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Supporting Information for the Paper

Iron-catalyzed domino indole fluorination/allenic aza–Claisen rearrangement

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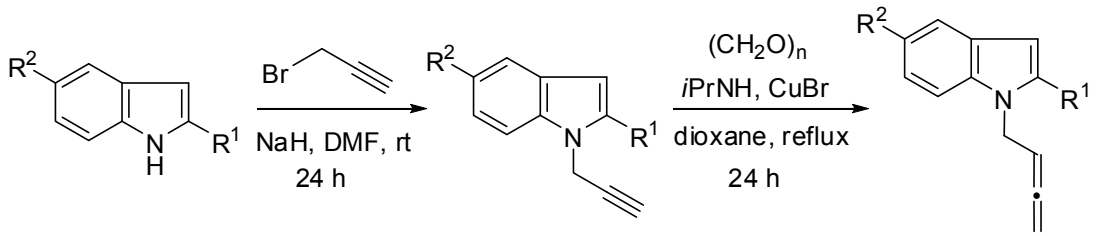
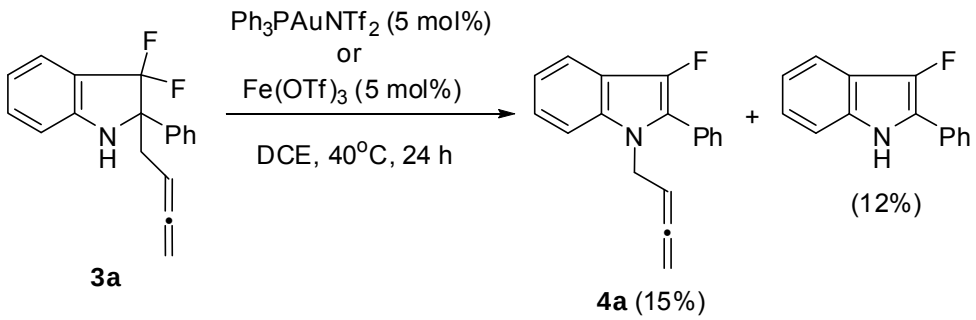
General methods: ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on a Bruker Avance-300 or Varian VRX-300S. NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{1}H, 7.27 ppm; ^{13}C, 76.9 ppm), or C_6D_6 (^{1}H, 7.16 ppm; ^{13}C, 128.0 ppm). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. All commercially available compounds were used without further purification.

2-Substituted indoles were commercially available except 2-(4-tolyl)-1*H*-indole and 2-(4-*tert*-butylphenyl)-1*H*-indole, which were readily obtained as described in the literature: G.-p. Lu, C. Cai, *Synlett* **2012**, *23*, 2992.



R^1 = Ph, R^2 = H	**1a** (82%)	**2a** (84%)
R^1 = 4-ClC_6H_4, R^2 = H	**1b** (73%)	**2b** (73%)
R^1 = 4-FC_6H_4, R^2 = H	**1c** (61%)	**2c** (64%)
R^1 = 4-MeC_6H_4, R^2 = H	**1d** (62%)	**2d** (61%)
R^1 = 4-*t*BuC_6H_4, R^2 = H	**1e** (52%)	**2e** (56%)
R^1 = naphthalen-2-yl, R^2 = H	**1f** (59%)	**2f** (51%)
R^1 = 4-MeC_6H_4, R^2 = Me	**1g** (57%)	**2g** (84%)
R^1 = 4-MeC_6H_4, R^2 = OMe	**1h** (69%)	**2h** (78%)
R^1 = 4-MeC_6H_4, R^2 = F	**1i** (48%)	**2i** (83%)
R^1 = Ph, R^2 = NO_2	**1j** (78%)	**2j** (68%)
R^1 = Ph, R^2 = CN	**1k** (69%)	**2k** (72%)
R^1 = Me, R^2 = H	**1l** (61%)	**2l** (78%)
R^1 = Me, R^2 = Me	**1m** (77%)	**2m** (52%)
R^1 = Me, R^2 = OMe	**1n** (51%)	**2n** (79%)
R^1 = Me, R^2 = Cl	**1o** (71%)	**2o** (86%)
R^1 = Me, R^2 = Br	**1p** (76%)	**2p** (87%)
R^1 = Me, R^2 = NO_2	**1q** (66%)	**2q** (72%)

Scheme S1 Synthesis of 1-(buta-2,3-dienyl)-2-substituted-1*H*-indoles **2a–m**.



Scheme S2 Treatment of 2-(allenyl)-2-phenyl-3,3-difluoroindoline **3a** under metal-catalyzed conditions.

General Procedure for the Preparation of 1-(Prop-2-ynyl)-2-substituted-1*H*-indoles 1. Sodium hydride (1.5 mmol) was added to a solution of the appropriate 2-substituted indole (1.0 mmol) in DMF (15 mL) at 0 °C. After 1 h stirring at rt the solution was cooled at 0 °C and propargyl bromide (1.5 mmol) was added. The

reaction was stirred at rt until disappearance of the starting material (TLC). Then water (10 mL) was added, before being being extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds. Spectroscopic and analytical data for some representative pure forms of **1** follow.

1-(Prop-2-ynyl)-2-phenyl-1*H*-indole 1a. From 1.0 g (5.17 mmol) of 2-phenyl-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **1a** (1.01 g, 82%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.65 (m, 3H), 7.53 (m, 4H), 7.32 (td, 1H, *J* = 7.0, 1.2 Hz), 7.21 (td, 1H, *J* = 7.8, 1.0 Hz), 6.61 (s, 1H), 4.85 (d, 2H, *J* = 2.5 Hz), 2.39 (t, 1H, *J* = 2.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 140.9, 137.6, 132.2, 130.6, 129.3 (2C), 128.7 (2C), 128.2, 122.1, 120.7, 120.5, 110.0, 102.5, 78.9, 72.7, 34.1; IR ($CHCl_3$, cm^{-1}): ν 3291; HRMS (ES): calcd for $C_{17}H_{13}N$ $[M]^+$: 231.1042; found: 231.1042.

1-(Prop-2-ynyl)-2-(4-chlorophenyl)-1*H*-indole 1b. From 250 mg (1.10 mmol) of 2-(4-chlorophenyl)-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **1b** (213 mg, 73%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.55 (d, 1H, *J* = 7.7 Hz), 7.38 (m, 5H), 7.22 (td, 1H, *J* = 7.1, 1.2 Hz), 7.12 (m, 1H), 6.49 (s, 1H), 4.70 (d, 2H, *J* = 2.5 Hz), 2.29 (t, 1H, *J* = 2.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 139.6; 137.6; 13.3; 131.8; 130.6; 130.4; 129.0 (2C); 128.1; 122.4; 120.8; 120.6; 110.0; 102.8; 78.7; 73.0; 34.0; IR ($CHCl_3$, cm^{-1}): ν 3293; HRMS (ES): calcd for $C_{17}H_{12}ClN$ $[M]^+$: 265.0652; found: 265.0657.

1-(Prop-2-ynyl)-2-(4-fluorophenyl)-1*H*-indole 1c. From 200 mg (0.9 mmol) of 2-(4-fluorophenyl)-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **1c** (136 mg, 61%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.73 (d, 1H, *J* = 7.7 Hz), 7.66 (m, 2H), 7.59 (d, 1H, *J* = 8.2 Hz), 7.38 (dt, 1H, *J* = 7.4, 1.2 Hz), 7.30 (t, 3H, *J* = 7.2 Hz),

6.63 (s, 1H), 4.86 (d, 2H, *J* = 2.5 Hz), 2.45 (t, 1H, *J* = 2.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 139.8, 137.5, 131.0, 130.9, 128.3 (2C), 122.3, 120.7, 116.0, 115.9, 115.7, 115.6, 110.0, 109.9, 105.6, 78.8, 33.9; ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –113.5 (s, 1F); IR ($CHCl_3$, cm^{-1}): ν 3292; HRMS (ES): calcd for $C_{17}H_{12}FN$ $[M]^+$: 249.0948; found: 249.0943.

1-(Prop-2-ynyl)-2-(4-methylphenyl)-1*H*-indole 1d. From 207 mg (0.99 mmol) of 2-(4-methylphenyl)-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent gave compound **1d** (151 mg, 62%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.55 (d, 1H, *J* = 7.9 Hz), 7.38 (m, 3H), 7.16 (m, 4H), 6.47 (d, 1H, *J* = 0.4 Hz), 4.73 (d, 2H, *J* = 2.5 Hz); 2.35 (s, 3H), 2.27 (t, 1H, *J* = 2.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 141.1, 138.2, 137.5, 130.5, 129.5 (2C), 129.2 (2C), 128.4, 122.0, 120.6, 120.5, 110.0, 102.2, 79.0, 72.7, 34.1, 21.4; IR ($CHCl_3$, cm^{-1}): ν 3290; HRMS (ES): calcd for $C_{18}H_{15}N$ $[M]^+$: 245.1198; found: 245.1201.

1-(Prop-2-ynyl)-2-(4-*tert*-butylphenyl)-1*H*-indole 1e. From 310 mg (1.24 mmol) of 2-(4-*tert*-butylphenyl)-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **1e** (184 mg, 52%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.52 (d, 2H, *J* = 8.6 Hz), 7.45 (m, 2H), 7.20 (m, 1H), 7.08 (m, 3H), 6.48 (d, 1H, *J* = 0.7 Hz), 4.75 (d, 2H, *J* = 2.5 Hz), 2.30 (t, 1H, *J* = 2.5 Hz); 1.31 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 151.3, 150.1, 141.0, 137.6, 137.1, 129.0, 127.6, 125.7, 122.0, 120.6, 120.5, 110.0, 102.2, 90.7, 79.1, 72.7, 34.8, 34.1, 31.4 (3C); IR ($CHCl_3$, cm^{-1}): ν 3291; HRMS (ES): calcd for $C_{21}H_{21}N$ $[M]^+$: 287.1668; found: 287.1684.

1-(Prop-2-ynyl)-2-(naphthalen-2-yl)-1*H*-indole 1f. From 200 mg (0.82 mmol) of 2-(naphthalen-2-yl)-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **1f** (135 mg, 59%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.00 (s, 1H), 7.69 (m, 2H), 7.64 (m, 3H), 7.43 (d, 1H, *J* = 8.1 Hz), 7.27 (m, 4H), 6.64 (d, 1H, *J* = 0.5 Hz), 4.30 (d, 2H,

J = 2.5 Hz), 1.83 (t, 1H, *J* = 2.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 140.9, 138.4, 133.9, 133.3, 130.3, 130.2, 129.1, 128.7, 128.6, 128.5, 127.2, 126.7, 126.6, 122.6, 121.2, 121.0, 110.5, 103.6, 79.3, 72.8, 33.9; IR ($CHCl_3$, cm^{-1}): ν 3292; HRMS (ES): calcd for $C_{21}H_{15}N$ $[M]^+$: 287.1198; found: 287.1207.

5-Methyl-1-(prop-2-ynyl)-2-(4-methylphenyl)-1*H*-indole 1g. From 247 mg (1.12 mmol) of 5-methyl-2-(4-methylphenyl)-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **1g** (166 mg, 57%) as a colorless solid; mp 108–109 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, acetone-d_6, 25 ^{o}C) δ: 7.52 (d, 2H, *J* = 8.2 Hz, Ar), 7.43 (d, 1H, *J* = 8.3 Hz, Ar), 7.36 (m, 1H, Ar), 7.34 (d, 2H, *J* = 8.5 Hz, Ar), 7.06 (dd, 1H, *J* = 8.3, 1.2 Hz, Ar), 6.46 (d, 1H, *J* = 0.7 Hz, Ar), 4.92 (d, 1H, *J* = 2.5 Hz, NCH_2), 2.90 (t, 1H, *J* = 2.5 Hz, ≡CH), 2.41 (s, 3H, Me), 2.40 (s, 3H, Me); ^{13}C-NMR (75 MHz, acetone-d_6, 25 ^{o}C) δ: 141.8, 138.8, 137.2, 130.5, 130.3 (Ar, 2CH), 130.0, 129.8, 129.7 (Ar, 2CH), 124.2 (Ar, CH), 121.0 (Ar, CH), 110.9 (Ar, CH), 102.5 (Ar, CH), 80.3, 74.1 (≡CH), 34.5 (NCH_2), 21.6 (Me), 21.3 (Me); IR ($CHCl_3$, cm^{-1}): ν 2919, 1474, 1330, 1163, 823, 789, 643; HRMS (ES): calcd for $C_{19}H_{17}N$ $[M]^+$: 259.1355; found: 259.1354.

5-Methoxy-1-(prop-2-ynyl)-2-(4-methylphenyl)-1*H*-indole 1h. From 159 mg (0.67 mmol) of 5-methoxy-2-(4-methylphenyl)-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **1h** (127 mg, 69%) as a colorless solid; mp 115–116 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, acetone-d_6, 25 ^{o}C) δ: 7.51 (d, 2H, *J* = 8.2 Hz, Ar), 7.44 (d, 1H, *J* = 8.8 Hz, Ar), 7.33 (d, 2H, *J* = 7.9 Hz, Ar), 7.10 (d, 1H, *J* = 2.5 Hz, Ar), 6.89 (dd, 1H, *J* = 8.8, 2.5 Hz, Ar), 6.48 (s, 1H, Ar), 4.90 (d, 1H, *J* = 2.5 Hz, NCH_2), 3.81 (s, 3H, OMe), 2.90 (t, 1H, *J* = 2.5 Hz, ≡CH), 2.40 (s, 3H, Me); ^{13}C-NMR (75 MHz, acetone-d_6, 25 ^{o}C) δ: 155.8, 142.3, 138.8, 133.9, 130.5, 130.3 (Ar, 2CH), 129.9, 129.8, 129.7 (Ar, 2CH), 112.7 (Ar, CH), 111.8 (Ar, CH), 103.0 (Ar, CH), 102.8 (Ar, CH), 80.3, 74.1 (≡CH), 55.9 (OMe), 34.6 (NCH_2), 21.3 (Me); IR ($CHCl_3$, cm^{-1}): ν 2852, 1619, 1474, 1216, 824, 740, 651; HRMS (ES): calcd for $C_{19}H_{17}NO$ $[M]^+$: 275.1304; found: 275.1319.

5-Fluoro-1-(prop-2-ynyl)-2-(4-methylphenyl)-1*H*-indole 1i. From 168 mg (0.75 mmol) of 5-fluoro-2-(4-methylphenyl)-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **1i** (94 mg, 48%) as a colorless solid; mp 113–114 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.46 (d, 2H, *J* = 8.2 Hz, Ar), 7.38 (m, 1H, Ar), 7.28 (d, 2H, *J* = 8.0 Hz, Ar), 7.19 (d, 1H, *J* = 2.5 Hz, Ar), 6.98 (m, 1H, Ar), 6.48 (s, 1H, Ar), 4.80 (d, 1H, *J* = 2.6 Hz, NCH_2), 2.41 (s, 3H, Me), 2.38 (t, 1H, *J* = 2.5 Hz, ≡CH); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 159.9, 156.8, 142.6, 138.4, 134.0, 130.3, 129.5 (Ar, 2CH), 129.0 (Ar, 2CH), 110.0 (Ar, CH), 109.9 (Ar, CH), 105.7 (Ar, CH), 101.9 (Ar, CH), 78.7, 73.7 (≡CH), 34.1 (NCH_2), 21.3 (Me); IR ($CHCl_3$, cm^{-1}): ν 2921, 1621, 1472, 1197, 824, 783, 645; HRMS (ES): calcd for $C_{18}H_{14}FN$ $[M]^+$: 263.1104; found: 263.1107.

5-Nitro-2-phenyl-1-(prop-2-ynyl)-1*H*-indole 1j. From 200 mg (0.84 mmol) of 5-nitro-2-phenyl-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **1j** (181 mg, 78%) as a colorless solid; mp 119–120 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.60 (d, 1H, *J* = 2.2 Hz, Ar), 8.20 (dd, 1H, *J* = 9.1, 2.3 Hz, Ar), 7.57 (m, 6H, Ar), 6.74 (s, 1H, Ar), 4.87 (d, 2H, *J* = 2.5 Hz, NCH_2), 2.46 (t, 1H, *J* = 2.5 Hz, ≡CH); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 144.1, 142.4, 140.1, 130.9, 129.3 (Ar, 2CH), 129.1 (Ar, CH), 129.0 (Ar, 2CH), 127.5, 117.7 (Ar, CH), 117.6 (Ar, CH), 110.0 (Ar, CH), 104.3 (Ar, CH), 77.7, 73.7 (≡CH), 34.4 (NCH_2); IR ($CHCl_3$, cm^{-1}): ν 2923, 1616, 1468, 1190, 834, 789, 640; HRMS (ES): calcd for $C_{17}H_{12}N_2O_2$ $[M]^+$: 276.0893; found: 276.0888.

2-Phenyl-1-(prop-2-ynyl)-1*H*-indole-5-carbonitrile 1k. From 120 mg (0.54 mmol) of 2-phenyl-1*H*-indole-5-carbonitrile, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **1k** (95 mg, 69%) as a pale yellow solid; mp 115–116 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.88 (t, 1H, *J* = 0.8 Hz, Ar), 7.44 (m, 7H, Ar), 6.54 (s, 1H, Ar), 4.75 (d, 1H, *J* = 2.5 Hz, NCH_2), 2.34 (t, 1H, *J* = 2.5 Hz, ≡CH); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C)

δ: 143.2, 138.9, 131.0, 129.3 (Ar, 2CH), 128.9 (Ar, CH), 128.9 (Ar, 2CH), 128.0, 126.0 (Ar, CH), 125.0 (Ar, CH), 120.6, 110.9 (Ar, CH), 103.6, 102.9 (Ar, CH), 77.8, 73.6 (≡CH), 34.2 (NCH_2); IR ($CHCl_3$, cm^{-1}): ν 2919, 1613, 1467, 1170, 820, 760, 670; HRMS (ES): calcd for $C_{18}H_{12}N_2$ $[M]^+$: 256.0995; found: 256.1007.

1-(Prop-2-ynyl)-2-methyl-1*H*-indole 1l. From 1.0 g (7.63 mmol) of 2-methyl-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **1l** (769 mg, 61%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.47 (d, 1H, *J* = 7.7 Hz), 7.28 (d, 1H, *J* = 8.2 Hz), 7.10 (m, 2H), 6.21 (br s, 1H), 4.74 (d, 2H, *J* = 2.5 Hz), 2.42 (s, 3H), 2.19 (t, 1H, *J* = 2.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 136.5, 136.0, 128.3, 120.9, 119.8 (2C), 108.8, 100.9, 78.2, 72.1, 32.3, 12.5; IR ($CHCl_3$, cm^{-1}): ν 3295; HRMS (ES): calcd for $C_{12}H_{11}N$ $[M]^+$: 169.0885; found: 169.0888.

2,5-Dimethyl-1-(prop-2-ynyl)-1*H*-indole 1m. From 500 mg (3.44 mmol) of 2,5-dimethyl-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **1m** (485 mg, 77%) as a colorless solid; mp 110–111 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, acetone-d_6, 25 ^{o}C) δ: 7.30 (d, 1H, *J* = 8.3 Hz, Ar), 7.23 (s, 1H, Ar), 6.93 (d, 1H, *J* = 8.3 Hz, Ar), 6.15 (s, 1H, Ar), 4.94 (d, 1H, *J* = 2.5 Hz, NCH_2), 2.79 (t, 1H, *J* = 2.5 Hz, ≡CH), 2.46 (s, 3H, Me), 2.37 (s, 3H, Me); ^{13}C-NMR (75 MHz, acetone-d_6, 25 ^{o}C) δ: 137.2, 136.2, 129.7, 129.1, 122.9 (Ar, CH), 120.3 (Ar, CH), 109.7 (Ar, CH), 101.1 (Ar, CH), 80.0, 73.4 (≡CH), 32.8 (NCH_2), 21.6 (Me), 12.6 (Me); IR ($CHCl_3$, cm^{-1}): ν 2943, 1632, 1471, 1234, 820, 763, 675; HRMS (ES): calcd for $C_{13}H_{13}N$ $[M]^+$: 183.1078; found: 183.1041.

5-Methoxy-2-methyl-1-(prop-2-ynyl)-1*H*-indole 1n. From 500 mg (3.10 mmol) of 5-methoxy-2-methyl-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **1n** (315 mg, 51%) as a colorless solid; mp 119–120 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, acetone-d_6, 25 ^{o}C) δ: 7.31 (d, 1H, *J* = 8.9 Hz, Ar), 6.97 (d, 1H, *J* = 2.3 Hz, Ar), 6.76

(dd, 1H, J = 8.9, 2.5 Hz, Ar), 6.17 (s, 1H, Ar), 4.94 (d, 1H, J = 2.5 Hz, NCH_2), 3.77 (s, 3H, OMe), 2.80 (t, 1H, J = 2.5 Hz, ≡CH), 2.45 (s, 3H, Me); ^{13}C-NMR (75 MHz, acetone-d_6, 25 ^{o}C) δ: 155.3, 137.7, 132.6, 129.9, 111.1 (Ar, CH), 110.6 (Ar, CH), 102.7 (Ar, CH), 101.3 (Ar, CH), 79.9, 73.4 (≡CH), 55.9 (OMe), 32.9 (NCH_2), 12.6 (Me); IR ($CHCl_3$, cm^{-1}): ν 2958, 1483, 1201, 849, 779; HRMS (ES): calcd for $C_{13}H_{13}NO$ $[M]^+$: 199.0991; found: 199.1004.

5-Chloro-2-methyl-1-(prop-2-ynyl)-1*H*-indole 1o. From 500 mg (3.08 mmol) of 5-chloro-2-methyl-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **1o** (444 mg, 71%) as a colorless solid; mp 127–128 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, acetone-d_6, 25 ^{o}C) δ: 7.47 (s, 1H, Ar), 7.45 (d, 1H, J = 8.6 Hz, Ar), 7.10 (dd, 1H, J = 8.8, 2.2 Hz, Ar), 6.26 (s, 1H, Ar), 5.00 (d, 1H, J = 2.5 Hz, NCH_2), 2.85 (t, 1H, J = 2.5 Hz, ≡CH), 2.49 (d, 3H, J = 0.9 Hz, Me); ^{13}C-NMR (75 MHz, acetone-d_6, 25 ^{o}C) δ: 139.2, 136.1, 130.5, 125.7, 121.4 (Ar, CH), 119.7 (Ar, CH), 111.4 (Ar, CH), 101.2 (Ar, CH), 79.4, 73.9 (≡CH), 33.0 (NCH_2), 12.6 (Me); IR ($CHCl_3$, cm^{-1}): ν 2911, 1621, 1478, 1190, 827, 763, 640; HRMS (ES): calcd for $C_{12}H_{10}NCl$ $[M]^+$: 203.0496; found: 203.0502.

5-Bromo-2-methyl-1-(prop-2-ynyl)-1*H*-indole 1p. From 400 mg (1.90 mmol) of 5-bromo-2-methyl-1*H*-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **1p** (359 mg, 76%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.66 (d, 1H, J = 1.6 Hz, Ar), 7.26 (m, 2H, Ar), 6.24 (s, 1H, Ar), 4.79 (d, 2H, J = 2.5 Hz, NCH_2), 2.49 (s, 3H, Me), 2.30 (t, 1H, J = 2.5 Hz, ≡CH); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 137.4, 135.1, 130.0, 123.7 (Ar, CH), 122.3 (Ar, CH), 113.1, 110.3 (Ar, CH), 100.5 (Ar, CH), 77.7, 72.5 (≡CH), 32.5 (NCH_2), 12.5 (Me); IR ($CHCl_3$, cm^{-1}): ν 2965, 1497, 1254, 850; HRMS (ES): calcd for $C_{12}H_{10}BrN$ $[M]^+$: 246.9991; found: 246.9994.

2-Methyl-5-nitro-1-(prop-2-ynyl)-1*H*-indole 1q. From 500 mg (2.84 mmol) of 2-methyl-5-nitro-1*H*-indole, and after chromatography of the residue using

hexanes/ethyl acetate (5:1) as eluent gave compound **1q** (404 mg, 66%) as a colorless solid; mp 97–99 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.45 (d, 1H, *J* = 2.2 Hz, Ar), 8.08 (dd, 1H, *J* = 9.1, 2.2 Hz, Ar), 7.35 (d, 1H, *J* = 9.1 Hz, Ar), 6.44 (s, 1H, Ar), 4.85 (d, 2H, *J* = 2.5 Hz, NCH_2), 2.52 (s, 3H, Me), 2.35 (t, 1H, *J* = 2.5 Hz, ≡CH); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 141.9, 139.6, 139.3, 127.5, 116.8 (Ar, CH), 108.7 (Ar, CH), 103.1 (Ar, CH), 77.4, 73.2 (≡CH), 32.9 (NCH_2), 12.7 (Me); IR ($CHCl_3$, cm^{-1}): ν 2956, 1490, 1234, 832; HRMS (ES): calcd for $C_{12}H_{10}N_2O_2$ $[M]^+$: 214.0736; found: 214.0733.

General Procedure for the Cu-Catalyzed Reaction of 1-(Prop-2-ynyl)-2-substituted-1*H*-indoles 1. Preparation of 1-(Buta-2,3-dienyl)-2-substituted-1*H*-indoles 2. A well stirred solution of $(CH_2O)_n$ (0.5 mmol), CuI (0.1 mmol), the appropriate 1-(prop-2-ynyl)-2-substituted-1*H*-indole (0.2 mmol), and *N*,*N*-diisopropylethylamine (Hüning's base) (0.36 mmol) in dioxane (1 mL) was refluxed under argon atmosphere. When the reaction was complete as monitored by TLC, it was cooled to RT. Water (5 mL) was added before being extracted with ethyl acetate (3 x 15 mL). The organic phase was washed with water (2 x 5 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure compounds **1**. Spectroscopic and analytical data for some representative pure forms of **2** follow.

1-(Buta-2,3-dienyl)-2-phenyl-1*H*-indole 2a. From 266 mg (1.15 mmol) of alkyne **1a**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2a** (236 mg, 84%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.67 (d, 1H, *J* = 7.7 Hz), 7.57 (t, 1H, *J* = 2.0 Hz), 7.55 (m, 1H), 7.45 (m, 4H), 7.27 (td, 1H, *J* = 7.0, 1.2 Hz), 7.18 (td, 1H, *J* = 7.8, 0.9 Hz), 6.58 (br s, 1H), 5.33 (m, 1H), 4.78 (d, 2H, *J* = 2.8 Hz), 4.77 (s, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 141.3, 137.7, 132.8, 129.4 (2C), 128.5 (2C), 128.2, 128.0, 121.7, 120.5, 120.0, 110.3, 102.2, 88.1, 77.3, 42.9; IR ($CHCl_3$, cm^{-1}): ν 1956; HRMS (ES): calcd for $C_{18}H_{15}N$ $[M]^+$: 245.1198; found: 245.1199.

1-(Buta-2,3-dienyl)-2-(4-chlorophenyl)-1*H*-indole 2b. From 290 mg (1.10 mmol) of alkyne **1b**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2b** (224 mg, 73%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.67 (d, 1H, *J* = 7.7 Hz), 7.57 (t, 1H, *J* = 2.0 Hz), 7.55 (m, 1H), 7.45 (m, 4H), 7.27 (td, 1H, *J* = 7.0, 1.2 Hz), 7.18 (td, 1H, *J* = 7.8, 0.9 Hz), 6.58 (br s, 1H), 5.33 (m, 1H), 4.78 (d, 2H, *J* = 2.8 Hz), 4.77 (s, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 141.3, 137.7, 132.8, 129.4 (2C), 128.5 (2C), 128.2, 128.0, 121.7, 120.5, 120.0, 110.3, 102.2, 88.1, 77.3, 42.9; IR ($CHCl_3$, cm^{-1}): ν 1954; HRMS (ES): calcd for $C_{18}H_{14}ClN$ $[M]^+$: 279.0809; found: 279,0812.

1-(Buta-2,3-dienyl)-2-(4-fluorophenyl)-1*H*-indole 2c. From 200 mg (0.90 mmol) of alkyne **1c**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2c** (136 mg, 64%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.70 (d, 1H, *J* = 7.0 Hz), 7.27 (m, 3H), 7.21 (m, 2H), 6.82 (t, 2H, *J* = 8.6Hz), 6.50 (s, 1H), 4.89 (q, 1H, *J* = 5.9 Hz), 4.39 (m, 2H), 4.21(m, 2H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.4, 140.0, 138.3, 131.4, 131.2, 129.4, 128.9, 127.8, 122.3, 121.1, 120.6, 115.8, 115.5, 110.6, 102.9, 88.4, 77.7, 42.5; ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –113.5 (s, 1F); IR ($CHCl_3$, cm^{-1}): ν 1955; HRMS (ES): calcd for $C_{18}H_{14}FN$ $[M]^+$: 263.1104; found: 263.1108.

1-(Buta-2,3-dienyl)-2-(4-methylphenyl)-1*H*-indole 2d. From 150 mg (0.61 mmol) of alkyne **1d**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **2d** (96 mg, 61%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.54 (m, 1H), 7.32 (m, 3H), 7.12 (m, 4H, 6.44 (d, 1H, *J* = 0.8 Hz), 5.22 (m, 1H), 4.65 (m, 4H), 2.34 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.6, 141.4, 138.0, 137.7, 129.9, 129.3 (2C), 129.2 (2C), 128.3, 121.6, 120.5, 120.0, 110.3, 101.9, 88.2, 77.4, 42.9, 21.3; IR ($CHCl_3$, cm^{-1}): ν 1955; HRMS (ES): calcd for $C_{19}H_{17}N$ $[M]^+$: 259.1355; found: 259.1365.

1-(Buta-2,3-dienyl)-2-(4-*tert*-butylphenyl)-1*H*-indole 2e. From 149 mg (0.52 mmol) of alkyne **1e**, and after chromatography of the residue using hexanes/ethyl

acetate (70:1) as eluent gave compound **2e** (88 mg, 56%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.55 (m, 2H), 7.35 (m, 3H), 7.10 (m, 3H), 6.45 (d, 1H, *J* = 0.7 Hz), 5.21 (m, 1H), 4.66 (m, 4H), 1.30 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.6, 151.1, 141.4, 137.7, 130.3, 129.1 (2C), 125.5 (2C), 121.6, 120.5, 119.9, 110.3, 101.9, 91.0, 88.3, 77.3, 43.0, 34.7, 31.4 (3C); IR ($CHCl_3$, cm^{-1}): ν 1954; HRMS (ES): calcd for $C_{22}H_{23}N$ $[M]^+$: 301.1824; found: 301.1822.

1-(Buta-2,3-dienyl)-2-(naphthalen-2-yl)-1*H*-indole 2f. From 133 mg (0.47 mmol) of alkyne **1f**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2f** (64 mg, 51%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.92 (s, 1H), 7.75 (m, 1H), 7.64 (m, 3H), 7.56 (dd, 1H, *J* = 6.9, 1.5 Hz), 7.31 (m, 5H), 6.70 (s, 1H), 5.00 (q, 1H, *J* = 6.4 Hz), 4.43 (m, 2H), 4.35 (m, 2H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.5, 141.3, 138.6, 133.8, 133.3, 130.8, 129.2, 128.6 (2C), 128.5, 128.4, 127.5, 126.7, 126.5, 122.3, 121.2, 120.6, 110.6, 103.4, 88.6, 77.3, 42.9; IR ($CHCl_3$, cm^{-1}): ν 1958; HRMS (ES): calcd for $C_{22}H_{17}N$ $[M]^+$: 295.1355; found: 295.1358.

1-(Buta-2,3-dienyl)-5-methyl-2-(4-methylphenyl)-1*H*-indole 2g. From 126 mg (0.49 mmol) of alkyne **1g**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **2g** (112 mg, 84%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.17 (d, 2H, *J* = 8.0 Hz, Ar), 7.04 (m, 4H, Ar), 6.81 (dd, 1H, *J* = 8.5, 1.8 Hz, Ar), 6.20 (d, 1H, *J* = 0.6 Hz, Ar), 5.05 (m, 1H, =CH), 4.51 (m, 2H, =CH_2), 4.45 (m, 2H, NCH_2), 2.23 (s, 3H, Me), 2.18 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 141.4, 137.8, 136.0, 130.5, 129.9, 129.1 (Ar, 2CH), 129.0 (Ar, 2CH), 128.5, 123.1 (Ar, CH), 120.0 (Ar, CH), 109.9 (Ar, CH), 101.3 (Ar, CH), 88.2 (=CH), 77.4 (=CH_2), 42.9 (NCH_2), 21.4 (Me), 21.3 (Me); IR ($CHCl_3$, cm^{-1}): ν 2920, 1957, 1474, 1341, 849, 827, 790; HRMS (ES): calcd for $C_{20}H_{19}N$ $[M]^+$: 273.1511; found: 273.1523.

1-(Buta-2,3-dienyl)-5-methoxy-2-(4-methylphenyl)-1*H*-indole 2h. From 142 mg (0.52 mmol) of alkyne **1h**, and after chromatography of the residue using

hexanes/ethyl acetate (20:1) as eluent gave compound **2h** (116 mg, 78%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.39 (d, 2H, *J* = 8.2 Hz, Ar), 7.28 (m, 1H, Ar), 7.26 (m, 2H, Ar), 7.08 (d, 1H, *J* = 2.6 Hz, Ar), 6.88 (m, 1H, Ar), 6.43 (d, 1H, *J* = 0.6 Hz, Ar), 5.27 (m, 1H, =CH), 4.72 (m, 2H, =CH_2), 4.66 (m, 2H, NCH_2), 3.86 (s, 3H, OMe), 2.41 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 154.4, 141.9, 137.8, 132.9, 130.4, 129.8, 129.2 (Ar, 2CH), 129.1 (Ar, 2CH), 111.7 (Ar, CH), 111.0 (Ar, CH), 102.1 (Ar, CH), 101.4 (Ar, CH), 88.2 (=CH), 77.3 (=CH_2), 55.9 (OMe), 43.0 (NCH_2), 21.3 (Me); IR ($CHCl_3$, cm^{-1}): ν 2932, 1960, 1472, 1367, 852, 830, 784; HRMS (ES): calcd for $C_{20}H_{19}NO$ $[M]^+$: 289.1461; found: 289.1466.

1-(Buta-2,3-dienyl)-5-fluoro-2-(4-methylphenyl)-1*H*-indole 2i. From 80 mg (0.30 mmol) of alkyne **1i**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **2i** (69 mg, 83%) as a colorless solid; mp 106–107 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.42 (d, 2H, *J* = 8.0 Hz, Ar), 7.28 (m, 4H, Ar), 6.98 (dd, 1H, *J* = 9.0, 2.6 Hz, Ar), 6.48 (s, 1H, Ar), 5.30 (m, 1H, =CH), 4.77 (m, 2H, =CH_2), 4.70 (m, 2H, NCH_2), 2.44 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 159.7, 156.6, 142.9, 138.2, 134.2, 130.5, 129.5 (Ar, 2CH), 129.3 (Ar, 2CH), 110.8 (Ar, CH), 109.6 (Ar, CH), 105.3 (Ar, CH), 101.7 (Ar, CH), 88.0 (=CH), 77.5 (=CH_2), 43.0 (NCH_2), 21.3 (Me); IR ($CHCl_3$, cm^{-1}): ν 2954, 1952, 1476, 1376, 846, 823, 776; HRMS (ES): calcd for $C_{19}H_{16}FN$ $[M]^+$: 277.1261; found: 277.1260.

1-(Buta-2,3-dienyl)-5-nitro-2-phenyl-1*H*-indole 2j. From 129 mg (0.47 mmol) of alkyne **1j**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2j** (93 mg, 68%) as a colorless solid; mp 121–122 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.59 (d, 1H, *J* = 2.2 Hz, Ar), 8.15 (dd, 1H, *J* = 9.1, 2.2 Hz, Ar), 7.51 (m, 5H, Ar), 7.42 (d, 1H, *J* = 9.1 Hz, Ar), 6.71 (s, 1H, Ar), 5.31 (m, 1H, =CH), 4.76 (m, 4H, =CH_2 + NCH_2); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 144.5, 142.0, 140.4, 131.4, 129.3 (Ar, 2CH), 128.9 (Ar, CH), 128.8 (Ar, 2CH), 127.3, 117.6 (Ar, CH), 117.3 (Ar, CH), 110.1 (Ar, CH), 104.1 (Ar, CH), 87.6 (=CH), 78.1 (=CH_2), 43.0 (NCH_2); IR ($CHCl_3$, cm^{-1}): ν

2970, 1947, 1475, 1387, 838, 808, 753; HRMS (ES): calcd for $C_{18}H_{14}N_2O_2$ $[M]^+$: 290.1049; found: 290.1053.

1-(Buta-2,3-dienyl)-2-phenyl-1*H*-indole-5-carbonitrile 2k. From 80 mg (0.31 mmol) of alkyne **1k**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2k** (61 mg, 72%) as a colorless solid; mp 113–114 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.97 (s, 1H, Ar), 7.50 (m, 7H, Ar), 6.61 (s, 1H, Ar), 5.30 (qu, 1H, *J* = 6.6 Hz, =CH), 4.75 (m, 4H, $=CH_2$ + NCH_2); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.4, 143.5, 139.1, 131.5, 129.3 (Ar, 2CH), 128.7 (Ar, CH), 128.7 (Ar, 2CH), 127.8, 125.8 (Ar, CH), 124.5 (Ar, CH), 120.8, 111.0 (Ar, CH), 102.9, 102.6 (Ar, CH), 87.6 (=CH), 78.0 ($=CH_2$), 42.9 (NCH_2); IR ($CHCl_3$, cm^{-1}): ν 2959, 1956, 1470, 1350, 840, 813, 756; HRMS (ES): calcd for $C_{19}H_{14}N_2$ $[M]^+$: 270.1151; found: 270.1157.

1-(Buta-2,3-dienyl)-2-methyl-1*H*-indole 2l. From 350 mg (2.12 mmol) of alkyne **1l**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2l** (303 mg, 78%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.44 (d, 1H, *J* = 7.5 Hz), 7.20 (d, 1H, *J* = 8.0 Hz), 7.06 (td, 1H, *J* = 6.7 Hz, 1.0 Hz), 6.99 (t, 1H, *J* = 7.0 Hz), 6.12 (br s, 1H), 5.14 (q, 1H, *J* = 6.4 Hz), 4.70 (m, 2H), 4.60 (m, 2H), 2.35 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.6, 136.6, 136.3, 128.2, 120.7, 120.5, 119.7, 109.0, 100.2, 87.5, 77.4, 41.8, 12.7; IR ($CHCl_3$, cm^{-1}): ν 1956; HRMS (ES): calcd for $C_{13}H_{13}N$ $[M]^+$: 183.1042; found: 183.1042.

1-(Buta-2,3-dienyl)-2,5-dimethyl-1*H*-indole 2m. From 178 mg (0.97 mmol) of alkyne **1m**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2m** (100 mg, 52%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.36 (s, 1H, Ar), 7.22 (d, 1H, *J* = 8.3 Hz, Ar), 7.02 (dd, 1H, *J* = 8.2, 1.2 Hz, Ar), 6.05 (s, 1H, Ar), 5.26 (m, 1H, *J* = 6.6 Hz, =CH), 4.83 (m, 2H, $=CH_2$), 4.73 (m, 2H, NCH_2), 2.49 (s, 3H, Me), 2.47 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 136.5, 135.0, 128.5, 128.4, 122.0 (Ar, CH), 119.5 (Ar,

CH), 108.7 (Ar, CH), 99.6 (Ar, CH), 87.5 (=CH), 77.4 (=CH_2), 41.8 (NCH_2), 21.4 (Me), 12.7 (Me); IR ($CHCl_3$, cm^{-1}): ν 2954, 1956, 1475, 1369, 843, 821, 758; HRMS (ES): calcd for $C_{14}H_{15}N$ $[M]^+$: 197.1198; found: 197.1205.

1-(Buta-2,3-dienyl)-5-methoxy-2-methyl-1*H*-indole 2n. From 180 mg (0.90 mmol) of alkyne **1n**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **2n** (151 mg, 79%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.18 (d, 1H, *J* = 8.8 Hz, Ar), 7.02 (d, 1H, *J* = 2.5 Hz, Ar), 6.81 (dd, 1H, *J* = 8.8, 2.5 Hz, Ar), 6.19 (s, 1H, Ar), 5.23 (qu, 1H, *J* = 6.5 Hz, =CH), 4.80 (m, 2H, =CH_2), 4.66 (m, 2H, NCH_2), 3.86 (s, 3H, OMe), 2.43 (d, 3H, *J* = 0.6 Hz, Me); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 153.9, 136.9, 131.8, 128.5, 110.2 (Ar, CH), 109.6 (Ar, CH), 101.9 (Ar, CH), 99.9 (Ar, CH), 87.5 (=CH), 77.0 (=CH_2), 55.9 (OMe), 41.9 (NCH_2), 12.7 (Me); IR ($CHCl_3$, cm^{-1}): ν 2932, 1484, 1227, 1202, 847; HRMS (ES): calcd for $C_{14}H_{15}NO$ $[M]^+$: 213.1148; found: 213.1146.

1-(Buta-2,3-dienyl)-5-chloro-2-methyl-1*H*-indole 2o. From 355 mg (1.74 mmol) of alkyne **1o**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2o** (327 mg, 86%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.48 (d, 1H, *J* = 1.9 Hz Ar), 7.19 (d, 1H, *J* = 8.8 Hz, Ar), 7.09 (dd, 1H, *J* = 8.6, 2.0 Hz, Ar), 6.20 (s, 1H, Ar), 5.22 (qu, 1H, *J* = 6.5 Hz, =CH), 4.79 (m, 2H, =CH_2), 4.66 (m, 2H, NCH_2), 2.44 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 137.8, 135.0, 129.1, 125.0, 120.7 (Ar, CH), 119.1 (Ar, CH), 109.9 (Ar, CH), 99.9 (Ar, CH), 87.2 (=CH), 77.4 (=CH_2), 41.9 (NCH_2), 12.7 (Me); IR ($CHCl_3$, cm^{-1}): ν 2953, 1954, 1474, 1360, 842, 810, 782; HRMS (ES): calcd for $C_{13}H_{12}NCl$ $[M]^+$: 217.0652; found: 217.0657.

1-(Buta-2,3-dienyl)-5-bromo-2-methyl-1*H*-indole 2p. From 327 mg (1.32 mmol) of alkyne **1p**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **2p** (301 mg, 87%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.64 (d, 1H, *J* = 1.7Hz, Ar), 7.22 (dd, 1H, *J* = 8.6, 1.8 Hz, Ar), 7.15 (d, 1H, *J* = 8.6 Hz, Ar), 6.20 (s, 1H, Ar), 5.21 (qu, 1H, *J* = 6.4 Hz, =CH), 4.79

(m, 2H, =CH_2), 4.66 (m, 2H, NCH_2), 2.43 (s, 3H, Me); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.5, 137.7, 135.3, 129.8, 123.2 (Ar, CH), 122.1 (Ar, CH), 112.6, 110.4 (Ar, CH), 99.9 (Ar, CH), 87.2 (=CH), 77.4 (=CH_2), 41.9 (NCH_2), 12.6 (Me); IR ($CHCl_3$, cm^{-1}): ν 2924, 1480, 1218, 1200, 850; HRMS (ES): calcd for $C_{13}H_{12}BrN$ $[M]^+$: 261.0147; found: 261.0146.

1-(Buta-2,3-dienyl)-2-methyl-5-nitro-1*H*-indole 2q. From 380 mg (1.77 mmol) of alkyne **1q**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **2q** (289 mg, 72%) as a colorless solid; mp 96–97 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.45 (d, 1H, *J* = 2.2 Hz, Ar), 8.05 (dd, 1H, *J* = 9.0, 2.2 Hz, Ar), 7.27 (d, 1H, *J* = 9.1 Hz, Ar), 6.41 (s, 1H, Ar), 5.26 (m, 1H, *J* = 6.0 Hz, =CH), 4.78 (m, 2H, =CH_2), 4.72 (dt, 2H, *J* = 6.0, 2.9 Hz, NCH_2), 2.47 (d, 3H *J* = 0.5 Hz, Me); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 208.4, 141.5, 140.0, 139.6, 127.3, 116.7 (Ar, CH), 116.4 (Ar, CH), 108.7 (Ar, CH), 102.6 (Ar, CH), 86.9 (=CH), 77.9 (=CH_2), 42.1 (NCH_2), 12.8 (Me); IR ($CHCl_3$, cm^{-1}): ν 2968, 1967, 1430, 1348, 832; HRMS (ES): calcd for $C_{13}H_{12}N_2O_2$ $[M]^+$: 228.0893; found: 228.0904.

Reaction of 1-Allenyl-2-phenyl-indole 2a with Selectfluor. From 50 mg (0.20 mmol) of aminoallene **2a**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, 11 mg (20%) of the less polar compound **3a** and 4 mg (8%) of the more polar compound **4a** were obtained.

1-(Buta-2,3-dienyl)-3-fluoro-2-phenyl-1H-indole 4a. Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.57 (d, 1H, *J* = 7.7 Hz), 7.38 (m, 6H), 7.14 (m, 2H), 5.16 (q, 1H, *J* = 6.0 Hz), 4.65 (m, 2H), 4.59 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –175.4 (s, 1F); HRMS (ES): calcd for $C_{18}H_{14}FN$ $[M]^+$: 263.1104; found: 263.1118.

General Procedure for the Metal-Catalyzed Reaction of *N*-Allenyl-2-aryl Indoles 2a–i and Selectfluor. Synthesis of 2-(Allenyl)-2-aryl-3,3-difluoroindolines 3a–i. $Fe(OTf)_3$ or $[(Ph_3P)AuNTf_2]$ (0.05 mmol), Selectfluor (2.0 mmol), and $NaHCO_3$ (2.0 mmol) were sequentially added to a stirred solution of

the corresponding *N*-allenyl indole **2** (1.0 mmol) in acetonitrile (10 mL) under argon atmosphere. The resulting mixture was stirred at room temperature until disappearance of the starting material (TLC, typically 1 h). After filtration through a pad of Celite, water (5 mL) was added before being extracted with ethyl acetate (3 x 15 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave adducts **3**.

2-(Allenyl)-2-phenyl-3,3-difluoroindoline 3a. From 235 mg (0.96 mmol) of *N*-allenyl indole **2a**, and after chromatography of the residue using hexanes/ethyl acetate (15:1) as eluent gave compound **3a** (227 mg, 83%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.56 (m, 2H), 7.42 (m, 5H), 6.58 (t, 1H, *J* = 7.4 Hz), 6.76 (d, 1H, *J* = 8.0 Hz), 5.18 (q, 1H, *J* = 6.6 Hz), 4.80 (m, 2H), 3.78 (m, 1H), 3.68 (m, 1H), 3.18 (d, 1H, J = 4.3 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 209.0, 150.2, 134.8, 134.9, 133.4, 129.1 (2C), 128.2, 127.7, 126.3, 124.5, 119.5, 119.0, 108.6, 96.4 (t, *J* = 89.1 Hz), 87.9, 76.7, 42.3; ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –98.44 (d, 1H, *J* = 317.6 Hz), –110.6 (d, 1F, *J* = 317.6 Hz); IR ($CHCl_3$, cm^{-1}): ν 3525, 1955, 1157, 1133; HRMS (ES): calcd for $C_{18}H_{15}F_2N$ $[M]^+$: 283.1167; found: 283.1183.

2-(Allenyl)-2-(4-chlorophenyl)-3,3-difluoroindoline 3b. From 43 mg (0.15 mmol) of *N*-allenyl indole **2b**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **3b** (32 mg, 66%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.42 (d, 2H, *J* = 8.6 Hz), 7.34 (m, 2H), 7.28 (d, 2H, *J* = 8.8 Hz), 6.81 (t, 1H, *J* = 7.4 Hz), 6.66 (d, 1H, *J* = 8.1 Hz), 5.07 (q, 1H, *J* = 6.6 Hz), 4.71 (m, 2H), 3.68 (m, 1H), 3.55 (m, 1H), 3.09 (d, 1H, *J* = 4.0 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 209.0, 150.0, 135.2, 133.5 (2C), 129.2 (2C), 128.4 (2C), 126.2, 124.5, 122.8, 119.2, 108.8, 95.9 (t, *J* = 89.1 Hz), 87.8, 76.9, 42.2; ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –97.7 (d, 1F, *J* = 263.2 Hz), –110.2 (d, 1F, *J* = 268.1 Hz); IR ($CHCl_3$, cm^{-1}): ν 3525, 1953, 1155, 1135; HRMS (ES): calcd for $C_{18}H_{14}ClF_2N$ $[M]^+$: 317.0777; found: 317.0792.

2-(Allenyl)-2-(4-fluorophenyl)-3,3-difluoroindoline 3c. From 70 mg (0.27 mmol) of *N*-allenyl indole **2c**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **3c** (32 mg, 40%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.42 (m, 2H), 7.31 (dd, 1H, J = 6.0 Hz, J = 1.5 Hz), 7.13 (m, 1H), 6.74 (t, 2H, *J* = 8.9 Hz), 6.61 (t, 1H, *J* = 7.4 Hz), 6.56 (d, 1H, *J* = 8.0 Hz), 4.89 (q, 1H, *J* = 6.4 Hz), 4.51 (m, 2H), 3.48 (m, 1H), 3.35 (m, 1H), 2.61 (d, 1H, *J* = 3.5 Hz); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.8, 165.3, 162.0, 133.4, 130.3, 130.2, 127.0, 126.6, 125.9, 124.7, 119.4, 115.4, 115.1, 109.0, 96.3, 88.3, 76.5, 42.2; ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –95.5 (d, 1F, *J* = 263.2 Hz), –111.6 (d, 1F, *J* = 263.3 Hz), –113.1 (s, 1F); IR ($CHCl_3$, cm^{-1}): ν 3524, 1954, 1160, 1130; HRMS (ES): calcd for $C_{18}H_{14}F_3N$ $[M]^+$: 301.1072; found: 301.1089.

2-(Allenyl)-2-(4-methylphenyl)-3,3-difluoroindoline 3d. From 96 mg (0.37 mmol) of *N*-allenyl indole **2d**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **3d** (52 mg, 48%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.68 (d, 2H, *J* = 8.2 Hz); 7.47 (dd, 1H, *J* = 8.0, 1.3 Hz), 7.07 (m, 3H), 6.75 (m, 2H), 5.08 (m, 1H), 4.65 (m, 2H), 3.67 (m, 2H), 2.18 (s, 3H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 206.8, 136.6, 131.0, 130.2, 129.2 (2C), 128.3 (2C), 125.5, 124.6, 123.9, 122.4, 119.9, 116.8, 106.6, 86.2, 74.1, 40.1, 18.7; ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –96.2 (d, 1F, *J* = 263.2 Hz), –111.3 (d, 1F, *J* = 263.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 3525, 1952, 1161, 1136; HRMS (ES): calcd for $C_{19}H_{17}F_2N$ $[M]^+$: 297.1323; found: 297.1322.

2-(Allenyl)-2-(4-*tert*-butylphenyl)-3,3-difluoroindoline 3e. From 48 mg (0.16 mmol) of *N*-allenyl indole **2e**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **3e** (23 mg, 43%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.54 (d, 2H, *J* = 8.3 Hz), 7.39 (d, 1H, *J* = 8.6 Hz); 7.23 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.16 (d, 2H, *J* = 8.8 Hz); 6.52 (m, 2H), 4.86 (m, 1H), 4.43 (m, 2H), 3.43 (m, 2H), 1.06 (s, 9H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 207.7, 150.7, 142.3, 132.0, 131.1, 127.5, 126.9 (2C), 126.6 (2C),

126.0, 125.1, 124.3 (2C), 124.2, 123.4, 117.8, 107.5, 87.2, 75.1, 41.1, 29.9; ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –96.0 (d, 1F, *J* = 263.2 Hz), –110.9 (d, 1F, *J* = 263.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 3528, 1954, 1154, 1134; HRMS (ES): calcd for $C_{22}H_{23}F_2N$ [*M*]$^+$: 339.1793; found: 339.1790.

2-(Allenyl)-2-(naphthalen-2-yl)-3,3-difluoroindoline 3f. From 60 mg (0.25 mmol) of *N*-allenyl indole **2f**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **3f** (45 mg, 55%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 8.19 (s, 1H), 7.49 (m, 4H), 7.27 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.12 (m, 3H), 6.53 (d, 2H, *J* = 7.7 Hz); 4.86 (m, 1H), 4.42 (m, 2H), 3.42 (m, 2H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.2, 134.2, 133.6, 133.5, 133.1, 128.9, 128.3, 128.2 (2C), 127.9, 126.8, 126.4, 125.6 (2C), 124.9, 123.8, 120.5, 119.4, 109.0, 88.5, 76.5, 42.4; ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –95.4 (d, 1F, *J* = 268.1 Hz), –110.5 (d, 1F, *J* = 263.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 3525, 1951, 1152, 1132; HRMS (ES): calcd for $C_{22}H_{17}F_2N$ [*M*]$^+$: 333.1323; found: 333.1337.

5-Methyl-2-(allenyl)-2-(4-methylphenyl)-3,3-difluoroindoline 3g. From 49 mg (0.18 mmol) of *N*-allenyl indole **2g**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **3g** (29 mg, 52%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.59 (d, 2H, *J* = 8.2 Hz, Ar), 6.97 (d, 3H, *J* = 7.9 Hz, Ar), 6.85 (s, 1H, Ar), 6.66 (m, 1H, Ar), 5.22 (m, 1H, *J* = 6.4 Hz, =CH), 4.53 (m, 2H, =CH_2), 3.97 (m, 1H, CH*H*), 3.71 (m, 1H, C*H*H), 2.77 (d, 1H, *J* = 3.2 Hz, NH), 2.06 (s, 3H, Me), 1.84 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.1, 139.1 (Ar, CH), 138.9, 133.9, 132.8, 131.1, 129.3 (Ar, 2CH), 128.4 (Ar, 2CH), 125.3 (Ar, CH), 121.0, 120.7, 109.0 (Ar, CH), 97.1, 88.8 (=CH), 76.5 (=CH_2), 42.7 (CH_2), 21.1(Me), 20.5 (Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –94.7 (d, 1F, *J* = 268.1 Hz), –111.7 (d, 1F, *J* = 263.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 2925, 1713, 1501, 1328, 1272, 1095, 857, 823; HRMS (ES): calcd for $C_{20}H_{19}F_2N$ [*M*]$^+$: 311.1480; found: 311.1487.

5-Methoxy-2-(allenyl)-2-(4-methylphenyl)-3,3-difluoroindoline 3h. From 56 mg (0.19 mmol) of *N*-allenyl indole **2h**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **3h** (26 mg, 42%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.63 (d, 2H, *J* = 8.2 Hz, Ar), 7.03 (m, 1H, Ar), 6.99 (d, 2H, *J* = 8.0 Hz, Ar), 6.92 (m, 1H, Ar), 6.58 (d, 1H, *J* = 8.6 Hz, Ar), 5.03 (m, 1H, *J* = 6.3 Hz, =CH), 4.55 (m, 2H, =CH_2), 3.55 (m, 1H, CH*H*), 3.47 (m, 1H, C*H*H), 3.23 (s, 3H, OMe), 2.71 (d, 1H, *J* = 3.4 Hz, NH), 2.07(s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.1, 154.1, 145.0, 139.0, 132.7, 129.2 (Ar, 4CH), 128.9, 120.5 (Ar, CH), 113.0, 110.4 (Ar, CH), 109.4 (Ar, CH), 97.3, 88.9 (=CH), 76.4 (=CH_2), 55.5 (OMe), 43.0 (CH_2), 21.1(Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –96.0 (d, 1F, *J* = 263.3 Hz), –113.1 (d, 1F, *J* = 268.1 Hz); IR ($CHCl_3$, cm^{-1}): ν 2926, 1706, 1495, 1276, 1073, 825; HRMS (ES): calcd for $C_{20}H_{19}F_2NO$ $[M]^+$: 327.1429; found: 327.1434.

5-Fluoro-2-(allenyl)-2-(4-methylphenyl)-3,3-difluoroindoline 3i. From 32 mg (0.12 mmol) of *N*-allenyl indole **2i**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **3i** (16 mg, 44%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.52 (d, 2H, *J* = 8.2 Hz, Ar), 6.99 (m, 1H, Ar), 6.97 (d, 2H, *J* = 7.9 Hz, Ar), 6.81 (m, 1H, Ar), 6.33 (m, 1H, Ar), 4.92 (m, 1H, *J* = 6.4 Hz, =CH), 4.51 (m, 2H, =CH_2), 3.51 (m, 1H, CH*H*), 3.45 (m, 1H, C*H*H), 2.63 (d, 1H, *J* = 3.1 Hz, NH), 2.06 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.1, 139.2 (2C), 132.20, 132.16, 129.3 (Ar, 2CH), 128.2 (Ar, 2CH), 127.2, 126.6, 119.9 (d, *J* = 93.8 Hz, Ar, CH), 112.0 (d, *J* = 98.2 Hz, Ar, CH), 109.8 (d, *J* = 28.4 Hz, Ar, CH), 97.3 (dd, *J* = 124.4, 87.3 Hz, Ar, C), 87.3 (=CH), 76.6 (=CH_2), 42.7 (CH_2), 21.1(Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –96.2 (d, 1F, *J* = 268.1 Hz), –113.3 (d, 1F, *J* = 268.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 2924, 1700, 1492, 1266, 1187, 843, 814; HRMS (ES): calcd for $C_{19}H_{16}F_3N$ $[M]^+$: 315.1229; found: 315.1243.

