Electronic supplementary information

Heck reaction of arenediazonium salts with *N,N*-diprotected allylamines. Synthesis of cinnamylamines and indoles

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Contents:

1. General information S2
2. Characterization data of cinnamylamines **3a** – **3f** S2
3. Characterization data of cinnamylamines **3g** – **3o** S3
4. Characterization data of compounds **5a** – **5e** S5
5. Characterization data of indoles **7a** – **7d** S6
6. Characterization data of indoles **7e** – **7h** S7
7. One-pot synthesis of **12** S8
8. References S8
9. Scans of ^{1}H and ^{13}C NMR spectra S9

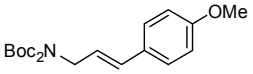
1. General information.

Reagents and methods. All the starting materials, catalysts, bases, and solvents are commercially available and were used as purchased, without further purification. All the products were purified on axially compressed columns, packed with SiO_2 25-40 μm, connected to a solvent delivery system and to a refractive index detector, and eluting with *n*-hexane/AcOEt mixtures.
2-(Alkynyl)trifluoroacetanilides,[1] arenediazonium tetrafluoroborates,[2] and *N,N*-di-Boc-allylamine[3] were prepared according to literature.

2. Cinnamylamines 3a - 3f.

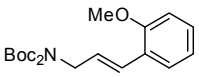
General procedure: an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged under argon with arenediazonium salt (0.5 mmol), *N,N*-$(Boc)_2$ allylamine (0.55 mmol), $Pd_2(dba)_3$ (0.01 mmol), NaOAc (1.5 mmol), and anhydrous MeCN (5 mL). The tube was protected from light with aluminum film, sealed and stirred at room temperature for the indicated time. Then, the reaction mixture was diluted with Et_2O, washed twice with H_2O, and with a saturated NaCl solution. The organic phase was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with a *n*-hexane/AcOEt mixture.

3a.



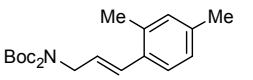
3 h, pale yellow liquid, yield: 90 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.10 (dt, *J* = 15.6 Hz, *J* = 6.4 Hz, 1H), 4.32 (dd, *J* = 5.6 Hz, *J* = 1.2 Hz, 2H), 3.82 (s, 3H), 1.53 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 152.4, 131.9, 129.6, 127.6, 122.9, 114.0, 82.3, 55.3, 48.3, 28.1;
IR (neat, cm^{-1}): 2979, 2935, 1745, 1695, 1608, 1542, 1367, 1250, 1146, 1114;
Anal. Calcd. for $C_{20}H_{29}NO_5$: C, 66.09; H, 8.04; Found: C, 66.19; H, 8.11.

3b.



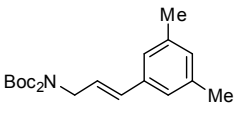
1.5 h, white solid, mp 65-66 °C, yield: 85 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 7.2 Hz, 1H), 7.24 (dt, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 6.95-6.87 (m, 3H), 6.22 (dt, *J* = 16.0 Hz, *J* = 6.4 Hz, 1H), 4.32 (d, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 1.54 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.7, 152.3, 128.6, 127.5, 126.9, 126.0, 125.6, 120.6, 110.8, 82.3, 55.3, 48.6, 28.1;
IR (KBr, cm^{-1}): 2981, 2931, 1745, 1718, 1369, 1352, 1250, 1147, 1118, 756;
Anal. Calcd. for $C_{20}H_{29}NO_5$: C, 66.09; H, 8.04; Found: C, 65.99; H, 8.13.

3c.



5 h, pale yellow liquid, yield: 83 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 7.6 Hz, 1H), 7.00 (m, 2H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.08 (dt, *J* = 15.6 Hz, *J* = 6.4 Hz, 1H), 4.35 (dd, *J* = 6.4 Hz, *J* = 1.2 Hz, 2H), 2.32 (s, 6H), 1.54 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 137.2, 135.2, 133.1, 131.0, 130.1, 126.8, 125.7, 125.5, 82.3, 48.4, 28.1, 21.0, 19.7;
IR (neat, cm^{-1}): 2979, 2931, 1747, 1697, 1367, 1352, 1225, 1147, 1117;
Anal. Calcd. for $C_{21}H_{31}NO_4$: C, 69.78; H, 8.64; Found: C, 69.69; H, 8.58.

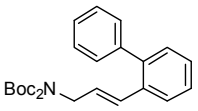
3d.



3 h, pale yellow liquid, yield: 72 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.01 (s, 2H), 6.91 (s, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.21 (dt, *J* = 15.6 Hz, *J* = 6.4 Hz, 1H), 4.34 (d, *J* = 6.0 Hz, 2H), 2.33 (s, 6H), 1.54 (s, 18H);

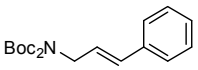
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 137.9, 136.8, 132.5, 129.3, 124.7, 124.3, 82.3, 48.2, 28.1, 21.2;
IR (neat, cm^{-1}): 2979, 2933, 1788, 1747, 1697, 1477, 1456, 1433, 1385, 1367, 1352, 1223, 1115, 1145, 852, 733;
Anal. Calcd. for $C_{21}H_{31}NO_4$: C, 69.78; H, 8.64; Found: C, 69.68; H, 8.68.

3e.



3 h, dark yellow liquid, yield: 61 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (m, 1H), 7.39-7.28 (m, 8H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.20 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 4.26 (dd, *J* = 6.4 Hz, *J* = 1.2 Hz, 2H), 1.48 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.3, 140.9, 140.8, 134.7, 131.1, 130.2, 129.8, 128.1, 127.5, 127.4, 127.0, 126.1, 126.0, 82.3, 48.2, 28.1;
IR (neat, cm^{-1}): 2979, 2933, 1747, 1695, 1475, 1454, 1433, 1385, 1369, 1223, 1144, 1115;
Anal. Calcd. for $C_{25}H_{31}NO_4$: C, 73.32; H, 7.63; Found: C, 73.22; H, 7.75.

3f. (Known compound)[4]

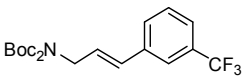


2.5 h, pale yellow liquid, yield: 80 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39-7.23 (m, 5H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.23 (dt, *J* = 15.6 Hz, *J* = 6.4 Hz, 1H), 4.35 (d, *J* = 6.0 Hz, 2H), 1.54 (s, 18H).

3. Cinnamylamines 3g – 3o.

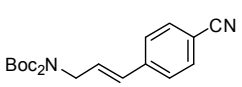
General procedure: an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged under argon with arenediazonium salt (0.5 mmol), *N,N*-$(Boc)_2$ allylamine (0.55 mmol), $Pd_2(dba)_3$ (0.01 mmol), $CaCO_3$ (0.75 mmol), and anhydrous MeOH (5 mL). The tube was protected from light with aluminum film, sealed, and stirred at room temperature for the indicated time. Then, the reaction mixture was diluted with Et_2O, washed twice with H_2O, and with a saturated NaCl solution. The organic phase was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with a *n*-hexane/AcOEt mixture.

3g.



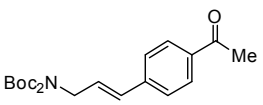
3.5 h, pale yellow liquid, yield: 83 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (s, 1H), 7.54-7.40 (m, 3H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.31 (dt, *J* = 15.6 Hz, *J* = 2.4 Hz, 1H), 4.36 (dd, *J* = 6.0 Hz, *J* = 1.2 Hz, 2H), 1.53 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.3, 137.6, 131.0 (q, *J* = 32.1 Hz), 130.7, 129.5, 129.0, 127.3, 124.6 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 271.2 Hz), 123.0 (q, *J* = 3.7 Hz), 82.5, 47.9, 28.1;
IR (neat, cm^{-1}): 2981, 2935, 1747, 1695, 1369, 1333, 1165, 1146, 1124;
Anal. Calcd. for $C_{20}H_{26}F_3NO_4$: C, 59.84; H, 6.53; Found: C, 59.76; H, 6.46.

3h.



1.5 h, white solid, mp 100-101 °C, yield: 83 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 4.37 (d, *J* = 5.6 Hz, 2H), 1.52 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.3, 141.3, 132.4, 130.4, 129.4, 126.7, 118.9, 110.8, 82.7, 47.8, 28.1;
IR (KBr, cm^{-1}): 2979, 2933, 2223, 1724, 1682, 1338, 1226, 1143, 1122;
Anal. Calcd. for $C_{20}H_{26}N_2O_4$: C, 67.02; H, 7.31; Found: C, 67.11; H, 7.22.

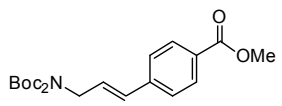
3i.



5 h, pale yellow liquid, yield: 70 %.

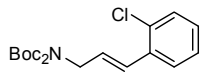
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 4.36 (d, *J* = 5.2 Hz, 2H), 2.58 (s, 3H), 1.51 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.4, 152.3, 141.4, 136.1, 131.0, 128.7, 128.3, 126.4, 82.6, 48.0, 28.1, 26.5;
IR (neat, cm^{-1}): 2979, 2933, 1747, 1685, 1602, 1367, 1267, 1224, 1145, 1118;
Anal. Calcd. for $C_{21}H_{29}NO_5$: C, 67.18; H, 7.79; Found: C, 67.26; H, 7.87.

3j.



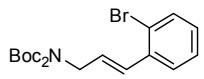
6 h, white solid, mp 77-78 °C, yield: 67 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 4.37 (d, *J* = 6.0 Hz, 2H), 3.92 (s, 3H), 1.52 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.8, 152.3, 141.3, 131.2, 129.9, 129.0, 128.0, 126.3, 82.6, 52.0, 48.0, 28.1;
IR (KBr, cm^{-1}): 2979, 2933, 2223, 1718, 1689, 1367, 1353, 1282, 1232, 1149, 1108;
Anal. Calcd. for $C_{21}H_{29}NO_6$: C, 64.43; H, 7.47; Found: C, 64.36; H, 7.31.

3k.



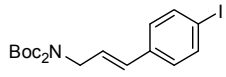
4 h, orange liquid, yield: 83 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.34 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.22-7.17 (m, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 4.38 (dd, *J* = 6.0 Hz, *J* = 1.2 Hz, 2H), 1.54 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 134.9, 133.0, 129.6, 128.6, 128.4, 128.0, 126.9, 126.8, 82.5, 48.0, 28.1;
IR (neat, cm^{-1}): 2979, 2933, 1747, 1697, 1367, 1351, 1224, 1147, 1109, 752;
Anal. Calcd. for $C_{19}H_{26}ClNO_4$: C, 62.03; H, 7.12; Found: C, 61.95; H, 7.00.

3l.



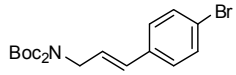
4 h, yellow liquid, yield: 74 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.49 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.19 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 4.37 (d, *J* = 5.6 Hz, 2H), 1.54 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 136.6, 132.9, 130.9, 128.9, 128.2, 127.5, 127.1, 123.5, 82.5, 48.0, 28.1;
IR (neat, cm^{-1}): 2979, 2933, 1747, 1697, 1465, 1434, 1384, 1367, 1351, 1145, 1120;
Anal. Calcd. for $C_{19}H_{26}BrNO_4$: C, 55.35; H, 6.36; Found: C, 55.43; H, 6.26.

3m.



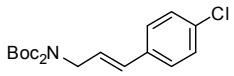
4 h, white solid, mp 68-69 °C, yield: 63 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.22 (dt, *J* = 16.0 Hz, *J* = 6.4 Hz, 1H), 4.32 (d, *J* = 6.4 Hz, 2H), 1.52 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 137.6, 136.3, 131.1, 128.2, 126.2, 92.8, 82.5, 48.0, 28.1;
IR (KBr, cm^{-1}): 2977, 2931, 1737, 1695, 1350, 1232, 1149, 1122;
Anal. Calcd. for $C_{19}H_{26}INO_4$: C, 49.68; H, 5.71; Found: C, 49.55; H, 5.66.

3n.



3 h, white solid, mp 64-65 °C, yield: 63 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.22 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 4.32 (d, *J* = 6.0 Hz, 2H), 1.52 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 135.7, 131.6, 131.0, 127.9, 126.0, 121.3, 82.4, 48.0, 28.1;
IR (KBr, cm^{-1}): 2979, 2931, 1739, 1695, 1348, 1234, 1149, 1124;
Anal. Calcd. for $C_{19}H_{26}BrNO_4$: C, 55.35; H, 6.36; Found: C, 55.26; H, 6.28.

3o.

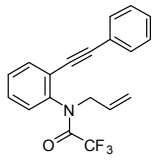


4 h, white solid, mp 51-52 °C, yield: 77 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (m, 4H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 15.6 Hz, *J* = 6.4 Hz, 1H), 4.33 (d, *J* = 6.4 Hz, 2H), 1.52 (s, 18H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 135.3, 133.2, 131.0, 128.7, 127.6, 125.9, 82.5, 48.0, 28.1;
IR (KBr, cm^{-1}): 2979, 2933, 1735, 1695, 1350, 1234, 1149, 1122;
Anal. Calcd. for $C_{19}H_{26}ClNO_4$: C, 62.03; H, 7.12; Found: C, 62.11; H, 7.01.

4. Compounds 5a – 5e.

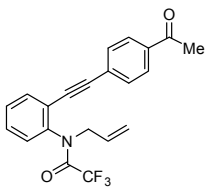
General procedure: an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged under argon with 2-(alkynyl)trifluoroacetanilide (1 equiv), allylbromide (1.5 equiv), K_2CO_3 (1.2 eq.), and anhydrous DMF (0.3 M). The tube was sealed and stirred at room temperature for the indicated period of time. Then, the reaction mixture was diluted with Et_2O, washed twice with H_2O, and with a saturated NaCl solution. The organic phase was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with a *n*-hexane/AcOEt mixture.

5a. (Known compound)[1]



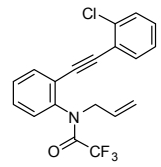
4 h, pale yellow liquid, yield: 89 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (m, 1H), 7.50 (m, 2H), 7.41 (m, 5H), 7.24 (m, 1H), 5.93 (m, 1H), 5.19 (m, 2H), 4.91 (dd, *J* = 14.4 Hz, *J* = 5.7 Hz, 1H), 4.01 (dd, *J* = 14.4 Hz, *J* = 7.6 Hz, 1H).

5b.



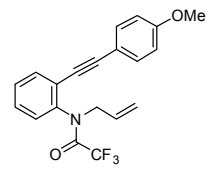
10 min, pale yellow liquid, yield: 90 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.4 Hz, 2H), 7.66-7.64 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.44-7.42 (m, 2H), 7.26 (m, 1H), 5.90 (m, 1H), 5.19 (m, 2H), 4.87 (dd, *J* = 14.4 Hz, *J* = 5.6 Hz, 1H), 3.99 (dd, *J* = 14.8 Hz, *J* = 7.6 Hz, 1H), 2.62 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.1, 157.0 (q, *J* = 36.8 Hz), 132.9, 131.7, 130.7, 129.7, 129.4, 129.2, 128.3, 127.0, 122.9, 120.1, 116.2 (q, *J* = 288.6 Hz), 94.4, 87.7, 53.7, 26.5;
IR (neat, cm^{-1}): 3072, 3004, 2927, 1687, 1602, 1484, 1452, 1403, 1359, 1265, 1187, 1155, 838, 755;
MS *m/z:* 274 (100), 344 (76), 232 (56), 246 (40), 190 (40), 302 (29), 371 (M^+, 20);
Anal. Calcd. for $C_{21}H_{16}F_3NO_2$: C, 67.92; H, 4.34; Found: C, 67.82; H, 4.26.

5c.



3 h, pale yellow liquid, yield: 83 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (m, 1H), 7.54 (m, 1H), 7.43 (m, 3H), 7.32-7.23 (m, 3H), 5.92 (m, 1H), 5.19 (dd, *J* = 17.2 Hz, *J* = 10.0 Hz, 2H), 4.98 (dd, *J* = 14.4 Hz, *J* = 6.0 Hz, 1H), 3.98 (dd, *J* = 14.4 Hz, *J* = 7.6 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.8 (q, *J* = 36.8 Hz), 139.9, 136.0, 133.4, 133.2, 130.8, 130.0, 130.0, 129.4, 129.2, 129.1, 126.6, 123.0, 122.4, 120.1, 116.3 (q, *J* = 288.6 Hz), 92.0, 89.6, 53.6;
IR (neat, cm^{-1}): 3074, 2931, 1701, 1492, 1471, 1452, 1438, 1207, 1190, 1155, 756;
MS *m/z*: 336 (100), 226 (85), 69 (79), 190 (61), 230 (59), 294 (59), 266 (53), 363 (M^+, 43);
Anal. Calcd. for $C_{19}H_{13}ClF_3NO$: C, 62.73; H, 3.60; Found: C, 62.65; H, 3.51.

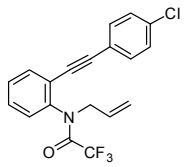
5d.



12 h, pale yellow liquid, yield: 91 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (m, 1H), 7.46-7.34 (m, 4H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 5.93 (m, 1H), 5.19 (m, 2H), 4.90 (dd, *J* = 14.4 Hz, *J* = 5.6 Hz, 3H), 3.99 (dd, *J* = 14.8 Hz, *J* = 7.6 Hz, 1H), 3.85 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 157.1 (q, *J* = 37.6 Hz), 139.8, 133.2, 132.5, 130.9, 129.6, 129.1, 128.3, 123.8, 119.9, 116.3 (q, *J* = 288.6 Hz), 114.4, 114.2, 95.8, 83.6, 55.3, 53.5;
IR (neat, cm^{-1}): 2935, 2840, 1697, 1606, 1512, 1454, 1251, 1205, 1188, 1155, 1030, 833;
MS *m/z:* 359 (M^+, 100), 262 (68), 290 (60), 235 (55), 332 (52);
Anal. Calcd. for $C_{20}H_{16}F_3NO_2$: C, 66.85; H, 4.49; Found: C, 66.72; H, 4.40.

5e.

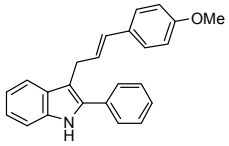


4 h, pale yellow liquid, yield: 88 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (m, 1H), 7.62-7.40 (m, 6H), 7.24 (m, 1H), 5.89 (m, 1H), 5.20 (m, 2H), 4.88 (dd, *J* = 14.4 Hz, *J* = 6.0 Hz, 1H), 3.99 (dd, *J* = 14.4 Hz, *J* = 7.2 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.1 (q, *J* = 37.6 Hz), 140.1, 135.1, 132.9, 132.8, 130.7, 129.7, 129.2, 129.0, 128.9, 123.2, 120.8, 120.1, 116.3 (q, *J* = 288.6 Hz), 94.3, 85.6, 53.6;
IR (neat, cm^{-1}): 3085, 2929, 1701, 1494, 1452, 1207, 1190, 1155, 1091, 829, 758;
MS *m/z*: 336 (100), 266 (82), 190 (66), 294 (65), 253 (58), 328 (58), 231 (54), 363 (M^+, 54);
Anal. Calcd. for $C_{19}H_{13}ClF_3NO$: C, 62.73; H, 3.60; Found: C, 62.62; H, 3.49.

