045500
H	-1.16341400	4.18363100	-2.25490900
H	-0.28648100	4.88755400	-0.85725500
H	2.61148800	1.25203800	2.55450900
H	1.19676100	0.06622700	-1.00724700
H	2.57470700	1.55694100	0.82299600

C	-0.54611100	-1.25144500	0.08087100
C	-1.19828900	-2.50203100	-0.03357000
C	-2.51996700	-2.61465800	-0.40730900
H	-3.23829000	0.66871100	-0.79735200
H	-2.96054300	-3.60271100	-0.50036100
O	-0.51383600	-3.68231300	0.17226900
C	-0.39592400	-4.02266500	1.53810600
H	-1.38901600	-4.18636800	1.98121300
H	0.17773400	-4.95168900	1.58260000
H	0.14089900	-3.24780200	2.09067200
C	-4.68255500	-1.55675600	-1.13323700
H	-5.11598500	-0.57330000	-1.33012400
H	-4.76699500	-2.15816900	-2.04538800
H	-5.29066700	-2.05073900	-0.36692800
O	1.61029500	-2.07975200	0.78568500
C	-1.36601400	2.50851300	0.18498100
O	-0.89158300	3.54022800	0.67084400
O	-2.66710400	2.56932900	-0.29053300
C	-3.29175900	3.81930100	-0.10139400
H	-2.75944900	4.61683100	-0.62853100
H	-4.30339700	3.71515600	-0.50077500
H	-3.33166600	4.09195000	0.95751600
H	1.46995300	3.35403100	0.67985300
H	1.28603400	0.23221700	-1.20429200
H	1.41079000	2.68299600	-0.94825700

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C	-1.03829800	-0.57439400	1.31422500
C	0.18332100	-1.45151900	0.97851200
C	-0.10519600	1.42524100	0.18396900
C	-2.41416300	-1.25613200	1.34428300
C	-1.26173200	0.46345100	0.19344900
C	-3.40234700	-0.07516500	1.23800500
C	-2.67038200	1.03579100	0.41946400
H	0.51893000	-1.95933500	1.88907700
H	-4.34405700	-0.37912700	0.77659800
H	-2.57754400	1.94858700	1.01582700
C	-3.31915700	1.40875800	-0.89727100
C	-3.39441400	2.68179500	-1.28226700
H	-3.02052500	3.48144900	-0.65060500
H	-3.81078600	2.95897100	-2.24629700
C	-3.80918300	0.28271500	-1.77292500
H	-4.03997300	0.64077100	-2.77812100
H	-3.06017300	-0.51468700	-1.85734100
H	-4.71546700	-0.17806000	-1.36564200
C	-0.76734000	0.11453200	2.66273400
H	-1.50965200	0.88739800	2.87776000
H	-0.79992100	-0.62357800	3.47003800
H	0.21828500	0.58928900	2.68041800
H	-3.65363100	0.30098100	2.23326800
C	3.70581600	-0.60338200	-0.17764200
C	2.58443700	-1.26407600	0.31891400
C	1.35081900	-0.62433700	0.43649500
C	1.22368400	0.73093100	0.07563200
C	2.36013600	1.39727900	-0.42387700
C	3.57475500	0.73454200	-0.55092800
H	2.66446900	-2.30789900	0.61634000
H	4.41545700	1.28652400	-0.96221200
O	2.28510200	2.68783400	-0.86200800
C	2.55523600	3.65665500	0.14347800
H	3.57465600	3.53503100	0.53049600
H	2.46060600	4.63083800	-0.33626900
H	1.82849400	3.57987000	0.95559000
C	5.03212900	-1.30460000	-0.30879900
H	4.95048800	-2.36084800	-0.04560100
H	5.40946800	-1.23434600	-1.33285600
H	5.77952400	-0.84747500	0.34659600
O	-0.23240300	2.62610500	0.30183700
C	-0.12781100	-2.59631800	0.02592800
O	-0.04337800	-3.76310100	0.31784800

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C	4.76436400	0.27805400	0.09766100
C	3.87999400	0.84493500	1.01368300
C	2.51455200	0.61236800	0.90713200
C	2.00148600	-0.18099200	-0.12870200
C	2.90377100	-0.75816600	-1.03153800
C	4.27073500	-0.52906800	-0.92364600
H	5.83100300	0.45567400	0.18704700
H	4.25847600	1.46009200	1.82391300
H	1.83961700	1.02959000	1.64816200
H	2.52104800	-1.38515800	-1.83246500
H	4.95152500	-0.98210000	-1.63723400
C	0.56167100	-0.42579300	-0.29840300
H	0.29952300	-1.28378300	-0.91615800
C	-0.42404500	0.33497300	0.20207700
H	-0.14681300	1.24621600	0.73212300
C	-1.86306900	0.07170900	0.07135800
C	-2.42969400	-1.18418000	0.22251600
O	-3.71952400	-1.38078600	0.06837800
C	-2.76648400	1.18040900	-0.20072800
O	-3.99050300	1.01483900	-0.34988400
C	-2.21207400	2.57942600	-0.31154300
H	-1.80442500	2.90275100	0.65170200
H	-1.39782600	2.61634400	-1.03983300
H	-3.01551900	3.25262700	-0.60676200
C	-1.69445100	-2.43204100	0.60256300
H	-1.47781800	-3.02574800	-0.29118200
H	-0.75549600	-2.21203700	1.10841800
H	-2.34714200	-3.02837400	1.24286700
H	-4.11647900	-0.46832400	-0.15313400

O	-0.50571300	-2.17371000	-1.19372400
C	-0.81421900	-3.21545300	-2.12195600
H	-1.63800500	-3.82611000	-1.74612300
H	-1.09458700	-2.71519400	-3.04691700
H	0.05714900	-3.85430900	-2.27608300
H	-2.56829500	-1.87048900	2.23669200
H	-1.22787800	-0.07782100	-0.75917100
H	-2.52245400	-1.90533900	0.46637000

$ATS1_{22}$			
C	-0.49891600	-0.13456500	0.13776700
C	0.81003400	-0.84430600	0.14575300
C	1.35414100	-1.18816200	1.41643200
C	-1.67242600	-0.75542600	-0.02571700
C	0.92269200	-0.47491800	2.64087500
H	1.55908900	-0.74320000	3.48279700
O	2.28297500	-2.08002500	1.53484200
H	2.40162700	-2.48834000	0.60080800
C	1.17613300	-1.71303500	-0.98828100
O	2.03947900	-2.59367900	-0.85398900
H	0.97413000	0.60439600	2.42671400
C	4.23556400	1.31932600	-0.75957600
C	3.34865200	0.25157000	-0.60496900
C	2.13538200	0.64537600	-0.06526800
C	1.69893600	1.80364300	0.36259500
C	2.60802700	2.86348000	0.18907000
C	3.86536900	2.61126400	-0.36504200
H	3.61733700	-0.75550100	-0.90544300
H	4.57702400	3.42403600	-0.48602500
H	-0.12284000	-0.71257200	2.85641200
H	-1.69288200	-1.84157700	-0.13094200
C	-2.99189400	-0.10287200	-0.06186900
C	-3.14269700	1.28619600	-0.17707700
C	-4.14230900	-0.89540900	0.02159200
C	-4.40743800	1.85912600	-0.18815800
H	-2.26540500	1.91837200	-0.27178900
C	-5.40941600	-0.32182300	0.00916400
H	-4.03744000	-1.97421400	0.10337900
C	-5.54574900	1.05899100	-0.09328500
H	-4.50756400	2.93589900	-0.27924000
H	-6.28912000	-0.95353400	0.07803500
H	-6.53215900	1.51089000	-0.10631100
H	-0.42065400	0.94304100	0.30381800
H	5.21626300	1.13896800	-1.18883900
H	2.36374100	3.88030100	0.49385600
C	0.55518900	-1.47534800	-2.33472900
H	-0.45390300	-1.89504400	-2.36357500
H	0.46787300	-0.40269200	-2.52243100
H	1.16961200	-1.95825400	-3.09372600

$AI1_{22}$			
C	-0.46135200	-0.06604000	0.09594800
C	0.91431900	-0.68118100	0.11359500
C	1.36239100	-1.09048000	1.44701200
C	-1.61022700	-0.74181800	-0.00148200
C	0.92174000	-0.33531100	2.63183700
H	1.53773500	-0.57646700	3.49681800
O	2.20536300	-2.04737700	1.59646900
H	2.31676300	-2.48559900	0.67374500
C	1.18677000	-1.68507300	-0.97503600
O	1.94500300	-2.63673800	-0.77506400
H	0.97309500	0.73615000	2.35300500
C	4.18692900	1.24839000	-0.80627300
C	3.27599500	0.21250500	-0.63976600
C	2.03864700	0.54959300	-0.07496400
C	1.65343500	1.77180000	0.40346900
C	2.59900400	2.79066600	0.18132300
C	3.84137500	2.54146800	-0.40035400
H	3.54000600	-0.79038500	-0.96688300
H	4.56009000	3.34834600	-0.52558900
H	-0.13090500	-0.56075200	2.82989200
H	-1.60826100	-1.83325200	-0.04598100
C	-2.94372500	-0.11340600	-0.05152300
C	-3.11207700	1.27148800	-0.19958600
C	-4.08517600	-0.91623600	0.04827900
C	-4.38262200	1.82948500	-0.22794900
H	-2.24421400	1.91443900	-0.30359500
C	-5.35926600	-0.35710000	0.01711300
H	-3.96959000	-1.99169400	0.15681300
C	-5.51221400	1.01883600	-0.11858400
H	-4.49366900	2.90284200	-0.34315800
H	-6.23153400	-0.99761000	0.09830600
H	-6.50390800	1.45838700	-0.14511300
H	-0.41288500	1.01867900	0.21150200
H	5.15610800	1.04987700	-1.25304400
H	2.38398800	3.81172500	0.49915000
C	0.59028300	-1.46309500	-2.33216800
H	-0.42976900	-1.85689500	-2.35197700
H	0.53497300	-0.39406400	-2.54820300
H	1.19368600	-1.98775000	-3.07227800

$ATS2_{22}$			
C	-0.42938300	0.09643400	-0.02716200
C	0.91826000	-0.57054400	0.07829300
C	1.29579600	-0.87767600	1.50214200
C	-1.58357600	-0.57830300	-0.00015600
C	0.64272100	-0.28240800	2.69670600
H	1.38673700	-0.16877600	3.48557200
O	2.13507400	-1.81232000	1.73249600
H	2.29376200	-2.30876300	0.84288400
C	1.12719600	-1.74129800	-0.85736300
O	1.87876900	-2.66593700	-0.54987200
H	0.20092800	0.67659400	2.45298900
C	4.05002000	1.23772300	-1.28335900
C	3.07250800	0.26296900	-1.14816300
C	2.09251300	0.47022000	-0.16507200
C	2.04208900	1.50952700	0.77071000
C	3.10818000	2.42617600	0.60605000
C	4.05900100	2.32873600	-0.40498200
H	3.09134800	-0.60777100	-1.80169100
H	4.82994400	3.08896300	-0.51311500

$AI2_{22}$			
C	-5.67714600	-0.87154300	-0.01625200
C	-4.65053700	-1.80121700	-0.17859300
C	-3.32337400	-1.39563800	-0.13457400
C	-2.99403200	-0.04796200	0.06580300
C	-4.03426400	0.87234400	0.24026100
C	-5.36411800	0.46730100	0.19673000
H	-6.71316700	-1.19238500	-0.04757000
H	-4.88715700	-2.84932600	-0.33151800
H	-2.53464200	-2.13423800	-0.23896500
H	-3.79191900	1.91831700	0.40831900
H	-6.15529800	1.19773600	0.33151000
C	-1.60426500	0.43370400	0.09976200
H	-1.47100000	1.44906200	0.48062400
C	-0.51304400	-0.23344500	-0.29253700
H	-0.59091800	-1.24540100	-0.68682100
C	0.86333900	0.35272600	-0.17757800
C	1.51431900	0.48439400	1.31006700
O	1.66975000	1.75231400	1.85021500
C	1.05468000	1.61615700	-1.02932000

H	-0.11192000	-1.00828700	3.03360400
H	-1.55658700	-1.66630100	0.10256300
C	-2.93599500	-0.00400700	-0.08022400
C	-3.16447700	1.35011000	-0.36194200
C	-4.03955400	-0.83768200	0.13318800
C	-4.45812400	1.85077800	-0.41381300
H	-2.32568300	2.01275900	-0.54904700
C	-5.33610300	-0.33666800	0.08069900
H	-3.87512700	-1.89057900	0.34765500
C	-5.54923700	1.01082600	-0.19162800
H	-4.61810700	2.90141000	-0.63320100
H	-6.17845100	-0.99898900	0.25194300
H	-6.55873500	1.40610400	-0.23515200
H	-0.37847300	1.18178900	-0.04973700
H	4.80439900	1.14738200	-2.05895300
H	3.19918900	3.26581900	1.29767400
C	0.52098500	-1.68275200	-2.22799300
H	-0.52383600	-2.00160700	-2.18798000
H	0.53256800	-0.65285900	-2.59303700
H	1.08037900	-2.34379400	-2.88954700

AI3$_{22}$

C	5.41450200	-0.34084900	-0.45496800
C	4.79490800	0.87926200	-0.18282000
C	3.41247000	0.98785100	-0.13655900
C	2.57188800	-0.12683500	-0.36120400
C	3.22453100	-1.35041400	-0.63303800
C	4.60704200	-1.45553000	-0.67937600
H	6.49661400	-0.41983000	-0.48966500
H	5.40107300	1.76440800	-0.00403200
H	2.97259900	1.95769000	0.07561700
H	2.61118000	-2.23160100	-0.80361200
H	5.06084200	-2.42075200	-0.89114600
C	1.12324200	-0.08747100	-0.33203800
H	0.62994900	-1.03083900	-0.55483600
C	0.36600000	1.02377700	-0.06828500
H	0.92977300	1.93200600	0.13868100
C	-1.04318100	1.19720500	-0.04004900
C	-1.01764400	-1.51080700	1.47503800
O	-0.62094700	-2.64887800	1.66120700
C	-1.61308900	2.50489400	0.14428600
O	-2.82787300	2.75275900	0.11121900
C	-0.67849200	3.69325500	0.42350400
H	-0.05322800	3.52618200	1.30625600
H	-0.01065200	3.89240300	-0.42054500
H	-1.31238500	4.56429600	0.59158200
C	-0.74528200	-0.45095800	2.52449300
H	0.26396100	-0.06284900	2.36370800
H	-1.44664200	0.38149900	2.47036500
H	-0.78030400	-0.94240000	3.49945000
C	-3.62824300	-2.07290700	-1.14470500
C	-2.67411900	-2.25541700	-0.15914100
C	-1.87121100	-1.19247300	0.28256000
C	-1.96310000	0.07988100	-0.32594100
C	-2.96249000	0.24289400	-1.30804500
C	-3.78030200	-0.80111800	-1.70521500
H	-4.25466100	-2.89975300	-1.46662900
H	-2.53686400	-3.22014700	0.31943400
H	-3.07195000	1.22405300	-1.75425100
H	-4.53332400	-0.63085000	-2.47077900

AI4$_{22}$

C	5.04626200	0.13388800	-0.08759200
C	4.26422700	1.17837700	0.39322900
C	2.87728300	1.13830200	0.25352100
C	2.24462300	0.06765500	-0.38630100
C	3.04313000	-0.99636200	-0.83688800
C	4.42421400	-0.95917400	-0.69196500
H	6.12726600	0.16328300	0.01851200
H	4.73072100	2.02687700	0.88721400
H	2.28462200	1.94866100	0.67016100
H	2.53216800	-1.86097600	-1.24602000

O	1.80062400	2.51526800	-0.69532700
C	0.35075800	1.65756600	-2.36602000
H	0.39391700	0.67869100	-2.85255800
H	-0.70649600	1.89318400	-2.22048600
H	0.81635100	2.42009800	-2.98940400
C	0.77811100	-0.34675000	2.34804200
H	-0.17743600	0.12488300	2.58917500
H	0.59472600	-1.36241100	1.99156600
H	1.39017500	-0.38781300	3.25258300
H	2.04430300	2.31183500	1.15156900
C	4.55974400	-1.54774300	0.01630200
C	3.97623200	-0.74898800	1.00655400
C	2.71232400	-0.25994400	0.72115200
C	2.07107300	-0.53087900	-0.47822500
C	2.62518400	-1.33196600	-1.46299100
C	3.89849000	-1.84063700	-1.18173000
H	5.55032100	-1.96079400	0.17979700
H	4.49422500	-0.53833200	1.93647300
H	2.12710100	-1.55622800	-2.40169800
H	4.39308600	-2.47242600	-1.91282400

ATS3$_{22}$

C	5.05926100	0.06935100	-0.17535900
C	4.31661600	1.14009000	0.31571800
C	2.93030101	1.15256500	0.19420800
C	2.24457200	0.10895400	-0.44857500
C	3.00718800	-0.98136200	-0.90577300
C	4.38953800	-0.99719700	-0.77483500
H	6.14114700	0.05858200	-0.07860100
H	4.81852200	1.96985100	0.80732300
H	2.37338600	1.98321700	0.61987200
H	2.47653200	-1.82689300	-1.33056400
H	4.95181200	-1.85395200	-1.13738700
C	0.78112600	0.03491500	-0.55827700
H	0.44904000	-0.57827100	-1.39719800
C	-0.01714400	1.22284800	-0.36819300
H	0.49638400	2.17591200	-0.24618200
C	-1.37563500	1.19731000	-0.22969700
C	0.16822600	-1.23729100	0.66053300
O	0.80850300	-2.32419200	0.50043000
C	-2.11666900	2.44651000	-0.00687200
O	-3.32893600	2.49813300	0.16595700
C	-1.34171800	3.76628000	0.01537000
H	-0.59469100	3.77425000	0.81450800
H	-0.81904200	3.94133100	-0.92855700
H	-2.06379200	4.56426600	0.18730700
C	0.34855200	-0.56265300	2.03279100
H	1.42082800	-0.44404300	2.21592000
H	-0.15460700	0.40509900	2.12322700
H	-0.05556000	-1.24390300	2.78977000
C	-3.25855700	-2.66440900	-0.17554100
C	-1.92772000	-2.50669300	0.20958000
C	-1.31731100	-1.25801200	0.20427600
C	-2.05541200	-0.12564800	-0.20731300
C	-3.39030500	-0.29326900	-0.59439300
C	-3.98977900	-1.55174800	-0.57311000
H	-3.71519400	-3.65126200	-0.17679500
H	-1.30368300	-3.34759900	0.49752400
H	-3.96059500	0.57467900	-0.89980300
H	-5.02780500	-1.65604200	-0.87869200

AI5$_{22}$

C	5.02397200	0.21043900	0.03098000
C	4.16848400	1.04344100	0.74746200
C	2.79250800	0.96790900	0.55213400
C	2.24804800	0.06325800	-0.36517900
C	3.11780800	-0.77040700	-1.07604900
C	4.49463600	-0.69885500	-0.88047300
H	6.09679700	0.27111800	0.18141000
H	4.57275200	1.75286100	1.46244800
H	2.13146500	1.61278400	1.12610200
H	2.70386800	-1.47553500	-1.79221000

H	5.02343600	-1.79392900	-1.04626000
C	0.76105500	-0.06052900	-0.52973800
H	0.52792900	-0.50824800	-1.50619600
C	-0.01950900	1.19026600	-0.37625200
H	0.51586400	2.13713500	-0.39156900
C	-1.36088400	1.20069400	-0.19609800
C	0.19627600	-1.25340600	0.45733000
O	0.78700800	-2.39748600	0.22580100
C	-2.05634400	2.49841000	-0.00517500
O	-3.24841600	2.59015900	0.24037600
C	-1.24682000	3.79064800	-0.10553600
H	-0.46570800	3.82639300	0.65884200
H	-0.76167600	3.88327700	-1.08050300
H	-1.93750000	4.62036700	0.04235400
C	0.37112200	-0.77389700	1.92591700
H	1.44355000	-0.72468800	2.14031200
H	-0.09285000	0.19465600	2.15296400
H	-0.07015900	-1.53865700	2.57238300
C	-3.31327000	-2.61711700	-0.15131700
C	-1.95210100	-2.49874700	0.11549900
C	-1.32945900	-1.25559500	0.12993800
C	-2.08457900	-0.09824400	-0.14716600
C	-3.45351900	-0.22330400	-0.42206300
C	-4.06411900	-1.47494200	-0.41643700
H	-3.78661900	-3.59641600	-0.16697000
H	-1.30027200	-3.34989400	0.29286600
H	-4.03831700	0.66254100	-0.63291900
H	-5.12673000	-1.55330300	-0.63203300

H	5.15379000	-1.34950700	-1.44622100
C	0.75503300	-0.07960100	-0.55465700
H	0.57540500	-0.45959200	-1.57278000
C	-0.01440900	1.20243000	-0.40864200
H	0.53833000	2.13255600	-0.50213800
C	-1.34292900	1.21070800	-0.20084900
C	0.15347600	-1.17296600	0.37197400
O	0.72858100	-2.42510000	0.04445100
C	-2.05010300	2.52127500	-0.00947900
O	-3.18768700	2.57536700	0.41072100
C	-1.30321100	3.80550300	-0.32709000
H	-0.47221700	3.95320200	0.36872000
H	-0.89393300	3.78902000	-1.34012600
H	-2.00427200	4.63203400	-0.22194900
C	0.36912200	-0.88024000	1.86030900
H	1.43701300	-0.84476600	2.10025500
H	-0.08324500	0.07220600	2.14854400
H	-0.09734000	-1.67819600	2.44217400
C	-3.35120800	-2.57724900	-0.11075500
C	-1.97876800	-2.49350400	0.10702600
C	-1.33796100	-1.25947000	0.08809100
C	-2.07537000	-0.07991100	-0.13530600
C	-3.45426400	-0.17990100	-0.35530000
C	-4.08507700	-1.41970700	-0.34305000
H	-3.84220000	-3.54521400	-0.10335000
H	-1.38572900	-3.38450900	0.27824900
H	-4.03291600	0.71667100	-0.52964300
H	-5.15457100	-1.47634700	-0.51784000
H	1.65112900	-2.39984600	0.33010000

ATS4$_{22}$

C	4.94786500	0.32089200	0.77917800
C	3.92932300	0.75264600	1.62373700
C	2.59907900	0.64303600	1.22738200
C	2.25810300	0.10884300	-0.02105500
C	3.29778300	-0.30565300	-0.86348900
C	4.62790700	-0.21058000	-0.46798300
H	5.98510400	0.40324500	1.08708600
H	4.16945000	1.17149700	2.59591100
H	1.80285900	0.97039100	1.89059200
H	3.05775900	-0.69242200	-1.85189500
H	5.41575800	-0.53677600	-1.13954100
C	0.81917600	0.02158200	-0.42691100
H	0.61712000	-0.35586600	-1.81554600
C	0.01845800	1.19698100	-0.29350400
H	0.56616300	2.13267000	-0.35978000
C	-1.34319300	1.22214600	-0.15517700
C	0.09236900	-1.29166900	-0.43333100
O	-0.02973800	-1.32398600	-2.10398600
C	-2.03458300	2.53343800	-0.20778200
O	-3.24525400	2.66218500	-0.12486000
C	-1.19653200	3.79525300	-0.39291700
H	-0.47372200	3.91984200	0.41806100
H	-0.64440200	3.77560400	-1.33611600
H	-1.88382900	4.63979800	-0.39546600
C	0.91413200	-2.51534900	-0.08570600
H	1.91875100	-2.44123200	-0.50342700
H	1.01241900	-2.57917100	1.00103900
H	0.44751300	-3.43325200	-0.44663800
C	-3.26869000	-2.48947400	0.81866700
C	-1.94595000	-2.46325600	0.41807700
C	-1.31852800	-1.26537500	0.04221300
C	-2.03731800	-0.04406600	0.10075200
C	-3.39149900	-0.09988600	0.49600500
C	-3.99177100	-1.29605400	0.84446200
H	-3.73557300	-3.42799200	1.09824000
H	-1.39463200	-3.39586300	0.39009700
H	-3.95671500	0.81904700	0.53075900
H	-5.03384200	-1.29835300	1.14886800
H	0.47296500	-2.05749000	-2.49718300

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C	-5.16372300	0.05518300	-0.05185000
C	-4.49884400	-0.57247200	-1.10260500
C	-3.10876300	-0.61011200	-1.12676700
C	-2.36107100	-0.02385700	-0.09944600
C	-3.03959700	0.61086900	0.94601000
C	-4.43044900	0.64750000	0.97236300
H	-6.24823300	0.08385900	-0.03296800
H	-5.06387900	-1.02832200	-1.90923800
H	-2.58971600	-1.08643600	-1.95376700
H	-2.46816200	1.06506700	1.75102500
H	-4.94126300	1.13598500	1.79587100
C	-0.87216500	-0.01689600	-0.13871200
C	-0.23148600	1.24440500	-0.04290800
H	-0.87606100	2.11112600	0.05832300
C	1.13341400	1.40613700	-0.07350100
C	-0.10487400	-1.16135100	-0.26585000
O	1.24969200	-2.69182500	2.40653000
C	1.68407100	2.79416200	0.08874800
O	2.85357800	3.01147200	0.33713700
C	0.73012900	3.96992000	-0.04789200
H	0.14689300	3.91146900	-0.96986600
H	0.02968100	4.00071200	0.79187200
H	1.32767200	4.88013700	-0.04048700
C	-0.71290400	-2.54137500	-0.25950100
H	-1.77906500	-2.50441500	-0.04299900
H	-0.57884300	-3.04346000	-1.22379900
H	-0.22597600	-3.14594700	0.51185200
C	3.49908000	-2.09842100	-0.61467600
C	2.13243900	-2.18742200	-0.54109100
C	1.32380000	-1.03087300	-0.35327100
C	1.96208500	0.24219300	-0.24438400
C	3.38185100	0.29899100	-0.33002200
C	4.12656400	-0.83963100	-0.50763100
H	4.09492600	-2.99327900	-0.76327700
H	1.65586400	-3.15648400	-0.62993200
H	3.86968900	1.25799500	-0.24177200
H	5.20763700	-0.76889600	-0.56903800
H	0.84326500	-1.81908200	2.36122800
H	2.07207300	-2.57889600	1.91554700

ATS4$_{42}$

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C	-4.85932900	-0.84791300	-0.23396100	C	-4.65229700	-1.01470600	-0.62400100
C	-3.91048400	-0.94724800	-1.25010200	C	-3.59396600	-0.80585300	-1.50832900
C	-2.55449900	-0.89716000	-0.95051300	C	-2.32678800	-0.51006800	-1.02139000
C	-2.11689400	-0.76482500	0.37504600	C	-2.09941900	-0.42073400	0.35535700
C	-3.08156900	-0.64357000	1.38269600	C	-3.16088500	-0.63047700	1.23259200
C	-4.43910000	-0.68982000	1.08385400	C	-4.43425000	-0.92512500	0.74627300
H	-5.91775500	-0.88018900	-0.47031600	H	-5.64250600	-1.24333600	-1.00440900
H	-4.22928500	-1.04711900	-2.28280500	H	-3.75936600	-0.87125600	-2.57897200
H	-1.82499900	-0.92534600	-1.75501900	H	-1.50015000	-0.33394900	-1.70565600
H	-2.75751500	-0.51937300	2.41254100	H	-2.99212600	-0.55956800	2.30414400
H	-5.16971600	-0.60047300	1.88142200	H	-5.25357300	-1.08304600	1.44030900
C	-0.68615800	-0.69409500	0.72505100	C	-0.69863800	-0.11919900	0.86508500
H	-0.48137000	-0.26862500	1.69877300	H	-0.74983300	-0.09881500	1.96556100
C	0.28652500	-1.31599900	-0.00431500	C	0.22359200	-1.24778500	0.49117400
H	-0.06563000	-1.83827700	-0.88930100	H	-0.21264400	-2.24176000	0.55760700
C	1.71290700	-1.23693200	0.12184400	C	1.49574600	-1.09159800	0.11059700
C	2.39526800	-0.70584900	1.23271200	C	2.17212300	0.27420100	0.08670000
O	3.68976400	-0.56173700	1.22159600	O	3.02644400	0.40650800	-1.03389600
C	2.53473900	-1.62038900	-1.02302800	C	2.34646700	-2.28463900	-0.17826000
O	3.76800200	-1.45568300	-1.02553300	O	3.54983600	-2.16662100	-0.34925200
C	1.91417100	-2.22840700	-2.25858200	C	1.71270200	-3.65861000	-0.24348600
H	1.24407000	-1.51028100	-2.73992500	H	1.32124700	-3.94890000	0.73557300
H	2.71790400	-2.49048700	-2.94466800	H	0.88292900	-3.67475700	-0.95425800
H	1.33253500	-3.12083800	-2.01371700	H	2.47845500	-4.36990800	-0.54892000
C	1.78108300	-0.41799200	2.56944400	C	2.97969500	0.44992200	1.38643000
H	2.58206100	-0.37958900	3.30770000	H	3.48880200	1.41673900	1.35996900
H	1.26848700	0.54590100	2.55291900	H	2.32229600	0.42143600	2.26011200
H	1.06376300	-1.19757700	2.83693900	H	3.72513000	-0.34527900	1.47598700
H	4.00051200	-0.85959000	0.28656500	H	3.68415200	-0.29957000	-0.95273700
C	1.25330600	1.72540300	0.10483700	C	1.14697800	1.39276400	-0.01389500
C	1.72745200	2.99041200	-0.24252800	C	1.57890100	2.64178700	-0.47174800
C	0.01416100	1.46594500	0.02772000	C	-0.18059400	1.22765600	0.38379000
C	0.73845700	3.88173100	-0.68423100	C	0.70905700	3.72150600	-0.51563600
H	2.76913400	3.29441100	-0.19059700	H	2.60607800	2.74014700	-0.80567600
C	-1.05635100	2.23939800	-0.36490200	C	-1.05157000	2.32184200	0.33591100
C	-0.61608600	3.51860700	-0.74309200	C	-0.61308800	3.56289100	-0.10206600
H	1.02514900	4.88441100	-0.98964500	H	1.05778200	4.68436900	-0.87501900
H	-2.09865400	1.93934500	-0.38956500	H	-2.08752500	2.18483600	0.63333200
H	-1.34641500	4.24527500	-1.08749300	H	-1.30198200	4.40087400	-0.13236200

VII. References:

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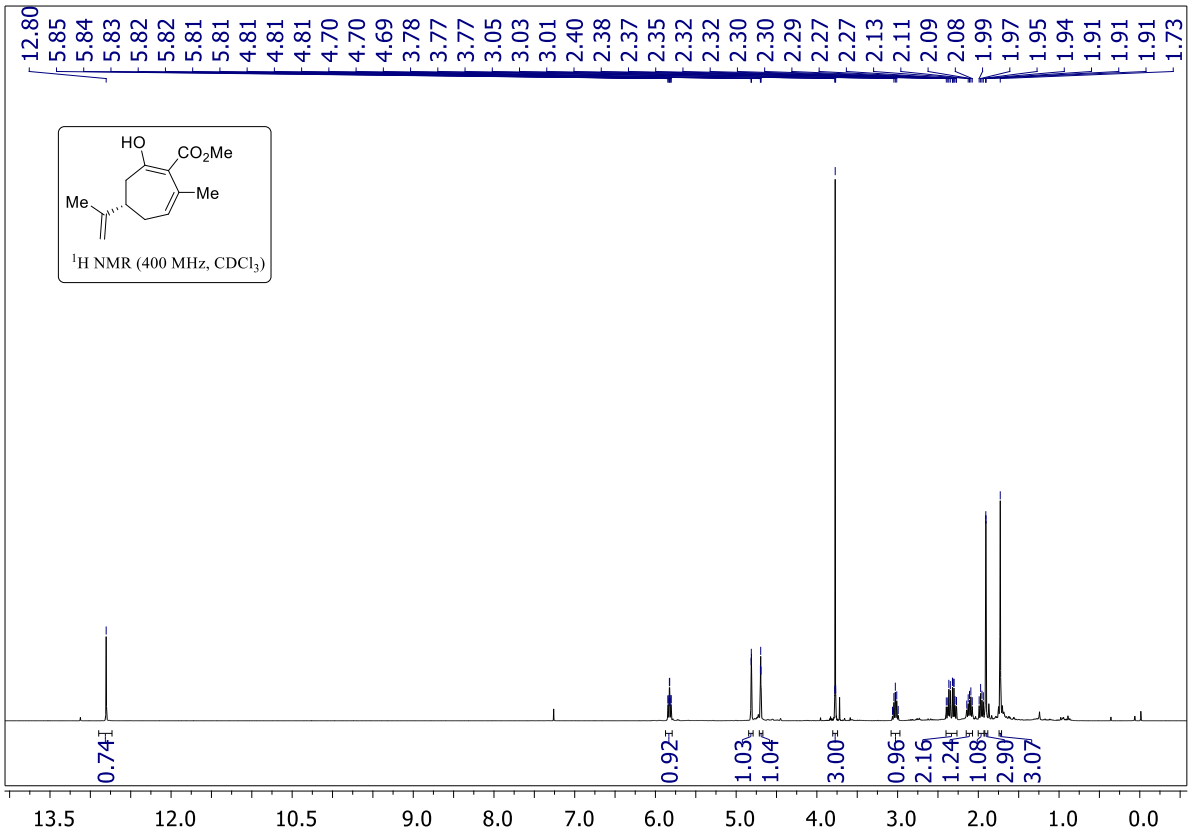
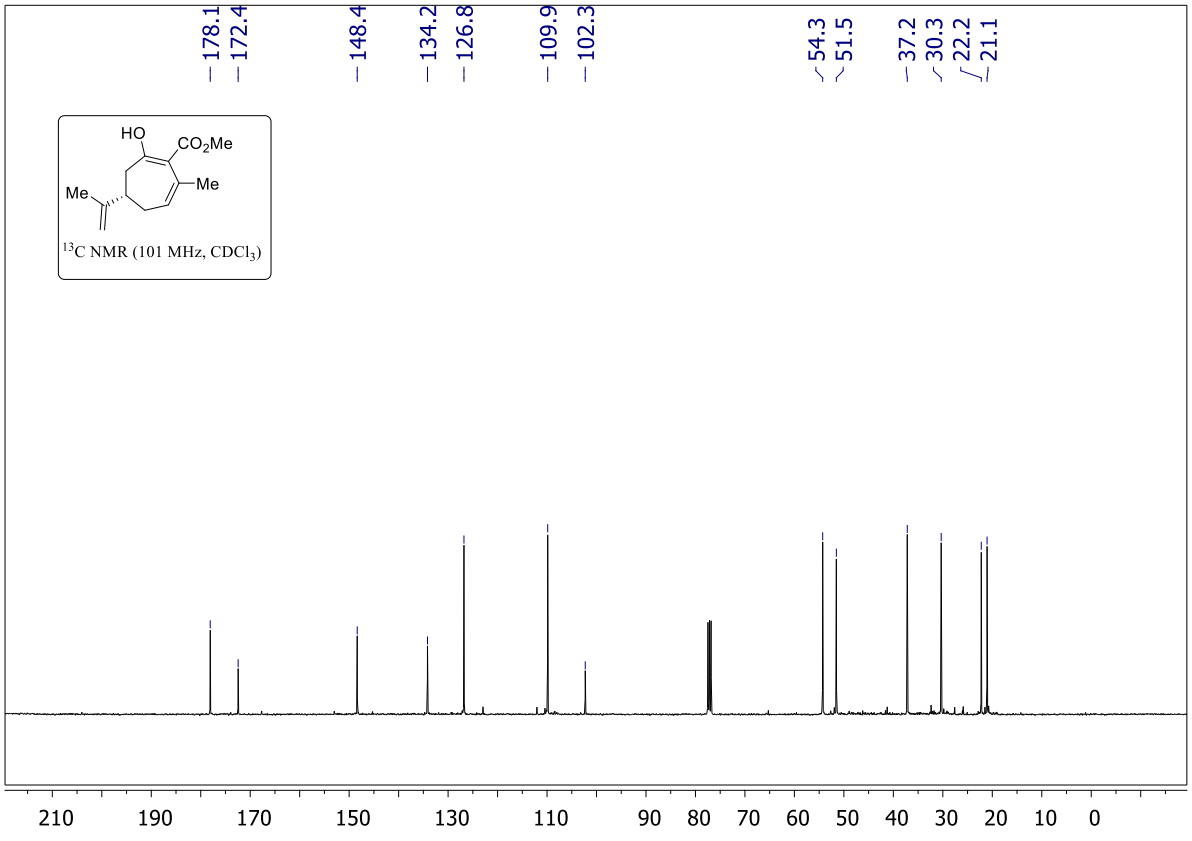
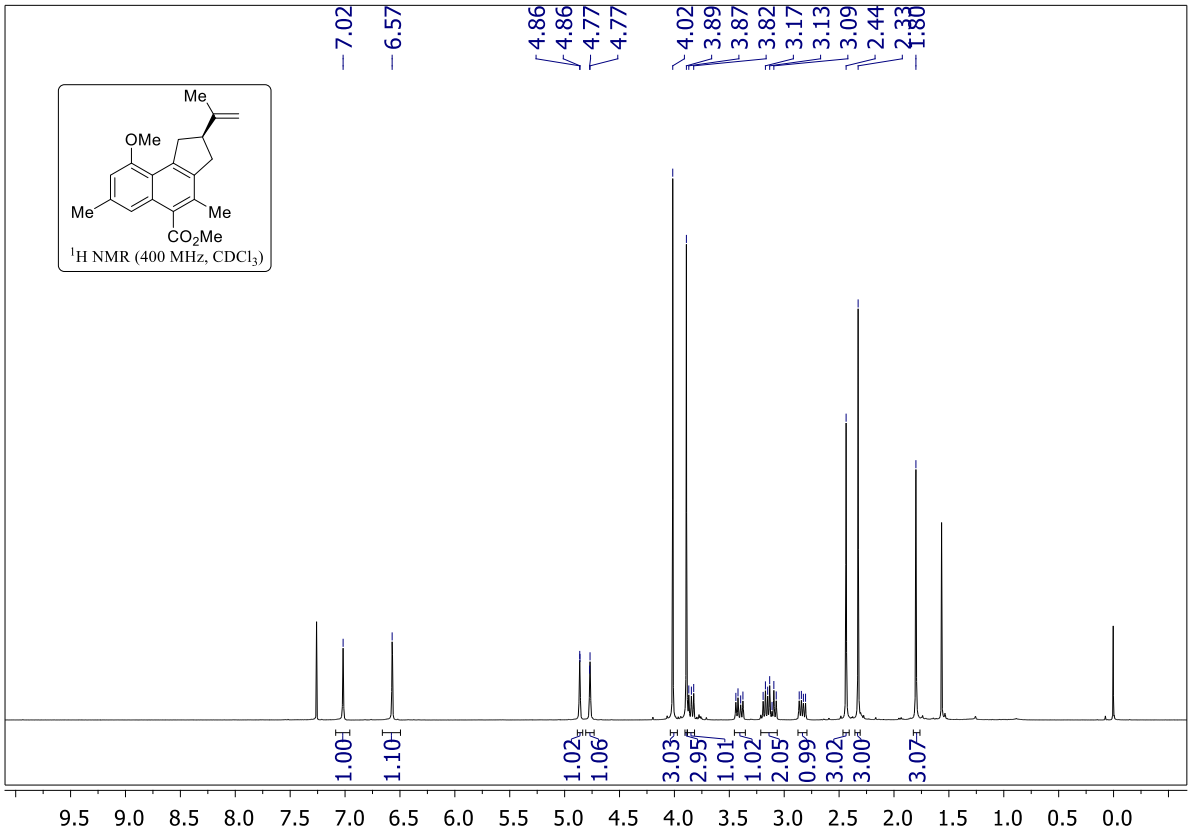
VIII. ^{1}H NMR & ^{13}C NMR Spectra:

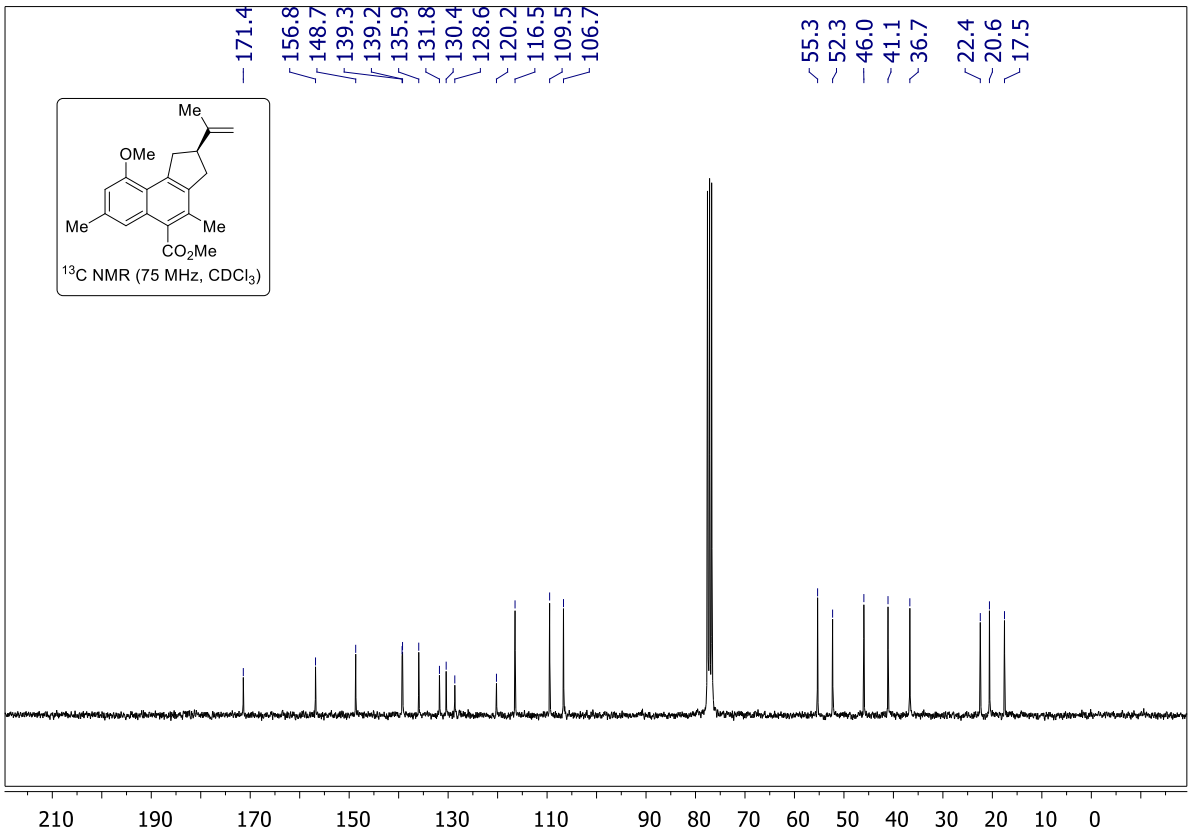
Methyl (*S*)-2-hydroxy-7-methyl-4-(prop-1-en-2-yl)cyclohepta-1,6-diene-1-carboxylate (7a):