2-(Buta-2,3-dienyl)-3,3-difluoro-5-nitro-2-phenylindoline 3j. From 47 mg (0.16 mmol) of *N*-allenyl indole **2j**, 49 mg (92%) of compound **3j** was obtained as a pale yellow solid; mp 123–124 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, C_6D_6, 25

^{o}C) δ: 8.15 (d, 1H, *J* = 1.8 Hz, Ar), 7.98 (dd, 1H, *J* =8.9, 2.3 Hz, Ar), 7.41 (m, 2H, Ar), 7.12 (m, 3H, Ar), 6.06 (d, 1H, *J* = 9.1 Hz, Ar), 4.74 (qu, 1H, *J* = 6.4 Hz, =CH), 4.48 (m, 2H, =CH_2), 3.30 (m, 2H, CH_2), 3.03 (br s, 1H, NH); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.1, 154.4 (t, *J* = 24.0 Hz, C), 140.4, 134.2, 130.2, 129.8 (Ar, 2CH), 128.9 (Ar, CH), 127.9 (Ar, 2CH), 125.0, 121.7 (Ar, CH), 120.0 (t, *J* = 102.5 Hz, C), 107.3 (Ar, CH), 97.1 (dd, *J* = 124.3, 89.4 Hz, Ar, C), 87.3 (=CH), 77.1 (=CH_2), 41.7(CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –97.9 (d, 1F, *J* = 251.1 Hz), –108.5 (d, 1F, *J* = 252.3 Hz); IR ($CHCl_3$, cm^{-1}): ν 2930, 1622, 1507, 1328, 1269, 1099, 758, 707; HRMS (ES): calcd for $C_{18}H_{14}F_2N_2O_2$ $[M]^+$: 328.1017; found: 328.1038.

2-(Buta-2,3-dienyl)-3,3-difluoro-2-phenylindoline-5-carbonitrile 3k. From 30 mg (0.11 mmol) of *N*-allenyl indole **2k**, 33 mg (97%) of compound **3k** was obtained as a colorless solid; mp 118–119 °C (*n*-hexane/ethyl acetate); ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.48 (d, 2H, *J* = 7.7 Hz, Ar), 7.11 (m, 3H, Ar), 7.03 (s, 1H, Ar), 7.00 (d, 1H, *J* = 9.3 Hz, Ar), 6.13 (d, 1H, *J* = 8.3 Hz, Ar), 4.79 (m, 1H, *J* = 6.4 Hz, =CH), 4.48 (m, 2H, =CH_2), 3.33 (m, 3H, CH_2 + NH); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.1, 152.9 (t, *J* = 26.2 Hz, Ar, C), 137.7 (Ar, CH), 134.5 (d, *J* = 10.9 Hz, Ar, C), 129.6 (Ar, CH), 128.9 (Ar, CH), 128.6 (Ar, 2CH), 128.3 (Ar, CH), 127.9 (Ar, 2CH), 125.5 (t, *J* = 113.5 Hz, Ar, C), 120.8 (t, *J* = 102.5 Hz, Ar, C), 119.0, 108.6 (Ar, CH), 101.8, 96.7 (dd, *J* = 124.3, 89.4 Hz, Ar, C), 87.4 (=CH), 76.9 (=CH_2), 41.8 (CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –96.9 (d, 1F, *J* = 251.9 Hz), –109.4 (d, 1F, *J* = 251.9 Hz); IR ($CHCl_3$, cm^{-1}): ν 2858, 2224, 1626, 1499, 1178, 1097, 856, 735; HRMS (ES): calcd for $C_{19}H_{14}F_2N_2$ $[M]^+$: 308.1119; found: 308.1112.

Procedure for the Iron-Catalyzed Reaction of 1-(Allenyl)-2-methyl-1*H*-indoles 2l–q and Selectfluor. Synthesis of 2-(Allenyl)-3,3-difluoro-2-methyl indolines 3l, 3m, and 3o–q. $Fe(OTf)_3$ (0.0715 mmol), Selectfluor (2.86 mmol), and $NaHCO_3$ (2.86 mmol) were sequentially added at 0 ^{o}C to a stirred solution of the appropriate *N*-allenyl-2-methyl indole **2** (1.43 mmol) in acetonitrile (14 mL) under argon atmosphere. The resulting mixture was stirred at 0 ^{o}C until disappearance of the

starting material (TLC, 5 min). After filtration through a pad of Celite, water (7 mL) was added before being extracted with ethyl acetate (3 x 20 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave adducts **3**.

2-(Buta-2,3-dienyl)-2-methyl-3,3-difluoroindoline 3l. From 88 mg (0.48 mmol) of aminoallene **2l**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **3l** (50 mg, 47%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.35 (d, 1H, *J* = 7.4 Hz, Ar), 7.07 (t, 1H, *J* = 7.6 Hz, Ar), 6.56 (d, 1H, *J* = 8.0 Hz, Ar), 6.38 (d, 1H, *J* = 8.0 Hz, Ar), 4.91 (m, 1H, *J* = 6.5 Hz, =CH), 4.52 (m, 2H, =CH_2), 3.50 (m, 2H, CH_2), 2.11 (br s, 1H, NH), 1.32 (d, 3H, *J* = 2.9 Hz, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.0, 149.4, 133.3 (Ar, CH), 124.5 (Ar, CH), 123.8, 120.1, 118.7 (Ar, CH), 108.4 (Ar, CH), 93.4 (dd, *J* = 115.7, 93.8 Hz, Ar, C), 88.4 (=CH), 76.5 (=CH_2), 40.6 (CH_2), 18.2 (d, *J* = 30.6 Hz, Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –107.7 (d, 1F, *J* = 268.2 Hz), –108.9 (d, 1F, *J* = 268.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 2930, 1623, 1480, 1249, 1065, 843, 814; HRMS (ES): calcd for $C_{13}H_{13}F_2N$ $[M]^+$: 221.1010; found: 221.1021.

2-(Buta-2,3-dienyl)-3,3-difluoro-5-methyl-2-methylindoline 3m. From 40 mg (0.20 mmol) of aminoallene **2m**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **3m** (23 mg, 48%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.16 (s, 1H, Ar), 6.92 (d, 1H, *J* = 8.5 Hz, Ar), 6.37 (d, 1H, *J* = 8.0 Hz, Ar), 4.96 (m, 1H, *J* = 6.5 Hz, =CH), 4.55 (m, 2H, =CH_2), 3.53 (m, 2H, CH_2), 2.01 (s, 3H, Me), 1.35 (d, 3H, *J* = 3.7 Hz, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 209.0 147.5 (t, *J* = 26.1 Hz, Ar, C), 133.8 (Ar, CH), 124.9 (Ar, CH), 123.9, 120.3 (t, *J* = 106.9 Hz, Ar, C), 108.5 (Ar, CH), 93.7 (dd, *J* = 115.6, 93.8 Hz, Ar, C), 88.6 (=CH), 76.4 (=CH_2), 40.9 (CH_2), 20.5 (Me), 18.1 (d, *J* = 30.5 Hz, Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –107.8 (d, 1F, *J* = 267.9 Hz), –109.3 (d, 1F, *J* = 268.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 2937, 1713, 1470, 1245, 1157, 823; HRMS (ES): calcd for $C_{14}H_{15}F_2N_2$ $[M]^+$: 235.1167; found: 235.1189.

2-(Buta-2,3-dienyl)-5-chloro-3,3-difluoro-2-methylindoline 3o. From 67 mg (0.31 mmol) of aminoallene **2o**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **3o** (33 mg, 41%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.29 (d, 1H, *J* = 1.7 Hz, Ar), 7.02 (d, 1H, *J* = 8.6 Hz, Ar), 6.06 (d, 1H, *J* = 8.5 Hz, Ar), 4.81 (m, 1H, *J* = 6.4 Hz, =CH), 4.49 (m, 2H, =CH_2), 3.36 (m, 2H, CH_2), 2.02 (br s, 1H, NH), 1.25 (dd, 3H, *J* = 3.6, 0.9 Hz, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.9, 147.8 (t, *J* = 25.0 Hz, Ar, C), 133.2 (Ar, CH), 126.2, 124.7 (Ar, CH), 123.1 (d, *J* = 150.5 Hz, Ar, C), 121.2 (t, *J* = 100.4 Hz, Ar, C), 109.5 (Ar, CH), 93.5 (dd, *J* = 111.2, 93.8 Hz, Ar, C), 87.9 (=CH), 76.8 (=CH_2), 40.4 (CH_2), 18.2 (dd, *J* = 28.3, 6.5 Hz, Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –108.0 (d, 1F, *J* = 268.2 Hz), –109.2 (d, 1F, *J* = 268.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 2926, 1614, 1483, 1256, 1069, 851, 808; HRMS (ES): calcd for $C_{13}H_{12}NClF_2$ $[M]^+$: 255.0620; found: 255.0637.

2-(Buta-2,3-dienyl)-5-bromo-3,3-difluoro-2-methylindoline 3p. From 80 mg (0.31 mmol) of aminoallene **2p**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **3p** (38 mg, 42%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.44 (dd, 1H, *J* = 3.3, 1.6 Hz, Ar), 7.14 (m, 1H, Ar), 6.02 (d, 1H, *J* = 8.5 Hz, Ar), 4.80 (m, 1H, *J* = 6.4 Hz, =CH), 4.49 (dt, 2H, *J* = 6.3, 3.0 Hz, NCH_2), 3.36 (m, 2H, CH_2), 2.11 (br s, 1H, NH), 1.23 (dd, 3H, *J* = 3.5, 0.9 Hz, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.9, 148.2 (t, *J* = 26.0 Hz, Ar, C), 136.0 (Ar, CH), 126.1, 122.8, 121.9 (t, *J* = 100.4 Hz, Ar, C), 110.0 (Ar, CH), 93.4 (dd, *J* = 113.5, 94.1 Hz, Ar, C), 87.9 (=CH), 76.8 (=CH_2), 40.3 (CH_2), 18.2 (d, *J* = 28.8 Hz, Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –107.9 (d, 1F, *J* = 251.8 Hz), –109.1 (d, 1F, *J* = 251.6 Hz); IR ($CHCl_3$, cm^{-1}): ν 2924, 1610, 1472, 1254, 1084, 853, 802; HRMS (ES): calcd for $C_{13}H_{12}NBrF_2$ $[M]^+$: 299.0115; found: 299.0137.

2-(Buta-2,3-dienyl)-3,3-difluoro-5-nitro-2-methylindoline 3q. From 73 mg (0.32 mmol) of aminoallene **2q**, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound **3q** (49 mg, 57%) as a

colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 8.18 (dd, 1H, *J* = 3.8, 1.8 Hz, Ar), 7.91 (dd, 1H, *J* = 9.0, 2.3 Hz, Ar), 5.85 (dd, 1H, *J* = 9.0, 1.2 Hz, Ar), 4.72 (m, 1H, *J* = 6.5 Hz, =CH), 4.49 (m, 2H, =CH_2), 3.35 (m, 2H, CH_2), 2.41 (br s, 1H, NH), 1.22 (d, 3H, *J* = 4.0 Hz, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.9, 153.0 (t, *J* = 24.0 Hz, Ar, C), 139.7, 130.2 (Ar, CH), 125.1, 121.5 (Ar, CH), 119.5 (t, *J* = 103.4 Hz, Ar, C), 106.8 (Ar, CH), 93.7 (dd, *J* = 119.0, 91.2 Hz, Ar, C), 87.1 (=CH), 77.4 (=CH_2), 39.8 (CH_2), 18.6(d, *J* = 28.8 Hz, Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –106.7 (d, 1F, *J* = 252.9 Hz), –108.4 (d, 1F, *J* = 252.9 Hz); IR ($CHCl_3$, cm^{-1}): ν 2932, 1702, 1490, 1242, 1150, 830; HRMS (ES): calcd for $C_{13}H_{12}N_2O_2F_2$ $[M]^+$: 266.0861; found: 266.0851.

Procedure for the Iron-Catalyzed Reaction of 1-(Allenyl)-2-methyl-1*H*-indoles 2l–q and Selectfluor. Synthesis of 2-(Allenyl)-3,3-difluoro-2-(fluoromethyl)indolines 5l, 5m, and 5o–q. $Fe(OTf)_3$ (0.0715 mmol), Selectfluor (5.00 mmol), and $NaHCO_3$ (5.00 mmol) were sequentially added to a stirred solution of the appropriate *N*-allenyl-2-methyl indole **2** (1.43 mmol) in acetonitrile (14 mL) under argon atmosphere. The resulting mixture was stirred at room temperature until disappearance of the starting material (TLC, 5 min). After filtration through a pad of Celite, water (7 mL) was added before being extracted with ethyl acetate (3 x 20 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave adducts **5**.

2-(Buta-2,3-dienyl)-3,3-difluoro-2-(fluoromethyl)indoline 5l. From 88 mg (0.48 mmol) of aminoallene **2l**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **5l** (55 mg, 48%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.28 (d, 1H, *J* = 7.4, 1.2 Hz, Ar), 7.03 (td, 1H, *J* = 8.2, 1.2 Hz, Ar), 6.53 (t, 1H, *J* = 7.4 Hz, Ar), 6.37 (d, 1H, *J* = 8.2 Hz, Ar), 4.91 (m, 1H, *J* = 6.3Hz, =CH), 4.51 (m, 2H, =CH_2), 4.45 (d, 1H, *J* = 1.5 Hz, CH*H*F), 4.30 (d, 1H, *J* = 1.3 Hz, C*H*HF), 3.61 (m, 1H, CH*H*), 3.46 (m, 1H, C*H*H), 2.62 (br s, 1H, NH); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.9, 150.0, 133.5 (Ar,

CH), 124.3 (Ar, CH), 123.9, 119.8, 119.1 (Ar, CH), 108.5 (Ar, CH), 91.6 (dd, *J* = 122.2, 87.3 Hz, Ar, C), 88.3 (=CH), 80.4 (dd, *J* = 709.1, 37.1 Hz, Ar, CH_2F), 76.7 (=CH_2), 41.1 (CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –103.5 (d, 1F, *J* = 273.0 Hz), –107.0 (dd, 1F, *J* = 273.0, 14.6 Hz), –230.5 (d, 1F, *J* = 14.6 Hz); IR ($CHCl_3$, cm^{-1}): ν 2930, 1614, 1480, 1260, 1084, 846, 809; HRMS (ES): calcd for $C_{13}H_{12}NF_3$ $[M]^+$: 239.0916; found: 239.0922.

2-(Buta-2,3-dienyl)-3,3-difluoro-2-(fluoromethyl)-5-methylindoline 5m. From 46 mg (0.23 mmol) of aminoallene **2m**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **5m** (30 mg, 51%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.11 (s, 1H, Ar), 6.88 (d, 1H, *J* = 7.9 Hz, Ar), 6.35 (d, 1H, *J* = 8.2 Hz, Ar), 4.96 (m, 1H, *J* = 6.6Hz, =CH), 4.52 (m, 2H, =CH_2), 4.49 (d, 1H, *J* = 2.5 Hz, CH*H*F), 4.33 (d, 1H, *J* = 2.5 Hz, C*H*HF), 3.64 (m, 1H, CH*H*), 3.50 (m, 1H, C*H*H), 2.63 (br s, 1H, NH), 1.96 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.9, 148.0 (t, *J* = 26.1 Hz, Ar, C), 145.7, 134.1 (Ar, CH), 124.7 (Ar, CH), 124.0, 120.0, 108.5 (Ar, CH), 91.8, 88.5 (=CH), 80.7 (dd, *J* = 709.1, 39.3 Hz, Ar, C), 76.6 (=CH_2), 41.4 (CH_2), 20.4 (Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –103.9 (d, 1F, *J* = 273.0 Hz), –106.6 (dd, 1F, *J* = 273.0, 9.6 Hz), –230.5 (d, 1F, *J* = 9.9 Hz); IR ($CHCl_3$, cm^{-1}): ν 2926, 1708, 1486, 1260, 1157, 828; HRMS (ES): calcd for $C_{14}H_{14}NF_3$ $[M]^+$: 253.1072; found: 253.1077.

2-(Buta-2,3-dienyl)-5-chloro-3,3-difluoro-2-(fluoromethyl)indoline 5o. From 67 mg (0.31 mmol) of aminoallene **2o**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **5o** (36 mg, 45%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.22 (d, 1H, *J* = 1.9 Hz, Ar), 6.98 (d, 1H, *J* = 8.1 Hz, Ar), 6.05 (d, 1H, *J* = 8.5 Hz, Ar), 4.82 (qu, 1H, *J* = 6.3Hz, =CH), 4.47 (m, 2H, =CH_2), 4.37 (d, 1H, *J* = 2.3 Hz, CH*H*F), 4.21 (d, 1H, *J* = 2.3 Hz, C*H*HF), 3.48 (m, 1H, CH*H*), 3.32 (m, 1H, C*H*H), 2.50 (br s, 1H, NH); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.8, 148.4 (t, *J* = 26.1 Hz, Ar, C), 133.5 (Ar, CH), 124.5 (Ar, CH), 124.0, 122.9, 121.1, 109.6 (Ar, CH), 92.1 (dd, *J* = 120.0, 87.3 Hz, Ar, C), 87.8 (=CH), 80.4 (dd, *J* = 709.1, 37.1 Hz, Ar, CH_2F), 76.9 (=CH_2), 40.9 (CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –103.5 (d, 1F, *J* = 273.0 Hz), –108.0 (dd, 1F, *J* = 273.0, 9.8 Hz), –230.6 (d, 1F, *J* = 9.8 Hz); IR ($CHCl_3$, cm^{-1}): ν 2925, 1620, 1488, 1260, 1080, 853, 811; HRMS (ES): calcd for $C_{13}H_{11}NClF_3$ [*M*]$^{+}$: 273.0526; found: 273.0530.

2-(Buta-2,3-dienyl)-5-bromo-3,3-difluoro-2-(fluoromethyl)indoline 5p. From 76 mg (0.29 mmol) of aminoallene **2p**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **5p** (50 mg, 54%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.38 (d, 1H, *J* = 1.7 Hz, Ar), 7.13 (d, 1H, *J* = 9.8 Hz, Ar), 6.02 (d, 1H, *J* = 8.5 Hz, Ar), 4.85 (m, 1H, *J* = 6.4 Hz, =CH), 4.48 (m, 2H, =CH_2), 4.39 (t, 1H, *J* = 2.55 Hz, CH*H*F), 4.24 (t, 1H, *J* = 2.6 Hz, C*H*HF), 3.52 (m, 1H, CH*H*), 3.34 (m, 1H, C*H*H), 3.02 (br s, 1H, NH); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.9, 148.8 (t, *J* = 26.2 Hz, Ar, C), 136.2 (Ar, CH), 128.0 (Ar, CH), 121.7 (t, *J* = 25.1 Hz, Ar, C), 110.5, 110.0 (Ar, CH), 92.0 (dd, *J* = 171.3, 85.5 Hz, Ar, C), 87.8 (=CH), 81.6 (dd, *J* = 709.9, 37.8 Hz, Ar, CH_2F), 76.9 (=CH_2), 40.9(CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –102.2 (d, 1F, *J* = 257.2 Hz), –107.0 (dd, 1F, *J* = 257.4, 9.6 Hz), –229.4 (d, 1F, *J* = 9.2 Hz); IR ($CHCl_3$, cm^{-1}): ν 2923, 1608, 1476, 1256, 1059, 867, 805; HRMS (ES): calcd for $C_{13}H_{11}NBrF_3$ [*M*]$^{+}$: 317.0021; found: 317.0041.

2-(Buta-2,3-dienyl)-3,3-difluoro-5-nitro-2-(fluoromethyl)indoline 5q. From 50 mg (0.22 mmol) of aminoallene **2q**, 57 mg (91%) of compound **5q** was obtained as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 8.16 (dd, 1H, *J* = 3.7, 1.8Hz, Ar), 7.89 (dd, 1H, *J* = 9.0, 2.2 Hz, Ar), 5.89 (d, 1H, *J* = 9.0 Hz, Ar), 4.81 (m, 1H, *J* = 6.5 Hz, =CH), 4.51 (m, 2H, =CH_2), 4.48 (m, 1H, CH*H*F), 4.19 (d, 1H, C*H*HF), 3.51 (m, 1H, CH*H*), 3.35 (m, 1H, C*H*H); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 208.9, 153.7, 140.2, 130.3 (Ar, CH), 121.8, 121.1(Ar, CH), 119.6 (t, *J* = 101.3 Hz, Ar, C), 107.0 (Ar, CH), 92.3 (dd, *J* = 205.5, 84.2 Hz, Ar, C), 86.9 (=CH), 80.0 (dd, *J* = 712.7, 37.3 Hz, Ar, CH_2F), 77.3 (=CH_2), 40.3 (CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –100.9 (d, 1F, *J* = 258.9 Hz), –110.8 (dd, 1F, *J* = 258.9, 12.5 Hz), –230.0 (d, 1F, *J* = 12.3 Hz); IR ($CHCl_3$, cm^{-1}): ν 2940, 1680, 1474, 1264, 1080, 846, 800; HRMS (ES): calcd for $C_{13}H_{11}N_2O_2F_3$ $[M]^+$: 284.0767; found: 284.0791.

Procedure for the Pd(II)-Catalyzed Cyclization of 2-Allenyl-1*H*-indoles 3 in Presence of Allyl Bromide. Preparation of 7-allyl-9a-(4-substituted)-10,10-difluoro-6,9,9a,10-tetrahydropyrido[1,2-*a*]indoles 11. Palladium(II) chloride (0.004 mmol) was added to a stirred solution of the appropriate β-aminoallene **3** (0.08 mmol) and allyl bromide (0.40 mmol) in *N*,*N*-dimethylformamide (0.5 mL). The reaction was stirred under argon atmosphere until disappearance of the starting material (TLC, 24 h). Water (0.4 mL) was added before being extracted with ethyl acetate (3 x 4 mL). The organic phase was washed with water (2 x 2 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave adducts **11**.

10,10-Difluoro-tetrahydropyrido[1,2-*a*]indole 11a. From 48 mg (0.17 mmol) of β-aminoallene **3a**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **11a** (28 mg, 50%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.66 (d, 2H, *J* = 7.7 Hz, Ar), 6.93 (m, 6H, Ar), 6.73 (d, 1H, *J* = 7.9 Hz, Ar), 5.58 (m, 1H, =CH), 4.92 (m, 2H, =CH_2), 4.88 (dd, 2H, *J* = 11.3, 1.4 Hz, CH_2), 3.38 (dd, 2H, *J* = 11.1, 2.9 Hz, CH_2), 3.37 (s, 2H, CH_2), 2.42 (d, 2H, *J* = 6.3 Hz, CH_2); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 138.4, 135.5, 135.0 (Ar,

CH), 134.2, 132.2 (Ar, 2CH), 129.1 (Ar, CH), 128.6 (Ar, 2CH), 128.0 (=CH), 126.5 (=CH), 125.9 (Ar, CH), 124.6 (Ar, CH), 120.0 (Ar, CH), 116.4 (=CH_2), 115.6, 114.9, 62.4 (CH_2), 60.7 (CH_2), 33.4 (CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –92.6 (s, 2F); IR (C_6D_6, cm^{-1}): ν 2927, 1703, 1499, 1256, 1180, 840, 810; HRMS (ES): calcd for $C_{21}H_{19}F_2N$ [*M*]$^+$: 323.1480; found: 323.1469.

10,10-Difluoro-tetrahydropyrido[1,2-*a*]indole 11b. From 26 mg (0.08 mmol) of β-aminoallene **3b**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **11b** (13 mg, 46%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.87 (d, 1H, *J* = 7.9 Hz), 7.67 (d, 2H, *J* = 8.5 Hz), 7.50 (t, 1H, *J* = 7.5 Hz); 7.37 (t, 1H, *J* = 7.5 Hz), 7.28 (d, 2H, *J* = 8.6 Hz), 7.22 (d, 1H, *J* = 8.0 Hz), 5.76 (m, 1H), 5.25 (br s, 1H), 5.05 (m, 2H), 3.47 (br s, 2H), 3.38 (br s, 2H), 2.72 (d, 2H, *J* = 6.0 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 148.9, 138.7, 138.2, 134.6, 133.5, 132.4, 132.3, 131.8, 129.6, 128.5 (2C), 126.2 (2C), 125.2, 124.4, 119.6, 116.6, 78.5, 62.1, 60.6, 33.2; ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –95.5 (d, 1F, *J* = 263.2 Hz), –111.6 (d, 1F, *J* = 263.3 Hz); HRMS (ES): calcd for $C_{21}H_{18}ClF_2N$ [*M*]$^+$: 357.1090; found: 357.1089.

10,10-Difluoro-tetrahydropyrido[1,2-*a*]indole 11l. From 30 mg (0.14 mmol) of β-aminoallene **3l**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **11l** (28 mg, 32%) as a colorless oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ^{o}C) δ: 7.71 (d, 2H, *J* = 7.8 Hz, Ar), 7.05 (t, 1H, *J* = 7.3 Hz, Ar), 6.88 (dd, 1H, *J* = 12.4, 7.8 Hz, Ar), 5.62 (m, 1H, =CH), 4.98 (m, 2H, =CH_2), 4.97 (m, 2H, CH_2), 3.60 (dd, 2H, *J* = 19.2, 2.7 Hz, CH_2), 3.59 (m, 2H, CH_2), 2.47 (d, 2H, *J* = 6.0 Hz, CH_2), 2.12 (d, 3H, *J* = 1.2 Hz, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ^{o}C) δ: 138.9, 135.0 (Ar, CH), 132.3 (=CH), 128.9, 126.9 (=CH), 126.2 (Ar, CH), 125.7 (Ar, CH), 125.1, 124.9, 120.4 (Ar, CH), 116.6 (=CH_2), 63.5 (CH_2), 62.1 (CH_2), 33.4 (CH_2), 23.6 (Me); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –99.7 (s, 2F); IR (C_6D_6, cm^{-1}): ν 2935, 1634, 1474, 1245, 1056, 840; HRMS (ES): calcd for $C_{16}H_{17}F_2N$ [*M*]$^+$: 261.1323; found: 261.1348.

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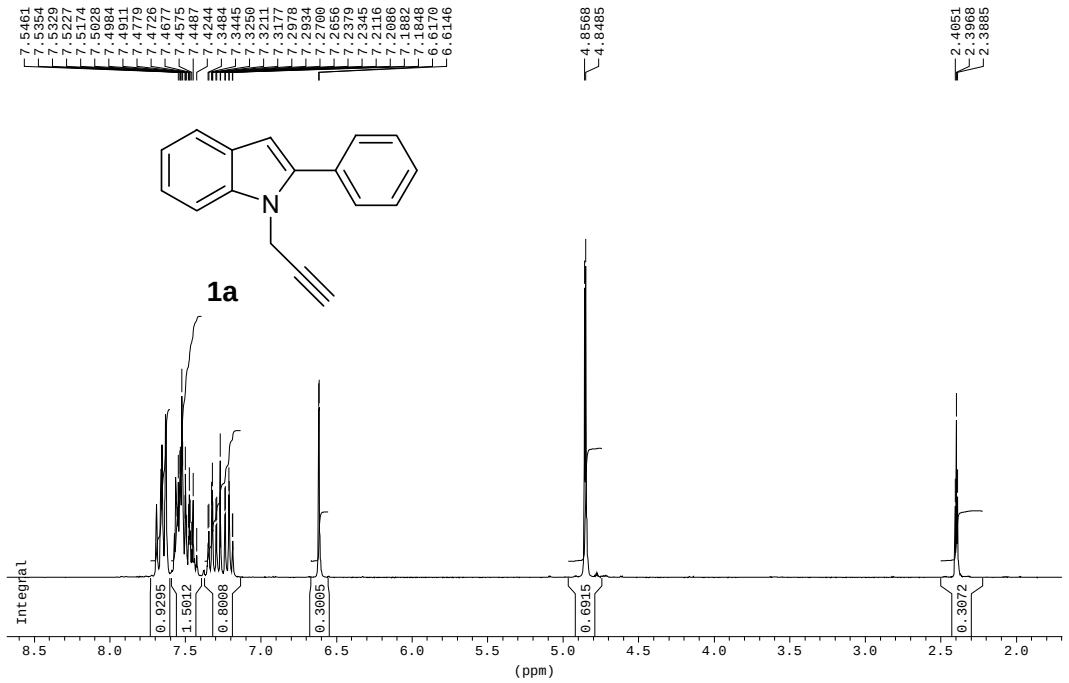

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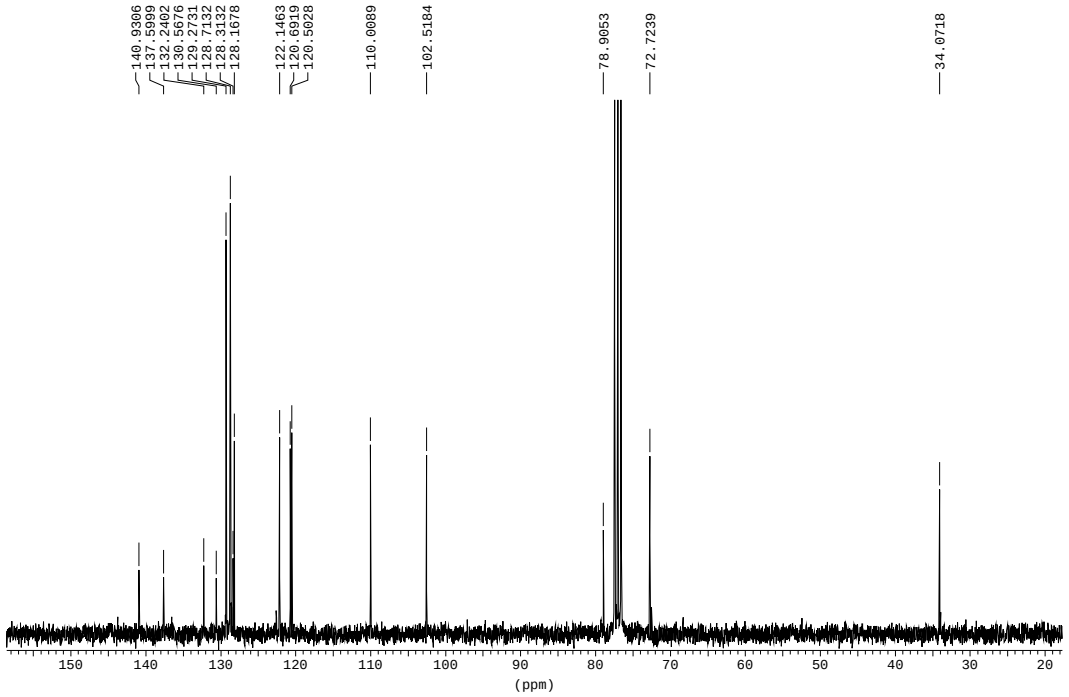

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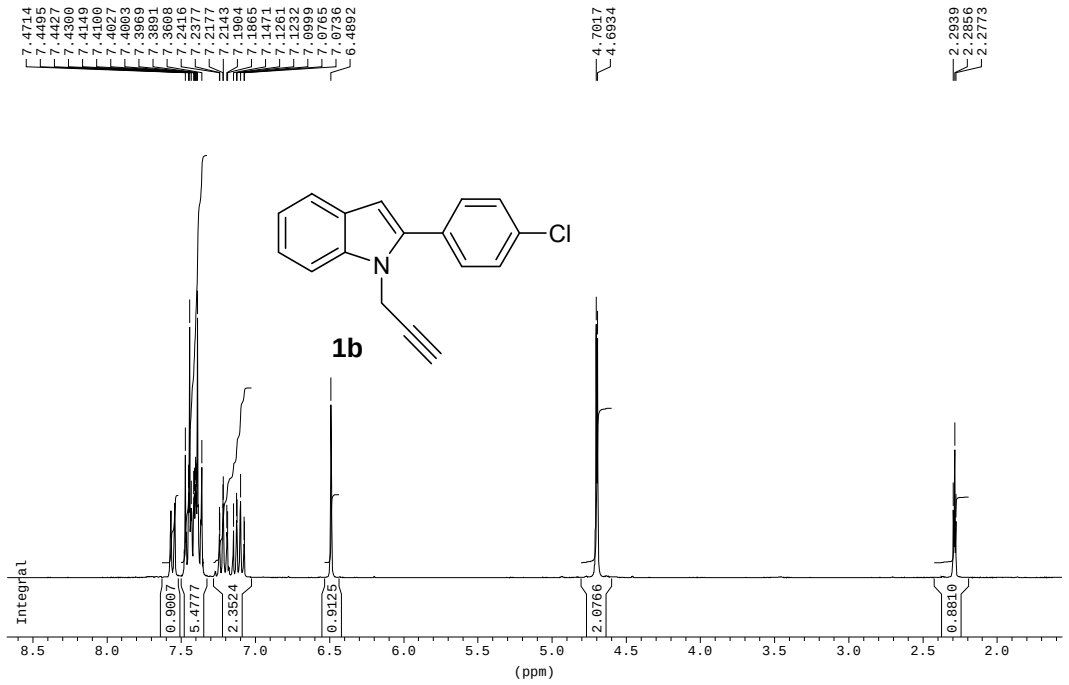

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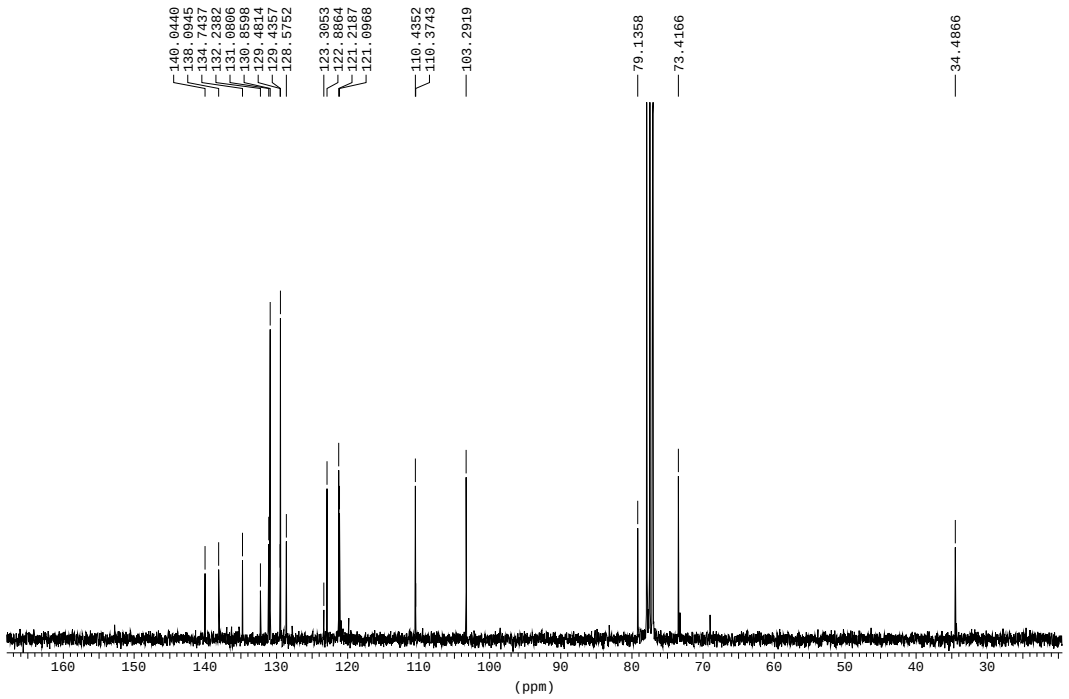

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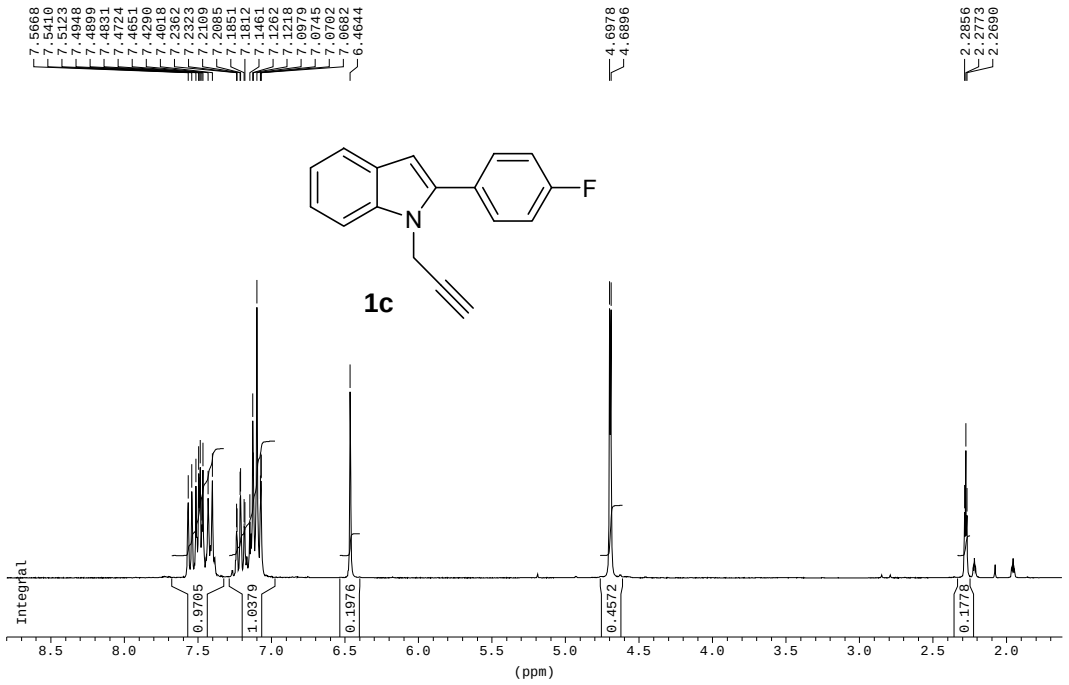

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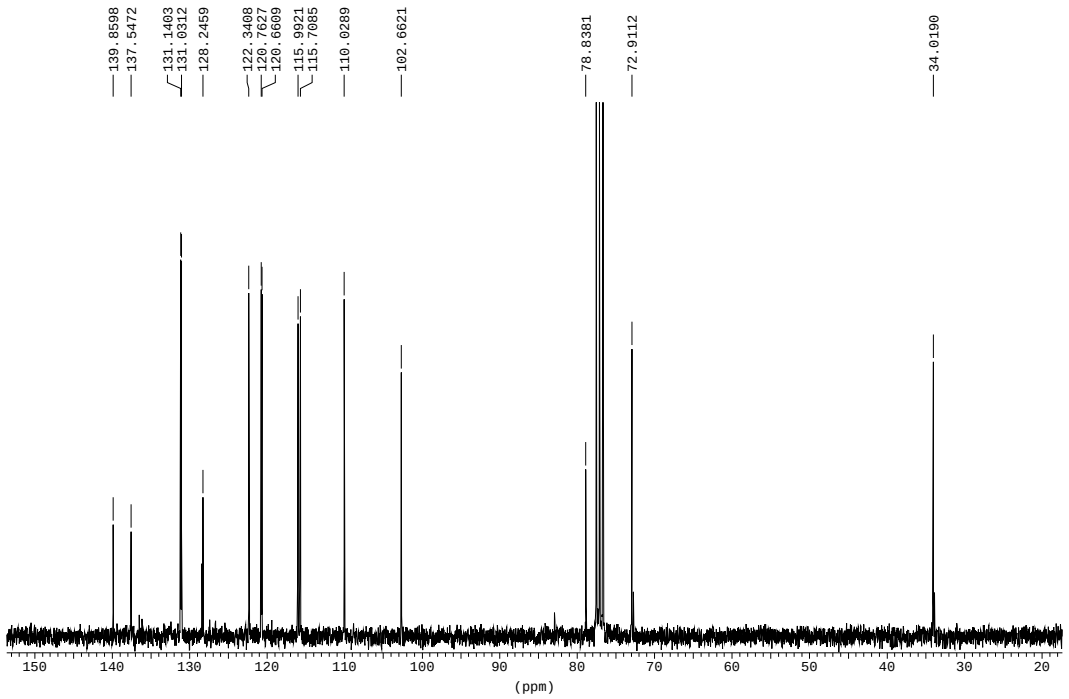

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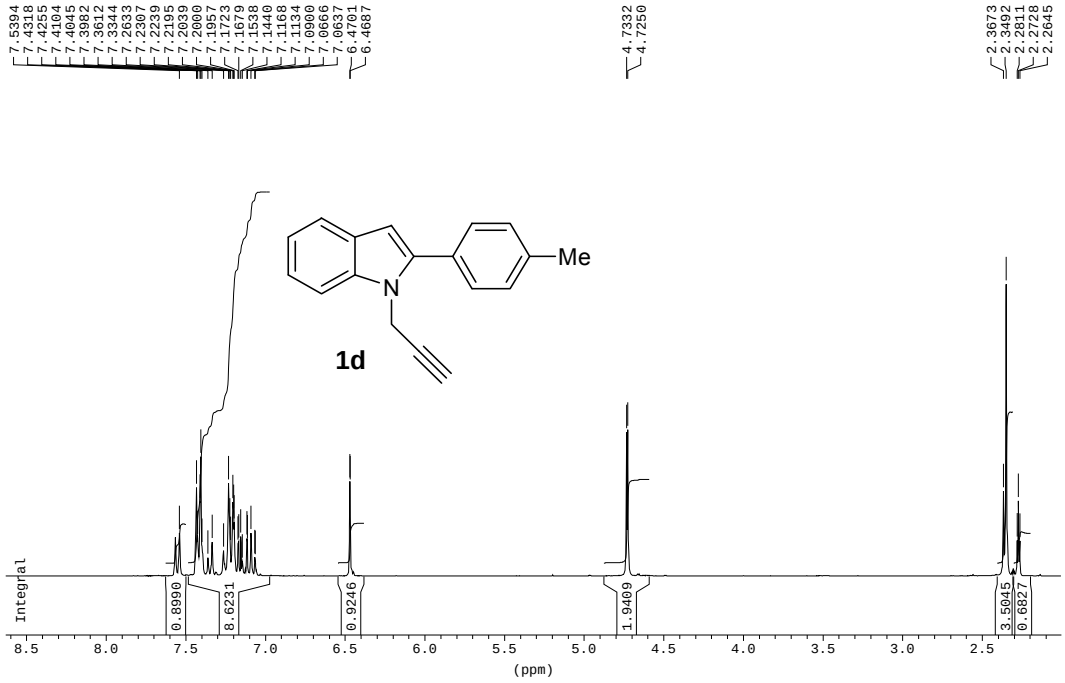

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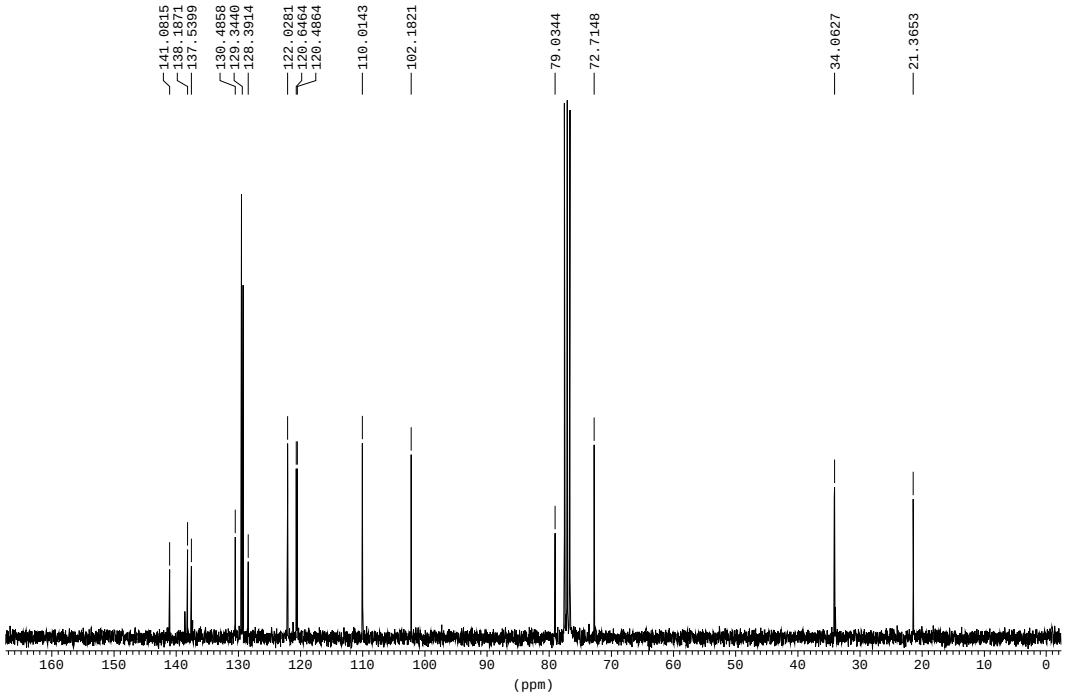

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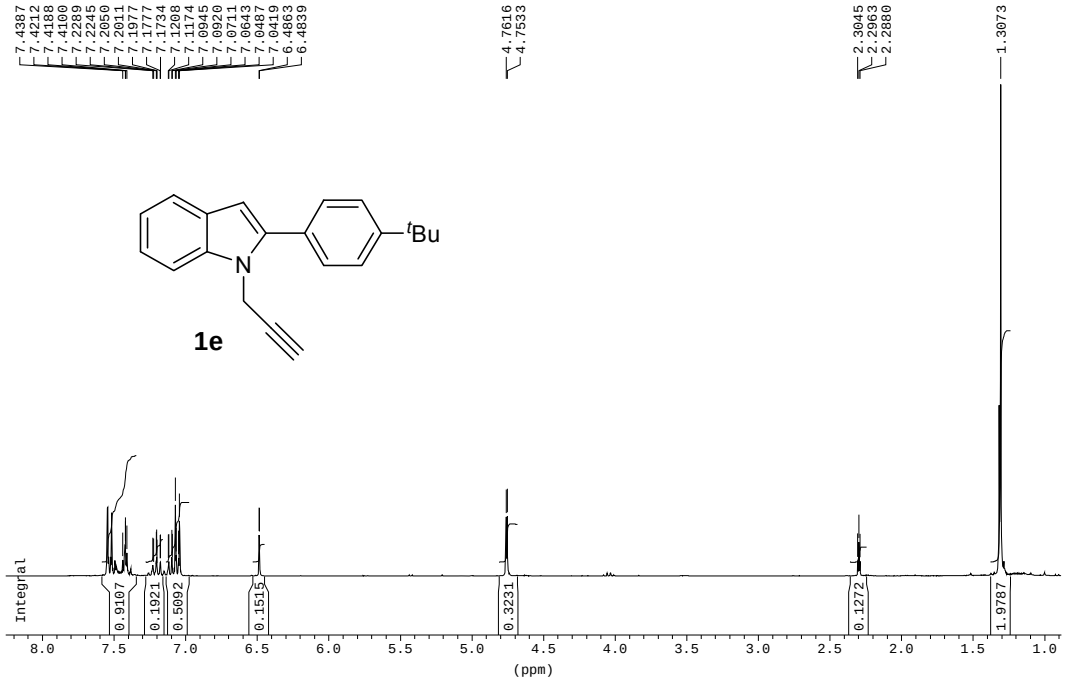

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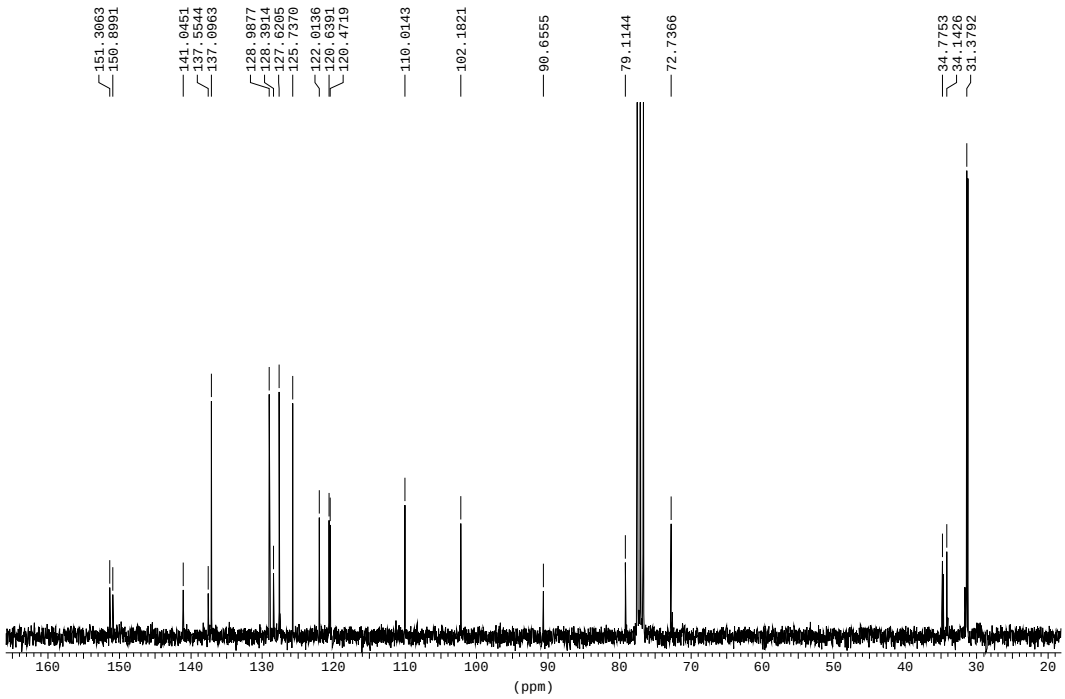

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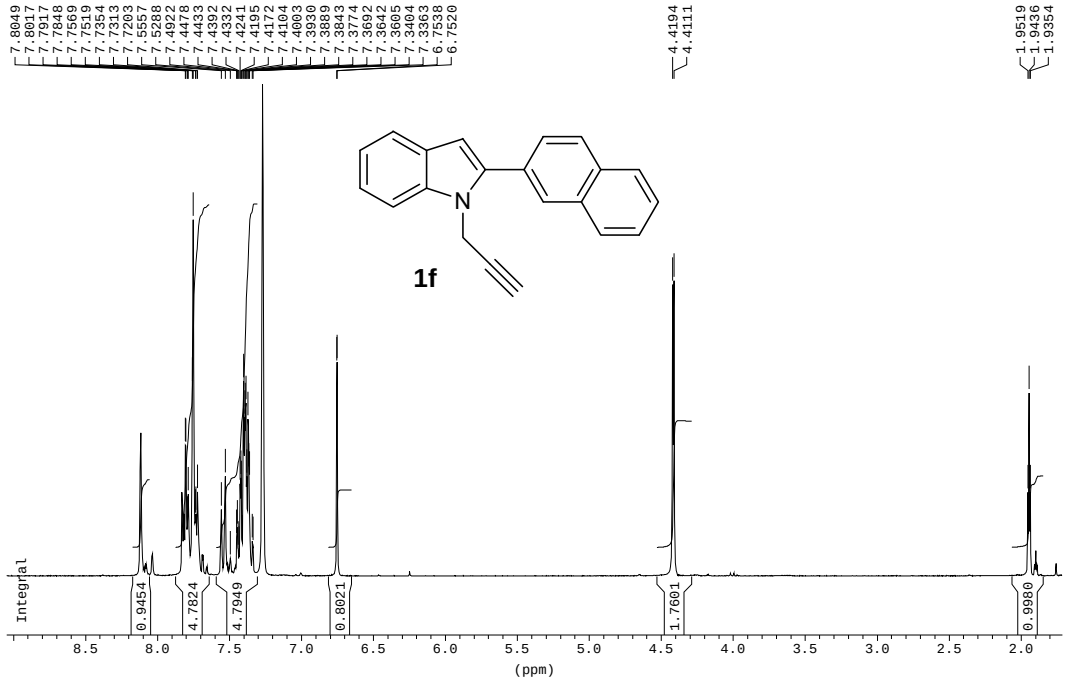

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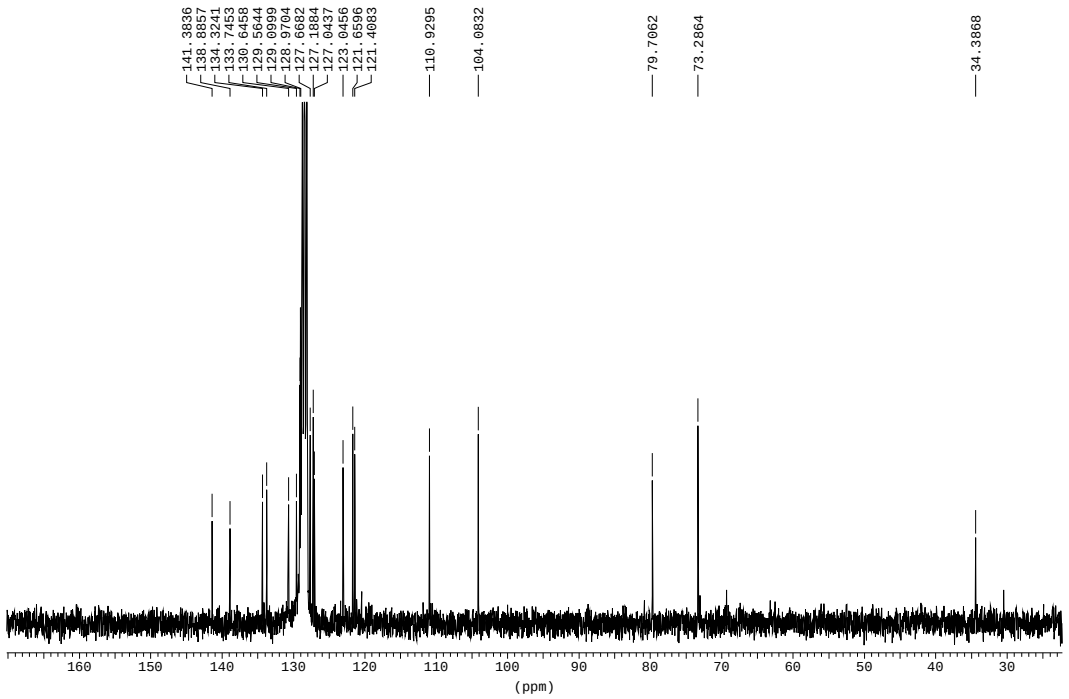

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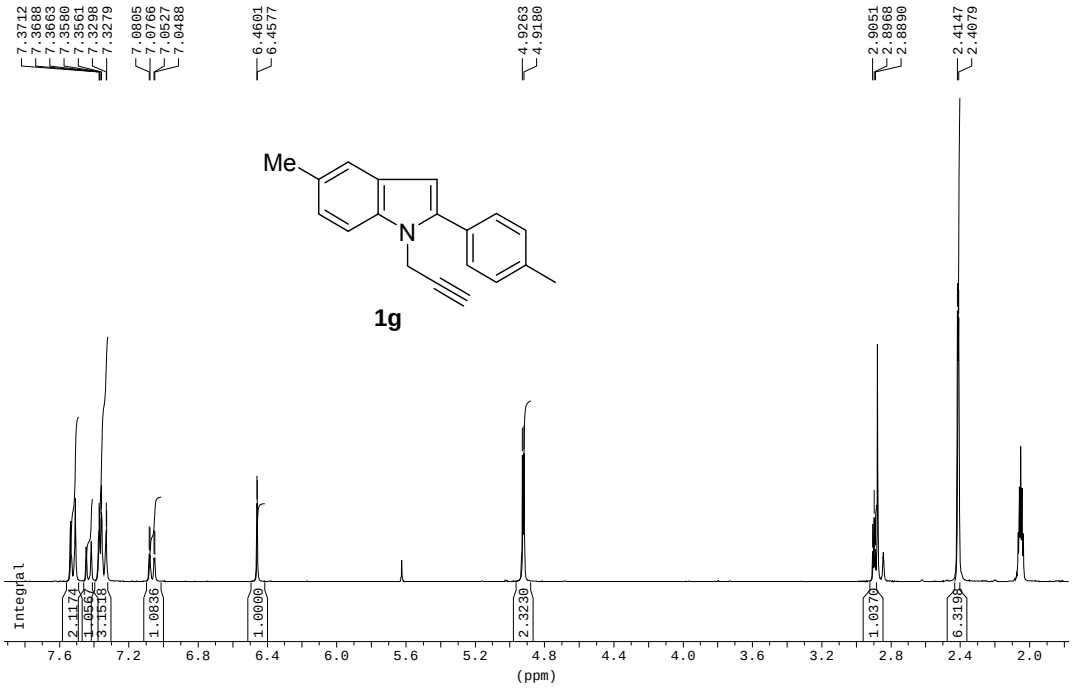