5. Indoles 7a – 7d.

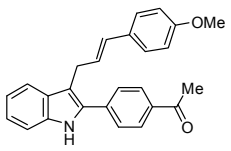
General procedure: an oven-dried Schlenk tube equipped with a magnetic starring bar was charged under argon with arenediazonium salt (0.275 mmol), 2-alkynyl-*N*-(allyl)trifluoroacetanilide (0.25 mmol), $Pd_2(dba)_3$ (0.005 mmol), sodium acetate (0.75 mmol) and anhydrous MeCN (2.5 mL). The tube was protected from light with aluminum film, sealed, and stirred at room temperature for the indicated time. Then, K_2CO_3 (0.5 mmol) and PPh_3 (0.04 mmol) were added. The tube was sealed and stirred at 100 °C for the indicated time. The reaction was diluted with Et_2O, washed twice with H_2O, and with a saturated NaCl solution. The organic phase was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with a *n*-hexane/AcOEt mixture.

7a. (Known compound)[1]



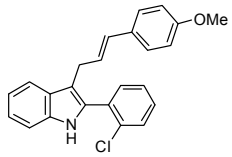
2 + 8 h, yellow solid, yield: 68 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (bs, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.44 (m, 2H), 7.30 (m, 3H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.46 (m, 2H), 3.80 (m, 5H).

7b.



1.5 + 12 h, yellow solid, mp 146-147 °C, yield: 79 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (bs, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.70 (m, 3H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.28 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.41 (m, 2H), 3.81 (m, 5H), 2.66 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.5, 158.9, 137.5, 136.4, 135.8, 133.5, 130.4, 129.9, 129.4, 129.0, 127.2, 126.9, 123.2, 120.1, 119.8, 113.9, 112.8, 111.0, 55.3, 28.2, 26.6;
IR (KBr, cm^{-1}): 3336, 1672, 1604, 1510, 1261;
Anal. Calcd. for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; Found: C, 81.69; H, 6.12.

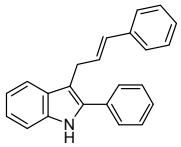
7c.



1 + 12 h, yellow wax, yield: 88 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (bs, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.54 (m, 2H), 7.38 (m, 3H), 7.28 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 15.6 Hz, *J* = 6.0 Hz, 1H), 3.82 (m, 3H), 3.68 (d, *J* = 5.6 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 135.9, 133.9, 132.7, 132.1, 131.7, 130.7, 130.1, 129.6, 128.3, 127.3, 127.2, 126.8, 122.5, 119.8, 119.6, 113.9, 112.7, 110.9, 55.3, 28.4;
IR (neat, cm^{-1}): 3407, 3056, 2931, 1606, 1510, 1454, 1245, 1035, 744;

MS *m/z:* 373 (M^+, 100), 121 (61), 375 (35), 217 (35), 234 (29);
Anal. Calcd. for $C_{24}H_{20}ClNO$: C, 77.10; H, 5.39; Found: C, 76.99; H, 5.45.

7d. (Known compound)[1]

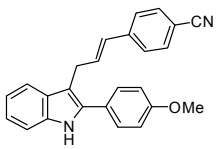


0.5 + 12 h, yellow waxy solid, yield: 81 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (bs, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.46-7.18 (m, 9H), 6.63-6.50 (m, 2H), 3.86 (d, *J* = 4.8 Hz, 2H).

6. Indoles 7e – 7h.

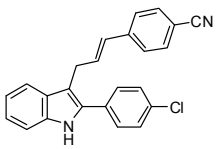
General procedure: an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged under argon with arenediazonium salt (0.275 mmol), 2-alkynyl-*N*-(allyl) trifluoroacetanilide (0.25 mmol), $Pd_2(dba)_3$ (0.005 mmol), $CaCO_3$ (0.375 mmol), and anhydrous MeOH (2.5 mL). The tube was protected from light with aluminum film, sealed, and stirred at room temperature for the indicated period of time. Then, the solvent was evaporated under reduced pressure and K_2CO_3 (0.5 mmol), PPh_3 (0.04 mmol), and anhydrous MeCN (2.5 mL) were added. The tube was sealed and stirred at 100 °C for the indicated period of time. The reaction was diluted with Et_2O, washed twice with H_2O, and with a saturated NaCl solution. The organic phase was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with an *n*-hexane/AcOEt mixture.

7e.



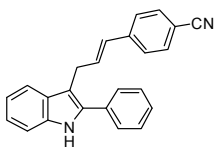
2 + 12 h, yellow waxy solid, yield: 69 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (bs, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56-7.50 (m, 4H), 7.42 (m, 3H), 7.25 (t, *J* = 6.8 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.68 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.89 (s, 3H), 3.82 (d, *J* = 6.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 142.3, 135.8, 135.2, 134.2, 132.3, 129.3, 129.2, 128.8, 126.6, 125.3, 122.2, 119.8, 119.1, 119.0, 114.4, 110.8, 110.0, 108.8, 55.4, 28.3;
IR (KBr, cm^{-1}): 3394, 3033, 2925, 2837, 2225, 1602, 1508, 1458, 1250, 1176, 835, 744;
MS *m/z:* 364 (M^+, 100), 236 (49), 363 (32), 365 (30);
Anal. Calcd. for $C_{25}H_{20}N_2O$: C, 82.39; H, 5.35; Found: C, 82.27; H, 5.26.

7f.



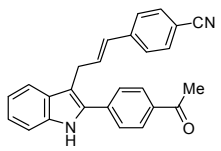
1 + 6 h, yellow waxy solid, yield: 72 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (bs, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.56-7.38 (m, 9H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.67 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.83 (d, *J* = 5.6 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1, 136.1, 134.0, 133.9, 133.7, 132.3, 131.2, 129.2, 129.1, 129.1, 129.0, 126.6, 122.9, 120.1, 119.3, 119.1, 111.1, 110.1, 110.1, 28.3;
IR (KBr, cm^{-1}): 3398, 3057, 2923, 2225, 1602, 1485, 1456, 1093, 833, 742, 547;
MS *m/z:* 368 (M^+, 100), 240 (49), 217 (36), 369 (32), 370 (31), 204 (31);
Anal. Calcd. for $C_{24}H_{17}ClN_2$: C, 78.15; H, 4.65; Found: C, 78.08; H, 4.51.

7g.



1 + 10 h, orange waxy solid, yield: 73 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (bs, 1H), 7.66-7.38 (m, 11H), 7.28 (dt, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.41 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 3.87 (d, *J* = 5.6 Hz, *J* = 1.6 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 136.0, 135.2, 134.0, 132.9, 132.8, 132.3, 129.2, 129.0, 128.9, 127.9, 126.6, 122.5, 119.9, 119.2, 119.1, 111.0, 110.0, 109.6, 28.3;
IR (KBr, cm^{-1}): 3396, 3056, 2923, 2225, 1602, 1450, 744, 689;
MS *m/z:* 334 (M^+, 100), 206 (51), 218 (46), 333 (26);
Anal. Calcd. for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; Found: C, 86.06; H, 5.40.

7h.

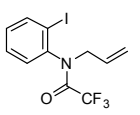


1 + 12 h, yellow solid, mp 182-183 °C, yield: 73 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (bs, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.32 (m, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.69 (dt, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.88 (d, *J* = 5.6 Hz, *J* = 1.6 Hz, 2H), 2.66 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.4, 142.0, 137.3, 136.4, 136.0, 133.8, 133.4, 132.3, 129.2, 129.2, 129.0, 127.6, 126.6, 123.4, 120.3, 119.5, 119.0, 111.5, 111.1, 110.3, 28.3, 26.6;
IR (KBr, cm^{-1}): 3352, 2923, 2221, 1668, 1603, 1275;
Anal. Calcd. for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; Found: C, 82.88; H, 5.42.

7. One-pot synthesis of 12.

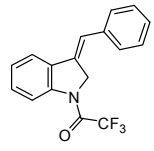
General procedure: an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged under argon with benzenediazonium tetrafluoroborate (52.8 mg, 0.25 mmol), 2-iodo-*N*-(allyl)trifluoroacetanilide (88.8 mg, 0.275 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), $CaCO_3$ (61.5 mg, 0.75 mmol), and anhydrous MeCN (2.5 mL). The tube was protected from light with aluminum film, sealed, and stirred at room temperature for 1 h. Then, the solvent was evaporated under reduced pressure and $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol), P(*o*-tol)$_3$ (15.2 mg, 0.05 mmol), Et_3N (174 µL, 1.25 mmol), and anhydrous MeCN (2.5 mL) were added. The tube was sealed and stirred at 80 °C overnight. The reaction was diluted with Et_2O, washed twice with H_2O, and with a saturated NaCl solution. The organic phase was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with a *n*-hexane/AcOEt 90/10 v/v.

10.



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 5.93-5.83 (m, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 5.15 (d, *J* = 16.8 Hz, 1H), 4.96 (dd, *J* = 14.4 Hz, *J* = 5.6 Hz, 1H), 3.61 (dd, *J* = 14.4 Hz, *J* = 8.0 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.4 (q, *J* = 36.8 Hz), 140.9, 140.1, 131.0, 130.7, 130.2, 128.8, 120.6, 116.0 (q, *J* = 288.5 Hz), 99.5, 53.3;
IR (neat, cm^{-1}): 3085, 2931, 1700, 1471, 1438, 1411, 1211, 1187, 1155, 727;
Anal. Calcd. for $C_{11}H_9F_3INO$: C, 37.21; H, 2.55; Found: C, 37.10; H, 2.27.

12.

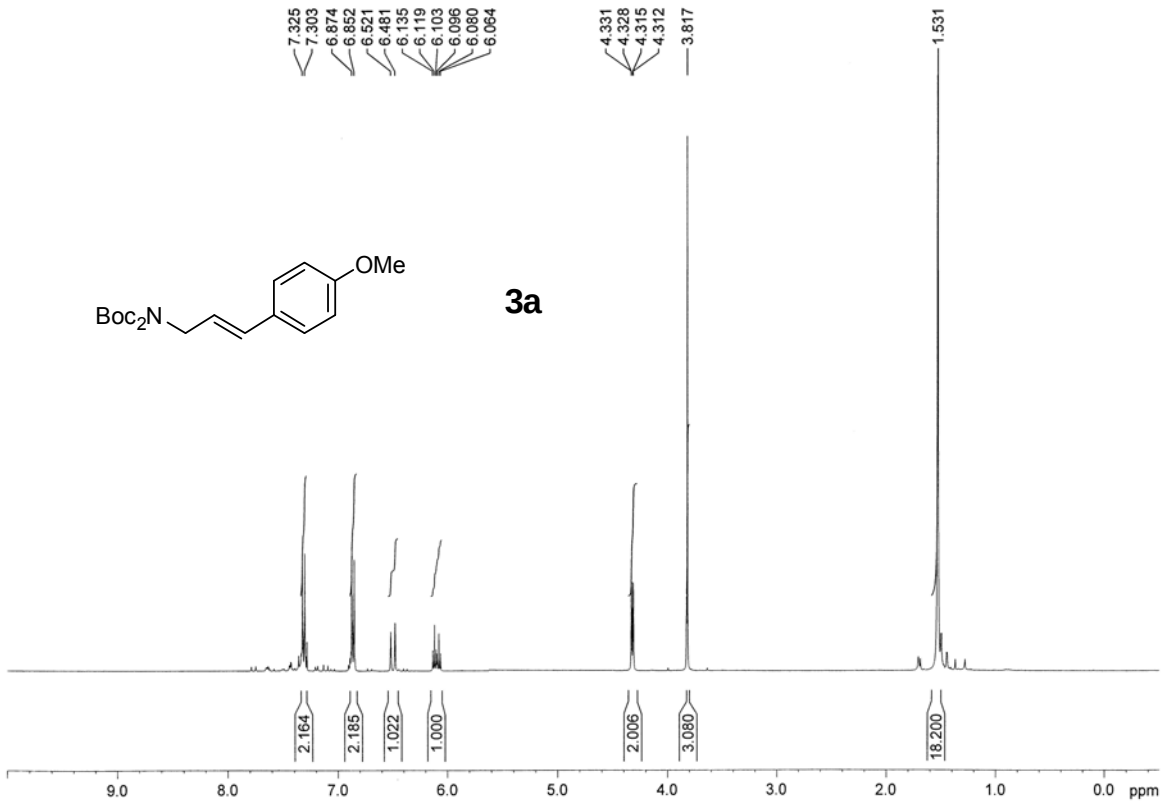


1 + 12 h, white solid, mp 147-148 °C, yield: 50 %.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.38-7.24 (m, 5H), 6.97 (t, *J* = 2.8 Hz, 1H), 5.15 (d, *J* = 2.8 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.7 (q, *J* = 38.5 Hz), 142.8, 136.0, 131.5, 131.3, 129.9, 129.0, 128.3, 127.6, 126.1, 119.9, 119.1, 118.3, 116.0 (q, *J* = 288.1 Hz), 52.5;
IR (KBr, cm^{-1}): 2925, 1693, 1467, 1434, 1234, 1199, 1151, 1095, 763, 690;
MS *m/z:* 69 (100), 303 (M^+, 99), 206 (47), 226 (45), 204 (31), 302 (31), 178 (22);
Anal. Calcd. for $C_{17}H_{12}F_3NO$: C, 67.32; H, 3.99; Found: C, 67.21; H, 4.09.

8. References.

1) Cacchi S., Fabrizi G., Pace P. *J. Org. Chem.* **1998**, *63*, 1001-1011.
2) Roe A. *Org. React*. **1949**, *5*, 193.
3) Arcadi A., Bernocchi E., Cacchi S., Caglioti L., Marinelli F. *Tetrahedron Lett.* **1990**, *31*, 2463-2466.
4) Donnell R. D., Rein T., Åkermark B., Helquist P. *J. Org. Chem.* **1988**, *53*, 3845-3849.