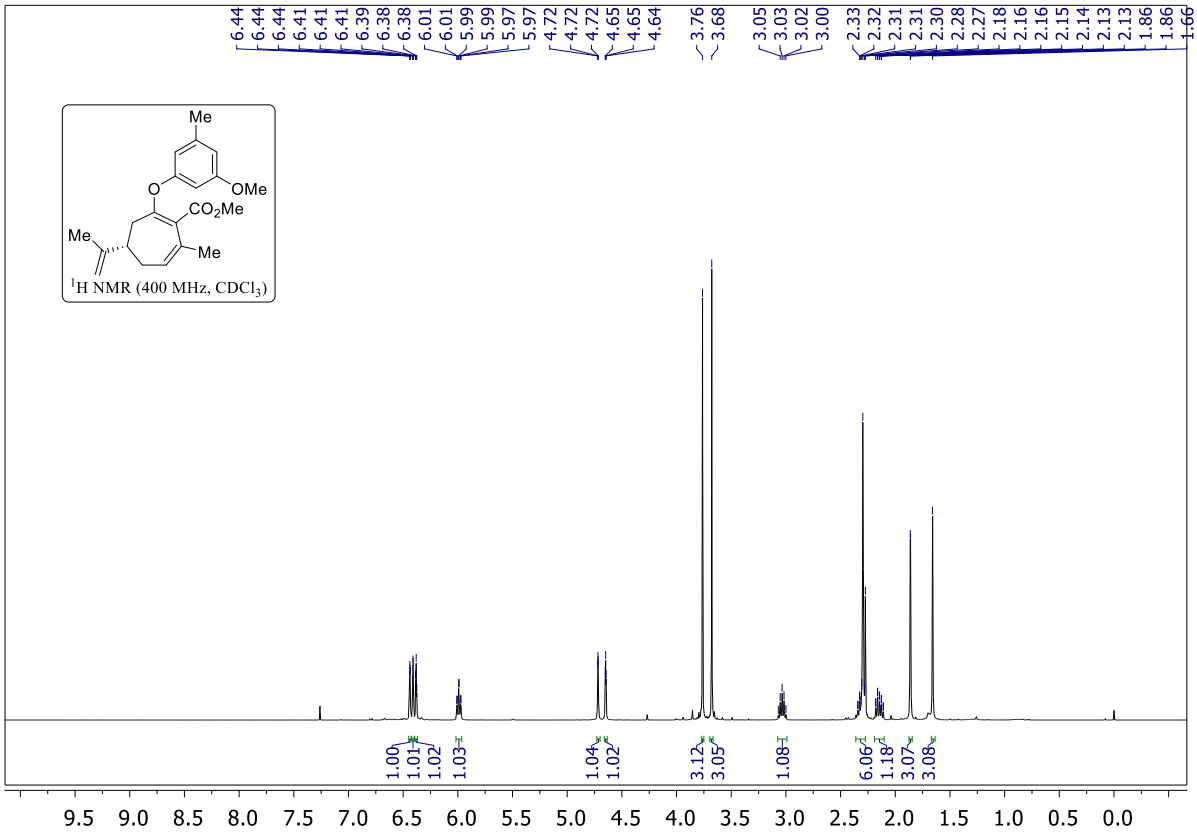


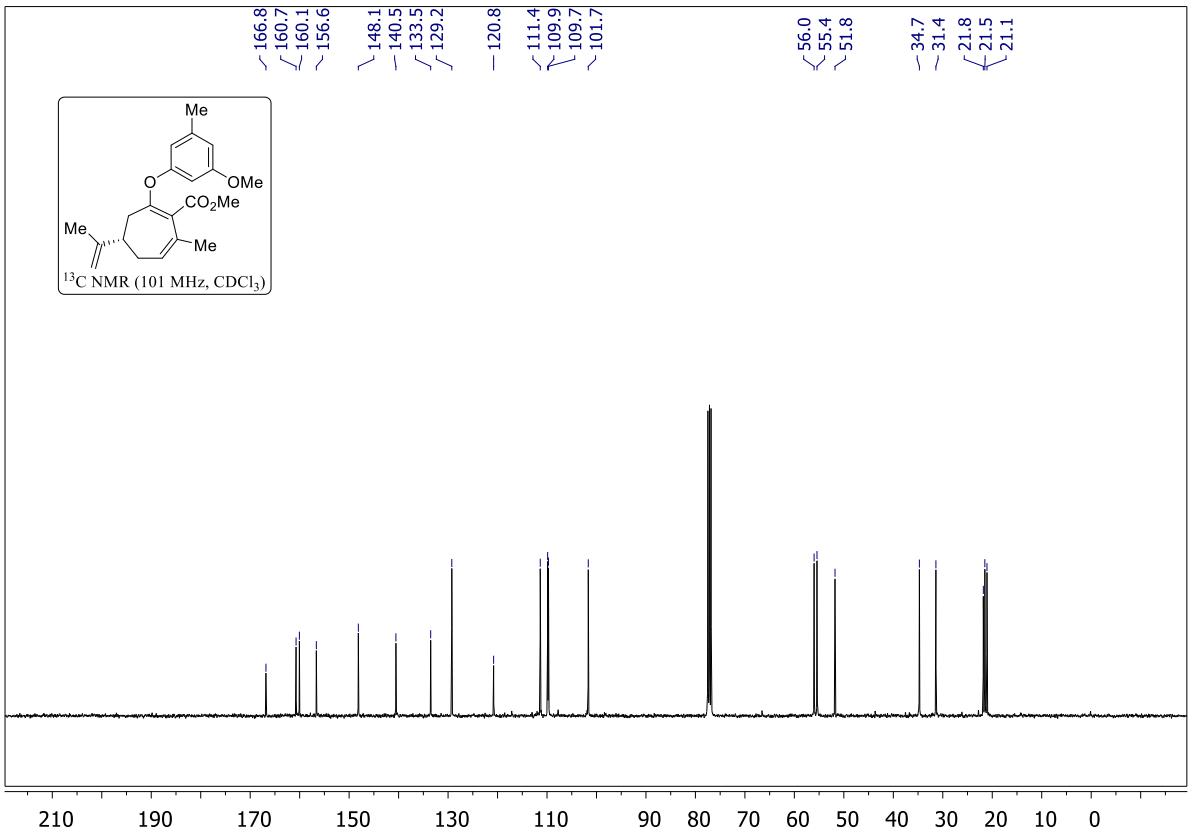
Methyl (*S*)-9-methoxy-4,7-dimethyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8a):



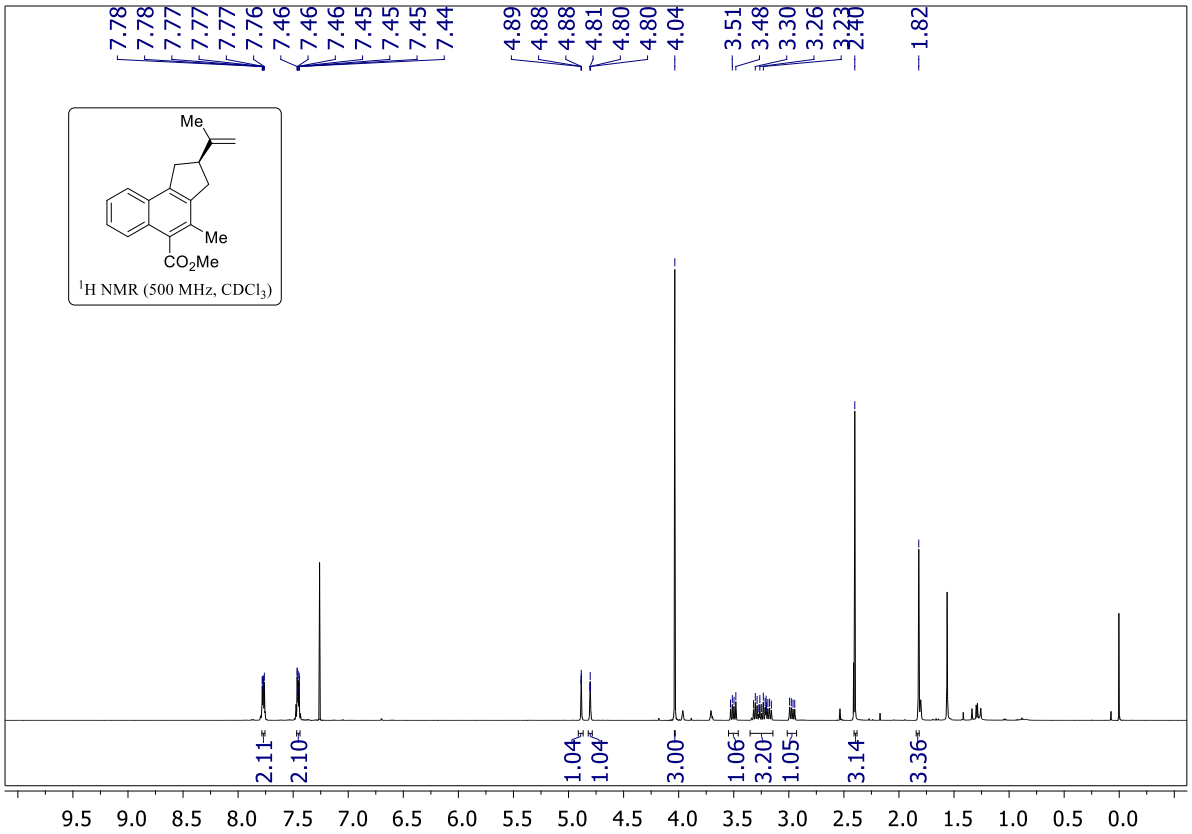


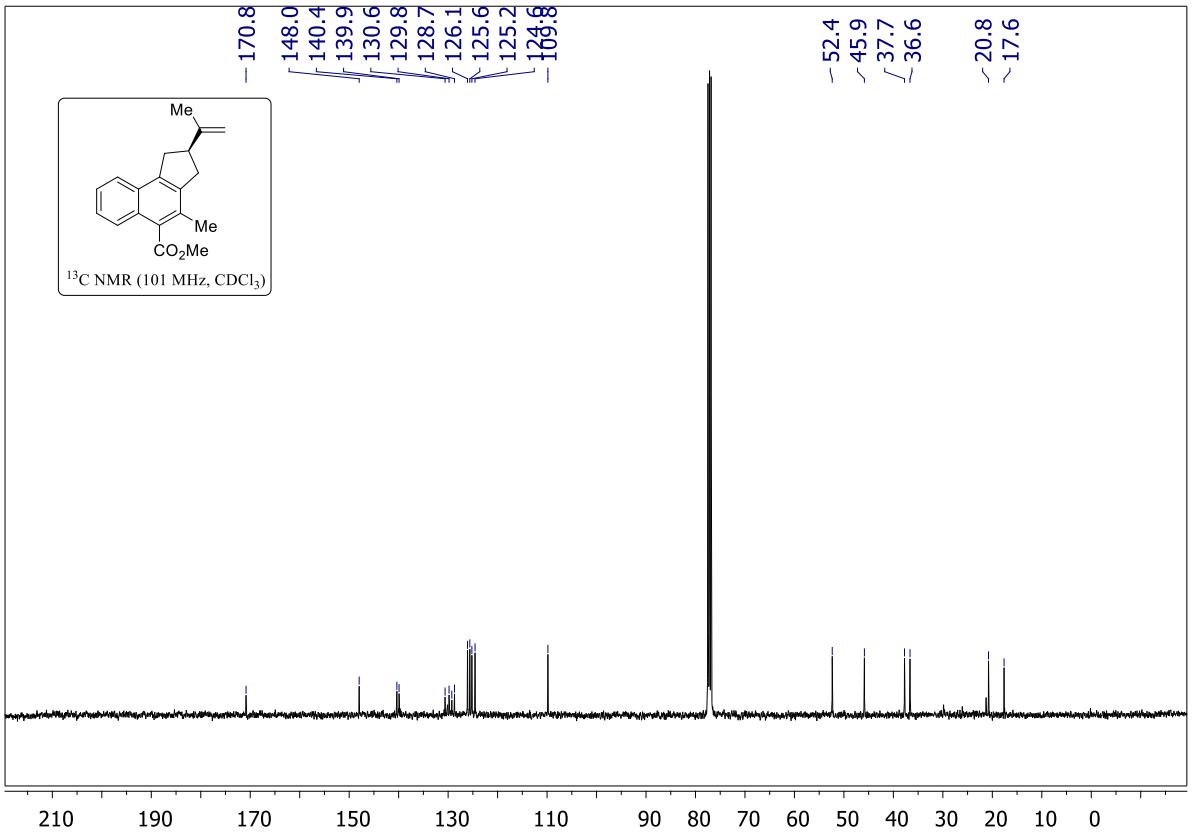
Methyl (*S*)-2-(3-methoxy-5-methylphenoxy)-7-methyl-4-(prop-1-en-2-yl)cyclohepta-1,6-diene-1-carboxylate (9):



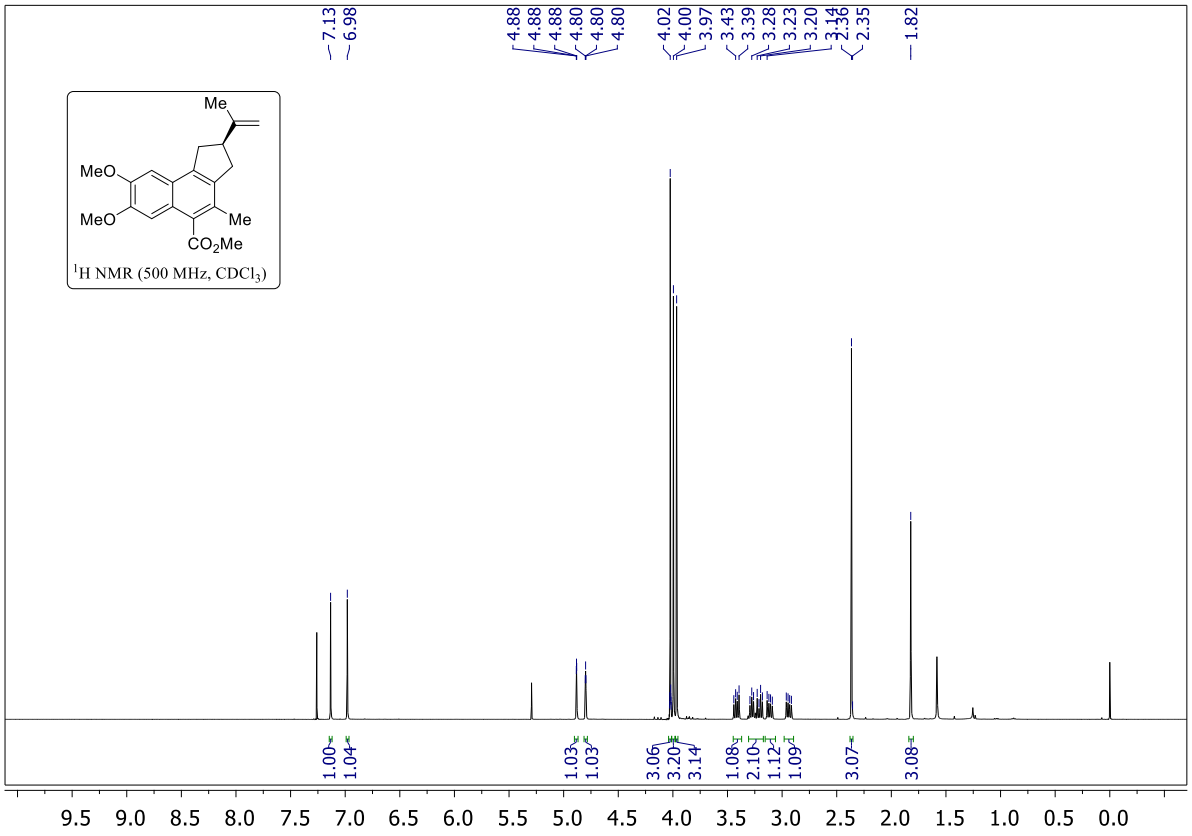


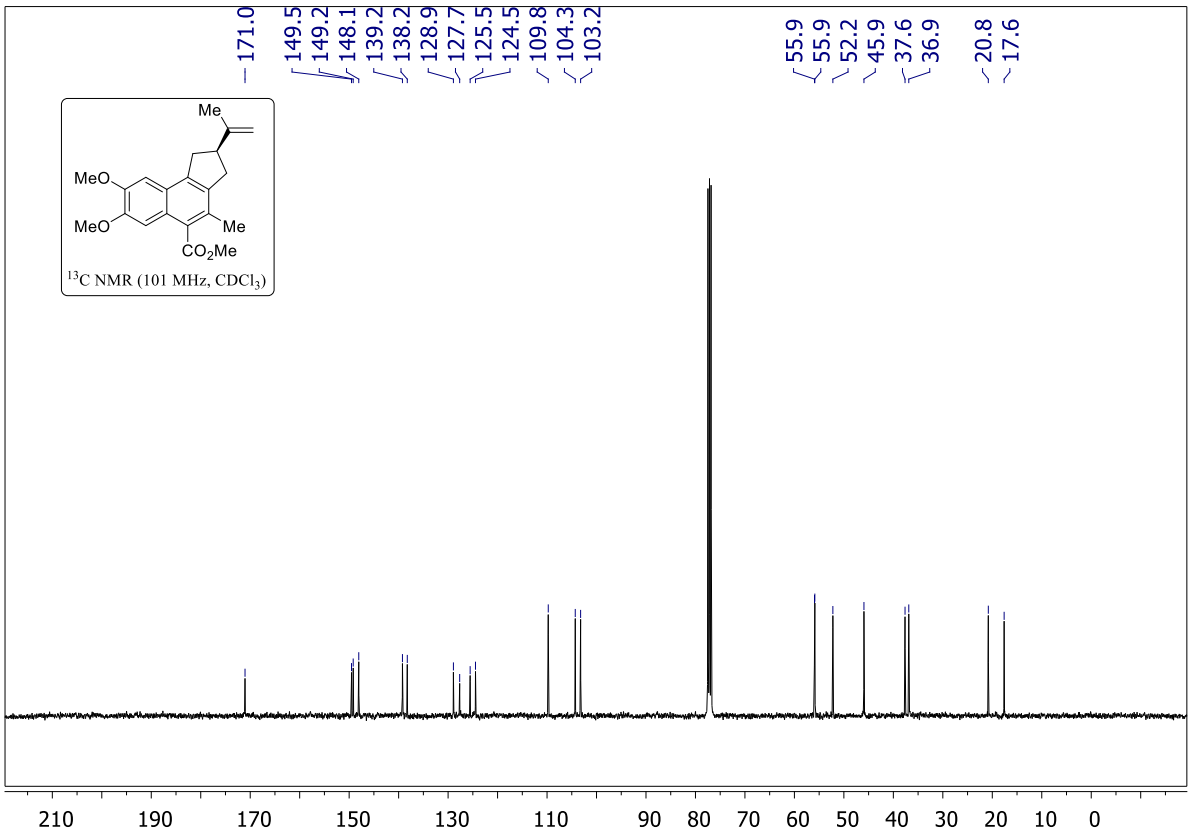
Methyl (*S*)-4-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8b):



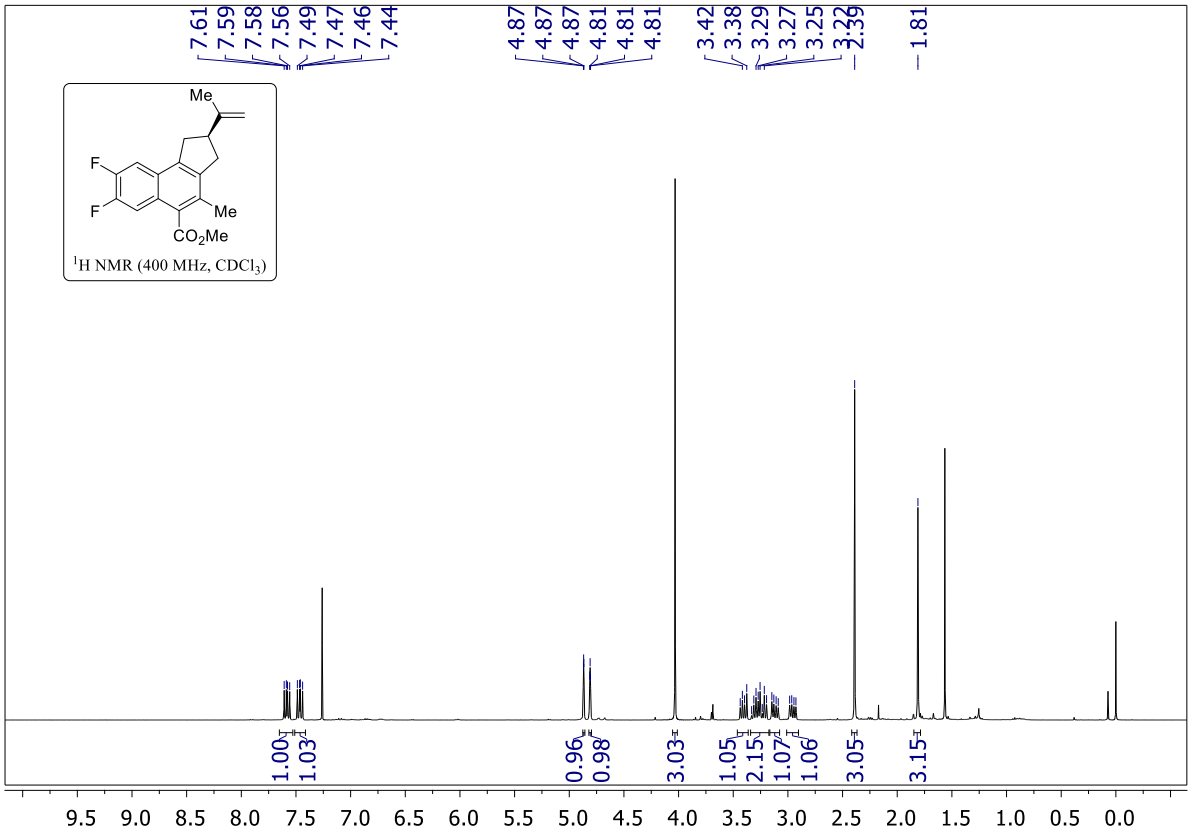


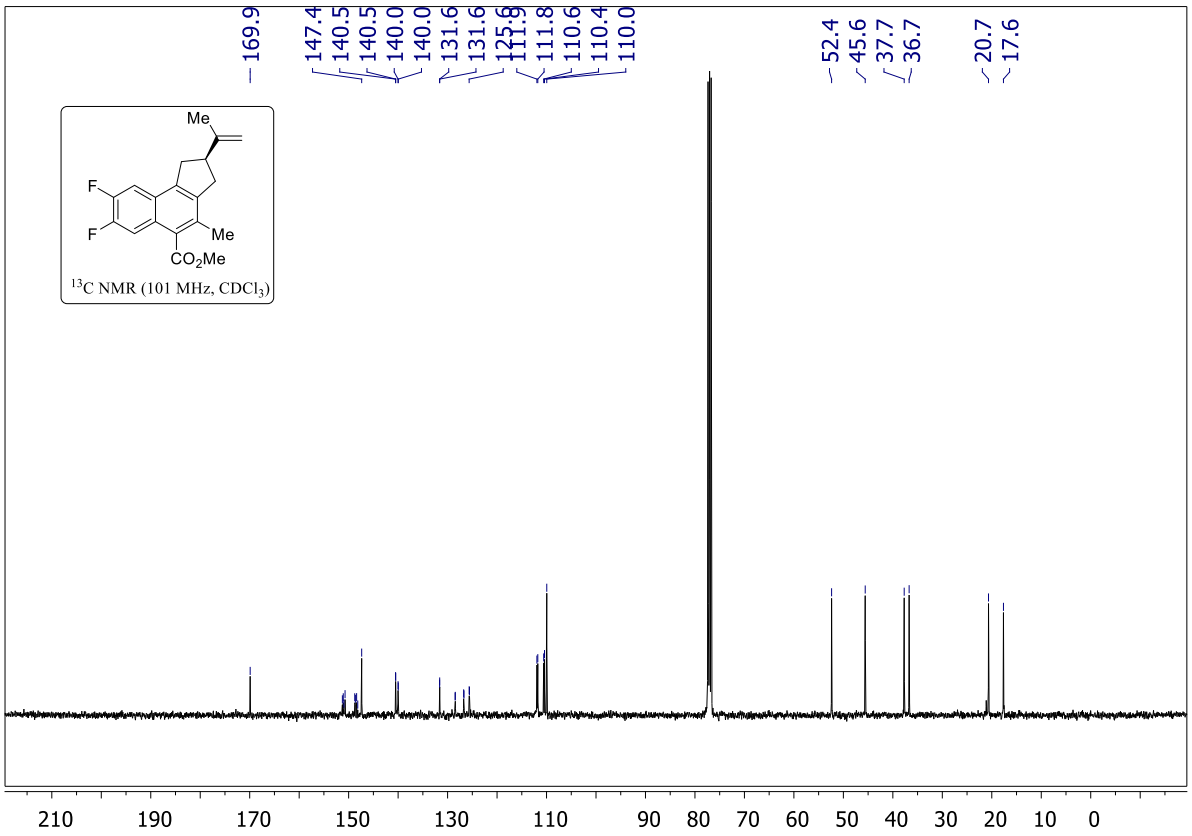
Methyl (*S*)-7,8-dimethoxy-4-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8c):

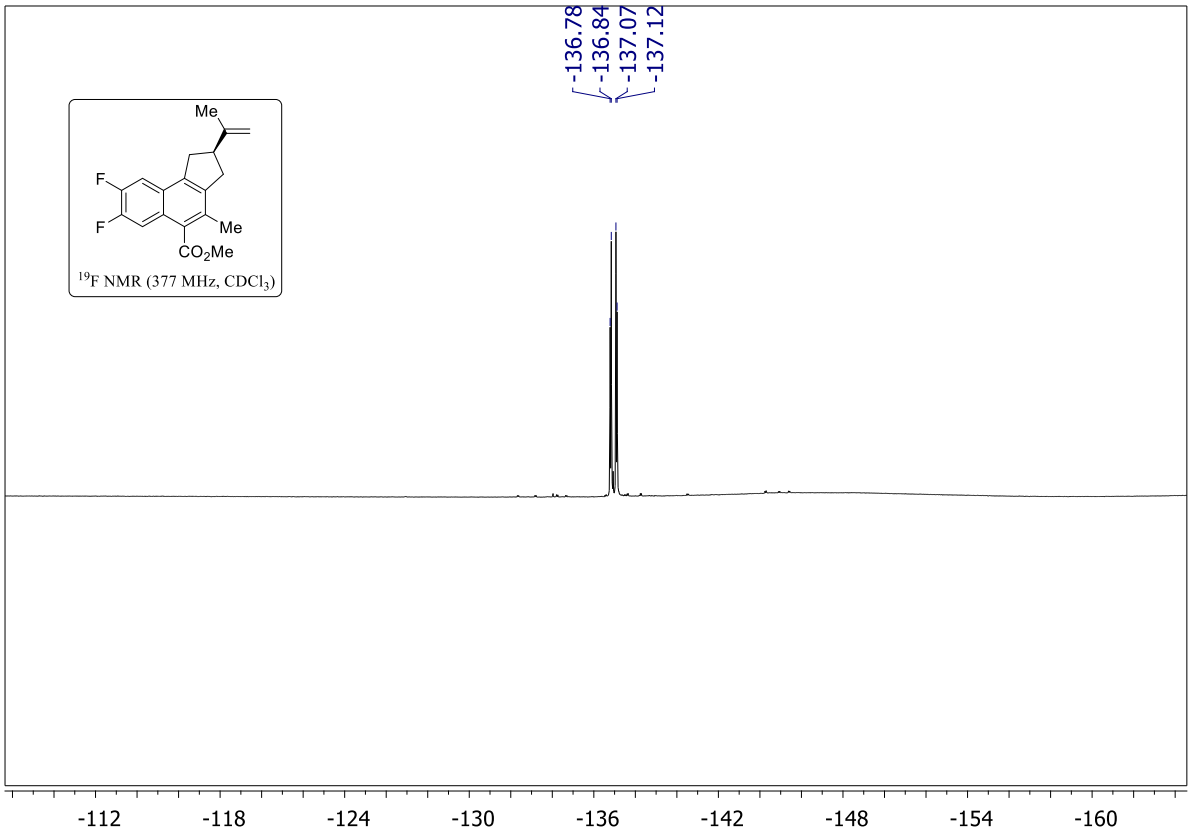




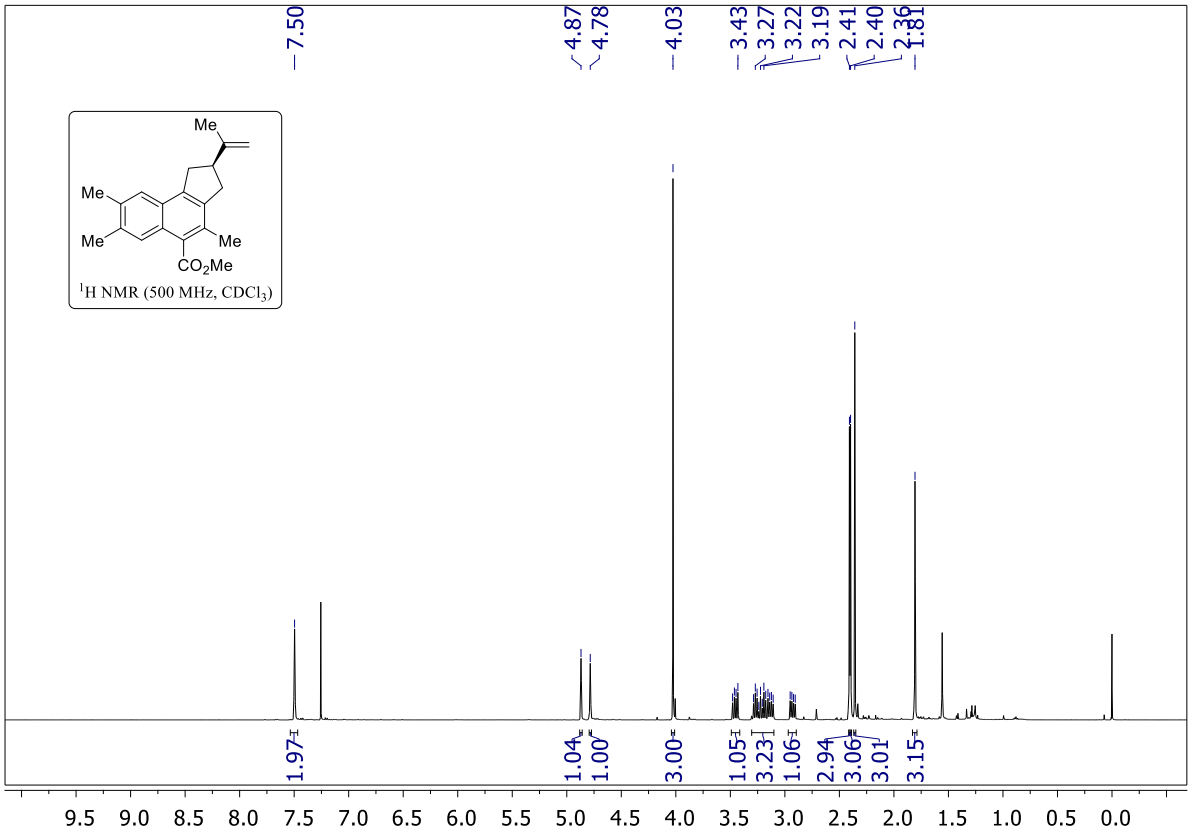
Methyl (*S*)-7,8-difluoro-4-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8d):

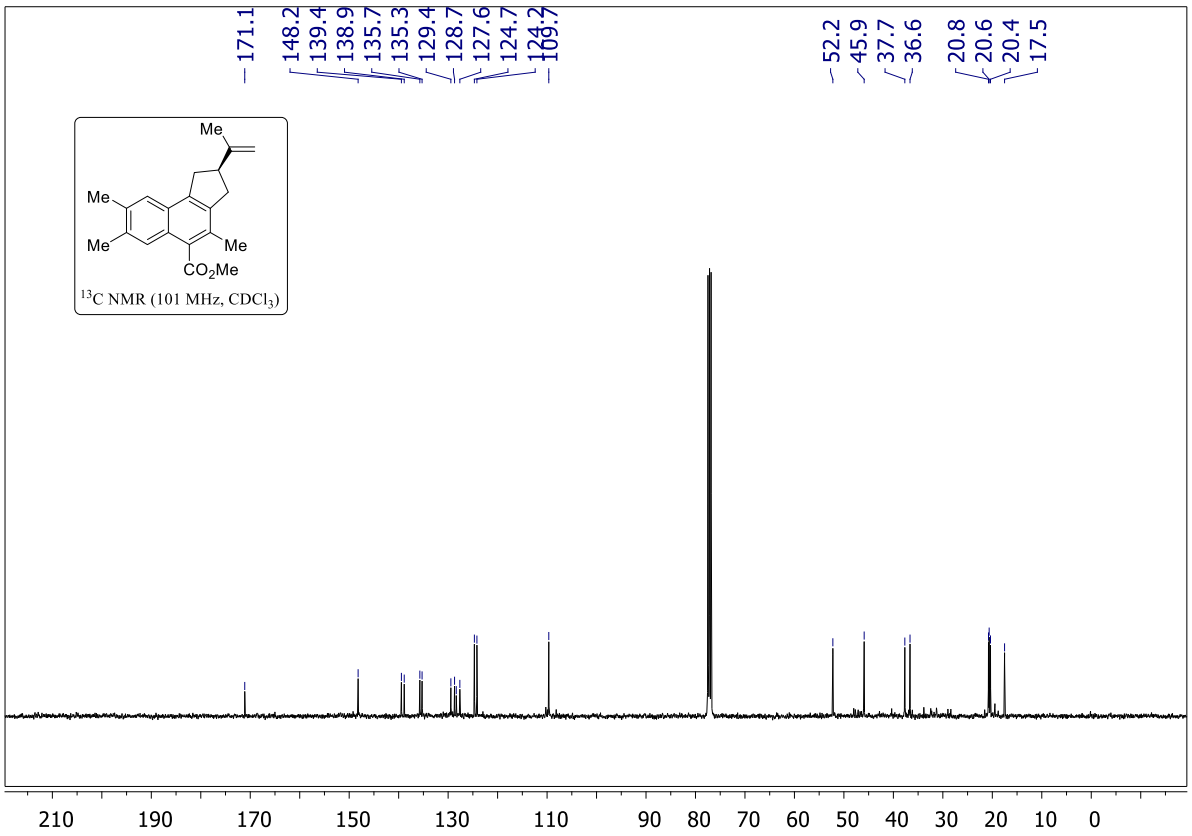




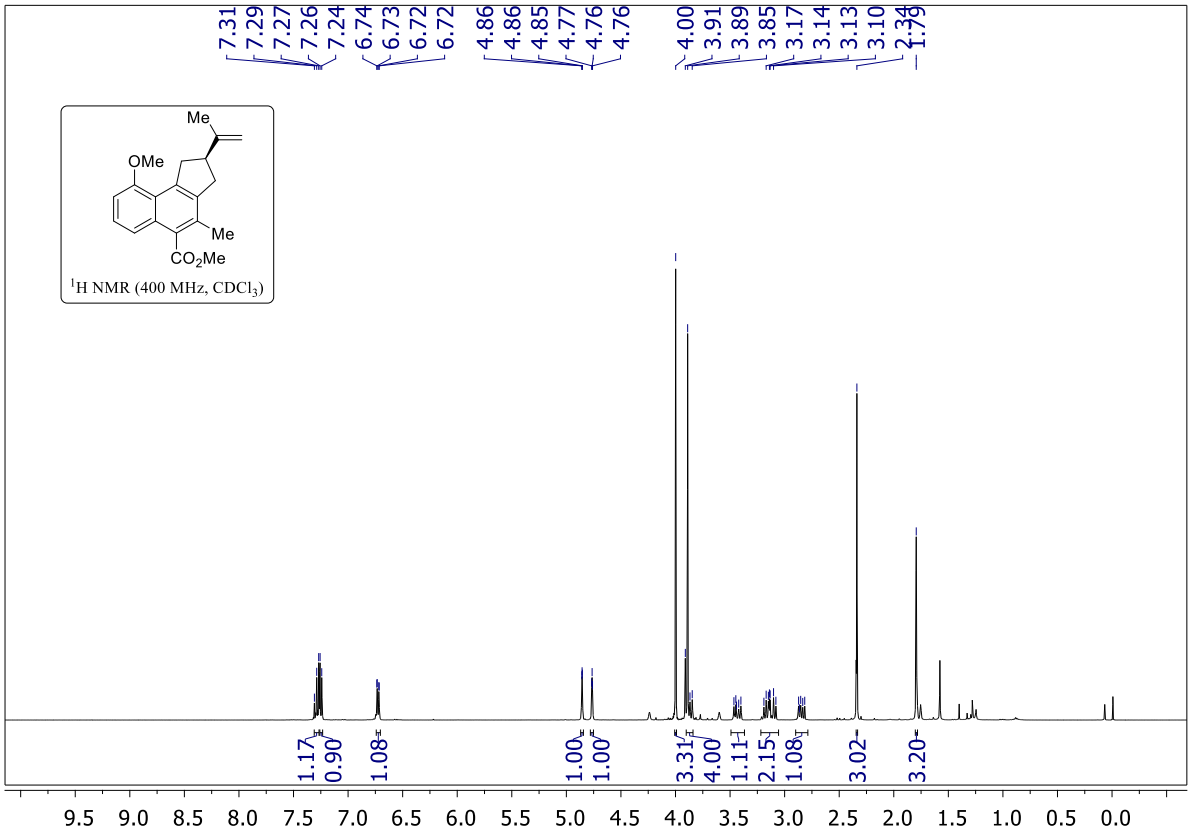

-136.78
-136.84
-137.07
-137.12
Me
F
F
Me
CO2Me
19F NMR (377 MHz, CDCl3)
-112
-118
-124
-130
-136
-142
-148
-154
-160

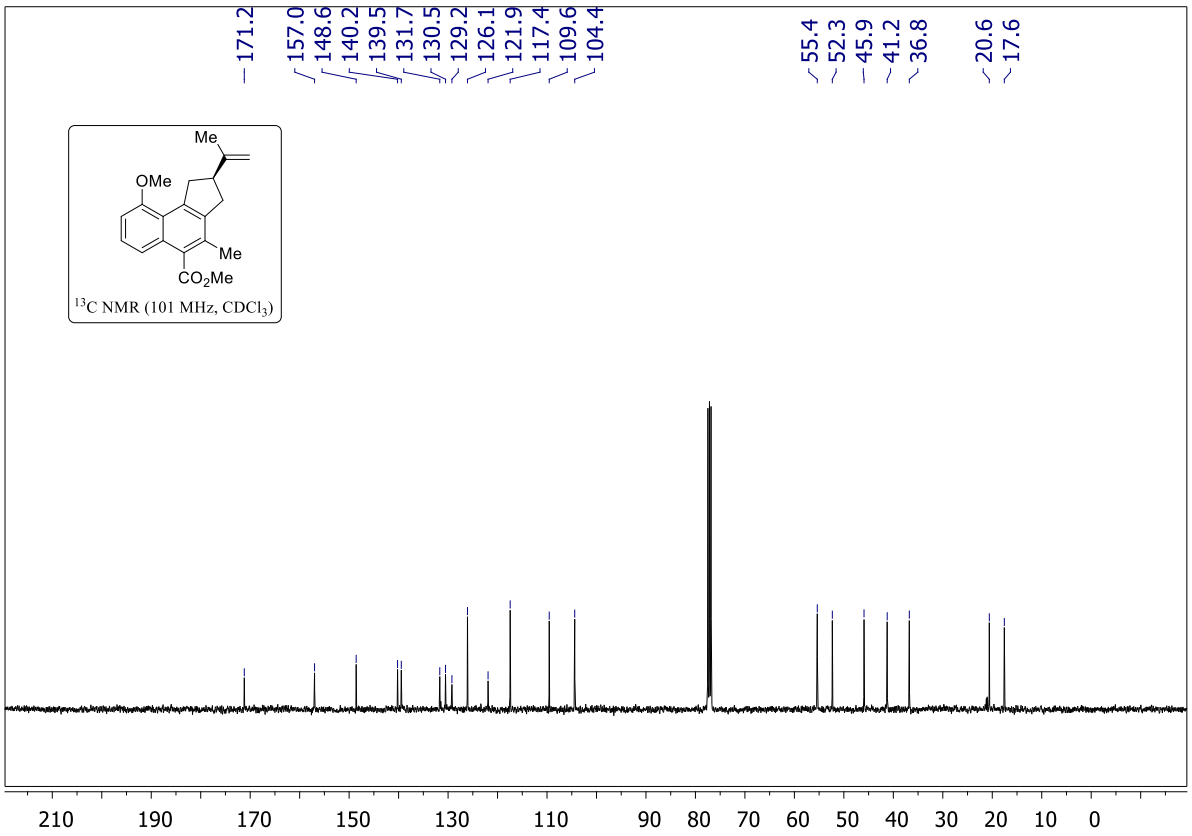
Methyl (*S*)-4,7,8-trimethyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8e):



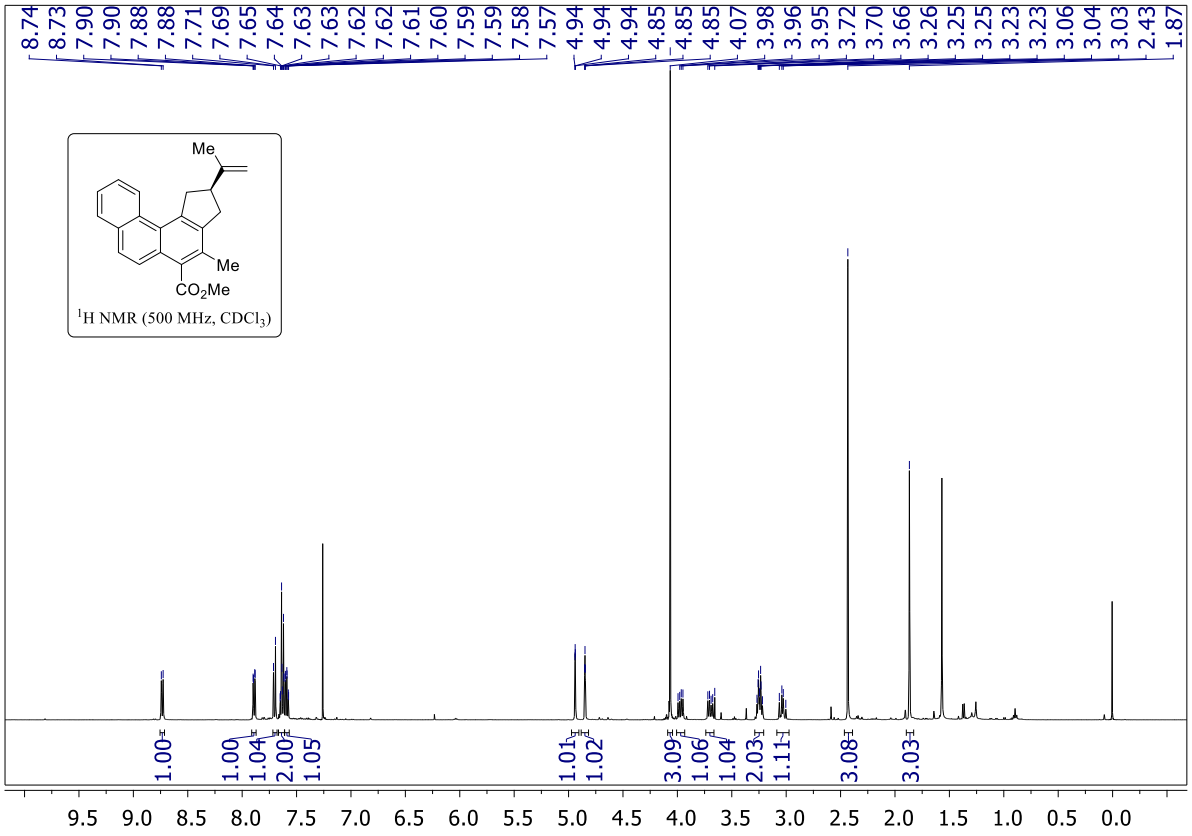


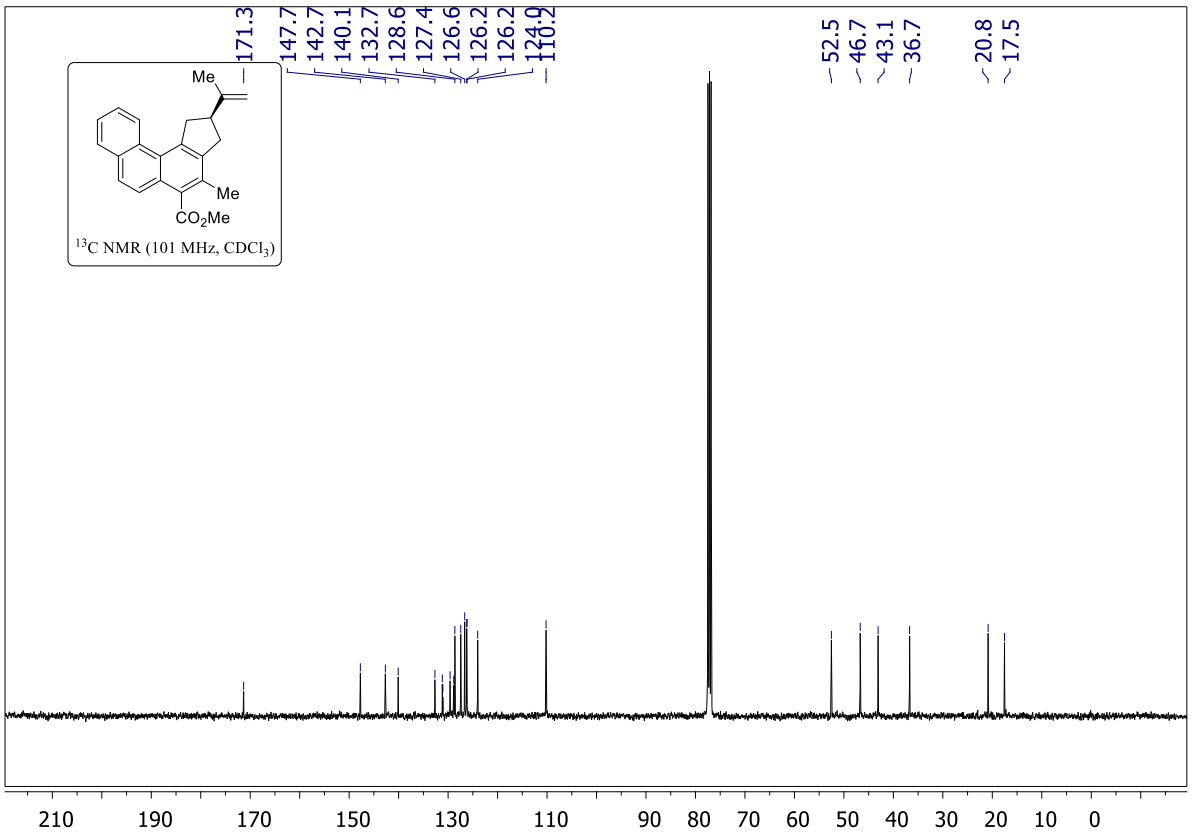
Methyl (*S*)-9-methoxy-4-methyl-2-(prop-1-en-2-yl)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (8f):



