Electronic Supplementary Information (ESI)

Palladium-catalyzed cross-coupling reactions of aryl fluorides with *N*-tosylhydrazones *via* C-F bond activation

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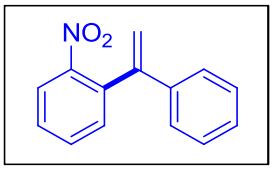
1. General

All the palladium-catalyzed cross-coupling reactions were carried out in oven-dried glassware sealed with rubber septa under nitrogen condition. All solvents were distilled under nitrogen atmosphere prior to use. $Pd(PPh_3)_4$, Cs_2CO_3 and other metal salts were commercially available. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh, from Qingdao, China). NMR spectra were measured on a Bruker ARX 400 (^1H at 400 MHz, ^{13}C at 100 MHz) magnetic resonance spectrometer. Chemical shifts are reported in *ppm* using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet). Infrared spectra were recorded on a Nicolet Avatar 330 Fourier transform spectrometer (FT-IR) and are reported in wave numbers (cm^{-1}). MS data were obtained on an Agilent 5975C inert 350 EI mass spectrometer (GC-MS). HRMS data were obtained on a VG ZAB-HS mass spectrometer, Brucker Apex IV FTMS spectrometer. Compounds described in the literature were characterized by comparison of their ^1H, and/or ^{13}C NMR spectra to the previously reported data. EA: ethyl acetate; PE: petroleum ether.

2. General procedure for the Pd-catalyzed cross-coupling reaction

Under an argon atmosphere, $Pd(PPh_3)_4$ (17.3 mg, 0.015 mmol, 5 mol%), Cs_2CO_3 (293.2 mg, 0.9 mmol, 3.0 equiv), TBAC (16.7 mg, 20 mol%), *N*-tosylhydrazone (0.6 mmol, 2.0 equiv) and aryl fluoride (0.30 mmol, 1.0 equiv) were successively added to a flame-dried 10 mL Schleck tube. The reaction flask was degassed three times with nitrogen, and then dry DMF (3.0 mL) was added using a syringe. Note that the aryl fluoride in a liquid form was added to the reaction tube by syringe after being dissolved in solvent. The reaction was heated at 90 ℃ with stirring for 8 h, and then cooled down to room temperature. After completion of the reaction, the reaction was quenched with water and extracted with diethyl ether (25 ml × 3). The organic layers were combined and washed with brine twice. It was dried over anhydrous Na_2SO_4 and solvent was removed in *vacuo* to leave a crude mixture, which is purified by silica gel column chromatography to afford the pure desired product.

3. Characterization data

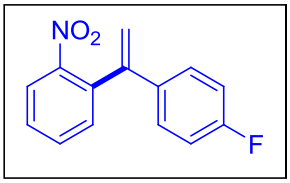


1-nitro-2-(1-phenylvinyl)benzene (3a)[1]

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 78%; yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.53-7.42 (m, 2H), 7.34-7.15 (m, 5H), 5.73 (s, 1H), 5.30 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 146.5, 139.1, 137.0, 132.9, 132.5, 128.7, 128.5, 128.2, 126.6, 124.4, 115.6.
IR (film): 2926, 1527, 1353, 908, 861, 782, 763, 705.



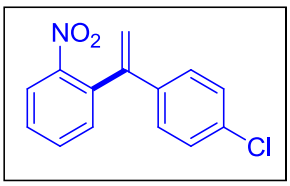
1-(1-(4-fluorophenyl)vinyl)-2-nitrobenzene (3b)[2]

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 60%; pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (1H, dd, *J* = 8.1, 1.1 Hz), 7.63 (1H, td, *J* = 7.6, 1.3 Hz), 7.50 (1H, td, *J* = 7.8, 1.3 Hz), 7.44 (1H, dd, *J* = 7.6, 1.4 Hz), 7.19-7.23 (2H, m), 6.94-6.99 (2H, m), 5.67 (1H, s), 5.29 (1H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (*J* = 248 Hz), 148.9, 145.6, 136.8, 135.4 (*J* = 3.8 Hz), 133.0, 132.4, 128.9, 128.3 (*J* = 7.7 Hz), 124.4, 115.5, 115.2.

HRMS (ESI) *m/e* calcd for $C_{14}H_{11}FNO_2$ ($M+H^+$) 244.0768, found 244.0766.
IR (film): 1604, 1528, 1509, 1351, 1234, 1160, 1014, 909, 863, 843, 789, 766.



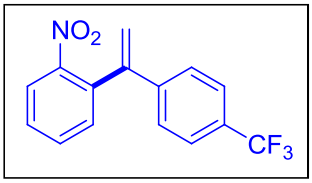
1-(1-(4-chlorophenyl)vinyl)-2-nitrobenzene (3c)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 74%; pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 5.64 (s, 1H), 5.24 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 145.5, 137.7, 136.5, 134.1, 133.1, 132.4, 129.0, 128.6, 127.8, 124.5, 116.0.

HRMS (ESI) *m*/*e* calcd for $C_{14}H_{11}ClNO_2$ ($M+H^+$) 260.0473, found 260.0471.
IR (film): 1526, 1491, 1348, 1260, 1094, 1013, 837, 798, 766, 750, 709.



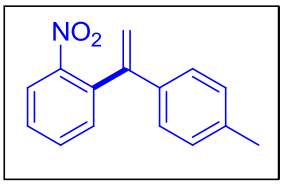
1-nitro-2-(1-(4-(trifluoromethyl)phenyl)vinyl)benzene (3d)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 61%; pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.67 (dt, *J* = 7.6, 3.8 Hz, 1H), 7.54-7.57 (m, 3H), 7.46 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.82 (s, 1H), 5.42 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 145.5, 142.6, 136.1, 133.2, 132.5, 130.0 (q, *J* = 32.6 Hz), 129.1, 126.8, 125.5 (q, *J* = 3.7 Hz), 124.6, 121.4 (q, *J* = 272.5 Hz), 117.5.

HRMS (ESI) *m*/*e* calcd for $C_{15}H_{11}F_3NO_2$ ($M+H^+$) 294.0736, found 294.0736.
IR (film): 1528, 1348, 1324, 1167, 1117, 1067, 1016, 849, 787, 769, 725.



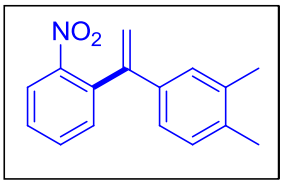
1-nitro-2-(1-*p*-tolylvinyl)benzene (3e)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 67%; light brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.61 (td, *J* = 7.5, 1.2 Hz, 1H), 7.57-7.37 (m, 2H), 7.19-7.01 (m, 4H), 5.70 (s, 1H), 5.25 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 146.3, 138.1, 137.2, 136.3, 132.8, 132.5, 129.1, 128.59, 126.4, 124.3, 114.7, 21.2.

HRMS (ESI) *m/e* calcd for $C_{15}H_{14}NO_2$ ($M+H^+$) 240.1019, found 240.1017.
IR (film): 1527, 1352, 906, 862, 826, 786, 766, 657.



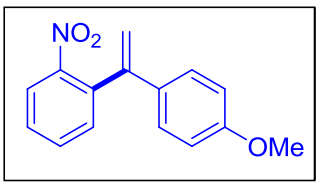
1,2-dimethyl-4-(1-(2-nitrophenyl)vinyl)benzene (3f)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 61%; pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.62 (td, *J* = 7.5, 1.3 Hz, 1H), 7.56-7.42 (m, 2H), 7.11-6.89 (m, 3H), 5.71 (s, 1H), 5.25 (s, 1H), 2.24 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 146.4, 137.2, 136.8, 136.7, 136.6, 132.8, 132.5, 129.7, 128.5, 127.7, 124.3, 124.0, 114.5, 19.9, 19.5.

HRMS (ESI) *m/e* calcd for $C_{16}H_{16}NO_2$ ($M+H^+$) 254.1176, found 254.1174.
IR (film): 1527, 1350, 904, 858, 826, 786, 766, 717, 705.



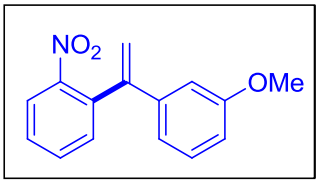
1-(1-(4-methoxyphenyl)vinyl)-2-nitrobenzene (3g)

Purified by column chromatography over silica gel (eluent: PE:EA=20:1); yield: 73%; yellow solid; m.p. 80-81 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.19 – 7.15 (m, 2H), 6.83– 6.80 (m, 2H), 5.65 (s, 1H), 5.21 (s, 1H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 145.8, 137.2, 132.8, 132.4, 131.8, 128.6, 127.8, 124.3, 113.8, 113.8, 55.3.

HRMS (ESI) *m/e* calcd for $C_{15}H_{14}NO_3$ ($M+H^+$) 256.0968, found 256.0966.
IR (film): 2957, 2917, 2849, 1607, 1528, 1512, 1353, 1250, 1182, 837, 786, 660.



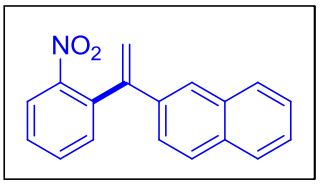
1-(1-(3-methoxyphenyl)vinyl)-2-nitrobenzene (3h)

Purified by column chromatography over silica gel (eluent: PE:EA=20:1); yield: 62%; pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.63 (td, *J* = 7.5, 1.3 Hz, 1H), 7.55-7.43 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.95-6.75 (m, 3H), 5.76 (s, 1H), 5.32 (s, 1H), 3.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 148.9, 146.4, 140.6, 136.9, 132.9, 132.5, 129.4, 128.7, 124.4, 119.1, 115.7, 113.4, 112.6, 55.2.

HRMS (ESI) *m/e* calcd for $C_{15}H_{14}NO_3$ ($M+H^+$) 256.0968, found 256.0966.
IR (film): 2954, 2923, 2851, 1577, 1527, 1352, 1288, 1238, 1047, 911, 857, 788, 765, 710, 667.



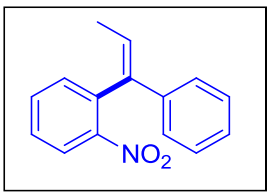
2-(1-(2-nitrophenyl)vinyl)naphthalene (3i)

Purified by column chromatography over silica gel (eluent: PE:EA=40:1); yield: 36%; yellow solid; m.p. 41-43 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.74-7.62 (m, 2H), 7.57-7.51 (m, 4H), 7.49 – 7.39 (m, 2H), 5.89 (s, 1H), 5.41 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 146.4, 137.0, 136.6, 133.2, 133.1, 133.0, 132.6, 128.8, 128.3, 128.3, 127.6, 126.3, 126.3, 125.7, 124.5, 116.0.

HRMS (ESI) *m/e* calcd for $C_{18}H_{14}NO_2$ ($M+H^+$) 276.1019, found 276.1018.
IR (film): 1525, 1349, 896, 857, 821, 785, 753, 708.



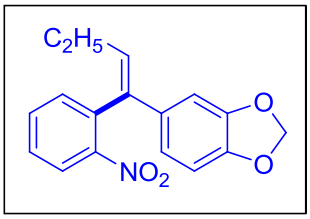
(*Z*)-1-nitro-2-(1-phenylprop-1-enyl)benzene (3j)[1]

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 63%; yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.64 (td, *J* = 7.5, 1.3 Hz, 1H), 7.53-7.45 (m, 1H), 7.32 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.29-7.14 (m, 5H), 6.27 (q, *J* = 7.0 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 140.4, 138.5, 135.0, 132.9, 132.8, 128.4, 128.3, 127.2, 126.4, 125.2, 124.5, 15.6.

IR (film): 1526, 1351, 850, 787, 760, 696.

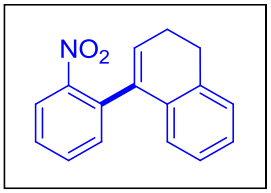


(*Z*)-1-nitro-2-(1-phenylbut-1-enyl)benzene (3k)

Purified by column chromatography over silica gel (eluent: PE:EA=40:1); yield: 48%; yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1, 0.8 Hz, 1H), 7.63 (td, *J* = 7.5, 1.1 Hz, 1H), 7.53-7.45 (m, 1H), 7.30 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.77 (d, *J* = 1.7 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.57 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.04 (t, *J* = 7.6 Hz, 1H), 5.92 (s, 2H), 1.91 (p, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).

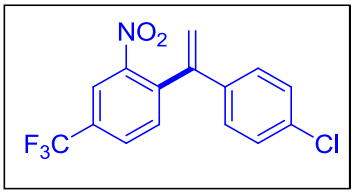
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 147.8, 146.9, 136.5, 135.3, 134.9, 132.9, 132.7, 131.2, 128.4, 124.5, 120.4, 108.0, 107.0, 101.1, 23.3, 14.0.
HRMS (ESI) *m/e* calcd for $C_{17}H_{16}NO_4$ ($M+H^+$) 298.1074, found 298.1073.
IR (film): 2967, 1526, 1503, 1489, 1443, 1350, 1247, 1227, 1039, 936, 856, 809, 788, 757, 732.



4-(2-nitrophenyl)-1,2-dihydronaphthalene (3l)[1]

Purified by column chromatography over silica gel (eluent: PE:EA=40:1); yield: 61%; yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.63 (td, *J* = 7.5, 1.2 Hz, 1H), 7.50 (td, *J* = 8.0, 1.4 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.16 (ddd, *J* = 11.9, 8.4, 4.0 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 6.02 (t, *J* = 4.6 Hz, 1H), 3.13-2.72 (br. d, 2H), 2.44 (br. s, 2H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 136.7, 136.0, 135.7, 134.3, 132.9, 132.5, 128.3, 128.0, 127.7, 127.4, 126.5, 124.3, 123.7, 27.8, 23.4;
IR (film): 2930, 1525, 1350, 1020, 860, 787, 769, 752, 739, 711.



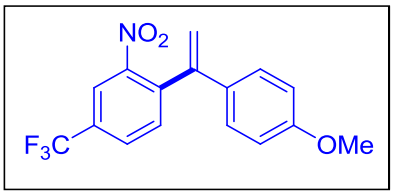
1-(1-(4-chlorophenyl)vinyl)-2-nitro-4-(trifluoromethyl)benzene (3m)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 57%; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 0.7 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.29-7.26 (m, 2H), 7.16-7.13 (m, 2H), 5.80 (s, 1H), 5.36 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 144.4, 140.0, 136.8, 134.6, 133.3, 131.6 (q, *J* = 34.5 Hz), 129.5 (q, *J* = 3.5 Hz), 128.8, 127.8, 122.8 (q, *J* = 272.8 Hz), 121.9 (q, *J* = 3.8 Hz), 117.1;

HRMS (ESI) *m/e* calcd for $C_{15}H_{10}ClF_3NO_2$ ($M+H^+$) 328.0347, found 328.0347.
IR (film): 1540, 1492, 1358, 1324, 1178, 1137, 1089, 836.



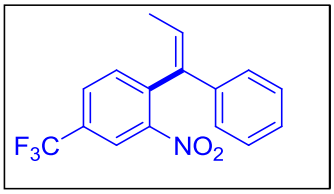
1-(1-(4-methoxyphenyl)vinyl)-2-nitro-4-(trifluoromethyl)benzene (3n)

Purified by column chromatography over silica gel (eluent: PE:EA=20:1); yield: 65%; yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 0.7 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.16-7.12 (m, 2H), 6.84-6.81 (m, 2H), 5.71 (s, 1H), 5.25 (s, 1H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 149.0, 144.8, 140.8, 133.3, 131.2 (q, *J* = 34.3 Hz), 131.0, 129.2(q, *J* = 3.4 Hz), 127.8, 122.9 (q, *J* = 272.8 Hz), 121.7 (q, *J* = 3.8 Hz), 114.9, 114.0, 55.3.

HRMS (ESI) *m/e* calcd for $C_{16}H_{13}F_3NO_3$ ($M+H^+$) 324.0842, found 324.0842.
IR (film): 1539, 1512, 1324, 1252, 1180, 1135, 837, 706.



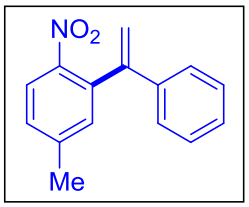
(*Z*)-2-nitro-1-(1-phenylprop-1-enyl)-4-(trifluoromethyl)benzene (3o)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 75%; yellow solid; m.p. 79-81 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.82 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.22-7.14 (m, 3H), 7.07 (dd, *J* = 7.9, 1.5 Hz, 2H), 6.25 (q, *J* = 7.1 Hz, 1H), 1.57 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 139.6, 138.8, 137.4, 133.9, 131.0 (q, *J* = 34.3 Hz), 129.4 (q, *J* = 3.5 Hz), 128.5, 127.6, 126.4, 126.2, 122.9 (q, *J* = 270.9), 121.91 (q, *J* = 3.8 Hz), 15.6.

