Toward Chemical Propulsion: Synthesis of ROMP-propelled Nanocars—Supporting Information

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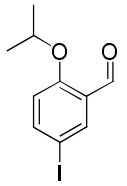
General Methods

^{1}H NMR and ^{13}C NMR spectra were recorded at 400 or 500 and 100 or 125 MHz, respectively. Chemical shifts (δ) are reported in ppm from residual signal of $CDCl_3$ (δ 7.26 ppm). ^{31}P NMR spectra were recorded at 202 MHz. Chemical shifts of the phosphorus resonances were determined relative to 85% phosphoric acid as the external standard (H_3PO_4: δ 0.0 ppm). All

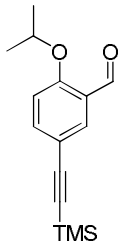
MALDI-TOF experiments were performed using alpha cyano-4-hydroxy-cinnamic acid as the matrix in positive ion mode (+eV). FTIR spectra were recorded using a Nicolet FTIR Infrared Microscope with ATR objective with 2 cm^{-1} resolution. Melting points of compounds **3**, **4** and **5** were recorded on a MEL-TEMP Electrothermal melting point apparatus. The other solid compounds did not melt below 200 °C. Reagent grade tetrahydrofuran (THF) was distilled from sodium benzophenoneketyl. Triethylamine (Et_3N) and dichloromethane (CH_2Cl_2) were distilled from CaH_2 under N_2 atmosphere. THF and Et_3N were degassed with a stream of argon for 30 min before being used in Sonogashira coupling reactions. *cis,cis*-1,5-Cyclooctadiene was distilled from CaH_2 under a nitrogen atmosphere. Trimethylsilylacetylene (TMSA) was donated by FAR Research Inc. or Petra Research. All other chemicals were purchased from commercial suppliers and used without further purification. The reactions were conducted under nitrogen atmosphere. Flash column chromatography was performed using 230-400 mesh silica gel from EM Science for all compounds except for nanocars **1** and **2**, which were purified using 40-63 μm Geduran silica gel 60 from EMD Chemicals. Thin layer chromatography (TLC) was performed using aluminum plates pre-coated with silica gel 60 F_{254} 0.20 mm layer thickness purchased from Sigma-Aldrich. The syntheses of **6**,[1] **7**,[1] **S3**,[2] and **S9**[3] were performed according to reported protocols.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Iodide Using a Palladium-Catalyzed Cross-Coupling (Sonogashira) Protocol. To an oven-dried round-bottom flask or Schlenk tube equipped with a magnetic stir bar were added the aryl halide, the terminal alkyne, $PdCl_2(PPh_3)_2$ (ca. 5 mol% per aryl halide) and CuI (ca. 10 mol% per aryl halide). A solvent system of THF:Et_3N 3:1 was well-degassed under argon for 30 min prior to

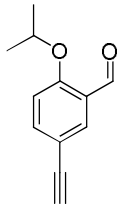
addition to the reaction mixture. Upon completion, the reaction was quenched with a saturated solution of NH_4Cl. The organic layer was then diluted with CH_2Cl_2 (2×) and washed with water or saturated NH_4Cl (1×). The combined aqueous layers were extracted with CH_2Cl_2 (2×). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed from the filtrate *in vacuo* to afford the crude product, that was purified by column chromatography.



Compound 3. A Schlenk tube equipped with a stir bar was charged with 5-iodosalicyladehyde (823 mg, 3.32 mmol), cesium carbonate (2.14 g, 6.64 mmol), and DMF (30 mL). Then isopropyl iodide (1.2 mL, 11.6 mmol) was added and the mixture stirred overnight at 50 ºC. The reaction was quenched with water (50 mL), and then was extracted with diethyl ether (50 mL). The organic layer was washed with water (50 mL ×5). After drying the organic layer with $MgSO_4$ the solvent was removed *in vacuo* to give **3** as a white solid (824 mg, 86%): mp 54−56 °C. FTIR (neat) 3338, 3092, 3059, 2977, 2860, 2758, 2545, 2482, 2362, 2053, 1877, 1831, 1780, 1677, 1609, 1582, 1463, 1423, 1404, 1390, 1382, 1372, 1352, 1335, 1272, 1237, 1183, 1142, 1105 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 10.35 (s, 1H), 7.08 (d, 1H, J = 2.4 Hz), 7.76 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 6.77 (d, 1H, J = 8.8 Hz), 4.65 (sep, 1H, J = 6.0 Hz), 1.39 (d, 6H, J = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 188.8, 160.3, 144.1, 137.2, 127.6, 116.6, 82.8, 71.7, 22.1, 1.2; EI-HRMS *m*/*z* calcd for $C_{10}H_{11}IO_2$ 289.9804, found 289.9803.

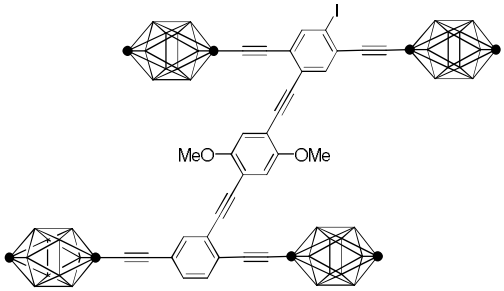


Compound 4. See the general procedure for the Pd/Cu coupling reaction. The materials used were **3** (824 mg, 2.84 mmol), $Pd(PPh_3)_2Cl_2$ (60 mg, 0.085 mmol), CuI (32 mg, 0.17 mmol), THF (18 mL), and Et_3N (6 mL). TMSA (0.81 mL, 5.68 mmol) was added via syringe and the mixture was stirred at rt overnight. The residue was purified by flash column chromatography (silica gel, 40% CH_2Cl_2 in hexanes) to provide **4** as a light-yellow solid (715 mg, 2.74 mmol, 97%): mp 56−58 °C. FTIR (neat) 3655, 3334, 3047, 2963, 2900, 2876, 2765, 2512, 2325, 2188, 2153, 2011, 1979, 1943, 1879, 1799, 1678, 1603, 1569, 1482, 1410, 1393, 1384, 1374, 1354, 1273, 1247, 1217, 1178, 1159, 1138, 1115, 1101 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 10.39 (s, 1H), 7.90 (d, 1H, J = 2.4 Hz), 7.56 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 6.89 (d, 1H, J = 8.4 Hz), 4.66 (sep, 1H, J = 6.0 Hz), 1.38 (d, 6H, J = 6.0 Hz), 0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 189.3, 160.4, 138.9, 132.4, 125.5, 115.6, 113.9, 103.9, 93.8, 71.5, 22.1, 0.11; EI-HRMS *m*/*z* calcd for $C_{15}H_{20}O_2Si$ 260.1233, found 260.1228.



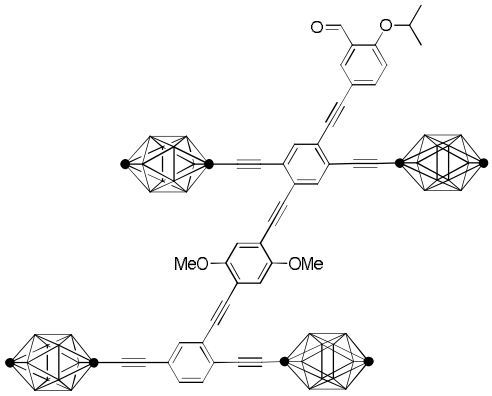
Compound 5. A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with **4** (80 mg, 0.307 mmol), MeOH (5 mL), and THF (5 mL). K_2CO_3 was added (100 mg, 1.00 mmol) and the mixture was stirred at room temperature for 2 h. The reaction was quenched with 15% NH_4Cl (20 mL) and then extracted with CH_2Cl_2 (20 mL ×2). The combined organic fractions were dried with $MgSO_4$ and evaporated *in vacuo*. The residue was purified by column

chromatography (silica gel, 40% CH_2Cl_2 in hexanes) to provide **5** as a white solid (54 mg, 0.29 mmol, 94%): mp 84−85 °C. FTIR (neat) 3343, 3258, 3046, 2988, 2491, 2912, 2874, 2764, 2101, 1911, 1822, 1680, 1602, 1565, 1485, 1450, 1417, 1388, 1351, 1335, 1282, 1250, 1212, 1183, 1164, 1131, 1113, 1104 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 10.41 (s, 1H), 7.93 (d, 1H, *J* = 2.0 Hz), 7.60 (dd, 1H, J_1 = 9.0 Hz, J_2 = 2.0 Hz), 6.93 (d, 1H, *J* = 9.0 Hz), 4.69 (sep, 1H, *J* = 6.0 Hz), 3.01 (s, 1H), 1.40 (d, 6H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 189.3, 160.7, 139.2, 132.5, 125.6, 114.5, 114.1, 82.6, 76.9, 71.6, 22.1; EI-HRMS *m*/*z* calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0838.

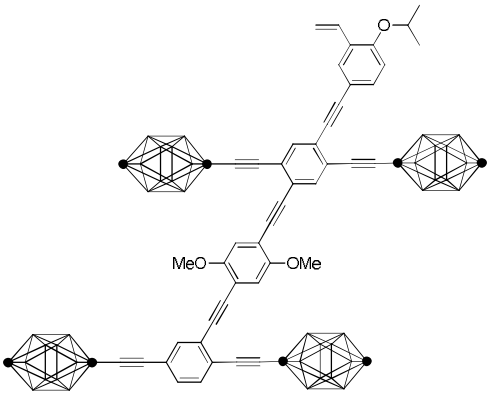


Compound 8. See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **6**[1] (257 mg, 0.43 mmol), **7**[1] (477 mg, 0.72 mmol), $PdCl_2(PPh_3)_2$ (25 mg, 36.0 μmol), CuI (14.0 mg, 72 μmol), THF (45 mL), and Et_3N (15 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, 20% CH_2Cl_2 in hexanes) to yield **8** as a yellow solid (154 mg, 32%). FTIR (neat) 3062, 2825, 2854, 2611, 2360, 2212, 2212, 1726, 1595, 1504, 1487, 1463, 1411, 1362, 1281, 1221, 1140, 1064, 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.47 (d, 1H, *J* = 1.0 Hz), 7.41 (s, 1H), 7.23 (d, 1H, *J* = 8.0 Hz), 7.14 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.5 Hz), 7.06 (d, 2H, *J* = 6.5 Hz), 3.99 (s, 6H), 3.20-1.60 (br m, 44H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 142.0, 135.5, 135.4, 132.3, 131.2, 128.6, 126.7, 126.3, 124.9, 124.0, 122.2, 115.9, 115.8, 113.8, 113.2, 99.7, 92.3, 92.1, 92.0, 91.5, 91.21, 91.17, 90.9, 88.1,

80.7, 78.1, 78.0, 77.2, 76.5, 69.7, 69.3, 69.1, 60.9, 60.7, 60.5, 56.7, 56.6; MALDI-TOF MS (+eV) *m*/*z* calcd for $C_{40}H_{57}B_{40}IO_2$ 1129.2, found 1129.6.

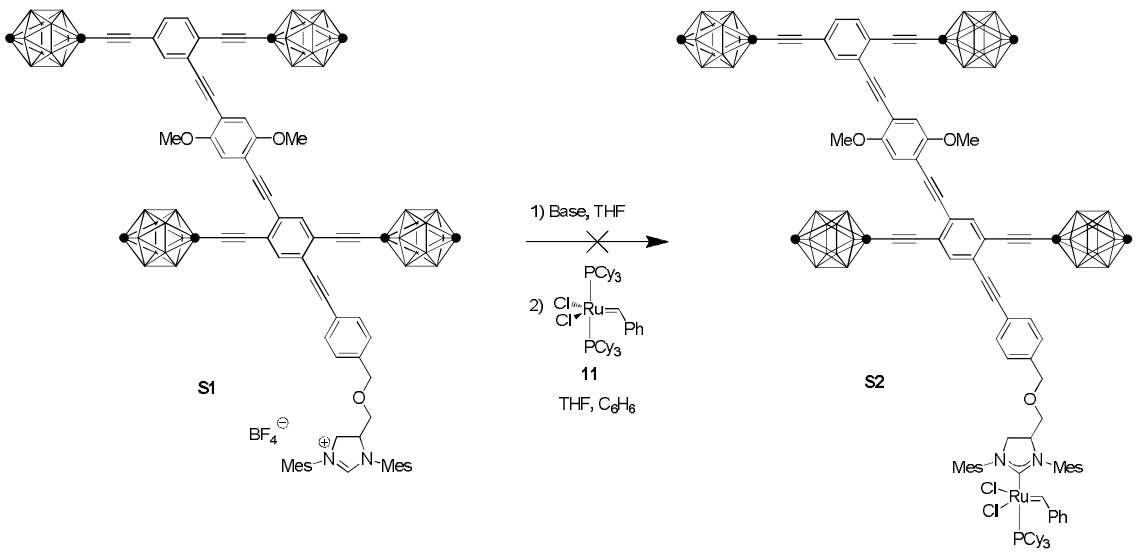


Compound 9. See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **8** (84 mg, 0.074 mmol), **5** (28 mg, 0.15 mmol), $PdCl_2(PPh_3)_2$ (5.0 mg, 7.1 μmol), CuI (2.5 mg, 13.1 μmol), THF (10 mL), and Et_3N (10 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, 5% EtOAc in hexanes) to yield **9** as a yellow solid (80 mg, 91%). FTIR (neat) 3063, 2978, 2864, 2610, 2213, 1688, 1603, 1504, 1464, 1412, 1386, 1271, 1221, 1184, 1138, 1109, 1063, 1043, 1007 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 10.48 (s, 1H), 8.03 (d, 1H, *J* = 2.4 Hz), 7.68 (dd, 1H, *J* = 8.8 Hz, *J* = 2.0 Hz), 7.49 (s, 1H), 7.48 (d, 1H, *J* = 1.6 Hz), 7.44 (s, 1H), 7.23 (d, 1H, *J* = 8.4 Hz), 7.14 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 7.07 (m, 2H), 7.03 (d, 1H, *J* = 9.2 Hz), 4.77 (sep, 1H, *J* = 6.0 Hz), 4.00 (s, 6H), 3.20-1.60 (br m, 44H), 1.45 (d, 6H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 160.9, 154.28, 154.26, 138.8, 135.8, 135.5, 135.43, 135.39, 132.47, 132.34, 131.18, 130.49, 127.90, 127.86, 126.7, 125.8, 125.7, 124.04, 124.00, 123.96, 122.2, 115.8, 114.9, 114.2, 113.7, 113.4, 95.1, 92.4, 92.3, 92.1, 91.5, 91.3, 91.2, 90.9, 88.0, 86.2, 78.1, 78.0, 77.3, 71.7, 69.4, 60.5, 56.7, 29.9, 22.2; MALDI-TOF MS (+eV) *m*/*z* calcd for $C_{52}H_{68}B_{40}O_4$ 1189.5, found 1189.8.



Compound 10. $MePPh_3Br$ (217 mg, 0.61 mmol) was dried at 60 ºC *in vacuo* for 2 h in a 50 mL round-bottom flask equipped with a stir bar. THF was added (20 mL) and the resultant suspension was cooled to 0 ºC. BuLi (2.5 M in hexane, 0.24 mL, 0.61 mmol) was added drop wise and the mixture was stirred for 30 min at 0 ºC. A yellow solution was obtained. Only 5.0 mL of this solution were transferred via syringe to a solution of compound **9** (120 mg, 0.101 mmol) in THF (10 mL) cooled to 0 ºC. The mixture was allowed to warm at rt and stirred overnight. The solvent was removed. The crude product was purified by column chromatography (silica gel, 15% CH_2Cl_2 in hexanes) to yield **10** as a yellow solid (84 mg, 69%). FTIR (neat) 3062, 2964, 2612, 2211, 1689, 1600, 1504, 1464, 1411, 1385, 1279, 1242, 1221, 1111, 1064, 1043 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, 1H, J = 2.0 Hz), 7.49 (d, 1H, J = 0.5 Hz), 7.48 (d, 1H, J = 1.0 Hz), 7.44 (s, 1H), 7.39 (dd, 1H, J_1= 8.6 Hz, J_2 = 2.0 Hz), 7.23 (dd, 1H, J_1 = 8.0 Hz, J_2 = 0.5 Hz), 7.14 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.6 Hz), 7.09-7.00 (m, 3H), 6.88 (d, 1H, J = 8.7 Hz), 5.85 (dd, 1H, J_1 = 17.8 Hz, J_2 = 1.1 Hz), 5.33 (dd, 1H, J_1 = 11.2 Hz, J_2 = 1.2 Hz), 4.63 (sep, 1H, J = 6.0 Hz), 4.00 (s, 6H), 3.20-1.60 (br m, 44H), 1.39 (d, 6H, J = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 154.3, 135.8, 135.5, 135.4, 132.6, 132.3, 131.3, 131.2, 130.6, 128.3, 126.7, 126.4, 125.3, 124.0, 123.9, 123.8, 122.2, 115.84, 115.80, 115.3, 114.5, 113.7, 113.6, 113.5, 96.7, 92.2, 91.2, 91.0, 88.0, 85.4, 78.2, 78.0, 77.8, 71.0, 69.6, 69.4, 60.6, 56.7, 22.4; MALDI-TOF MS (+eV) m/z calcd for $C_{53}H_{70}B_{40}O_3$ 1187.6, found 1187.8.

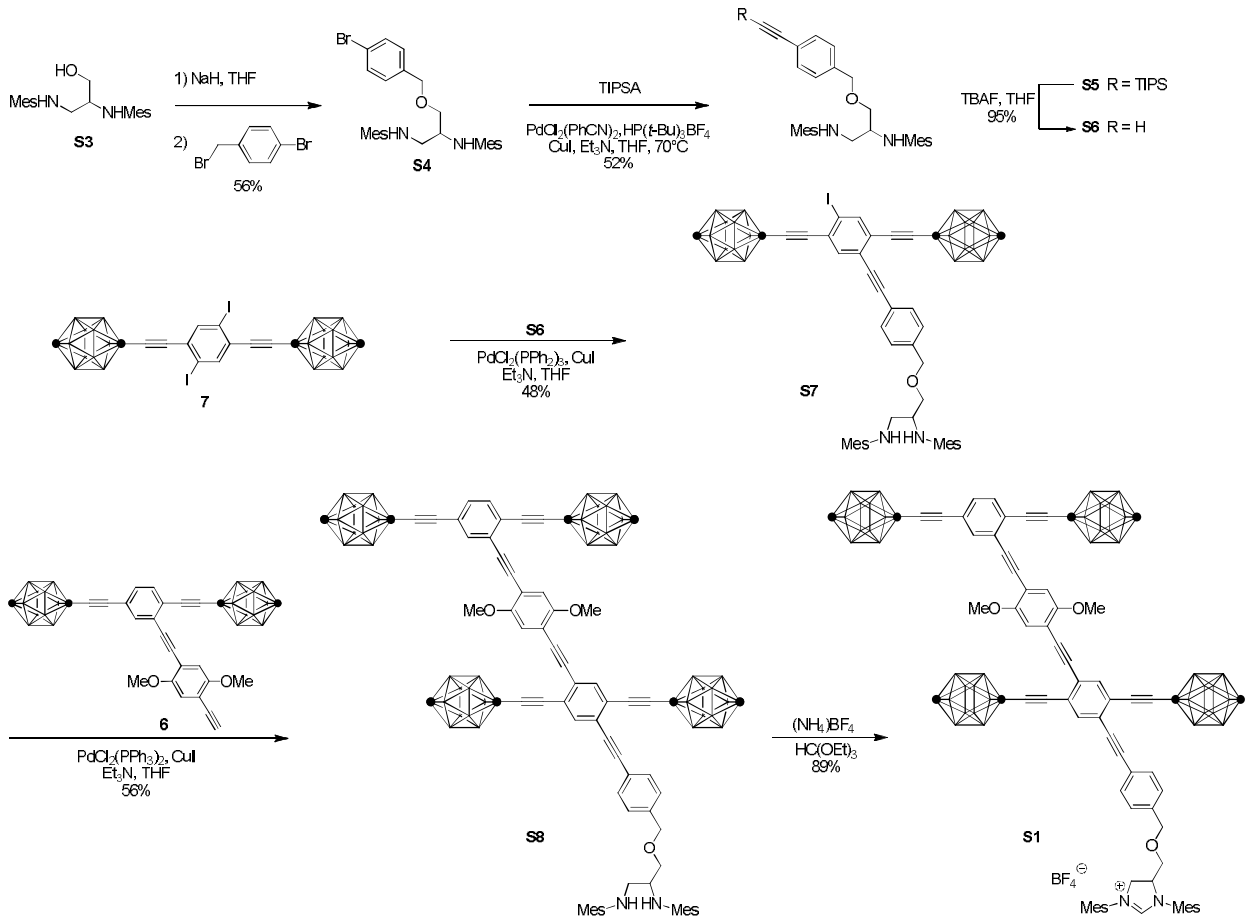
Other approaches investigated toward synthesis of ROMP-propelled nanocars



Scheme S1. Failed attempts to form Ru complexes with **S1** to synthesize nanocar **S2**.

A) Permanent binding

We envisioned that a ligand exchange between ruthenium complex **11** and the corresponding carbene from the dihydroimidazolium tetrafluoroborate **S1** (Scheme S1) would produce nanocar **S2**. The synthesis of **S1** (Scheme S2) began with alkylation of the hydroxybismesityl **S3**[2] with 4-bromobenzyl bromide. Coupling of the bromide in **S4** with triisopropylsilylacetylene (TIPSA) using the Fu-modified Sonogashira method[4] afforded the TIPS-protected alkyne **S5**, which upon alkyne deprotection gave **S6**. To assemble the nanocar moiety, alkyne **S6** was coupled to diiodide axle **7**[1] using conventional Sonogashira conditions. The resultant iodide **S7** was then coupled to half-nanocar **6**.[1] Finally, condensation of the ethane-1,2-diamine **S8** with triethylorthoformate in the presence of $(NH_4)BF_4$ provided the desired dihydroimidazolium tetrafluoroborate nanocar **S1** in 89% yield.[5]



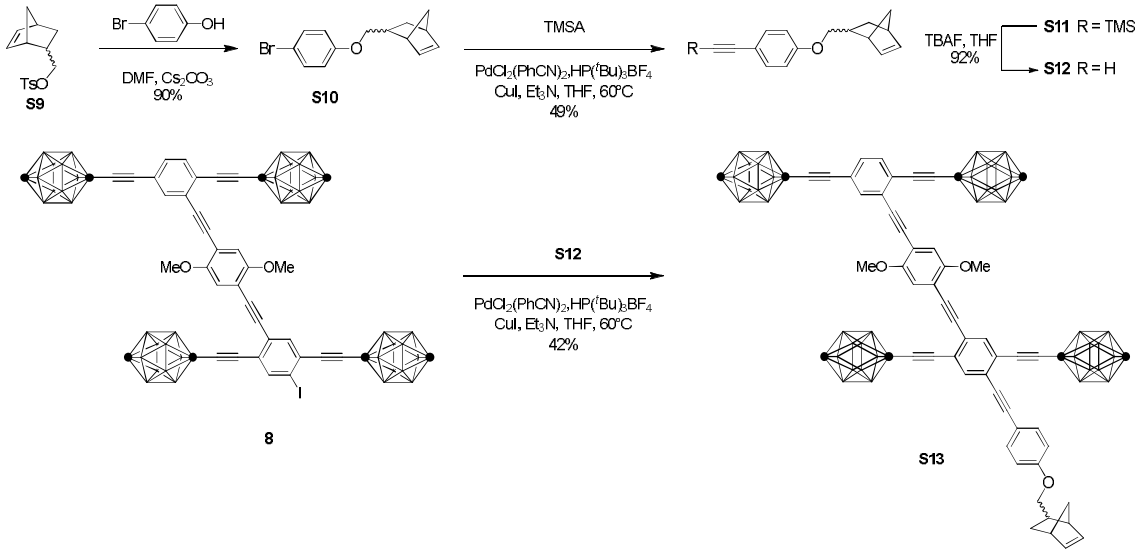
Scheme S2. Synthesis of dihydroimidazolium tetrafluoroborate nanocar **S1**.

As shown in Scheme S1, however, all attempts at preparing nanocar **S2** failed. Deprotonation of **S1** with either KHMDS or *t*-BuOK in THF at room temperature afforded the correspondent carbene, as monitored by ^{1}H NMR. However, no reaction occurred with ruthenium complex **11** in either benzene or THF at ambient temperature or 80 ºC. Only dimerization and/or decomposition of the carbene were observed.

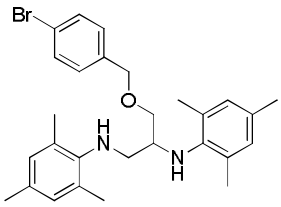
B) Temporary binding

We also prepared a norbornenyl-substituted nanocar for *in situ* ROMP catalyst generation. Activation of the nanocar as a ROMP initiator could be achieved by mixing it in solution with a ruthenium complex such as **11**; the mixture could be then deposited in a surface and exposed to a

strained cyclic olefin.[6] The synthesis started with a nucleophilic substitution on the mixture of *endo*/*exo* norbornenyl tosylate **S9**[3] with 4-bromophenol. The resultant bromide **S10** was then coupled with TMSA to give **S11**, followed by alkyne deprotection, producing the norbornenyl terminal alkyne **S12**. Coupling of **S12** with iodide nanocar **8** afforded nanocar **S13** in a 42% yield (Scheme S3).

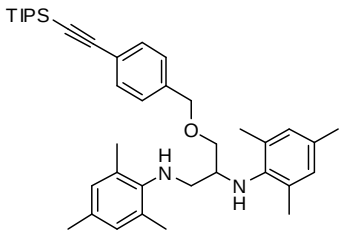


Scheme S3. Synthesis of norbornenyl nanocar **S13**.



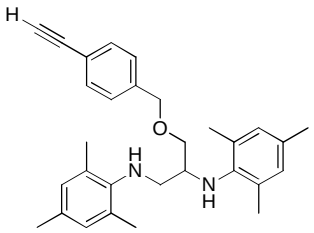
Compound S4. A 100 mL three-neck round-bottom flask equipped with a stir bar was charged with **S3**[2] (1.0 g, 3.07 mmol) and THF (10 mL). The mixture was cooled to 0 ºC, then NaH (122 mg, 3.07 mmol, 60% in mineral oil). After stirring 10 min at 0 ºC, 4-bromobenzyl bromide (766 mg, 3.07 mmol) was added. The mixture was allowed to warm at room temperature and stirred overnight. The reaction was quenched with water (20 mL) and extracted with CH_2Cl_2 (30 mL).