9. Copy of ^{1}H and ^{13}C spectra.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6.874
6.852
6.521
6.481
6.135
6.119
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6.096
6.080
6.064
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4.328
4.315
4.312
3.817
1.531
OMe
Boc2N
3a
2.164
2.185
1.022
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2.006
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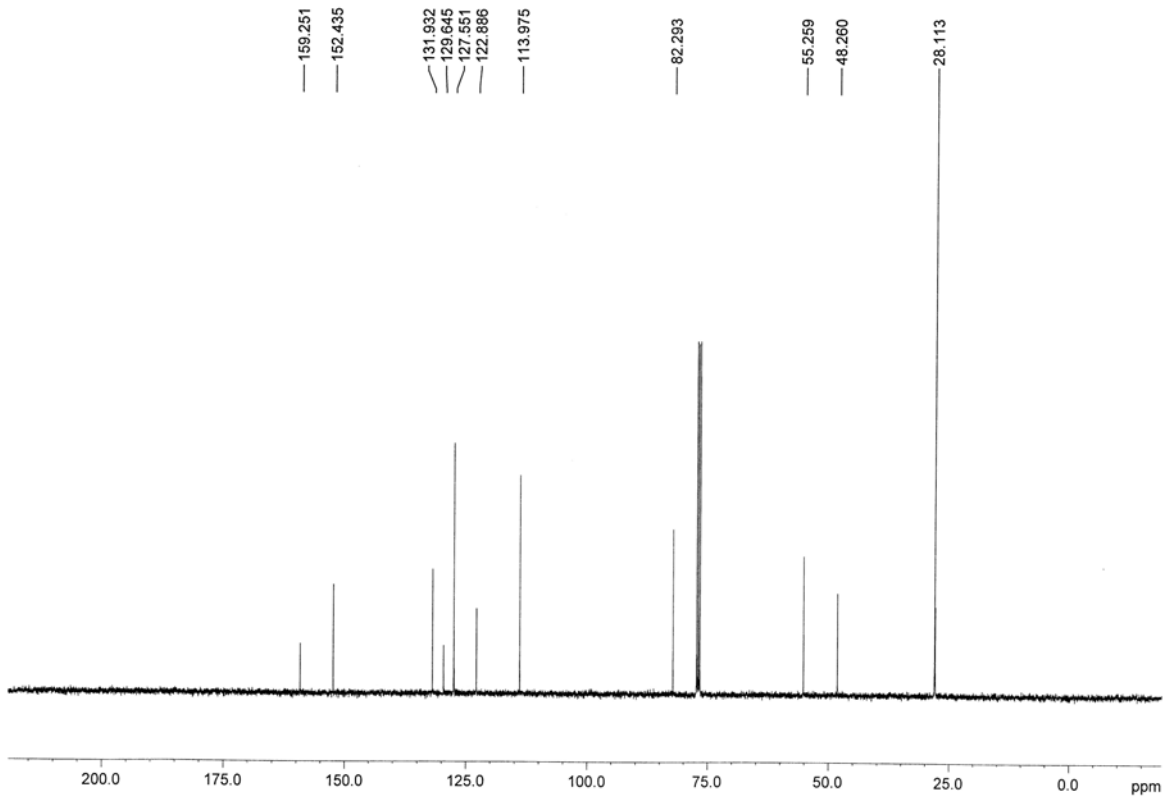
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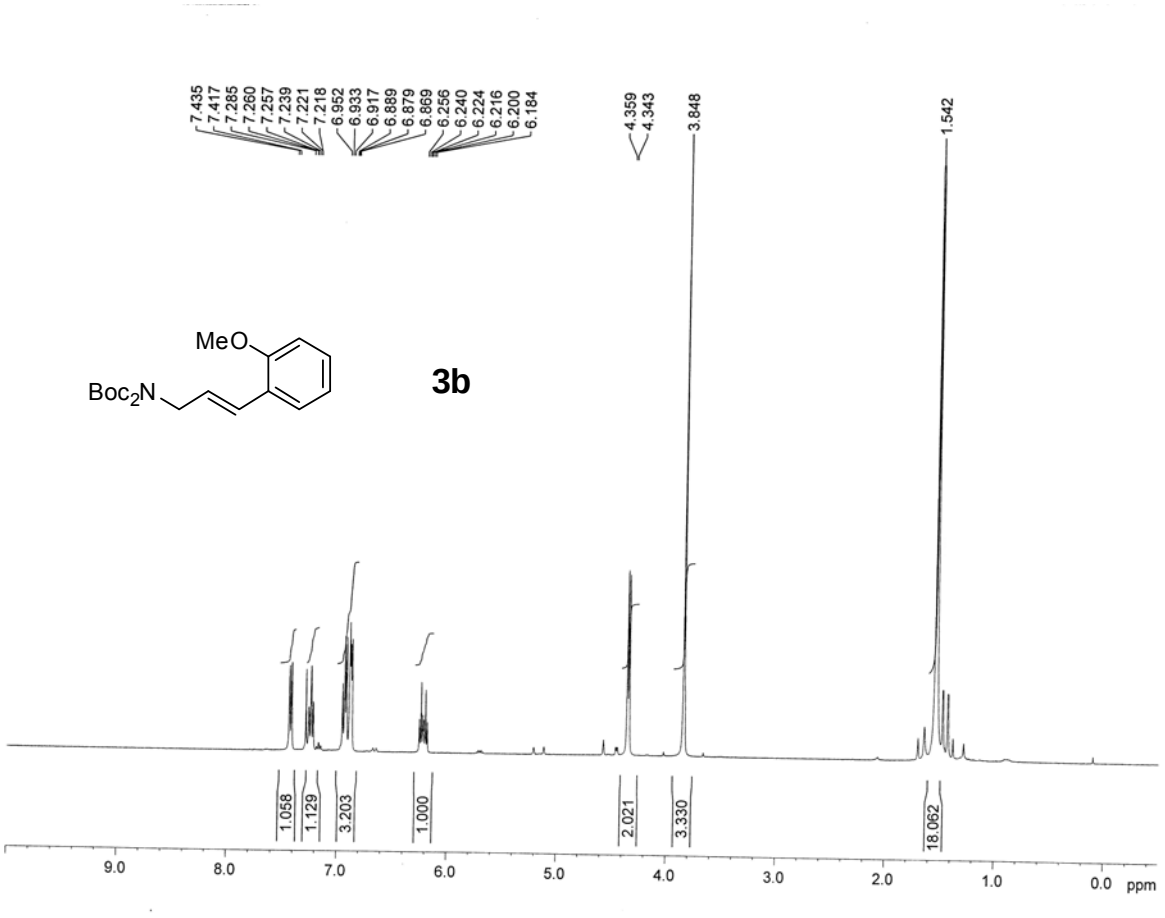
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6.879
6.869
6.256
6.240
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6.216
6.200
6.184
4.359
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3.848
1.542
MeO
Boc2N
3b
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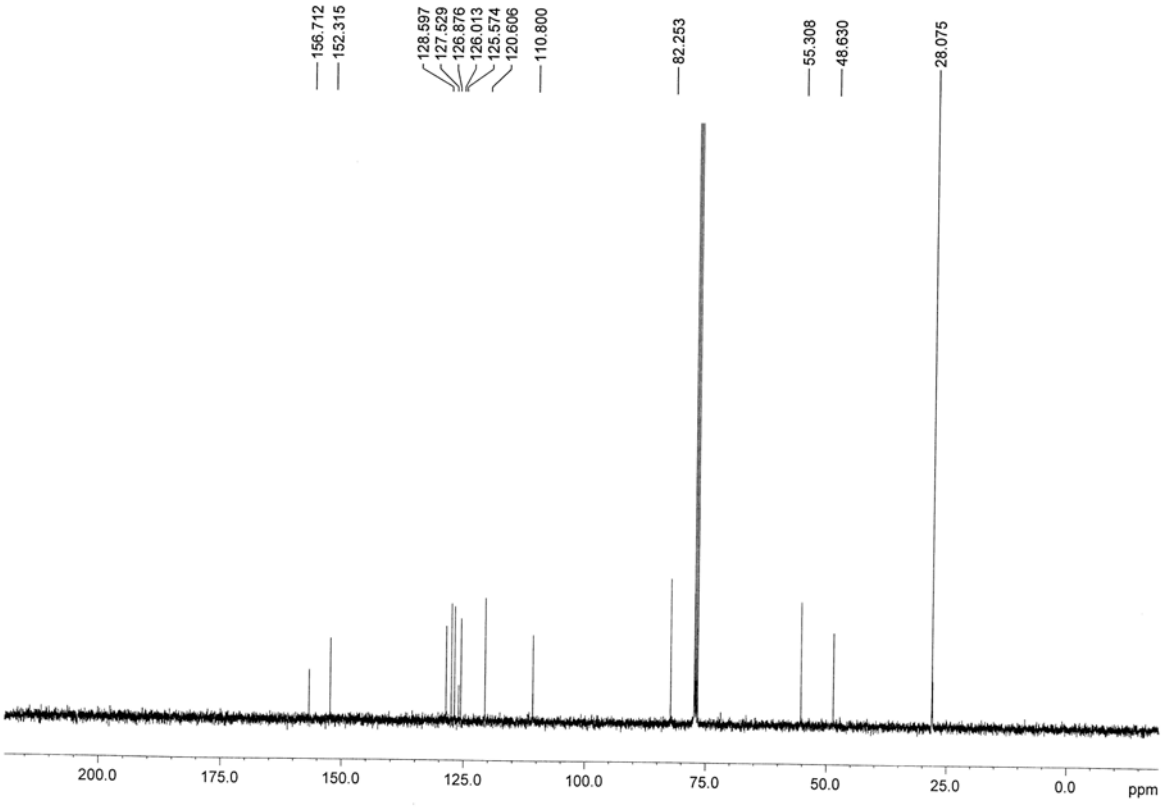
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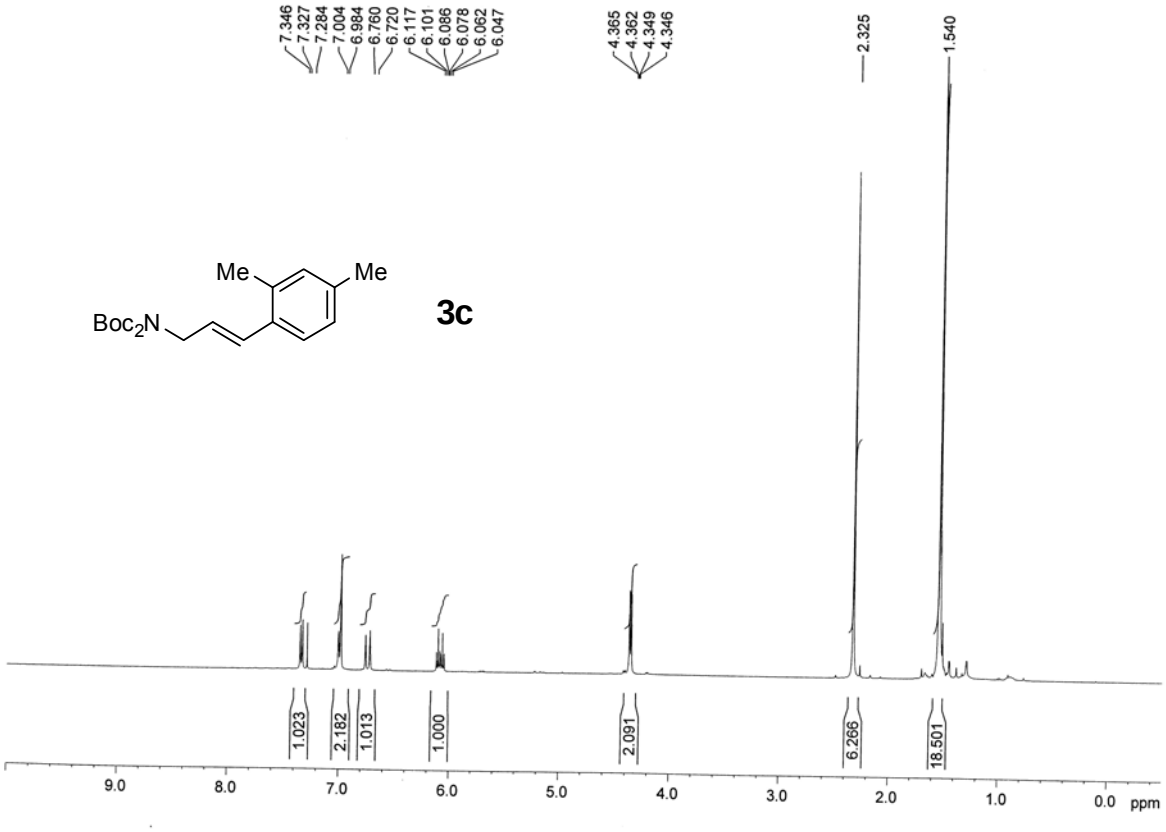
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4.362
4.349
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Me
Me
Boc2N
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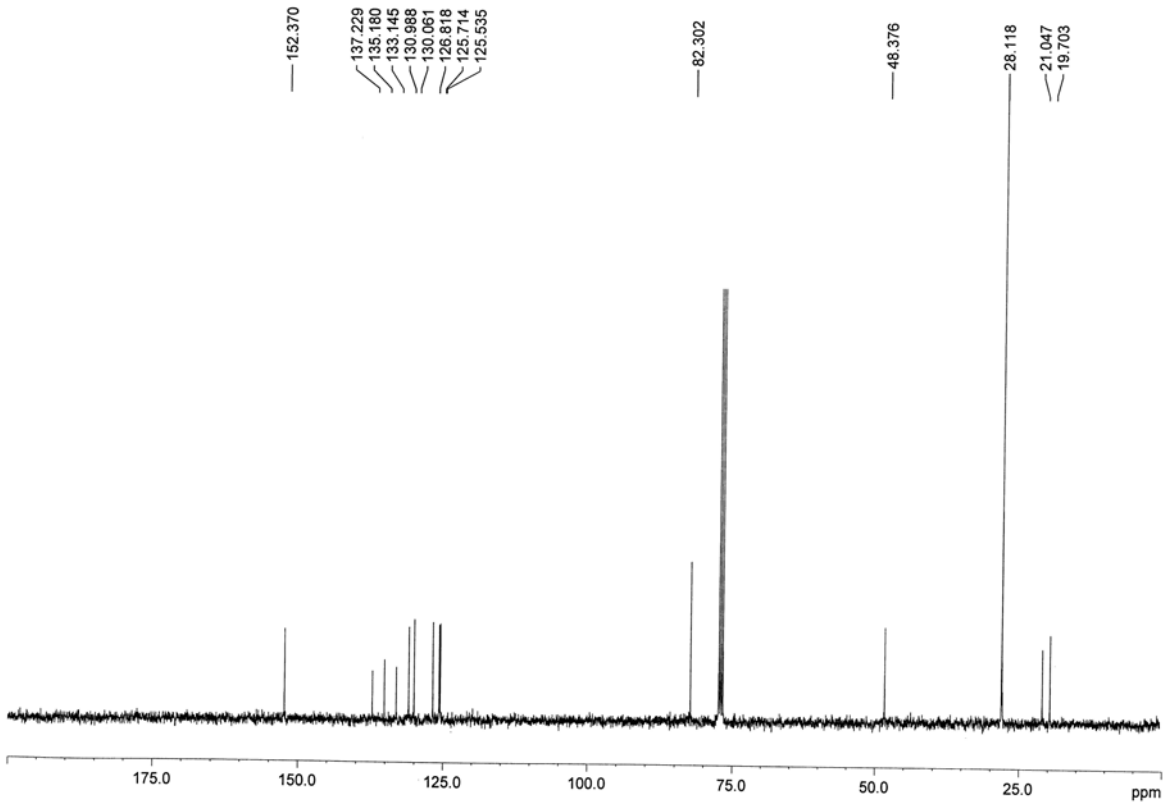
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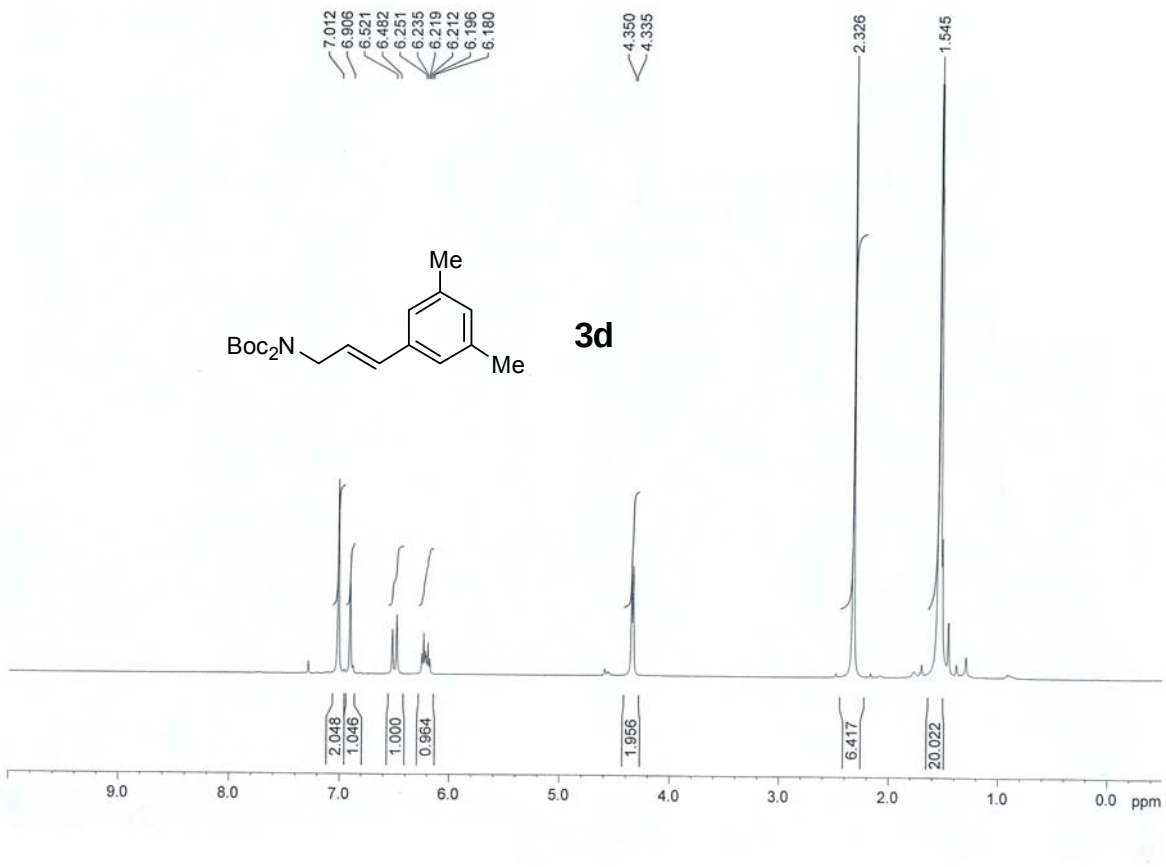
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1.545
Me
Boc2N
Me
3d
