Electronic Supplementary Material (ESI) for ChemComm.

Sulfur-directed carbon-sulfur bond cleavage for Rh-catalyzed regioselective alkynylthiolation of alkynes

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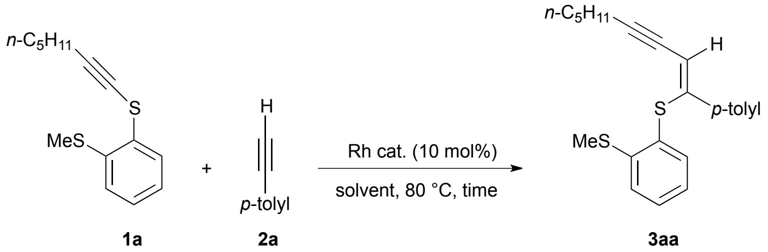
Table of Contents

i) Condition screening for the intermolecular reaction of 1a with 2a



Entry[a]	Rh catalyst[b]	Solvent	Time (h)	Yield (%)
1	$[Rh(cod)_2]OTf$ + BIPHEP	DCE	1	19
2	$[\mathbf{Ir}(cod)_2]OTf$ + BIPHEP	DCE	1	ND
3	$1/2\mathbf{[RhCl(cod)]_2}$ + BIPHEP	DCE	1	ND
4	$[Rh(cod)_2]OTf + 2PPh_3$	DCE	1	ND
5	$[Rh(cod)_2]OTf$ + 2P(cyclohexyl)$_3$	DCE	1	ND
7	$[Rh(cod)_2]OTf$ + DPPE	DCE	0.25	86
8	$[Rh(cod)_2]$ OTf + DPPE	toluene	0.25	72
9	$[Rh(cod)_2]$ OTf + DPPE	1,4-dioxane	0.25	81

[a] The ratio of sulfide **1a**/alkyne **2a** was 1/3. [b] BIPHEP: 2,2'-bis(diphenylphosphino)-1,1'-biphenyl, DPPE: 1,2-bis(diphenylphosphino)ethane, DPPE: 1,2-bis(diphenylphosphino)ethane.

ii) Condition screening for the intramolecular reaction of 6a

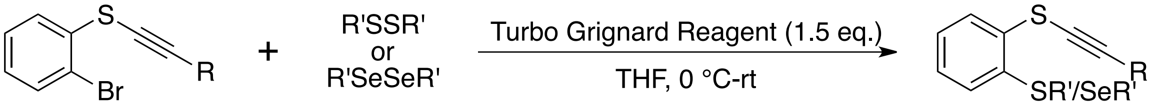
Entry	Rh catalyst	x (mol%)	n (M)[a]	Yield (%)
1	[Rh(cod)(dppe)]OTf	10	0.10	22
2	$[Rh(cod)_2]OTf$ + *rac*-BINAP	10	0.10	78
3	$[Rh(cod)_2]OTf$ + *rac*-BINAP	10	0.05	85
4	$[Rh(cod)_2]OTf$ + *rac*-BINAP	50	0.05	44
5	$[Rh(cod)_2]OTf$ + *rac*-BINAP	5	0.10	93

[a] The initial concentration of diyne **6a**.

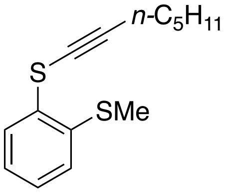
iii) Experimental details and characterization data for new compounds

General: ^1H NMR spectra were recorded on JEOL ECX-500 (500 MHz) spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; dt, doublet of triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained by JEOL ECX-500 (125 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.16 ppm in $CDCl_3$). $CDCl_3$ was used as a NMR solvent. High-resolution mass spectra (HRMS) were measured on an ESI (Electro Spray Ionization) – Orbitrap mass spectrometer method. X-ray structures were obtained by a Rigaku R-AXIS RAPID diffractometer. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF254) prepared in our laboratory, Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air and backfilled under argon at room temperature. Unless otherwise noted, all reactions were performed under an argon atmosphere. All reagents were purchased from Wako, Kanto, Aldrich and TCI and used without further purification.

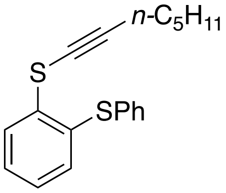
General procedure for the syntheses of substrate (GP):



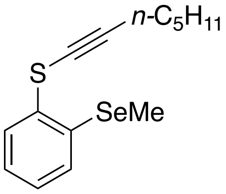
Tetrahydrofuran (3.0 ml) was added to bromide derivatives (1.0 mmol) and Turbo Grignard Reagent (1.5 eq.) in round-bottom flask at 0 ℃, then stirred for 2 hours at room temperature. Disulfide (or diselenide) (2.0 eq.) was added to the reaction vessel at 0 ℃, then the mixture was stirred at room temperature for 2 hours. After reaction was completed, water was added and the mixture was extracted with AcOEt. The extract was dried (Na_2SO_4), and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel.



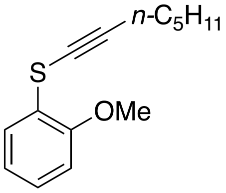
[Hept-1-ynyl][2-(methylsulfanyl)phenyl]sulfane (1a). GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a yellow oil (65%). ^{1}H NMR δ 7.68 (dd, J = 1.3, 7.9 Hz, 1H), 7.32 (dd, J = 1.3, 7.6 Hz, 1H), 7.26 (dt, J_d = 1.4 Hz, J_t = 7.6 Hz, 1H), 7.16 (dt, J_d = 1.4 Hz, J_t = 7.9 Hz, 1H), 2.46 (t, J = 7.5 Hz, 2H), 2.44 (s, 3H), 1.66-1.57 (m, 2H), 1.46-1.32 (m, 4H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 136.4, 134.0, 130.4, 127.6, 126.6, 126.3, 101.2, 64.9, 31.2, 28.5, 22.4, 20.5, 17.9, 14.2; HRMS(ESI) calcd for $C_{14}H_{19}S_2$ (M+H): 251.0923; found: 251.0923.



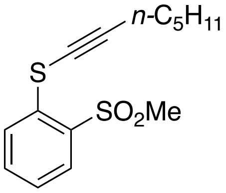
[Hept-1-ynyl][2-(Phenylsulfanyl)phenyl]sulfane (1b). GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a pale yellow oil (20 %). ^{1}H NMR δ 7.77 (dd, J = 1.3, 8.0 Hz, 1H), 7.44-7.37 (m, 2H), 7.27-7.22 (m, 2H), 7.20-7.15 (m, 4H), 2.46 (t, J = 7.0 Hz, 2H), 1.65-1.57 (m, 2H), 1.47-1.30 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 140.0, 135.7, 135.4, 129.6, 129.3, 129.1, 128.7, 126.5, 126.4, 126.2, 101.5, 64.7, 31.1, 28.3, 22.2, 20.3, 14.0; HRMS(ESI) calcd for $C_{19}H_{21}S_2$ (M+H): 313.1079; found: 313.1080.



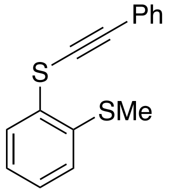
[Hept-1-ynyl][2-(methylselenyl)phenyl]sulfane (1c). GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a yellow oil (63%). ^{1}H NMR δ 7.68 (dd, J = 1.2, 7.7 Hz, 1H), 7.46 (dd, J = 1.4, 7.7 Hz, 1H), 7.29 (dt, J_d = 1.4 Hz, J_t = 7.5 Hz, 1H), 7.11 (dt, J_d = 1.4 Hz, J_t = 7.5 Hz, 1H), 2.46 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.64-1.59 (m, 2H), 1.46-1.33 (m, 4H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 137.9, 133.1, 127.9, 127.9, 126.2, 125.9, 100.6, 65.0, 30.8, 28.0, 21.9, 20.0, 13.7, 8.4; HRMS(ESI) calcd for $C_{14}H_{19}SSe$ (M+H): 299.0367; found: 299.0368.



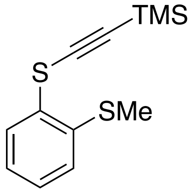
[Hept-1-ynyl][2-methoxyphenyl]sulfane (1d). Tetrahydrofuran (4.0 ml) was added to 1-heptyne (2.0 mmol) and *n*-BuLi (0.9 eq.) in round-bottom flask at -78 ℃, then stirred for 1 hour. Bis(2-methoxyphenyl) disulfide (0.7 eq.) in tetrahydrofuran (3 ml) was added to the reaction, then the mixture was stirred and warmed to room temperature. After reaction was completed, water was added and the mixture was extracted with diethyl ether. The extract was dried (Na_2SO_4), and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 3/1) to give title compound (47%) as a colorless oil. ^{1}H NMR δ 7.60 (dd, J = 1.6, 7.8 Hz, 1H), 7.19-7.15 (m, 1H), 7.01 (dt, J_d = 1.2 Hz, J_t = 7.7 Hz, 1H), 6.82 (dd, J = 1.1, 8.1 Hz, 1H), 3.87 (s, 3H), 2.46 (t, J = 7.0 Hz, 2H), 1.66-1.58 (m, 2H), 1.47-1.32 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 155.0, 126.8, 126.2, 122.5, 121.5, 110.2, 100.5, 64.2, 55.8, 31.1, 28.4, 22.2, 20.3, 13.9; HRMS(ESI) calcd for $C_{14}H_{19}OS$ (M+H): 235.1151; found: 235.1152.



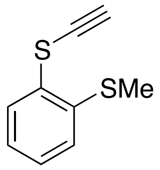
[Hept-1-ynyl][2-(methylsulfonyl)phenyl]sulfane (1e). Tetrahydrofuran (2.0 ml) was added to (2-bromophenyl)(hept-1-ynyl)sulfane (1.0 mmol) and Turbo Grignard Reagent (1.5 eq.) in round-bottom flask at 0 ℃, then stirred for 2 hour at room temperature. Methanesulfonyl chloride (2.2 eq.) was added to the reaction, then the mixture was stirred and warmed to room temperature. After reaction was completed, saturated aq.$NaHCO_3$ was added and the mixture was extracted with diethyl ether. The extract was dried (Na_2SO_4), and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (hexane/EtOAc = 5/1) to give title compound (17%) as a colorless oil. ^{1}H NMR δ 8.03-7.99 (m, 2H), 7.63 (dt, J_d = 1.3 Hz, J_t = 7.4 Hz, 1H), 7.41-7.36 (m, 1H), 3.17 (s, 3H), 2.49 (t, J = 7.1 Hz, 2H), 1.67-1.62 (m, 2H), 1.48-1.33 (m, 4H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 136.2, 136.0, 134.0, 129.9, 128.4, 126.4, 102.3, 63.7, 42.1, 31.1, 28.1, 22.1, 20.3, 14.0; HRMS(ESI) calcd for $C_{14}H_{18}O_2NaS_2$ (M+Na): 305.0640; found: 305.0640.



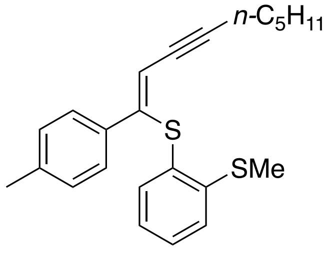
[2-(Methylsulfanyl)phenyl][phenylethynyl]sulfane (1f). GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a pale yellow oil (78%). ^{1}H NMR δ 7.75 (dd, J = 1.1, 7.9 Hz, 1H), 7.53-7.50 (m, 2H), 7.36-7.33 (m, 4H), 7.27 (dt, J_d = 1.4 Hz, J_t = 7.5 Hz, 1H), 7.19 (dt, J_d = 1.4 Hz, J_t = 7.5 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR δ 135.6, 134.5, 131.9, 130.7, 128.8, 128.5, 127.8, 127.1, 126.8, 123.0, 98.8, 75.8, 18.0; HRMS(ESI) calcd for $C_{15}H_{13}S_2$ (M+H): 257.0453; found: 257.0454.



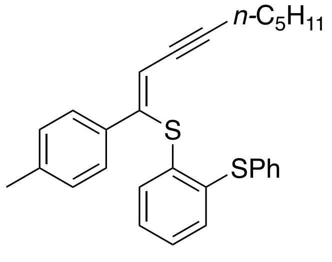
[2-(Methylsulfanyl)phenyl][trimethylsilylethynyl]sulfane (1g). GP was used. Isolated by preparative TLC (hexane only). The title compound was obtained as a pale yellow oil (73%). ^{1}H NMR δ 7.68 (dd, J = 1.3, 7.8 Hz, 1H), 7.37-7.34 (m, 1H), 7.32-7.27 (m, 1H), 7.23-7.18 (m, 1H), 2.45 (s, 3H), 0.27 (s, 9H); ^{13}C NMR δ 135.1, 134.3, 130.8, 127.9, 127.0, 126.4, 107.3, 90.5, 18.0, 0.0; HRMS(ESI) calcd for $C_{12}H_{17}S_2Si$ (M+H): 253.0535; found: 253.0536.



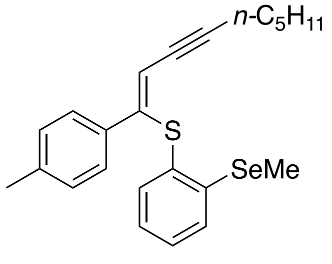
[Ethynyl][2-(methylsulfanyl)phenyl]sulfane (1h). Substrate (**1g**, 252.5 mg, 1.0 mmol) was dissolved in methanol (4.0 ml) and tetrahydrofuran (2.0 ml). After addition of KOH (62.1 mg, 1.1 mmol) and water (1.4 ml), the mixture was stirred at room temperature. After 2 h, the solvents were removed, and the residue was purified by preparative TLC (hexane/toluene = 5/1) to give corresponding substrate (**1h**, 94%) as a yellow oil. ^{1}H NMR δ 7.71 (dd, J = 1.0, 7.7 Hz, 1H), 7.36-7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.20 (dt, J_d = 1.2 Hz, J_t = 7.5 Hz, 1H), 3.28 (s, 1H), 2.44 (s, 3H); ^{13}C NMR δ 134.9, 133.9, 130.4, 127.6, 127.3, 127.0, 87.7, 71.2, 17.8; HRMS(ESI) calcd for $C_9H_9S_2$ (M+H): 181.0140; found: 181.0140.



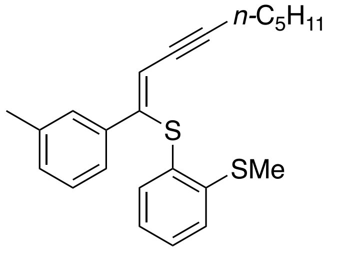
(Z)-[2-(Methylsulfanyl)phenyl][1-(4-methylphenyl)non-1-en-3-ynyl]sulfane (3aa). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (98%). ^{1}H NMR δ 7.37 (d, *J* = 7.9 Hz, 2H), 7.10-7.03 (m, 3H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.87 (dt, J_d = 1.4 Hz, J_t = 7.4 Hz, 1H), 6.22 (t, *J* = 2.2 Hz, 1H), 2.47 (s, 3H), 2.37 (dt, J_d = 2.2 Hz, J_t = 7.1 Hz, 2H), 2.25 (s, 3H), 1.57-1.51 (m, 2H), 1.41-1.29 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR δ 144.8, 139.3, 138.3, 135.6, 133.6, 131.4, 128.8, 127.5, 126.9, 125.9, 125.1, 113.0, 100.1, 78.5, 31.1, 28.3, 22.2, 21.1, 20.0, 16.2, 14.0; HRMS(ESI) calcd for $C_{23}H_{26}NaS_2$ (M+Na): 389.1368; found: 389.1368.



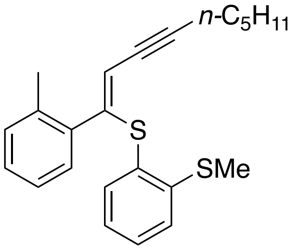
(Z)-[2-(Phenylsulfanyl)phenyl][1-(4-methylphenyl)non-1-en-3-ynyl]sulfane (3ba). Purified by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound and dimer of **1b** were obtained as a mixture, and the yield was determined to be 67% by the NMR analysis using tetrachloroethylene as an internal standard. Only the discriminable ^{1}H NMR and ^{13}C NMR peaks for compound **3ba** were listed. ^{1}H NMR δ 6.19 (t, *J* = 2.0 Hz, 1H), 2.36 (dt, J_d = 2.0 Hz, J_t = 7.0 Hz, 2H), 2.25 (s, 3H), 1.56-1.46 (m, 2H), 1.41-1.26 (m, 4H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR δ 100.4, 78.8, 31.3, 28.5, 22.4, 21.3, 20.2, 14.2; HRMS(ESI) calcd for $C_{28}H_{28}NaS_2$ (M+Na): 451.1525; found: 451.1526.



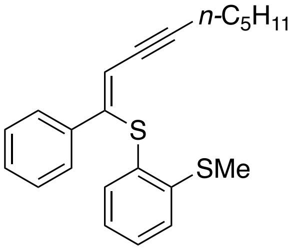
(Z)-[2-(Methylselenyl)phenyl][1-(4-methylphenyl)non-1-en-3-ynyl]sulfane (3ca). Isolated by preparative TLC (hexane/CH_2Cl_2 = 4/1). The title compound was obtained as a yellow oil (89%). ^{1}H NMR δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.06 (dd, *J* = 1.4, 7.8 Hz, 1H), 7.01-6.98 (m, 3H), 6.90 (dt, J_d = 1.4 Hz, J_t = 7.6 Hz, 1H), 6.12 (t, *J* = 2.2 Hz, 1H), 2.38 (dt, J_d = 2.2 Hz, J_t = 7.0 Hz, 2H), 2.32 (s, 3H), 2.25 (s, 3H), 1.58-1.52 (m, 2H), 1.42-1.29 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 145.1, 138.3, 135.5, 135.3, 134.9, 131.7, 128.8, 128.6, 127.5, 127.1, 125.8, 112.9, 100.2, 78.5, 31.1, 28.4, 22.2, 21.1, 20.0, 14.0, 7.1; HRMS(ESI) calcd for $C_{23}H_{26}NaSSe$ (M+Na): 437.0810; found: 437.0811.



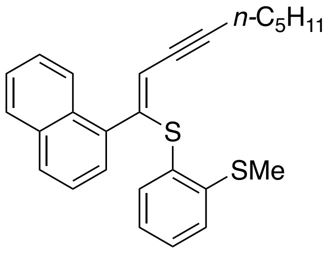
(Z)-[2-(Methylsulfanyl)phenyl][1-(3-methylphenyl)non-1-en-3-ynyl]sulfane (3ab). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (89%). ^{1}H NMR δ 7.30-7.26 (m, 2H), 7.09-7.03 (m, 4H), 6.98 (d, J = 7.4 Hz, 1H), 6.89-6.86 (m, 1H), 6.15-6.14 (m, 1H), 2.47 (s, 3H), 2.37 (dt, J_d = 2.2 Hz, J_t = 7.1 Hz, 2H), 2.24 (s, 3H), 1.57-1.51 (m, 2H), 1.42-1.29 (m, 4H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 145.2, 139.6, 138.4, 137.6, 133.4, 131.7, 129.1, 128.3, 127.9, 127.0, 125.9, 125.0, 124.8, 113.3, 100.3, 78.4, 31.1, 28.3, 22.2, 21.3, 20.0, 16.2, 14.0; HRMS(ESI) calcd for $C_{23}H_{26}NaS_2$ (M+Na): 389.1368; found: 389.1368.



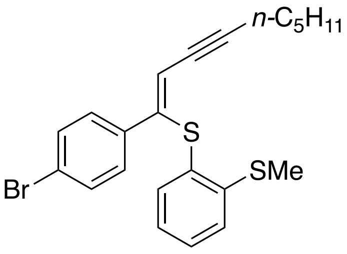
(Z)-[2-(Methylsulfanyl)phenyl][1-(2-methylphenyl)non-1-en-3-ynyl]sulfane (3ac). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a red brown oil (96%). ^{1}H NMR δ 7.18-7.14 (m, 2H), 7.10 (dt, J_d = 1.4 Hz, J_t = 7.5 Hz, 1H), 7.03-6.98 (m, 3H), 6.95-6.91 (m, 1H), 6.83 (dt, J_d = 1.3 Hz, J_t = 7.4 Hz, 1H), 5.72-5.71 (m, 1H), 2.46 (dt, J_d = 2.2 Hz, J_t = 7.1 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 1.66-1.60 (m, 2H), 1.51-1.45 (m, 2H), 1.40-1.36 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 146.6, 143.4, 137.9, 136.2, 135.1, 129.9, 129.8, 129.8, 128.5, 127.8, 124.8, 124.3, 124.1, 110.9, 99.7, 77.4, 31.1, 28.5, 22.3, 20.0, 20.0, 15.7, 14.1; HRMS(ESI) calcd for $C_{23}H_{26}NaS_2$ (M+Na): 389.1368; found: 389.1368.



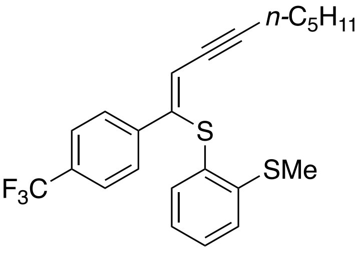
(Z)-[2-(Methylsulfanyl)phenyl][1-(phenyl)non-1-en-3-ynyl]sulfane (3ad). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (96%). ^{1}H NMR δ 7.48-7.44 (m, 2H), 7.20-7.14 (m, 3H), 7.08-7.00 (m, 3H), 6.87-6.82 (m, 1H), 6.14 (t, J = 1.8 Hz, 1H), 2.45 (s, 3H), 2.38 (dt, J_d = 1.8 Hz, J_t = 6.8 Hz, 2H), 1.58-1.50 (m, 2H), 1.43-1.27 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 145.3, 139.9, 138.6, 133.2, 132.0, 128.5, 128.2, 127.8, 127.3, 125.9, 125.1, 113.6, 100.6, 78.6, 31.3, 28.5, 22.4, 20.2, 16.3, 14.2; HRMS(ESI) calcd for $C_{22}H_{24}NaS_2$ (M+Na): 375.1212; found: 375.1212.



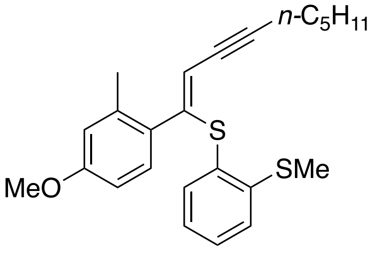
(Z)-[2-(Methylsulfanyl)phenyl][1-(1-naphthyl)non-1-en-3-ynyl]sulfane (3ae). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (83%). ^{1}H NMR δ 8.34-8.33 (m, 1H), 7.68-7.66 (m, 1H), 7.57-7.56 (m, 1H), 7.48-7.44 (m, 1H), 7.41-7.37 (m, 1H), 7.35 (dd, J = 1.1, 7.1 Hz, 1H), 7.18-7.15 (m, 1H), 6.97 (dd, J = 1.3, 7.7 Hz, 1H), 6.91 (dt, J_d = 1.4 Hz, J_t = 7.9 Hz, 1H), 6.84 (dd, J = 1.3, 7.9 Hz, 1H), 6.52 (dt, J_d = 1.4 Hz, J_t = 7.5 Hz, 1H), 5.88 (t, J = 2.2 Hz, 1H), 2.48 (dt, J_d = 2.2 Hz, J_t = 7.1 Hz, 2H), 2.34 (s, 3H), 1.67-1.62 (m, 2H), 1.52-1.46 (m, 2H), 1.41-1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 145.9, 143.7, 135.9, 135.5, 133.1, 131.5, 129.5, 128.6, 128.2, 127.9, 127.1, 125.9, 125.8, 125.6, 124.5, 124.2, 123.8, 111.2, 100.1, 77.5, 31.1, 28.5, 22.3, 20.0, 15.7, 14.0; HRMS(ESI) calcd for $C_{26}H_{26}NaS_2$ (M+Na): 425.1368; found: 425.1368.



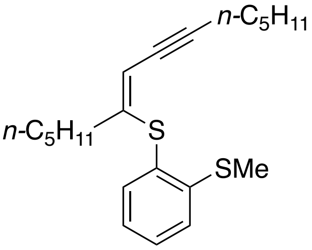
(Z)-[2-(Methylsulfanyl)phenyl][1-(4-bromophenyl)non-1-en-3-ynyl]sulfane (3af). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (87%). ^{1}H NMR δ 7.33-7.28 (m, 4H), 7.09-7.03 (m, 3H), 6.89-6.85 (m, 1H), 6.10 (t, J = 2.2 Hz, 1H), 2.45-2.44 (m, 3H), 2.39 (dt, J_d = 2.2 Hz, J_t = 7.2 Hz, 2H), 1.59-1.52 (m, 2H), 1.43-1.27 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 144.2, 140.1, 137.4, 132.2, 132.0, 131.2, 129.2, 127.5, 125.5, 125.0, 122.3, 113.8, 101.0, 78.3, 31.1, 28.3, 22.2, 20.0, 16.0, 14.0; HRMS(ESI) calcd for $C_{22}H_{23}BrNaS_2$ (M+Na): 453.0317; found: 453.0318.



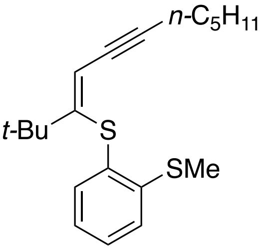
(Z)-[2-(Methylsulfanyl)phenyl][1-(4-trifluoromethylphenyl)non-1-en-3-ynyl]sulfane (3ag). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (81%). ^{1}H NMR δ 7.56 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.09-7.07 (m, 3H), 6.89-6.86 (m, 1H), 6.17 (t, J = 2.3 Hz, 1H), 2.47 (s, 3H), 2.41 (dt, J_d = 2.3 Hz, J_t = 7.2 Hz, 2H), 1.60-1.54 (m, 2H), 1.44-1.29 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 143.9, 142.0 (d, $J_{C\text{-}F}$ = 1.5 Hz), 140.3, 132.1, 131.9, 130.0 (q, $J_{C\text{-}F}$ = 32.8 Hz), 127.9, 127.6, 125.6, 125.0 (q, $J_{C\text{-}F}$ = 3.9 Hz), 123.9 (d, $J_{C\text{-}F}$ = 276.9 Hz), 115.0, 101.8, 78.1, 31.1, 28.2, 22.2, 20.0, 16.0, 13.9 (a pair of peaks at the aromatic region is overlapped); HRMS(ESI) calcd for $C_{23}H_{23}F_3NaS_2$ (M+Na): 443.1088; found: 443.1089.



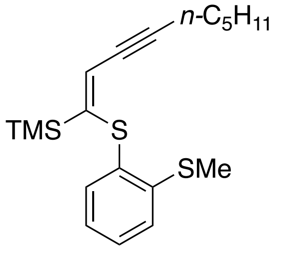
(Z)-[2-(Methylsulfanyl)phenyl][1-(2-methyl-4-methoxyphenyl)non-1-en-3-ynyl]sulfane (3ah). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a pale yellow oil (95%). ^1H NMR δ 7.14-7.12 (m, 1H), 7.08-7.05 (m, 2H), 6.97-6.95 (m, 1H), 6.83-6.79 (m, 1H), 6.52-6.51 (m, 1H), 6.46 (dd, J = 2.4, 8.3 Hz, 1H), 5.66 (t, J = 2.1 Hz, 1H), 3.67 (s, 3H), 2.42 (dt, J_d = 2.1 Hz, J_t = 7.1 Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H), 1.62-1.55 (m, 2H), 1.47-1.29 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 159.1, 146.5, 143.2, 138.0, 135.0, 131.2, 130.7, 130.5, 128.5, 124.5, 124.3, 115.3, 111.1, 110.4, 99.7, 77.7, 55.2, 31.3, 28.6, 22.4, 20.5, 20.1, 15.9, 14.2; HRMS(ESI) calcd for $C_{24}H_{28}ONaS_2$ (M+Na): 419.1474; found: 419.1472.



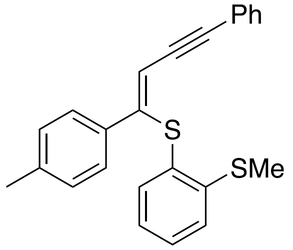
(Z)-[2-(Methylsulfanyl)phenyl][1-(pentyl)non-1-en-3-ynyl]sulfane (3ai). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (81%). ^1H NMR δ 7.42 (dd, J = 1.1, 7.7 Hz, 1H), 7.30-7.29 (m, 1H), 7.15-7.13 (m, 1H), 7.09-7.05 (m, 1H), 5.66-5.64 (m, 1H), 2.44 (s, 3H), 2.36 (dt, J_d = 2.0 Hz, J_t = 6.9 Hz, 2H), 2.02 (t, J = 7.1 Hz, 2H), 1.58-1.51 (m, 2H), 1.43-1.28 (m, 6H), 1.21-1.07 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H), 0.80 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 147.5, 143.4, 134.6, 129.7, 129.6, 128.4, 124.2, 107.6, 97.4, 77.1, 35.2, 30.8, 30.7, 28.2, 27.8, 22.0, 21.9, 19.5, 15.3, 13.7, 13.6; HRMS(ESI) calcd for $C_{21}H_{30}NaS_2$ (M+Na): 369.1681; found: 369.1681.



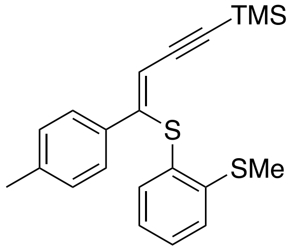
(Z)-[2-(Methylsulfanyl)phenyl][1-(2-methyl-2-propanyl)non-1-en-3-ynyl]sulfane (3aj). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (86%). ^1H NMR δ 7.20-7.16 (m, 2H), 7.11-7.03 (m, 2H), 6.12 (t, J = 2.3 Hz, 1H), 2.49 (s, 3H), 2.04 (dt, J_d = 2.3 Hz, J_t = 7.0 Hz, 2H), 1.23 (s, 9H), 1.22-1.09 (m, 6H), 0.81 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 154.6, 136.7, 136.4, 127.7, 126.9, 125.6, 125.6, 114.5, 99.2, 78.1, 39.4, 30.9, 29.2, 28.0, 22.2, 19.6, 16.4, 13.9; HRMS(ESI) calcd for $C_{20}H_{28}NaS_2$ (M+Na): 355.1525; found: 355.1525.



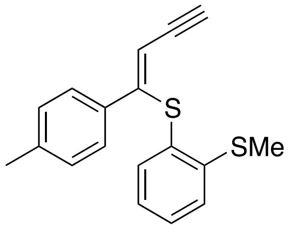
(Z)-[2-(Methylsulfanyl)phenyl][1-(trimethylsilyl)non-1-en-3-ynyl]sulfane (3ak). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (76%). ^{1}H NMR δ 7.31 (dd, *J* = 1.4, 7.5 Hz, 1H), 7.21-7.18 (m, 1H), 7.14 (dd, *J* = 1.3, 7.6 Hz, 1H), 7.04 (dt, J_d = 1.4 Hz, J_t = 7.5 Hz, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 2.46 (s, 3H), 2.23 (dt, J_d = 2.3 Hz, J_t = 7.2 Hz, 2H), 1.45-1.38 (m, 2H), 1.32-1.24 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.04 (s, 9H); ^{13}C NMR δ 148.6, 142.2, 134.4, 133.7, 128.6, 126.2, 125.6, 123.9, 102.2, 79.1, 32.1, 29.2, 23.2, 20.8, 16.9, 15.0, 0.0; HRMS(ESI) calcd for $C_{19}H_{28}NaS_2Si$ (M+Na): 371.1294; found: 371.1295.



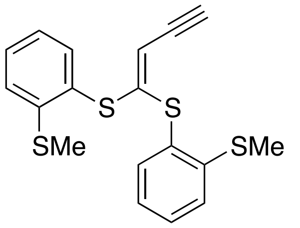
(Z)-[1-(4-Methylphenyl)-4-(phenyl)but-1-en-3-ynyl][2-(methylsulfanyl)phenyl]sulfane (3fa). Isolated by preparative TLC (hexane/CH_2Cl_2 = 4/1). The title compound was obtained as a pale yellow solid (91%). Mp 103 ℃; ^{1}H NMR δ 7.45-7.42 (m, 4H), 7.30-7.28 (m, 3H), 7.13-7.02 (m, 5H), 6.90-6.86 (m, 1H), 6.32 (s, 1H), 2.47 (s, 3H), 2.26 (s, 3H); ^{13}C NMR δ 147.1, 139.8, 138.7, 135.5, 133.1, 131.9, 131.6, 128.9, 128.2, 127.6, 127.3, 125.8, 125.1, 123.5, 111.6, 98.1, 87.6, 21.2, 16.1 (a pair of peaks at the aromatic region is overlapped); HRMS(ESI) calcd for $C_{24}H_{20}NaS_2$ (M+Na): 395.0899; found: 395.0900.



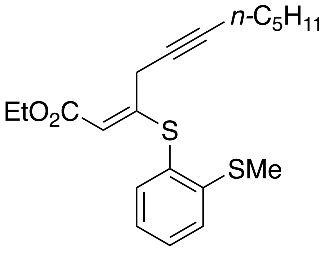
(Z)-[1-(4-Methylphenyl)-4-(trimethylsilyl)but-1-en-3-ynyl][2-(methylsulfanyl)phenyl]sulfane (3ga). Isolated by preparative TLC (hexane/CH_2Cl_2 = 4/1). The title compound was obtained as a yellow oil (90%). ^{1}H NMR δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.09-7.06 (m, 3H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.89-6.85 (m, 1H), 6.09 (s, 1H), 2.47 (s, 3H), 2.25 (s, 3H), 0.19 (s, 9H); ^{13}C NMR δ 148.6, 140.0, 138.8, 135.5, 133.1, 132.3, 129.0, 127.8, 127.4, 125.9, 125.1, 111.2, 104.1, 102.4, 21.3, 16.3, 0.0; HRMS(ESI) calcd for $C_{21}H_{24}NaS_2Si$ (M+Na): 391.0981; found: 391.0982.



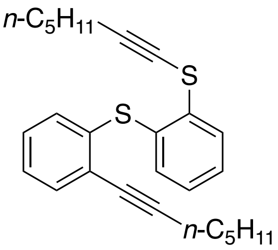
(Z)-[1-(4-Methylphenyl)but-1-en-3-ynyl][2-(methylsulfanyl)phenyl]sulfane (3ha). Isolated by preparative TLC (hexane/CH_2Cl_2 = 3/1). The title compound was obtained as a yellow oil (12%). ^1H NMR δ 7.35 (d, J = 8.1 Hz, 2H), 7.11-7.06 (m, 3H), 7.00 (d, J = 8.1 Hz, 2H), 6.91-6.85 (m, 1H), 6.05 (d, J = 2.2 Hz, 1H), 3.45 (dt, J = 2.2 Hz, 1H), 2.47 (s, 3H), 2.25 (s, 3H); ^{13}C NMR δ 149.5, 140.4, 138.9, 134.9, 132.5, 132.1, 128.9, 127.7, 127.6, 125.6, 124.9, 110.1, 85.5, 81.1, 21.2, 16.1; HRMS(ESI) calcd for $C_{18}H_{16}NaS_2$ (M+Na): 319.0586; found: 319.0587.



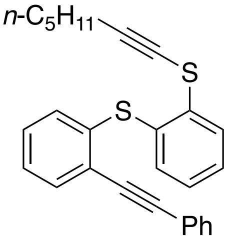
[1-((2-Methylsulfanylphenyl)sulfanyl)but-1-en-3-ynyl][2-(methylsulfanyl)phenyl]sulfane (3hh). Isolated by preparative TLC (hexane/CH_2Cl_2 = 3/1). The title compound was obtained as a yellow oil (64%). ^1H NMR δ 7.43 (dd, J = 1.3, 7.7 Hz, 1H), 7.36-28 (m, 3H), 7.20 (dd, J = 1.0, 7.7 Hz, 1H), 7.14 (dd, J = 1.2, 7.9 Hz, 1H), 7.12-7.06 (m, 2H), 5.48 (d, J = 2.5 Hz, 1H), 3.42 (d, J = 2.5 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H); ^{13}C NMR δ 146.5, 144.2, 143.4, 135.6, 134.6, 130.0, 129.6, 129.2, 128.9, 125.6, 125.3, 125.2, 124.9, 107.9, 85.5, 80.1, 16.1, 15.6; HRMS(ESI) calcd for $C_{18}H_{16}NaS_4$ (M+Na): 383.0027; found: 383.0027.



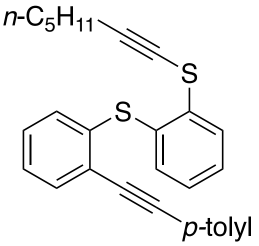
Ethyl (E)-3-((2-(methylsulfanyl)phenyl)sulfanyl)undec-2-en-5-ynoate (5). Isolated by preparative TLC (hexane/EtOAc = 5/1). The title compound was obtained as a yellow oil (54%). ^1H NMR δ 7.51 (dd, J = 1.4, 7.5 Hz, 1H), 7.43 (dt, J_d = 1.6 Hz, J_t = 7.8 Hz, 1H), 7.24-7.21 (m, 1H), 7.17 (dt, J_d = 1.2 Hz, J_t = 7.5 Hz, 1H), 5.08-5.07 (m, 1H), 4.07 (q, J = 7.2 Hz, 2H), 3.95-3.93 (m, 2H), 2.44 (s, 3H), 2.23-2.18 (m, 2H), 1.57-1.50 (m, 2H), 1.44-1.30 (m, 4H), 1.20 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 165.0, 158.0, 146.1, 137.6, 131.1, 126.5, 125.3, 124.9, 110.6, 83.5, 75.1, 60.0, 31.2, 28.6, 23.4, 22.4, 19.0, 15.4, 14.4, 14.2; HRMS(ESI) calcd for $C_{20}H_{26}O_2NaS_2$ (M+Na): 385.1266; found: 385.1267.



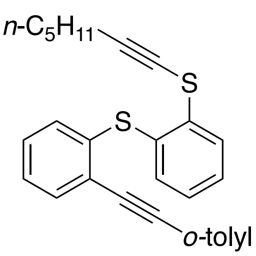
[Hept-1-ynyl][(2-((2-(hept-1-ynyl)phenyl)sulfanyl)phenyl)]sulfane (6a). Tetrahydrofuran solution (2.5 ml) of [Hept-1-ynyl][(2-((2-bromophenyl)sulfanyl)phenyl)]sulfane (1.48 g, 3.8 mmol) was added to a dry and argon-flushed flask, then cooled to -20 ℃. *i*PrMgCl・LiCl (tetrahydrofuran solution (abt. 14%), 4.7 ml, 4.9 mmol) was added at –20 ℃ and the resulting mixture was stirred for 2 h warming to rt. Then, a solution of I_2 (2.45 g, 9.6 mmol) in THF (9.0 ml) was added and stirred for 15 min. The reaction mixture was quenched with sat. $Na_2S_2O_3$ and the resulting mixture was extracted with diethyl ether. The combined organic layer was dried (Na_2SO_4), and concentrated under reduced pressure. Tetrahydrofuran 1.9 mL) and diisopropylamine (0.7 mL) were added to a part of crude mixture (303.0 mg, 0.6 mmol), $Pd(PPh_3)Cl_2$ (56.4 mg, 0.08 mmol) and CuI (30.8 mg, 0.16 mmol) under an Ar atmosphere. 1-heptyne (0.25 ml, 1.8 mmol) was added, and the resulting mixture was stirred at 60 ℃. After 4 h, the solvents were removed, and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 5/1) to give diyne (106.6 mg,44%) as a yellow oil. ^{1}H NMR δ 7.84-7.78 (m, 1H), 7.48-7.41 (m, 2H), 7.40-7.35 (m, 1H), 7.24-7.18 (m, 1H), 7.09-7.04 (m, 2H), 6.67-6.62 (m, 1H), 2.52-2.44 (m, 4H), 1.67-1.59 (m, 4H), 1.51-1.28 (m, 8H), 0.92 (t, J = 7.2 Hz, 6H); ^{13}C NMR δ 141.1, 138.8, 136.3, 132.4, 130.0, 128.0, 128.0, 126.5, 126.1, 126.1, 125.3, 122.6, 101.6, 97.7, 78.0, 64.8, 31.1, 31.1, 28.3, 22.2, 22.2, 20.3, 19.7, 14.0, 14.0 (a pair of peaks at the aliphatic region is overlapped); HRMS(ESI) calcd for $C_{26}H_{30}NaS_2$ (M+Na): 429.1681; found: 429.1682.



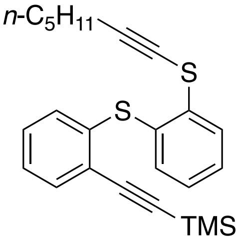
[Hept-1-ynyl][(2-((2-(phenylethynyl)phenyl)sulfanyl)phenyl)]sulfane (6b). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a pale yellow oil (39%). ^{1}H NMR δ 7.82 (dd, J = 1.1, 8.0 Hz, 1H), 7.61-7.30 (m, 8H), 7.21 (dt, J_d = 1.3 Hz, J_t = 7.5 Hz, 1H), 7.14-7.10 (m, 2H), 6.72-6.68 (m, 1H), 2.45 (t, J = 7.0 Hz, 2H), 1.65-1.57 (m, 2H), 1.46-1.30 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 141.3, 139.4, 136.6, 132.5, 131.8, 130.3, 128.9, 128.6, 128.4, 127.8, 126.7, 126.4, 126.3, 125.6, 123.1, 121.8, 101.9, 96.1, 86.9, 64.8, 31.2, 28.4, 22.3, 20.4, 14.1; HRMS(ESI) calcd for $C_{27}H_{24}NaS_2$ (M+Na): 435.1212; found: 435.1212.



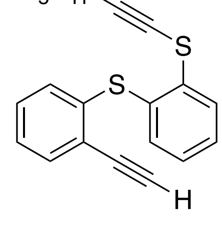
[Hept-1-ynyl][(2-((2-(4-methylphenylethynyl)phenyl)sulfanyl)phenyl)]sulfane (6c). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (40%). ^{1}H NMR δ 7.81 (dd, *J* = 0.9, 7.9 Hz, 1H), 7.50-7.41 (m, 5H), 7.23-7.09 (m, 5H), 6.70-6.67 (m, 1H), 2.45 (t, *J* = 7.1 Hz, 2H), 2.36(s, 3H), 1.64-1.59 (m, 2H), 1.46-1.30 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 141.3, 139.2, 138.7, 136.5, 132.4, 131.6, 130.2, 129.2, 128.7, 127.9, 126.7, 126.4, 126.2, 125.5, 122.0, 120.0, 101.8, 96.4, 86.2, 64.8, 31.1, 28.4, 22.3, 21.6, 20.4, 14.1; HRMS(ESI) calcd for $C_{28}H_{26}NaS_2$ (M+Na): 449.1368; found: 449.1368.