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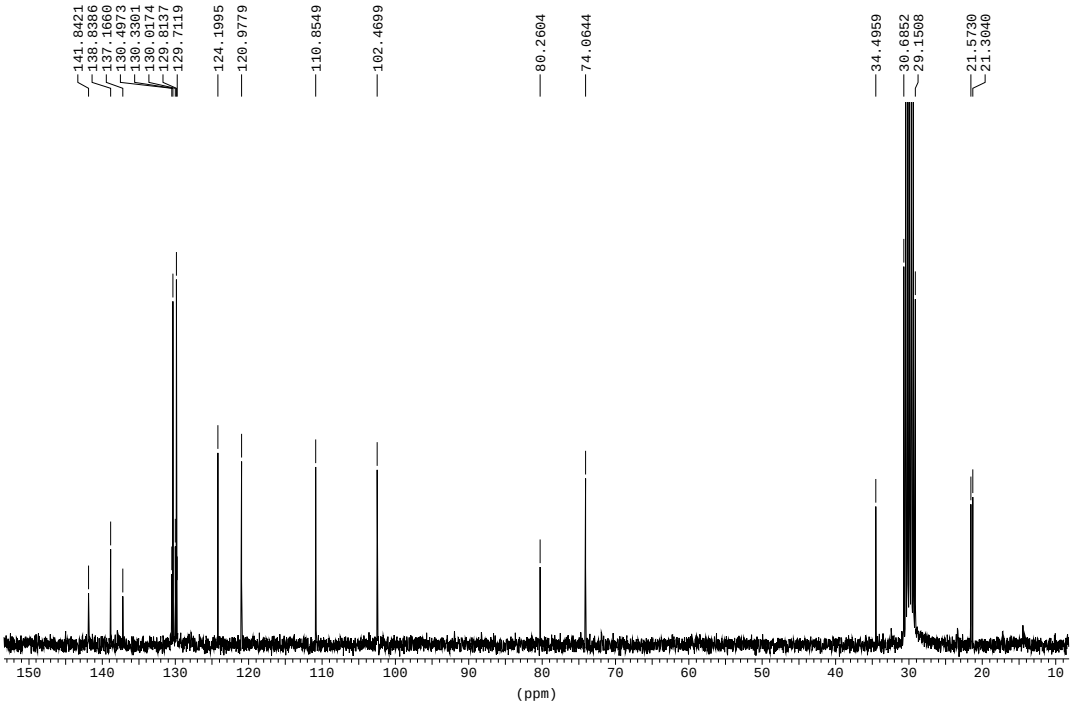

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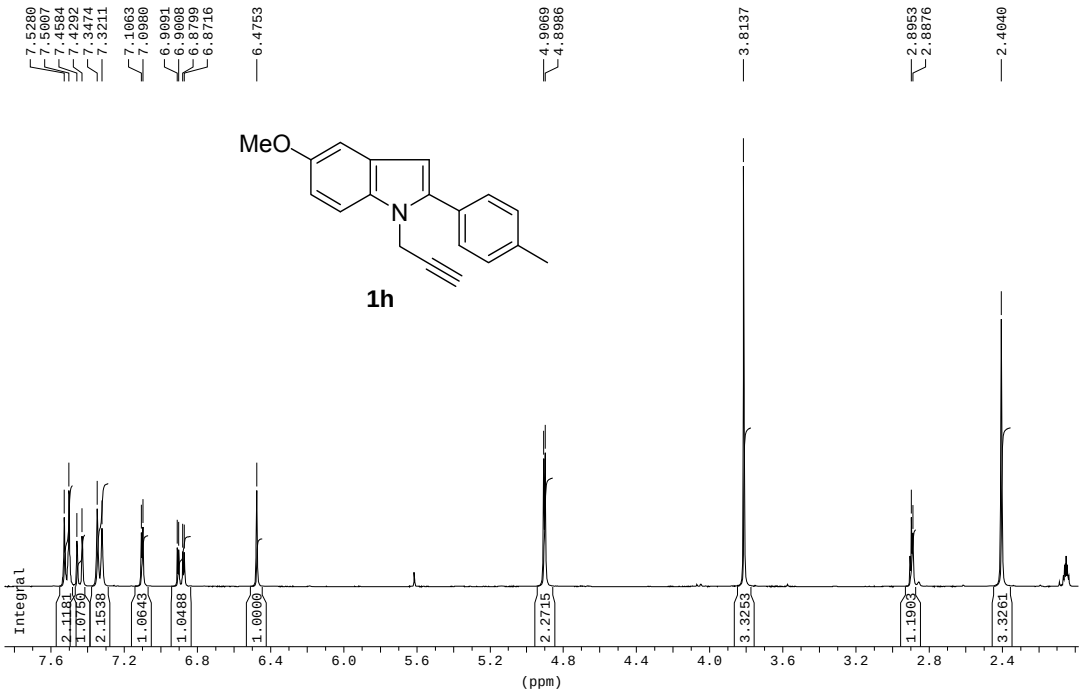

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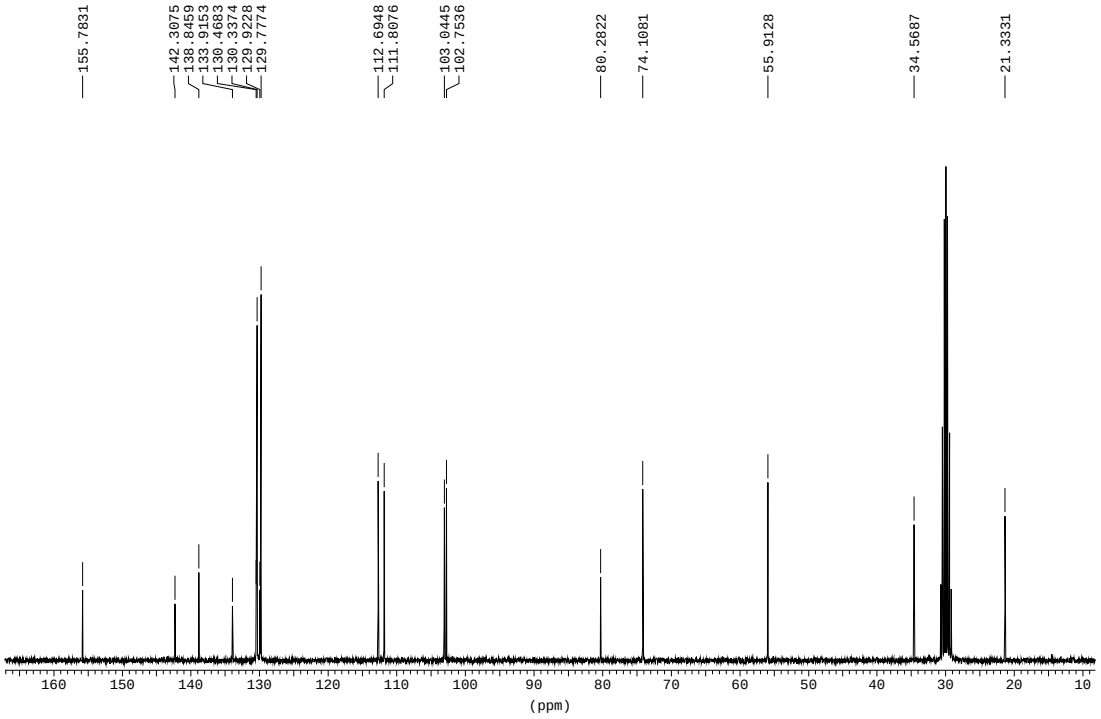

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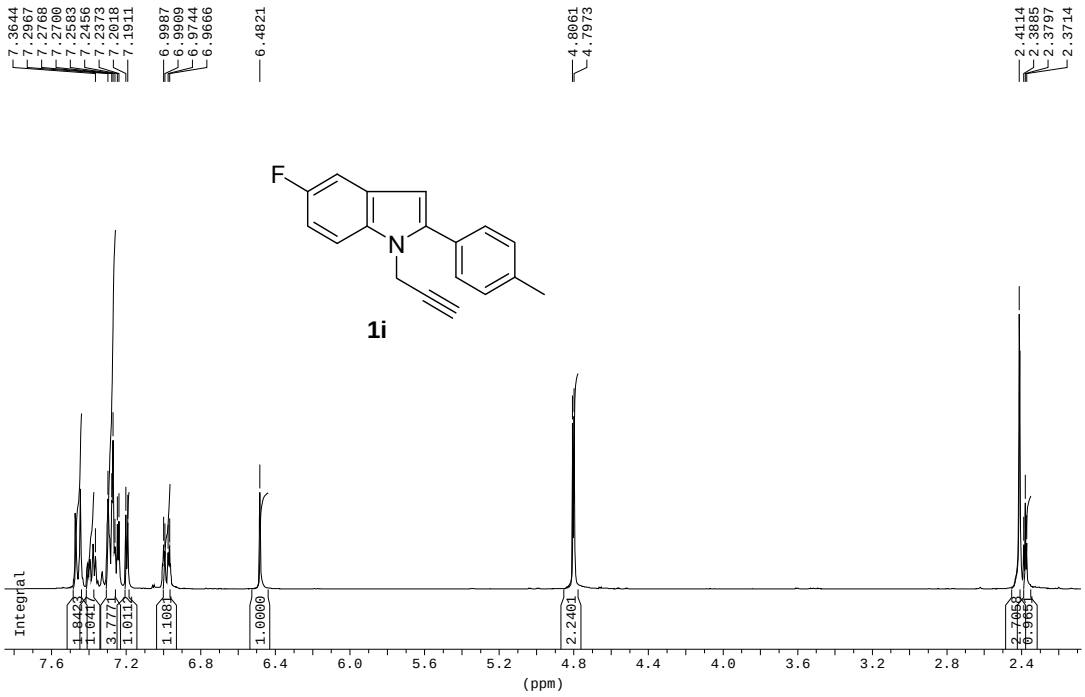

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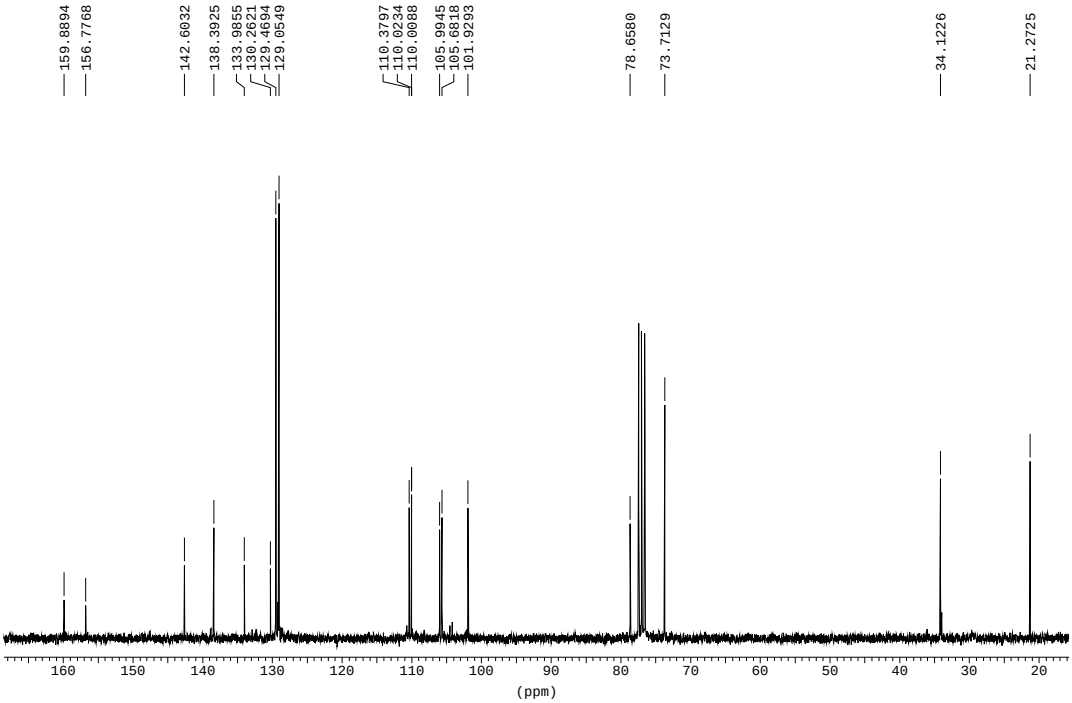

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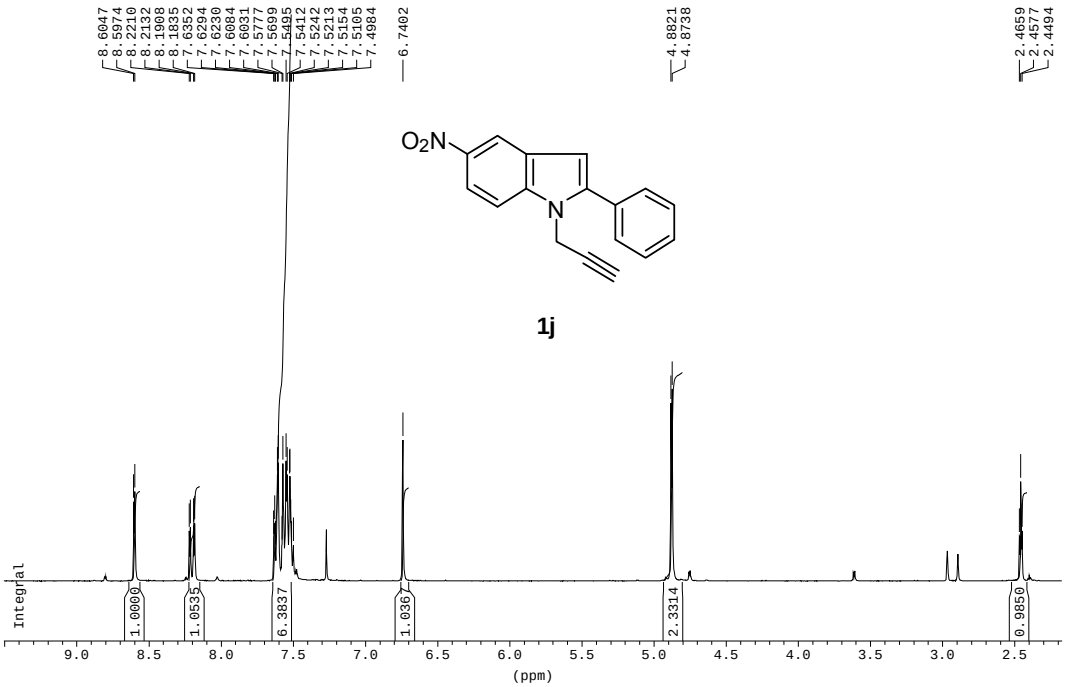

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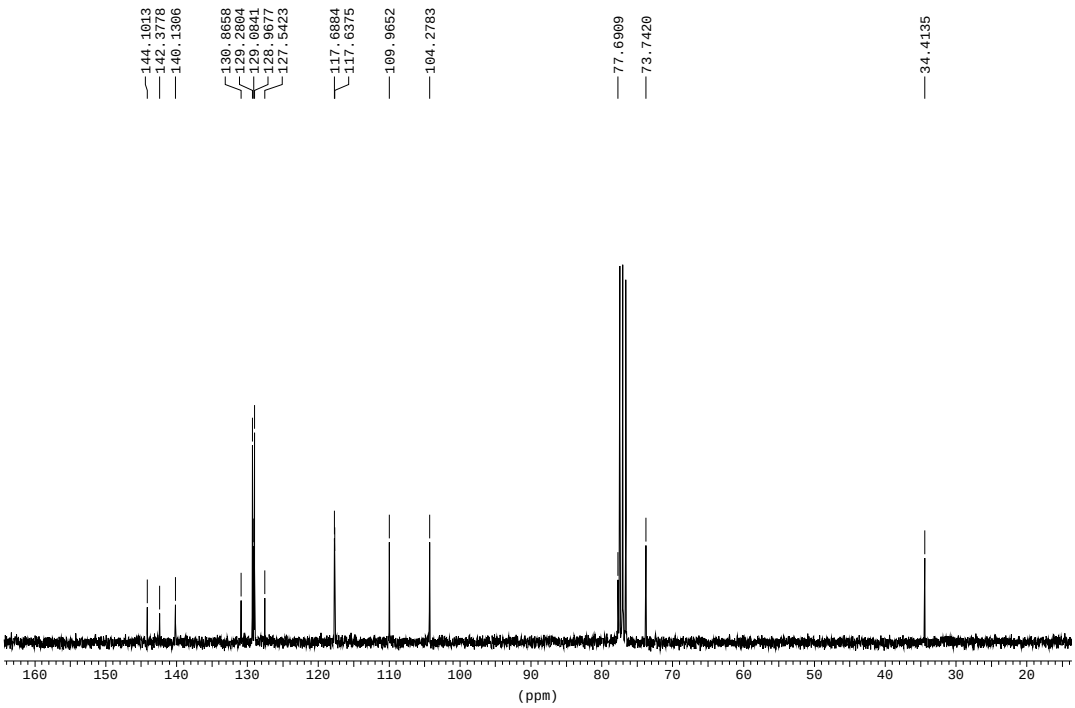

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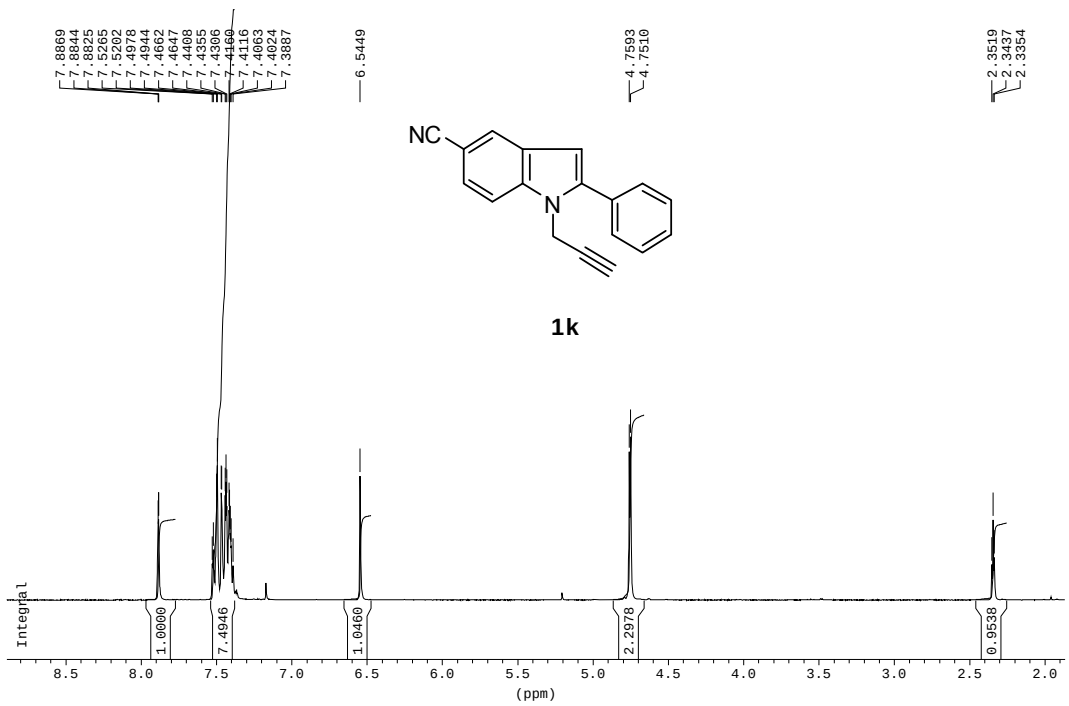

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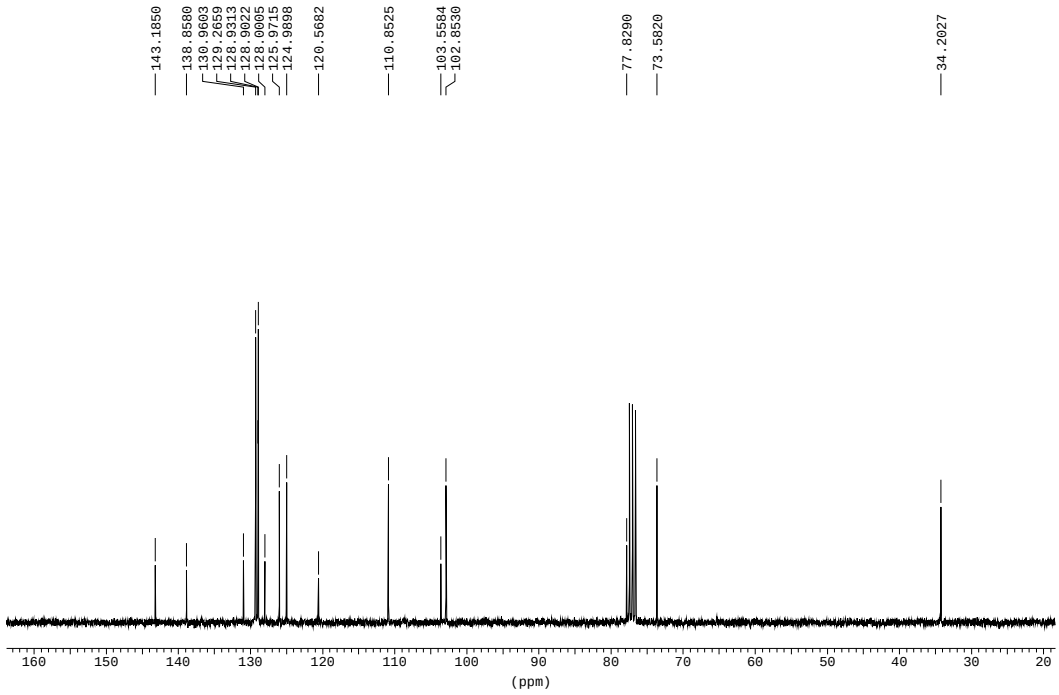

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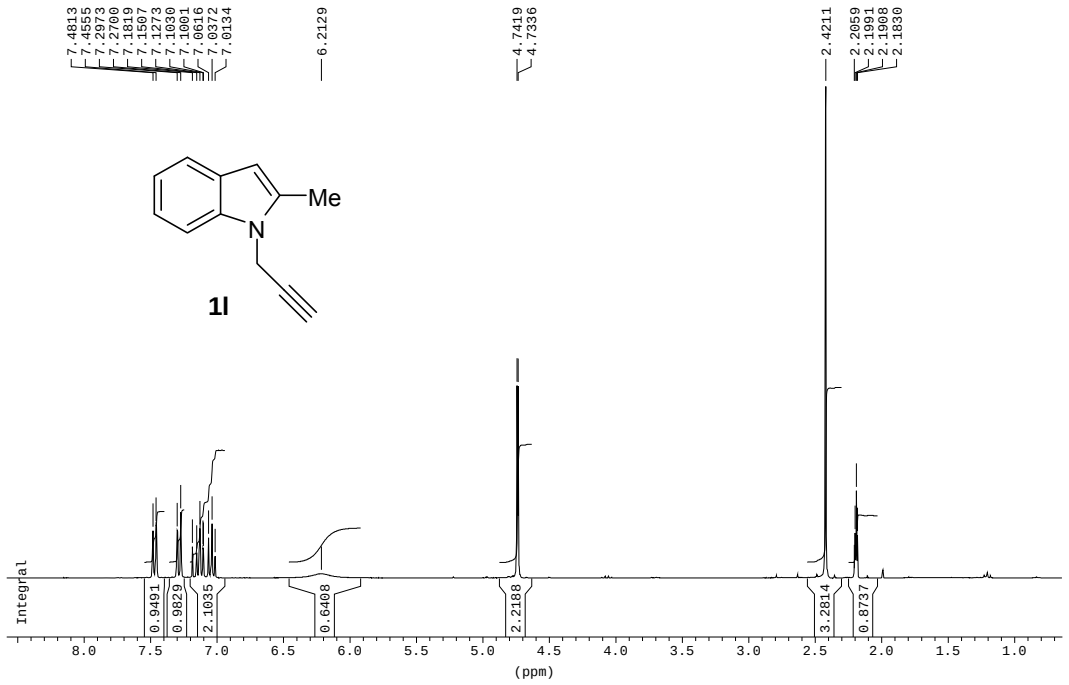

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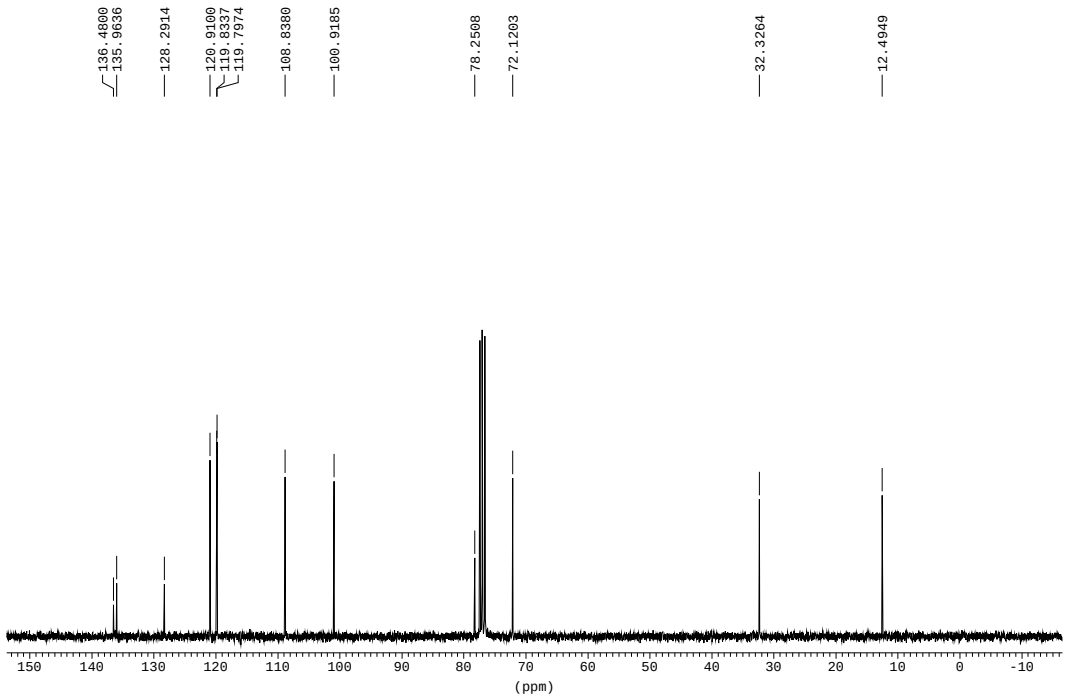

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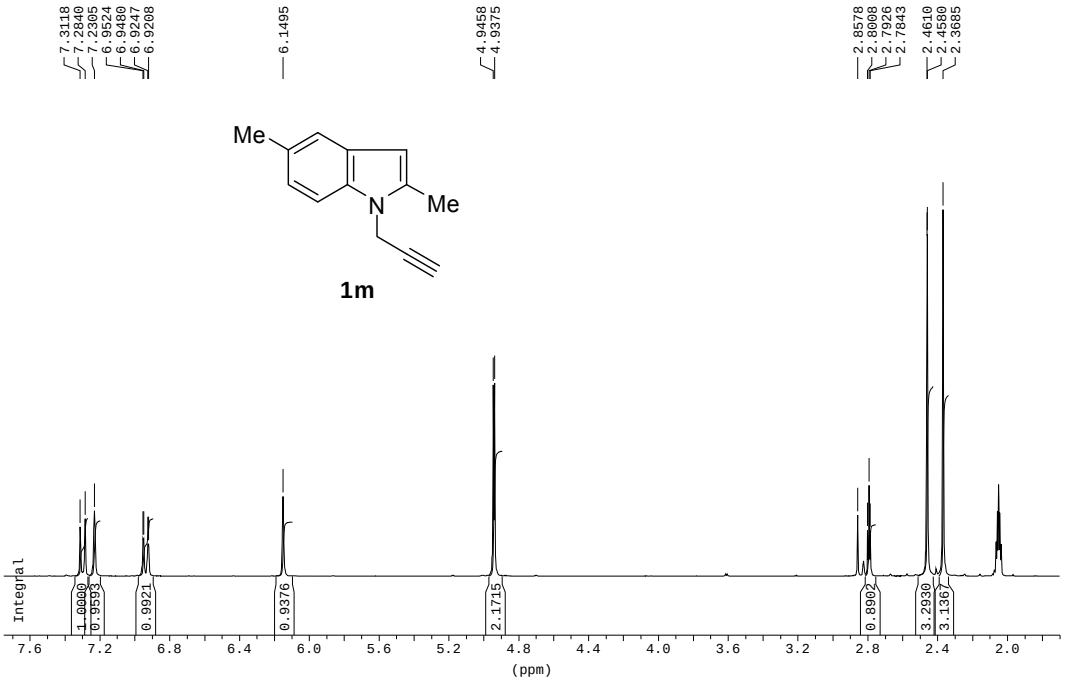

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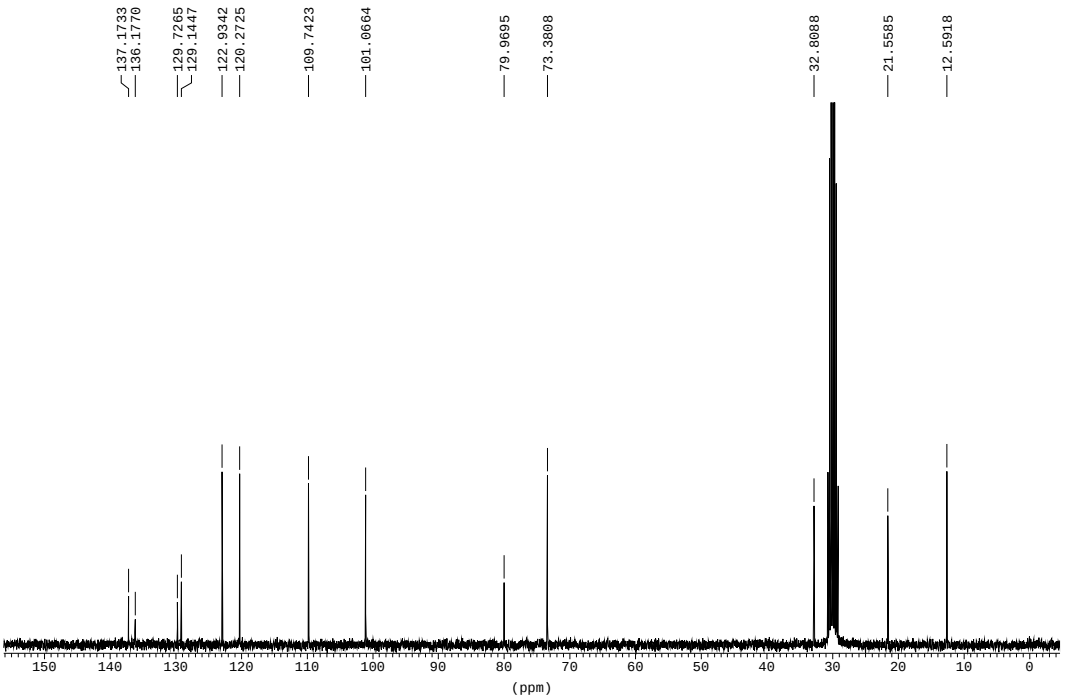

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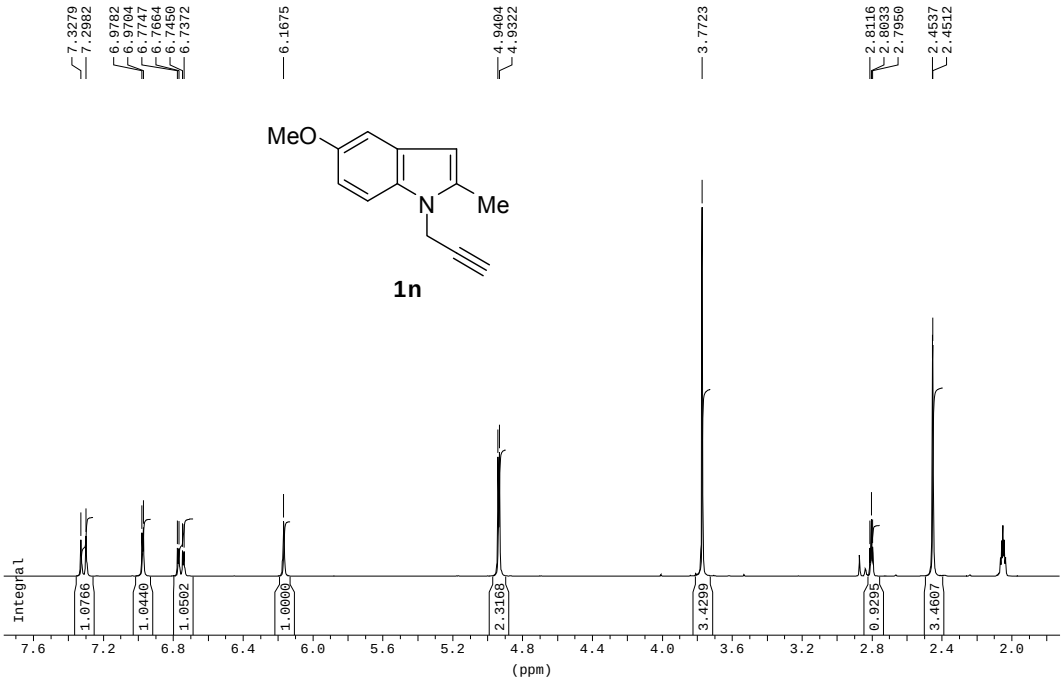

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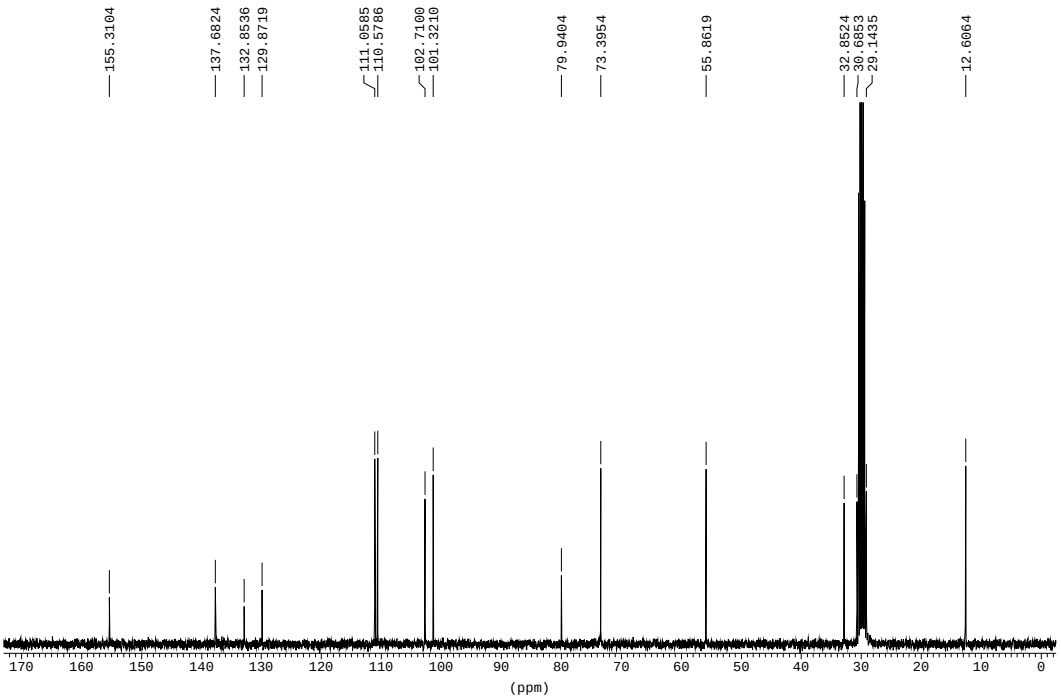

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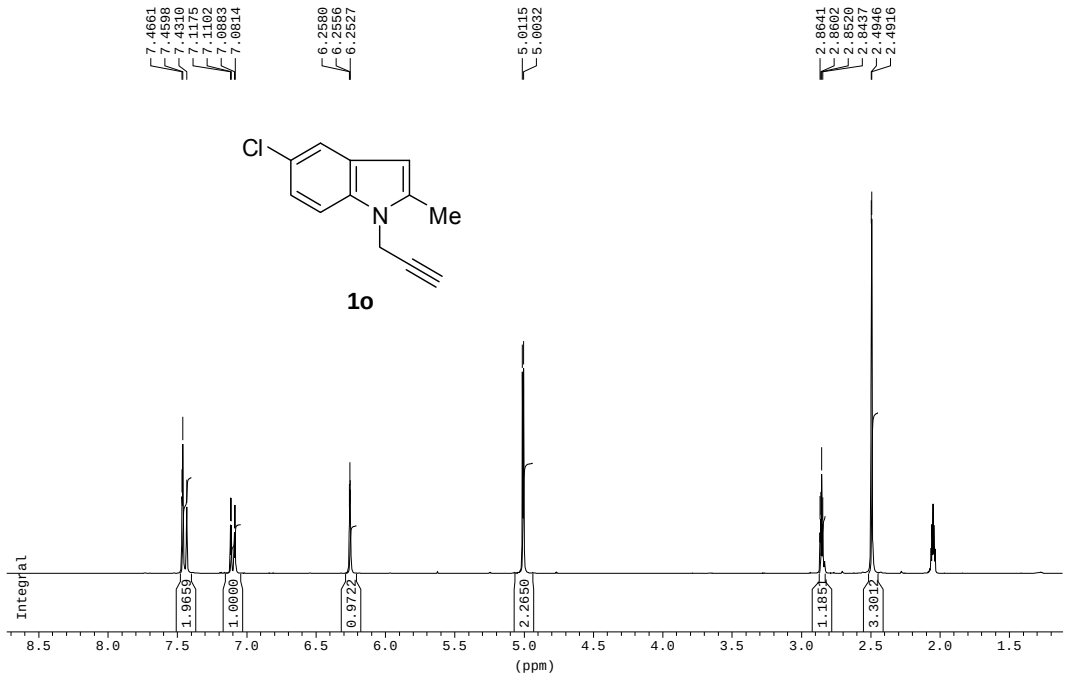

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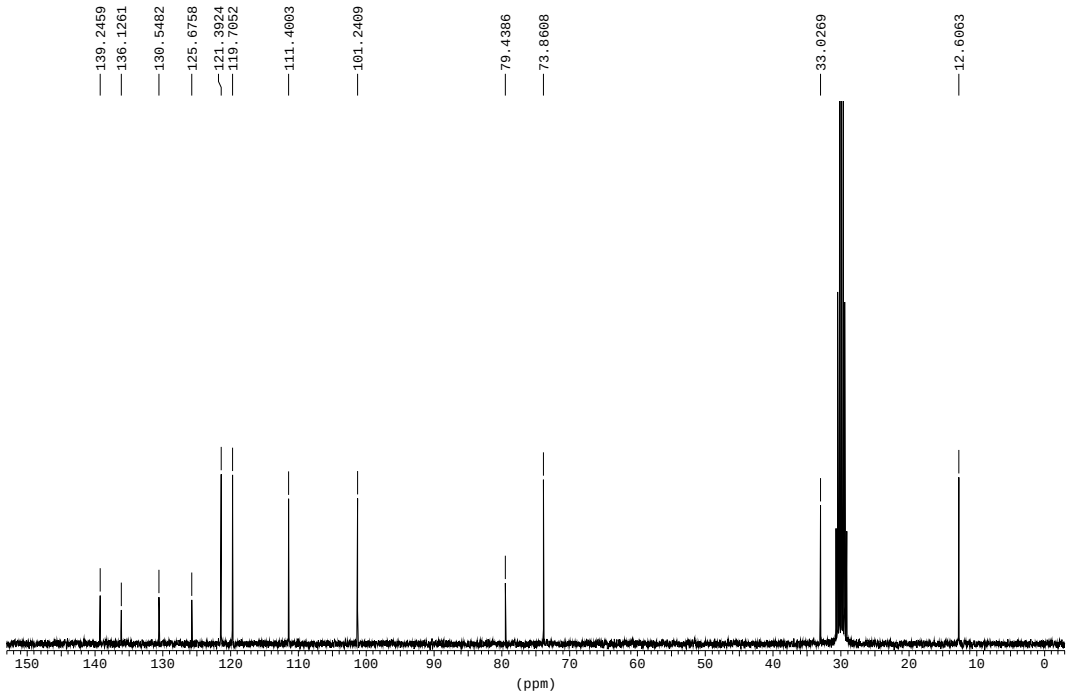

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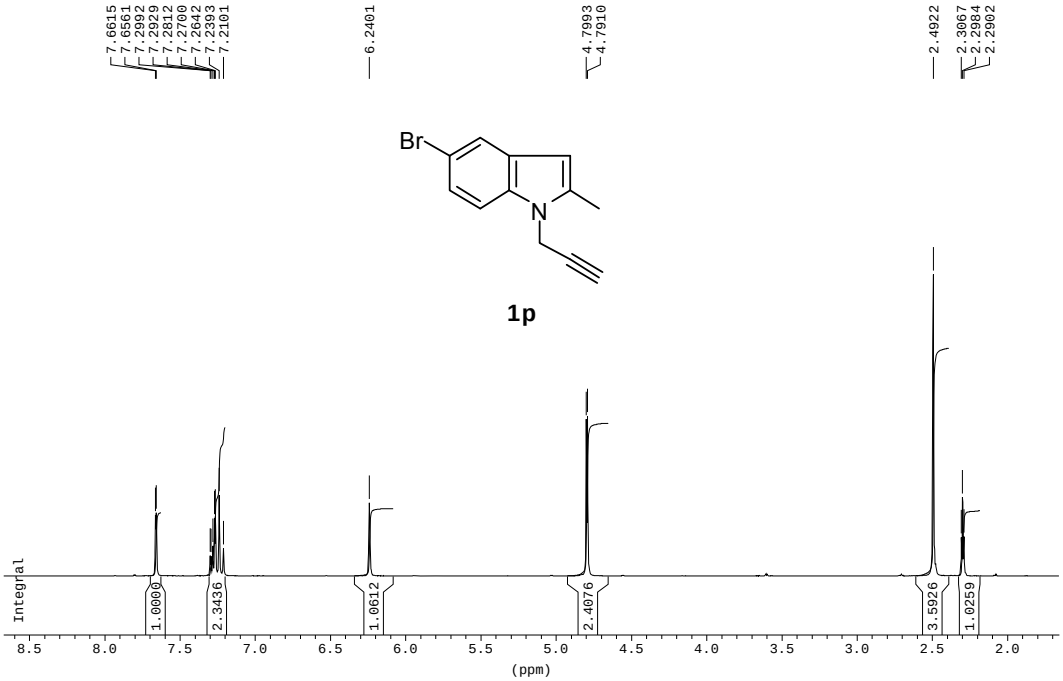

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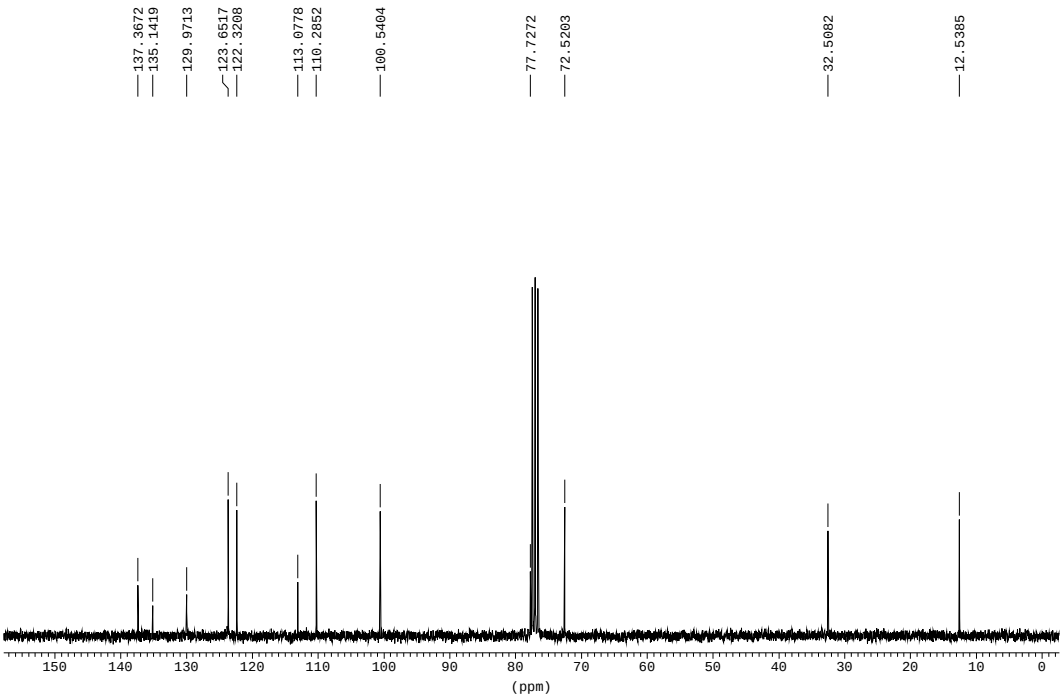

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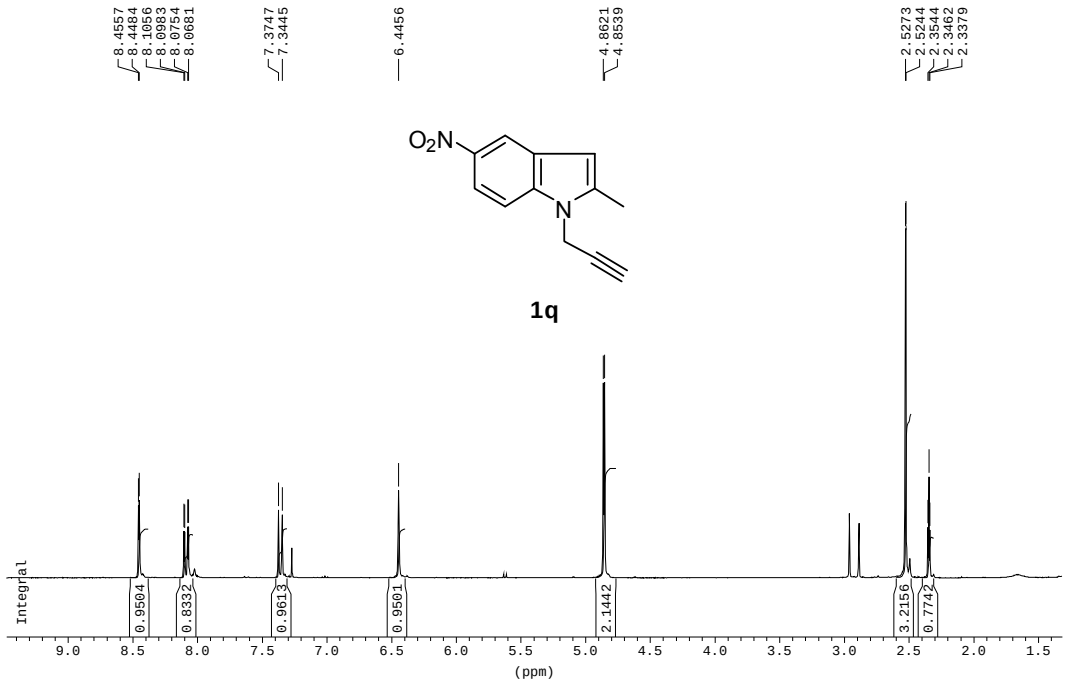

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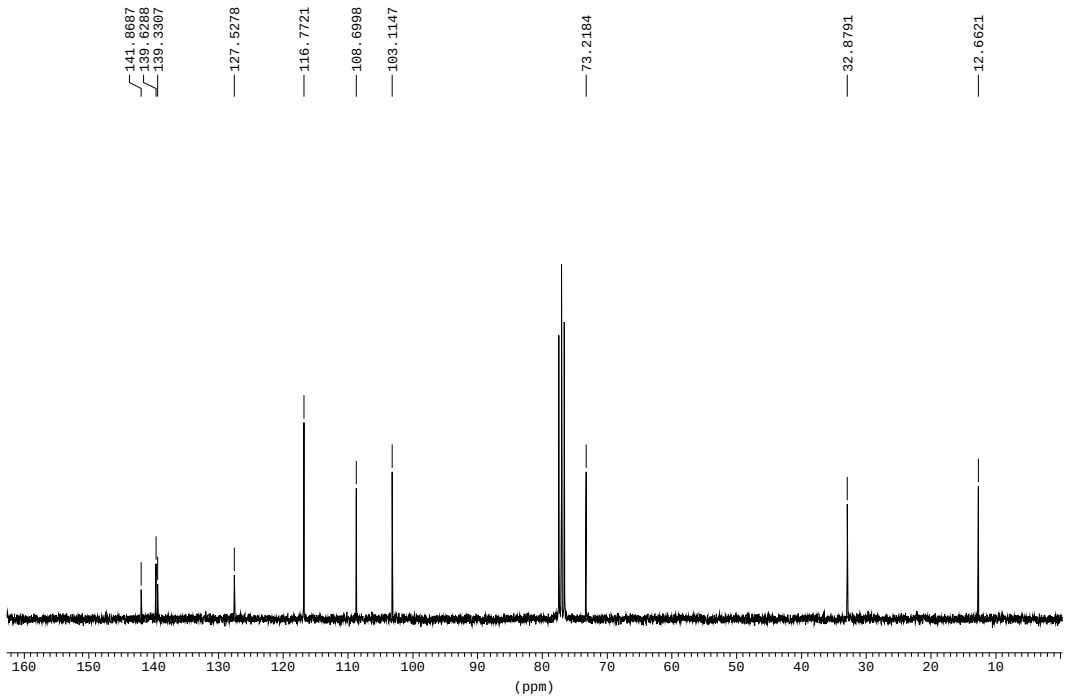

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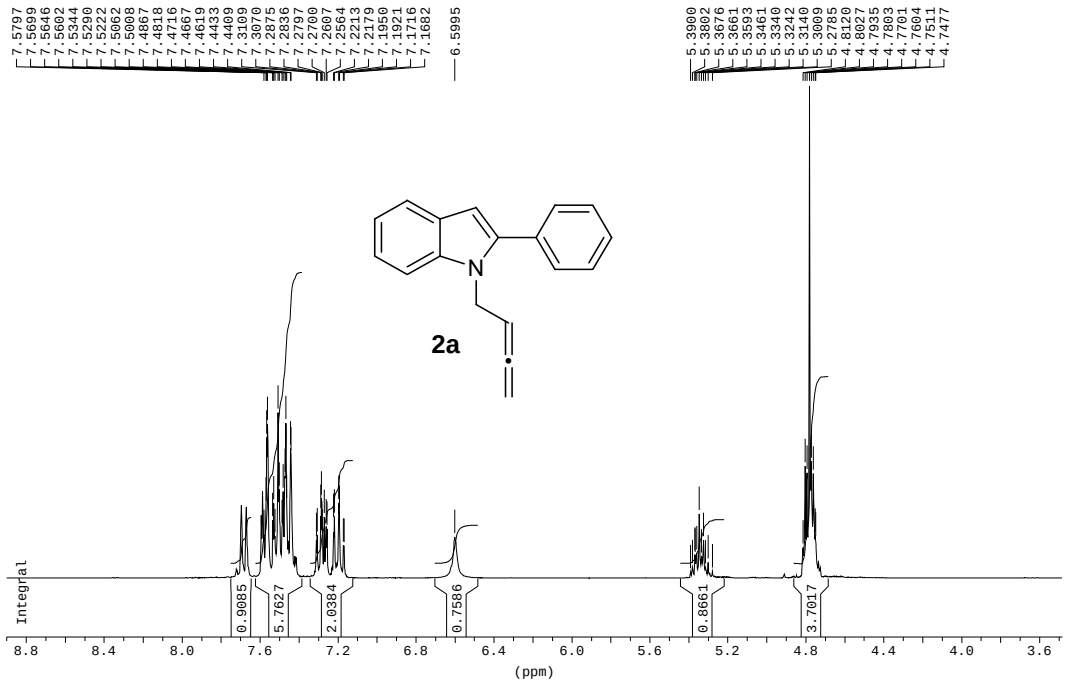

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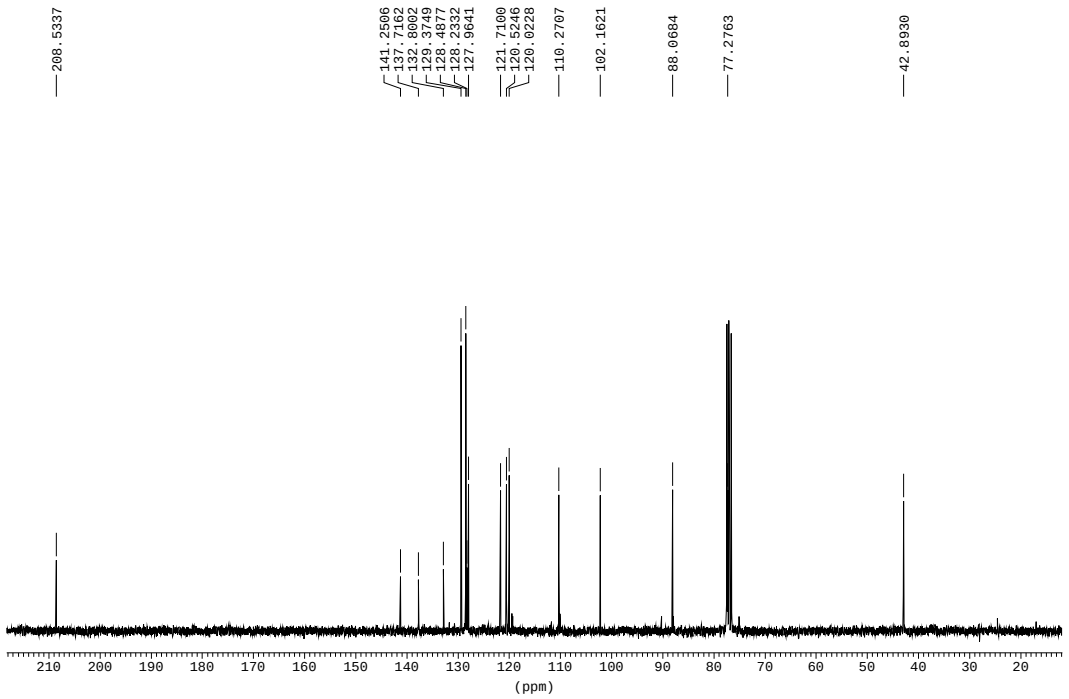

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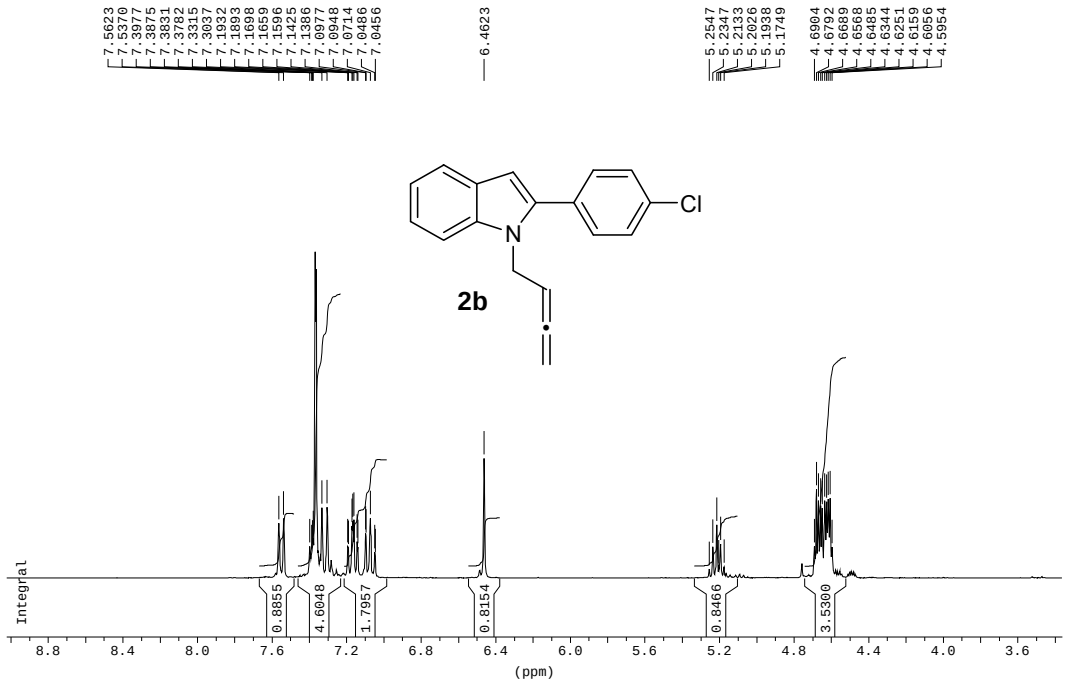

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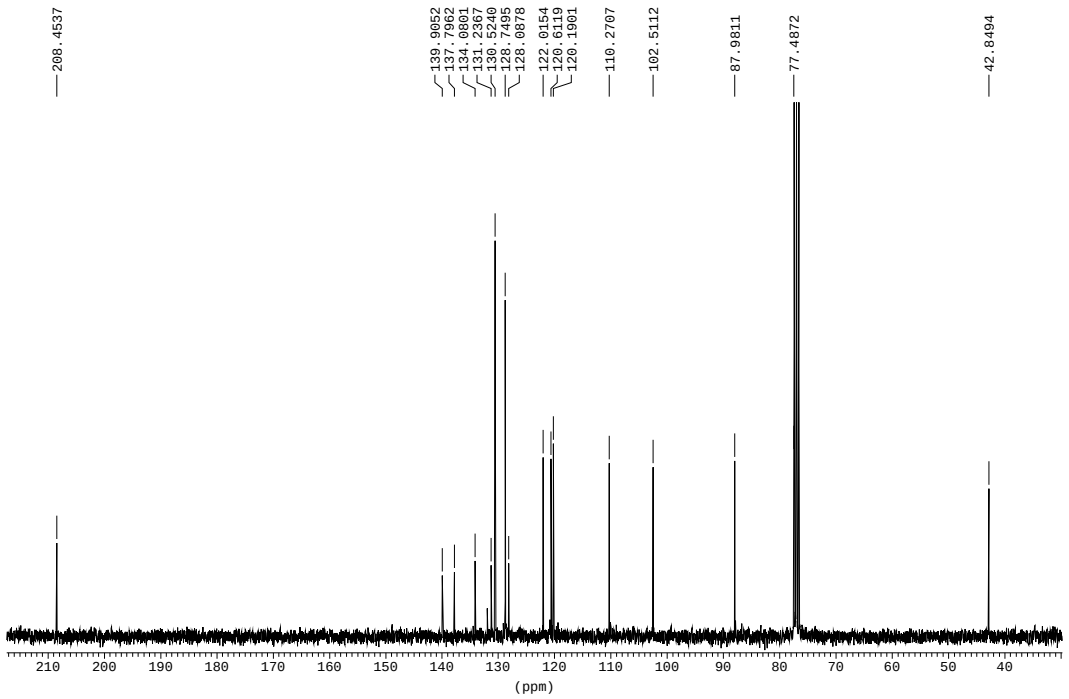