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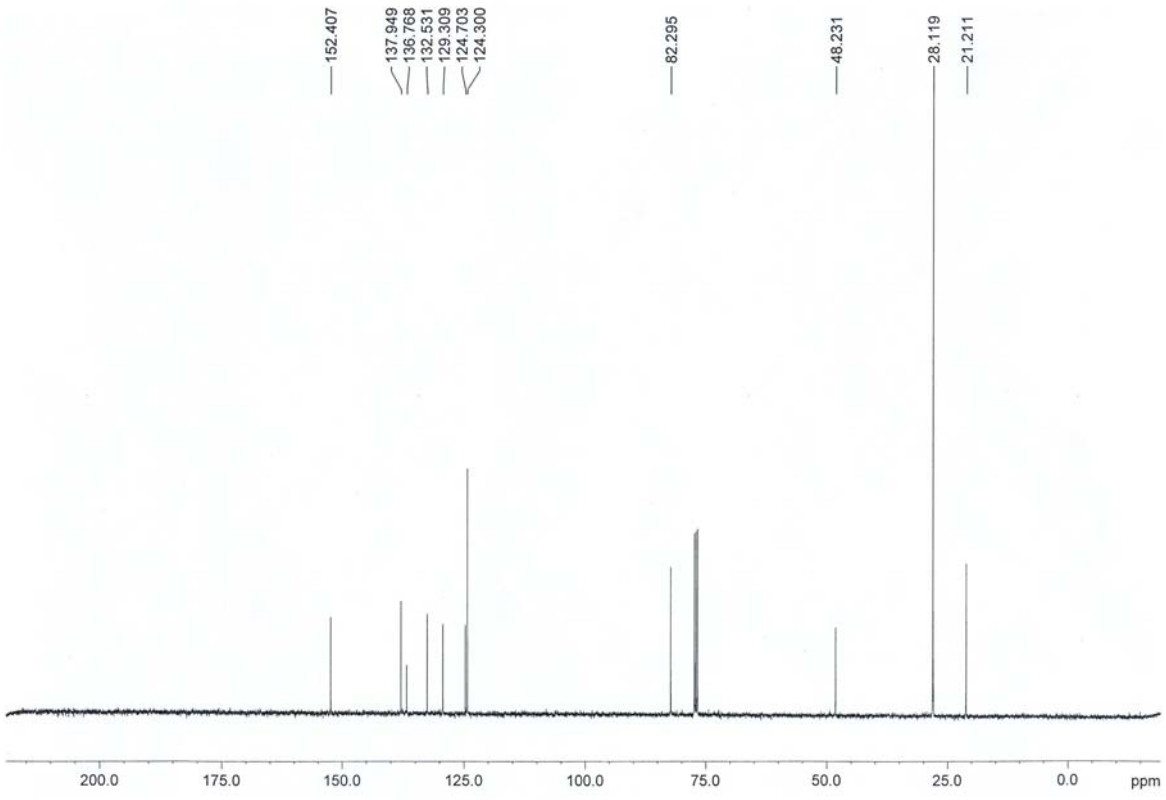
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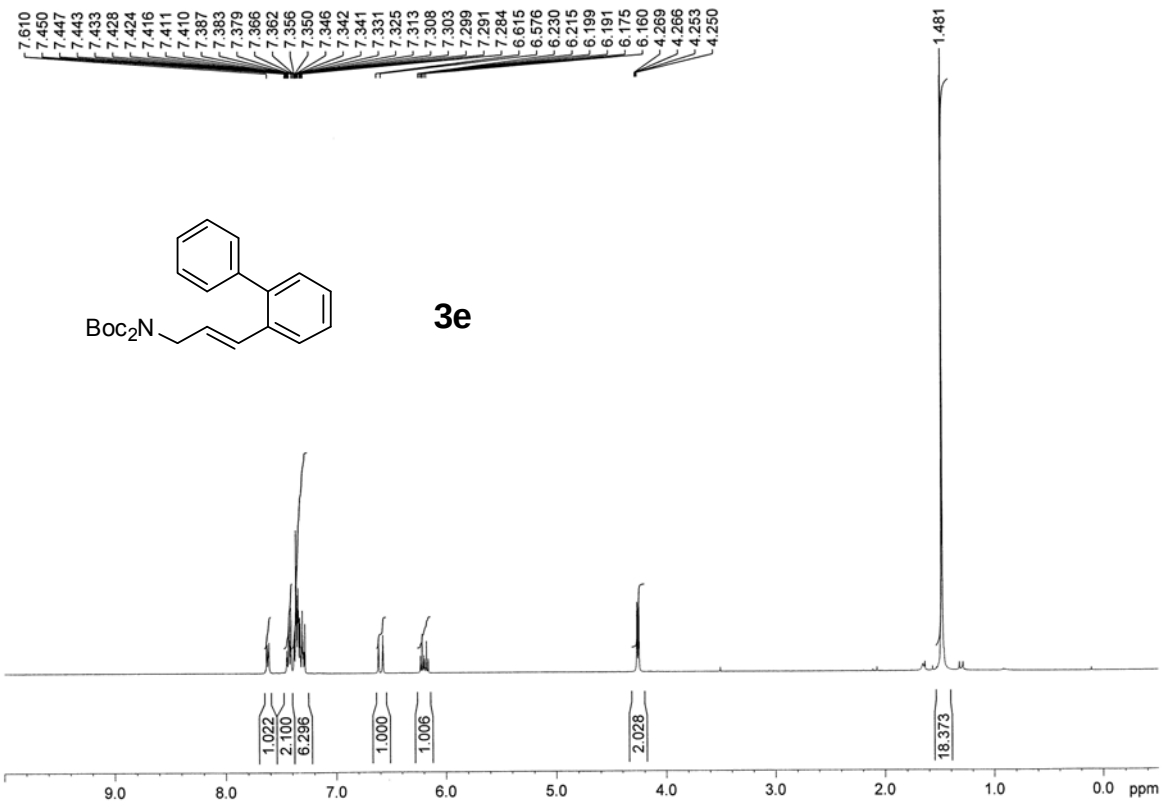
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7.366
7.362
7.356
7.350
7.346
7.342
7.341
7.331
7.325
7.313
7.308
7.303
7.299
7.291
7.284
6.615
6.576
6.230
6.215
6.199
6.191
6.175
6.160
4.269
4.266
4.253
4.250
1.481
Boc2N
3e
1.022
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6.296
1.000
1.006
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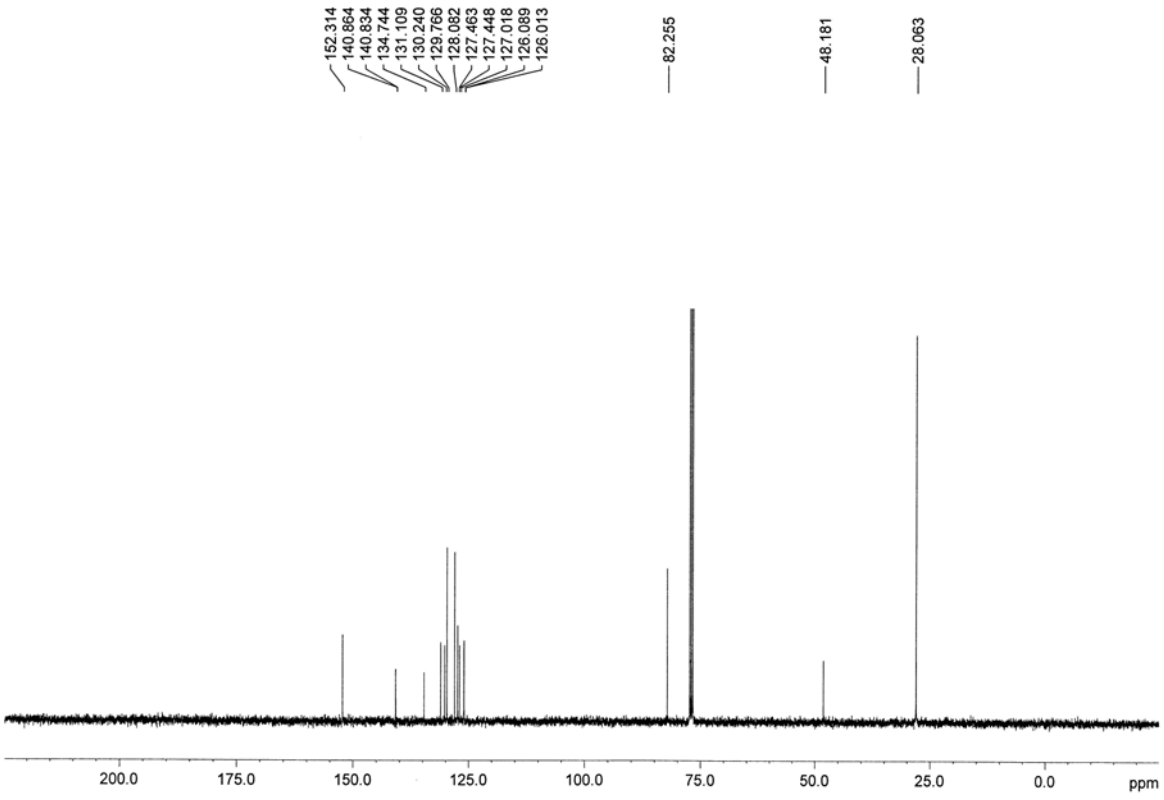
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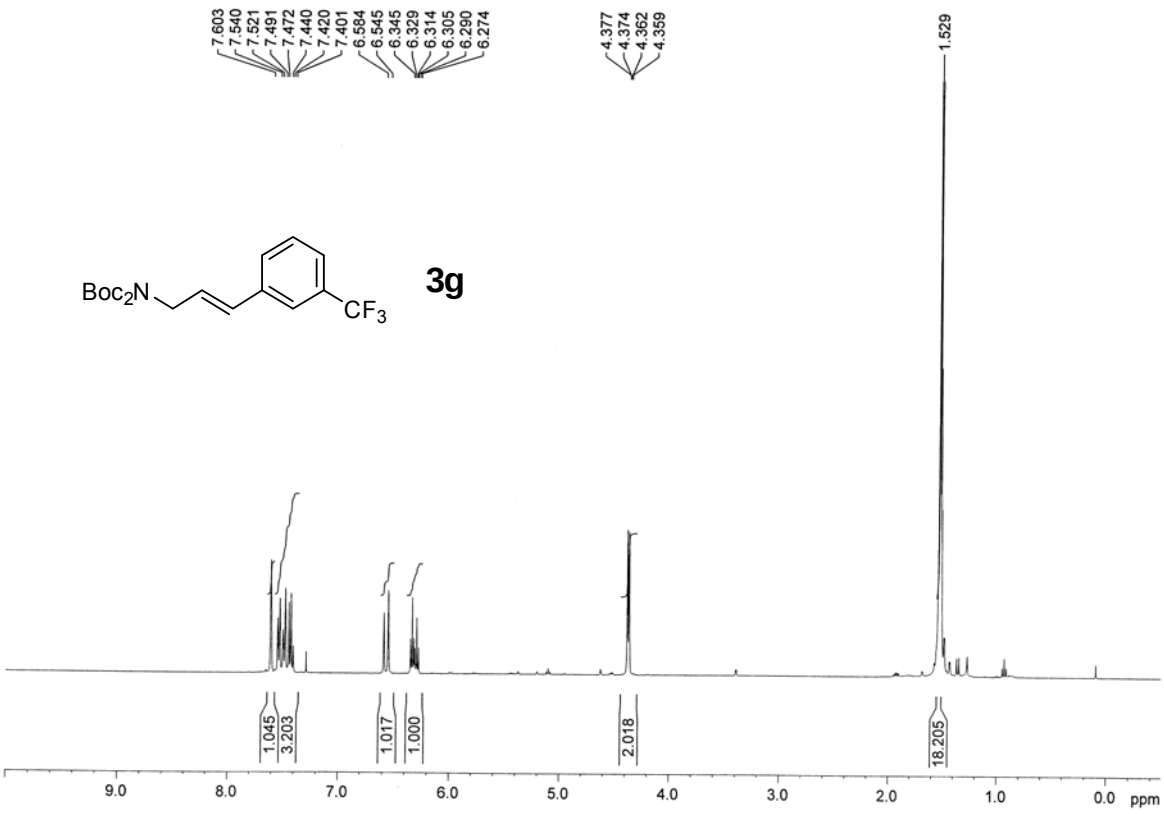
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6.290
6.274
4.377
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4.359
1.529
Boc2N
CF3
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1.000
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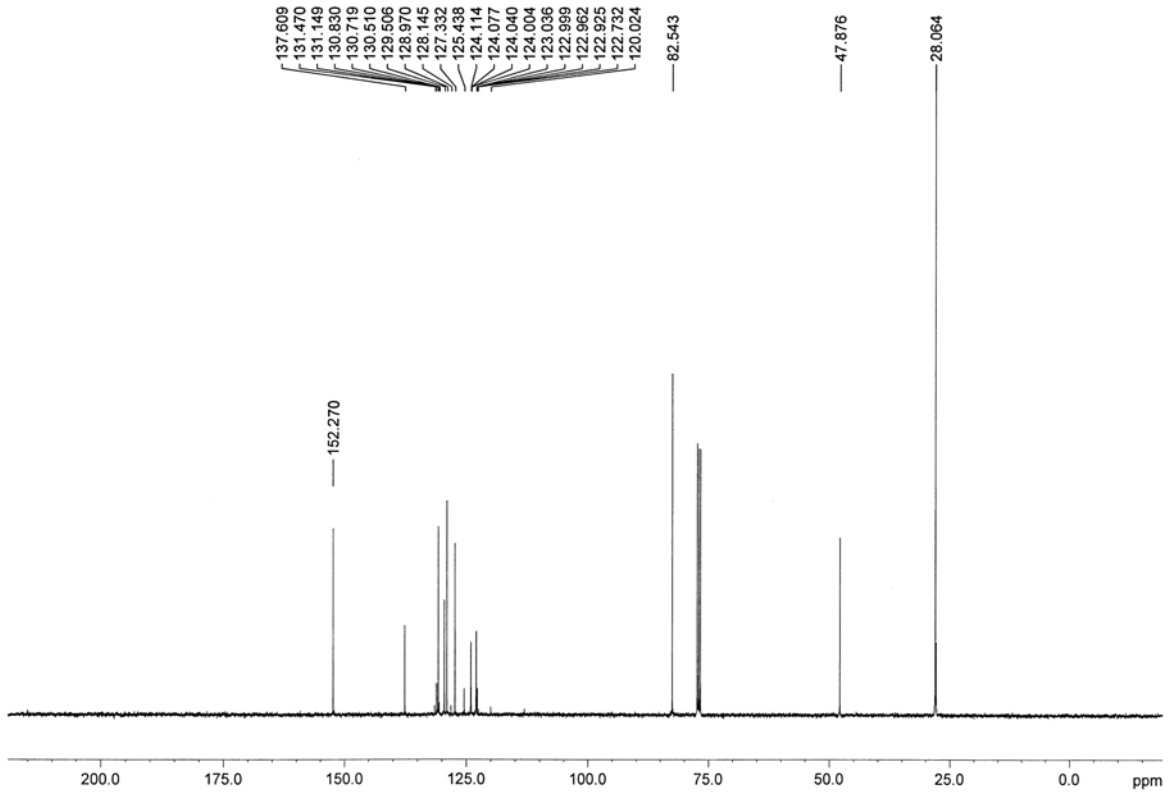
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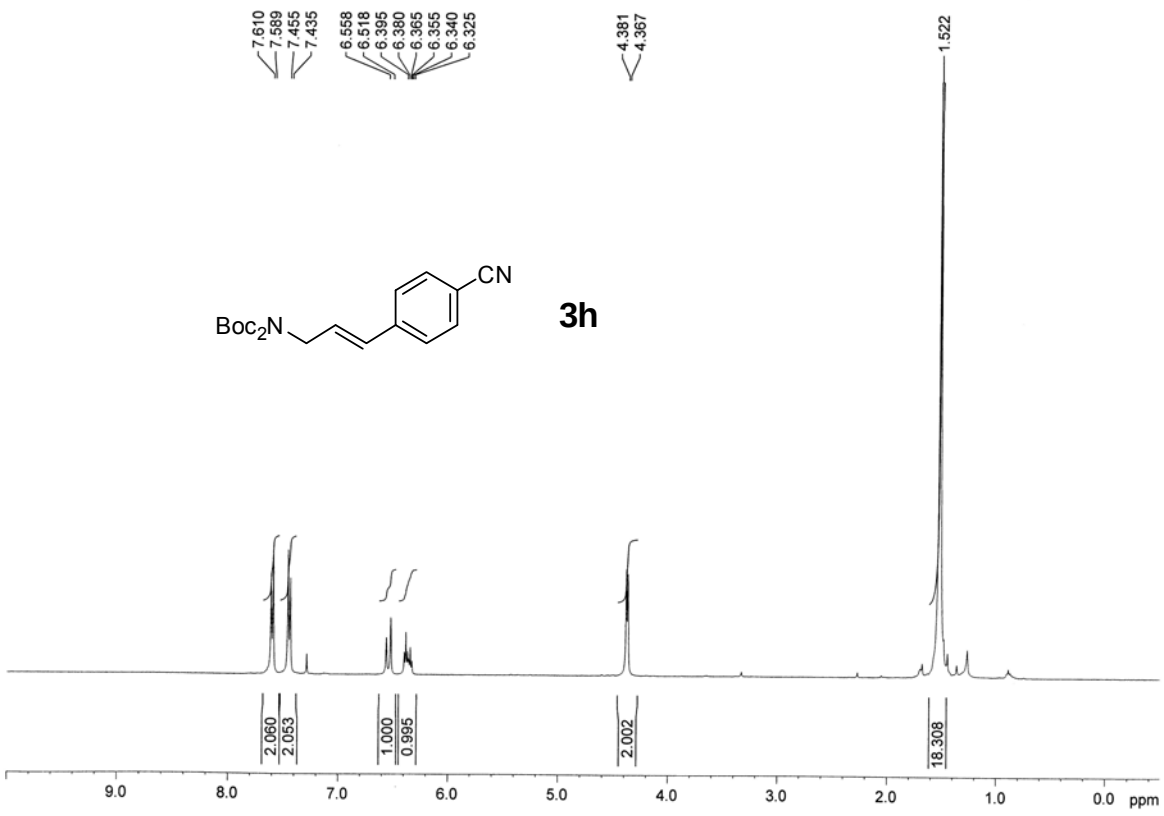
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6.340
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CN
Boc2N
3h
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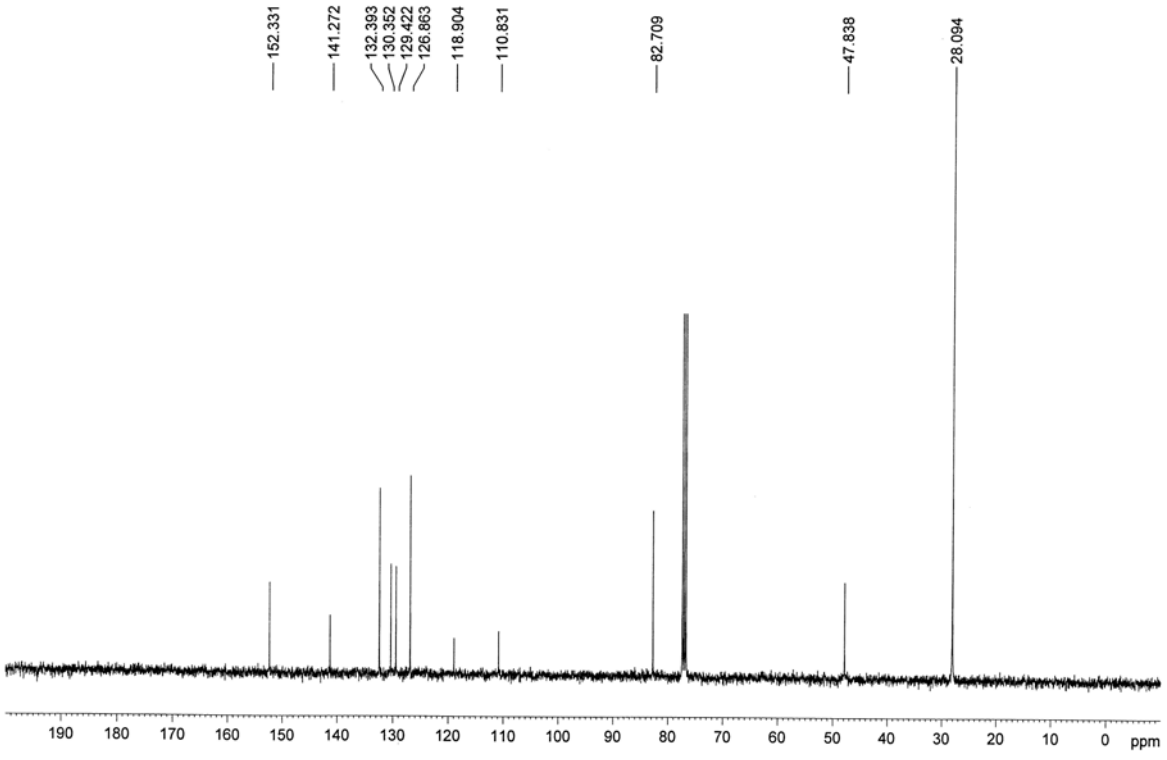
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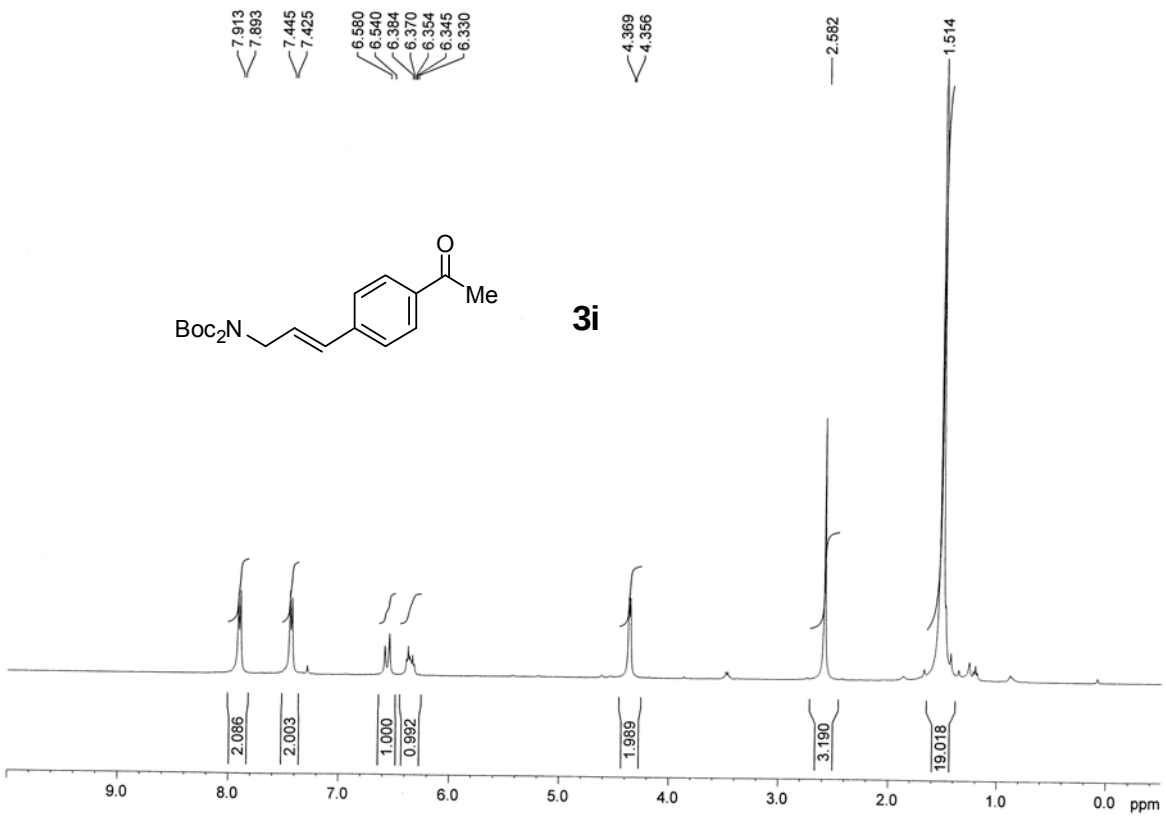
