Ruthenium-catalysed cyclisation reactions of 1,11-dien-6-ynes leading to biindenes

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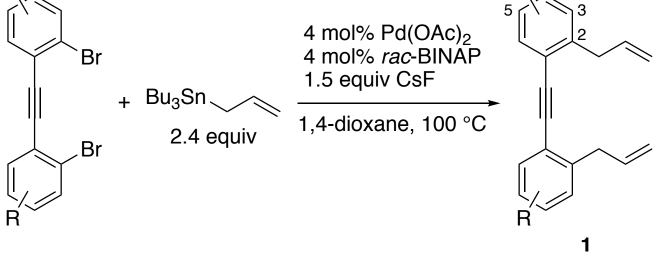
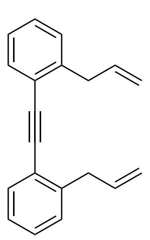
Supporting Information

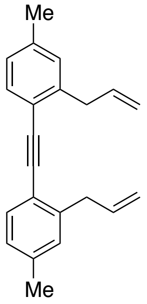
General. All reactions were carried out with standard Schlenk techniques under a nitrogen or an argon atmosphere. Column chromatography was carried out on Wakogel® C-200 (75–150 μm). Preparative thin-layer chromatography (TLC) was performed on Wakogel® B-5F. Proton chemical shifts (δ) were referenced to residual $CHCl_3$ (at 7.26 ppm). Carbon chemical shifts (δ) were referenced to $CDCl_3$ (at 77.0 ppm).

Preparation of 1,11-Dien-6-ynes 1.

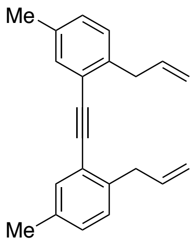




1a 65%



1b 83%



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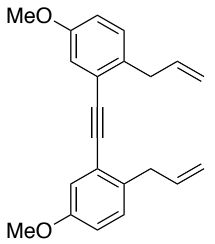
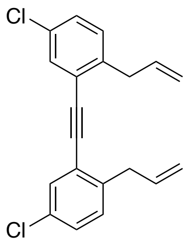


1d 78%



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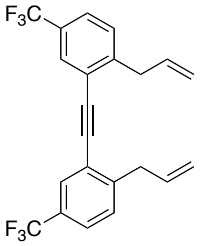

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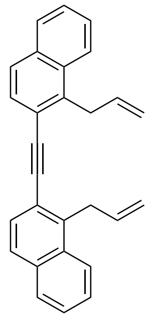

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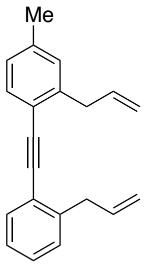
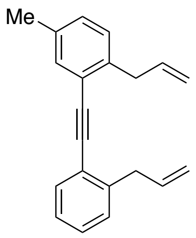
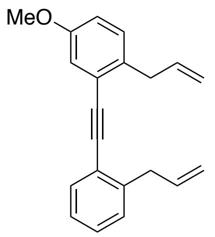


1h 85%



1i 81%



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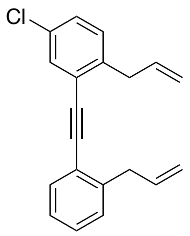

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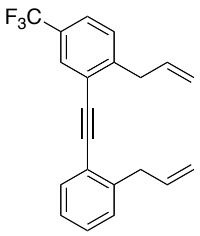
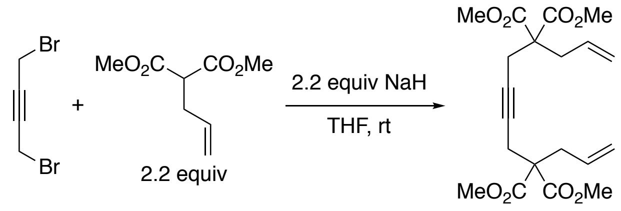


1l 97%



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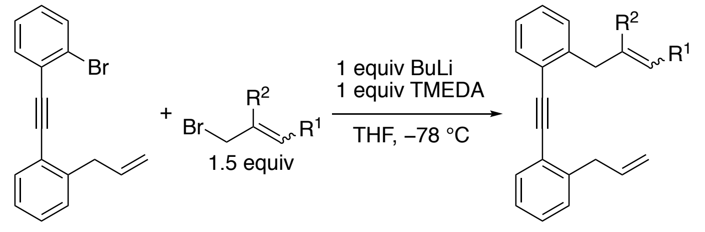
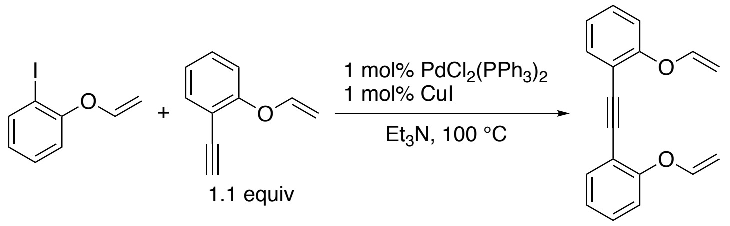
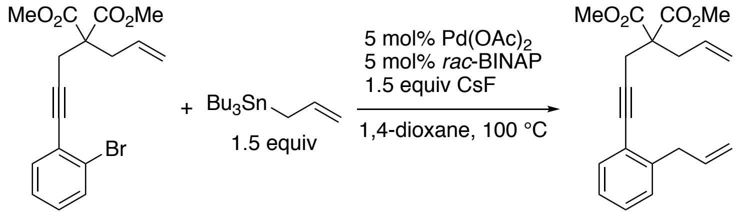


1n (R^1 = Me, R^2 = H) 82%
1o (R^1 = H, R^2 = Me) 81%



1p 91%



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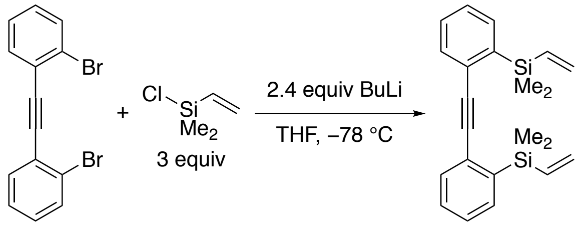
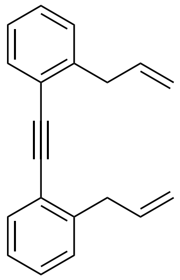
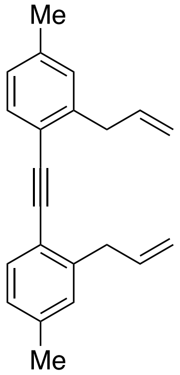


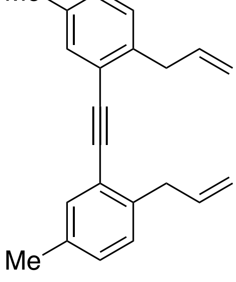
1r 84%



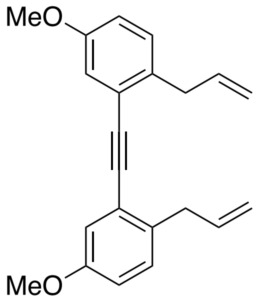
1,2-Bis(2-allylphenyl)ethyne (1a). Yellow oil; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.34–7.18 (m, 6H), 6.13–5.97 (m, 2H), 5.16–5.05 (m, 4H), 3.66 (d, *J* = 5.7 Hz, 4H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 141.8, 136.6, 132.2, 128.8, 128.5, 126.1, 122.9, 116.0, 91.8, 38.8; HRMS (ESI) calcd for $C_{20}H_{18}Na$ [M + Na]$^+$ 281.1301, found 281.1297.



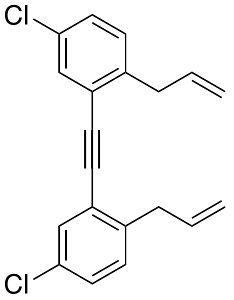
1,2-Bis(2-allyl-4-methylphenyl)ethyne (1b). Yellow oil; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.06–6.98 (m, 4H), 6.04 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 2H), 5.15–5.04 (m, 4H), 3.61 (d, *J* = 6.6 Hz, 4H), 2.34 (s, 6H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 141.5, 138.4, 136.8, 132.1, 129.6, 126.9, 120.1, 115.8, 91.3, 38.8, 21.5; HRMS (ESI) calcd for $C_{22}H_{22}Na$ [M + Na]$^+$ 309.1614, found 309.1613.



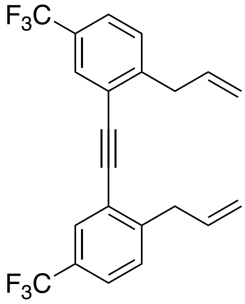
1,2-Bis(2-allyl-5-methylphenyl)ethyne (1c). Yellow oil; ^{1}H NMR (399 MHz, CDCl$_3$) δ 7.36–7.33 (m, 2H), 7.15–7.07 (m, 4H), 6.03 (ddt, *J* = 16.8, 8.4, 6.6 Hz, 2H), 5.12–5.04 (m, 4H), 3.61 (d, *J* = 6.8 Hz, 4H), 2.33 (s, 6H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 138.7, 136.9, 135.6, 132.6, 129.3, 128.7, 122.7, 115.7, 91.6, 38.3, 20.8; HRMS (ESI) calcd for $C_{22}H_{22}Na$ [M + Na]$^+$ 309.1614, found 309.1614.



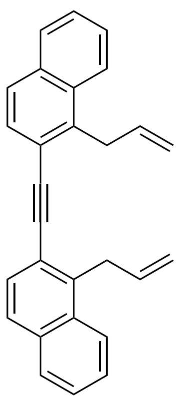
1,2-Bis(2-allyl-5-methoxyphenyl)ethyne (1d). Yellow oil; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.14 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 2.7 Hz, 2H), 6.86 (dd, J = 8.4, 2.7 Hz, 2H), 6.01 (ddt, J = 17.6, 9.4, 6.5 Hz, 2H), 5.11–5.02 (m, 4H), 3.82 (s, 6H), 3.58 (d, J = 6.6 Hz, 4H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 157.6, 137.0, 134.1, 129.9, 123.5, 116.7, 115.6, 115.2, 91.5, 55.4, 37.9; HRMS (ESI) calcd for $C_{22}H_{22}NaO_2$ [M + Na]$^+$ 341.1512, found 341.1513.



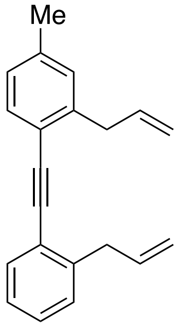
1,2-Bis(2-allyl-5-chlorophenyl)ethyne (1e). Yellow solid, mp 46–48 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.49 (d, J = 1.8 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.30–7.24 (m, 2H), 5.99 (ddt, J = 17.1, 10.2, 6.6 Hz, 2H), 5.15–5.03 (m, 4H), 3.59 (d, J = 6.6 Hz, 4H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 140.3, 135.8, 131.78, 131.76, 130.2, 128.9, 124.0, 116.6, 91.4, 38.1; HRMS (ESI) calcd for $C_{20}H_{16}Cl_2Na$ [M + Na]$^+$ 349.0521, found 349.0519.



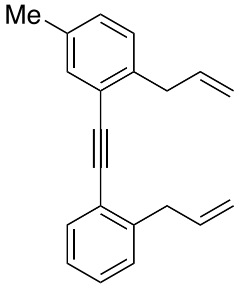
1,2-Bis[2-allyl-5-(trifluoromethyl)phenyl]ethyne (1f). Pale yellow solid, mp 36–39 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.82–7.76 (m, 2H), 7.55 (dd, J = 7.8, 1.5 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 6.02 (ddt, J = 17.1, 10.2, 7.1 Hz, 2H), 5.20–5.06 (m, 4H), 3.69 (d, J = 6.3 Hz, 4H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 145.7 (q, $^4J_{C-F}$ = 1.5 Hz), 135.2, 129.5, 129.2 (q, $^3J_{C-F}$ = 3.9 Hz), 128.9 (q, $^2J_{C-F}$ = 33.0 Hz), 125.4 (q, $^3J_{C-F}$ = 3.6 Hz), 123.8 (q, $^1J_{C-F}$ = 272.4 Hz), 123.1, 117.1, 91.6, 38.6; HRMS (ESI) calcd for $C_{22}H_{16}F_6Na$ [M + Na]$^+$ 417.1048, found 417.1047.



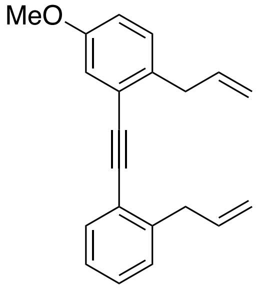
1,2-Bis(1-allyl-2-naphthyl)ethyne (1g). Pale yellow solid, mp 119–124 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.88–7.82 (m, 2H), 7.77–7.64 (m, 4H), 7.59–7.47 (m, 4H), 6.16 (ddt, *J* = 16.8, 10.5, 5.9 Hz, 2H), 5.13 (dd, *J* = 7.3, 1.6 Hz, 2H), 5.08 (s, 2H), 4.23 (d, *J* = 6.0 Hz, 4H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 138.5, 136.1, 133.4, 131.9, 128.8, 128.6, 126.8, 126.5, 126.2, 124.6, 120.7, 115.9, 93.4, 35.2; HRMS (ESI) calcd for $C_{28}H_{22}Na$ [M + Na]$^+$ 381.1614, found 381.1614.



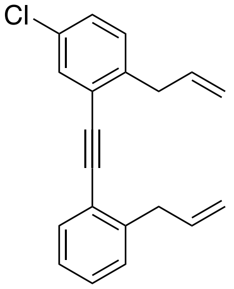
1-(2-Allyl-4-methylphenyl)-2-(2-allylphenyl)ethyne (1h). Yellow oil; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.52 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.32–7.16 (m, 3H), 7.07–7.00 (m, 2H), 6.12–5.97 (m, 2H), 5.15–5.05 (m, 4H), 3.67–3.59 (m, 4H), 2.35 (s, 3H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 141.7, 141.6, 138.6, 136.7, 136.6, 132.2, 132.1, 129.6, 128.8, 128.3, 127.0, 126.1, 123.1, 119.9, 116.0, 115.9, 92.0, 91.1, 38.80, 38.77, 21.5; HRMS (ESI) calcd for $C_{21}H_{20}Na$ [M + Na]$^+$ 295.1457, found 295.1462.



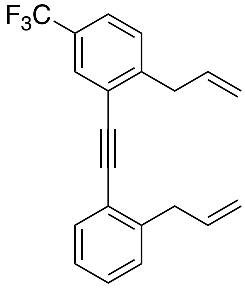
1-(2-Allyl-5-methylphenyl)-2-(2-allylphenyl)ethyne (1i). Yellow oil; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.35 (s, 1H), 7.32–7.07 (m, 5H), 6.12–5.95 (m, 2H), 5.04–5.15 (m, 4H), 3.65 (d, *J* = 6.9 Hz, 2H), 3.61 (d, *J* = 6.6 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 141.8, 138.8, 136.9, 136.6, 135.7, 132.7, 132.3, 129.4, 128.82, 128.78, 128.4, 126.1, 123.0, 122.7, 116.0, 115.8, 92.0, 91.4, 38.8, 38.4, 20.8; HRMS (ESI) calcd for $C_{21}H_{20}Na$ [M + Na]$^+$ 295.1457, found 295.1457.



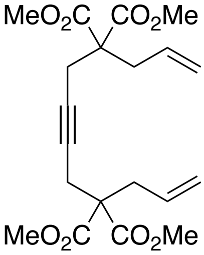
1-(2-Allyl-5-methoxyphenyl)-2-(2-allylphenyl)ethyne (1j). Yellow oil; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.5, 0.9 Hz, 1H), 7.33–7.18 (m, 3H), 7.15 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 2.7 Hz, 1H), 6.86 (dd, J = 8.4, 3.0 Hz, 1H), 6.12–5.95 (m, 2H), 5.14–5.03 (m, 4H), 3.82 (s, 3H), 3.68–3.63 (m, 2H), 3.61–3.56 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 157.6, 141.8, 137.0, 136.5, 134.1, 132.3, 129.9, 128.8, 128.6, 126.1, 123.6, 122.8, 116.6, 116.0, 115.6, 115.1, 91.8, 91.5, 55.4, 38.8, 37.9; HRMS (ESI) calcd for $C_{21}H_{20}NaO$ [M + Na]$^+$ 83.1093, found 311.1403.



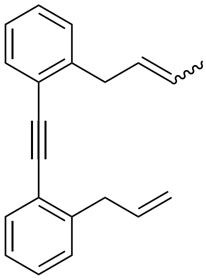
1-(2-Allyl-5-chlorophenyl)-2-(2-allylphenyl)ethyne (1k). Yellow oil; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.54–7.49 (m, 2H), 7.34–7.15 (m, 5H), 6.11–5.92 (m, 2H), 5.11 (t, J = 1.4 Hz, 2H), 5.10–5.04 (m, 2H), 3.66–3.58 (m, 4H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 141.9, 140.2, 136.4, 136.0, 132.4, 131.70, 131.68, 130.1, 128.93, 128.87, 128.6, 126.2, 124.6, 122.4, 116.4, 116.2, 92.9, 90.4, 38.7, 38.1; HRMS (ESI) calcd for $C_{20}H_{17}ClNa$ [M + Na]$^+$ 315.0911, found 315.0911.



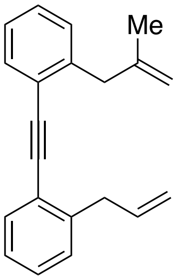
1-[2-Allyl-5-(trifluoromethyl)phenyl]-2-(2-allylphenyl)ethyne (1l). Yellow oil; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.78–7.75 (m, 1H), 7.57–7.49 (m, 2H), 7.39–7.20 (m, 4H), 6.11–5.95 (m, 2H), 5.17–5.05 (m, 4H), 3.69 (d, J = 6.3 Hz, 2H), 3.68–3.62 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 145.6, 142.0, 136.4, 135.4, 132.4, 129.4, 129.3, 129.00, 128.97 (q, $^{3}J_{C\text{–}F}$ = 3.9 Hz), 128.8 (q, $^{2}J_{C\text{–}F}$ = 32.7 Hz), 126.2, 124.9 (q, $^{3}J_{C\text{–}F}$ = 3.9 Hz), 123.9 (q, $^{1}J_{C\text{–}F}$ = 271.9 Hz), 123.8, 122.3, 116.9, 116.2, 93.3, 90.3, 38.7, 38.6; HRMS (ESI) calcd for $C_{21}H_{17}F_3Na$ [M + Na]$^+$ 349.1175, found 349.1174.



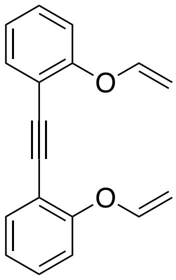
Tetramethyl dodeca-1,11-dien-6-yne-4,4,9,9-tetracarboxylate (1m). Colorless liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.60 (ddt, *J* = 17.2, 9.7, 7.4, 2H), 5.17 (dd, *J* = 17.3, 1.8 Hz, 2H), 5.12 (dd, *J* = 10.5, 1.5 Hz, 2H), 3.73 (s, 12H), 2.74–2.78 (m, 8H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.1, 131.8, 119.7, 77.7, 56.9, 52.6, 36.4, 22.8; HRMS (ESI) calcd for $C_{20}H_{26}NaO_8$ [M + Na]$^+$ 417.1520, found 417.1520; IR (*ν*/cm^{-1}): 1740, 1220.



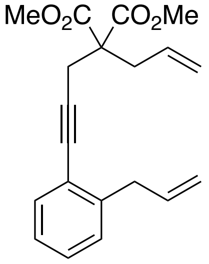
(*E*)- and (*Z*)-1-(2-Allylphenyl)-2-[2-(2-butenyl)phenyl]ethyne (1n). Colorless oil; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.57–7.50 (m, 2H; major + minor), 7.38–7.16 (m, 6H; major + minor), 6.05 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H; major + minor), 5.73–5.47 (m, 2H; major + minor), 5.17–5.05 (m, 2H; major + minor), 3.70–3.55 (m, 4H; major + minor), 1.74 (d, *J* = 5.1 Hz, 3H; minor), 1.68 (dd, *J* = 6.0, 1.2 Hz, 3H; major); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 142.9, 142.8, 141.8, 136.59, 136.55, 132.4, 132.23, 132.20, 131.4, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.45, 128.37, 128.2, 126.6, 126.4, 126.1, 125.9, 125.8, 125.2, 123.0, 122.9, 122.8, 122.7, 116.04, 116.00, 113.5, 91.94, 91.92, 91.7, 38.8, 37.6, 31.9, 18.0, 13.0; HRMS (ESI) calcd for $C_{21}H_{20}Na$ [M + Na]$^+$ 295.1457, found 295.1460.



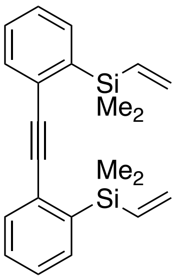
1-(2-Allylphenyl)-2-[2-(2-methallyl)phenyl]ethyne (1o). Colorless oil; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.56–7.50 (m, 2H), 7.33–7.17 (m, 6H), 6.04 (ddt, *J* = 16.9, 10.4, 6.6 Hz, 1H), 5.15–5.06 (m, 2H), 4.86–4.82 (m, 1H), 4.68 (q, *J* = 1.2 Hz, 1H), 3.68–3.62 (m, 2H), 3.60 (s, 2H), 1.76 (s, 3H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 144.5, 141.8, 141.4, 136.6, 132.3, 132.2, 129.3, 128.8, 128.5, 128.3, 126.1, 123.4, 122.9, 116.1, 112.1, 92.1, 91.4, 42.5, 38.8, 22.5; HRMS (ESI) calcd for $C_{21}H_{20}Na$ [M + Na]$^+$ 295.1457, found 295.1456.



1,2-Bis[2-(vinyloxy)phenyl]ethyne (1p). Yellow solid, mp 45–46 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.56 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.31 (dt, *J* = 1.8, 8.0 Hz, 2H), 7.08 (dt, *J* = 1.1, 7.6 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.71 (dd, *J* = 13.8, 6.0 Hz, 2H), 4.80 (dd, *J* = 13.8, 1.8 Hz, 2H), 4.47 (dd, *J* = 6.2, 2.0 Hz, 2H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 156.9, 148.5, 133.5, 129.7, 123.2, 117.0, 114.6, 95.1, 89.6; HRMS (ESI) calcd for $C_{18}H_{14}NaO_2$ [M + Na]$^+$ 285.0886, found 285.0888.

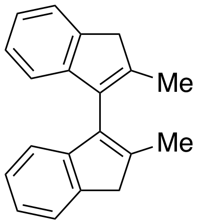


Dimethyl 2-allyl-2-[3-(2-allylphenyl)-2-propynyl]malonate (1q). Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 (d, *J* = 7.5 Hz, 1H), 7.23 (dt, *J* = 1.7, 7.6 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.15 (dt, *J* = 1.0, 7.5 Hz, 1H), 5.98 (ddt, *J* = 16.5, 10.5, 7.1 Hz, 1H), 5.68 (ddt, *J* = 17.3, 9.7, 7.4 Hz, 1H), 5.23–5.13 (m, 2H), 5.08–5.02 (m, 2H), 3.76 (s, 6H), 3.51 (d, *J* = 6.5 Hz, 2H), 3.07 (s, 2H), 2.87 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 170.3, 141.8, 136.6, 132.4, 131.8, 128.7, 128.2, 125.9, 122.6, 119.8, 115.8, 87.9, 82.1, 57.2, 52.8, 38.5, 36.8, 23.8; HRMS (ESI) calcd for $C_{20}H_{22}NaO_4$ [M + Na]$^+$ 349.1410, found 349.1410; IR (ν/cm^{-1}): 1740, 1220.

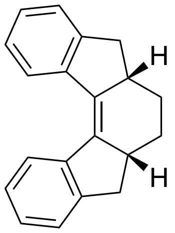


1,2-Bis{2-[dimethyl(vinyl)silyl]phenyl}ethyne (1r). Pale yellow solid, mp 48–50 ºC; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.56–7.53 (m, 4H), 7.37 (dt, *J* = 2.0, 7.5 Hz, 2H), 7.32 (dt, *J* = 1.2, 7.4 Hz, 2H), 6.50 (dd, *J* = 20.5, 14.5 Hz, 2H), 6.07 (dd, *J* = 14.8, 3.7 Hz, 2H), 5.81 (dd, *J* = 20.5, 3.5 Hz, 2H), 0.51 (s, 12H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 140.7, 137.9, 134.6, 132.7, 131.9, 129.0, 128.8, 127.4, 93.8, −2.6; HRMS (ESI) calcd for $C_{22}H_{26}NaSi_2$ [M + Na]$^+$ 369.1465, found 369.1463.

General Procedure for the Ruthenium-Catalysed Cycloisomerisation of 1,11-Dien-6-ynes 1 (GP-1 and GP-2). A Schlenk tube was charged with [GP-1: Cp*RuCl(cod) (3.8 mg, 0.010 mmol) and $P(C_6F_5)_3$ (10.6 mg, 0.020 mmol); GP-2: $[Cp^*Ru(MeCN)_3]PF_6$ (5.0 mg, 0.010 mmol)], and the tube was evacuated and backfilled with nitrogen. Methanol (1.0 mL) was added via a syringe through the septum, and the mixture was stirred at room temperature. After 10 min, dienyne **1** (0.200 mmol) and methanol (1.0 mL) were added successively, and the mixture was heated at 40 °C. After 24 h, the reaction mixture was filtered through a plug of Florisil® eluting with hexane–AcOEt (10:1), and the filtrate was concentrated. The residue was purified by preparative TLC (hexane–AcOEt) to afford product **2**.

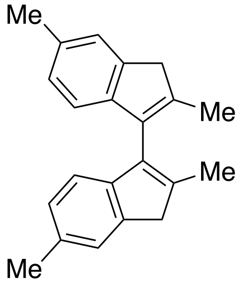


2,2′-Dimethyl-3*H*,3′*H*-1,1′-biindene (2a). The general procedure (GP-1) was followed by using **1a** (12.7/52.0 mg, 0.049/0.201 mmol). Purification by preparative TLC (hexane) yielded **2a** (11.0/42.5 mg, 0.043/0.164 mmol, 87%/82%) as a pale yellow solid. Mp 156–158 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.22–7.11 (m, 4H), 7.04–7.00 (m, 2H), 3.52 (s, 4H), 2.03 (s, 6H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 146.2, 142.6, 142.5, 132.8, 126.0, 123.7, 123.2, 120.0, 42.9, 15.4; HRMS (ESI) calcd for $C_{20}H_{18}Na$ $[M + Na]^+$ 281.1301, found 281.1302.

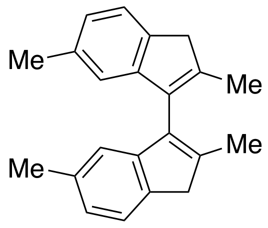


(5a*R,7a*S**)-5,5a,6,7,7a,8-Hexahydrodibenz[*a*,*i*]-*as*-indacene (3a).** The general procedure (GP-1) was followed by using **1a** (12.8 mg, 0.050 mmol), but at 40 °C in *i*-PrOH. Purification by preparative TLC (hexane) yielded **3a** (9.6 mg, 0.037 mmol, 75%) and **2a** (1.8 mg, 0.007 mmol, 14%). **3a:** Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 7.5 Hz, 2H), 7.29–7.17 (m, 6H), 3.23 (dd, J = 16.0, 9.0 Hz, 2H), 3.04–2.96 (m, 2H), 2.72 (dd, J = 16.3, 7.3 Hz, 2H), 2.11–2.03 (m, 2H), 1.53–1.46

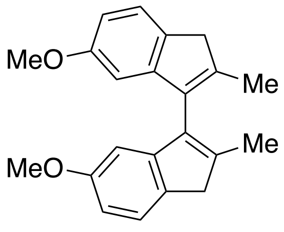
(m, 2H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 146.5, 140.3, 139.0, 127.3, 126.1, 125.1, 123.7, 42.2, 38.5, 27.4; HRMS (ESI) calcd for $C_{20}H_{18}Na$ [M + Na]$^+$ 281.1301, found 281.1306.



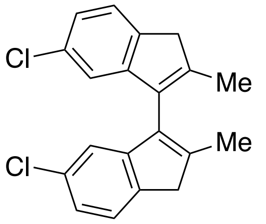
2,2′,5,5′-Tetramethyl-3*H*,3′*H*-1,1′-biindene (2b). The general procedure (GP-1) was followed by using **1b** (57.0/57.2 mg, 0.199/0.200 mmol). Purification by preparative TLC (hexane) yielded **2b** (39.7/37.2 mg, 0.139/0.130 mmol, 70%/65%) as an orange solid. Mp 110–115 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.28–7.25 (m, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 3.46 (s, 4H), 2.38 (s, 6H), 1.99 (s, 6H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 143.7, 142.9, 141.3, 133.2, 132.7, 126.6, 124.2, 119.7, 42.7, 21.4, 15.4; HRMS (ESI) calcd for $C_{22}H_{22}Na$ [M + Na]$^+$ 309.1614, found 309.1610.



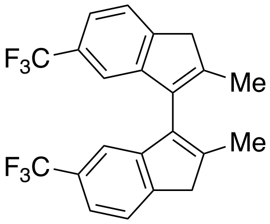
2,2′,6,6′-Tetramethyl-3*H*,3′*H*-1,1′-biindene (2c). The general procedure (GP-1) was followed by using **1c** (57.1/57.2 mg, 0.199/0.200 mmol). Purification by preparative TLC (hexane) yielded **2c** (40.4/42.0 mg, 0.141/0.147 mmol, 71%/73%) as a yellow solid. Mp 130–138 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.33 (d, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.2 Hz, 2H), 6.84 (s, 2H), 3.47 (s, 4H), 2.29 (s, 6H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.6, 142.8, 139.6, 135.7, 132.9, 124.5, 122.9, 120.7, 42.5, 21.4, 15.4; HRMS (ESI) calcd for $C_{22}H_{22}Na$ [M + Na]$^+$ 309.1614, found 309.1618.



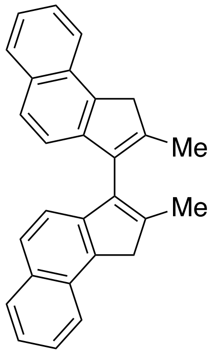
6,6′-Dimethoxy-2,2′-dimethyl-3*H*,3′*H*-1,1′-biindene (2d). The general procedure (GP-1) was followed by using **1d** (63.5/63.6 mg, 0.199/0.200 mmol). Purification by preparative TLC (hexane:AcOEt = 20:1) yielded **2d** (42.1/37.4 mg, 0.132/0.117 mmol, 66%/59%) as a brown solid. Mp 70–75 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 6.72 (dd, *J* = 7.8, 2.4 Hz, 2H), 6.62 (d, *J* = 2.4 Hz, 2H), 3.74 (s, 6H), 3.47 (s, 4H), 2.04 (s, 6H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 158.8, 147.6, 144.3, 134.6, 132.7, 123.5, 109.6, 105.8, 55.5, 42.2, 15.6; HRMS (ESI) calcd for $C_{22}H_{22}NaO_2$ [M + Na]$^+$ 341.1512, found 341.1508.



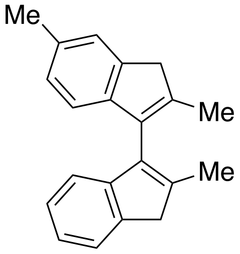
6,6′-Dichloro-2,2′-dimethyl-3*H*,3′*H*-1,1′-biindene (2e). The general procedure (GP-2) was followed by using **1e** (65.4/65.6 mg, 0.200/0.200 mmol), but at 60 °C. Purification by preparative TLC (hexane) yielded **2e** (29.4/28.3 mg, 0.090/0.0.086 mmol, 45%/43%) as a brown solid. Mp 138–141 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.11 (dd, *J* = 8.1, 2.1 Hz, 2H), 6.92 (d, *J* = 2.1 Hz, 2H), 3.49 (s, 4H), 2.01 (s, 6H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 147.6, 145.2,15.4, 140.7, 132.3, 131.7, 124.2, 123.8, 119.8, 42.5; HRMS (ESI) calcd for $C_{20}H_{16}Cl_2Na$ [M + Na]$^+$ 349.0521, found 349.0522.



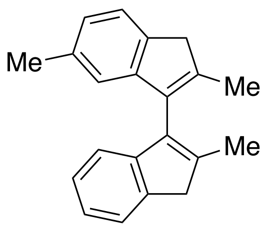
2,2′-Dimethyl-6,6′-bis(trifluoromethyl)-3*H*,3′*H*-1,1′-biindene (2f). The general procedure (GP-2) was followed by using **1f** (78.6/78.5 mg, 0.199/0.199 mmol). Purification by preparative TLC (hexane) yielded **2f** (21.8/23.0 mg, 0.055/0.0.058 mmol, 28%/29%) as a brown solid. Brown solid, mp 148–154 ºC; ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.16 (s, 2H), 3.60 (s, 4H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.3, 146.2, 145.3, 131.7, 128.9 (q, $^2J_{C\text{–}F}$ = 31.8 Hz), 124.7 (q, $^1J_{C\text{–}F}$ = 272.0 Hz), 123.4, 121.0 (q, $^3J_{C\text{–}F}$ = 3.8 Hz), 116.3 (q, $^3J_{C\text{–}F}$ = 3.8 Hz), 43.0, 15.5; HRMS (ESI) calcd for $C_{22}H_{16}F_6Na$ [M + Na]+ 417.1048, found 417.1048.



2,2′-Dimethyl-1*H*,1′*H*-3,3′-bi(cyclopenta[*a*]naphthalene) (2g). The general procedure (GP-1) was followed by using **1g** (71.5/71.6 mg, 0.199/0.200 mmol), but at 80 °C in MeOH (0.05 M). Purification by preparative TLC (hexane, then hexane:$CHCl_3$ = 10:1) yielded **2g** (30.9/25.5 mg, 0.086/0.071 mmol, 43%/36%) as a yellow solid. Mp 280 ºC (decomp.); ^1H NMR (399 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.50 (ddd, J = 8.2, 6.8, 1.4 Hz, 2H), 7.37 (ddd, J = 8.2, 7.0, 1.0 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 3.87 (s, 4H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.2, 138.5, 133.5, 131.2, 129.9, 128.8, 126.8, 126.1, 124.1, 123.3, 120.0, 41.8, 15.6; HRMS (ESI) calcd for $C_{28}H_{22}Na$ $[M + Na]^+$ 381.1614, found 381.1613.

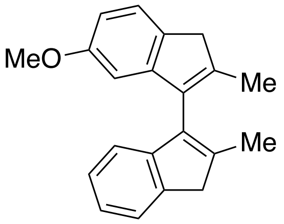


2,2′,5-Trimethyl-3*H*,3′*H*-1,1′-biindene (2h). The general procedure (GP-1) was followed by using **1h** (54.3/54.7 mg, 0.199/0.201 mmol). Purification by preparative TLC (hexane) yielded **2h** (49.9/48.6 mg, 0.183/0.178 mmol, 92%/89%) as an orange solid. Mp 98–100 ºC; ^1H NMR (301 MHz, $CDCl_3$) δ 7.47–7.42 (m, 1H), 7.30–7.26 (m, 1H), 7.20–7.09 (m, 2H), 7.04–6.95 (m, 2H), 6.90 (d, J = 7.5 Hz, 1H), 3.50 (s, 2H), 3.48 (s, 2H), 2.39 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 146.3, 143.6, 142.9, 142.5, 142.4, 141.4, 133.3, 133.0, 132.6, 126.6, 126.0, 124.2, 123.7, 123.2, 120.1, 119.7, 42.9, 42.7, 21.4, 15.4; HRMS (ESI) calcd for $C_{21}H_{20}Na$ $[M + Na]^+$ 295.1457, found 295.1459.

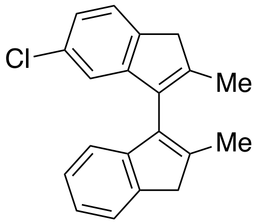


2,2′,6-Trimethyl-3*H*,3′*H*-1,1′-biindene (2i). The general procedure (GP-1) was followed by using **1i** (54.7/54.6 mg, 0.201/0.200 mmol). Purification by preparative TLC (hexane) yielded **2i** (47.9/46.0 mg, 0.176/0.169 mmol, 88%/84%) as a pale yellow solid. Mp 146–148 ºC; ^1H

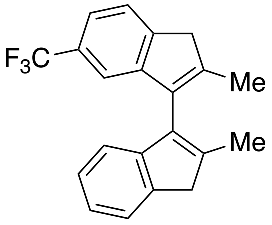
NMR (301 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.9 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.28–7.17 (m, 2H), 7.09 (d, *J* = 6.6 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.91 (s, 1H), 3.57 (s, 2H), 3.53 (s, 2H), 2.35 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 146.5, 146.3, 142.9, 142.53, 142.50, 139.6, 135.6, 133.0, 132.8, 126.0, 124.5, 123.7, 123.2, 122.9, 120.7, 120.1, 42.9, 42.5, 21.5, 15.42, 15.38; HRMS (ESI) calcd for $C_{21}H_{20}Na$ $[M + Na]^+$ 295.1457, found 295.1458.



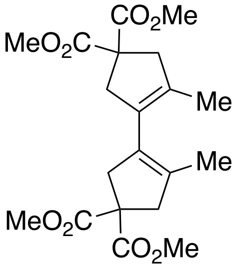
6-Methoxy-2,2′-dimethyl-3*H*,3′*H*-1,1′-biindene (2j). The general procedure (GP-1) was followed by using **1j** (57.8/57.8 mg, 0.200/0.200 mmol). Purification by preparative TLC (hexane:AcOEt = 20:1) yielded **2j** (49.7/47.9 mg, 0.172/0.166 mmol, 86%/83%) as a yellow solid. Mp 92–97 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.3 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.21–7.09 (m, 2H), 7.04–7.01 (m, 1H), 6.69 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.57 (d, *J* = 2.4 Hz, 1H), 3.70 (s, 3H), 3.51 (s, 2H), 3.45 (s, 2H), 2.02 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 158.8, 147.7, 146.1, 144.2, 142.6, 142.5, 134.6, 132.81, 132.78, 126.0, 123.7, 123.5, 123.2, 120.0, 109.6, 105.8, 55.4, 42.9, 42.2, 15.6, 15.4; HRMS (ESI) calcd for $C_{21}H_{20}NaO$ $[M + Na]^+$ 311.1406, found 311.1405.



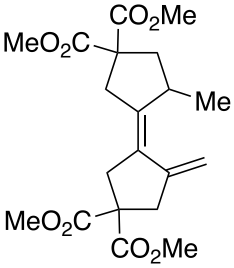
6-Chloro-2,2′-dimethyl-3*H*,3′*H*-1,1′-biindene (2k). The general procedure (GP-1) was followed by using **1k** (58.5/58.6 mg, 0.200/0.200 mmol). Purification by preparative TLC (hexane) yielded **2k** (30.1/34.5 mg, 0.103/0.118 mmol, 51%/59%) as an orange solid. Mp 74–75 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.48–7.43 (m, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.23–7.07 (m, 3H), 7.00–6.95 (m, 2H), 3.52 (s, 2H), 3.48 (s, 2H), 2.02 (s, 6H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 148.0, 145.8, 144.7, 143.1, 142.5, 140.7, 132.4, 132.21, 132.16, 126.2, 124.1, 123.9, 123.6, 123.3, 120.0, 119.8, 42.9, 42.4, 15.5, 15.4: HRMS (ESI) calcd for $C_{20}H_{17}ClNa$ [M + Na]$^+$ 315.0911, found 315.0916.



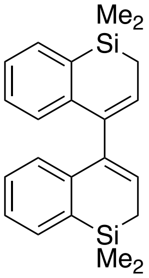
2,2′-Dimethyl-6-(trifluoromethyl)-3*H*,3′*H*-1,1′-biindene (2l). The general procedure (GP-1) was followed by using **1l** (65.0/65.6 mg, 0.199/0.201 mmol). Purification by preparative TLC (hexane) yielded **2l** (27.9/30.5 mg, 0.085/0.093 mmol, 43%/46%) as a yellow oil. ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.52 (d, J = 7.5 Hz, 1H), 7.49–7.44 (m, 1H), 7.43–7.37 (m, 1H), 7.21 (s, 1H), 7.20–7.12 (m, 2H), 6.98–6.93 (m, 1H), 3.56 (s, 2H), 3.54 (d, J = 2.1 Hz, 2H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 146.2, 145.8, 144.6, 143.3, 142.5, 132.5, 132.1, 128.7 (q, $^2J_{C–F}$ = 31.8 Hz), 126.2, 124.7 (q, $^1J_{C–F}$ = 272.0 Hz), 124.0, 123.4, 123.3, 120.8 (q, $^3J_{C–F}$ = 3.8 Hz), 119.7, 116.5 (q, $^3J_{C–F}$ = 3.8 Hz), 43.0, 42.9, 15.5, 15.4; HRMS (ESI) calcd for $C_{21}H_{17}F_3Na$ [M + Na]$^+$ 349.1175, found 349.1175.



Tetramethyl 5,5′-dimethyl-[1,1′-bi(cyclopentane)]-5,5′-diene-3,3,3′,3′-tetracarboxylate (2m). The general procedure (GP-2) was followed by using **1m** (79.3/79.2 mg, 0.201/0.201 mmol). Purification by preparative TLC (hexane:AcOEt = 3:1) yielded **2m** (64.5/66.1 mg, 0.164/0.168 mmol, 81%/83%) as a colorless oil. ^{1}H NMR (301 MHz, $CDCl_3$) δ 3.73 (s, 12H), 3.03–2.97 (m, 8H), 1.54 (s, 6H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 172.6, 132.3, 128.6, 57.7, 52.8, 45.6, 43.3, 15.0; HRMS (ESI) calcd for $C_{20}H_{26}NaO_8$ [M + Na]$^+$ 417.1520, found 417.1523; IR (ν/cm^{-1}): 1736, 1266.



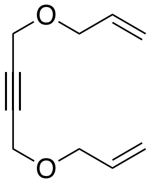
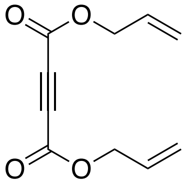
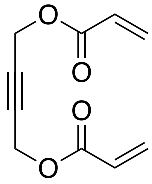
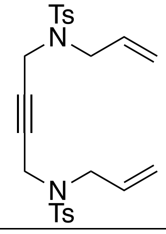
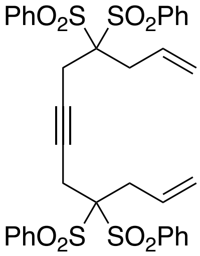
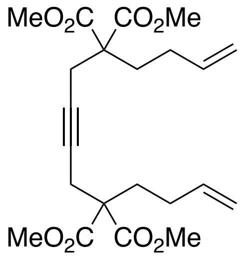
Tetramethyl (*Z*)-5-methyl-5′-methylene-[1,1′-bi(cyclopentylidene)]-3,3,3′,3′-tetracarboxylate (4m). The general procedure (GP-2) was followed by using **1m** (19.8 mg, 0.050 mmol), but at 0 °C for 1 h. Purification by preparative TLC (hexane:AcOEt = 3:1) yielded **4m** (10.8 mg, 0.027 mmol, 55%) as a colorless oil. ^{1}H NMR (301 MHz, CDCl$_3$) δ 5.11–5.02 (m, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.722 (s, 3H), 3.715 (s, 3H), 3.19–2.80 (m, 7H), 2.67 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.09 (dd, *J* = 13.5, 3.9 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.6, 172.2, 171.8, 171.7, 143.9, 141.9, 127.7, 109.1, 58.3, 57.3, 52.85, 52.81, 52.78, 43.2, 42.2, 40.7, 40.5, 35.5, 18.2; HRMS (ESI) calcd for $C_{20}H_{26}NaO_8$ [M + Na]$^+$ 417.1520, found 417.1516; IR (ν/cm^{-1}): 1737, 1263.



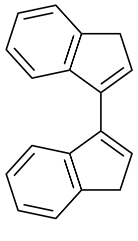
1,1,1′,1′-Tetramethyl-1,1′,2,2′-tetrahydro-4,4′-bibenzo[*b*]siline (5). A Schlenk tube was charged with **1r** (17.4 mg, 0.050 mmol) and Cp*RuCl(PPh$_3$)$_2$ (2.0 mg, 0.0025 mmol), and the tube was evacuated and backfilled with nitrogen. Ethanol (0.5 mL) was added via a syringe through the septum, and the mixture was stirred at 60 °C. After 3 h, the reaction mixture was filtered through a plug of Florisil® eluting with hexane–AcOEt (10:1), and the filtrate was concentrated. The residue was purified by preparative TLC (hexane) to afford product **5** (7.5 mg, 0.022 mmol, 43%) as a yellow oil. ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.50–7.46 (m, 2H), 7.16–7.09 (m, 4H), 7.01–7.07 (m, 2H), 6.16 (t, *J* = 5.9 Hz, 2H), 1.67 (d, *J* = 5.4 Hz, 4H), 0.37 (s, 12H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 142.9, 142.7, 134.3, 132.5, 129.5, 127.3, 127.1, 126.1, 13.4; HRMS (ESI) calcd for $C_{22}H_{26}NaSi_2$ [M + Na]$^+$ 369.1465, found 369.1466.

Dienynes that Failed to Undergo the Ruthenium-Catalysed Cycloisomerisation

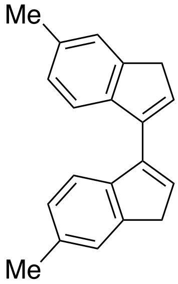
Conditions **A**: [Cp*Ru(MeCN)$_3$]PF$_6$; **B**: Cp*RuCl(cod)–P(C$_6$F$_5$)$_3$

	**A:** complex mixture **B:** complex mixture		**A:** complex mixture **B:** complex mixture
	**A:** complex mixture **B:** decomposition		**A:** complex mixture **B:** complex mixture
	**A:** no reaction **B:** no reaction		**A:** no reaction

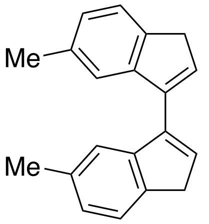
General Procedure for the Ruthenium-Catalysed Tandem Ring-Closing Metathesis of 1,11-Dien-6-ynes 1 (GP-3). A Schlenk tube was charged with Hoveyda–Grubbs 2nd generation catalyst (3.8 mg, 0.006 mmol), and the tube was evacuated and backfilled with nitrogen. Dienyne **1** (0.200 mmol) and toluene (10 mL) was added successively via a syringe through the septum, and the mixture was heated at 100 °C for 6 h. After cooling to room temperature, the reaction mixture was filtered through a plug of Florisil® eluting with hexane–AcOEt (10:1), and the filtrate was concentrated. The residue was purified by preparative TLC or column chromatography on silica gel (hexane–ACOEt) to afford product **6**.



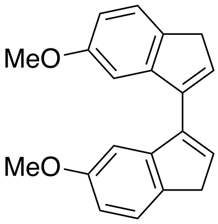
3*H*,3′*H*-1,1′-Biindene (6a). The general procedure (GP-3) was followed by using **1a** (12.9/51.8 mg, 0.050/0.200 mmol). Purification by preparative TLC (hexane) yielded **6a** (9.4/37.9 mg, 0.041/0.165 mmol, 82%/82%) as a pale yellow solid. Mp 128–132 ºC; ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.58–7.53 (m, 4H), 7.34–7.24 (m, 4H), 6.77 (t, *J* = 1.8 Hz, 2H), 3.58 (d, *J* = 1.6 Hz, 4H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 144.3, 144.2, 138.9, 131.3, 126.1, 124.9, 123.9, 120.7, 38.4; HRMS (ESI) calcd for $C_{18}H_{14}Na$ $[M + Na]^+$ 253.0988, found 253.0991.



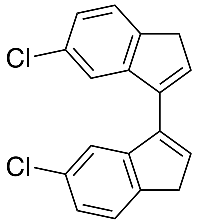
5,5′-Dimethyl-3*H*,3′*H*-1,1′-biindene (6b). The general procedure (GP-3) was followed by using **1b** (57.0/57.4 mg, 0.199/0.200 mmol). Purification by preparative TLC (hexane) yielded **6b** (37.1/39.2 mg, 0.144/0.152 mmol, 72%/76%) as an orange solid. Mp 146–148 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.37 (s, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.72–6.57 (m, 2H), 3.53 (s, 4H), 2.43 (s, 6H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 144.6, 141.7, 138.9, 134.6, 130.1, 126.8, 124.8, 120.4, 38.2, 21.4; HRMS (ESI) calcd for $C_{20}H_{18}Na$ $[M + Na]^+$ 281.1301, found 281.1297.



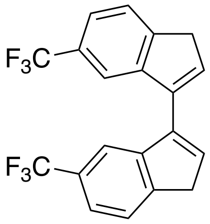
6,6′-Dimethyl-3*H*,3′*H*-1,1′-biindene (6c). The general procedure (GP-3) was followed by using **1c** (57.1/57.2 mg, 0.199/0.200 mmol). Purification by preparative TLC (hexane) yielded **6c** (45.1/43.8 mg, 0.175/0.170 mmol, 88%/85%) as a pale yellow solid. Mp 140–142 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.36 (s, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.73 (s, 2H), 3.54 (s, 4H), 2.40 (s, 6H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 144.6, 141.3, 138.9, 135.7, 131.5, 125.7, 123.6, 121.3, 38.0, 21.5; HRMS (ESI) calcd for $C_{20}H_{18}Na$ $[M + Na]^+$ 281.1301, found 281.1306.



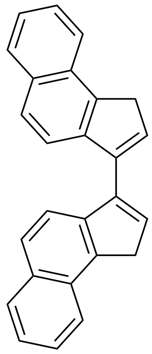
6,6′-Dimethoxy-3*H*,3′*H*-1,1′-biindene (6d). The general procedure (GP-3) was followed by using **1d** (63.6/63.7 mg, 0.200/0.200 mmol). Purification by column chromatography on silica gel (hexane:AcOEt = 20:1) yielded **6d** (36.7/36.9 mg, 0.126/0.127 mmol, 63%/64%) as a brown oil. ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 2.4 Hz, 2H), 6.83 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.77 (t, *J* = 1.8 Hz, 2H), 3.81 (s, 6H), 3.52 (d, *J* = 1.5 Hz, 4H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 158.8, 145.7, 138.8, 136.3, 132.7, 124.3, 111.0, 106.3, 55.6, 37.7; HRMS (ESI) calcd for $C_{20}H_{18}NaO_2$ $[M + Na]^+$ 313.1199, found 313.1199.



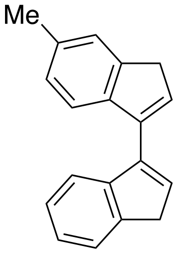
6,6′-Dichloro-3*H*,3′*H*-1,1′-biindene (6e). The general procedure (GP-3) was followed by using **1e** (65.2/65.4 mg, 0.199/0.200 mmol). Purification by column chromatography on silica gel (hexane:$CHCl_3$ = 20:1) yielded **6e** (57.5/57.5 mg, 0.192/0.192 mmol, 96%/96%) as a yellow solid. Mp 154–156 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.8 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.27–7.21 (m, 2H), 6.81 (t, *J* = 1.8 Hz, 2H), 3.57 (d, *J* = 1.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 142.3, 137.7, 133.1, 132.4, 125.1, 124.9, 120.7, 38.1; HRMS (ESI) calcd for $C_{18}H_{12}Cl_2Na$ $[M + Na]^+$ 321.0208, found 321.0208.