HRMS (ESI) *m/e* calcd for $C_{16}H_{13}F_3NO_2$ ($M+H^+$) 308.0893, found 308.0893.
IR (film): 1539, 1355, 1177, 1134, 1088, 790, 760, 717, 696.



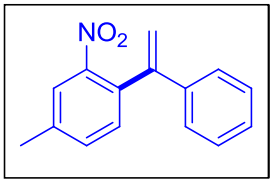
4-methyl-1-nitro-2-(1-phenylvinyl)benzene (4b)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 56%; pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.23 (m, 7H), 5.72 (s, 1H), 5.28 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 144.1, 139.2, 137.1, 133.0, 129.2, 128.4, 128.1, 126.5, 124.6, 115.0, 21.4.

HRMS (ESI) *m/e* calcd for $C_{15}H_{13}NNaO_2$ ($M+Na^+$) 262.0839, found 262.0841.
IR (film): 1606, 1583, 1519, 1495, 1346, 903, 840, 780, 760, 704.



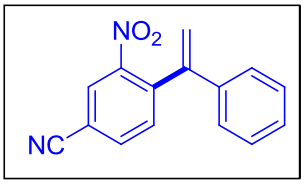
4-methyl-2-nitro-1-(1-phenylvinyl)benzene (4c)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 36%; yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.37-7.12 (m, 6H), 5.71 (s, 1H), 5.28 (s, 1H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) 148.8, 146.4, 139.3, 139.2, 134.1, 133.6, 132.3, 128.4, 128.1, 126.5, 124.7, 115.3, 21.0.

HRMS (ESI) *m/e* calcd for $C_{15}H_{14}NO_2$ ($M+H^+$) 240.1019, found 240.1017.
IR (film): 2919, 1530, 1354, 907, 841, 798, 782, 706, 667, 653.

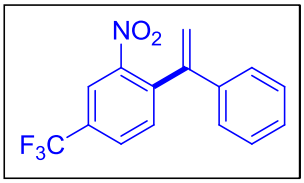


3-nitro-4-(1-phenylvinyl)benzonitrile (4d)

Purified by column chromatography over silica gel (eluent: PE:EA=15:1); yield: 40%; pale yellow solid; m.p. 115-117 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.4 Hz, 1H), 7.89 (dt, *J* = 25.5, 12.7 Hz, 1H), 7.60 (t, *J* = 8.9 Hz, 1H), 7.34-7.29 (m, 3H), 7.18-7.21 (m, 2H), 5.83 (s, 1H), 5.37 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 145.1, 141.5, 138.0, 135.7, 133.6, 128.8, 128.7, 128.0, 126.6, 117.2, 116.5, 113.0.

HRMS (ESI) *m/e* calcd for $C_{15}H_{11}N_2O_2$ ($M+H^+$) 251.0815, found 251.0812.
IR (film): 2960, 2921, 2849, 2236, 1620, 1552, 1534, 1354, 908, 785, 768, 707.



2-nitro-1-(1-phenylvinyl)-4-(trifluoromethyl)benzene (4f)

Purified by column chromatography over silica gel (eluent: PE:EA=50:1); yield: 70%; pale yellow solid; m.p. 89-91 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.89 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.46-7.28 (m, 3H), 7.21-7.24 (m, 2H), 5.82 (s, 1H), 5.36 (s, 1H).

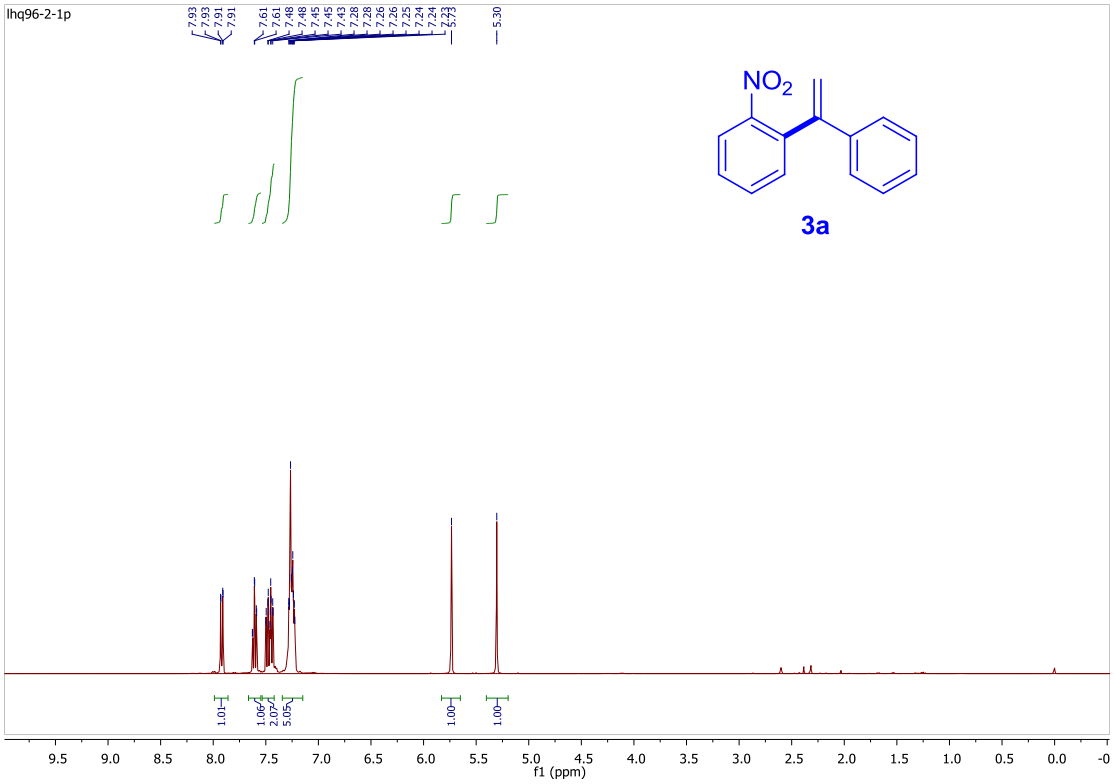
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 145.4, 140.5, 138.3, 133.4, 131.3 (q, *J* = 34.3 Hz), 129.3 (q, *J* = 3.7 Hz), 128.6 (s), 128.6 (s), 126.5 (s), 122.8 (q, *J* = 271 Hz), 121.8 (q, *J* = 3.8 Hz), 116.6.

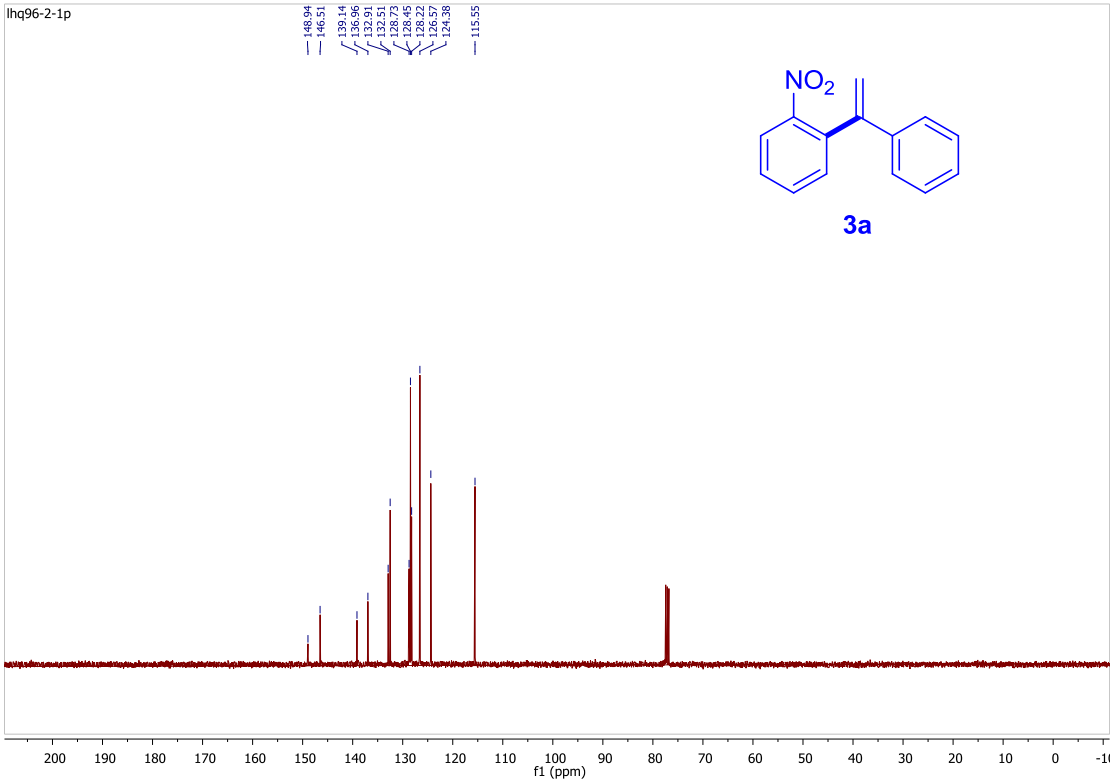
HRMS (ESI) *m/e* calcd for $C_{15}H_{11}F_3NO_2$ ($M+H^+$) 294.0736, found 294.0735.
IR (film): 2927, 1541, 1361, 1326, 1178, 1140, 1086, 906, 786, 772, 704, 657, 652.

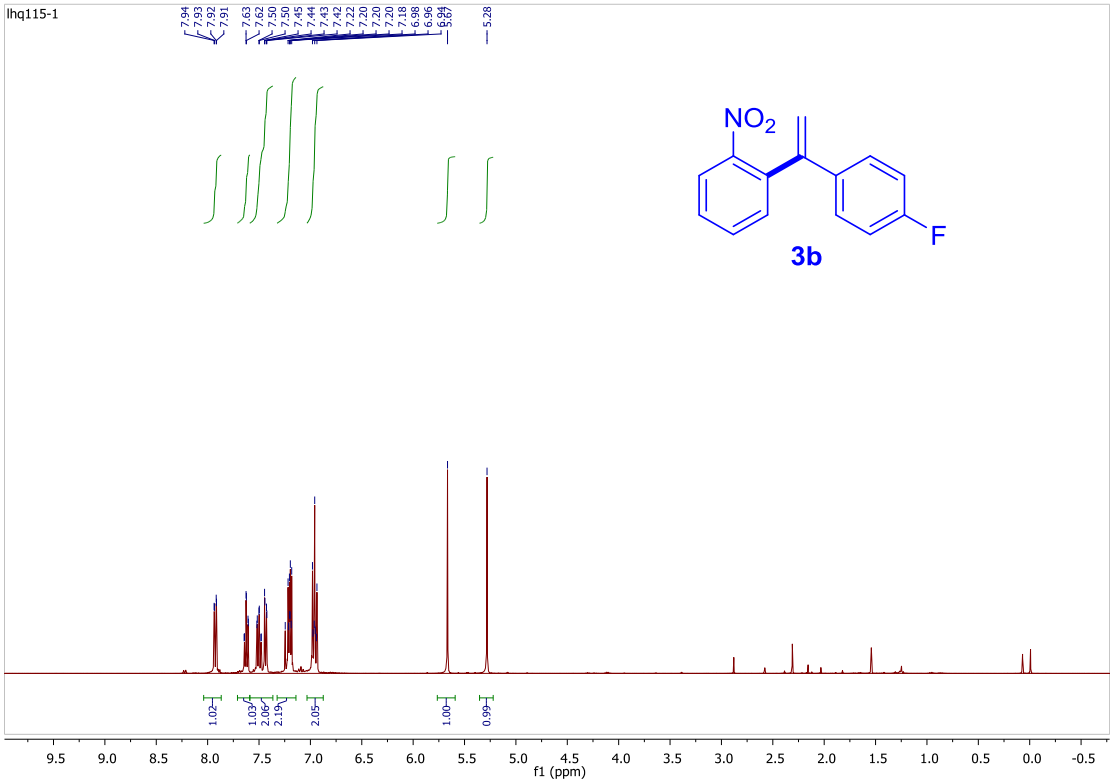
4. References

1) Tang, J.; Lukas J. Goo ßen, L. J. *Org. Lett.* **2014**, *16*, 2664-2667.
2) Fang, Y. Q.; Lautens. M. *J. Org. Chem.* **2008**, *73*, 538-549.

