Photoinduced Electron Transfer as a Probe for the Folding Behavior of Dimethylsilylene-Spaced Alternating Donor-Acceptor Oligomers and Polymers

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Supplementary Information

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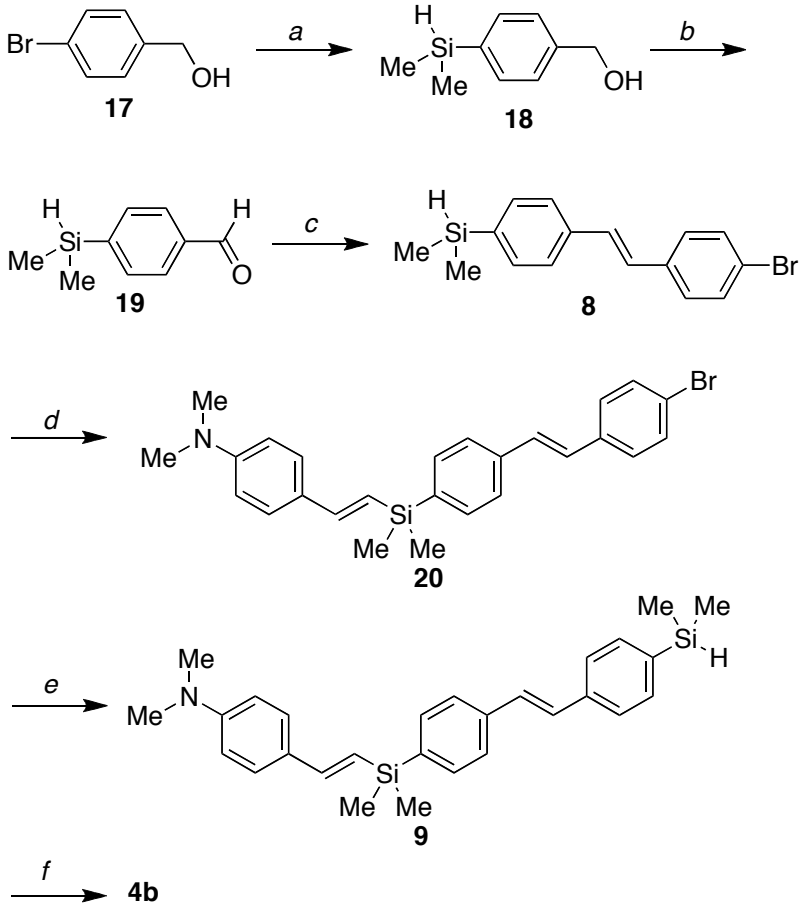
Experimental details



Scheme S1. *a* *n*-BuLi, $ClMe_2SiH$, 81%; *b* MnO_2, 83%; *c* $(EtO)_2POCH_2C_6H_4Br$-4, NaH, 65%; *d* NaI, $Rh(PPh_3)_3Cl$, $Me_2NC_6H_4C{\equiv}CH$ (**7**), 56%; *e* *n*-BuLi, Me_2SiHCl, 99%; *f* NaI, $Rh(PPh_3)_3Cl$, $HC{\equiv}CC_6H_4NMe(CH_2)_3NMeC_6H_4C{\equiv}CH$ (**10**), 41%.

4-(Dimethylsilyl)benzyl alcohol (18). Under N_2, to a solution of **17** (5.61 g, 30.0 mmol) in THF (200 mL) was added *n*-BuLi in hexane (46.9 mL, 1.6 M, 75.0 mmol) at -78 ºC and the mixture was stirred under N_2 for 1 h. $ClMe_2SiH$ (4.5 mL, 40 mmol) was then introduced and the mixture was gradually warmed to rt. After further stirring for 1 h, the mixture was quenched with sat. $NaHCO_3$. The organic layer was washed with water, brine and dried (Na_2SO_4). After evaporation of the solvent in vacuo, the residue was chromatographed on silica gel (25% EtOAc/hexane) to give **18** (4.05 g, 81%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.37 (d, J = 3.6 Hz, 6 H), 1.68 (t, J = 6.0 Hz, 1 H), 4.44 (sept, J = 3.6 Hz, 1 H), 4.71 (d, J = 6.0 Hz, 2

H), 7.37 (d, J = 7.6 Hz, 2 H), 7.55 (d, J = 7.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -3.6, 65.3, 126.3, 134.2, 136.7, 141.7; IR (KBr) ν 3328, 3063, 3015, 2959, 2901, 2118, 1397, 1249, 1109, 1016, 882 cm^{-1}; HRMS (FAB) (M - H) cacld for $C_9H_{13}OSi$: 165.0736; Found: 165.0736.

4-(Dimethylsilyl)benzaldehyde (19). Under N_2, a solution of **18** (2.00 g, 12.0 mmol) in dry CH_2Cl_2 (30 mL) was added to a suspension of activated MnO_2 (10.46 g, 120.0 mmol) in dry CH_2Cl_2 (30 mL) at rt, and the mixture was stirred for 5 h under N_2. After passing through a silica gel bed, the filtrate was evaporated in vacuo to give **19** (1.63 g, 83%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.40 (d, J = 3.7 Hz, 6 H), 4.47 (sept, J = 3.7 Hz, 1 H), 7.71 (d, J = 8.0 Hz, 2 H), 7.85 (d, J = 8.0 Hz, 2 H), 10.02 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -3.9, 128.6, 134.4, 136.6, 145.9, 192.2; IR (KBr) ν 3028, 2957, 2823, 2734, 2124, 1702, 1596, 1557, 1381, 1251, 1211, 1104, 881 cm^{-1}. HRMS (FAB) (M + H) cacld for $C_9H_{13}OSi$: 165.0736; Found: 165.0735.

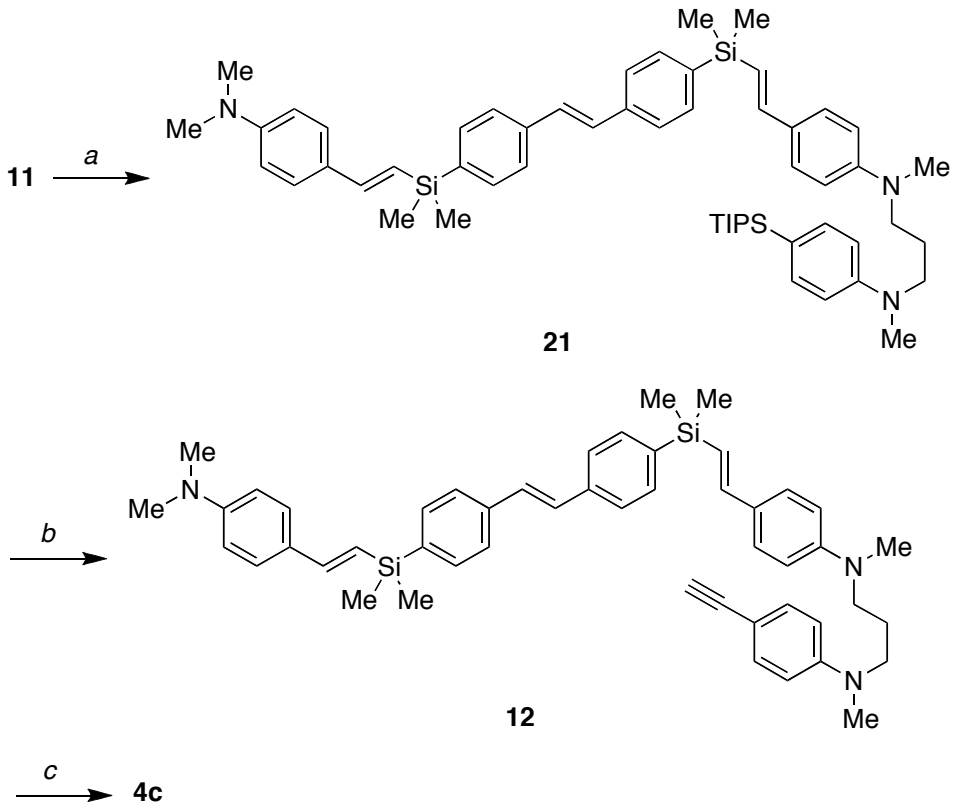
(*E*)-4-bromo-4'-(dimethylsilyl)stilbene (8). Under N_2, a solution of 4-bromobenzyl phosphonate[S1] (1.46 g, 4.75 mmol) in dry THF (15 mL) was added to a suspension of NaH (0.1741 g, 60 wt%, 4.35 mmol) in dry THF (10 mL) at rt. After refluxed for 1 h, **19** (0.65 g, 3.96 mmol) in dry THF (15 mL) was introduced under N_2 and the mixture was refluxed under N_2 for 3 h. After cooling to rt, the mixture was washed with water, brine and dried ($MgSO_4$). After evaporation of the solvent in vacuo, the residue was chromotographed on silica gel (hexane) to give **8** (0.81 g, 65%) as a white solid: mp 141-142 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.38 (d, J = 3.7 Hz, 6 H), 4.45 (sept, J = 3.7 Hz, 1 H), 7.06 (d, J = 16.4 Hz, 1 H), 7.10 (d, J = 16.4 Hz, 1 H), 7.38 (d, J = 8.5 Hz, 2 H), 7.48 (d, J = 8.5 Hz, 2 H), 7.50 (d, J = 8.1 Hz, 2 H), 7.54 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -3.6, 121.3, 125.8, 127.7, 127.9, 129.2, 131.6, 134.3, 136.1, 137.2, 137.6; IR (KBr) ν 3063, 3040, 3015, 2958, 2111, 1482, 1401, 1325, 1251, 967, 887, 825 cm^{-1}. HRMS (EI) (M) cacld for $C_{16}H_{17}{}^{79}BrSi$: 316.0283; Found: 316.0275.

4-Bromo-4'-[dimethyl(4-N,N-dimethylamino-*E*-styryl)silyl]-*E*-stilbene (20). Under N_2, to a solution of **8** (0.95 g, 3.0 mmol), NaI (0.45 g, 3.0 mmol), and $Rh(PPh_3)_3Cl$ (0.14 g, 0.16 mmol) in dry THF (22 mL) was added 4-ethynyl-*N*,*N*-dimethylaniline[S2] (0.49 g, 3.4 mmol) in dry THF (8 ml) slowly and the mixture was refluxed under N_2 for 5 h. After cooling to rt, the mixture was poured into methanol. The precipitate was collected and flash-chromatographed on silica gel (33% CH_2Cl_2/hexane) to give **20** (0.77 g, 56%) as a white solid: mp 161-162 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.44 (s, 6 H), 2.98 (s, 6 H), 6.31 (d, *J* = 19.0 Hz, 1 H), 6.69 (d, *J* = 8.9 Hz, 2 H), 6.88 (d, *J* = 19.0 Hz, 1 H), 7.06 (d, *J* = 16.3 Hz, 1 H), 7.11 (d , *J* = 16.3 Hz, 1 H), 7.36 (d, J = 8.9 Hz, 2 H), 7.38 (d, *J* = 8.8 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.49, (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -2.1, 40.5, 112.1, 120.7, 121.2, 125.7, 126.7, 127.45, 127.47, 127.9, 129.4, 131.6, 134.3, 136.2, 137.2, 139.2, 145.3, 150.4; IR (KBr) ν 3012, 2981, 2946, 2882, 2803, 1600, 1519, 1354, 1244, 971, 821 cm^{-1}; HRMS (FAB) (M) cacld for $C_{26}H_{28}N^{79}BrSi$: 461.1174; Found: 461.1176.

4-Dimethylsilyl-4'-[dimethyl(4-N,N-dimethylamino-*E*-styryl)silyl]-*E*-stilbene (9). Under N_2, to a solution of **20** (0.70 g, 1.51 mmol) in dry THF (15 mL) was added *n*-BuLi in hexane (1.3 mL, 1.6 M, 2.0 mmol) at -78 ^oC and the mixture was stirred under N_2. After 1 h, a freshly distilled chlorodimethylsilane (0.21 mL, 1.82 mmol) was added under N_2 and the mixture was gradually warmed to rt. After further stirring for 2 h, the mixture was quenched with sat. $NaHCO_3$. The organic layer was washed with water, brine and dried ($MgSO_4$). After evaporation of the solvent in vacuo, the residue was dissolved in dichloromethane and reprecipitated in methanol to give **9** (0.66 g, 99%) as a white solid: mp 114-115 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.37 (d, *J* = 3.6 Hz, 6 H), 0.43 (s, 6 H), 2.98 (s, 6 H), 4.44 (sept, *J* = 3.6 Hz, 1 H), 6.31 (d, *J* = 19.0 Hz, 1 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 6.87 (d, *J* = 19.0 Hz, 1 H), 7.14 (ABq, *J* = 16.4 Hz, 2 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 7.50 (d, *J* = 7.9 Hz, 2 H), 7.50 (d, *J* = 8.3 Hz, 2 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.57 (d, *J* = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100

MHz) δ -3.6, -2.1, 40.6, 112.2, 121.0, 125.7, 125.8, 127.5, 128.65, 128.73, 129.1, 134.2, 136.8, 137.6, 138.0, 138.9, 145.2, 151.3; IR (KBr) ν 3060, 3014, 2954, 2898, 2800, 2115, 1598, 1553, 1519, 1355, 1247, 1181, 1112, 882 cm^{-1}; HRMS (FAB) (M) cacld for $C_{28}H_{35}NSi_2$: 441.2308; Found: 441.2309.

Compound 4b. Under N_2, to a solution of **9** (0.26 g, 0.60 mmol), NaI (73 mg, 0.48 mmol), and $Rh(PPh_3)_3Cl$ (22 mg, 0.024 mmol) in dry THF (2 mL) was added 2,6-Bis(4-ethynylphenyl)-2,6-diazaheptane (**10**)[S2] (73 mg, 0.24 mmol) in dry THF (1 ml) slowly and the mixture was refluxed under N_2 for 5 h. After cooling to rt, the mixture was poured into methanol. The precipitate was collected and dissolved in THF, and then reprecipitated with MeOH and hexane, respectively, to give **4b** (0.130 g, 41%) as a white solid: mp 126-127 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.41 (s, 24 H), 1.88 (quint, J = 7.3 Hz, 2 H), 2.94 (s, 6 H), 2.97 (s, 12 H), 3.38 (t, *J* = 7.3 Hz, 4 H), 6.30 (d, *J* = 19.0 Hz, 1 H), 6.31 (d, *J* = 19.0 Hz, 2 H), 6.64, (d, *J* = 8.7 Hz, 4 H), 6.68 (d, *J* = 8.7 Hz, 4 H), 6.86 (d, *J* = 19.0 Hz, 2 H), 6.88 (d, *J* = 19.0 Hz, 2 H), 7.14 (s, 4 H), 7.33 (d, *J* = 8.7 Hz, 4 H), 7.35, (d, *J* = 8.7 Hz, 4 H), 7.50 (d, *J* = 7.7 Hz, 4 H), 7.57 (d, *J* = 7.7 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -2.3, 24.3, 38.4, 40.4, 50.3, 112.1, 112.2, 121.0, 125.8, 126.8, 126.9, 127.6, 127.8, 129.0, 134.4, 137.8, 138.86, 138.91, 145.3, 145.4, 149.3, 150.6; IR (KBr) ν 3060, 3011, 2951, 2892, 2802, 1600, 1518, 1354, 1246, 1181, 1109, 985, 853, 811 cm^{-1}; HRMS (FAB) (M) cacld for $C_{77}H_{92}N_4Si_4$: 1184.6399; Found: 1184.6399.



Scheme S2. *a* NaI, **9**, $Rh(PPh_3)_3Cl$, 35%; *b* TBAF, 97%; *c* NaI, $Rh(PPh_3)_3Cl$, **6**, 51%.

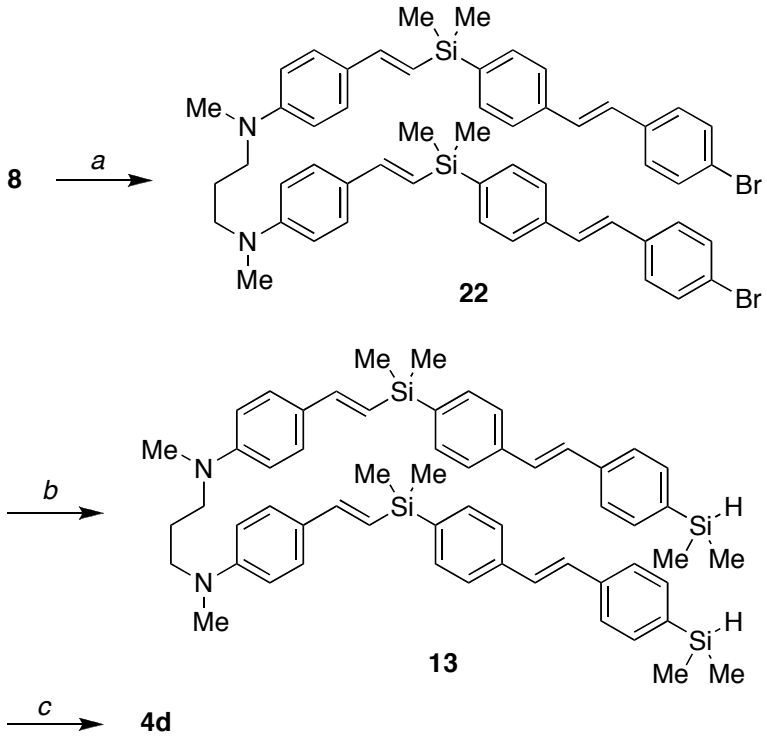
Compound 21. Under N_2, to a solution of **9** (0.66 g, 1.5 mmol), NaI (0.68 g, 4.5 mmol), and $Rh(PPh_3)_3Cl$ (70 mg, 0.08 mmol) in THF (10 mL) was added N,N'-Dimethyl-N-[4-(triisopropylsilyl)ethynylphenyl]-N'-[4-(ethynyl)phenyl]-propan e-1,3-diamine (**11**)[S3] (0.89 g, 1.9 mmol) in dry THF (5 ml) slowly and the mixture was refluxed under N_2 for 5 h. After cooling to rt, the mixture was poured into methanol. The precipitate was collected and flash-chromatographed on silica gel (50% CH_2Cl_2/hexane) to give **21** (0.47 g, 35%) as a white solid: mp 141-142 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.44 (s, 12 H), 1.13-1.14 (m, 21 H), 1.88 (quint, *J* = 7.0 Hz, 2 H), 2.94 (s, 3 H), 2.95 (s, 3 H), 2.98 (s, 6 H), 3.38 (t, *J* = 7.0 Hz, 4 H), 6.31 (d, *J* = 19.2 Hz, 1 H), 6.32 (d, *J* = 19.2 Hz, 1 H), 6.58 (d, *J* = 8.8 Hz, 2 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 6.69 (d, *J* = 8.8 Hz, 2 H), 6.87 (d, *J* = 19.2 Hz, 1 H), 6.88 (d, *J* = 19.2 Hz, 1 H), 7.15 (s, 2 H), 7.33-7.37 (m, 6 H), 7.339 (d, *J* = 8.8 Hz, 2 H), 7.341 (d, J = 8.8 Hz, 2 H), 7.36 (d, *J* = 8.8 Hz, 2 H) 7.51 (d, *J* = 7.4 Hz, 4 H), 7.57 (d, *J* = 7.4 Hz, 4 H); ^{13}C

NMR ($CDCl_3$, 100 MHz) δ -2.1, 11.6, 18.9, 24.4, 38.4, 38.5, 40.5, 50.2, 50.3, 87.3, 108.2, 110.5, 111.5, 112.0, 112.1, 120.9, 121.0, 125.7, 126.8, 127.5, 127.6, 128.8, 133.2, 134.2, 137.7, 138.8, 145.1, 145.2, 148.7, 149.1, 150.4; IR (KBr) ν 3091, 3060, 2953, 2863, 2145, 1605, 1518, 1355, 1246, 1182, 1109, 985, 836, 812 cm^{-1}; HRMS (MALDI) (M + H) cacld for $C_{58}H_{78}N_3Si_3$: 900.5504; Found: 900.5525.

Compound 12. Under N_2, to a solution of **21** (0.20 g, 0.22 mmol) in THF (2 mL) was added tetrabutylammonium chloride trihydrate (84 mg, 0.26 mmol) in THF (1 mL) and the mixture was stirred under N_2. After 30 min, the mixture was poured into diethyl ether to give **12** (0.16 g, 97%) as a white solid: mp 146-147 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.42 (s, 6 H), 0.44 (s, 6 H), 0.42 (s, 12 H), 1.88 (quint, *J* = 7.2 Hz, 2 H), 2.948 (s, 3 H), 2.951 (s, 3 H), 2.98 (s, 7 H), 3.39 (t, *J* = 7.2 Hz, 4 H), 6.32 (d, *J* = 19.0 Hz, 1 H), 6.32 (d, *J* = 19.0 Hz, 1 H), 6.58 (d, J = 9.2 Hz, 2 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 6.87 (d, *J* = 19.0 Hz, 1 H), 6.88 (d, *J* = 19.0 Hz, 1 H), 7.15 (s, 2 H), 7.32-7.36 (m, 6 H), 7.34 (d, *J* = 8.8 Hz, 2 H), 7.35 (d, *J* = 9.2 Hz, 2 H), 7.36 (d, *J* = 8.8 Hz, 2 H), 7.51 (d, *J* = 8.2 Hz, 4 H), 7.58 (d, *J* = 8.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -1.7, 24.6, 38.6, 38.8, 40.7, 50.3, 50.4, 74.8, 84.7, 108.5, 111.3, 111.85, 111.91, 120.6, 120.8, 125.5, 126.5, 127.2, 127.4, 128.6, 132.9, 133.9, 137.3, 138.40, 138.44, 144.7, 144.9, 148.6, 148.7, 150.0; IR (KBr) ν 3297, 3060, 3012, 2952, 2895, 2822, 2097, 1606, 1518, 1356, 1246, 1181, 1109, 985, 836, 812 cm^{-1}. HRMS (MALDI) (M + H) cacld for $C_{49}H_{58}N_3Si_2$: 744.4169; Found: 744.4186.

Compound 4c. Under N_2, to a solution of $\mathbf{6}^{S2}$ (20.7 mg, 0.07 mmol), NaI (63 mg, 0.42 mmol), and $Rh(PPh_3)_3Cl$ (6.5 mg, 0.007 mmol) in THF (1 mL) was added slowly **12** (0.11g, 0.15 mmol) in THF (1 mL) and the mixture was refluxed under N_2 for 16 h. After cooling to rt, the mixture was poured into MeOH. The precipitate was collected and dissolved in THF, and then reprecipitated with MeOH and hexane, respectively, to give **4c** (0.063 g, 51%) as a white solid: mp 138-139 ^oC; ^1H NMR

(CD_2Cl_2, 400 MHz): δ 0.42 (s, 36 H), 1.88 (quint, *J* = 7.2 Hz, 6 H), 2.94 (s, 12 H), 2.96 (s, 12 H), 3.38 (t, *J* = 7.2 Hz, 12 H), 6.28-6.36 (m, 6 H), 6.64-6.68 (m, 12 H), 6.85-6.90 (m, 6 H), 7.16 (s, 6 H), 7.31-7.35 (m, 12 H), 7.52 (d, *J* = 7.6 Hz, 12 H), 7.58 (d, *J* = 7.6 Hz, 12 H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ -2.0, 24.9, 38.8, 40.7, 50.8, 112.55, 112.61, 121.2, 121.3, 126.4, 127.2, 127.3, 128.1, 128.2, 129.4, 134.9, 138.3, 139.6, 145.96, 146.03, 150.0, 151.3; IR (KBr) ν 3061, 3014, 2953, 2896, 2821, 1600, 1519, 1363, 1247, 1182, 1109, 985, 836, 812 cm^{-1}; HRMS (MALDI) (M + Na) cacld for $C_{116}H_{138}N_6Si_6Na$: 1805.9496; Found: 1805.9542.



Scheme S3. *a* NaI, HC≡CC_6H_4NMe$(CH_2)_3$NMeC_6H_4C≡CH (**10**), 63%; *b* *n*-BuLi, Me_2SiHCl, 40%; *c* **12**, NaI, $Rh(PPh_3)_3Cl$, 39%.

Compound 22. Under N_2, to a solution of **8** (0.91 g, 2.88 mmol), NaI (0.43 g, 2.88 mmol), and $Rh(PPh_3)_3Cl$ (0.13 g, 0.14 mmol) in dry THF (20 mL) was added 2,6-Bis(4-ethynylphenyl)-2,6-diazaheptane (**10**)[S2] (0.41 g, 1.4 mmol) in dry THF (5 ml) slowly and the mixture was refluxed under N_2 for 5 h. After cooling to rt, the mixture was poured into methanol. The precipitate was collected and

flash-chromatographed on silica gel (50% CH_2Cl_2/hexane) to give **22** (0.80 g, 63%) as a white solid: mp 176-178 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.43 (s, 12 H), 1.89 (quint, *J* = 7.2 Hz, 2 H), 2.95 (s, 6 H), 3.39 (t, *J* = 7.2 Hz, 4 H), 6.30 (d, *J* = 19.0 Hz, 2 H), 6.64 (d, *J* = 8.8 Hz, 4 H), 6.87 (d, *J* = 19.0 Hz, 2 H), 7.05 (d, *J* = 16.4 Hz, 2 H), 7.10 (d, *J* = 16.4 Hz, 2 H), 7.34 (d, *J* = 8.8 Hz, 4 H), 7.38 (d, *J* = 8.5 Hz, 4 H), 7.47 (d, *J* = 8.5 Hz, 4 H), 7.48 (d, *J* = 8.1 Hz, 4 H), 7.57 (d, *J* = 8.1 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -2.1, 24.4, 38.5, 50.4, 112.0, 120.8, 121.2, 125.7, 126.7, 127.5, 127.6, 127.9, 129.4, 131.6, 134.3, 136.2, 137.2, 139.1, 145.2, 149.1; IR (KBr) ν 3060, 3015, 2953, 2895, 2819, 1600, 1517, 1485, 1377, 1246, 1181, 1105, 1072, 965, 814 cm^{-1}; HRMS (MALDI) (M + H) cacld for $C_{53}H_{57}{}^{79}Br_2N_2Si_2$: 935.2427; Found: 935.2448.

Compound 13. Under N_2, to a solution of **22** (0.52 g, 0.56 mmol) in dry THF (5 mL) was added *n*-BuLi in hexane (0.9 mL, 1.6 M, 1.3 mmol) at -78 ^oC and the mixture was stirred under N_2. After 1 h, a freshly distilled chlorodimethylsilane (0.2 mL, 1.80 mmol) was added under N_2 and the mixture was gradually warmed to rt. After further stirring for 2 h, the mixture was quenched with sat. $NaHCO_3$. The organic layer was washed with water, brine and dried ($MgSO_4$). After evaporation of the solvent in vacuo, the residue was dissolved in dichloromethane and reprecipitated in methanol to give **13** (0.20 g, 40%) as a white solid: mp 121-122 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 0.38 (d, *J* = 4.0 Hz, 12 H), 0.44 (s, 12 H), 1.90 (quint, *J* = 7.2 Hz, 2 H), 2.95 (s, 6 H), 3.39 (t, *J* = 7.2 Hz, 4 H), 4.46 (sept, *J* = 4.0 Hz, 2 H), 6.31 (d, *J* = 19.0 Hz, 2 H), 6.65 (d, *J* = 8.7 Hz, 4 H), 6.87 (d, *J* = 19.0 Hz, 2 H), 7.15 (ABq, *J* = 16.0 Hz, 4 H), 7.35 (d, *J* = 8.7 Hz, 4 H), 7.51(d, *J* = 8.1 Hz, 4 H), 7.52 (d, *J* = 8.2 Hz, 4 H), 7.55 (d, *J* = 8.2 Hz, 4 H), 7.58 (d, *J* = 8.1 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -3.2, -1.7, 24.6, 38.7, 50.5, 111.8, 120.6, 125.5, 125.6, 126.4, 127.4, 128.4, 128.8, 133.9, 136.4, 137.2, 137.7, 138.5, 144.8, 148.7; IR (KBr) ν 3060, 3015, 2955, 2898, 2822, 2116, 1598, 1518, 1377, 1247, 1181, 1112, 985, 965, 882, 837, 814 cm^{-1}; HRMS (MALDI) (M + H) cacld for $C_{57}H_{71}N_2Si_4$: 895.4694; Found: 865.4713.