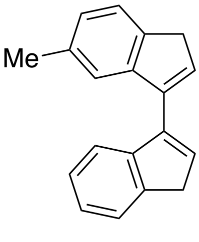
6,6′-Bis(trifluoromethyl)-3*H*,3′*H*-1,1′-biindene (6f). The general procedure (GP-3) was followed by using **1f** (78.8/79.0 mg, 0.200/0.200 mmol). Purification by column chromatography on silica gel (hexane) yielded **6f** (63.6/58.1 mg, 0.174/0.159 mmol, 87%/79%) as a yellow solid. Mp 154–158 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 6.93–6.88 (m, 2H), 3.69 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 144.5, 137.7, 133.2, 129.0 (q, $^2J_{C–F}$ = 32.0 Hz), 124.6 (q, $^1J_{C–F}$ = 272.3 Hz), 124.2, 122.2 (q, $^3J_{C–F}$ = 4.0 Hz), 117.2 (q, $^3J_{C–F}$ = 3.6 Hz), 38.6; HRMS (ESI) calcd for $C_{20}H_{12}F_6Na$ $[M + Na]^+$ 389.0735, found 389.0739.



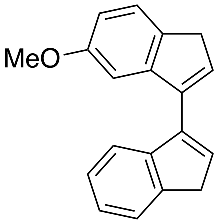
1*H*,1′*H*-3,3′-Bi(cyclopenta[*a*]naphthalene) (6g). The general procedure (GP-3) was followed by using **1g** (71.5/71.8 mg, 0.199/0.200 mmol). Purification by column chromatography on silica gel (hexane:CHCl$_3$ = 20:1) yielded **6g** (42.7/47.3 mg, 0.129/0.143 mmol, 65%/71%) as a brown solid. Mp 182 ºC (decomp.); ^{1}H NMR (301 MHz, CDCl$_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.54 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 2H), 7.44 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 2H), 6.92–6.89 (m, 2H), 3.94 (d, *J* = 1.5 Hz, 4H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 141.8, 141.0, 139.8, 131.7, 130.6, 130.1, 128.8, 127.0, 126.2, 124.8, 123.6, 120.0, 37.4; HRMS (ESI) calcd for $C_{26}H_{18}Na$ [M + Na]$^+$ 353.1301, found 353.1306.



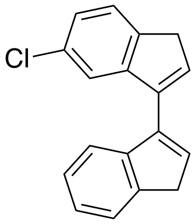
5-Methyl-3*H*,3′*H*-1,1′-biindene (6h). The general procedure (GP-3) was followed by using **1h** (54.5/54.7 mg, 0.200/0.201 mmol). Purification by preparative TLC (hexane) yielded **6h** (43.6/44.6 mg, 0.178/0.183 mmol, 89%/91%) as a brown oil. ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.59–7.52 (m, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.37 (s, 1H), 7.35–7.20 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.76 (t, *J* = 2.1 Hz, 1H), 6.70 (t, *J* = 2.1 Hz, 1H), 3.57 (s, 2H), 3.55 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (75.6 MHz, CDCl$_3$) δ 144.5, 144.3, 144.2, 141.7, 139.1, 138.7, 134.6, 131.1, 130.2, 126.8, 126.1, 124.84, 124.82, 123.9, 120.7, 120.3, 38.4, 38.2, 21.4; HRMS (ESI) calcd for $C_{19}H_{16}Na$ [M + Na]$^+$ 267.1144, found 267.1147.



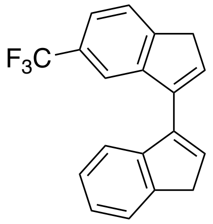
6-Methyl-3*H*,3′*H*-1,1′-biindene (6i). The general procedure (GP-3) was followed by using **1i** (54.5/54.3 mg, 0.200/0.199 mmol). Purification by preparative TLC (hexane) yielded **6i** (39.2/36.1 mg, 0.160/0.148 mmol, 80%/74%) as a brown oil. ^{1}H NMR (301 MHz, CDCl$_3$) δ 7.58–7.53 (m, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.37 (s, 1H), 7.35–7.23 (m, 2H), 7.08 (d, J = 8.1 Hz, 1H), 6.78–6.73 (m, 2H), 3.59 (d, J = 1.8 Hz, 2H), 3.54 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 144.6, 144.4, 144.2, 141.3, 139.0, 138.8, 135.7, 131.6, 131.2, 126.1, 125.8, 124.9, 123.9, 123.6, 121.3, 120.7, 38.4, 38.0, 21.6; HRMS (ESI) calcd for $C_{19}H_{16}Na$ [M + Na]$^+$ 267.1144, found 267.1139.



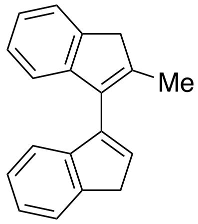
6-Methoxy-3*H*,3′*H*-1,1′-biindene (6j). The general procedure (GP-3) was followed by using **1j** (57.7/57.4 mg, 0.200/0.199 mmol). Purification by column chromatography on silica gel (hexane:AcOEt = 20:1) yielded **6j** (40.6/36.0 mg, 0.156/0.138 mmol, 78%/69%) as a brown oil. ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.61–7.55 (m, 2H), 7.45 (d, J = 7.8 Hz, 1H), 7.38–7.27 (m, 2H), 7.14 (d, J = 2.4 Hz, 1H), 6.85 (dd, J = 8.4, 2.4 Hz, 1H), 6.81 (t, J = 2.1 Hz, 1H), 6.78 (t, J = 2.1 Hz, 1H), 3.83 (s, 3H), 3.60 (d, J = 1.5 Hz, 2H), 3.54 (d, J = 1.5 Hz, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 158.8, 145.8, 144.3, 144.2, 138.9, 138.8, 136.3, 132.7, 131.2, 126.1, 124.9, 124.3, 123.9, 120.7, 110.9, 106.4, 55.6, 38.4, 37.7; HRMS (ESI) calcd for $C_{19}H_{16}NaO$ [M + Na]$^+$ 283.1093, found 283.1088.



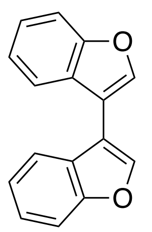
6-Chloro-3*H*,3′*H*-1,1′-biindene (6k). The general procedure (GP-3) was followed by using **1k** (58.4/58.8 mg, 0.199/0.201 mmol). Purification by column chromatography on silica gel (hexane) yielded **6k** (40.3/44.8 mg, 0.152/0.169 mmol, 76%/84%) as a yellow solid. Mp 66–69 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.59–7.50 (m, 3H), 7.45 (d, J = 7.8 Hz, 1H), 7.35–7.20 (m, 3H), 6.82 (t, J = 2.1 Hz, 1H), 6.76 (t, J = 2.3 Hz, 1H), 3.59 (d, J = 1.5 Hz, 2H), 3.56 (d, J = 1.8 Hz, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 146.1, 144.2, 143.9, 142.4, 138.29, 138.28, 132.8, 132.3, 131.6, 126.2, 125.0, 124.8, 124.7, 124.0, 120.8, 120.4, 38.4, 38.0; HRMS (ESI) calcd for $C_{18}H_{13}ClNa$ $[M + Na]^+$ 287.0598, found 287.0600.



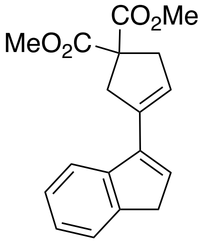
6-(Trifluoromethyl)-3*H*,3′*H*-1,1′-biindene (6l). The general procedure (GP-3) was followed by using **1l** (65.4/65.1 mg, 0.200/0.199 mmol). Purification by column chromatography on silica gel (hexane) yielded **6l** (49.2/52.6 mg, 0.165/0.176 mmol, 82%/88%) as a yellow solid. Mp 90–93 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.66–7.50 (m, 4H), 7.26–7.37 (m, 2H), 6.88 (t, *J* = 2.1 Hz, 1H), 6.79 (t, *J* = 2.1 Hz, 1H), 3.65 (s, 2H), 3.64–3.60 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 144.9, 144.2, 143.9, 138.4, 138.2, 132.7, 131.8, 128.8 (q, $^2J_{C-F}$ = 31.6 Hz), 126.2, 125.2, 124.7 (q, $^1J_{C-F}$ = 272.3 Hz), 124.1, 124.0, 121.9 (q, $^3J_{C-F}$ = 4.0 Hz), 120.4, 117.4 (q, $^3J_{C-F}$ = 3.6 Hz), 38.51, 38.48; HRMS (ESI) calcd for $C_{19}H_{13}F_3Na$ $[M + Na]^+$ 321.0862, found 321.0862.



2-Methyl-3*H*,3′*H*-1,1′-biindene (6o). The general procedure (GP-3) was followed by using **1o** (54.7/54.6 mg, 0.201/0.200 mmol). Purification by preparative TLC (hexane) yielded **6o** (35.7/38.1 mg, 0.146/0.156 mmol, 73%/78%) as a pale yellow solid. Mp 110–115 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.59–7.52 (m, 1H), 7.42–7.48 (m, 1H), 7.28–7.11 (m, 6H), 6.53 (t, *J* = 2.1 Hz, 1H), 3.59 (s, 2H), 3.50 (d, *J* = 4.8 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 144.8, 144.1, 142.4, 142.3, 138.9, 133.3, 132.6, 126.1, 126.0, 124.6, 123.83, 123.78, 123.2, 121.1, 119.8, 43.0, 38.6, 15.4; HRMS (ESI) calcd for $C_{19}H_{16}Na$ [M + Na]+ 267.1144, found 267.1139.

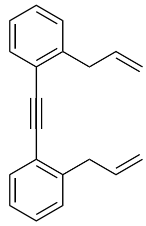


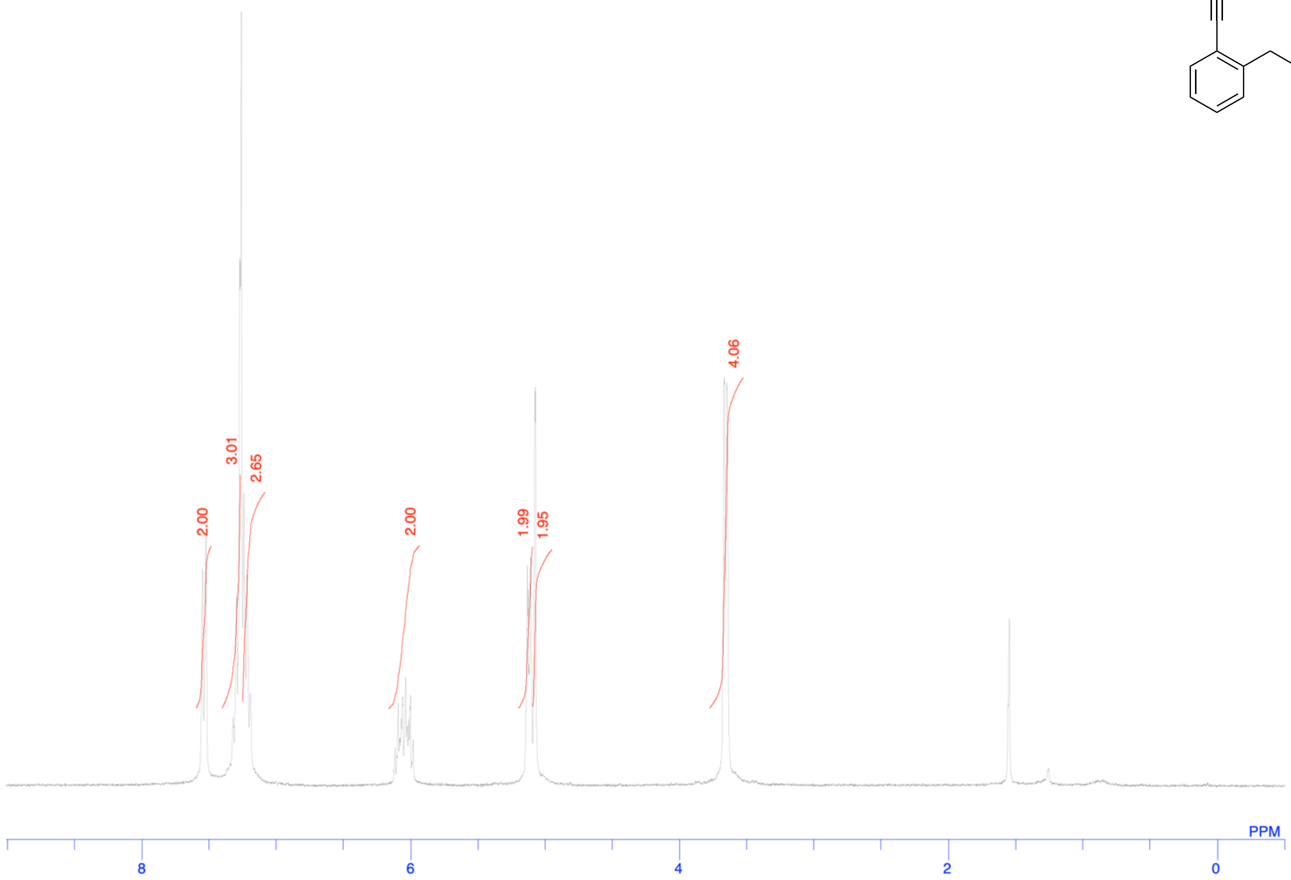
3,3′-Bibenzofuran (6p). The general procedure (GP-3) was followed by using **1p** (52.6/52.3 mg, 0.201/0.199 mmol). Purification by column chromatography on silica gel (hexane:AcOEt = 20:1) yielded **6p** (45.1/42.1 mg, 0.193/0.180 mmol, 96%/90%) as a yellow solid. Mp 136–139 ºC; ^{1}H NMR (301 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.77–7.72 (m, 2H), 7.62–7.57 (m, 2H), 7.40 (dt, *J* = 1.5, 7.5 Hz, 2H), 7.34 (dt, *J* = 1.3, 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 141.6, 126.5, 124.9, 123.1, 120.5, 112.4, 111.8; HRMS (ESI) calcd for $C_{16}H_{10}NaO_2$ [M + Na]+ 257.0573, found 257.0574.



Dimethyl 3-(1*H*-inden-3-yl)-3-cyclopentene-1,1-dicarboxylate (6q). The general procedure (GP-3) was followed by using **1q** (65.0/65.4 mg, 0.199/0.200 mmol). Purification by column chromatography on silica gel (hexane:AcOEt = 10:1) yielded **6q** (51.9/49.4 mg, 0.174/0.166 mmol, 87%/83%) as a brown oil. ^{1}H NMR (301 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.31 (dt, *J* = 1.2, 7.7 Hz, 1H), 7.22 (dt, *J* = 1.2, 7.3 Hz, 1H), 6.44–6.48 (m, 1H), 6.18 (s, 1H), 3.77 (s, 6H), 3.41–3.45 (m, 4H), 3.29 (s, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 172.4, 144.5, 143.0, 139.0, 135.1, 131.6, 126.1, 124.8, 123.9, 123.1, 120.9, 58.0, 52.9, 42.7, 41.7, 37.8; HRMS (ESI) calcd for $C_{18}H_{18}NaO_4$ [M + Na]$^+$ 321.1097, found 321.1101; IR (*v*/cm^{-1}): 1735, 1260.

1a

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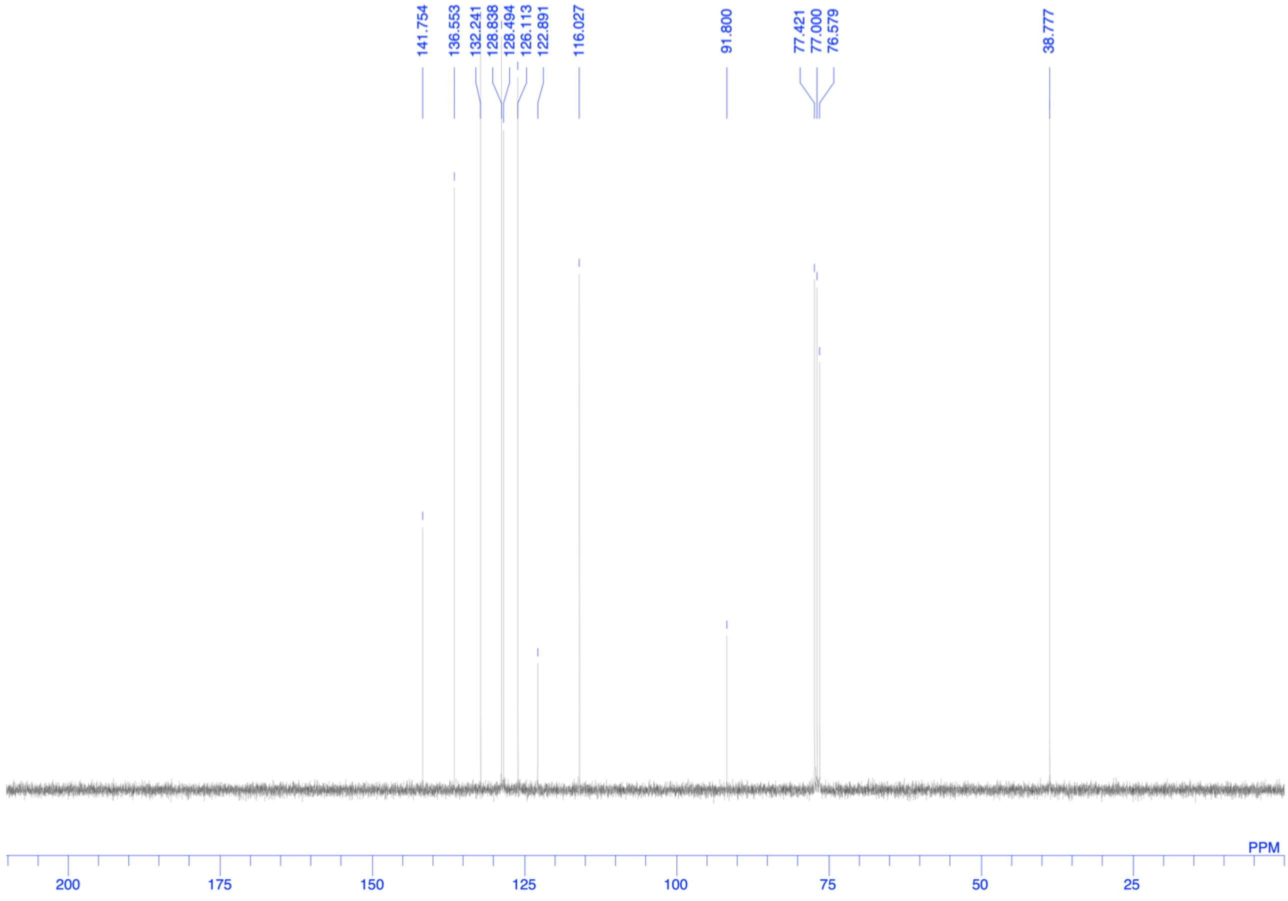
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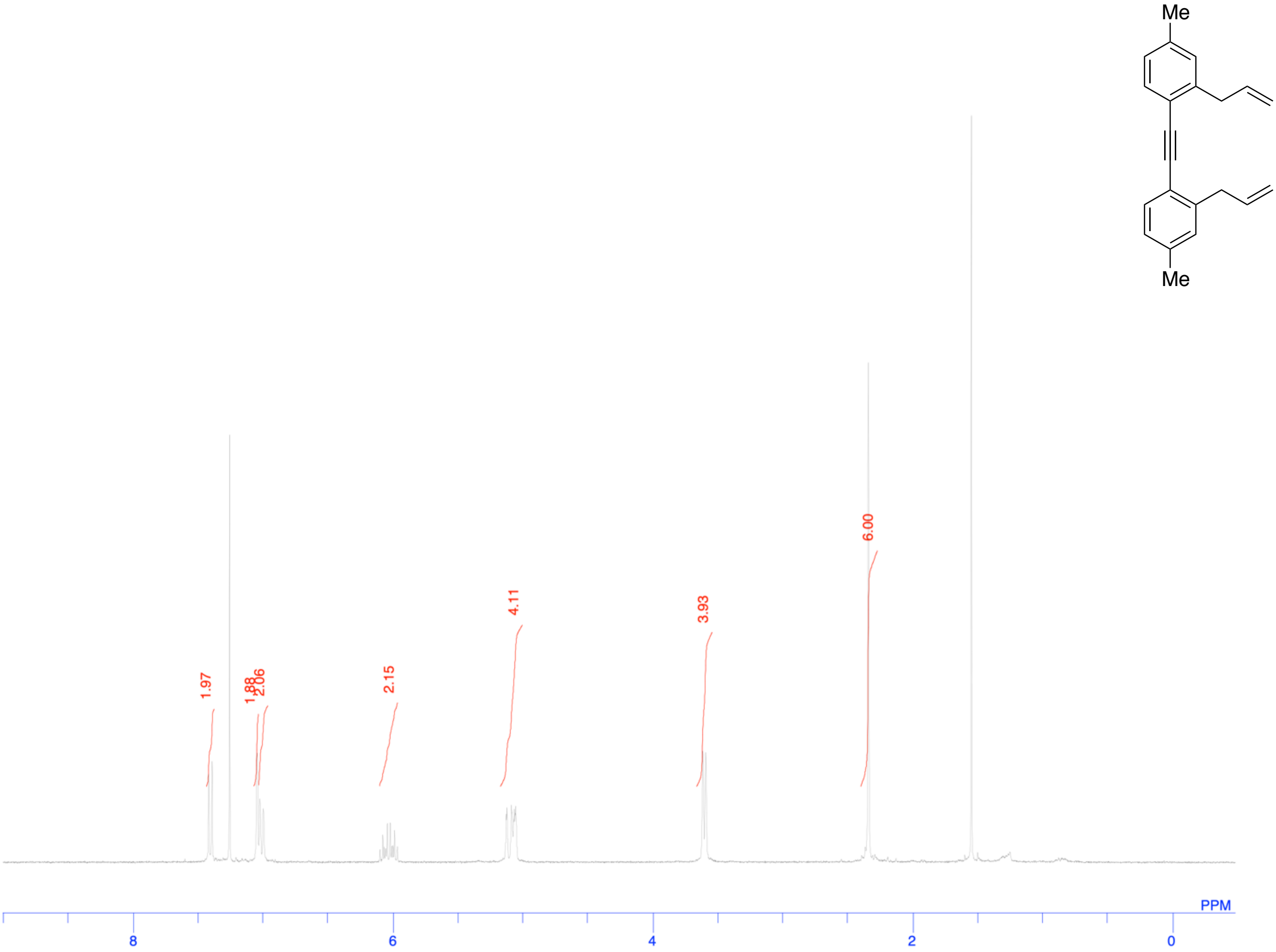
1b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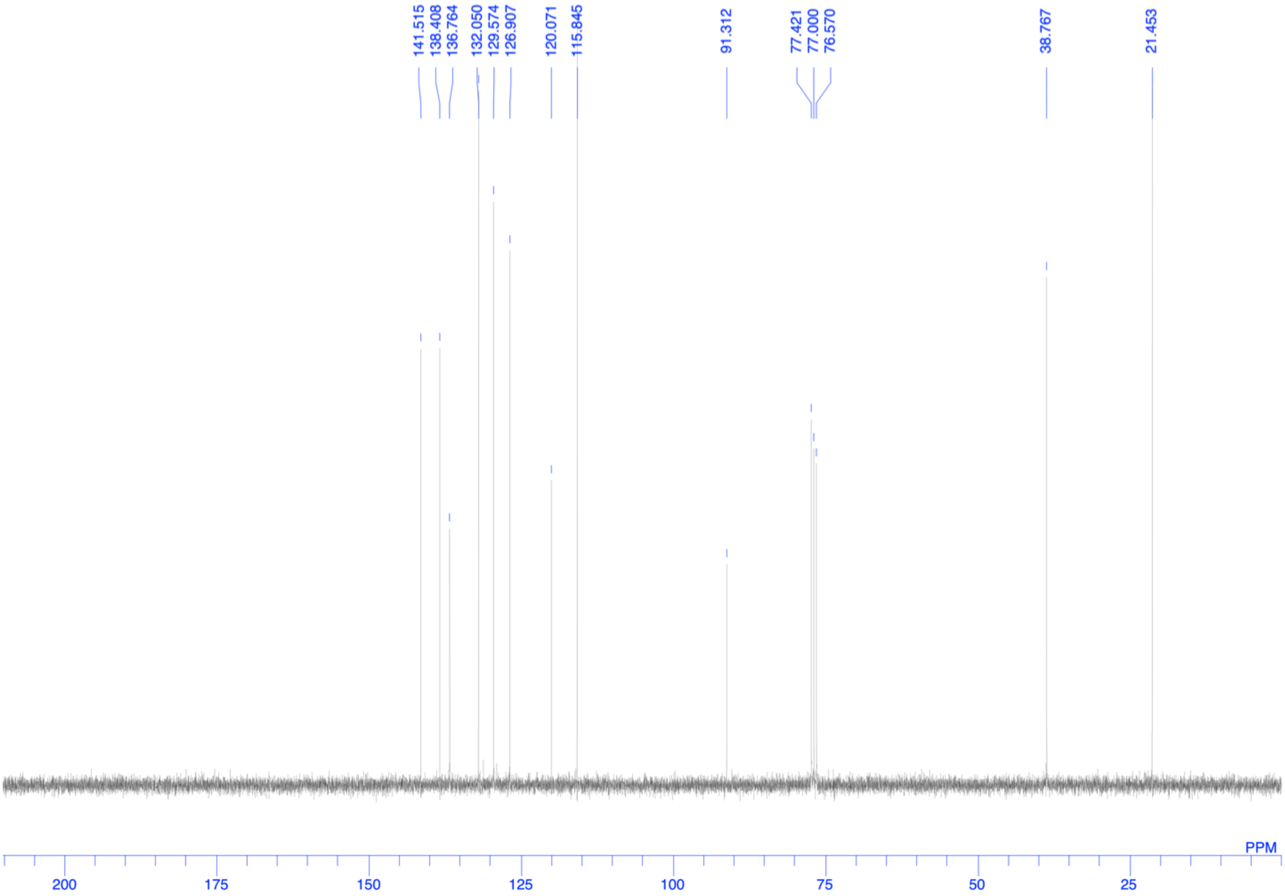
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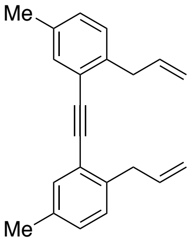
25

1c


Me
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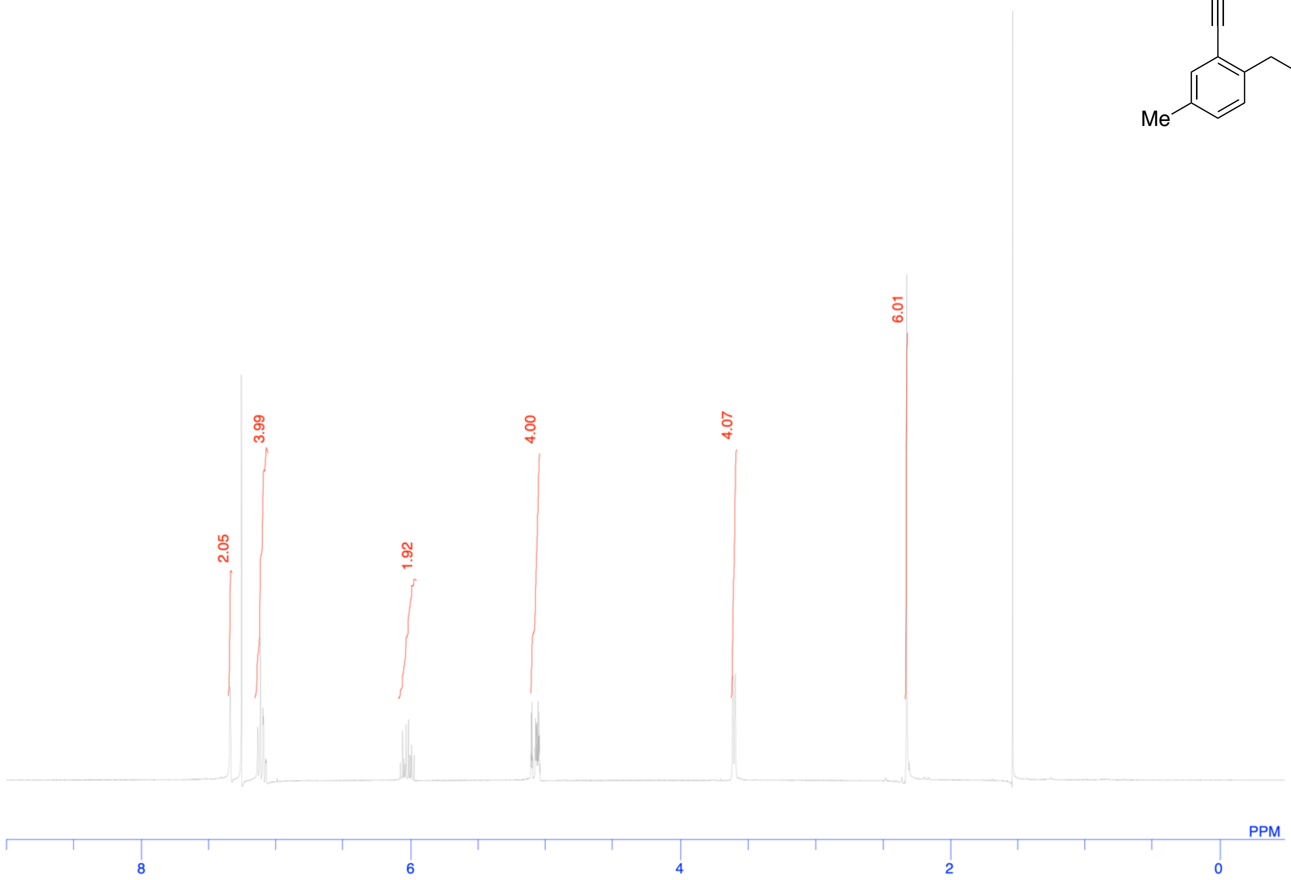
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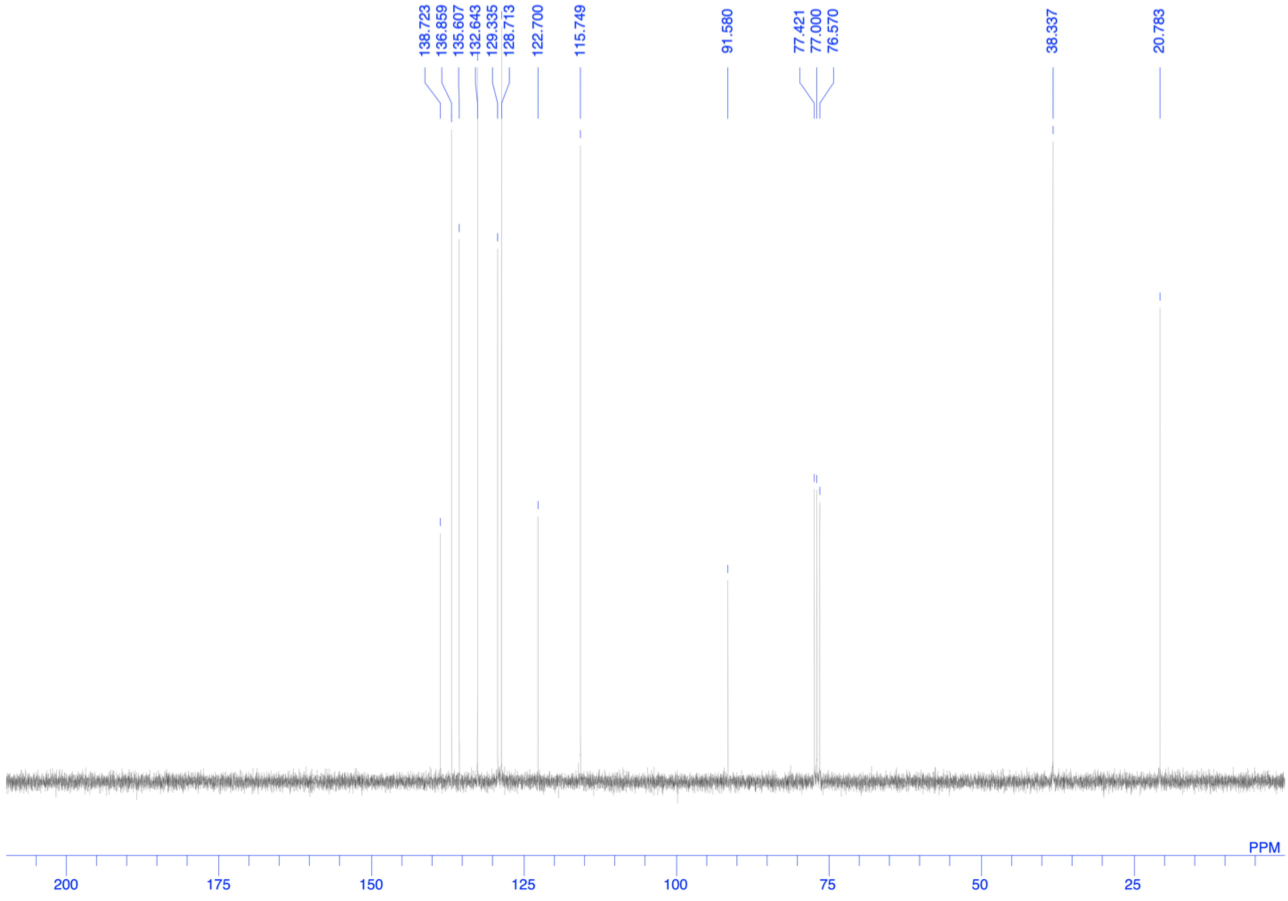
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25

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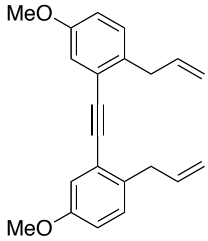
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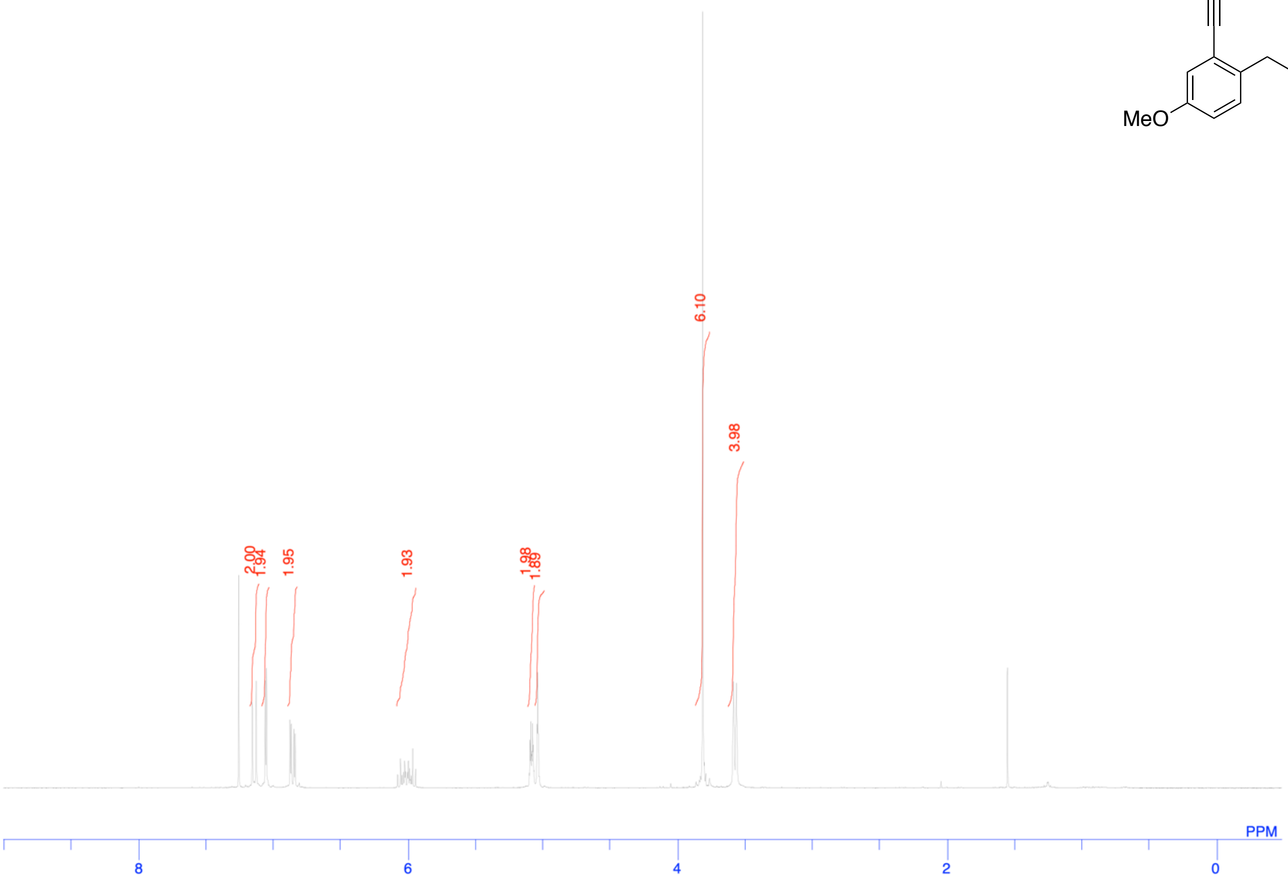
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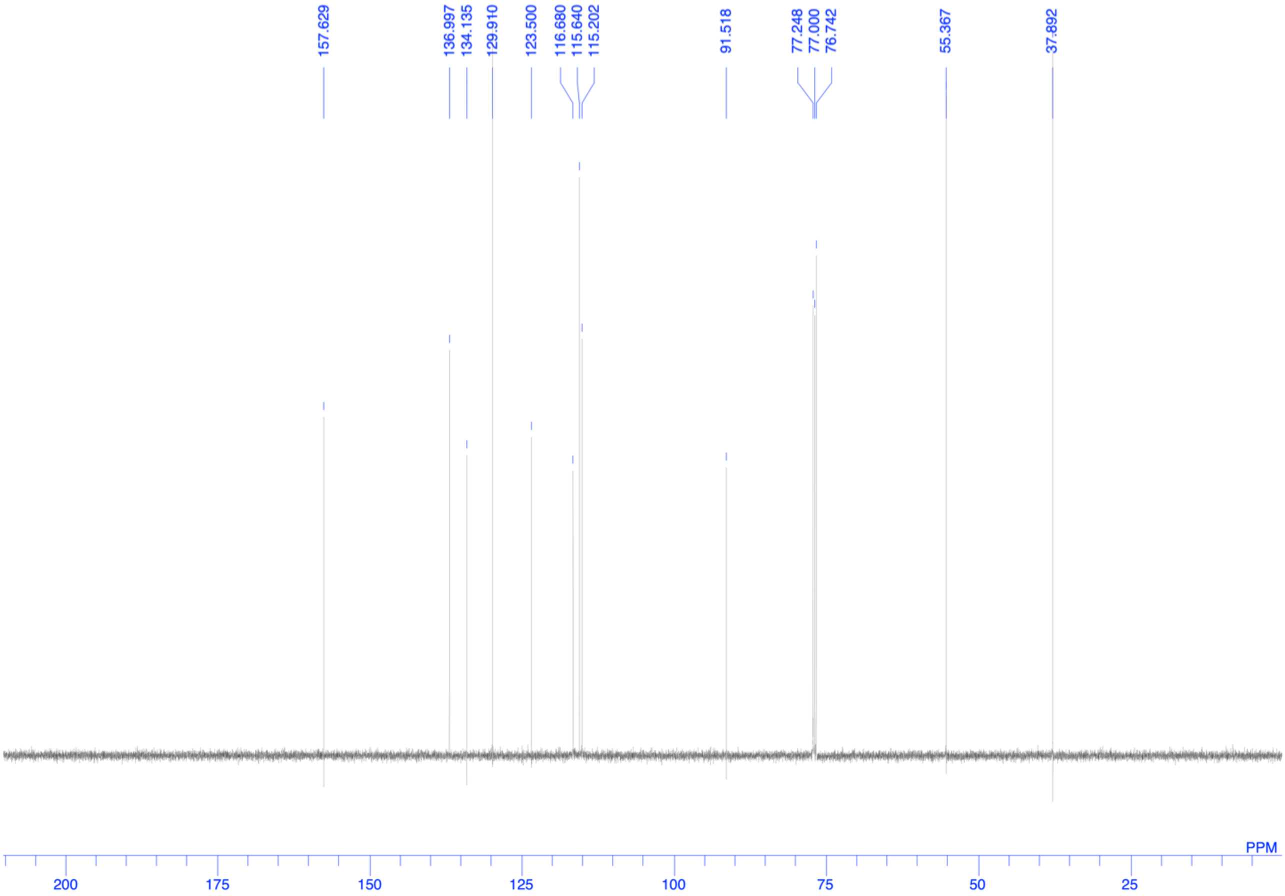
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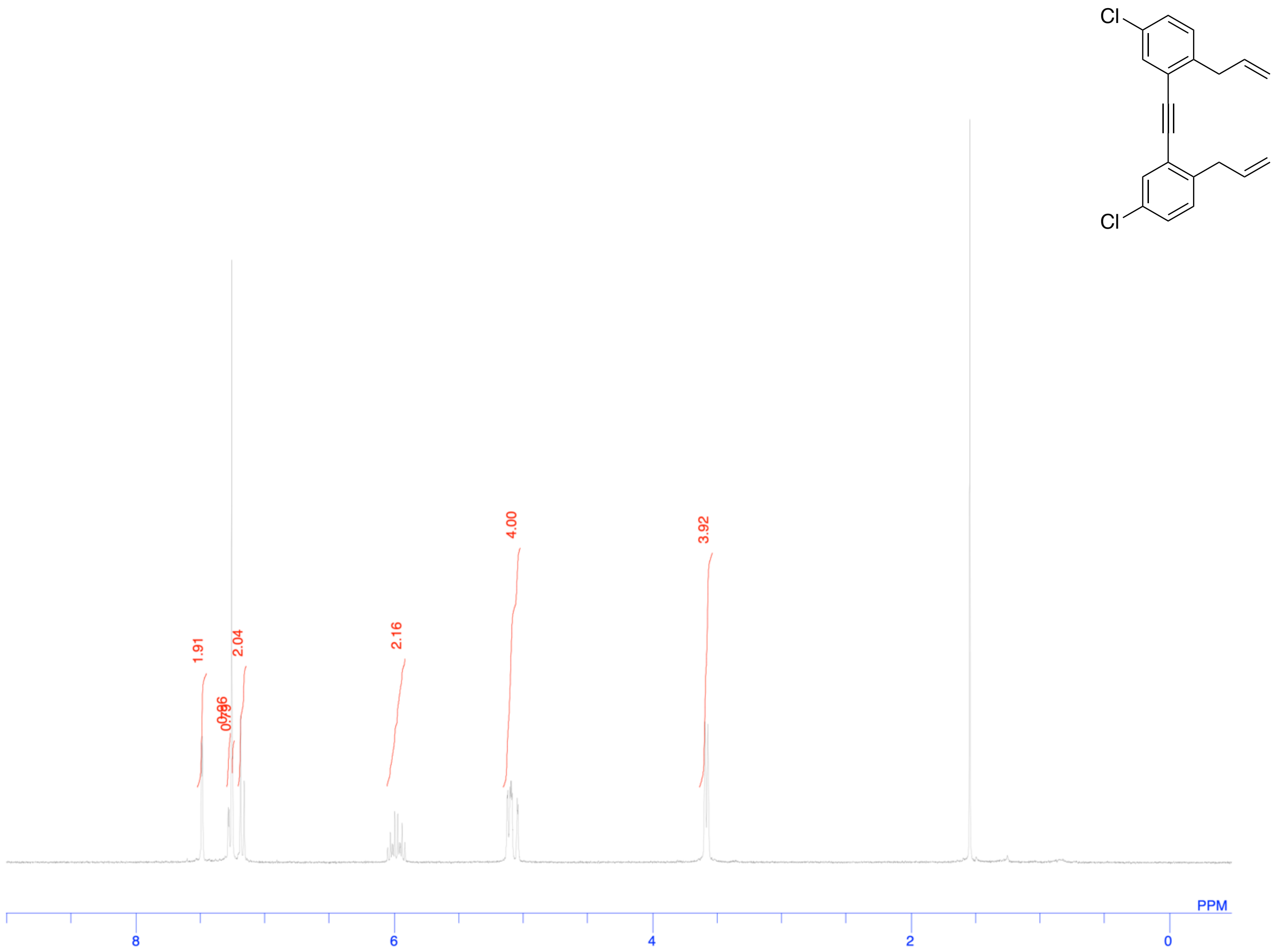

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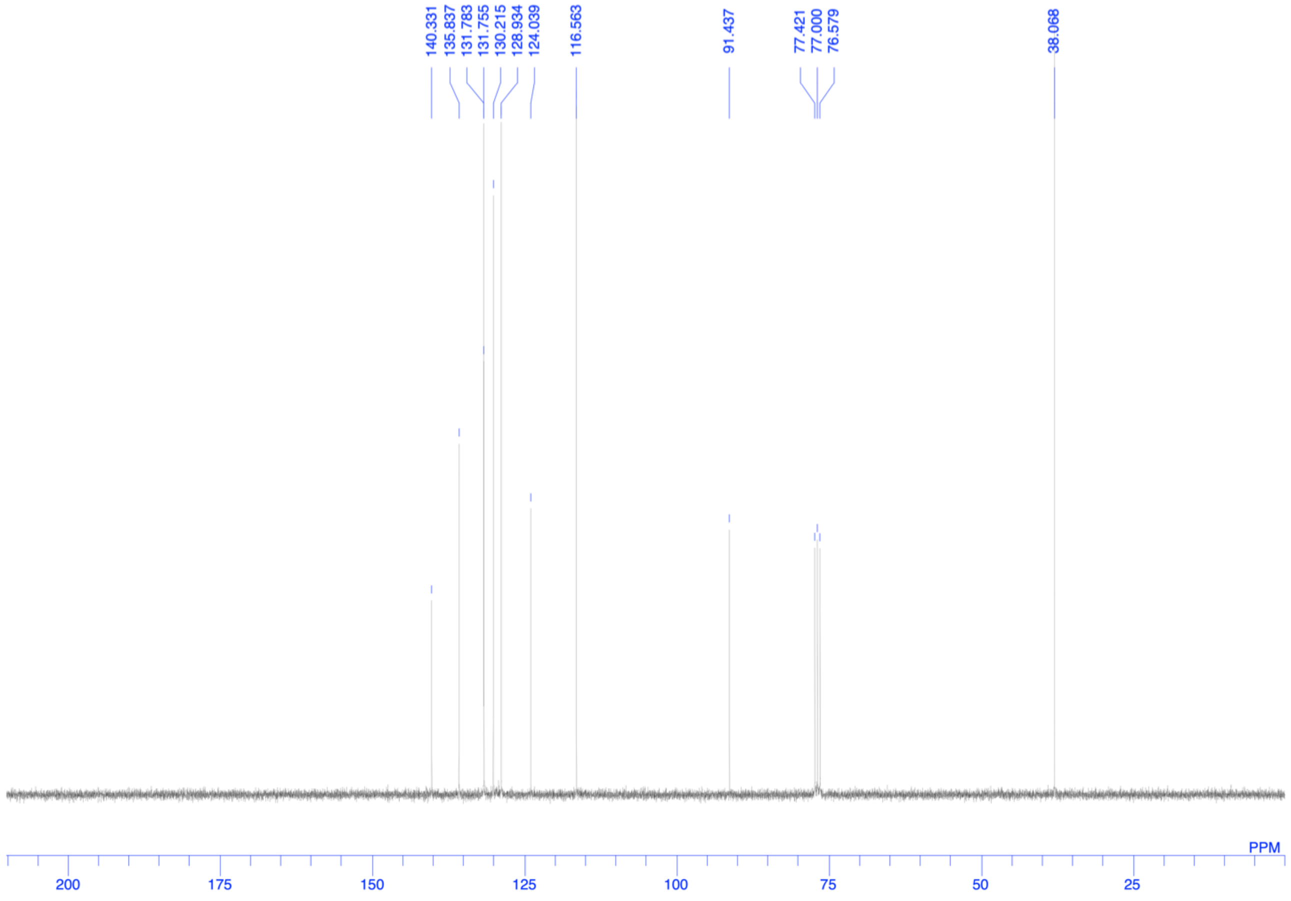

