Supporting Information

For the article entitled

Regio- and Stereo-Selective Olefinic C-H Functionalization of Aryl Alkenes in Ethanol

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Supporting Information

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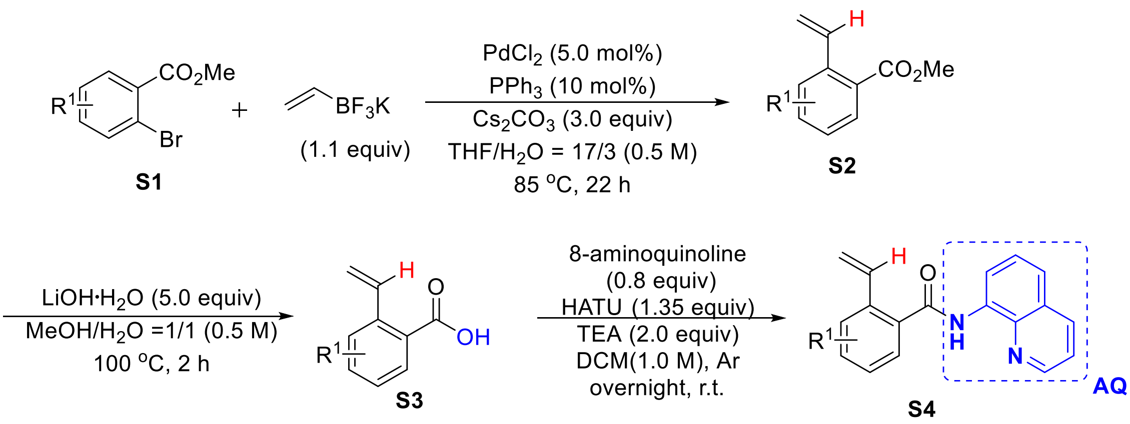
1. General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent), and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). The enantiomeric excesses (ee) of the products were determined by chiral stationary phase HPLC with Chiralpak (AD-H, OD-H, IA-H, IC-H, IB-H). Optical rotations were measured with Rudolph Autopol IVT. $Pd(OAc)_2$ were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification. Aroylsilanes were prepared from aroyl chlorides by reported method.

2. General Procedure for Substrate Synthesis

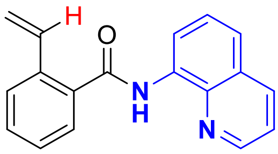
2.1 General Procedure A for Substrate Synthesis



General Procedure A for Heck Reaction[1]: A solution of potassium vinyltrifluoroborate (1.1 equiv), $PdCl_2$ (5.0 mol%), PPh_3 (10.0 mol%), Cs_2CO_3 (3.0 equiv), and substituted ester **(S1)** (5.0 mmol) in THF/H_2O (17:3) (0.5 M) was heated at 85 °C under N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to rt and diluted with H_2O (3 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crud product was purified by silica gel chromatography (SiO_2, PE/EA = 98/2) to obtain the corresponding product.

General Procedure A for Ester Hydrolysis[2] : The appropriate alkenyl ester **(S2)** was dissolved in a 1 : 1 mixture of MeOH and H_2O, and LiOH·H_2O (5.0 equiv) was added. The reaction was stirred vigorously at 100 °C for 2 h, and reaction progress was monitored by GC-MS. When full conversion was observed, the resulting mixture was diluted with water and washed with EA (×2). The organic layer was discarded. The aqueous layer was acidified with 2 M HCl solution and extracted with EA (×3). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the resulting acid **(S3)** was used in the next step without further purification.

General Procedure A for AQ Amide Preparation: The appropriate carboxylic acid (**S3**), 8-aminoquinoline (0.8 equiv), HATU (1.35 equiv) and TEA (2.0 equiv) were dissolved in DCM (1 M) and stirred at room temperature, and reaction progress was monitored by GC-MS. After 8-aminoquinoline was fully consumed (approximately 16 h), the resulting mixture was washed with 1 M HCl (aq.) solution, and the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the resulting residue was purified by silica gel column chromatography (PE/EA = 4/1).



_N_-(Quinolin-8-yl)-2-vinylbenzamide (1a)

Following the general procedure A, **1a** was obtained as a white solid (0.98 g, 72% yield for three steps, m.p. = 117-118 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.24 (s, 1H), 8.95 (d, *J* = 7.5 Hz, 1H), 8.76 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.18 (d, *J* = 9.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.25 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.80 (d, *J* = 17.5 Hz, 1H), 5.37 (d, *J* = 11.0 Hz, 1H).

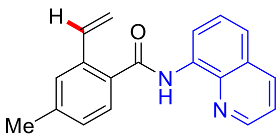
^{13}C NMR (125 MHz, $CDCl_3$)

δ 167.62, 148.27, 138.64, 136.61, 136.33, 135.63, 134.69, 134.57, 130.57, 128.00, 127.86, 127.64, 127.42, 126.65, 121.89, 121.67, 117.01, 116.63.

HRMS (ESI) for $C_{18}H_{14}N_2ONa$ $[M+Na]^+$: 297.0998, found: 298.1006.

FTIR (KBr, cm^{-1})

3565.42, 3506.54, 3475.70, 3385.98, 3357.94, 2959.81, 2926.17, 2850.47, 2331.78, 1684.11, 1653.27, 1636.45, 1574.77, 1557.94, 1454.21, 1384.11, 1328.04, 1257.94.



4-Methyl-_N_-(quinolin-8-yl)-6-vinylbenzamide (1b)

Following the general procedure A, **1b** was obtained as a white solid (0.99 g, 68% yield for three steps, m.p. = 79-80 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.24 (s, 1H), 8.94 (d, *J* = 7.5 Hz, 1H), 8.76 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.17 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.26 (d, *J* = 17.5 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 5.78 (dd, *J* = 17.5, 1.1 Hz, 1H), 5.36 (dd, *J* = 11.0, 1.0 Hz, 1H), 2.44 (s, 3H).

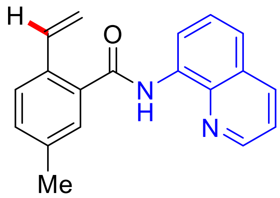
^{13}C NMR (125 MHz, $CDCl_3$)

δ 167.65, 148.23, 140.76, 138.66, 136.73, 136.30, 134.84, 134.81, 132.88, 128.60, 127.99, 127.78, 127.43, 127.33, 121.74, 121.64, 116.72, 116.54, 21.49.

HRMS (ESI) for $C_{19}H_{16}N_2ONa$ $[M+Na]^+$: 311.1155, found: 311.1147.

FTIR (KBr, cm^{-1})

3565.42, 3509.35, 3472.90, 3444.86, 3383.18, 2354.21, 1684.11, 1670.09, 1653.27, 1636.45, 1616.82, 1557.94, 1538.32, 1521.50, 1507.48, 1473.83, 1457.01, 1420.56, 1260.75, 1145.79, 828.97, 792.52.



5-Methyl-*N*-(quinolin-8-yl)-2-vinylbenzamide (1c)

Following the general procedure A, **1c** was obtained as a white solid (0.35 g, 24% yield for three steps, m.p. = 91-92 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.20 (s, 1H), 8.95 (d, *J* = 7.5 Hz, 1H), 8.77 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.52 (s, 1H), 7.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.30 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.18 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.75 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.31 (dd, *J* = 11.0, 1.0 Hz, 1H), 2.43 (s, 3H).

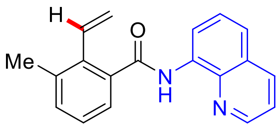
^{13}C NMR (125 MHz, $CDCl_3$)

δ 168.73, 148.20, 138.58, 136.90, 136.85, 136.30, 136.10, 134.81, 133.97, 131.93, 128.00, 127.45, 127.21, 125.61, 121.69, 121.62, 120.60, 116.52, 20.65.

HRMS (ESI) for $C_{19}H_{16}N_2ONa$ $[M+Na]^+$: 311.1155, found: 311.1158.

FTIR (KBr, cm^{-1})

3565.42, 3509.35, 3475.70, 3444.86, 3416.82, 2354.21, 1672.90, 1633.64, 1616.82, 1557.94, 1521.50, 1487.85, 1457.01, 1384.11, 1322.43, 1260.75, 1196.26, 826.17.



3-Methyl-*N*-(quinolin-8-yl)-2-vinylbenzamide (1d)

Following the general procedure A, **1d** was obtained as a white solid (0.28 g, 19% yield for three steps, m.p. = 125-126 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.12 (s, 1H), 8.91 (d, *J* = 7.5 Hz, 1H), 8.76 (d, *J* = 6.0 Hz, 1H), 8.17 (d, *J* = 10.0 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.55 – 7.53 (m, 2H), 7.44 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.33 – 7.27 (m, 2H), 6.99 (dd, *J* = 17.5, 11.5 Hz, 1H), 5.47 (dd, *J* = 13.5, 1.5 Hz, 1H), 5.44 (dd, *J* = 7.5, 1.5 Hz, 1H), 2.40 (s, 3H).

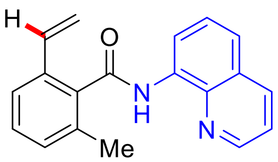
^{13}C NMR (125 MHz, $CDCl_3$)

δ 167.84, 148.27, 138.65, 137.85, 136.32, 135.60, 134.72, 134.35, 133.68, 131.33, 128.13, 128.00, 127.43, 126.52, 121.85, 121.66, 116.65, 116.13, 21.17.

HRMS (ESI) for $C_{19}H_{16}N_2ONa$ $[M+Na]^+$: 311.1155, found: 311.1149.

FTIR (KBr, cm^{-1})

3646.73, 3629.91, 3565.42, 3419.63, 3555.14, 2920.56, 2359.81, 1670.09, 1521.50, 1485.05, 1384.14, 1325.23, 1271.96, 826.17, 792.52, 761.68.



2-Methyl-*N*-(quinolin-8-yl)-6-vinylbenzamide (1e)

Following the general procedure A, **1e** was obtained as a green solid (0.23g, 16% yield for three steps, m.p. = 77-78 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.95 (s, 1H), 9.00 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.73 (dd, *J* = 4.0, 1.5

Hz, 1H), 8.18 (dd, J = 8.0, 1.5 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 6.93 (dd, J = 17.5, 11.0 Hz, 1H), 5.78 (dd, J = 17.5, 1.0 Hz, 1H), 5.26 (dd, J = 11.0, 1.0 Hz, 1H), 2.44 (s, 3H).

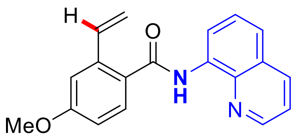
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.25, 151.91, 140.83, 137.34, 137.27, 135.06, 135.06, 133.41, 132.93, 131.68, 129.80, 129.41, 126.25, 123.40, 121.54, 120.90, 118.55, 117.60, 20.12.

HRMS (ESI) for $C_{19}H_{16}N_2ONa$ $[M+Na]^+$: 311.1155, found: 311.1163.

FTIR (KBr, cm^{-1})

3568.22, 3453.27, 3419.63, 2923.36, 2853.27, 1644.86, 1636.45, 1557.94, 1541.12, 1504.67, 1400.93, 1381.31, 1204.67, 963.55.



4-Methoxy-*N*-(quinolin-8-yl)-2-vinylbenzamide (1f)

Following the general procedure A, **1f** was obtained as a white solid (0.65 g, 43% yield for three steps, m.p. = 109-110 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.25 (s, 1H), 8.93 (dd, J = 7.5, 1.0 Hz, 1H), 8.77 (dd, J = 4.0, 1.5 Hz, 1H), 8.17 (dd, J = 8.0, 1.5 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 7.30 (dd, J = 17.5, 11.0 Hz, 1H), 7.14 (d, J = 2.5 Hz, 1H), 6.93 (dd, J = 8.5, 2.5 Hz, 1H), 5.78 (dd, J = 17.5, 1.0 Hz, 1H), 5.39 (dd, J = 11.0, 1.0 Hz, 1H), 3.90 (s, 3H).

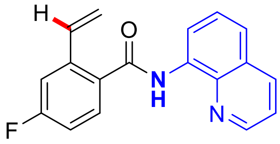
^{13}C NMR (125 MHz, $CDCl_3$)

δ 167.21, 161.32, 148.22, 139.04, 138.69, 136.32, 135.03, 134.87, 129.68, 128.21, 128.00, 127.45, 121.66, 121.64, 117.13, 116.49, 113.26, 112.04, 55.46.

HRMS (ESI) for $C_{19}H_{16}N_2O_2Na$ $[M+Na]^+$: 327.1104, found: 327.1095.

FTIR (KBr, cm^{-1})

3478.50, 3419.63, 2351.40, 1670.09, 1597.20, 1524.30, 1482.24, 1423.36, 1384.11, 1325.23, 1260.75, 1235.51.



4-Fluoro-*N*-(quinolin-8-yl)-2-vinylbenzamide (1g)

Following the general procedure A, **1g** was obtained as a white solid (0.53 g, 36% yield for three steps, m.p. = 108-109 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.22 (s, 1H), 8.92 (dd, *J* = 7.0, 1.0 Hz, 1H), 8.77 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.19 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.74 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.46 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.34 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.27–7.21 (m, 1H), 7.11–7.09 (m, 1H), 5.80 (d, *J* = 17.0 Hz, 1H), 5.43 (d, *J* = 11.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.57, 162.90 (d, J_{CF} = 248.6 Hz), 147.29, 138.48 (d, J_{CF} = 8.3 Hz), 137.57, 135.34, 133.51, 132.74, 130.78 (d, J_{CF} = 2.9 Hz), 128.95 (d, J_{CF} = 9.0 Hz), 126.96, 126.36, 120.98, 120.70, 117.12, 115.61, 113.82 (d, J_{CF} = 21.8 Hz), 112.29 (d, J_{CF} = 22.3 Hz).

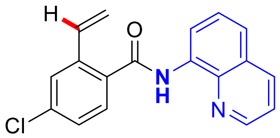
^{19}F NMR (471 MHz, $CDCl_3$)

δ -109.61.

HRMS (ESI) for $C_{18}H_{13}N_2OFNa$ $[M+Na]^+$: 315.0904, found: 315.0897.

FTIR (KBr, cm^{-1})

3571.03, 3509.35, 3453.27, 3416.82, 3385.98, 2926.17, 2351.40, 1675.70, 1656.07, 1633.64, 1541.12, 1521.50, 1485.05, 1386.92, 1328.04, 1263.55, 1128.97, 826.17, 786.92.



4-Chloro-*N*-(quinolin-8-yl)-2-vinylbenzamide (1h)

Following the general procedure A, **1h** was obtained as a white solid (0.71 g, 46% yield for three steps, m.p. = 123-124 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.23 (s, 1H), 8.92 (dd, *J* = 7.5, 1.0 Hz, 1H), 8.77 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.46 (dd, *J* = 8.0, 4.2 Hz, 1H), 7.37 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.20 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.81 (dd, *J* = 17.5, 1.0 Hz, 1H), 5.43 (dd, *J* = 11.0, 1.0 Hz, 1H).

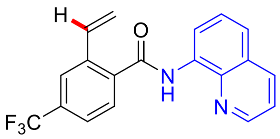
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.52, 148.35, 138.58, 138.47, 136.71, 136.37, 134.47, 133.88, 133.56, 129.16, 127.99, 127.88, 127.39, 126.72, 122.10, 121.75, 118.32, 116.69.

HRMS (ESI) for $C_{18}H_{13}N_2OCl$ Na $[M+Na]^+$: 331.0609, found: 331.0618.

FTIR (KBr, cm^{-1})

3458.88, 3419.63, 1656.07, 1650.47, 1636.45, 1622.43, 1560.75, 1538.32, 1507.48, 1457.01, 1400.93.



***N*-(Quinolin-8-yl)-4-(trifluoromethyl)-2-vinylbenzamide (1i)**

Following the general procedure A, **1i** was obtained as a white solid (0.87 g, 51% yield for three steps, m.p. = 101-102 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.26 (s, 1H), 8.93 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.77 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.91 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.676 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.47 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.23 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.89 (d, *J* = 17.5 Hz, 1H), 5.49 (d, *J* = 11.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.27, 148.42, 138.55, 137.24, 136.41, 134.28, 133.35, 132.52 (q, J_{CF} = 32.8 Hz), 130.82, 128.24, 128.00, 127.37, 124.52 (q, J_{CF} = 3.6 Hz), 123.71 (q, J_{CF} = 271.0 Hz), 123.59 (q, J_{CF} = 3.9 Hz), 122.34, 121.82, 118.85, 116.82.

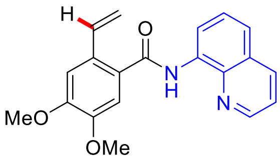
^{19}F NMR (471 MHz, $CDCl_3$)

δ -62.99.

HRMS (ESI) for $C_{19}H_{13}N_2OF_2Na$ $[M+ Na]^+$: 365.0872, found: 365.0865.

FTIR (KBr, cm^{-1})

3458.88, 3447.66, 3414.02, 2923.36, 2850.47, 2357.01, 2331.78, 1684.11, 1656.07, 1633.64, 1563.55, 1541.12, 1510.28, 1406.54, 1392.52.



4,5-Dimethoxy-*N*-(quinolin-8-yl)-2-vinylbenzamide (1j)

Following the general procedure A, **1j** was obtained as a kelly solid (0.13 g, 8% yield for three steps, m.p. = 126-127 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.24 (s, 1H), 8.93 (d, *J* = 7.0 Hz, 1H), 8.77 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.46 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.27 (s, 1H), 7.23 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.11 (s, 1H), 5.73 (dd, *J* = 17.5, 1.0 Hz, 1H), 5.33 (dd, *J* = 11.0, 1.0 Hz, 1H), 3.99 (s, 3H), 3.96 (s, 3H).

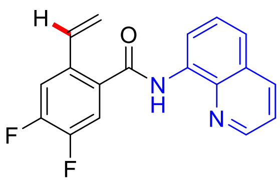
^{13}C NMR (125 MHz, $CDCl_3$)

δ 167.16, 150.78, 148.70, 148.28, 138.71, 136.31, 134.75, 134.50, 130.05, 128.20, 128.01, 127.44, 121.77, 121.66, 116.57, 115.78, 110.91, 108.99, 56.18, 56.05.

HRMS (ESI) for $C_{20}H_{18}N_2O_3Na$ $[M+Na]^+$: 357.1210, found: 357.1213.

FTIR (KBr, cm^{-1})

3509.35, 3458.88, 3447.66, 3414.02, 3385.98, 2926.17, 2354.21, 2331.78, 1686.92, 1670.09, 1656.07, 1636.45, 1560.75, 1535.51, 1507.48, 1398.13, 1384.11, 1274.77, 1213.08.



4,5-Difluoro-*N*-(quinolin-8-yl)-2-vinylbenzamide (1k)

Following the general procedure A, **1k** was obtained as a white solid (0.75 g, 82% yield for three steps, m.p. = 144-145

°C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.22 (s, 1H), 8.89 (dd, *J* = 7.0, 2.0 Hz, 1H), 8.78 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.49 – 7.43 (m, 2H), 7.16 (dd, *J* = 18.0, 11.5 Hz, 1H), 5.75 (d, *J* = 17.5 Hz, 1H), 5.42 (d, *J* = 11.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.21, 151.60 (d, J_{CF} = 264.4 Hz), 151.49 (d, J_{CF} = 264.4 Hz), 148.43, 138.57, 136.41, 134.25 (d, J_{CF} = 1.0 Hz), 134.25, 132.87, 132.00 (d, J_{CF} = 4.0 Hz), 127.99, 127.36, 122.29, 121.82, 118.18, 117.17 (d, J_{CF} = 17.5 Hz), 116.78, 115.55 (d, J_{CF} = 17.9 Hz).

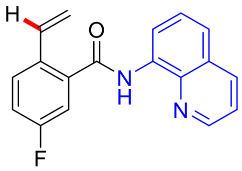
^{19}F NMR (471 MHz, $CDCl_3$)

δ -133.98, -137.52.

HRMS (ESI) for $C_{18}H_{12}N_2OF_2Na$ $[M+Na]^+$: 333.0810, found: 333.0805.

FTIR (KBr, cm^{-1})

3747.66, 3649.53, 3627.10, 3565.42, 3383.18, 2351.40, 1686.92, 1653.27, 1636.45, 1541.12, 1510.28, 1409.35, 1392.52, 1314.02.



5-Fluoro-*N*-(quinolin-8-yl)-2-vinylbenzamide (1l)

Following the general procedure A, **1l** was obtained as a white solid (0.22 g, 15% yield for three steps, m.p. = 110-111 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.23 (s, 1H), 8.92 (dd, *J* = 7.5, 1.0 Hz, 1H), 8.78 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.19 (d, *J* = 10.0 Hz, 1H), 7.64 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.47 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.43 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.22 – 7.13 (m, 2H), 5.74 (d, *J* = 17.5 Hz, 1H), 5.36 (d, *J* = 11.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.14, 161.98 (d, J_{CF} = 247.5 Hz), 148.39, 138.60, 137.07 (d, J_{CF}

= 6.5 Hz), 136.37, 134.38, 133.54, 132.74 (d, J_{CF} = 3.5 Hz), 128.68 (d, J_{CF}= 7.8 Hz), 127.99, 127.37, 122.19, 121.77, 117.72 (d, J_{CF} = 21.3 Hz), 117.03, 116.77, 114.64 (d, J_{CF} = 22.8 Hz).

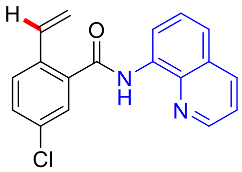
^{19}F NMR (471 MHz, $CDCl_3$)

δ -113.32.

HRMS (ESI) for $C_{18}H_{13}N_2OFNa$ $[M+Na]^+$: 315.0904, found: 315.0907.

FTIR (KBr, cm^{-1})

3568.22, 3509.35, 3453.27, 3383.18, 3332.71, 2920.56, 2856.07, 1684.11, 1653.27, 1633.64, 1560.75, 1538.32, 1487.85, 1400.93, 1384.11, 1269.16, 823.36.



5-chloro-*N*-(quinolin-8-yl)-2-vinylbenzamide (1m)

Following the general procedure A, **1m** was obtained as a white solid (0.77 g, 46% yield for three steps, m.p. = 116-117 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.21 (s, 1H), 8.91 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.78 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.62 – 7.56 (m, 3H), 7.48 – 7.44 (m, 2H), 7.15 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.79 (dd, *J* = 17.5, 1.0 Hz, 1H), 5.39 (dd, *J* = 11.0, 1.0 Hz, 1H).

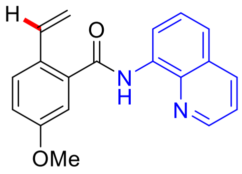
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.10, 148.40, 138.58, 136.93, 136.37, 134.94, 134.36, 133.63, 133.46, 130.63, 128.03, 127.99, 127.65, 127.36, 122.22, 121.78, 117.65, 116.80.

HRMS (ESI) for $C_{18}H_{13}N_2OClNa$ $[M+Na]^+$: 331.0609, found: 331.0612.

FTIR (KBr, cm^{-1})

3568.22, 3509.35, 3444.86, 3419.63, 2920.56, 2850.47, 2354.21, 1695.33, 1684.11, 1670.09, 1653.27, 1636.45, 1541.12, 1521.50, 1487.85, 1457.01, 1384.11, 1328.04, 826.17, 792.52.



5-Methoxy-*N*-(quinolin-8-yl)-2-vinylbenzamide (1n)

Following the general procedure A, **1n** was obtained as a white solid (0.76 g, 50% yield for three steps, m.p. = 159-160 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.22 (s, 1H), 8.95 (dd, *J* = 7.0, 1.0 Hz, 1H), 8.77 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.56 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.04 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.69 (dd, *J* = 17.5, 1.0 Hz, 1H), 5.27 (dd, *J* = 11.0, 1.0 Hz, 1H), 3.88 (s, 3H).

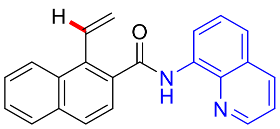
^{13}C NMR (125 MHz, $CDCl_3$)

δ 167.40, 159.16, 148.32, 138.64, 136.75, 136.31, 134.61, 133.88, 128.99, 127.99, 127.96, 127.39, 121.96, 121.70, 116.74, 116.67, 115.21, 112.48, 55.57.

HRMS (ESI) for $C_{19}H_{17}N_2O_2$ $[M+H]^+$: 305.1285, found: 305.1304.

FTIR (KBr, cm^{-1})

3571.03, 3475.70, 3458.88, 3419.63, 1670.09, 1636.45, 1616.82, 1541.12, 1521.50, 1400.93, 1381.31, 1328.04, 826.17, 792.52, 615.89.



***N*-(Quinolin-8-yl)-1-vinyl-2-naphthamide (1o)**

Following the general procedure A, **1o** was obtained as a kelly solid (0.8 g, 49% yield for three steps, m.p. = 114-115 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.27 (s, 1H), 8.96 (d, *J* = 7.5 Hz, 1H), 8.74 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.27 – 8.24 (m, 1H), 8.17 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 (dd, *J* = 9.0, 3.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.63 – 7.54 (m, 4H), 7.45 – 7.38 (m, 2H), 5.72 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.69 (dd, *J* = 14.5, 1.5 Hz, 1H).

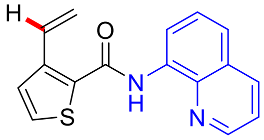
^{13}C NMR (125 MHz, $CDCl_3$)

δ 168.47, 148.24, 138.64, 136.30, 134.95, 134.82, 134.18, 133.25, 133.02, 131.46, 128.31, 128.02, 128.00, 127.48, 127.04, 126.77, 126.25, 124.77, 122.79, 121.77, 121.64, 116.55.

HRMS (ESI) for $C_{22}H_{16}N_2ONa$ $[M+Na]^+$: 347.1155, found: 347.1150.

FTIR (KBr, cm^{-1})

3624.30, 3571.03, 3475.70, 3456.07, 3447.66, 3422.43, 1667.29, 1656.07, 1633.64, 1622.43, 1616.82, 1560.75, 1538.32, 1507.48, 1454.21, 1406.54, 1384.11.



***N*-(Quinolin-8-yl)-3-vinylthiophene-2-carboxamide (1p)**

Following the general procedure A, **1p** was obtained as a white solid (0.5 g, 36% yield for three steps, m.p. = 93-94 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.45 (s, 1H), 8.85 – 8.81 (m, 2H), 8.16 (dd, J = 8.5, 1.5 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 7.40 (d, J = 5.0 Hz, 1H), 7.33 (d, J = 5.0 Hz, 1H), 5.79 (dd, J = 17.5, 1.0 Hz, 1H), 5.51 (dd, J = 11.0, 1.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

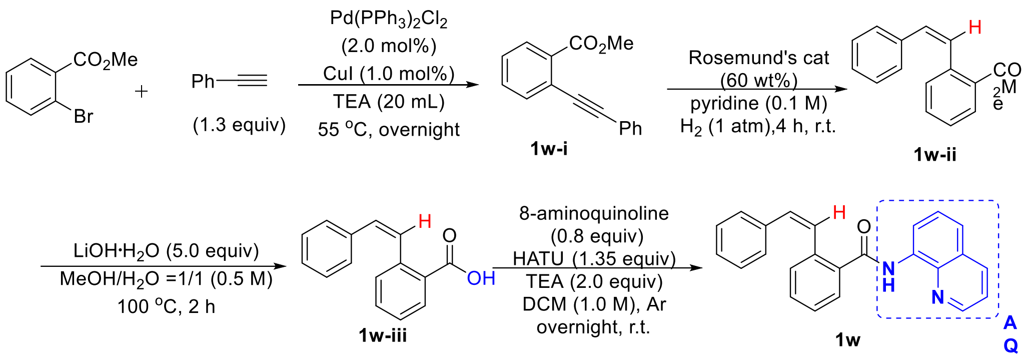
δ 160.88, 148.36, 142.49, 138.65, 136.33, 134.59, 132.83, 130.06, 127.98, 127.71, 127.41, 127.25, 121.79, 121.71, 118.27, 116.64.

HRMS (ESI) for $C_{16}H_{12}N_2OSNa$ $[M+Na]^+$: 303.0563, found: 303.0563.

FTIR (KBr, cm^{-1})

3571.03, 3478.50, 3444.86, 3419.63, 2923.36, 1670.09, 1664.49, 1653.27, 1636.45, 1619.63, 1541.12, 1510.28, 1457.01, 1400.93.

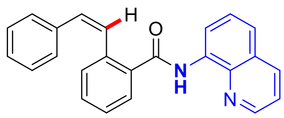
Procedure for 1w Synthesis



Alkynylation Reaction[3]: A solution of $Pd(PPh_3)_2Cl_2$ (1.0 mol%), CuI (1.0 mol%), methyl 2-bromobenzoate (5.00 mmol) and ethynylbenzene (6.00 mmol) in TEA (0.4 M) was stirred at 55 °C overnight, then cooled to rt and diluted with H_2O (20 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crud product was purified by silica gel chromatography (SiO_2, PE / EA) to obtain the corresponding product.

Hydrogenation Reaction: Following a slight modification from a previously reported procedure, a solution of alkyne (**1w-i)** (3.9 mmol, 1.0 equiv) in pyridine (39 mL) was vacuum purged three times, backfilling with N_2. Rosemund's catalyst (5% Pd on $BaSO_4$, 0.521 g) was added and the solution was vacuumed purged once more, backfilling with H_2. The solution was allowed to stir at room temperature for 4 h until reaction completion (monitored by TLC). The reaction was vacuum purged and backfilled with N_2, upon which the reaction was filtered through Celite, rinsing with EtOAc (200 mL). The organic solution was concentrated in vacuo to give an orange oil, which was dissolved in 50 mL EtOAc. The organic solution was washed with HCl (2 M, 30 mL × 2), water (50 mL), and brine (50 mL). The organic layer was then dried with Na2SO4 and concentrated in vacuo to afford the crude olefin. Purification by column chromatography (PE/EA) afforded olefin (**1w-ii)**

Ester Hydrolysis and **AQ Amide Preparation** were performed according to the general procedure A.



(*Z*)-*N*-(quinolin-8-yl)-2-styrylbenzamide (1w)

Following the procedure, **1w** was obtained as a colorless oil (0.39 g, 22% yield for four steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.57 (s, 1H), 8.92 (dd, J = 7.5, 1.5 Hz, 1H), 8.56 (dd, J = 4.0, 1.5 Hz, 1H), 8.14 (dd, J = 8.0, 1.5 Hz, 1H), 7.91 (dd, J = 7.5, 1.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.52 (dd, J = 8.5, 1.5 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.24 – 7.23 (m, 2H), 7.20 – 7.16 (m, 2H), 7.15 – 7.12 (m, 1H), 6.98 (d, J = 12.0 Hz, 1H), 6.74 (d, J = 12.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

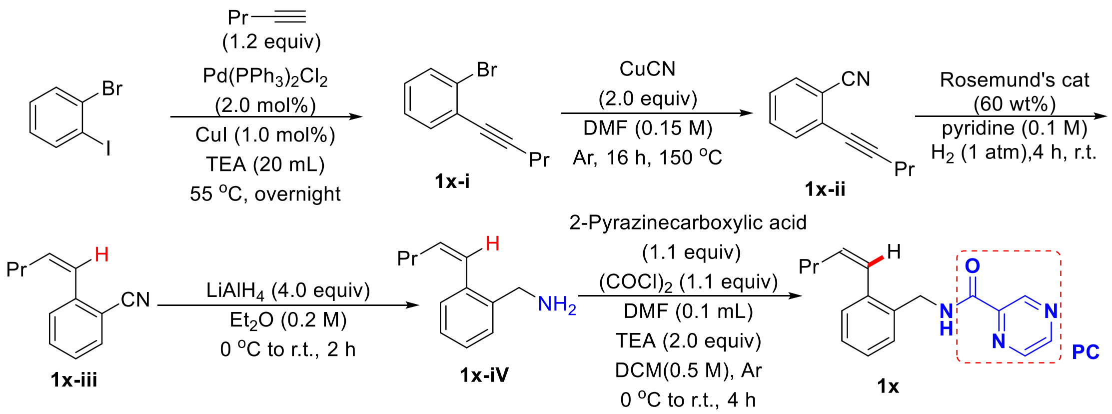
δ 165.92, 147.03, 137.68, 135.58, 135.42, 135.14, 134.76, 133.81, 131.17, 129.61, 129.59, 128.17, 127.57, 127.56, 127.11, 126.88, 126.54, 126.39, 126.17, 120.65, 120.55, 115.49.

HRMS (ESI) for $C_{24}H_{18}N_2ONa$ $[M+Na]^+$: 373.1311, found: 373.1304.

FTIR (KBr, cm^{-1})

3854.21, 3744.86, 3649.53, 3624.30, 3562.62, 2348.60, 1734.58, 1686.92, 1656.07, 1560.75, 1541.12, 1507.48, 1459.81, 1398.13, 1022.43, 666.36.

Procedure for 1x Synthesis

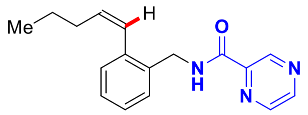


Alkynylation Reaction and **Hydrogenation Reaction** was following the Procedure for **1w** Synthesis.

Cyanation Reaction[4]: To a solution of CuCN (2.0 equiv)in DMF (0.15 M) was added 1-bromo-2-(pent-1-yn-1-yl)benzene **(1x-i)** at 150°C and stirred for 16 h. then cooled to rt and diluted with H_2O (20 mL) followed by extraction with EtOAc (30 mL x 3). Combined the organic layers and dried over Na_2SO_4, The solvent was removed in vacuo, and the resulting residue was purified by silica gel column chromatography

(PE / EA).

Benzonitrile Reduction and **PC Amide Preparation** was following the general procedure **B.**



(*Z*)-*N*-(2-(pent-1-en-1-yl)benzyl)pyrazine-2-carboxamide (1x)

Following the **1w** procedure and the general procedure **B**, **1x** was obtained as a white solid (1.08g, 77% yield for five steps, m.p. = 75-76 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.43 (d, *J* = 1.5 Hz, 1H), 8.73 (d, *J* = 2.5 Hz, 1H), 8.47 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.99 (s, 1H), 7.37 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.23 (dd, *J* = 7.0, 1.5 Hz, 1H), 6.55 (d, *J* = 11.5 Hz, 1H), 5.83 – 5.78 (m, 1H), 4.65 (d, *J* = 6.0 Hz, 2H), 2.13 – 2.08 (m, 2H), 1.43 – 1.36 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

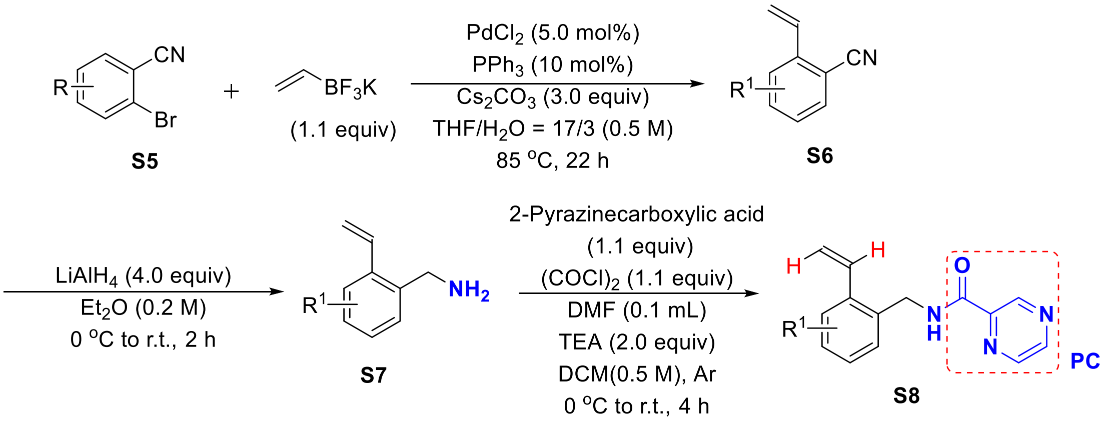
δ 161.60, 146.20, 143.47, 143.44, 141.42, 135.90, 134.34, 133.60, 128.85, 127.71, 126.48, 126.22, 125.64, 40.68, 29.43, 21.78, 12.75.

HRMS (ESI) for $C_{17}H_{19}N_3ONa$ $[M+Na]^+$: 304.1420, found: 304.1414.

FTIR (KBr, cm^{-1})

3851.40, 3747.66, 3627.10, 3565.42, 3444.86, 3416.82, 1653.27, 1639.2,5 1557.94, 1543.93, 1504.67, 1406.54, 1384.11, 1022.43.

2.2 General Procedure B for Substrate Synthesis

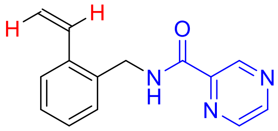


Heck Reaction: A solution of potassium vinyltrifluoroborate (1.1 equiv), $Pd(OAc)_2$ (5.0 mol%), PPh_3 (10.0 mol%), Cs_2CO_3 (3.0 equiv), and substituted benzonitrile **(S5)** (5.00 mmol) in THF/H_2O (17:3) (0.5 M) was heated at 85 °C under N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to rt and diluted with H_2O (10 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crud product was purified by silica gel chromatography (SiO_2, PE / EA = 98 / 2) to obtain the corresponding product (**S6**).

Benzonitrile Reduction[5]: To a solution of substituted benzonitrile **(S6)** in Et_2O (0.2 M) was added dropwise $LiAlH_4$ (4.0 equiv) over 30 min at 0°C and stirred for 2 h at r.t. 4 M NaOH was added slowly to until a clear solution was obtained. The Et_2O layer was separated and the aqueous phase was extracted with Et_2O (20 mL x 3). Combined the organic layers and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with EtOAc and the resulting amine **(S7)** was used in the next step without further purification.

PC Amide Preparation[6]: 2-Pyrazinecarboxylic acid (1.1 equiv) was dissolved in dry DCM (0.5 M) by adding 2 to 3 drops of dry DMF. To this reaction mixture oxalyl chloride (1.1 equiv.) was added at 0 °C slowly and the resultant reaction mixture was stirred at rt for 2 h under a nitrogen atm. After this period, the reaction mixture was concentrated in vacuum to remove excess oxalyl chloride and solvent. The resultant acid chloride was dissolved in DCM (25 mL) and this reaction mixture was added to a separate flask which contained the corresponding amine (**S7**), TEA (2.0 equiv) in

DCM (5 mL) at 0 °C and the resultant reaction mixture was stirred at rt for 4 h under a nitrogen atm. After this period, the reaction mixture was diluted with DCM and then washed with water followed by saturated aqueous $NaHCO_3$ solution and the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the resulting residue was purified by silica gel column chromatography (PE / EA = 2 / 1).



N-(2-vinylbenzyl)pyrazine-2-carboxamide (4a)

Following the general procedure B, **4a** was obtained as a yellow solid (0.67 g, 56% yield for three steps for three steps, m.p.= 86-87 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.45 (s, 1H), 8.74 (t, *J* = 3.0 Hz, 1H), 8.48 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.95 (s, 1H), 7.55 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.02 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.69 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.37 (dd, *J* = 11.0, 1.0 Hz, 1H), 4.74 (d, *J* = 5.5 Hz, 2H).

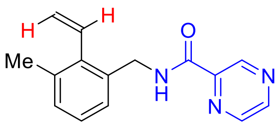
^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.55, 146.27, 143.47, 143.31, 141.49, 136.08, 133.30, 132.60, 128.33, 127.28, 127.08, 125.26, 116.04, 40.45.

HRMS (ESI) for $C_{14}H_{14}N_3O$ $[M+H]^+$: 240.1131, found: 240.1139.

FTIR (KBr, cm^{-1})

3568.22, 3472.90, 3456.07, 3450.47, 3422.43, 2357.01, 1689.72, 1664.49, 1653.27, 1642.06, 1566.36, 1541.12, 1507.48, 1476.64, 1406.54, 1381.31.



N-(3-methyl-2-vinylbenzyl)pyrazine-2-carboxamide (4g)

Following the general procedure B, **4g** was obtained as a white solid (0.83 g, 66% yield for three steps, m.p. = 109-110 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.44 (d, *J* = 9.0 Hz, 1H), 8.73 (s, 1H), 8.48 (s, 1H), 8.01 (s, 1H), 7.25 – 7.24 (m, 1H), 7.16 (d, J = 3.5 Hz, 1H), 7.11 (dd, J = 14.0, 6.5 Hz, 1H), 6.79 (dd, J = 17.5, 10.5 Hz, 1H), 5.62 (dd, J = 11.5, 1.5 Hz, 1H), 5.32 (dd, J = 18.0, 1.5 Hz, 1H), 4.70 (d, J = 6.0 Hz, 2H), 2.31 (s, 3H).

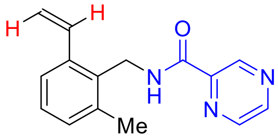
^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.56, 146.24, 146.19, 143.48, 141.48, 140.14, 136.98, 135.79, 135.47, 133.95, 133.79, 133.19, 129.28, 128.56, 126.22, 125.46, 125.02, 119.64, 40.87, 19.66.

HRMS (ESI) for $C_{15}H_{15}N_3ONa$ $[M+Na]^+$: 276.1107, found: 276.1102.

FTIR (KBr, cm^{-1})

3649.53, 3624.30, 3568.22, 3416.82, 3355.14, 2926.17, 2351.40, 1667.29, 1642.06, 1560.75, 1541.12, 1513.08, 1471.03, 1406.54, 1381.31, 1022.43.



***N*-(2-methyl-6-vinylbenzyl)pyrazine-2-carboxamide (4h)**

Following the general procedure B, **4h** was obtained as a yellow solid (0.39 g, 31% yield for three steps, m.p. = 107-108 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.43 (d, J = 1.5 Hz, 1H), 8.70 (d, J = 2.5 Hz, 1H), 8.44 (dd, J = 2.5, 1.5 Hz, 1H), 7.76 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 7.09 (dd, J = 6.5, 4.0 Hz, 1H), 5.66 (dd, J = 17.0, 1.0 Hz, 1H), 5.36 (dd, J = 11.0, 1.5 Hz, 1H), 4.75 (d, J = 5.0 Hz, 2H), 2.44 (s, 3H).

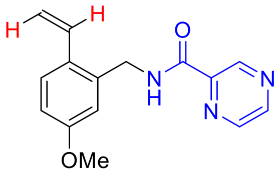
^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.56, 146.19, 143.34, 143.29, 141.45, 137.39, 136.54, 133.49, 131.31, 129.16, 127.24, 123.46, 116.44, 36.63, 18.77.

HRMS (ESI) for $C_{15}H_{15}N_3ONa$ [M+Na]+: 276.1107, found: 276.1105.

FTIR (KBr, cm^{-1})

3565.42, 3512.15, 3481.31, 3453.27, 3419.63, 2926.17, 1686.92, 1675.70, 1667.29, 1653.27, 1642.06, 1622.43, 1557.94, 1543.93, 1507.48, 1457.01, 1403.74, 1381.31.



N-(5-methoxy-2-vinylbenzyl)pyrazine-2-carboxamide (4i)

Following the general procedure B, **4i** was obtained as a white solid (0.96g, 71% yield for three steps, m.p. = 73-74 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.44 (dd, *J* = 5.5, 1.5 Hz, 1H), 8.74 (d, *J* = 2.5 Hz, 1H), 8.49 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.96 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 6.94 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.59 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.26 (dd, *J* = 11.0, 1.0 Hz, 1H), 4.71 (d, *J* = 5.5 Hz, 2H), 3.81 (d, *J* = 3.5 Hz, 3H).

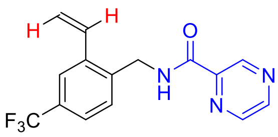
^{13}C NMR (125 MHz, $CDCl_3$)

δ 162.60, 159.43, 147.31, 144.49, 144.32, 142.54, 135.75, 132.96, 129.61, 127.51, 115.06, 114.68, 113.58, 55.36, 41.50.

HRMS (ESI) for $C_{15}H_{15}N_3O_2Na$ $[M+ Na]^+$: 292.1056, found: 292.1058.

FTIR (KBr, cm^{-1})

3453.27, 3442.06, 3422.43, 3405.61, 3388.79, 2928.97, 1684.11, 1667.29, 1605.61, 1521.50, 1510.28, 1465.42, 1400.93, 1300.00, 1257.94, 1165.42, 1022.43.



N-(4-(trifluoromethyl)-2-vinylbenzyl)pyrazine-2-carboxamide (4j)

Following the general procedure B, **4j** was obtained as a white solid (0.72 g, 47% yield for three steps, m.p. = 87-88 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.44 (s, 1H), 8.76 (d, *J* = 2.5 Hz, 1H), 8.51 (d, *J* = 2.0 Hz, 1H), 8.06 (s, 1H), 7.76 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.03 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.77 (d, *J* = 17.5 Hz, 1H), 5.49 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.79, 146.50, 143.51, 141.55, 137.14 (d, J_{CF} = 8.8 Hz), 136.69, 131.58, 129.24 (q, J_{CF} = 32.1 Hz), 128.33, 127.85, 123.56 (q, J_{CF} = 37.5 Hz), 122.94 (q, J_{CF} = 270.5 Hz), 122.25 (q, J_{CF} = 3.9 Hz), 117.87, 39.95.

^{19}F NMR (471 MHz, $CDCl_3$)

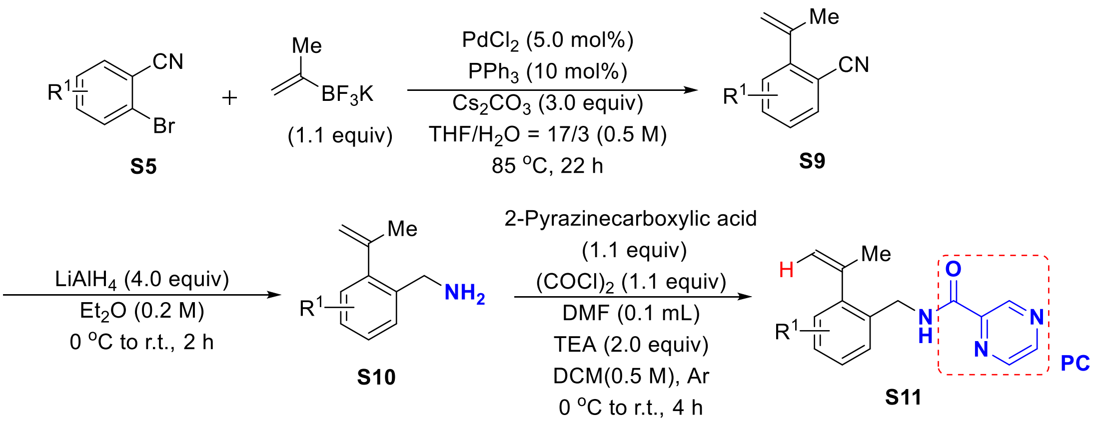
δ -62.71.

HRMS (ESI) for $C_{15}H_{12}N_3OF_3Na$ [M+ Na]$^+$: 330.0825, found: 330.0823.

FTIR (KBr, cm^{-1})

3568.22, 3512.15, 3444.86, 3383.18, 2959.81, 2928.97, 2357.01, 2326.17, 1681.31, 1667.29, 1656.07, 1622.43, 1541.12, 1507.48, 1476.64, 1398.13, 1330.84, 1128.97, 1019.63.

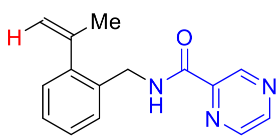
2.3 General Procedure C for Substrate Synthesis



Heck Reaction: A solution of potassium isopropenyl trifluoroborate (1.1 equiv), $PdCl_2$ (5.0 mol%), PPh_3 (10.0 mol%), Cs_2CO_3 (3.0 equiv), and substituted benzonitrile **(S5)** (5.0 mmol) in THF/H_2O (17:3) (0.5 M) was heated at 85 °C under N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to rt and diluted with H_2O (10 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crud product was purified by silica gel chromatography (SiO_2, PE / EA = 98 / 2) to obtain the corresponding product **(S9)**.

Benzonitrile Reduction: To a solution of substituted benzonitrile **(S9)** in Et_2O (0.2 M) was added dropwise $LiAlH_4$ (4.0 equiv) over 30 min at 0°C and stirred for 2 h at r.t. 4 M NaOH was added slowly to until a clear solution was obtained. The Et_2O layer was separated and the aqueous phase was extracted with Et_2O (20 mL × 3). Combined the organic layers and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with EtOAc and the resulting amine **(S10)** was used in the next step without further purification.

PC Amide Preparation: 2-Pyrazinecarboxylic acid (1.1 equiv) was dissolved in dry DCM (0.5 M) by adding 2 to 3 drops of dry DMF. To this reaction mixture oxalyl chloride (1.1 equiv.) was added at 0 °C slowly and the resultant reaction mixture was stirred at rt for 2 h under a nitrogen atm. After this period, the reaction mixture was concentrated in vacuum to remove excess oxalyl chloride and solvent. The resultant acid chloride was dissolved in DCM (0.5 M) and this reaction mixture was added to a separate flask which contained the corresponding amine (**S10**), Et_3N (2.0 equiv) in DCM (5 mL) at 0 °C and the resultant reaction mixture was stirred at rt for 4 h under a nitrogen atm. After this period, the reaction mixture was diluted with DCM and then washed with water followed by saturated aqueous $NaHCO_3$ solution and the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the resulting residue was purified by silica gel column chromatography (PE / EA = 2 / 1).



***N*-(2-(prop-1-en-2-yl)benzyl)pyrazine-2-carboxamide (6a)**

Following the general procedure C, **6a** was obtained as a white solid (0.78 g, 62% yield for three steps, m.p. = 95-96 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.44 (s, 1H), 8.74 (d, *J* = 2.5 Hz, 1H), 8.50 – 8.49 (m, 1H), 8.03 (s, 1H), 7.41 – 7.39 (m, 1H), 7.28 – 7.26 (m, 2H), 7.20 – 7.18 (m, 1H), 5.28 (s, 1H), 4.93 (s, 1H), 4.70 (d, *J* = 6.0 Hz, 2H), 2.09 (s, 3H).

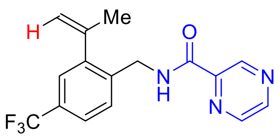
^{13}C NMR (125 MHz, $CDCl_3$)

δ 162.68, 147.25, 144.64, 144.49, 143.78, 142.53, 134.07, 128.93, 128.33, 127.61, 127.40, 115.82, 41.35, 25.13.

HRMS (ESI) for $C_{15}H_{15}N_3ONa$ $[M+Na]^+$: 276.1107, found: 276.1099.

FTIR (KBr, cm^{-1})

3472.90, 3461.68, 3419.63, 3385.98, 1667.29, 1636.45, 1619.63, 1529.91, 1406.54, 1294.39, 1025.23, 775.70.



N-(2-(prop-1-en-2-yl)-4-(trifluoromethyl)benzyl)pyrazine-2-carboxamide (6i)

Following the general procedure C, **6i** was obtained as a yellow solid (1.0 g, 63% yield for three steps, m.p. = 88-89 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.41 (d, J = 1.5 Hz, 1H), 8.74 (d, J = 2.5 Hz, 1H), 8.49 (dd, J = 2.5, 1.5 Hz, 1H), 8.14 (s, 1H), 7.52 – 7.46 (m, 2H), 7.41 (s, 1H), 5.35 – 5.33 (m, 1H), 4.96 (m, 1H), 4.72 (d, J = 6.0 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.93, 146.44, 143.47, 143.16 (d, J = 6.5 Hz), 142.44, 141.57, 137.32 (d, J = 1.0 Hz), 128.75 (q, J = 32.3 Hz), 128.00, 124.13 (q, J = 37.5 Hz), 123.10 (q, J = 37.5 Hz), 122.95 (q, J = 270.6 Hz), 115.92, 112.26, 39.84, 23.77.

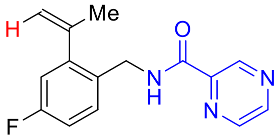
^{19}F NMR (471 MHz, $CDCl_3$)

δ -62.57.

HRMS (ESI) for $C_{16}H_{15}N_3OF$ $[M+H]^+$: 322.1162, found: 322.1139.

FTIR (KBr, cm^{-1})

3419.63, 3405.61, 2968.22, 2923.36, 1684.11, 1675.70, 1633.64, 1616.82, 1560.75, 1541.12, 1524.30, 1403.74, 1342.06, 1291.59, 1271.96, 1120.56, 1095.33, 1028.04, 901.87.



***N*-(2-(prop-1-en-2-yl)-4-(fluoromethyl)benzyl)pyrazine-2-carboxamide (6j)**

Following the general procedure C, **6j** was obtained as a yellow oil (0.76 g, 56% yield for three steps, m.p. = 105-106 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.43 (s, 1H), 8.75 (s, 1H), 8.50 (d, *J* = 1.5 Hz, 1H), 8.02 (s, 1H), 7.38 (dd, *J* = 8.5, 6.0 Hz, 1H), 6.97 – 6.93 (m, 1H), 6.89 (dd, *J* = 9.5, 2.5 Hz, 1H), 5.30 (d, *J* = 1.5 Hz, 1H), 4.95 (s, 1H), 4.65 (d, *J* = 6.0 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.67, 160.90 (d, *J* = 245.5 Hz), 146.30, 144.75 (d, *J* = 32.3 Hz), 143.46, 143.34, 142.63 (d, *J* = 1.4 Hz), 141.51, 129.77 (d, *J* = 8.4 Hz), 128.98 (d, *J* = 3.1 Hz), 115.36, 114.09 (d, *J* = 21.1 Hz), 113.17 (d, *J* = 21.0 Hz), 39.67, 23.81.

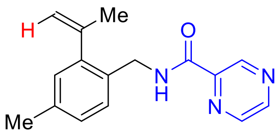
^{19}F NMR (471 MHz, $CDCl_3$)

δ -114.86.

HRMS (ESI) for $C_{15}H_{14}N_3OF_3Na$ $[M+ Na]^+$: 294.1013, found: 294.1010.

FTIR (KBr, cm^{-1})

3419.63, 3405.61, 3388.79, 2968.22, 2923.36, 2357.01, 1695.33, 1684.11, 1675.70, 1560.75, 1541.12, 1524.30, 1403.74, 1342.06, 1291.59, 1271.96, 1171.03, 1120.56, 1095.33, 1028.04, 901.87.



***N*-(4-methyl-2-(prop-1-en-2-yl)benzyl)pyrazine-2-carboxamide (6k)**

Following the general procedure C, **6k** was obtained as a white solid (0.99 g, 74% yield for three steps, m.p. = 97-98 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.36 (d, *J* = 1.5 Hz, 1H), 8.66 (d, *J* = 2.5 Hz, 1H), 8.41 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.92 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 4.0, 1.0 Hz, 1H), 6.93 (d, *J* = 1.0 Hz, 1H), 5.20 – 5.18 (m, 1H), 4.84 (dd, *J* = 2.0, 1.0 Hz, 1H), 4.58 (d, *J* = 6.0 Hz, 2H), 2.27 (s, 3H), 2.01 (s, 3H).

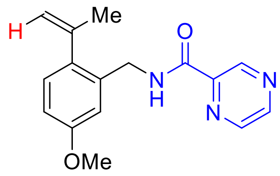
^{13}C NMR (125 MHz, $CDCl_3$)

δ 162.60, 147.20, 144.76, 144.53, 144.47, 143.71, 142.51, 137.35, 131.06, 129.09, 128.96, 128.11, 115.59, 41.15, 25.15, 21.06.

HRMS (ESI) for $C_{16}H_{17}N_3ONa$ $[M+Na]^+$: 290.1264, found: 290.1274.

FTIR (KBr, cm^{-1})

3461.68, 3444.86, 3425.23, 3405.61, 2923.36, 2348.60, 1675.70, 1636.45, 1516.82, 1529.91, 1406.54, 1300.00, 1058.88, 1025.23, 994.39.



***N*-(5-methoxy-2-(prop-1-en-2-yl)benzyl)pyrazine-2-carboxamide (6l)**

Following the general procedure C, **6l** was obtained as a yellow solid (1.1 g, 77% yield for three steps, m.p. = 78-79 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.43 (d, J = 1.5 Hz, 1H), 8.74 (d, J = 2.5 Hz, 1H), 8.50 (dd, J = 2.5, 1.5 Hz, 1H), 8.04 (s, 1H), 7.12 (d, J = 8.5 Hz, 1H), 6.94 (d, J = 2.5 Hz, 1H), 6.82 (dd, J = 8.5, 2.5 Hz, 1H), 5.27 – 5.25 (m, 1H), 4.90 (s, 1H), 4.67 (d, J = 6.0 Hz, 2H), 3.79 (s, 3H), 2.07 (s, 3H).

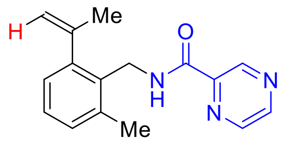
^{13}C NMR (125 MHz, $CDCl_3$)

δ 162.70, 158.71, 147.26, 144.49, 144.46, 144.27, 142.54, 136.15, 135.50, 129.43, 115.87, 114.28, 112.89, 55.33, 41.48, 25.30.

HRMS (ESI) for $C_{16}H_{17}N_3O_2Na$ $[M+Na]^+$: 306.1213, found: 306.1210.

FTIR (KBr, cm^{-1})

3442.06, 3416.82, 3405.61, 3383.18, 1695.33, 1684.11, 1653.27, 1633.64, 1616.82, 1577.57, 1560.75, 1538.32, 1510.28, 1462.62, 1400.93, 1389.72, 1285.98, 1019.63.



N-(2-methyl-6-(prop-1-en-2-yl)benzyl)pyrazine-2-carboxamide (6m)

Following the general procedure C, **6m** was obtained as a yellow solid (0.81 g, 60% yield for three steps, m.p. = 97-98 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.43 (d, J = 1.5 Hz, 1H), 8.72 (d, J = 2.5 Hz, 1H), 8.46 (dd, J = 2.5, 1.5 Hz, 1H), 7.74 (s, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 5.26 – 5.24 (m, 1H), 4.90 (dd, J = 2.0, 1.0 Hz, 1H), 4.68 (d, J = 5.0 Hz, 2H), 2.42 (s, 3H), 2.08 (s, 3H).

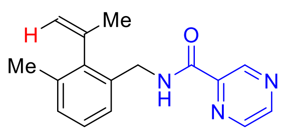
^{13}C NMR (125 MHz, $CDCl_3$)

δ 162.38, 147.21, 145.44, 145.42,144.42, 144.40, 142.52, 138.02, 131.76, 129.48, 127.86, 126.17, 115.58, 38.86, 25.74, 19.71.

HRMS (ESI) for $C_{16}H_{17}N_3ONa$ $[M+Na]^+$: 290.1264, found: 290.1269.

FTIR (KBr, cm^{-1})

3458.88, 3442.05, 3425.23, 3408.41, 3397.22, 2973.83, 2926.17, 1653.27, 1633.64, 1524.30, 1398.13, 1151.40, 1019.63, 901.87, 800.93.



N-(3-methyl-2-(prop-1-en-2-yl)benzyl)pyrazine-2-carboxamide (6n)

Following the general procedure C, **6n** was obtained as a white solid (0.83 g, 62% yield for three steps, m.p. = 97-98 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.43 (d, J = 1.5 Hz, 1H), 8.73 (d, J = 2.5 Hz, 1H), 8.49 (dd, J = 2.5, 1.5 Hz, 1H), 8.00 (s, 1H), 7.26 – 7.24 (m, 1H), 7.18 – 7.14 (m, 2H), 5.37 (d, J = 3.0 Hz, 1H), 4.89 (m, 1H), 4.76 (dd, J = 14.5, 6.6 Hz, 1H), 4.48 (dd, J = 14.5, 5.0 Hz, 1H), 2.29 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

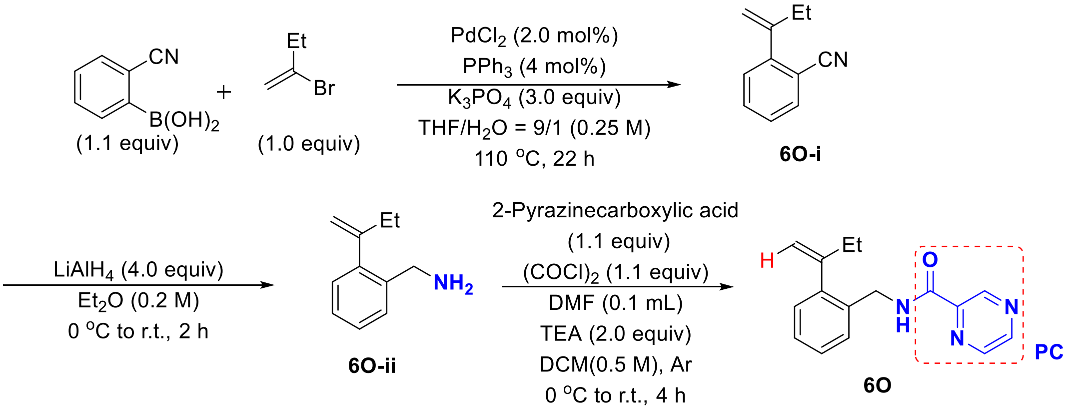
δ 162.57, 147.19, 144.55, 144.49, 143.84, 143.02, 142.52, 135.37, 134.27, 129.40, 127.09, 126.25, 116.07, 41.55, 24.28, 19.45.

HRMS (ESI) for $C_{16}H_{17}N_3OK$ [M+K]+: 290.1264, found: 290.1274.

FTIR (KBr, cm^{-1})

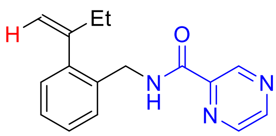
3458.88, 3442.06, 3425.23, 3388.79, 3088.79, 2968.22, 2923.36, 1667.29, 1653.27, 1557.94, 1527.10, 1420.56, 1294.39, 1028.04, 772.90, 641.12.

Procedure for 6O Synthesis



Suzuki Reaction[7]: A solution of 2-cyanobenzeneboronic acid (5.5 mmol, 1.1 equiv), $PdCl_2$ (0.1 mmol, 2.0 mol%), PPh_3 (0.2 mmol, 4.0 mol%), K_3PO_4 (15.0 mmol, 3.0 equiv), and 2-bromobut-1-ene (5.00 mmol) in THF/H_2O (9:1) (20 mL) was heated at 110 °C under N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 110 °C for 22 h, then cooled to rt and diluted with H_2O (20 mL) followed by extraction with EtOAc (30 mL x 3). The solvent was removed in vacuo, and the crude product was purified by silica gel chromatography (SiO_2, PE/EtOAc) to obtain the corresponding product(**6o-i**).

Benzonitrile Reduction and **PC Amide Preparation** was performed following the general procedure C.



***N*-(2-(but-1-en-2-yl)benzyl)pyrazine-2-carboxamide (6o)**

Following the procedure, **6o** was obtained as a yellow solid (0.95 g, 53% yield for three steps, m.p. = 63-64 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.43 (d, *J* = 1.5 Hz, 1H), 8.74 (d, *J* = 2.5 Hz, 1H), 8.49 (dd, *J* = 2.5, 1.5 Hz, 1H), 8.01 (s, 1H), 7.42 – 7.39 (m, 1H), 7.28 – 7.26 (m, 1H), 7.16 – 7.13 (m, 1H), 5.26 (q, J = 1.5 Hz, 1H), 4.95 – 4.94 (m, 1H), 4.67 (d, J = 6.0 Hz, 2H), 2.37 (q, J = 7.5 Hz, 2H), 1.07 (d, J = 15.0 Hz, 3H).

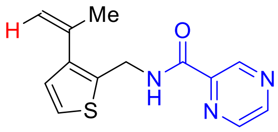
^{13}C NMR (125 MHz, $CDCl_3$)

δ 162.66, 150.37, 147.24, 144.49, 143.34, 142.52, 134.42, 128.82, 128.70, 127.42, 127.35, 113.56, 41.31, 31.24, 12.26.

HRMS (ESI) for $C_{16}H_{17}N_3ONa$ $[M+Na]^+$: 290.1264, found: 290.1262.

FTIR (KBr, cm^{-1})

3475.70, 3461.68, 3416.82, 1670.09, 1656.07, 1636.45, 1616.82, 1538.32, 1524.30, 1400.93, 1016.82.



N-((3-(prop-1-en-2-yl)thiophen-2-yl)methyl)pyrazine-2-carboxamide (6q)

Following the general procedure C, **6q** was obtained as a yellow solid (0.71 g, 55% yield for three steps, m.p. = 79-80 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.44 (d, J = 1.5 Hz, 1H), 8.75 (d, J = 2.5 Hz, 1H), 8.51 – 8.50 (m, 1H), 8.07 (s, 1H), 7.19 (d, J = 5.0 Hz, 1H), 6.96 (d, J = 5.0 Hz, 1H), 5.24 (t, J = 2.0 Hz, 1H), 4.98 (dd, J = 2.0, 1.0 Hz, 1H), 4.87 (d, J = 5.5 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

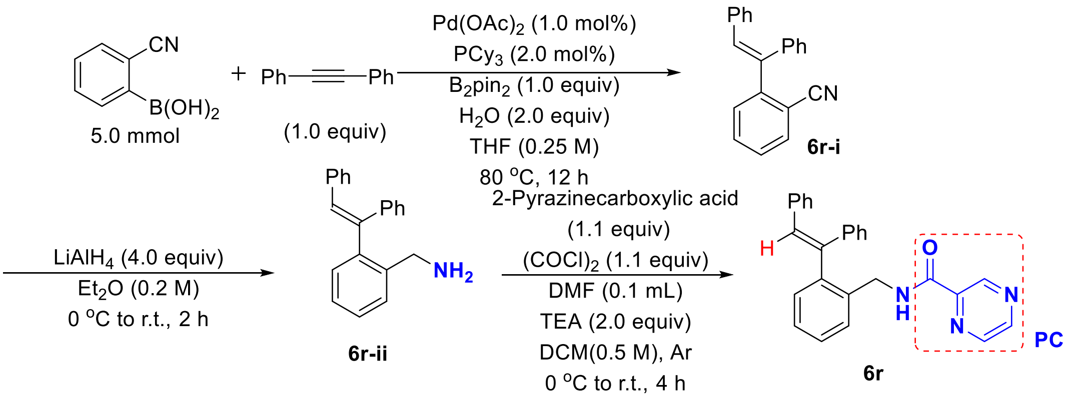
δ 162.60, 147.37, 144.51, 144.25, 142.57, 142.12, 139.47, 134.35, 127.75, 123.83, 115.72, 37.10, 24.13.

HRMS (ESI) for $C_{13}H_{13}N_3OSNa$ $[M+Na]^+$: 282.0672, found: 282.0682.

FTIR (KBr, cm^{-1})

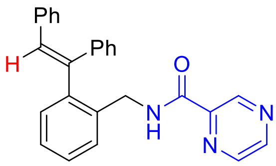
3422.43, 3408.41, 3397.20, 3383.18, 2968.22, 2928.97, 1675.70, 1521.50, 1398.13, 1285.98, 1171.03, 1022.43, 899.07, 775.70.

Procedure for 6r Synthesis



Suzuki Reaction[8]: A solution of 2-cyanobenzeneboronic acid (5.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.05 mmol, 1.0 mol%), PCy_3 (0.1 mmol, 2.0 mol%), B_2pin_2 (5.0 mmol, 1.0 equiv), H_2O (10.0 mmol, 2.0 equiv) and 1,2-diphenylethyne (5.0 mmol) in THF (20 mL) was heated at 80 °C under N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 80 °C for 12 h, then cooled to rt and diluted with H_2O (20 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crude product was purified by silica gel chromatography (SiO_2, PE/EtOAc) to obtain the corresponding product(**6r-i**).

Benzonitrile Reduction and **PC Amide Preparation** was follwing the general procedure C.



(*E*)-*N*-(2-(1,2-diphenylvinyl)benzyl)pyrazine-2-carboxamide (6r)

Following the procedure, **6r** was obtained as a yellow solid (0.54 g, 28% yield for three steps, m.p. = 90-91 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.34 (d, *J* = 1.5 Hz, 1H), 8.70 (d, *J* = 2.5 Hz, 1H), 8.43 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.69 (s, 1H), 7.42 – 7.39 (m, 2H), 7.35 – 7.32 (m, 2H), 7.21 – 7.16 (m, 8H), 7.13 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.71 (s, 1H), 4.46 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.43, 146.05, 143.46, 143.35, 142.86, 141.28, 140.79, 138.77, 135.90, 134.65, 130.04, 129.83, 128.74, 128.67, 128.38, 127.53, 127.13, 127.07, 126.75, 126.55, 126.08, 40.60.

HRMS (ESI) for $C_{26}H_{21}N_3ONa$ [M+Na]+: 414.1577, found: 414.1586.

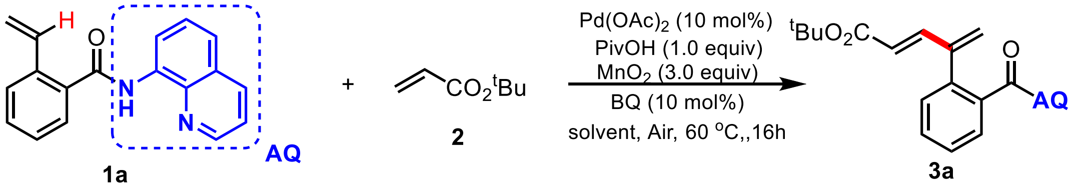
FTIR (KBr, cm^{-1})

3747.66, 3649.53, 3629.91, 3565.42, 3416.82, 2962.62, 2351.40, 1686.92, 1656.07, 1560.75, 1543.93, 1504.67, 1406.54, 1384.11, 1025.23.

3. Optimization of Reaction Conditions

3.1 Optimization of Conditions for the Cross-Coupling-1

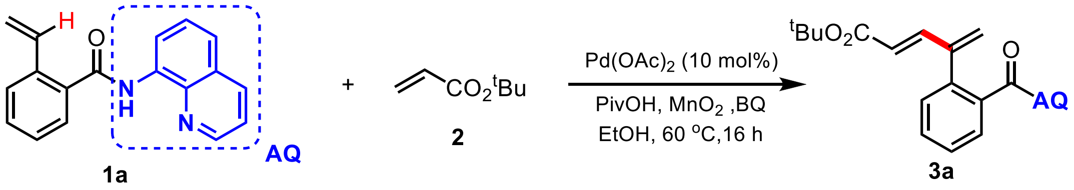
Table S1. Preliminary Screening of Solvents [a]



Entry	Solvent	Yield (%)[b]
1	MeCN	13
2	DCM	32
3	toluene	28
4	DME	16
5	EA	23
6	DMF	Trace
7	DMSO	Trace
8	MeOH	30
9	HFIP	Trace
10	CF_3CH_2OH	Trace
11	**EtOH**	**49**

[a]Reactions conditions: **1a** (0.1 mmol), **2** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), PivOH (1.0 equiv), MnO_2 (3.0 equiv), BQ (10 mol%) in a solvent (0.1 M) under air at 60 °C for 16 h. [b]Isolated yields.

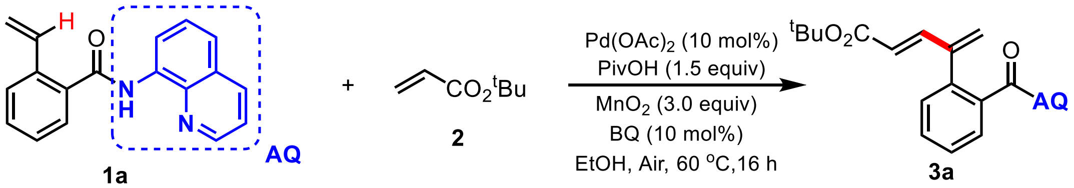
Table S2. Preliminary Screening of Additives-1 [a]



Entry	Additive-1	Yield (%)[b]
1	**PivOH (1.5 equiv)**	**51**
2	PivOH (2.0 equiv)	49
3	PivOH (2.5 equiv)	51
4	BQ (20 mol%)	47
5	BQ (50 mol%)	30
6	No BQ	28
7	MnO_2 (1.0 equiv)	26
8	MnO_2 (2.0 equiv)	33
9	Ar	47
10	O_2(1.0 atm)	50

[a]Reactions conditions: **1a** (0.1 mmol), **2** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), additives, in EtOH (0.1 M) at 60 °C for 16 h. [b]Isolated yields.

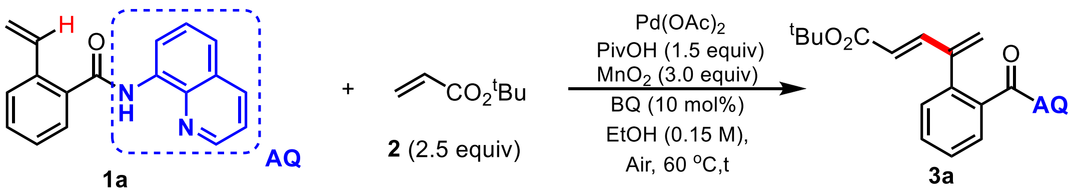
Table S3. Preliminary Screening of Additives-2[a]



Entry	Additive-2	Yield (%)[b]
1	**2** (1.5 equiv)	48
2	**2 (2.5 equiv)**	**63**
3	**2** (3.0 equiv)	56
4	C = 0.05 M	25
5	**C = 0.15 M**	**54**
6	C = 0.2 M	48

[a]Reactions conditions: **1a** (0.1 mmol), **2** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), PivOH (1.5 equiv), MnO_2 (3.0 equiv), BQ (10 mol%) in EtOH under air at 60 °C for 16 h. [b]Isolated yields.

Table S4. Preliminary Screening of Catalyst Loading and Time[a]

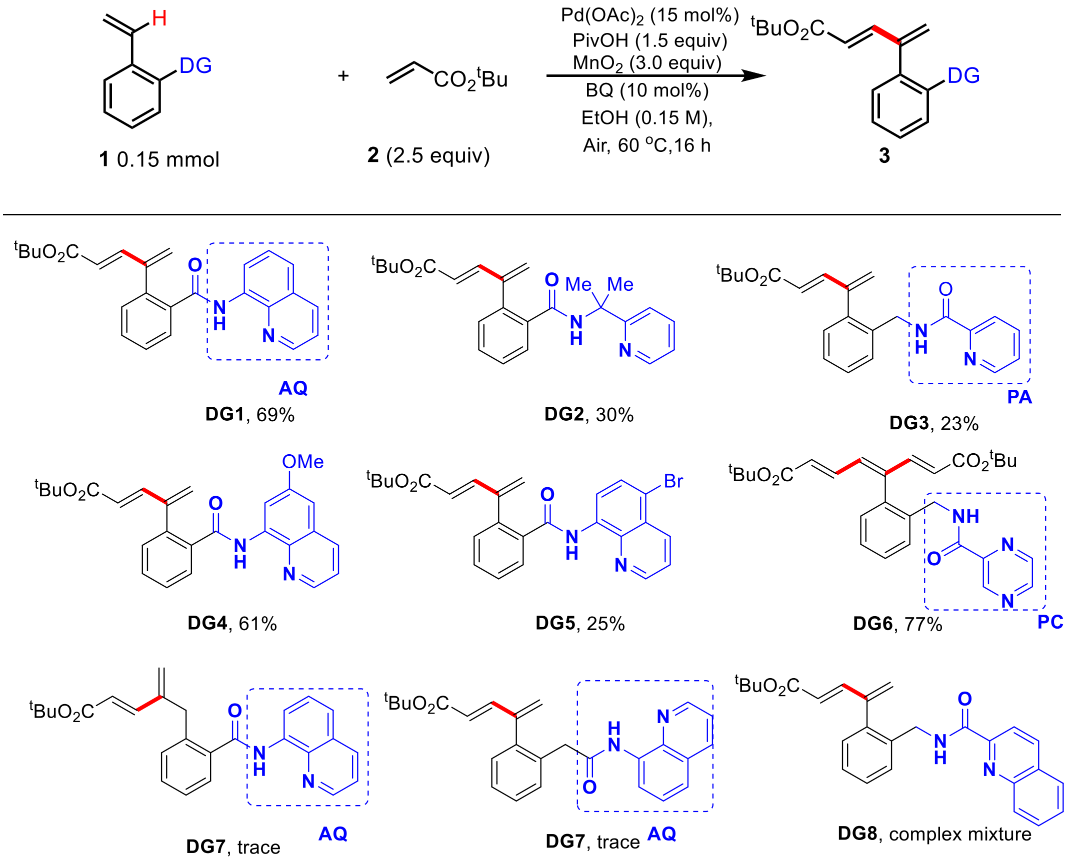


Entry	Catalyst and time	Yield (%)[b]
1	$Pd(OAc)_2$ (10 mol%), 16 h	42

2	Pd(OAc)$_2$ (10 mol%), 24 h	54
3	Pd(OAc)$_2$ (10 mol%), 36 h	52
4	Pd(OAc)$_2$ (15 mol%), 16 h	51
5	**Pd(OAc)$_2$ (15 mol%), 24 h**	**69**
6	Pd(OAc)$_2$ (15 mol%), 36 h	59

[a] Reactions conditions: **1a** (0.15 mmol), **2a** (2.5 equiv), Pd(OAc)$_2$, PivOH (1.5 equiv), MnO_2 (3.0 equiv), BQ (10 mol%) in EtOH (0.15 M) under air at 60 °C. [b]Isolated yields.

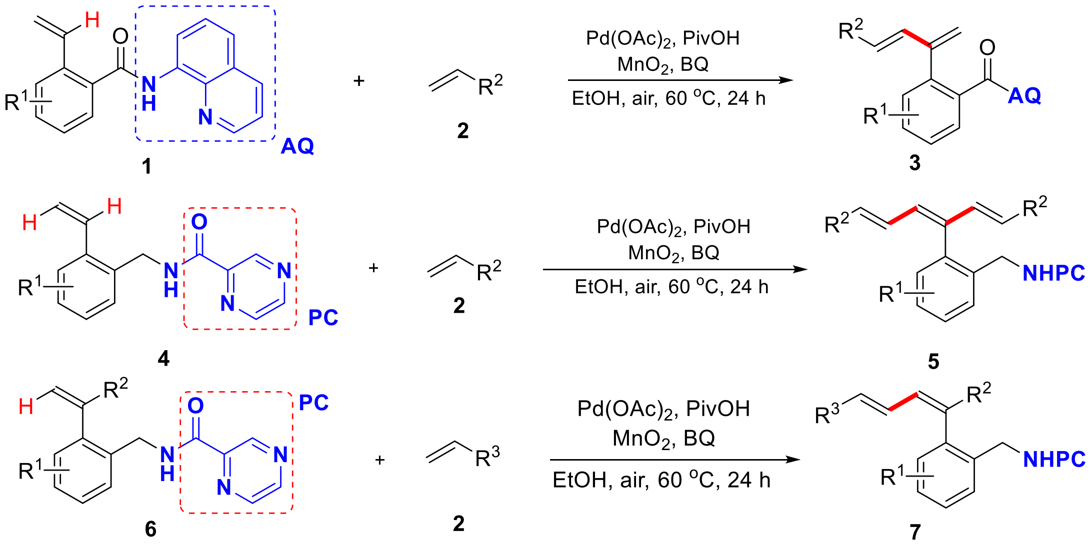
Table S5. Preliminary Screening of Directing Group[a]



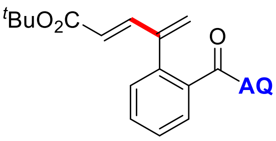
[a] Reactions conditions: **1a** (0.15 mmol), **2a** (2.5 equiv), Pd(OAc)$_2$ (15 mol%), PivOH (1.5 equiv), MnO_2 (3.0 equiv), BQ (10 mol%) in EtOH (0.15 M) under air at 60 °C for 24 h. [b]Isolated yields·.

4. General Procedure 1 for Alkenyl C-H Alkenylation

4.1 General Procedure 1 for Cross-Coupling Between Amides and Alkenes



An screw-cap vial was charged with $Pd(OAc)_2$ (15 mol%, 0.023 mmol) , MnO_2 (3.0 equiv, 0.45 mmol), BQ (10 mol%, 0.015 mmol), amide **1, 4 or 6** (1.0 equiv, 0.15 mmol), EtOH (1.0 mL). Then, pivalic acid (1.5 equiv, 0.23 mmol), and olefin **2** (2.5 equiv, 0.38 mmol) were added into the solution in sequence. The vial was sealed under air and heated to 60 °C with stirring for 24 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures).



Tert-butyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3a)

Following the general procedure 1, **3a** was obtained as a colorless oil (41.5 mg, 69% yield).

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$)

δ 10.22 (s, 1H), 8.83 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.73 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.54 – 7.50 (m, 4H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.42 (q, *J* = 4.0 Hz, 1H), 7.31 – 7.29 (m, 1H), 5.73 (s, 1H), 5.64 (d, *J* = 15.5 Hz, 1H), 5.61 (s, 1H), 1.37 (s, 9H).

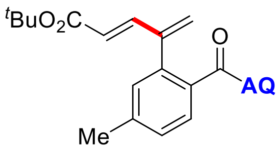
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.87, 165.09, 147.08, 144.22, 144.02, 137.61, 135.78, 135.40, 135.17, 133.71, 129.49, 129.41, 127.73, 127.34, 126.90, 126.35, 124.89, 122.81, 120.69, 120.56, 115.48, 79.32, 27.00.

HRMS (ESI) for $C_{25}H_{25}N_2O_3$ $[M+H]^+$: 401.1860, found: 401.1851.

FTIR (KBr, cm^{-1})

3416.82, 2359.81, 2340.19, 1681.31, 1650.47, 1406.54, 1028.04, 671.96.



Tert-butyl (*E*)-4-(5-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3b)

Following the general procedure 1, **3b** was obtained as a white oil (38.3 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.23 (s, 1H), 8.82 (dd, *J* = 7.5, 1.0 Hz, 1H), 8.73 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.42 (q, *J* = 4.0 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.09 (s, 1H), 5.73 (s, 1H), 5.62 (d, *J* = 15.5 Hz, 1H), 5.60 (s, 1H), 2.44 (s, 3H), 1.37 (s, 9H).

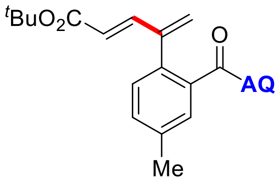
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.81, 165.14, 147.02, 144.48, 144.14, 139.87, 137.66, 135.82, 135.14, 133.87, 132.50, 130.00, 128.03, 127.91, 126.90, 126.37, 124.70, 122.72, 120.53, 120.51, 115.43, 79.28, 27.01, 20.34.

HRMS (ESI) for $C_{26}H_{27}N_2O_4$ $[M+H]^+$: 415.2016, found: 415.2023.

FTIR (KBr, cm^{-1})

3388.79, 2923.36, 2853.27, 2354.21, 1681.31, 1664.49, 1650.47, 1557.94, 1541.12, 1504.67, 1398.13, 1025.23.



Tert-butyl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3c)

Following the general procedure 1, **3c** was obtained as a colorless oil (44.1 mg, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.19 (s, 1H), 8.82 (d, *J* = 7.0 Hz, 1H), 8.73 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.14 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.69 (s, 1H), 7.56 – 7.50 (m, 2H), 7.46 – 7.41 (m, 2H), 7.33 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 5.70 (s, 1H), 5.65 (d, *J* = 16.0 Hz, 1H), 5.59 (s, 1H), 2.46 (s, 3H), 1.37 (s, 9H).

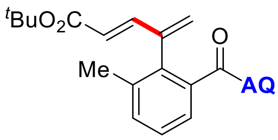
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.08, 165.15, 147.05, 144.22, 144.14, 137.63, 137.28, 135.26, 135.14, 133.78, 132.79, 130.19, 129.32, 128.28, 126.90, 126.35, 124.83, 122.72, 120.61, 120.52, 115.47, 79.24, 27.02, 20.12.

HRMS (ESI) for $C_{26}H_{27}N_2O_3$ $[M+H]^+$: 415.2016, found: 415.2013.

FTIR (KBr, cm^{-1})

3747.66, 3646.73, 3627.1, 3568.22, 3212.15, 3178.5, 3007.48, 2962.62, 2351.4, 1653.27, 1535.51, 1504.67, 1403.74, 1028.04.



Tert-butyl (*E*)-4-(2-methyl-6-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3d)

Following the general procedure 1, **3d** was obtained as a white solid (57.2 mg, 92% yield, m.p.= 94-95 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.10 (s, 1H), 8.83 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.72 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.66 – 7.65 (m, 1H), 7.56 – 7.50 (m, 2H), 7.45 (d, *J* = 15.5 Hz, 1H), 7.42 – 7.38 (m, 3H), 5.79 (s, 1H), 5.53 (d, *J* = 10.5 Hz, 1H), 5.52 (d, *J* = 3.5 Hz, 1H), 2.26 (s, 3H), 1.43 (s, 9H).

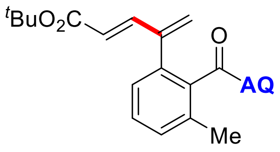
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.52, 165.19, 147.13, 143.79, 143.06, 137.56, 136.42, 136.02, 135.15, 134.62, 133.75, 131.11, 127.03, 126.90, 126.33, 125.38, 124.87, 122.54, 120.63, 120.49, 115.49, 79.37, 27.11, 18.92.

HRMS (ESI) for $C_{26}H_{27}N_2O_3$ $[M+H]^+$: 415.2016, found: 415.2011.

FTIR (KBr, cm^{-1})

3414.0, 3383.18, 2923.36, 2853.27, 1731.78, 1633.64, 1653.27, 1557.94, 1538.32, 1504.67, 1403.74, 1028.04.



Tert-butyl (*E*)-4-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3e)

Following the general procedure 1, **3e** was obtained as a white oil (31.8 mg, 51% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.84 (s, 1H), 8.83 (d, *J* = 7.0 Hz, 1H), 8.66 (d, *J* = 4.0 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.39 (q, *J* = 4.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 15.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 5.71 (d, *J* = 16.0 Hz, 1H), 5.59 (s, 1H), 5.54 (s, 1H), 2.50 (s, 3H), 1.42 (s, 9H).

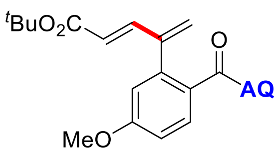
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.51, 165.14, 147.12, 144.23, 143.59, 137.37, 136.27, 135.17, 134.94, 134.87, 133.43, 129.00, 127.87, 126.92, 126.33, 126.07, 125.03, 123.12, 120.76, 120.51, 115.39, 79.26, 27.09, 18.73.

HRMS (ESI) for $C_{26}H_{26}N_2O_3Na$ $[M+Na]^+$: 437.1836, found: 437.1838.

FTIR (KBr, cm^{-1})

3655.14, 3629.91, 3573.83, 3528.97, 3489.72, 3453.27, 1709.35, 1678.5, 1656.07, 1630.84, 1524.3, 1482.24, 1385.92, 1328.04, 1271.96, 1151.4.



Tert-butyl (*E*)-4-(5-methoxy-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3f)

Following the general procedure 1, **3f** was obtained as a white oil (40.4 mg, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.25 (s, 1H), 8.82 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.75 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.43 (q, 4.0 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 5.76 (s, 1H), 5.64 (d, *J* = 5.0 Hz, 1H), 5.63 (d, *J* = 10.5 Hz, 1H), 3.89 (s, 3H), 1.38 (s, 9H).

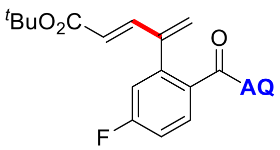
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.30, 165.11, 160.13, 146.99, 144.40, 143.89, 137.80, 137.71, 135.15, 133.99, 130.01, 127.58, 126.92, 126.39, 124.79, 122.79, 120.50, 120.43, 115.40, 114.91, 112.46, 79.35, 54.50, 27.02.

HRMS (ESI) for $C_{26}H_{27}N_2O_4$ $[M+H]^+$: 431.1965, found: 431.1955.

FTIR (KBr, cm^{-1})

3441.33, 3417.07, 3383.91, 2920.56, 2853.27, 2354.21, 1650.47, 1636.45, 1406.54, 1019.63.



Tert-butyl (*E*)-4-(5-fluoro-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3g)

Following the general procedure 1, **3g** was obtained as a white oil (35.7 mg, 57% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.21 (s, 1H), 8.80 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.74 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.16 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.92 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.45 – 7.42 (m, 2H), 7.22 – 7.18 (m, 1H), 7.00 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.76 (s, 1H), 5.65 (d, *J* = 4.5 Hz, 1H), 5.63 (d, *J* = 11.5 Hz, 1H), 1.39 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.86, 164.73, 162.49 (d, J_{CF} = 250.6 Hz), 147.12, 143.33, 143.26, 138.38 (d, J_{CF} = 8.3 Hz), 137.60, 135.21, 133.61, 131.55 (d, J_{CF} = 3.3 Hz), 130.35 (d, J_{CF} = 8.9 Hz), 126.91, 126.34, 125.26, 123.04, 120.81, 120.61, 116.32 (d, J_{CF} = 21.9 Hz), 115.51, 114.45 (d, J_{CF} = 21.3 Hz), 79.52, 27.01.

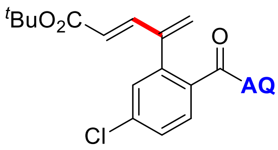
^{19}F NMR (471 MHz, $CDCl_3$)

δ -109.23.

HRMS (ESI) for $C_{25}H_{24}N_2O_3F$ $[M+H]^+$: 419.1765, found: 419.1755.

FTIR (KBr, cm^{-1})

3419.63, 3385.98, 2926.17, 2853.27, 2348.60, 1653.27, 1633.64, 1400.93, 1028.04.



Tert-butyl (*E*)-4-(5-chloro-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3h)

Following the general procedure 1, **3h** was obtained as a yellow oil (33.4 mg, 51% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.23 (s, 1H), 8.80 (dd, *J* = 6.5, 2.0 Hz, 1H), 8.74 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.16 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.48 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.29 (d, *J* = 2.0 Hz, 1H), 5.77 (s, 1H), 5.64 (s, 1H), 5.61 (d, *J* = 16.0 Hz, 1H), 1.38 (s, 9H).

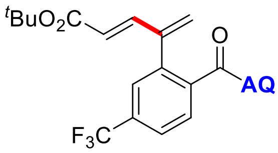
^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.84, 164.65, 147.14, 143.35, 143.13, 137.59, 137.49, 135.54, 135.22, 133.72, 133.54, 129.43, 129.29, 127.58, 126.91, 126.33, 125.40, 123.11, 120.90, 120.63, 115.57, 79.54, 27.00.

HRMS (ESI) for $C_{25}H_{24}N_2O_3Cl$ $[M+H]^+$: 435.147, found: 435.148.

FTIR (KBr, cm^{-1})

3444.50, 3417.71, 3383.11, 2920.31, 2856.07, 1684.11, 1653.27, 1633.64, 1541.12, 1471.03, 1398.13, 1022.43.



Tert-butyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)-5-(trifluoromethyl)phenyl)penta-2,4-dienoate (3i)

Following the general procedure 1, **3i** was obtained as a white solid (35.2 mg, 50% yield, m.p. = 137-138 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.26 (s, 1H), 8.80 (q, *J* = 3.0 Hz, 1H), 8.74 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.17 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.57 – 7.55 (m, 3H), 7.46 – 7.43 (m, 2H), 5.80 (s, 1H), 5.67 (s, 1H), 5.57 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 9H).

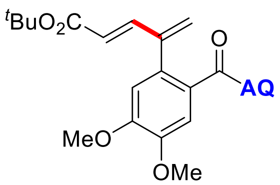
^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.72, 164.42, 147.22, 143.20, 143.05, 138.61, 137.54, 136.53, 135.26, 133.32, 131.48 (q, J_{CF} = 32.6 Hz), 128.43, 126.91, 126.31, 126.24 (q, J_{CF} = 3.9 Hz), 125.71, 124.34 (q, J_{CF} = 3.6 Hz), 123.21, 122.506 (q, J_{CF} = 271.0 Hz), 121.14, 120.69, 115.67, 79.60, 26.98.

HRMS (ESI) for $C_{26}H_{24}N_2O_3F_3$ $[M+H]^+$: 469.1734, found: 469.1730.

FTIR (KBr, cm^{-1})

3507.53, 3472.90, 3444.73, 3417.40, 3383.33, 3362.80, 2917.76, 2853.27, 2354.21, 1557.94, 1656.07, 1636.45, 1507.48, 1471.03, 1409.35, 1022.43.



Tert-butyl (*E*)-4-(4,5-dimethoxy-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3j)

Following the general procedure 1, **3j** was obtained as a colorless oil (50.9 mg, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.29 (s, 1H), 8.83 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.74 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.47 (d, *J* = 15.5 Hz, 1H), 7.42 (q, *J* = 4.0 Hz, 1H), 6.72 (s, 1H), 5.78 (s, 1H), 5.67 (s, 1H), 5.66 (d, *J* = 15.5 Hz, 1H), 3.99 (s, 3H), 3.95 (s, 3H), 1.41 (s, 9H).

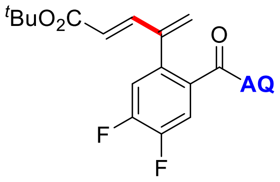
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.25, 165.17, 149.58, 147.66, 147.00, 144.28, 144.14, 137.75, 135.12, 133.98, 128.81, 127.36, 126.92, 126.36, 125.44, 122.94, 120.54, 120.52, 115.41, 111.77, 111.13, 79.43, 55.15, 55.11, 27.06.

