

Pd@GO catalyzed stereo- and regio-selective addition of arenes to alkynes and synthesis of coumarins via C-H functionalization

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General Information

All necessary chemicals were purchased from Sigma-Aldrich, Spectrochem, and TCI and utilized without further purification. Infrared (IR) spectra were recorded on a Spectrum BX Fourier transform infrared (FT-IR) instrument (PerkinElmer) (ν_{\max} in cm^{-1}) on KBr disks. ^1H and ^{13}C NMR (400 and 100 MHz, respectively) spectra were recorded on a Bruker Avance II-400 spectrometer in CDCl_3 (chemical shifts in δ with TMS as internal standard). Mass spectra were recorded on a Waters Xevo-G2-XS QT of Mass Spectrometer. Transmission electron microscopy (TEM) images were recorded on a JEOL JSM 100CX instrument. Scanning electron microscopy (SEM) images and Energy Dispersive X-ray (EDX) were recorded on a JSM-6360 instrument (JEOL). Powder XRD was recorded on a Bruker D8 Advance XRD Instrument SWAX. Thermogravimetric Analysis (TGA) was recorded on a Perkin Elmer Precisely STA 6000 simultaneous thermal analyzer. XPS analysis was carried out on an Escalab Xi+ XPS Instrument. Silica gel (E-Merck, 100-200 mesh) was used for column chromatography. Hexane refers to the fraction boiling between 60 °C and 80 °C.

Preparation of Pd@GO

Synthesis of GO: Graphite oxide was first prepared according to the modified Hummer's method^{1,2}. 1 g of graphite powder was added to 20 mL of conc. H_2SO_4 in an ice bath. Then, 500 mg of NaNO_3 was added to the mixture, followed by 4 g of KMnO_4 in portions over an hour. The solution was then allowed to stir for another one hour. After that, it was heated to 45 °C and allowed to stir for another period of an hour. The solution was turned viscous at this point. Then, 50 mL of water was added and stirred for another 30 min, followed by the addition of 150 mL of water. Hydrogen peroxide (H_2O_2 30 %) was then slowly added until the solution turned yellowish green. Then the solution was centrifuged, filtered, and washed with water, ethanol, and diethyl ether and finally dried.

Synthesis of Pd@GO³: 600 mg of graphite oxide was mixed with 100 mg of palladium acetate in a 250 mL round bottom flask. The mixture was then kept under a vacuum for 1 h. Then, under a N_2 atmosphere, 100 mL of dry toluene was added, and it was sonicated at room temperature for 1h. Then, the mixture was heated at 100 °C under a N_2 atmosphere for 4h. It was cooled to room temperature (20 °C), centrifuged and filtered. The residue was washed sufficiently with ethanol, acetone, and finally diethyl ether, and dried.

General procedure for the C-H functionalization of arenes:

Arenes (**1a-1e**, 2 mmol) or phenols (**4a-4j**, 2 mmol), alkynes (**2a-2e**, 1 mmol), and Pd@GO (2.3 mol %, 15 mg) were taken in a 25 mL round bottom flask. TFA/DCM (1:1, 2 mL) was added to it, and the reaction mixture was stirred at room temperature for the time mentioned in Tables 3 and 5. After that, the reaction mixture was neutralised with a saturated NaHCO₃ solution. The catalyst was separated by centrifugation followed by filtration. The recovered catalyst was washed with water, ethanol, and diethyl ether, and dried. This purified catalyst was used in another set of reactions. The products were extracted from filtrate with CHCl₃ (3 X 10 mL). The organic layer was then washed with water (3 X10 mL), brine (1 X10 mL) and dried over anhydrous Na₂SO₄. The organic solvent was removed under reduced pressure and the crude reaction mass was purified by column chromatography using ethyl acetate/ hexane as the eluent.

Characterization of the catalyst

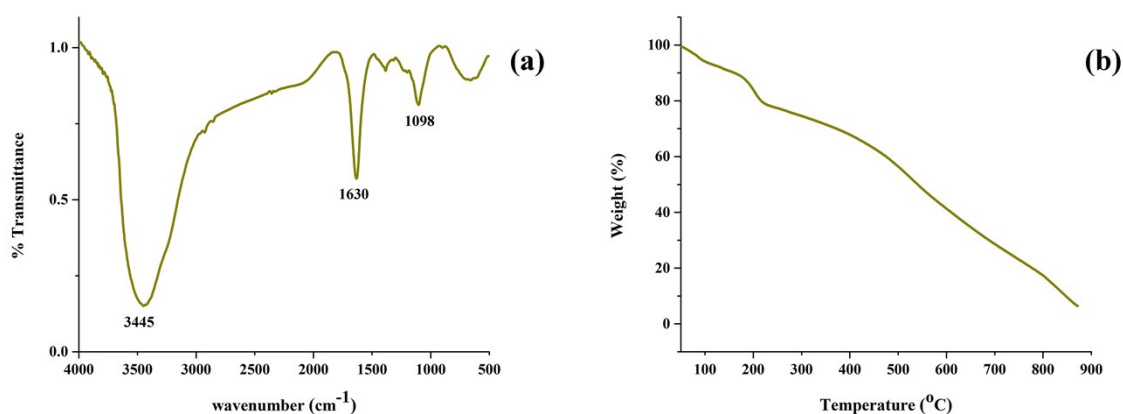


Fig S1. FT-IR Spectra (a) and TGA thermogram (b) of Pd@GO

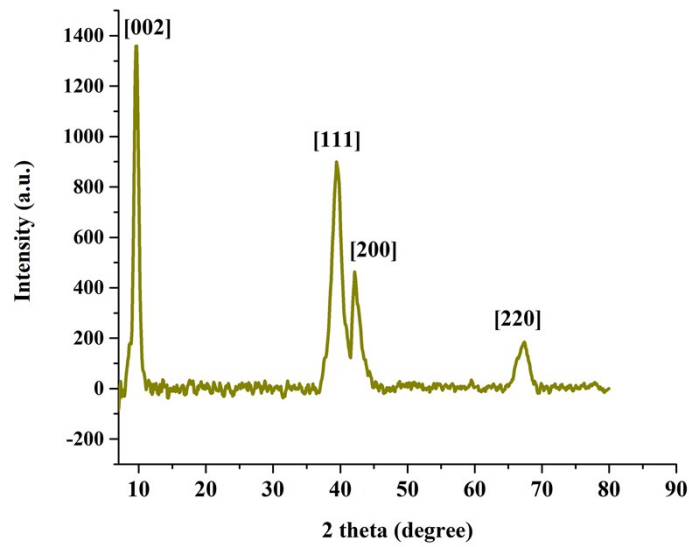


Fig S2. P-XRD Spectra of Pd@GO

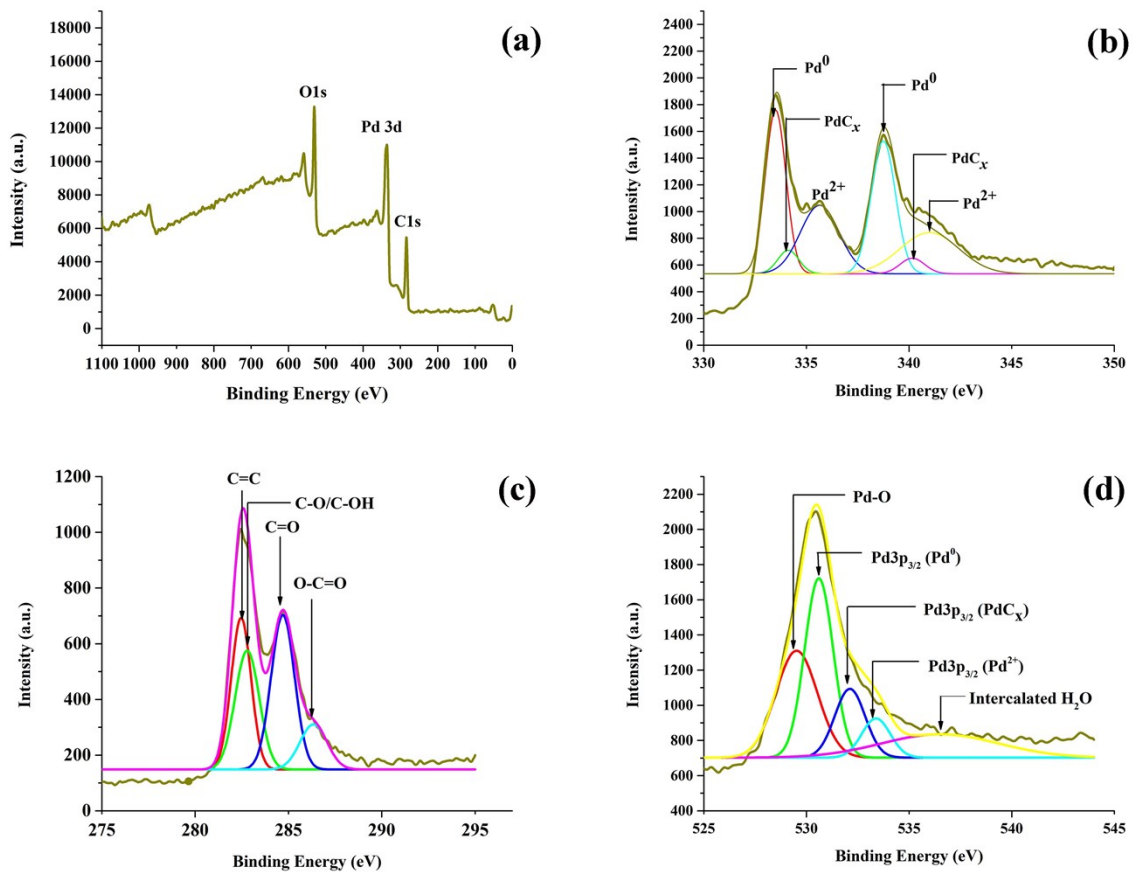


Fig S3. XPS Spectra showing (a) Survey Spectrum (b) Pd 3d (c) C 1s and (d) O 1s level of Pd@GO

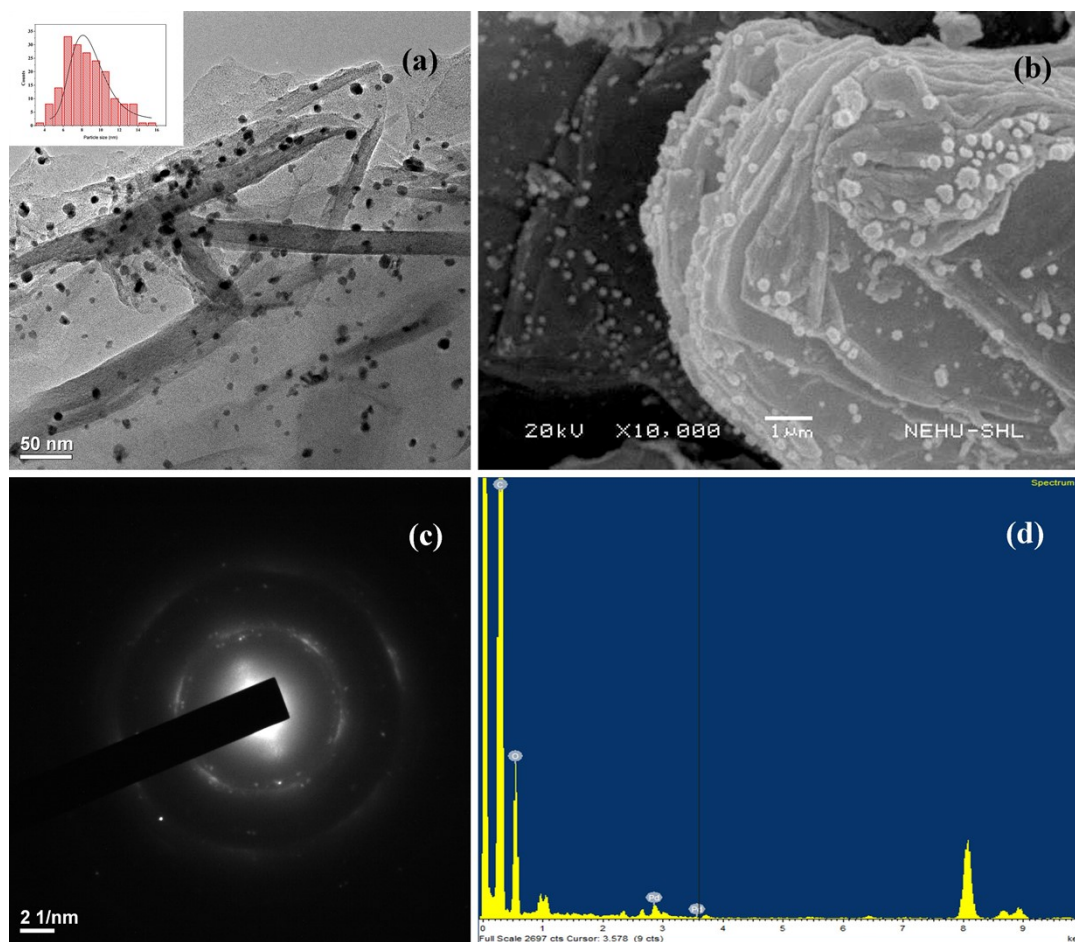


Fig S4. TEM image (a) SEM image (b) SAED (c) and EDX Spectra (c) of the recycled Pd@GO

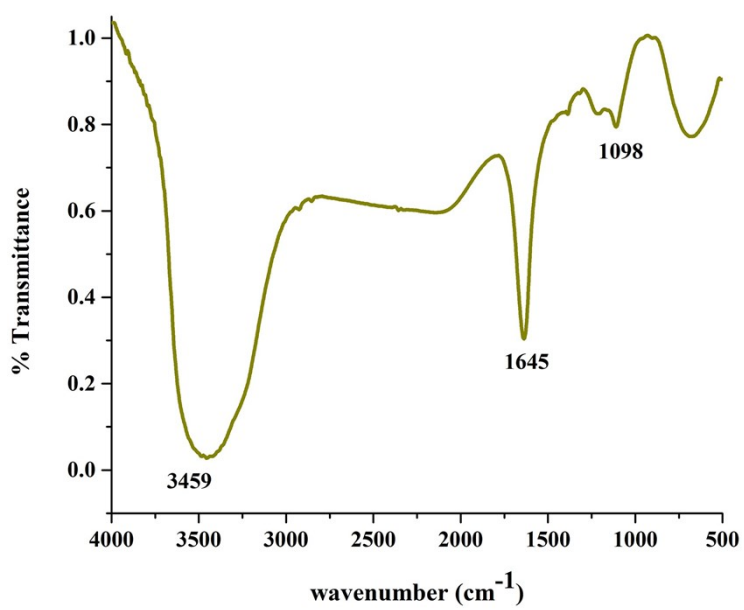
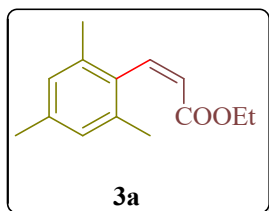
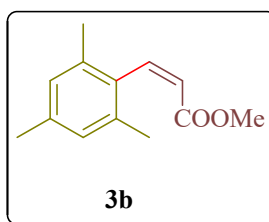


Fig S5. FT-IR Spectra of the recycled Pd@GO

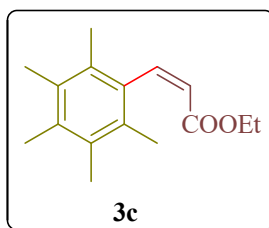
Spectral data of the compounds



Colourless liquid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.03$ (d, $J = 12$ Hz, 1H), 6.83 (s, 2H), 6.12 (d, $J = 12$ Hz, 1H), 4.05 (q, $J = 7.0$ Hz, 2H), 2.26 (s, 3H), 2.15 (s, 6H), 1.11 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 165.5, 144.2, 136.7, 134.5, 132.8, 127.8, 122.8, 59.9, 21.0, 20.1, 14.0$. HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 241.1205, Found 241.1190.⁴

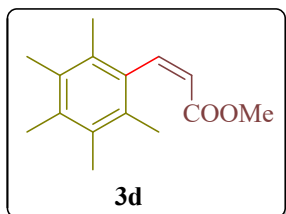


Colourless liquid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.09$ (d, $J = 12$ Hz, 1H), 6.89 (s, 2H), 6.18 (d, $J = 12$ Hz, 1H), 3.63 (s, 3H), 2.31 (s, 3H), 2.19 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 165.8, 144.5, 136.8, 134.5, 132.5, 127.9, 122.2, 51.2, 21.0, 20.1$. HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 227.1048, Found 227.1033.⁴

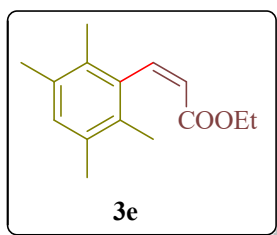


White solid. M.p.: 65-68 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.14$ (d, $J = 12$ Hz, 1H), 6.14 (d, $J = 12$ Hz, 1H), 4.04 (q, $J = 7$ Hz, 2H), 2.22 (s, 3H), 2.20 (s, 6H), 2.14 (s, 6H), 1.12 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 165.4, 146.5, 133.9, 133.2, 131.9, 129.7, 122.1,$

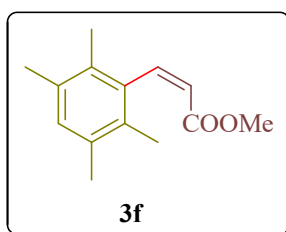
59.8, 17.6, 16.7, 16.3, 14.0. HRMS (ESI) m/z calcd. for $C_{16}H_{22}O_2$ $[M+Na]^+$ 269.1518, Found 269.1510.⁴



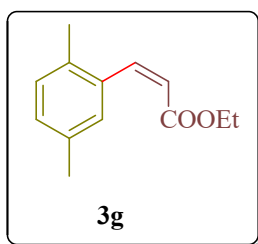
White solid. M.p.: 98-100 °C. 1H NMR ($CDCl_3$, 400 MHz): δ = 7.15 (d, J = 12 Hz, 1H), 6.16 (d, J = 12 Hz, 1H), 3.58 (s, 3H), 2.22 (s, 3H), 2.20 (s, 6H), 2.13 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.7, 147.0, 134.1, 133.0, 132.0, 129.8, 121.5, 51.1, 17.6, 16.8, 16.4. HRMS (ESI) m/z calcd. for $C_{15}H_{20}O_2$ $[M+Na]^+$ 255.1361, Found 255.1342.⁴



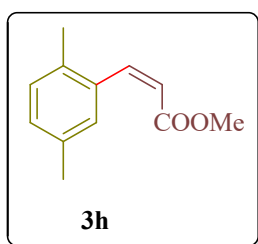
Colourless liquid. 1H NMR ($CDCl_3$, 400 MHz): δ = 7.11 (d, J = 12 Hz, 1H), 6.90 (s, 1H), 6.15 (d, J = 12 Hz, 1H), 4.03 (q, J = 7.0 Hz, 2H), 2.21 (s, 6H), 2.08 (s, 6H), 1.08 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.5, 145.6, 135.7, 133.0, 130.5, 130.2, 122.4, 59.8, 20.0, 16.5, 13.9.^{4,5}



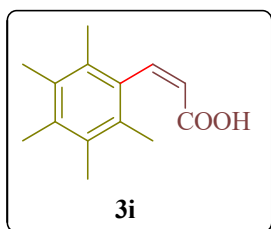
Colourless liquid. 1H NMR ($CDCl_3$, 300 MHz): δ = 7.12 (d, J = 12 Hz, 1H), 6.90 (s, 1H), 6.18 (d, J = 12 Hz, 1H), 3.58 (s, 3H), 2.22 (s, 6H), 2.07 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.7, 146.0, 135.4, 133.1, 130.7, 130.2, 121.8, 51.1, 19.9, 16.4. HRMS (ESI) m/z calcd. for $C_{14}H_{18}O_2$ $[M+Na]^+$ 241.1205, Found 241.1190.⁴



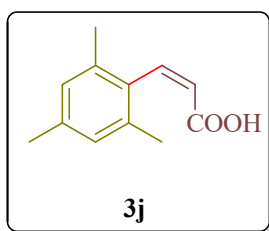
Colourless liquid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.11$ (s, 1H), 7.10 (d, $J = 12$ Hz, 1H), 7.05-7.01 (m, 2H), 6.01 (d, $J = 12$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 2.29 (s, 3H), 2.23 (s, 3H), 1.16 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 166.1$, 142.9, 134.8, 134.4, 132.6, 129.5, 129.2, 129.1, 120.9, 60.1, 20.9, 19.3, 13.9. HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 227.1048, Found 227.1042.⁵



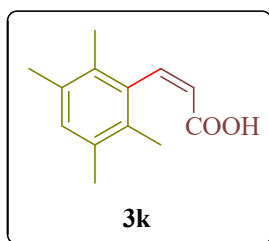
Colourless liquid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.13$ (s, 1H), 7.11 (d, $J = 12$ Hz, 1H), 7.06-7.02 (m, 2H), 6.02 (d, $J = 12$ Hz, 1H), 3.63 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 166.4$, 143.4, 134.65, 134.61, 132.7, 129.6, 129.28, 129.21, 120.3, 51.2, 20.9, 19.3.



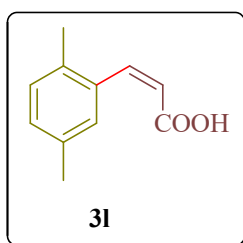
White solid. M.p.: 210-214 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.22$ (d, $J = 12$ Hz, 1H), 6.15 (d, $J = 12$ Hz, 1H), 2.22 (s, 3H), 2.19 (s, 6H), 2.13 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 148.2$, 134.6, 132.3, 129.9, 121.7, 17.6, 16.8, 16.4. HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 241.1204, Found 241.1222.⁴



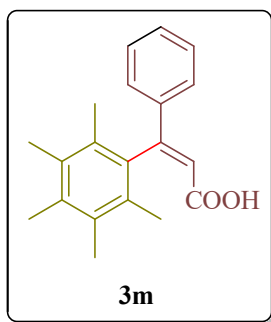
White solid. M.p.: 133-135 °C. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.10 (d, J = 12 Hz, 1H), 6.82 (s, 2H), 6.10 (d, J = 12 Hz, 1H), 2.26 (s, 3H), 2.14 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 171.0, 146.3, 137.1, 134.6, 132.1, 128.0, 122.2, 21.0, 20.1. HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 213.0891, Found 213.0896.⁶



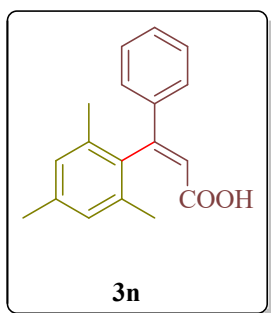
White solid. M.p.: 180-182 °C. ^1H NMR (CDCl_3 , 300 MHz): δ = 7.18 (d, J = 12 Hz, 1H), 6.90 (s, 1H), 6.15 (d, J = 12 Hz, 1H), 2.20 (s, 6H), 2.07 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 168.5, 147.3, 134.7, 133.5, 131.0, 130.4, 121.9, 19.9, 16.5. HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 227.1048, Found 227.1033.⁶



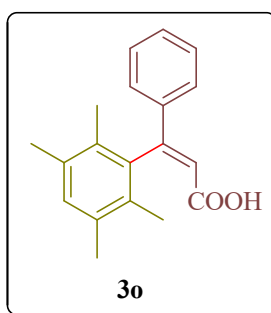
White solid. M.p.: 68-70 °C. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.19 (d, J = 12.4 Hz, 1H), 7.12 (s, 1H), 7.06-7.00 (m, 2H), 5.99 (d, J = 12.4 Hz, 1H), 2.27 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 171.4, 145.8, 134.7, 134.3, 132.8, 129.7, 129.5, 129.4, 119.9, 20.9, 19.4. HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 199.0735, Found 199.0727.⁶



White solid. M.p.: 235-238 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.34\text{-}7.30$ (m, 5H), 6.64 (s, 1H), 2.27 (s, 3H), 2.21 (s, 6H), 2.01 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 168.4, 158.1, 138.6, 135.0, 133.9, 132.8, 130.3, 129.8, 128.7, 127.2, 117.1, 17.5, 16.9, 16.5$. HRMS (ESI) m/z calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 317.1518, Found 317.1519.⁴

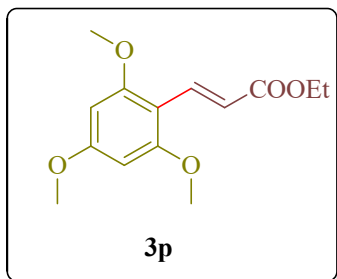


White solid. M.p.: 192-193 °C. ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.36\text{-}7.30$ (m, 5H), 6.90 (s, 2H), 6.60 (s, 1H), 2.32 (s, 3H), 2.02 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 168.3, 156.8, 138.1, 137.3, 134.8, 134.2, 129.8, 128.8, 128.7, 128.3, 127.1, 116.8, 21.1, 19.7$. HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 289.1204, Found 289.1202.⁵

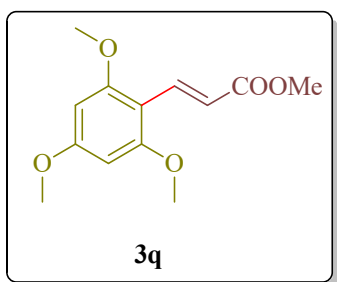


White solid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.37\text{-}7.28$ (m, 5H), 6.99 (s, 1H), 6.64 (s, 1H), 2.23 (s, 6H), 1.96 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 169.3, 158.0, 138.4, 136.9, 133.6$.

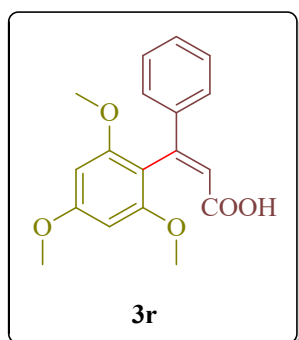
131.1, 130.6, 129.8, 128.7, 127.2, 116.9, 20.0, 16.3. HRMS (ESI) m/z calcd. for $C_{19}H_{20}O_2$ $[M+Na]^+$ 303.1361, Found 303.1378. ⁶



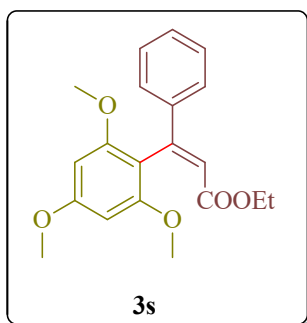
White solid. M.p.: 75-78 °C. ¹H NMR ($CDCl_3$, 400 MHz): δ = 8.10 (d, J = 16 Hz, 1H), 6.77 (d, J = 16 Hz, 1H), 6.11 (s, 2H), 4.27 (q, J = 7.2 Hz, 2H), 3.86 (s, 6H), 3.84 (s, 3H), 1.34 (t, J = 7 Hz, 3H). ¹³C NMR ($CDCl_3$, 100 MHz): δ = 169.0, 162.7, 161.2, 135.4, 117.5, 105.8, 90.3, 59.9, 55.7, 55.3, 14.4. HRMS (ESI) m/z calcd. for $C_{14}H_{18}O_5$ $[M+Na]^+$ 289.1052, Found 289.1041. ⁶



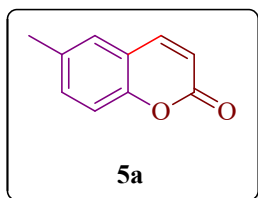
White solid. M.p.: 132-134 °C. ¹H NMR ($CDCl_3$, 400 MHz): δ = 8.11 (d, J = 16.4 Hz, 1H), 6.78 (d, J = 16.4 Hz, 1H), 6.11 (s, 2H), 3.86 (s, 6H), 3.84 (s, 3H), 3.77 (s, 3H). ¹³C NMR ($CDCl_3$, 100 MHz): δ = 169.4, 162.7, 161.2, 135.7, 117.1, 105.9, 90.4, 55.7, 55.3, 51.3. HRMS (ESI) m/z calcd. for $C_{13}H_{16}O_5$ $[M+Na]^+$ 275.0895, Found 275.0888.