Compound 4d. Under N_2, to a solution of **13** (44.8 mg, 0.050 mmol), NaI (30.0 mg, 0.20 mmol), and $Rh(PPh_3)_3Cl$ (4.7 mg, 0.005 mmol) in dry THF (1 mL) was added slowly **12** (78.2 mg, 0.11 mmol) in THF (1 mL) and the mixture was refluxed under N_2 for 16 h. After cooling to rt, the mixture was poured into MeOH. The precipitate was collected and dissolved in THF, and then reprecipitated with MeOH and hexane, respectively, to give **4d** (0.046 g, 39%) as a white solid: mp 143-144 ^oC; ^1H NMR (CD_2Cl_2, 400 MHz): δ 0.41 (s, 48 H), 1.87 (quint, J = 7.2 Hz, 6 H), 2.93 (s, 18 H), 2.95 (s, 12 H), 3.38 (t, J = 7.2 Hz, 12 H), 6.27-6.33 (m, 8 H), 6.63-6.68 (m, 16 H), 6.84-6.90 (m, 8 H), 7.16 (s, 8 H), 7.31-7.34 (m, 16 H), 7.51 (d, J = 8.0 Hz, 16 H), 7.57 (d, J = 8.0 Hz, 16 H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ -2.1, 24.8, 38.8, 40.7, 50.8, 112.5, 112.6, 121.20, 121.25, 126.3, 127.2, 127.3, 128.1, 128.2, 129.4, 134.9, 138.3, 139.6, 145.9, 146.0, 150.0, 151.3; IR (KBr) ν 3059, 3012, 2951, 2893, 1599, 1518, 1354, 1246, 1181, 1109, 984, 835, 811 cm^{-1}; HRMS (MALDI) (M + Na) cacld for $C_{155}H_{184}N_8Si_8Na$: 2404.2695; Found: 2404.2744.

***N,N',2,2*-Tetramethyl-*N,N'*-diphenylpropane-1,3-diamine (14b).** Under N_2, a CH_2Cl_2 solution (50 mL) of 2,2-Dimethylmalonic acid (6.6 g, 50 mmol) was slowly added a CH_2Cl_2 solution (50 mL) of oxalyl chloride (12.9 mL, 150 mmol) at 0 ^oC. After being refluxed for 20 h, the mixture was cooled to rt, and the solvent and residual oxalyl chloride were removed in vacuo to give the residue (7.9 g), which was used directly for the next reaction. Under N_2, a THF solution (250 mL) of *N*-methylaniline (10.8 mL, 100 mmol) and K_2CO_3 (27.6 g, 200 mmol) was slowly added a THF solution (100 mL) of the above residue (8.1 g) at 0 ^oC. After being stirred at rt for 12 h, the mixture was poured into iced water (300 mL). The aqueous layer was separated and extracted with ether (200 mL × 3), and the combined organic layer was washed with water (200 mL × 2) and brine (200 mL × 2), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was further dissolved in CH_2Cl_2 (200 mL) and slowly added to a slurry of LAH (10 g, 250 mmol) in ether

(200 mL) at 0 °C. After being stirred at rt for 10 h, the reaction was carefully quenched with water (25 mL). The insoluble salt was removed by filtration and washed with CH_2Cl_2 (150 mL × 2). The filtrate was collected, dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was chromatographed on silica gel (hexane/CH_2Cl_2 = 2/1) to give **14b** (8.9 g, 65% over 3 steps) as a sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 6 H), 2.98 (s, 6 H), 3.26 (s, 4 H), 6.64-6.67 (m, 2 H), 6.73-6.76 (m, 4 H), 7.17-7.21 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 47.8, 42.6, 62.2, 111.9, 115.9, 128.8, 150.5; IR (KBr) ν 3097, 3060, 3022, 2970, 2812, 2819, 1935, 1913, 1598, 1502, 1451, 1344, 1289, 1265, 1092, 1035, 990, 966, 862, 745, 691, 514 cm^{-1}; HRMS (FAB) (M) calcd for $C_{19}H_{26}N_2$ 282.2103, found 282.2096.

***N,N'*-Bis(4-(2-trimethylsilyl)ethynylphenyl)-*N,N'*-dimethylethylenediamine (15a).** *N*-Bromosuccinimde (1.06 g, 6.0 mmol) was added to a $CHCl_3$ solution (30 mL) of *N,N'*-Dimethyl-*N,N'*-diphenylethylenediamine[S4] (0.72 g, 3 mmol) at 0 °C. After being stirred at 0 °C for 2 h, the mixture was poured into water (100 mL), and the aqueous layer was separated and extracted with $CHCl_3$ (100 mL × 2). The combined organic layer was washed with water (100 mL × 2) and brine (100 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was recrystalized from CH_2Cl_2/hexane (1/10) to give *N,N'*-Di(4-bromophenyl)-*N,N'*-dimethylethylenediamine (0.90g, 75%) as a white solid: mp 165-167 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 2.87 (s, 6 H), 3.48 (s, 4 H), 6.50-6.51 (m, 4 H), 7.25-7.28 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 49.9, 108.0, 113.1, 131.5, 147.1; IR (KBr) ν 3067, 2988, 2952, 2933, 2876, 2820, 2799, 1867, 1583, 1500, 1374, 960, 583, 505 cm^{-1}; HRMS (FAB) (M) calcd for $C_{16}H_{18}N_2{}^{79}Br_2$ 395.9842, found 395.9837. Under N_2, a piperidine solution (50 mL) of *N,N'*-Di(4-bromophenyl)-*N,N'*-dimethylethylenediamine (2.00 g, 5.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol), CuI (0.19 g, 1.0 mmol), PPh_3 (0.66 g, 2.5 mmol), and trimethylsilylethyne (2.15 mL, 15.0 mmol) was refluxed for 16 h, and the mixture was cooled to rt, passed through a celite bed (4 cm), and washed with $CHCl_3$ (200 mL). The filtrate was washed with water

(150 mL × 2) and brine (150mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was chromatographed on silica gel (hexane/CH_2Cl_2 = 3/1) to give **15a** (1.88 g, 87%) as a white solid: mp 137-139 ^oC; ^1H NMR (400MHz, $CDCl_3$) δ 0.25 (s, 18 H), 2.90 (s, 6 H), 3.55 (s, 4 H), 6.52 (d, *J* = 9.0 Hz, 4 H), 7.32 (d, *J* = 9.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.4, 38.8, 49.4, 91.4, 106.2, 109.9, 111.0, 133.2, 148.3; IR (KBr) ν 3045, 2956, 2917, 2851, 2149, 1605, 1515, 1380, 1248, 863, 841, 759 cm^{-1}; HRMS (FAB) (M) calcd for $C_{26}H_{36}N_2Si_2$ 432.2408, found 432.2417.

***N,N'*-Bis(4-(2-trimethylsilyl)ethynylphenyl)-*N,N',2,2*-tetramethylpropane-1,3-diamine (15b).** *N*-Bromosuccinimide (1.42 g, 8.0 mmol) was added to a $CHCl_3$ solution (40 mL) of **14b** (1.13 g, 4.0 mmol) at 0 ^oC. After being stirred at 0 ^oC for 2 h, the mixture was poured into water (100 mL), and the aqueous layer was separated and extracted with ether (100 mL × 3). The combined organic layer was washed with water (100 mL × 2) and brine (100 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was then recrystalized from CH_2Cl_2/hexane (1/10) to give *N,N'*-di(4-bromophenyl)-*N,N',2,2*-tetramethylpropane-1,3-diamine (1.09 g, 62%) as a white solid: mp 165-166 ^oC; ^1H NMR (400MHz, $CDCl_3$) δ 1.04 (s, 6 H), 2.99 (s, 6 H), 3.24 (s, 4 H), 6.62 (d, *J* = 8.0 Hz, 4 H), 7.27 (d, *J* = 8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 42.0, 42.9, 62.0, 107.8, 113.6, 131.4, 149.3; IR (KBr) ν 3091, 2956, 2873, 2821, 1858, 1585, 1497, 1378, 1343, 1310, 1192, 1092, 965, 806, 644, 506 cm^{-1}; HRMS (FAB) (M) calcd for $C_{19}H_{24}{}^{79}Br_2N_2$ 438.0306, found 438.0298. Under N_2, a piperidine solution (50 mL) of *N,N'*-di(4-bromophenyl)-*N,N',2,2*- tetramethylpropane-1,3-diamine (2.20 g, 5.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol), CuI (0.19 g, 1.0 mmol), PPh_3 (0.66 g, 2.5 mmol), and trimethylsilylethyne (2.15 mL, 15.0 mmol) was refluxed for 16 h, and the mixture was cooled to rt, passed through a celite bed (4 cm), and washed with $CHCl_3$ (150 mL). The filtrate was washed with water (150 mL × 2) and brine (150 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was chromatographed on silica gel (hexane/CH_2Cl_2 = 2/1) to give **15b** (2.16 g, 91%) as a

white solid: mp 122-123 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.24 (s, 18 H), 1.02 (s, 6 H), 3.02 (s, 6 H), 3.28 (s, 4 H), 6.62 (d, *J* = 8.8 Hz, 4 H), 7.31 (d, *J* = 8.8 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.4, 25.6, 41.8, 43.1, 61.5, 91.2, 106.3, 109.6, 111.4, 132.8, 150.1; IR (KBr) ν 3098, 3010, 2954, 2869, 2812, 2144, 1606, 1514, 1376, 1297, 1245, 1174, 1087, 968, 871, 759, 636, 543 cm^{-1}; HRMS (FAB) (M) calcd for $C_{29}H_{42}N_2Si_2$ 474.2887, found 474.2887.

***N,N'*-Dimethyl-*N,N'*-bis(4-(2-trimethylsilyl)ethynylphenyl)butane-1,4-diamine (15c).** *N*-Bromosuccinimide (1.42 g, 8.0 mmol) was added to a $CHCl_3$ solution (40 mL) of *N,N'*-Dimethyl-*N,N'*-diphenylbutane-1,4-diamine[S5] (1.07 g, 4.0 mmol) at 0 °C. After being stirred at 0 °C for 2 h, the mixture was poured into water (100 mL), and the aqueous layer was separated and extracted with ether (100 mL × 3). The combined organic layer was washed with water (100 mL × 2) and brine (100 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was then recrystallized from CH_2Cl_2/hexane (1/10) to give *N,N'*-Dimethyl-*N,N'*-di(4-bromophenyl)butane-1,4-diamine (1.11 g, 65%) as a white solid: mp 129-130 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.58 (m, 4 H), 2.89 (s, 6 H), 3.30 (t, *J* = 8.6 Hz, 4 H), 6.54 (d, *J* = 9.2 Hz, 4 H), 7.28 (d, *J* = 9.2 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 38.5, 52.7, 107.9, 113.7, 131.7, 148.0; IR (KBr) ν 3082, 3040, 2932, 2887, 2827, 2798, 1867, 1591, 1499, 1429, 1378, 1302, 1221, 1189, 1100, 1012, 952, 807, 759, 612, 507 cm^{-1}; HRMS (FAB) (M) calcd for $C_{18}H_{22}{}^{79}Br_2N_2$ 424.0150, found 424.0152. Under N_2, a piperidine solution (50 mL) of *N,N'*-Dimethyl-*N,N'*- di(4-bromophenyl) butane-1,4-diamine (2.13 g, 5.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol), CuI (0.19 g, 1.0 mmol), PPh_3 (0.66 g, 2.5 mmol), and trimethylsilylethyne (2.15 mL, 15.0 mmol) was refluxed for 16h, and the mixture was cooled to rt, passed through a celite bed (4 cm), and washed with $CHCl_3$ (150 mL). The filtrate was washed with water (150 mL × 2) and brine (150mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was chromatographed on silica gel (hexane/CH_2Cl_2 = 2/1) to give **15c** (2.07 g, 90%) as a white solid: mp 150-152 °C; ^{1}H NMR (400MHz, $CDCl_3$)

δ 0.24 (s, 18 H), 1.58 (m, 4 H), 2.93 (s, 6 H), 3.34 (m, 4 H), 6.55 (d, *J* = 8.6 Hz, 4 H), 7.32 (d, *J* = 8.6 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.4, 24.5, 38.4, 52.3, 91.1, 106.4, 109.5, 111.3, 133.1, 148.8; IR (KBr) ν 3093, 3040, 2953, 2896, 2829, 2148, 1875, 1607, 1518, 1469, 1376, 1302, 1248, 1183, 1095, 1004, 953, 864, 812, 756, 632, 537 cm^{-1}; HRMS (FAB) (M) calcd for $C_{28}H_{40}N_2Si_2$ 460.2730, found 460.2726.

***N,N'*-Bis(4-(2-(trimethylsilyl)ethynyl)phenyl)piperazine (15d).** *N*-Bromosuccinimide (1.42 g, 8.0 mmol) was added to a $CHCl_3$ solution (40 mL) of *N,N'*-Diphenylpiperazine[S6] (1.03 g, 4.0 mmol) at 0 °C. After being stirred at 0 °C for 2 h, the mixture was poured into water (100 mL), and the aqueous layer was separated and extracted with ether (100 mL × 3). The combined organic layer was washed with water (100 mL × 2) and brine (100 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was then recrystallized from CH_2Cl_2/hexane (1/10) to give *N,N'*-Di(4-bromophenyl)piperazine (0.91 g, 53%) as a white solid: mp 260 °C dec.; ^{1}H NMR (400MHz, $CDCl_3$) δ 3.28 (s, 8 H), 6.84 (d, *J* = 9.2 Hz, 4 H), 7.37 (d, *J* = 9.2 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.2, 112.3, 117.8, 131.8, 149.9; IR (KBr) ν 3091, 3040, 2954, 2879, 2831, 1877, 1582, 1491, 1449, 1331, 1226, 940, 815, 512 cm^{-1}; HRMS (FAB) (M) calcd for $C_{16}H_{16}{}^{79}Br_2N_2$ 393.9683, found 393.9680. Under N_2, a piperidine solution (10 mL) of *N,N'*-Di(4-bromophenyl)piperazine (396 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), CuI (38 mg, 0.2 mmol), PPh_3 (132 mg, 0.5 mmol), and trimethylsilylethyne (0.43 mL, 3.0 mmol) was refluxed for 16 h, and the mixture was cooled to rt, passed through a celite bed (3 cm), and washed with $CHCl_3$ (100 mL). The filtrate was washed with water (100 mL × 2) and brine (100 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was chromatographed on silica gel (hexane/CH_2Cl_2 = 2/1) to give **15d** (344 mg, 80%) as a white solid: mp 162 °C (dec); ^{1}H NMR (400MHz, $CDCl_3$) δ 0.26 (s, 18 H), 3.37 (s, 8 H), 6.85 (d, *J* = 8.4 Hz, 4 H), 7.38 (d, *J* = 8.4 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.3, 48.3, 92.2, 105.6, 113.5, 115.0, 133.0, 150.5; IR (KBr) ν 3036, 2999, 2957, 2897, 2834, 2153, 1603, 1509, 1385, 1239, 1151, 866,

837, 550 cm^{-1}; HRMS (FAB) (M) calcd for $C_{26}H_{34}N_2Si_2$ 430.2260, found 430.2261.

***N,N'*-Di(4-ethynylphenyl)-*N,N'*-dimethylethylenediamine (16a).** Under N_2, a THF/MeOH (1/1) solution (30 mL) of **15a** (250 mg, 0.58 mmol) and K_2CO_3 (320 mg, 2.32 mmol) was stirred at rt for 4 h, and the mixture was poured into water (50 mL). The aqueous layer was separated and extracted with ether (50 mL × 3), and the combined organic layer was washed with water (50 mL × 2) and brine (50 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was flash-chromatographed on silica gel (hexane/CH_2Cl_2 = 5/4) to give **16a** (134 mg, 80%) as a white solid: mp 144-145 ^oC; ^1H NMR (400MHz, $CDCl_3$) δ 2.92 (s, 6 H), 2.99 (s, 2 H), 3.56 (s, 4 H), 6.56 (d, *J* = 9.2 Hz, 4 H) , 7.35 (d, *J* = 9.2 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.8, 49.5, 74.9, 84.6, 108.8, 111.1, 133.3, 148.5; IR (KBr) ν 3296, 3075, 3046, 2940, 2826, 2093, 1606, 1514, 1385, 1321, 1239, 653, 560 cm^{-1}; HRMS (FAB) (M) calcd for $C_{20}H_{20}N_2$ 288.1623, found 288.1626.

***N,N'*-Di(4-ethynylphenyl)-*N,N',2,2*-Tetramethylpropane-1,3-diamine (16b).** Under N_2, a THF/MeOH (1/1) solution (30 mL) of **15b** (250 mg, 0.53 mmol) and K_2CO_3 (366 mg, 2.65 mmol) was stirred at rt for 4 h, and the mixture was poured into water (50 mL). The aqueous layer was separated and extracted with ether (50 mL × 3), and the combined organic layer was washed with water (50 mL × 2) and brine (50 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was flash-chromatographed on silica gel (hexane/CH_2Cl_2 = 3/2) to give **16b** (144 mg, 82%) as a white solid: mp 130-131^oC; ^1H NMR (400MHz, $CDCl_3$) δ 1.05 (s, 6 H), 2.98 (s, 2 H), 3.03 (s, 6 H), 3.30 (s, 4 H), 6.66 (d, *J* = 9.0 Hz, 4 H), 7.34 (d, *J* = 9.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 41.8, 43.0, 61.6, 74.8, 84.7, 108.6, 111.5, 132.9, 150.3; IR (KBr) ν 3282, 3098, 3010, 2967, 2944, 2867, 2813, 2095, 1606, 1516, 1460, 1375, 1343, 1299, 1217, 1169, 1087, 898, 817, 670, 563, 532 cm^{-1}; HRMS (FAB) (M) calcd for $C_{23}H_{26}N_2$ 330.2096, found 330.2099.

***N,N'*-Di(4-ethynylphenyl) -*N,N'*-dimethylbutane-1,4-diamine (16c).** Under N_2, a THF/MeOH (1/1) solution (30 mL) of **15c** (250 mg, 0.54 mmol) and K_2CO_3 (369 mg, 2.71 mmol) was stirred at rt for 4 h, and the mixture was poured into water (50 mL). The aqueous layer was separated and extracted with ether (50 mL × 3), and the combined organic layer was washed with water (50 mL × 2) and brine (50 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was flash-chromatographed on silica gel (hexane/CH_2Cl_2 = 3/2) to give **16c** (145 mg, 85%) as a white solid: mp 125-126 ^oC; ^1H NMR (400MHz, $CDCl_3$) δ 1.59 (m, 6 H), 2.92 (s, 6 H), 2.96 (s, 2 H), 3.33 (t, *J* = 6.8 Hz, 4 H), 6.56 (d, *J* = 8.4 Hz, 4 H), 7.33 (d, *J* = 8.4 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 38.4, 52.3, 74.7, 84.8, 108.4, 111.3, 133.2, 148.9; IR (KBr) ν 3270, 3093, 3042, 2943, 2892, 2095, 1608, 1518, 1466, 1378, 1305, 1225, 1177, 1094, 1008, 955, 905, 819,670, 591, 531 cm^{-1}; HRMS (FAB) (M) calcd for $C_{22}H_{24}N_2$ 316.1939, found 316.1932.

***N,N'*-Di(4-ethynylphenyl)piperazine (16d).** Under N_2, a THF/MeOH (2/1) solution (40 mL) of **15d** (155 mg, 0.36 mmol) and K_2CO_3 (200 mg, 1.44 mmol) was stirred at rt for 4 h, and the mixture was poured into water (50 mL). The aqueous layer was separated and extracted with ether (50 mL × 3), and the combined organic layer was washed with water (50 mL × 2) and brine (50 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue, which was flash-chromatographed on silica gel (hexane/CH_2Cl_2 = 2/1) to give **16d** (89 mg, 86%) as a white solid: mp 201-202 ^oC; ^1H NMR (400MHz, $CDCl_3$) δ 3.01 (s, 2 H), 3.39 (s, 8 H), 6.87 (d, *J* = 8.8 Hz, 4 H), 7.42 (d, *J* = 8.8 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.3, 75.6, 84.0, 112.4, 115.1, 133.1, 150.7; IR (KBr) ν 3294, 3037, 2960, 2923, 2847, 2816, 2364, 2099, 1602, 1509, 1229, 943, 820, 655 cm^{-1}; HRMS (FAB) (M) calcd for $C_{20}H_{18}N_2$ 286.1473, found 286.1470.

Polymer 5a. A mixture of **16a** (58 mg, 0.2 mmol), **6** (70 mg, 0.2 mmol), NaI (60 mg, 0.4 mmol), and $RhCl(PPh_3)_3$ (9 mg, 0.01 mmol) in THF (2 mL) was refluxed for

16 h. After being cooled to rt, the mixture was poured into MeOH (100 mL). The precipitate was collected, dissolved in THF (0.5 mL), and then reprecipitated from MeOH (100mL). The solid was collected by filtration and washed with MeOH (50 mL) (88 mg, 75%); Mn = 4600, PDI = 1.65; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.41 (br, 12 H), 2.92 (br, 6 H), 3.54 (br, 4 H), 6.27-6.32 (br, 2 H), 6.60-6.62 (br, 4 H), 6.83-6.87 (br, 2 H), 7.12 (br, 2H), 7.31-7.34 (br, 4 H), 7.47-7.56 (br, 8 H); IR (KBr) ν 3061, 3012, 2952, 2896, 2826, 2361, 1560, 1517, 1377, 1245, 1181, 1110, 985, 964, 835, 811, 665, 541 cm^{-1}.

Polymer 5b. A mixture of **16b** (66 mg, 0.2 mmol), **6** (70 mg, 0.2 mmol), NaI (60 mg, 0.4 mmol), and $RhCl(PPh_3)_3$ (9 mg, 0.01 mmol) in THF (2 mL) was refluxed for 16 h. After being cooled to rt, the mixture was poured into MeOH (100 mL). The precipitate was collected, dissolved in THF (0.5 mL), and then reprecipitated from MeOH (100 mL). The solid was collected by filtration and washed with MeOH (50 mL) (106 mg, 78%); Mn = 6800, PDI = 2.05; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.40 (br, 12 H), 1.03 (br, 6 H), 3.01 (br, 6 H), 3.28 (br, 4 H), 6.25-6.29 (br, 2 H), 6.67-6.69 (br, 4 H), 6.81-6.86 (br, 2 H), 7.11 (br, 2H), 7.29-7.31 (br, 4 H), 7.46-7.56 (br, 8 H); IR (KBr) ν 3061, 3012, 2951, 2896, 2822, 1600, 1517, 1376, 1246, 1179, 1110, 985, 966, 835, 811, 666, 540 cm^{-1}.

Polymer 5c. A mixture of **16c** (63 mg, 0.2 mmol), **6** (70 mg, 0.2 mmol), NaI (60 mg, 0.4 mmol), and $RhCl(PPh_3)_3$ (9 mg, 0.01 mmol) in THF (2 mL) was refluxed for 16 h. After being cooled to rt, the mixture was poured into MeOH (100 mL). The precipitate was collected, dissolved in THF (0.5 mL), and then reprecipitated from MeOH (100mL). The solid was collected by filtration and washed with MeOH (50 mL) (100 mg, 75%); Mn = 5500, PDI = 1.81; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.40 (br, 12 H), 1.58 (br, 4 H), 2.92 (br, 6 H), 3.33 (br, 4 H), 6.25-6.30 (br, 2 H), 6.60-6.62 (br, 4 H), 6.82-6.87 (br, 2 H), 7.11 (br, 2H), 7.30-7.33 (br, 4 H), 7.47-7.55 (br, 8 H); IR (KBr) ν 3061, 3010, 2953, 2873, 2822, 1602, 1553, 1516, 1479, 1420, 1378, 1344,

1298, 1247, 1179, 1109, 984, 966, 835, 811, 666, 540 cm^{-1}.

Polymer 5d. A mixture of **16d** (56 mg, 0.2 mmol), **6** (70 mg, 0.2 mmol), NaI (60 mg, 0.4 mmol), and $RhCl(PPh_3)_3$ (9 mg, 0.01 mmol) in THF (2 mL) was stirred at 45 ^oC for 10 h. After being cooled to rt, the mixture was poured into MeOH (100 mL). The precipitate was collected, dissolved in THF (0.5 mL), and then reprecipitated from MeOH (100mL). The solid was collected by filtration and washed with MeOH (50 mL) (87 mg, 75%): Mn = 3400, PDI = 1.43; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (br, 12 H), 3.30-3.37 (br, 8 H), 6.38-6.42 (br, 2 H), 6.86-6.94 (br, 6 H), 7.13-7.15 (br, 2 H), 7.36-7.40 (br, 4 H), 7.50-7.60 (br, 8H); IR (KBr) ν 3059, 3014, 2953, 2897, 2828, 2104, 1912, 1602, 1511, 1450, 1385, 1331, 1242, 1182, 1110, 1041, 986, 944, 834, 812, 667, 612 cm^{-1}.