HRMS (ESI) for $C_{27}H_{29}N_2O_5$ $[M+H]^+$: 461.2071, found: 461.2067.

FTIR (KBr, cm^{-1})

3444.86, 3417.79, 3385.98, 2920.56, 2850.47, 2357.01, 1684.11, 1650.47, 1633.64, 1538.32, 1405.54, 1022.43, 795.33.



Tert-butyl (*E*)-4-(4,5-difluoro-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3k)

Following the general procedure 1, **3k** was obtained as a colorless oil (26.8mg, 41% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.24 (s, 1H), 8.78 (dd, *J* = 5.5, 3.5 Hz, 1H), 8.74 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.16 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.78 (dd, *J* = 10.5, 8.0 Hz, 1H), 7.55 – 7.54 (m, 2H), 7.46 – 7.42 (m, 2H), 7.11 (dd, *J* = 10.0, 7.5 Hz, 1H), 5.78 (s, 1H), 5.65 (s, 1H), 5.61 (d, *J* = 15.5 Hz, 1H), 1.40 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.74, 163.30, 148.50 (dd, J_{CF} = 165.0, 12.5 Hz), 147.19, 144.08 (dd, J_{CF} = 223.0, 3.5 Hz), 143.25, 142.40, 137.58, 135.24, 133.36, 132.80 (d, J_{CF} = 4.6 Hz), 132.09 (d, J_{CF} = 4.1 Hz), 126.91, 126.30, 125.88, 123.24, 121.09, 120.69, 118.39 (d, J_{CF} = 17.6 Hz), 117.66 (d, JCF = 18.6 Hz), 115.65, 79.66, 27.01.

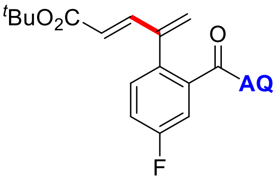
^{19}F NMR (471 MHz, $CDCl_3$)

δ -133.48, -136.73.

HRMS (ESI) for $C_{25}H_{23}N_2O_3F_2$ $[M+H]^+$: 437.1671, found: 437.1678.

FTIR (KBr, cm^{-1})

3507.53, 3472.90, 3444.73, 3417.40, 3383.33, 3362.80, 2917.76, 2853.27, 2354.21, 1557.94, 1656.07, 1636.45, 1507.48, 1471.03, 1409.35, 1022.43.



Tert-butyl (*E*)-4-(4-fluoro-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3l)

Following the general procedure 1, **3l** was obtained as a white oil (29.7 mg, 47% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.24 (s, 1H), 8.80 (dd, *J* = 6.5, 2.5 Hz, 1H), 8.74 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.16 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.61 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.46 – 7.42 (m, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.21 (m, 1H), 5.75 (s, 1H), 5.62 (s, 1H), 5.60 (d, *J* = 15.5 Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.95, 164.34, 161.25 (d, J_{CF} = 247.5 Hz), 147.17, 143.92, 143.25, 137.60, 137.21 (d, J_{CF} = 6.8 Hz), 135.21, 133.45, 131.61 (d, J_{CF} = 3.5 Hz), 131.29 (d, J_{CF} = 7.9 Hz), 126.91, 126.32, 125.47, 122.99, 120.98, 120.64, 116.61 (d, J_{CF} = 21.2 Hz), 115.63, 114.97 (d, J_{CF} = 23.0 Hz), 79.46, 27.01.

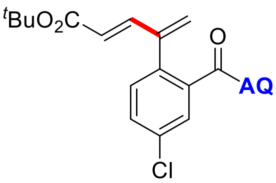
^{19}F NMR (471 MHz, $CDCl_3$)

δ -112.63.

HRMS (ESI) for $C_{25}H_{24}N_2O_3F$ $[M+H]^+$: 419.1765, found: 419.1766.

FTIR (KBr, cm^{-1})

3629.91, 3442.06, 3419.63, 2926.17, 2357.01, 1737.38, 1681.31, 1651.38, 1557.10, 1538.04, 1504.82, 1392.52, 1022.43.



Tert-butyl (*E*)-4-(4-chloro-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3m)

Following the general procedure 1, **3m** was obtained as a white oil (38.8 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.21 (s, 1H), 8.79 (dd, *J* = 6.5, 2.5 Hz, 1H), 8.74 (dd, *J* = 4.0, 1.5

Hz, 1H), 8.16 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.88 (d, *J* = 2.0 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.49 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 5.74 (s, 1H), 5.63 – 5.59 (m, 2H), 1.38 (s, 9H).

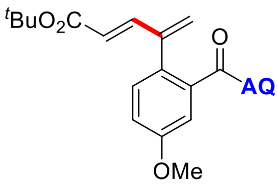
^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.89, 164.30, 147.18, 143.62, 143.14, 137.57, 136.86, 135.21, 134.06, 133.42, 130.77, 129.57, 127.94, 126.90, 126.31, 125.36, 123.05, 121.00, 120.64, 115.63, 79.48, 27.00.

HRMS (ESI) for $C_{25}H_{24}N_2O_3Cl$ $[M+H]^+$: 435.147, found: 435.1479.

FTIR (KBr, cm^{-1})

3447.66, 3416.82, 3385.98, 2923.36, 2853.27, 1684.11, 1656.07, 1636.45, 1560.75, 1541.12, 1403.04, 1022.43.



Tert-butyl (*E*)-4-(4-methoxy-2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3n)

Following the general procedure 1, **3n** was obtained as a colorless oil (51.9 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.22 (s, 1H), 8.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.73 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.46 – 7.41 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.06 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.70 (s, 1H), 5.66 (d, *J* = 16.0 Hz, 1H), 5.60 (s, 1H), 3.90 (s, 3H), 1.38 (s, 9H).

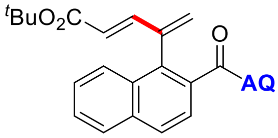
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.66, 165.16, 158.37, 147.08, 144.42, 143.81, 137.63, 136.50, 135.13, 133.70, 130.66, 127.86, 126.90, 126.33, 125.06, 122.73, 120.72, 120.56, 115.84, 115.48, 112.44, 79.27, 54.54, 27.03.

HRMS (ESI) for $C_{26}H_{27}N_2O_4$ $[M+H]^+$: 431.1965, found: 431.1955.

FTIR (KBr, cm^{-1})

3385.98, 3355.14, 2926.17, 2847.66, 1653.27, 1633.64, 1402.90, 1137.38, 1044.86.



Tert-butyl (*E*)-4-(3-(quinolin-8-ylcarbamoyl)naphthalen-2-yl)penta-2,4-dienoate (3o)

Following the general procedure 1, **3o** was obtained as a colorless oil (42.9 mg, 64% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.29 (s, 1H), 8.90 (dd, *J* = 7.5, 1.0 Hz, 1H), 8.73 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.16 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.91 (m, 2H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 16.0 Hz, 1H), 7.60 – 7.52 (m, 4H), 7.42 (q, *J* = 4.0 Hz, 1H), 6.03 (s, 1H), 5.72 (s, 1H), 5.43 (d, *J* = 15.5 Hz, 1H), 1.40 (s, 9H).

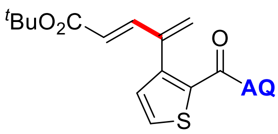
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.41, 165.13, 147.19, 144.38, 141.95, 137.64, 135.16, 133.77, 133.17, 133.09, 132.95, 130.42, 127.79, 127.10, 127.07, 126.93, 126.36, 126.19, 126.07, 126.00, 124.15, 123.63, 120.76, 120.53, 115.59, 79.45, 27.07.

HRMS (ESI) for $C_{29}H_{27}N_2O_3$ $[M+H]^+$: 451.2016, found: 451.2006.

FTIR (KBr, cm^{-1})

3383.09, 3354.97, 2968.22, 2920.56, 1684.11, 1670.09, 1656.07, 1560.75, 1535.51, 1406.54, 1137.38, 1042.06, 994.39, 924.30, 837.38.



Tert-butyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)thiophen-3-yl)penta-2,4-dienoate (3p)

Following the general procedure 1, **3p** was obtained as a yellow solid (25.2 mg, 41% yield, m.p. = 105-106 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.62 (s, 1H), 8.82 – 8.80 (m, 2H), 8.15 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.63 (d, *J* = 15.5 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.45 (q, *J* = 4.0 Hz, 1H), 6.97 (d, *J* = 5.0 Hz, 1H), 6.07 (s, 1H), 5.81 (s, 1H), 5.61 (d, *J* = 16.0 Hz, 1H), 1.41 (s, 9H).

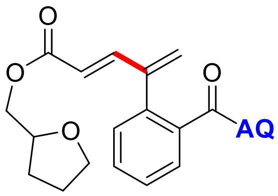
^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.92, 158.99, 147.01, 143.39, 139.61, 137.82, 137.61, 136.40, 135.11, 133.79, 129.64, 128.79, 127.16, 126.90, 126.35, 123.36, 120.69, 120.58, 115.76, 79.62, 27.03.

HRMS (ESI) for $C_{23}H_{23}N_2O_3$ $[M+H]^+$: 407.1424, found: 407.1432.

FTIR (KBr, cm^{-1})

3444.44, 3417.24, 3383.14, 2923.36, 2850.47, 1653.27, 1633.64, 1560.75, 1535.51, 1507.48, 1473.83 , 1025.23.



(Tetrahydrofuran-2-yl)methyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3q)

Following the general procedure 1, **3q** was obtained as a white oil (38.3 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.21 (s, 1H), 8.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.73 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.59 (d, *J* = 15.5 Hz, 1H), 7.56 – 7.50 (m, 4H), 7.43 (q, *J* = 4.0 Hz, 1H), 7.29 – 7.27 (m, 1H), 5.78 (s, 1H), 5.76 (d, *J* = 15.5 Hz, 1H), 5.66 (s, 1H), 4.16 (dd, *J* = 10.5, 3.5 Hz, 1H), 4.06 – 4.03 (m, 1H), 4.02 – 3.98 (m, 1H), 3.84 – 3.80 (m, 1H), 3.76 – 3.71 (m, 1H), 1.96 – 1.90 (m, 1H), 1.88 – 1.81 (m, 2H), 1.55 – 1.50 (m, 1H).

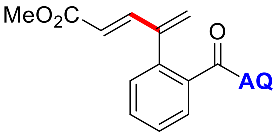
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.73, 165.69, 147.15, 145.60, 144.17, 137.62, 135.46, 135.36, 135.15, 133.69, 129.55, 129.41, 127.85, 127.45, 126.90, 126.34, 125.65, 120.70, 120.62, 120.58, 115.51, 75.43, 67.34, 65.43, 26.94, 24.55.

HRMS (ESI) for $C_{26}H_{25}N_2O_4$ $[M+H]^+$: 429.1809, found: 429.1815.

FTIR (KBr, cm^{-1})

3444.28, 3417.37, 3383.59, 2926.17, 2850.47, 1653.27, 1636.45 1557.94, 1535.51, 1507.48 ,1400.93, 1016.82.



Methyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3r)

Following the general procedure 1, **3r** was obtained as a yellow oil (31.7 mg, 59% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.21 (s, 1H), 8.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.71 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 – 7.89 (m, 1H), 7.57 – 7.51 (m, 5H), 7.43 (q, *J* = 4.0 Hz, 1H), 7.30 – 7.28 (m, 1H), 5.77 (s, 1H), 5.71 (d, *J* = 15.5 Hz, 1H), 5.67 (s, 1H), 3.66 (s, 3H).

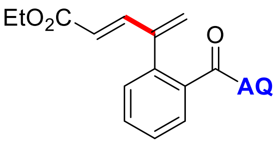
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.22, 165.74, 147.06, 145.29, 144.20, 137.62, 135.43, 135.40, 135.20, 133.66, 129.57, 129.35, 128.89, 127.86, 127.47, 126.92, 126.36, 125.55, 120.74, 120.59, 115.53, 50.51.

HRMS (ESI) for $C_{22}H_{19}N_2O_3$ $[M+H]^+$: 359.1390, found: 359.1386.

FTIR (KBr, cm^{-1})

3442.06, 3419.63, 3383.18, 3175.70, 2351.40, 1656.07, 1557.94, 1541.12, 1504.67, 1457.01, 1402.85, 1030.84.



Ethyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3s)

Following the general procedure 1, **3s** was obtained as a yellow oil (36.3 mg, 65% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.21 (s, 1H), 8.82 (d, *J* = 7.5 Hz, 1H), 8.71 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 (dd, *J* = 6.5, 2.5 Hz, 1H), 7.57 - 7.49 (m, 5H), 7.43 (q, *J* = 4.0 Hz, 1H), 7.29 (dd, *J* = 7.0, 1.5 Hz, 1H), 5.77 (s, 1H), 5.70 (d, *J* = 15.5 Hz, 1H), 5.66 (s, 1H), 4.12 (q, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

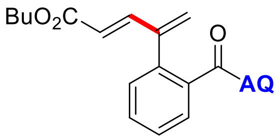
δ 165.78, 165.75, 147.06, 145.03, 144.22, 137.62, 135.53, 135.40,

135.19, 133.68, 129.55, 129.37, 127.84, 127.44, 126.92, 126.36, 125.39, 121.04, 120.72, 120.58, 115.52, 59.34, 13.15.

HRMS (ESI) for $C_{23}H_{21}N_2O_3$ $[M+H]^+$: 373.1547, found: 373.1540.

FTIR (KBr, cm^{-1})

3851.40, 3744.86, 3646.73, 3587.85, 3178.50, 2926.17, 2850.47, 2354.21, 1656.07, 1636.45, 1504.67, 1402.84, 1022.43.



Butyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3t)

Following the general procedure 1, **3t** was obtained as a colorless oil (36.4 mg, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.22 (s, 1H), 8.82 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.71 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 (dd, *J* = 6.5, 2.5 Hz, 1H), 7.56 – 7.50 (m, 5H), 7.43 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.30 (dd, *J* = 6.5, 2.5 Hz, 1H), 5.77 (s, 1H), 5.70 (d, *J* = 15.5 Hz, 1H), 5.66 (s, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 1.55 – 1.50 (m, 2H), 1.32 – 1.29 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H).

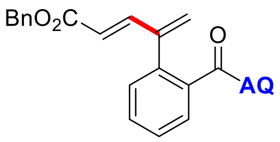
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.90, 165.77, 147.07, 144.98, 144.24, 137.61, 135.56, 135.39, 135.19, 133.67, 129.58, 129.39, 127.81, 127.44, 126.91, 126.35, 125.39, 120.98, 120.73, 120.57, 115.51, 63.27, 29.60, 18.04, 12.64.

HRMS (ESI) for $C_{25}H_{25}N_2O_3$ $[M+H]^+$: 401.186, found: 401.1863.

FTIR (KBr, cm^{-1})

3750.47, 3627.36, 3568.22, 3422.43, 3383.18, 3357.94, 3144.86, 2965.42, 2923.36, 2357.01, 2320.56, 1653.27, 1557.94, 1541.12, 1403.74, 1025.23.



Benzyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3u)

Following the general procedure 1, **3u** was obtained as a white oil (37.7 mg, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.19 (s, 1H), 8.82 (dd, *J* = 7.0, 1.0 Hz, 1H), 8.59 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.88 (dd, *J* = 6.0, 2.5 Hz, 1H), 7.59 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.50 (m, 4H), 7.37 (q, *J* = 4.0 Hz, 1H), 7.32 – 7.27 (m, 6H), 5.77 (d, *J* = 7.5 Hz, 1H), 5.76 (d, *J* = 8.5 Hz, 1H), 5.65 (s, 1H), 5.12 (s, 2H).

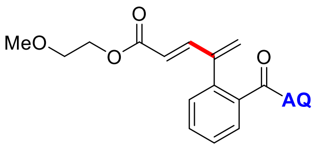
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.74, 165.59, 147.09, 145.63, 144.15, 137.58, 137.39, 135.43, 135.41, 135.13, 134.84, 133.65, 129.54, 129.35, 127.85, 127.48, 127.28, 127.16, 126.89, 126.34, 125.72, 120.72, 120.64, 120.58, 115.50, 65.23.

HRMS (ESI) for $C_{28}H_{23}N_2O_3$ $[M+H]^+$: 435.1703, found: 435.1707.

FTIR (KBr, cm^{-1})

3742.53, 3646.33, 3626.88, 3564.79, 3444.86, 3383.18, 3212.15, 3147.66, 2351.40, 1650.47, 1557.94, 1541.12, 1504.67, 1406.54, 1022.43, 798.13.



2-Methoxyethyl (*E*)-4-(2-(quinolin-8-ylcarbamoyl)phenyl)penta-2,4-dienoate (3v)

Following the general procedure 1, **3v** was obtained as a yellow oil (32.0 mg, 53% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.21 (s, 1H), 8.82 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.72 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 (dd, *J* = 6.0, 2.5 Hz, 1H), 7.59 (d, *J* = 15.5 Hz, 1H), 7.56 – 7.49 (m, 4H), 7.43 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.28 (dd, *J* = 6.0, 3.0 Hz, 1H), 5.78 (s, 1H), 5.77 (d, *J* = 15.5 Hz, 1H), 5.66 (s, 1H), 4.23 (t, *J* = 5.0 Hz, 2H), 3.55 (t, *J* = 5.0 Hz, 2H), 3.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

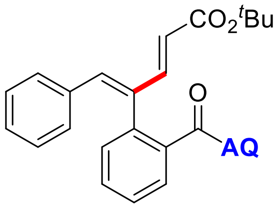
δ 165.76, 165.70, 147.13, 145.65, 144.16, 137.62, 135.45, 135.38,

135.17, 133.68, 129.55, 129.40, 127.87, 127.45, 126.91, 126.35, 125.69, 120.72, 120.61, 120.59, 115.52, 69.38, 62.44, 57.93.

HRMS (ESI) for $C_{24}H_{23}N_2O_4$ $[M+H]^+$: 403.1652, found: 403.1657.

FTIR (KBr, cm^{-1})

3565.42, 3442.06, 3416.82, 2962.62, 2354.21, 1653.27, 1560.75, 1543.93, 1507.48, 1409.35, 1028.04.



Tert-butyl (2*E*,4*Z*)-5-phenyl-4-(2-(quinolin-8-ylcarbamoyl) phenyl)penta-2,4-dienoate (3w)

Following the general procedure 1, **3w** was obtained as a white solid (62.0 mg, 87% yield, m.p. = 57-58 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.33 (s, 1H), 8.78 (dd, *J* = 7.5, 2.0 Hz, 1H), 8.50 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.64 (d, *J* = 16.0 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.50 – 7.44 (m, 2H), 7.35 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.11 – 7.08 (m, 3H), 7.04 (s, 1H), 6.99 – 6.97 (m, 2H), 5.47 (d, *J* = 15.5 Hz, 1H), 1.40 (s, 9H).

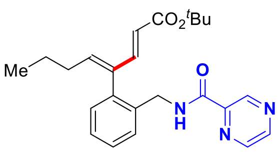
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.35, 164.92, 147.15, 146.78, 138.59, 137.63, 136.54, 135.27, 134.97, 134.56, 134.28, 133.87, 130.67, 129.76, 128.78, 128.75, 127.61, 127.32, 127.28, 126.74, 126.26, 121.30, 120.53, 120.40, 115.55, 79.18, 27.08.

HRMS (ESI) for $C_{31}H_{28}N_2O_3Na$ $[M+Na]^+$: 499.1992, found: 499.1977.

FTIR (KBr, cm^{-1})

3851.40, 3744.86, 3629.91, 3568.22, 3468.22, 3458.88, 3442.06, 3416.82, 3385.98, 1686.92, 1653.27, 1636.45, 1538.32, 1510.28, 1403.74, 1025.23.



Tert-butyl (2*E*,4*Z*)-4-(2-((pyrazine-2-carboxamido)methyl) phenyl)octa-2,4-dienoate (3x)

Following the general procedure 1, **3x** was obtained as a yellow oil (56.0 mg, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.40 (d, *J* = 1.5 Hz, 1H), 8.72 (d, *J* = 2.5 Hz, 1H), 8.47 – 8.46 (m, 1H), 7.91 (s, 1H), 7.49 – 7.47 (m, 1H), 7.44 (d, *J* = 15.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.04 – 7.02 (m, 1H), 6.24 (t, *J* = 7.5 Hz, 1H), 5.13 (d, *J* = 15.5 Hz, 1H), 4.52 (dd, *J* = 15.0, 6.0 Hz, 1H), 4.45 (dd, *J* = 14.5, 5.5 Hz, 1H), 1.96 – 1.85 (m, 2H), 1.42 (s, 9H), 1.40 – 1.37 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H).

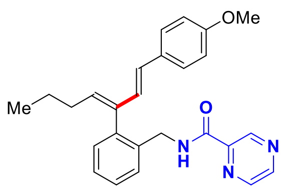
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.39, 161.56, 146.17, 143.41, 143.33, 142.28, 141.45, 137.37, 135.14, 134.63, 129.12, 128.04, 127.21, 127.06, 119.84, 104.78, 79.14, 40.27, 30.88, 27.11, 21.15, 12.81.

HRMS (ESI) for $C_{24}H_{29}N_3O_3Na$ $[M+Na]^+$: 430.2101, found: 430.2101.

FTIR (KBr, cm^{-1})

3854.21, 3747.56, 3635.51, 3416.82, 3332.71, 3192.52, 3063.55, 3004.67, 2957.01, 2923.36, 1737.38, 1686.92, 1653.27, 1557.94, 1507.48, 1459.81, 1400.93, 1025.23.



***N*-(2-((1*E*,3*Z*)-1-(4-methoxyphenyl)hepta-1,3-dien-3-yl)benzyl)pyrazine-2-carboxamide (3y)**

Following the general procedure 1, **3y** was obtained as a brown oil (50.7 mg, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.32 (d, *J* = 1.5 Hz, 1H), 8.54 (d, *J* = 2.5 Hz, 1H), 8.01 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.98 (s, 1H), 7.54 – 7.51 (m, 1H), 7.38 – 7.34 (m, 2H), 7.17 – 7.14 (m, 2H), 7.12 – 7.10 (m, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.78 – 6.75 (m, 2H), 5.94 (t, *J* = 7.5 Hz, 1H), 5.76 (d, *J* = 16.0 Hz, 1H), 4.62 (dd, *J* = 14.5, 6.5 Hz, 1H), 4.46 (dd, *J* = 14.5, 5.5 Hz, 1H), 3.79 (s, 3H), 1.93 – 1.79 (m, 2H), 1.43 – 1.35 (m, 2H), 0.85 (t,

J = 7.5 Hz, 3H).

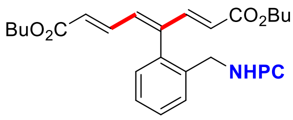
^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.42, 157.89, 145.82, 143.31, 143.16, 141.20, 138.72, 136.93, 134.84, 133.69, 130.04, 129.39, 129.19, 128.45, 128.05, 126.95, 126.78, 126.40, 112.83, 54.28, 40.63, 30.53, 21.62, 12.86.

HRMS (ESI) for $C_{26}H_{28}N_3O_2Na$ $[M+ Na]^+$: 436.1995, found: 436.1979.

FTIR (KBr, cm^{-1})

3854.21, 3744.86, 3649.53, 3624.30, 3565.42, 3444.86, 3315.89, 3060.75, 2957.01, 2354.21, 1681.31, 1653.27, 1563.55, 1535.51, 1507.48 ,1459.81, 1395.33, 1022.43, 666.36.



Dibutyl (2*E*,4*Z*,6*E*)-4-(2-((pyrazine-2-carboxamido)methyl)phenyl)octa-2,4,6-trienedioate (5a)

Following the general procedure 1, **5a** was obtained as a colorless oil (73.7mg, 81% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.35 (d, J = 1.0 Hz, 1H), 8.69 (d, J = 2.5 Hz, 1H), 8.39 (q, J = 1.5 Hz, 1H), 7.86 (t, J = 5.5 Hz, 1H), 7.57 (d, J = 15.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.06 (dd, J = 7.5, 1.0 Hz, 1H), 6.92 (dd, J = 15.0, 11.5 Hz, 1H), 6.79 (d, J = 12.0 Hz, 1H), 6.05 (d, J = 15.0 Hz, 1H), 5.45 (d, J = 15.5 Hz, 1H), 4.51 – 4.38 (m, 2H), 4.09 – 4.05 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.37 – 1.33 (m, 2H), 1.32 – 1.28 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H), 0.88 (d, J = 7.5 Hz, 3H).

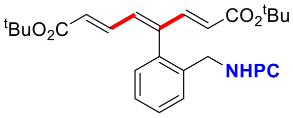
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.41, 165.15, 161.37, 146.10, 145.13, 144.37, 143.35, 143.17, 141.35, 138.48, 135.13, 134.73, 133.46, 129.06, 128.74, 128.17, 127.34, 124.93, 122.81, 63.55, 63.45, 40.40, 29.61, 29.53, 18.09, 18.07, 12.67, 12.66.

HRMS (ESI) for $C_{28}H_{33}N_3O_5Na$ $[M+Na]^+$: 514.2312, found: 514.2308.

FTIR (KBr, cm^{-1})

3481.31, 3456.07, 3428.04, 3422.43, 3405.61, 2357.01, 2331.78, 1644.86, 1633.64, 1628.04, 1619.63, 1608.41, 1543.93, 1507.48, 1403.74, 1395.33, 1381.31.



Di-tert-butyl (2*E*,4*Z*,6*E*)-4-(2-((pyrazine-2-carboxamido)methyl)phenyl)octa-2,4,6-trienedioate (5b)

Following the general procedure 1, **5b** was obtained as a colorless oil (73.7 mg, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.36 (d, *J* = 1.5 Hz, 1H), 8.69 (d, *J* = 2.5 Hz, 1H), 8.43 – 8.42 (m, 1H), 7.87 (s, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 15.5 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.06 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.86 (dd, *J* = 15.0, 12.0 Hz, 1H), 6.73 (d, *J* = 11.5 Hz, 1H), 5.98 (d, *J* = 15.0 Hz, 1H), 5.36 (d, *J* = 15.0 Hz, 1H), 4.52 – 4.39 (m, 2H), 1.42 (s, 9H), 1.39 (s, 9H).

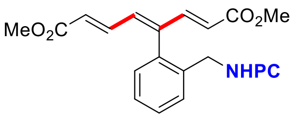
^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.68, 164.54, 146.11, 144.38, 144.05, 143.33, 141.44, 137.72, 134.80, 134.68, 133.69, 129.13, 128.56, 128.04, 127.26, 126.61, 124.44, 98.96, 79.75, 79.69, 40.38, 28.68,27.05, 27.02.

HRMS (ESI) for $C_{28}H_{33}N_3O_5Na$ $[M^{+}Na]^{+}$: 514.2312, found: 514.2306.

FTIR (KBr, cm^{-1})

3512.15, 3472.90, 3458.88, 3444.86, 3414.02, 3405.61, 2354.21, 2328.97, 1675.7, 1658.88, 1653.27, 1644.86, 1633.64, 1619.63, 1616.82, 1557.94, 1541.12, 1510.28, 1459.81, 1403.74, 1392.52, 1386.92.



Dimethyl (2*E*,4*Z*,6*E*)-4-(2-((pyrazine-2-carboxamido)methyl)phenyl)octa-2,4,6-trienedioate (5c)

Following the general procedure 1, **5c** was obtained as a yellow oil (61.1 mg, 54% yield, m.p. = 135-136 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.35 (d, J = 1.5 Hz, 1H), 8.70 (d, J = 2.5 Hz, 1H), 8.40 – 8.39 (m, 1H), 7.86 (s, 1H), 7.58 (d, J = 15.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.06 (d, J = 8.5 Hz, 1H), 6.91 (dd, J = 15.0, 11.5 Hz, 1H), 6.78 (d, J = 11.5 Hz, 1H), 6.04 (d, J = 15.0 Hz, 1H), 5.45 (d, J = 15.5 Hz, 1H), 4.50 – 4.38 (m, 2H), 3.67 (s, 3H), 3.62 (s, 3H).

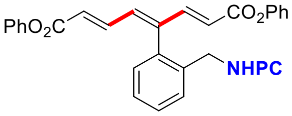
<u>^{13}C NMR</u> (125 MHz, $CDCl_3$)

δ 165.69, 165.43, 161.37, 146.12, 145.39, 144.41, 143.38, 143.15, 141.34, 138.59, 135.23, 134.73, 133.35, 129.04, 128.78, 128.24, 127.38, 124.60, 122.43, 50.65, 40.40, 28.68.

<u>HRMS (ESI)</u> for $C_{22}H_{21}N_3O_5Na$ $[M+Na]^+$: 430.1373, found: 430.1363.

<u>FTIR</u> (KBr, cm^{-1})

3514.95, 3472.90, 3456.07, 3444.86, 3425.23, 3414.02, 2359.81, 2334.58, 1661.638, 1653.27, 1636.45, 1625.23, 1538.32, 1510.28, 1406.54, 1395.33.



Diphenyl (2*E*,4*Z*,6*E*)-4-(2-((pyrazine-2-carboxamido)methyl)phenyl)octa-2,4,6-trienedioate (5d)

Following the general procedure 1, **5d** was obtained as a yellow oil (53.0 mg, 66% yield).

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$)

δ 9.39 (d, J = 1.5 Hz, 1H), 8.65 (d, J = 2.5 Hz, 1H), 8.35 (dd, J = 2.5, 1.5 Hz, 1H), 7.93 (t, J = 5.5 Hz, 1H), 7.79 (d, J = 15.5 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.34 (m, 4H), 7.25 – 7.20 (m, 2H), 7.16 – 7.15 (m, 1H), 7.12 (dd, J = 13.0, 9.0 Hz, 1H), 7.04 – 7.00 (m, 4H), 6.93 (d, J = 11.5 Hz, 1H), 6.28 (d, J = 15.0 Hz, 1H), 5.69 (d, J = 15.5 Hz, 1H), 4.58 – 4.48 (m, 2H).

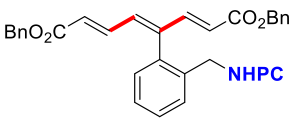
<u>^{13}C NMR</u> (125 MHz, $CDCl_3$)

δ 163.62, 163.33, 161.42, 149.46, 149.44, 146.80, 146.28, 145.05, 143.36, 143.08, 141.50, 140.03, 135.70, 134.77, 133.09, 129.08, 128.89, 128.50, 128.44, 128.34, 127.52, 124.89, 124.84, 124.46, 122.37, 120.31, 40.44, 28.68.

HRMS (ESI) for $C_{32}H_{26}N_3O_5$ $[M+H]^+$: 532.1867, found: 532.1873.

FTIR (KBr, cm^{-1})

3475.70, 3447.66, 3422.43, 2357.01, 1656.07, 1650.47, 1633.64, 1619.63, 1400.93.



Dibenzyl (2*E*,4*Z*,6*E*)-4-(2-((pyrazine-2-carboxamido)methyl)phenyl)octa-2,4,6-trienedioate (5e)

Following the general procedure 1, **5e** was obtained as a yellow oil (46.1 mg, 55% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.31 (d, *J* = 1.5 Hz, 1H), 8.54 (d, *J* = 2.5 Hz, 1H), 8.14 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.82 (t, *J* = 5.5 Hz, 1H), 7.61 (d, *J* = 15.5 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.39 – 7.31 (m, 9H), 7.30 – 7.27 (m, 2H), 7.05 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.97 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.78 (d, *J* = 11.5 Hz, 1H), 6.08 (d, *J* = 15.0 Hz, 1H), 5.50 (d, *J* = 15.5 Hz, 1H), 5.11 – 5.04 (m, 4H), 4.48 – 4.38 (m, 2H).

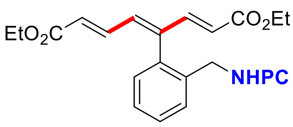
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.07, 164.84, 161.32, 146.09, 145.64, 144.61, 143.23, 143.04, 141.31, 139.05, 135.25, 134.72, 134.71, 134.58, 133.36, 129.06, 128.87, 128.25, 127.59, 127.53, 127.43, 127.41, 127.39, 127.26, 127.14, 124.55, 122.55, 65.52, 65.28, 40.42.

HRMS (ESI) for $C_{34}H_{29}N_3O_5Na$ $[M+Na]^+$: 582.1999, found: 582.1997.

FTIR (KBr, cm^{-1})

3509.35, 3475.70, 3456.07, 3442.06, 3422.43, 3408.41, 2354.21, 2320.56, 1684.11, 1672.90, 1658.88, 1656.07, 1633.64, 1622.43, 1611.21, 1557.94, 1538.32, 1504.67, 1417.76, 1403.74, 1392.52, 1384.11.



Diethyl (2*E*,4*Z*,6*E*)-4-(2-((pyrazine-2-carboxamido)meth

yl)phenyl)octa-2,4,6-trienedioate (5f)

Following the general procedure 1, **5f** was obtained as a yellow oil (46.2 mg, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.35 (d, *J* = 1.5 Hz, 1H), 8.69 (d, *J* = 2.5 Hz, 1H), 8.40 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.86 (t, *J* = 5.5 Hz, 1H), 7.57 (d, *J* = 15.5 Hz, 1H), 7.52 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.06 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.92 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.78 (d, *J* = 11.5 Hz, 1H), 6.04 (d, *J* = 15.5 Hz, 1H), 5.44 (d, *J* = 15.5 Hz, 1H), 4.50 – 4.39 (m, 2H), 4.15– 4.10 (m, 2H), 4.08 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.20 (t, *J* = 7.5 Hz, 3H).

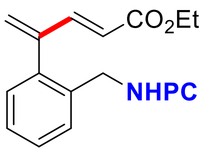
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.30, 165.07, 161.37, 146.10, 145.21, 144.33, 143.36, 143.18, 141.34, 138.42, 135.18, 134.72, 133.44, 129.07, 128.74, 128.19, 127.35, 125.01, 122.79, 59.54, 40.40, 13.17.

HRMS (ESI) for $C_{24}H_{25}N_3O_5Na$ $[M+Na]^+$: 458.1686, found: 458.1684.

FTIR (KBr, cm^{-1})

3565.42, 3512.15, 3456.07, 3444.86, 2354.21, 2326.17, 1684.11, 1670.09, 1650.47, 1636.45, 1622.43, 1557.94, 1538.32, 1507.48, 1473.83, 1454.21, 1395.33, 1386.92.



Ethyl (*E*)-4-(2-((pyrazine-2-carboxamido)methyl)phenyl)penta-2,4-dienoate (5f')

Following the general procedure 1, **5f'** was obtained as a white oil (10.8 mg, 21% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.40 (d, *J* = 1.5 Hz, 1H), 8.72 (d, *J* = 2.5 Hz, 1H), 8.46 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.94 (s, 1H), 7.57 (d, *J* = 15.5 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.12 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.85 (d, *J* = 1.5 Hz, 1H), 5.51 (d, *J* = 1.5 Hz, 1H), 5.41 (d, *J* = 15.5 Hz, 1H), 4.56 (d, *J* = 6.0 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 1.23 (d, *J* = 7.0 Hz, 3H).

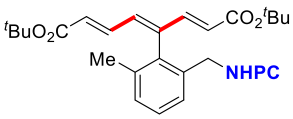
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.61, 161.55, 146.20, 145.28, 144.26, 143.43, 143.30, 141.44, 136.83, 134.31, 128.84, 128.06, 127.49, 126.87, 125.35, 121.23, 59.48, 40.27, 13.18.

HRMS (ESI) for $C_{19}H_{19}N_3O_3Na$ $[M+Na]^+$: 360.1319, found: 360.1308.

FTIR (KBr, cm^{-1})

3509.35, 3472.90, 3456.07, 3442.06, 3422.43, 3405.61, 2354.21, 2340.19, 1658.88, 1653.27, 1633.64, 1625.23, 1616.82, 1560.75, 1541.12, 1510.28, 1406.54, 1392.52, 1384.11.



Di-tert-butyl (2*E*,4*Z*,6*E*)-4-(2-methyl-6-((pyrazine-2-carboxamido)methyl)phenyl)octa-2,4,6-trienedioate (5g)

Following the general procedure 1, **5g** was obtained as a yellow solid (45.7 mg, 60% yield, m.p. = 149-150 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.36 (d, *J* = 1.5 Hz, 1H), 8.68 (d, *J* = 2.5 Hz, 1H), 8.42 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.83 (t, *J* = 5.5 Hz, 1H), 7.47 (d, *J* = 15.5 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 6.80 – 6.74 (m, 2H), 6.01 – 5.94 (m, 1H), 5.33 (d, *J* = 15.5 Hz, 1H), 4.45 – 4.35 (m, 2H), 2.08 (s, 3H), 1.42 (s, 9H), 1.39 (s, 9H).

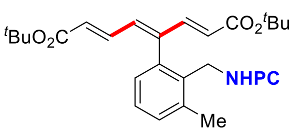
^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.74, 164.52, 161.27, 146.04, 143.58, 143.30, 143.26, 143.23, 141.44, 137.41, 135.74, 135.02, 134.45, 133.09, 128.96, 127.79, 126.86, 125.99, 123.46, 79.76, 79.68, 40.67, 27.05,27.02, 18.58.

HRMS (ESI) for $C_{29}H_{36}N_3O_5$ $[M+H]^+$: 506.2649, found: 506.2662.

FTIR (KBr, cm^{-1})

3481.31, 3456.07, 3444.86, 2357.01, 1653.27, 1650.47, 1633.64, 1622.43, 1417.76, 1403.74, 1395.33.



Di-tert-butyl (2*E*,4*Z*,6*E*)-4-(3-methyl-2-((pyrazine-2-carb

oxamido)methyl)phenyl)octa-2,4,6-trienedioate (5h)

Following the general procedure 1, **5h** was obtained as a yellow solid (46.8 mg, 51% yield, m.p. = 61-62 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.34 (d, *J* = 1.5 Hz, 1H), 8.66 (d, *J* = 2.5 Hz, 1H), 8.38 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.59 (t, *J* = 4.5 Hz, 1H), 7.48 (d, *J* = 15.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 5.5 Hz, 1H), 6.91 – 6.86 (m, 2H), 6.72 (d, *J* = 12.0 Hz, 1H), 5.94 (s, 1H), 5.36 (d, *J* = 15.5 Hz, 1H), 4.51 – 4.41 (m, 2H), 2.48 (s, 3H), 1.42 (s, 9H), 1.39 (s, 9H).

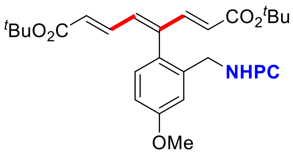
^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.64, 164.58, 161.15, 145.99, 144.83, 144.80, 143.20, 141.41, 137.84, 137.37, 135.03, 134.78, 132.33, 130.16, 130.14, 127.43, 126.83, 126.37, 124.53, 79.71, 79.64, 37.58, 27.05, 27.04, 18.74.

HRMS (ESI) for $C_{29}H_{35}N_3O_5Na$ $[M+Na]^+$: 528.2469, found: 528.2453.

FTIR (KBr, cm^{-1})

3565.42, 3414.02, 2317.76, 1748.60, 1731.78, 1712.15, 1656.07, 1636.45, 1622.43.



Di-tert-butyl (2*E*,4*Z*,6*E*)-4-(4-methoxy-2-((pyrazine-2-carboxamido)methyl)phenyl)octa-2,4,6-trienedioate (5i)

Following the general procedure 1, **5i** was obtained as a white oil (47.1 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.36 (d, *J* = 1.5 Hz, 1H), 8.69 (d, *J* = 2.5 Hz, 1H), 8.43 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.87 (t, *J* = 5.5 Hz, 1H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.72 (d, *J* = 11.5 Hz, 1H), 5.98 (d, *J* = 15.0 Hz, 1H), 5.40 (d, *J* = 15.5 Hz, 1H), 4.47 – 4.35 (m, 2H), 3.84 (s, 3H), 1.43 (s, 9H), 1.40 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$)

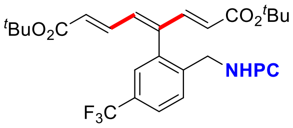
δ 164.76, 164.65, 161.44, 158.90, 146.12, 144.80, 144.02, 143.33,

143.22, 141.45, 137.93, 136.15, 135.12, 130.29, 126.35, 125.60, 124.36, 114.04, 112.57, 79.69, 79.67, 54.36, 40.51, 28.68, 27.04.

HRMS (ESI) for $C_{29}H_{35}N_3O_6K$ $[M+K]^+$: 560.2157, found: 560.2164.

FTIR (KBr, cm^{-1})

3568.22, 3512.15, 3475.70, 3456.07, 3447.66, 2351.40, 2326.17, 1684.11, 1670.09, 1653.27, 1636.45, 1622.43, 1538.32, 1504.67, 1406.54, 1400.93.



Di-tert-butyl (2*E*,4*Z*,6*E*)-4-(2-((pyrazine-2-carboxamido)methyl)-5-(trifluoromethyl)phenyl)octa-2,4,6-trienedioate (5j)Following the general procedure 1, **5j** was obtained as a white solid (61.6 mg, 73% yield, m.p. = 89-90 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.30 (d, *J* = 1.5 Hz, 1H), 8.65 (d, *J* = 2.5 Hz, 1H), 8.38 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.88 (t, *J* = 6.0 Hz, 1H), 7.60 (d, *J* = 1.0 Hz, 2H), 7.42 (d, *J* = 15.5 Hz, 1H), 7.26 (s, 1H), 6.74 – 6.66 (m, 2H), 5.96 (d, *J* = 14.0 Hz, 1H), 5.24 – 5.21 (m, 1H), 4.49 – 4.37 (m, 2H), 1.37 (s, 9H), 1.32 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.39, 164.26, 161.67, 146.36, 143.66, 143.38, 142.92, 142.24, 141.49, 136.84 (d, J_{CF} = 1.4 Hz), 136.79, 135.37, 134.36, 199.61 (q, J_{CF} = 32.8 Hz), 128.99, 127.70, 125.78 (q, J_{CF} = 3.9 Hz), 125.48 (q, J_{CF} = 254.7 Hz), 125.00 (q, J_{CF} = 3.5 Hz), 124.58, 80.05, 79.96, 39.91, 27.04, 26.98.

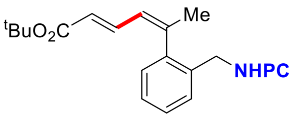
^{19}F NMR (471 MHz, $CDCl_3$)

δ -62.51.

HRMS (ESI) for $C_{29}H_{32}N_3O_5F_3K$ $[M+K]^+$: 598.1926, found: 598.1927.

FTIR (KBr, cm^{-1})

3453.23, 3439.25, 2362.62, 2326.17, 1667.29, 1656.07, 1633.64, 1557.94, 1535.51, 1504.67.



Tert-butyl (2*E*,4*Z*)-5-(2-((pyrazine-2-carboxamido)methyl)phenyl)hexa-2,4-dienoate (7a)

Following the general procedure 1, **7a** was obtained as a white solid (54.8 mg, 96% yield, m.p. = 62-63 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.39 (s, 1H), 8.71 (d, *J* = 2.5 Hz, 1H), 8.46 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.98 (s, 1H), 7.45 – 7.41 (m, 1H), 7.33 – 7.30 (m, 2H), 7.07 (dd, *J* = 5.5, 3.5 Hz, 1H), 6.81 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.32 (d, *J* = 12.0 Hz, 1H), 5.74 (d, *J* = 15.5 Hz, 1H), 4.65 (dd, *J* = 15.0, 6.0 Hz, 1H), 4.45 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.17 (s, 3H), 1.39 (s, 9H).

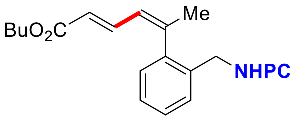
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.38, 161.60, 146.16, 146.12, 143.36, 143.33, 141.49, 139.27, 139.21, 133.35, 128.05, 127.50, 127.15, 127.03, 125.90, 121.54, 79.04, 40.21, 27.08, 25.60.

HRMS (ESI) for $C_{22}H_{26}N_3O_3$ $[M+H]^+$: 380.1969, found: 380.1960.

FTIR (KBr, cm^{-1})

3481.31, 3458.88, 3444.86, 3425.23, 2357.01, 2258.88, 1661.68, 1656.07, 1647.66, 1633.64, 1628.04, 1622.43, 1412.15, 1403.74, 1395.33.



Butyl (2*E*,4*Z*)-5-(2-((pyrazine-2-carboxamido)methyl)phenyl)hexa-2,4-dienoate (7b)

Following the general procedure 1, **7b** was obtained as a white oil (49.5 mg, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.39 (s, 1H), 8.71 (d, *J* = 2.5 Hz, 1H), 8.44 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.97 (s, 1H), 7.47 – 7.44 (m, 1H), 7.35 – 7.31 (m, 2H), 7.10 – 7.06 (m, 1H), 6.87 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.35 (d, *J* = 12.0 Hz, 1H), 5.80 (d, *J* = 15.5 Hz, 1H), 4.66 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.43 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 2.19 (s, 3H), 1.56 – 1.50 (m, 2H), 1.33 – 1.27 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H).

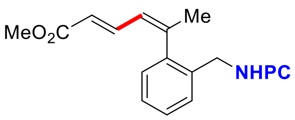
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.98, 161.58, 146.82, 146.14, 143.35, 143.31, 141.45, 140.20, 139.15, 133.38, 128.21, 127.44, 127.22, 127.07, 125.93, 119.69, 63.04, 40.23, 29.60, 25.64, 18.09, 12.67.

HRMS (ESI) for $C_{22}H_{26}N_3O_3$ $[M^+H]^+$: 380.1969, found: 380.1961.

FTIR (KBr, cm^{-1})

3484.11, 3475.70, 3453.27, 3442.06, 3422.43, 2357.01, 2328.97, 1664.49, 1656.07, 1647.66, 1633.64, 1628.04, 1622.43, 1614.02, 1409.35, 1400.93, 1389.72.



Methyl (2*E*,4*Z*)-5-(2-((pyrazine-2-carboxamido)methyl)phenyl)hexa-2,4-dienoate (7c)

Following the general procedure 1, **7c** was obtained as a light yellow oil (45.4 mg, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.39 (d, *J* = 1.5 Hz, 1H), 8.71 (d, *J* = 2.5 Hz, 1H), 8.44 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.97 (s, 1H), 7.48 – 7.45 (m, 1H), 7.36 – 7.32 (m, 2H), 7.09 – 7.07 (m, 1H), 6.86 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.36 (d, *J* = 12.0 Hz, 1H), 5.80 (d, *J* = 15.5 Hz, 1H), 4.65 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.44 (dd, *J* = 14.5, 5.5 Hz, 1H), 3.59 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

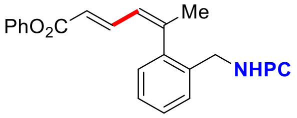
δ 167.27, 162.61, 148.00, 147.18, 144.39, 144.32, 142.46, 141.36, 140.13, 134.40, 129.30, 128.44, 128.27, 128.12, 126.98, 120.34, 51.34, 41.26, 26.73.

HRMS (ESI) for $C_{19}H_{20}N_3O_3$ $[M+H]^+$: 338.1499, found: 338.1504.

FTIR (KBr, cm^{-1})

3475.70, 3456.07, 3439.25, 3416.82, 2359.81, 2334.58, 1658.88, 1656.07, 1647.66, 1633.64, 1622.43, 1611.21, 1420.56, 1403.74, 1395.33.

Phenyl (2*E*,4*Z*)-5-(2-((pyrazine-2-carboxamido)methyl)phenyl)hexa-2,4-dienoate



(7d)

Following the general procedure 1, **7d** was obtained as a brown solid (50.5 mg, 84% yield, m.p. = 103-104 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.40 (d, *J* = 2.0 Hz, 1H), 8.67 (d, *J* = 2.5 Hz, 1H), 8.40 – 8.39 (m, 1H), 8.00 (s, 1H), 7.45 (dt, *J* = 7.5, 4.0 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.05 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.44 (d, *J* = 11.5 Hz, 1H), 5.99 (d, *J* = 15.5 Hz, 1H), 4.68 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.46 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.22 (s, 3H).

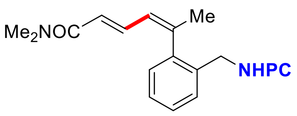
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.20, 162.65, 150.68, 149.28, 147.27, 144.38, 144.27, 143.08, 142.56, 139.97, 134.39, 129.28, 129.26, 128.42, 128.41, 128.15, 126.92, 125.58, 121.47, 119.77, 41.25, 26.85.

HRMS (ESI) for $C_{24}H_{22}N_3O_3$ $[M+H]^+$: 400.1656, found: 400.1649.

FTIR (KBr, cm^{-1})

3478.50, 3458.88, 3422.43, 3402.80, 3388.79, 2359.81, 2334.58, 1647.66, 1644.86, 1633.64, 1614.02, 1608.41, 1417.76, 1406.54, 1392.52.



N-(2-((2*Z*,4*E*)-6-(dimethylamino)-6-oxohexa-2,4-dien-2-yl)benzyl)pyrazine-2-carboxamide (7e)

Following the general procedure 1, **7e** was obtained as a brown oil (46.7 mg, 89% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.38 (d, *J* = 1.5 Hz, 1H), 8.70 (d, *J* = 2.5 Hz, 1H), 8.47 (dd, *J* = 2.5, 1.5 Hz, 1H), 8.05 (s, 1H), 7.42 – 7.38 (m, 1H), 7.32 – 7.29 (m, 2H), 7.10 – 7.06 (m, 1H), 6.87 (dd, *J* = 14.5, 11.5 Hz, 1H), 6.37 – 6.34 (m, 1H), 6.23 (d, *J* = 15.0 Hz, 1H), 4.64 (dd, *J* = 14.5, 6.0 Hz, 1H), 4.46 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.99 (s, 3H), 2.90 (s, 3H), 2.16

(s, 3H).

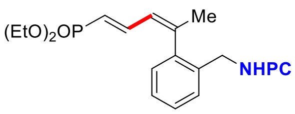
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.64, 162.63, 147.02, 145.85, 144.50, 144.28, 142.59, 140.38, 139.15, 134.33, 128.88, 128.57, 128.08, 127.30, 119.85, 41.25, 37.22, 35.64, 26.65.

HRMS (ESI) for $C_{20}H_{23}N_4O_2$ $[M+H]^+$: 351.1816, found: 351.1814.

FTIR (KBr, cm^{-1})

3568.22, 3523.36, 3512.15, 3475.70, 3456.07, 31416.82, 3385.98, 2362.62, 2326.17, 1664.49, 1656.07, 1644.86, 1633.64, 1625.23, 1614.02, 1417.76, 1403.74, 1392.52, 1384.11.



Diethyl ((1*E*,3*Z*)-4-(2-((pyrazine-2-carboxamido)methyl) phenyl)penta-1,3-dien-1-yl)phosphonate (7f)

Following the general procedure 1, **7f** was obtained as a colorless oil (61.9 mg, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.40 (d, *J* = 1.5 Hz, 1H), 8.74 (d, *J* = 2.5 Hz, 1H), 8.53 (dd, *J* = 2.5, 1.5 Hz, 1H), 8.05 (s, 1H), 7.44 – 7.41 (m, 1H), 7.34 – 7.29 (m, 2H), 7.09 – 7.05 (m, 1H), 6.72 – 6.62 (m, 1H), 6.32 (d, *J* = 11.0 Hz, 1H), 5.65 (dd, *J* = 20.0, 16.5 Hz, 1H), 4.67 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.44 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.99 – 3.93 (m, 4H), 2.17 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 6H).

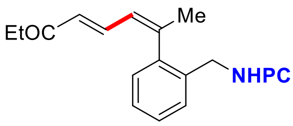
^{13}C NMR (125 MHz, $CDCl_3$)

δ 161.75, 146.27, 145.93, 143.82, 143.76, 143.33, 143.28, 141.66, 138.83, 133.36, 127.80, 127.48, 127.25, 127.01, 126.84, 116.29, 114.77, 60.62, 40.08, 25.44, 15.20.

HRMS (ESI) for $C_{21}H_{27}N_3O_4P$ $[M+H]^+$: 416.1734, found: 416.1737.

FTIR (KBr, cm^{-1})

3472.90, 3453.27, 3442.06, 3422.43, 3385.98, 2357.01, 2337.38, 1654.49, 1656.07, 1647.66, 1636.45, 1619.63, 1614.02, 1417.76, 1400.93, 1384.11.



***N*-(2-((2*Z*,4*E*)-6-oxoocta-2,4-dien-2-yl)benzyl)pyrazine-2-carboxamide (7g)**

Following the general procedure 1, **7g** was obtained as a yellow oil (38.1 mg, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.38 (d, *J* = 1.5 Hz, 1H), 8.71 (d, *J* = 2.5 Hz, 1H), 8.43 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.97 (s, 1H), 7.48 – 7.46 (m, 1H), 7.37 – 7.33 (m, 2H), 7.10 – 7.08 (m, 1H), 6.75 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.36 (d, *J* = 11.0 Hz, 1H), 6.09 (d, *J* = 15.5 Hz, 1H), 4.65 (dd, *J* = 14.5, 6.0 Hz, 1H), 4.45 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.34 (q, *J* = 7.5 Hz, 2H), 2.20 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 3H).

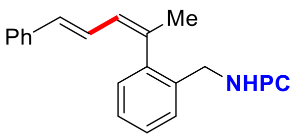
^{13}C NMR (125 MHz, $CDCl_3$)

δ 201.01, 162.60, 148.62, 147.28, 144.37, 144.24, 142.51, 140.19, 138.79, 134.43, 129.28, 128.91, 128.40, 128.34, 128.12, 127.49, 41.22, 33.52, 26.81, 8.02.

HRMS (ESI) for $C_{20}H_{22}N_3O_2$ $[M+H]^+$: 336.1707, found: 336.1716.

FTIR (KBr, cm^{-1})

3509.35, 3489.72, 3472.90, 3453.27, 3416.82, 3385.98, 2359.81, 2328.97, 1667.29, 1656.07, 1647.66, 1639.25, 1622.43, 1614.02, 1403.74, 1400.93, 1392.52.



***N*-(2-((2*Z*,4*E*)-5-phenylpenta-2,4-dien-2-yl)benzyl)pyrazine-2-carboxamide (7h)**

Following the general procedure 1, **7h** was obtained as a yellow oil (44.7 mg, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.31 (d, *J* = 1.5 Hz, 1H), 8.46 (d, *J* = 2.5 Hz, 1H), 7.97 (s, 1H), 7.90 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.37 – 7.32 (m, 2H), 7.18 – 7.10 (m, 6H), 6.44 (d, *J* = 15.5 Hz, 1H), 6.39 (dd, *J* = 10.5, 1.5 Hz, 1H), 6.31 (dd, *J* = 15.5, 10.5 Hz, 1H), 4.70 (dd, *J* =

14.5, 6.5 Hz, 1H), 4.46 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.16 (s, 3H).

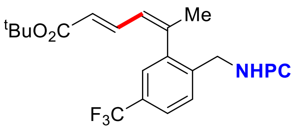
^{13}C NMR (125 MHz, $CDCl_3$)

δ 162.52, 146.85, 144.22, 144.11, 142.28, 141.60, 138.94, 137.24, 134.94, 131.71, 129.68, 129.05, 128.88, 128.36, 128.12, 127.74, 127.25, 126.25, 125.82, 41.48, 26.35.

HRMS (ESI) for $C_{23}H_{22}N_3O$ $[M+H]^+$: 356.1757, found: 356.1765.

FTIR (KBr, cm^{-1})

3509.35, 3472.90, 3458.88, 3447.66, 3416.82, 3385.98, 2357.01, 2328.97, 2258.88, 1672.90, 1661.68, 1644.86, 1639.25, 1622.43, 1611.21, 1403.74, 1398.13.



Tert-butyl (2*E*,4*Z*)-5-(2-((pyrazine-2-carboxamido)methyl)-5-(trifluoromethyl)phenyl)hexa-2,4-dienoate (7i)

Following the general procedure 1, **7i** was obtained as a yellow oil (55.6 mg, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.40 (d, *J* = 1.0 Hz, 1H), 8.74 (d, *J* = 2.5 Hz, 1H), 8.49 (dd, *J* = 2.0, 1.5 Hz, 1H), 8.09 (s, 1H), 7.57 (s, 2H), 7.35 (s, 1H), 6.73 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.39 (d, *J* = 12.0 Hz, 1H), 5.81 (d, *J* = 15.0 Hz, 1H), 4.72 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.46 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.20 (s, 3H), 1.39 (s, 9H).

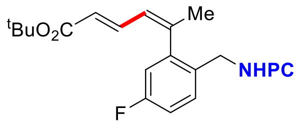
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.12, 161.86, 146.41, 144.02, 143.39, 143.05, 141.56, 139.70, 138.26, 137.73 (d, J_{CF} = 0.9 Hz), 129.28 (q, J_{CF} = 32.5 Hz), 128.30, 126.64, 124.23 (q, J_{CF} = 3.8 Hz), 123.98 (q, J_{CF} = 3.6 Hz), 122.793 (q, J_{CF}= 270.8 Hz), 122.71, 79.32, 39.76, 27.04, 25.34.

HRMS (ESI) for $C_{23}H_{24}N_3O_3F_3Na$ $[M+ Na]^+$: 470.1662, found: 470.1671.

FTIR (KBr, cm^{-1})

3564.69, 3454.39, 3444.63, 2351.40, 1686.92, 1653.27, 1633.64, 1560.75, 1543.93, 1504.67, 1409.35, 1400.93, 1171.03.



Tert-butyl (2E,4Z)-5-(5-fluoro-2-((pyrazine-2-carboxamido)methyl)phenyl)hexa-2,4-dienoate (7j)

Following the general procedure 1, **7j** was obtained as a yellow oil (52.1 mg, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.39 (d, *J* = 1.5 Hz, 1H), 8.72 (d, *J* = 2.5 Hz, 1H), 8.47 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.98 (s, 1H), 7.42 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.81 – 6.76 (m, 2H), 6.34 – 6.32 (m, 1H), 5.77 (d, *J* = 15.5 Hz, 1H), 4.61 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.40 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.16 (s, 3H), 1.39 (s, 9H).

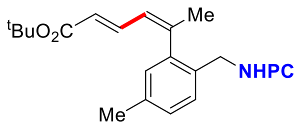
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.23, 162.66, 162.11 (d, J_{CF} = 246.8 Hz), 147.26, 145.52, 144.36, 144.23, 142.53, 142.25 (d, J_{CF} = 7.6 Hz), 139.65, 131.05 (d, J_{CF} = 8.5 Hz), 130.41 (d, J_{CF} = 3.3 Hz), 127.23, 123.25, 115.38 (d, J_{CF} = 21.4 Hz), 115.02 (d, J_{CF} = 21.0 Hz), 112.83 (d, J_{CF} = 21.1 Hz), 80.23, 40.55, 28.08, 26.29.

HRMS (ESI) for $C_{22}H_{24}N_3O_3FNa$ $[M+Na]^+$: 420.1694, found: 420.1698.

FTIR (KBr, cm^{-1})

3475.70, 3453.27, 3442.06, 2357.01, 2331.78, 2258.88, 1667.29, 1661.68, 1656.07, 1647.66, 1633.64, 1619.63, 1611.21, 1420.56, 1403.74, 1395.33.



Tert-butyl (2*E*,4*Z*)-5-(5-methyl-2-((pyrazine-2-carboxamido)methyl)phenyl)hexa-2,4-dienoate (7k)

Following the general procedure 1, **7k** was obtained as a yellow oil (50.2 mg, 85% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.39 (d, *J* = 1.5 Hz, 1H), 8.70 (d, *J* = 2.5 Hz, 1H), 8.46 (dd, *J* = 2.0, 1.5 Hz, 1H), 7.93 (s, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 1H), 6.88 (s, 1H), 6.83 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.30 (d, *J* = 11.5 Hz, 1H), 5.74 (d, *J* = 15.5 Hz, 1H), 4.59 (dd, *J* = 14.5, 6.0 Hz, 1H), 4.41 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.33 (s, 3H), 2.15 (s, 3H), 1.39 (s, 9H).

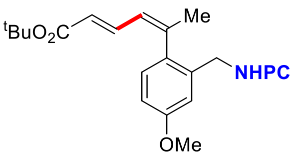
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.43, 161.51, 146.37, 146.09, 143.39, 143.32, 141.47, 139.44, 139.13, 136.78, 130.30, 128.15, 127.96, 127.86, 125.72, 121.36, 79.00, 40.00, 27.09, 25.67, 20.04.

HRMS (ESI) for $C_{23}H_{27}N_3O_3Na$ $[M+Na]^+$: 416.1945, found: 416.1941.

FTIR (KBr, cm^{-1})

3568.22, 3453.40, 3444.63, 2362.62, 2337.38, 1737.38, 1684.11, 1653.27, 1633.64, 1557.94, 1538.32, 1400.93, 1137.38.



Tert-butyl (2*E*,4*Z*)-5-(4-methoxy-2-((pyrazine-2-carboxmido)methyl)phenyl)hexa-2,4-dienoate (7l)

Following the general procedure 1, **7l** was obtained as a yellow oil (61.0 mg, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.43 (d, J = 1.5 Hz, 1H), 8.72 (d, J = 2.5 Hz, 1H), 8.47 – 8.46 (m, 1H), 7.99 (s, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.96 (d, J = 2.5 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.32 (d, J = 11.5 Hz, 1H), 5.75 (d, J = 15.5 Hz, 1H), 4.62 (dd, J = 15.0, 6.5 Hz, 1H), 4.41 (dd, J = 15.0, 5.5 Hz, 1H), 3.81 (s, 3H), 2.15 (s, 3H), 1.40 (s, 9H).

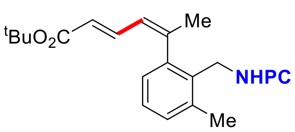
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.48, 161.63, 158.29, 146.17, 146.13, 143.34, 143.32, 141.50, 139.52, 134.85, 131.33, 128.67, 126.17, 121.25, 113.53, 112.30, 79.01, 54.32, 40.33, 27.10, 25.78.

HRMS (ESI) for $C_{23}H_{27}N_3O_4Na$ $[M+Na]^+$: 432.1894, found: 432.1892.

FTIR (KBr, cm^{-1})

3507.88, 3473.10, 3444.05, 3423.18, 2357.01, 2261.687, 1656.07, 1644.85, 1636.45, 1628.04, 1614.02, 1460.75, 1541.12, 1507.48, 1398.13.



Tert-butyl (2*E*,4*Z*)-5-(3-methyl-2-((pyrazine-2-carboxam

ido)methyl)phenyl)hexa-2,4-dienoate (7m)

Following the general procedure 1, **7m** was obtained as a yellow solid (41.1 mg, 70% yield, m.p. = 78-79 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.38 (d, *J* = 1.5 Hz, 1H), 8.68 (d, *J* = 2.5 Hz, 1H), 8.42 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.68 (s, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.0 Hz, 1H), 6.83 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.32 (dd, *J* = 11.5, 0.5 Hz, 1H), 5.73 (d, *J* = 15.5 Hz, 1H), 4.66 (dd, *J* = 14.0, 5.5 Hz, 1H), 4.45 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.44 (s, 3H), 2.16 (s, 3H), 1.38 (s, 9H).

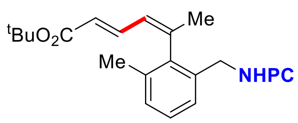
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.39, 162.39, 147.89, 147.07, 144.31, 144.25, 142.50, 141.73, 140.36, 138.21, 131.97, 130.28, 128.34, 127.03, 126.26, 122.34, 79.99, 38.78, 28.12, 27.17, 19.65.

HRMS (ESI) for $C_{23}H_{27}N_3O_3Na$ $[M+Na]^+$: 416.1945, found: 416.1936.

FTIR (KBr, cm^{-1})

3475.70, 3456.07, 3444.86, 2354.21, 1653.27, 1650.47, 1633.64, 1622.43, 1406.54.



Tert-butyl (2*E*,4*Z*)-5-(2-methyl-6-((pyrazine-2-carboxamido)methyl)phenyl)hexa-2,4-dienoate (7n)

Following the general procedure 1, **7n** was obtained as a white oil (48.7 mg, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.39 (d, *J* = 1.5 Hz, 1H), 8.70 (d, *J* = 2.0 Hz, 1H), 8.46 (dd, *J* = 2.0, 1.5 Hz, 1H), 7.94 (s, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 1H). 6.70 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.38 (d, *J* = 12.0 Hz, 1H), 5.73 (d, *J* = 15.5 Hz, 1H), 4.61 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.39 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 1.38 (s, 9H).

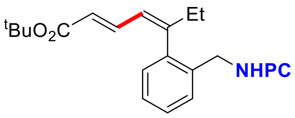
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.37, 162.51, 147.11, 146.41, 144.40, 144.34, 142.51, 139.95, 139.32, 135.26, 134.16, 129.77, 127.90, 127.39, 126.48, 122.71, 80.03, 41.44, 28.11, 25.19, 19.40.

HRMS (ESI) for $C_{23}H_{27}N_3O_3Na$ [M+Na]+: 416.1945, found: 416.1943.

FTIR (KBr, cm^{-1})

3475.70, 3453.27, 3442.06, 2357.01, 2331.78, 2258.88, 1667.29, 1661.68, 1656.07, 1647.66, 1633.64, 1619.63, 1611.21, 1420.56, 1403.74, 1395.33.



Tert-butyl (2*E*,4*Z*)-5-(2-((pyrazine-2-carboxamido)methyl)phenyl)hepta-2,4-dienoate (7o)

Following the general procedure 1, **7o** was obtained as a yellow oil (58.5 mg, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.40 (d, *J* = 1.5 Hz, 1H), 8.71 (d, *J* = 2.5 Hz, 1H), 8.47 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.98 (s, 1H), 7.44 – 7.42 (m, 1H), 7.34 – 7.28 (m, 2H), 7.06 – 7.04 (m, 1H), 6.84 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.31 (d, *J* = 11.5 Hz, 1H), 5.77 (d, *J* = 15.5 Hz, 1H), 4.64 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.44 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.53 – 2.39 (m, 2H), 1.38 (s, 9H), 1.09 (t, *J* = 7.5 Hz, 3H).

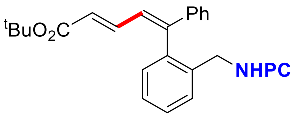
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.38, 161.62, 151.77, 146.14, 143.33, 141.50, 139.37, 138.47, 133.64, 127.97, 127.85, 127.10, 126.74, 124.00, 121.73, 79.00, 40.13, 31.63, 27.07, 11.17.

HRMS (ESI) for $C_{23}H_{27}N_3O_3Na$ $[M+Na]^+$: 416.1945, found: 416.1953.

FTIR (KBr, cm^{-1})

3509.35, 3472.90, 3456.07, 2354.21, 1670.09, 1658.88, 1644.86, 1633.64, 1619.63, 1398.13.



Tert-butyl (2*E*,4*Z*)-5-phenyl-5-(2-((pyrazine-2-carboxamido)methyl)phenyl)penta-2,4-dienoate (7p)

Following the general procedure 1, **7p** was obtained as a yellow oil (43.5 mg, 66% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.29 (d, *J* = 1.5 Hz, 1H), 8.65 (d, *J* = 2.5 Hz, 1H), 8.34 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.67 (s, 1H), 7.51 – 7.50 (m, 1H), 7.43 – 7.38 (m, 2H), 7.30 – 7.28 (m, 2H), 7.26 – 7.18 (m, 4H), 7.03 – 6.96 (m, 2H), 6.01 – 5.94 (m, 1H), 4.44 – 4.33 (m, 2H), 1.41 (s, 9H).

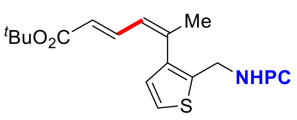
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.16, 161.32, 146.94, 145.92, 143.25, 143.21, 141.24, 139.40, 138.65, 136.64, 135.07, 129.87, 128.68, 127.79, 127.65, 127.02, 125.80, 125.05, 123.82, 79.26, 40.49, 27.08.

HRMS (ESI) for $C_{27}H_{27}N_3O_3Na$ $[M+Na]^+$: 464.1945, found: 464.1948.

FTIR (KBr, cm^{-1})

3565.42, 3509.35, 3447.66, 2354.21, 1695.33, 1681.31, 1653.27, 1557.94, 1535.51, 1510.28, 1454.21.



Tert-butyl (2*E*,4*Z*)-5-(2-((pyrazine-2-carboxamido)methyl)thiophen-3-yl)hexa-2,4-dienoate (7q)

Following the general procedure 1, **7q** was obtained as a yellow oil (46.2 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.40 (d, *J* = 1.5 Hz, 1H), 8.73 (d, *J* = 2.5 Hz, 1H), 8.50 (dd, *J* = 2.5, 1.5 Hz, 1H), 8.08 (s, 1H), 7.26 (s, 1H), 7.03 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.84 (d, *J* = 5.0 Hz, 1H), 6.34 (d, *J* = 12.0 Hz, 1H), 5.81 (d, *J* = 15.5 Hz, 1H), 4.66 (d, *J* = 6.0 Hz, 2H), 2.15 (s, 3H), 1.41 (s, 9H).

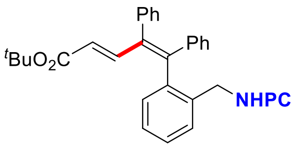
^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.52, 162.73, 147.29, 144.46, 144.27, 142.57, 142.47, 140.45, 138.99, 135.77, 127.81, 127.28, 125.01, 122.73, 80.16, 36.89, 28.12, 25.96.

HRMS (ESI) for $C_{20}H_{23}N_3O_3SNa$ $[M+Na]^+$: 408.1352, found: 408.1355.

FTIR (KBr, cm^{-1})

3475.70, 3453.27, 3419.63, 2354.21, 2256.07, 1656.07, 1647.66, 1633.64, 1622.43, 1614.02, 1403.74, 1392.52.



***Tert*-butyl (2*E*,4*E*)-4,5-diphenyl-5-(2-((pyrazine-2-carboxamido)methyl)phenyl)penta-2,4-dienoate (7r)**

Following the general procedure 1, **7r** was obtained as a yellow oil (58.8 mg, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.35 (d, *J* = 1.5 Hz, 1H), 8.68 (d, *J* = 2.5 Hz, 1H), 8.40 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.65 (t, *J* = 5.0 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.42 – 7.39 (m, 2H), 7.35 – 7.32 (m, 2H), 7.27 – 7.26 (m, 1H), 7.26 – 7.24 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.01 – 6.98 (m, 3H), 6.92 – 6.90 (m, 2H), 5.49 (d, *J* = 15.5 Hz, 1H), 4.53 (dd, *J* = 14.5, 6.0 Hz, 1H), 4.45 (dd, *J* = 14.5, 5.5 Hz, 1H), 1.34 (s, 9H).

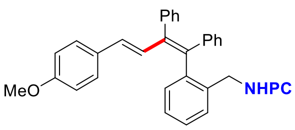
^{13}C NMR (125 MHz, $CDCl_3$)

δ 165.35, 161.41, 146.03, 145.73, 143.37, 143.28, 143.25, 141.27, 139.45, 139.25, 137.56, 137.31, 135.03, 130.54, 129.84, 129.38, 128.91, 127.83, 127.35, 126.89, 126.67, 126.30, 126.26, 123.06, 79.10, 40.48, 27.02.

HRMS (ESI) for $C_{33}H_{31}N_3O_3Na$ [M+Na]+: 540.2258, found: 540.224.

FTIR (KBr, cm^{-1})

3850.97, 3742.29, 3627.10, 3565.42, 2359.81, 1790.65, 1731.78, 1684.11, 1651.44, 1633.64, 1507.48, 1457.01, 669.16.



***N*-(2-((1*E*,3*E*)-4-(4-methoxyphenyl)-1,2-diphenylbuta-1,3-dien-1-yl)benzyl)pyrazine-2-carboxamide (7s)**

Following the general procedure 1, **7s** was obtained as a brown oil (48.7 mg, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.31 (d, *J* = 1.5 Hz, 1H), 8.55 (d, *J* = 2.5 Hz, 1H), 8.11 (dd, *J* =

2.5, 1.5 Hz, 1H), 7.81 (t, J = 6.0 Hz, 1H), 7.54 (dd, J = 6.0, 2.5 Hz, 1H), 7.41 – 7.39 (m, 3H), 7.30 – 7.25 (m, 3H), 7.25 – 7.23 (m, 2H), 7.01 – 6.96 (m, 5H), 6.92 – 6.90 (m, 2H), 6.71 – 6.68 (m, 3H), 6.15 (d, J = 16.0 Hz, 1H), 4.55 (d, J = 6.0 Hz, 2H), 3.75 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

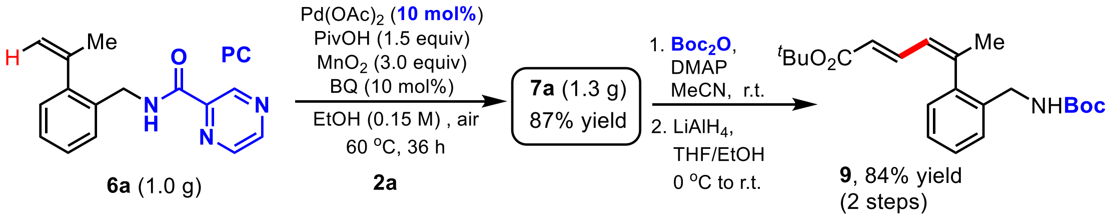
δ 161.45, 158.21, 145.84, 143.33, 143.14, 141.15, 140.74, 140.03, 139.57, 138.45, 138.31, 135.45, 131.72, 130.88, 130.25, 129.33, 129.08, 128.97, 127.41, 127.17, 127.10, 126.88, 126.72, 126.53, 125.96, 125.30, 112.87, 54.24, 40.72.

HRMS (ESI) for $C_{35}H_{29}N_3O_2K$ $[M+K]^+$: 562.1891, found: 562.1877.

FTIR (KBr, cm^{-1})

3565.42, 3422.43, 3383.18, 3335.51, 3276.64, 3122.43, 3063.55, 2959.81, 2354.21, 1689.72, 1653.27, 1636.45, 1538.32, 1510.28, 1403.74, 1022.43.

5. Scaled-up Preparation and Directing Group Removal

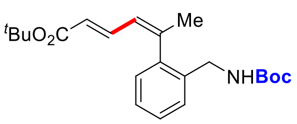


5.1 Scaled-up preparation

An screw-cap tube was charged with $Pd(OAc)_2$ (10 mol%, 0.39 mmol) , MnO_2 (3.0 equiv, 11.7 mmol), BQ (10 mol%, 0.39 mmol), amide **6a** (1.0 equiv, 3.9 mmol), EtOH (26.0 mL). Then, pivalic acid (1.5 equiv, 5.98 mmol), and olefin **2** (2.5 equiv, 9.88 mmol) were added into the solution in sequence. The vial was sealed under air and heated to 60 °C with stirring for 36 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA). Product **7a** was obtained as a white solid (1.3 g, 87% yield).

5.2 Directing Group Removal Reaction[10]

Boc-anhydride (5.0 equiv, 1.0 mmol) was added to a solution of **7a** (75.8 mg, 0.2 mmol) and DMAP (2.0 equiv, 0.4 mmol) in MeCN (2 mL) and the rection mixture was stirred overnight. The reaction mixture was quenched with sat. aq NH_4Cl (5 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), concentrated under reduced pressure and purified by column chromatography (PE / EA) to give amide (**9-i**). Then to a solution of amide in THF/EtOH (1:1, 0.02 M) was added dropwise $LiAlH_4$ (2.0 equiv) over 30 min at 0°C and stirred at r.t. for 2 h, and 2 M NaOH was added slowly until a clear solution was obtained. The layer was separated and the aqueous phase was extracted with Et_2O (20 mL × 3). Combined the organic layers and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with EtOAc and the resulting amine (**9**) was purified by silica gel chromatography (SiO_2, PE/EA = 2/1).



Tert-butyl (2*E*,4*Z*)-5-(2-(((tert-butoxycarbonyl)amino)methyl)phenyl)hexa-2,4-dienoate (9)

Following the procedure, **12** was obtained as a white solid (63.0 mg, 84% yield for two steps, m.p. = 118-119 °C).

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$)

δ 7.36 (d, *J* = 7.0 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.03 –7.02 (m, 1H), 6.79 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.29 (d, *J* = 12.0 Hz, 1H), 5.77 (d, *J* = 15.5 Hz, 1H), 4.76 (s, 1H), 4.30 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.08 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.14 (s, 3H), 1.43 (s, 9H), 1.41 (s, 9H).

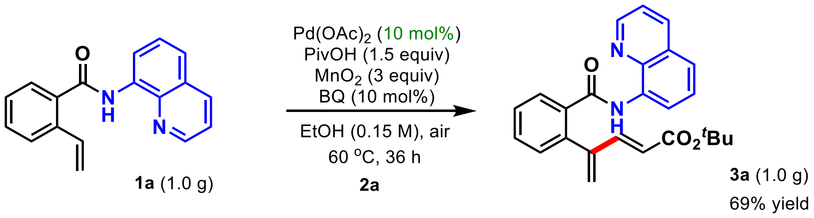
<u>^{13}C NMR</u> (125 MHz, $CDCl_3$)

δ 166.56, 155.71, 147.42, 140.52, 139.77, 135.58, 128.50, 128.28, 127.98, 127.56, 126.54, 122.27, 80.09, 79.33, 42.15, 28.39,28.13, 26.56.

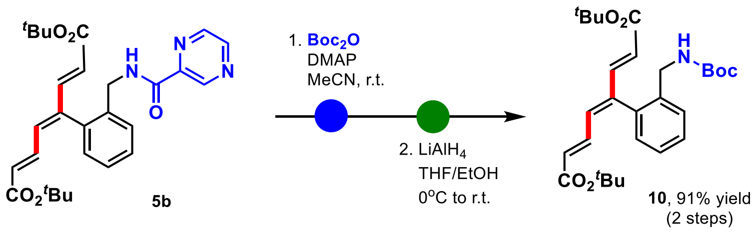
<u>HRMS (ESI)</u> for $C_{22}H_{32}NO_4$ $[M+H]^+$: 374.2326, found: 374.2316.

<u>FTIR</u> (KBr, cm^{-1})

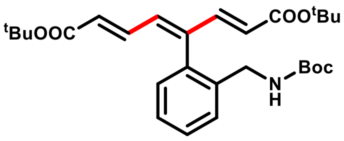
3417.26, 2926.17, 2856.07, 1651.63, 1644.90, 1633.89, 1557.38, 1538.50, 1505.23, 806.54.



An screw-cap vial was charged with $Pd(OAc)_2$ (81.9 mg, 10 mol%, 0.365 mmol) , MnO_2 (3.0 equiv, 10.9 mmol), BQ (39.4 mg, 10 mol%, 0.365 mmol), amide **1a** (1.0 g, 1.0 equiv, 3.65 mmol), EtOH (25 mL). Then, pivalic acid (0.559 g, 1.5 equiv, 5.48 mmol), and olefin **2a** (1.16 g, 2.5 equiv, 9.1 mmol) were added into the solution in sequence. The vial was sealed under air and heated to 60 °C with stirring for 36 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) to afford **3a** in 69% yield (1 g).



Boc-anhydride (5.0 equiv, 0.5 mmol) was added to a solution of **5b** (49.2 mg, 0.1 mmol) and DMAP (2.0 equiv, 0.2 mmol) in MeCN (1 mL) and the rection mixture was stirred 4 h. The reaction mixture was quenched with sat. aq NH_4Cl (5 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), concentrated under reduced pressure and purified by column chromatography (SiO_2, PE / EA = 20:1 to 10: 1) to give amide. Then to a solution of amide in THF/EtOH (1:1, 0.02 M) was added dropwise $LiAlH_4$ (2.0 equiv) over 30 min at 0°C and stirred at r.t. for 2 h, and 2 M NaOH was added slowly until a clear solution was obtained. The layer was separated and the aqueous phase was extracted with Et_2O (20 mL × 3). Combined the organic layers and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with EtOAc and the resulting amine (**10**) was purified by silica gel chromatography (SiO_2, PE/EA = 20:1).



di-Tert-butyl (2E,4Z,6E)-4-(2-(((tert-butoxycarbonyl) amino) methyl)phenyl) octa-2,4,6-trienedioate (10)

Following the procedure, **10** was obtained as a white solid (44.4 mg, 91% yiel d for two steps, m.p. = 47-48 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.46 (d, J = 15.4 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.01 (d, J = 7.3 Hz, 1H), 6.85 (dd, J = 15.2, 11.7 Hz, 1H), 6.69 (d, J = 11.7 Hz, 1H), 6.01 (d, J = 15.2 Hz, 1H), 5.34 (d, J = 15.5 Hz, 1H), 4.62 (s, 1H), 4.15 (dd, J = 14.9, 5.9 Hz, 1H), 4.05 (dd, J = 14.7, 5.6 Hz, 1H), 1.45 (s, 9H), 1.42 (s, 9H), 1.41 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 164.81, 164.66, 154.54, 144.53, 144.19, 137.87, 135.85, 134.57, 133.23, 128.91, 127.88, 127.81, 126.75, 126.41, 124.19, 79.73, 79.66, 78.29, 41.26, 27.33, 27.07, 27.04.

HRMS (ESI) for Na $[M+Na]^+$:508.2670, found: 508.2676.

