

Supporting information

The Reaction of Dimethylalkynylaluminum Reagents With Trimethylsilyldiazomethane: Original Reactivity Leading to New α -Silylated Alkynyl Hydrazones

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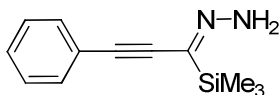
General Remarks

All reactions were carried out under argon atmosphere in flame-dried glassware and with dry solvents: toluene and 1,2-dichloroethane from Sigma-Aldrich or distilled THF (over sodium/benzophenone). Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by TLC carried out on 0.2 mm E. Merck silica gel plates (60F-254) using UV lamp as visualizing agent and Nihidrin solution as developing agent. Flash column chromatography was performed on neutral alumina (Alumine oxide activated, neutral, Brockmann Activity I particle size : 0.05-0.15 mm) or basic alumina (Alumine oxide activated, basic, Brockmann Activity I, particle size : 150 mesh). ^1H (250 or 500 MHz) and ^{13}C (62.5 or 125 MHz) NMR spectra were recorded on a Bruker Nanobay Avance III 250 or a Bruker Avancell 500 in CDCl_3 and calibrated using residual undeuterated solvent as an internal reference. Chemical shift (δ) are given in ppm relative to tetramethylsilane (0 ppm). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), sex (sextuplet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants J are reported in Hz. High Resolution mass spectra were recorded on a ThermoFischer Exactive Orbitrap spectrometer.

General procedure for synthesis of α -Silyl Alkynyl Hydrazones

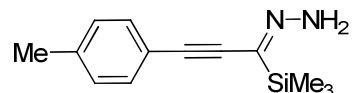
The preparation of **2a** is representative. The preparation of **2a** is representative. To a solution of dimethylphenylalkynylaluminium (1 mmol, prepared according to ref. 7c in toluene) in 1,2-dichloroethane (3 mL) were added TMS diazomethane solution (0.75 mL, 1.5 mmol, 2 M solution in diethyl ether) and AlMe_3 (0.5 mL, 1.0 mmol, 2 M solution in toluene) sequentially. The reaction mixture was heated under argon atmosphere 24 h at 60 °C. After cooling to room temperature, the reaction mixture was slowly poured into a cooled 2 M aqueous solution of Rochelle's salts (3 mL, CAUTION: gas evolution). The organic layer was separated and aqueous layer was extracted with EtOAc (3 \times 15 mL) and combined organic layers were dried over anhydrous MgSO_4 . The solvent was evaporated and the crude residue was purified by column chromatography on neutral or basic alumina (cHex/ EtOAc 94:6) to give **2a** as a yellow oil (199 mg, 92%).

3-Phenyl-1-(trimethylsilyl)prop-2-ynylidenehydrazine **2a**



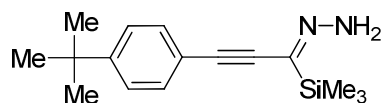
Yellow oil; Yield 92% (199 mg); IR (neat, cm^{-1}) 3394 (w), 3274 (w), 2974 (w), 2183 (w), 1596 (w), 1486 (m), 1247 (m), 1098 (w), 841 (vs); ^1H NMR (500 MHz, CDCl_3) δ 0.25 (s, 9H), 6.65 (broad s, 2H), 7.34-7.36 (m, 3H), 7.46-7.48 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.0, 81.5, 104.4, 122.8, 128.6, 129.0, 131.8, 137.6; HRMS (ESI) m/z : calcd for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{Si}$ (MH^+) 217.1155, found 217.1149.

3-p-Tolyl-1-(trimethylsilyl)prop-2-ynylidene)hydrazine 2b



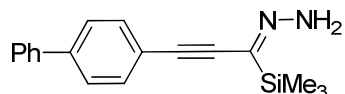
Yellow oil; Yield 86% (198 mg); IR (neat, cm^{-1}) 3419 (w), 3275 (w), 2952 (w), 2183 (w), 1603 (w), 1508 (w), 1247 (m), 1077 (w), 835 (vs); ^1H NMR (500 MHz, CDCl_3) δ 0.25 (s, 9H), 2.3 (s, 3H), 6.67 (broad s, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.0, 21.7, 81.1, 104.7, 119.8, 129.4, 131.7, 137.8, 139.3; HRMS (ESI) m/z : calcd for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{Si}$ (MH^+) 231.1312, found 231.1307.

3-(4-Tert-butylphenyl)-1-(trimethylsilyl)prop-2-ynylidene)hydrazine 2c



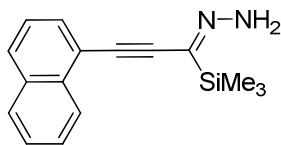
Yellow oil; Yield 87% (237 mg); IR (neat, cm^{-1}) 3394 (w), 2961 (w), 2178 (w), 1599 (w), 1502 (m), 1247 (m), 1110 (w), 837 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.26 (s, 9H), 1.33 (s, 9H), 6.70 (broad s, 2H), 7.38 (d, $J = 6.5, 1.9$ Hz, 2H), 7.42 (dd, $J = 6.5, 1.9$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.1, 31.3, 35.0, 81.0, 104.6, 119.7, 125.6, 131.5, 137.7, 152.4; HRMS (ESI) m/z : calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{Si}$ (MH^+) 273.1781, found 273.1782.

3-(Biphenyl-4-yl)-1-(trimethylsilyl)prop-2-ynylidene)hydrazine 2d



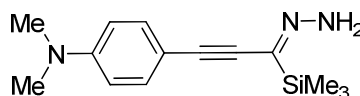
Yellow oil; Yield 76% (222 mg); IR (neat, cm^{-1}) 3397 (w), 3265 (w), 2952(w), 2178 (w), 1599 (w), 1484 (m), 1248 (m), 1107 (w), 761 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.29 (s, 9H), 6.75 (broad s, 2H), 7.38 (t, $J = 7.3$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.55-7.56 (m, 2H), 7.59-7.61 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.0, 82.2, 104.2, 121.6, 127.2, 127.3, 127.9, 129.1, 132.2, 137.4, 140.3, 141.8; HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{Si}$ (MH^+) 293.1468, found 293.1456.

(3-(Naphthalen-1-yl)-1-(trimethylsilyl)prop-2-ynylidene)hydrazine 2e



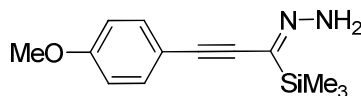
Yellow oil; Yield 91% (242 mg); IR (neat, cm^{-1}) 3414 (w), 3270 (w), 2957 (w), 2168 (w), 1596 (w), 1488 (w), 1247 (m), 1121 (w), 877 (w), 798 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.33 (s, 9H), 6.82 (broad s, 2H), 7.44-7.47 (m, 1H), 7.52-7.56 (m, 1H), 7.58-7.61 (m, 1H), 7.72 (dd, $J = 7.1, 1.1$ Hz, 1H), 7.87 (dd, $J = 7.0, 1.2$ Hz, 2H), 8.31 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ -1.9, 86.3, 102.4, 120.4, 125.4, 126.1, 126.8, 127.3, 128.6, 129.6, 131.0, 132.9, 133.4, 137.6; HRMS (ESI) m/z : calcd for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{Si}$ (MH^+) 267.1312, found 267.1304.

4-(3-Hydrazono-3-(trimethylsilyl)prop-1-ynyl)-N,N-dimethylaniline 2f



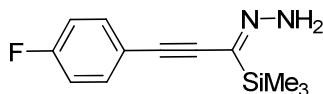
Yellow oil; Yield 61% (158 mg); IR (neat, cm^{-1}) 3404 (w), 2956 (w), 2174 (w), 1606 (s), 1522 (m), 1362 (m), 1246 (w), 1191 (w), 835 (vs); ^1H NMR (500 MHz, CDCl_3) δ 0.25 (s, 9H), 2.99 (s, 6H), 6.58 (broad s, 2H), 6.63 (dd, $J = 6.9, 2.0$ Hz, 2H), 7.34 (d, $J = 6.9, 2.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.0, 40.3 ($\times 2$), 80.2, 106.4, 109.3, 111.9, 133.1, 139.1, 150.7; HRMS (ESI) m/z : calcd for $\text{C}_{14}\text{H}_{22}\text{N}_3\text{Si}$ (MH^+) 260.1577, found 260.1570.

(3-(4-Methoxyphenyl)-1-(trimethylsilyl)prop-2-ynylidene)hydrazine 2g



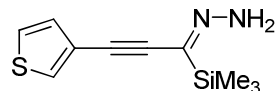
Yellow oil; Yield 45% (111 mg); IR (neat, cm^{-1}) 3414 (w), 3270 (w), 2957 (w), 2180 (w), 1603 (w), 1509 (w), 1247 (m), 1173 (w), 1030 (w), 830 (vs); ^1H NMR (500 MHz, CDCl_3) δ 0.25 (s, 9H), 3.80 (s, 3H), 6.77 (broad s, 2H), 7.39 (d, $J = 2.1$ Hz, 2H), 7.41 (d, $J = 2.1$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.1, 55.4, 80.5, 104.6, 114.2, 114.8, 133.3, 137.9, 160.2; HRMS (ESI) m/z : calcd for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{OSi}$ (MH^+) 247.1261, found 247.1261.

(3-(4-Fluorophenyl)-1-(trimethylsilyl)prop-2-ynylidene)hydrazine 2h



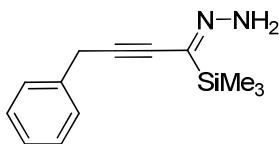
Yellow oil; Yield 80% (187 mg); IR (neat, cm^{-1}) 3409 (w), 3280 (w), 2958 (w), 2178 (w), 1599 (w), 1506 (s), 1247 (s), 1231 (s), 1156 (w), 1093 (w); ^1H NMR (500 MHz, CDCl_3) δ 0.24 (s, 9H), 6.69 (broad s, 2H), 7.02-7.06 (m, 2H), 7.43-7.46 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.0, 81.4, 103.2, 116.0 (d, $J_{\text{C-F}} = 21$ Hz), 118.9 (d, $J_{\text{C-F}} = 2$ Hz), 133.8 (d, $J_{\text{C-F}} = 9$ Hz), 137.4, 163.0 (d, $J_{\text{C-F}} = 249$ Hz); HRMS (ESI) m/z : calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{FSi}$ (MH^+) 235.1061, found 235.1057.

(3-(Thiophen-3-yl)-1-(trimethylsilyl)prop-2-ynylidene)hydrazine 2i



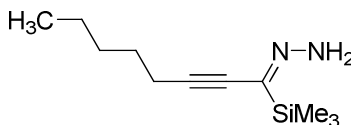
Yellow oil; Yield 75% (167 mg); IR (neat, cm^{-1}) 3409 (w), 3275 (w), 2957 (w), 2173 (w), 1597 (w), 1487 (w), 1247 (m), 1189 (w), 1085 (w), 841 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.12 (s, 9H), 6.63 (broad s, 2H), 6.99 (d, $J = 5.0$ Hz, 1H), 7.14-7.15 (m, 1H), 7.34 (d, $J = 2.9$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.1, 81.3, 99.1, 121.6, 125.7, 129.2, 129.7, 136.7; HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_{15}\text{N}_2\text{SSi}$ (MH^+) 223.0719, found 223.07155.

4-Phenyl-1-(trimethylsilyl)but-2-ynylidene)hydrazine 2j



Yellow oil; Yield 85% (196 mg); IR (neat, cm^{-1}) 3424 (w), 3275 (w), 2957 (w), 2193 (w), 1603 (w), 1495 (w), 1247 (w), 1169 (w), 1030 (w), 838 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.0 (s, 9H), 3.68 (s, 2H), 6.36 (broad s, 2H), 7.02-7.03 (m, 1H), 7.10-7.16 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.1, 26.3, 75.6, 103.3, 126.9, 127.9, 128.8, 136.4, 138.3; HRMS (ESI) m/z : calcd for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{Si}$ (MH^+) 231.1312, found 231.1304.

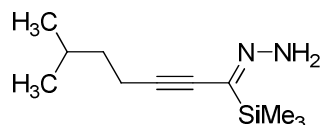
1-(Trimethylsilyl)oct-2-ynylidene)hydrazine 2k



Yellow oil; Yield 81% (170 mg); IR (neat, cm^{-1}) 3414 (w), 3270 (w), 2957 (m), 2193 (w), 1597 (w), 1497 (w), 1246 (m), 1176 (w), 1097 (w), 755 (m); ^1H NMR (500 MHz, CDCl_3) δ 0.16 (s, 9H), 0.89 (t, $J = 7.2$ Hz, 3H), 1.3-1.42 (m, 4H), 1.57 (quint., $J = 7.2$ Hz, 2H), 2.43 (t, $J = 7.1$ Hz,

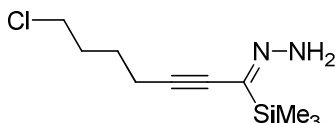
2H), 6.50 (broad s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.2, 14.1, 19.8, 22.2, 28.5, 31.1, 73.7, 106.4, 138.9; HRMS (ESI) m/z : calcd for $\text{C}_{11}\text{H}_{23}\text{N}_2\text{Si}$ (MH^+) 211.1625, found 211.1619.

(6-Methyl-1-(trimethylsilyl)hept-2-ynylidene)hydrazine 2l



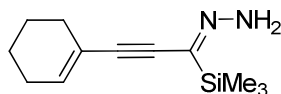
Yellow oil; Yield 82% (172 mg); IR (neat, cm^{-1}) 3399 (w), 2956 (m), 2198 (w), 1700 (w), 1574 (w), 1493 (w), 1247 (m), 1172 (w), 1016 (w); ^1H NMR (500 MHz, CDCl_3) δ 0.16 (s, 9H), 0.90 (d, $J = 6.6$ Hz, 6H), 1.46 (q, $J = 7.3$ Hz, 2H), 1.71 (septet, $J = 6.6$ Hz, 1H), 2.45 (t, $J = 7.3$ Hz, 2H), 6.49 (broad s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.2, 17.9, 22.3, 27.4, 37.8, 73.6, 106.5, 139.1; HRMS (ESI) m/z : calcd for $\text{C}_{11}\text{H}_{23}\text{N}_2\text{Si}$ (MH^+) 211.1625, found 211.1622.

7-chloro-1-(trimethylsilyl)hept-2-ynylidene)hydrazine 2m



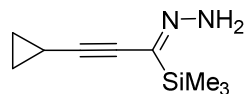
Yellow oil; Yield 77% (177 mg); IR (neat, cm^{-1}) 3419 (w), 3191 (w), 2954 (m), 2208 (w), 1696 (w), 1607 (w), 1448 (w), 1248 (m), 1169 (w), 1046 (w), 757 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.17 (s, 9H), 1.76 (pentet, $J = 7.0$ Hz, 2H), 1.92 (pentet, $J = 6.5$ Hz, 2H), 2.52 (t, $J = 7.0$ Hz, 2H), 3.57 (t, $J = 6.5$ Hz, 2H), 6.50 (broad s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.1, 19.4, 26.1, 31.8, 44.6, 74.3, 105.3, 138.8; HRMS (ESI) m/z : calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{ClSi}$ (MH^+) 231.1078, found 231.1072.

(3-Cyclohexenyl-1-(trimethylsilyl)prop-2-ynylidene)hydrazine 2n



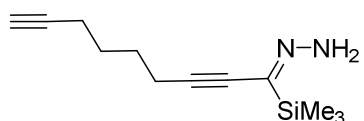
Yellow oil; Yield 88% (194 mg); IR (neat, cm^{-1}) 3394 (w), 3270 (w), 2935 (m), 2163 (w), 1693 (w), 1596 (w), 1493 (w), 1246 (s), 1097 (m), 839 (m), 755 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.14 (s, 9H), 1.53-1.58 (m, 2H), 1.60-1.65 (m, 2H), 2.07-2.11 (m, 2H), 2.12-2.16 (m, 2H), 6.14 (septet, $J = 2.0$ Hz, 1H), 6.56 (broad s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.2, 21.5, 22.3, 25.9, 29.4, 79.1, 106.4, 120.6, 136.3, 137.7; HRMS (ESI) m/z : calcd for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{Si}$ (MH^+) 221.1468, found 221.1462.

3-Cyclopropyl-1-(trimethylsilyl)prop-2-yn-1-ylidene)hydrazine **2o**



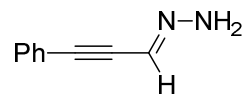
Yellow oil; Yield 79% (142 mg); IR (neat, cm^{-1}) 3404 (w), 2957 (w), 2195 (w), 1597 (w), 1496 (w), 1247 (m), 1089 (w), 755 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.12 (s, 9H), 0.72-0.76 (m, 2H), 0.86-0.90 (m, 2H), 1.42-1.47 (m, 1H), 6.47 (broad s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.2, 0.6, 9.6, 68.8, 109.8, 138.7; HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{17}\text{N}_2\text{Si}$ (MH^+) 181.1155, found 181.1160.

1-(Trimethylsilyl)nona-2,8-diyn-1-ylidene)hydrazine **2p**



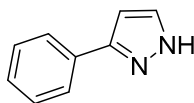
Yellow oil; Yield 82% (172 mg); IR (neat, cm^{-1}) 3424 (w), 3295 (w), 2950 (w), 2193 (w), 2109 (w), 1598 (w), 1497 (w), 1247 (m), 1176 (w), 841 (m); ^1H NMR (500 MHz, CDCl_3) δ 0.15 (s, 9H), 1.62-1.73 (m, 4H), 1.93 (t, $J = 2.6$ Hz, 1H), 2.21 (td, $J = 6.7, 2.6$ Hz, 2H), 2.48 (t, $J = 6.7$ Hz, 2H), 6.50 (broad s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.2, 18.0, 19.4, 27.6, 27.7, 68.8, 73.9, 83.9, 105.6, 138.7; HRMS (ESI) m/z : calcd for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{Si}$ (MH^+) 221.1468, found 221.1465.

(3-Phenylprop-2-yn-1-ylidene)hydrazine (**3**)



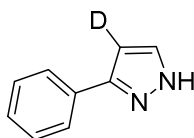
To a stirred solution of 3-Phenyl-1-(trimethylsilyl)prop-2-ynylidene)hydrazine **2a** (216 mg, 1 mmol) in methanol (5 mL) was added acetic acid (60 μL , 1 mmol). Reaction mixture was stirred at room temperature until the complete consumption of starting material (checked by TLC). After completion of reaction, solvent was evaporated under vacuo and the crude residue was directly subjected to silica gel column chromatography (cHex/ EtOAc 90:10) to afford pure product **3** as colorless oil. Yield 75% (108 mg); IR (neat, cm^{-1}) 3409 (w), 2957 (w), 2193 (w), 1698 (w), 1569 (w), 1496 (m), 1247 (m), 1171(w), 838 (s); ^1H NMR (500 MHz, CDCl_3) δ 6.37 (broad s, 2H), 6.64 (s, 1H), 7.35-7.38 (m, 3H), 7.48-7.50 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 76.9, 101.6, 119.9, 121.9, 128.7, 129.5, 131.9; HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_9\text{N}_2$ (MH^+) 145.0760, found 145.0761.

3-phenyl-1H-pyrazole (**5**)



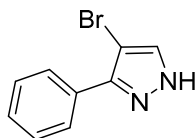
To a stirred solution of (3-Phenylprop-2-yn-1-ylidene)hydrazine **3** (72 mg, 0.5 mmol) in 1,2-DCE (5 mL) was added AlMe_3 (1 mmol, 0.5 mL solution of 2 M in toluene) and the reaction mixture was refluxed for 8 h. After cooling to room temperature, reaction mixture was poured into the cooled 2 M solution of Rochelle's salt (2 mL). The organic layer was separated and aqueous layer was extracted with EtOAc (4×10 mL) and combined organic layers were dried over anhydrous MgSO_4 . The solvent was evaporated and the crude residue was purified by silica gel column chromatography on (cHex/ EtOAc 65:35) to give **5** as a yellow solid. Yield 95% (69 mg); mp 76-78 °C; IR (neat, cm^{-1}) 3170 (m), 2963 (m), 2923 (m), 1725 (w), 1604 (w), 1456 (s), 1353 (w), 1199 (w), 1046 (m), 949 (vs); ^1H NMR (500 MHz, CDCl_3) δ 6.61 (d, $J = 2.0$ Hz, 1H), 7.33 (tt, $J = 7.3, 1.2$ Hz, 1H), 7.38-7.42 (m, 2H), 7.60 (d, $J = 2.0$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 102.8, 126.0, 128.0, 128.9, 132.3, 133.5, 149.3; HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_9\text{N}_2$ (MH^+) 145.0760, found 145.0757.