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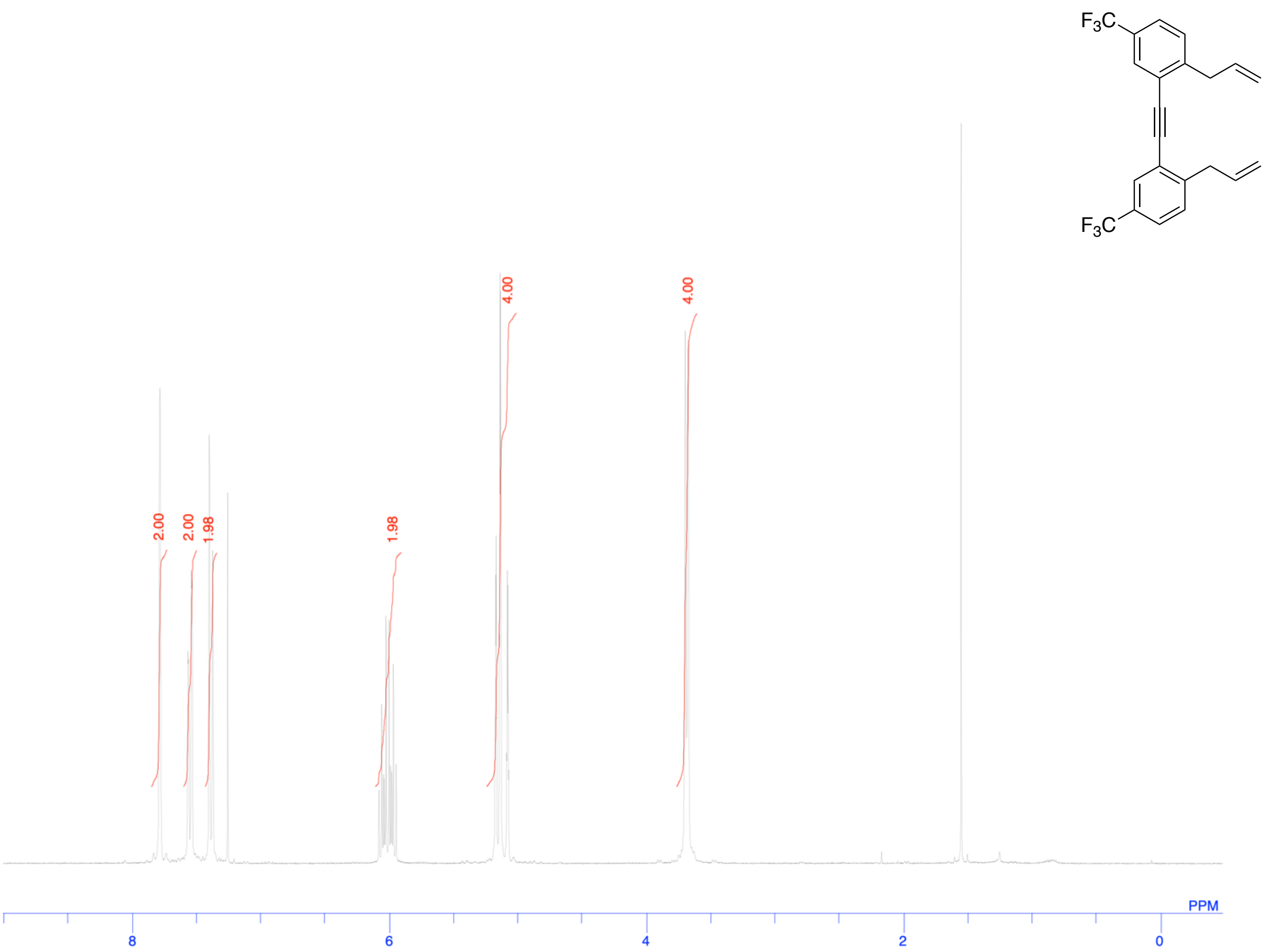
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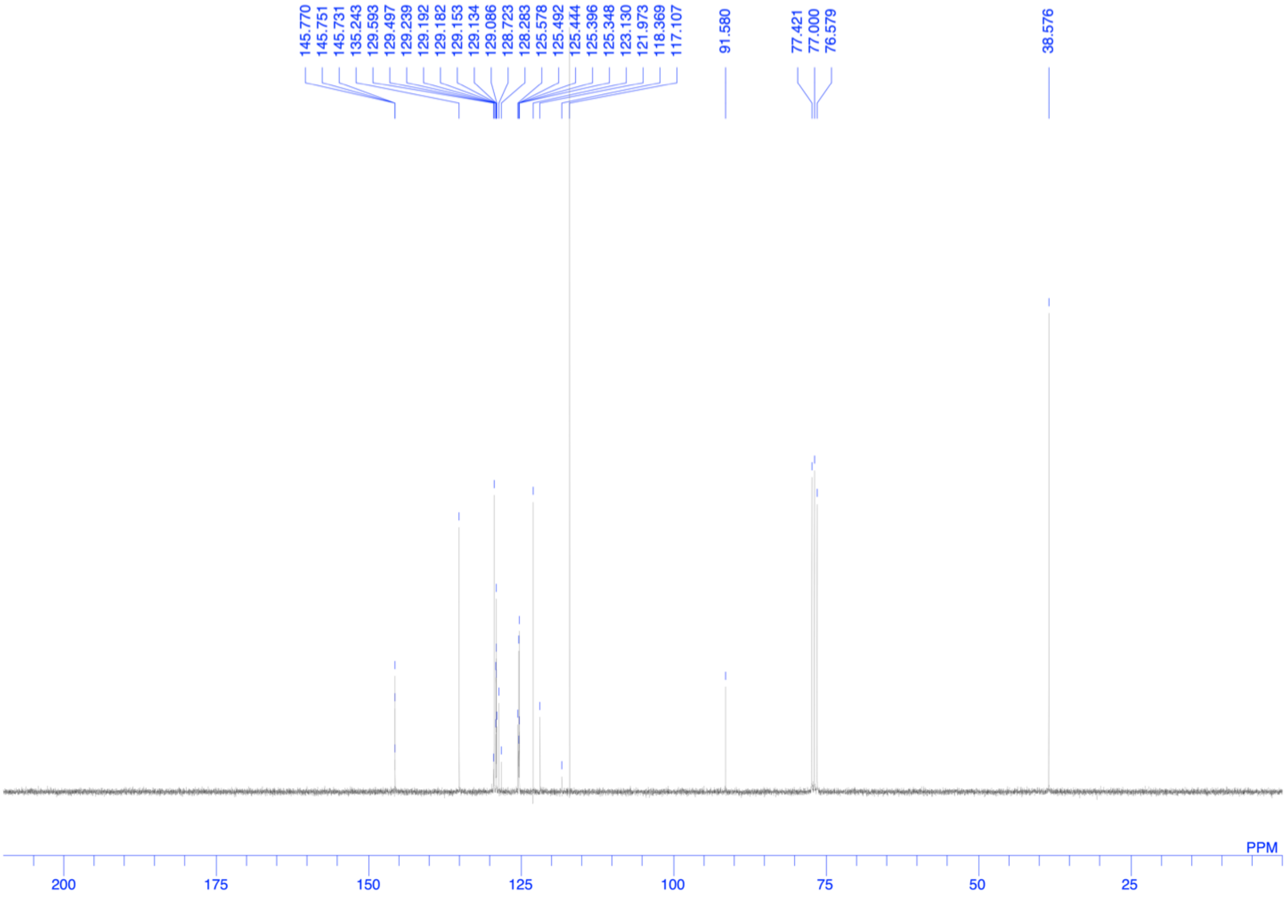
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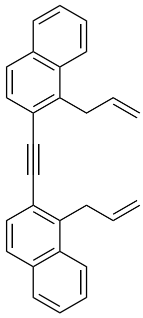

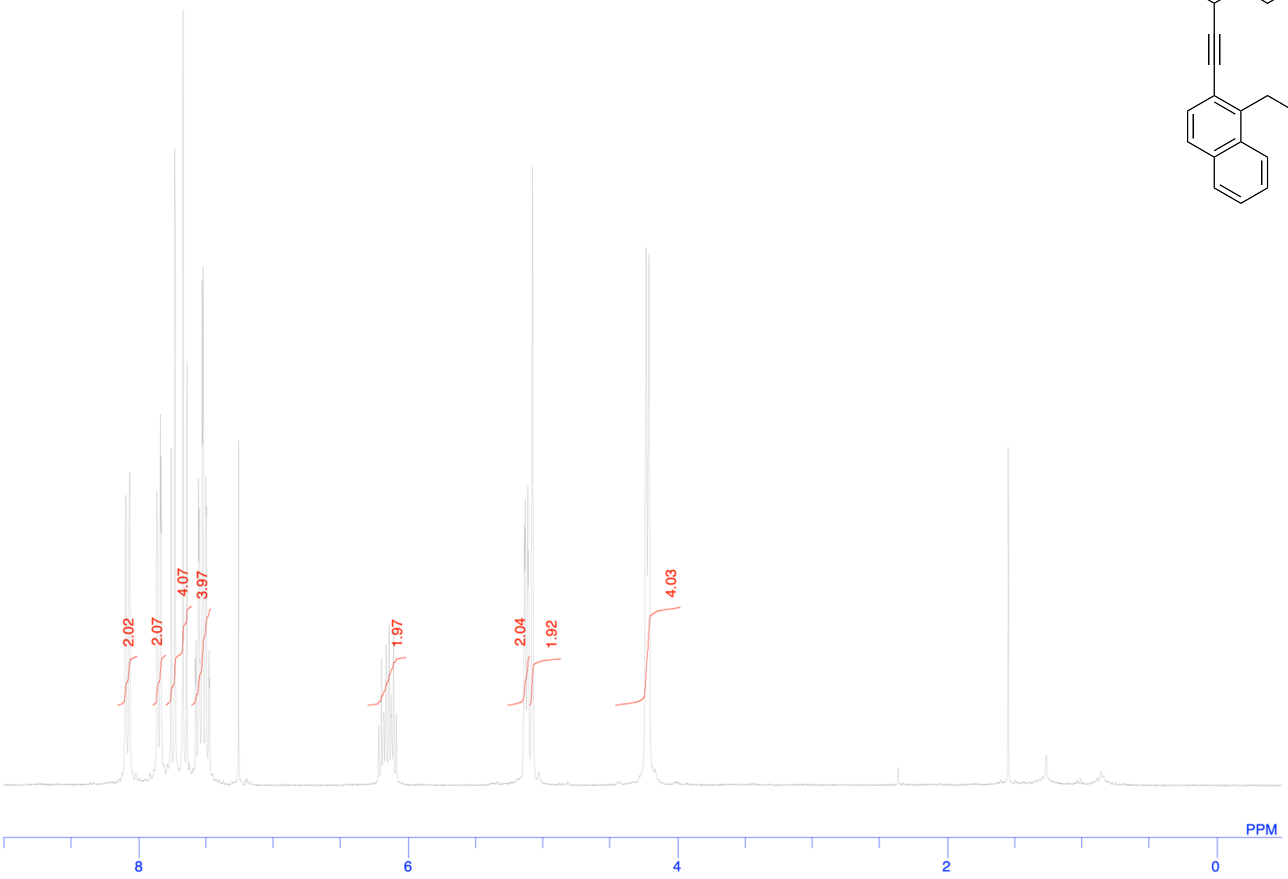
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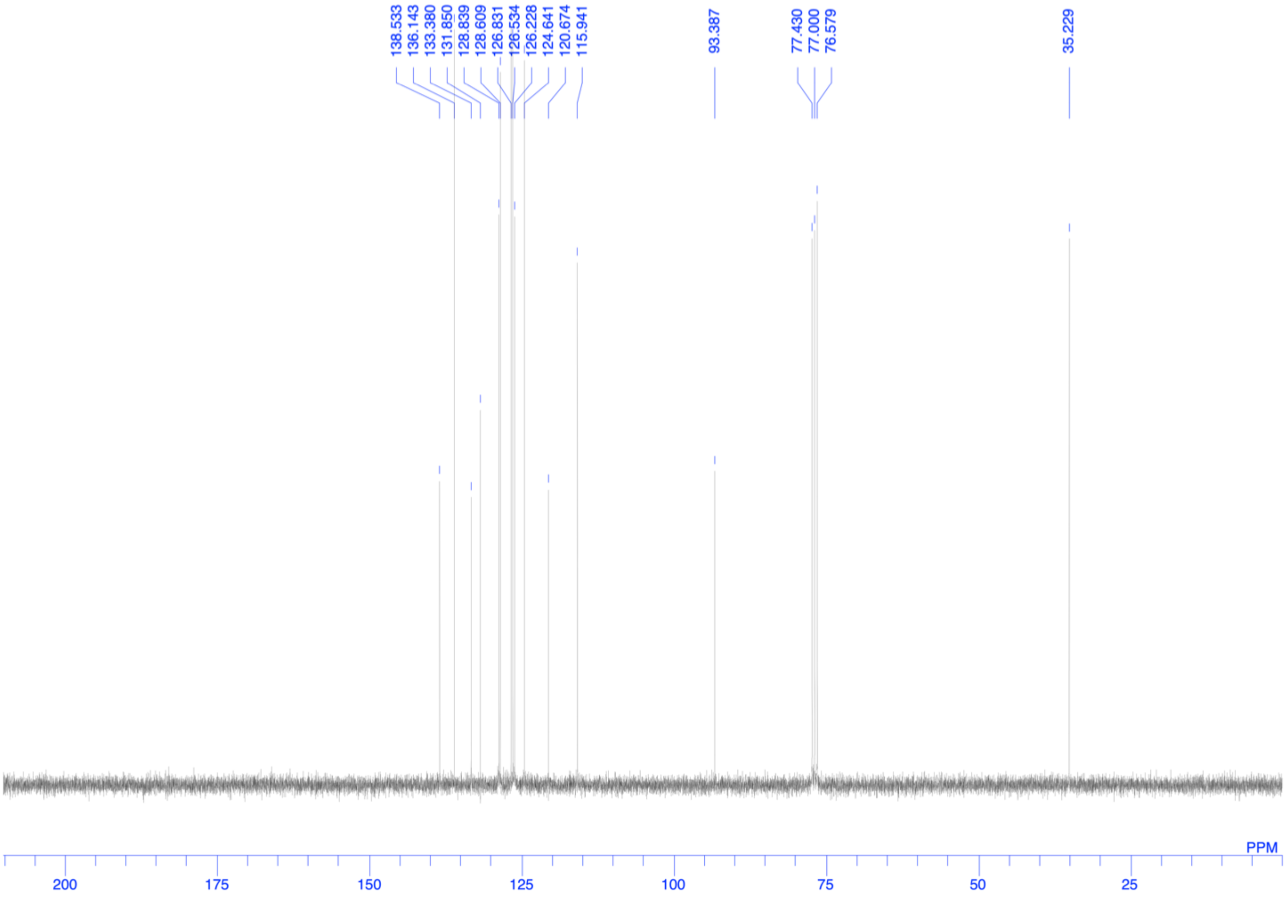
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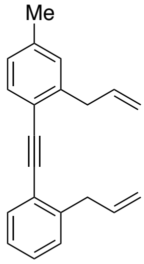
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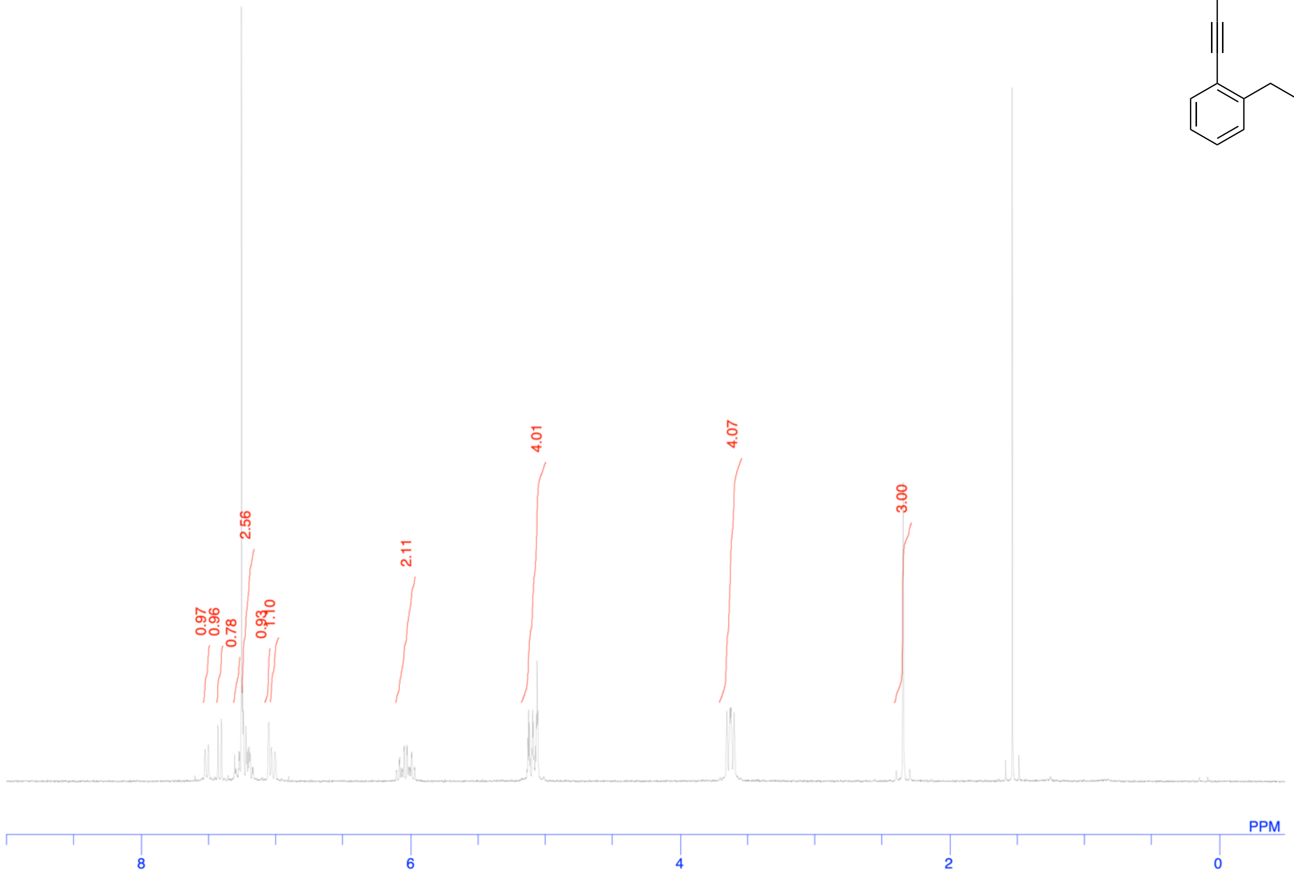
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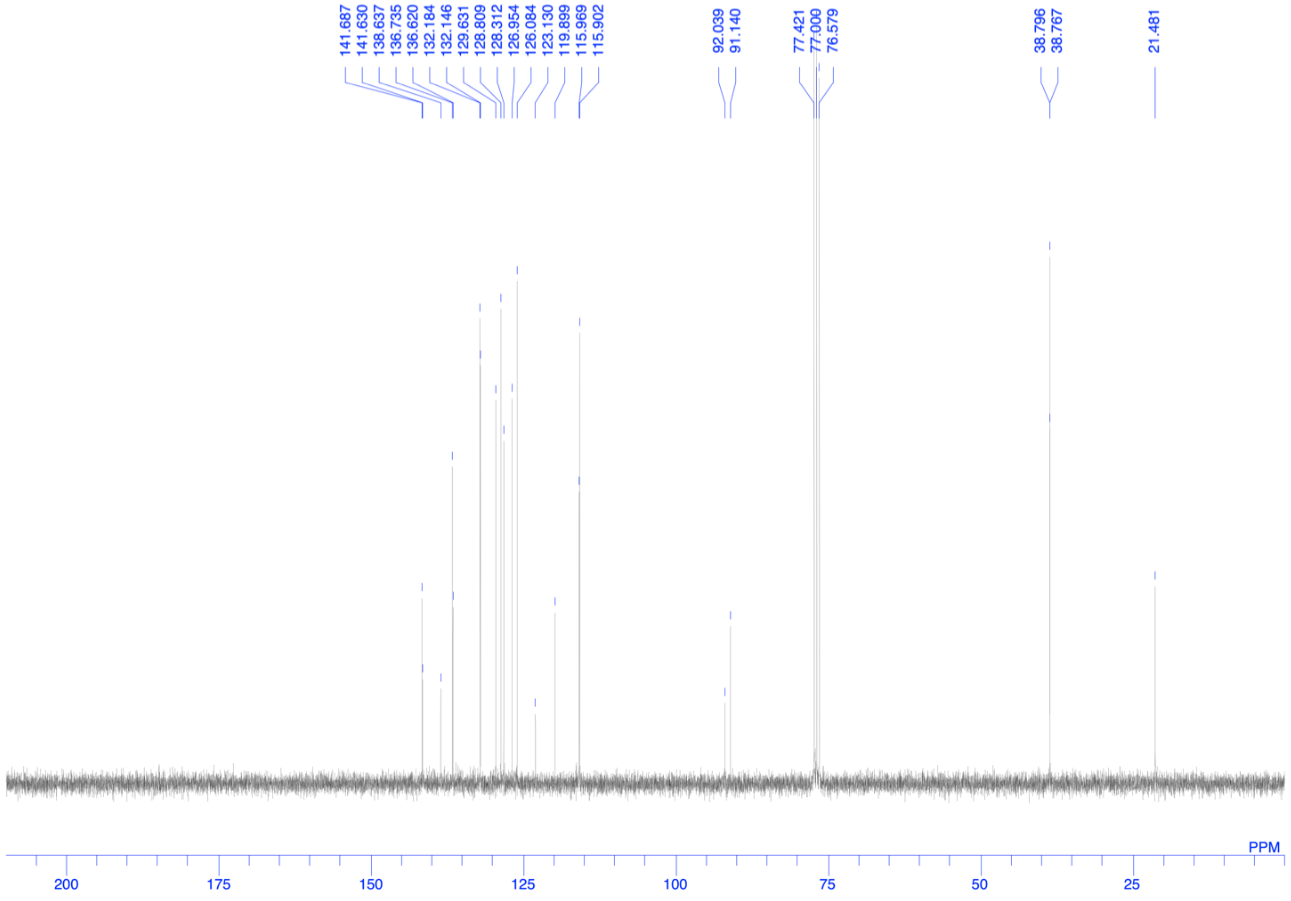
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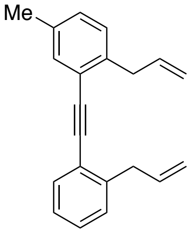
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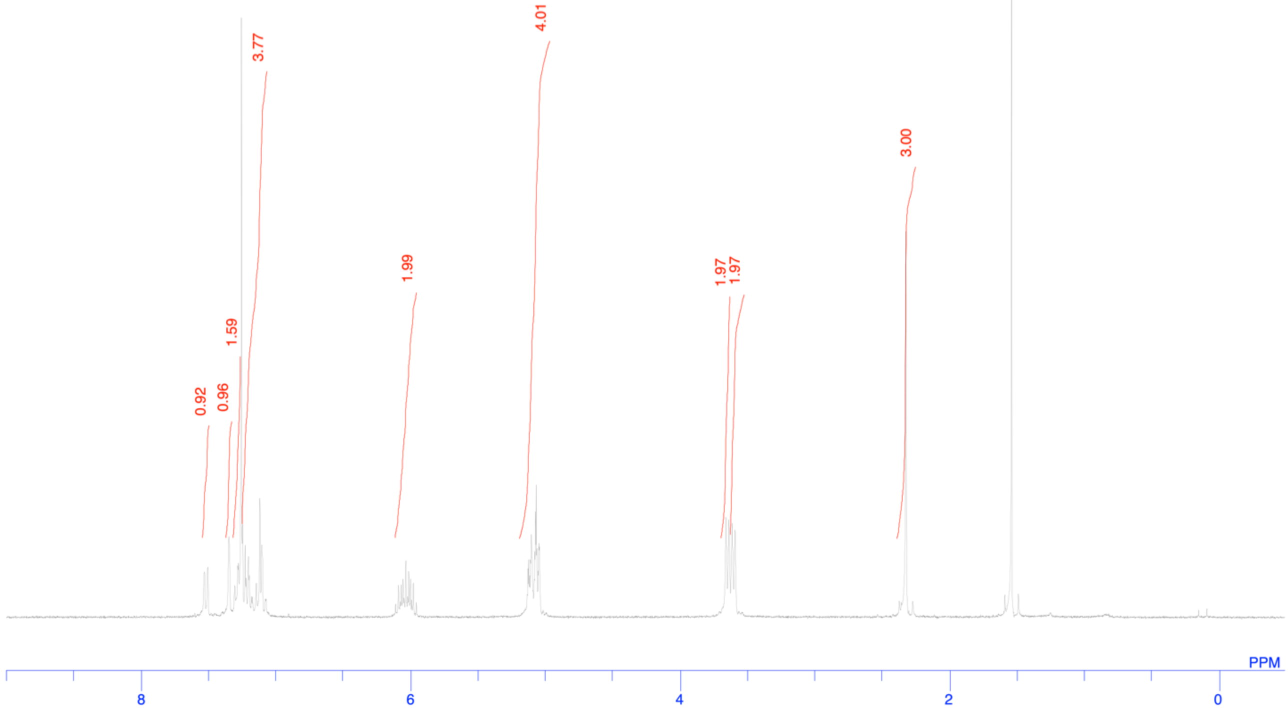
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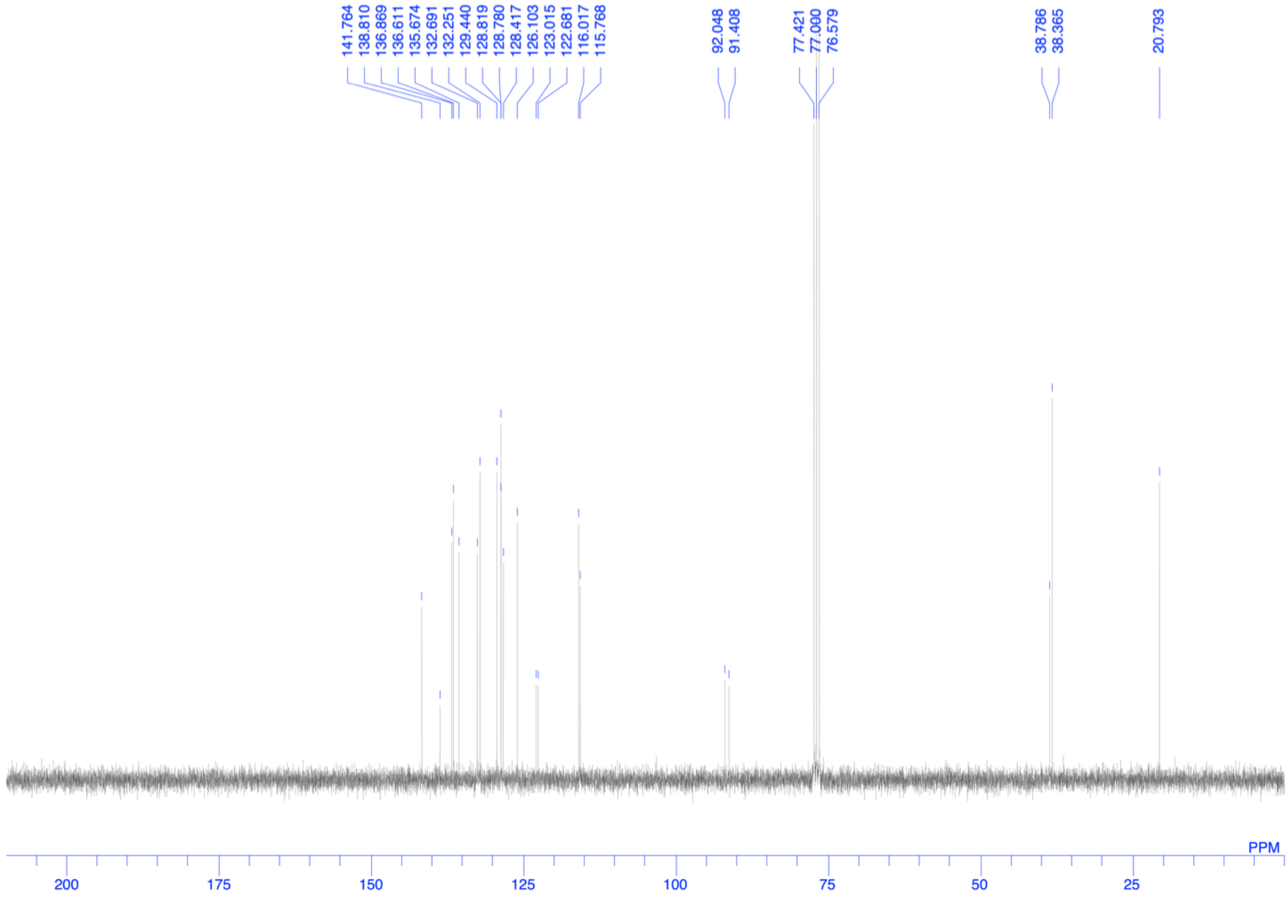
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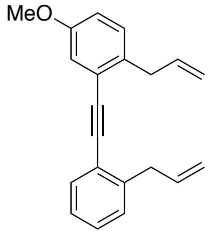
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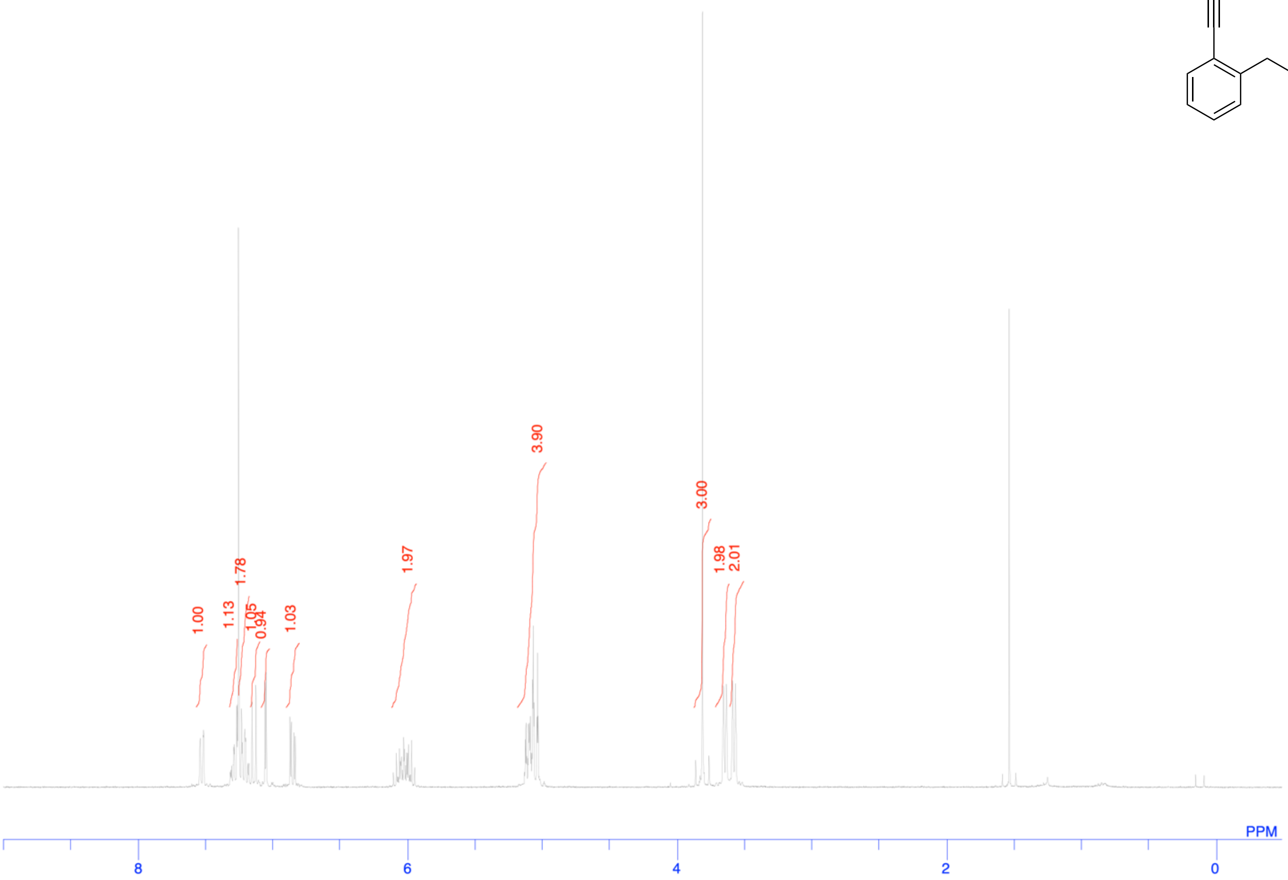
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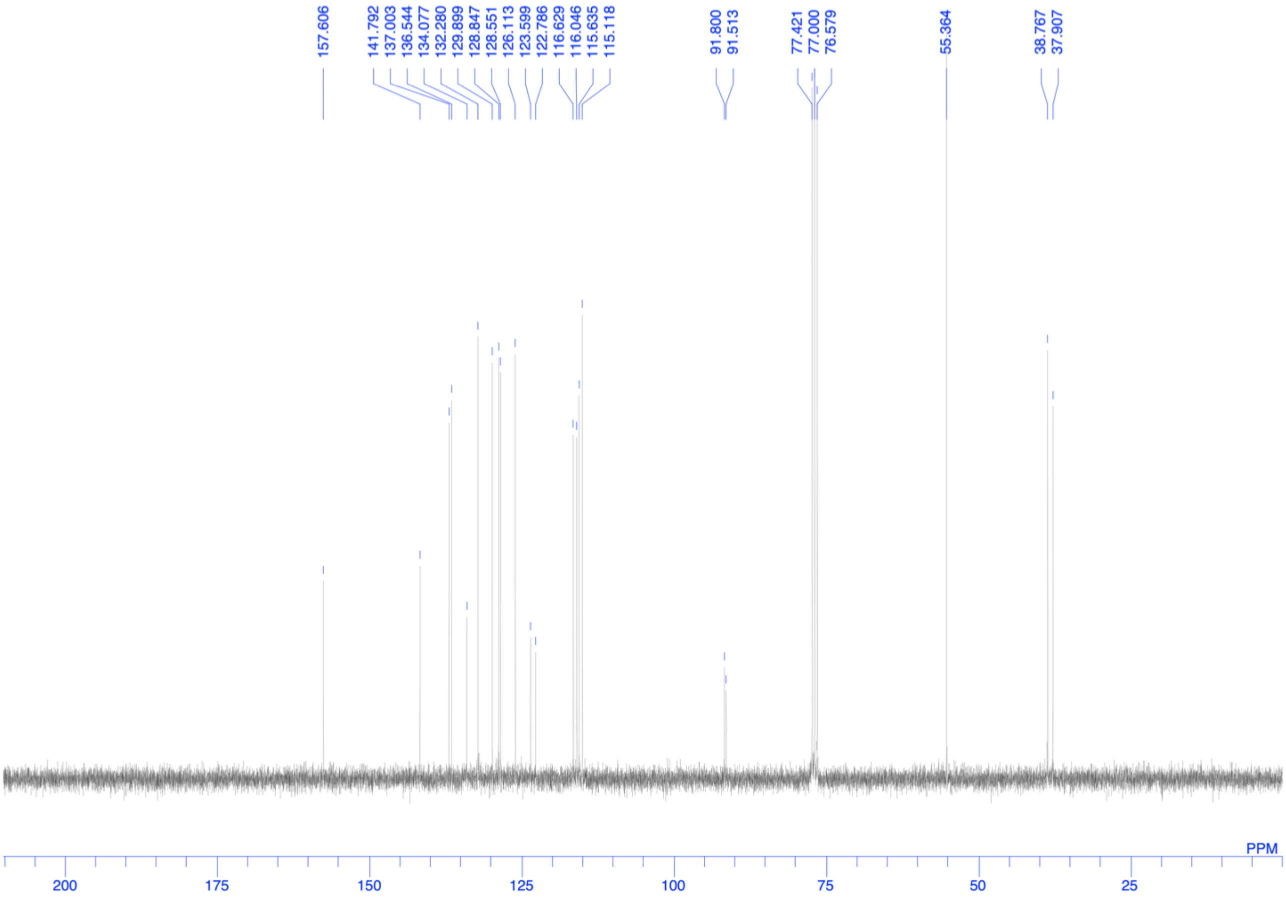
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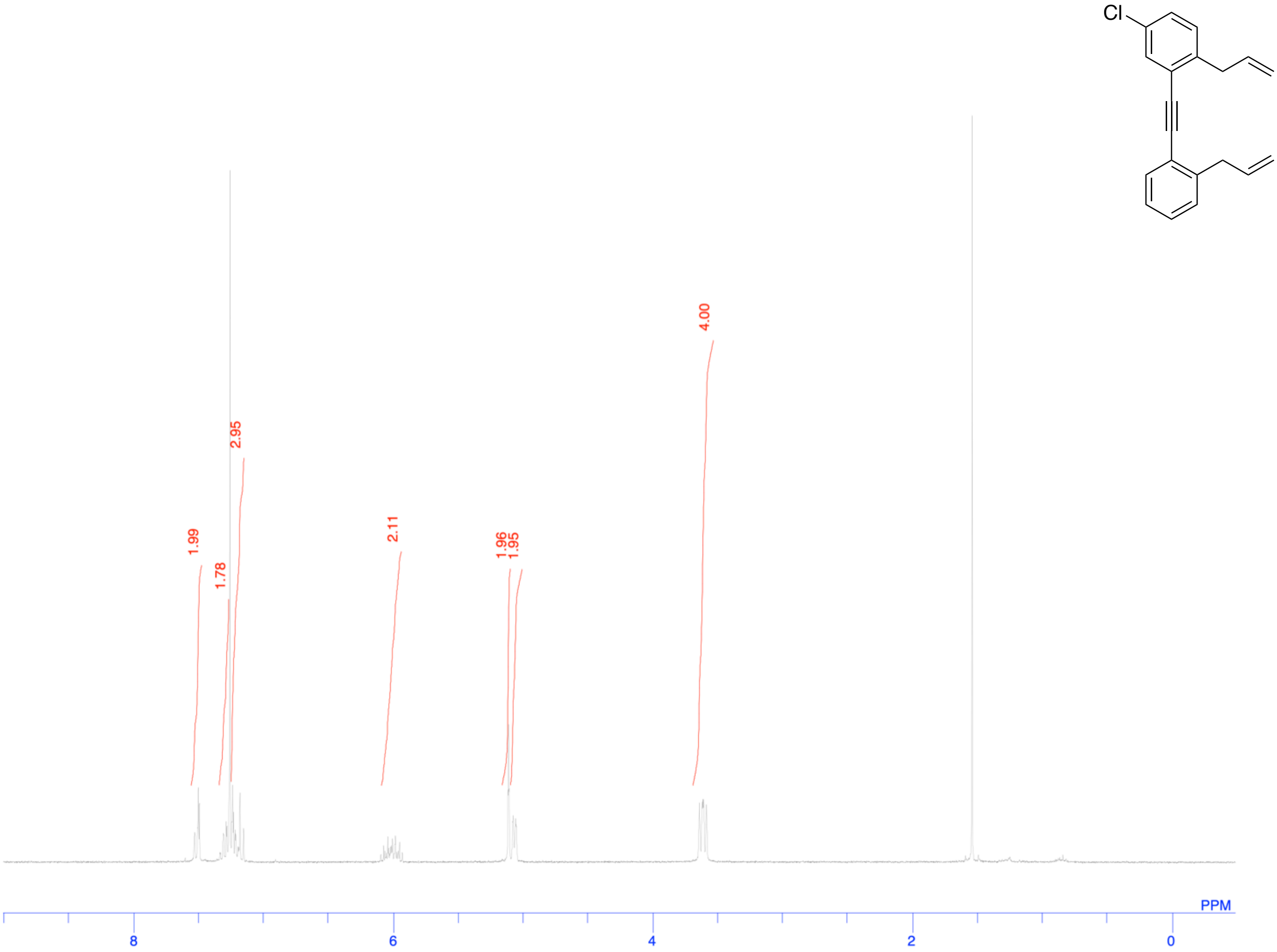
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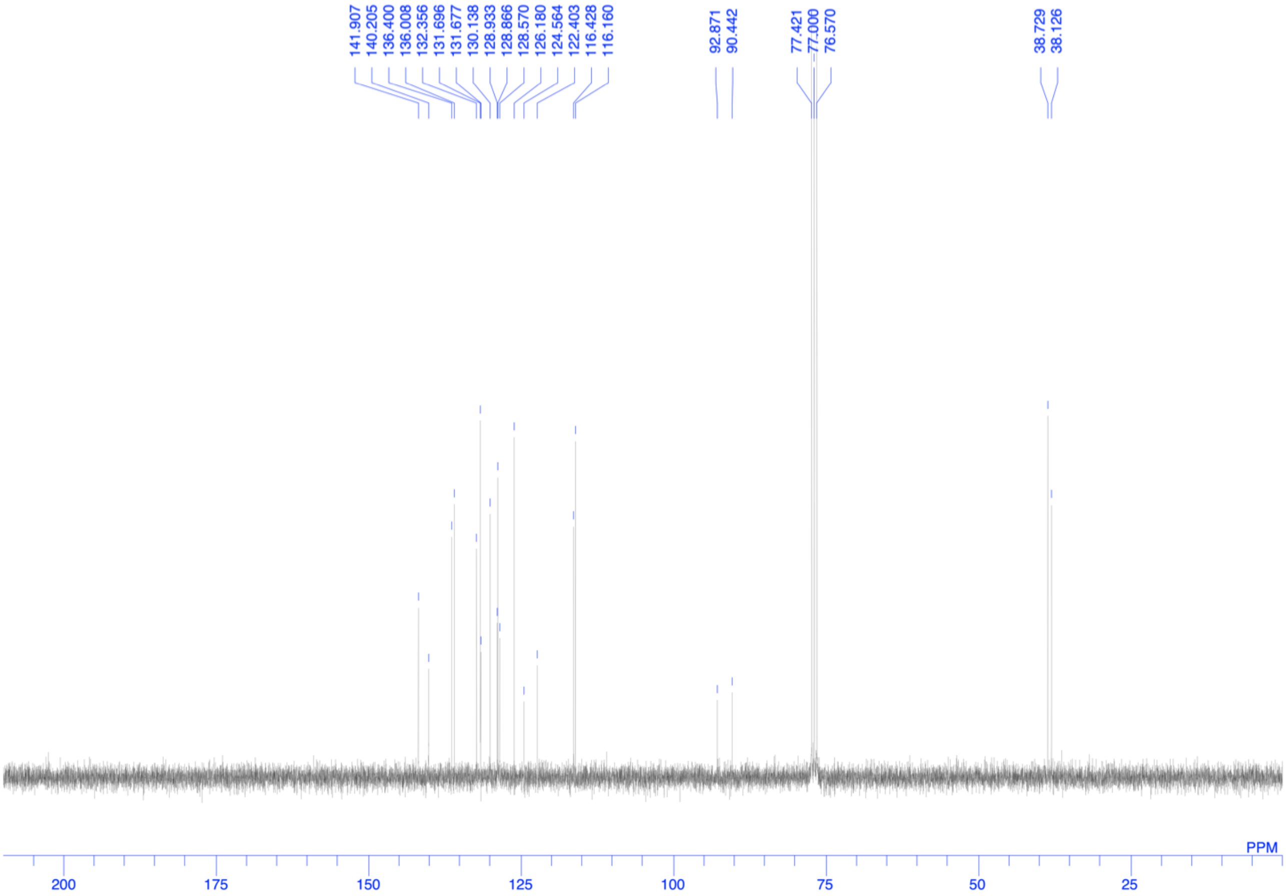
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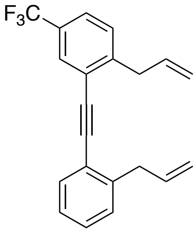
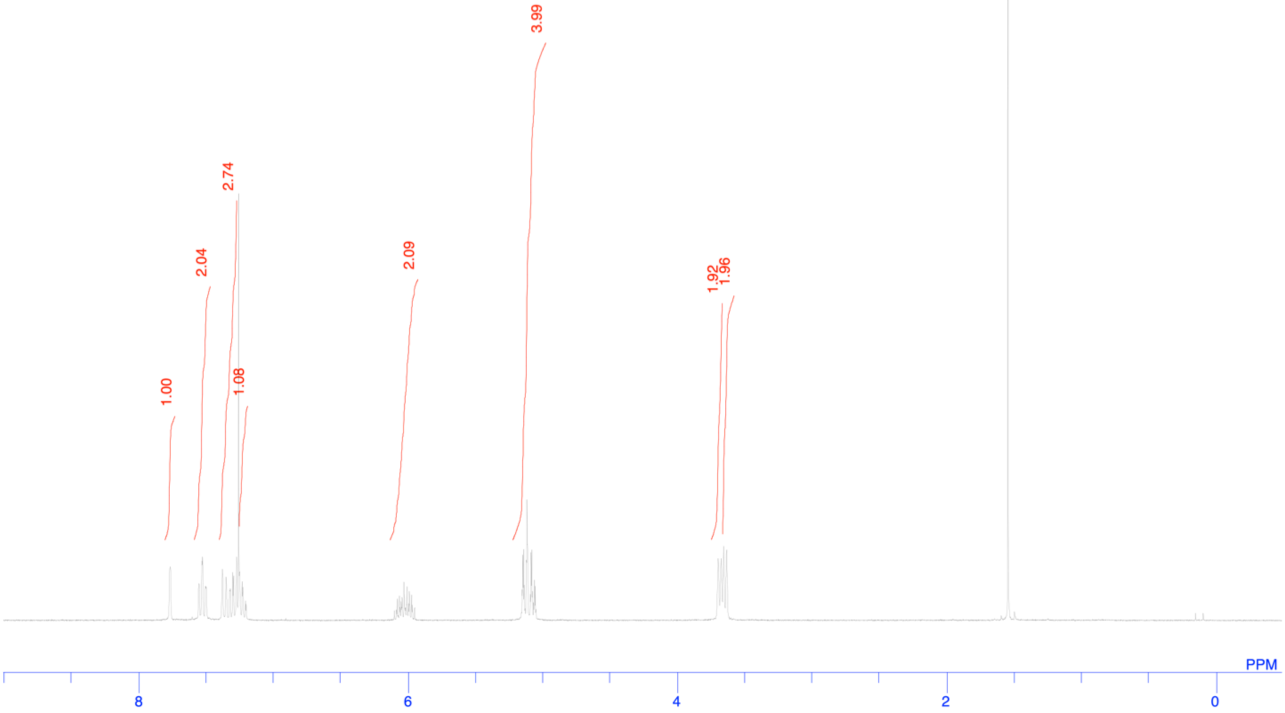

F$_3$C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2.74
1.08
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1.92
1.96
PPM
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6
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2
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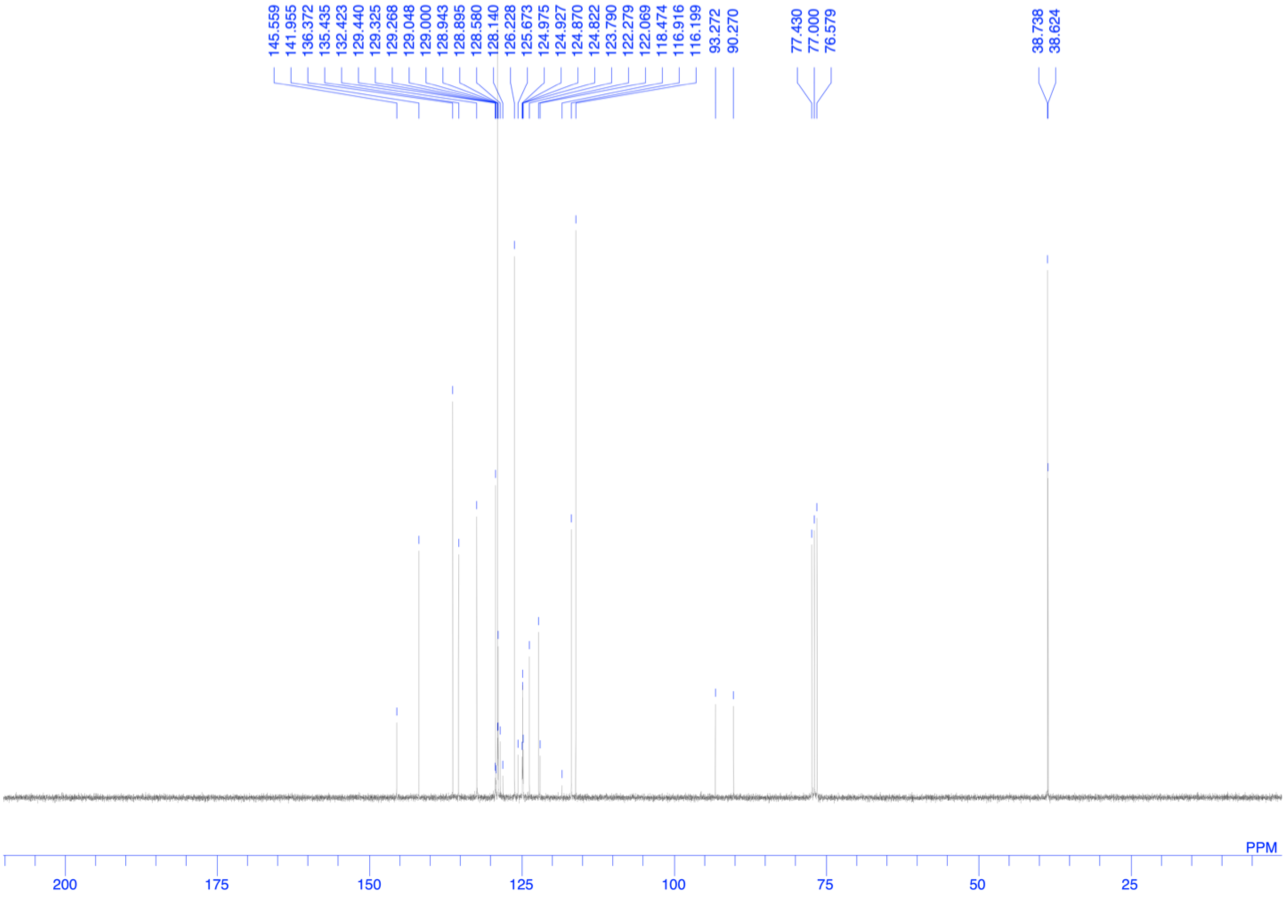
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132.423
129.440
129.325
129.268
129.048
129.000
128.943
128.895
128.580
128.140
126.228
125.673
124.975
124.927
124.870
124.822
123.790
122.279
122.069
118.474
116.916
116.199
93.272
90.270
77.430
77.000
76.579
38.738
38.624
PPM
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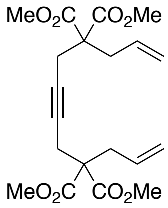
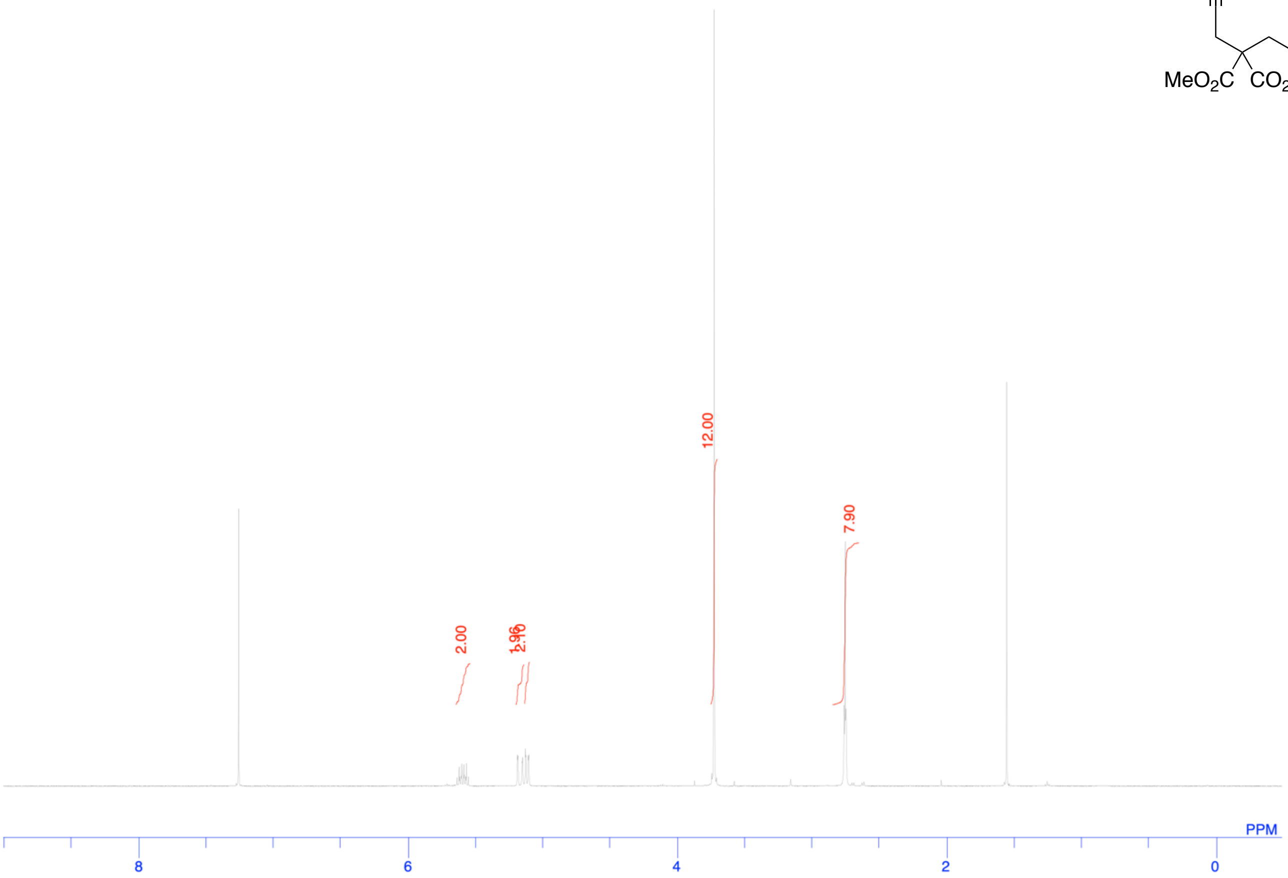
175
150
125
100
75
50
25