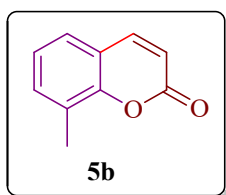
White solid. M.p.: 190-192 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.35\text{-}7.28$ (m, 5H), 6.48 (s, 1H), 6.18 (s, 2H), 3.85 (s, 3H), 3.64 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 169.8, 161.6, 158.0, 150.9, 140.4, 129.0, 128.2, 126.9, 118.7, 108.7, 90.9, 55.9, 55.3$. HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{17}\text{O}_5$ $[\text{M}+\text{Na}]^+$ 313.1076, Found 313.1093.⁶



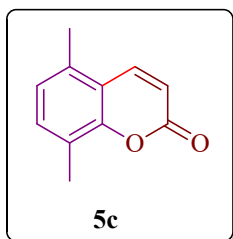
White solid. M.p.: 80-83 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.35$ (s, 2H), 7.27 (s, 3H), 6.49 (s, 1H), 6.18 (s, 2H), 4.05-4.02 (m, 2H), 3.83 (s, 3H), 3.63 (s, 6H), 1.14 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 165.8, 161.3, 157.9, 149.4, 140.4, 128.8, 128.2, 126.8, 119.3, 90.8, 59.6, 55.8, 55.2, 14.2$.



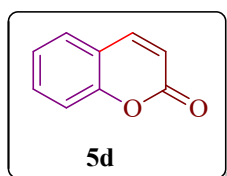
White solid. M.p.: 55-57 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.60$ (d, $J = 9.2$ Hz, 1H), 7.82 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.4$ Hz, 1H), 7.20-7.19 (m, 2H), 7.17 (d, $J = 8.4$ Hz, 1H), 6.34 (d, $J = 9.6$ Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.1, 152.1, 143.4, 134.1, 132.8, 127.6, 118.5, 116.62, 116.60, 20.7$. HRMS (ESI) m/z calcd. for $\text{C}_{10}\text{H}_9\text{O}_2$ $[\text{M}+\text{H}]^+$ 161.0603, Found 161.0583.⁷



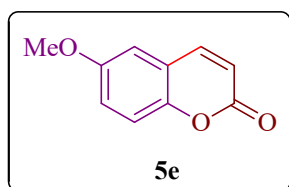
White solid. M.p.: 90-92 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.64$ (d, $J = 9.6$ Hz, 1H), 7.32-7.30 (m, 1H), 7.26 (dd, $J_1 = 1.6$ Hz, $J_2 = 7.6$ Hz, 1H), 7.12 (t, $J = 7.6$ Hz, 1H), 6.35 (d, $J = 9.6$ Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.1$, 152.3, 143.8, 133.1, 126.3, 125.6, 124.0, 118.5, 116.2, 15.4. HRMS (ESI) m/z calcd. for $\text{C}_{10}\text{H}_9\text{O}_2$ $[\text{M}+\text{H}]^+$ 161.0603, Found 161.0590.



White solid. M.p.: 98-100 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.95$ (d, $J = 10$ Hz, 1H), 7.28-7.26 (m, 2H), 7.03 (d, $J = 8$ Hz, 1H), 6.45 (d, $J = 10$ Hz, 1H), 2.51 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.0$, 152.8, 140.8, 133.4, 132.8, 125.2, 124.0, 117.3, 115.5, 18.1, 15.3.

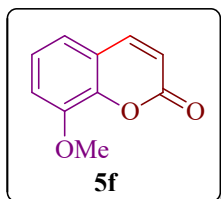


White solid. M.p.: 53-56 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.73$ (d, $J = 9.6$ Hz, 1H), 7.56-7.48 (m, 2H), 7.34-7.26 (m, 2H), 6.44 (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 160.0$, 154.0, 143.4, 131.8, 127.8, 124.4, 118.8, 116.9, 116.7.⁸

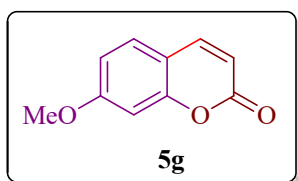


Light Yellow solid. M.p.: 98-100 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.67$ (d, $J = 9.2$ Hz, 1H), 7.29-7.27 (m, 1H), 7.13 (dd, $J_1 = 3$ Hz, $J_2 = 9$ Hz, 1H), 6.92 (d, $J = 2.8$ Hz, 1H), 6.44 (d,

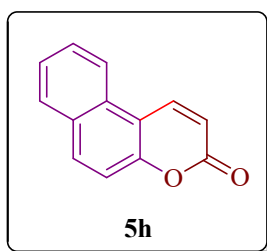
$J = 9.6$ Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.0, 156.0, 148.4, 143.2, 119.4, 119.1, 117.9, 117.1, 110.0, 55.8$.⁹



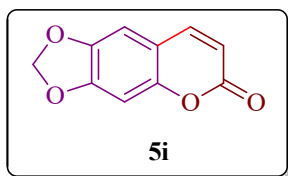
Yellow solid. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.72$ (d, $J = 9.6$ Hz, 1H), 7.24 (t, $J = 8$ Hz, 1H), 7.11-7.06 (m, 2H), 6.46 (d, $J = 9.6$ Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 160.2, 147.2, 143.7, 143.6, 124.3, 119.4, 119.2, 116.9, 113.7, 56.2$.



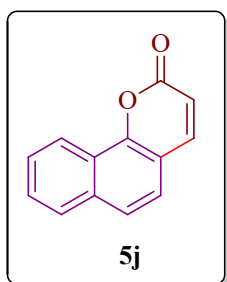
Yellow solid. M.p.: 98-101 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.67$ (d, $J = 9.6$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 1H), 6.88-6.83 (m, 2H), 6.28 (d, $J = 9.2$ Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 162.8, 161.2, 155.9, 143.4, 128.7, 113.1, 112.6, 112.5, 100.8, 55.7$.^{7,9,10}



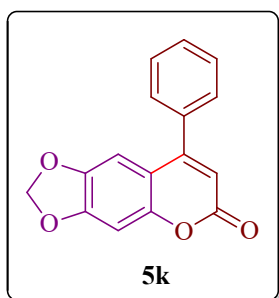
Yellow solid. M.p.: 103-105 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.52$ -8.48 (m, 1H), 8.25-8.22 (m, 1H), 8.01-7.98 (m, 1H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.71-7.68 (m, 1H), 7.59-7.56 (m, 1H), 7.49-7.45 (m, 1H), 6.60-6.57 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 160.9, 153.9, 139.1, 133.1, 130.3, 129.0, 128.3, 126.0, 121.3, 117.1, 115.6, 113.0$.¹¹



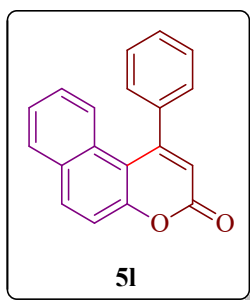
Yellow solid. M.p.: 206-208 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.53$ (d, $J = 9.6$ Hz, 1H), 6.76 (d, $J = 7.2$ Hz, 2H), 6.21 (d, $J = 9.6$ Hz, 1H), 6.00 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.3, 151.3, 151.2, 144.9, 143.6, 113.3, 112.6, 105.0, 102.3, 98.3$.¹¹



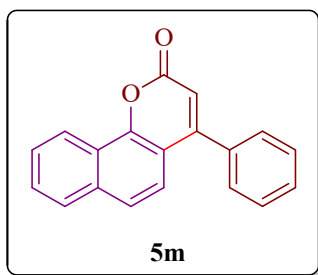
White solid. M.p.: 120-122 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.56$ -8.52 (m, 1H), 7.89-7.86 (m, 1H), 7.84 (d, $J = 9.2$ Hz, 1H), 7.69 (d, $J = 8.8$ Hz, 1H), 7.66-7.62 (m, 2H), 7.46 (d, $J = 8.8$ Hz, 1H), 6.53 (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.0, 151.3, 144.2, 134.8, 128.7, 127.8, 127.2, 124.4, 123.9, 123.1, 122.3, 115.9, 114.2$. HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_9\text{O}_2$ $[\text{M}+\text{H}]^+$ 197.0603, Found 197.0592.⁸



Brown solid. M.p.: 112-115 °C. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.43$ -7.40 (m, 3H), 7.33-7.29 (m, 2H), 6.78 (s, 1H), 6.73 (s, 1H), 6.13 (s, 1H), 5.95 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 161.3, 156.0, 151.3, 151.2, 144.9, 135.6, 129.6, 128.9, 128.2, 112.8, 112.1, 104.3, 102.4, 98.5, 98.3$.⁹



White solid. M.p.: 160-162 °C. ^1H NMR (CDCl_3 , 400 MHz): δ = 8.00 (d, J =9.2 Hz, 1H), 7.85-7.83 (m, 1H), 7.53-7.47 (m, 4H), 7.41-7.37 (m, 1H), 7.36-7.33 (m, 2H), 7.23 (s, 1H), 7.17-7.12 (m, 1H) 6.38 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.5, 156.6, 154.7, 139.5, 134.0, 131.3, 129.3, 129.2, 129.1, 129.0, 127.4, 126.7, 125.9, 125.4, 117.4, 116.7, 113.0.¹¹



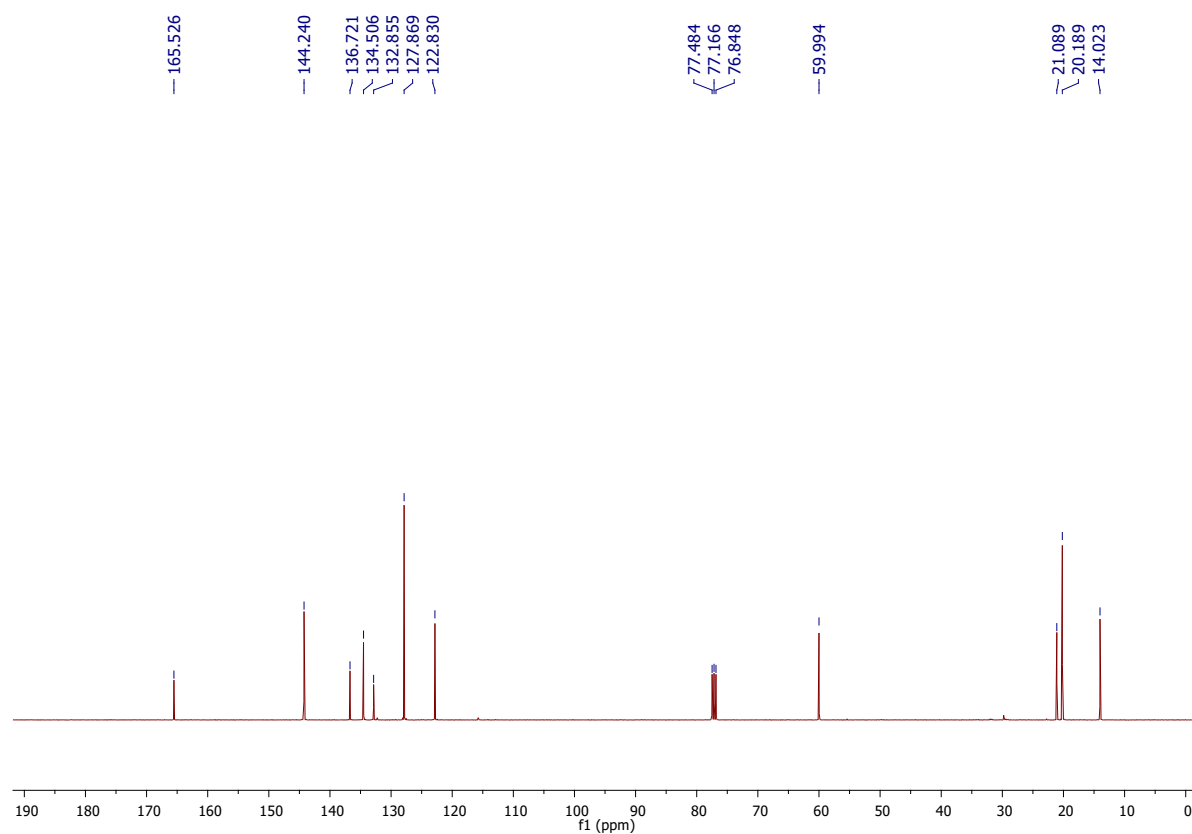
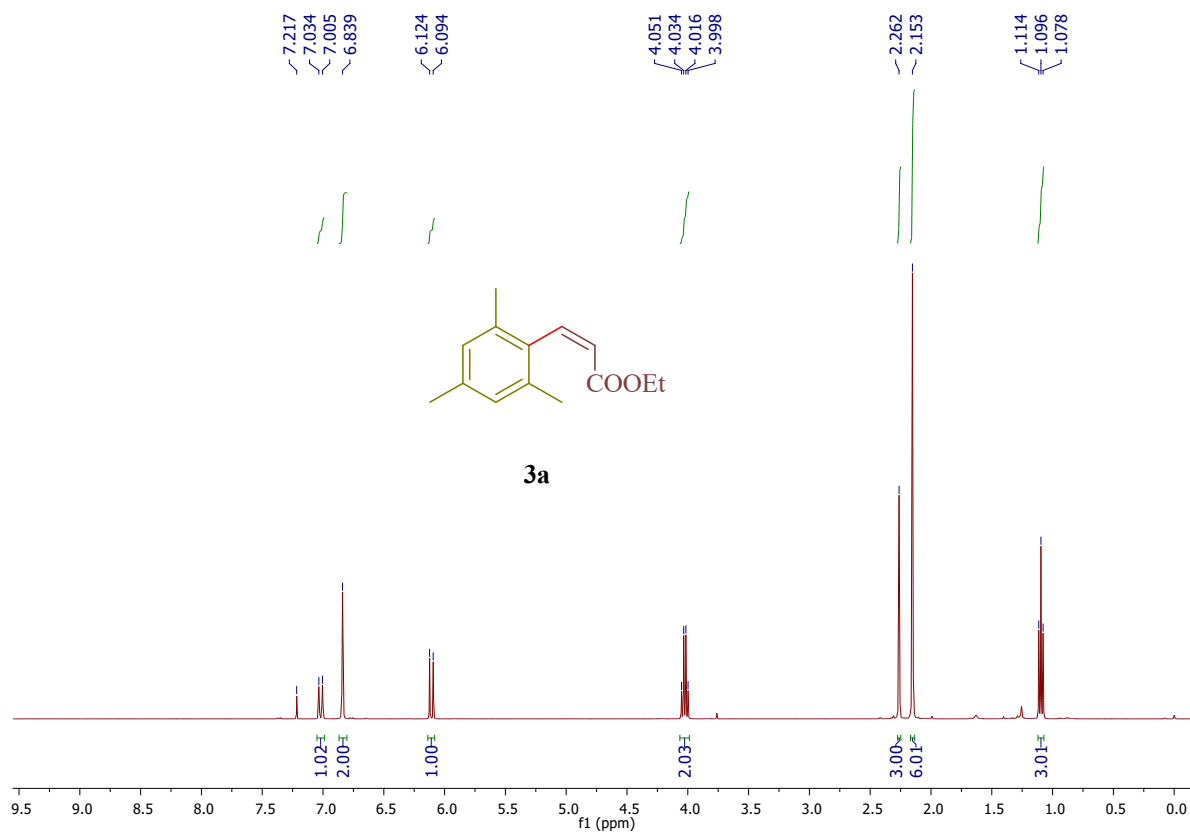
White solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.99 (d, J = 8.8 Hz, 1H), 7.84 (d, J =7.6 Hz, 1H), 7.55-7.47 (m, 4H), 7.41-7.37 (m, 1H), 7.35-7.33 (m, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.16-7.12 (m, 1H), 6.366 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.4, 156.5, 154.7, 139.5, 134.0, 131.3, 129.3, 129.2, 129.1, 129.0, 127.4, 126.7, 125.9, 125.4, 117.4, 116.8, 113.0.

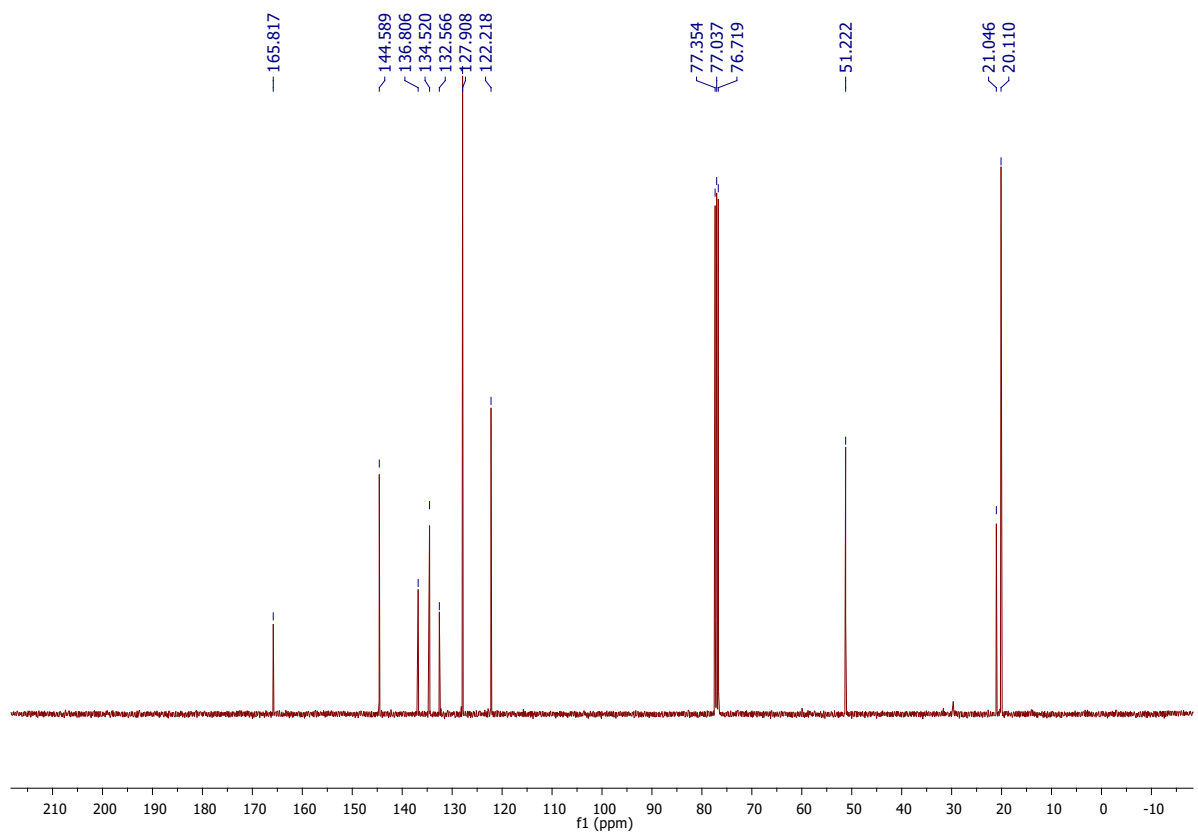
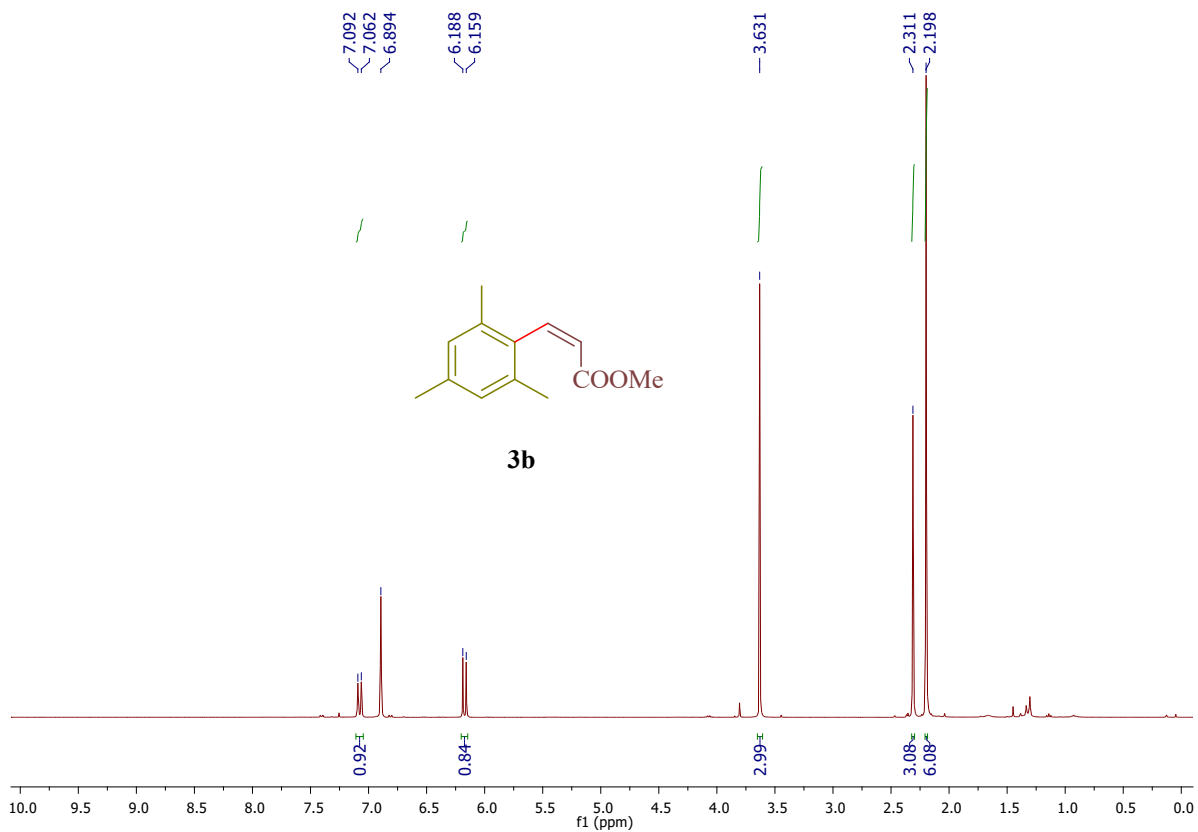
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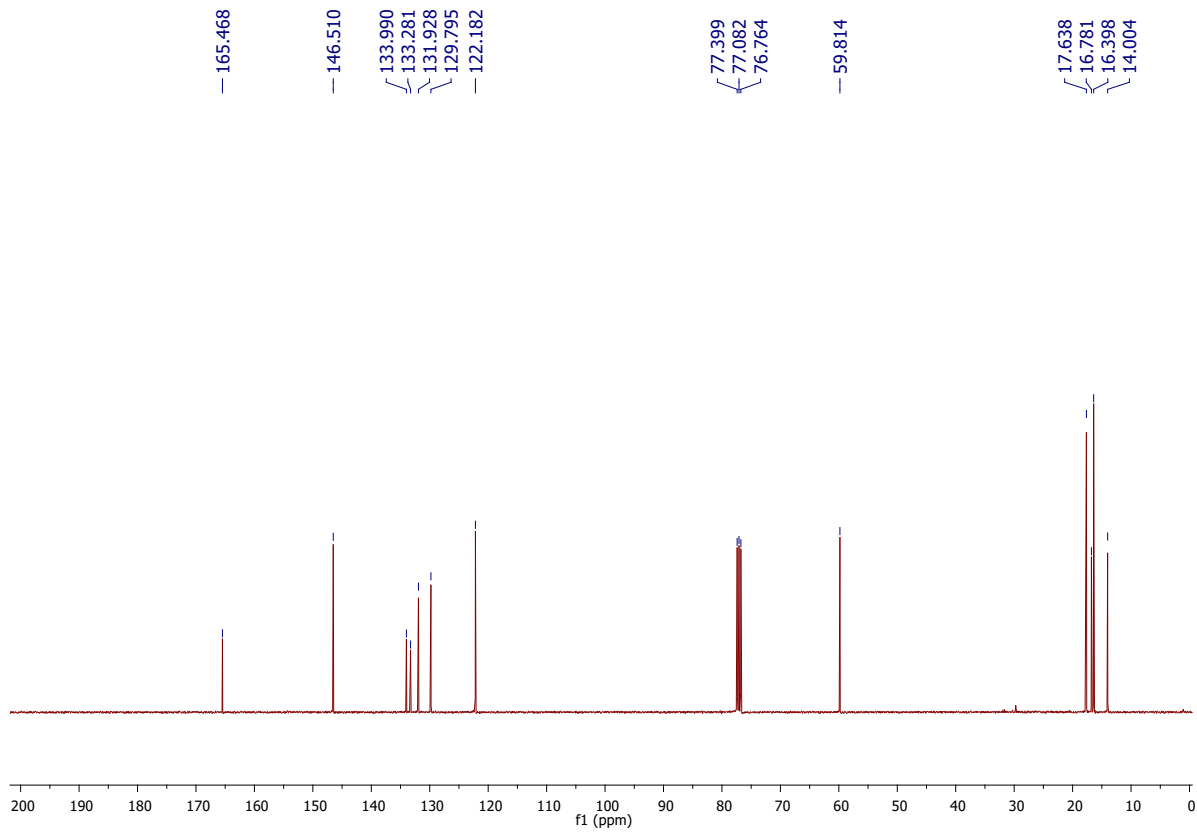
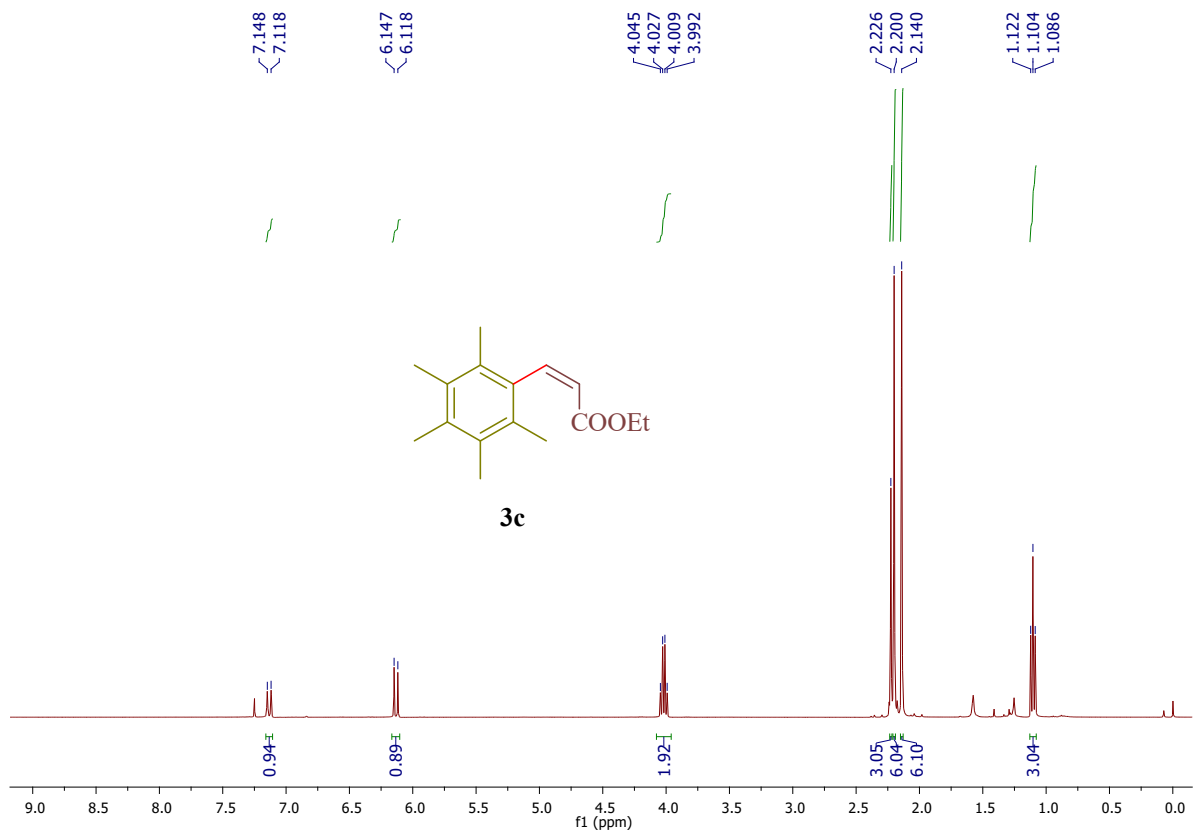
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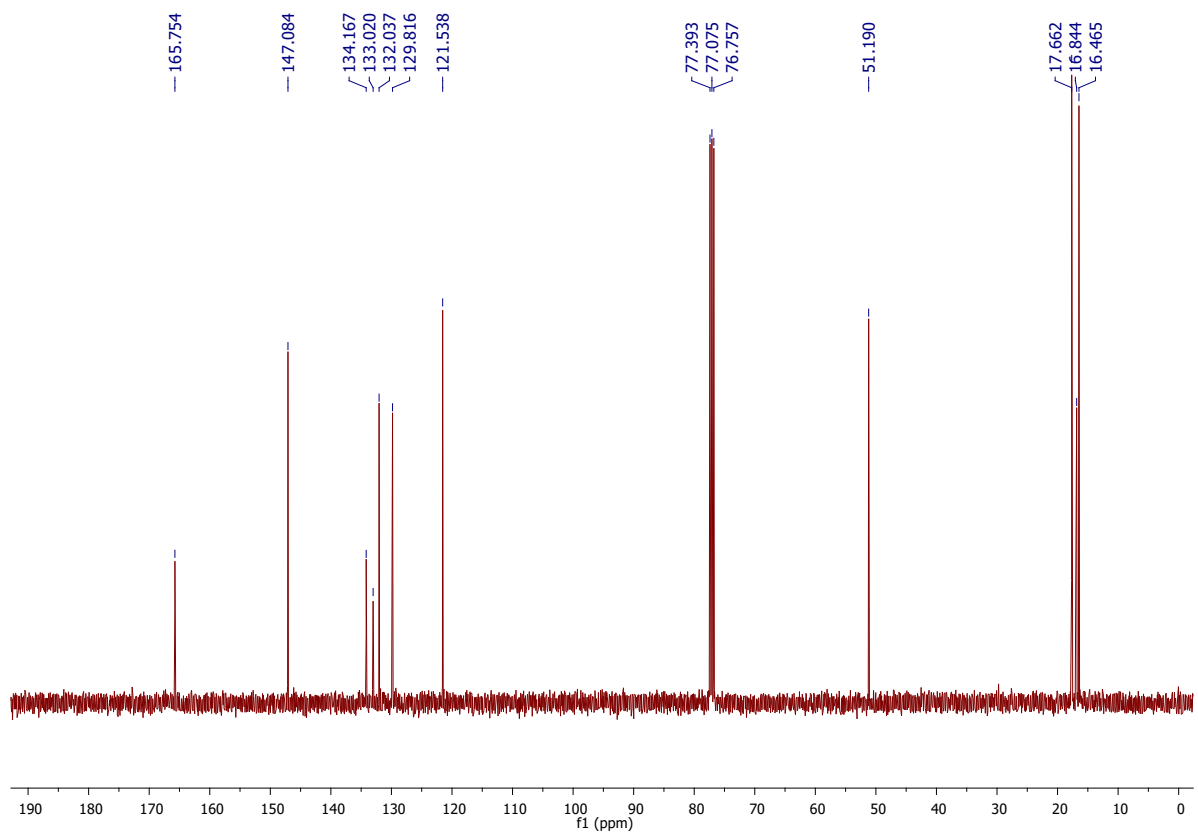
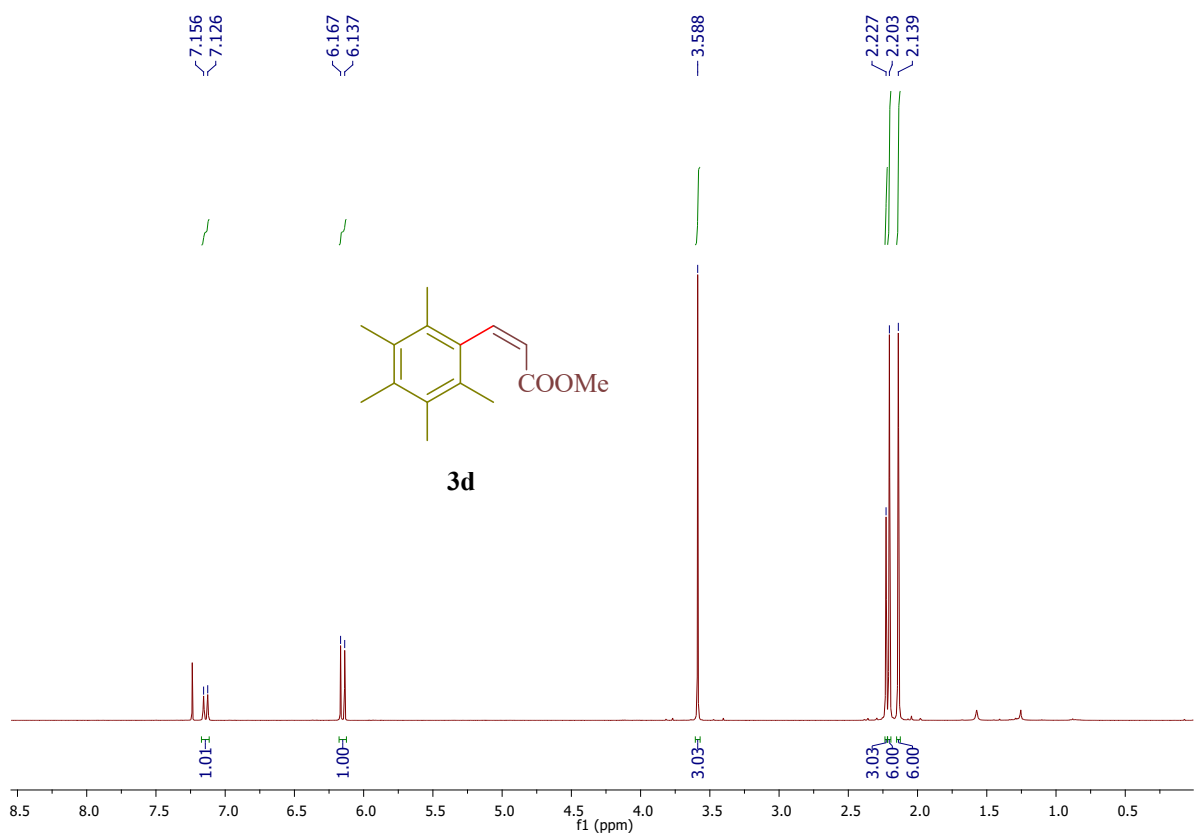
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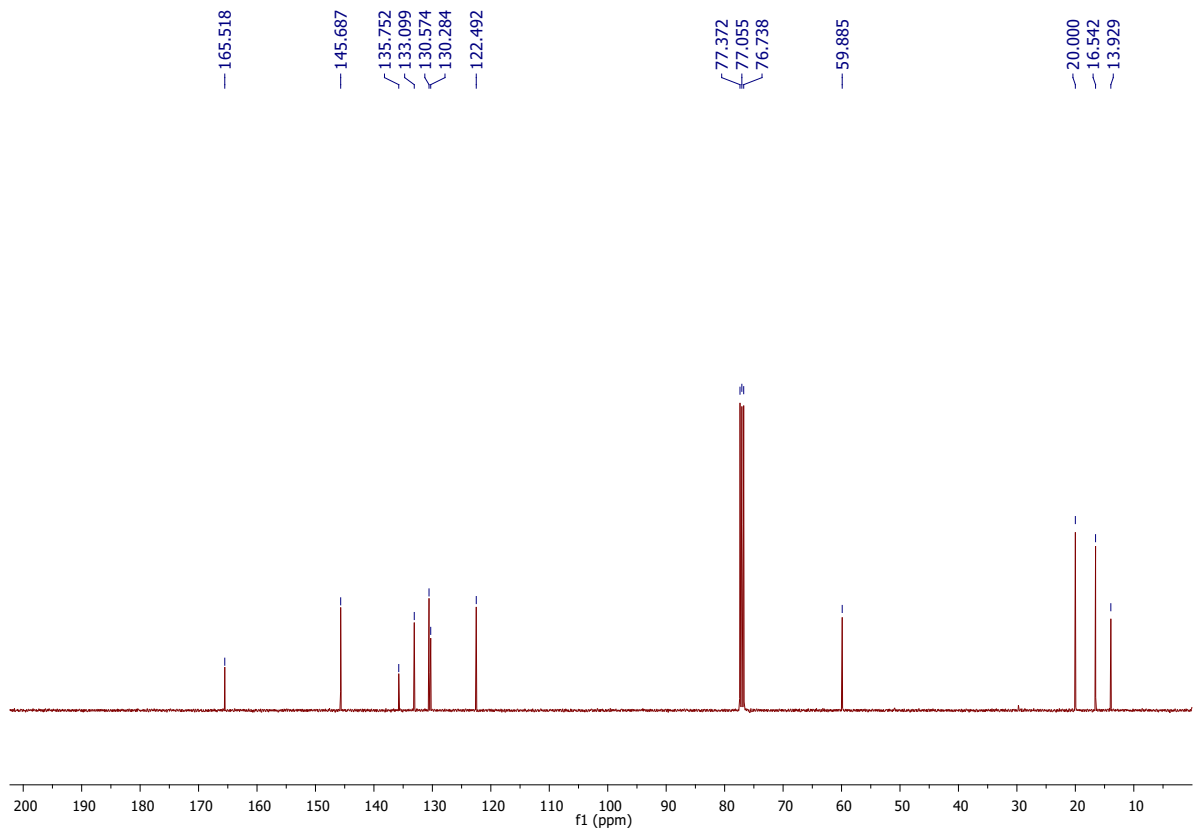
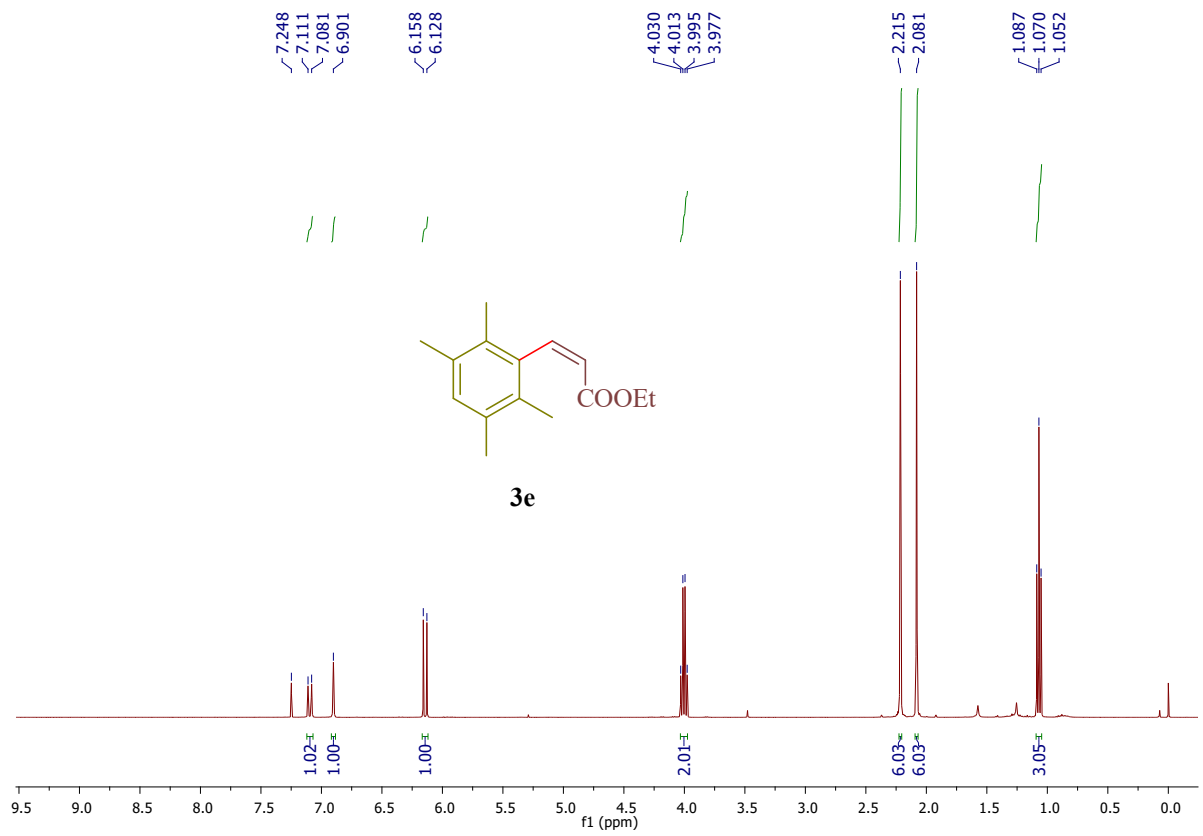
¹H and ¹³C NMR spectra of the compounds