3-phenyl-1H-pyrazole-4-*d* (6)



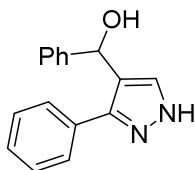
To a stirred solution of (3-Phenylprop-2-yn-1-ylidene)hydrazine **3** (72 mg, 0.5 mmol) in 1,2-DCE (5 mL) was added AlMe_3 (1 mmol, 0.5 mL solution of 2 M in toluene) and the reaction mixture was refluxed for 8 h. After cooling to room temperature, reaction mixture was quenched with MeOD (2 mL) acidified by DCl (0.1 mL DCl for 10 mL MeOD) and stirred overnight at 50 °C. The solvent was evaporated and the crude residue was directly subjected to silica gel column chromatography (cHex/ EtOAc 65:35) to give the deuterated pyrazole **6** (77% incorporation of deuterium observed) as a white solid. Yield 87% (64 mg); mp 56-58°C; IR (neat, cm^{-1}) 3169 (w), 2925 (w), 1686 (w), 1604 (w), 1455 (m), 1352 (w), 1175 (w), 1072 (m), 974 (w), 759 (s); ^1H NMR (500 MHz, CDCl_3) δ 6.61 (d, $J = 2.1$ Hz, 1H), 7.33 (tt, $J = 7.3, 1.2$ Hz, 1H), 7.38-7.41 (m, 2H), 7.59 (s, 1H), 7.76-7.77 (m, 2H), 9.90 (broad s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 102.8, 126.0, 128.1, 128.9, 132.3, 133.4, 149.2; HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_8\text{DN}_2$ (MH^+) 146.0829, found 146.0818.

4-Bromo-3-phenyl-1H-pyrazole (7)



To a stirred solution of (3-Phenylprop-2-yn-1-ylidene)hydrazine **3** (72 mg, 0.5 mmol) in 1,2-DCE (5 mL) was added AlMe₃ (1 mmol, 0.5 mL solution of 2 M in toluene) and the reaction mixture was refluxed for 8 h. After cooling to room temperature, reaction mixture was quenched with NBS (356 mg, 2 mmol) and stirred overnight at 50 °C. The reaction mixture was poured into the cooled 2 M solution of Rochelle's salt (2 mL). The organic layer was separated and aqueous layer was extracted with EtOAc (4×10 mL) and combined organic layers were dried over anhydrous MgSO₄. The solvent was evaporated and the crude residue was purified by silica gel column chromatography on (cHex/ EtOAc 65:35) to give the pure bromo pyrazole **7** as a yellow solid. Yield 62% (69 mg); mp 110-112 °C (litt.: 116.5, 103.9 °C)¹; IR (neat, cm⁻¹) 3156 (w), 3106 (w), 2943(w), 1720 (w), 1498 (w), 1438 (m), 1320 (w), 1099 (w), 973 (m), 940 (s), 766 (s); ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.45 (m, 3H), 7.53 (s, 1H), 7.74-7.76 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 92.3, 127.8, 128.8, 129.0, 129.8, 136.8, 144.5; HRMS (ESI) *m/z* : calcd for C₉H₈BrN₂ (MH⁺) 222.9865, found 222.9871.

Phenyl (3-phenyl-1H-pyrazol-4-yl)methanol (**8**)

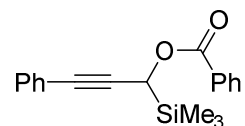


To a stirred solution of (3-Phenylprop-2-yn-1-ylidene)hydrazine **3** (72 mg, 0.5 mmol) in 1,2-DCE (5 mL) was added AlMe₃ (1 mmol, 0.5 mL solution of 2 M in toluene) and the reaction mixture was refluxed for 8 h. After cooling to room temperature, reaction mixture was quenched with PhCHO (212 mg, 2 mmol) and stirred for 4 h at 50 °C. The reaction mixture was poured into the cooled 2 M solution of Rochelle's salt (2 mL). The organic layer was separated and aqueous layer was extracted with EtOAc (4×10 mL) and combined organic layers were dried over anhydrous MgSO₄. The solvent was evaporated and the crude residue was purified by silica gel column chromatography on (cHex/ EtOAc 50:50) to give the pyrazole **8** as a yellow oil. Yield 69% (86 mg); IR (neat, cm⁻¹) 3203 (w), 2967 (w), 1720 (w), 1602 (w), 1493 (m), 1448 (w), 1275 (w), 1022 (m), 952 (w), 739 (s); ¹H NMR (500 MHz, CDCl₃) δ 5.87 (s, 1H), 7.20-7.24 (m, 2H), 7.27-7.29

¹ Garcie, M. Angeles, Cabildo, P.; Claramunt, R. M.; Pinilla, E.; Torres, M. R.; Alkorta, I.; Elguero, J. *Inorg. Chem. Acta* **2010**, 363, 1332.

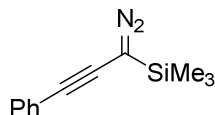
(m, 5H), 7.33-7.34 (m, 2H), 7.51-7.53 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 68.2, 121.9, 126.5, 127.6, 128.2, 128.5, 128.6, 128.9, 131.1, 131.3, 134.8, 143.7; HRMS (ESI) m/z : calcd for $\text{C}_{16}\text{H}_{15}\text{ON}_2(\text{MH}^+)$ 251.1178, found 251.1183.

3-Phenyl-1-(trimethylsilyl)prop-2-yn-1-yl benzoate (10)



To a stirred solution of 3-Phenyl-1-(trimethylsilyl)prop-2-ynylidene)hydrazine **2a** (54 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) was added MnO_2 (86 mg, 1 mmol) at 0 °C. After 1 h, cooling bath was removed and the reaction mixture was stirred at room temperature until the complete consumption of starting material (confirmed by TLC). Benzoic acid (61 mg, 0.5 mmol) was added to reaction mixture and stirred it for further 3 h. After the completion of reaction, the mixture was filter through a pad of celite and solvent was evaporated. The crude residue was directly subjected to silica gel column chromatography (cHex/ EtOAc 95:05) to afford the pure product **10** as a yellow solid. Yield 78% (60 mg); mp 54-56 °C; IR (neat, cm^{-1}) 3062 (w), 2952 (w), 2213 (w), 1720 (m), 1600 (w), 1490 (m), 1314 (w), 1251 (s), 1094 (m), 756 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.29 (s, 9H), 5.67 (s, 1H), 7.28-7.30 (m, 3H), 7.42-7.47 (m, 4H), 7.57 (tt, $J = 7.3, 1.2$ Hz, 1H), 8.08-8.10 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -3.5, 59.4, 86.3, 87.9, 123.3, 128.3, 128.4, 128.6, 129.9, 130.5, 131.9, 131.1, 166.4; HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{21}\text{O}_2\text{Si}(\text{MH}^+)$ 309.1305, found 309.1302.

Attempts of characterisation of (1-diazo-3-phenylprop-2-yn-1-yl)trimethylsilane (9)



To further confirm the formation of diazo compound, we recorded the IR and NMR data of the crude material. It shows the formation of diazo compound with approximate 80-85% purity.

IR (neat, cm^{-1}) 2959 (w), 2191 (w), 2044 (s, diazo characteristic peak), 1662 (w), 1596 (w), 1489 (m), 1251 (m), 1172 (s), 1070 (m), 845 (s); ^1H NMR (500 MHz, CDCl_3) δ 0.32 (s, 9H), 7.28-7.28-7.38 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ -1.8, 78.9, 95.2, 124.5, 127.2, 128.4, 130.5.

α -Silyl alkynyl diazo crude compound can be store for several weeks at -20 °C without further degradation, showing that its instability is mainly thermal. All attempts of further purification at

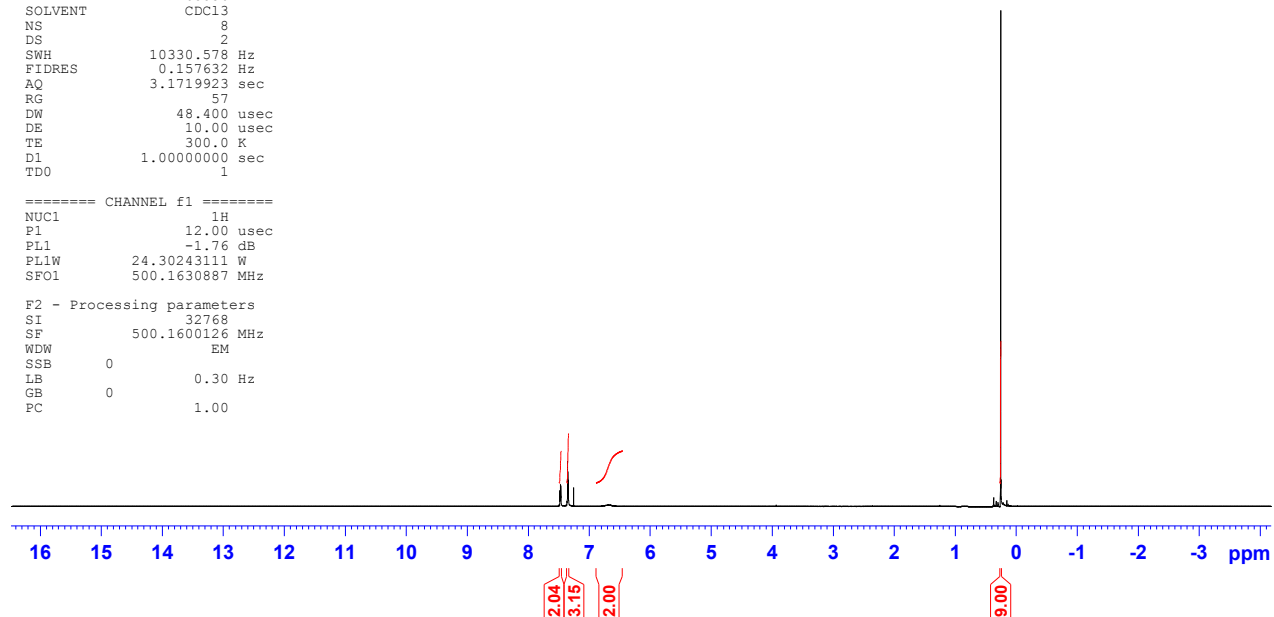
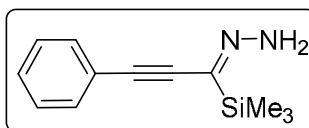
room temperature through column chromatography using neutral or basic alumina or triethylamine passed silica led to decomposition.

```
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EXPNO     10
PROCNO    1

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PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         2
SWH        10330.578 Hz
FIDRES     0.157632 Hz
AQ         3.1719923 sec
RG         57
DW         48.400 usec
DE         10.00 usec
TE         300.0 K
D1         1.00000000 sec
TDO        1

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P1         12.00 usec
PL1        -1.76 dB
PL1W       24.30243111 W
SFO1       500.1630887 MHz

F2 - Processing parameters
SI         32768
SF         500.1600126 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
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rk-18-Ph
 Current Data Parameters
 NAME rk-18-Ph
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140701
 Time_ 21.31
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 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 350
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
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 WDW EM
 SSB 0
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 PC 1.40

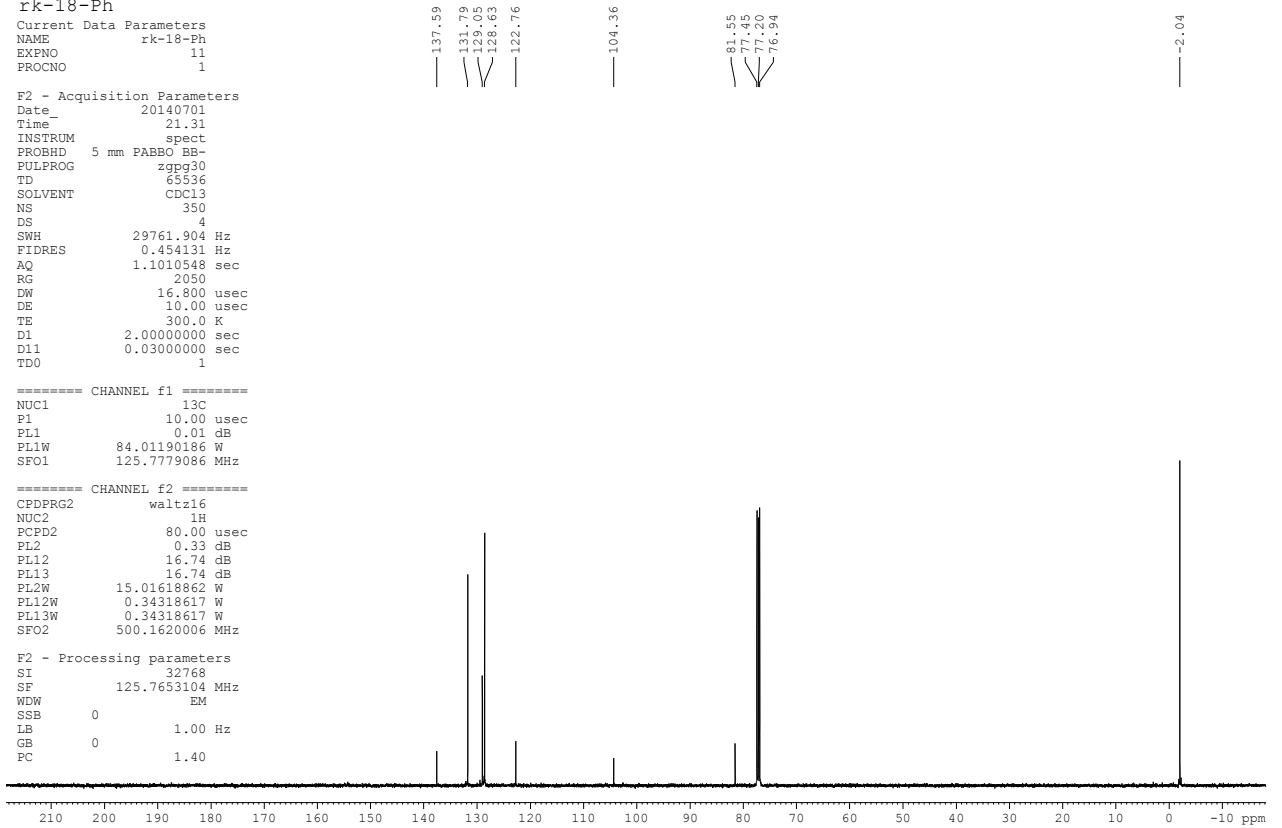


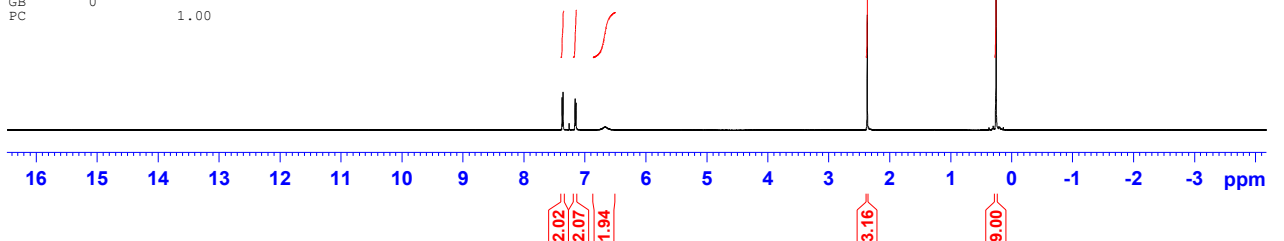
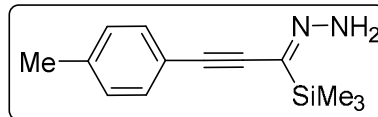
Fig S1. ¹H and ¹³C NMR Spectrum of 2a

rk-52-methyl
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 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
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 Time_ 18.54
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 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 25.4
 DW 48.400 usec
 DE 10.00 usec
 TE 310.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600119 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-52-methyl

Current Data Parameters
NAME rk-52
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140327
Time 19.02
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 310.0 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653083 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

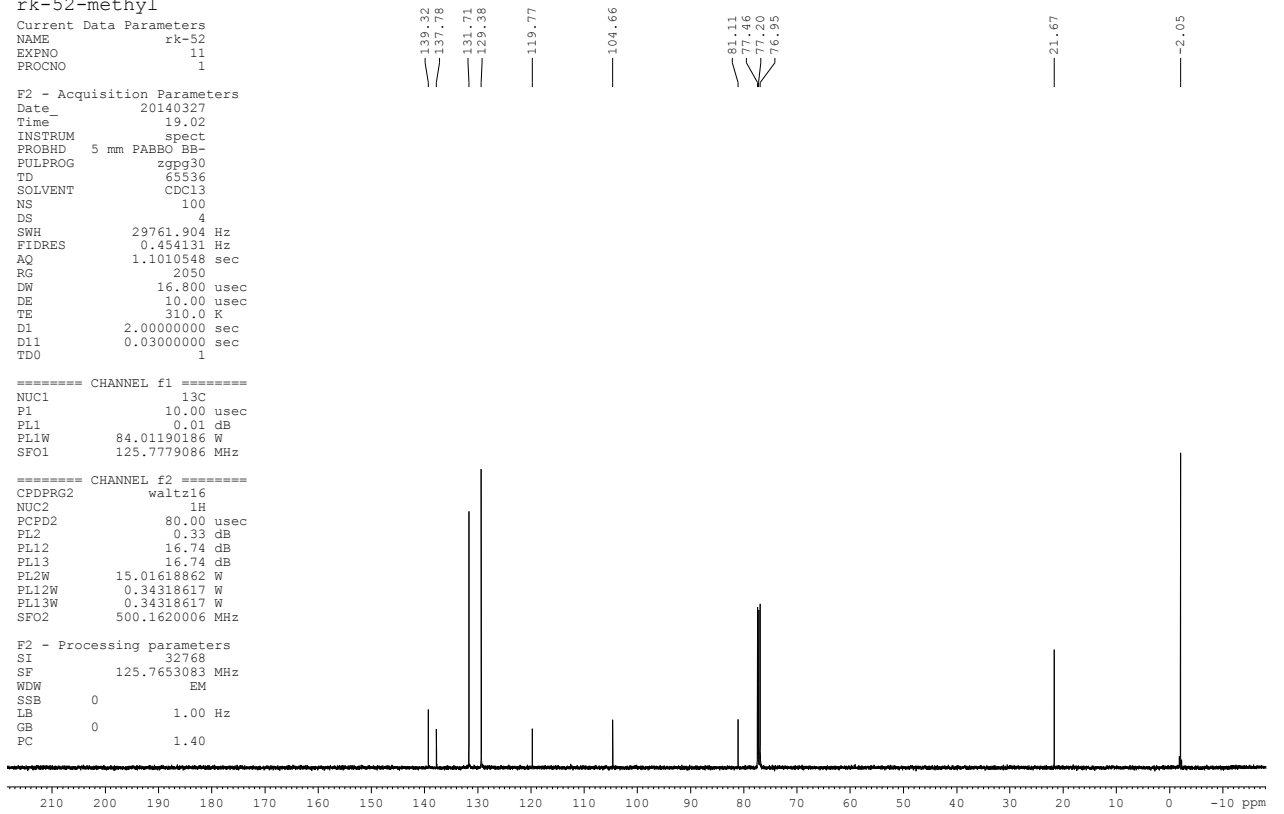


Fig S4. ¹H and ¹³C NMR Spectrum of 2b

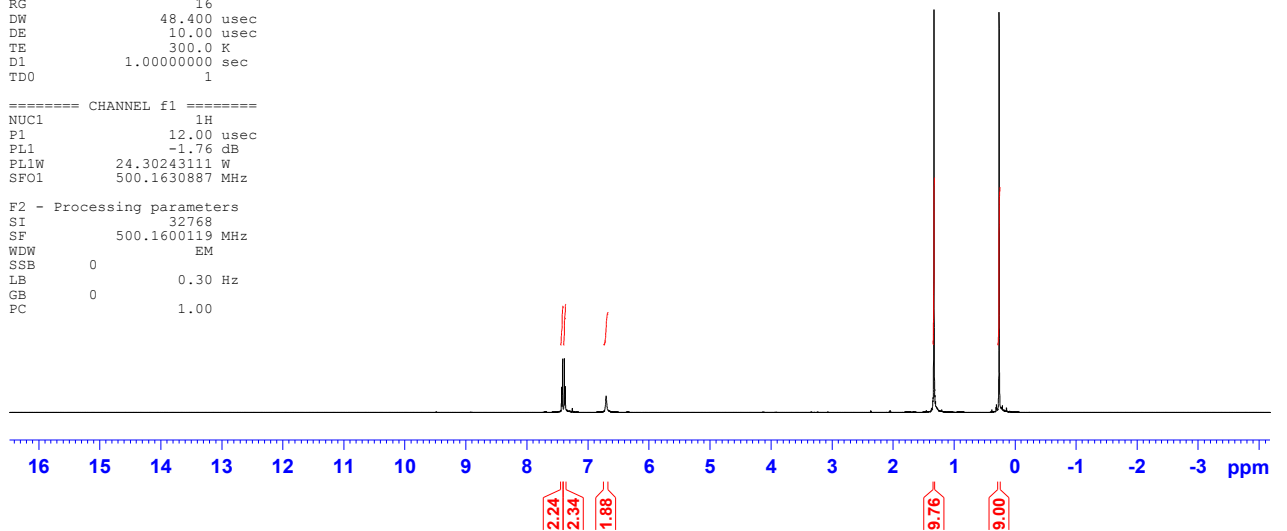
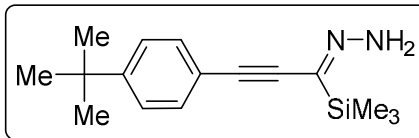
rk46

Current Data Parameters
NAME rk46
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140321
Time 13.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 16
DW 48.400 usec
DE 10.00 usec
TE 300.0 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -1.76 dB
PL1W 24.30243111 W
SFO1 500.1630887 MHz

F2 - Processing parameters
SI 32768
SF 500.1600119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



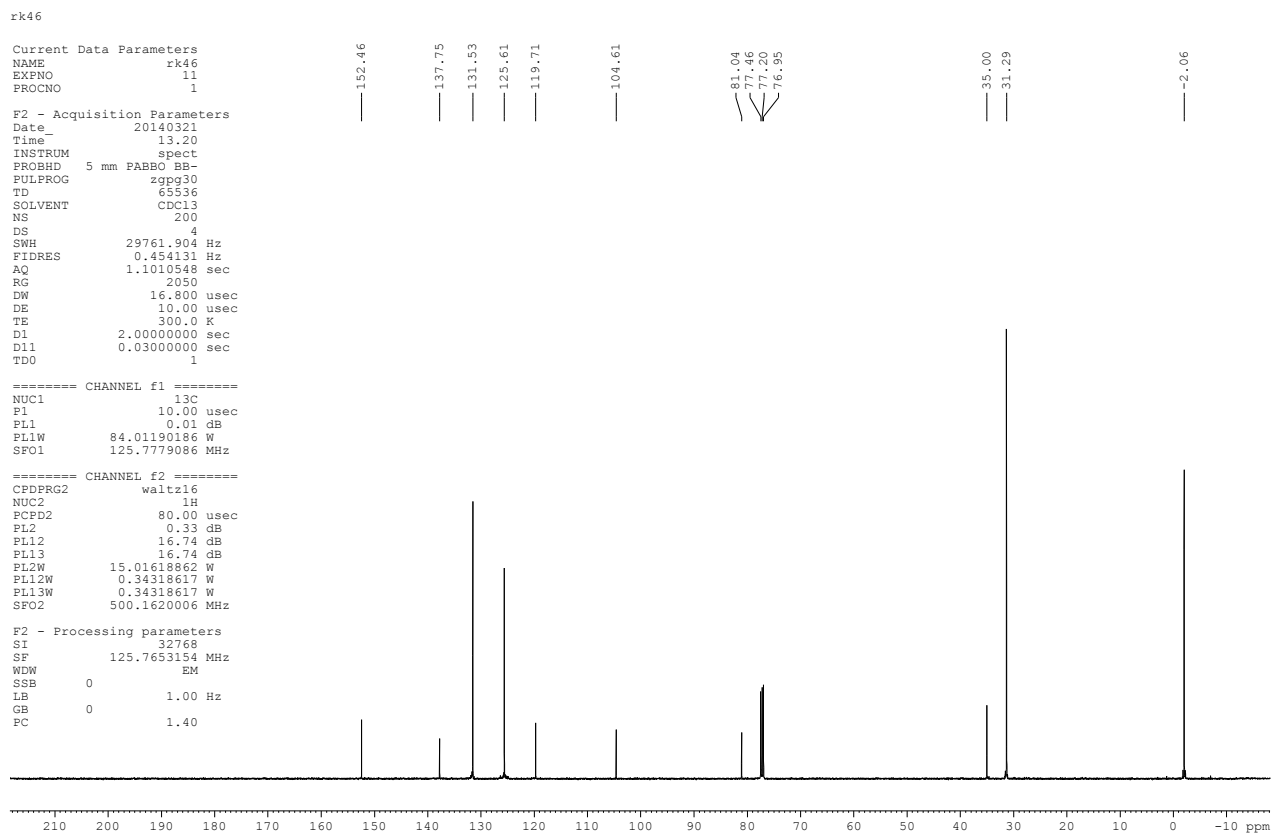


Fig S5. ^1H and ^{13}C NMR Spectrum of **2c**

rk-57-biphenyl