1m



MeO$_2$C
CO$_2$Me
MeO$_2$C
CO$_2$Me



2.00
1.96
2.10
12.00
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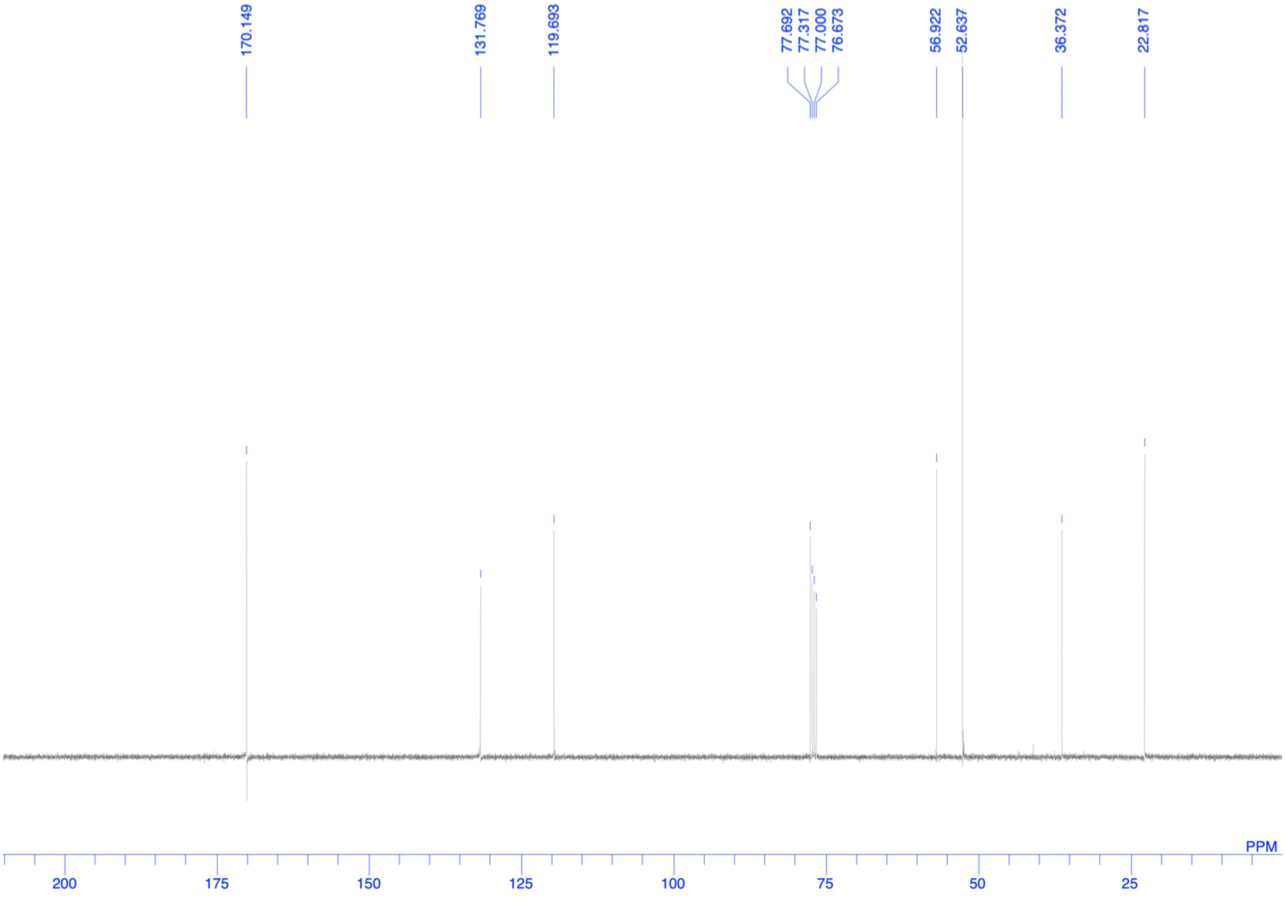
PPM
8
6
4
2
0



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131.769
119.693
77.692
77.317
77.000
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36.372
22.817
PPM
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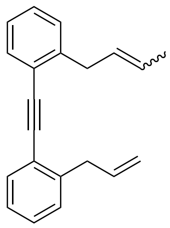
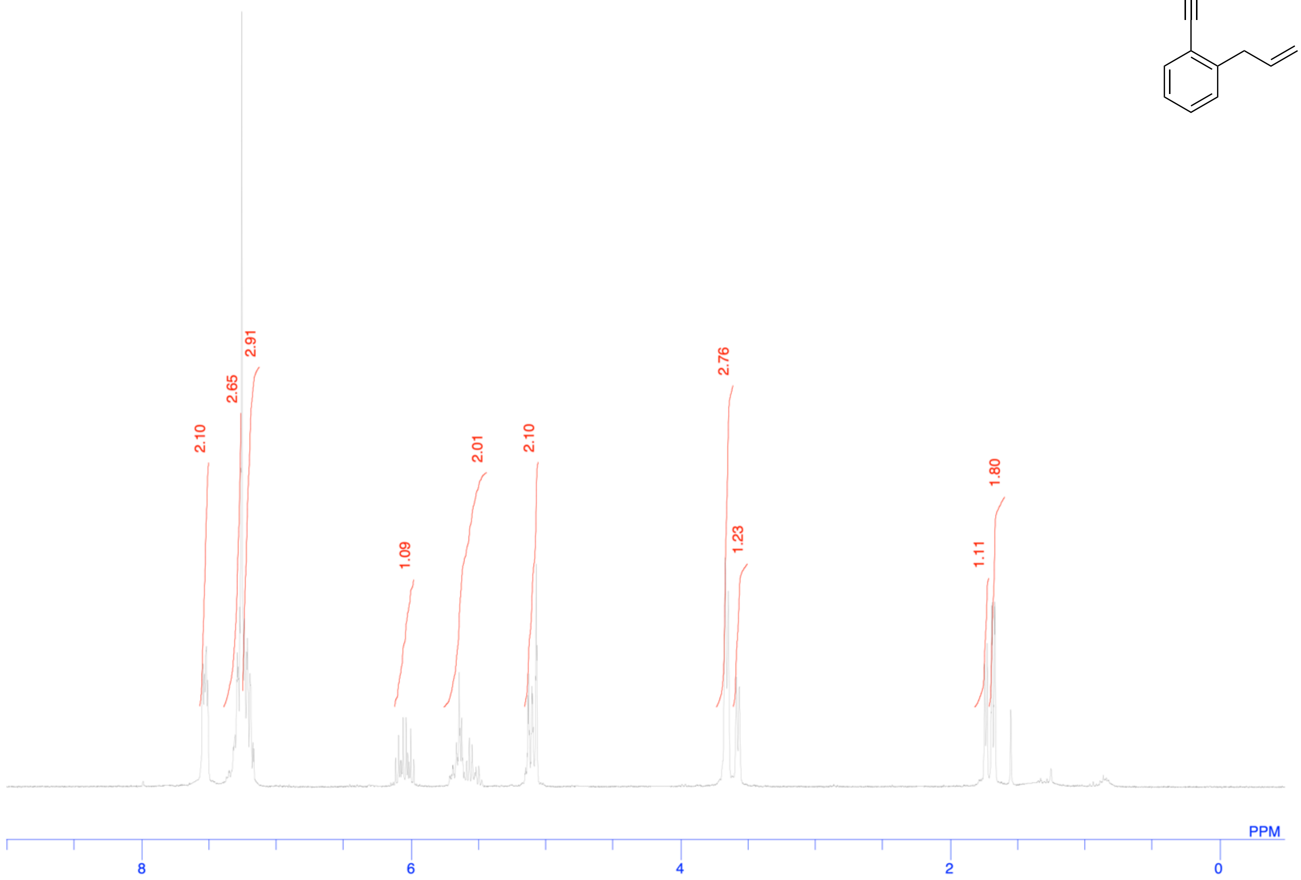
50
25

1n

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1.23
1.11
1.80
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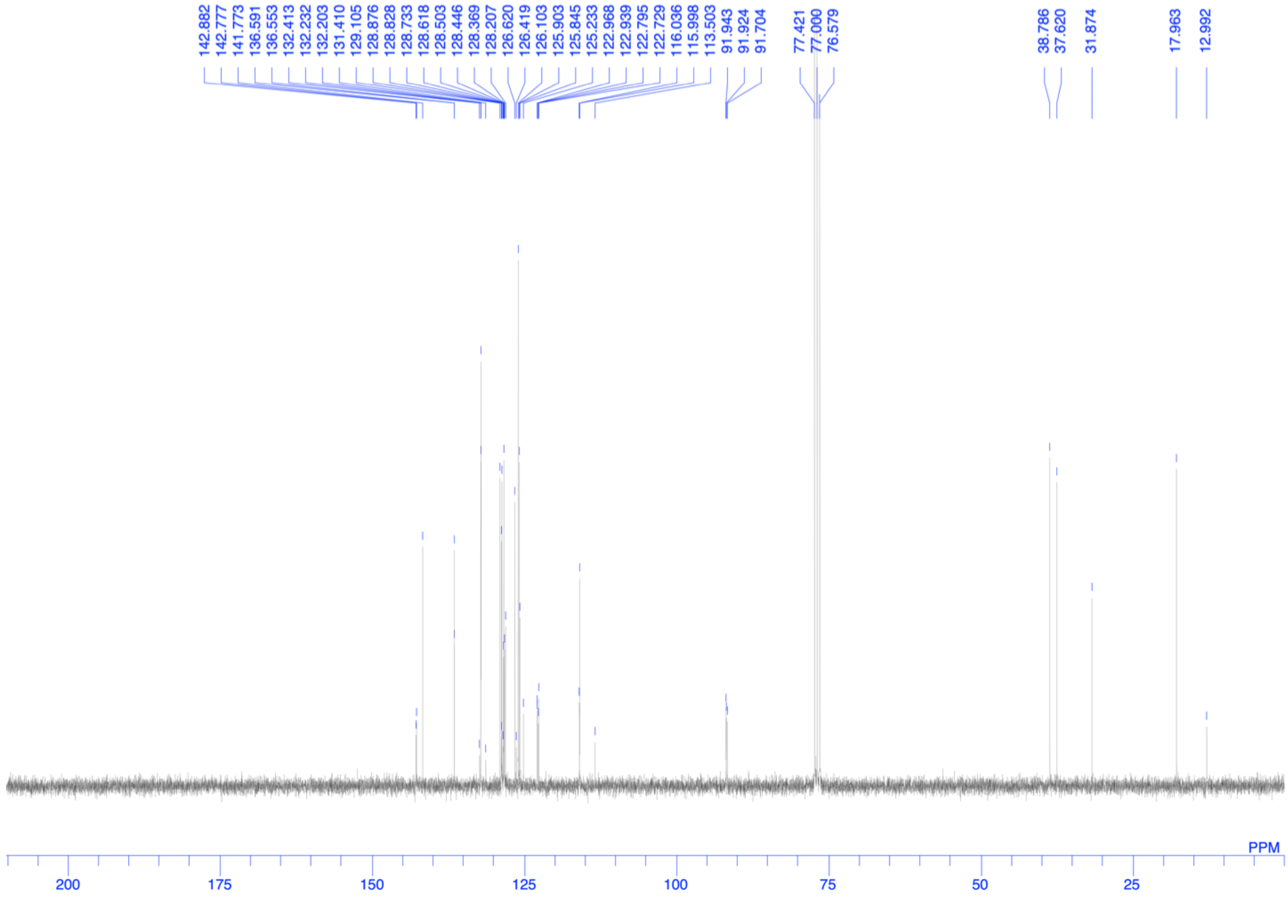
4
2
0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132.413
132.232
132.203
131.410
129.105
128.876
128.828
128.733
128.618
128.503
128.446
128.369
128.207
126.620
126.419
126.103
125.903
125.845
125.233
122.968
122.939
122.795
122.729
116.036
115.998
113.503
91.943
91.924
91.704
77.421
77.000
76.579
38.786
37.620
31.874
17.963
12.992
PPM
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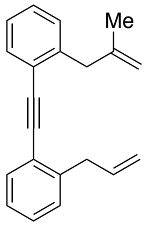
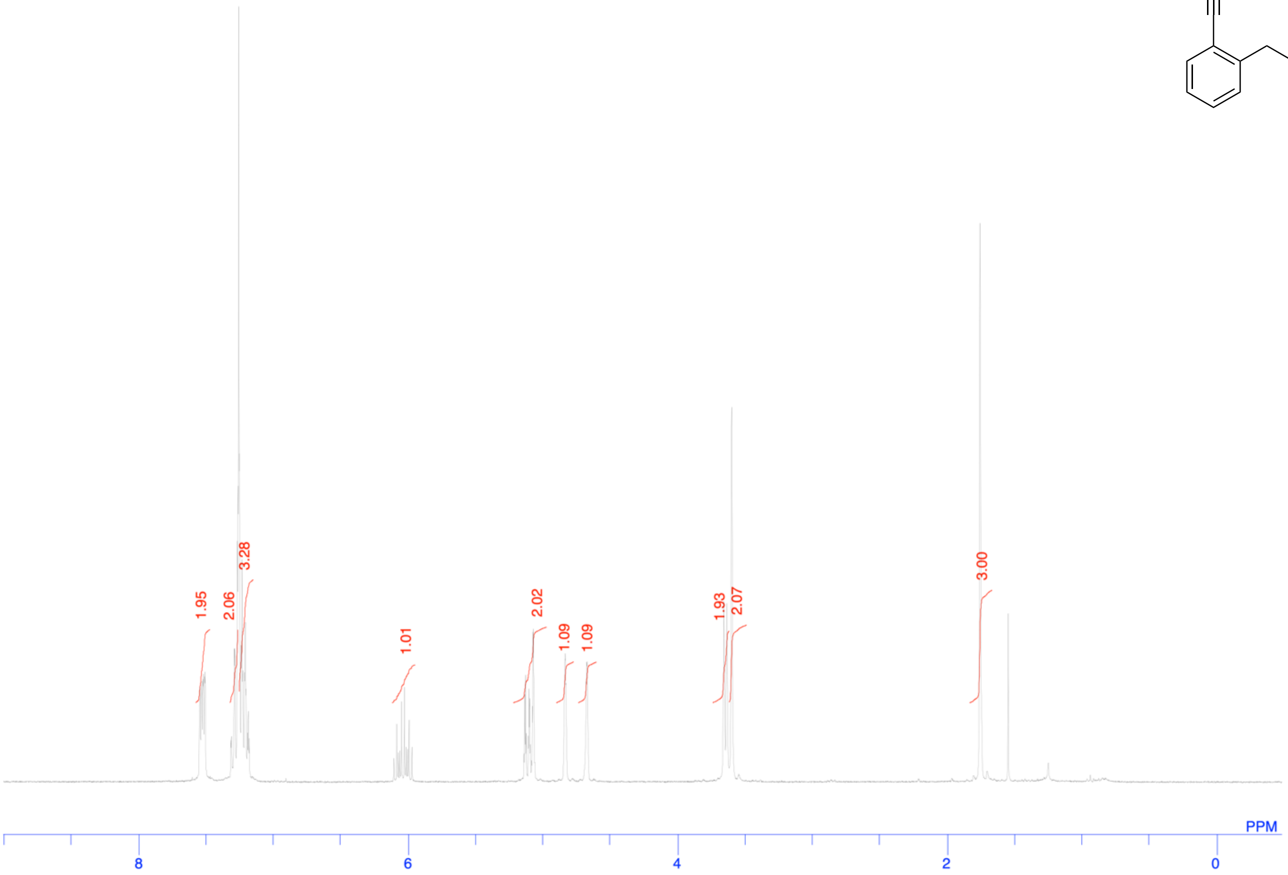
175
150
125
100
75
50
25

1o


Me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2.06
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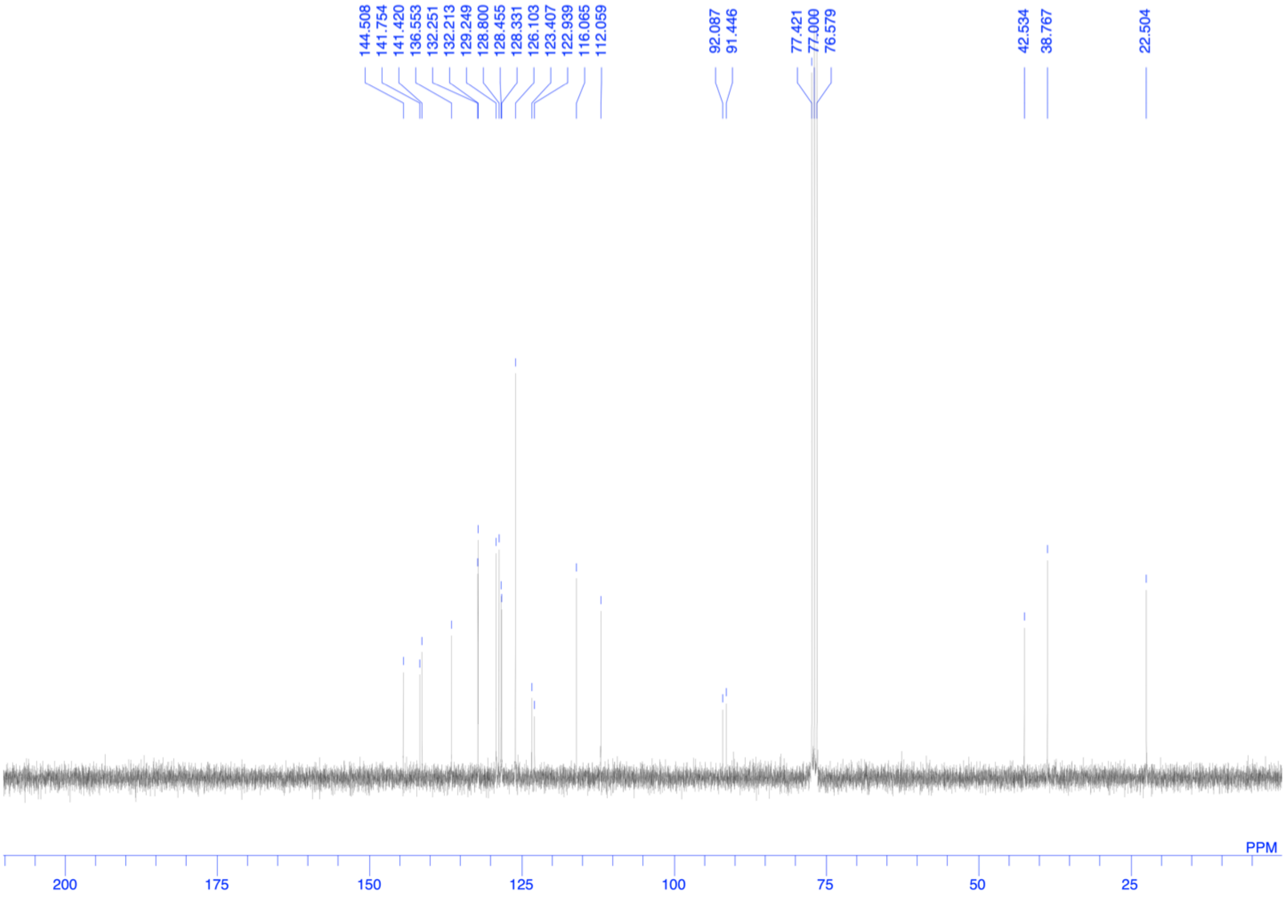
1.01
2.02
1.09
1.09
1.93
2.07
3.00
8
6
4
2
0
PPM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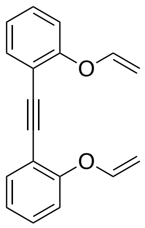
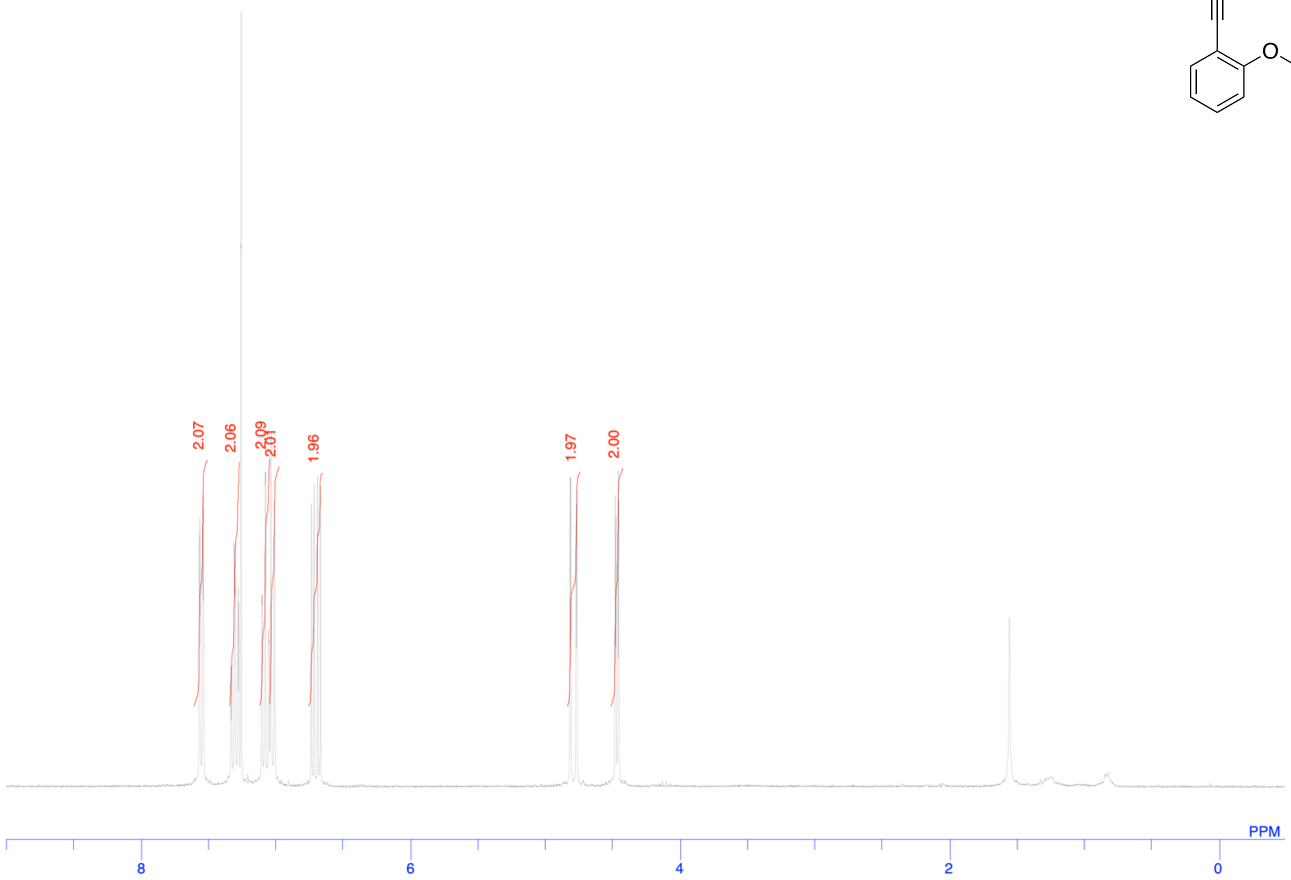
141.754
141.420
136.553
132.251
132.213
129.249
128.800
128.455
128.331
126.103
123.407
122.939
116.065
112.059
92.087
91.446
77.421
77.000
76.579
42.534
38.767
22.504
200
175
150
125
100
75
50
25
PPM

1p


O
O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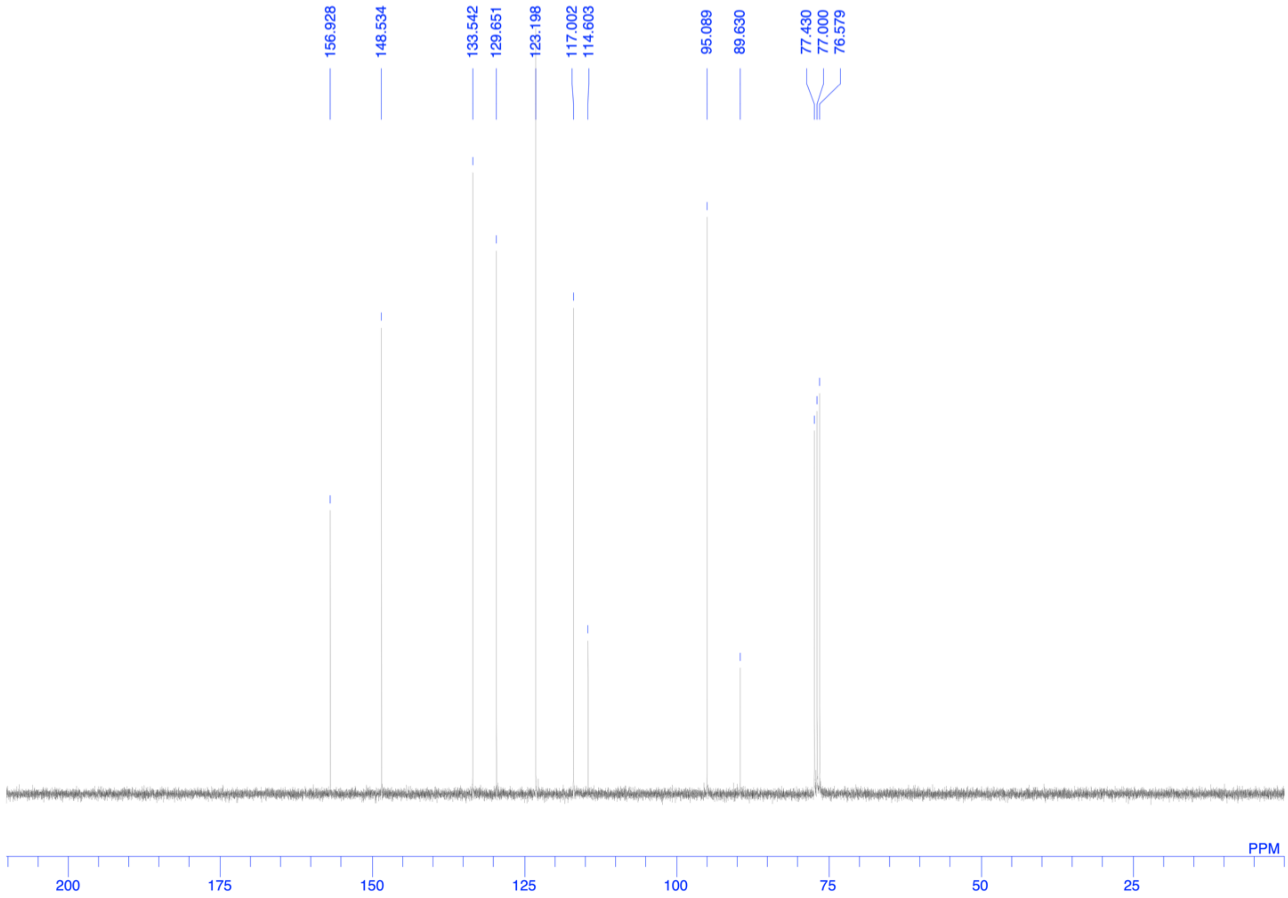
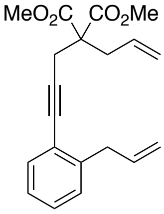
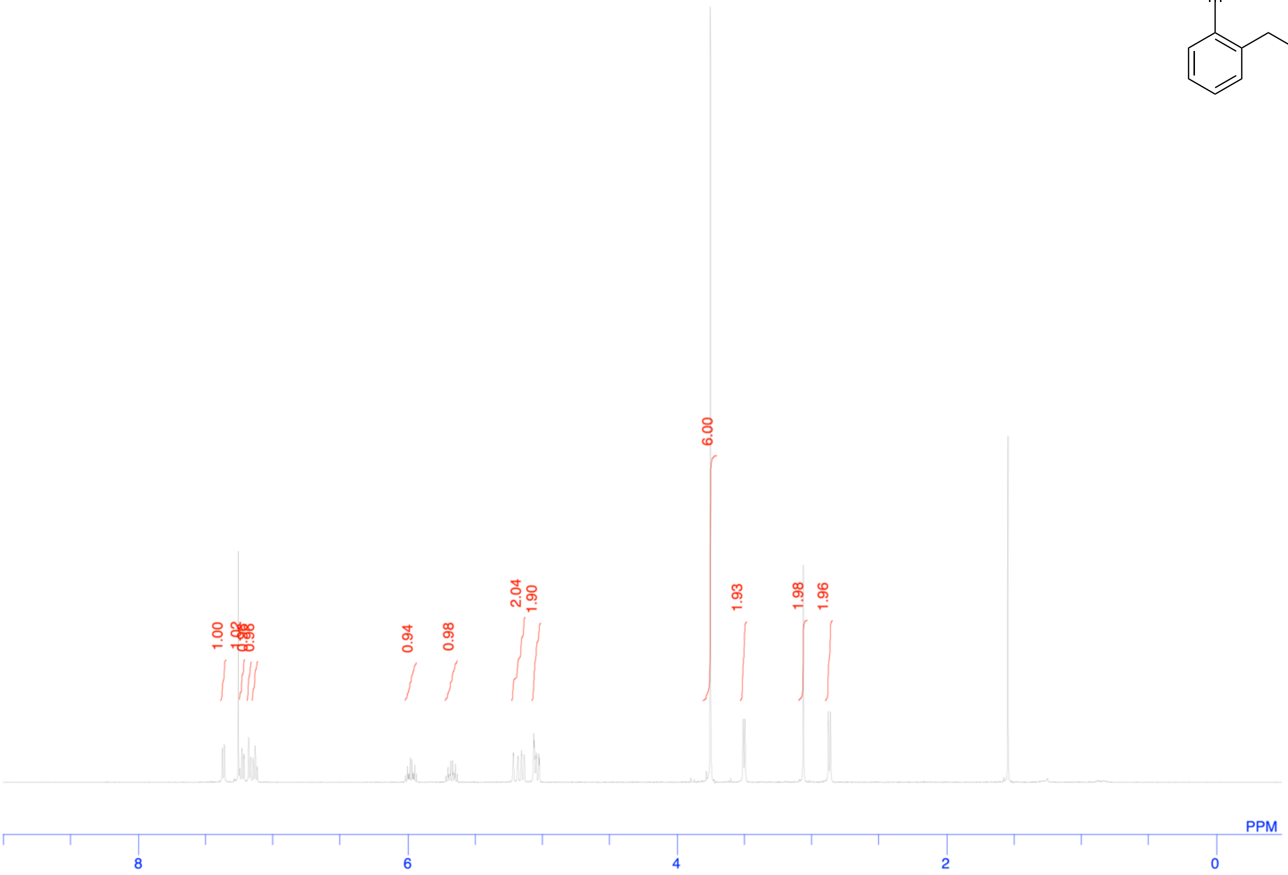
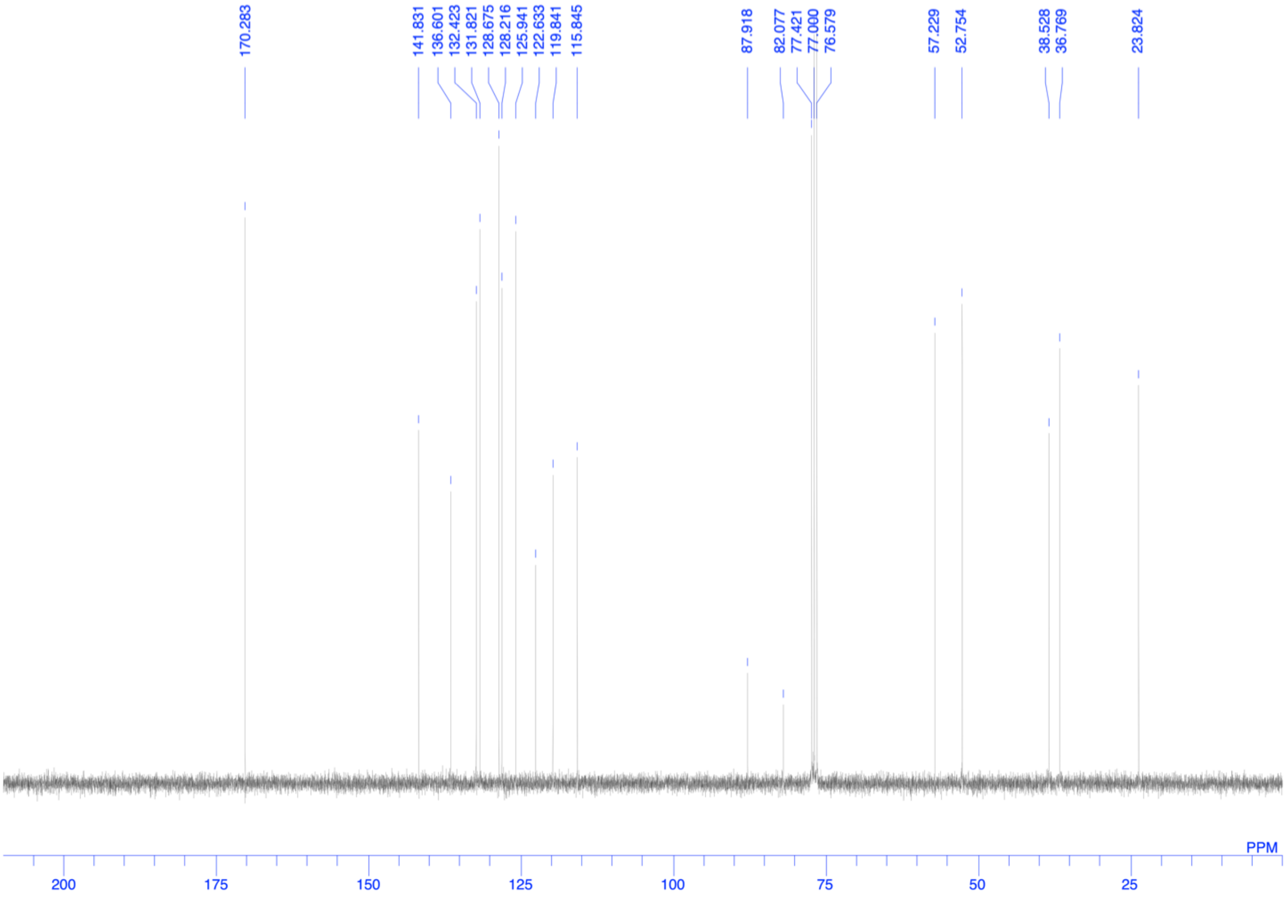
2.06
2.09
2.01
1.96
1.97
2.00
PPM
8
6
4
2
0


156.928
148.534
133.542
129.651
123.198
117.002
114.603
95.089
89.630
77.430
77.000
76.579
PPM
200
175
150
125
100
75
50
25

1q


MeO$_2$C
CO$_2$Me


1.00
1.02
0.96
0.98
0.94
0.98
2.04
1.90
6.00
1.93
1.98
1.96
PPM
8
6
4
2
0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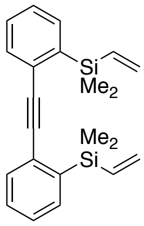
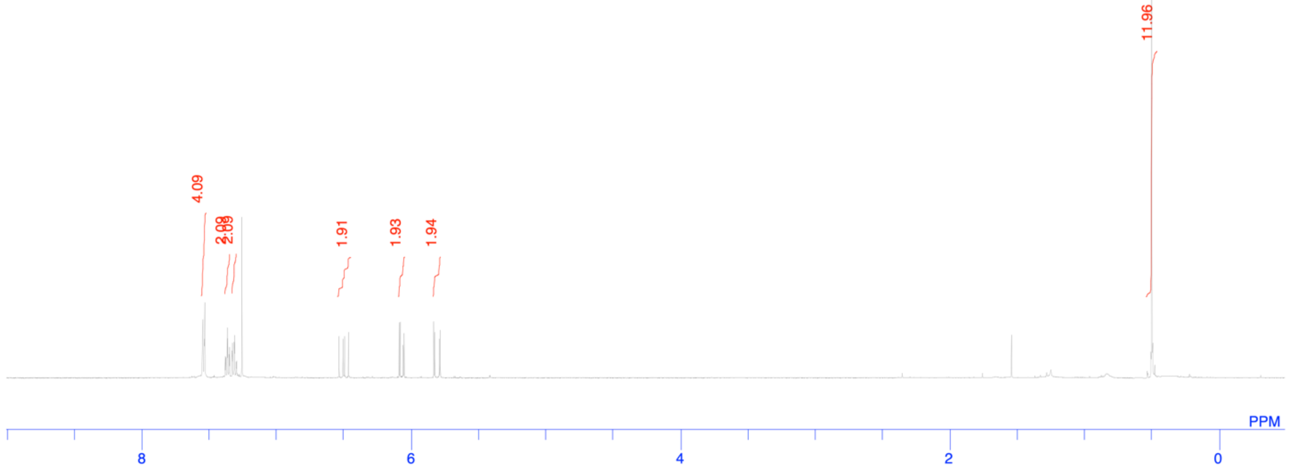
136.601
132.423
131.821
128.675
128.216
125.941
122.633
119.841
115.845
87.918
82.077
77.421
77.000
76.579
57.229
52.754
38.528
36.769
23.824
PPM
200
175
150
125
100
75
50
25

1r


Si
Me$_2$
Me$_2$
Si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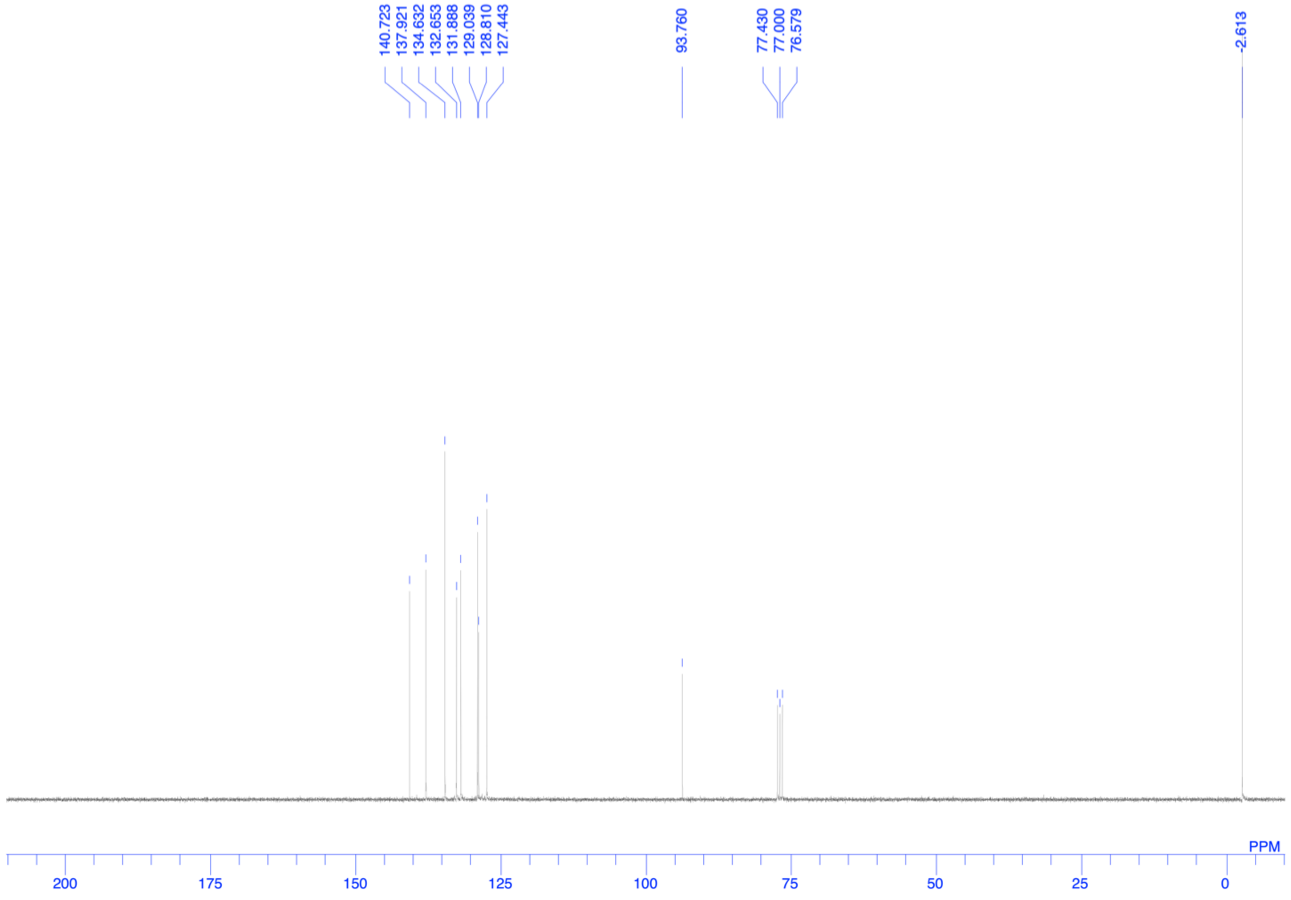
2.08
2.09
1.91
1.93
1.94
11.96
PPM
8
6
4
2
0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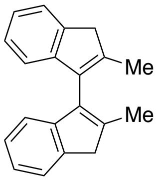
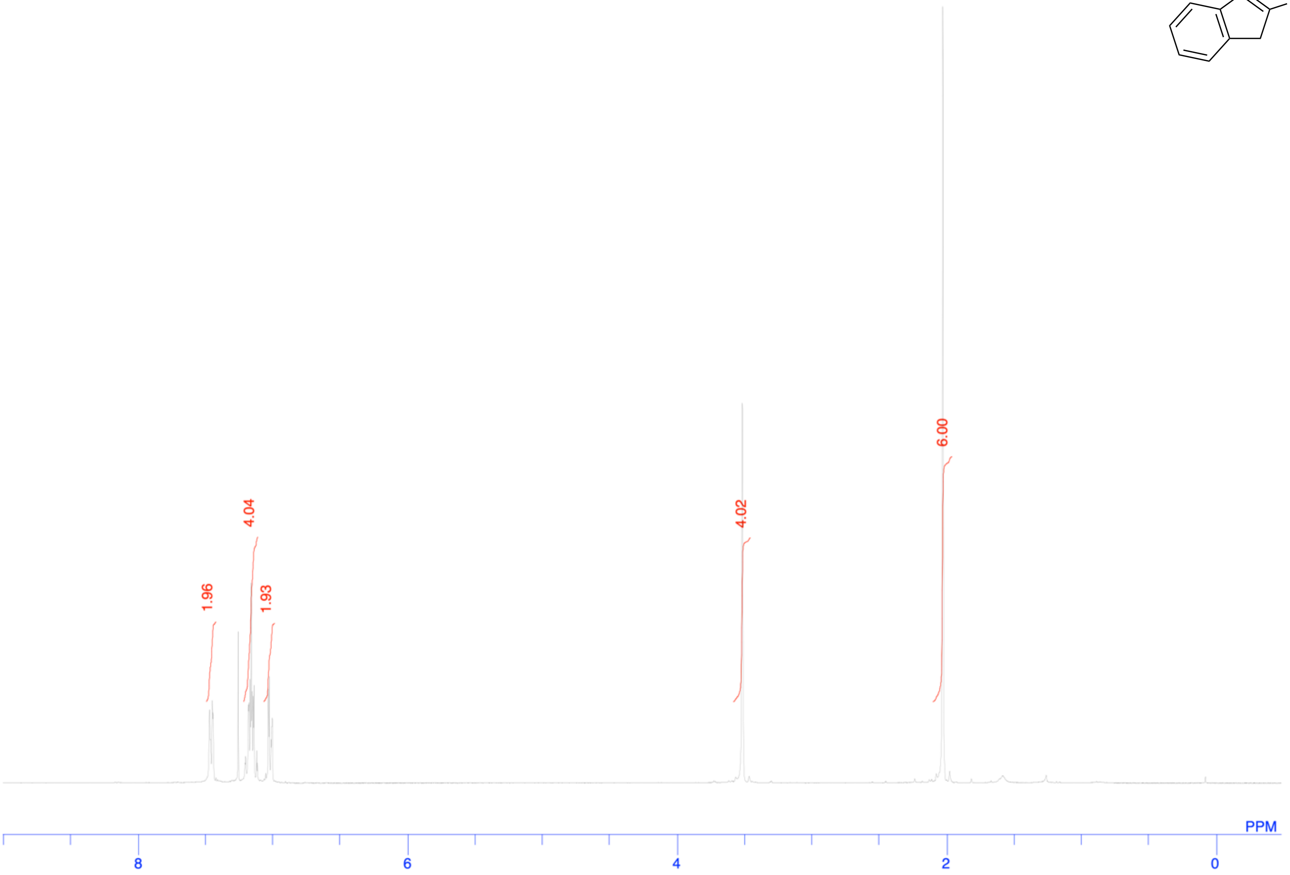
137.921
134.632
132.653
131.888
129.039
128.810
127.443
93.760
77.430
77.000
76.579
-2.613
PPM
200
175
150
125
100
75
50
25
0

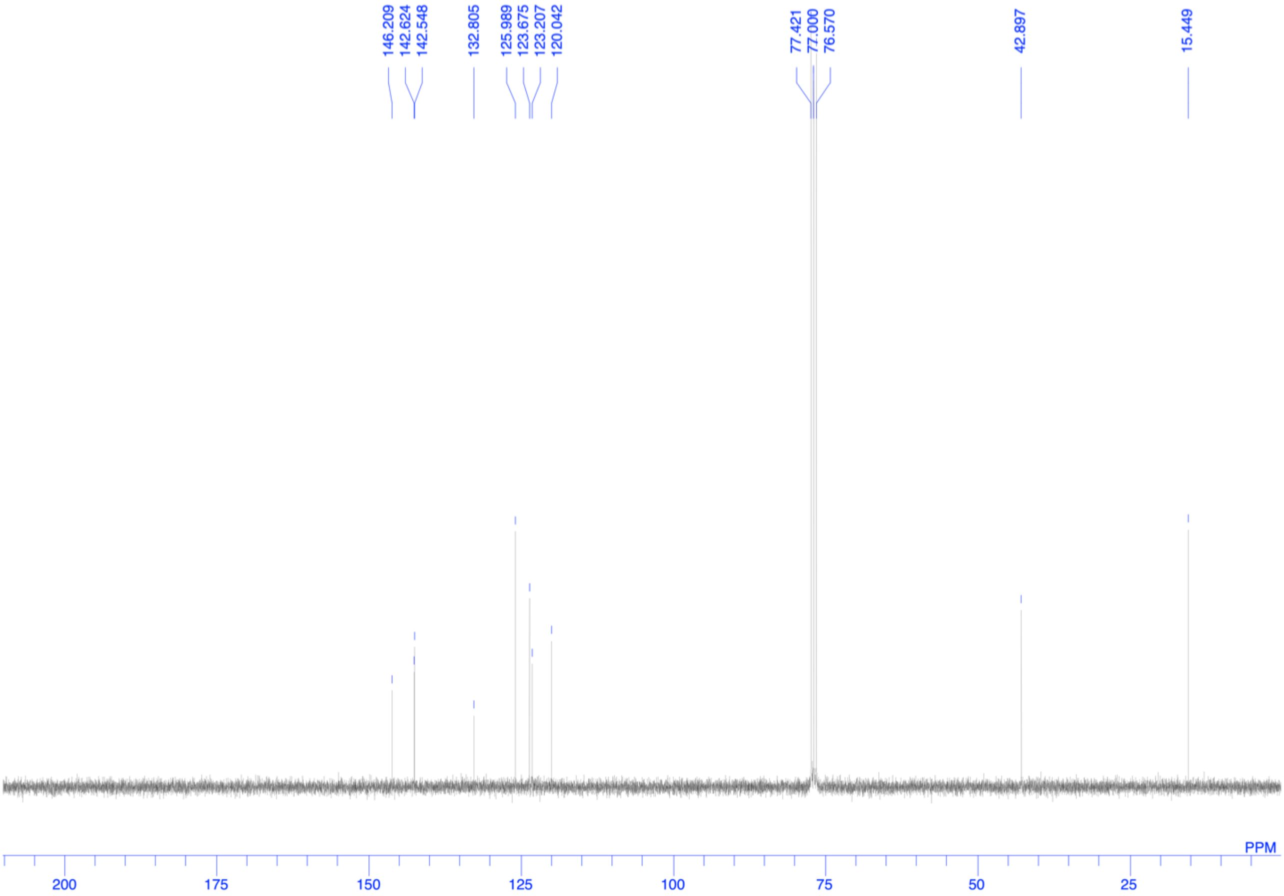
2a



Me
Me



1.96
4.04
1.93
4.02
6.00
PPM
8
6
4
2
0



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142.624
142.548
132.805
125.989
123.675
123.207
120.042
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77.000
76.570
42.897
15.449
PPM
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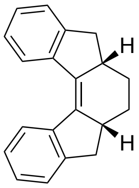
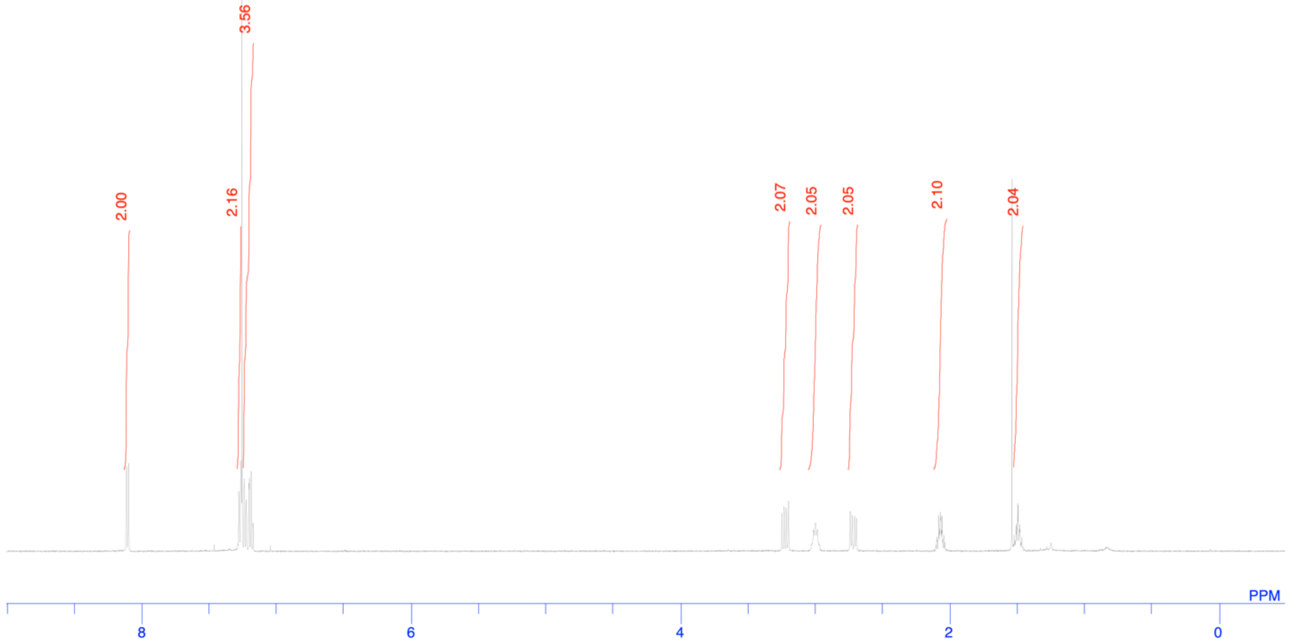
175
150
125
100
75
50
25