The aqueous layer was washed with CH_2Cl_2 (20 mL). The combined organic layers were dried with $MgSO_4$ and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (silica gel, 20% Et_2O in hexanes) to provide **S4** (850 mg, 1.72 mmol, 56%) as a yellow oil. FTIR (neat) 3366, 2942, 2913, 2856, 2341, 1593, 1484, 1373, 1302, 1231, 1156, 1094, 1070, 1031, 1011, 854, 803 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 (d, 2H, J = 8.4 Hz), 7.15 (d, 2H, J = 8.4 Hz), 6.82 (s, 4H), 4.41 (q, 2H, J = 12.0 Hz) 3.55 (m, 2H), 3.49 (t, 1H, J = 5.2 Hz), 3.30 (dd, 1H, J_1 = 12.0 Hz, J_2 = 5.2 Hz), 3.04 (dd, 1H, J_1 = 12.0 Hz, J_2 = 6.0 Hz), 2.27 (s, 6H), 2.25 (s, 3H), 2.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.8, 141.8, 137.2, 131.5, 131.0, 130.0, 129.4, 121.8, 72.8, 71.2, 51.0, 20.8, 20.7, 19.0, 18.5; EI-HRMS *m*/*z* calcd for $C_{28}H_{35}BrN_2O$: 494.1933, found: 494.1917.

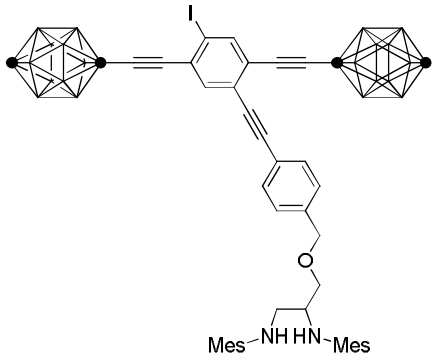


Compound S5. See the general procedure for the Pd/Cu coupling reaction. The materials used were **S4** (800 mg, 1.62 mmol), $Pd(PhCN)_2Cl_2$ (30 mg, 0.08 mmol), CuI (15 mg, 0.08 mmol), (*tert*-Bu)$_3PHBF_4$ (46 mg, 0.15 mmol), THF (10 mL) and Et_3N (10 mL). TIPSA (0.43 mL, 1.94 mmol) was added via syringe and the mixture was stirred at 70 ºC overnight. The residue was purified by flash column chromatography (silica gel, 10% CH_2Cl_2 in hexanes) to provide **S5** (500 mg, 0.84 mmol, 52%) as a pale yellow oil. FTIR (neat) 3368, 2942, 2863, 2721, 2361, 2155, 1483, 1362, 1303, 1231, 1094, 1017, 883, 853 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.55 (d, 2H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.4 Hz), 6.91 (d, 4H, J = 2.0 Hz), 4.53 (q, 2H, J = 12.0 Hz), 3.73 (br m, 2H), 3.64 (d, 2H, J = 7.4 Hz), 3.56 (dd, 1H, J_1 = 9.4 Hz, J_2 = 4.2 Hz), 3.40 (dd, 1H,

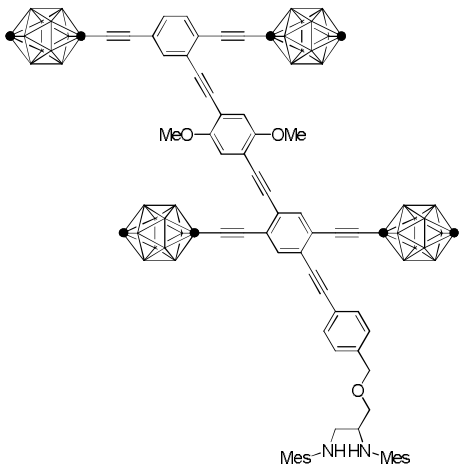
J_1 = 12.0 Hz, J_2 = 5.6 Hz), 3.15 (dd, 1H, J_1 = 12.0 Hz, J_2 = 5.6 Hz), 2.37 (s, 6H), 2.34 (s, 3H), 2.33 (s, 9H), 1.25 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.8, 141.8, 138.4, 132.3, 131.4, 131.0, 130.0, 129.8, 129.6, 129.4, 127.6, 123.1, 107.1, 90.8, 73.2, 71.1, 56.8, 51.0, 20.75, 20.72, 19.0, 18.9, 18.5, 11.5; EI-HRMS *m*/*z* calcd for $C_{39}H_{56}N_2OSi$ 596.4162, found 596.4173.



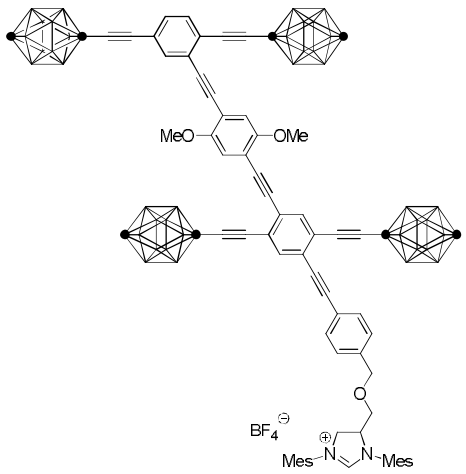
Compound S6. A 25 mL round-bottom flask equipped with a magnetic stir bar was charged with **S5** (100 mg, 0.17 mmol), THF (5 mL), and TBAF (0.2 mL, 0.2 mmol, 1.0 M in THF). The mixture was stirred 2 h at rt. The resulting reaction mixture was passed through a plug of silica gel using 1:1 CH_2Cl_2:hexanes as eluent, and concentrated to afford the title compound **S6** as a colorless oil (71 mg, 0.16 mmol, 95%). FTIR 3366, 3288, 3028, 2997, 2941, 2915, 2855, 1480, 1456, 1448, 1302, 1231, 1094, 1031, 1018, 854 (neat) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 2H, *J* = 8.4 Hz), 6.79 (d, 4H, *J* = 2.8 Hz), 4.43 (q, 2H, *J* = 12.0 Hz), 3.54 (m, 2H), 3.47 (t, 1H, *J* = 5.2 Hz), 3.27 (d, 1H, *J* = 5.2 Hz), 3.05 (s, 1H), 3.03 (d, 1H, *J* = 6.0 Hz), 2.24 (s, 6H), 2.22 (s, 3H), 2.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.7, 141.8, 138.9, 132.3, 131.4, 131.0, 130.0, 129.8, 129.6, 129.4, 127.6, 121.6, 83.6, 77.5, 73.1, 71.2, 56.8, 50.9, 20.71, 20.69, 18.9, 18.5, 17.9, 12.5; EI-HRMS *m*/*z* calcd for $C_{30}H_{36}N_2O$ 440.2828, found 440.2830.



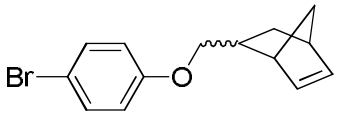
Compound S7. See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **7**[1] (175 mg, 0.26 mmol), **S6** (72 mg, 0.16 mmol), $PdCl_2(PPh_3)_2$ (9 mg, 13 μmol), CuI (5 mg, 26 μmol), THF (15 mL), and Et_3N (5 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, 10% EtOAc in hexanes) to yield **S7** as a yellow solid (76 mg, 48%). FTIR (neat) 3366, 3055, 2917, 2859, 2611, 2361, 2216, 1700, 1602, 1482, 1380, 1303, 1264, 1233, 1095, 1064, 1010, 971, 895, 854, 821, 737, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.37 (s, 1H), 7.31 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 6.4 Hz, 4H), 4.49 (q, J = 12.0 Hz, 2H), 3.75-3.48 (m, 5H), 3.33 (dd, J_1 = 12.0 Hz, J_2 = 5.2 Hz, 1H), 3.20-1.80 (br m, 41H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 142.0, 141.8, 139.2, 135.2, 132.0, 131.4, 131.0, 130.0, 129.8, 129.6, 129.5, 128.6, 127.7, 126.3, 125.0, 121.9, 99.6, 95.5, 92.0, 91.1, 86.1, 80.7, 76.4, 73.2, 71.4, 60.8, 56.9, 51.0, 34.9, 25.5, 20.9, 20.7, 19.0, 18.5, 17.9; EI-HRMS m/z calcd for $C_{44}H_{60}B_{20}IN_2O$ [M + H] 976.5753, found 976.5771.



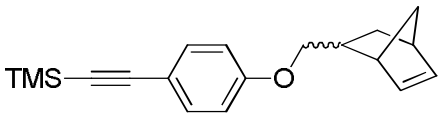
Compound S8. See the general procedure for the Pd/Cu Sonogashira coupling reaction. The materials used were **S7** (100 mg, 0.10 mmol), **6**[1] (79 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (8 mg, 0.01 mmol), CuI (4 mg, 0.02 mmol), THF (9 mL), and Et_3N (3 mL) at rt overnight. The crude product was purified by column chromatography (silica gel, 10% EtOAc in hexanes) to yield **S8** as a yellow solid (82 mg, 56%). FTIR 3062, 2956, 2922, 2851, 2610, 2208, 1723, 1705, 1594, 1540, 1501, 1463, 1411, 1394, 1282, 1264, 1221, 1183, 1147, 1141, 1064, 1041, 1008, 974, 892, 860, 830 (neat) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (m, 3H), 7.48 (d, 1H, J = 1.4 Hz), 7.46 (s, 1H), 7.31 (d, 2H, J = 8.3 Hz), 7.24 (d, 1H, J = 8.2 Hz), 7.14 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.6 Hz), 7.07 (d, 2H, J = 2.4 Hz), 6.82 (d, 4H, J = 6.1 Hz), 4.50 (q, 2H, J = 12.1 Hz), 4.006 (s, 3H), 4.004 (s, 3H), 3.55 (m, 5H), 3.20-1.80 (br m, 64H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.29, 154.27, 141.9, 139.2, 135.8, 135.6, 135.5, 132.4, 132.36, 132.29, 132.1, 131.7, 131.2, 131.1, 130.1, 129.8, 129.7, 129.5, 129.0, 128.8, 128.7, 127.8, 126.7, 125.9, 125.8, 124.1, 124.05, 123.96, 122.2, 122.0, 115.83, 115.79, 113.7, 113.3, 96.0, 92.5, 92.3, 92.1, 91.4, 91.3, 91.2, 90.9, 88.1, 86.7, 78.1, 78.0, 77.5, 77.4, 77.3, 73.3, 72.9, 71.4, 71.2, 60.7, 60.5, 56.9, 56.7, 51.0, 29.9, 20.78, 20.77, 19.04, 18.6; ESI-LRMS m/z calcd for $C_{70}H_{93}B_{40}N_2O_3$ [M + H] 1442.9, found: 1443.1.



Compound S1. A 5 mL round-bottom flask equipped with a stir bar was charged with **S8** (82 mg, 0.057 mmol), NH_4BF_4 (6 mg, 0.057 mmol) and $HC(OEt)_3$ (1 mL). The mixture was stirred at 120 ºC overnight. The solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 10% MeOH in CH_2Cl_2) to yield **S1** as a yellow solid (78 mg, 89%). FTIR (neat) 3063, 2926, 2856, 2613, 2212, 1980, 1722, 1630, 1503, 1484, 1463, 1411, 1385, 1266, 1220, 1063, 898, 857, 733, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.53 (d, 2H, J = 8.0 Hz), 7.51 (s, 1H), 7.47 (s, 2H), 7.32 (d, 2H, J = 8.5 Hz), 7.23 (d, 1H, J = 8.0 Hz), 7.14 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.5 Hz), 7.06 (d, 2H, J = 4.5 Hz), 6.99 (d, 2H, J = 3.5 Hz), 6.92 (s, 2H), 5.25 (t, 1H, J = 10.5 Hz), 4.74 (t, 1H, J = 10.0 Hz), 4.55 (dd, 2H, J_1 = 11.2 Hz, J_2 = 8.8 Hz), 4.43 (dd, 1H, J_1 = 12.0 Hz, J_2 = 8.0 Hz), 3.999 (s, 3H), 3.995 (s, 3H), 3.81 (dd, 1H, J_1 = 9.5 Hz, J_2 = 2.1 Hz), 3.61 (d, 1H, J = 12.0 Hz), 3.20-1.50 (br m, 62H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 154.25, 154.21, 141.0, 140.8, 137.5, 135.8, 135.7, 135.6, 135.5, 135.4, 132.3, 132.1, 131.2, 130.9, 130.3, 130.2, 128.9, 128.5, 126.6, 125.9, 125.6, 124.1, 124.0, 122.7, 122.1, 115.8, 115.7, 113.7, 113.2, 95.6, 92.6, 92.3, 92.0, 91.4, 91.2, 90.8, 88.0, 87.1, 78.1, 77.9, 77.8, 77.5, 77.2, 77.0, 73.8, 69.6, 69.3, 67.2, 64.2, 60.5, 56.6, 53.6, 52.9, 29.9, 21.2, 18.4, 17.7, 17.5; MALDI-TOF (+eV) m/z calcd for $C_{71}H_{91}B_{40}N_2O_3^+$ (cation only) 1452.9, found 1453.0.

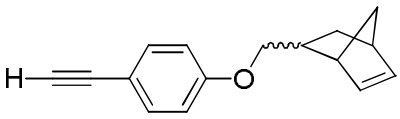


Compound S10. A Schlenk tube equipped with a stir bar was charged with **S9**[3] (1.3 g, 4.67 mmol), 4-bromophenol (800 mg, 4.62 mmol), cesium carbonate (2.25 g, 6.93 mmol), and DMF (7 mL). The mixture was heated at 80 °C overnight. The reaction was quenched by adding water (50 mL) and then it was extracted with diethyl ether (50 mL). The organic layer was washed with water (50 mL ×5). After drying the organic layer with $MgSO_4$ the solvent was removed *in vacuo* to give **S10** as a mixture of two isomers (1.16 g, 90%) as a yellow oil. FTIR (neat) 3137, 3058, 2966, 2867, 2361, 2051, 1867, 1590, 1577, 1488, 1467, 1390, 1346, 1285, 1240, 1169, 1101, 1072, 1021, 1002 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ Major isomer 7.36 (d, 2H, J = 8.5 Hz), 6.77 (d, 2H, J = 8.5 Hz), 6.21 (m, 1H), 5.96 (m, 1H), 3.68 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.5 Hz), 3.52 (t, 1H, J = 9.0 Hz), 3.05 (m, 1H), 2.87 (m, 1H), 2.56 (m, 1H), 1.95 – 1.90 (m, 1H), 1.51 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.0 Hz), 1.40 – 1.21 (m, 1H), 0.65 – 0.62 (m, 1H); Minor isomer δ 7.37 (d, 2H, J = 8.5 Hz), 6.80 (d, 2H, J = 8.5 Hz), 6.17 (m, 1H), 6.13 (m, 1H), 3.99 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.5 Hz), 3.80 (t, 1H, J = 9.0 Hz), 2.87 (m, 2H), 1.93 (m, 1H), 1.40 – 1.21 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) mixture of isomers δ 158.40, 137.75, 137.01, 136.54, 132.41, 132.32, 132.27, 116.49, 112.77, 112.66, 72.65, 71.85, 49.59, 45.22, 44.03, 43.84, 42.40, 41.76, 38.66, 38.45, 29.79, 29.18; EI-HRMS m/z calcd for $C_{14}H_{15}BrO$ 278.0306, found 278.0302.



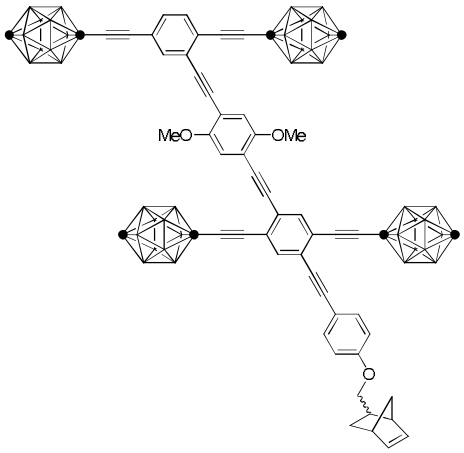
Compound S11. See the general procedure for the Pd/Cu coupling reaction. The materials used were **S10** (700 mg, 2.51 mmol), $Pd(PhCN)_2Cl_2$ (48 mg, 0.12 mmol), CuI (46 mg, 0.24 mmol), (*tert*-Bu)$_3$PHBF$_4$ (109 mg, 0.38 mmol), THF (12 mL), and Et_3N (4 mL). TMSA (0.42 mL, 3.01

mmol) was added via syringe and the mixture was stirred at 60 ºC overnight. The residue was purified by flash column chromatography (silica gel, 10% CH_2Cl_2 in hexanes) to provide **S11** as a mixture of two isomers (364 mg, 1.23 mmol, 49%) as a yellow oil. FTIR (neat) 3059, 2960, 2868, 2155, 1605, 1569, 1506, 1467, 1390, 1287, 1246, 1169, 1108, 1021, 864, 832, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ major isomer 7.38 (d, 2H, J = 8.9 Hz), 6.78 (d, 2H, J = 8.9 Hz), 6.17 (m, 1H), 5.94 (m, 1H), 3.69 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.5 Hz), 3.53 (t, 1H, J = 9.0 Hz), 3.02 (m, 1H), 2.86 (m, 1H), 2.56 (m, 1H), 1.93 – 1.88 (m, 1H), 1.48 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.0 Hz), 1.40 – 1.21 (m, 1H), 0.64 – 0.60 (m, 1H), 0.24 (s, 9H); minor isomer δ 7.40 (d, 2H, J = 8.9 Hz), 6.82 (d, 2H, J = 8.9 Hz), 6.15 (m, 1H), 6.11 (m, 1H), 4.02 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.5 Hz), 3.83 (t, 1H, J = 9.0 Hz), 2.86 (m, 2H), 1.91 (m, 1H), 1.40 – 1.21 (m, 4H), 0.24 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) mixture of isomers δ 159.57, 159.55, 137.82, 137.08, 136.63, 133.66, 133.61, 132.52, 116.56, 115.27, 115.16, 114.59, 105.54, 105.51, 92.53, 92.46, 72.49, 71.72, 49.66, 45.27, 44.09, 43.90, 42.45, 41.81, 38.73, 38.53, 29.85, 29.26, 0.30; EI-HRMS *m*/*z* calcd for $C_{19}H_{24}OSi$ 296.1596, found 295.1595.



Compound S12. A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with **S11** (360 mg, 1.21 mmol), THF (10 mL), and TBAF (1.3 mL, 1.3 mmol, 1.0 M in THF). The mixture was stirred 2 h at rt. The resulting reaction mixture was passed through a plug of silica gel using 1:1 CH_2Cl_2:hexanes as eluent, and concentrated to afford the title compound **S12** as a yellow oil (250 mg, 1.11 mmol, 92%). FTIR 3313, 3290, 3057, 2965, 2941, 2868, 2106, 1605, 1569, 1500, 1490, 1466, 1389, 1288, 1244, 1190, 1108, 1020, 831 (neat) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) major isomer δ 7.40 (d, 2H, J = 8.9 Hz), 6.81 (d, 2H, J = 8.9 Hz), 6.16

(m, 1H), 5.95 (m, 1H), 3.70 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.5 Hz), 3.54 (t, 1H, J = 9.0 Hz), 3.03 (m, 1H), 2.99 (s, 1H), 2.85 (m, 1H), 2.54 (m, 1H), 1.95 – 1.88 (m, 1H), 1.48 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.0 Hz), 1.380 – 1.26 (m, 1H), 0.64 – 0.60 (m, 1H); minor isomer δ 7.42 (d, 2H, J = 8.9 Hz), 6.85 (d, 2H, J = 8.9 Hz), 6.15 (m, 1H), 6.10 (m, 1H), 4.02 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.5 Hz), 3.84 (t, 1H, J = 9.0 Hz), 3.00 (s, 1H), 2.85 (m, 2H), 1.91 (m, 1H), 1.40 – 1.21 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) mixture of isomers δ 159.77, 137.84, 137.09, 136.62, 133.78, 133.73, 132.50, 114.70, 114.03, 83.99, 75.91, 75.85, 72.52, 71.73, 49.65, 45.26, 44.08, 43.89, 42.45, 41.81, 38.71, 38.50, 29.85, 29.24; EI-HRMS *m*/*z* calcd for $C_{16}H_{16}O$ 224.1201, found 224.1200.



Compound S13. See the general procedure for the Pd/Cu coupling reaction. The materials used were **8** (26 mg, 0.023 mmol), **S12** (6.2 mg, 0.028 mmol), $Pd(PhCN)_2Cl_2$ (2 mg, 5 μmol), CuI (1 mg, 5 μmol), (*tert*-Bu)$_3$PHBF$_4$ (4.3 mg, 15 μmol), THF (6 mL) and Et_3N (2 mL). The mixture was stirred at 60 ºC overnight. The residue was purified by flash column chromatography (silica gel, 10% CH_2Cl_2 in hexanes) to provide **S13** (12 mg, 9.7 μmol, 42%) as a yellow solid. FTIR (neat) 3062, 2928, 2855, 2611, 2361, 2208, 1605, 1511, 1464, 1411, 1387, 1283, 1263, 1246, 1220, 1171, 1147, 1064, 1041, 975, 898, 830, 735, 706 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.48 (d, 1H, J = 1.5 Hz), 7.46 (s, 1H), 7.43 (d, 2H, J = 8.9 Hz), 7.23 (d, J = 8.2 Hz, 1H), 7.14, (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H), 7.07 (s, 1H), 7.06 (s, 1H), 6.90 (d, 2H, J = 8.9 Hz), 6.20 (m,

1H), 5.80 (m, 1H), 4.00 (s, 6H), 3.76 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.5 Hz), 3.60 (t, 1H, J = 9.0 Hz), 3.2-1.6 (br m, 49 H); 1.48 (dd, 1H, J_1 = 8.1 Hz, J_2 = 2.0 Hz), 1.38 – 1.26 (m, 1H), 0.64 – 0.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 160.07, 154.25, 154.19, 137.88, 137.13, 136.66, 135.84, 135.54, 135.44, 135.38, 133.76, 133.59, 133.55, 132.60, 132.56, 132.34, 131.19, 128.86, 126.73, 126.67, 126.38, 125.21, 124.29, 124.04, 123.90, 123.79, 122.39, 122.16, 115.85, 115.80, 115.77, 115.66, 114.87, 114.84, 114.64, 114.49, 113.59, 113.43, 113.27, 96.75, 93.15, 92.23, 92.17, 91.19, 90.94, 90.81, 89.99, 88.88, 88.03, 85.50, 84.97, 78.14, 77.99, 77.81, 72.60, 71.82, 69.56, 60.54, 56.65, 56.59, 49.69, 45.30, 44.16, 44.13, 43.94, 42.49, 41.85, 38.81, 38.76, 38.60, 38.56, 34.89, 32.15, 30.39, 29.93, 29.89, 29.59, 29.29, 26.93, 25.50, 22.92; MALDI-TOF MS (+eV) *m*/*z* calcd for $C_{56}H_{72}B_{40}O_3$ 1225.6, found 1225.9.

ROMP of 1,5 cyclooctadiene

Catalytic activity of 1. 102 μL of a 4.0 mM solution, 0.70 mL of CD_2Cl_2.

Table S1. Conversion to polymer product using **1**.

Time (min)	Conversion (%)
3.8	1.9
4.8	2.5
5.8	2.5
6.8	2.8
7.8	3.1
8.8	3.0
9.8	3.3
10.8	3.3
11.8	3.6
12.8	3.7
13.8	3.6
14.8	3.9
15.8	3.7
16.8	3.9
17.8	4.0
18.8	3.9

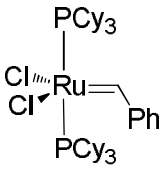
Time (min)	Conversion (%)
19.8	4.1
20.8	3.9
21.8	4.3
22.8	4.2
23.8	4.0
24.8	4.3
25.8	4.3
26.8	4.1
27.8	4.4
28.8	4.3
29.8	4.4
30.8	4.5
31.8	4.3
32.8	4.4
33.8	4.5
34.8	4.6
35.8	4.6
36.8	4.5
37.8	4.6
38.8	4.6
39.8	4.8
40.8	4.6
41.8	4.6
42.8	4.6
43.8	4.7
44.8	4.7
45.8	4.9
46.8	4.8
47.8	5.0
48.8	5.0
49.8	4.9
50.8	5.0
51.8	5.0
52.8	5.0
53.8	5.1
54.8	5.2
55.8	5.0
56.8	5.3
57.8	5.1
58.8	5.1
59.8	5.3
60.8	5.2

Catalytic activity of 2. 120 μL of a 3.3 mM solution, 0.68 mL of CD_2Cl_2.

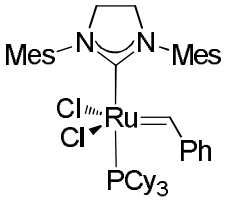
Table S2. Conversion to polymer product using **2**.

Time (min)	Conversion (%)
3.0	99.4
4.0	99.8
5.0	99.9
6.0	99.9
7.0	100.0
8.0	100.0
9.0	100.0
10.0	100.0
11.0	99.9
12.0	100.0
13.0	100.0
14.0	100.0
15.0	100.0
16.0	100.0
17.0	100.0
18.0	100.0

In order to determine if our experimental setup was in good agreement with the standard system developed by Grubbs[4] and therefore producing comparable results, we measured the activity of catalysts **11** and 1**2**.