```

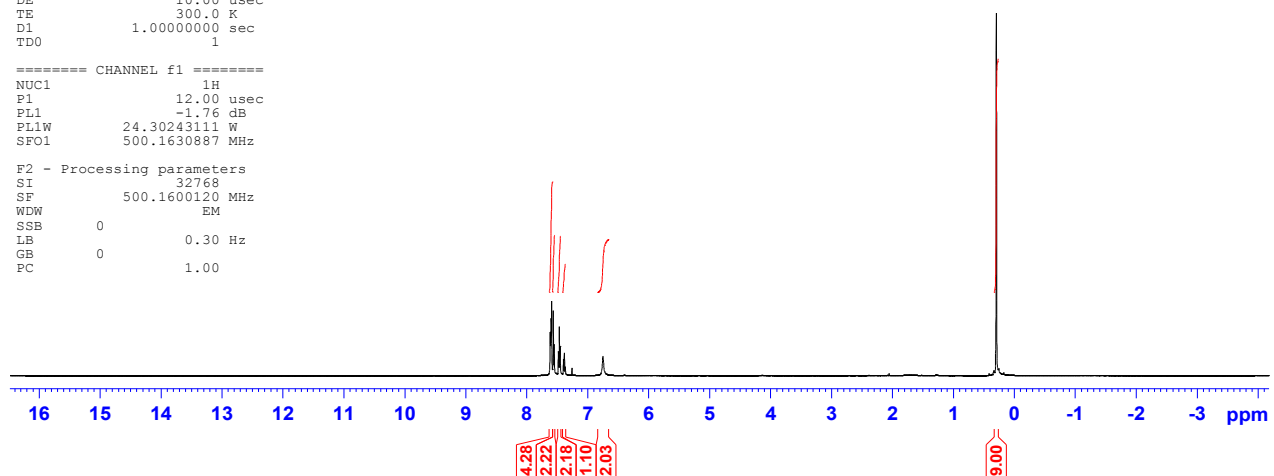
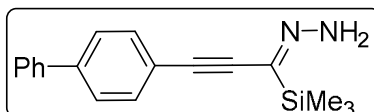
Current Data Parameters
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EXPNO    10
PROCNO   1

F2 - Acquisition Parameters
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Time     17.41
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       8
DS       2
SWH      10330.578 Hz
FIDRES   0.157632 Hz
AQ       3.1719923 sec
RG       22.6
DW       48.400 usec
DE       10.00 usec
TE       300.0 K
D1       1.00000000 sec
TD0      1

===== CHANNEL f1 =====
NUC1     1H
P1       12.00 usec
PL1      -1.76 dB
PL1W     24.30243111 W
SFO1     500.1630887 MHz