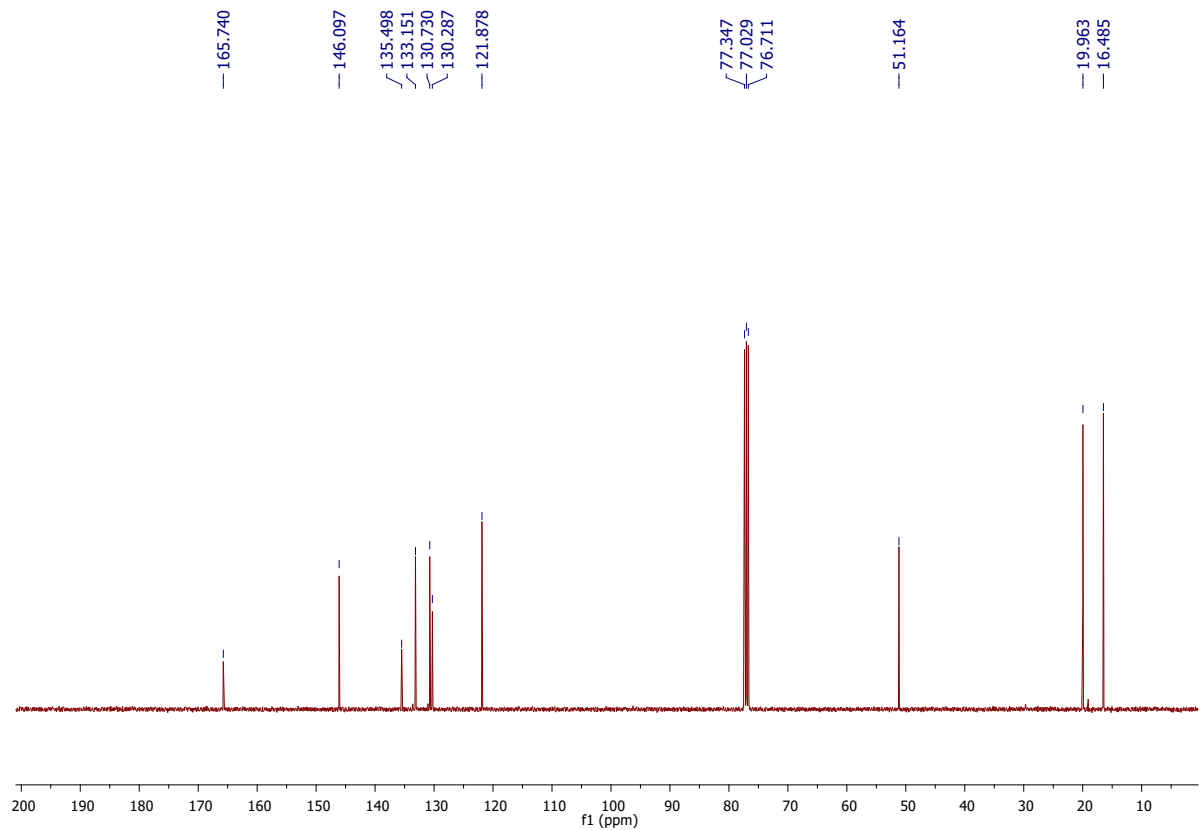
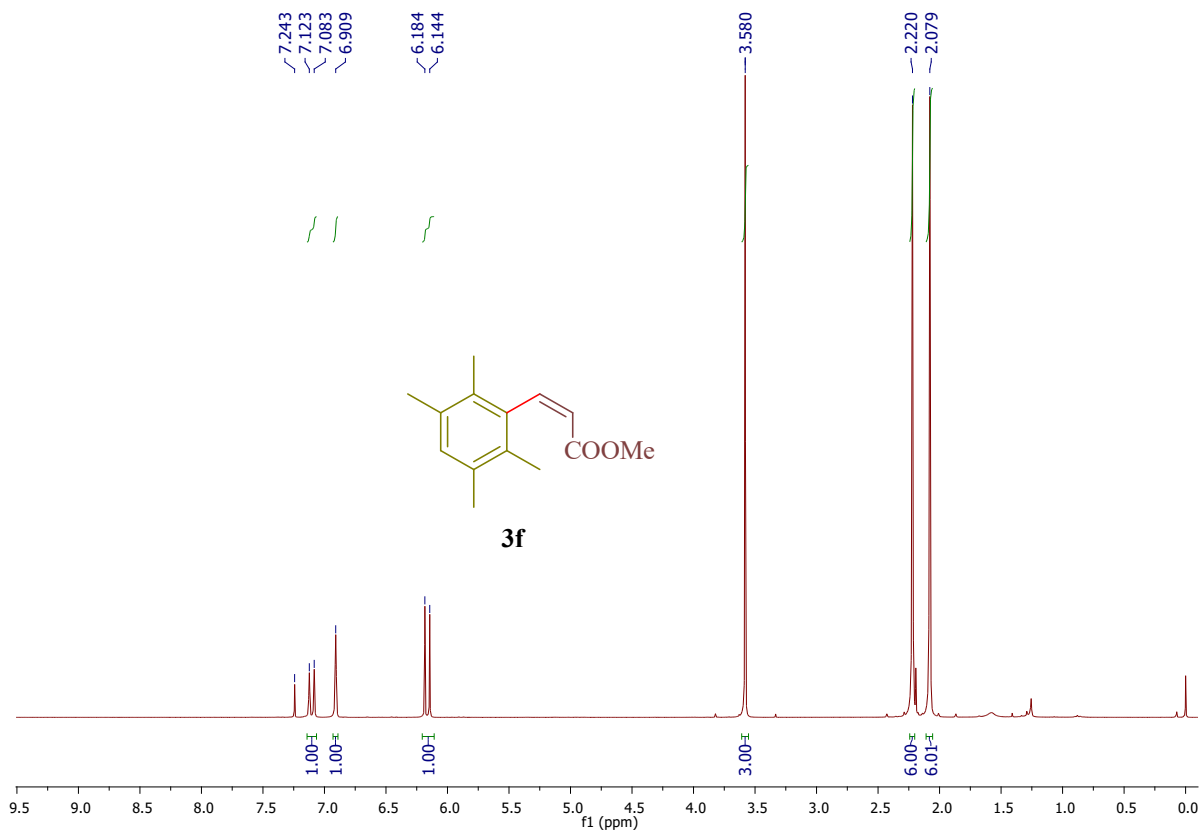


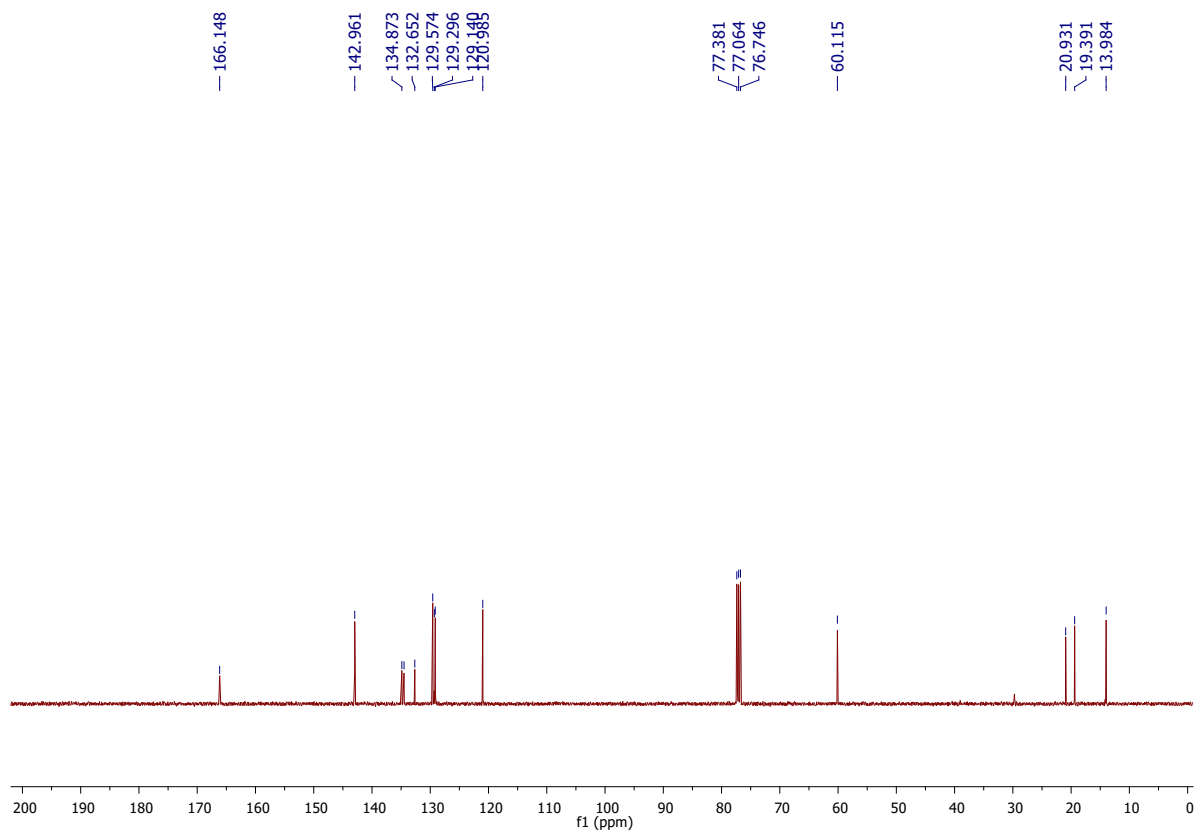
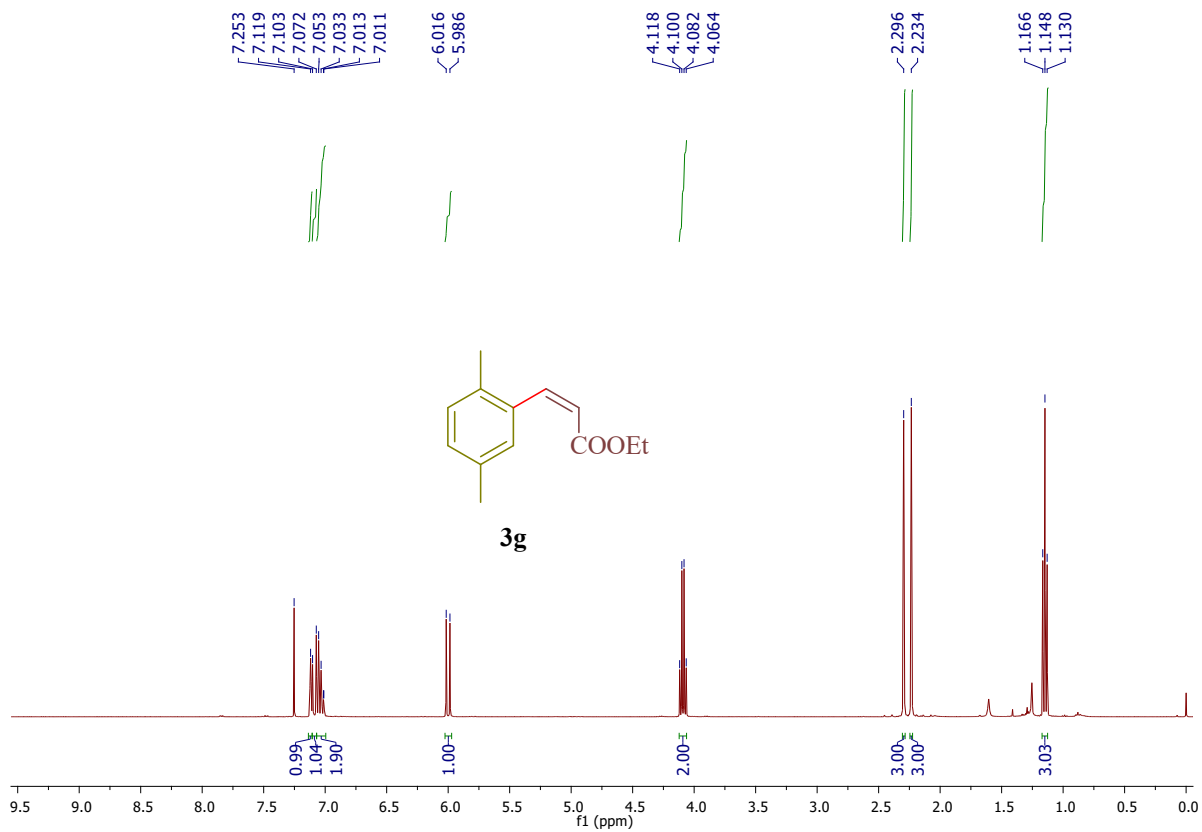


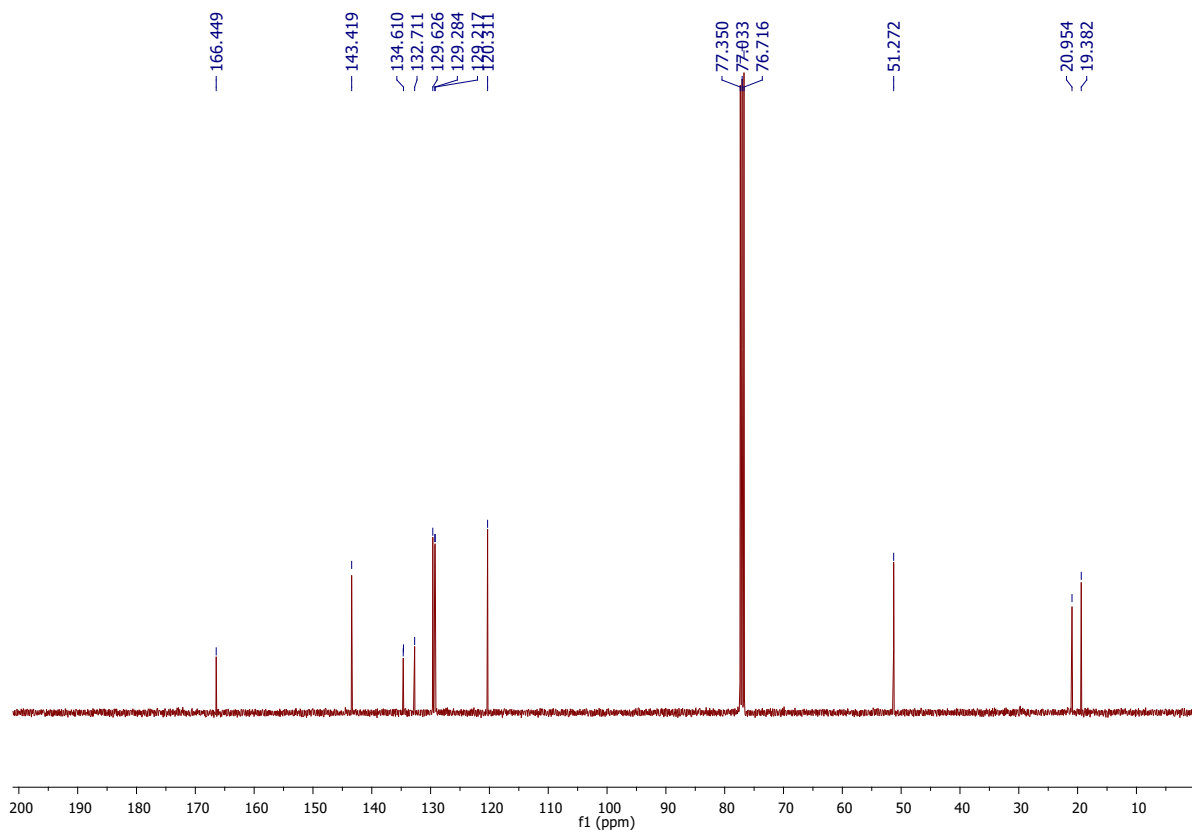
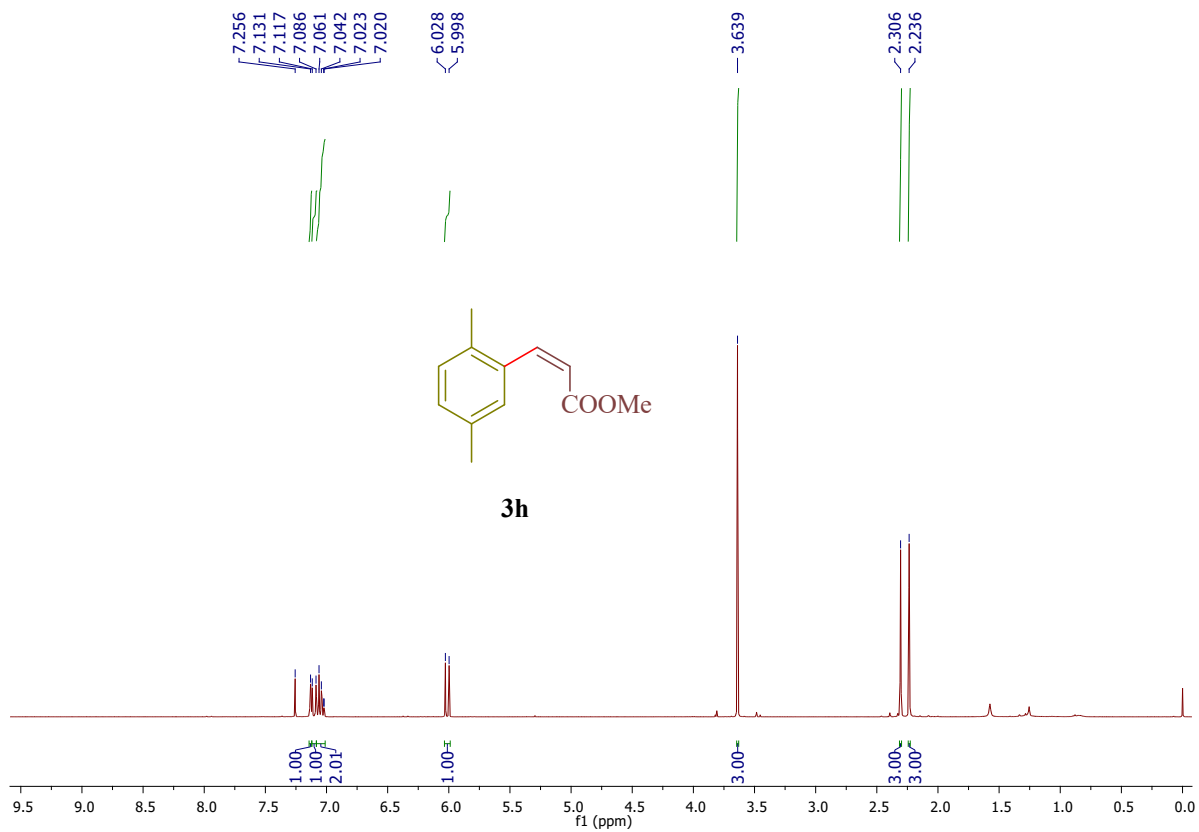