6. References

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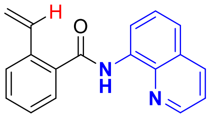
7. ^{1}H / ^{13}C NMR Charts

7.1 ^{1}H / ^{13}C NMR Charts of Substrates



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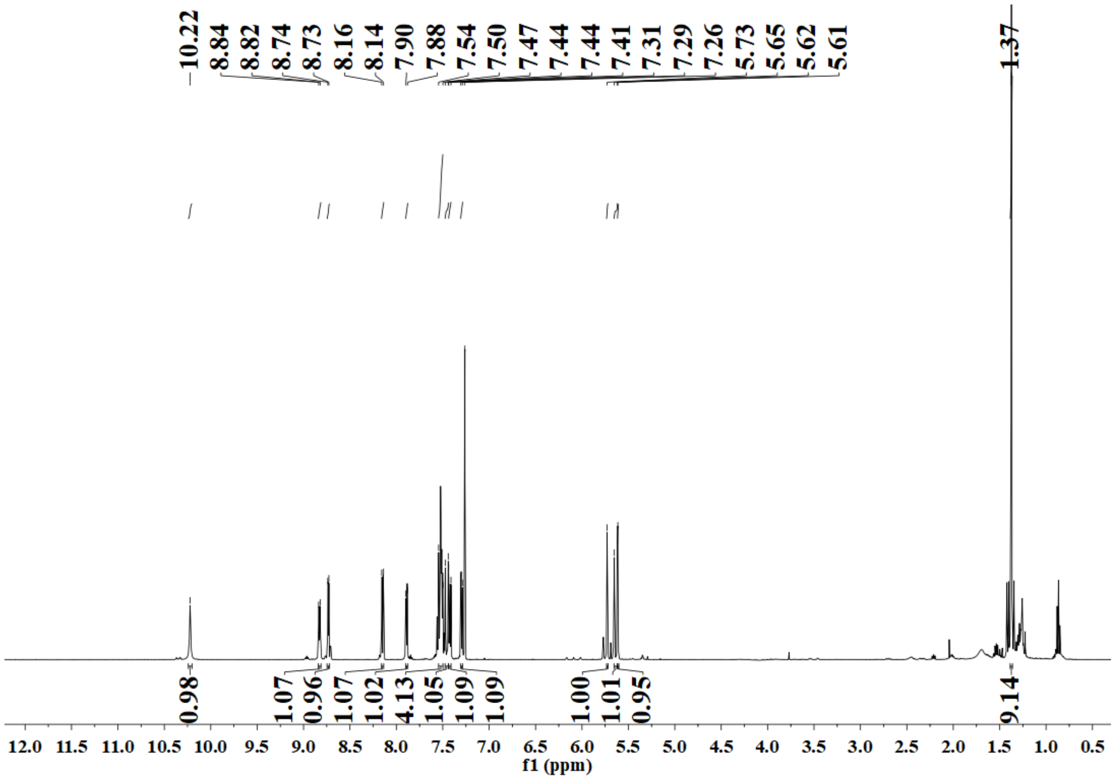
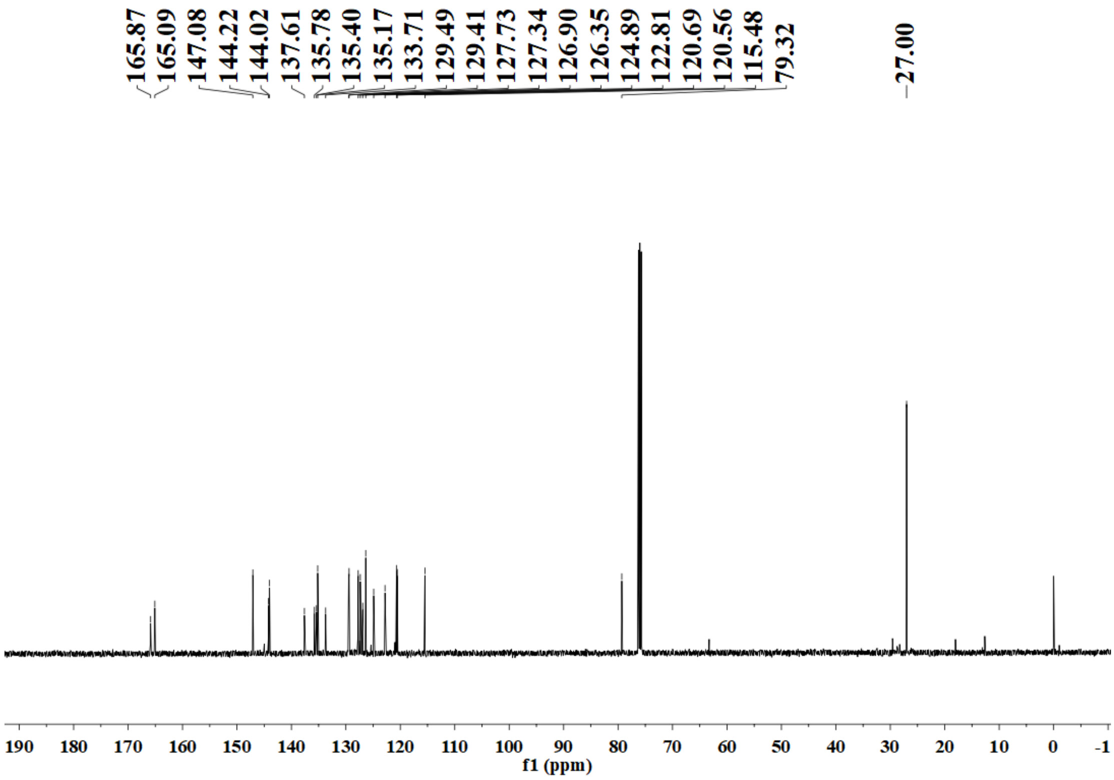
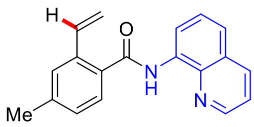
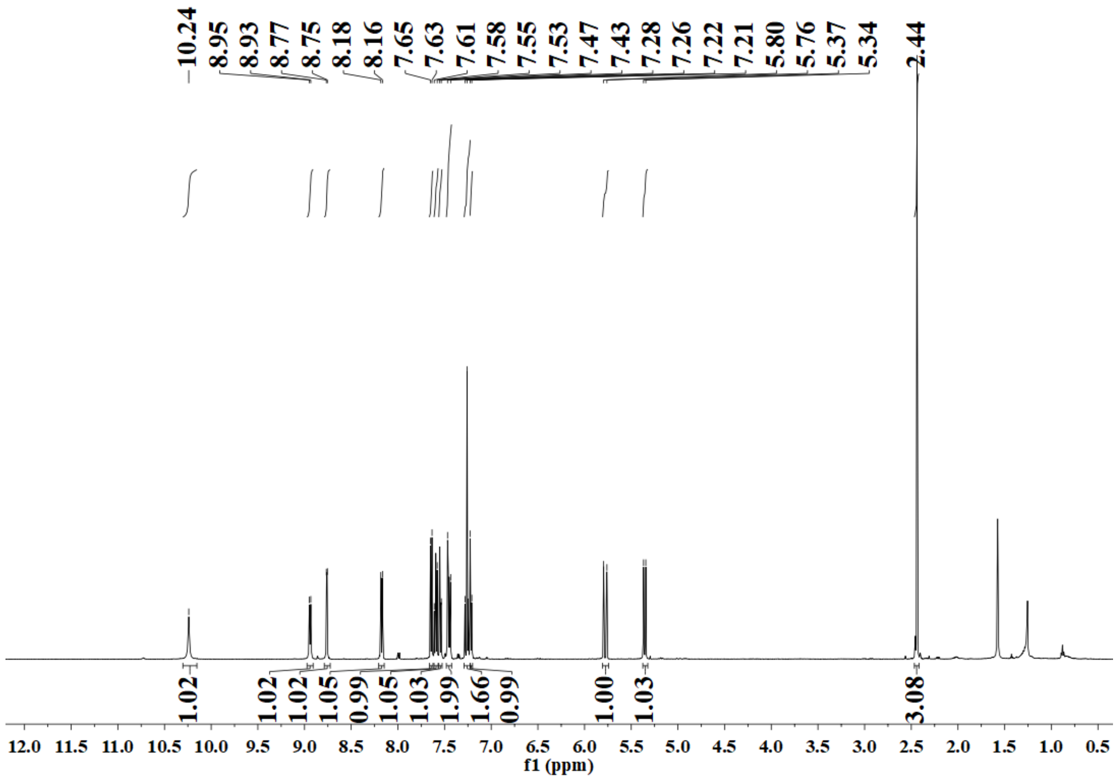






H
O
N
H
Me
N

(1b)



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8.18
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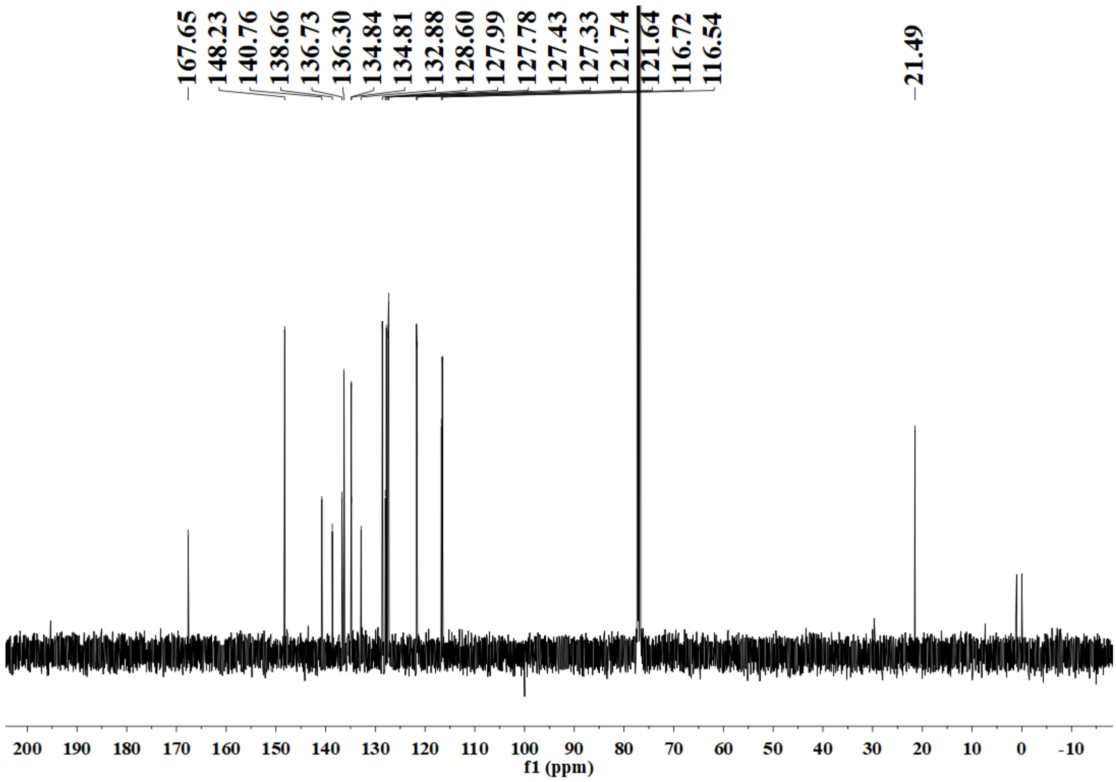
7.47
7.43
7.28
7.26
7.22
7.21
5.80
5.76
5.37
5.34
2.44
1.02
1.02
1.02
1.05
0.99
1.05
1.03
1.99
1.66
0.99
1.00
1.03
3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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128.60
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127.78
127.43
127.33
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116.72
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21.49
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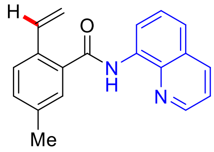
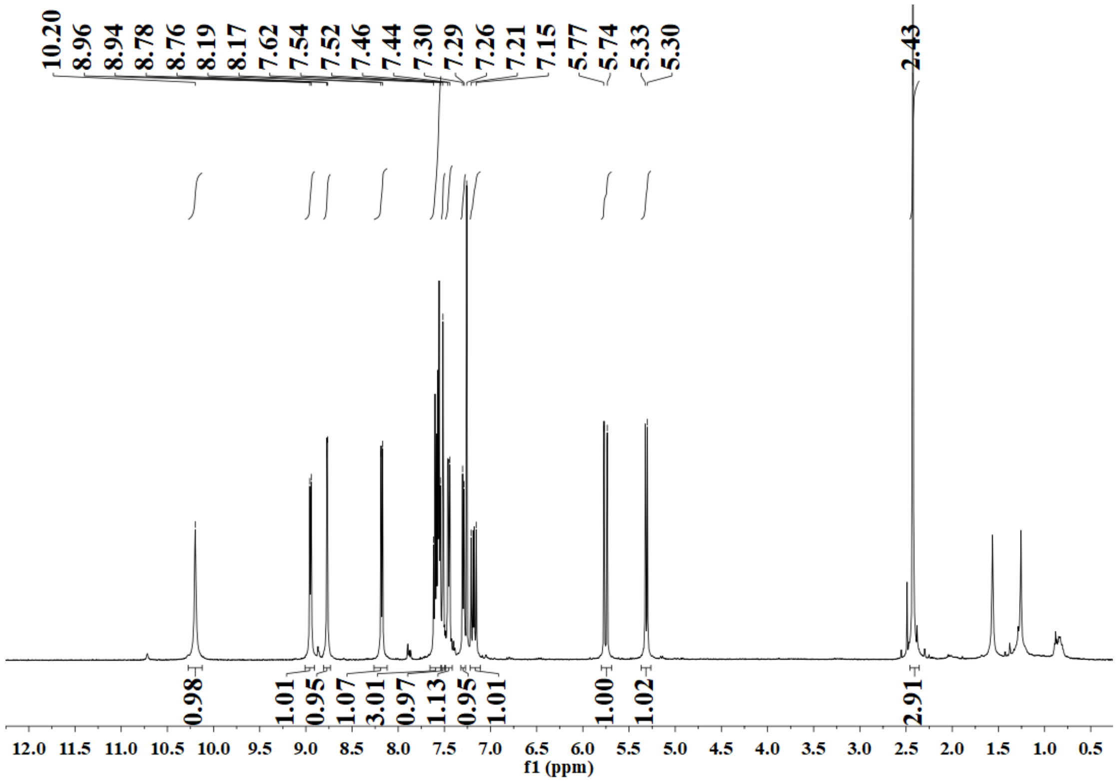
f1 (ppm)


H
O
N
H
N
Me

(1c)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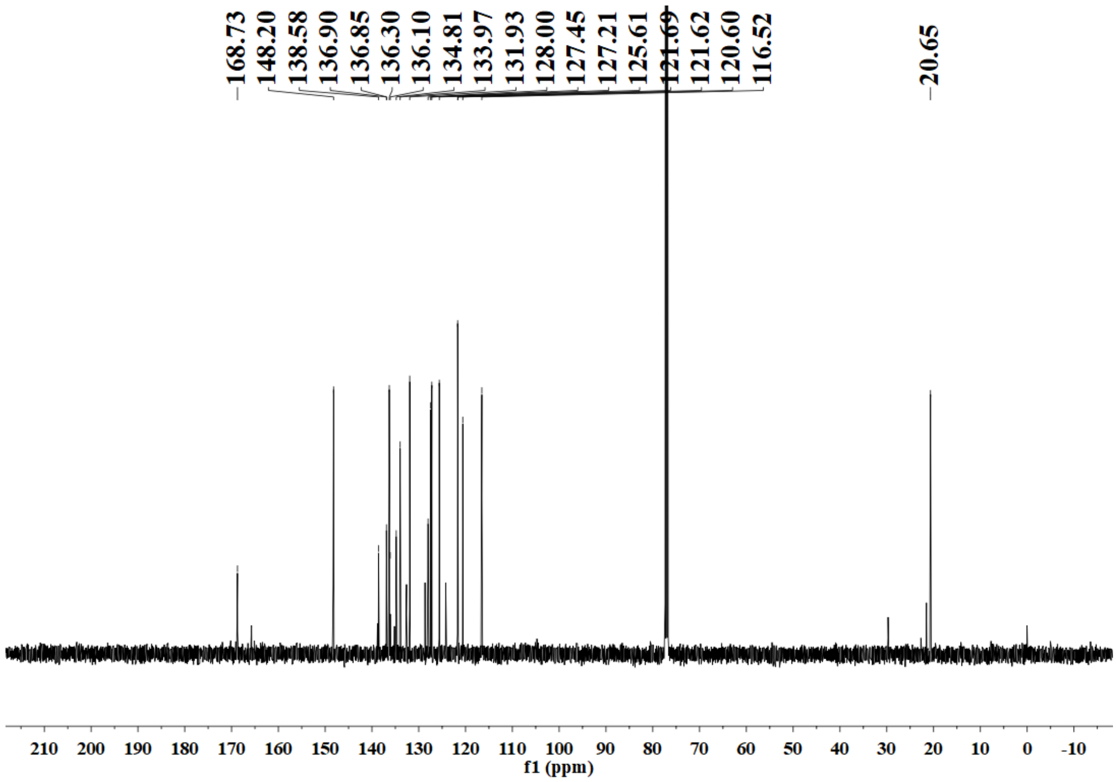
7.30
7.29
7.26
7.21
7.15
5.77
5.74
5.33
5.30
2.43
0.98
1.01
0.95
1.07
3.01
0.97
1.13
0.95
1.01
1.00
1.02
2.91
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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133.97
131.93
128.00
127.45
127.21
125.61
121.69
121.62
120.60
116.52
20.65
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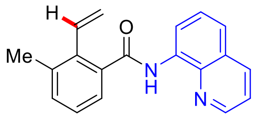
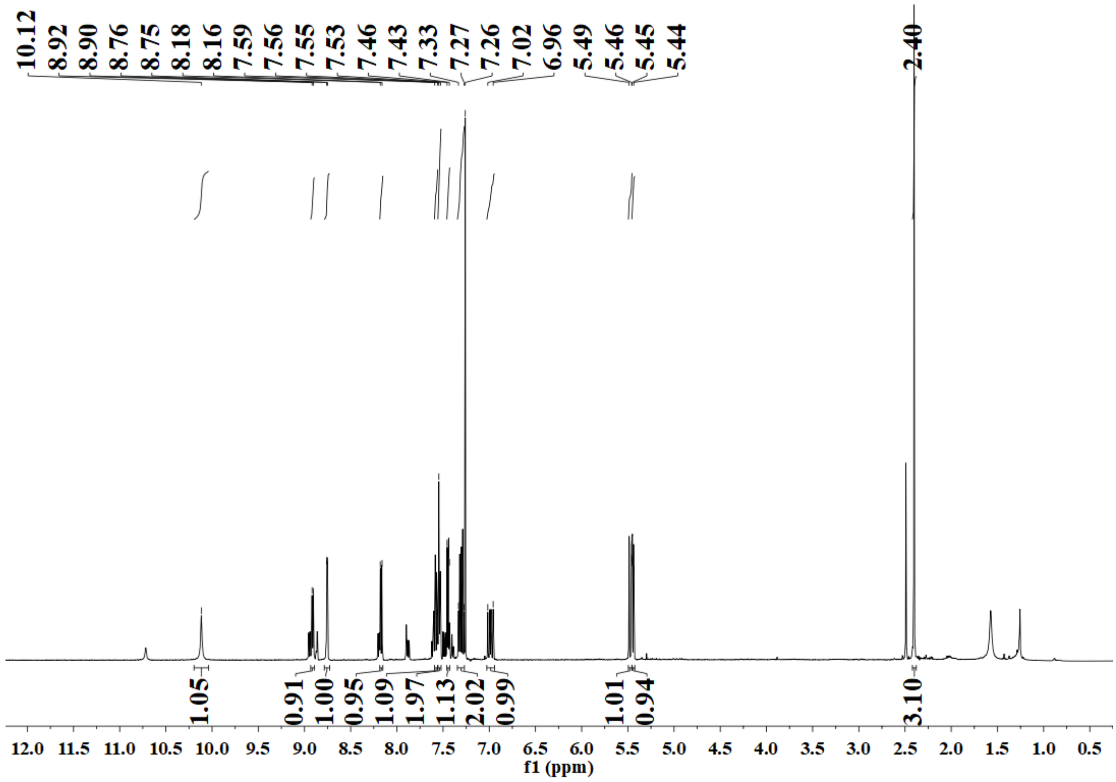
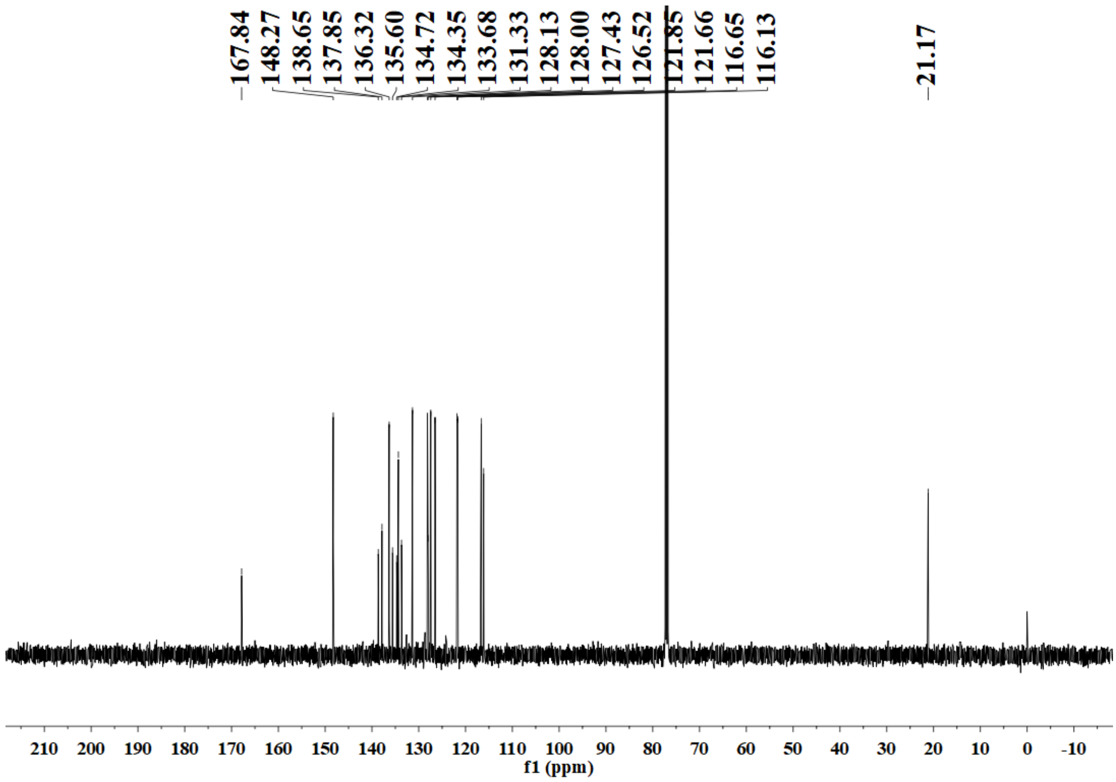
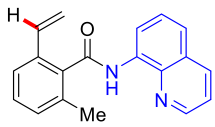
f1 (ppm)



(1d)







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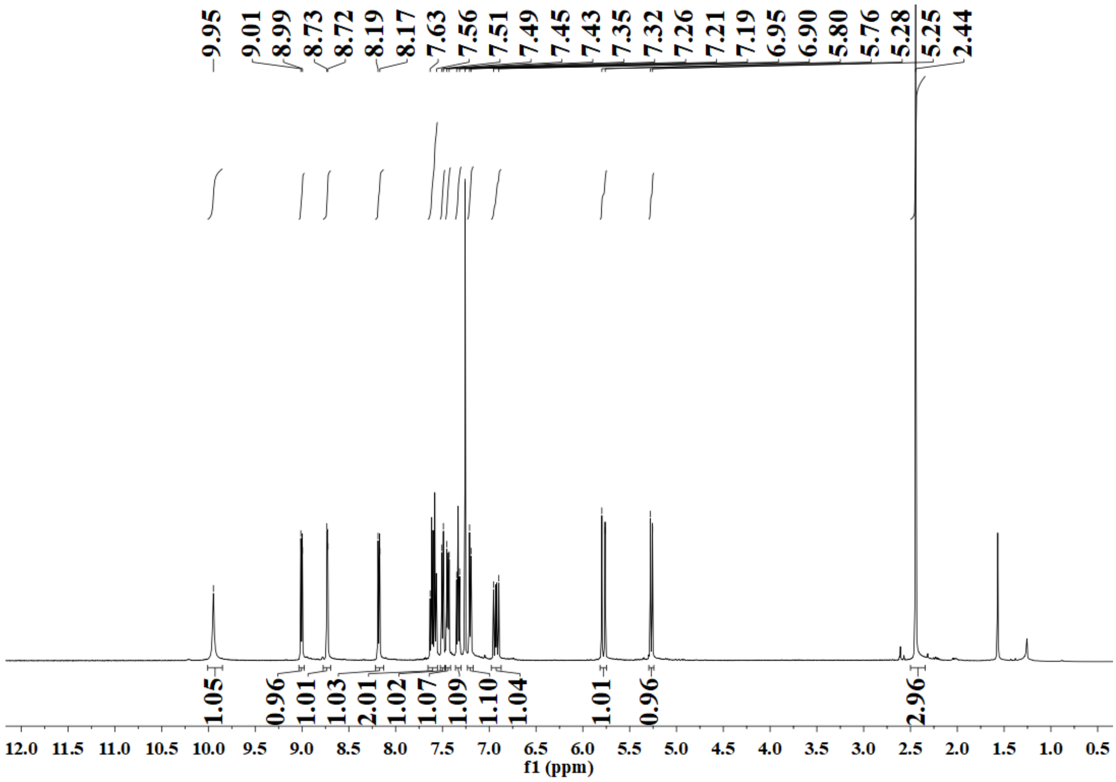

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5.80
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5.28
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0.96
1.01
1.03
2.01
1.02
1.07
1.09
1.10
1.04
1.01
0.96
2.96
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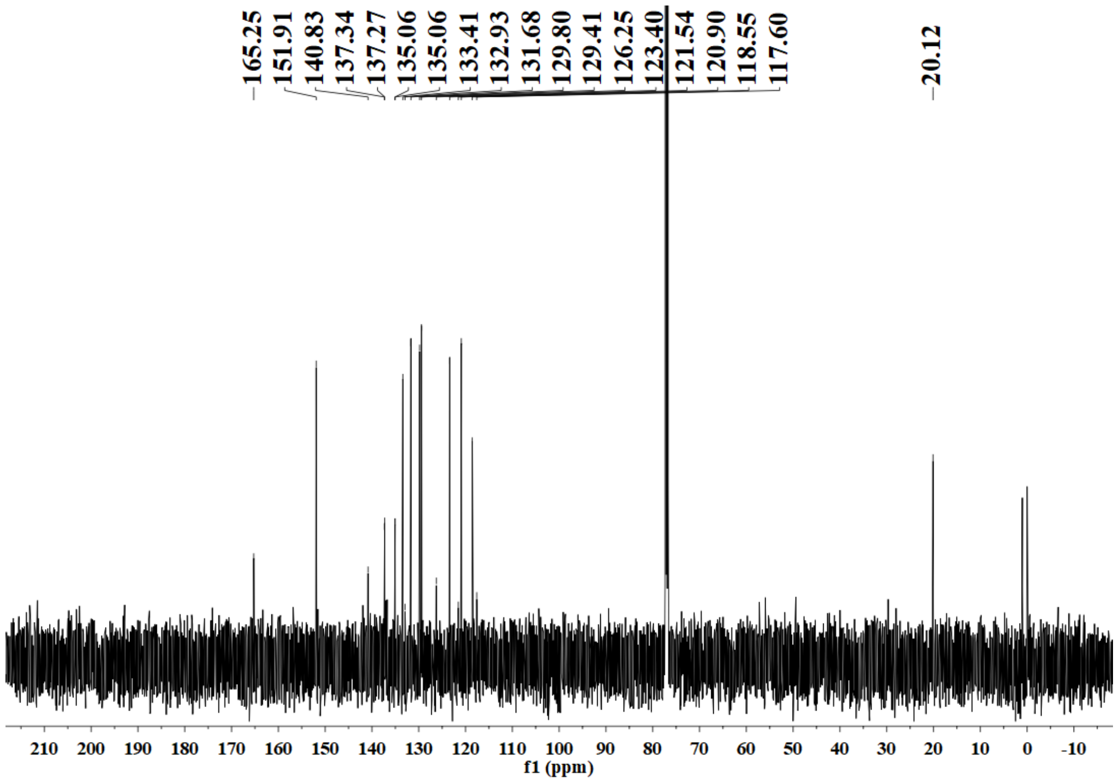
f1 (ppm)



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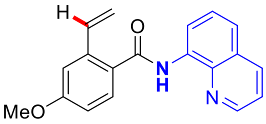
f1 (ppm)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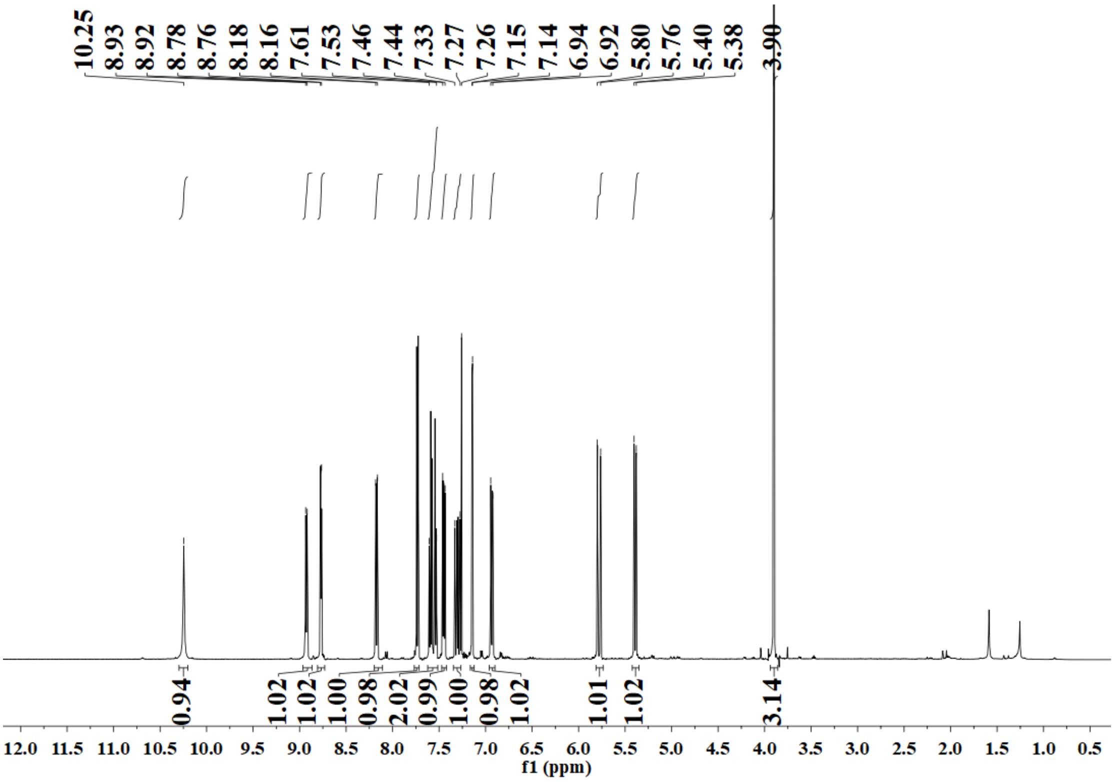
MeO

(1f)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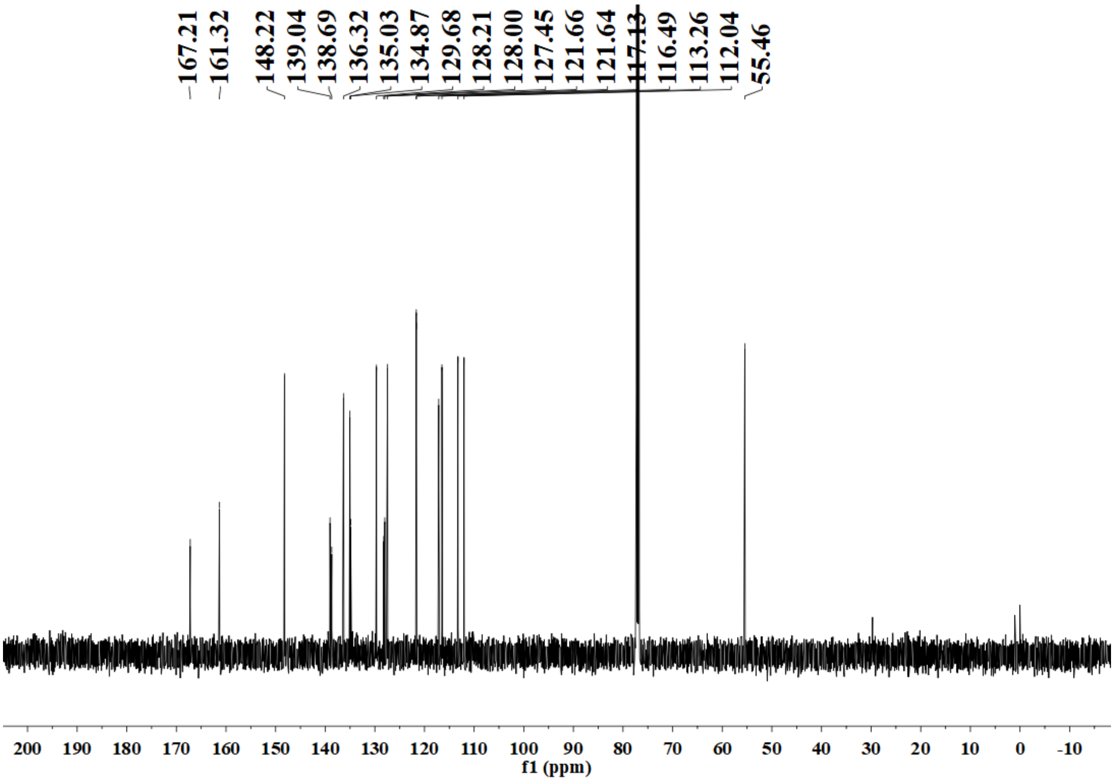
0.94 1.02 1.02 1.00 0.98 2.02 0.99 1.00 0.98 1.02 1.01 1.02 3.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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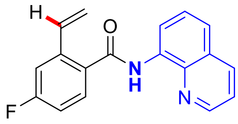
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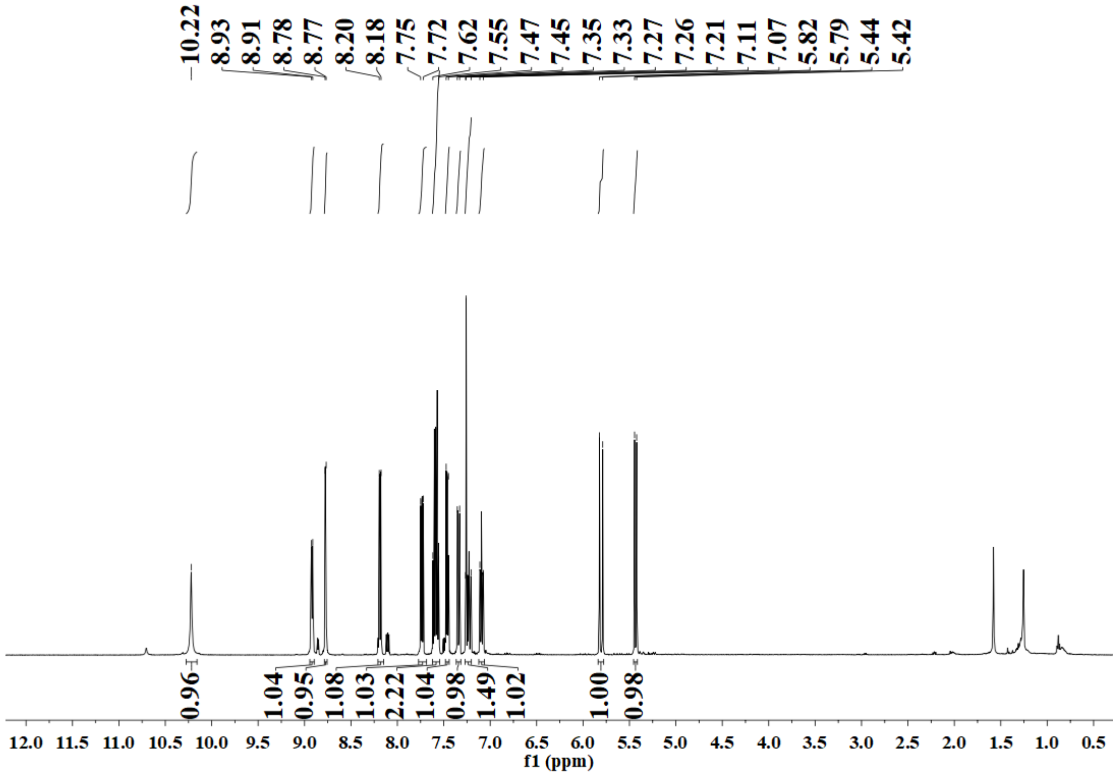
N
F

(1g)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5.44
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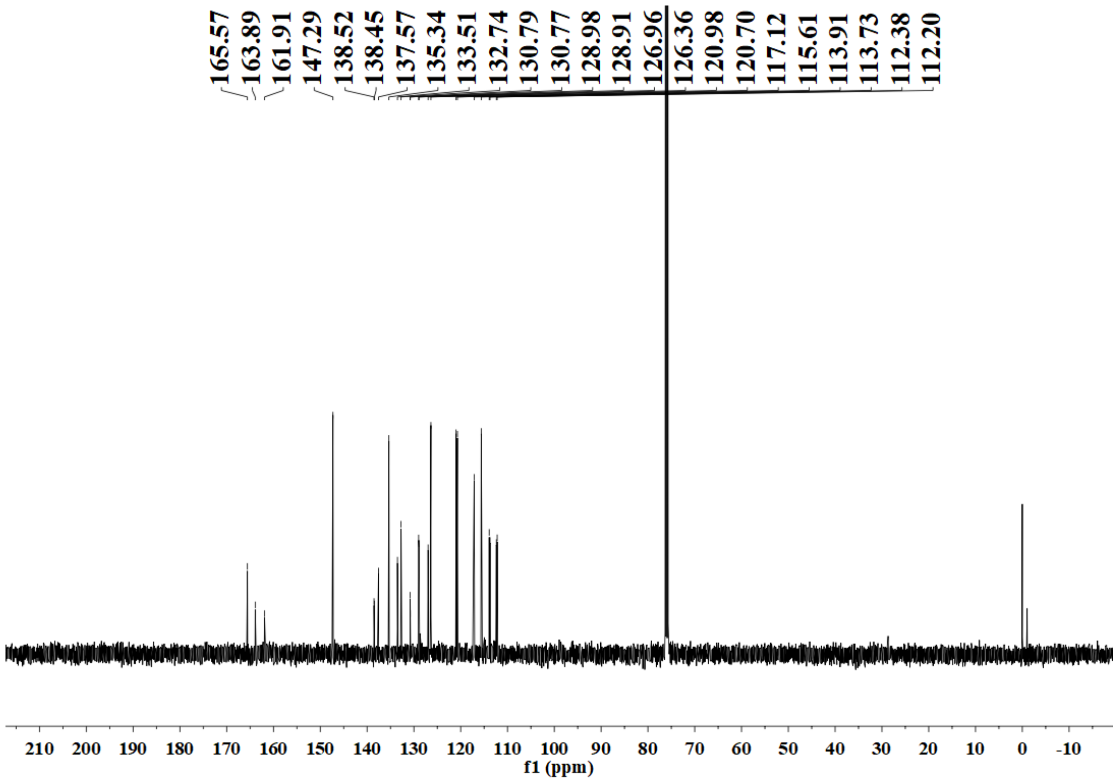
0.96
1.04
0.95
1.08
1.03
2.22
1.04
0.98
1.49
1.02
1.00
0.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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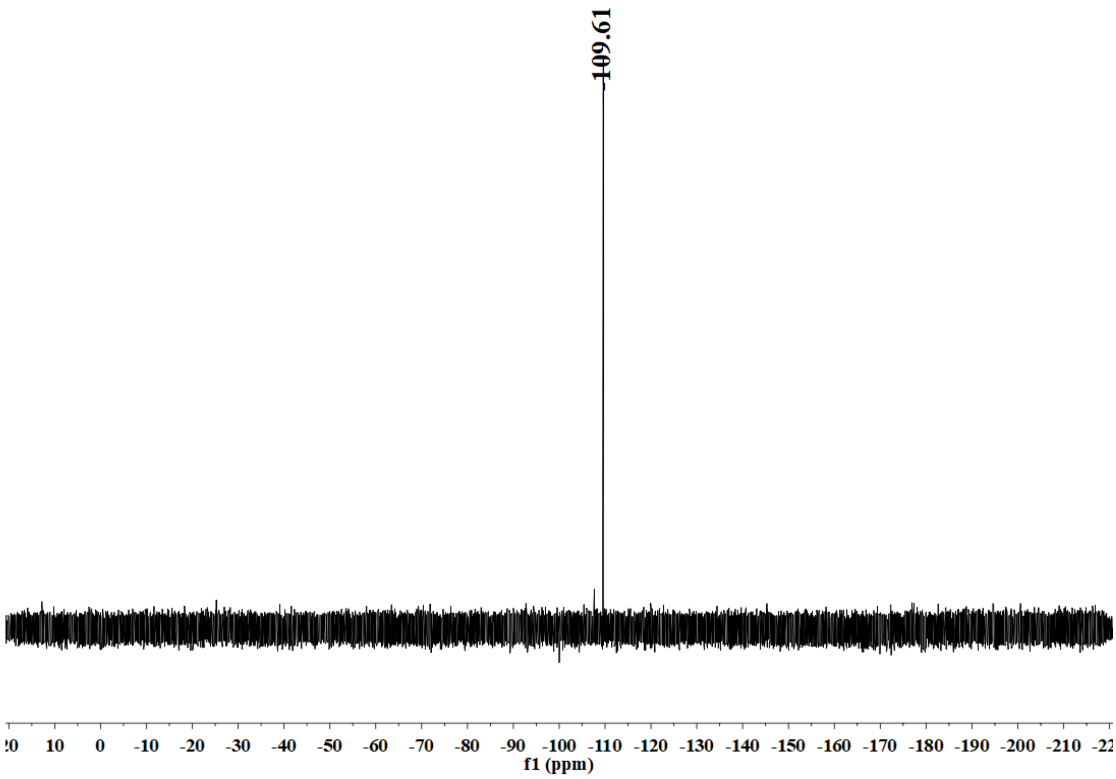
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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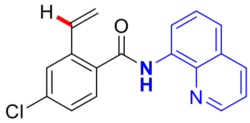
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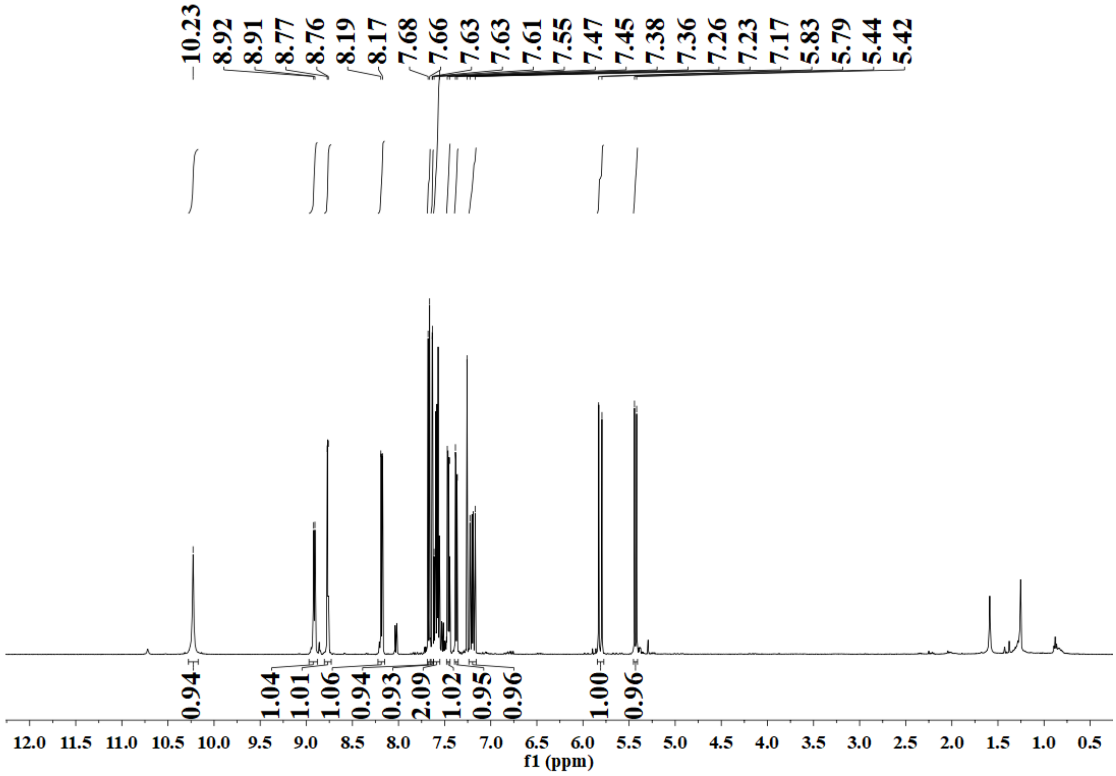
N
Cl

(1h)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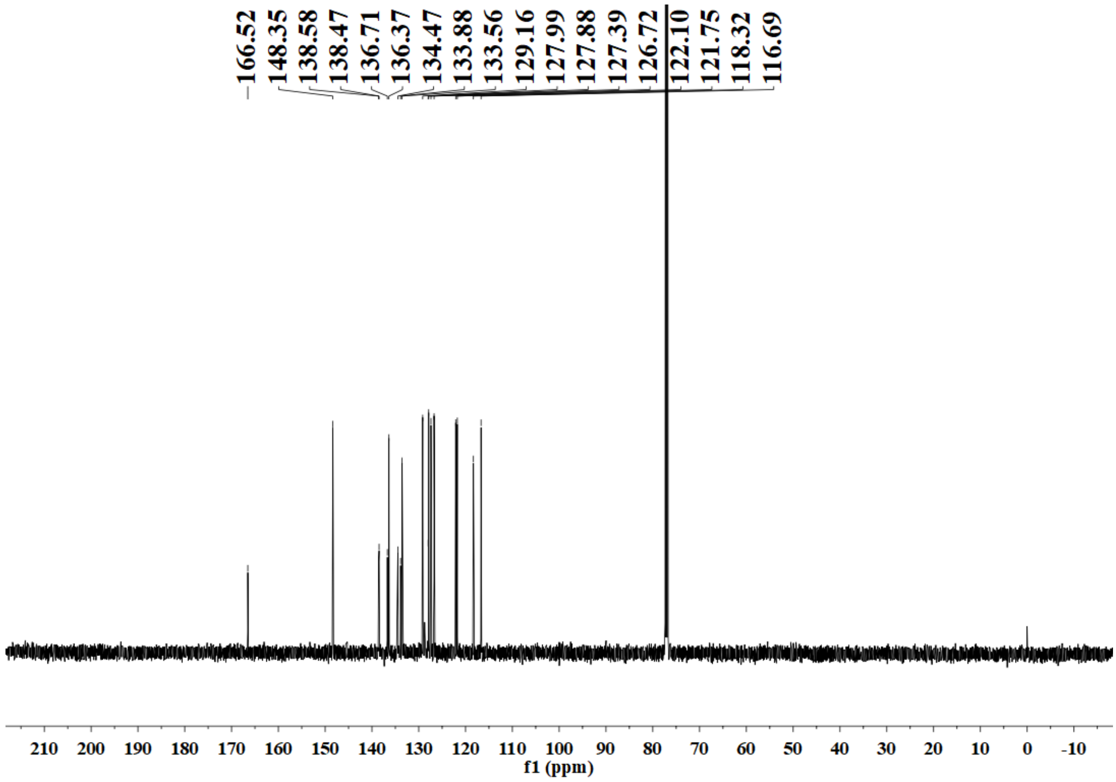
8.17
7.68
7.66
7.63
7.63
7.61
7.55
7.47
7.45
7.38
7.36
7.26
7.23
7.17
5.83
5.79
5.44
5.42
0.94
1.04
1.01
1.06
0.94
0.93
2.09
1.02
0.95
0.96
1.00
0.96
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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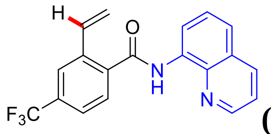
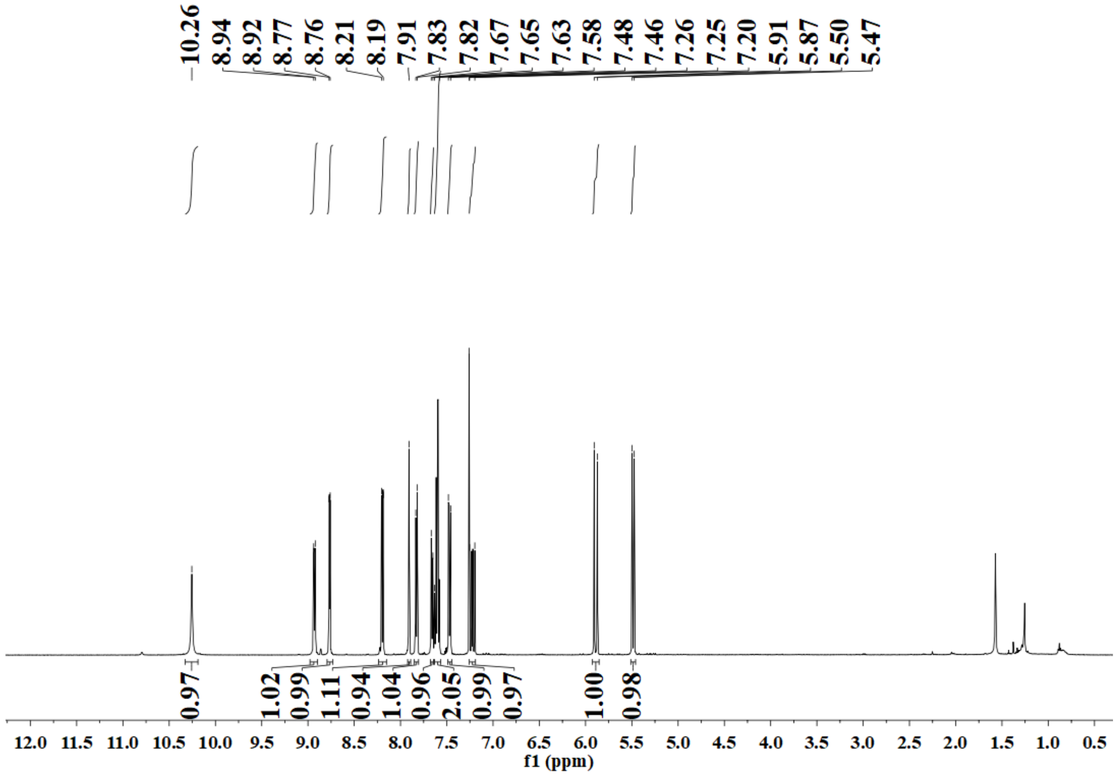
148.35
138.58
138.47
136.71
136.37
134.47
133.88
133.56
129.16
127.99
127.88
127.39
126.72
122.10
121.75
118.32
116.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



H
O
N
H
N
F_3C

(1i)



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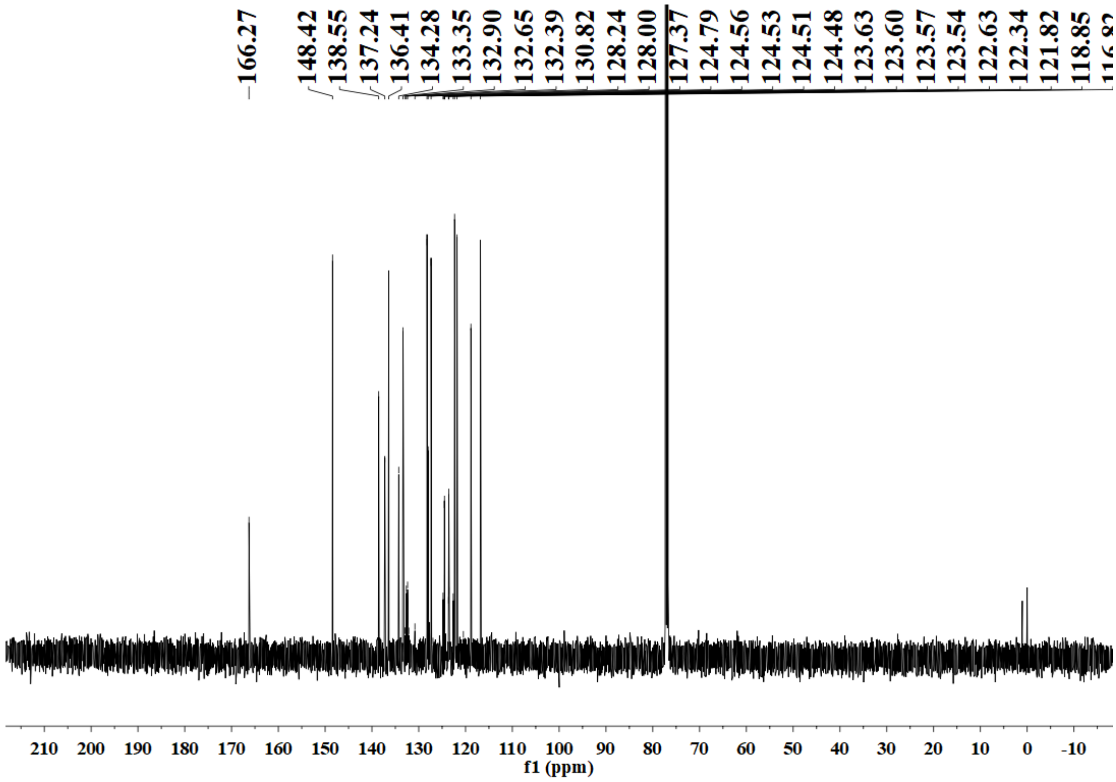
8.94
8.92
8.77
8.76
8.21
8.19
7.91
7.83
7.82
7.67
7.65
7.63
7.58
7.48
7.46
7.26
7.25
7.20
5.91
5.87
5.50
5.47
0.97
1.02
0.99
1.11
0.94
1.04
0.96
2.05
0.99
0.97
1.00
0.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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132.39
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128.24
128.00
127.37
124.79
124.56
124.53
124.51
124.48
123.63
123.60
123.57
123.54
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122.34
121.82
118.85
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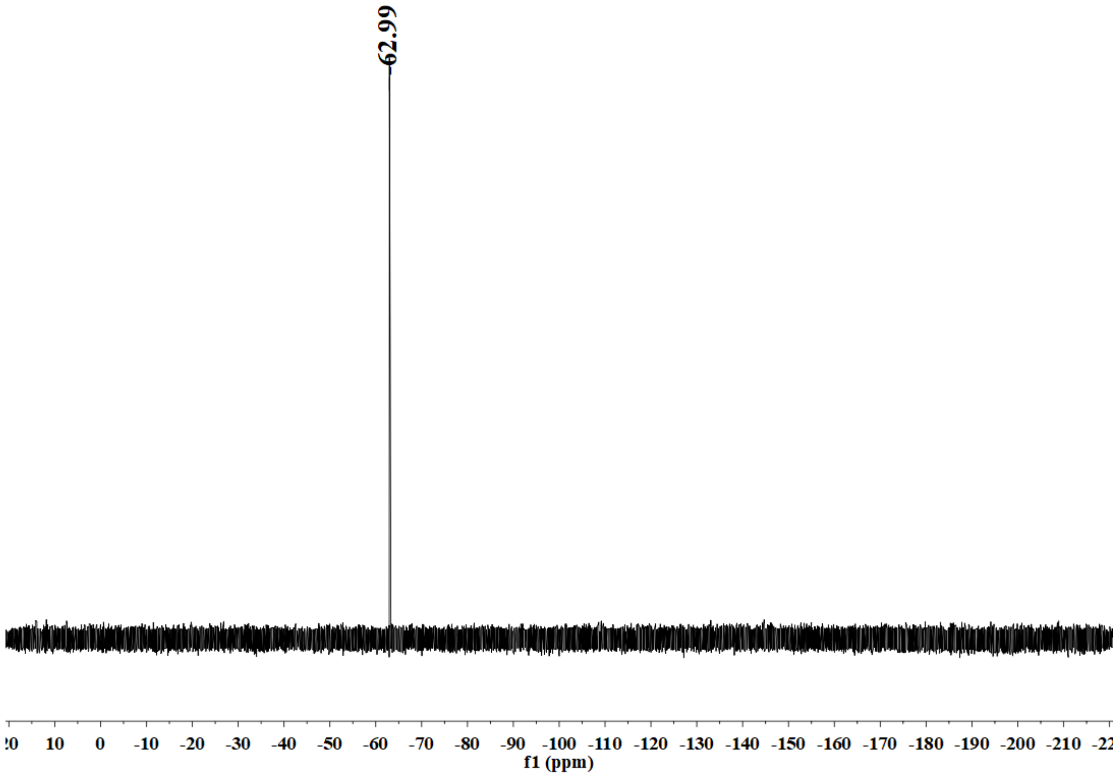
f1 (ppm)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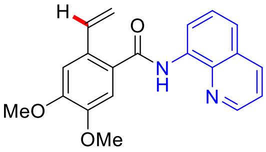
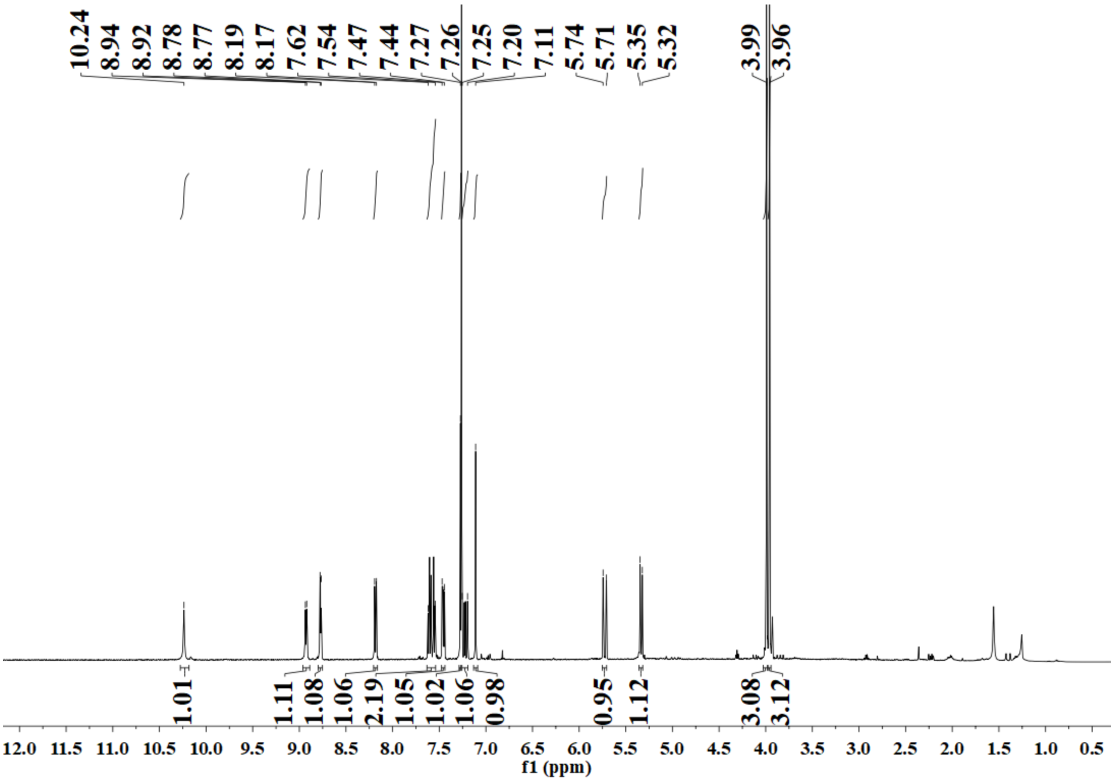
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


H
O
N
H
N
MeO
OMe

(1j)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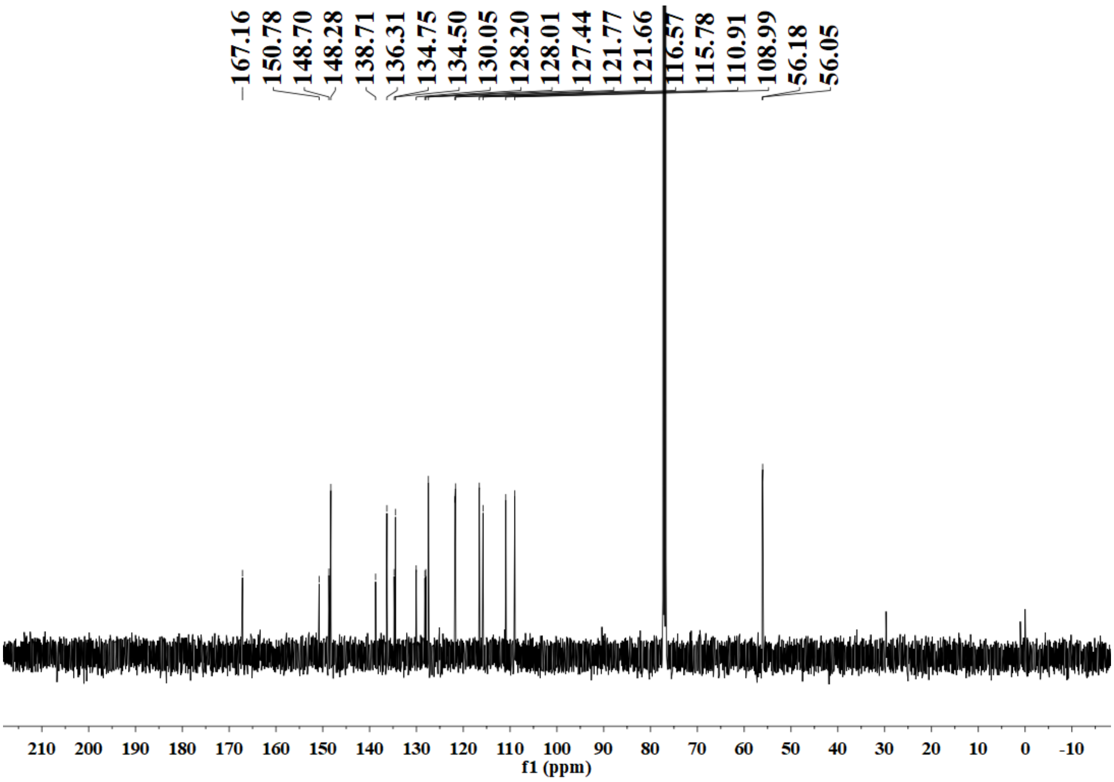
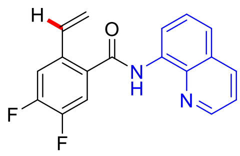
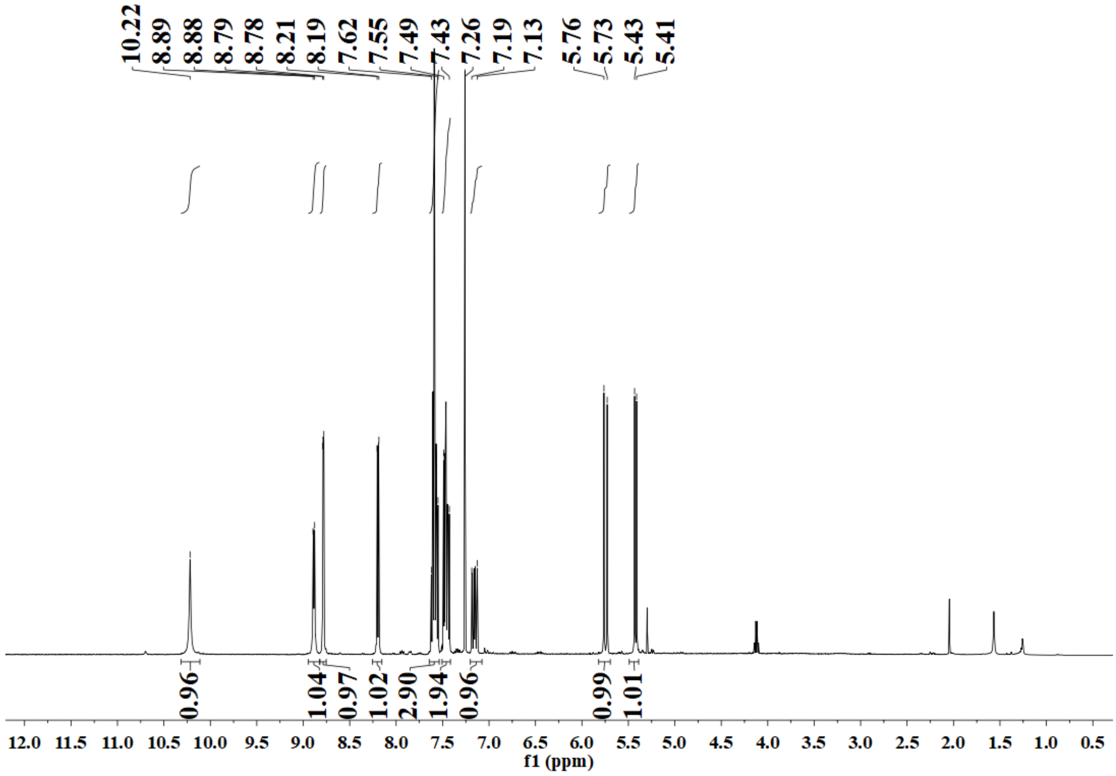
1.01 1.11 1.08 1.06 2.19 1.05 1.02 1.06 0.98 0.95 1.12 3.08 3.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


167.16 150.78 148.70 148.28 138.71 136.31 134.75 134.50 130.05 128.20 128.01 127.44 121.77 121.66 116.57 115.78 110.91 108.99 56.18 56.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
O
N
H
N
F
F

(1k)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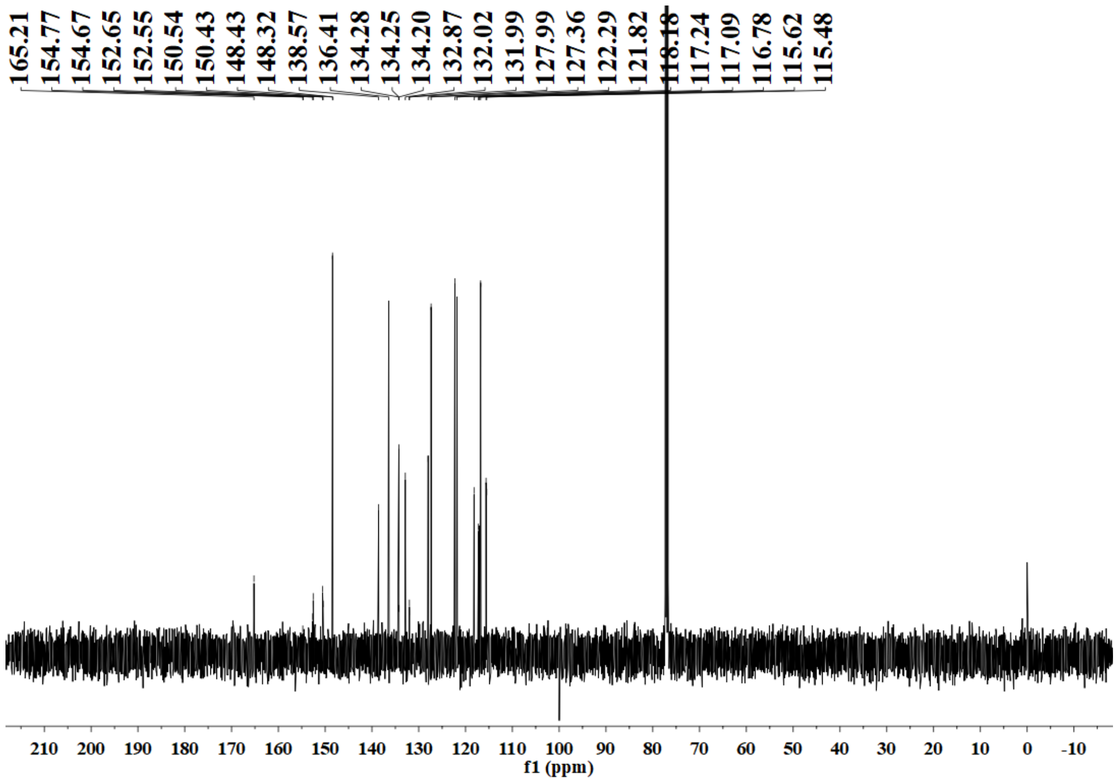
8.89
8.88
8.79
8.78
8.21
8.19
7.62
7.55
7.49
7.43
7.26
7.19
7.13
5.76
5.73
5.43
5.41
0.96
1.04
0.97
1.02
2.90
1.94
0.96
0.99
1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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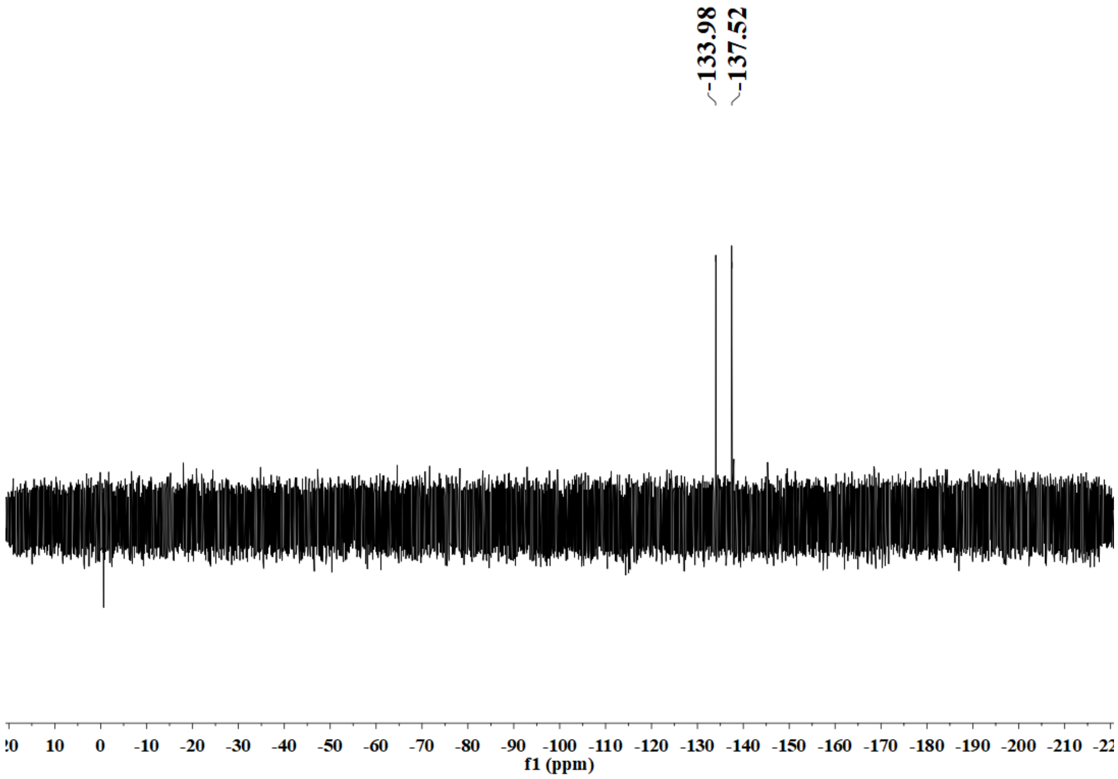
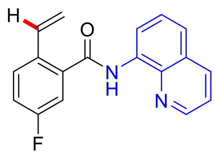
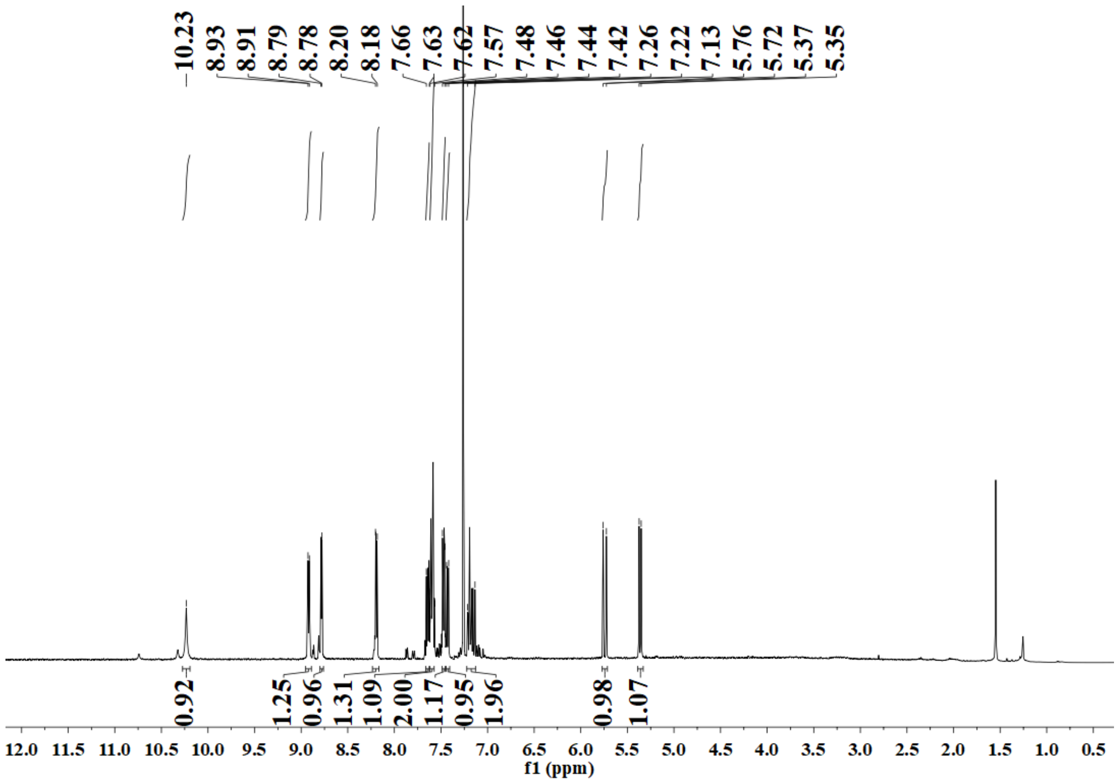
154.77
154.67
152.65
152.55
150.54
150.43
148.43
148.32
138.57
136.41
134.28
134.25
134.20
132.87
132.02
131.99
127.99
127.36
122.29
121.82
118.18
117.24
117.09
116.78
115.62
115.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-133.98
-137.52
f1 (ppm)



(1l)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8.91
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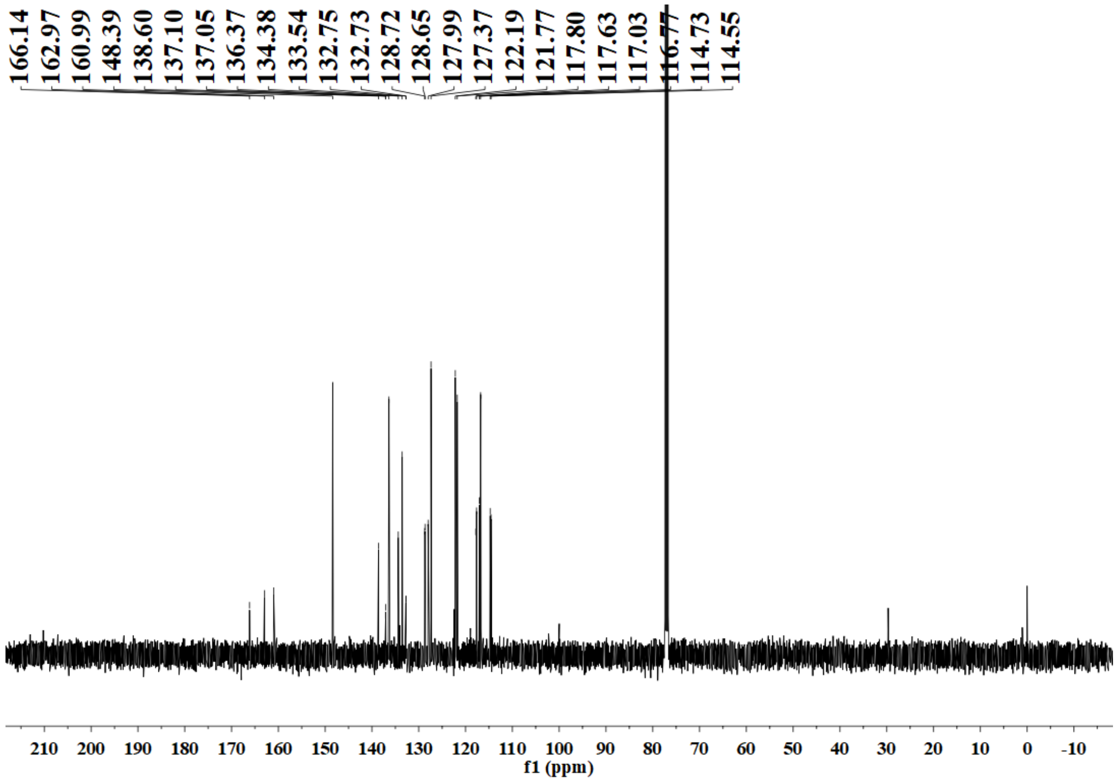
8.78
8.20
8.18
7.66
7.63
7.62
7.57
7.48
7.46
7.44
7.42
7.26
7.22
7.13
5.76
5.72
5.37
5.35
0.92
1.25
0.96
1.31
1.09
2.00
1.17
0.95
1.96
0.98
1.07
f1 (ppm)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160.99
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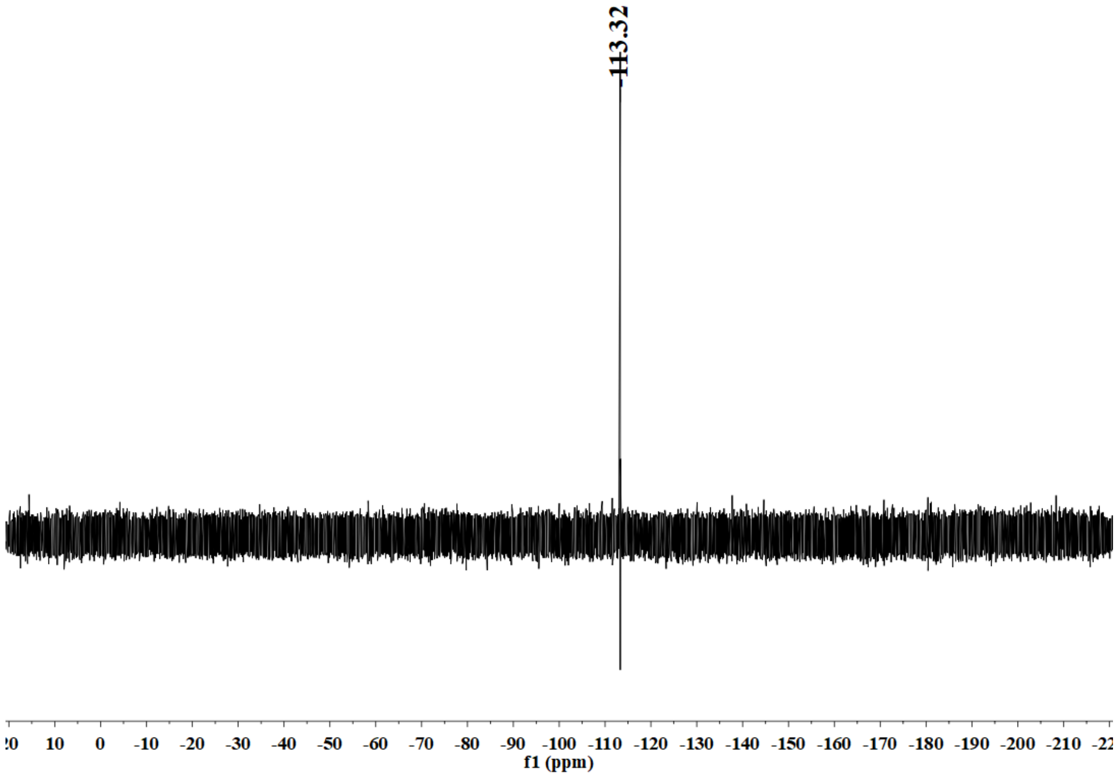
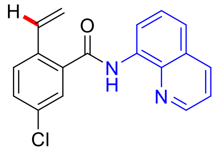
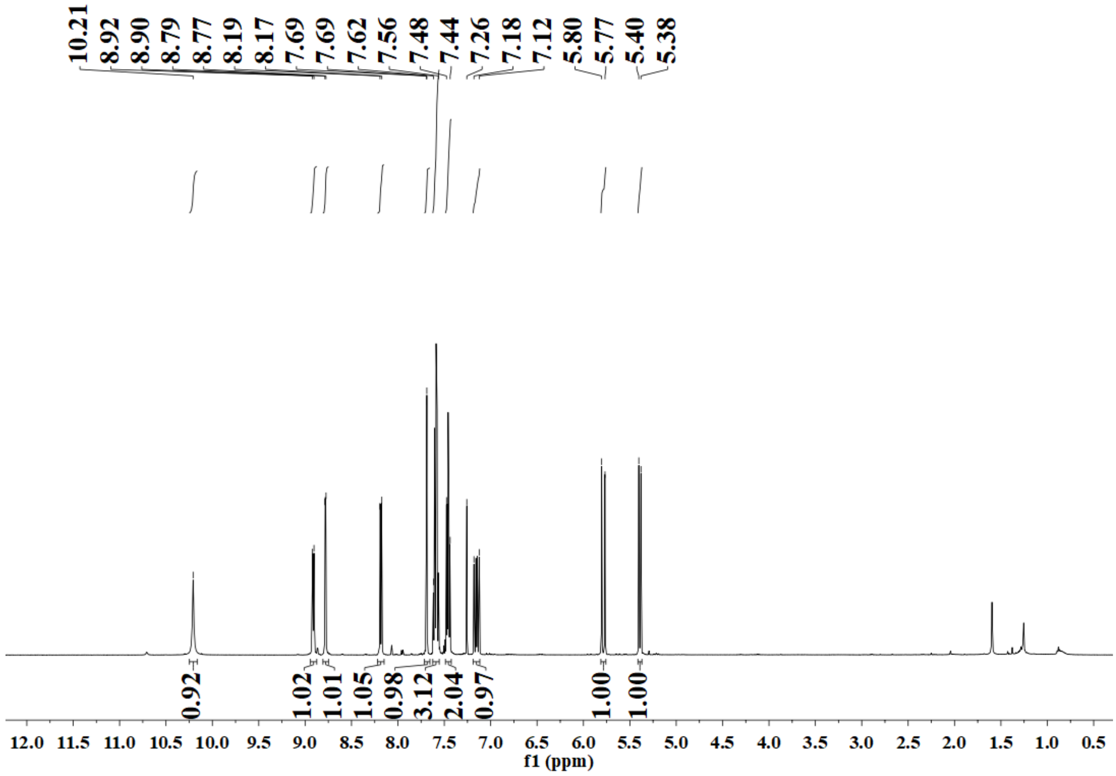
138.60
137.10
137.05
136.37
134.38
133.54
132.75
132.73
128.72
128.65
127.99
127.37
122.19
121.77
117.80
117.63
117.03
116.77
114.73
114.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-113.32
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


H
O
N
H
N
Cl

(1m)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8.92
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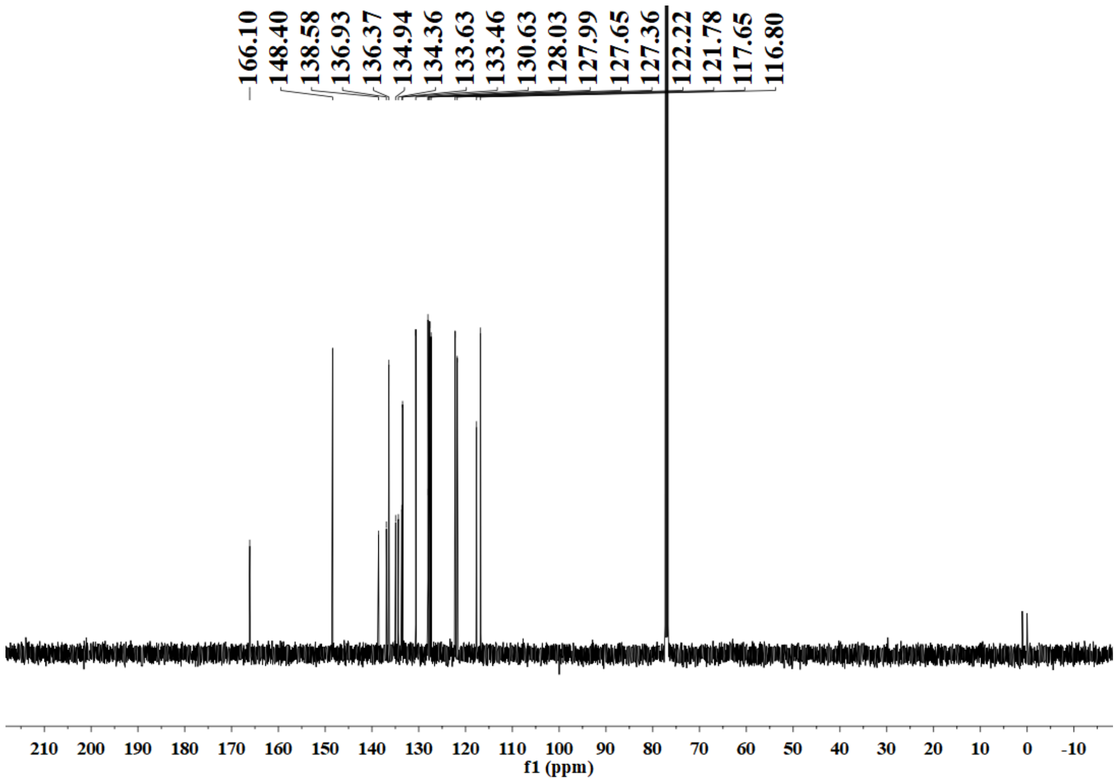
8.79
8.77
8.19
8.17
7.69
7.69
7.62
7.56
7.48
7.44
7.26
7.18
7.12
5.80
5.77
5.40
5.38
0.92
1.02
1.01
1.05
0.98
3.12
2.04
0.97
1.00
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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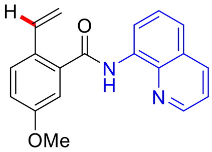
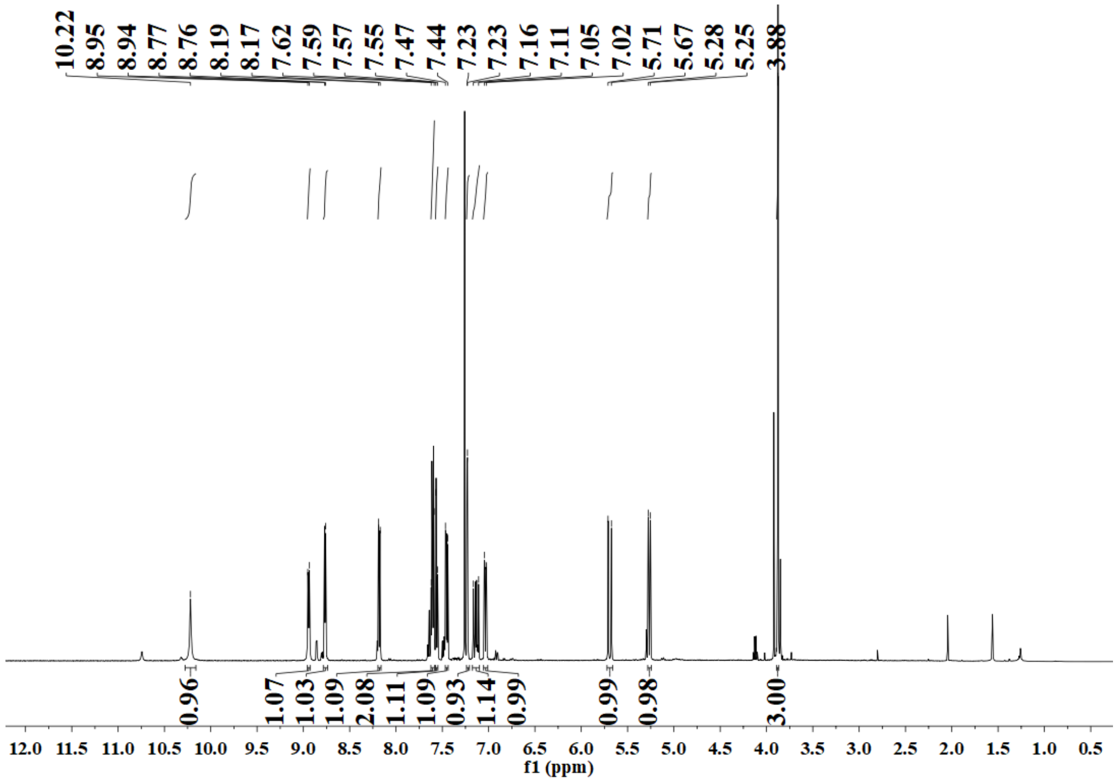
138.58
136.93
136.37
134.94
134.36
133.63
133.46
130.63
128.03
127.99
127.65
127.36
122.22
121.78
117.65
116.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
O
N
H
N
OMe

(1n)


10.22
8.95
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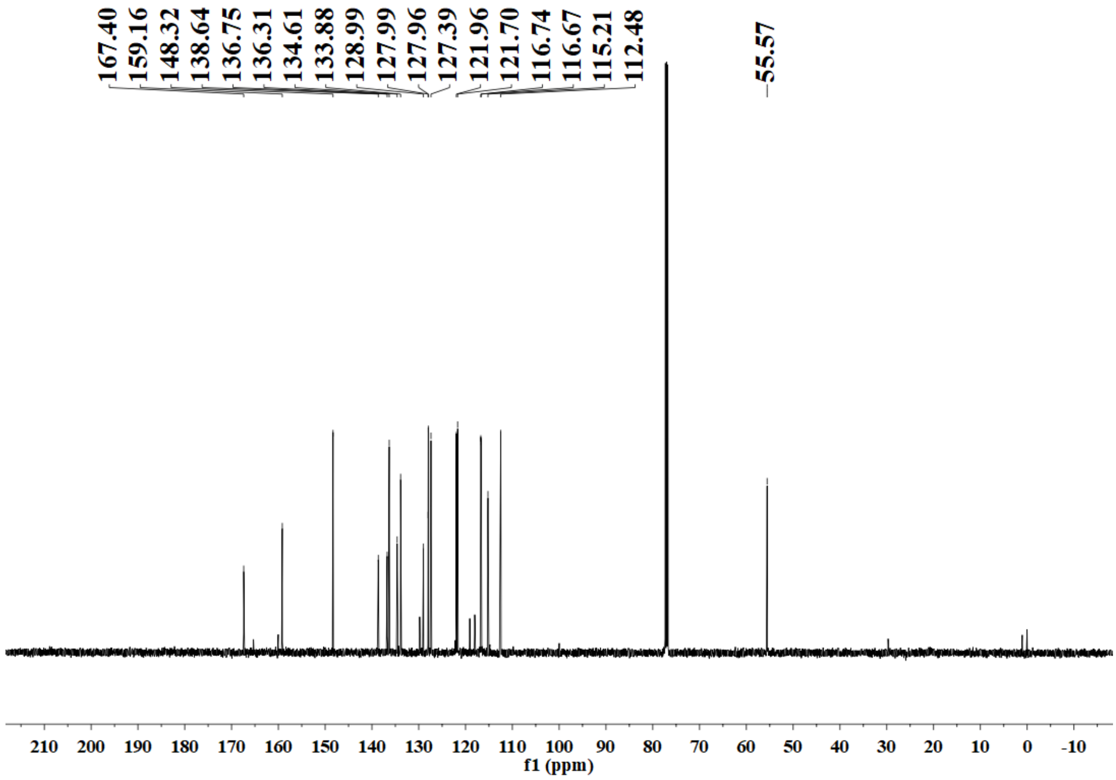
8.77
8.76
8.19
8.17
7.62
7.59
7.57
7.55
7.47
7.44
7.23
7.23
7.23
7.16
7.11
7.05
7.02
5.71
5.67
5.28
5.25
3.88
0.96
1.07
1.03
1.09
2.08
1.11
1.09
0.93
1.14
0.99
0.99
0.98
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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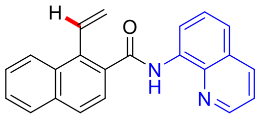
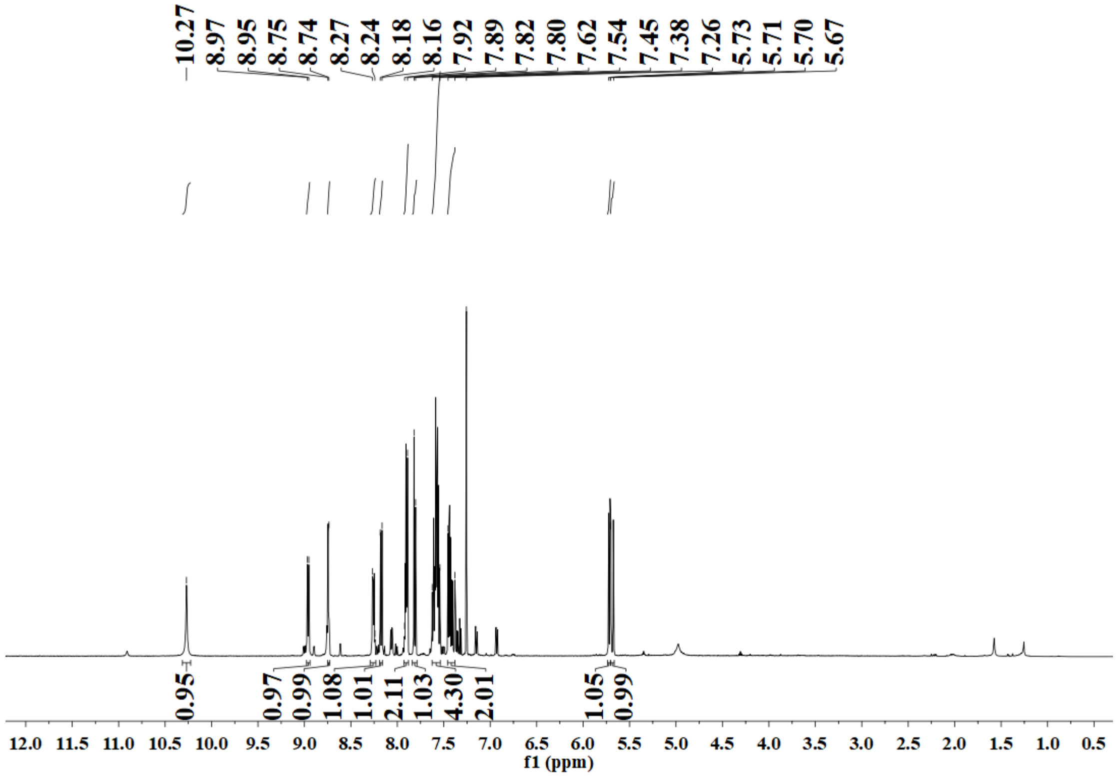
136.31
134.61
133.88
128.99
127.99
127.96
127.39
121.96
121.70
116.74
116.67
115.21
112.48
55.57
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
O
N
H
N

(1o)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8.16
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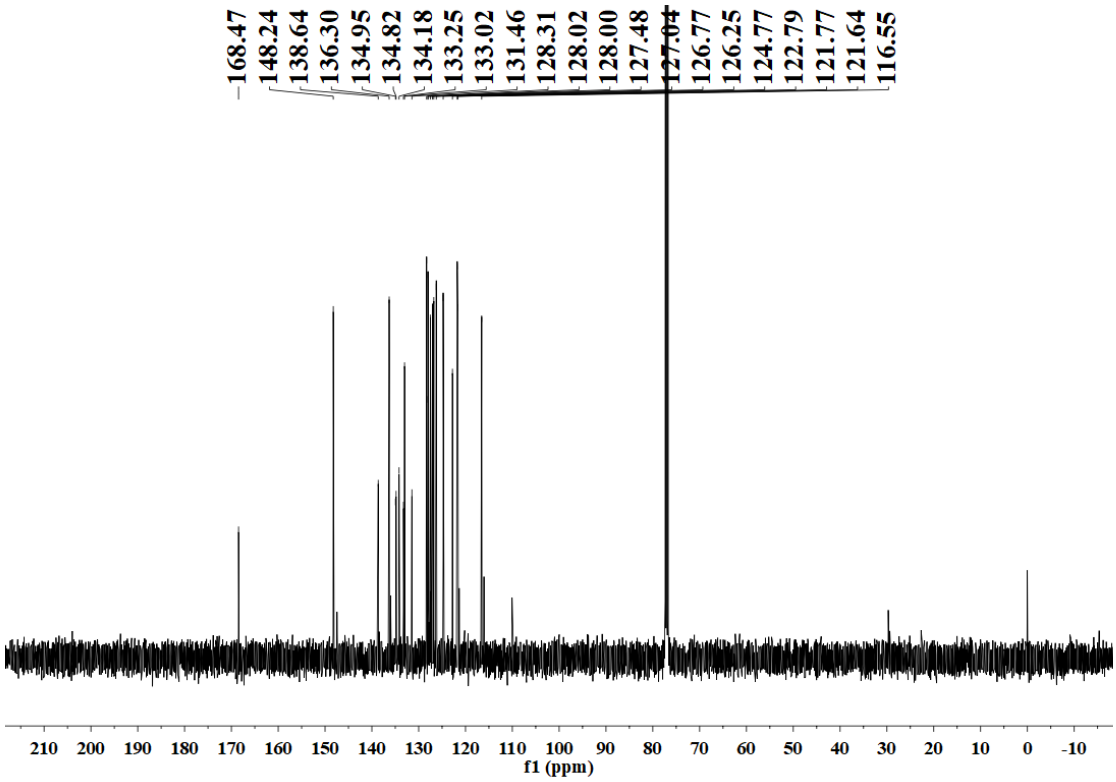
7.89
7.82
7.80
7.62
7.54
7.45
7.38
7.26
5.73
5.71
5.70
5.67
0.95
0.97
0.99
1.08
1.01
2.11
1.03
4.30
2.01
1.05
0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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133.02
131.46
128.31
128.02
128.00
127.48
127.04
126.77
126.25
124.77
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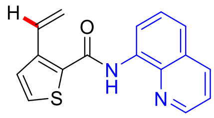
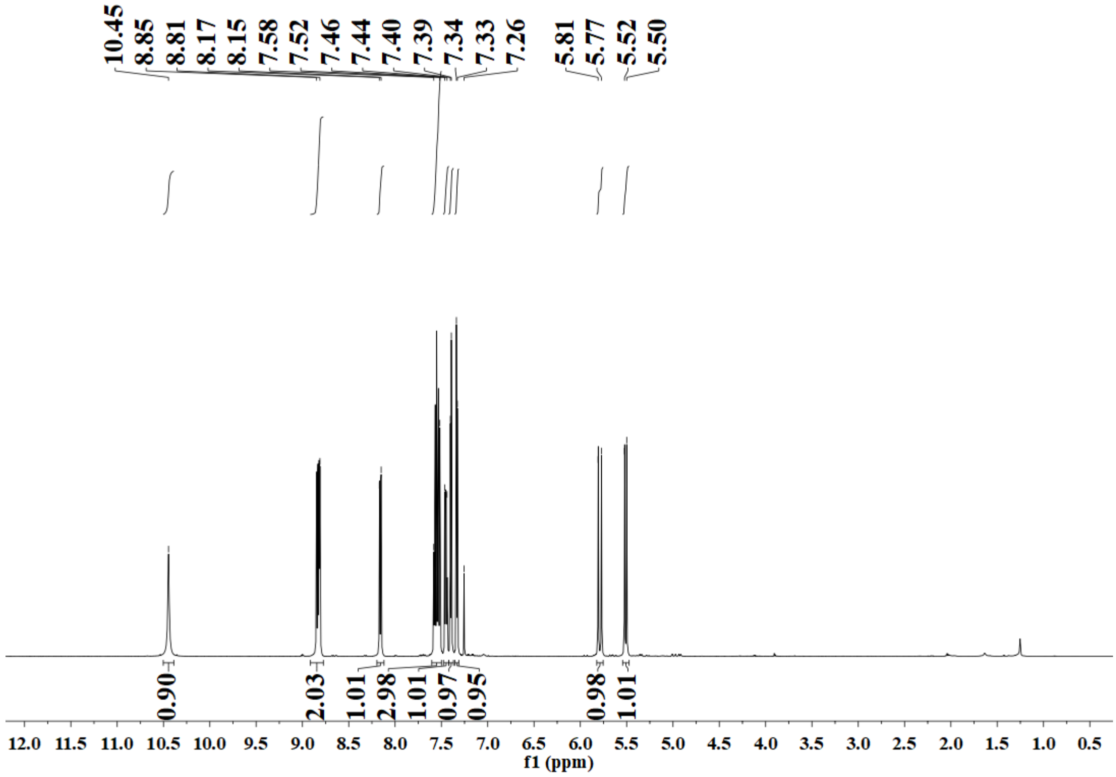
121.77
121.64
116.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
O
N
H
S
N

(1p)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7.46
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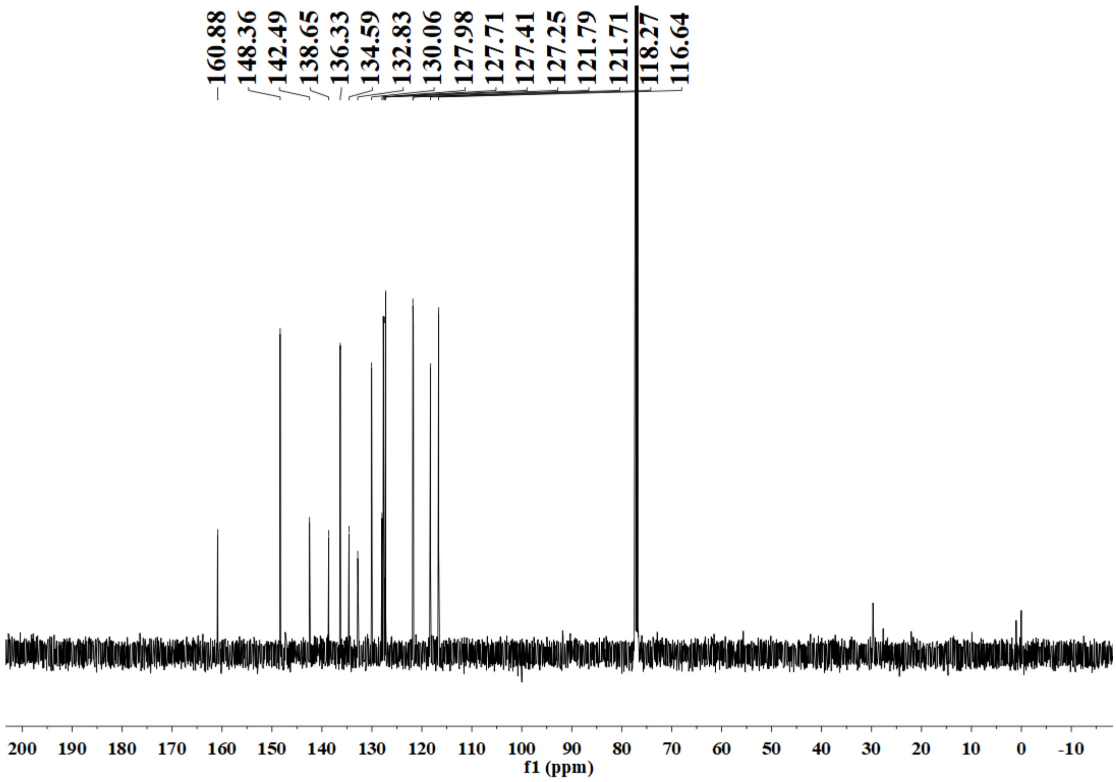
7.40
7.39
7.34
7.33
7.26
5.81
5.77
5.52
5.50
0.90
2.03
1.01
2.98
1.01
0.97
0.95
0.98
1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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127.71
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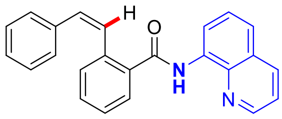
121.71
118.27
116.64
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
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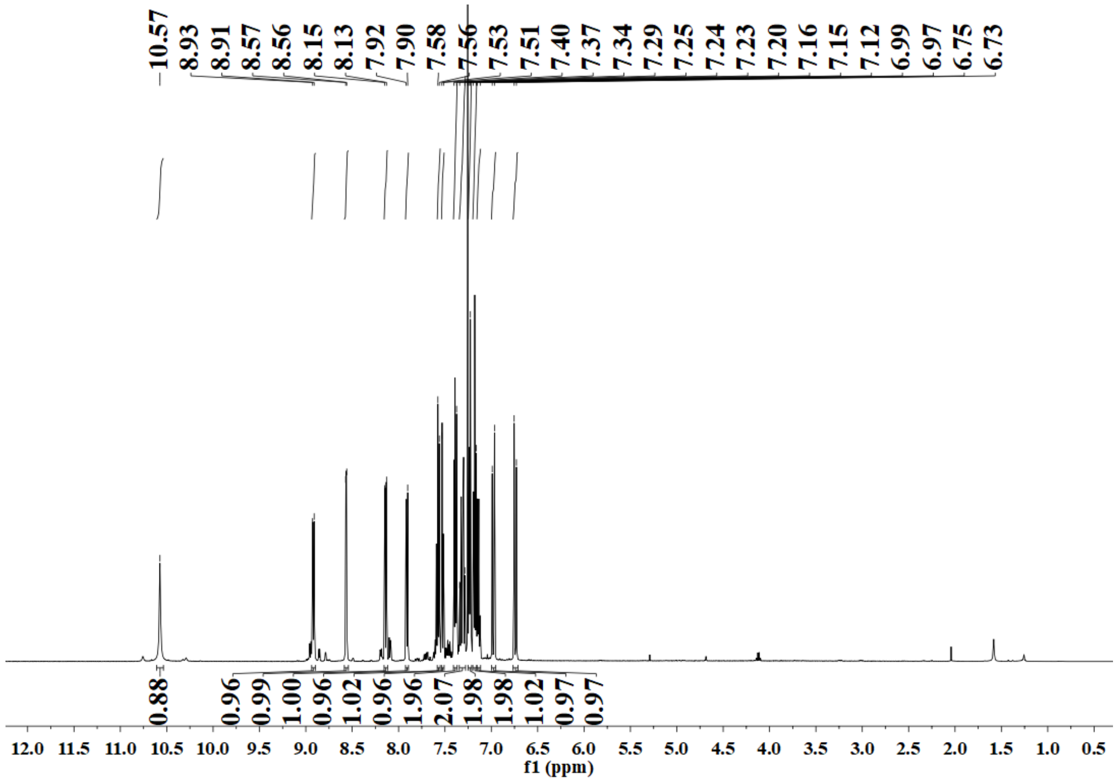
N
H
N