F2 - Processing parameters
SI       32768
SF       500.1600120 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00

```



rk-57-biphenyl

Current Data Parameters
 NAME rk-57-biphenyl
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140523
 Time 17.55
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 217
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653167 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

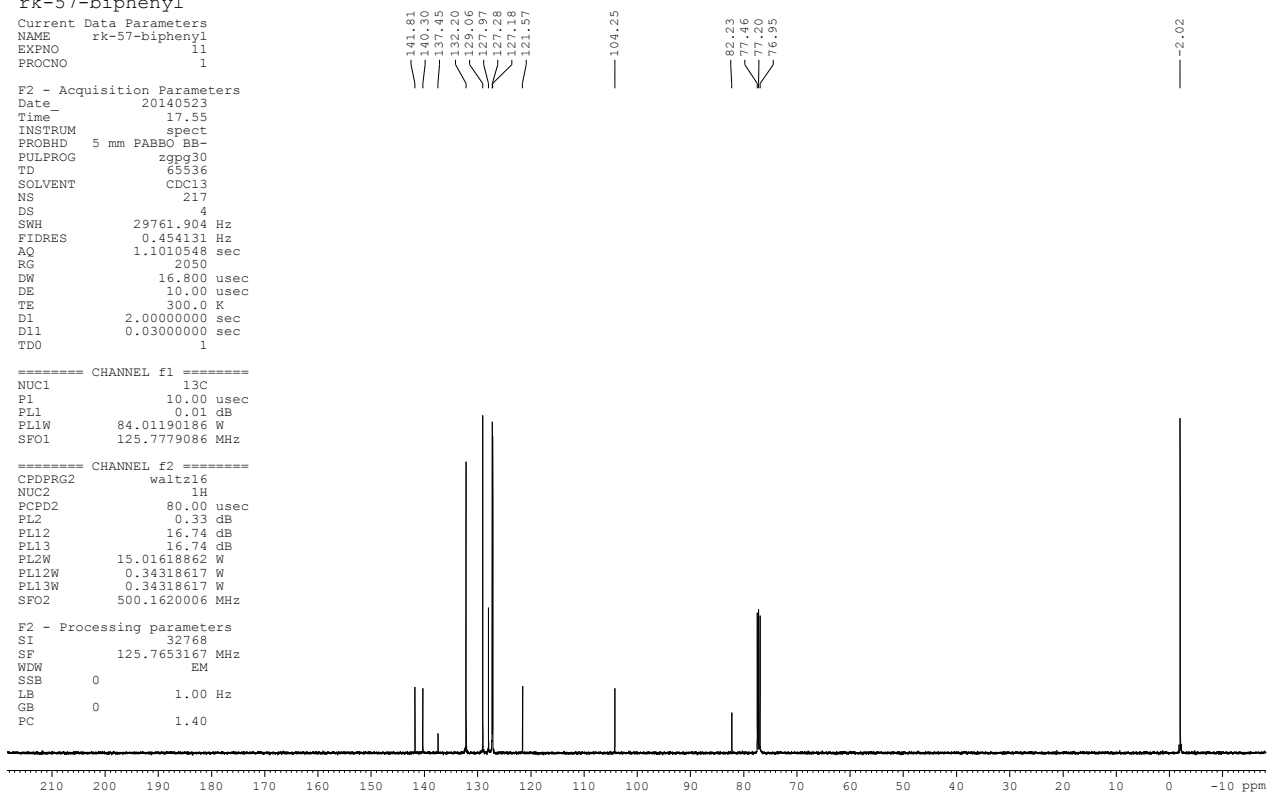


Fig S3. ¹H and ¹³C NMR Spectrum of 2d

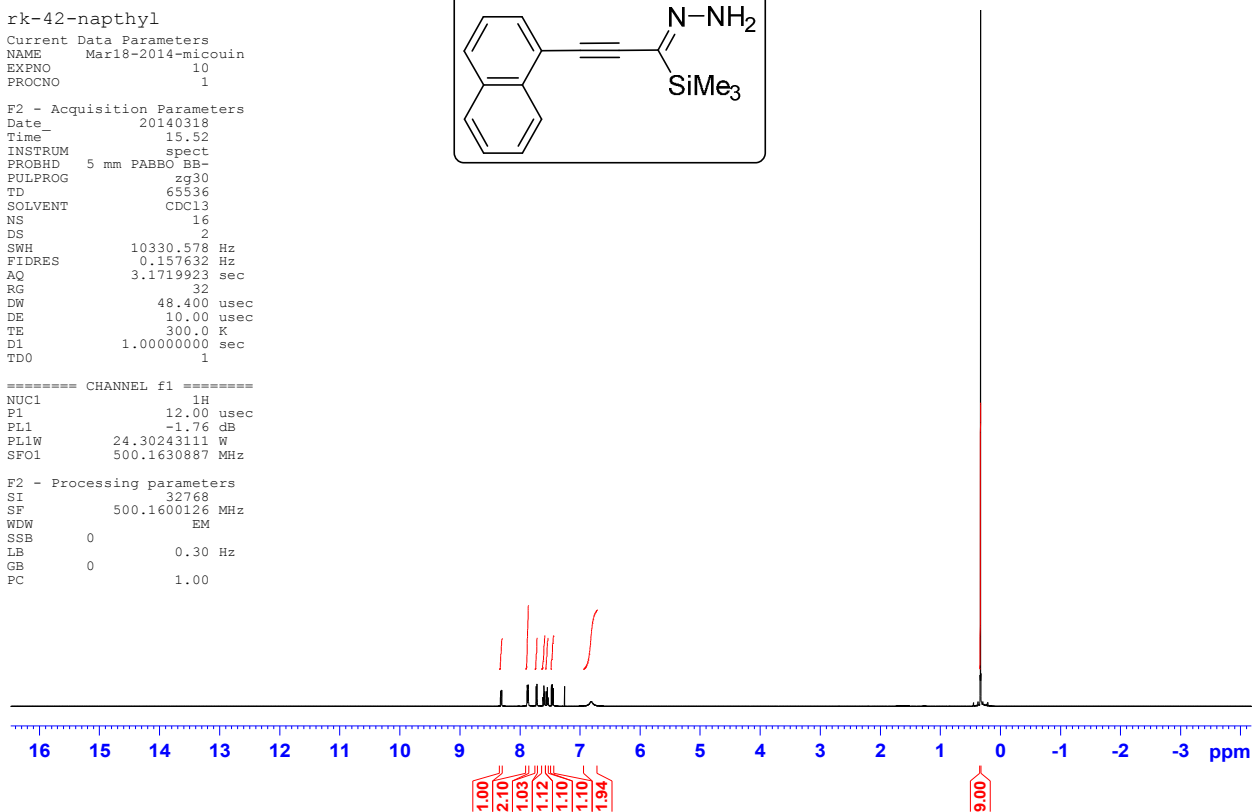
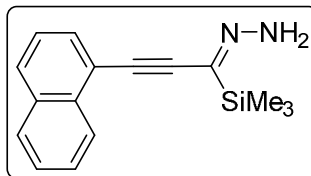
rk-42-naphthyl

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 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
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 INSTRUM spect
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 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 32
 DW 48.400 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600126 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-42-naphthyl

Current Data Parameters
NAME Marl8-2014-micouin
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140318
Time 16.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653116 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

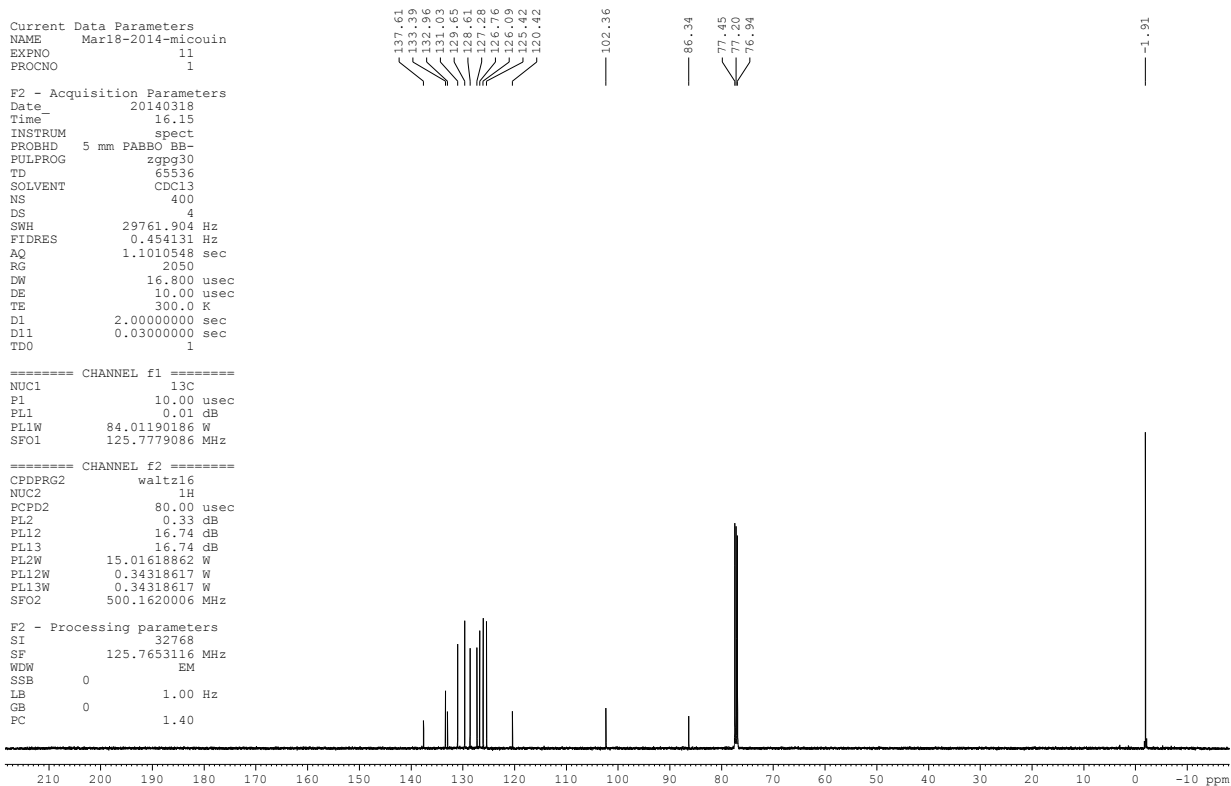


Fig S2. ¹H and ¹³C NMR Spectrum of 2e

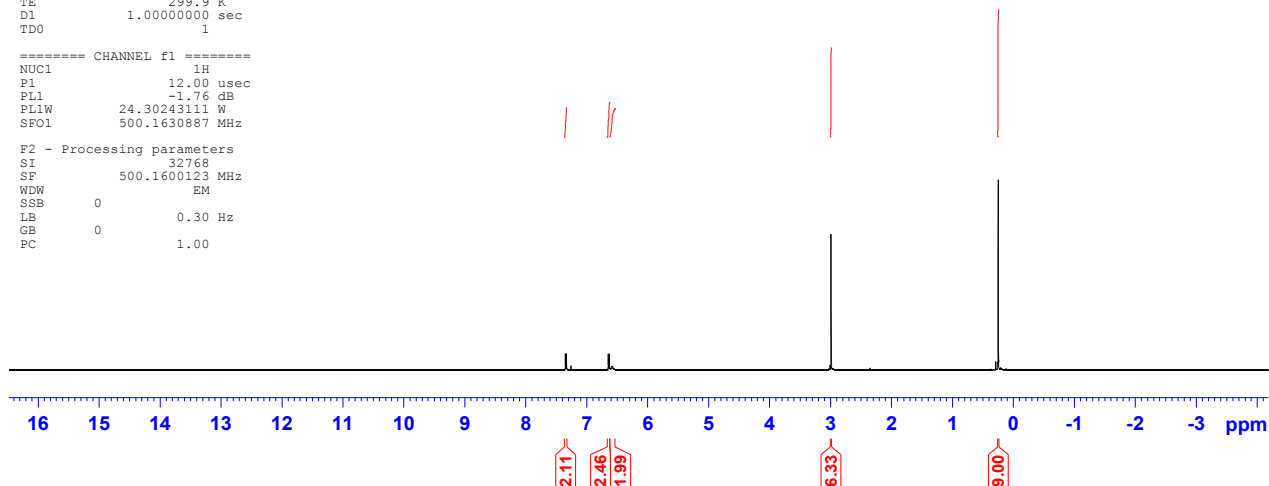
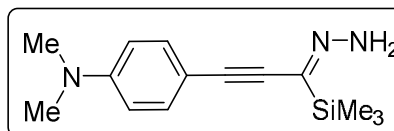
rk-56-N,N-Dimethyl Ph

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EXPNO 12
PROCNO 1

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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 28.5
DW 48.400 usec
DE 10.00 usec
TE 299.9 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -1.76 dB
PL1W 24.30243111 W
SFO1 500.1630887 MHz

F2 - Processing parameters
SI 32768
SF 500.1600123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



rk-56-n-N,N-Dimethyl Ph

Current Data Parameters
NAME rk-56-n,n-dimethyl Ph
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140401
Time 13.12
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

=====
CHANNEL f1
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

=====
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653126 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

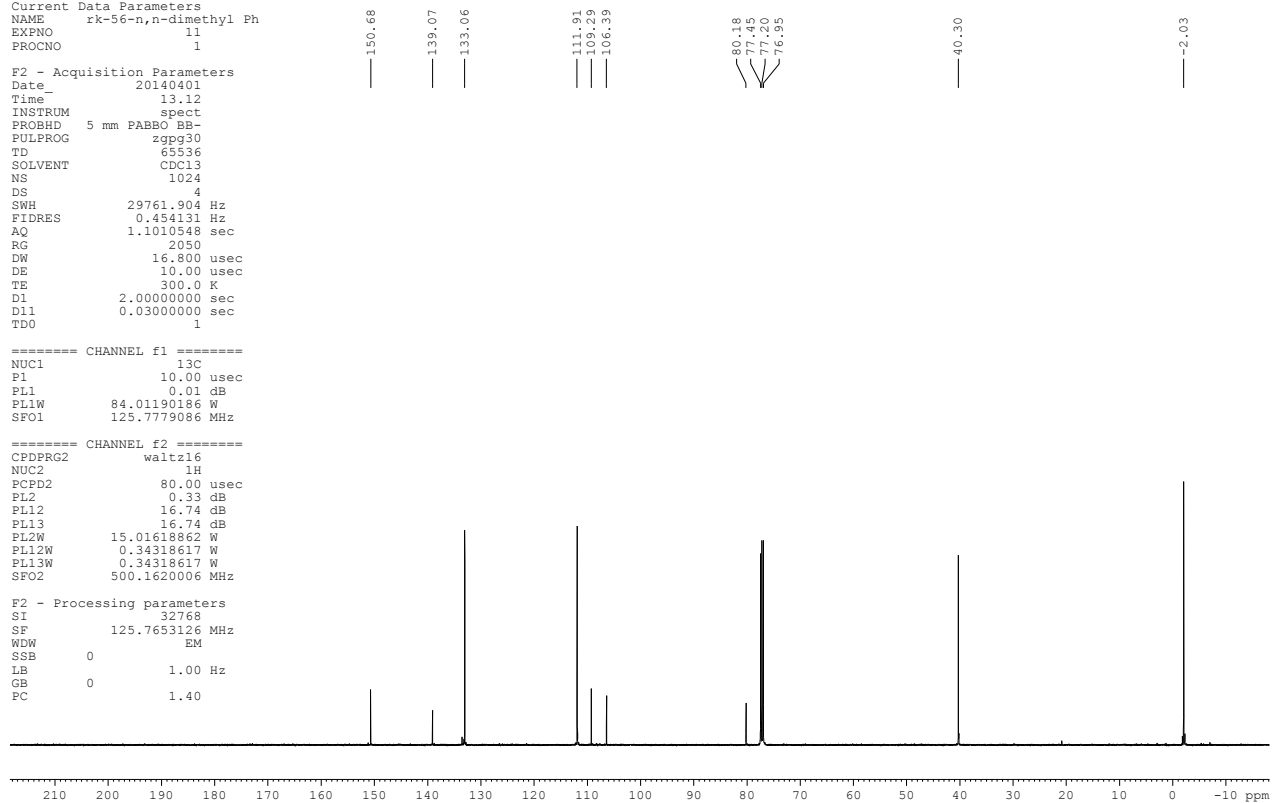


Fig S7. ¹H and ¹³C NMR Spectrum of 2f

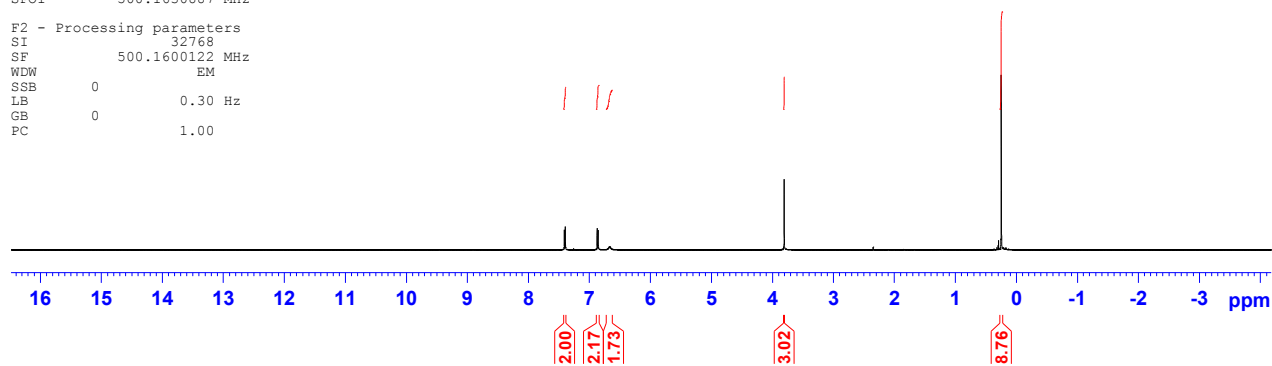
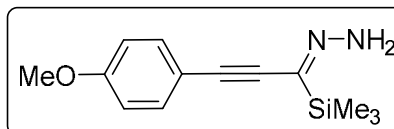
rk-55-OMe

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EXPNO 10
PROCNO 1

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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 16
DW 48.400 usec
DE 10.00 usec
TE 300.0 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -1.76 dB
PL1W 24.30243111 W
SFO1 500.1630887 MHz

F2 - Processing parameters
SI 32768
SF 500.1600122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



rk-55-OMe

Current Data Parameters
NAME rk-55-ome
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140404
Time_ 17.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL12W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653192 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

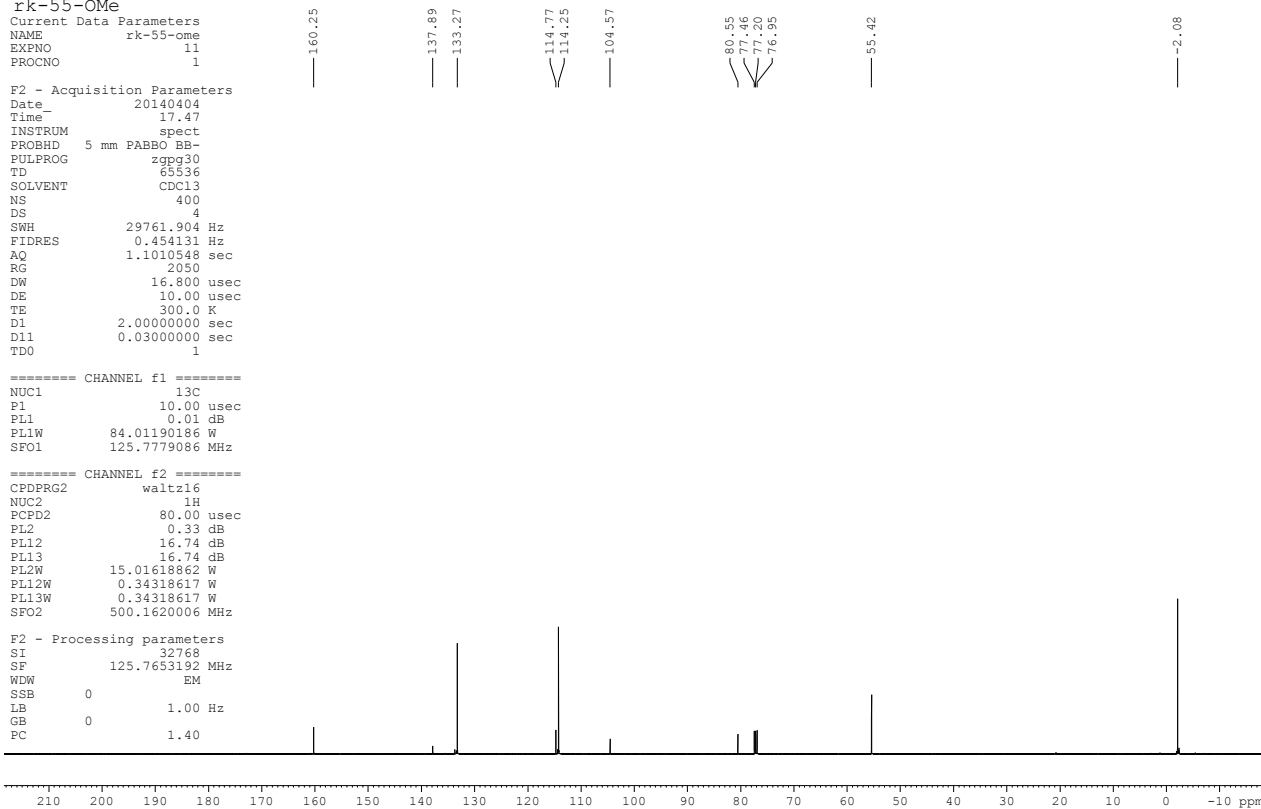


Fig S6. ¹H and ¹³C NMR Spectrum of 2g

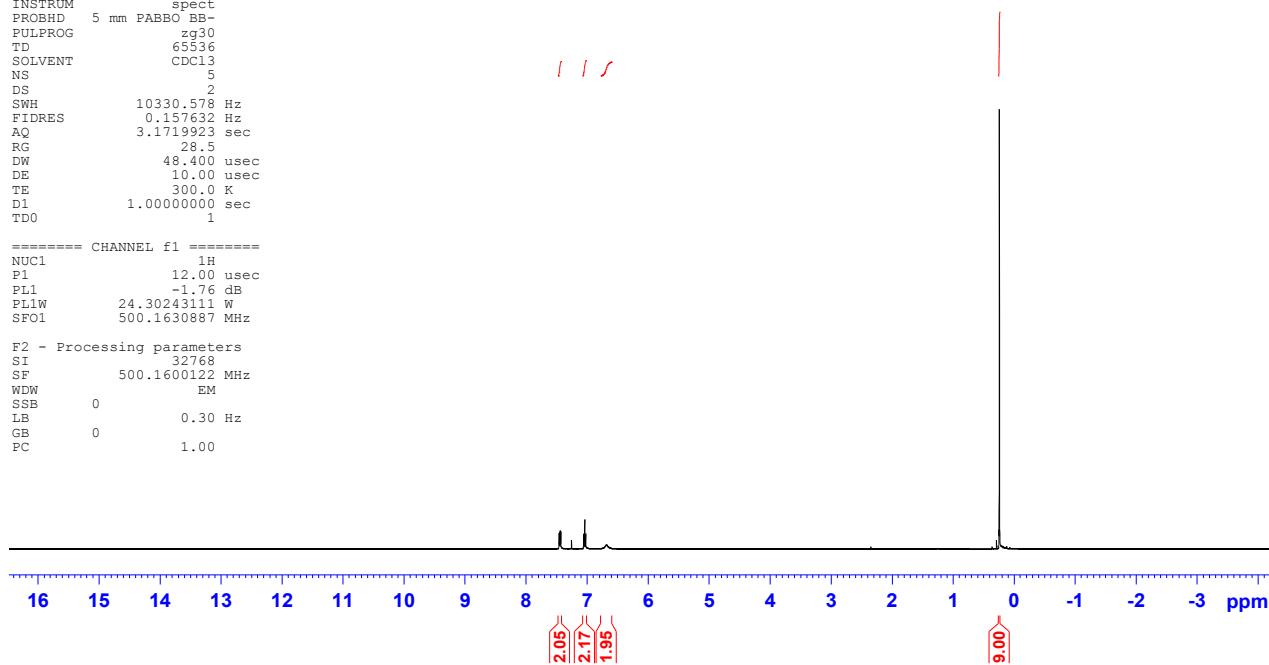
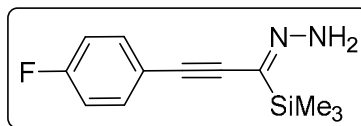
rk-53-fluoro

Current Data Parameters
NAME rk-53-fluro
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140328
Time 12.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 28.5
DW 48.400 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -1.76 dB
PL1W 24.30243111 W
SFO1 500.1630887 MHz

F2 - Processing parameters
SI 32768
SF 500.1600122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



rk-53-fluoro

Current Data Parameters
NAME rk-53-fluro
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140328
Time 12.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 200
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653023 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

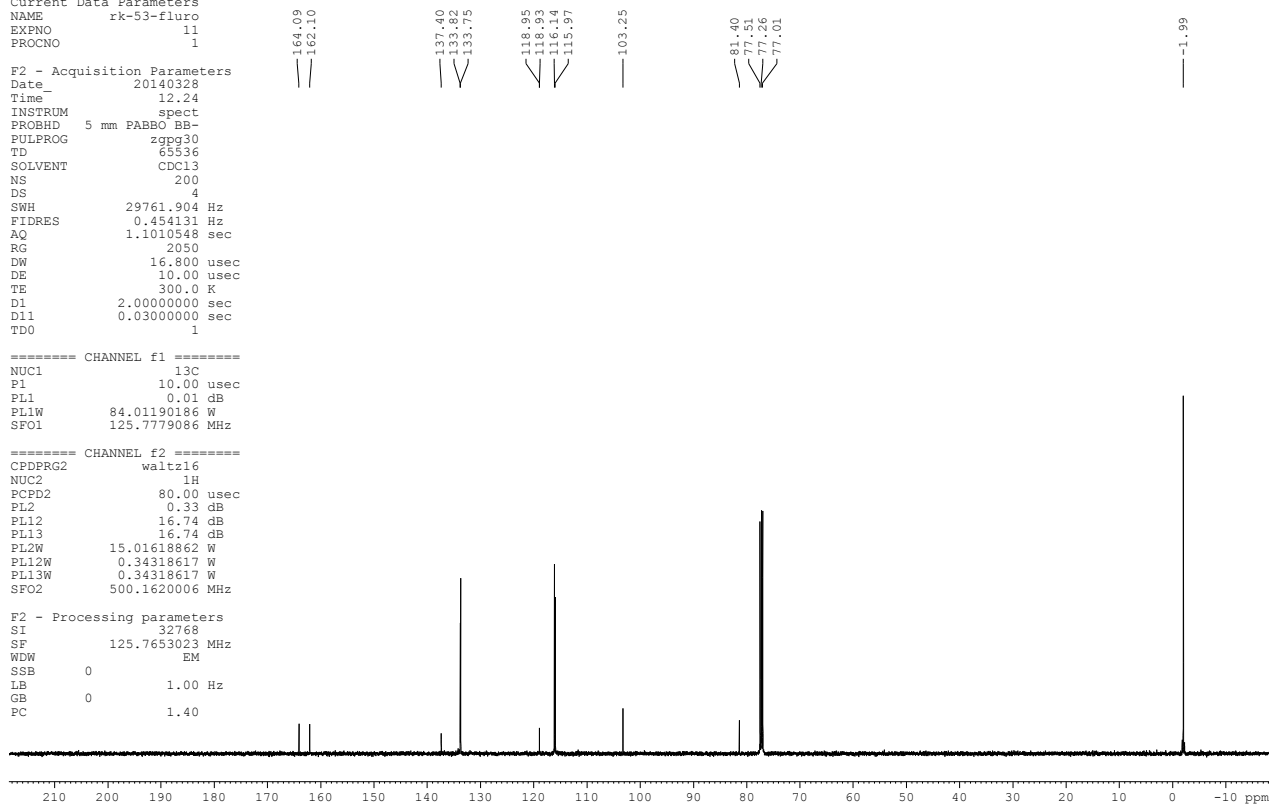


Fig S8. ¹H and ¹³C NMR Spectrum of 2h

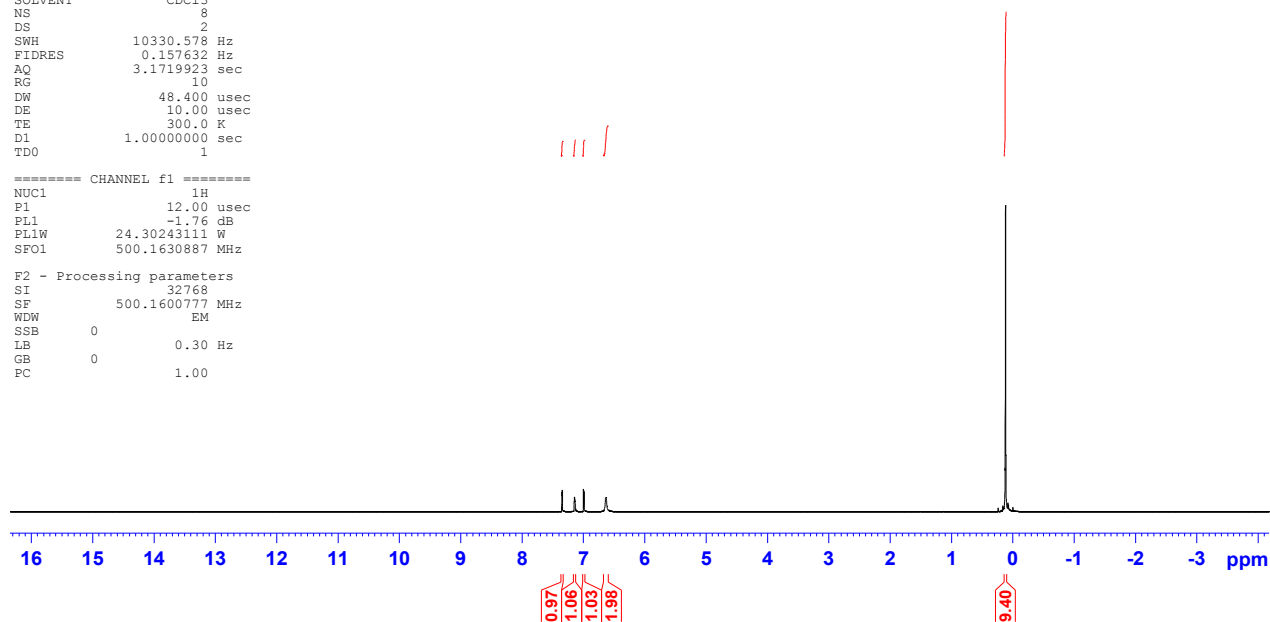
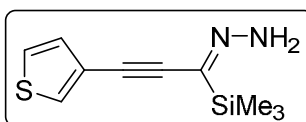
rk-47-thiophene-pure

Current Data Parameters
 NAME rk-47-thiophene-pure
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140516
 Time 13.12
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 8
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 10
 DW 48.400 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 FL1W 24.3024311 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600777 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-47-thiophene-pure

Current Data Parameters
 NAME rk-47-thiophene-pure
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140516
 Time 13.35
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 400
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 FL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 FCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653367 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

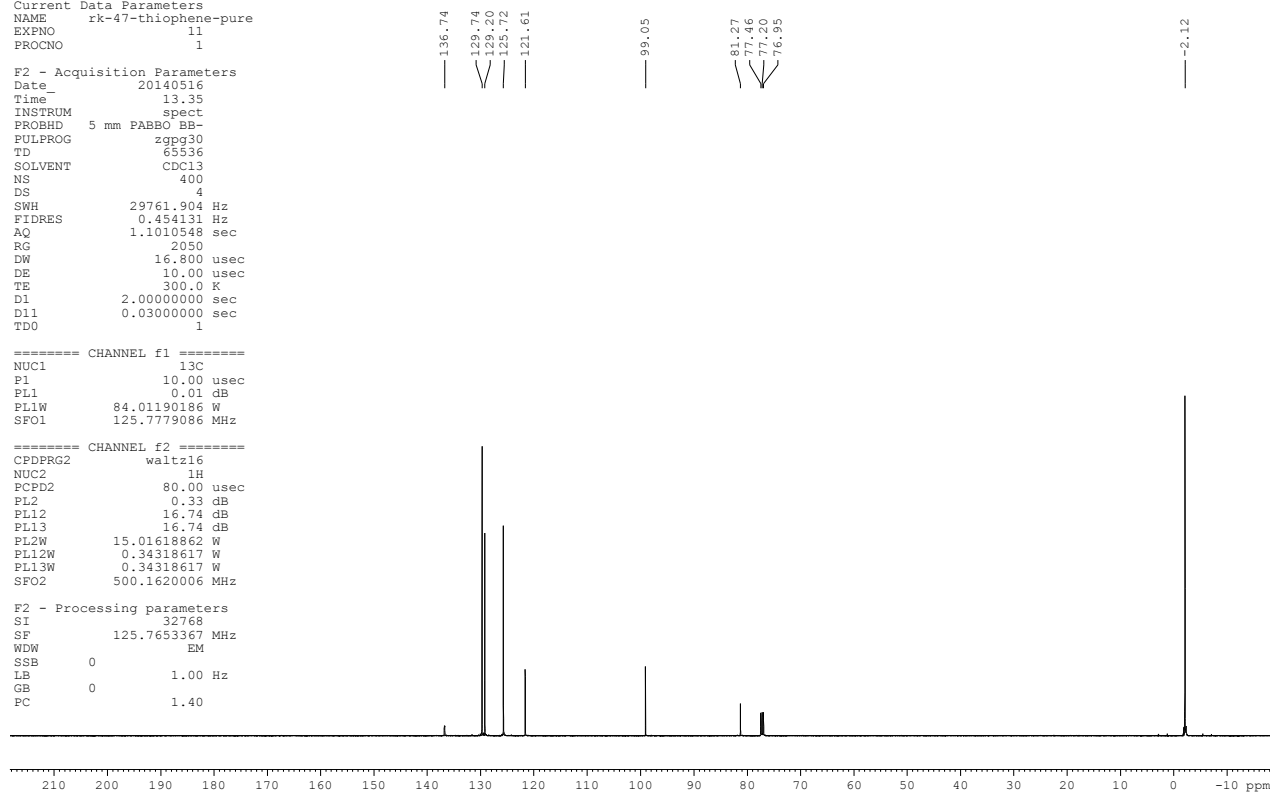


Fig S9. ¹H and ¹³C NMR Spectrum of 2i

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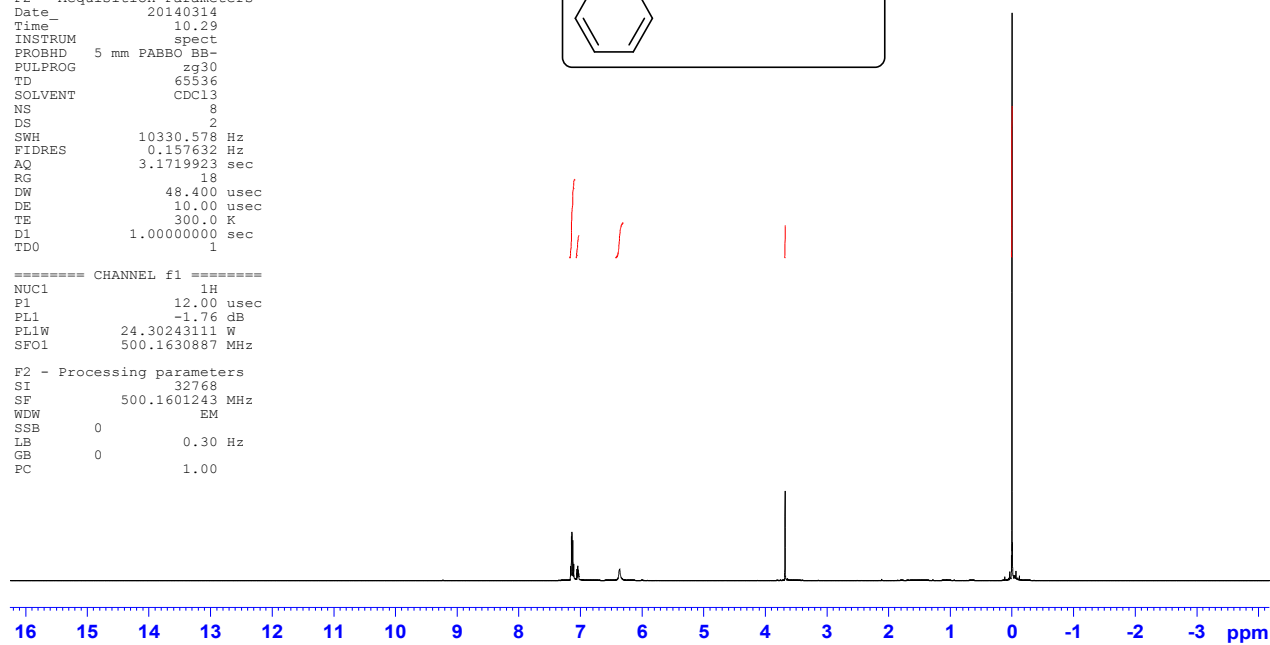
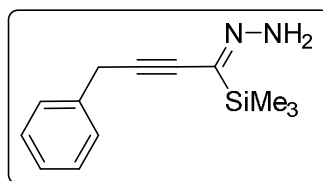
rk-34
Current Data Parameters
NAME      rk-34
EXPNO     10
PROCNO    1

F2 - Acquisition Parameters
Date_     20140314
Time      10.29
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         2
SWH        10330.578 Hz
FIDRES     0.157632 Hz
AQ         3.1719923 sec
RG         18
DW         48.400 usec
DE         10.00 usec
TE         300.0 K
D1         1.0000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         12.00 usec
PL1        -1.76 dB
PL1W       24.3024311 W
SFO1       500.1630887 MHz

F2 - Processing parameters
SI         32768
SF         500.1601243 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