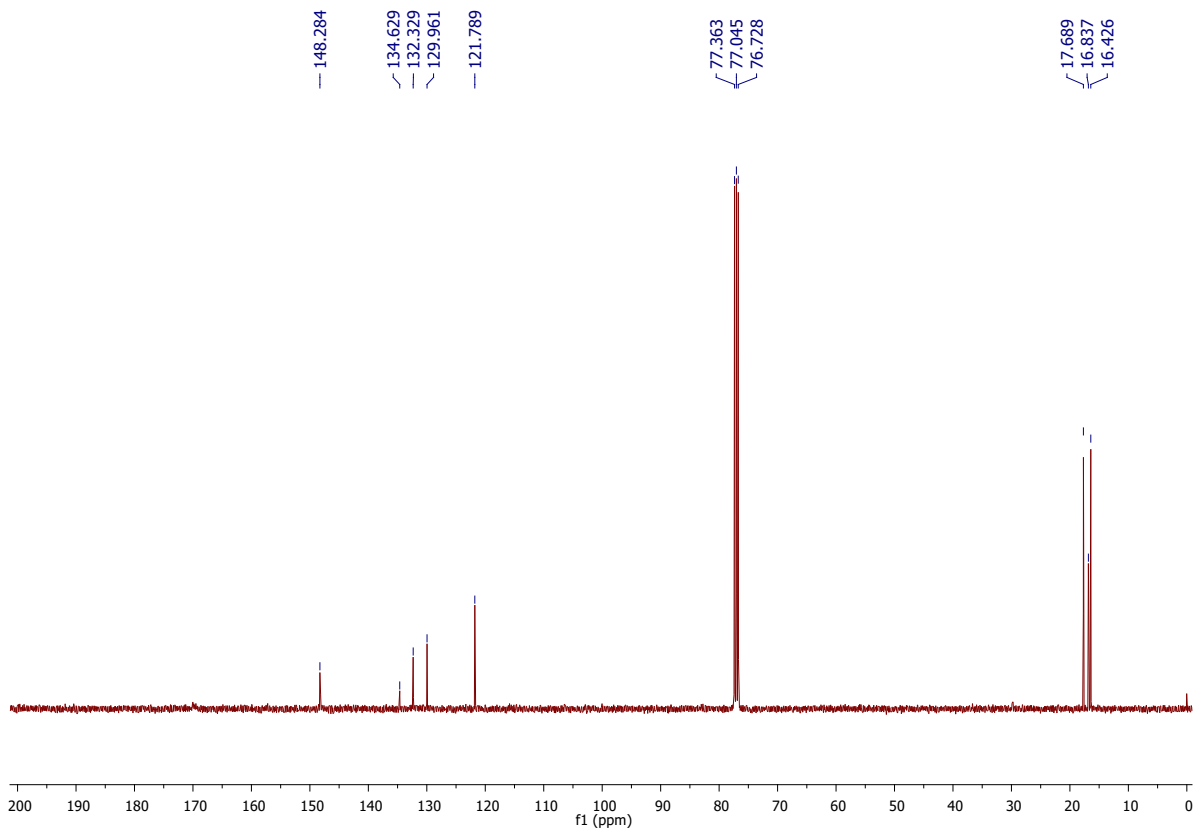
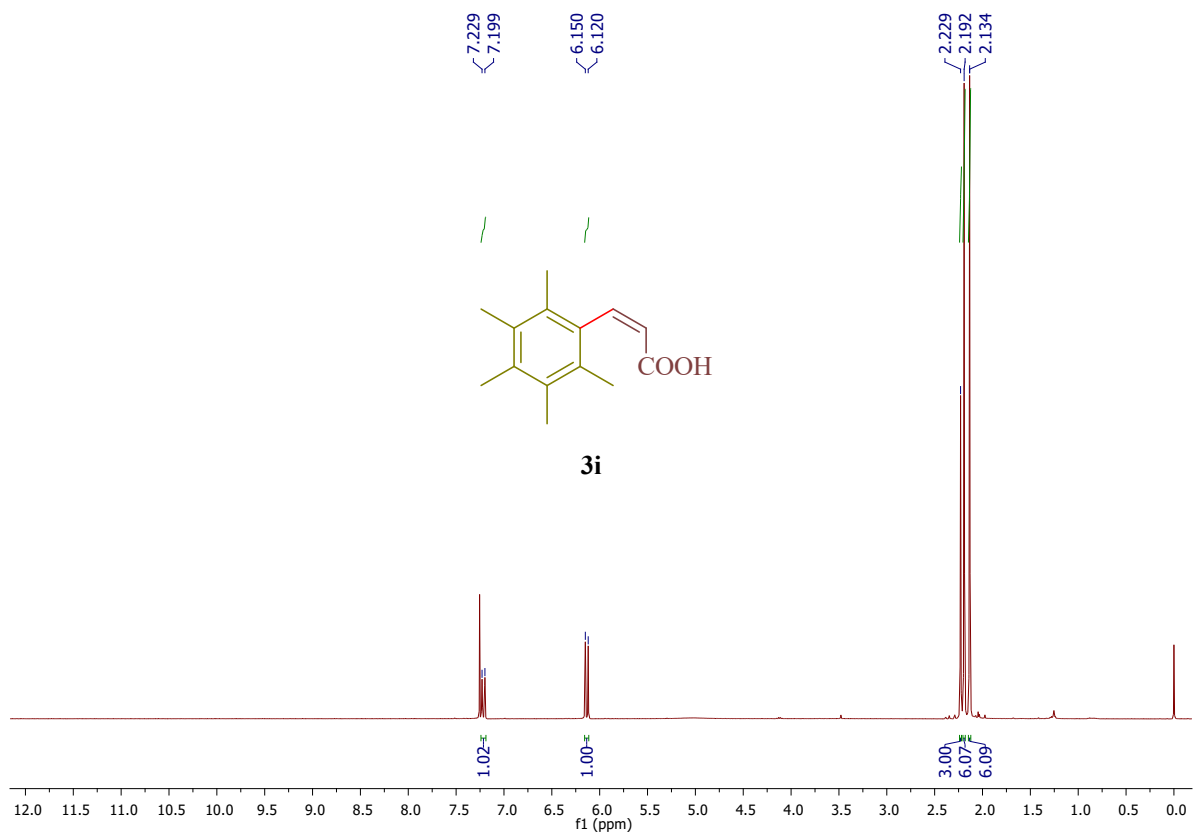


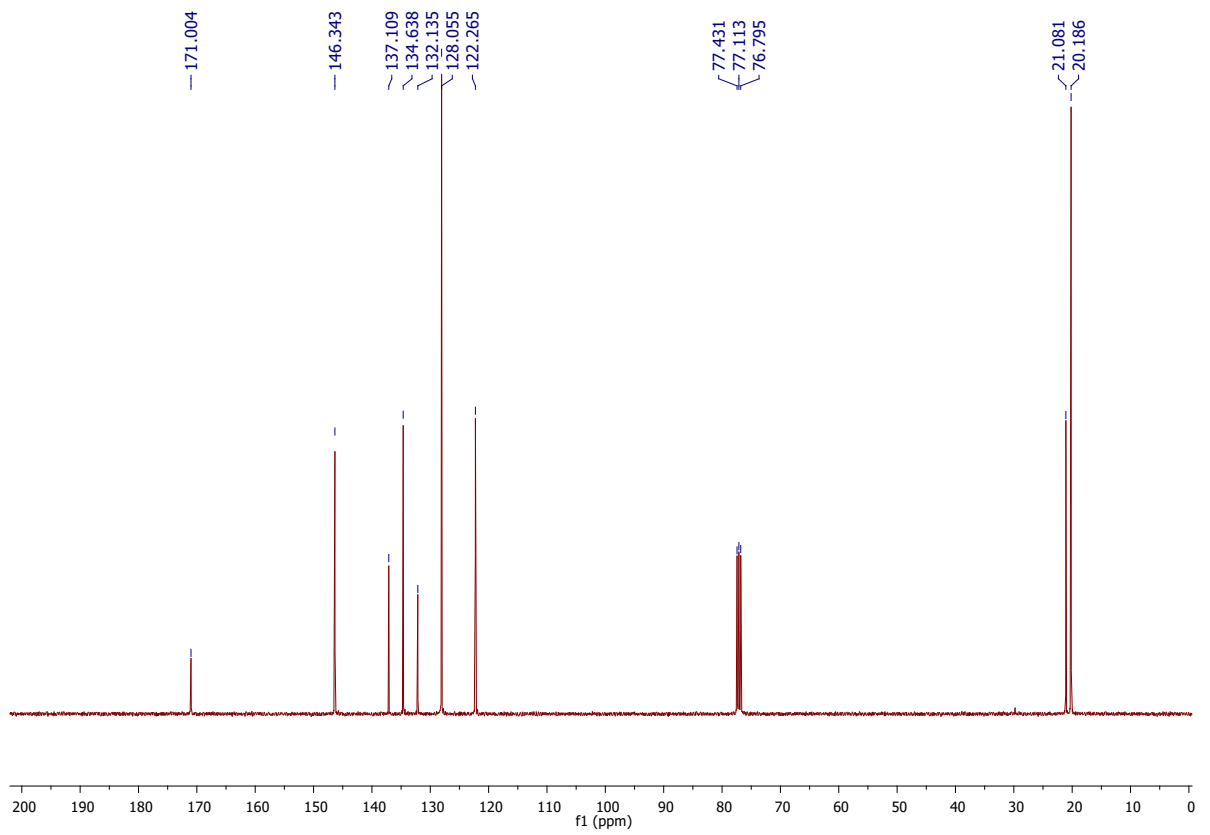
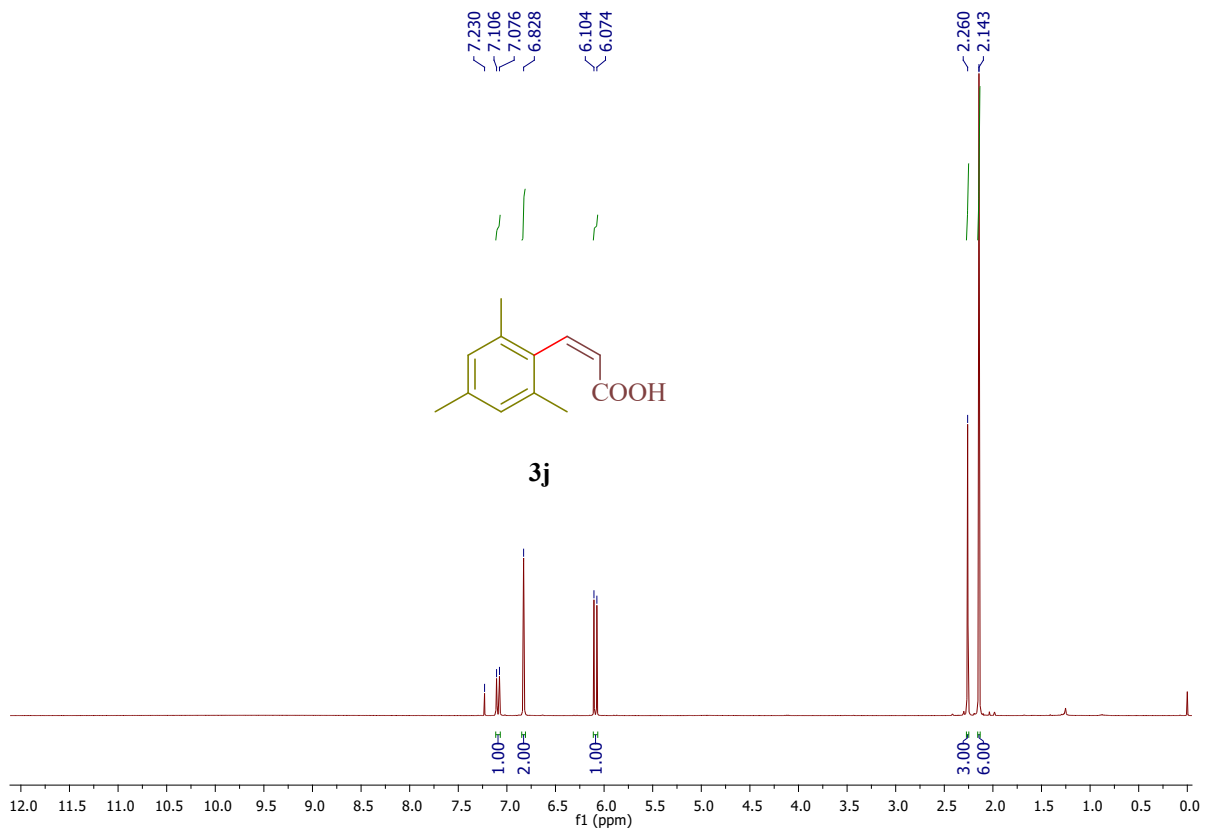


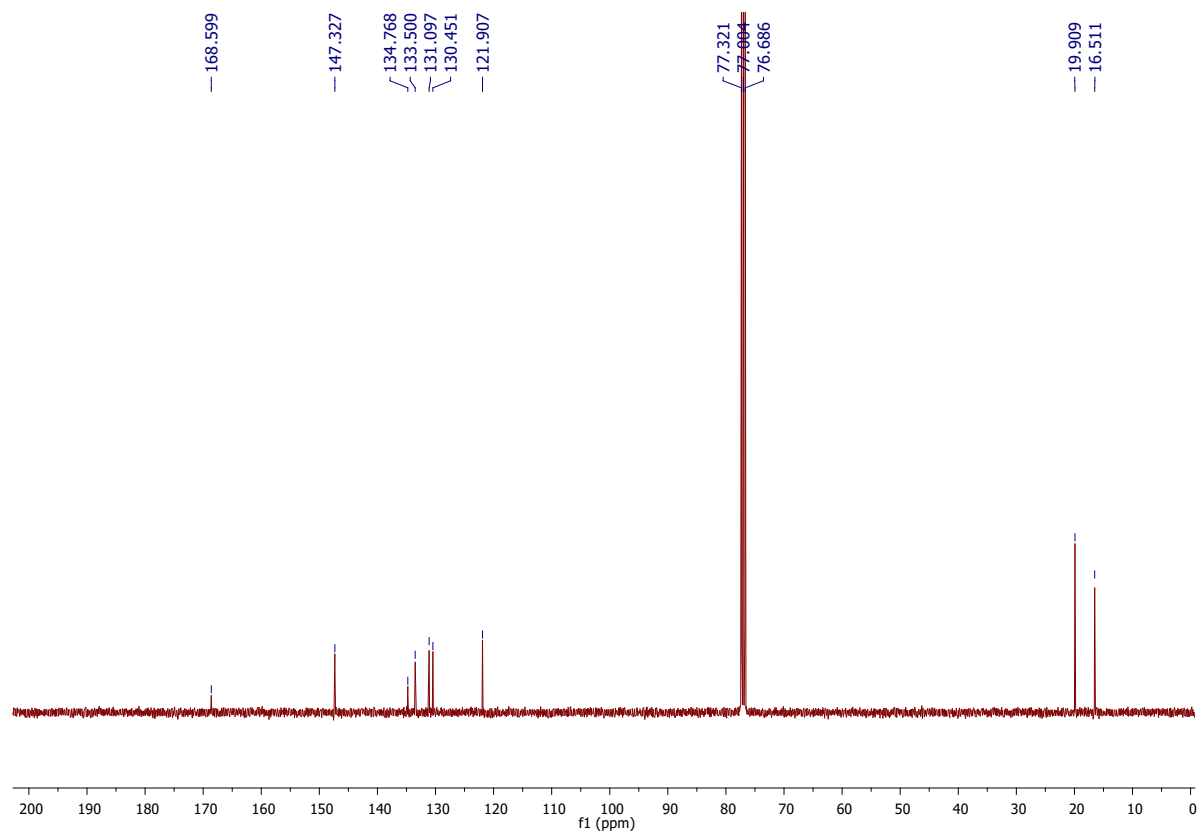
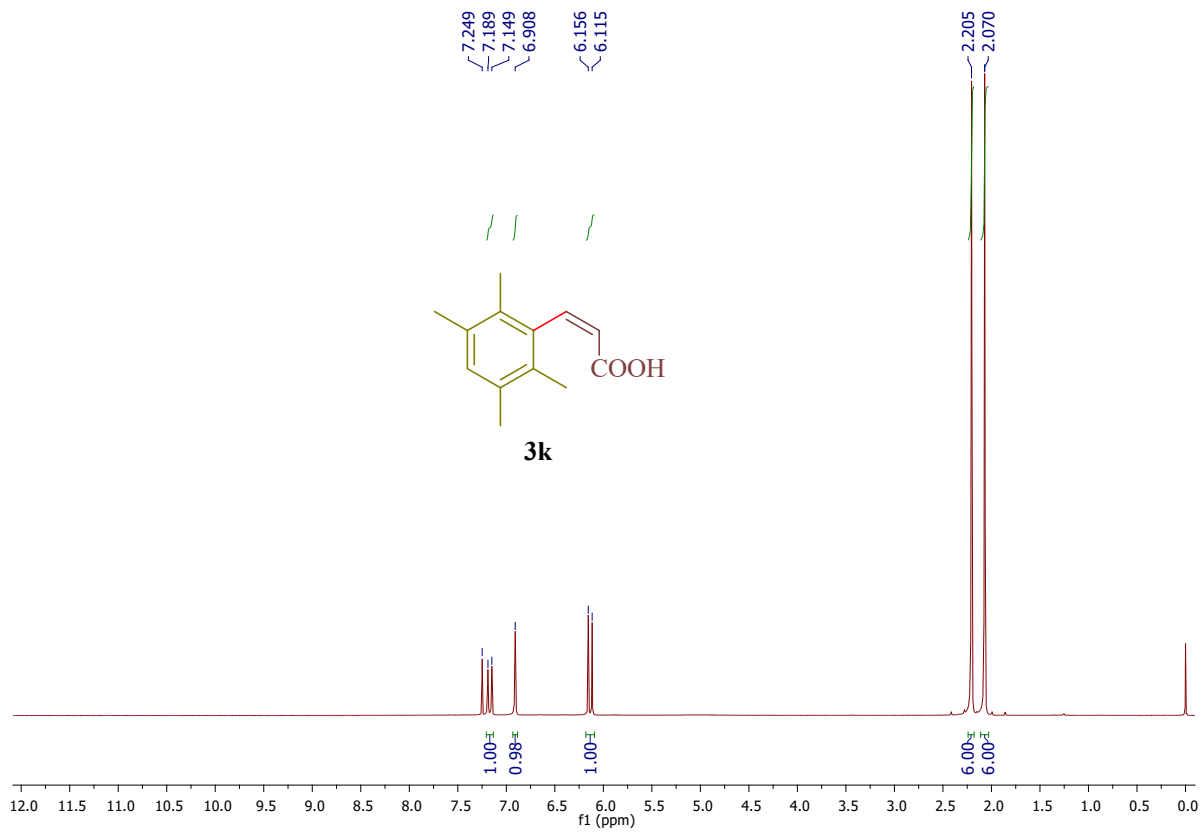


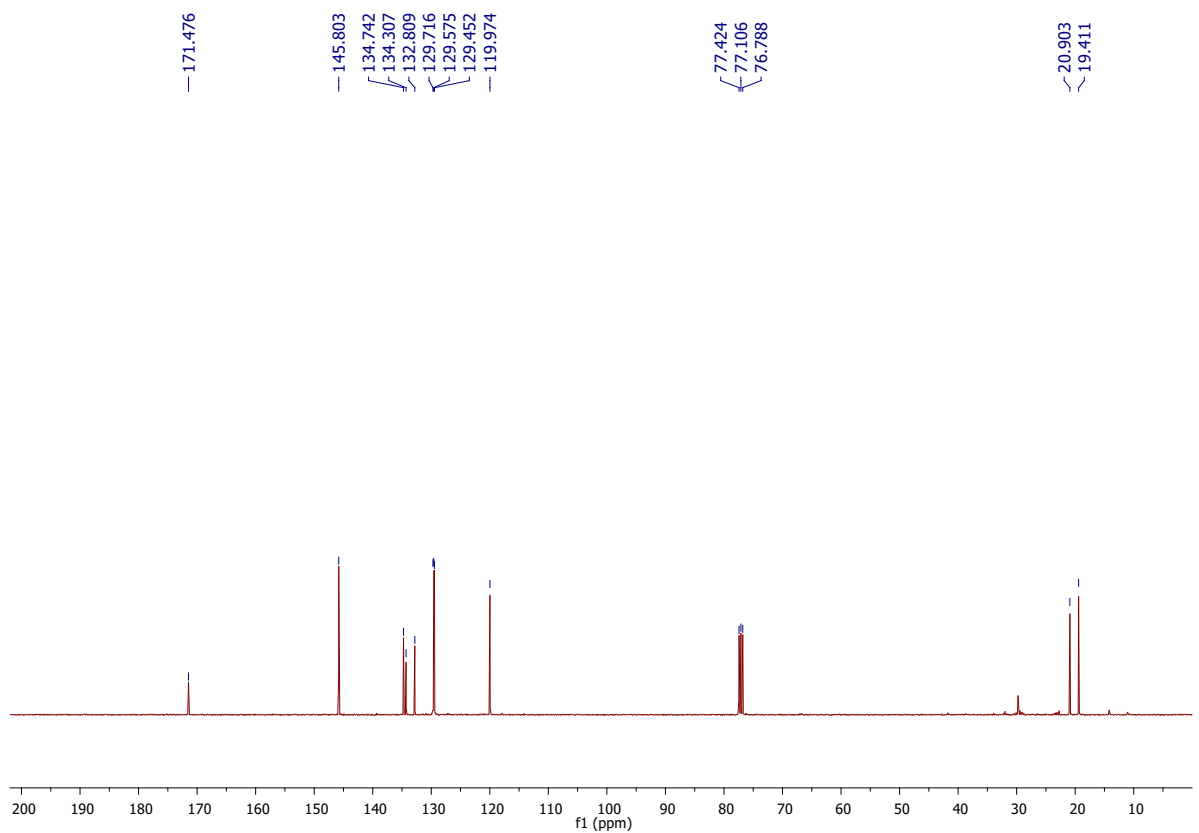
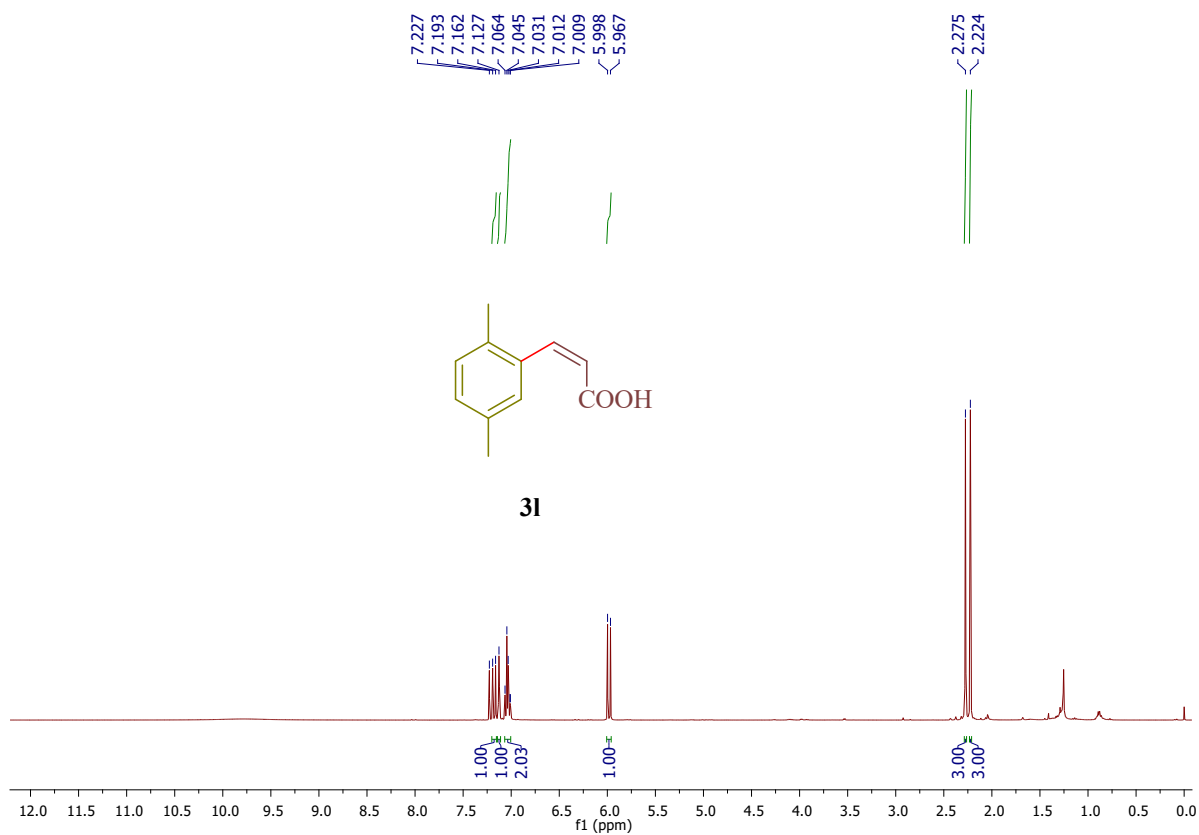