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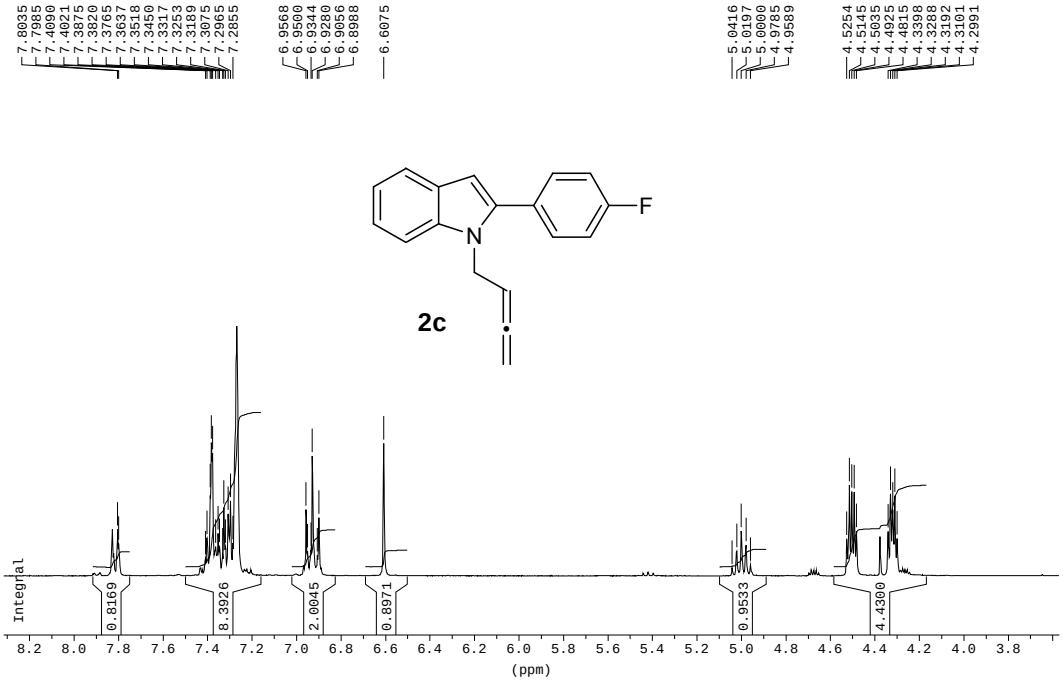

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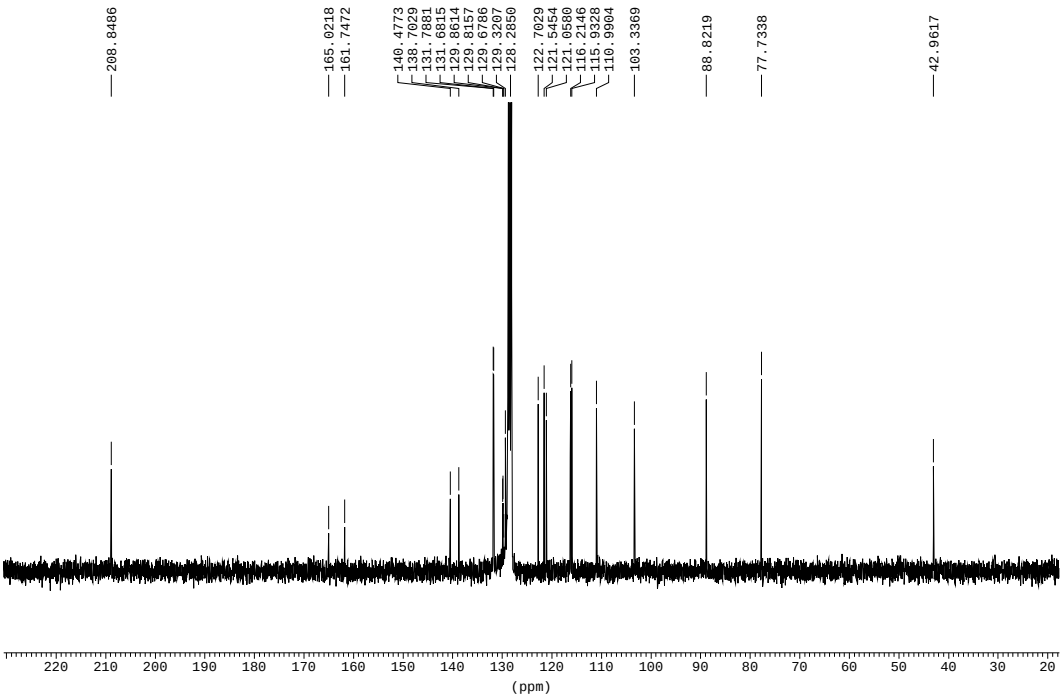

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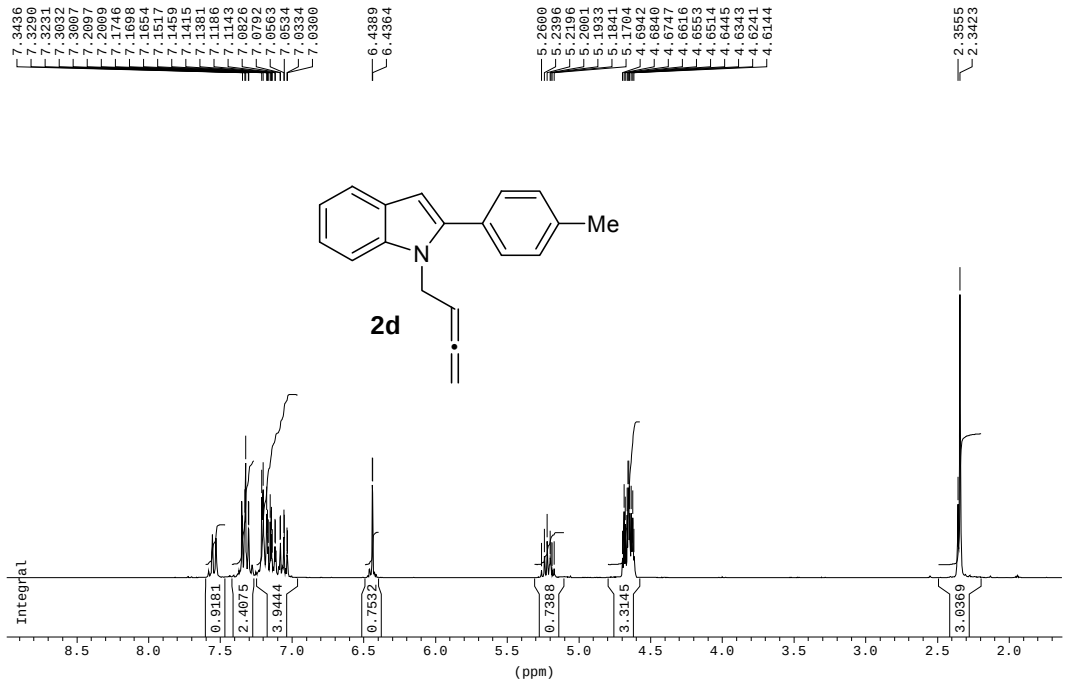

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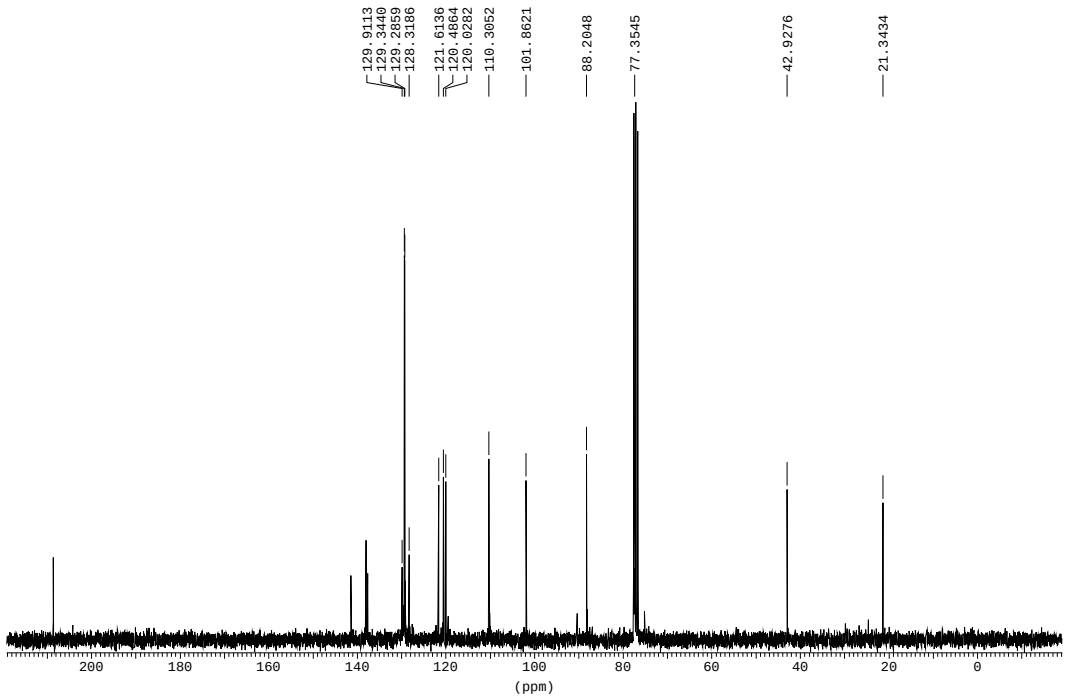

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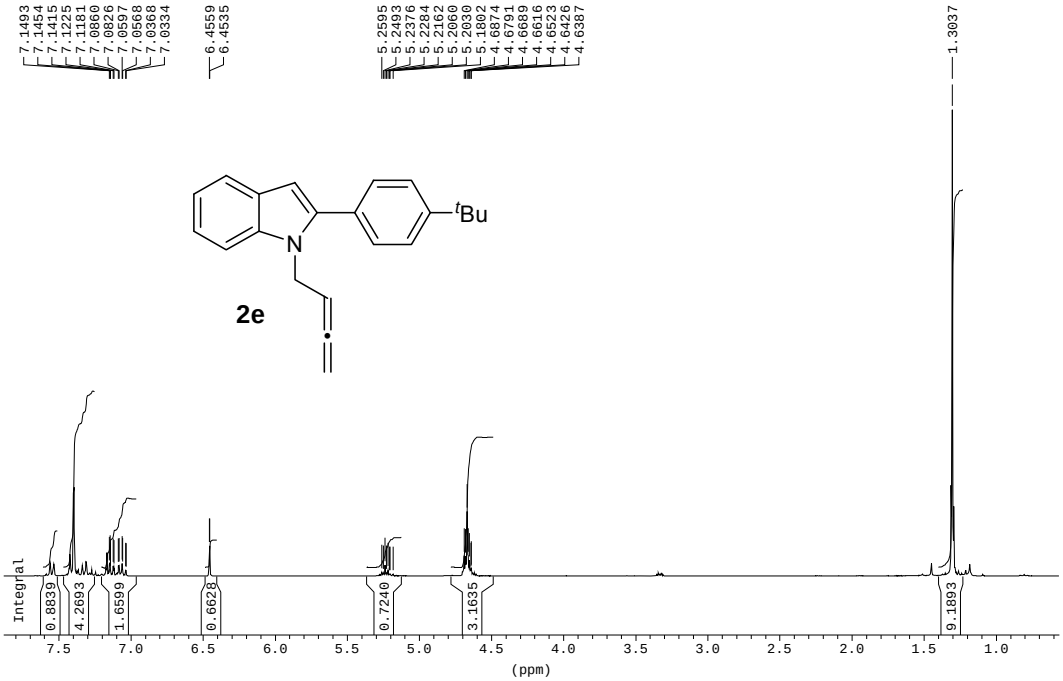

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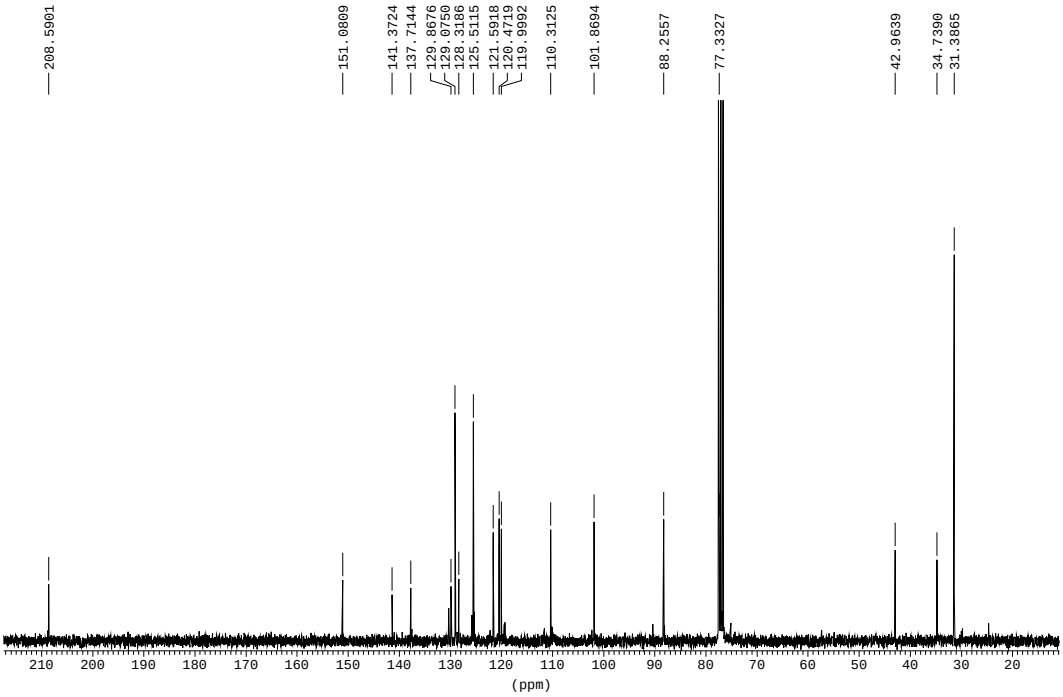

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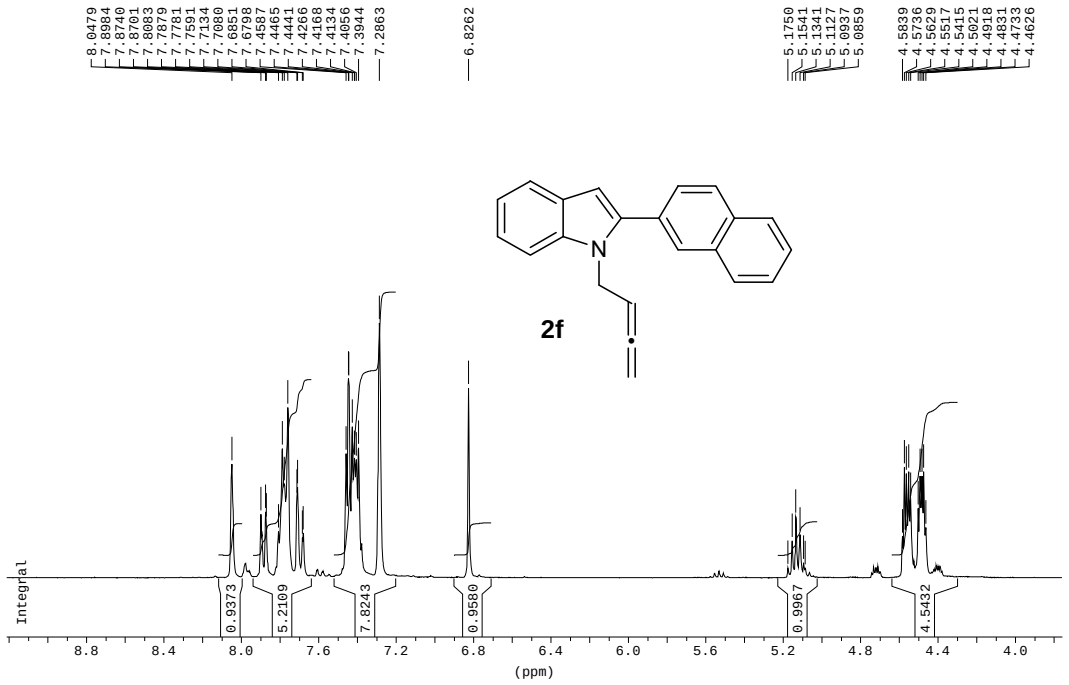

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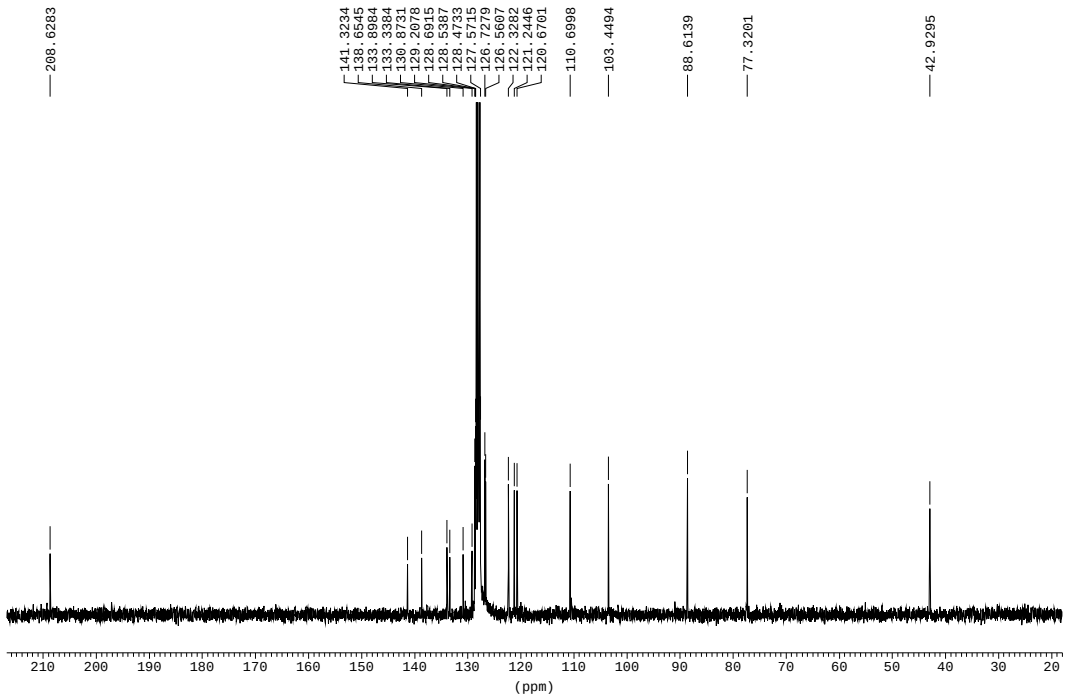

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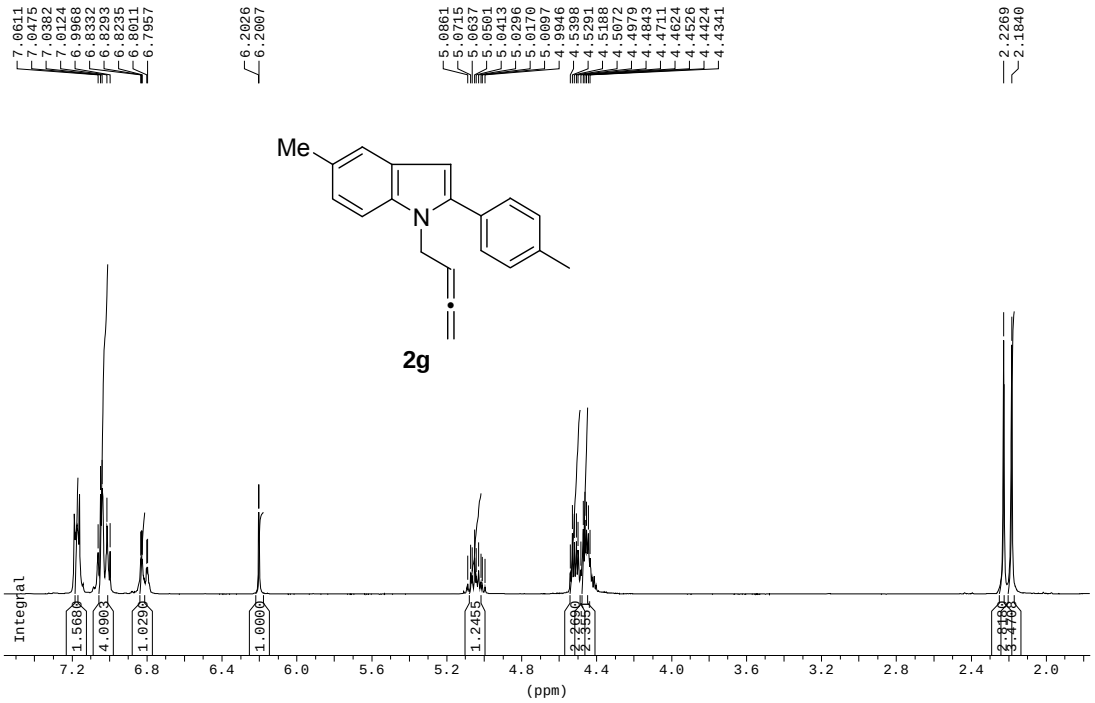

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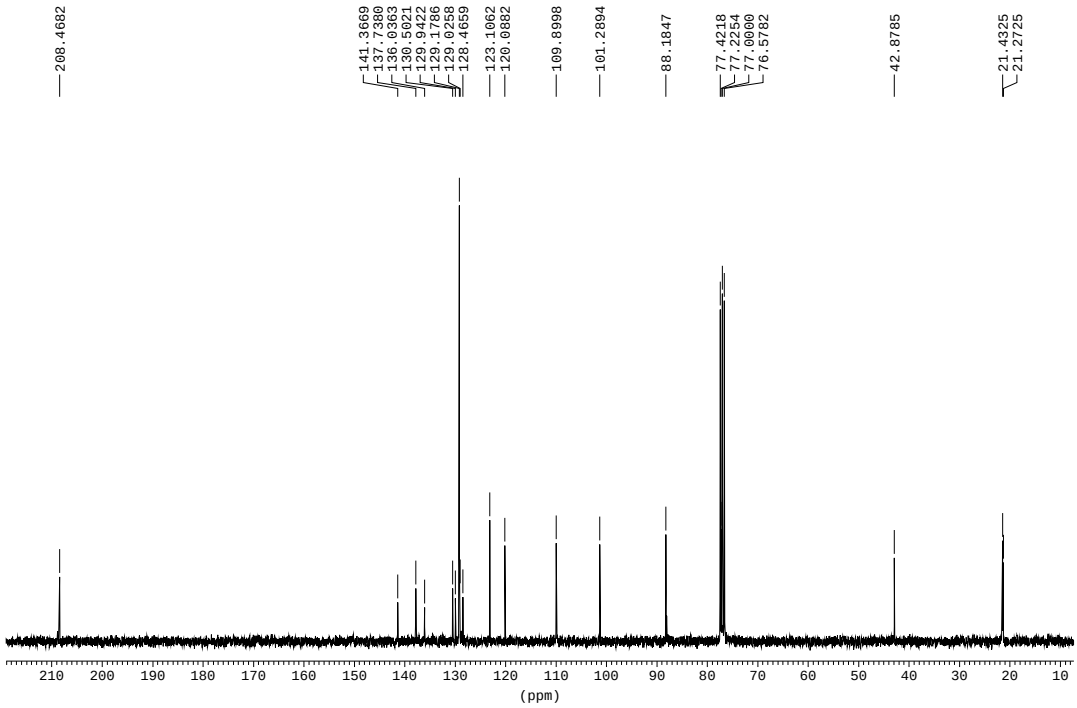

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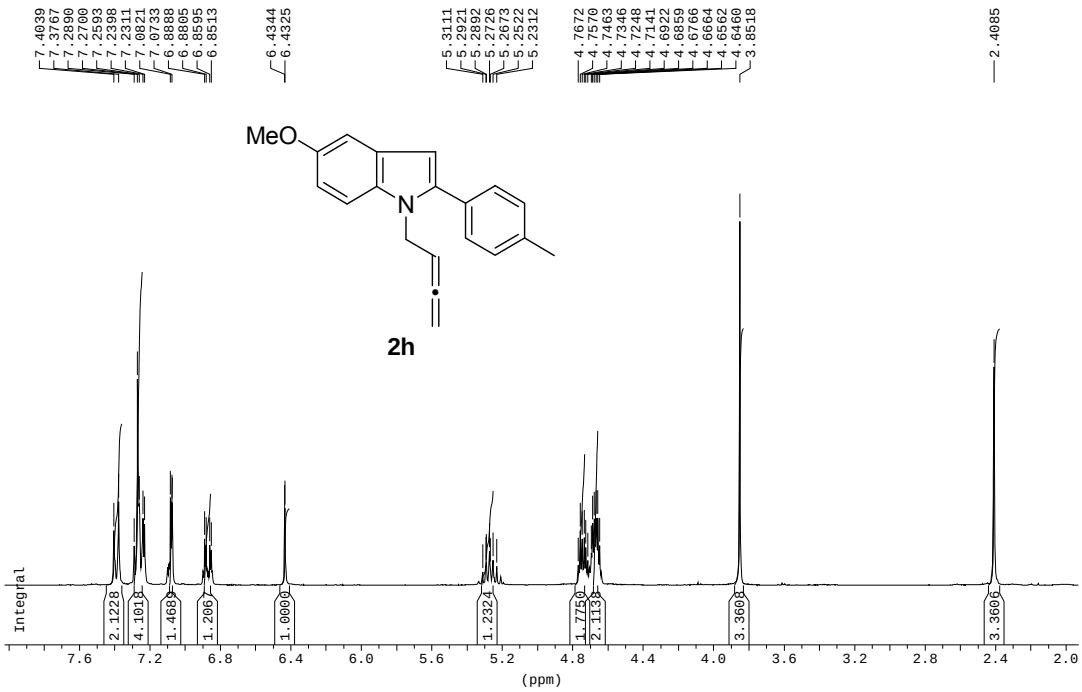

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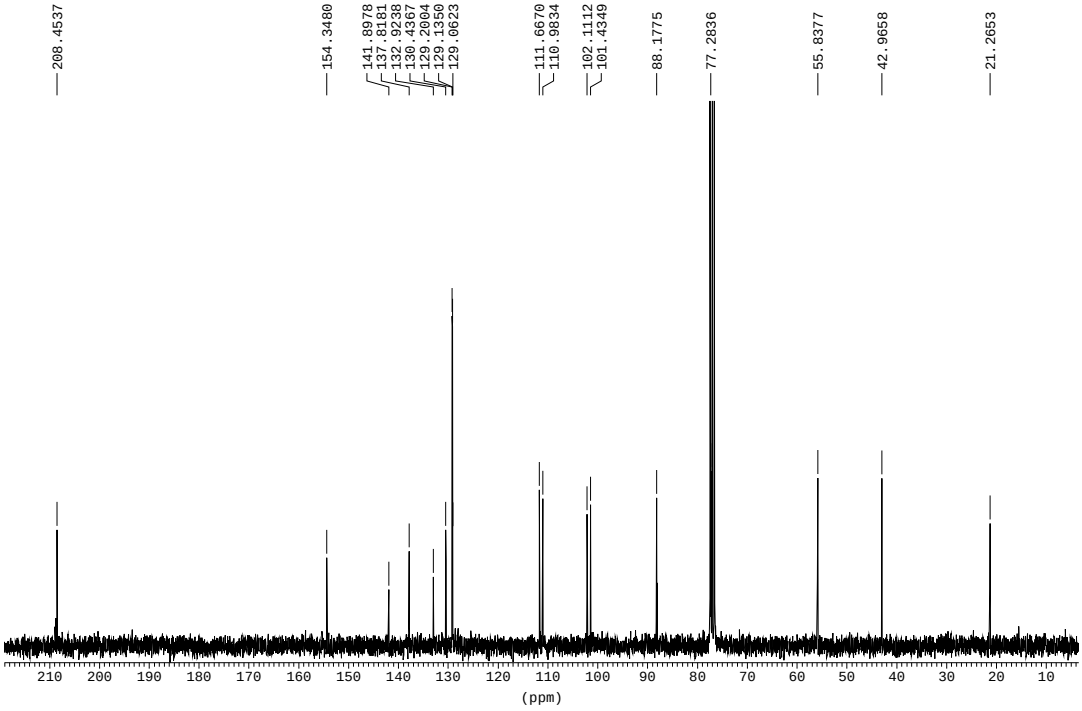

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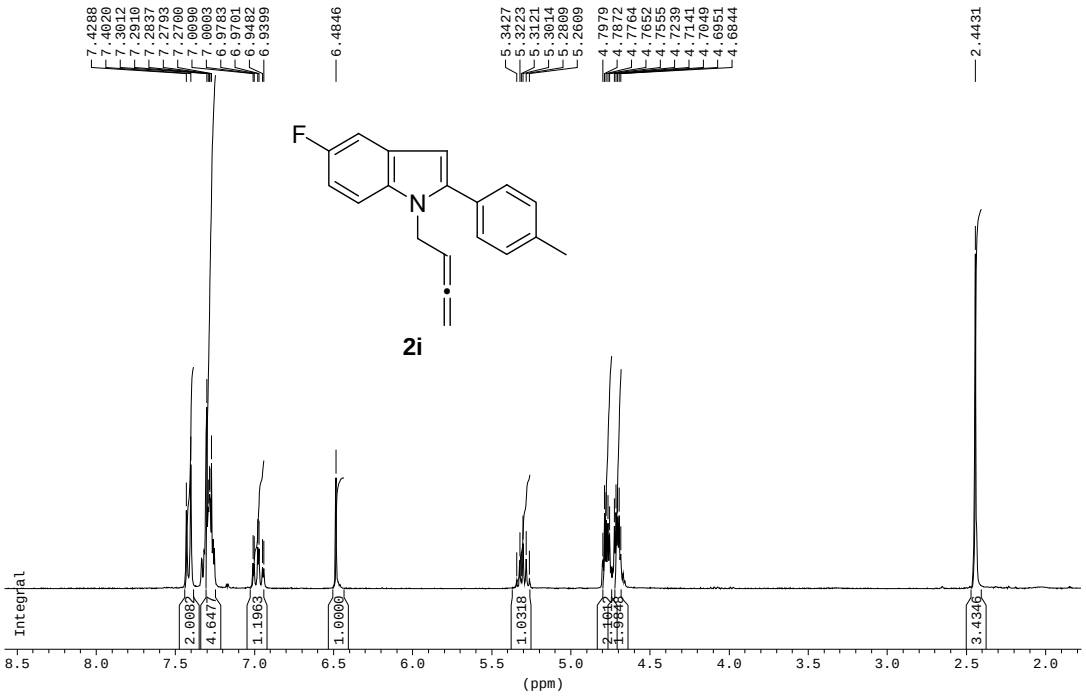

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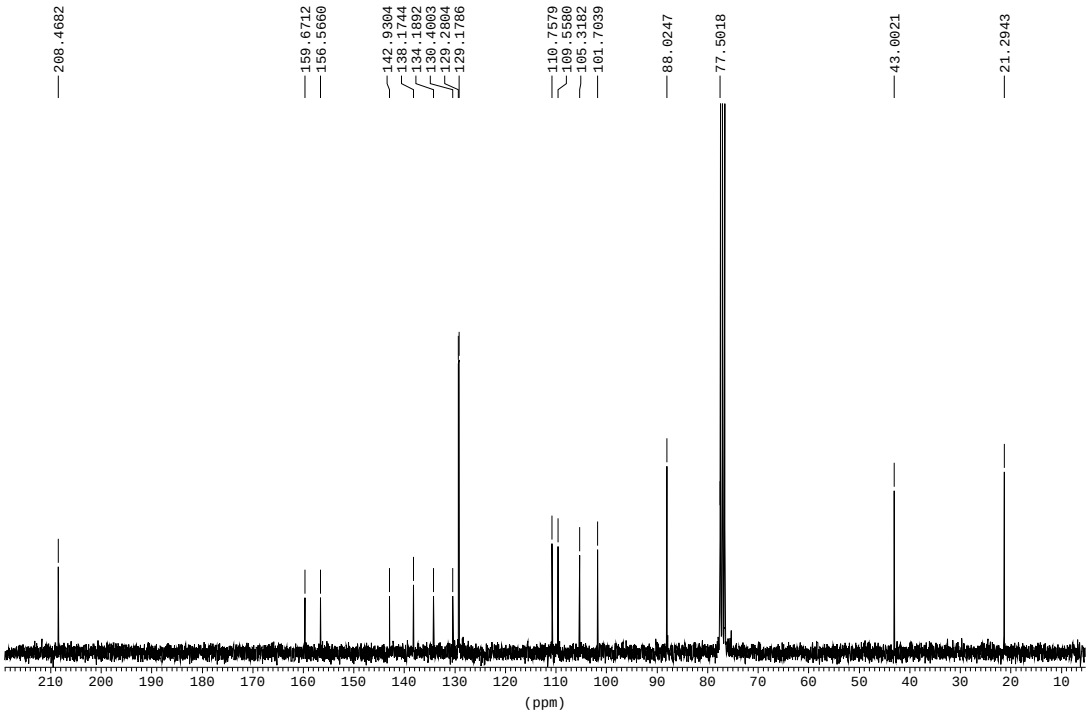

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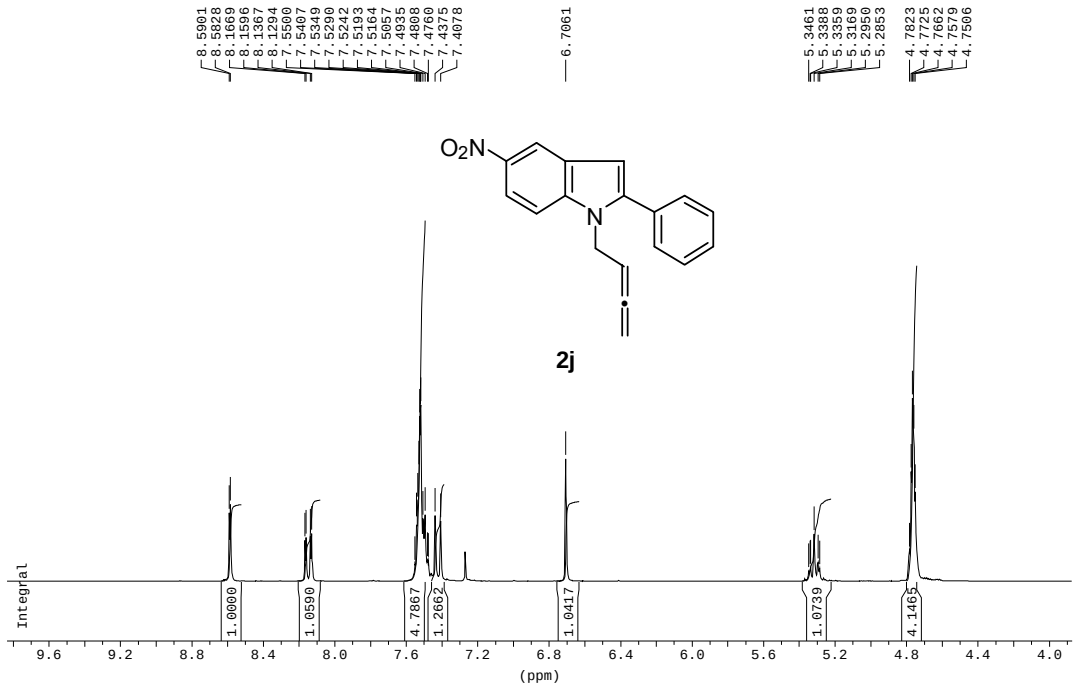

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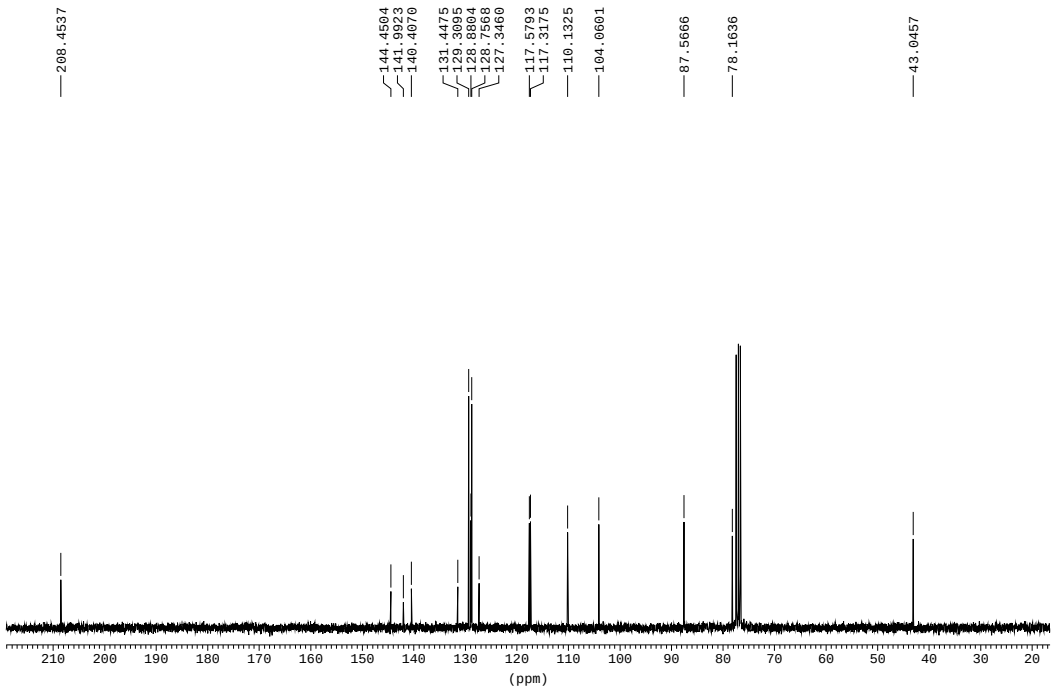

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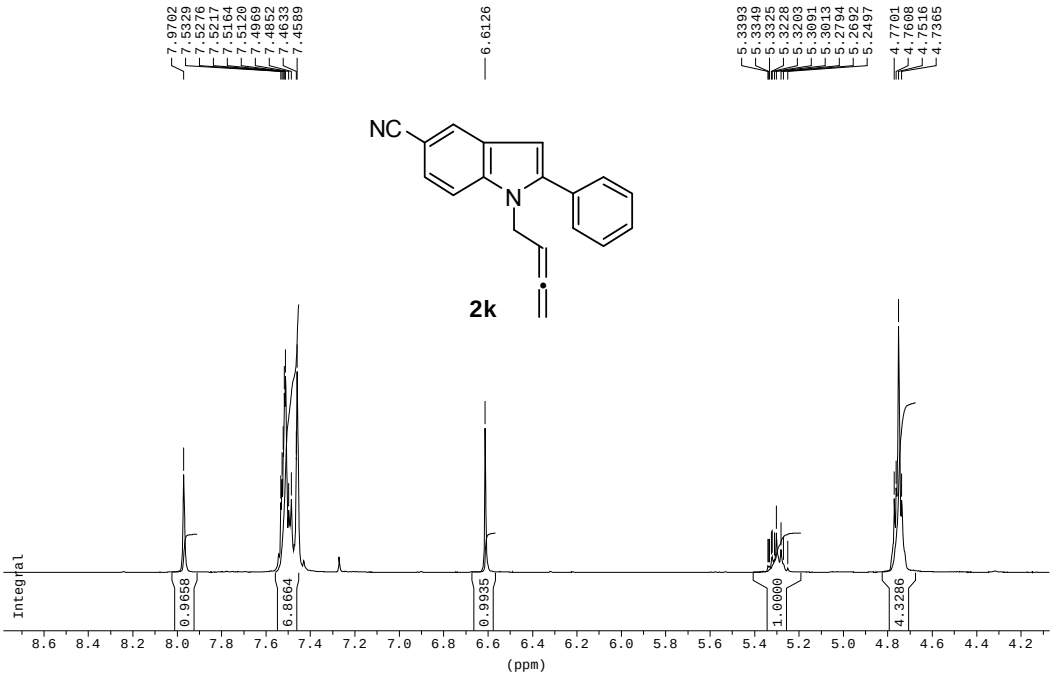

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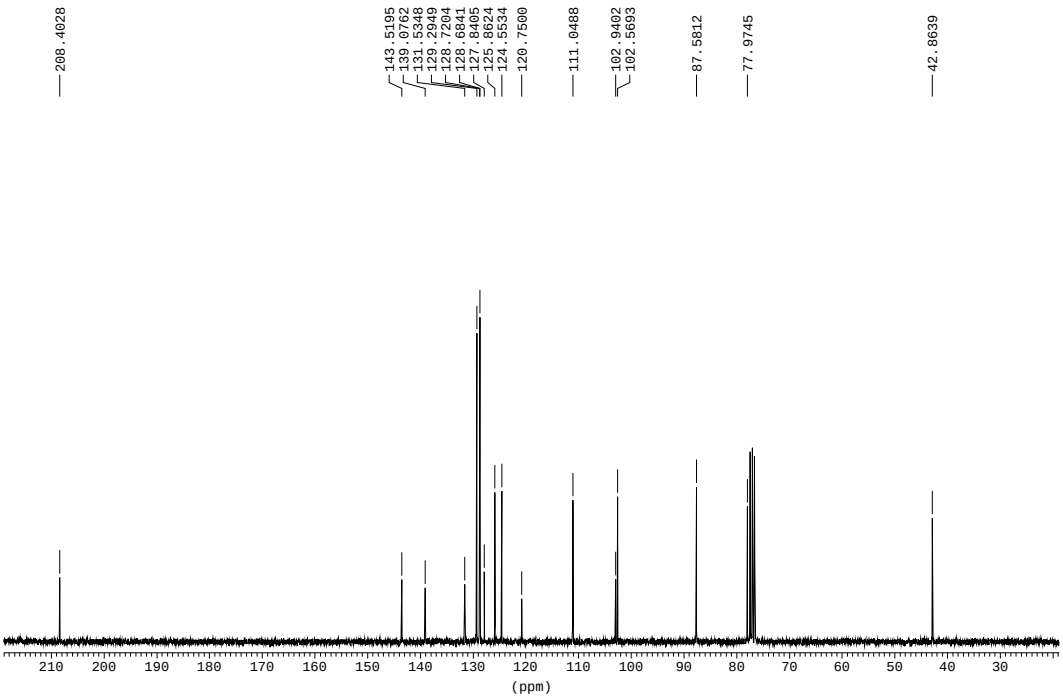

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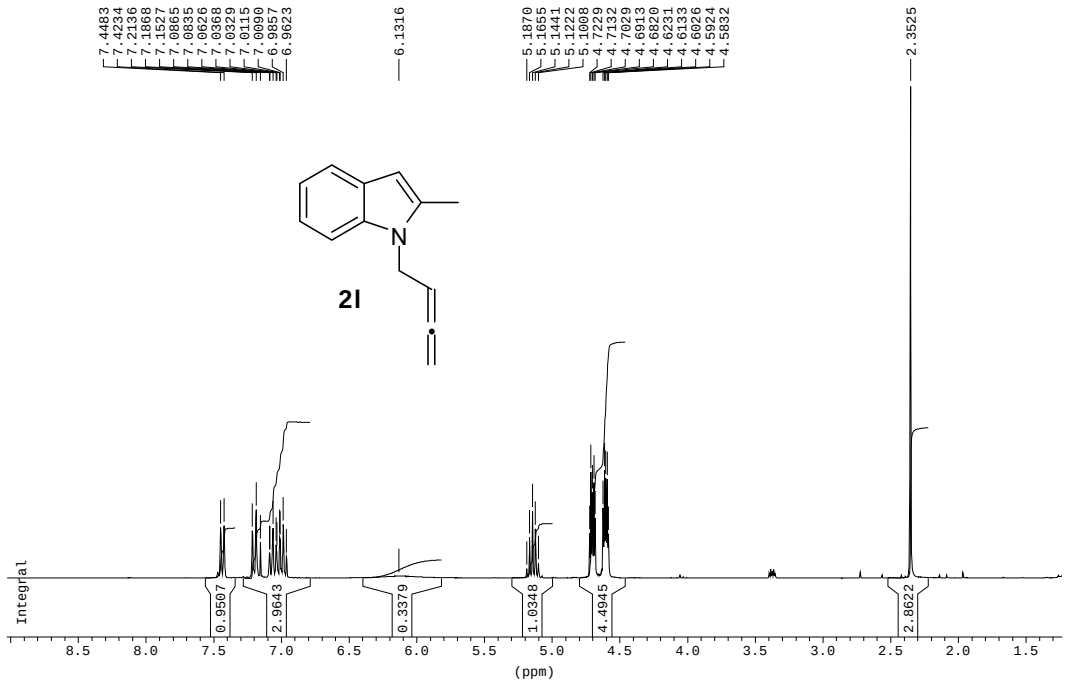

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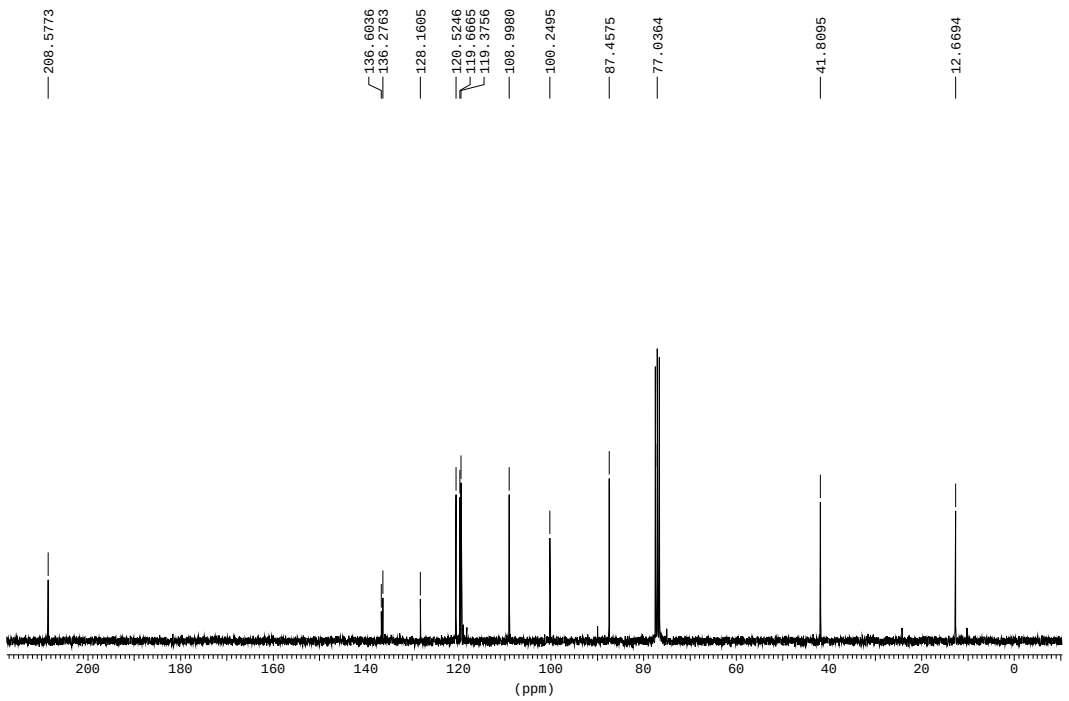

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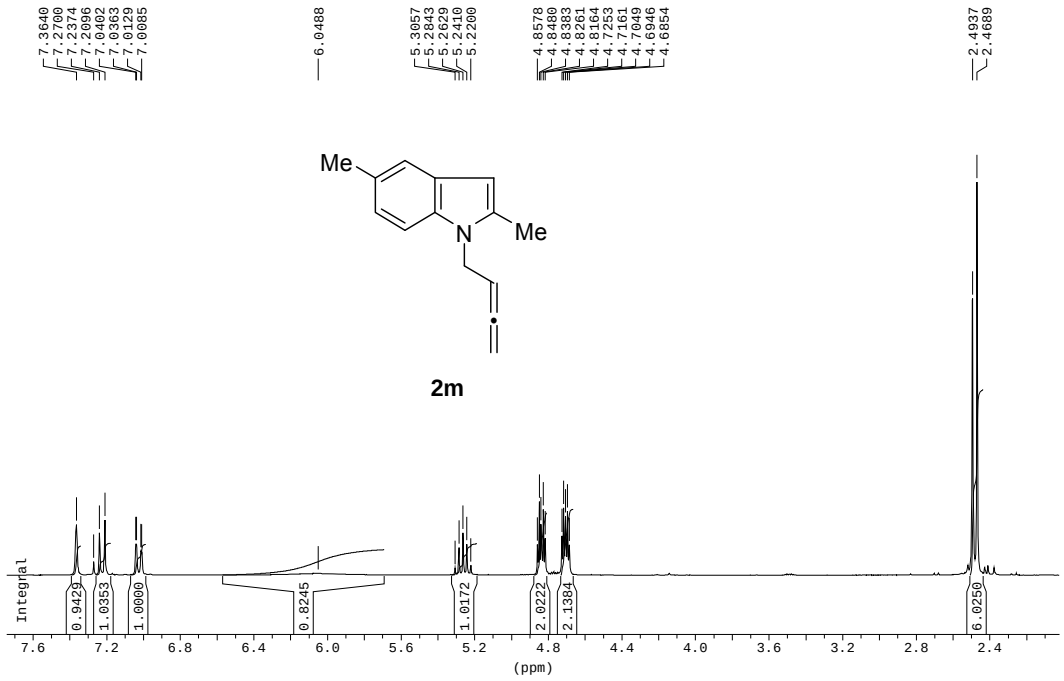

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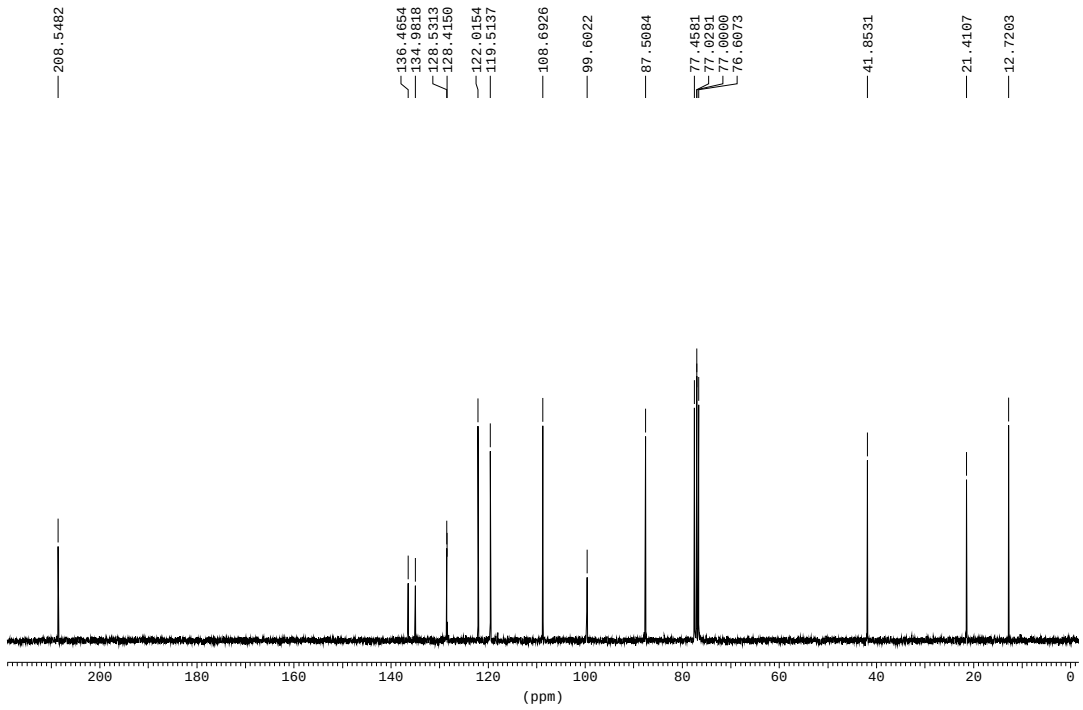

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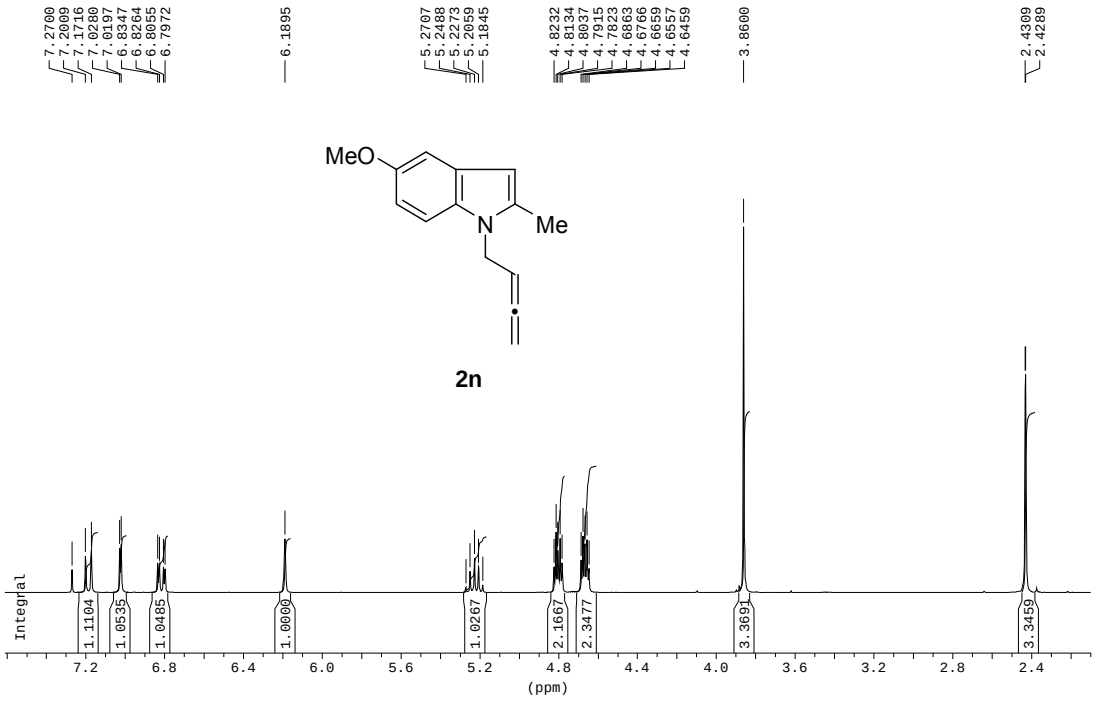

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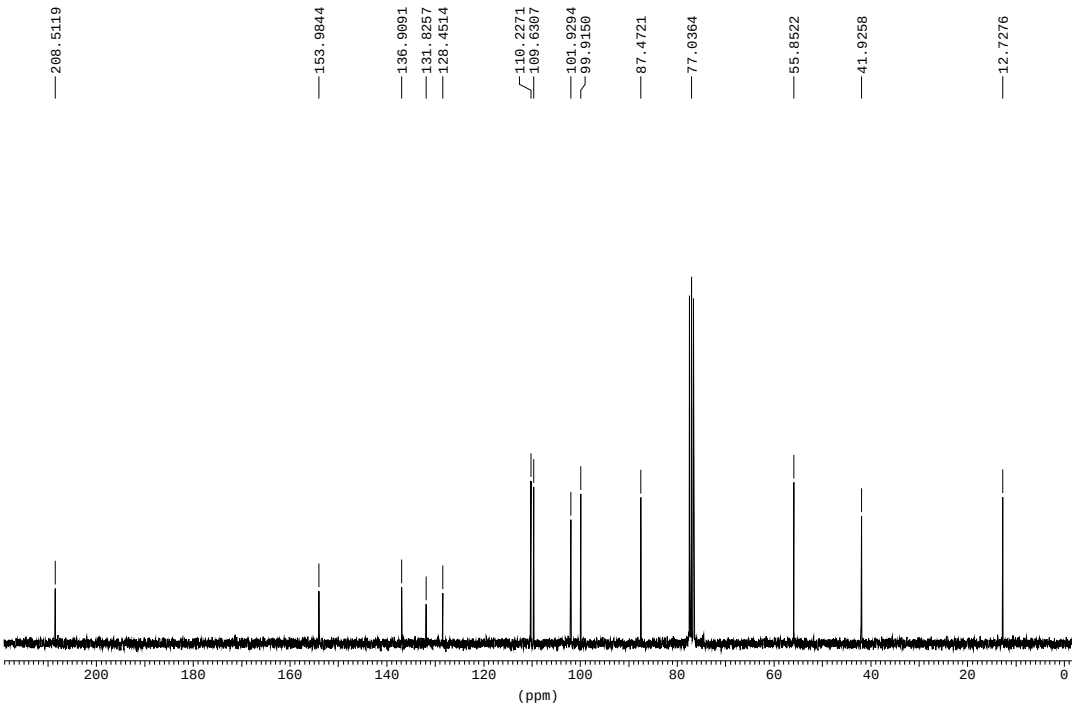