```

Current Data Parameters
NAME      rz-34
EXPNO     10
PROCNO    1

F2 - Acquisition Parameters
Date_     20140307
Time      12.01
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         396
DS         2
SWH        29761.904 Hz
FIDRES     0.454131 Hz
AQ         1.1010548 sec
RG         2050
DW         16.800 usec
DE         10.00 usec
TE         300.0 K
D1         2.0000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1         0.01 dB
PL1W       84.01190186 W
SFO1       125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        0.33 dB
PL12       16.74 dB
PL13       16.74 dB
PL2W       15.01618862 W
PL12W      0.34318617 W
PL13W      0.34318617 W
SFO2       500.1620006 MHz

F2 - Processing parameters
SI         32768
SF         125.7653180 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```

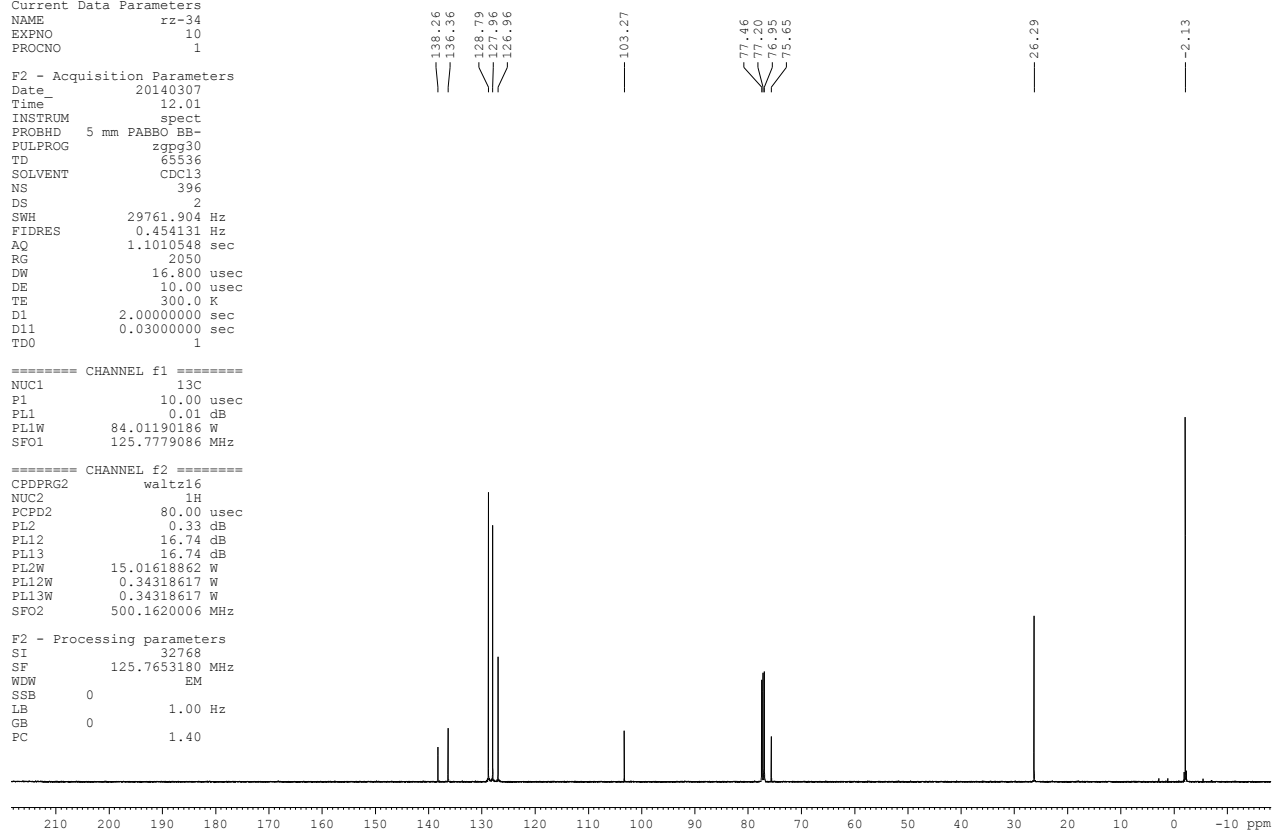


Fig S10. ¹H and ¹³C NMR Spectrum of 2j

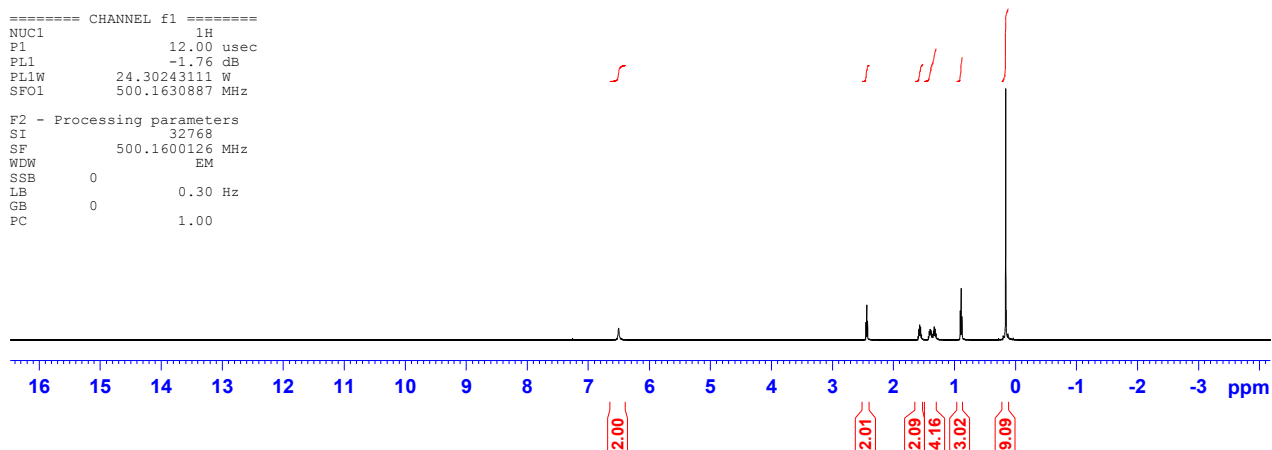
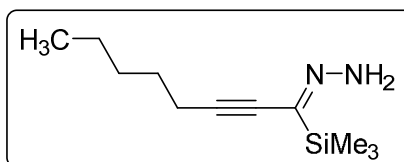
rk-43-heptyne

Current Data Parameters
NAME Mar18-2014-micouin
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140318
Time_ 16.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 12.7
DW 48.400 usec
DE 10.00 usec
TE 300.0 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -1.76 dB
PL1W 24.30243111 W
SFO1 500.1630887 MHz

F2 - Processing parameters
SI 32768
SF 500.1600126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



rk-43-heptyne

Current Data Parameters
NAME Mar18-2014-micouin
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140318
Time_ 16.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.0000000 sec
D11 0.03000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653149 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

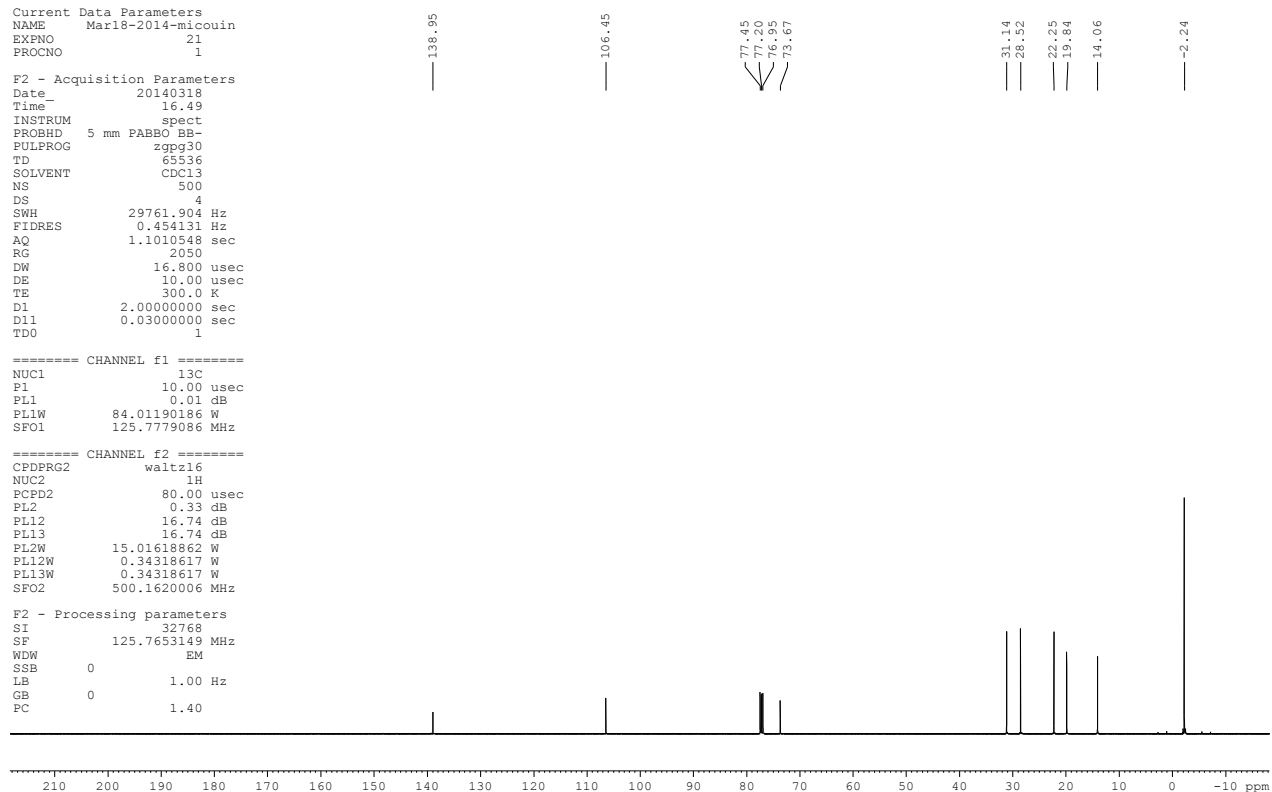


Fig S11. ¹H and ¹³C NMR Spectrum of 2k

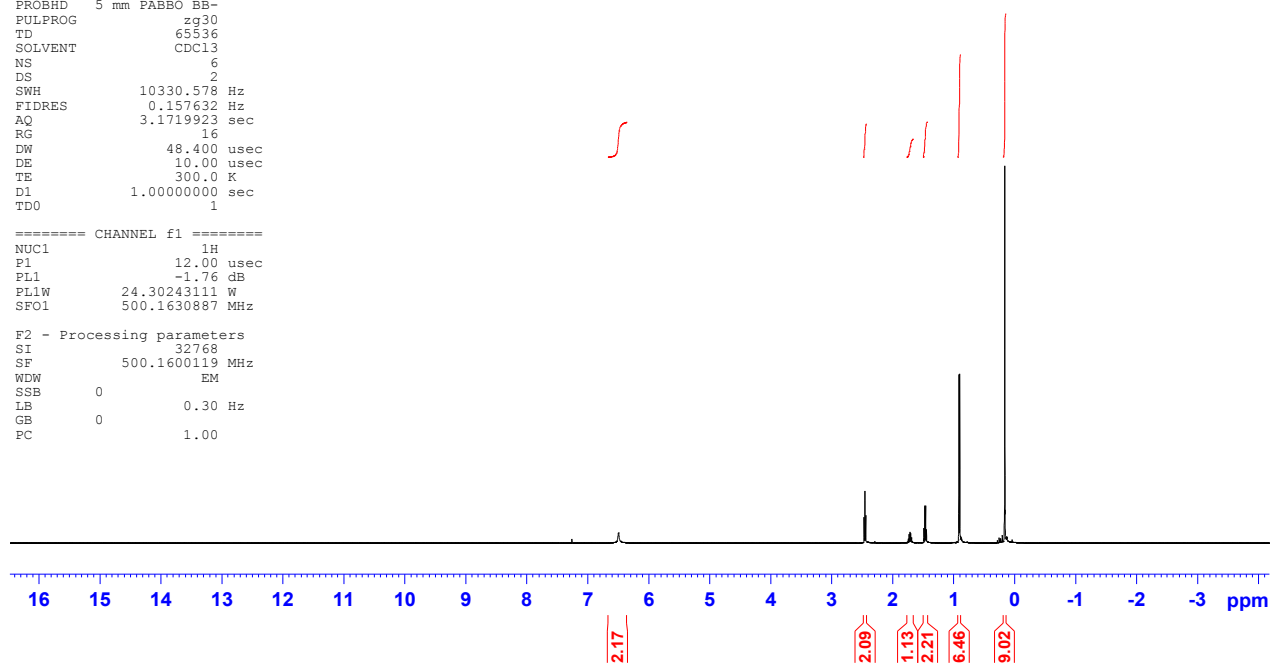
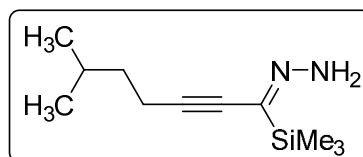
rk-45-Me-hexyne

Current Data Parameters
 NAME rk-45-Me-hexyne
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date 20140610
 Time 12.19
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 6
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 16
 DW 48.400 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600119 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-45-Me-hexyne

Current Data Parameters
 NAME rk-45-Me-hexyne
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date 20140610
 Time 12.23
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653133 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