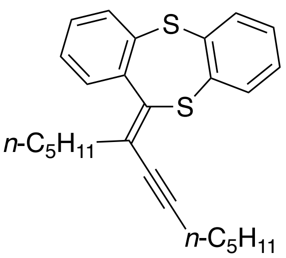
[Hept-1-ynyl][(2-((2-(2-methylphenylethynyl)phenyl)sulfanyl)phenyl)]sulfane (6d). Isolated by preparative TLC (hexane/CH_2Cl_2 = 5/1). The title compound was obtained as a yellow oil (38%). ^{1}H NMR δ 7.82 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.57-7.48 (m, 3H), 7.43 (dt, J_d = 1.5 Hz, J_t = 7.9 Hz, 1H), 7.24-7.20 (m, 3H), 7.19-7.14 (m, 1H), 7.12-7.08 (m, 2H), 6.70-6.66 (m, 1H), 2.58(s, 3H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.63-1.56 (m, 2H), 1.45-1.30 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 141.4, 140.5, 139.2, 136.6, 132.5, 132.1, 130.2, 129.5, 128.8, 128.5, 127.7, 126.6, 126.3, 126.1, 125.5, 125.4, 122.9, 121.9, 101.8, 95.0, 90.6, 64.8, 31.1, 28.3, 22.2, 21.1, 20.3, 14.0; HRMS(ESI) calcd for $C_{28}H_{26}NaS_2$ (M+Na): 449.1368; found: 449.1369.



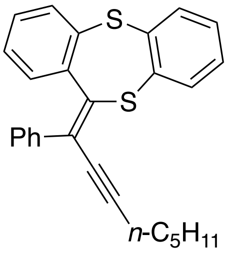
[Hept-1-ynyl][(2-((2-(trimethylsilylethynyl)phenyl)sulfanyl)phenyl)]sulfane (6e). Isolated by preparative TLC (hexane only). The title compound was obtained as a pale yellow oil (40%). ^{1}H NMR δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.48-7.41 (m, 3H), 7.22-7.18 (m, 1H), 7.11-7.04 (m, 2H), 6.66 (d, *J* = 7.8 Hz, 1H), 2.46 (t, *J* = 7.6 Hz, 2H), 1.64-1.57 (m, 2H), 1.46-1.32 (m, 4H), 0.92 (t, *J* = 7.7 Hz, 3H), 0.28 (s, 9H); ^{13}C NMR δ 141.3, 139.7, 136.4, 132.9, 130.1, 129.1, 128.0, 126.6, 126.4, 126.3, 125.4, 121.7, 102.0, 101.8, 101.7, 64.9, 31.2, 28.4, 22.3, 20.4, 14.1, 0.0; HRMS(ESI) calcd for $C_{24}H_{28}NaS_2Si$ (M+Na): 431.1294; found: 431.1294.



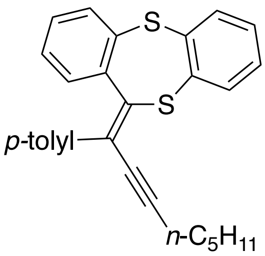
[Hept-1-ynyl][(2-((2-(ethynyl)phenyl)sulfanyl)phenyl)]sulfane (6f). Diyne having trimethylsilyl group (**6e**, 100.8 mg, 0.3 mmol) was dissolved in methanol (1.3 ml) and tetrahydrofuran (1.3 ml). After addition of KOH (30.5 mg, 0.5 mmol) and water (0.13 ml), the mixture was stirred at room temperature. After 2 h, the solvents were removed, and the residue was purified by preparative TLC (hexane/CH_2Cl_2) to give corresponding diyne (**6f**, 78%) as a yellow oil. ^{1}H NMR δ 7.87-7.85 (m, 1H), 7.54-7.48 (m, 3H), 7.29-7.24 (m, 1H), 7.19-7.10 (m, 2H), 6.70-6.68 (m, 1H), 3.53 (s, 1H), 2.50 (t, J = 7.1 Hz, 2H), 1.68-1.61 (m, 2H), 1.50-1.36 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 141.6, 139.9, 136.8, 133.4, 130.5, 129.5, 127.3, 126.8, 126.4, 126.2, 125.5, 120.5, 101.9, 83.9, 80.9, 64.8, 31.2, 28.4, 22.3, 20.4, 14.1; HRMS(ESI) calcd for $C_{21}H_{20}NaS_2$ (M+Na): 359.0899; found: 359.0899.



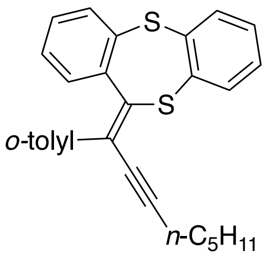
(Z)-11-(1-Pentyl-1-oct-2-ynylidene)-11H-dibenzo[*b*,*e*][1,4]dithiepine (7a). [Rh(cod)$_2$]OTf (3.1 mg, 0.005 mmol) and rac-BINAP (3.1 mg, 0.005 mmol) were placed in Schlenk tube, which was then evacuated and backfilled with argon (3×), the reaction vessel was filled with argon. 1,2-Dichloroethane (0.1 mL) was added to the flask and the mixture was stirred to give a yellowish solution. Then, a 1,2-dichloroethane solution (0.9 mL) of diyne (0.10 mmol) was added and the mixture was stirred at 80 ℃. The volatiles were removed under reduced pressure, and the crude products were isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a colorless oil (93%). ^{1}H NMR δ 7.60-7.55 (m, 1H), 7.52 (dd, J = 1.5, 7.6 Hz, 1H), 7.33 (m, 2H), 7.25-7.19 (m, 2H), 7.08 (dt, J_d = 1.6 Hz, J_t = 7.6 Hz, 1H), 7.01 (dt, J_d = 1.5 Hz, J_t = 7.4 Hz, 1H), 2.50 (t, J = 7.2 Hz, 2H), 2.03 (t, J = 7.9 Hz, 2H), 1.69-1.45 (m, 6H), 1.41-1.32 (m, 2H), 1.25-1.08 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H) ; ^{13}C NMR δ 140.4, 138.9, 137.4, 137.0, 136.9, 134.3, 133.8, 130.2, 130.2, 129.4, 129.2, 128.9, 126.9, 120.2, 100.2, 79.0, 33.8, 31.2, 31.1, 28.6, 28.2, 22.4, 22.3, 20.0, 14.2, 14.1; HRMS(ESI) calcd for $C_{26}H_{30}NaS_2$ (M+Na): 429.1681; found: 429.1681.



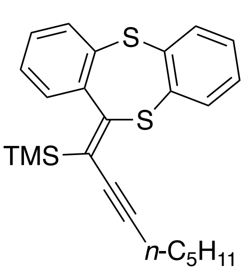
(Z)-11-(1-Phenyl-1-oct-2-ynylidene)-11H-dibenzo[*b*,*e*][1,4]dithiepine (7b). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a pale yellow oil (76%). ^{1}H NMR δ7.62 (dd, J = 1.6, 7.1 Hz, 1H), 7.56 (dd, J = 1.1, 7.8 Hz, 1H), 7.42 (dd, J = 1.7, 7.8 Hz, 1H), 7.17-7.01 (m, 8H), 6.96 (dt, J_d = 1.2 Hz, J_t = 7.5 Hz, 1H), 6.78 (dd, J = 1.1, 7.9 Hz, 1H), 2.56 (t, J = 7.2 Hz, 2H), 1.73-1.66 (m, 2H), 1.55-1.48 (m, 2H), 1.42-1.33 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H); ^{13}C NMR δ 138.9, 138.5, 136.2, 136.2, 136.0, 135.6, 132.1, 131.5, 129.7, 128.9, 127.6, 127.4, 127.1, 127.0, 125.6, 125.5, 124.6, 116.0, 99.5, 77.4, 29.2, 26.4, 20.2, 18.0, 12.1; HRMS(ESI) calcd for $C_{27}H_{24}NaS_2$ (M+Na): 435.1212; found: 435.1212.



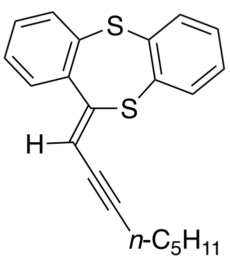
(Z)-11-(1-(4-Methylphenyl)-1-oct-2-ynylidene)-11H-dibenzo[*b*,*e*][1,4]dithiepine (7c). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a pale yellow oil (67%). ^{1}H NMR δ 7.62 (dd, J = 1.7, 7.2 Hz, 1H), 7.57 (dd, J = 1.1, 7.5 Hz, 1H), 7.41 (dd, J = 1.7, 7.8 Hz, 1H), 7.17-7.08 (m, 3H), 7.01-6.97 (m, 1H), 6.92-6.86 (m, 4H), 6.81 (dd, J = 1.3, 7.8 Hz, 1H), 2.55 (t, J = 7.3 Hz, 2H), 2.21 (s, 3H), 1.73-1.65 (m, 2H), 1.54-1.48 (m, 2H), 1.42-1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 140.9, 140.2, 138.5, 138.0, 137.6, 136.5, 135.4, 134.2, 133.7, 131.8, 131.0, 129.8, 129.4, 129.2, 129.1, 128.4, 127.6, 118.2, 101.5, 79.6, 31.4, 28.6, 22.4, 21.3, 20.2, 14.2; HRMS(ESI) calcd for $C_{28}H_{26}NaS_2$ (M+Na): 449.1368; found: 449.1368.



(E)-11-(1-(2-Methylphenyl)-1-oct-2-ynylidene)-11H-dibenzo[*b*,*e*][1,4]dithiepine (7d). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a pale yellow oil (59%). ^{1}H NMR δ 7.61 (dd, J = 1.5, 7.5 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.43 (dd, J = 1.3, 7.7 Hz, 1H), 7.17-7.13 (m, 1H), 7.12-7.08 (m, 1H), 7.03-6.97 (m, 3H), 6.95-6.85 (m, 3H), 6.71 (d, J = 7.4 Hz, 1H), 2.50 (t, J = 7.1 Hz, 2H), 2.31 (s, 3H), 1.68-1.62 (m, 2H), 1.50-1.44 (m, 2H), 1.39-1.32 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 141.8, 139.8, 138.3, 138.2, 138.0, 137.0, 136.8, 134.1, 133.4, 131.3, 131.0, 130.0, 129.9, 129.1, 129.0, 128.9, 127.6, 127.1, 125.3, 118.1, 102.0, 78.9, 31.2, 28.5, 22.3, 20.1, 19.9, 14.1; HRMS(ESI) calcd for $C_{28}H_{26}NaS_2$ (M+Na): 449.1368; found: 449.1368.



(E)-11-(1-Trimethylsilyl-1-oct-2-ynylidene)-11H-dibenzo[*b*,*e*][1,4]dithiepine (7e). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a pale yellow oil (90%). ^{1}H NMR δ 7.84 (dt, J_d = 1.7 Hz, J_t = 7.2 Hz, 1H), 7.82-7.80 (m, 1H), 7.65 (dd, J = 1.6, 7.4 Hz, 1H), 7.58-7.50 (m, 3H), 7.84 (dt, J_d = 1.7 Hz, J_t = 7.4 Hz, 1H), 7.35 (dt, J_d = 1.6 Hz, J_t = 7.3 Hz, 1H), 2.82 (t, J = 7.7 Hz, 2H), 1.97-1.88 (m, 2H), 1.84-1.60 (m, 4H), 1.20 (t, J = 7.7 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR δ 152.4, 142.1, 139.2, 139.0, 137.9, 134.5, 133.9, 131.3, 131.3, 130.2, 129.7, 129.3, 127.9, 120.4, 104.8, 80.7, 31.6, 29.1, 22.6, 20.6, 14.5, 0.0; HRMS(ESI) calcd for $C_{24}H_{28}NaS_2Si$ (M+Na): 431.1294 found: 431.1294.

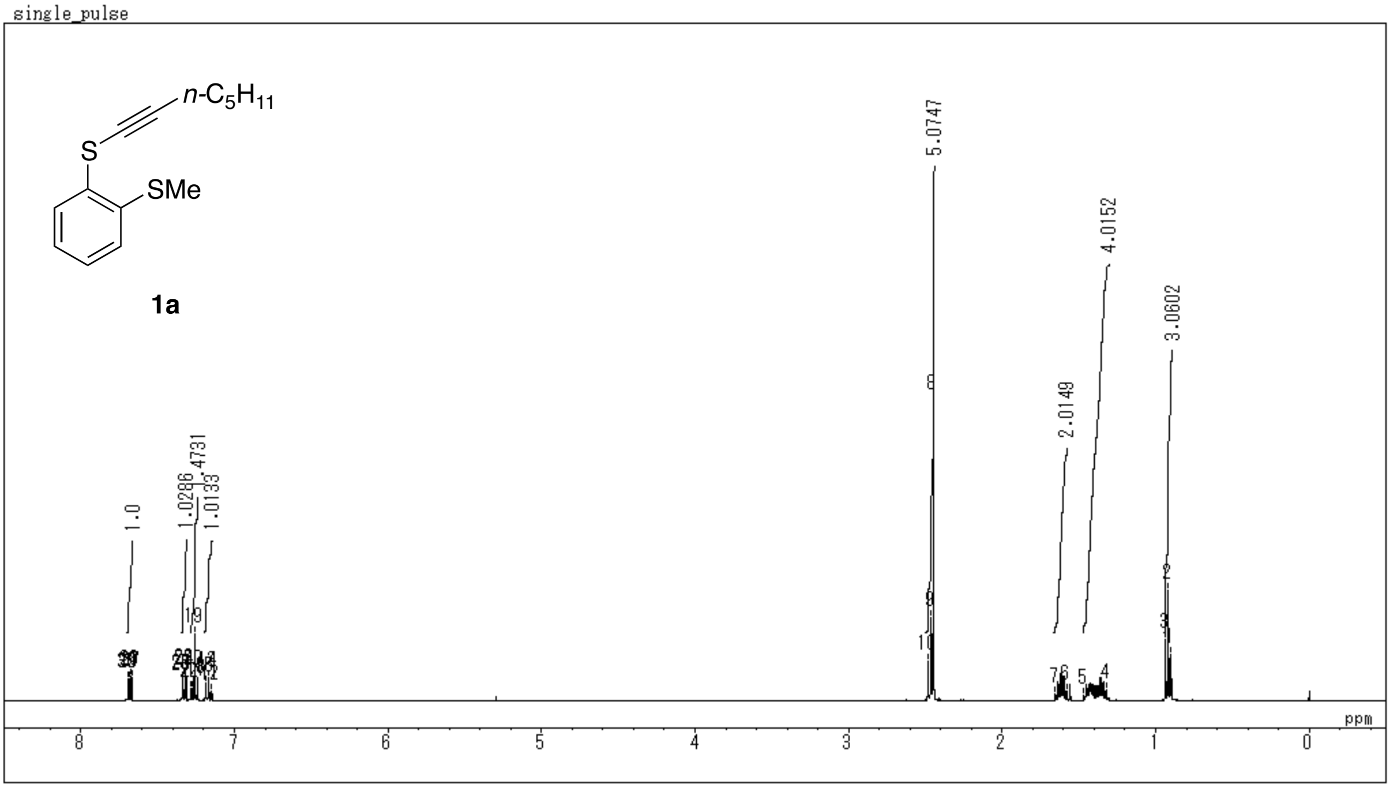


(Z)-11-(Oct-2-ynylidene)-11H-dibenzo[*b*,*e*][1,4]dithiepine (7f). Isolated by preparative TLC (hexane/toluene = 3/1). The title compound was obtained as a yellow oil (92%). ^{1}H NMR δ 7.63-7.62 (m, 1H), 7.56-7.54 (m, 1H), 7.49-7.48 (m, 1H), 7.31-7.28 (m, 2H), 7.23-7.19 (m, 1H), 7.18-7.13 (m, 2H), 5.50 (t, J = 2.3 Hz, 1H), 2.51 (dt, J_d = 2.3 Hz, J_t = 7.1 Hz, 2H), 1.68-1.63 (m, 2H), 1.52-1.46 (m, 2H), 1.41-1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 146.7, 141.3, 139.7, 137.2, 136.4, 133.9, 133.8, 131.8, 130.0, 129.7, 129.5, 129.3, 128.4, 105.6, 101.2, 77.0, 31.2, 28.5, 22.3, 20.0, 14.1; HRMS(ESI) calcd for $C_{21}H_{20}NaS_2$ (M+Na): 359.0899; found: 359.0899.

iv) Experimental details and characterization data for complex A

A 1,2-dichloroethane solution (0.5 mL)of sufide **1a** (7.5 mg, 0.01 mmol) and [Rh(cod)(dppe)]OTf (9.5 mg, 0.01 mmol) was stirred at 80 ℃ for 30 minutes. Then, acetonitrile (0.5 ml) was added and stirred at 80 ℃ for 2 h. After removing all volatiles under reduced pressure, reprecipitation using gave complex **A** (4.2 mg, 33%) as an orange solid: ^{1}H NMR δ 8.30-8.15 (m, 4H), 7.97-7.90 (m, 2H), 7.57-7.40 (m, 5H), 7.38-7.31 (m, 2H), 7.21-7.08 (m, 3H), 6.90-6.82 (m, 3H), 6.74-6.62 (m, 3H), 6.60-6.54 (m, 1H), 6.40-6.34 (m, 1H), 3.33-2.63 (m, 4H), 1.78 (s, 3H), 1.35 (t, J = 6.8 Hz, 2H), 1.03-0.93 (m, 2H), 0.80-0.64 (m, 4H), 0.71 (t, J = 7.5 Hz, 3H); ^{31}P NMR δ 48.94 (d, J_{PRh} = 100.3 Hz), 42.87 (d, J_{PRh} = 95.9 Hz). HRMS(ESI) calcd for $C_{40}H_{42}P_2RhS_2$ (M): 751.1253; found: 751.1248.

iv) Copies of ^{1}H NMR and ^{13}C NMR spectra for new compounds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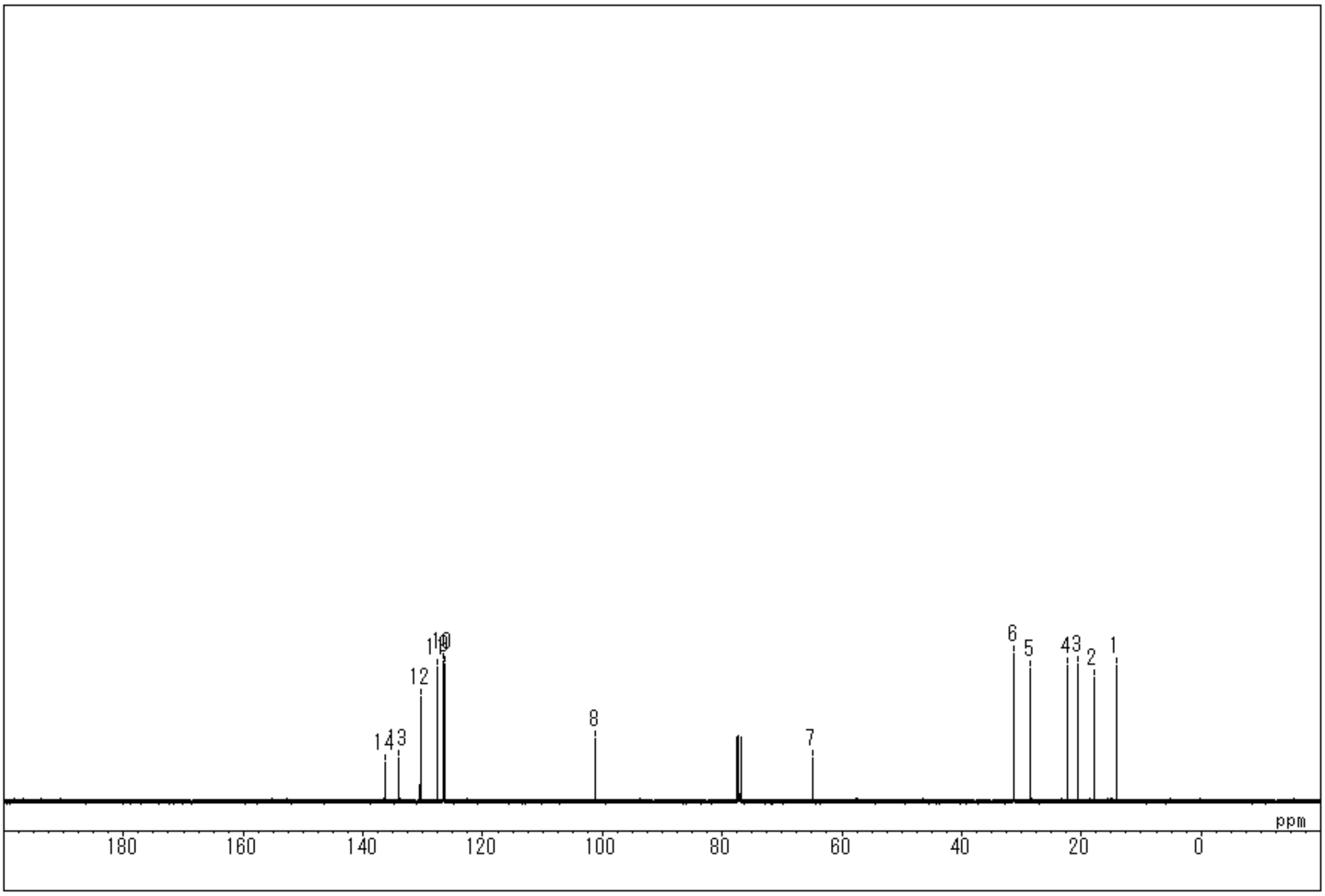

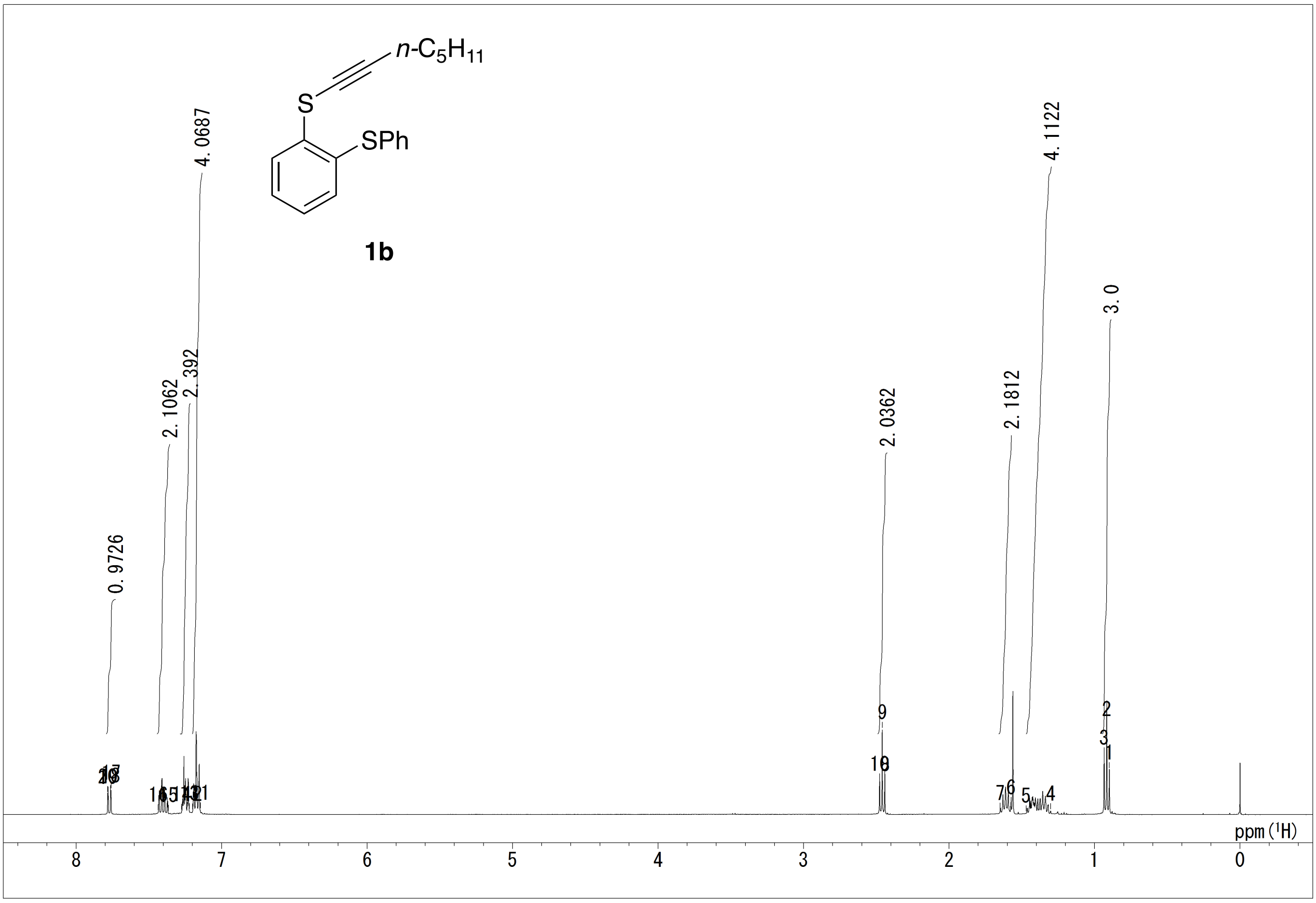

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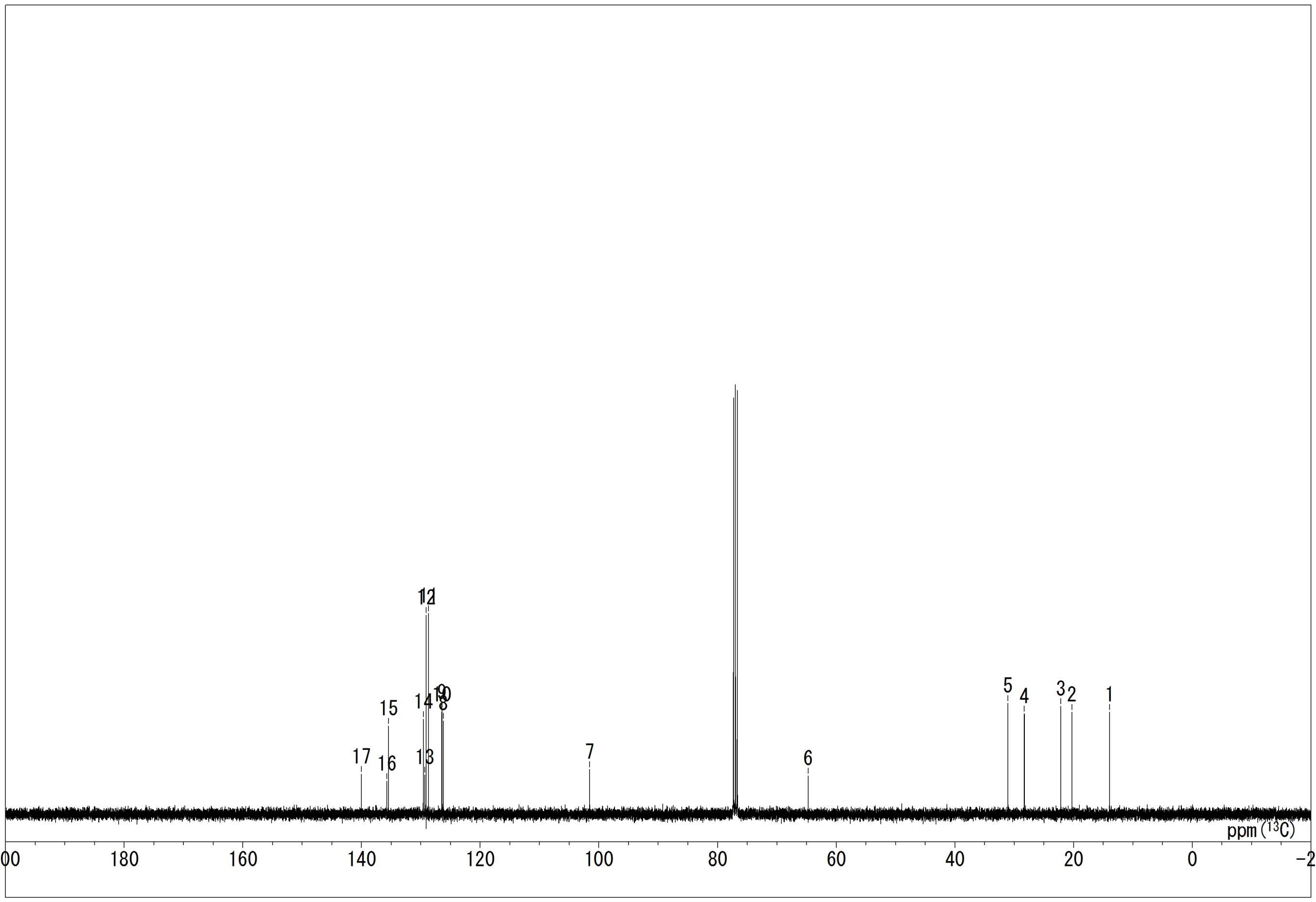