(1w)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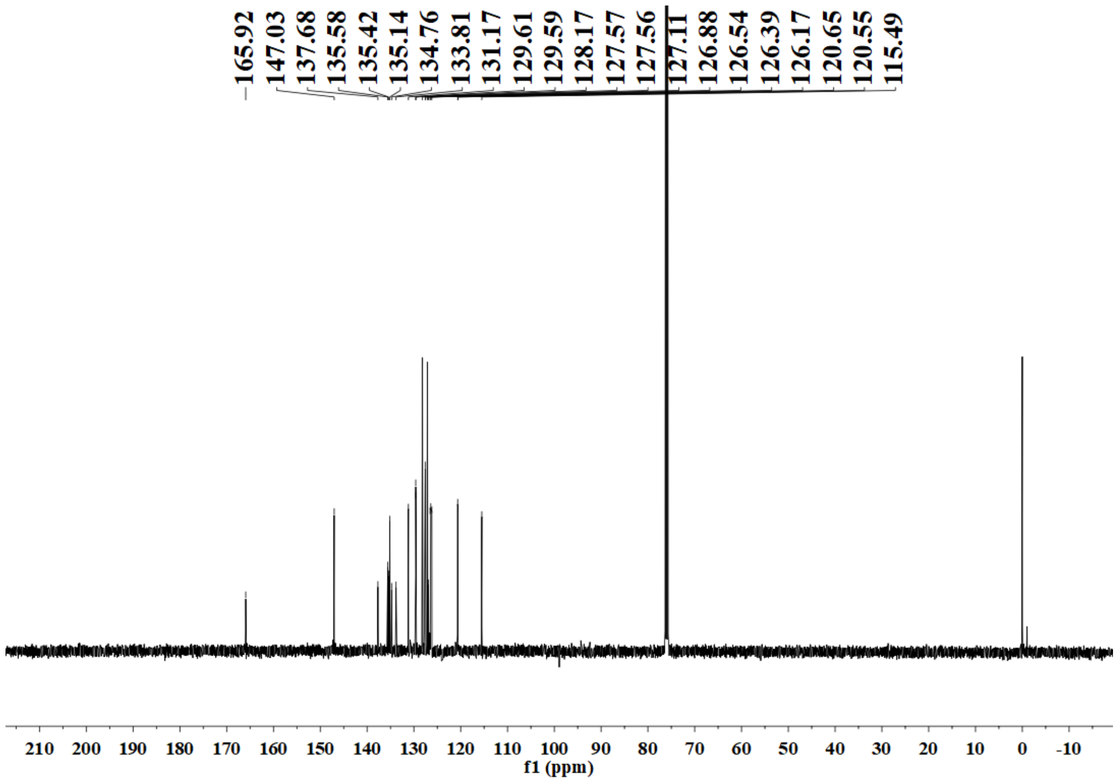
7.40
7.37
7.34
7.29
7.25
7.24
7.23
7.20
7.16
7.15
7.12
6.99
6.97
6.75
6.73
0.88
0.96
0.99
1.00
0.96
1.02
0.96
1.96
2.07
1.98
1.98
1.02
0.97
0.97
f1 (ppm)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129.59
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127.57
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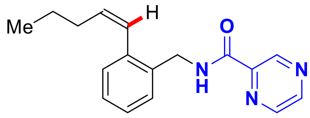
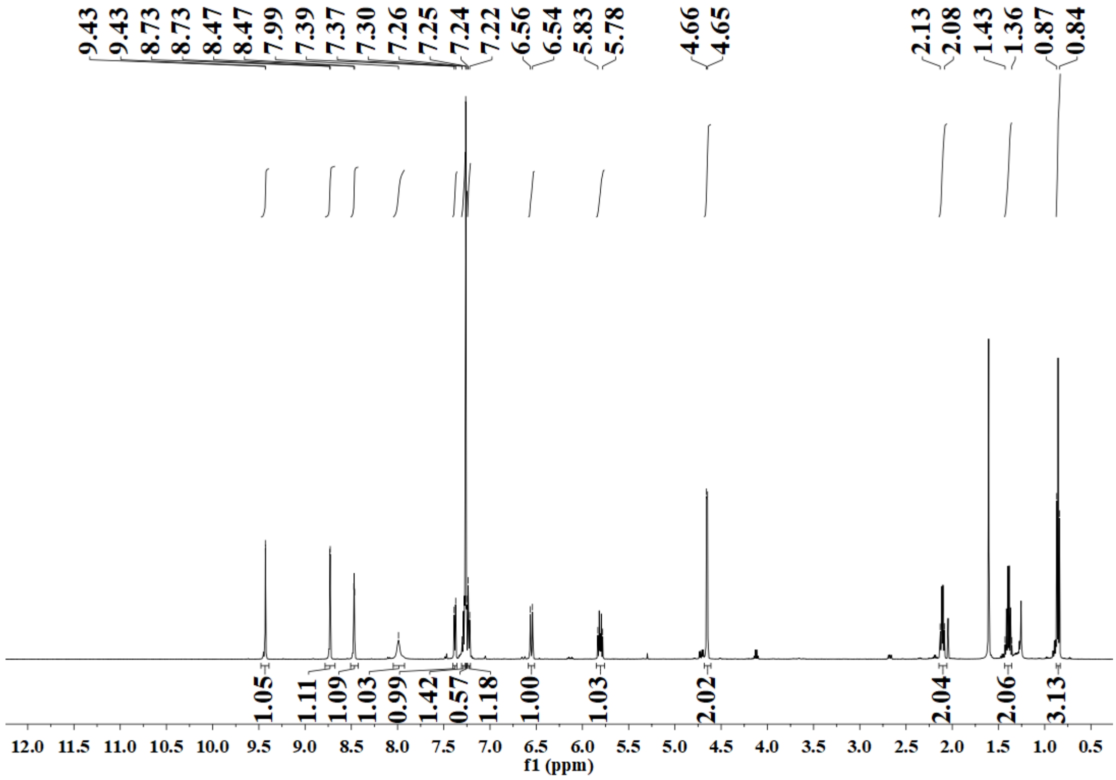
127.11
126.88
126.54
126.39
126.17
120.65
120.55
115.49
f1 (ppm)


Me
H
O
N
H
N
N

(1x)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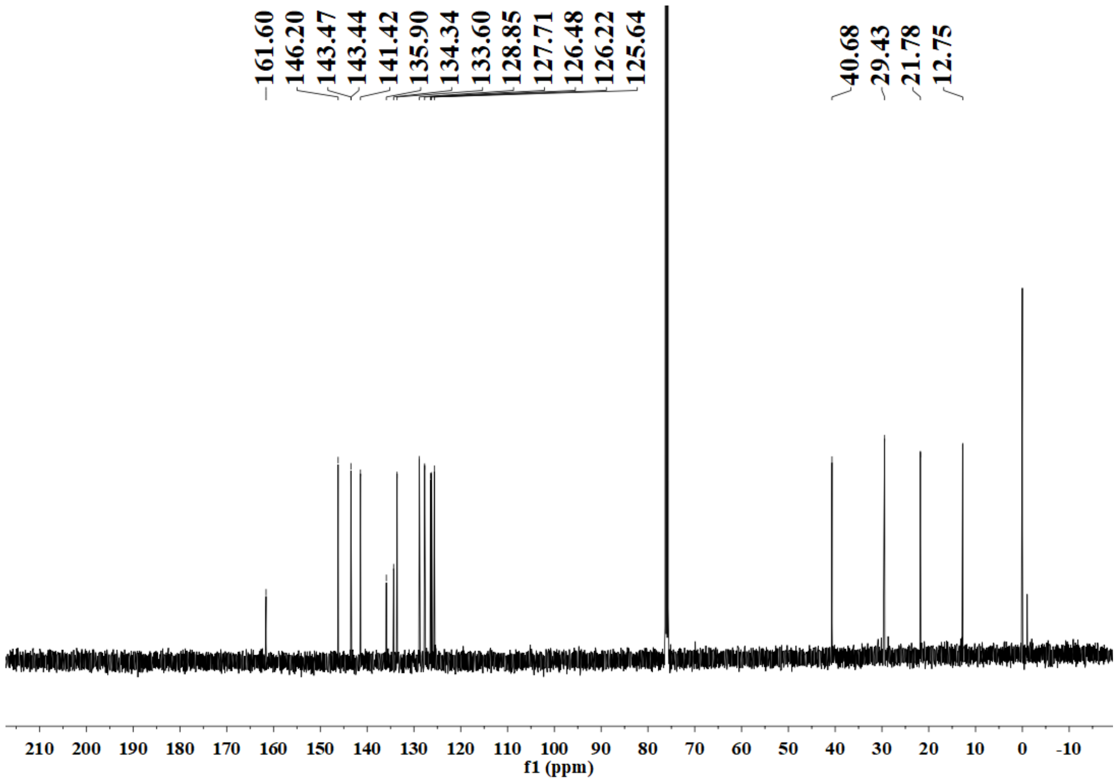
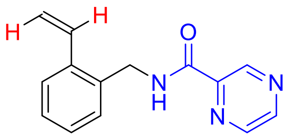
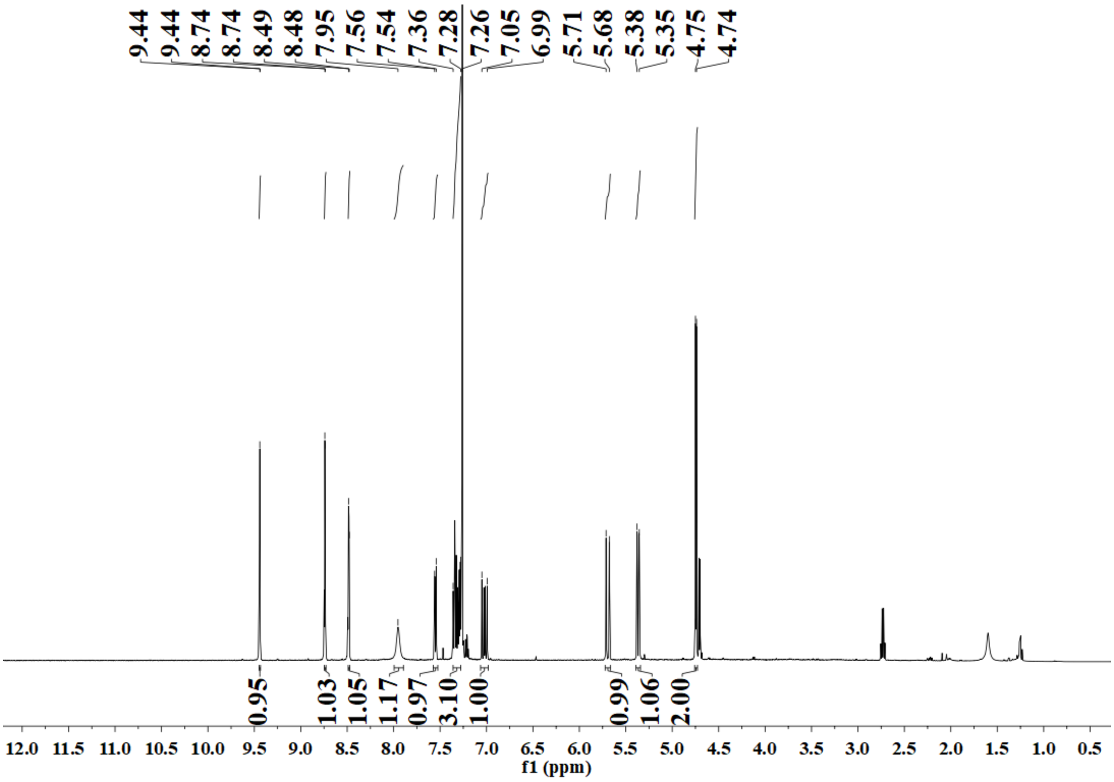
1.05 1.11 1.09 1.03 0.99 1.42 0.57 1.18 1.00 1.03 2.02 2.04 2.06 3.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


161.60 146.20 143.47 143.44 141.42 135.90 134.34 133.60 128.85 127.71 126.48 126.22 125.64
40.68 29.43 21.78 12.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



(4a)



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9.44
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8.74
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8.48
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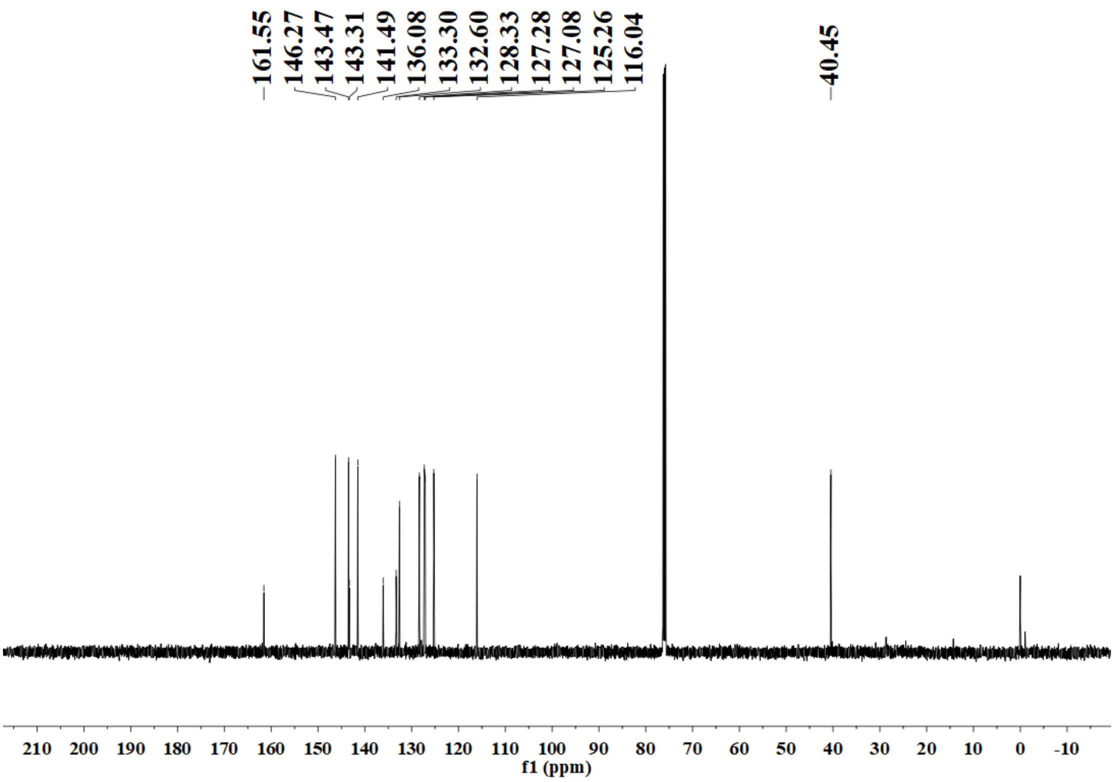
7.54
7.36
7.28
7.26
7.05
6.99
5.71
5.68
5.38
5.35
4.75
4.74
0.95
1.03
1.05
1.17
0.97
3.10
1.00
0.99
1.06
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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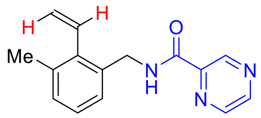
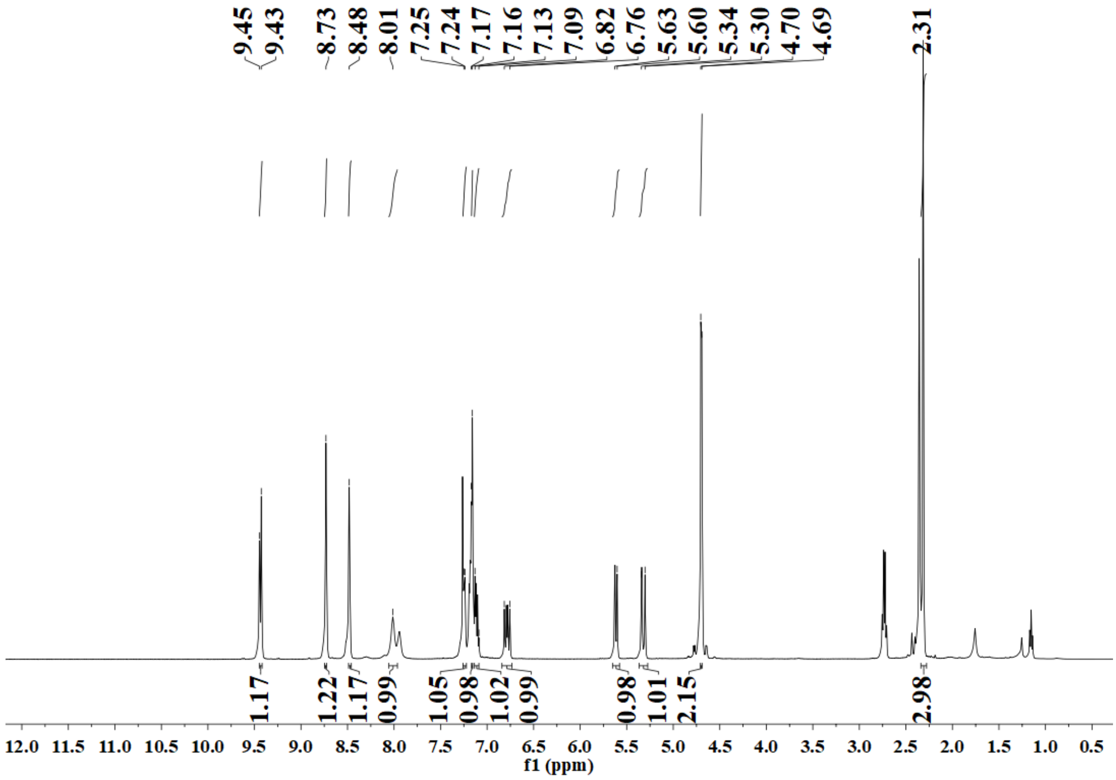
146.27
143.47
143.31
141.49
136.08
133.30
132.60
128.33
127.28
127.08
125.26
116.04
40.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
H
Me
O
N
H
N
N
(4g)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7.24
7.17
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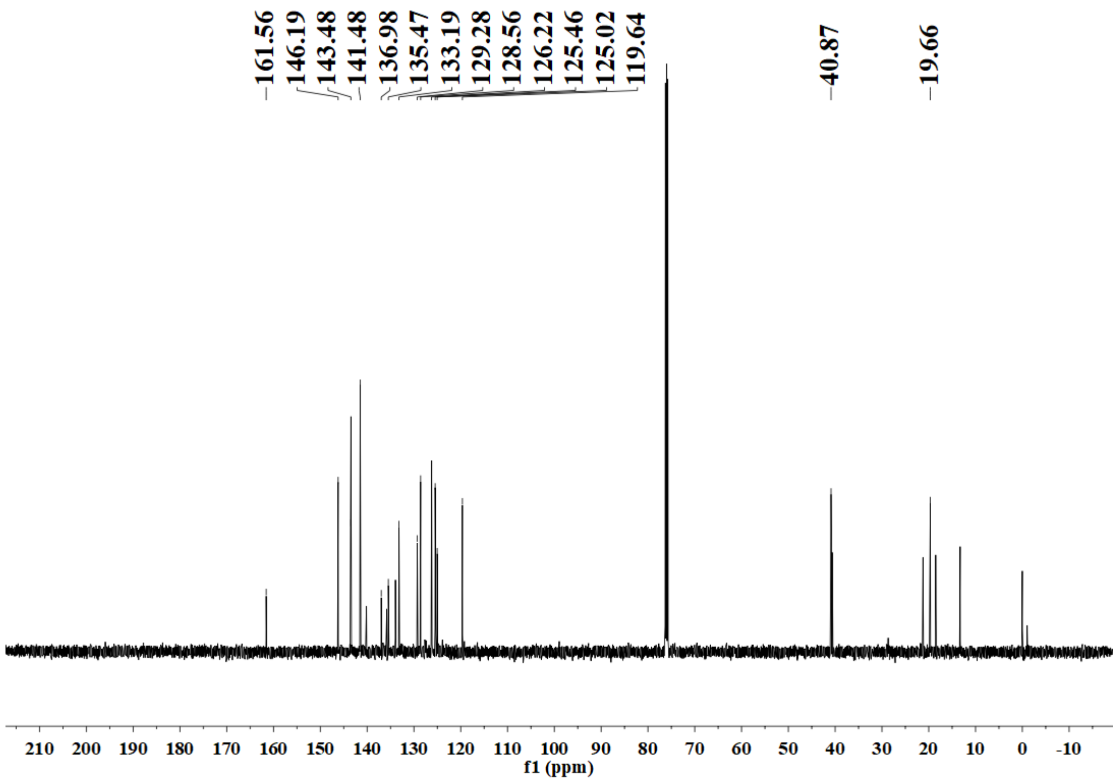
7.13
7.09
6.82
6.76
5.63
5.60
5.34
5.30
4.70
4.69
2.31
1.17
1.22
1.17
0.99
1.05
0.98
1.02
0.99
0.98
1.01
2.15
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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135.47
133.19
129.28
128.56
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119.64
40.87
19.66
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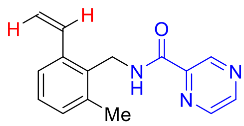
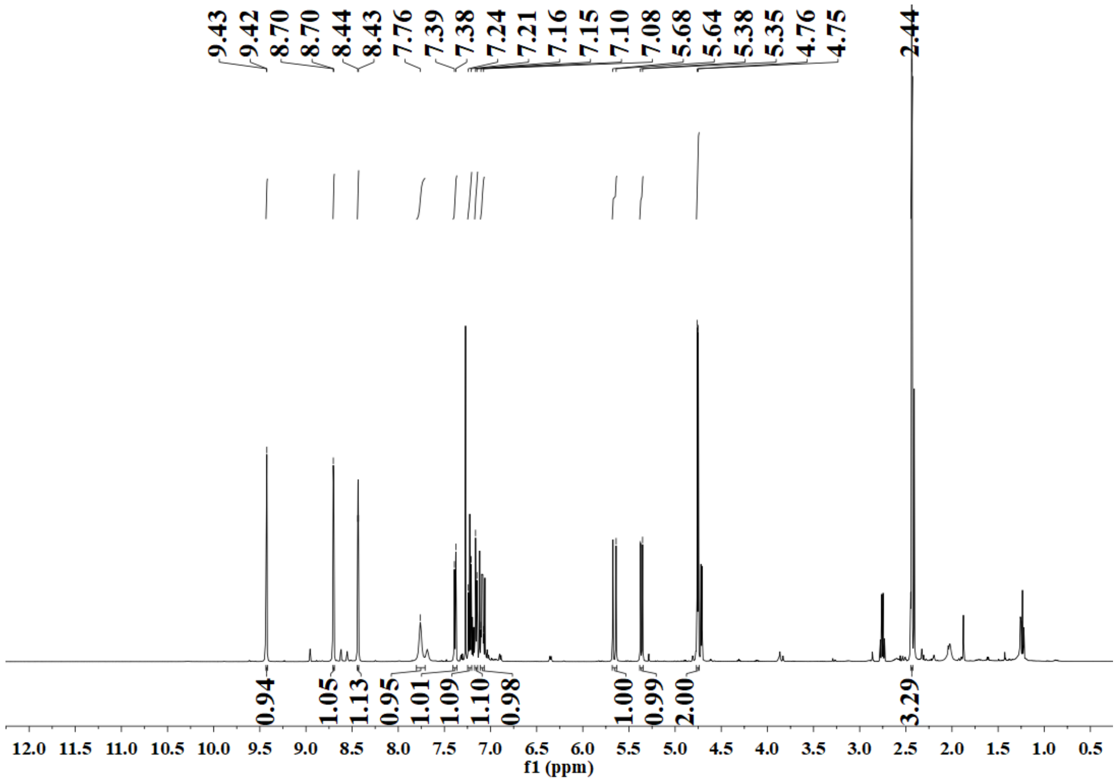
f1 (ppm)


H
H
O
N
H
N
N
Me

(4h)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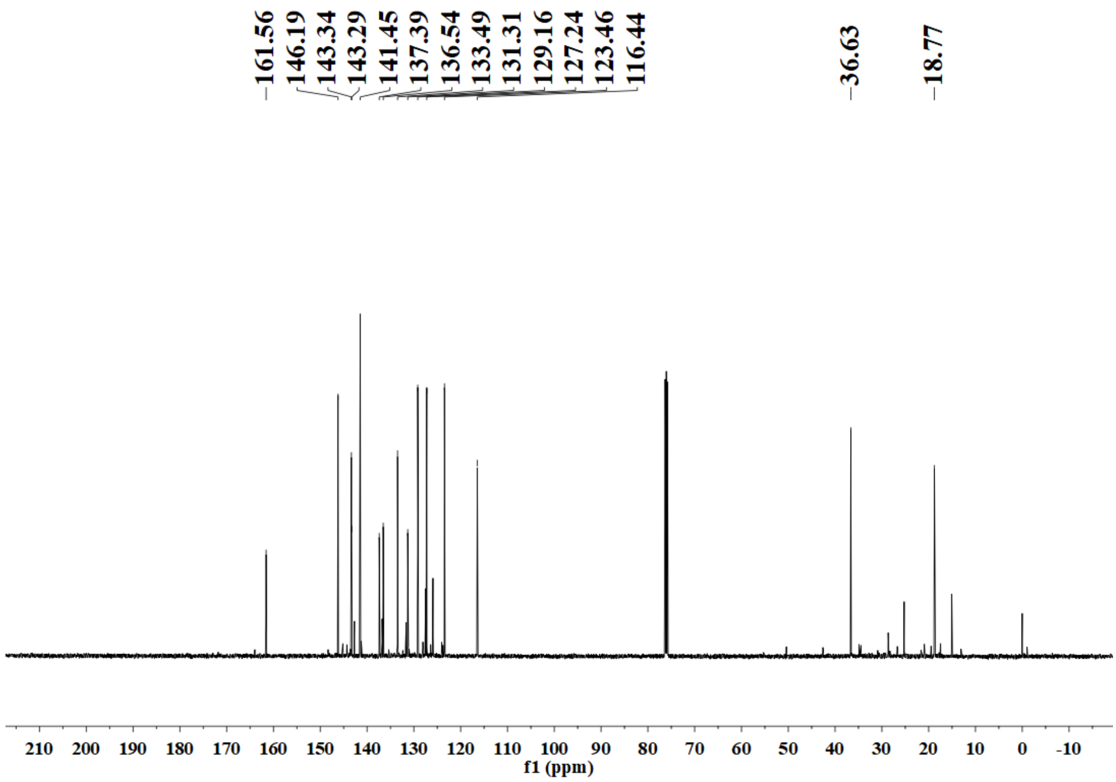
2.44
0.94 1.05 1.13 0.95 1.01 1.09 1.10 0.98 1.00 0.99 2.00 3.29
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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146.19 143.34 143.29 141.45 137.39 136.54 133.49 131.31 129.16 127.24 123.46 116.44
36.63
18.77
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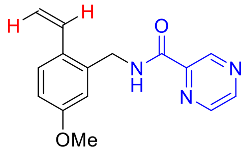
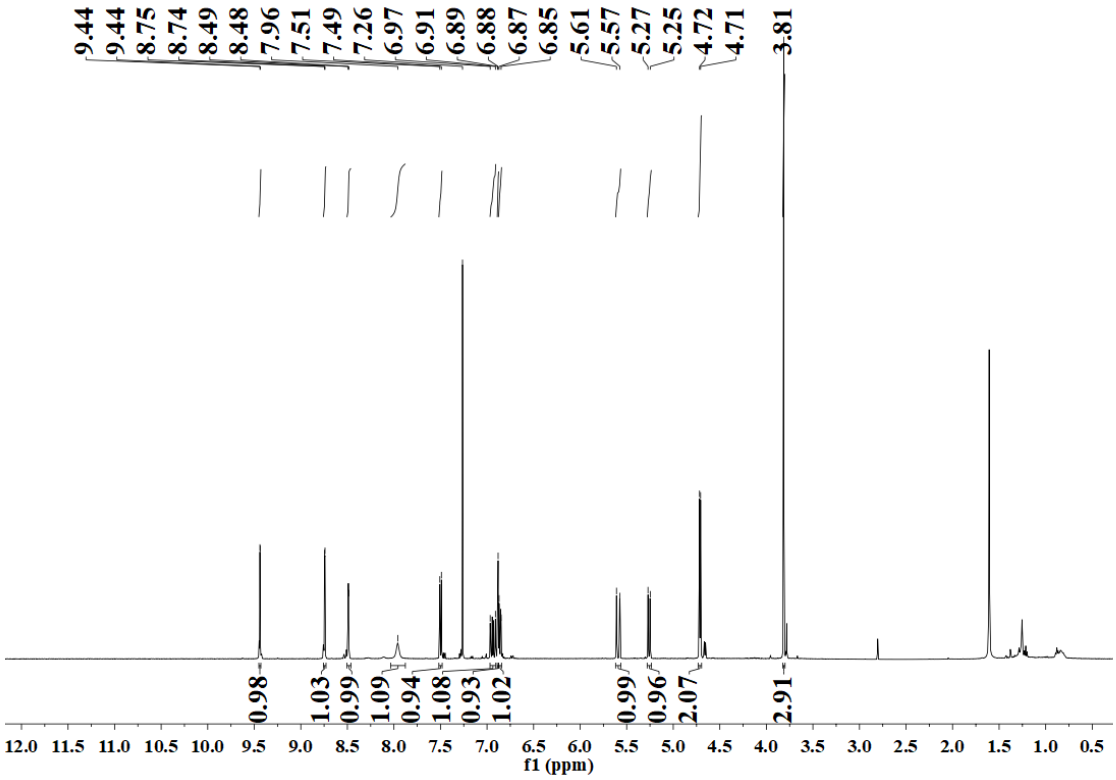
f1 (ppm)


H
H
O
N
H
N
N
OMe

(4i)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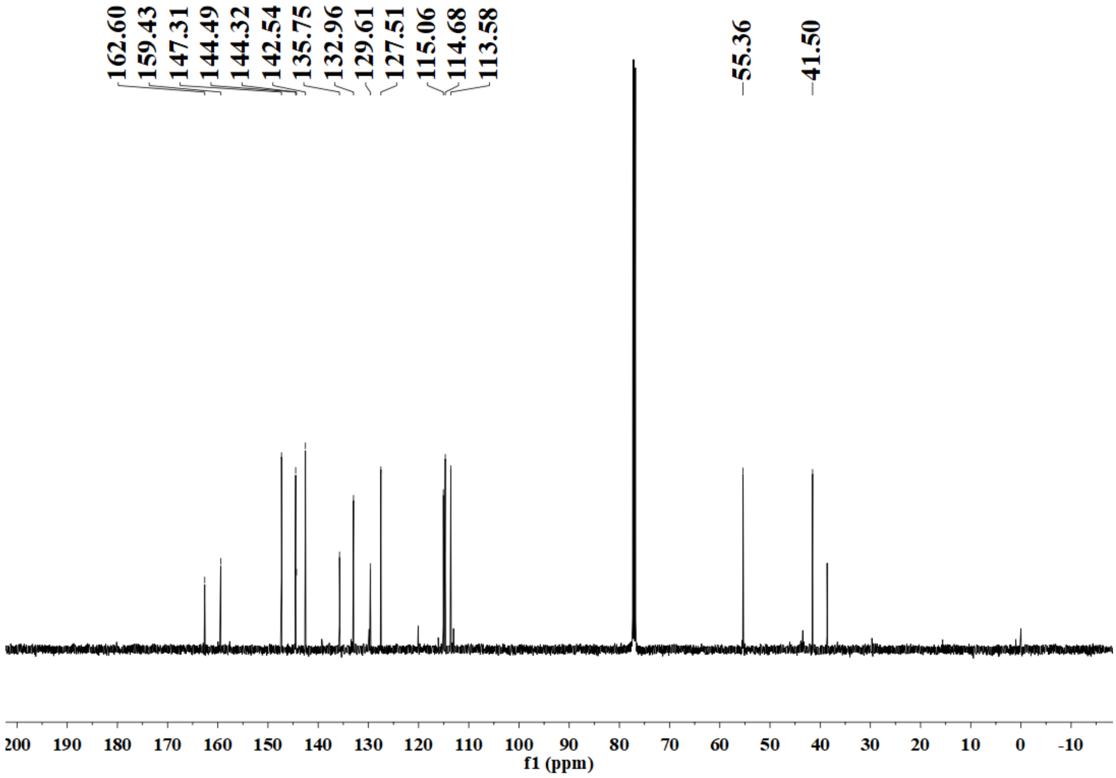
7.51
7.49
7.26
6.97
6.91
6.89
6.88
6.87
6.85
5.61
5.57
5.27
5.25
4.72
4.71
3.81
0.98
1.03
0.99
1.09
0.94
1.08
0.93
1.02
0.99
0.96
2.07
2.91
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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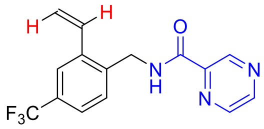
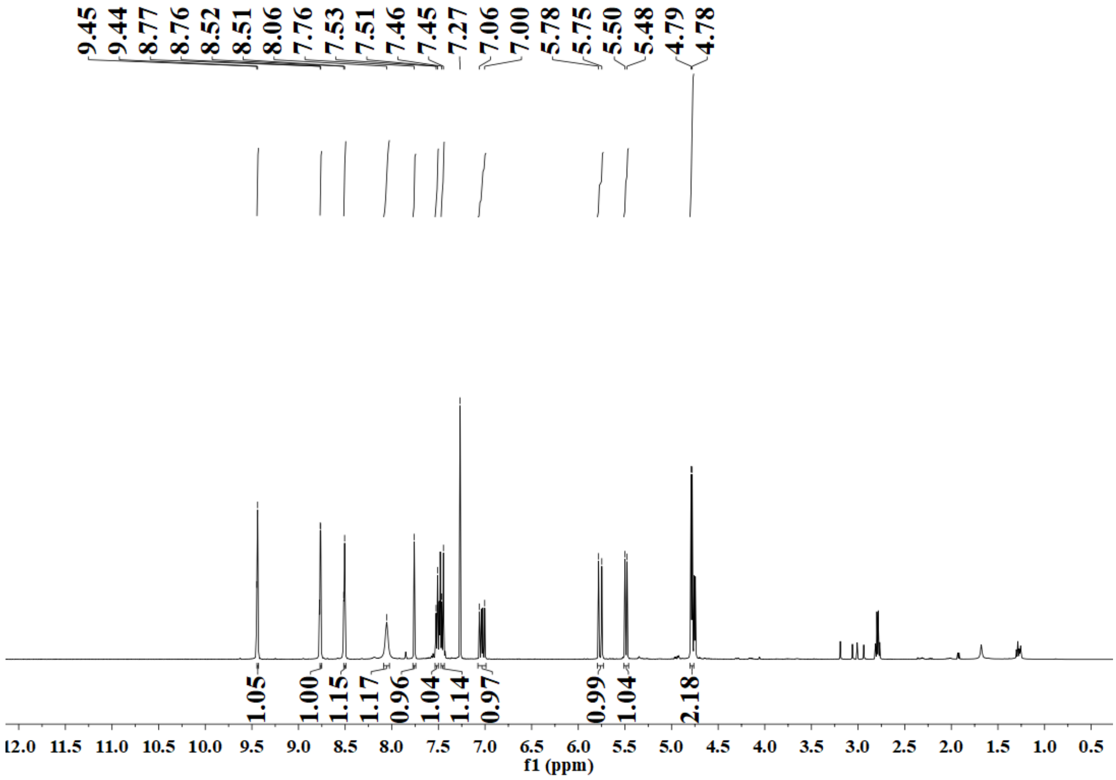
147.31
144.49
144.32
142.54
135.75
132.96
129.61
127.51
115.06
114.68
113.58
55.36
41.50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
H
O
N
H
N
N
F3C

(4j)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8.77
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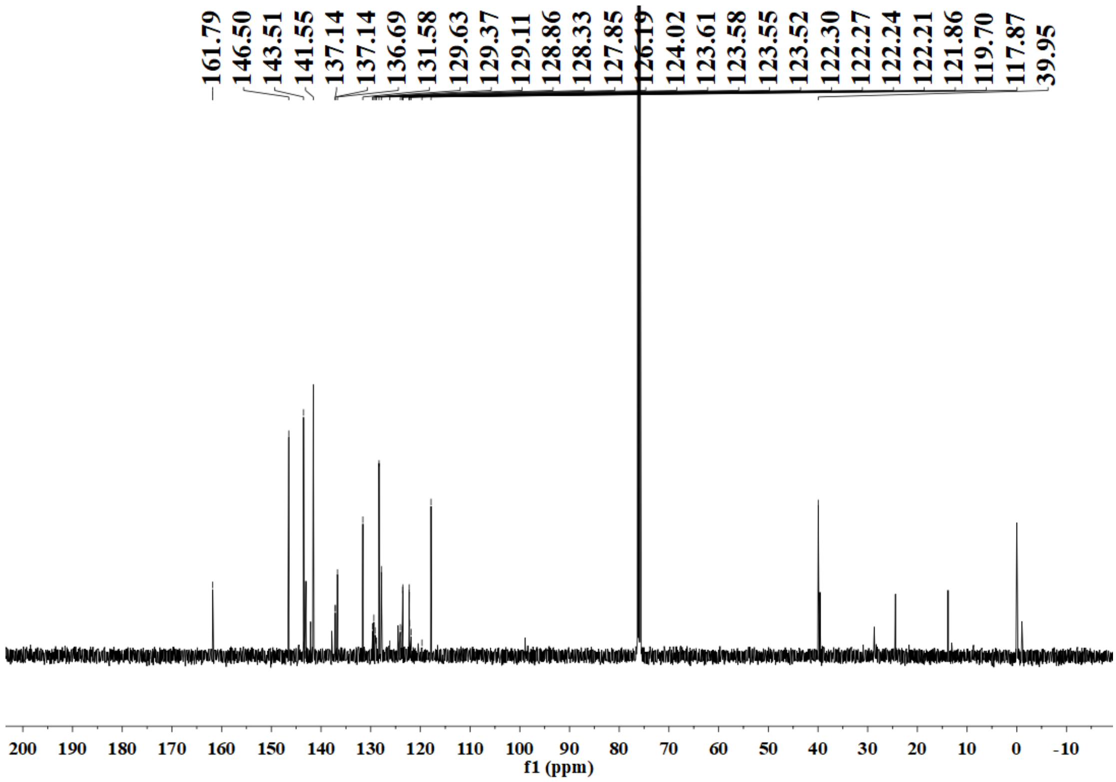
8.52
8.51
8.06
7.76
7.53
7.51
7.46
7.45
7.27
7.06
7.00
5.78
5.75
5.50
5.48
4.79
4.78
1.05
1.00
1.15
1.17
0.96
1.04
1.14
0.97
0.99
1.04
2.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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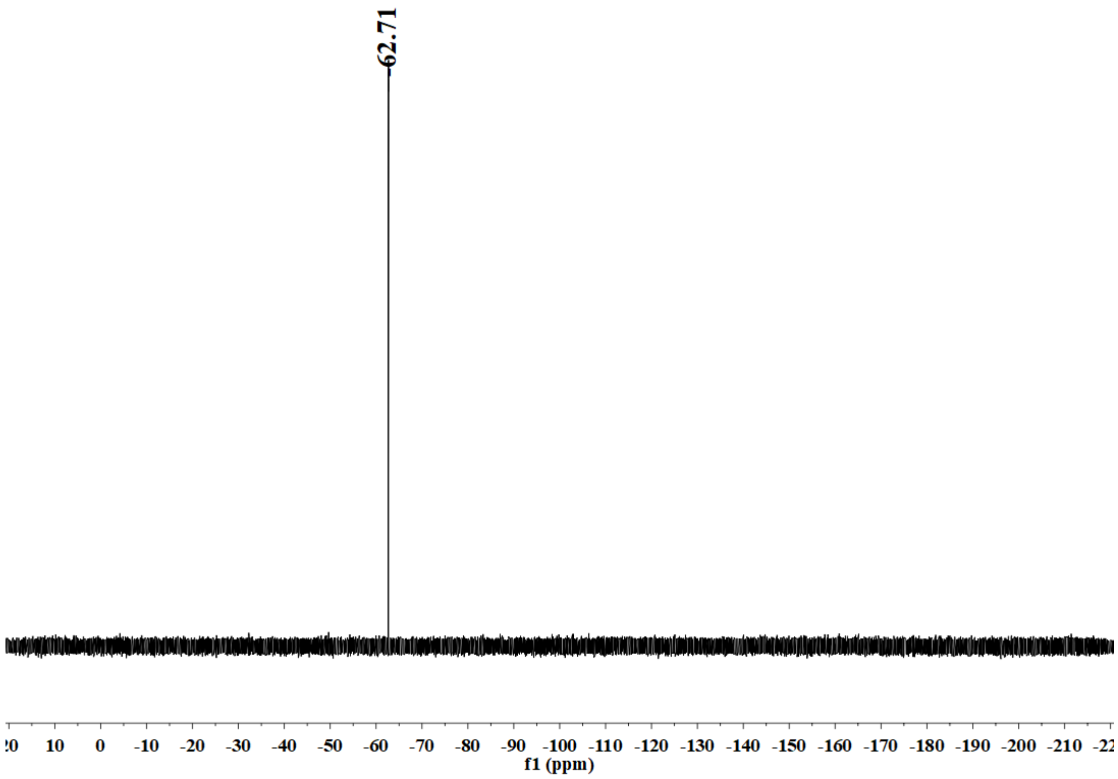
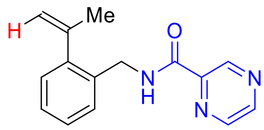
137.14
137.14
136.69
131.58
129.63
129.37
129.11
128.86
128.33
127.85
126.19
124.02
123.61
123.58
123.55
123.52
122.30
122.27
122.24
122.21
121.86
119.70
117.87
39.95
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

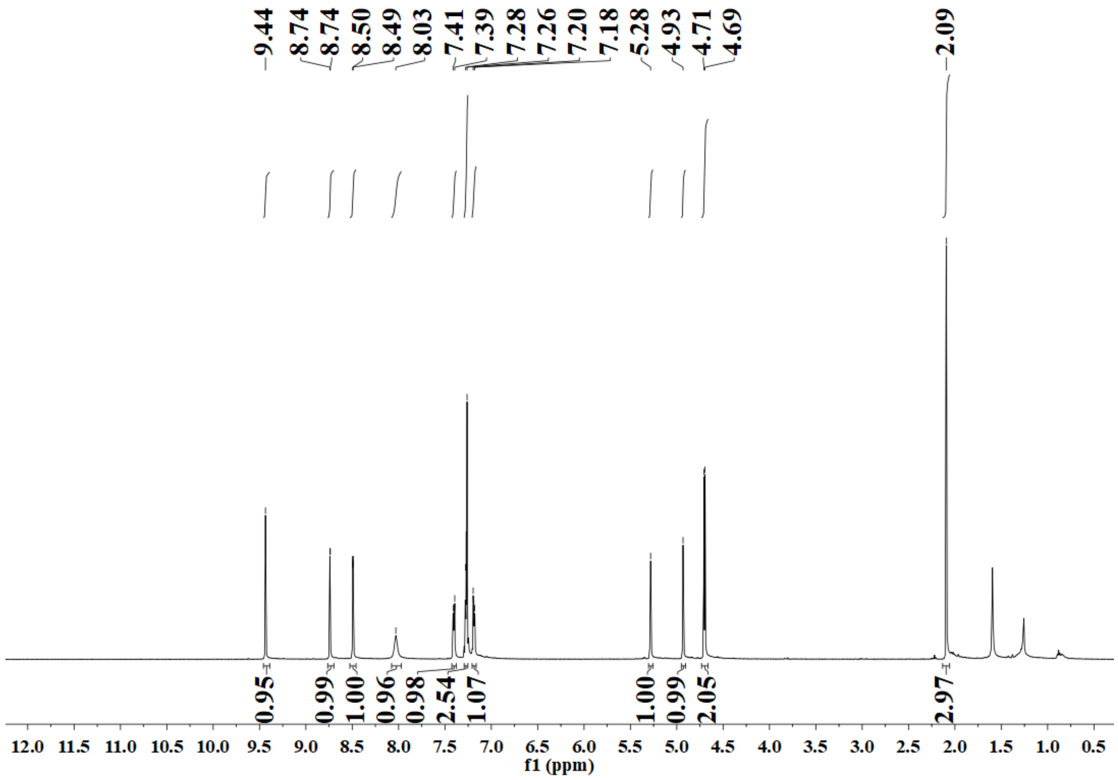


-62.71
f1 (ppm)

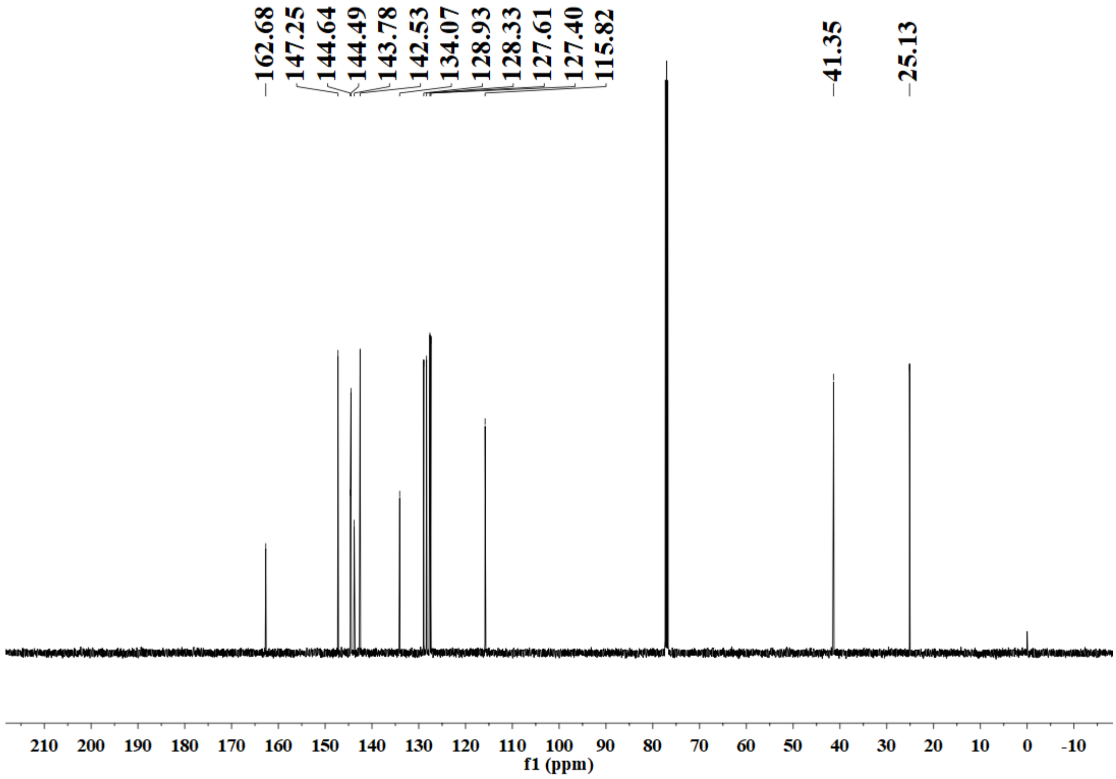


H
Me
O
N
H
N
N

(6a)



9.44
8.74
8.74
8.50
8.49
8.03
7.41
7.39
7.28
7.26
7.20
7.18
5.28
4.93
4.71
4.69
2.09
0.95
0.99
1.00
0.96
0.98
2.54
1.07
1.00
0.99
2.05
2.97
f1 (ppm)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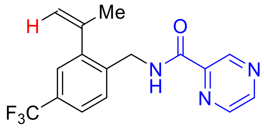
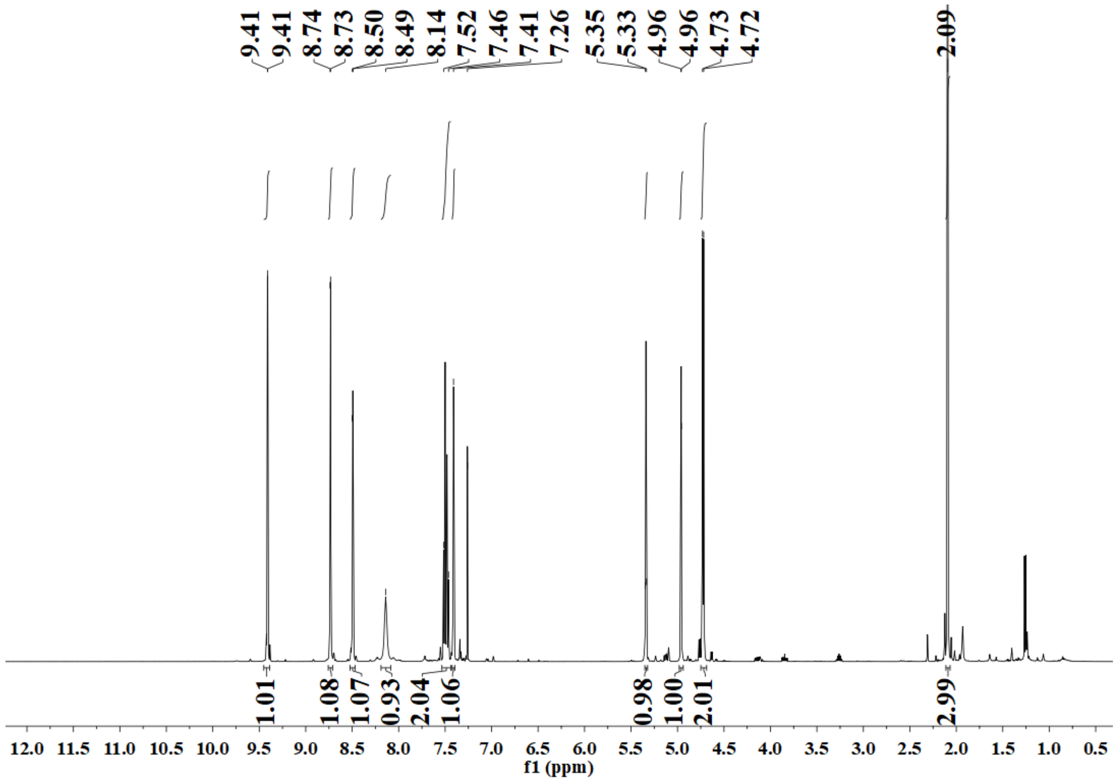
144.64
144.49
143.78
142.53
134.07
128.93
128.33
127.61
127.40
115.82
41.35
25.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
Me
O
N
H
N
N
F3C

(6i)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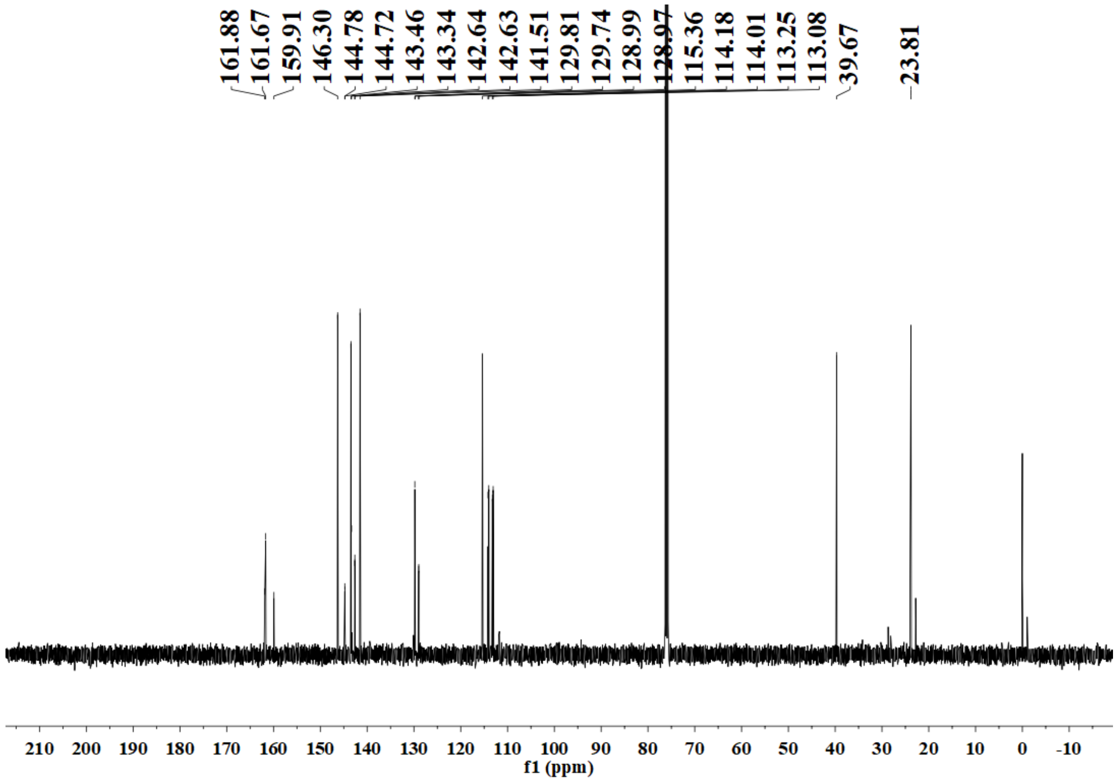
9.41
8.74
8.73
8.50
8.49
8.14
7.52
7.46
7.41
7.26
5.35
5.33
4.96
4.96
4.73
4.72
2.09
1.01
1.08
1.07
0.93
2.04
1.06
0.98
1.00
2.01
2.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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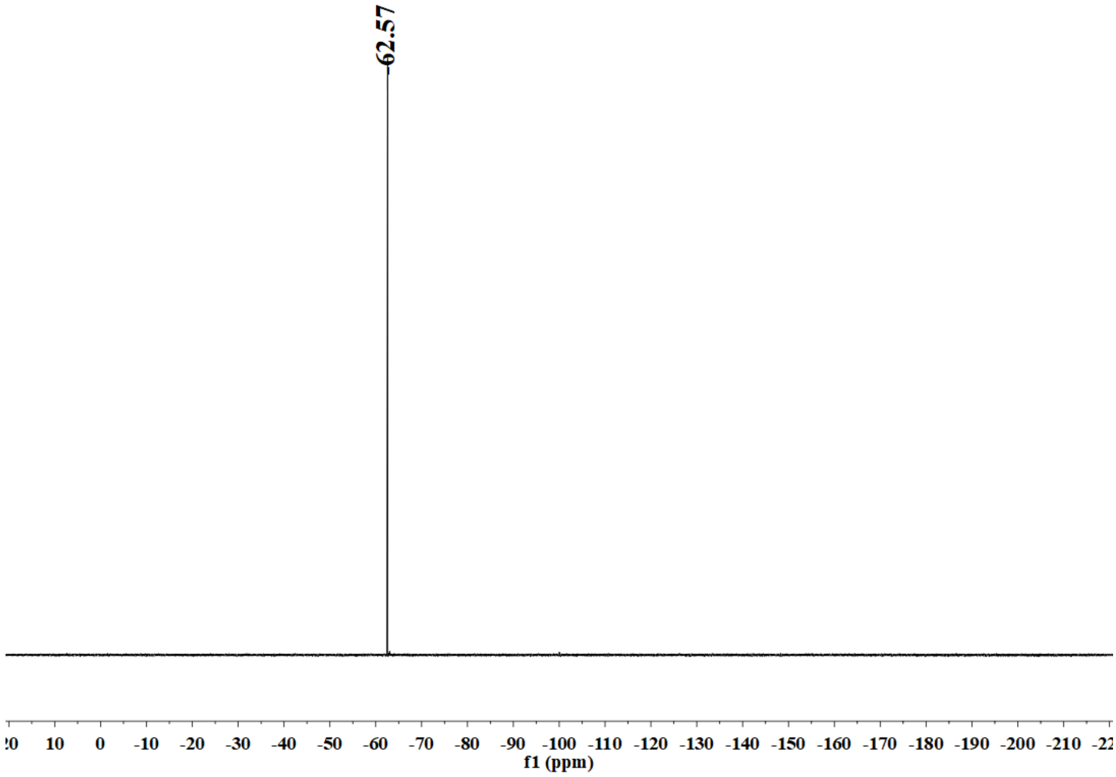
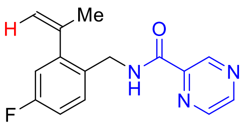
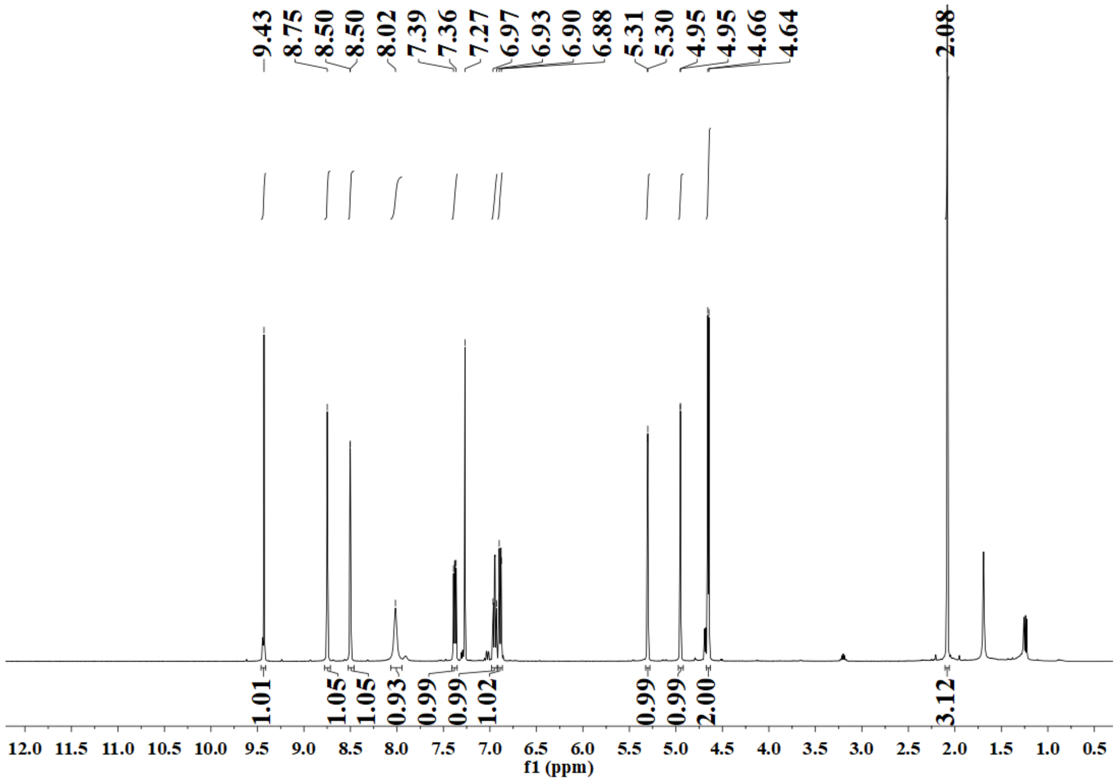
144.72
143.46
143.34
142.64
142.63
141.51
129.81
129.74
128.99
128.97
115.36
114.18
114.01
113.25
113.08
39.67
23.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.57
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



(6j)



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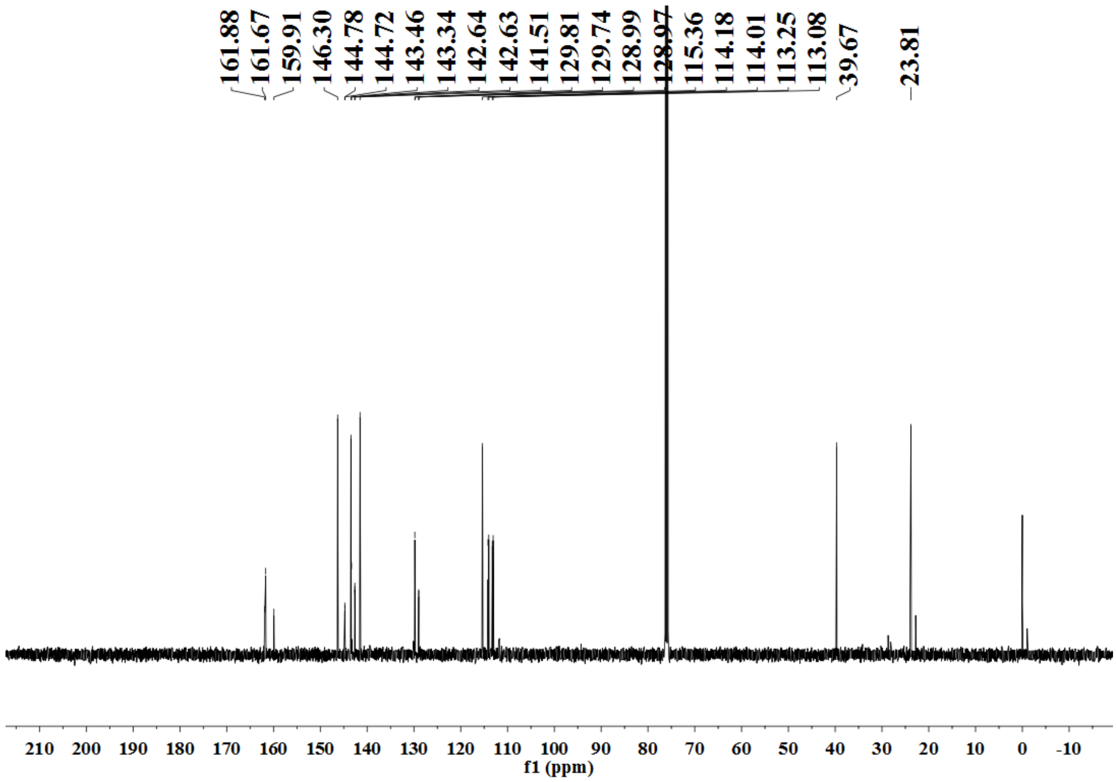
8.50
8.02
7.39
7.36
7.27
6.97
6.93
6.90
6.88
5.31
5.30
4.95
4.95
4.66
4.64
2.08
1.01
1.05
1.05
0.93
0.99
0.99
1.02
0.99
0.99
2.00
3.12
f1 (ppm)



161.88
161.67
159.91
146.30
144.78
144.72
143.46
143.34
142.64
142.63
141.51
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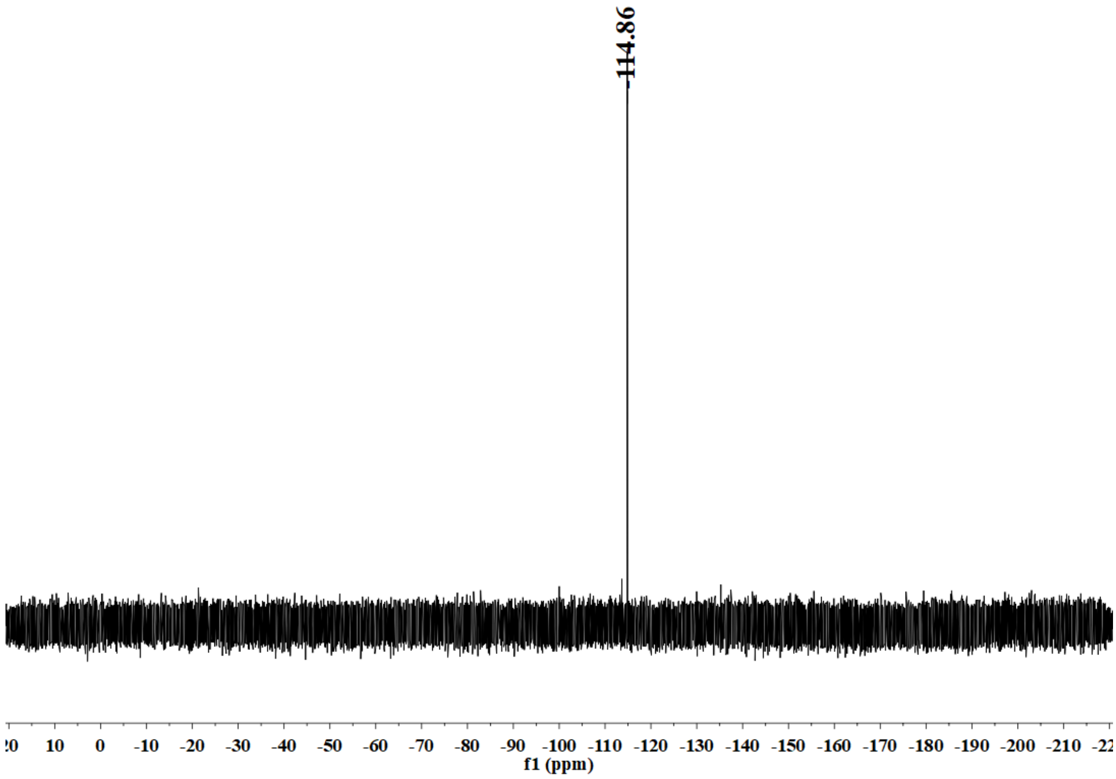
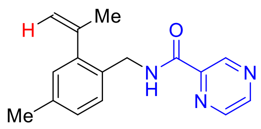
128.97
115.36
114.18
114.01
113.25
113.08
39.67
23.81
f1 (ppm)

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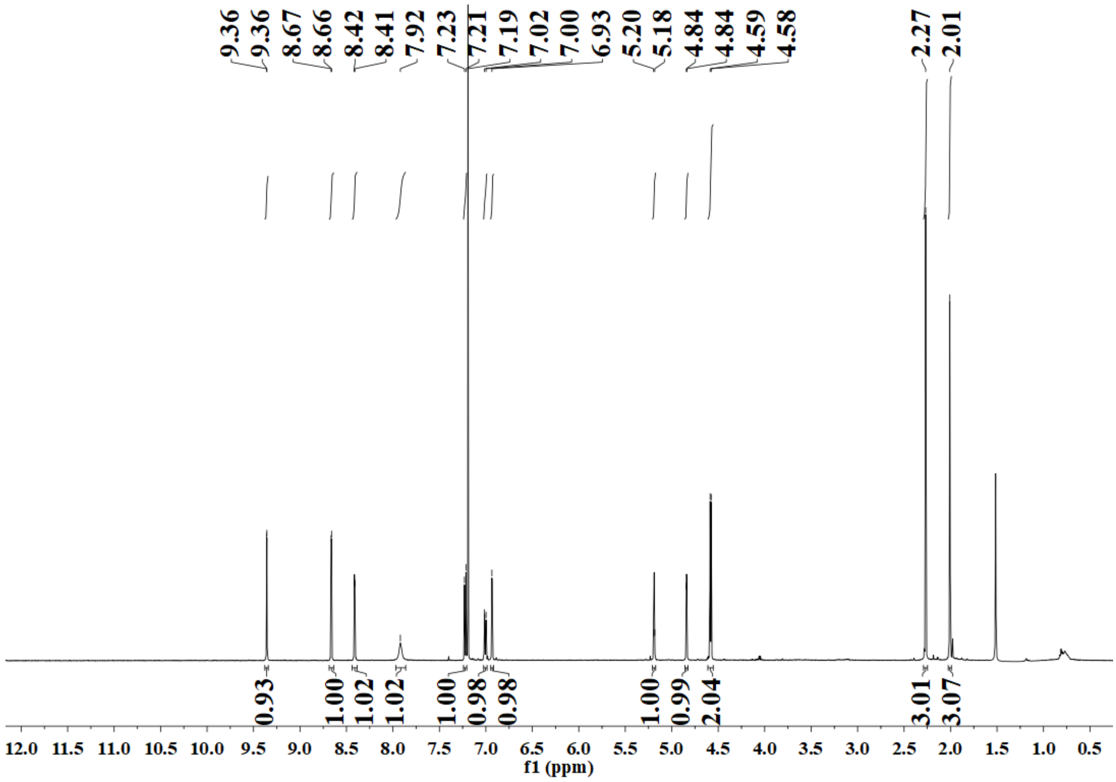

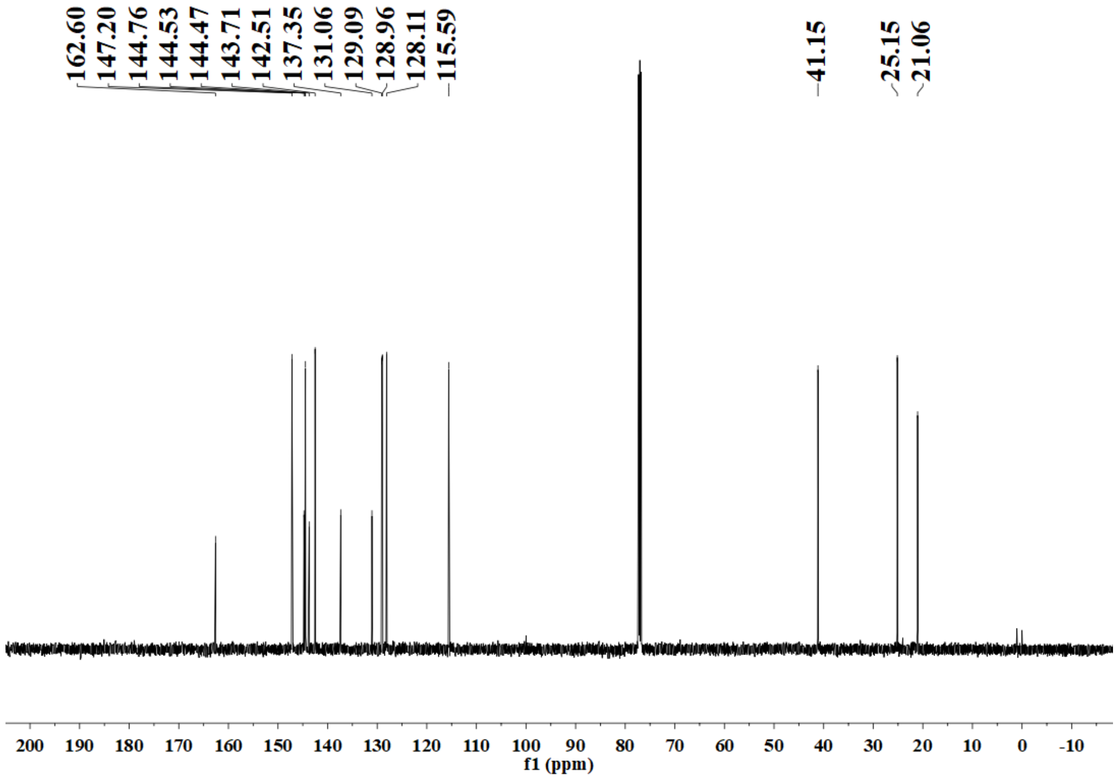
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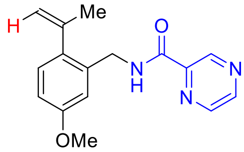
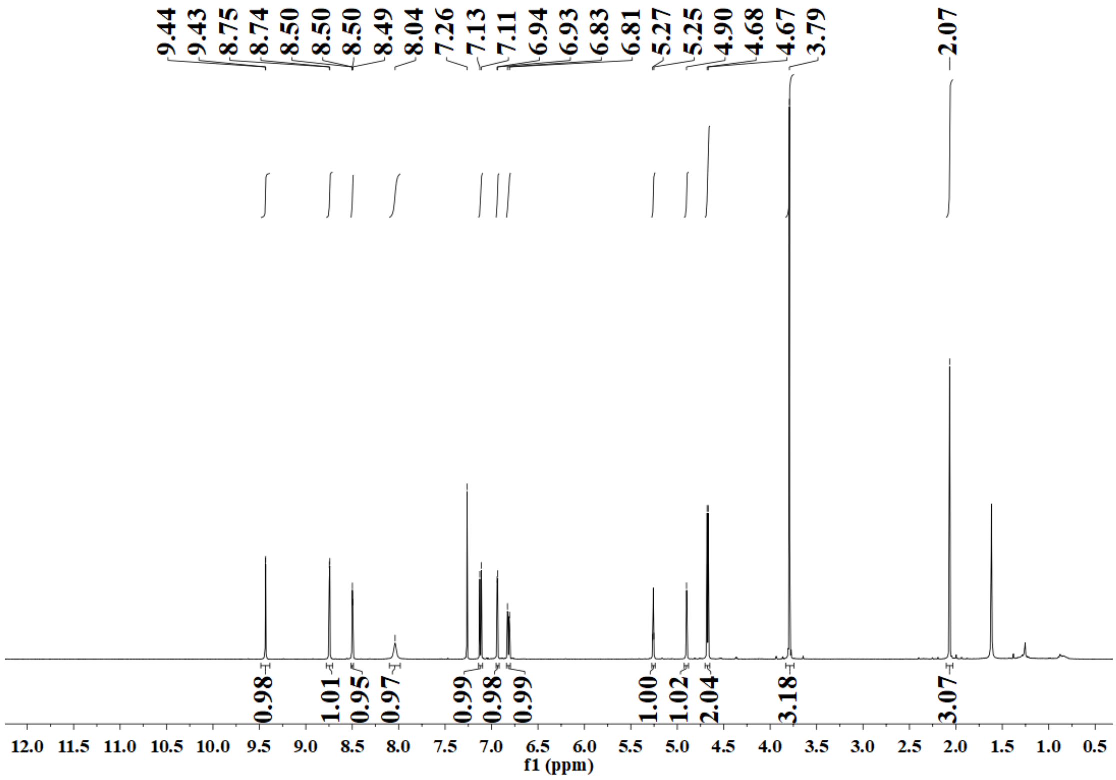
129.09
128.96
128.11
115.59
41.15
25.15
21.06
f1 (ppm)


H
Me
O
N
H
N
N
OMe

(6l)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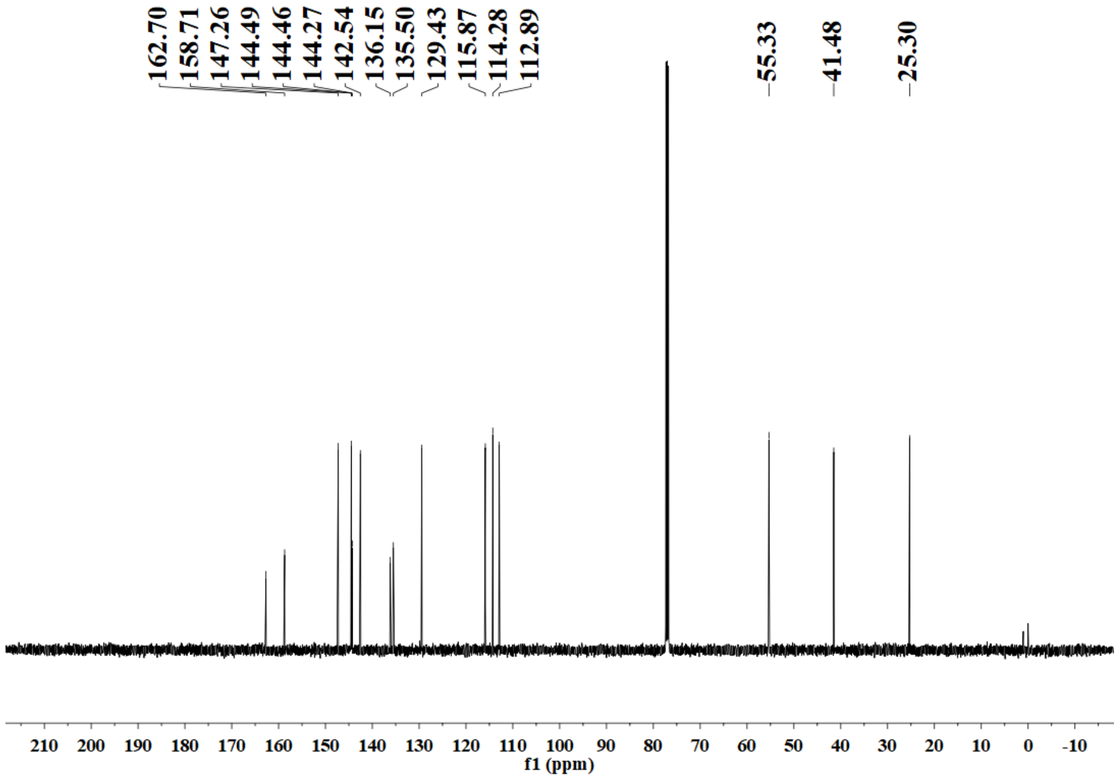
8.50
8.50
8.50
8.49
8.04
7.26
7.13
7.11
6.94
6.93
6.83
6.81
5.27
5.25
4.90
4.68
4.67
3.79
2.07
0.98
1.01
0.95
0.97
0.99
0.98
0.99
1.00
1.02
2.04
3.18
3.07
f1 (ppm)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144.46
144.27
142.54
136.15
135.50
129.43
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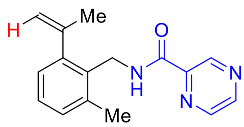
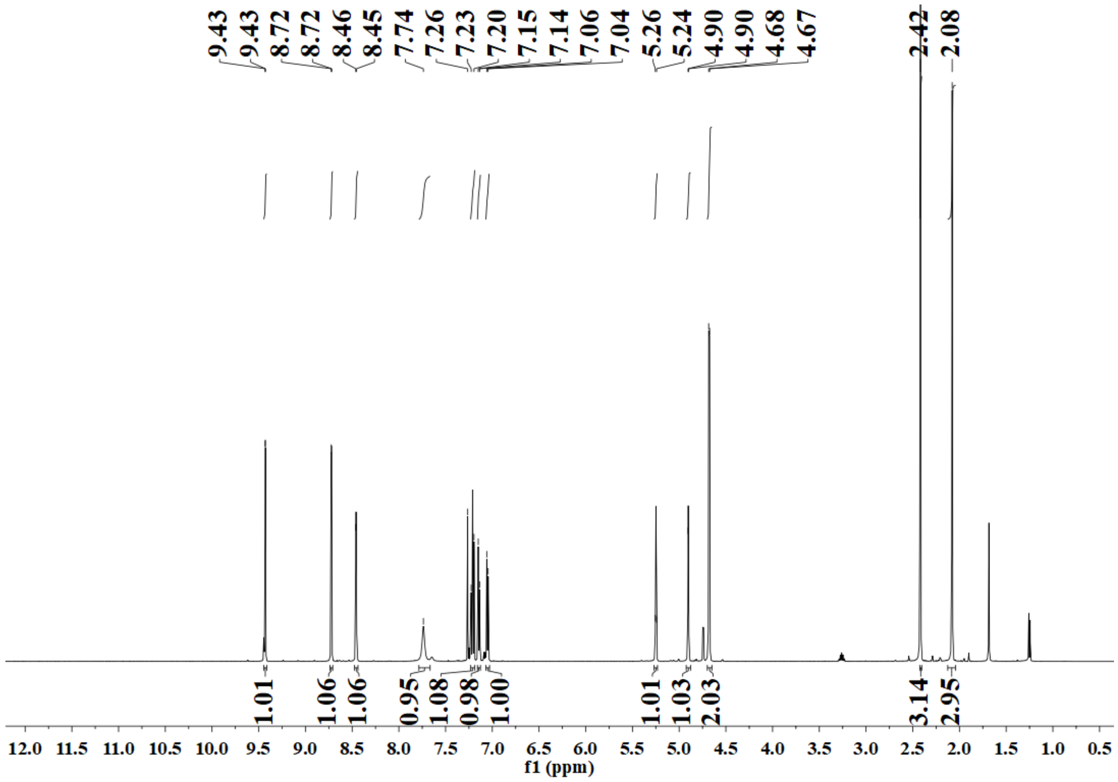
114.28
112.89
55.33
41.48
25.30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
Me
O
N
H
N
N
Me

(6m)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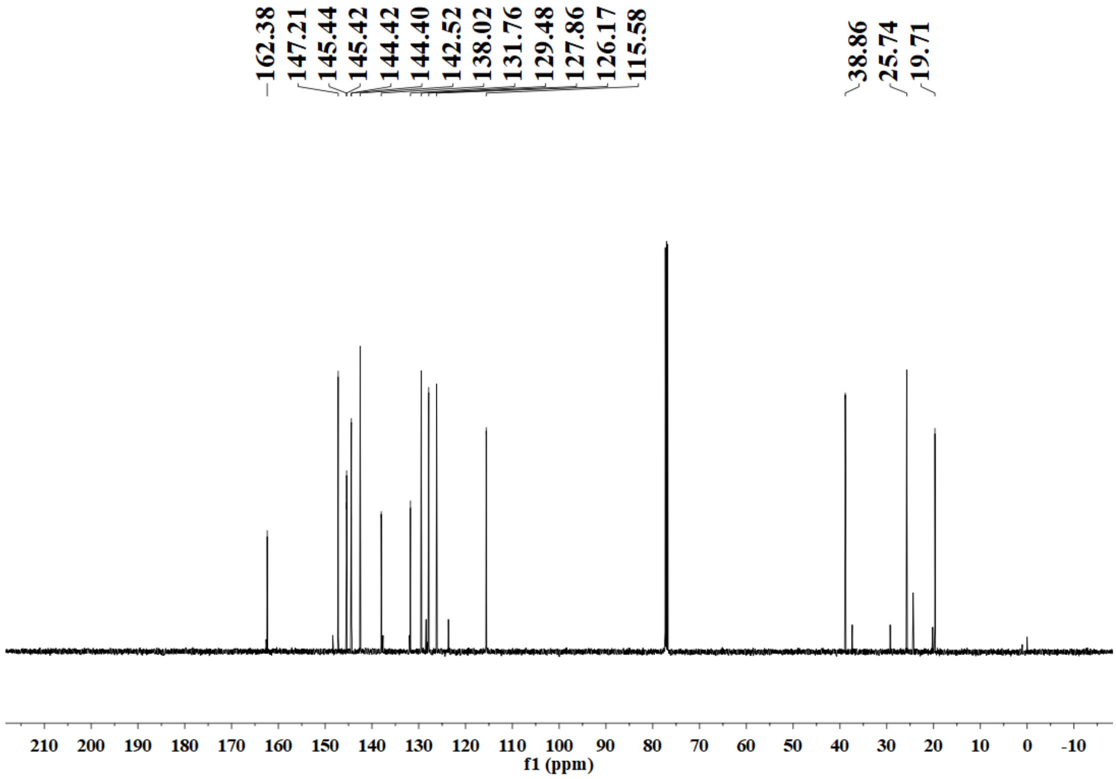
7.04
5.26
5.24
4.90
4.90
4.68
4.67
2.42
2.08
1.01
1.06
1.06
0.95
1.08
0.98
1.00
1.01
1.03
2.03
3.14
2.95
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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144.40
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138.02
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129.48
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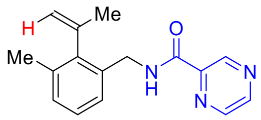
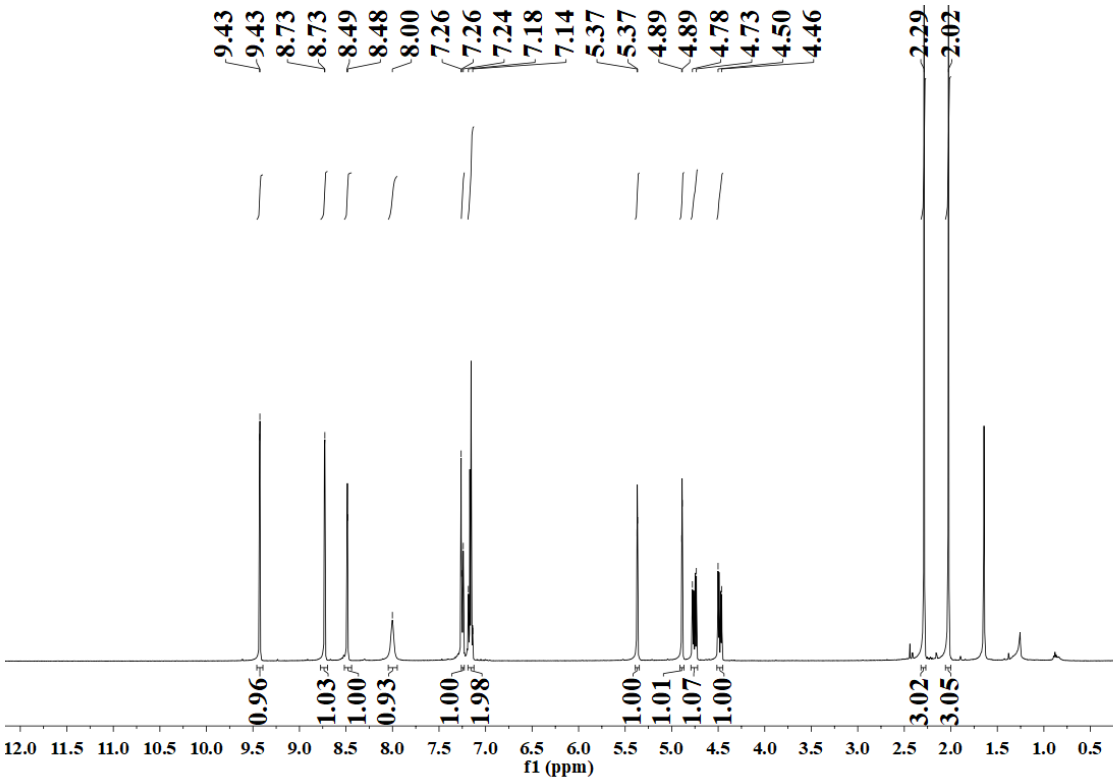
38.86
25.74
19.71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
Me
Me
O
N
H
N
N

(6n)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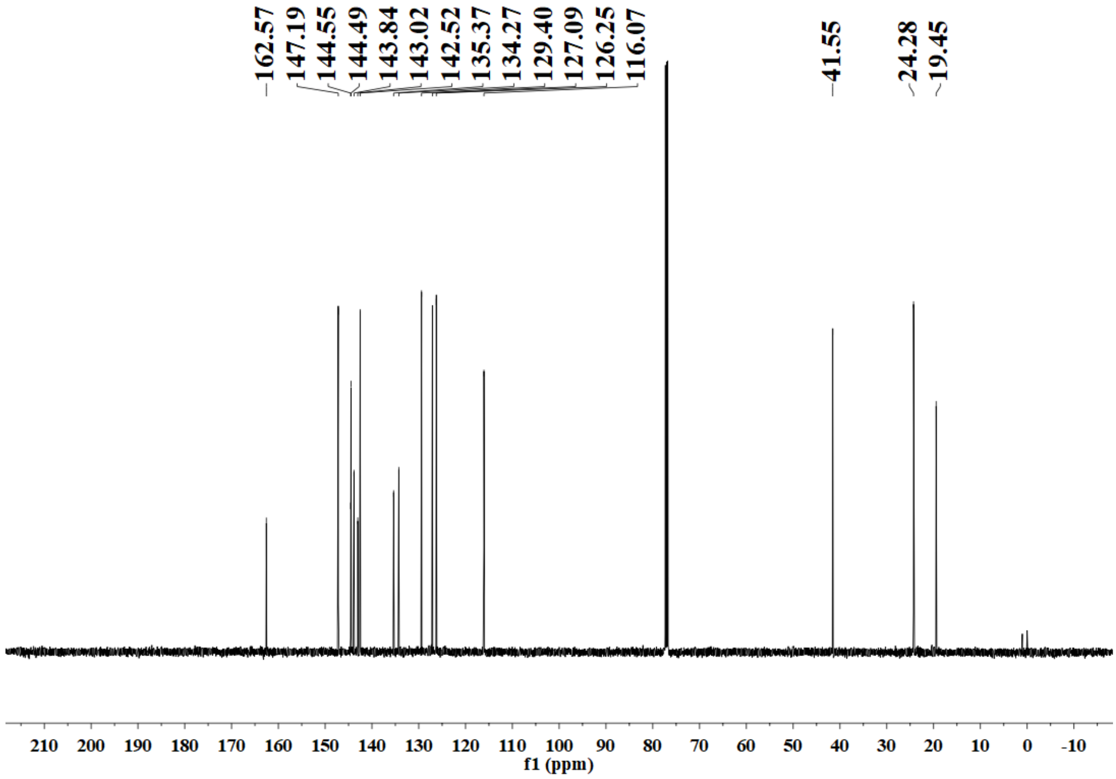
8.48
8.00
7.26
7.26
7.24
7.18
7.14
5.37
5.37
4.89
4.89
4.78
4.73
4.50
4.46
2.29
2.02
0.96
1.03
1.00
0.93
1.00
1.98
1.00
1.01
1.07
1.00
3.02
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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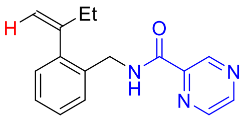
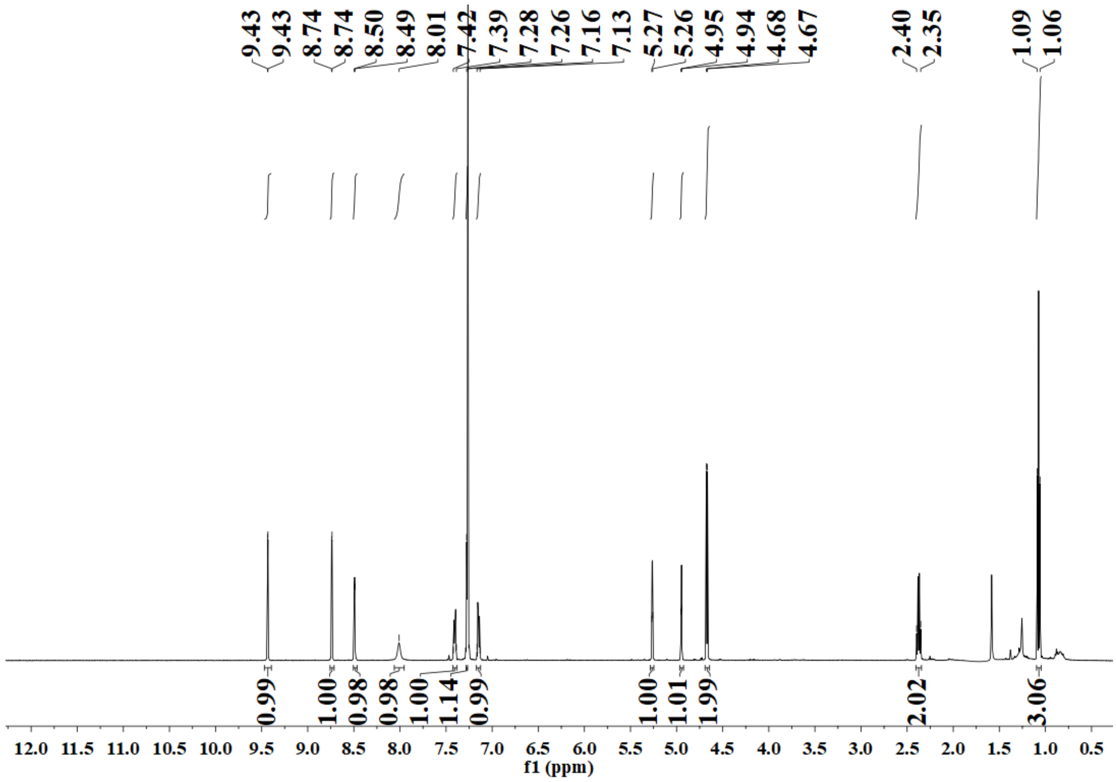
134.27
129.40
127.09
126.25
116.07
41.55
24.28
19.45
f1 (ppm)