3a


H
H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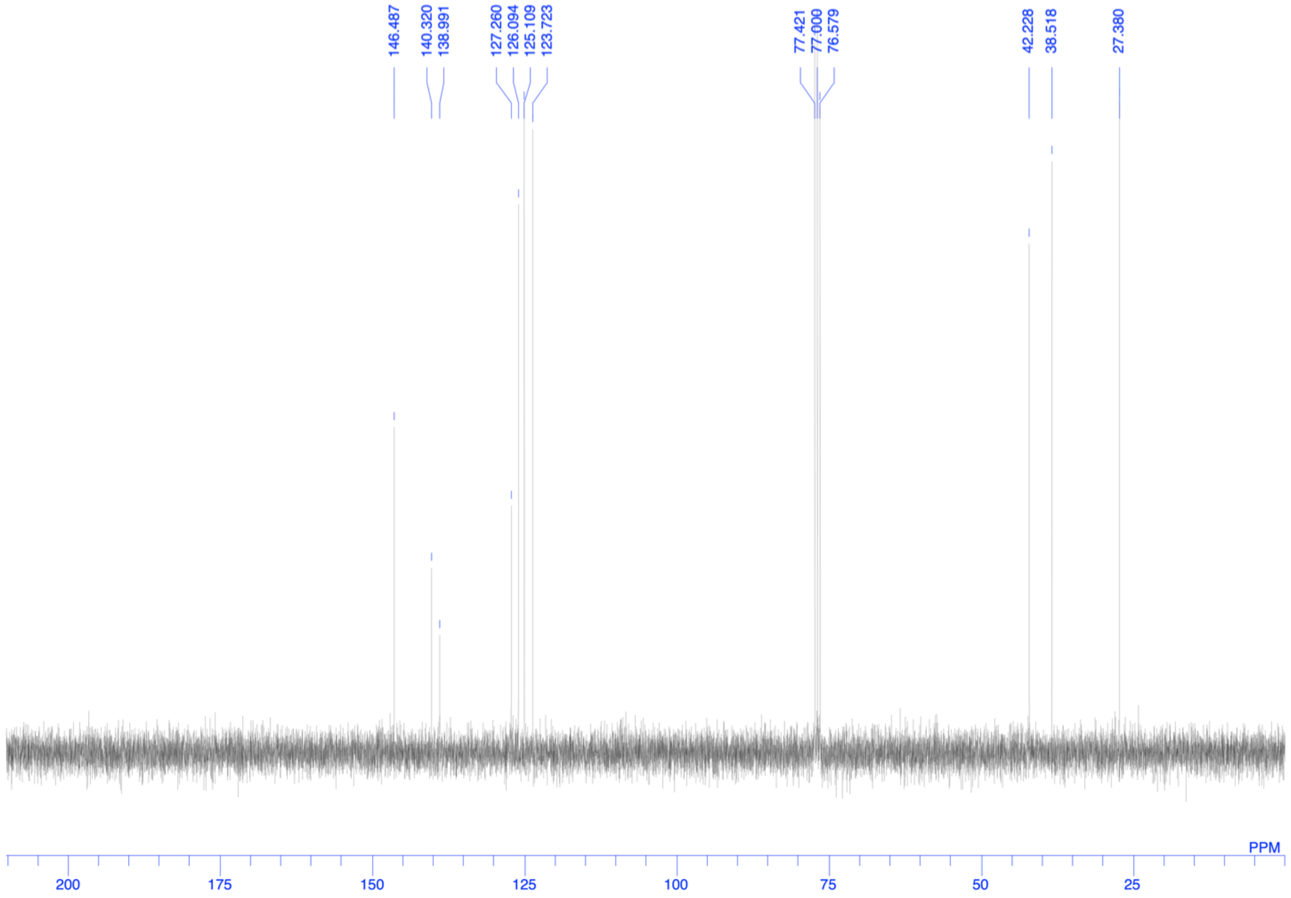
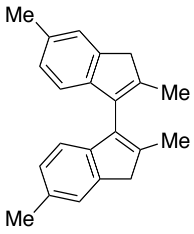
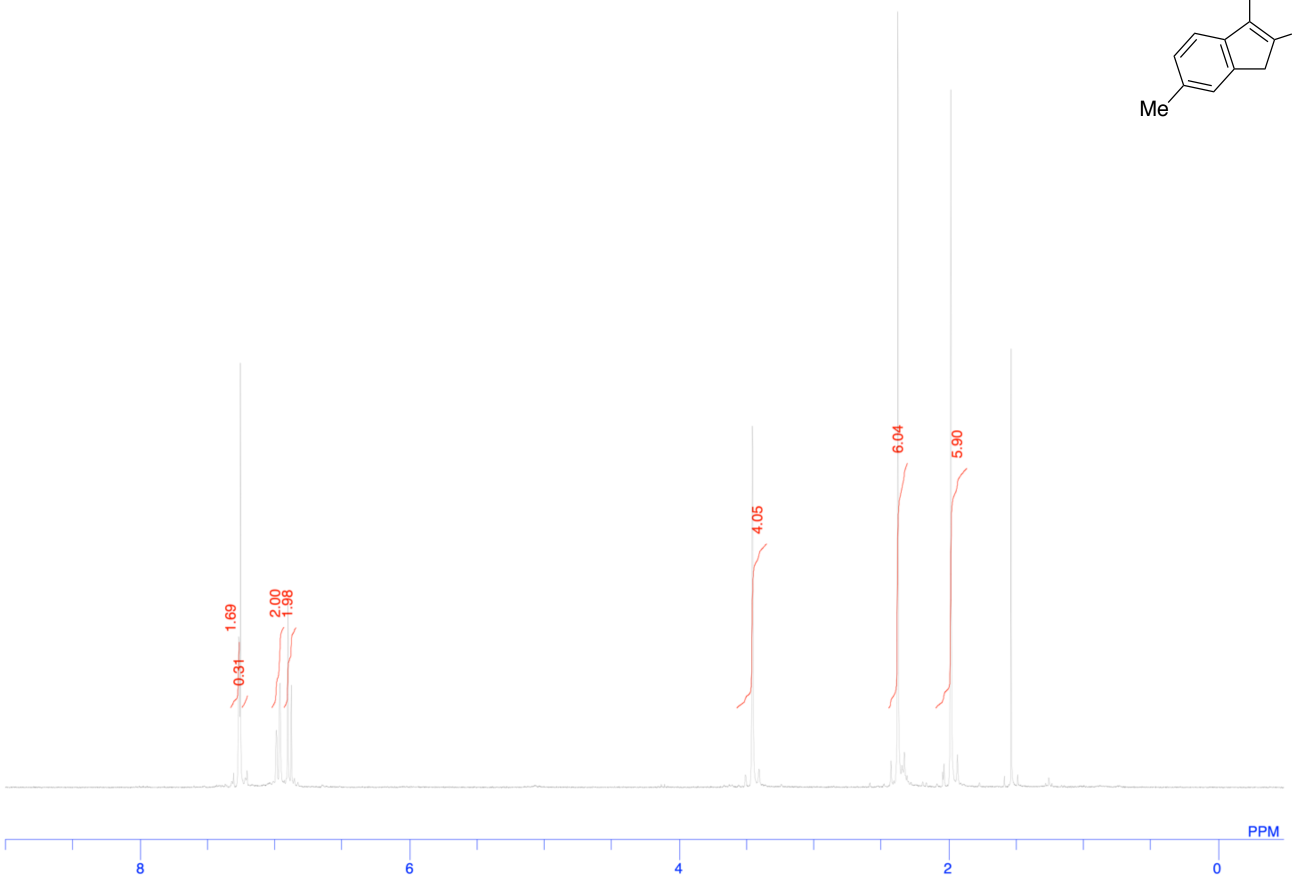
2.05
2.05
2.10
2.04
PPM
8
6
4
2
0


146.487
140.320
138.991
127.260
126.094
125.109
123.723
77.421
77.000
76.579
42.228
38.518
27.380
PPM
200
175
150
125
100
75
50
25

2b


Me
Me
Me
Me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2.00
1.98
4.05
6.04
5.90
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8
6
4
2
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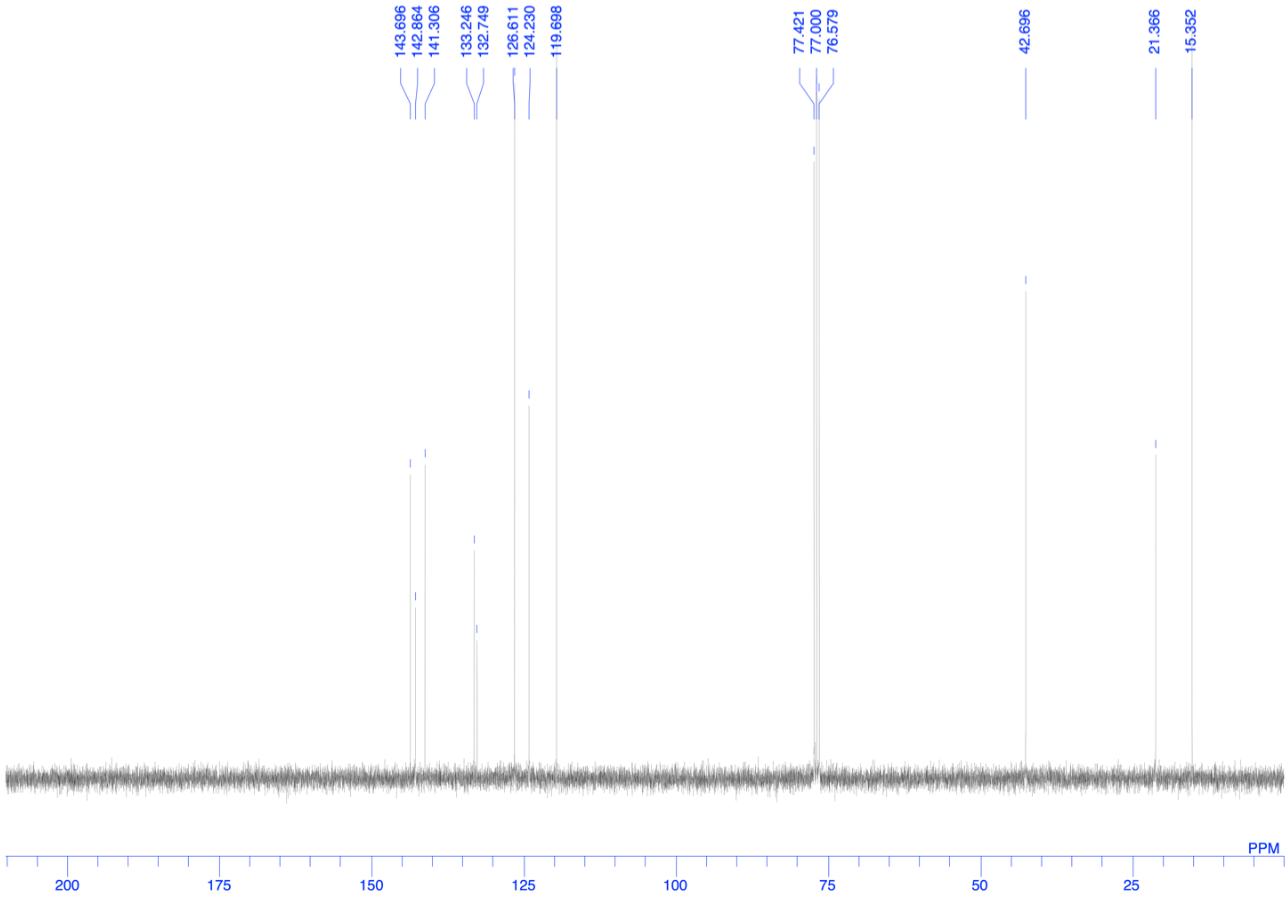
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141.306
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126.611
124.230
119.698
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42.696
21.366
15.352
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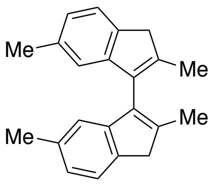
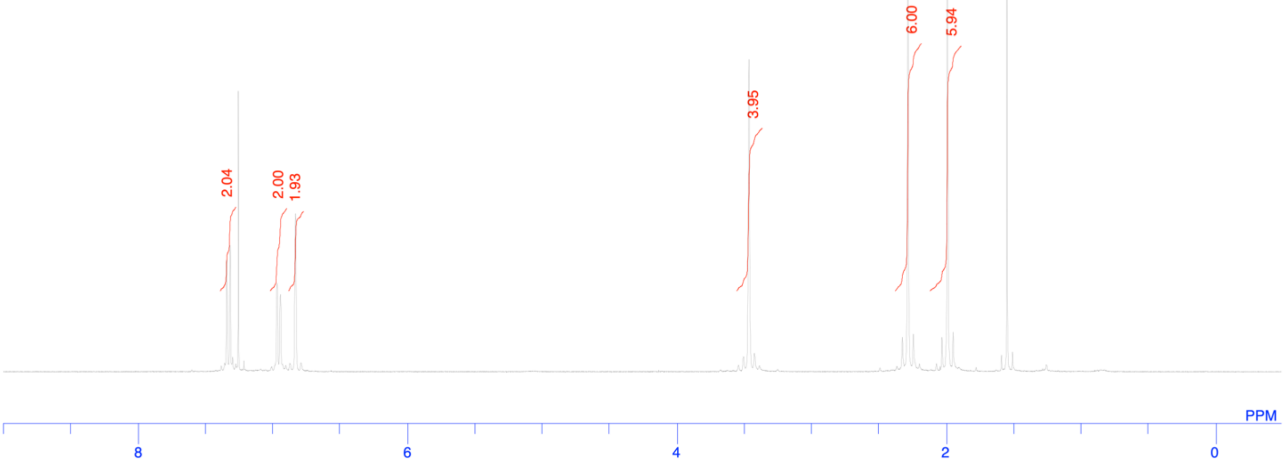
175
150
125
100
75
50
25

2c


Me
Me
Me
Me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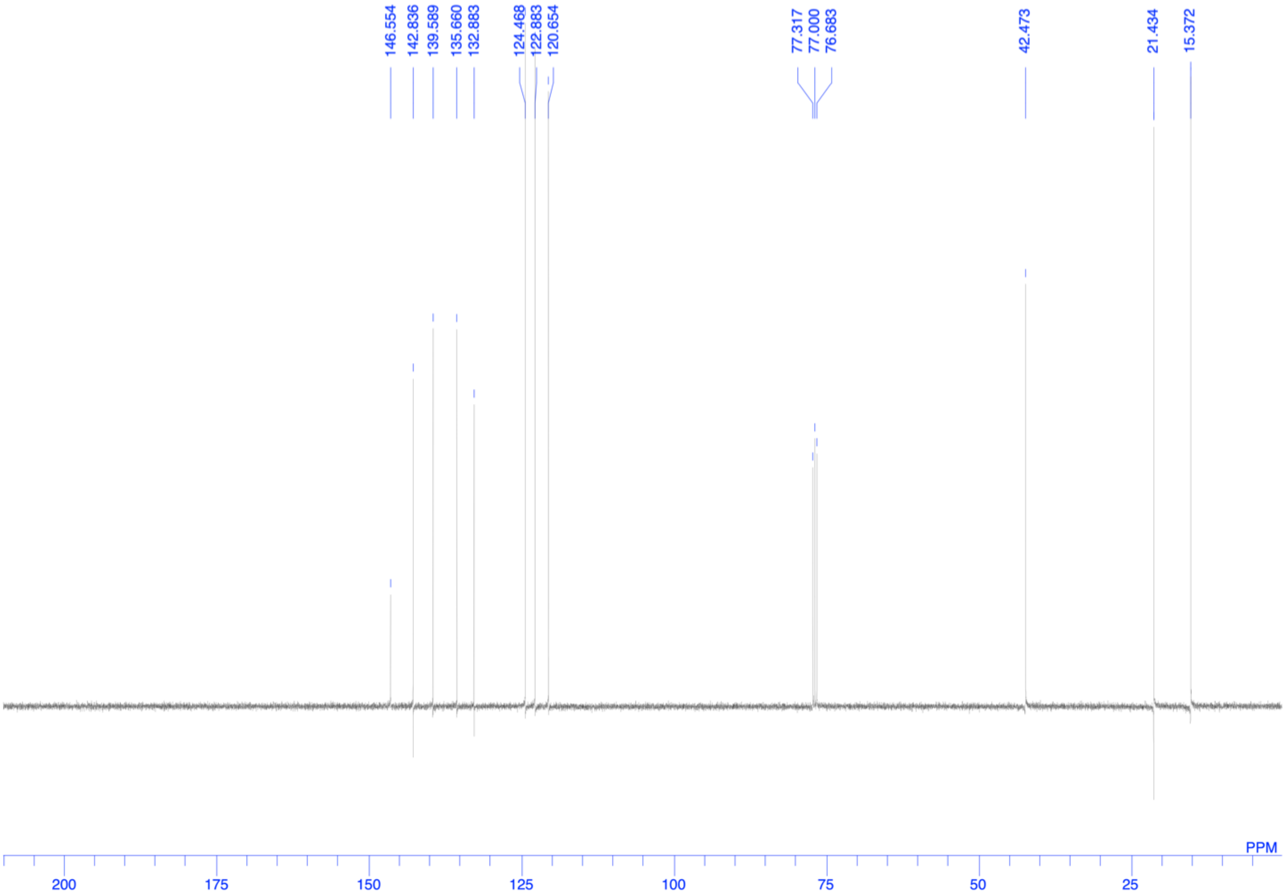
3.95
6.00
5.94
PPM
8
6
4
2
0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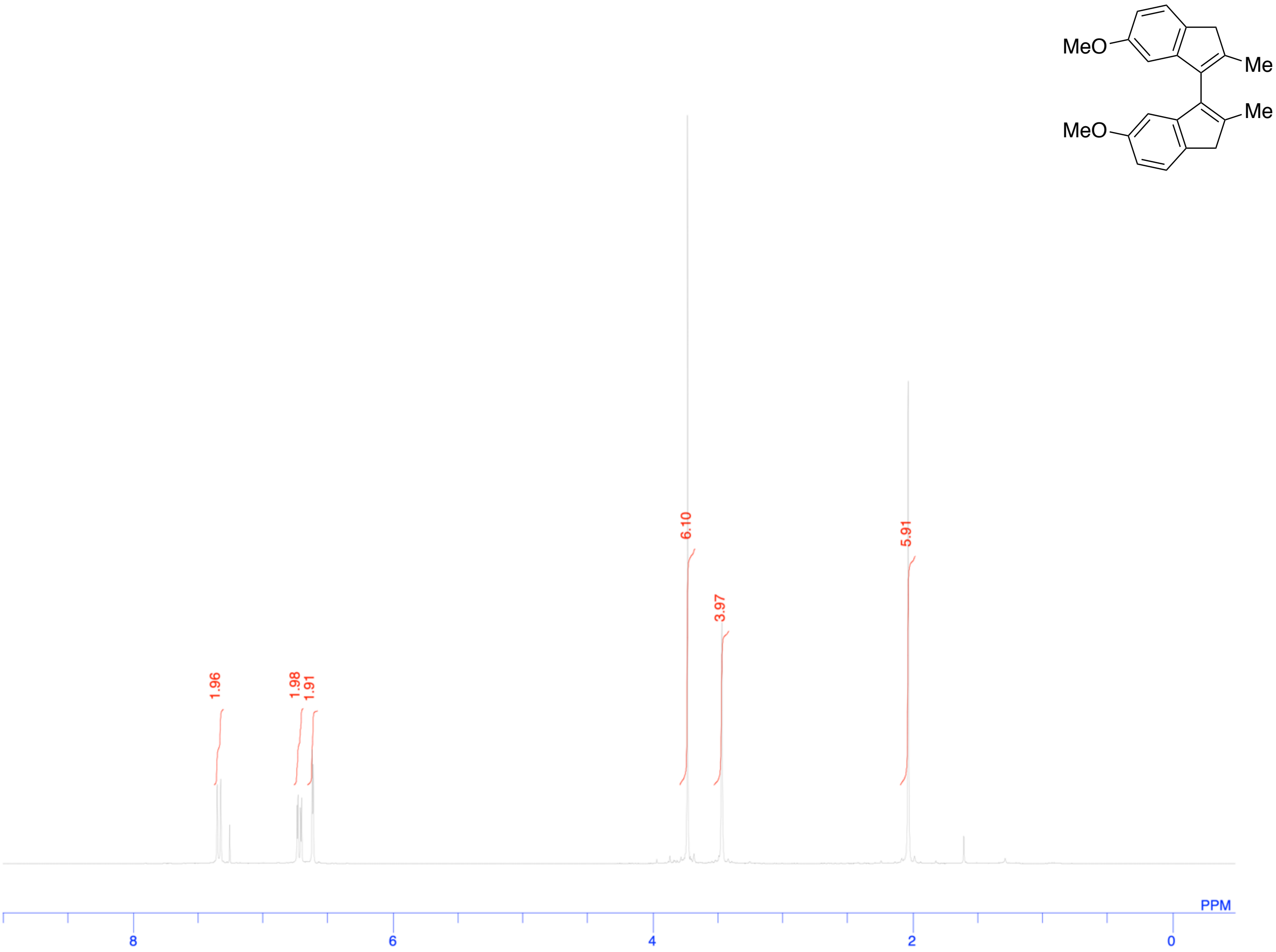
139.589
135.660
132.883
124.468
122.883
120.654
77.317
77.000
76.683
42.473
21.434
15.372
PPM
200
175
150
125
100
75
50
25

2d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Me
MeO
Me
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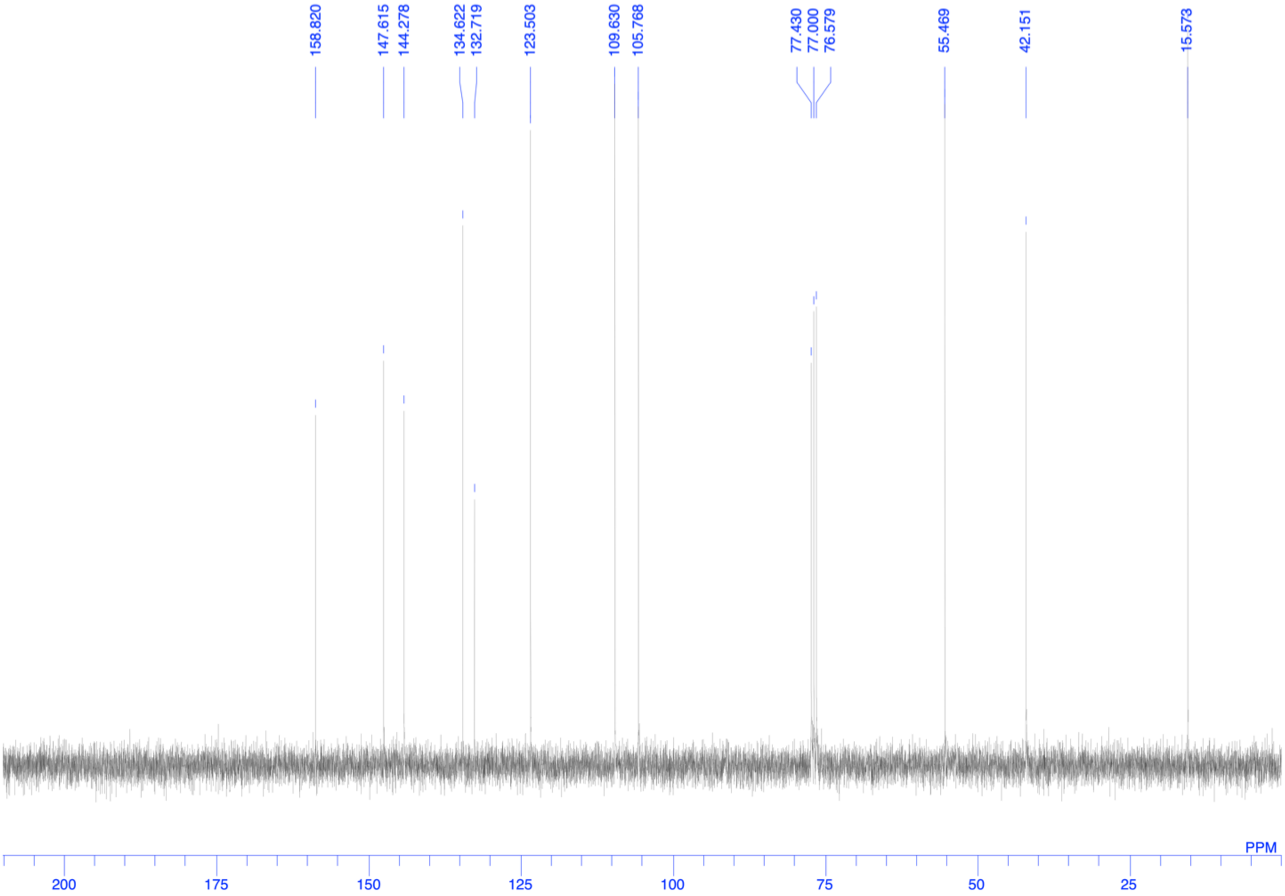
1.98
1.91
6.10
3.97
5.91
PPM
8
6
4
2
0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144.278
134.622
132.719
123.503
109.630
105.768
77.430
77.000
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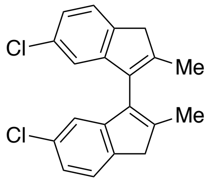
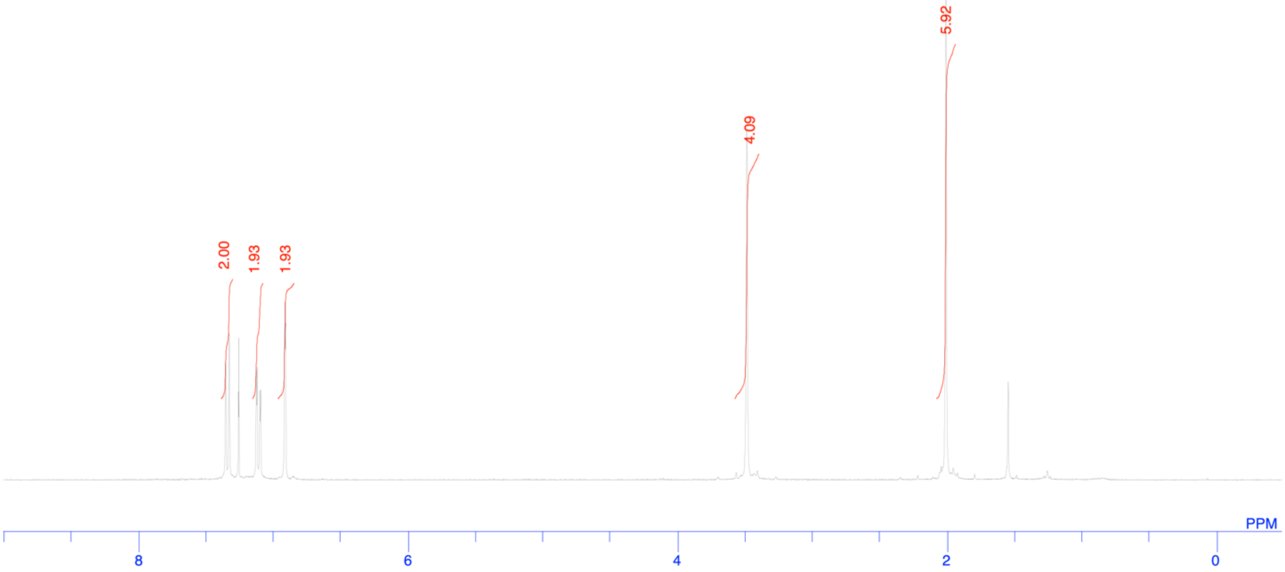
55.469
42.151
15.573
PPM
200
175
150
125
100
75
50
25

2e



Cl
Me
Cl
Me



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1.93
4.09
5.92
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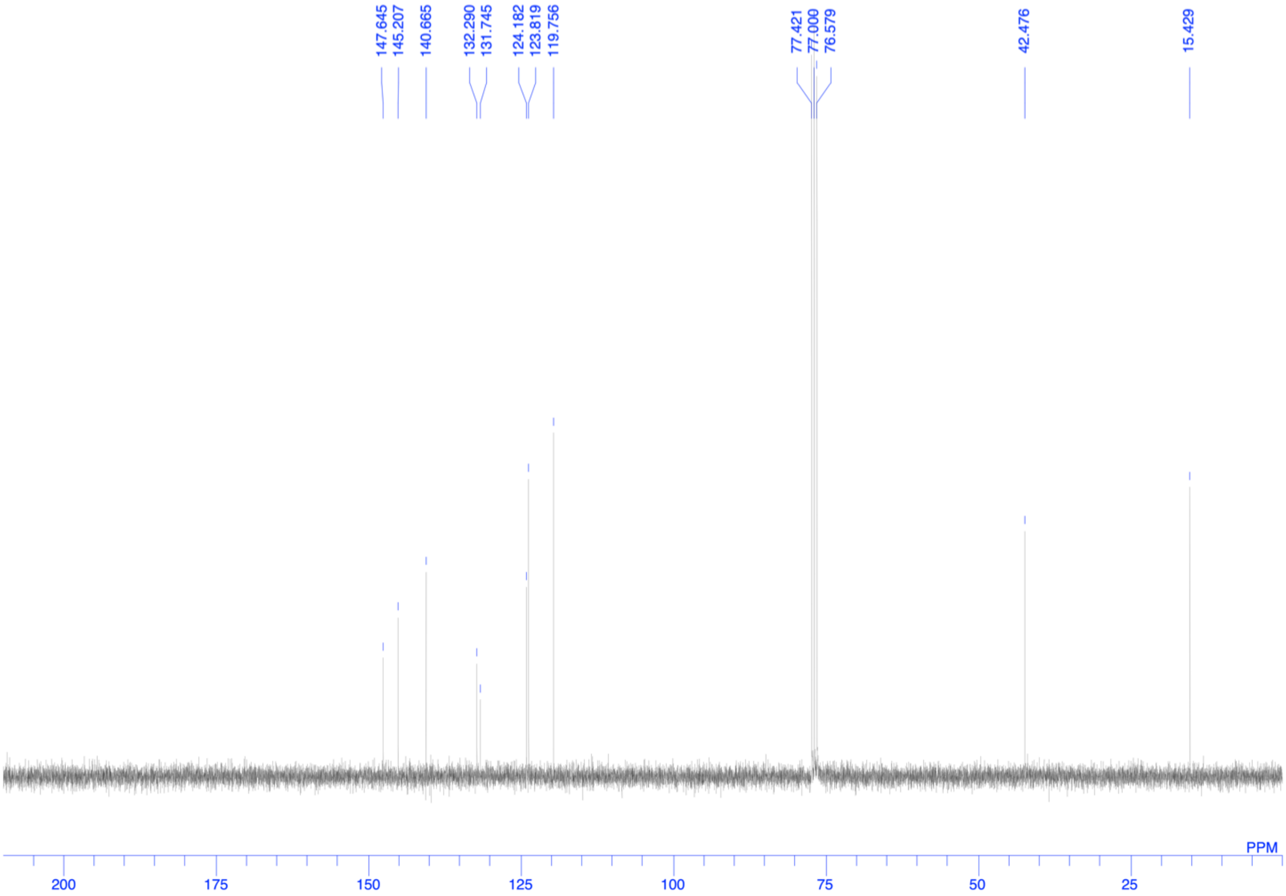
8
6
4
2
0



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124.182
123.819
119.756
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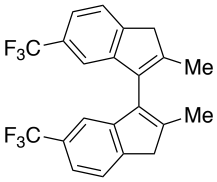
76.579
42.476
15.429
PPM
200
175
150
125
100
75
50
25

2f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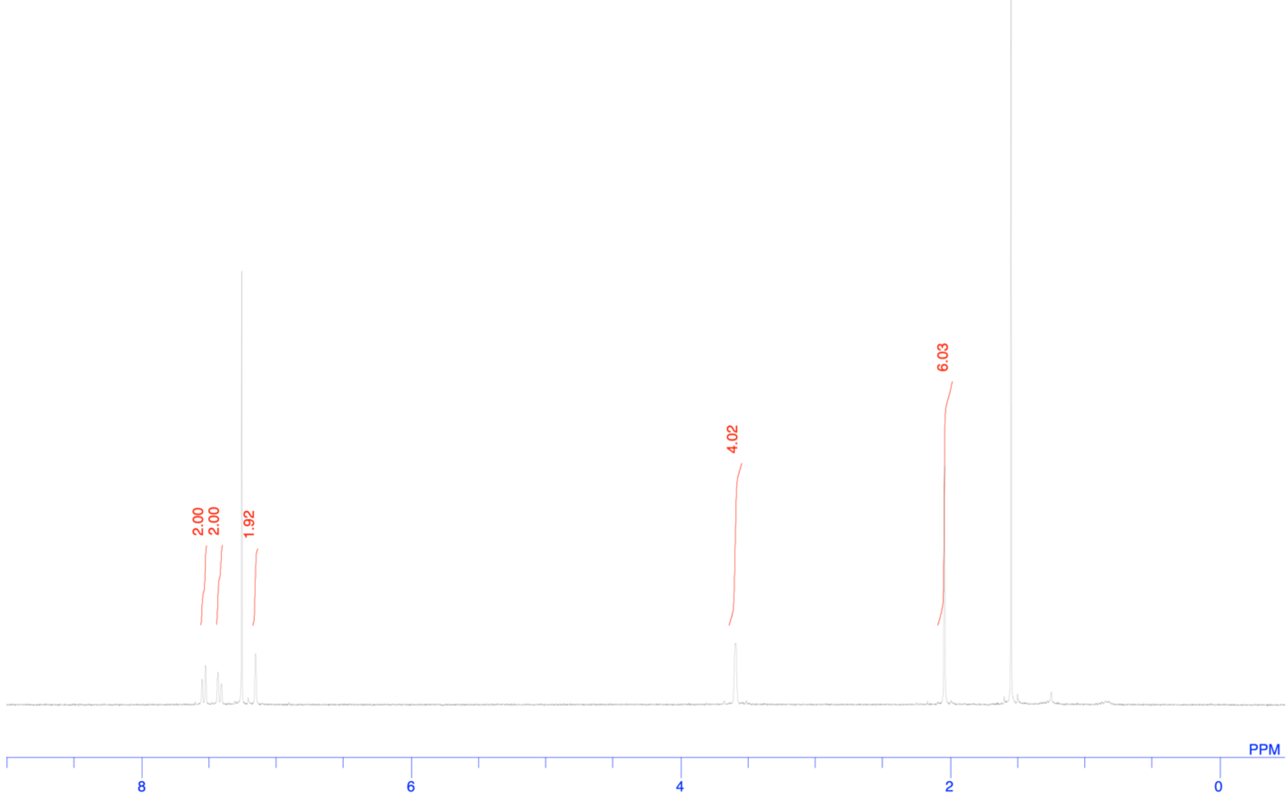
Me
Me
F3C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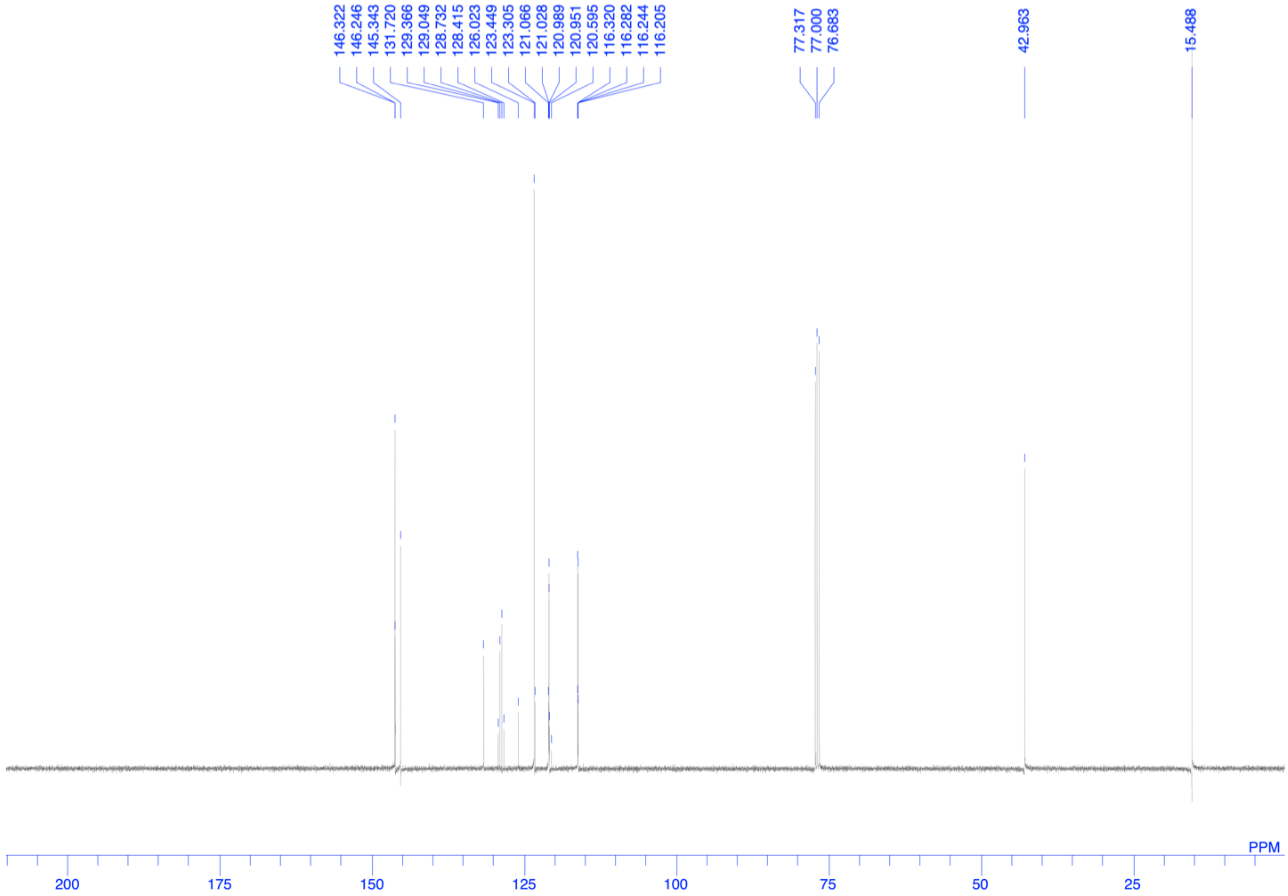
2.00
1.92
4.02
6.03
PPM
8
6
4
2
0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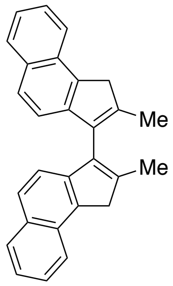
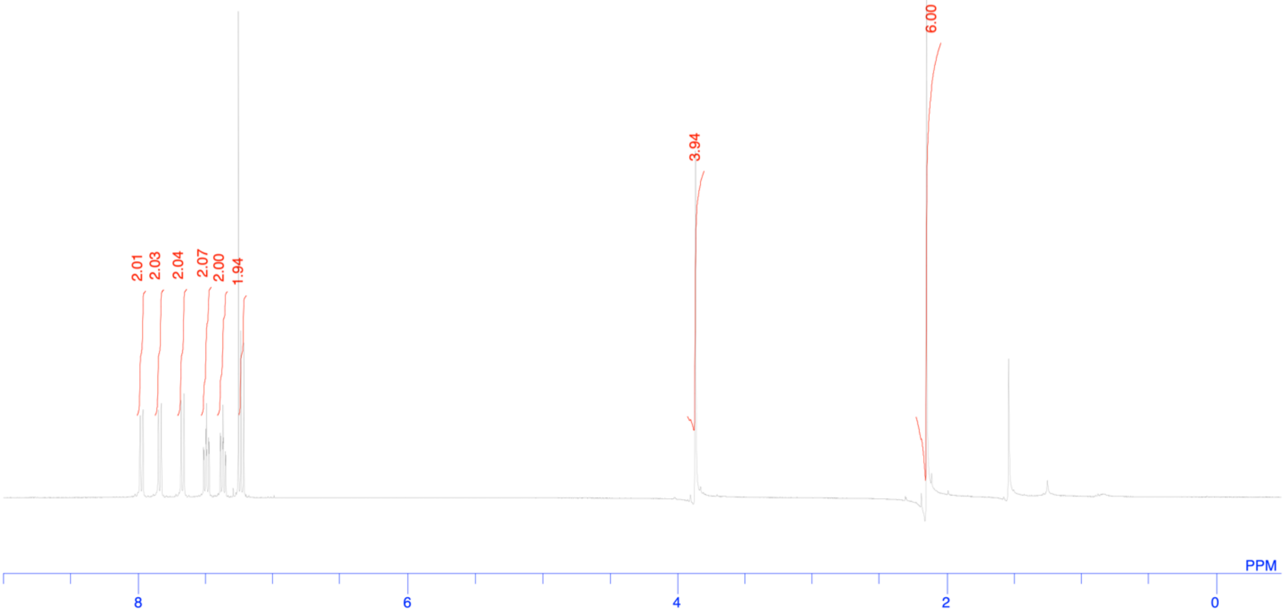
128.732
128.415
126.023
123.449
123.305
121.066
121.028
120.989
120.951
120.595
116.320
116.282
116.244
116.205
77.317
77.000
76.683
42.963
15.488
PPM
200
175
150
125
100
75
50
25

2g


Me
Me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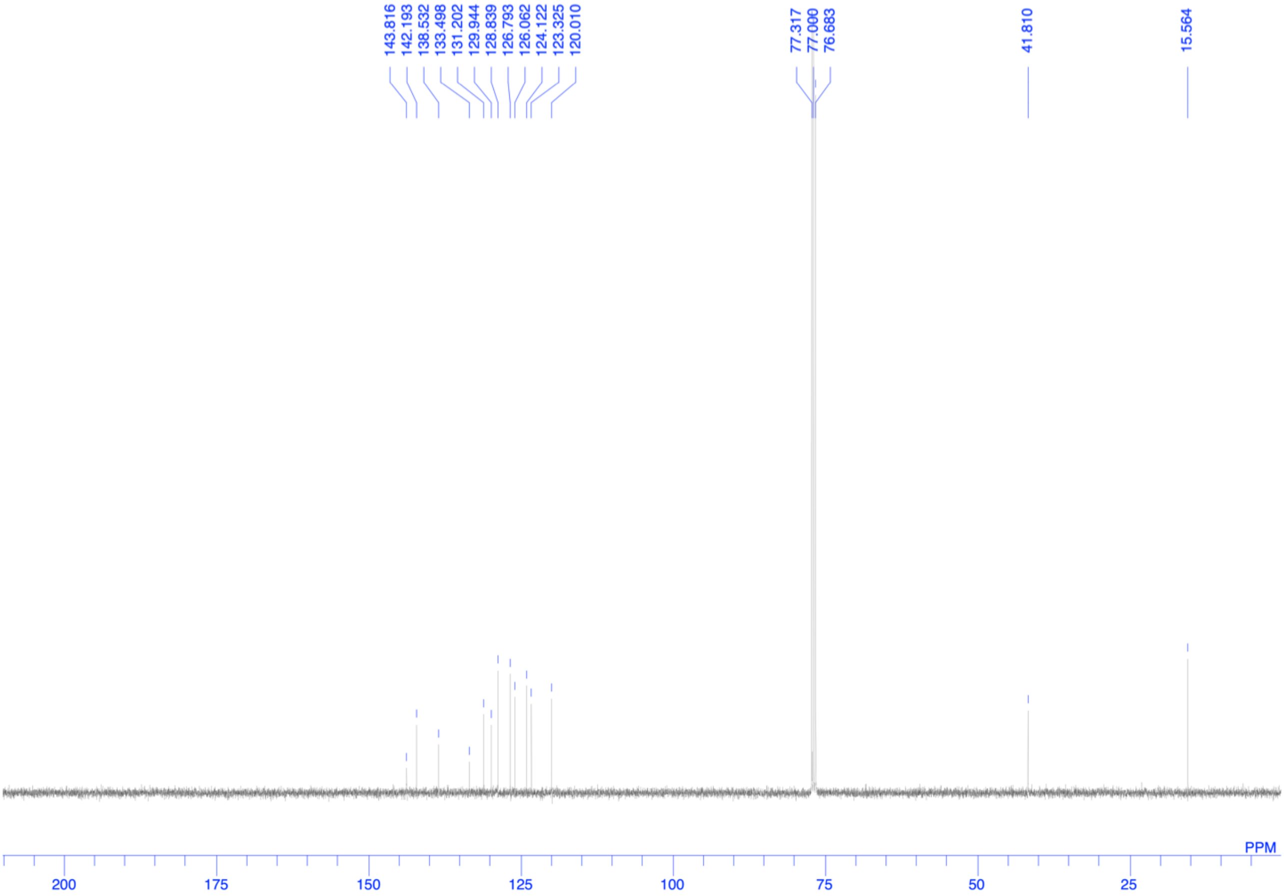
2.04
2.07
2.00
1.94
3.94
6.00
PPM
8
6
4
2
0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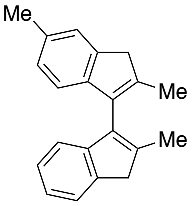
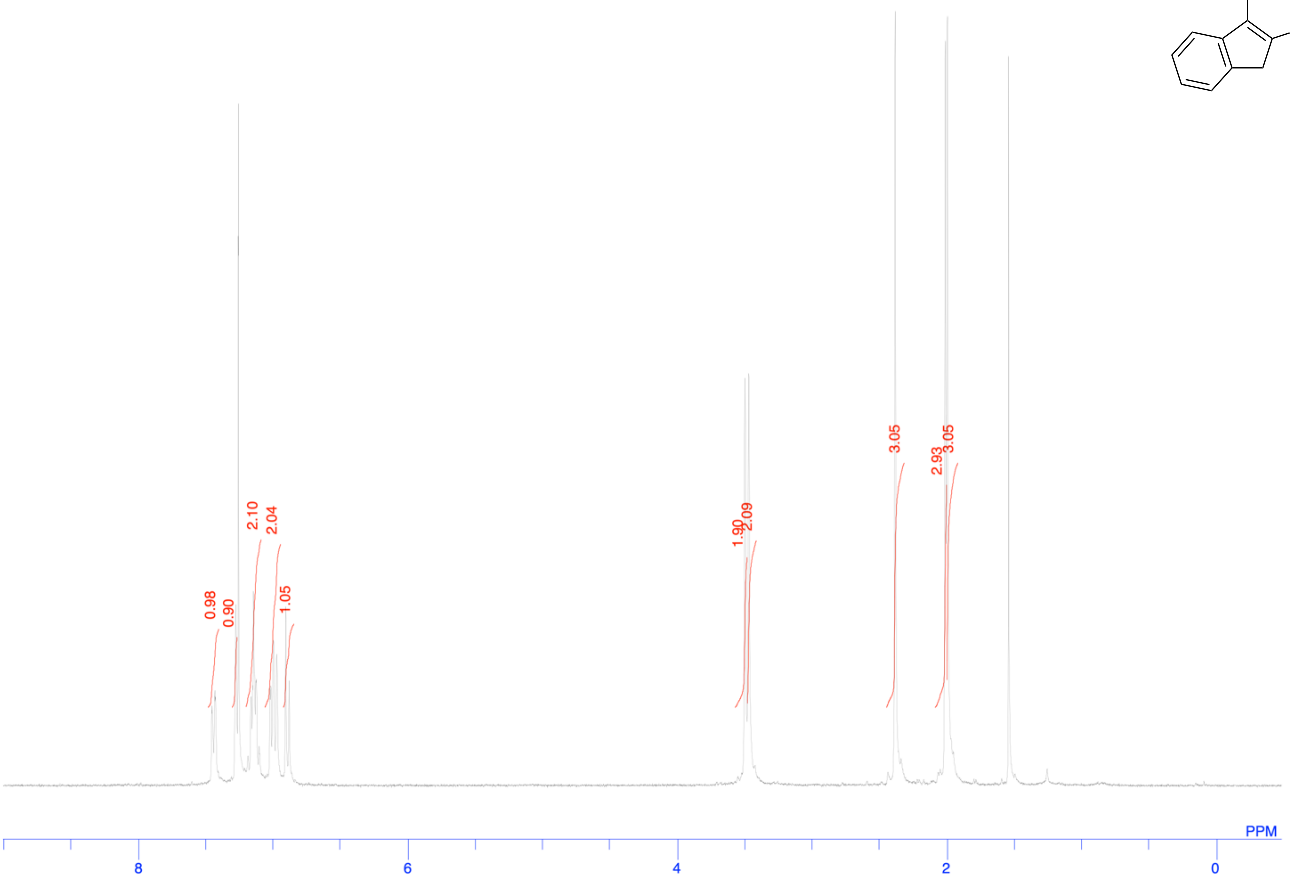
131.202
129.944
128.839
126.793
126.062
124.122
123.325
120.010
77.317
77.000
76.683
41.810
15.564
PPM
200
175
150
125
100
75
50
25

2h


Me
Me
Me


0.98
0.90
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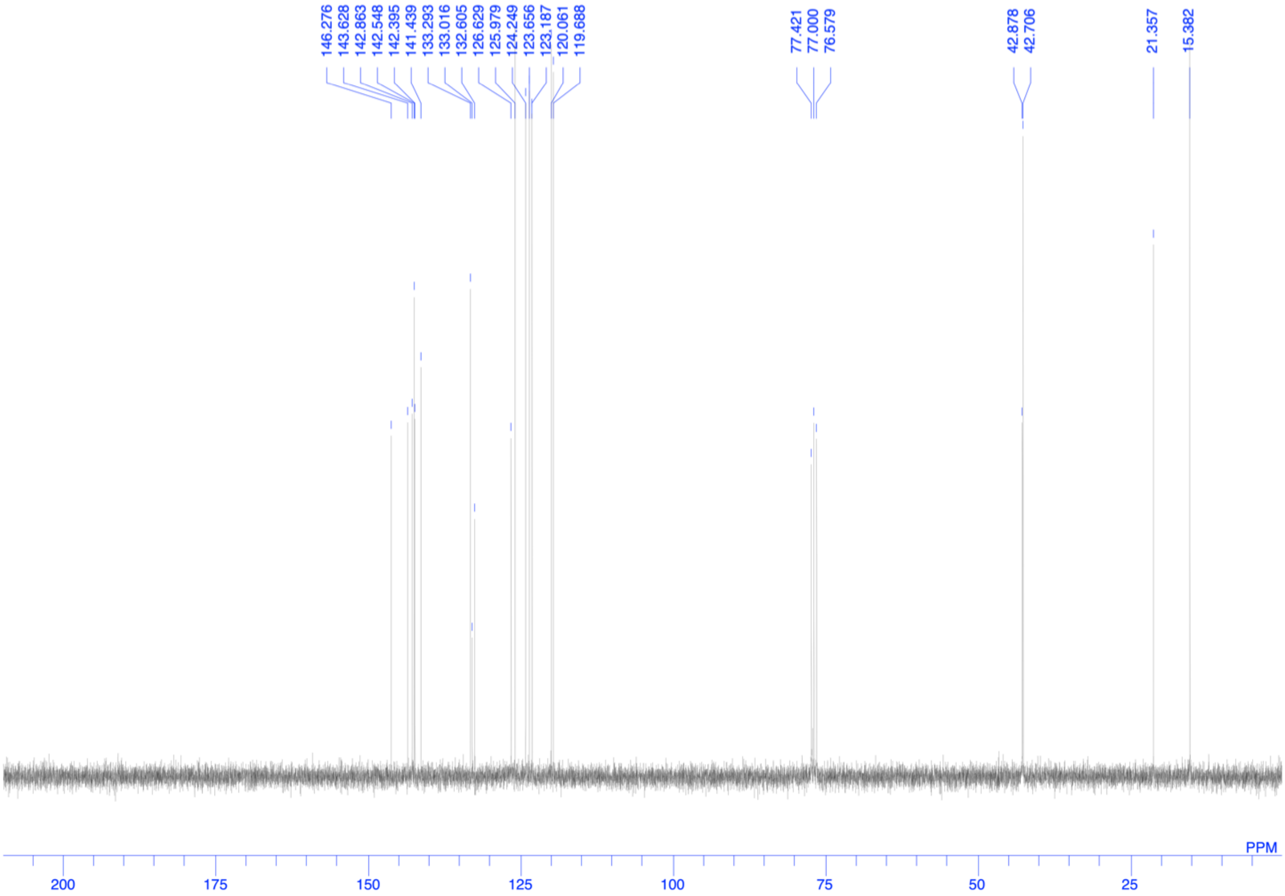
1.90
2.09
3.05
2.93
3.05
PPM
8
6
4
2
0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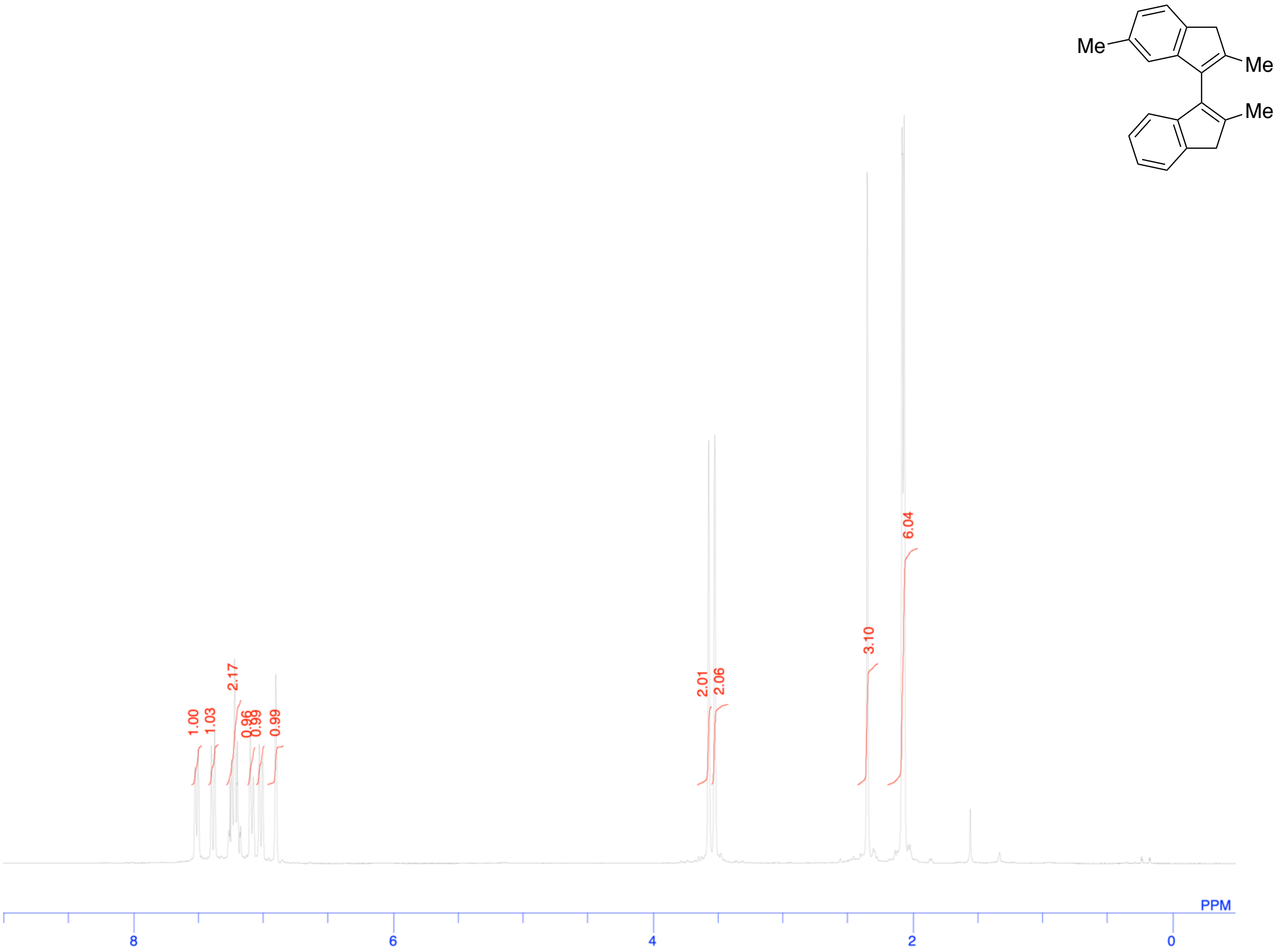
141.439
133.293
133.016
132.605
126.629
125.979
124.249
123.656
123.187
120.061
119.688
77.421
77.000
76.579
42.878
42.706
21.357
15.382
PPM
200
175
150
125
100
75
50
25