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4.356
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1.514
O
Me
Boc2N
3i
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1.000
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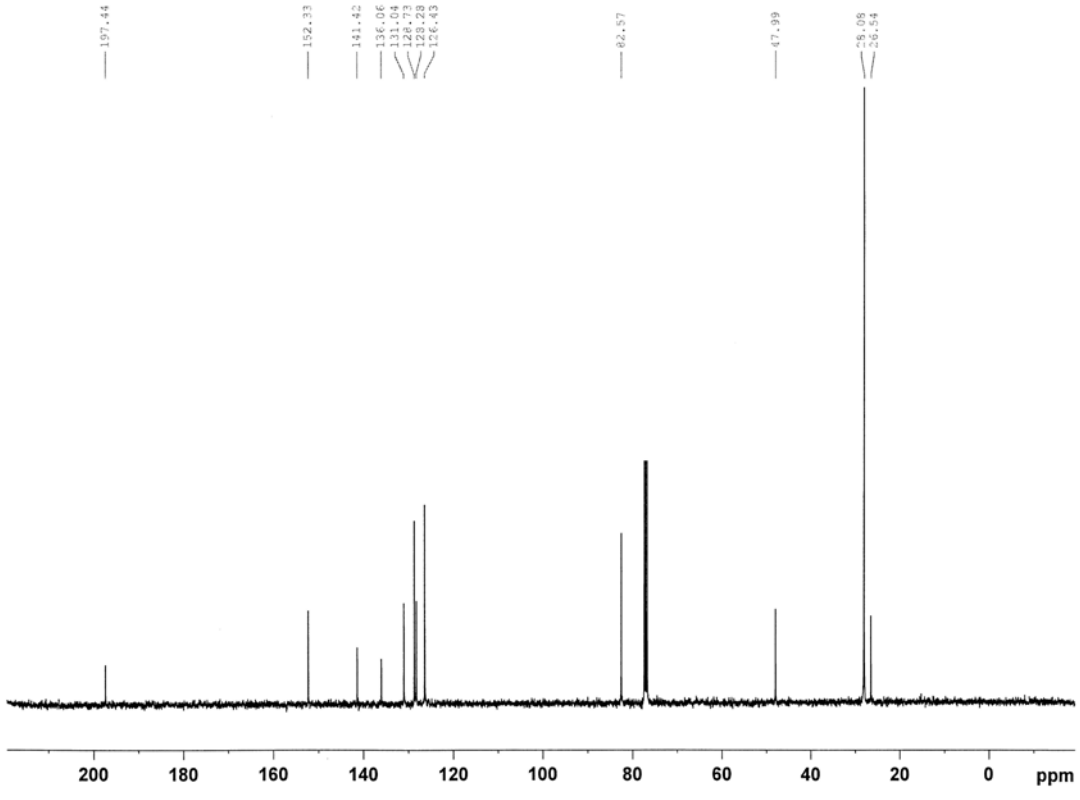
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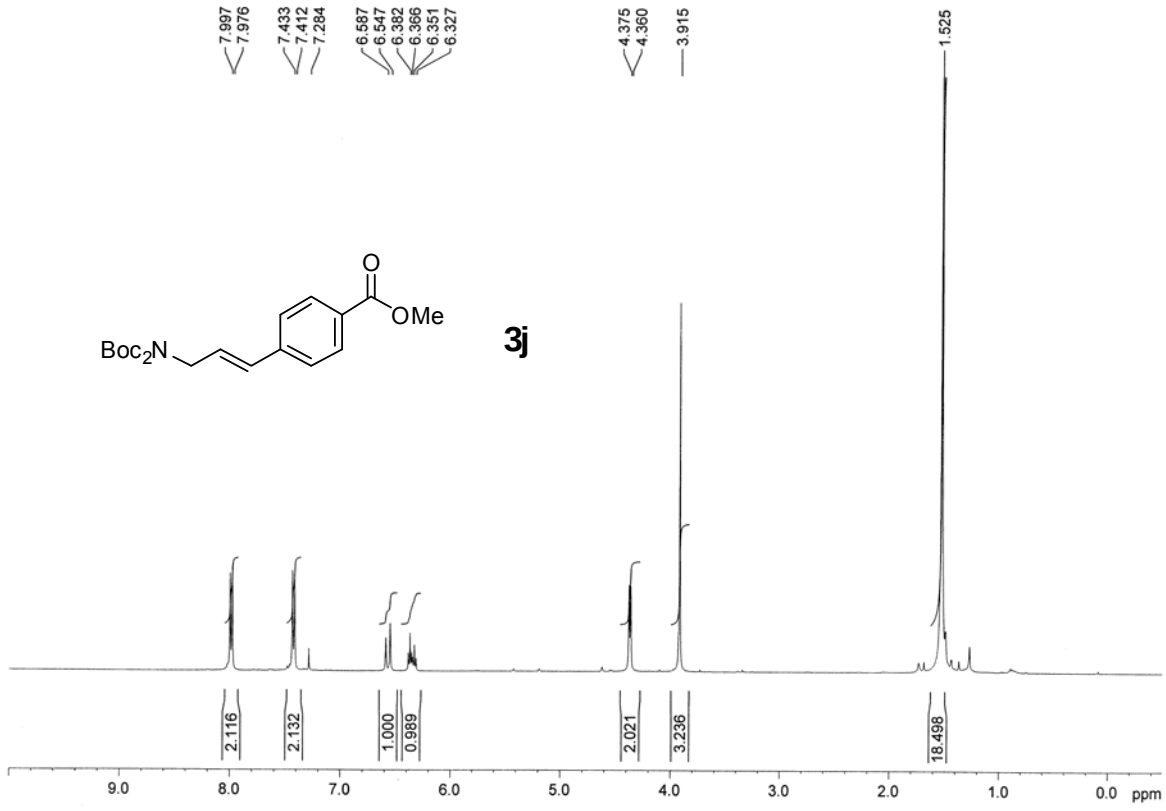
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1.525
O
OMe
Boc2N
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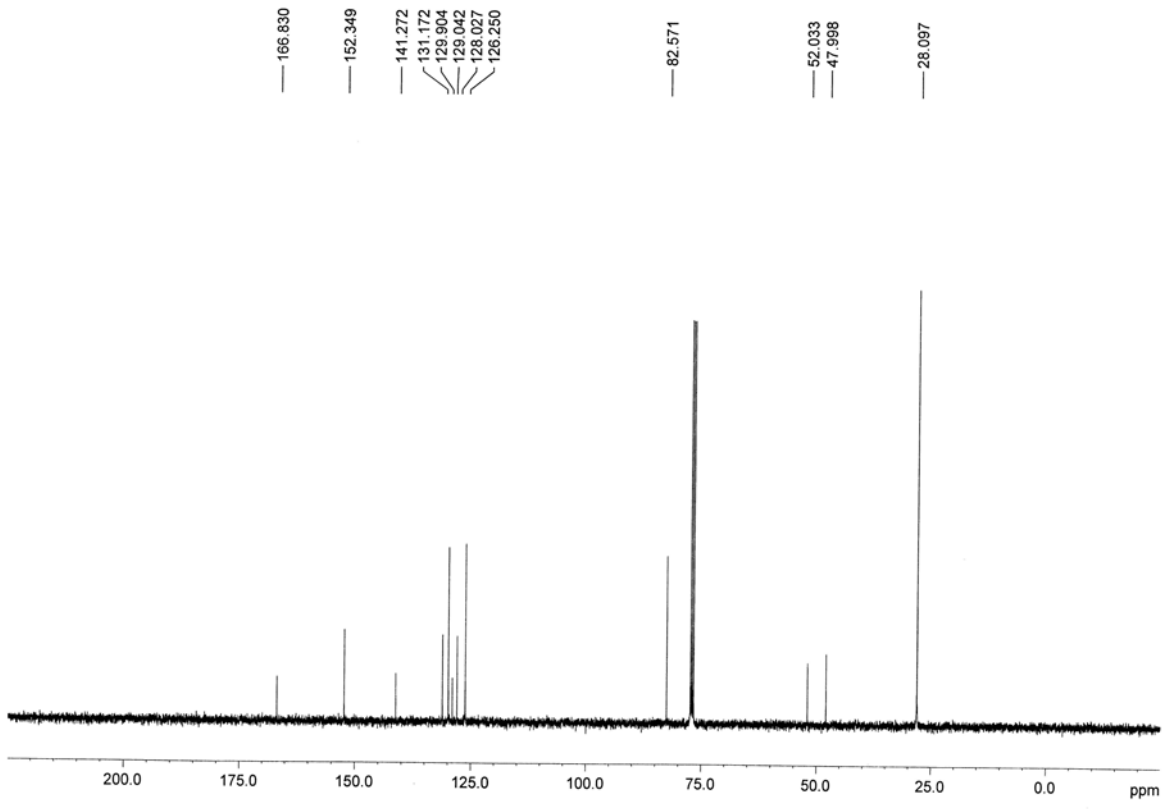
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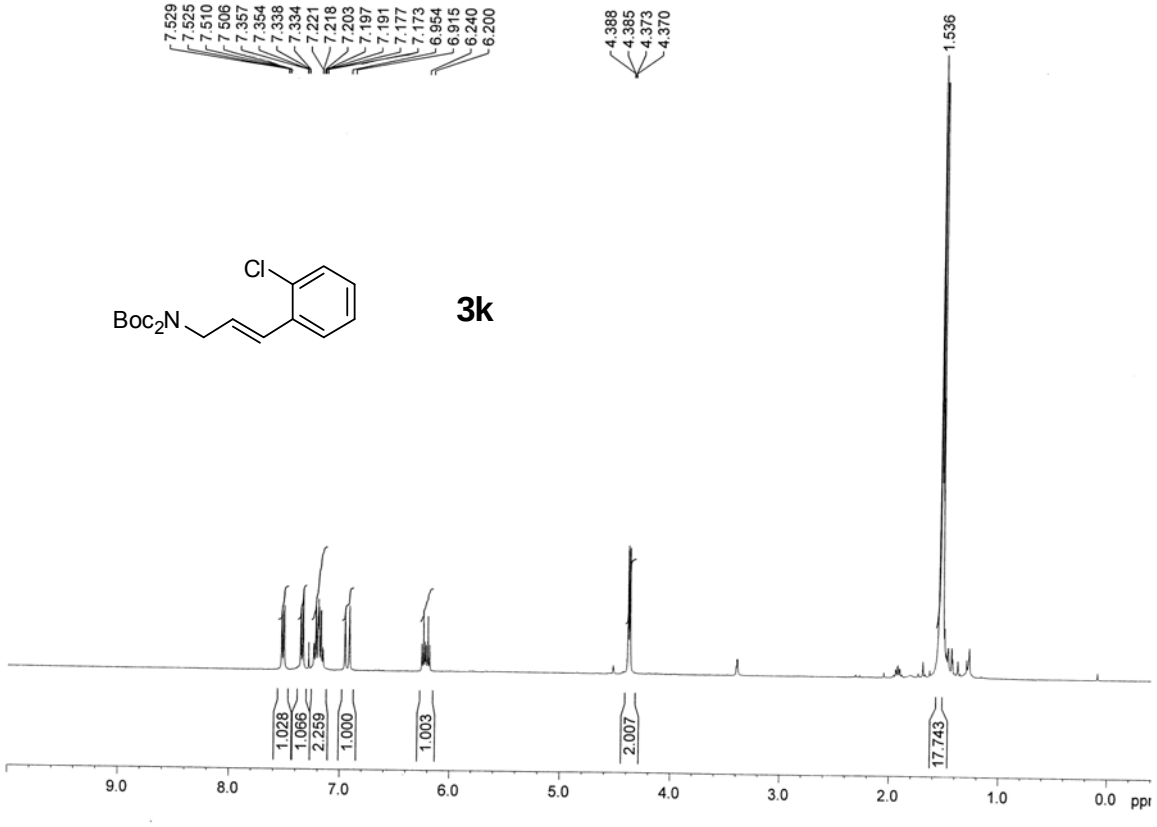
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7.177
7.173
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6.915
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6.200
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4.373
4.370
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Boc2N
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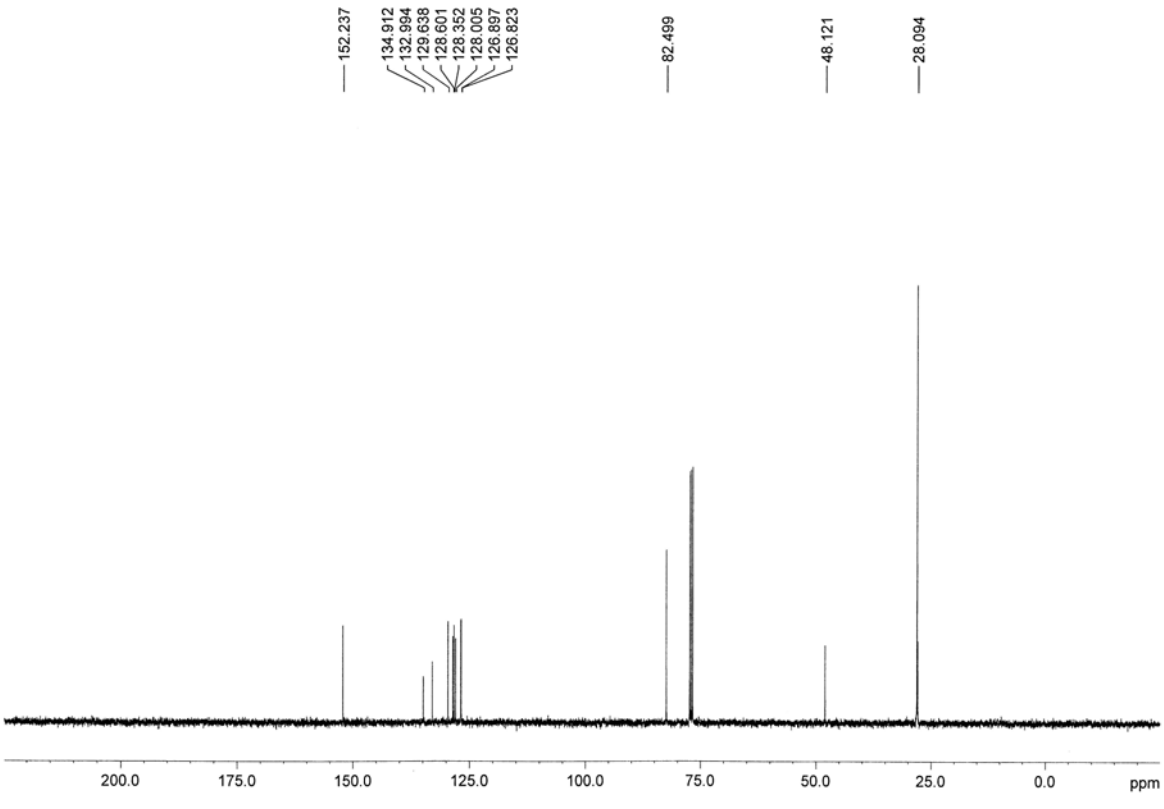
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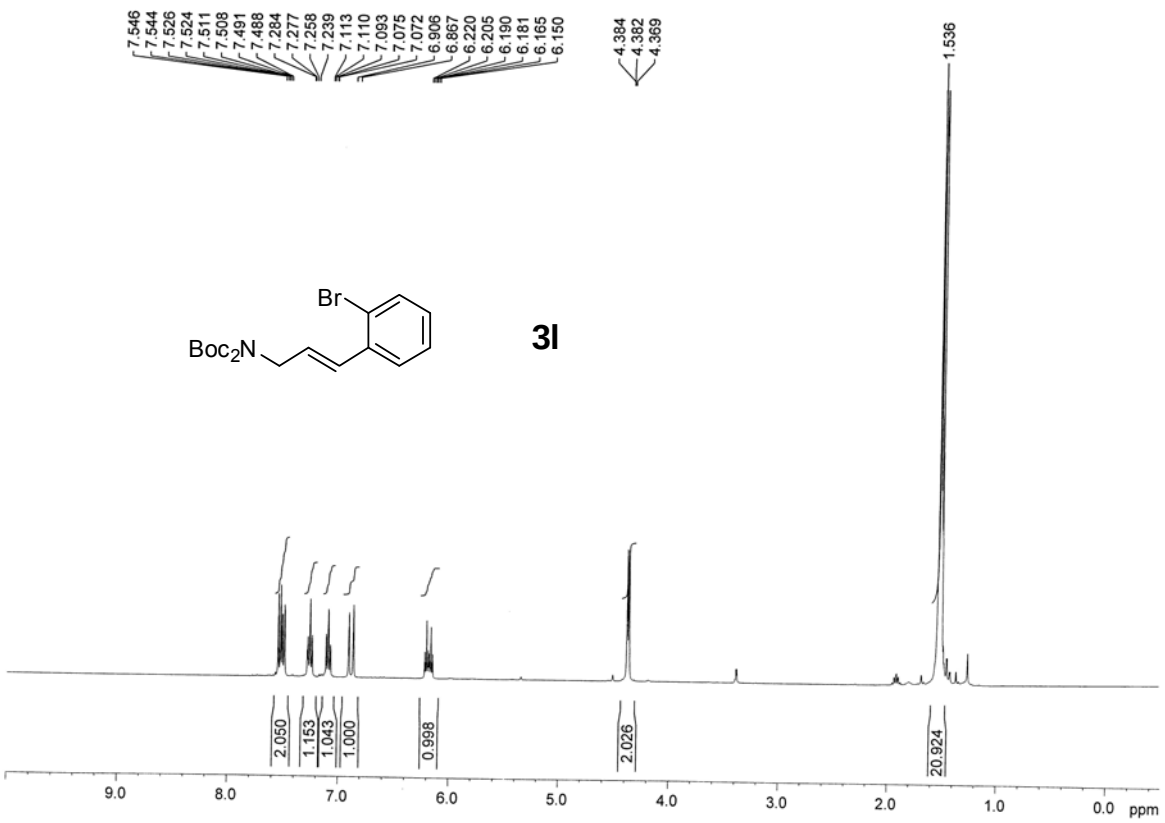
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7.075
7.072
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6.205
6.190
6.181
6.165
6.150
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4.382
4.369
1.536
Br
Boc2N
3l
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1.043