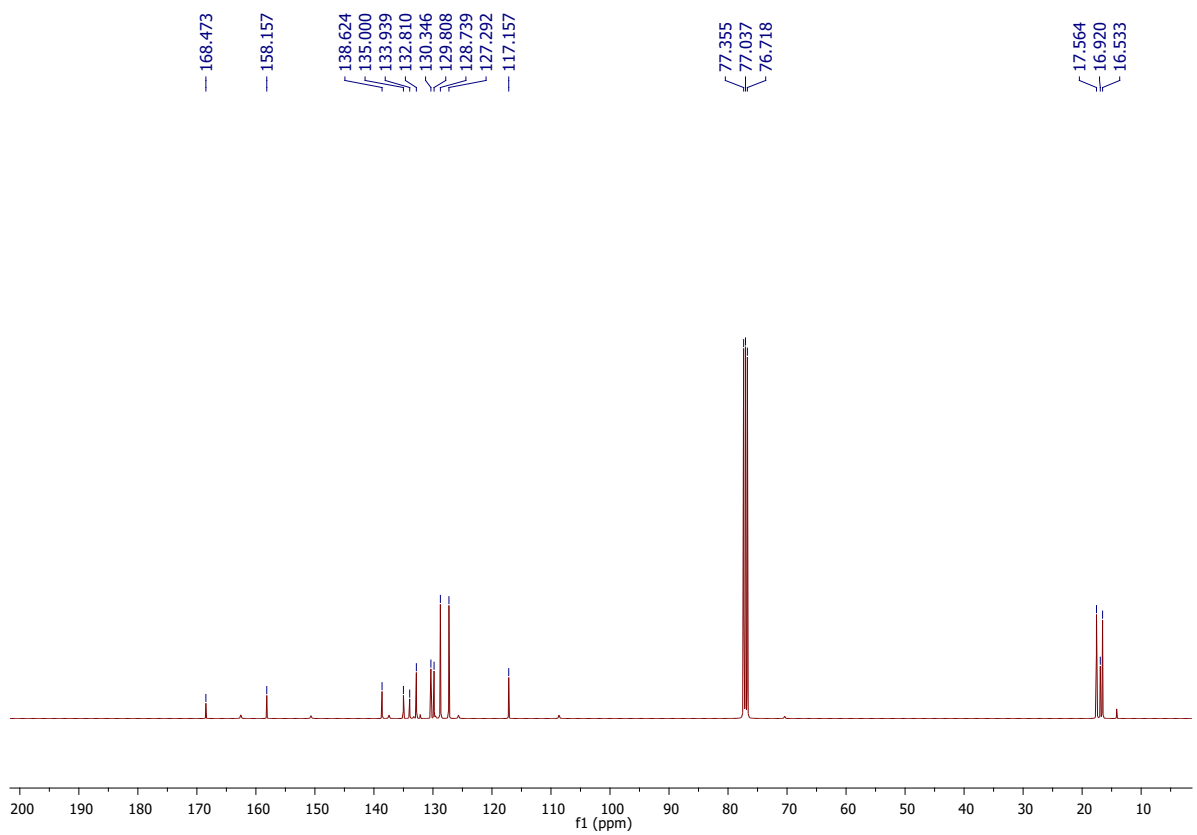
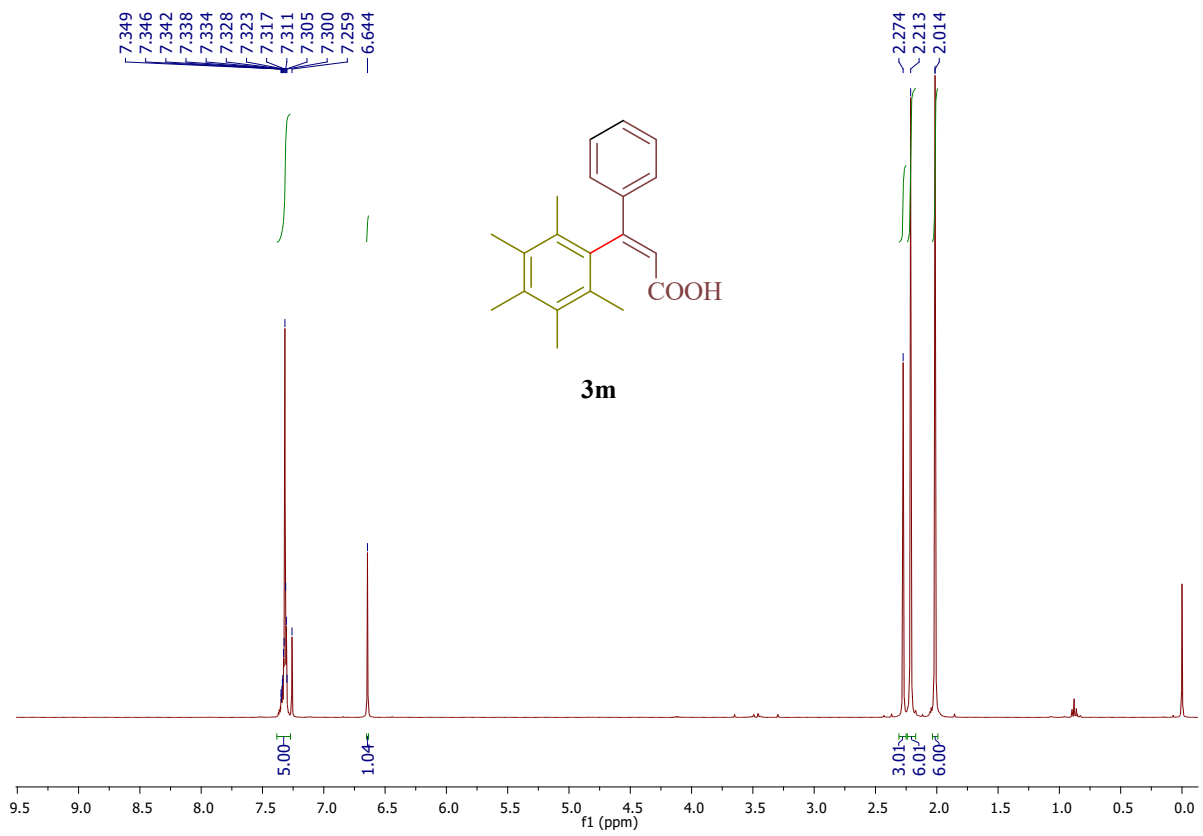


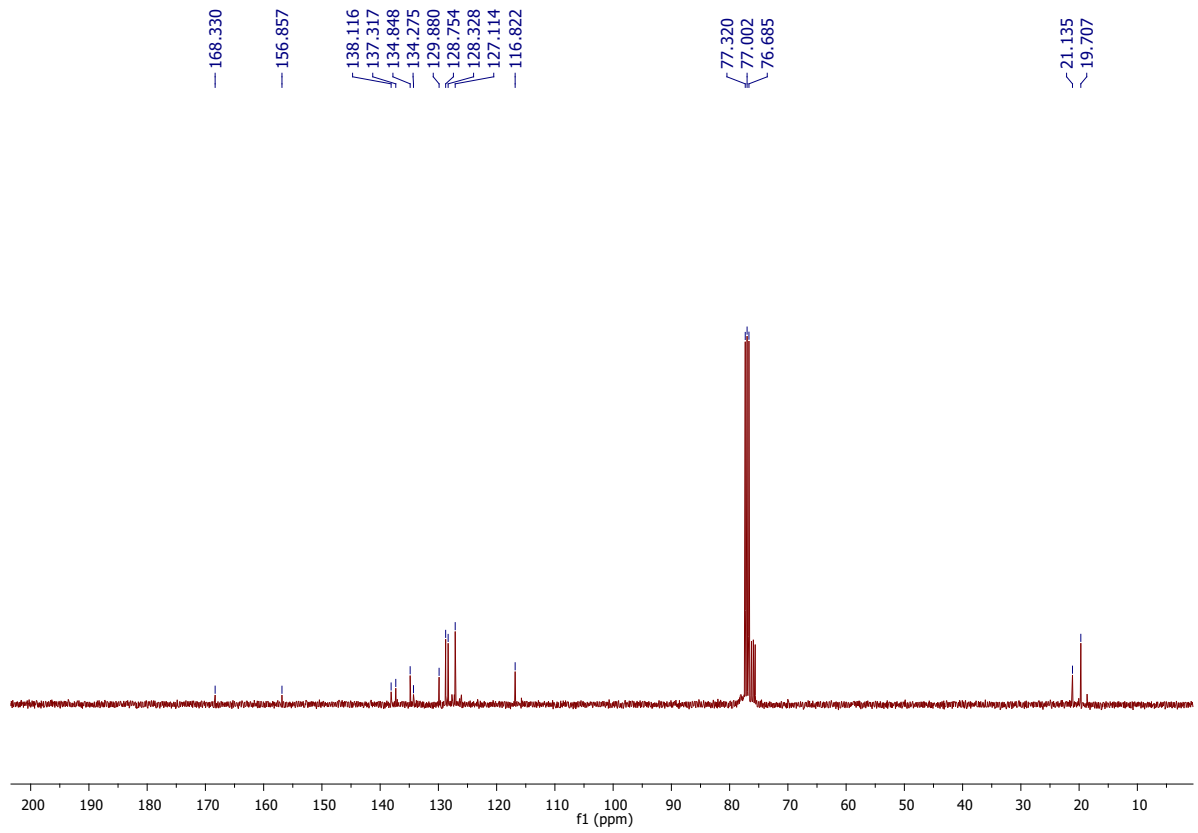
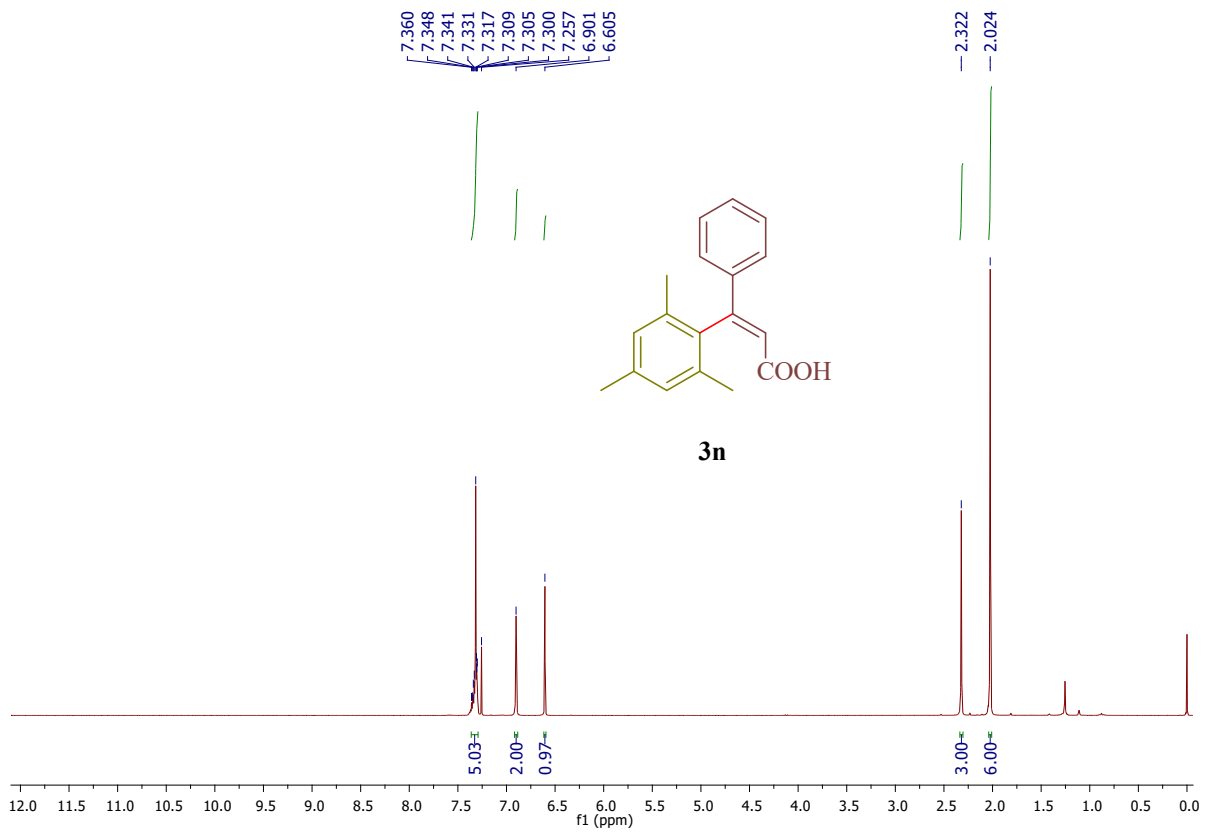


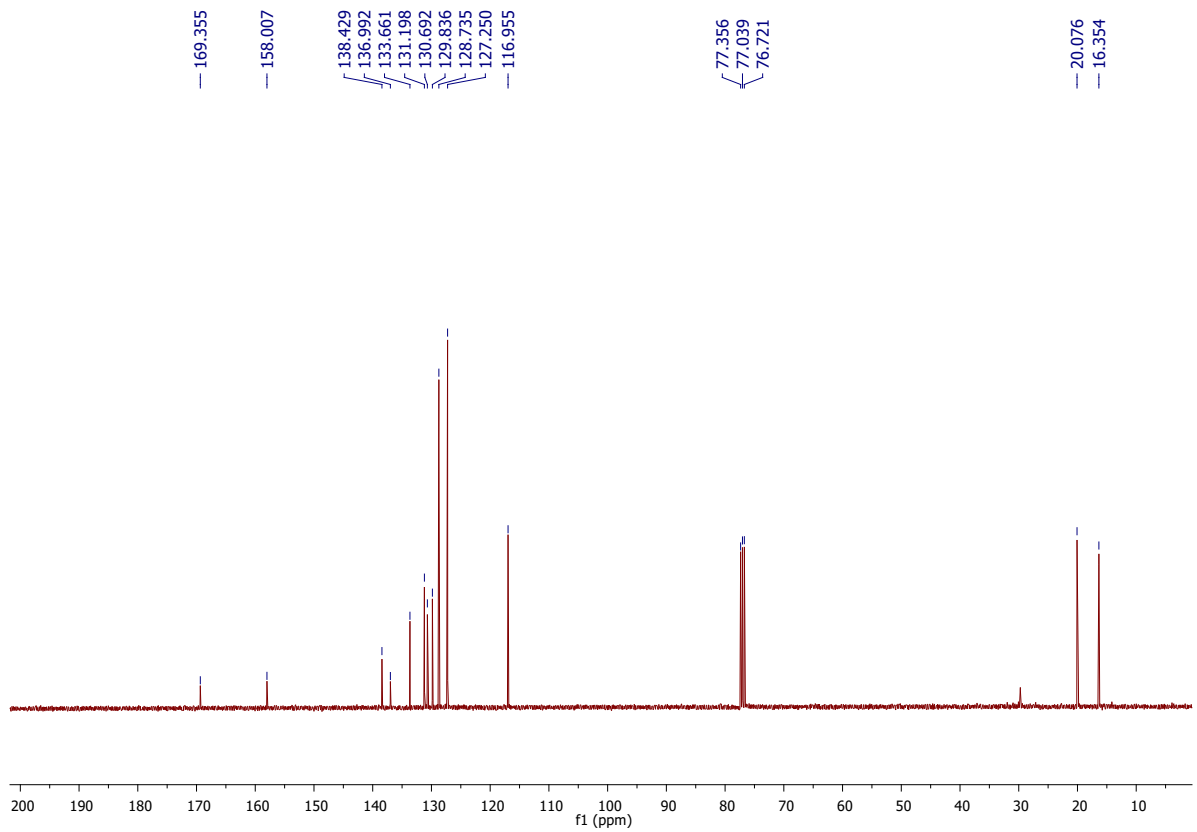
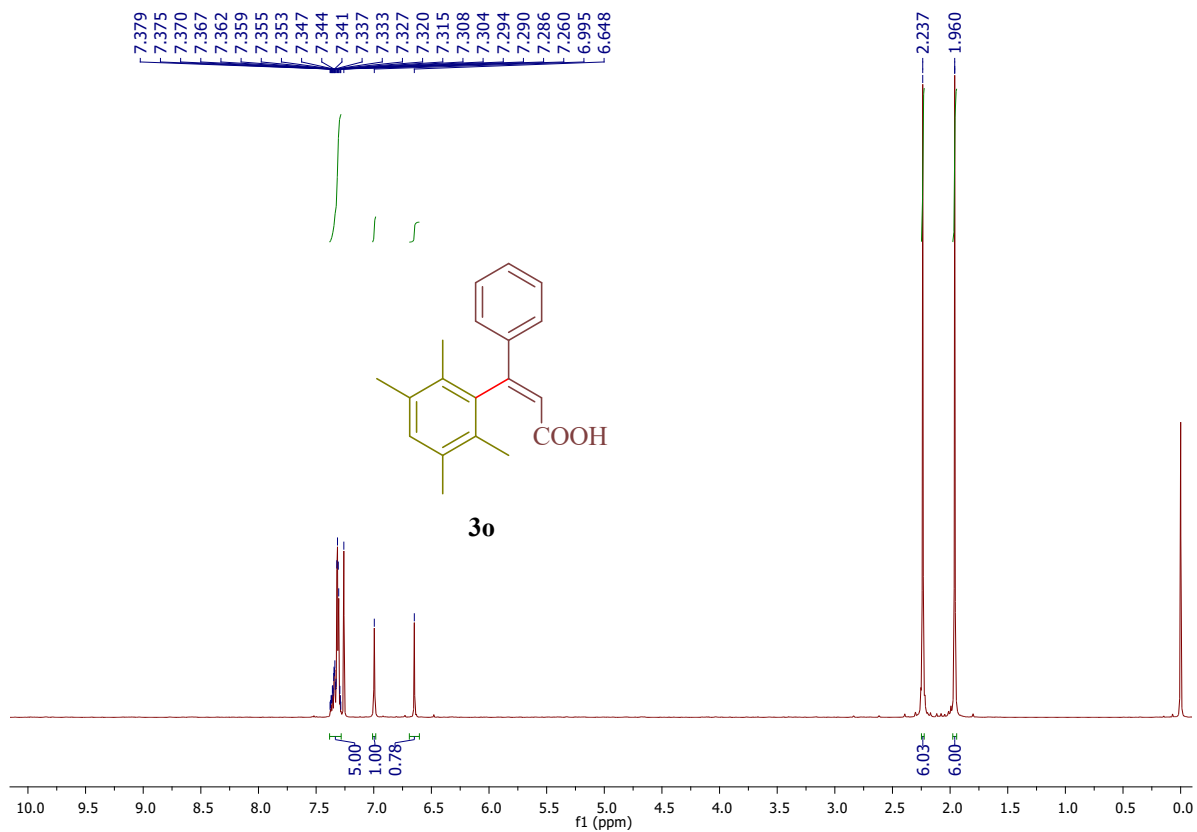


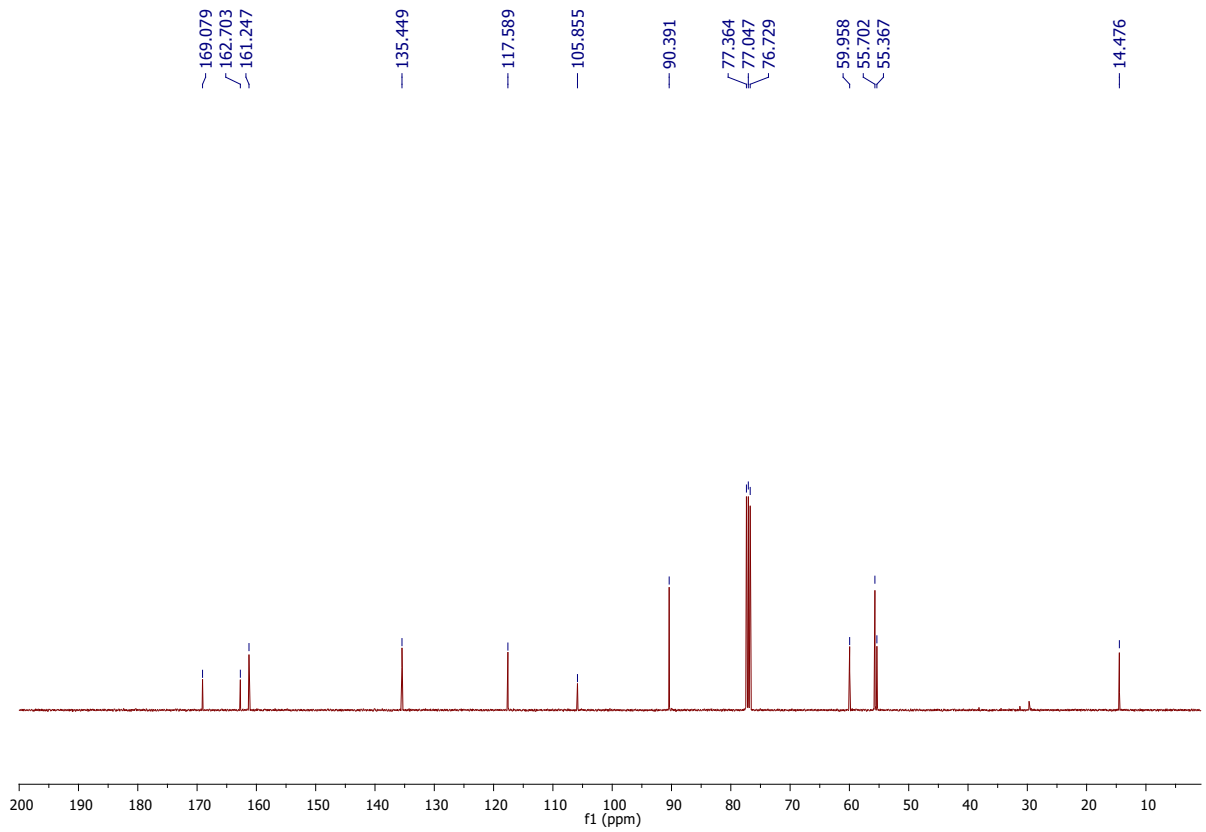
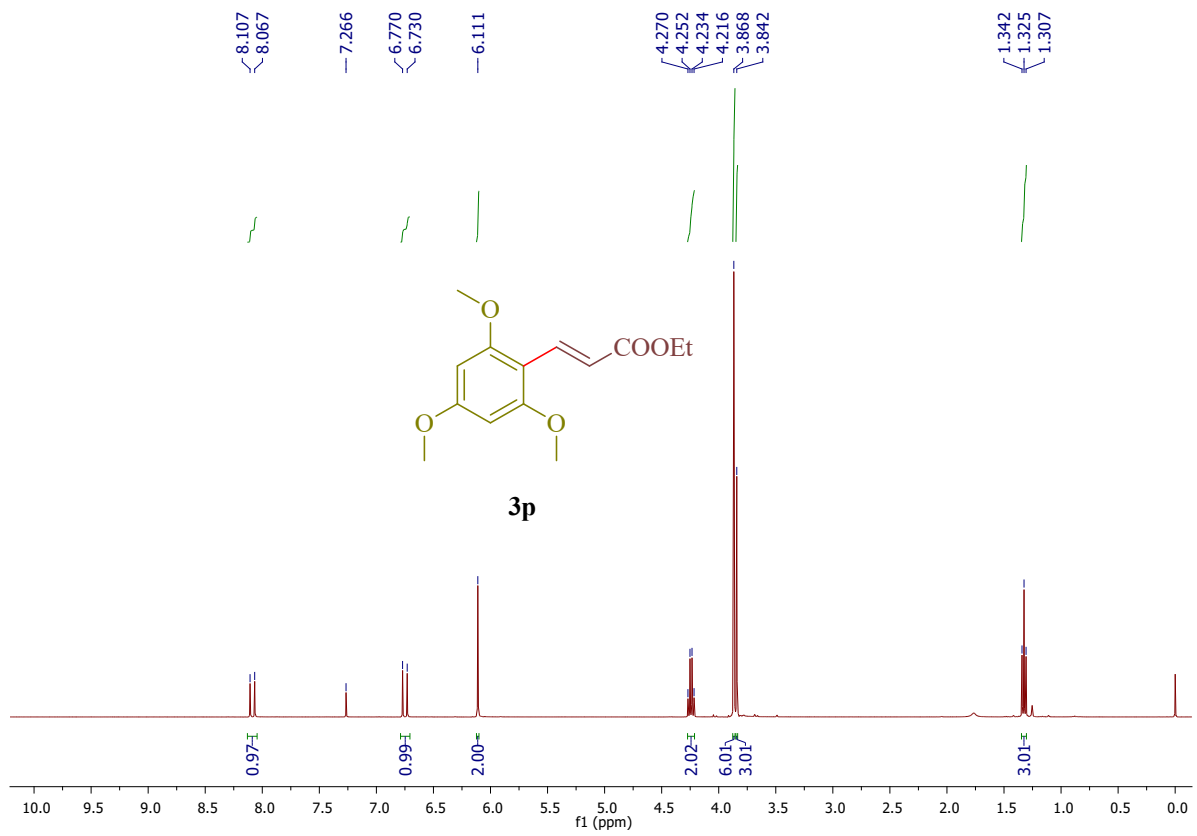


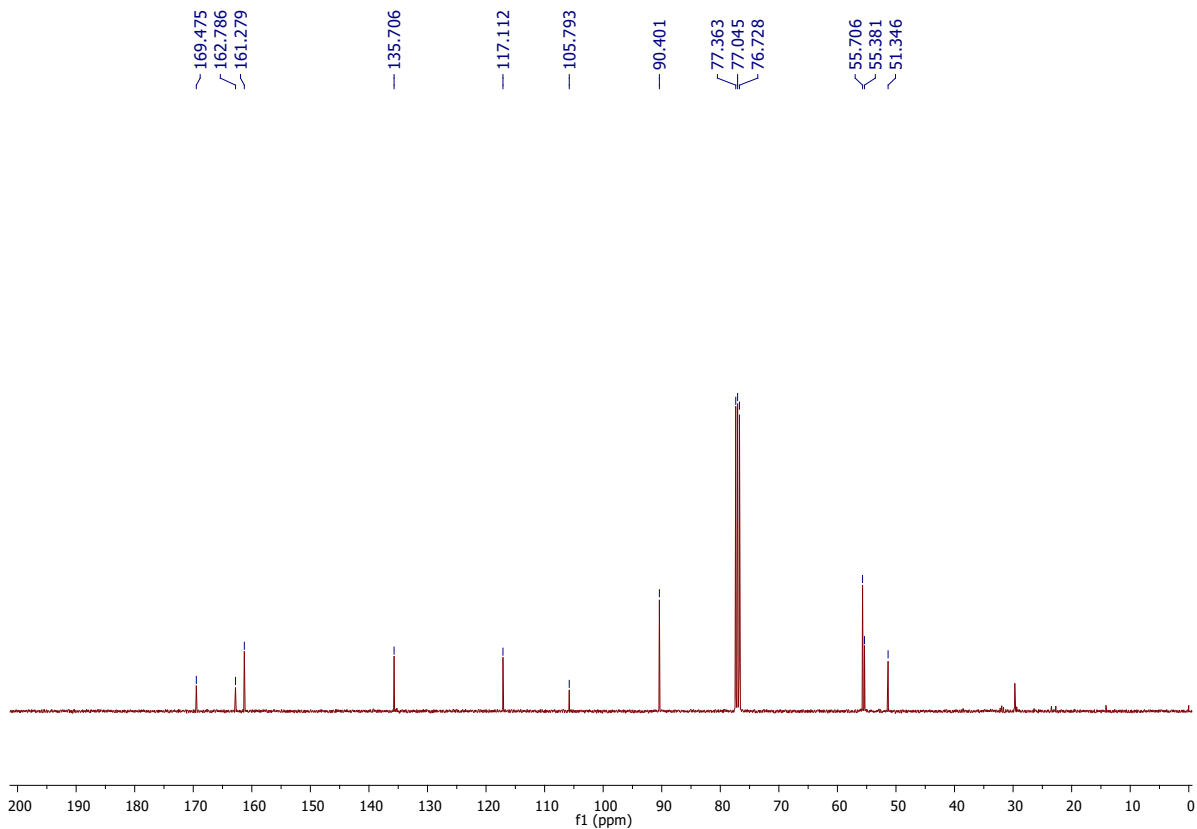
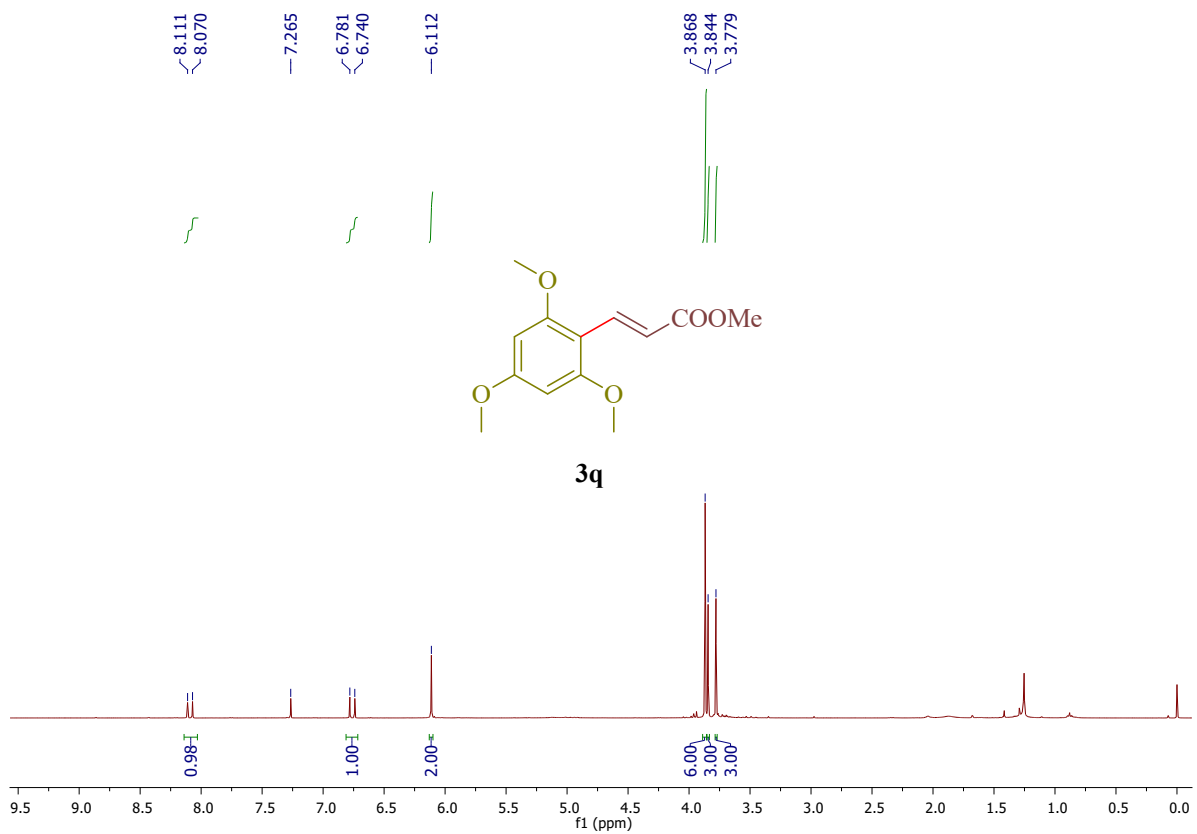