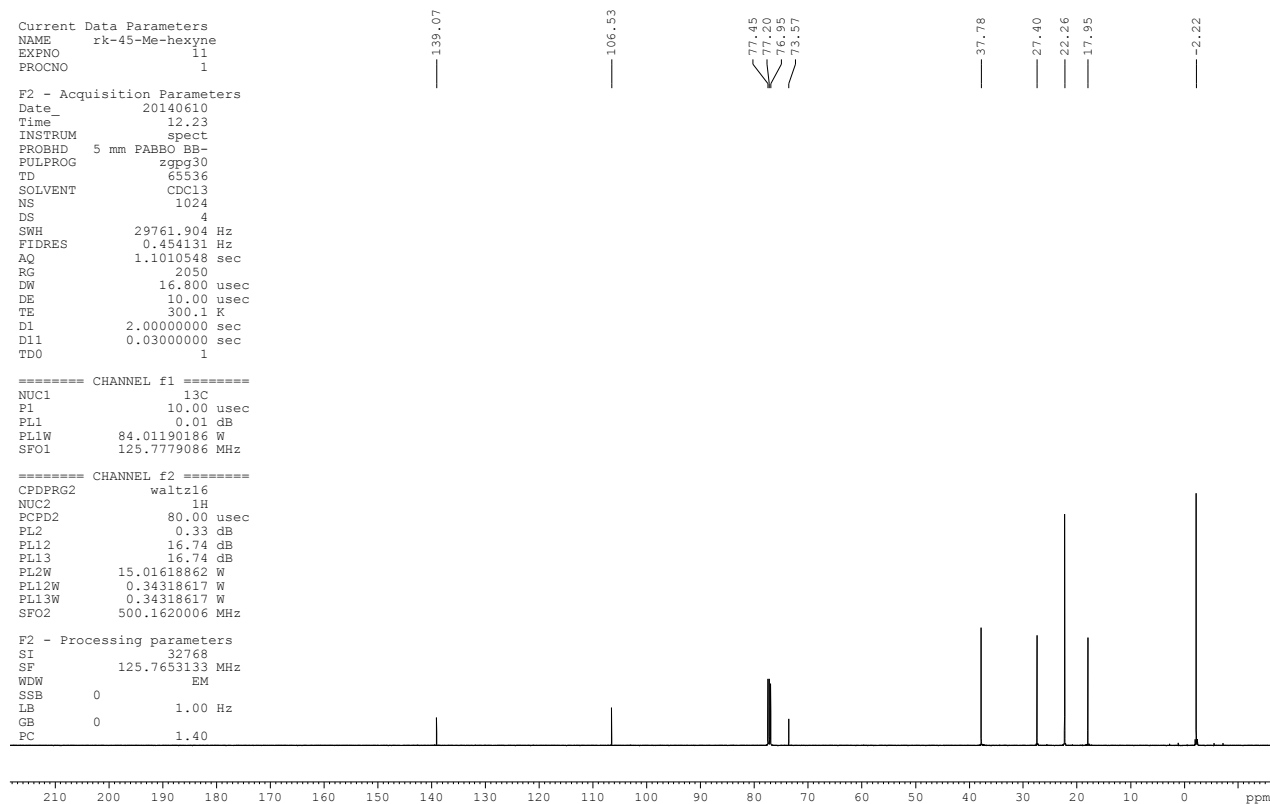


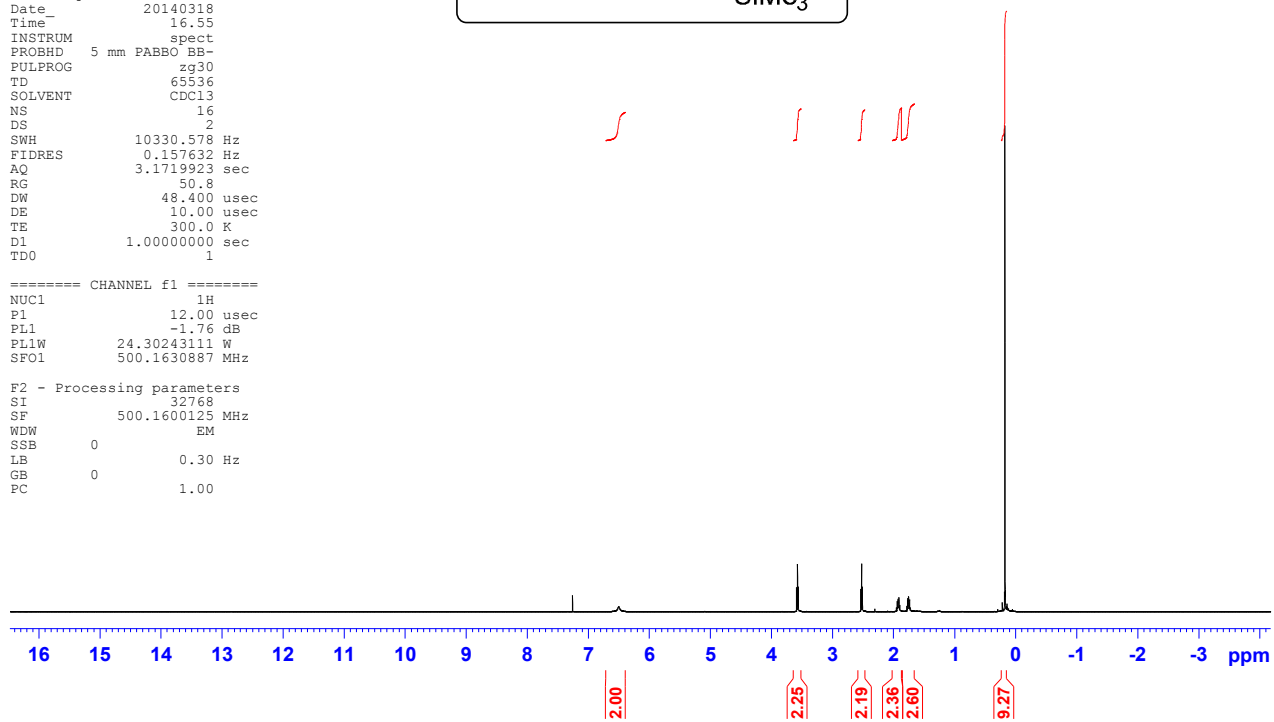
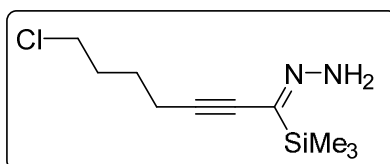
Fig S12. ¹H and ¹³C NMR Spectrum of 2l

rk-44-chlro-hexyne
 Current Data Parameters
 NAME Mar18-2014-micouin
 EXPNO 30
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140318
 Time_ 16.55
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 50.8
 DW 48.400 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600125 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-44-chlro-hexyne
 Current Data Parameters
 NAME Mar18-2014-micouin
 EXPNO 31
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140318
 Time_ 17.23
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 500
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653022 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

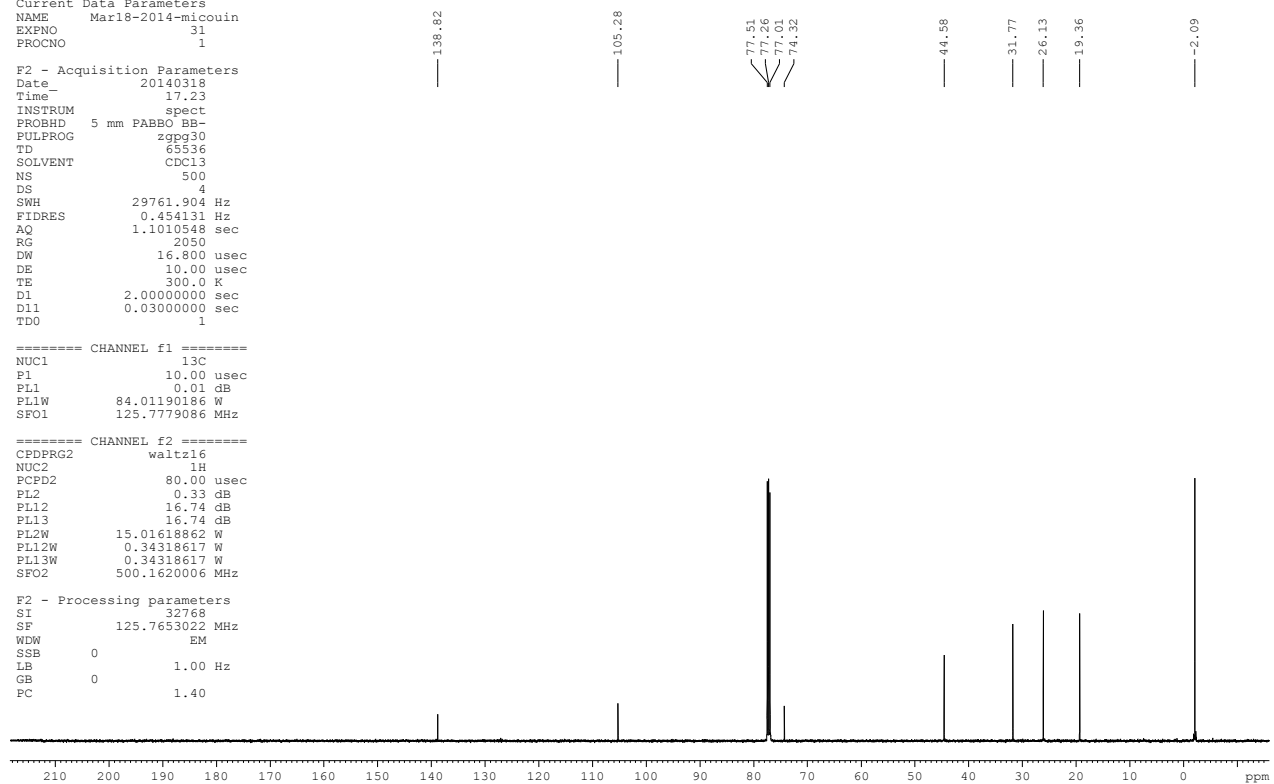


Fig S13. ¹H and ¹³C NMR Spectrum of 2m

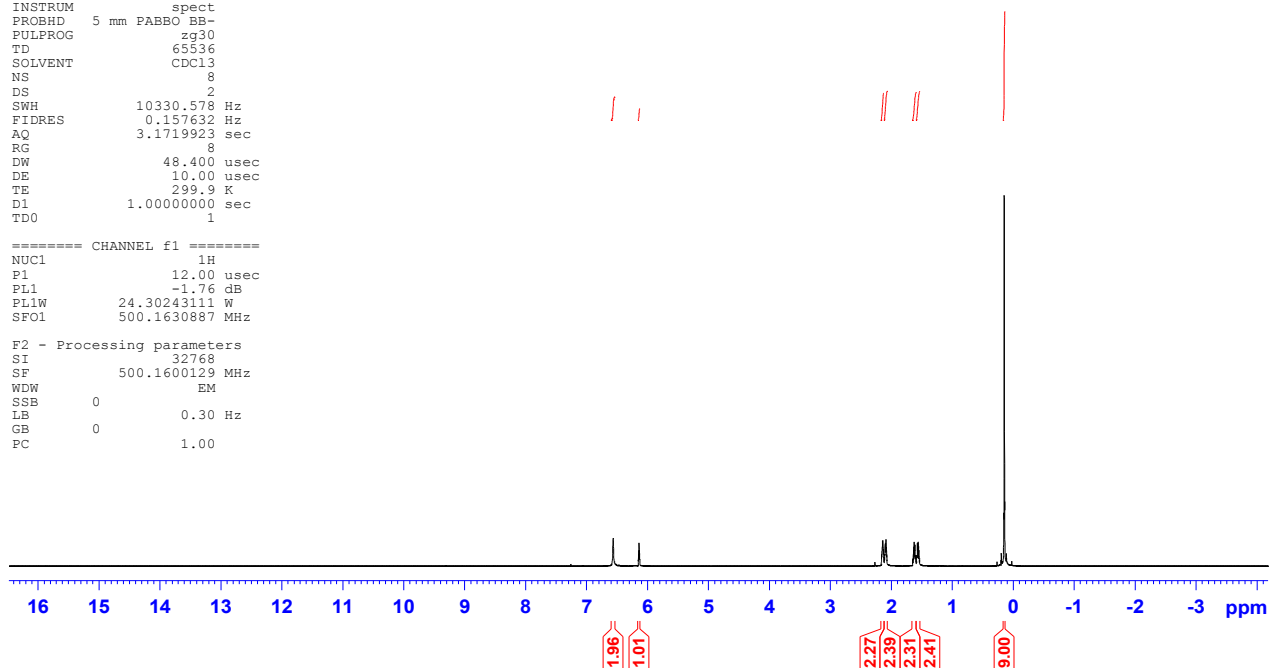
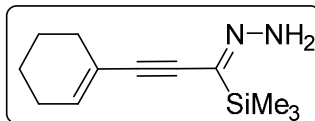
rk-41

Current Data Parameters
NAME rk-41
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140314
Time 10.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 8
DW 48.400 usec
DE 10.00 usec
TE 299.9 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -1.76 dB
PL1W 24.30243111 W
SFO1 500.1630887 MHz

F2 - Processing parameters
SI 32768
SF 500.1600129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



rk-41

Current Data Parameters
NAME rk-41
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140314
Time 10.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.0000000 sec
D11 0.03000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653197 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

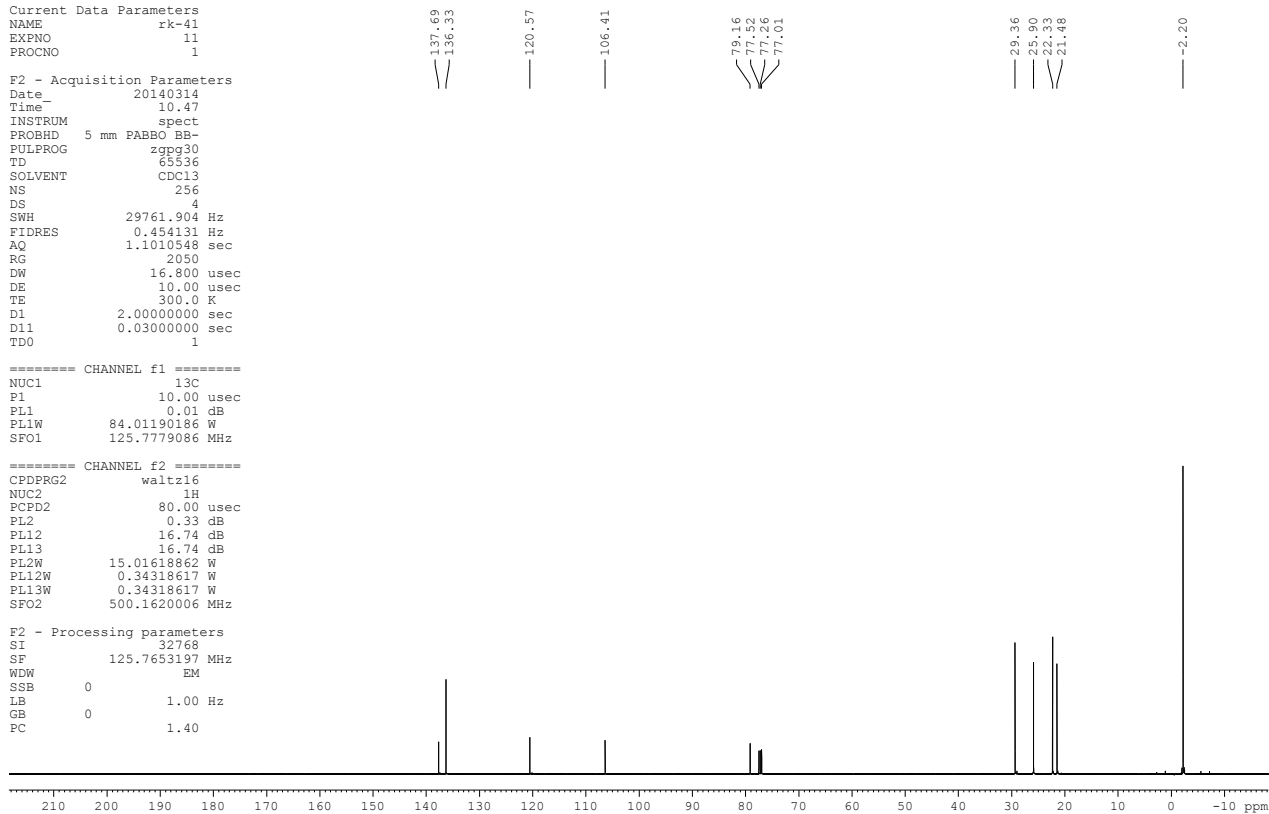
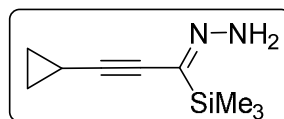


Fig S14. ¹H and ¹³C NMR Spectrum of 2n

rk-54-cyclo

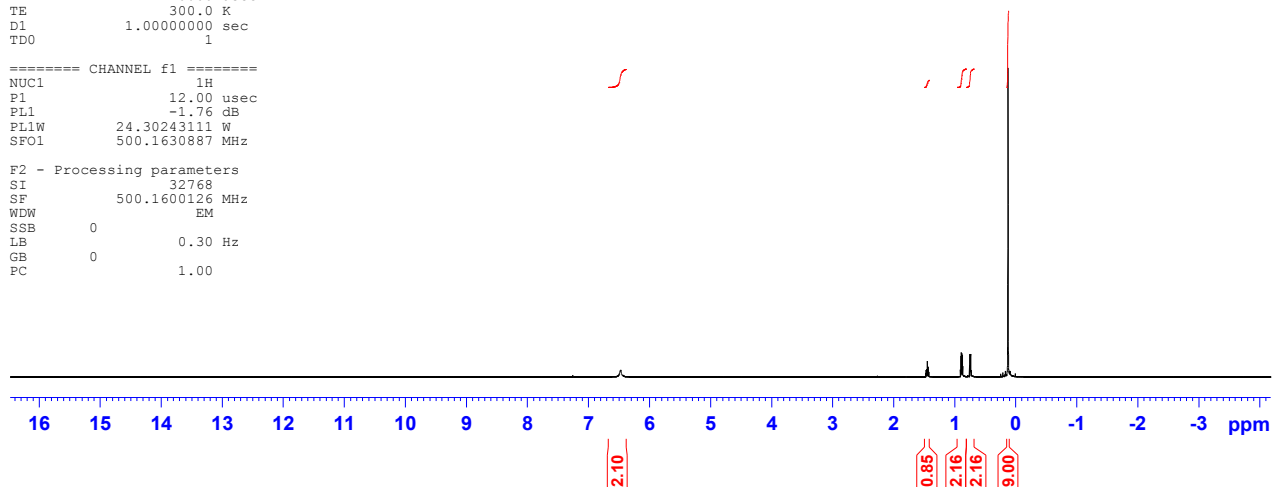
Current Data Parameters
NAME rk-54
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140404
Time_ 16.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 12.7
DW 48.400 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1



===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -1.76 dB
PL1W 24.30243111 W
SFO1 500.1630887 MHz

F2 - Processing parameters
SI 32768
SF 500.1600126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



rk-54-cyclo

Current Data Parameters
NAME rk-54
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140404
Time_ 17.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 750
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653184 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