2i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Me
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1.03
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0.99
0.99
2.01
2.06
3.10
6.04
PPM
8
6
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2
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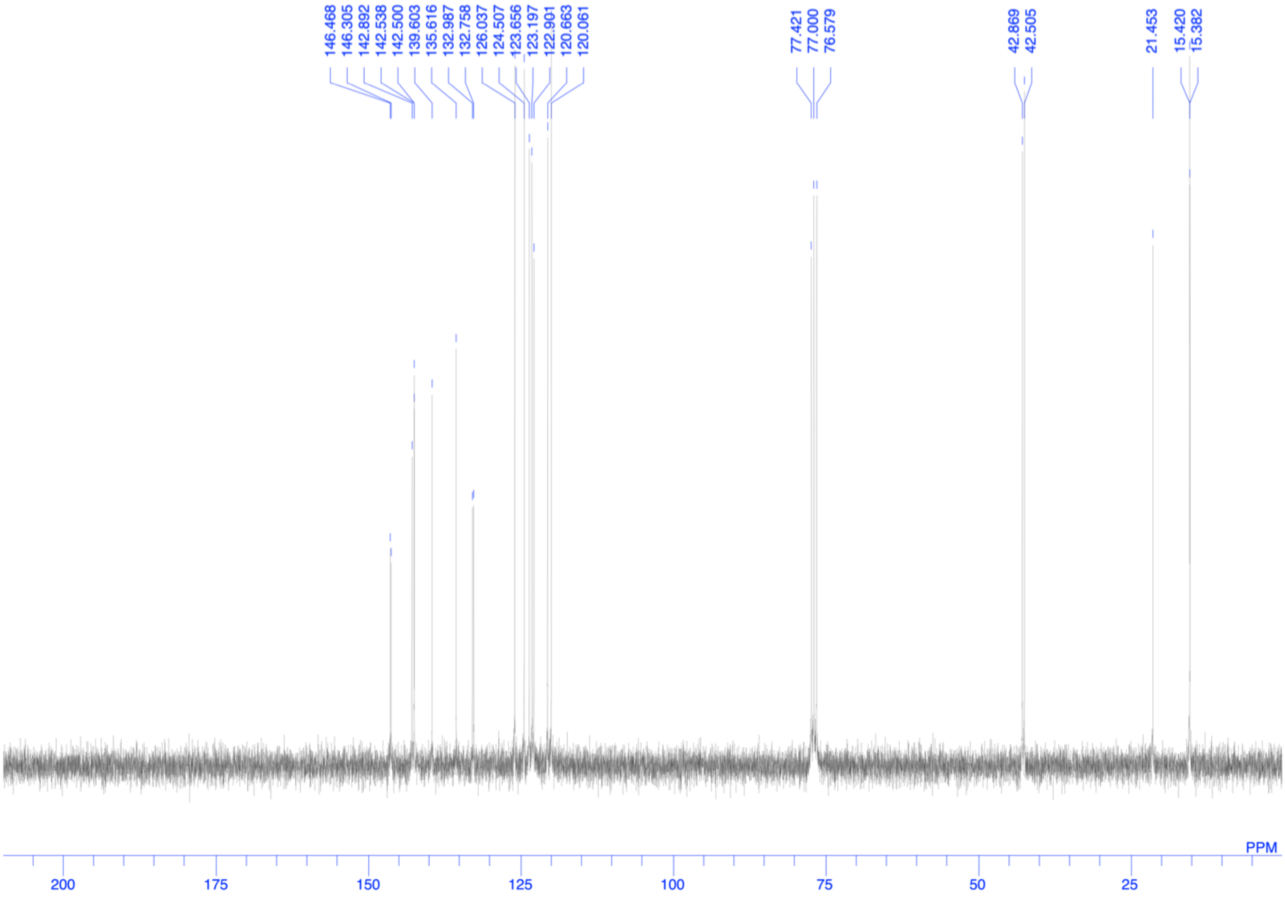
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142.892
142.538
142.500
139.603
135.616
132.987
132.758
126.037
124.507
123.656
123.197
122.901
120.663
120.061
77.421
77.000
76.579
42.869
42.505
21.453
15.420
15.382
PPM
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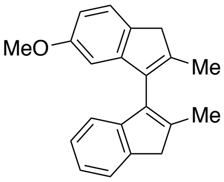
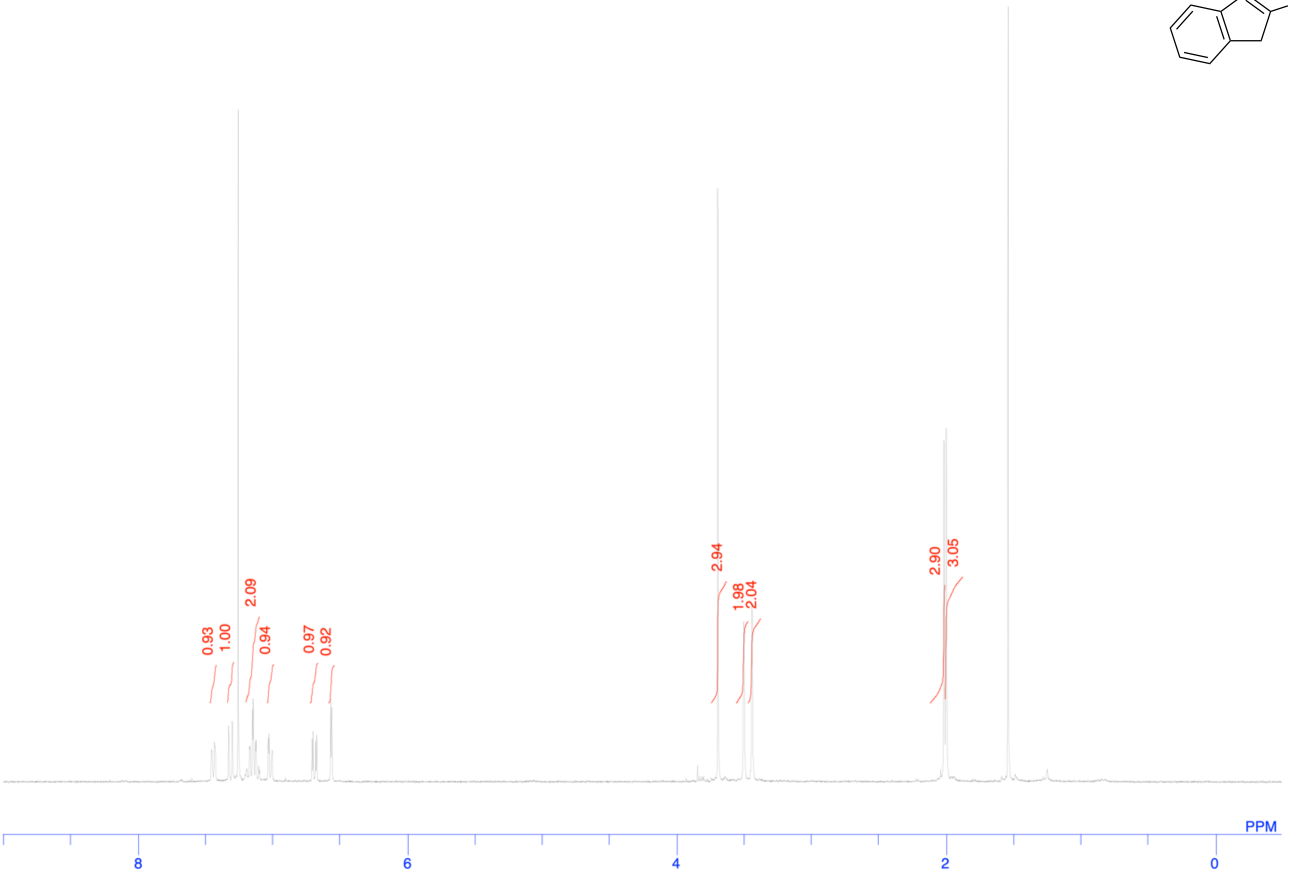
175
150
125
100
75
50
25

2j


MeO
Me
Me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3.05
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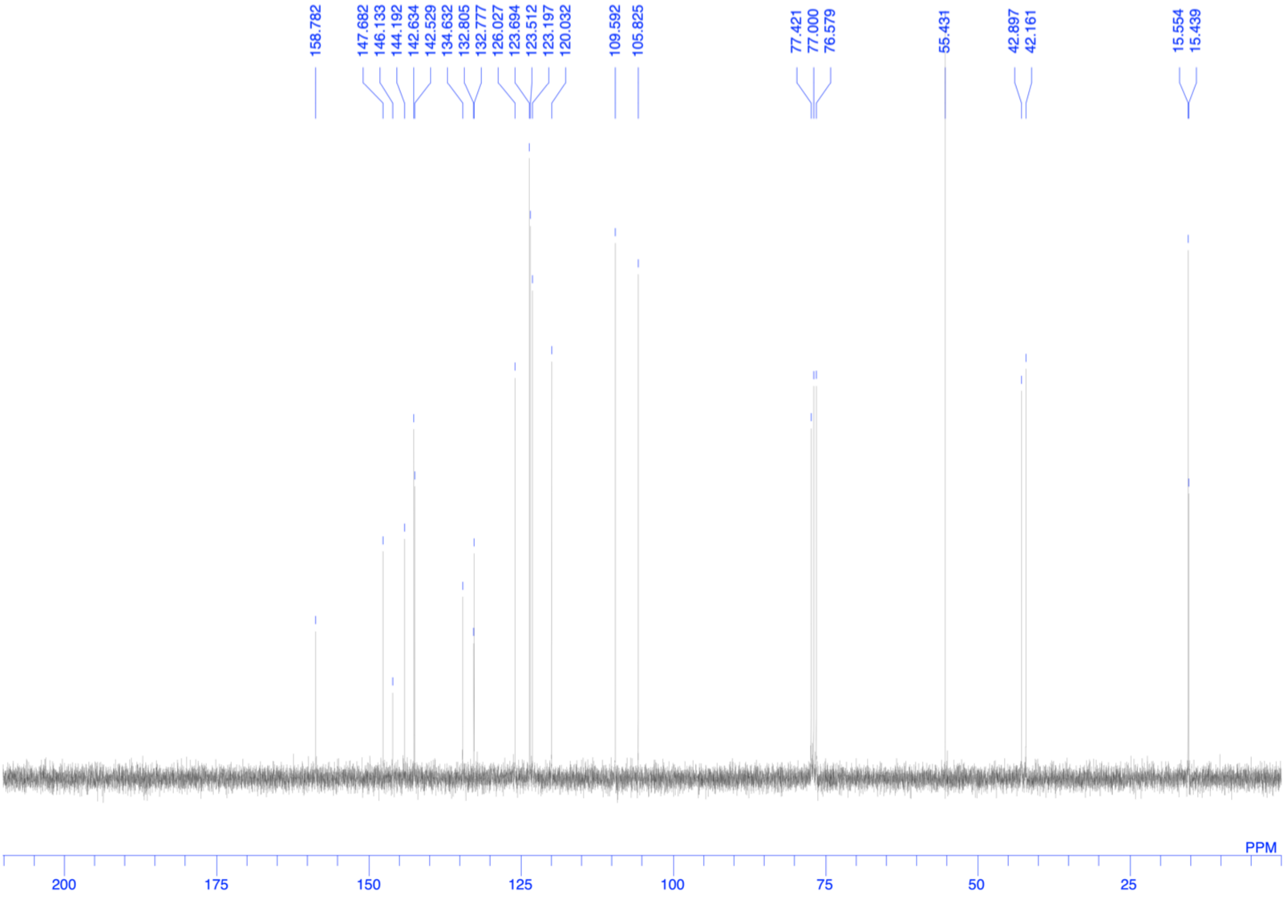
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132.805
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126.027
123.694
123.512
123.197
120.032
109.592
105.825
77.421
77.000
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15.439
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175
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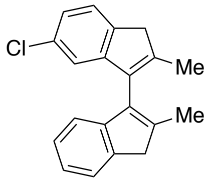
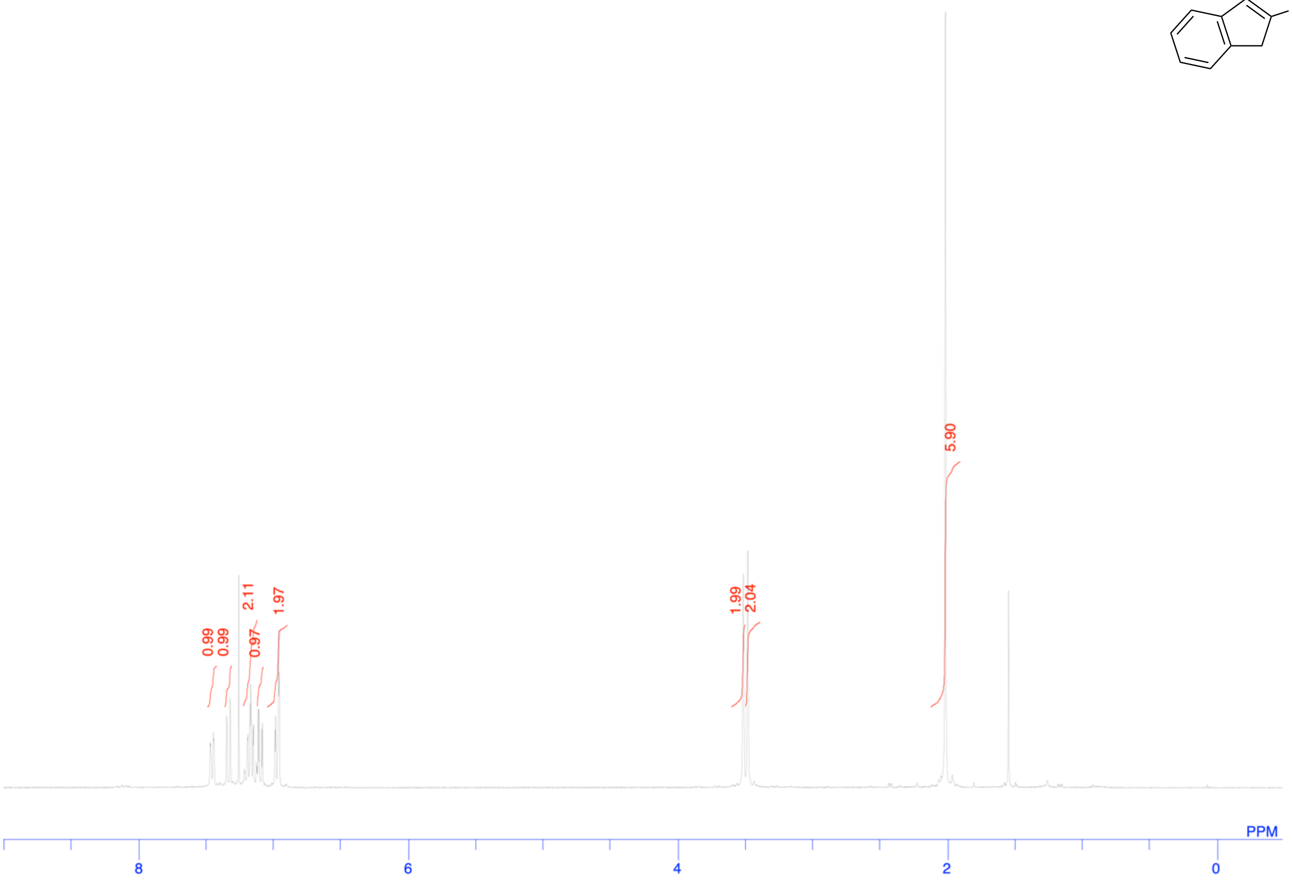
125
100
75
50
25

2k


Cl
Me
Me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1.99
2.04
5.90
PPM
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6
4
2
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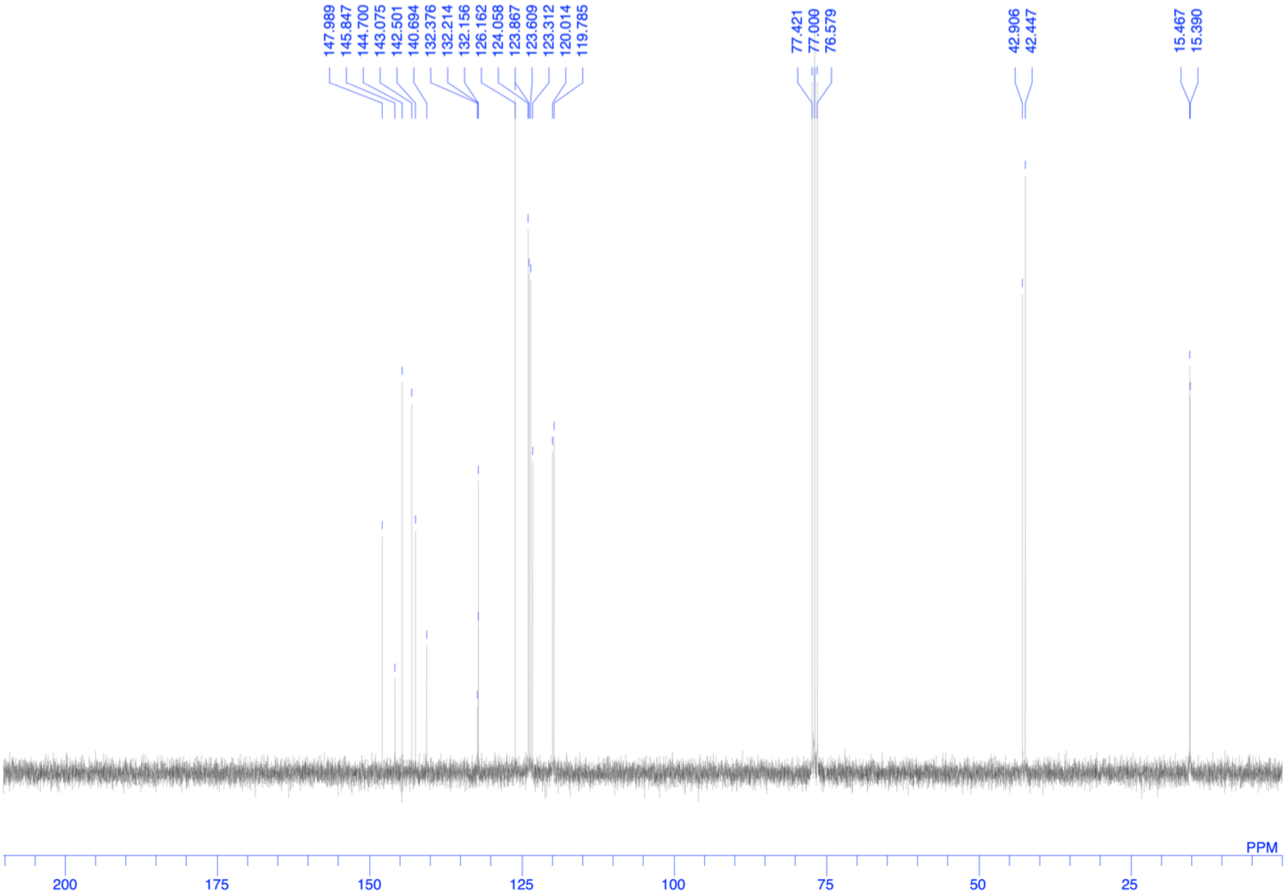
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144.700
143.075
142.501
140.694
132.376
132.214
132.156
126.162
124.058
123.867
123.609
123.312
120.014
119.785
77.421
77.000
76.579
42.906
42.447
15.467
15.390
PPM
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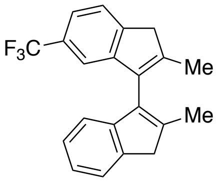
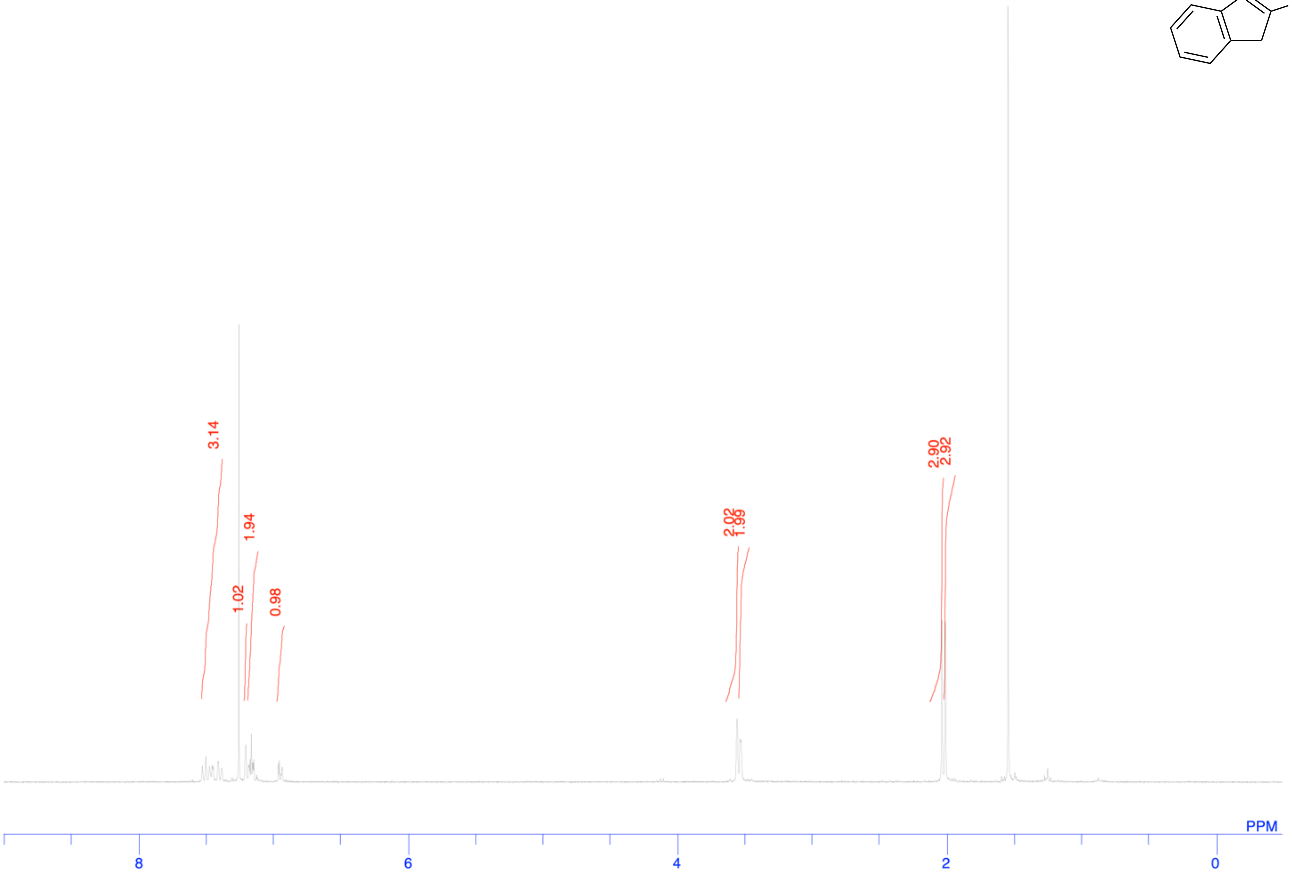
175
150
125
100
75
50
25

2l



F3C
Me
Me



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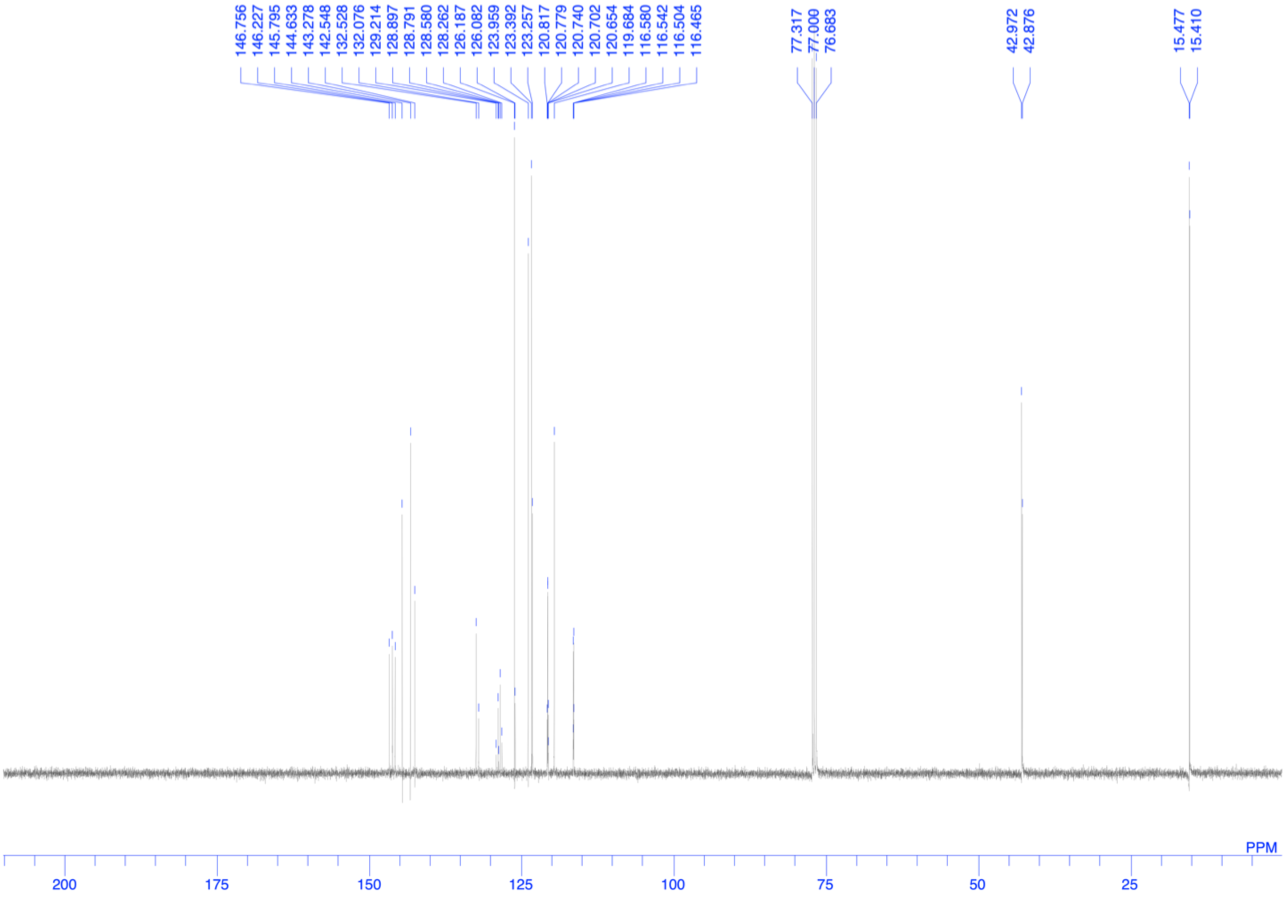
1.99
2.90
2.92
PPM
8
6
4
2
0



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146.227
145.795
144.633
143.278
142.548
132.528
132.076
129.214
128.897
128.791
128.580
128.262
126.187
126.082
123.959
123.392
123.257
120.817
120.779
120.740
120.702
120.654
119.684
116.580
116.542
116.504
116.465
77.317
77.000
76.683
42.972
42.876
15.477
15.410
PPM
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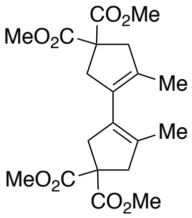
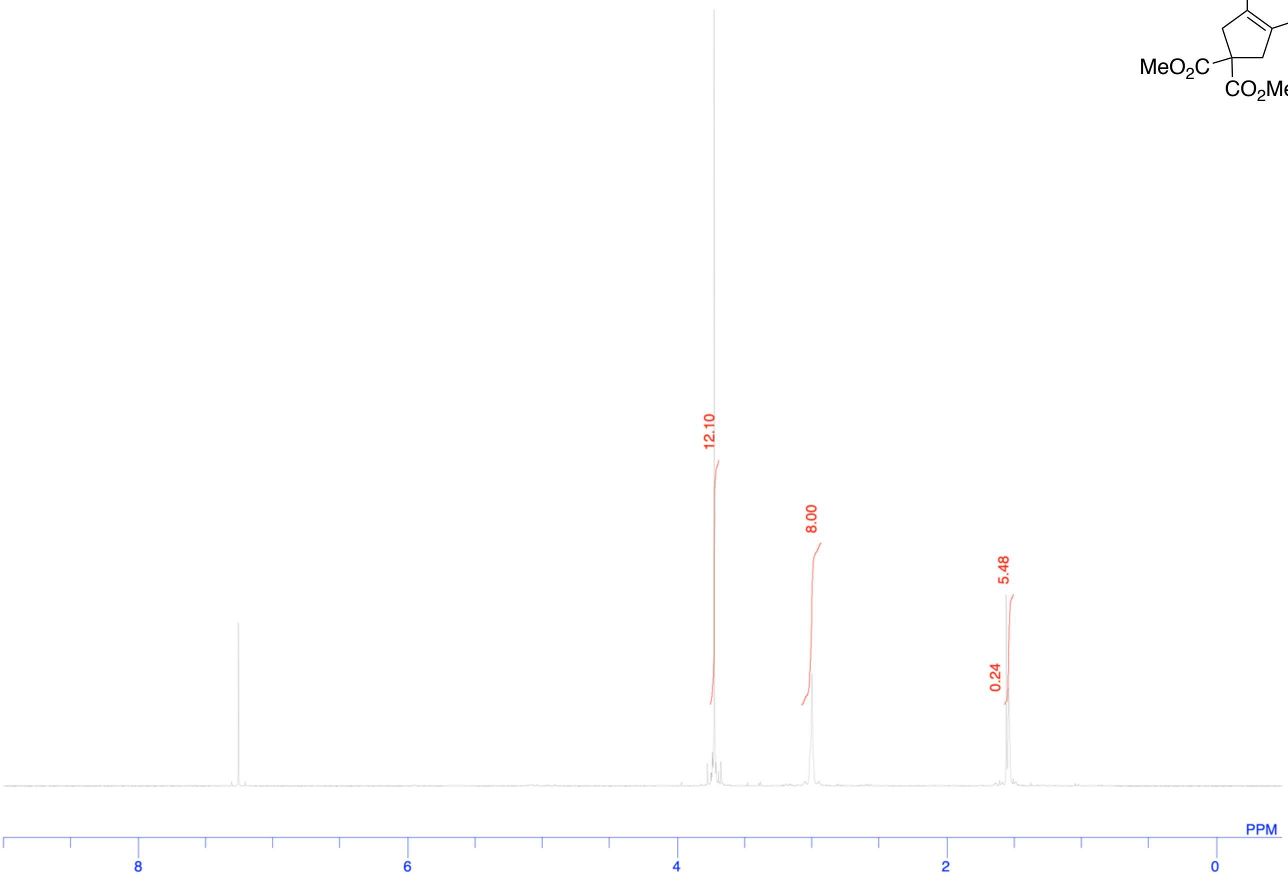
175
150
125
100
75
50
25

2m


CO2Me
MeO2C
Me
Me
MeO2C
CO2Me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8.00
5.48
0.24
PPM
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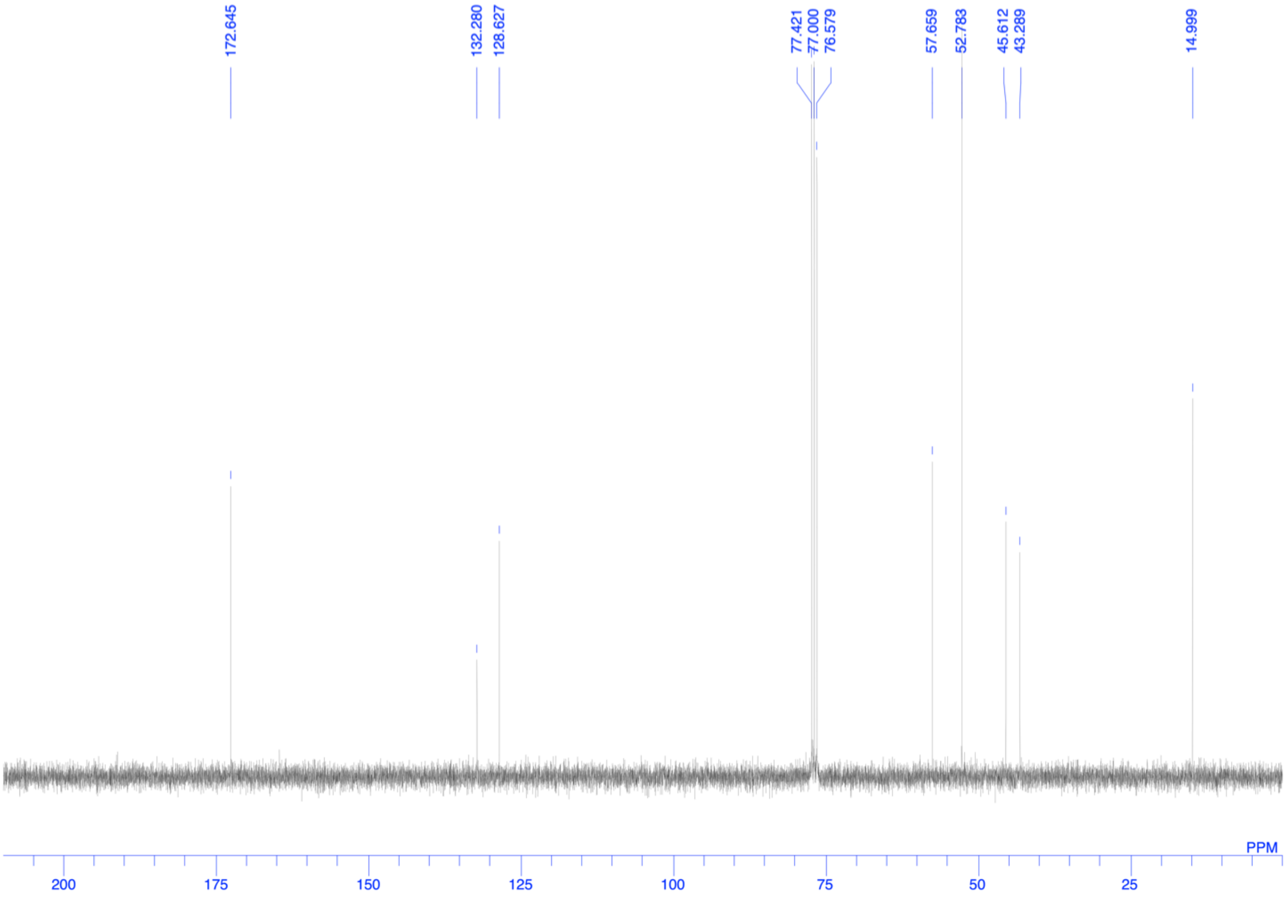
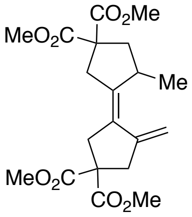
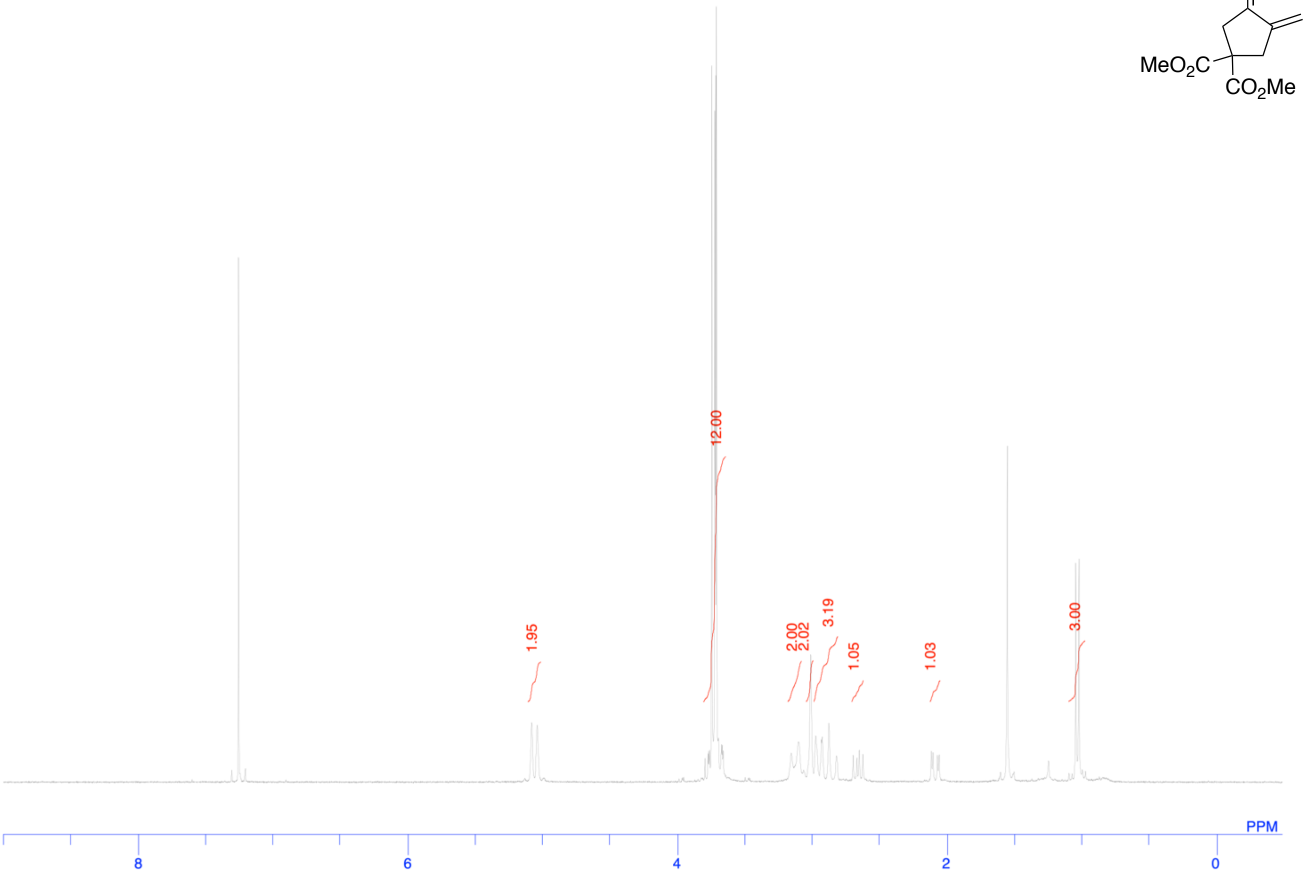
6
4
2
0


172.645
132.280
128.627
77.421
77.000
76.579
57.659
52.783
45.612
43.289
14.999
PPM
200
175
150
125
100
75
50
25

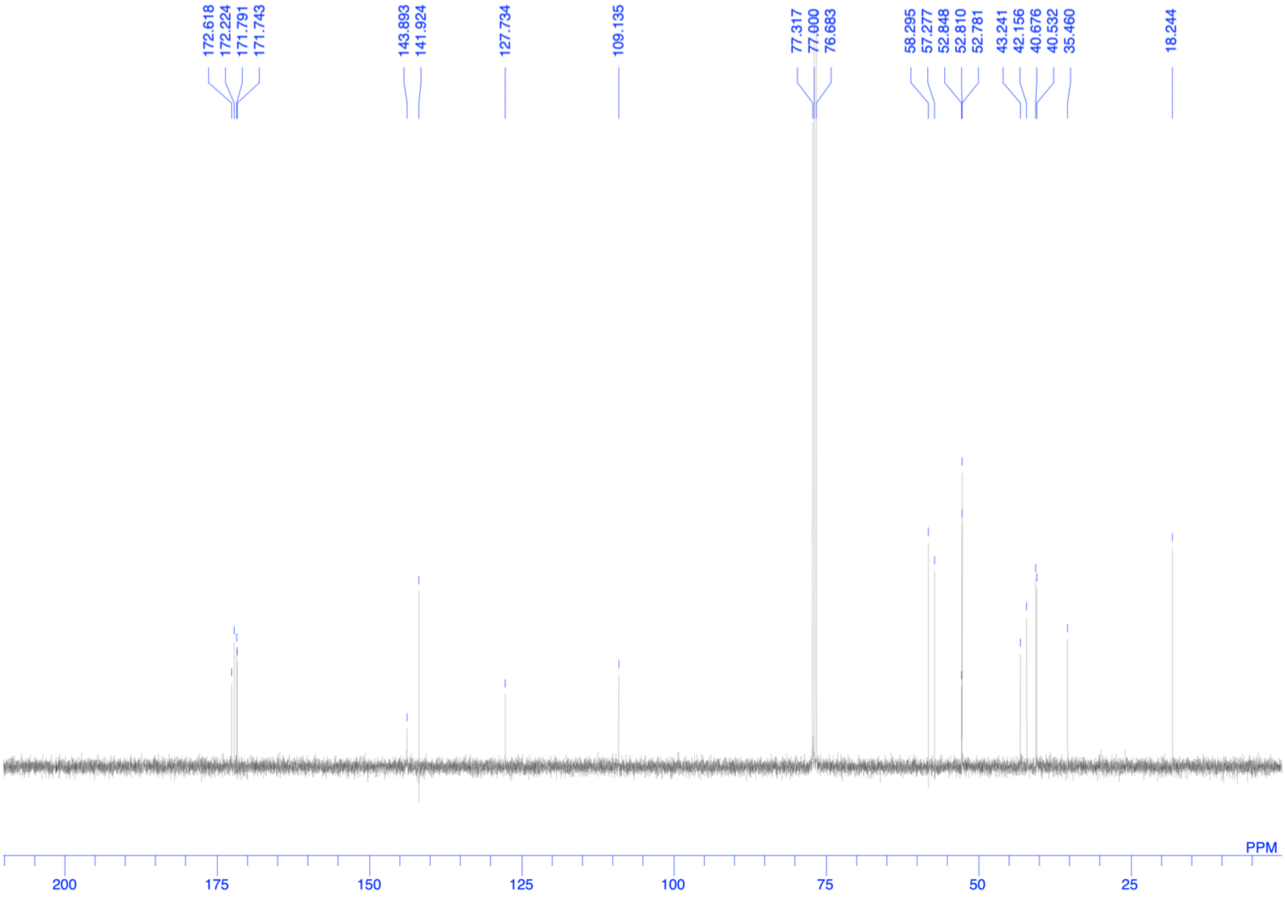
4m



CO2Me
MeO2C
Me
MeO2C
CO2Me

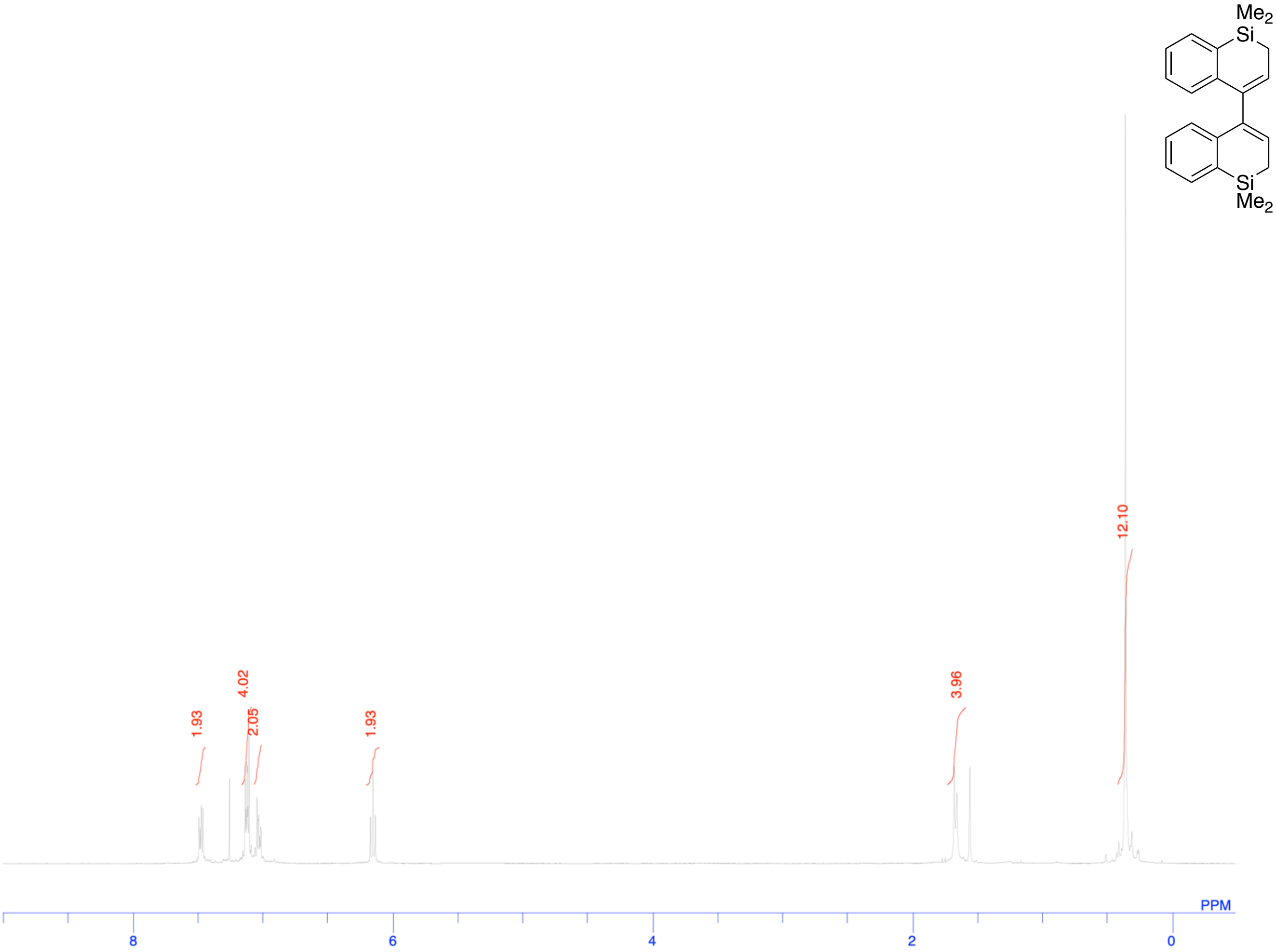


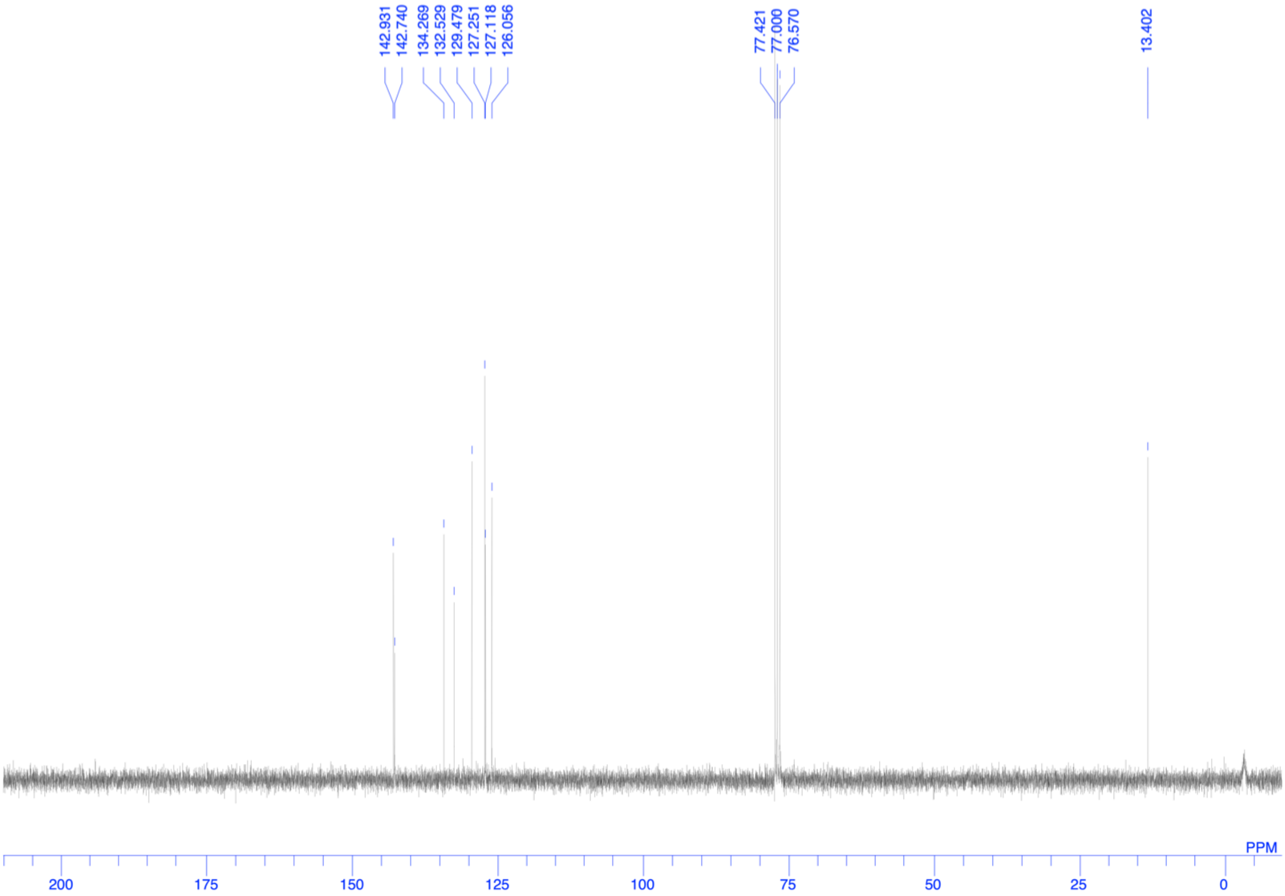
1.95
12.00
2.00
2.02
3.19
1.05
1.03
3.00
PPM
8
6
4
2
0