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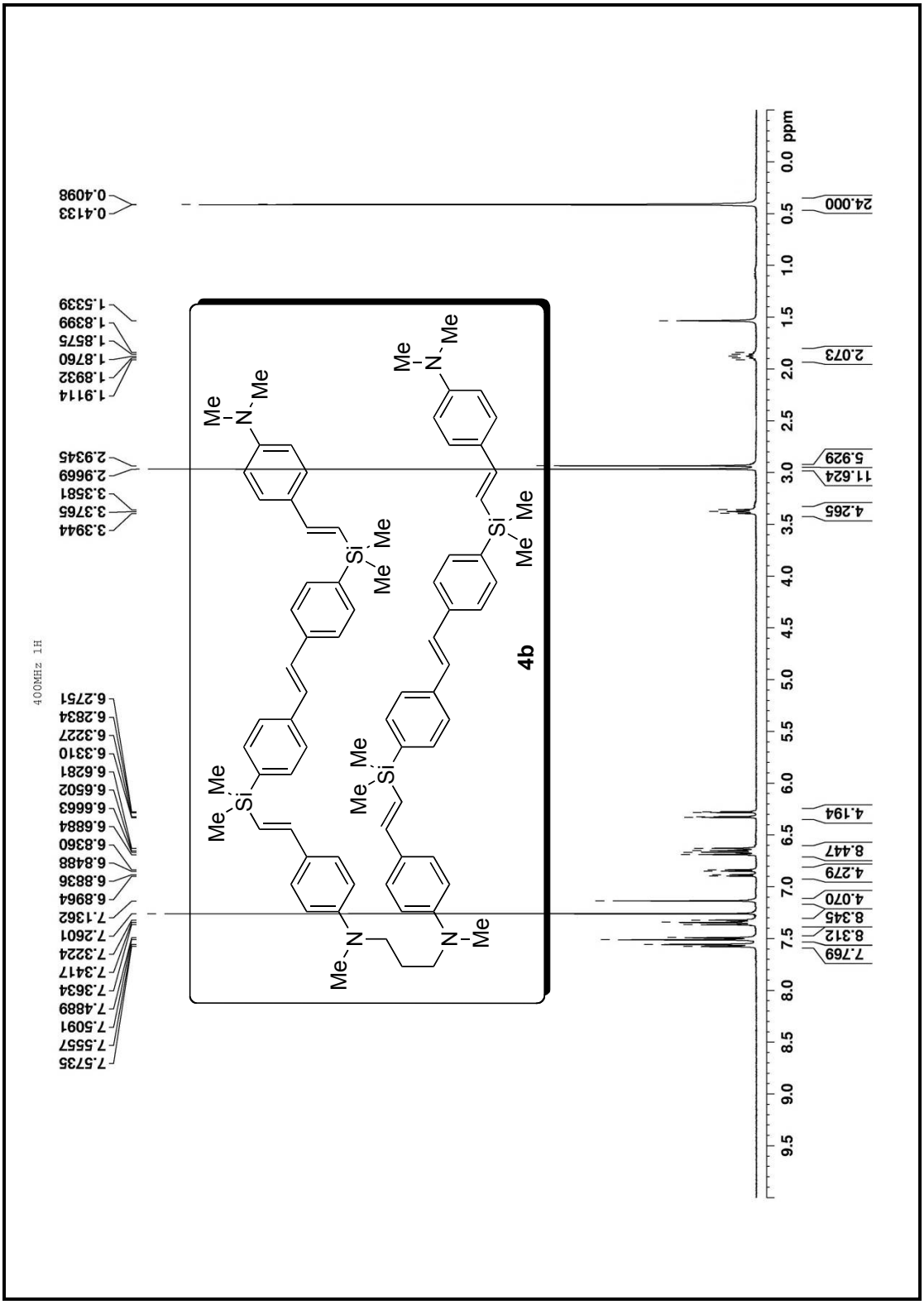