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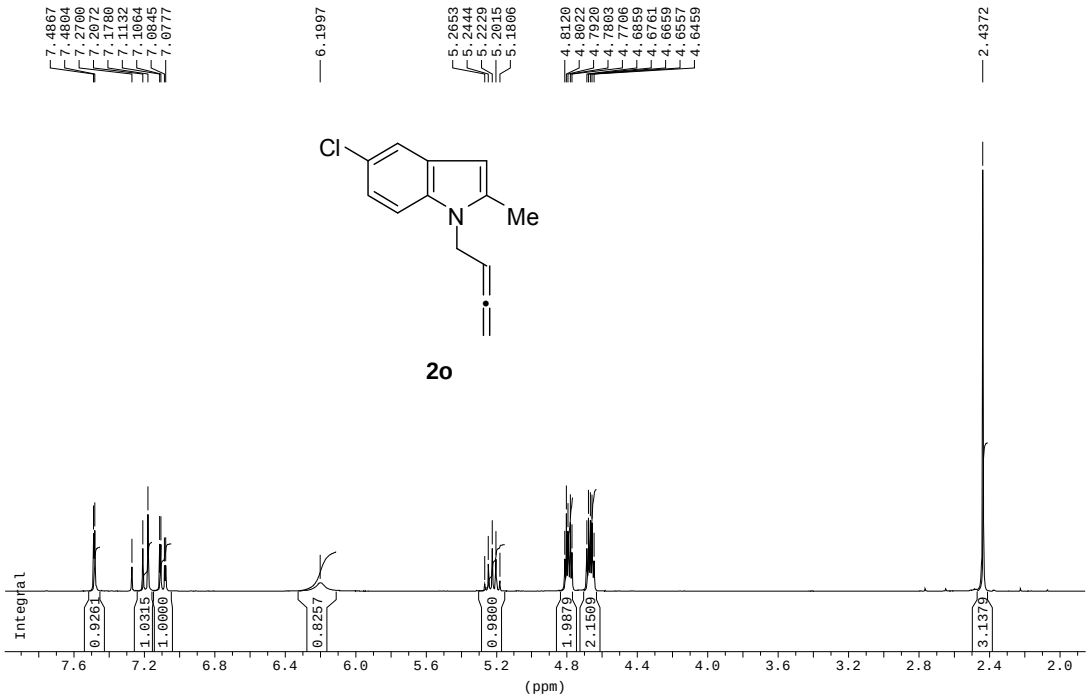

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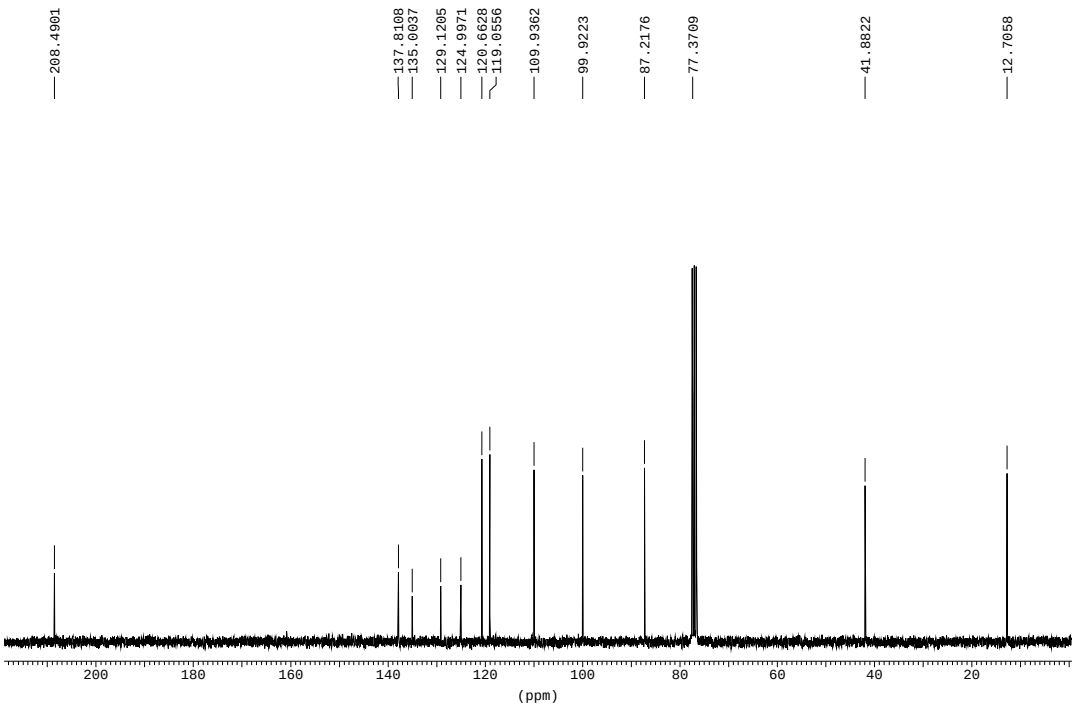

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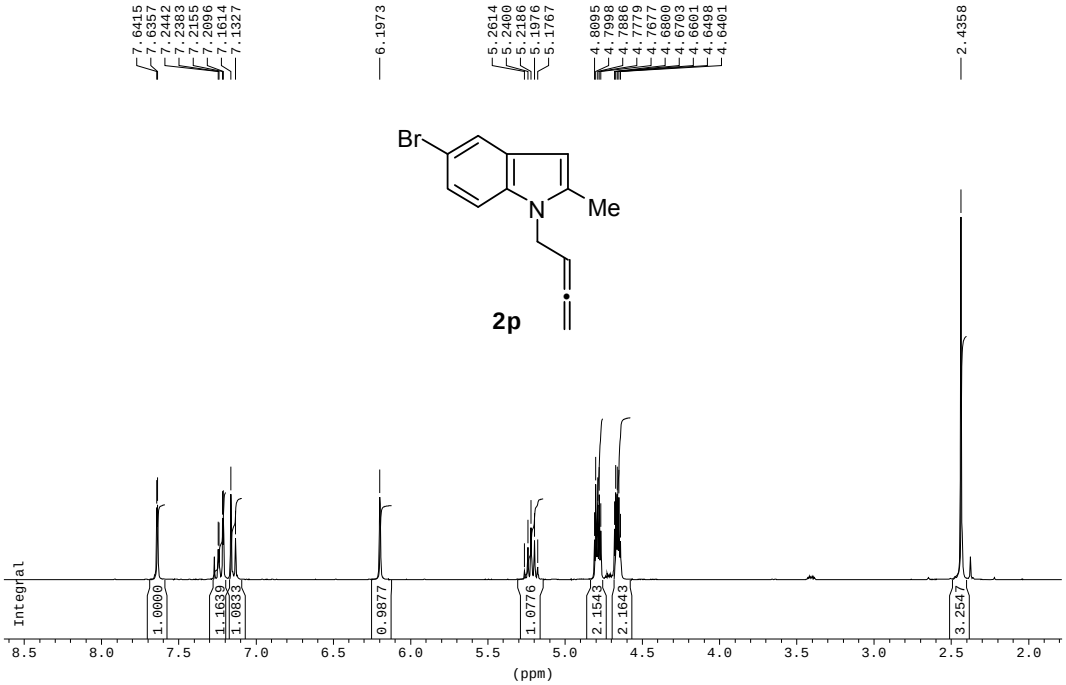

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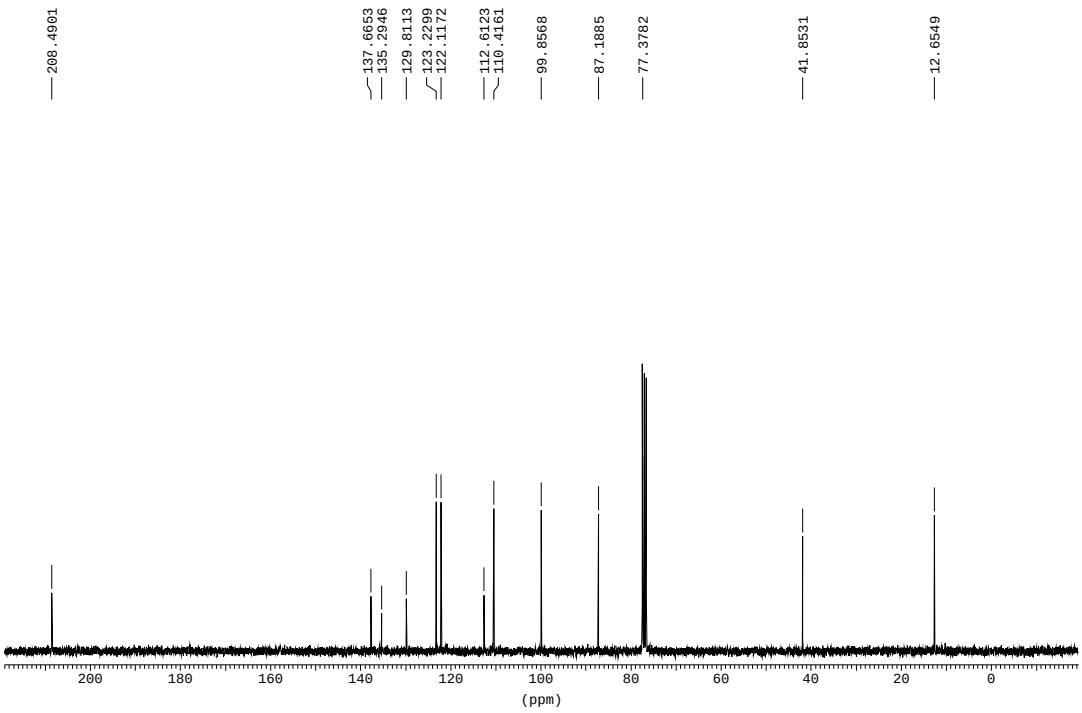

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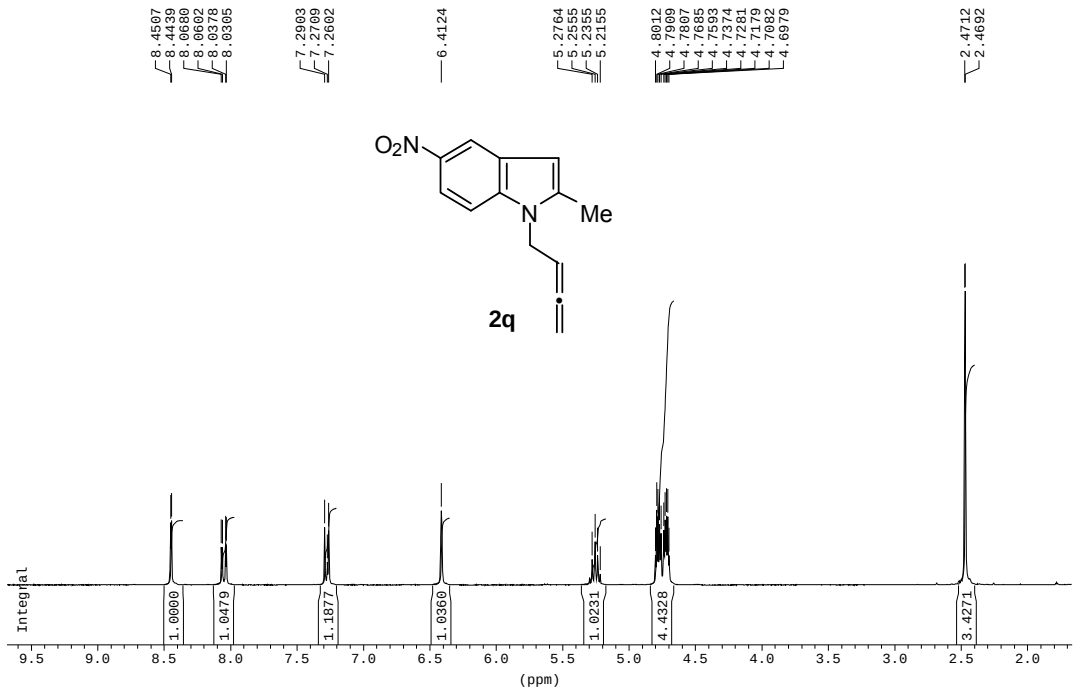

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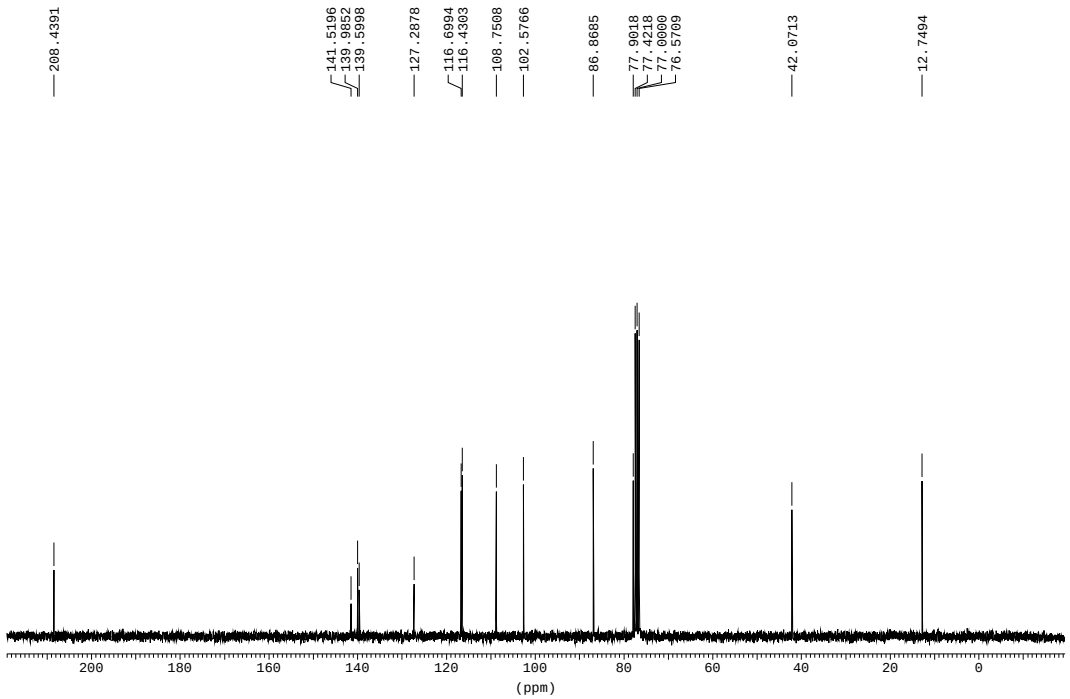

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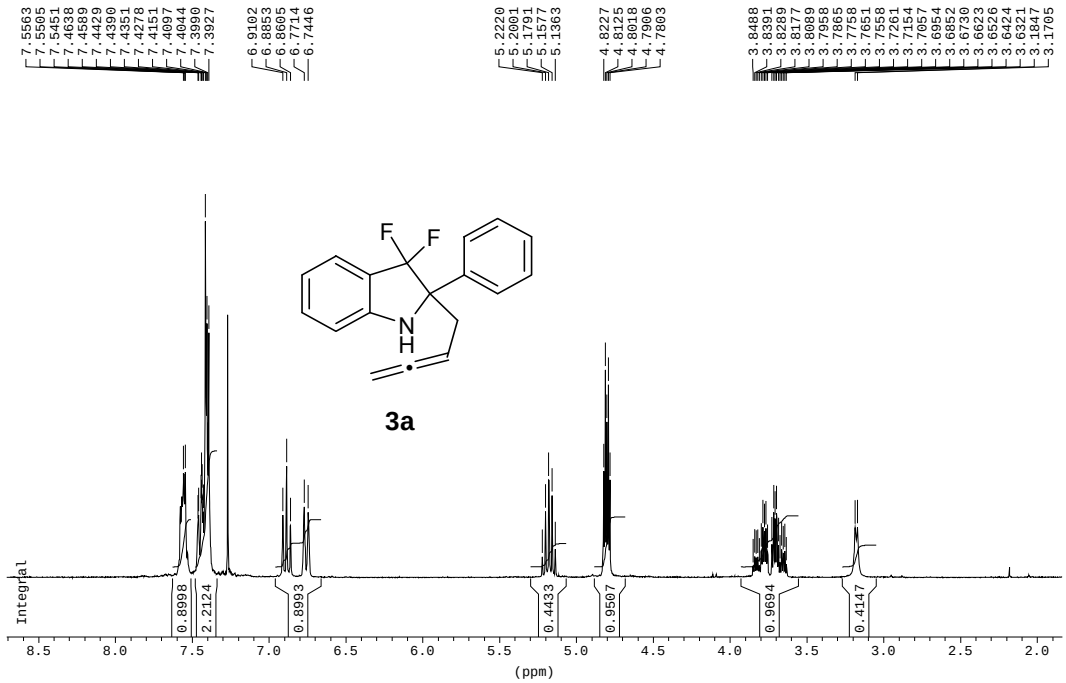

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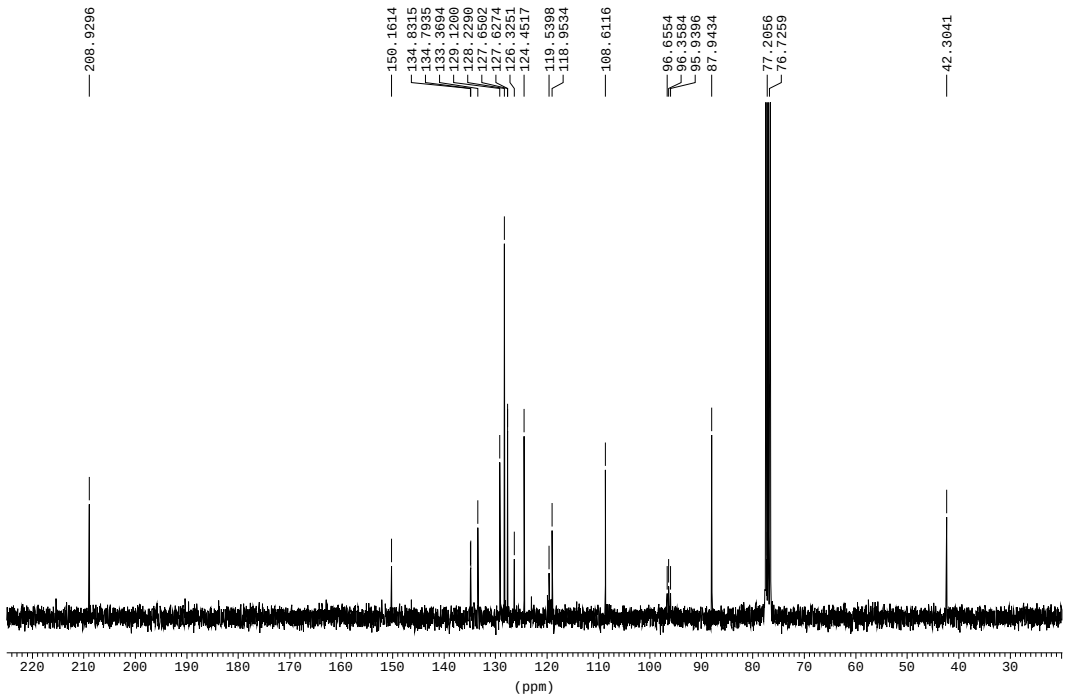

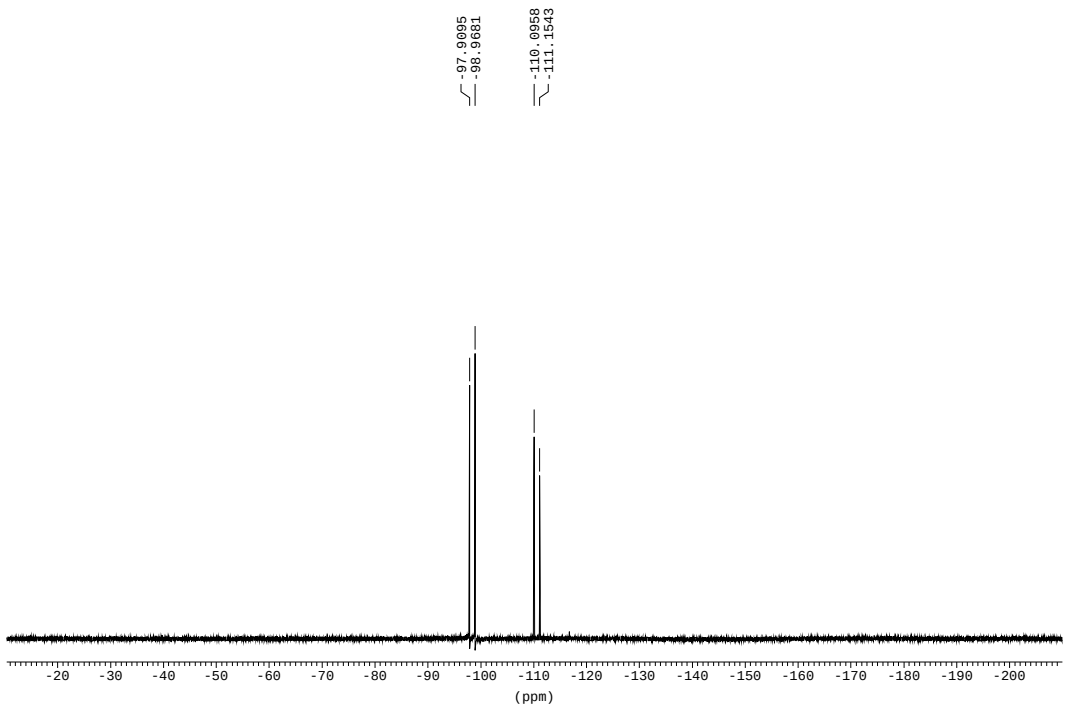
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(ppm)

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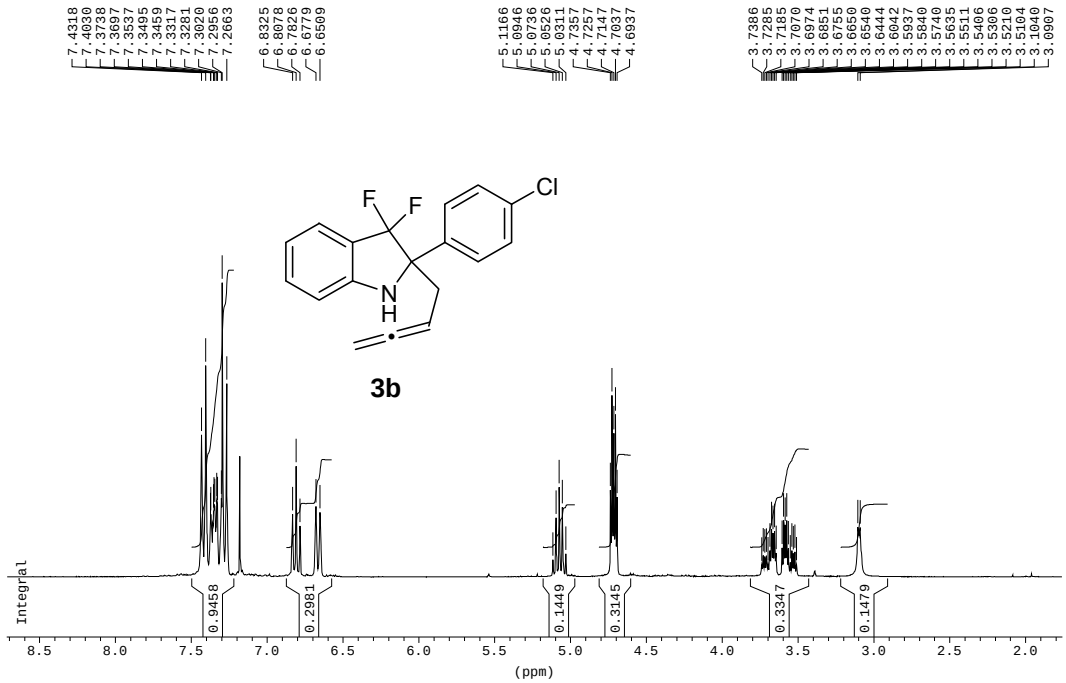

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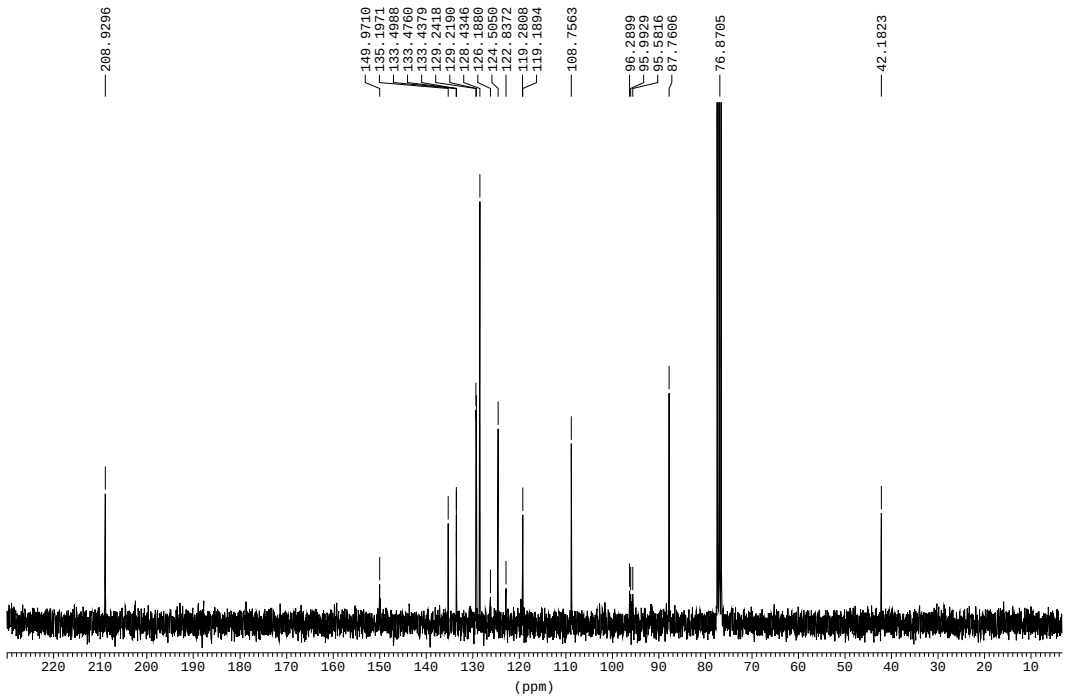

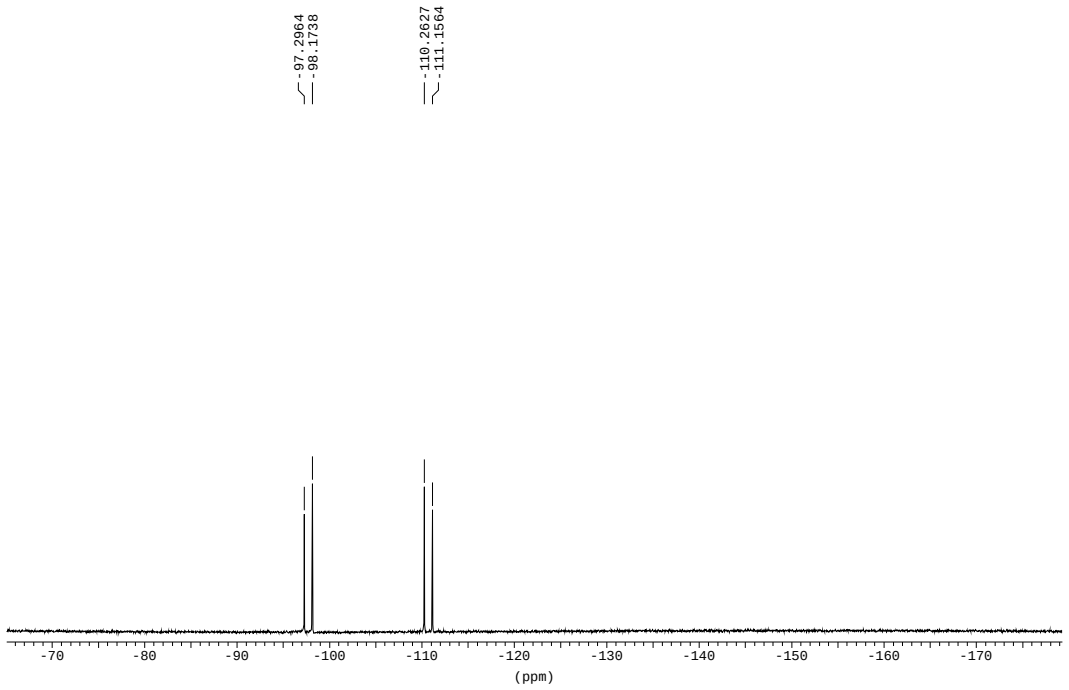
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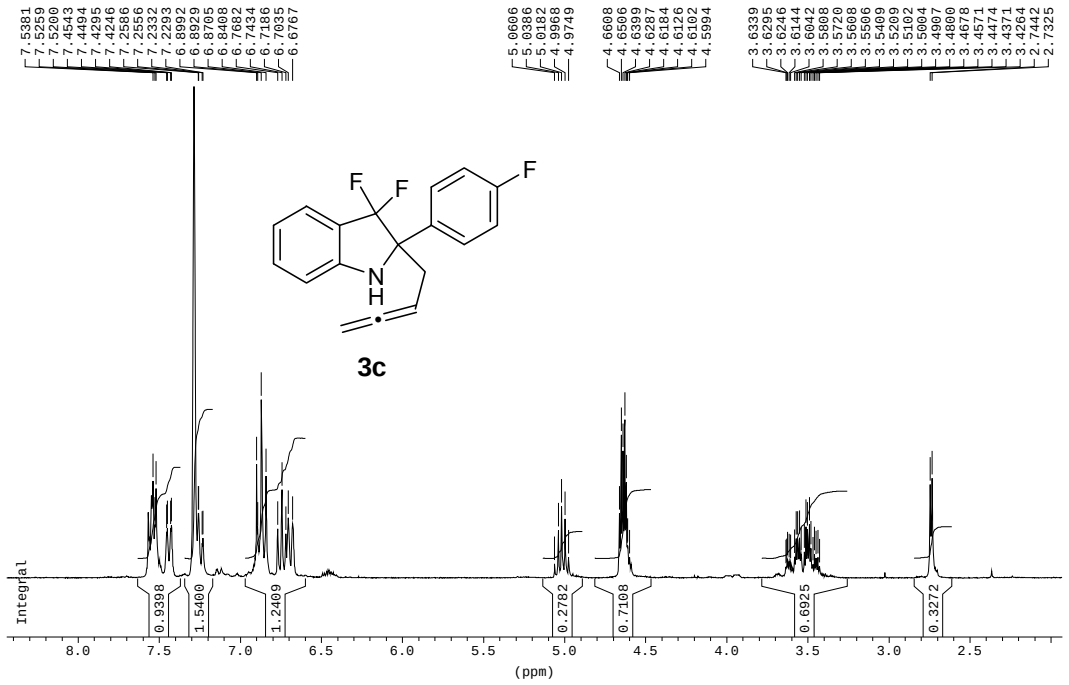
(ppm)

Q09MB90A



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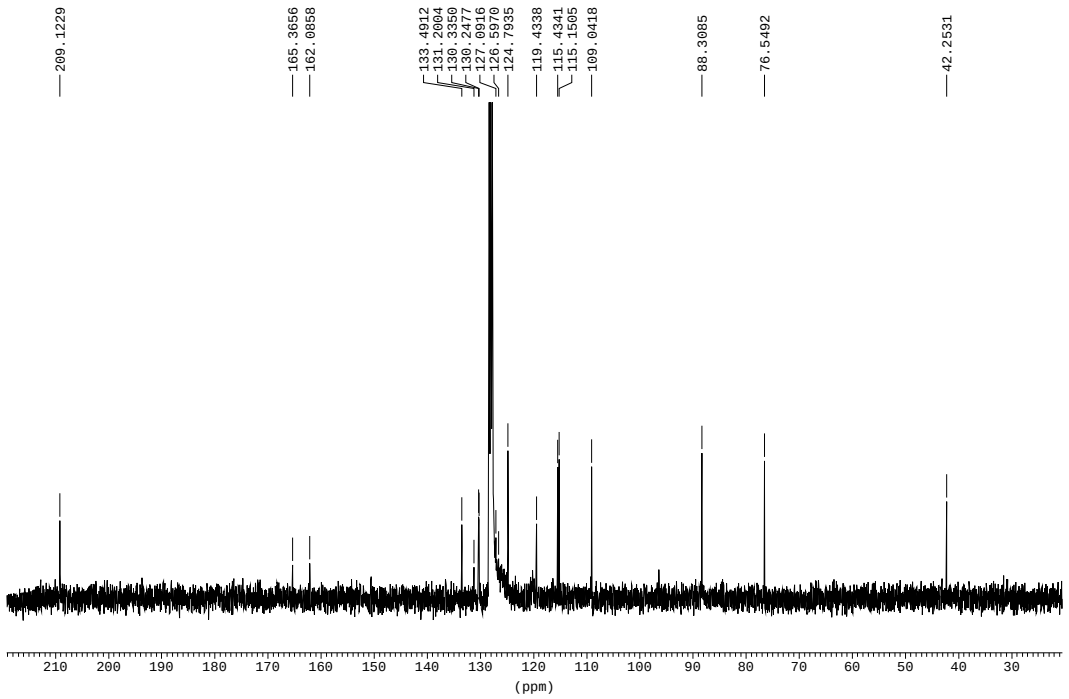

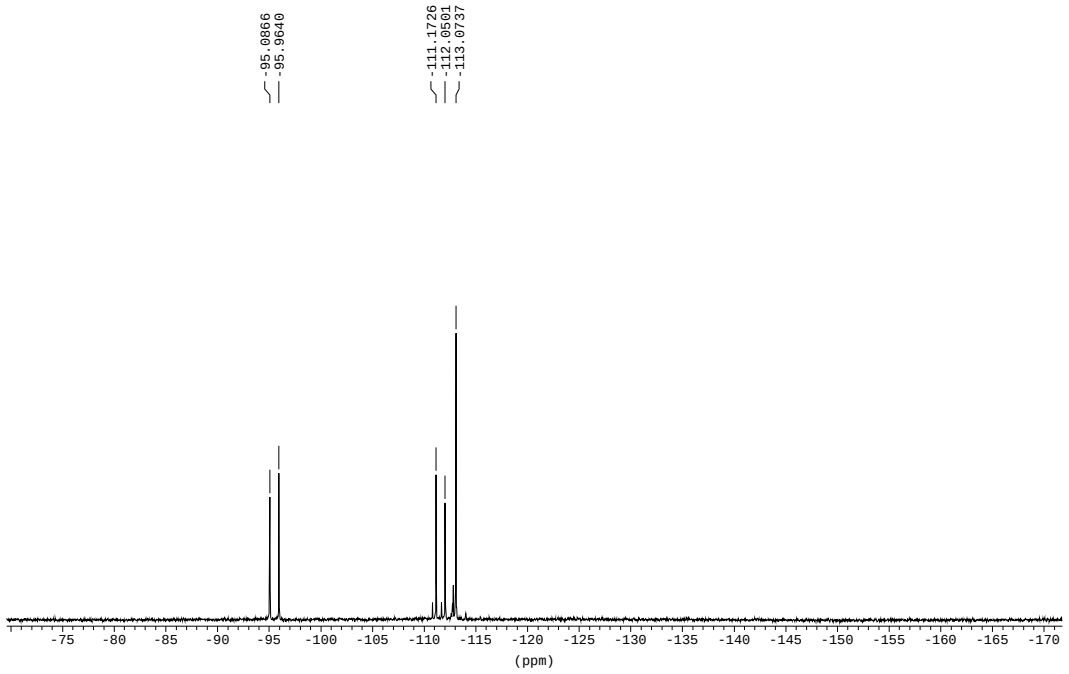
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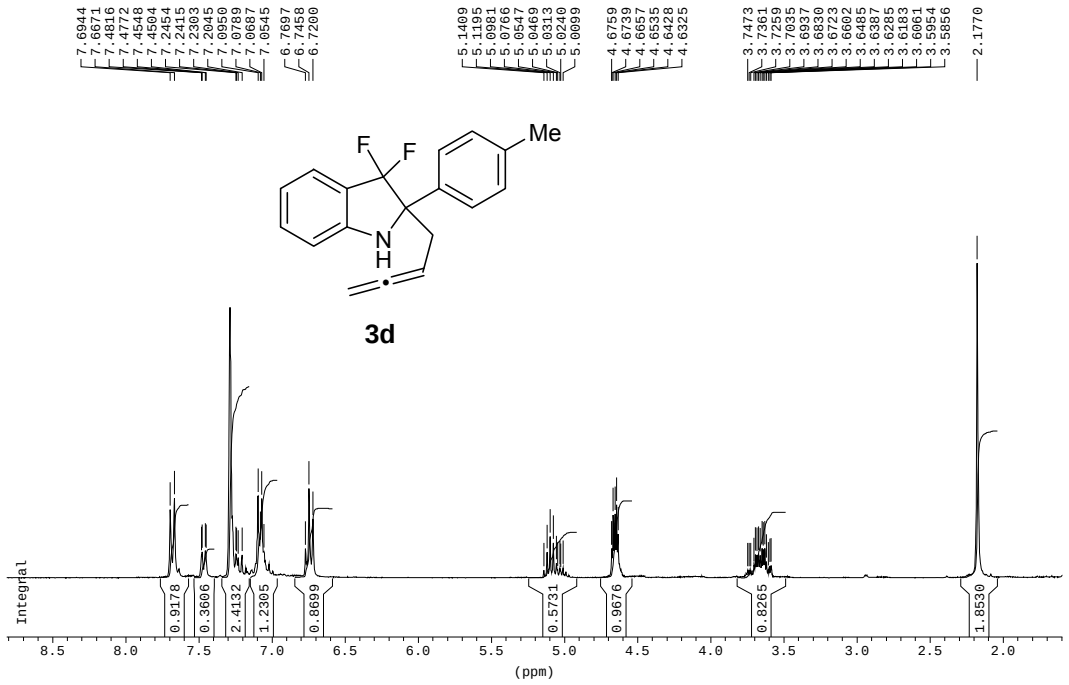

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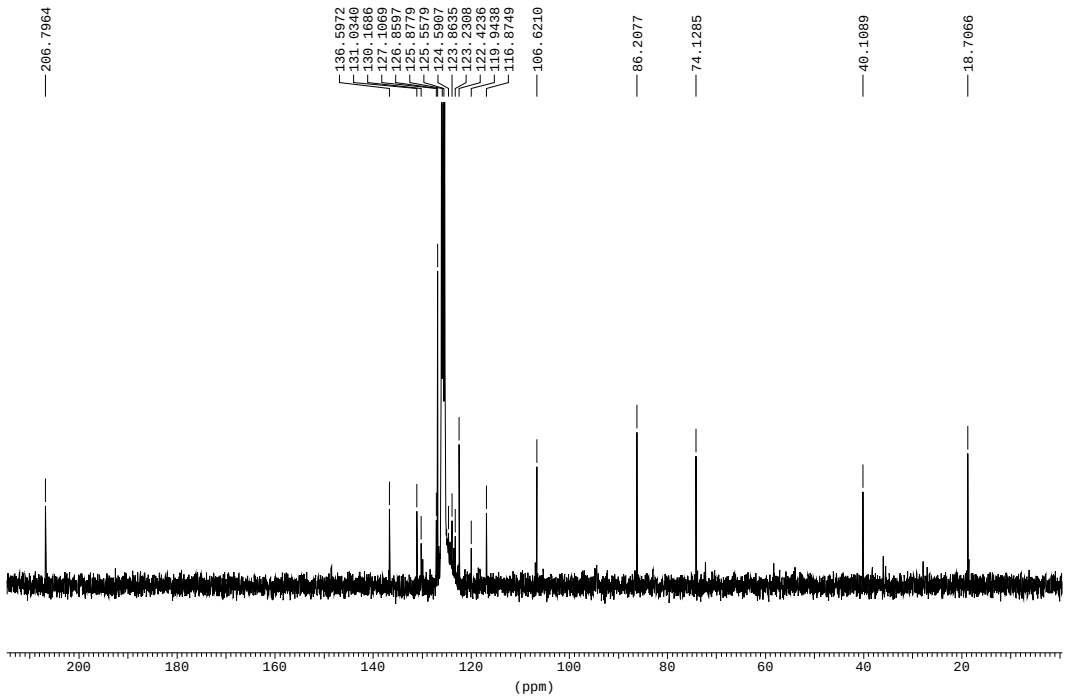

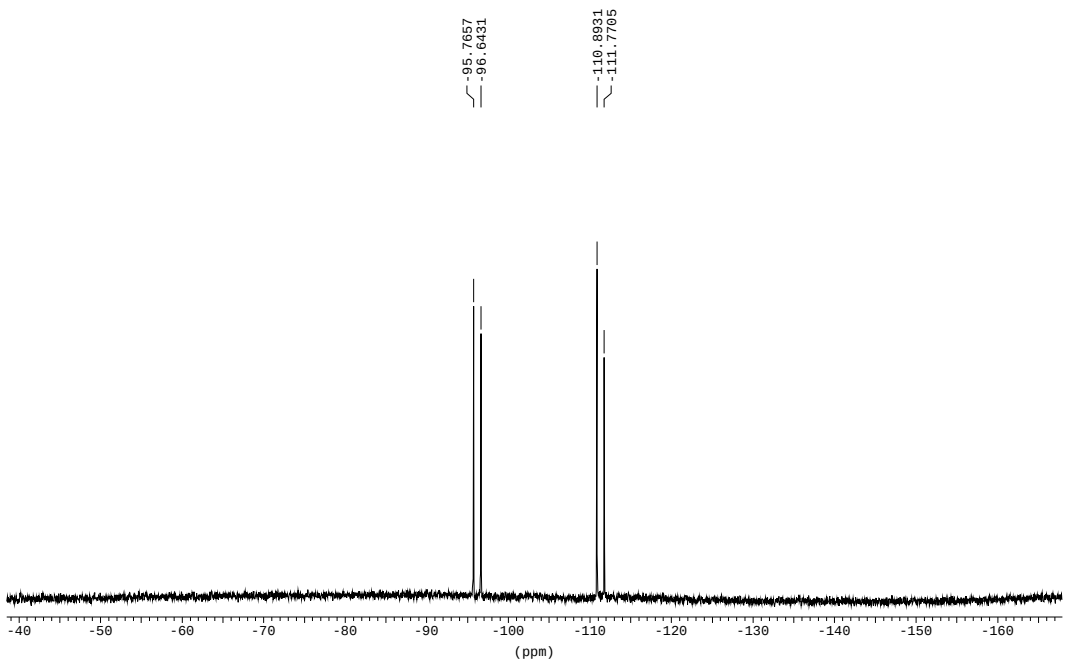
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(ppm)

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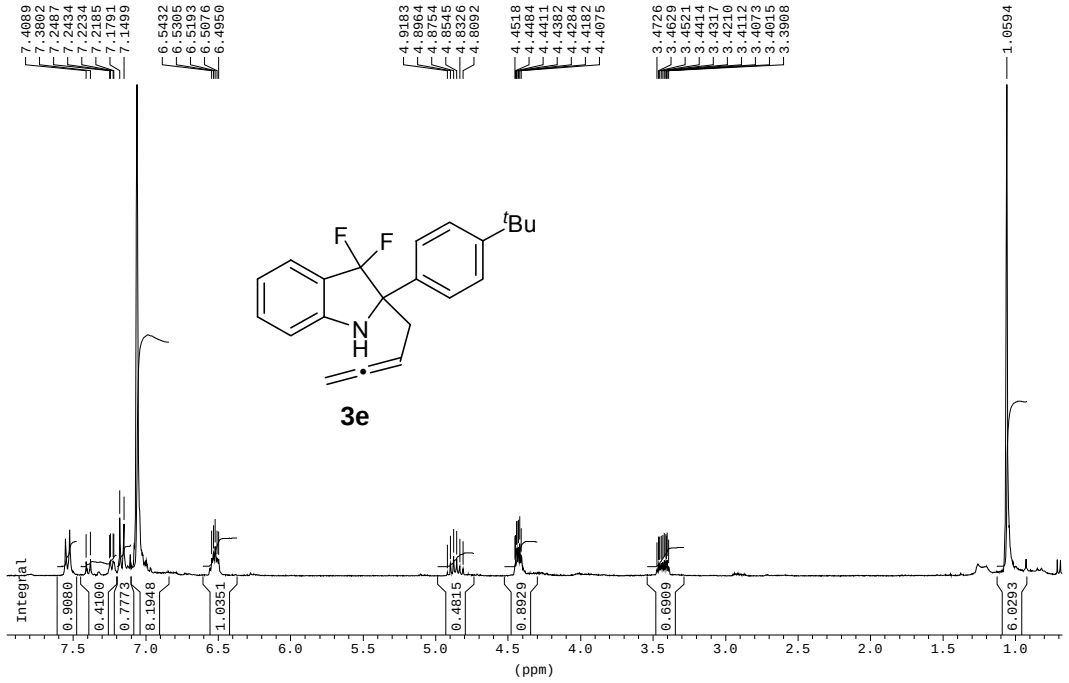

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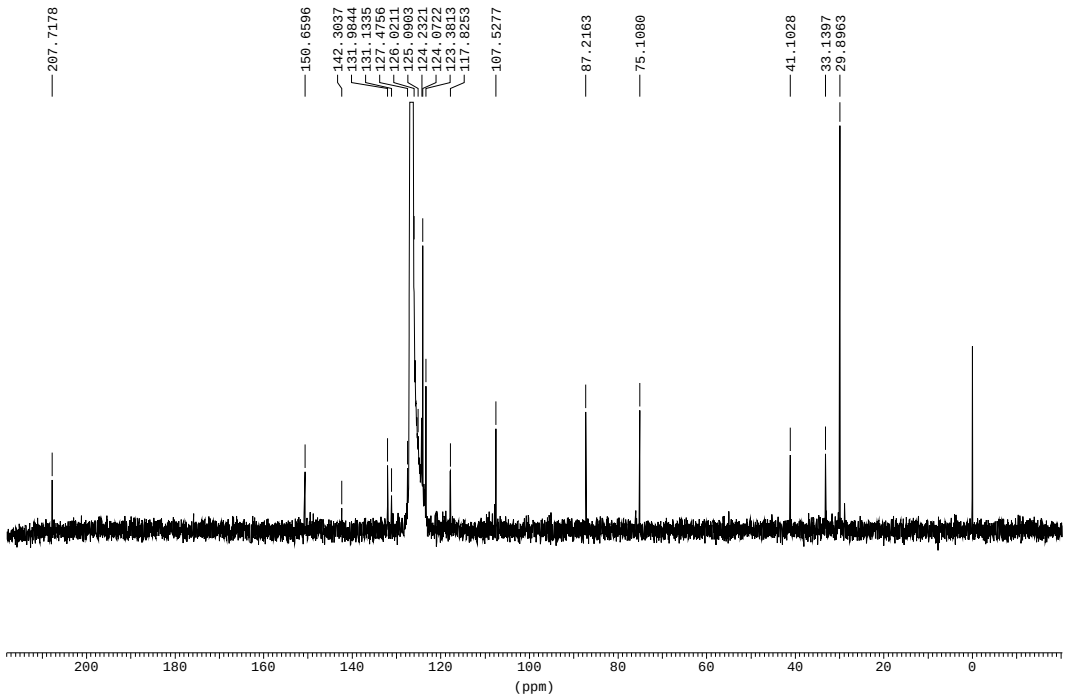

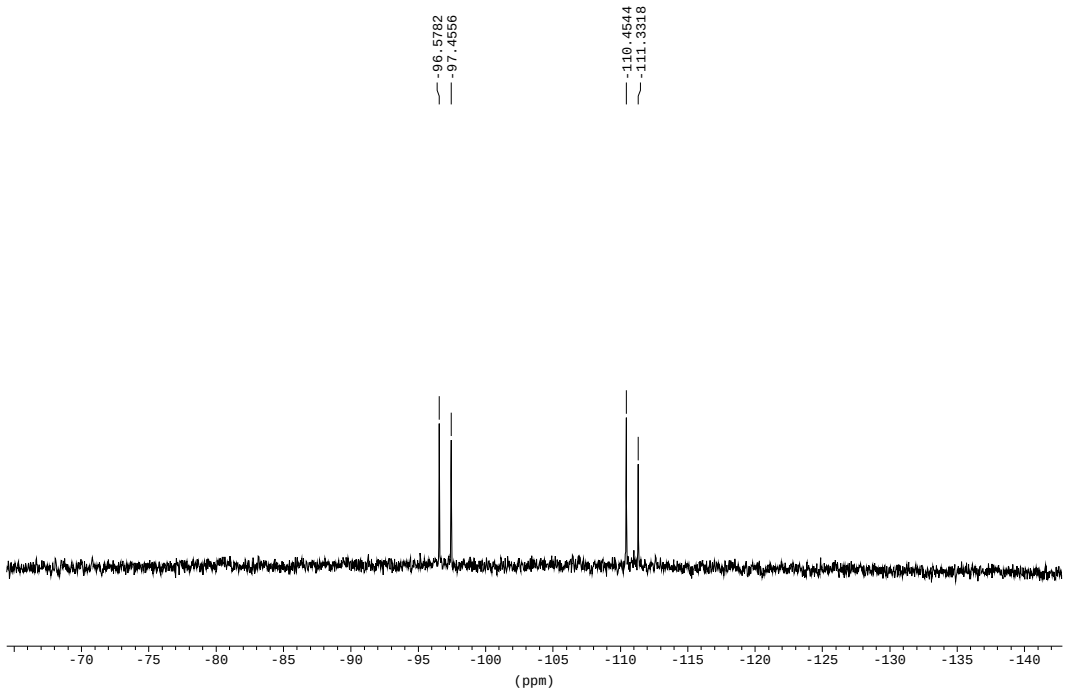
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(ppm)

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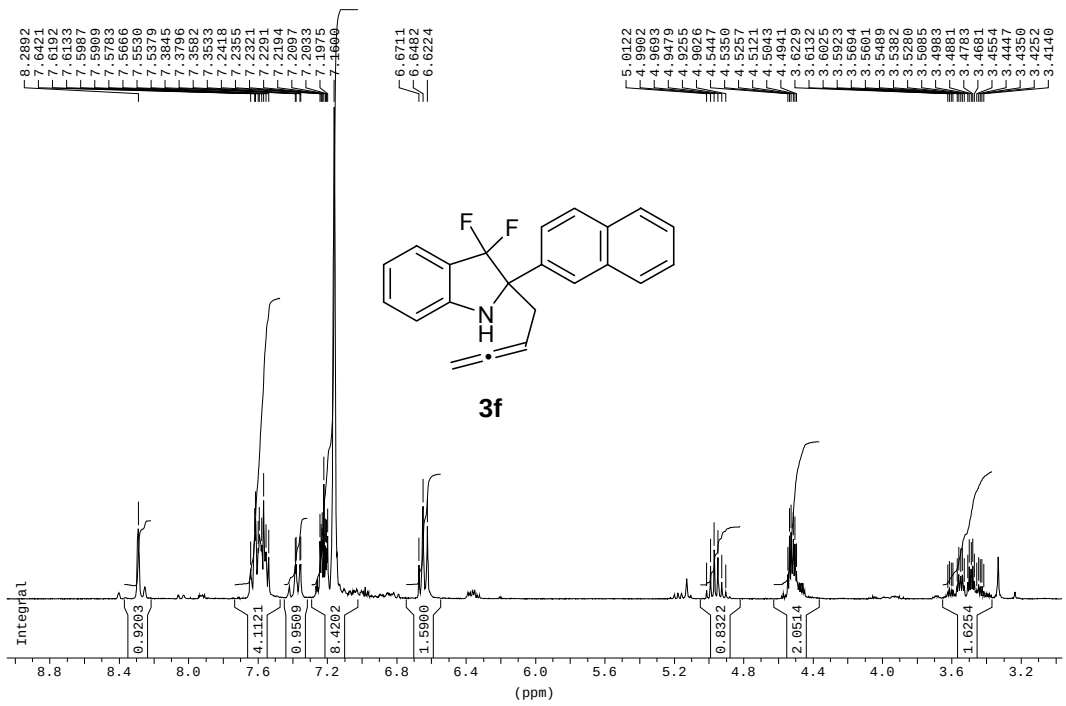

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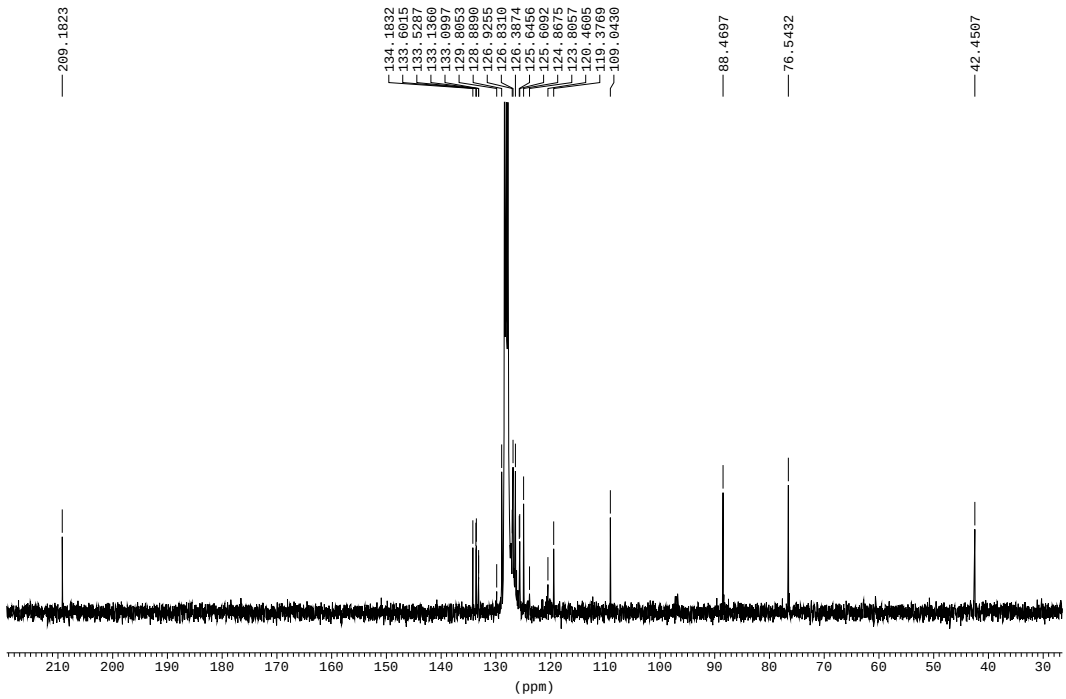

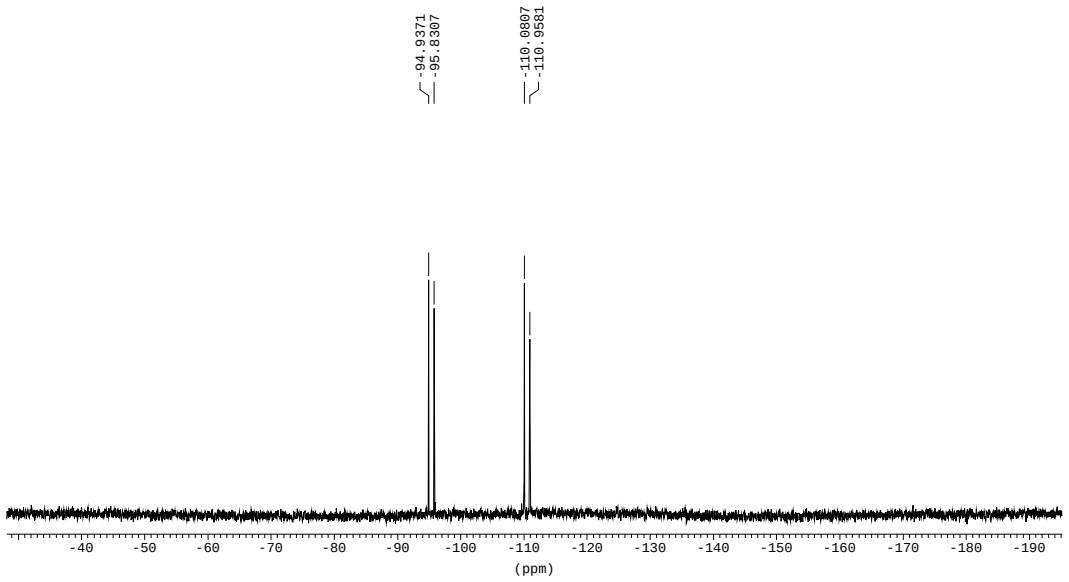
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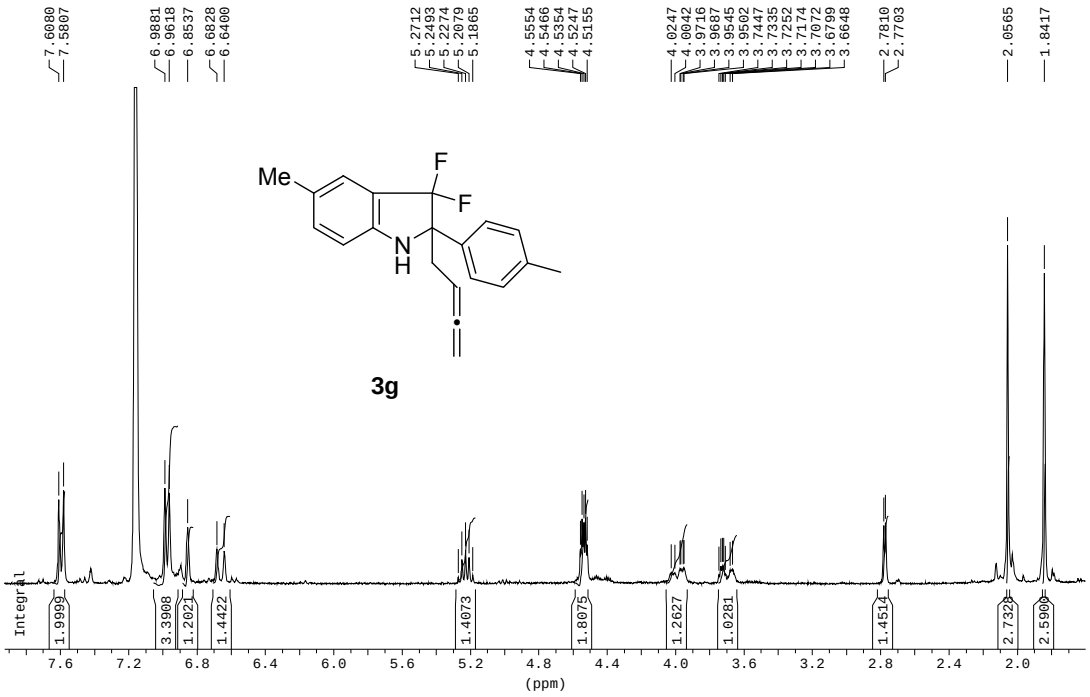
(ppm)