5. ^{1}H and ^{13}C NMR



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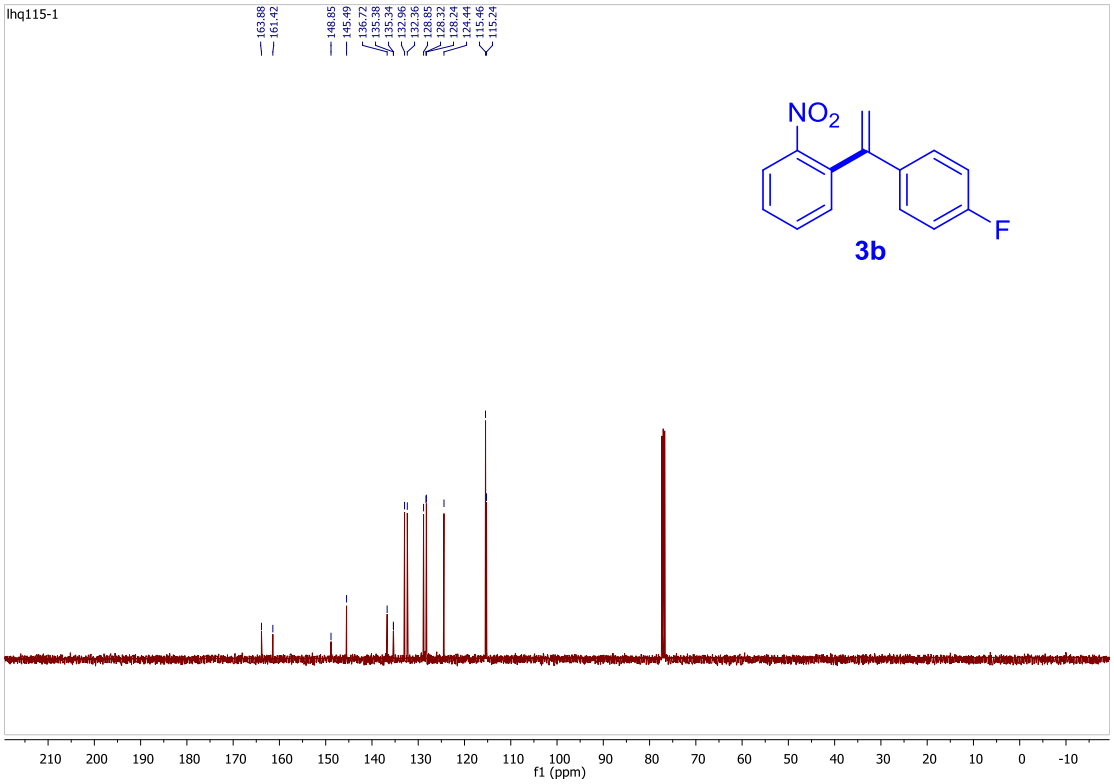
7.93
7.92
7.91
7.63
7.62
7.50
7.50
7.45
7.44
7.43
7.42
7.22
7.20
7.20
7.18
6.98
6.96
6.84
6.83
5.28
NO2
F
3b
1.02
1.03
2.06
2.19
2.05
1.00
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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161.42
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145.49
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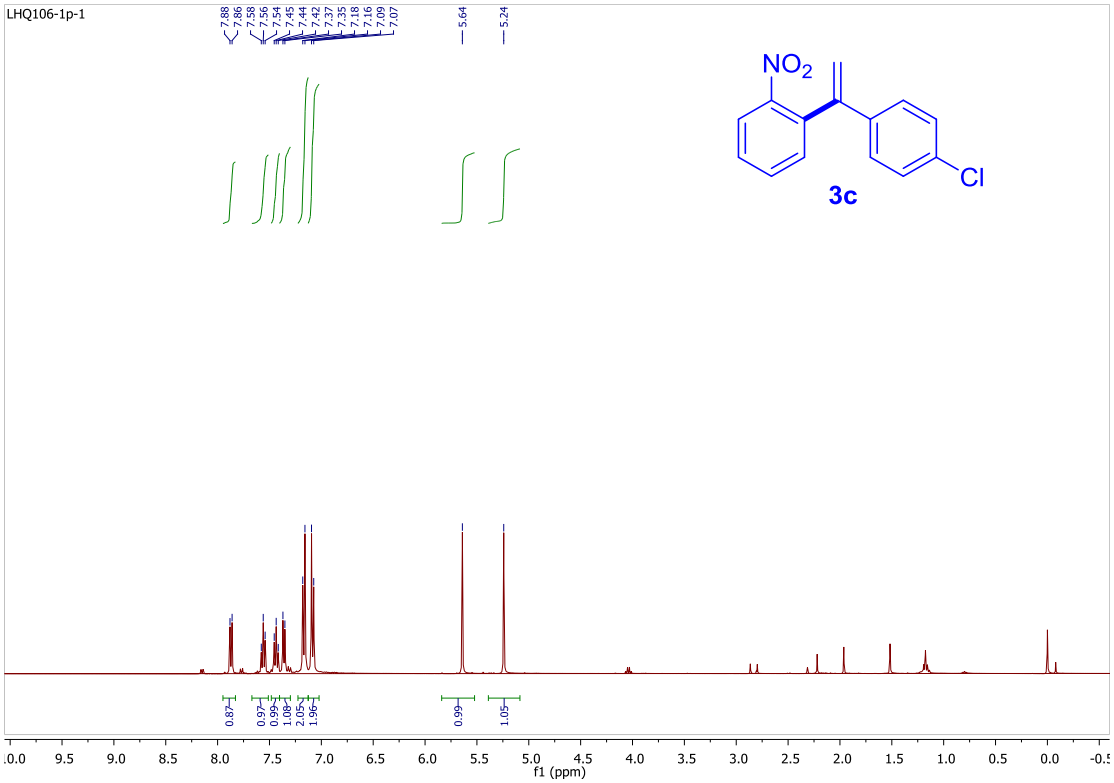
135.38
135.34
132.96
132.36
128.85
128.32
128.24
124.44
115.46
115.24
NO2
F
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.45
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7.42
7.37
7.35
7.18
7.16
7.09
7.07
5.64
5.24
NO2
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3c
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0.99
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1.96
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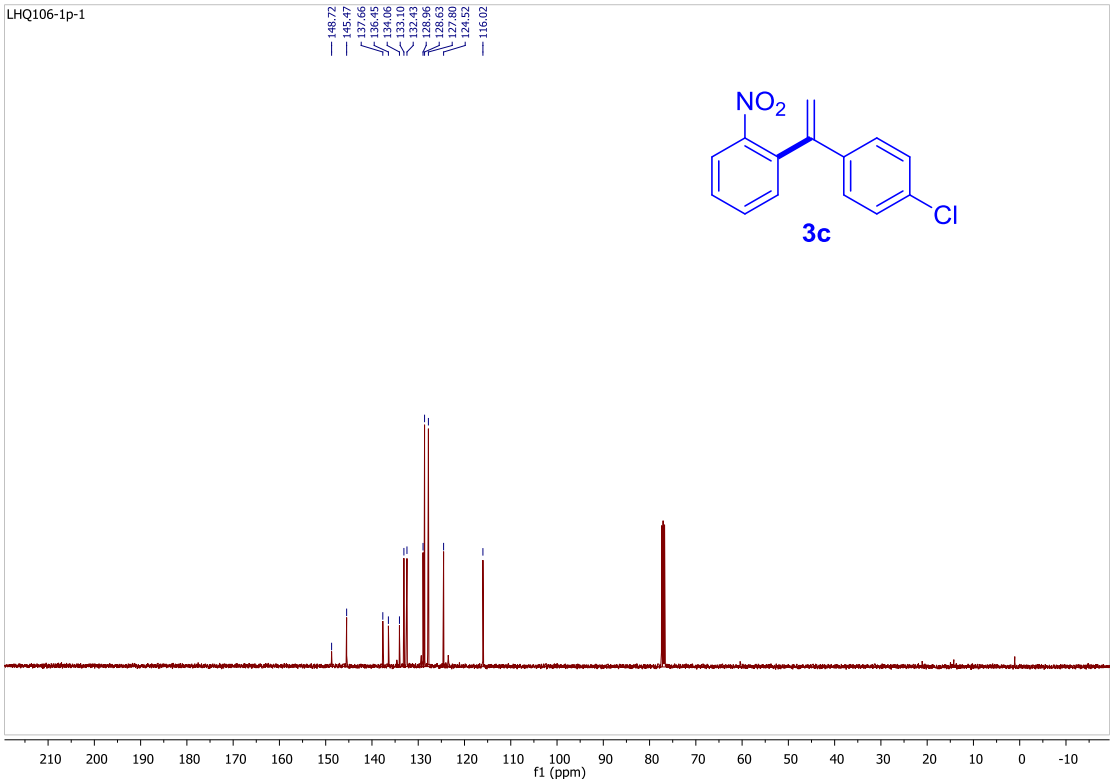
1.05
f1 (ppm)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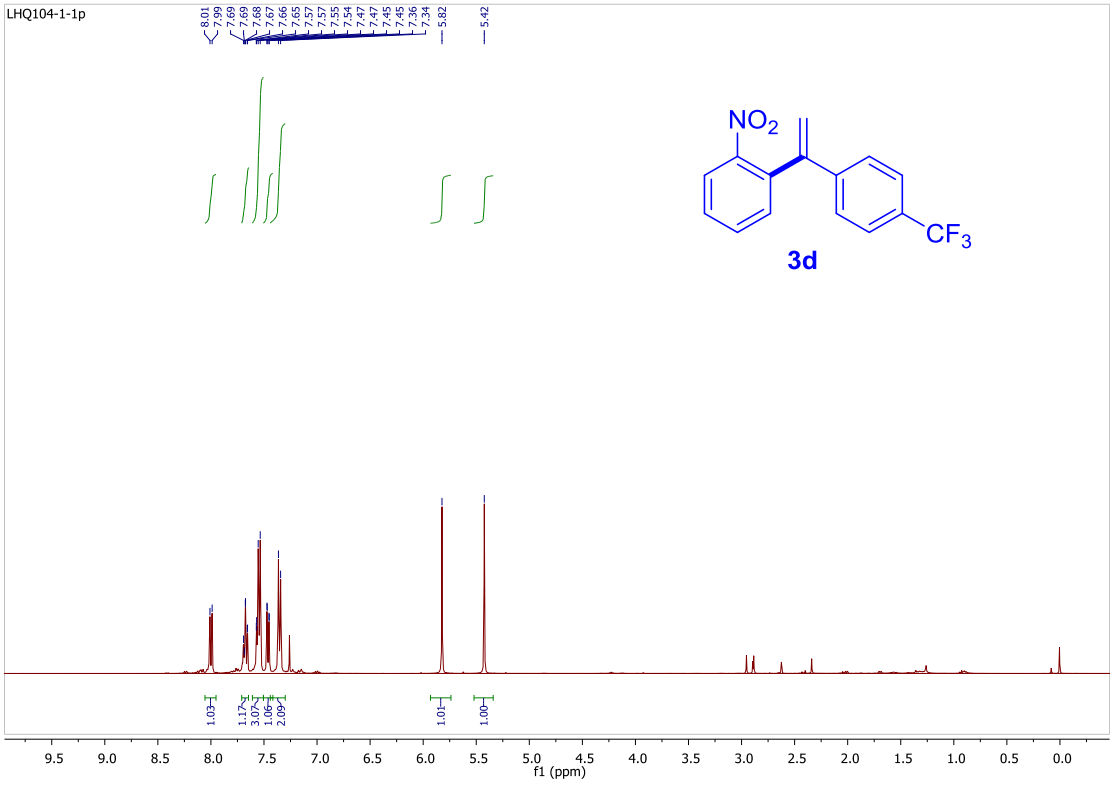
127.80
124.52
116.02
NO2
Cl
3c
f1 (ppm)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7.55
7.54
7.47
7.47
7.45
7.45
7.36
7.34
5.82
5.42
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CF3
3d
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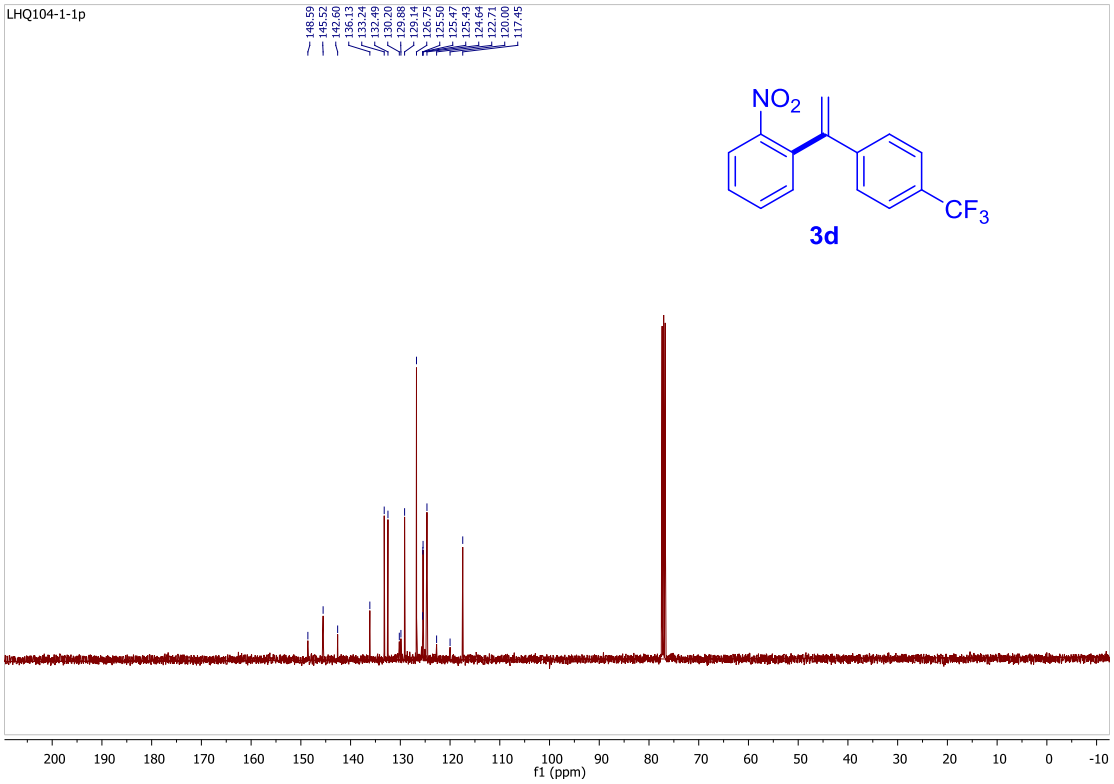
1.17
3.07
1.06
2.09
1.01
1.00
f1 (ppm)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117.45
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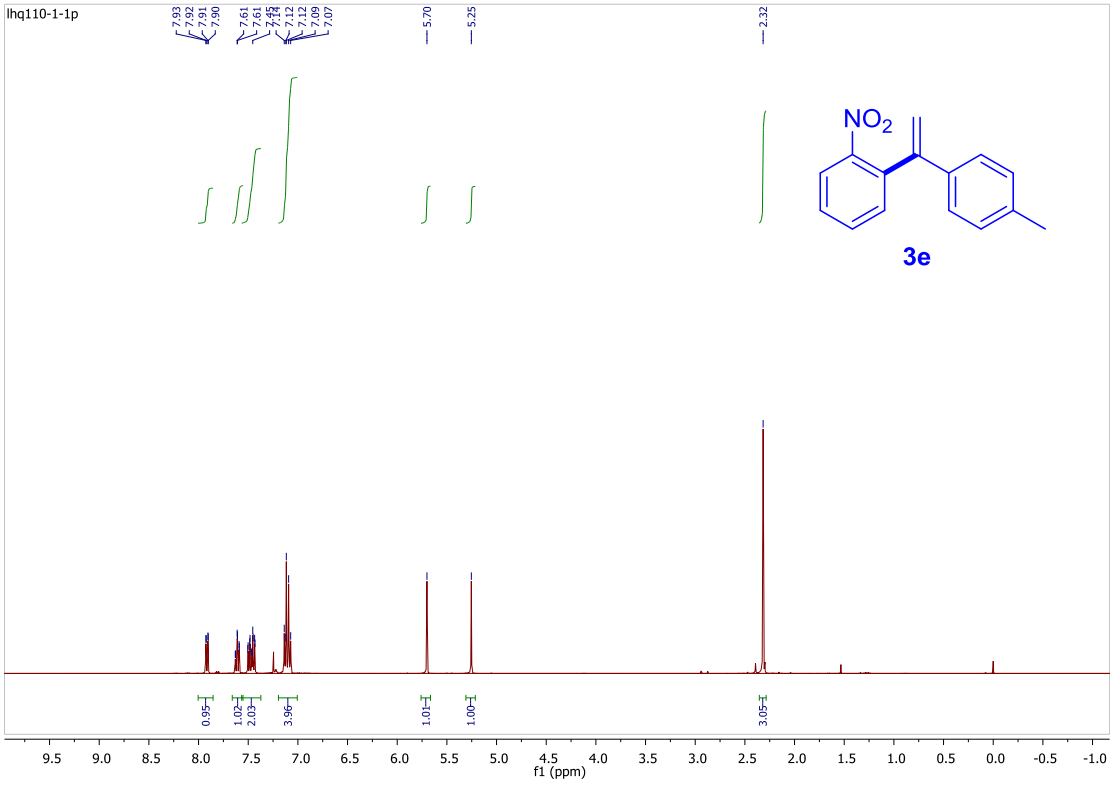
CF3
3d
f1 (ppm)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7.91