Figure S1. ^{1}H NMR spectrum of **4b**

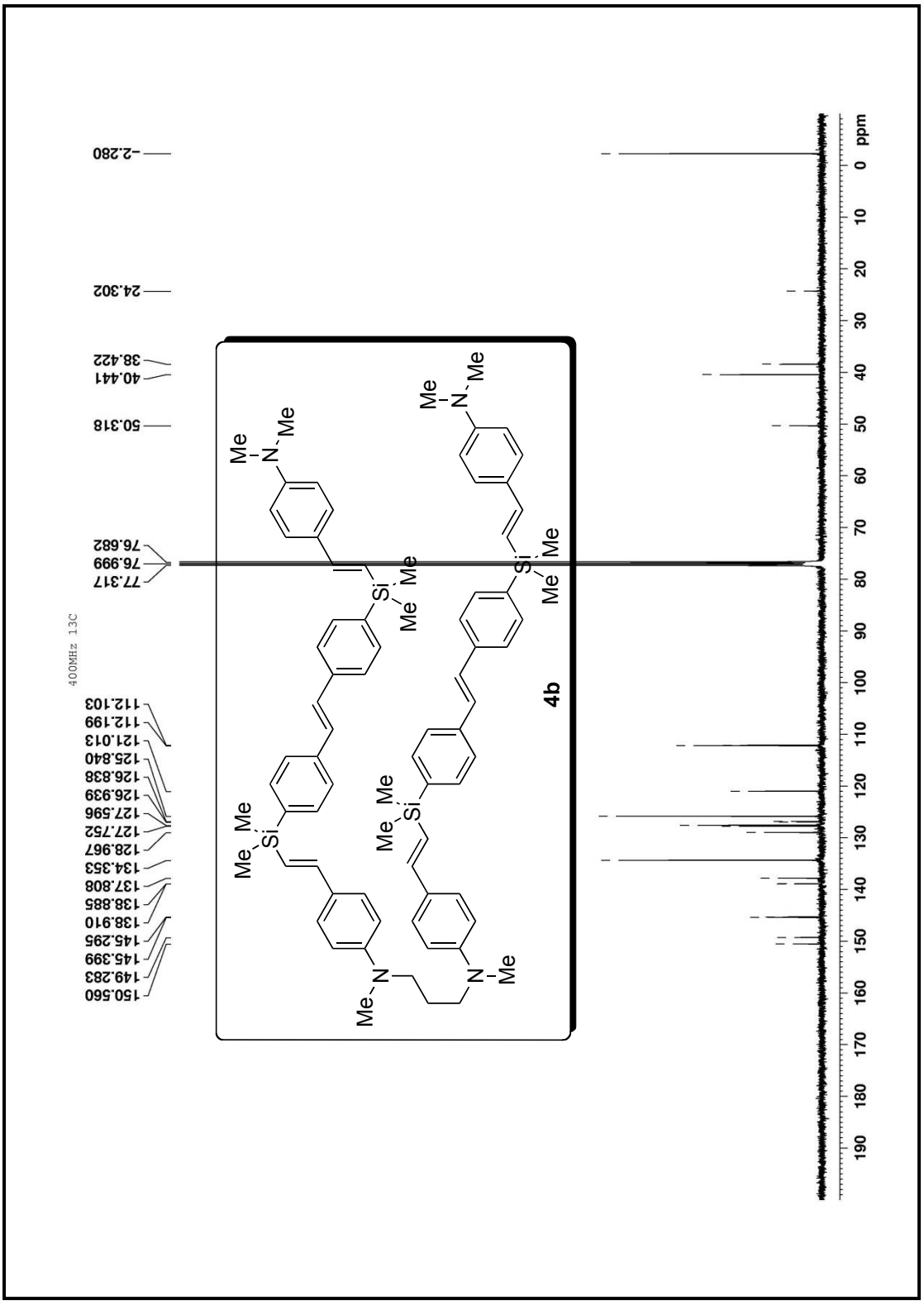

Figure S2. ^{13}C NMR spectrum of **4b**

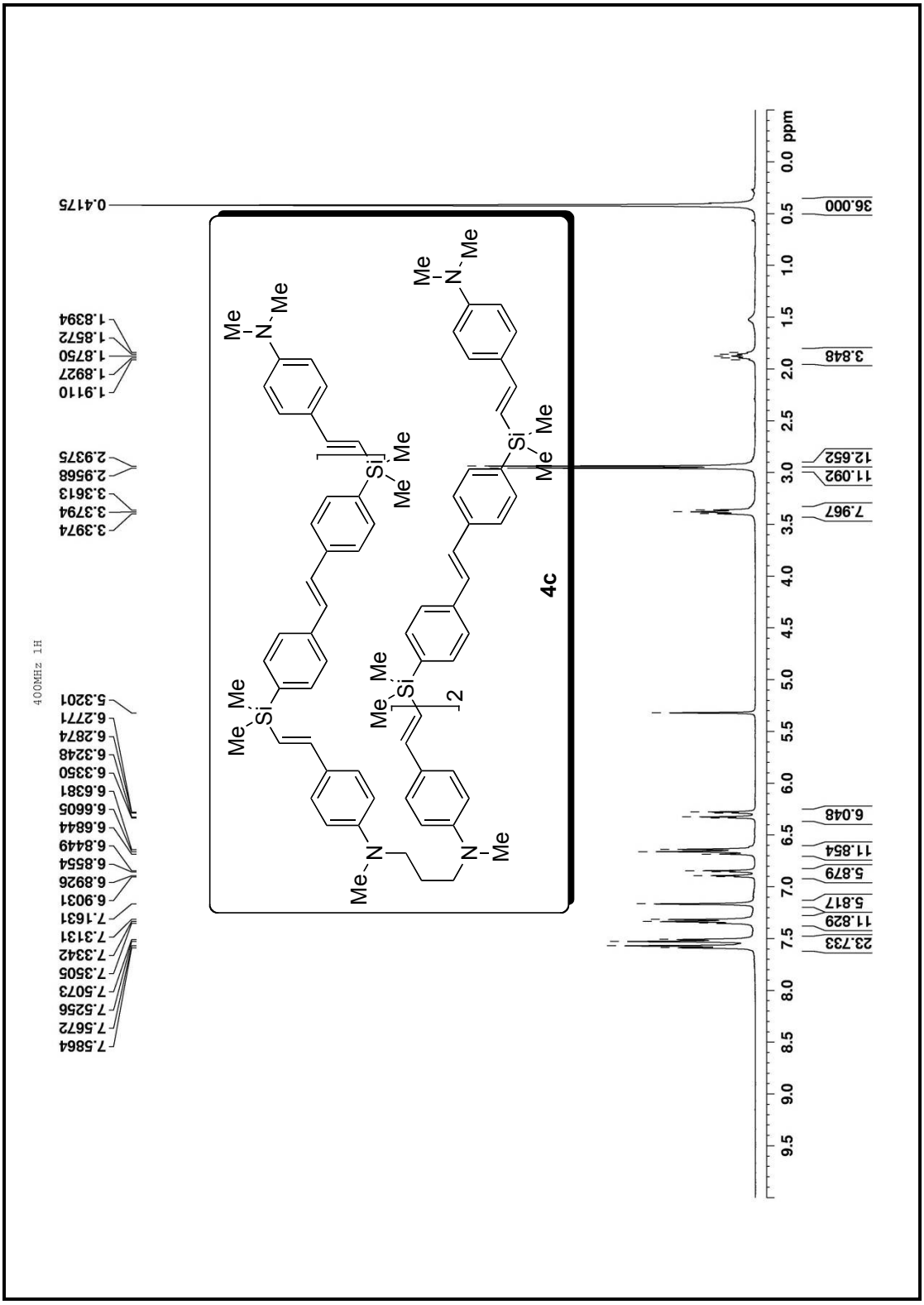

Figure S3. ^{1}H NMR spectrum of **4c**

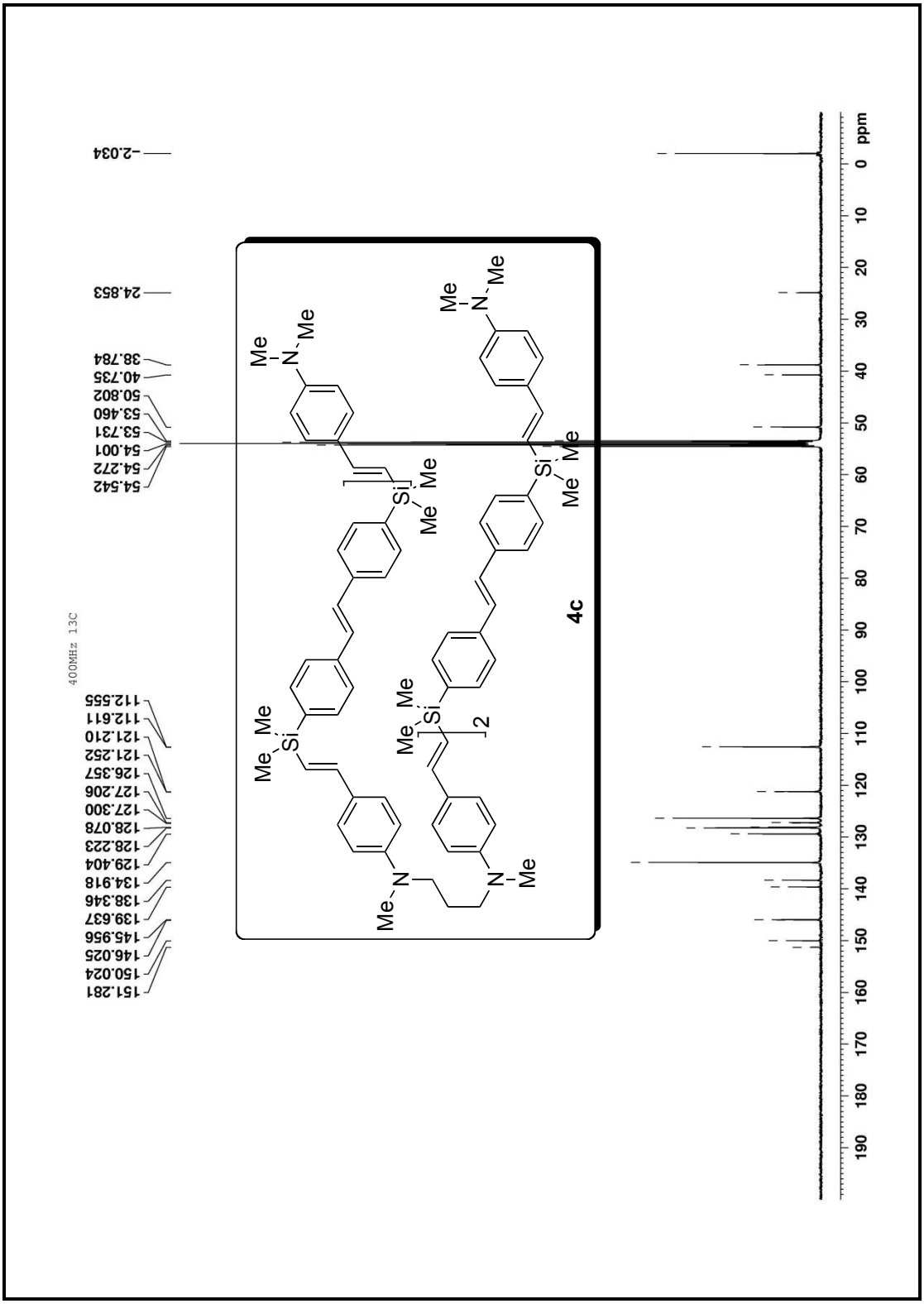

Figure S4. ^{13}C NMR spectrum of **4c**

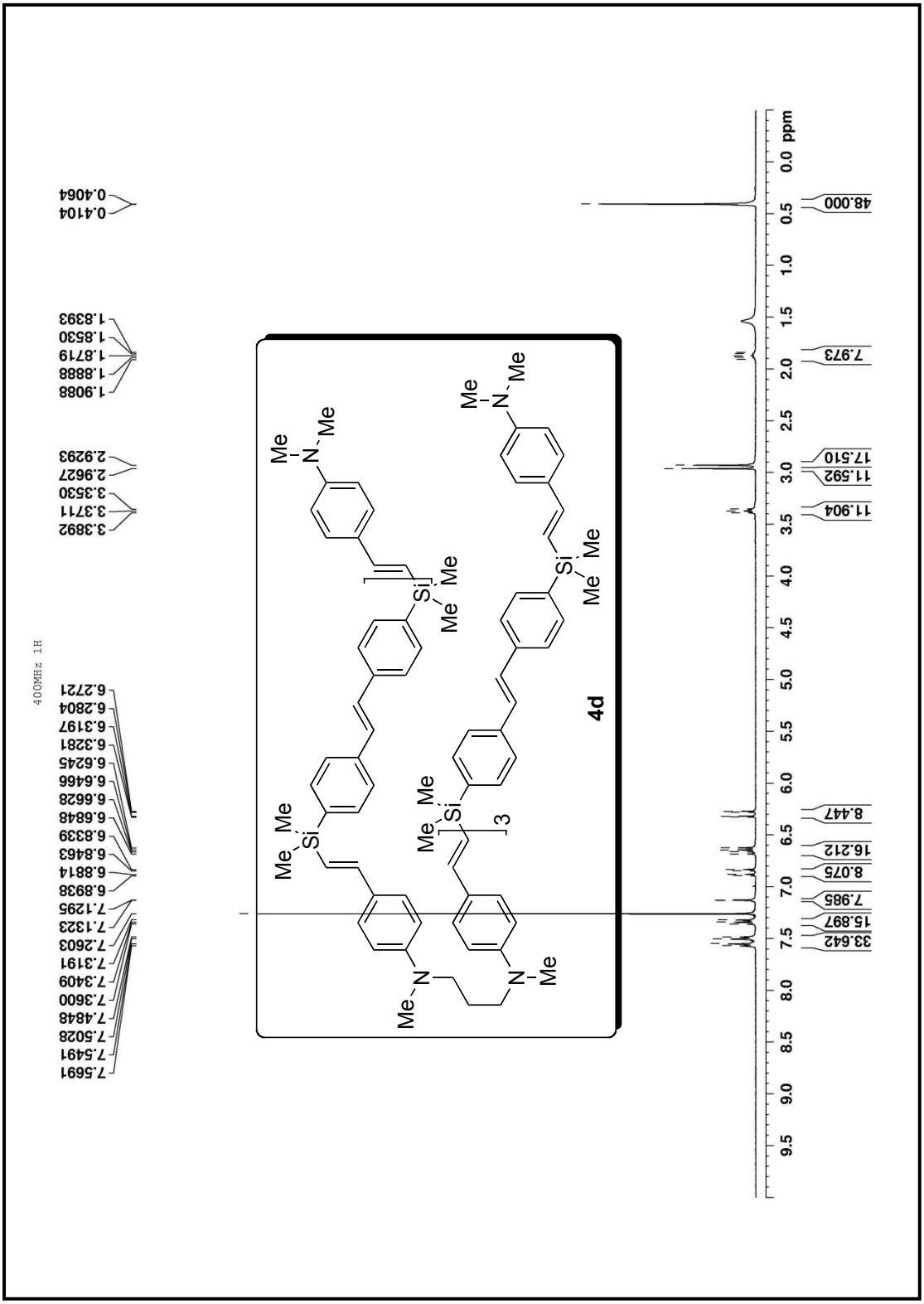

Figure S5. ^{1}H NMR spectrum of **4d**

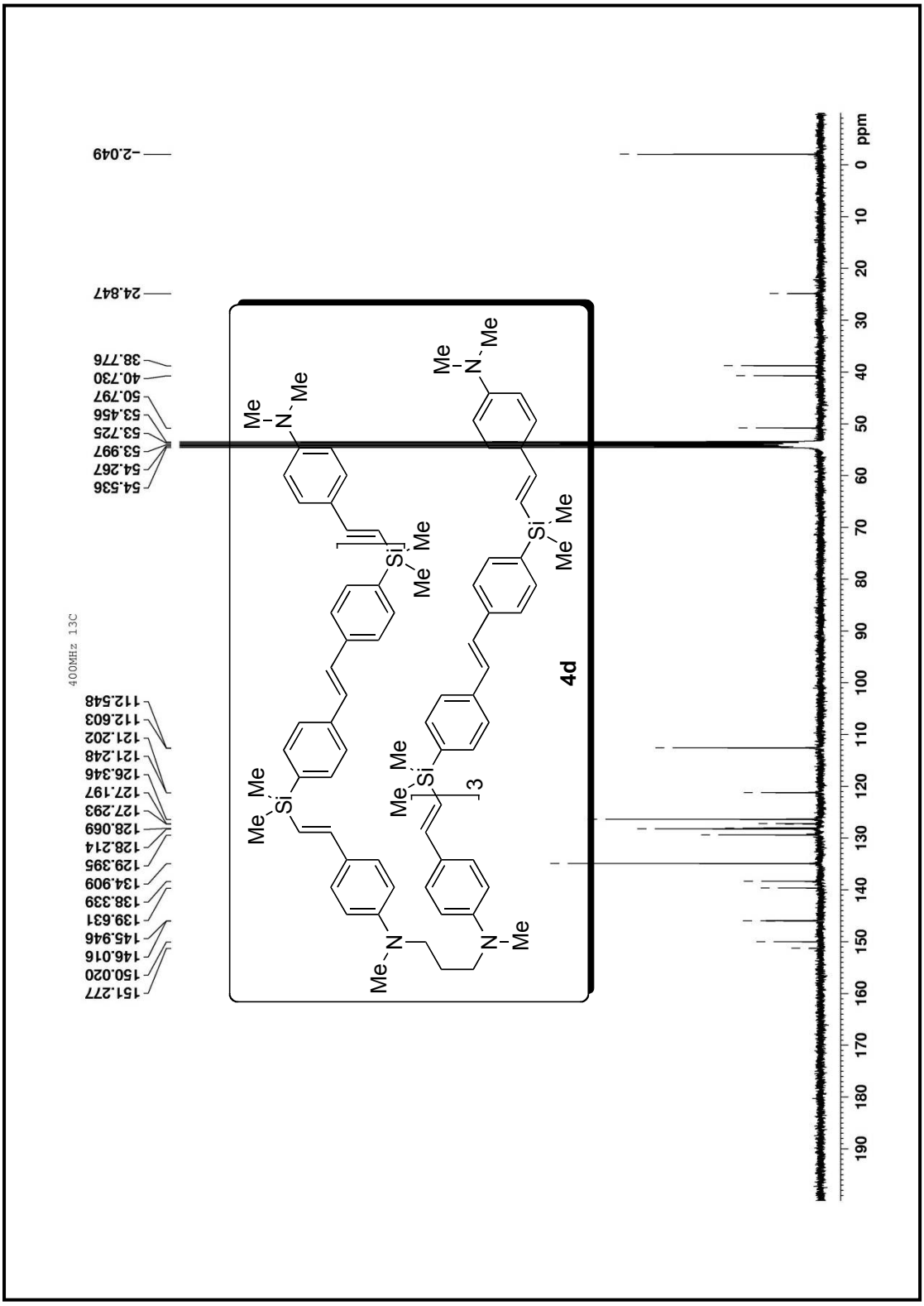

Figure S6. ^{13}C NMR spectrum of **4d**

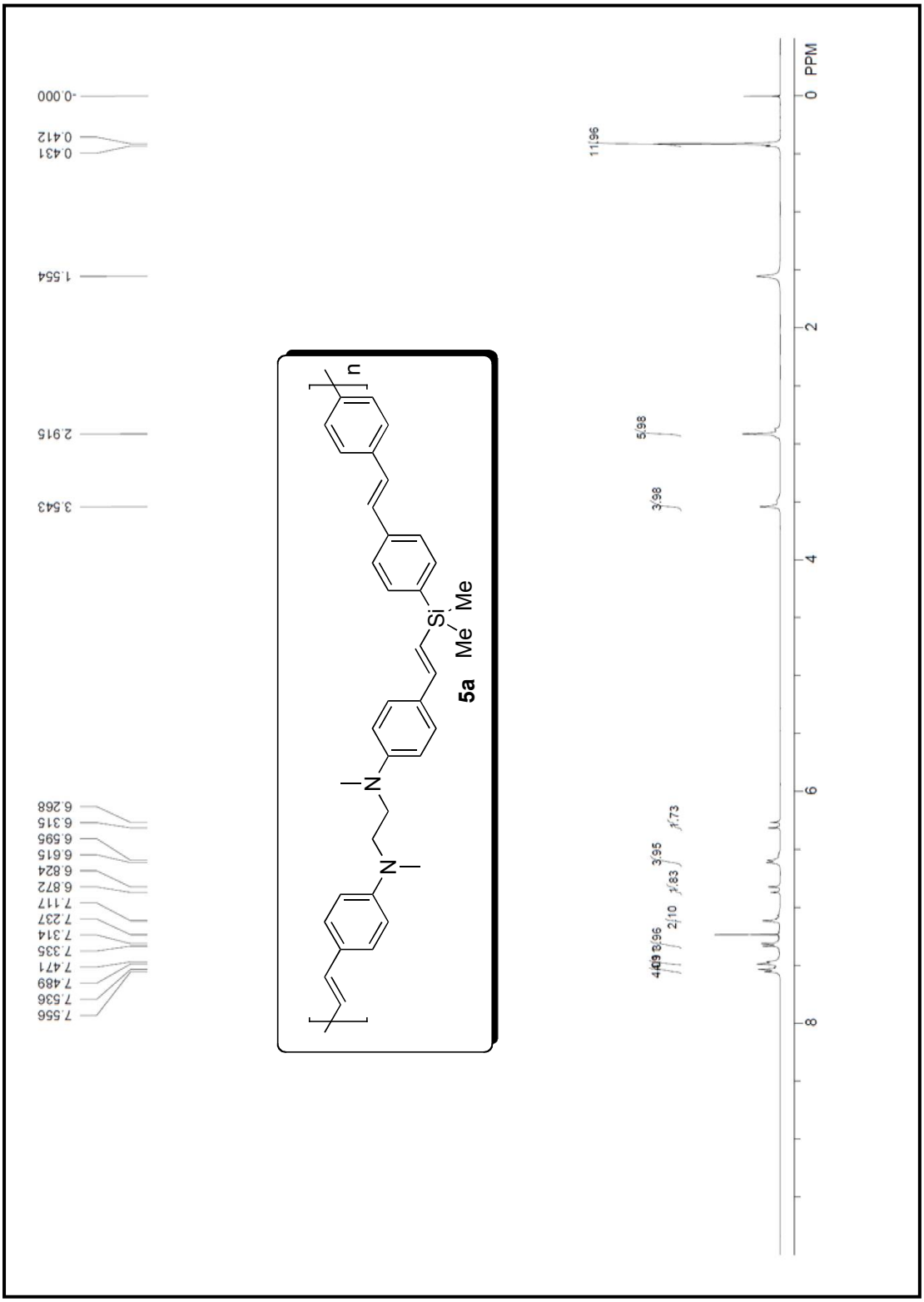

Figure S7. ^{1}H NMR spectrum of **5a**

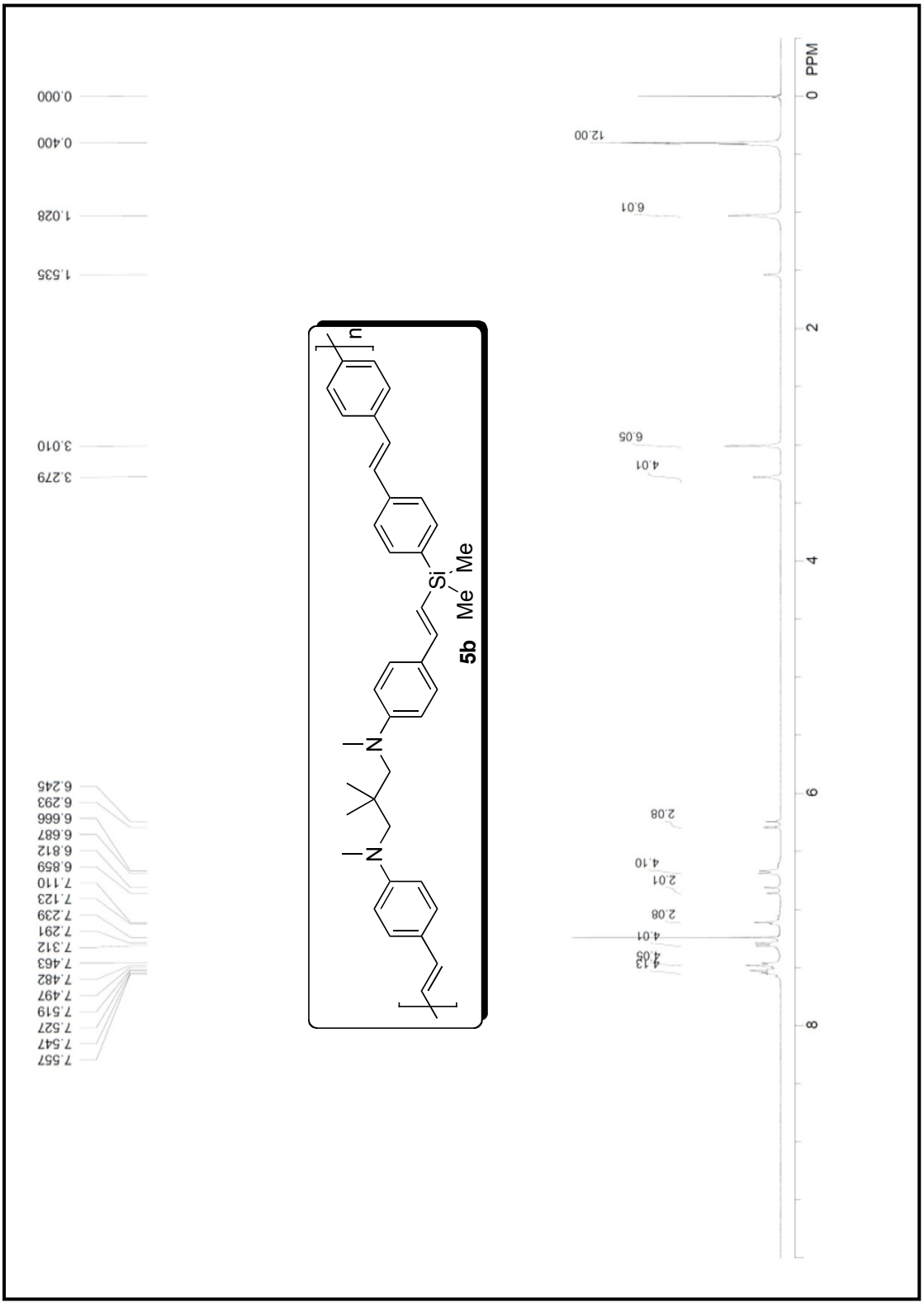

Figure S8. ^{1}H NMR spectrum of **5b**

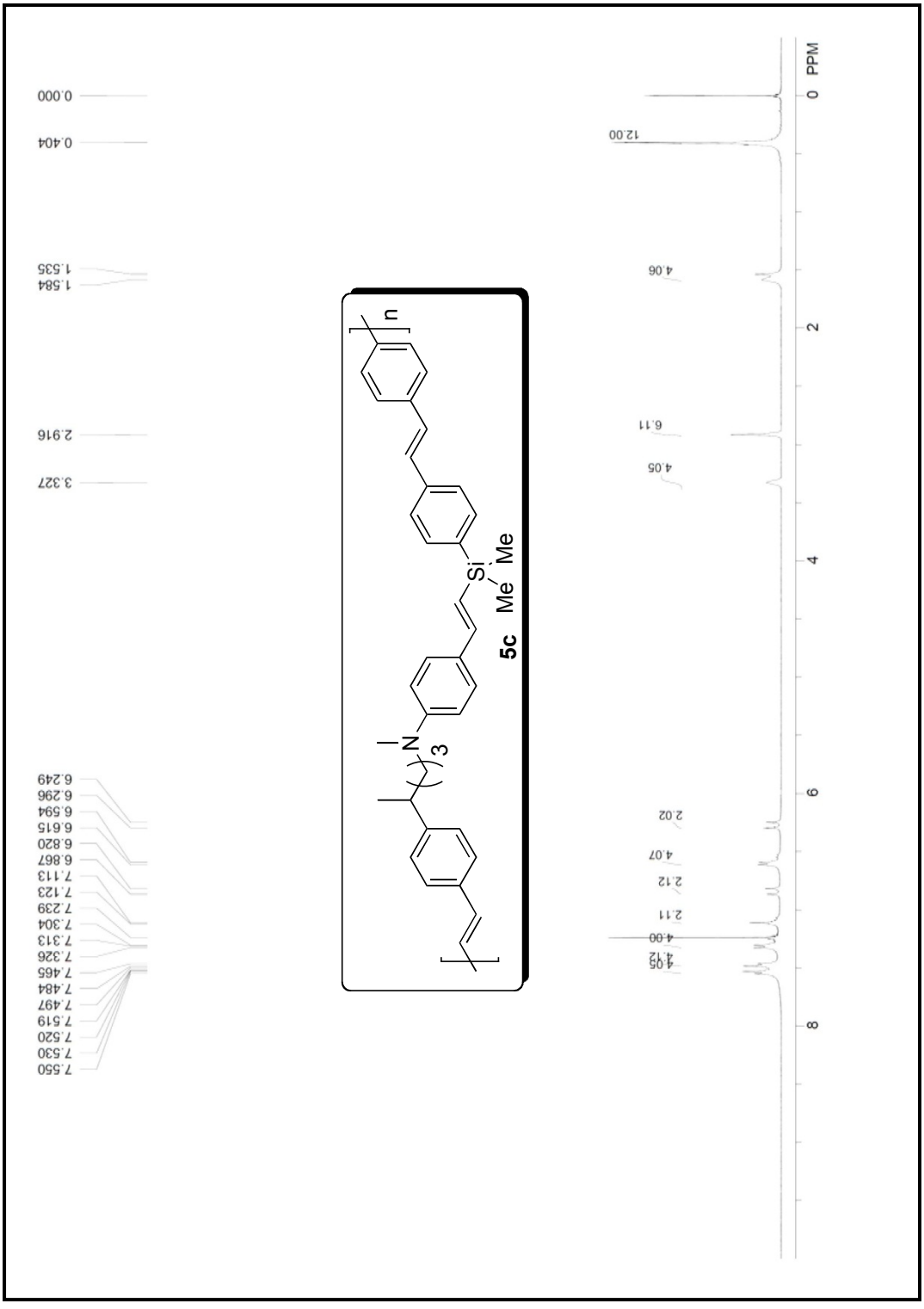

Figure S9. ^{1}H NMR spectrum of **5c**

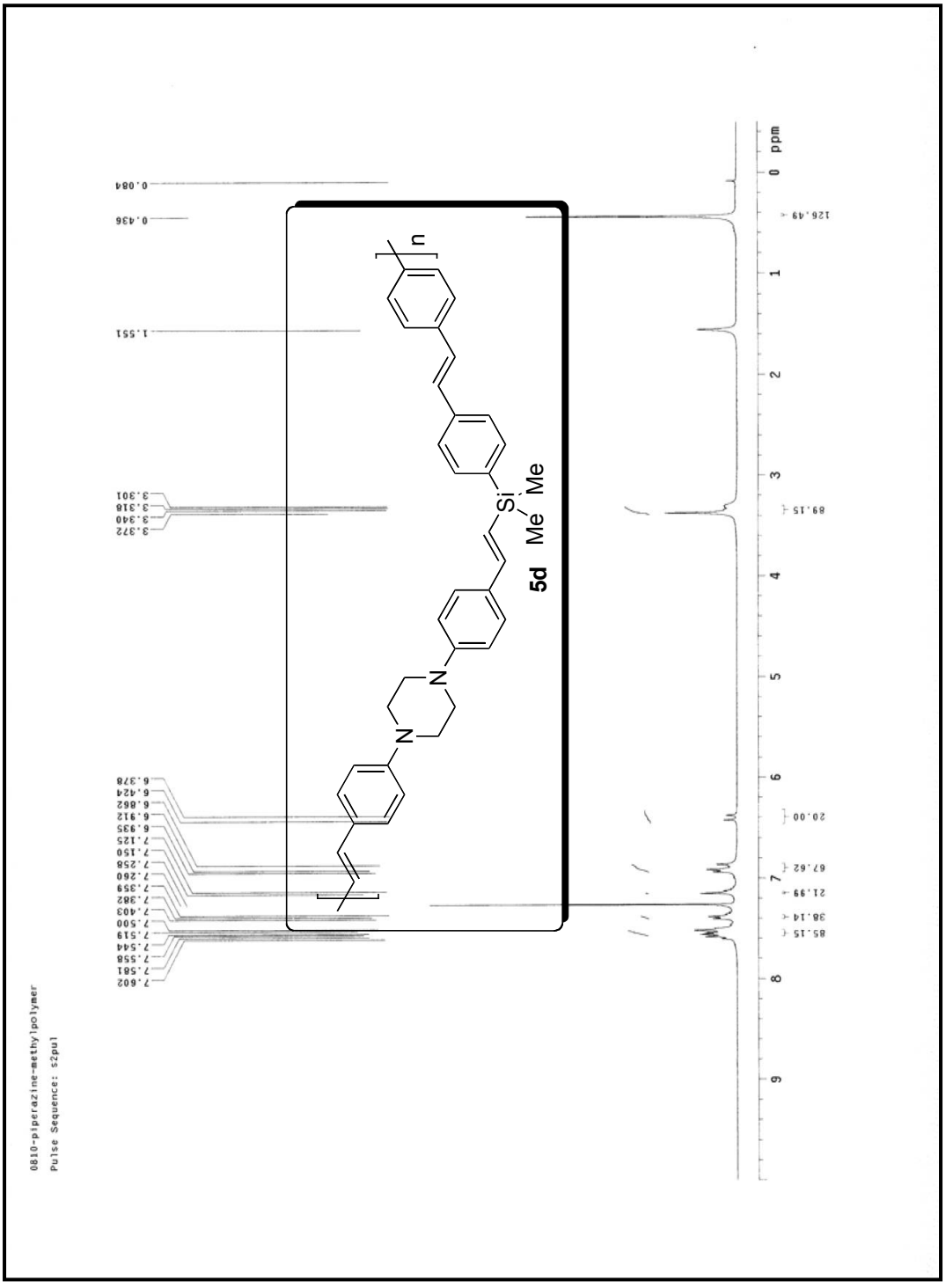