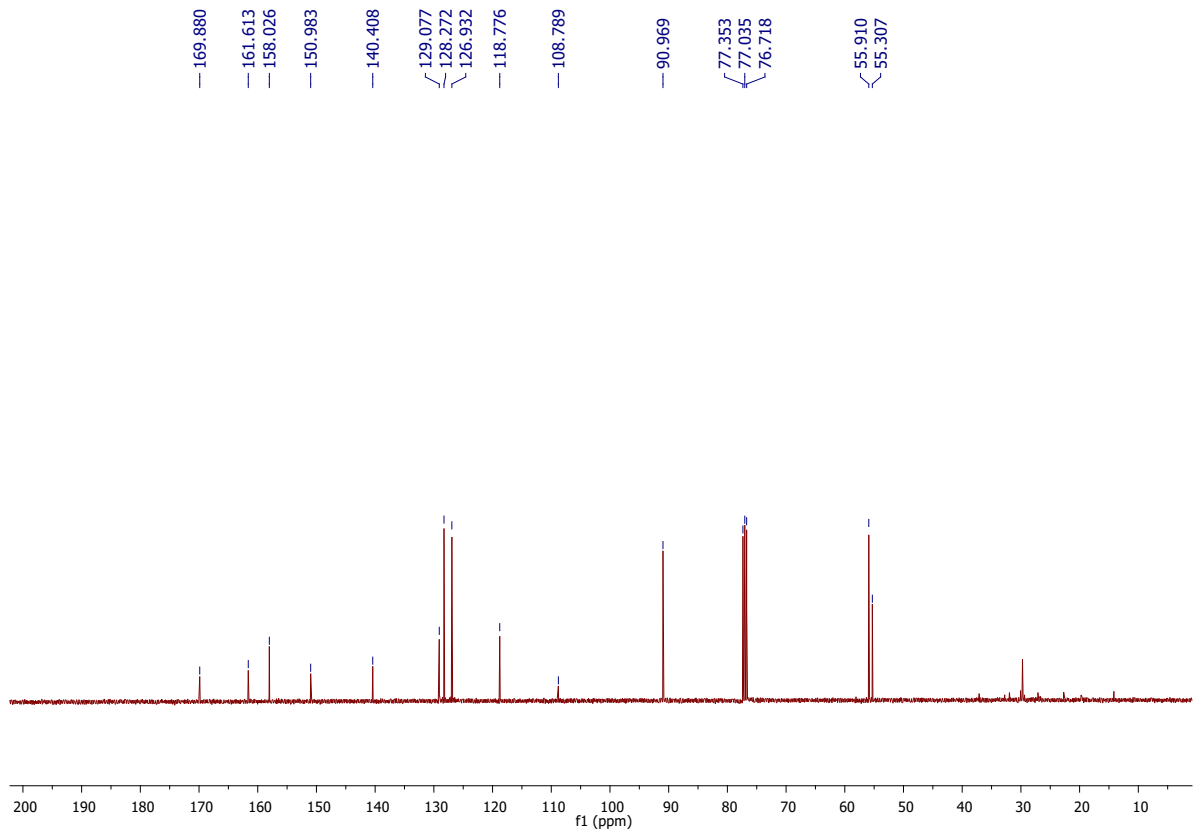
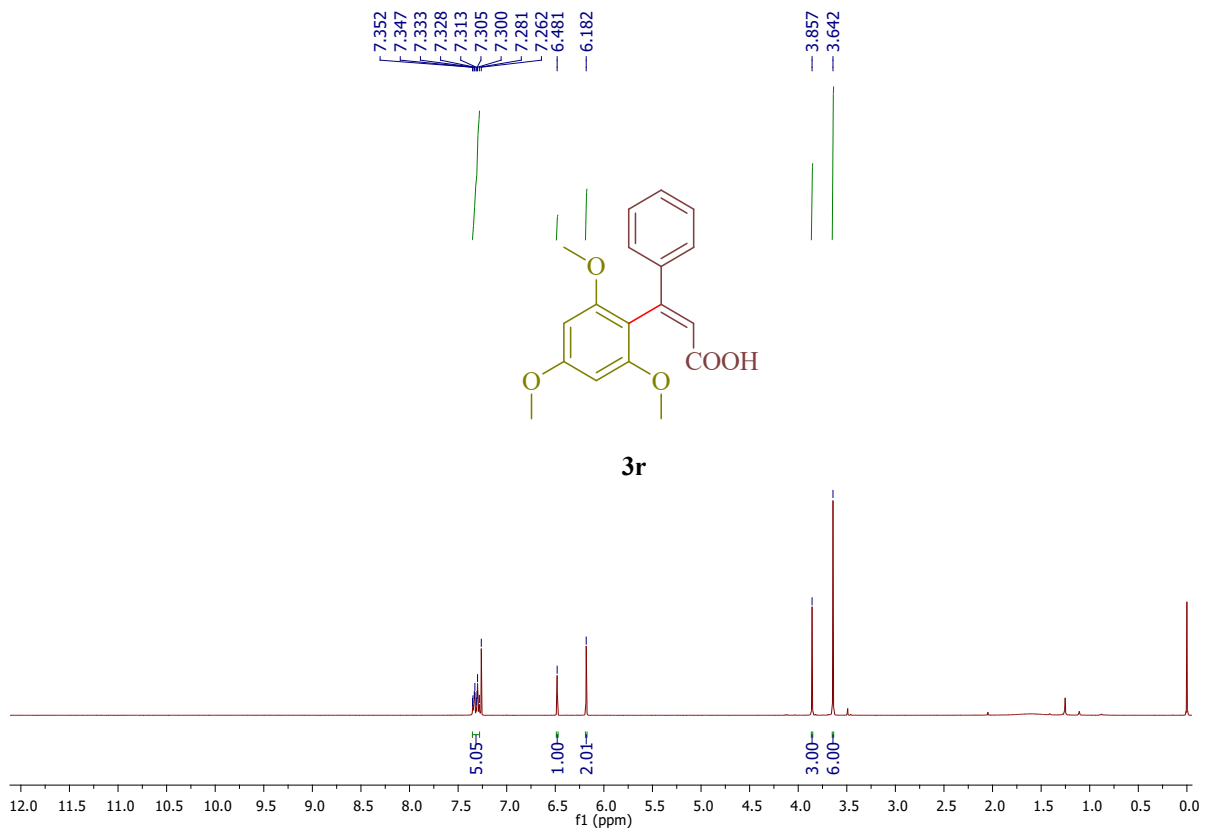


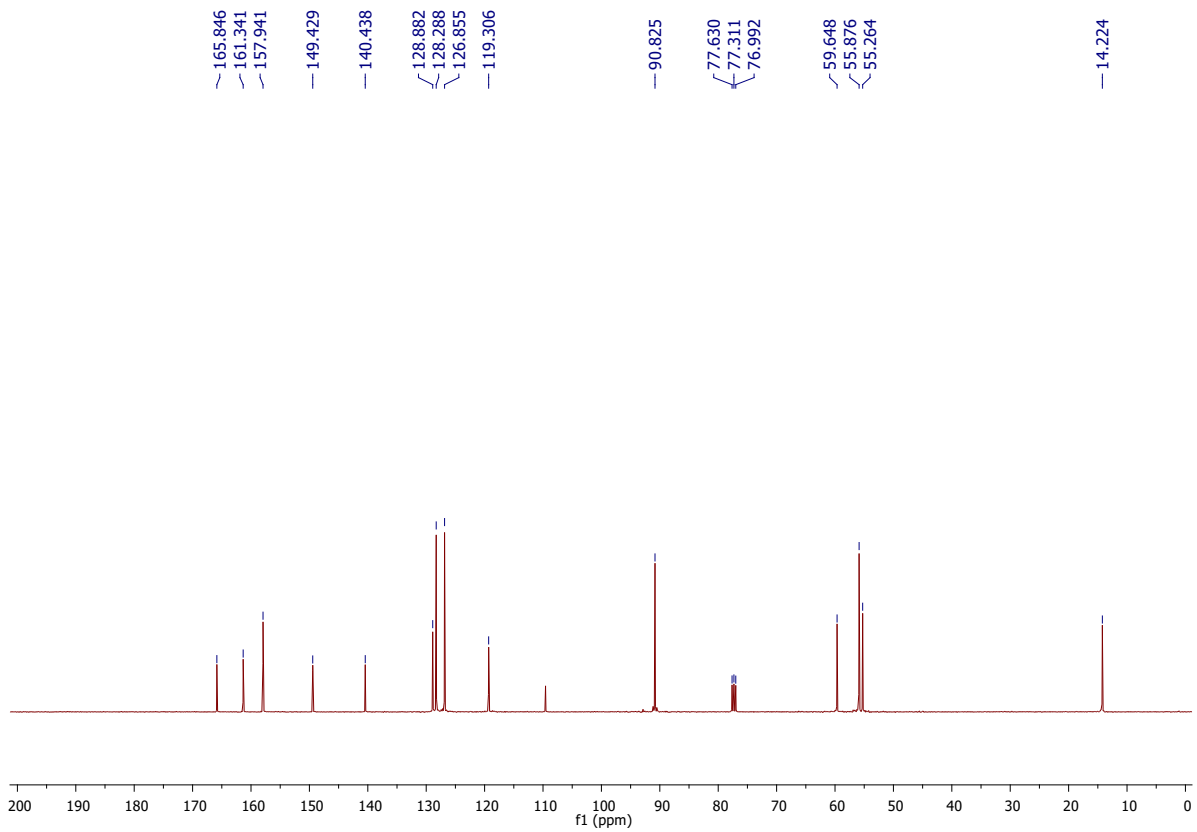
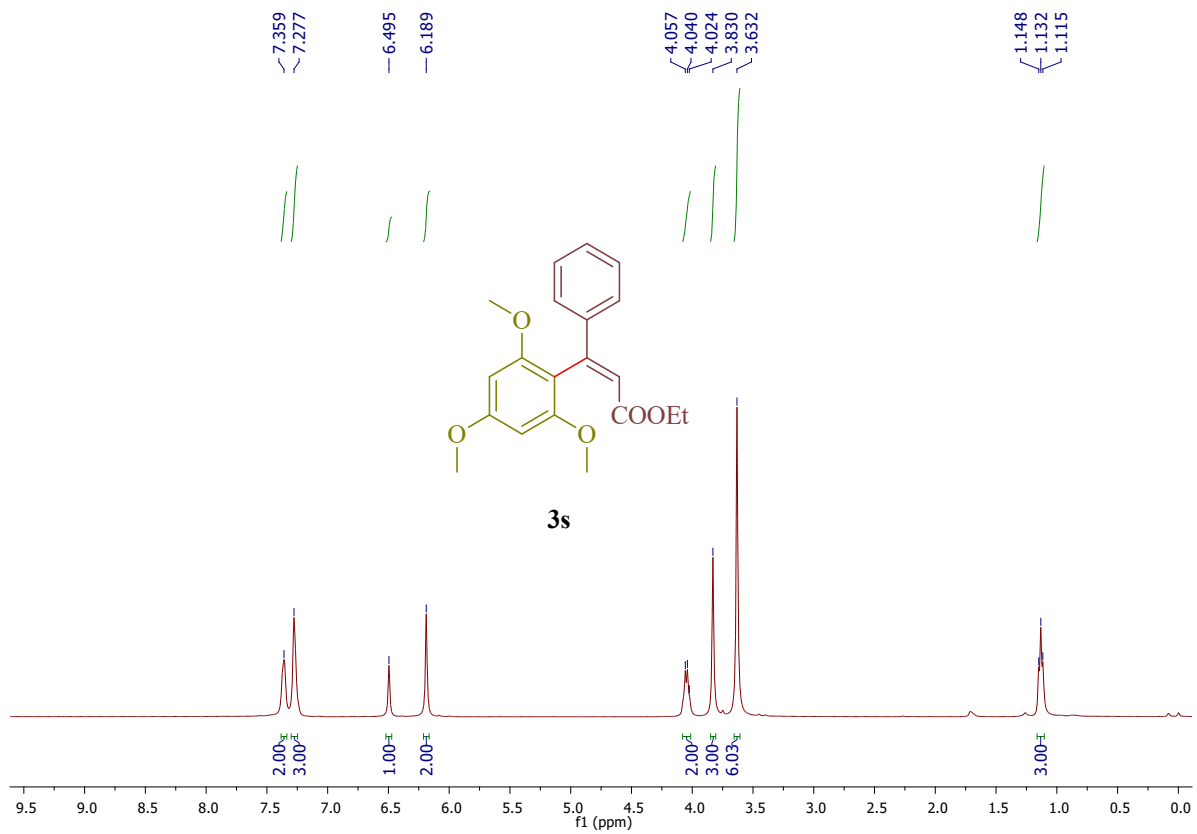


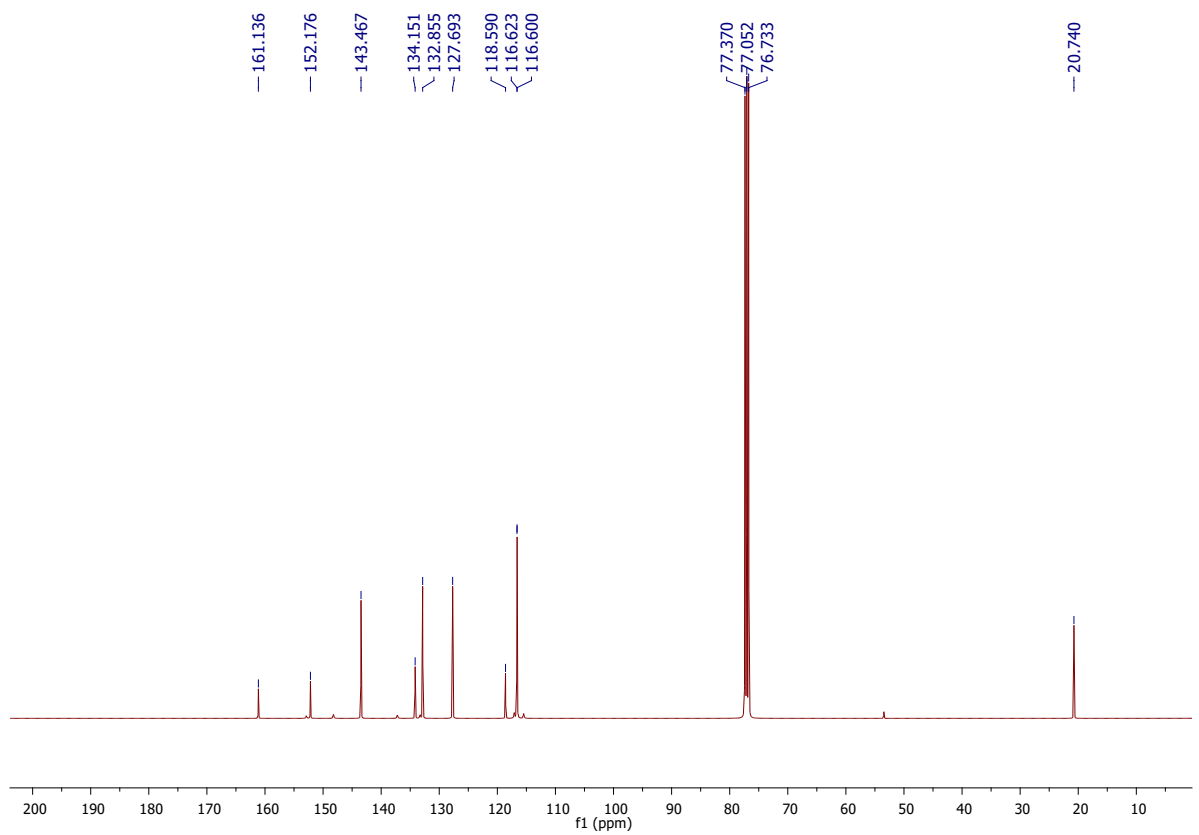
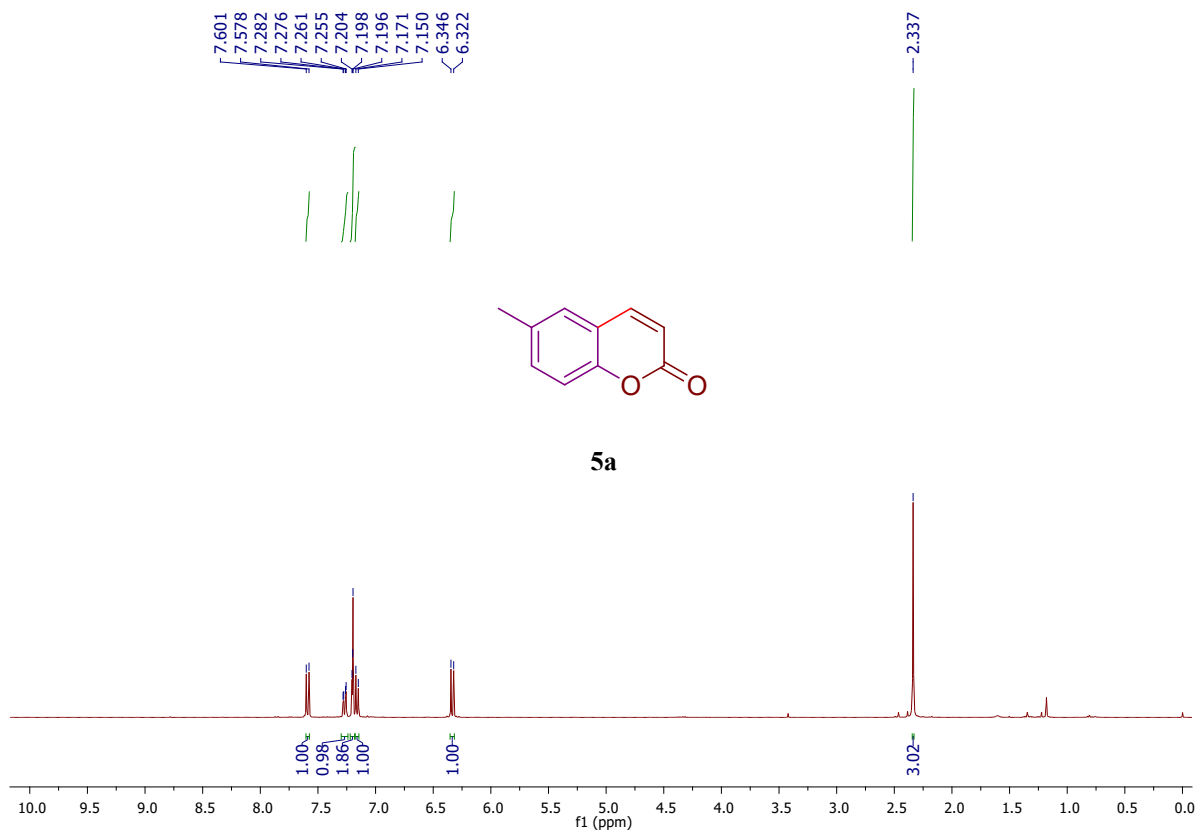


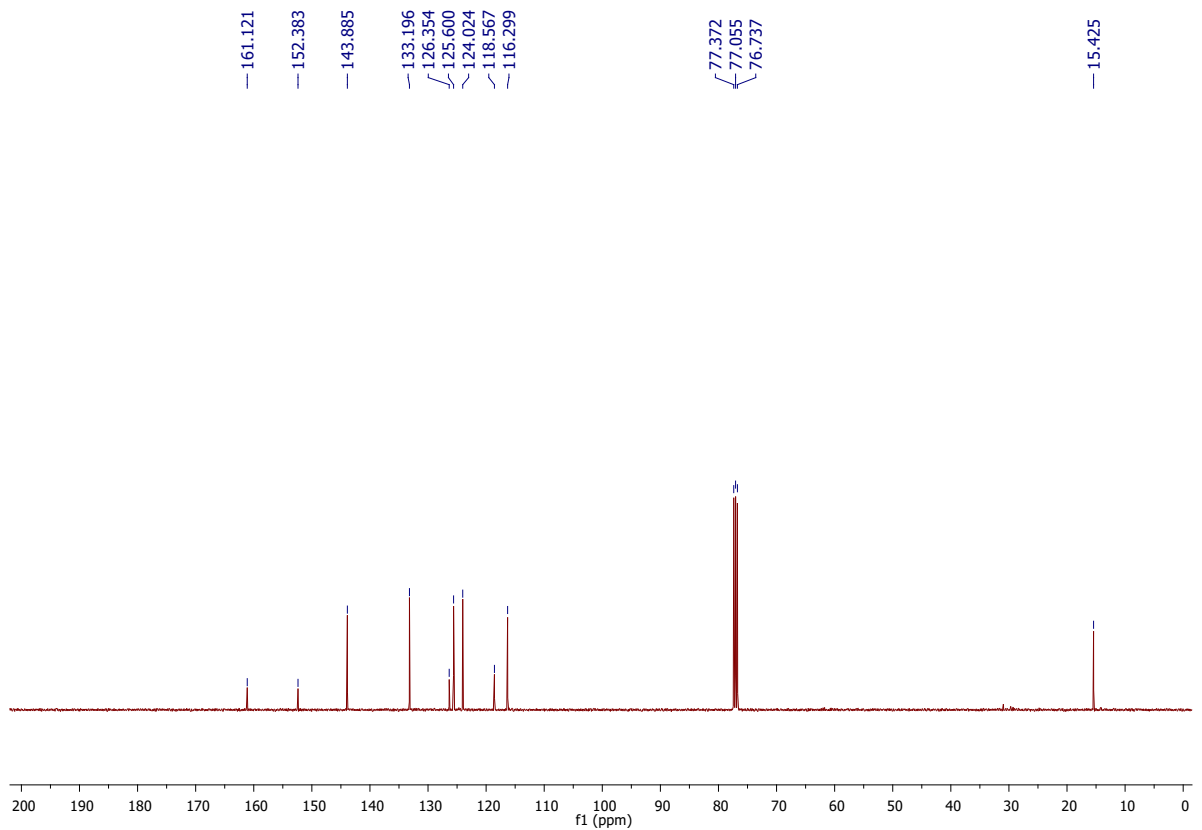
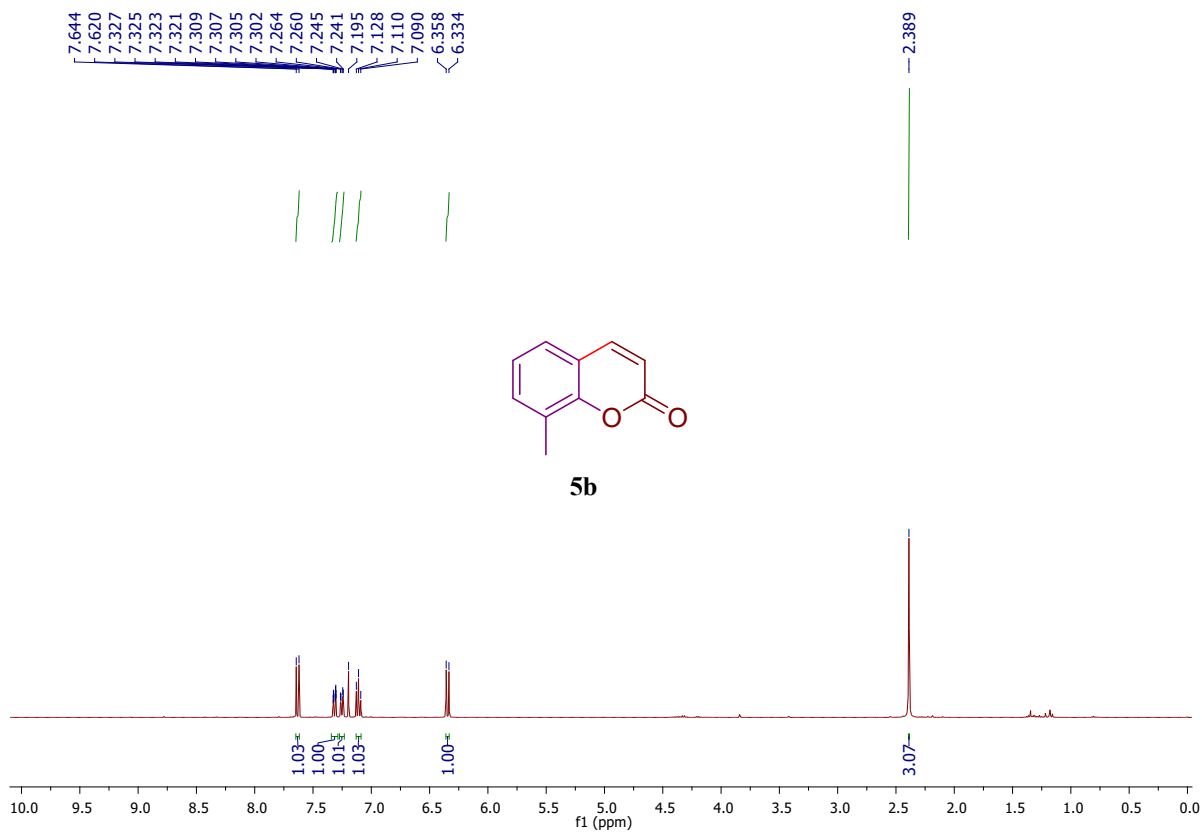