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7.61
7.44
7.44
7.12
7.09
7.07
5.70
5.25
2.32
NO2
3e
0.95
1.02
2.03
3.96
1.01
1.00
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
1.0
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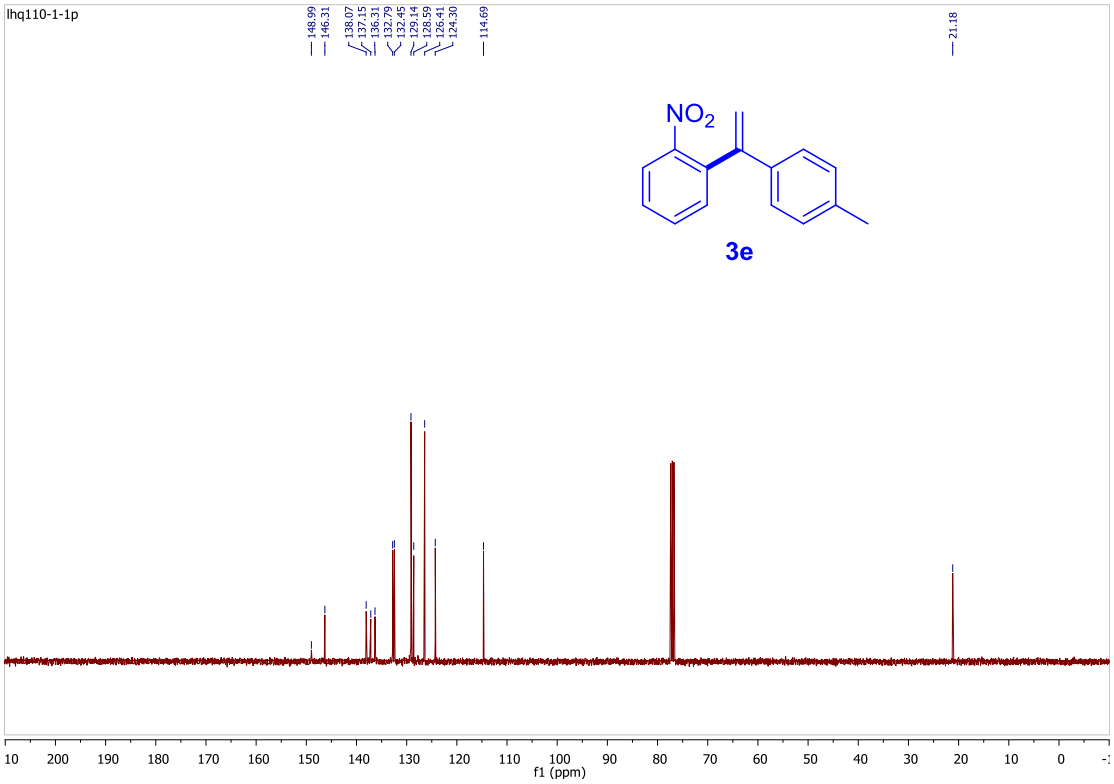
0.0
-0.5
-1.0
f1 (ppm)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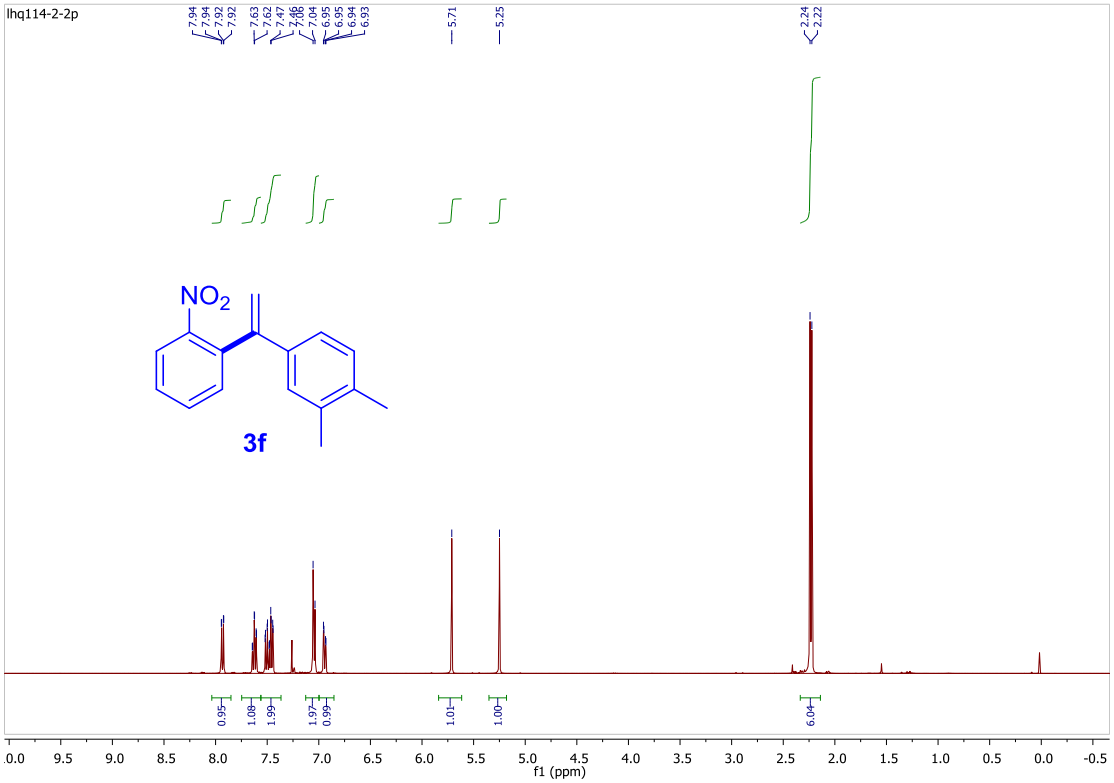
124.30
114.69
21.18
NO2
3e
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.04
6.95
6.95
6.94
6.93
5.71
5.25
2.24
2.22
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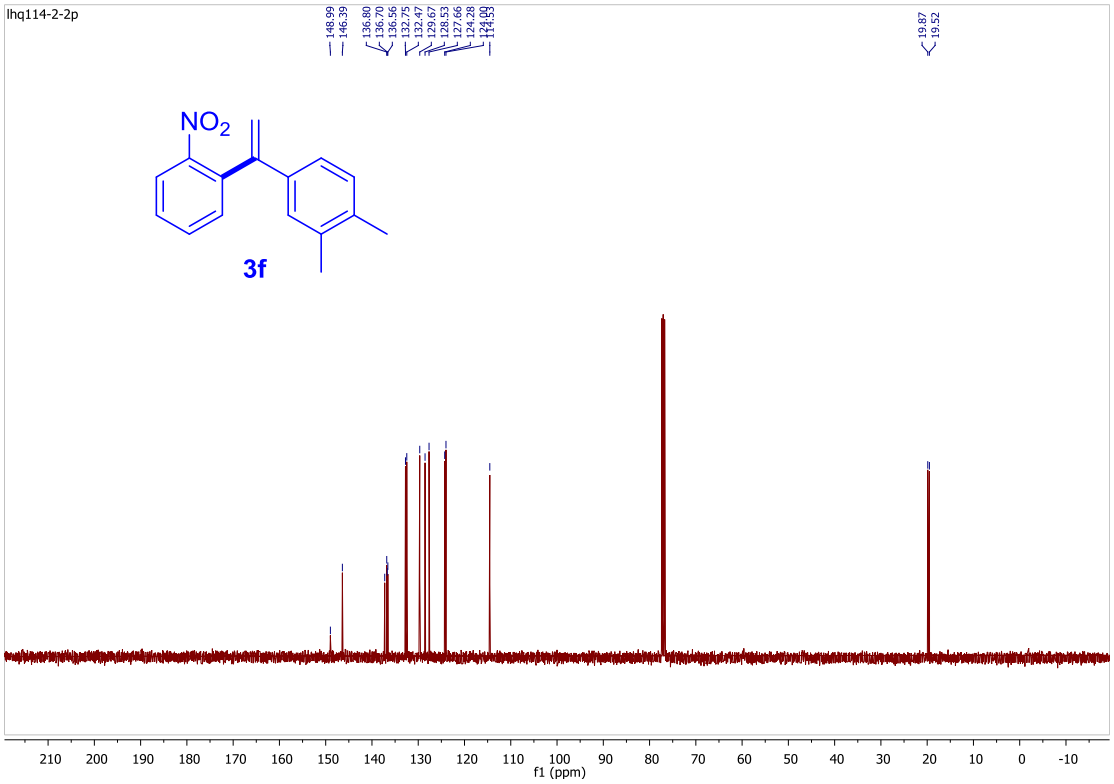
1.00
6.04
f1 (ppm)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19.52
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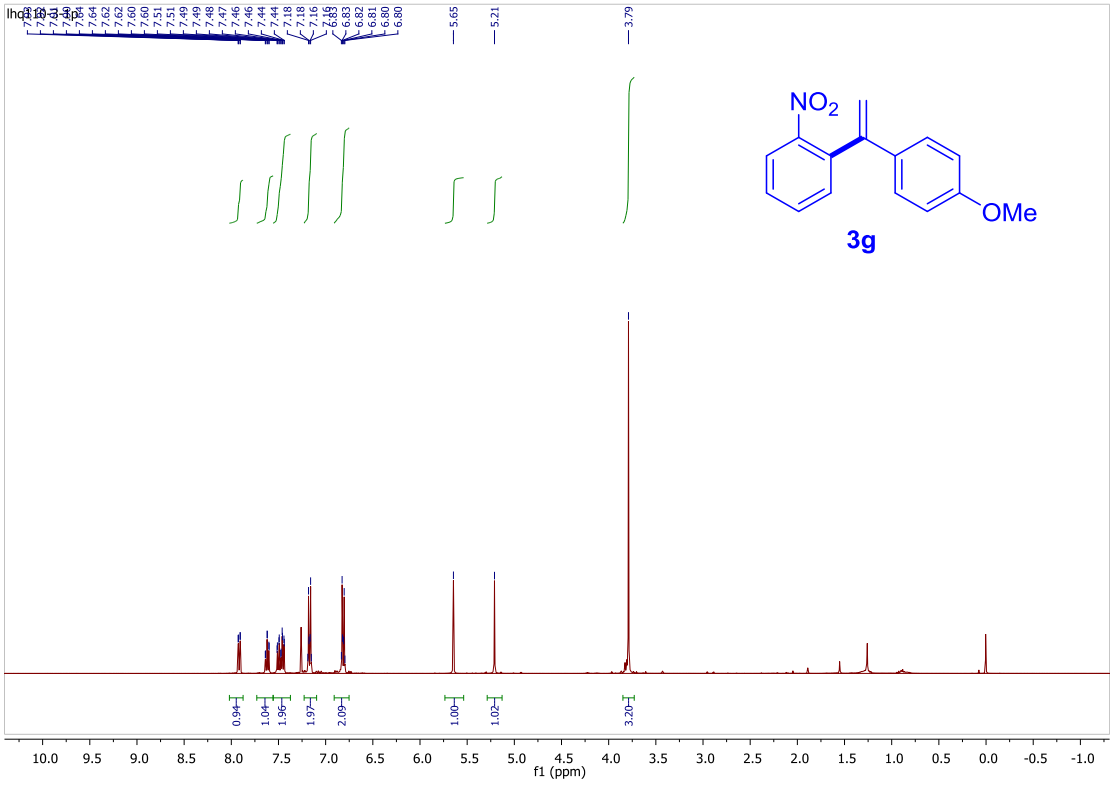
3f
f1 (ppm)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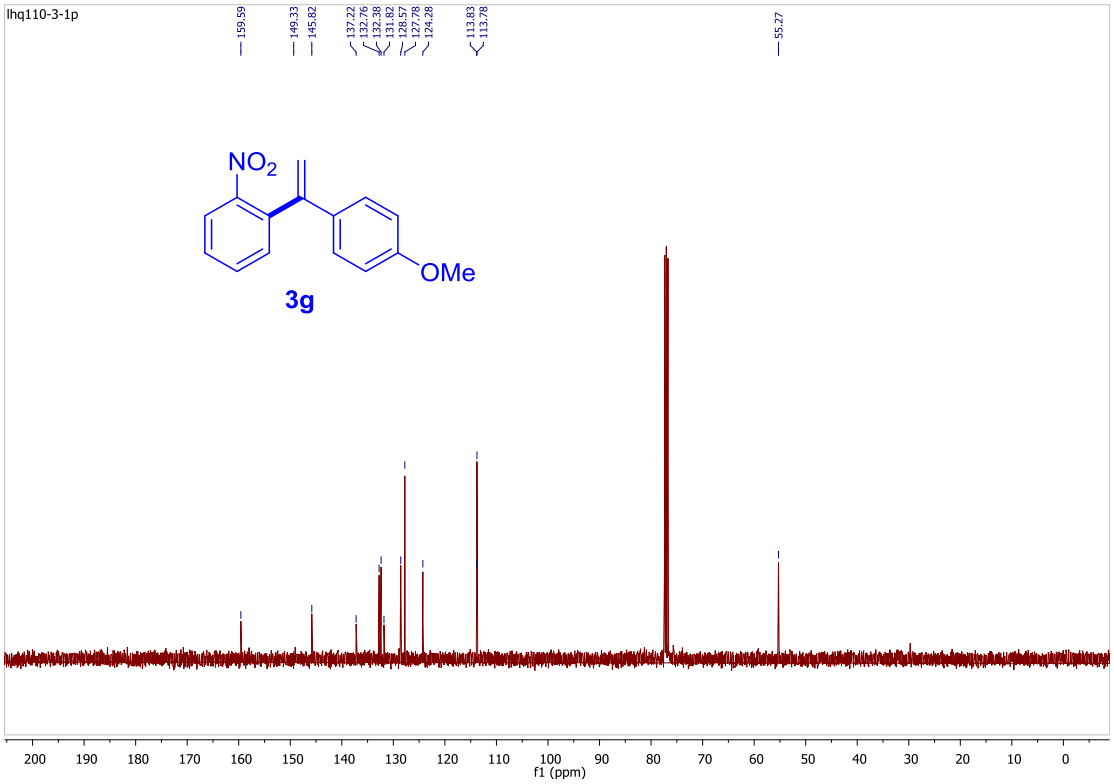
1.04
1.96
1.97
2.09
1.00
1.02
3.20
f1 (ppm)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113.78
55.27
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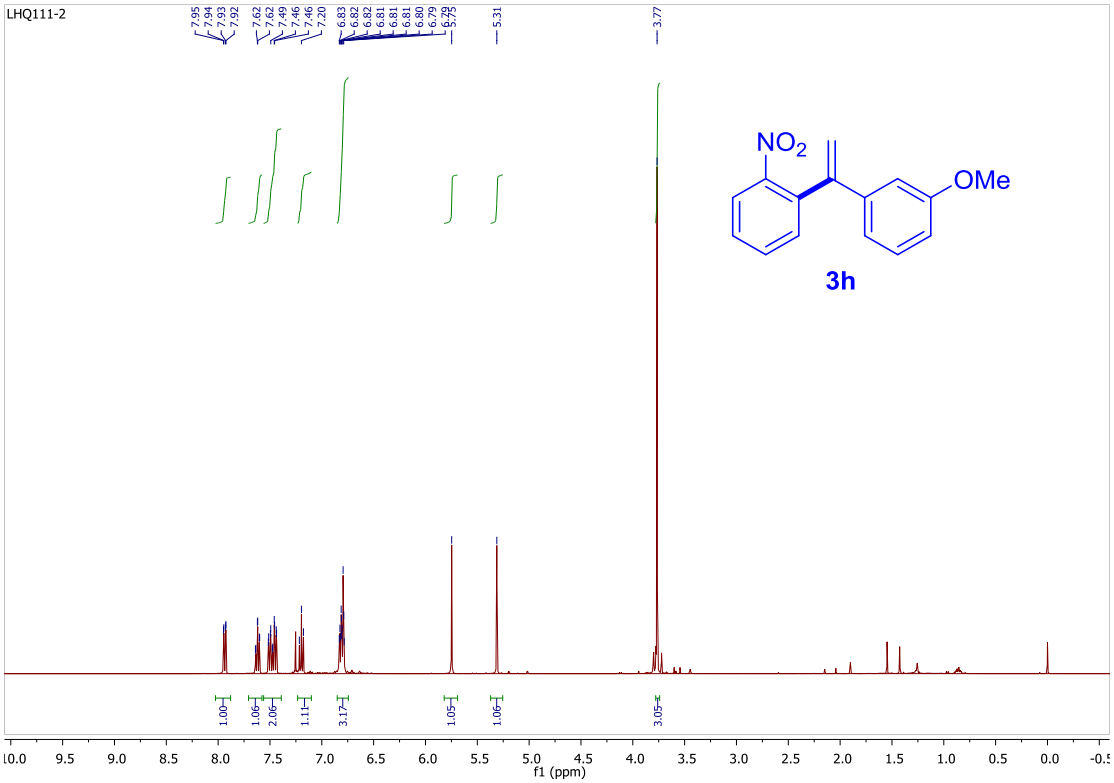
OMe
3g
f1 (ppm)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6.82
6.81
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6.81
6.80
6.79
6.79
5.75
5.31
3.77
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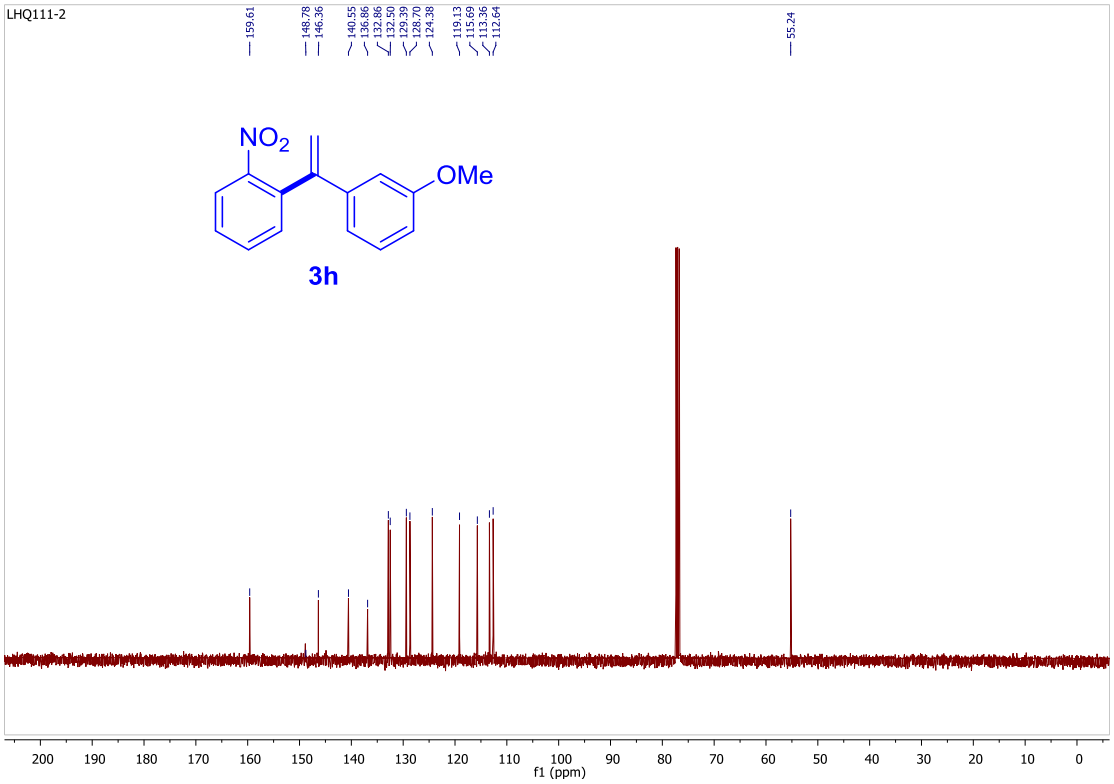
3.05
f1 (ppm)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55.24
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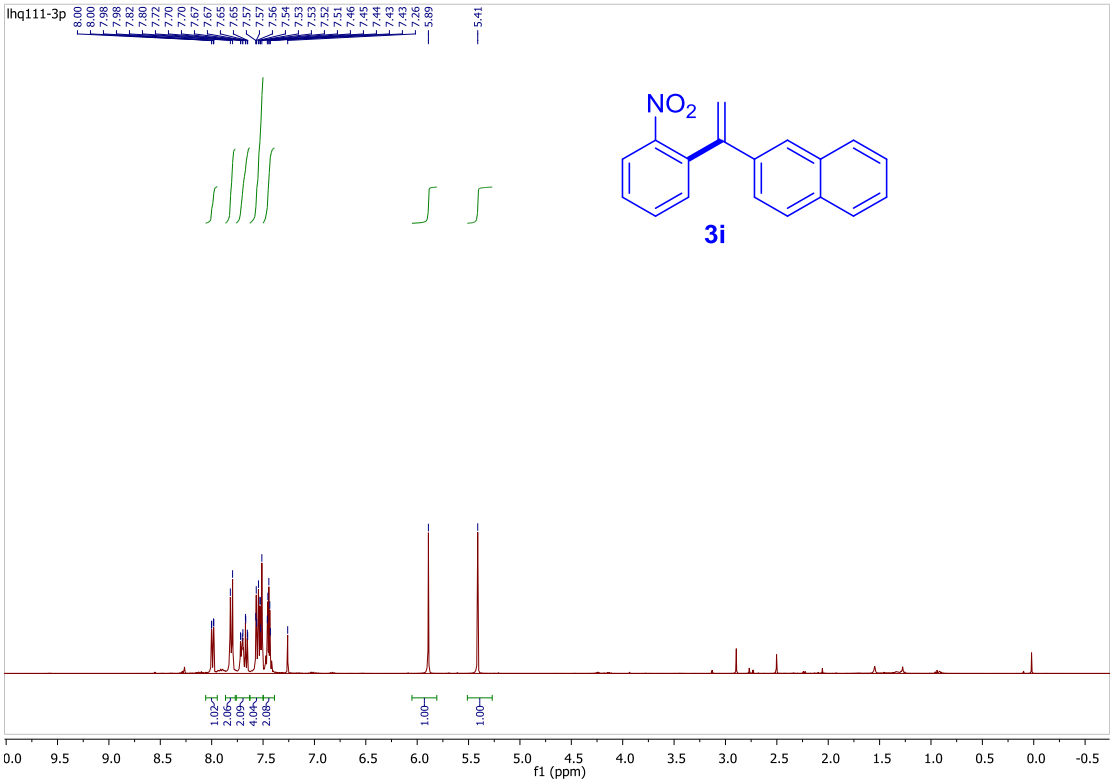
3h
f1 (ppm)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7.67