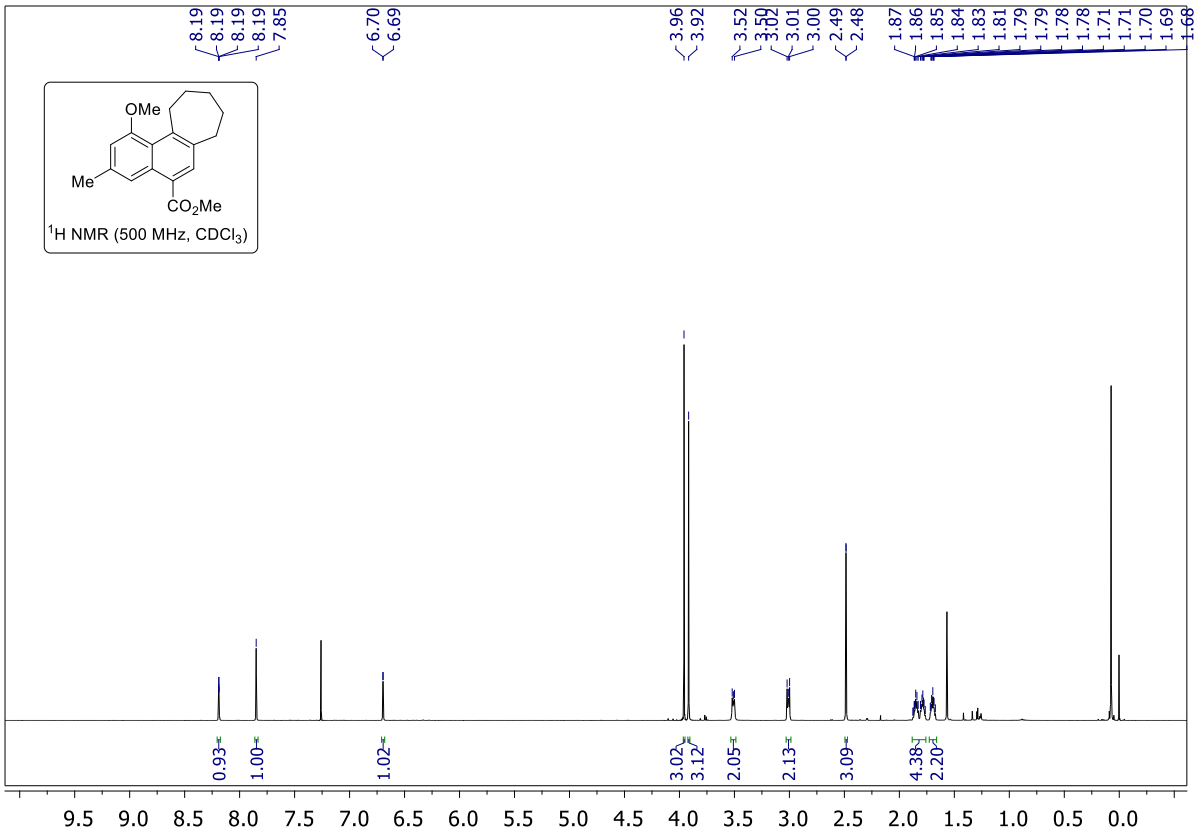


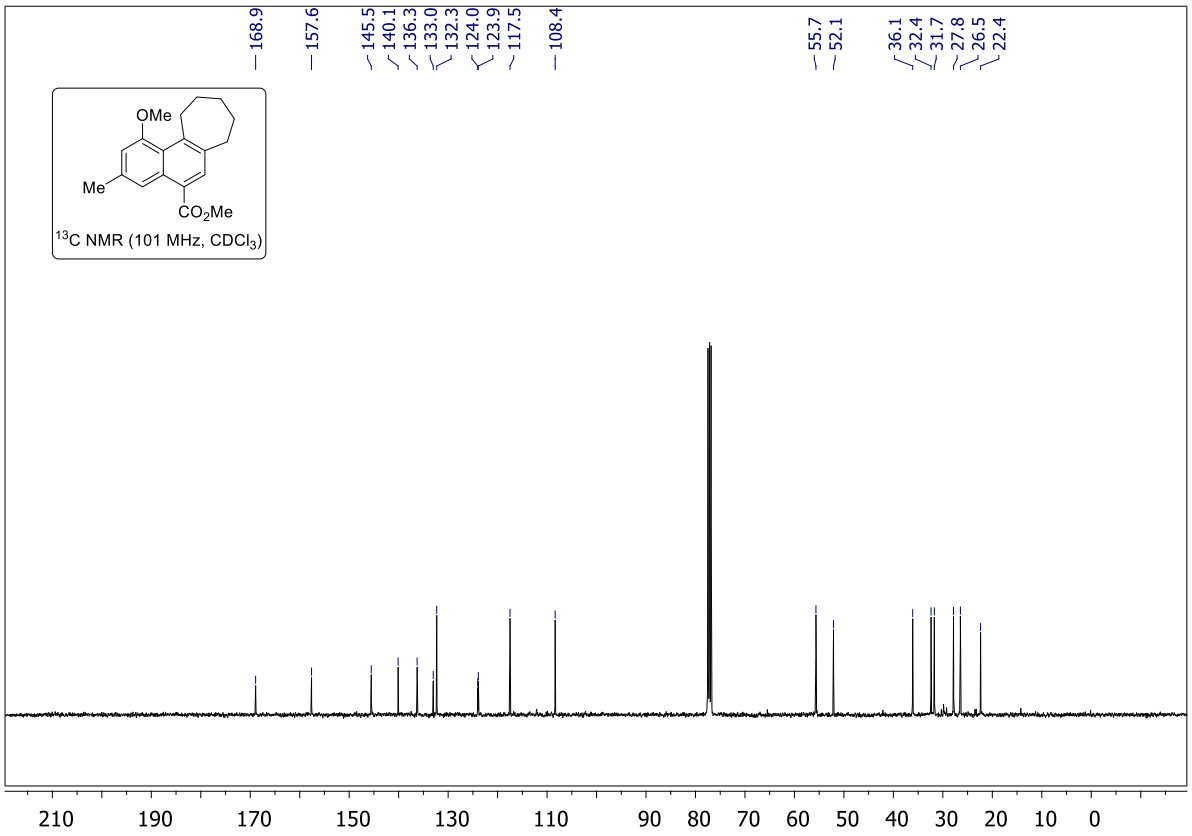
Methyl (*S*)-12-methyl-16-(prop-1-en-2-yl)-16,17-dihydro-15*H*-cyclopenta[*c*]phenanthrene-11-carboxylate (8g):



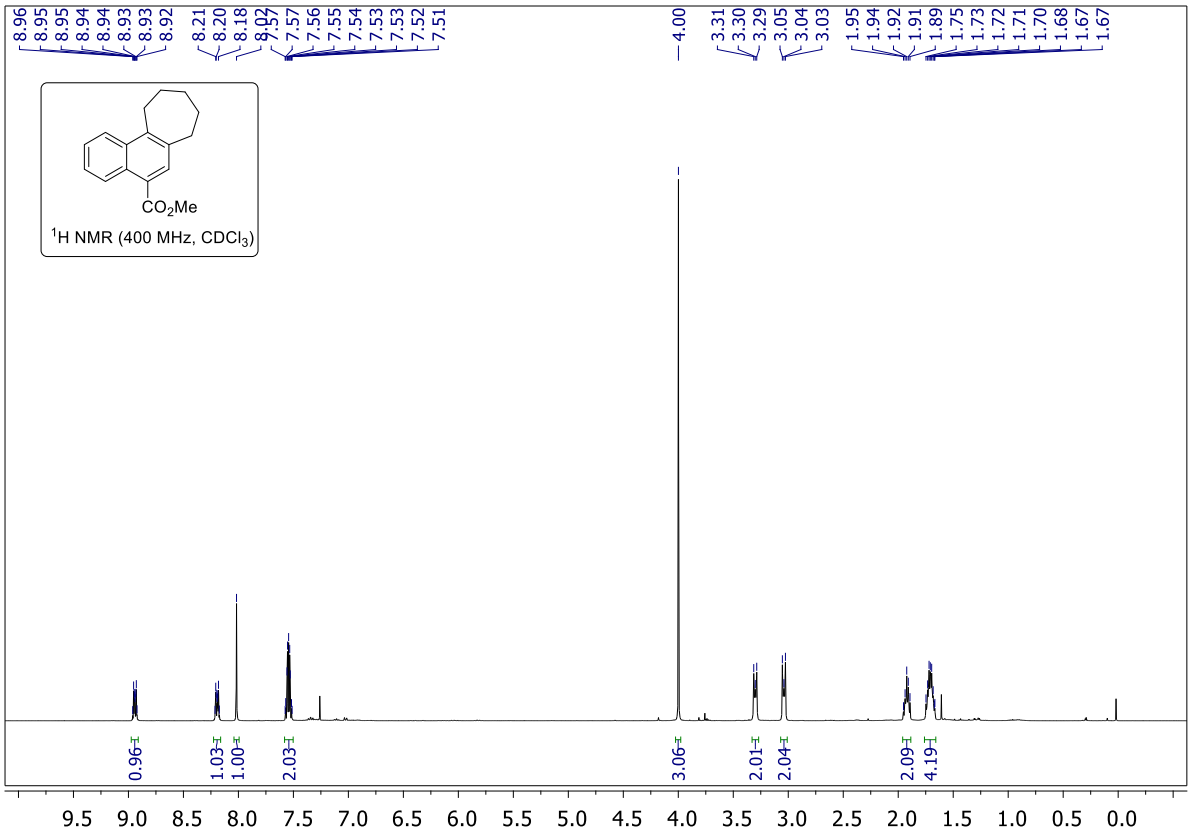


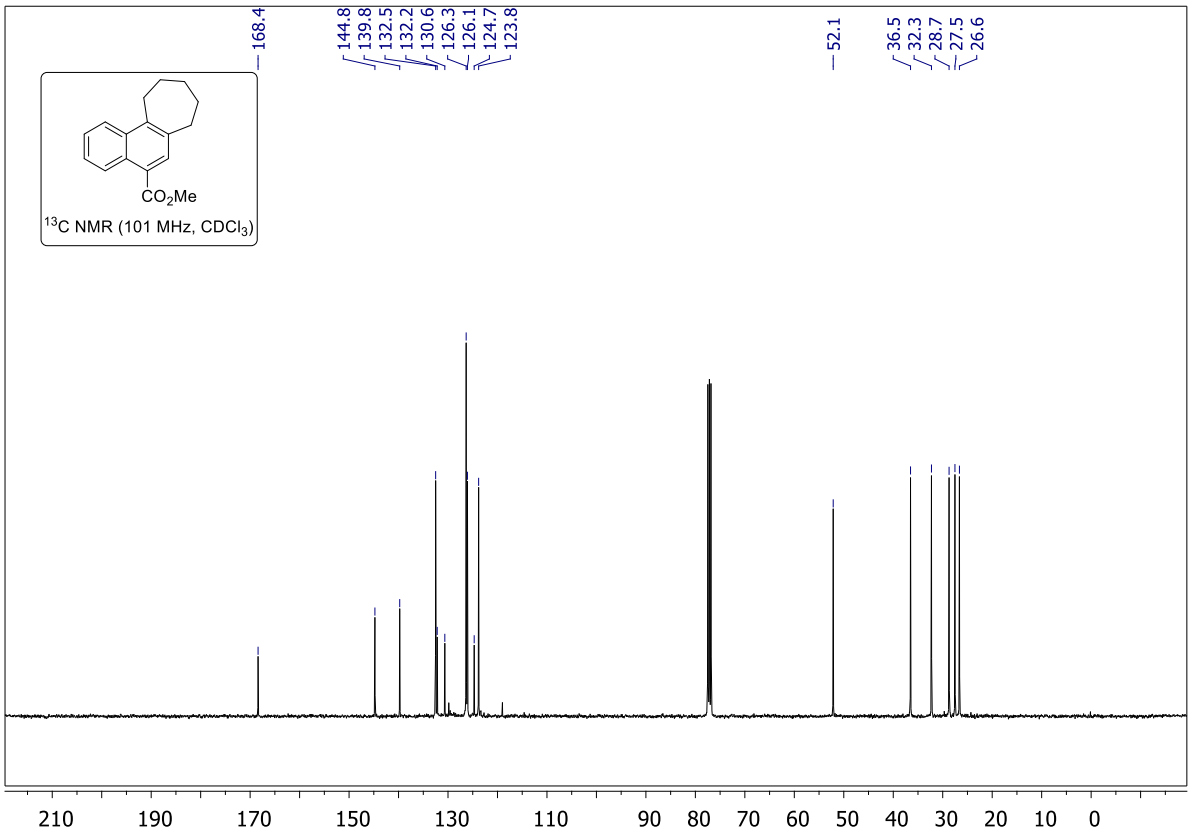
Methyl 1-methoxy-3-methyl-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11a):



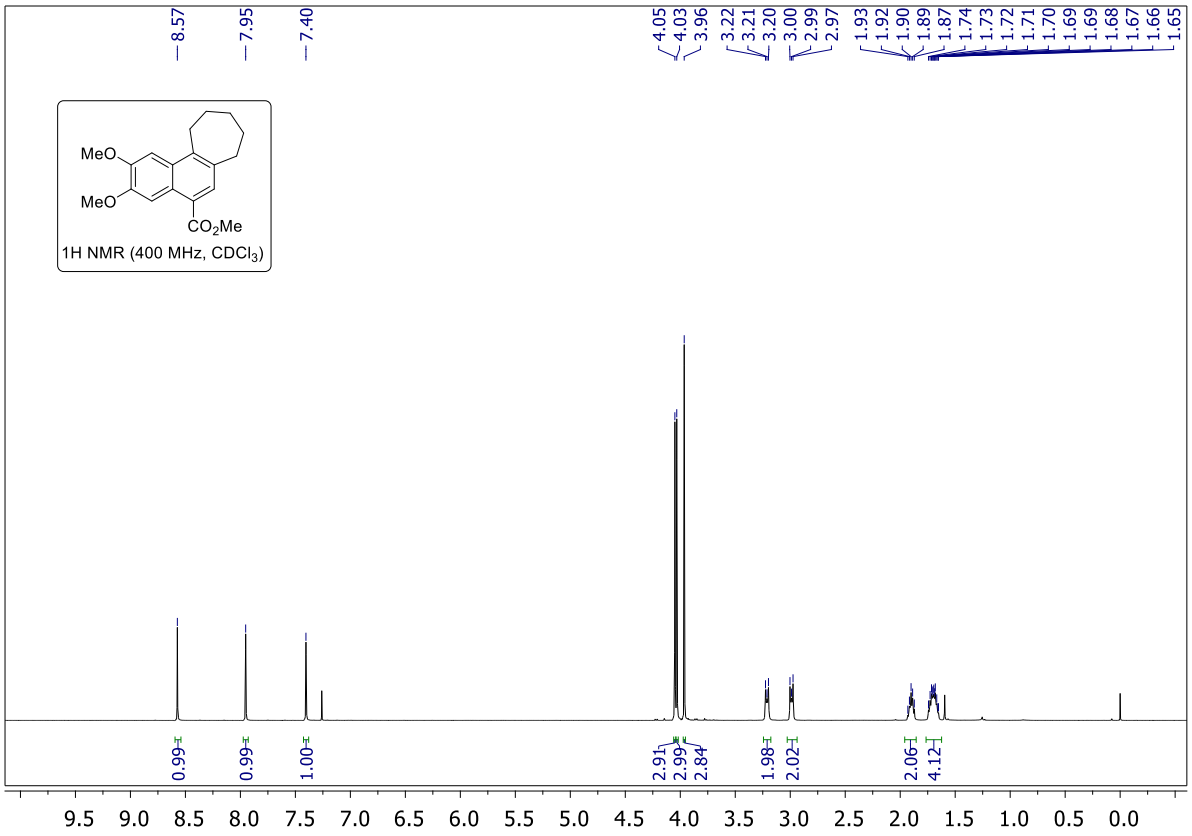


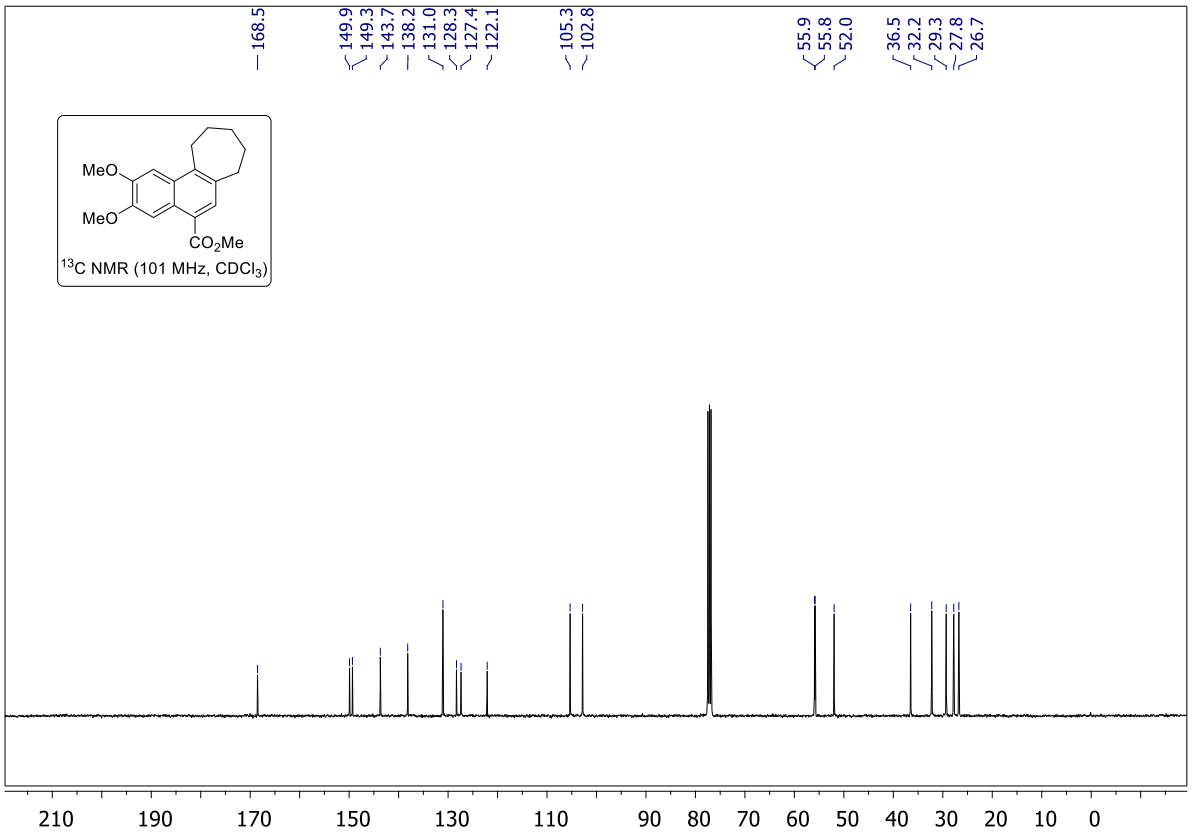
Methyl 8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11b):



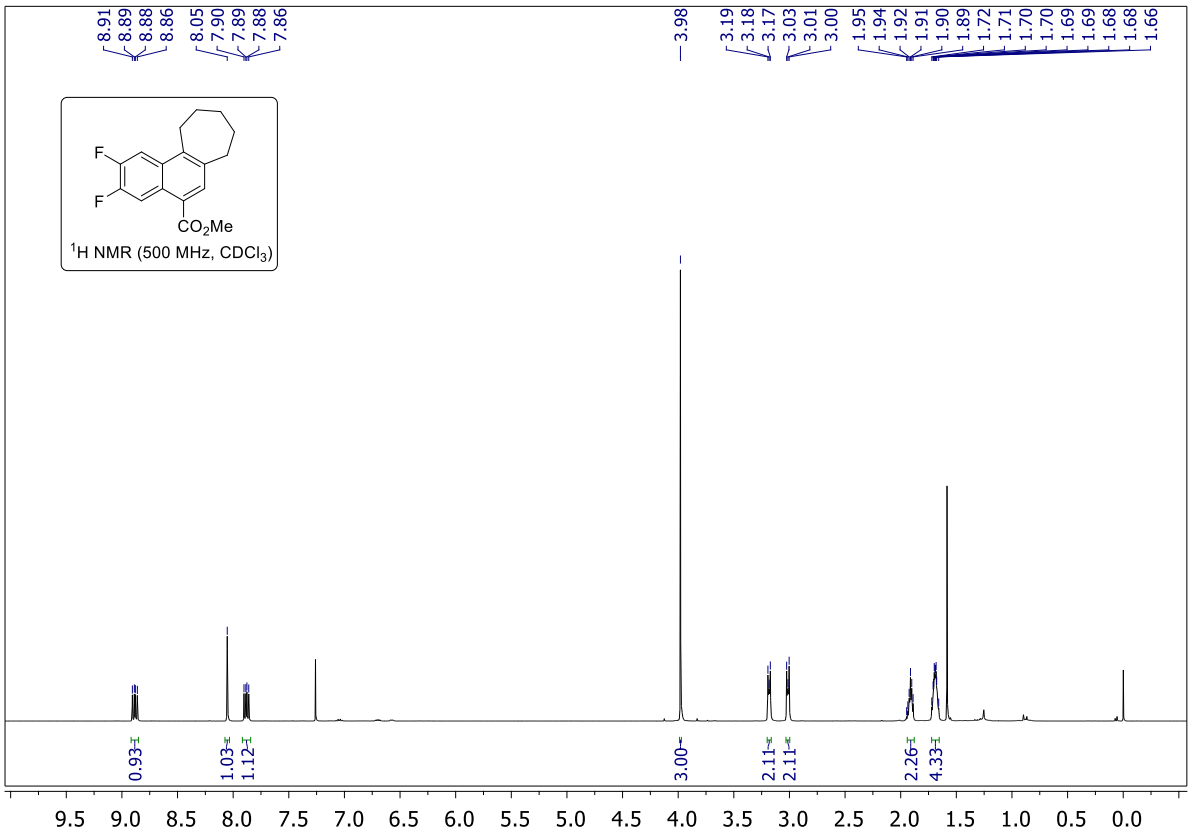


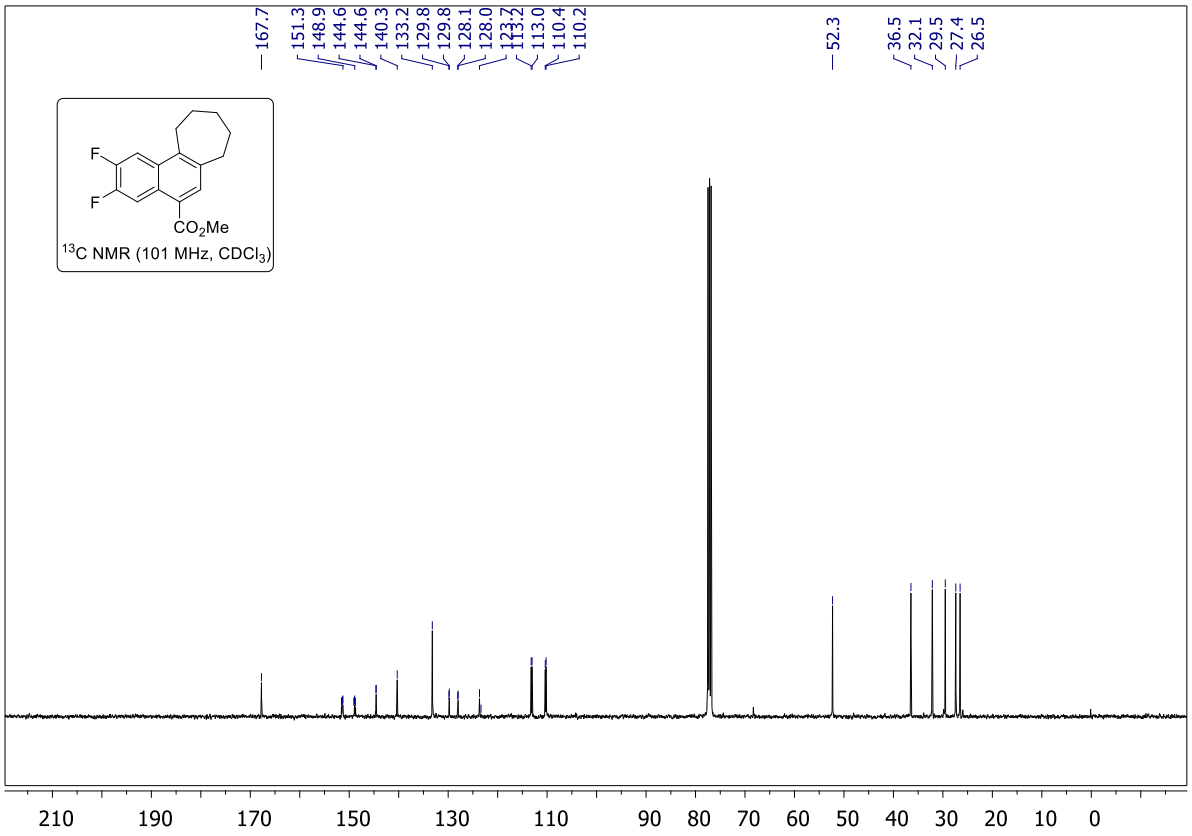
Methyl 2,3-dimethoxy-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11c):

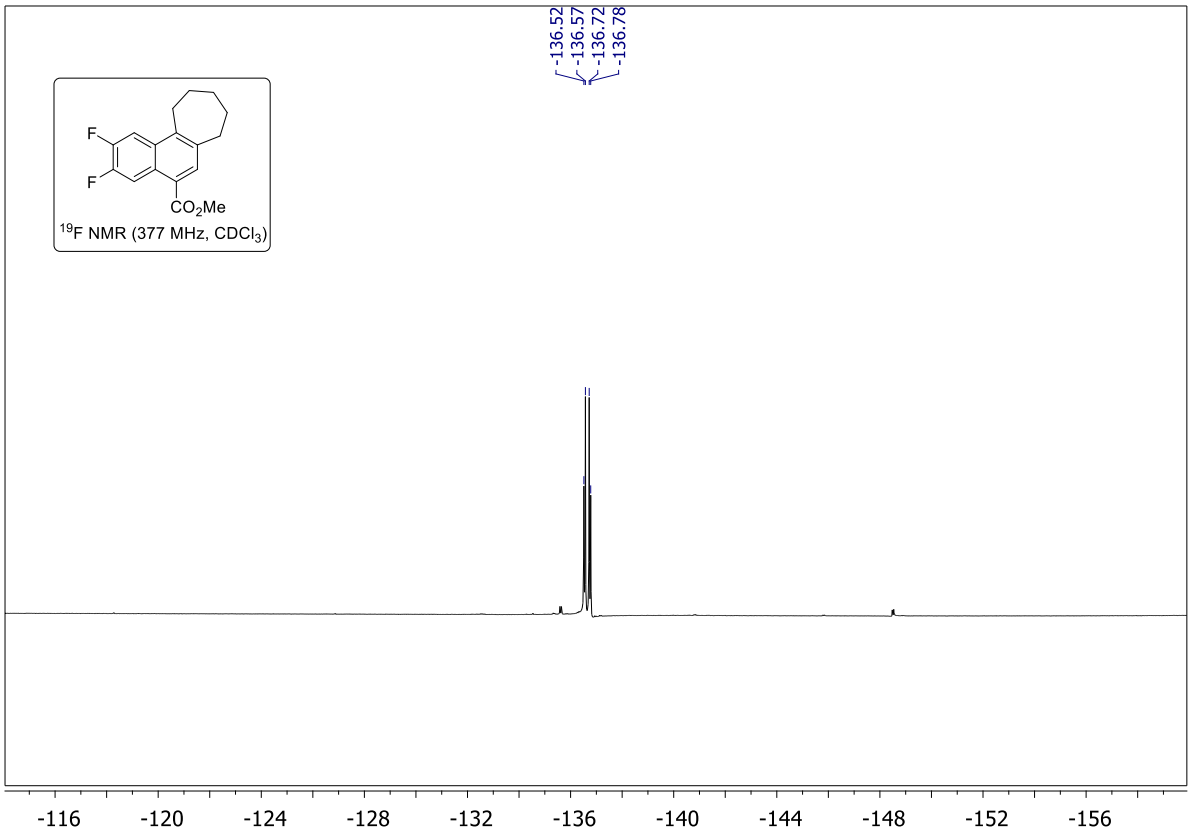




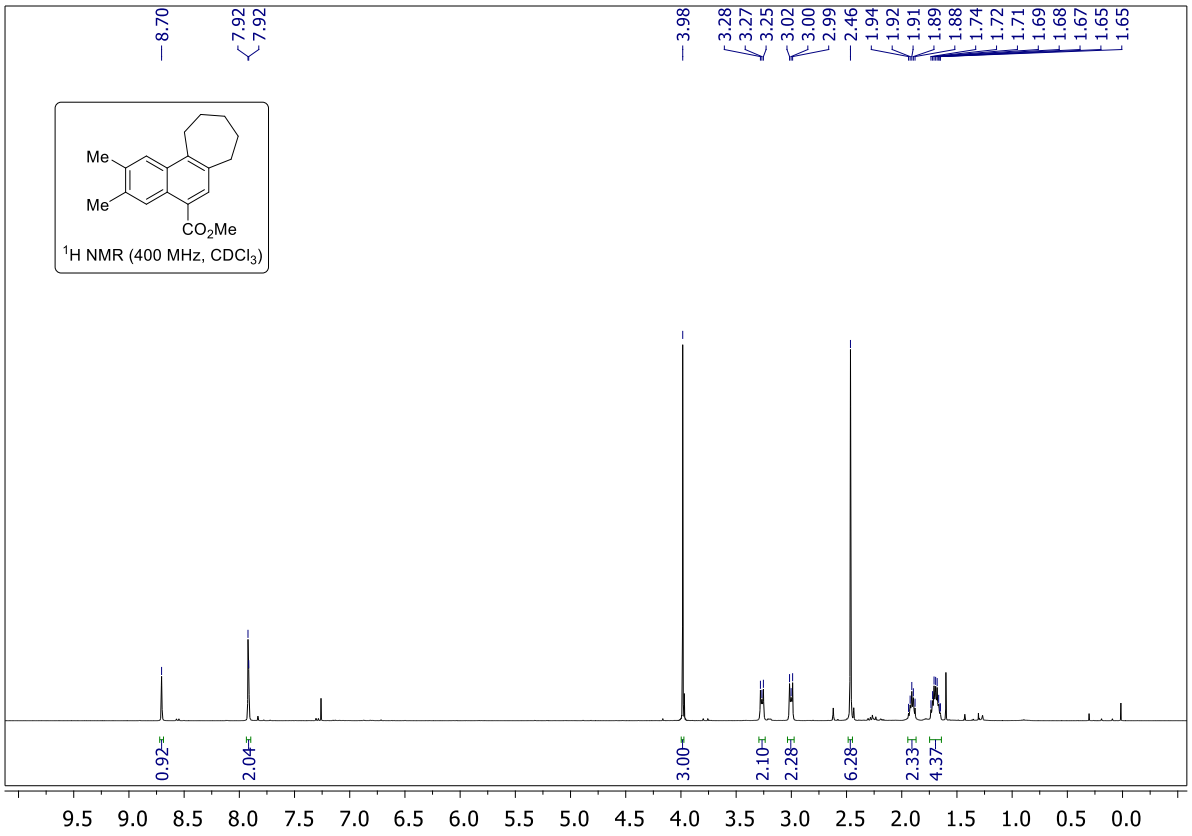
Methyl 2,3-difluoro-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11d):

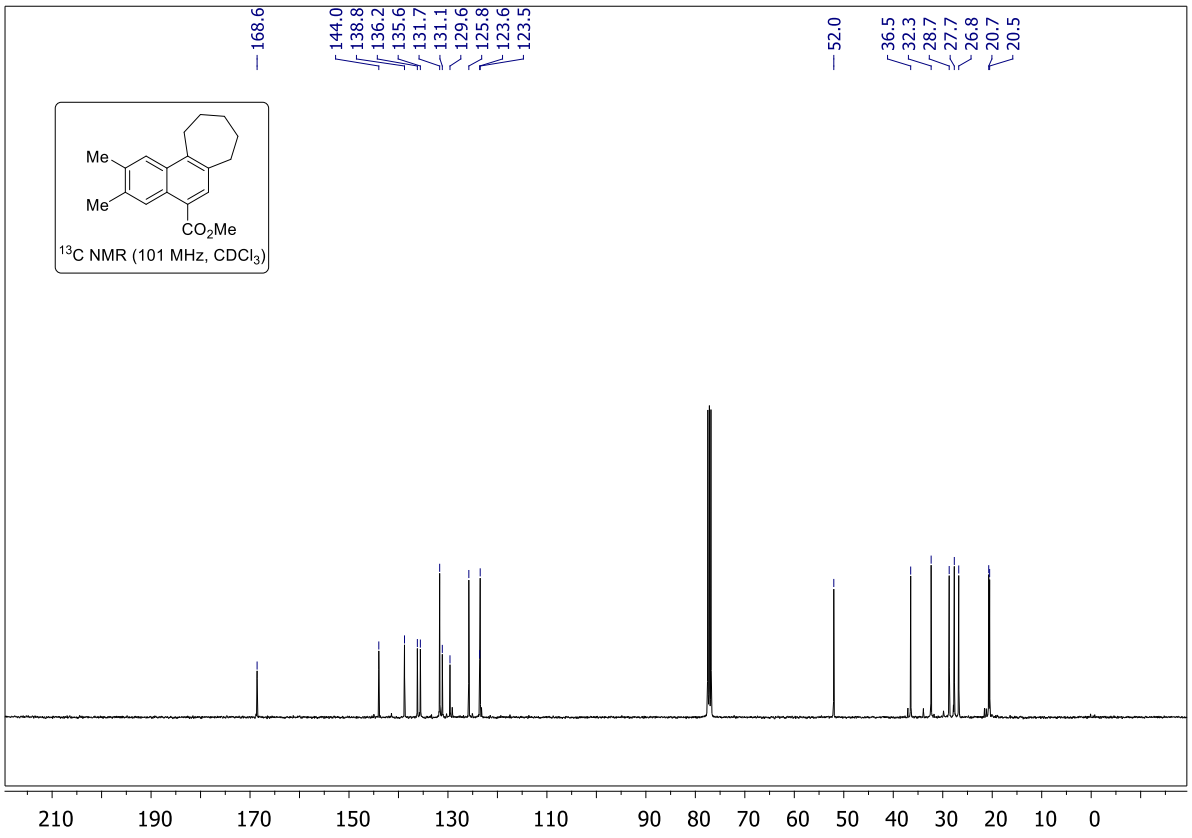




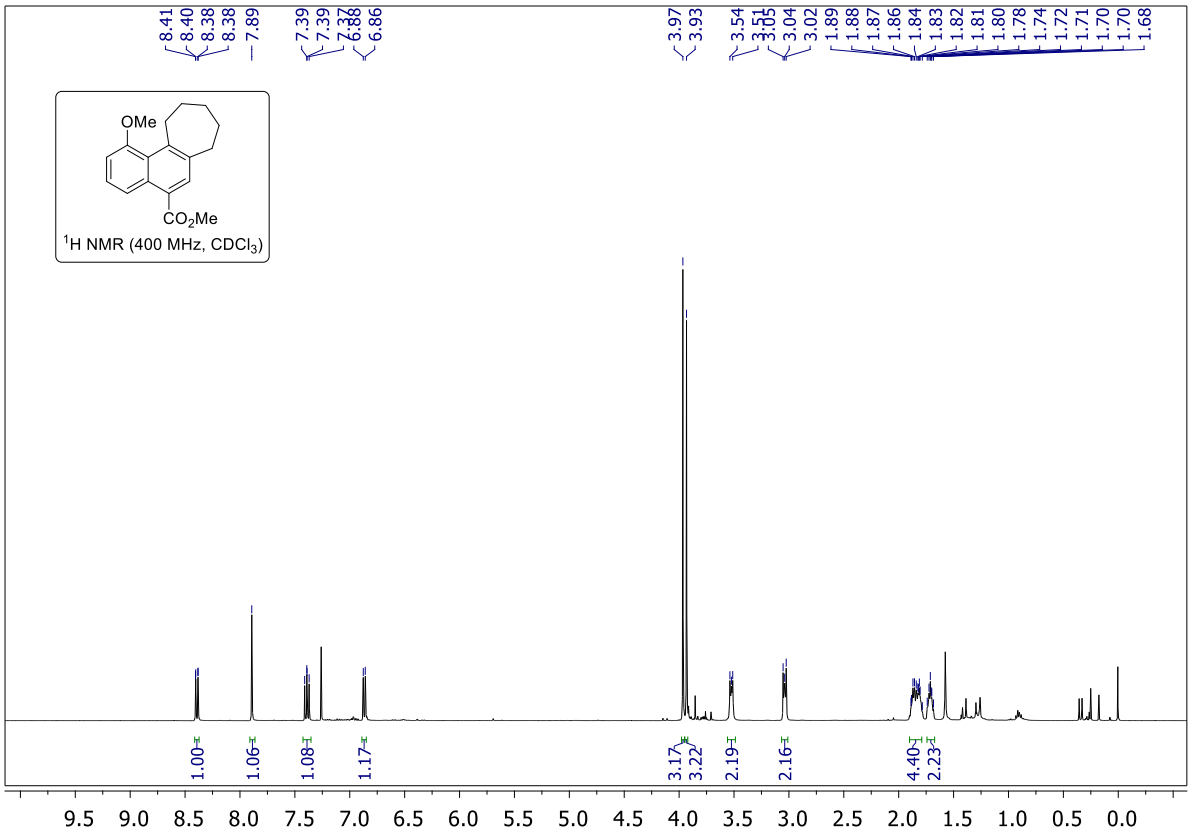

-136.52
-136.57
-136.72
-136.78
F
F
CO2Me
19F NMR (377 MHz, CDCl3)
-116
-120
-124
-128
-132
-136
-140
-144
-148
-152
-156

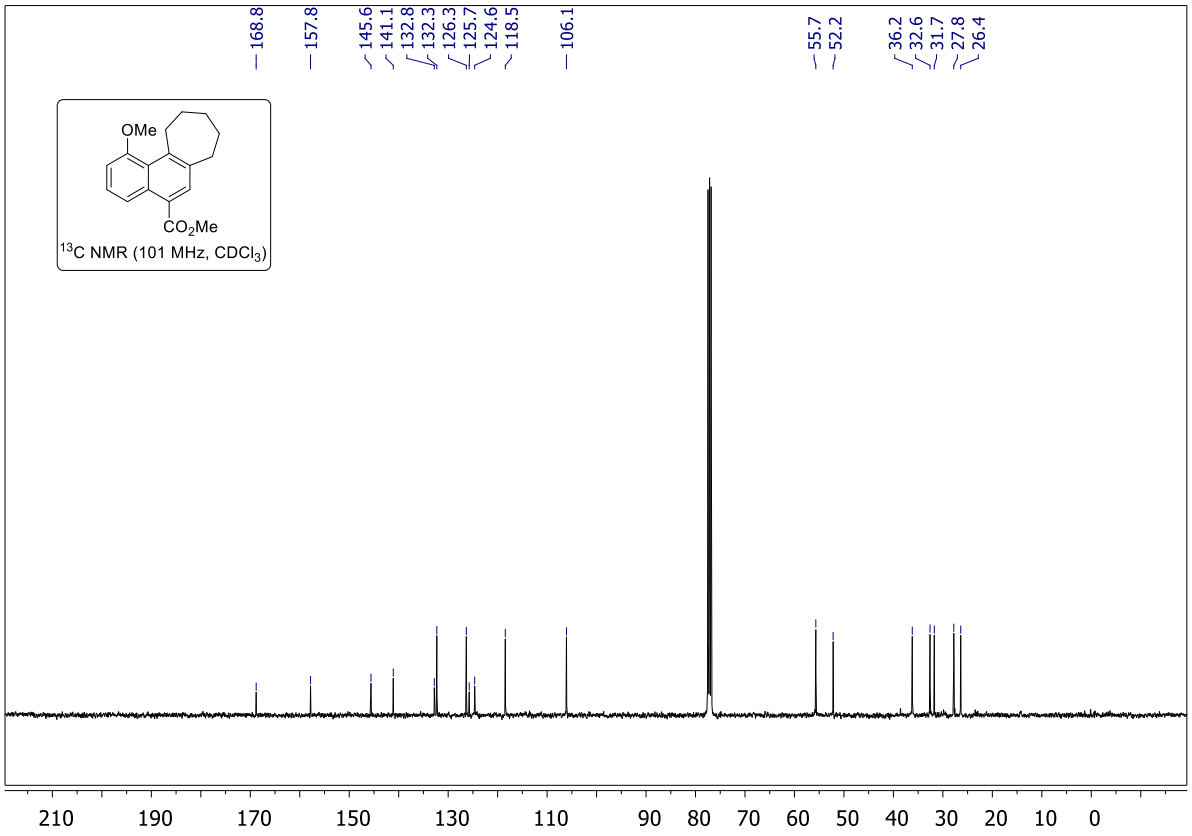
Methyl 2,3-dimethyl-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (14e):