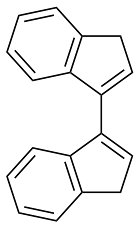
172.618
172.224
171.791
171.743
143.893
141.924
127.734
109.135
77.317
77.000
76.683
58.295
57.277
52.848
52.810
52.781
43.241
42.156
40.676
40.532
35.460
18.244
PPM
200
175
150
125
100
75
50
25

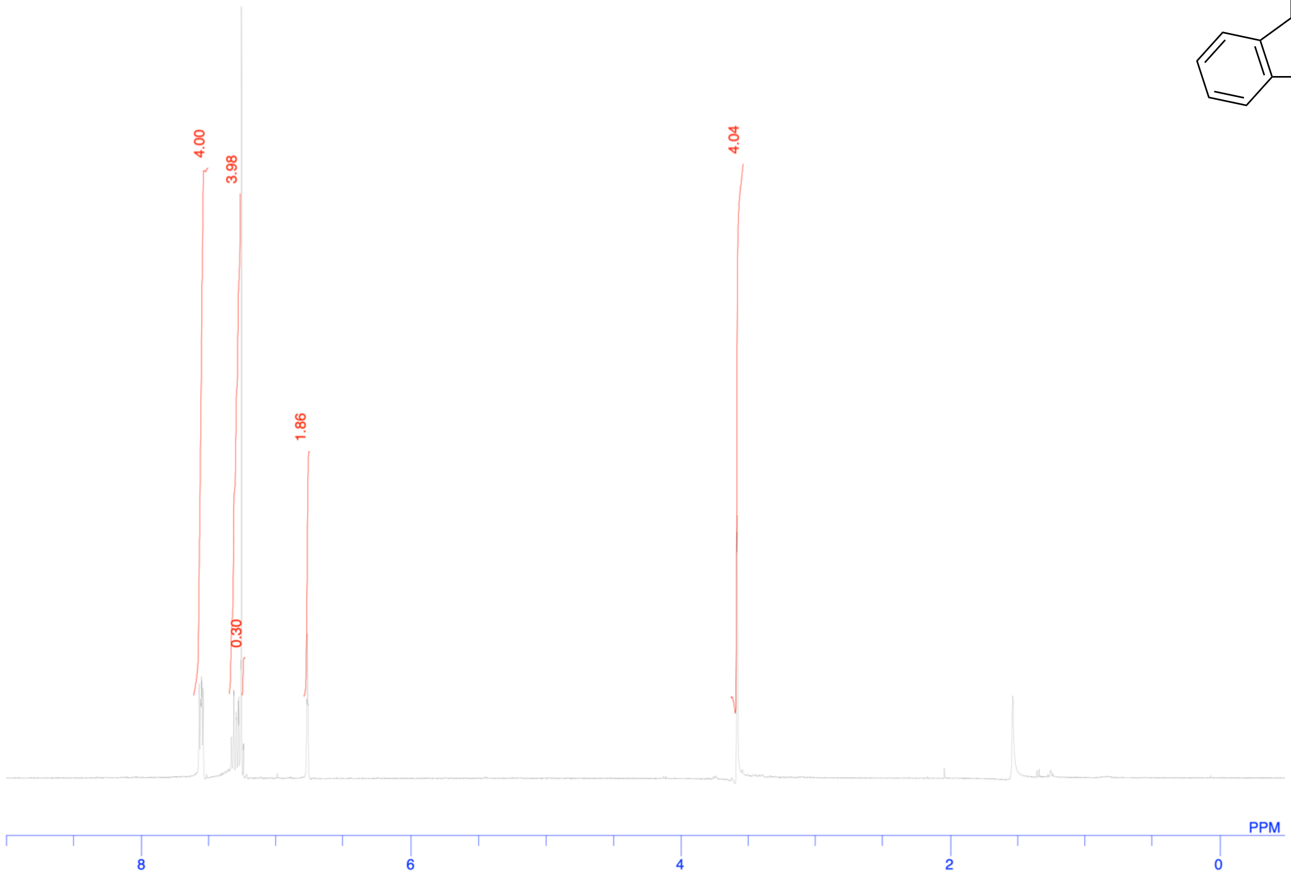
5


Me$_2$
Si
Si
Me$_2$
1.93
4.02
2.05
1.93
3.96
12.10
PPM
8
6
4
2
0


142.931
142.740
134.269
132.529
129.479
127.251
127.118
126.056
77.421
77.000
76.570
13.402
PPM
200
175
150
125
100
75
50
25
0

6a

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0.30
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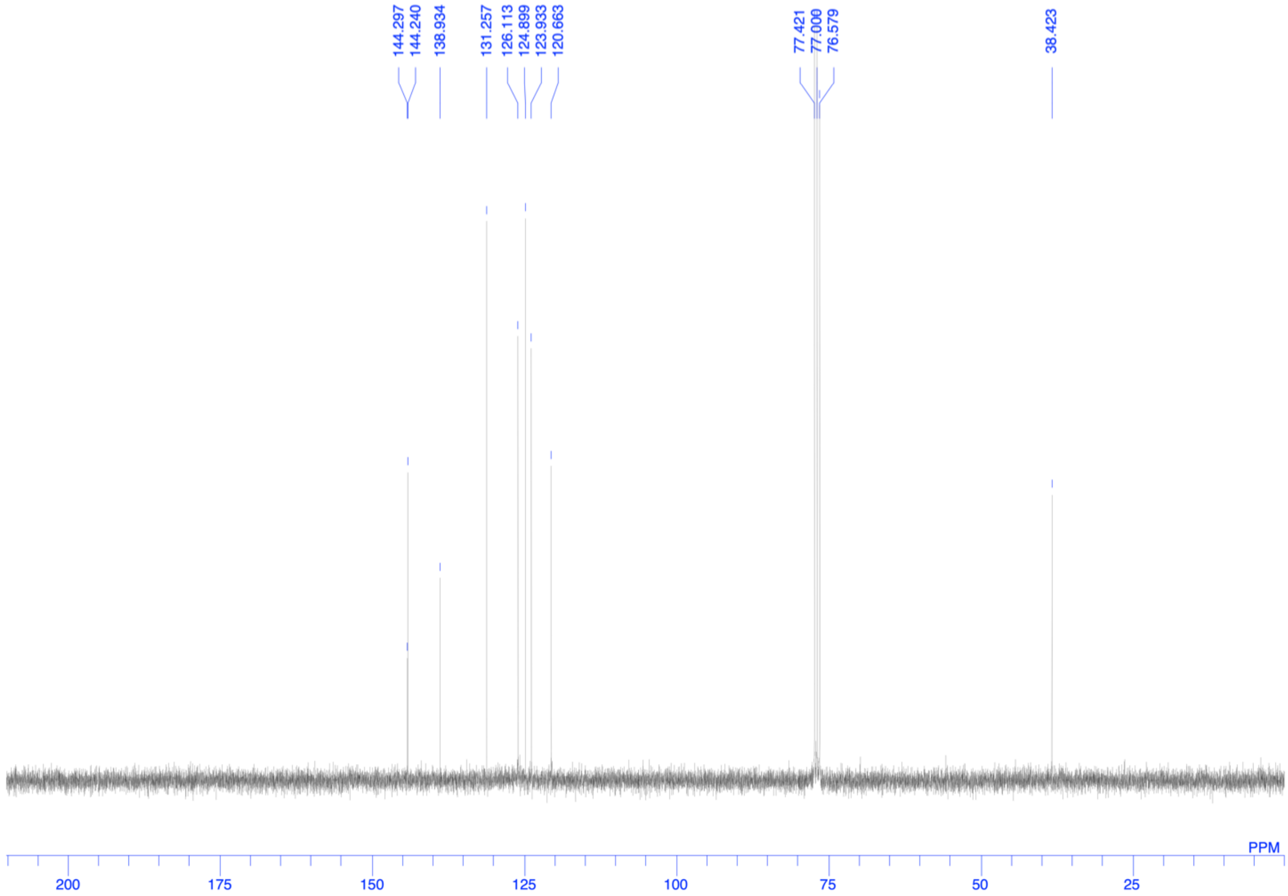
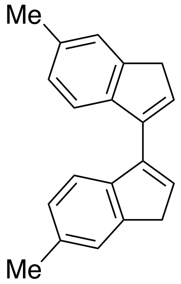
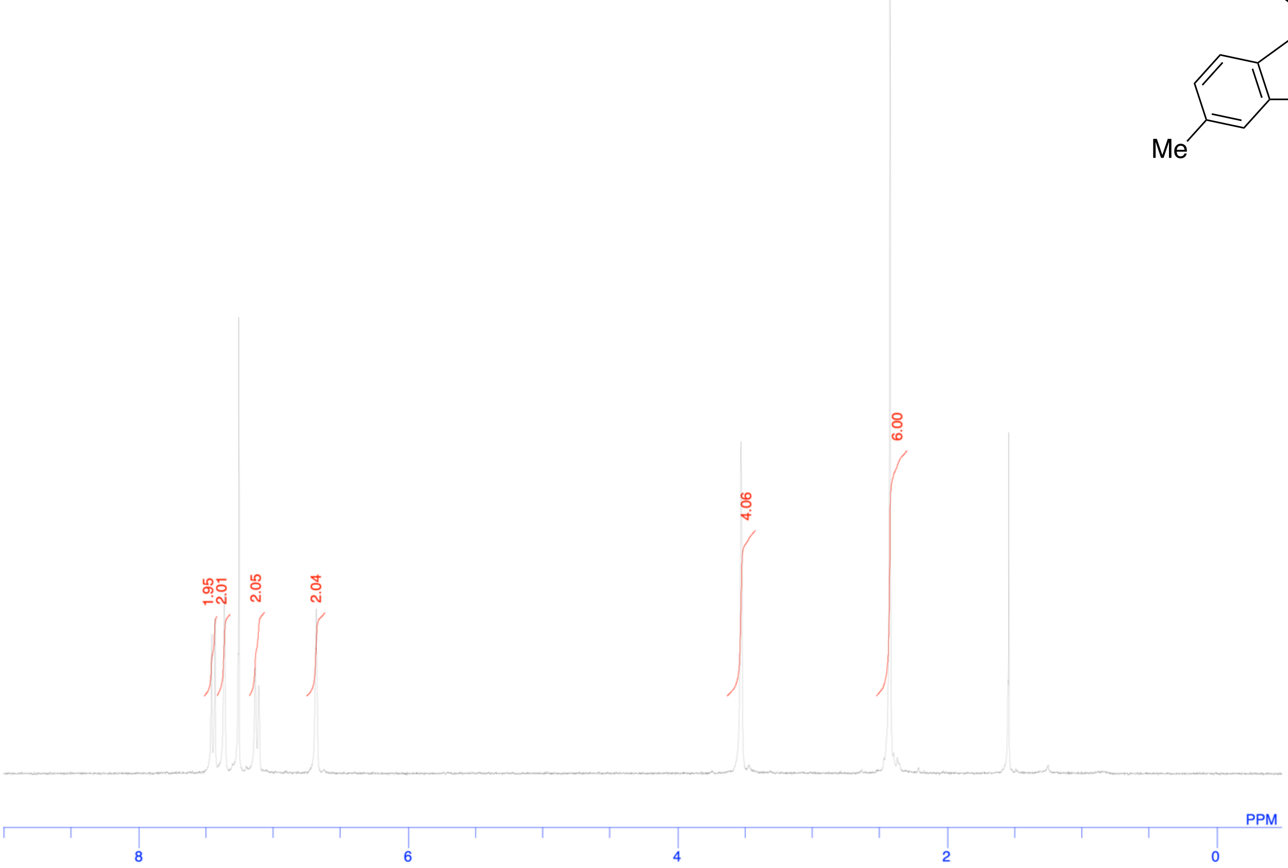
6
4
2
0


144.297
144.240
138.934
131.257
126.113
124.899
123.933
120.663
77.421
77.000
76.579
38.423
PPM
200
175
150
125
100
75
50
25

6b


Me
Me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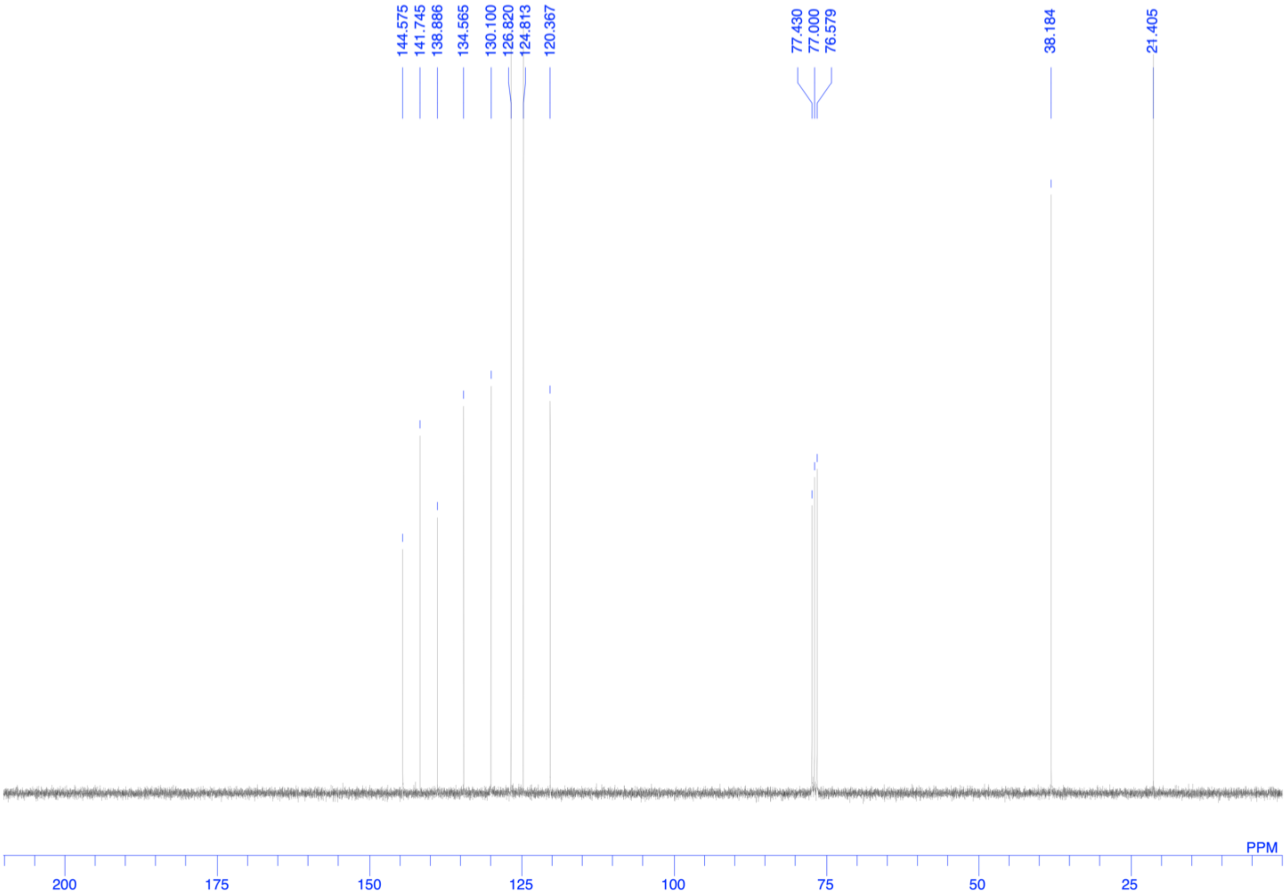
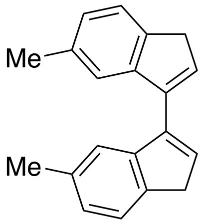
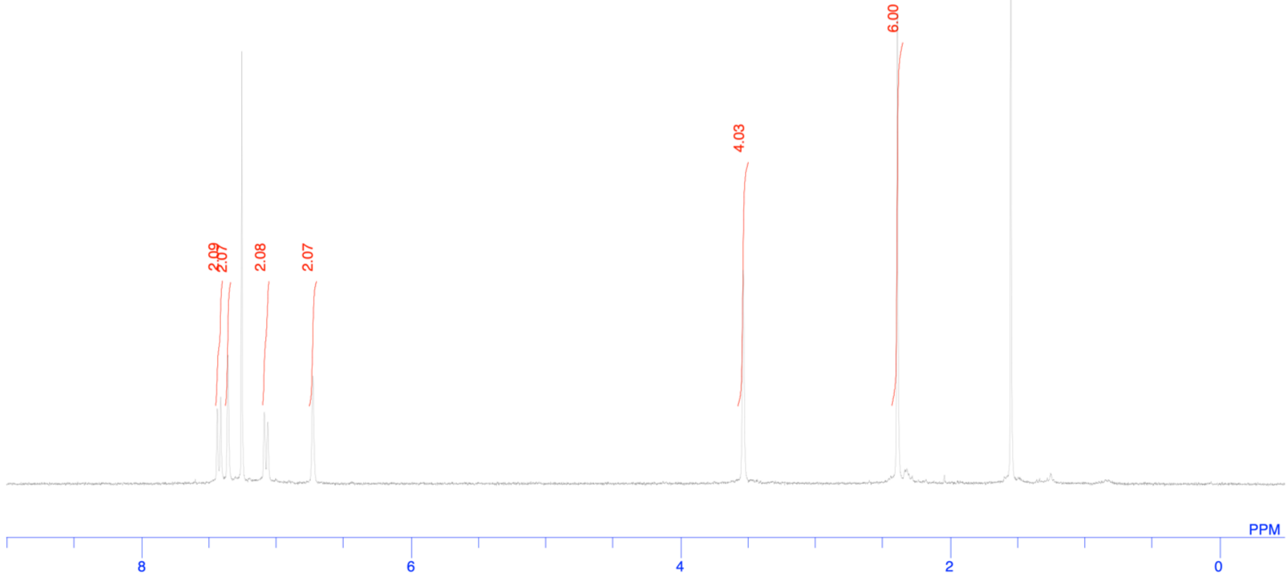
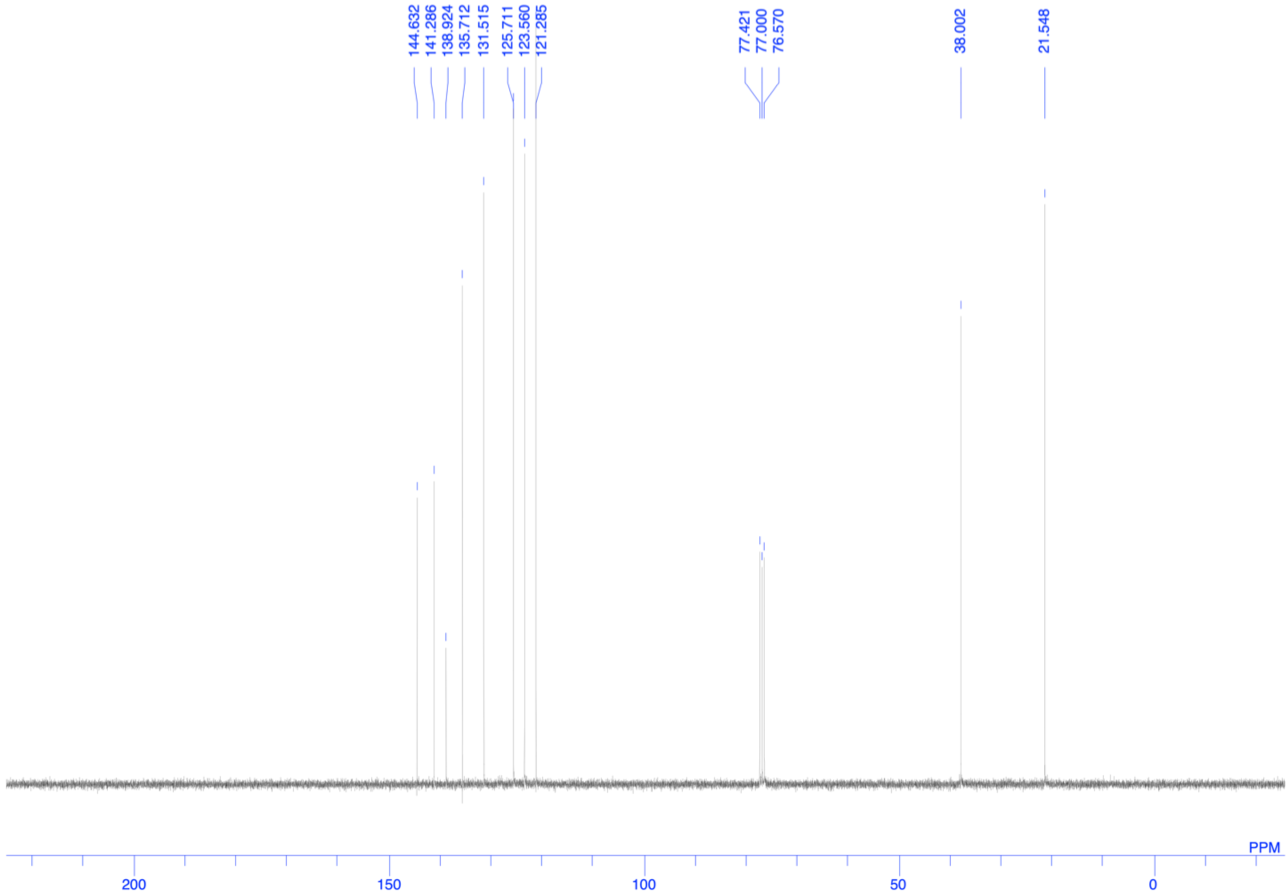
2.01
2.05
2.04
4.06
6.00
PPM
8
6
4
2
0


144.575
141.745
138.886
134.565
130.100
126.820
124.813
120.367
77.430
77.000
76.579
38.184
21.405
PPM
200
175
150
125
100
75
50
25

6c


Me
Me


2.09
2.07
2.08
2.07
4.03
6.00
PPM
8
6
4
2
0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141.286
138.924
135.712
131.515
125.711
123.560
121.285
77.421
77.000
76.570
38.002
21.548
PPM
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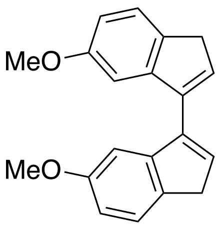
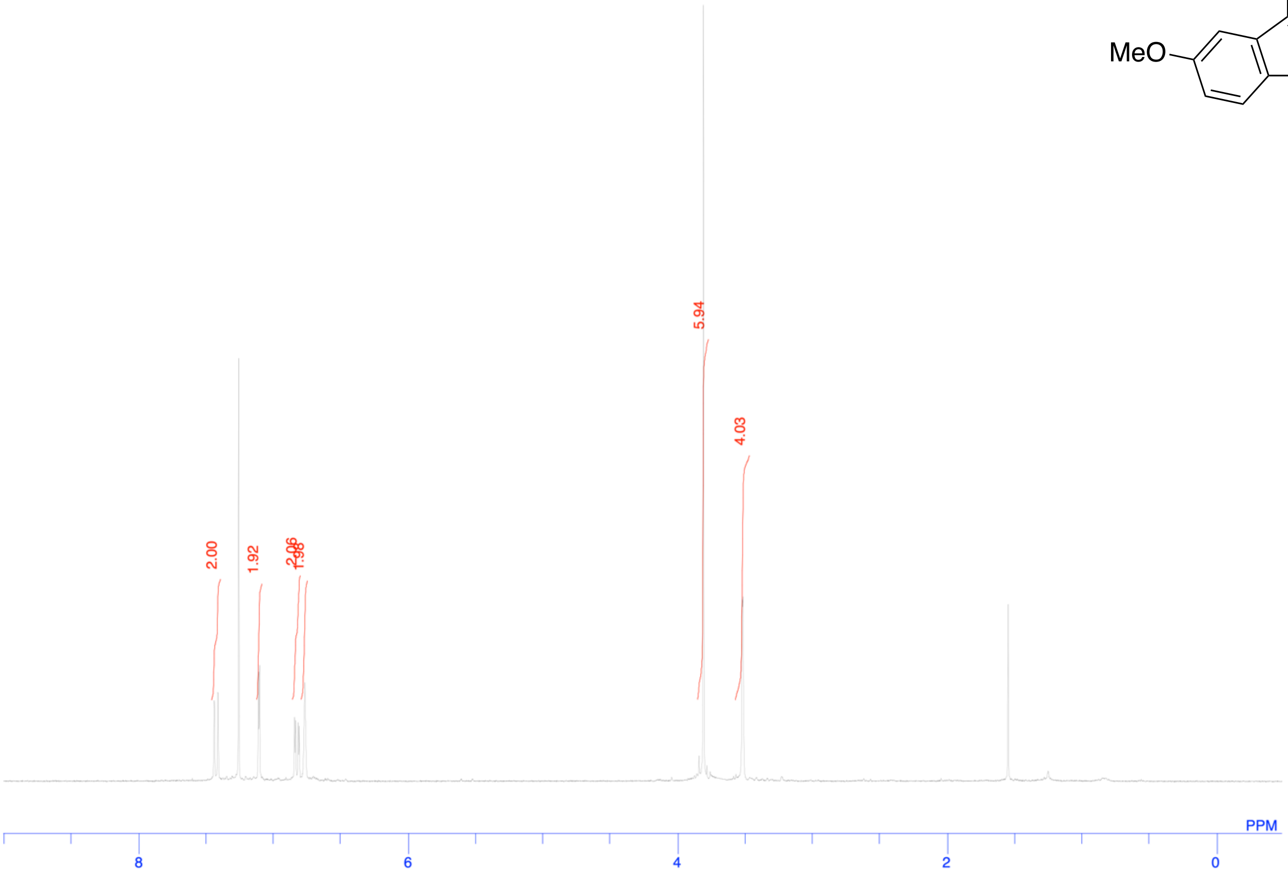
150
100
50
0

6d


MeO
MeO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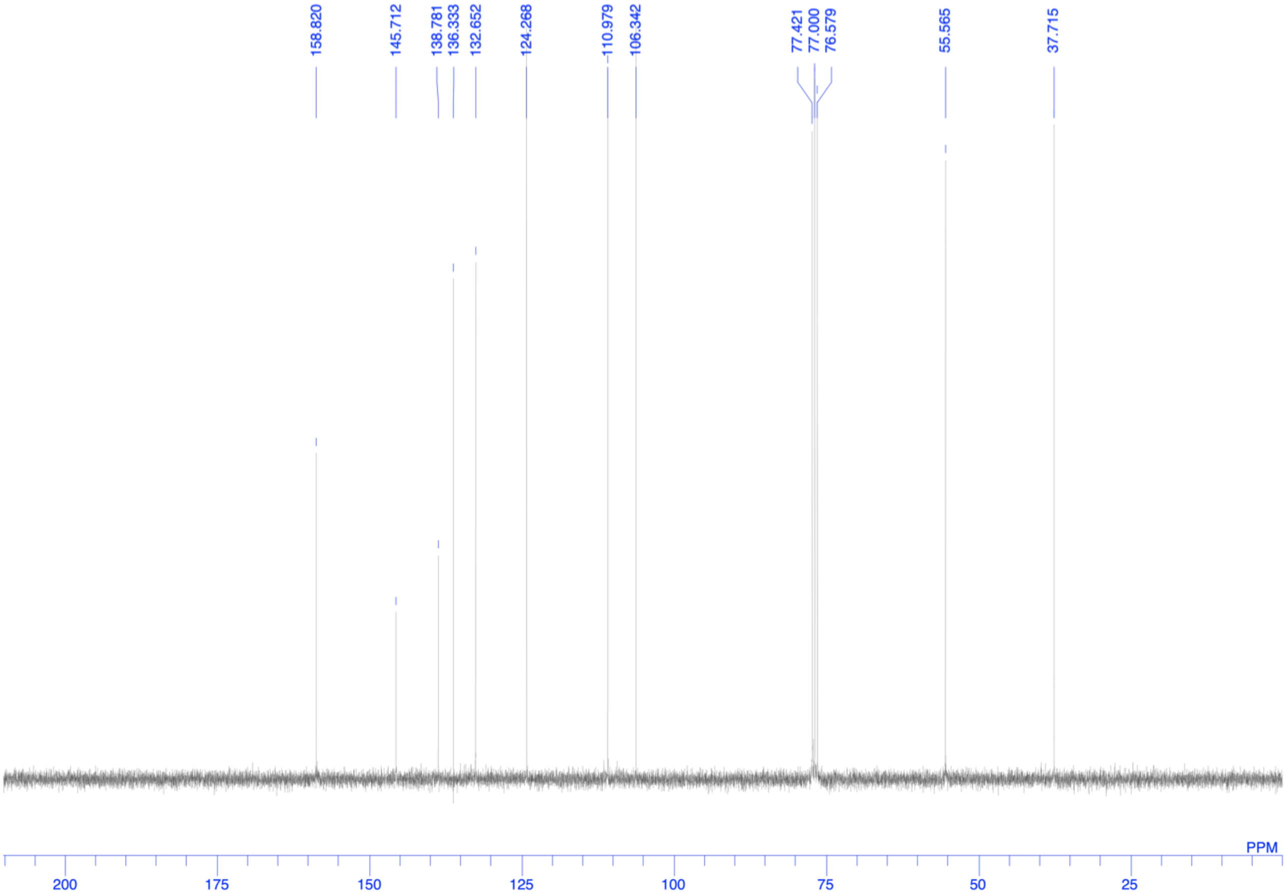
2.06
1.98
5.94
4.03
PPM
8
6
4
2
0


158.820
145.712
138.781
136.333
132.652
124.268
110.979
106.342
77.421
77.000
76.579
55.565
37.715
PPM
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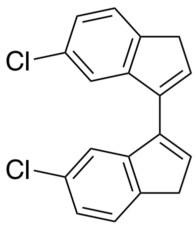
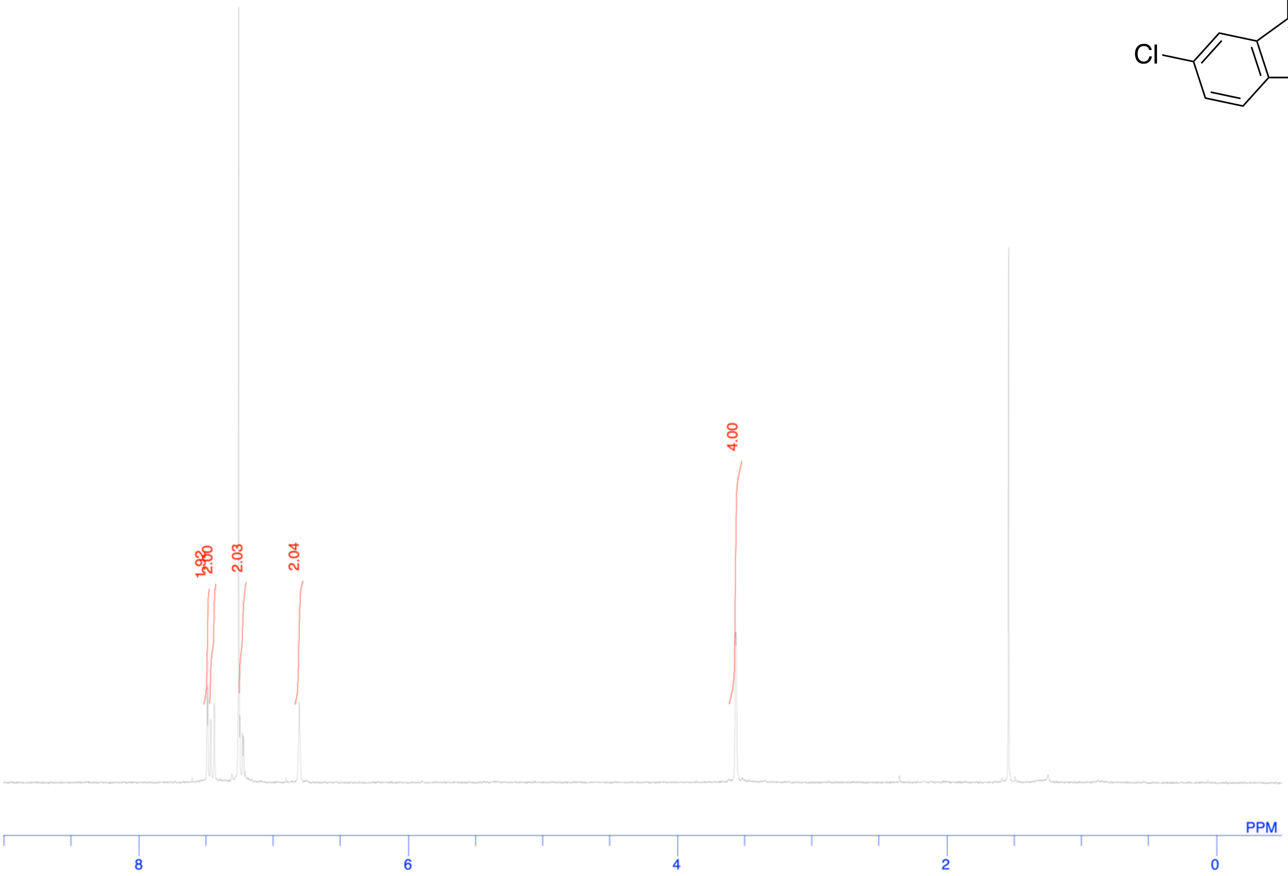
175
150
125
100
75
50
25

6e


Cl
Cl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2.03
2.04
4.00
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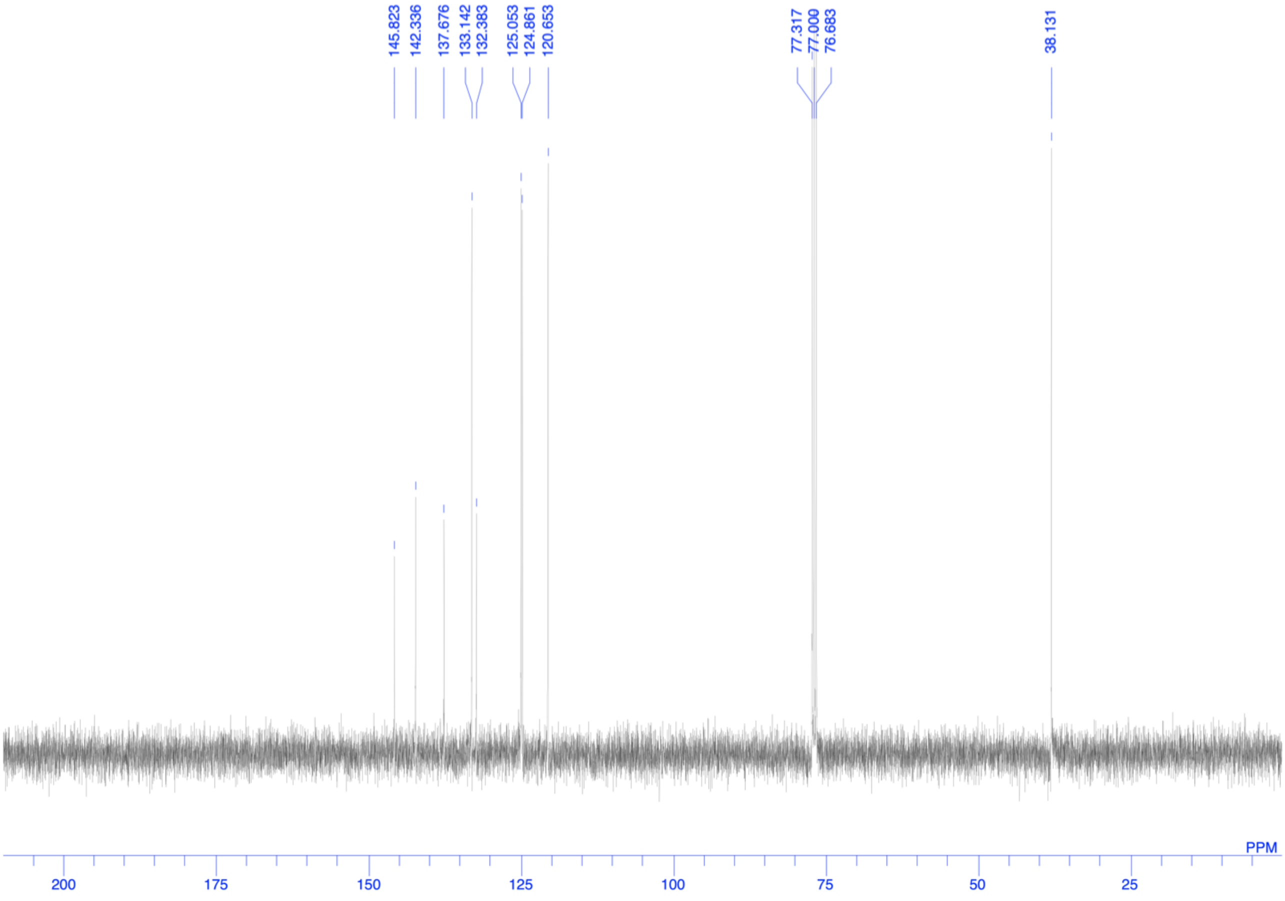
8
6
4
2
0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142.336
137.676
133.142
132.383
125.053
124.861
120.653
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77.000
76.683
38.131
PPM
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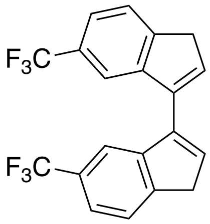
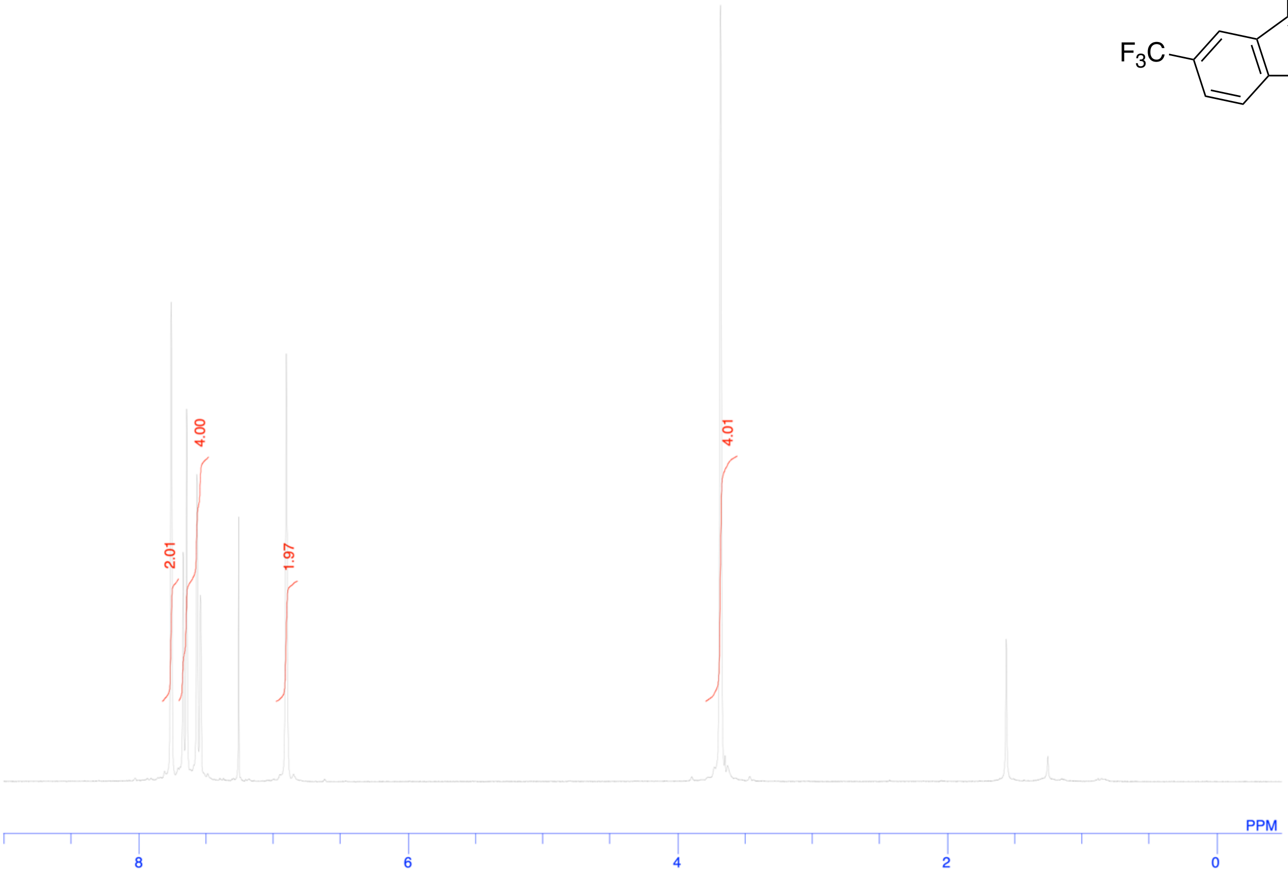
175
150
125
100
75
50
25

6f


F3C
F3C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4.00
1.97
4.01
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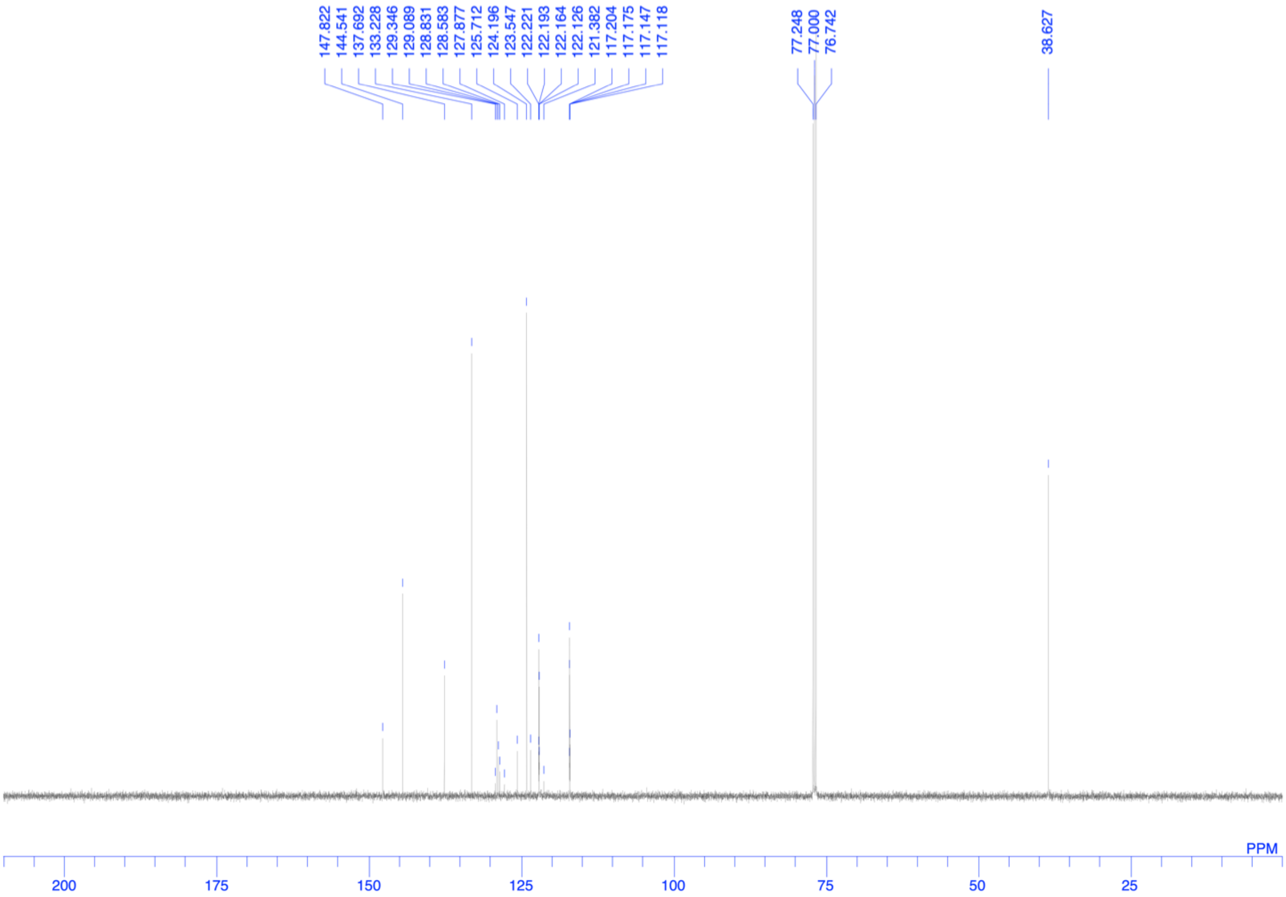
8
6
4
2
0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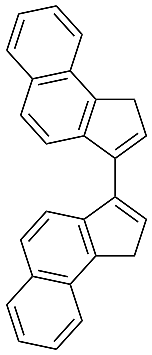
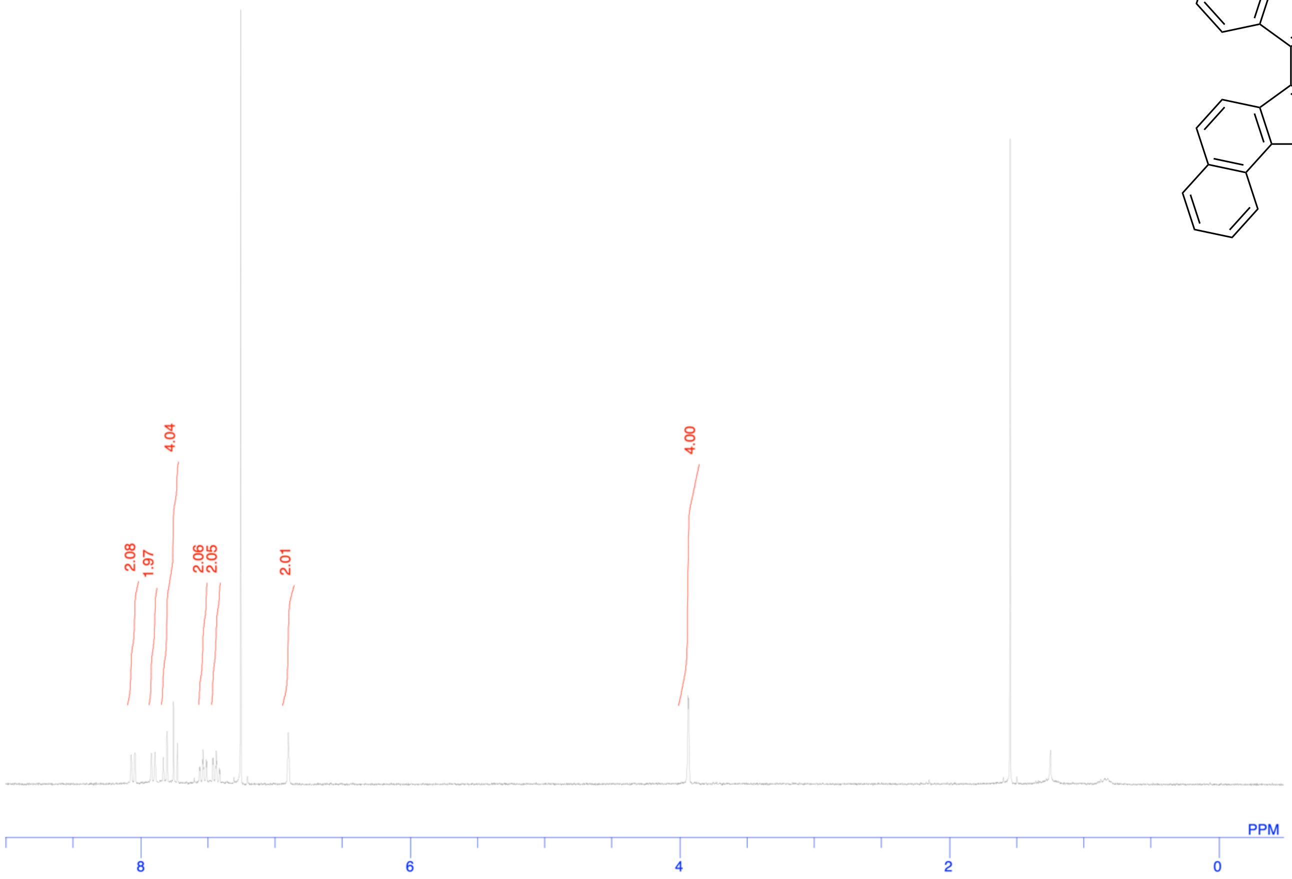
133.228
129.346
129.089
128.831
128.583
127.877
125.712
124.196
123.547
122.221
122.193
122.164
122.126
121.382
117.204
117.175
117.147
117.118
77.248
77.000
76.742
38.627
PPM
200
175
150
125
100
75
50
25