Q09SC1385P



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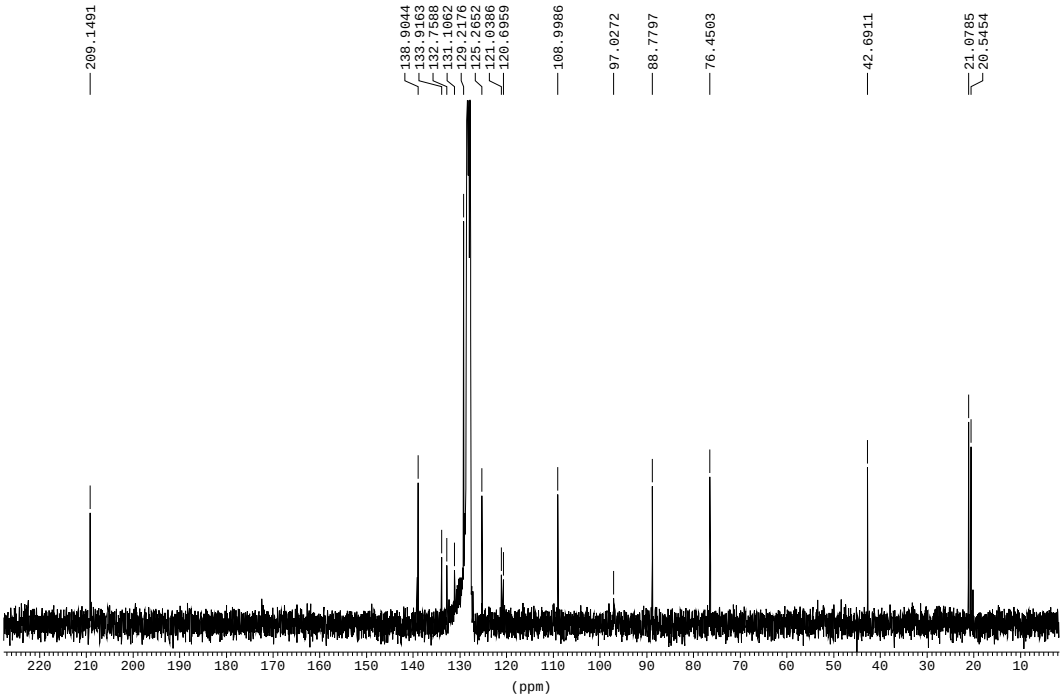

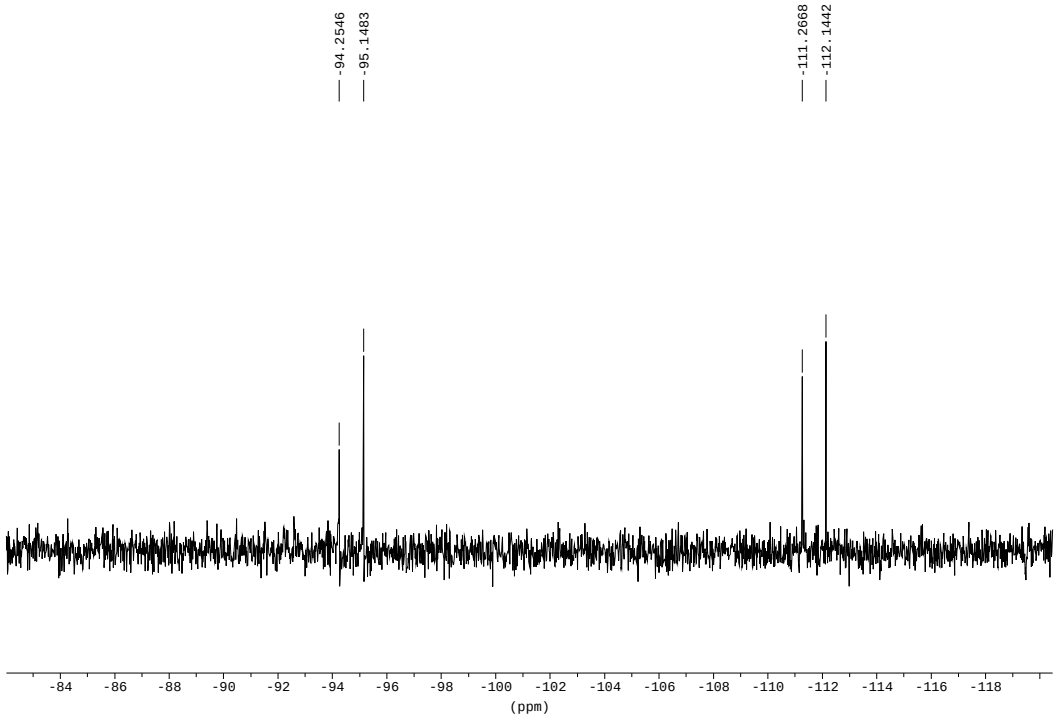
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(ppm)

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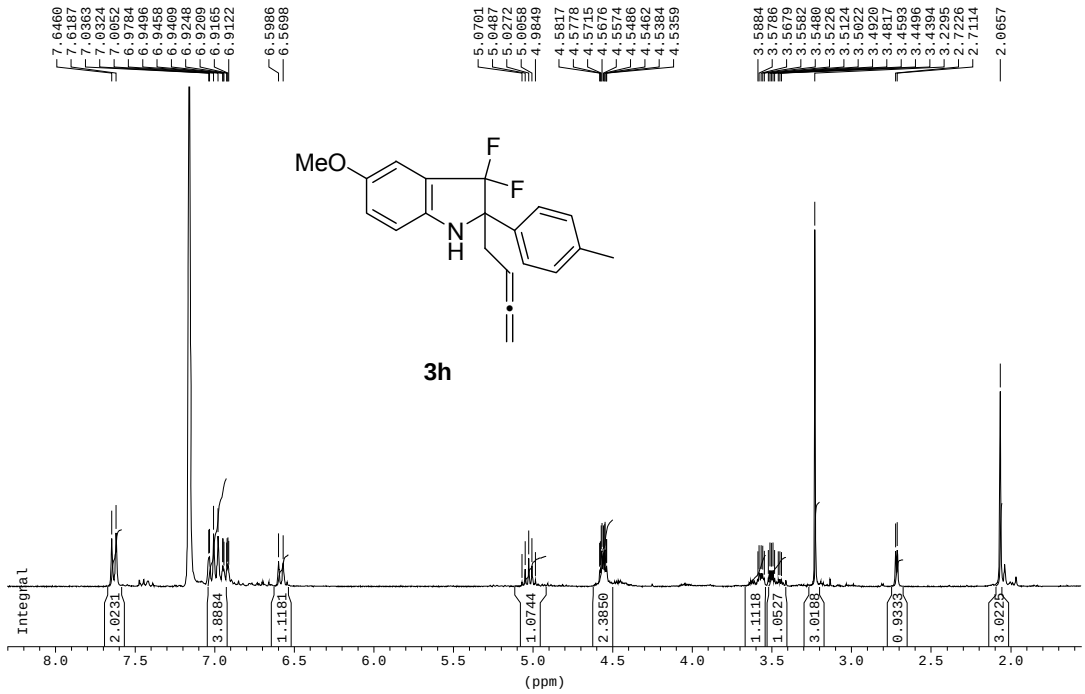

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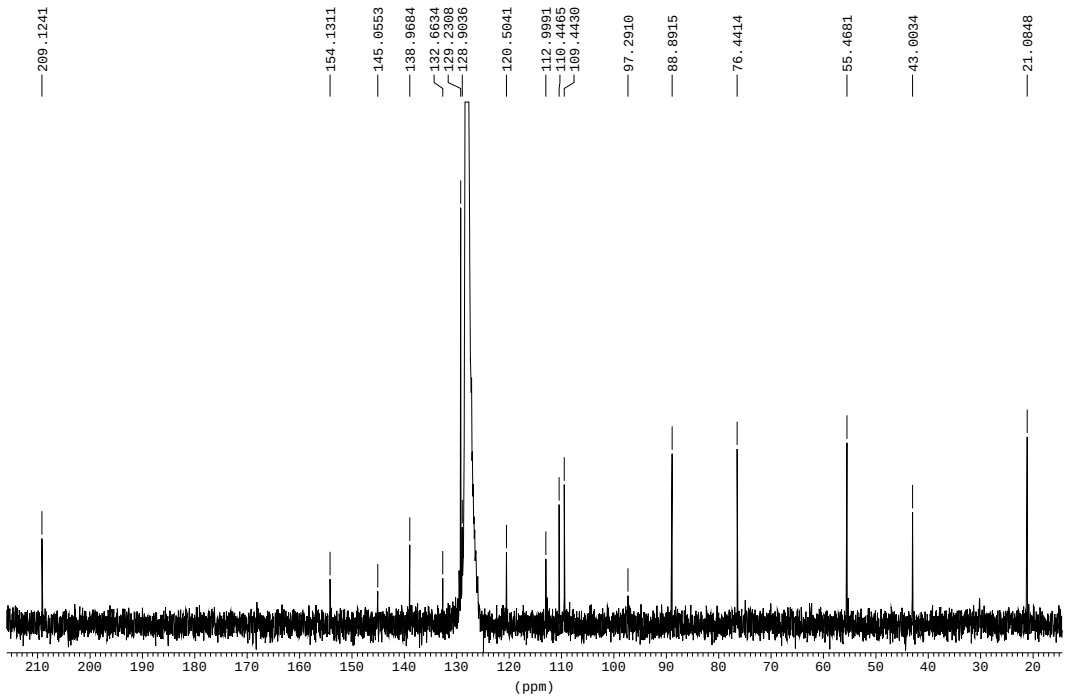

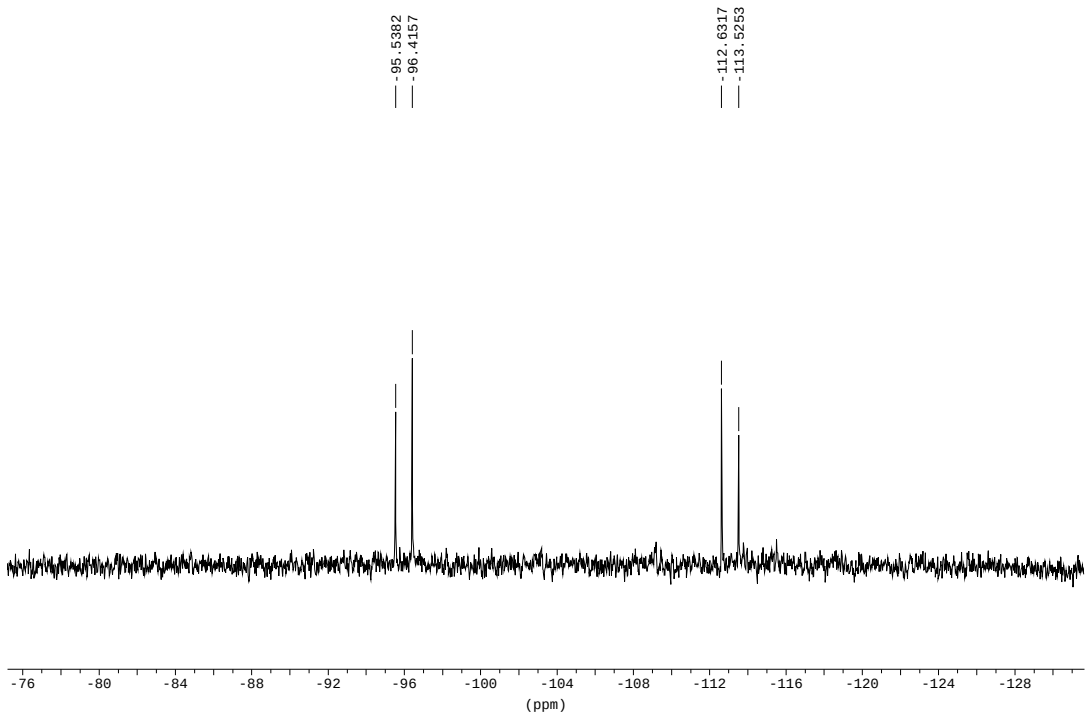
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-128
(ppm)

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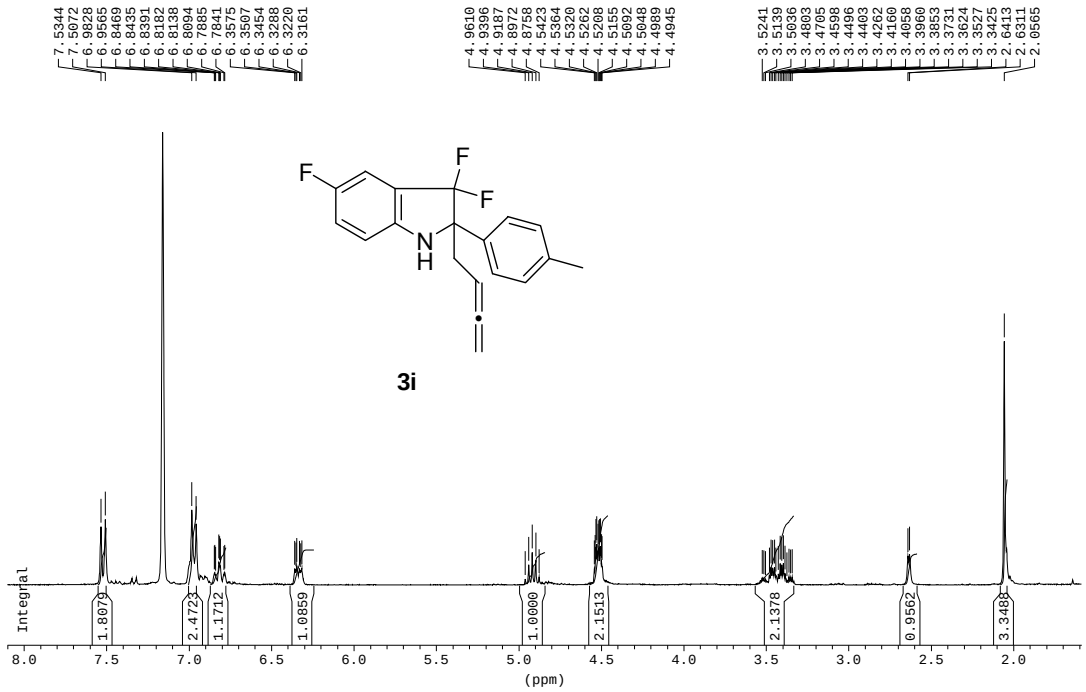

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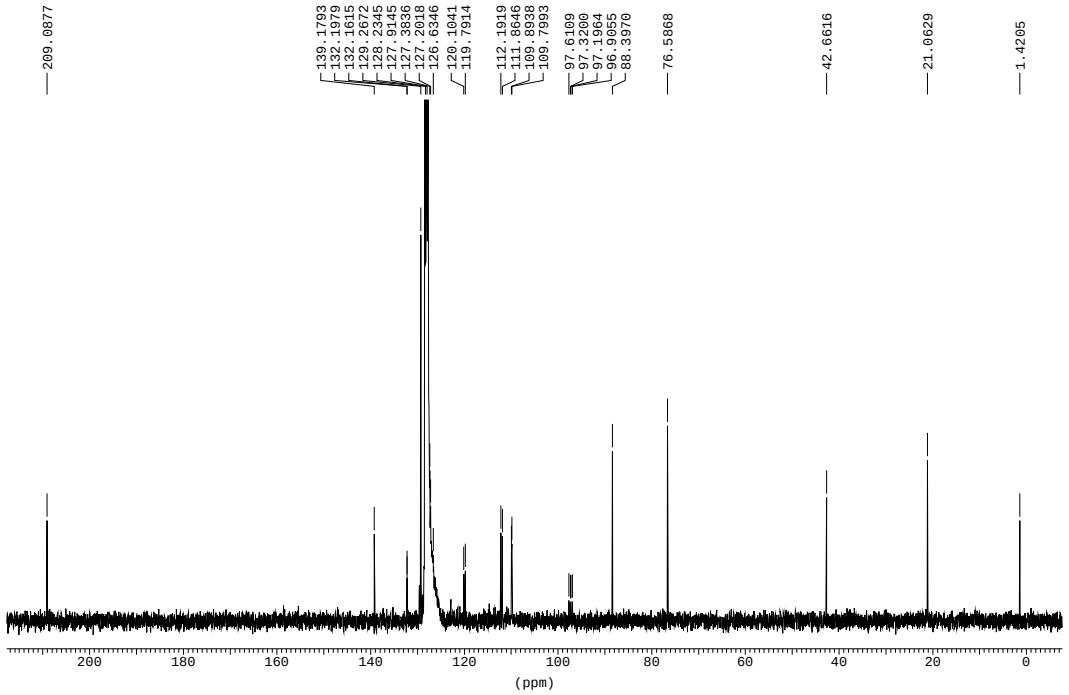

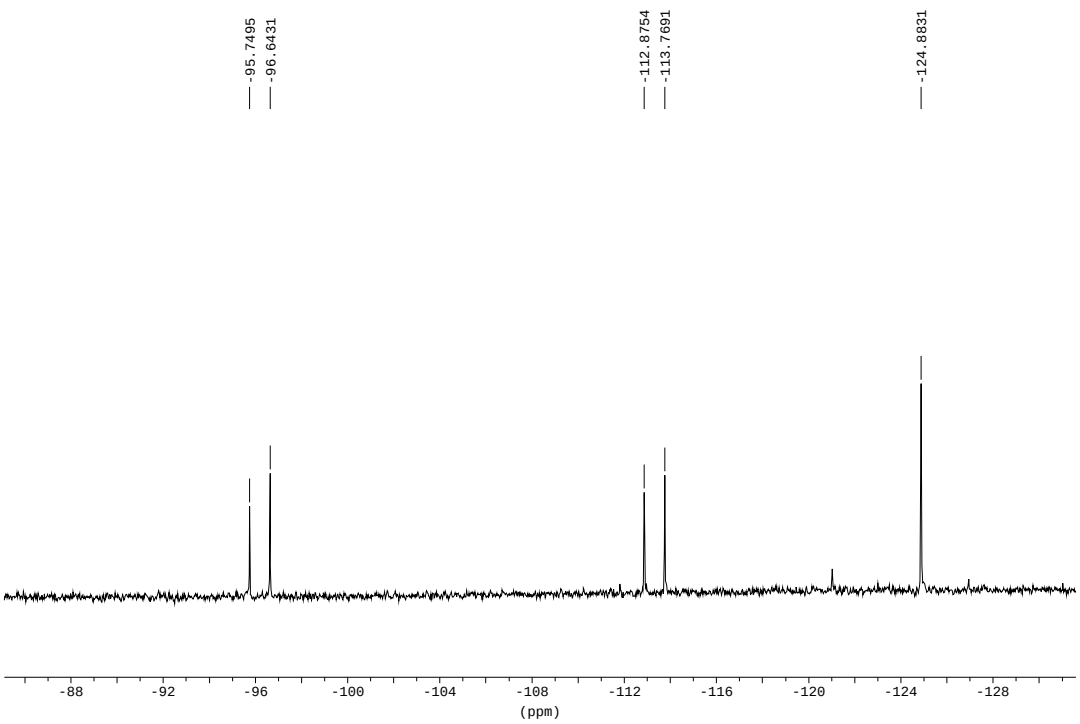
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(ppm)

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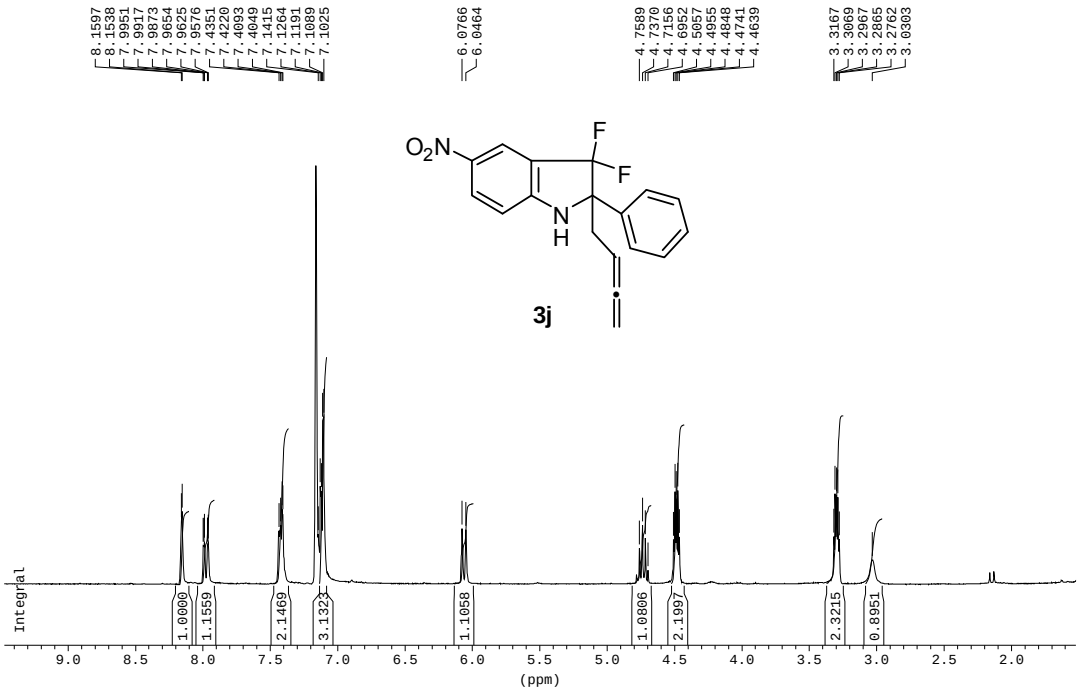

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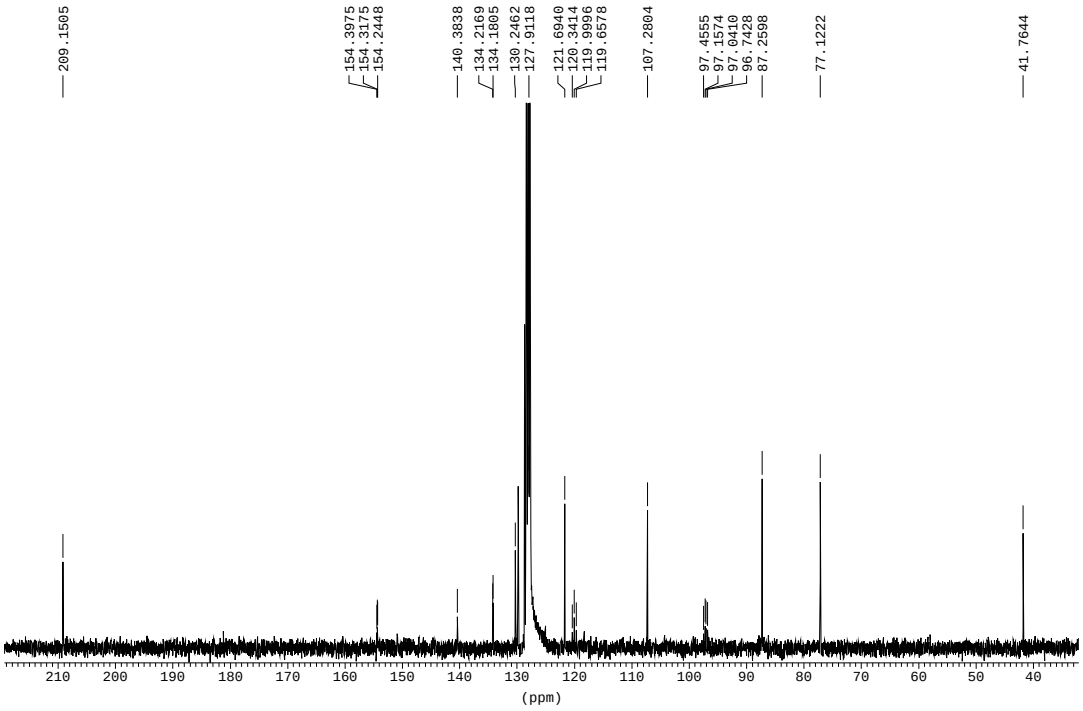

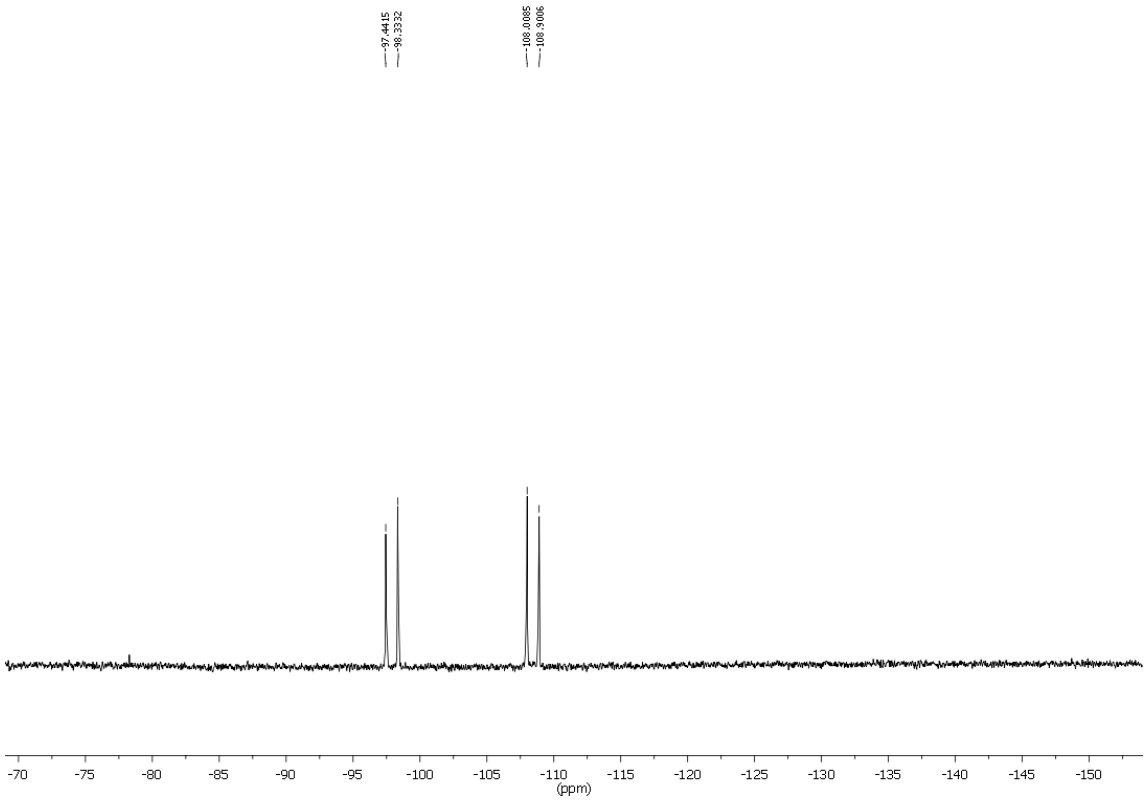
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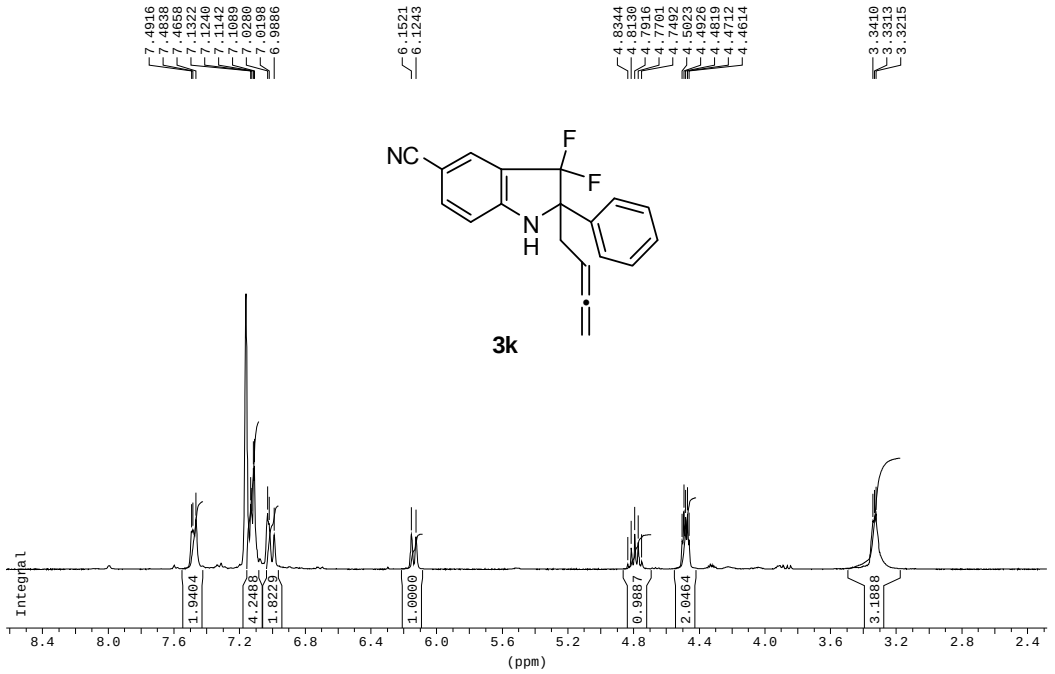

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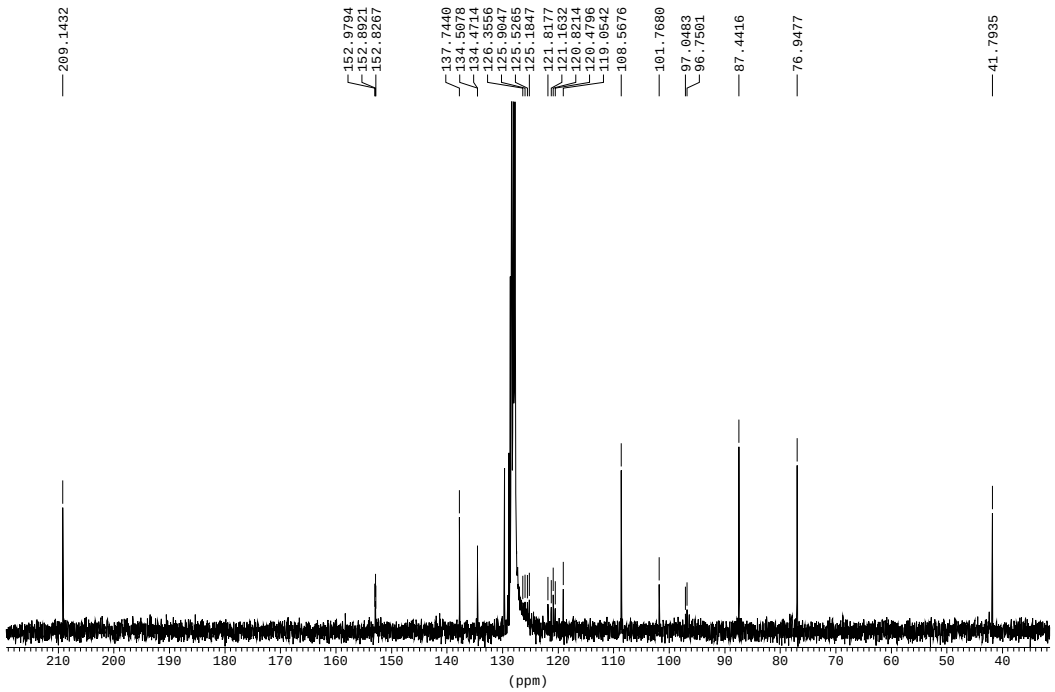

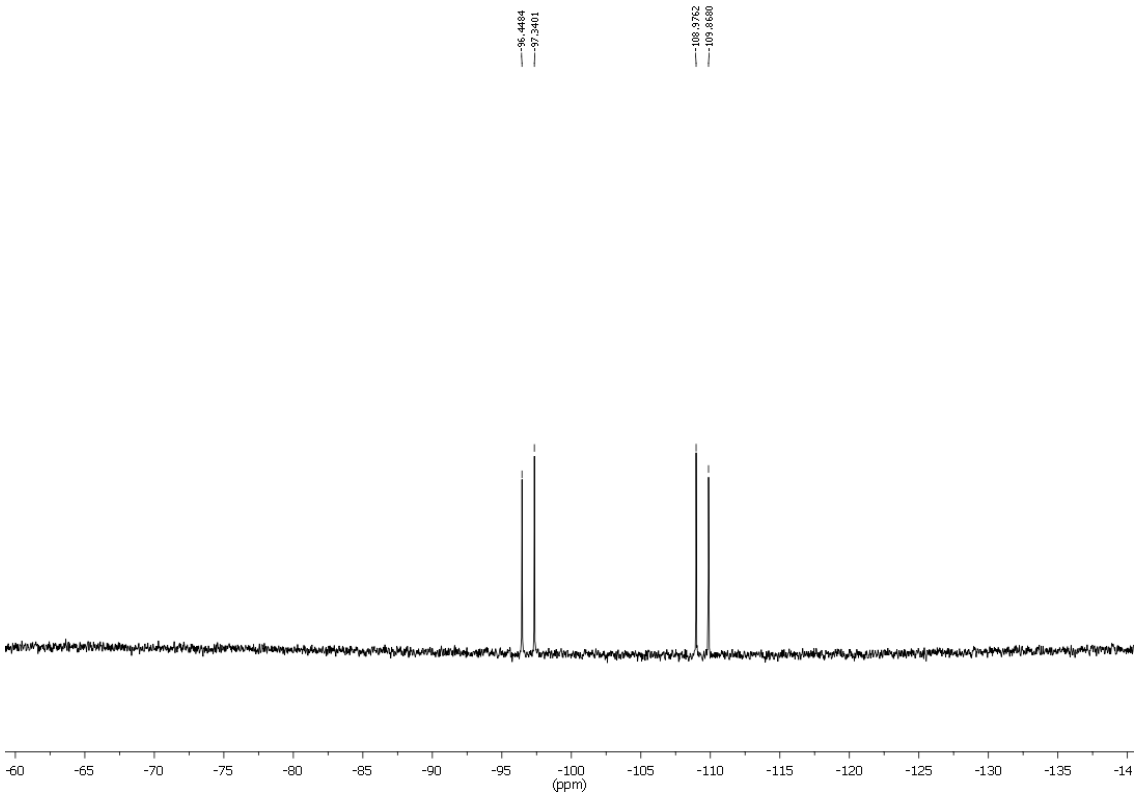
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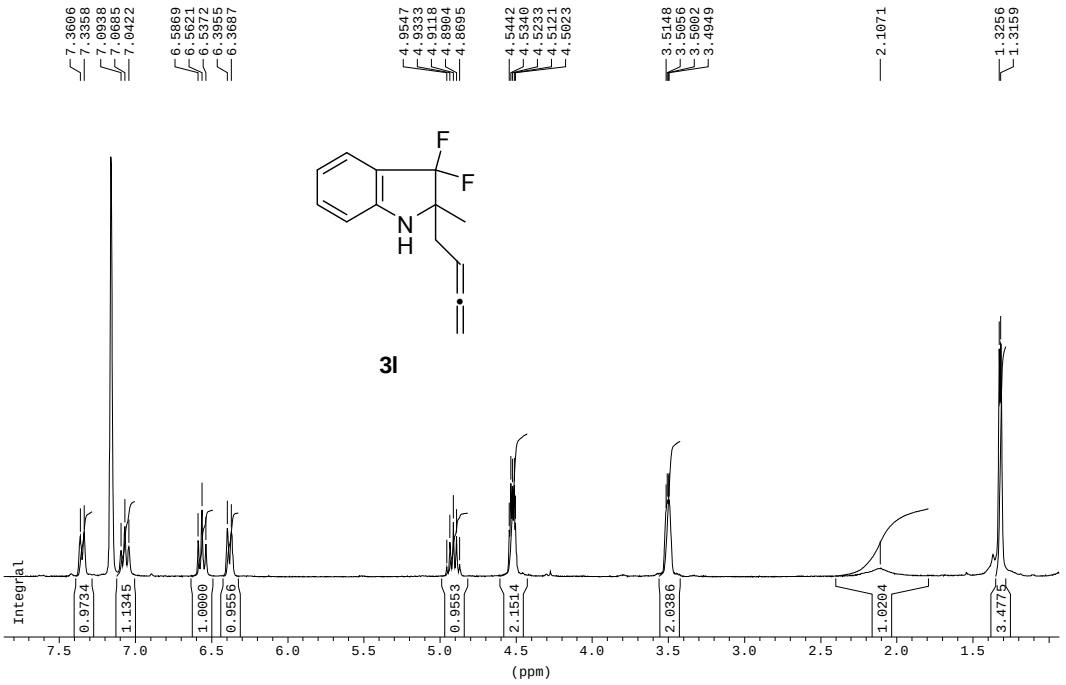
-97.3401
-108.9762
-109.8680
-60
-65
-70
-75
-80
-85
-90
-95
-100
(ppm)
-105
-110
-115
-120
-125
-130
-135
-14

Q09SC1431RA



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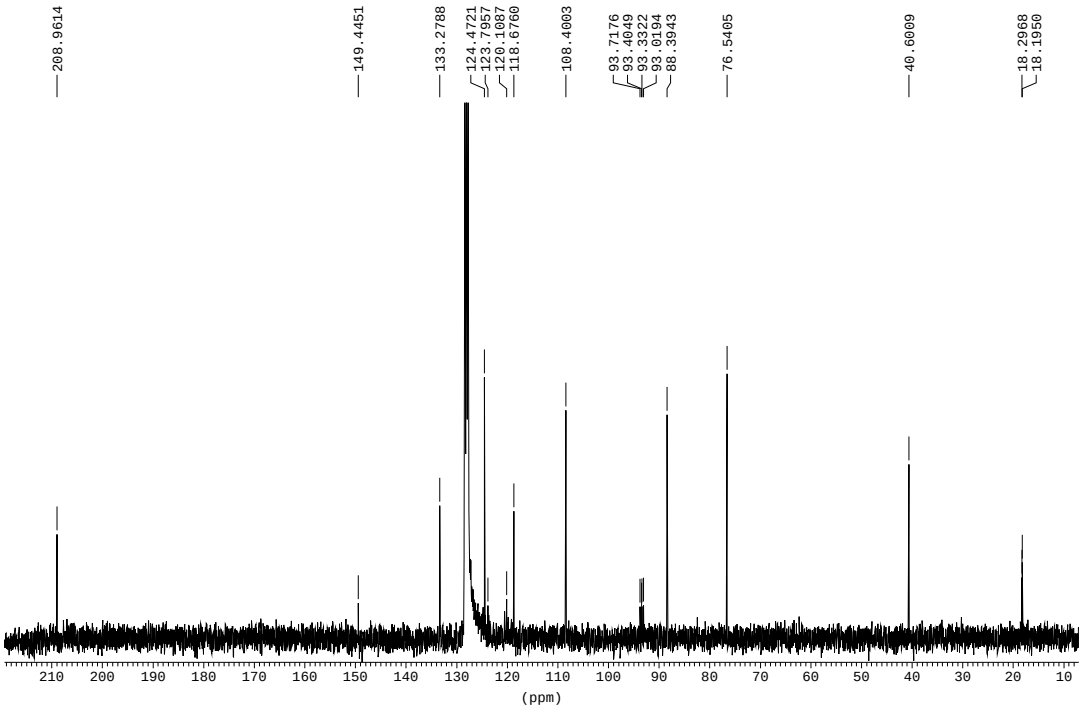

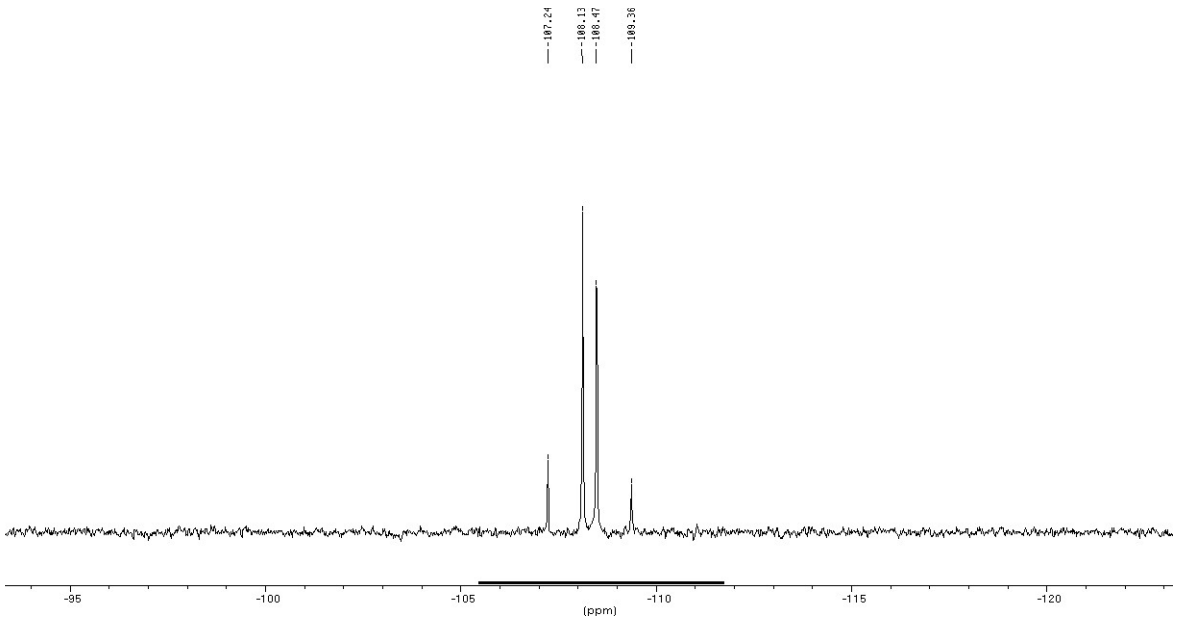
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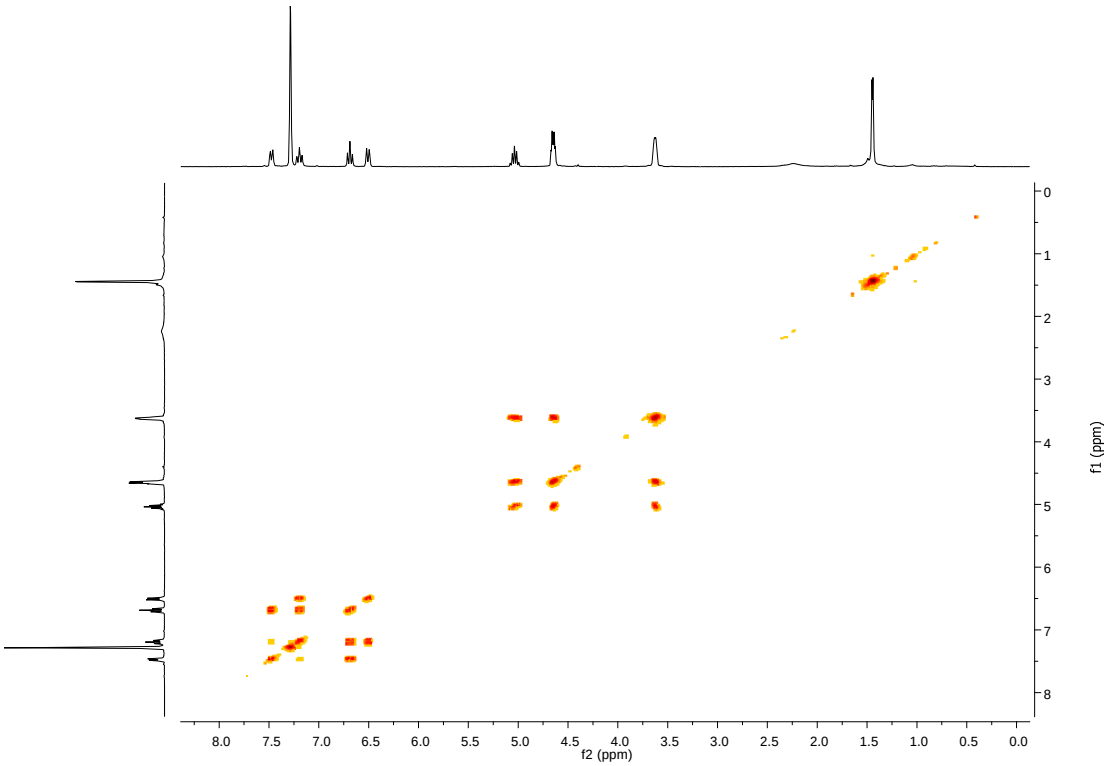
-108.47
-109.36
-95
-100
-105
-110
-115
-120
(ppm)

COSY: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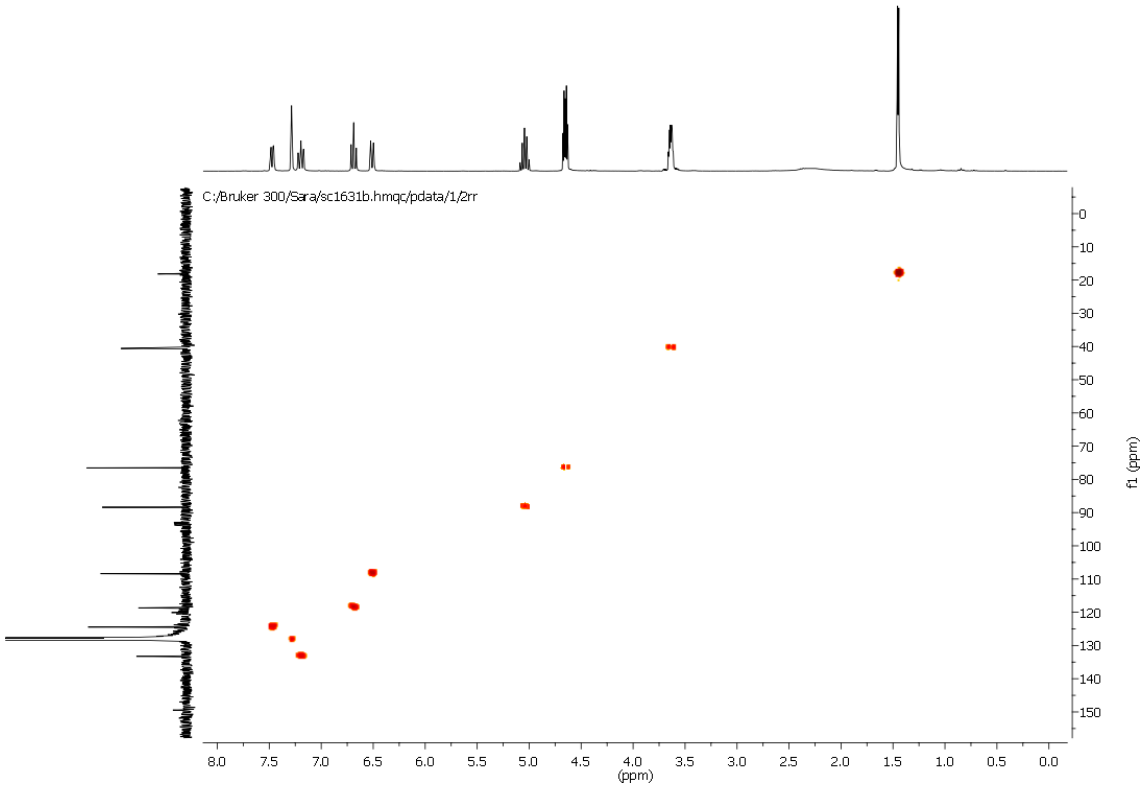
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

HMQC: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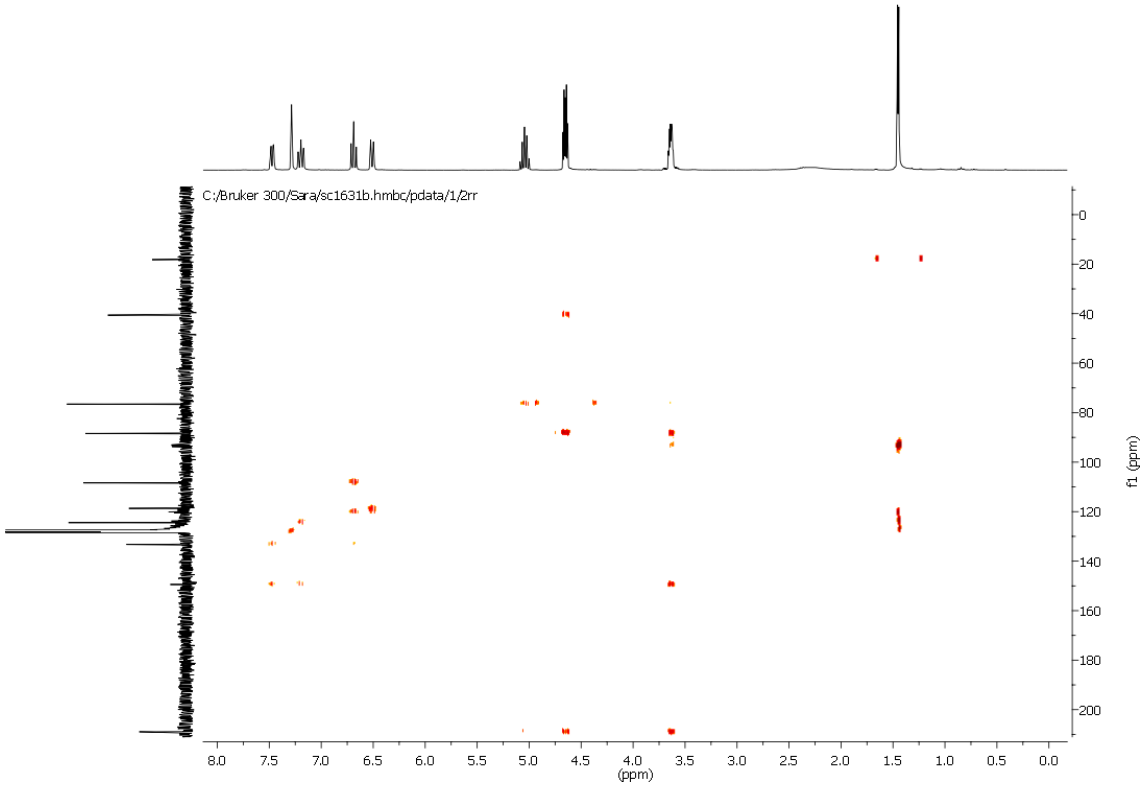
f1 (ppm)
(ppm)

HMBC: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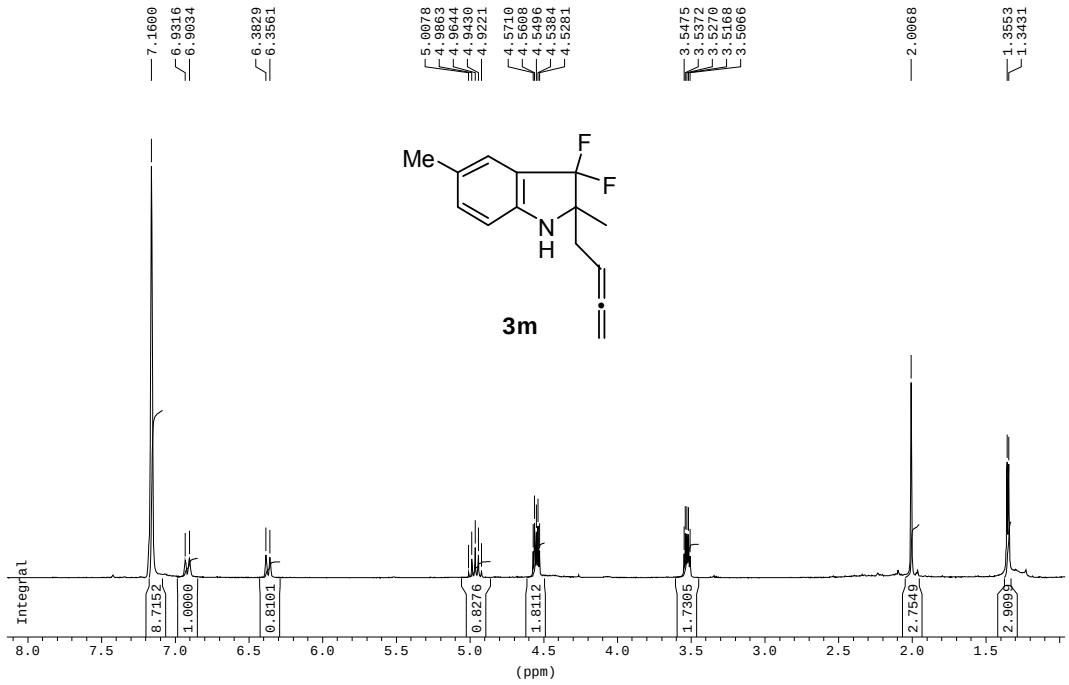
f1 (ppm)
(ppm)