11



12

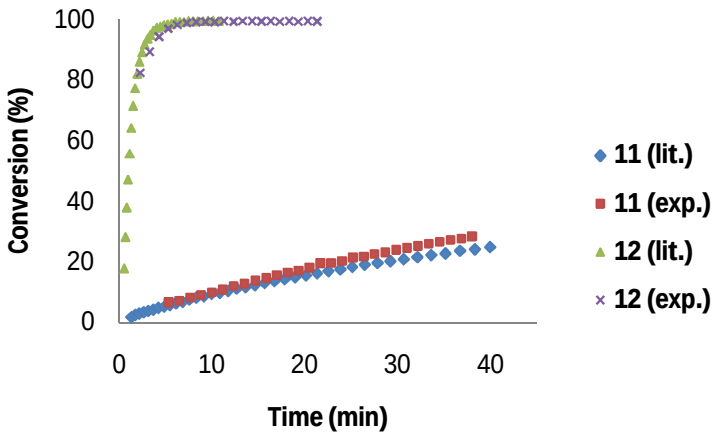
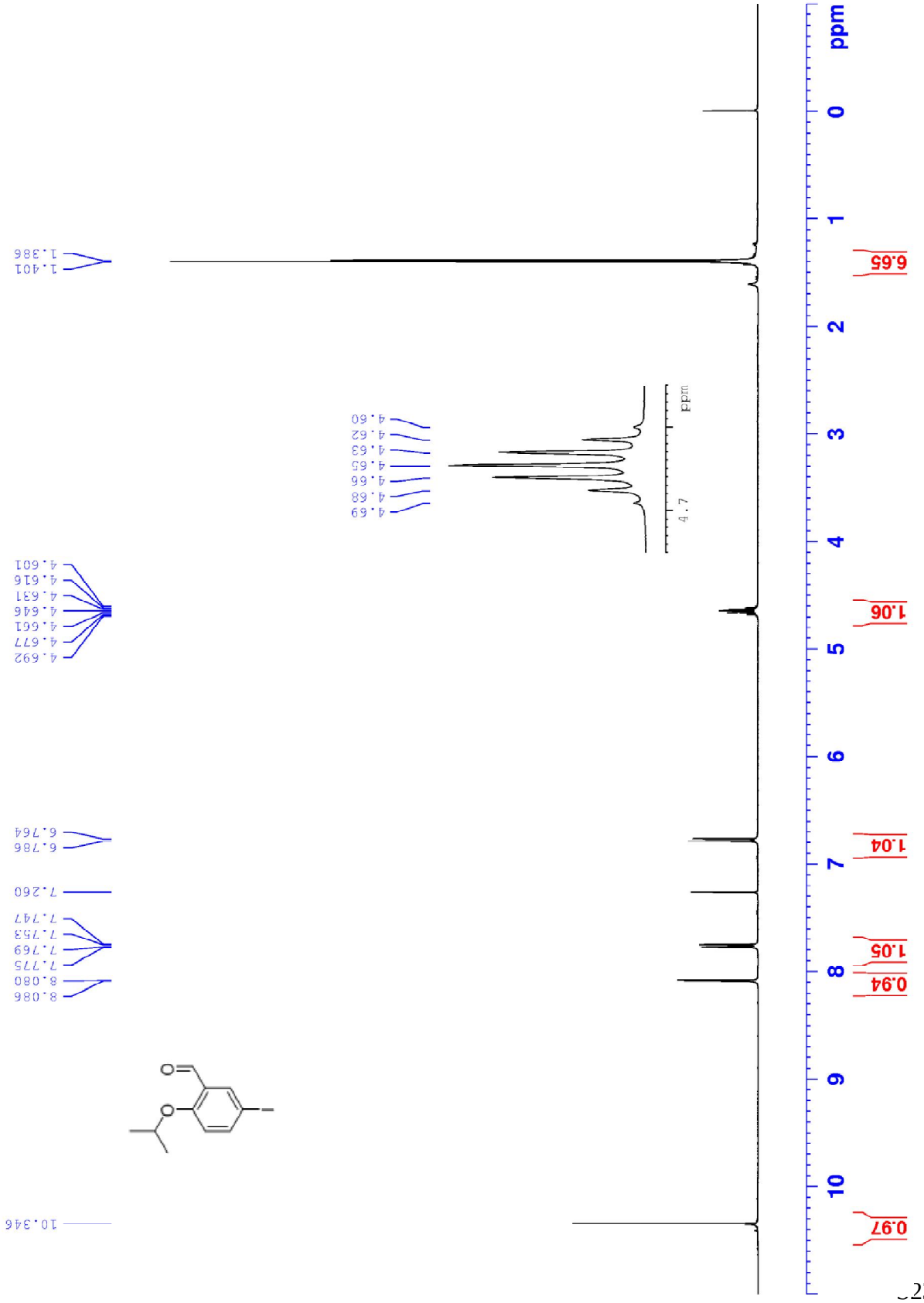


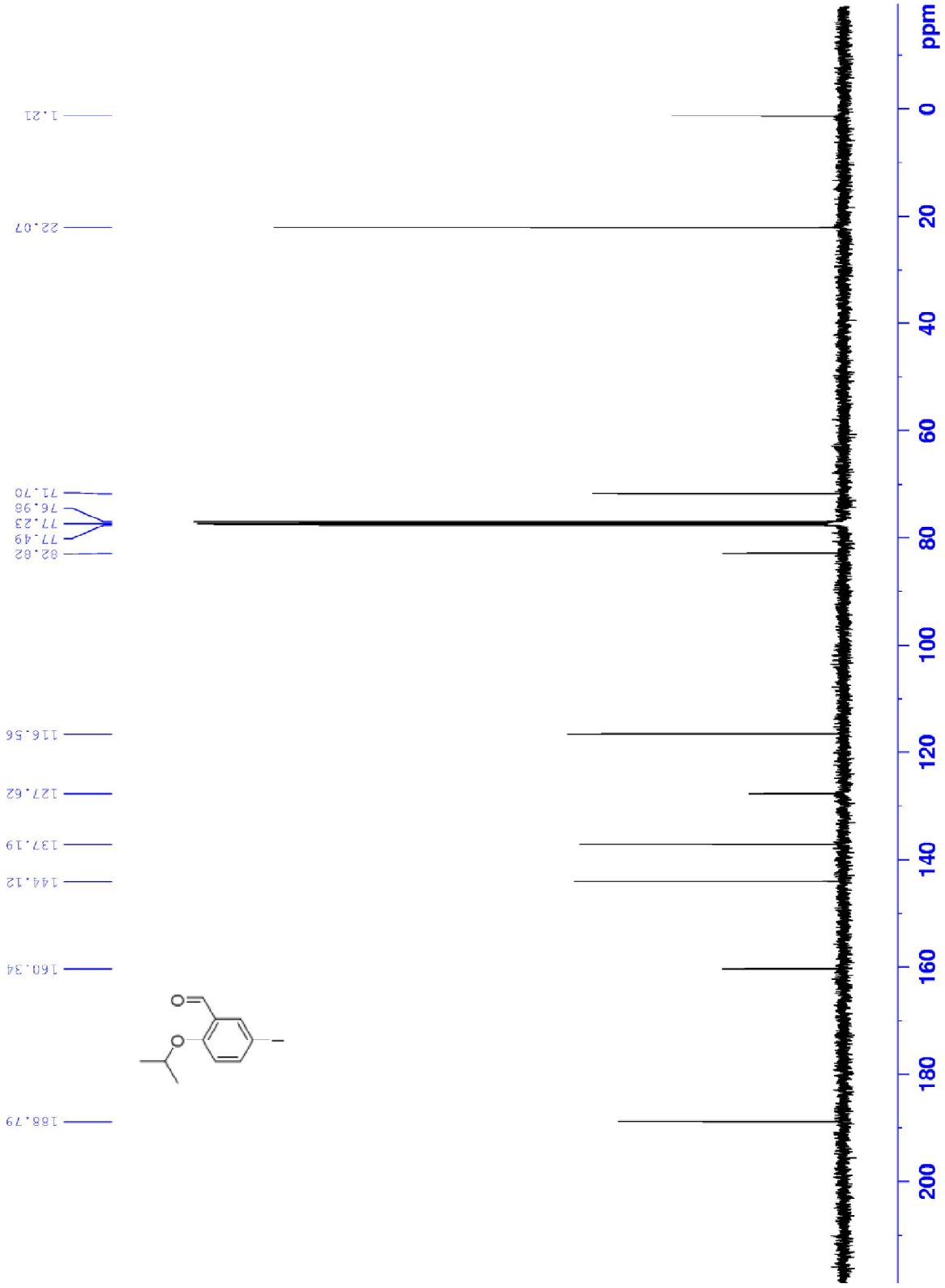
Figure S1. Observed polymerization (exp.) versus previously reported data (lit).

ROMP of norbornene with 1. A 3-neck 25 mL round-bottom flask equipped with a magnetic stir bar was charged with a solution of norbornene (35.3 mg, 0.37 mmol) in CH_2Cl_2 (6 mL). Complex **1** (100 μL of a 3.75 mM solution, 0.37 μmol) was added in one portion and the mixture was stirred 10 min at rt. The solvent was evaporated. The polymer was washed with MeOH to afford ring-opened polynorbornene (32.0 mg, 91%).

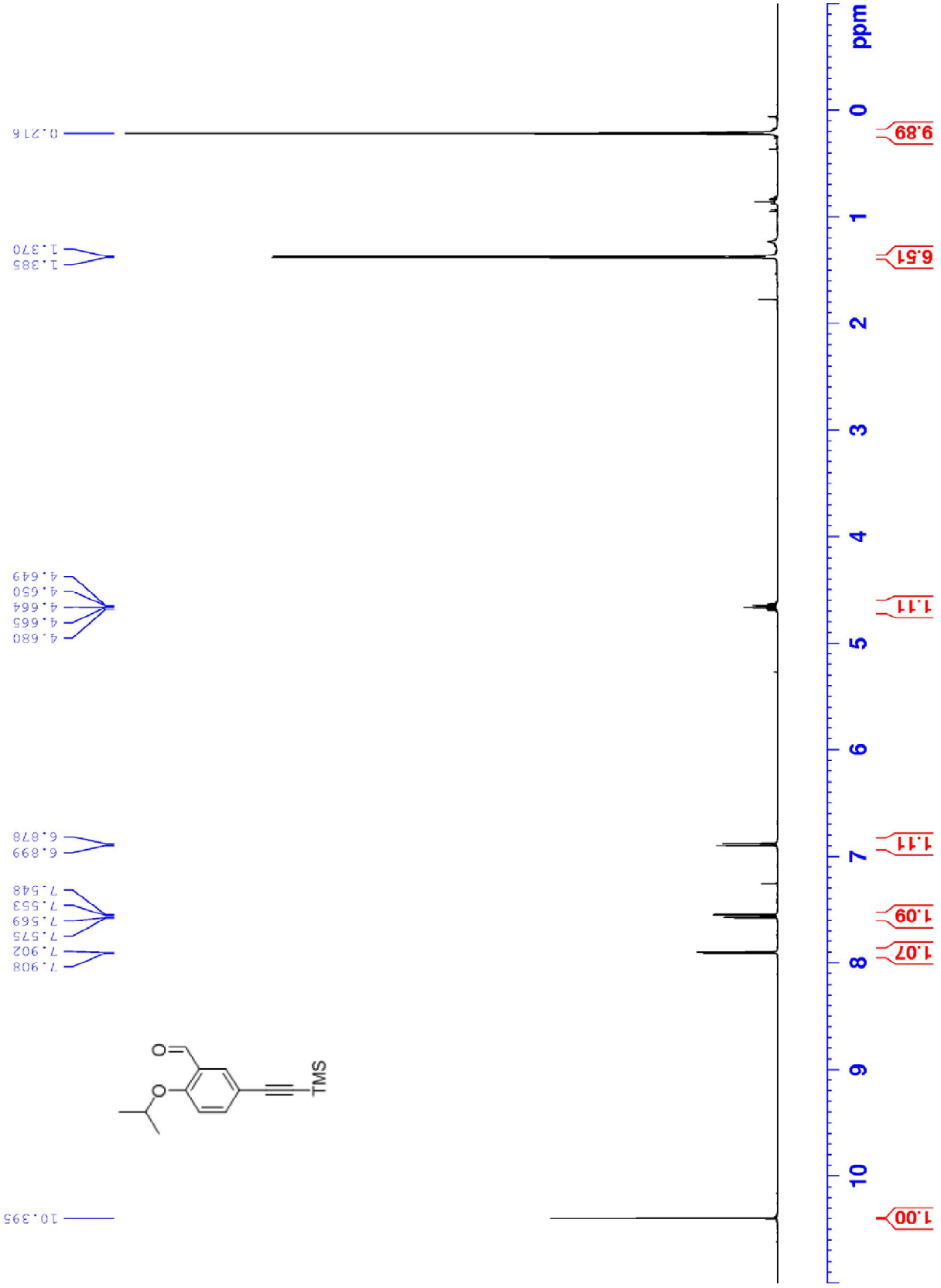
^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$)



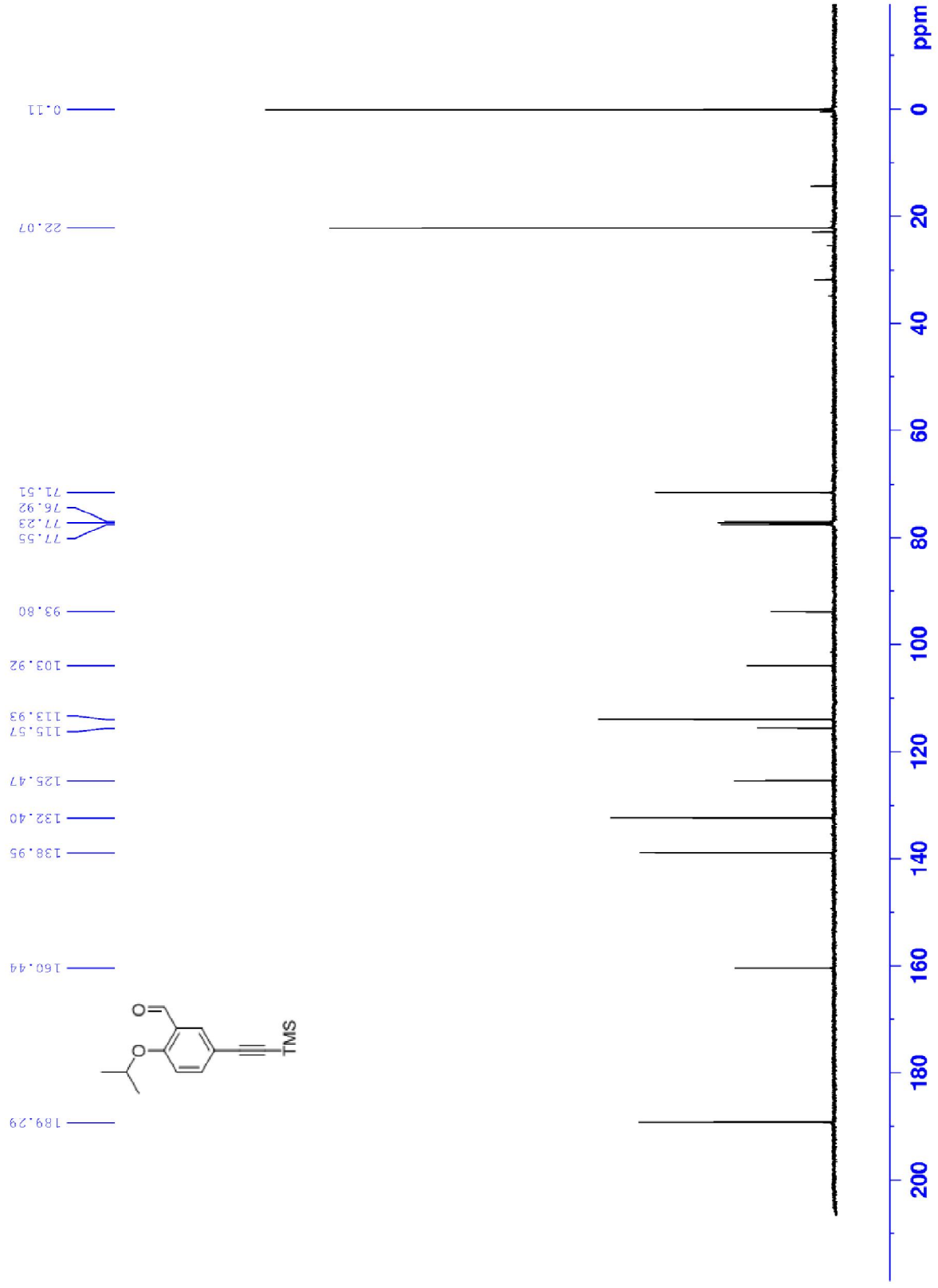
^{13}C NMR spectrum of **3** (125 MHz, $CDCl_3$)



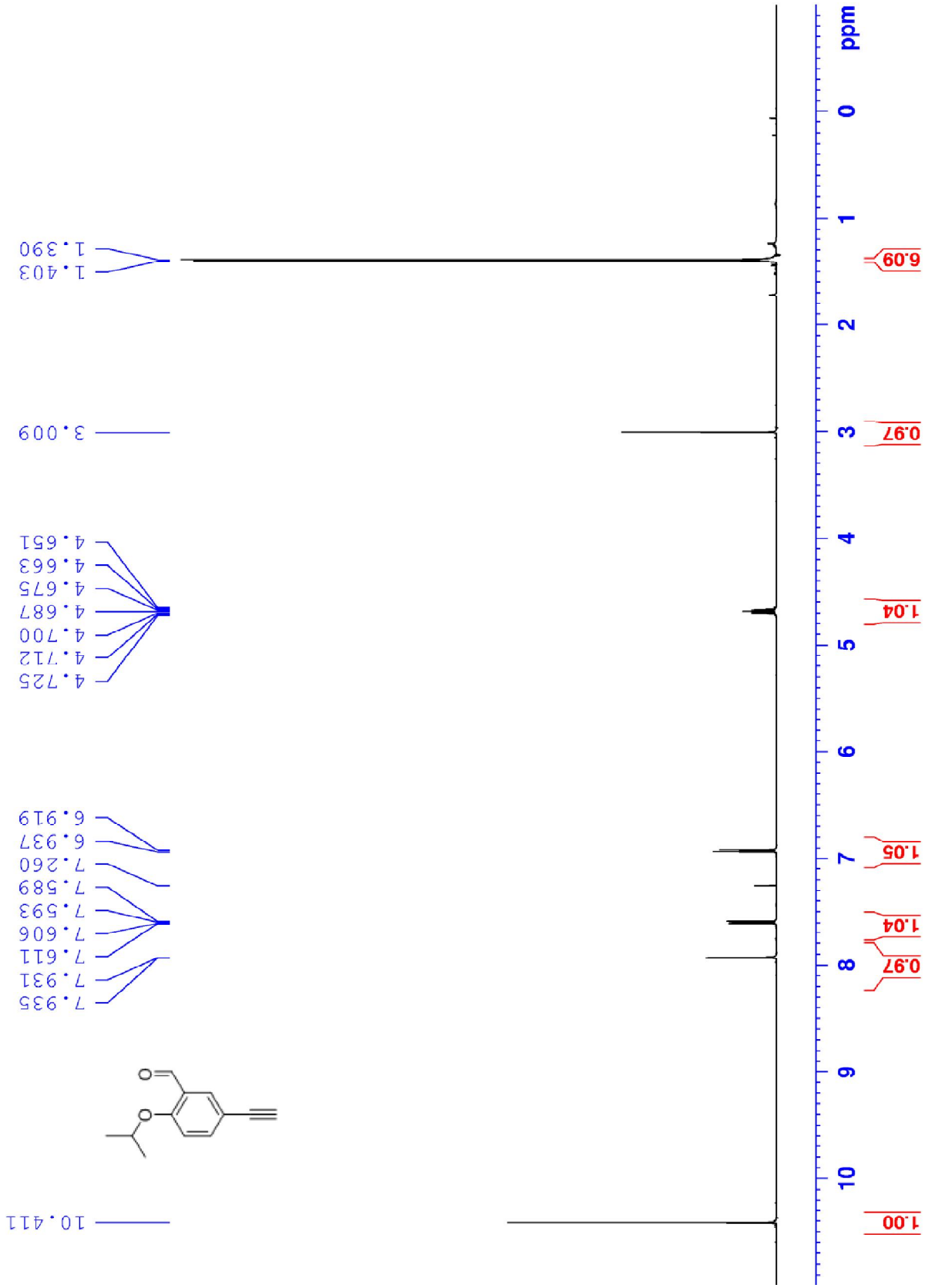
^{1}H NMR spectrum of **4** (500 MHz, $CDCl_3$)



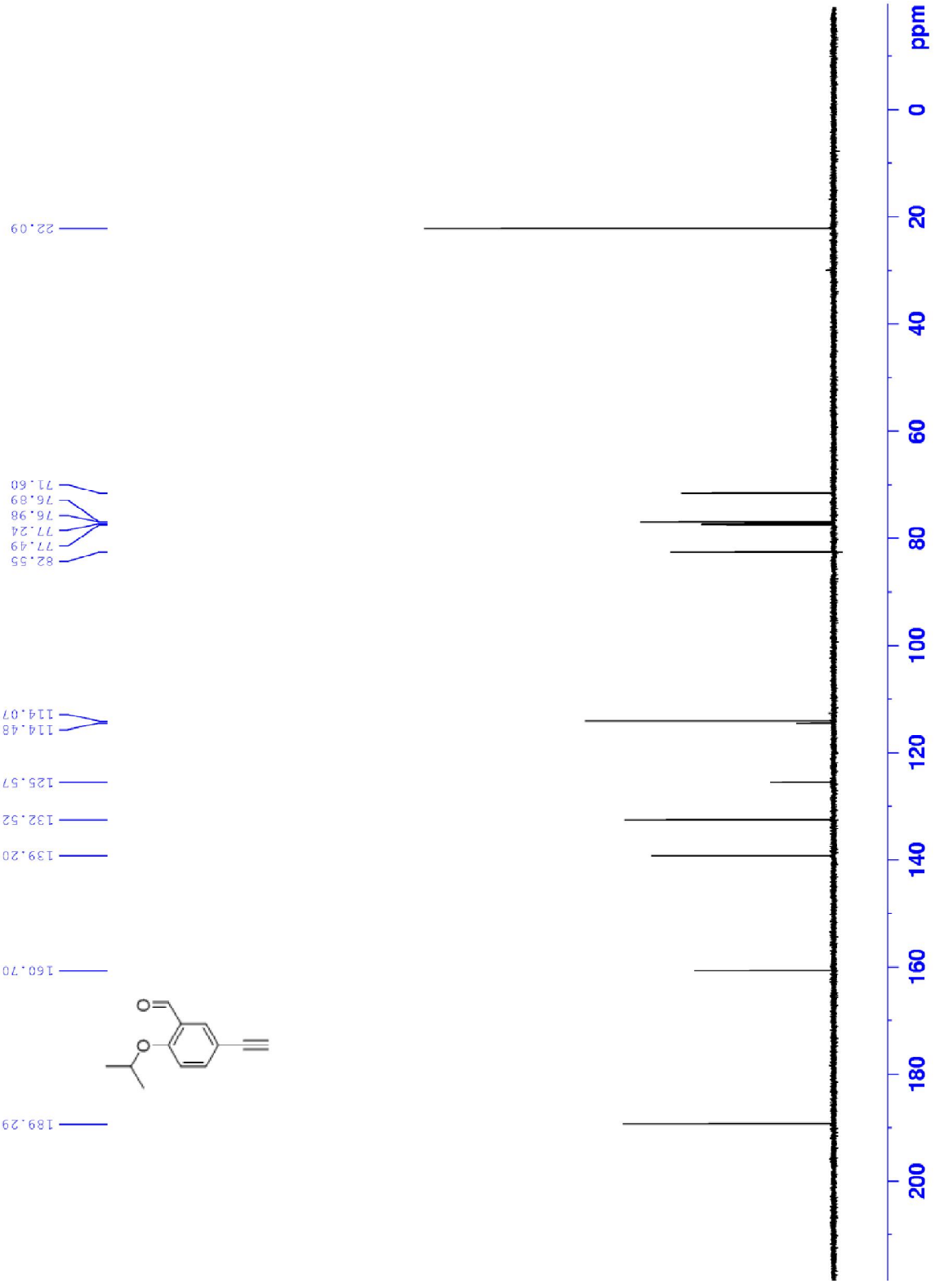
^{13}C NMR spectrum of **4** (125 MHz, $CDCl_3$)



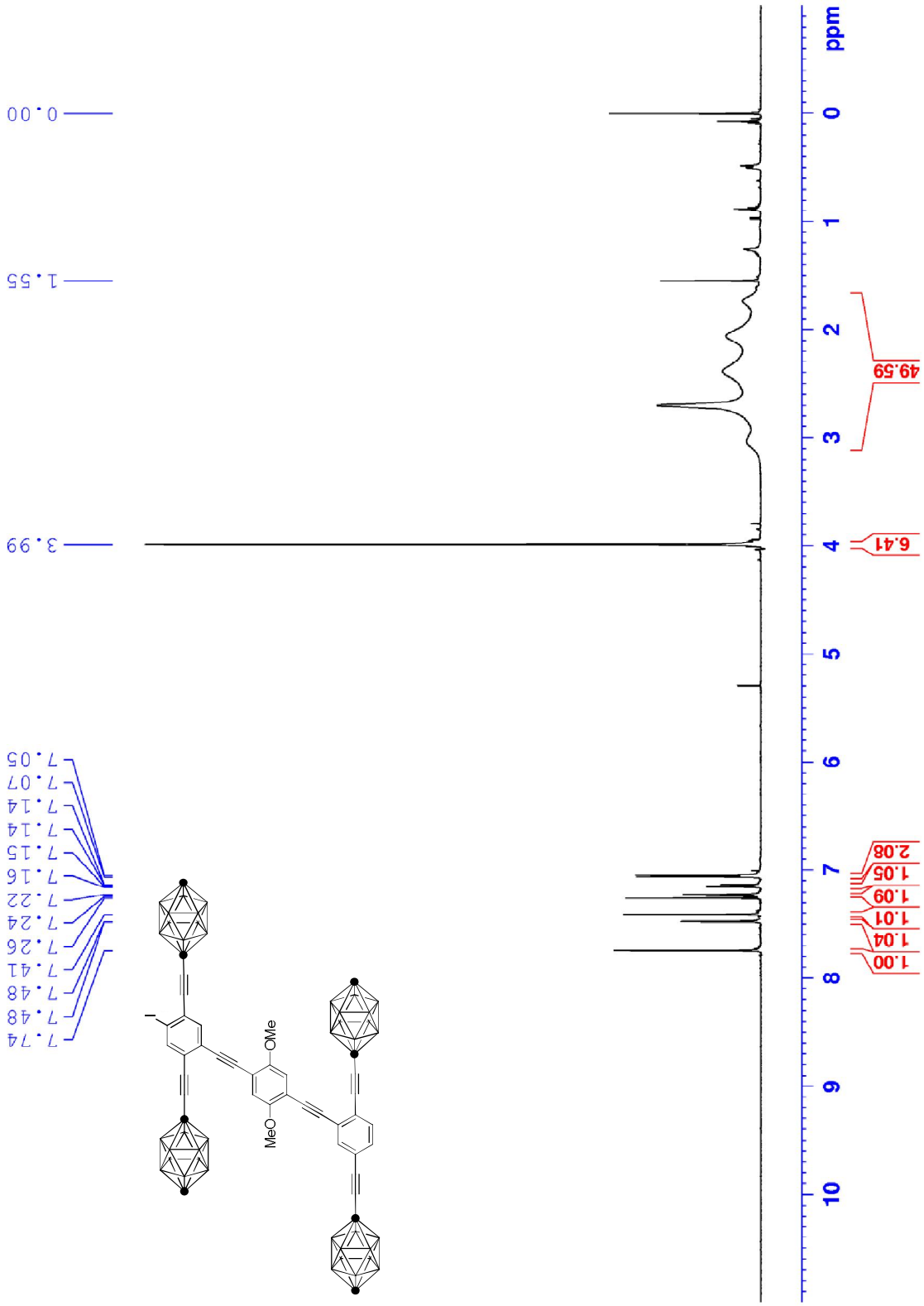
^{1}H NMR spectrum of **5** (500 MHz, $CDCl_3$)