6g

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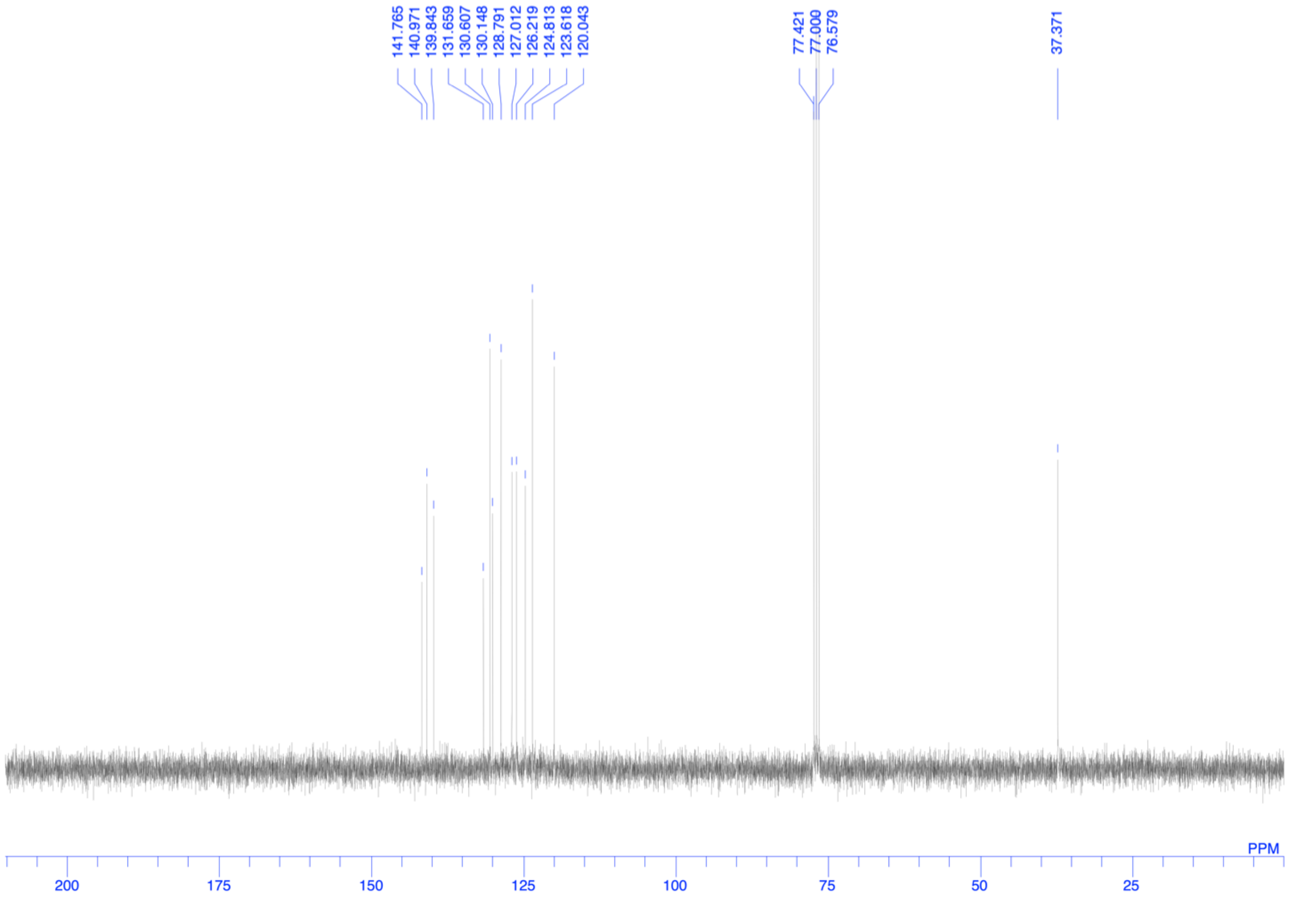
1.97
4.04
2.06
2.05
2.01
4.00
PPM
8
6
4
2
0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140.971
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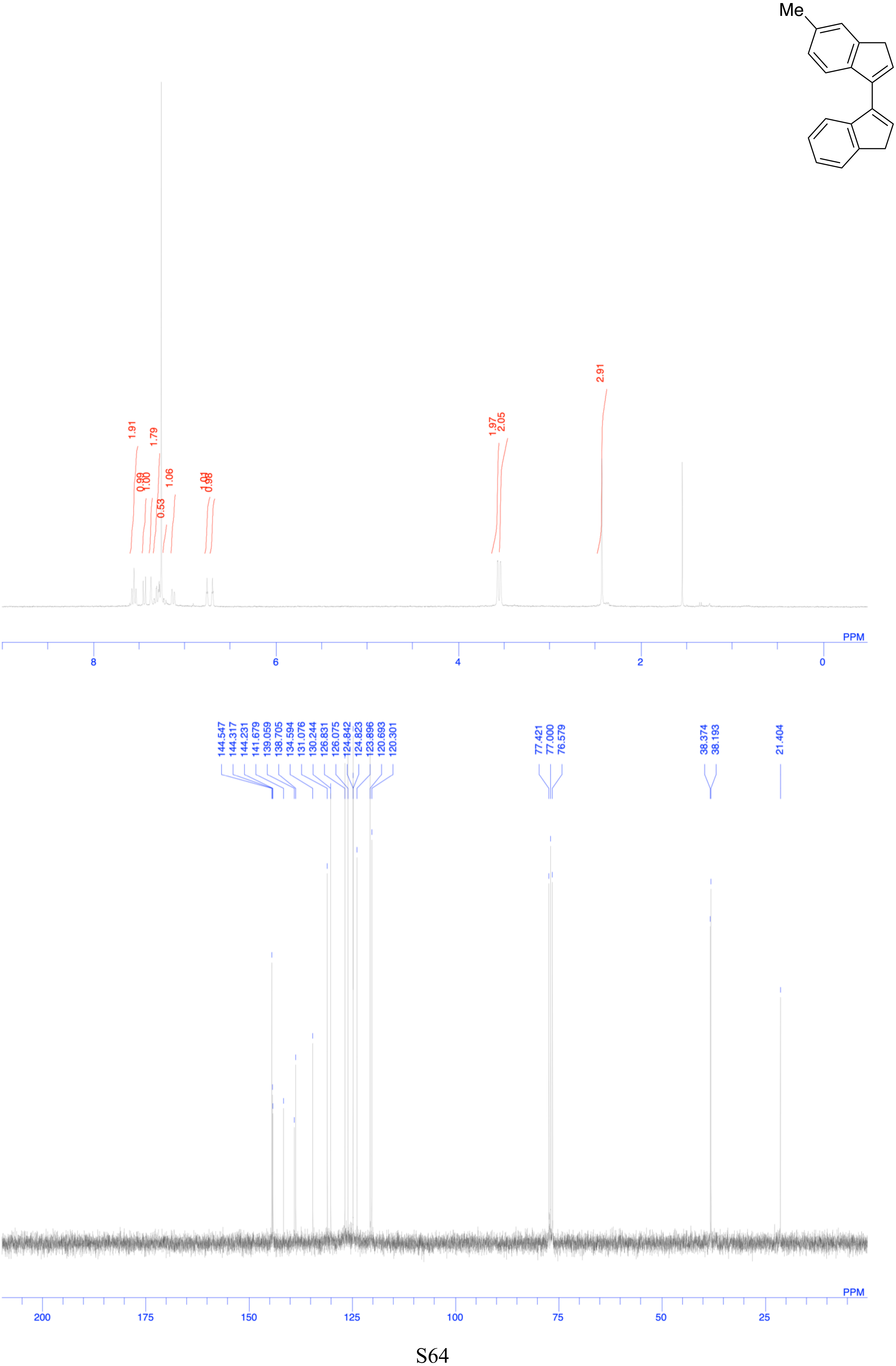
131.659
130.607
130.148
128.791
127.012
126.219
124.813
123.618
120.043
77.421
77.000
76.579
37.371
PPM
200
175
150
125
100
75
50
25

6h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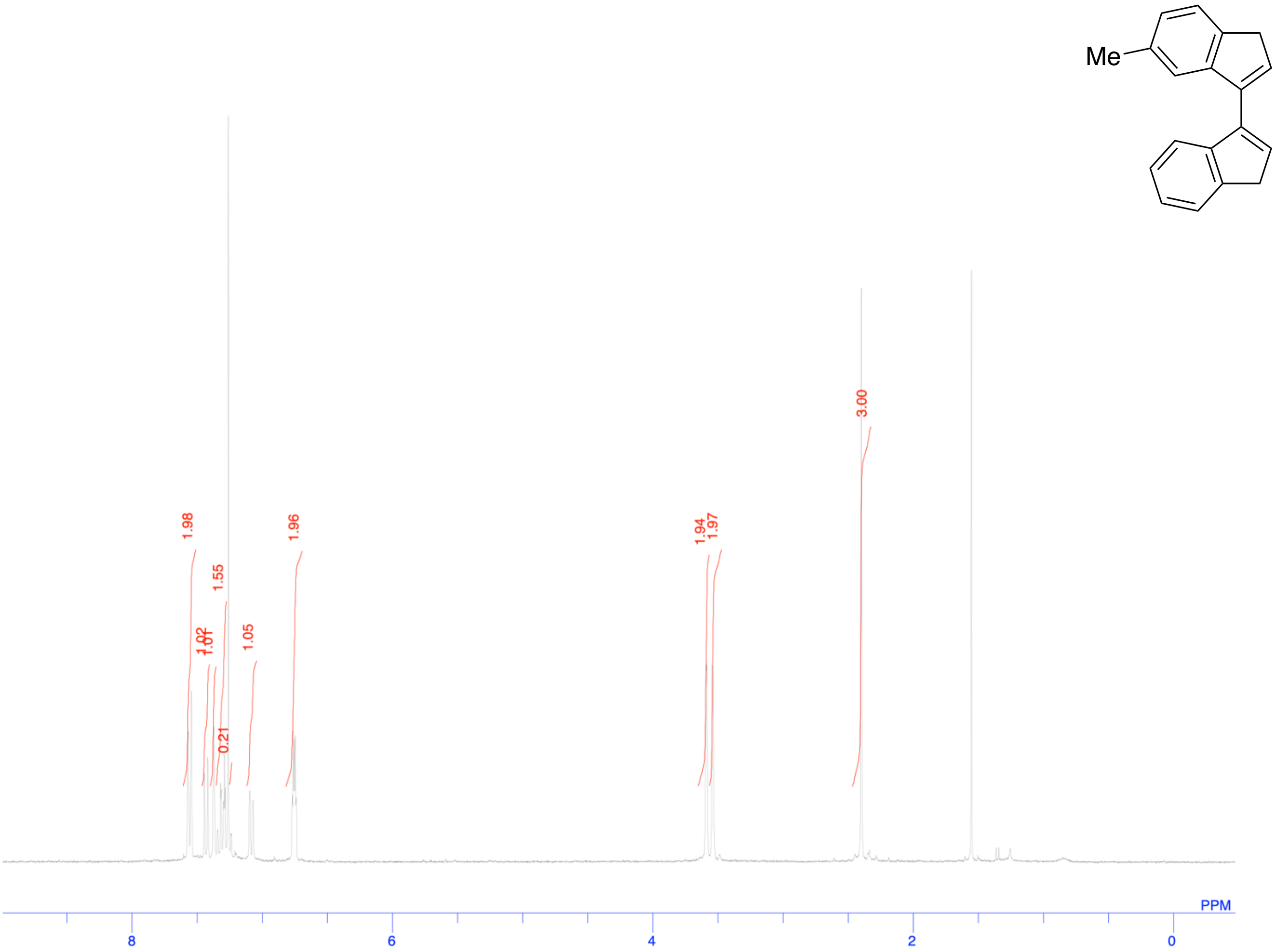
1.00
1.06
0.53
1.01
0.98
1.97
2.05
PPM
8
6
4
2
0
144.547
144.317
144.231
141.679
139.059
138.705
134.594
131.076
130.244
126.831
126.075
124.842
124.823
123.896
120.693
120.301
77.421
77.000
76.579
38.374
38.193
21.404
PPM
200
175
150
125
100
75
50
25

6i


Me
1.98
1.02
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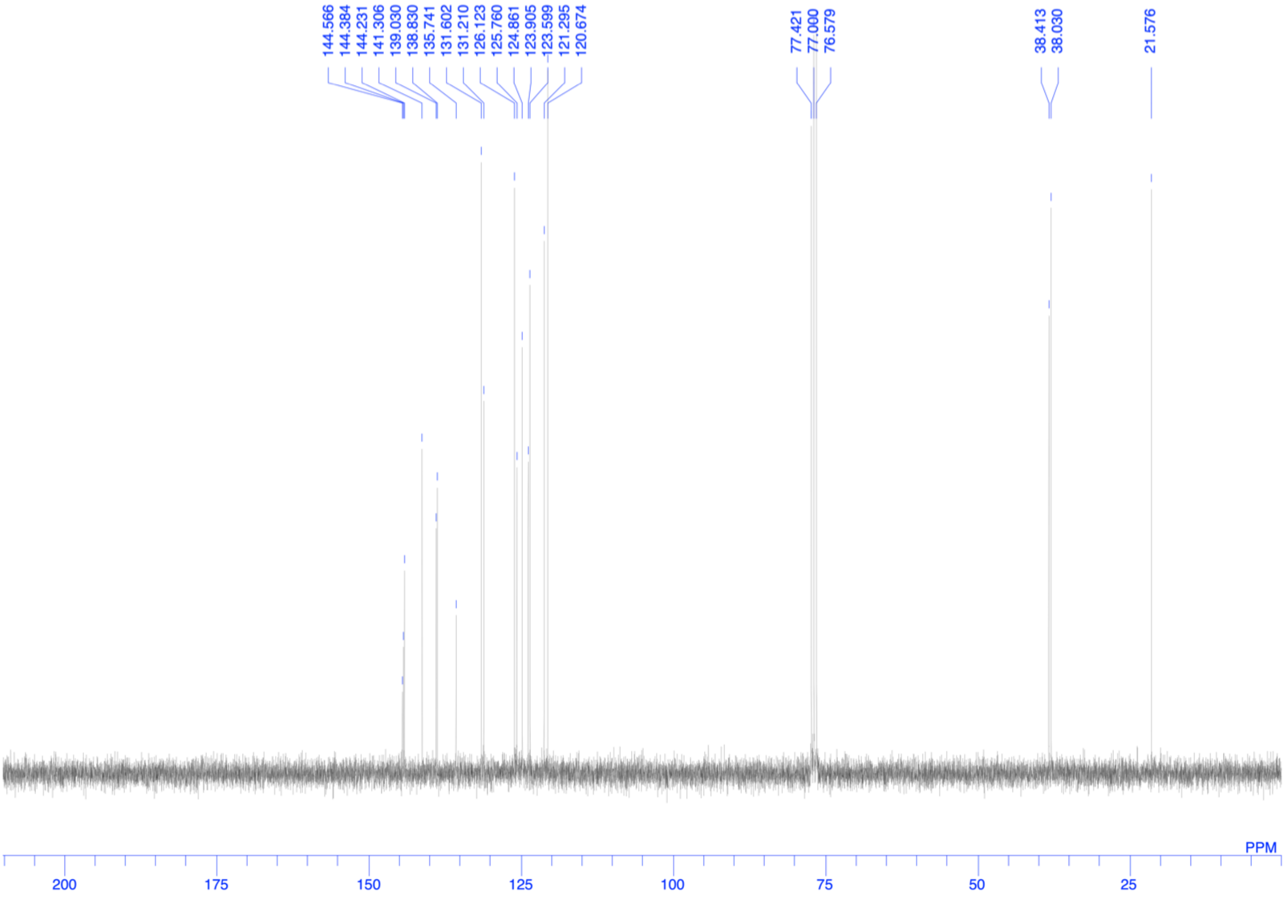
1.55
0.21
1.05
1.96
1.94
1.97
3.00
PPM
8
6
4
2
0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139.030
138.830
135.741
131.602
131.210
126.123
125.760
124.861
123.905
123.599
121.295
120.674
77.421
77.000
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38.030
21.576
PPM
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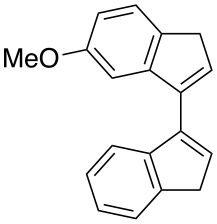
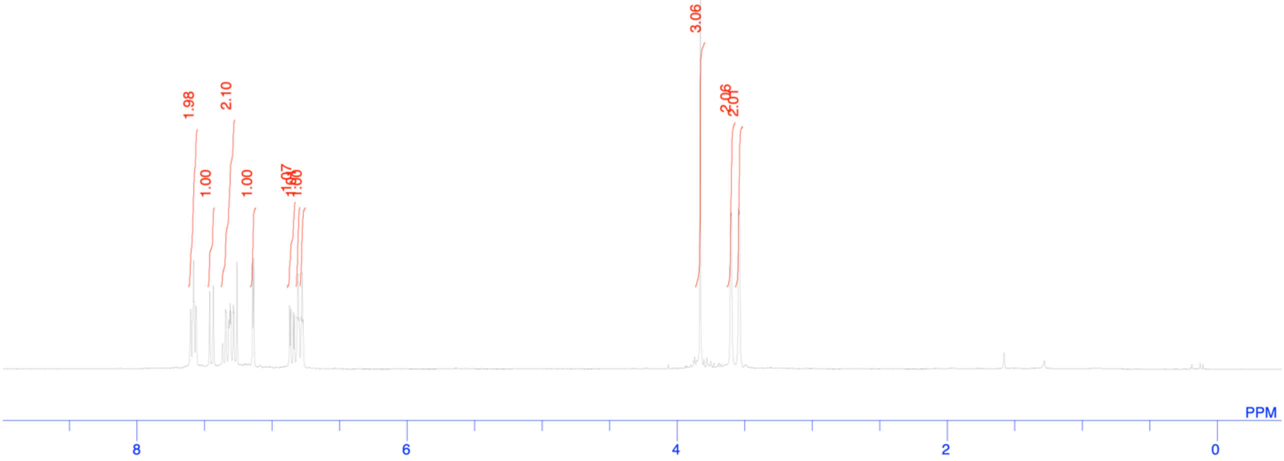
150
125
100
75
50
25

6j


MeO


1.98
1.00
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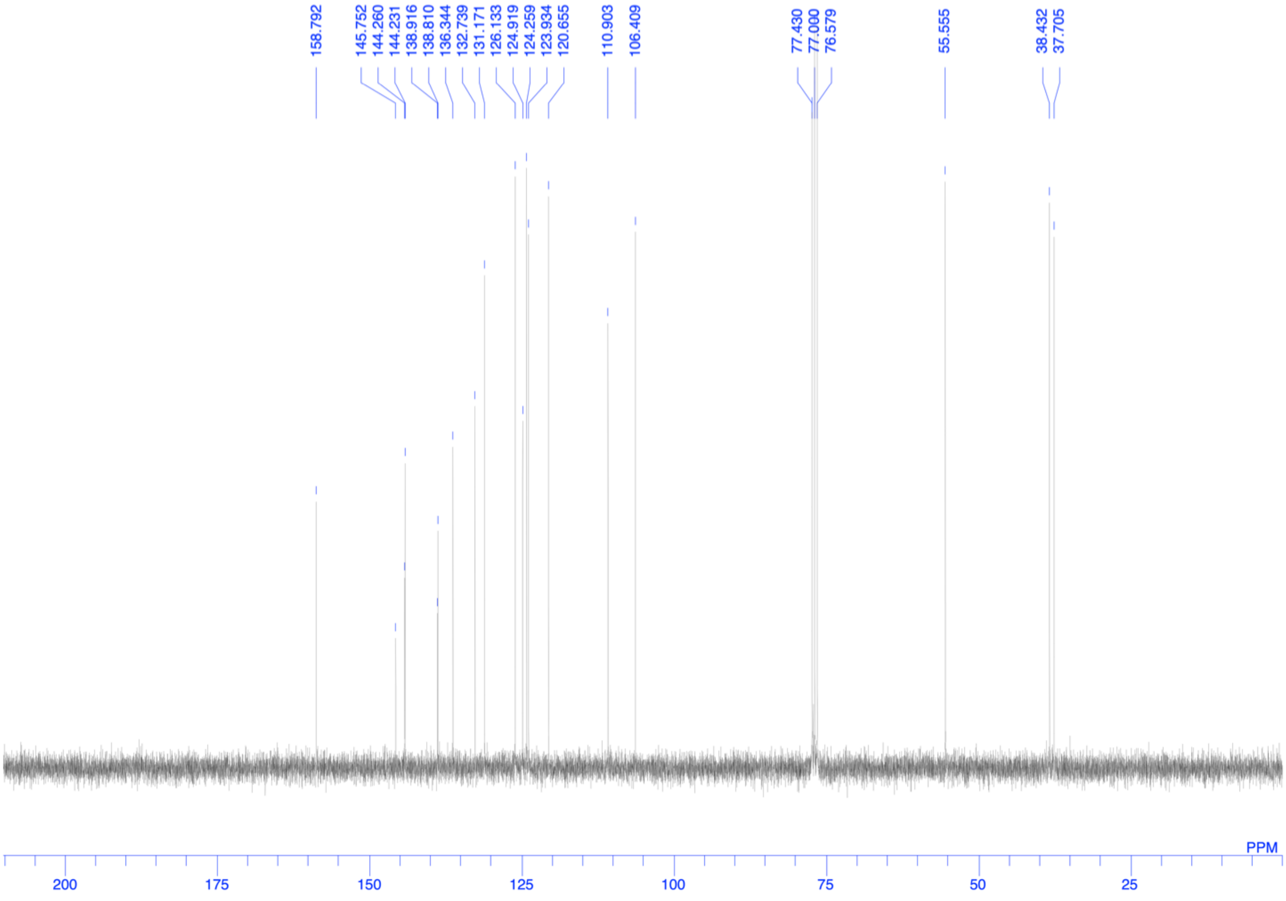
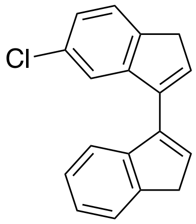
1.07
1.00
1.00
3.06
2.06
2.01
PPM
8
6
4
2
0


158.792
145.752
144.260
144.231
138.916
138.810
136.344
132.739
131.171
126.133
124.919
124.259
123.934
120.655
110.903
106.409
77.430
77.000
76.579
55.555
38.432
37.705
PPM
200
175
150
125
100
75
50
25

6k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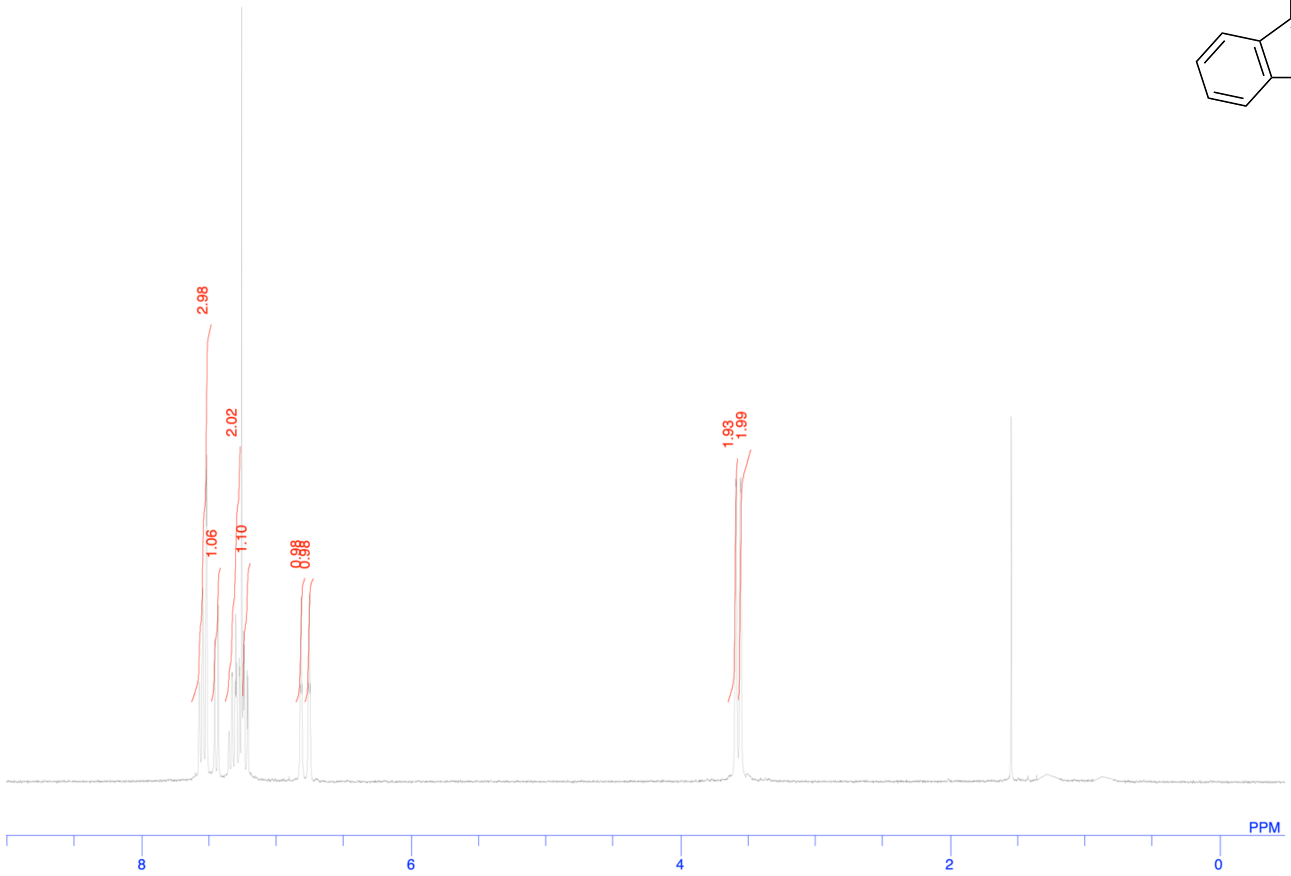
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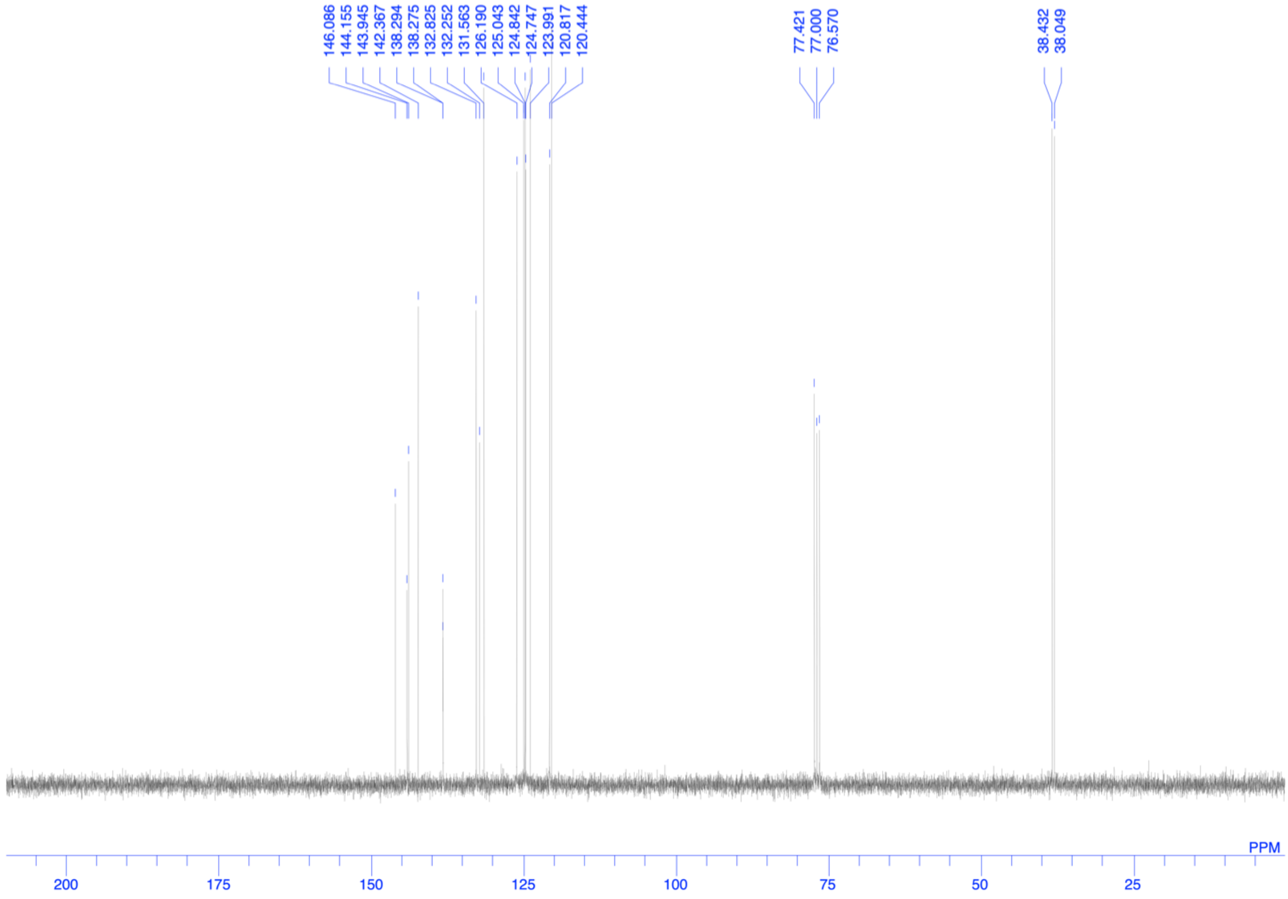
2.02
1.10
0.98
0.98
1.93
1.99
PPM
8
6
4
2
0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132.252
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124.747
123.991
120.817
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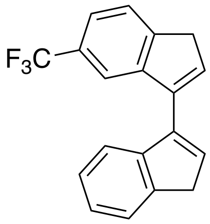
PPM
200
175
150
125
100
75
50
25

6l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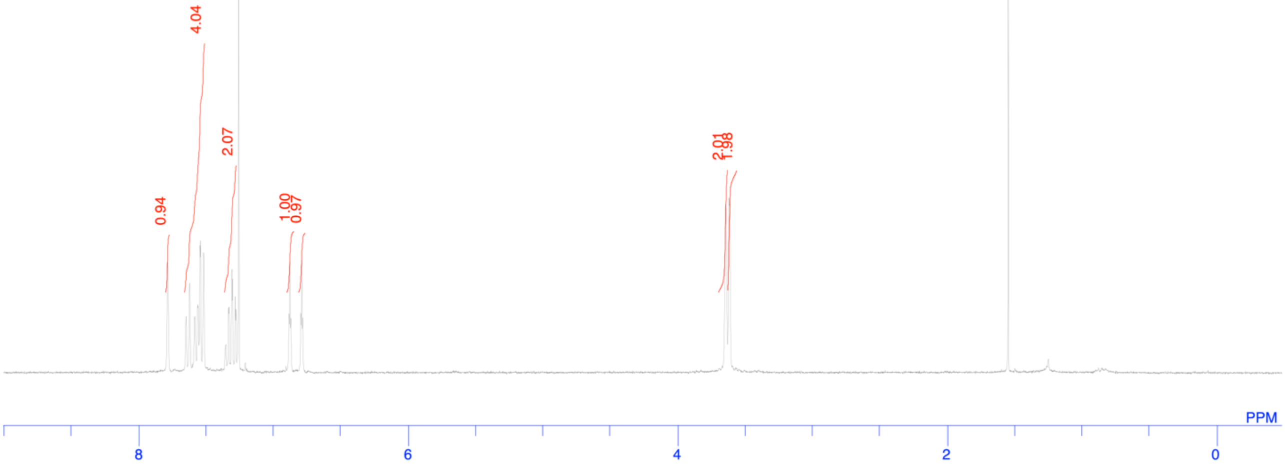
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1.98
PPM
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2
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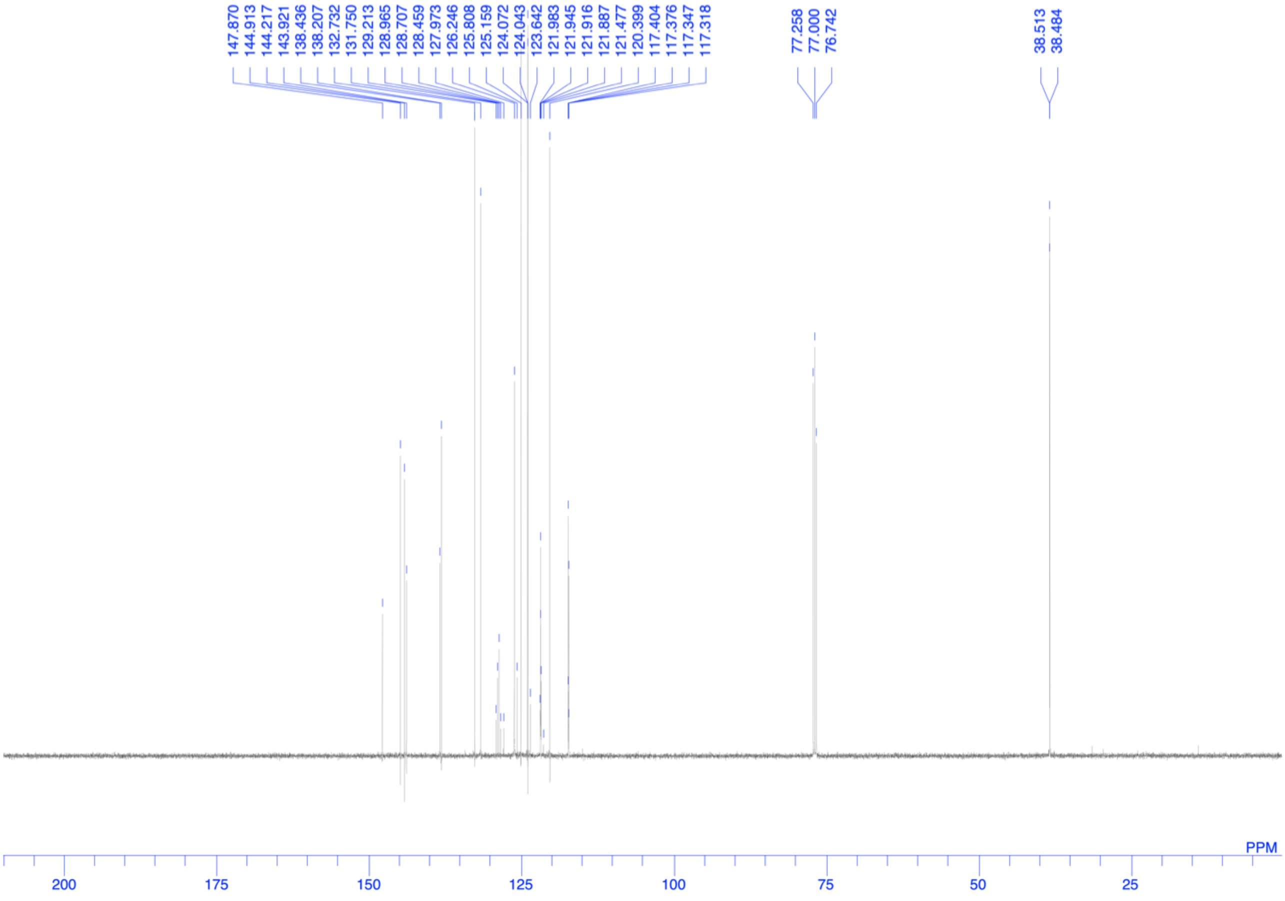
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126.246
125.808
125.159
124.072
124.043
123.642
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121.945
121.916
121.887
121.477
120.399
117.404
117.376
117.347
117.318
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76.742
38.513
38.484
PPM
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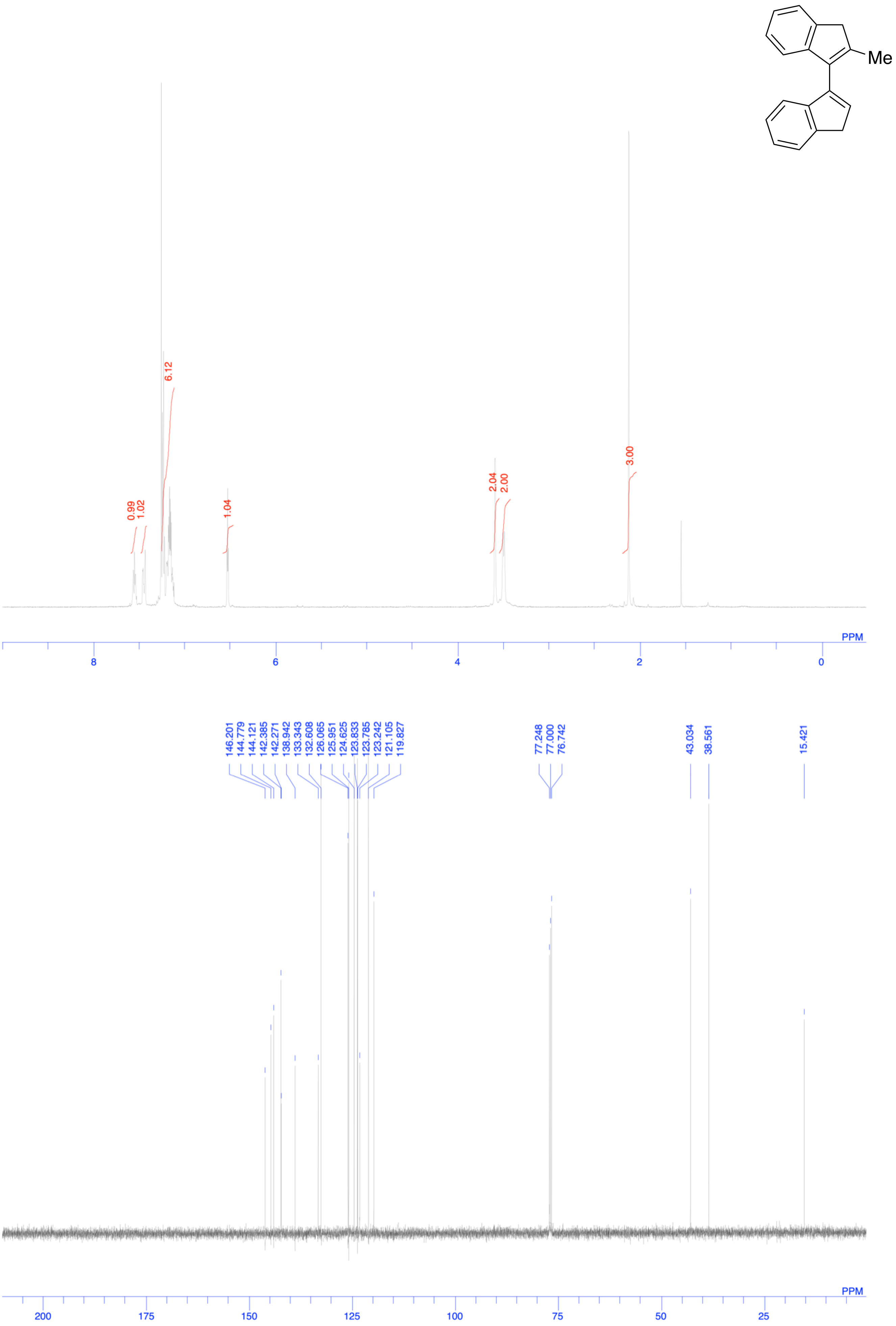
175
150
125
100
75
50
25

6o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2.04
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3.00
PPM
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6
4
2
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144.779
144.121
142.385
142.271
138.942
133.343
132.608
126.065
125.951
124.625
123.833
123.785
123.242
121.105
119.827
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77.000
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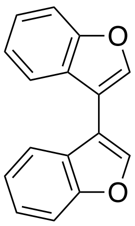
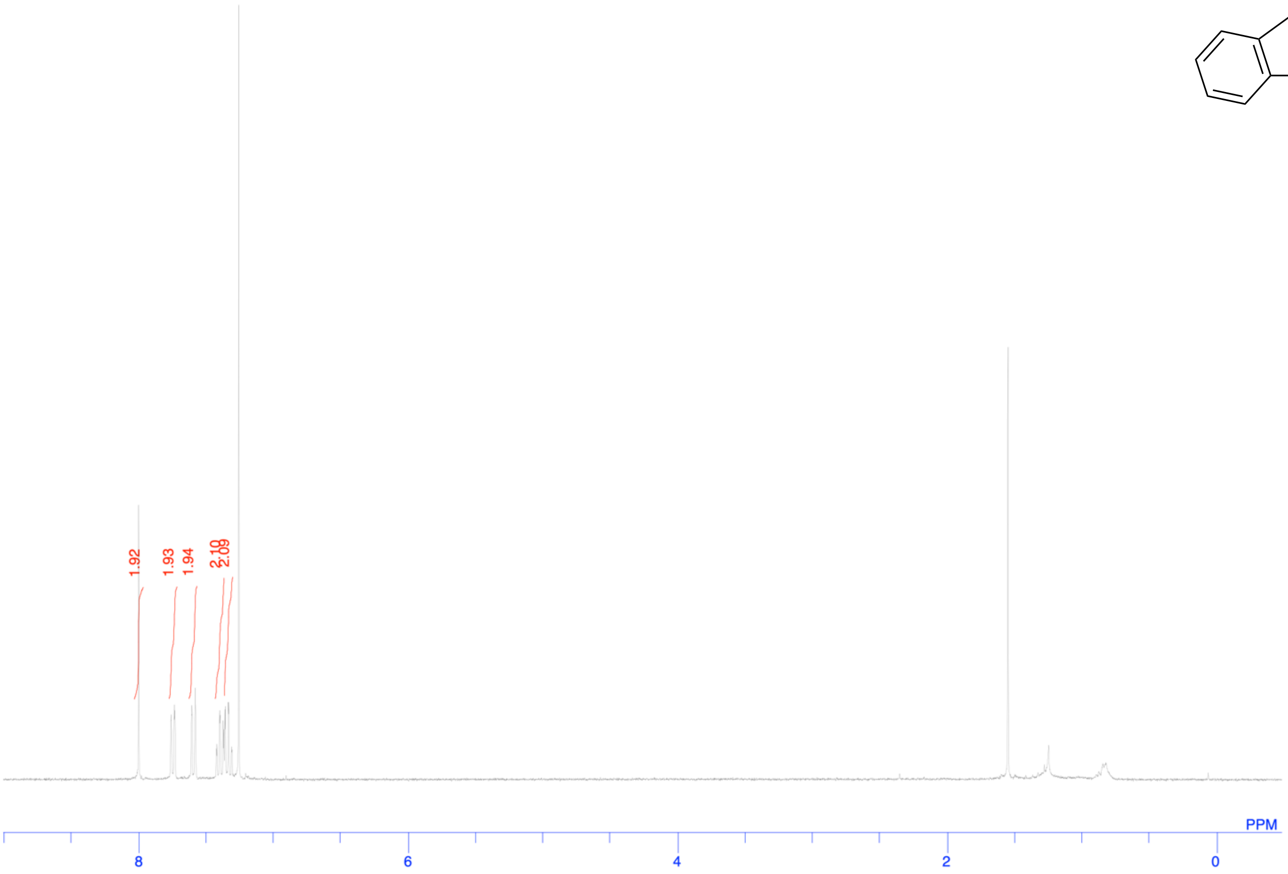
43.034
38.561
15.421
PPM
200
175
150
125
100
75
50
25

6p

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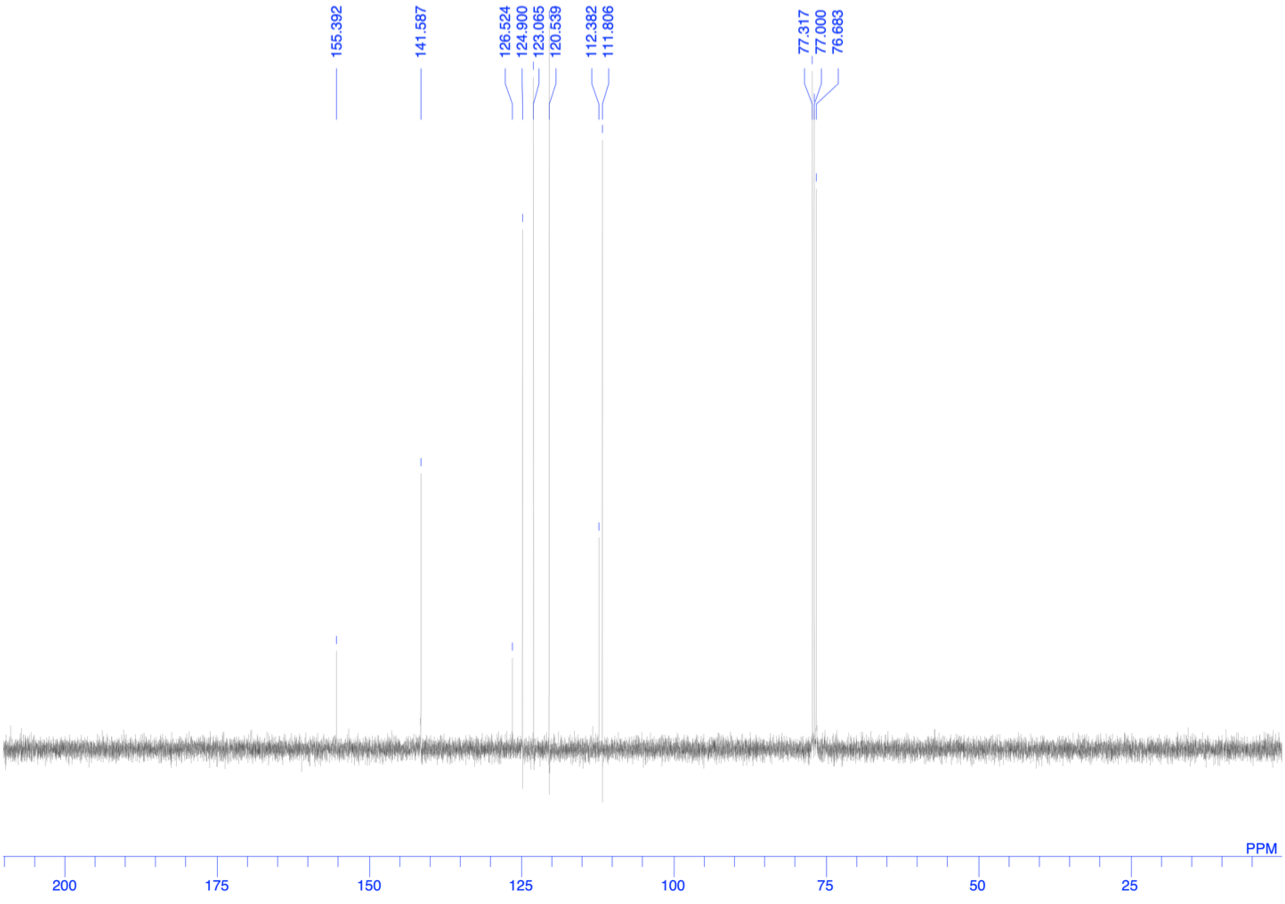
1.93
1.94
2.10
2.09
PPM
8
6
4
2
0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124.900
123.065
120.539
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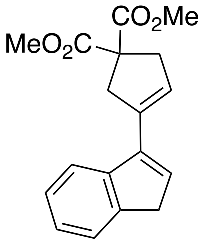
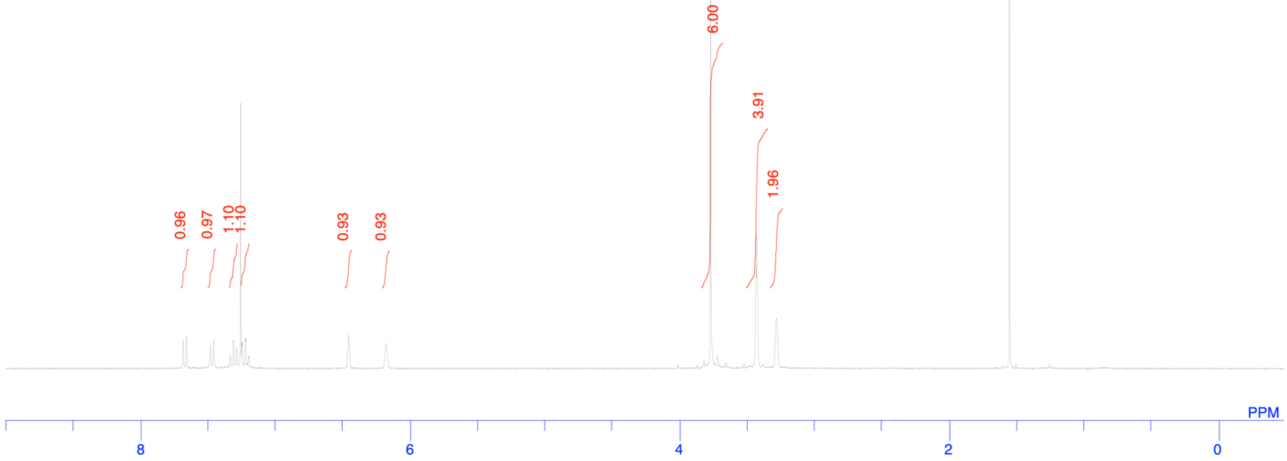
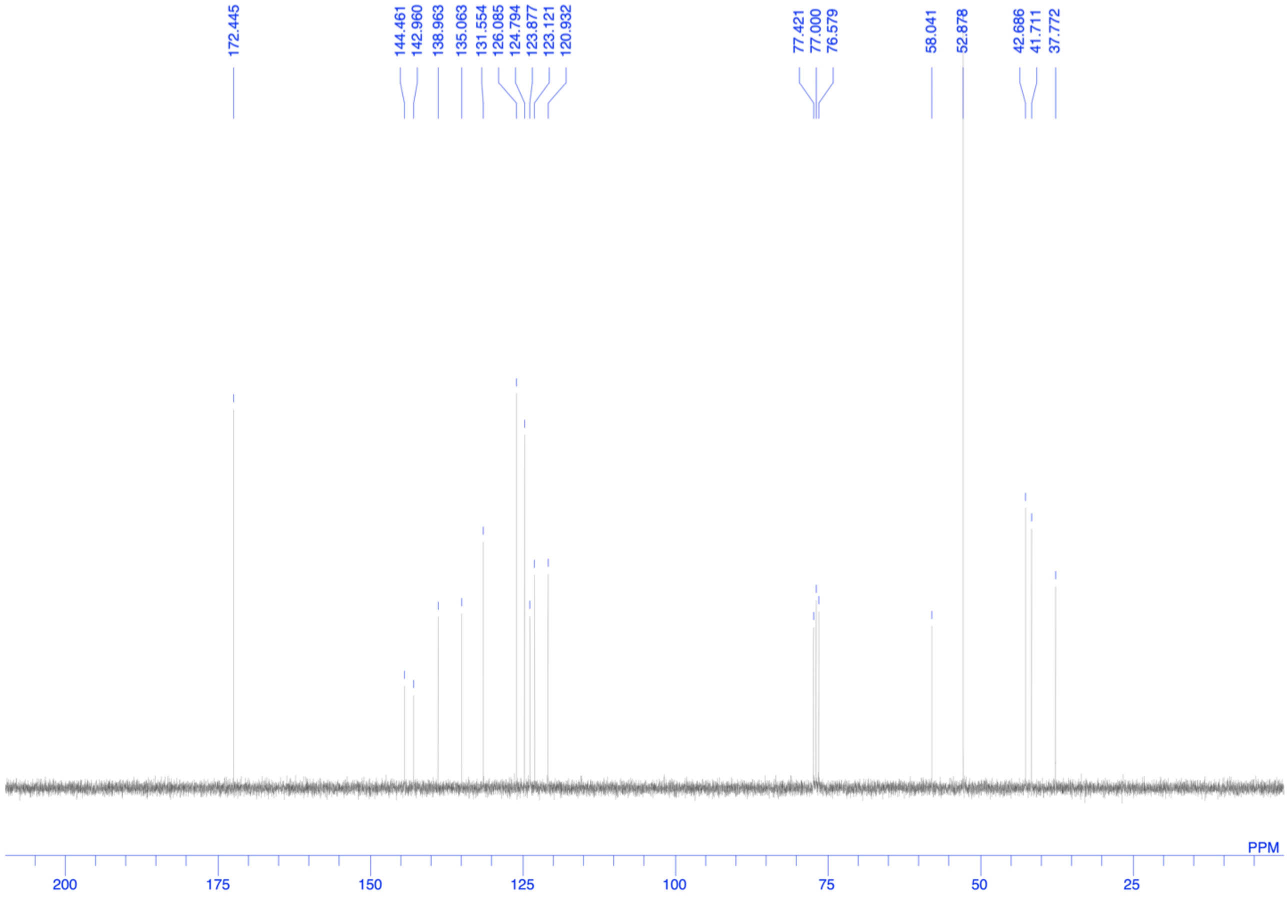
77.317
77.000
76.683
PPM
200
175
150
125
100
75
50
25

6q


CO2Me
MeO2C


0.96
0.97
1.10
1.10
0.93
0.93
6.00
3.91
1.96
PPM
8
6
4
2
0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138.963
135.063
131.554
126.085
124.794
123.877
123.121
120.932
77.421
77.000
76.579
58.041
52.878
42.686
41.711
37.772
PPM
200
175
150
125
100
75
50
25