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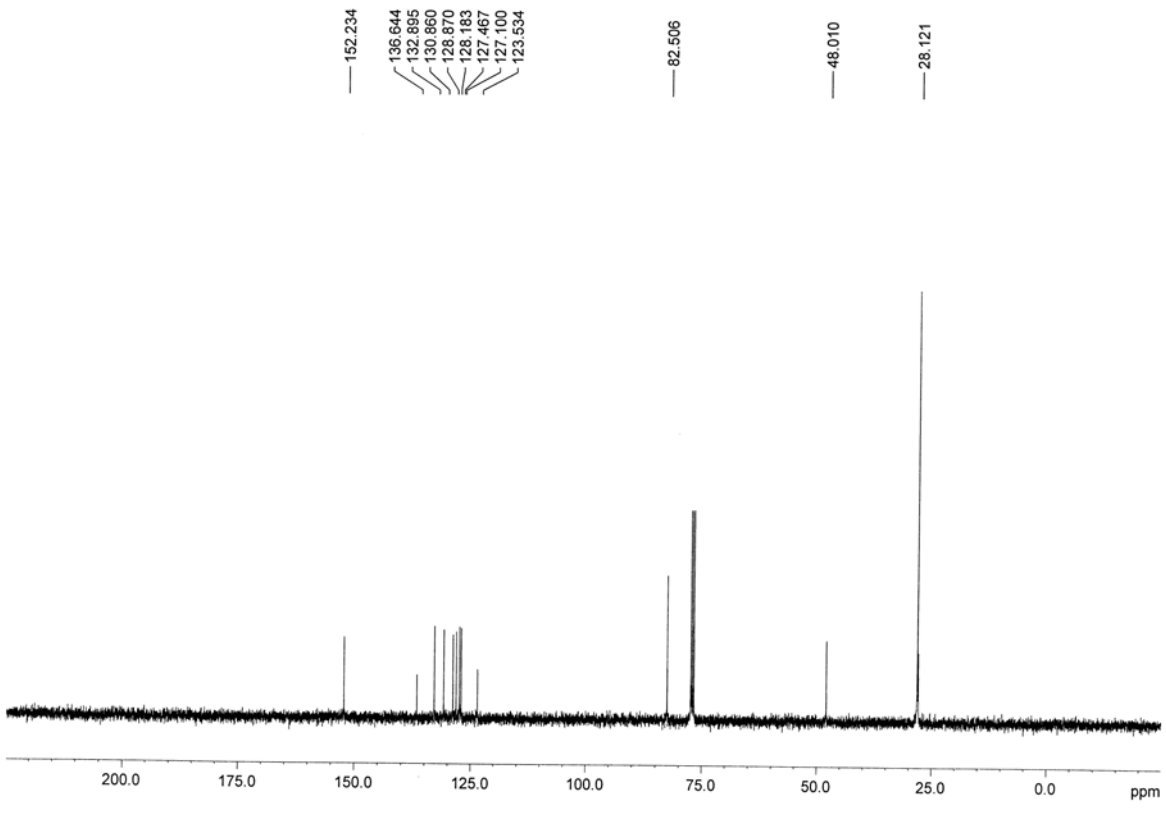
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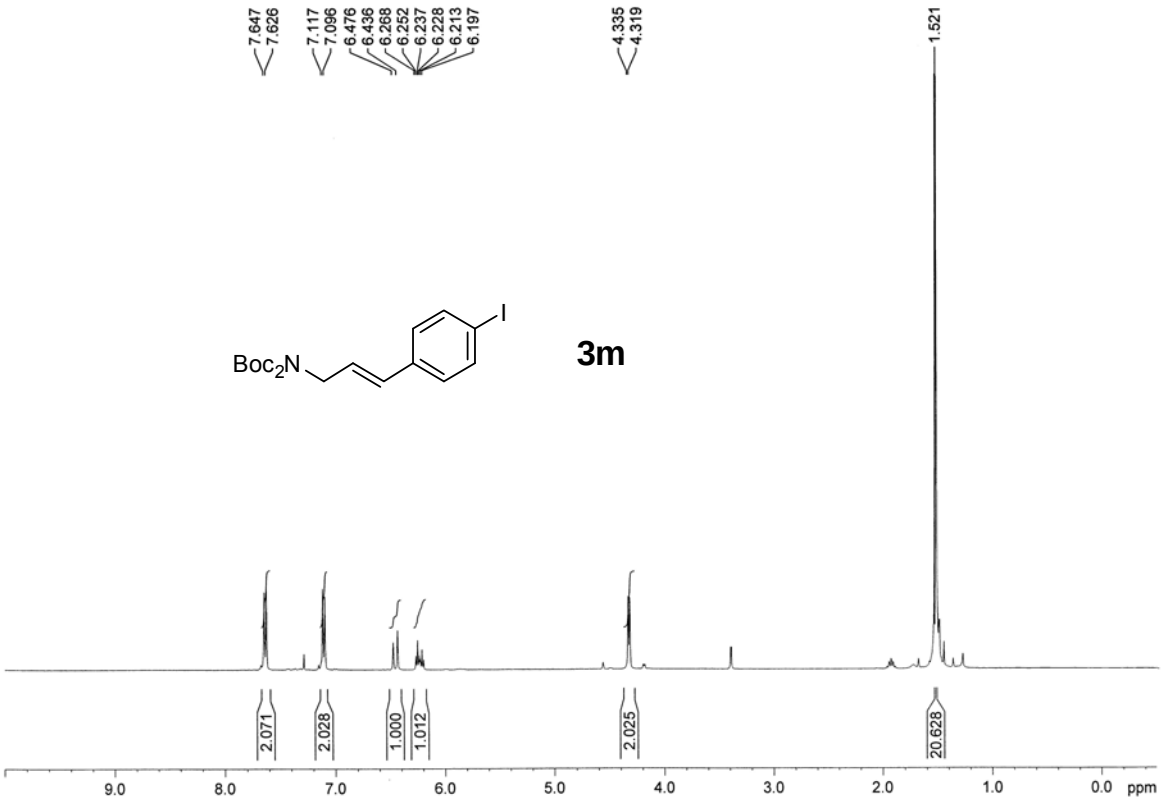
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6.197
4.335
4.319
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Boc2N
3m
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1.000
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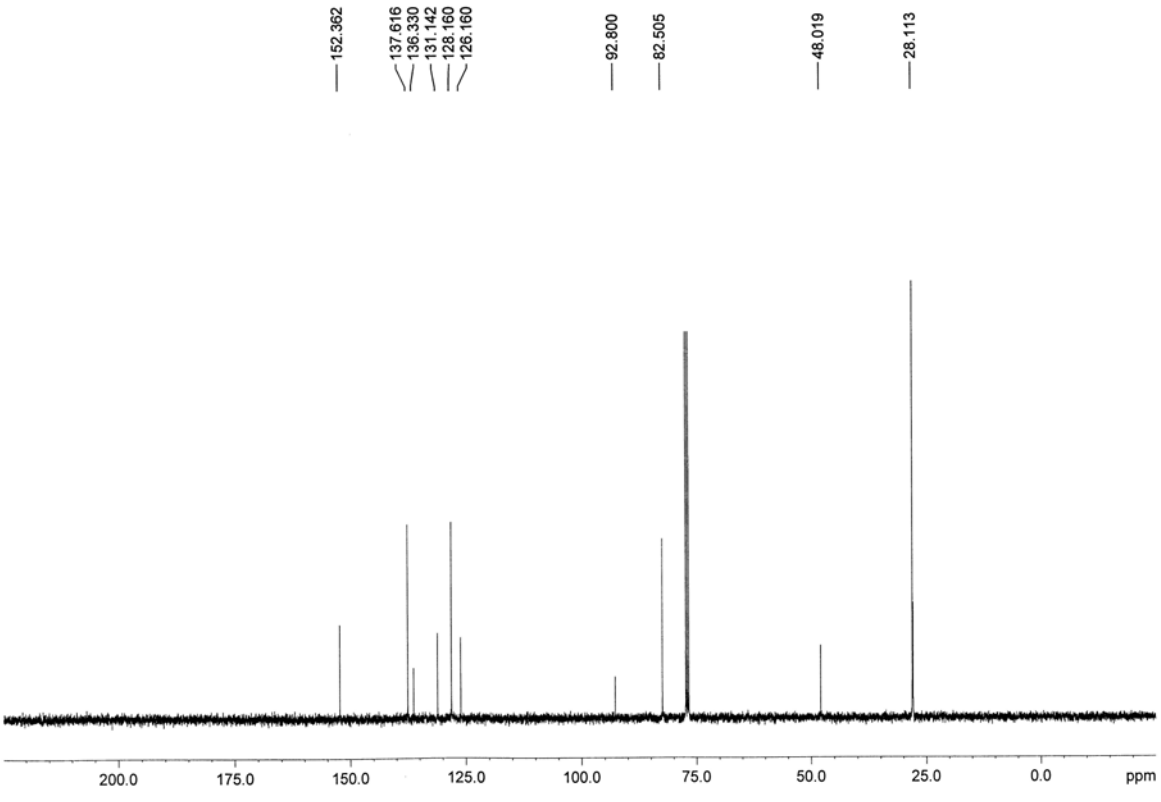
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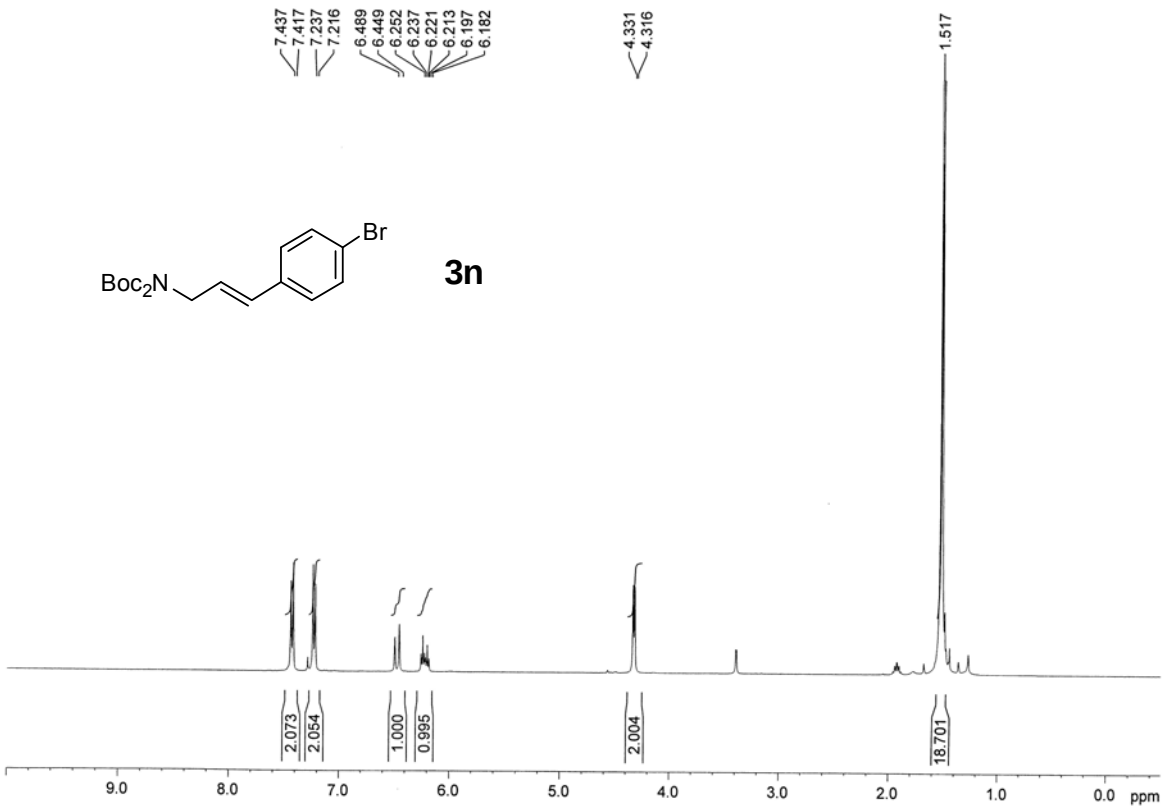
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6.197
6.182
4.331
4.316
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Br
Boc2N
3n
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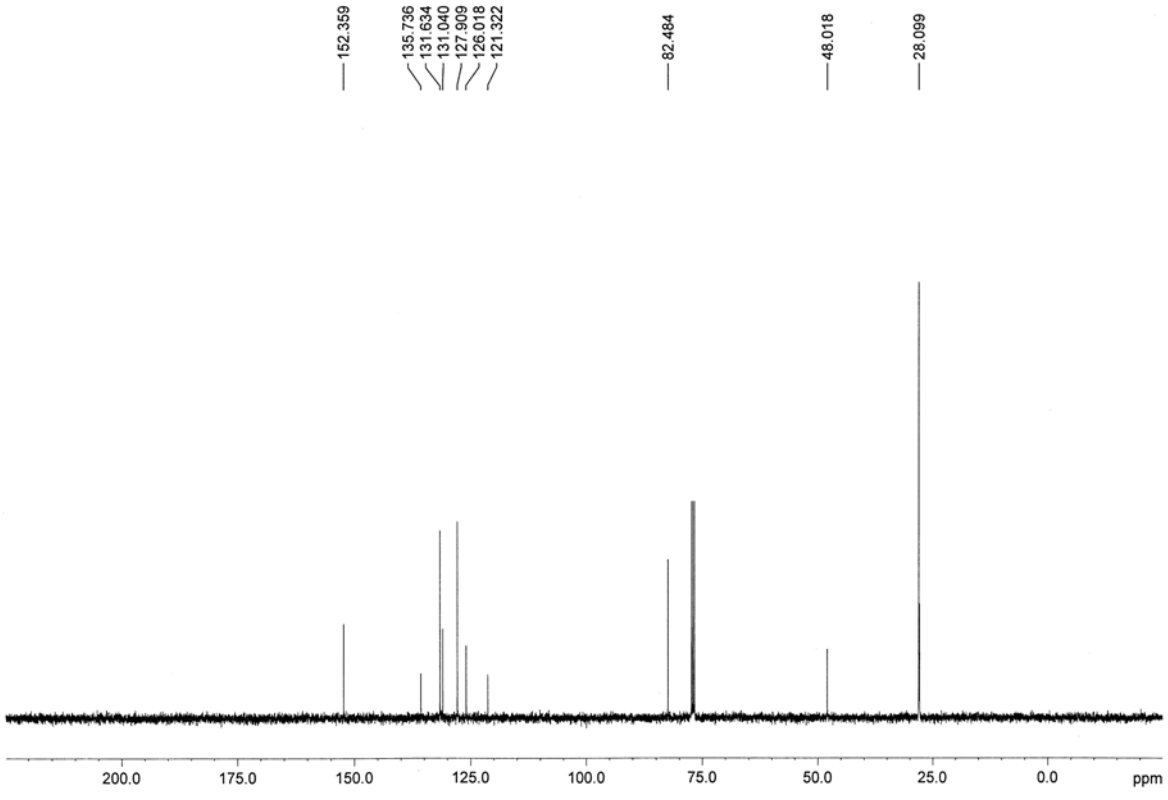
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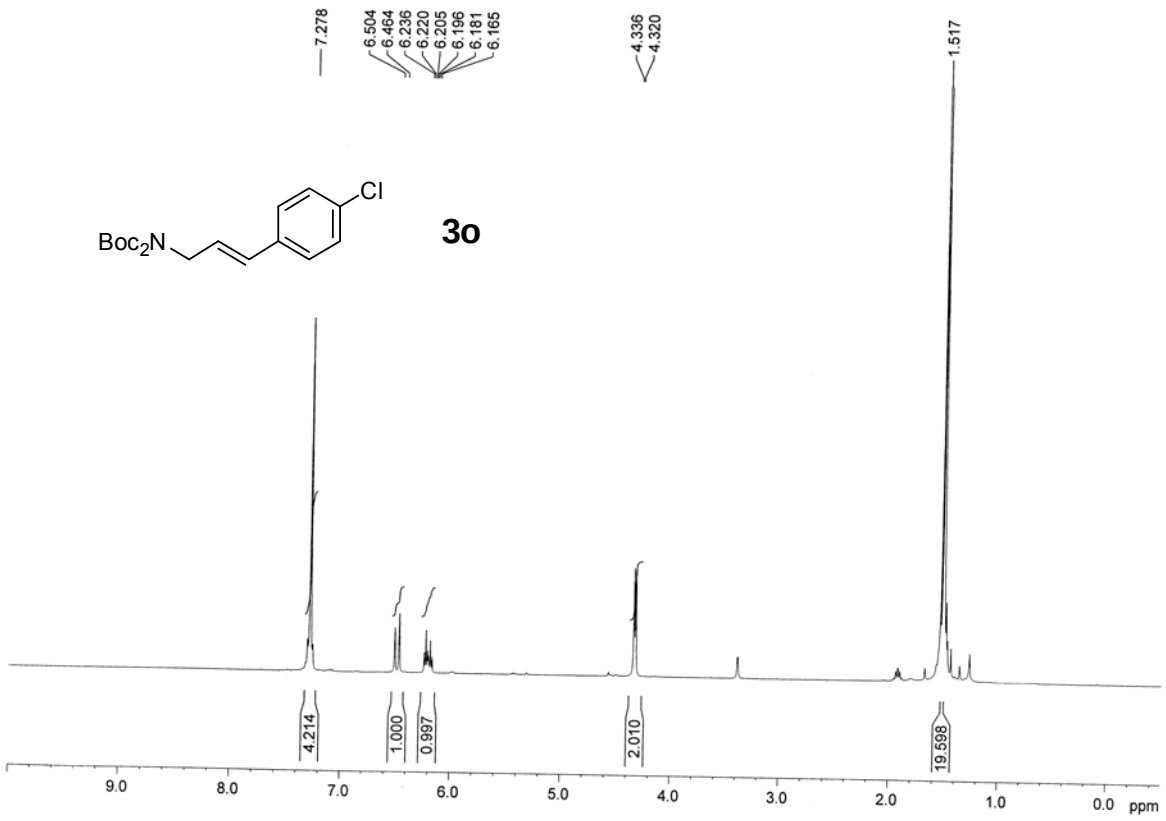
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Boc2N
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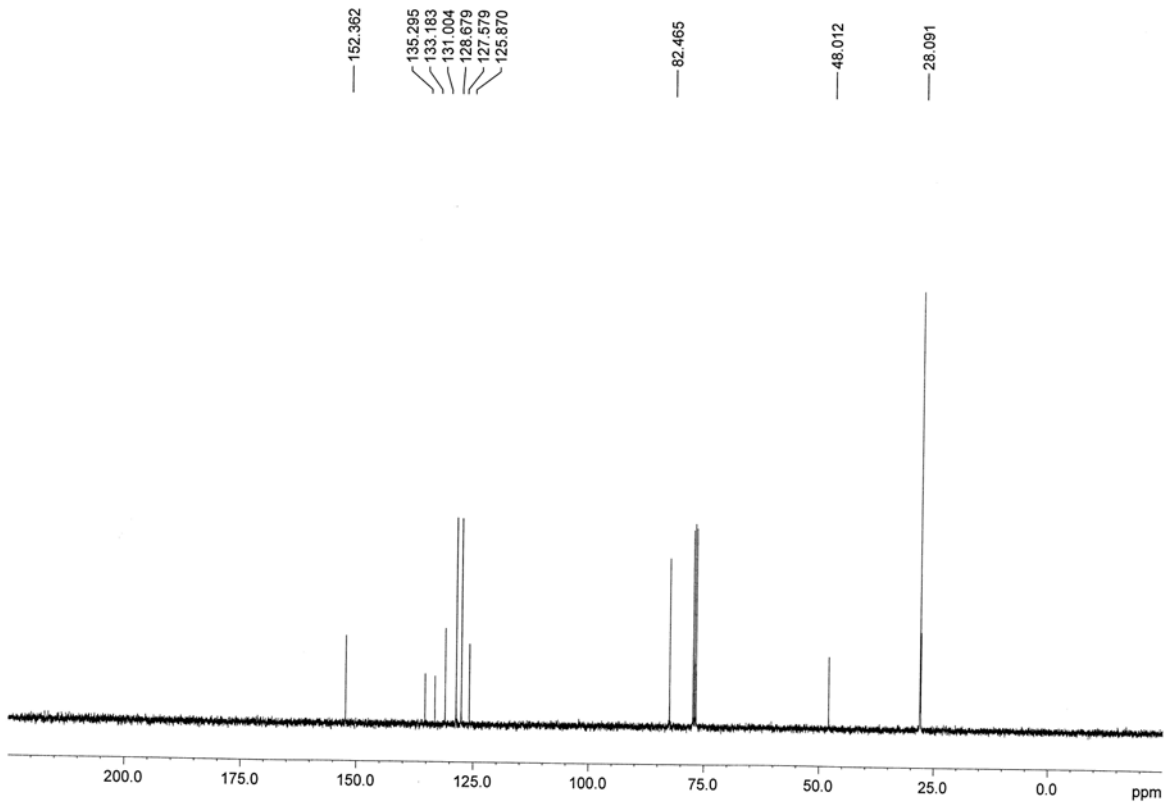
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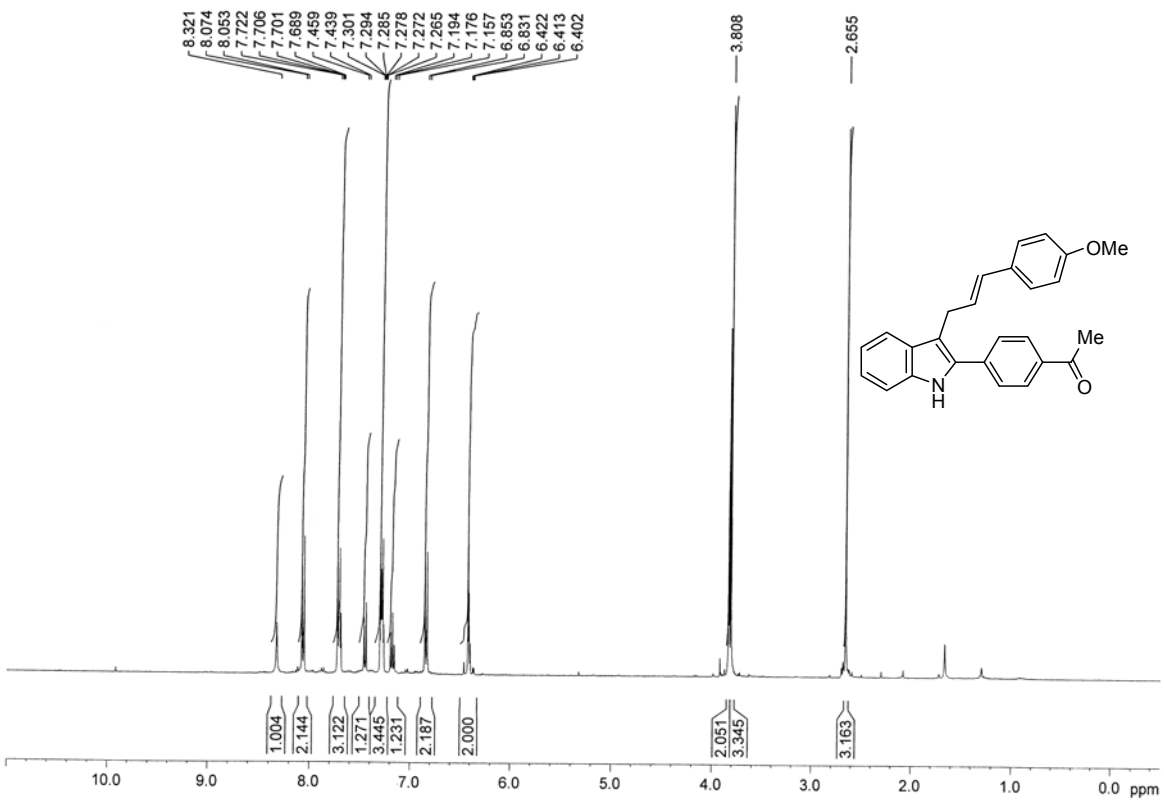
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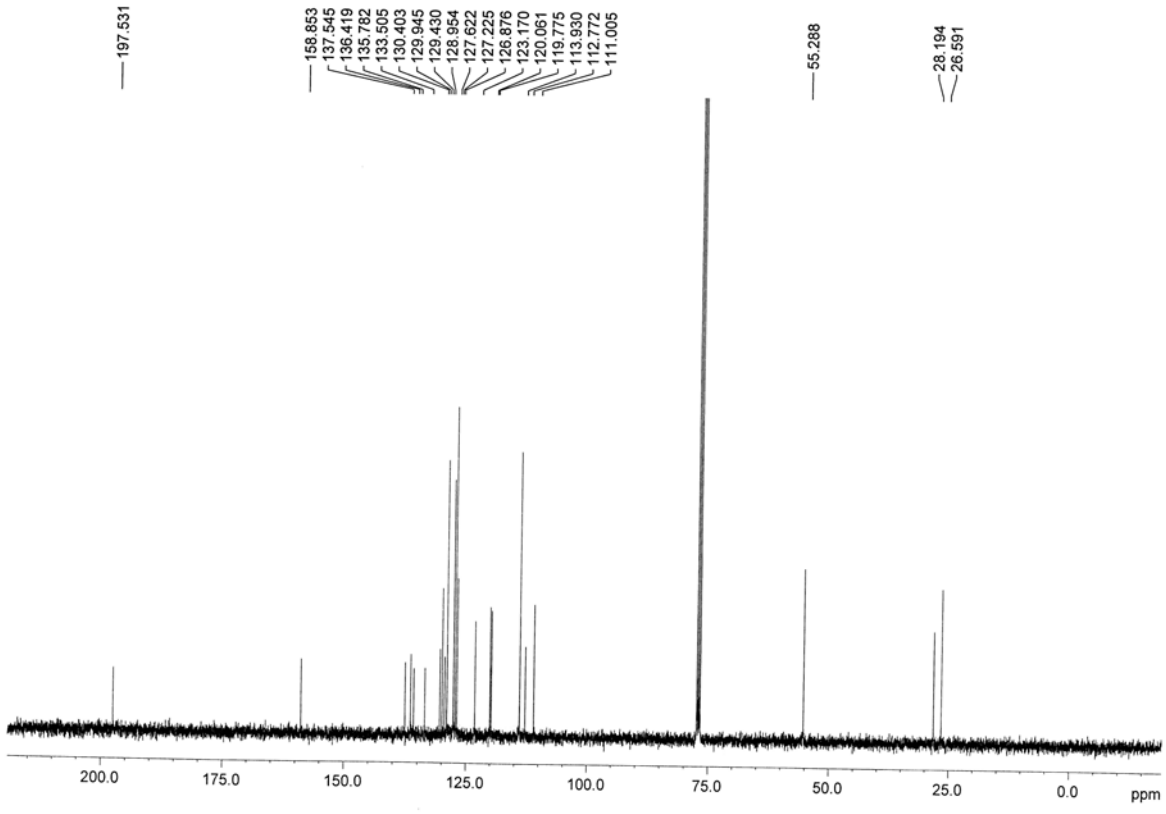
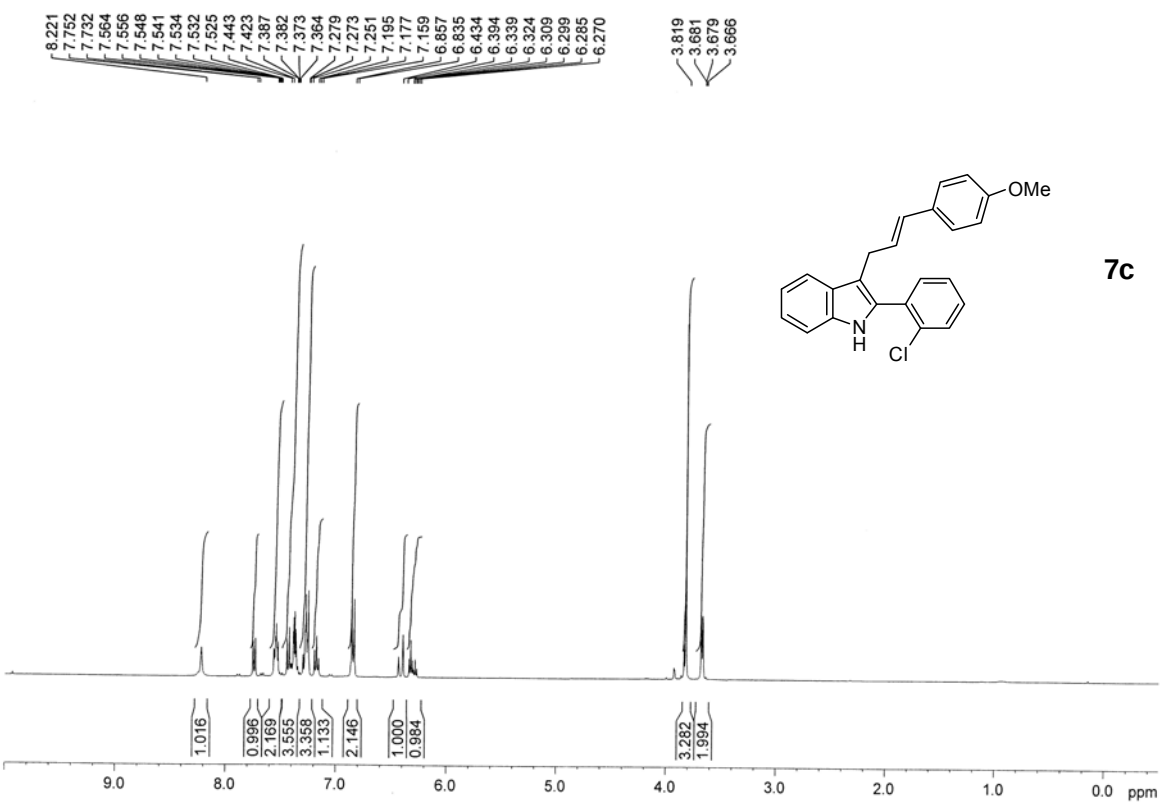
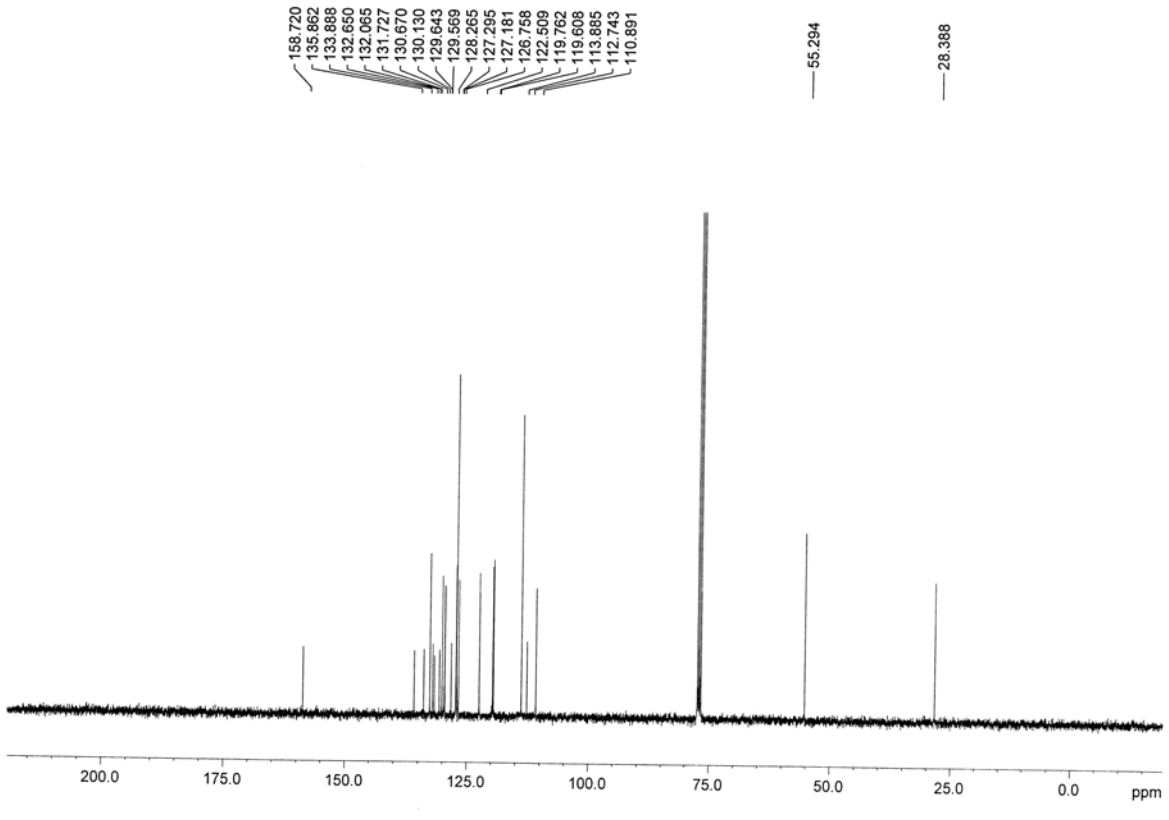
6.0
5.0
4.0
3.0
2.0
1.0
0.0 ppm
OMe
Me
O
N
H