H
Et
O
N
H
N
N

(6o)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8.01
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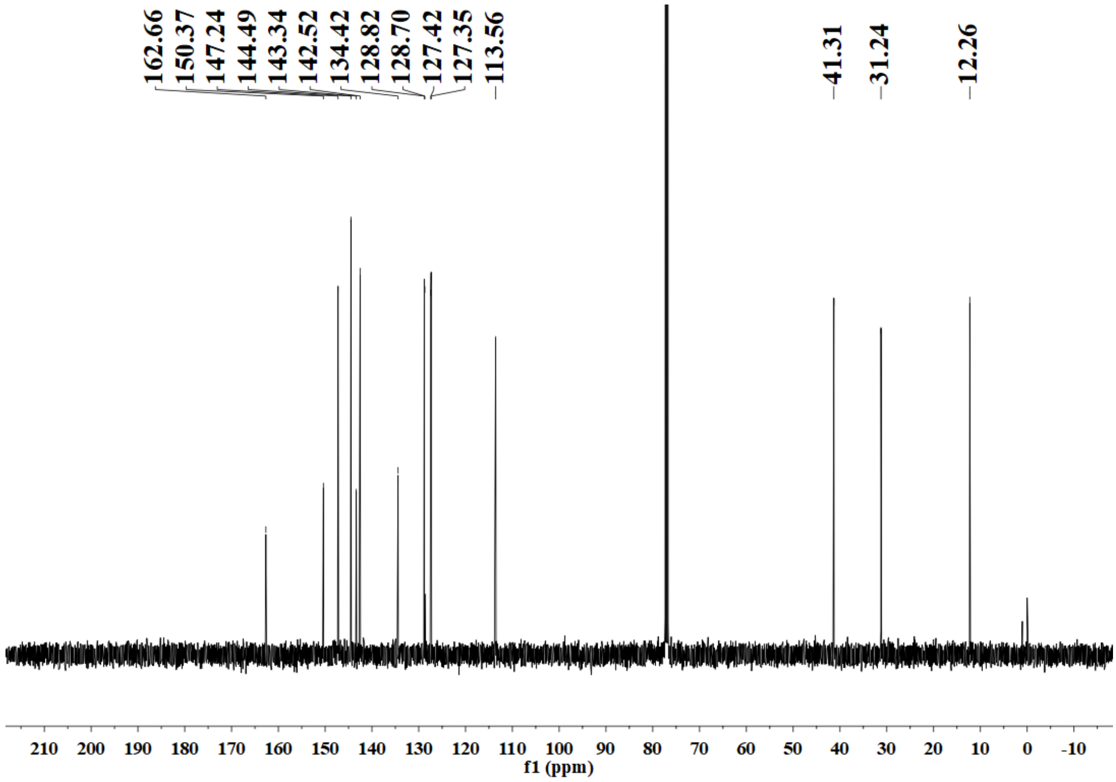
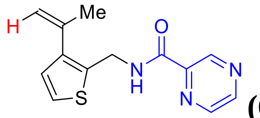
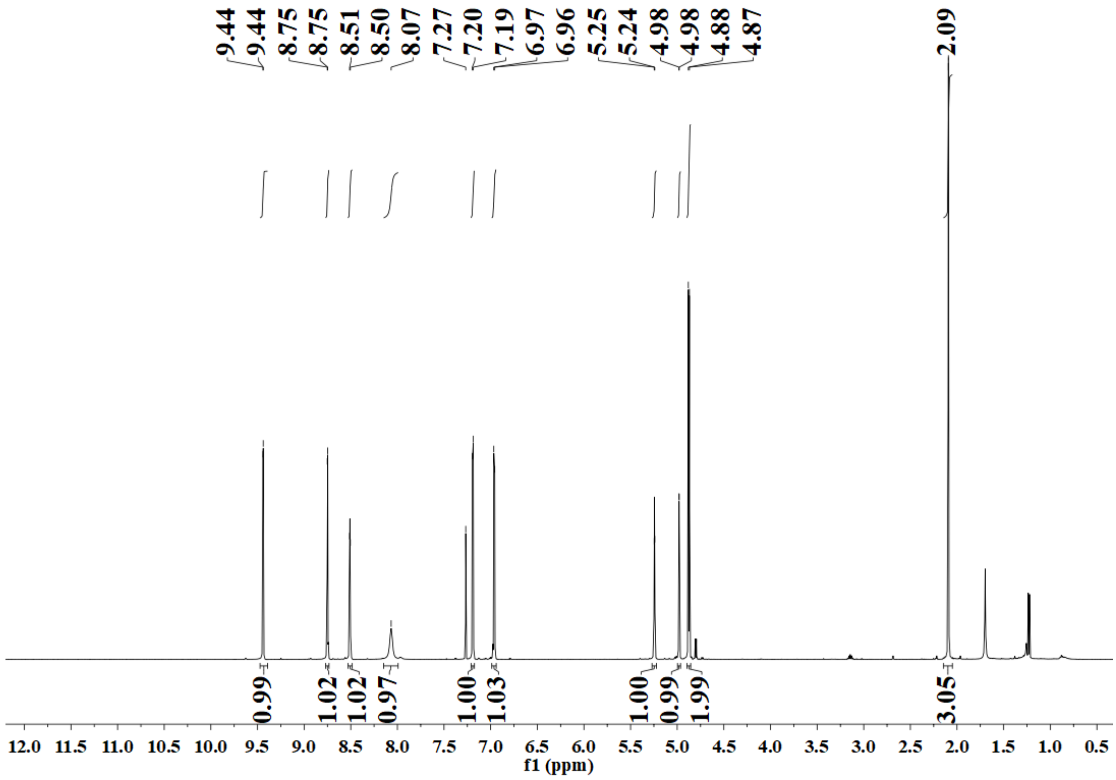
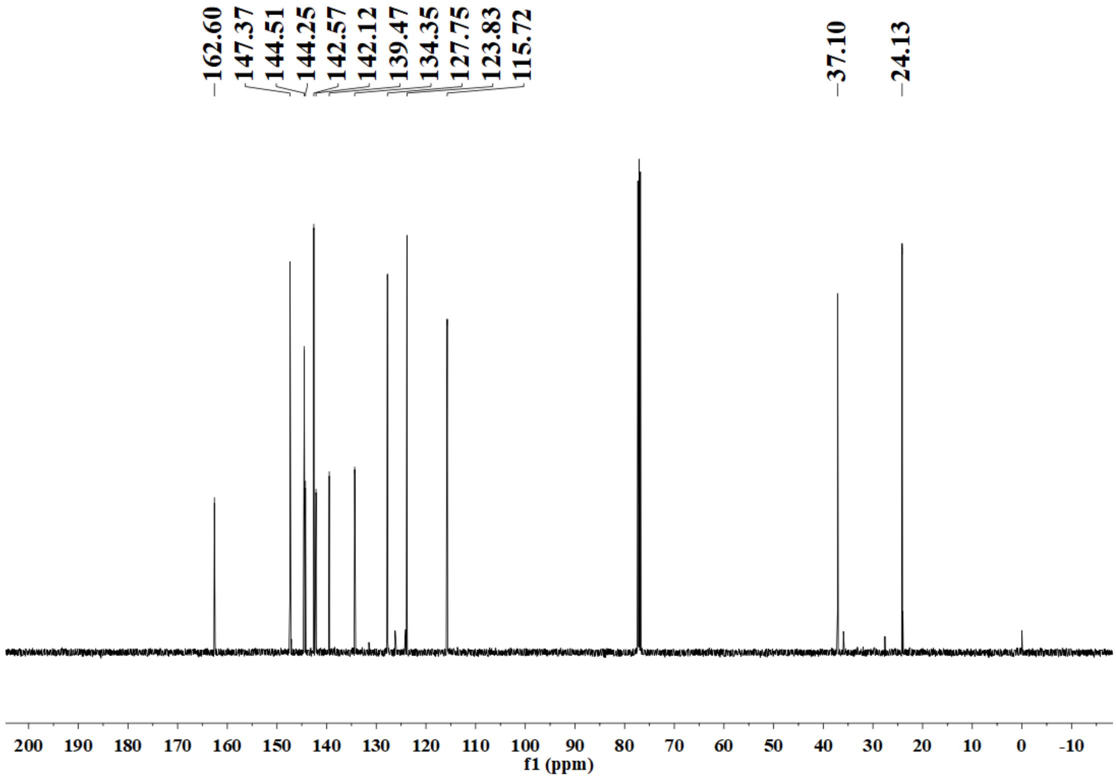
7.28
7.26
7.16
7.13
5.27
5.26
4.95
4.94
4.68
4.67
2.40
2.35
1.09
1.06
0.99
1.00
0.98
0.98
1.00
1.14
0.99
1.00
1.01
1.99
2.02
3.06
f1 (ppm)

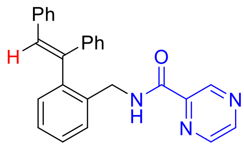

162.66
150.37
147.24
144.49
143.34
142.52
134.42
128.82
128.70
127.42
127.35
113.56
41.31
31.24
12.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

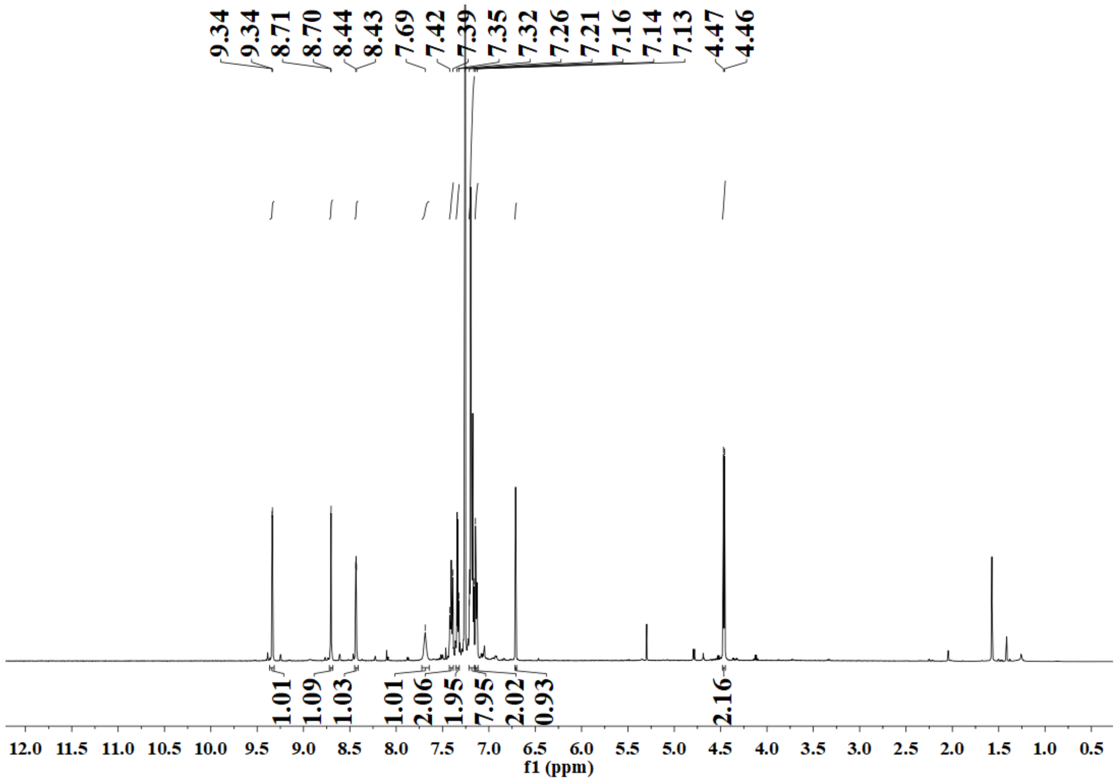


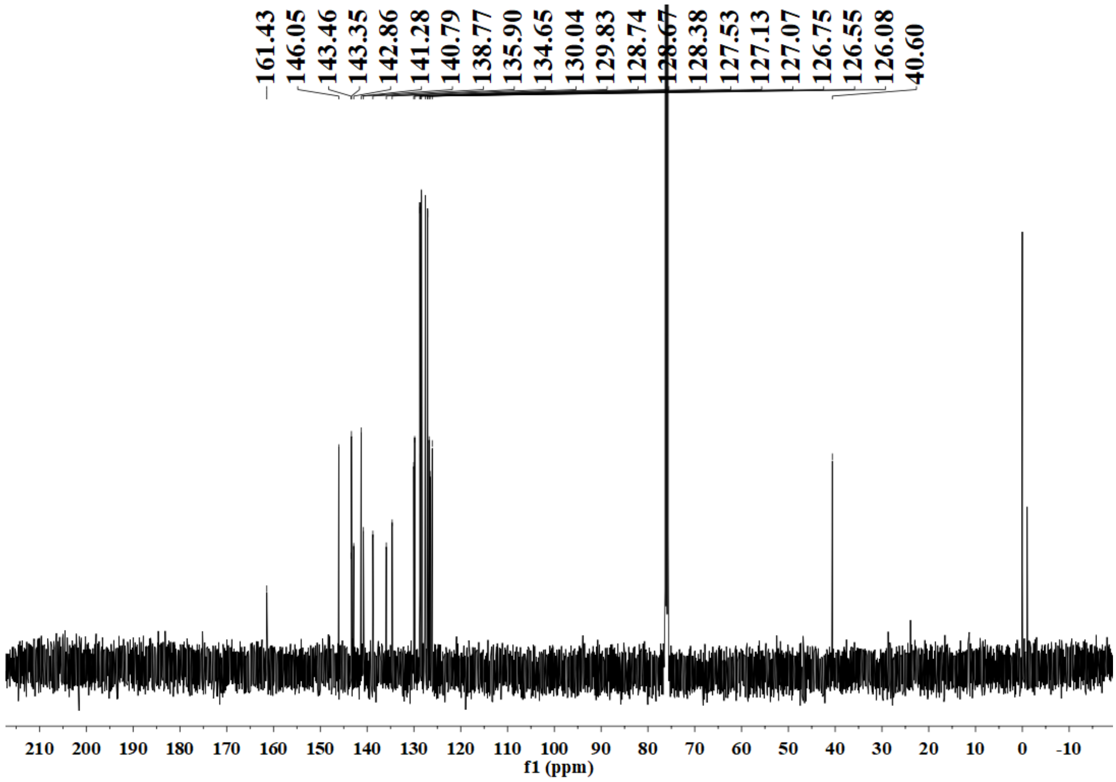
(6q)


9.44
9.44
8.75
8.75
8.51
8.50
8.07
7.27
7.20
7.19
6.97
6.96
5.25
5.24
4.98
4.98
4.88
4.87
2.09
0.99
1.02
1.02
0.97
1.00
1.03
1.00
0.99
1.99
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

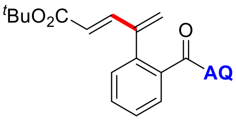

162.60
147.37
144.51
144.25
142.57
142.12
139.47
134.35
127.75
123.83
115.72
37.10
24.13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
Ph
H
O
N
H
N
N
(6r)

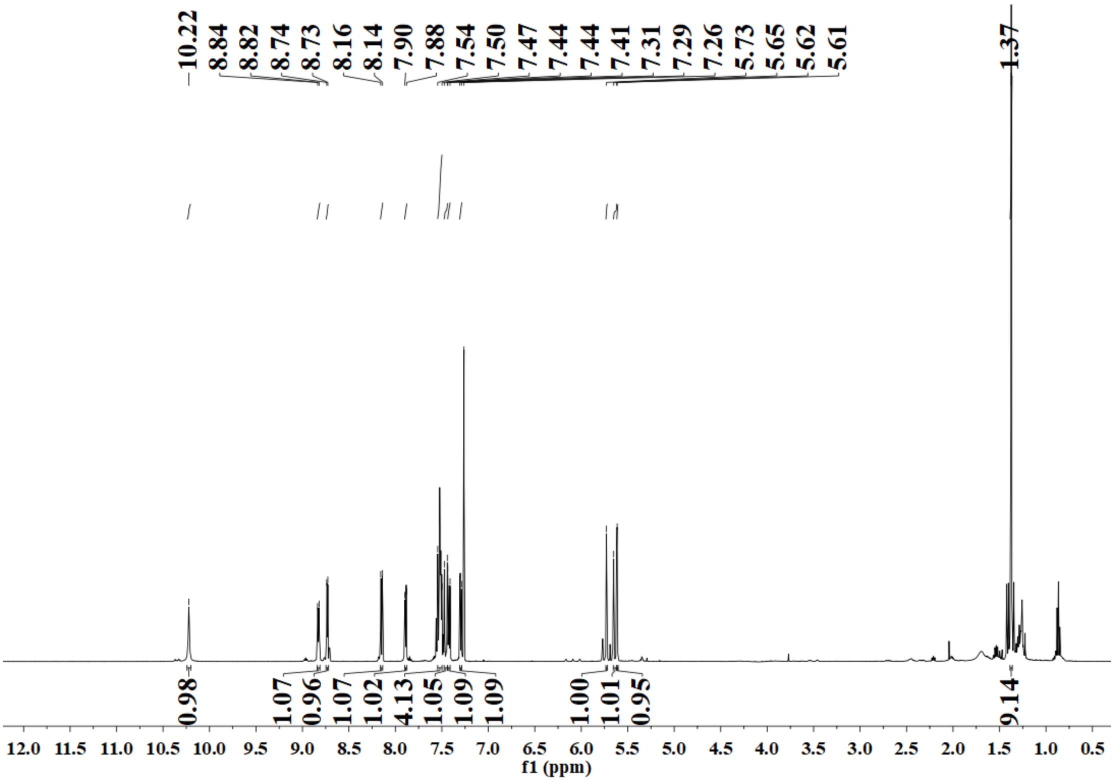

9.34
9.34
8.71
8.70
8.44
8.43
7.69
7.42
7.39
7.35
7.32
7.26
7.21
7.16
7.14
7.13
4.47
4.46
1.01
1.09
1.03
1.01
2.06
1.95
7.95
2.02
0.93
2.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

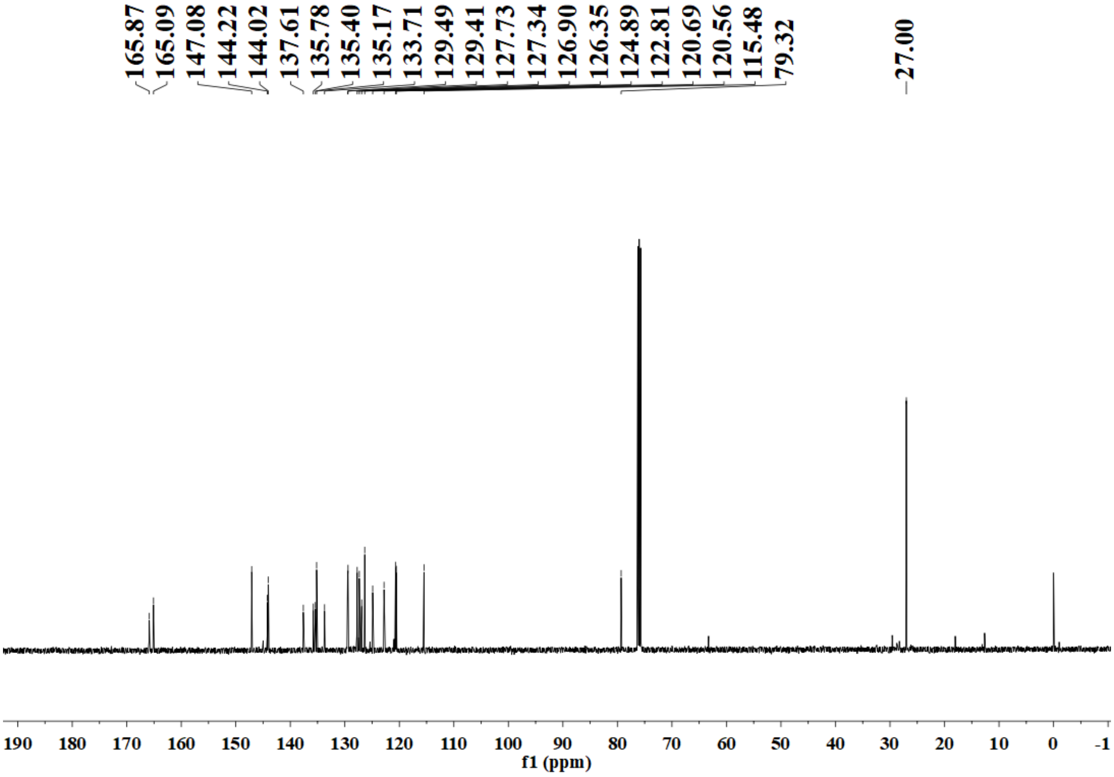

161.43
146.05
143.46
143.35
142.86
141.28
140.79
138.77
135.90
134.65
130.04
129.83
128.74
128.67
128.38
127.53
127.13
127.07
126.75
126.55
126.08
40.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

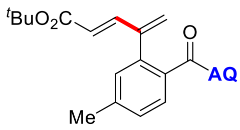
7.2 ^{1}H / ^{13}C NMR Charts of the Products



(3a)

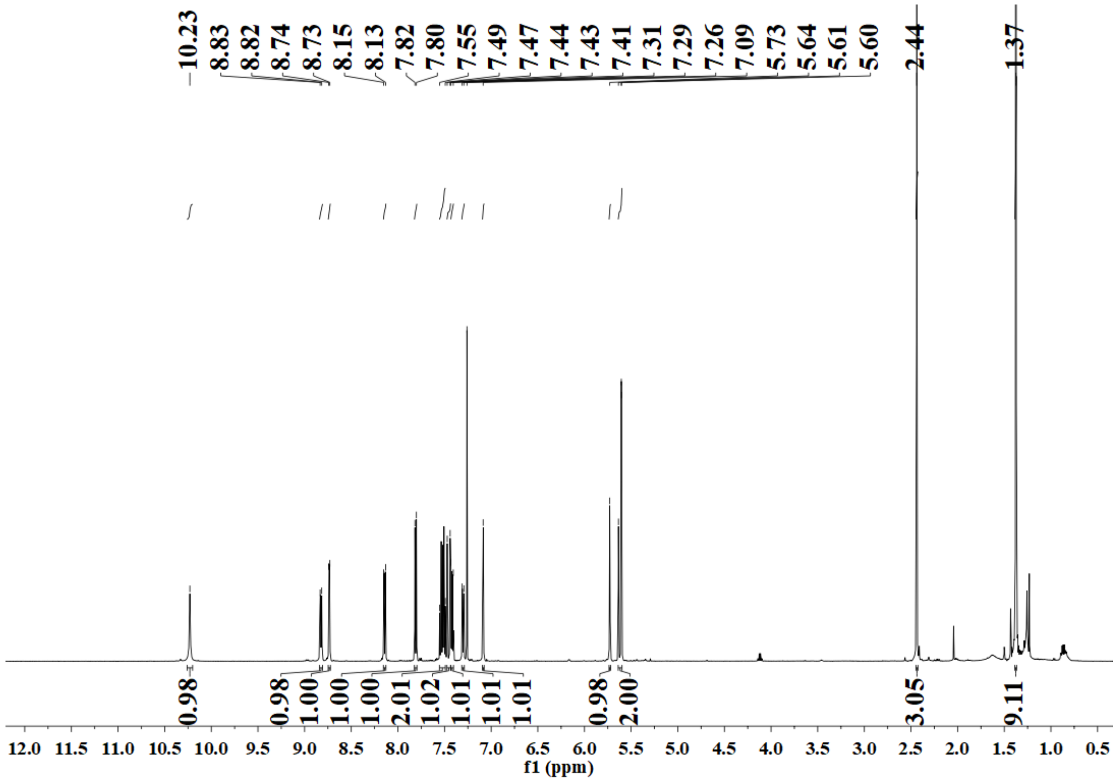




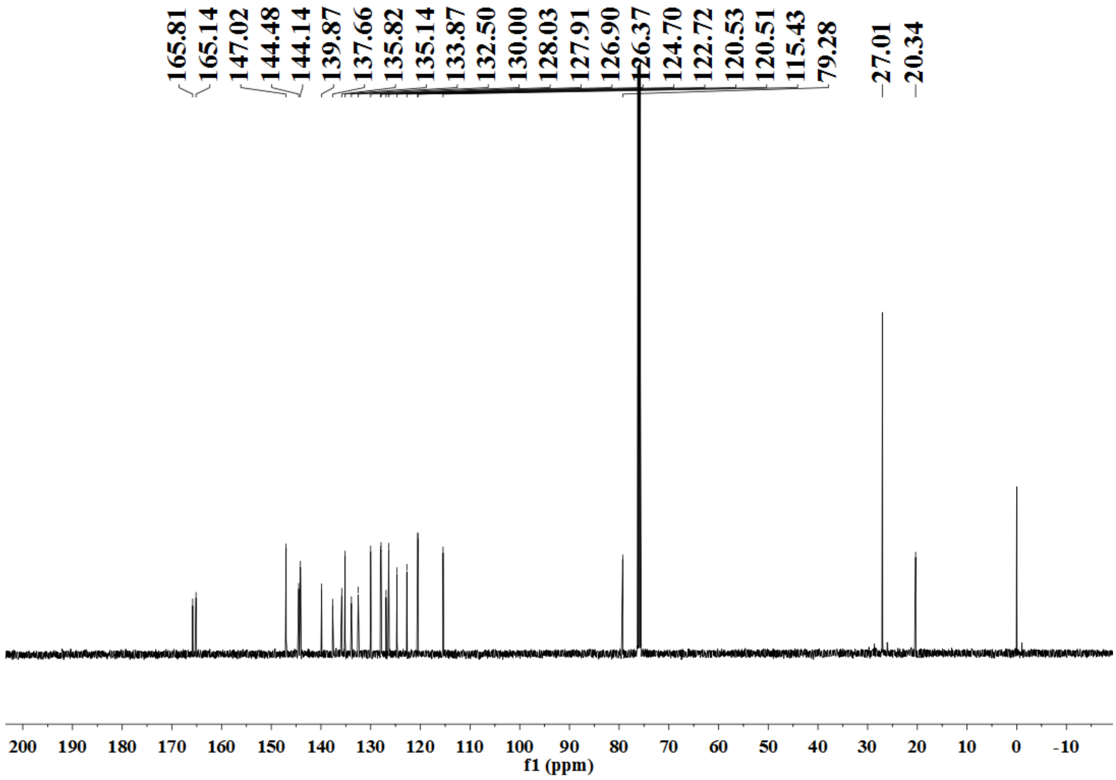


$^tBuO_2C$
O
AQ
Me

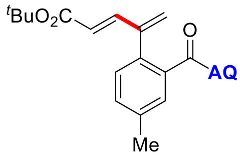
(3b)



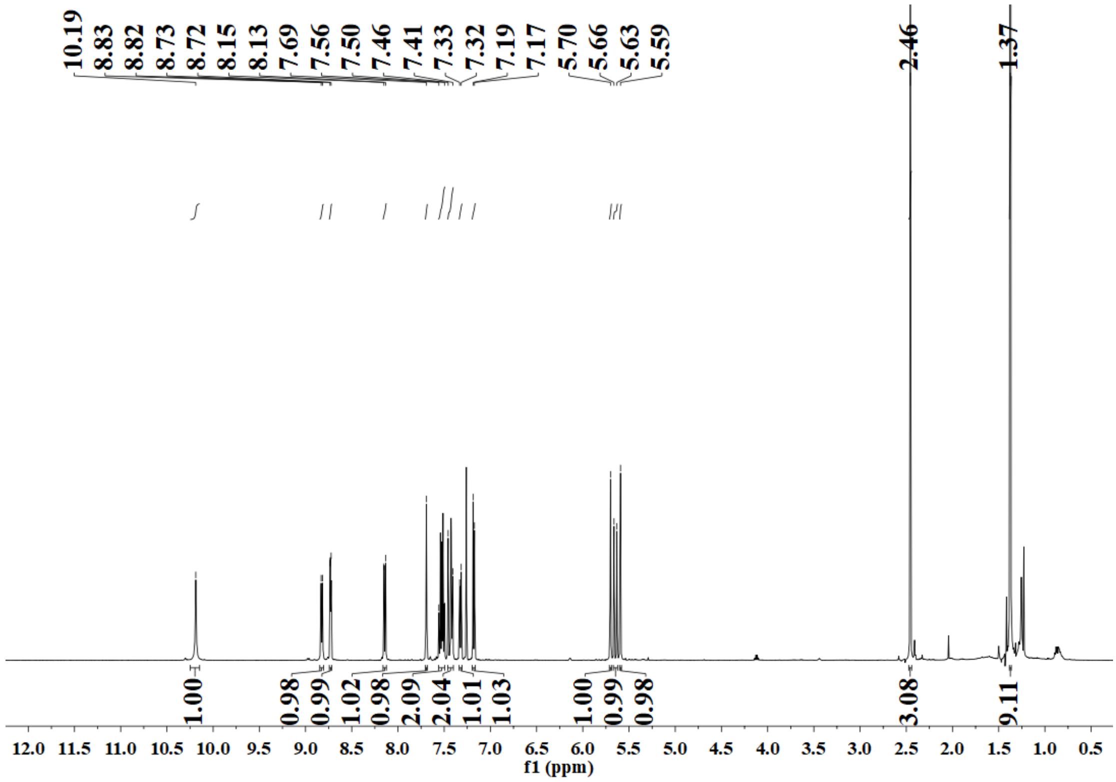
10.23
8.83
8.82
8.74
8.73
8.15
8.13
7.82
7.80
7.55
7.49
7.47
7.44
7.43
7.41
7.31
7.29
7.26
7.09
5.73
5.64
5.61
5.60
2.44
1.37
0.98
0.98
1.00
1.00
1.00
2.01
1.02
1.01
1.01
1.01
0.98
2.00
3.05
9.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

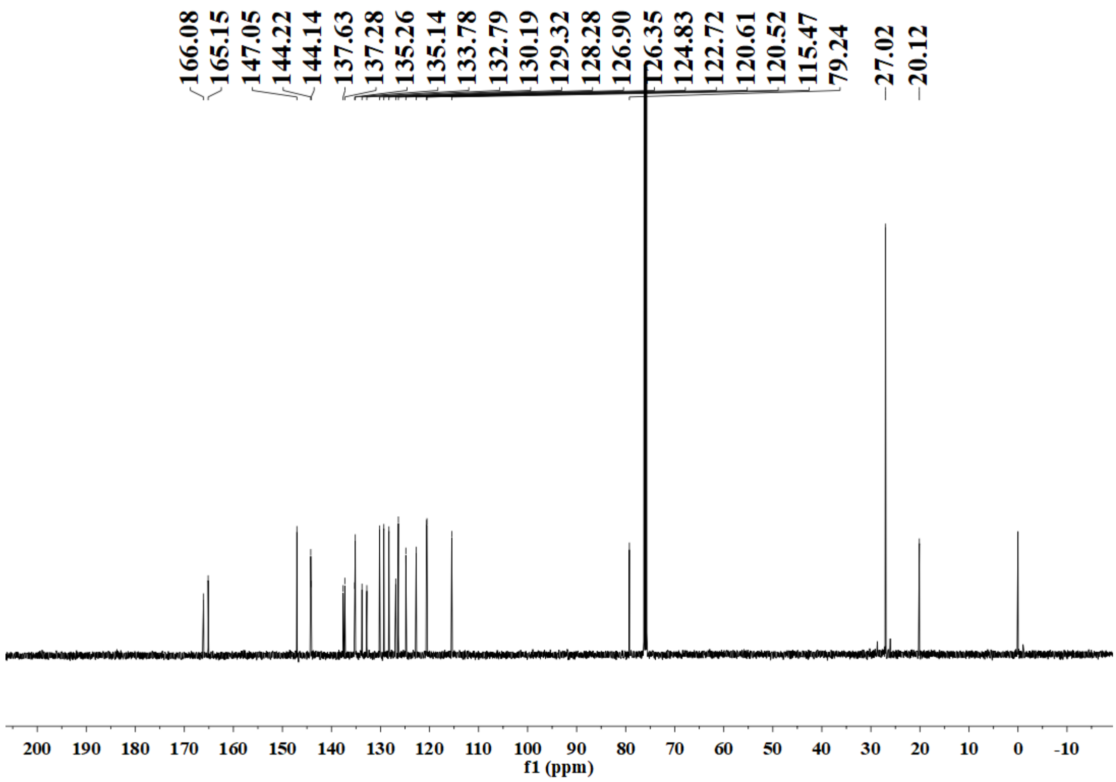


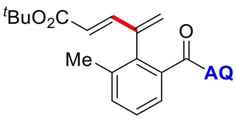
165.81
165.14
147.02
144.48
144.14
139.87
137.66
135.82
135.14
133.87
132.50
130.00
128.03
127.91
126.90
126.37
124.70
122.72
120.53
120.51
115.43
79.28
27.01
20.34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



(3c)

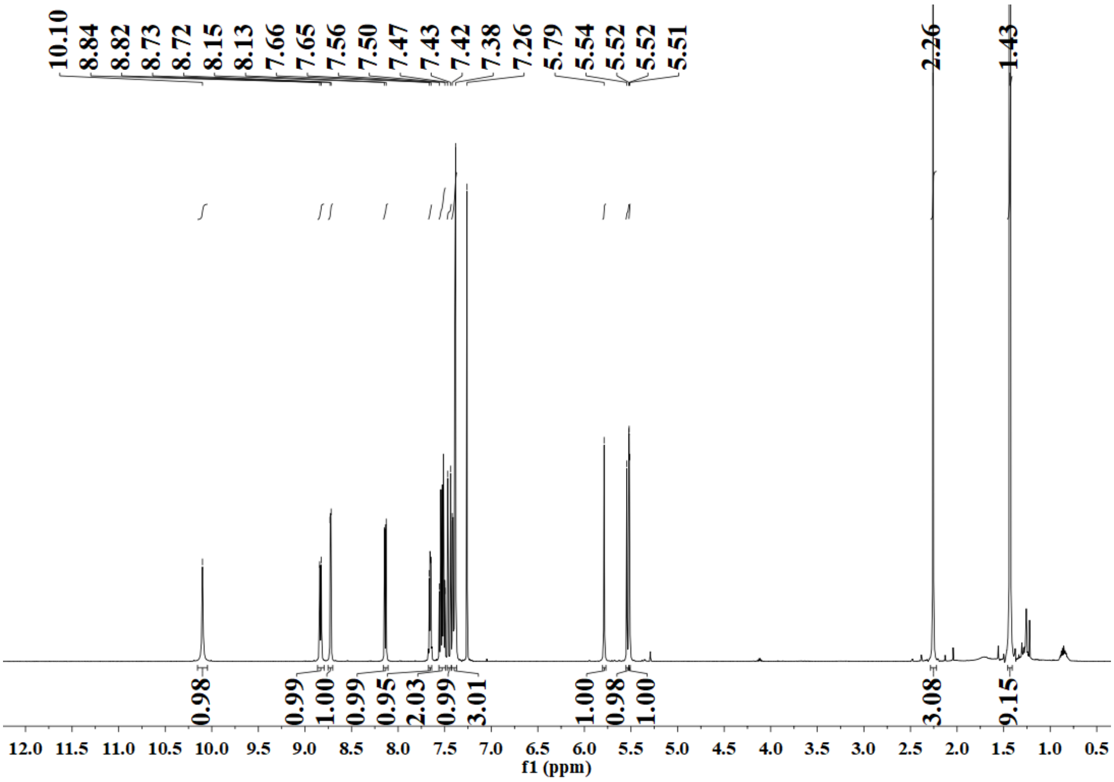




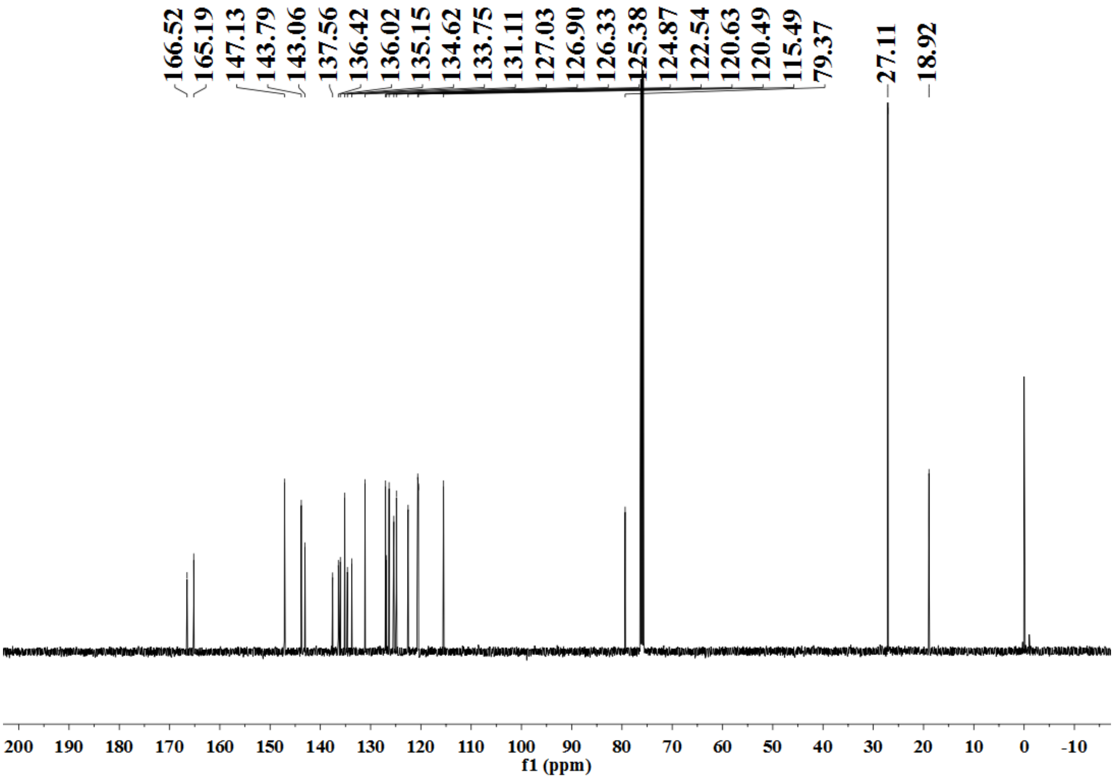


tBuO2C
Me
O
AQ

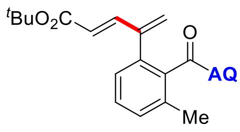
(3d)



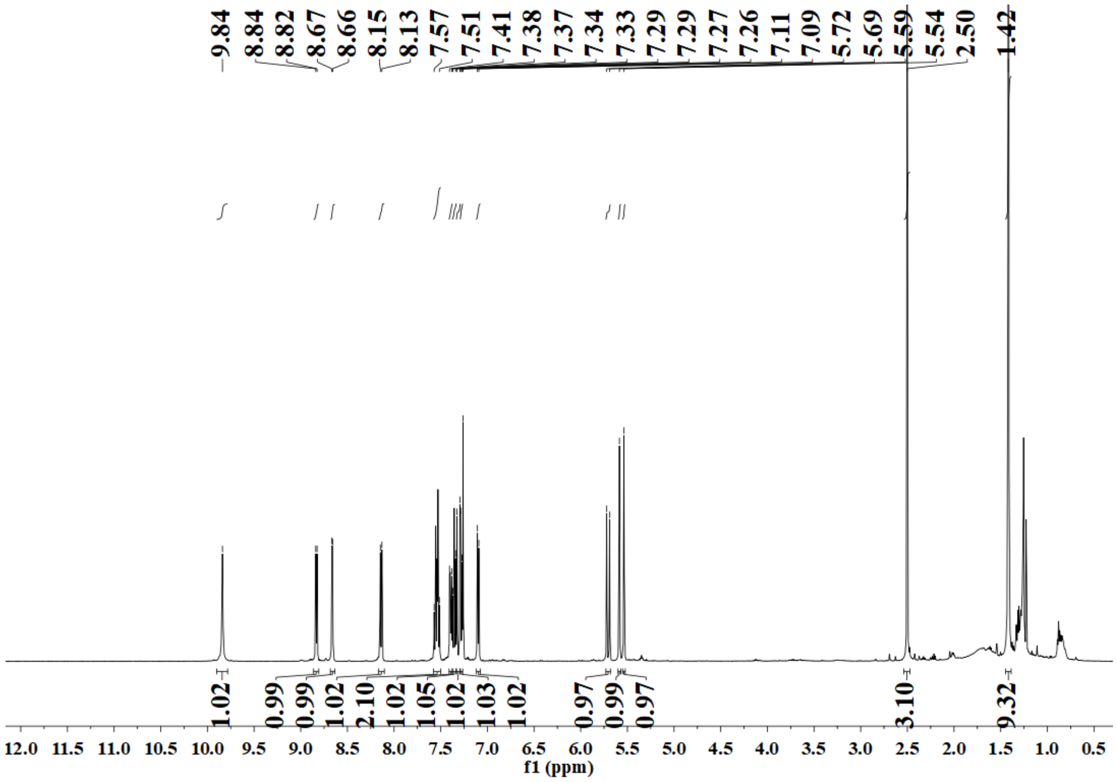
10.10
8.84
8.82
8.73
8.72
8.15
8.13
7.66
7.65
7.56
7.50
7.47
7.43
7.42
7.38
7.26
5.79
5.54
5.52
5.52
5.51
2.26
1.43
0.98
0.99
1.00
0.99
0.95
2.03
0.99
3.01
1.00
0.98
1.00
3.08
9.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

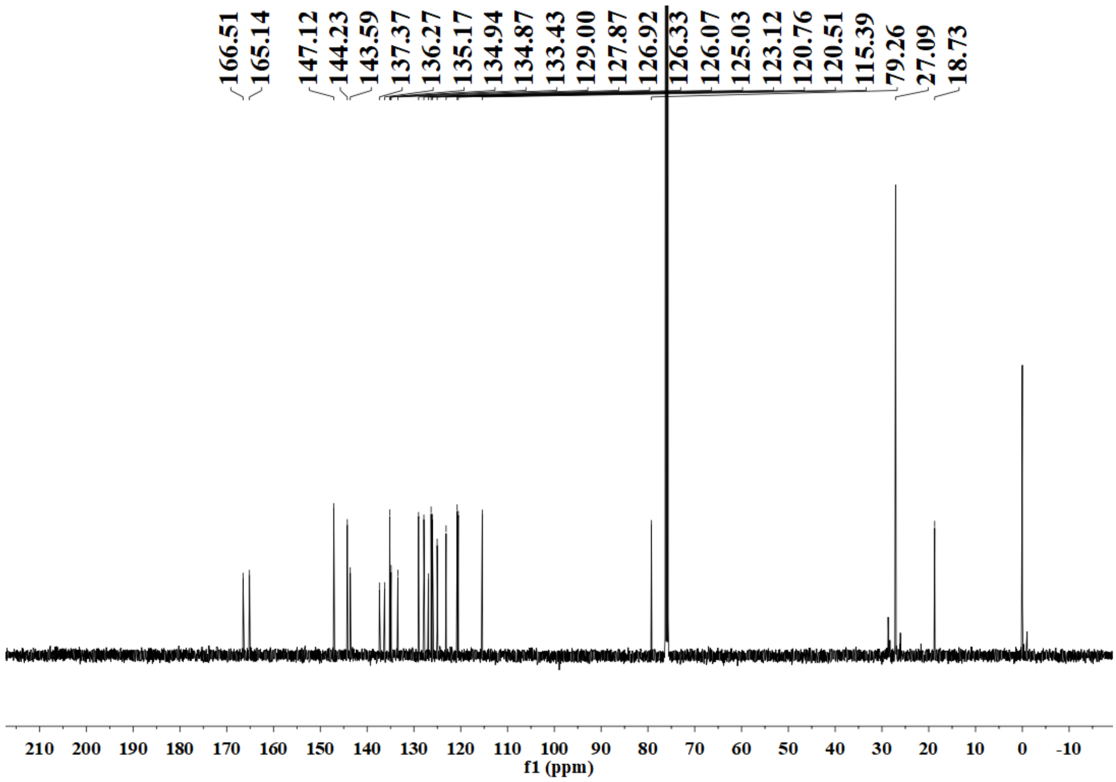


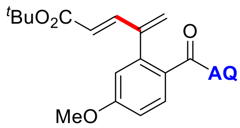
166.52
165.19
147.13
143.79
143.06
137.56
136.42
136.02
135.15
134.62
133.75
131.11
127.03
126.90
126.33
125.38
124.87
122.54
120.63
120.49
115.49
79.37
27.11
18.92
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



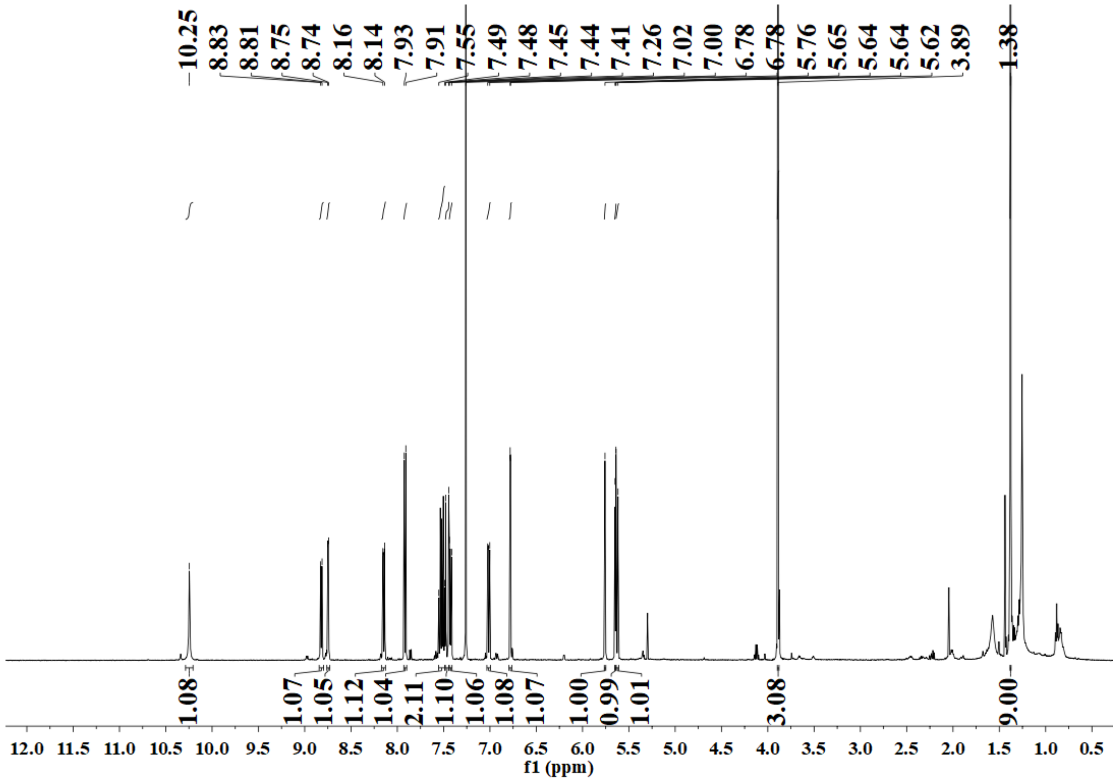
(3e)






tBuO2C
O
AQ
MeO

(3f)


10.25
8.83
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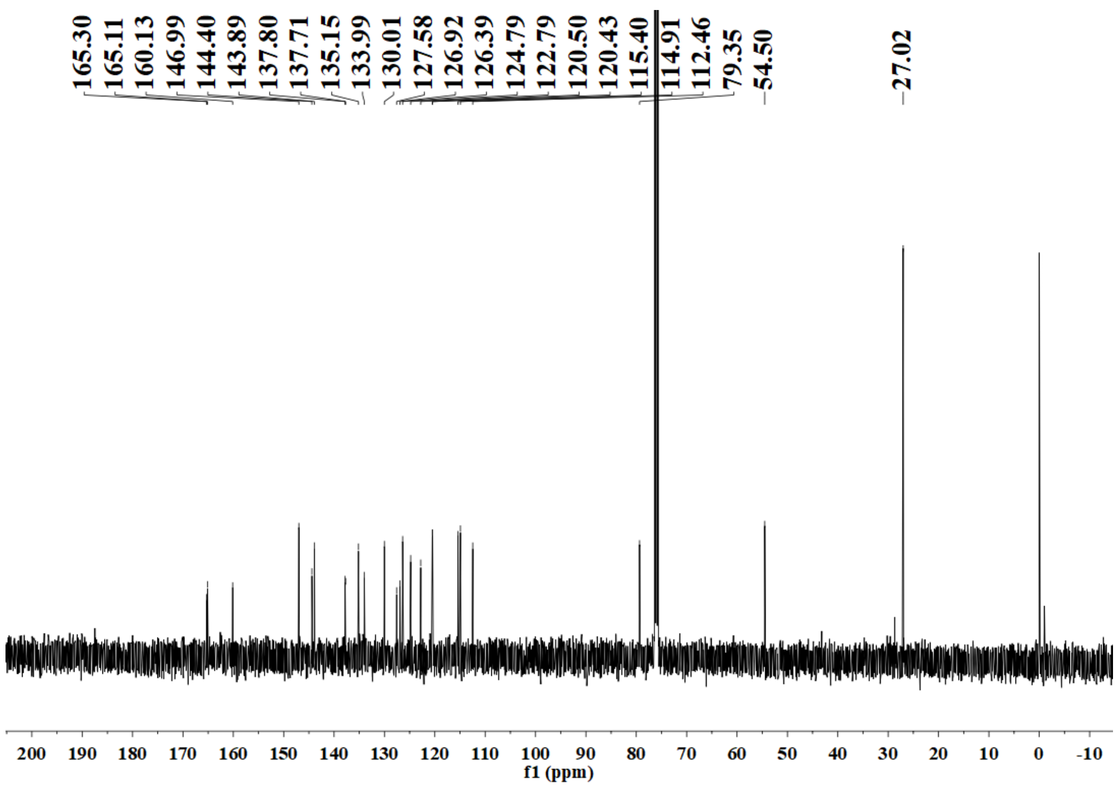
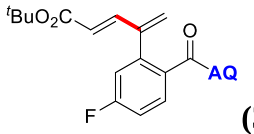
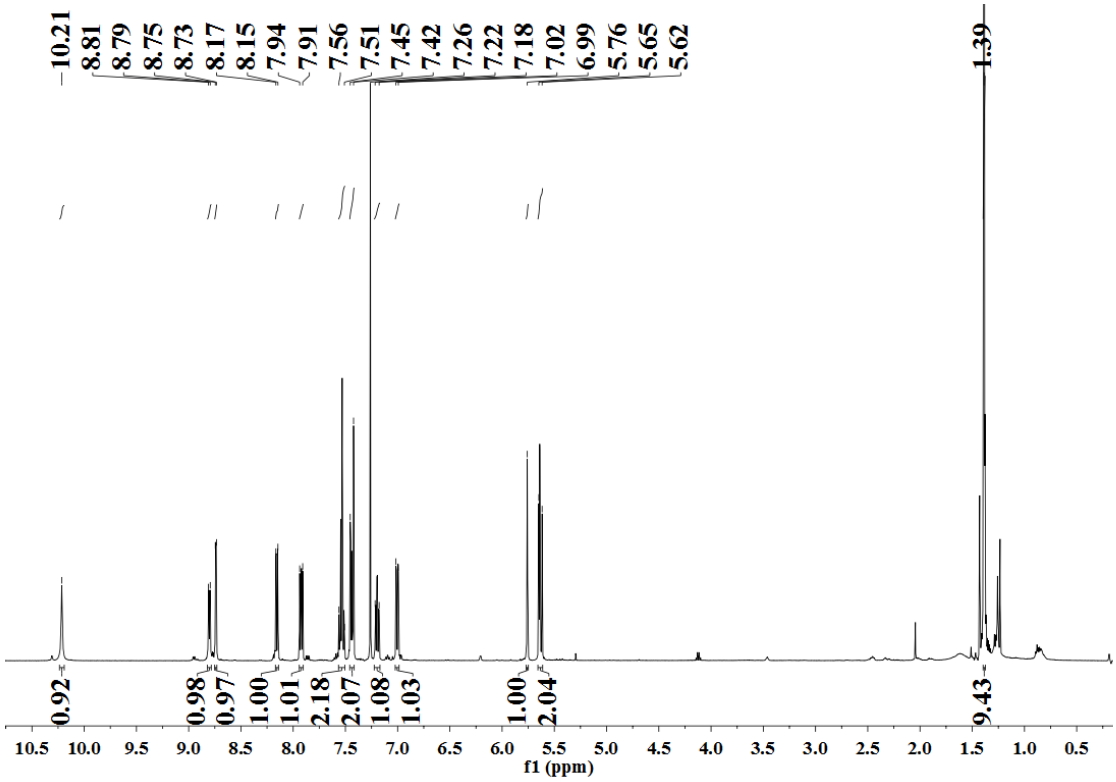
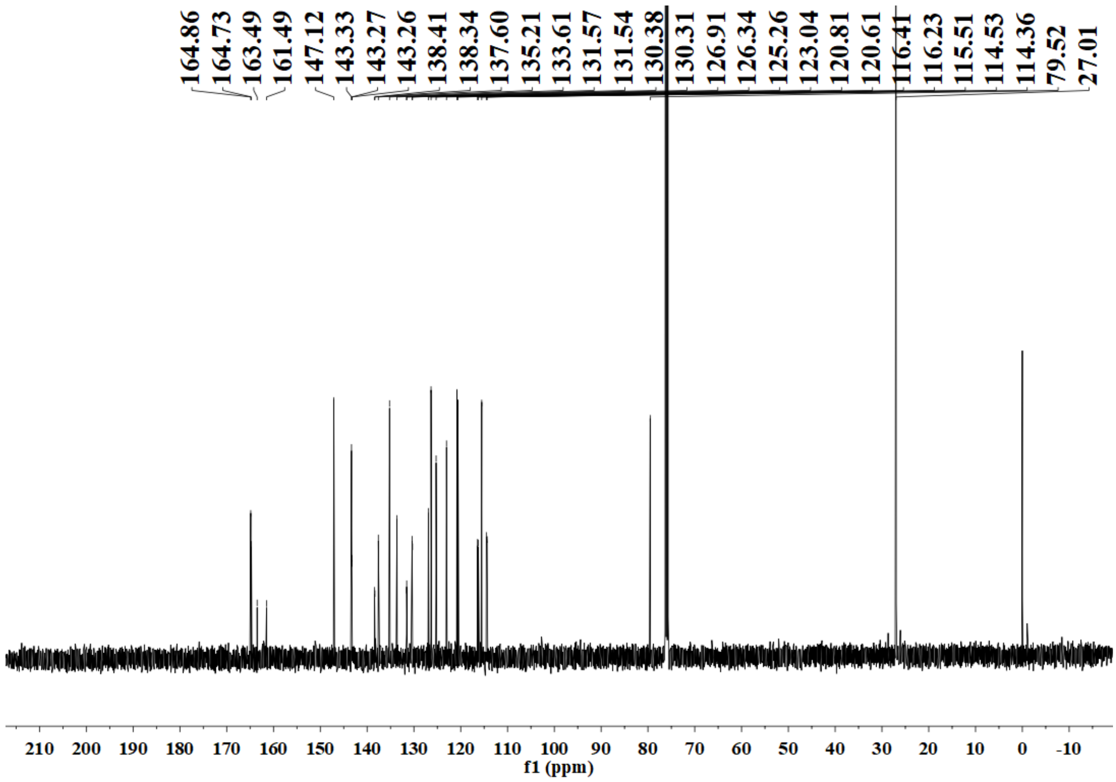
8.75
8.74
8.16
8.14
7.93
7.91
7.55
7.49
7.48
7.45
7.44
7.41
7.26
7.02
7.00
6.78
6.78
5.76
5.65
5.64
5.64
5.62
3.89
1.38
1.08
1.07
1.05
1.12
1.04
2.11
1.10
1.06
1.06
1.08
1.07
1.00
0.99
1.01
3.08
9.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

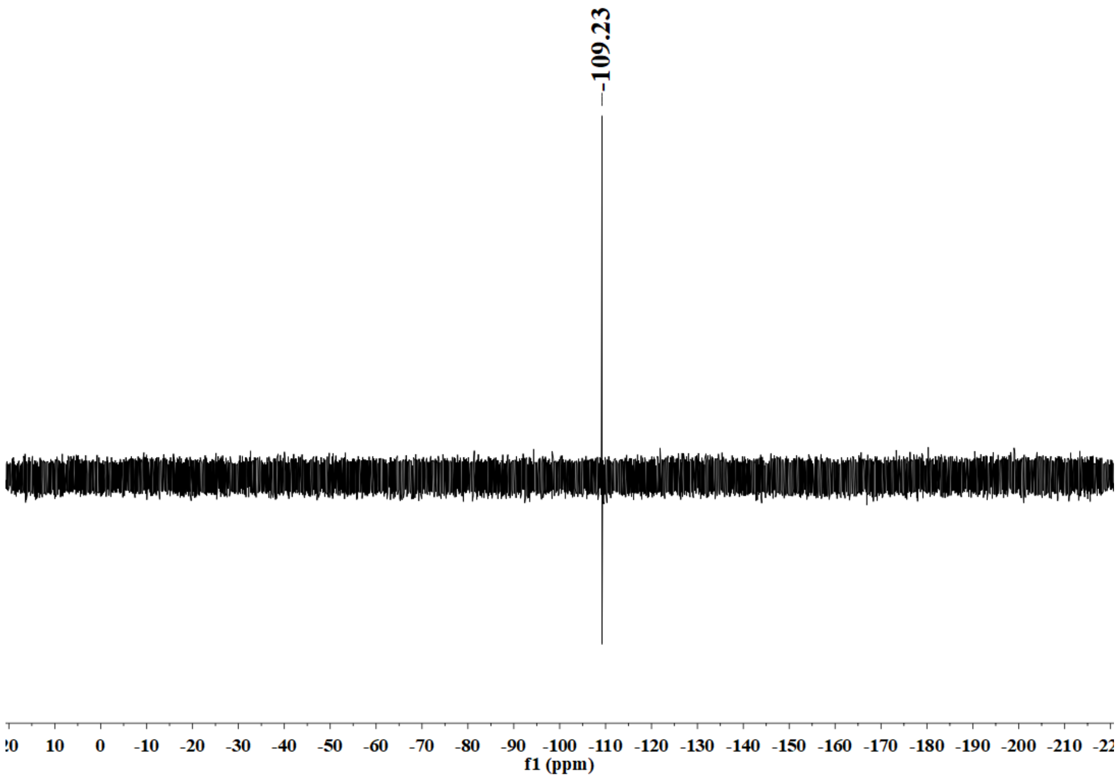

165.30
165.11
160.13
146.99
144.40
143.89
137.80
137.71
135.15
133.99
130.01
127.58
126.92
126.39
124.79
122.79
120.50
120.43
115.40
114.91
112.46
79.35
54.50
27.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

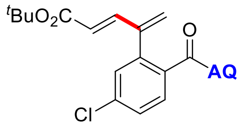

tBuO2C
O
AQ
F

(3g)

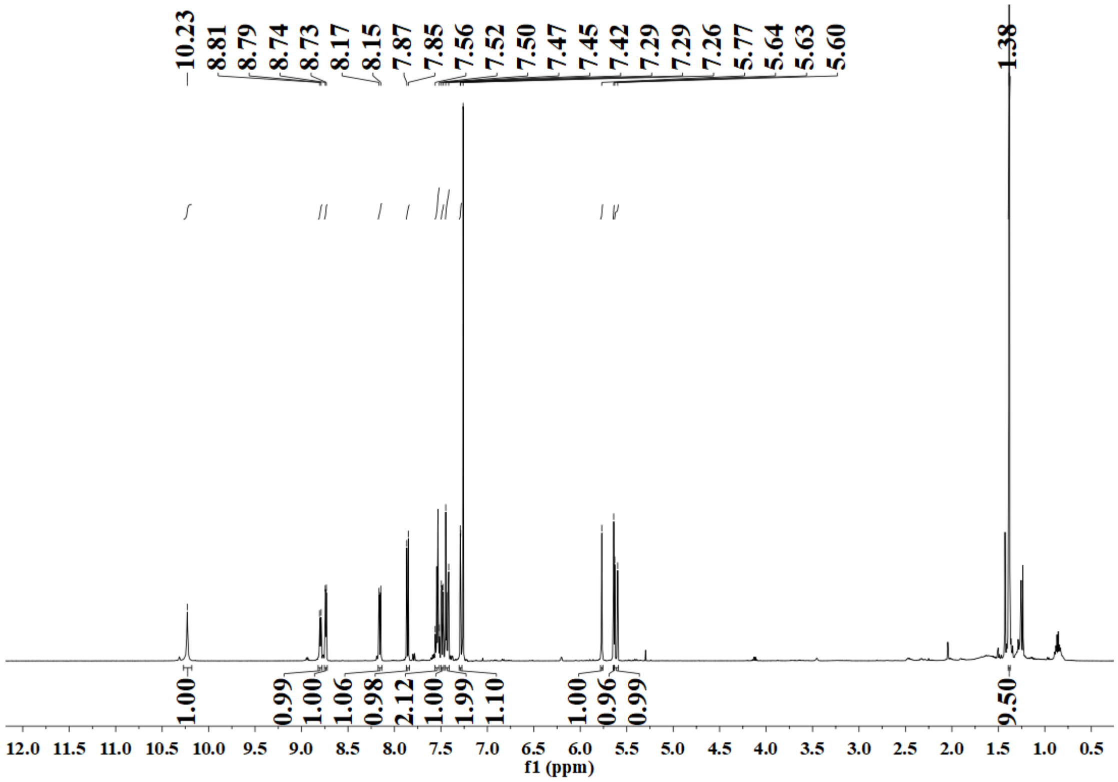

10.21
8.81
8.79
8.75
8.73
8.17
8.15
7.94
7.91
7.56
7.51
7.45
7.42
7.26
7.22
7.18
7.02
6.99
5.76
5.65
5.62
1.39
0.92
0.98
0.97
1.00
1.01
2.18
2.07
1.08
1.03
1.00
2.04
9.43
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

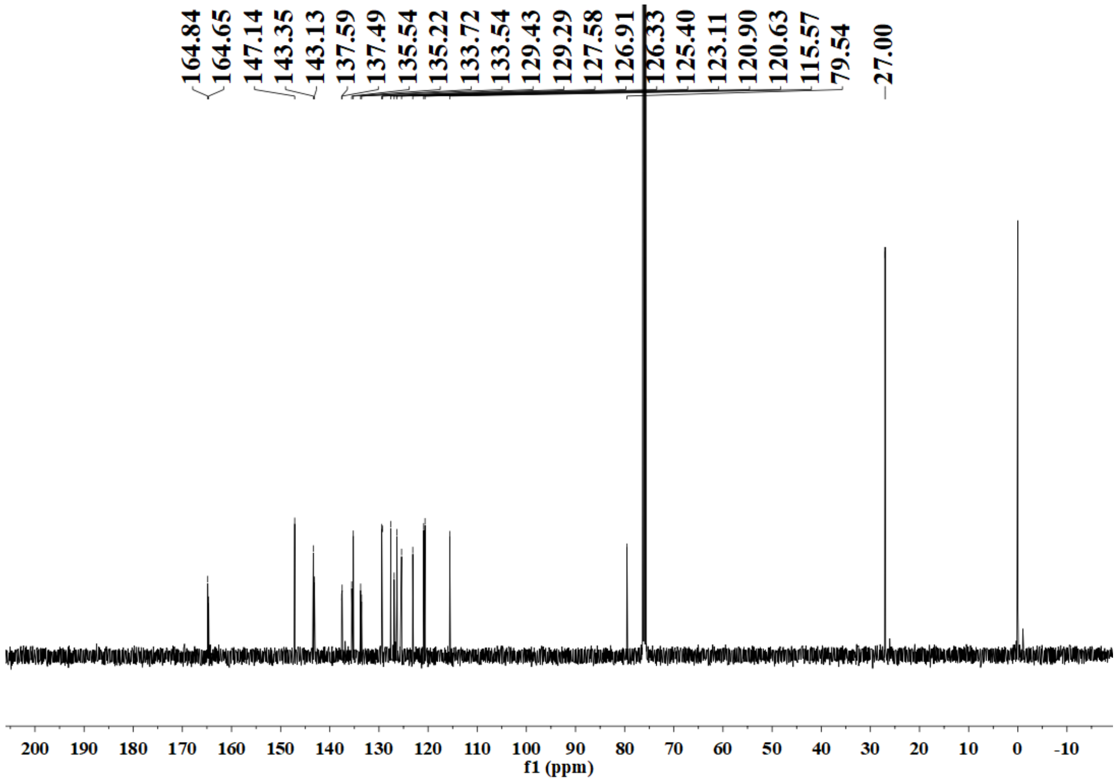

164.86
164.73
163.49
161.49
147.12
143.33
143.27
143.26
138.41
138.34
137.60
135.21
133.61
131.57
131.54
130.38
130.31
126.91
126.34
125.26
123.04
120.81
120.61
116.41
116.23
115.51
114.53
114.36
79.52
27.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-109.23
f1 (ppm)


ᵗBuO2C
O
AQ
Cl

(3h)


10.23
8.81
8.79
8.74
8.73
8.17
8.15
7.87
7.85
7.56
7.52
7.50
7.47
7.45
7.42
7.29
7.29
7.26
5.77
5.64
5.63
5.60
1.38
1.00
0.99
1.00
1.06
0.98
2.12
1.00
1.99
1.10
1.00
0.96
0.99
9.50
f1 (ppm)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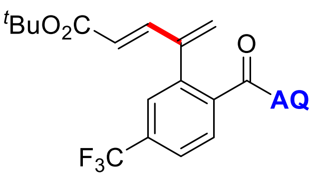
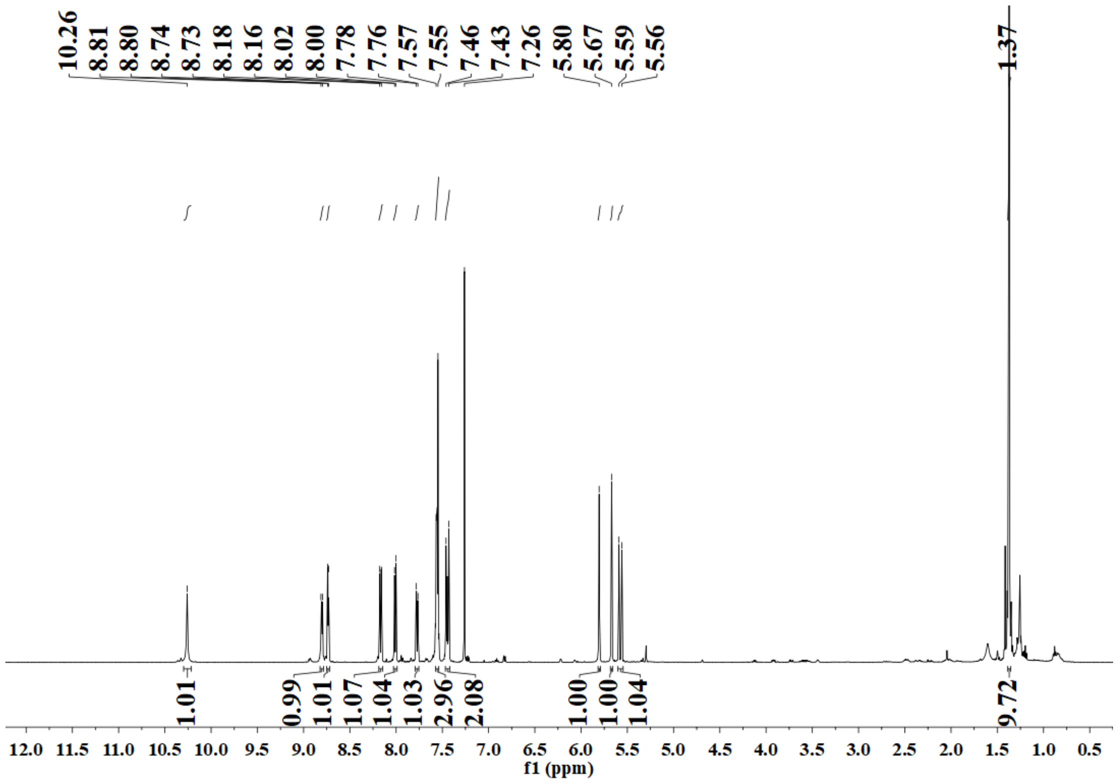
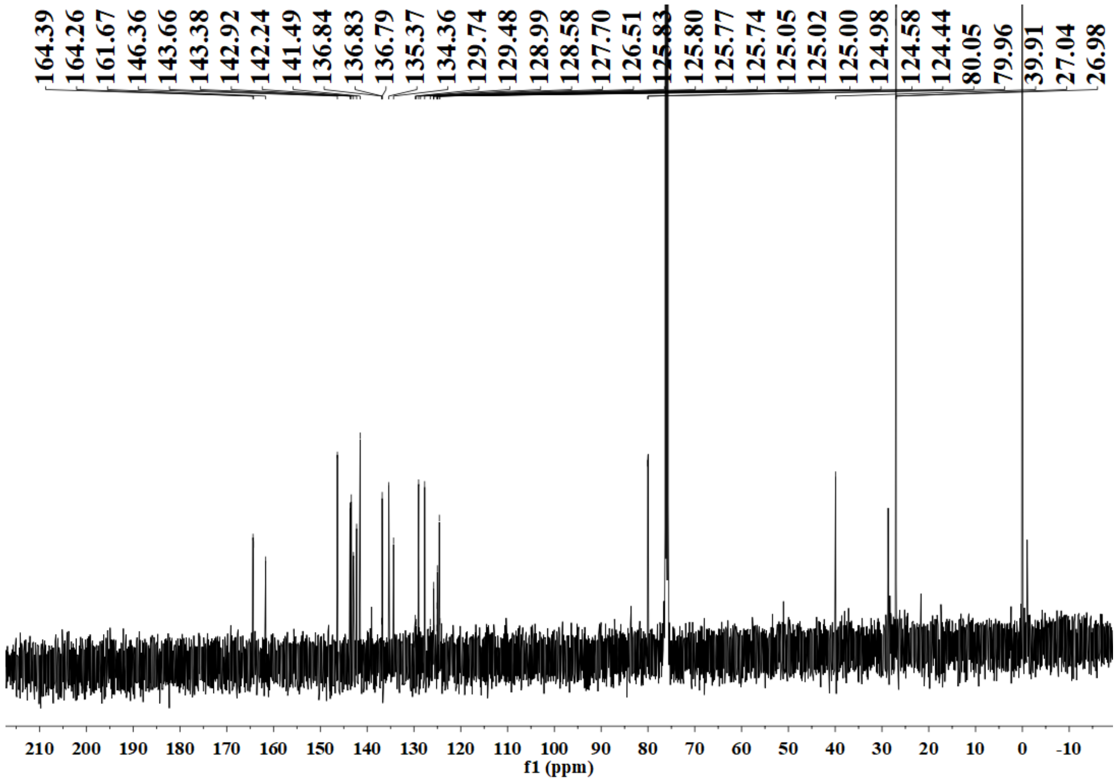
137.59
137.49
135.54
135.22
133.72
133.54
129.43
129.29
127.58
126.91
126.33
125.40
123.11
120.90
120.63
115.57
79.54
27.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


^{t}BuO$_2$C
O
AQ
F$_3$C

(3i)


10.26
8.81
8.80
8.74
8.73
8.18
8.16
8.02
8.00
7.78
7.76
7.57
7.55
7.46
7.43
7.26
5.80
5.67
5.59
5.56
1.37
1.01
0.99
1.01
1.07
1.04
1.03
2.96
2.08
1.00
1.00
1.04
9.72
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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164.26
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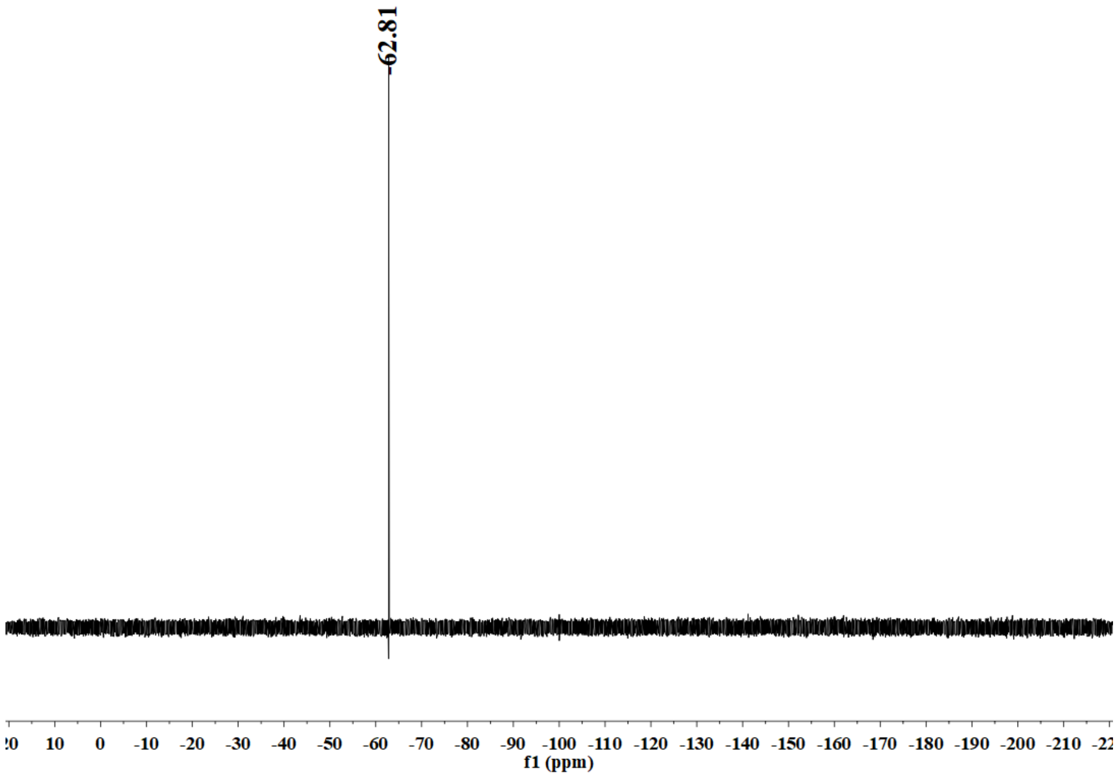
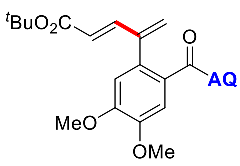
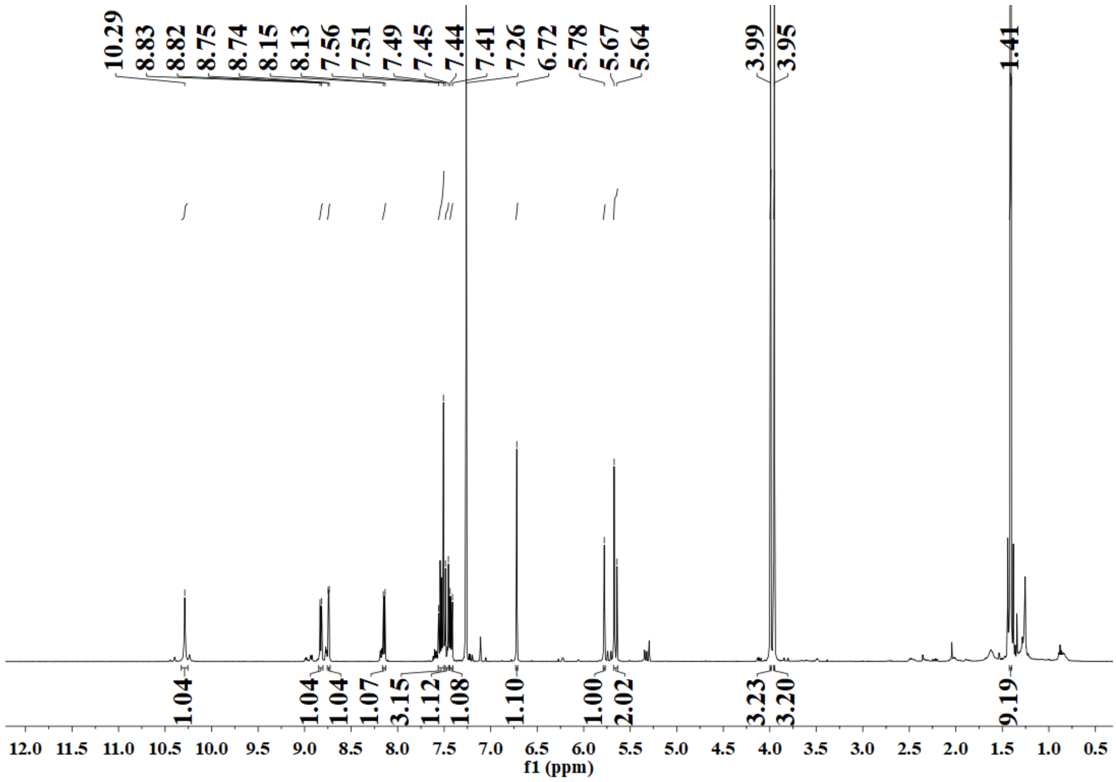
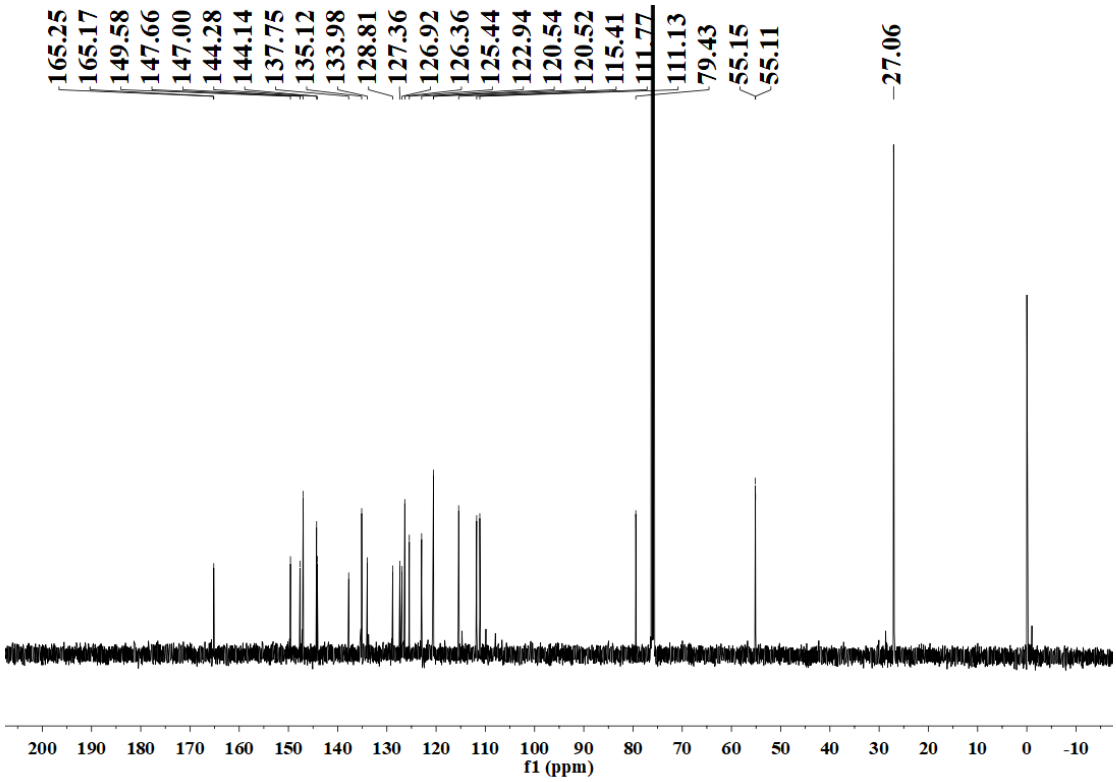
146.36
143.66
143.38
142.92
142.24
141.49
136.84
136.83
136.79
135.37
134.36
129.74
129.48
128.99
128.58
127.70
126.51
125.83
125.80
125.77
125.74
125.05
125.02
125.00
124.98
124.58
124.44
80.05
79.96
39.91
27.04
26.98
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

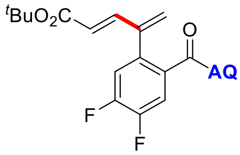

-62.81
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


tBuO2C
O
AQ
MeO
OMe

(3j)

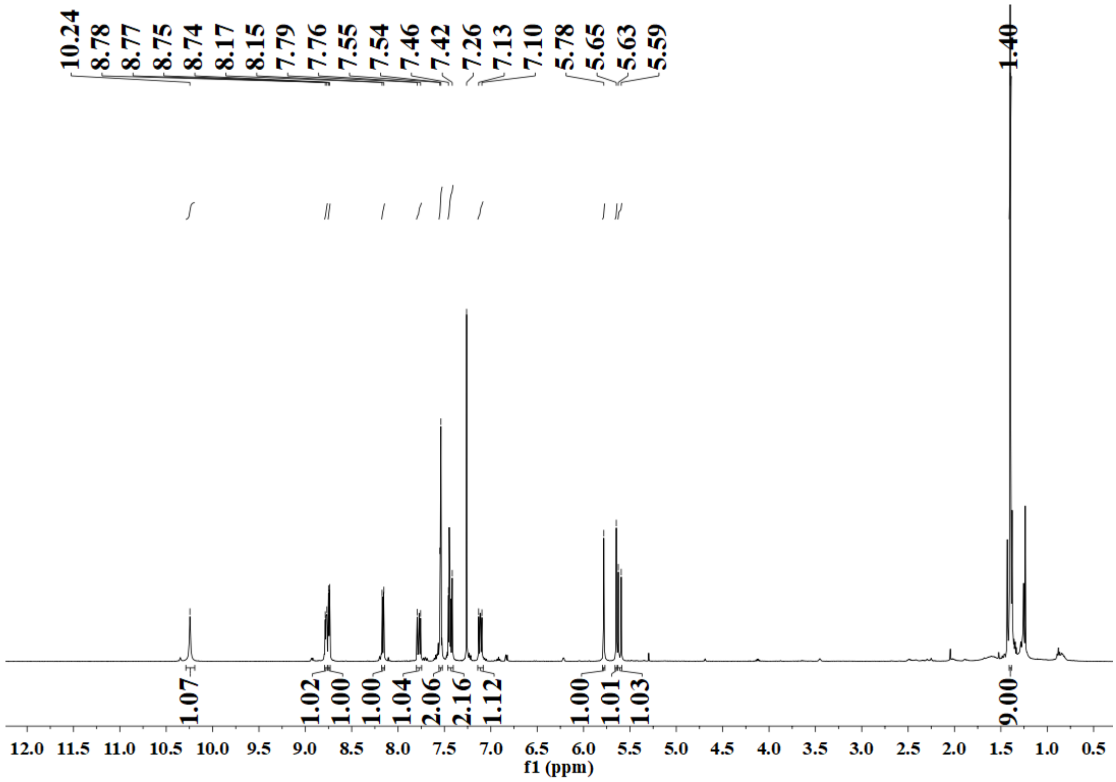

10.29
8.83
8.82
8.75
8.74
8.15
8.13
7.56
7.51
7.49
7.45
7.44
7.41
7.26
6.72
5.78
5.67
5.64
3.99
3.95
1.41
1.04
1.04
1.04
1.07
3.15
1.12
1.08
1.10
1.00
2.02
3.23
3.20
9.19
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


165.25
165.17
149.58
147.66
147.00
144.28
144.14
137.75
135.12
133.98
128.81
127.36
126.92
126.36
125.44
122.94
120.54
120.52
115.41
111.77
111.13
79.43
55.15
55.11
27.06
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



tBuO2C
O
AQ
F
F

(3k)