Figure S10. ^{1}H NMR spectrum of **5d**

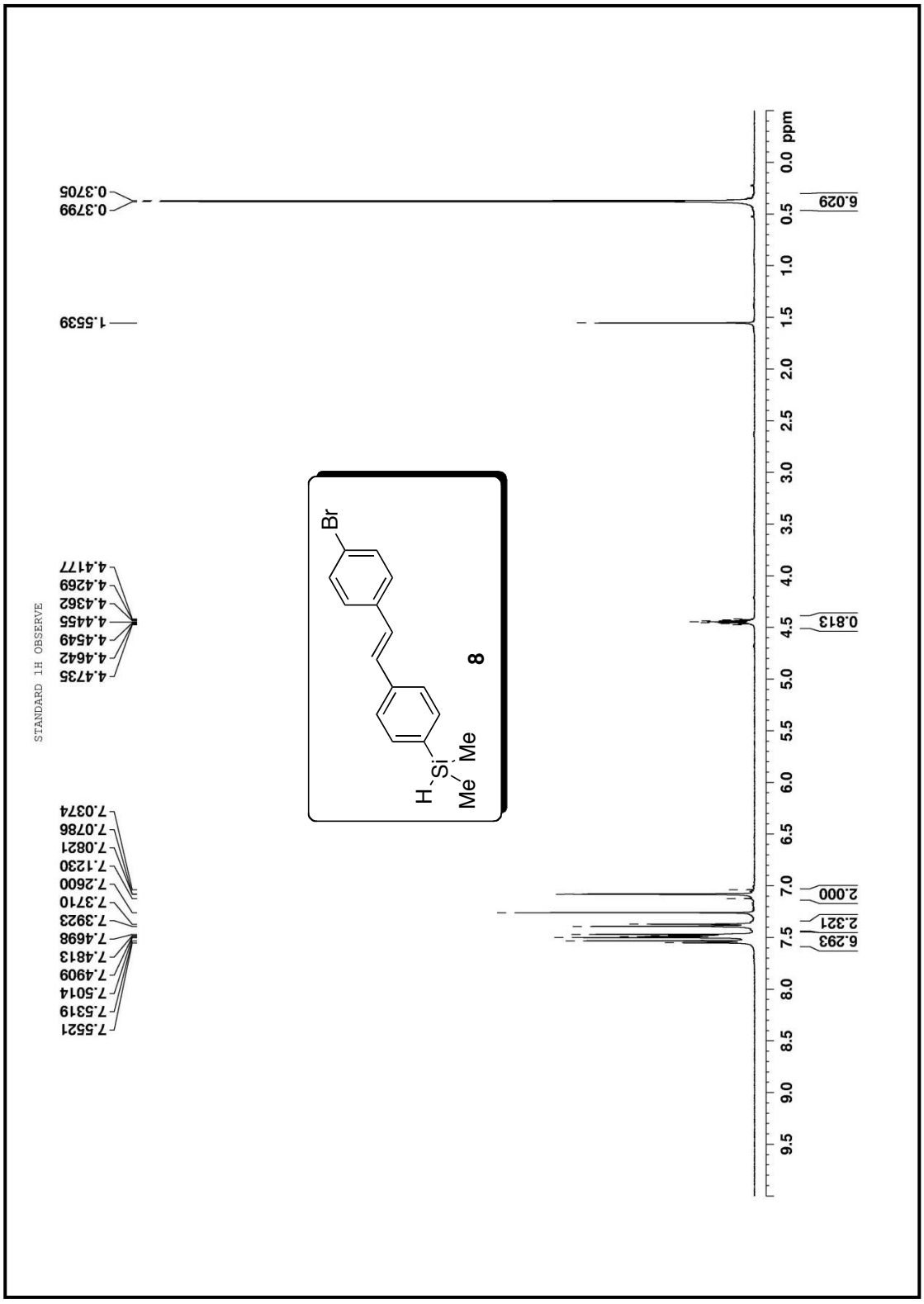

Figure S11. ^{1}H NMR spectrum of **8**

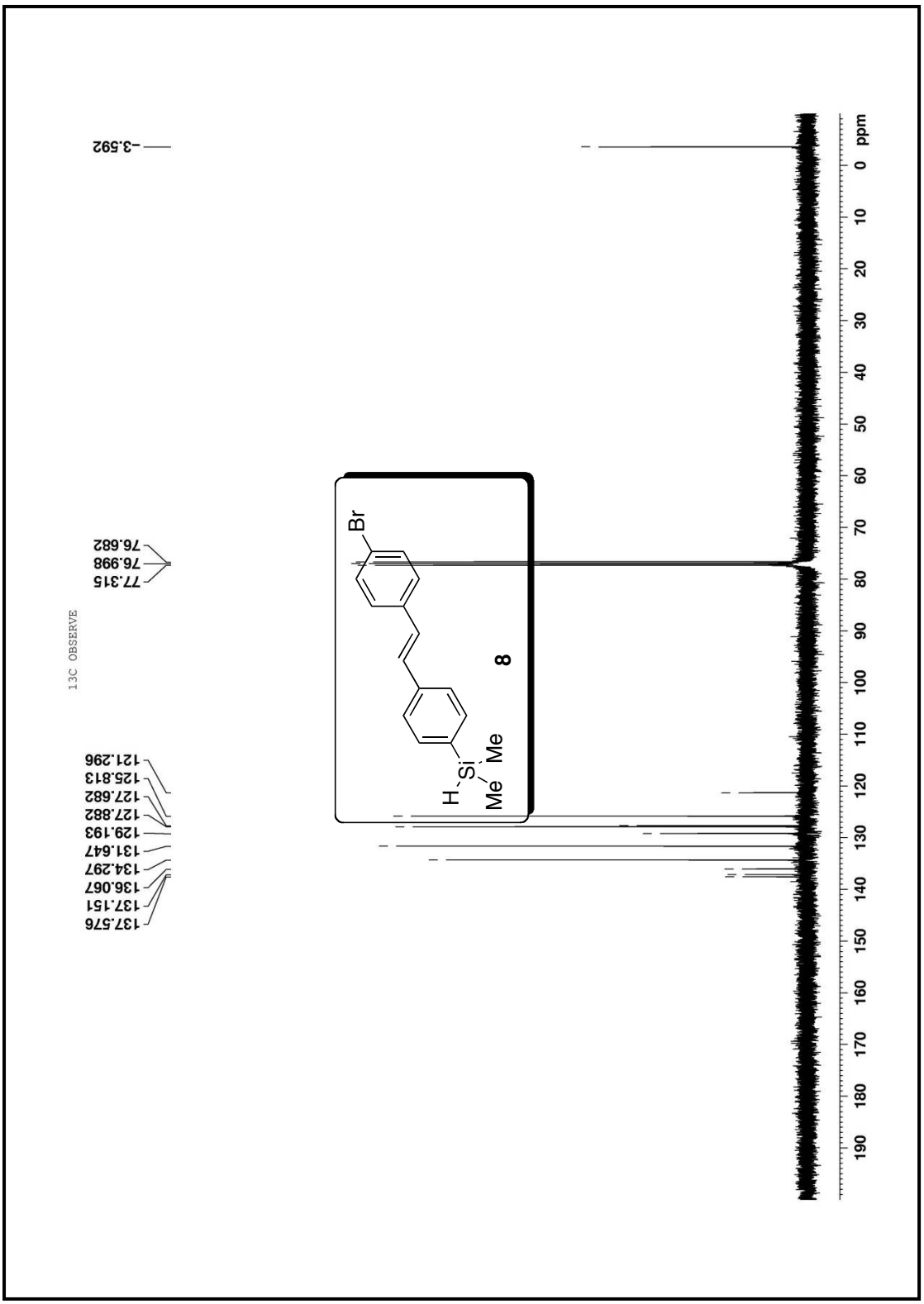

Figure S12. ^{13}C NMR spectrum of **8**

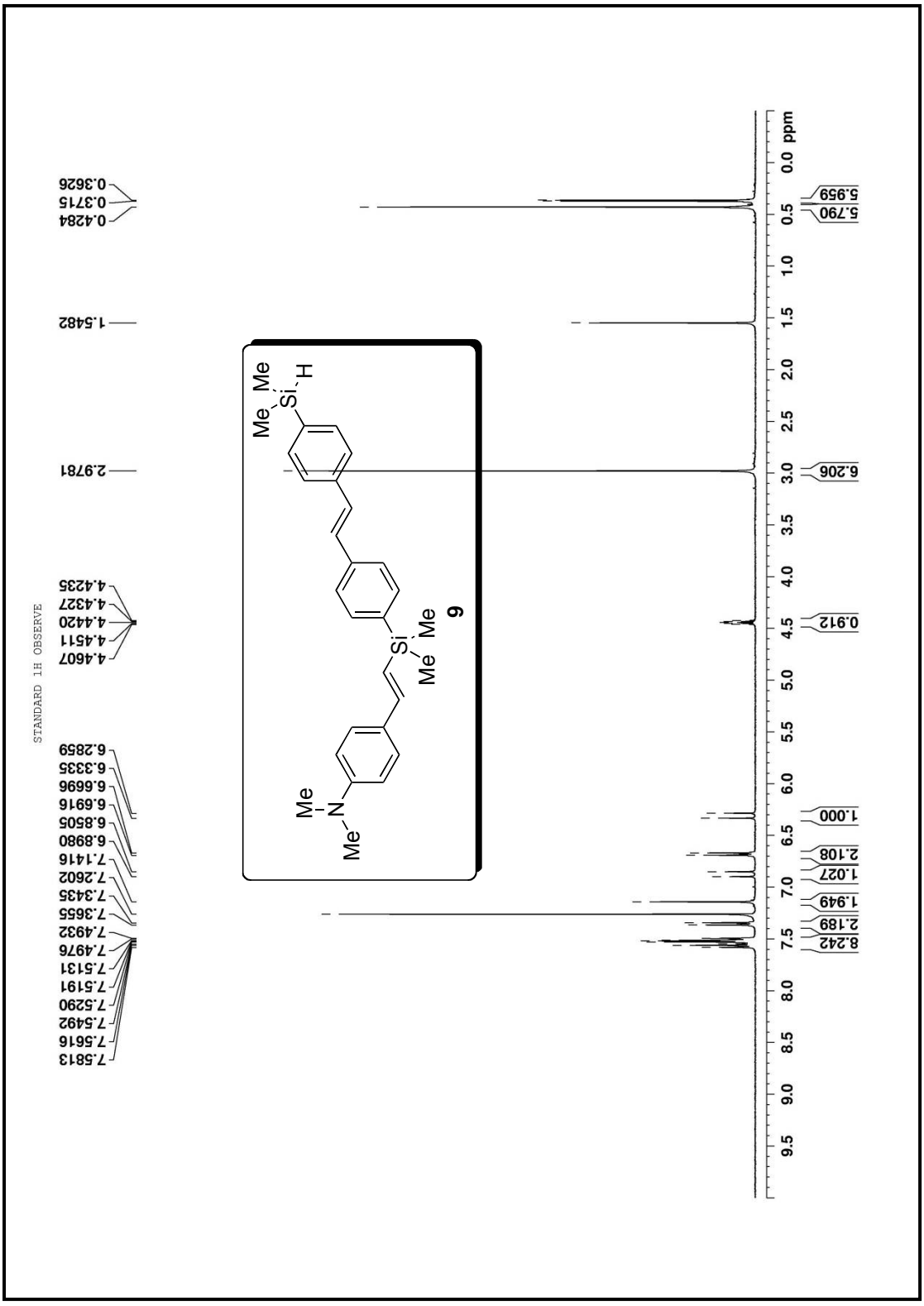

Figure S13. ^{1}H NMR spectrum of **9**

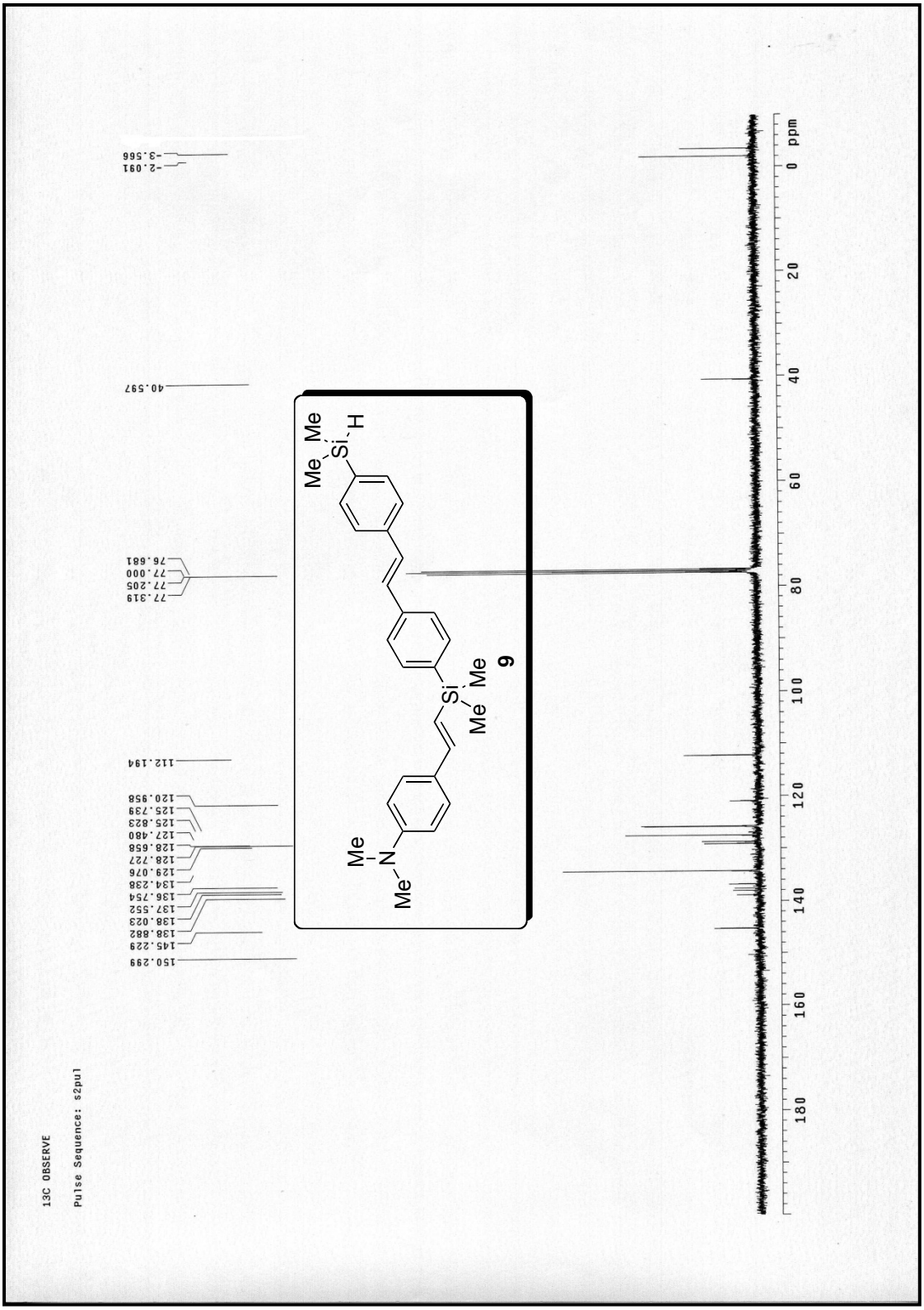

Figure S14. ^{13}C NMR spectrum of **9**

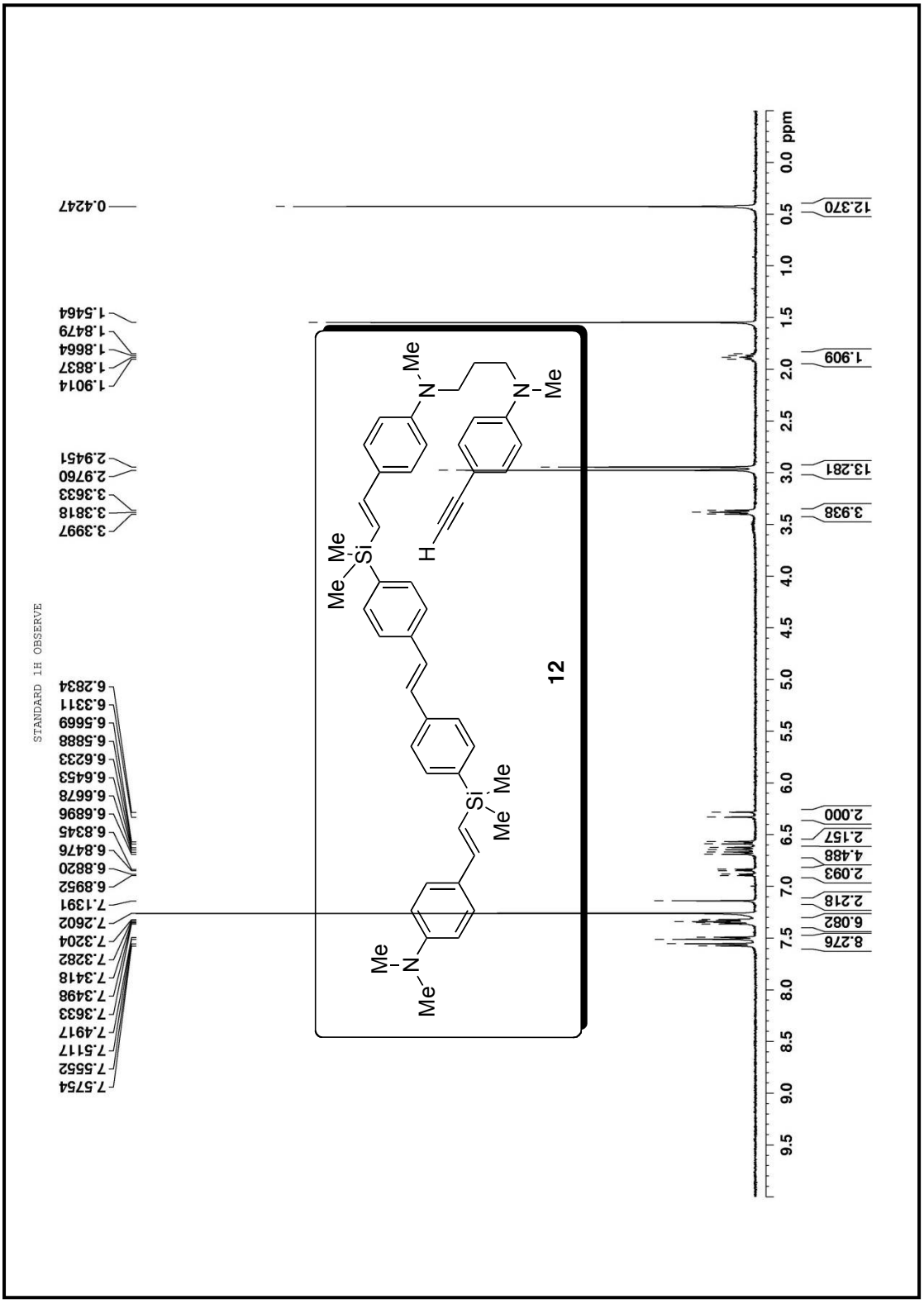

Figure S15. ^{1}H NMR spectrum of **12**

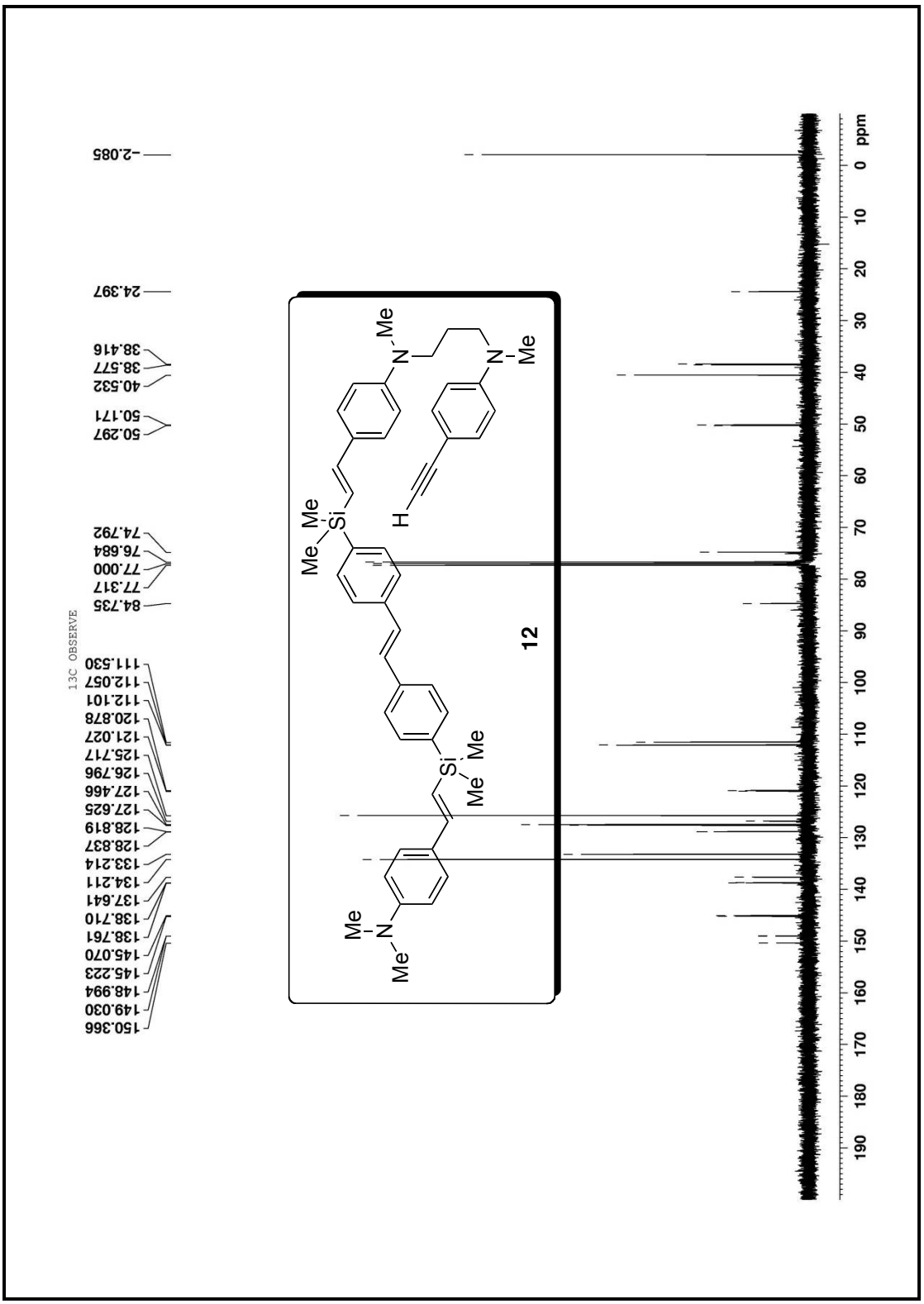

Figure S16. ^{13}C NMR spectrum of **12**

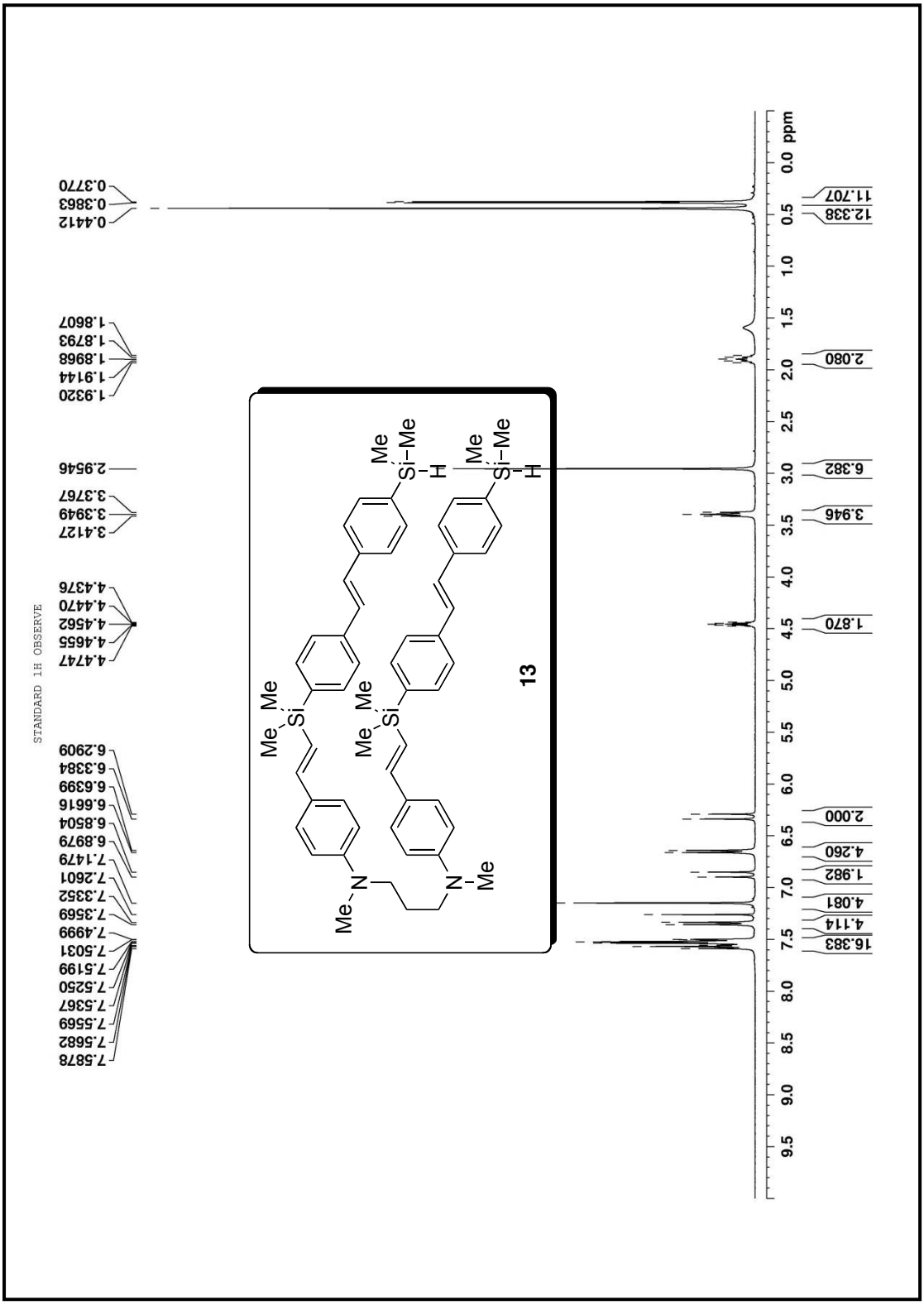

Figure S17. ^{1}H NMR spectrum of **13**

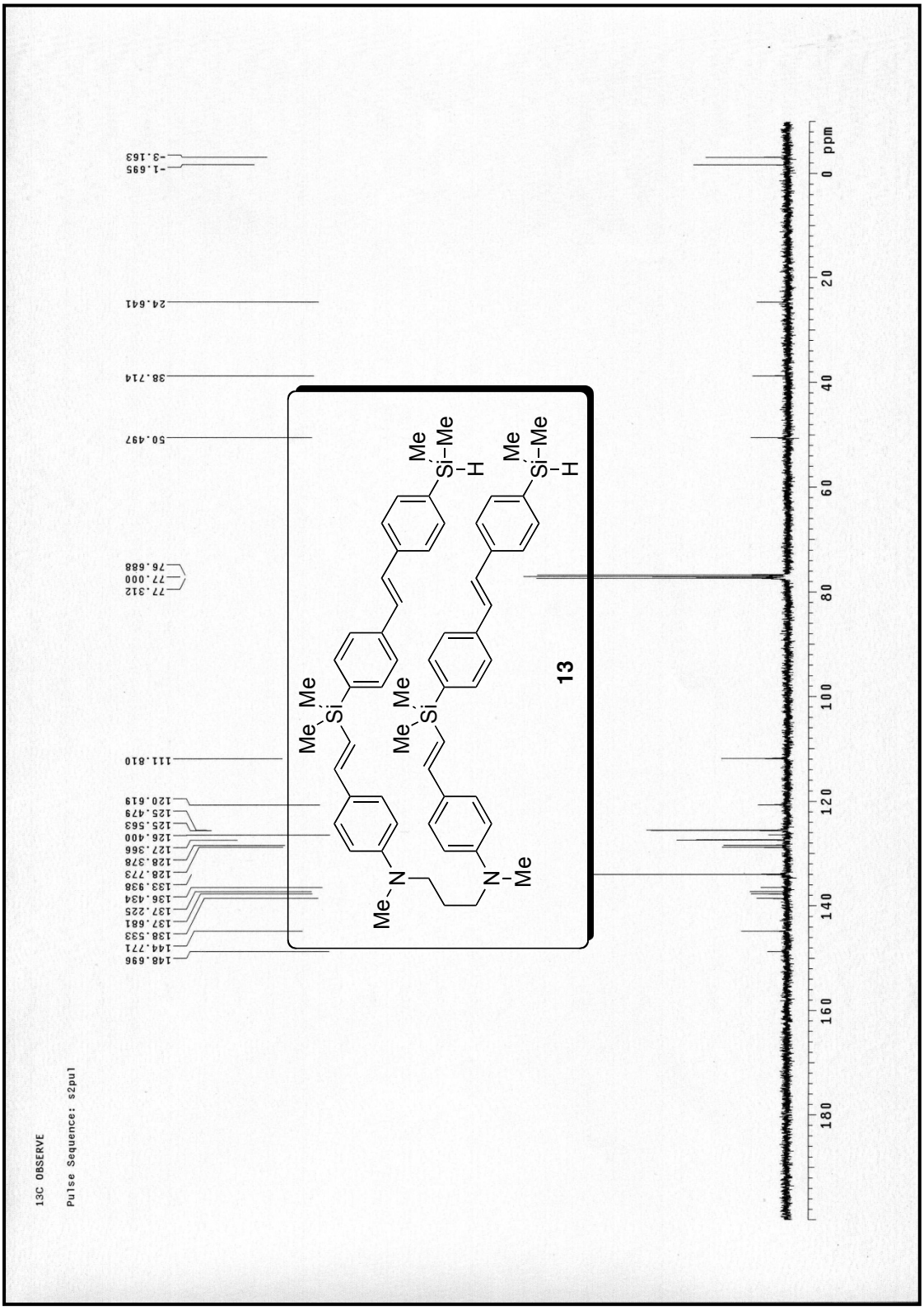

Figure S18. ^{13}C NMR spectrum of **13**

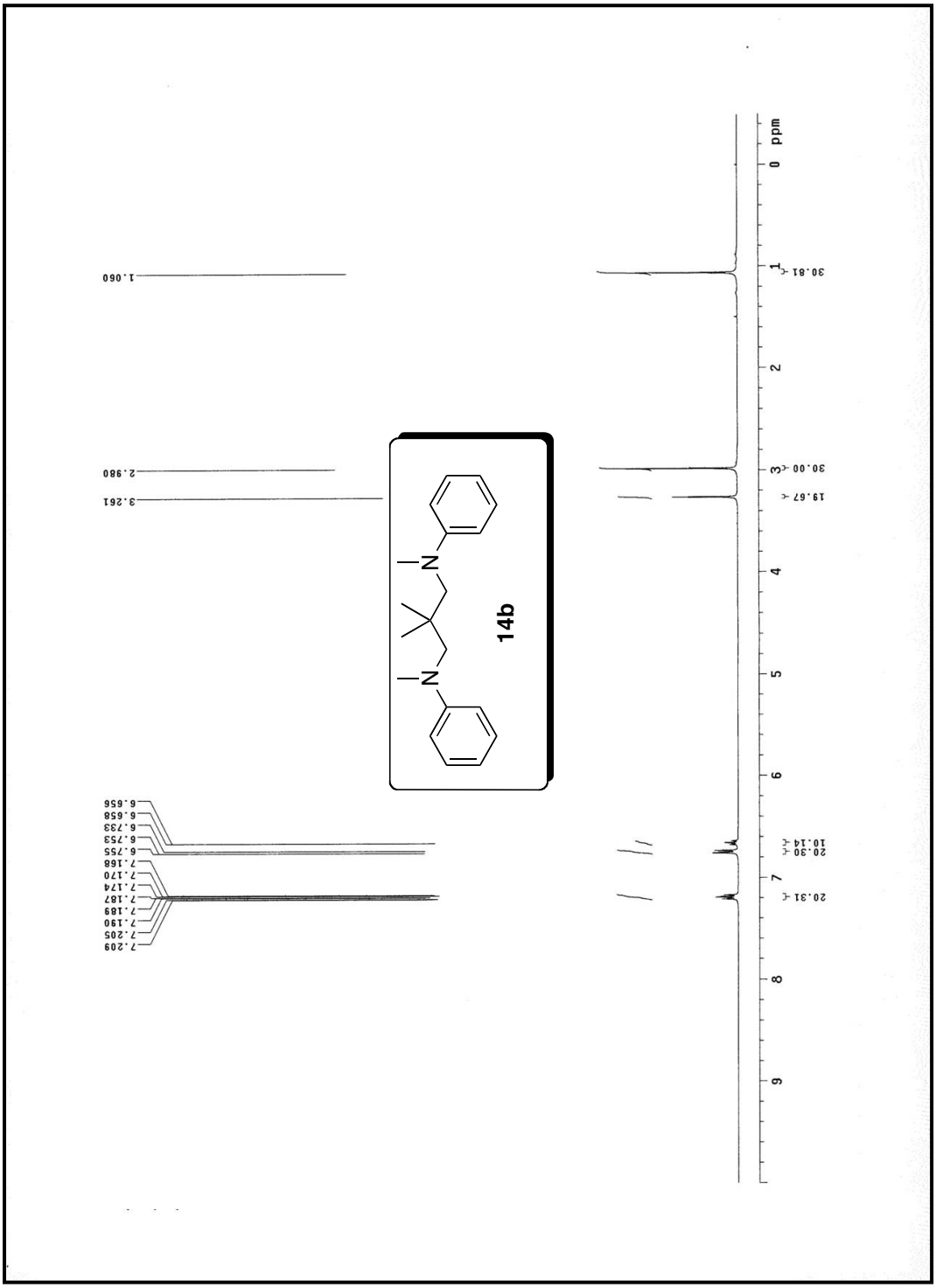

Figure S19. ^{1}H NMR spectrum of **14b**