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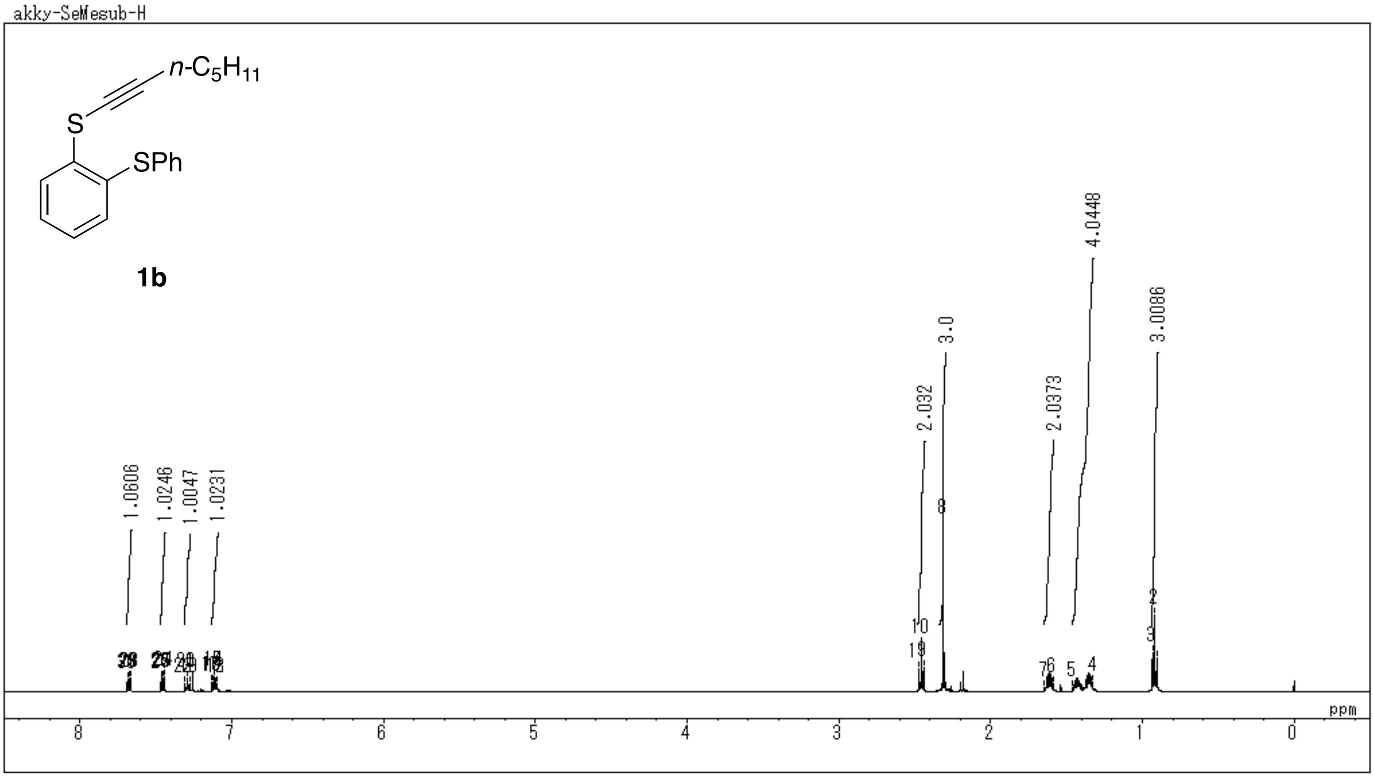
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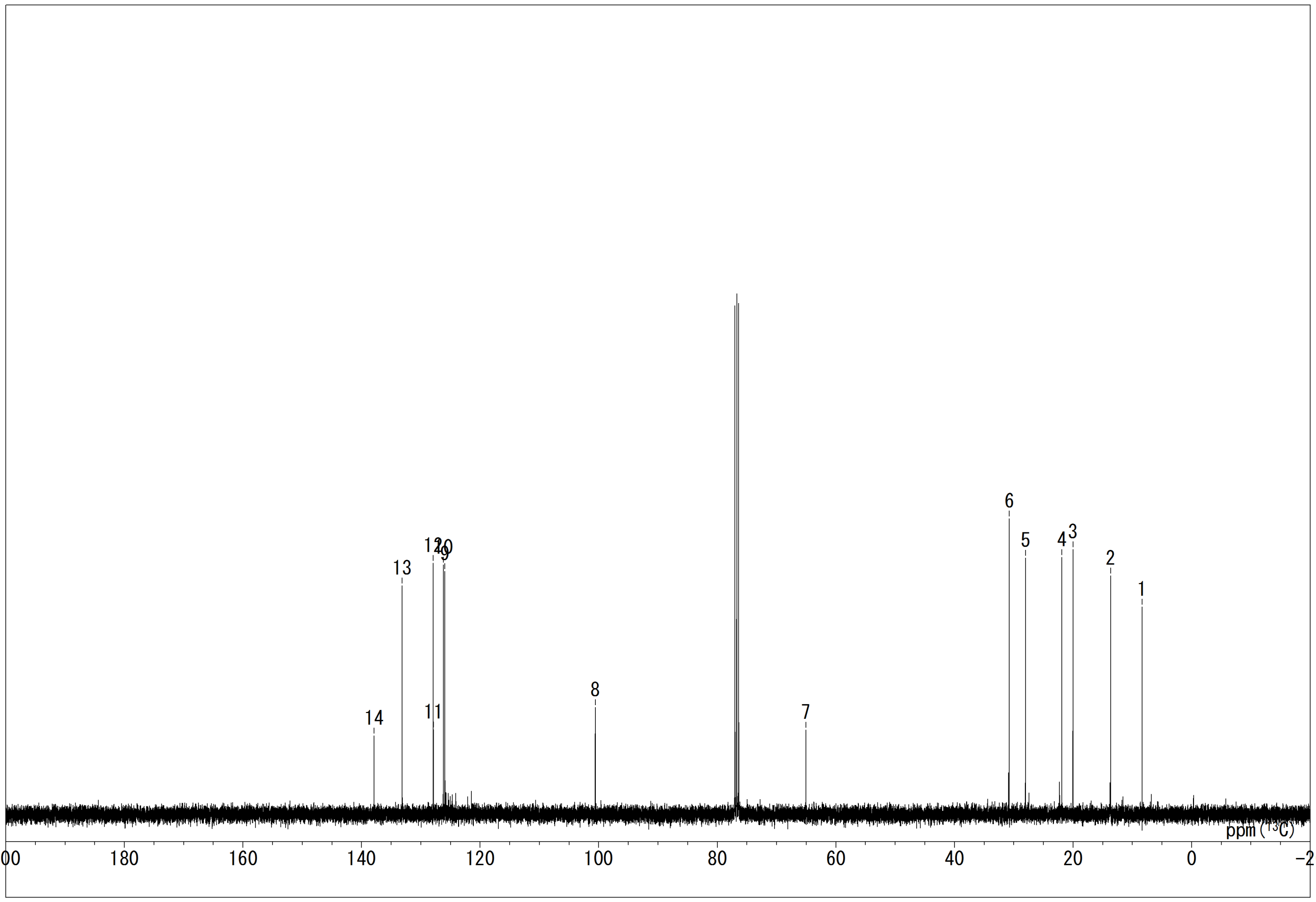
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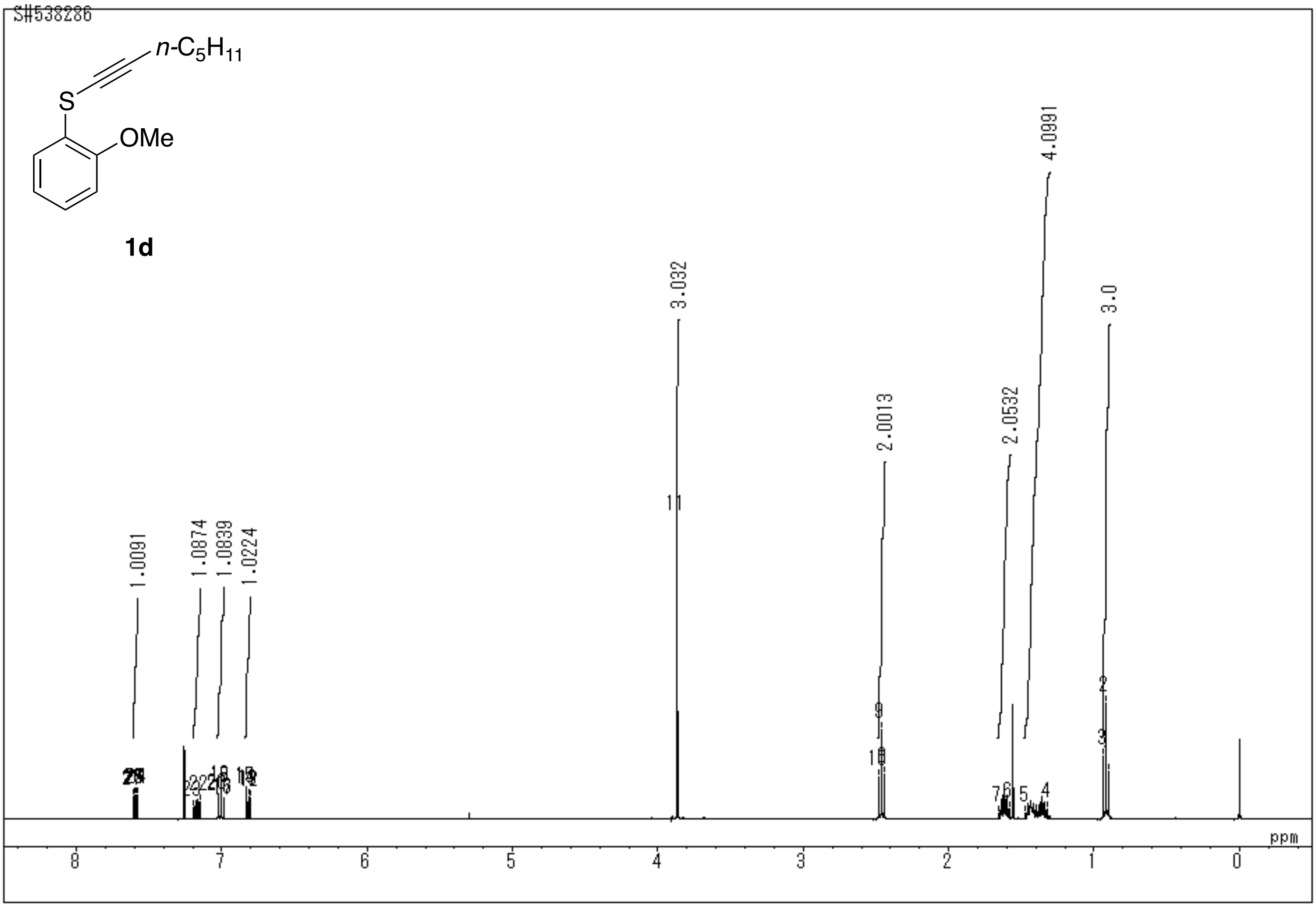
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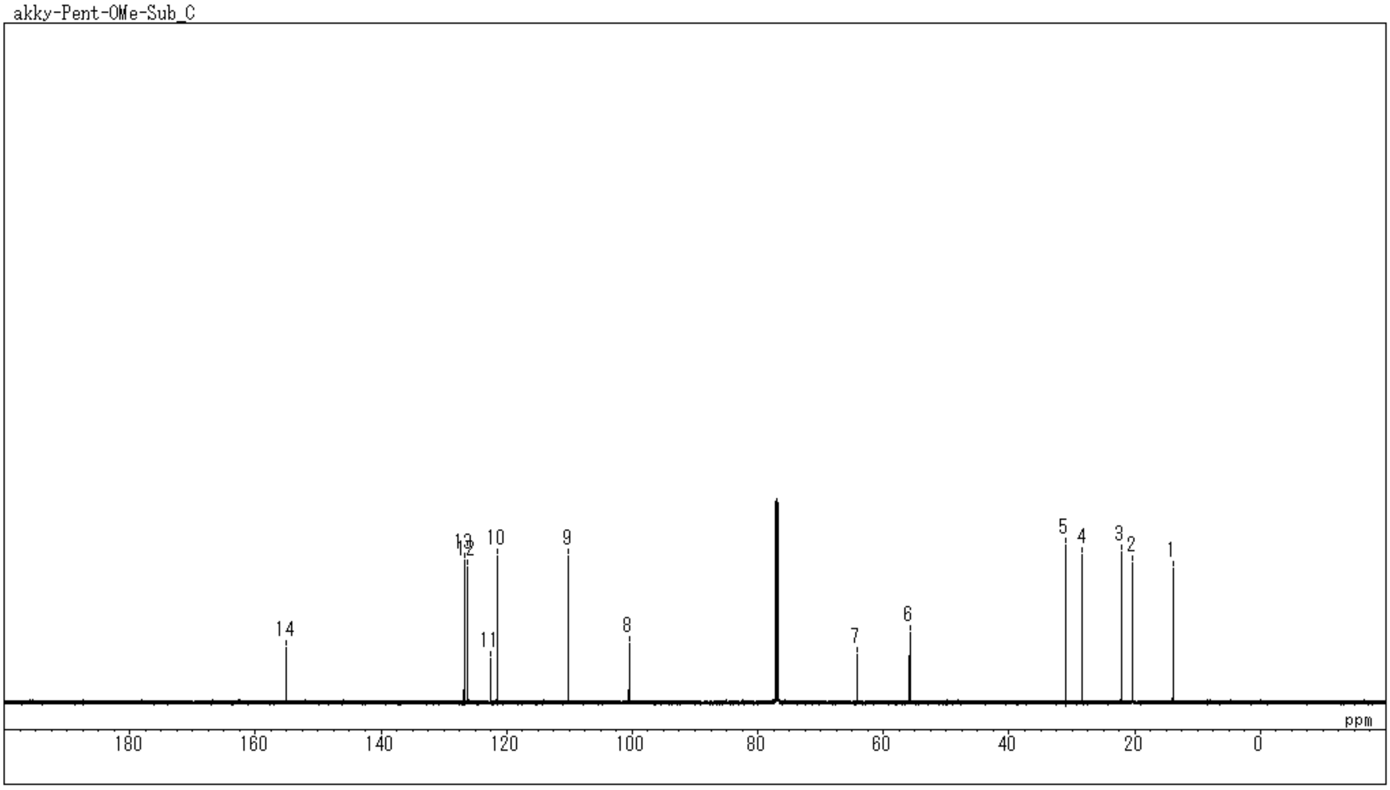
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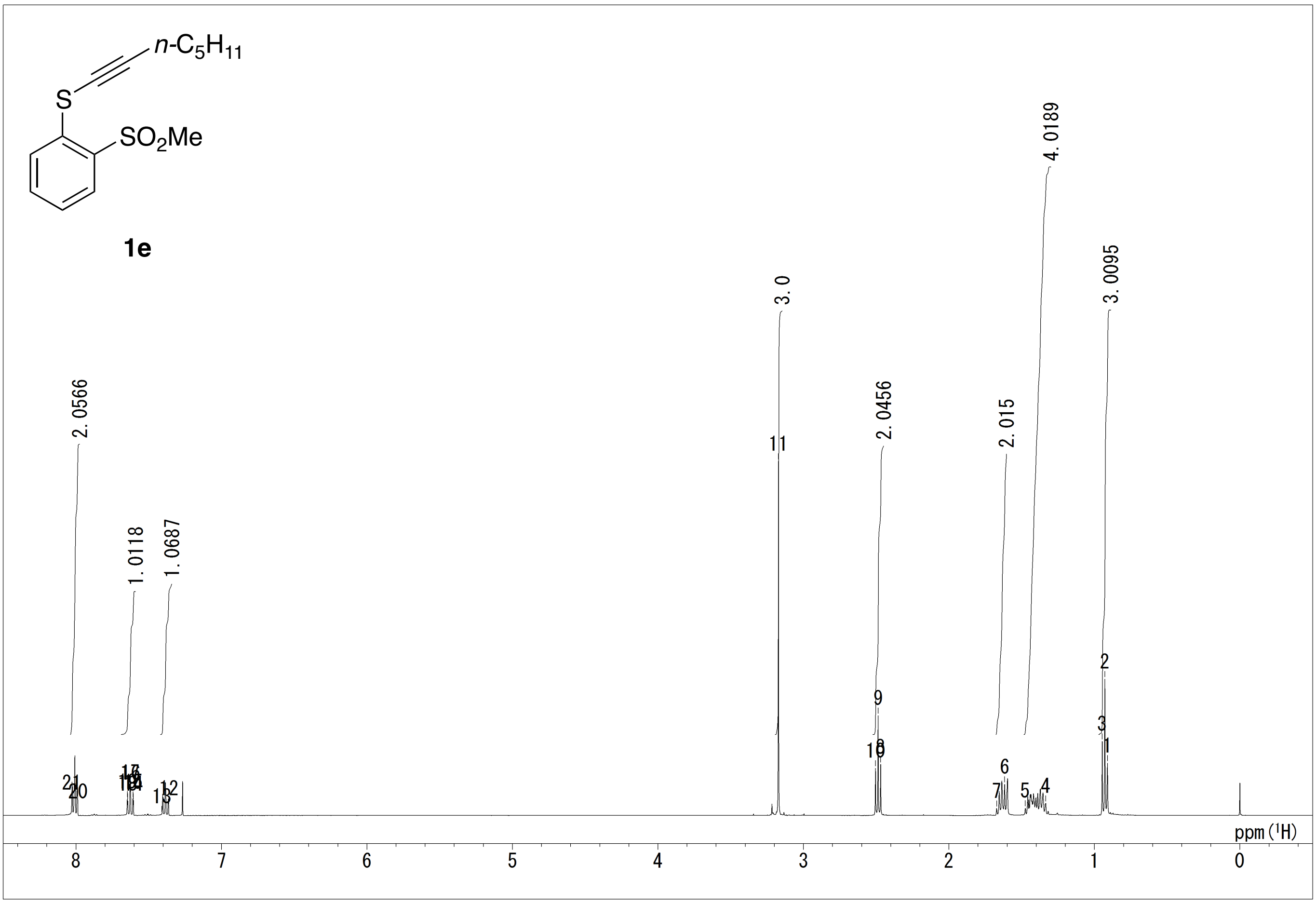
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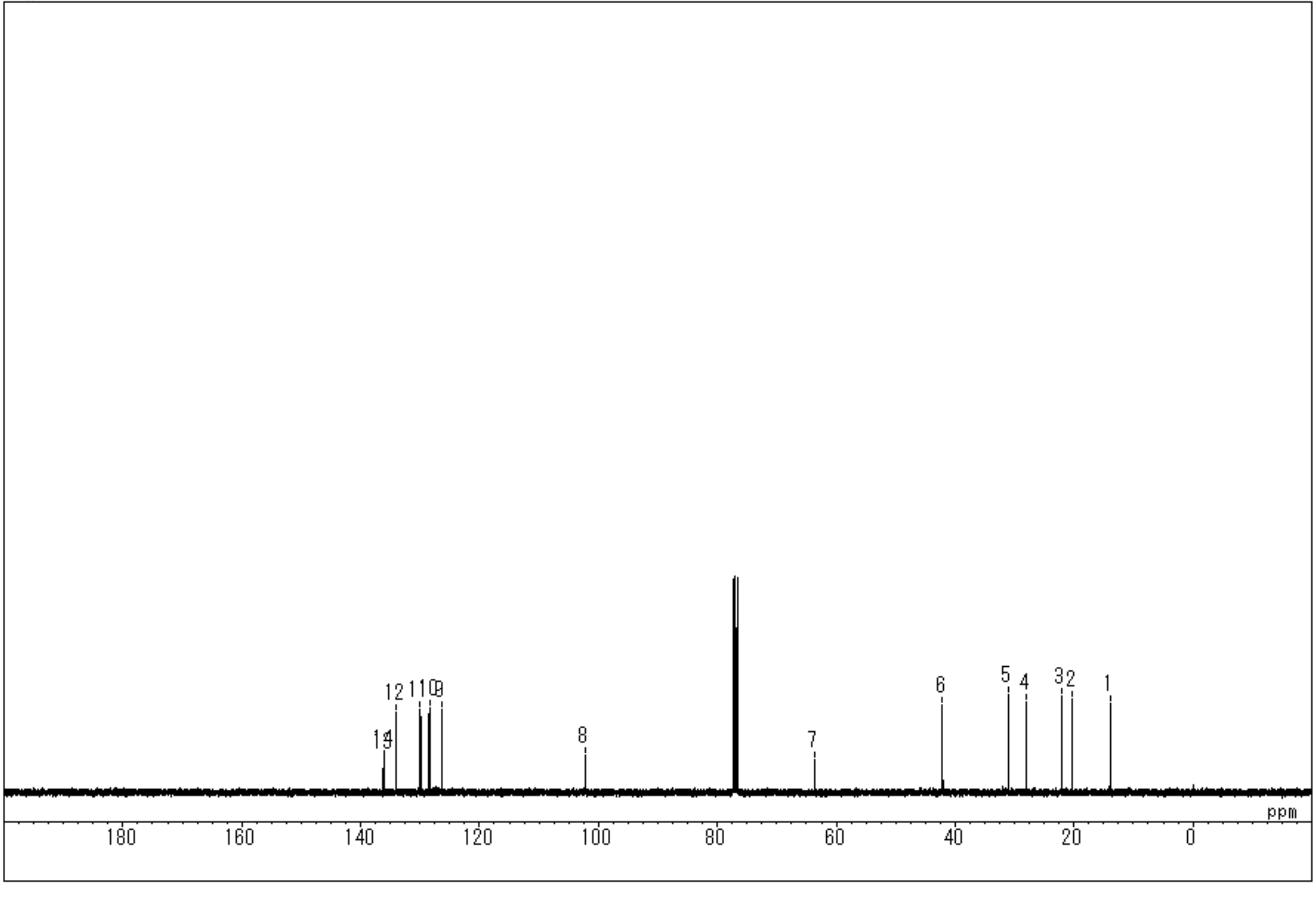
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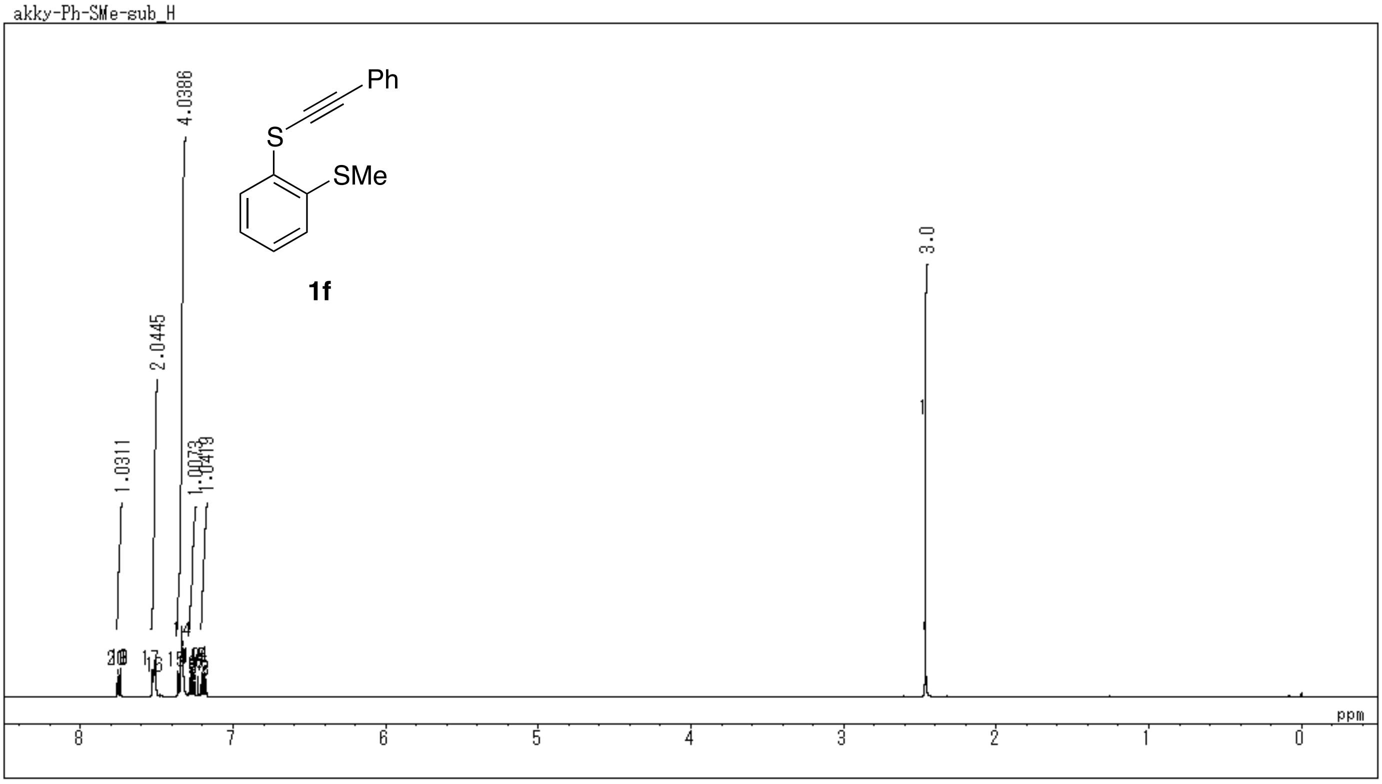
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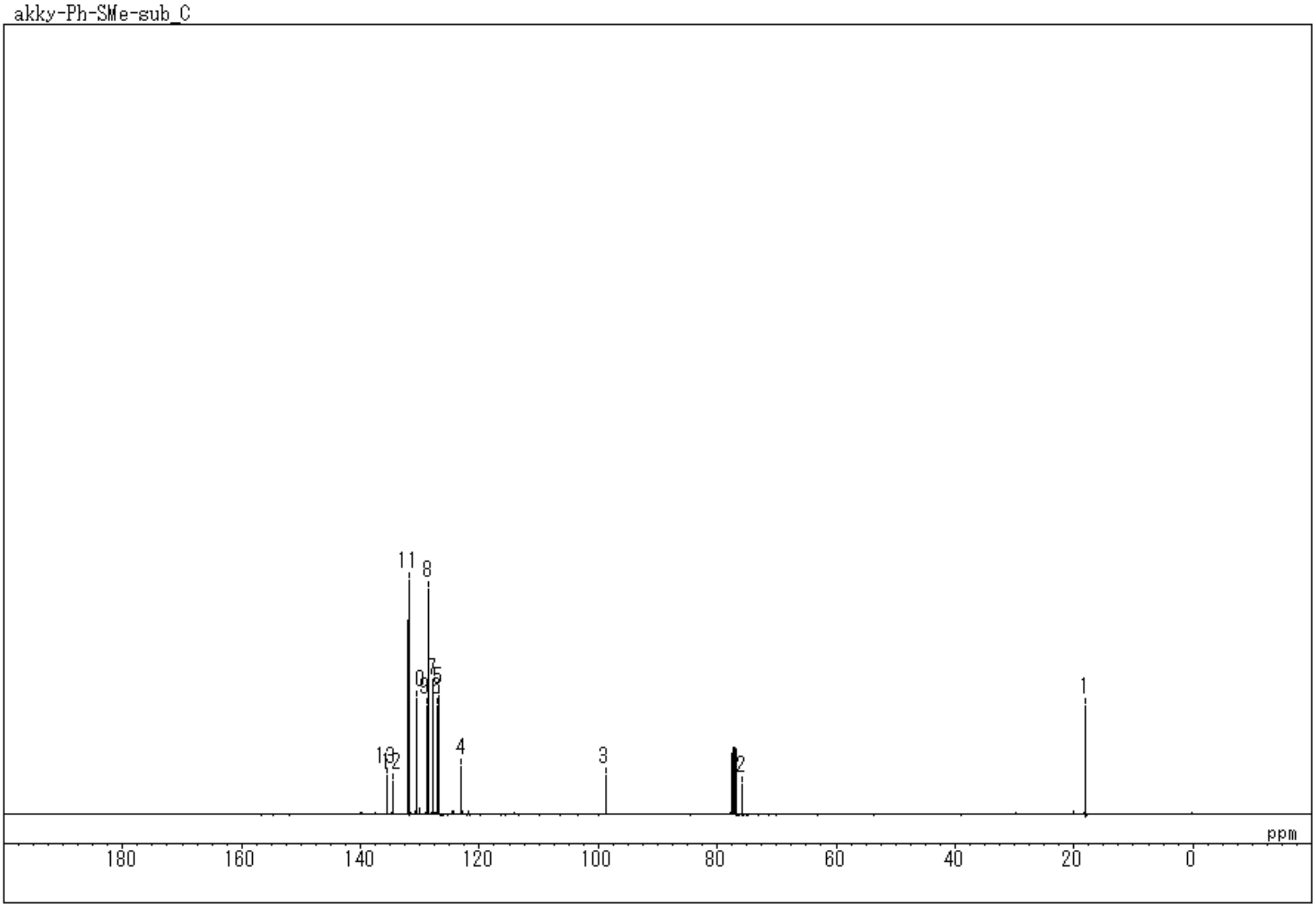
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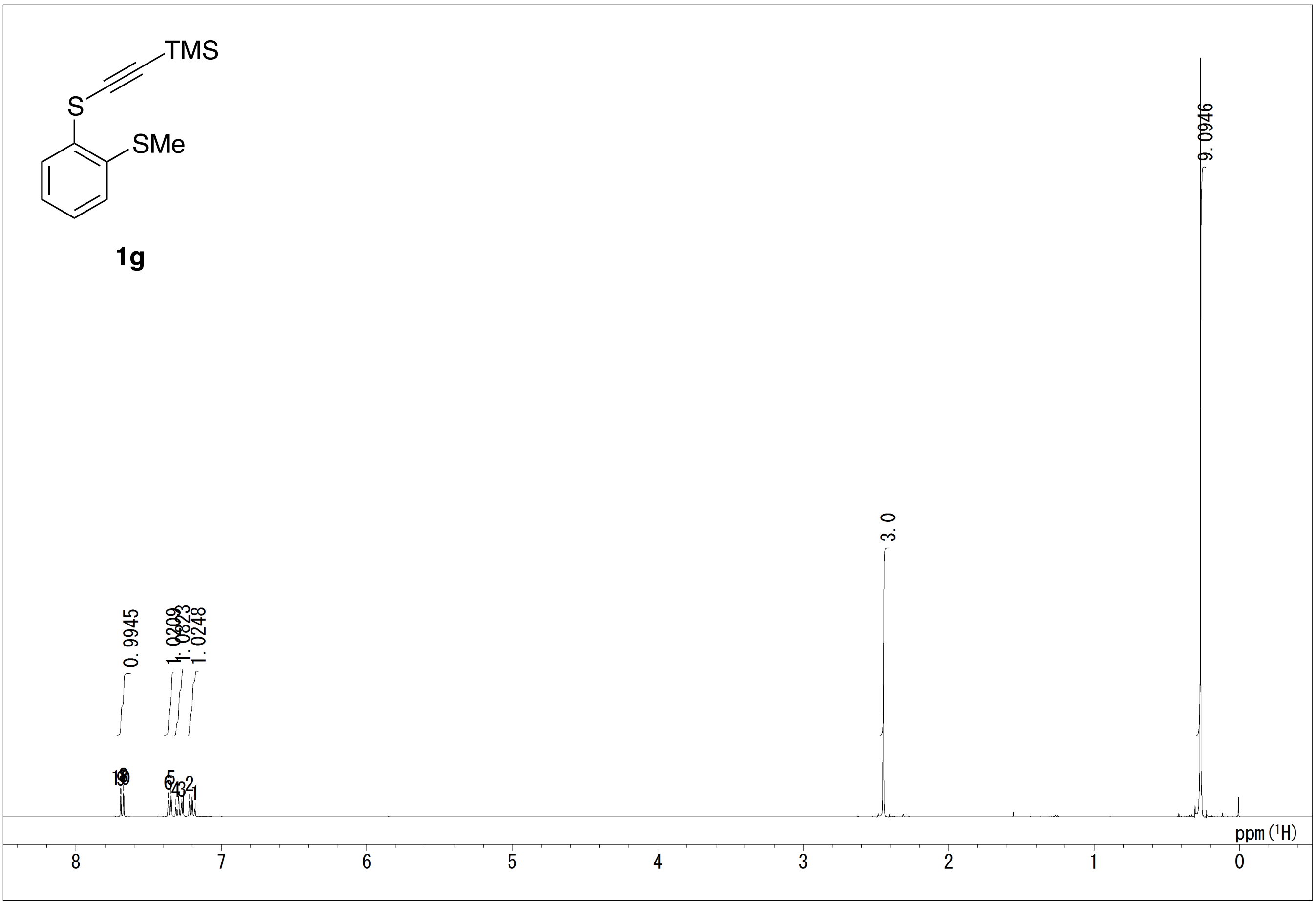
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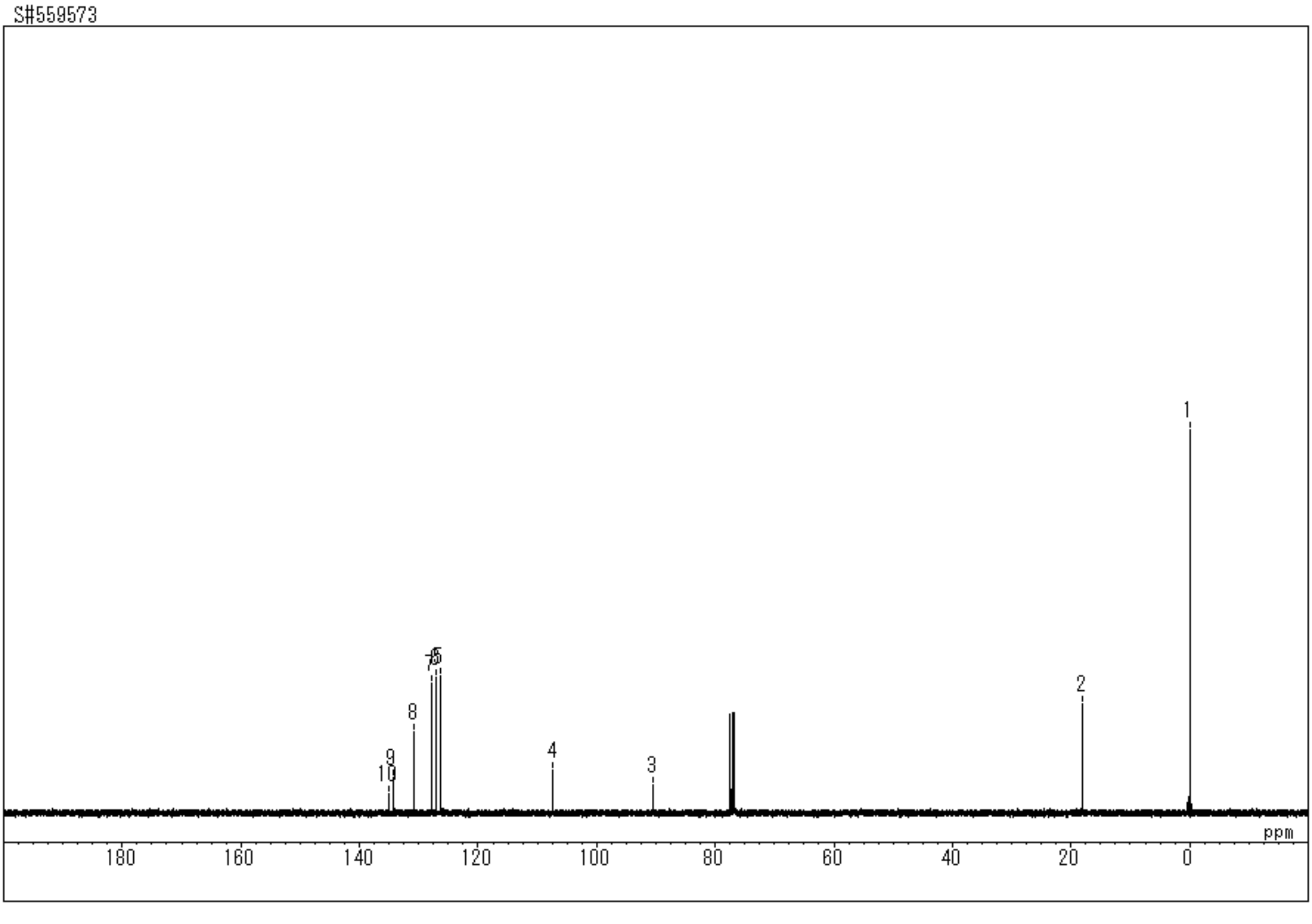
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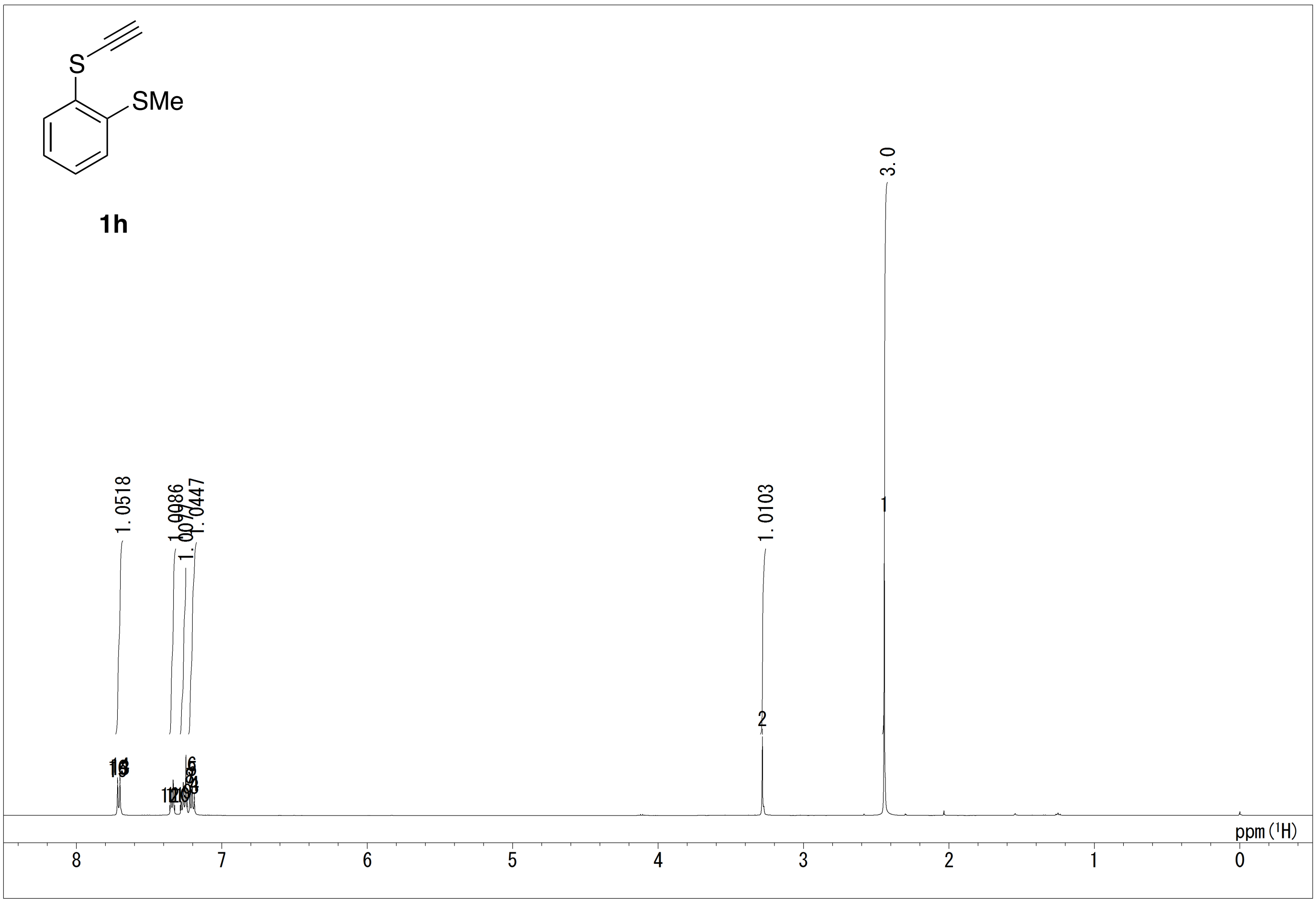

S
SMe
1h
3.0
1.0518
1.0986
1.0071
1.0447
1.0103
1
2
ppm (¹H)
8
7
6
5
4
3
2
1
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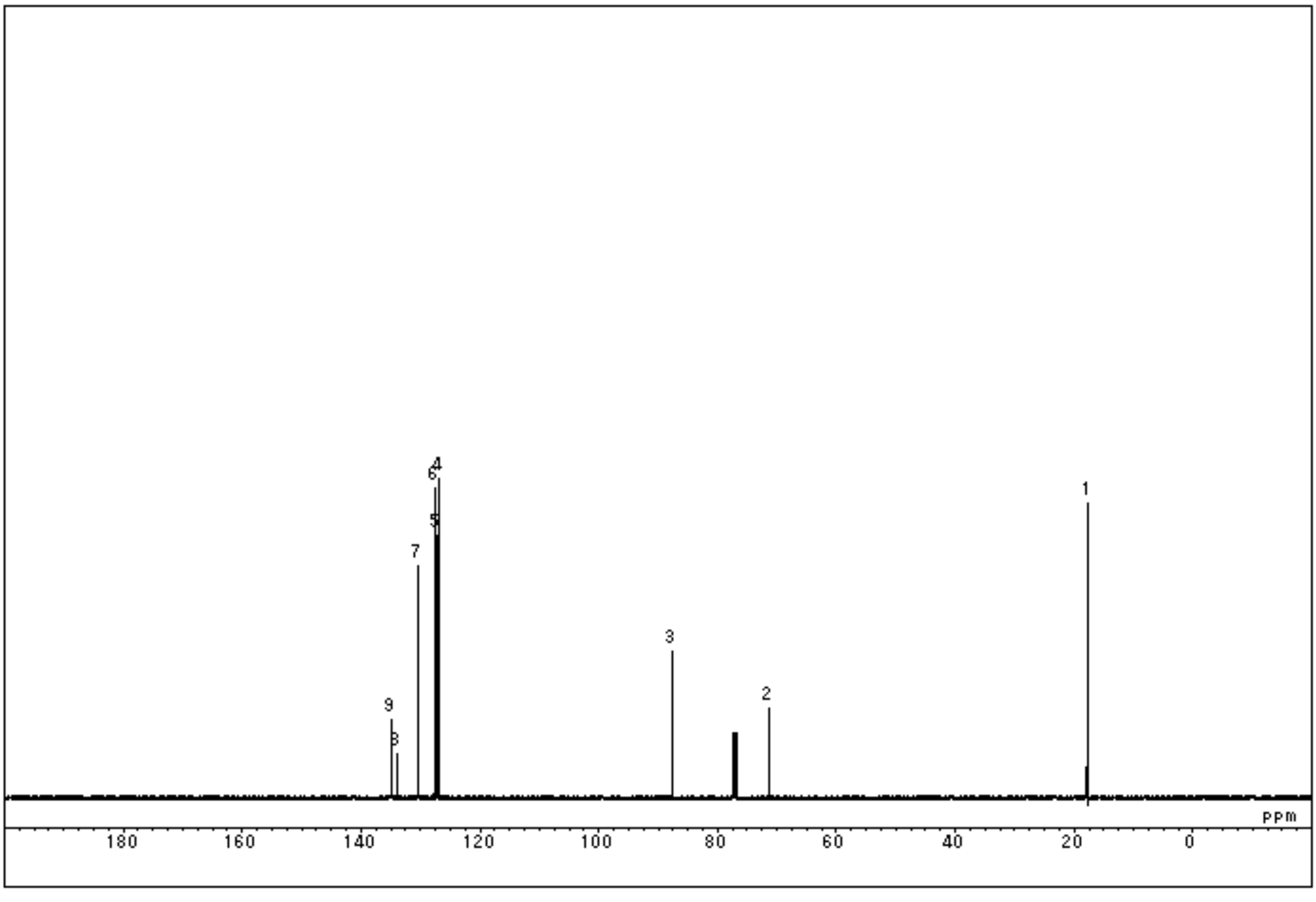

9
8
7
6
5
4
3
2
1
PPM
180
160
140
120
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60
40
20
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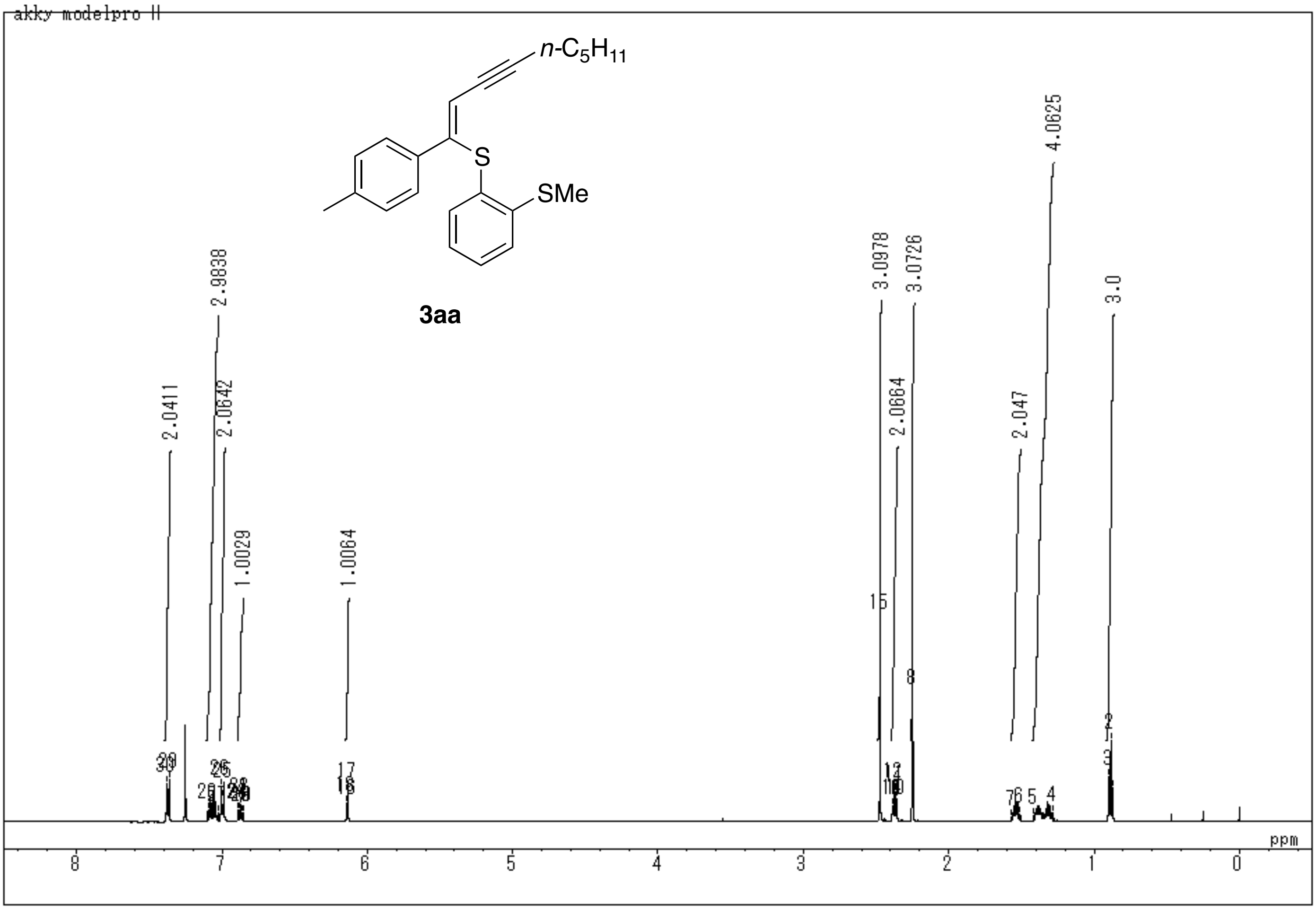
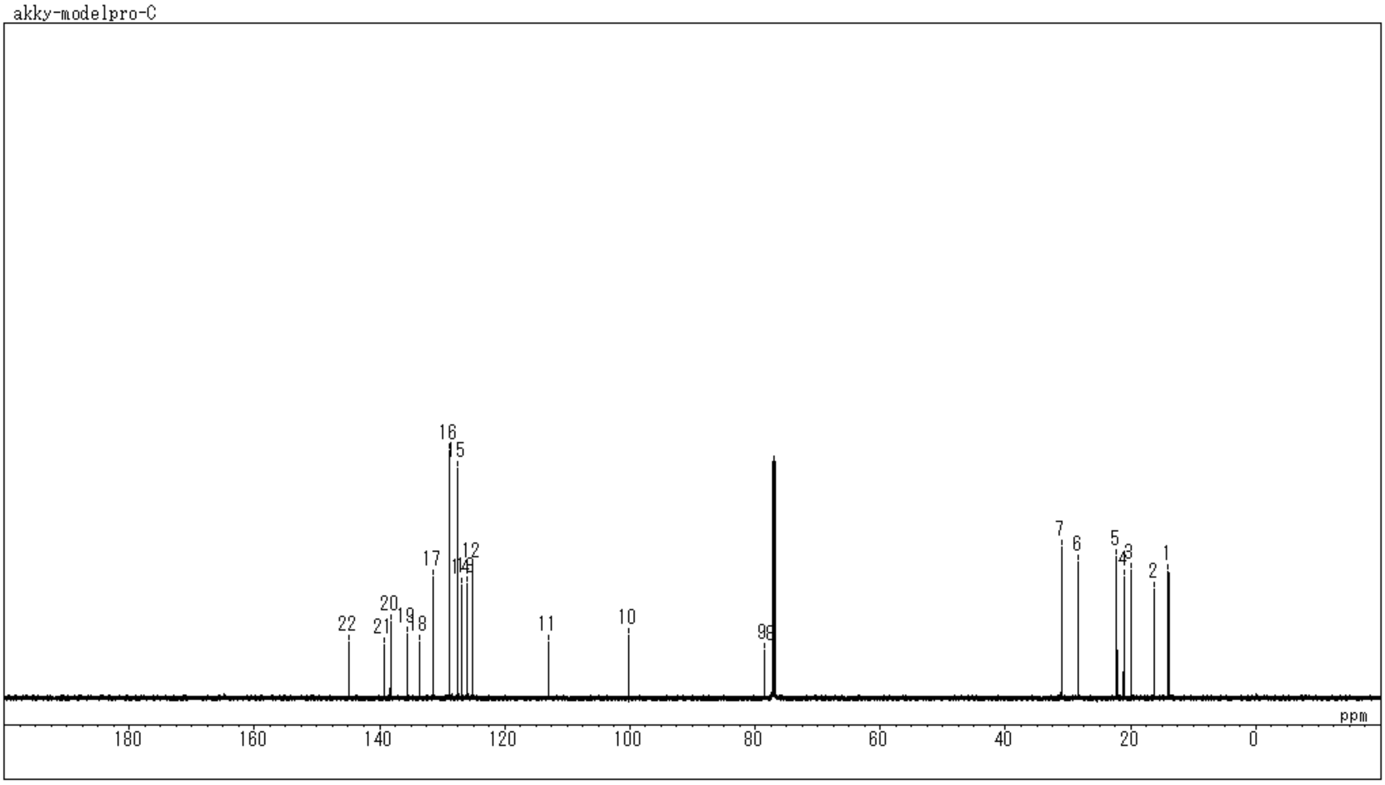
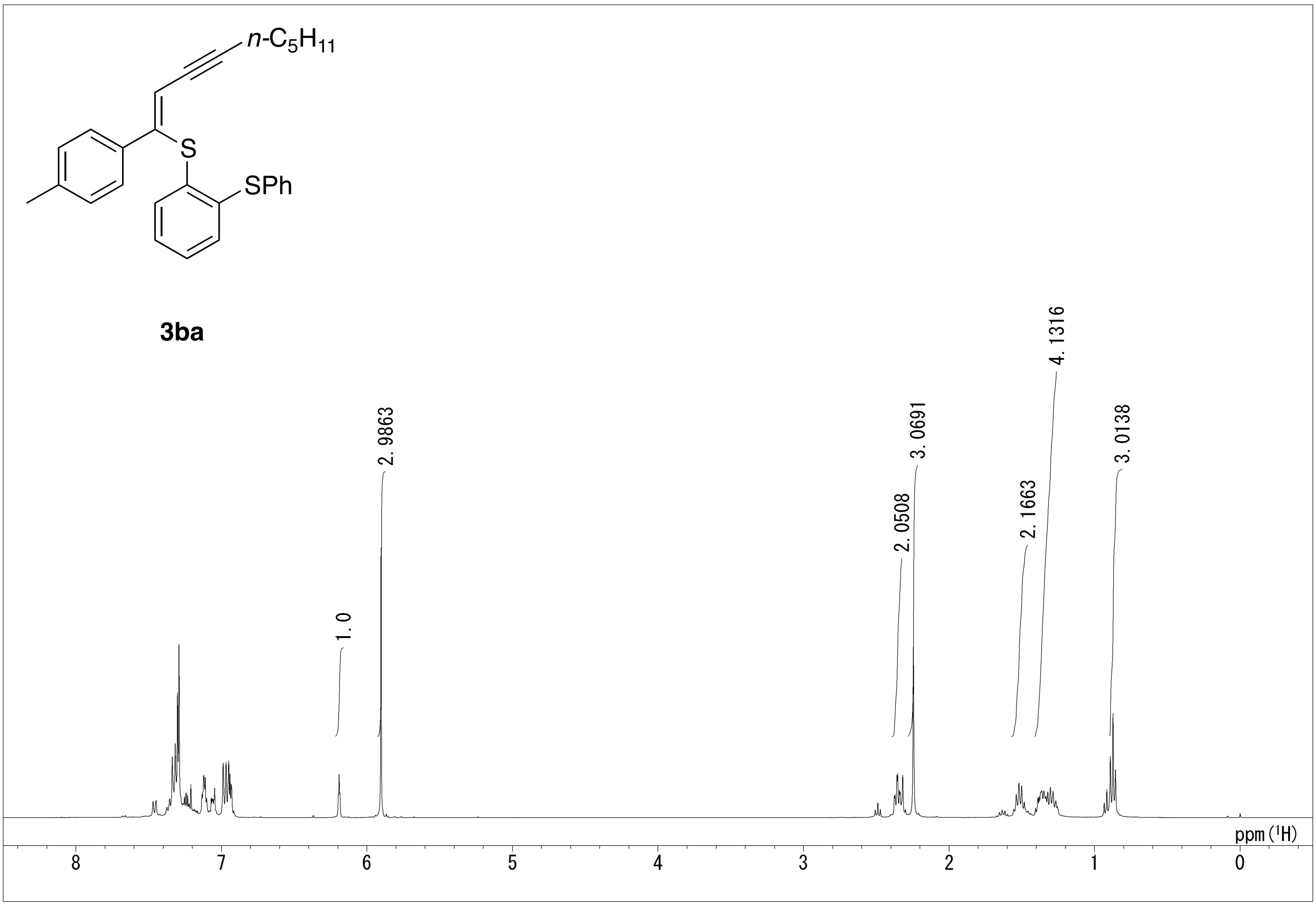
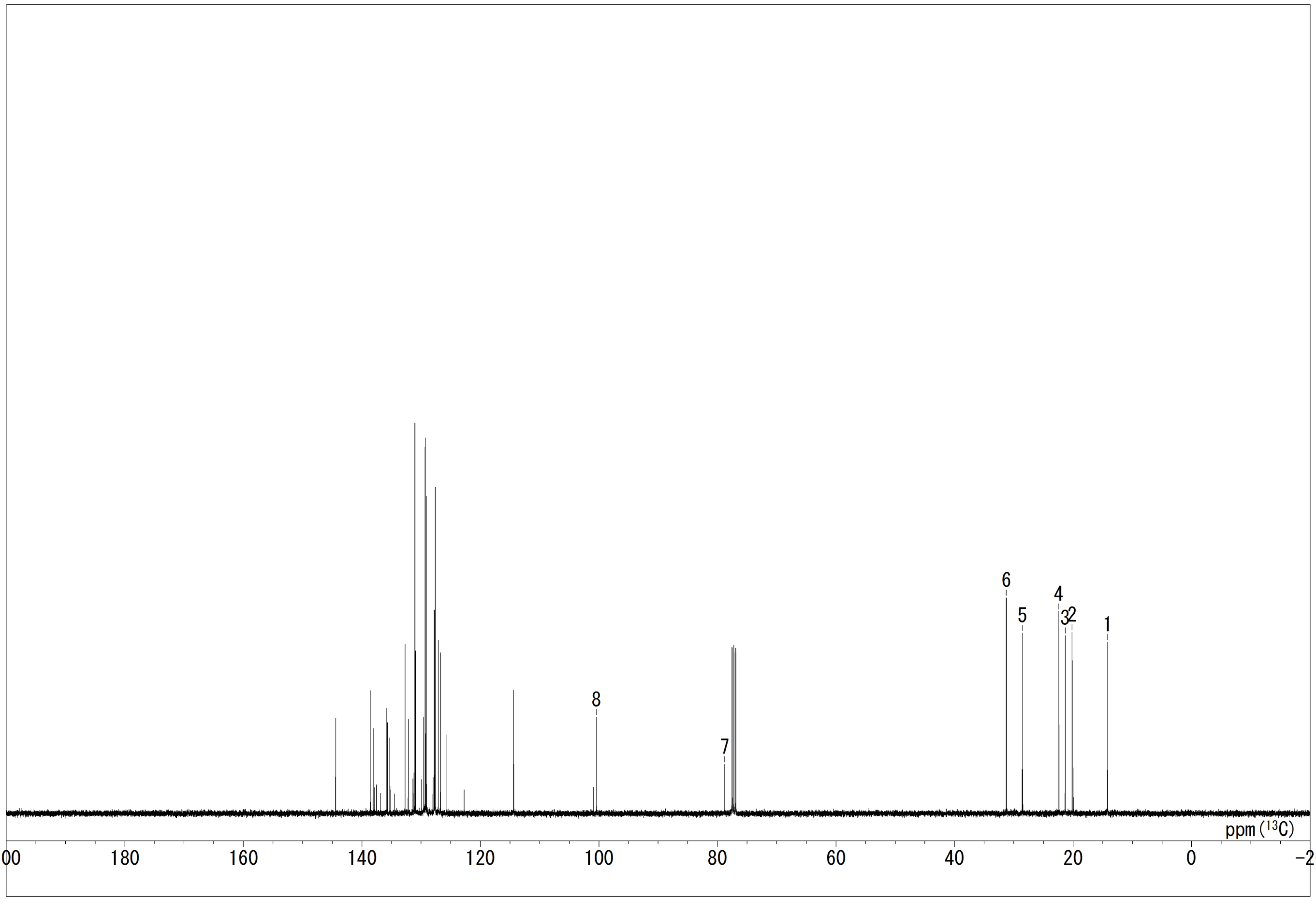
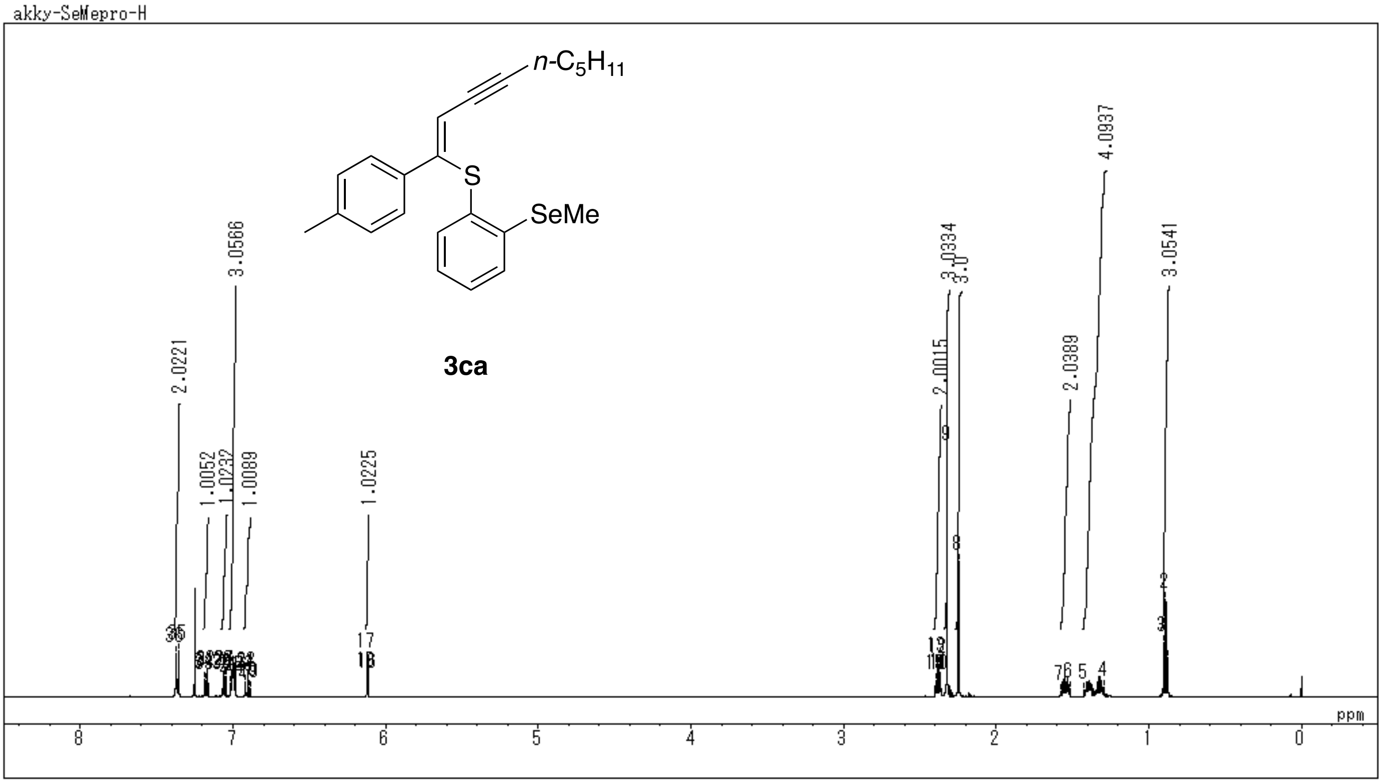