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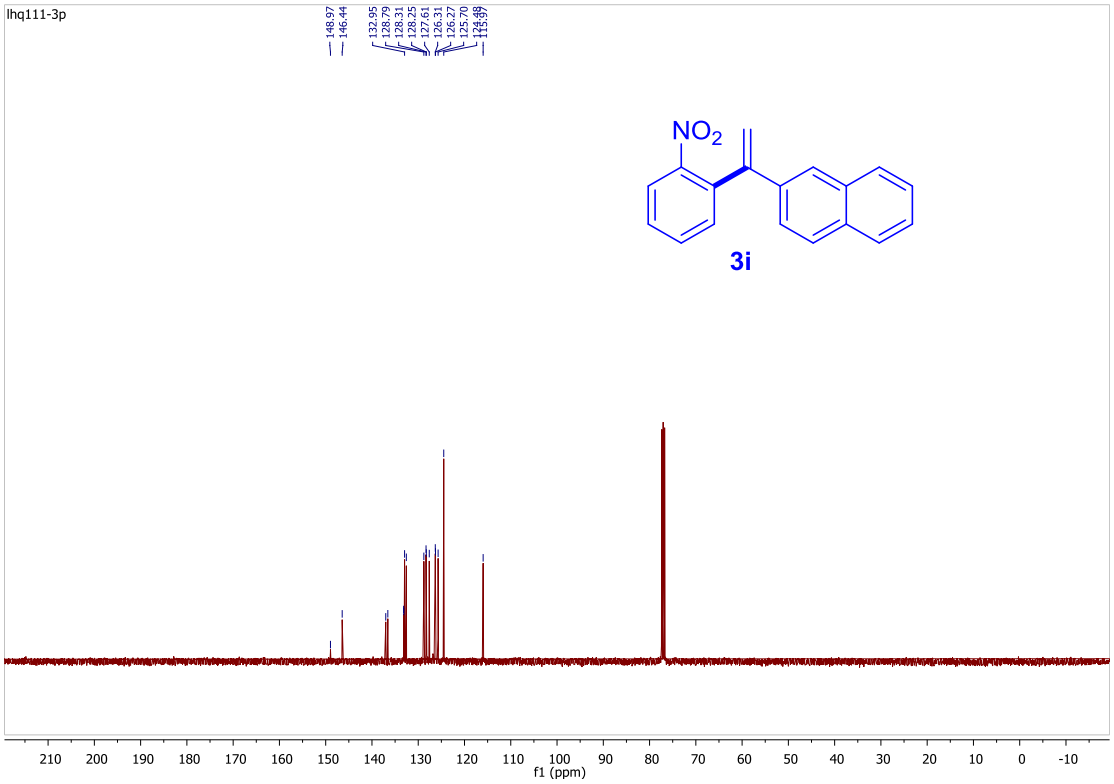
7.65
7.65
7.57
7.57
7.56
7.54
7.53
7.53
7.52
7.51
7.46
7.45
7.44
7.43
7.43
7.26
5.89
5.41
NO2
3i
1.02
2.06
2.09
4.04
2.08
1.00
1.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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115.99
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3i
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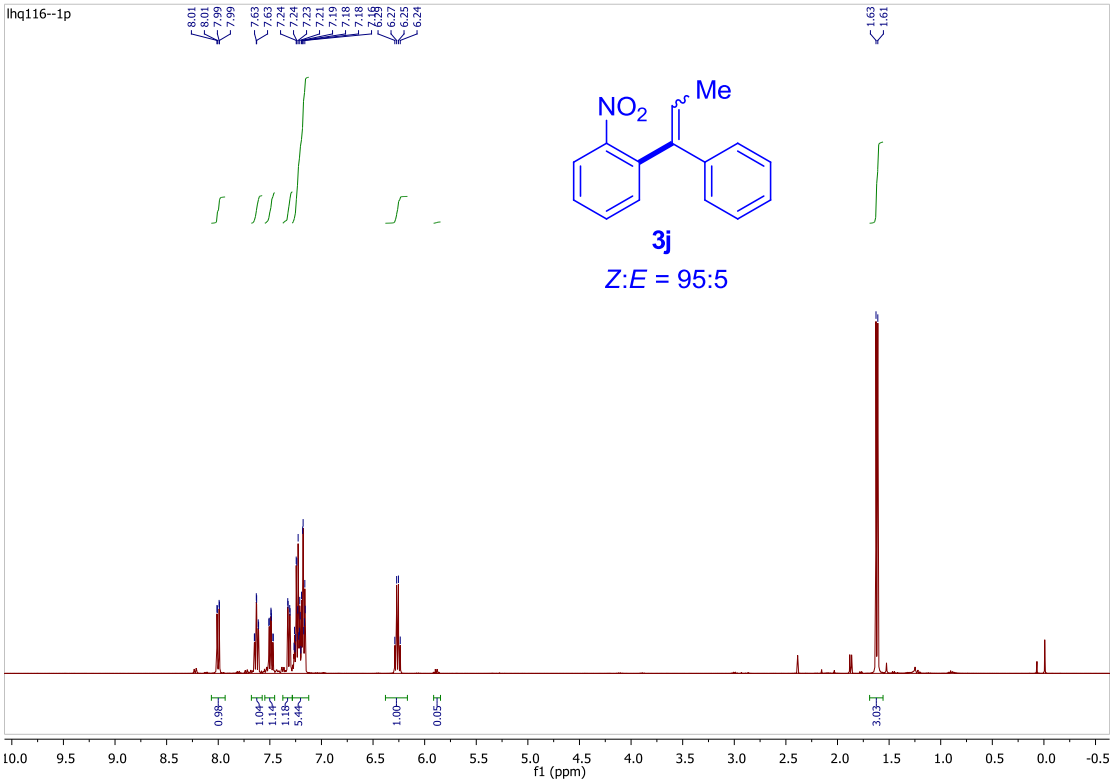
f1 (ppm)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8.01
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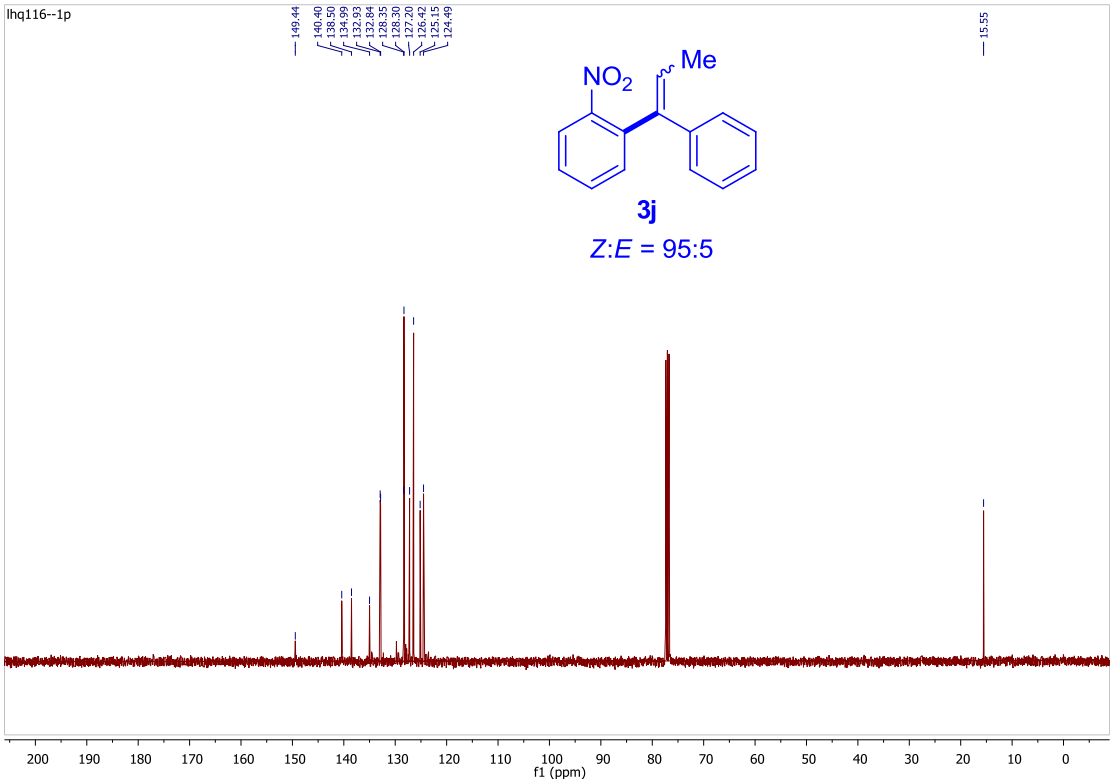
7.99
7.63
7.63
7.24
7.24
7.23
7.21
7.19
7.18
7.18
6.27
6.25
6.24
1.63
1.61
NO2
Me
3j
Z:E = 95:5
0.98
1.04
1.14
1.18
5.44
1.00
0.05
3.03
f1 (ppm)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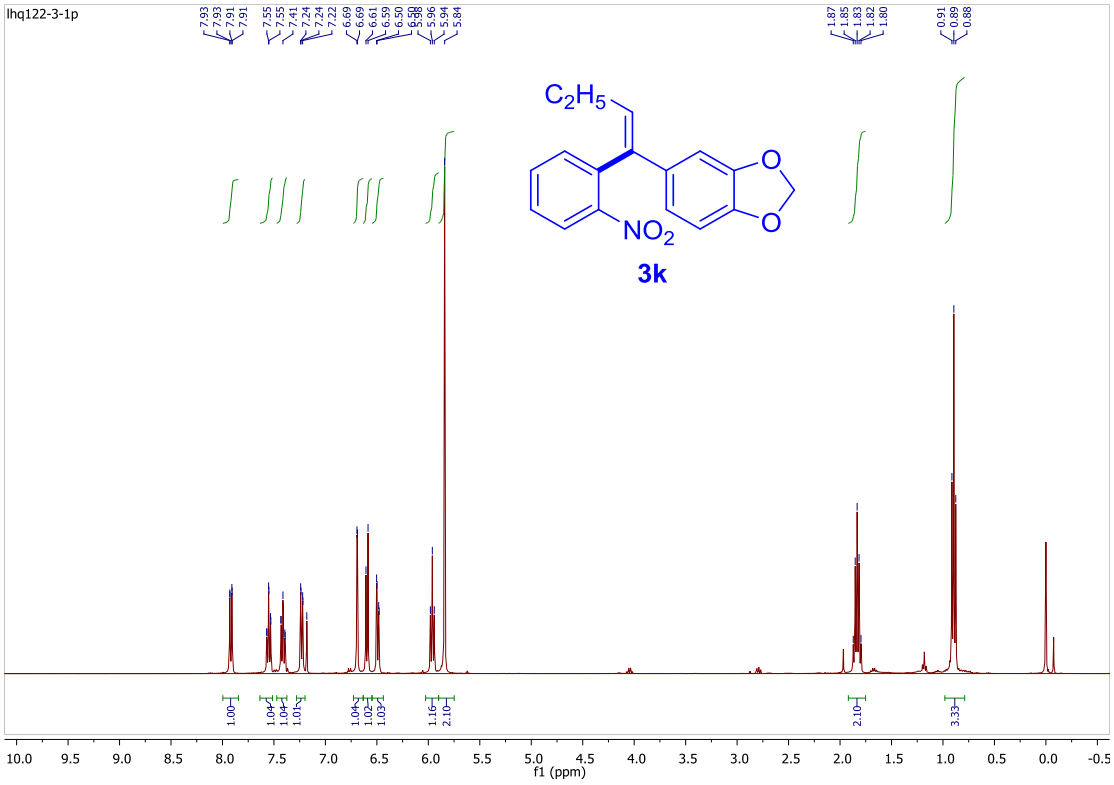
15.55
NO2
Me
3j
Z:E = 95:5
f1 (ppm)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7.93
7.91
7.91
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7.55
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7.24
7.24
7.22
6.69
6.69
6.61
6.59
6.50
5.96
5.94
5.84
1.87
1.85
1.83
1.82
1.80
0.91
0.89
0.88
C2H5
NO2
O
O
3k
1.00
1.04
1.04
1.01
1.04
1.02
1.02
1.16
2.10
2.10
3.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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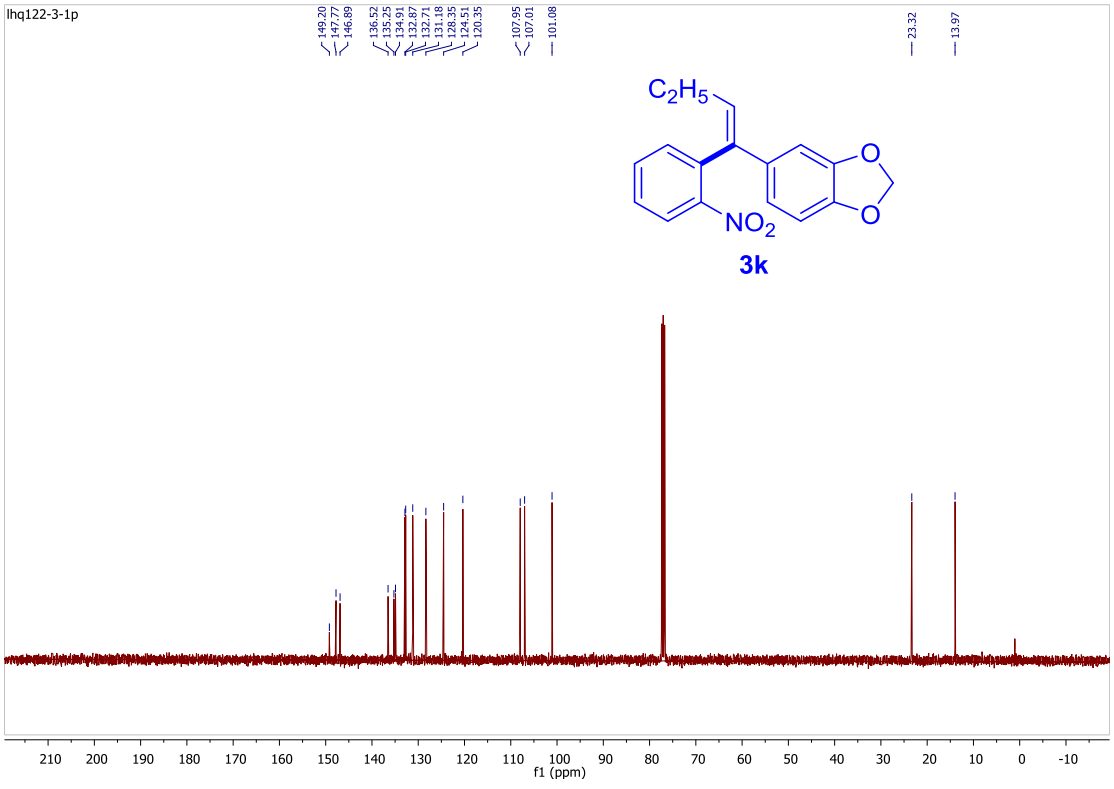
f1 (ppm)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120.35
107.95
107.01
101.08
23.32
13.97
C2H5
NO2
O
O
3k
210
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190
180
170
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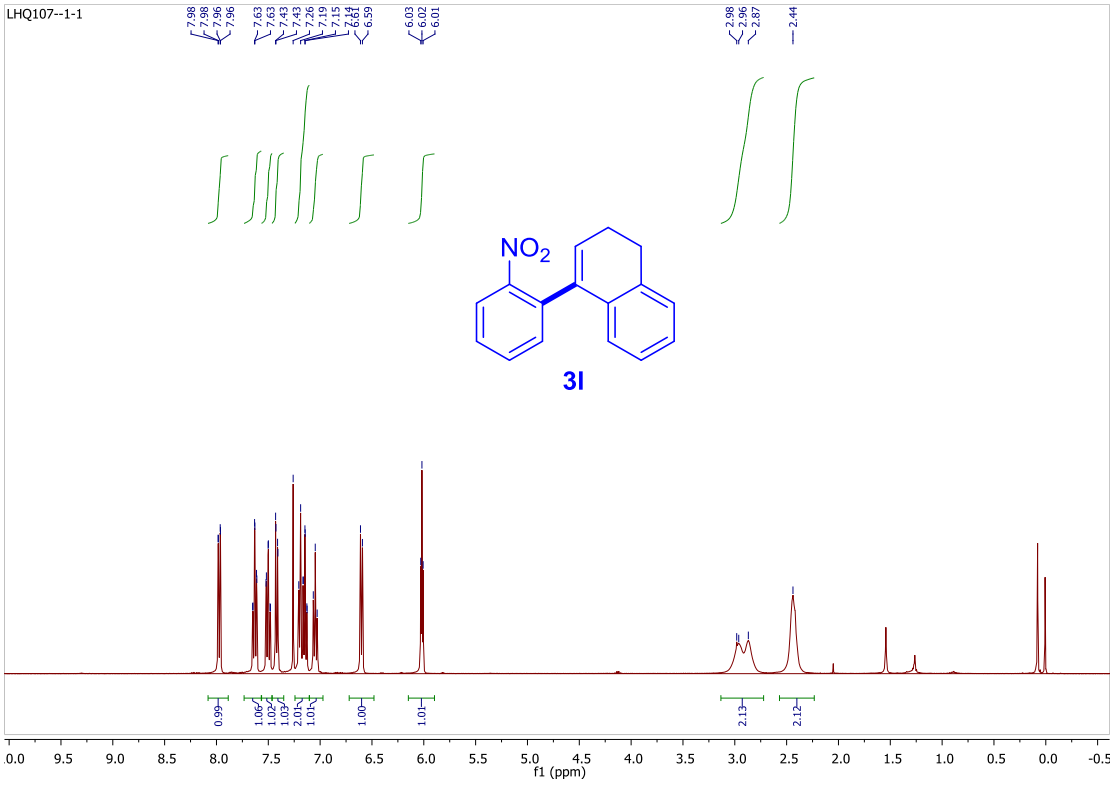
f1 (ppm)