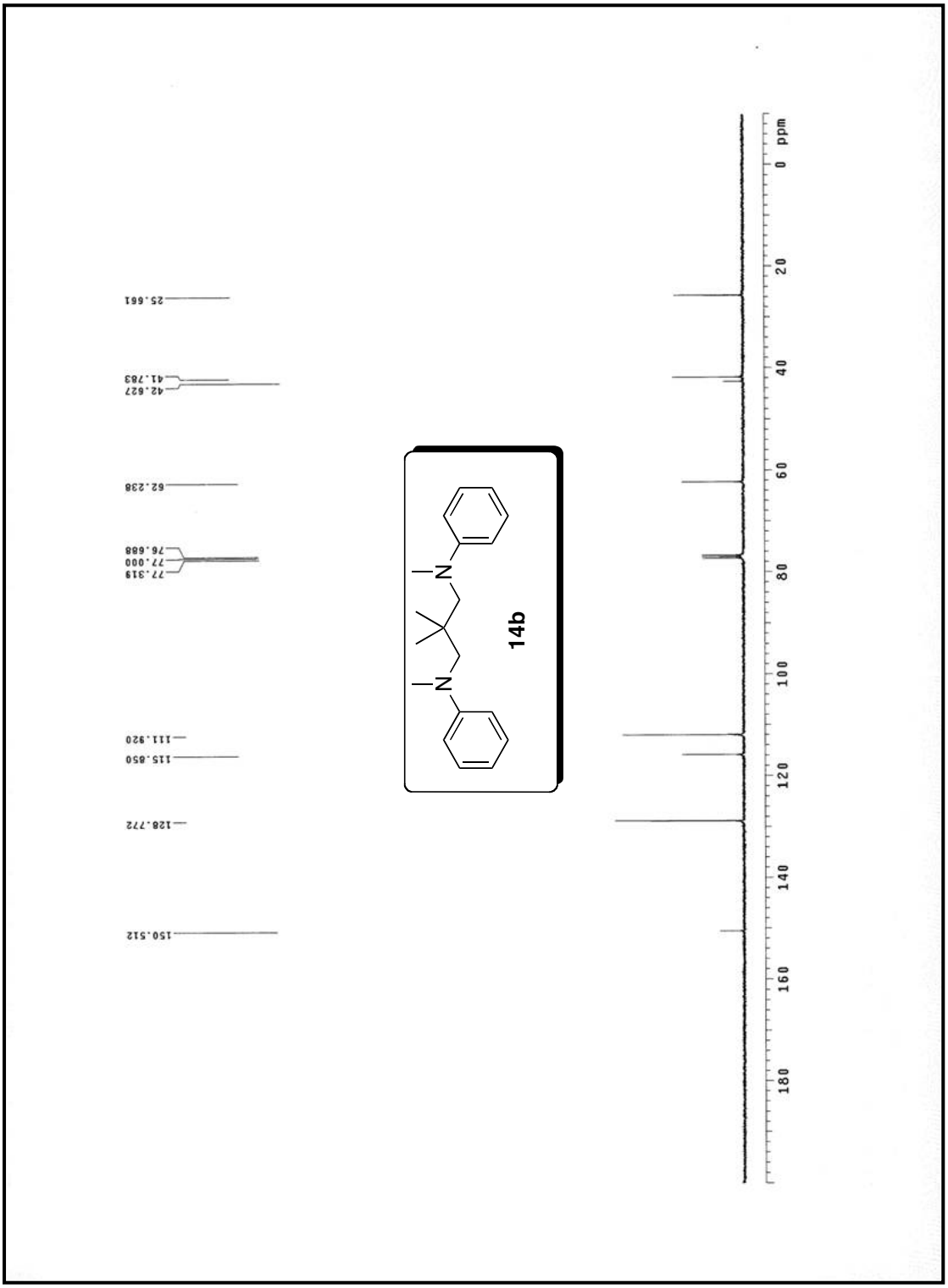

Figure S20. ^{13}C NMR spectrum of **14b**

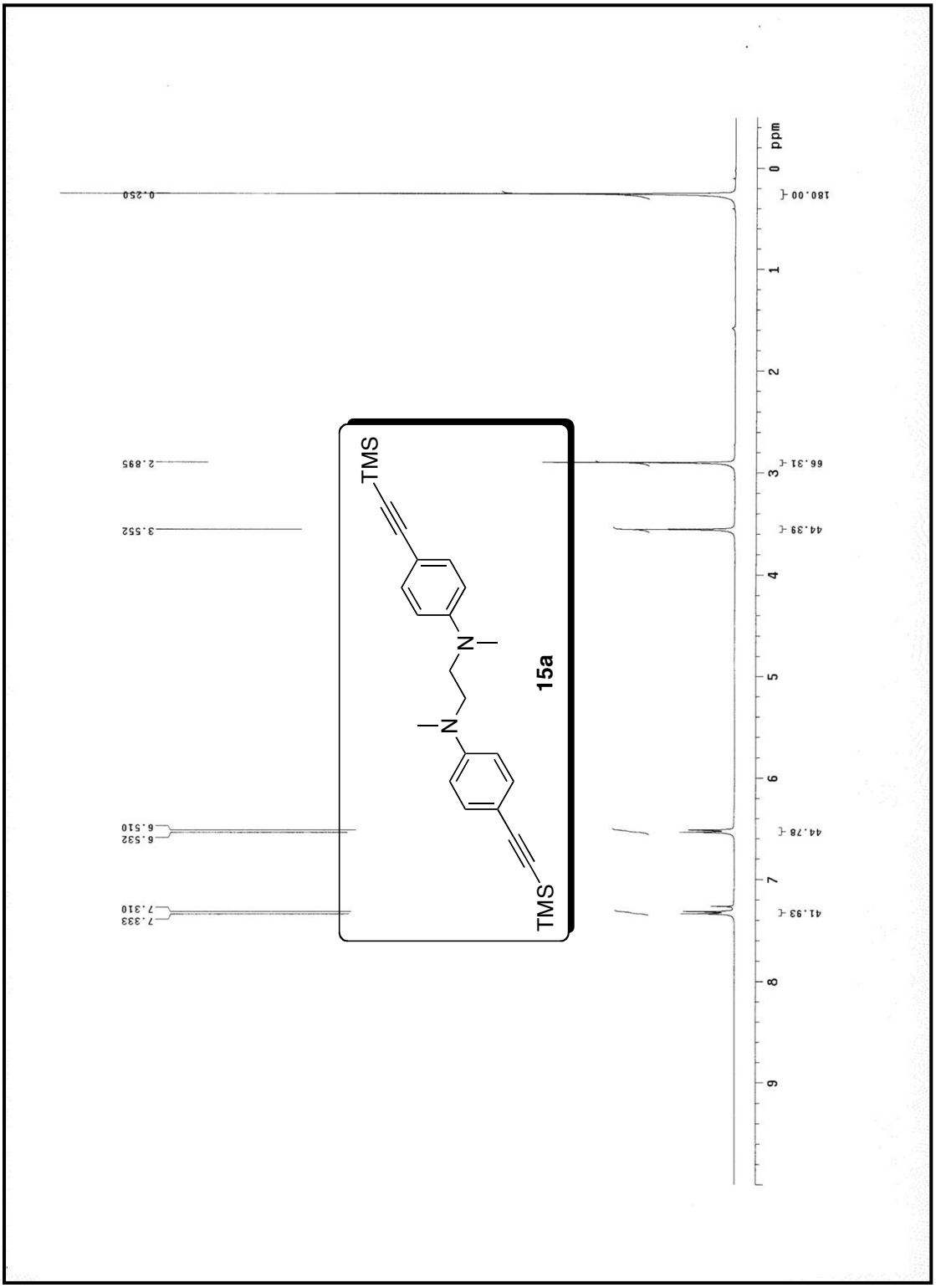

Figure S21. ^{1}H NMR spectrum of **15a**

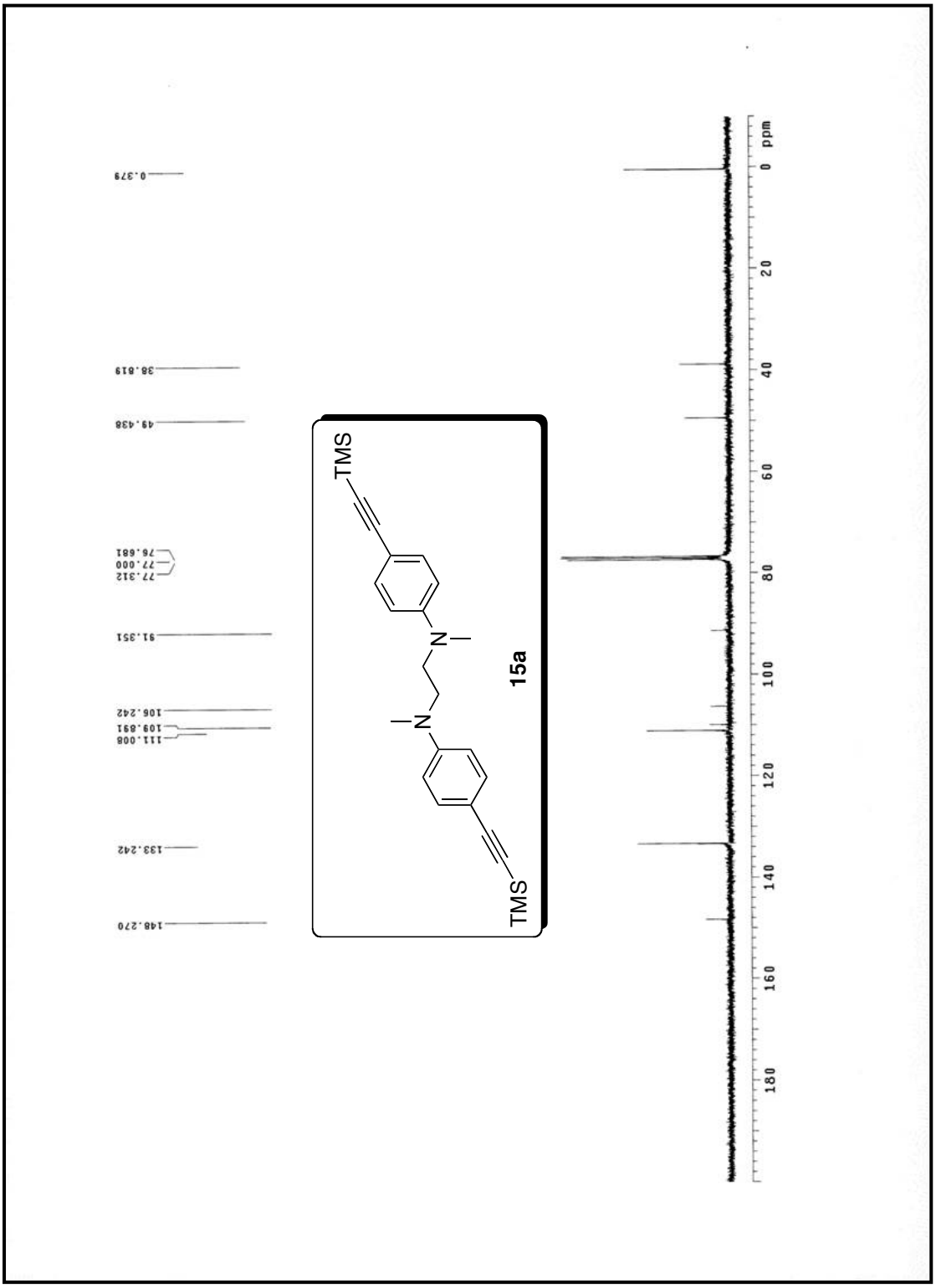

Figure S22. ^{13}C NMR spectrum of **15a**

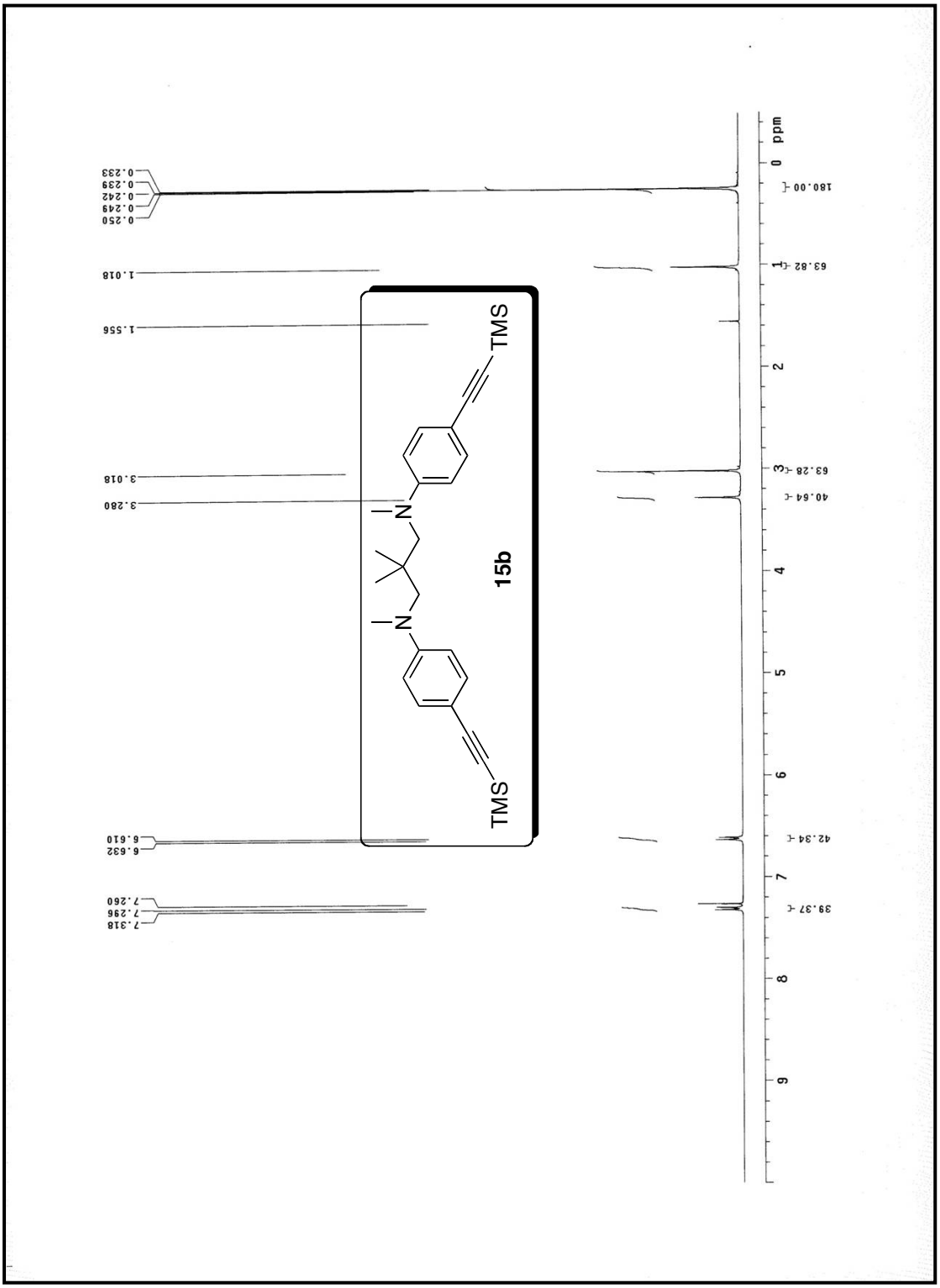

Figure S23. ^{1}H NMR spectrum of **15b**

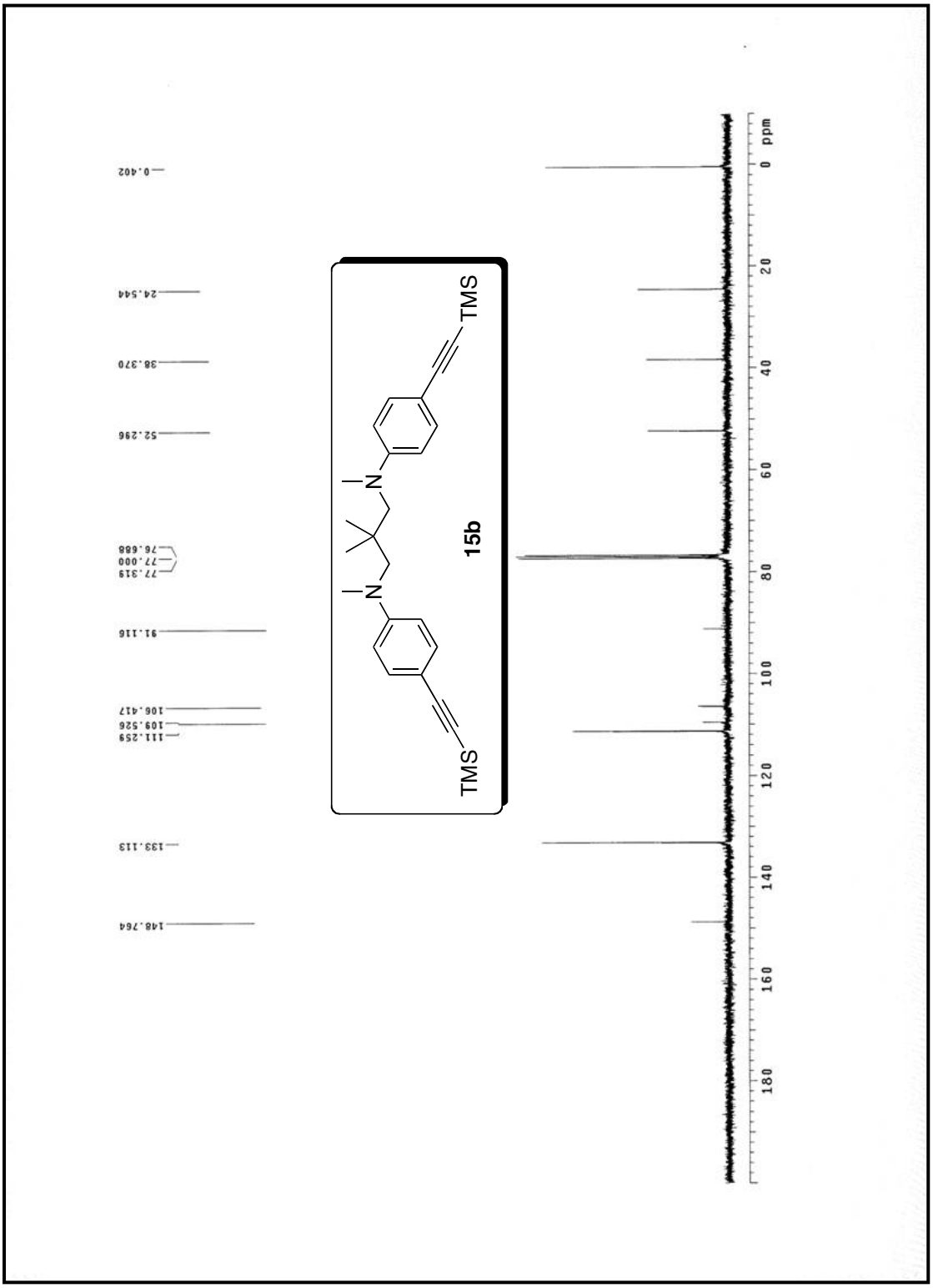

Figure S24. ^{13}C NMR spectrum of **15b**

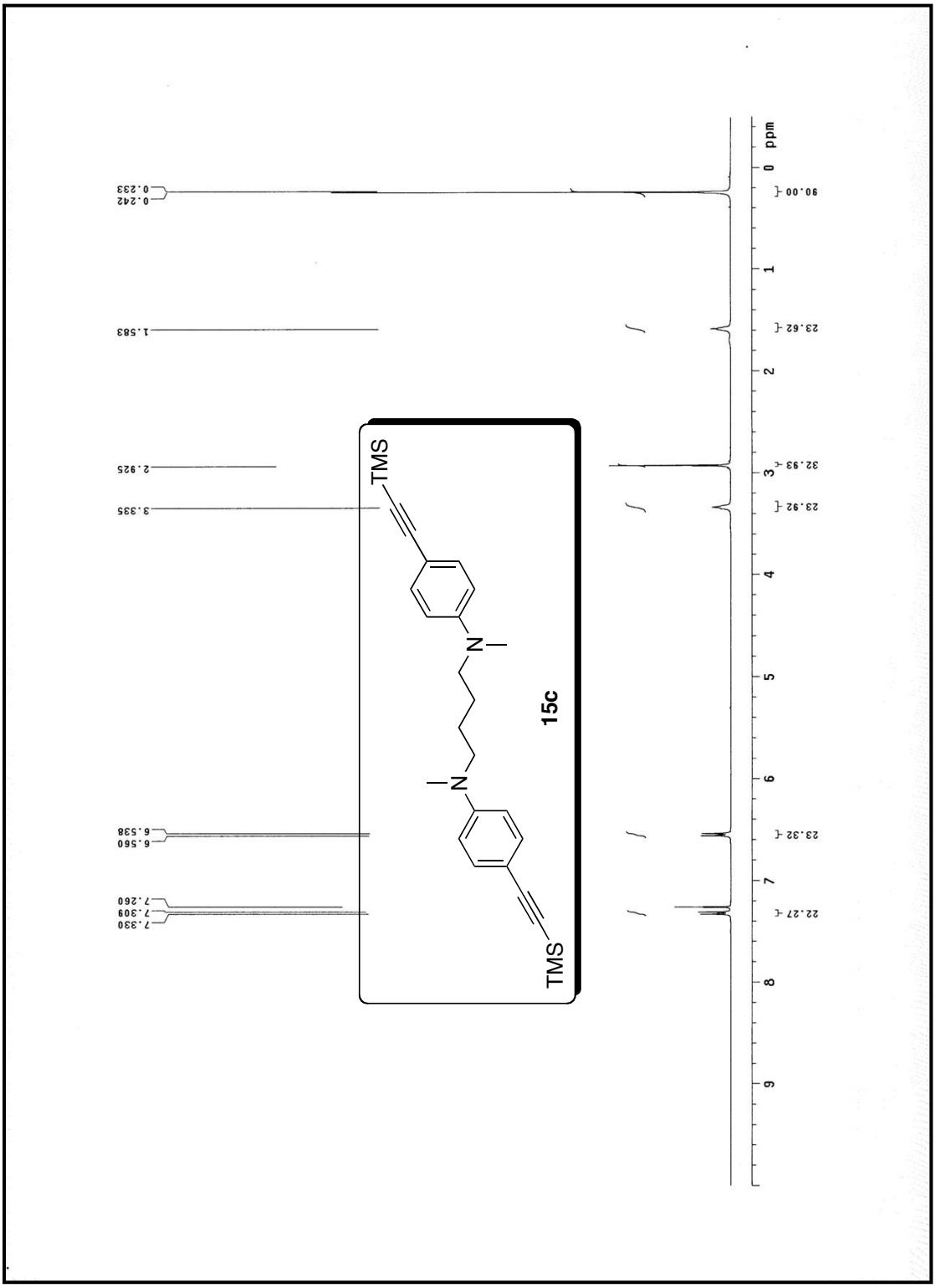

Figure S25. ^{1}H NMR spectrum of **15c**

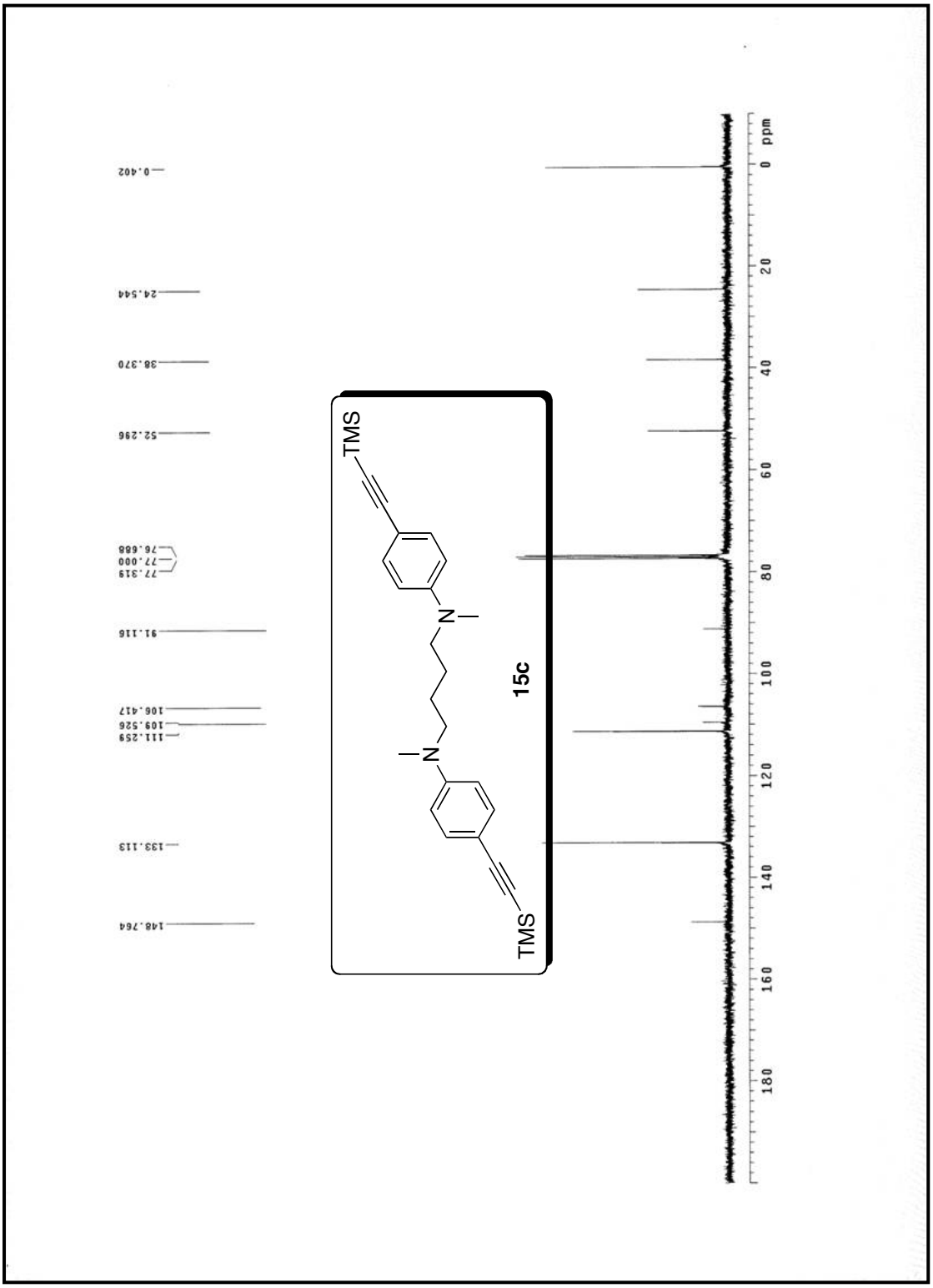

Figure S26. ^{13}C NMR spectrum of **15c**

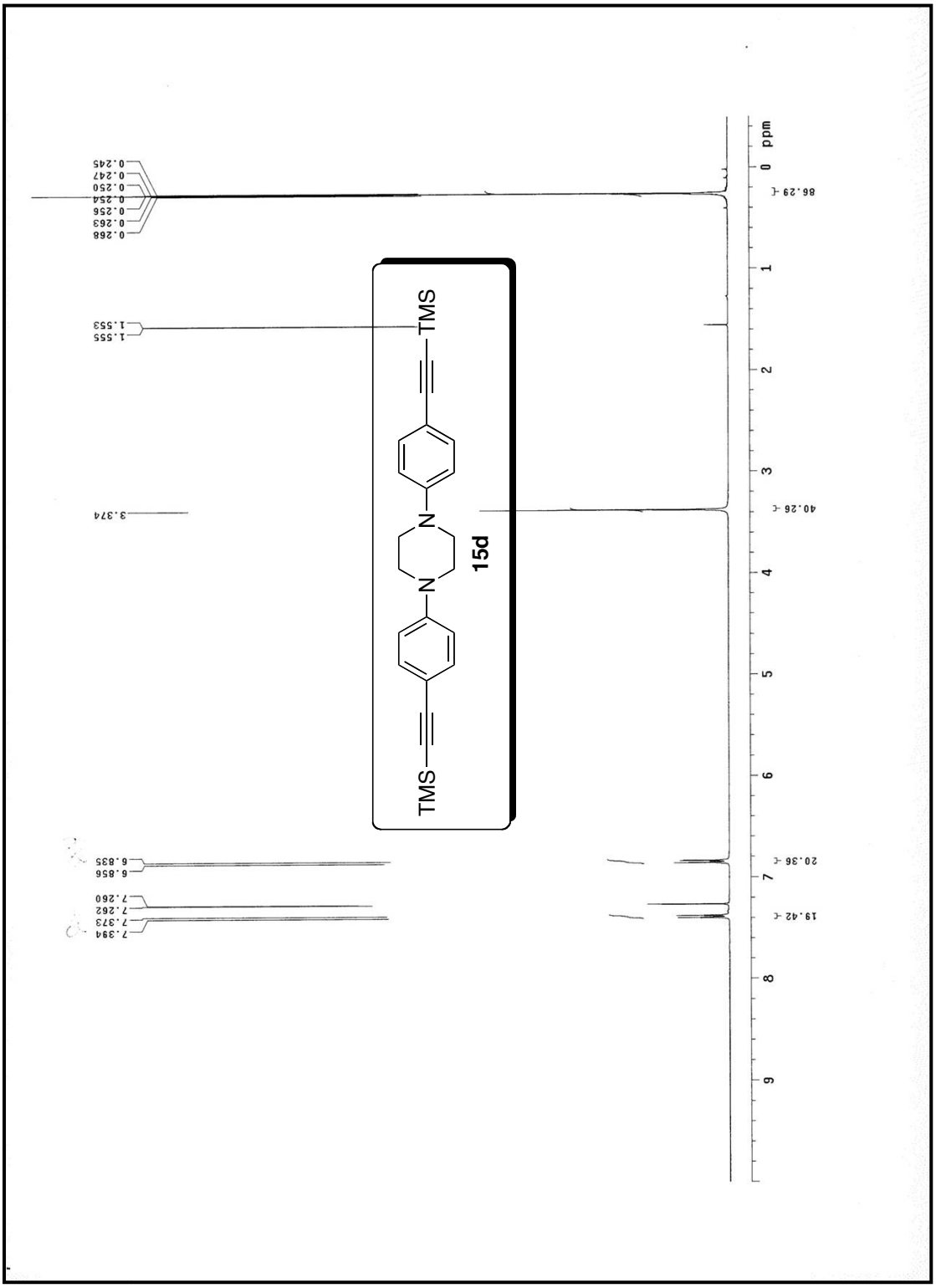

Figure S27. ^{1}H NMR spectrum of **15d**

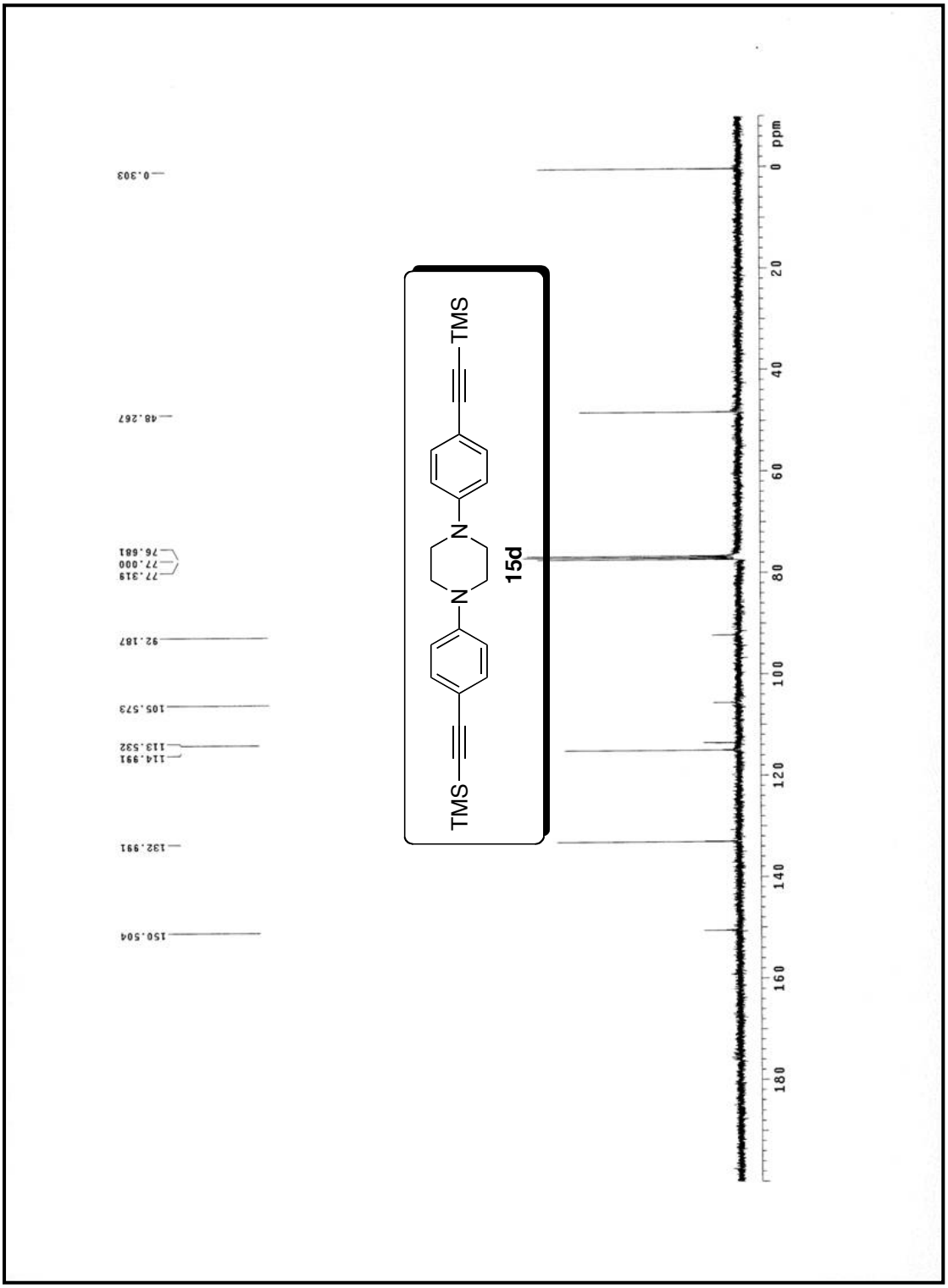

Figure S28. ^{13}C NMR spectrum of **15d**