akky modelpro H
n-C5H11
S
SMe
3aa
2.0411
2.9838
2.0642
1.0029
1.0064
3.0978
2.0664
3.0726
2.047
4.0625
3.0
ppm
8
7
6
5
4
3
2
1
0


akky-modelpro-C
ppm
180
160
140
120
100
80
60
40
20
0

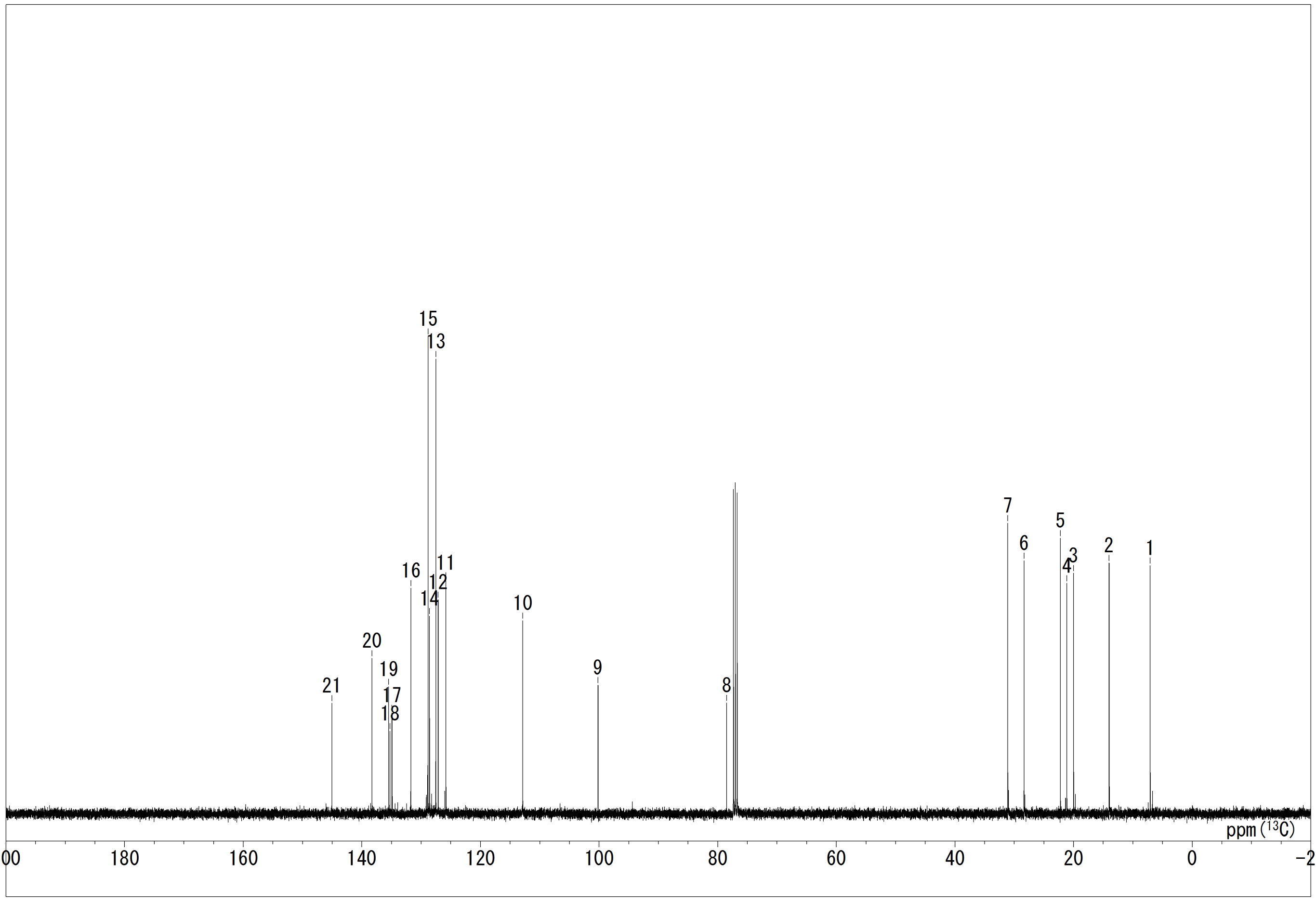

n-C5H11
S
SPh
3ba
1.0
2.9863
2.0508
3.0691
2.1663
4.1316
3.0138
ppm (1H)
8
7
6
5
4
3
2
1
0


8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
−20

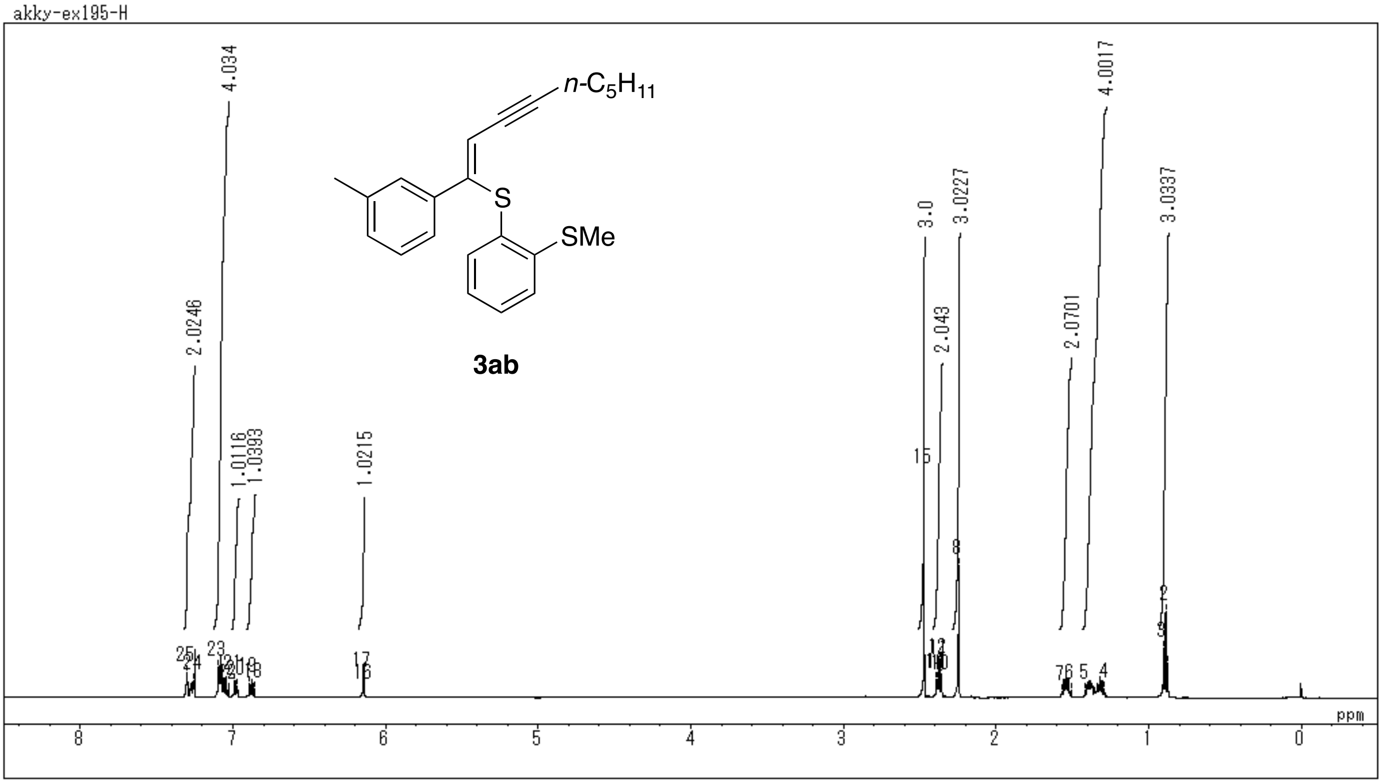


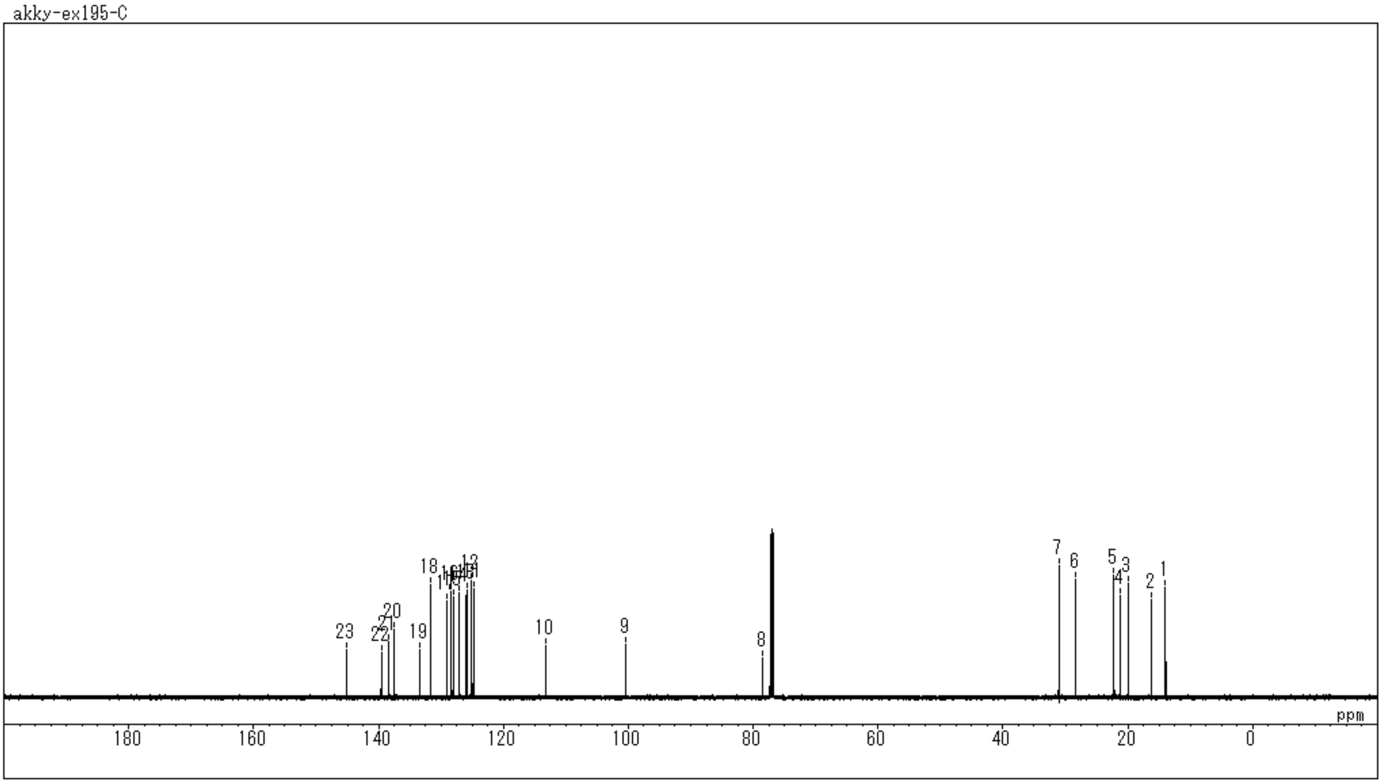
3ca

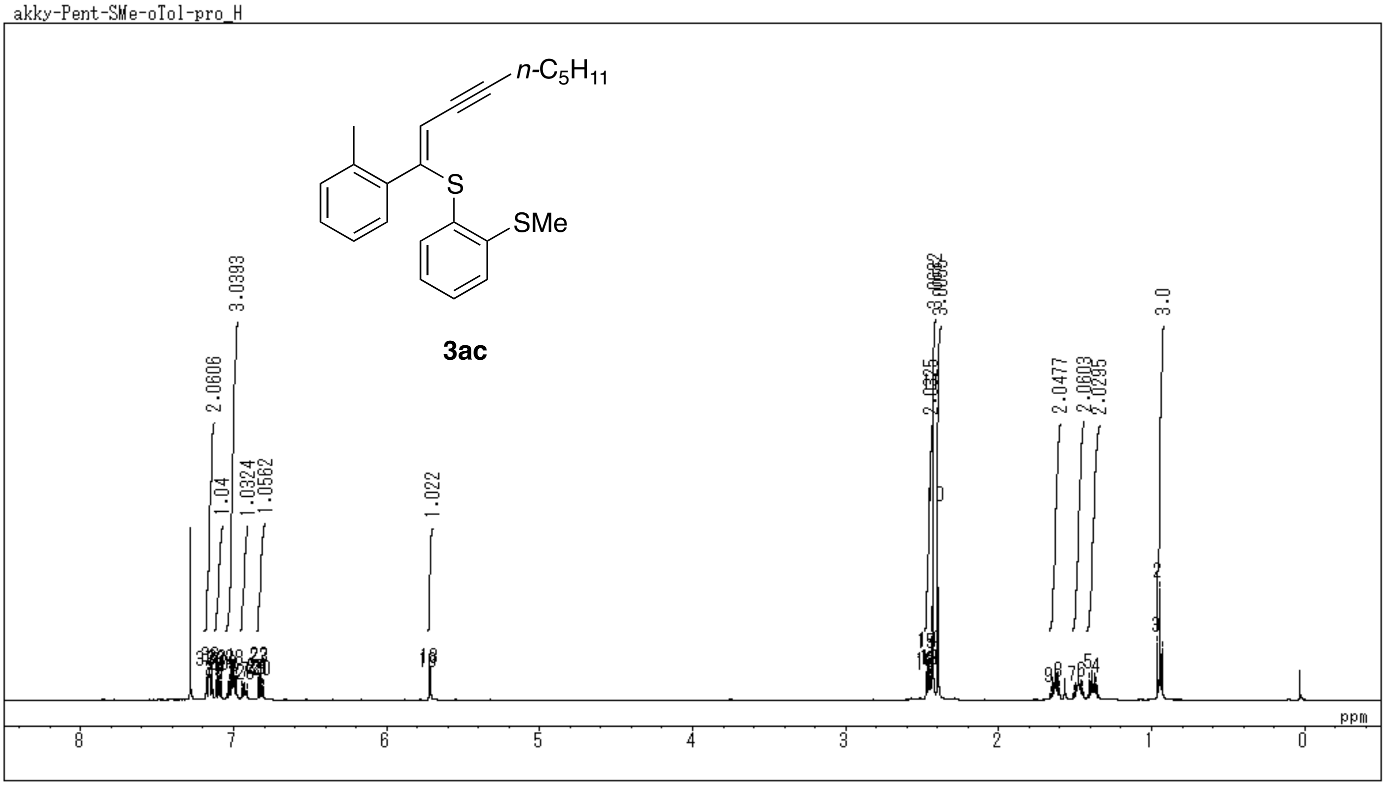
akky-SeMepro-H
n-C5H11
S
SeMe
2.0221
1.0052
1.0232
3.0566
1.0089
1.0225
2.0015
3.0334
3.0
2.0389
4.0937
3.0541
ppm
8
7
6
5
4
3
2
1
0

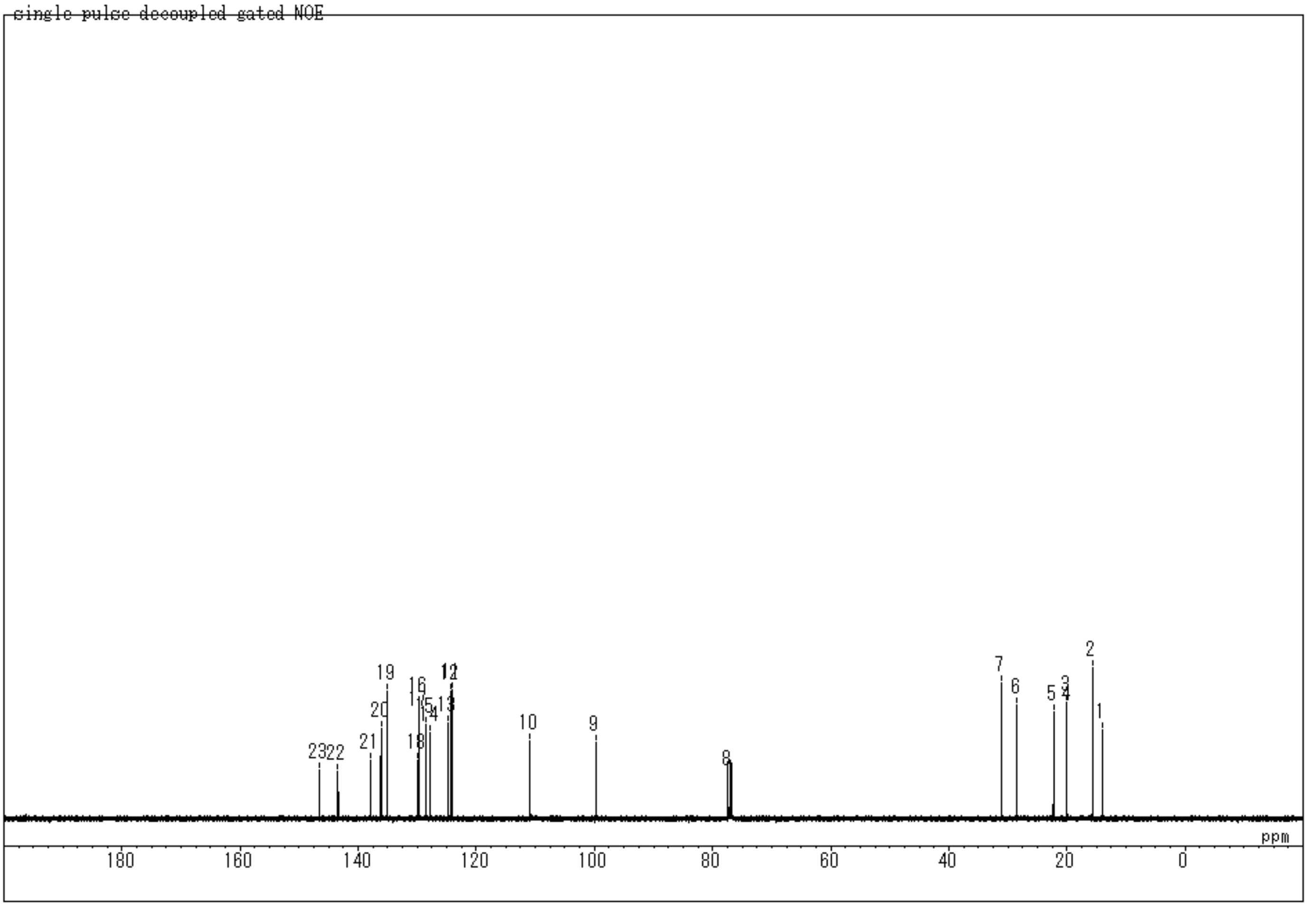


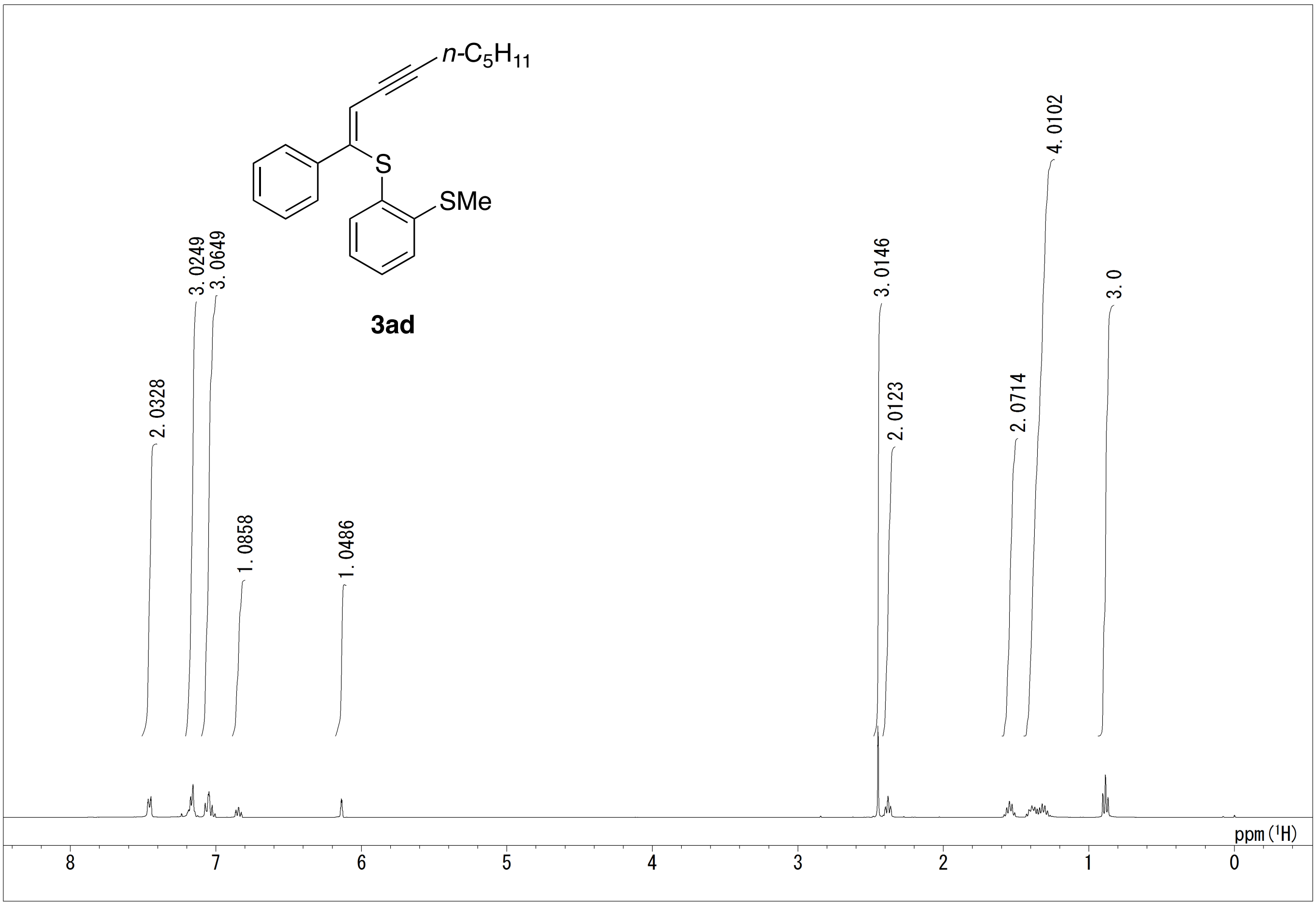
21
20
19
17
18
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
−20


akky-ex195-H
n-C5H11
S
SMe
3ab
2.0246
4.034
1.0116
1.0393
1.0215
3.0
2.043
3.0227
2.0701
4.0017
3.0337
ppm
8
7
6
5
4
3
2
1
0


akky-ex195-C
ppm
180
160
140
120
100
80
60
40
20
0

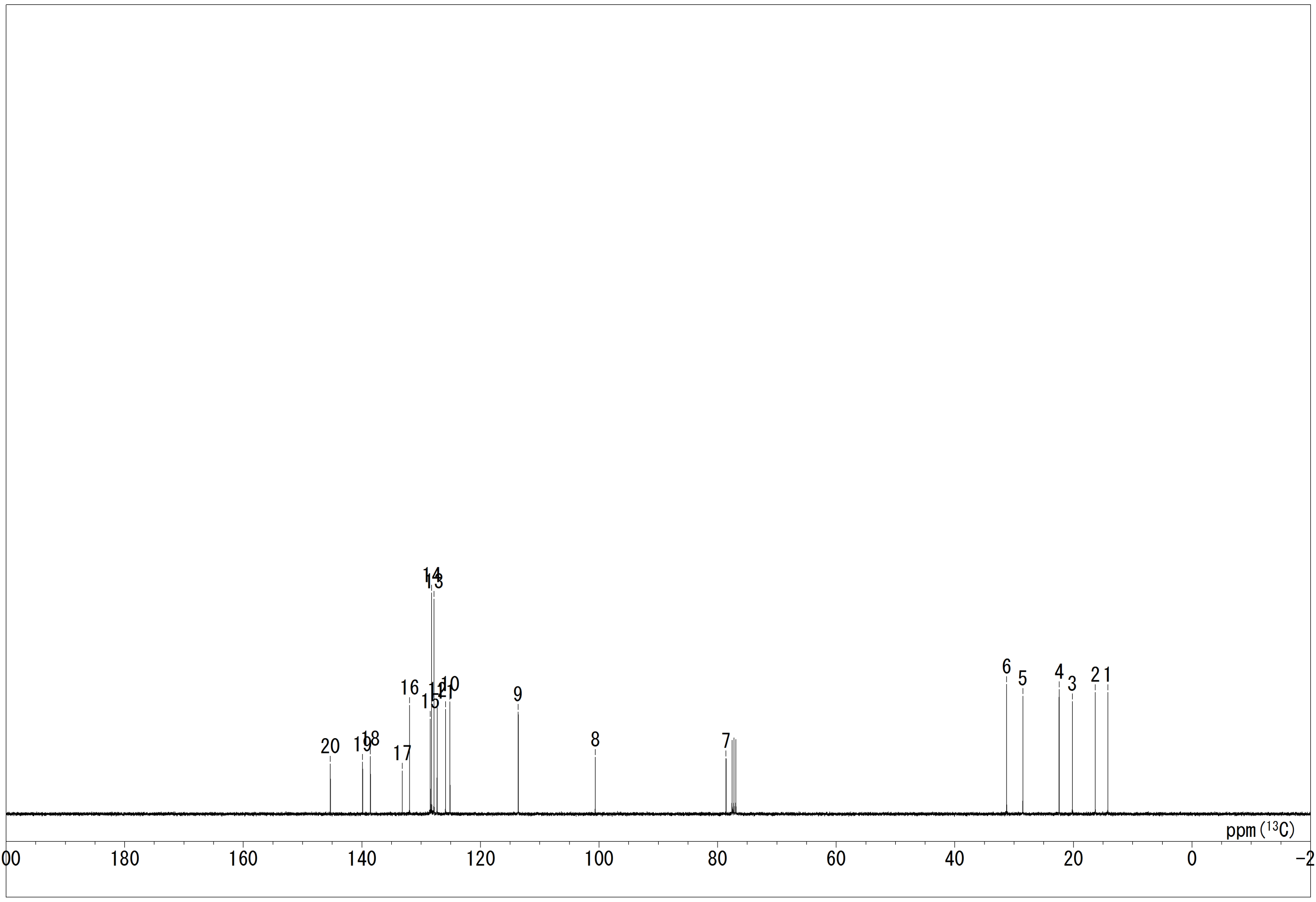

akky-Pent-SMe-oTol-pro_H
n-C$_5$H$_{11}$
S
SMe
3ac
2.0606
3.0393
1.04
1.0324
1.0562
1.022
2.0477
2.0603
2.0295
3.0
ppm
8
7
6
5
4
3
2
1
0


single pulse decoupled gated NOE
ppm
180
160
140
120
100
80
60
40
20
0



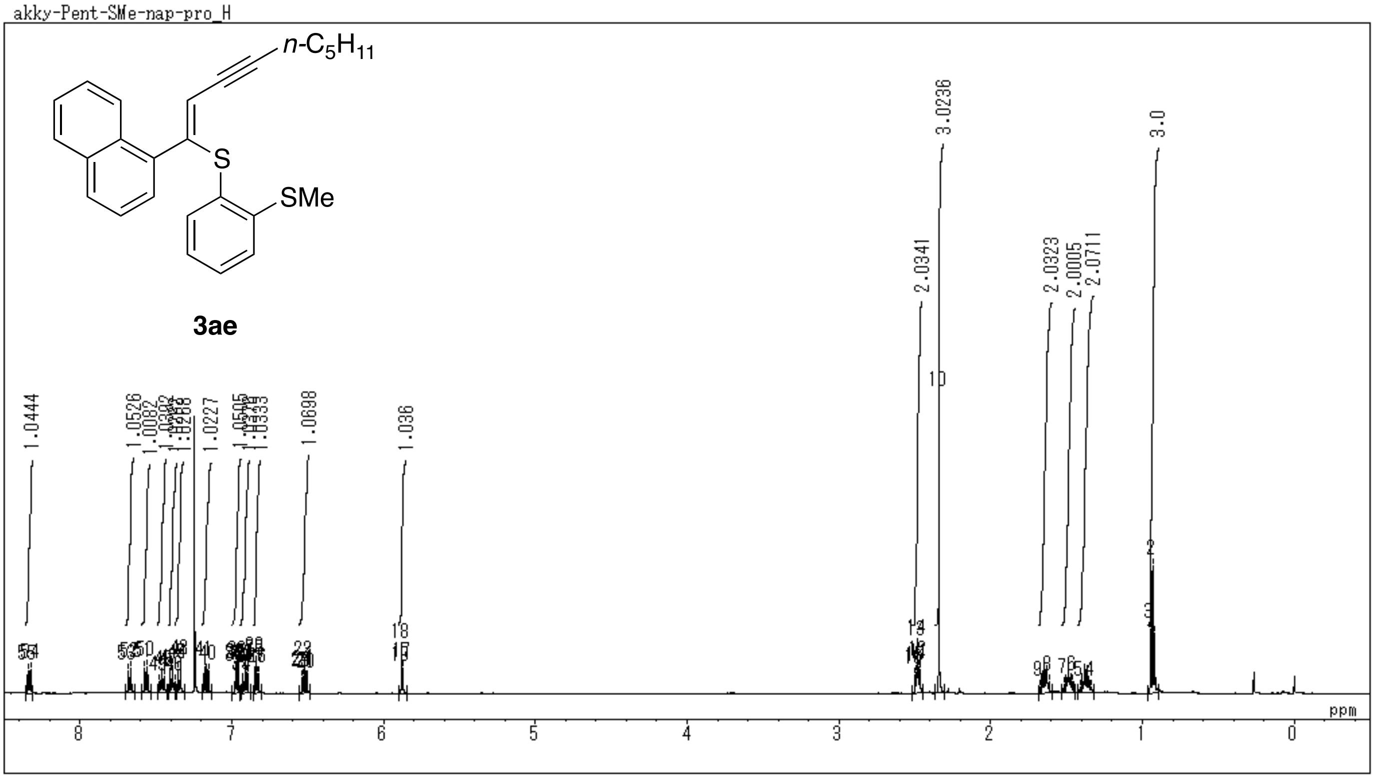
3ad

n-C5H11
S
SMe
2.0328
3.0249
3.0649
1.0858
1.0486
3.0146
2.0123
2.0714
4.0102
3.0
ppm (1H)
8
7
6
5
4
3
2
1
0

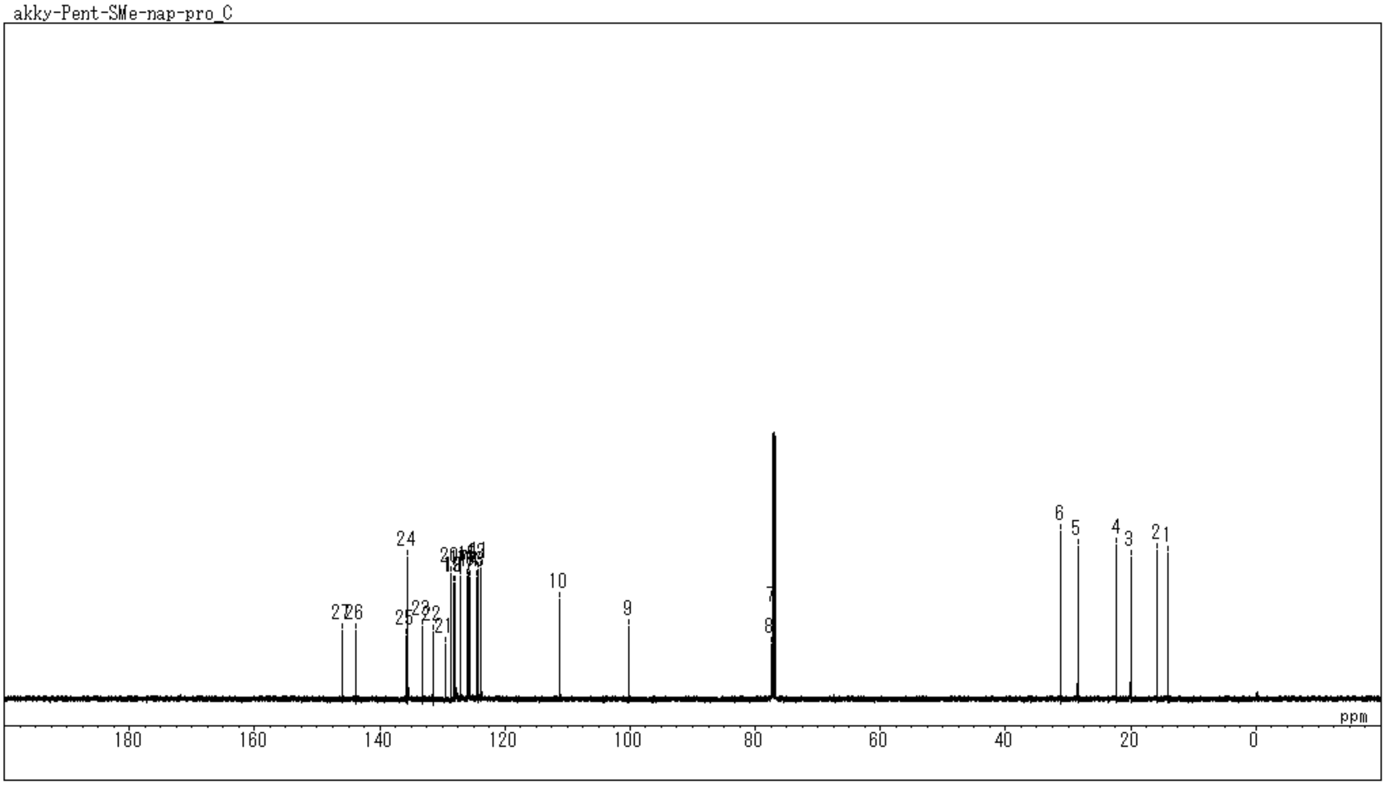


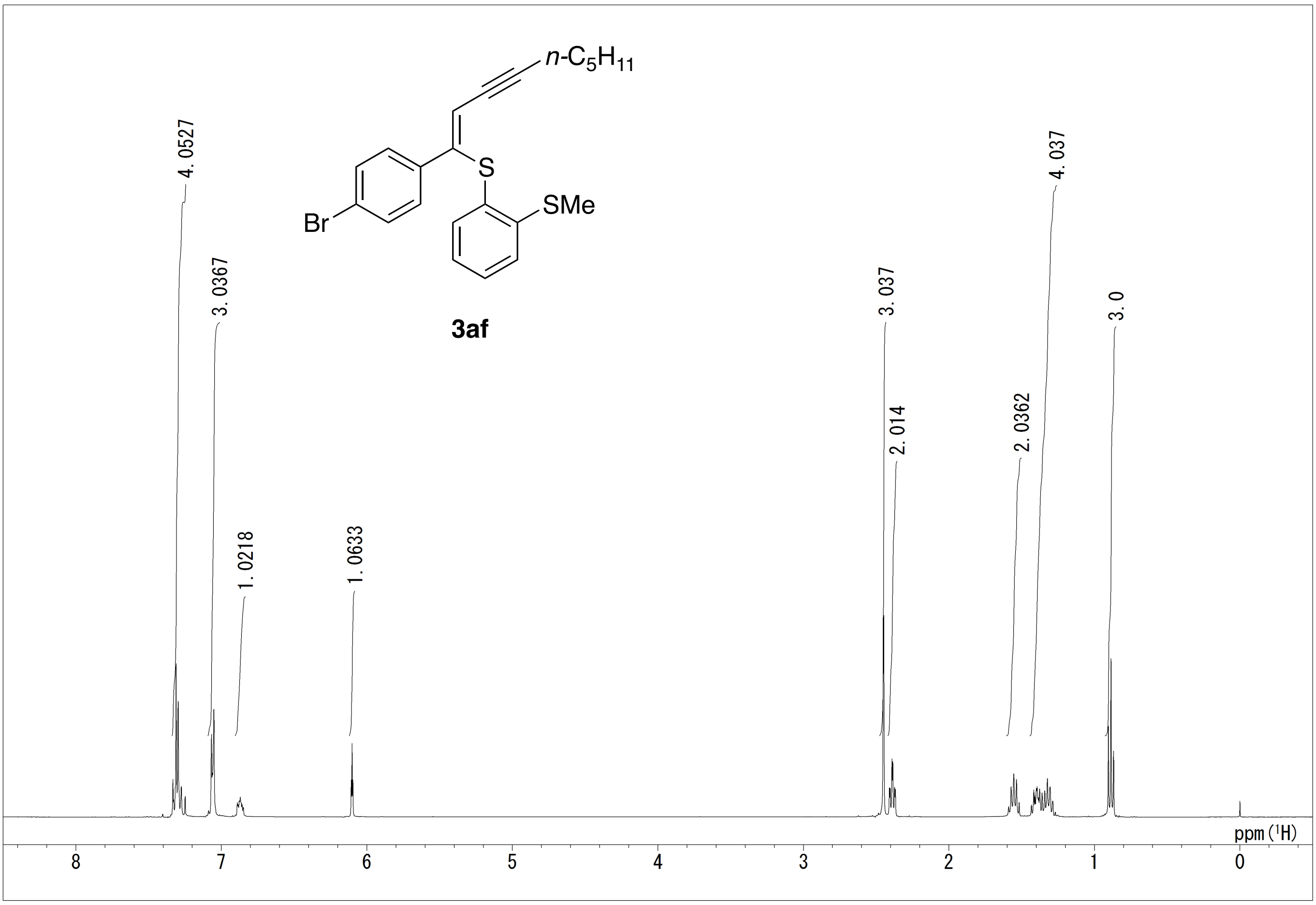
14
13
16
15
12
11
10
9
20
19
18
17
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
−20