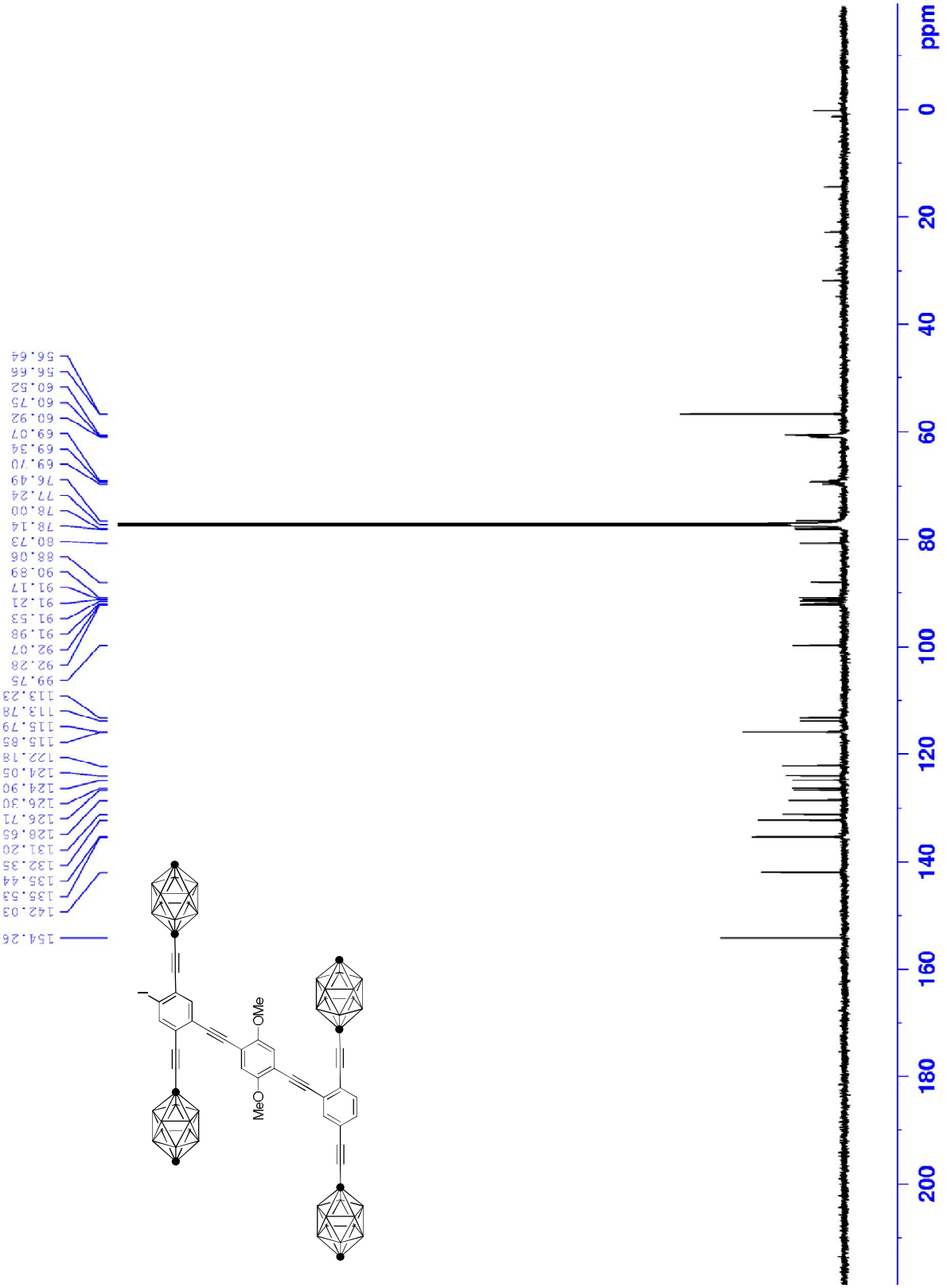
^{13}C NMR spectrum of **5** ($CDCl_3$)



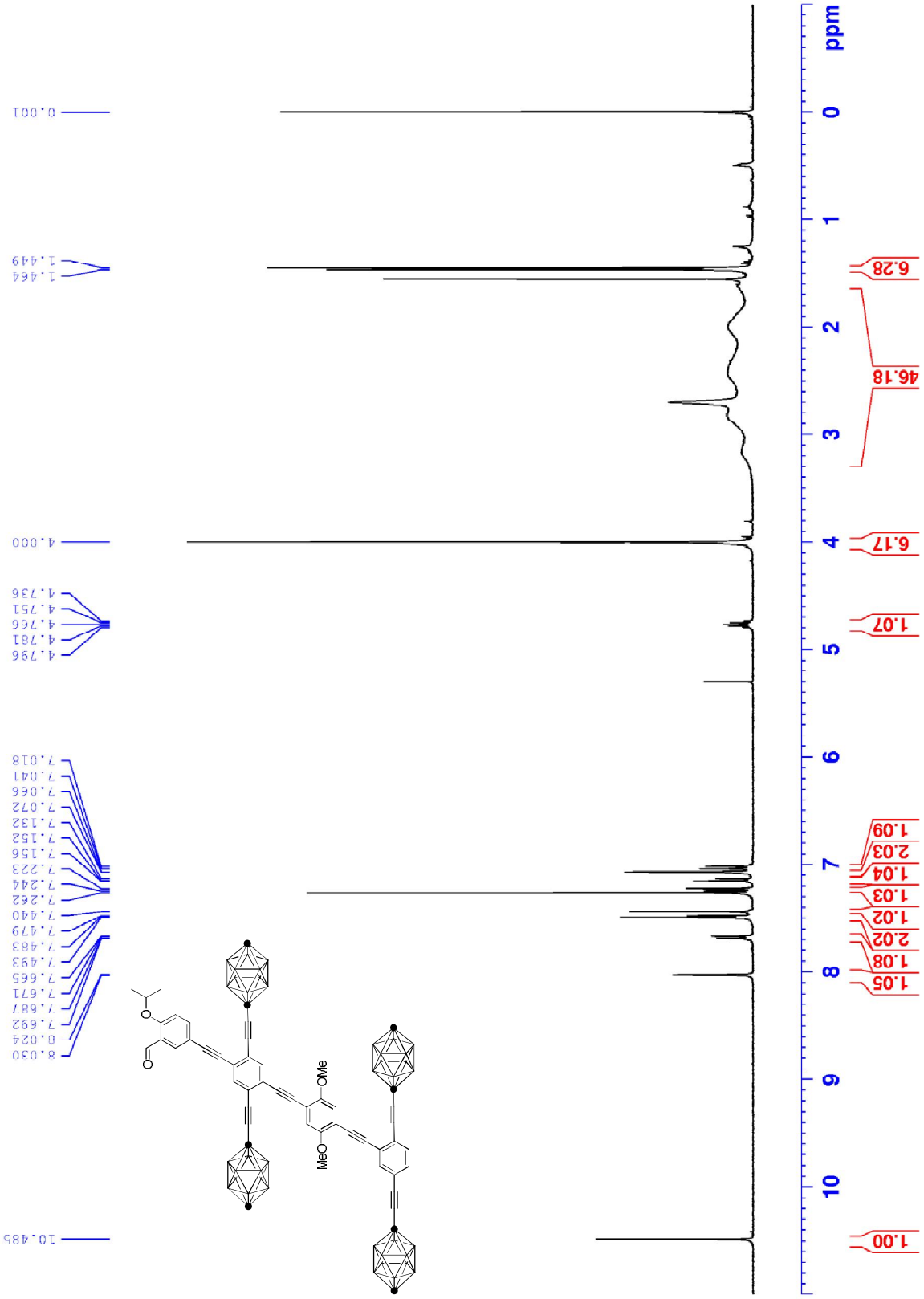
^{1}H NMR spectrum of **8** (500 MHz, $CDCl_3$)



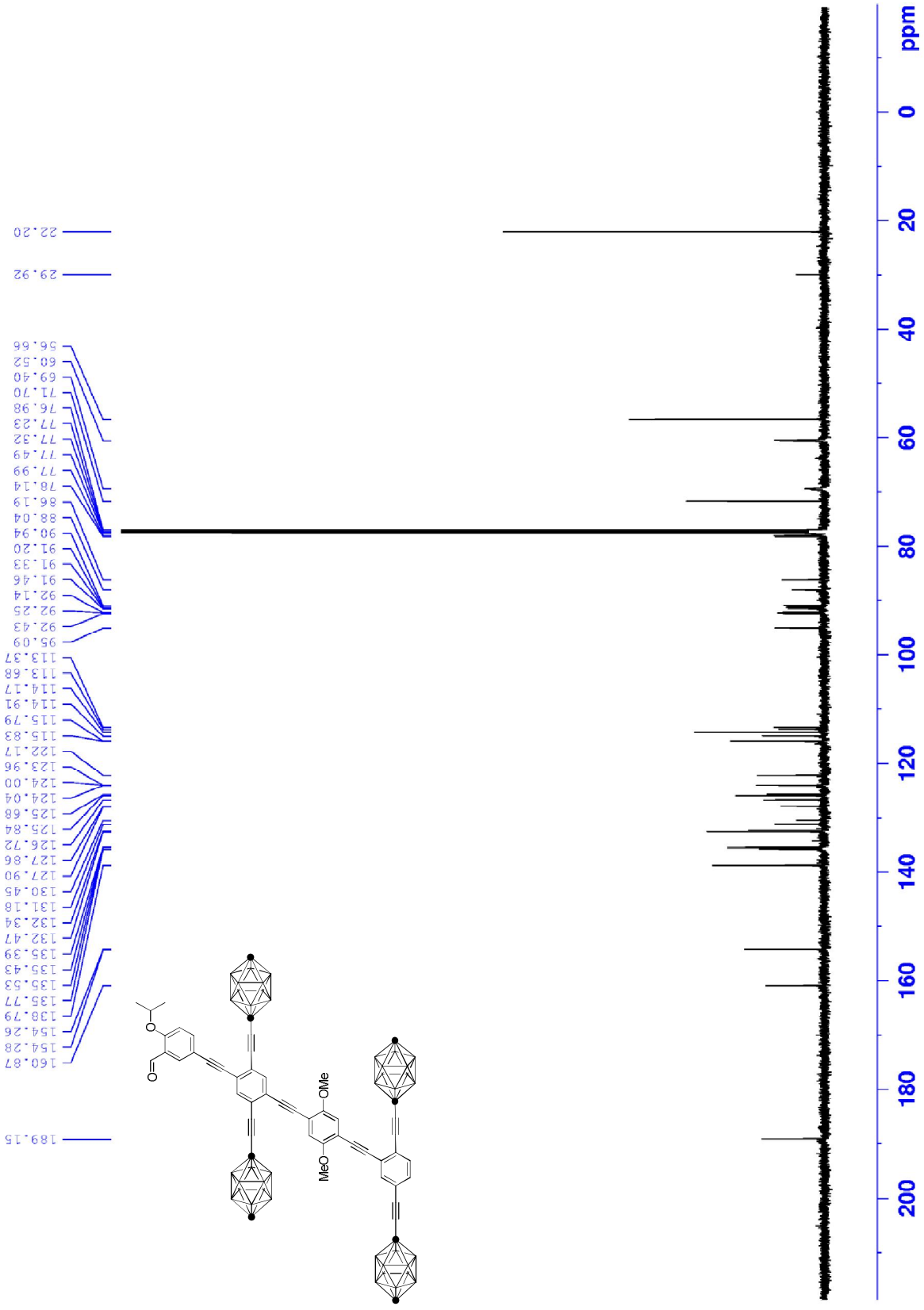
^{13}C NMR spectrum of **8** (125 MHz, $CDCl_3$)



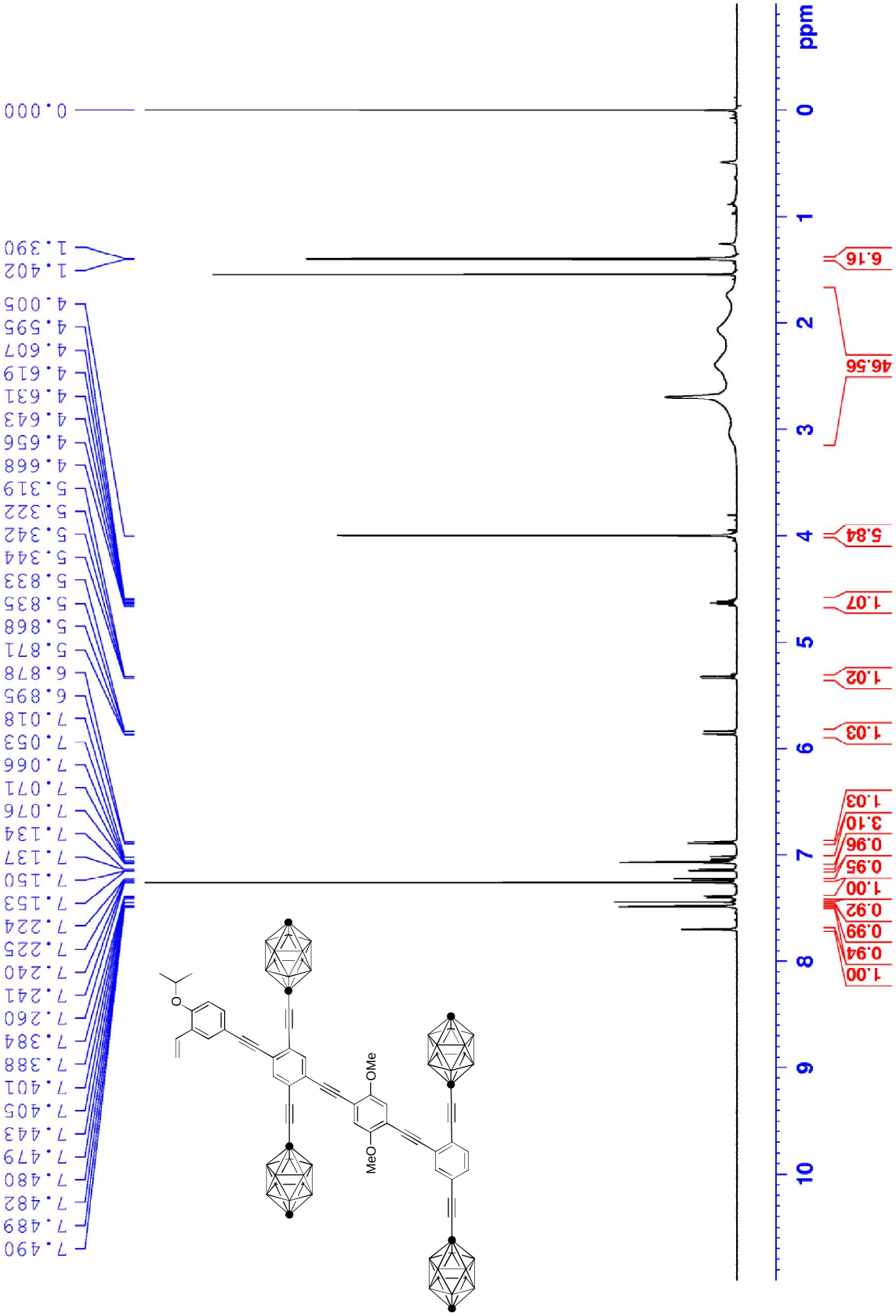
^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$)



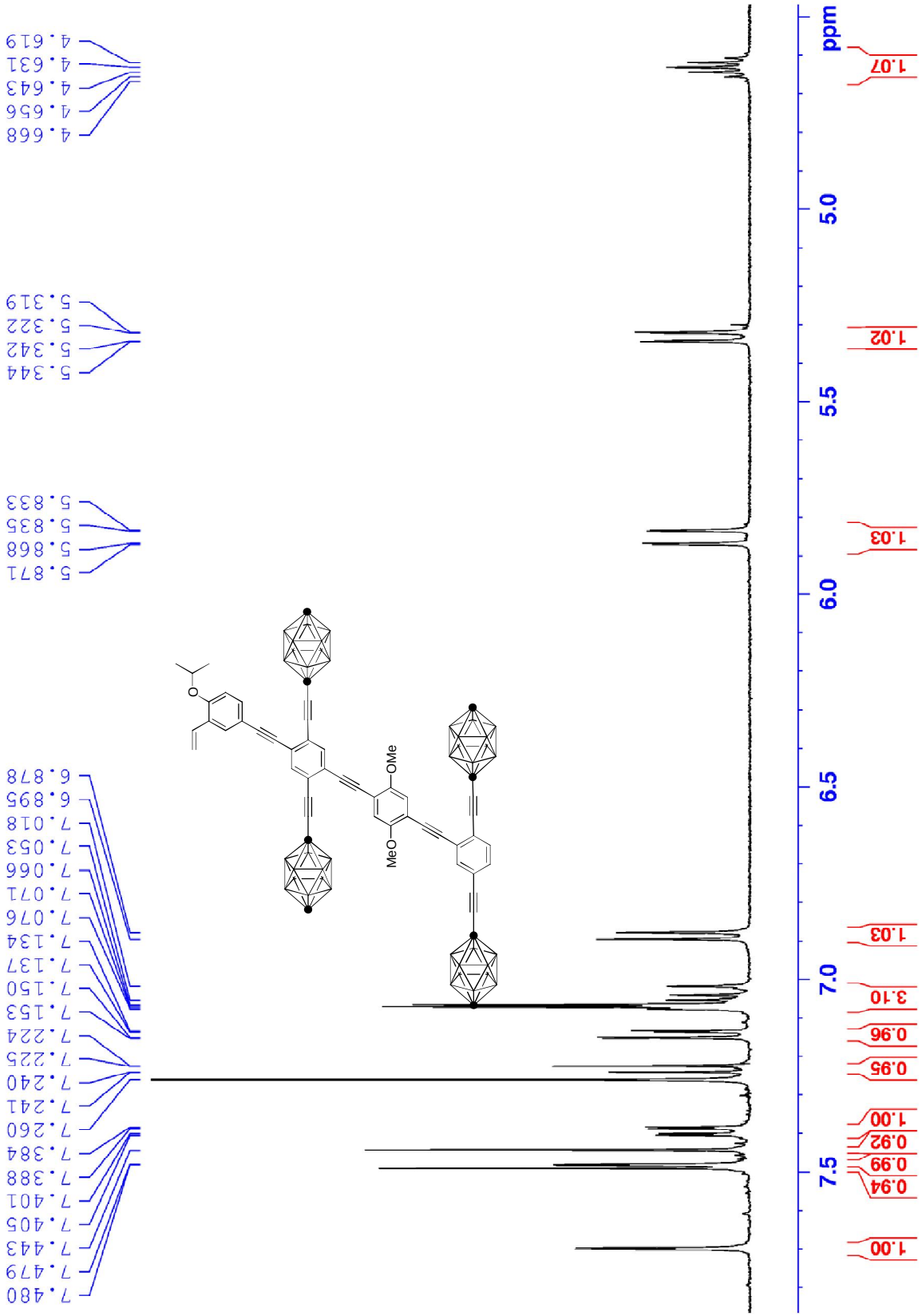
^{13}C NMR spectrum of **9** (125 MHz, $CDCl_3$)



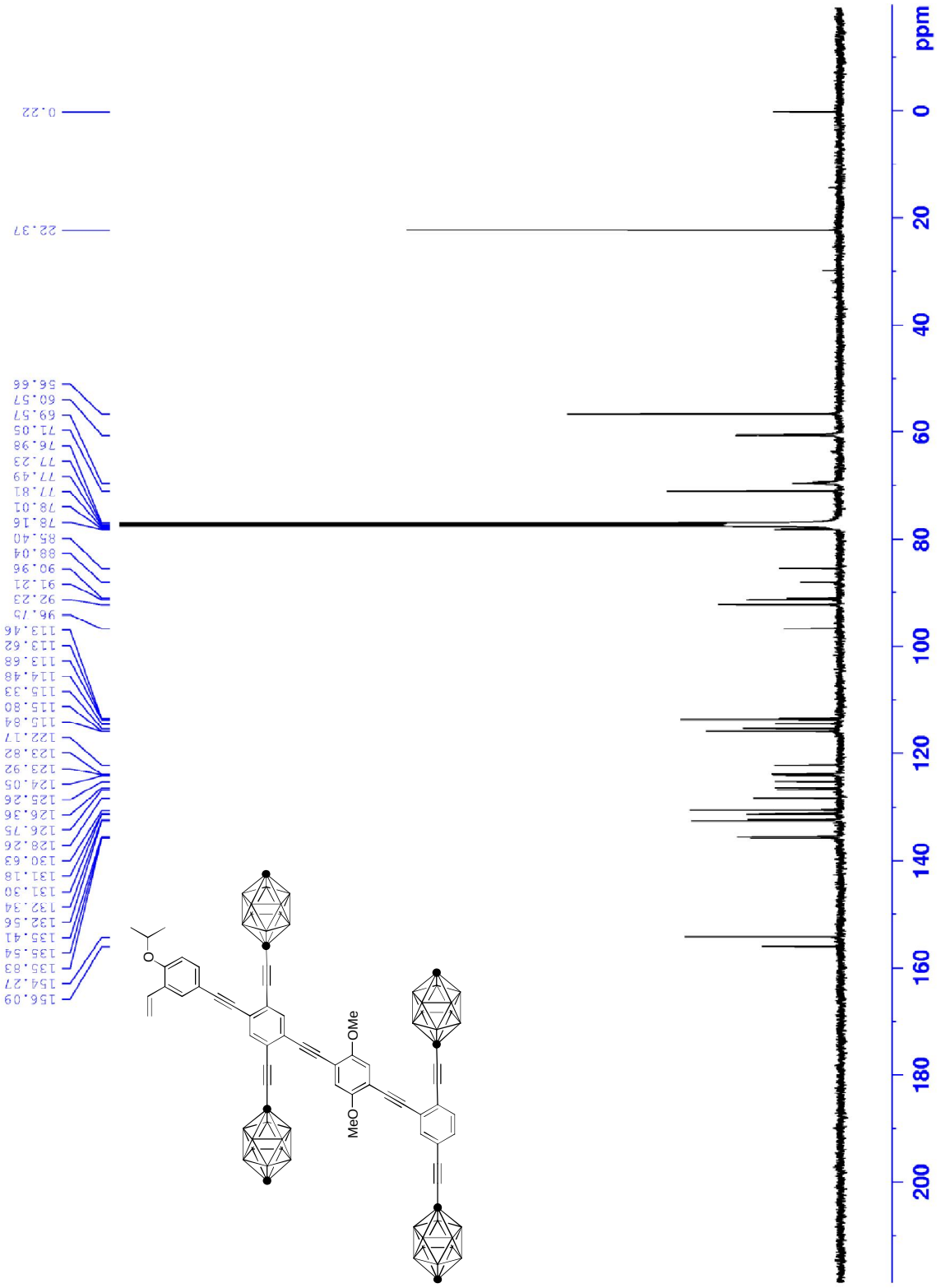
^{1}H NMR spectrum of **10** (500 MHz, $CDCl_3$)



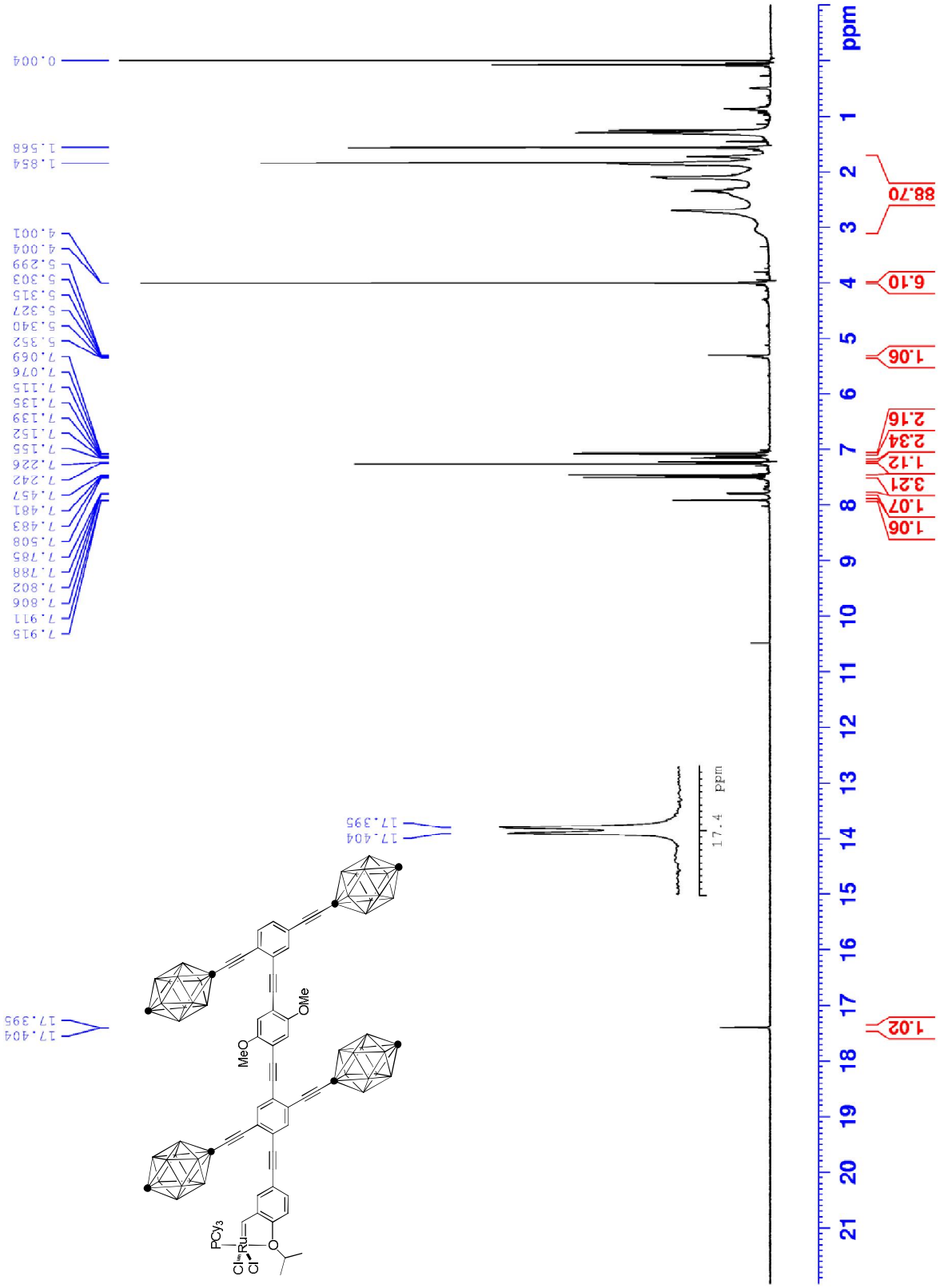
Amplification of ^{1}H NMR spectrum of **10** (500 MHz, $CDCl_3$)