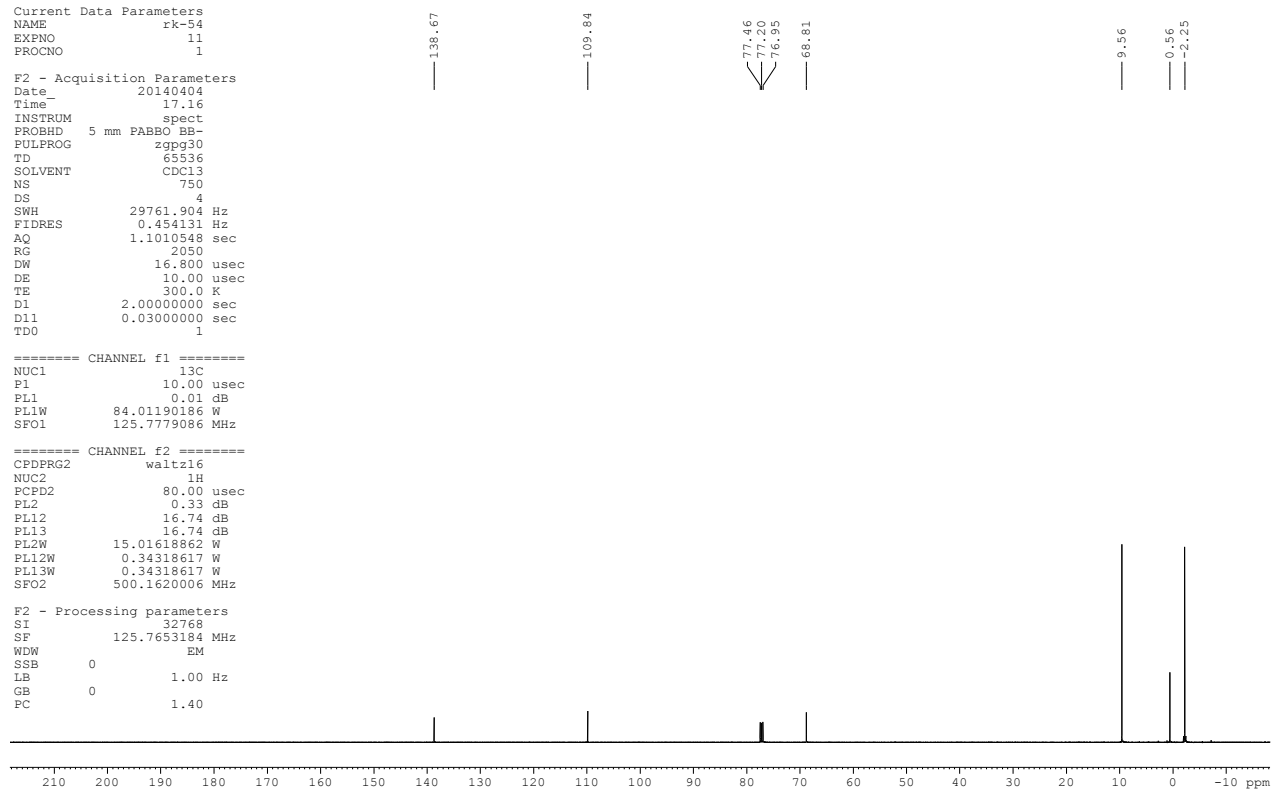


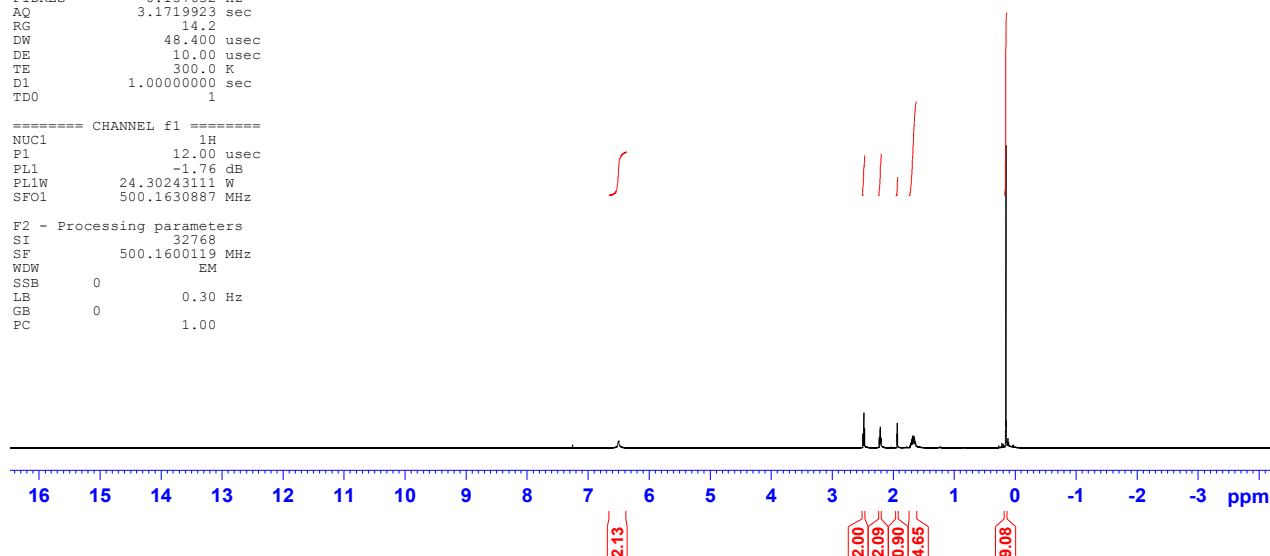
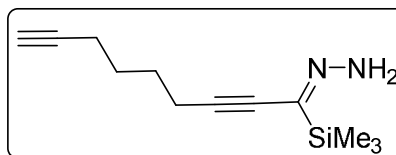
Fig S15. ¹H and ¹³C NMR Spectrum of 20

rk-59-octadiyne
 Current Data Parameters
 NAME rk-59-octadiyne
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140516
 Time 12.42
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 5
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 14.2
 DW 48.400 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600119 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-59-octadiyne

Current Data Parameters
 NAME rk-59-octadiyne
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140516
 Time 12.59
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 4
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653153 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

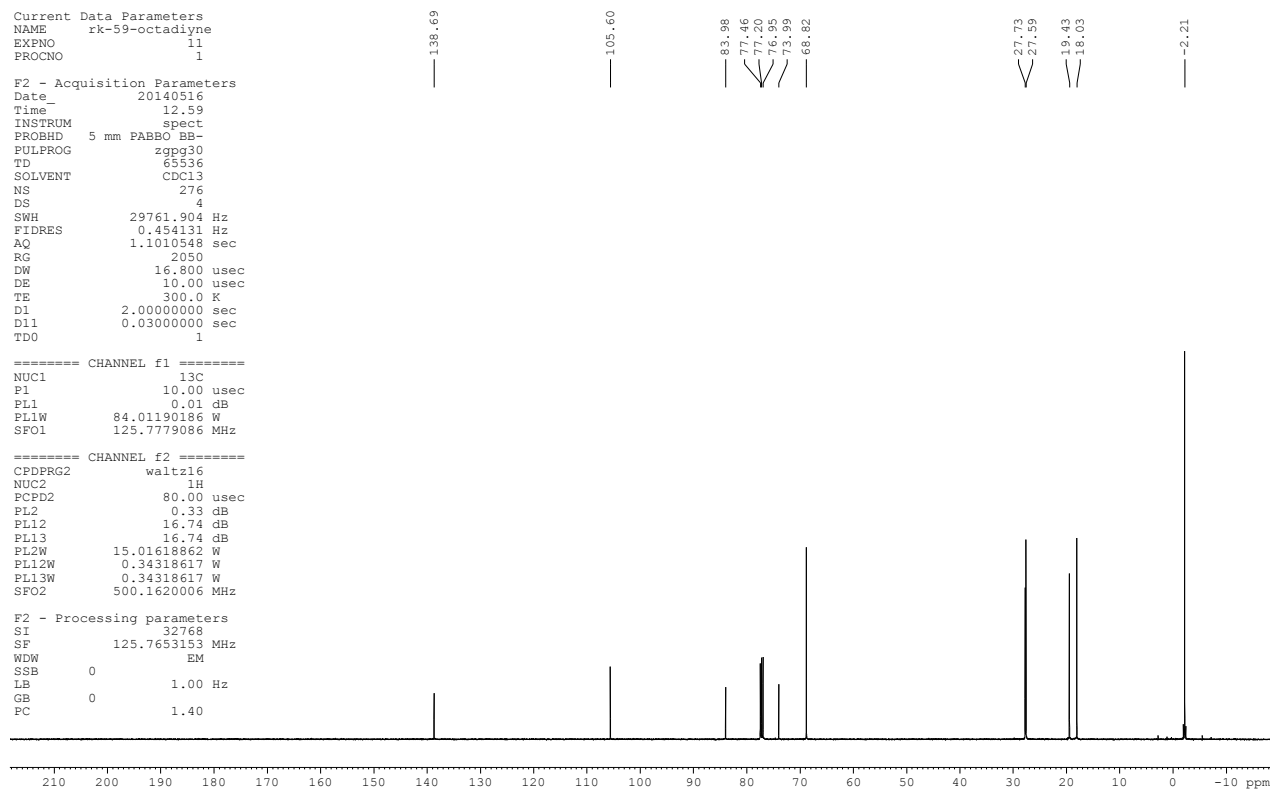


Fig S16. ¹H and ¹³C NMR Spectrum of 2p

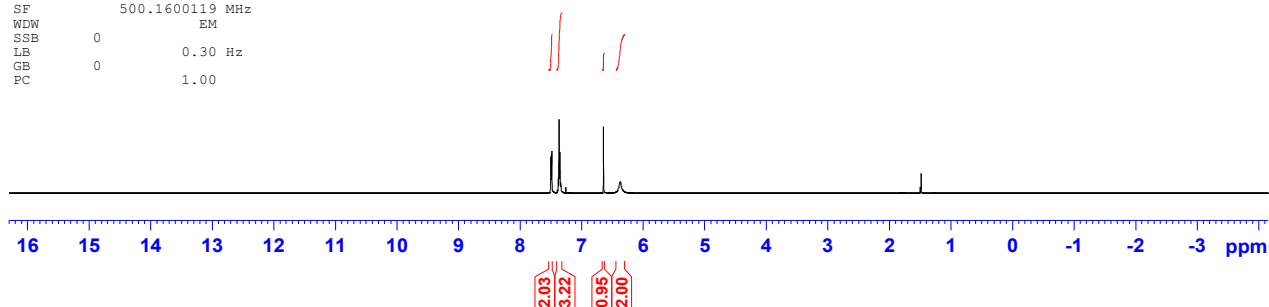
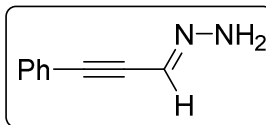
rk-21-desilylation

Current Data Parameters
 NAME rk-21-desilylation
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140516
 Time 14.01
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 28.5
 DW 48.400 usec
 DE 10.00 usec
 TE 299.9 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600119 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-21

Current Data Parameters
 NAME 06022014-micouin
 EXPNO 31
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140206
 Time_ 19.06
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 300
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653127 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

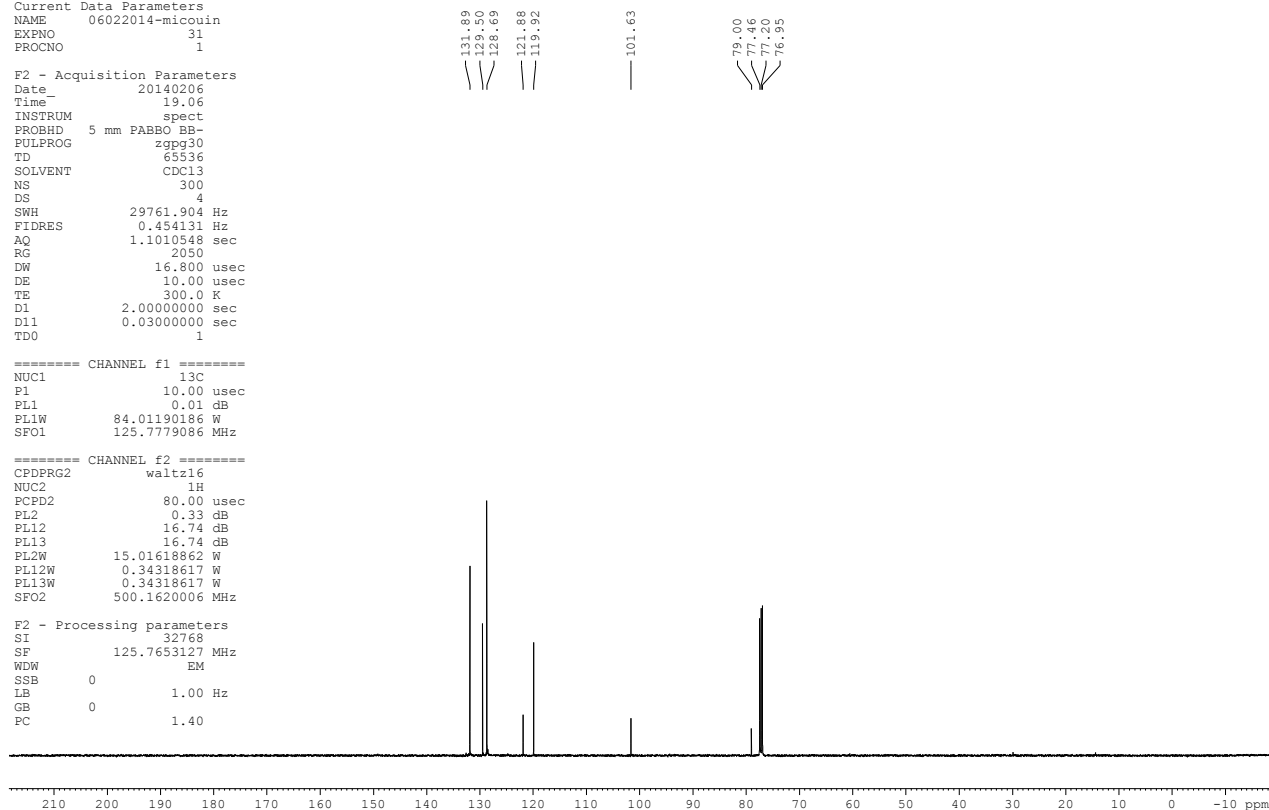
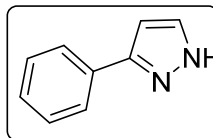


Fig S17. ¹H and ¹³C NMR Spectrum of 3

rk-pyrazole-1h

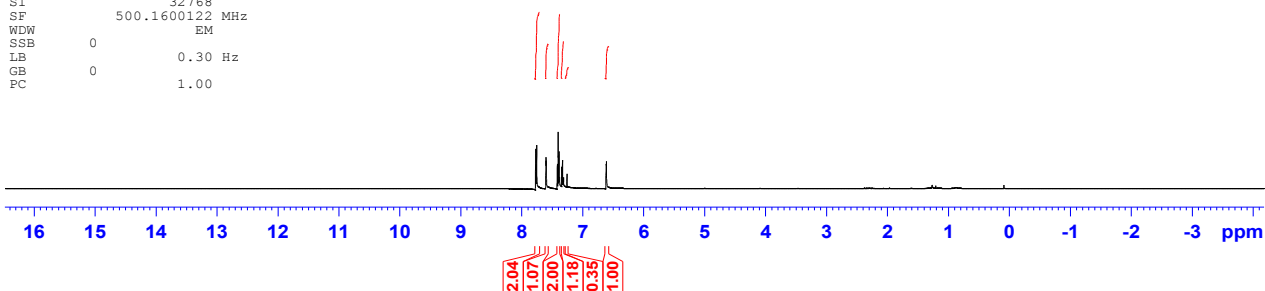
Current Data Parameters
 NAME rk-pyrazole
 EXPNO 10
 PROCNO 1



F2 - Acquisition Parameters
 Date_ 20140602
 Time_ 16.52
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 6
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 36
 DW 48.400 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600122 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-pyrazole-13c

Current Data Parameters
 NAME rk-pyrazole
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140602
 Time_ 16.58
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.1 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653125 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

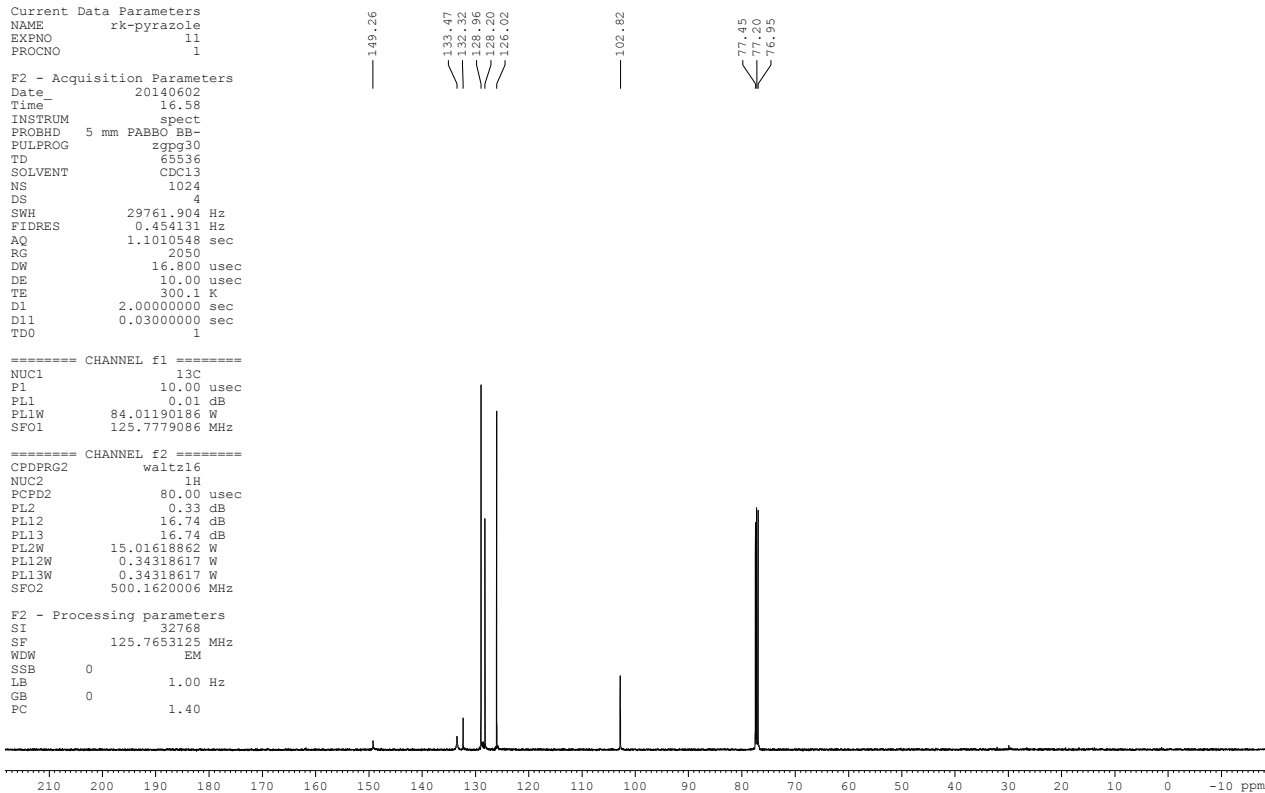


Fig S18. ¹H and ¹³C NMR Spectrum of 5

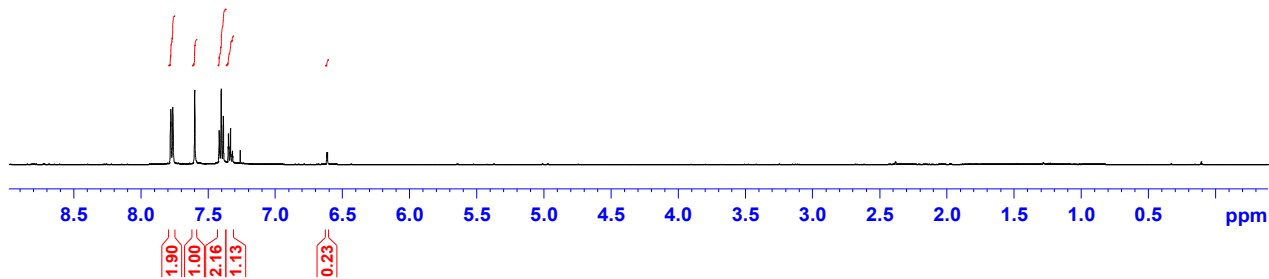
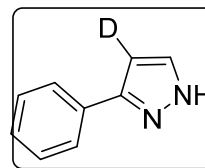
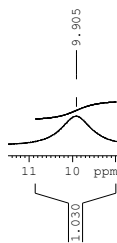
rk-63-D-pyrazole

Current Data Parameters
 NAME rk-63-deuterated pyrazole
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140610
 Time 15.13
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 6
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719922 sec
 RG 36
 DW 48.400 usec
 DE 10.00 usec
 TE 299.9 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600122 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-63-D-pyrazole

Current Data Parameters
 NAME rk-63-deuterated pyrazole
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140610
 Time 14.38
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPDZ 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653154 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