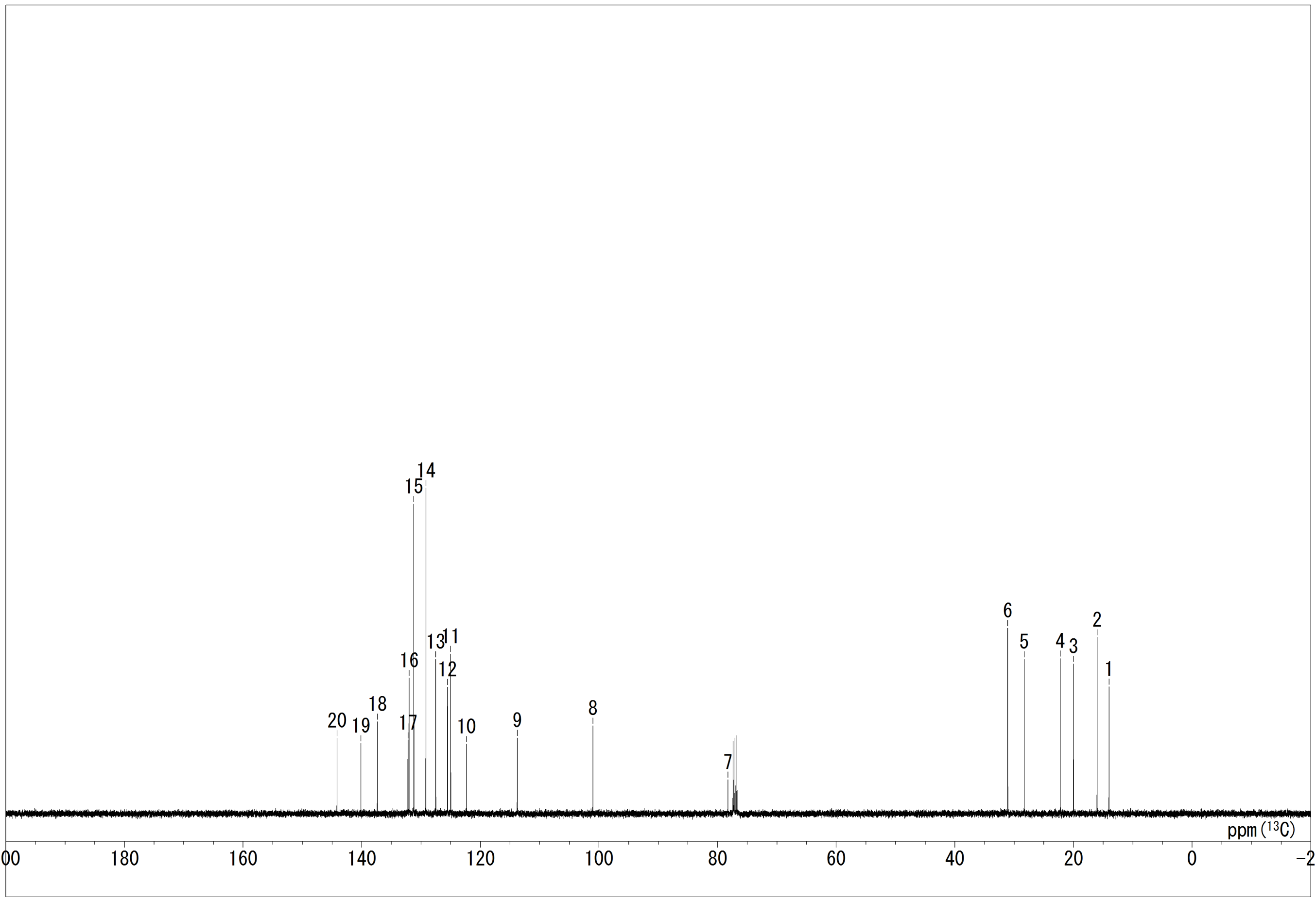
akky-Pent-SMe-nap-pro_H

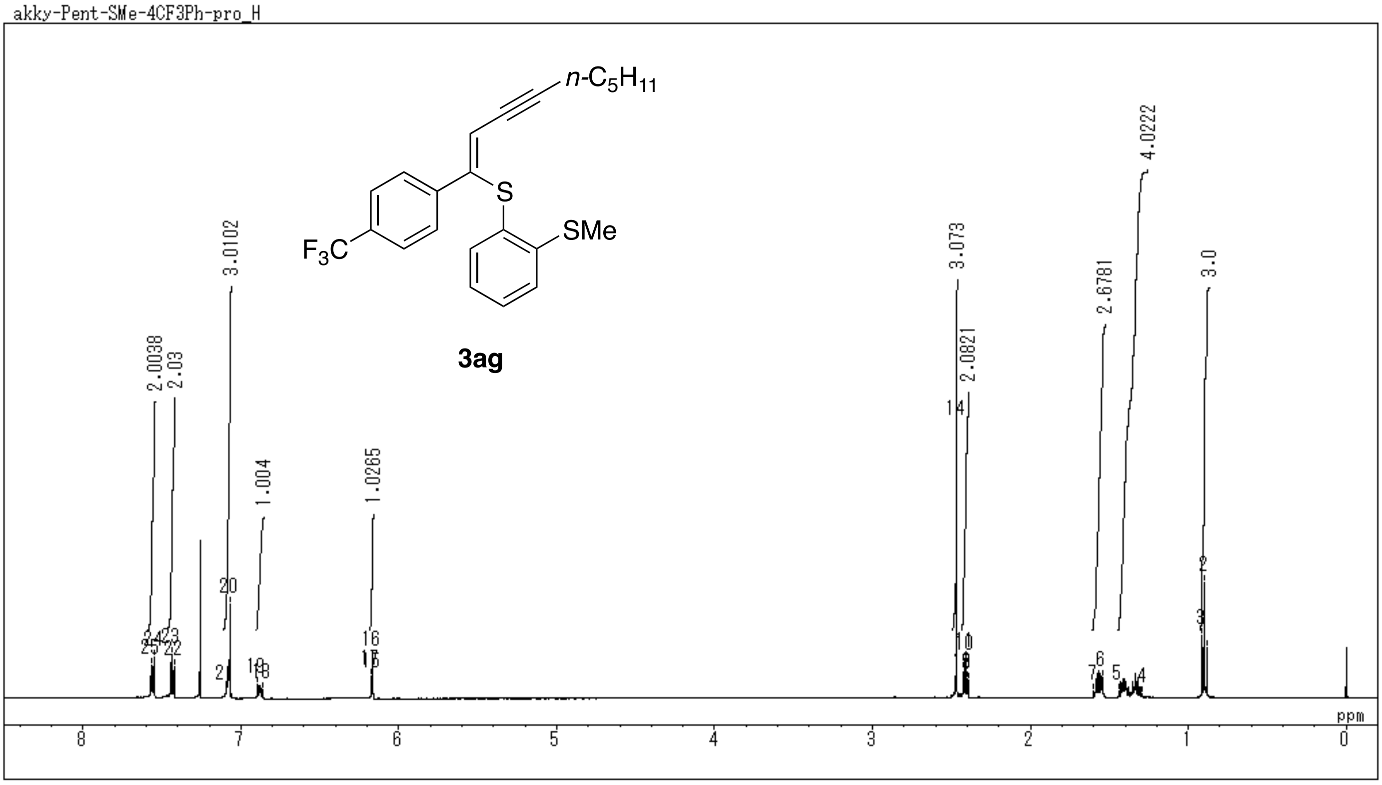


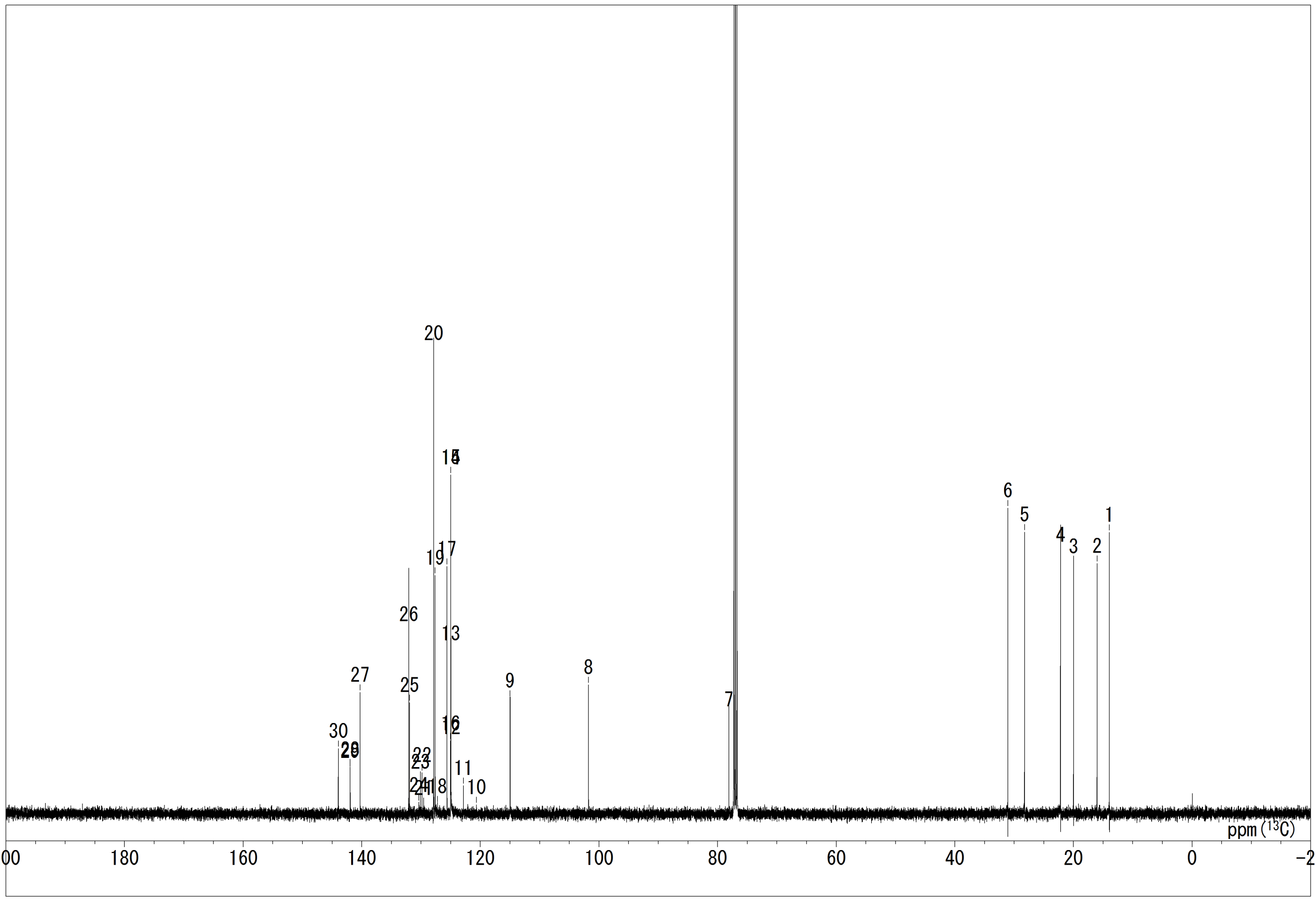
akky-Pent-SMe-nap-pro_C

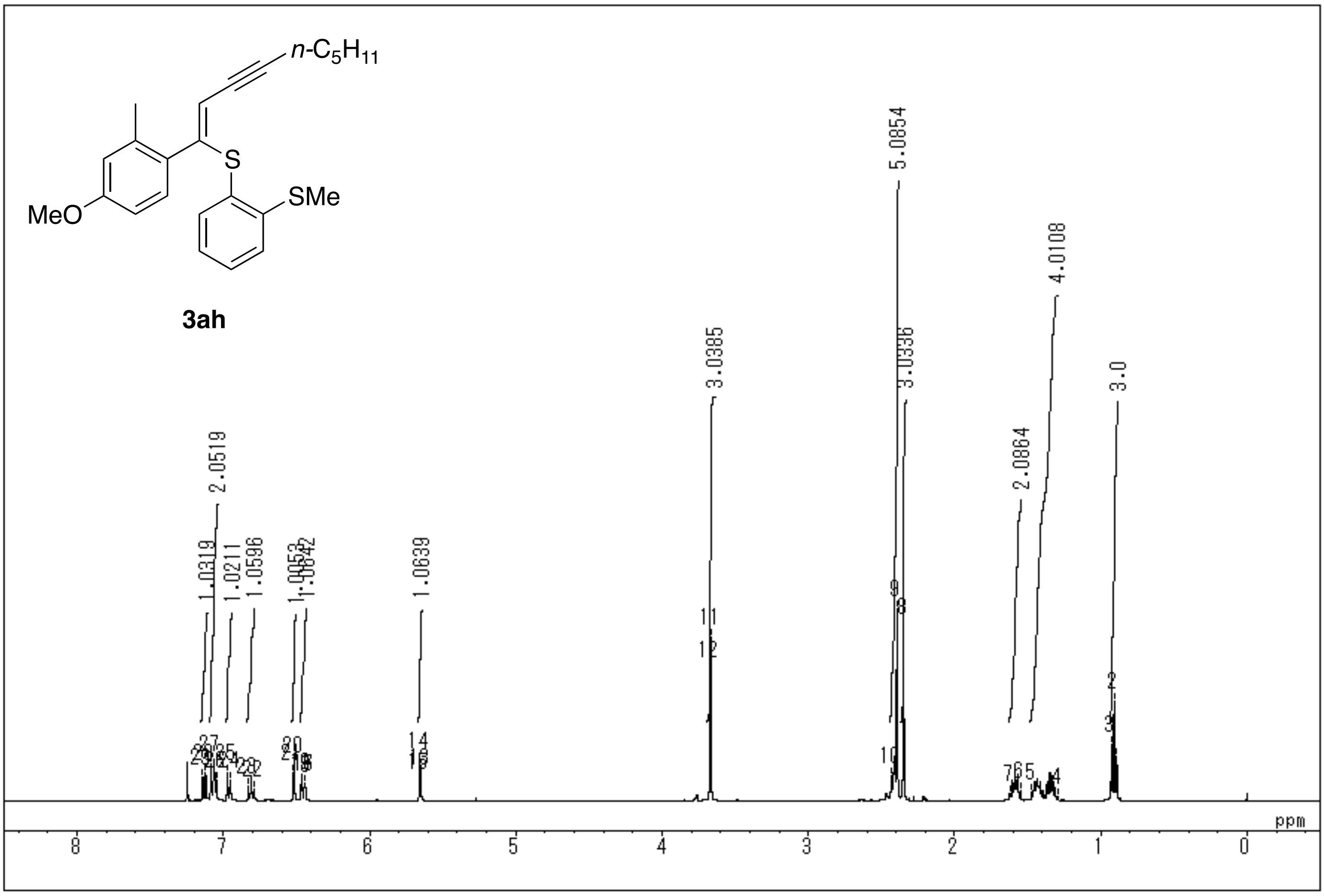


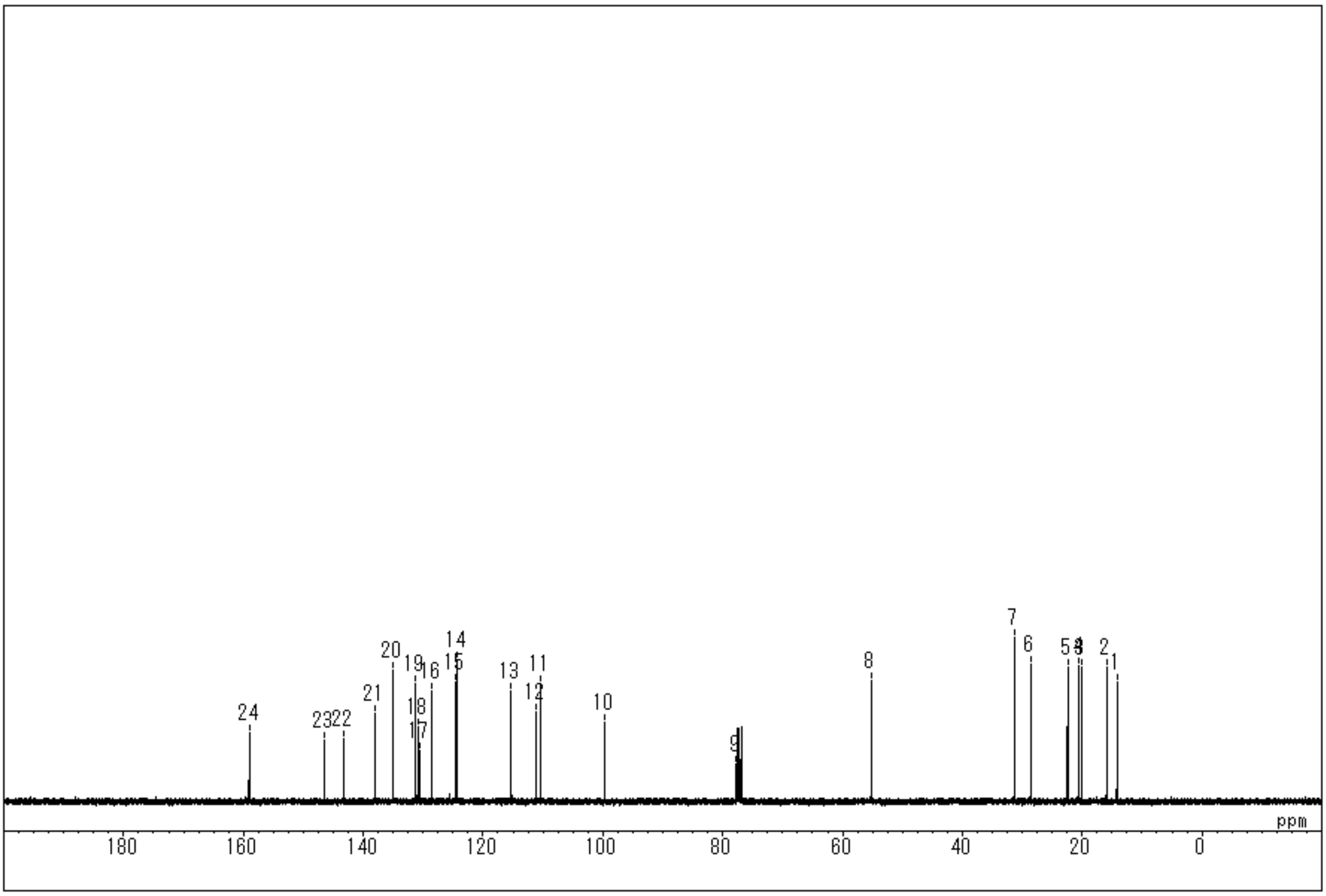

n-C5H11
S
SMe
Br
3af
4.0527
3.0367
1.0218
1.0633
3.037
2.014
2.0362
4.037
3.0
ppm (1H)
8
7
6
5
4
3
2
1
0

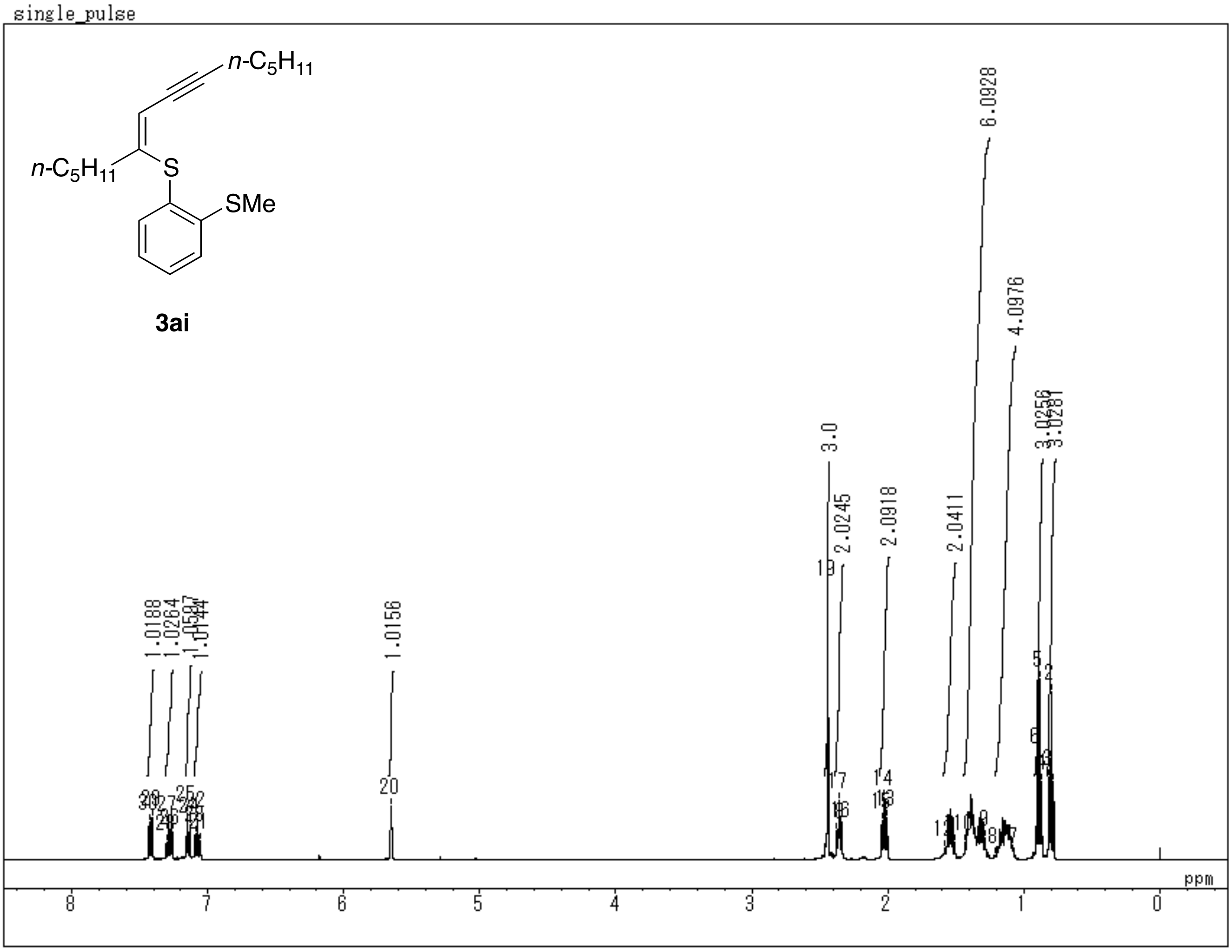

14
15
16
13
11
12
18
20
19
17
10
9
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
−20

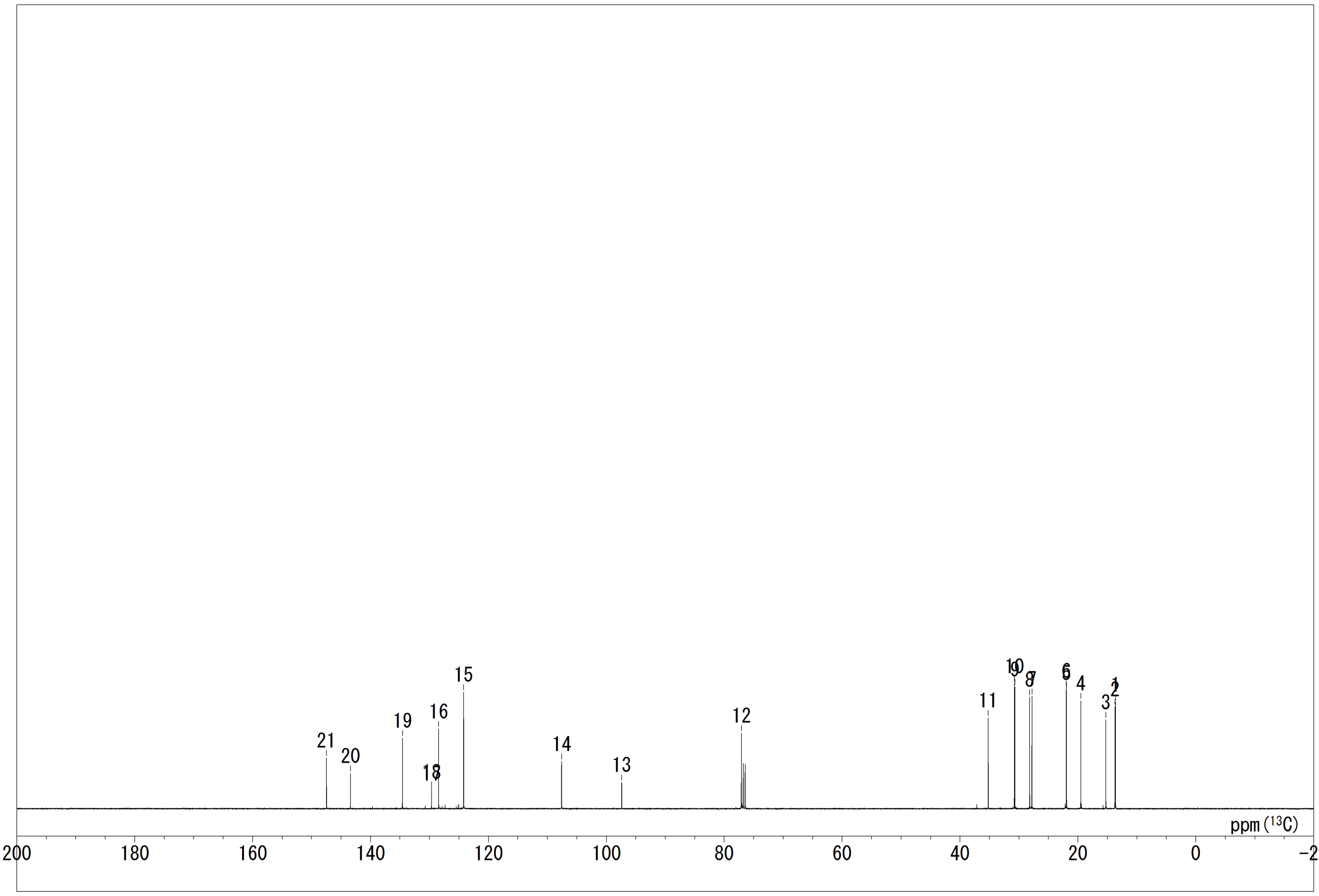

akky-Pent-SMe-4CF3Ph-pro_H
n-C5H11
S
SMe
F3C
3ag
2.0038
2.03
3.0102
1.004
1.0265
3.073
2.0821
2.6781
4.0222
3.0
ppm
8
7
6
5
4
3
2
1
0

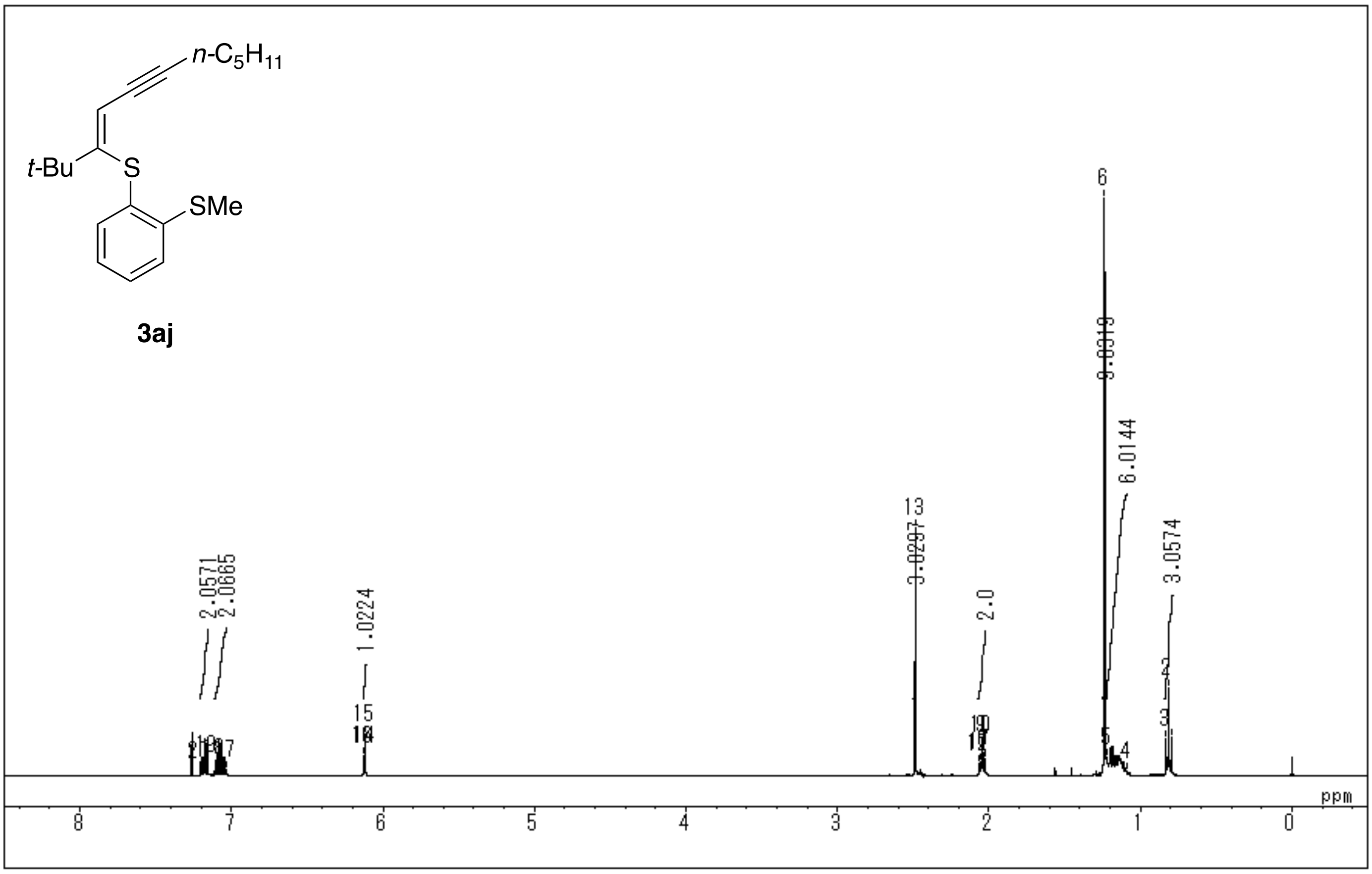

ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
−20

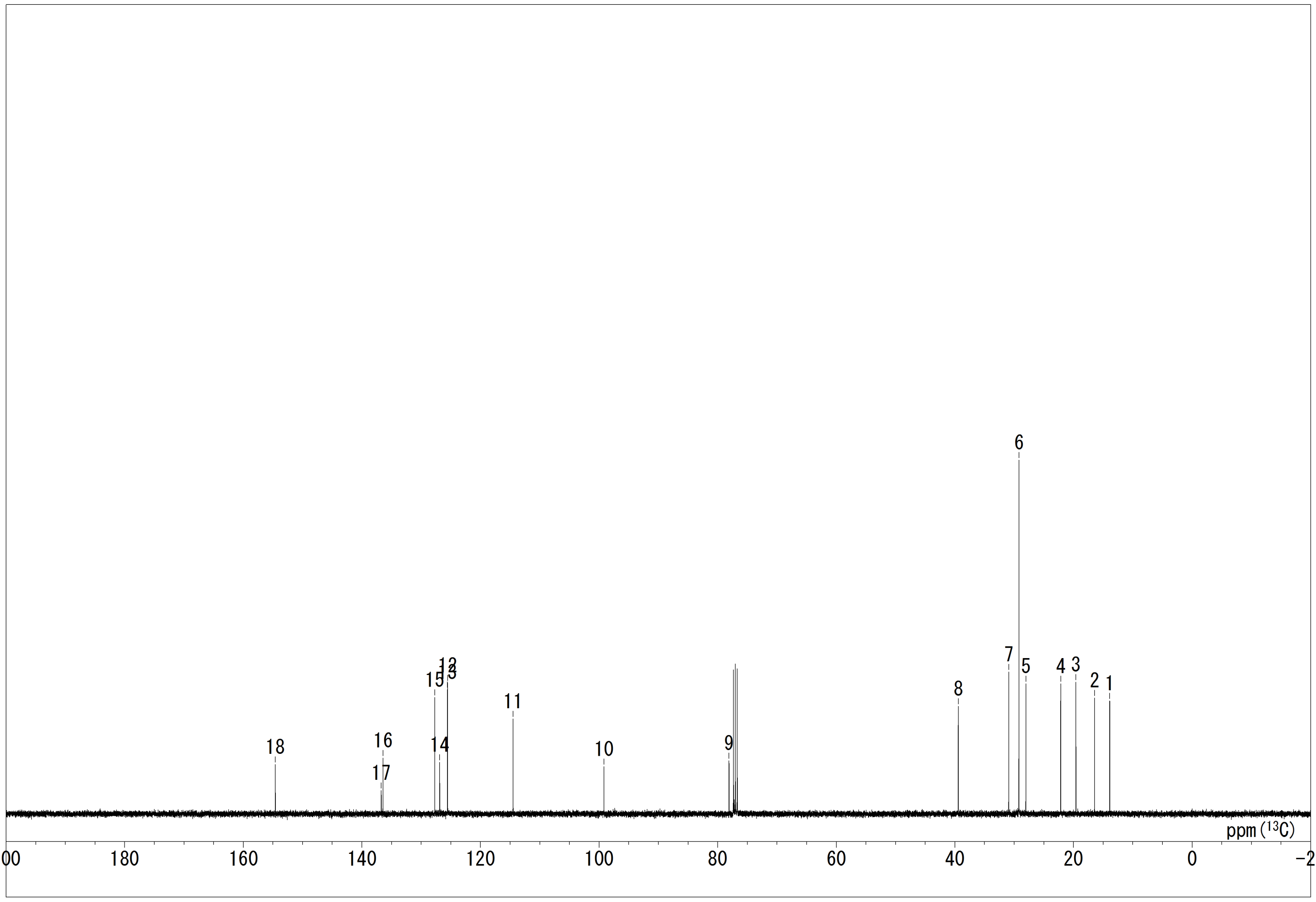

n-C5H11
S
SMe
MeO
3ah
1.0319
2.0519
1.0211
1.0596
1.0053
1.0042
1.0639
3.0385
5.0854
3.0336
2.0864
4.0108
3.0
ppm
8
7
6
5
4
3
2
1
0

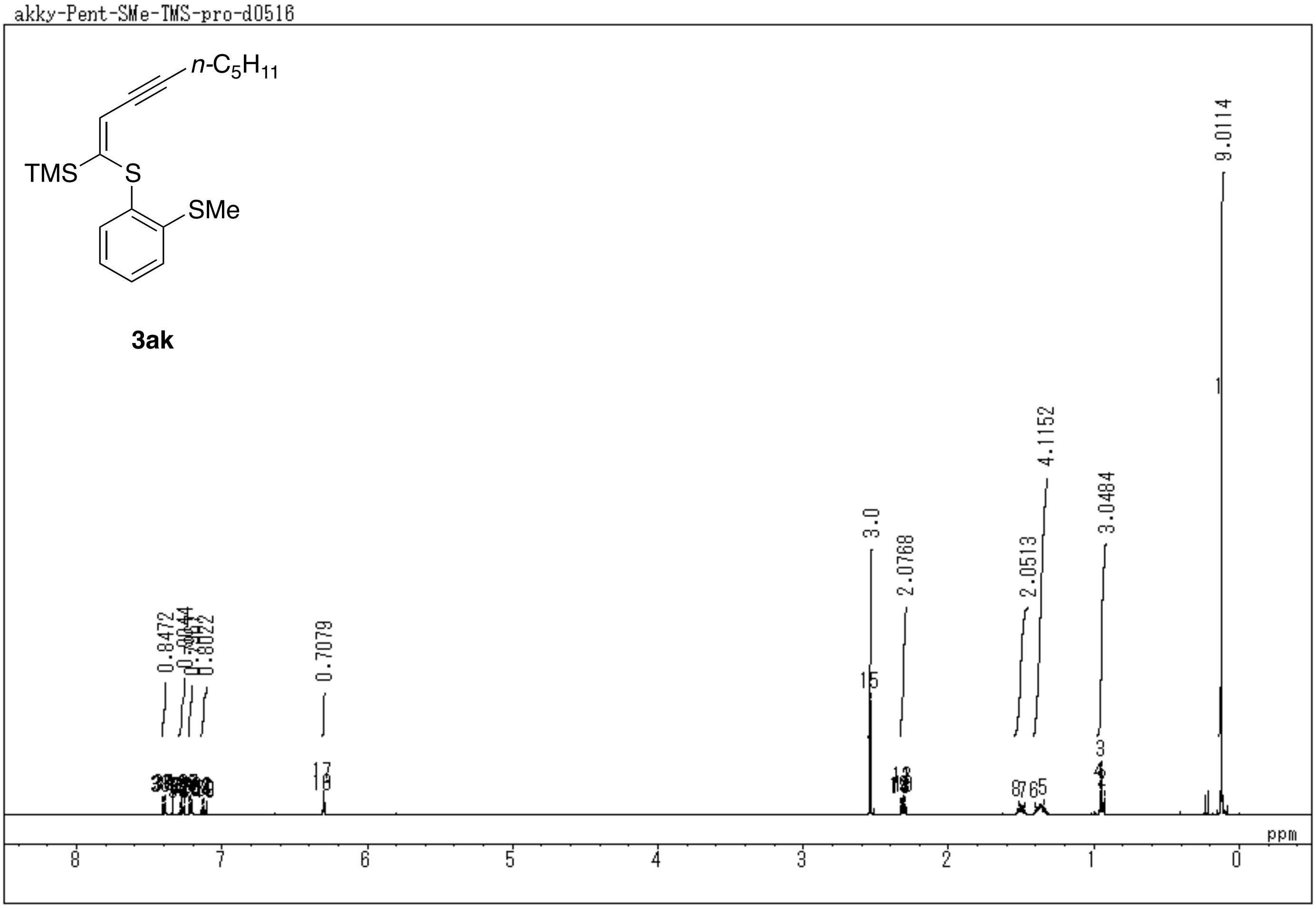

ppm
180
160
140
120
100
80
60
40
20
0

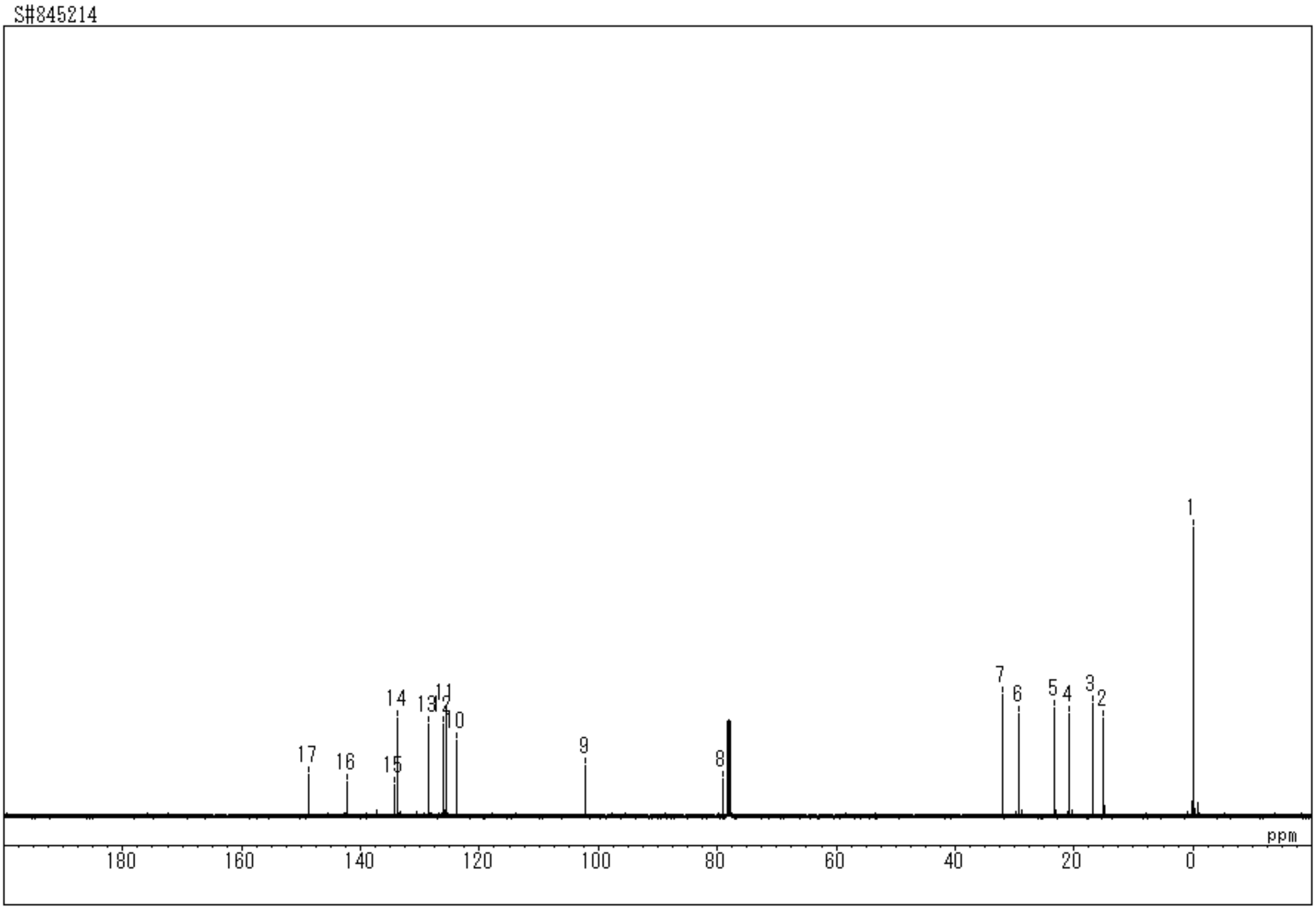

single_pulse
n-C5H11
n-C5H11
S
SMe
3ai
1.0188
1.0264
1.0597
1.0144
1.0156
3.0
2.0245
2.0918
2.0411
6.0928
4.0976
3.0256
3.0281
ppm
8
7
6
5
4
3
2
1
0