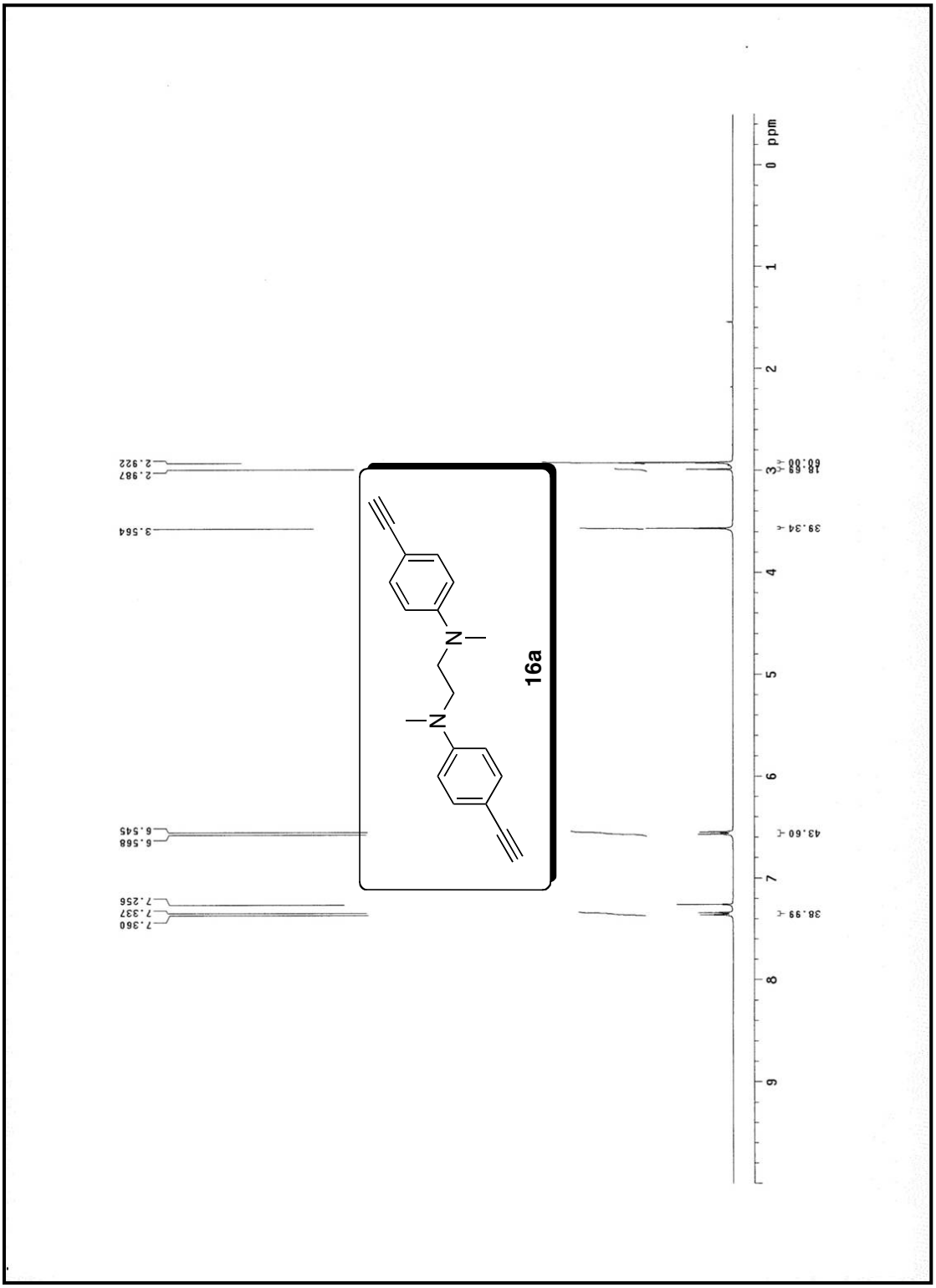

Figure S29. ^{1}H NMR spectrum of **16a**

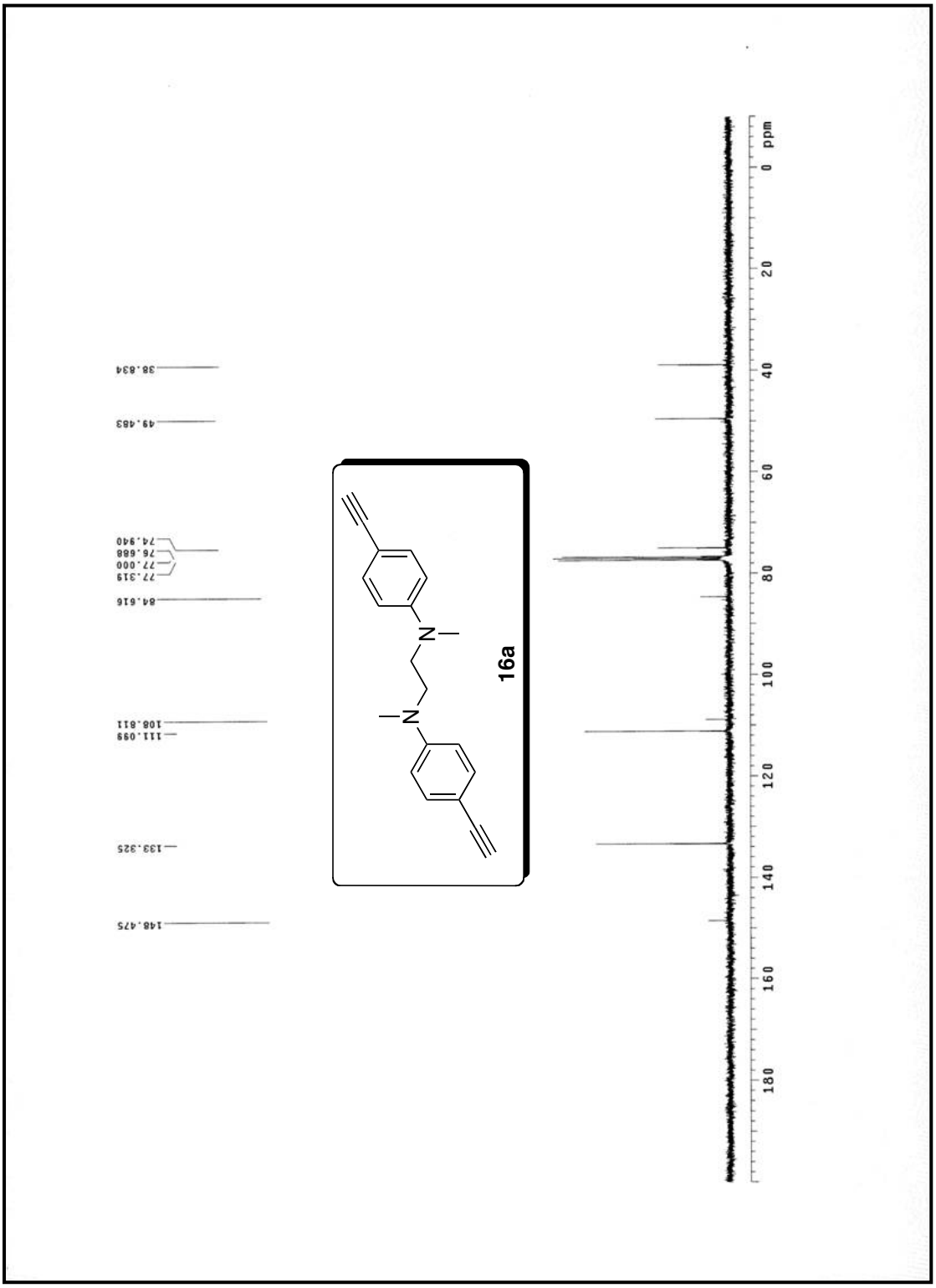

Figure S30. ^{13}C NMR spectrum of **16a**

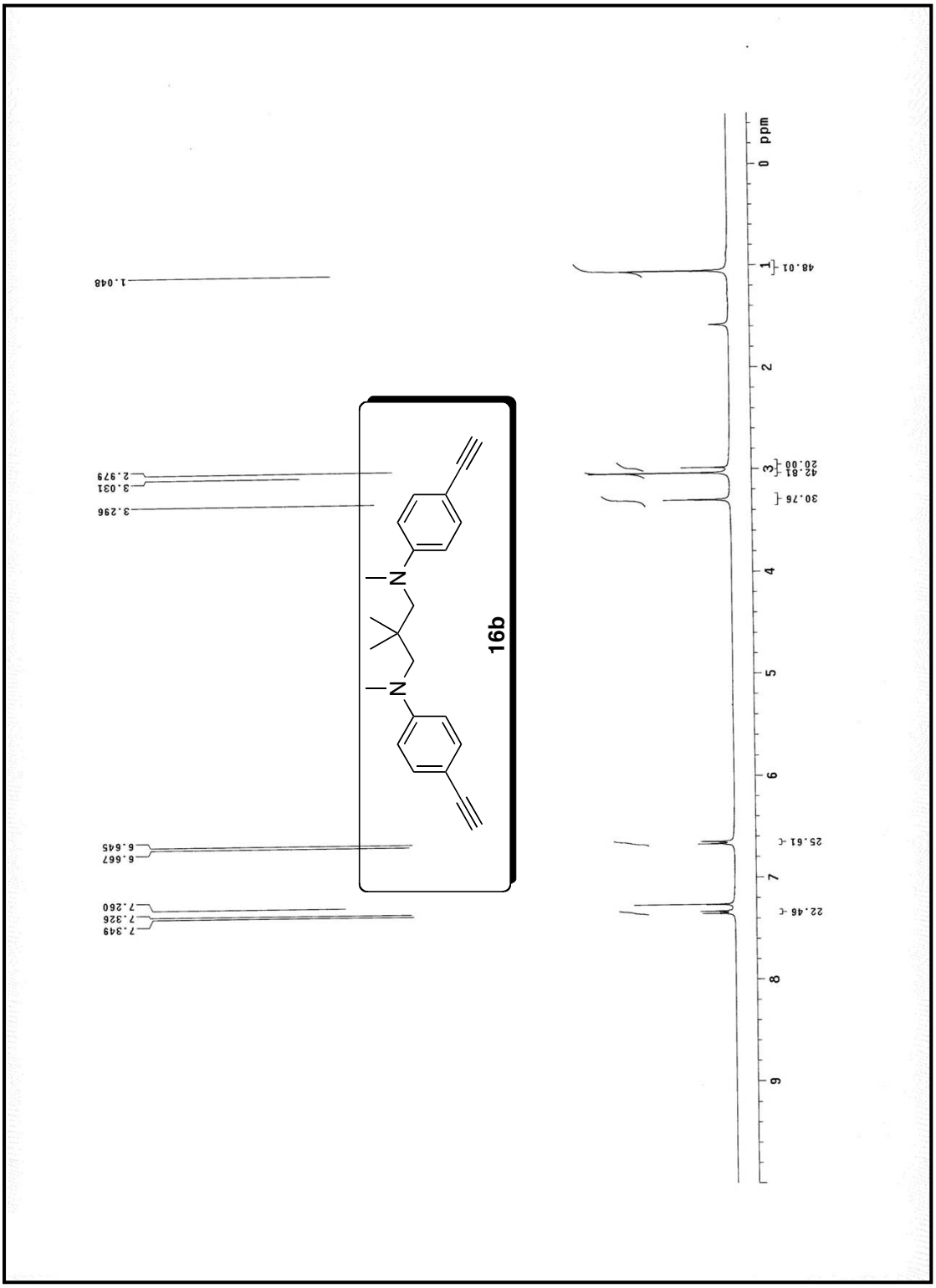

Figure S31. ^{1}H NMR spectrum of **16b**

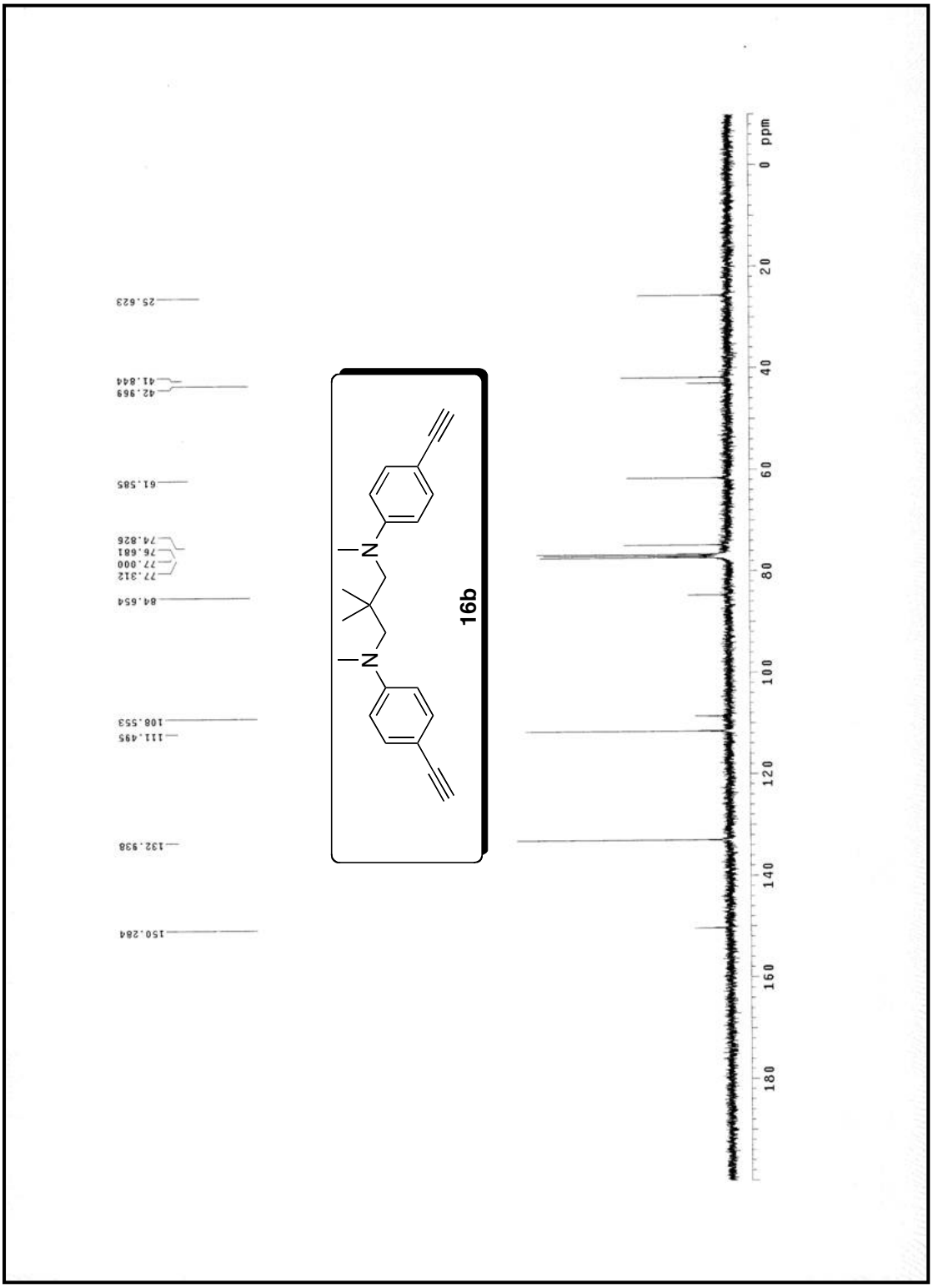

Figure S32. ^{13}C NMR spectrum of **16b**

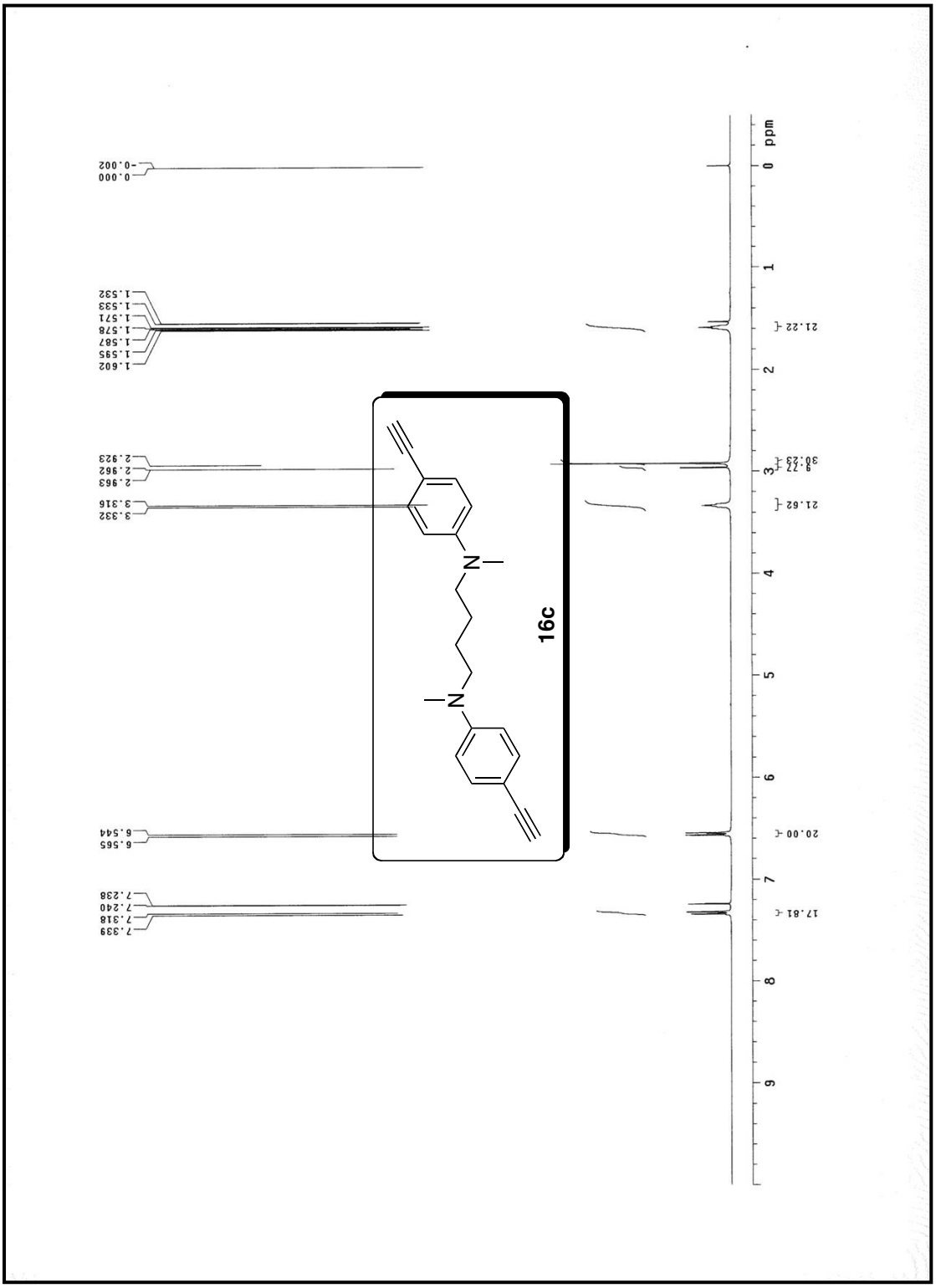

Figure S33. ^{1}H NMR spectrum of **16c**

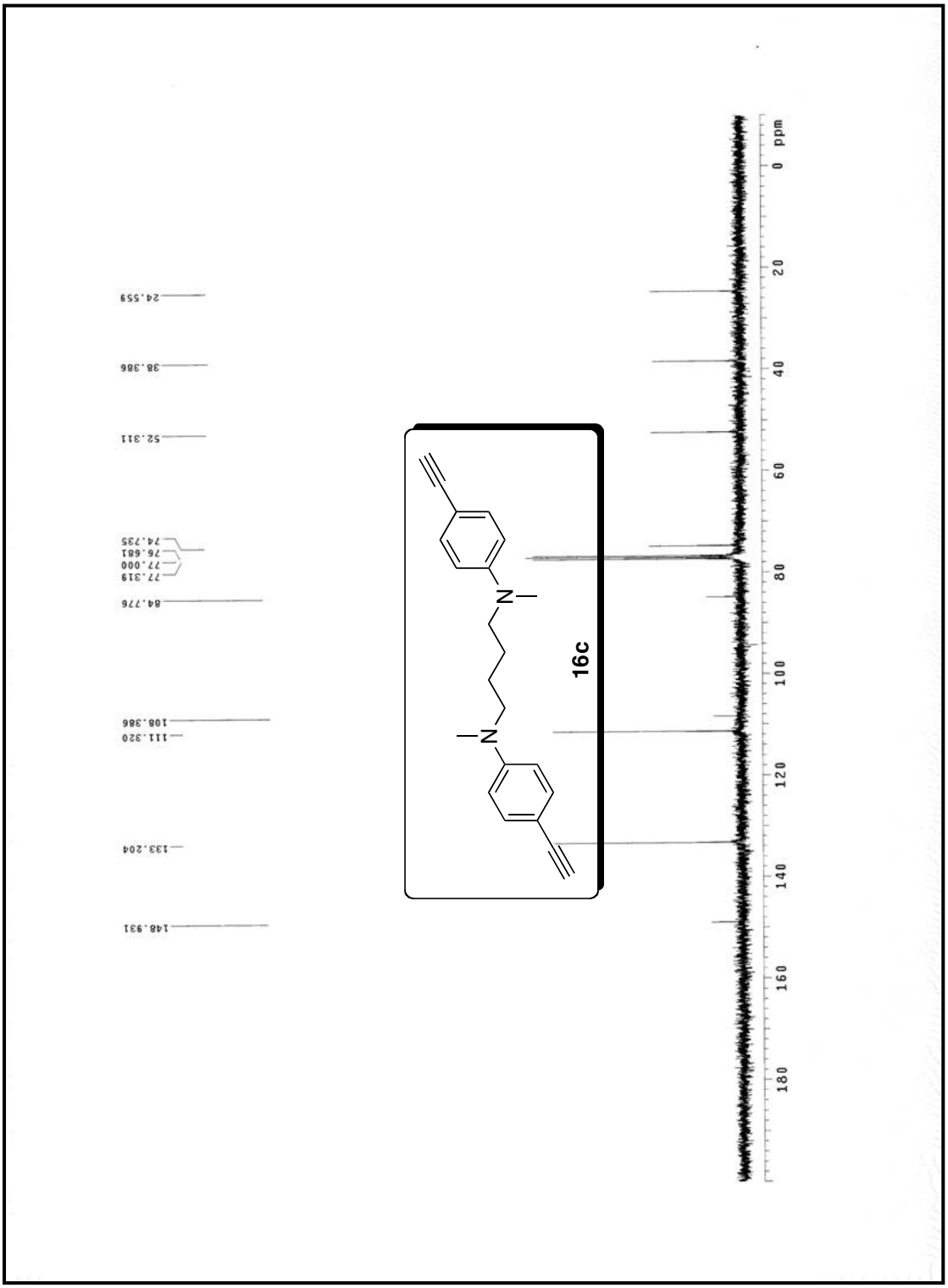

Figure S34. ^{13}C NMR spectrum of **16c**

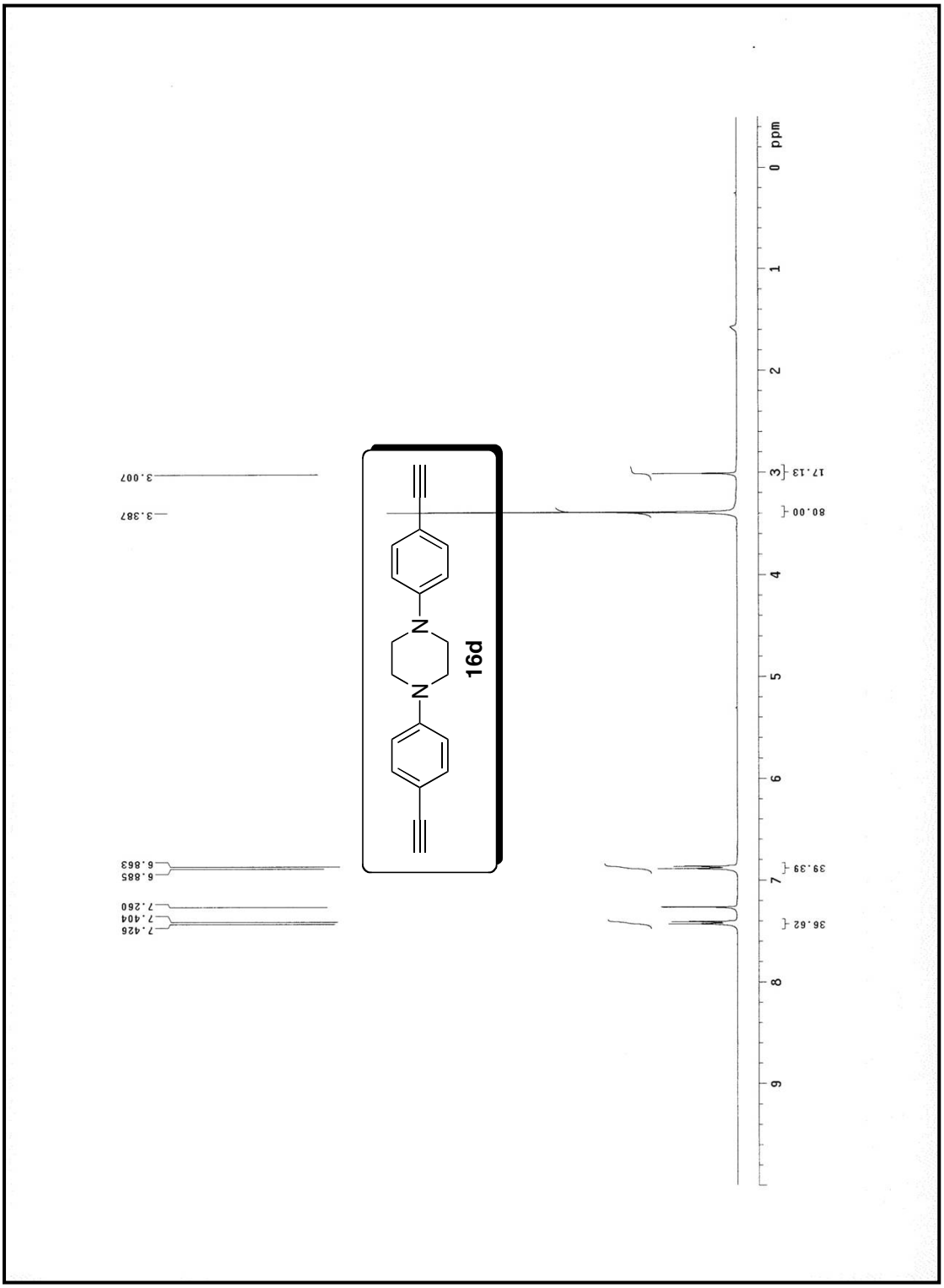

Figure S35. ^{1}H NMR spectrum of **16d**

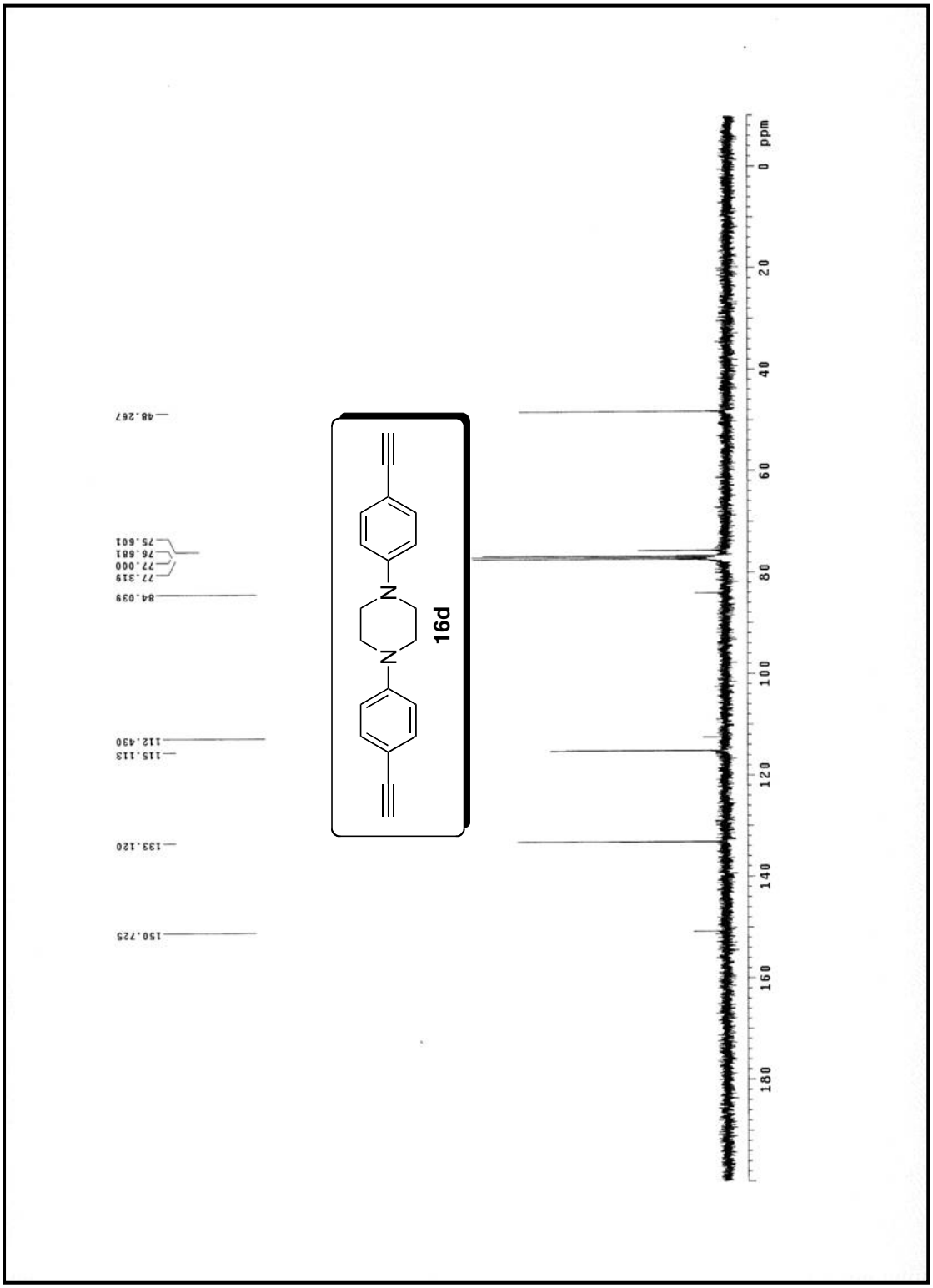

Figure S36. ^{13}C NMR spectrum of **16d**

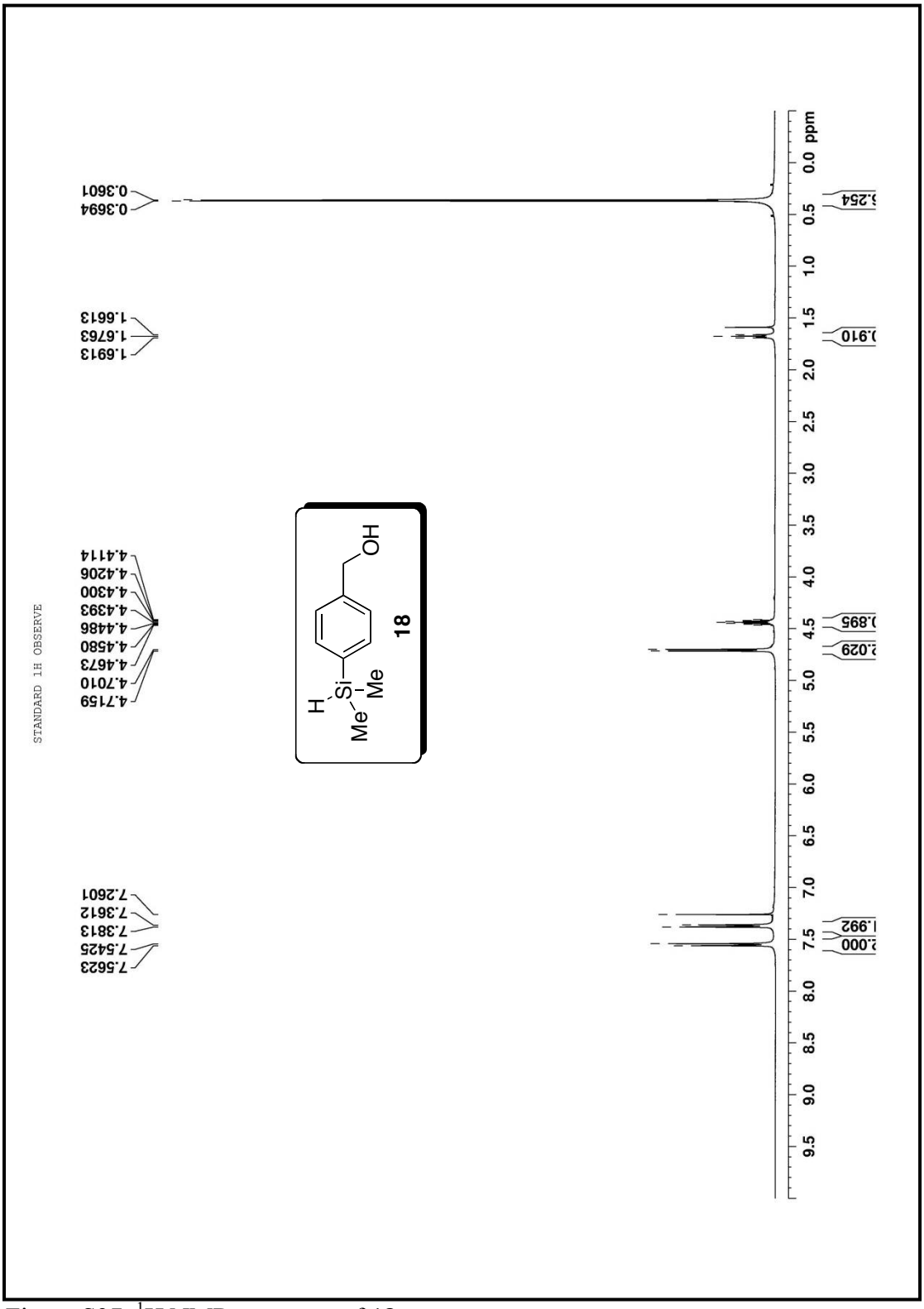

Figure S37. ^{1}H NMR spectrum of **18**