LHQ107--1-1
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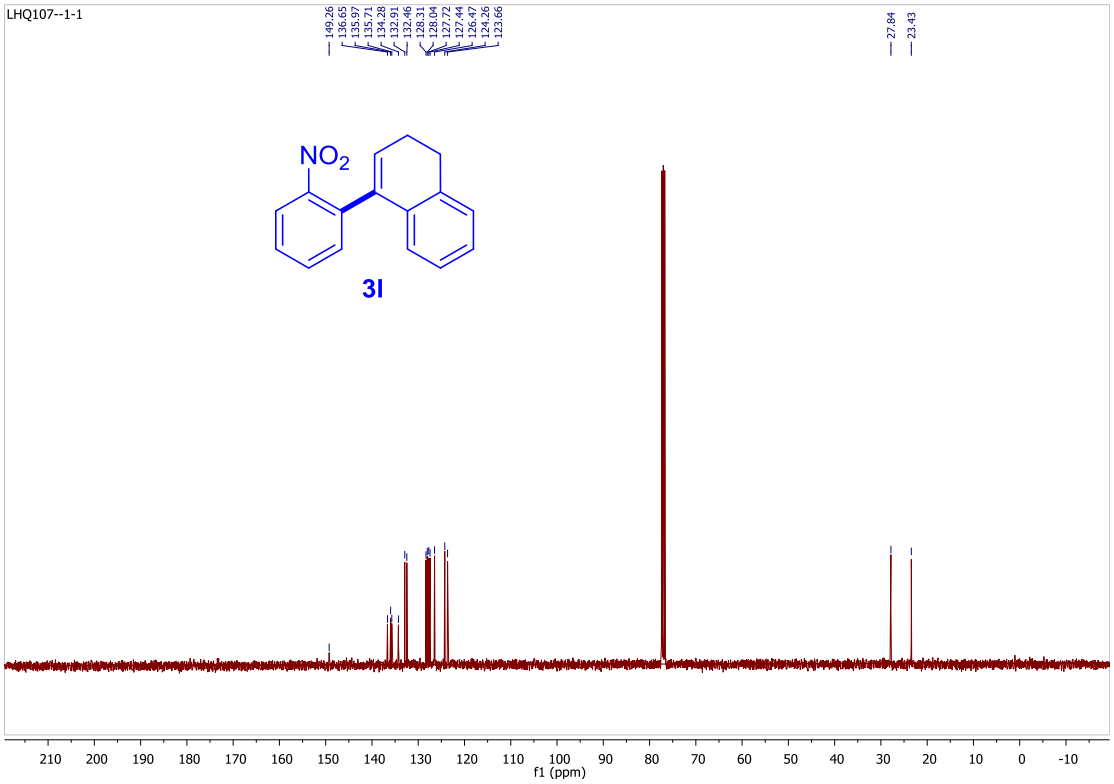
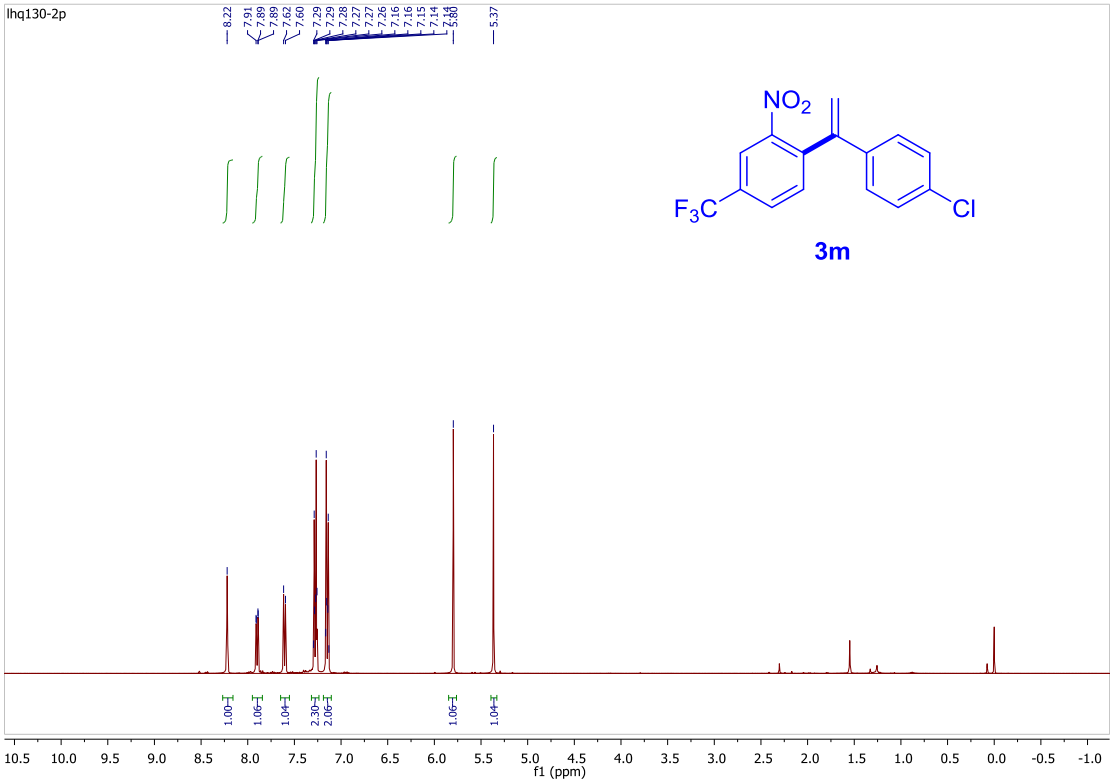
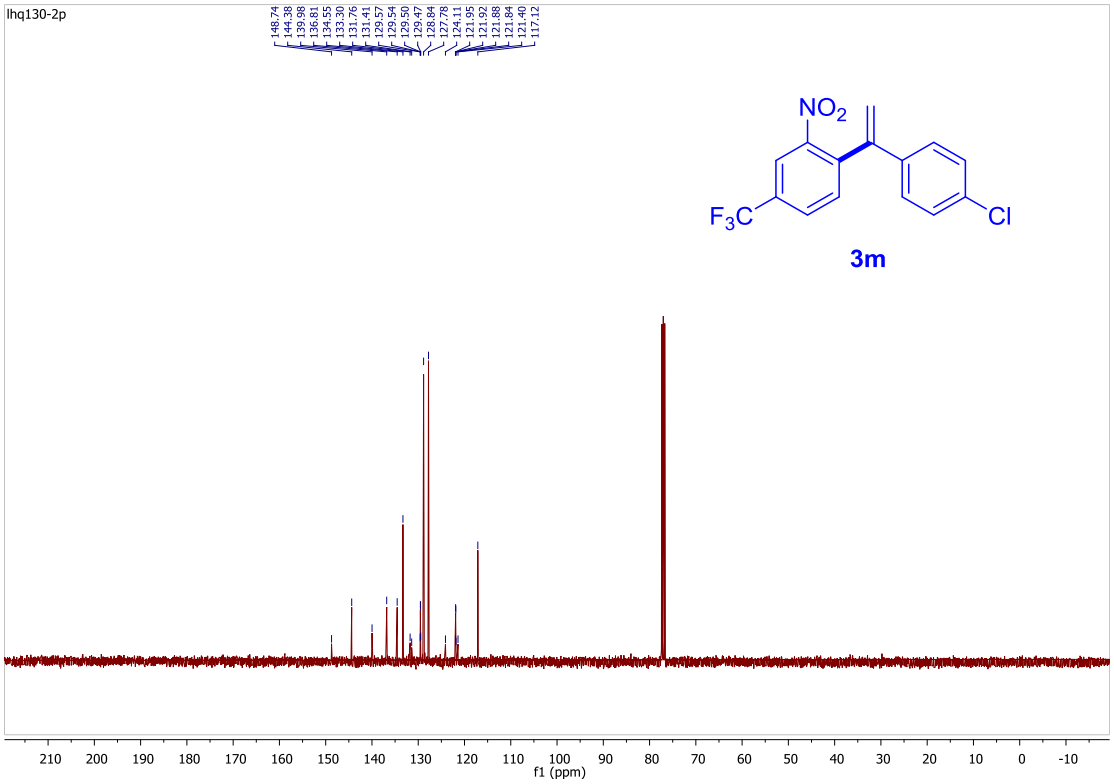
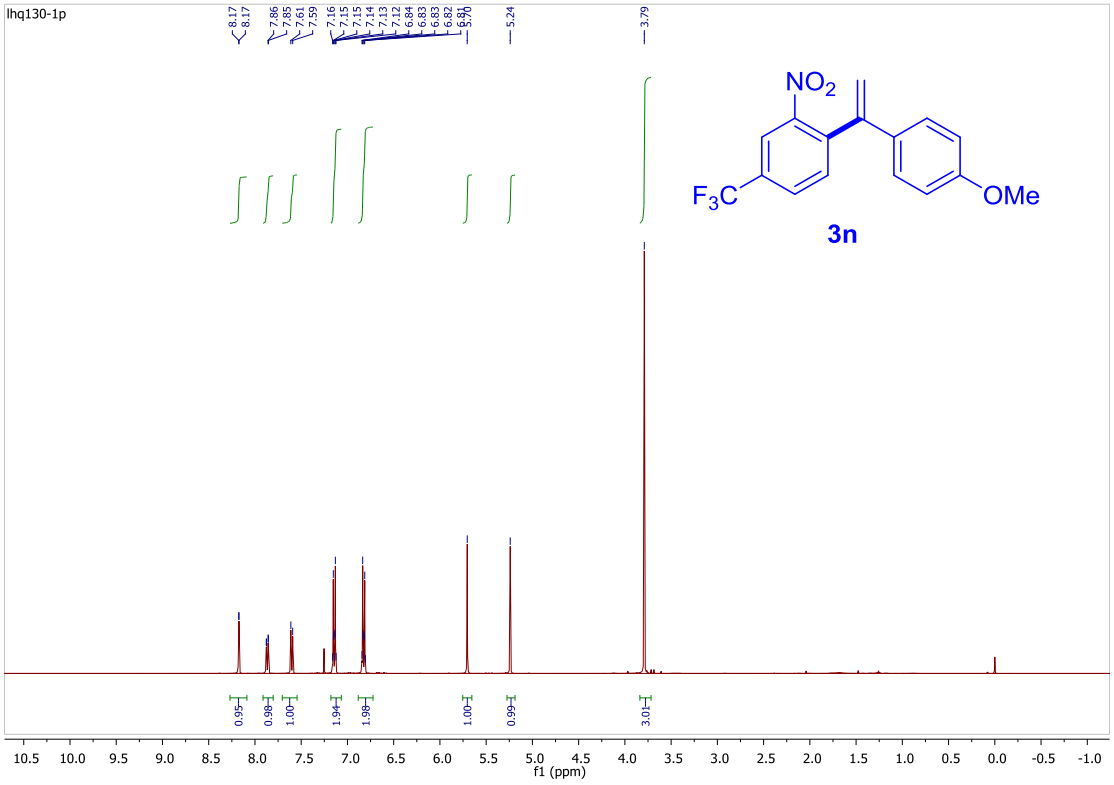
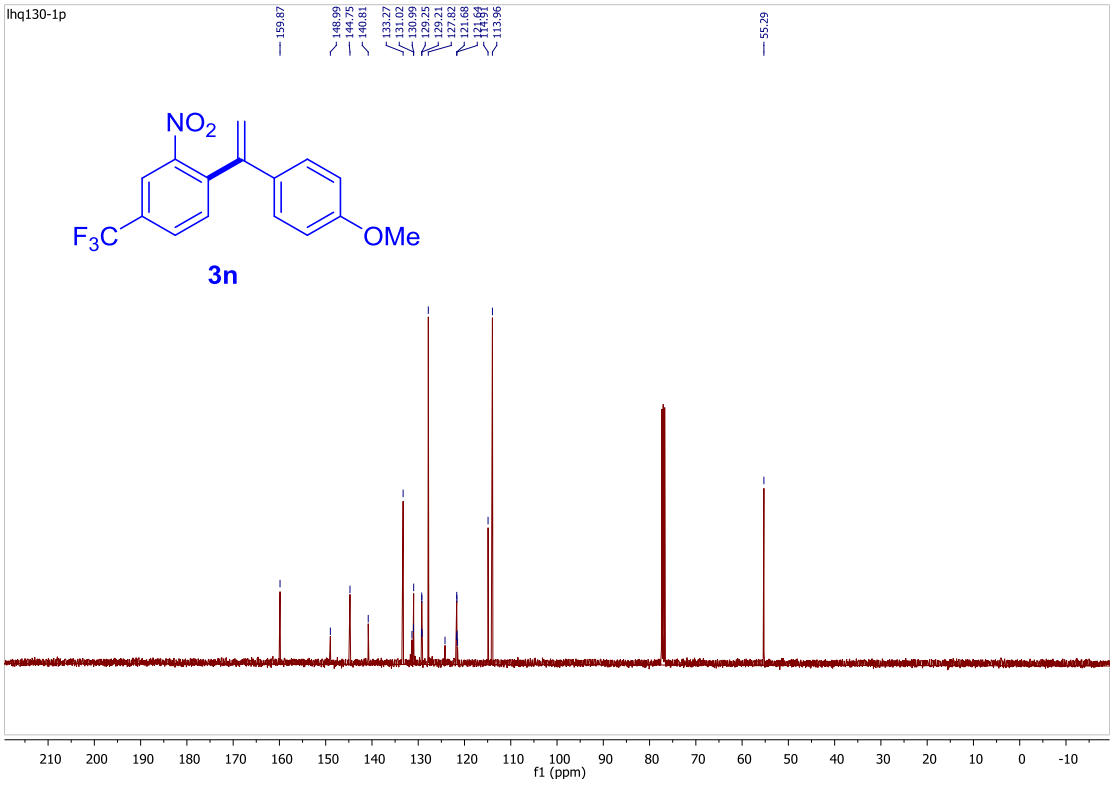
6.61
6.59
6.03
6.02
6.01
2.98
2.96
2.87
2.44
NO2
3l
0.99
1.06
1.02
1.03
2.01
1.01
1.00
1.01
2.13
2.12
f1 (ppm)