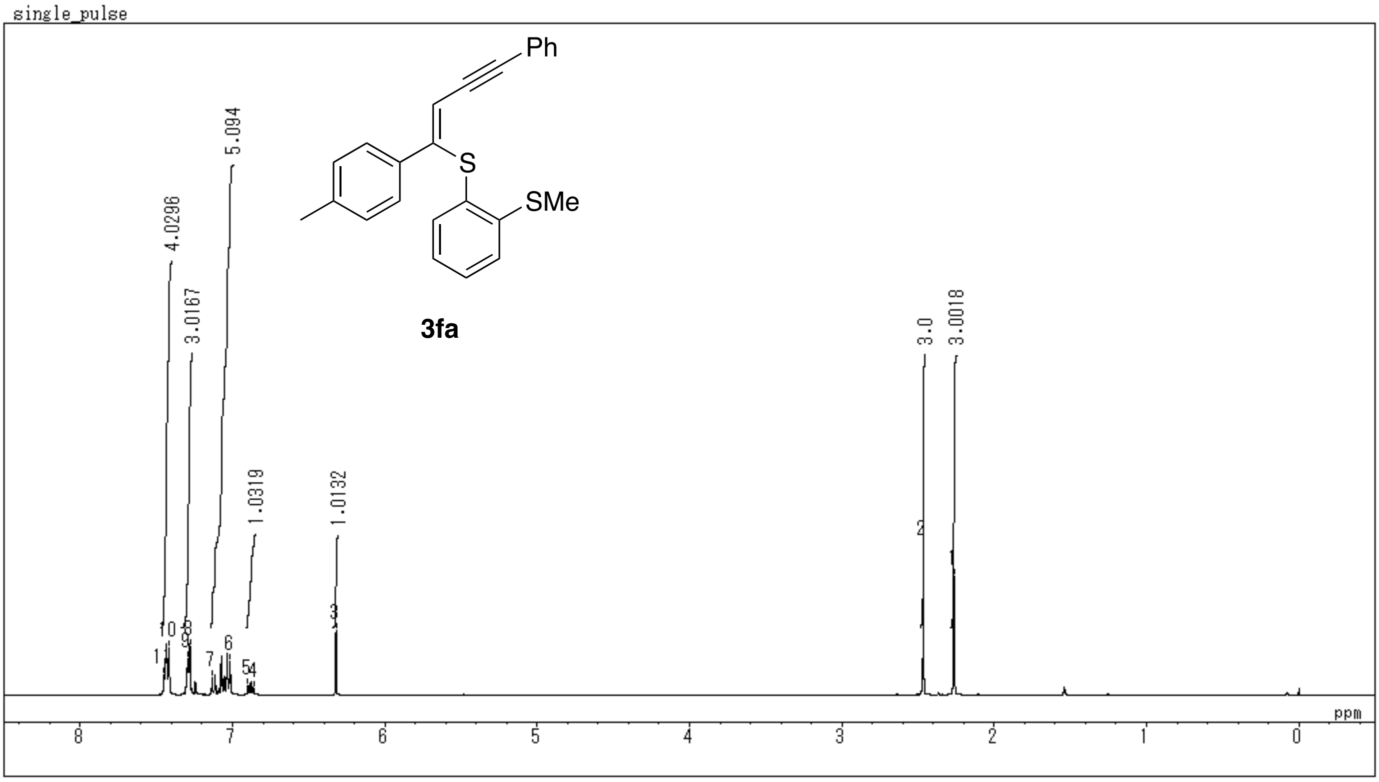

21
20
19
18
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
−20

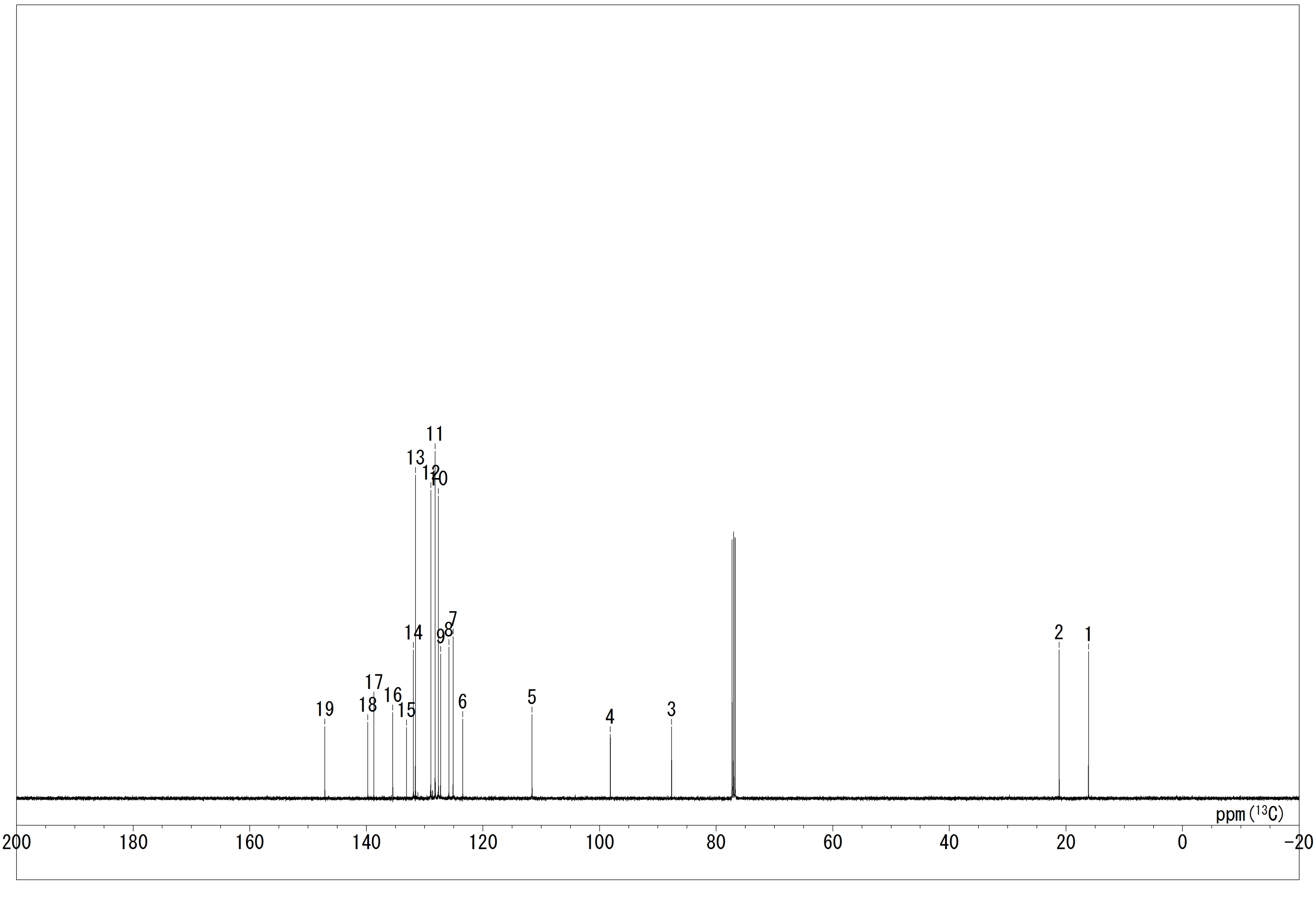

n-C5H11
t-Bu
S
SMe
3aj
2.0571
2.0665
1.0224
3.0297
2.0
9.0319
6.0144
3.0574
ppm
8
7
6
5
4
3
2
1
0

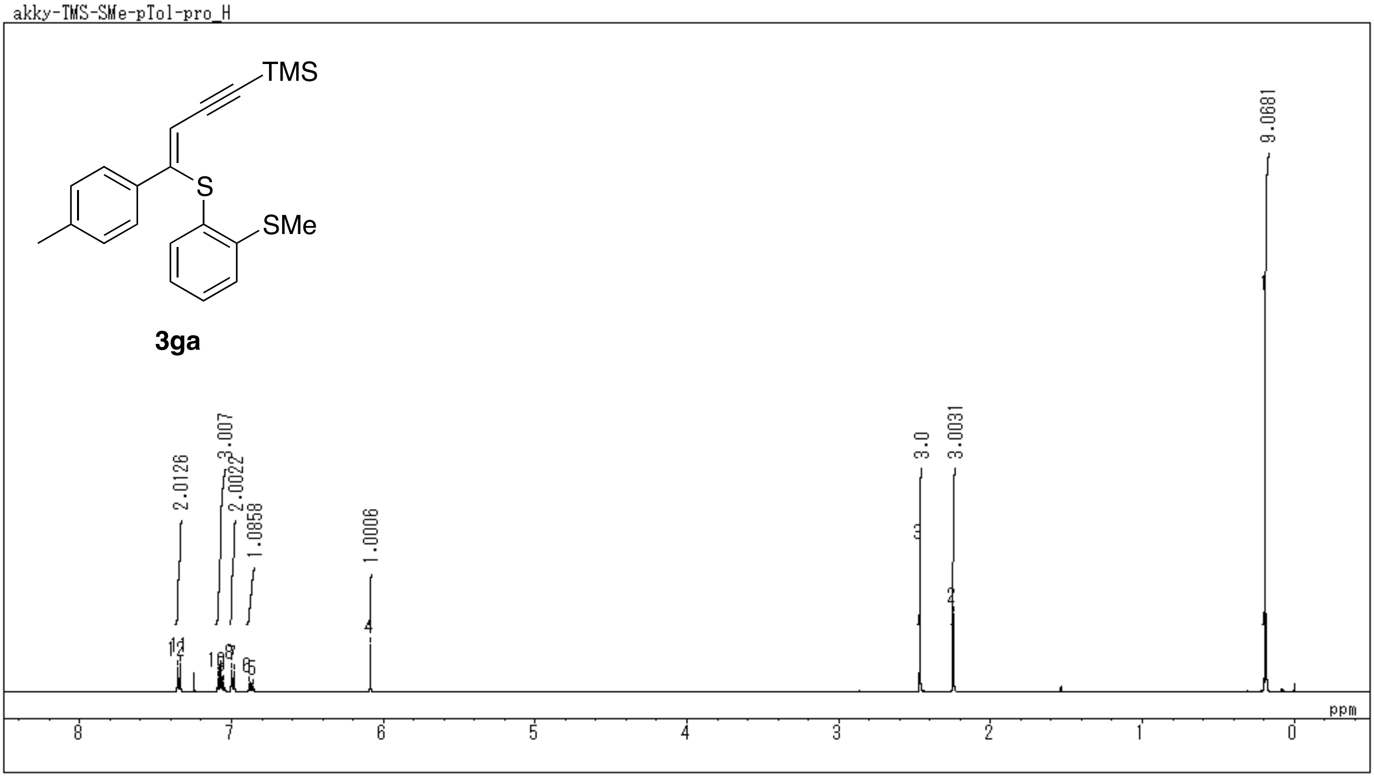

18
16
17
15
14
12
13
11
10
9
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
−20

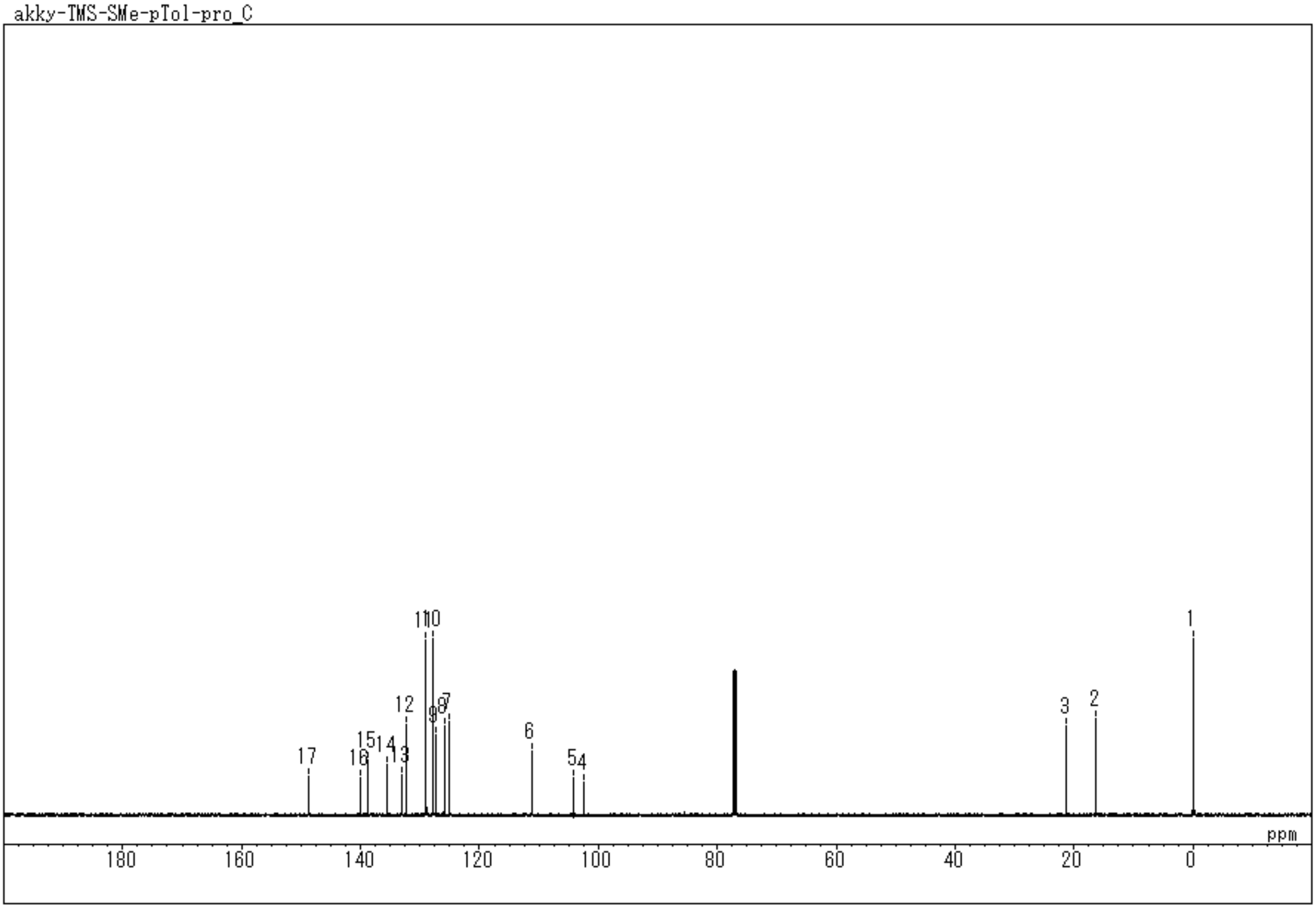

akky-Pent-SMe-TMS-pro-d0516
n-C5H11
TMS
S
SMe
3ak
0.8472
0.8022
0.7079
3.0
2.0768
2.0513
4.1152
3.0484
9.0114
17
15
8 7 6 5
3
1
ppm
8
7
6
5
4
3
2
1
0

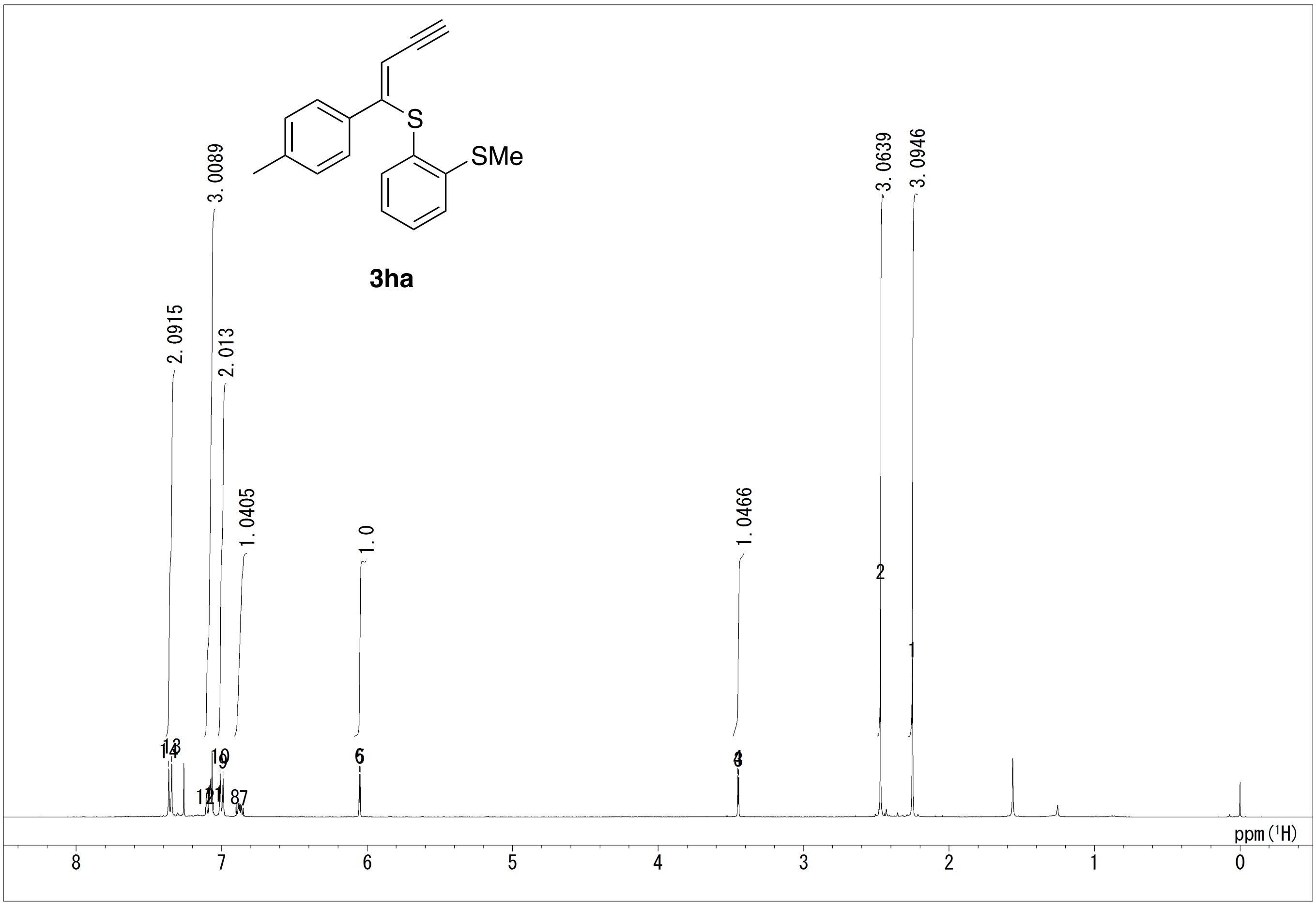

S#845214
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
180
160
140
120
100
80
60
40
20
0


single_pulse
Ph
S
SMe
3fa
4.0296
3.0167
5.094
1.0319
1.0132
3.0
3.0018
11
10
9
8
7
6
5
4
3
2
1
ppm
8
7
6
5
4
3
2
1
0

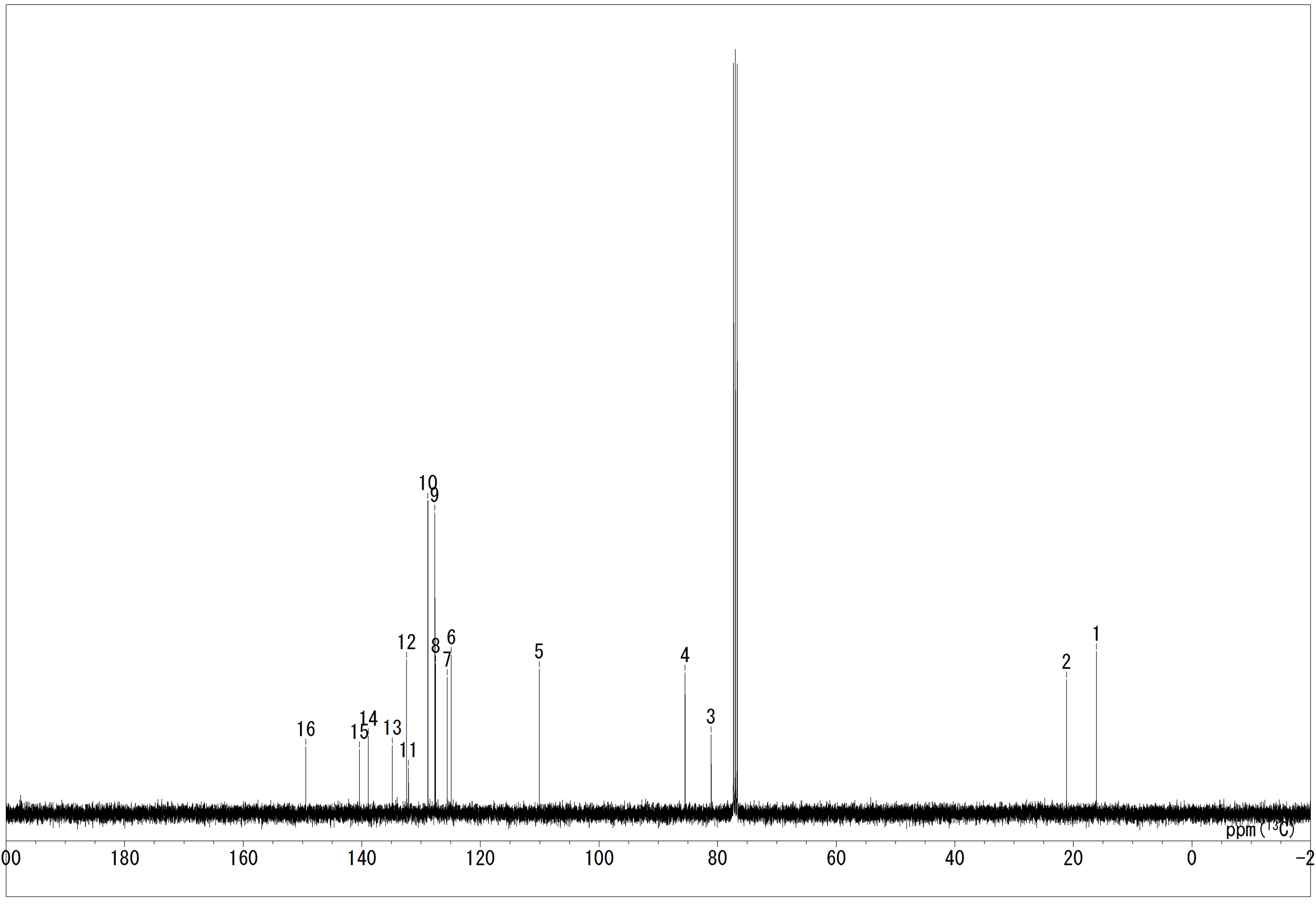

11
13
12
10
14
9
8
7
17
16
18
19
15
6
5
4
3
2
1
ppm (¹³C)
200
180
160
140
120
100
80
60
40
20
0
−20


akky-TMS-SMe-pTol-pro_H
TMS
S
SMe
3ga
2.0126
3.007
2.0022
1.0858
1.0006
3.0
3.0031
9.0681
ppm
8
7
6
5
4
3
2
1
0

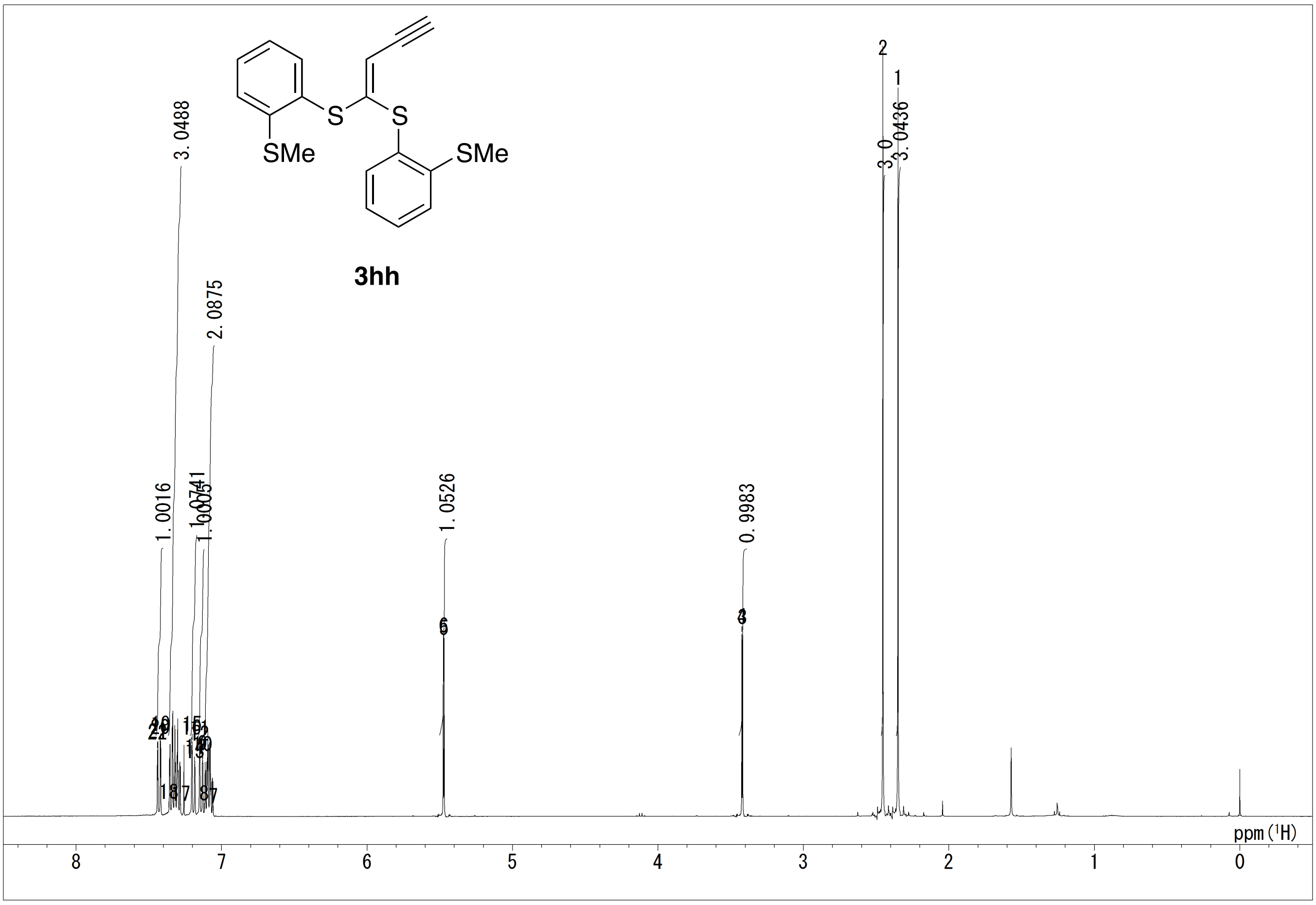

akky-TMS-SMe-pTol-pro_C
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
180
160
140
120
100
80
60
40
20
0

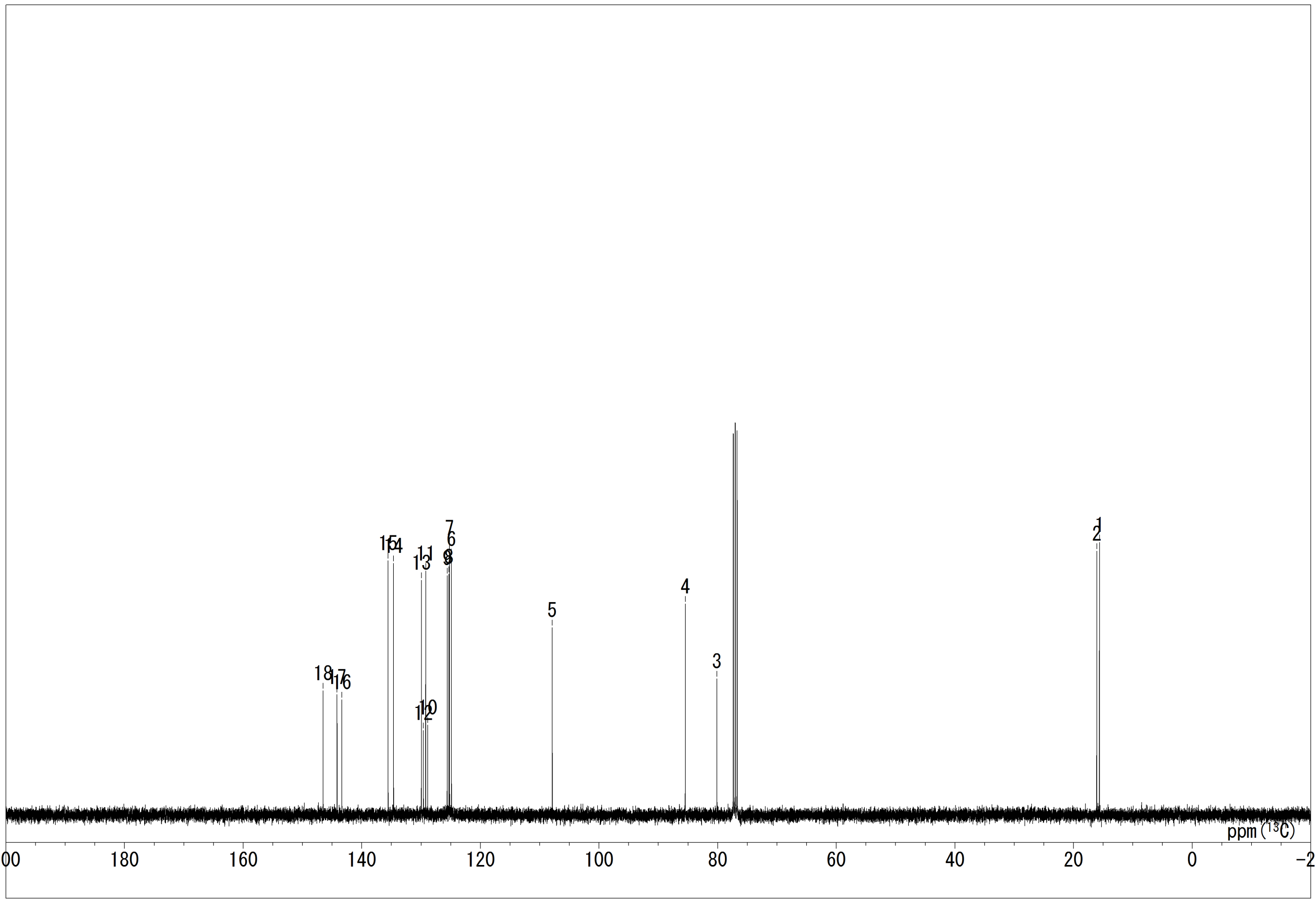

3ha

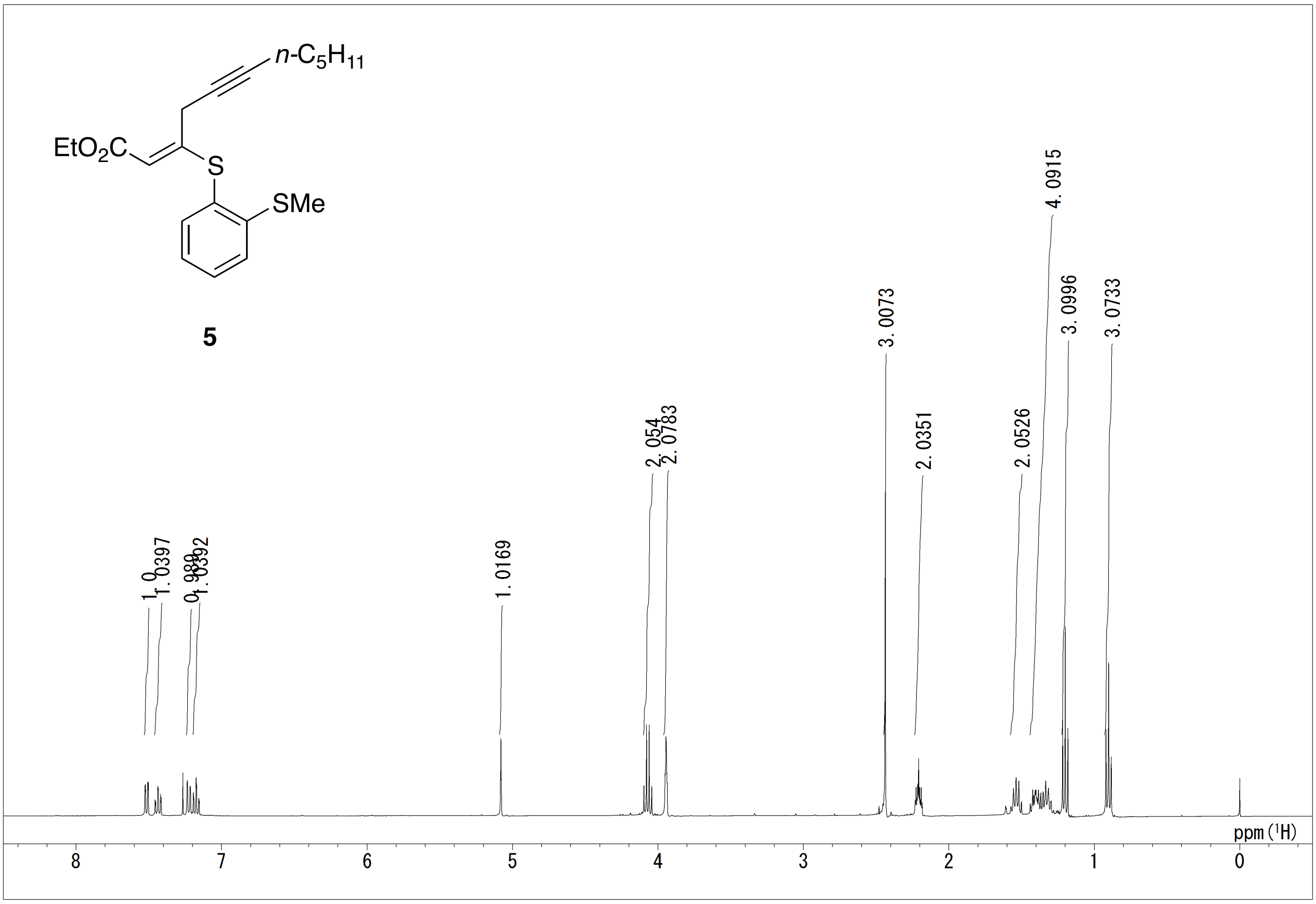
SMe
S
2.0915
3.0089
2.013
1.0405
1.0
1.0466
3.0639
3.0946
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (¹H)
8
7
6
5
4
3
2
1
0

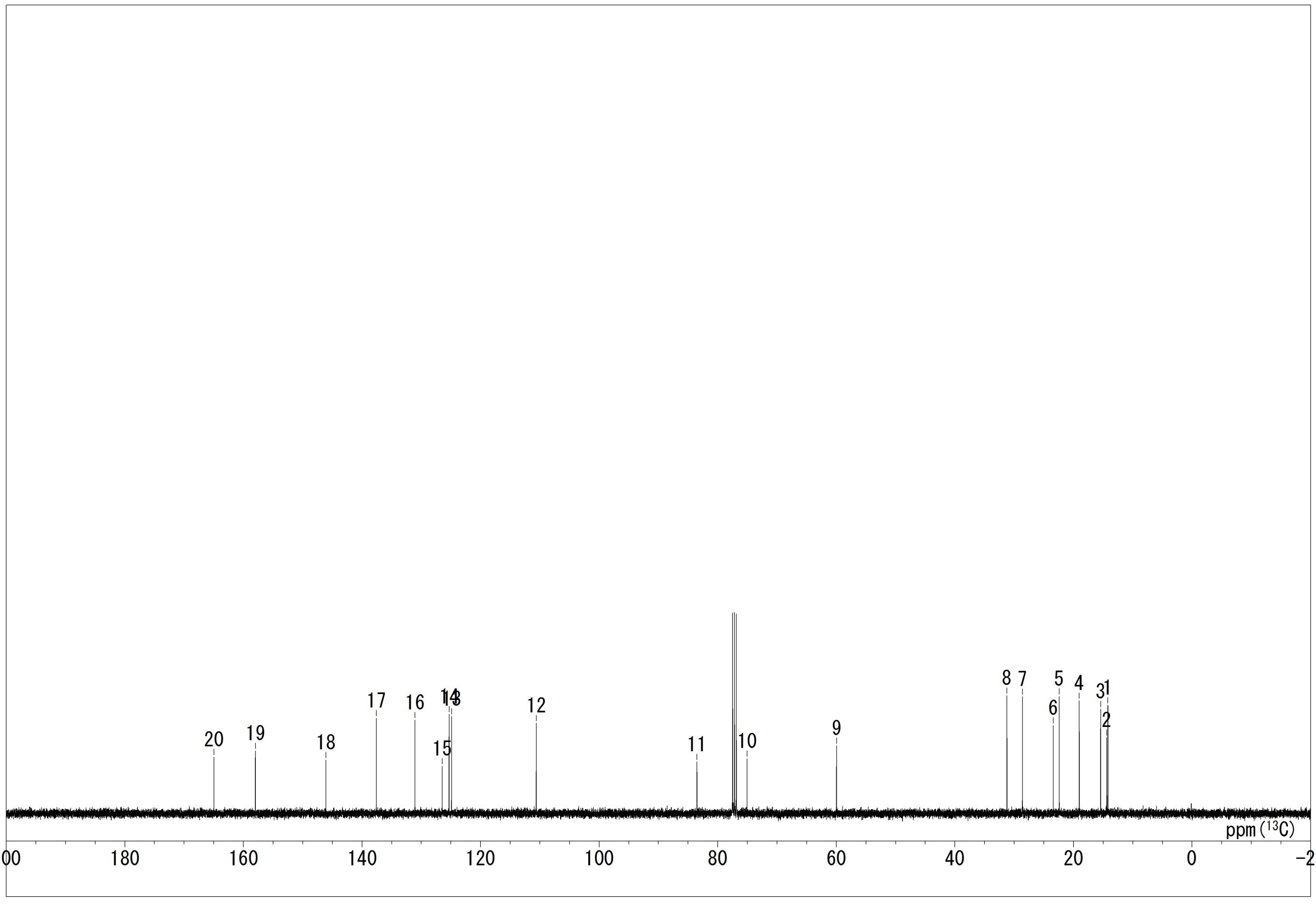


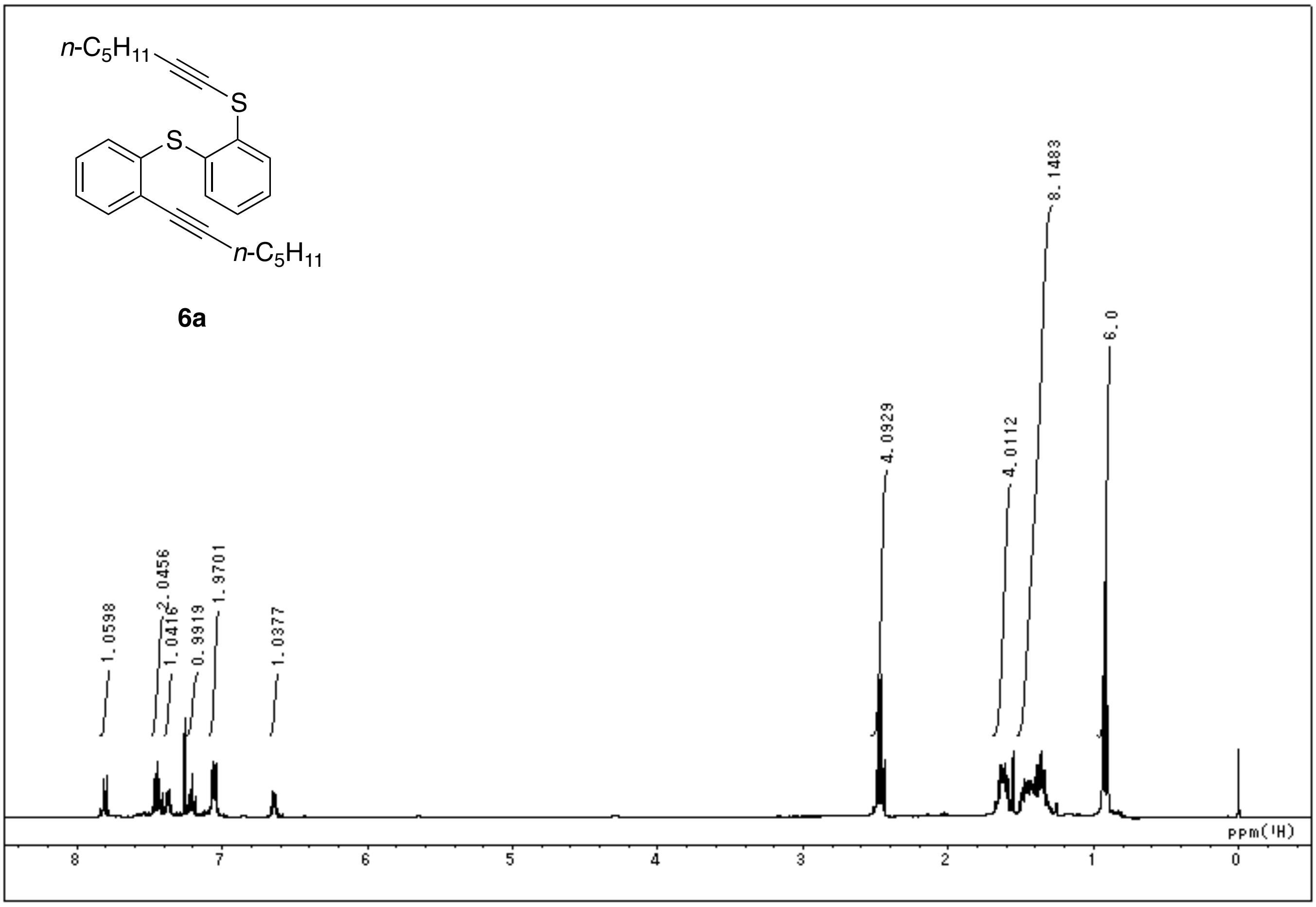
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (¹³C)
200
180
160
140
120
100
80
60
40
20
0
-20


SMe
S
S
SMe
3hh
1.0016
3.0488
1.0741
1.0005
2.0875
1.0526
0.9983
3.0
3.0436
ppm (¹H)
8
7
6
5
4
3
2
1
0


ppm (¹³C)
200
180
160
140
120
100
80
60
40
20
0
–20

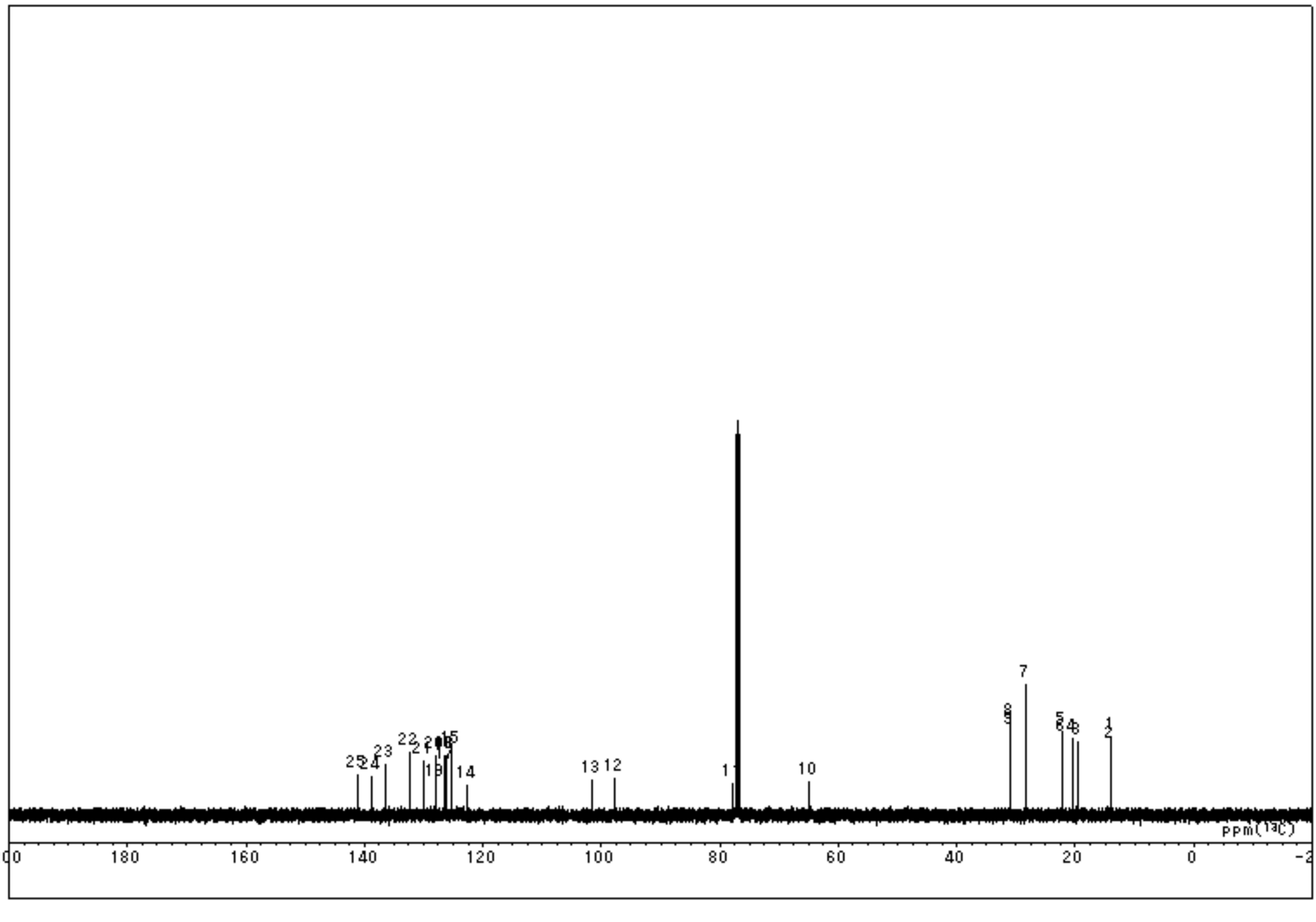

n-C5H11
EtO2C
S
SMe
5
1.0
1.0397
0.989
1.0392
1.0169
2.054
2.0783
3.0073
2.0351
2.0526
4.0915
3.0996
3.0733
ppm (1H)
8
7
6
5
4
3
2
1
0