Q09SC1648B



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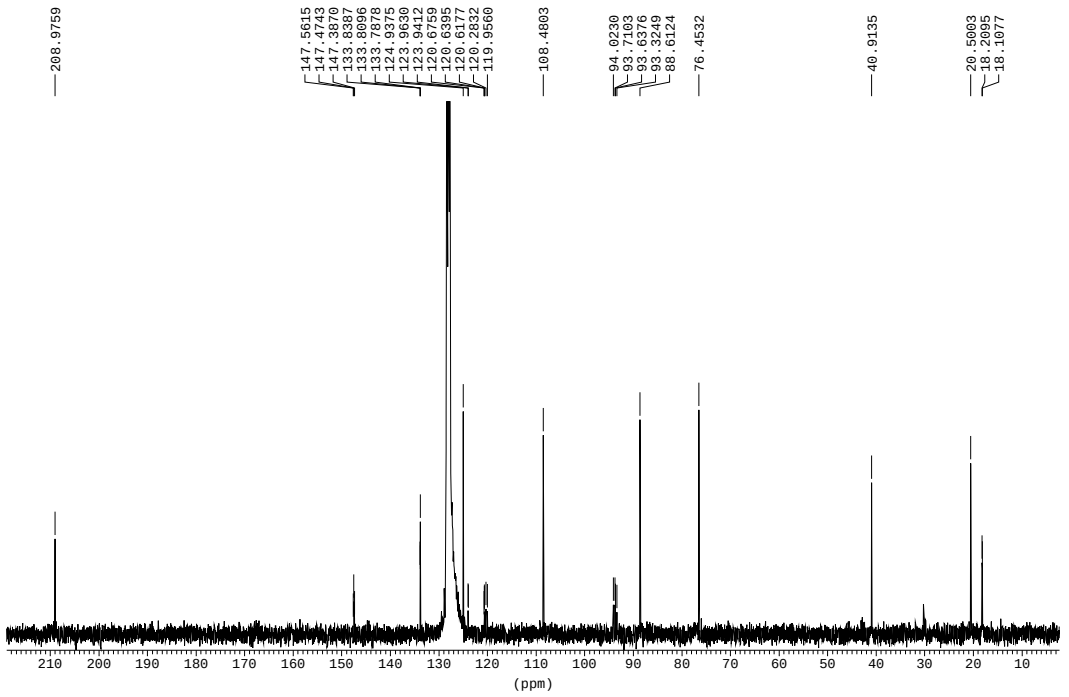
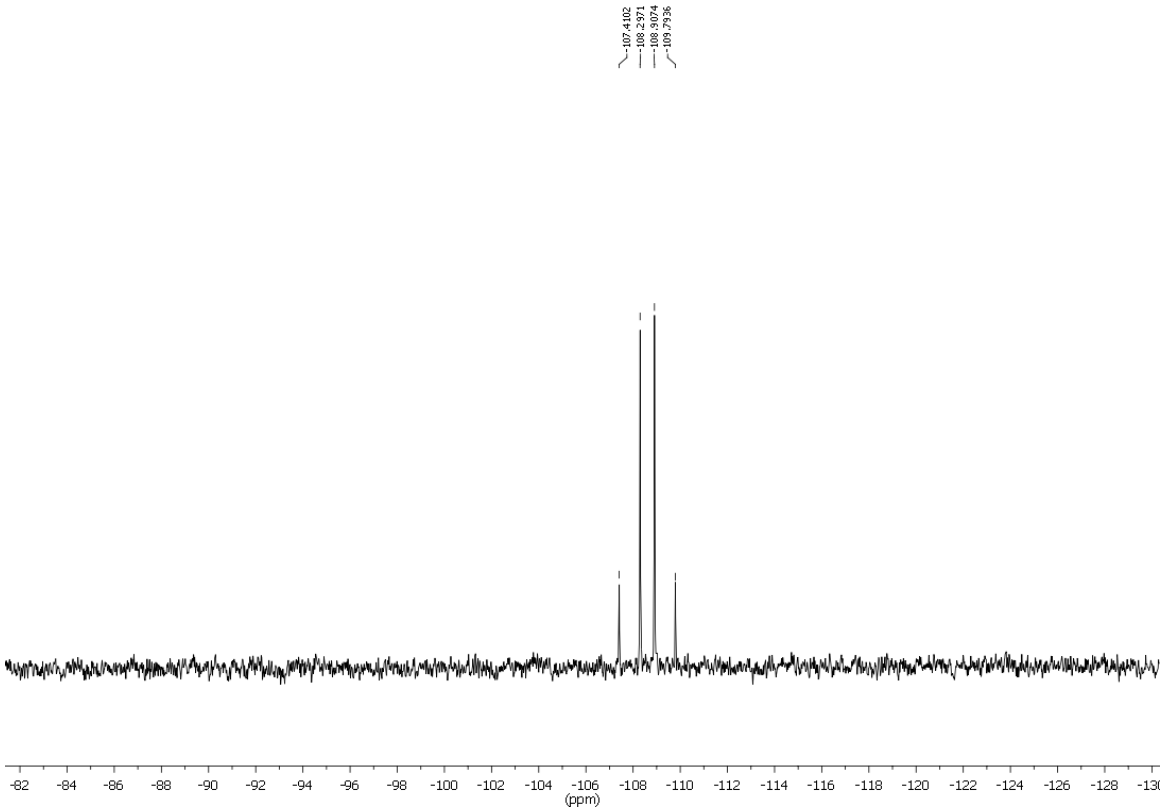
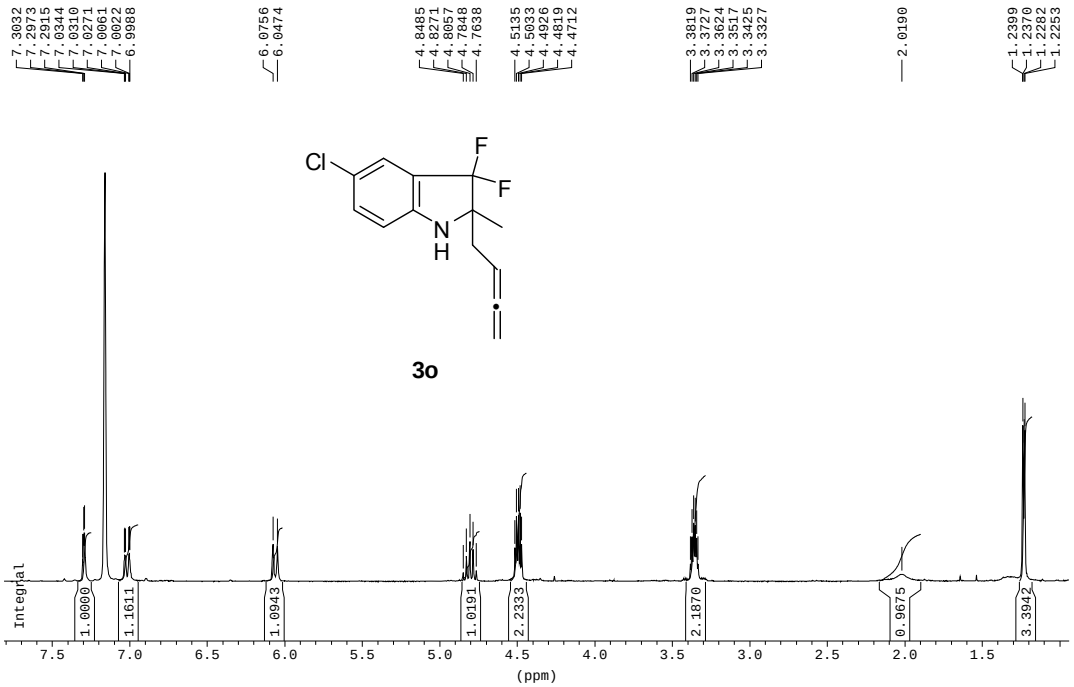
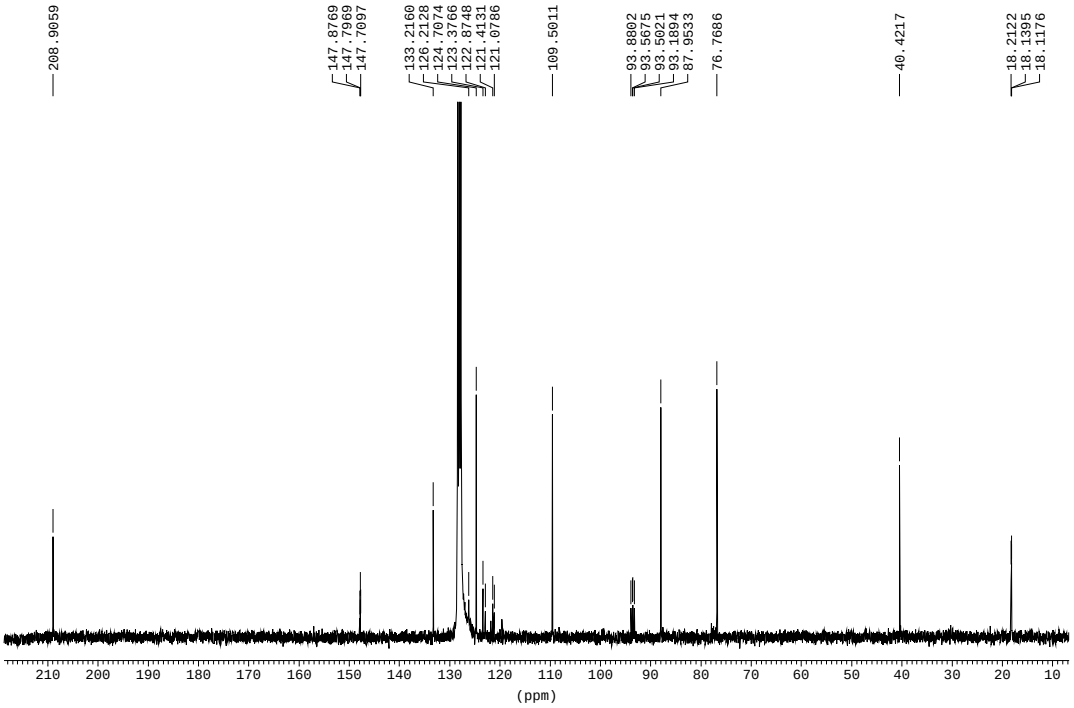


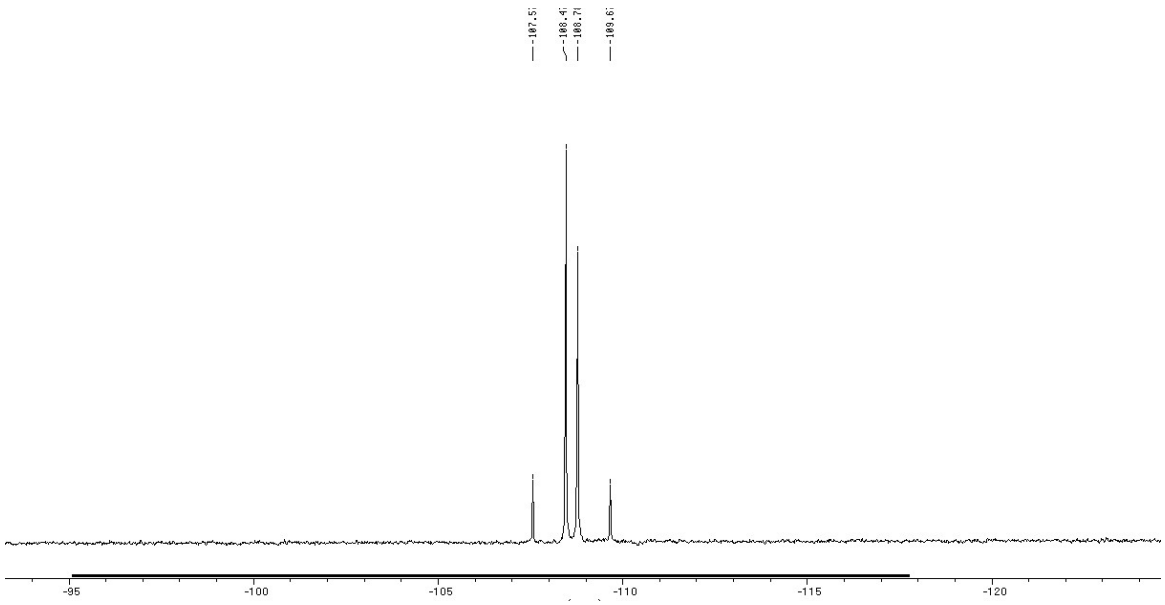

-107.4102
-108.2971
-108.9074
-109.7936
-82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128
(ppm)

Q09SC1428D1



Q09SC1428D

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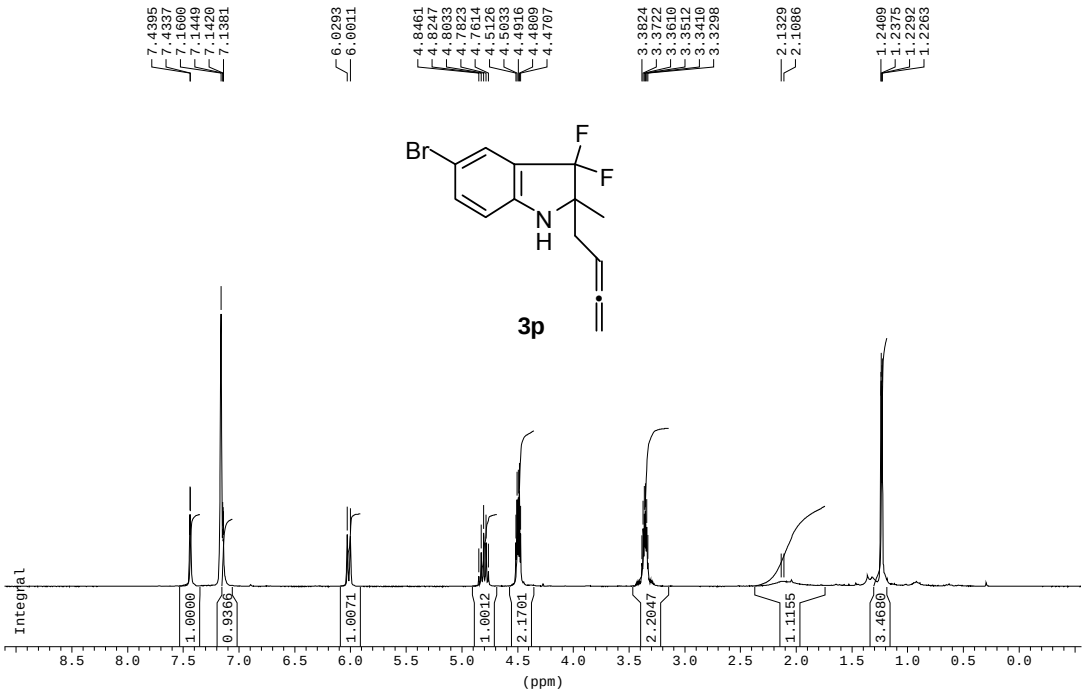
-108.46
-108.71
-109.61
-95
-100
-105
-110
-115
-120

Q09SC1662C



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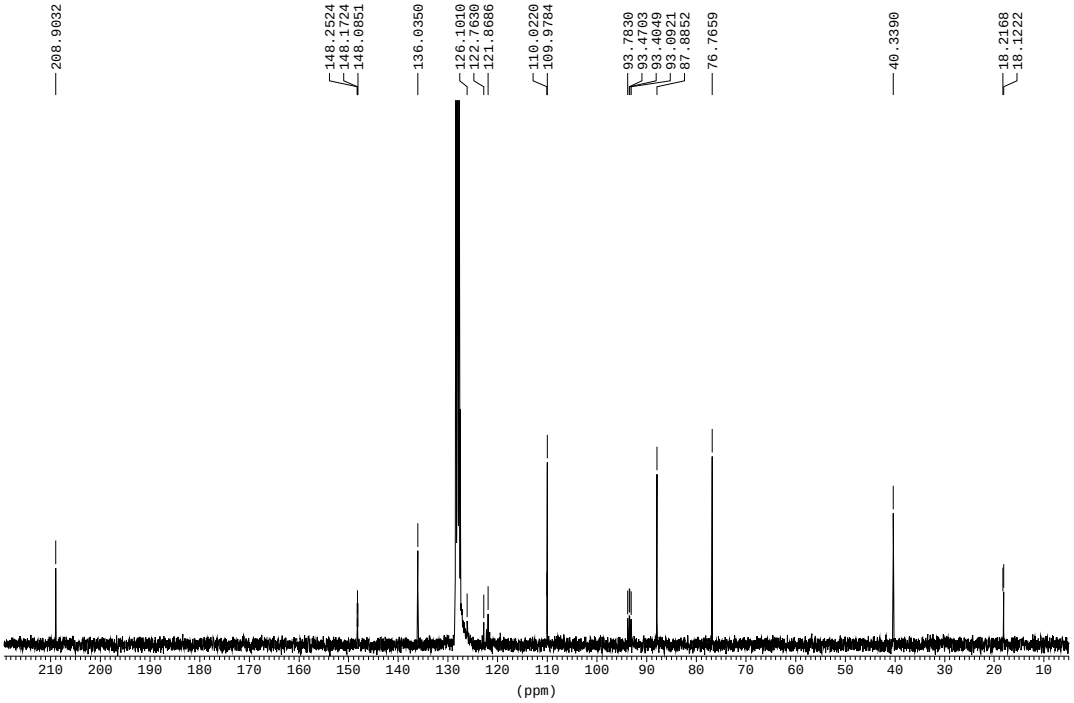

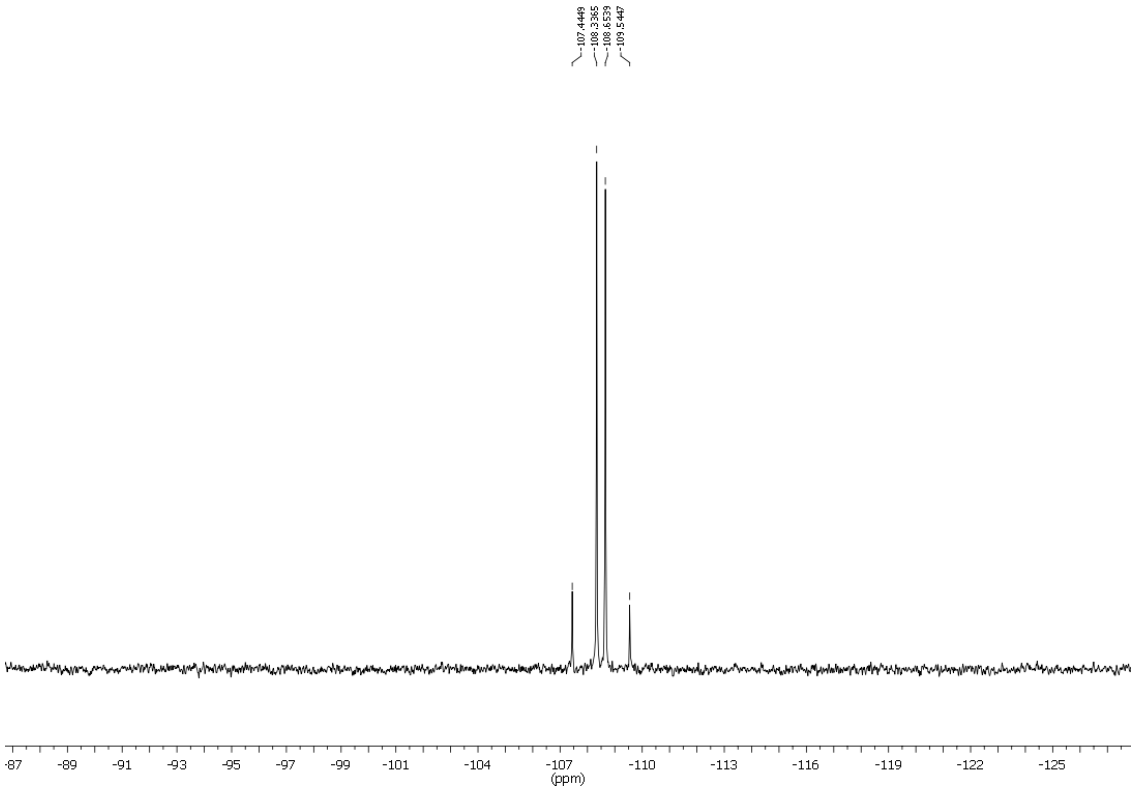
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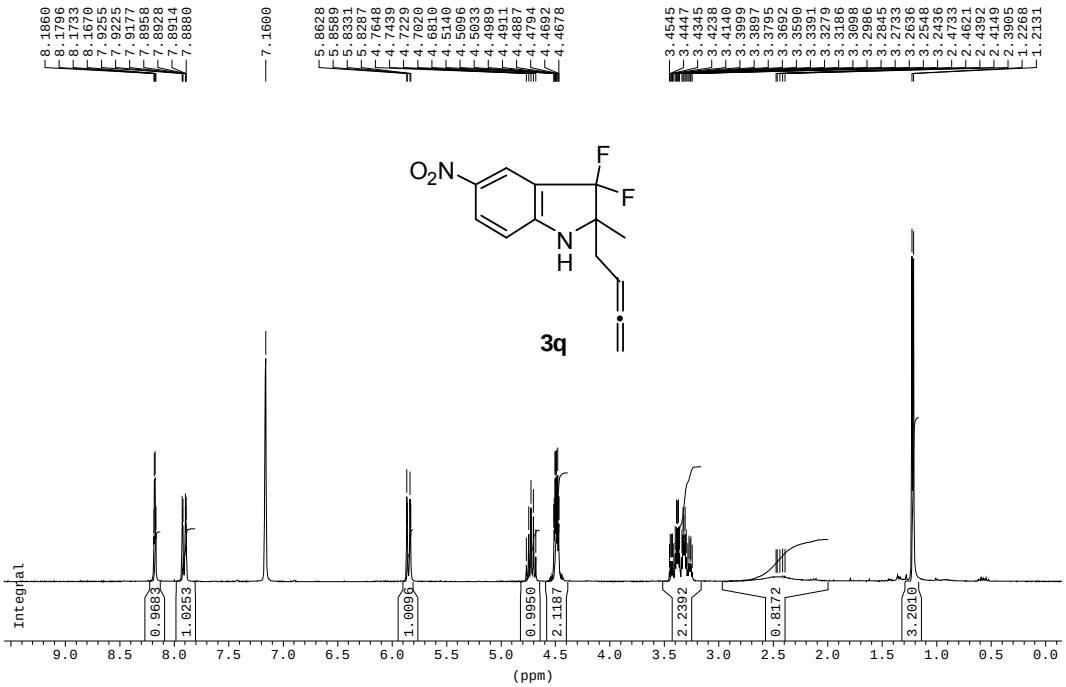
-108.3365
-108.6539
-109.5447
-87
-89
-91
-93
-95
-97
-99
-101
-104
-107
(ppm)
-110
-113
-116
-119
-122
-125

Q09SC1671B



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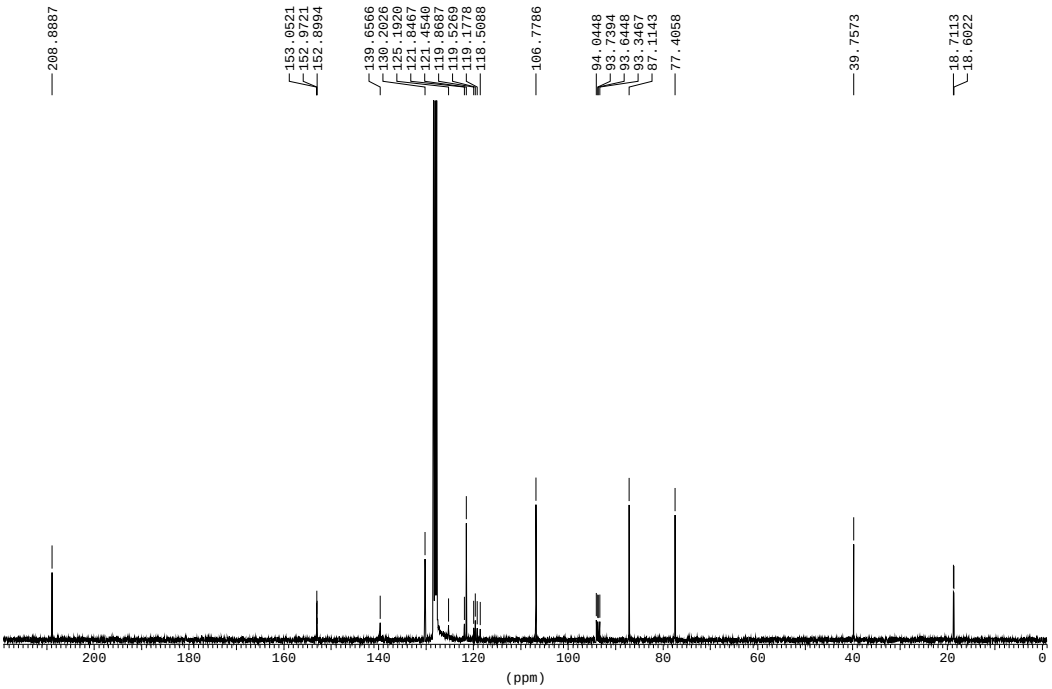
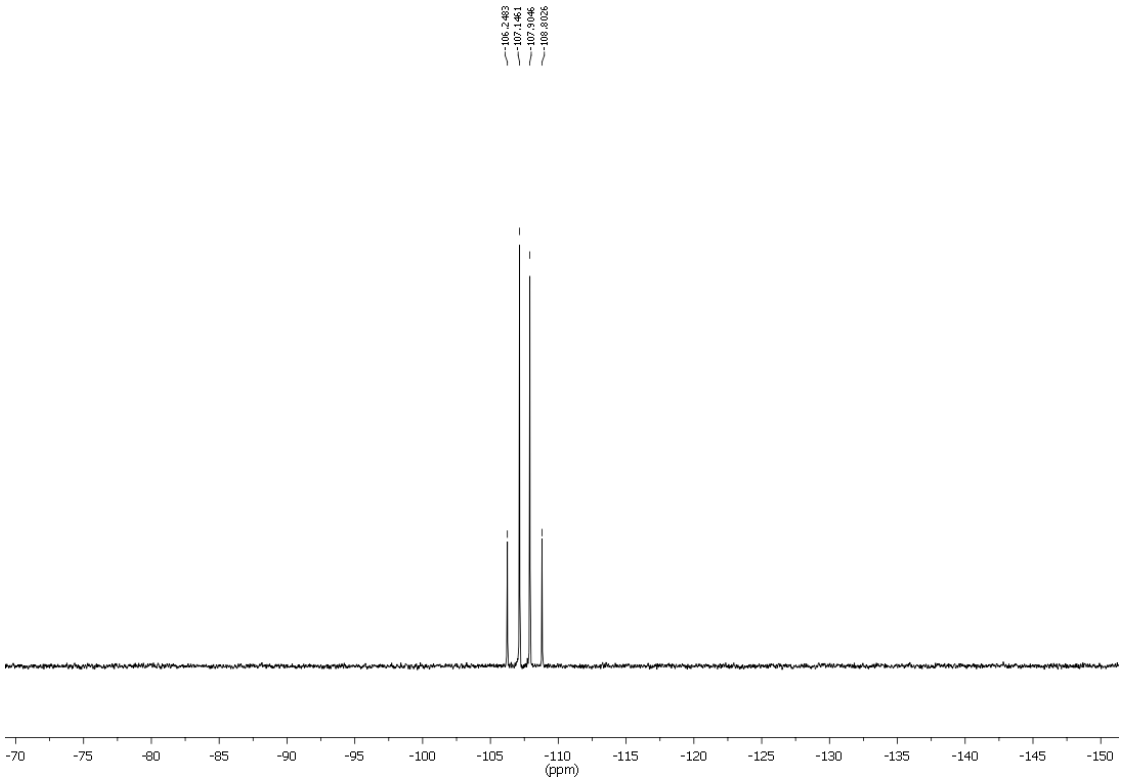
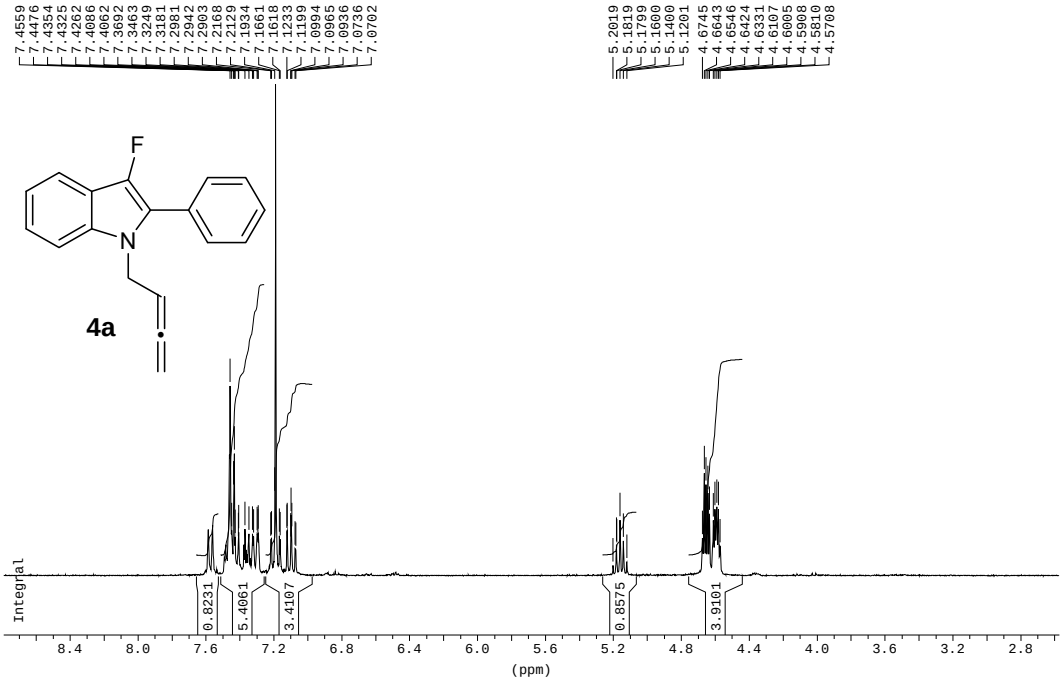
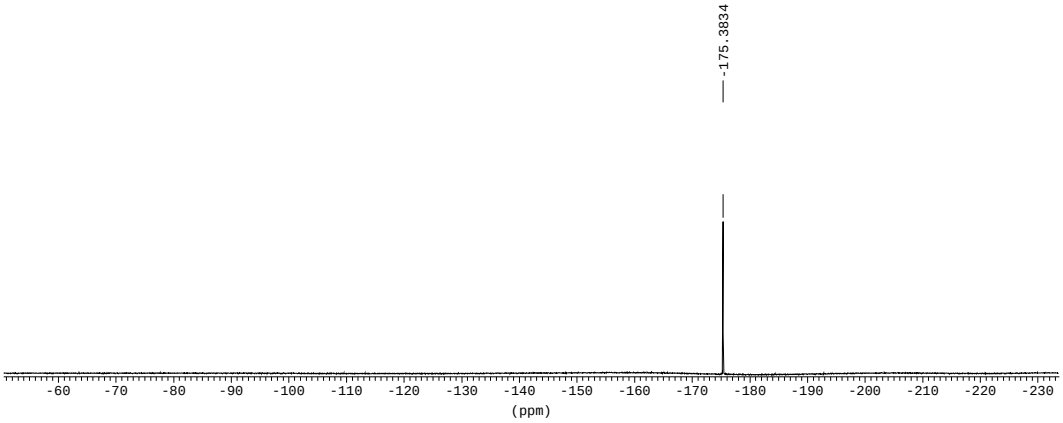



-106.2463
-107.7461
-107.9046
-108.8026
-70
-75
-80
-85
-90
-95
-100
-105
-110
(ppm)
-115
-120
-125
-130
-135
-140
-145
-150

Q09TM341C


7.4559
7.4476
7.4354
7.4325
7.4282
7.4086
7.4062
7.3692
7.3463
7.3249
7.3181
7.2981
7.2942
7.2903
7.2168
7.2129
7.1934
7.1661
7.1618
7.1233
7.1199
7.0994
7.0965
7.0936
7.0736
7.0702
5.2019
5.1819
5.1799
5.1600
5.1400
5.1201
4.6745
4.6643
4.6546
4.6424
4.6331
4.6107
4.6005
4.5908
4.5810
4.5708
F
N
4a
Integral
0.8231
5.4061
3.4107
0.8575
3.9101
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
(ppm)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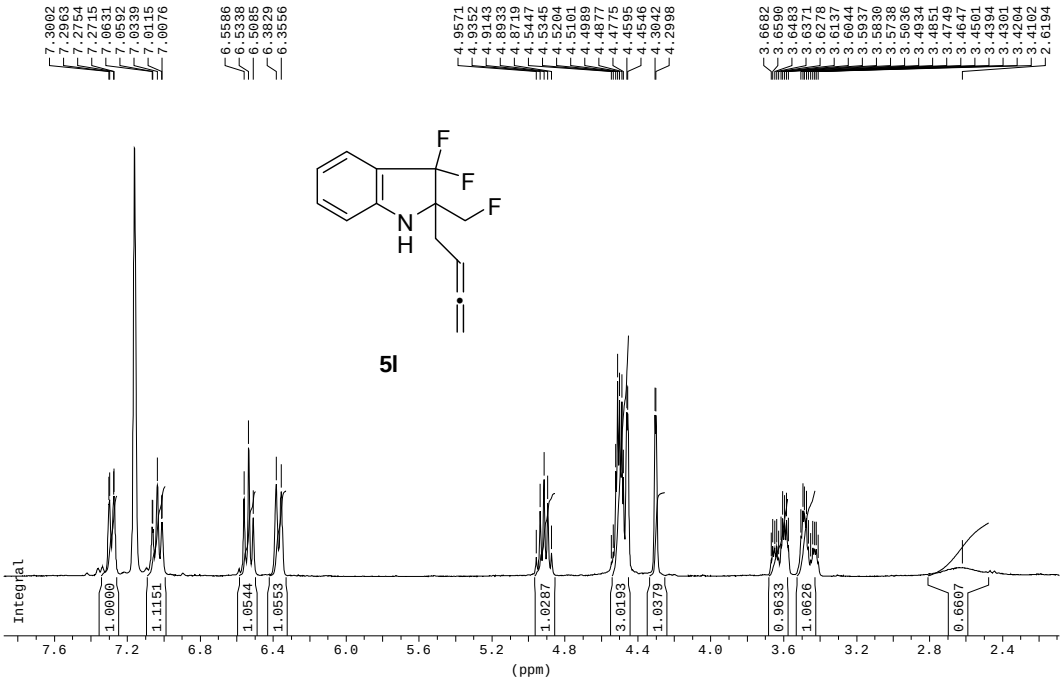
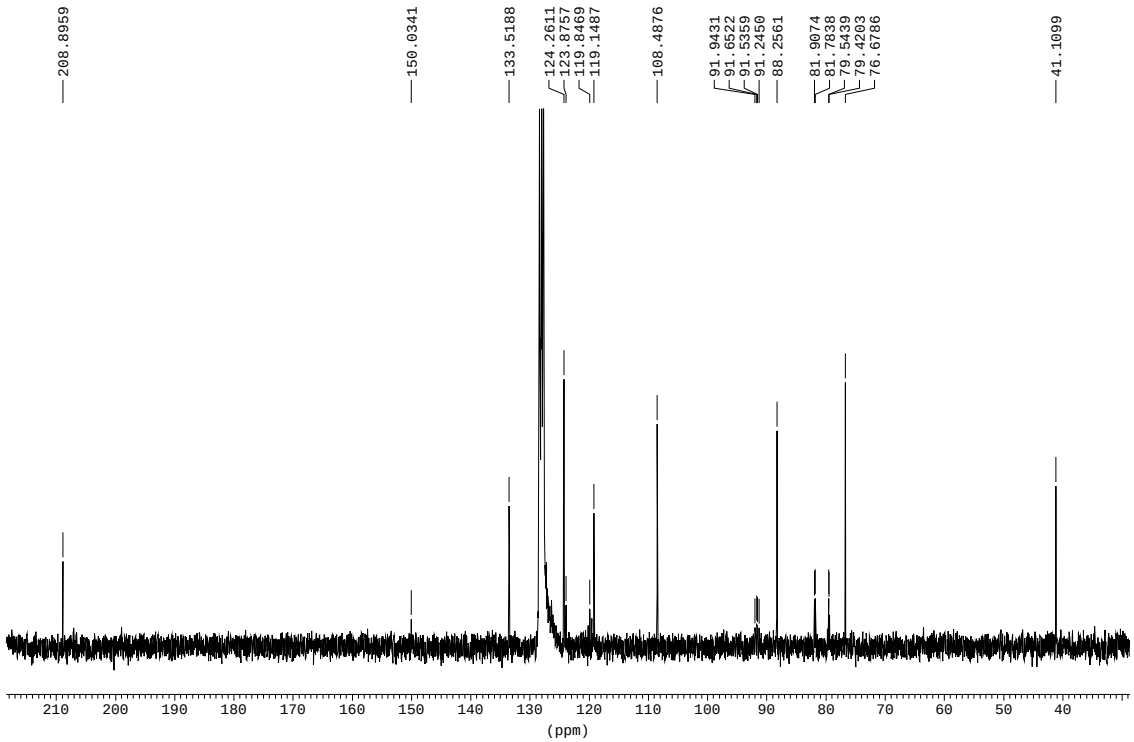
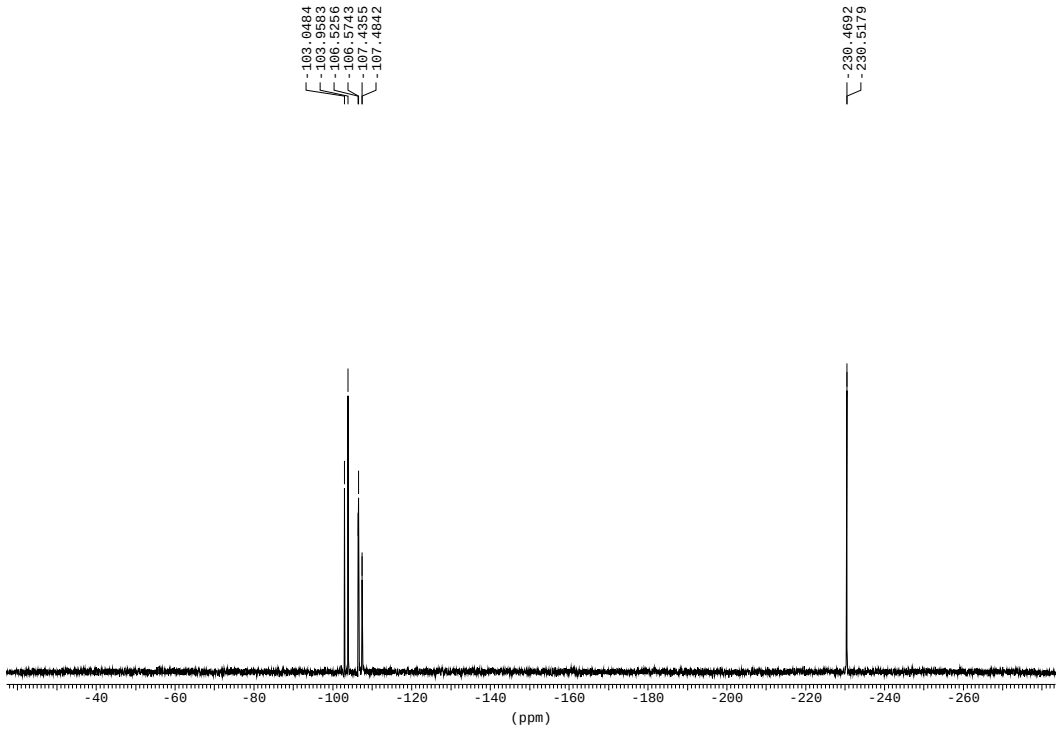
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
(ppm)

Q09SC1431A



Q09SC1431RB3

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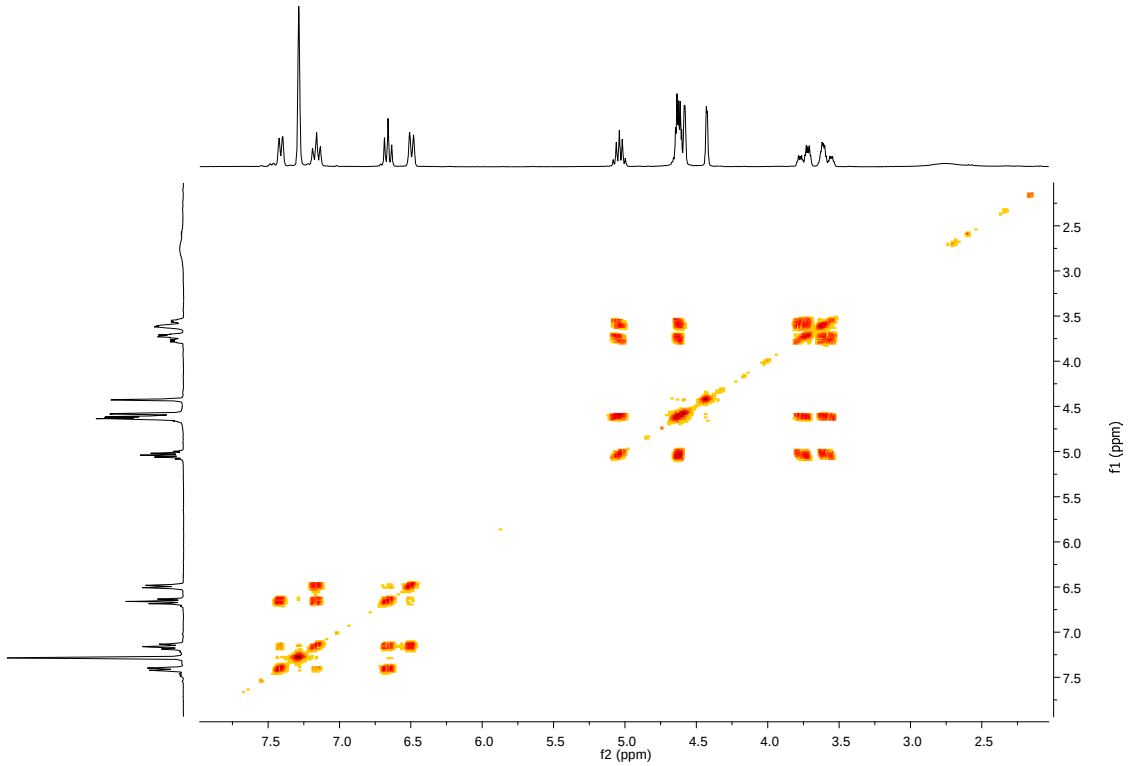
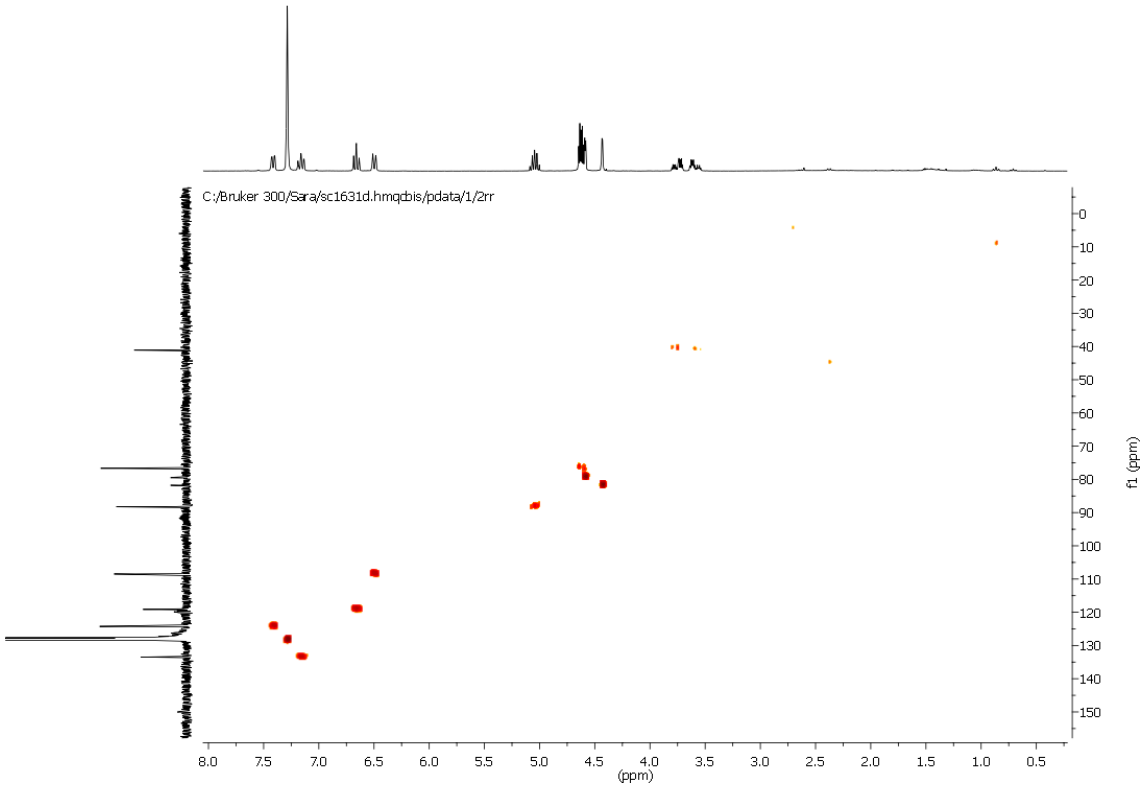
-103.9583
-106.5256
-106.5743
-107.4355
-107.4842
-230.4692
-230.5179
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
(ppm)

COSY:


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
f1 (ppm)

HMQC: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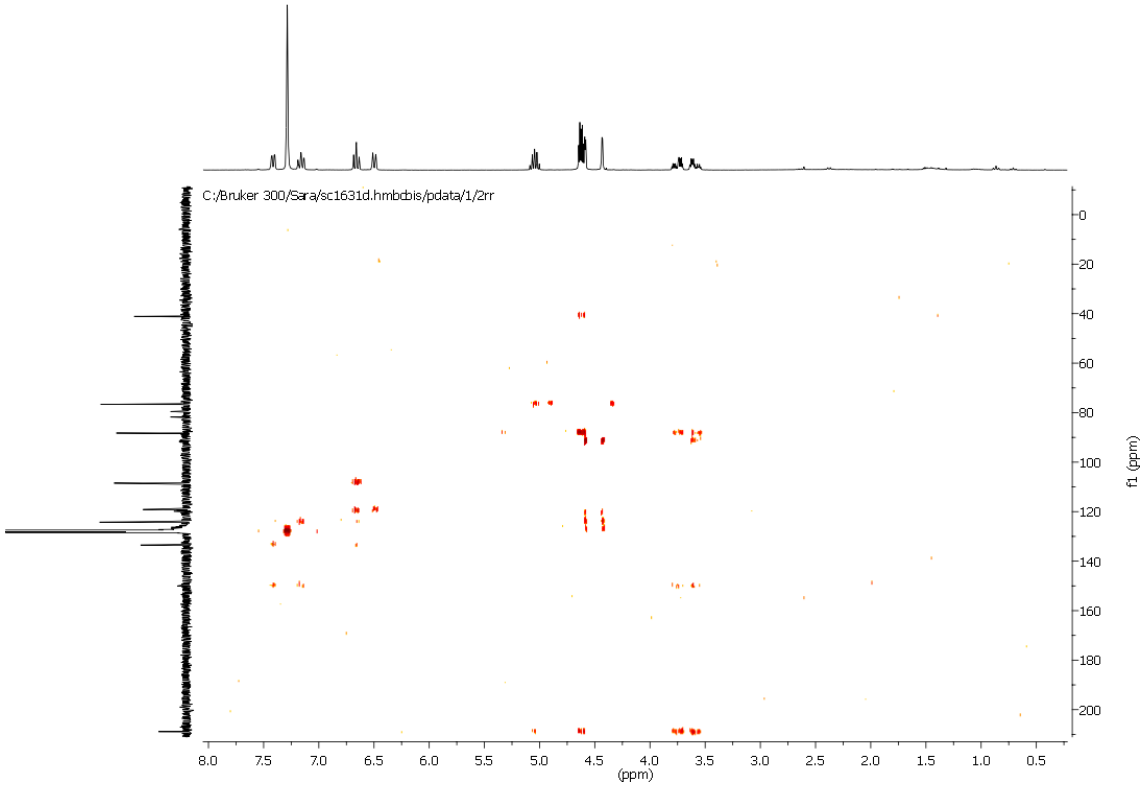
f1 (ppm)
(ppm)

HMBC: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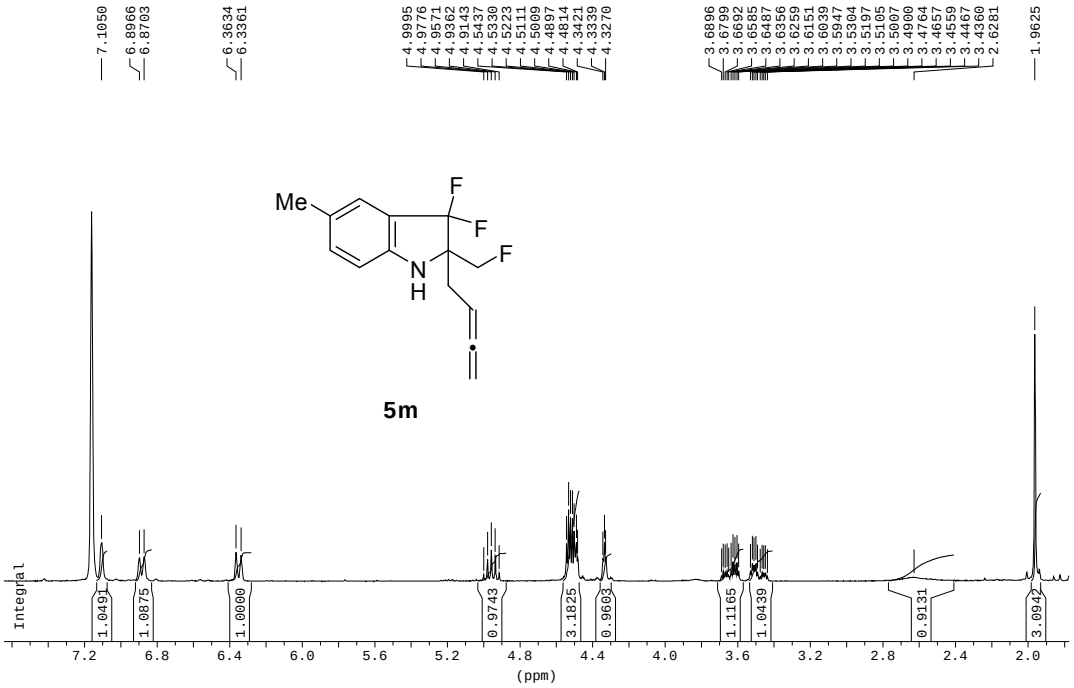
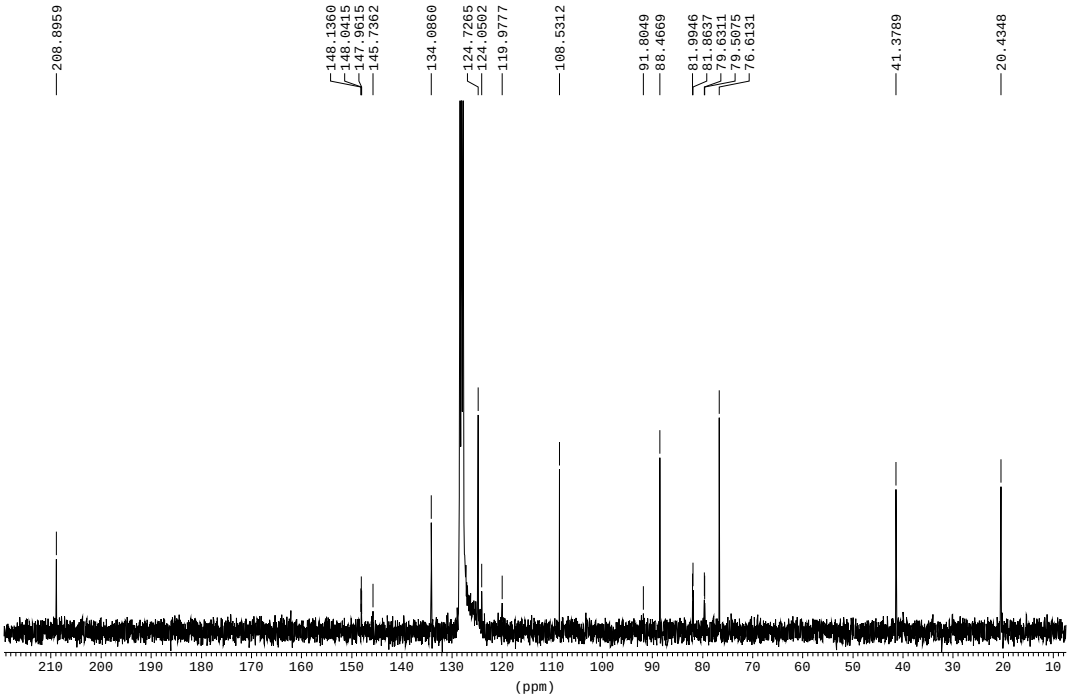
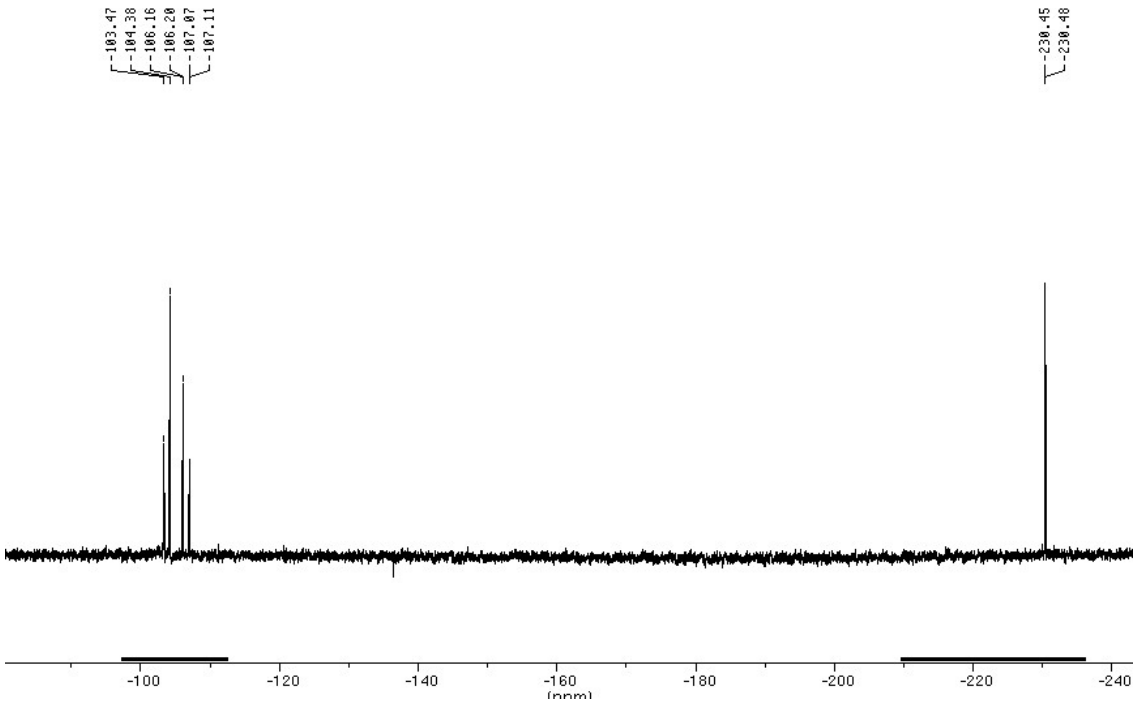
f1 (ppm)
(ppm)

Q09SC1429A

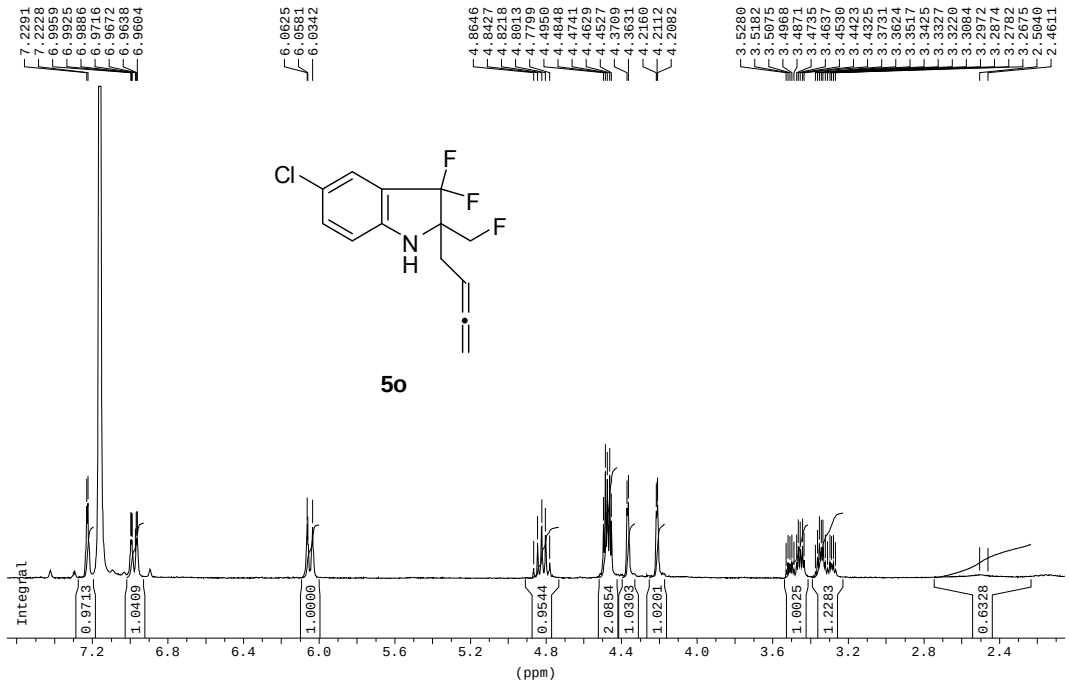


Q09SC1429A

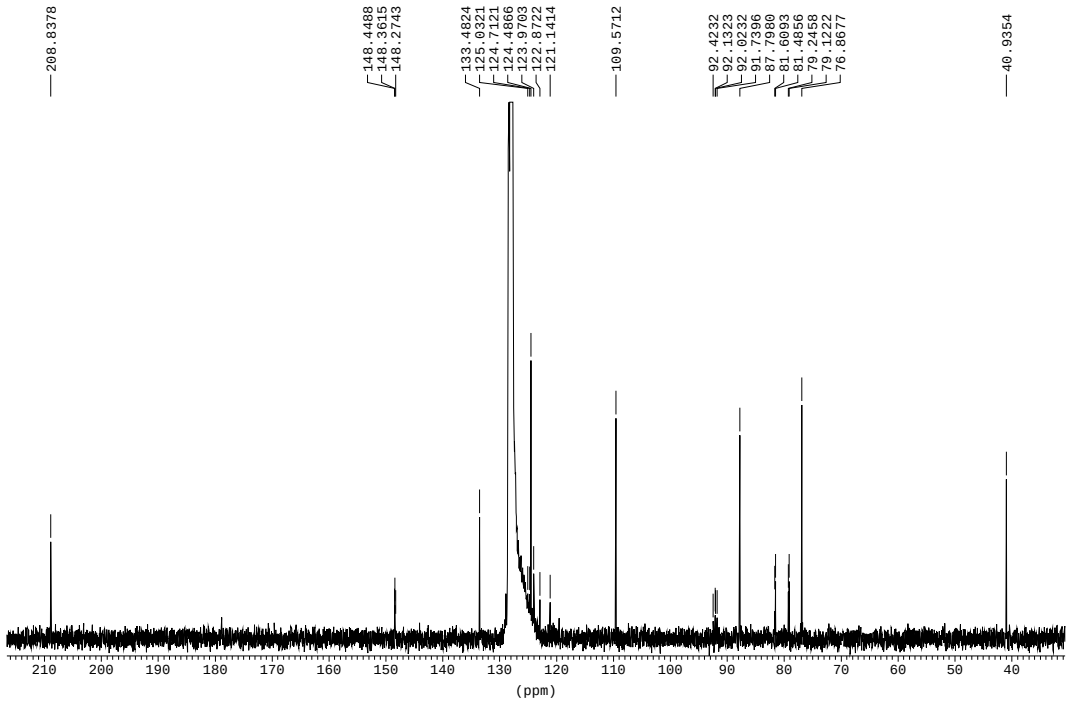


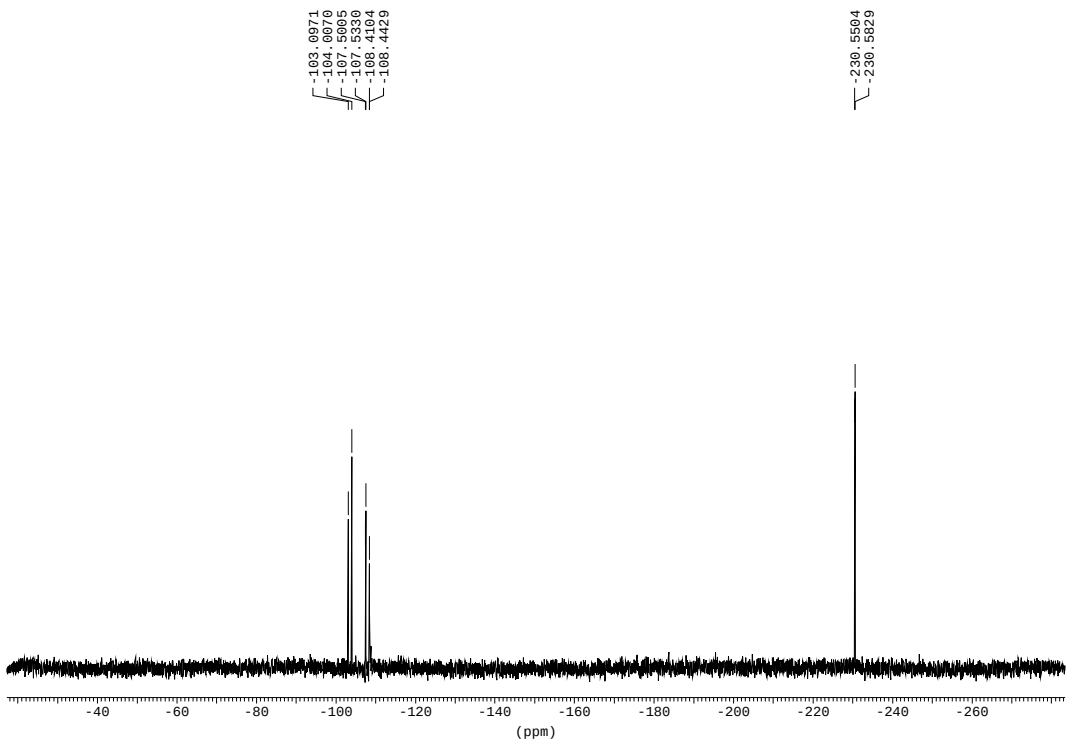

-103.47
-104.38
-106.16
-106.20
-107.07
-107.11
-230.45
-230.48
-100
-120
-140
-160
-180
-200
-220
-240
(ppm)