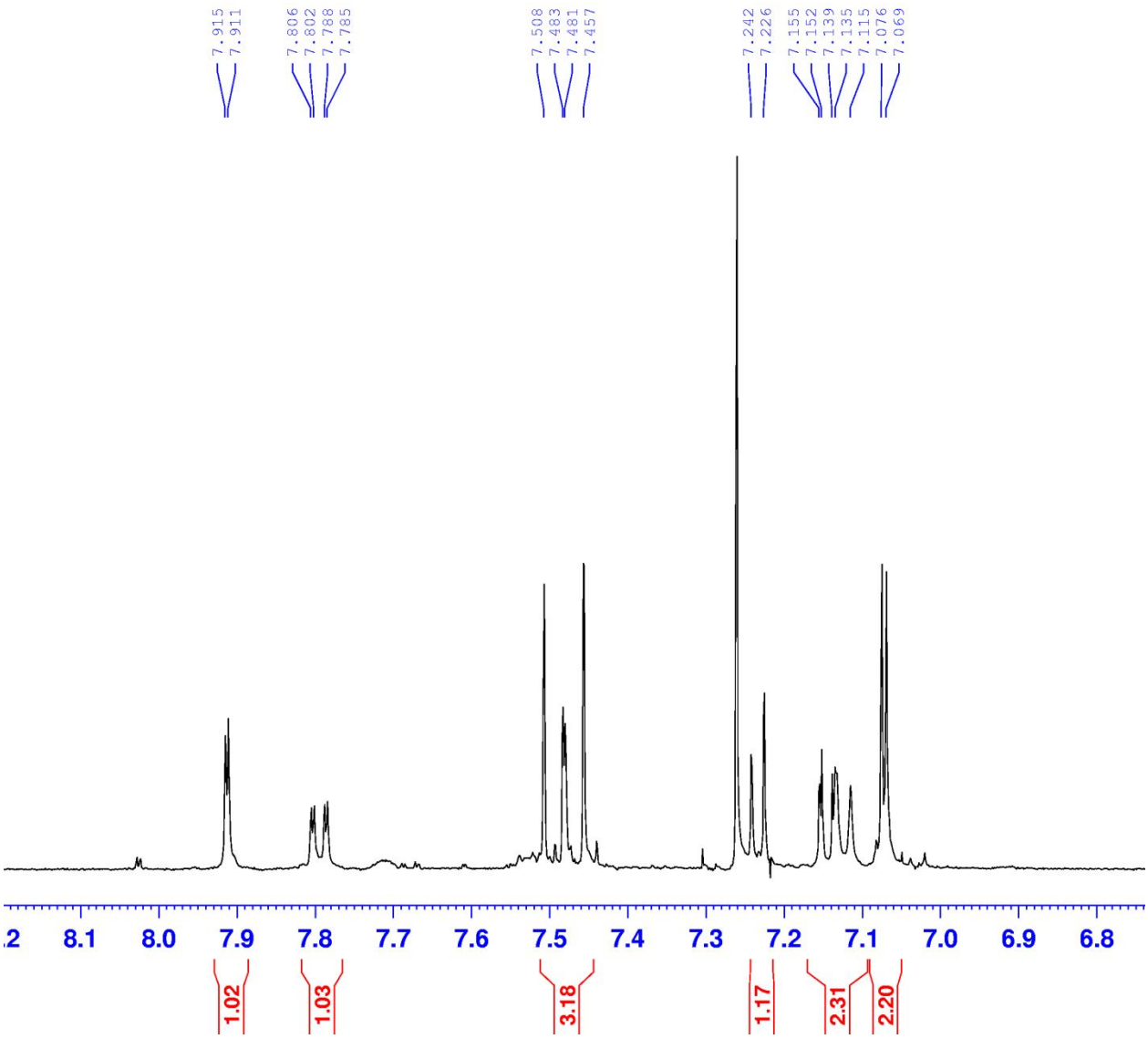
^{13}C NMR spectrum of **10** (125 MHz, $CDCl_3$)



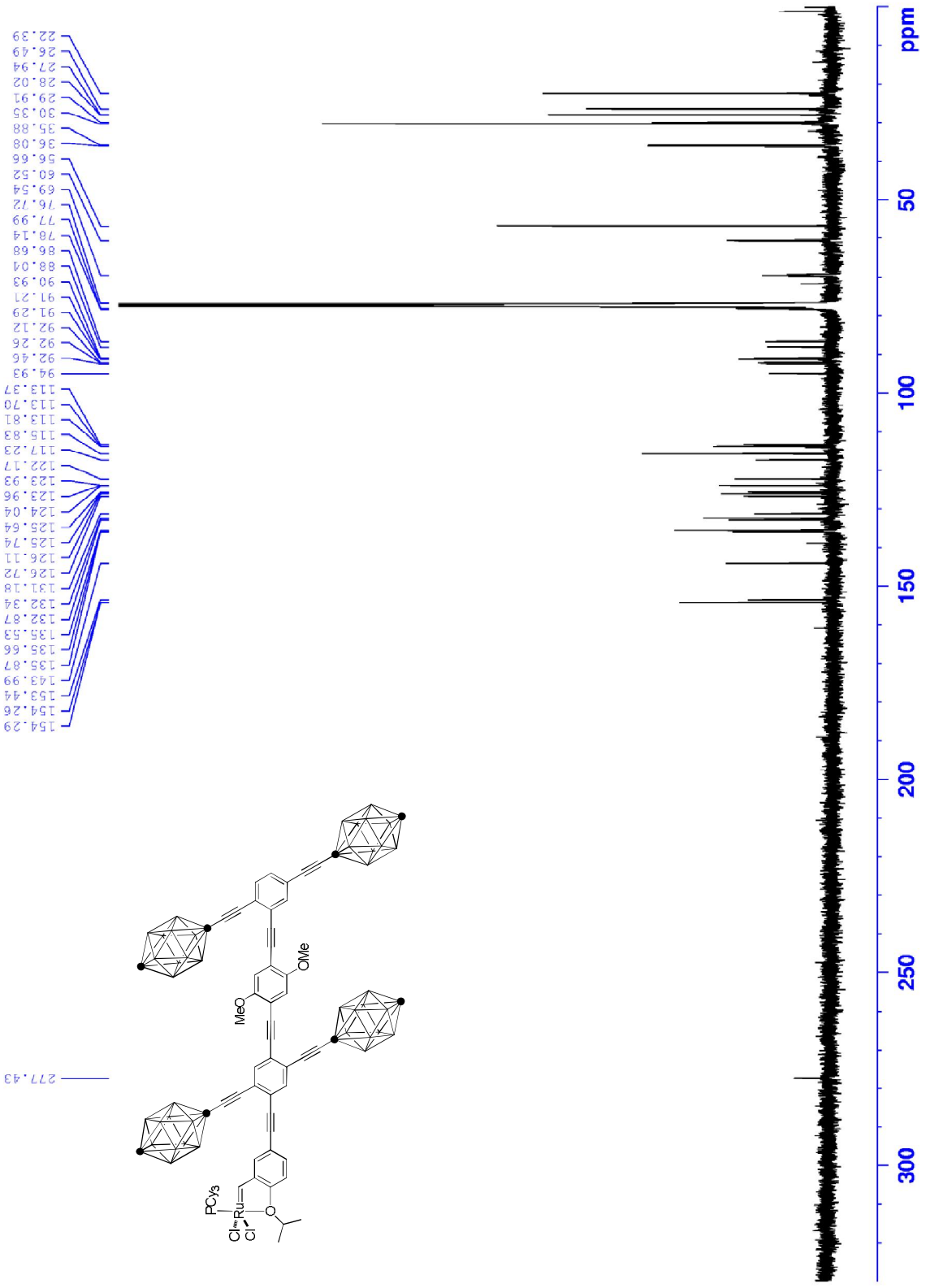
^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$)



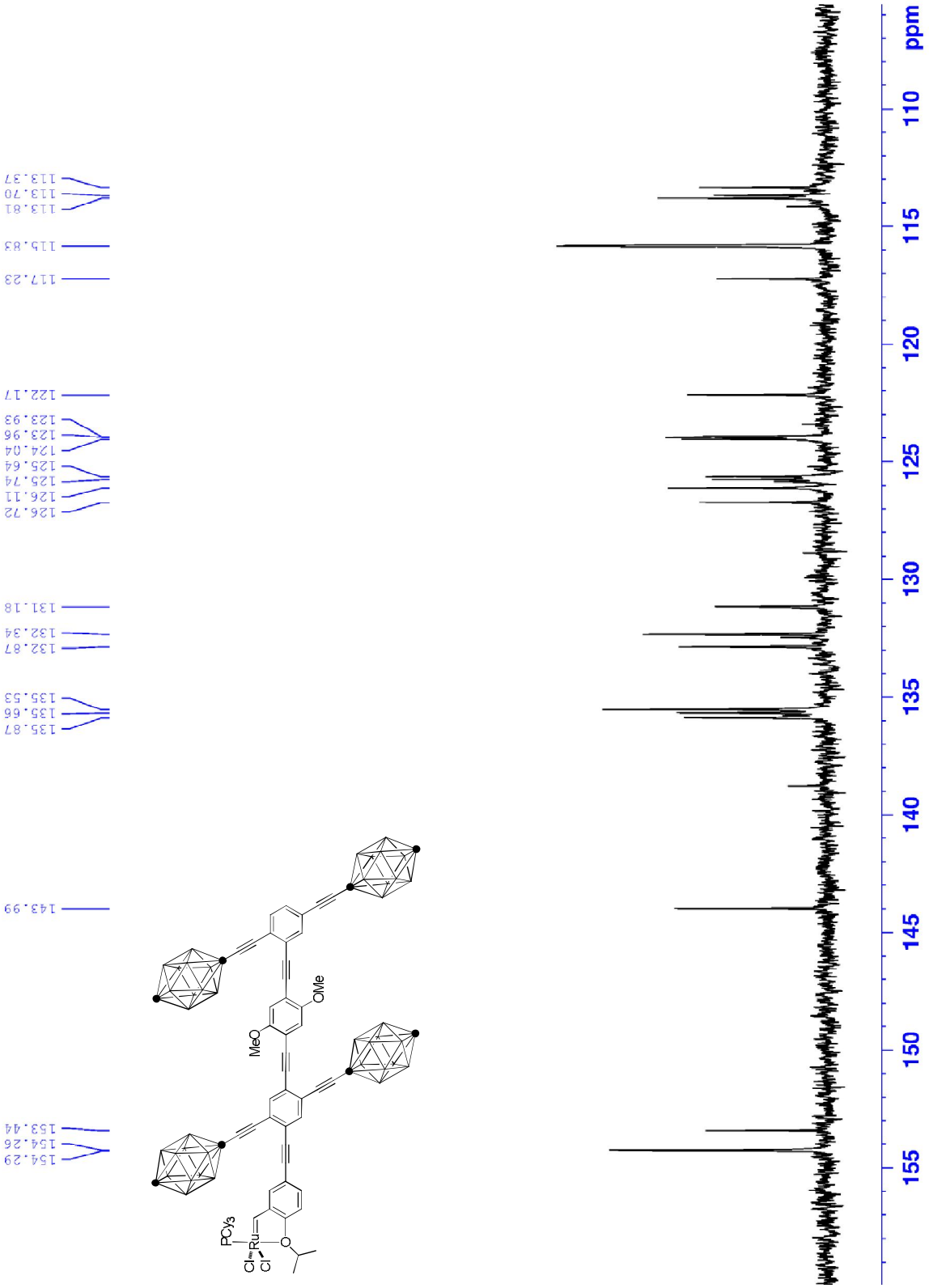
Amplification of ^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$)



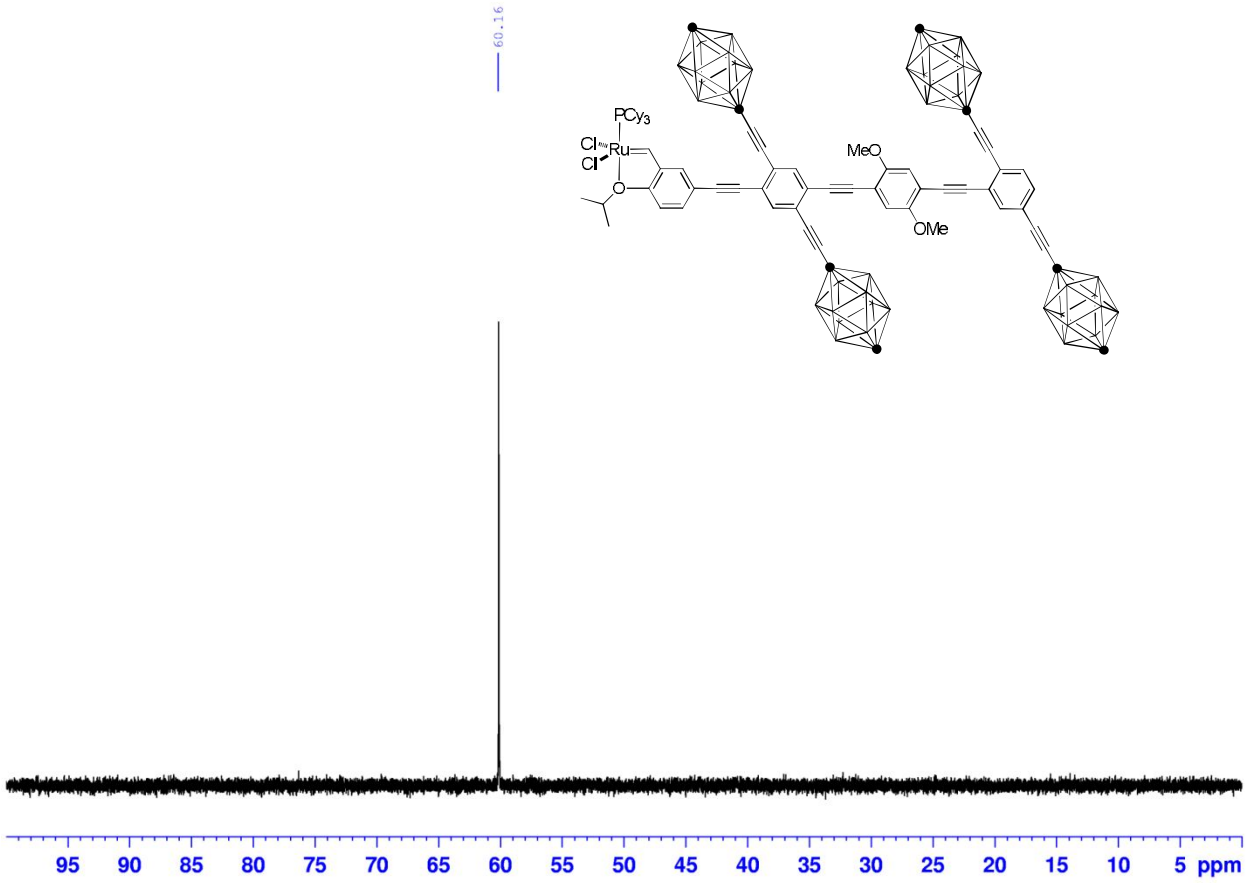
^{13}C NMR spectrum of **1** (125 MHz, $CDCl_3$)



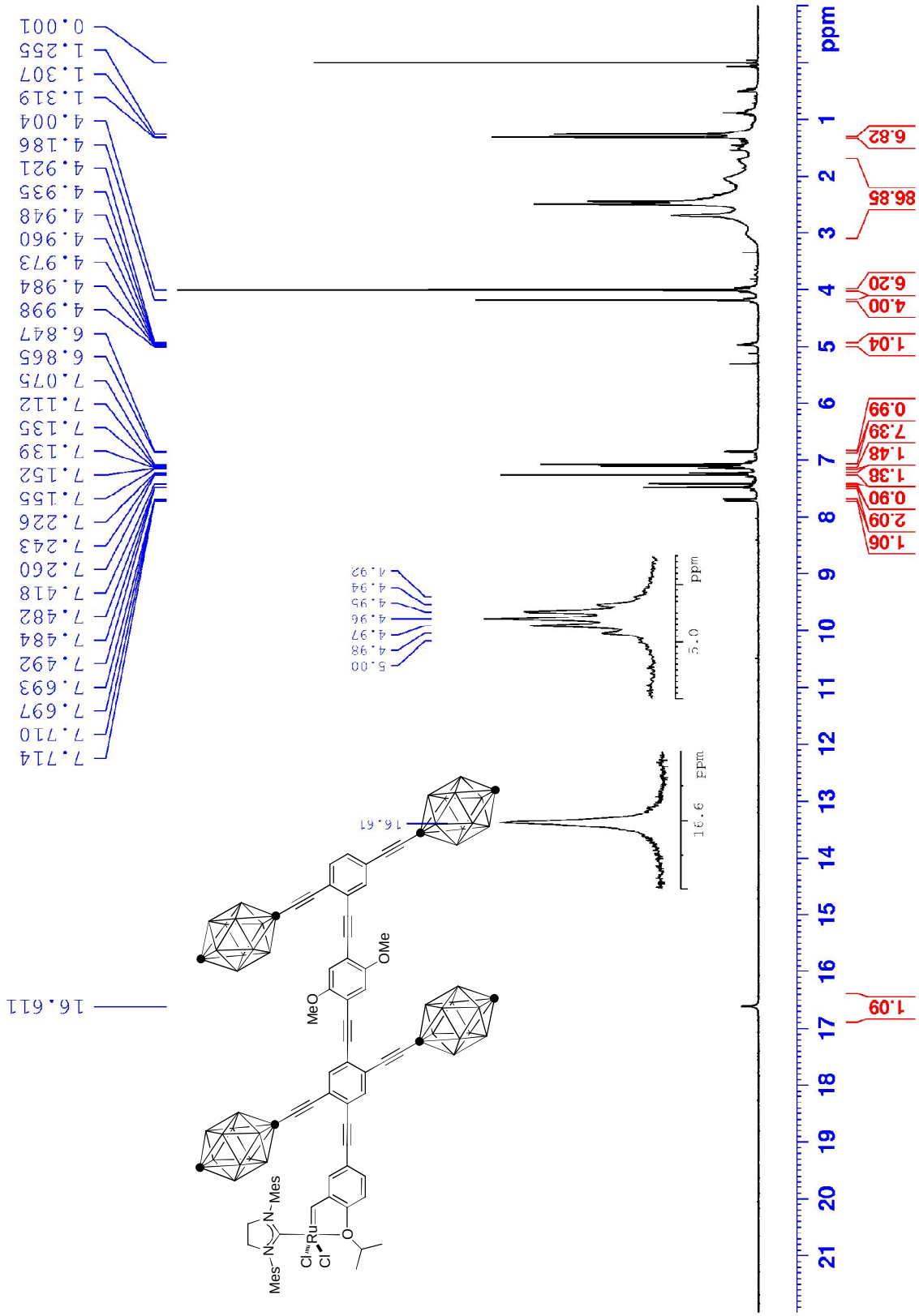
Amplification of ^{13}C NMR spectrum of **1** (125 MHz, $CDCl_3$)



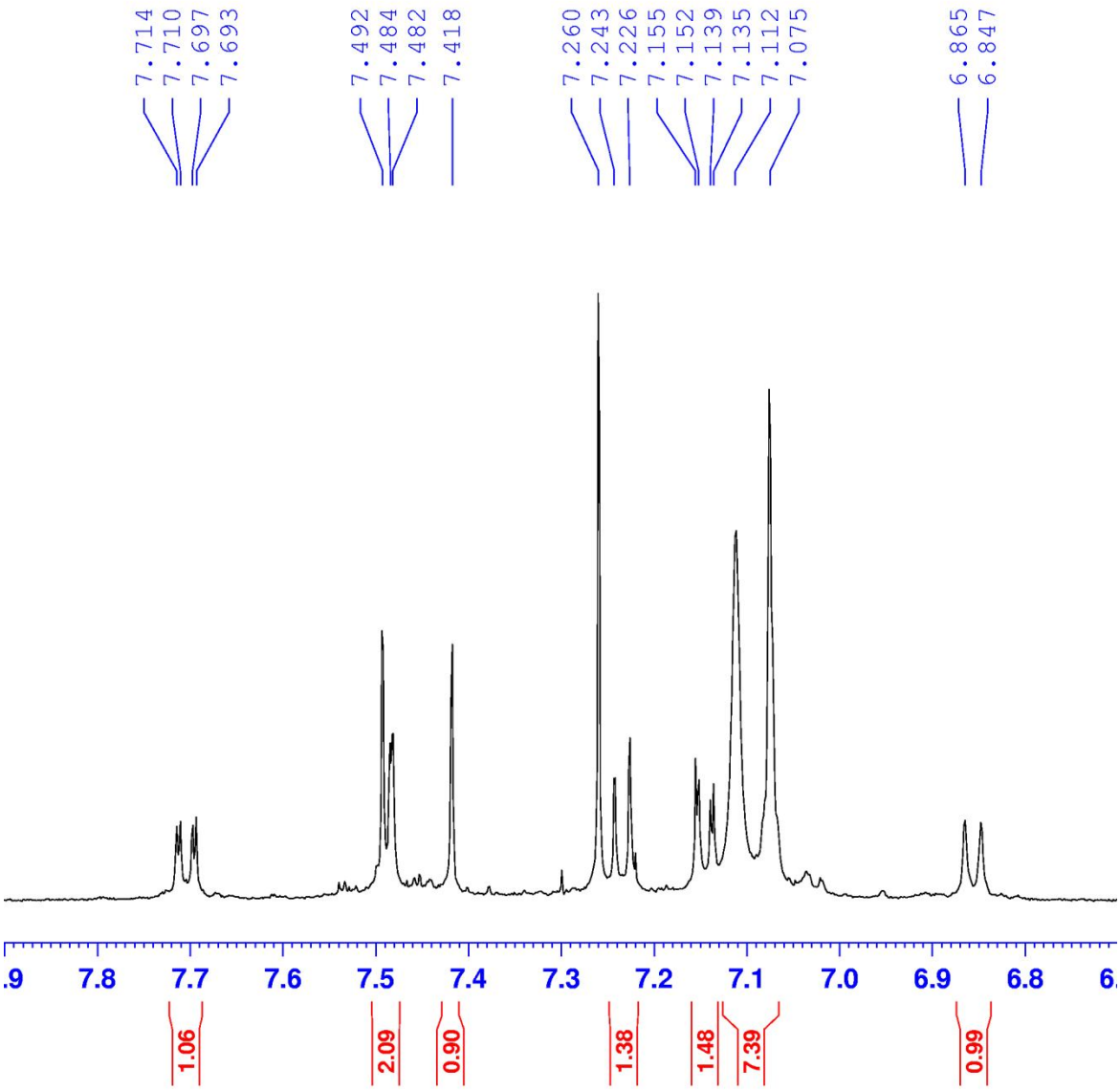
^{31}P NMR spectrum of **1** (202 MHz, $CDCl_3$)



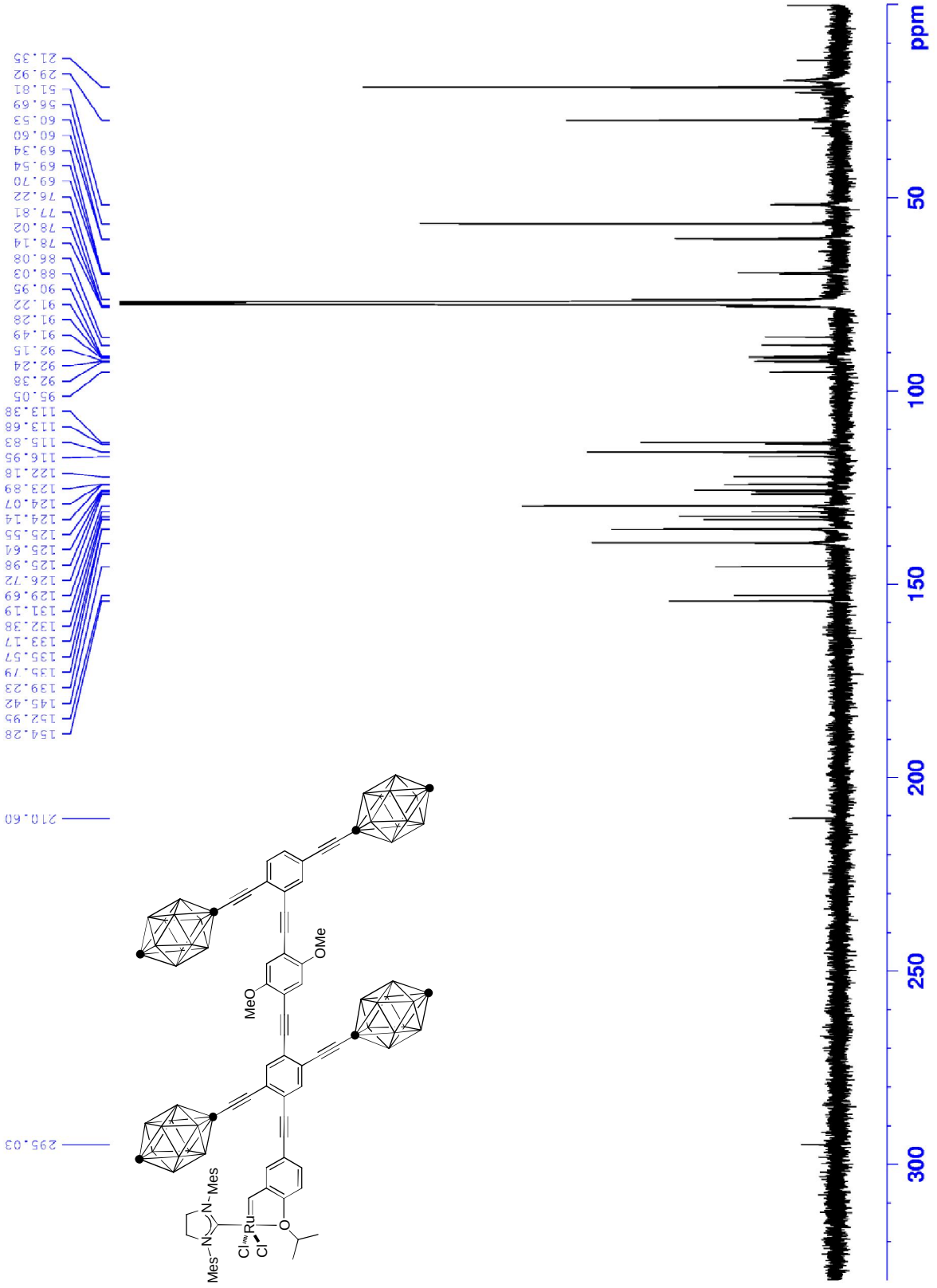
^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$)