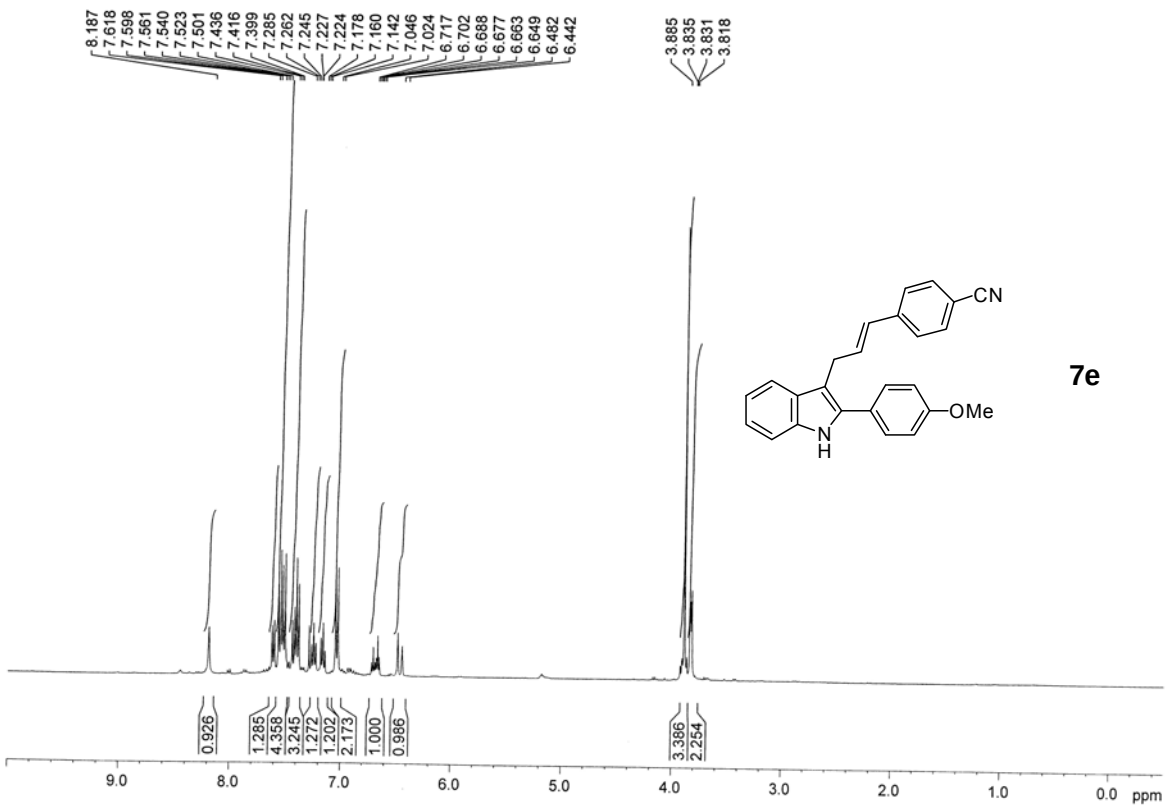
7b


197.531
158.853
137.545
136.419
135.782
133.505
130.403
129.945
129.430
128.954
127.622
127.225
126.876
123.170
120.061
119.775
113.930
112.772
111.005
55.288
28.194
26.591
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
ppm

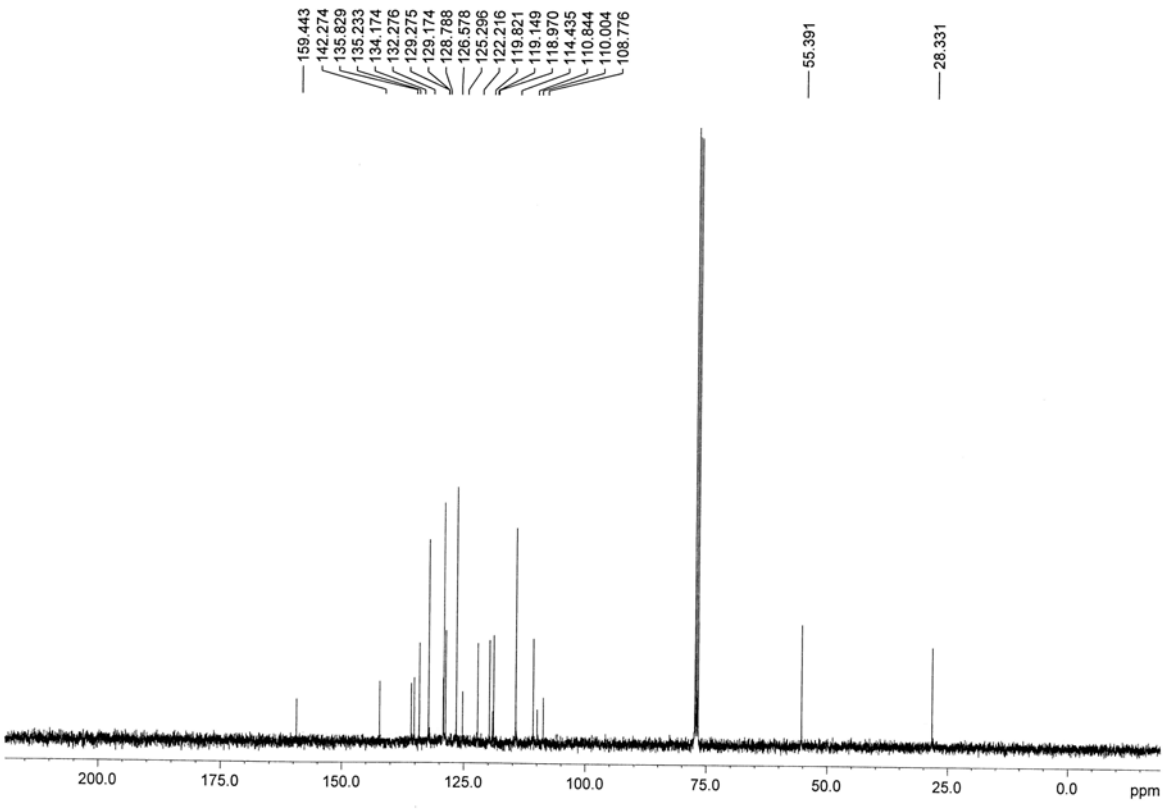

8.221
7.752
7.732
7.564
7.556
7.548
7.541
7.534
7.532
7.525
7.443
7.423
7.387
7.382
7.373
7.364
7.279
7.273
7.251
7.195
7.177
7.159
6.857
6.835
6.434
6.394
6.339
6.324
6.309
6.299
6.285
6.270
3.819
3.681
3.679
3.666
OMe
N
H
Cl
1.016
0.996
2.169
3.555
3.358
1.133
2.146
1.000
0.984
3.282
1.994
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