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7.79
7.76
7.55
7.54
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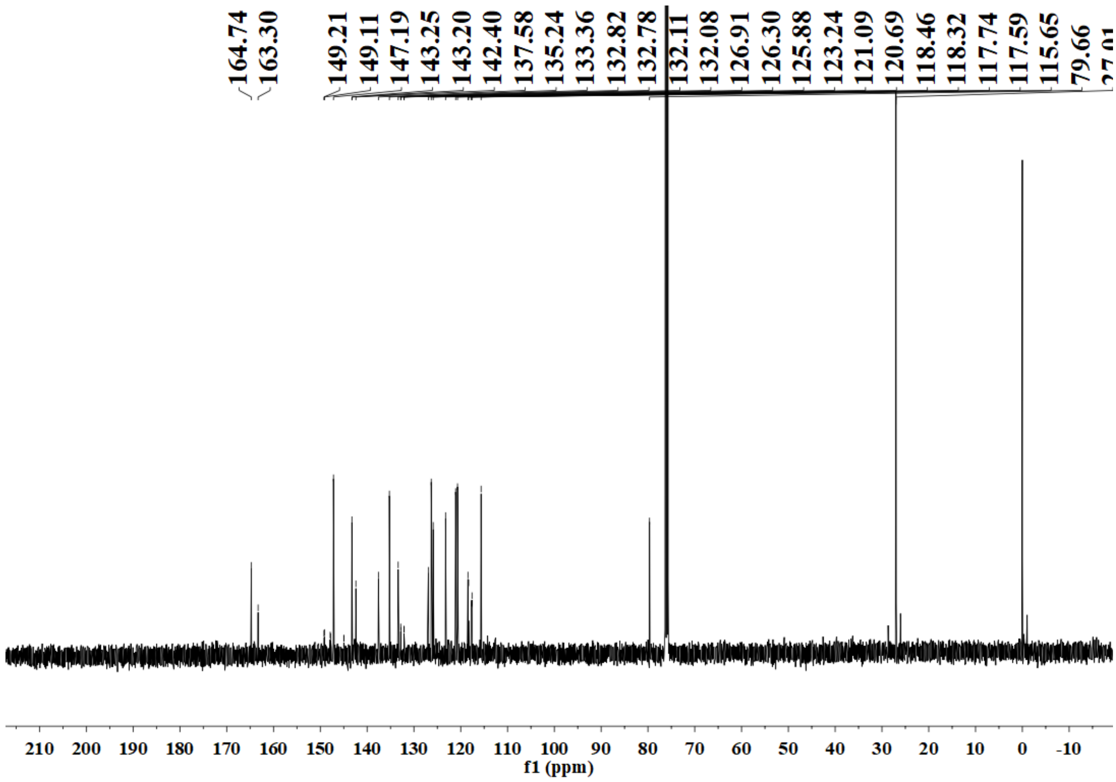
7.42
7.26
7.13
7.10
5.78
5.65
5.63
5.59
1.40
1.07
1.02
1.00
1.00
1.04
2.06
2.16
1.12
1.00
1.01
1.03
9.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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142.40
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135.24
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132.08
126.91
126.30
125.88
123.24
121.09
120.69
118.46
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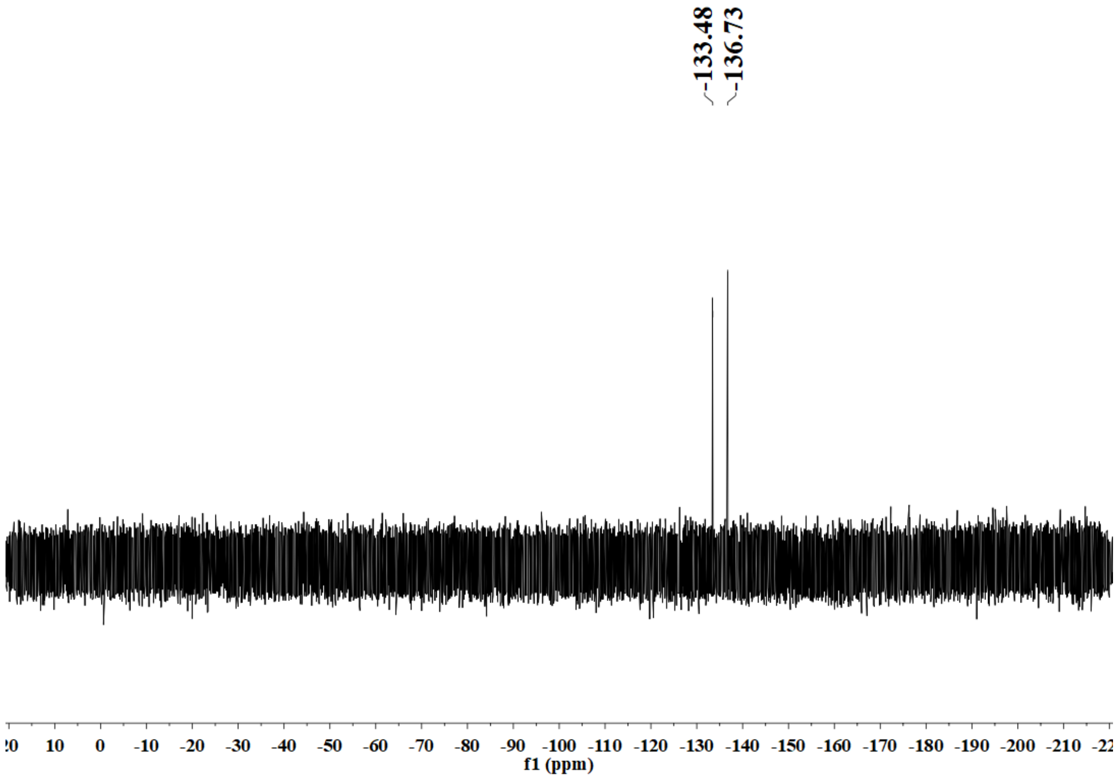
117.59
115.65
79.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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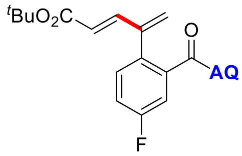
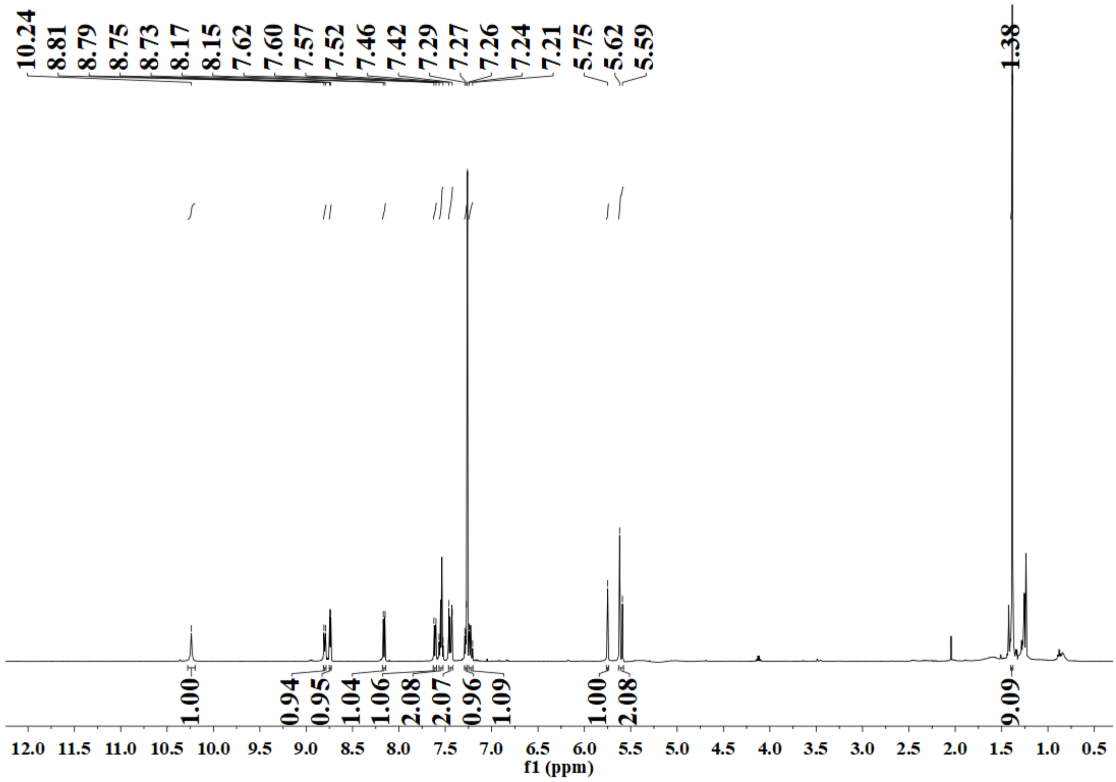

tBuO2C
O
AQ
F

(3l)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7.42
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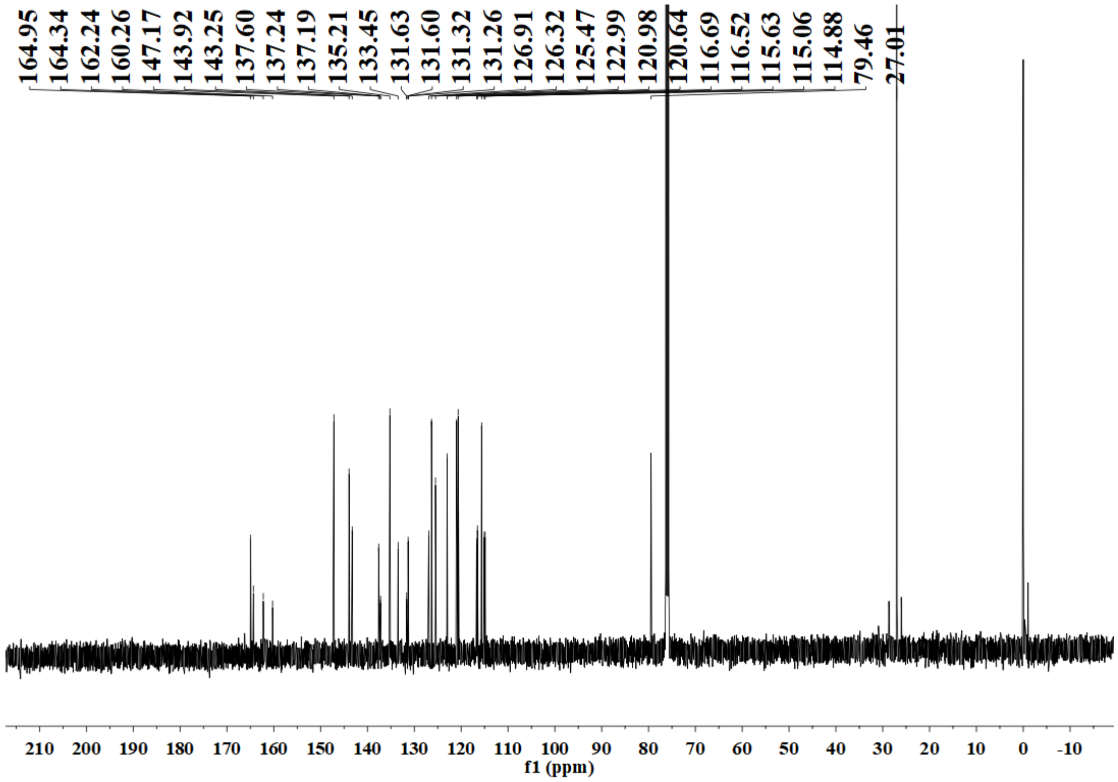
7.27
7.26
7.24
7.21
5.75
5.62
5.59
1.38
1.00
0.94
0.95
1.04
1.06
2.08
2.07
0.96
1.09
1.00
2.08
9.09
f1 (ppm)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131.63
131.60
131.32
131.26
126.91
126.32
125.47
122.99
120.98
120.64
116.69
116.52
115.63
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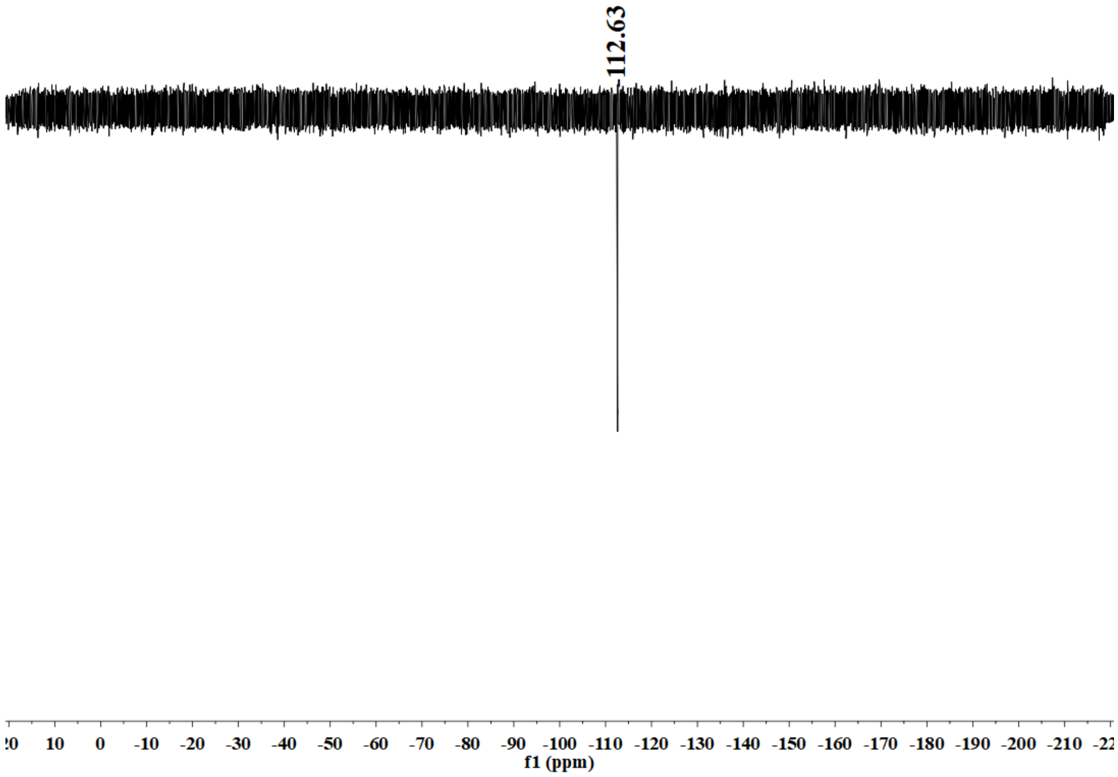
114.88
79.46
27.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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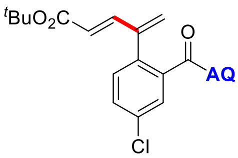
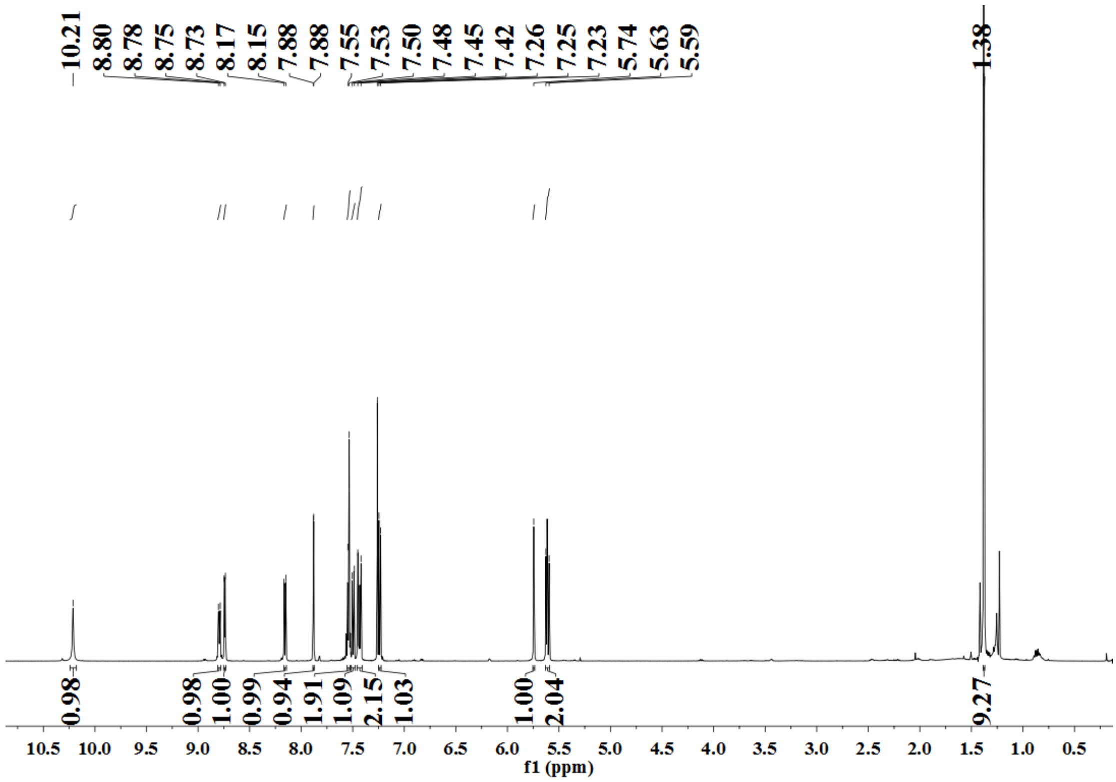
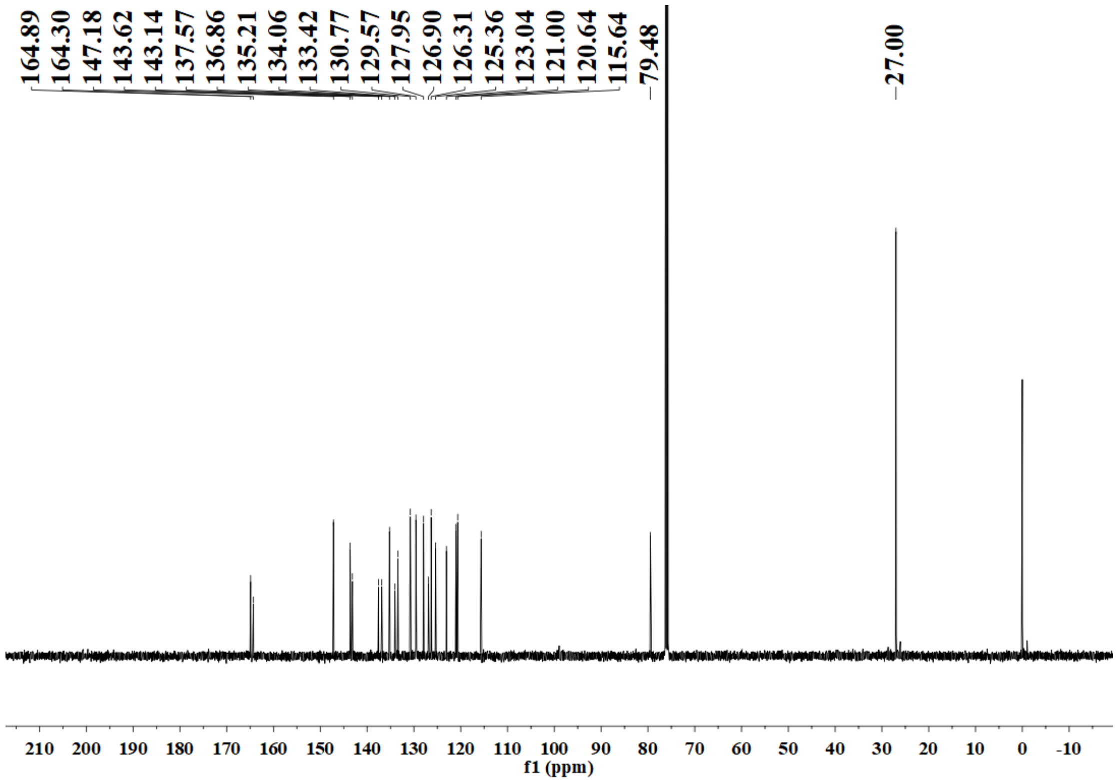
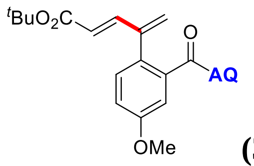
f1 (ppm)



(3m)

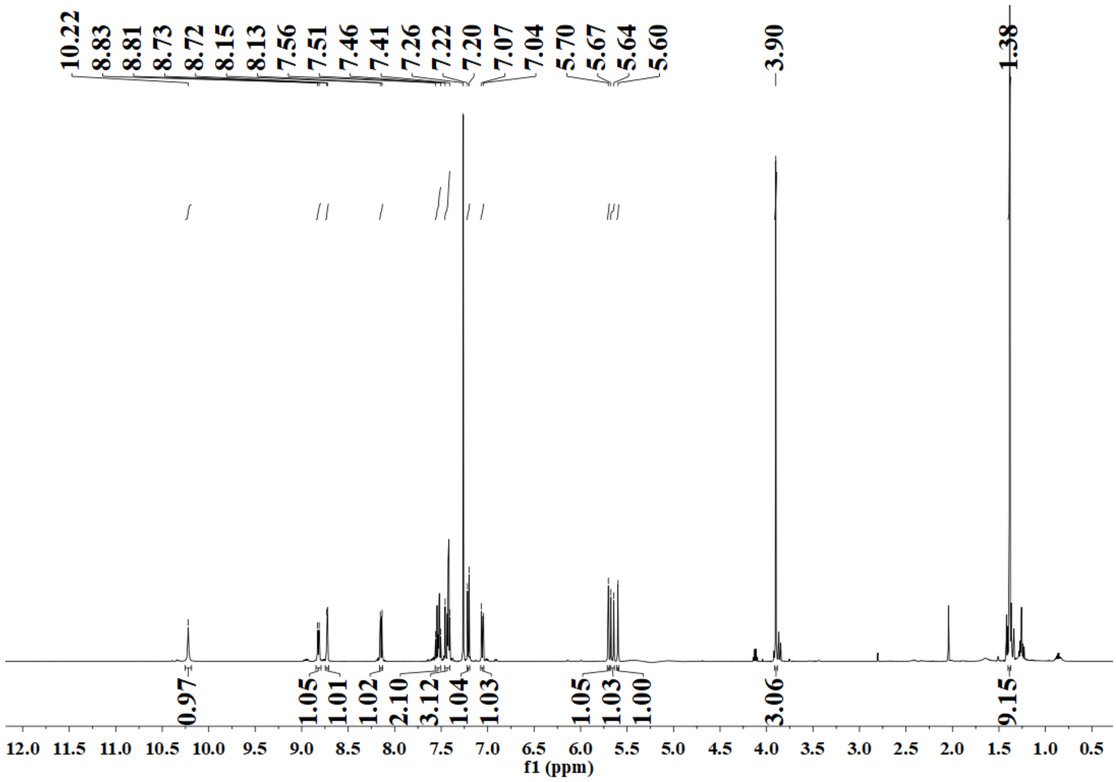




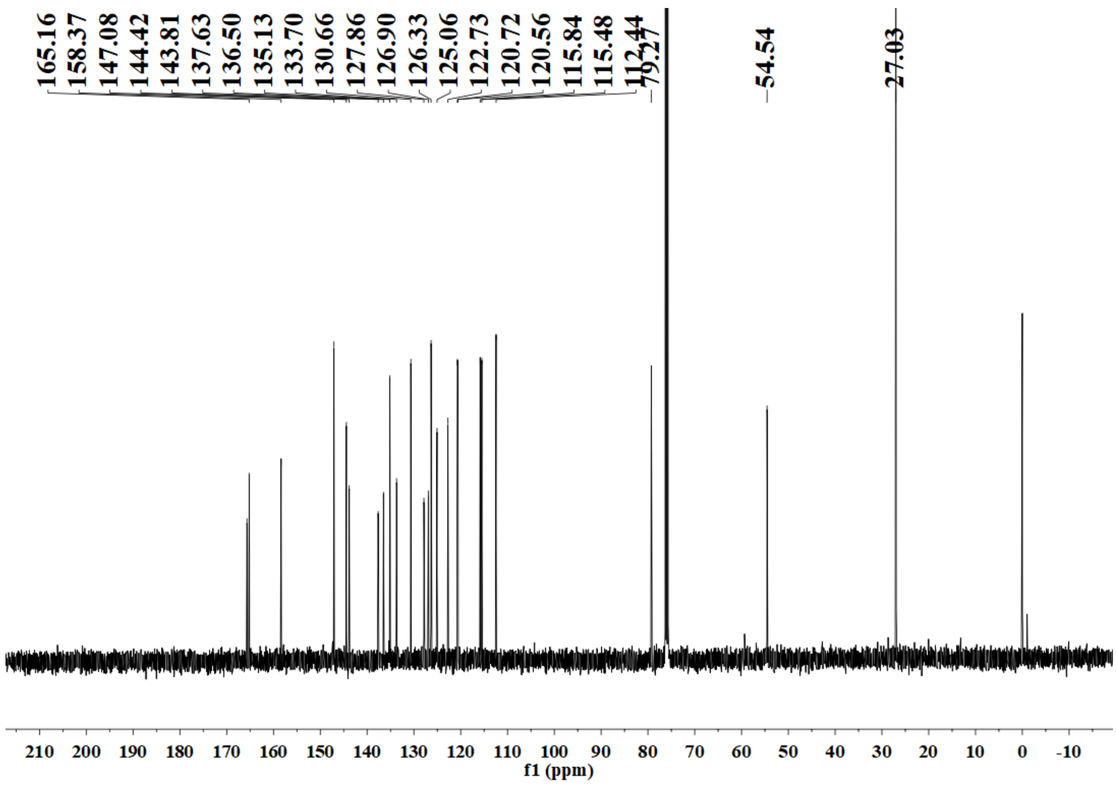


^{t}BuO$_2$C
O
AQ
OMe

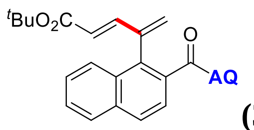
(3n)



10.22 8.83 8.81 8.73 8.72 8.15 8.13 7.56 7.51 7.46 7.41 7.26 7.22 7.20 7.07 7.04 5.70 5.67 5.64 5.60
3.90
1.38
0.97 1.05 1.01 1.02 2.10 3.12 1.04 1.03 1.05 1.03 1.00 3.06 9.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

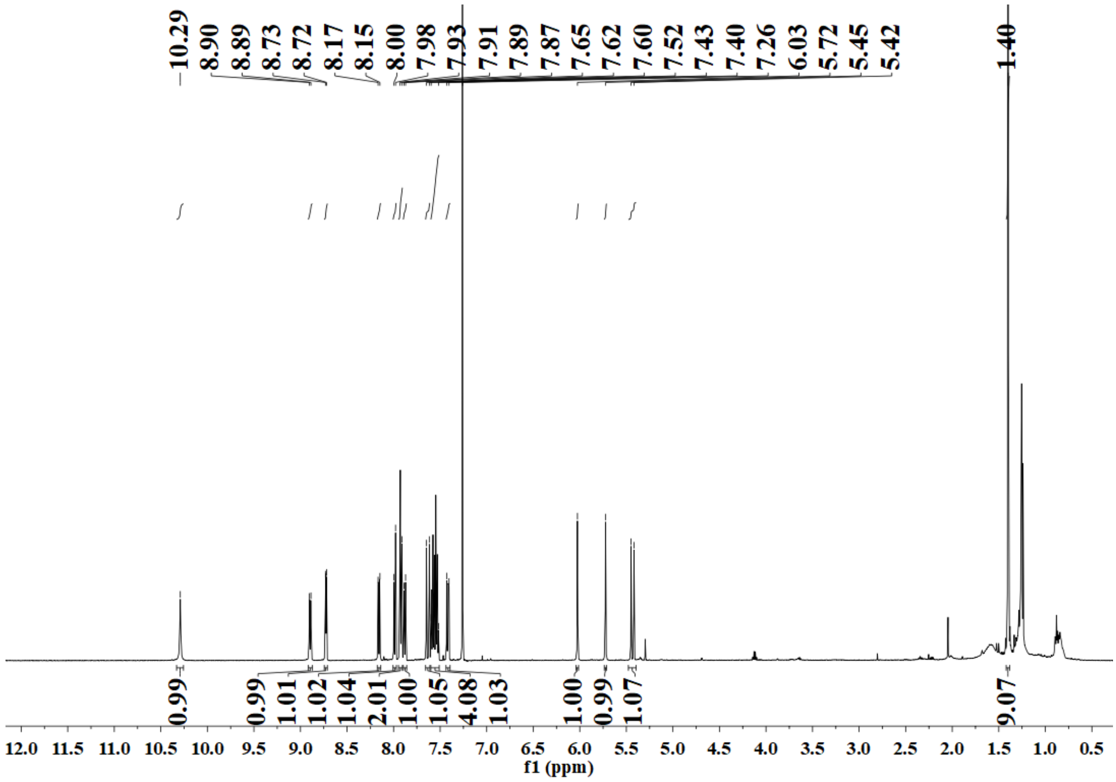


165.16 158.37 147.08 144.42 143.81 137.63 136.50 135.13 133.70 130.66 127.86 126.90 126.33 125.06 122.73 120.72 120.56 115.84 115.48 112.44 79.27
54.54
27.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



$^{t}BuO_2C$
O
AQ

(3o)



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8.17
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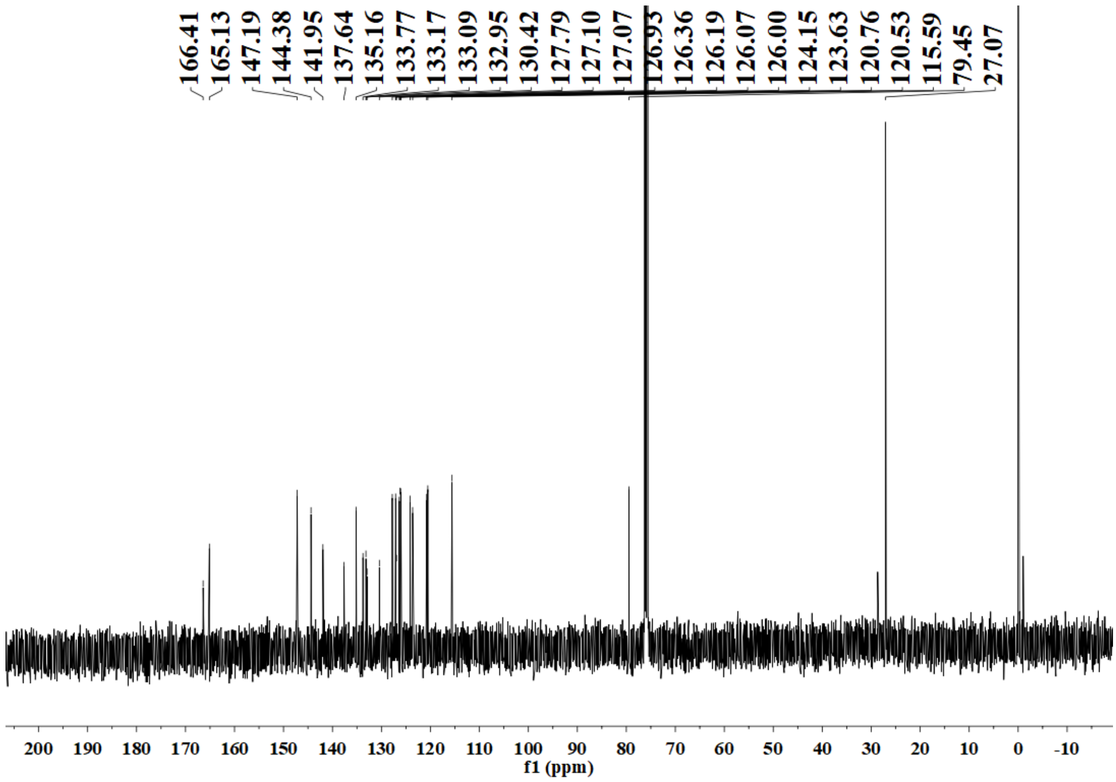
8.00
7.98
7.93
7.91
7.89
7.87
7.65
7.62
7.60
7.52
7.43
7.40
7.26
6.03
5.72
5.45
5.42
1.40
0.99
0.99
1.01
1.02
1.04
2.01
1.00
1.05
4.08
1.03
1.00
0.99
1.07
9.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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147.19
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133.17
133.09
132.95
130.42
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127.10
127.07
126.95
126.36
126.19
126.07
126.00
124.15
123.63
120.76
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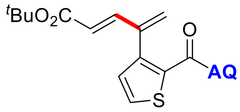
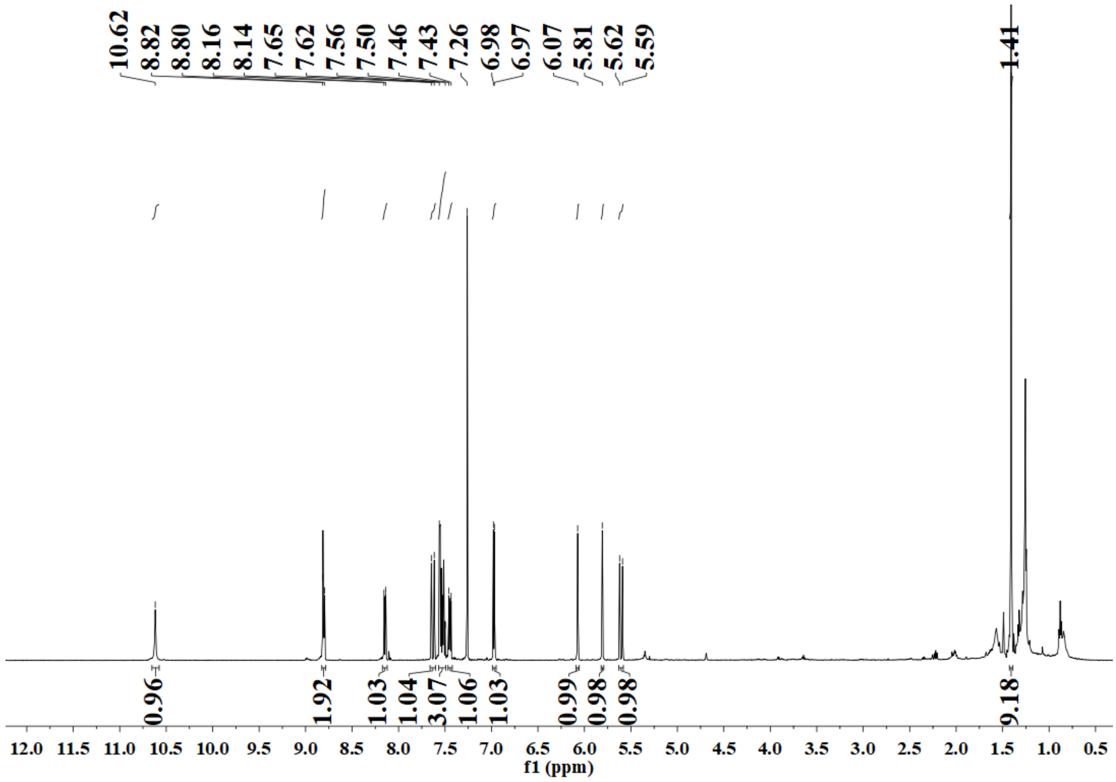
115.59
79.45
27.07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



$^tBuO_2C$
O
AQ
S

(3p)



10.62
8.82
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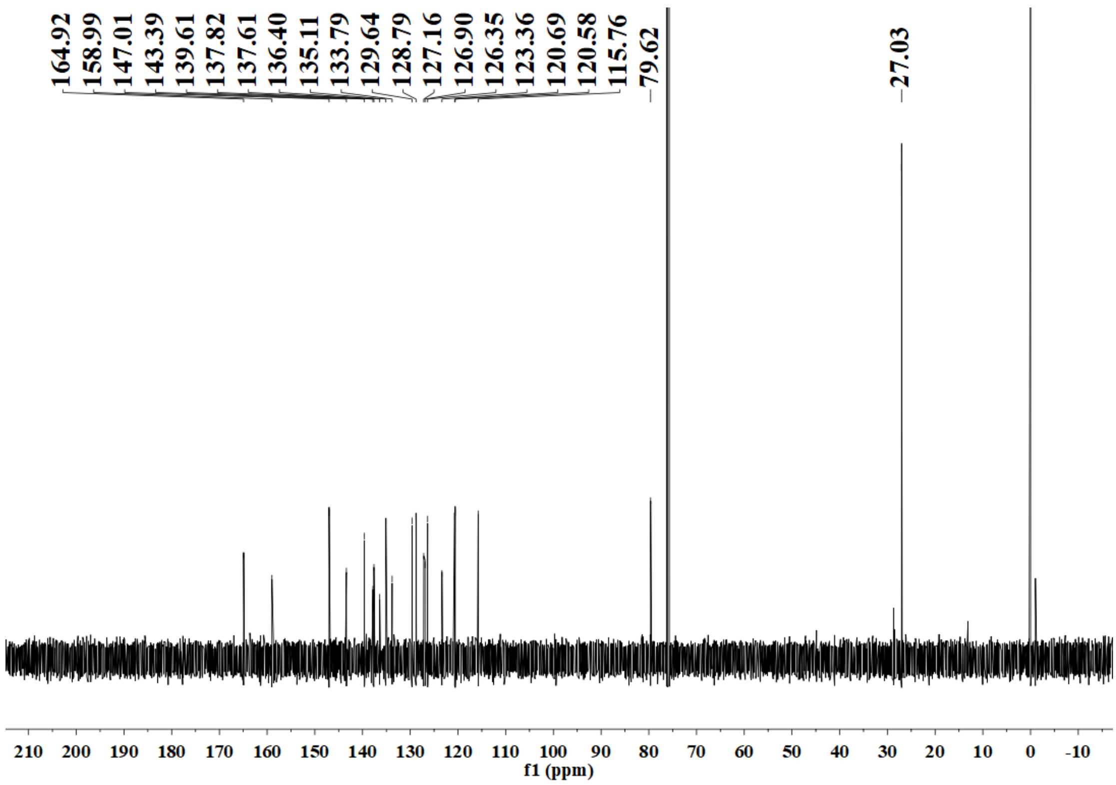
8.16
8.14
7.65
7.62
7.56
7.50
7.46
7.43
7.26
6.98
6.97
6.07
5.81
5.62
5.59
1.41
0.96
1.92
1.03
1.04
3.07
1.06
1.03
0.99
0.98
0.98
9.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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127.16
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126.35
123.36
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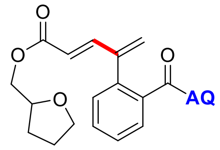
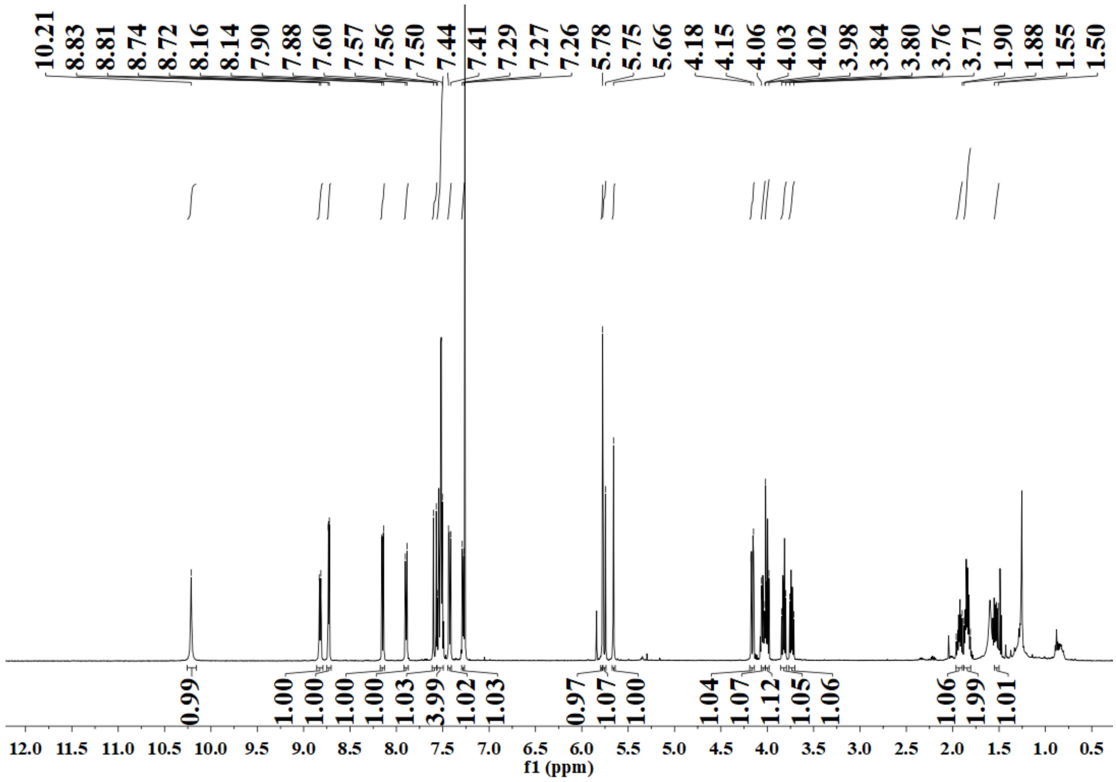
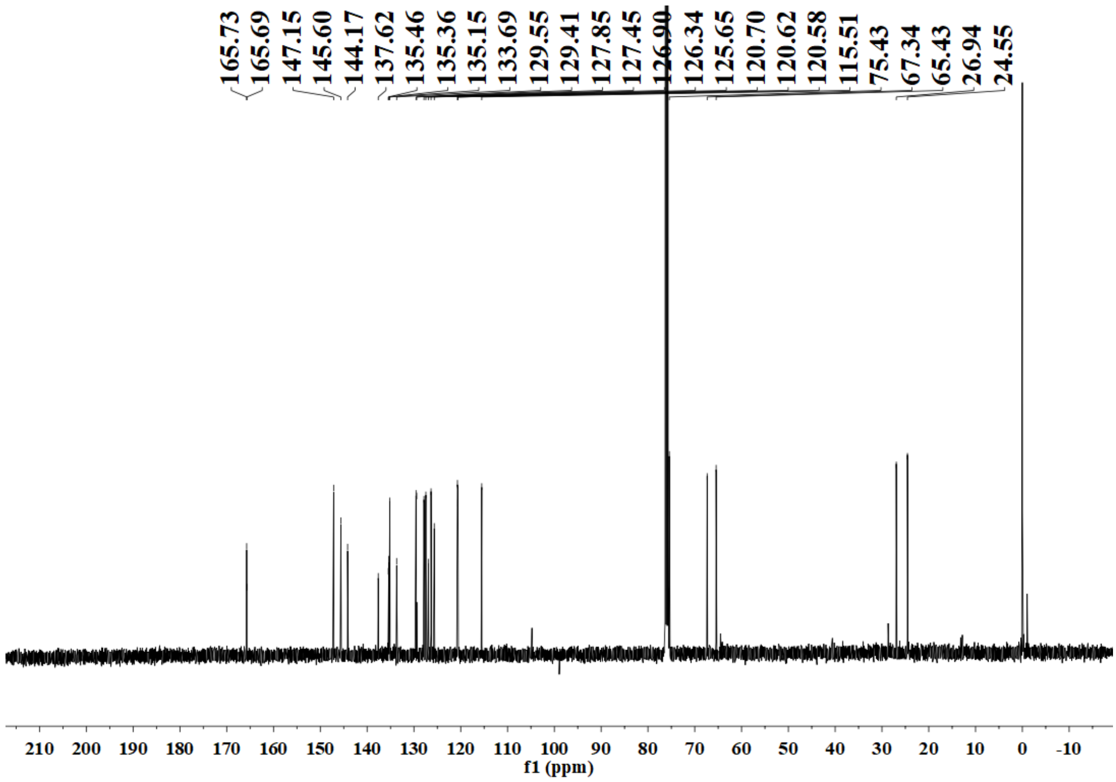
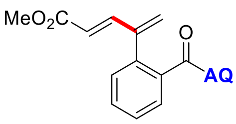
115.76
79.62
27.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


AQ

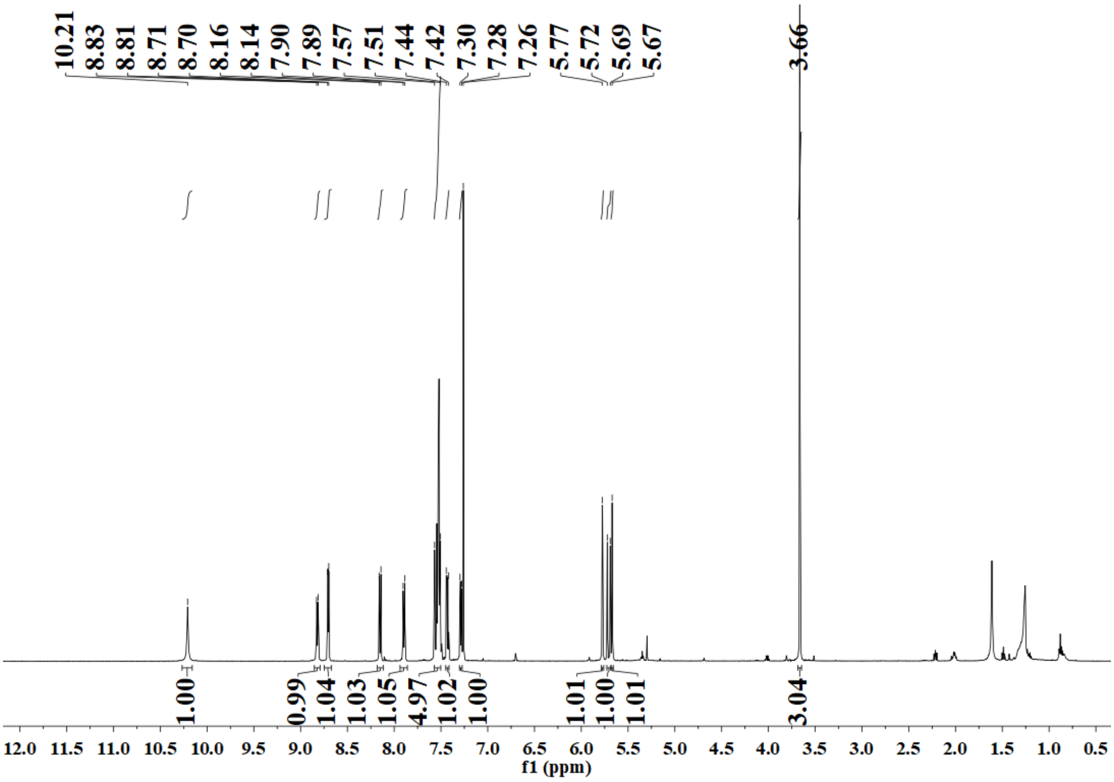
(3q)


10.21 8.83 8.81 8.74 8.72 8.16 8.14 7.90 7.88 7.60 7.57 7.56 7.50 7.44 7.41 7.29 7.27 7.26 5.78 5.75 5.66 4.18 4.15 4.06 4.03 4.02 3.98 3.84 3.80 3.76 3.71 1.90 1.88 1.55 1.50
0.99 1.00 1.00 1.00 1.00 1.03 3.99 1.02 1.03 0.97 1.07 1.00 1.04 1.07 1.12 1.05 1.06 1.06 1.99 1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


165.73 165.69 147.15 145.60 144.17 137.62 135.46 135.36 135.15 133.69 129.55 129.41 127.85 127.45 126.90 126.34 125.65 120.70 120.62 120.58 115.51 75.43 67.34 65.43 26.94 24.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO2C
O
AQ

(3r)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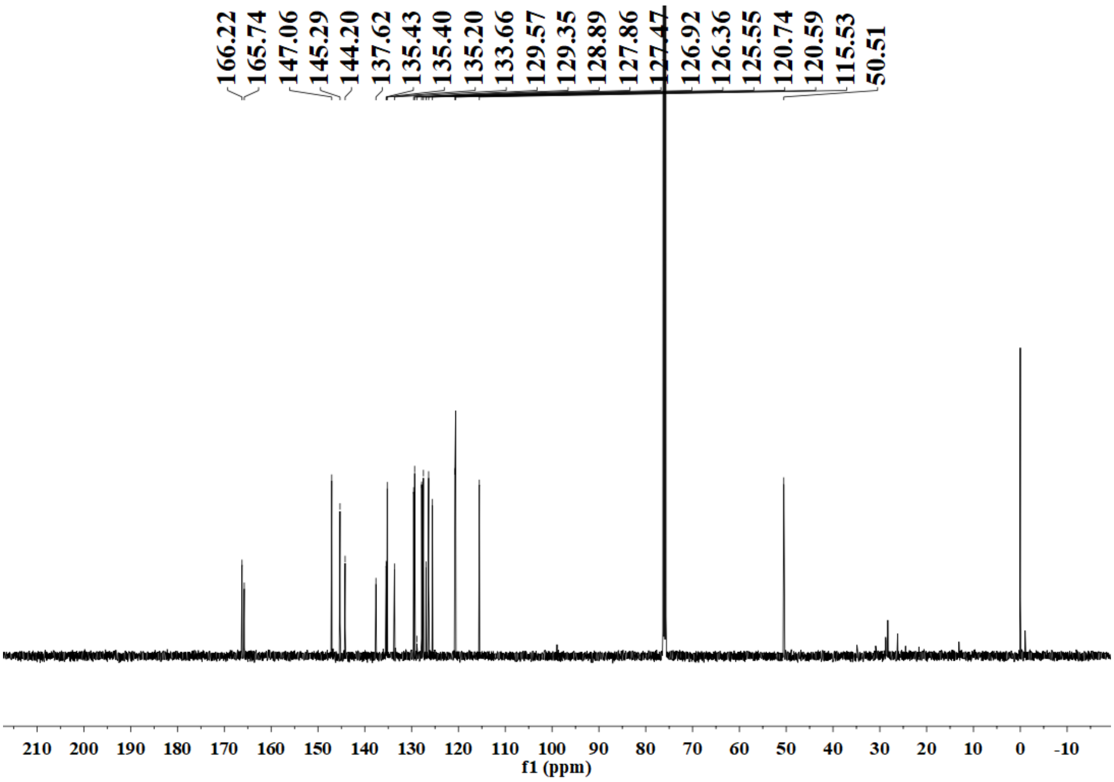
7.90
7.89
7.57
7.51
7.44
7.42
7.30
7.28
7.26
5.77
5.72
5.69
5.67
3.66
1.00
0.99
1.04
1.03
1.05
4.97
1.02
1.00
1.01
1.00
1.01
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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128.89
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127.47
126.92
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115.53
50.51
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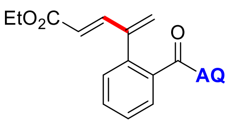
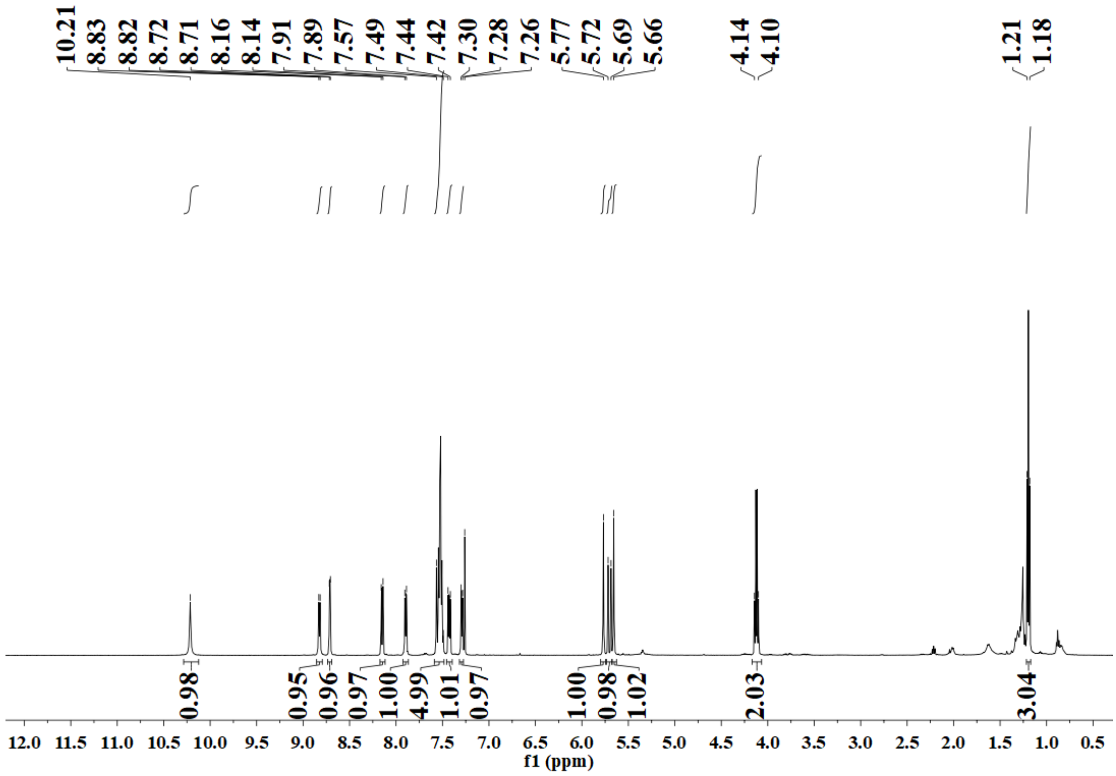
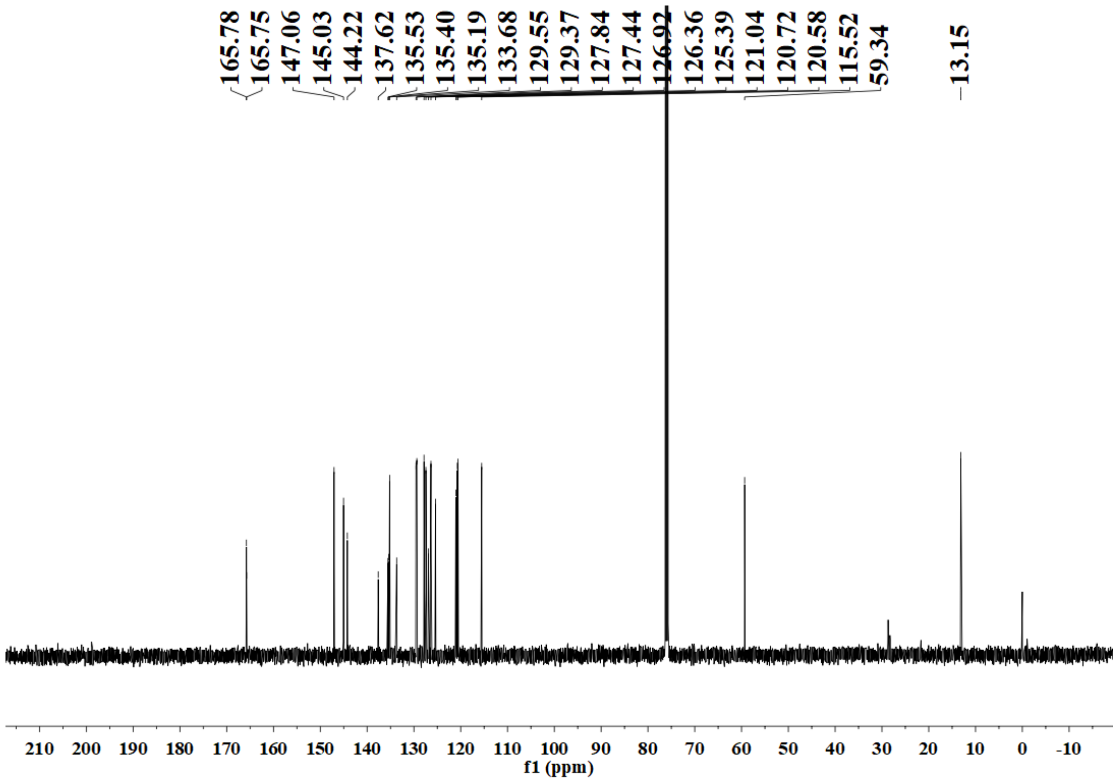
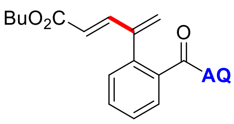
f1 (ppm)



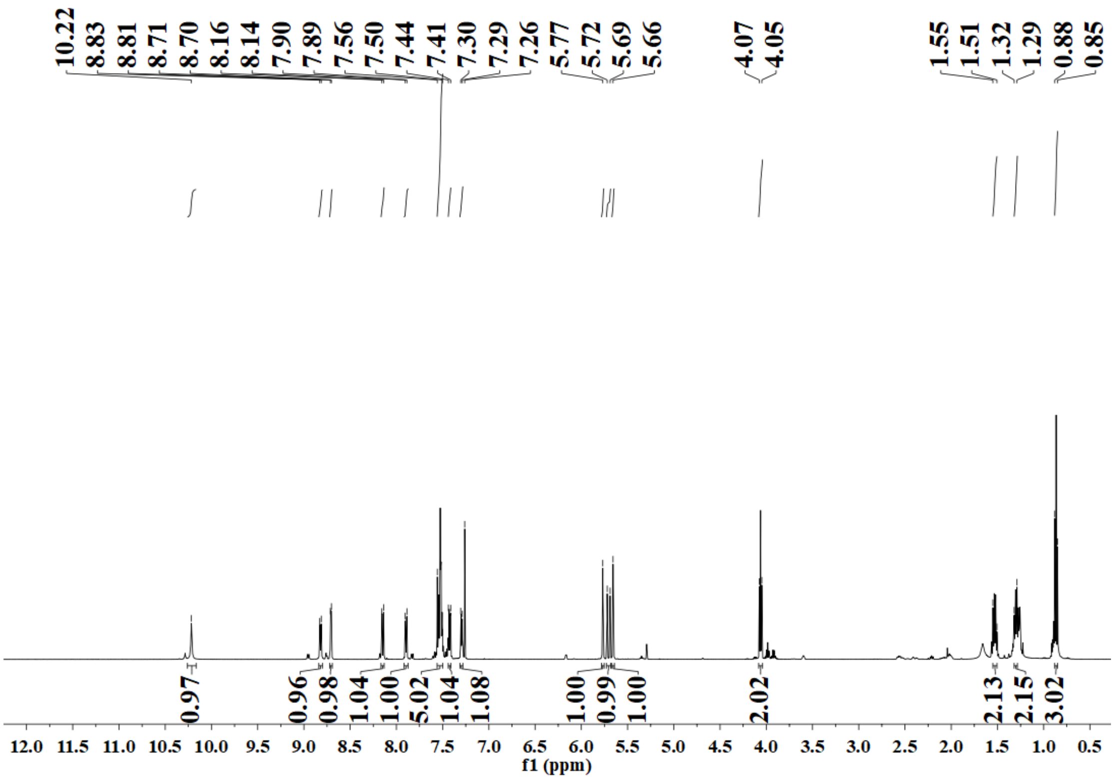
(3s)






BuO2C
O
AQ

(3t)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8.81
8.71
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7.90
7.89
7.56
7.50
7.44
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7.30
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7.26
5.77
5.72
5.69
5.66
4.07
4.05
1.55
1.51
1.32
1.29
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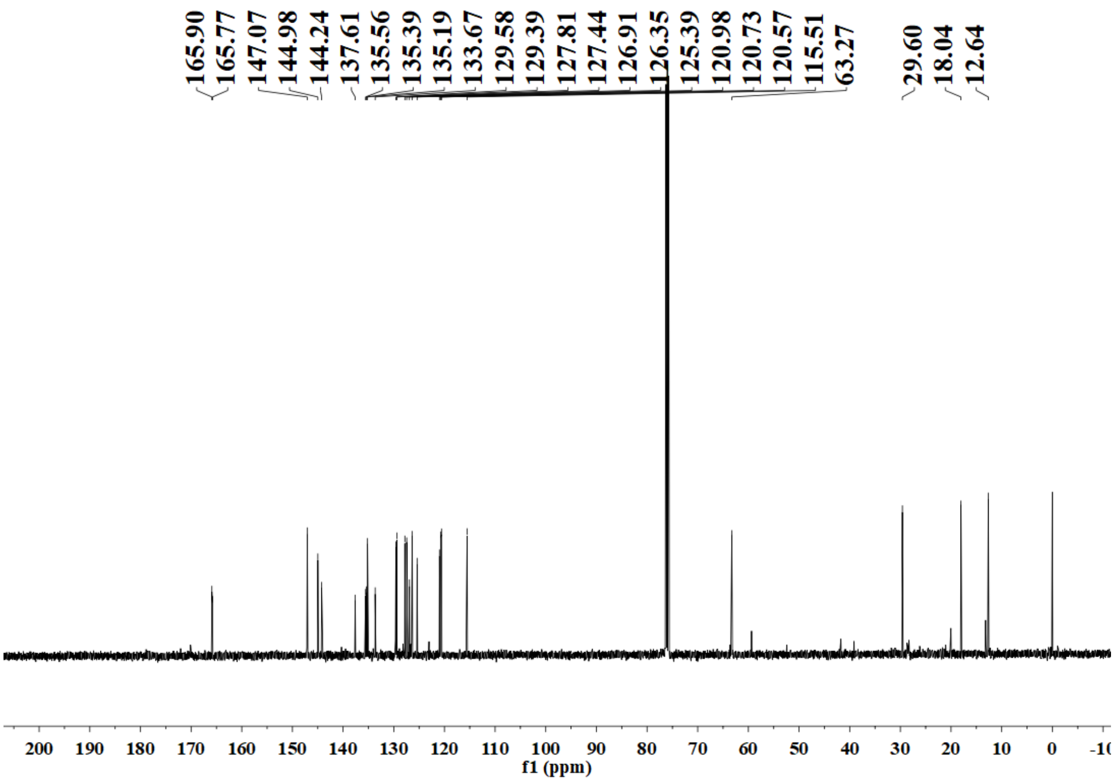
0.85
0.97
0.96
0.98
1.04
1.00
5.02
1.04
1.08
1.00
0.99
1.00
2.02
2.13
2.15
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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126.91
126.35
125.39
120.98
120.73
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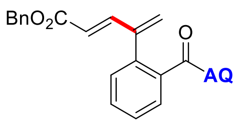
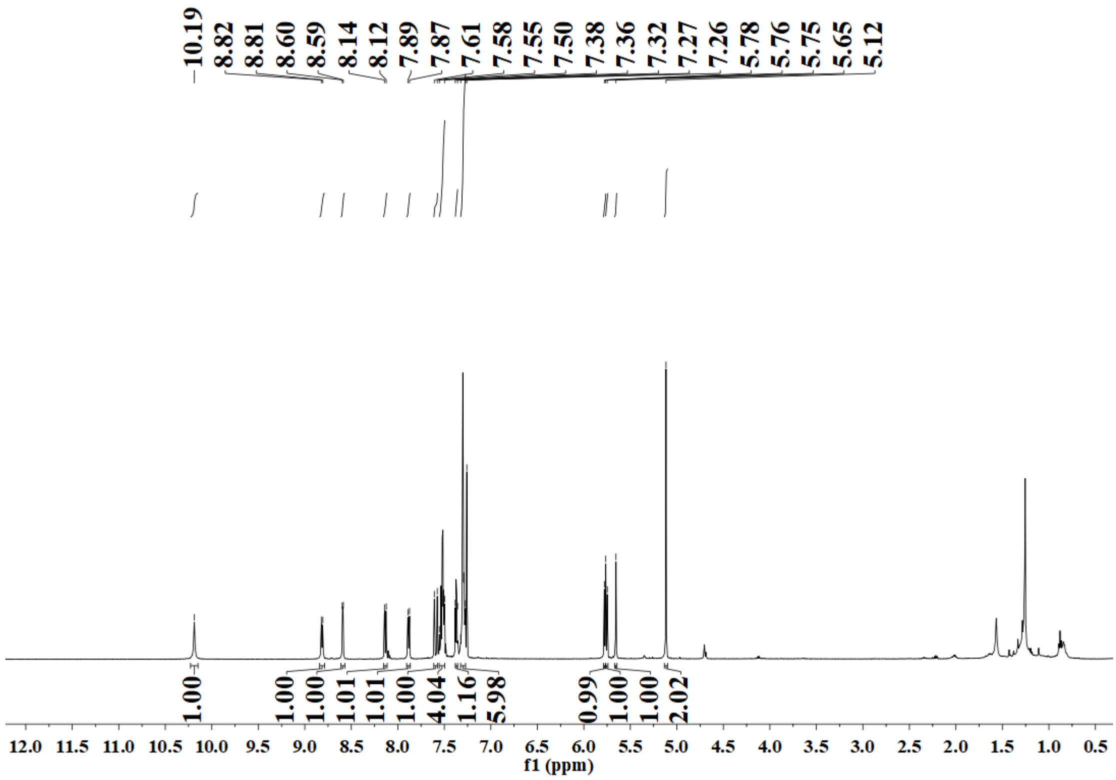
29.60
18.04
12.64
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


BnO2C
O
AQ

(3u)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7.50
7.38
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7.27
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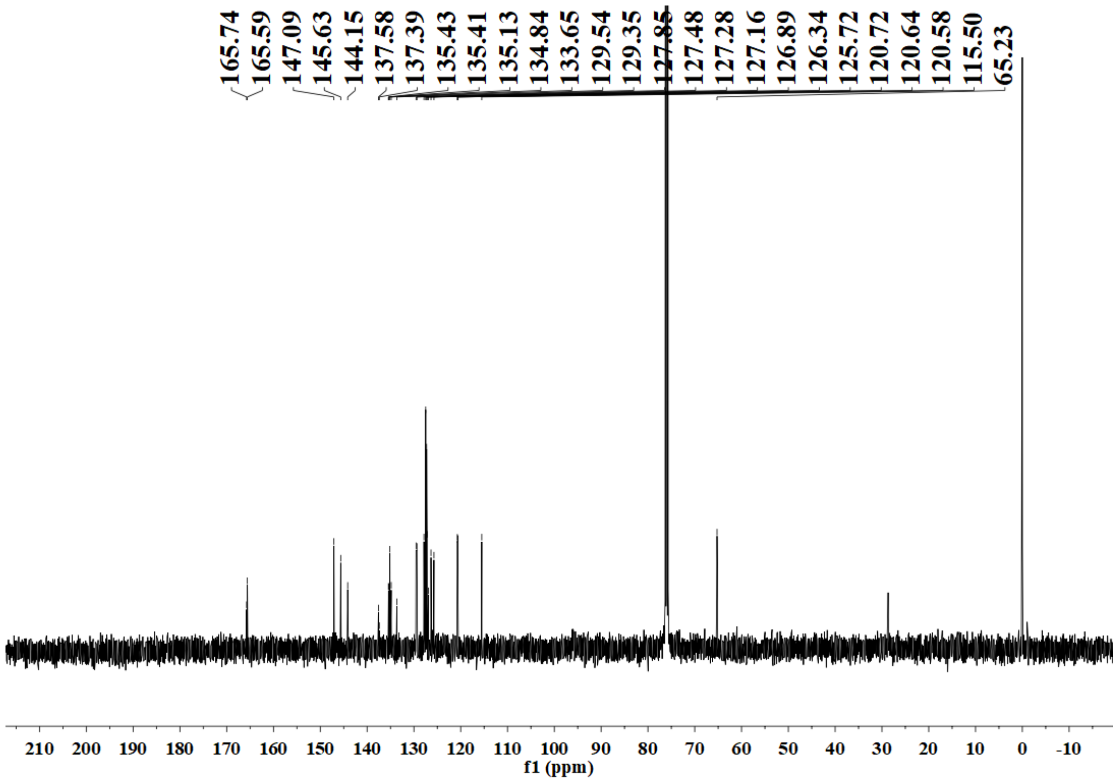
5.78
5.76
5.75
5.65
5.12
1.00
1.00
1.00
1.01
1.01
1.00
4.04
1.16
5.98
0.99
1.00
1.00
2.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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127.28
127.16
126.89
126.34
125.72
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120.58
115.50
65.23
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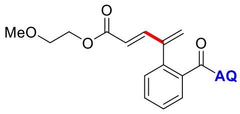
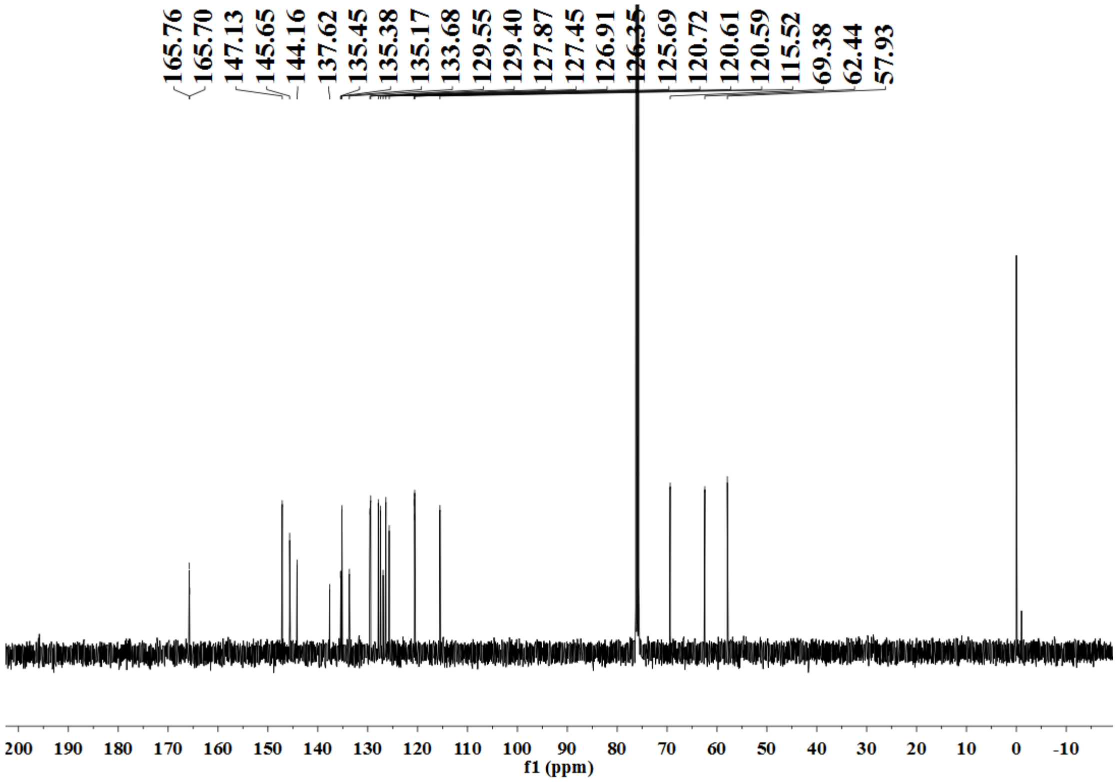
f1 (ppm)



MeO
O
O
O
AQ

(3v)



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127.87
127.45
126.91
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125.69
120.72
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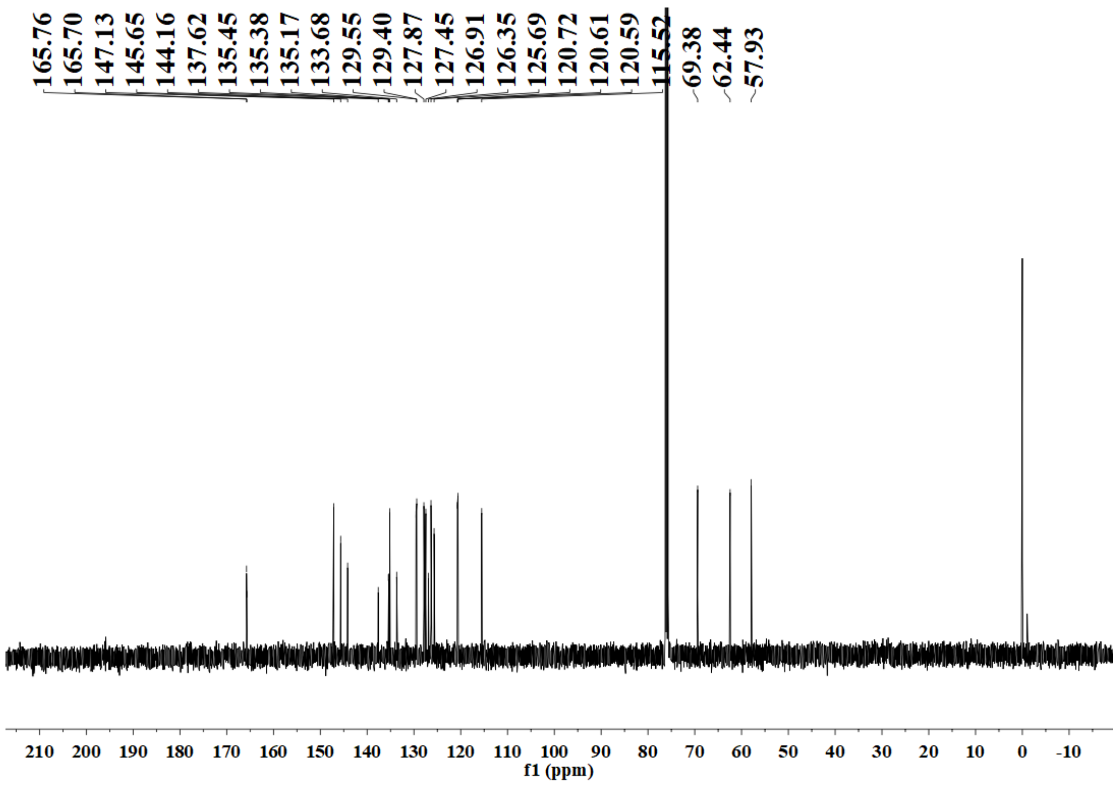
57.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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127.87
127.45
126.91
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120.72
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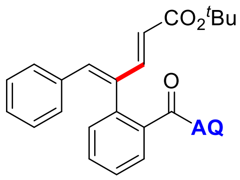
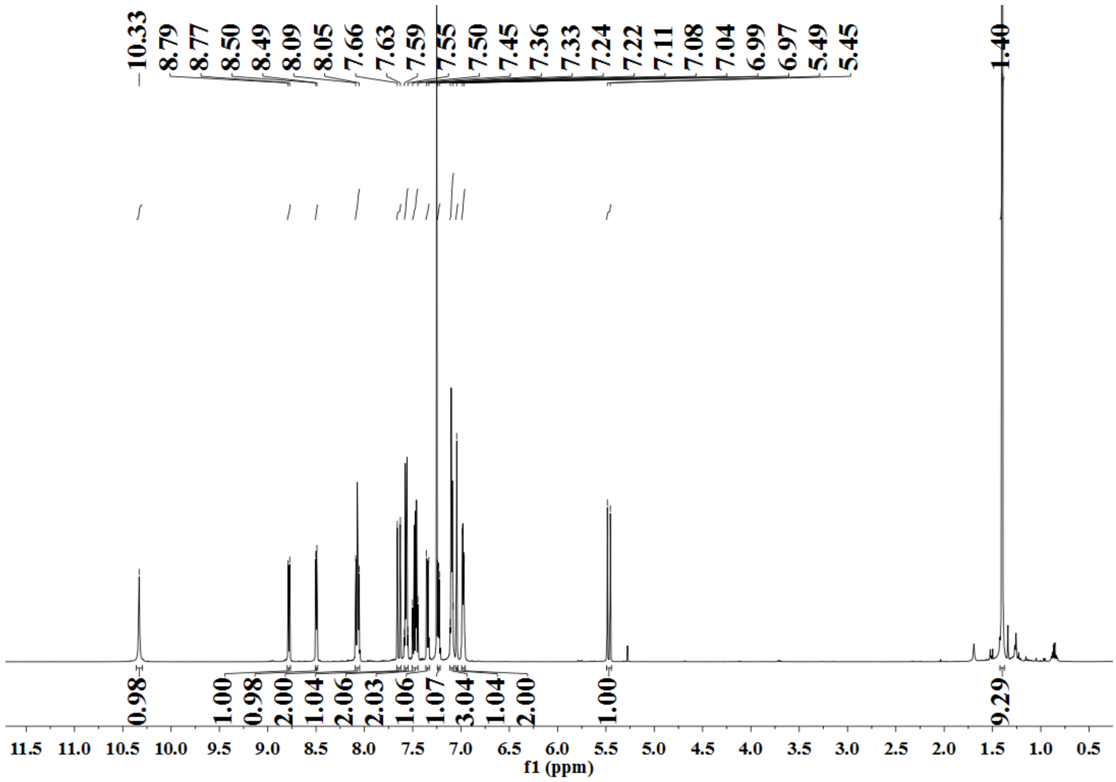
57.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CO2tBu
O
AQ

(3w)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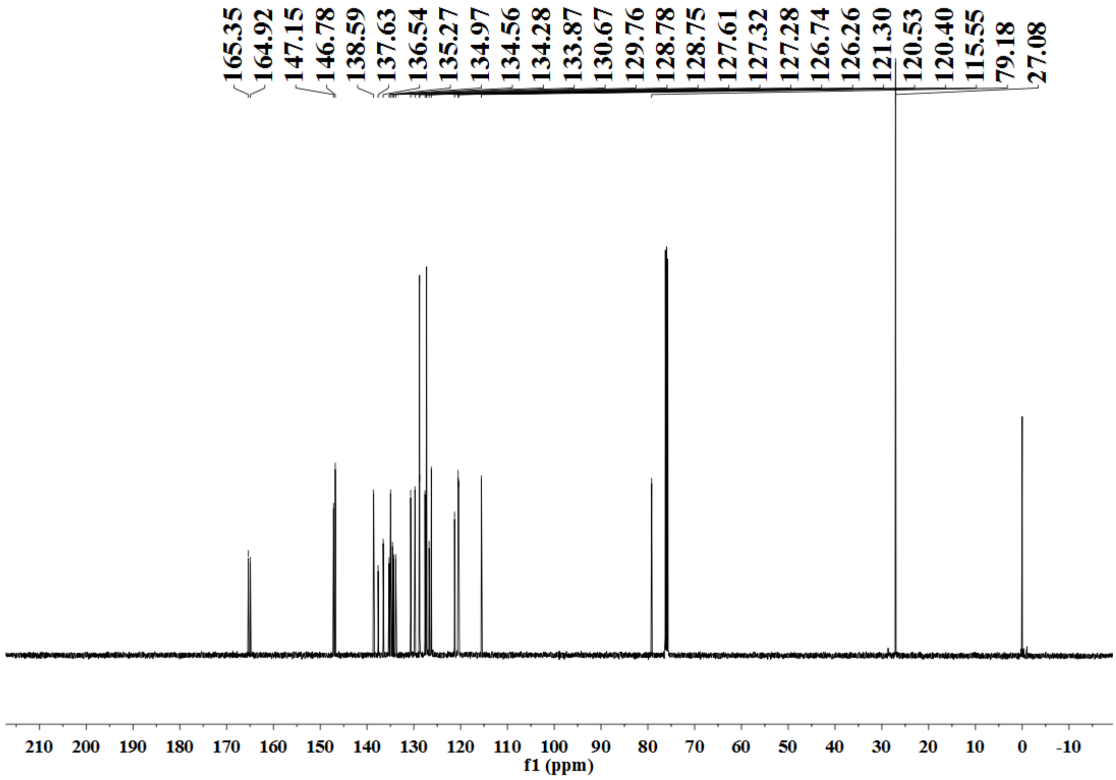
8.49
8.09
8.05
7.66
7.63
7.59
7.55
7.50
7.45
7.36
7.33
7.24
7.22
7.11
7.08
7.04
6.99
6.97
5.49
5.45
1.40
0.98
1.00
0.98
2.00
1.04
2.06
2.03
1.06
1.07
3.04
1.04
2.00
1.00
9.29
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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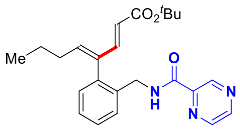
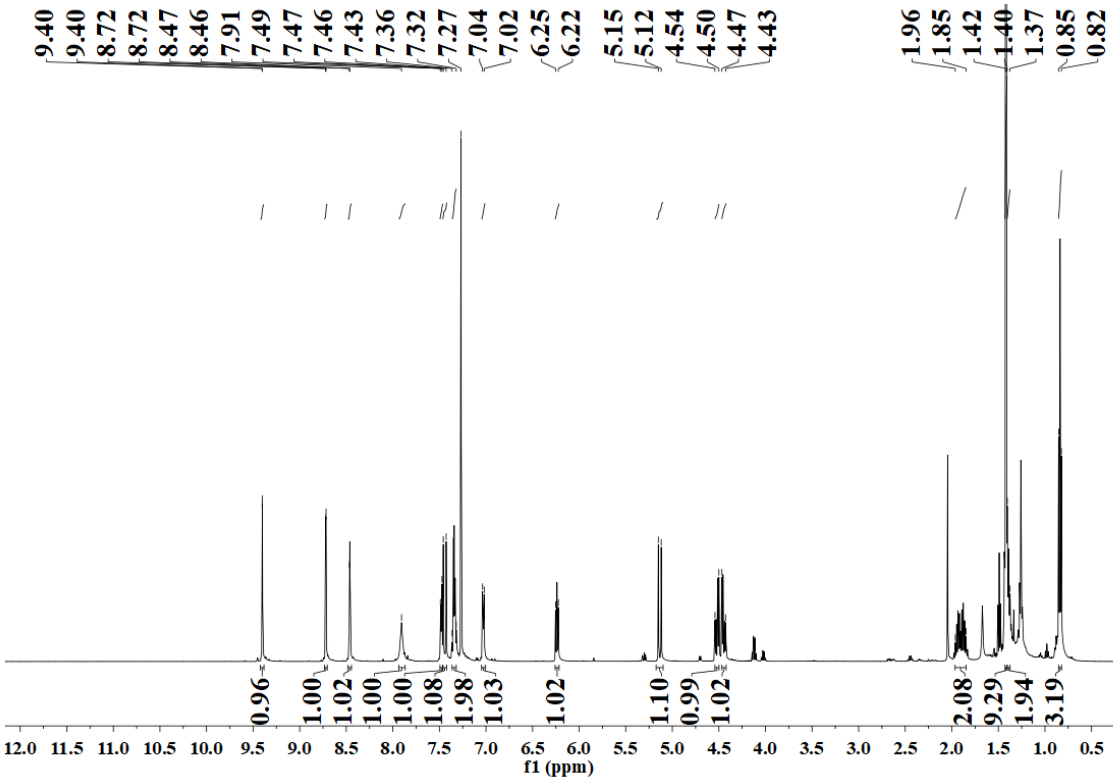
130.67
129.76
128.78
128.75
127.61
127.32
127.28
126.74
126.26
121.30
120.53
120.40
115.55
79.18
27.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CO2tBu
Me
O
N
H
N
N
(3x)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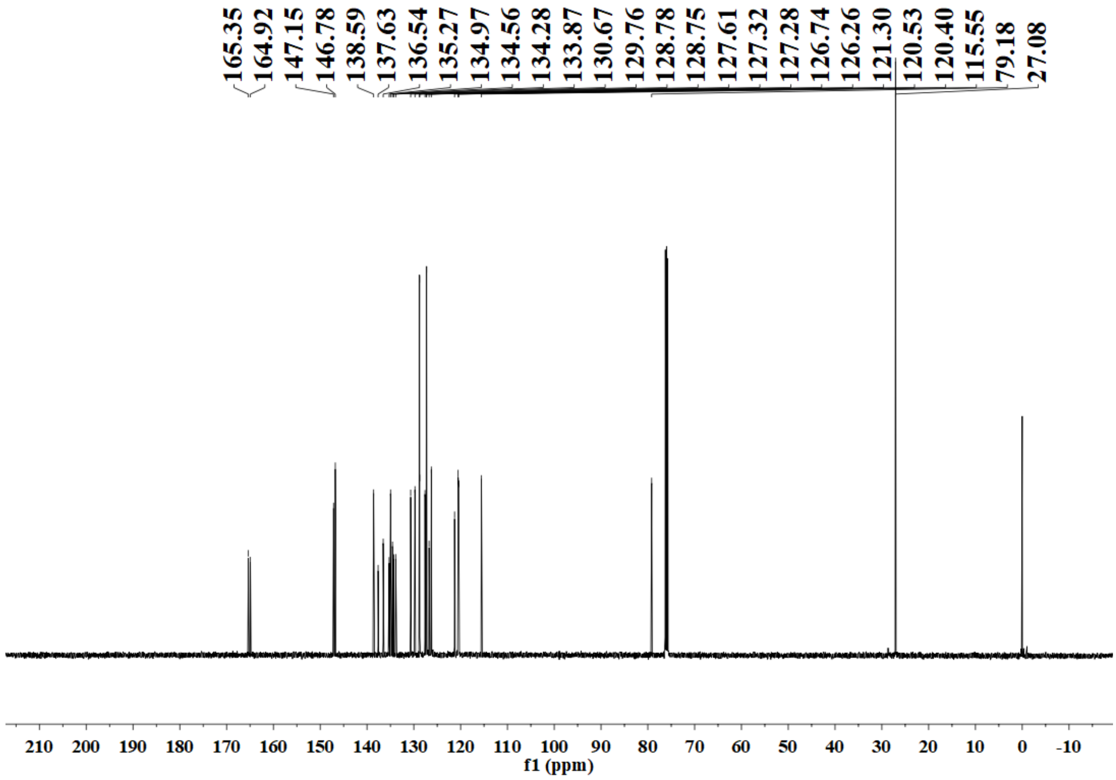
7.49
7.47
7.46
7.43
7.36
7.32
7.27
7.04
7.02
6.25
6.22
5.15
5.12
4.54
4.50
4.47
4.43
1.96
1.85
1.42
1.40
1.37
0.85
0.82
0.96
1.00
1.02
1.00
1.00
1.08
1.98
1.03
1.02
1.10
0.99
1.02
2.08
9.29
1.94
3.19
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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128.78
128.75
127.61
127.32
127.28
126.74
126.26
121.30
120.53
120.40
115.55
79.18
27.08
210
200
190
180
170
160
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140
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120
110
100
90
80
70
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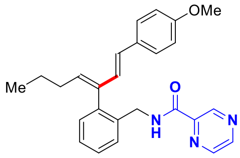
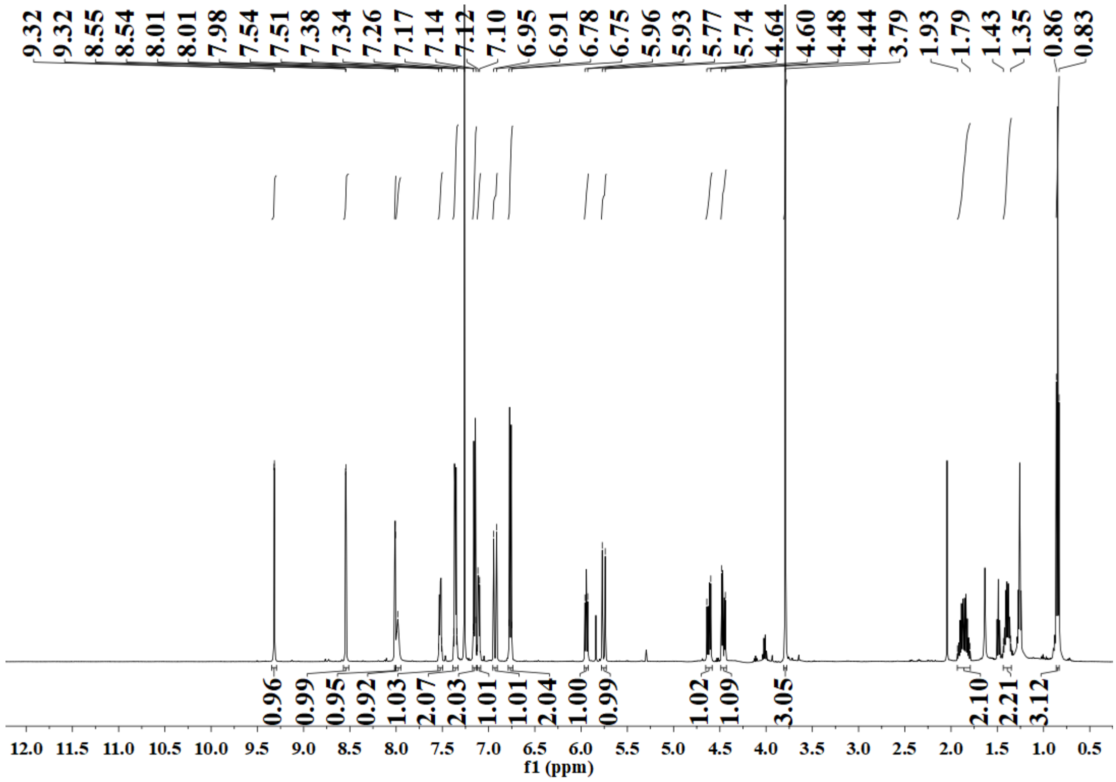
40
30
20
10
0
-10
f1 (ppm)


OMe
Me
O
N
H
N
N

(3y)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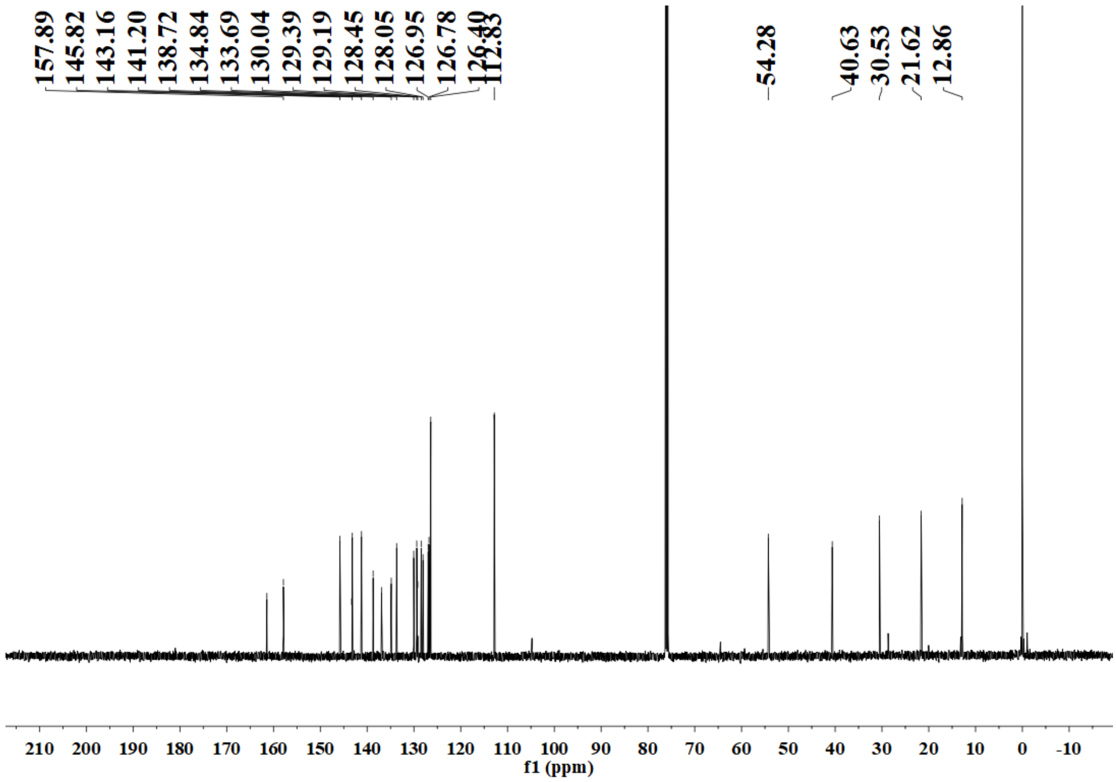
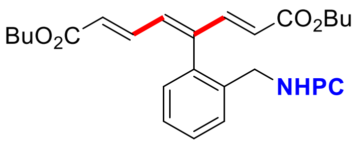
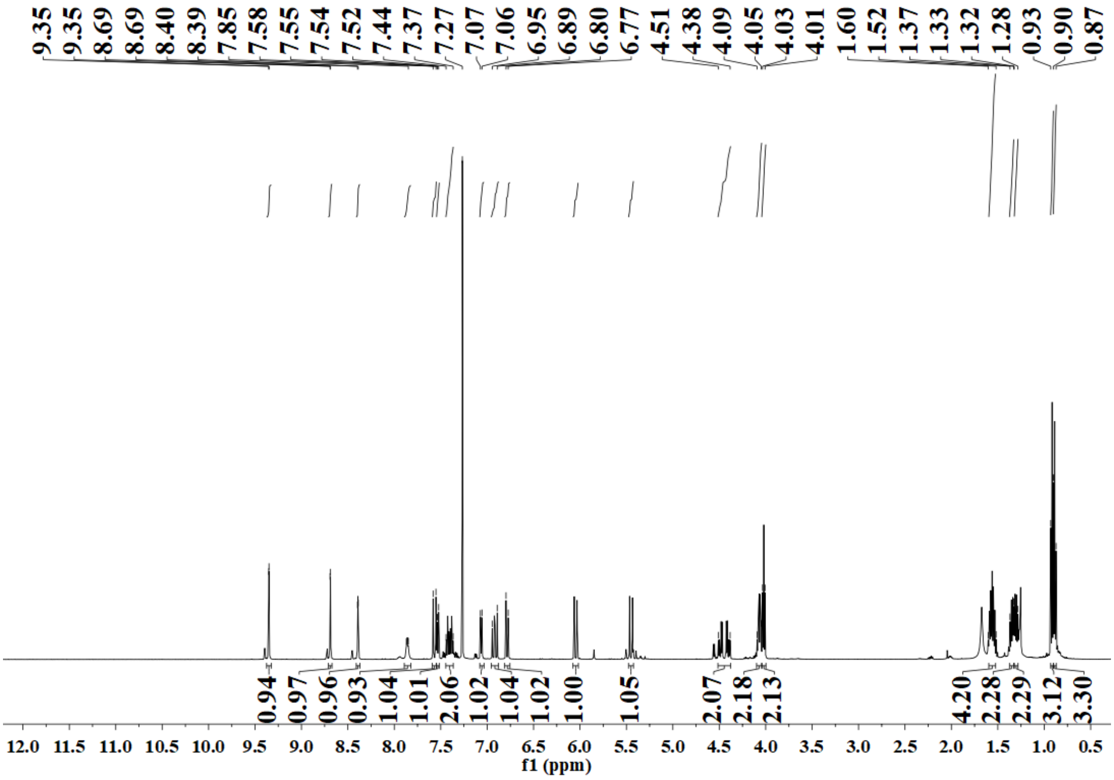
0.96 0.99 0.95 0.92 1.03 2.07 2.03 1.01 1.01 2.04 1.00 0.99 1.02 1.09 3.05 2.10 2.21 3.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


157.89 145.82 143.16 141.20 138.72 134.84 133.69 130.04 129.39 129.19 128.45 128.05 126.95 126.78 126.40 112.83
54.28
40.63 30.53 21.62 12.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


BuO2C
CO2Bu
NHPC

(5a)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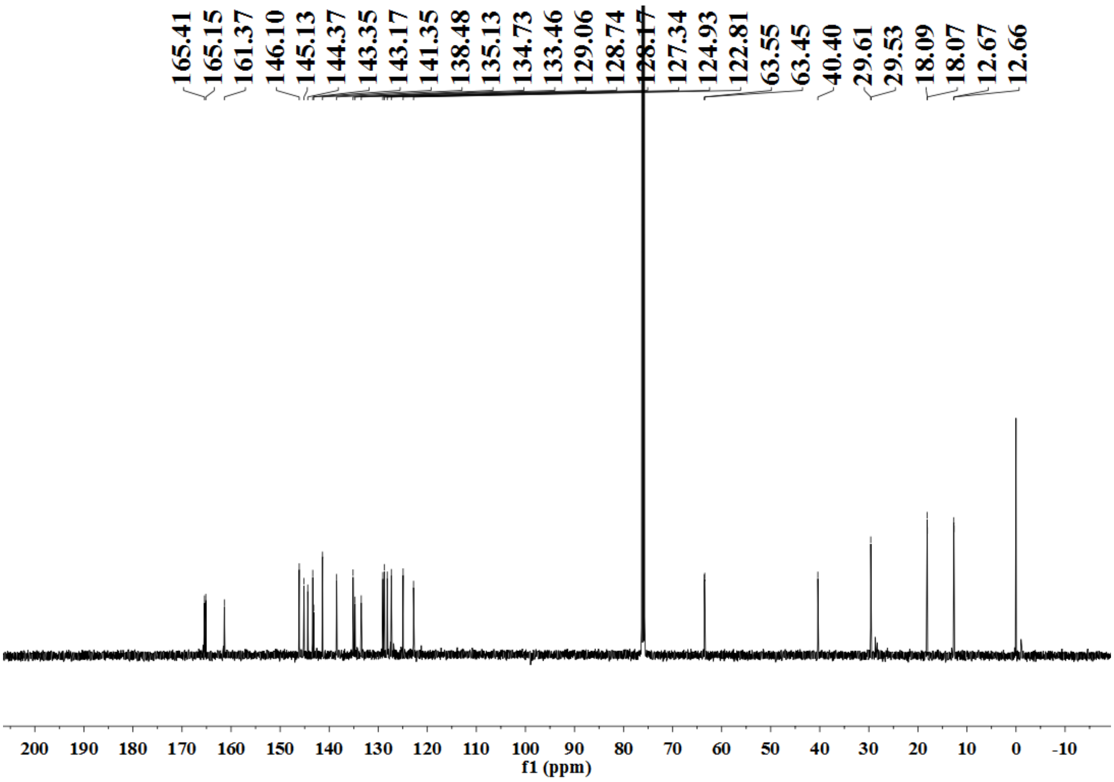
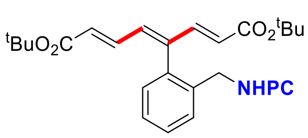
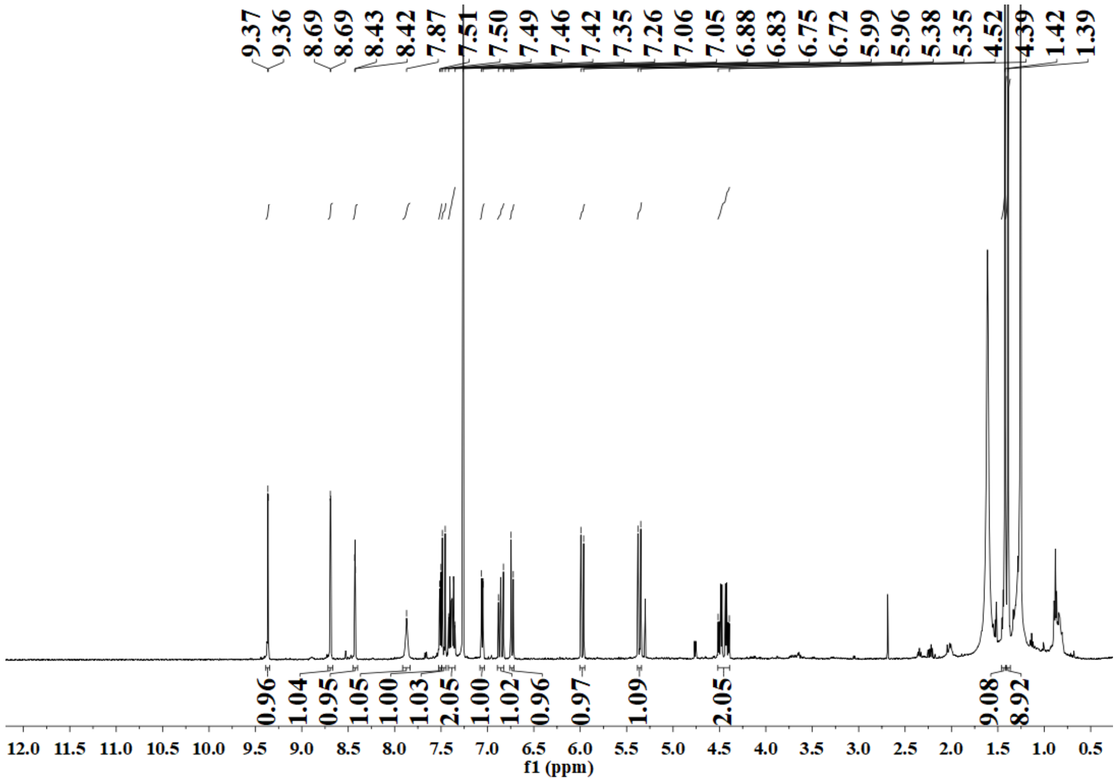
0.94 0.97 0.96 0.93 1.04 1.01 2.06 1.02 1.04 1.02 1.00 1.05 2.07 2.18 2.13 4.20 2.28 2.29 3.12 3.30
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


165.41 165.15 161.37 146.10 145.13 144.37 143.35 143.17 141.35 138.48 135.13 134.73 133.46 129.06 128.74 128.17 127.34 124.93 122.81 63.55 63.45 40.40 29.61 29.53 18.09 18.07 12.67 12.66
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



tBuO2C
CO2tBu
NHPC

(5b)