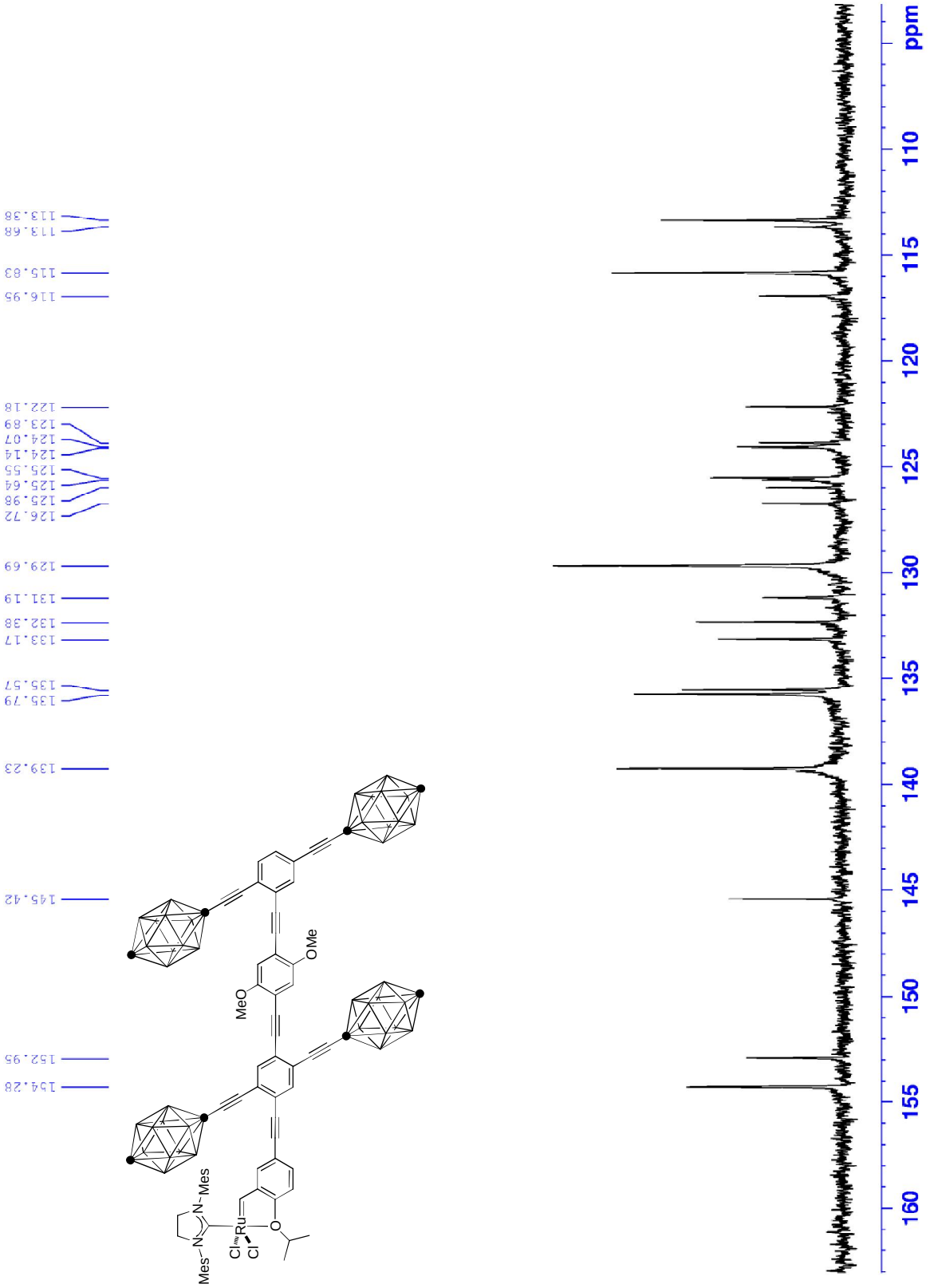
Amplification of ^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$)



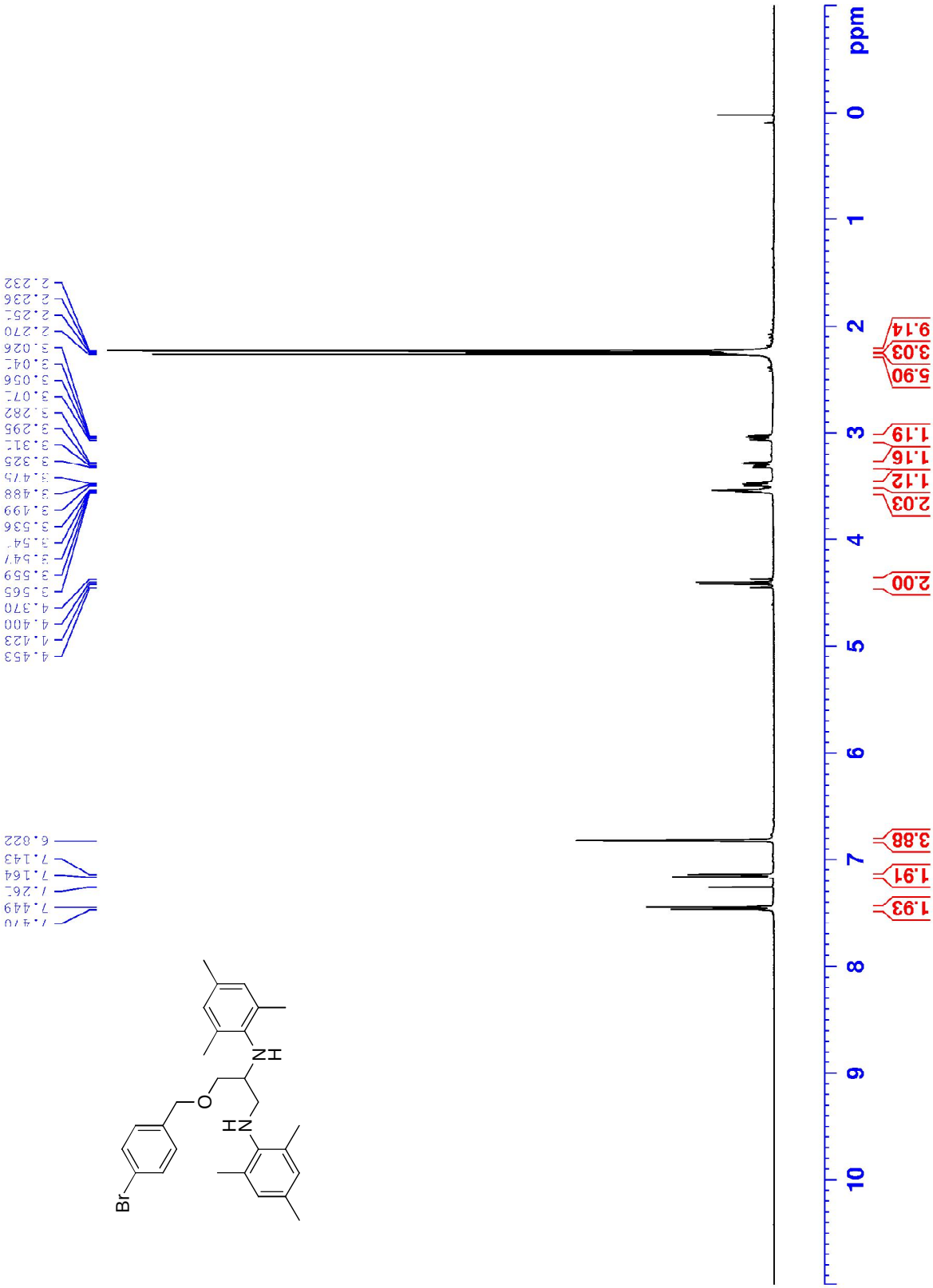
^{13}C NMR spectrum of **2** (125 MHz, $CDCl_3$)



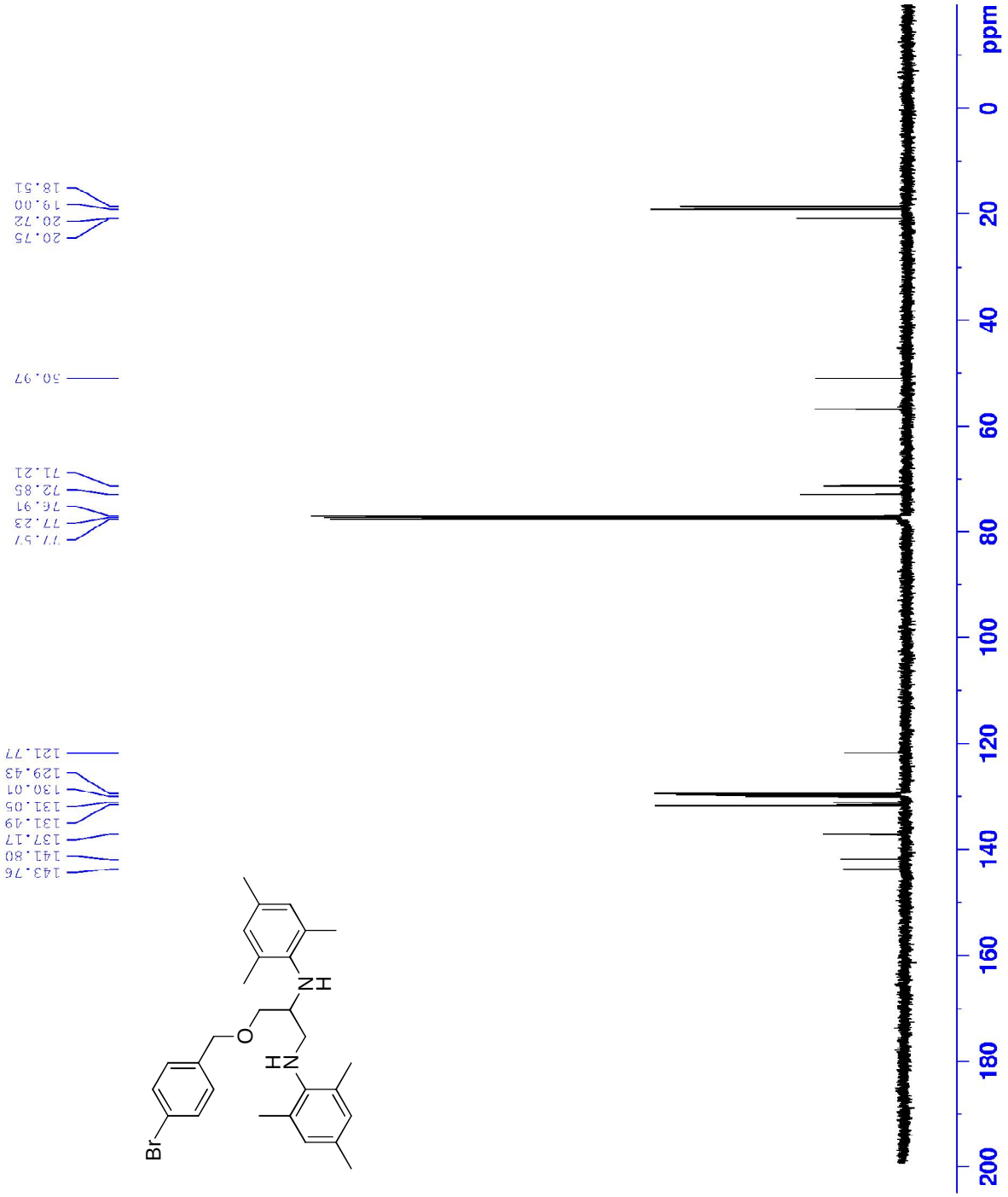
Amplification of ^{13}C NMR spectrum of **2** (125 MHz, $CDCl_3$)



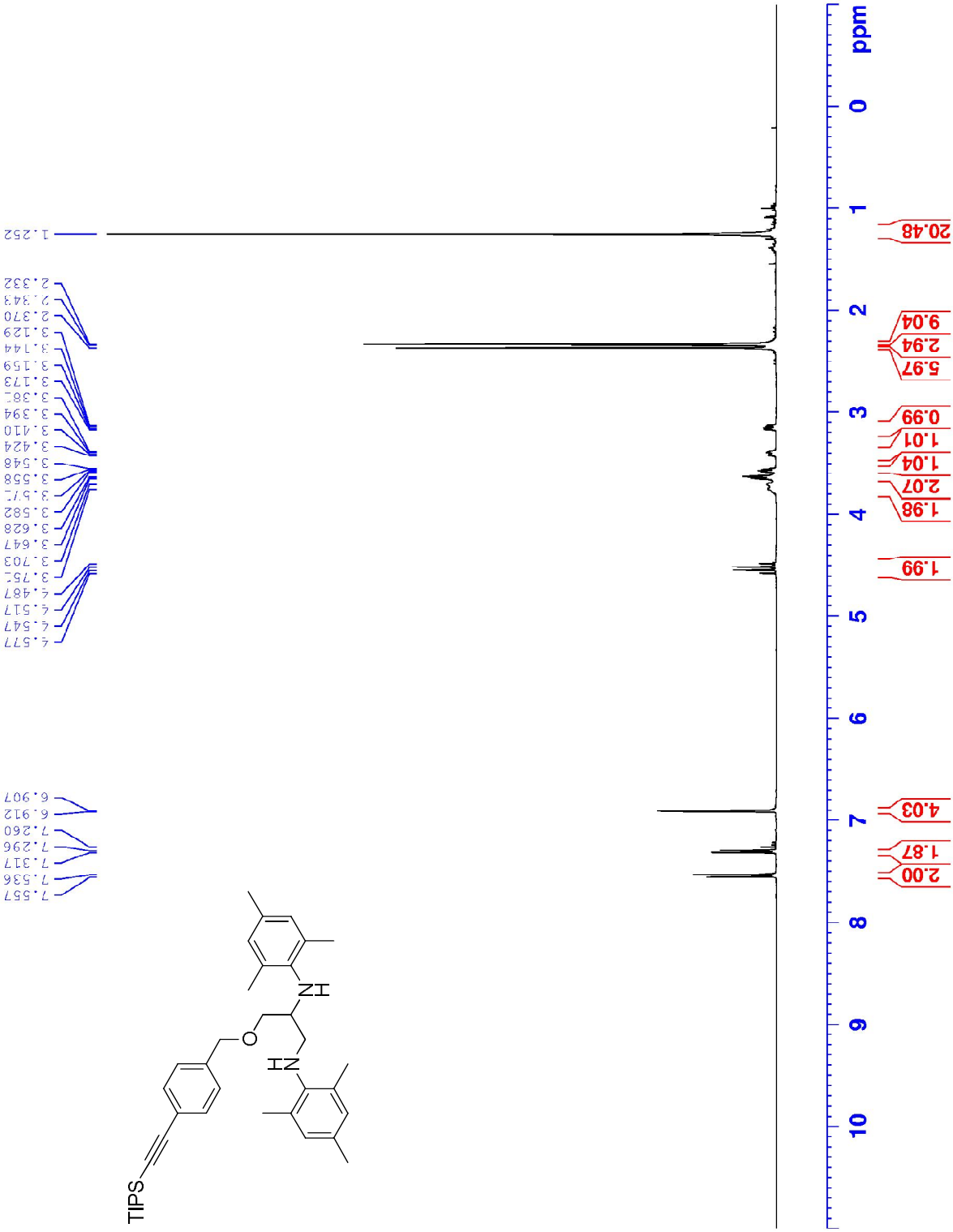
^{1}H NMR spectrum of **S4** (400 MHz, $CDCl_3$)



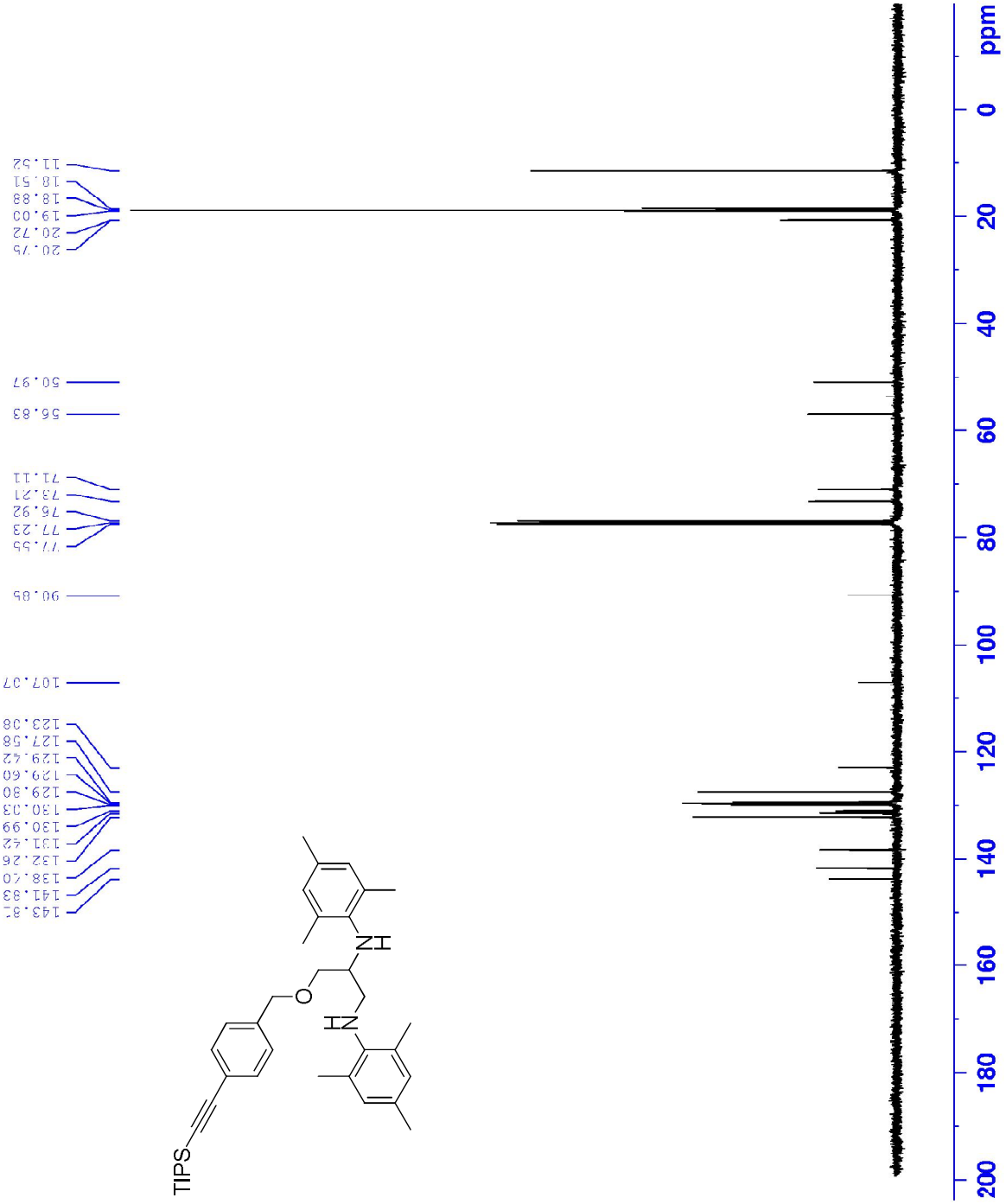
^{13}C NMR spectrum of **S4** (100 MHz, $CDCl_3$)



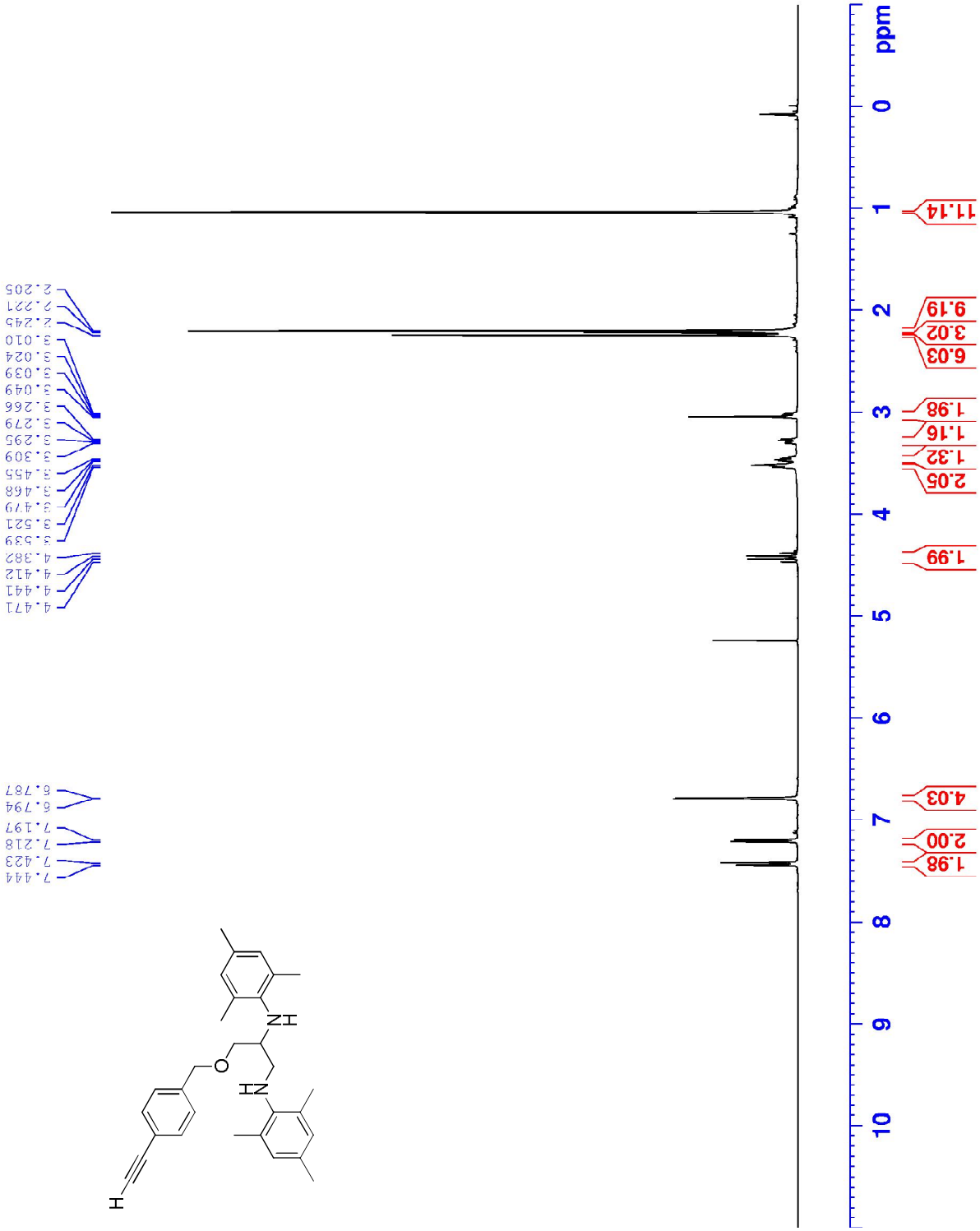
^{1}H NMR spectrum of **S5** (400 MHz, $CDCl_3$)



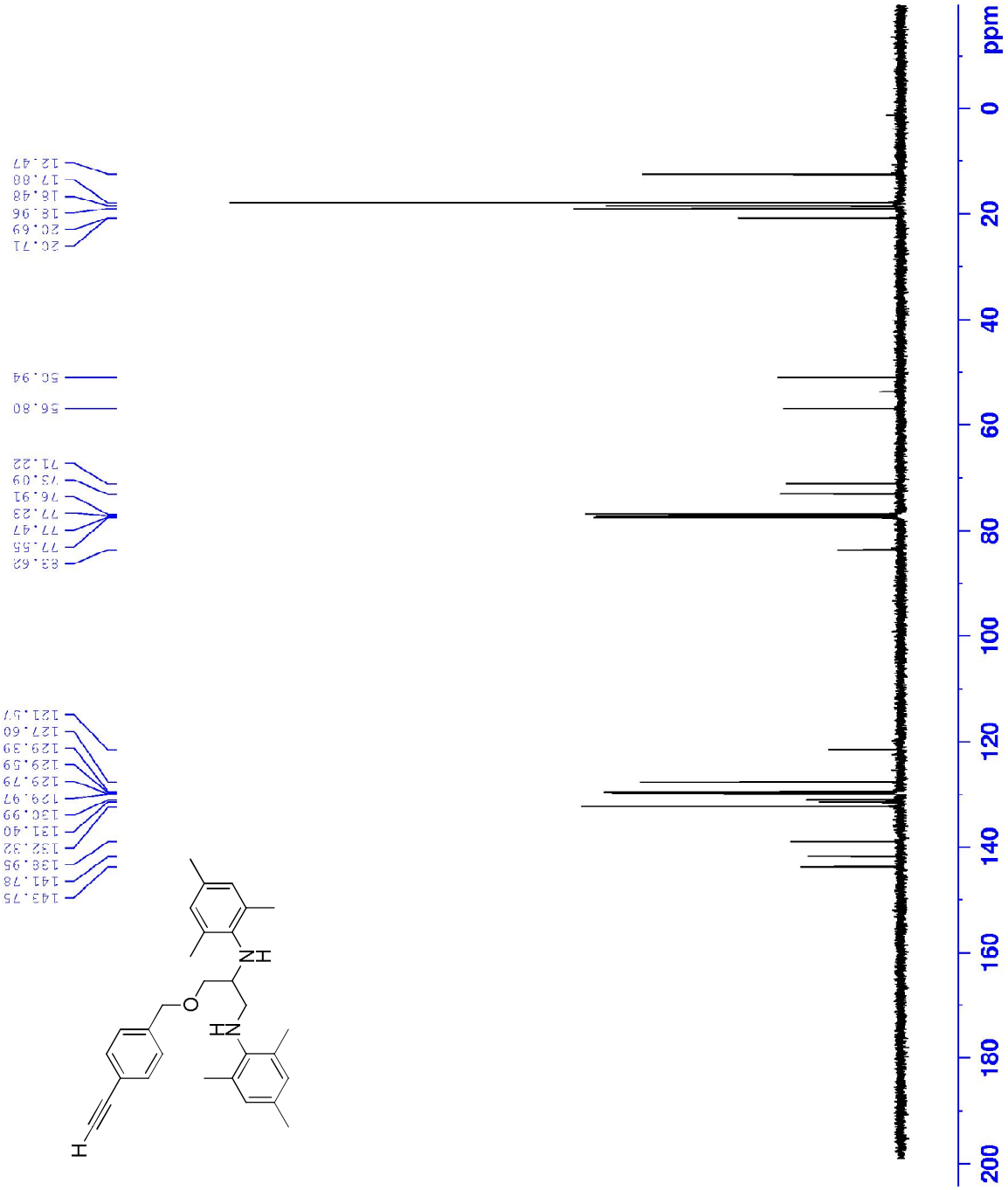
^{13}C NMR spectrum of **S5** (100 MHz, $CDCl_3$)