20
19
18
17
16
14
13
15
12
11
10
9
8
7
5
6
4
3
1
2
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
−20

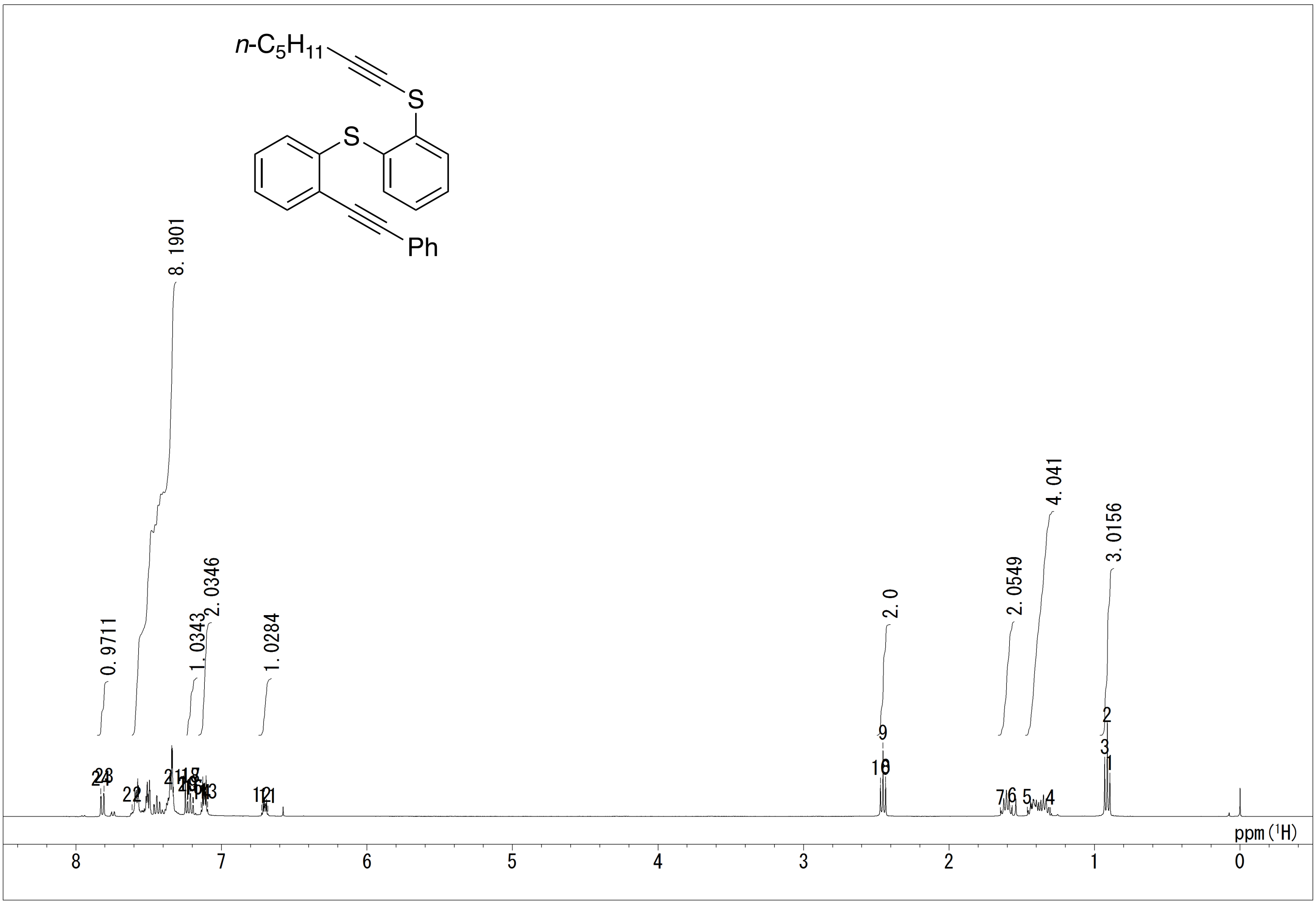


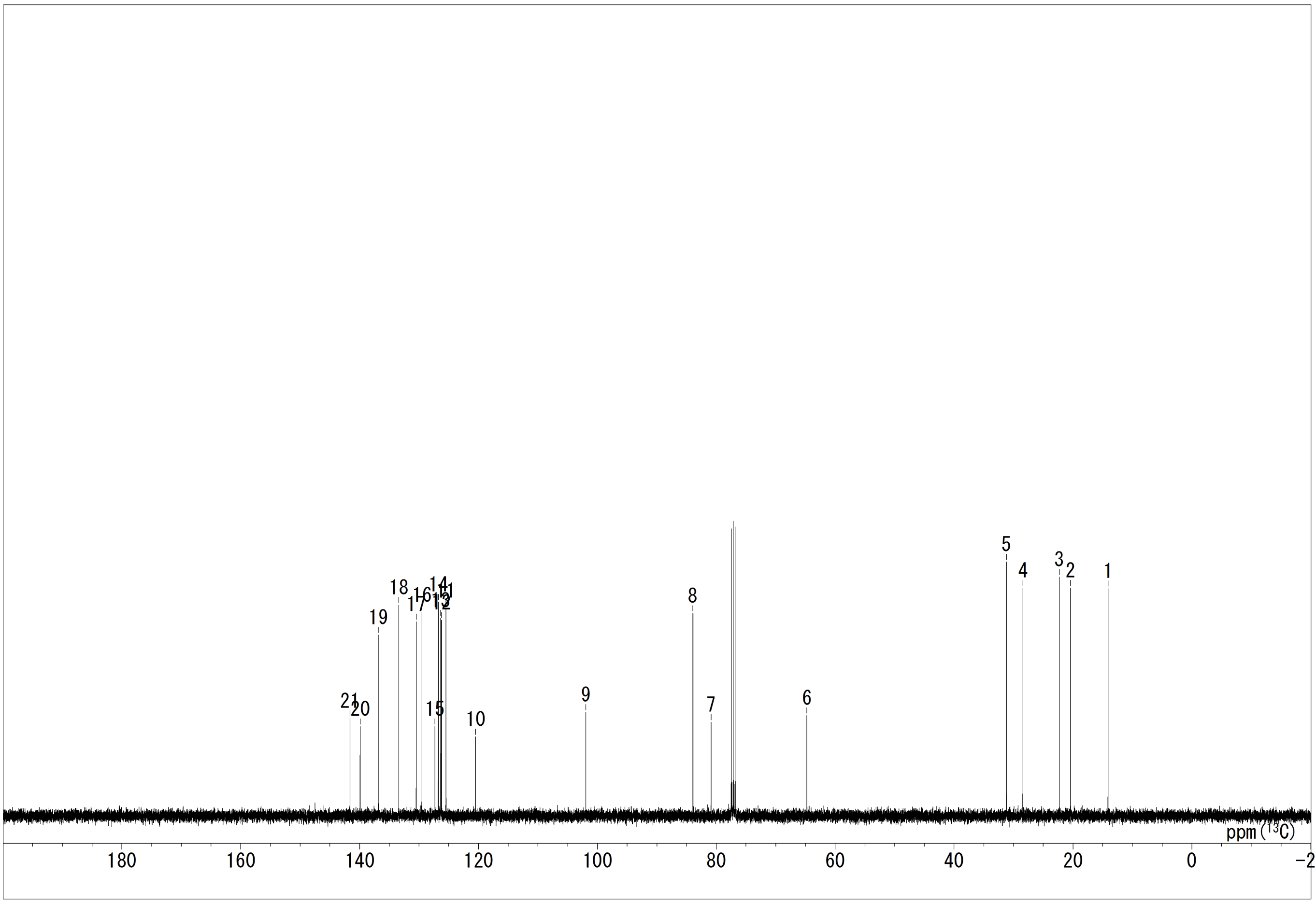
n-C5H11
S
S
n-C5H11
1.0598
2.0456
1.0416
0.9919
1.9701
1.0377
4.0929
4.0112
8.1483
6.0
ppm(¹H)
8
7
6
5
4
3
2
1
0

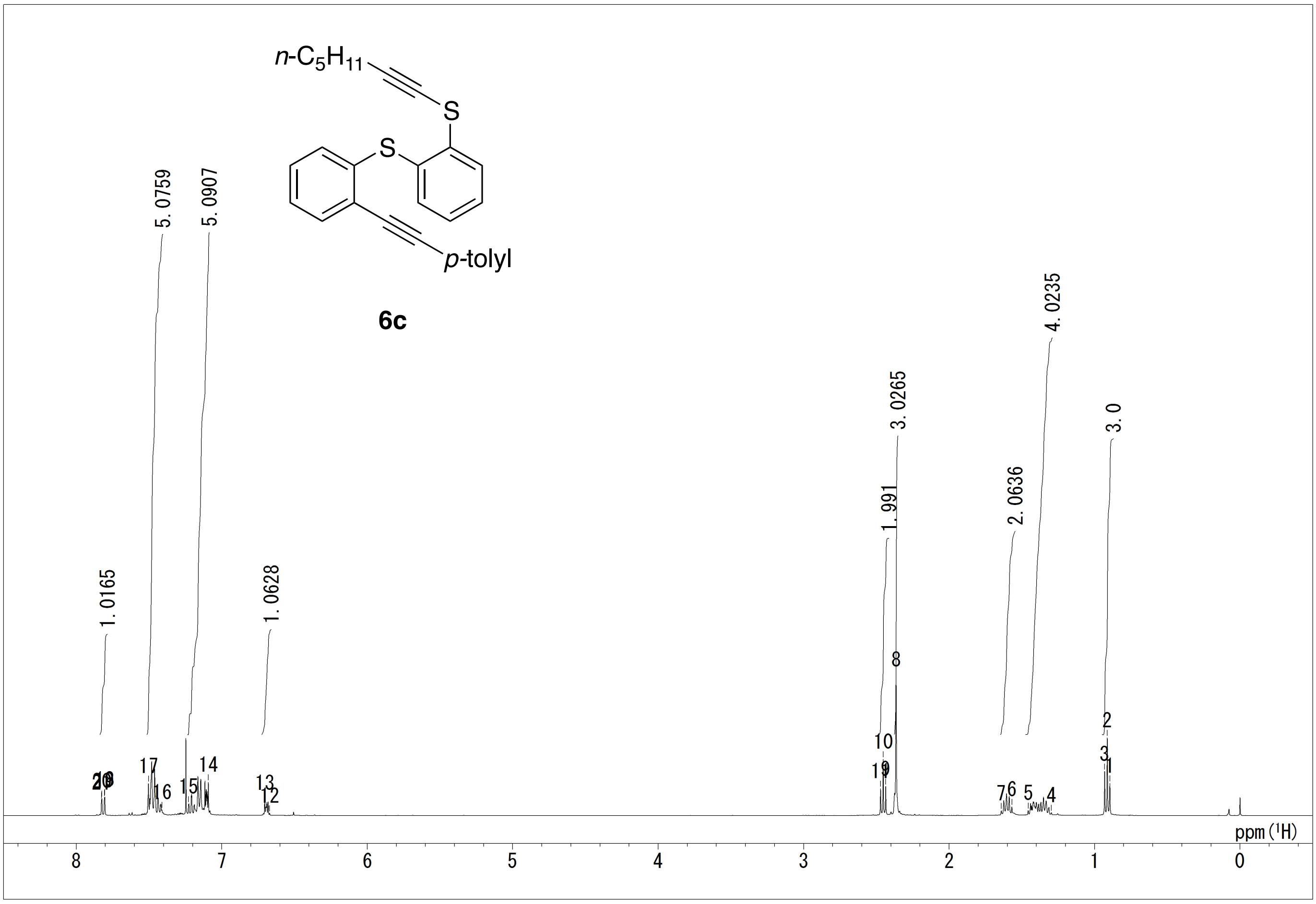
6a



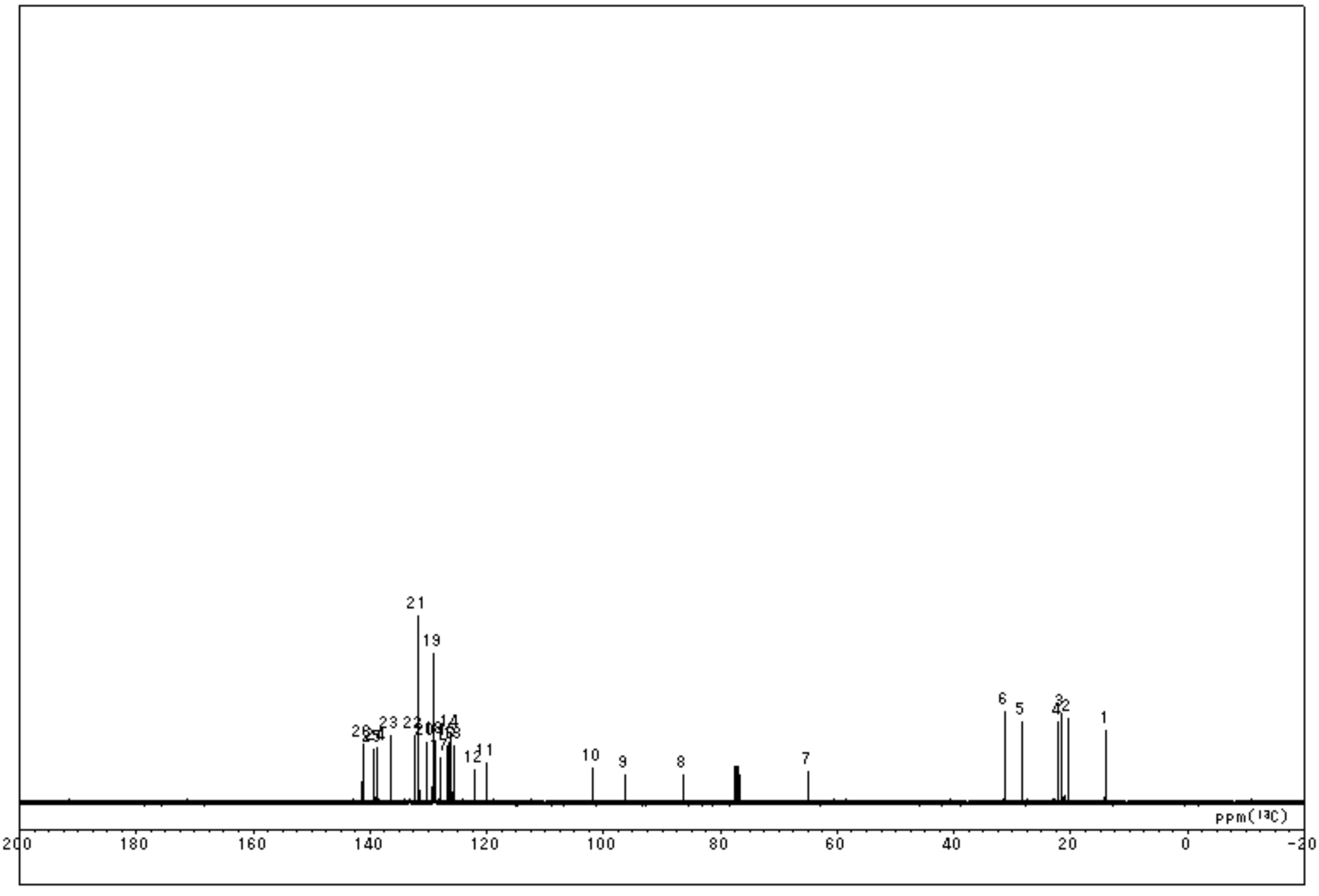
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm(¹³C)
200
180
160
140
120
100
80
60
40
20
0
-20


n-C5H11
S
S
Ph
0.9711
8.1901
1.0343
2.0346
1.0284
2.0
2.0549
4.041
3.0156
ppm (1H)
8
7
6
5
4
3
2
1
0

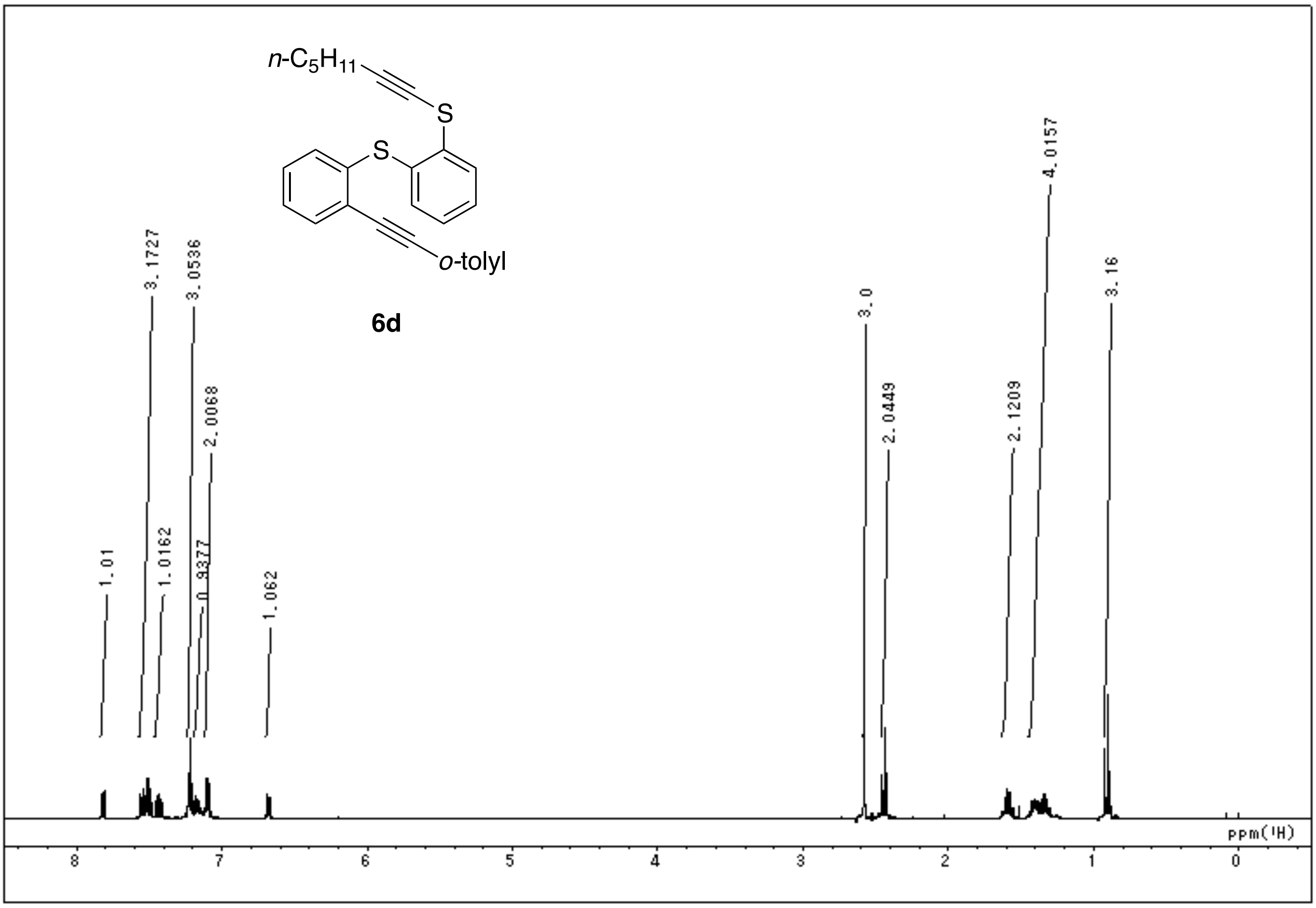

21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (13C)
180
160
140
120
100
80
60
40
20
0
−20


6c

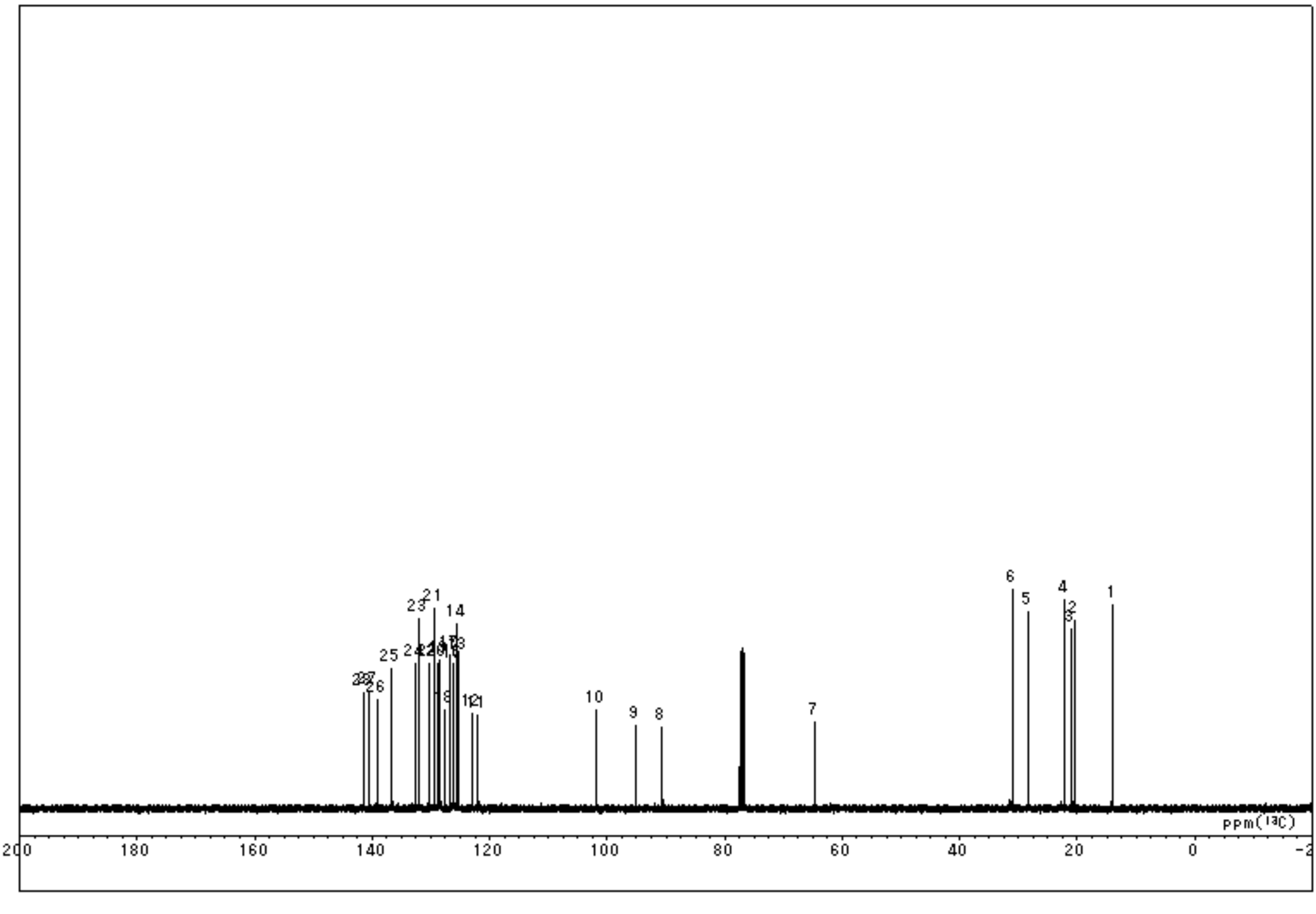
n-C5H11
S
S
p-tolyl
1.0165
5.0759
5.0907
1.0628
1.991
3.0265
2.0636
4.0235
3.0
20
17
16
15
14
13
12
10
19
8
7
6
5
4
3
2
1
ppm (1H)
8
7
6
5
4
3
2
1
0

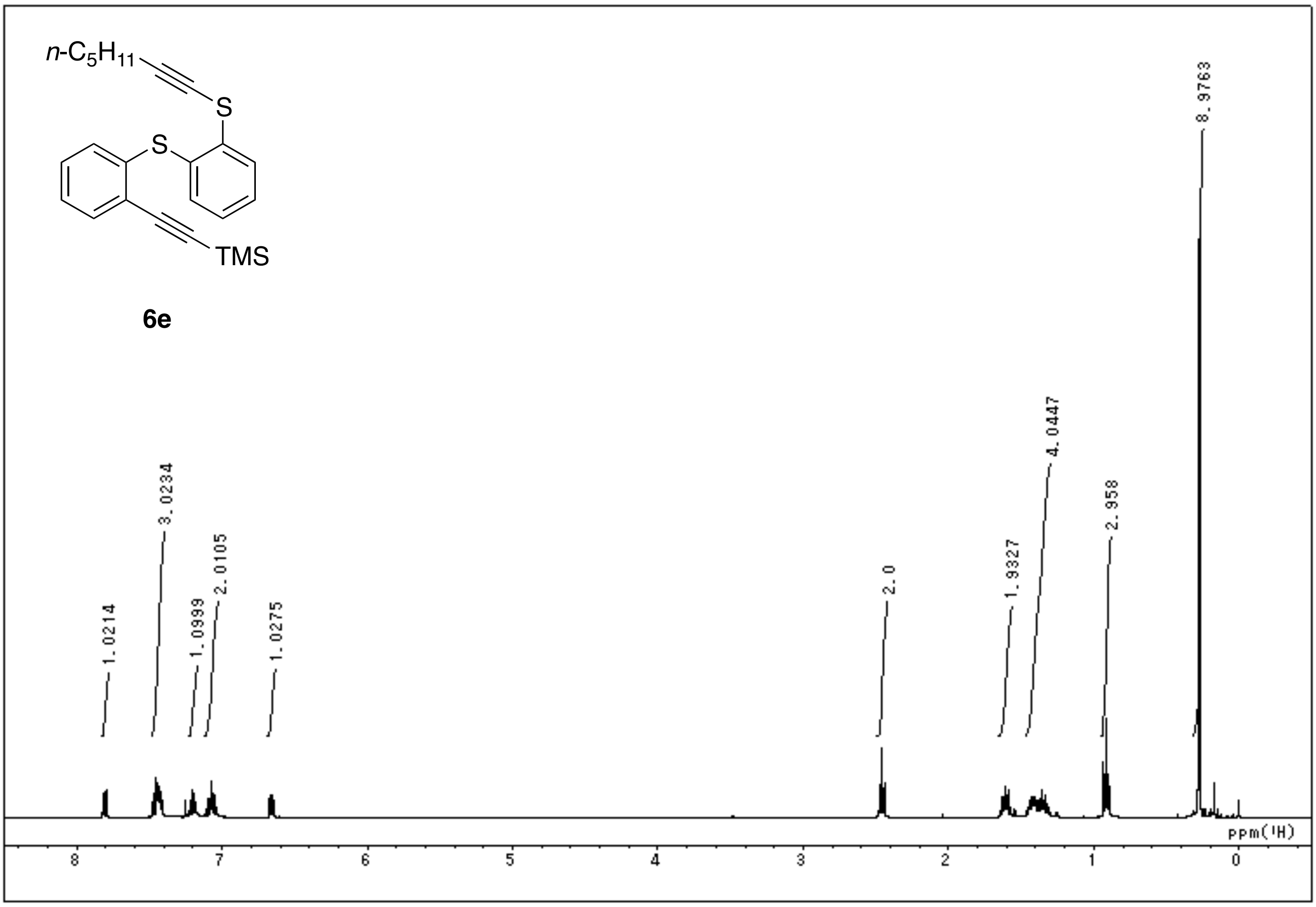


21
19
22
23
28
12
11
10
9
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
-20

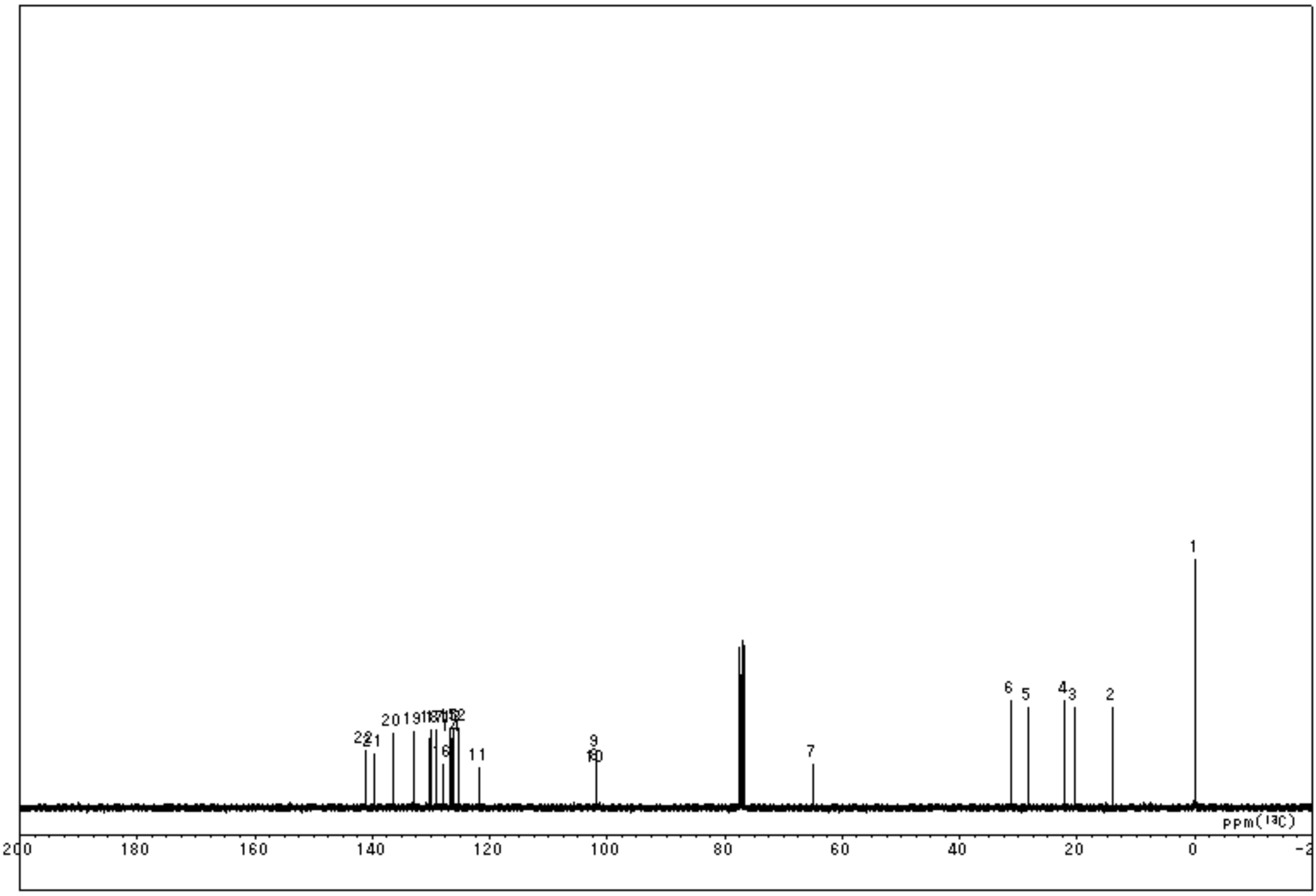

n-C5H11
S
S
o-tolyl
1.01
3.1727
1.0162
3.0536
0.9377
2.0068
1.062
3.0
2.0449
2.1209
4.0157
3.16
ppm (1H)
8
7
6
5
4
3
2
1
0

6d

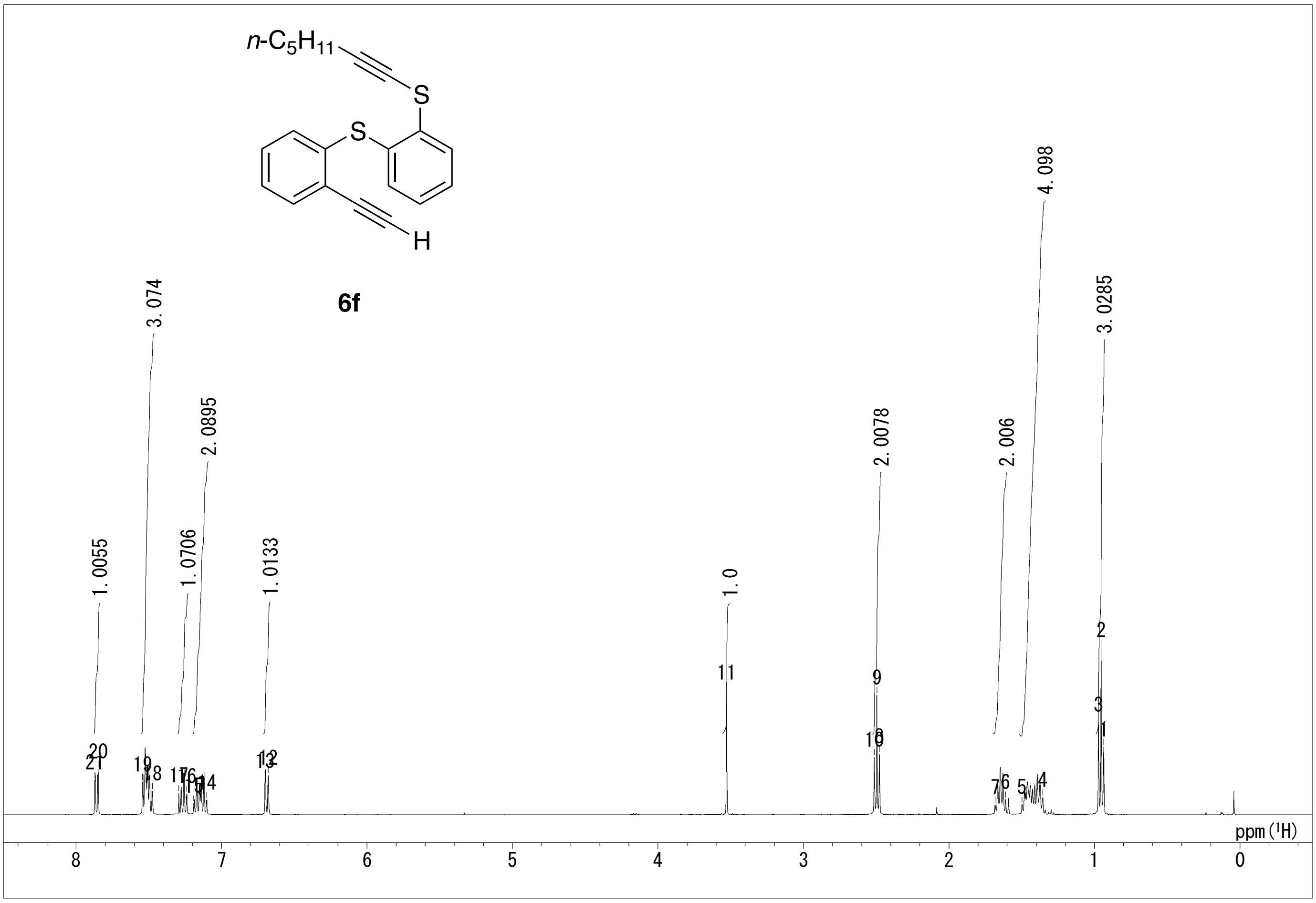

28
27
26
25
24
23
22
21
20
19
18
17
16
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
-20

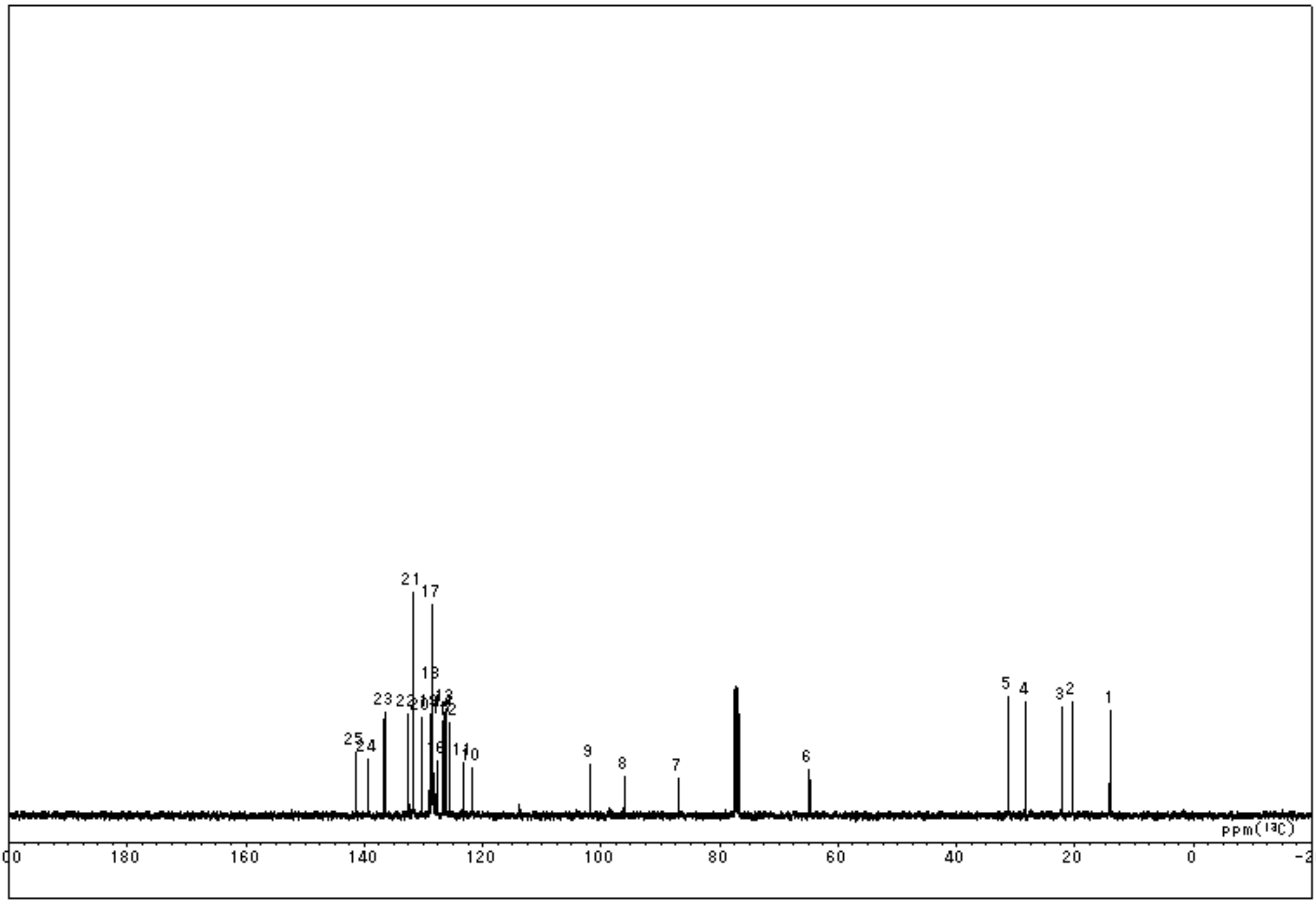

6e

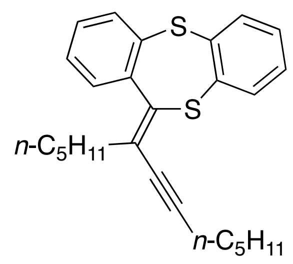
n-C5H11
S
S
TMS
1.0214
3.0234
1.0999
2.0105
1.0275
2.0
1.9327
4.0447
2.958
8.9763
ppm(1H)
8
7
6
5
4
3
2
1
0



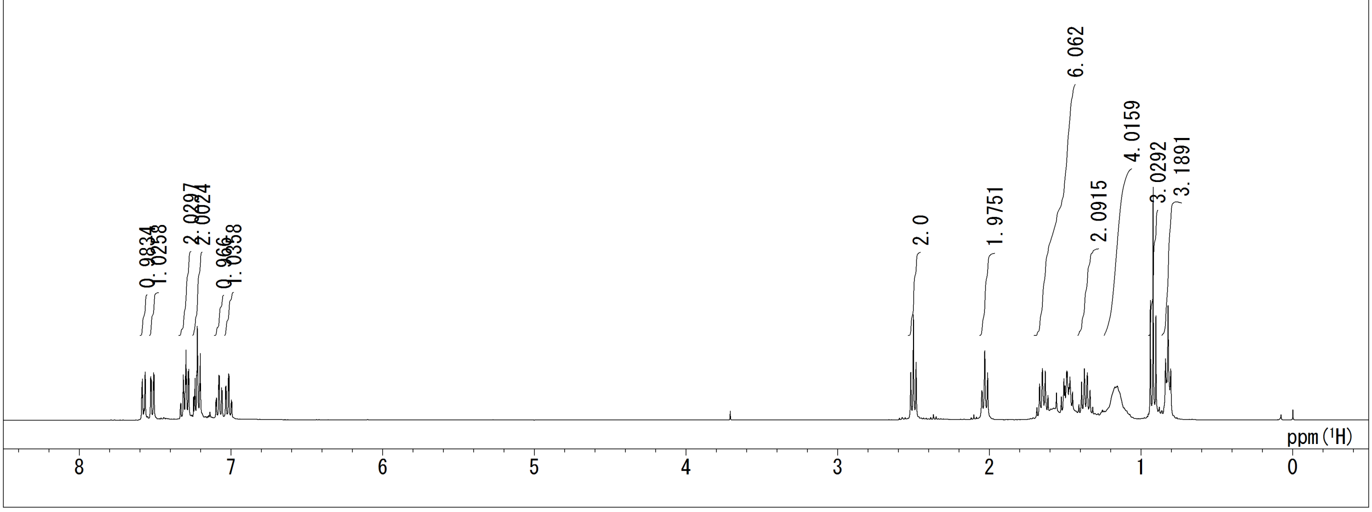
1
2
3
4
5
6
7
9
10
11
16
21
22
20
19
18
17
15
12
ppm(13C)
200
180
160
140
120
100
80
60
40
20
0
-20