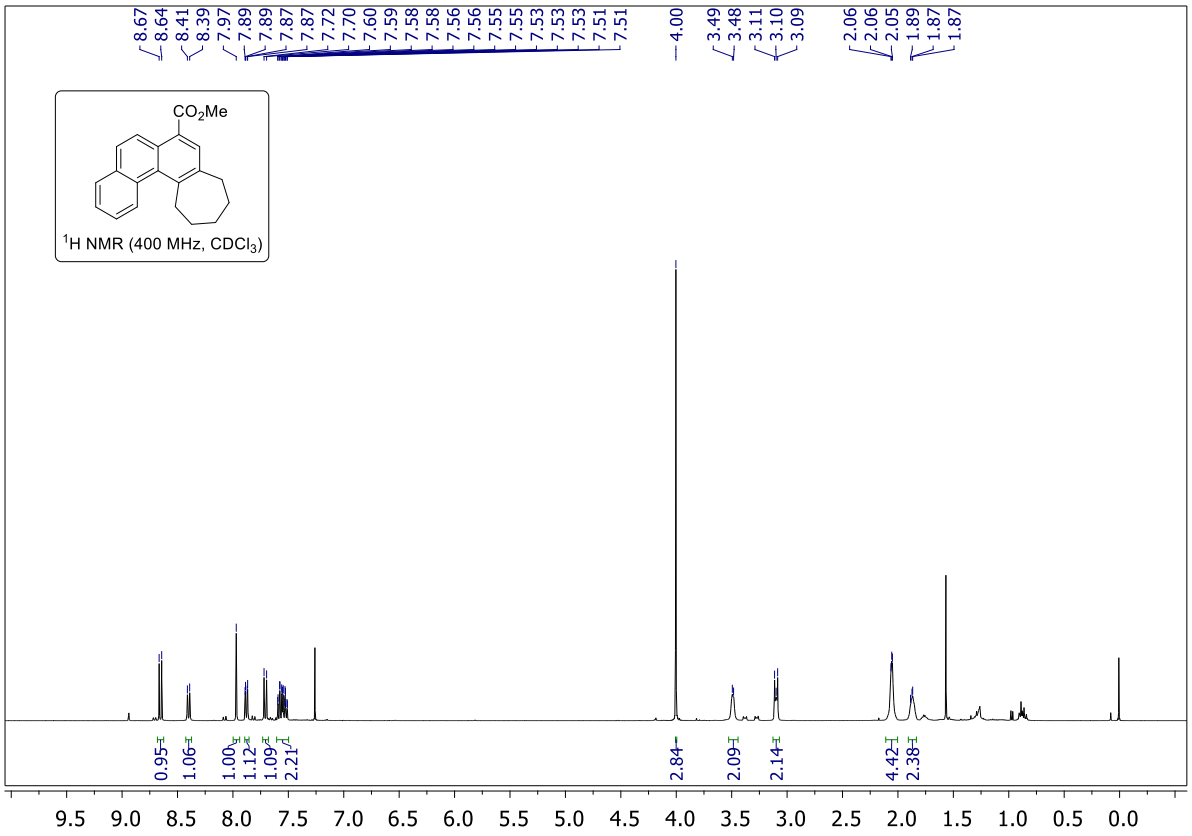


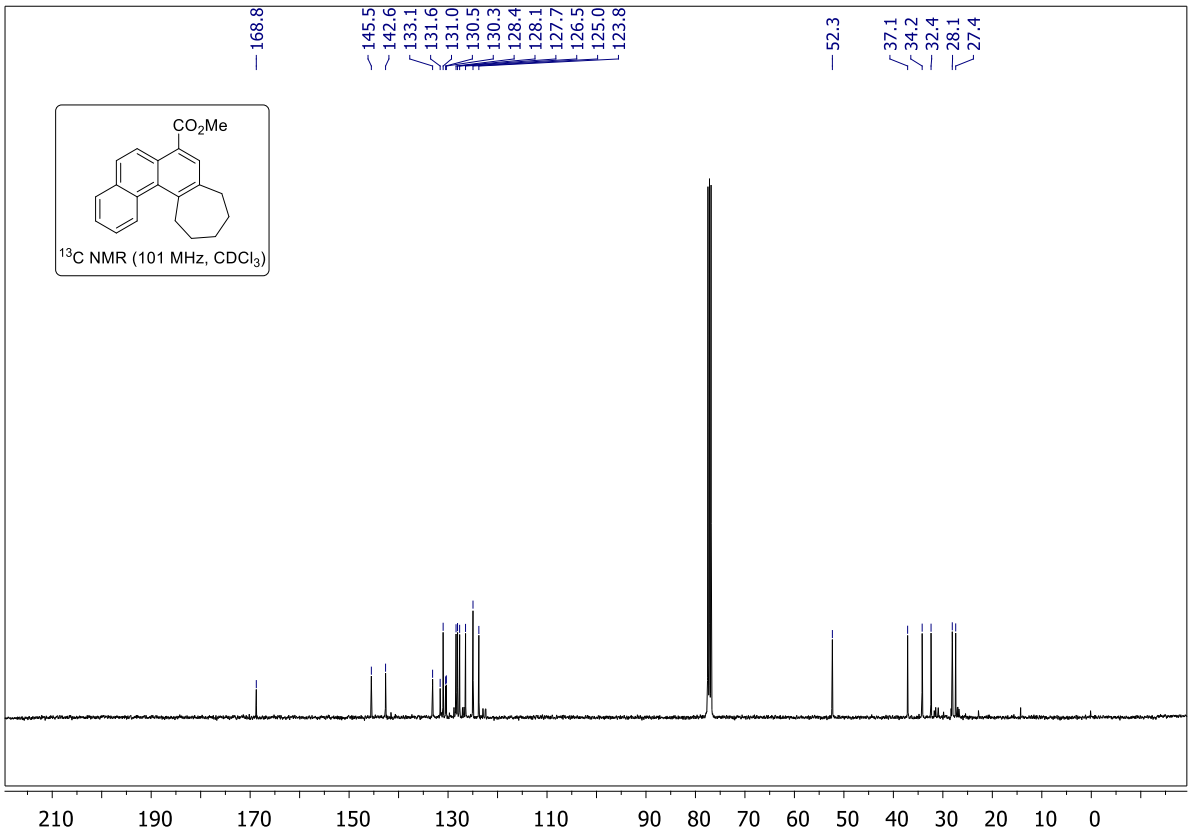
Methyl 1-methoxy-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11f):



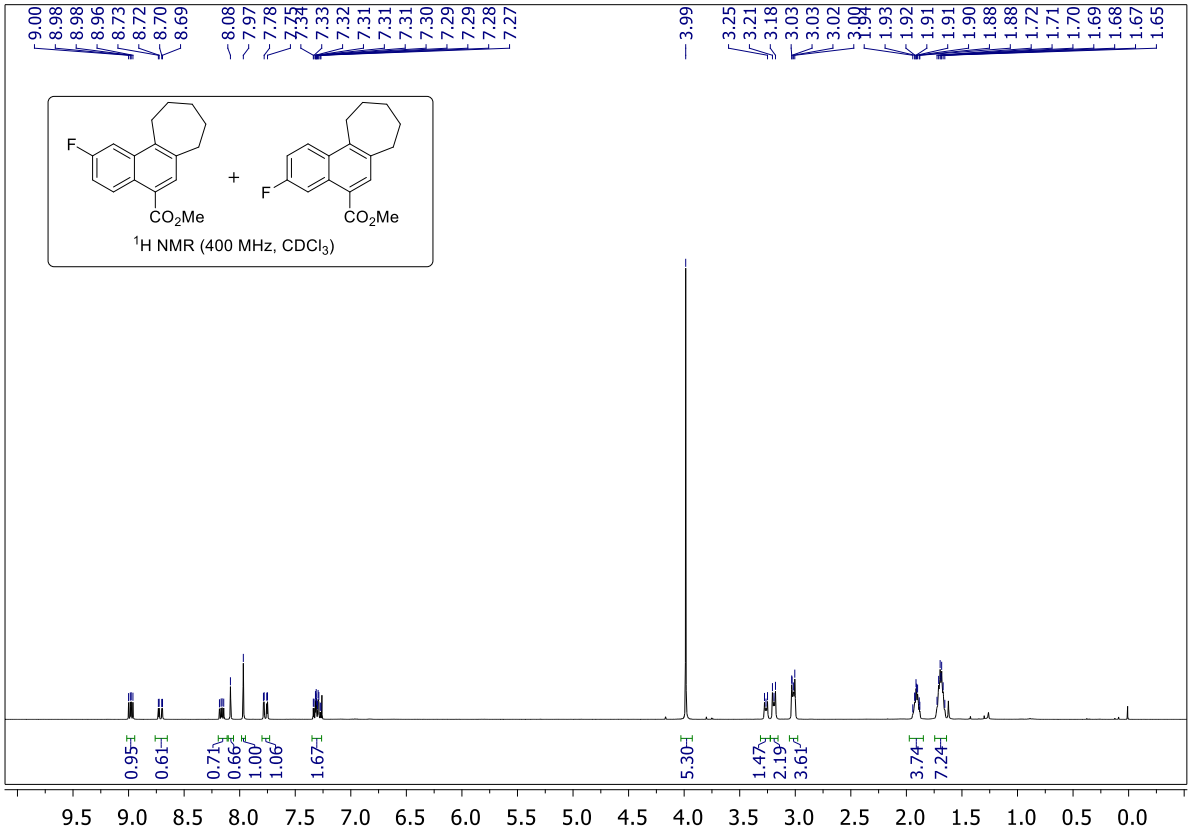


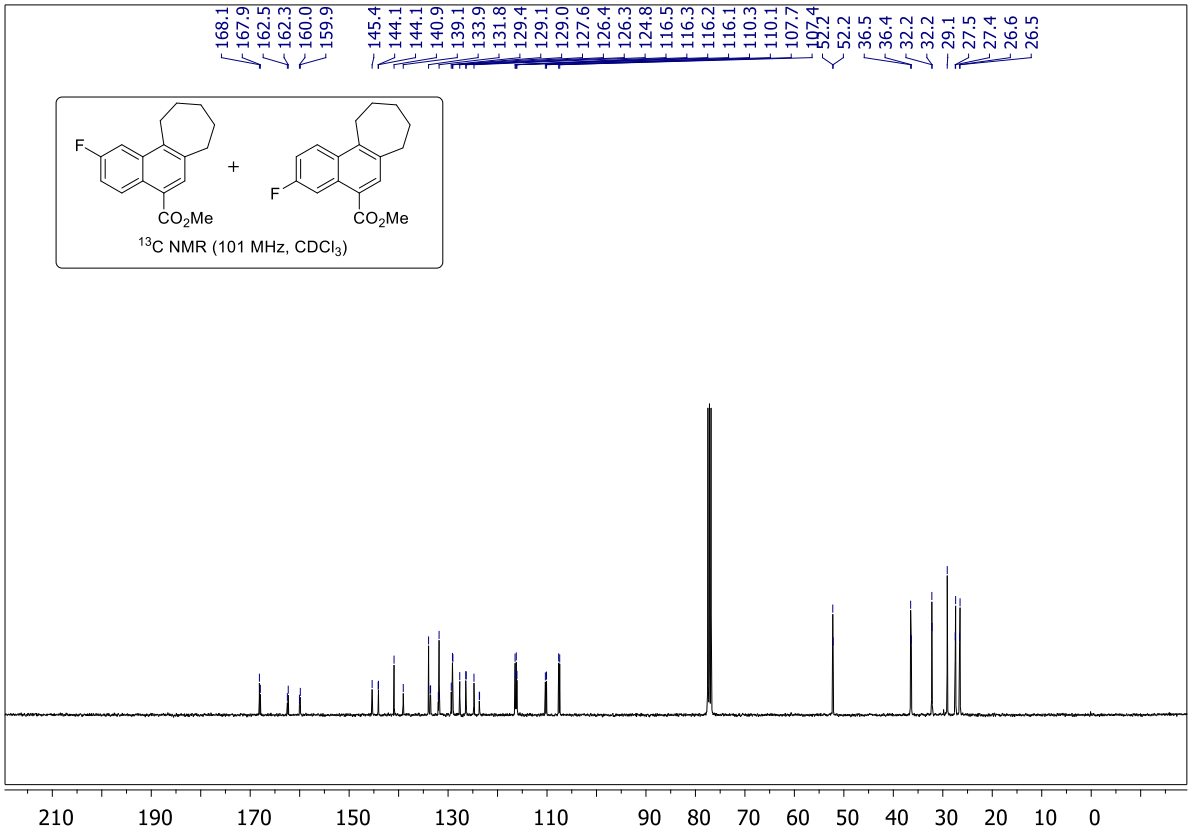
Methyl 10,11,12,13-tetrahydro-9*H*-cyclohepta[*c*]phenanthrene-7-carboxylate (11g):

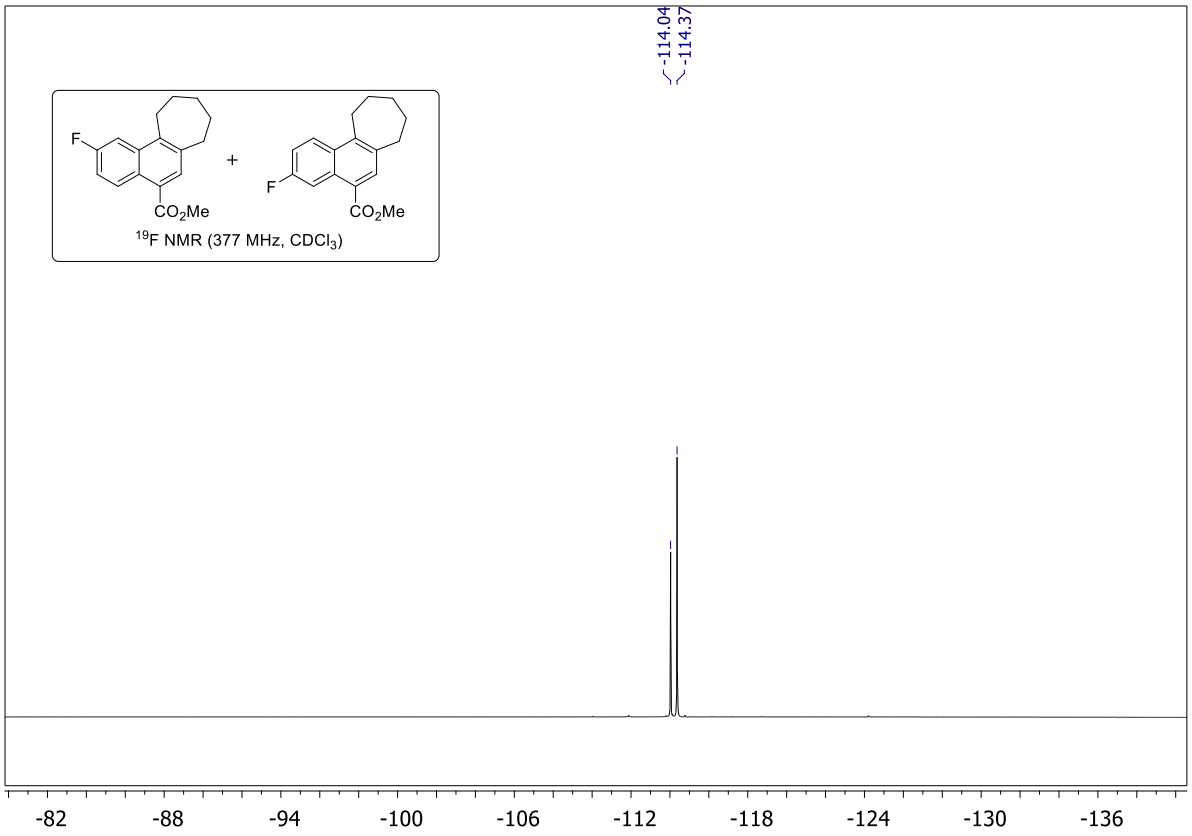




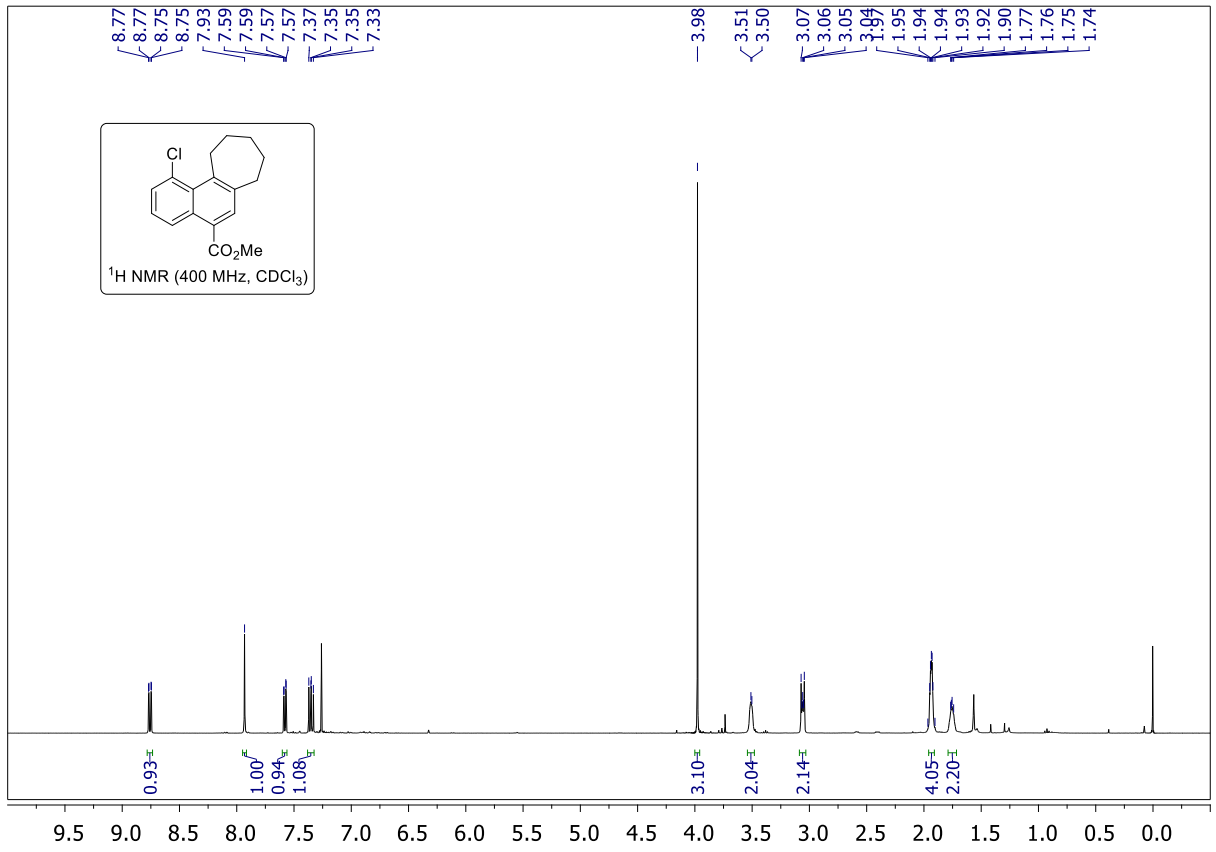
Methyl 2-fluoro-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11h) and Methyl 2-fluoro-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11h'):

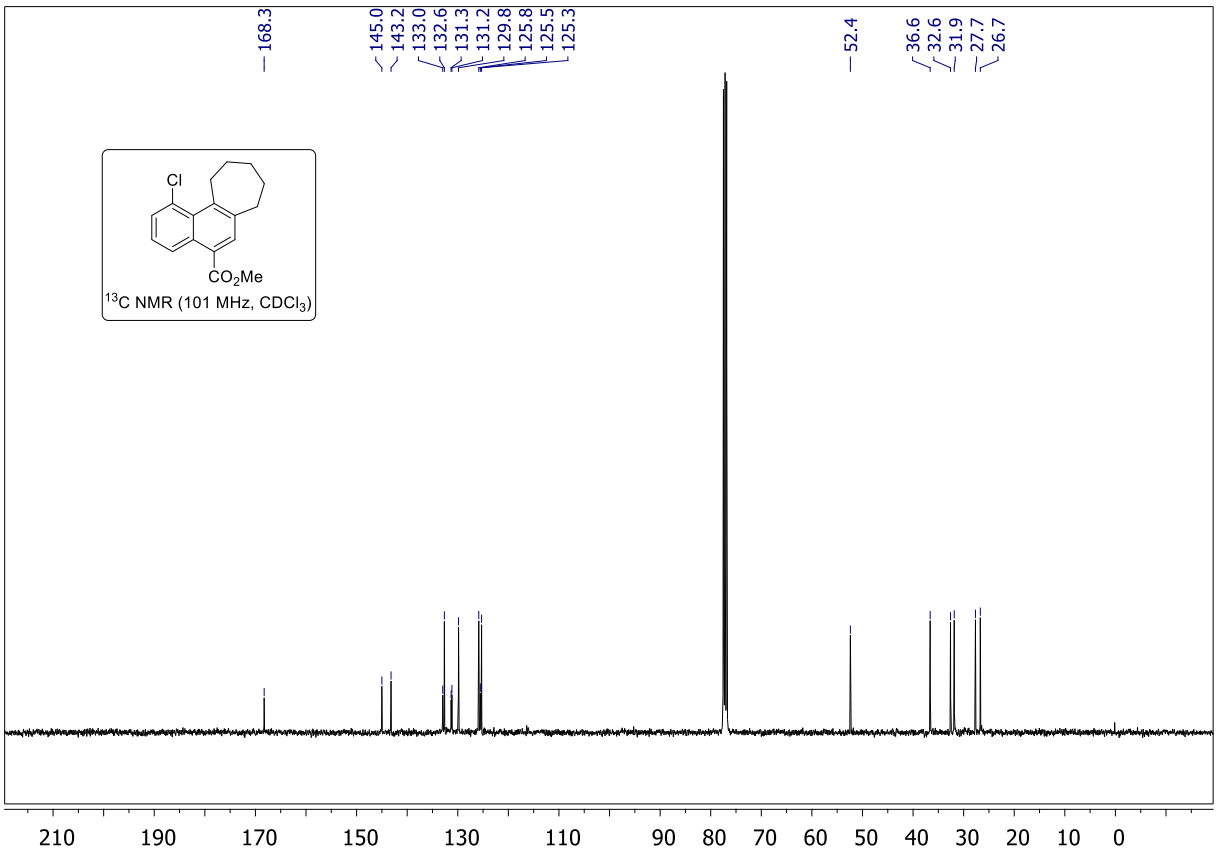




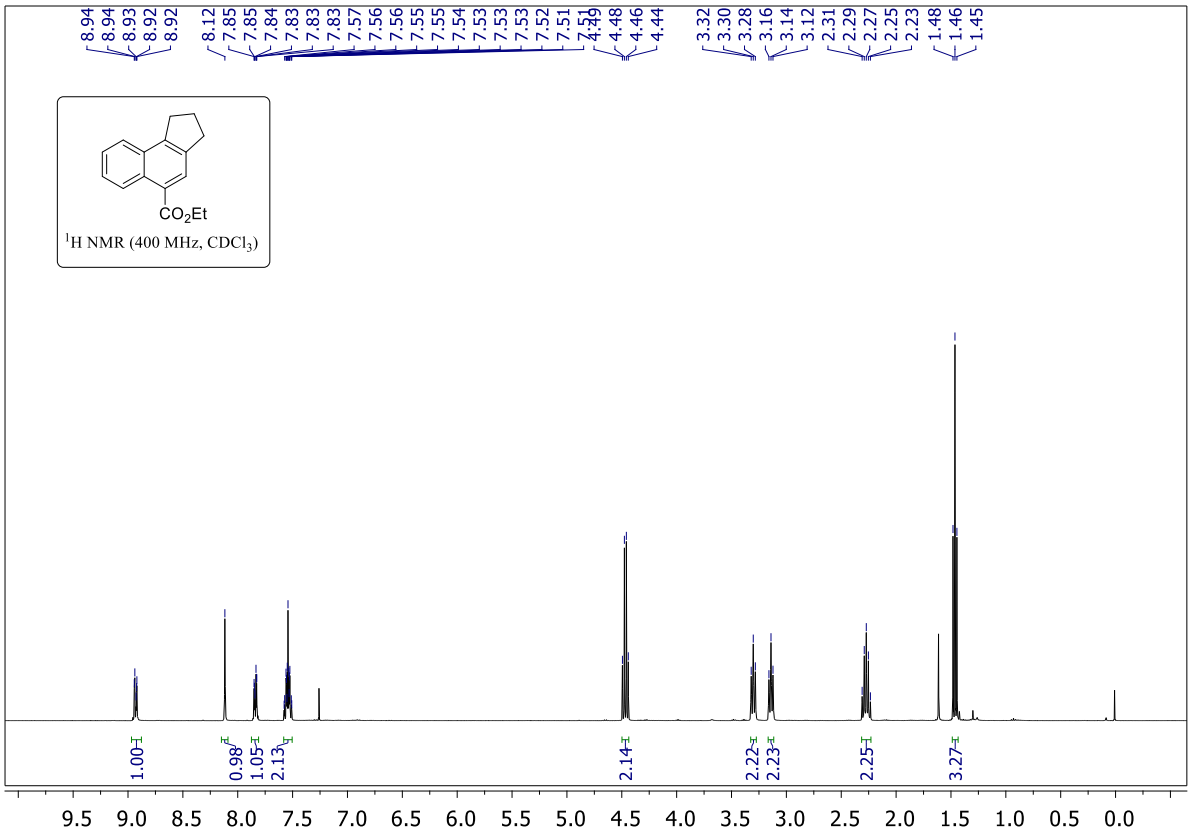

-114.04
-114.37
F
CO2Me
+
F
CO2Me
19F NMR (377 MHz, CDCl3)
-82
-88
-94
-100
-106
-112
-118
-124
-130
-136

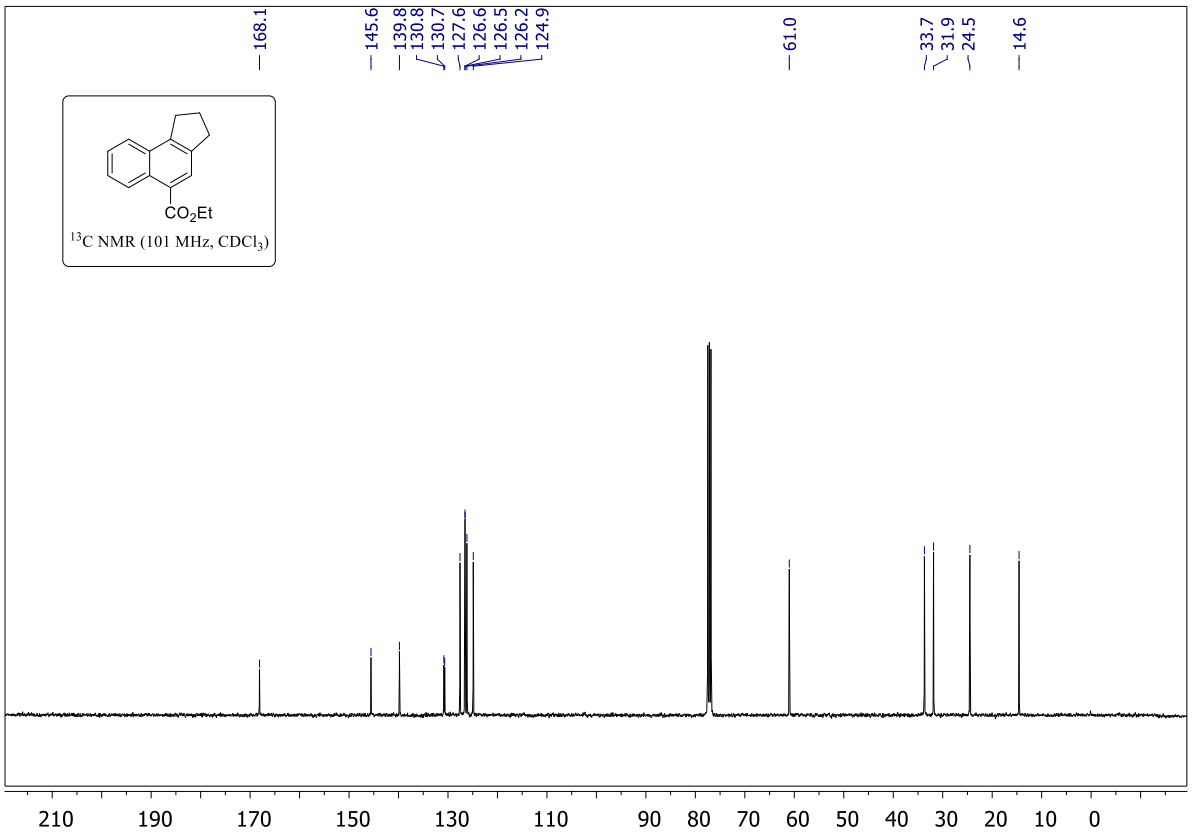
Methyl 1-chloro-8,9,10,11-tetrahydro-7*H*-cyclohepta[*a*]naphthalene-5-carboxylate (11i):



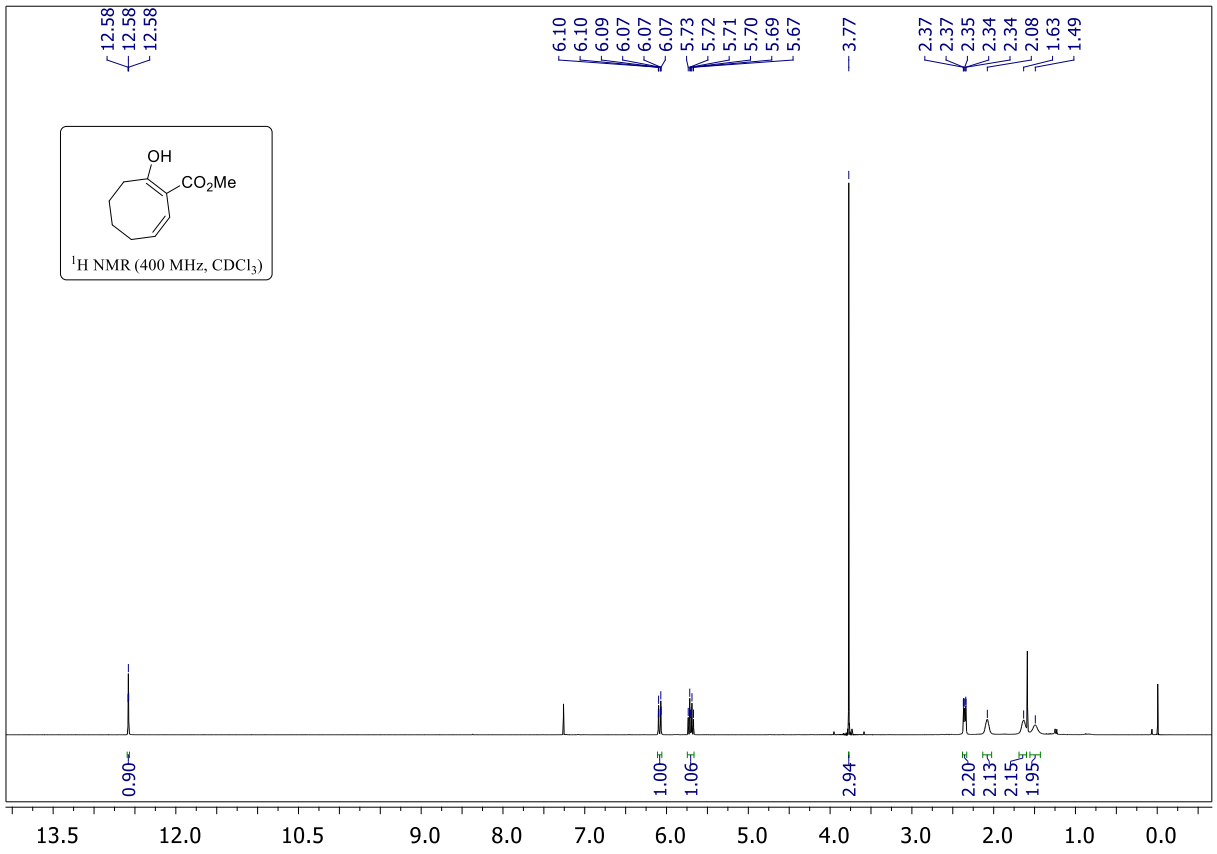


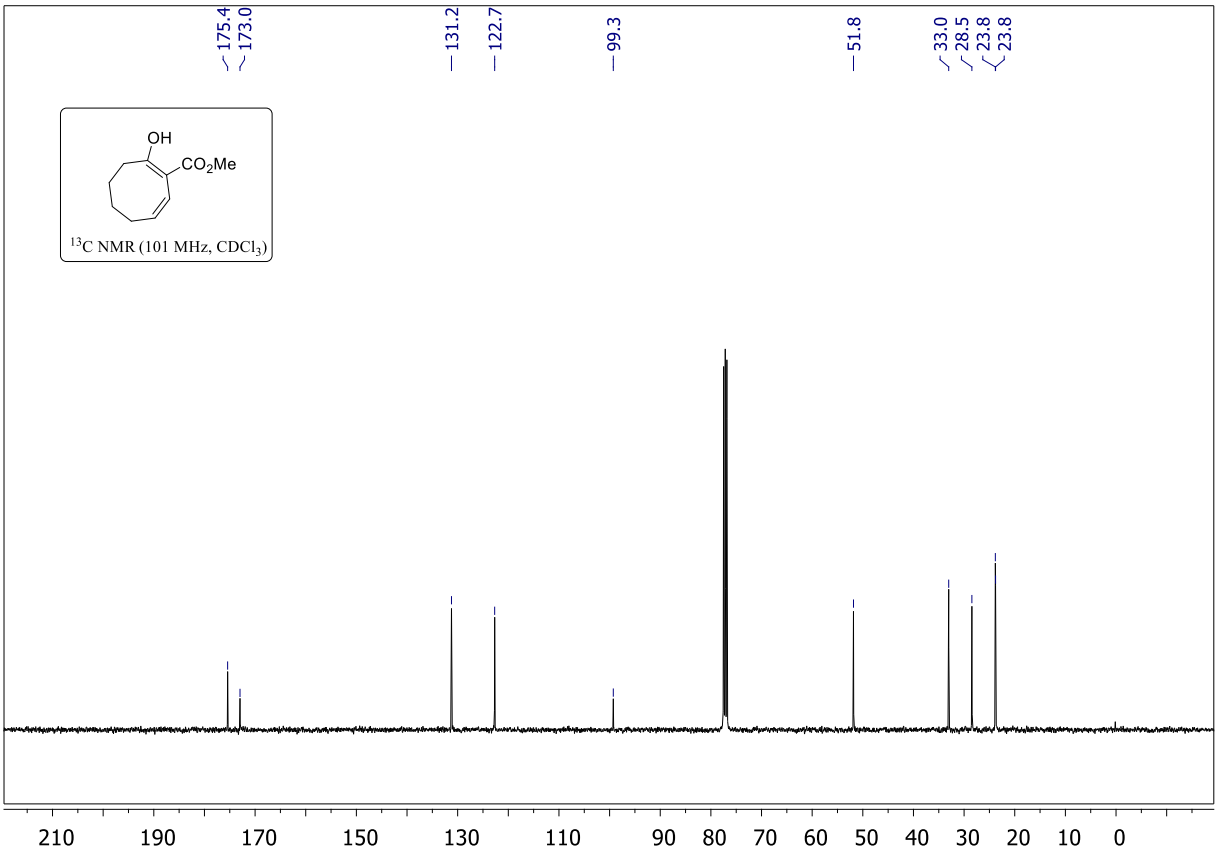
Ethyl 2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-5-carboxylate (11j):



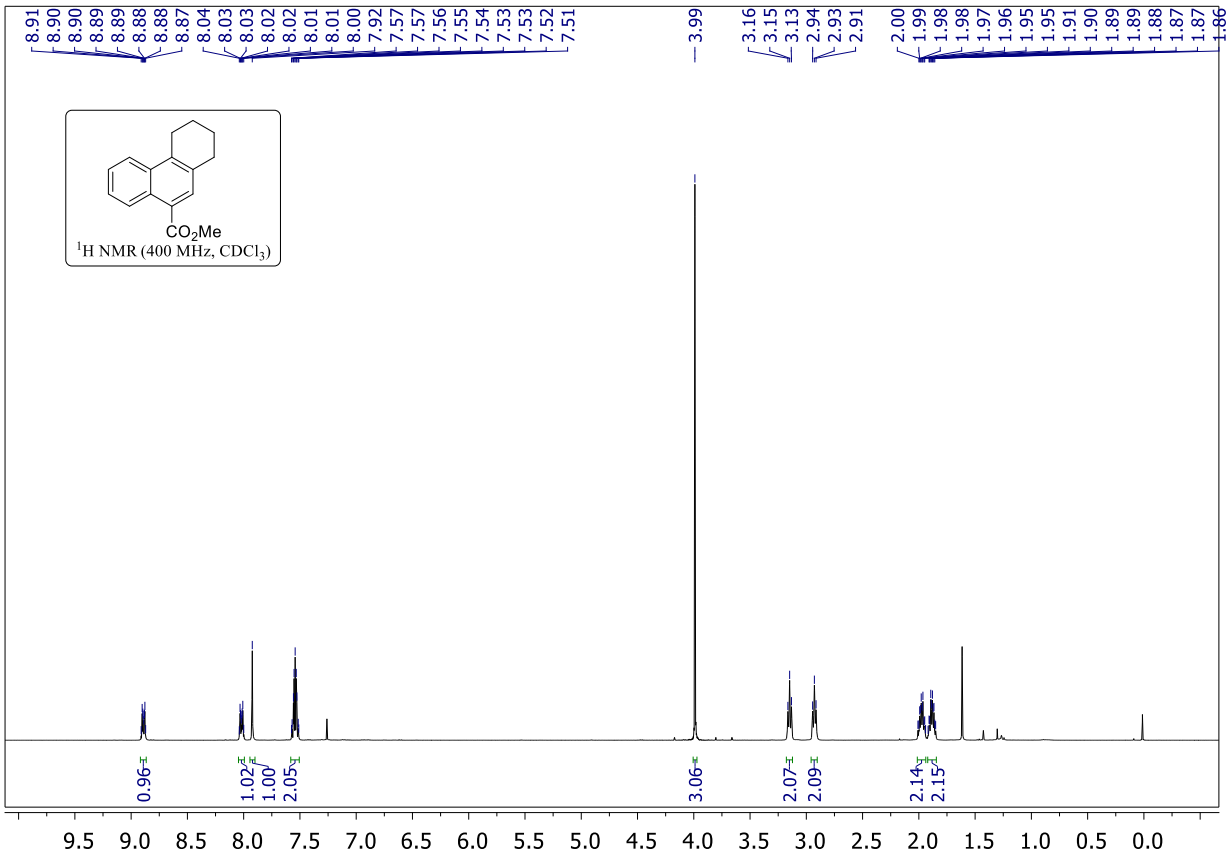


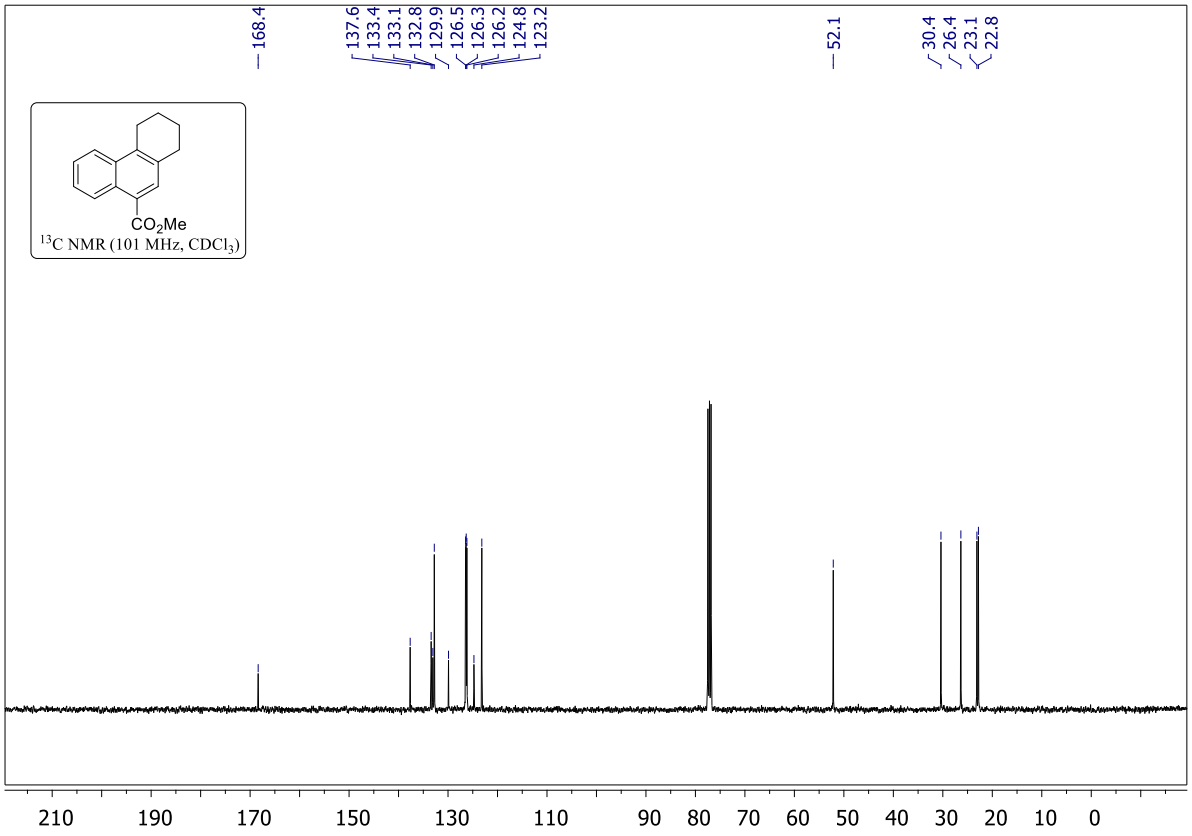
Methyl (1*Z*,7*Z*)-2-hydroxycycloocta-1,7-diene-1-carboxylate (7d):