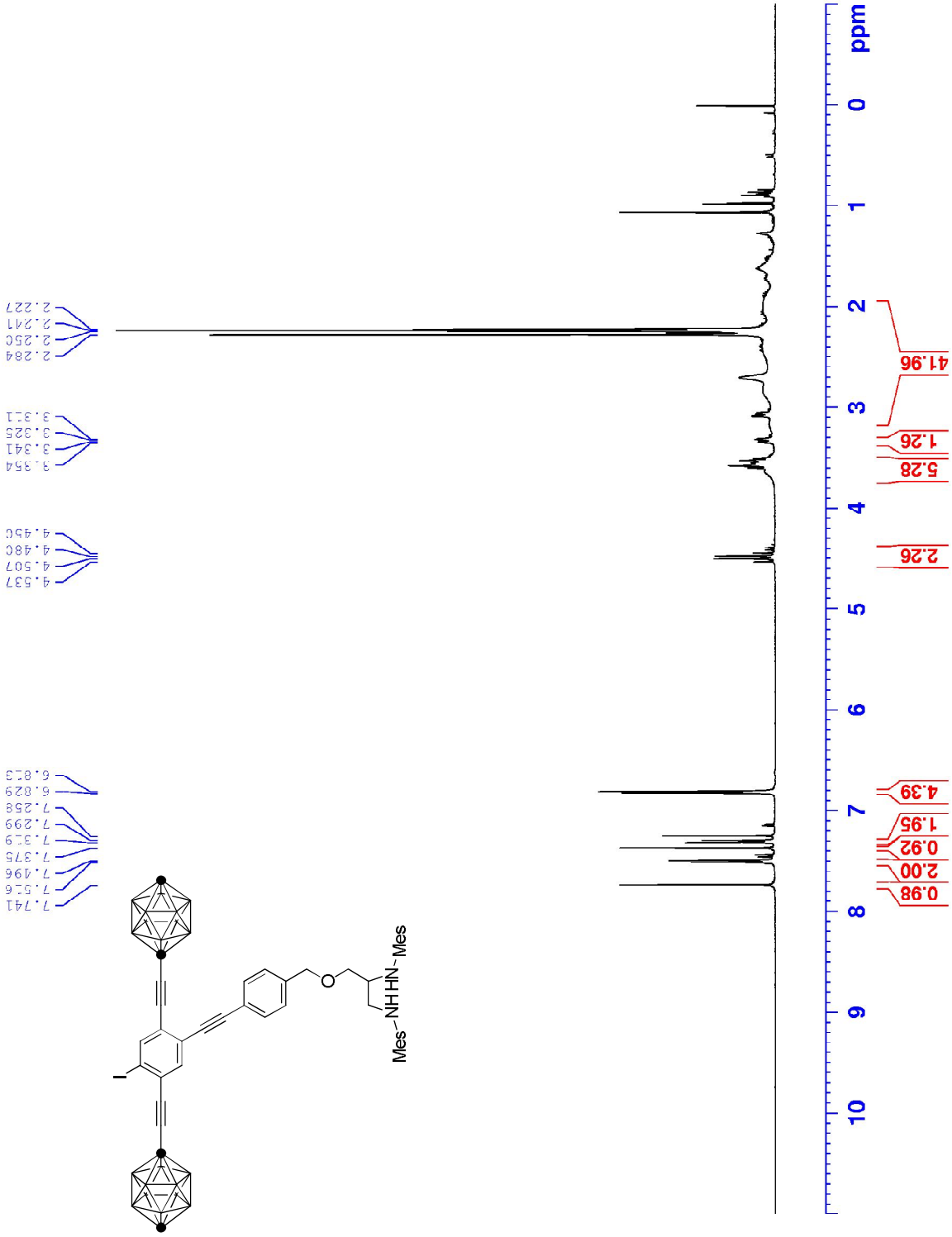
^{1}H NMR spectrum of **S6** (400 MHz, $CDCl_3$)



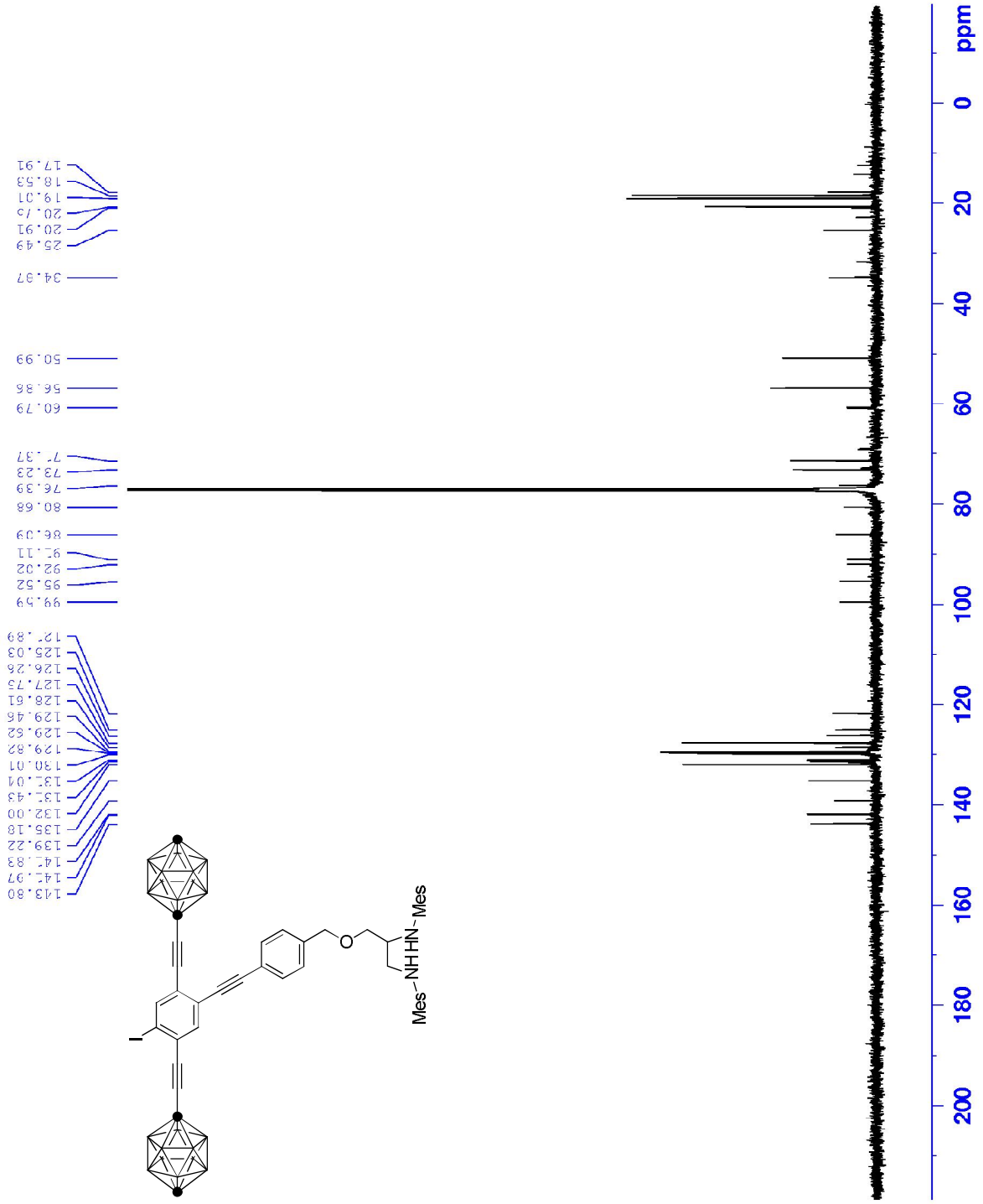
^{13}C NMR spectrum of **S6** (100 MHz, $CDCl_3$)



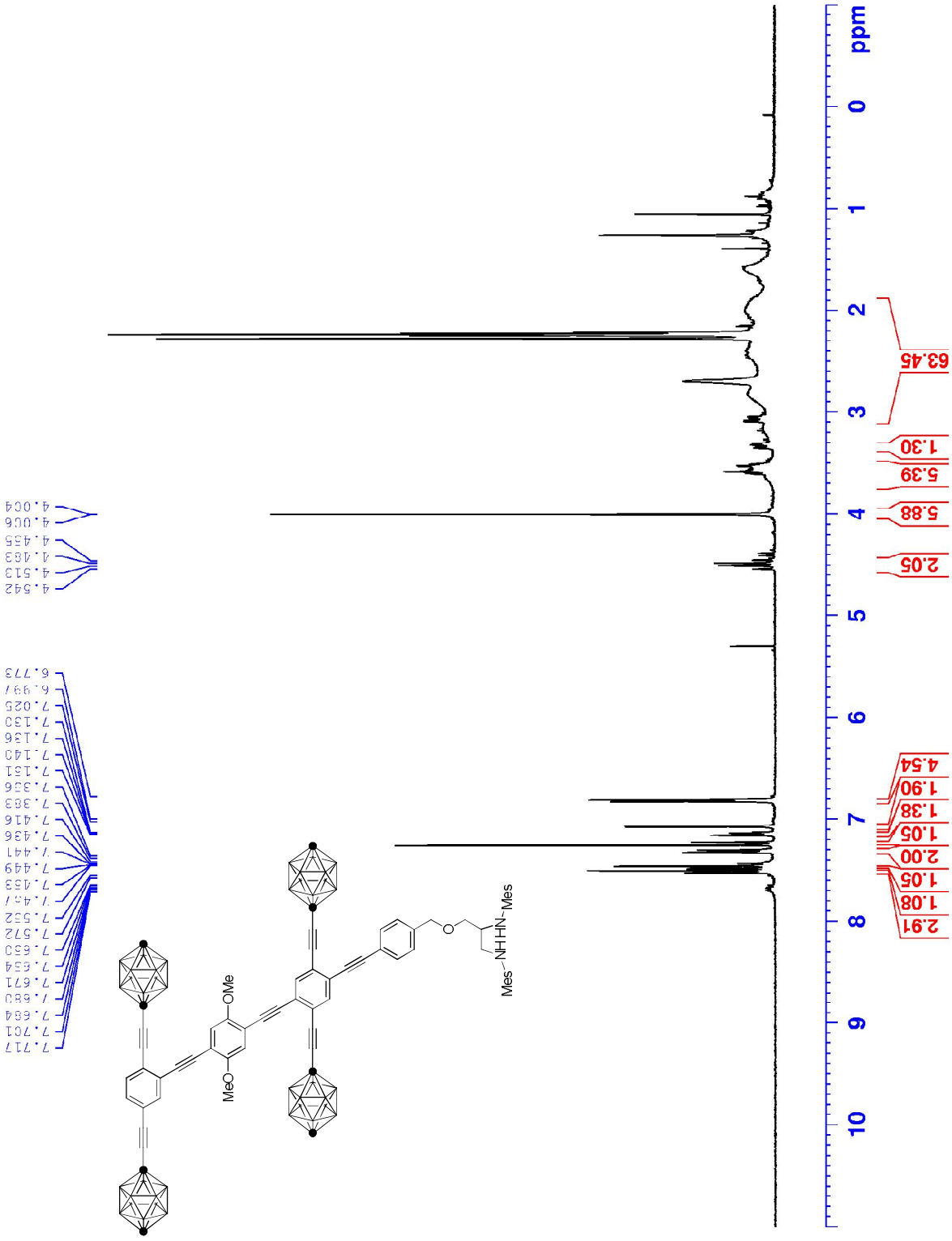
^{1}H NMR spectrum of **S7** (400 MHz, $CDCl_3$)



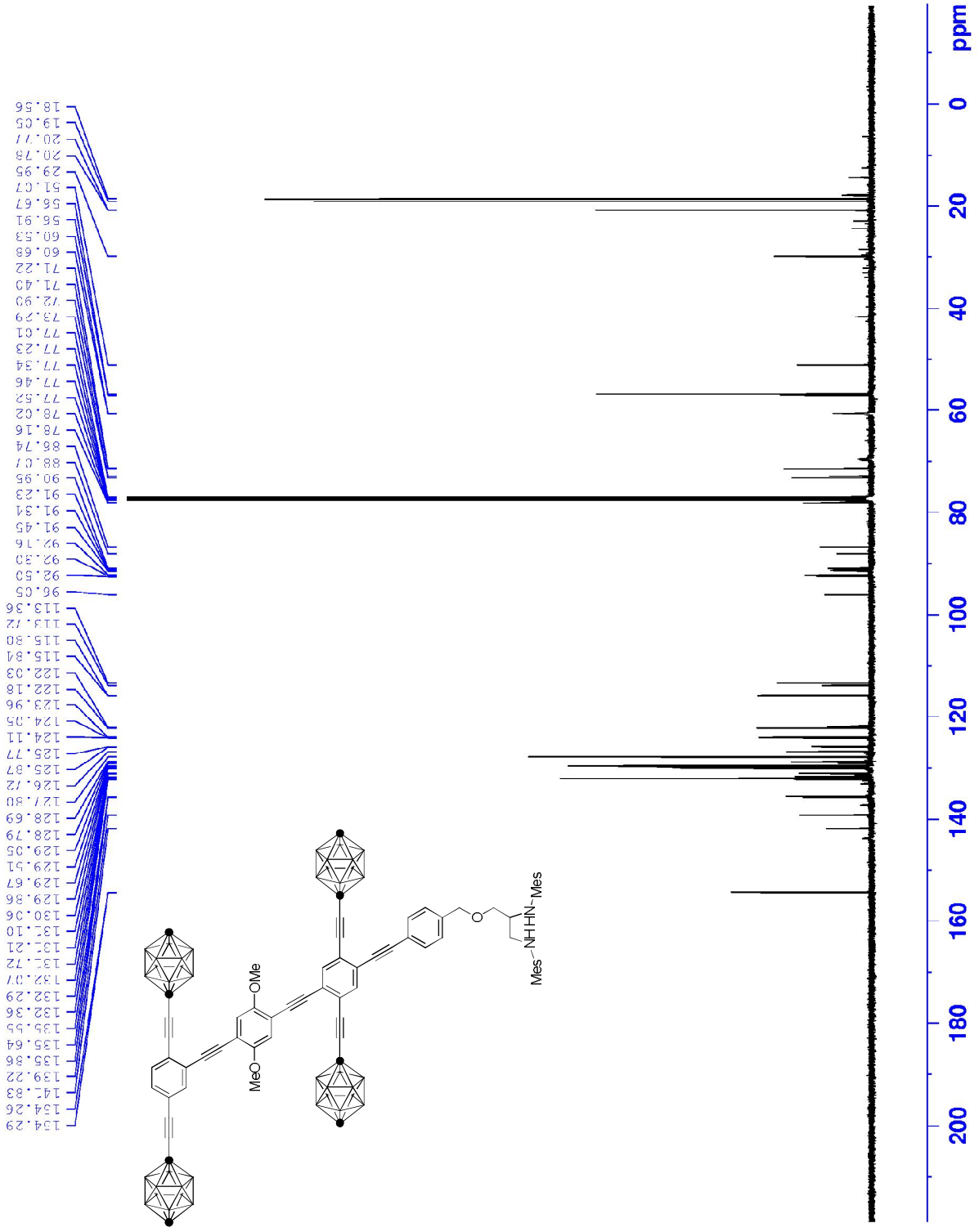
^{13}C NMR spectrum of **S7** (125 MHz, $CDCl_3$)



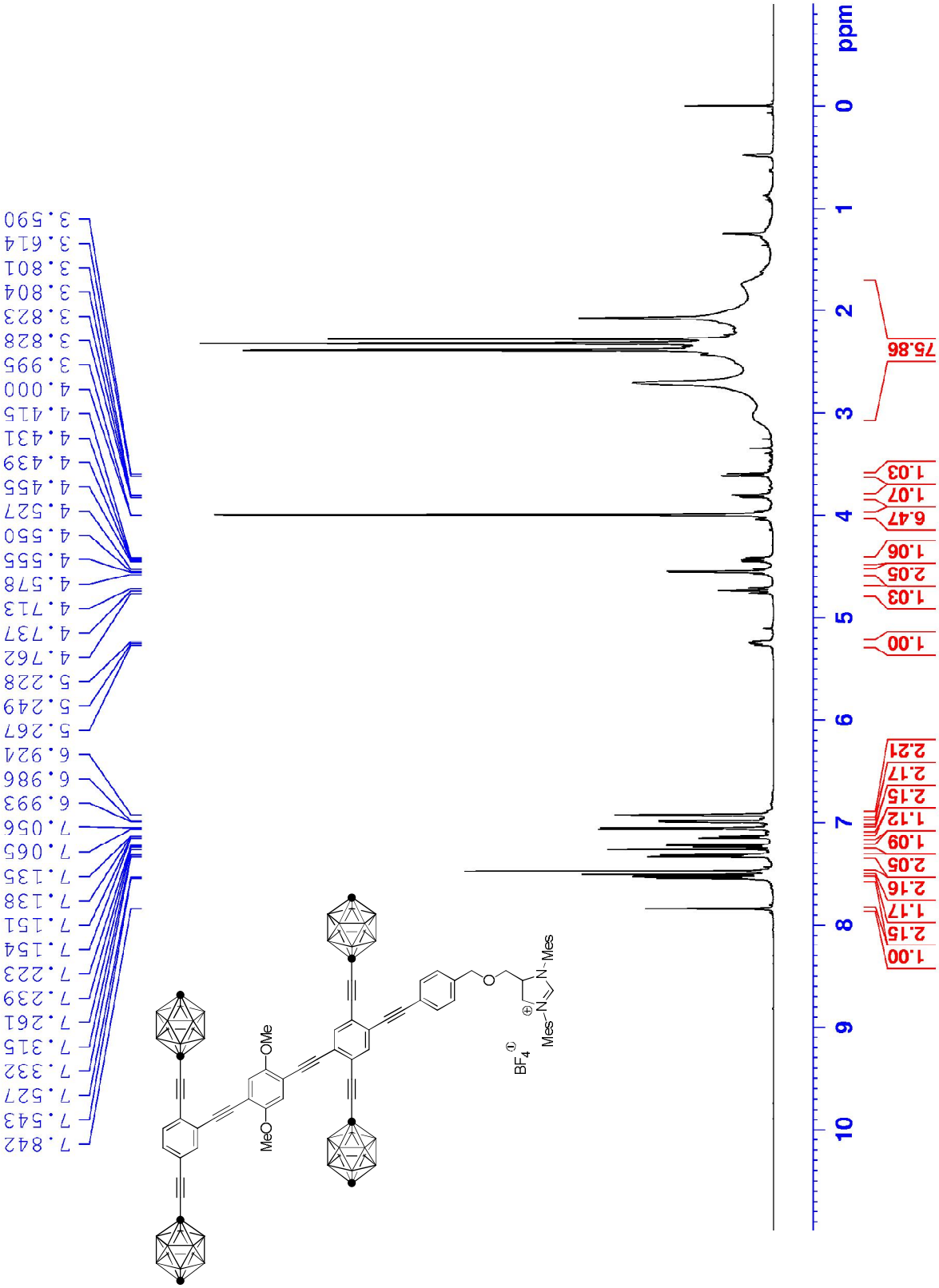
^{1}H NMR spectrum of **S8** (500 MHz, $CDCl_3$)



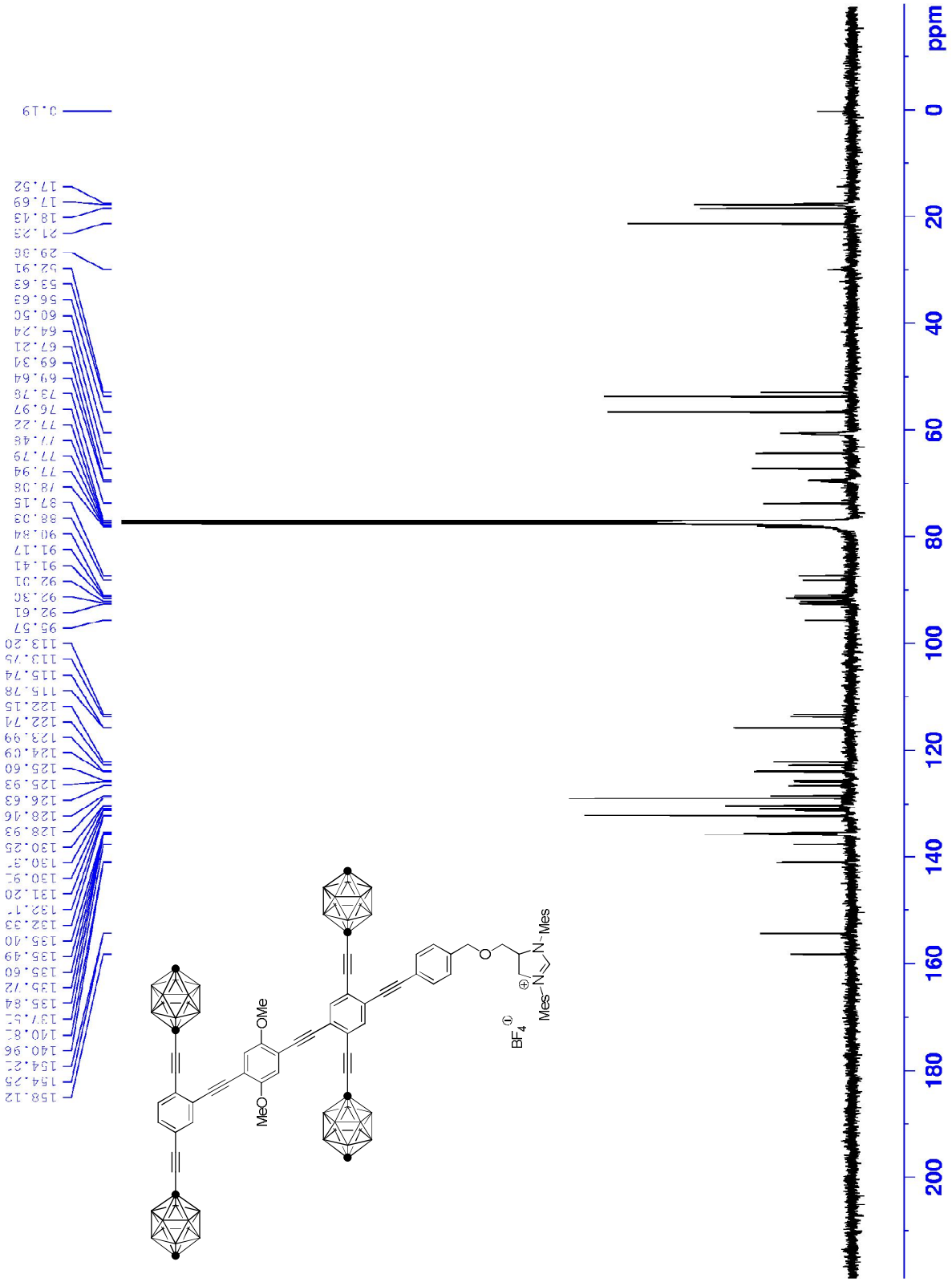
^{13}C NMR spectrum of **S8** (125 MHz, $CDCl_3$)



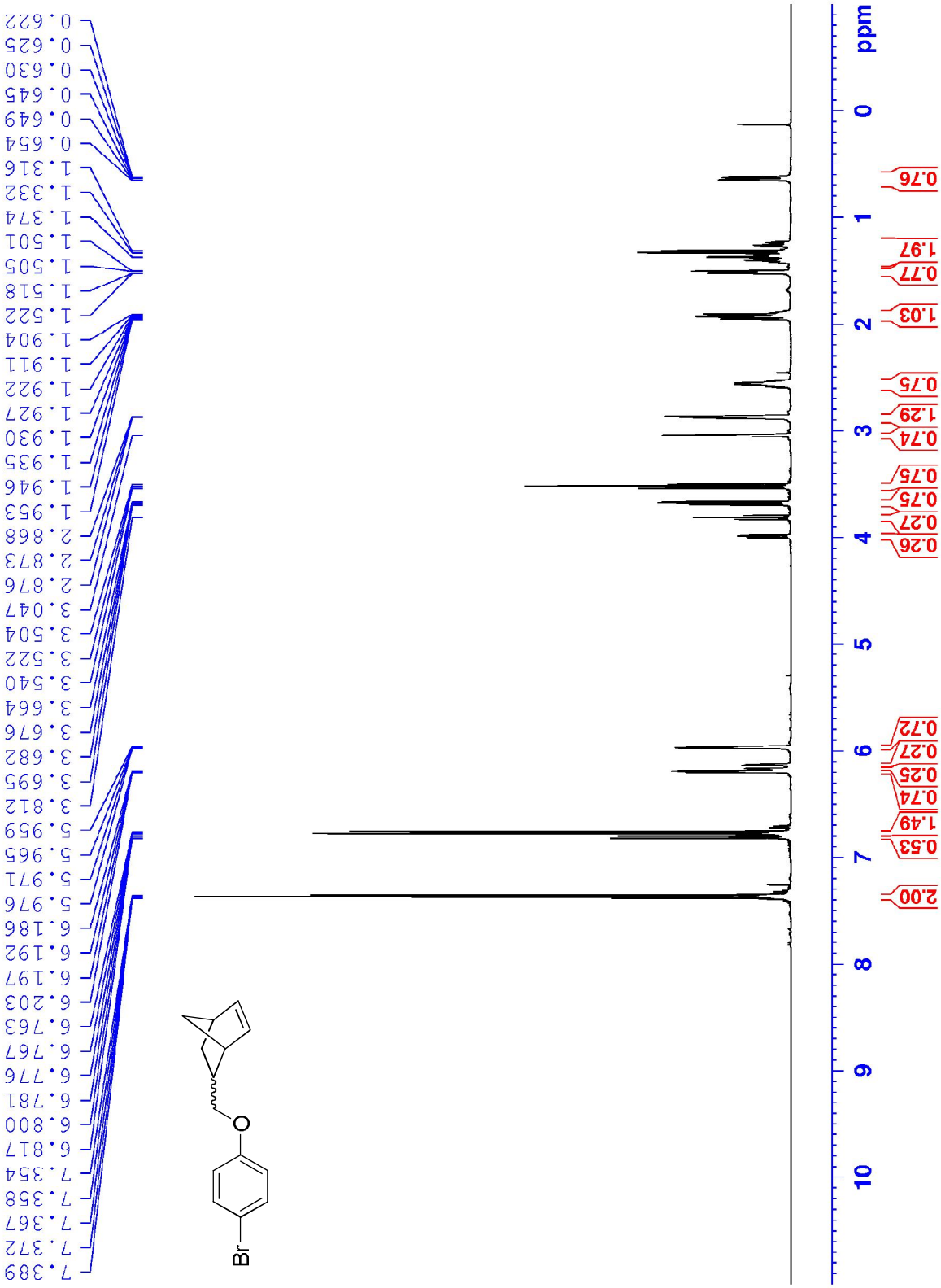
^{1}H NMR spectrum of **S1** (500 MHz, $CDCl_3$)