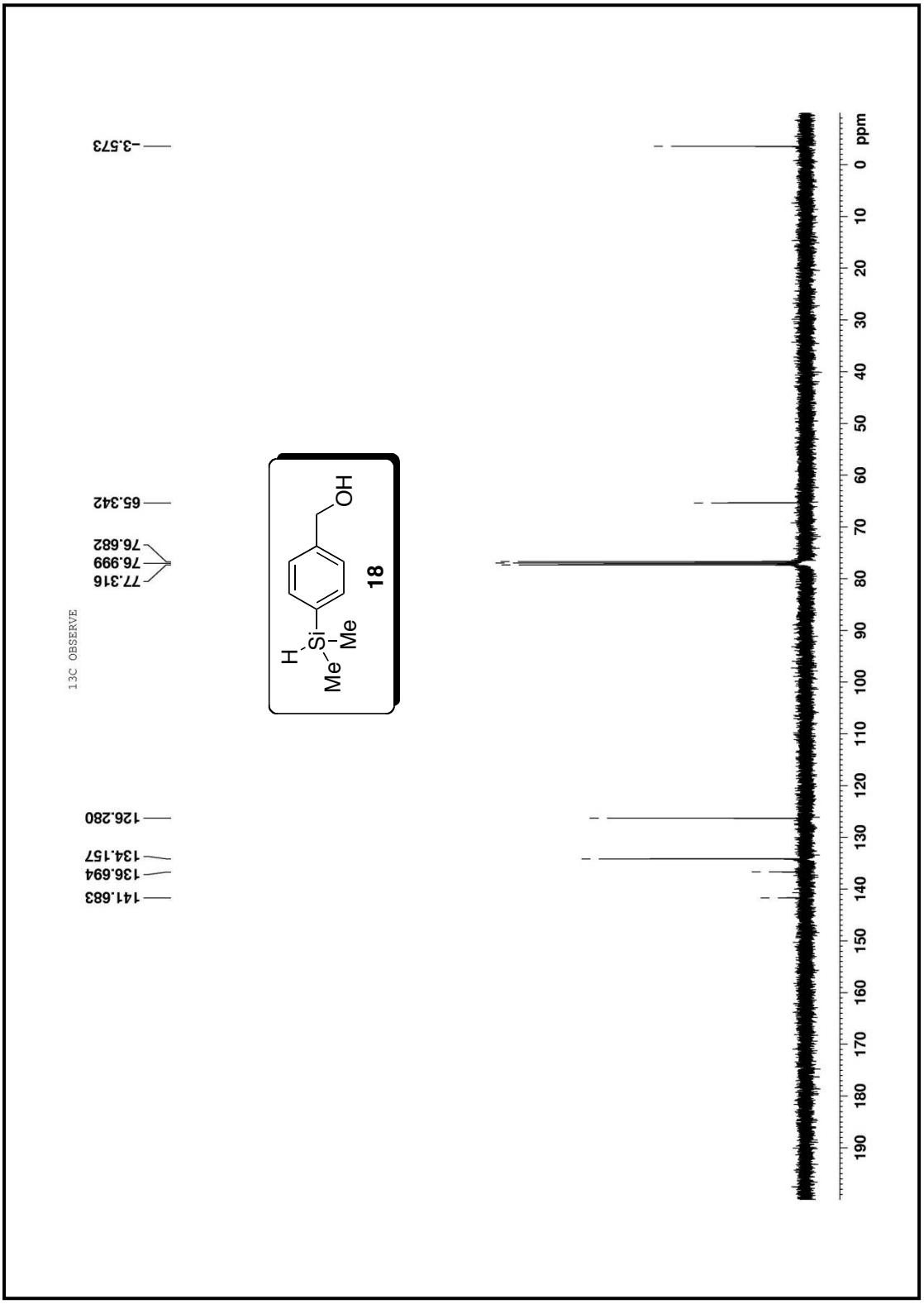

Figure S38. ^{13}C NMR spectrum of **18**

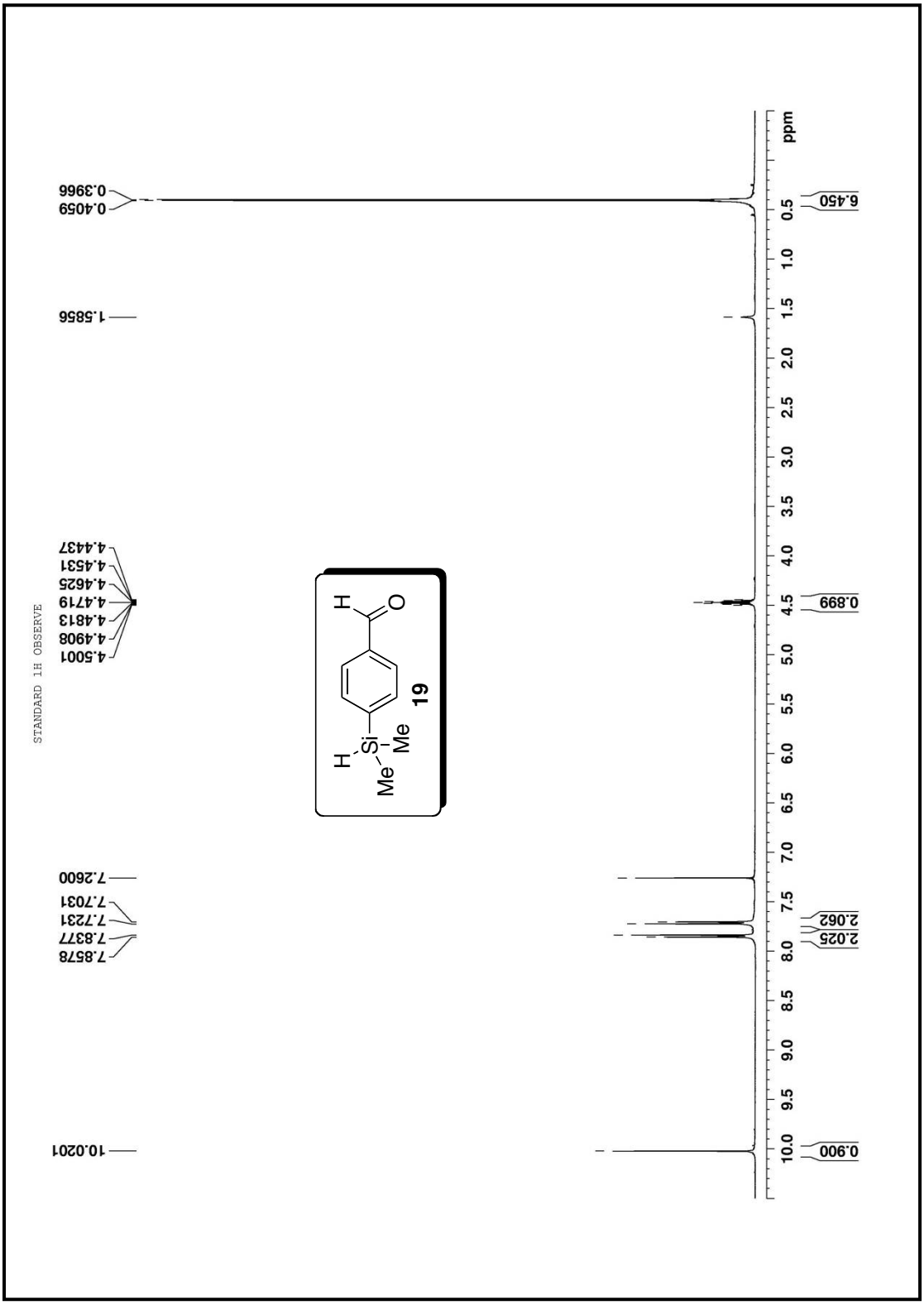

Figure S39. ^{1}H NMR spectrum of **19**

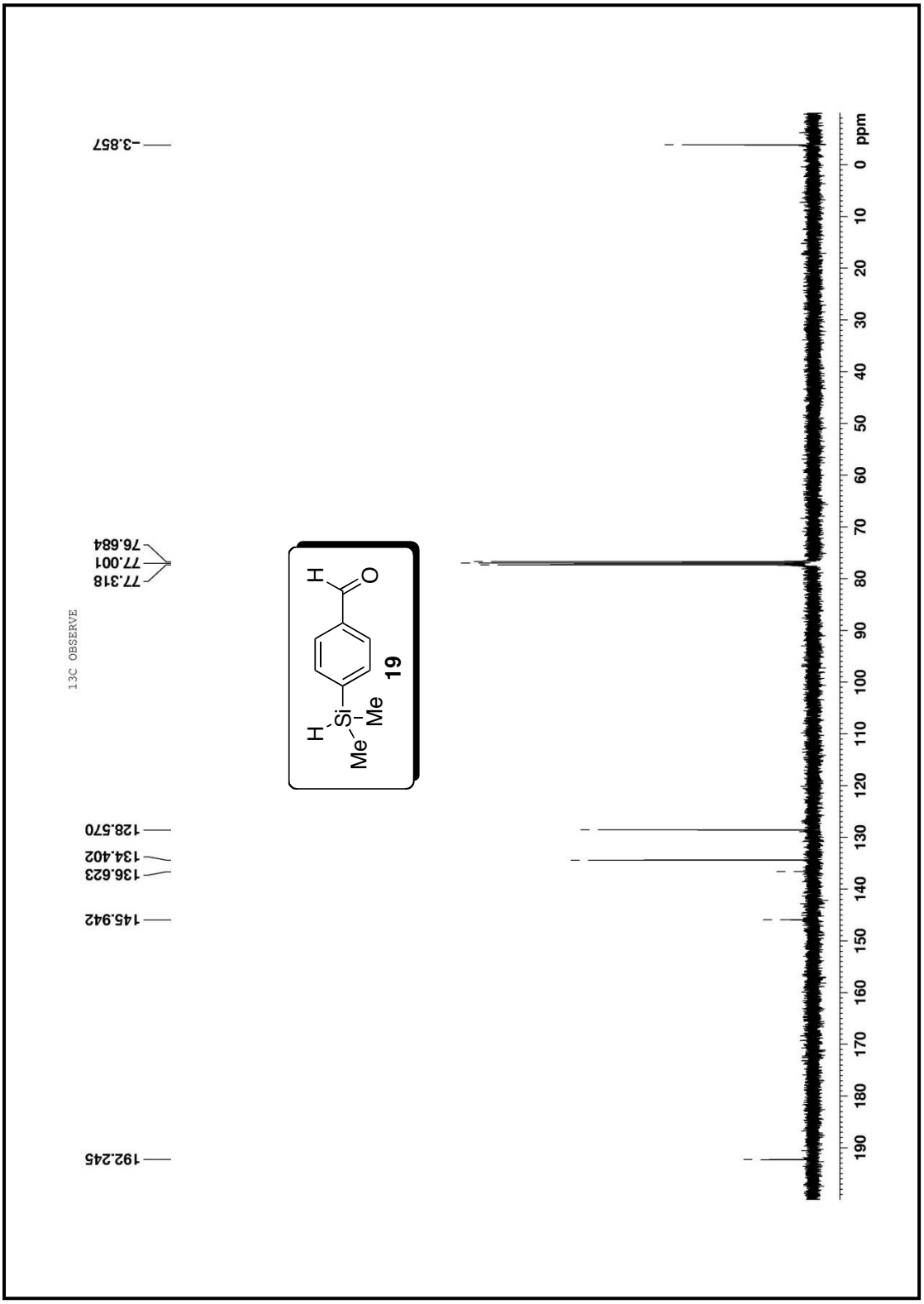

Figure S40. ^{13}C NMR spectrum of **19**

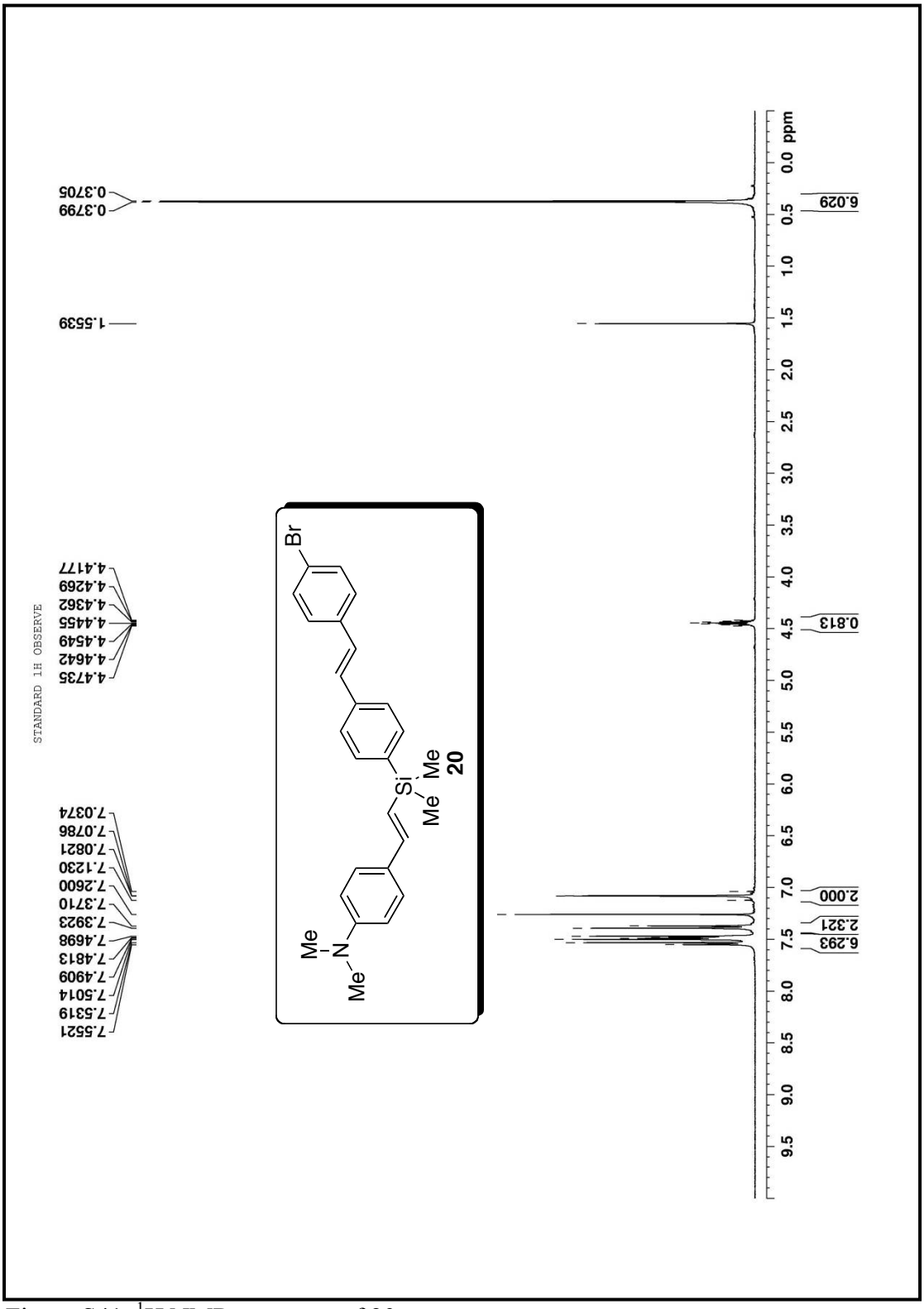

Figure S41. ^{1}H NMR spectrum of **20**

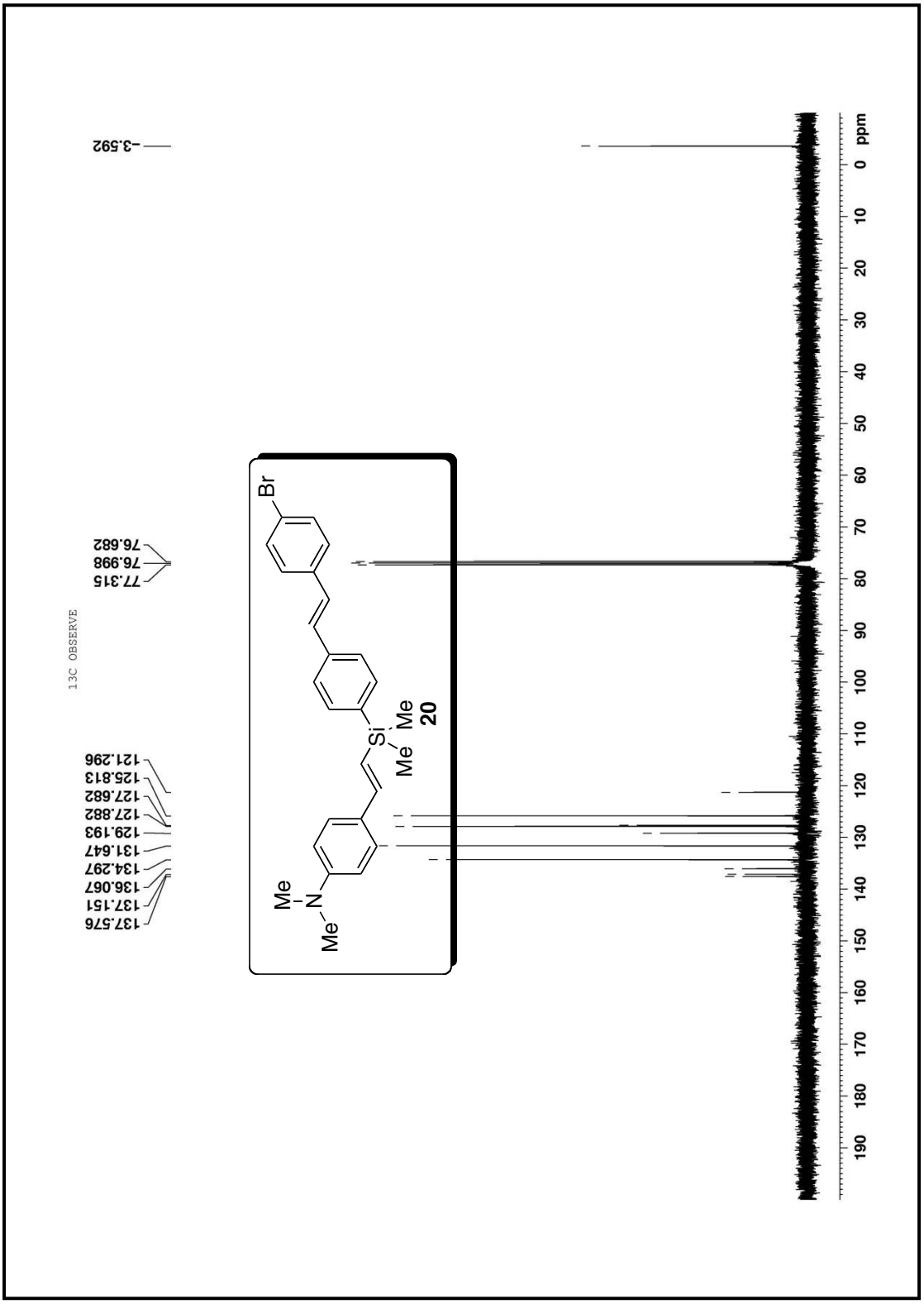

Figure S42. ^{13}C NMR spectrum of **20**

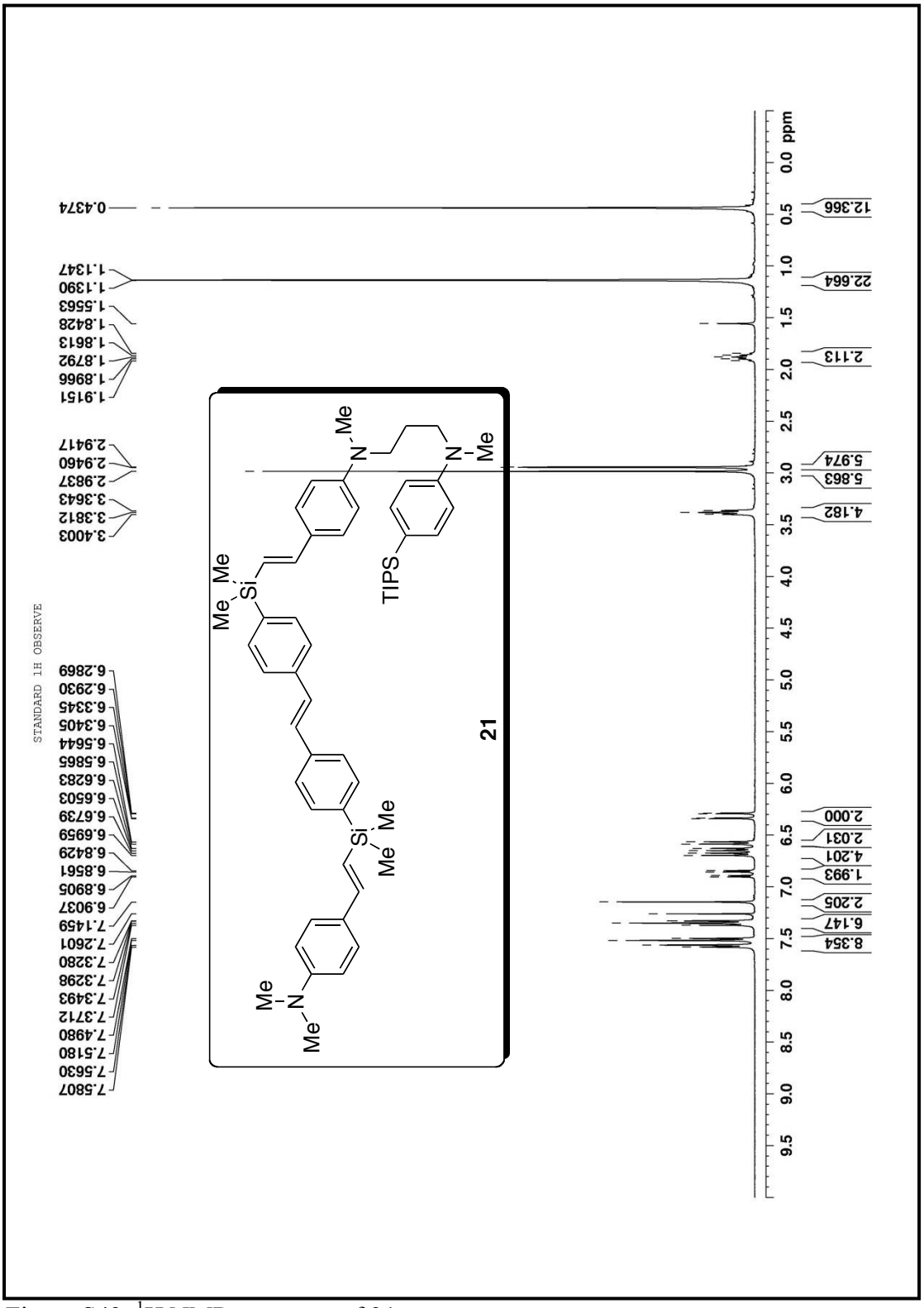

Figure S43. ^{1}H NMR spectrum of **21**

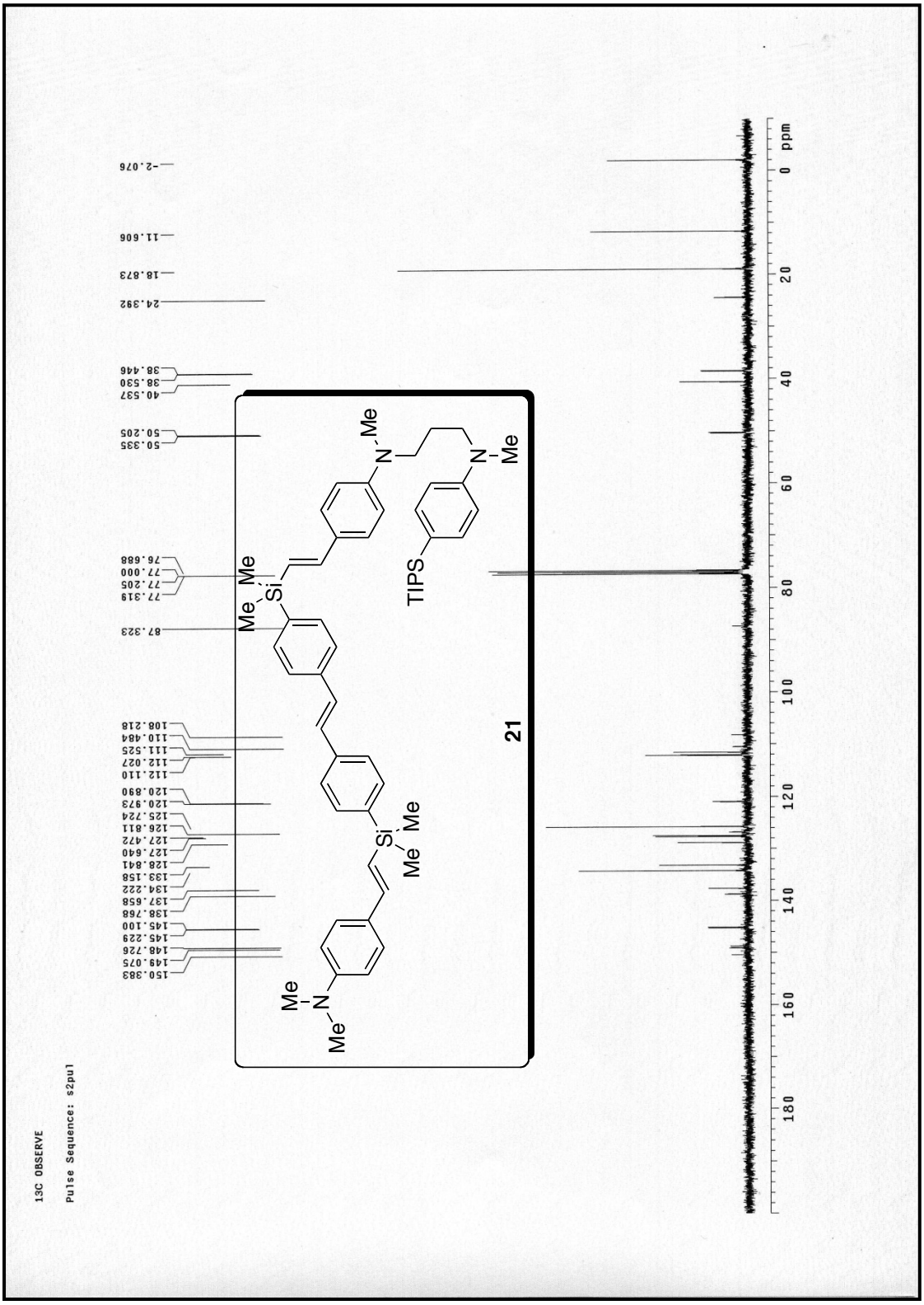

Figure S44. ^{13}C NMR spectrum of **21**

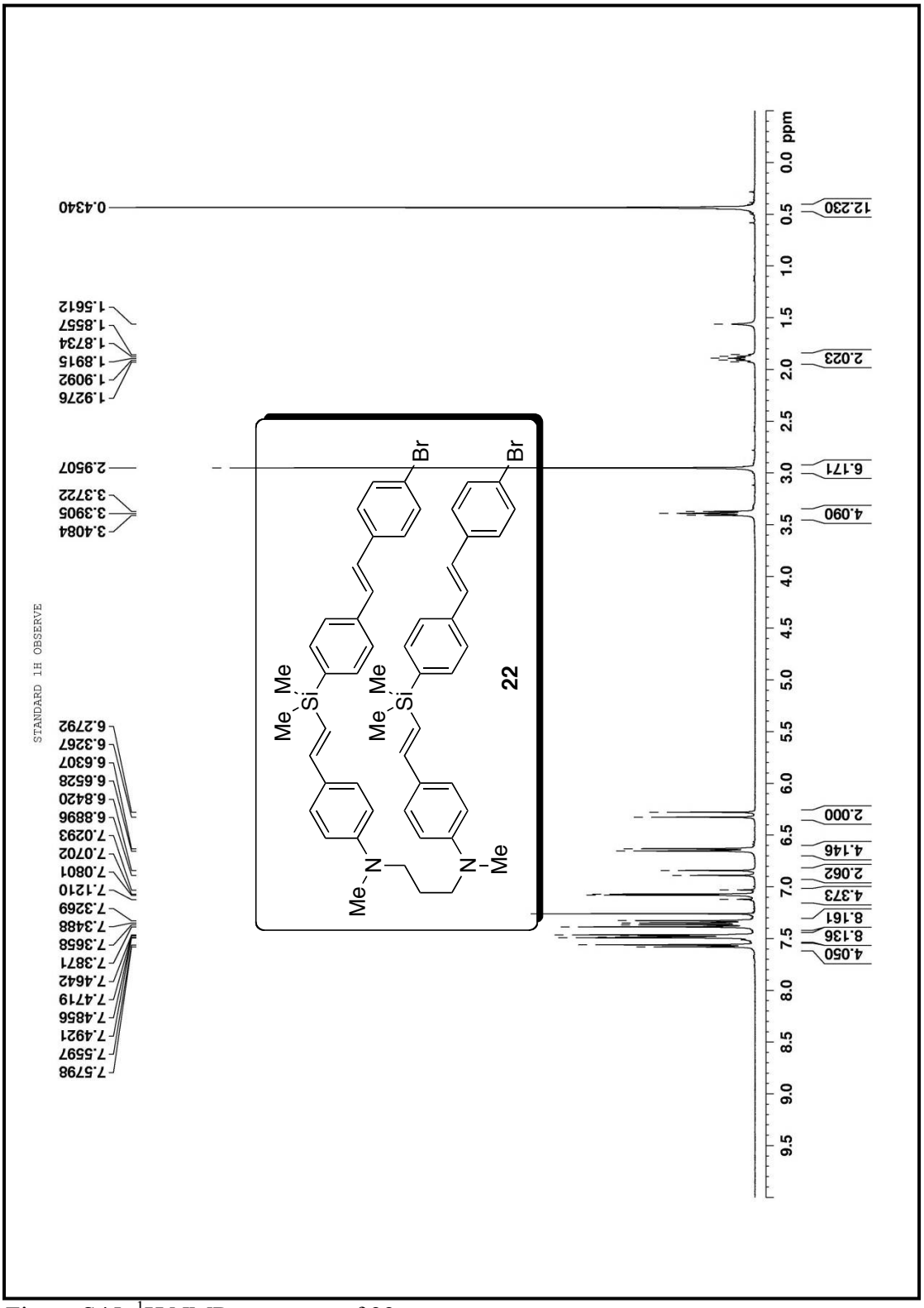

Figure S45. ^{1}H NMR spectrum of **22**

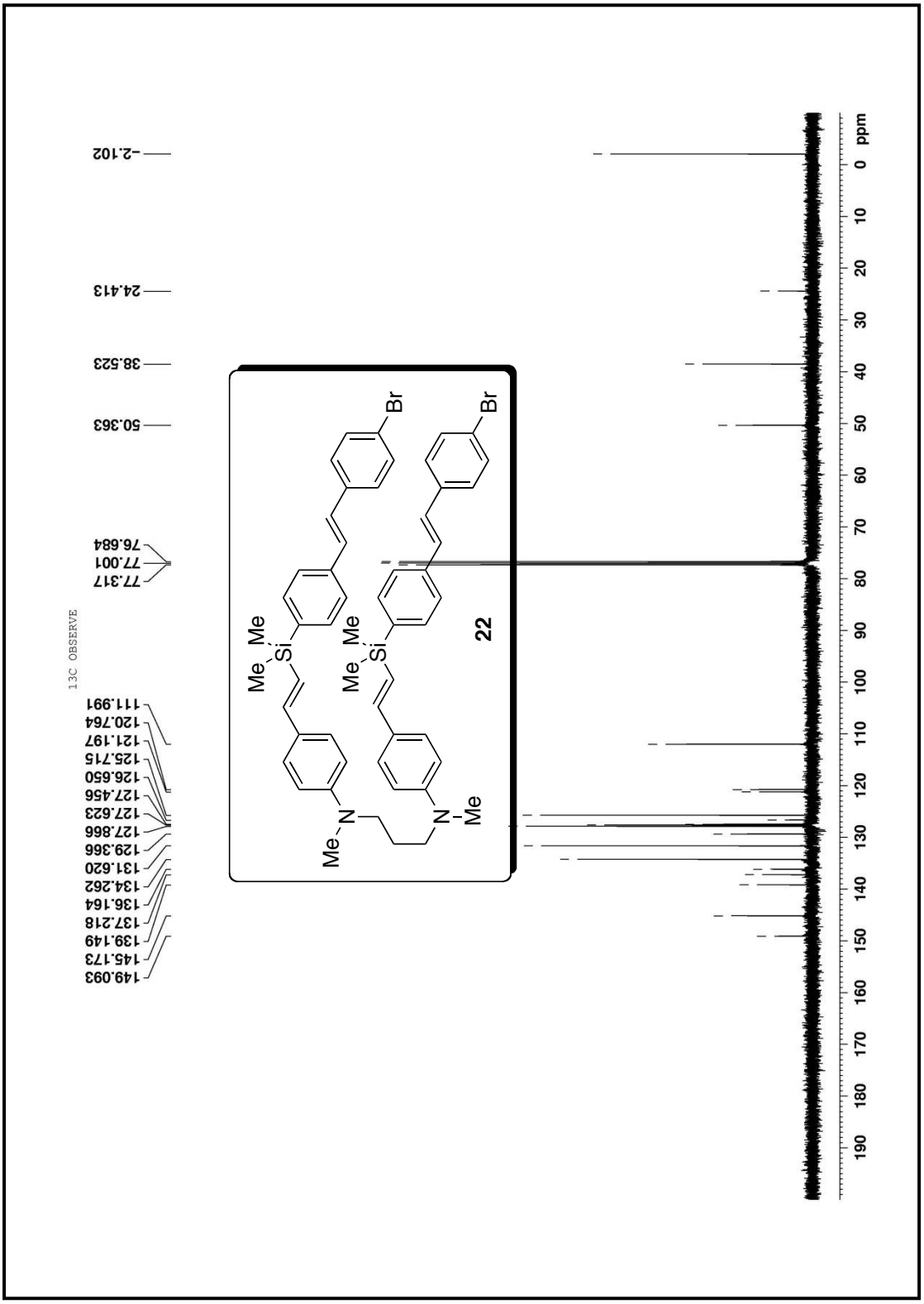

Figure S46. ^{13}C NMR spectrum of **22**