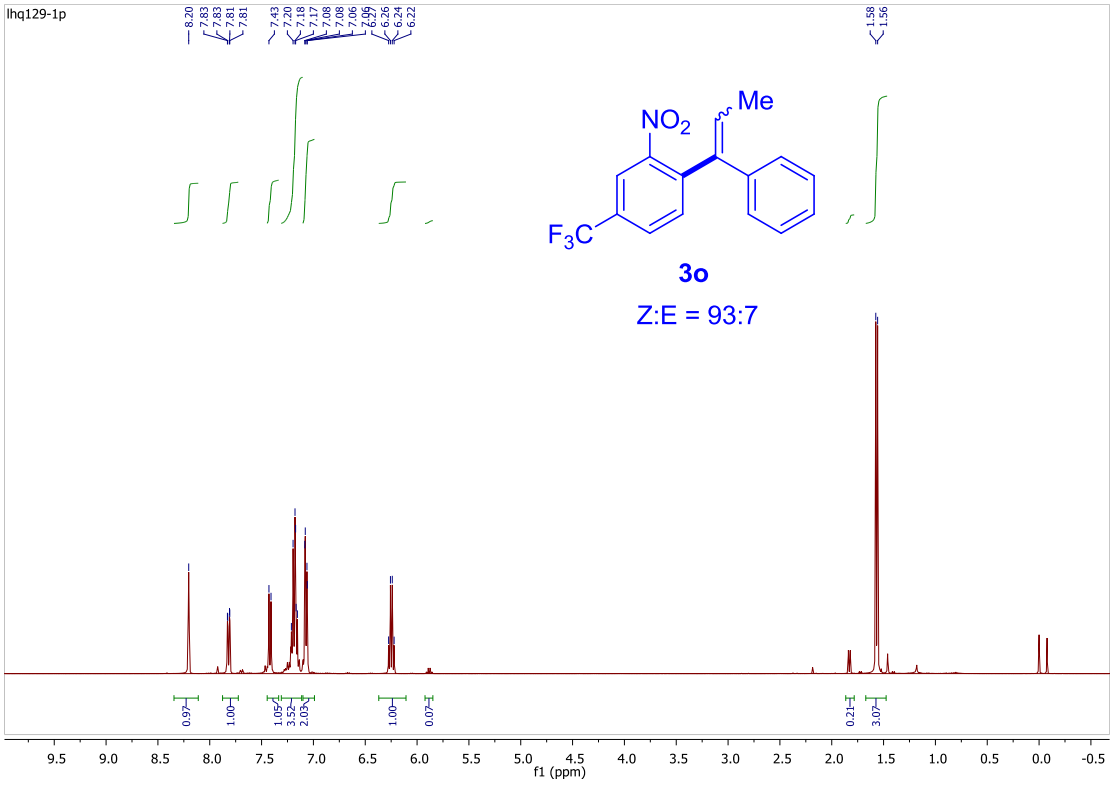

LHQ107--1-1
149.26
136.65
135.97
135.71
134.28
132.31
132.46
128.31
128.04
127.72
127.44
126.47
124.26
123.66
27.84
23.43
NO2
3l
f1 (ppm)

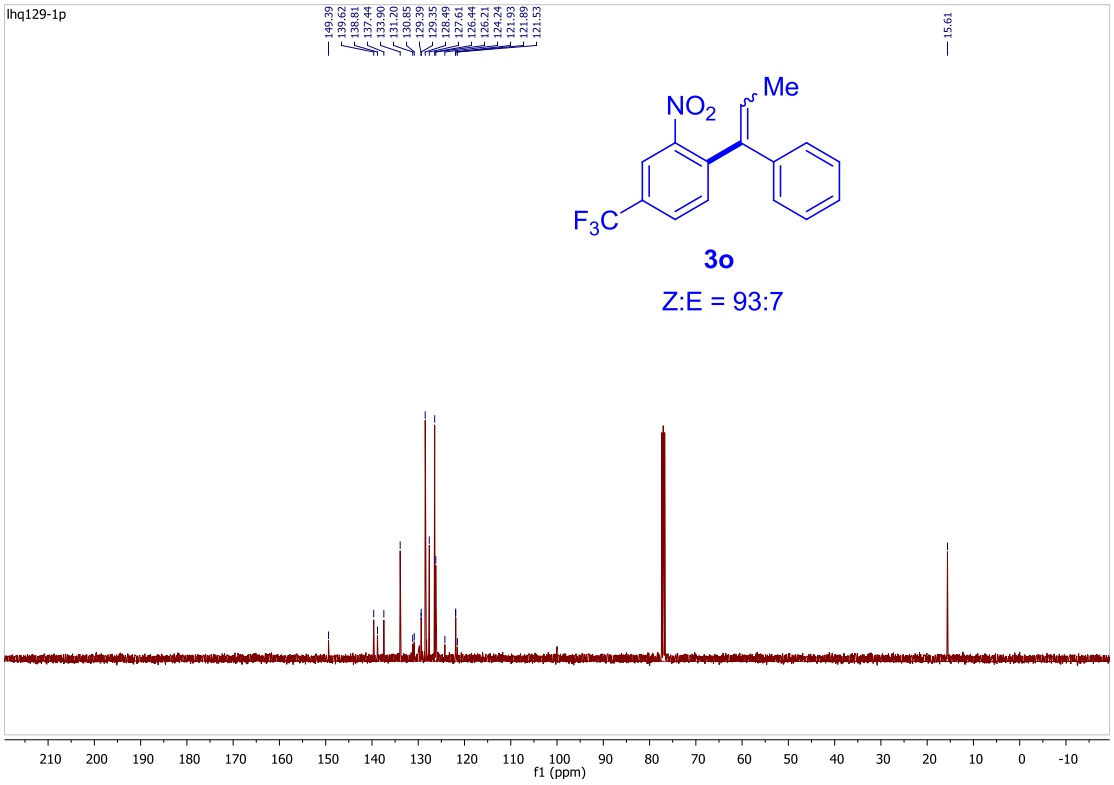

lhq130-2p
8.22
7.91
7.89
7.89
7.62
7.60
7.29
7.29
7.28
7.27
7.27
7.26
7.16
7.16
7.15
7.14
5.80
5.37
NO2
F3C
Cl
3m
1.00
1.06
1.04
2.30
2.06
1.06
1.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

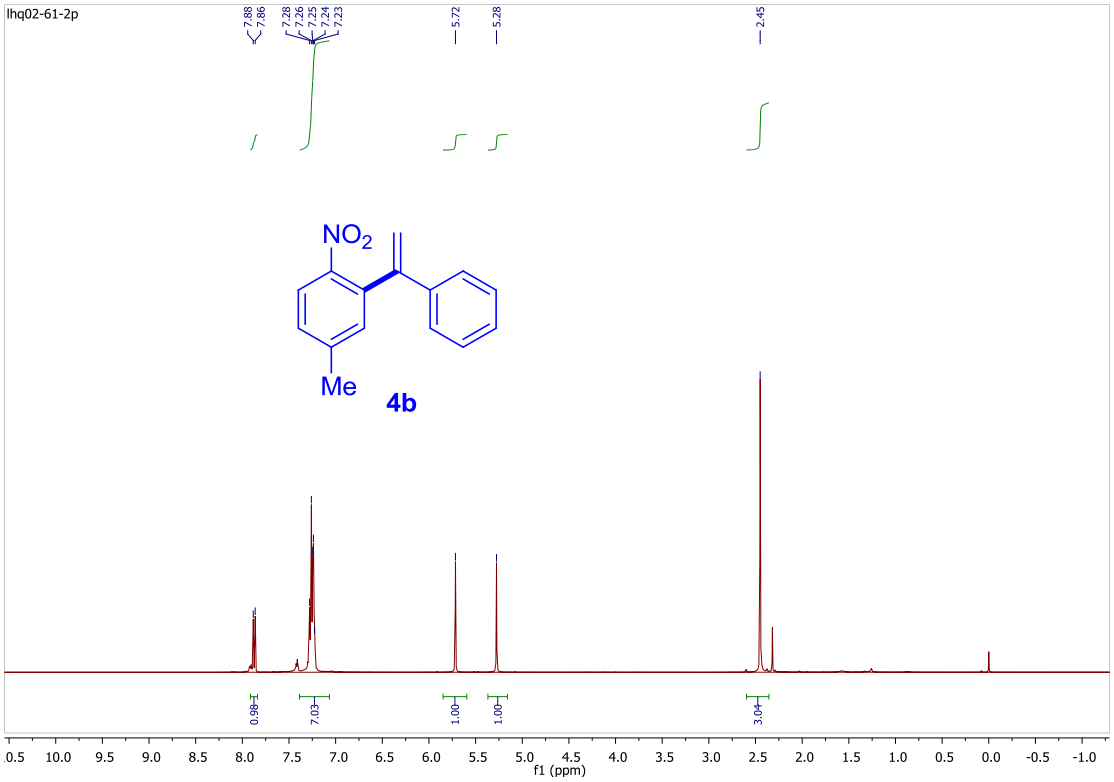

lhq130-2p
148.74
144.38
139.98
136.81
134.55
133.30
131.76
131.41
129.57
129.54
129.50
129.47
128.84
127.78
124.11
121.95
121.92
121.88
121.84
121.40
117.12
NO2
F3C
Cl
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

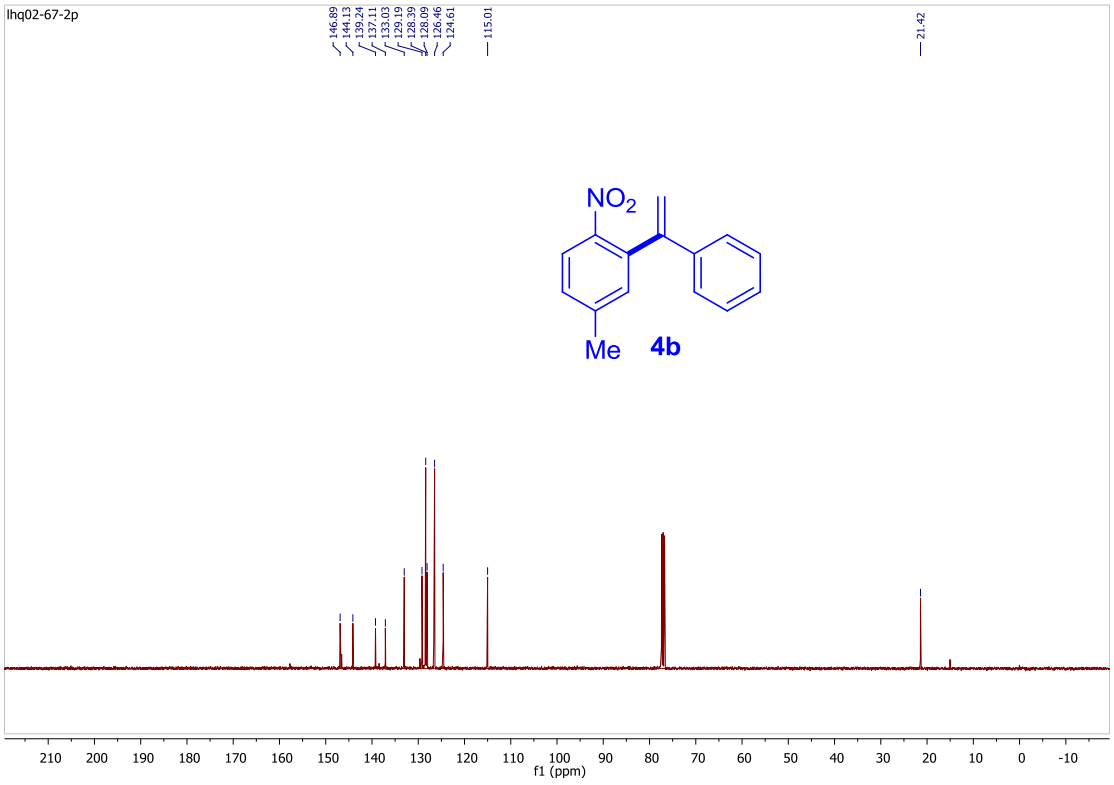

lhq130-1p
8.17
8.17
7.86
7.85
7.61
7.59
7.16
7.15
7.15
7.14
7.13
7.12
6.84
6.83
6.83
6.82
6.81
5.70
5.24
3.79
NO2
F3C
OMe
3n
0.95
0.98
1.00
1.94
1.98
1.00
0.99
3.01
f1 (ppm)

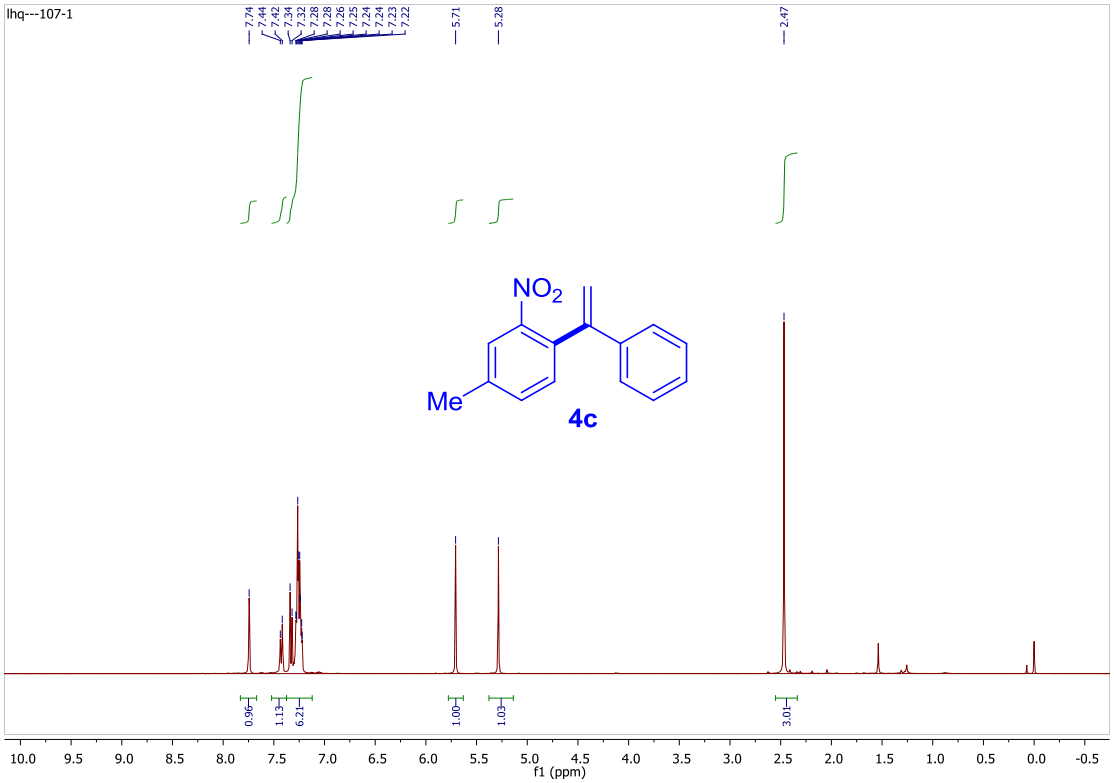

lhq130-1p
159.87
148.99
144.75
140.81
133.27
131.02
130.99
129.25
129.21
127.82
121.68
55.29
113.96
NO2
F3C
OMe
3n
f1 (ppm)