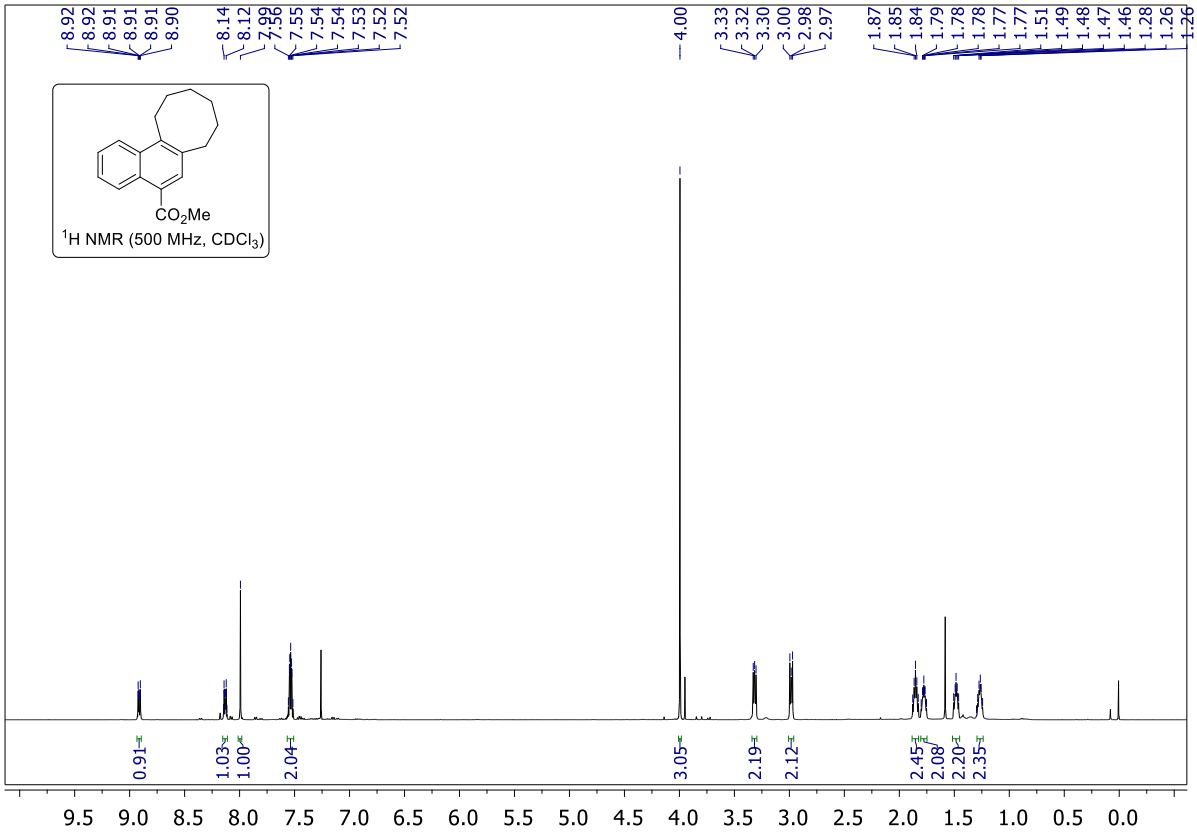


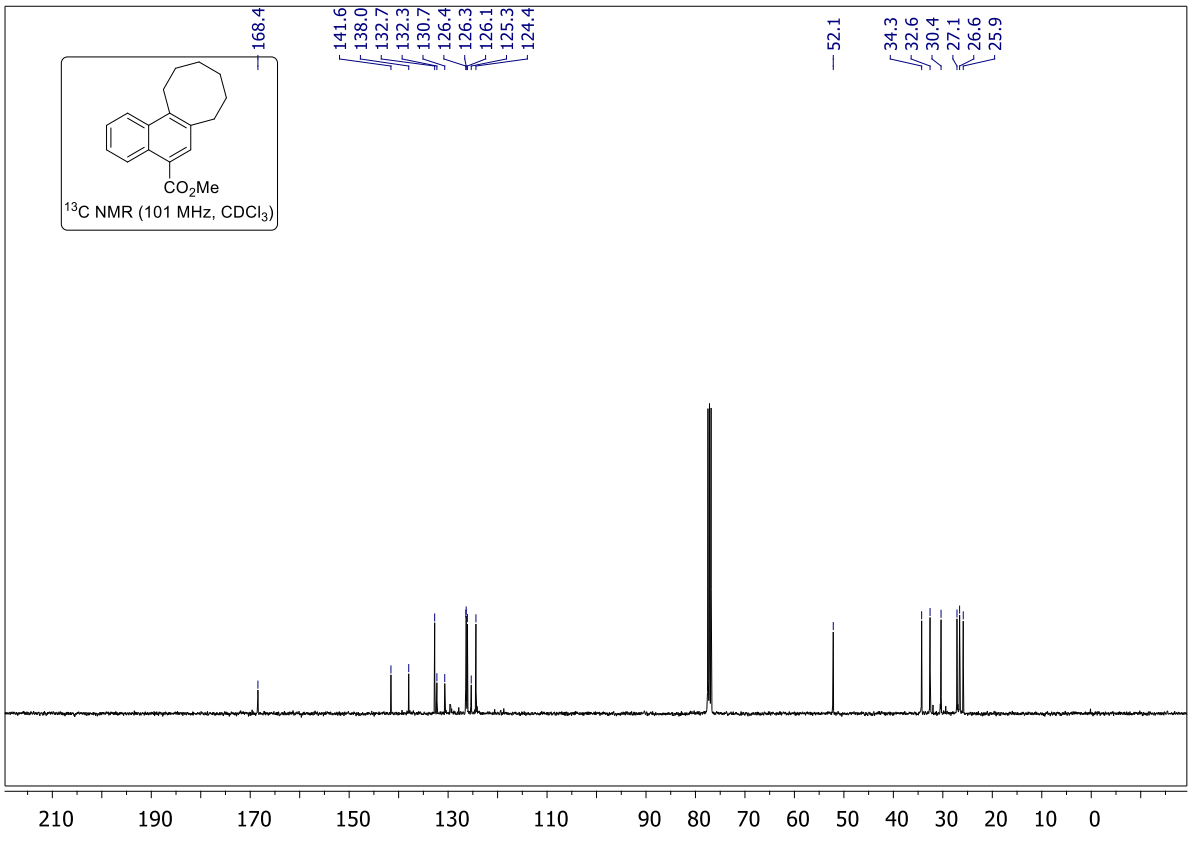
Methyl 1,2,3,4-tetrahydrophenanthrene-9-carboxylate (11k):



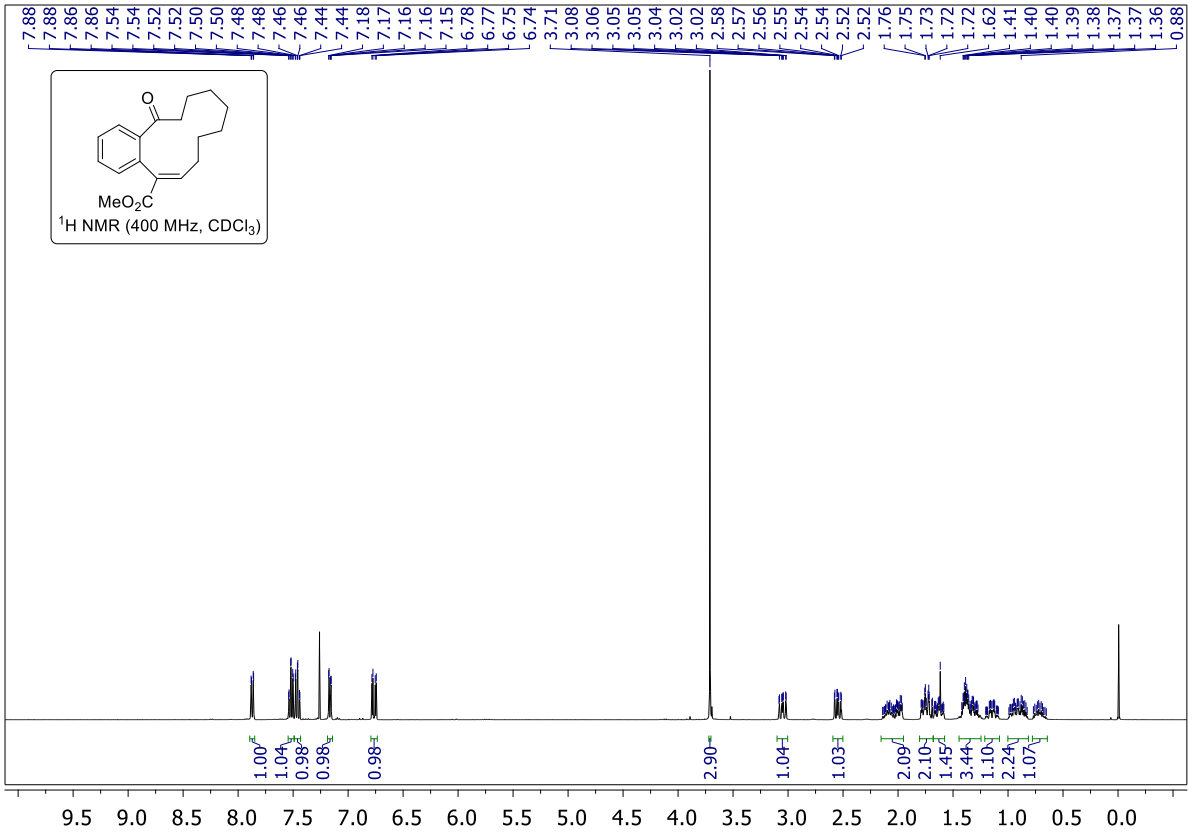


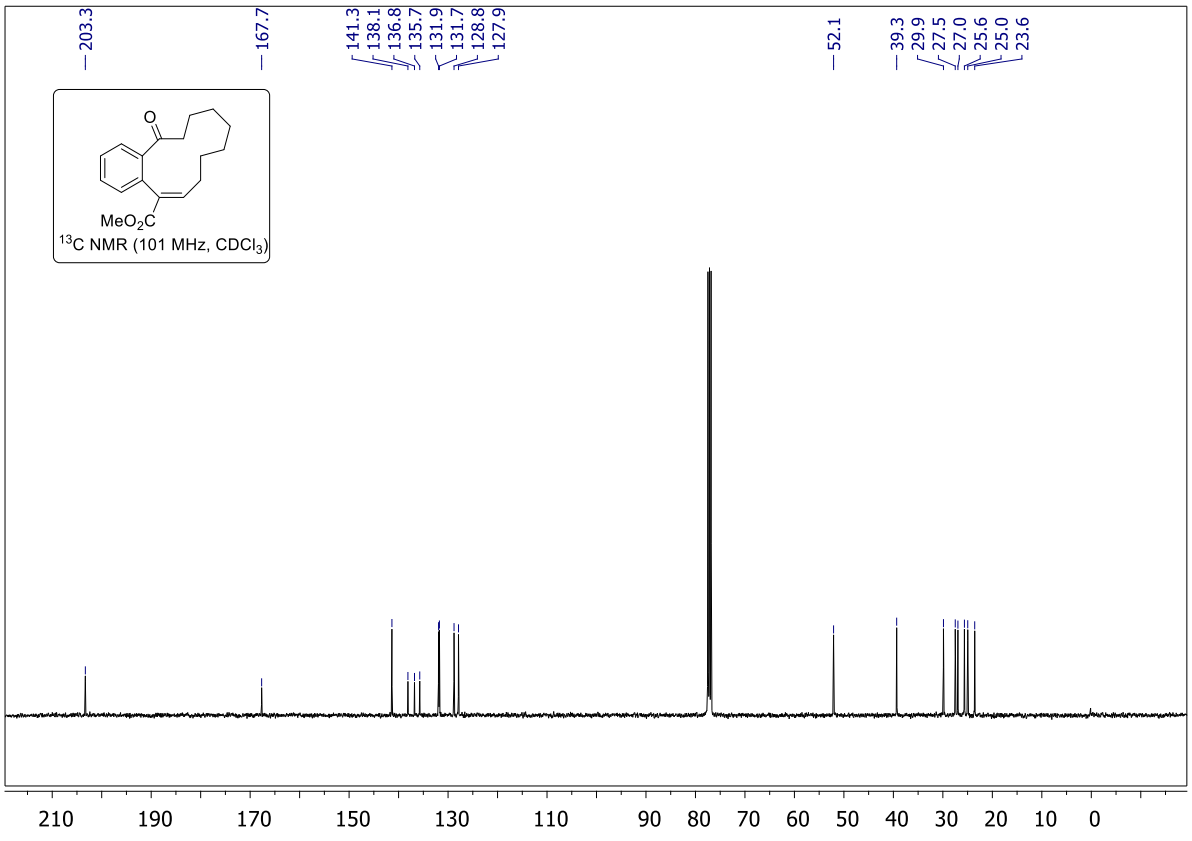
Methyl (*E*)-14-oxo-7,8,9,10,11,12,13,14-octahydrobenzo[12]annulene-5-carboxylate (11l):



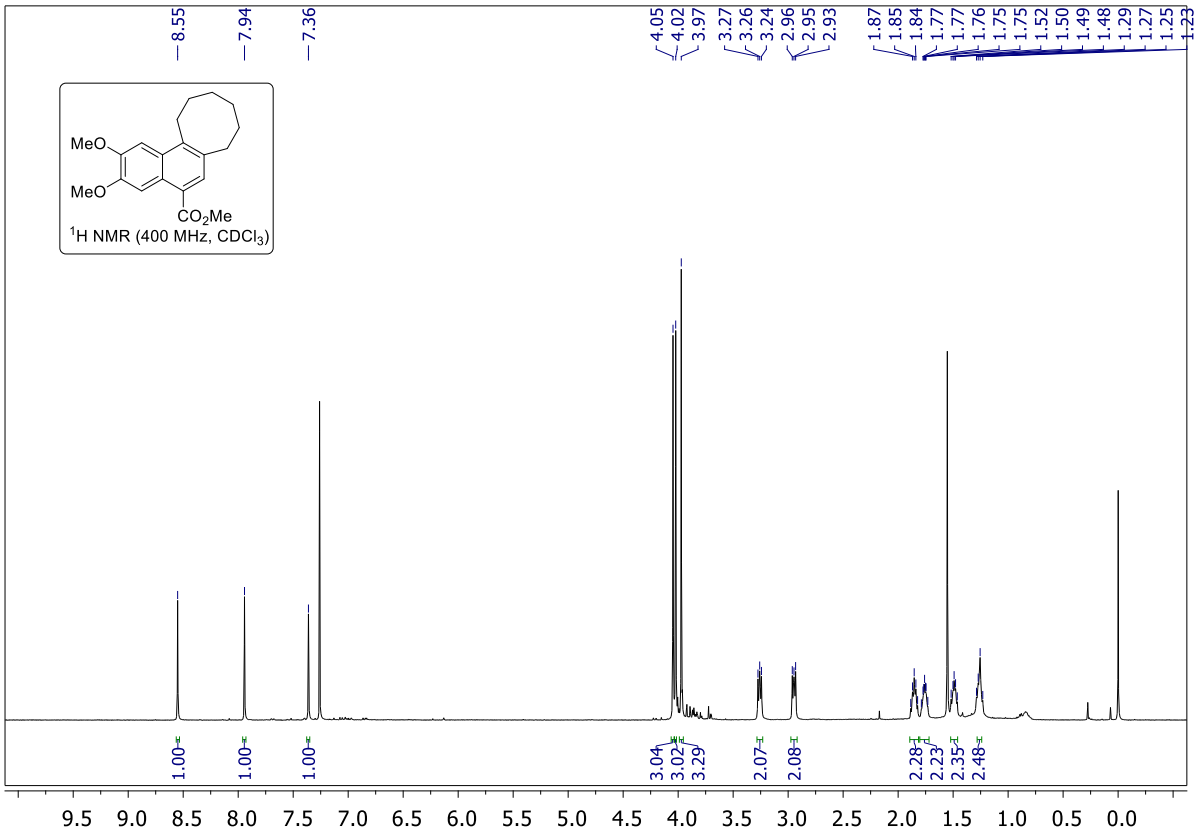


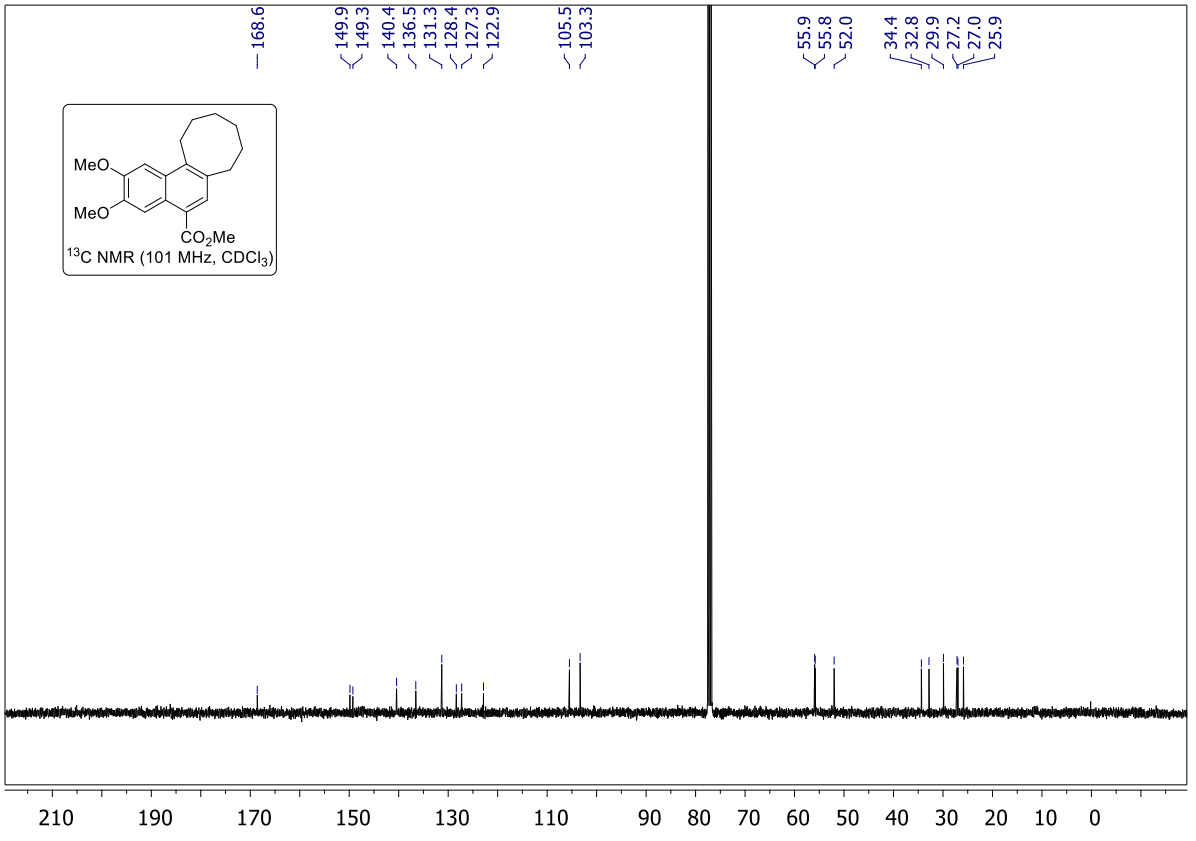
Methyl 7,8,9,10,11,12-hexahydrocycloocta[*a*]naphthalene-5-carboxylate (12a):



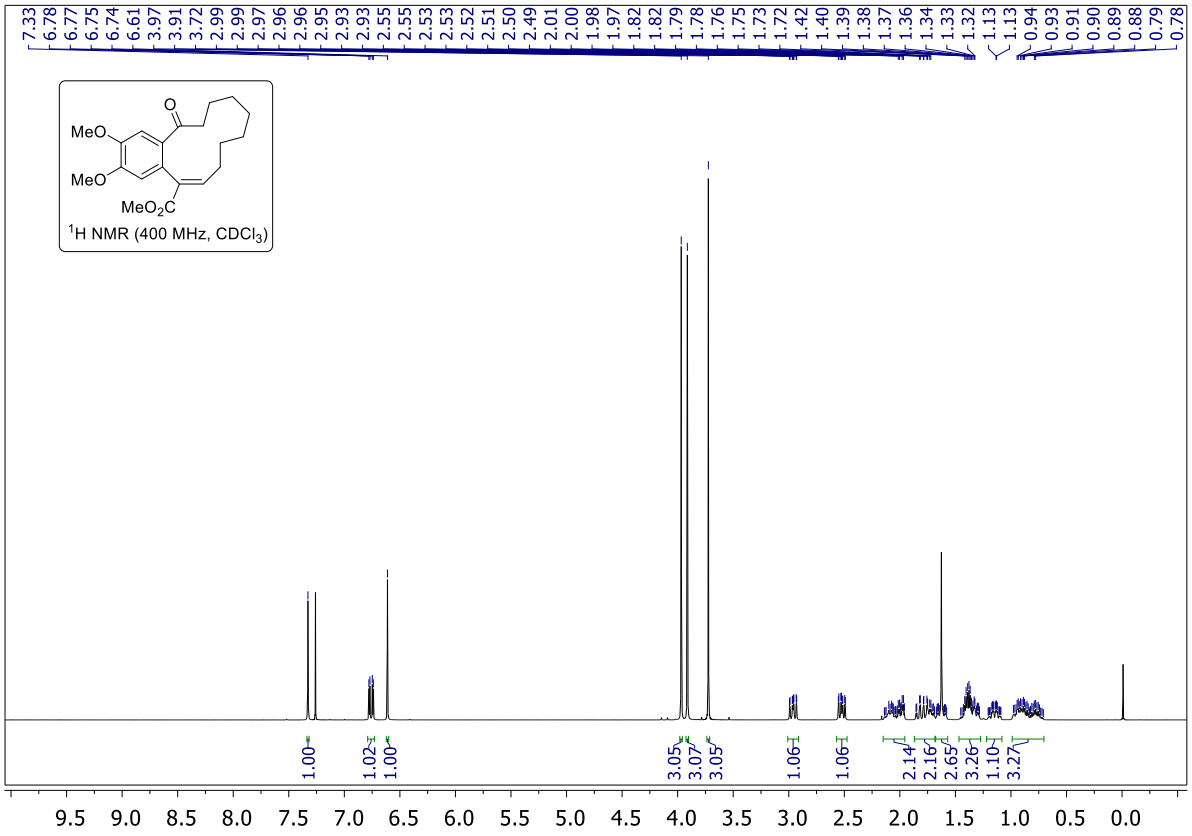


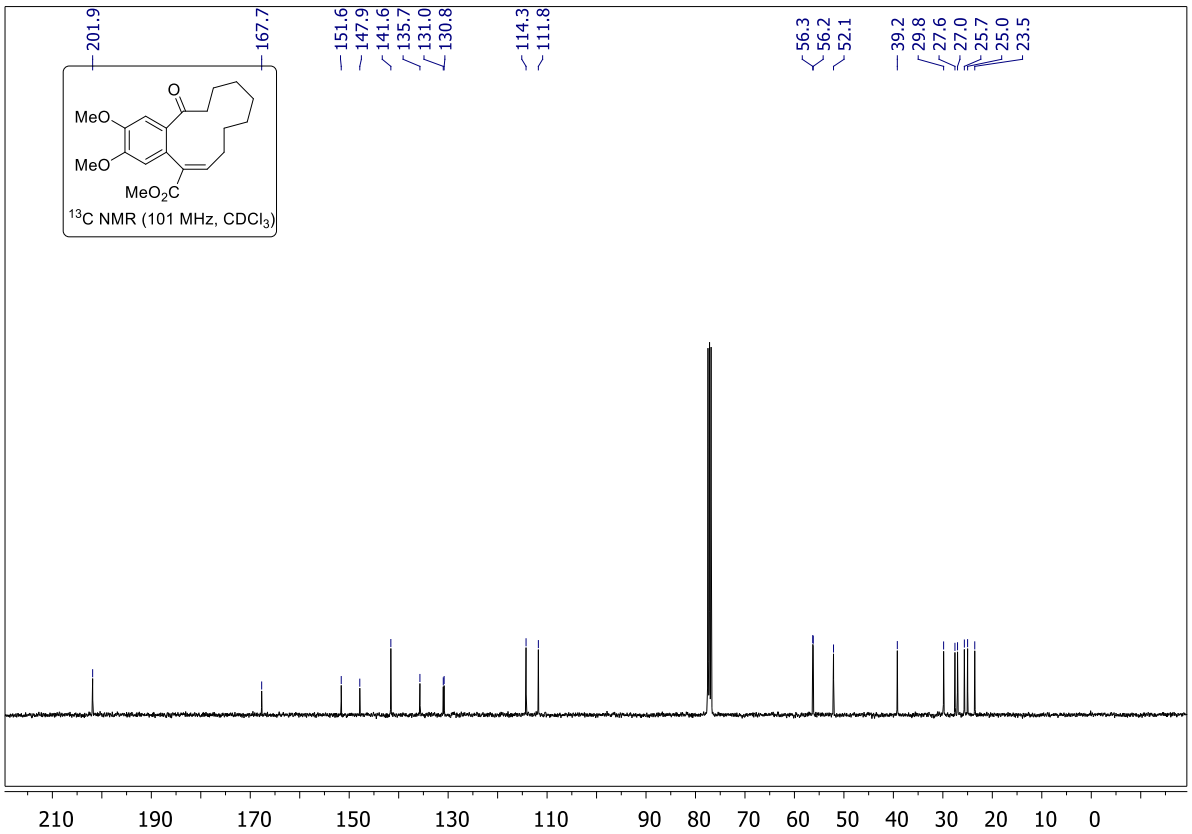
Methyl 2,3-dimethoxy-7,8,9,10,11,12-hexahydrocycloocta[*a*]naphthalene-5-carboxylate (11m):



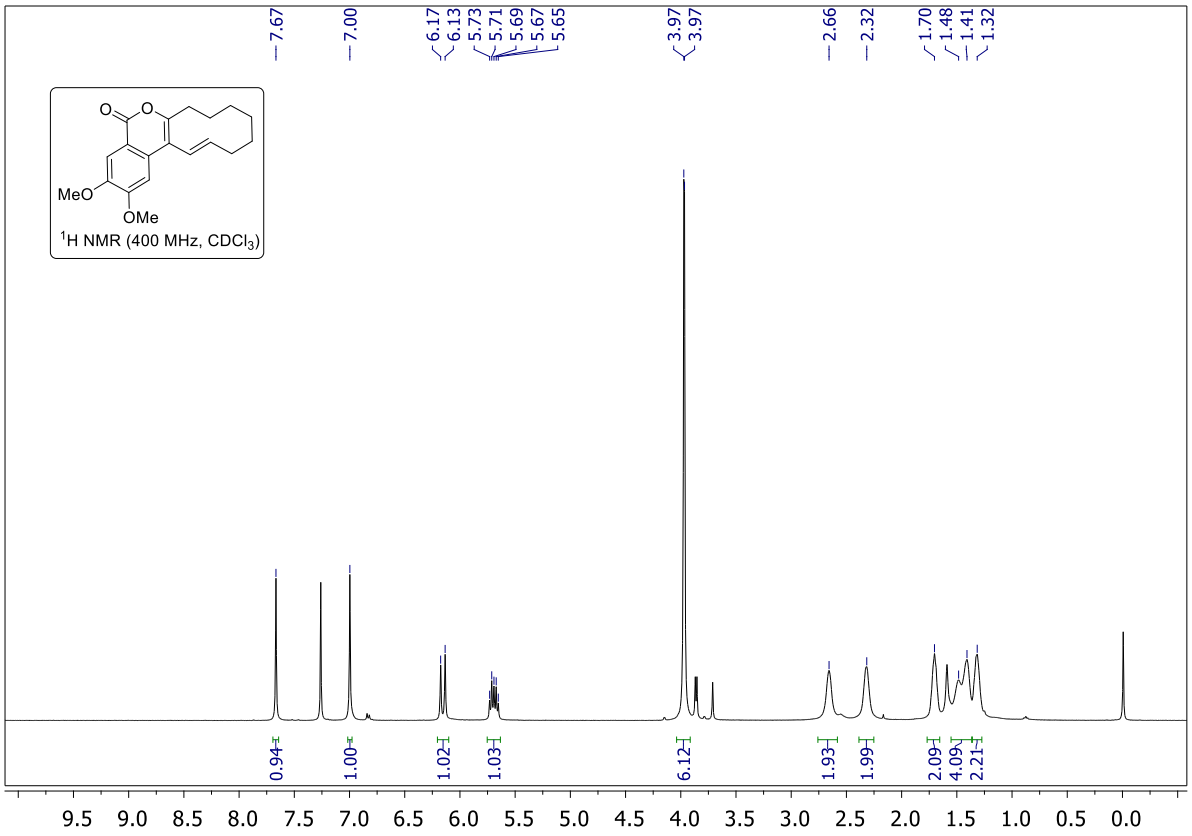


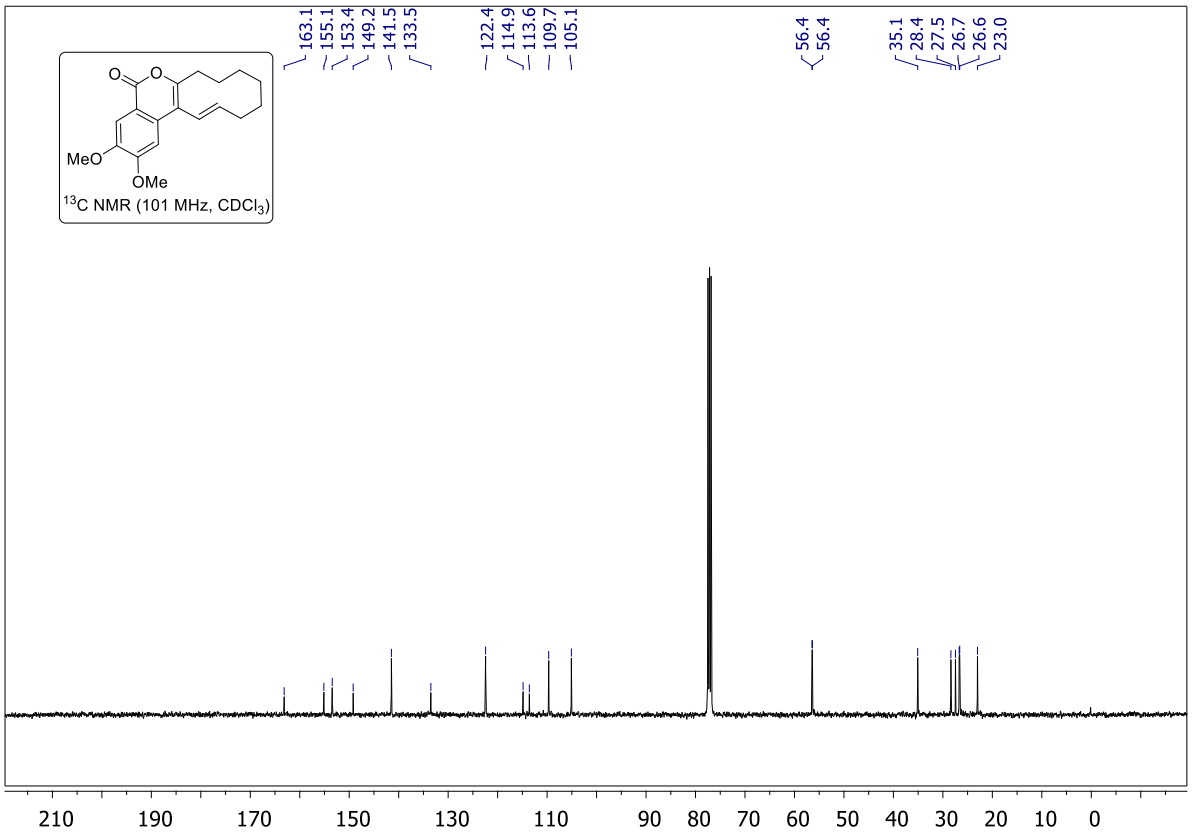
Methyl (*Z*)-2,3-dimethoxy-14-oxo-7,8,9,10,11,12,13,14-octahydrobenzo[12]annulene-5-carboxylate (12b):



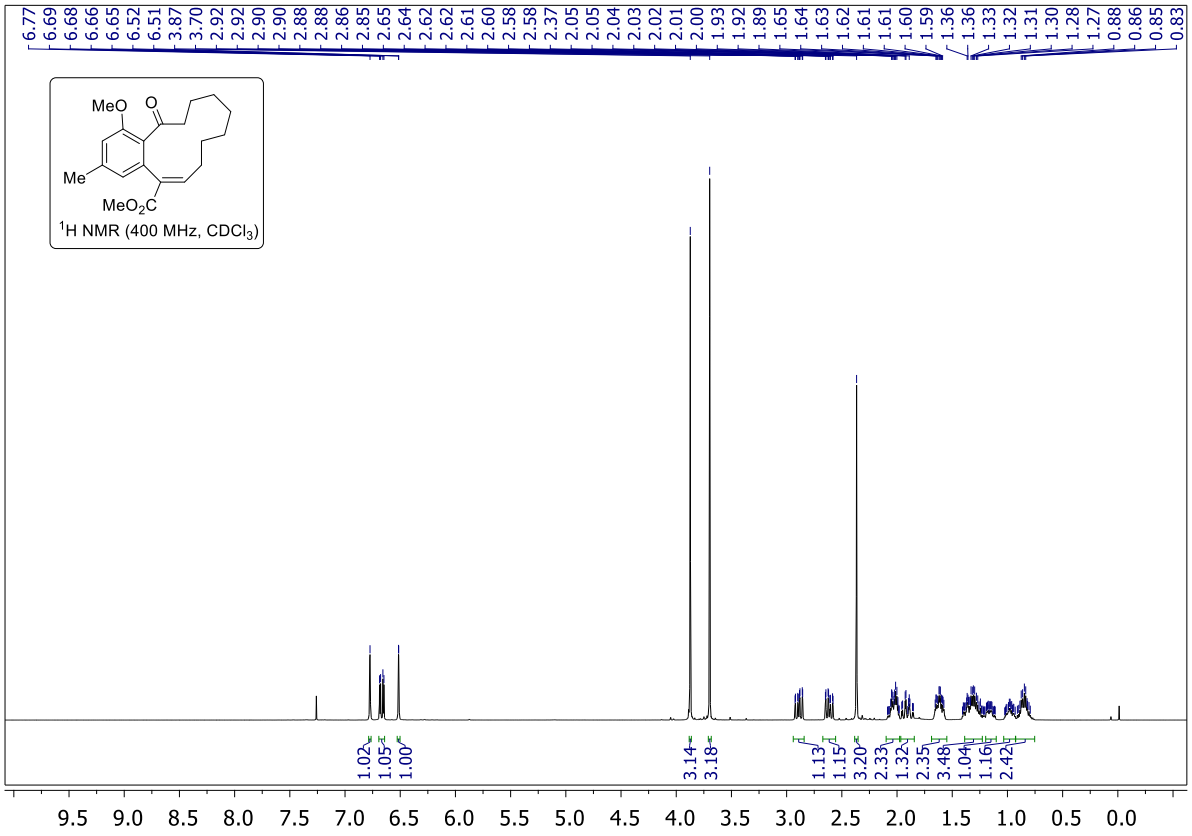


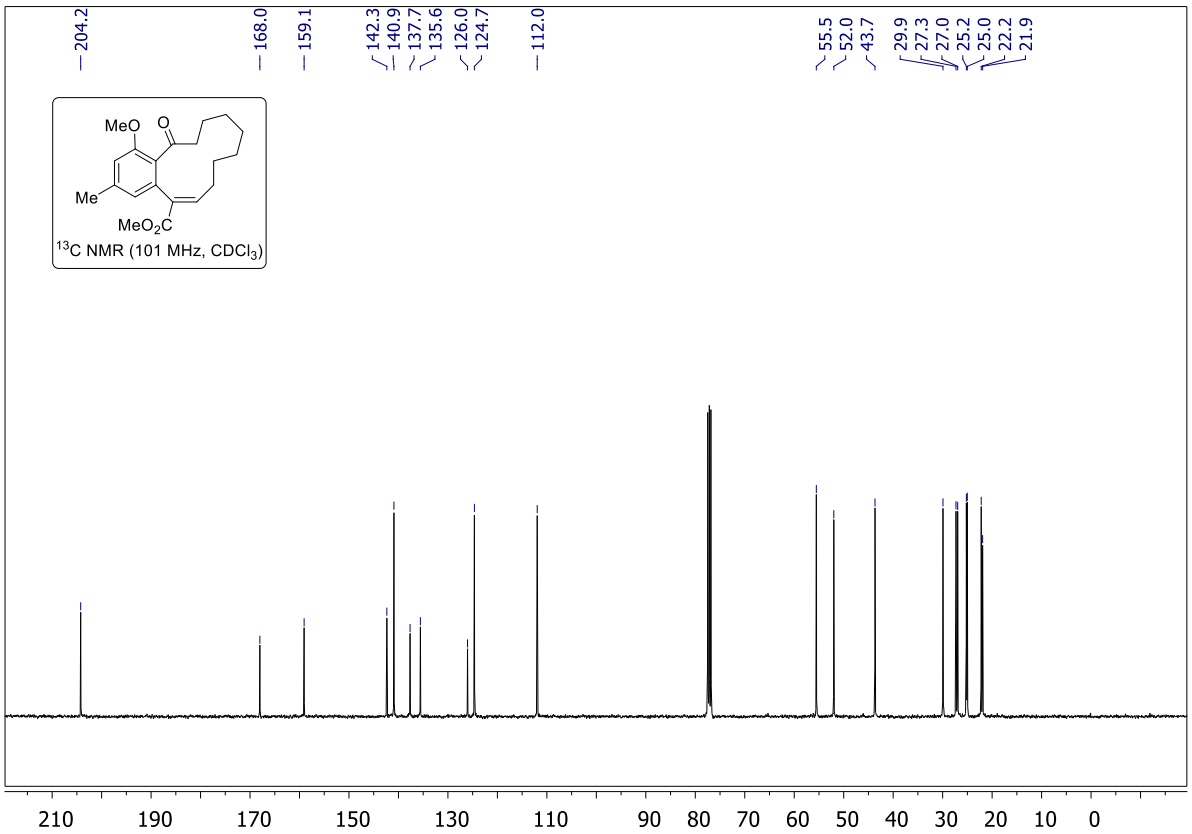
(*E*)-2,3-Dimethoxy-9,10,11,12,13,14-hexahydro-5*H*-cyclodeca[*c*]isochromen-5-one (13):



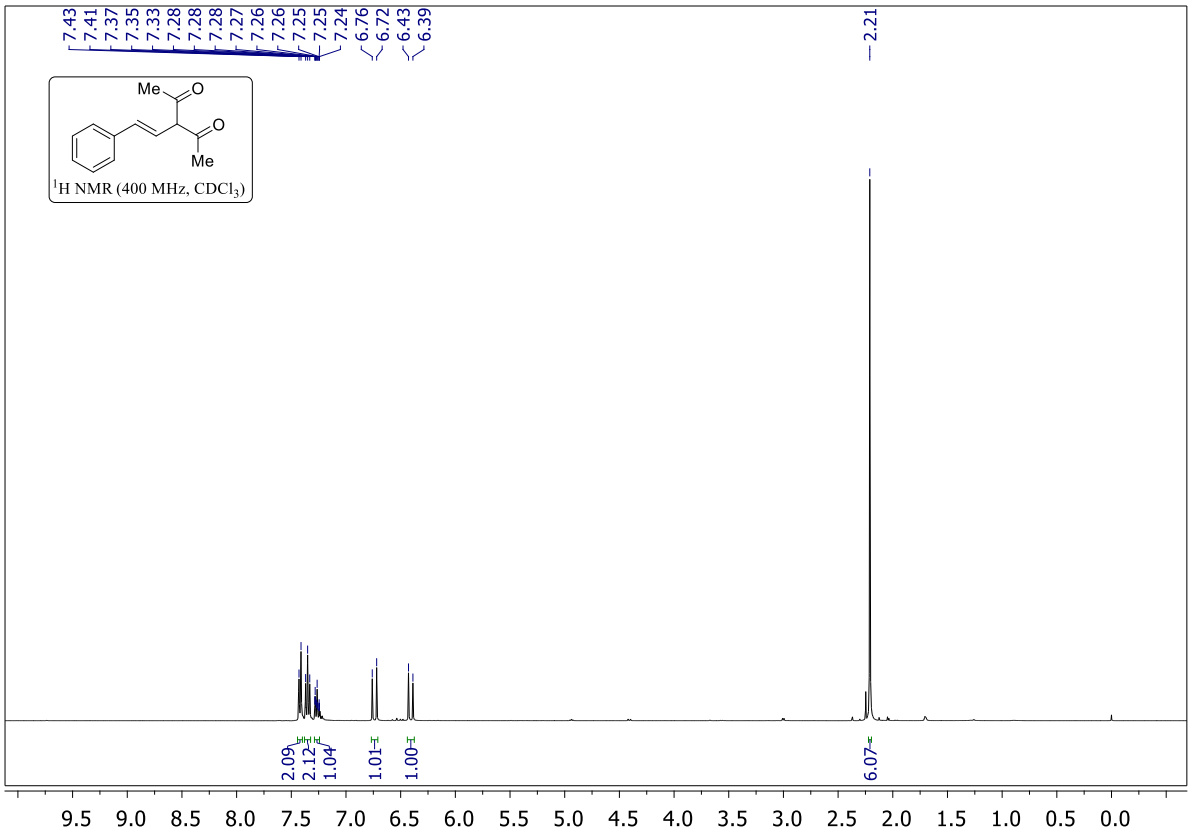


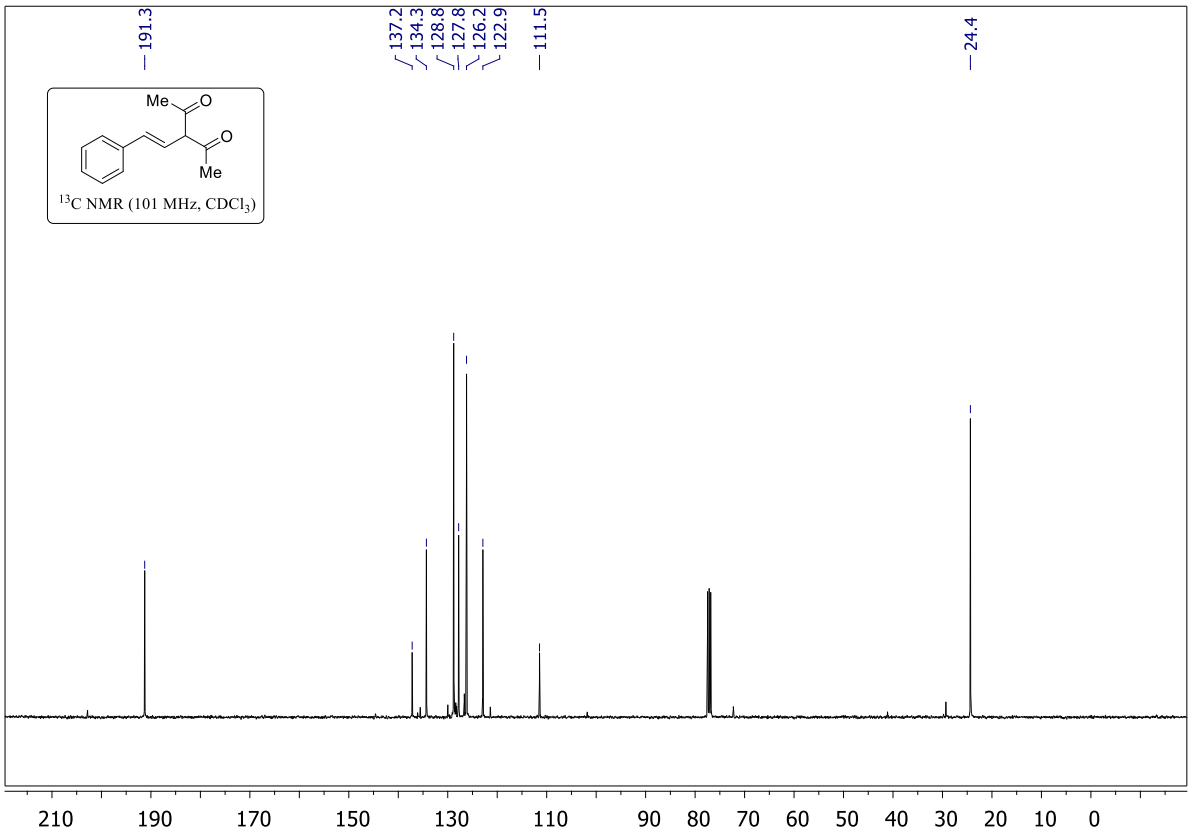
Methyl (*Z*)-1-methoxy-3-methyl-14-oxo-7,8,9,10,11,12,13,14-octahydrobenzo[12]annulene-5-carboxylate (12c):