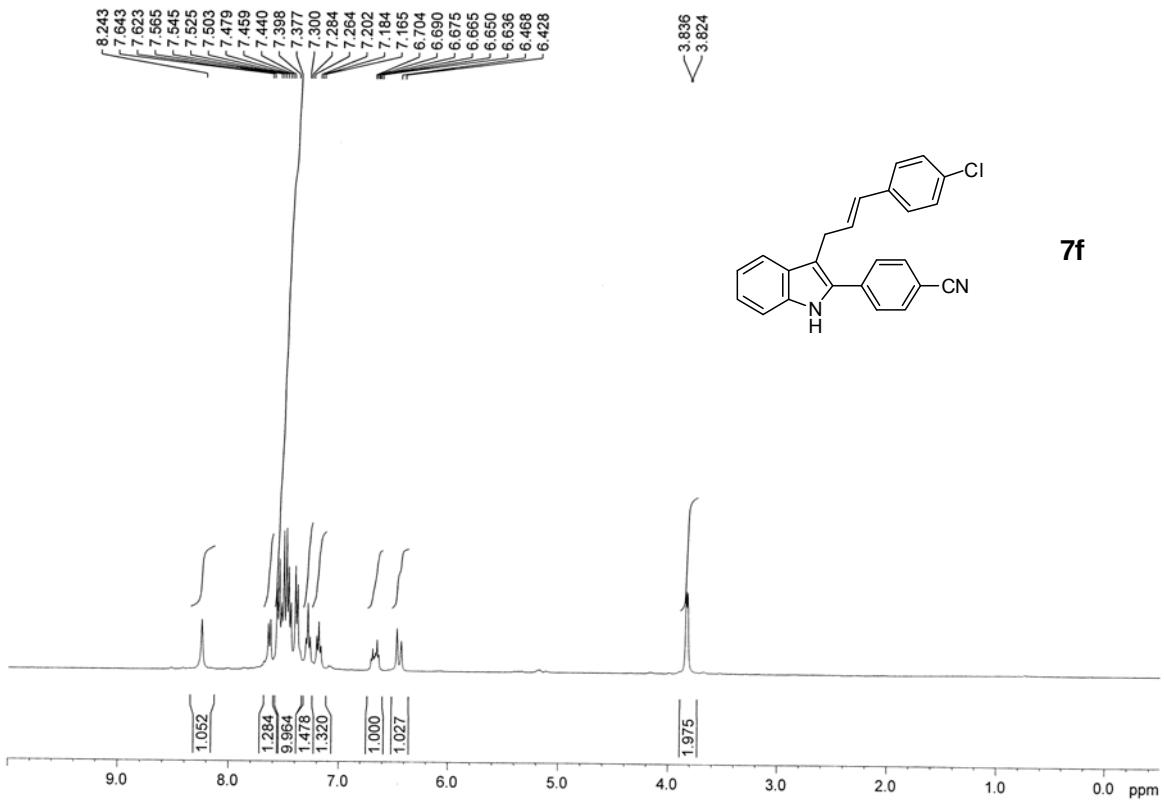
7c


158.720
135.862
133.888
132.650
132.065
131.727
130.670
130.130
129.643
129.569
128.265
127.295
127.181
126.758
122.509
119.762
119.608
113.885
112.743
110.891
55.294
28.388
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
ppm

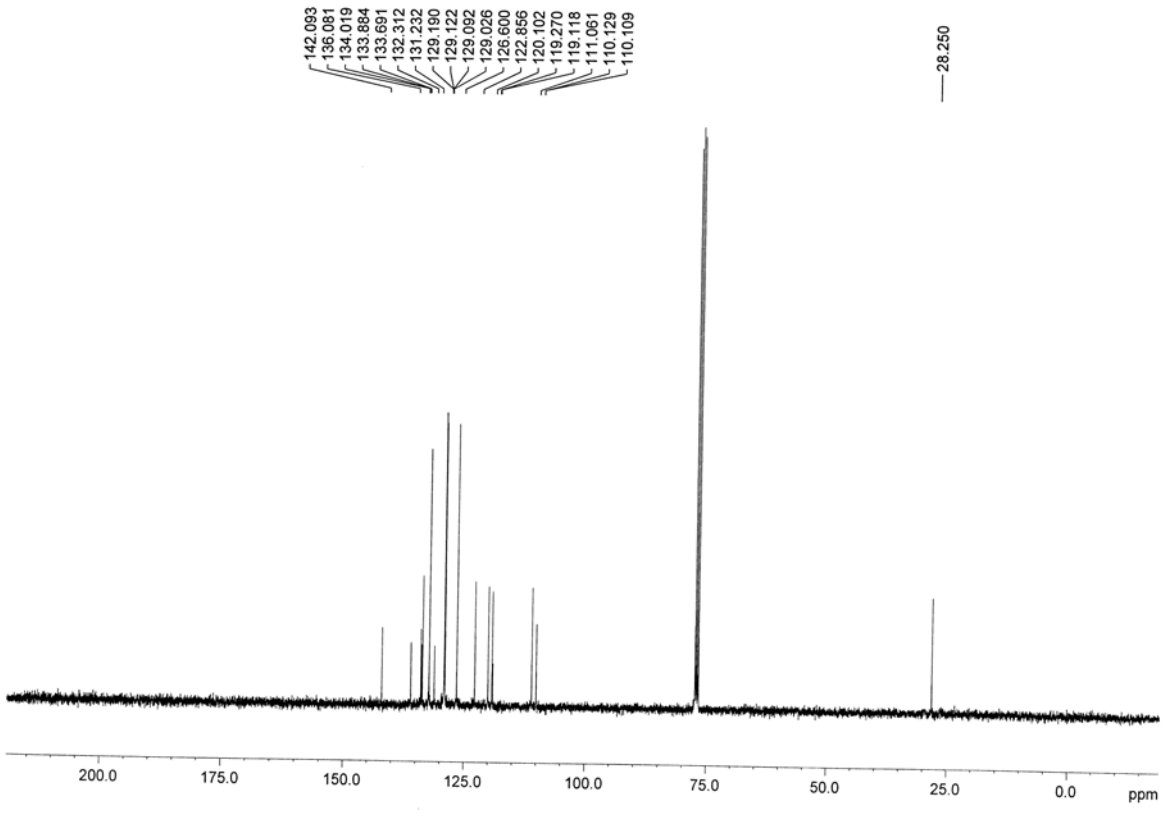

8.187
7.618
7.598
7.561
7.540
7.523
7.501
7.436
7.416
7.399
7.285
7.262
7.245
7.227
7.224
7.178
7.160
7.142
7.046
7.024
6.717
6.702
6.688
6.677
6.663
6.649
6.482
6.442
3.885
3.835
3.831
3.818
CN
OMe
N
H
0.926
1.285
4.358
3.245
1.272
1.202
2.173
1.000
0.986
3.386
2.254
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

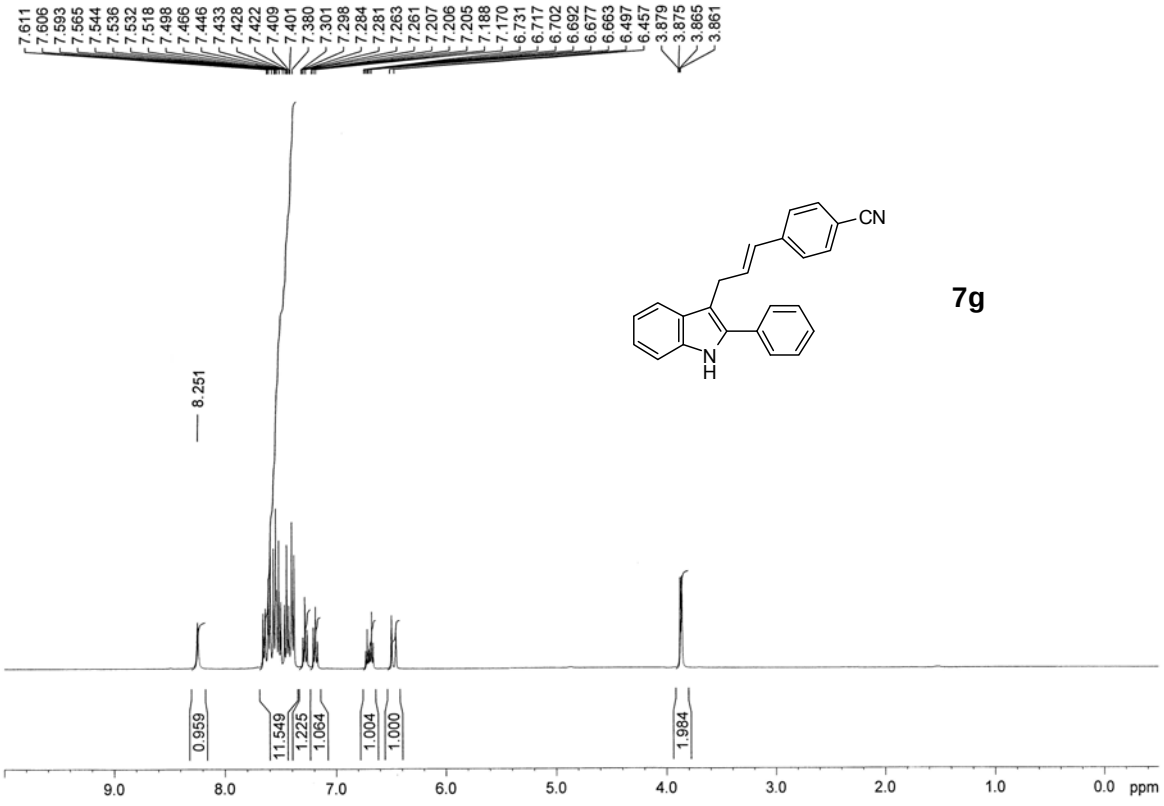
7e


159.443
142.274
135.829
135.233
134.174
132.276
129.275
129.174
128.788
126.578
125.296
122.216
119.821
119.149
118.970
114.435
110.844
110.004
108.776
55.391
28.331
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
ppm

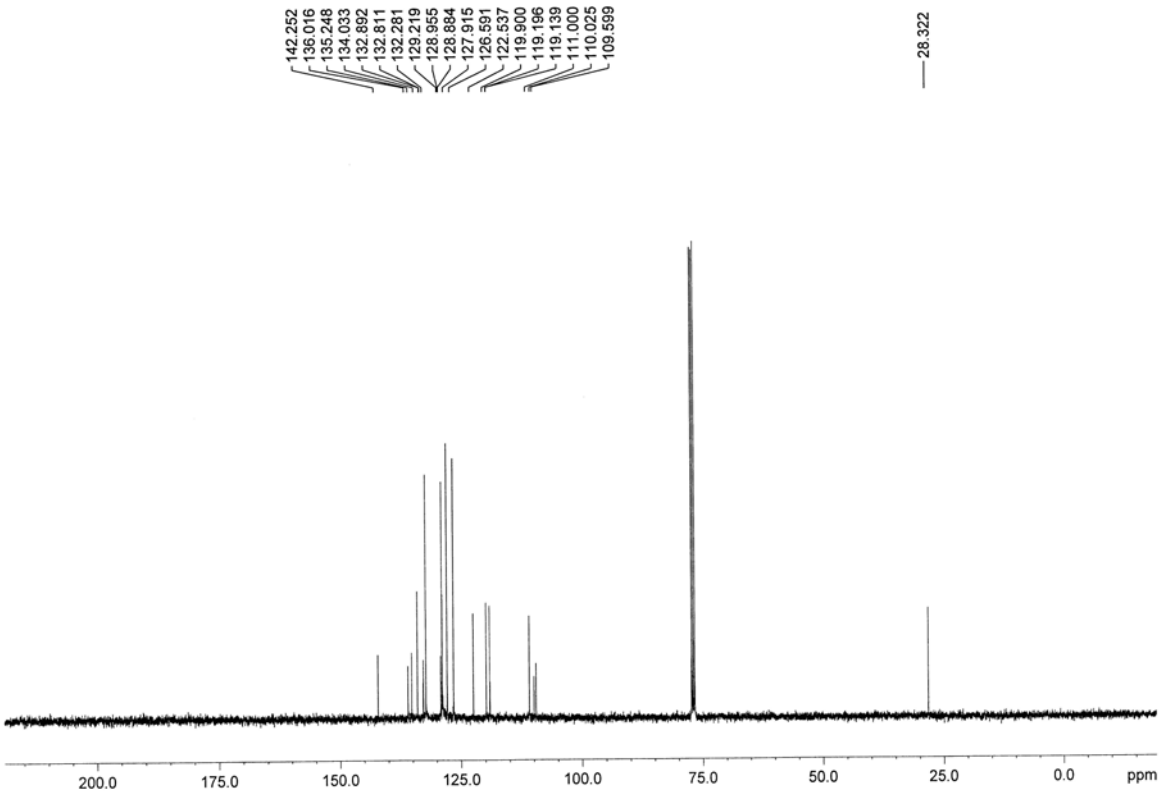

8.243
7.643
7.623
7.565
7.545
7.525
7.503
7.479
7.459
7.440
7.398
7.377
7.300
7.284
7.264
7.202
7.184
7.165
6.704
6.690
6.675
6.665
6.650
6.636
6.468
6.428
3.836
3.824
Cl
CN
N
H
1.052
1.284
9.964
1.478
1.320
1.000
1.027
1.975
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

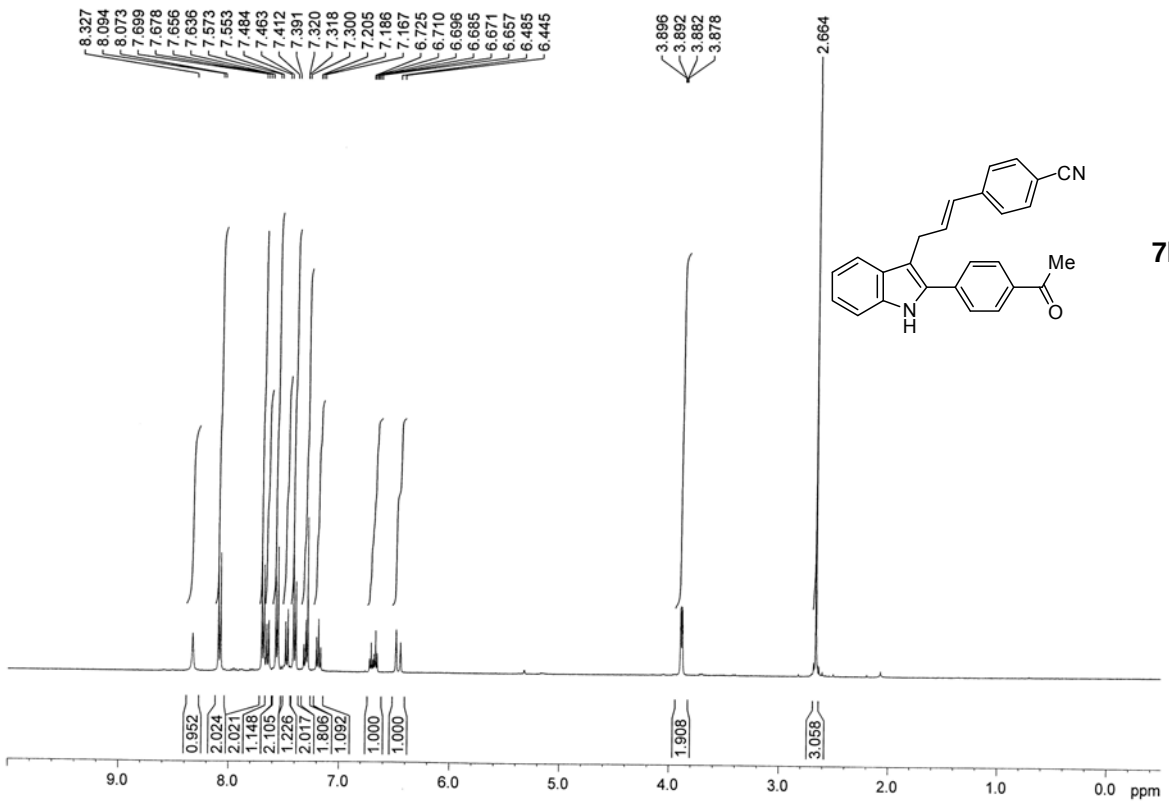
7f


142.093
136.081
134.019
133.884
133.691
132.312
131.232
129.190
129.122
129.092
129.026
126.600
122.856
120.102
119.270
119.118
111.061
110.129
110.109
28.250
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
ppm

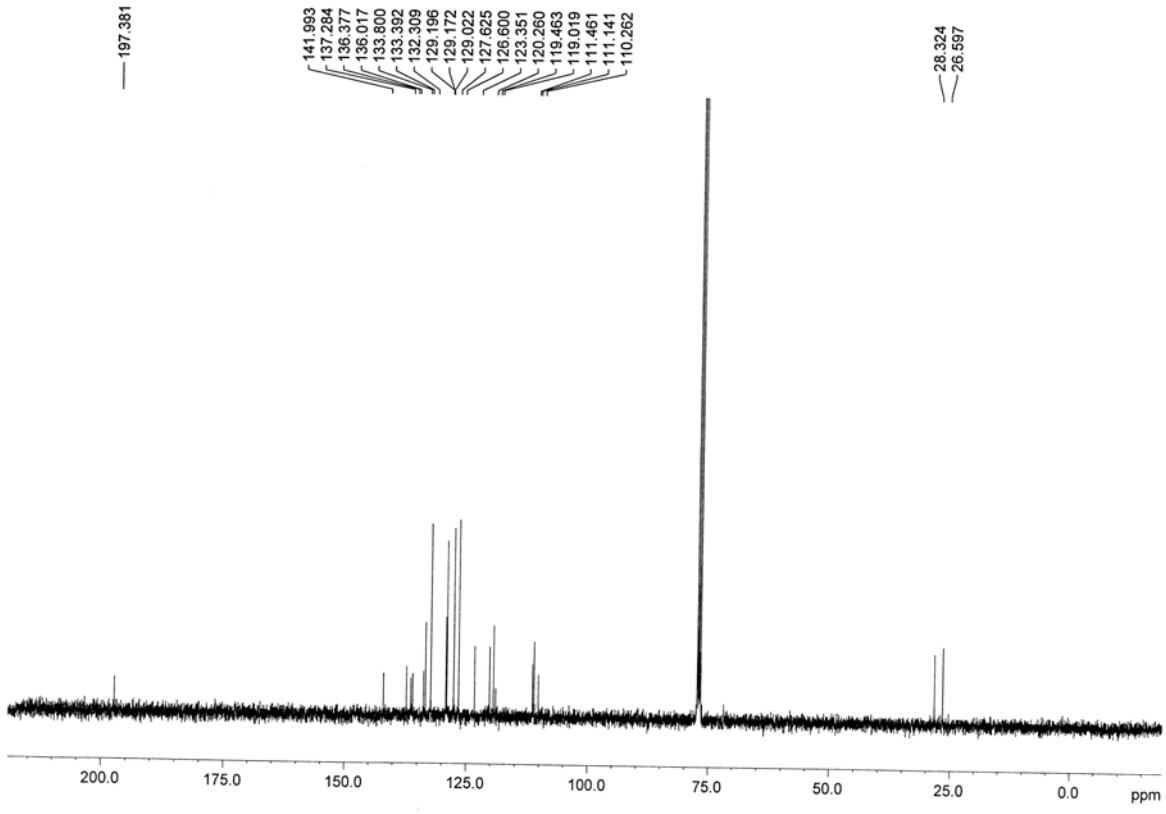

7.611
7.606
7.593
7.565
7.544
7.536
7.532
7.518
7.498
7.466
7.446
7.433
7.428
7.422
7.409
7.401
7.380
7.301
7.298
7.284
7.281
7.263
7.261
7.207
7.206
7.205
7.188
7.170
6.731
6.717
6.702
6.692
6.677
6.663
6.497
6.457
3.879
3.875
3.865
3.861
8.251
CN
N
H
0.959
11.549
1.225
1.064
1.004
1.000
1.984
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

7g


142.252
136.016
135.248
134.033
132.892
132.811
132.281
129.219
128.955
128.884
127.915
126.591
122.537
119.900
119.196
119.139
111.000
110.025
109.599
28.322
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
ppm


8.327
8.094
8.073
7.699
7.678
7.656
7.636
7.573
7.553
7.484
7.463
7.412
7.391
7.320
7.318
7.300
7.205
7.186
7.167
6.725
6.710
6.696
6.685
6.671
6.657
6.485
6.445
3.896
3.892
3.882
3.878
2.664
CN
Me
O
N
H
0.952
2.024
2.021
1.148
2.105
1.226
2.017
1.806
1.092
1.000
1.000
1.908
3.058
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

7h


197.381
141.993
137.284
136.377
136.017
133.800
133.392
132.309
129.196
129.172
129.022
127.625
126.600
123.351
120.260
119.463
119.019
111.461
111.141
110.262
28.324
26.597
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
ppm