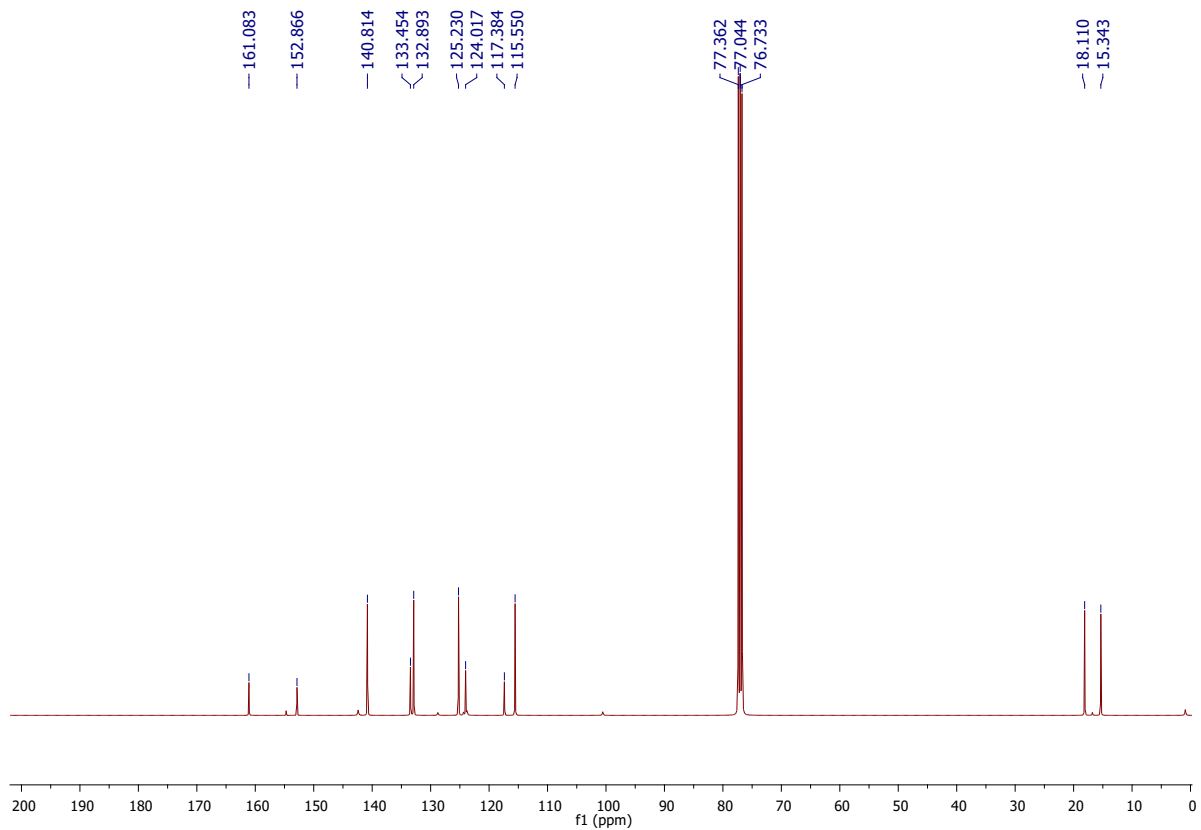
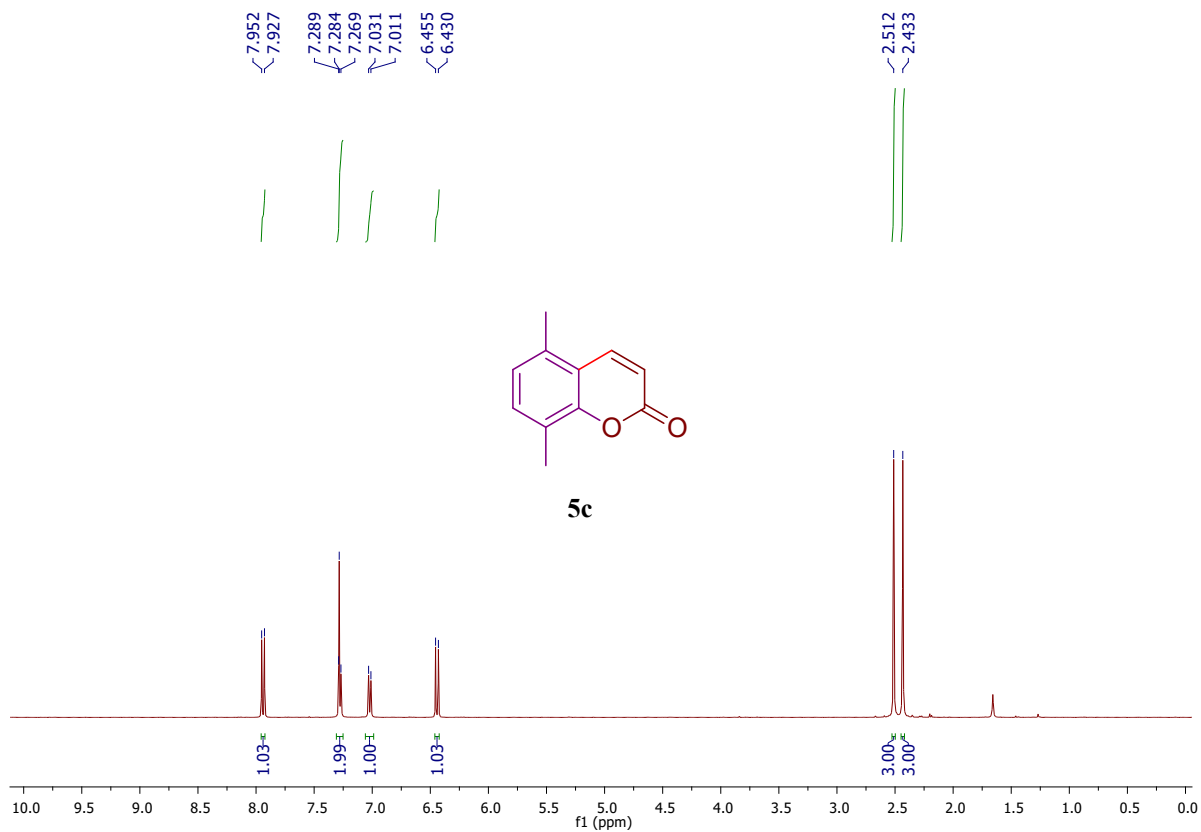




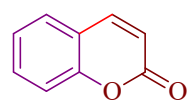




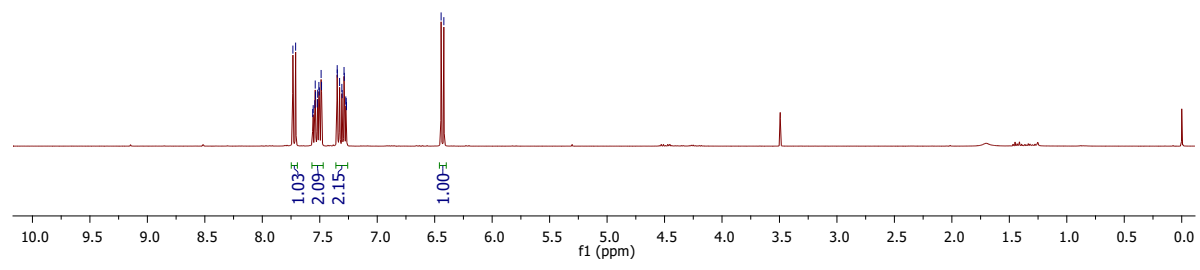




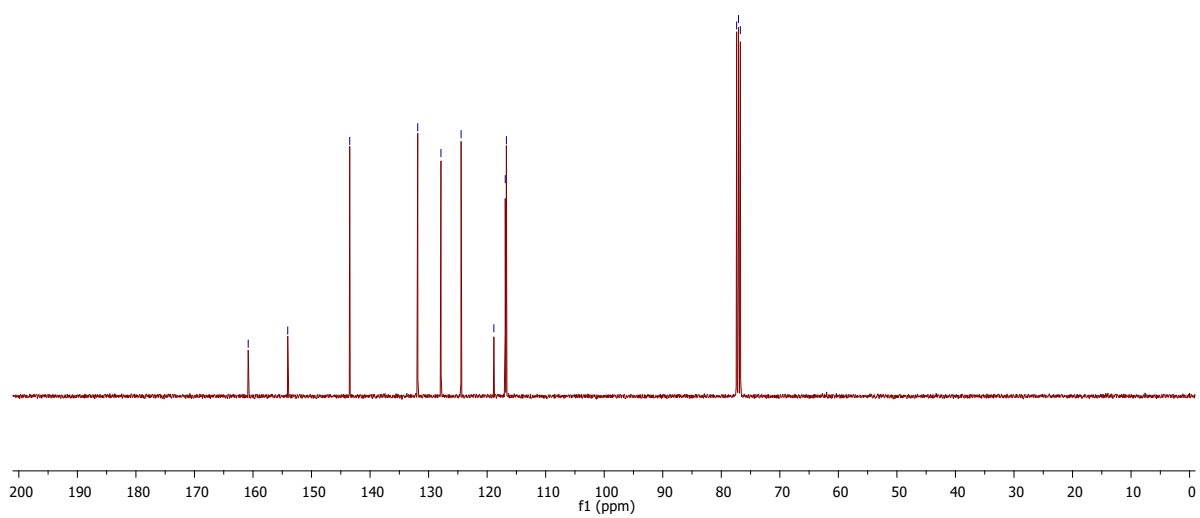
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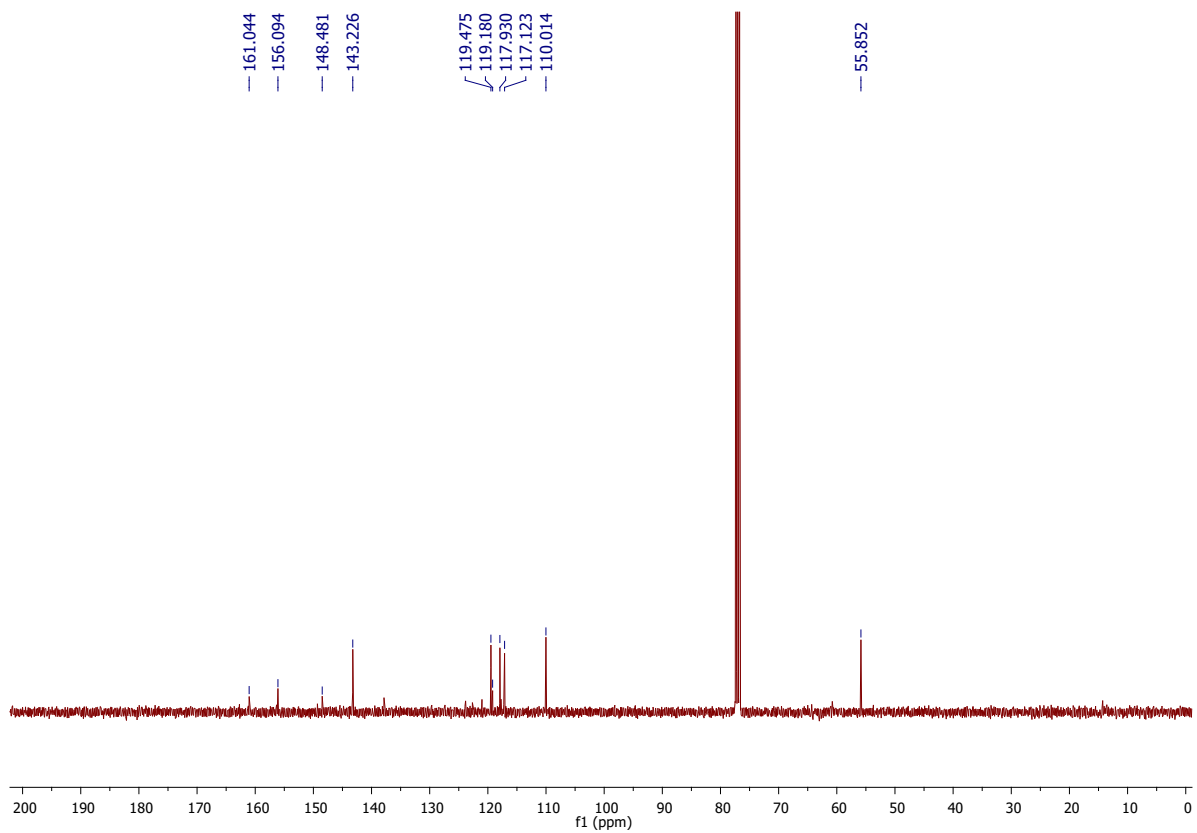
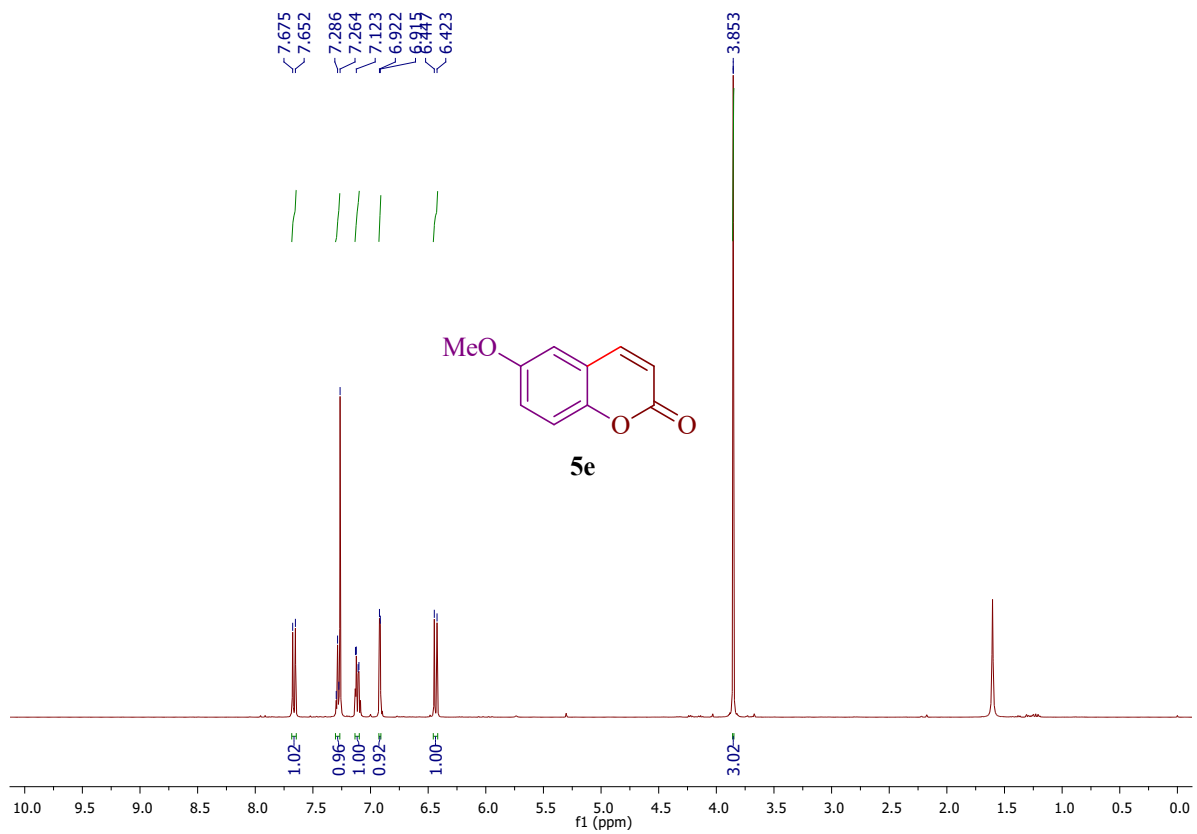


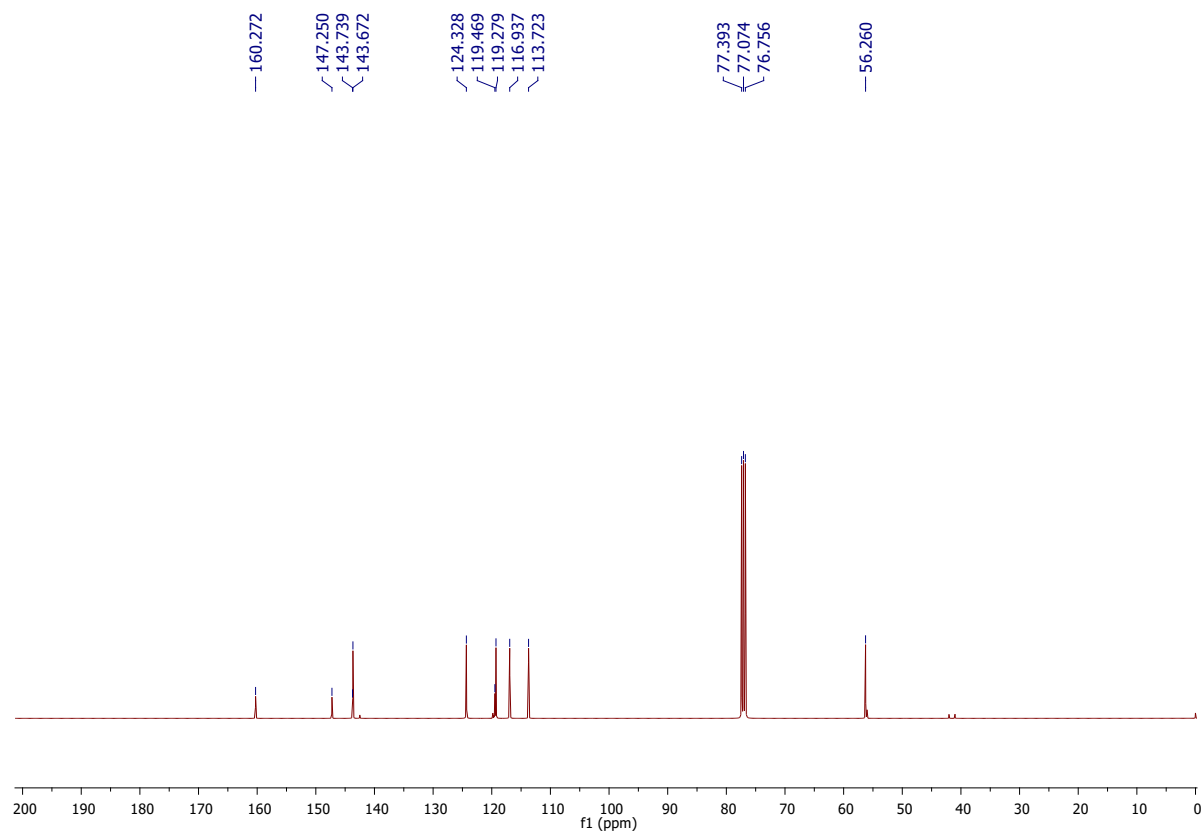
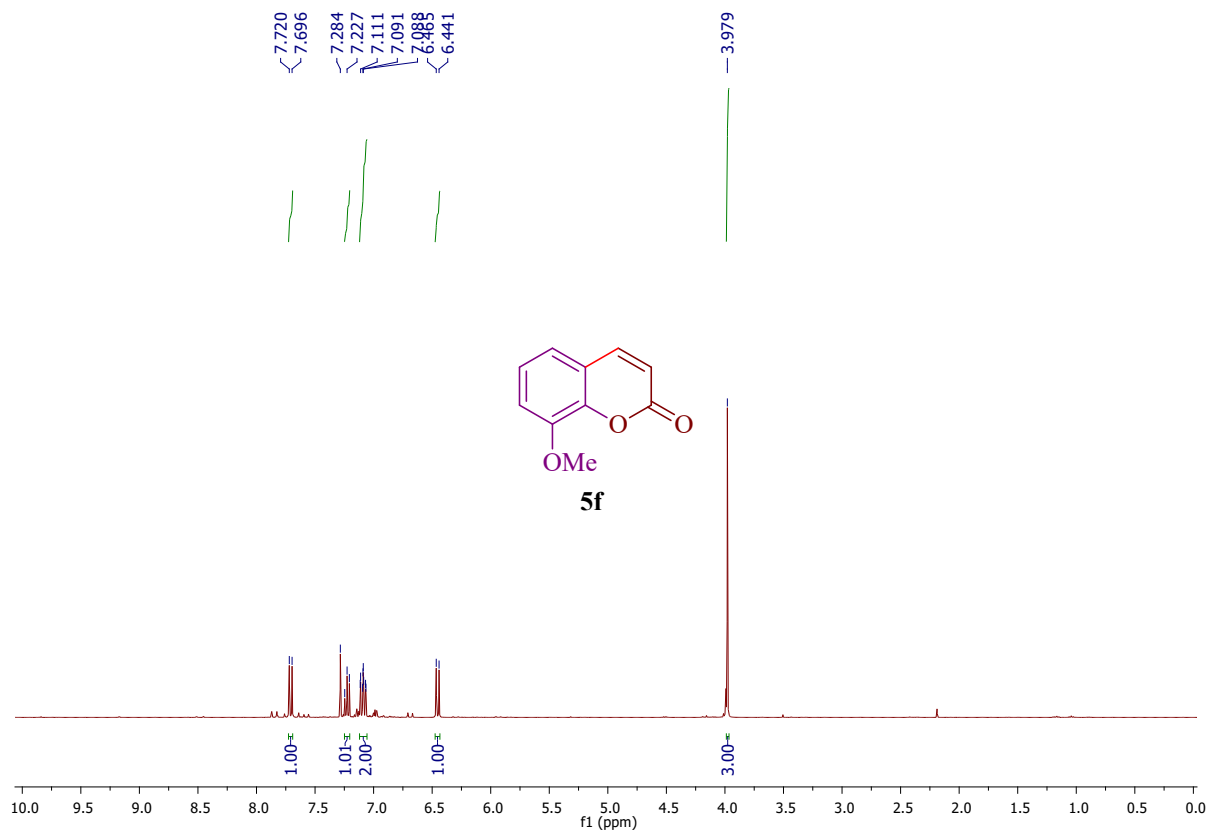
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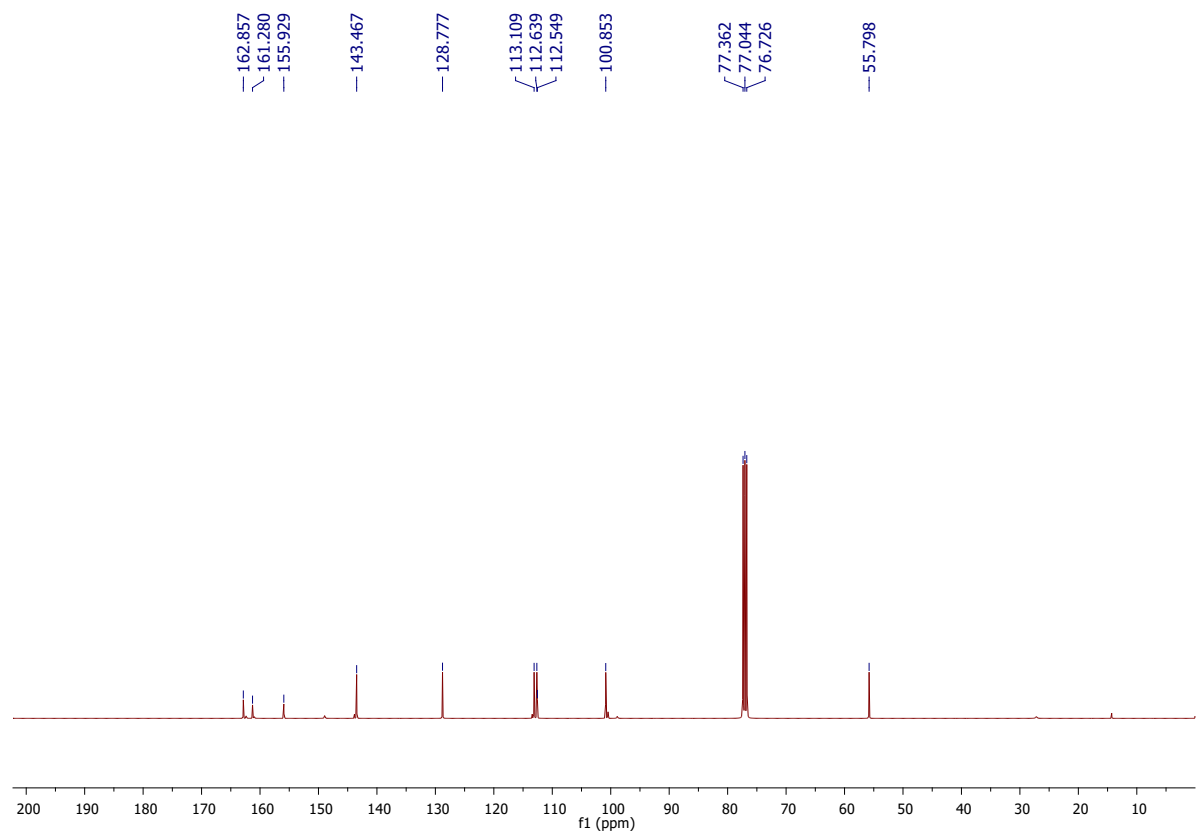
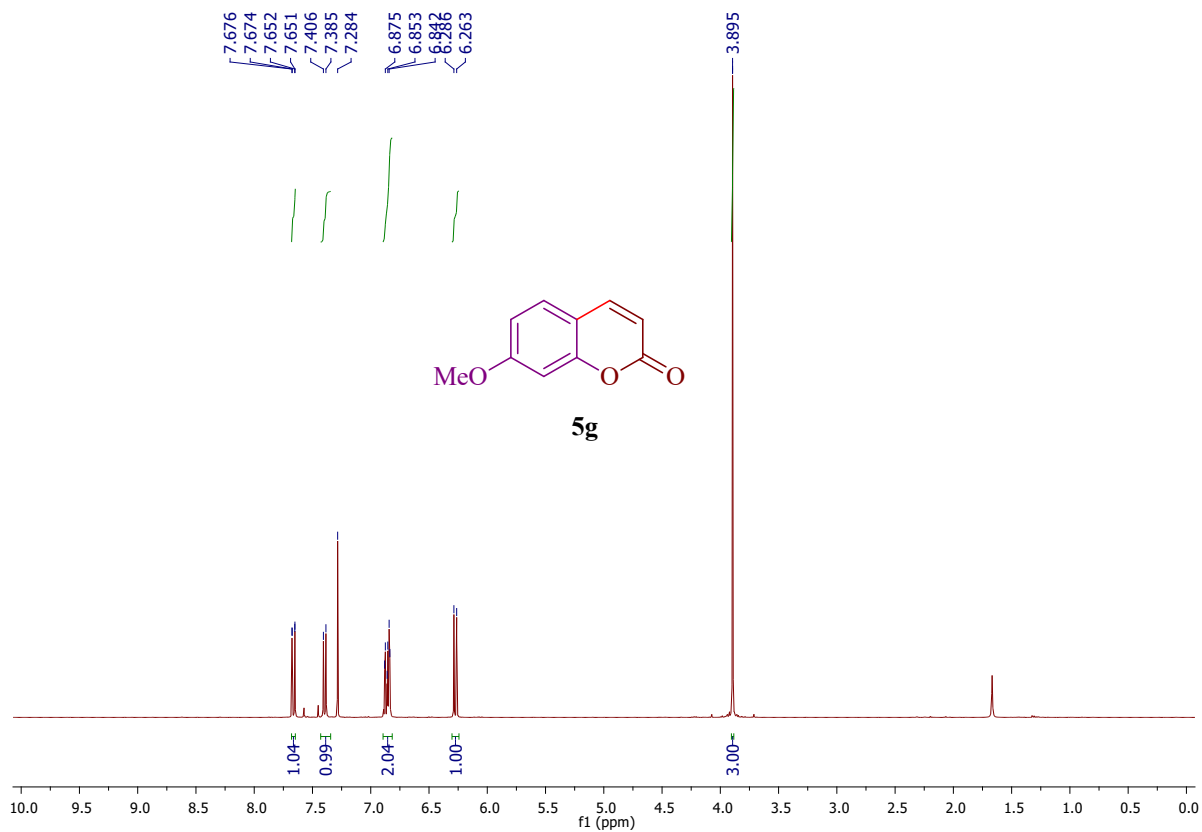