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7.51
7.50
7.49
7.46
7.42
7.35
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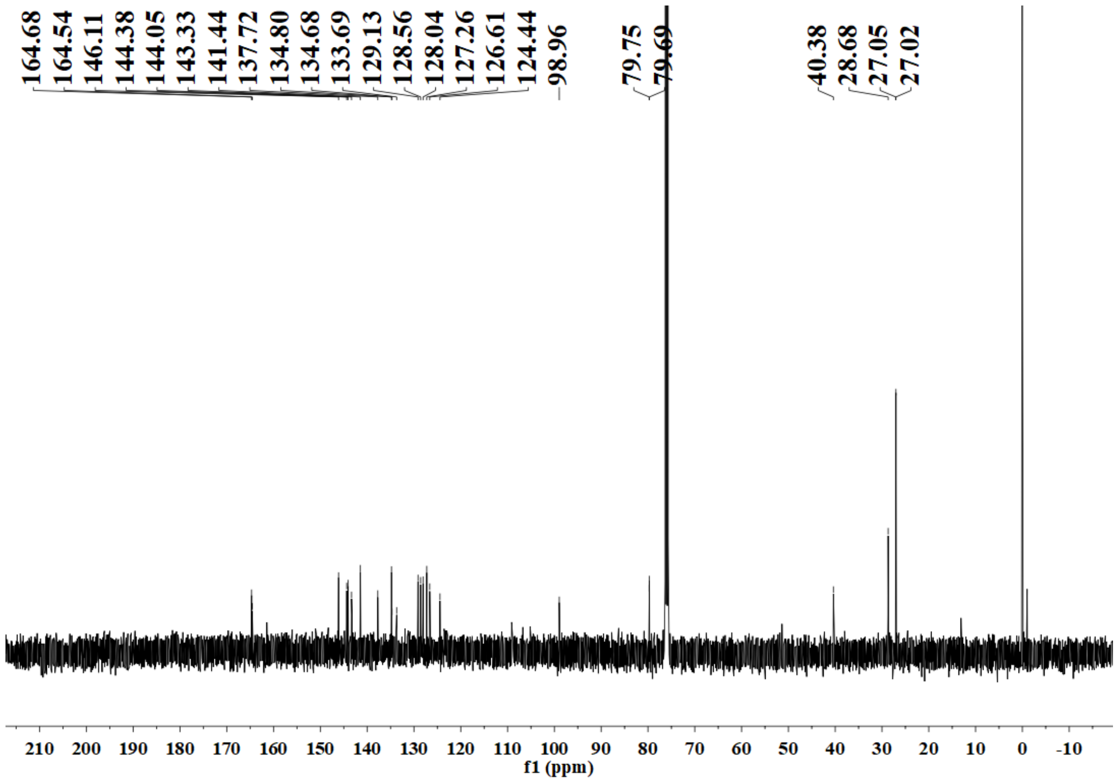
7.06
7.05
6.88
6.83
6.75
6.72
5.99
5.96
5.38
5.35
4.52
4.39
1.42
1.39
0.96
1.04
0.95
1.05
1.00
1.03
2.05
1.00
1.02
0.96
0.97
1.09
2.05
9.08
8.92
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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143.33
141.44
137.72
134.80
134.68
133.69
129.13
128.56
128.04
127.26
126.61
124.44
98.96
79.75
79.69
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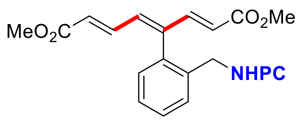
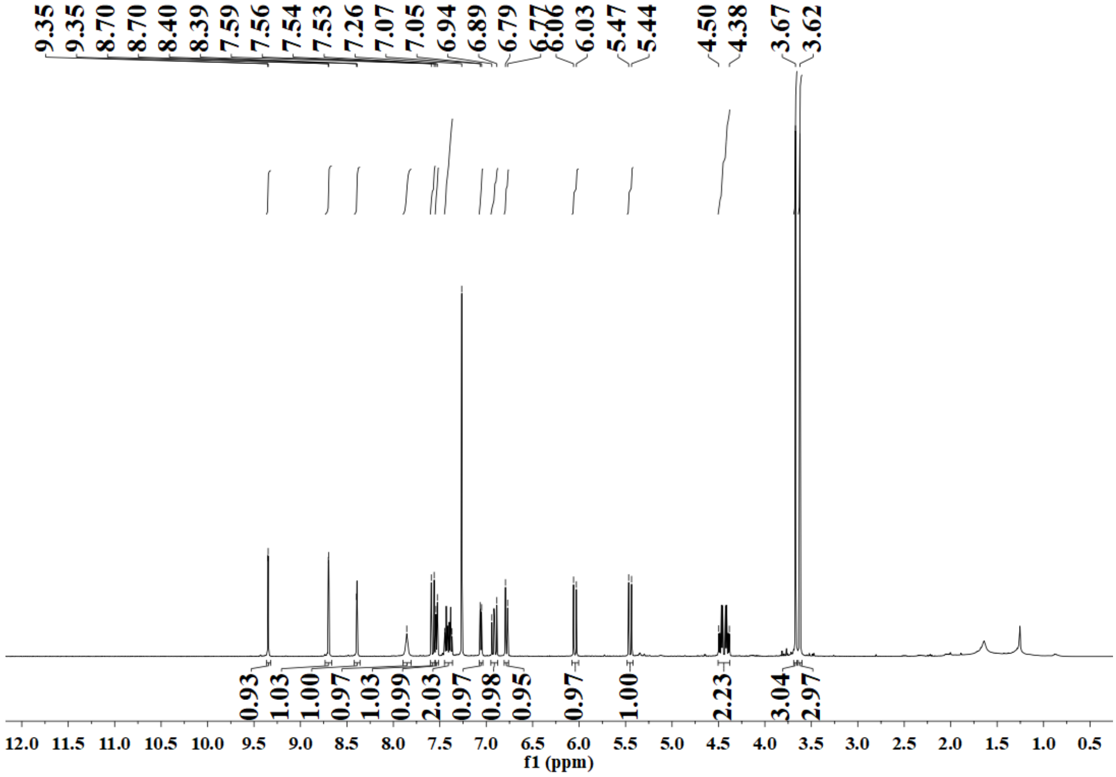
28.68
27.05
27.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO2C
CO2Me
NHPC

(5c)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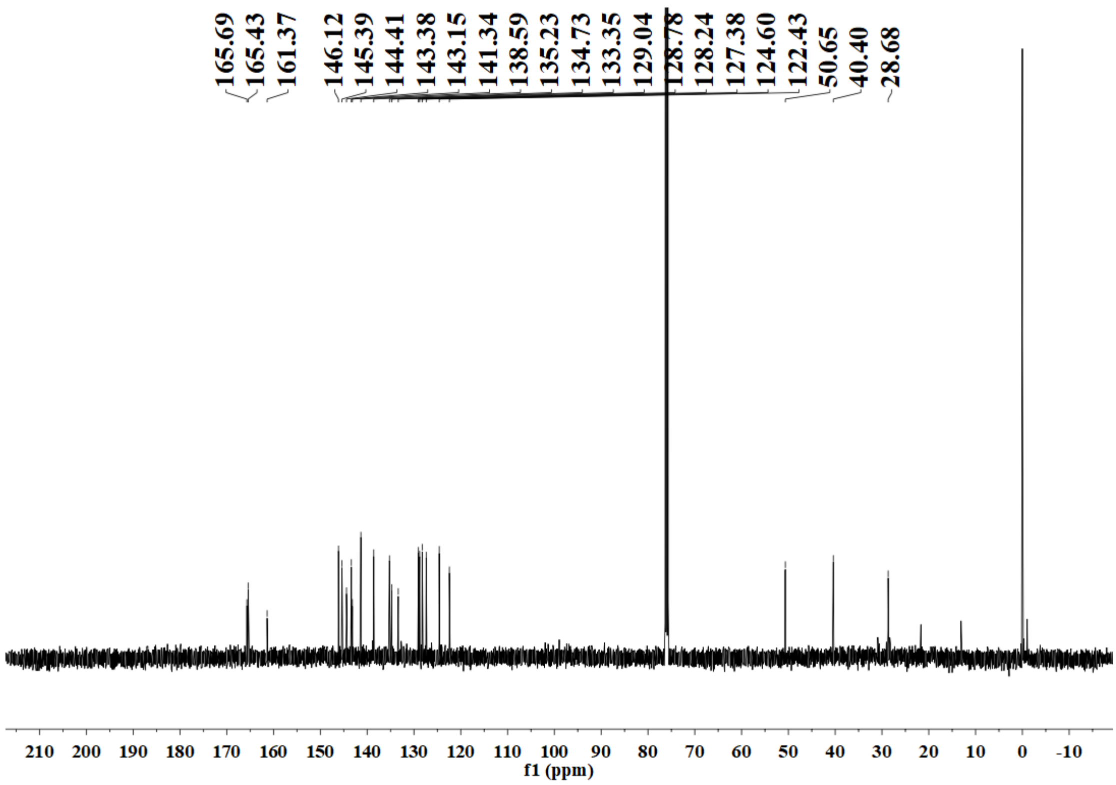
8.39
7.59
7.56
7.54
7.53
7.26
7.07
7.05
6.94
6.89
6.79
6.77
6.06
6.03
5.47
5.44
4.50
4.38
3.67
3.62
0.93
1.03
1.00
0.97
1.03
0.99
2.03
0.97
0.98
0.95
0.97
1.00
2.23
3.04
2.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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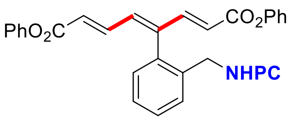
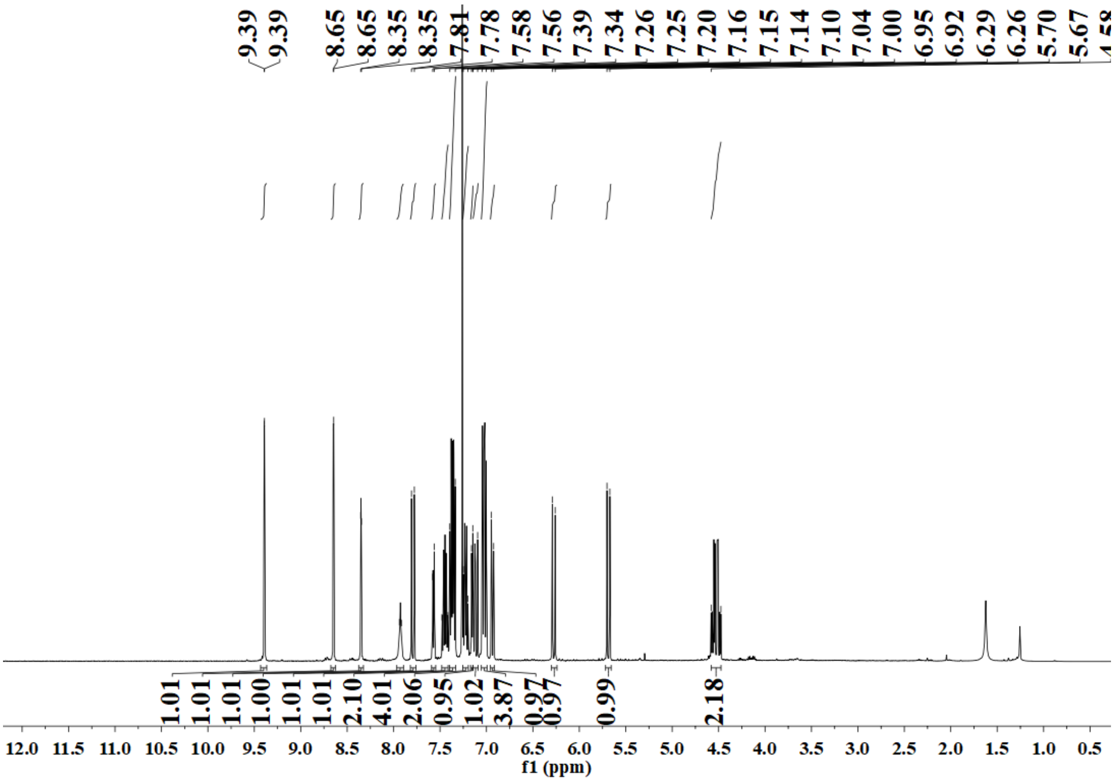
143.38
143.15
141.34
138.59
135.23
134.73
133.35
129.04
128.78
128.24
127.38
124.60
122.43
50.65
40.40
28.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


PhO2C
CO2Ph
NHPC

(5d)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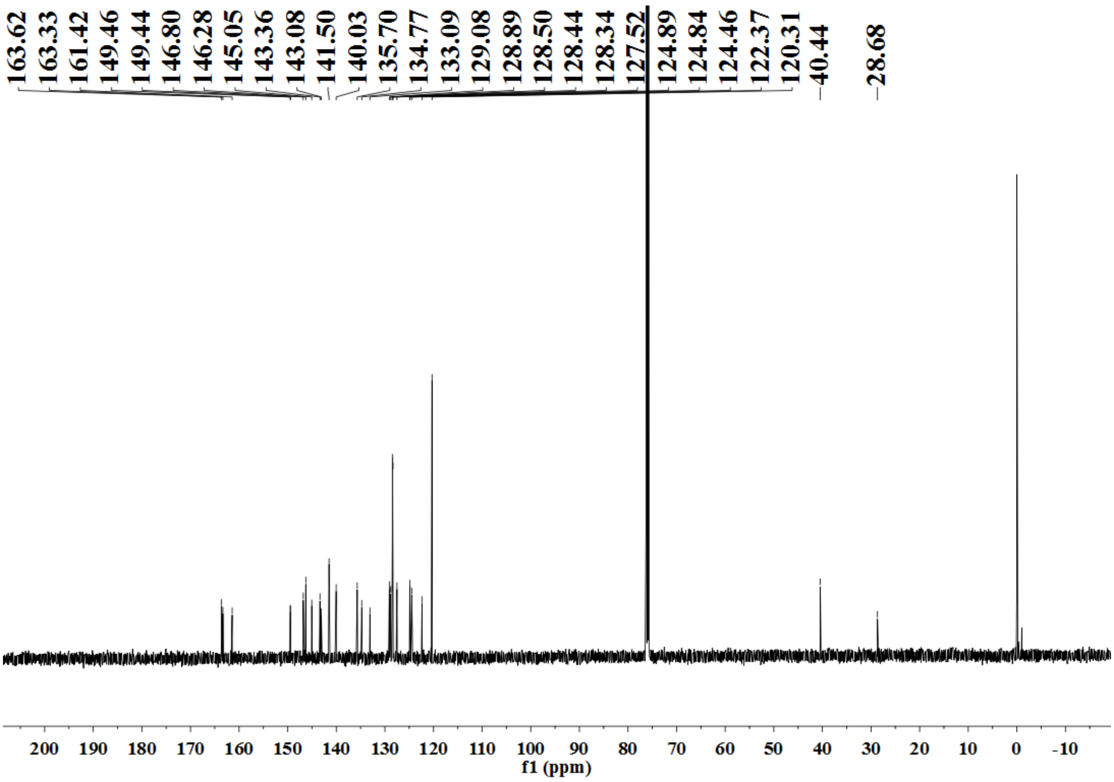
7.26
7.25
7.20
7.16
7.15
7.14
7.10
7.04
7.00
6.95
6.92
6.29
6.26
5.70
5.67
1.01
1.01
1.01
1.00
1.01
1.01
2.10
4.01
2.06
0.95
1.02
3.87
0.97
0.97
0.99
2.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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140.03
135.70
134.77
133.09
129.08
128.89
128.50
128.44
128.34
127.52
124.89
124.84
124.46
122.37
120.31
40.44
28.68
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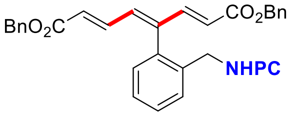
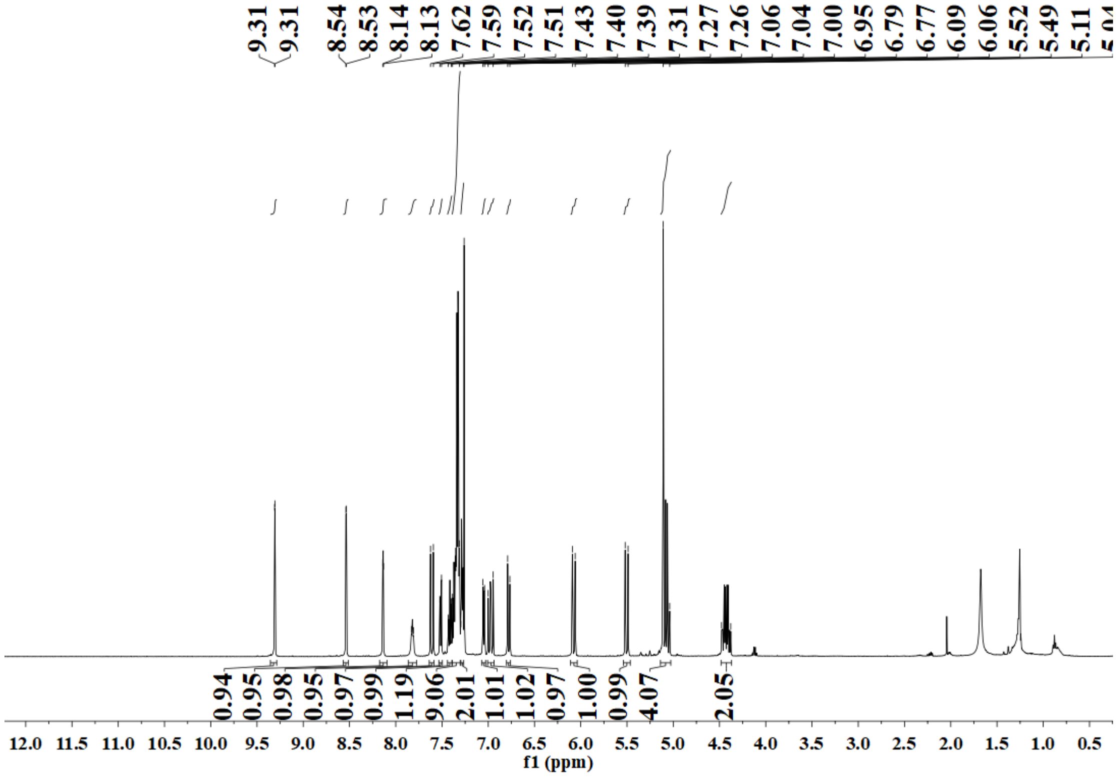
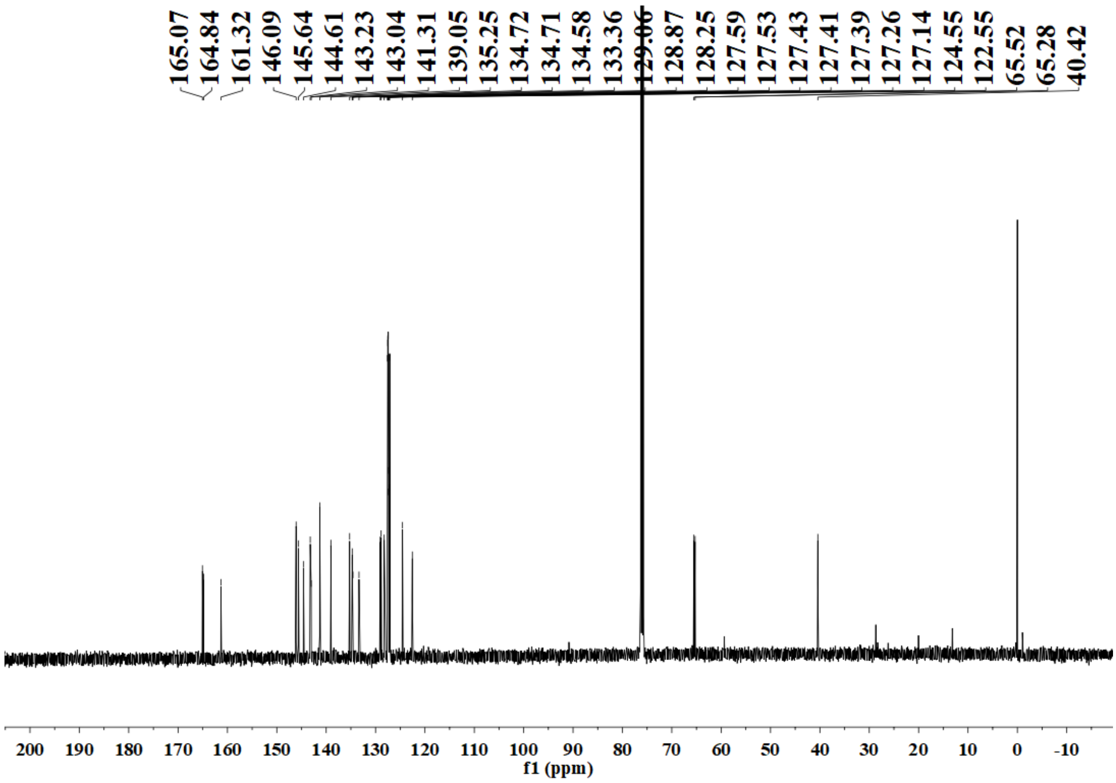
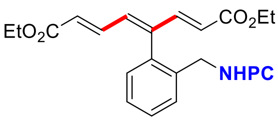
f1 (ppm)



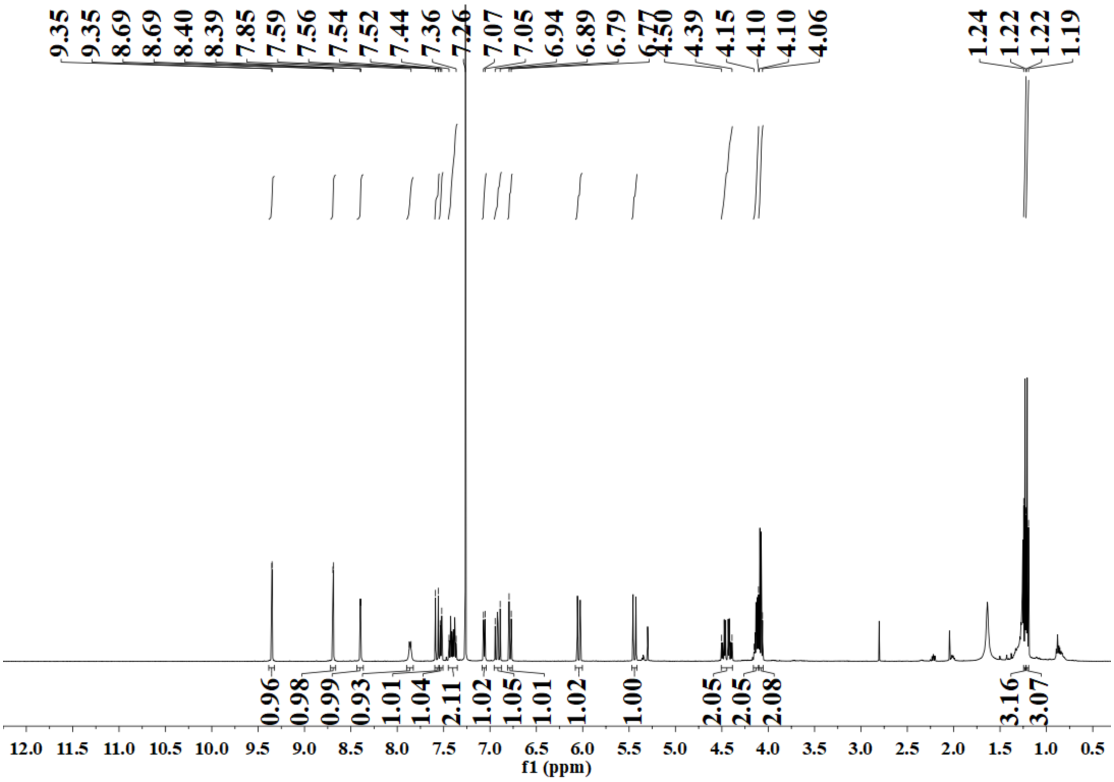
(5e)






EtO2C
CO2Et
NHPC

(5f)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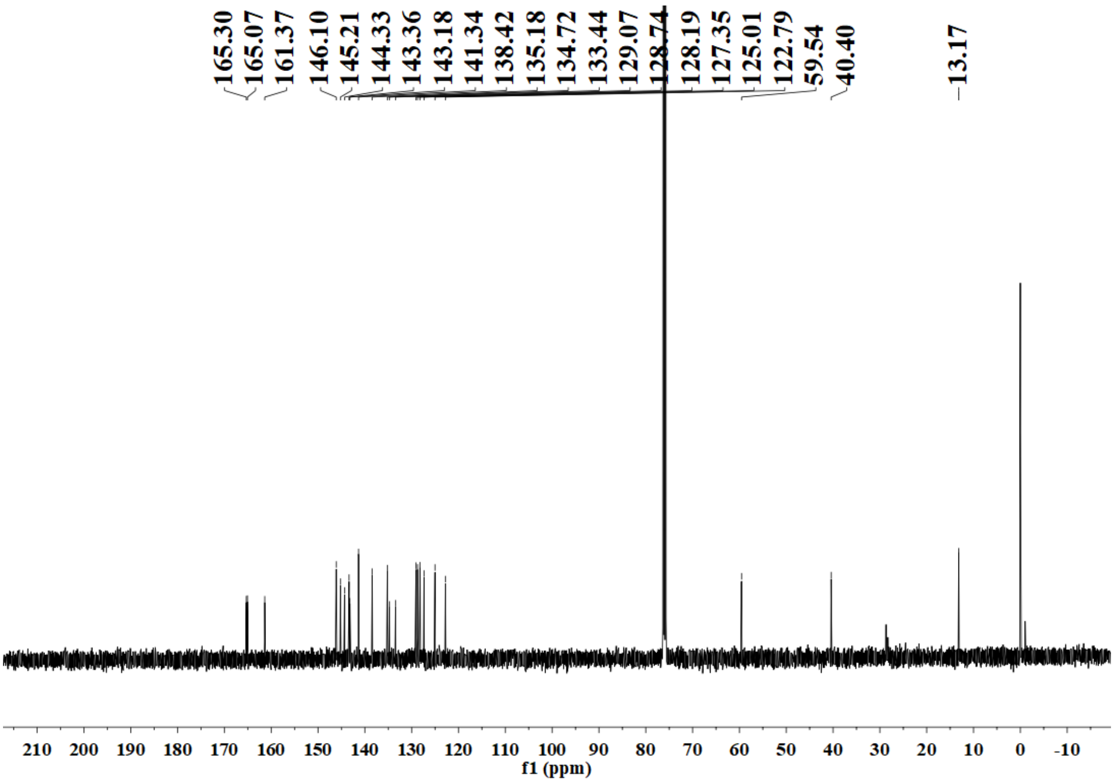
6.79
6.77
4.50
4.39
4.15
4.10
4.10
4.06
1.24
1.22
1.22
1.19
0.96
0.98
0.99
0.93
1.01
1.04
2.11
1.02
1.05
1.01
1.02
1.00
2.05
2.05
2.08
3.16
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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135.18
134.72
133.44
129.07
128.74
128.19
127.35
125.01
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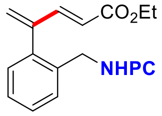
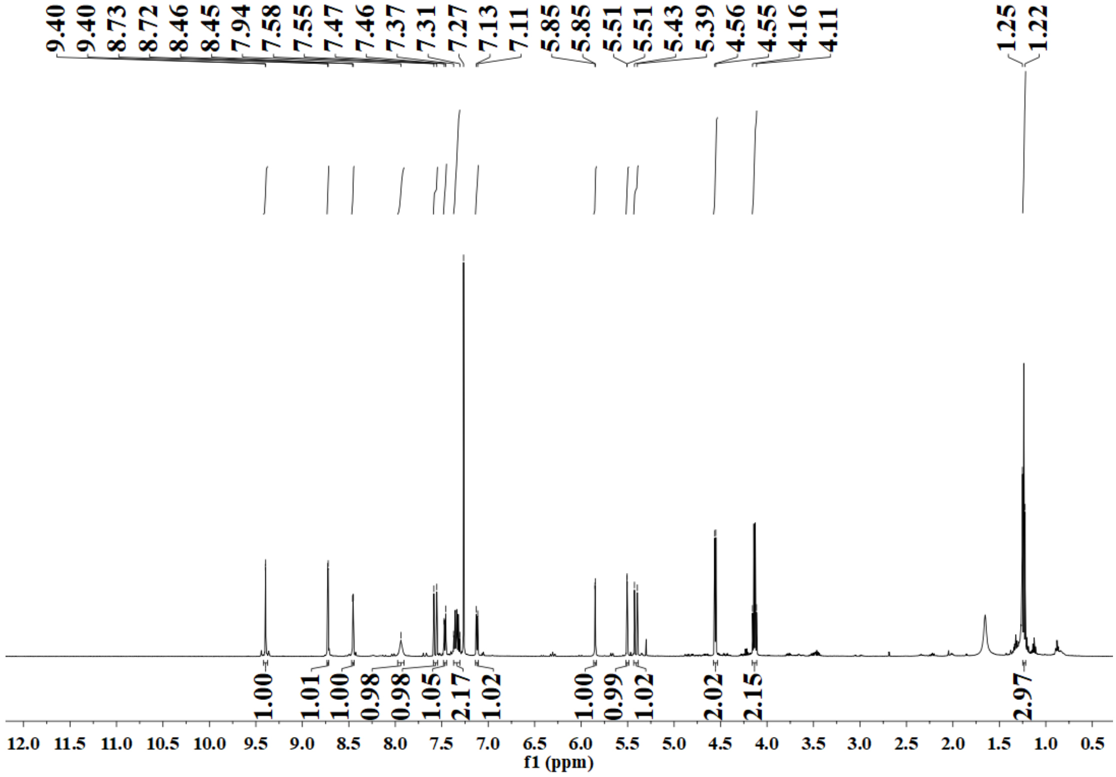
59.54
40.40
13.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



(5f')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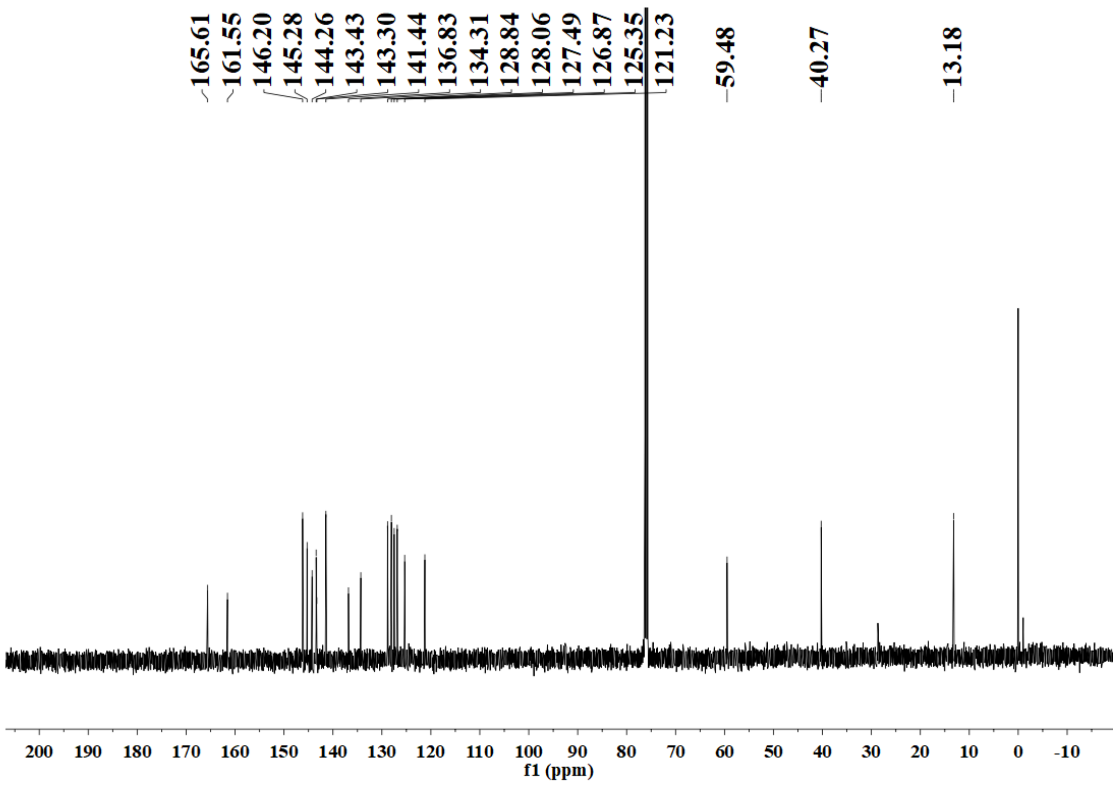
1.00 1.01 1.00 0.98 0.98 1.05 2.17 1.02 1.00 0.99 1.02 2.02 2.15 2.97
f1 (ppm)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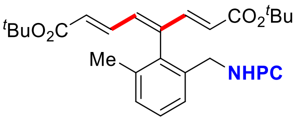
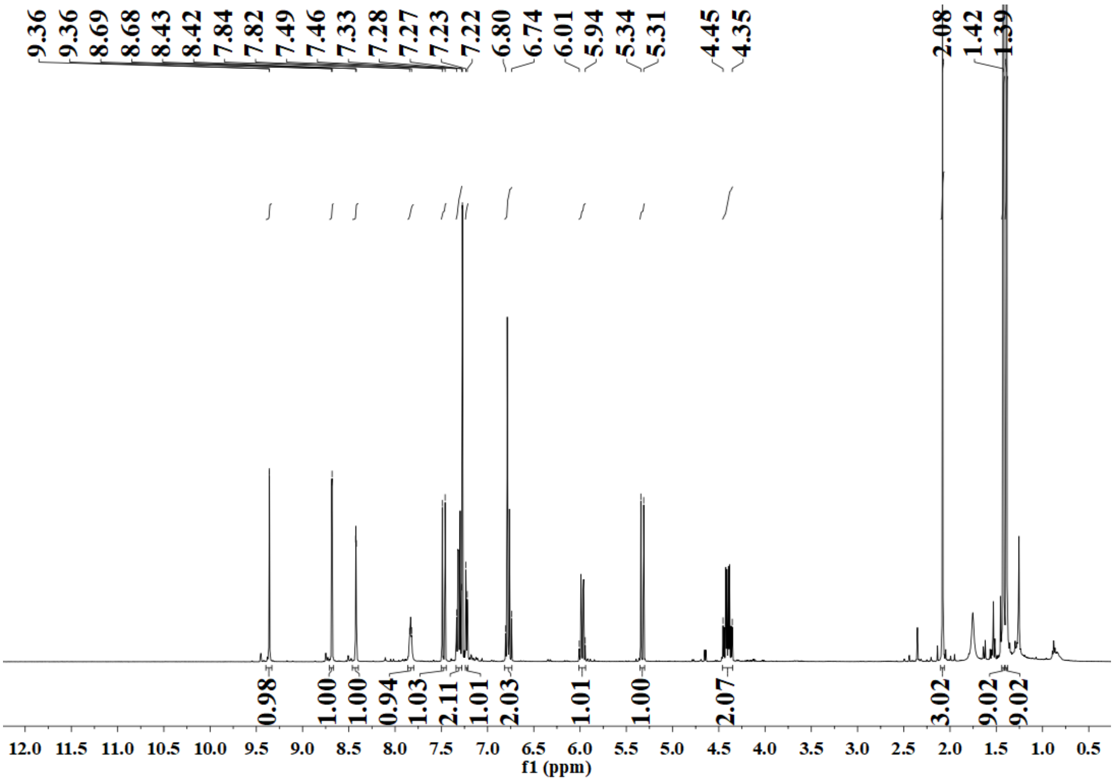
f1 (ppm)



tBuO2C
CO2tBu
Me
NHPC

(5g)



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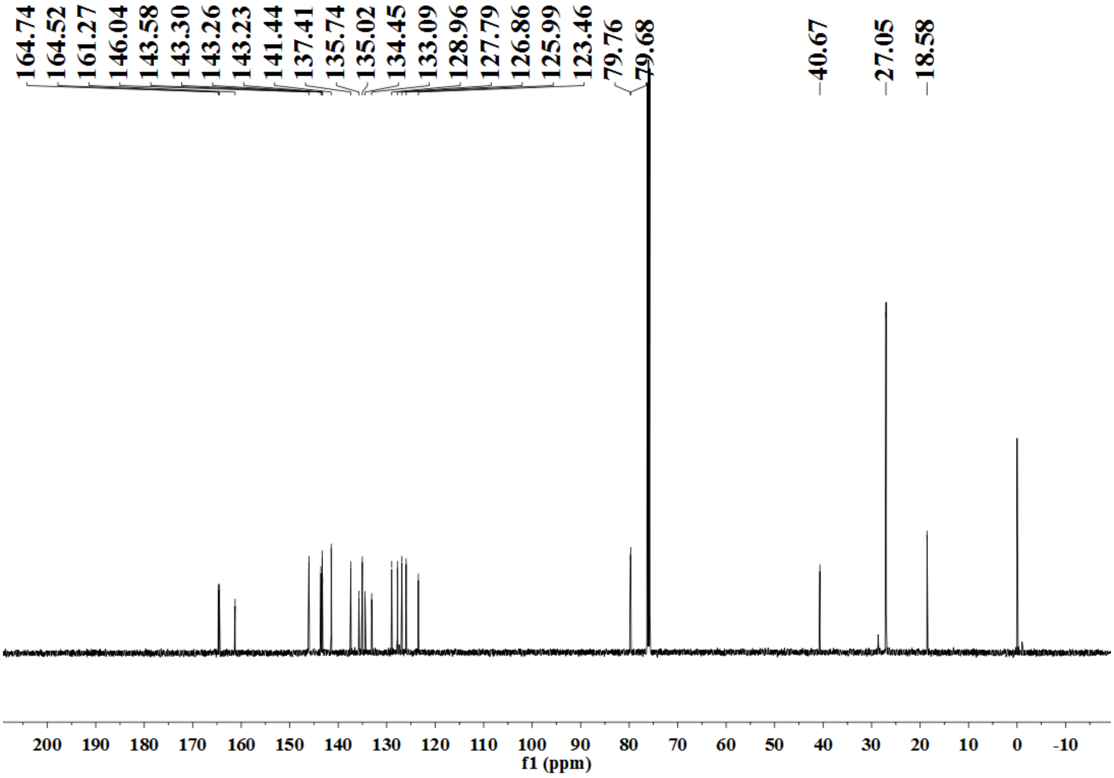
0.98 1.00 1.00 0.94 1.03 2.11 1.01 2.03 1.01 1.00 2.07 3.02 9.02 9.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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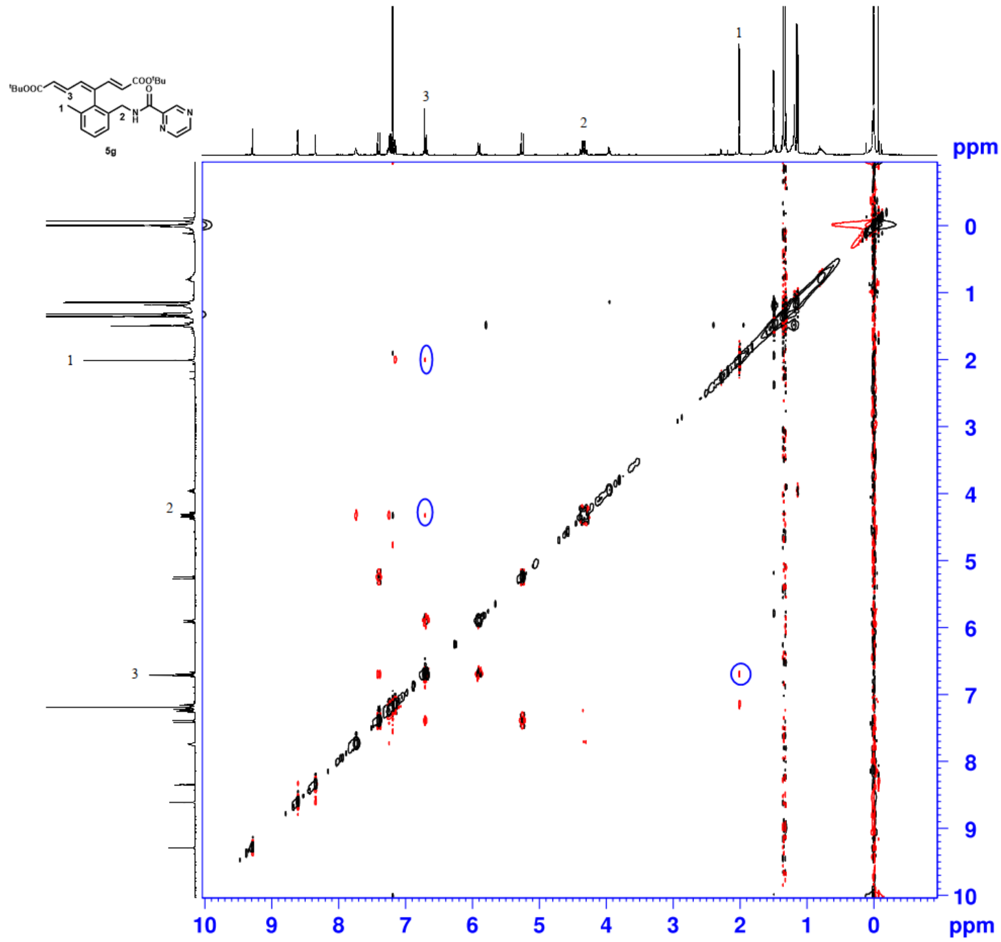
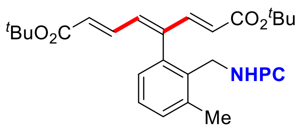
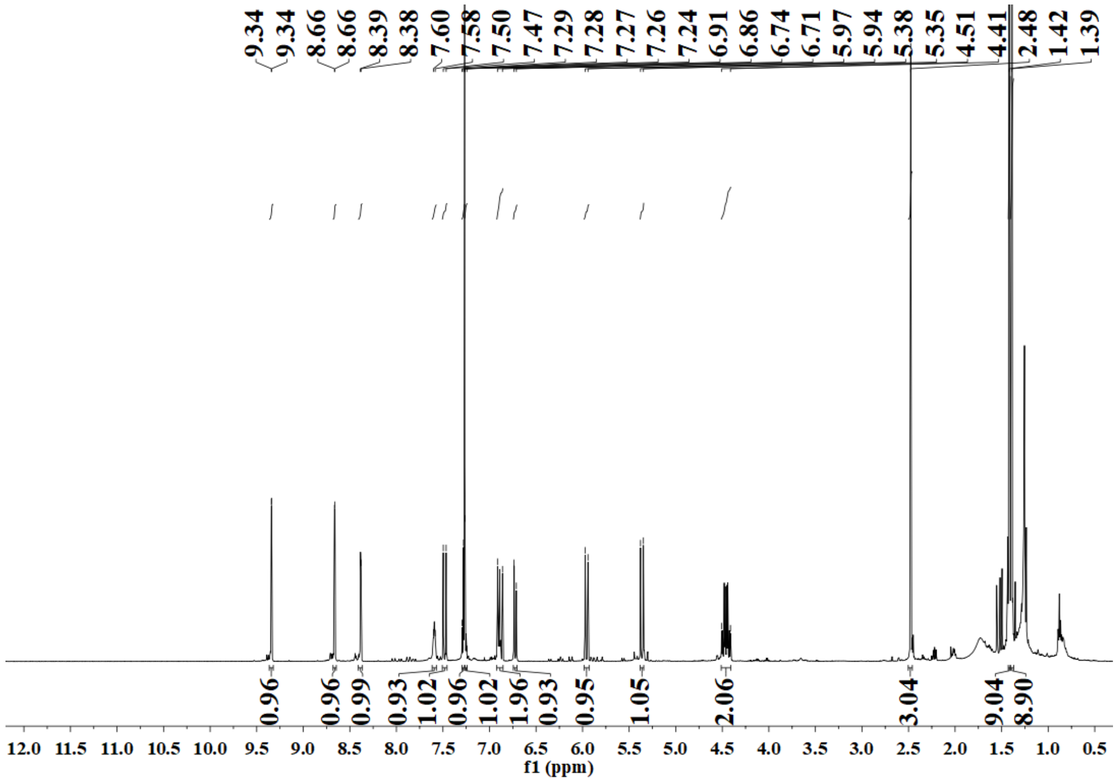
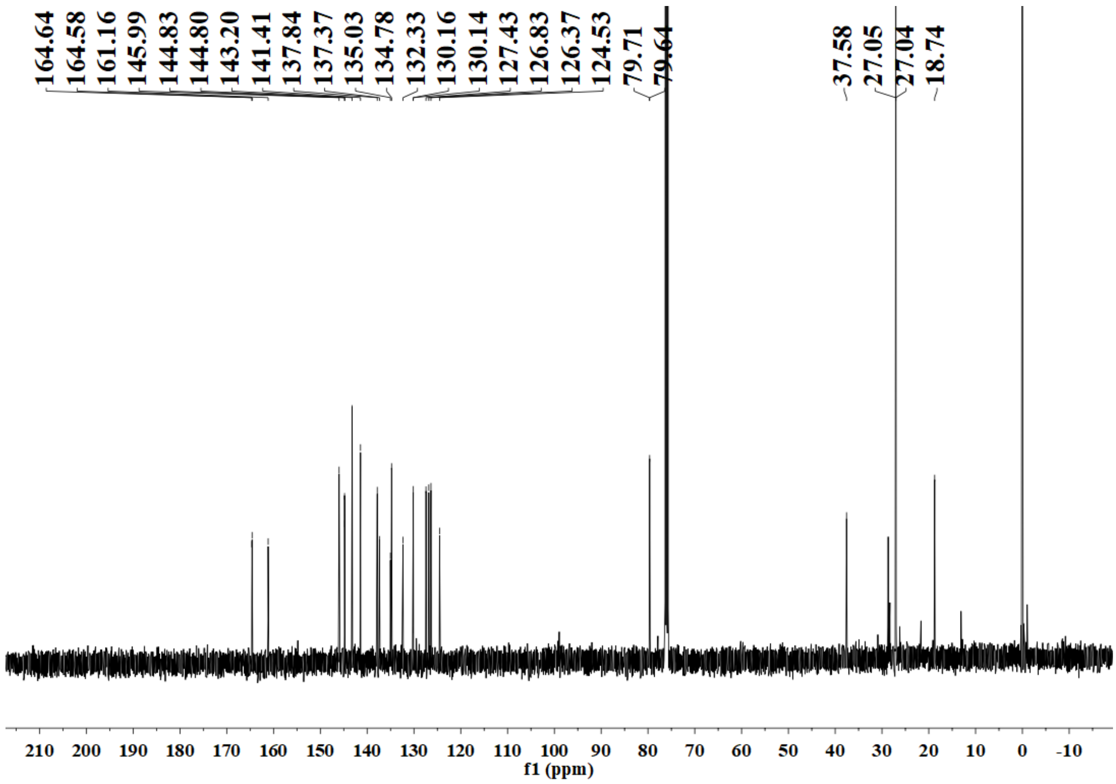
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

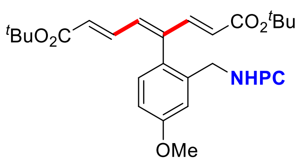




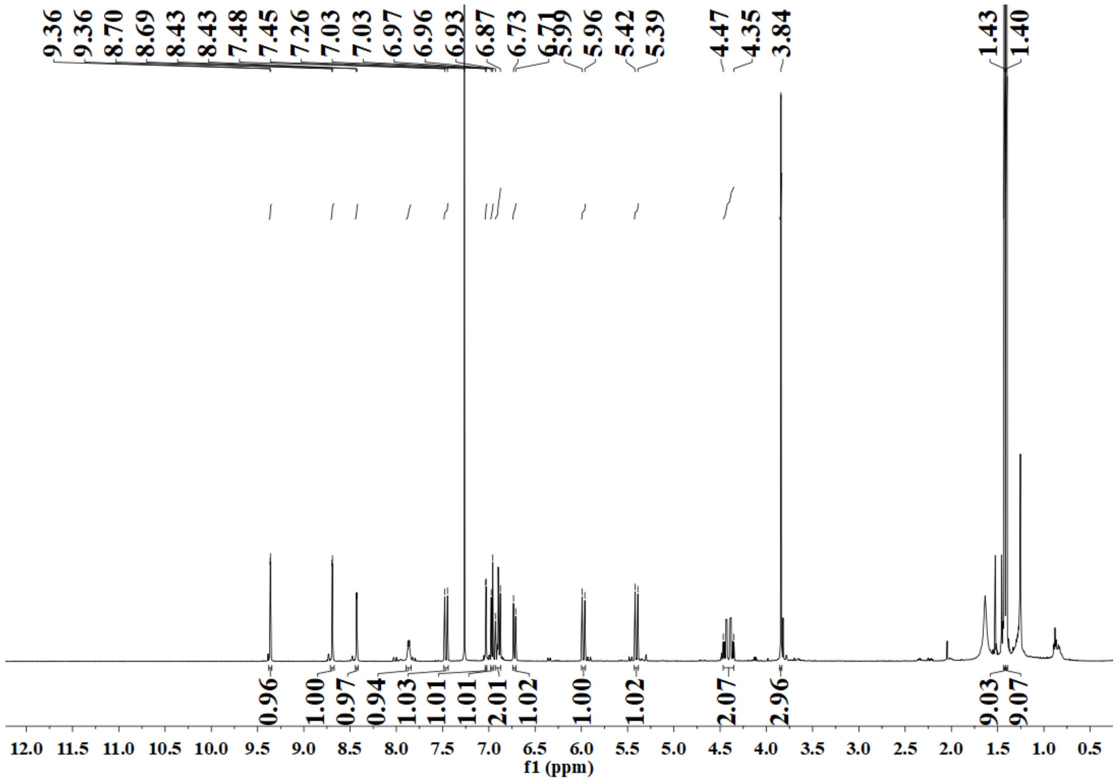
(5h)

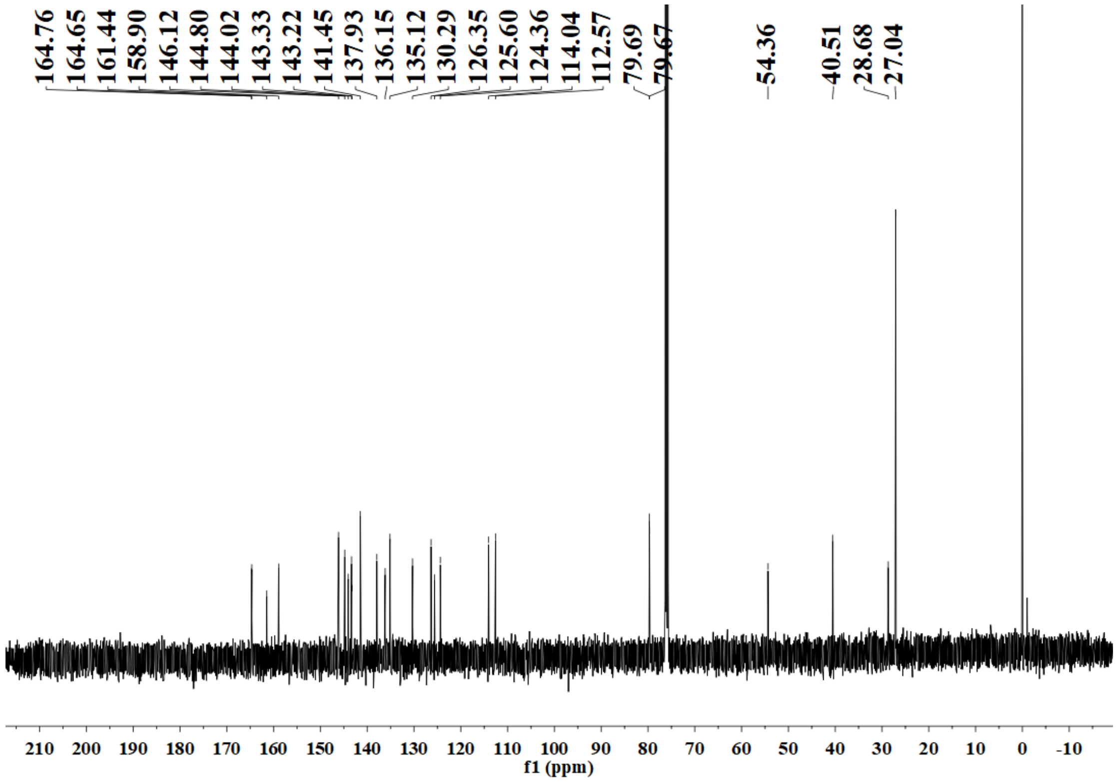






(5i)

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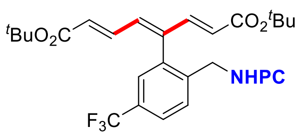
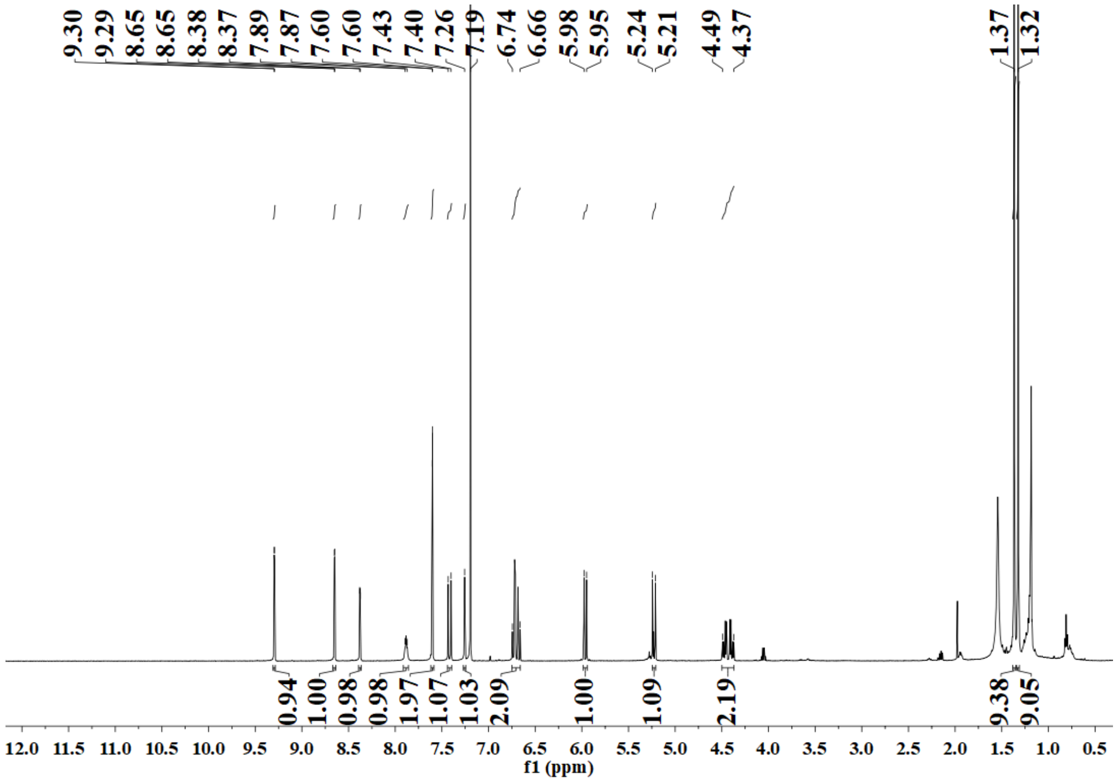
144.80
144.02
143.33
143.22
141.45
137.93
136.15
135.12
130.29
126.35
125.60
124.36
114.04
112.57
79.69
79.67
54.36
40.51
28.68
27.04
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


^{t}BuO$_2$C
CO$_2$^{t}Bu
NHPC
F$_3$C

(5j)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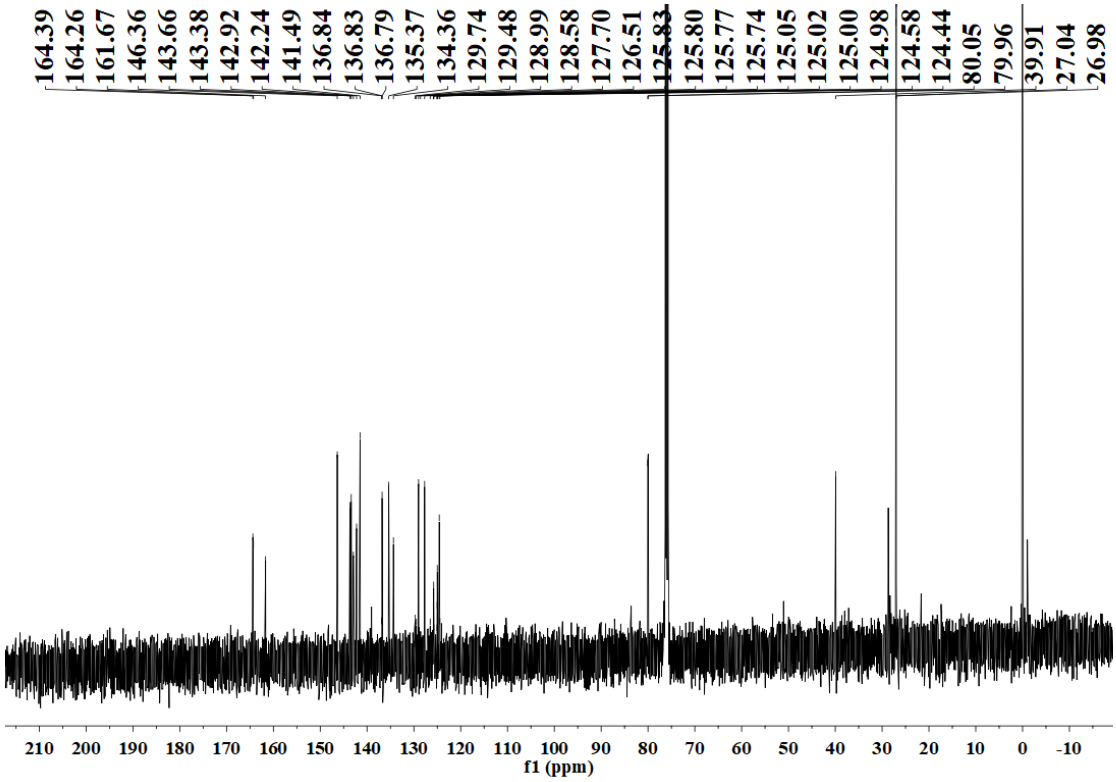
7.87
7.60
7.60
7.43
7.40
7.26
7.19
6.74
6.66
5.98
5.95
5.24
5.21
4.49
4.37
1.37
1.32
0.94
1.00
0.98
0.98
1.97
1.07
1.03
2.09
1.00
1.09
2.19
9.38
9.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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142.24
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135.37
134.36
129.74
129.48
128.99
128.58
127.70
126.51
125.83
125.80
125.77
125.74
125.05
125.02
125.00
124.98
124.58
124.44
80.05
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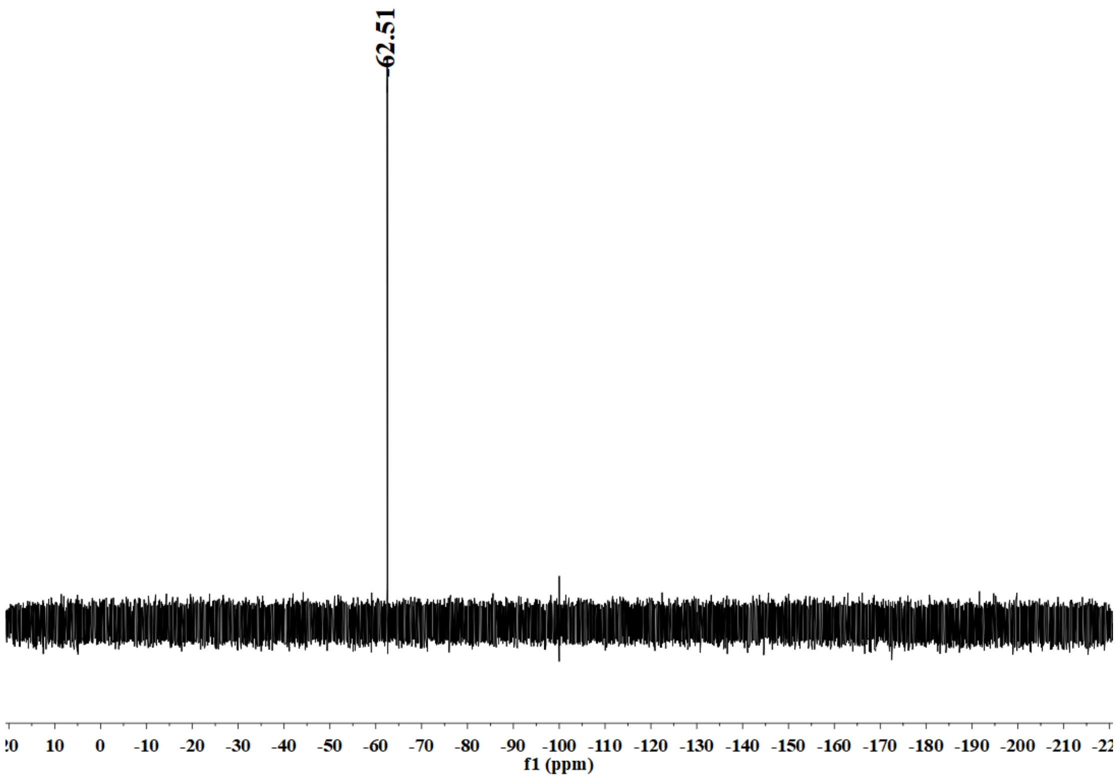
39.91
27.04
26.98
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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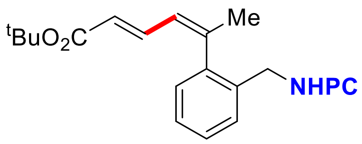
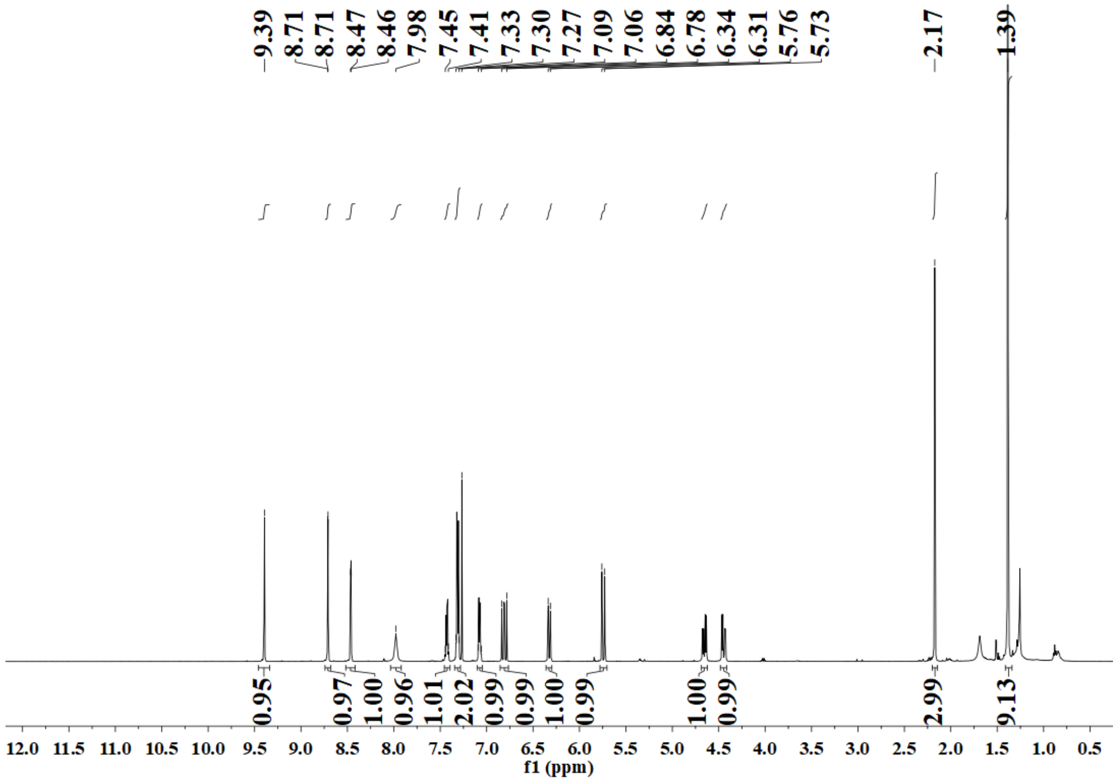
f1 (ppm)


tBuO2C
Me
NHPC

(7a)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7.45
7.41
7.33
7.30
7.27
7.09
7.06
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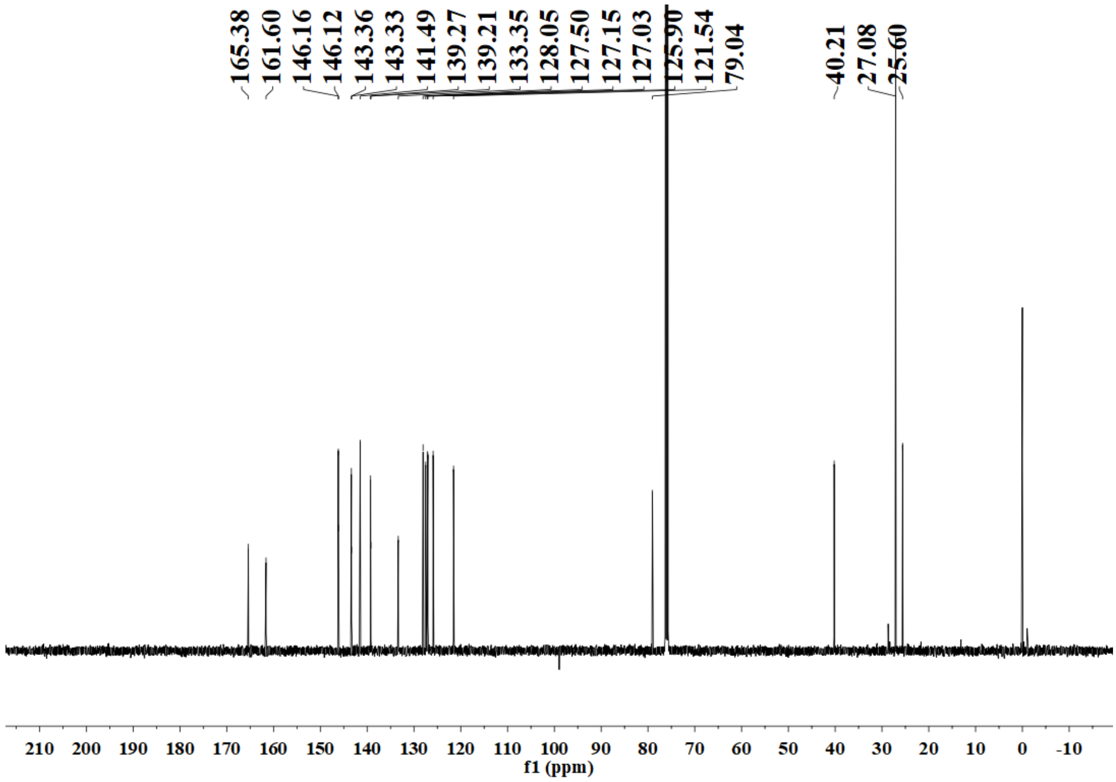
6.78
6.34
6.31
5.76
5.73
2.17
1.39
0.95
0.97
1.00
0.96
1.01
2.02
0.99
0.99
1.00
0.99
1.00
0.99
2.99
9.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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161.60
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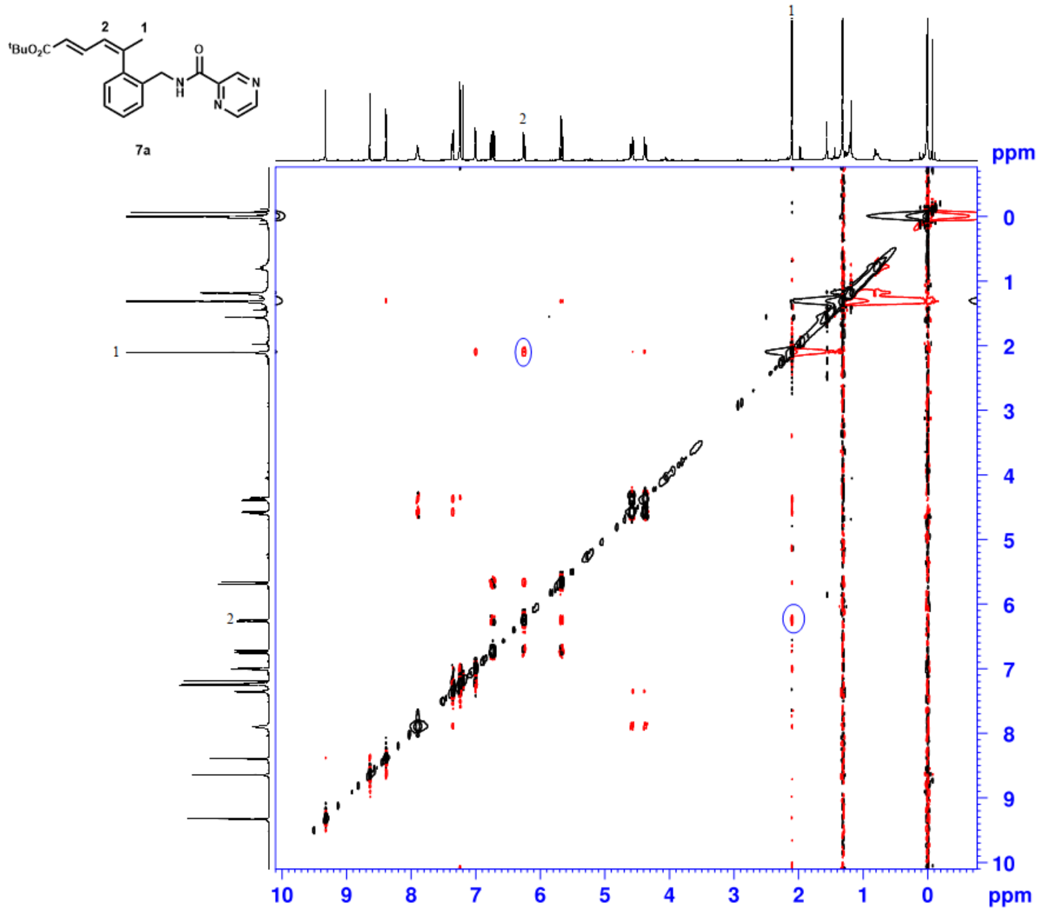
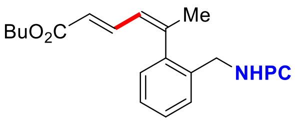
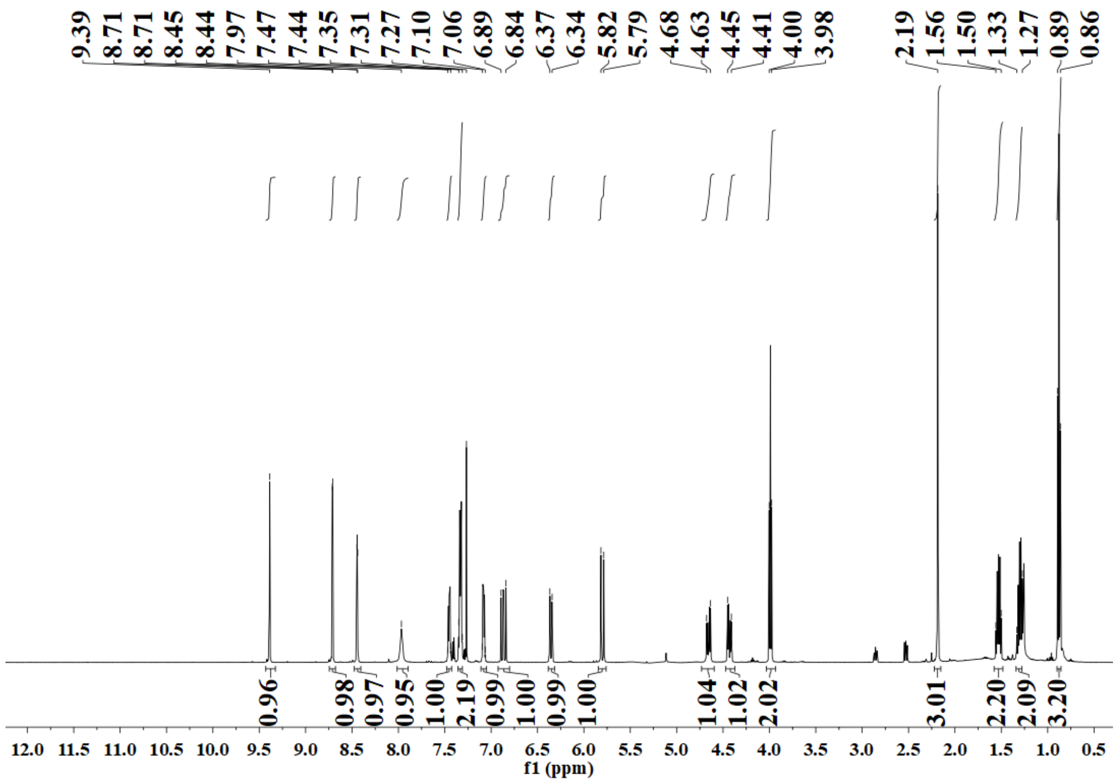
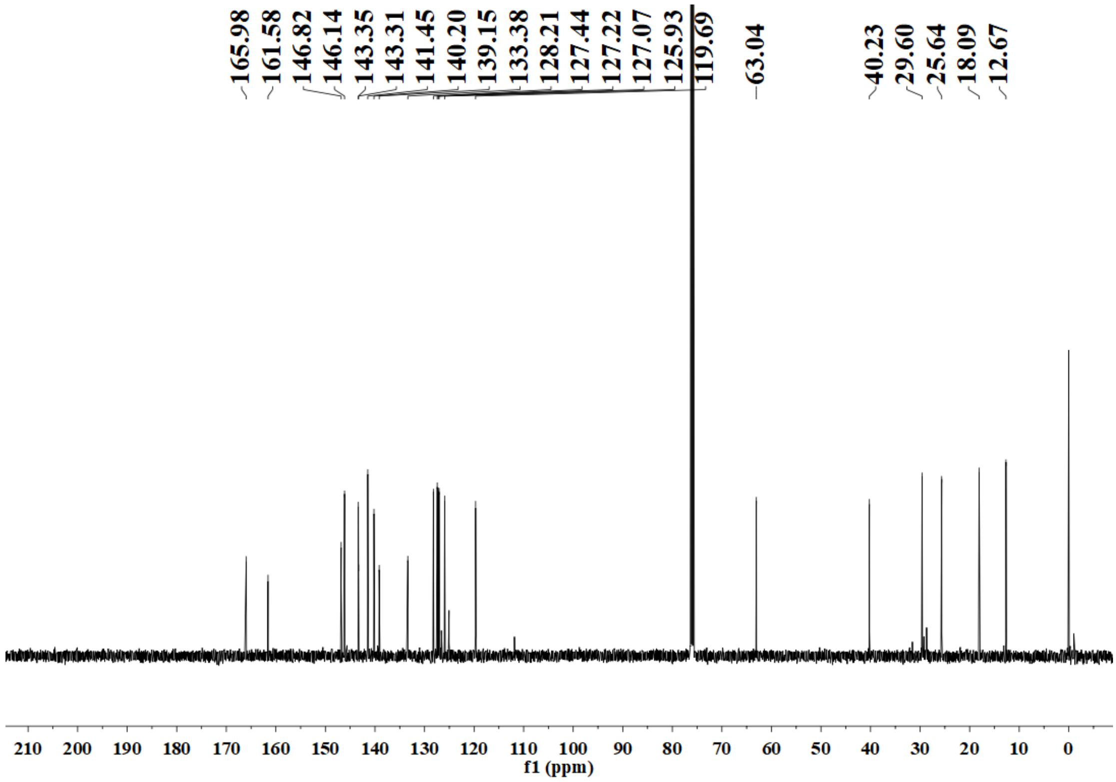
146.12
143.36
143.33
141.49
139.27
139.21
133.35
128.05
127.50
127.15
127.03
125.90
121.54
79.04
40.21
27.08
25.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)





(7b)

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146.14
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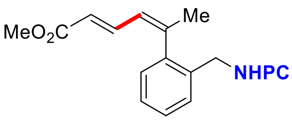
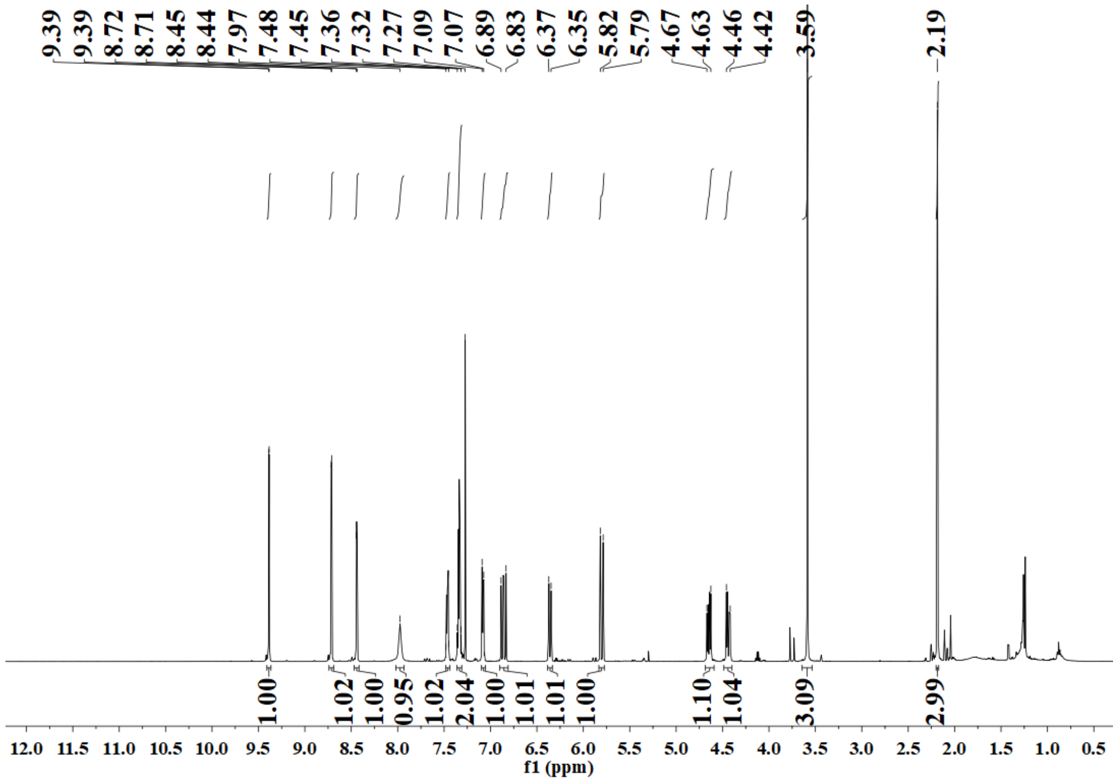
143.31
141.45
140.20
139.15
133.38
128.21
127.44
127.22
127.07
125.93
119.69
63.04
40.23
29.60
25.64
18.09
12.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO2C
Me
NHPC

(7c)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9.39
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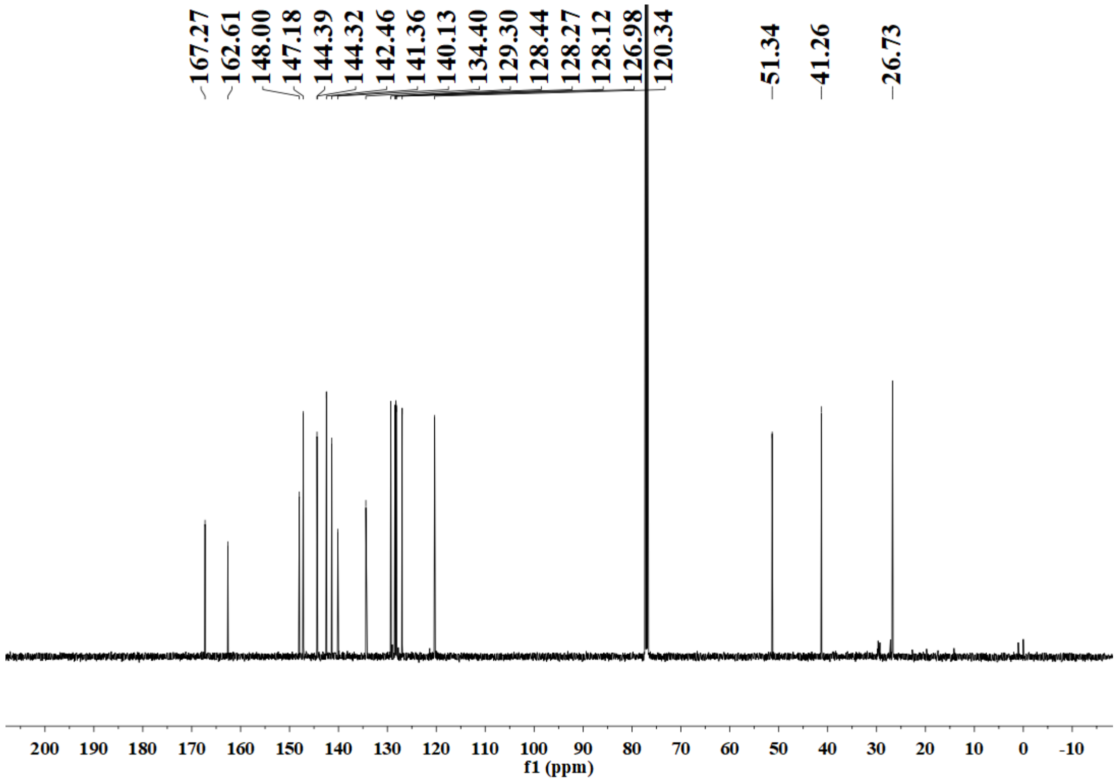
8.45
8.44
7.97
7.48
7.45
7.36
7.32
7.27
7.09
7.07
6.89
6.83
6.37
6.35
5.82
5.79
4.67
4.63
4.46
4.42
3.59
2.19
1.00
1.02
1.00
0.95
1.02
2.04
1.00
1.01
1.01
1.00
1.10
1.04
3.09
2.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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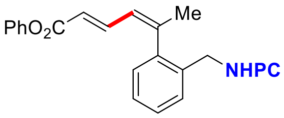
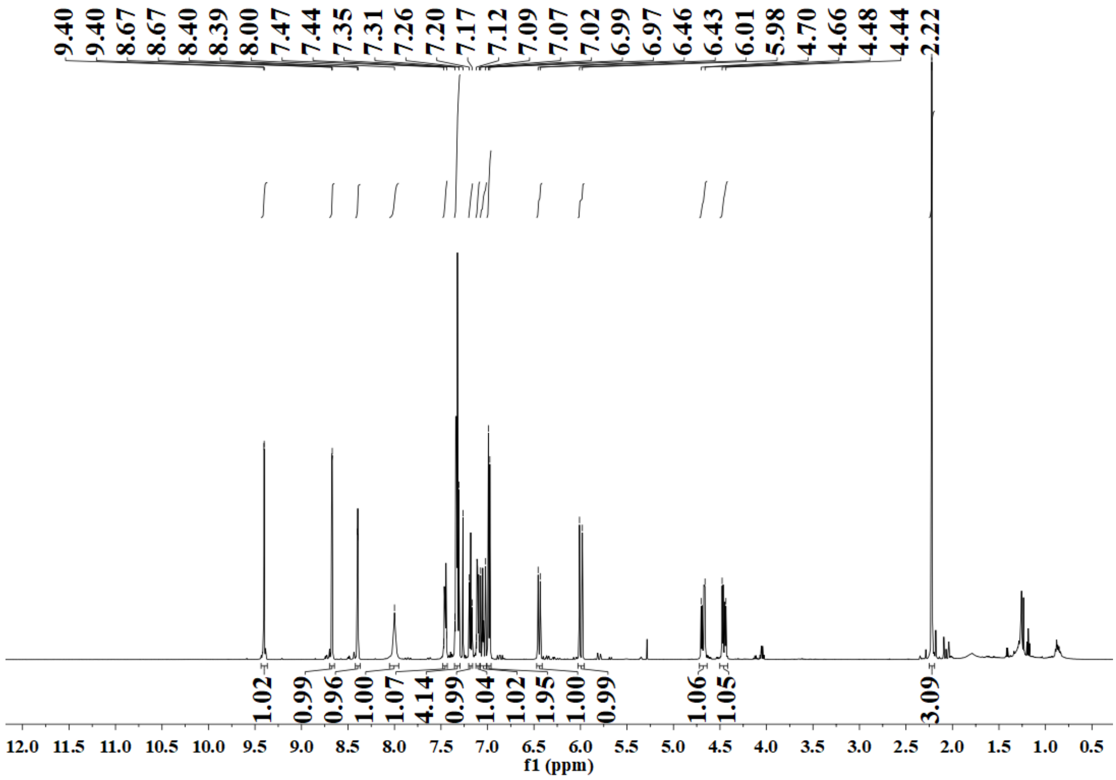
148.00
147.18
144.39
144.32
142.46
141.36
140.13
134.40
129.30
128.44
128.27
128.12
126.98
120.34
51.34
41.26
26.73
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


PhO2C
Me
NHPC

(7d)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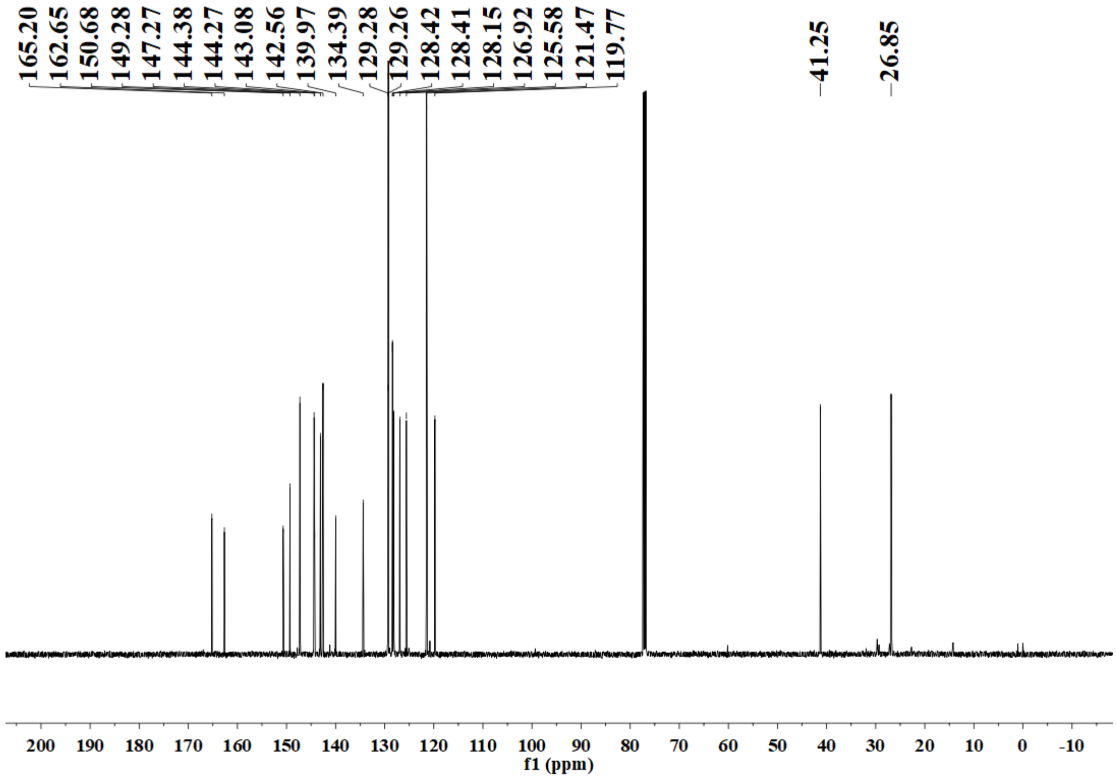
8.67
8.67
8.40
8.39
8.00
7.47
7.44
7.35
7.31
7.26
7.20
7.17
7.12
7.09
7.07
7.02
6.99
6.97
6.46
6.43
6.01
5.98
4.70
4.66
4.48
4.44
2.22
1.02
0.99
0.96
1.00
1.07
4.14
0.99
1.04
1.02
1.95
1.00
0.99
1.06
1.05
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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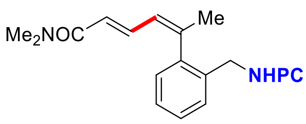
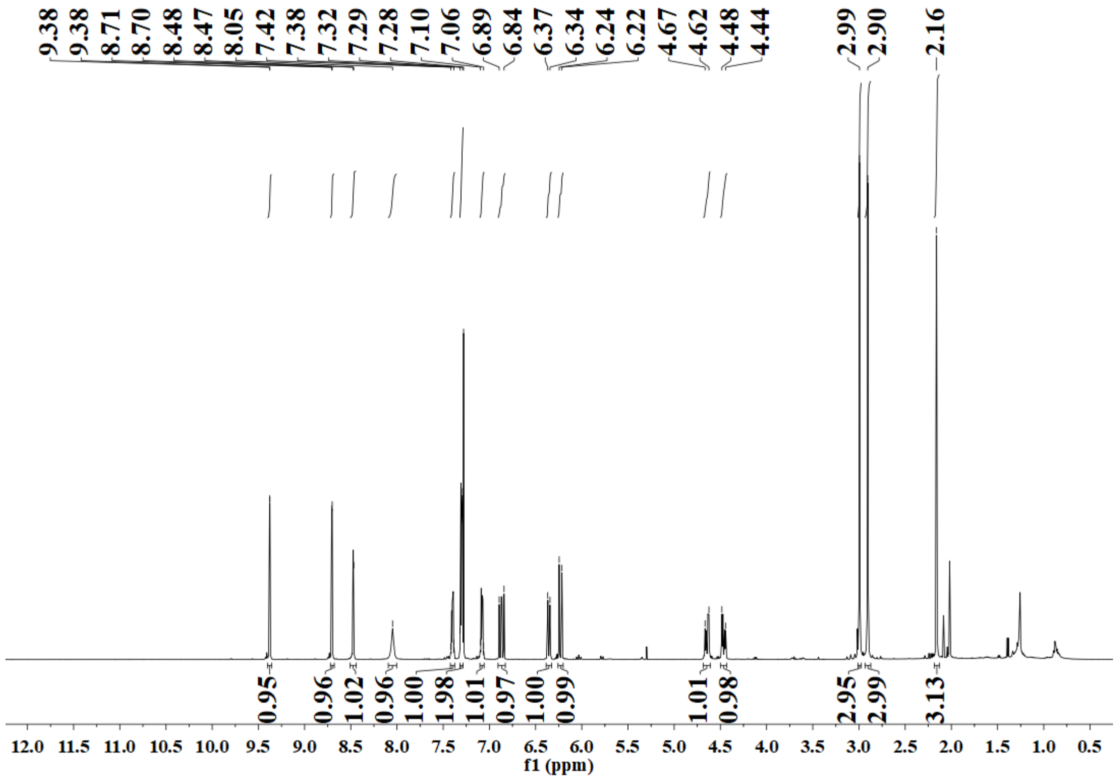
150.68
149.28
147.27
144.38
144.27
143.08
142.56
139.97
134.39
129.28
129.26
128.42
128.41
128.15
126.92
125.58
121.47
119.77
41.25
26.85
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me2NOC
NHPC

(7e)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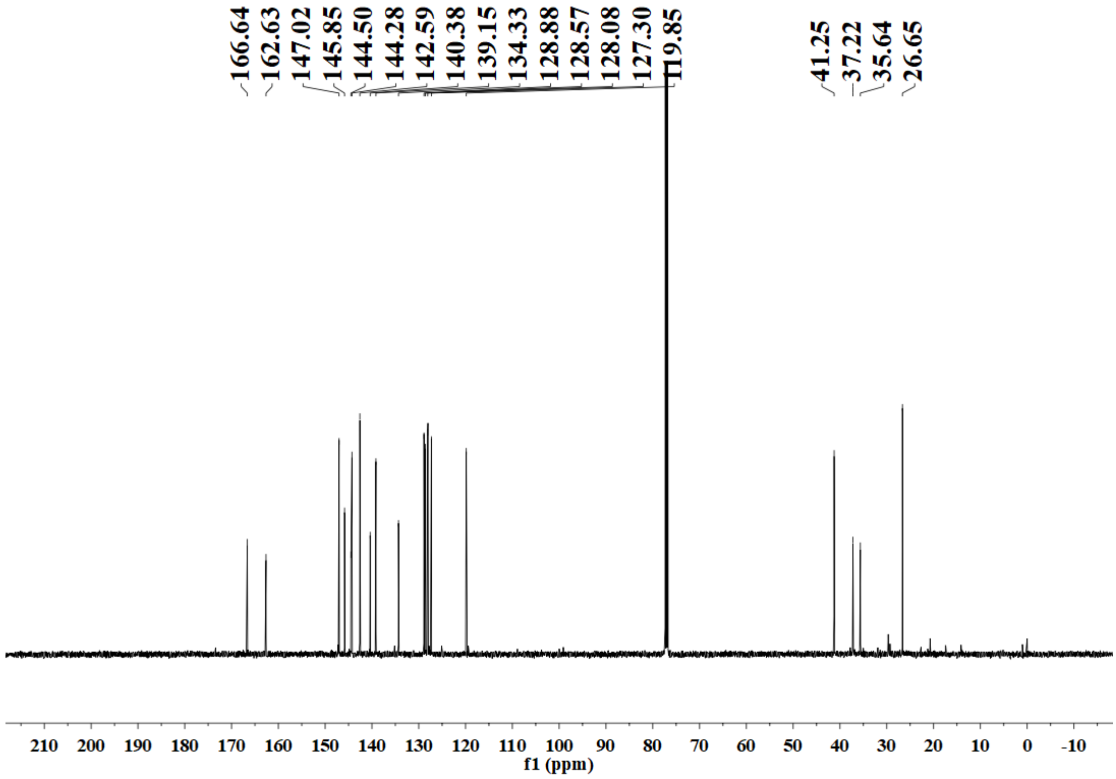
8.47
8.05
7.42
7.38
7.32
7.29
7.28
7.10
7.06
6.89
6.84
6.37
6.34
6.24
6.22
4.67
4.62
4.48
4.44
2.99
2.90
2.16
0.95
0.96
1.02
0.96
1.00
1.98
1.01
0.97
1.00
0.99
1.01
0.98
2.95
2.99
3.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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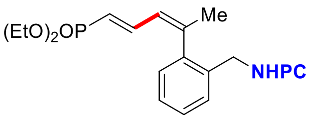
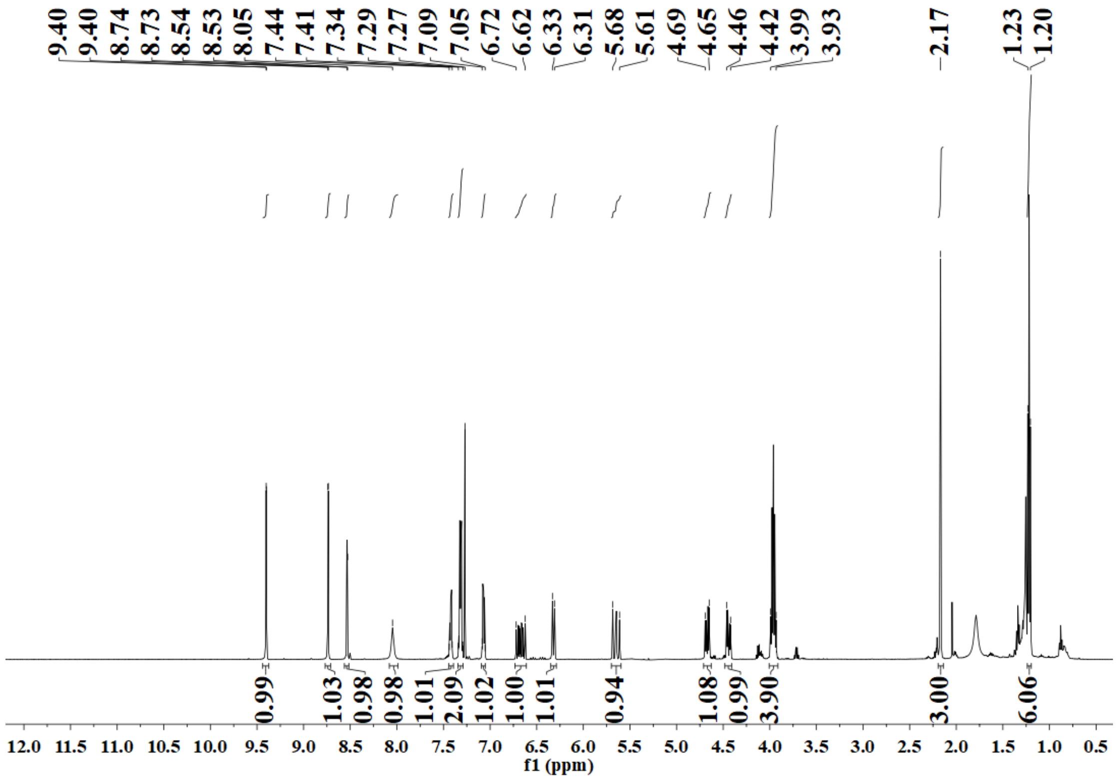
144.28
142.59
140.38
139.15
134.33
128.88
128.57
128.08
127.30
119.85
41.25
37.22
35.64
26.65
f1 (ppm)