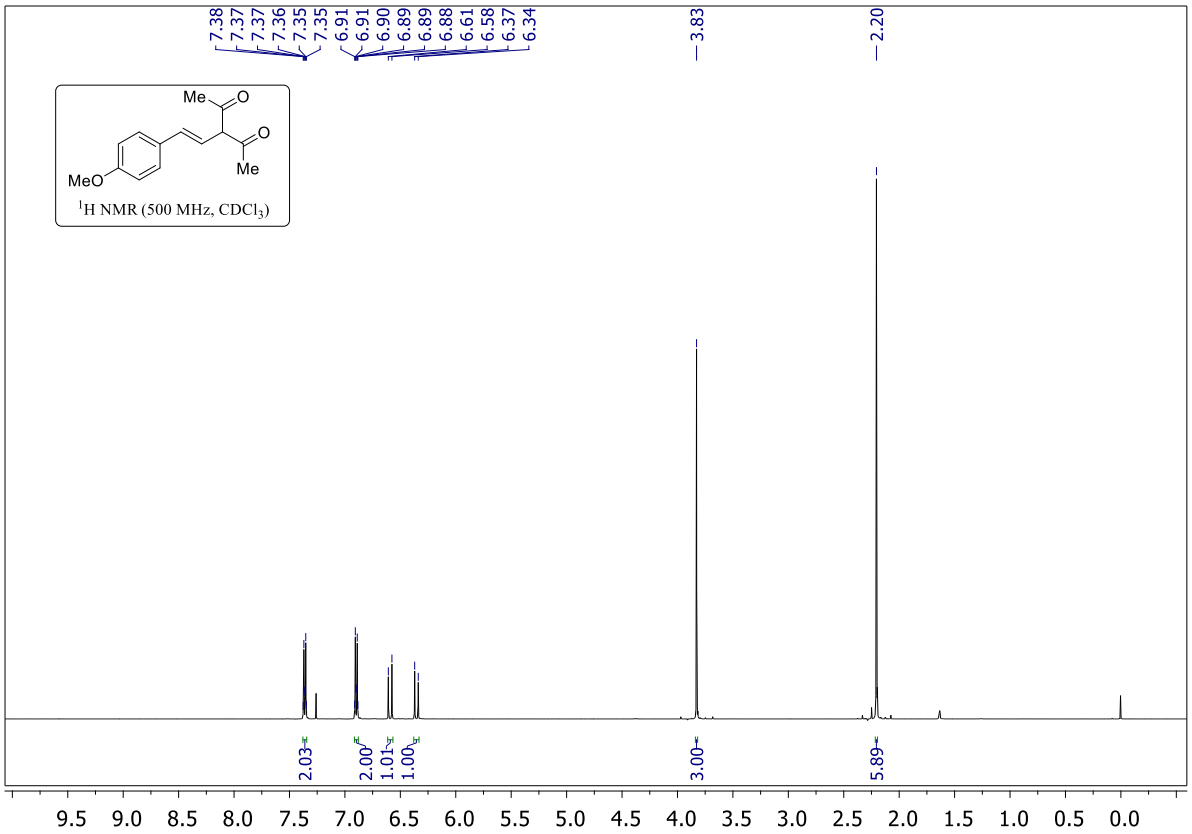


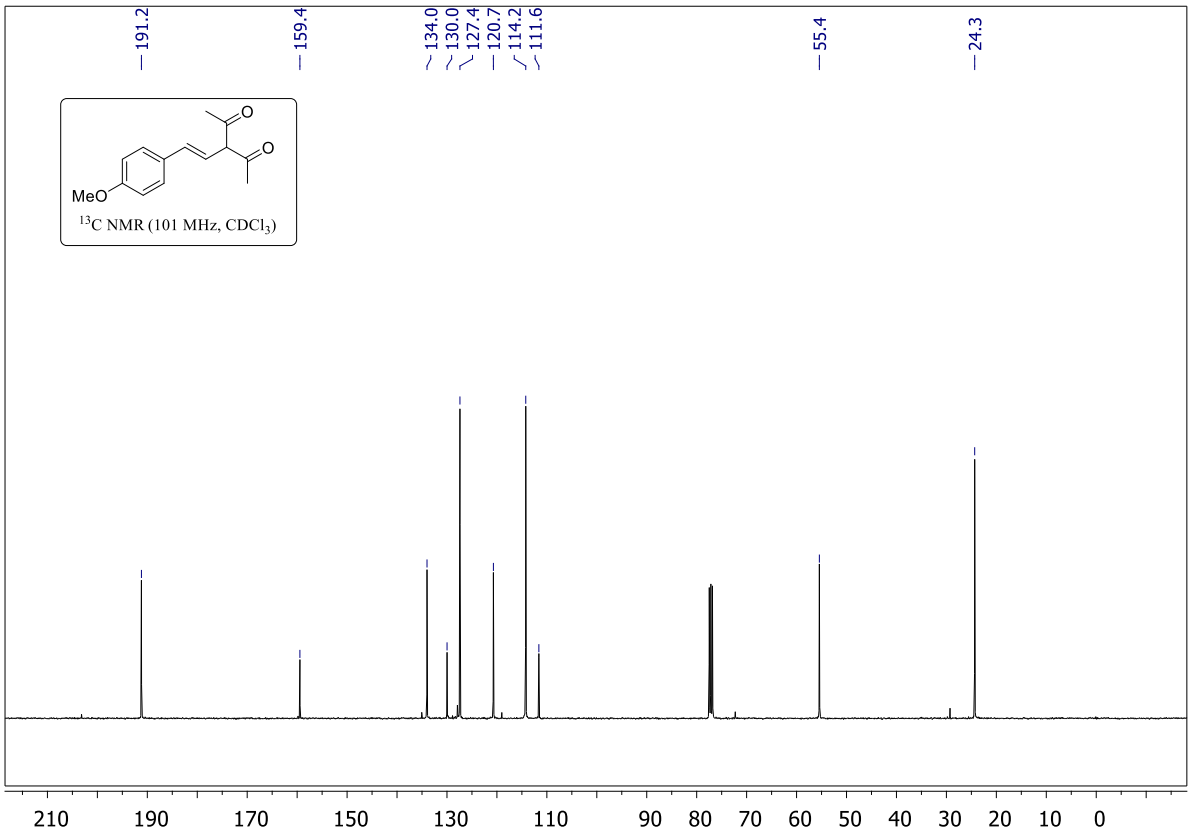
(*E*)-3-Styrylpentane-2,4-dione (14a):



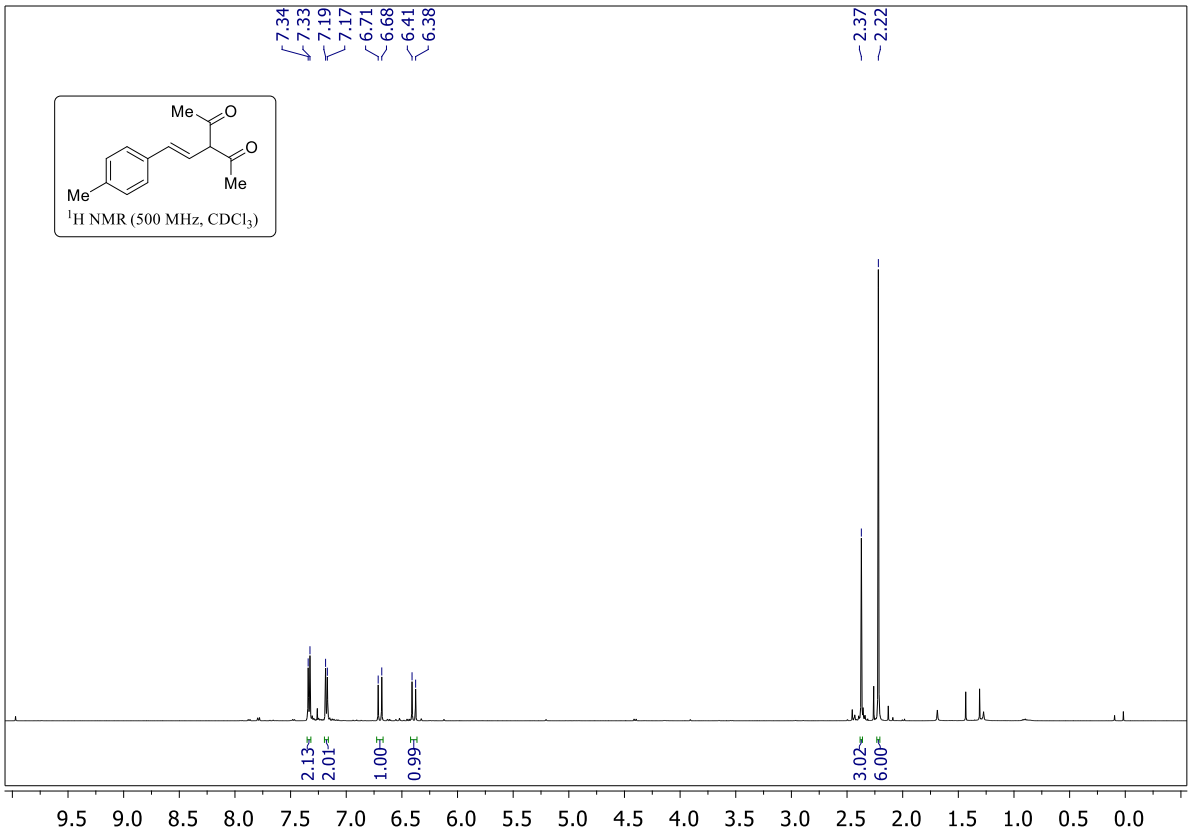


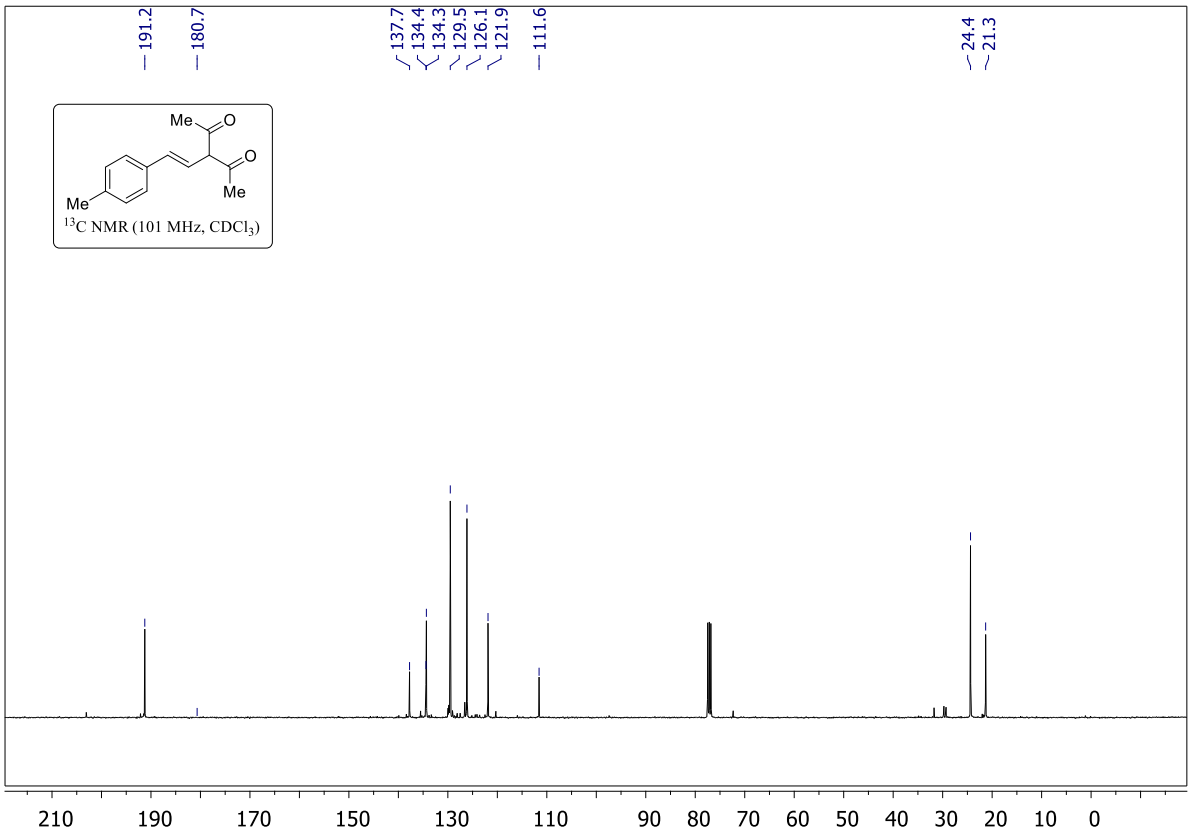
(*E*)-3-(4-Methoxystyryl)pentane-2,4-dione (14b):



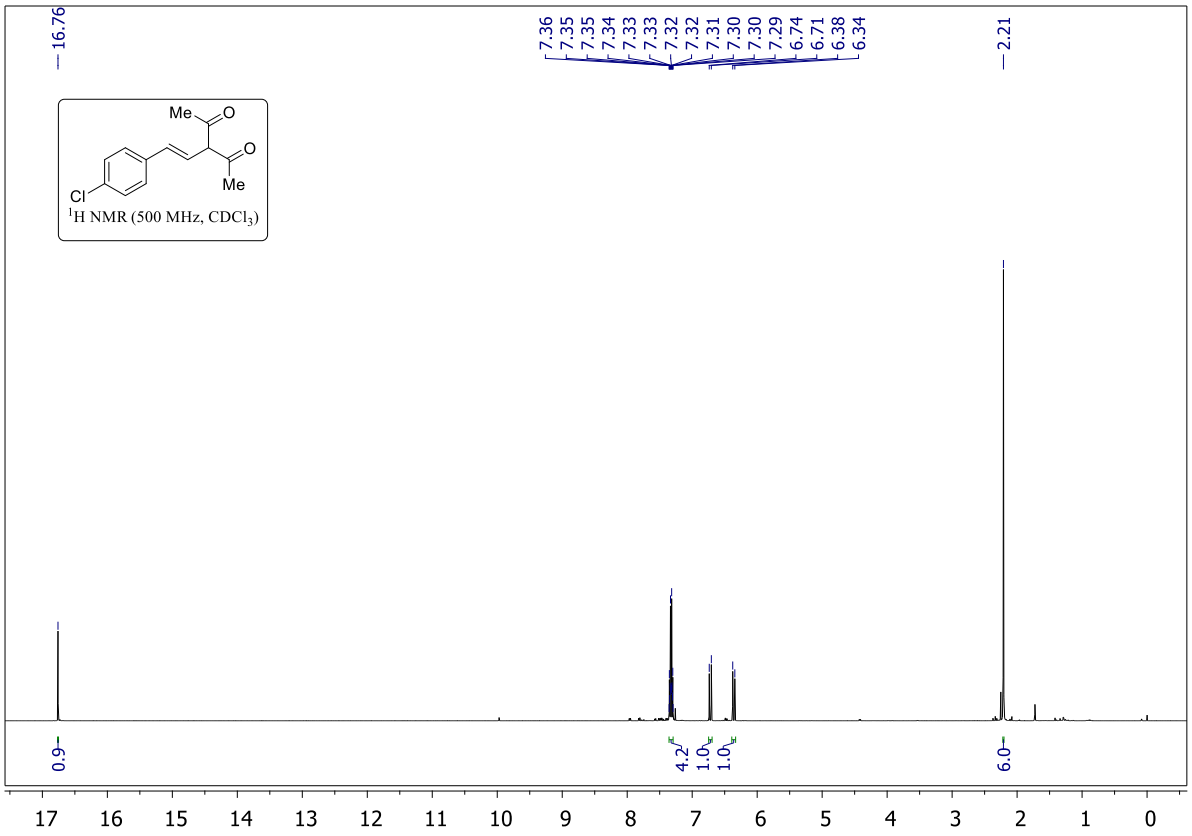


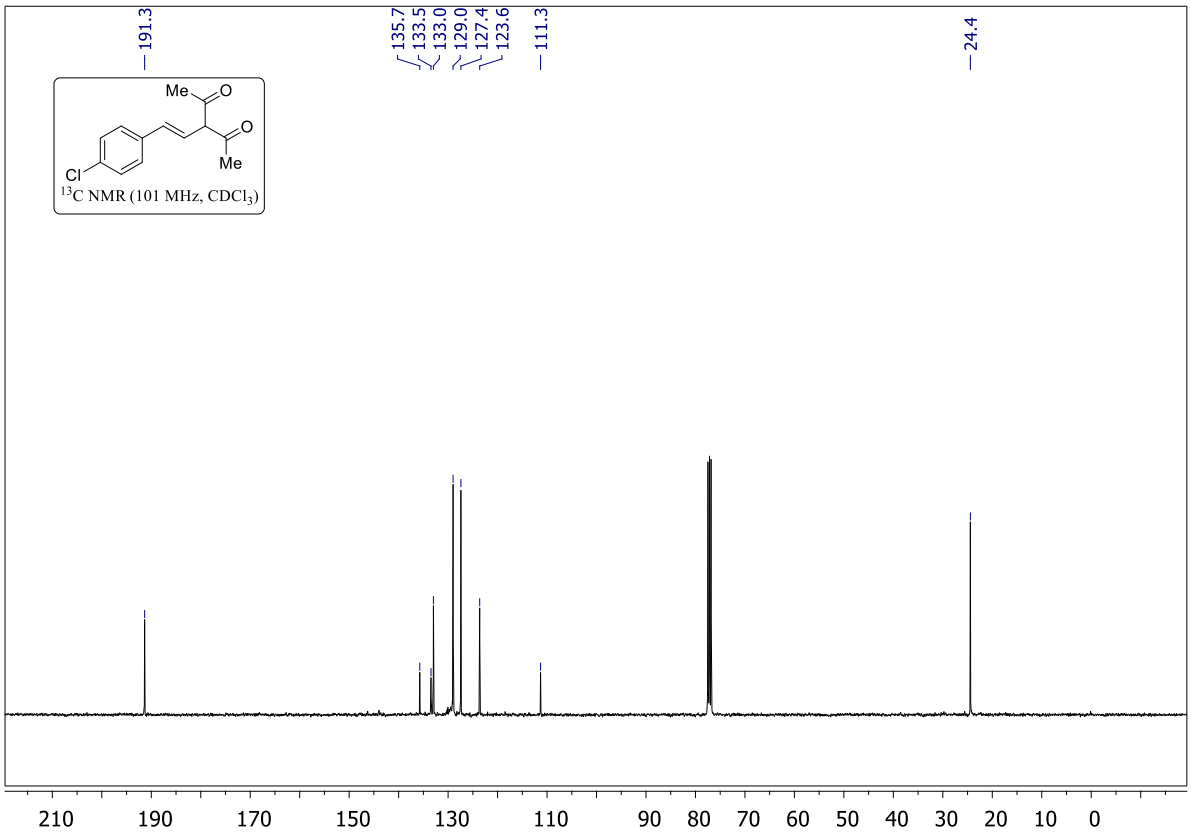
(*E*)-3-(4-Methylstyryl)pentane-2,4-dione (14c):



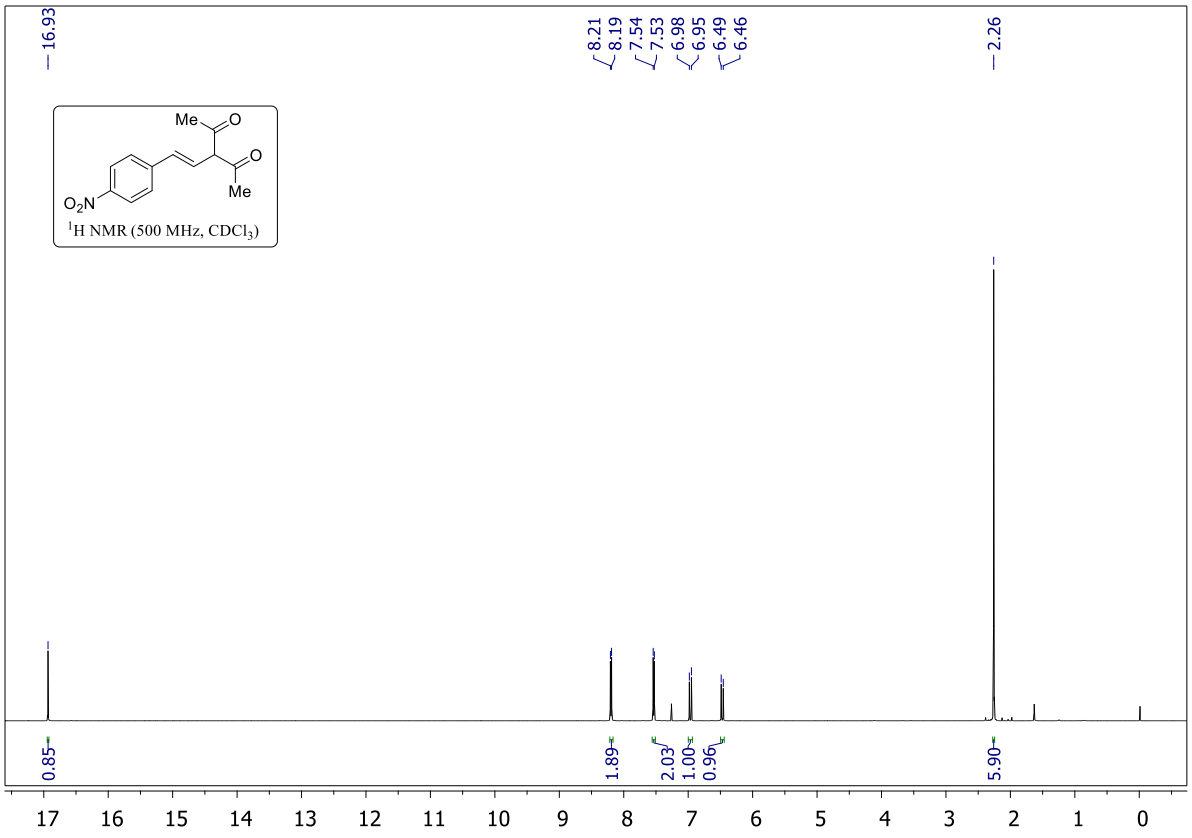


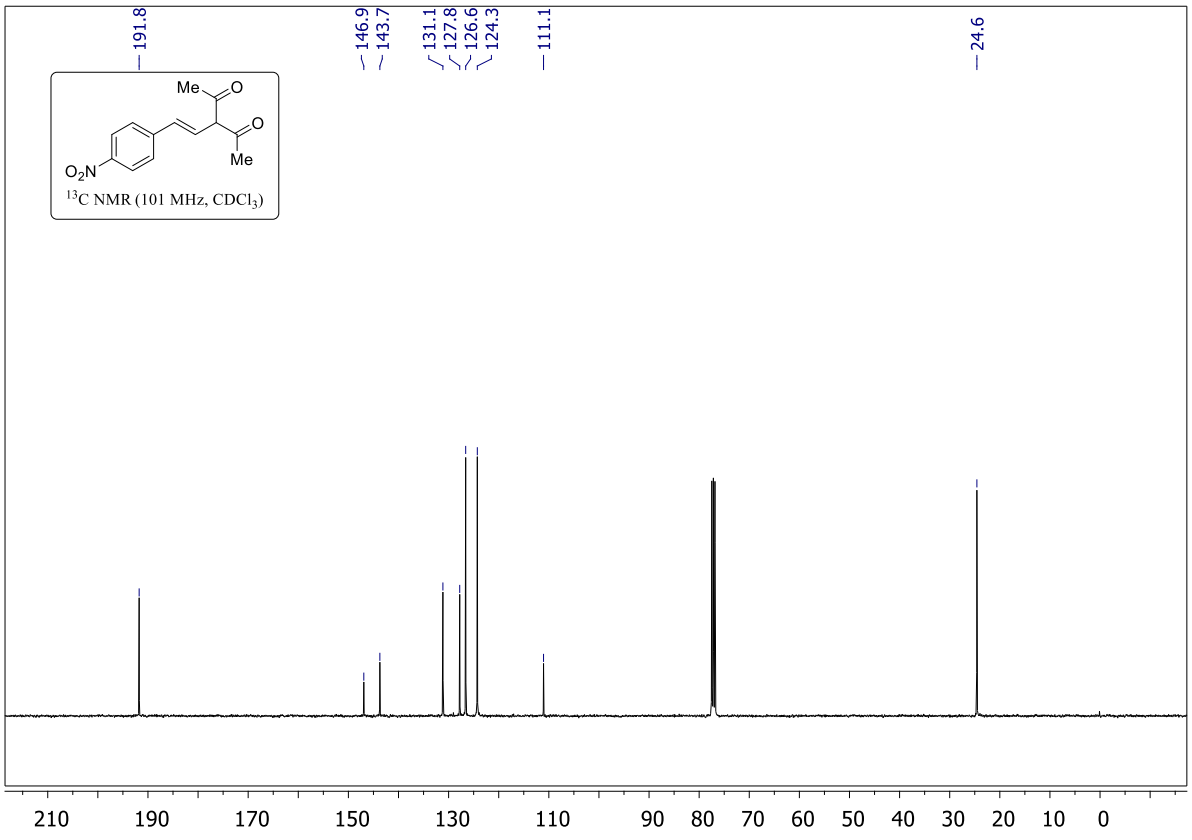
(*E*)-3-(4-Chlorostyryl)pentane-2,4-dione (14d):



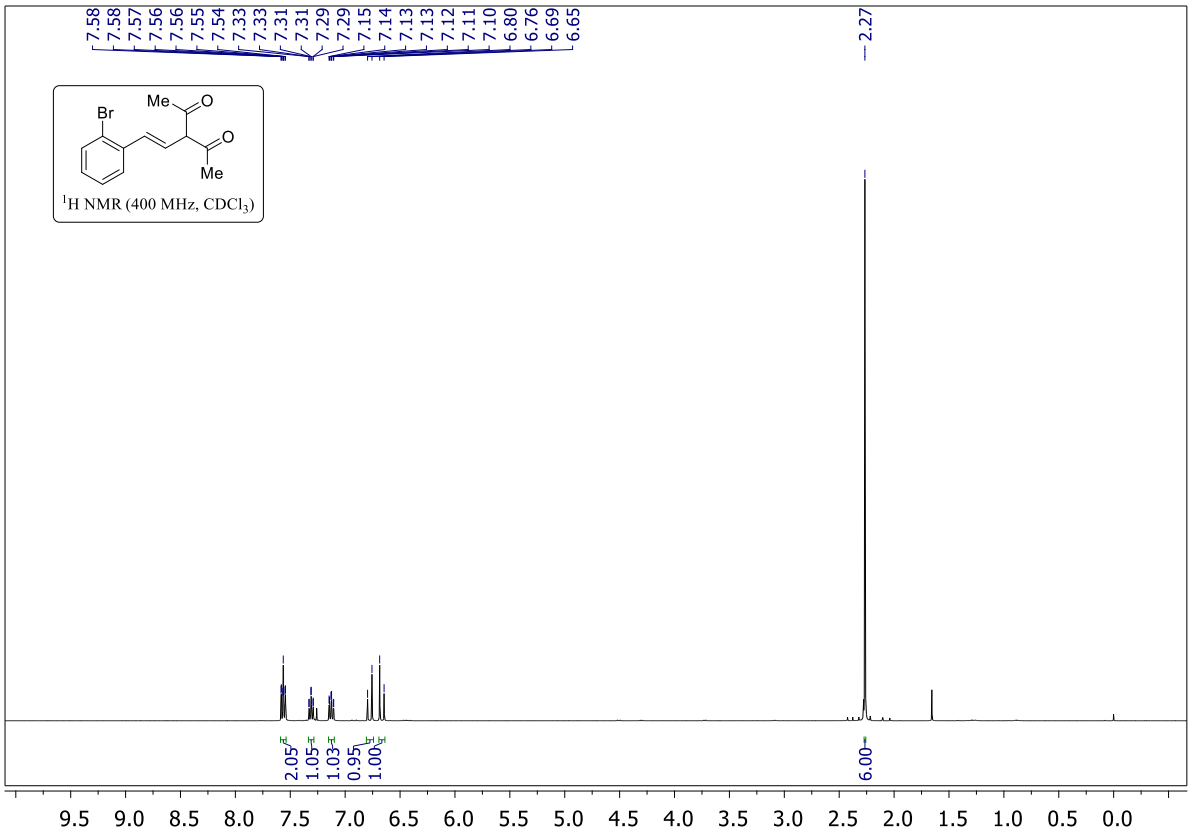


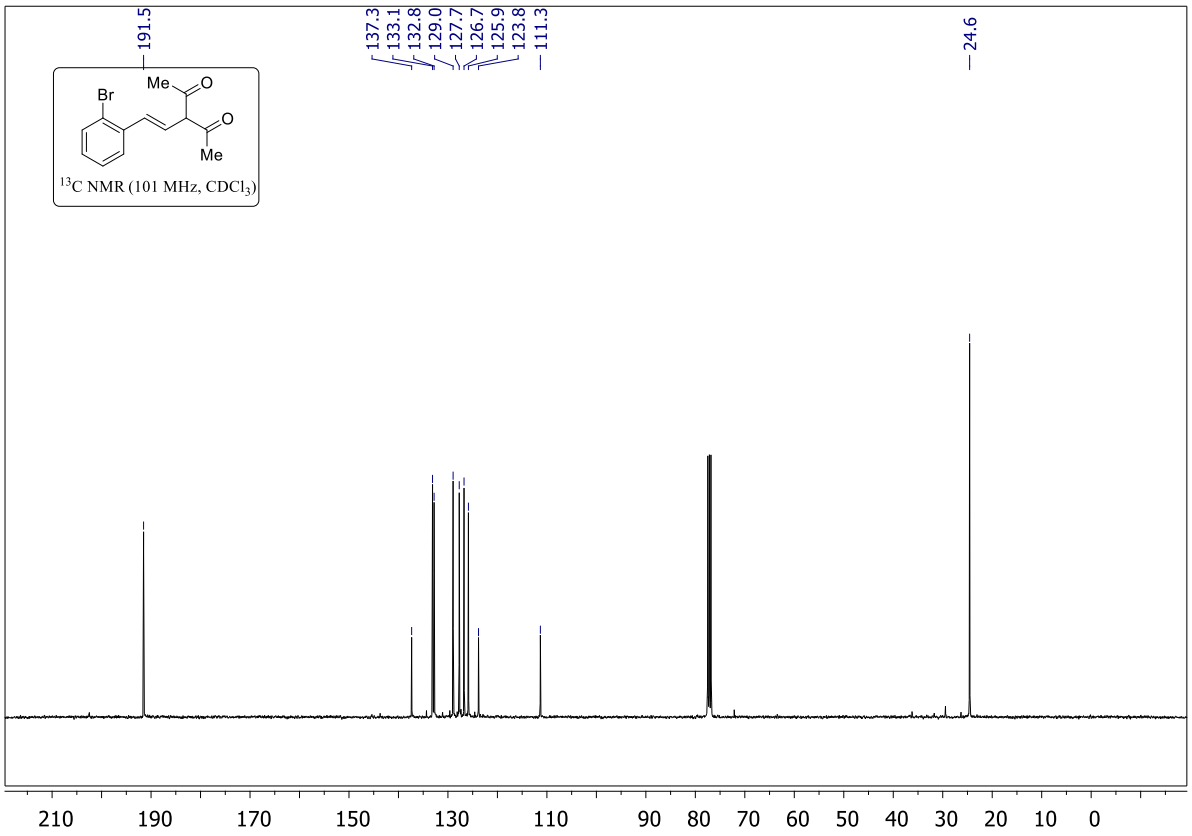
(*E*)-3-(4-Nitrostyryl)pentane-2,4-dione (14e):



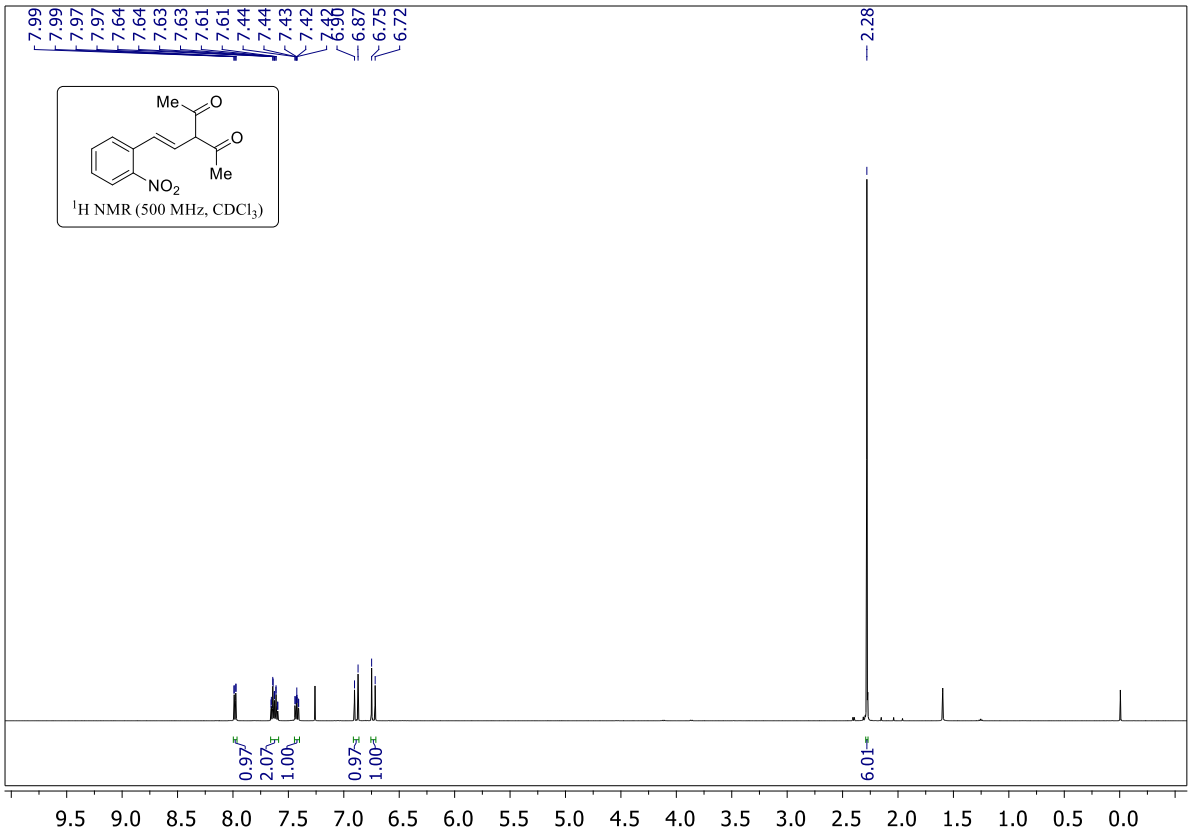


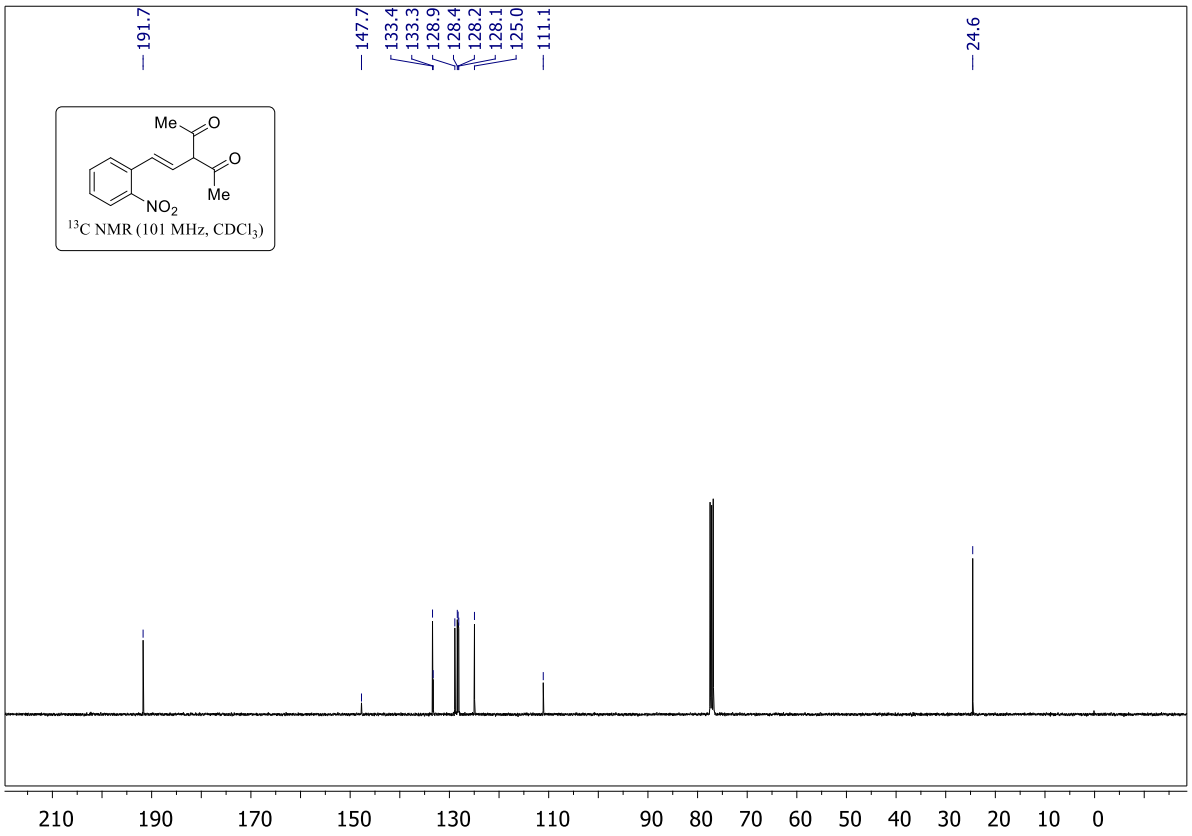
(*E*)-3-(2-Bromostyryl)pentane-2,4-dione (14f):



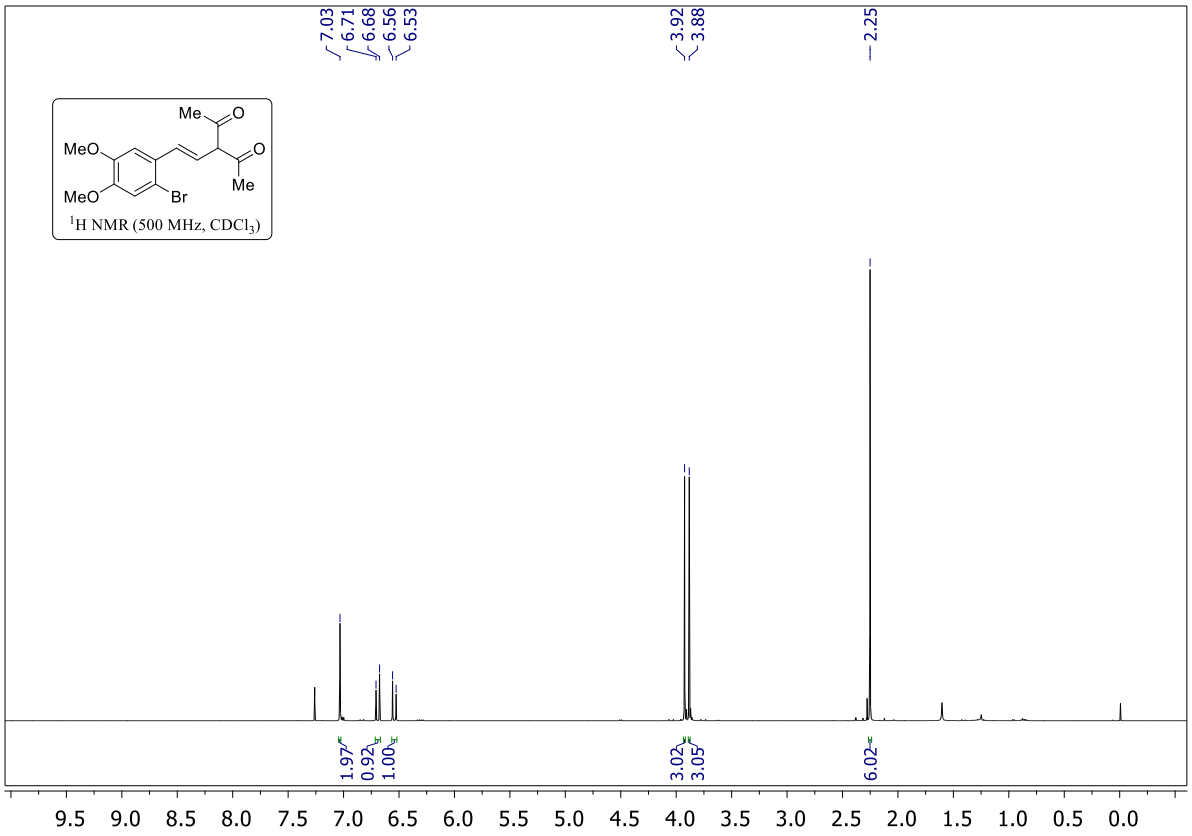


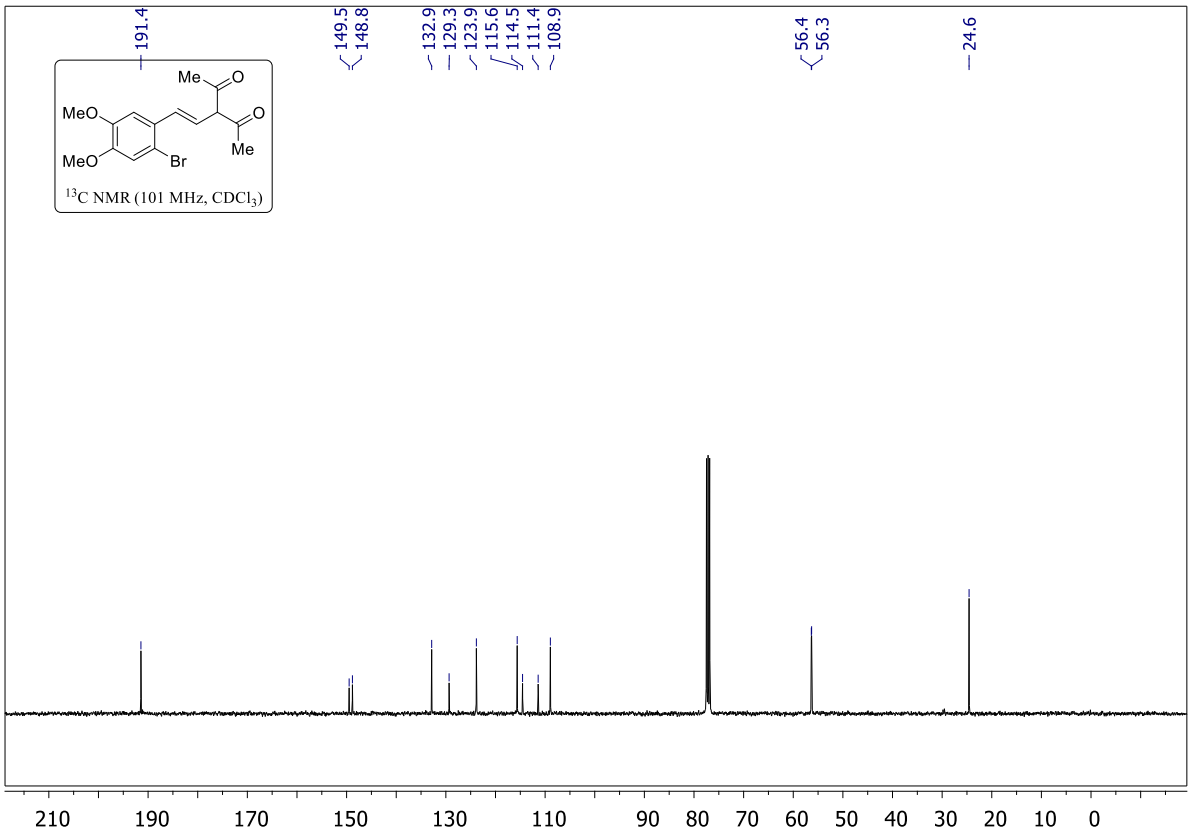
(*E*)-3-(2-Nitrostyryl)pentane-2,4-dione (14g):