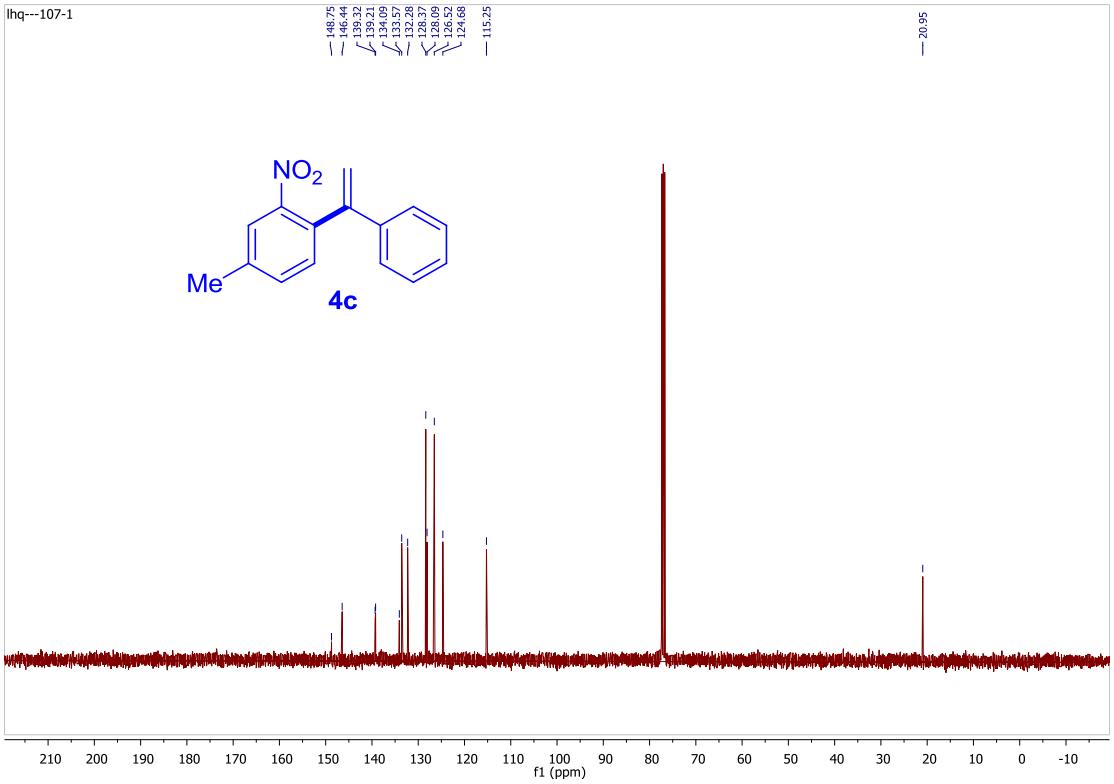

lhq129-1p
8.20
7.83
7.83
7.81
7.81
7.43
7.20
7.18
7.17
7.08
7.08
7.06
6.29
6.26
6.24
6.22
1.58
1.56
NO2
Me
F3C
3o
Z:E = 93:7
0.97
1.00
1.05
3.52
2.03
1.00
0.07
0.21
3.07
f1 (ppm)

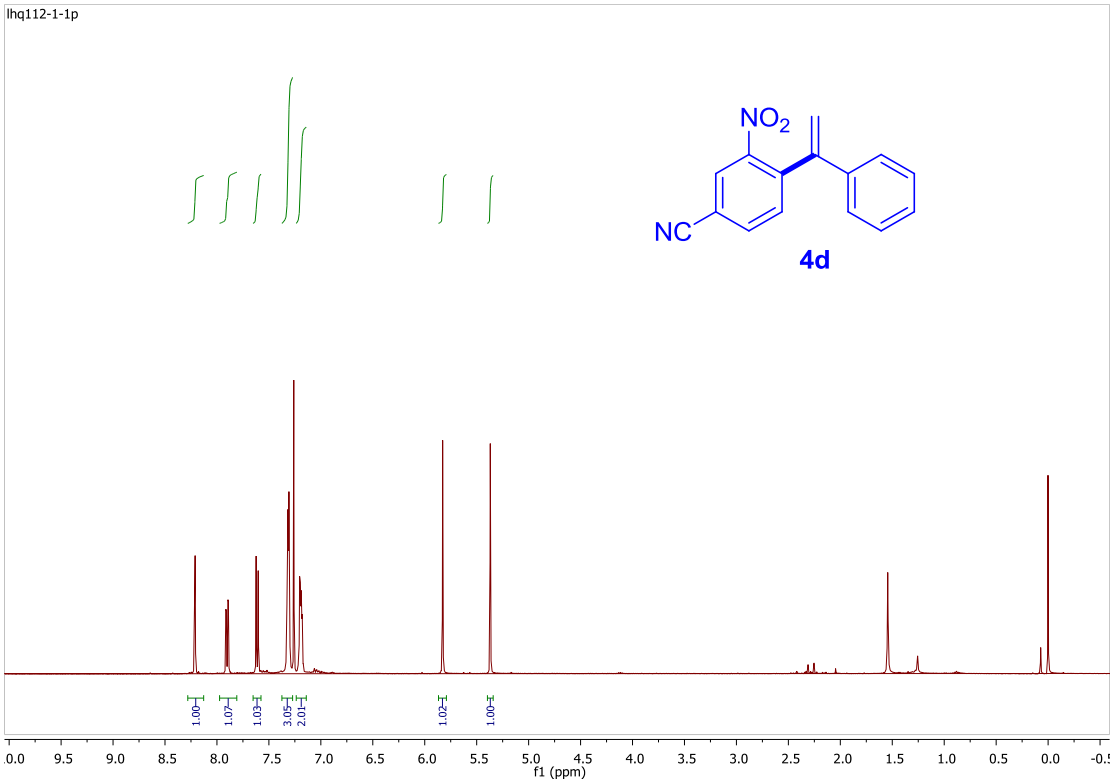

lhq129-1p
149.39
139.62
138.81
137.44
133.90
131.20
130.85
129.39
129.35
128.49
127.61
126.44
126.21
124.24
121.93
121.89
121.53
15.61
NO2
Me
F3C
3o
Z:E = 93:7
f1 (ppm)

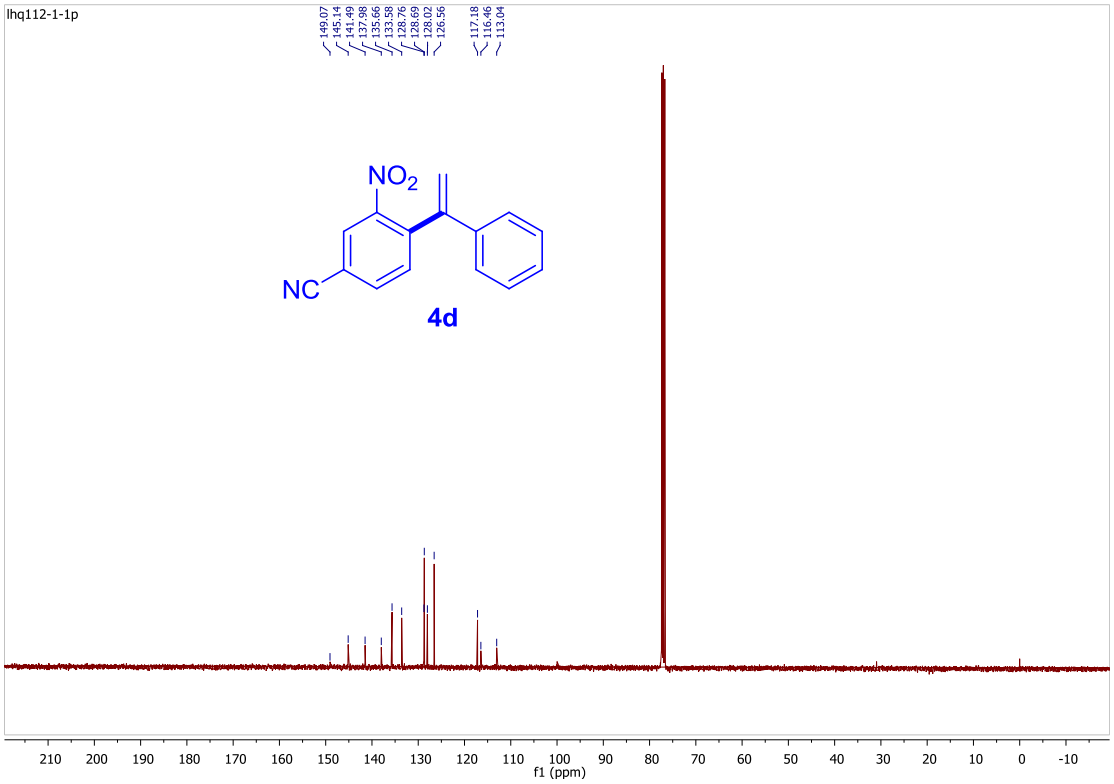

lhq02-61-2p
7.88
7.86
7.28
7.26
7.25
7.24
7.23
5.72
5.28
2.45
NO2
Me
4b
0.98
7.03
1.00
1.00
3.04
f1 (ppm)

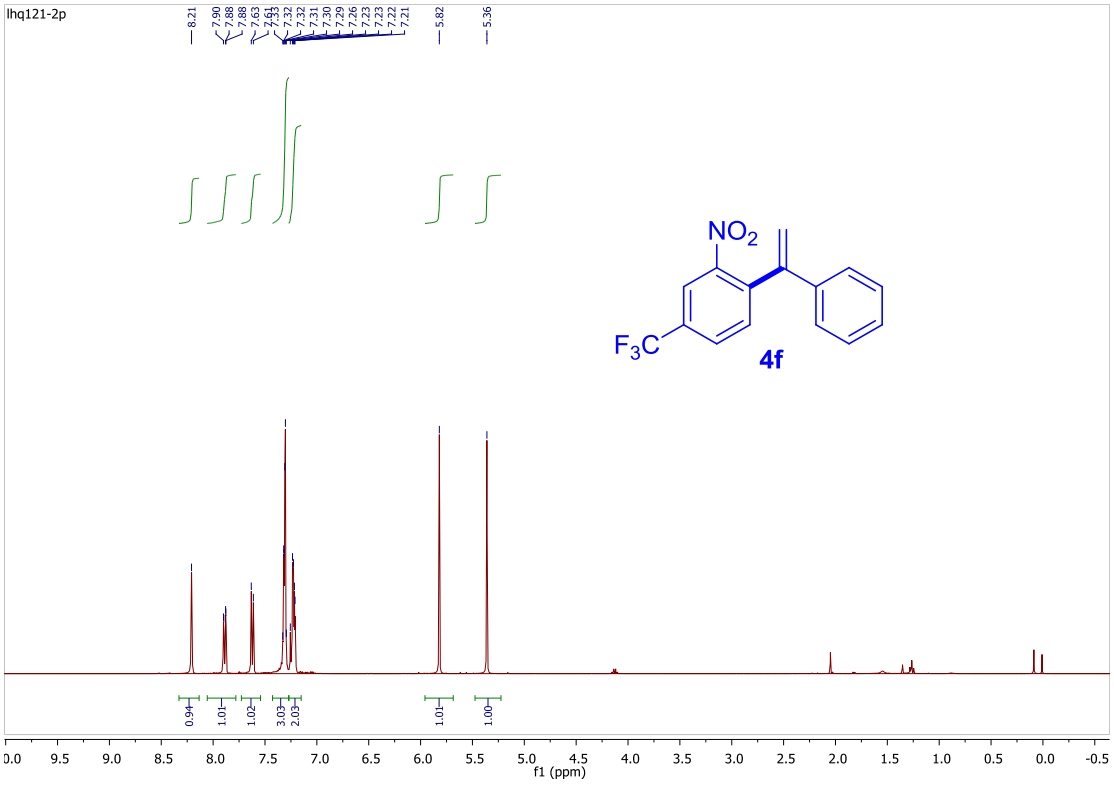

lhq02-67-2p
146.89
144.13
139.24
137.11
133.03
129.19
128.39
128.09
126.46
124.61
115.01
21.42
NO2
Me
4b
f1 (ppm)

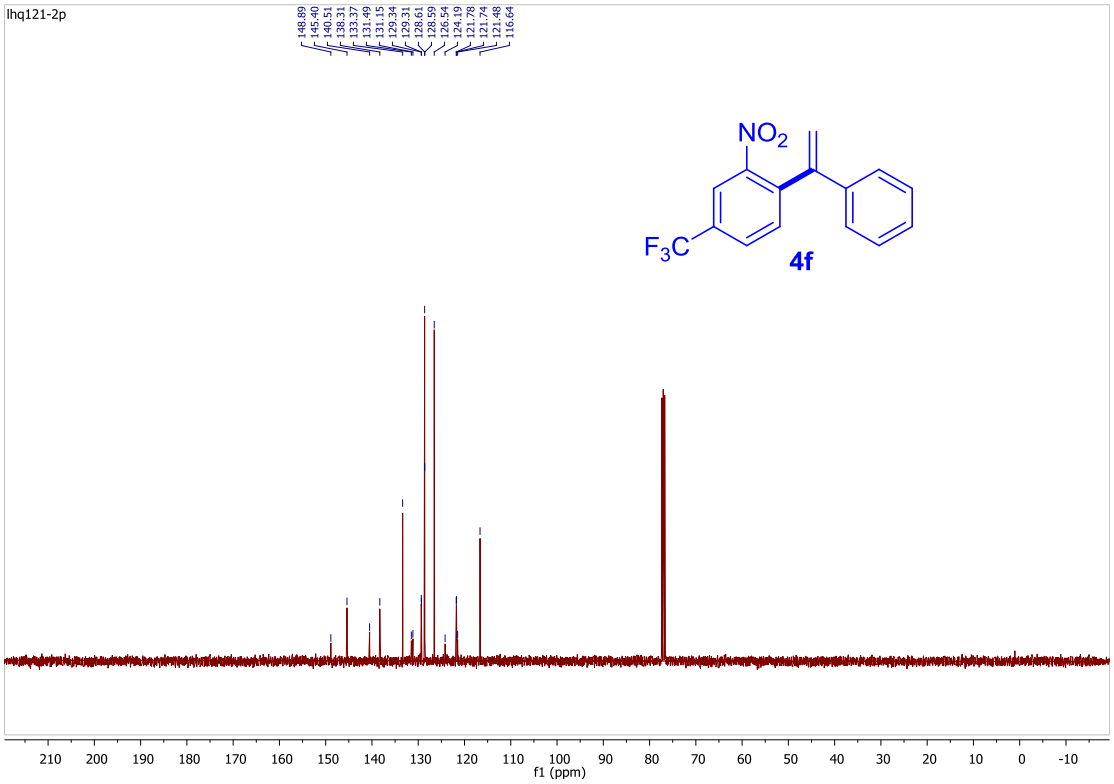

lhq---107-1
7.74
7.44
7.42
7.34
7.32
7.28
7.28
7.26
7.25
7.24
7.24
7.23
7.22
5.71
5.28
2.47
NO2
Me
4c
0.96
1.13
6.21
1.00
1.03
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


lhq---107-1
148.75
146.44
139.32
139.21
134.09
133.57
132.28
128.77
128.09
126.52
124.68
115.25
20.95
NO2
Me
4c
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)


lhq112-1-1p
NO2
NC
4d
1.00
1.07
1.03
3.05
2.01
1.02
1.00
f1 (ppm)


lhq112-1-1p
149.07
145.14
141.49
137.98
135.66
133.58
128.76
128.69
128.02
126.56
117.18
116.46
113.04
NO2
NC
4d
f1 (ppm)


lhq121-2p
8.21
7.90
7.88
7.88
7.63
7.61
7.33
7.32
7.32
7.31
7.30
7.29
7.26
7.23
7.22
7.21
5.82
5.36
NO2
F3C
4f
0.94
1.01
1.02
3.03
2.03
1.01
1.00
f1 (ppm)


lhq121-2p
148.89
145.40
140.51
138.31
133.37
131.49
131.15
129.34
129.31
128.61
128.59
126.54
124.19
121.78
121.74
121.48
116.64
NO2
F3C
4f
f1 (ppm)