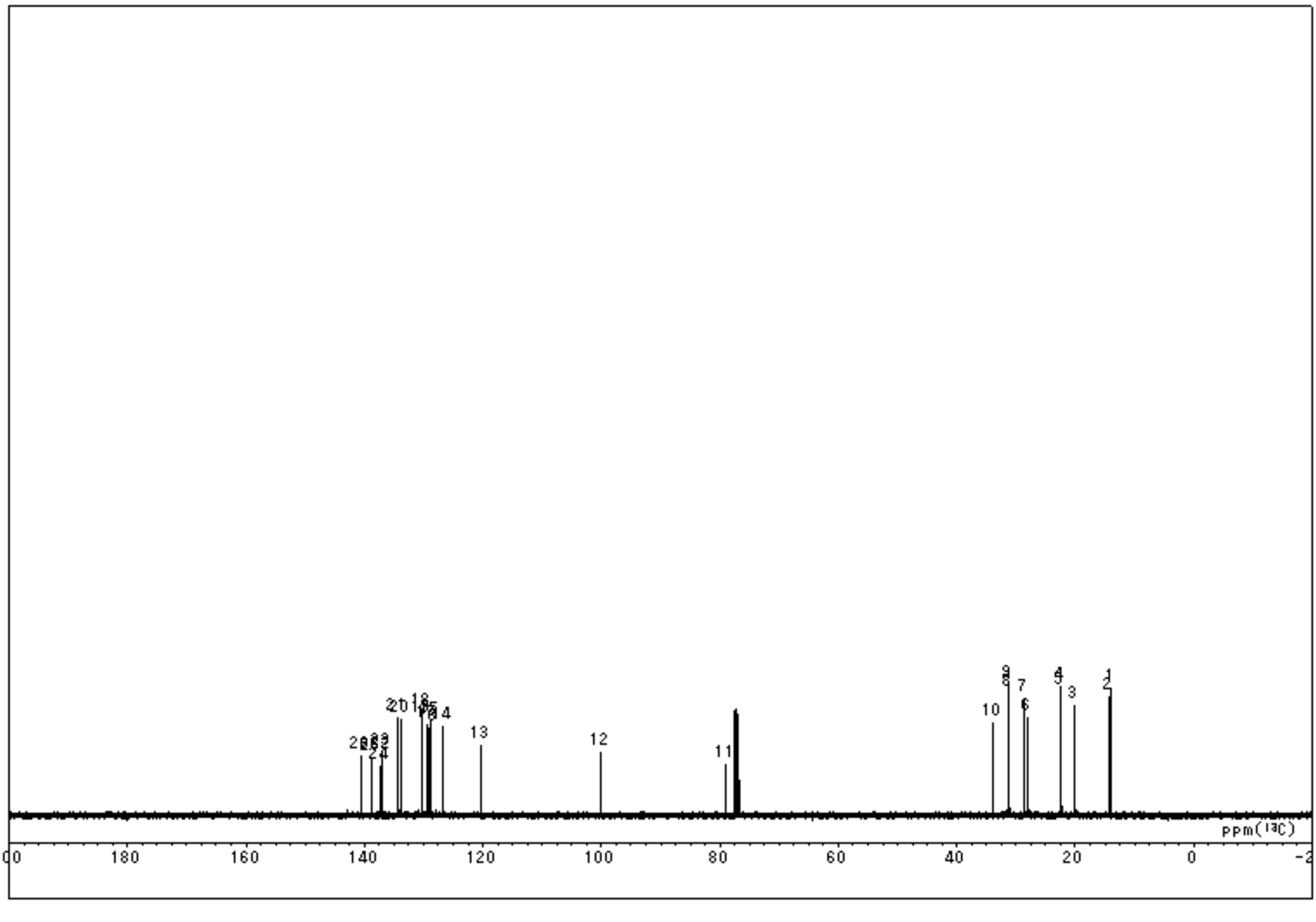

n-C_5H_{11}
S
S
H
6f
1.0055
3.074
1.0706
2.0895
1.0133
1.0
2.0078
2.006
4.098
3.0285
ppm (¹H)
8
7
6
5
4
3
2
1
0

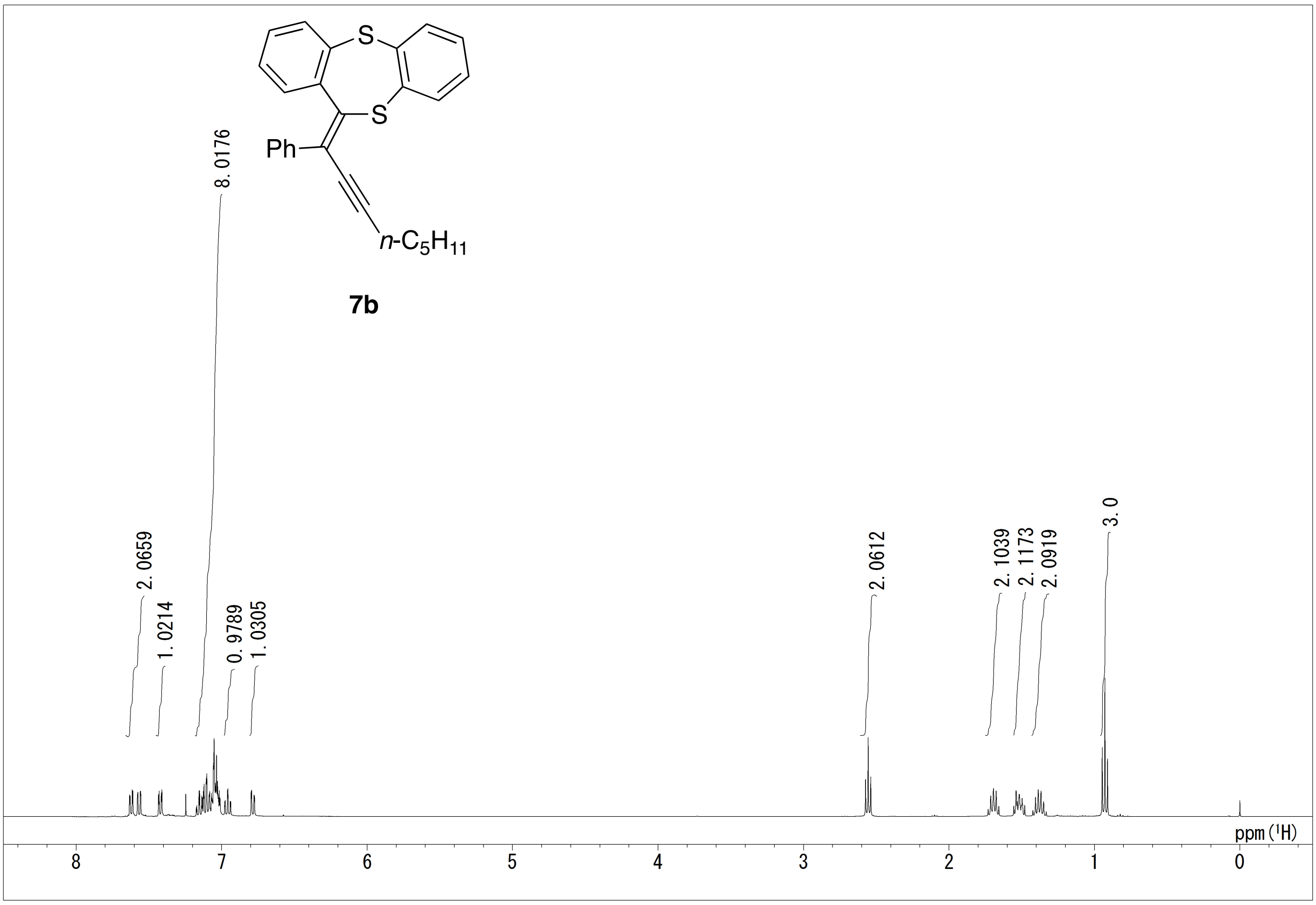

ppm (¹³C)
200
180
160
140
120
100
80
60
40
20
0
-20

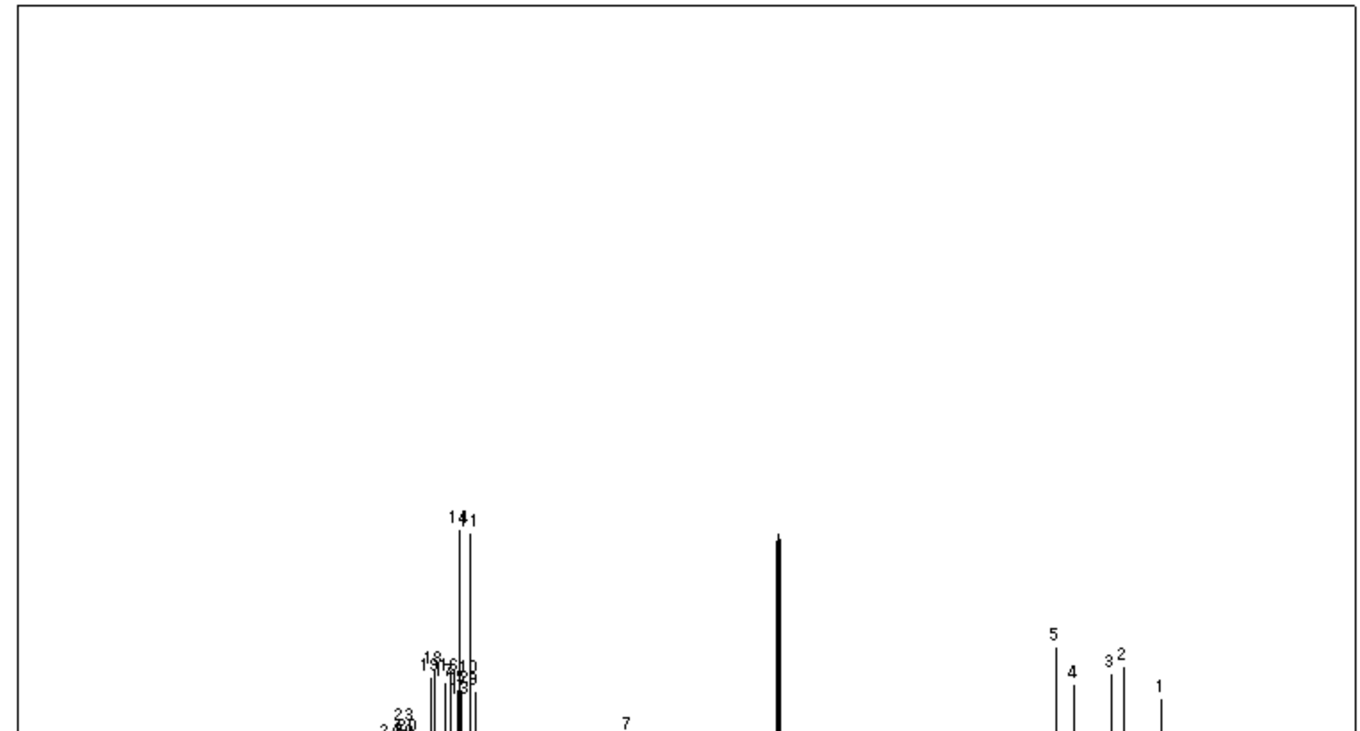

S
S
n-C5H11
n-C5H11

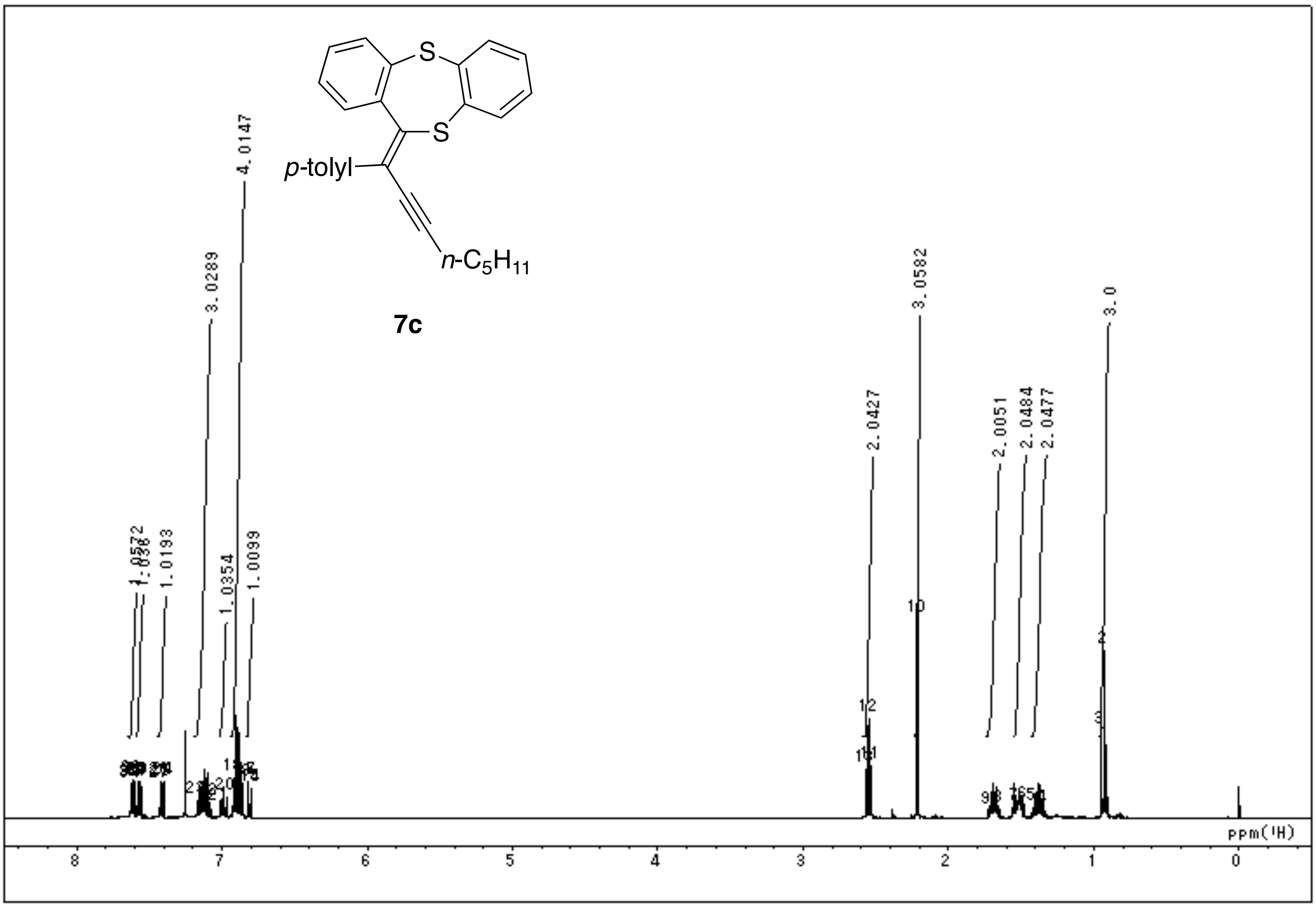
7a

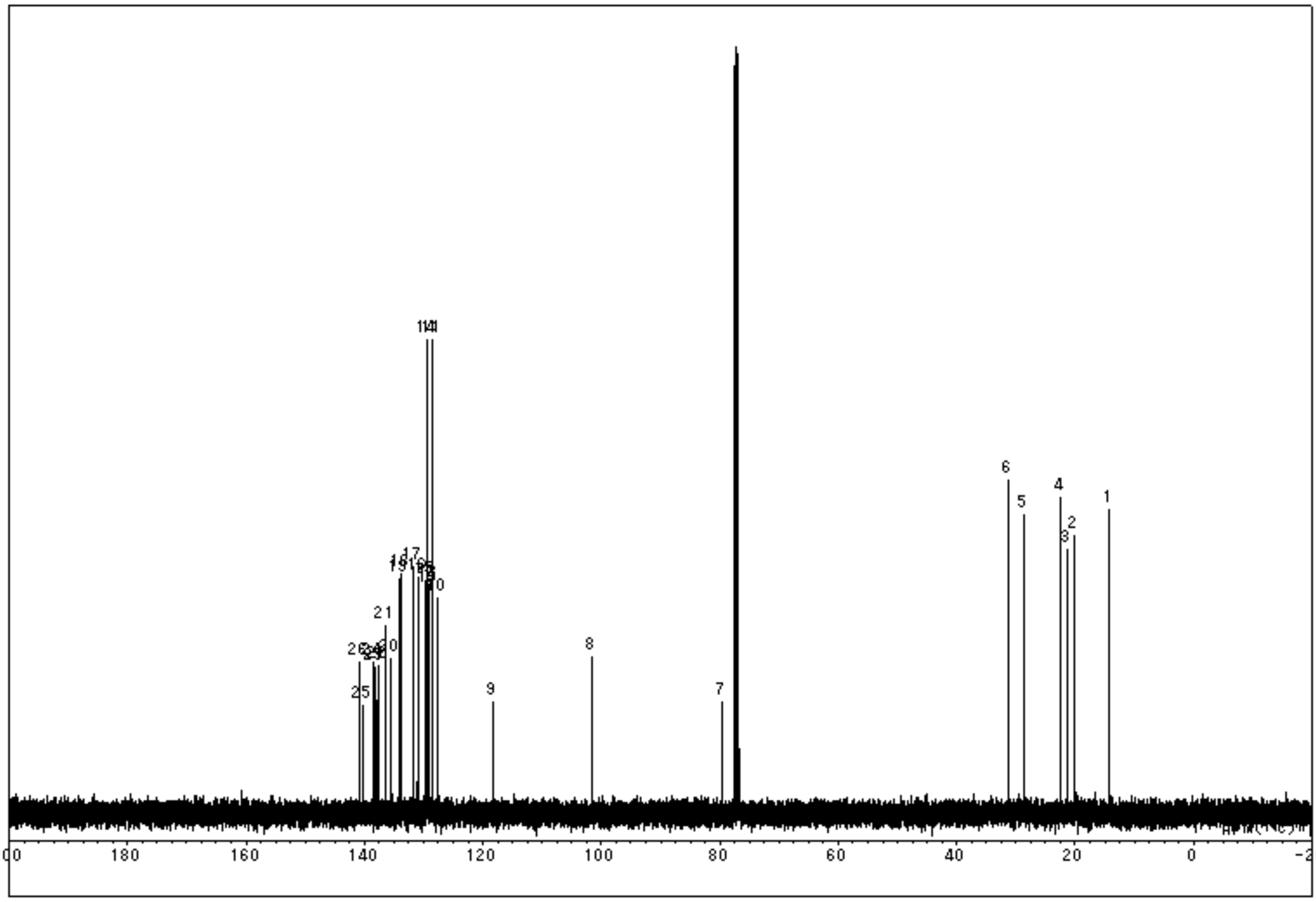

0.9834
1.0258
2.0297
2.0024
0.966
1.0358
2.0
1.9751
6.062
2.0915
4.0159
3.0292
3.1891
ppm (1H)
8
7
6
5
4
3
2
1
0

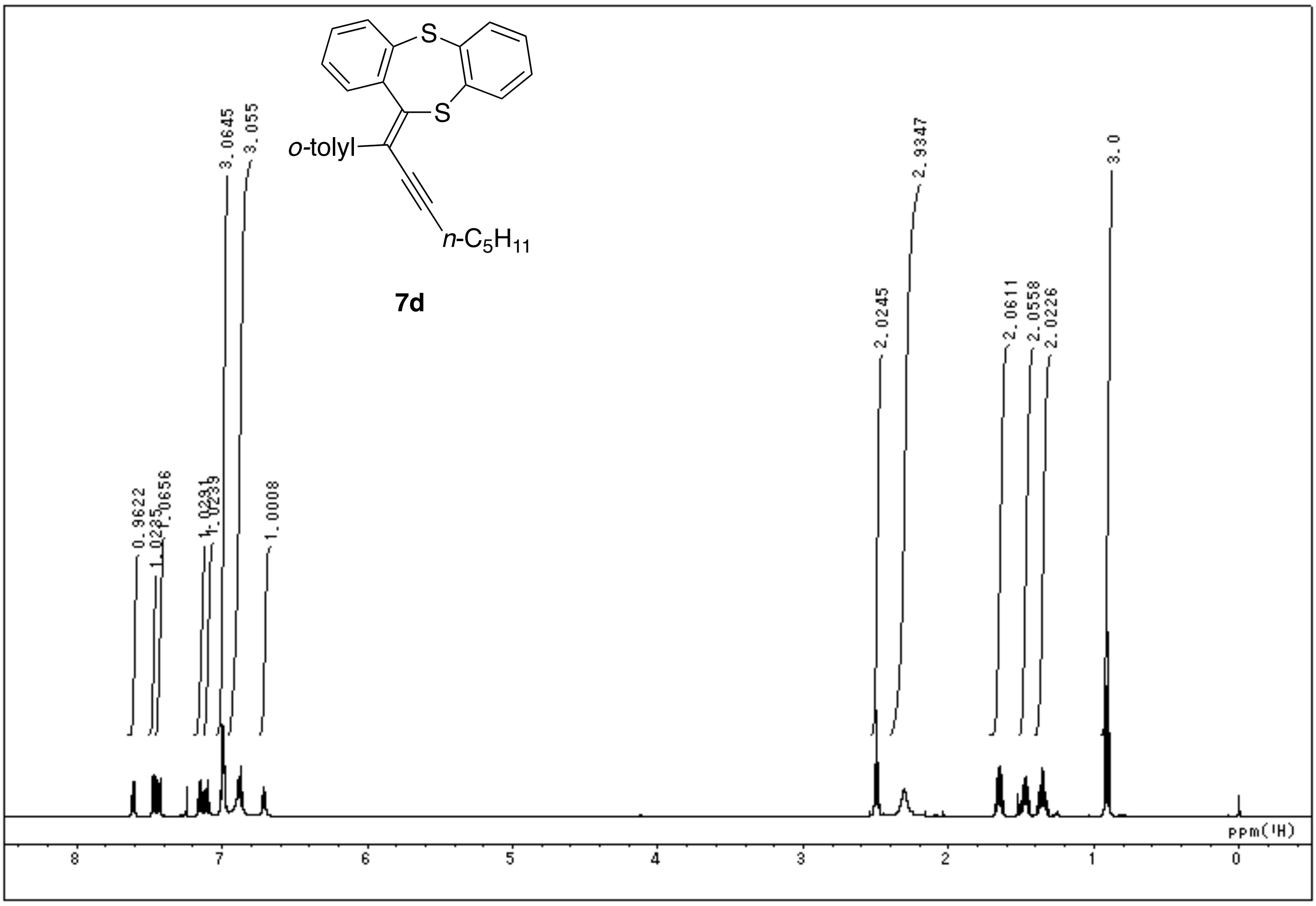

22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
-20


S
S
Ph
n-C5H11
7b
2.0659
1.0214
8.0176
0.9789
1.0305
2.0612
2.1039
2.1173
2.0919
3.0
ppm (1H)
8
7
6
5
4
3
2
1
0


25
24
23
20
19
18
17
16
10
12
13
9
14
11
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
-20

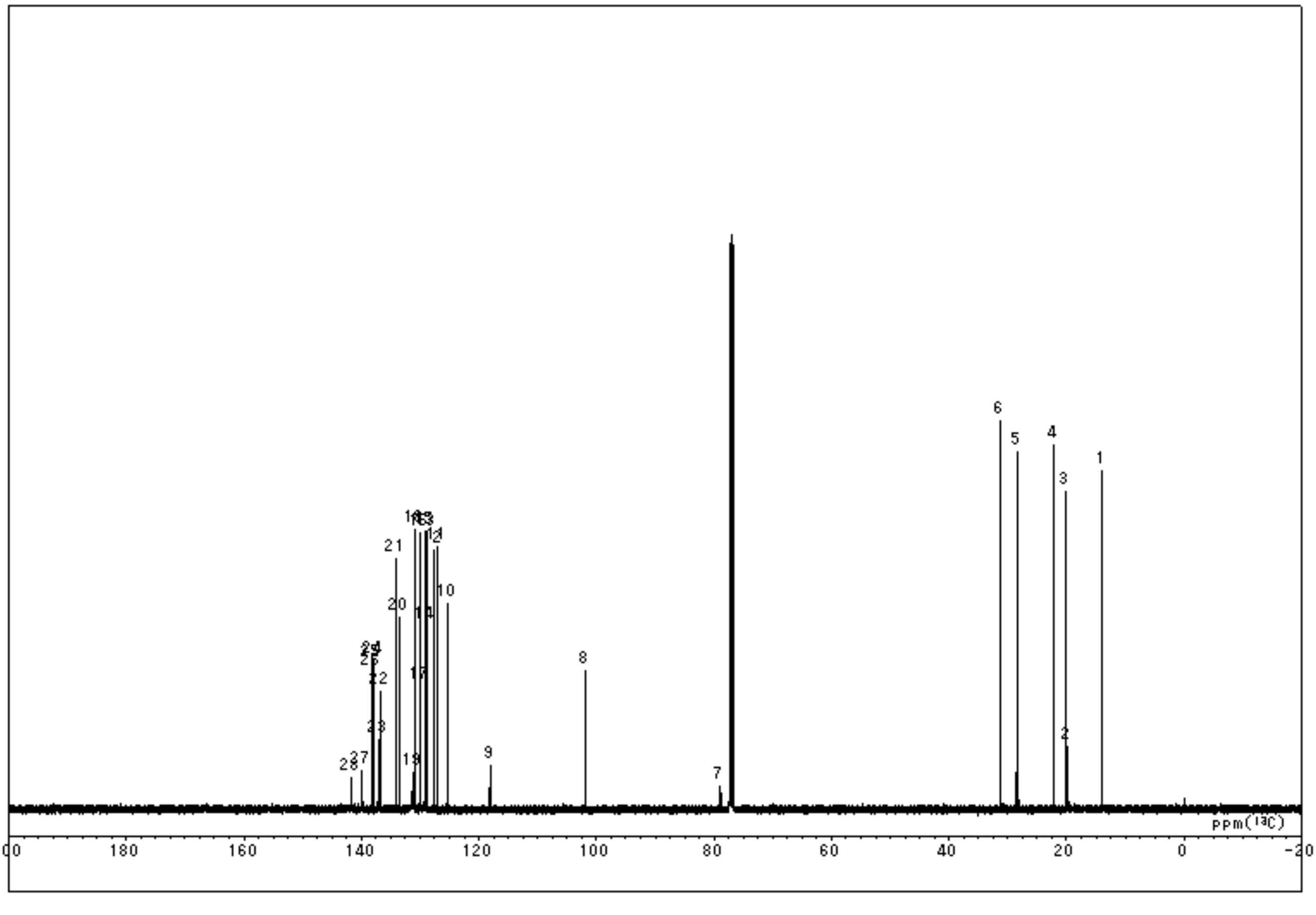

S
S
p-tolyl
n-C5H11
7c
1.0572
1.036
1.0193
3.0289
4.0147
1.0354
1.0099
2.0427
3.0582
2.0051
2.0484
2.0477
3.0
ppm(1H)
8
7
6
5
4
3
2
1
0


1
2
3
4
5
6
7
8
9
25
21
200
180
160
140
120
100
80
60
40
20
0
-20

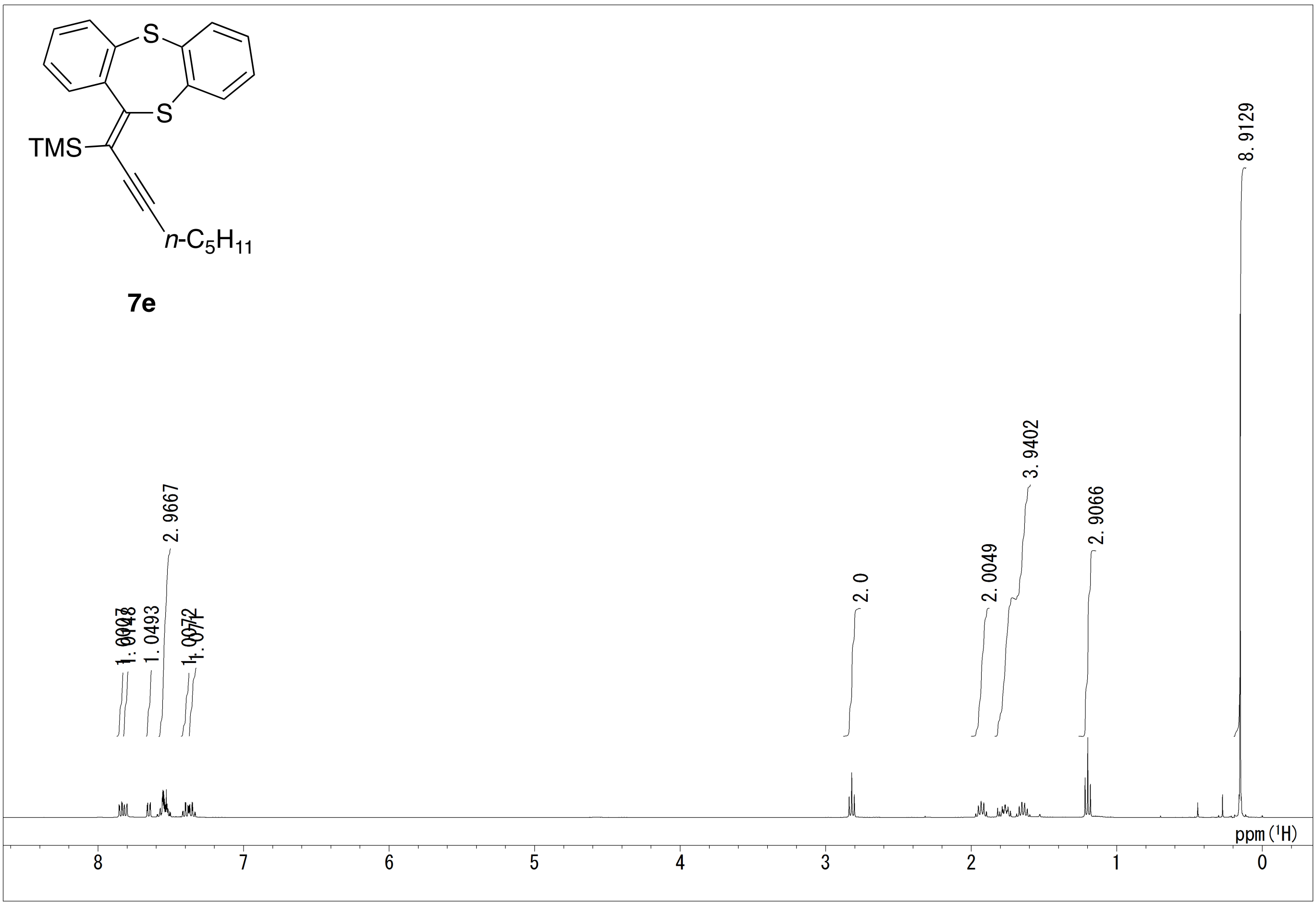


7d

S
S
o-tolyl
n-C5H11
0.9622
1.0285
1.0656
1.0231
1.0239
3.0645
3.055
1.0008
2.0245
2.9347
2.0611
2.0558
2.0226
3.0
ppm(1H)
8
7
6
5
4
3
2
1
0

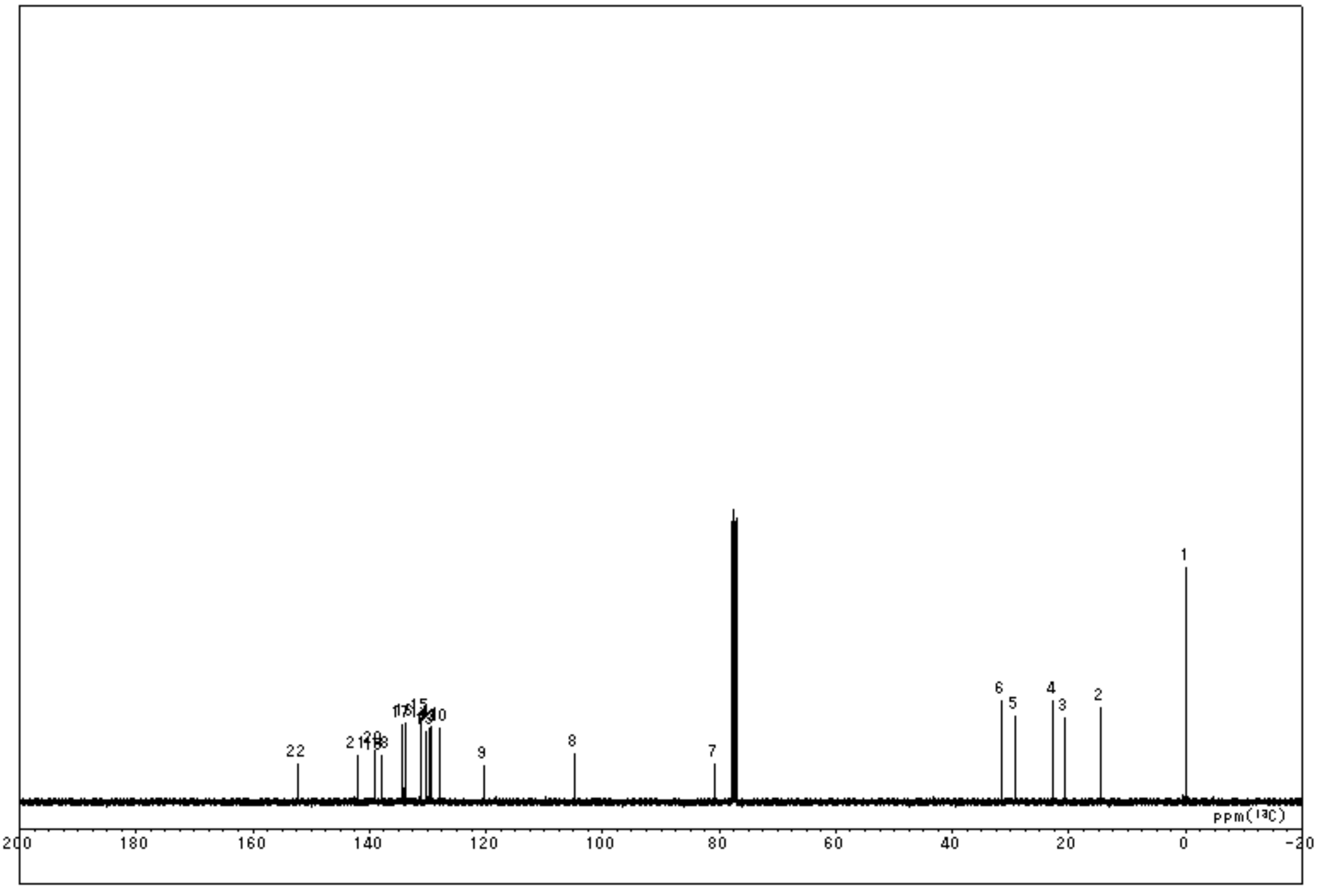


6
5
4
1
3
2
8
9
7
10
21
20
22
23
24
25
26
27
28
19
17
11
12
13
16
18
ppm(13C)
200
180
160
140
120
100
80
60
40
20
0
-20



S
S
TMS
n-C_5H_{11}
2.9667
1.0493
1.0072
2.0
2.0049
3.9402
2.9066
8.9129
ppm (^{1}H)
8
7
6
5
4
3
2
1
0

7e



22
21
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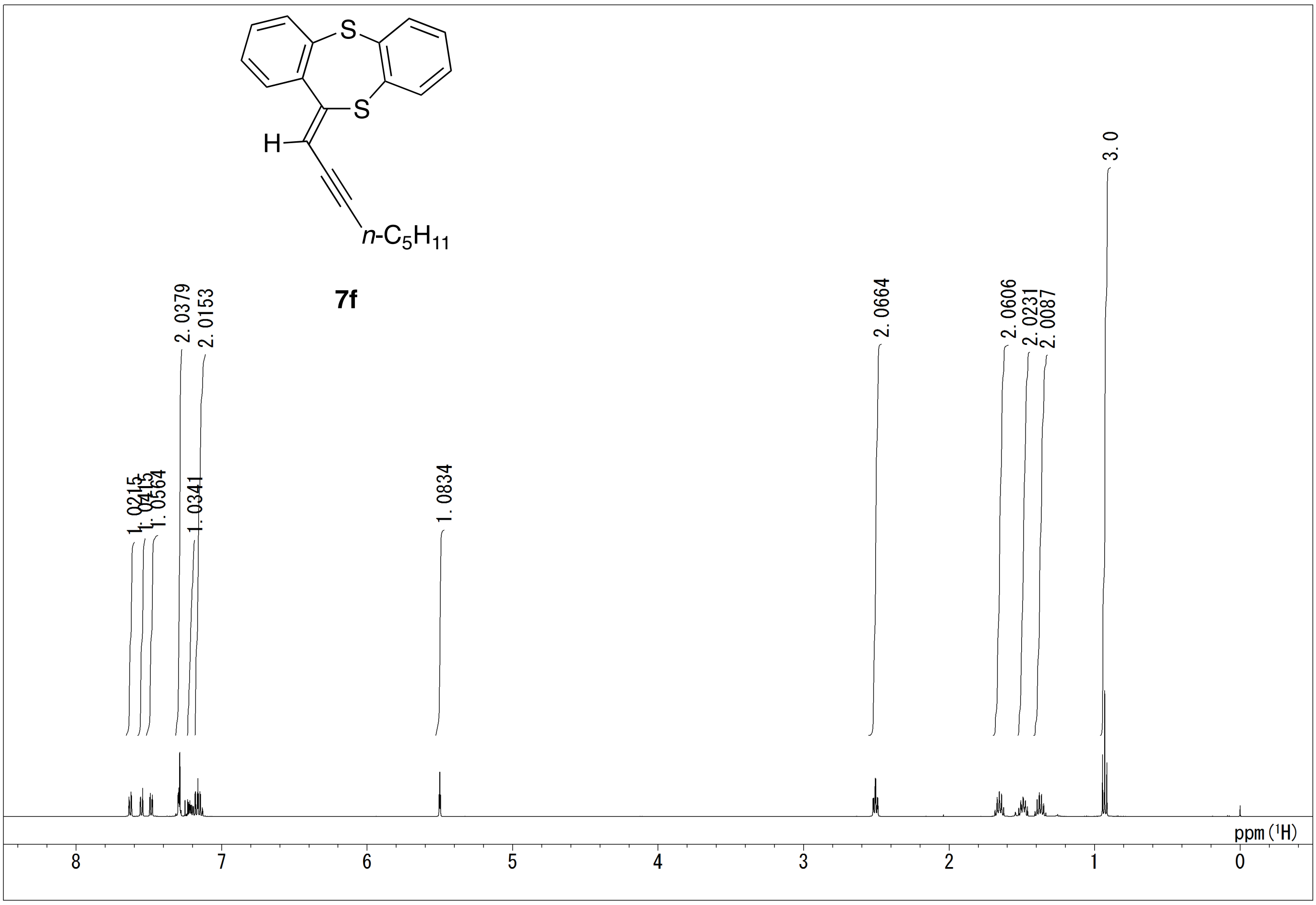
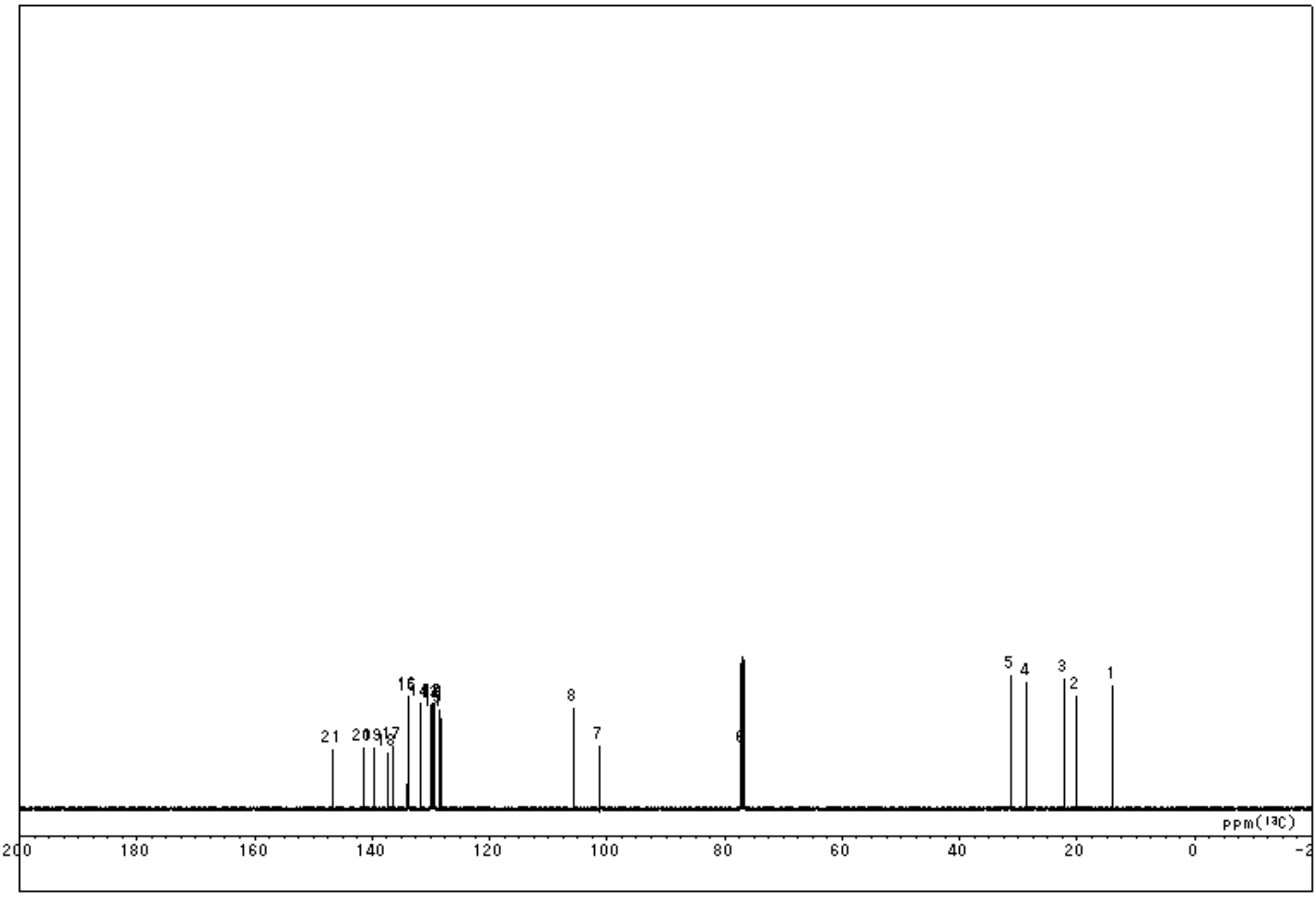
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (^{13}C)
200
180
160
140
120
100
80
60
40
20
0
-20



S
S
H
n-C5H11
1.0215
1.0415
1.0564
2.0379
1.0341
2.0153
1.0834
2.0664
2.0606
2.0231
2.0087
3.0
ppm (1H)
8
7
6
5
4
3
2
1
0

7f



21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm (13C)
200
180
160
140
120
100
80
60
40
20
0
-20

vi) Copies of ^{1}H NMR and ^{31}P NMR spectra for complex A