Q07SC1428E



Q09SC1428E

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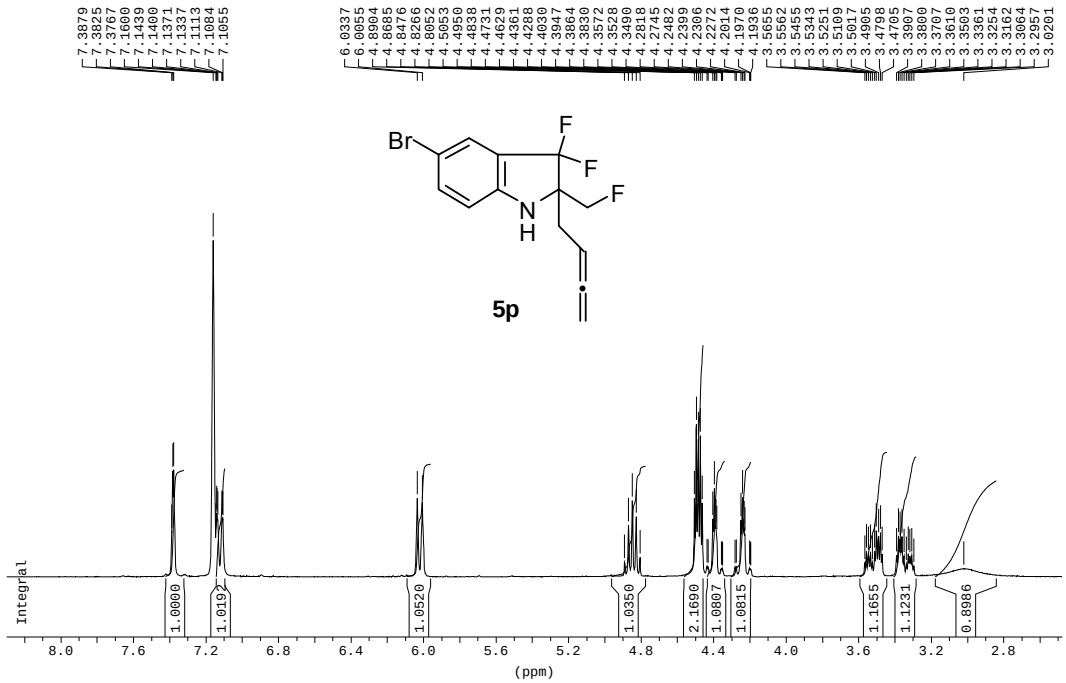
-104.0070
-107.5005
-107.5330
-108.4104
-108.4429
-230.5504
-230.5829
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
(ppm)

Q09SC1655B



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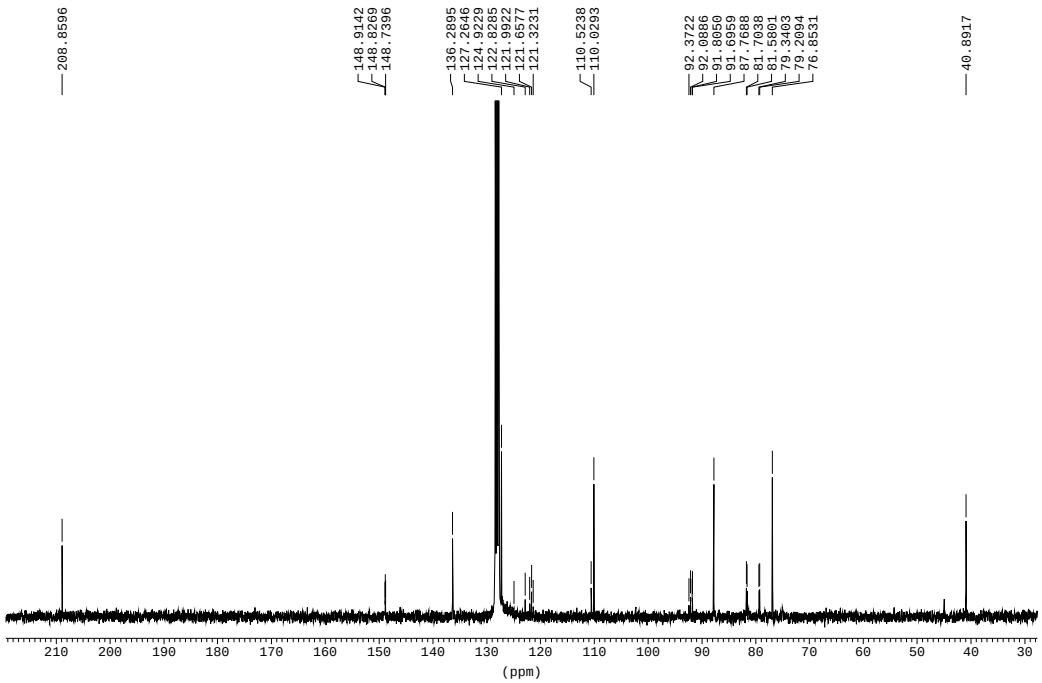
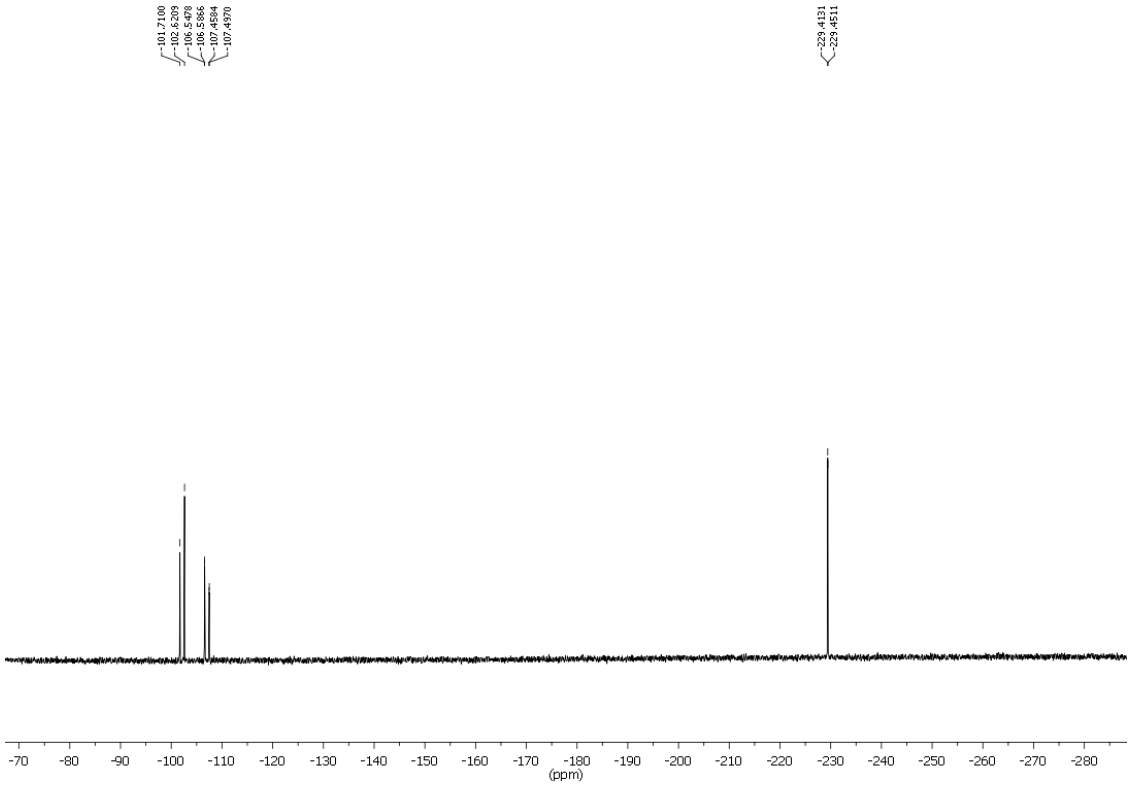
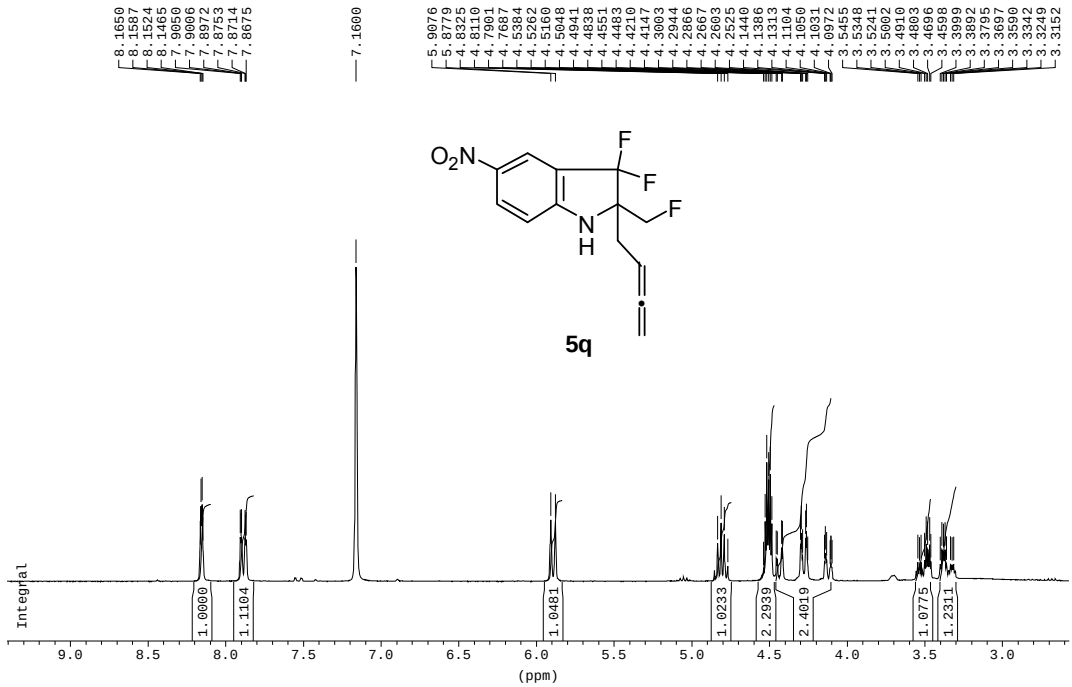
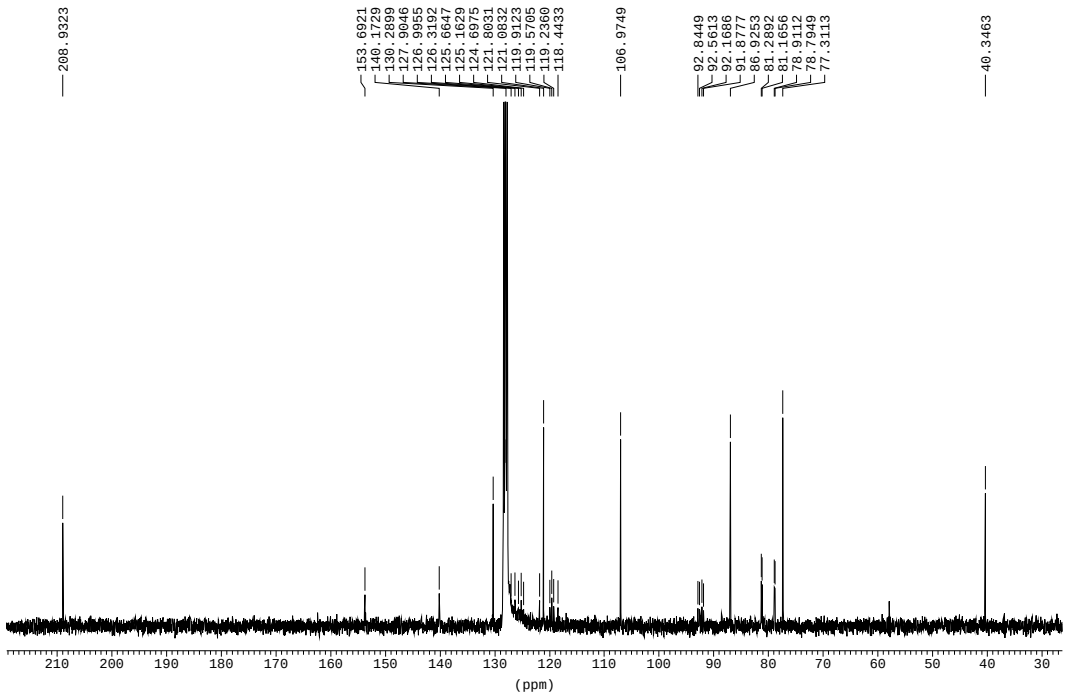


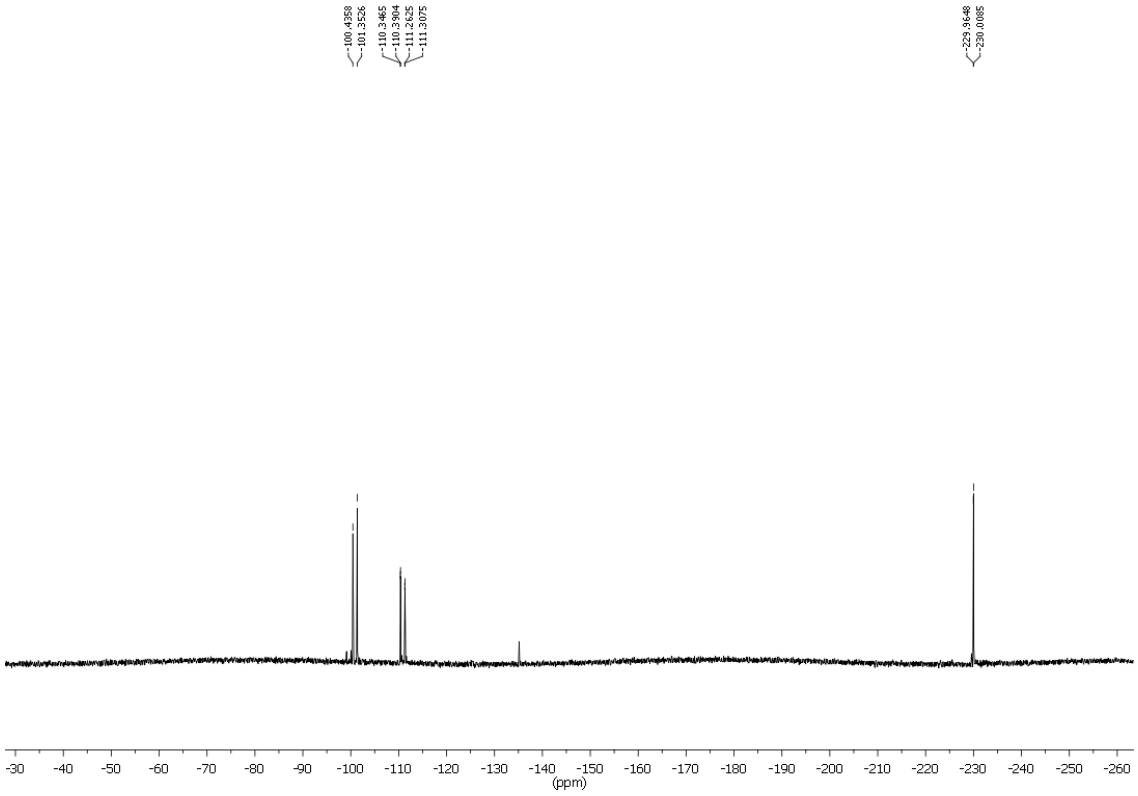

-101.7100
-102.6209
-106.5478
-106.5866
-107.4584
-107.4970
-229.4131
-229.4511
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280
(ppm)

Q09SC1676F



Q09SC1676F

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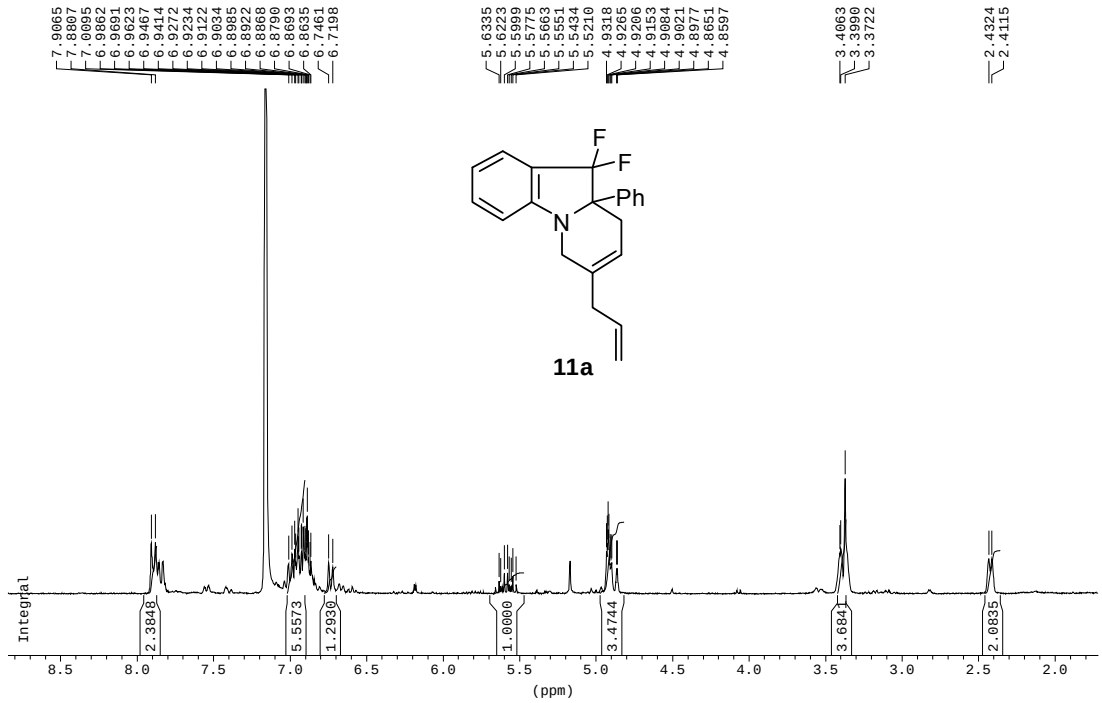
-101.3526
-110.3465
-110.3904
-111.2625
-111.3075
-229.9648
-230.0085
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260
(ppm)

Q09SC1635C



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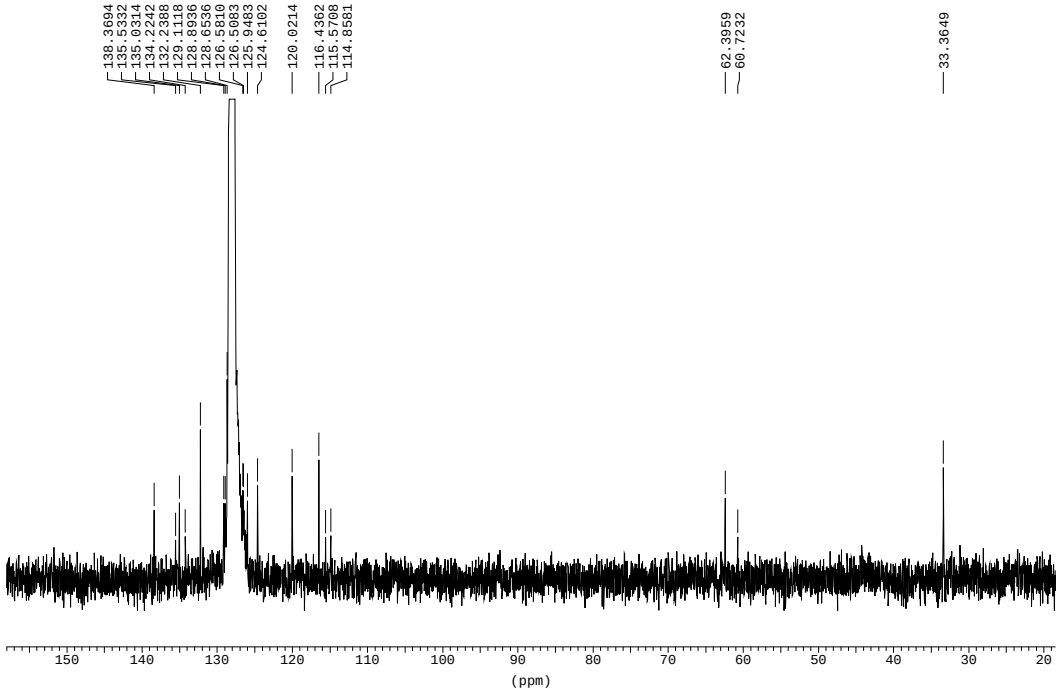
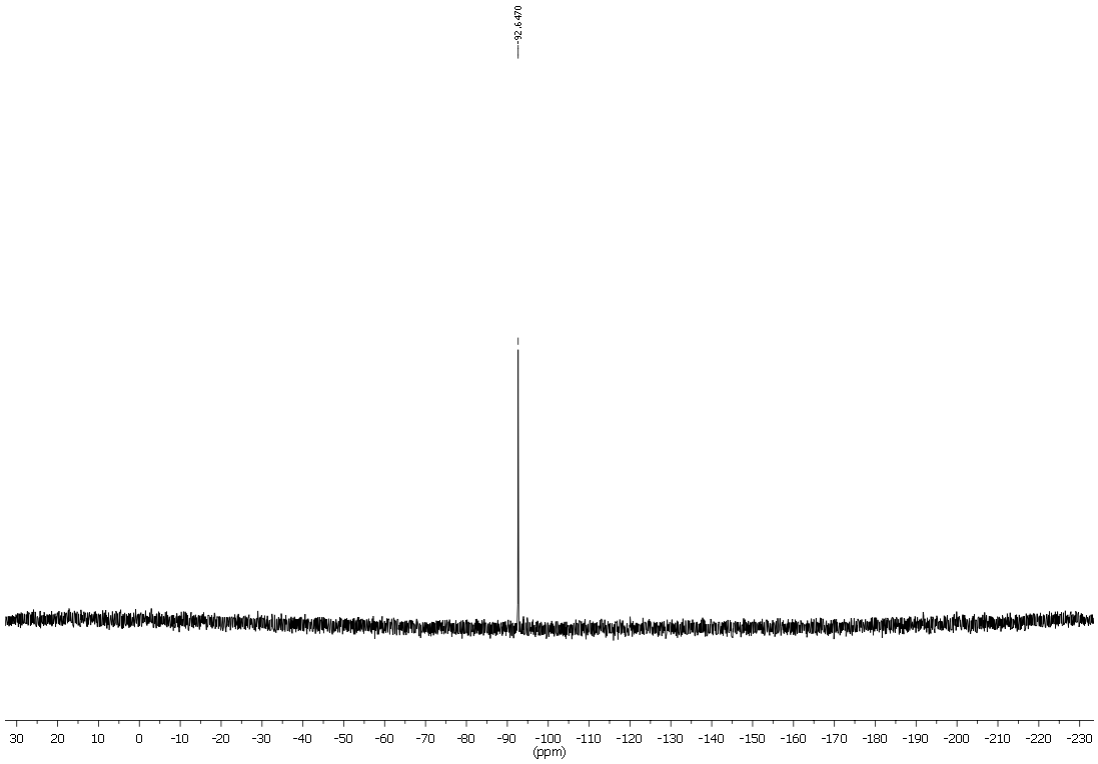
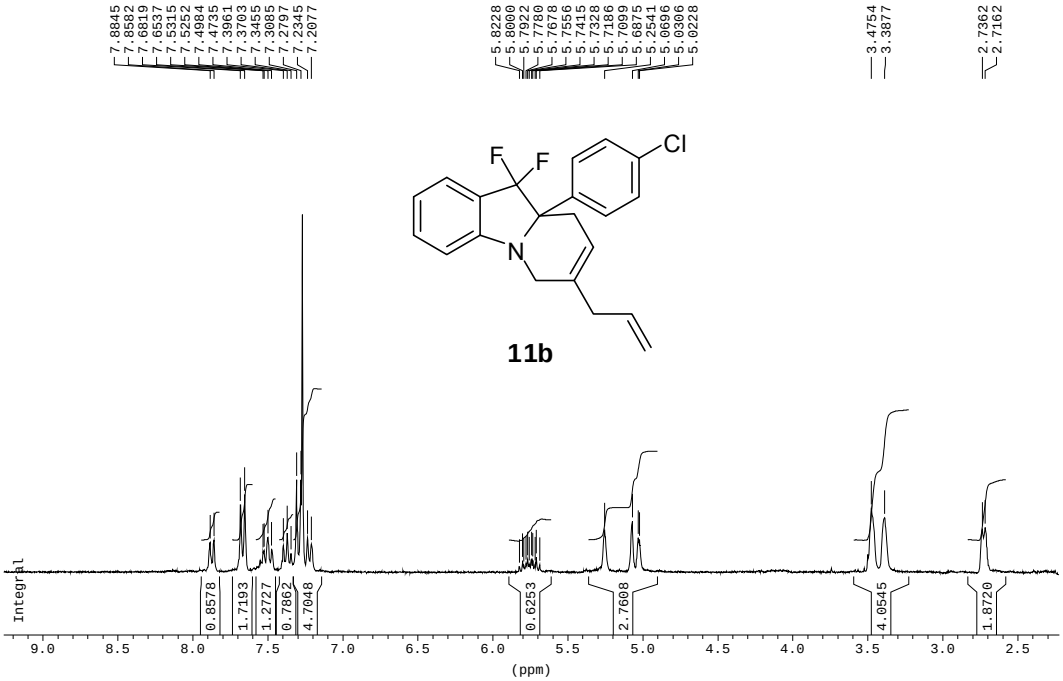



-92.6470
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
(ppm)

Q09MB36A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7.8582
7.6819
7.6537
7.5315
7.5252
7.4984
7.4735
7.3961
7.3703
7.3455
7.3085
7.2797
7.2345
7.2077
5.8228
5.8000
5.7922
5.7780
5.7678
5.7556
5.7415
5.7328
5.7186
5.7099
5.6875
5.2541
5.0696
5.0306
5.0228
3.4754
3.3877
2.7362
2.7162
F
F
Cl
N
11b
Integral
0.8578
1.7193
1.2727
0.7862
4.7048
0.6253
2.7608
4.0545
1.8720
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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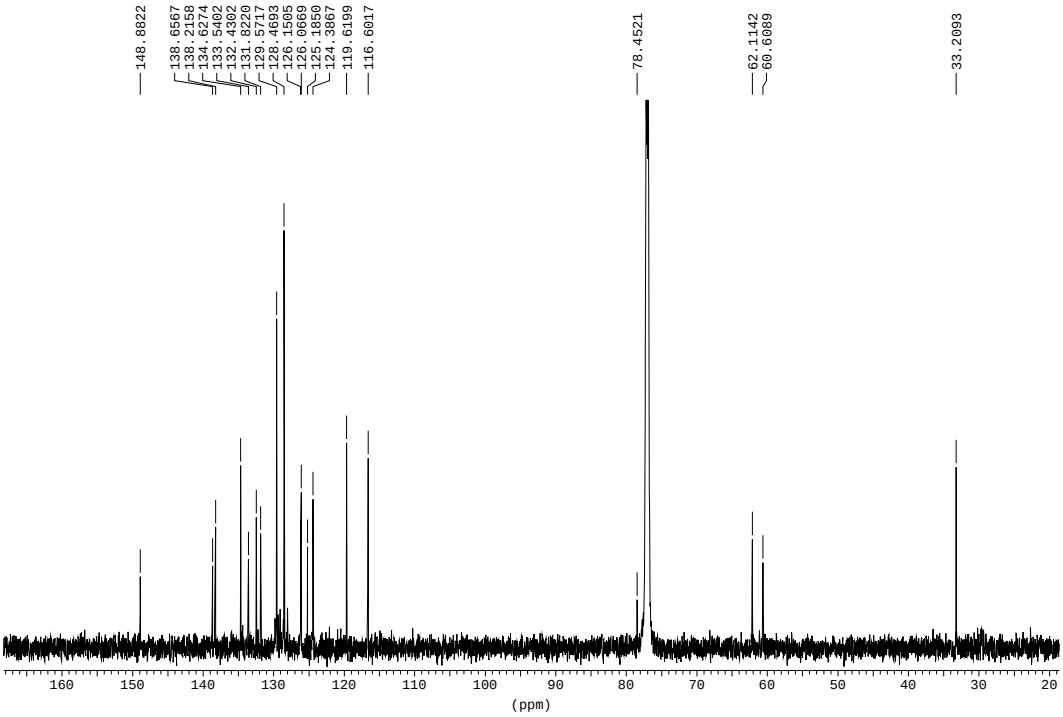
3.0
2.5
(ppm)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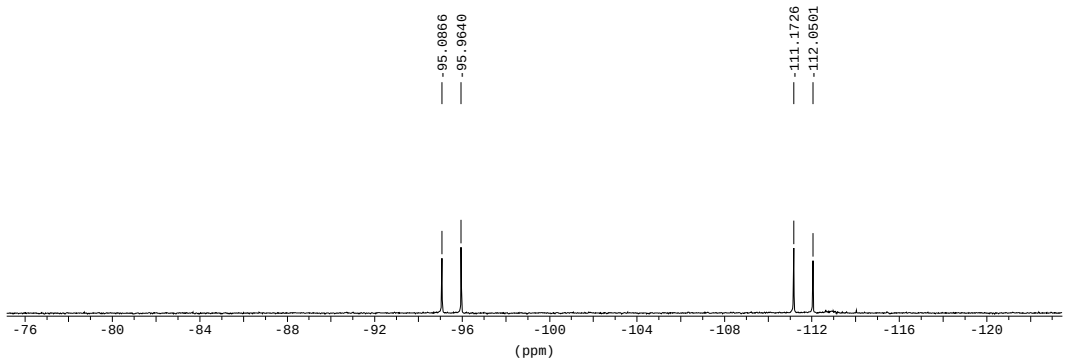
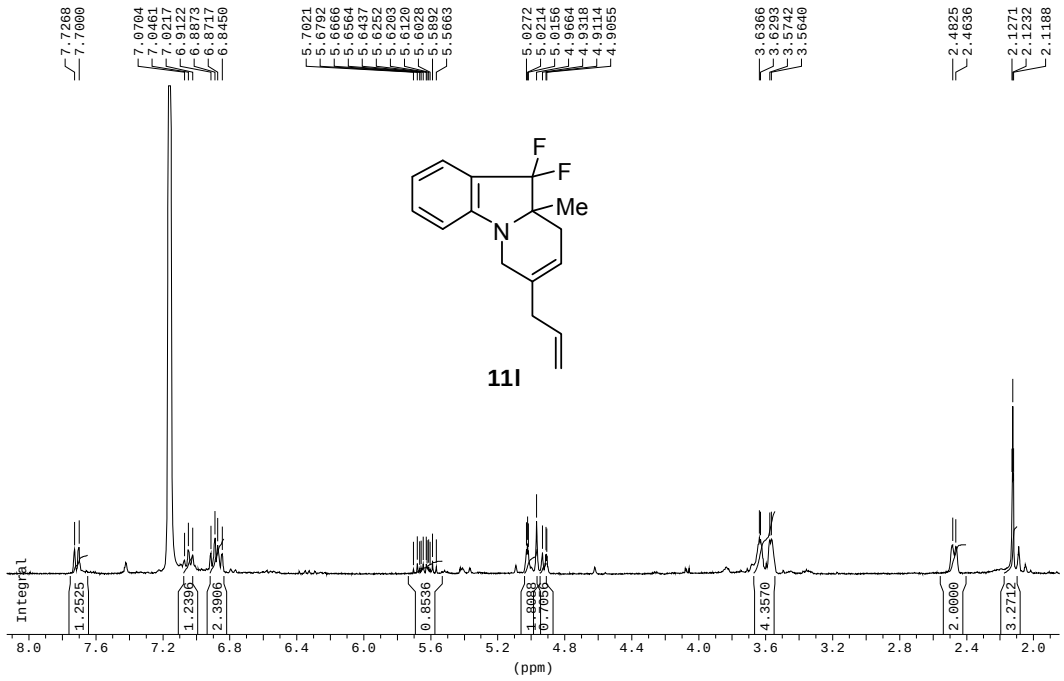
138.6567
138.2158
134.6274
133.5402
132.4302
131.8220
129.5717
128.4693
126.1505
126.0669
125.1850
124.3867
119.6199
116.6017
78.4521
62.1142
60.6089
33.2093
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)


-95.0866
-95.9640
-111.1726
-112.0501
-76
-80
-84
-88
-92
-96
-100
-104
-108
-112
-116
-120
(ppm)

Q09SC1649B



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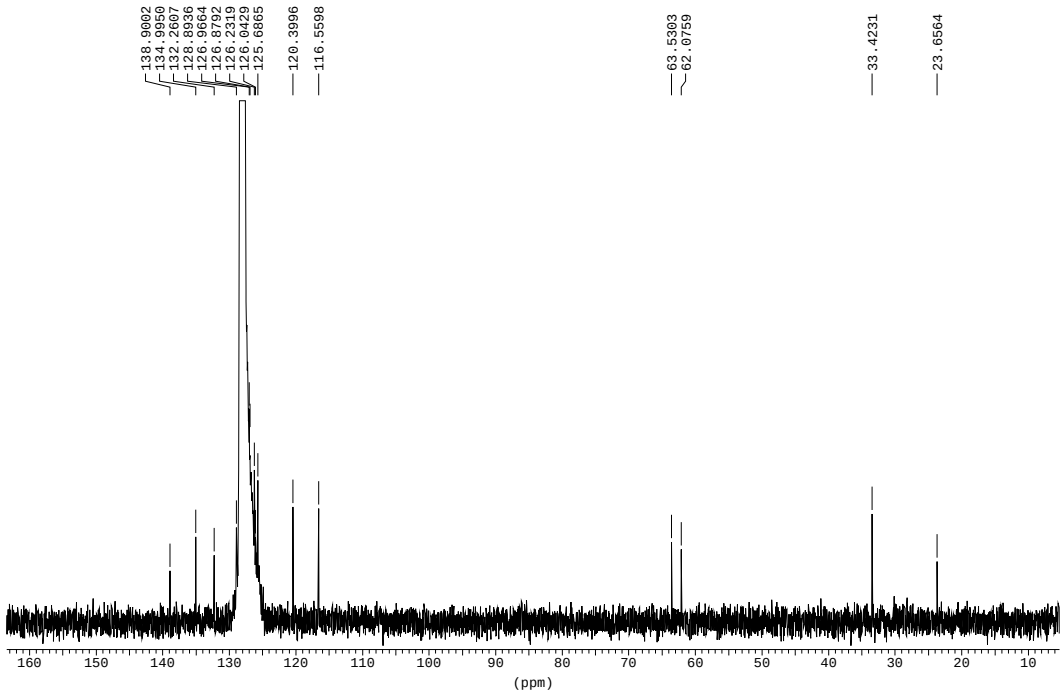
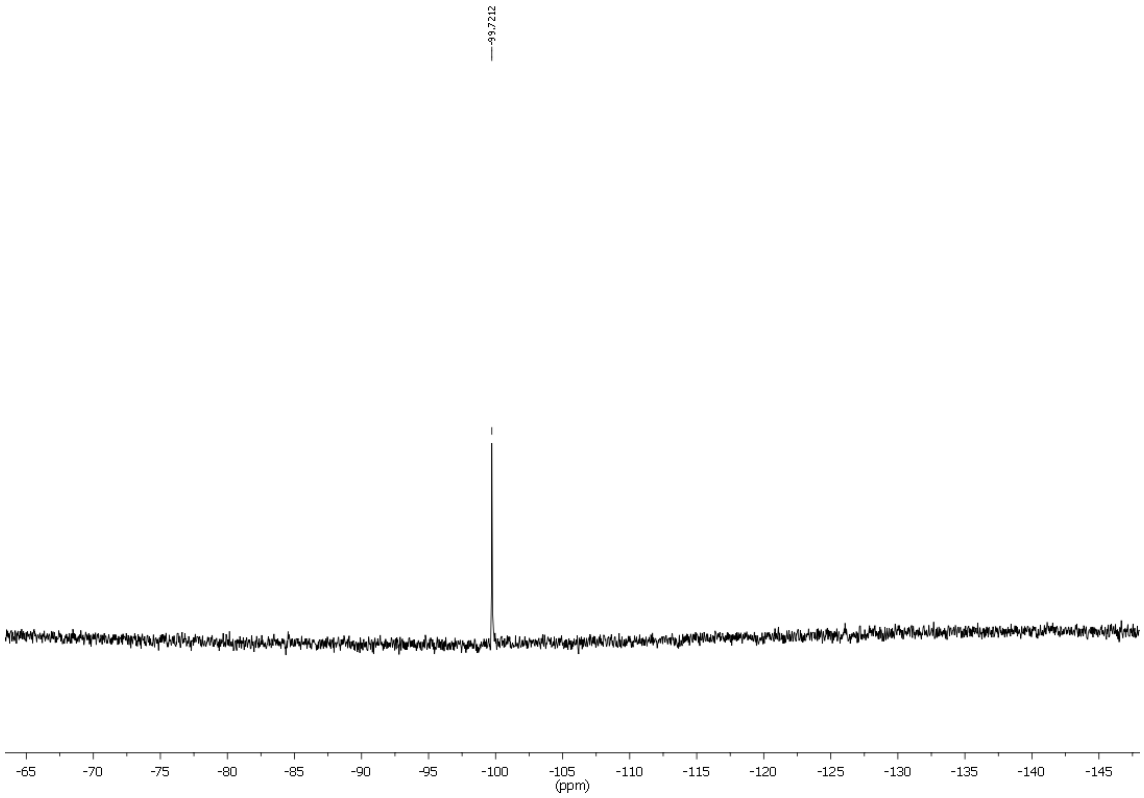
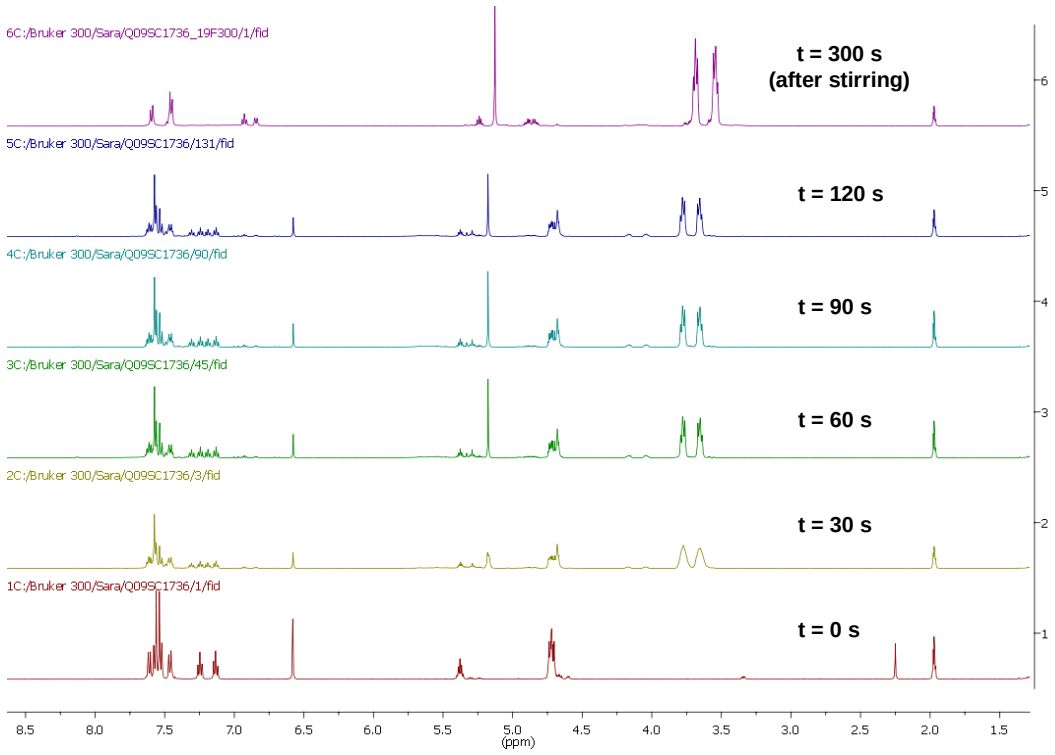



-99.7212
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
(ppm)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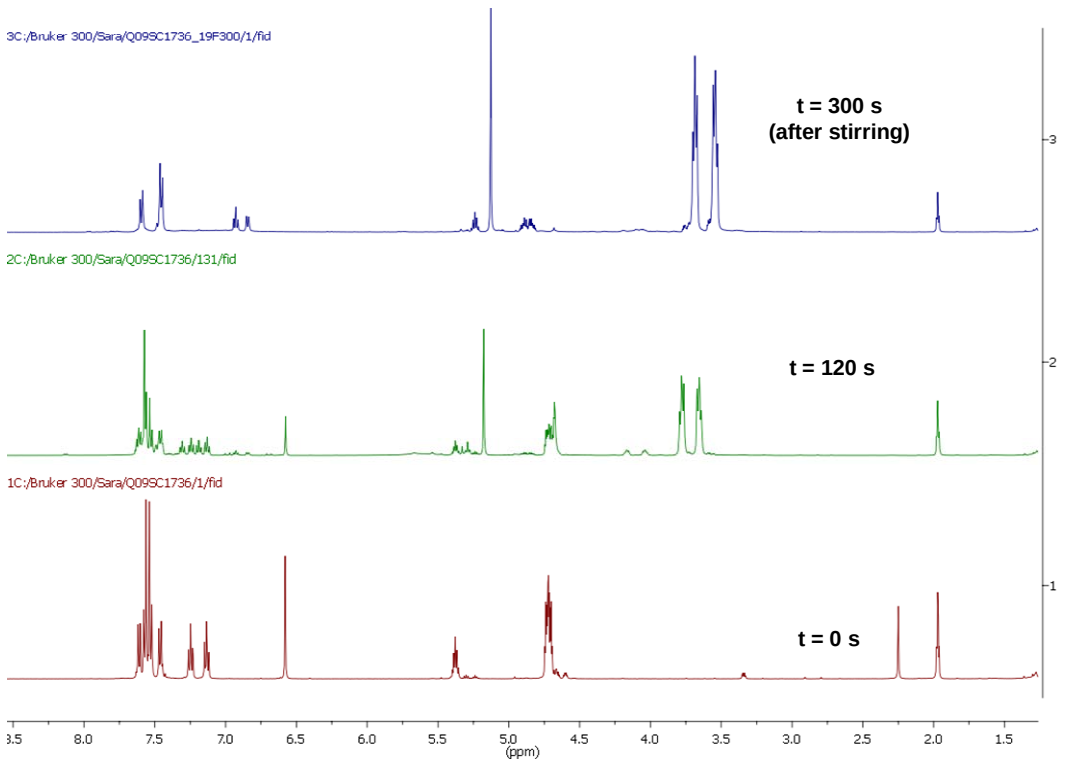
(after stirring)
5C:/Bruker 300/Sara/Q09SC1736/131/fid
t = 120 s
4C:/Bruker 300/Sara/Q09SC1736/90/fid
t = 90 s
3C:/Bruker 300/Sara/Q09SC1736/45/fid
t = 60 s
2C:/Bruker 300/Sara/Q09SC1736/3/fid
t = 30 s
1C:/Bruker 300/Sara/Q09SC1736/1/fid
t = 0 s
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)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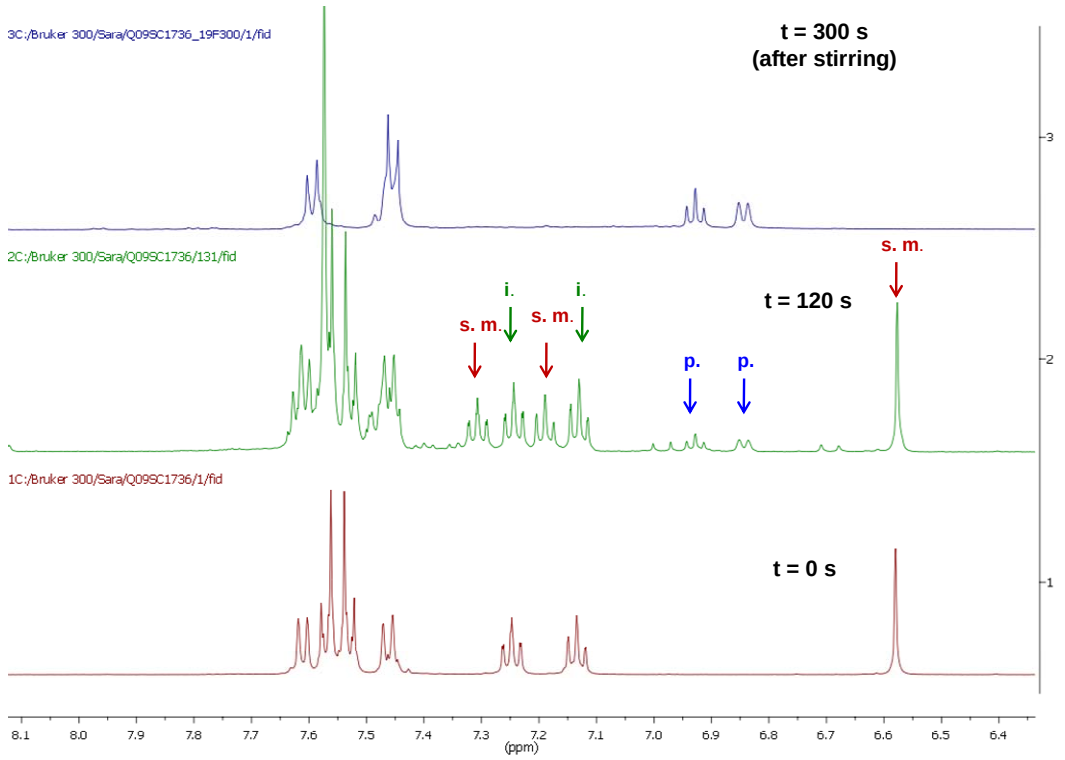
t = 300 s
(after stirring)
2C:/Bruker 300/Sara/Q09SC1736/131/fid
t = 120 s
1C:/Bruker 300/Sara/Q09SC1736/1/fid
t = 0 s
(ppm)


3C:/Bruker 300/Sara/Q09SC1736_19F300/1/fid
t = 300 s
(after stirring)
2C:/Bruker 300/Sara/Q09SC1736/131/fid
t = 120 s
s. m.
i.
i.
s. m.
s. m.
p.
p.
1C:/Bruker 300/Sara/Q09SC1736/1/fid
t = 0 s
(ppm)

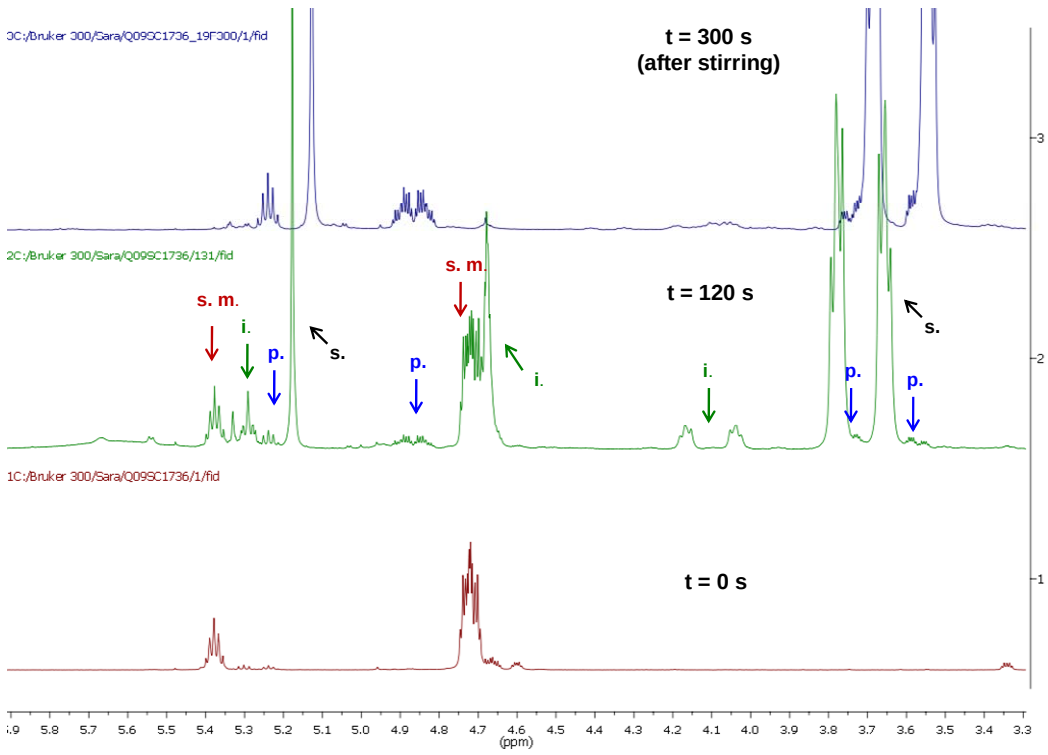
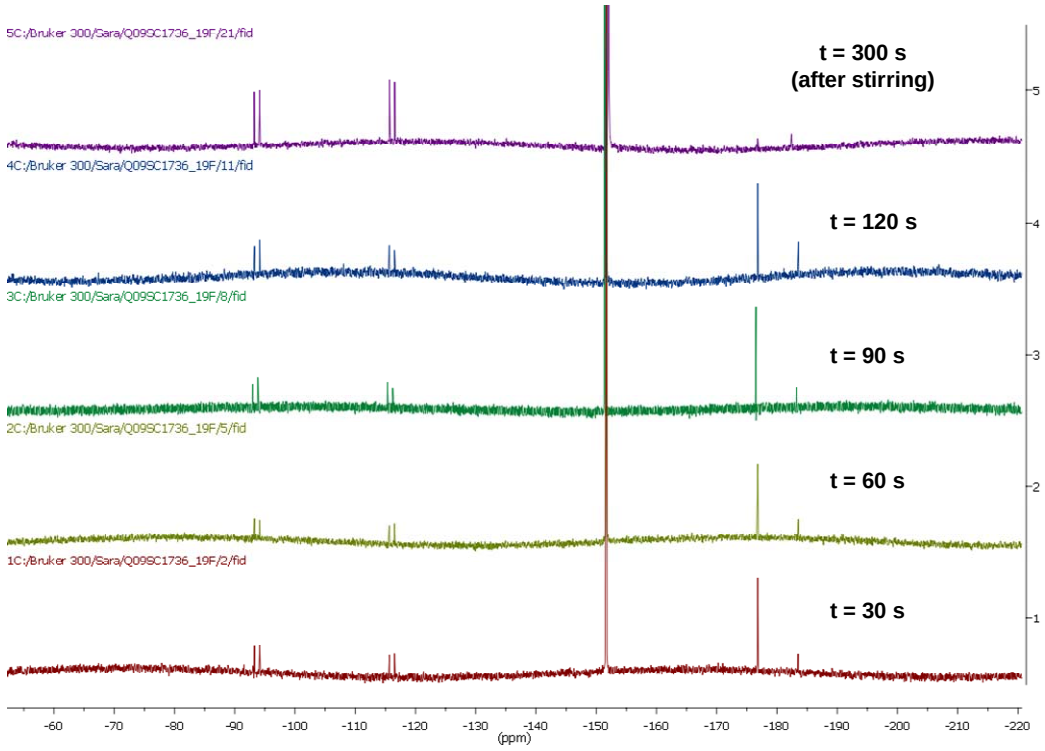


Figure S1 ^{1}H NMR evolution of the Selectfluor-promoted gold-catalyzed reaction of 2-(allenyl)-2-aryl-3,3-difluoroindoline **2b**; s.m. = starting material **2b**; i. = reaction intermediate; p. = product **3b**; s. = Selecfluor.



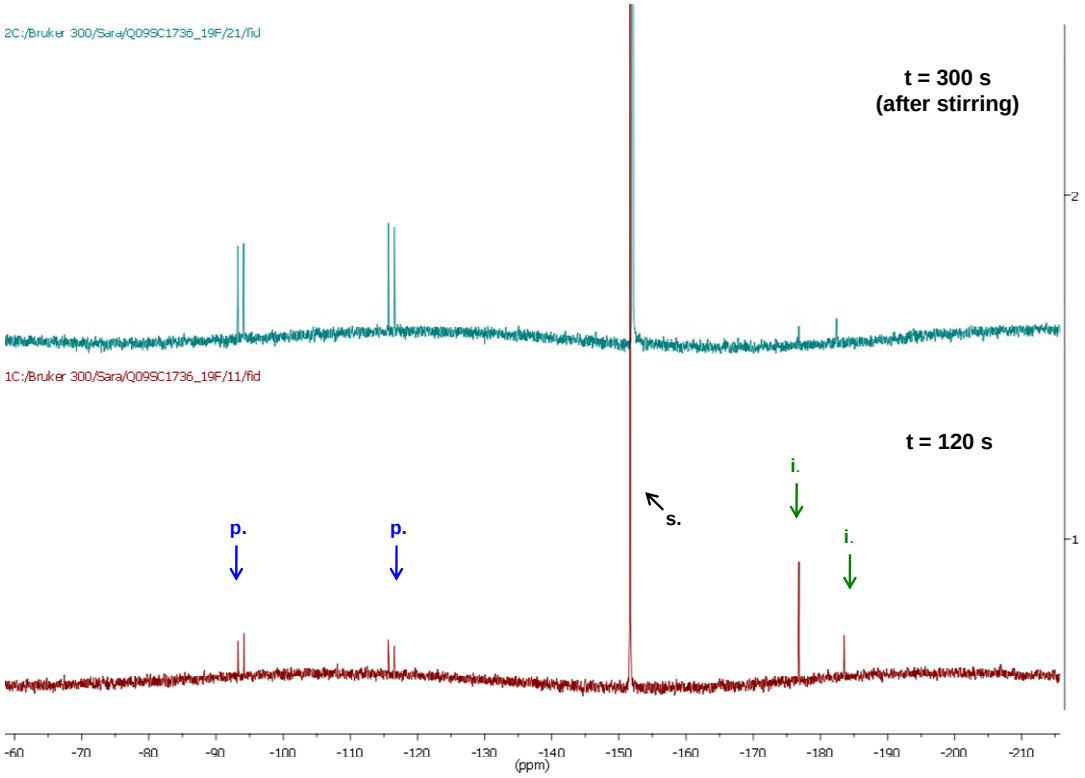


Figure S2 ^{19}F NMR evolution of the Selectfluor-promoted gold-catalyzed reaction of 2-(allenyl)-2-aryl-3,3-difluoroindoline **2b**; i. = reaction intermediate; p. = product **3b**; s. = Selecfluor.