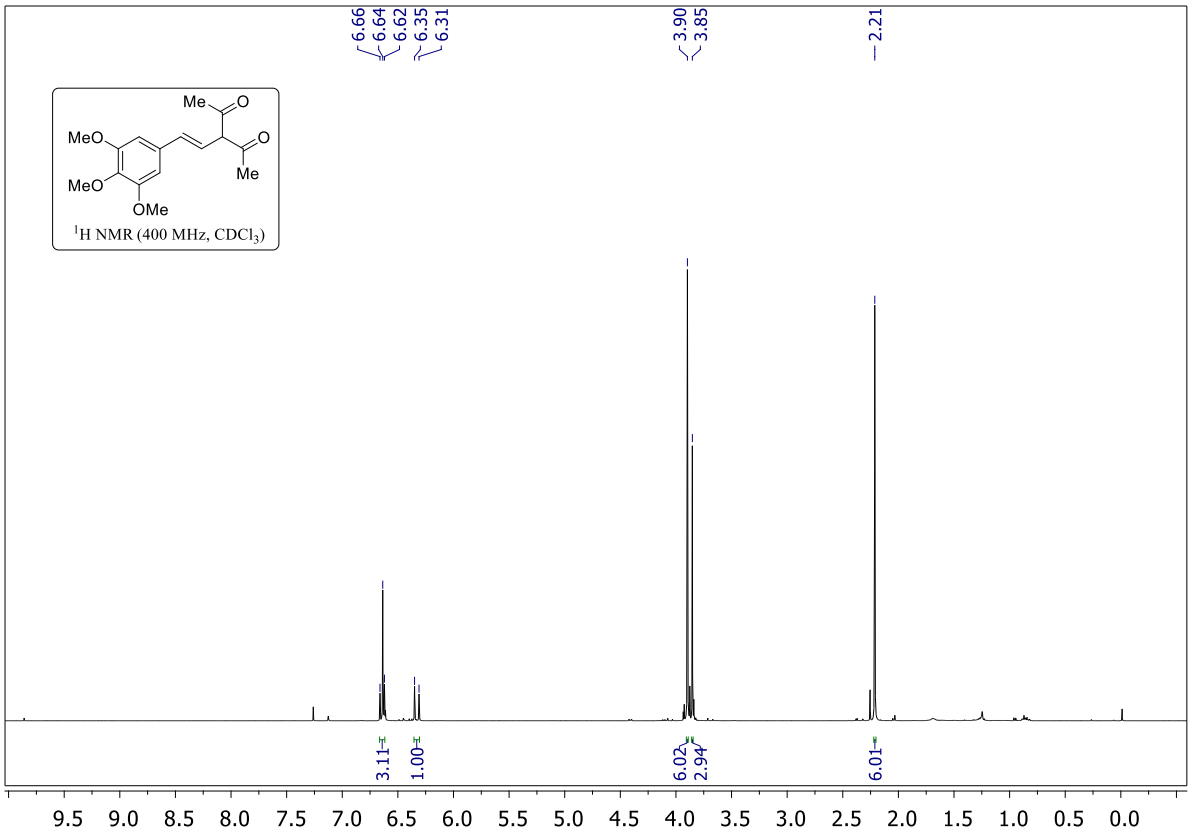


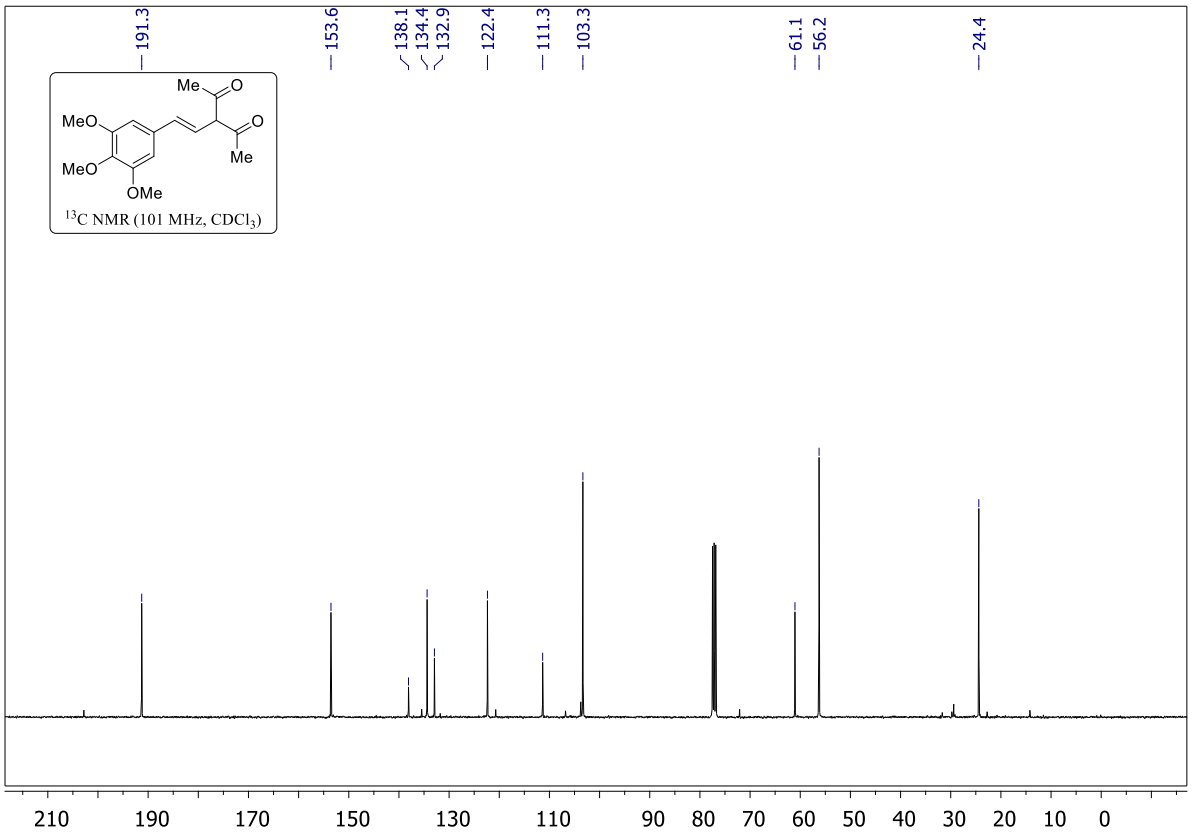
(*E*)-3-(2-Bromo-4,5-dimethoxystyryl)pentane-2,4-dione (14h):



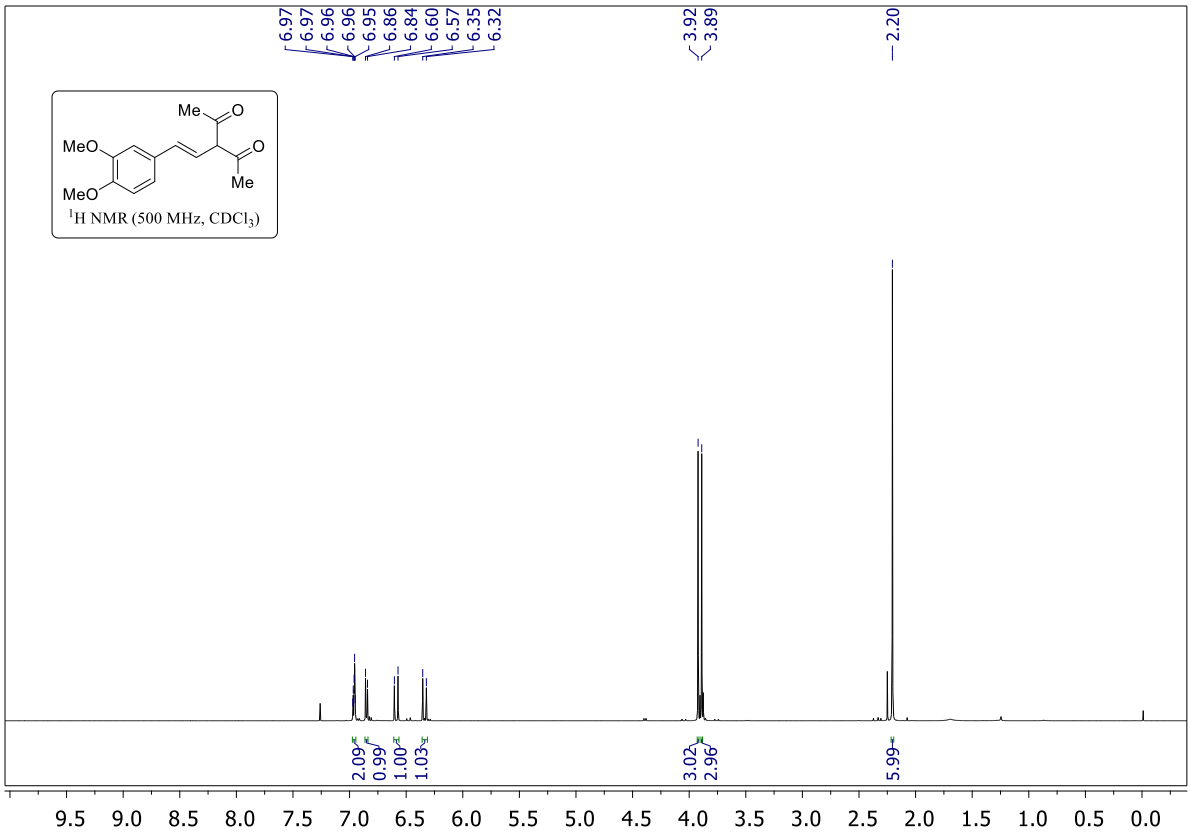


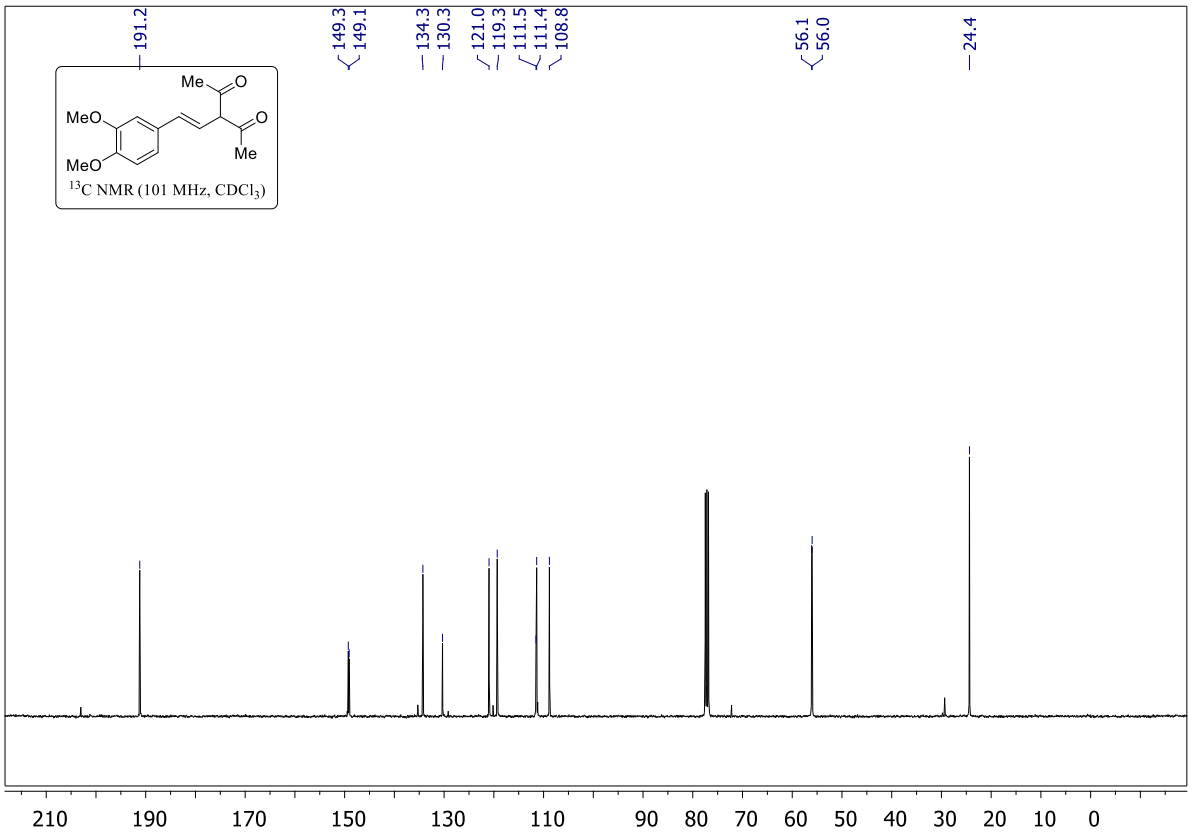
(*E*)-3-(3,4,5-Trimethoxystyryl)pentane-2,4-dione (14i):



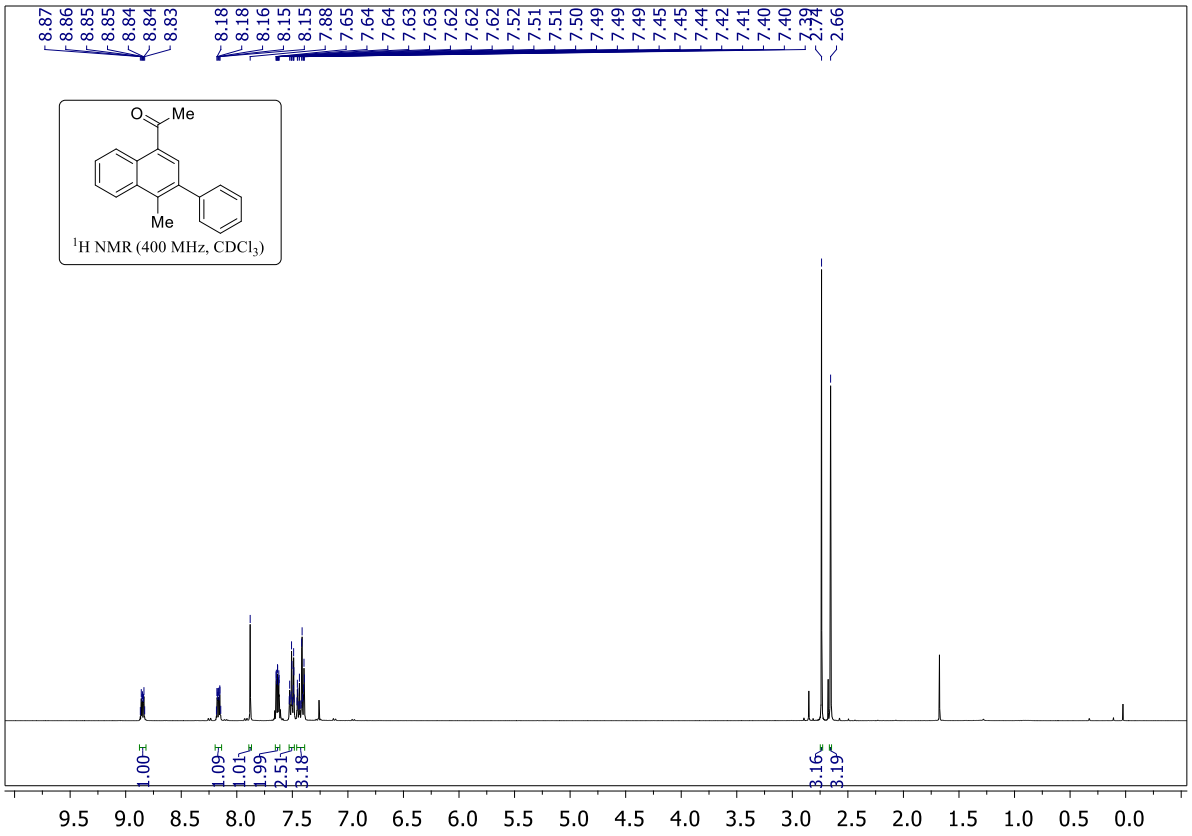


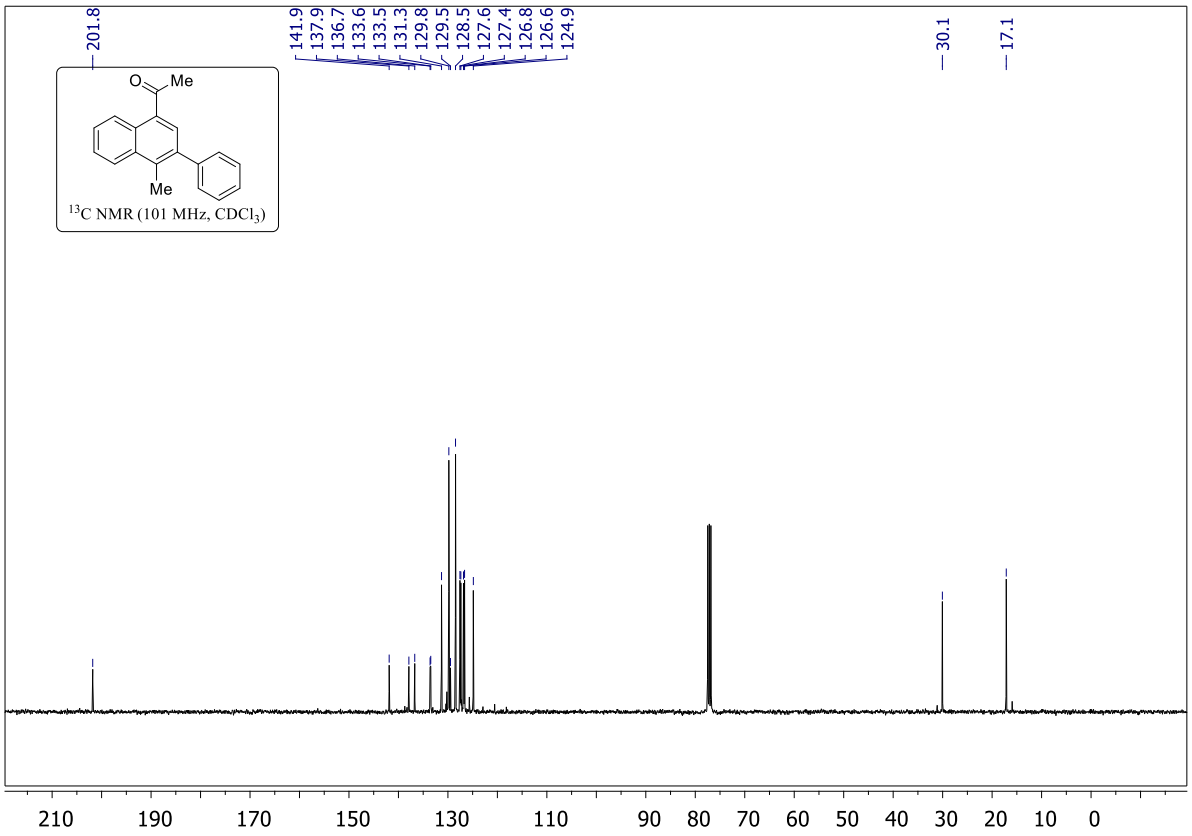
(*E*)-3-(3,4-Dimethoxystyryl)pentane-2,4-dione (14j):



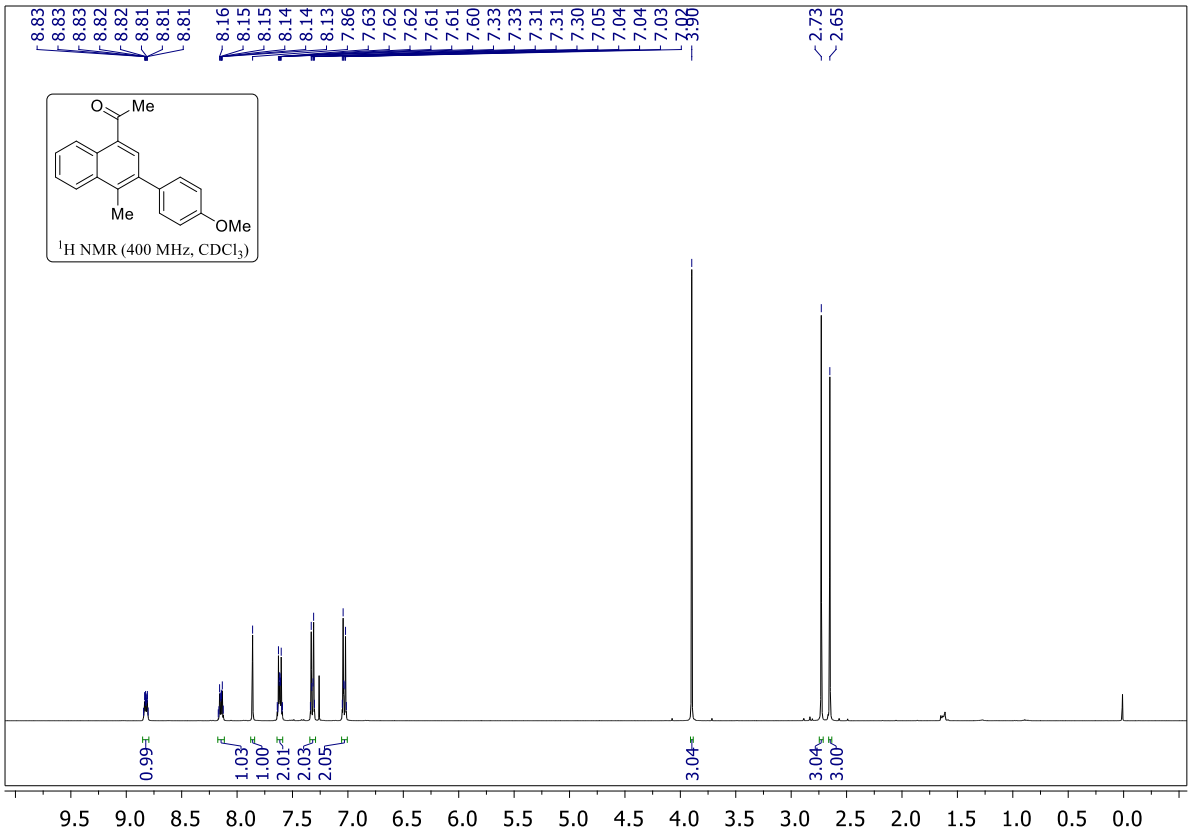


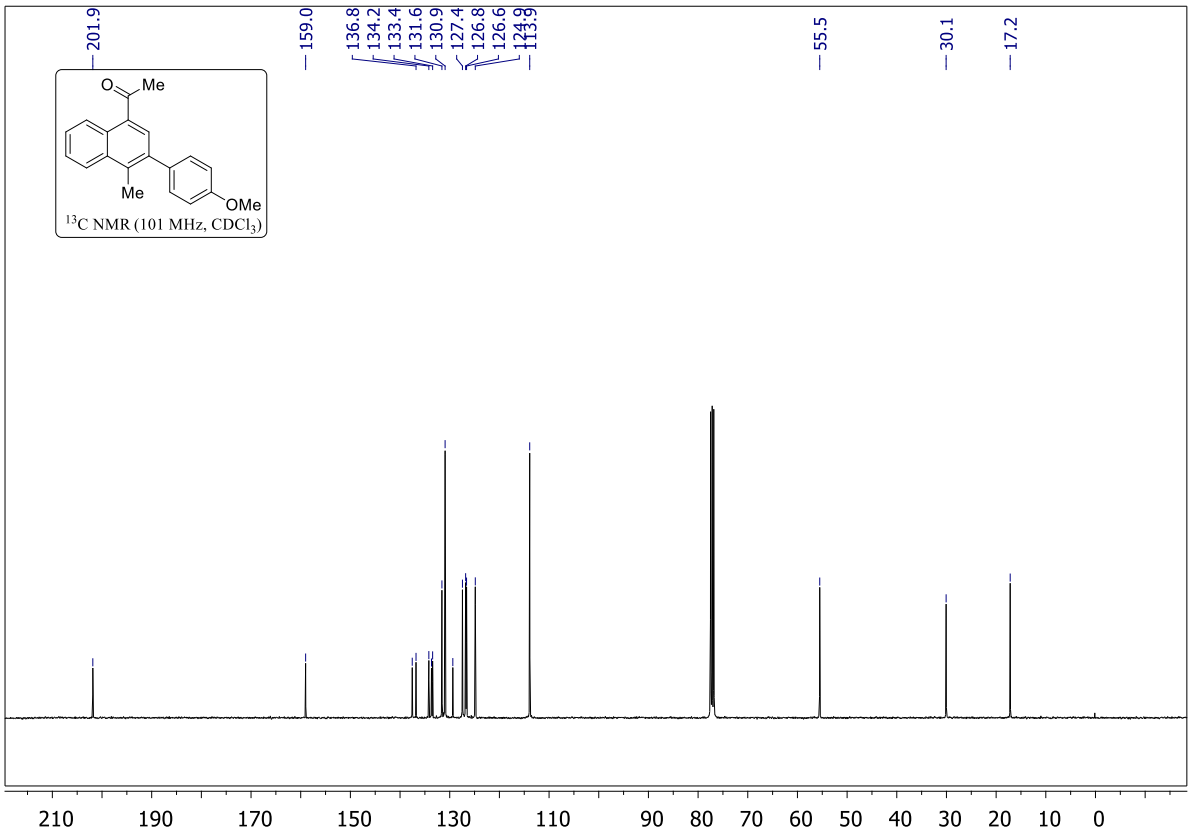
1-(4-Methyl-3-phenylnaphthalen-1-yl)ethan-1-one (15a):



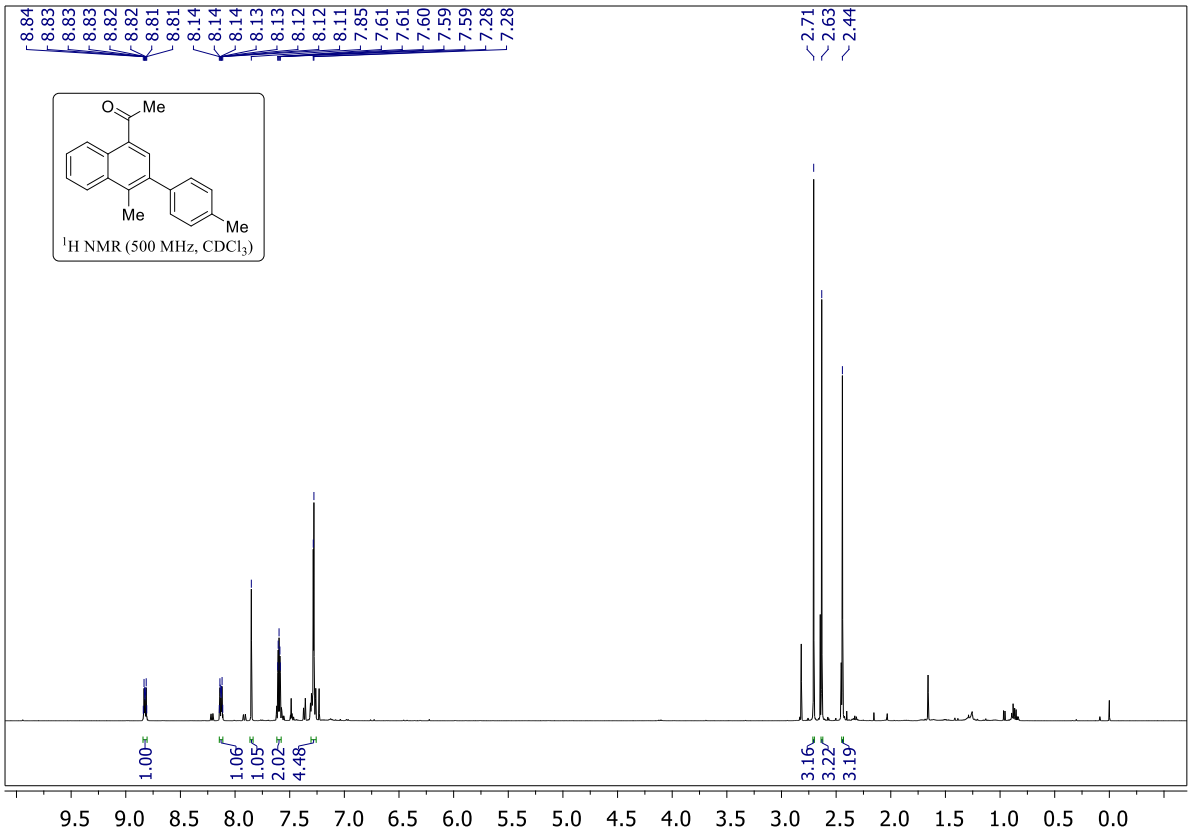


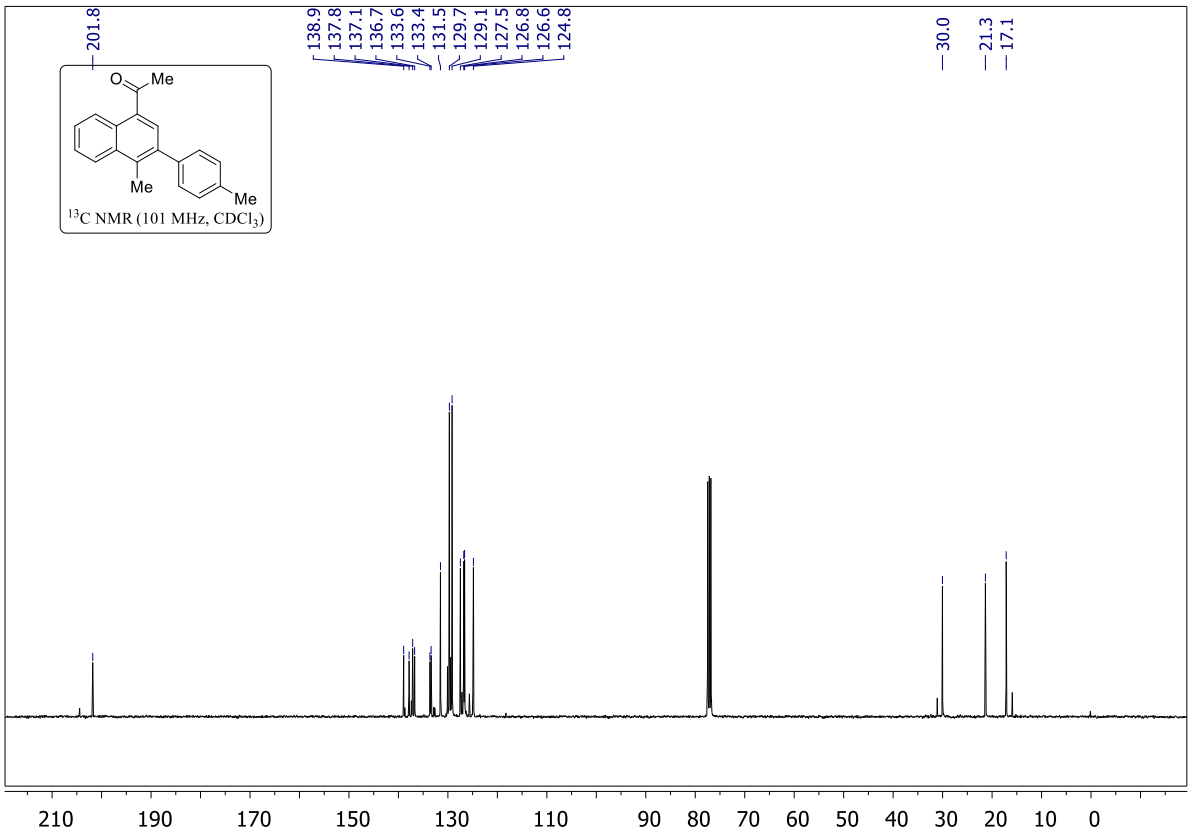
1-(3-(4-Methoxyphenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15b):



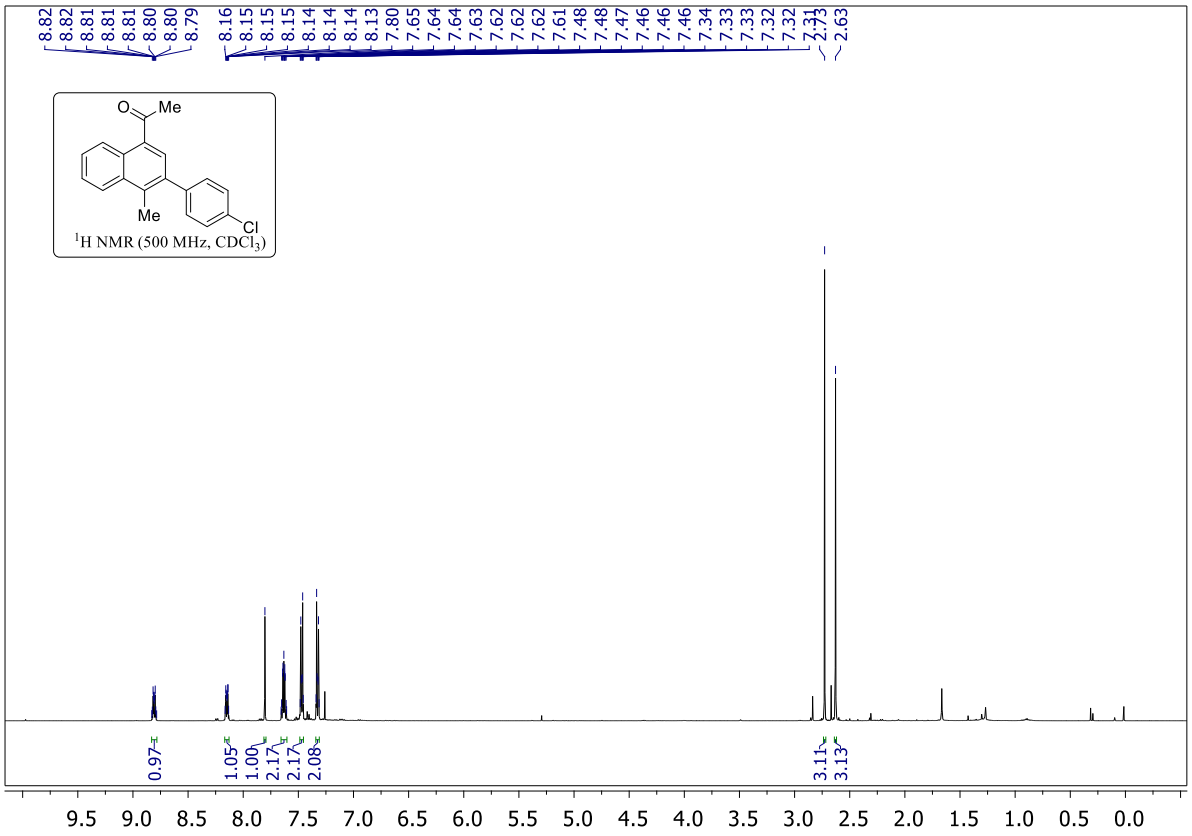


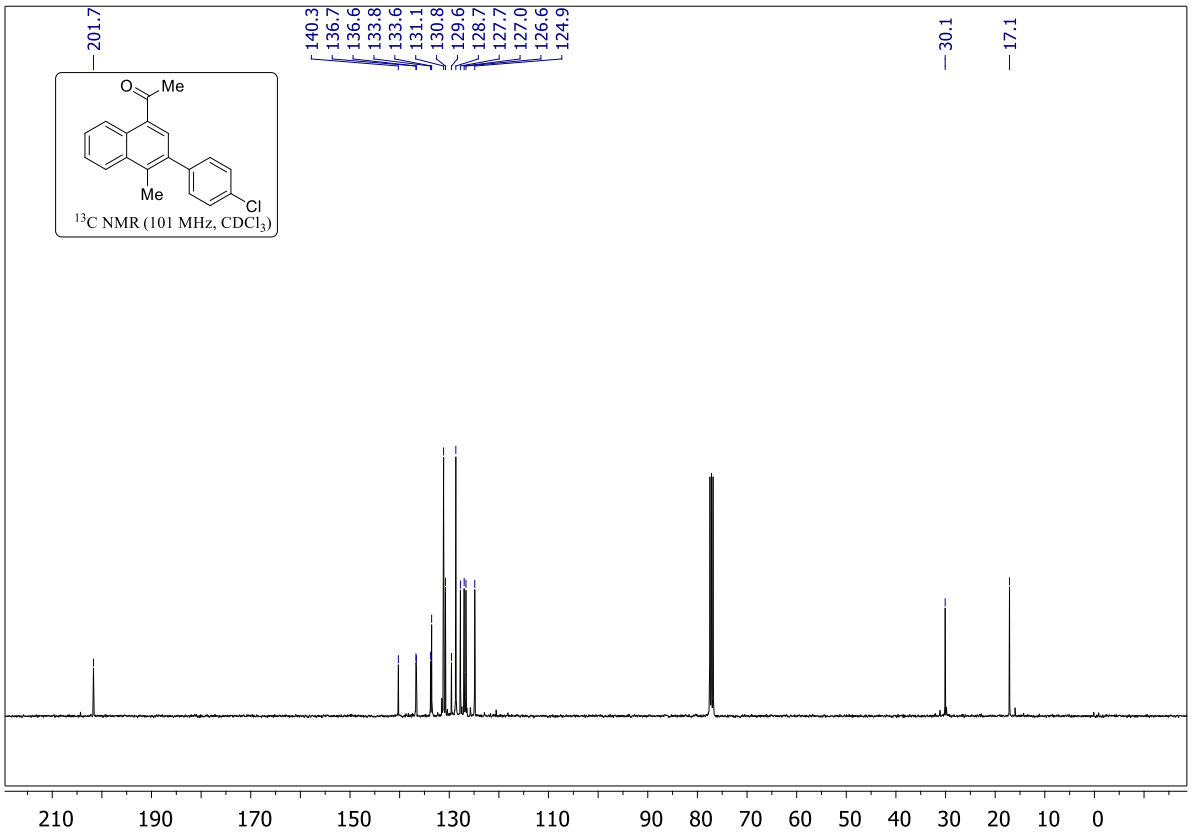
1-(4-Methyl-3-(*p*-tolyl)naphthalen-1-yl)ethan-1-one (15c):



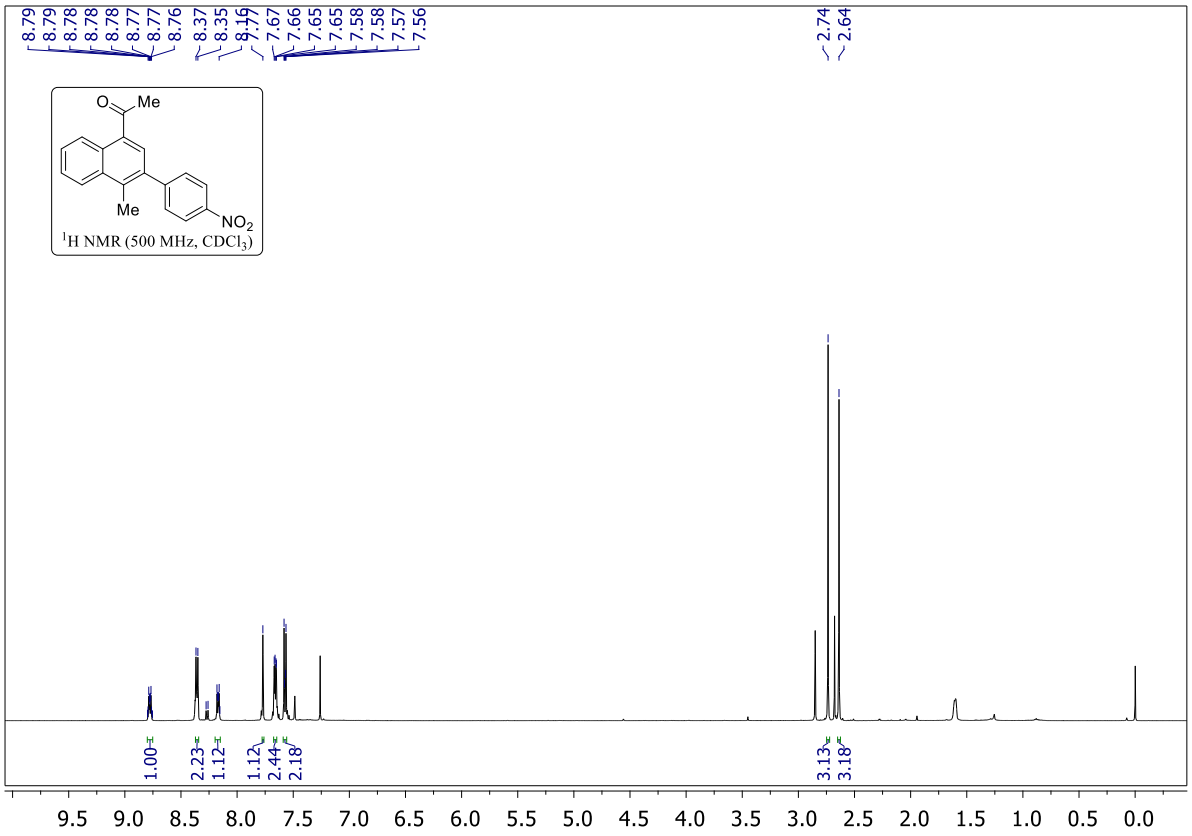


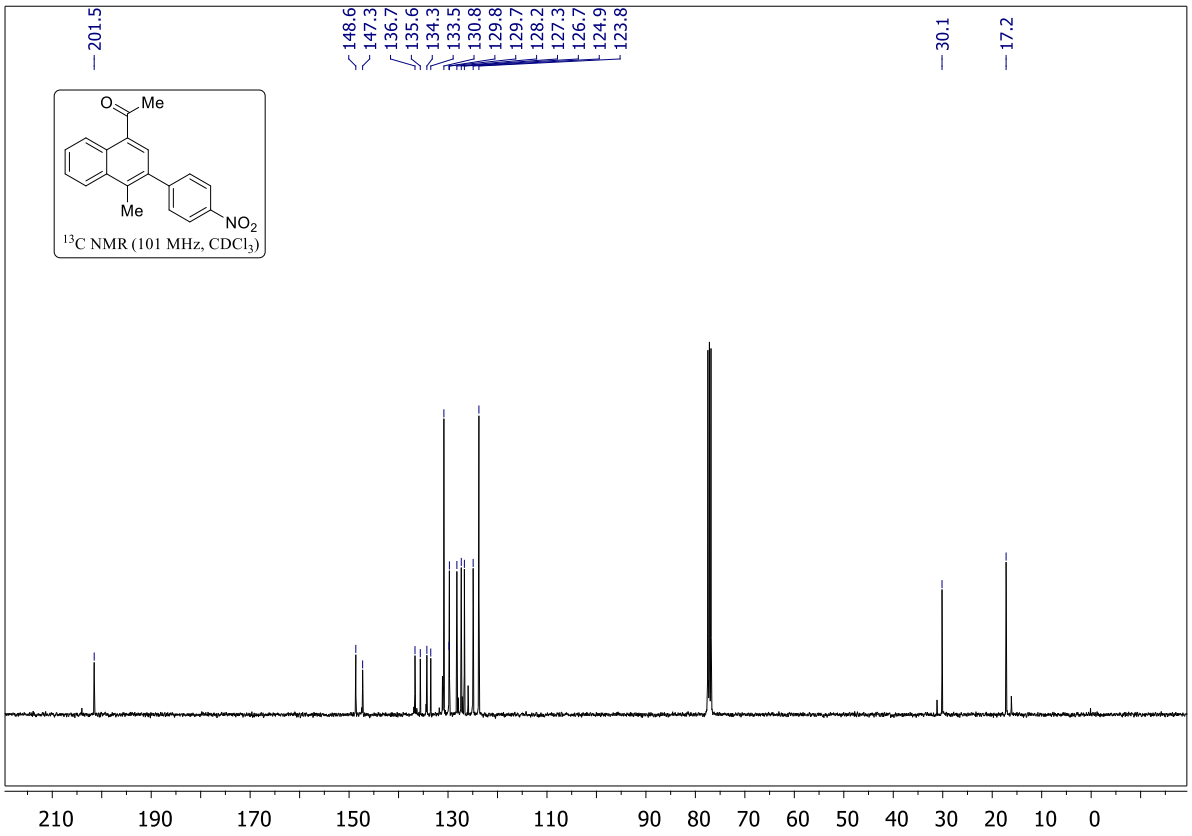
1-(3-(4-Chlorophenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15d):