(EtO)2OP
Me
NHPC

(7f)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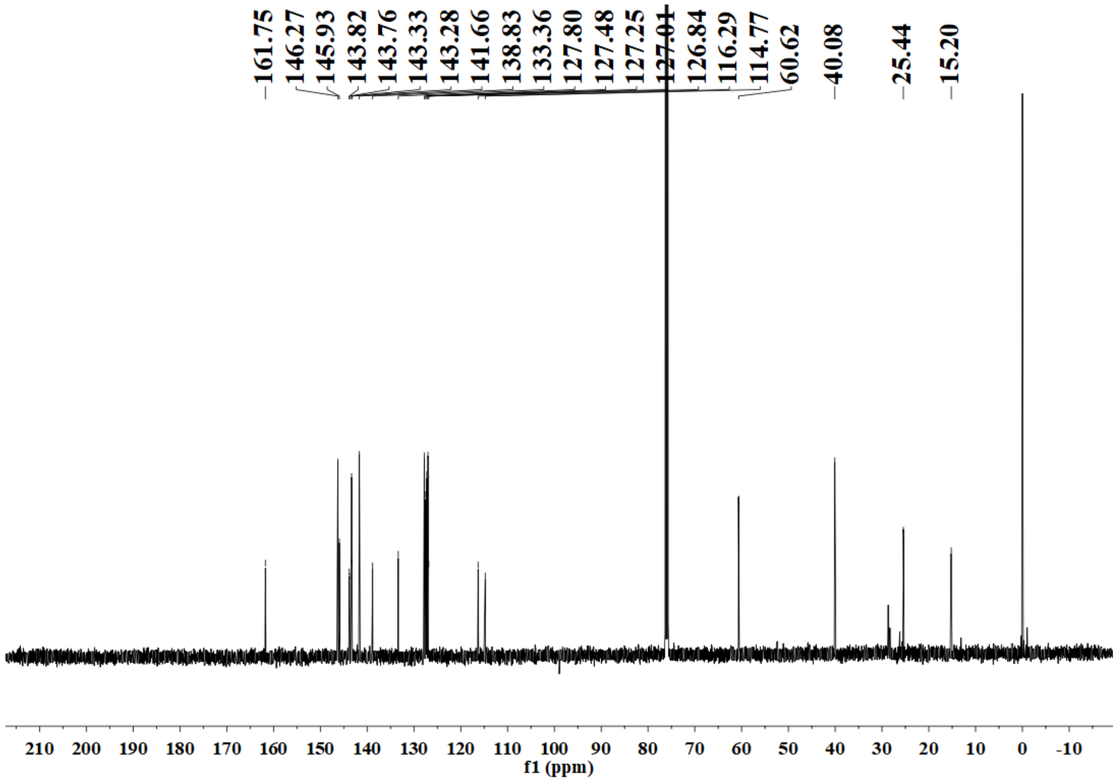
8.53
8.05
7.44
7.41
7.34
7.29
7.27
7.09
7.05
6.72
6.62
6.33
6.31
5.68
5.61
4.69
4.65
4.46
4.42
3.99
3.93
2.17
1.23
1.20
0.99
1.03
0.98
0.98
1.01
2.09
1.02
1.00
1.01
0.94
1.08
0.99
3.90
3.00
6.06
f1 (ppm)



161.75
146.27
145.93
143.82
143.76
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143.28
141.66
138.83
133.36
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127.48
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127.01
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116.29
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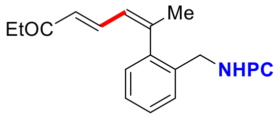
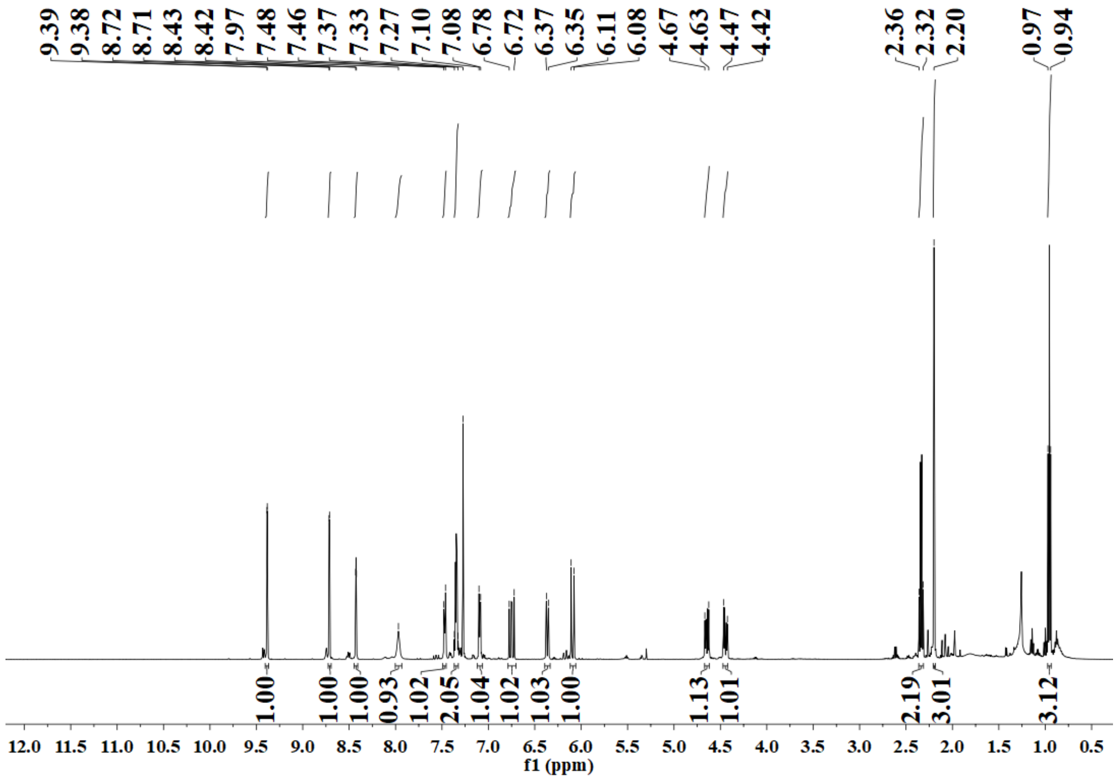
60.62
40.08
25.44
15.20
f1 (ppm)



EtOC
Me
NHPC

(7g)



9.39
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8.71
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8.42
7.97
7.48
7.46
7.37
7.33
7.27
7.10
7.08
6.78
6.72
6.37
6.35
6.11
6.08
4.67
4.63
4.47
4.42
2.36
2.32
2.20
0.97
0.94
1.00
1.00
1.00
0.93
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2.05
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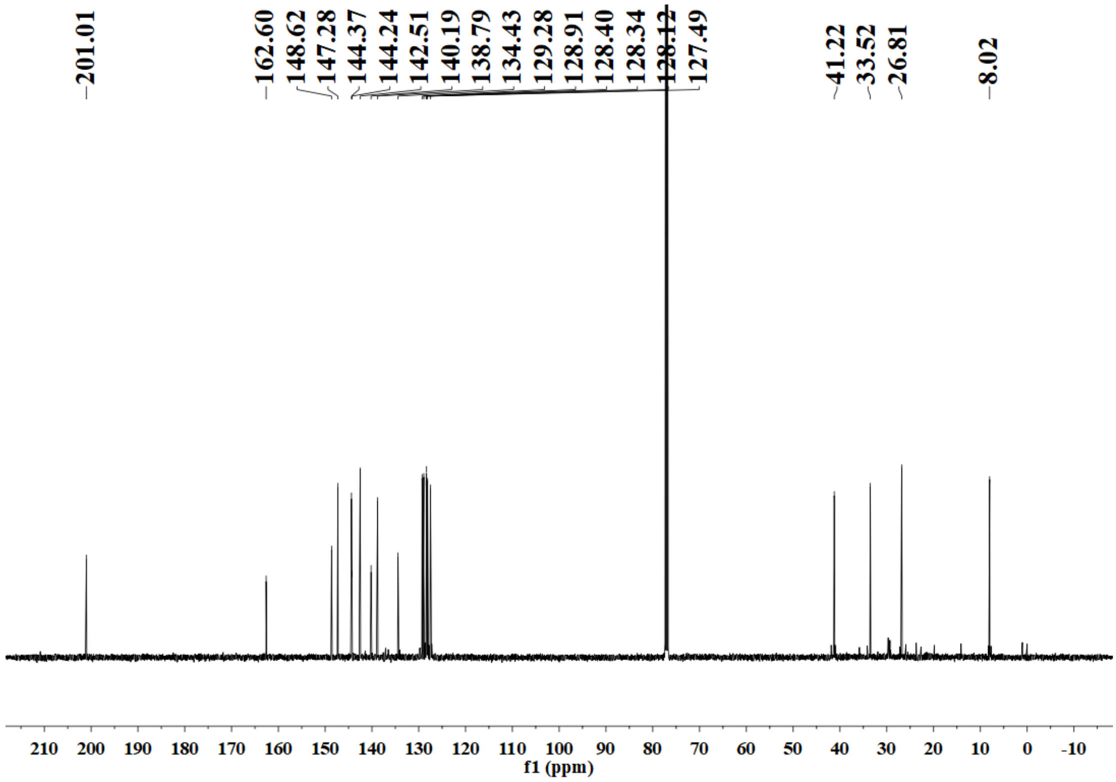
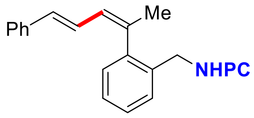
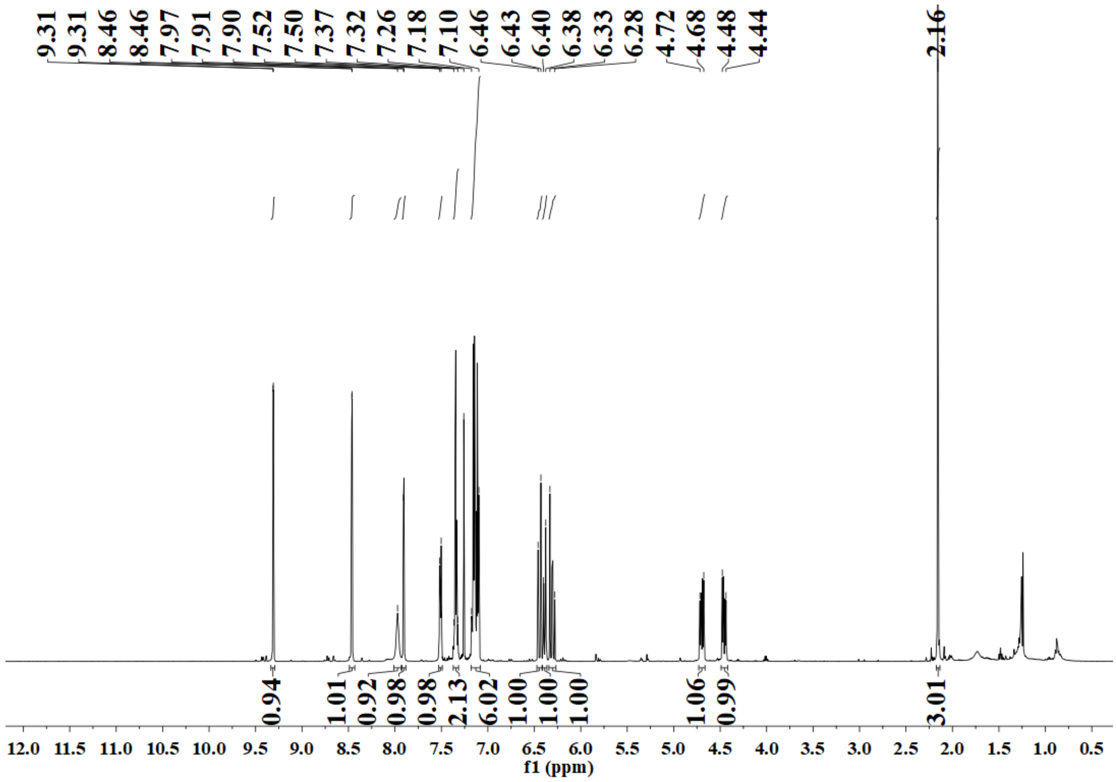
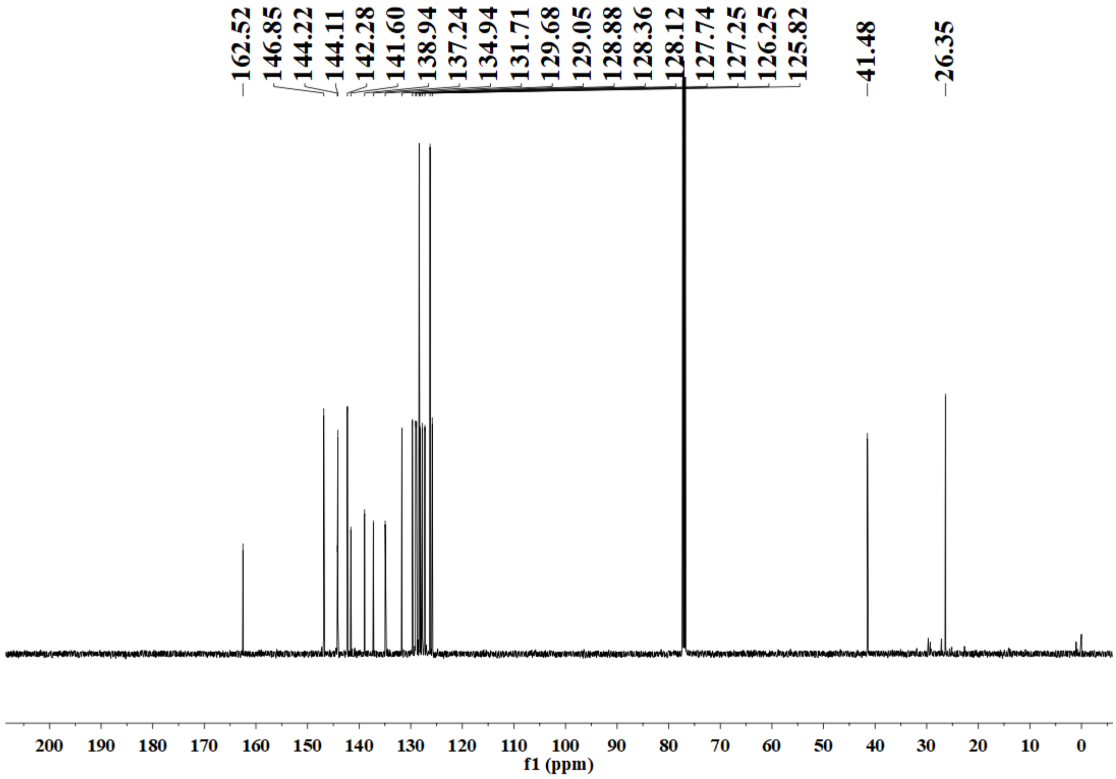
1.02
1.03
1.00
1.13
1.01
2.19
3.01
3.12
f1 (ppm)





(7h)





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144.22
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141.60
138.94
137.24
134.94
131.71
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129.05
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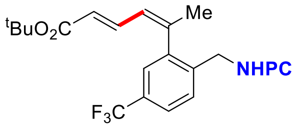
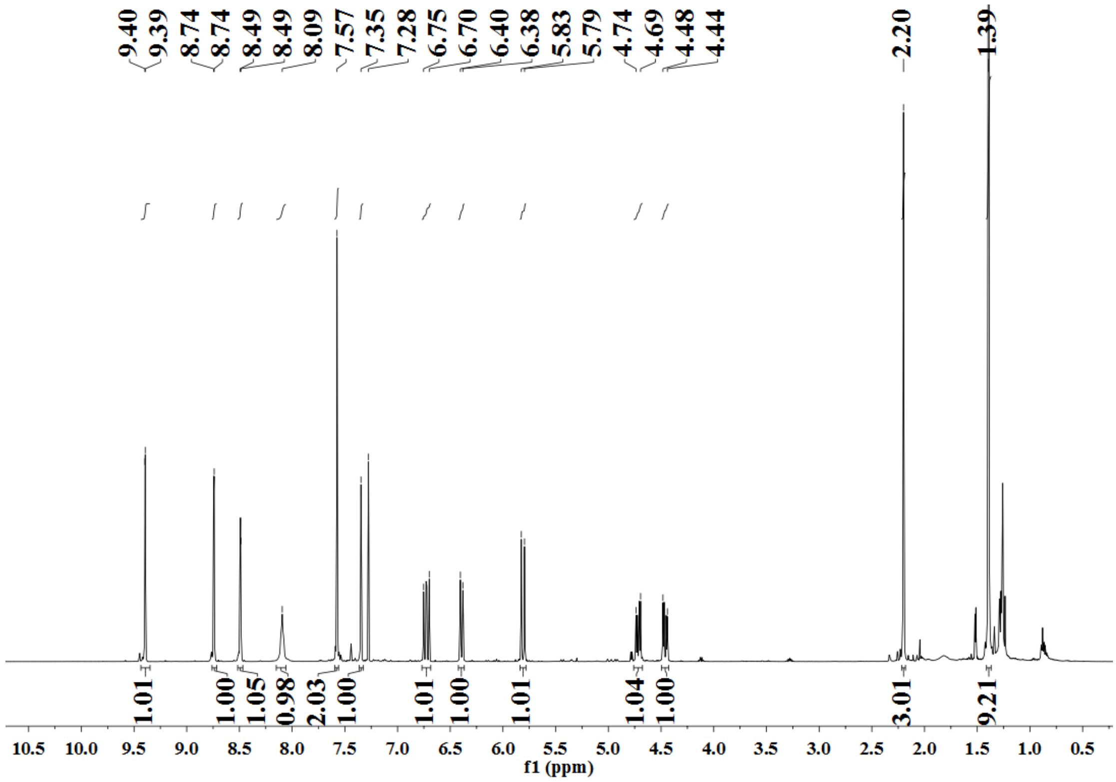
128.36
128.12
127.74
127.25
126.25
125.82
41.48
26.35
f1 (ppm)



^{t}BuO$_2$C
Me
NHPC
F$_3$C

(7i)



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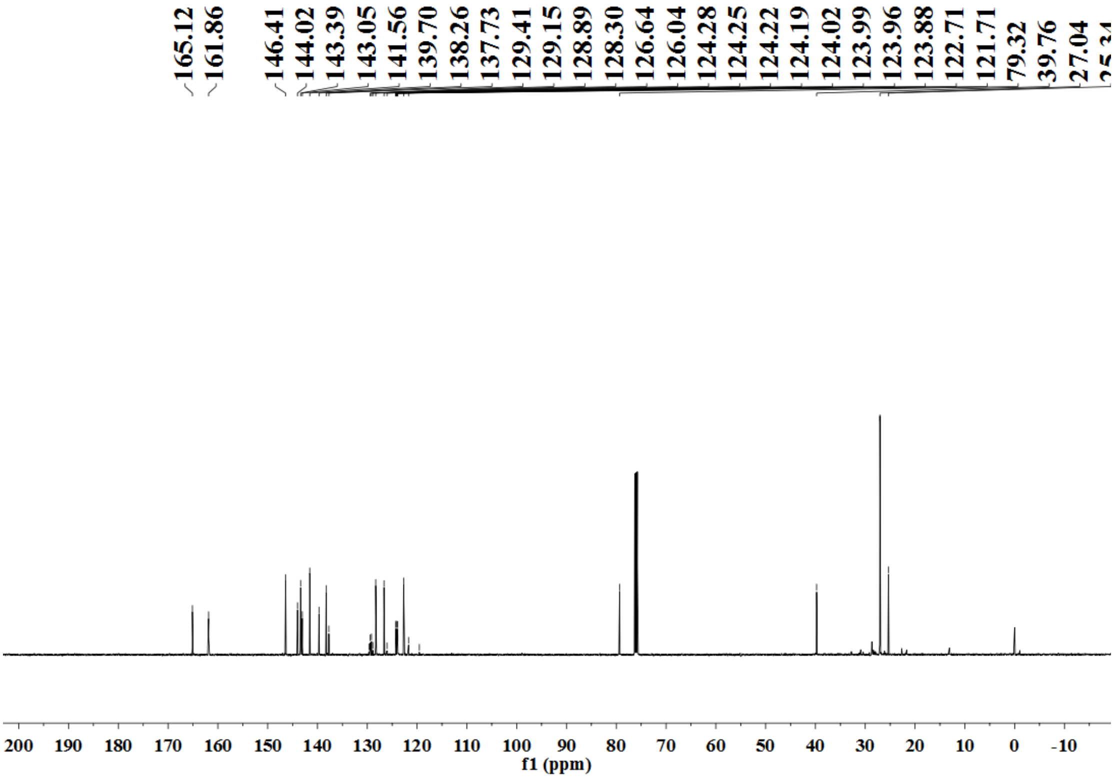
8.74
8.49
8.49
8.09
7.57
7.35
7.28
6.75
6.70
6.40
6.38
5.83
5.79
4.74
4.69
4.48
4.44
2.20
1.39
1.01
1.00
1.05
0.98
2.03
1.00
1.01
1.00
1.01
1.04
1.00
3.01
9.21
f1 (ppm)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143.05
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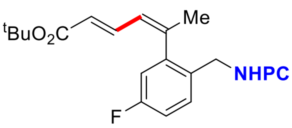
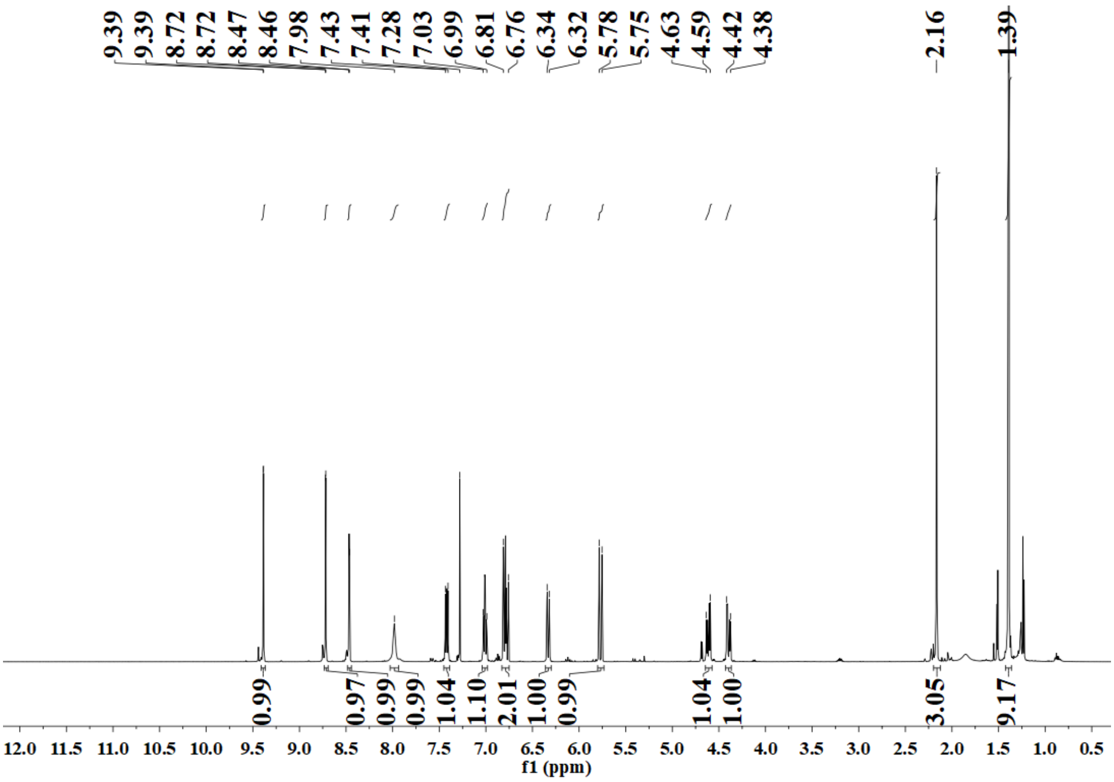
138.26
137.73
129.41
129.15
128.89
128.30
126.64
126.04
124.28
124.25
124.22
124.19
124.02
123.99
123.96
123.88
122.71
121.71
79.32
39.76
27.04
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


tBuO2C
Me
NHPC
F

(7j)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9.39
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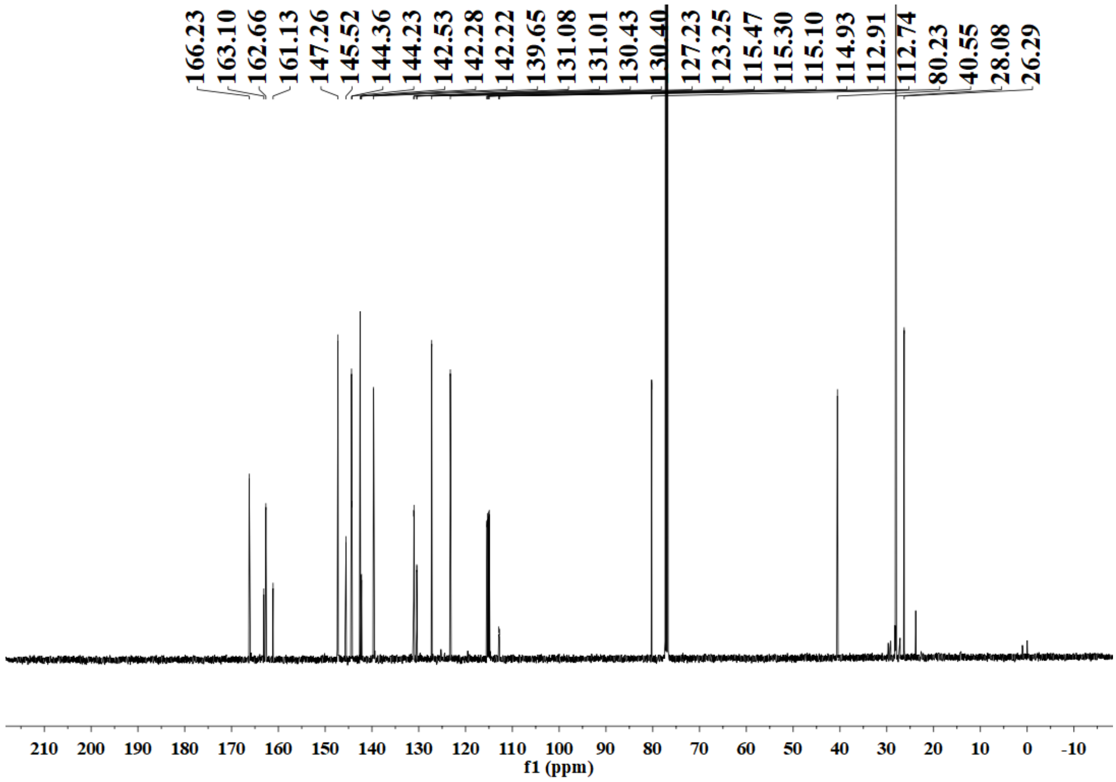
8.72
8.47
8.46
7.98
7.43
7.41
7.28
7.03
6.99
6.81
6.76
6.34
6.32
5.78
5.75
4.63
4.59
4.42
4.38
2.16
1.39
0.99
0.97
0.99
0.99
1.04
1.10
2.01
1.00
0.99
1.04
1.00
3.05
9.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


166.23
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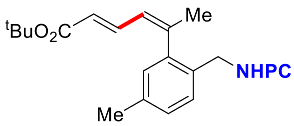
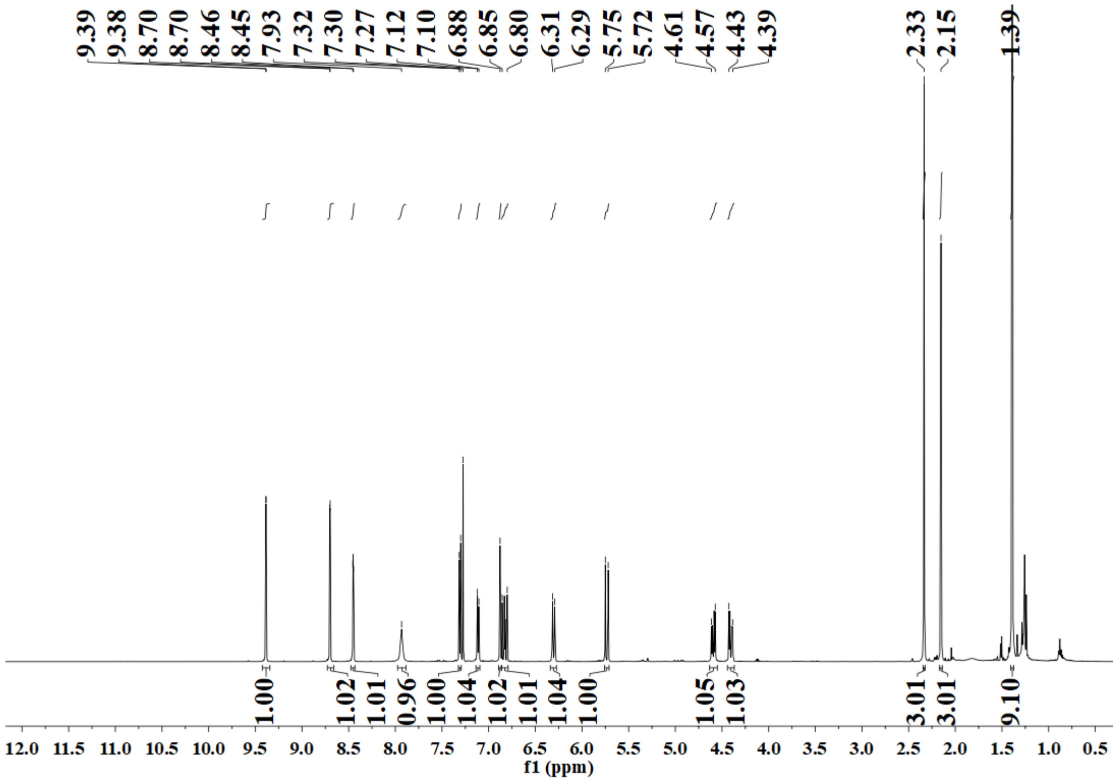
144.36
144.23
142.53
142.28
142.22
139.65
131.08
131.01
130.43
130.40
127.23
123.25
115.47
115.30
115.10
114.93
112.91
112.74
80.23
40.55
28.08
26.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


tBuO2C
Me
NHPC
Me

(7k)


9.39
9.38
8.70
8.70
8.46
8.45
7.93
7.32
7.30
7.27
7.12
7.10
6.88
6.85
6.80
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5.72
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4.57
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4.39
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2.15
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1.02
1.01
0.96
1.00
1.04
1.02
1.01
1.04
1.00
1.05
1.03
3.01
3.01
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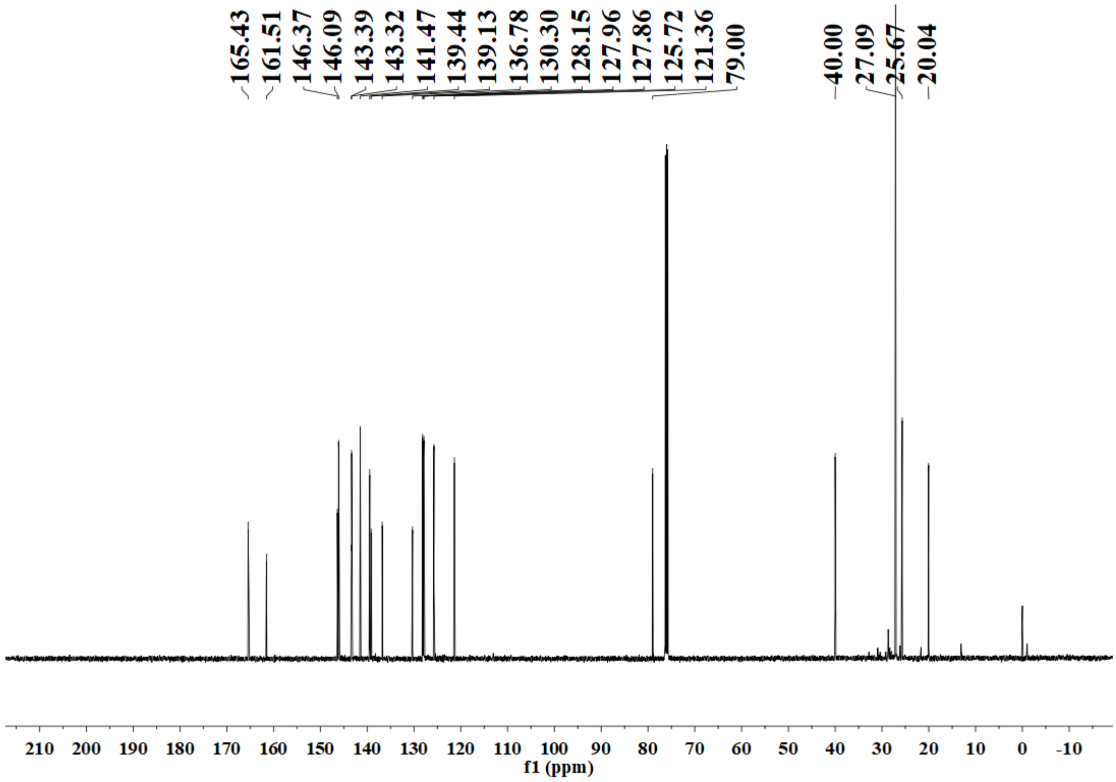
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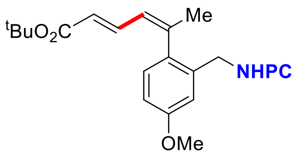
f1 (ppm)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NHPC
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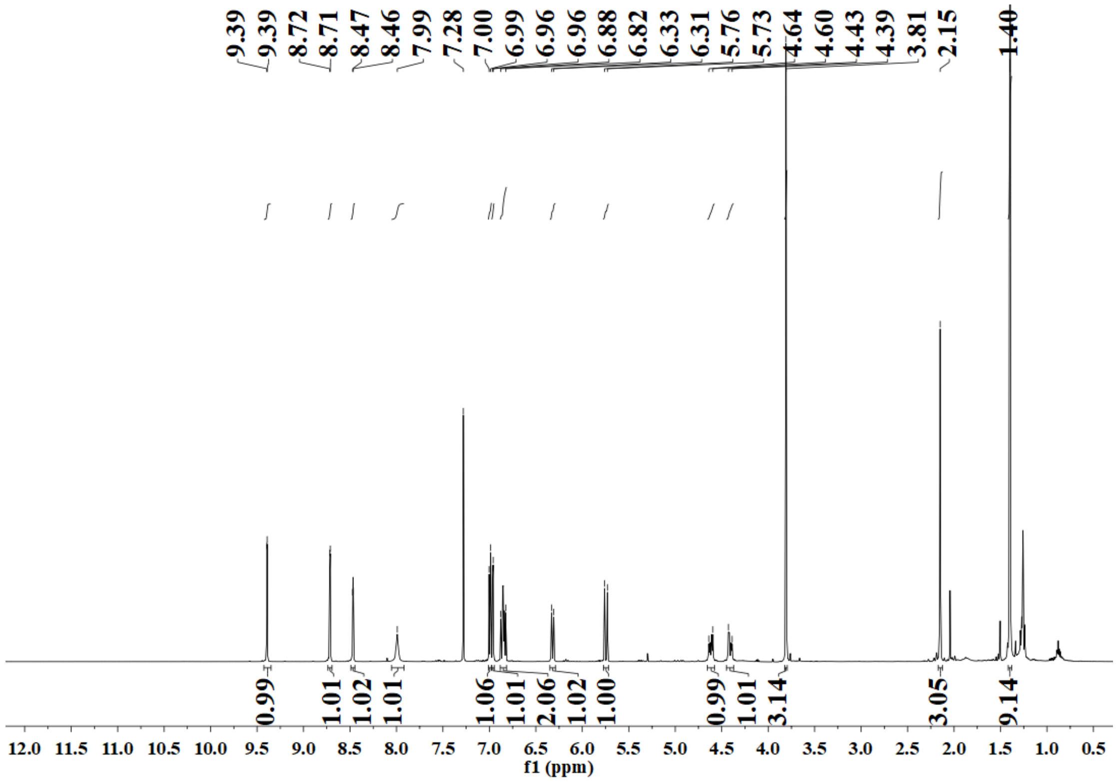
(7l)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6.31
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5.73
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4.60
4.43
4.39
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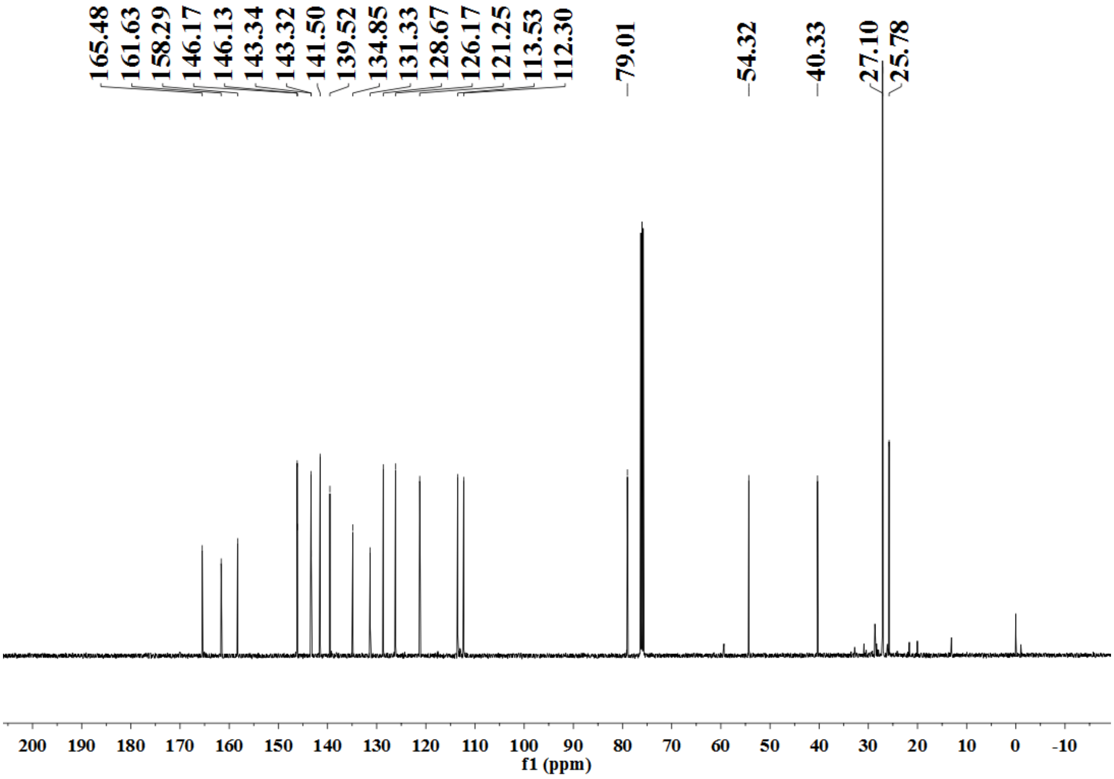
1.02
1.01
1.06
1.01
2.06
1.02
1.00
0.99
1.01
3.14
3.05
9.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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113.53
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27.10
25.78
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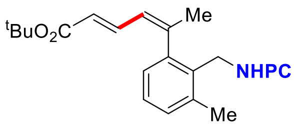
f1 (ppm)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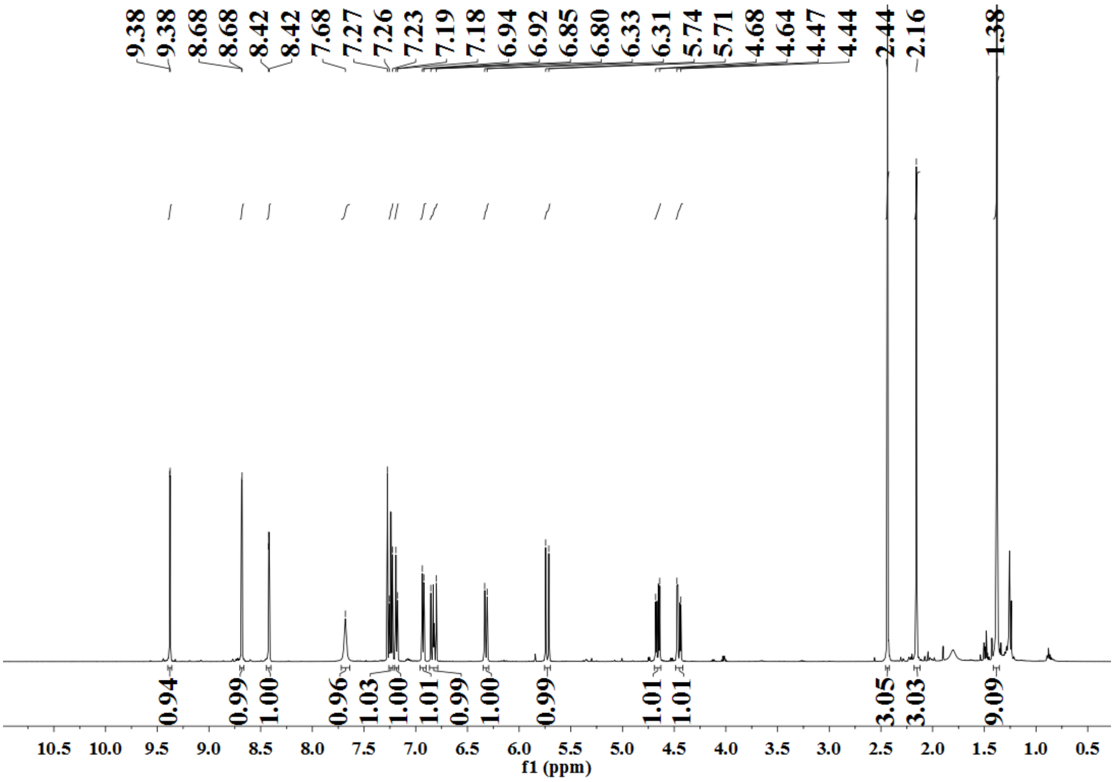
Me
NHPC
Me

(7m)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6.33
6.31
5.74
5.71
4.68
4.64
4.47
4.44
2.44
2.16
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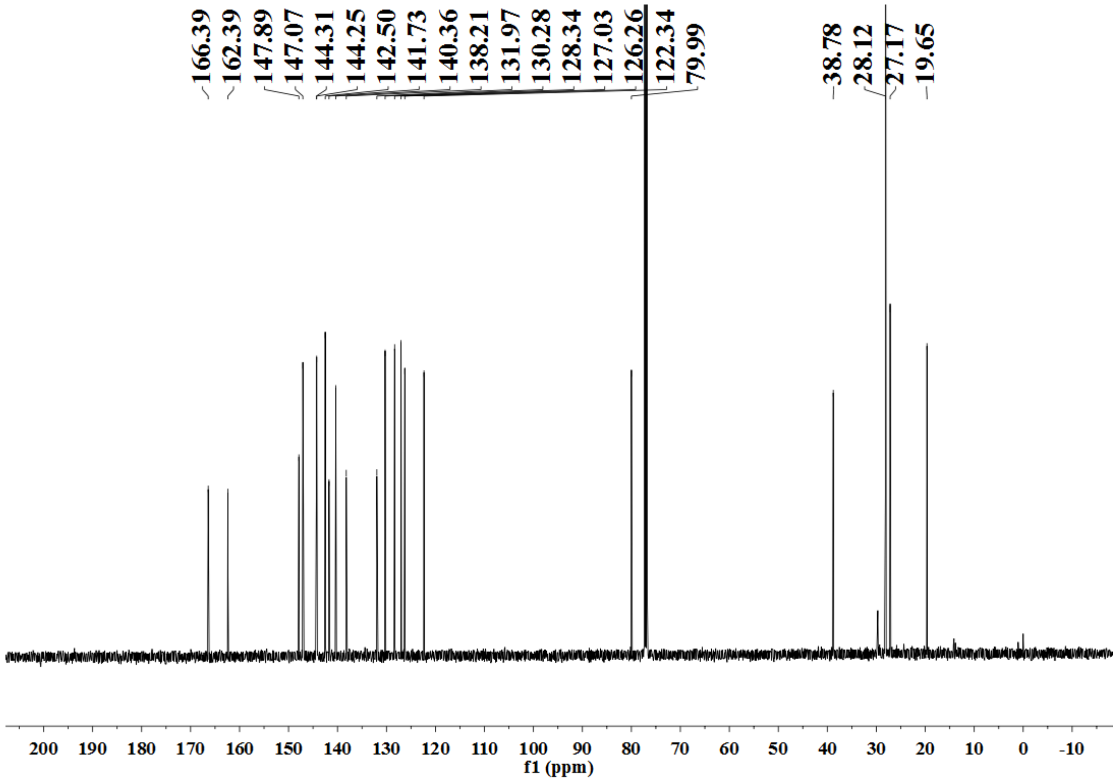
0.99
1.00
0.96
1.03
1.00
1.01
0.99
1.00
0.99
1.01
1.01
3.05
3.03
9.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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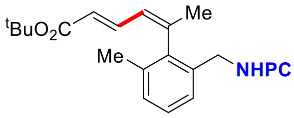
19.65
f1 (ppm)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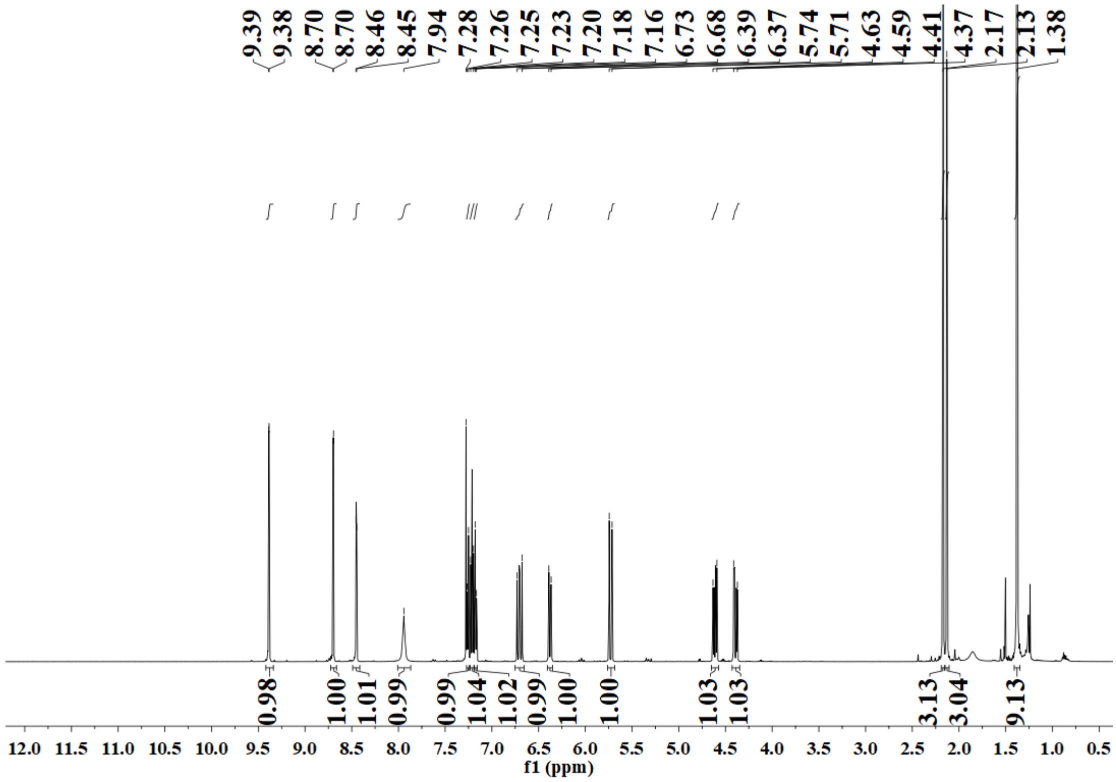
Me
NHPC

(7n)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7.18
7.16
6.73
6.68
6.39
6.37
5.74
5.71
4.63
4.59
4.41
4.37
2.17
2.13
1.38
0.98
1.00
1.01
0.99
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0.99
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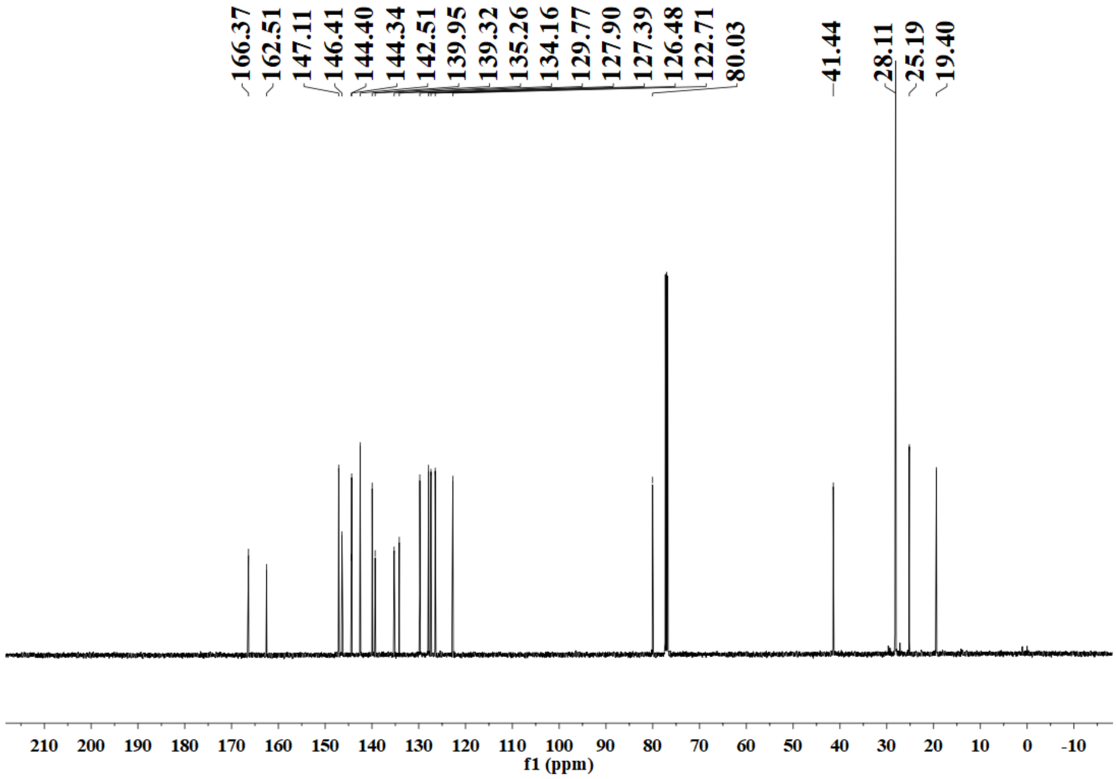
1.00
1.03
1.03
3.13
3.04
9.13
f1 (ppm)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126.48
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19.40
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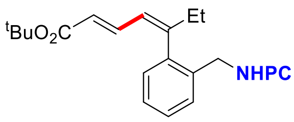
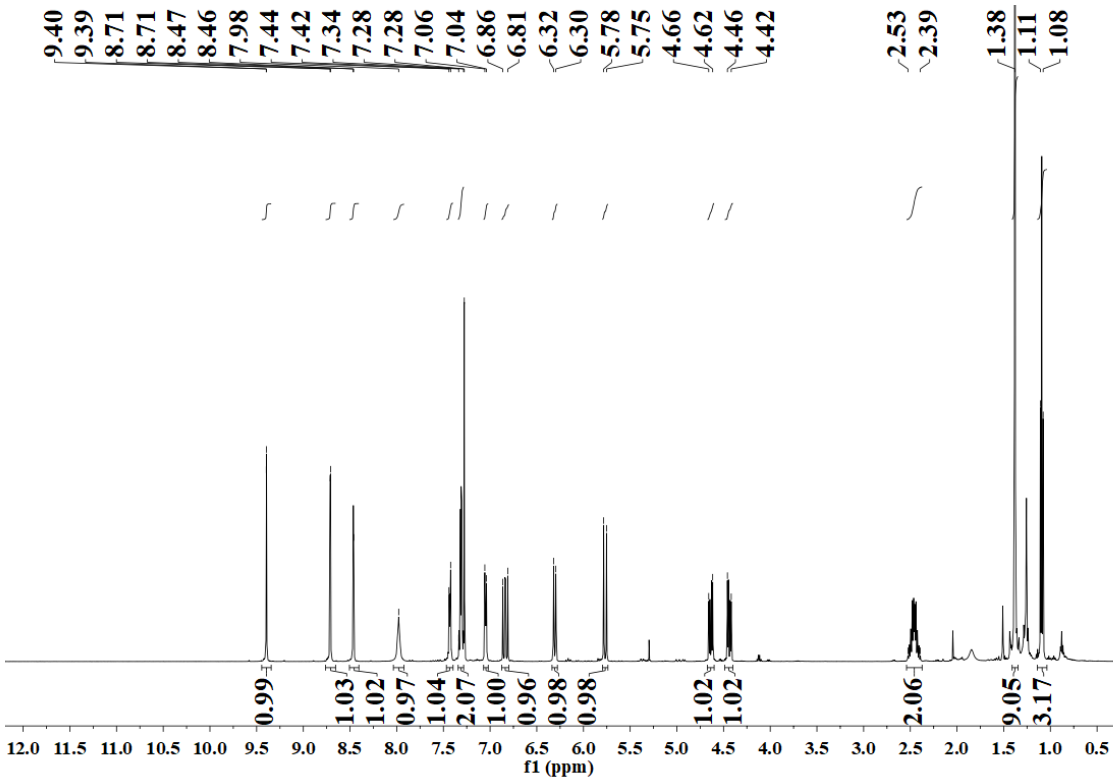
f1 (ppm)


tBuO2C
Et
NHPC

(7o)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7.04
6.86
6.81
6.32
6.30
5.78
5.75
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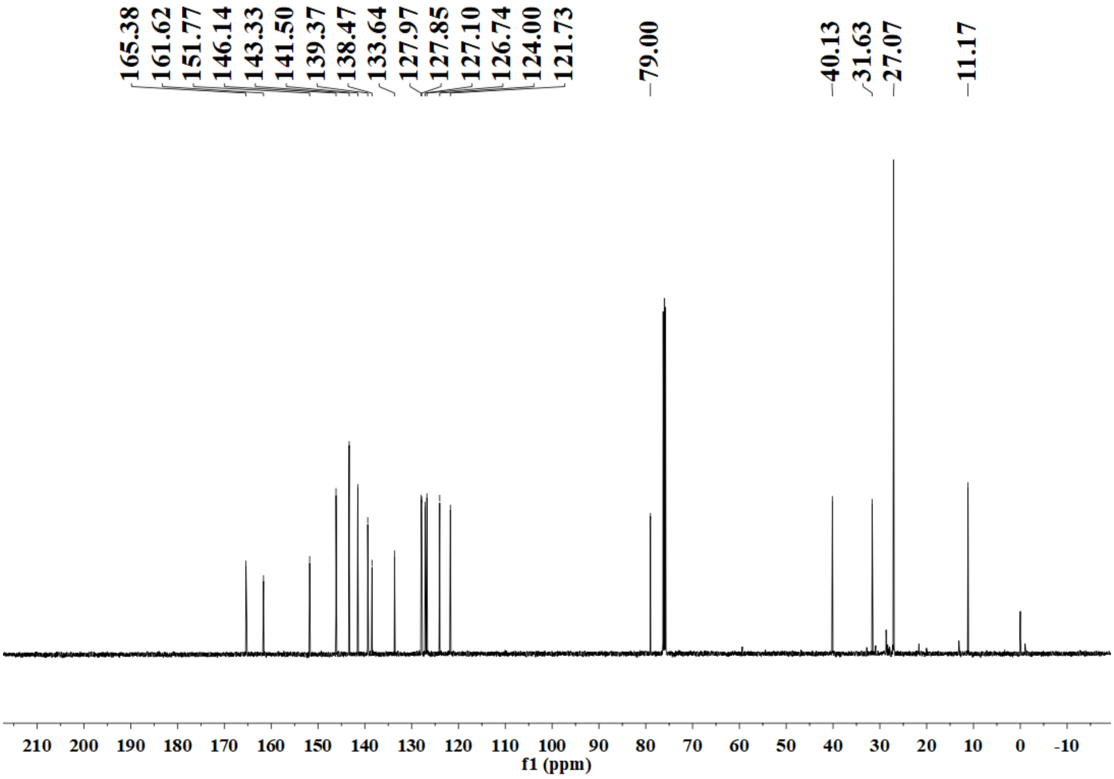
4.62
4.46
4.42
2.53
2.39
1.38
1.11
1.08
0.99
1.03
1.02
0.97
1.04
2.07
1.00
0.96
0.98
0.98
1.02
1.02
2.06
9.05
3.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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126.74
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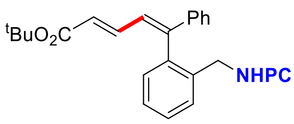
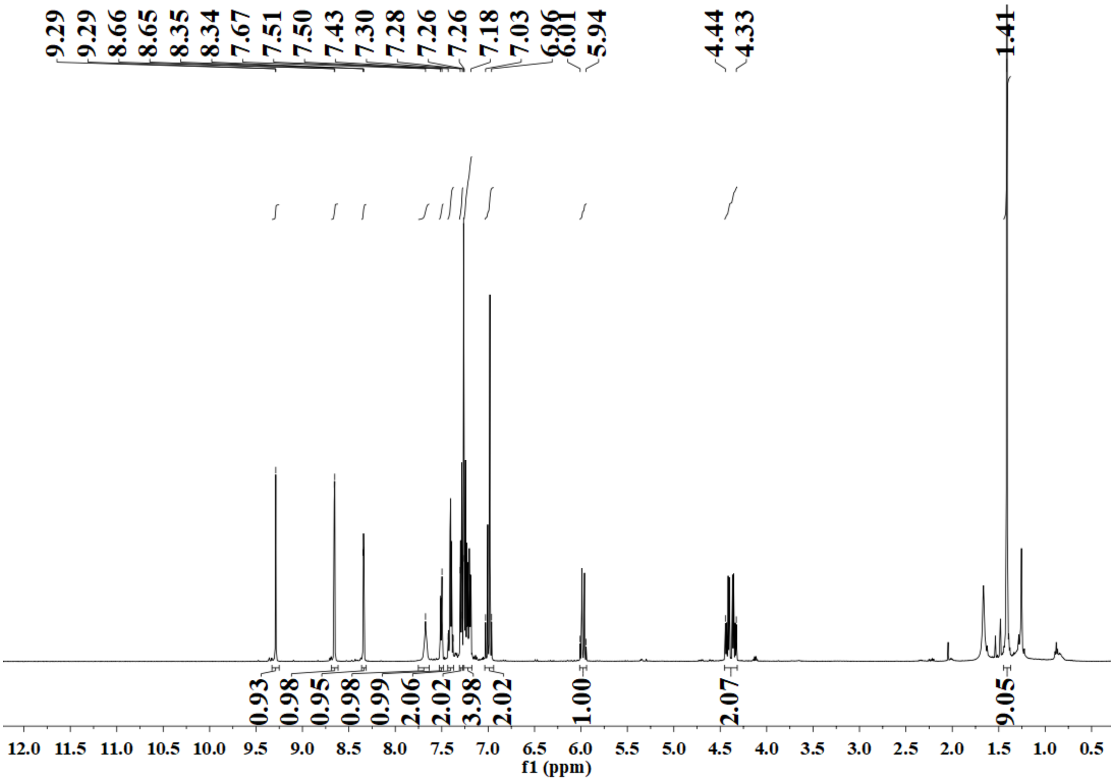
121.73
79.00
40.13
31.63
27.07
11.17
f1 (ppm)


tBuO2C
Ph
NHPC

(7p)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7.26
7.18
7.03
6.96
6.01
5.94
4.44
4.33
1.41
0.93
0.98
0.95
0.98
0.99
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2.02
3.98
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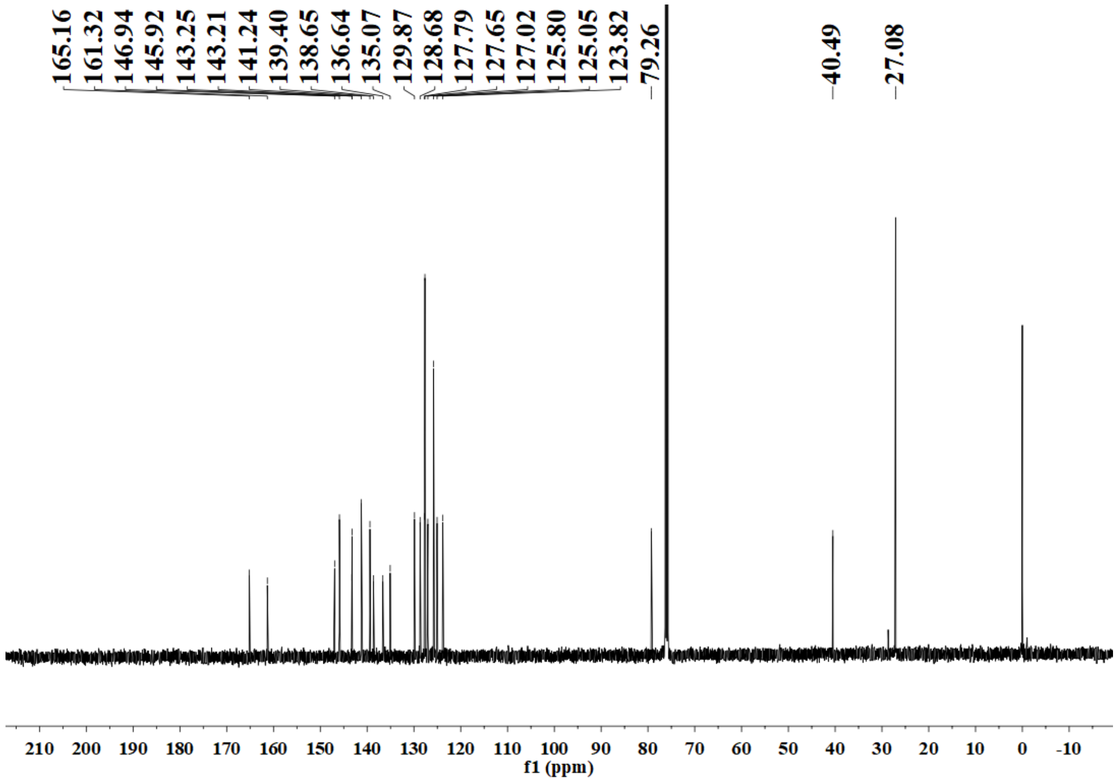
1.00
2.07
9.05
f1 (ppm)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127.65
127.02
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125.05
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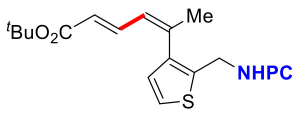
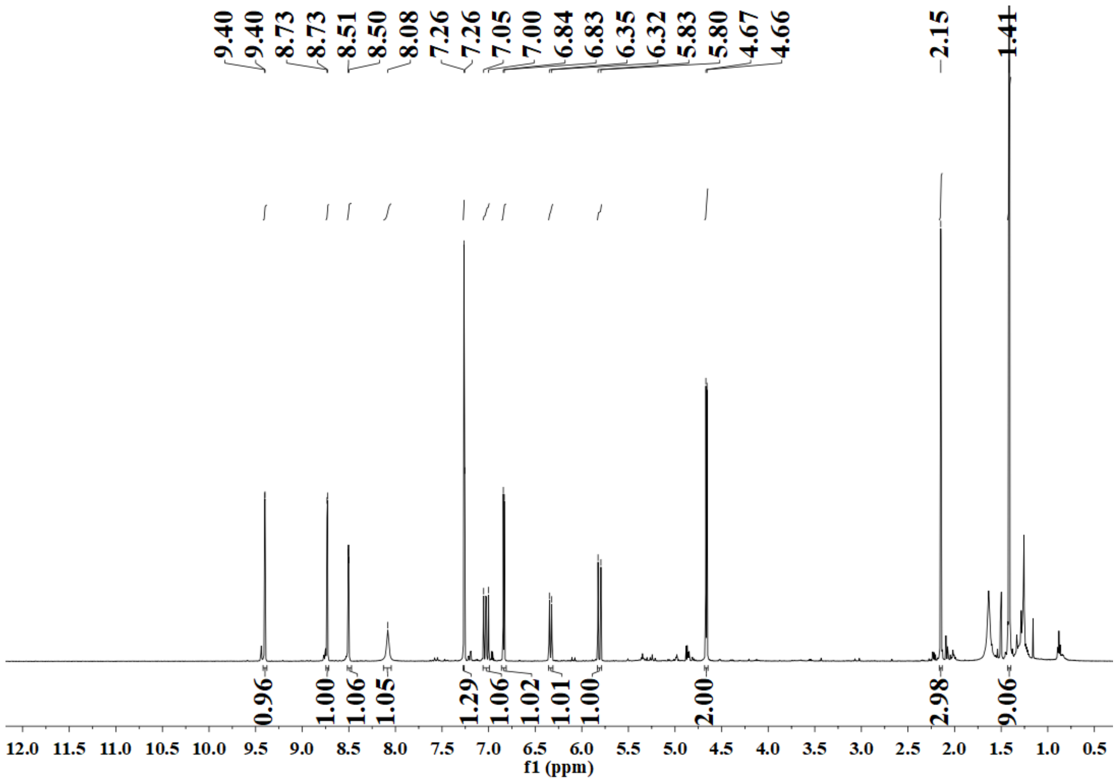
79.26
40.49
27.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


tBuO2C
Me
NHPC
S

(7q)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7.05
7.00
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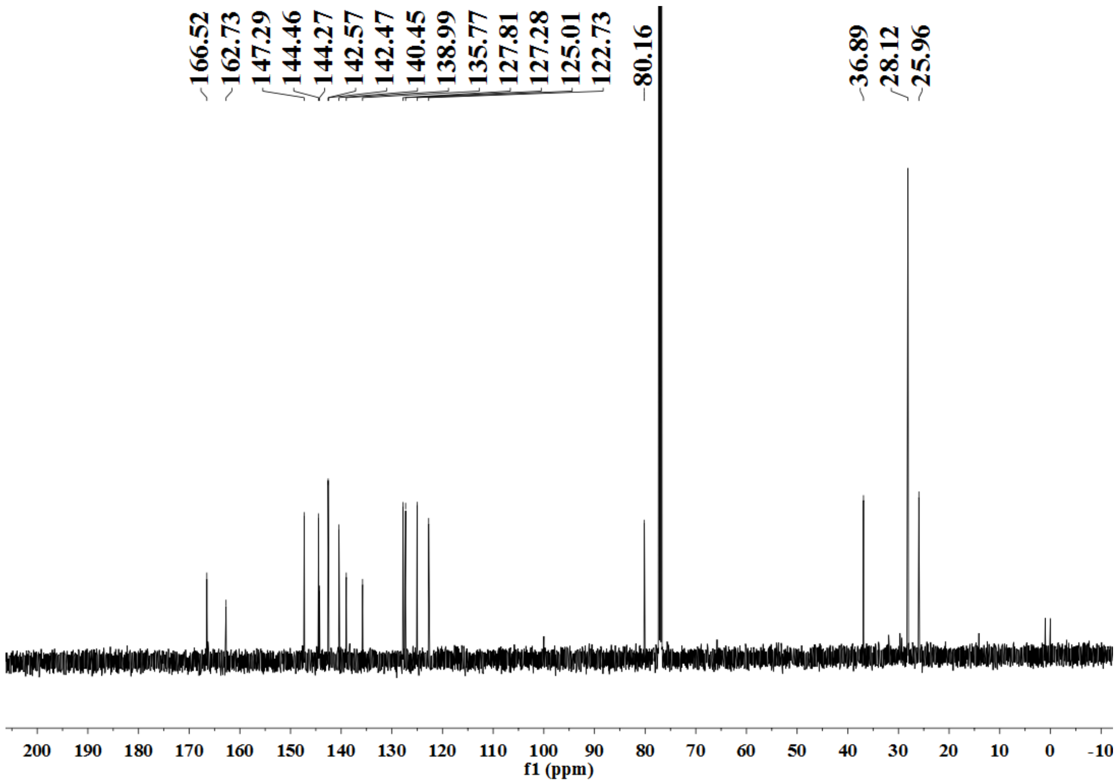
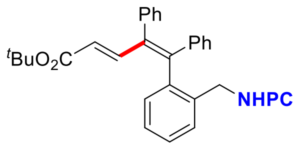
6.83
6.35
6.32
5.83
5.80
4.67
4.66
2.15
1.41
0.96
1.00
1.06
1.05
1.29
1.06
1.02
1.01
1.00
2.00
2.98
9.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)





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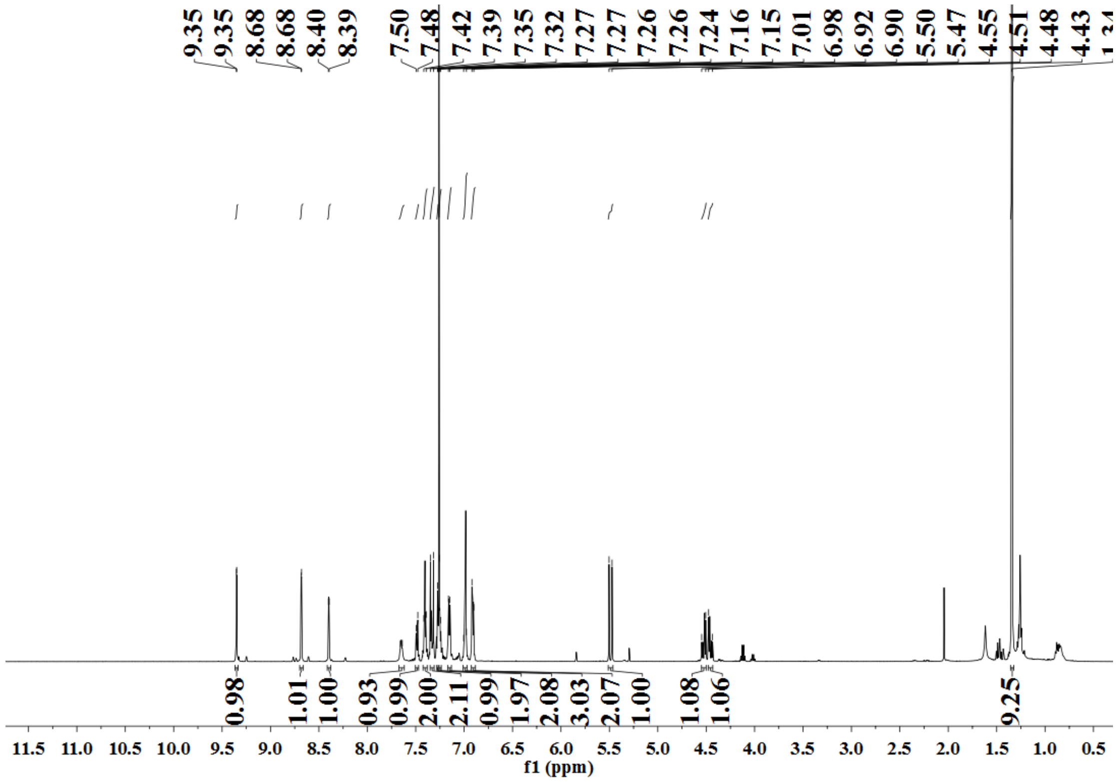

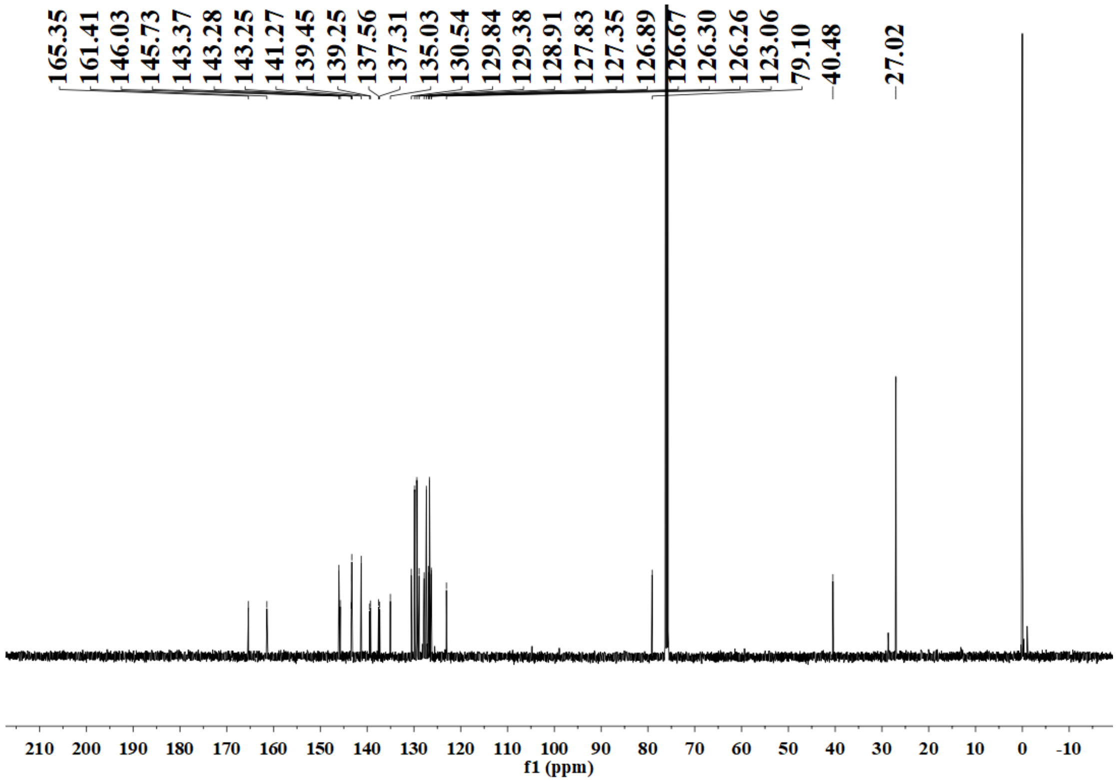
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130.54
129.84
129.38
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127.35
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126.67
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79.10
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27.02
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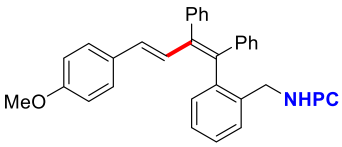
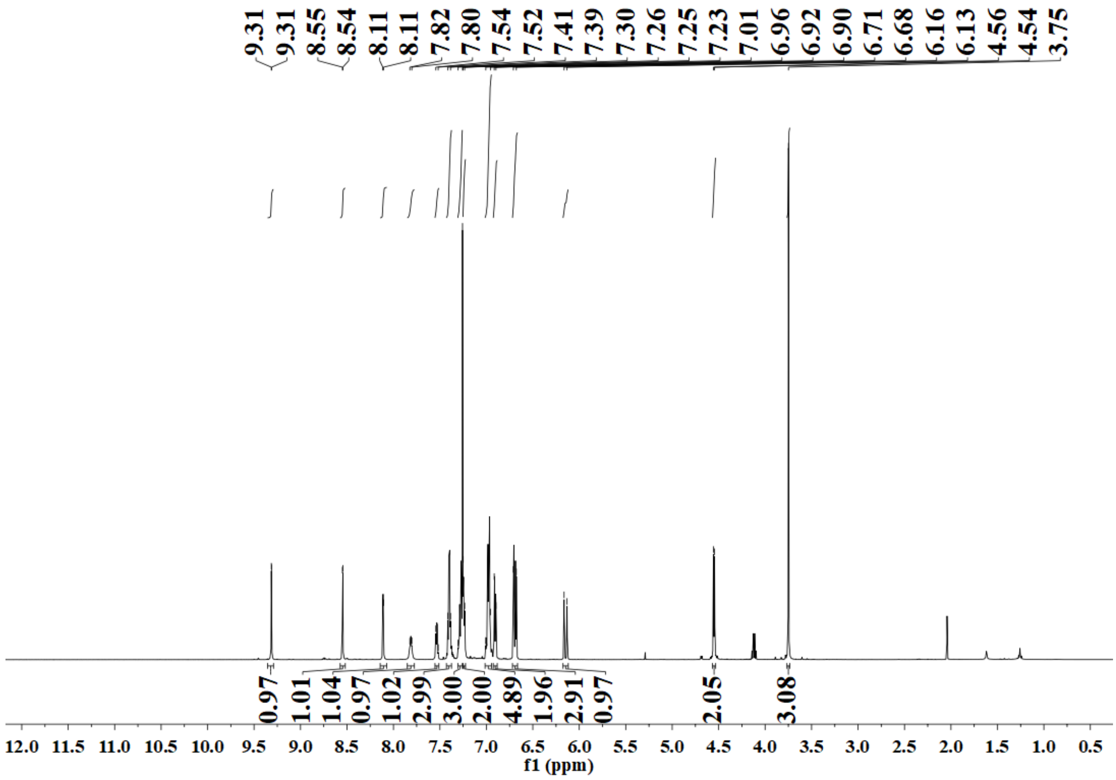
f1 (ppm)


Ph
Ph
MeO
NHPC

(7s)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1.02
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2.00
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1.96
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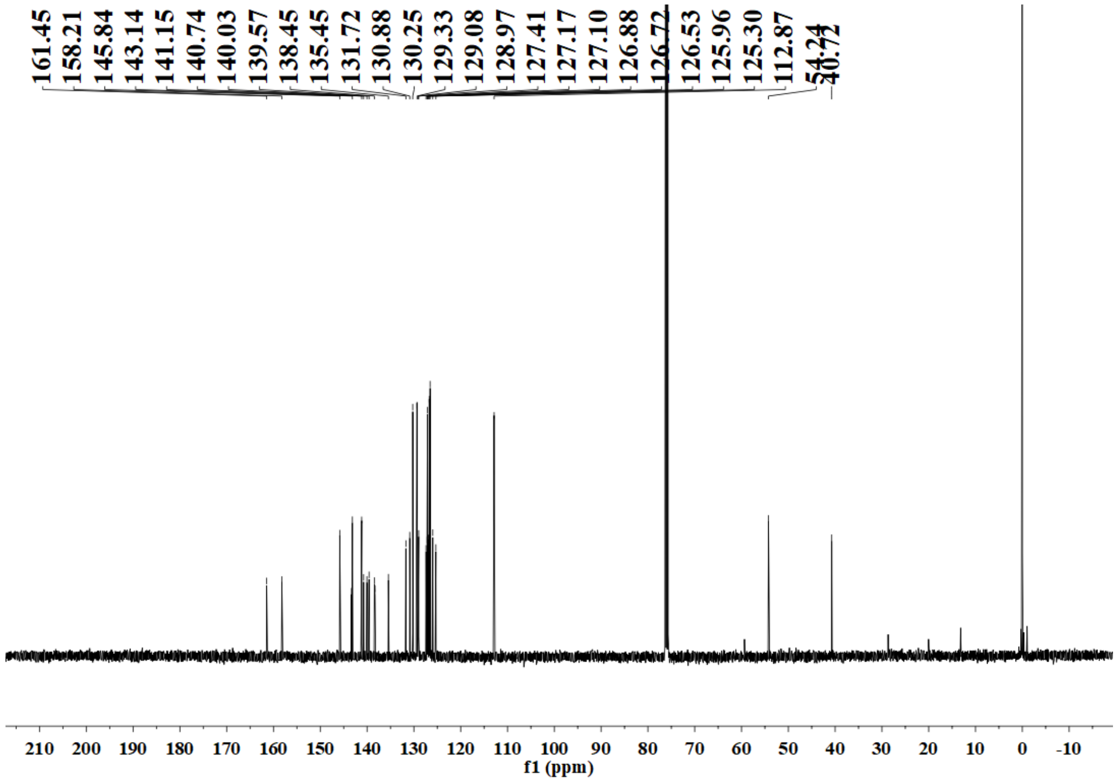
0.97
2.05
3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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126.72
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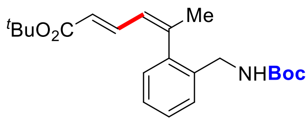
f1 (ppm)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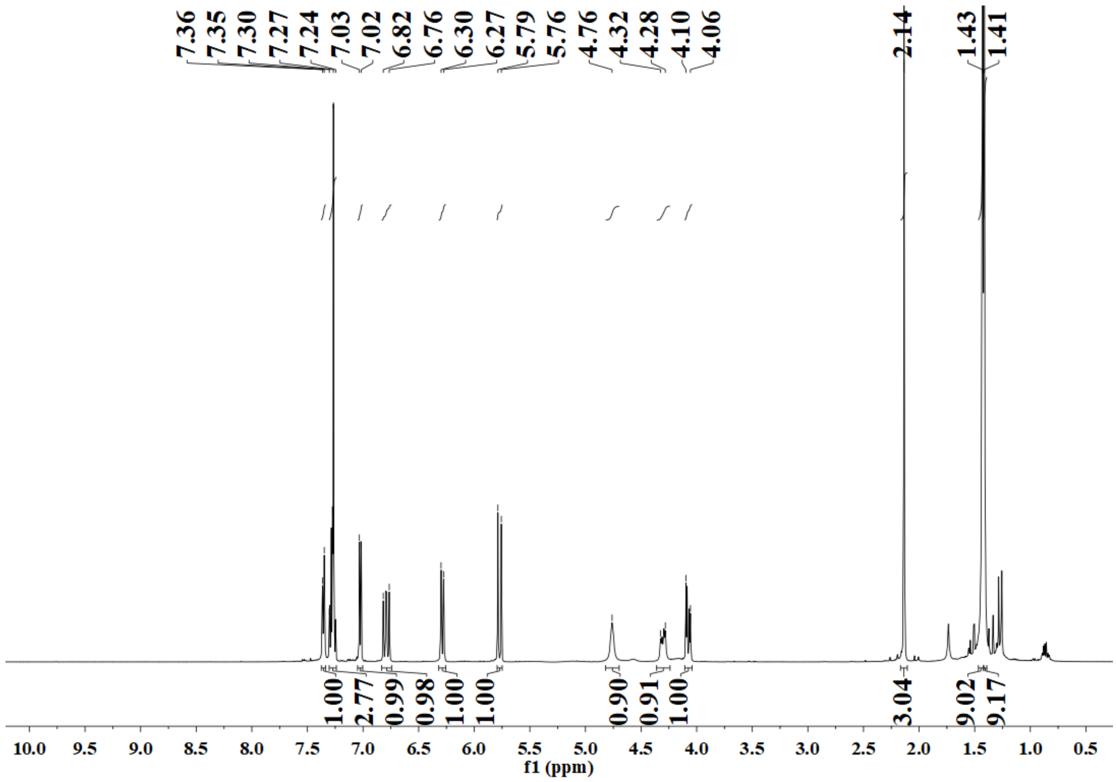
Me
NHBoc

(9)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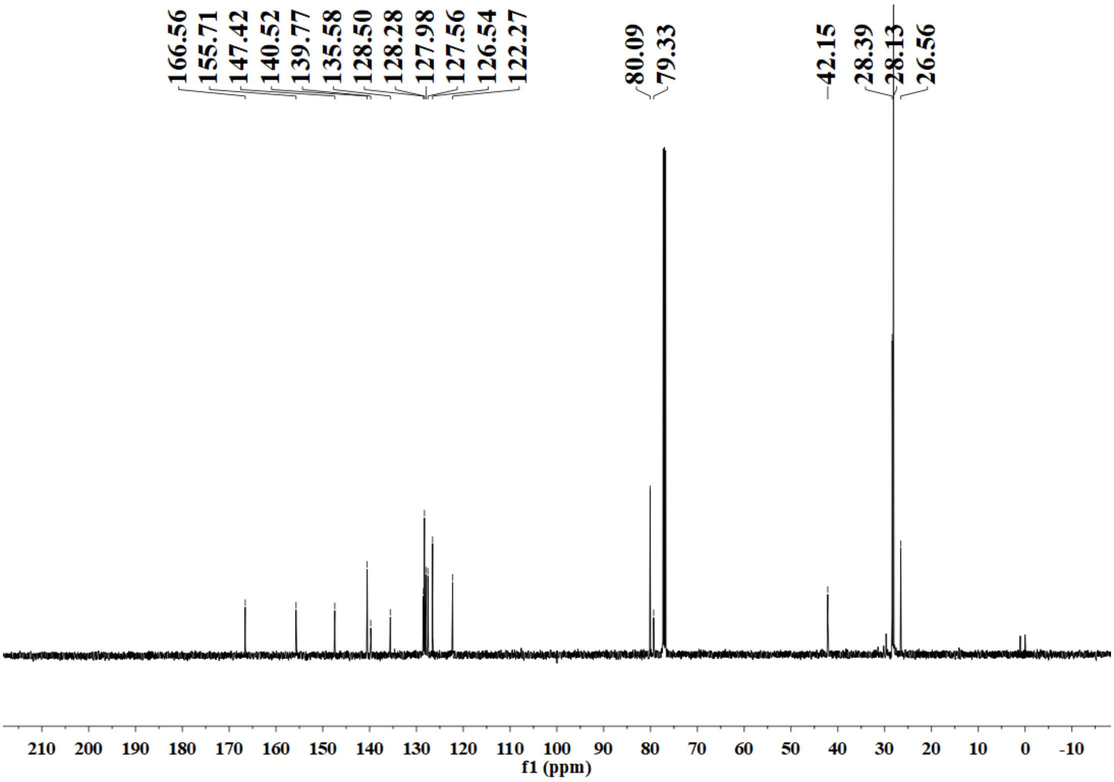
4.28
4.10
4.06
2.14
1.43
1.41
1.00
2.77
0.99
0.98
1.00
1.00
0.90
0.91
1.00
3.04
9.02
9.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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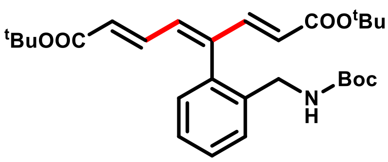
26.56
f1 (ppm)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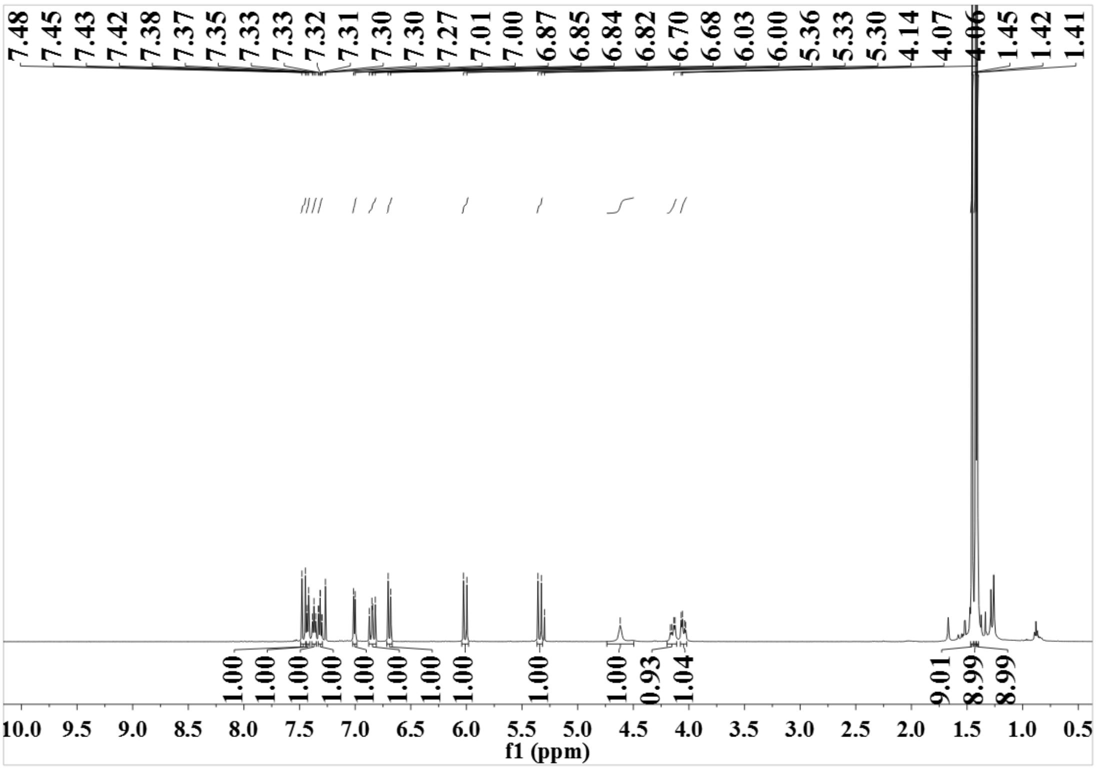
COOtBu
N
H
Boc

(10)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4.07
4.06
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1.42
1.41
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1.00
1.00
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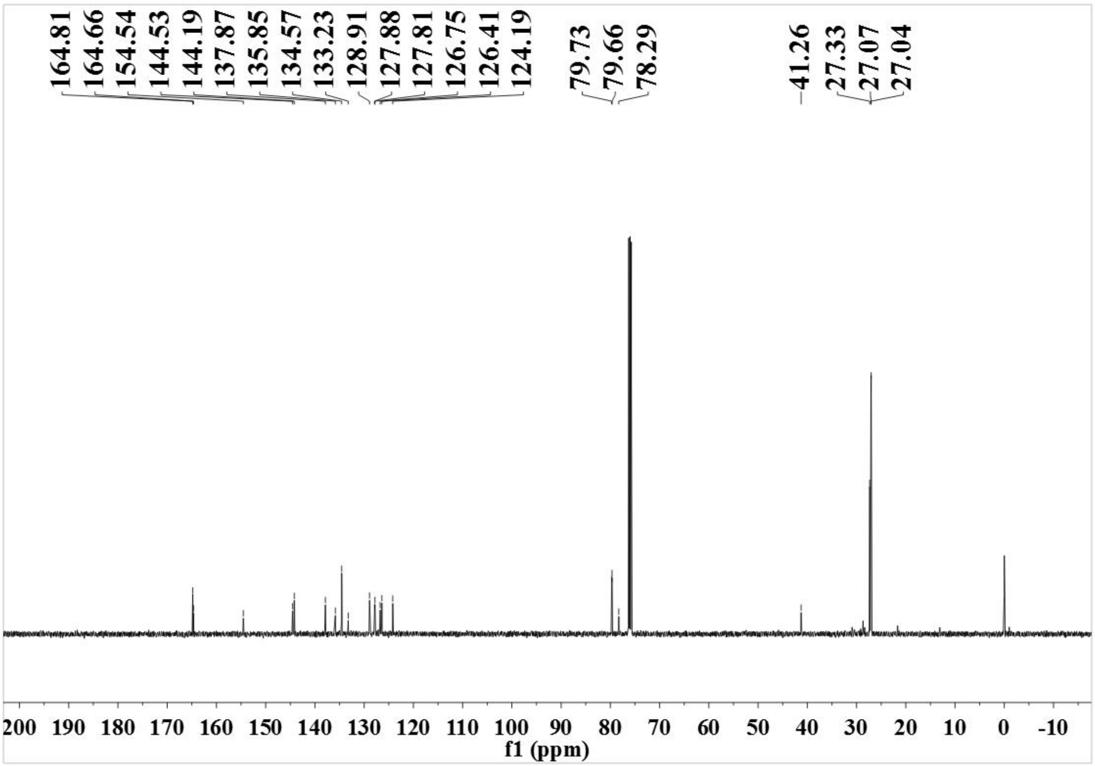
f1 (ppm)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124.19
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79.66
78.29
41.26
27.33
27.07
27.04
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)