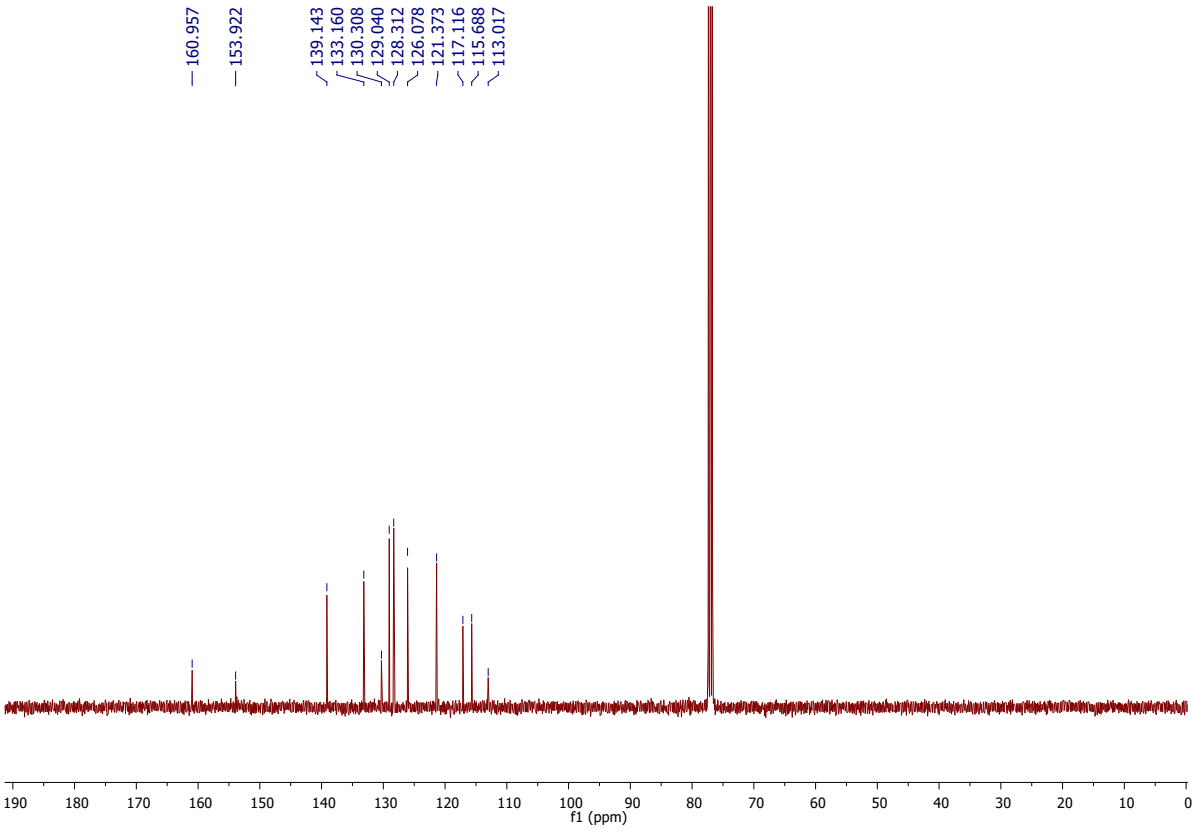
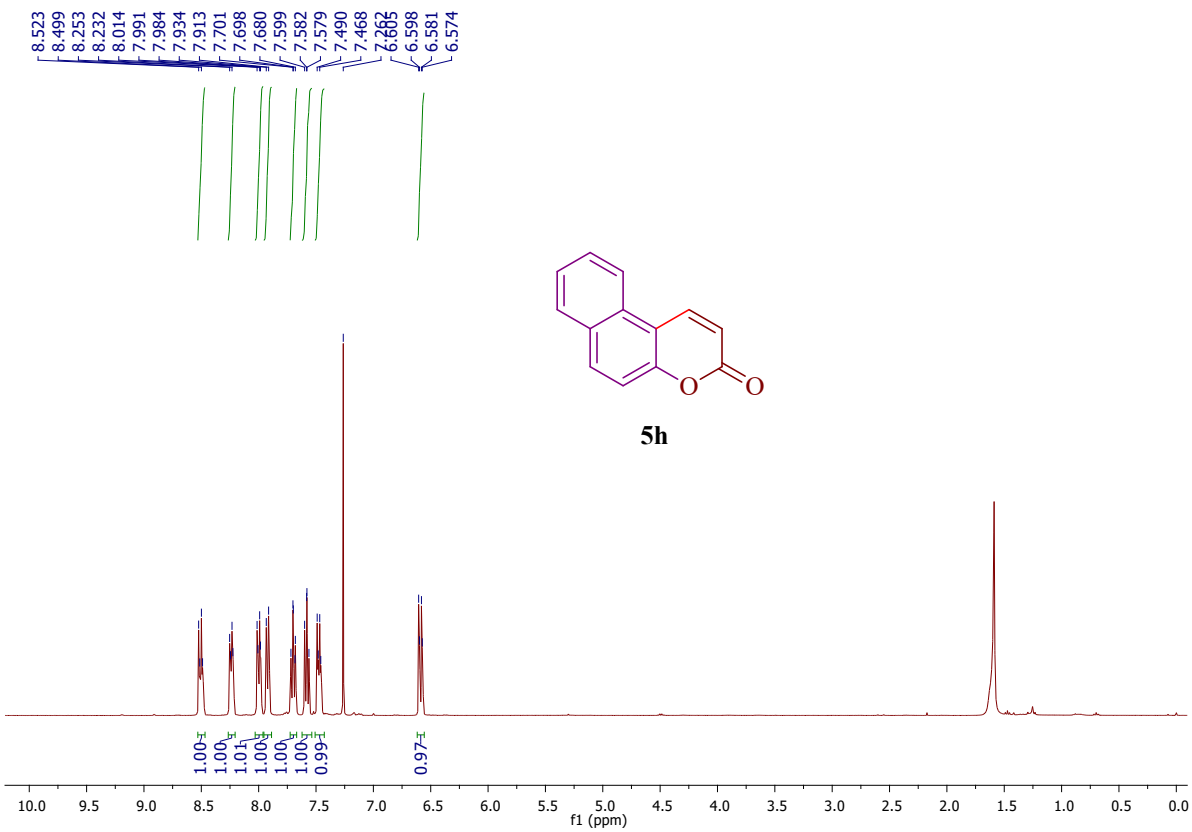
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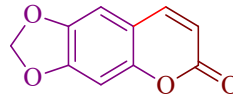
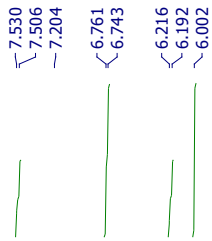




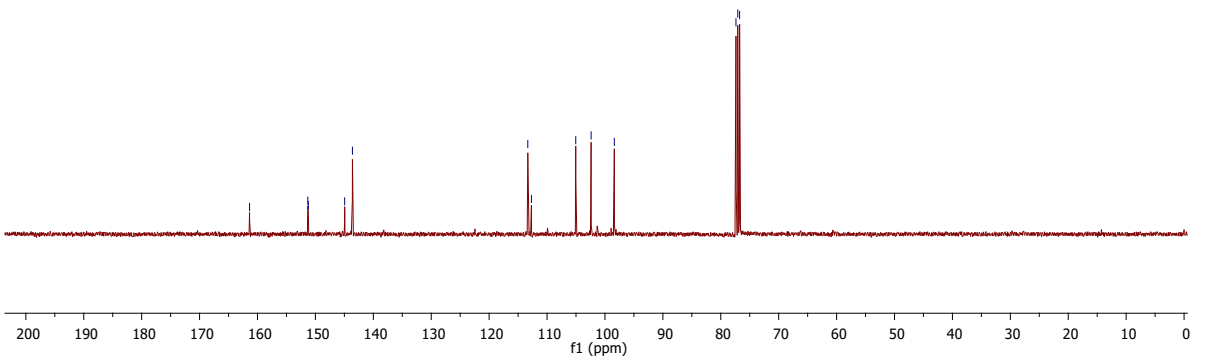
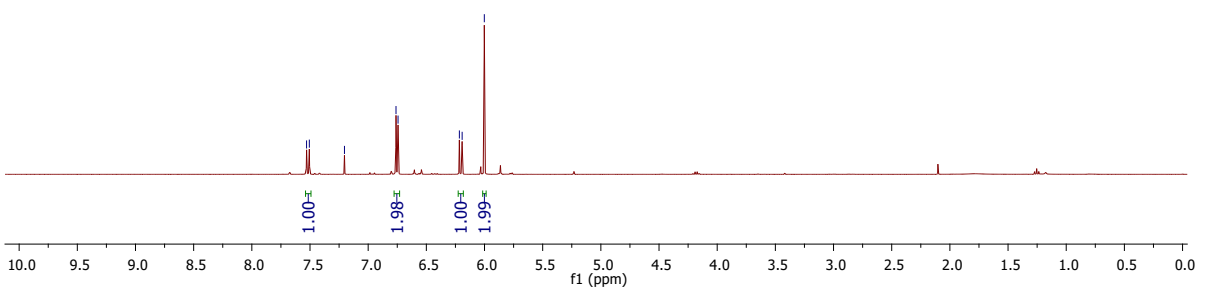


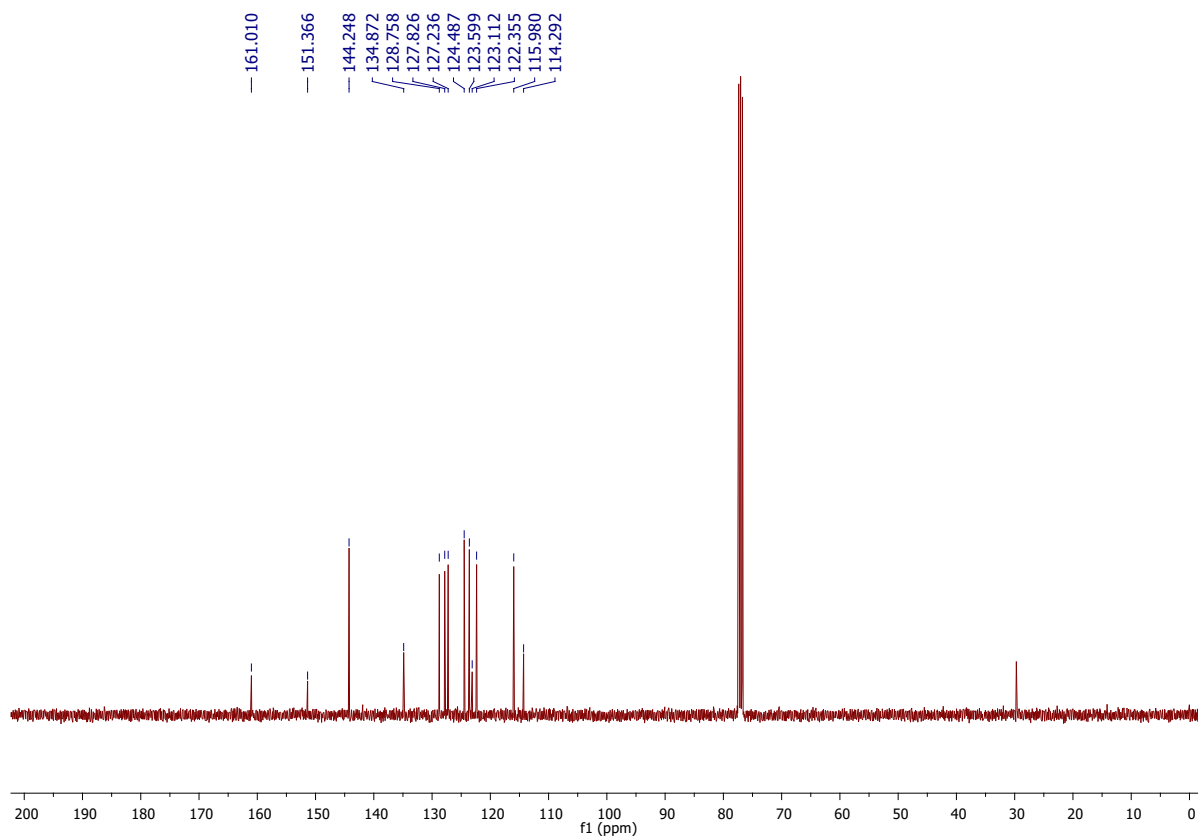
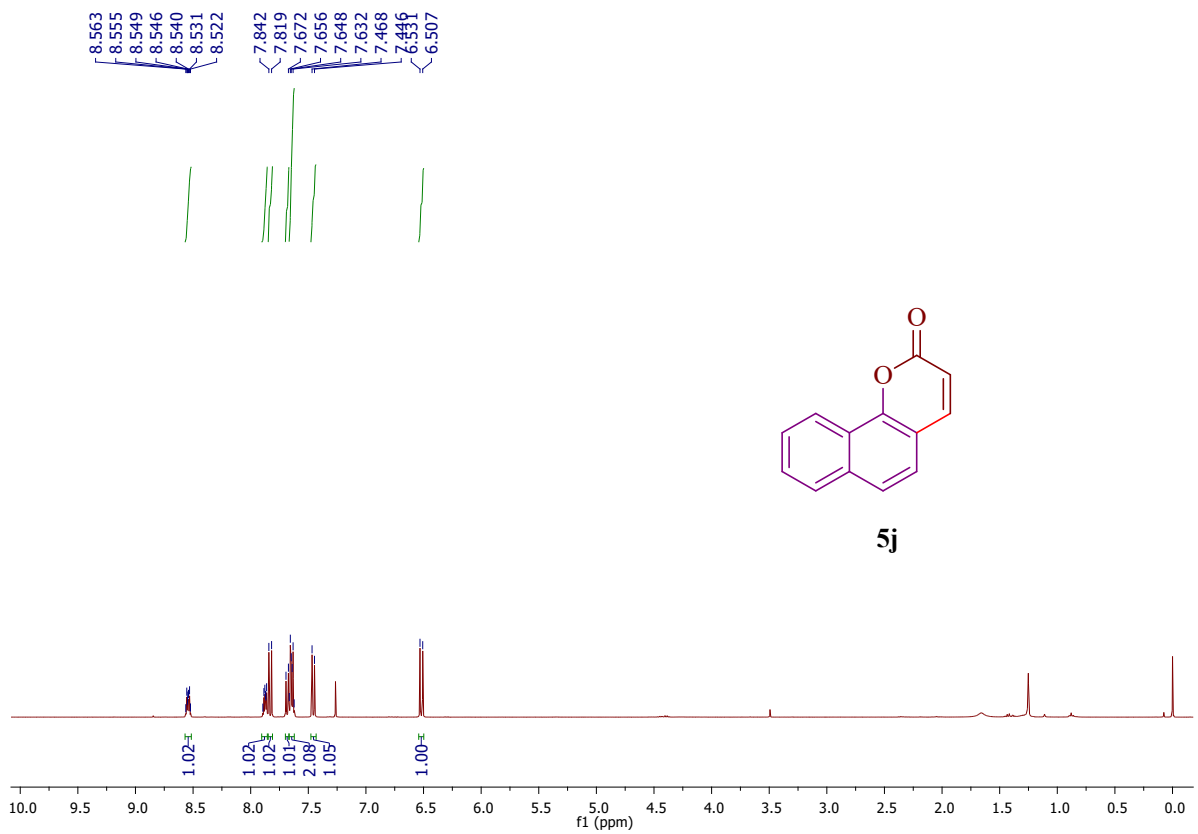


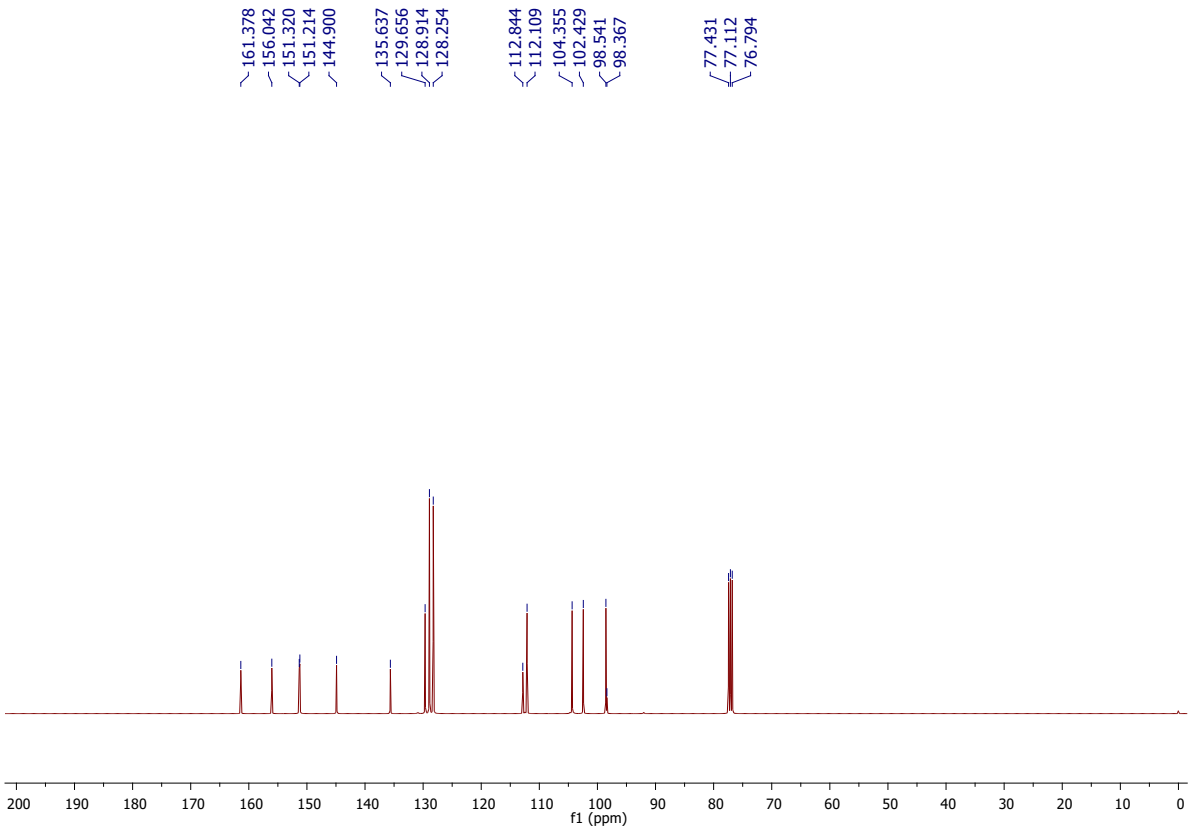
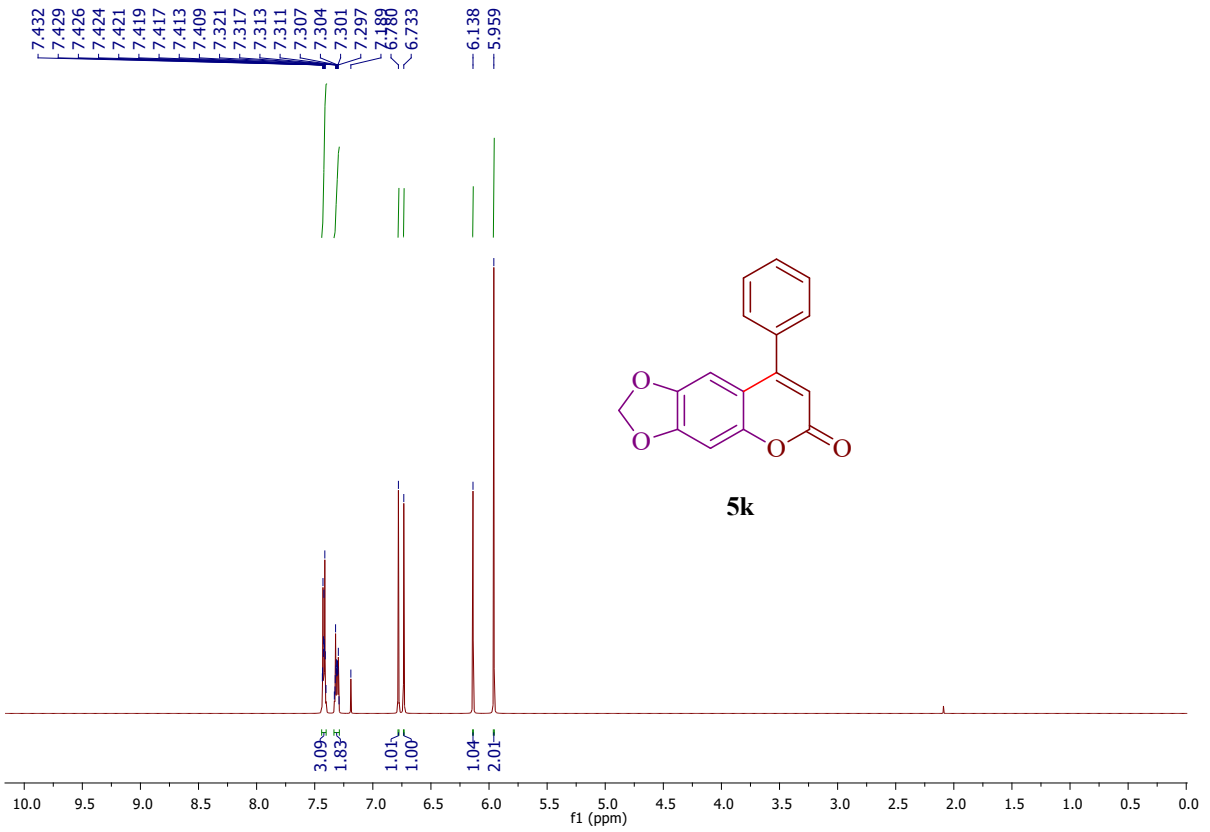


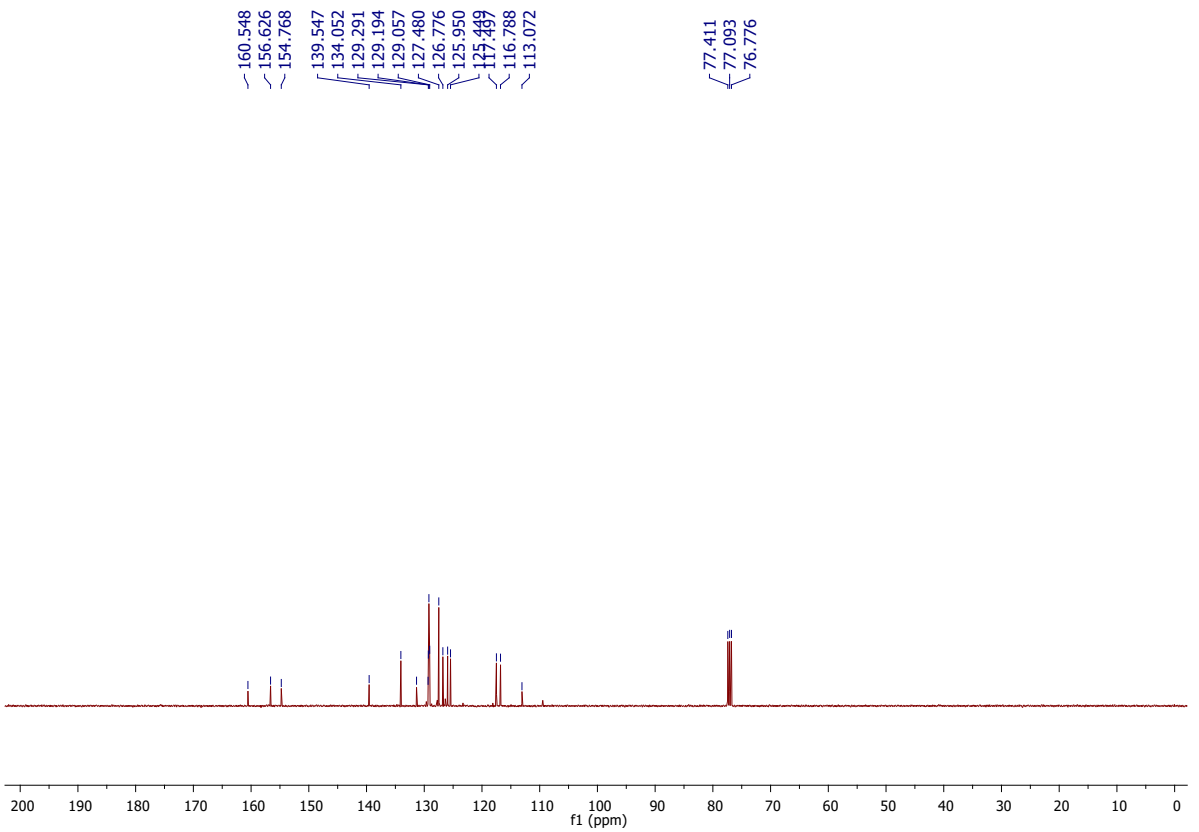
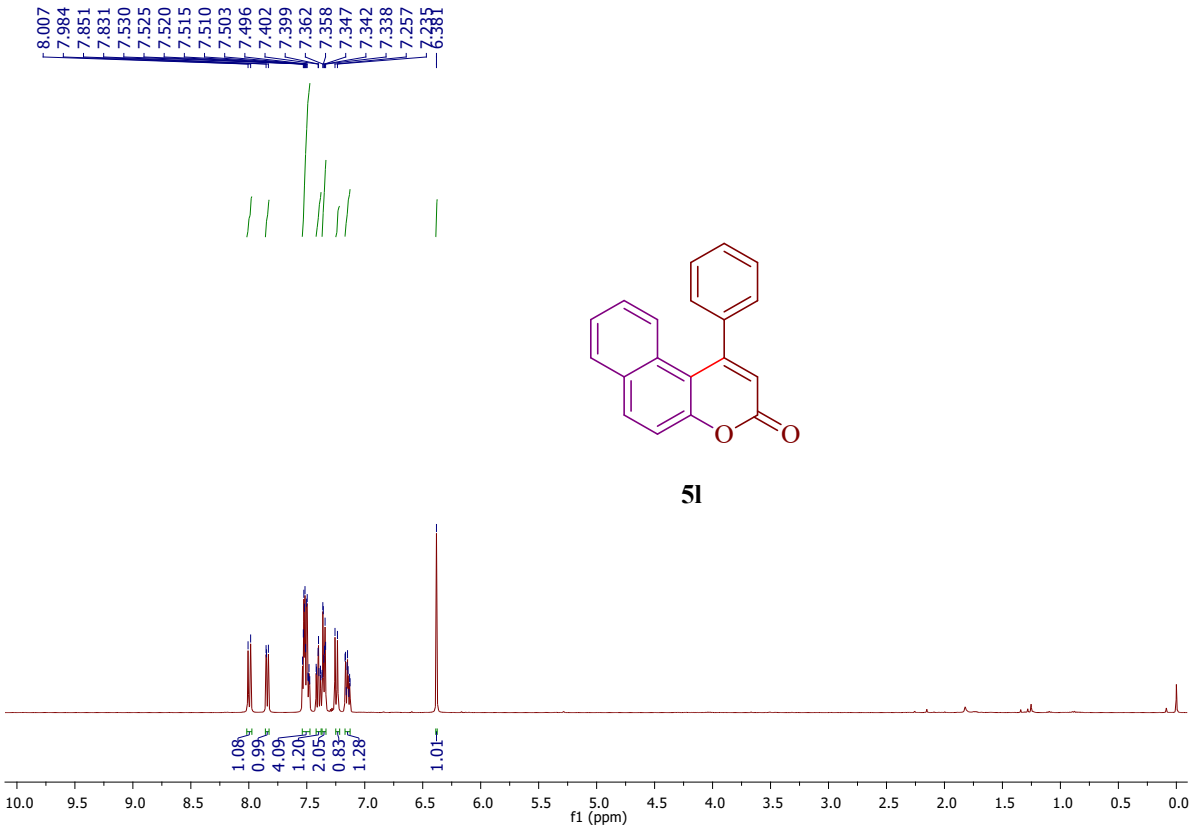


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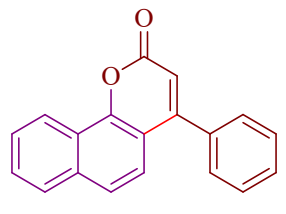
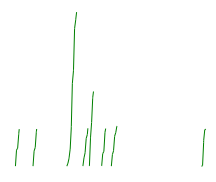




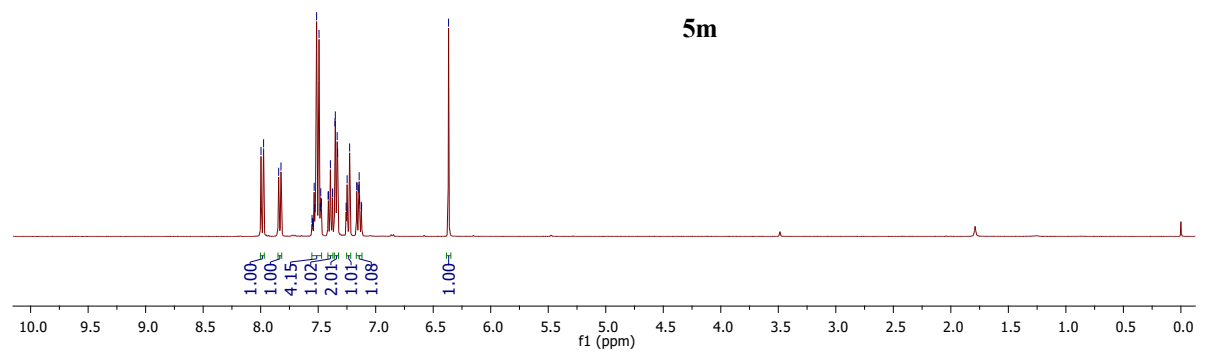




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5m



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