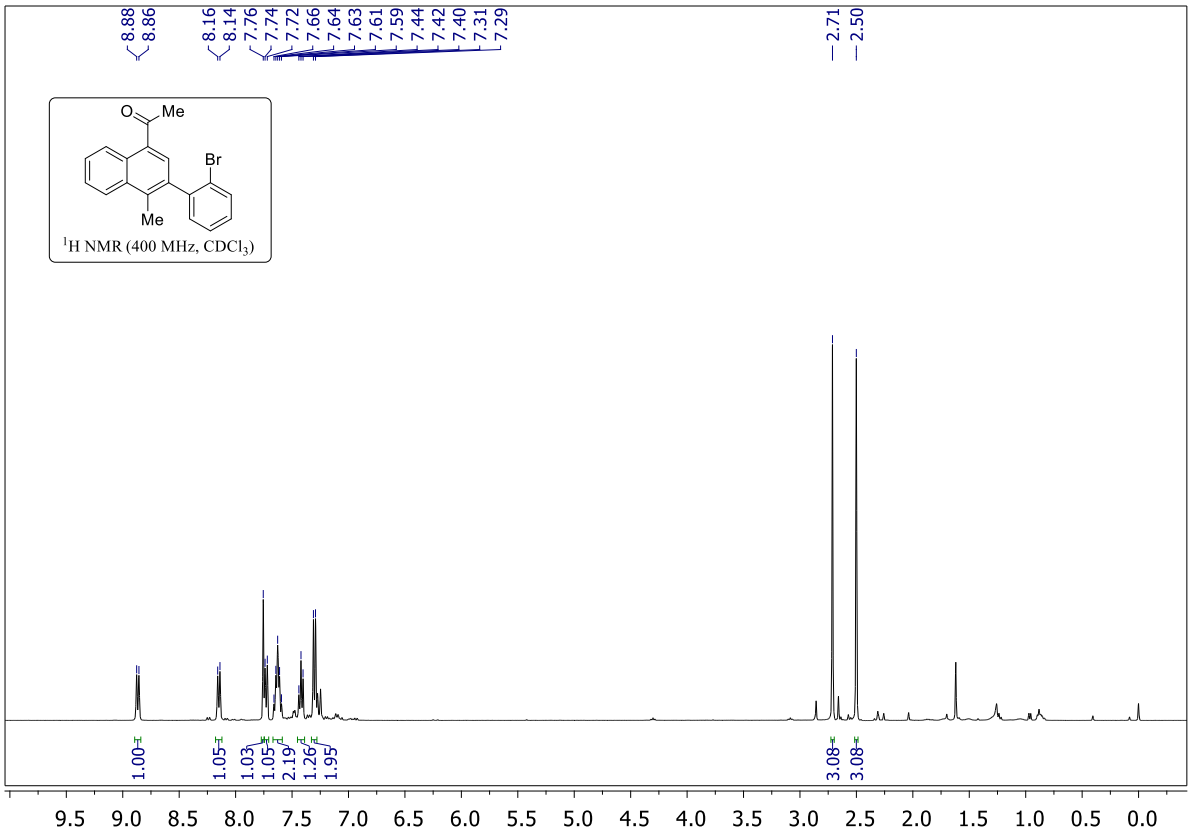


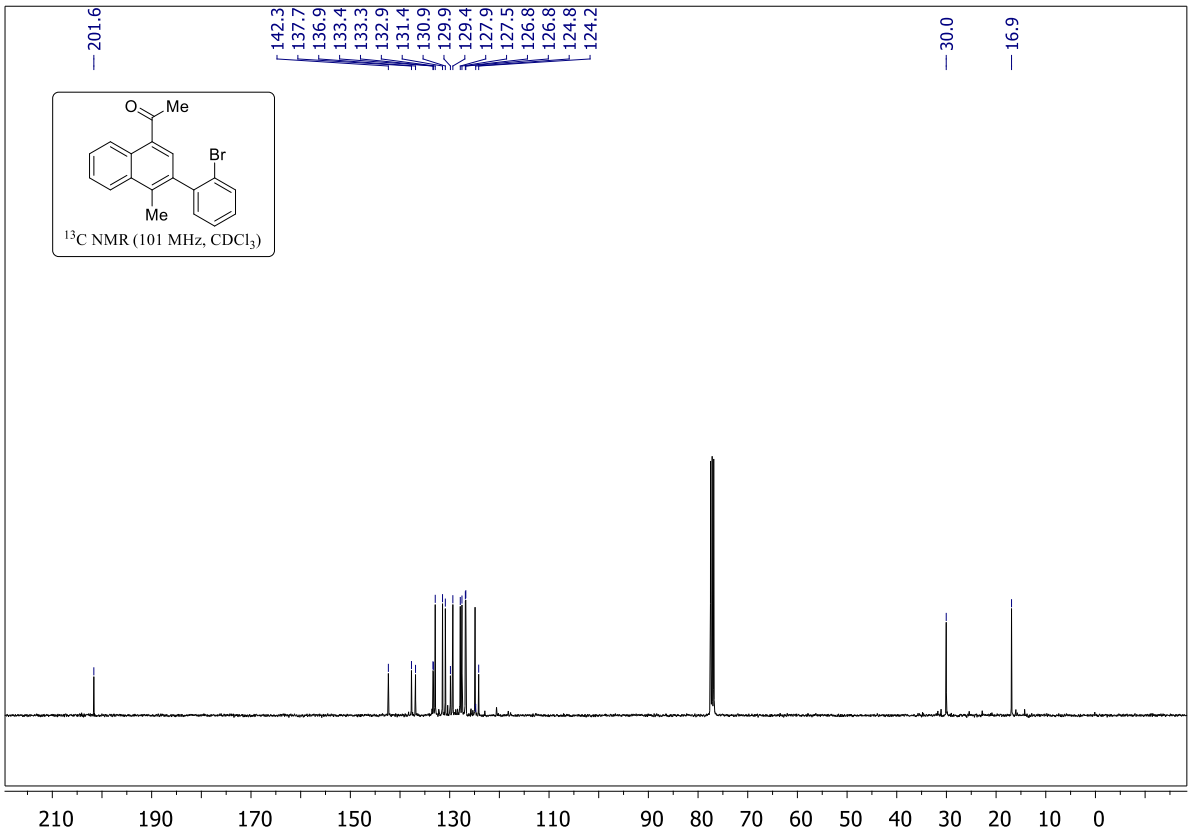
1-(4-Methyl-3-(4-nitrophenyl)naphthalen-1-yl)ethan-1-one (15e):



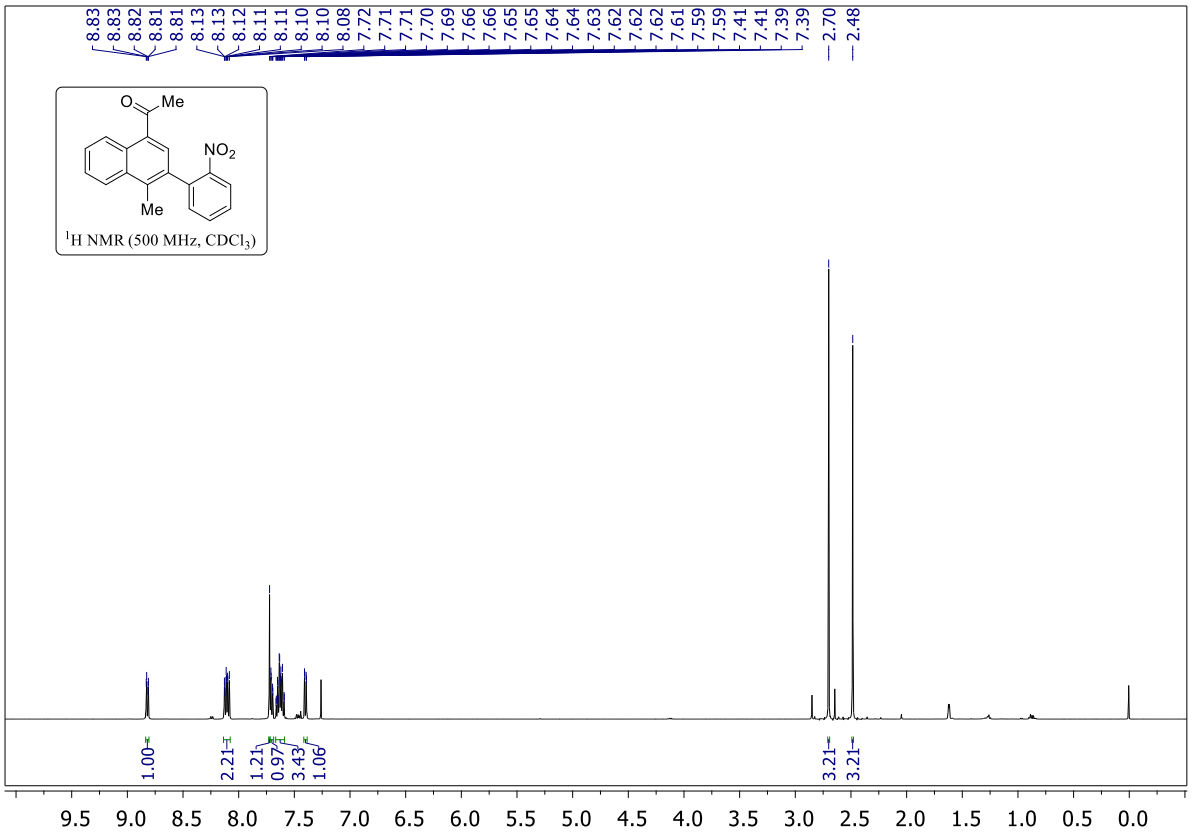


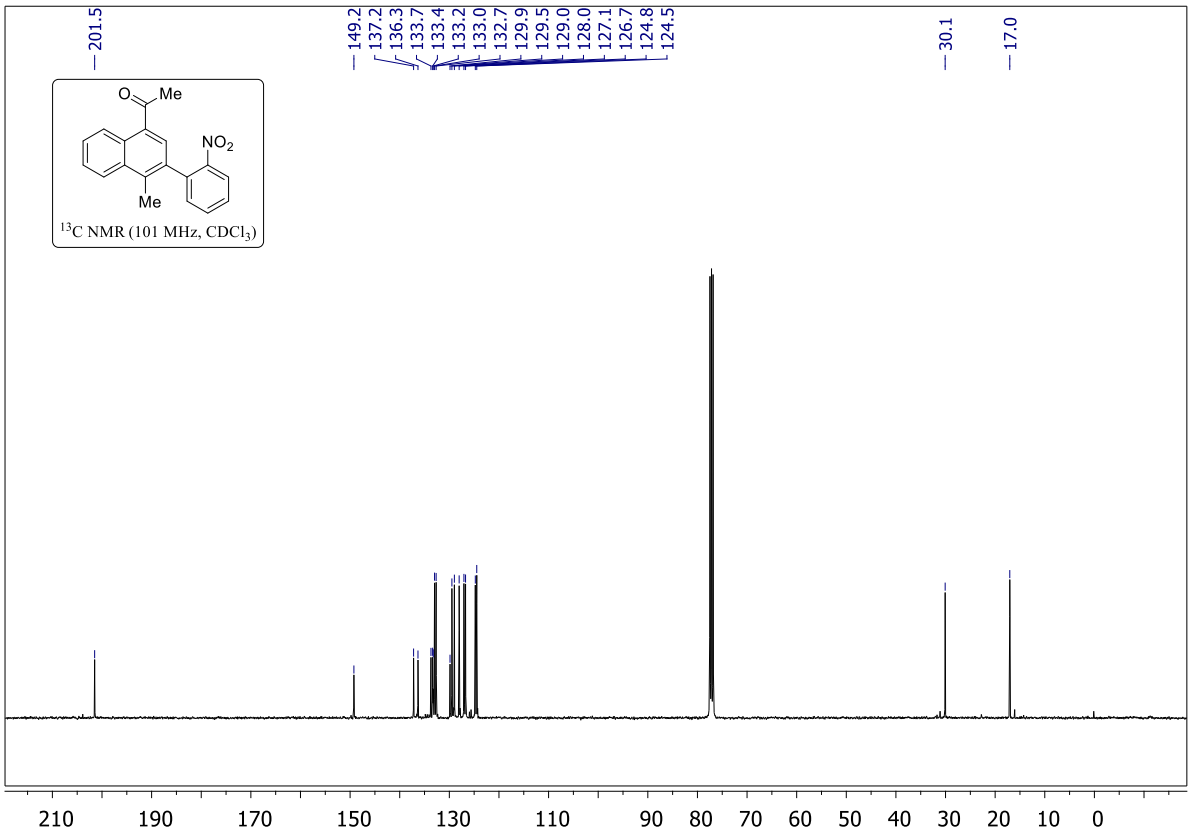
1-(3-(2-Bromophenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15f):



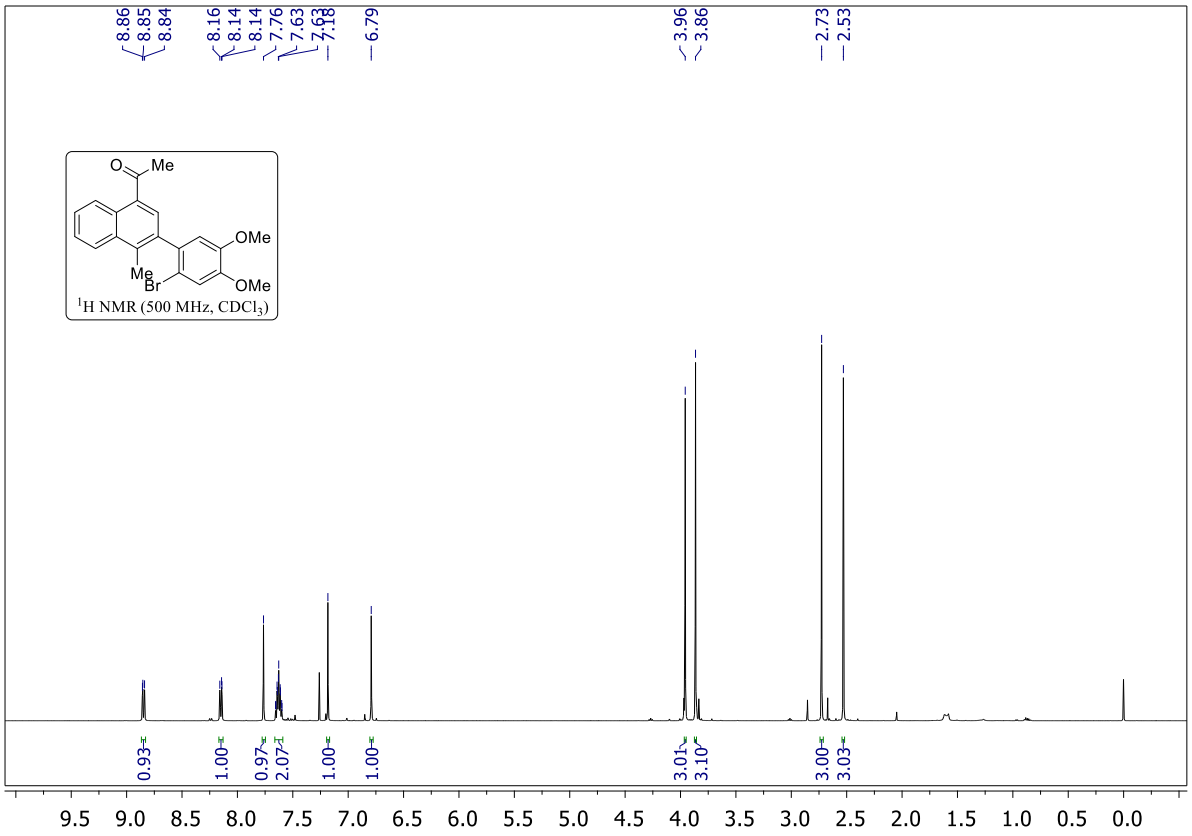


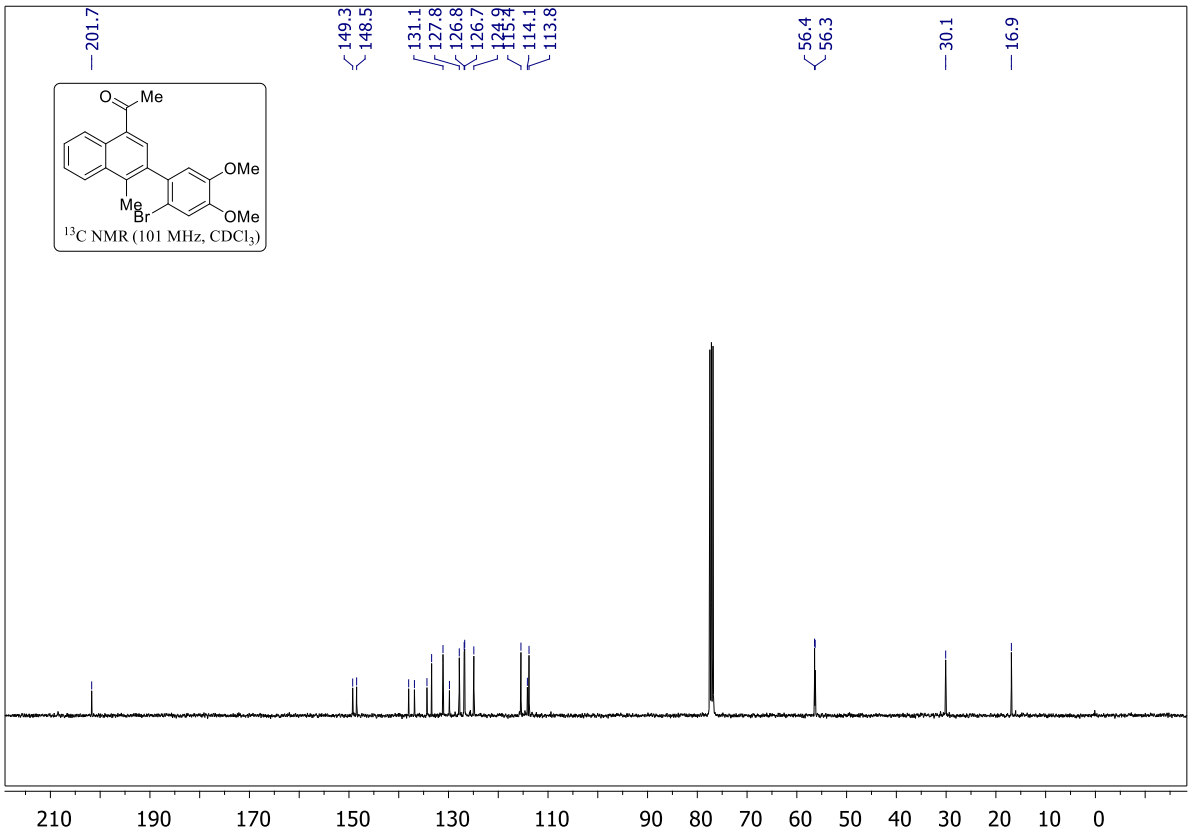
1-(4-Methyl-3-(2-nitrophenyl)naphthalen-1-yl)ethan-1-one (15g):



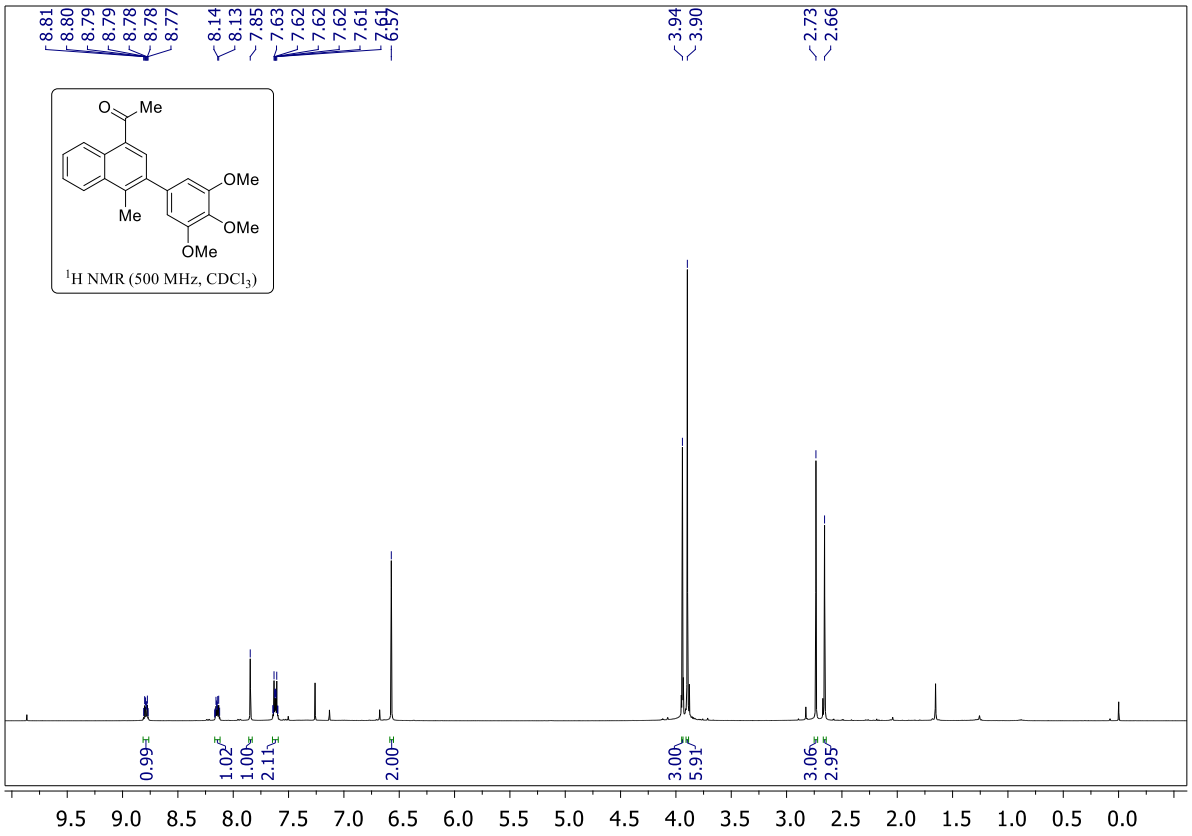


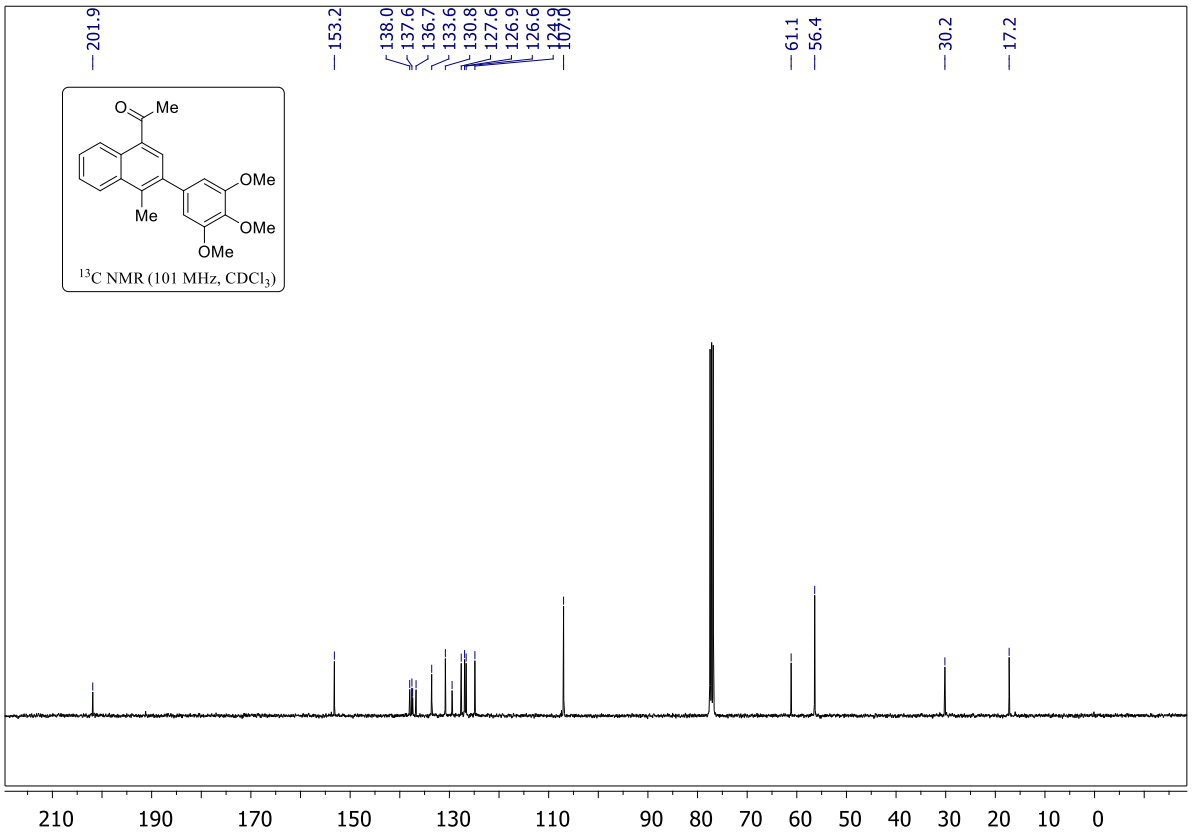
1-(3-(2-Bromo-4,5-dimethoxyphenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15h):



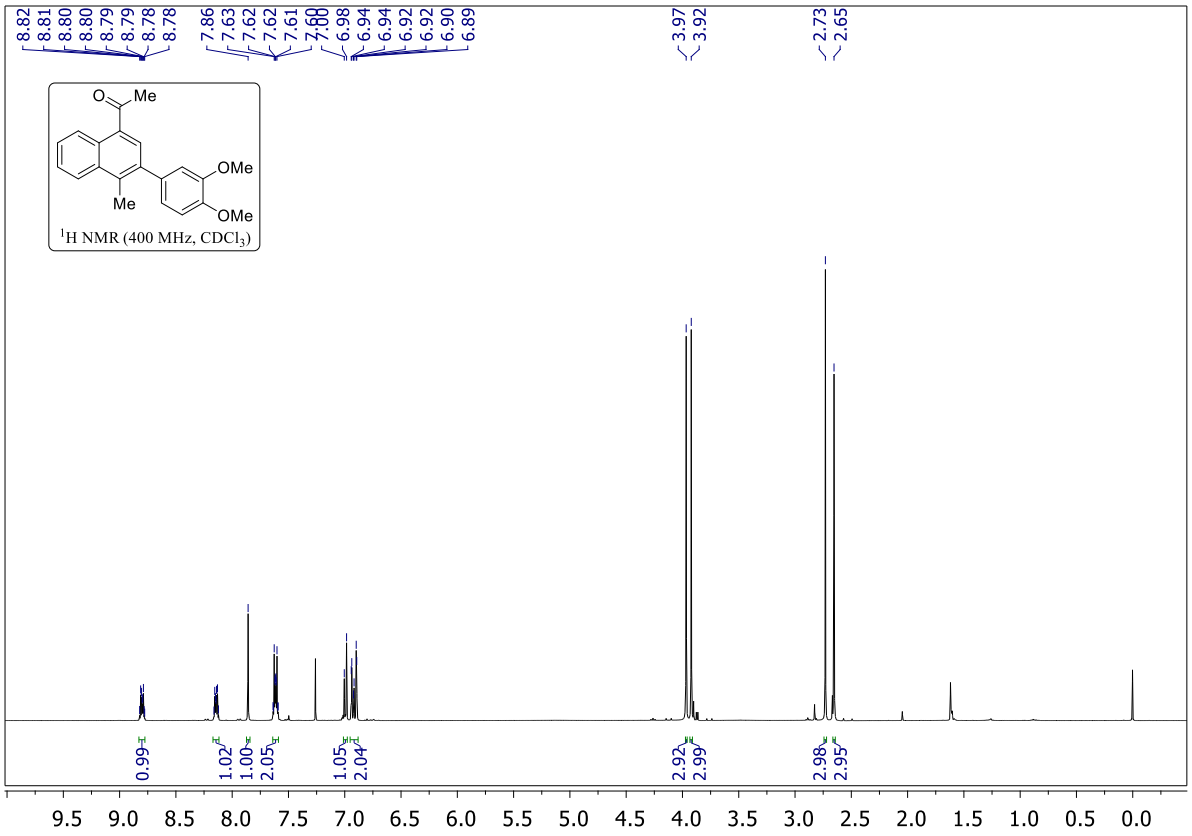


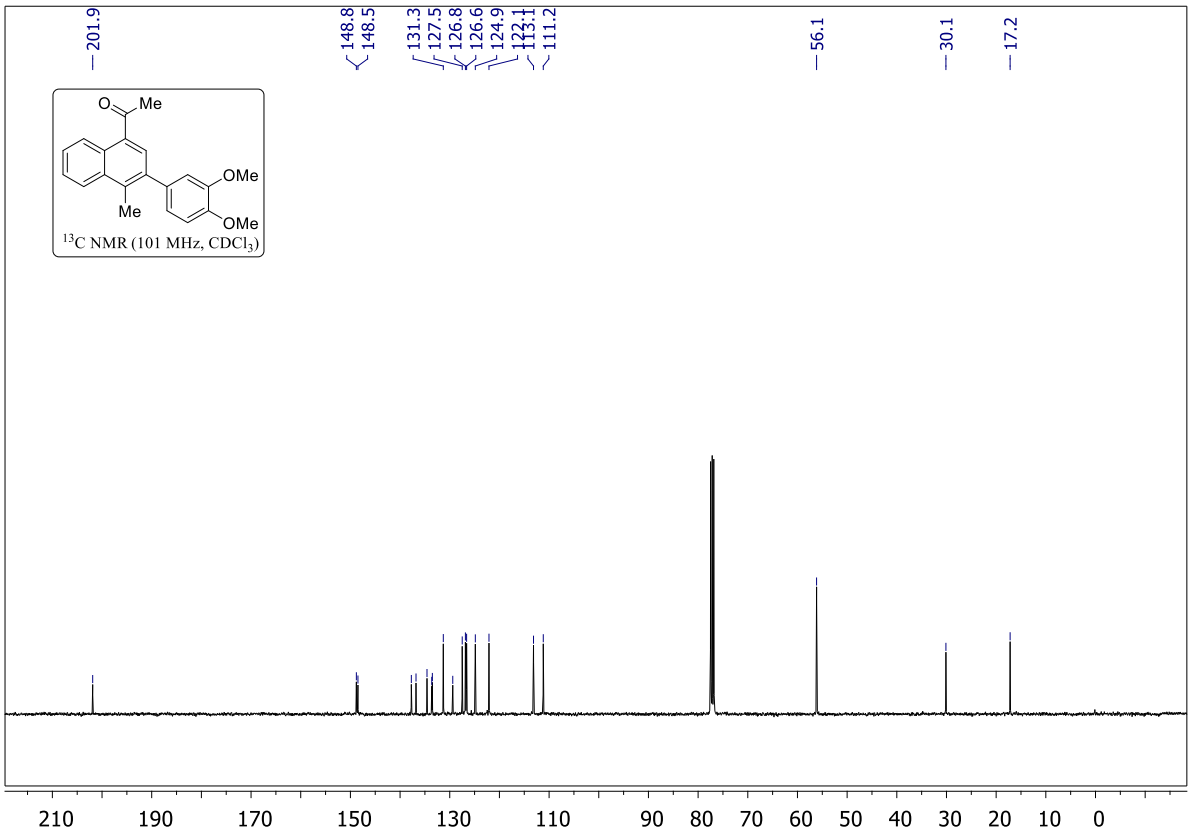
1-(4-Methyl-3-(3,4,5-trimethoxyphenyl)naphthalen-1-yl)ethan-1-one (15i):



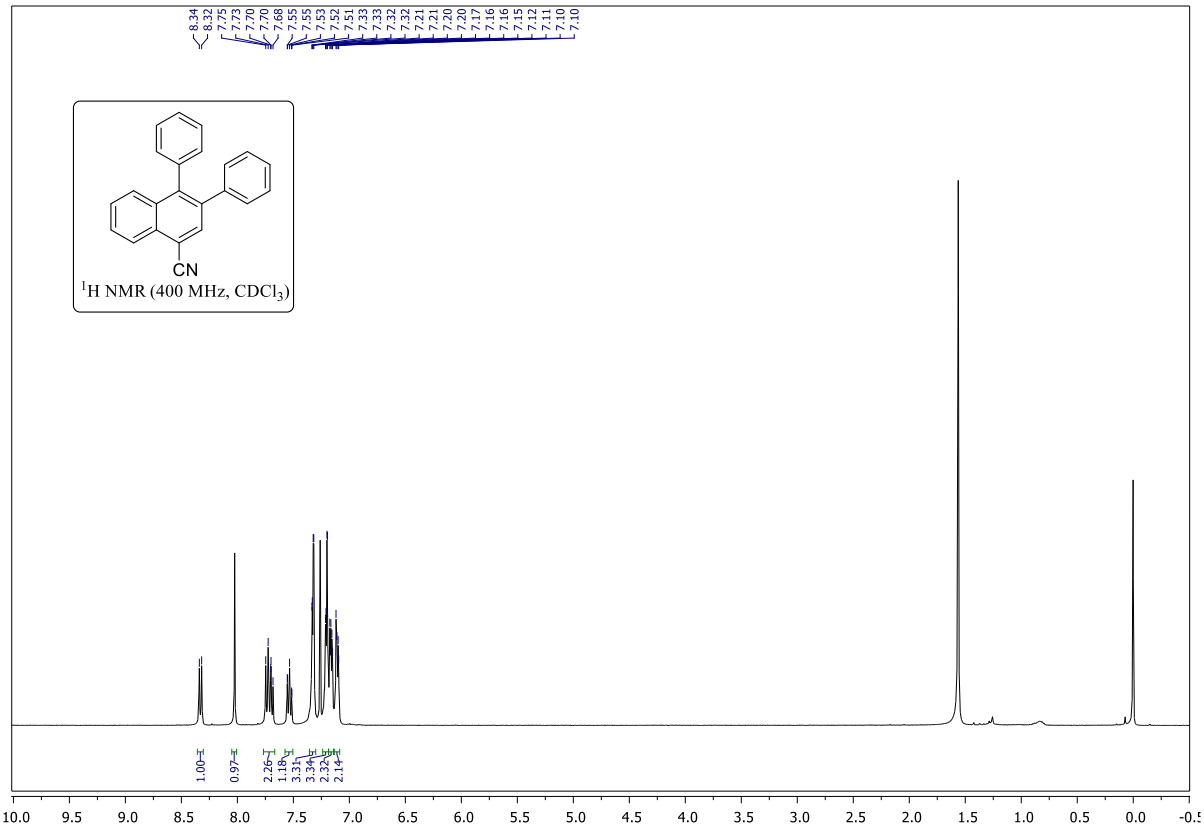


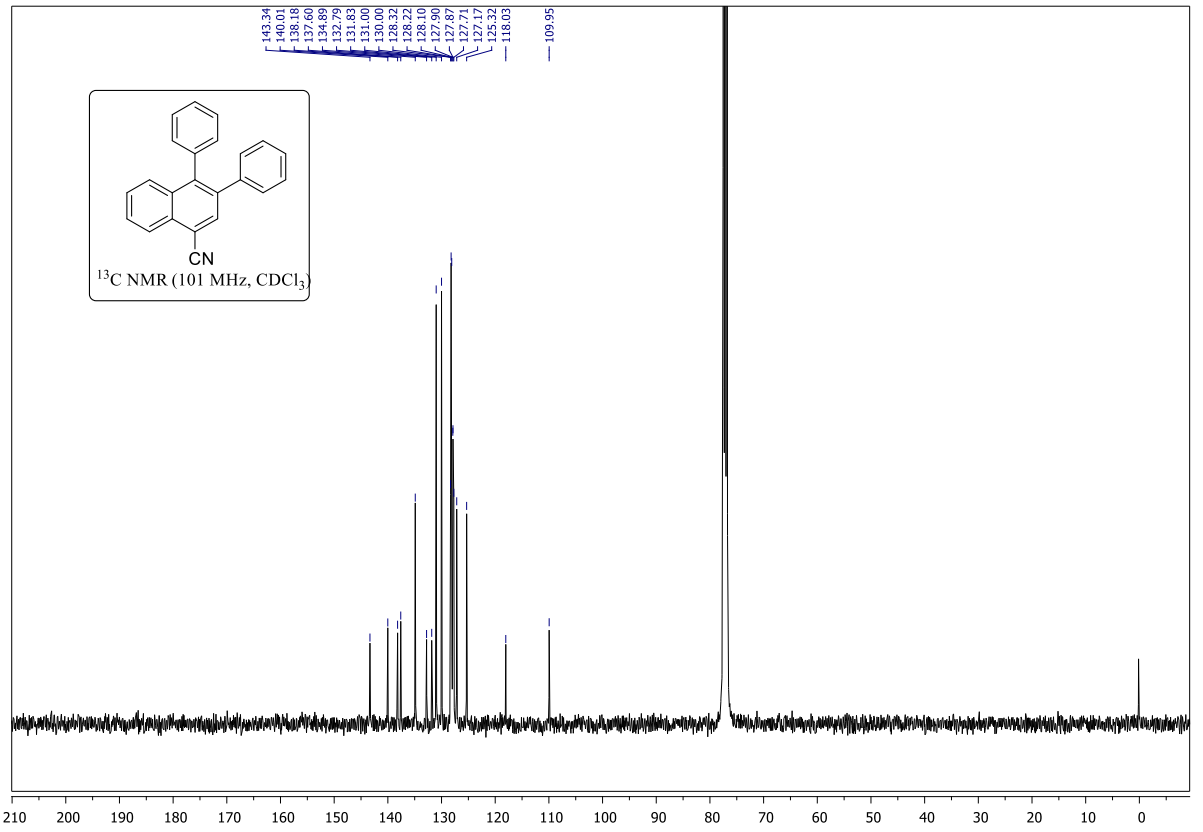
1-(3-(3,4-Dimethoxyphenyl)-4-methylnaphthalen-1-yl)ethan-1-one (15j):



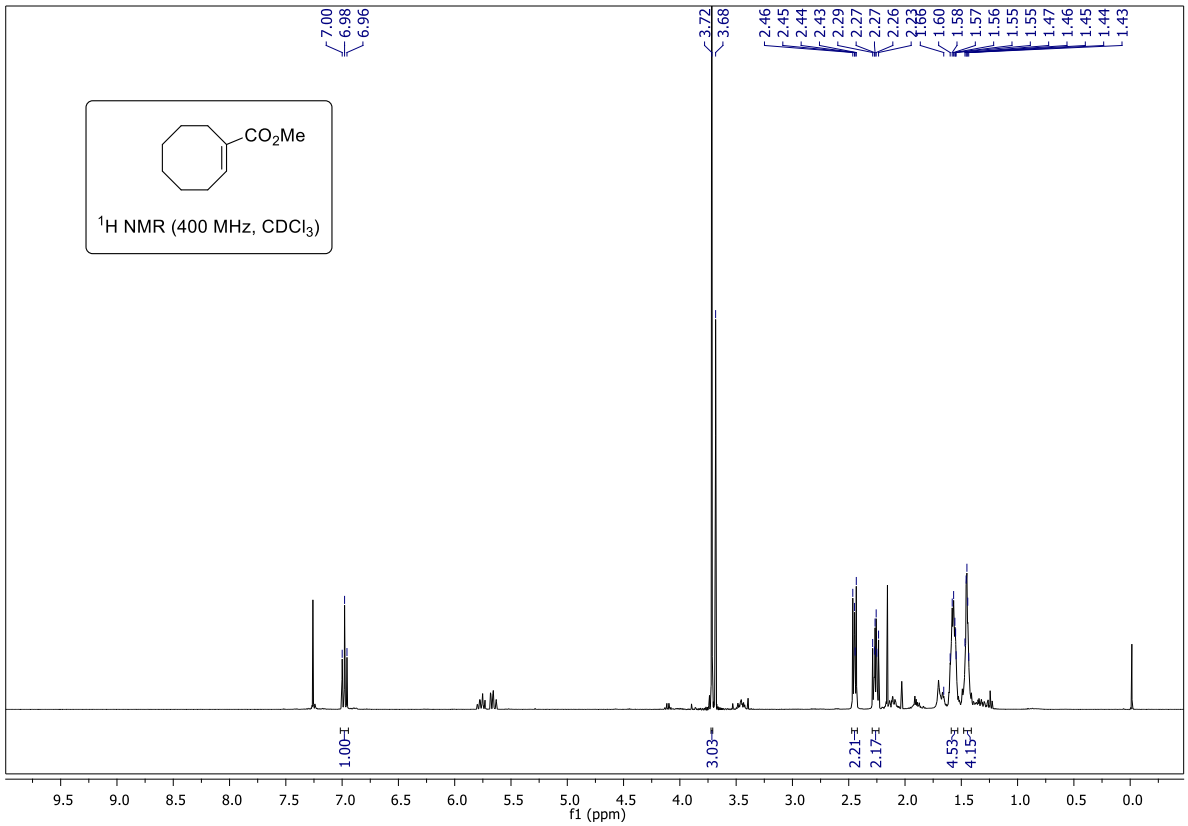


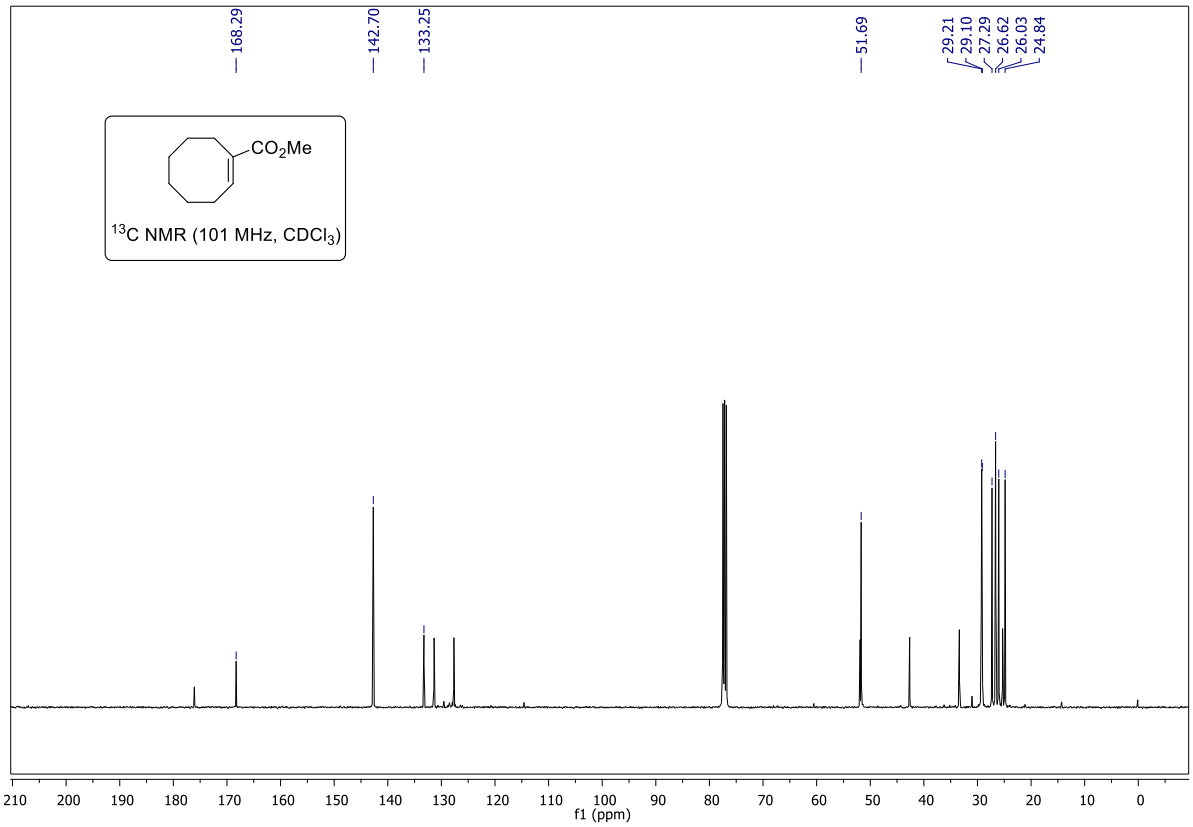
3,4-Diphenyl-1-naphthonitrile (15k):





Methyl (*Z*)-cyclooct-2-ene-1-carboxylate (16):





Biphenylene (17):