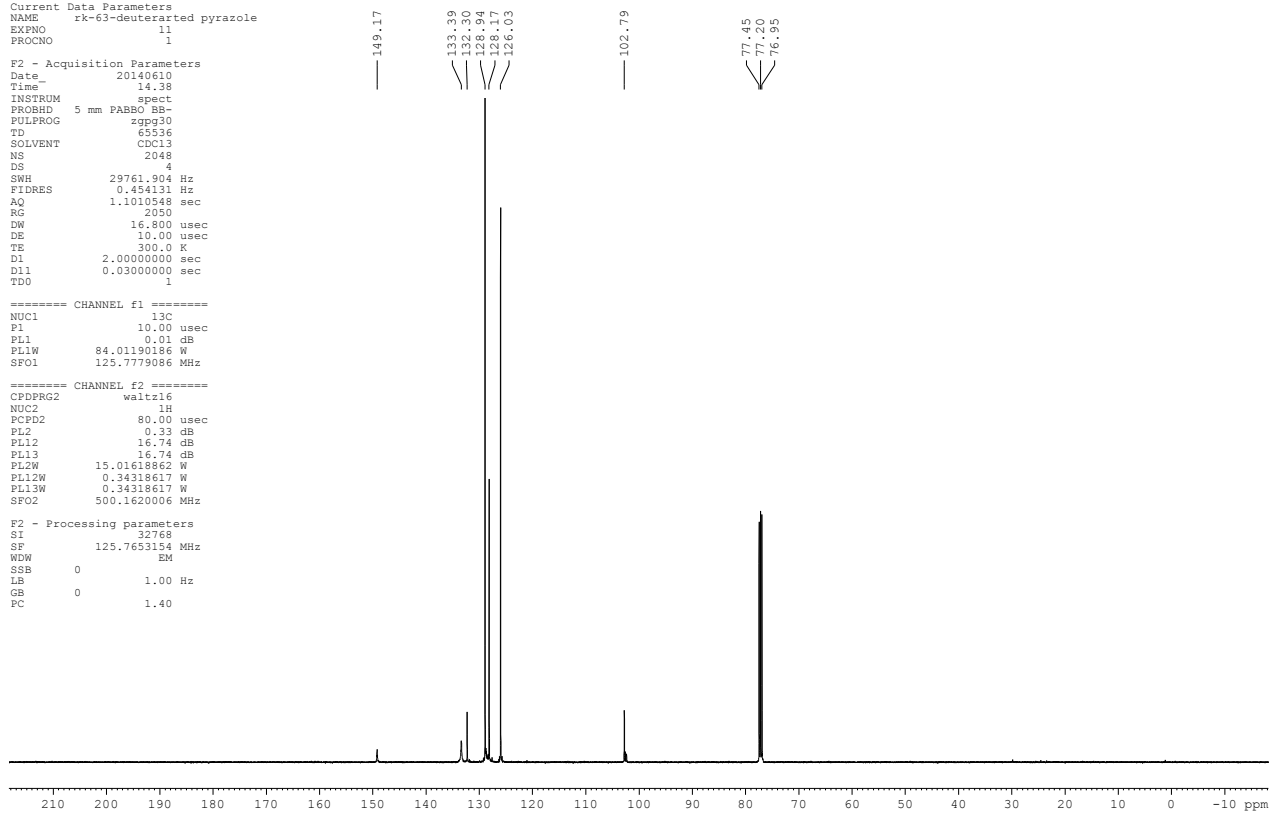
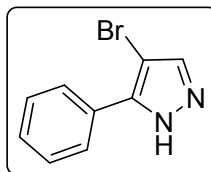


Fig S19. ¹H and ¹³C NMR Spectrum of 6

rk-62a-bromopyrazole

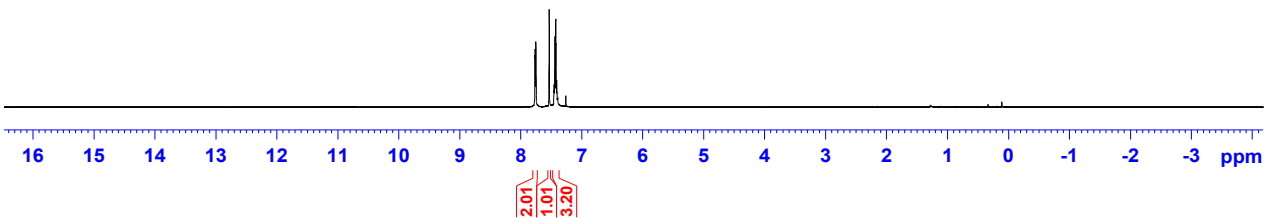
Current Data Parameters
 NAME rk-62a-bromopyrazole
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140602
 Time 15.50
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 28.5
 DW 48.400 usec
 DE 10.00 usec
 TE 300.1 K
 D1 1.00000000 sec
 TD0 1



===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600119 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



rk-62a-bromopyrazole

Current Data Parameters
 NAME rk-62a-bromopyrazole
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140602
 Time 15.53
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

144.53
 136.81
 129.83
 128.93
 127.77
 92.35
 77.45
 77.20
 76.95

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653160 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

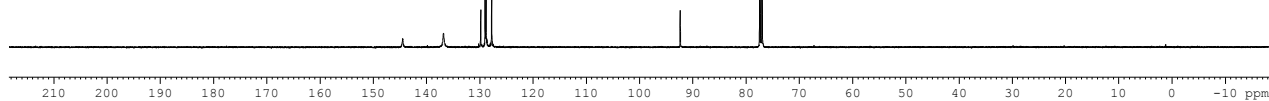


Fig S20. ¹H and ¹³C NMR Spectrum of 7

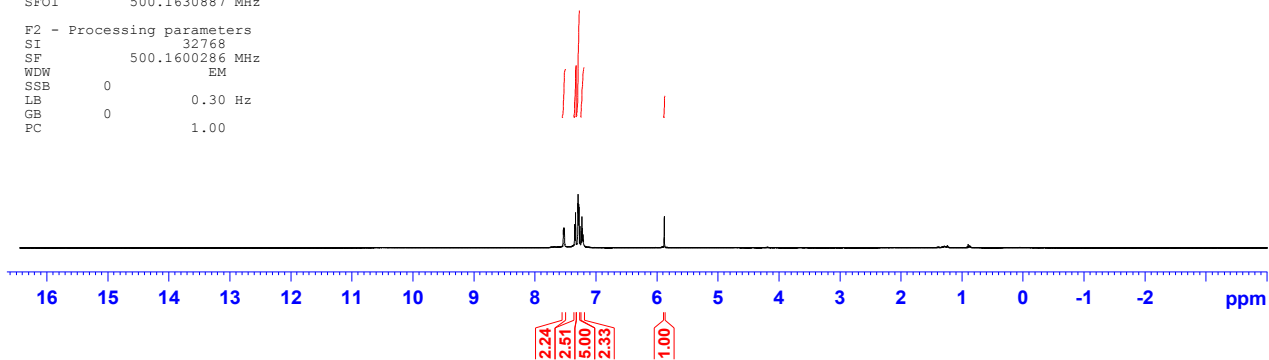
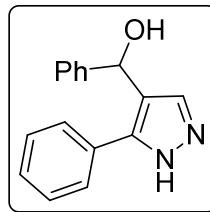
rk-62b-aldehyde

Current Data Parameters
 NAME rk-62b-aldehyde
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140523
 Time 18.13
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 64
 DW 48.400 usec
 DE 10.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -1.76 dB
 PL1W 24.30243111 W
 SFO1 500.1630887 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1600286 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 FC 1.00



rk-62b-aldehyde

Current Data Parameters
 NAME rk-62b-aldehyde
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140523
 Time 19.09
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010548 sec
 RG 2050
 DW 16.800 usec
 DE 10.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.01 dB
 PL1W 84.01190186 W
 SFO1 125.7779086 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.33 dB
 PL12 16.74 dB
 PL13 16.74 dB
 PL2W 15.01618862 W
 PL12W 0.34318617 W
 PL13W 0.34318617 W
 SFO2 500.1620006 MHz

F2 - Processing parameters
 SI 32768
 SF 125.7653113 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

143.74
 134.77
 131.31
 131.31
 131.06
 128.88
 128.88
 128.56
 128.23
 128.23
 127.66
 126.50
 121.91
 77.45
 77.20
 76.95
 68.18

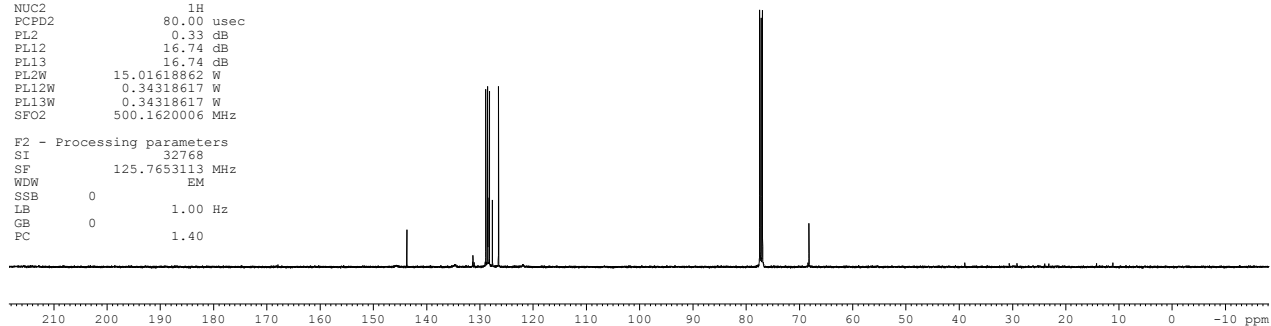


Fig S21. ¹H and ¹³C NMR Spectrum of 8

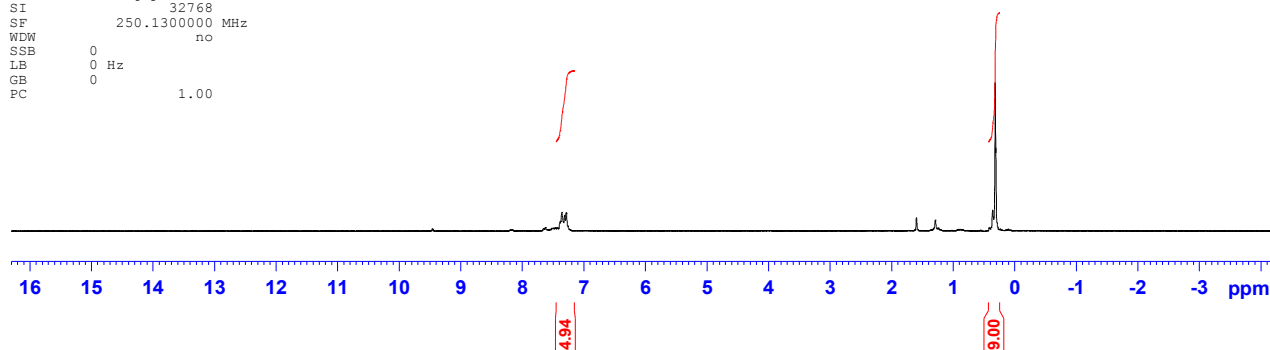
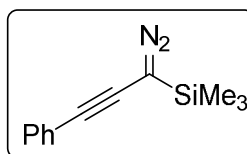
rk-66-Ph-diazo

Current Data Parameters
NAME rk-66-Ph-diazo
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140618
Time_ 11.28
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 8
DS 2
SWH 5165.289 Hz
FIDRES 0.315264 Hz
AQ 1.5860212 sec
RG 724
DW 96.800 usec
DE 6.50 usec
TE 300.5 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 6.50 usec
PLW1 20.00000000 W
SFO1 250.1315447 MHz

F2 - Processing parameters
SI 32768
SF 250.1300000 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



rk-60-crude

Current Data Parameters
NAME rk-60-diazo-crude
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140516
Time_ 14.29
INSTRUM spect
PROBHD 5 mm FABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SFO1 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653224 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

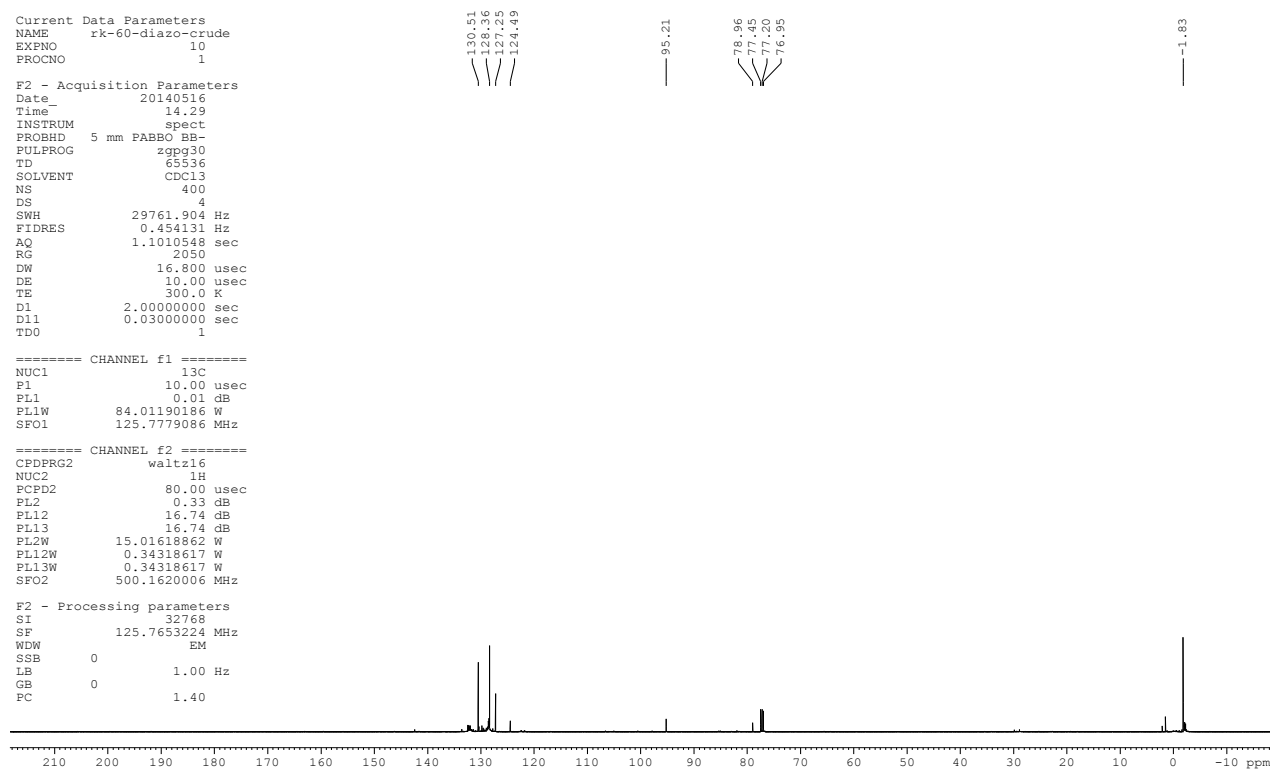


Fig S22. ¹H and ¹³C NMR Spectrum of Crude Compound 9

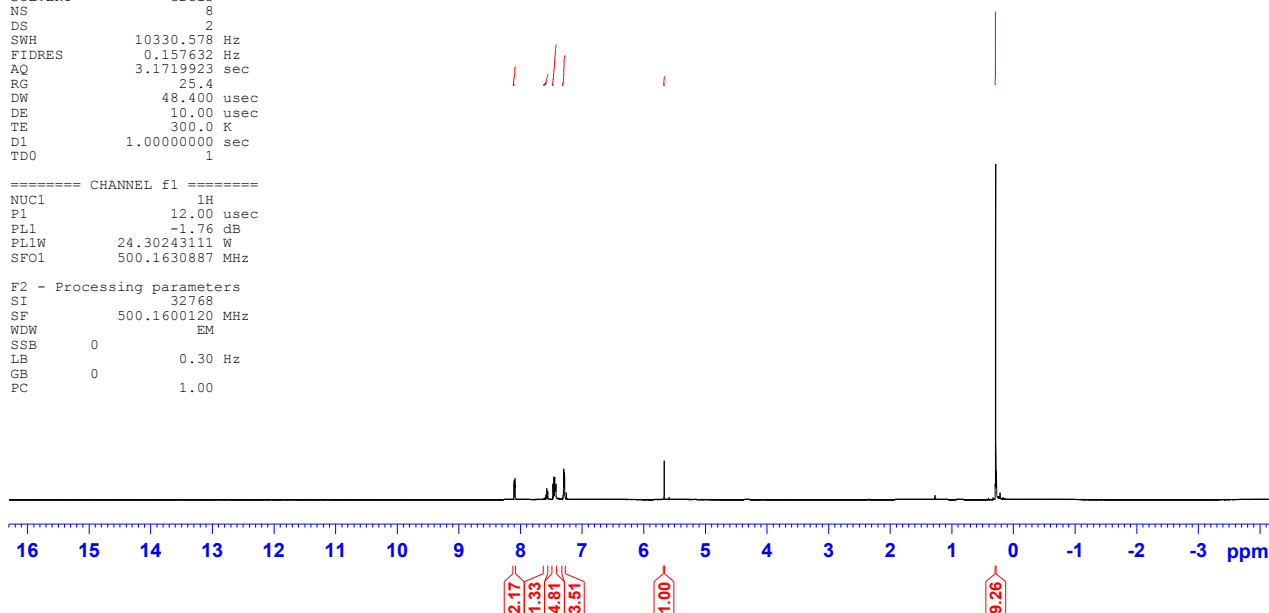
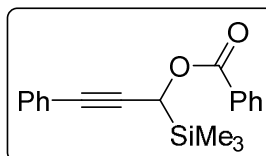
rk-phenylester-64

Current Data Parameters
NAME rk-69-phenylester
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140627
Time_ 13.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 25.4
DW 48.400 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -1.76 dB
PL1W 24.30243111 W
SF01 500.1630887 MHz

F2 - Processing parameters
SI 32768
SF 500.1600120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



rk-phenylester-64

Current Data Parameters
NAME rk-69-phenylester
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140627
Time_ 14.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 747
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.01 dB
PL1W 84.01190186 W
SF01 125.7779086 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.74 dB
PL13 16.74 dB
PL2W 15.01618862 W
PL12W 0.34318617 W
PL13W 0.34318617 W
SFO2 500.1620006 MHz

F2 - Processing parameters
SI 32768
SF 125.7653125 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

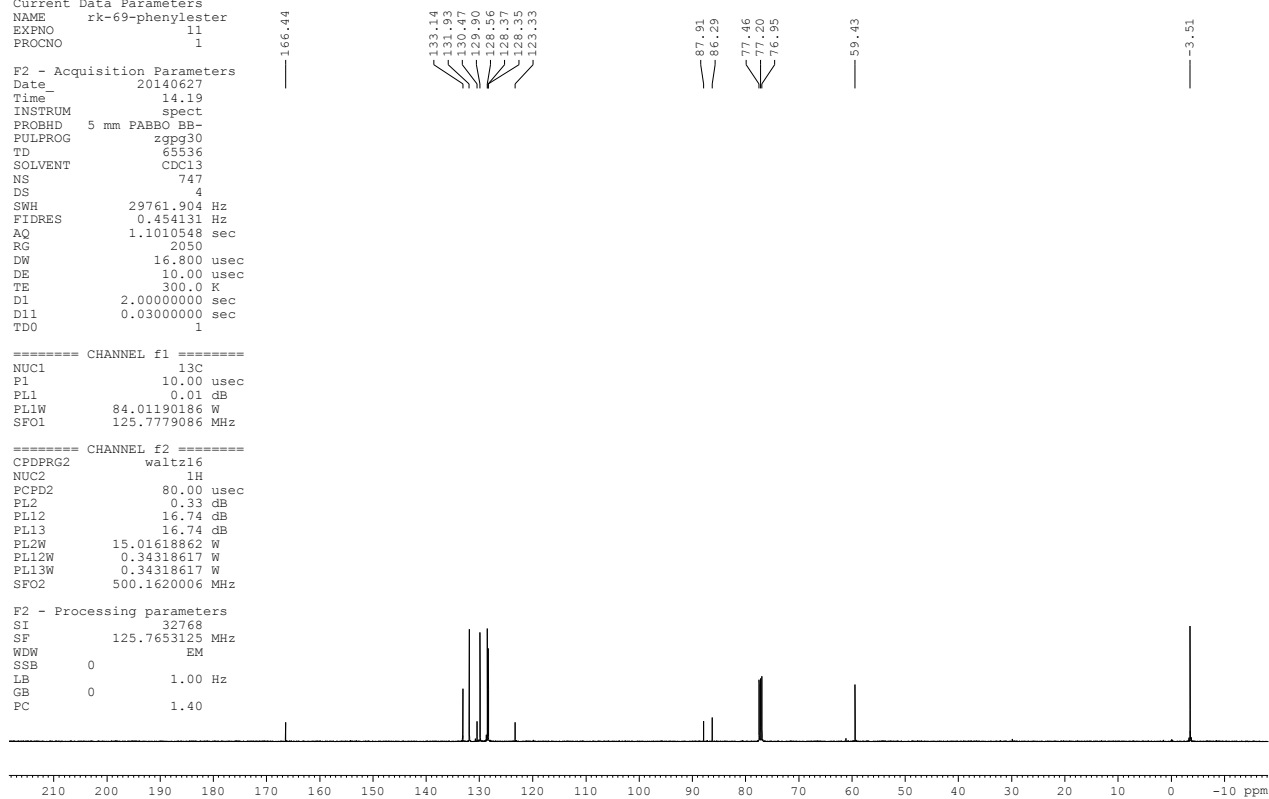


Fig S23. ¹H and ¹³C NMR Spectrum of 10