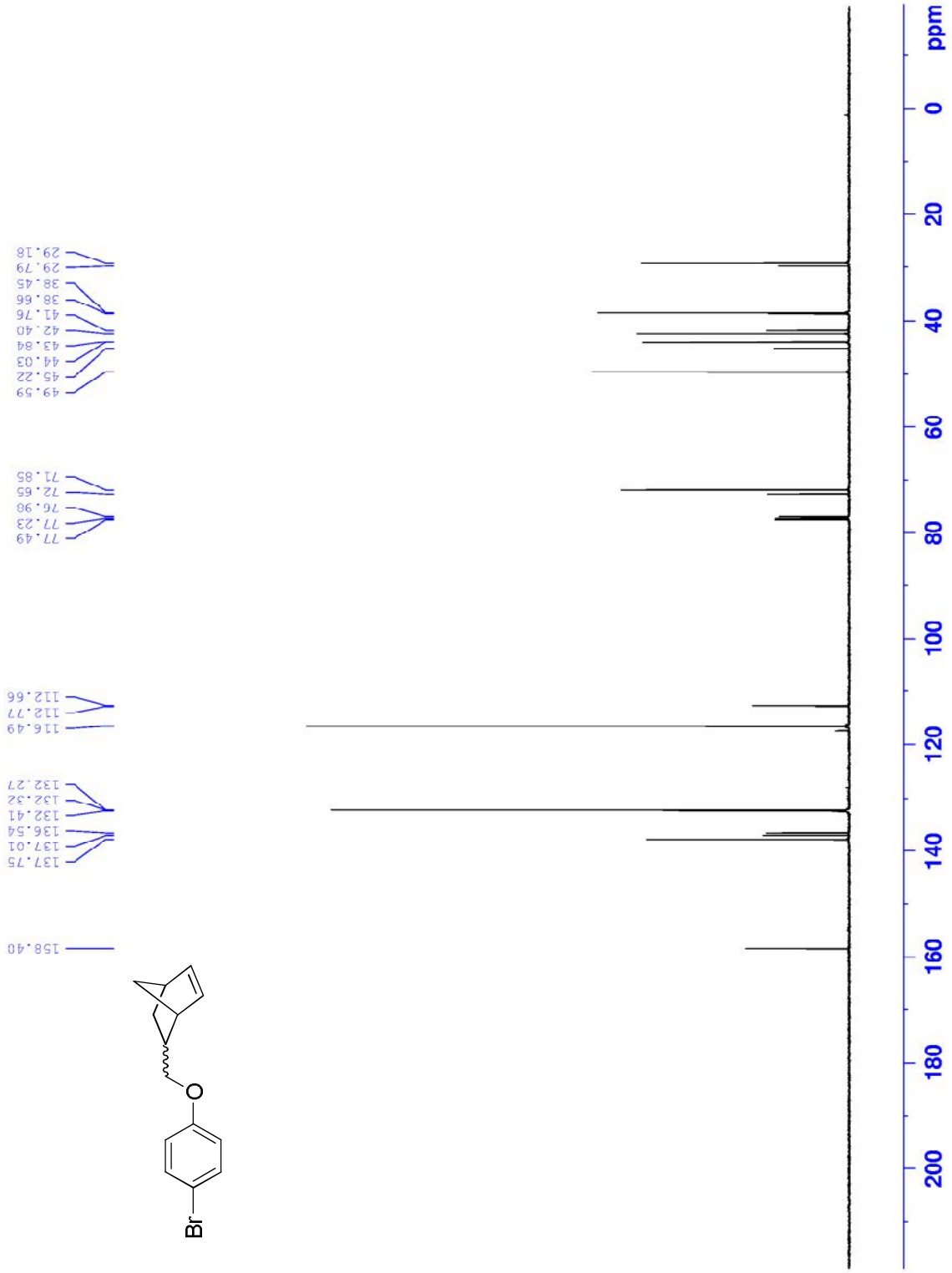
^{13}C NMR spectrum of **S1** (125 MHz, $CDCl_3$)



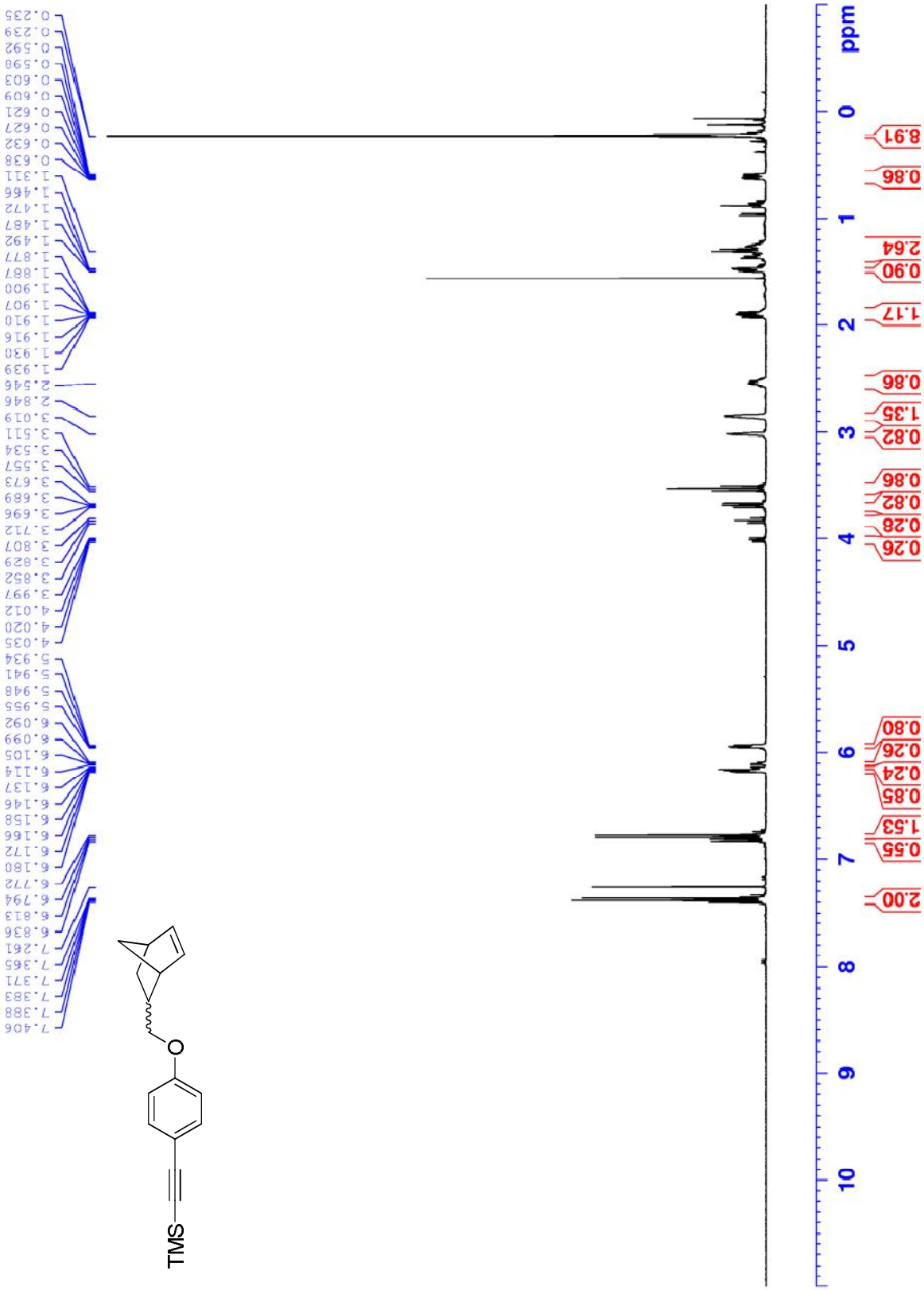
^{1}H NMR spectrum of **S10** (500 MHz, $CDCl_3$)



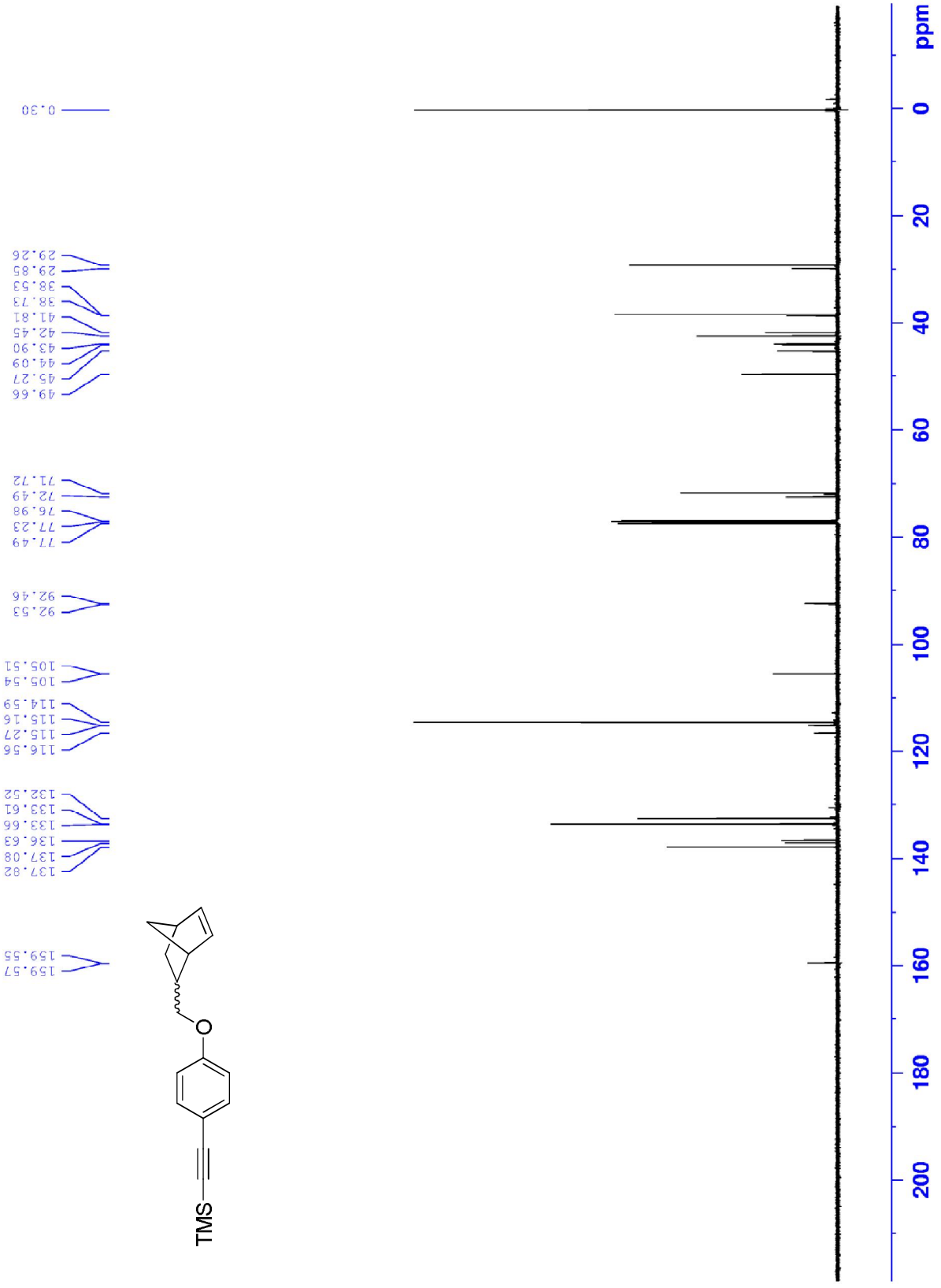
^{13}C NMR spectrum of **S10** (125 MHz, $CDCl_3$)



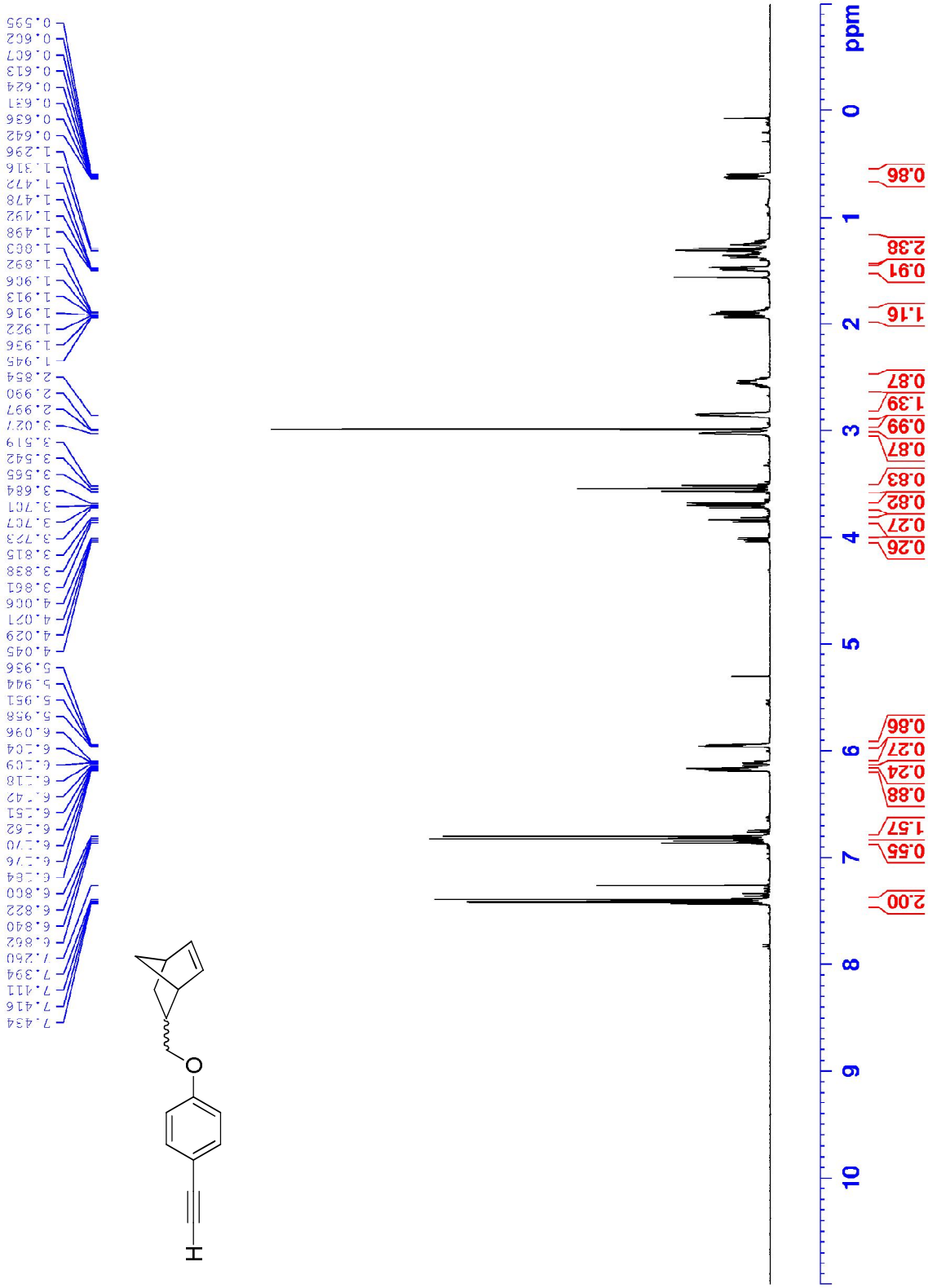
^{1}H NMR spectrum of **S11** (500 MHz, $CDCl_3$)



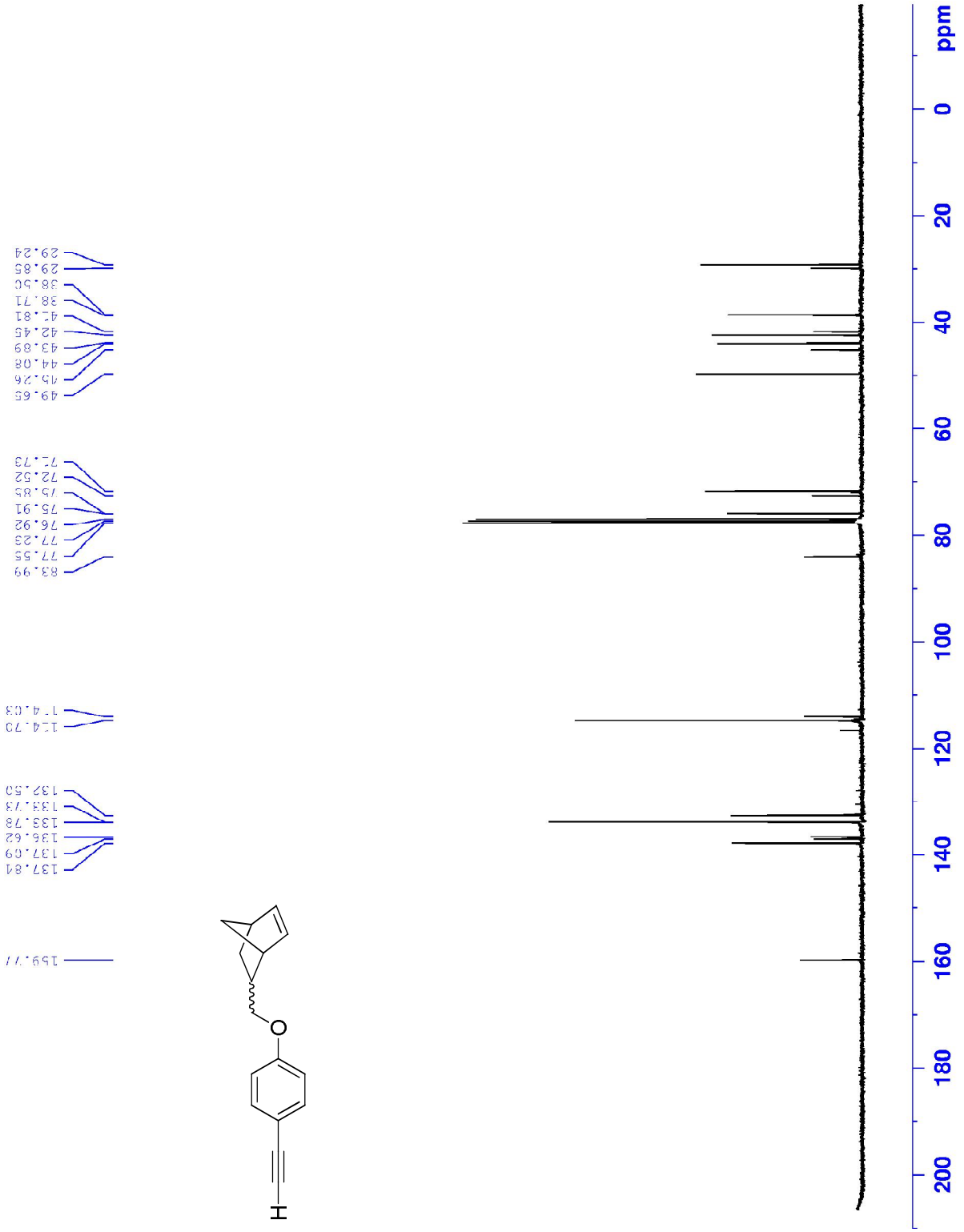
^{13}C NMR spectrum of **S11** (125 MHz, $CDCl_3$)



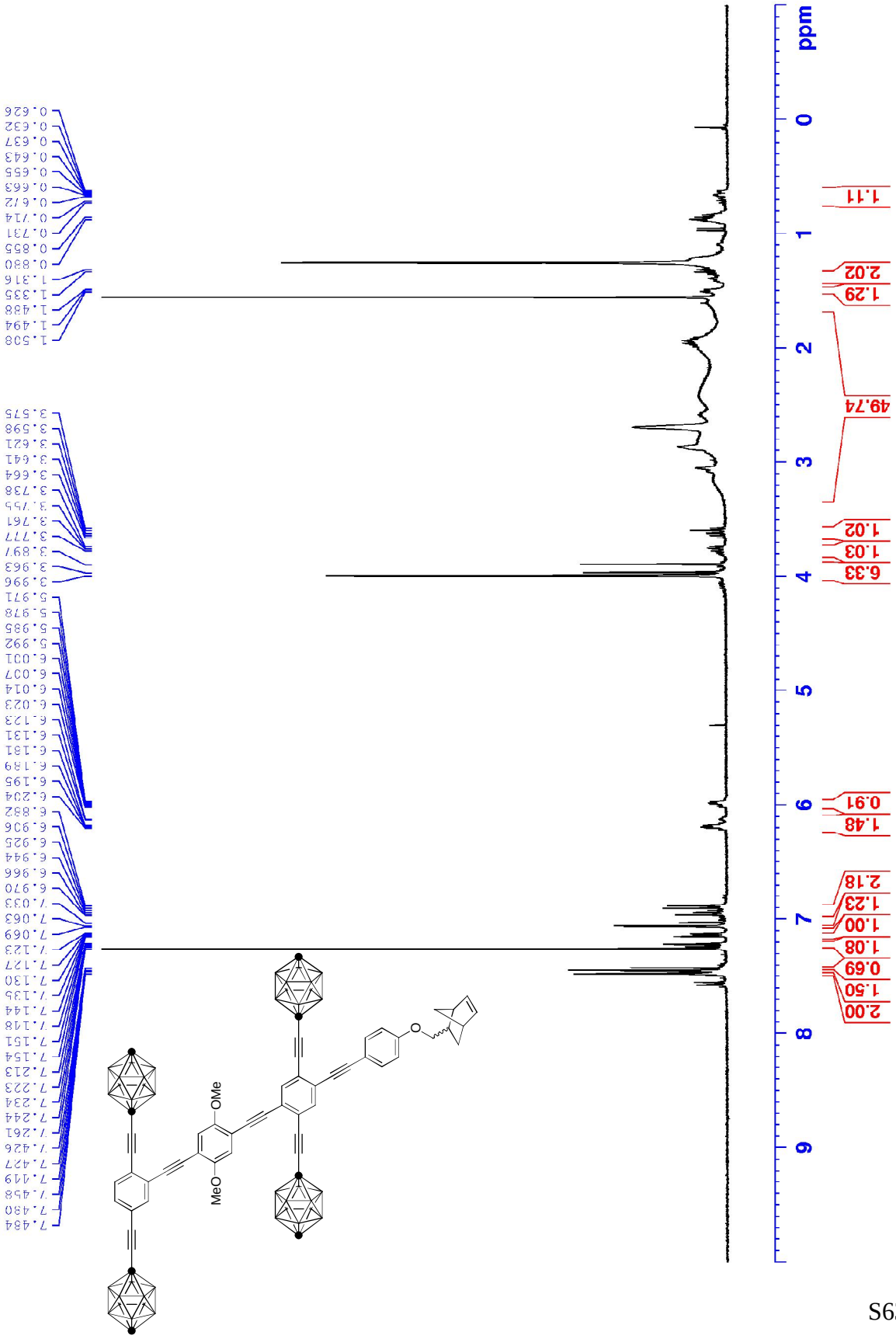
^{1}H NMR spectrum of **S12** (500 MHz, $CDCl_3$)



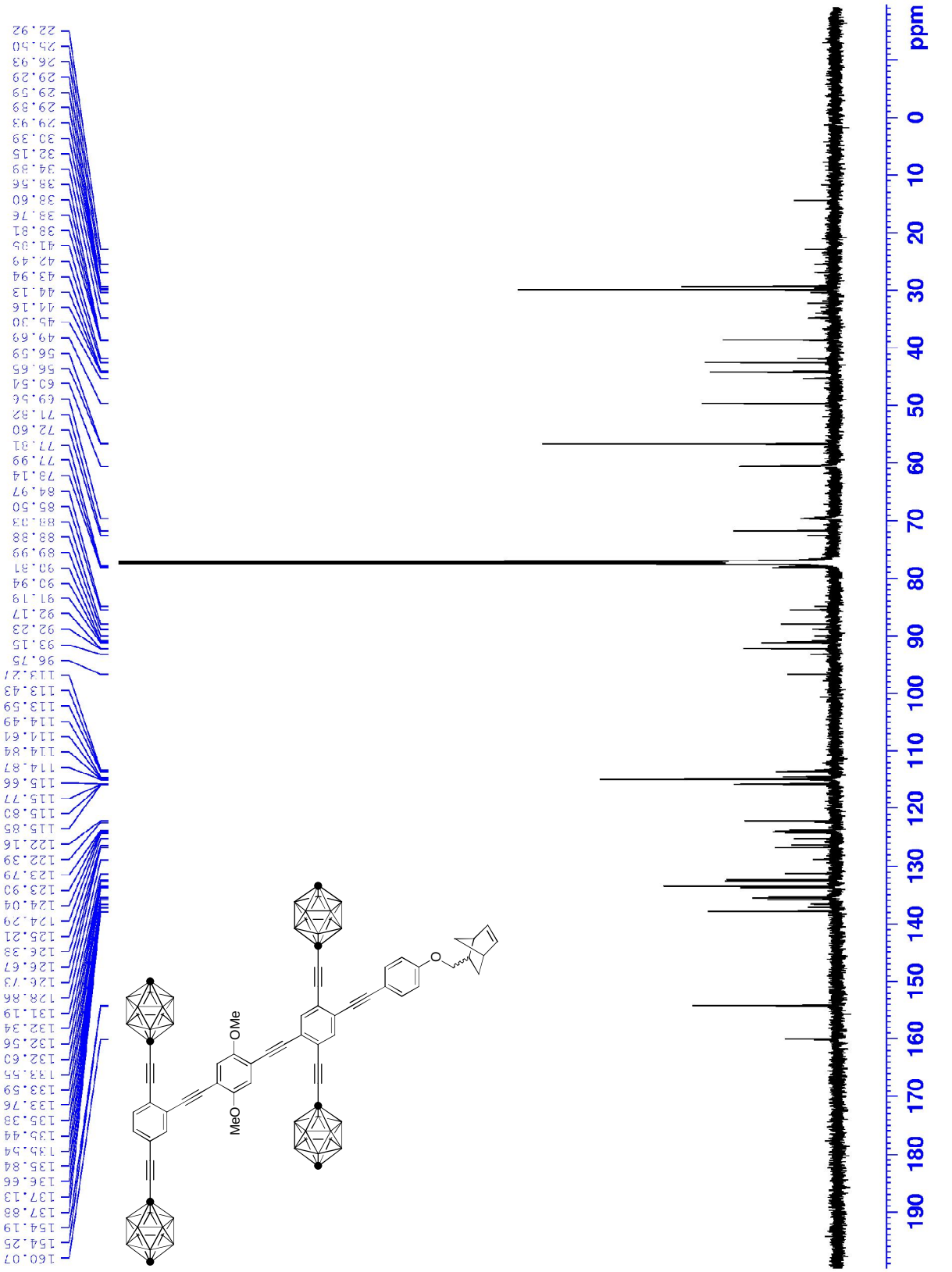
^{13}C NMR spectrum of **S12** (125 MHz, $CDCl_3$)



^{1}H NMR spectrum of **S13** (500 MHz, $CDCl_3$



^{13}C NMR spectrum of **S13** (125 MHz, $CDCl_3$)



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