Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Alkali-Amide-Catalyzed Divergent sp^2 and sp^3 C–H Alkylation of Alkylthiophenes with Alkenes

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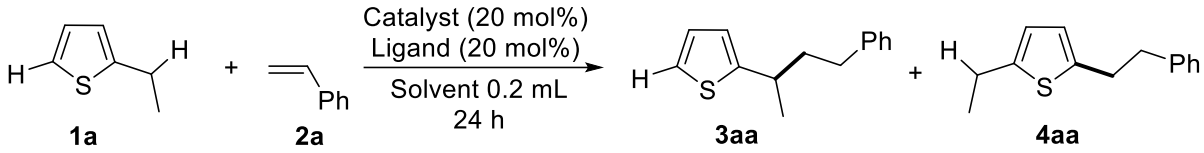
Table of Contents

1. General Information

All manipulations of air- and moisture-sensitive compounds were performed under an argon atmosphere by use of standard Schlenk techniques or a nitrogen atmosphere in a Mikrouna glovebox. THF, Et_2O, TBME and benzene were dried by distillation over sodium/benzophenone. THF-d^8, benzene-d^6, TMEDA, 18-crown-6, 12-crown-4, most thiophene and olefins purchased from innochem, J&K and TCI were dried over CaH_2, degassed and kept in a glovebox prior to use. $Li[N(SiMe_3)_2]$ (1.0 M in THF), $LiCH_2SiMe_3$ (0.55 M in hexane) and lithium diisopropylamide (LDA) (2.0 M solution in THF/ hexane) were purchased from J&K. After a process for removing the solvents in vacuum, the metal amides were kept as solids under -30 ℃ in a glove box. NaDA[1], KDA[1], thiophene derivatives[2], 5-D-2-butylthiophene[3] (**1c-D**), 2-(butyl-1,1-D_2)thiophene[4] (**1c-D'**) and 2-butylthiophene lithium (**1c-Li**)[3] were prepared according to procedures described in the literatures. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max}= 254 nm). Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AV 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C) instrument in $CDCl_3$ with tetramethylsilane as an internal standard. Data were reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. High resolution mass spectra (HRMS) were recorded on an Agilent GCQTOF 7200 GC/MS with Electron Ionization (EI) resource.

2. Optimization of Reaction Conditions

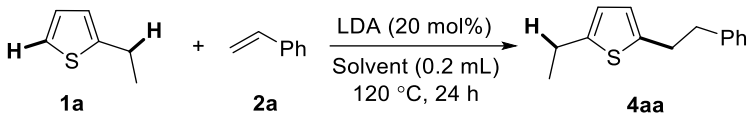
Table S1. Optimization of reaction conditions[a]



Entry	Catalyst	T (ºC)	Solvent	Additive	Yield (%)[b] **3aa**/**4aa**	Ratio **3aa** / **4aa**[c]
1	LiHMDS	120	TMEDA	-	0/0	0/0
2	NaHMDS	120	TMEDA	-	0/0	0/0
3	KHMDS	120	TMEDA	-	5/0	4.4/1
4	LDA	120	TMEDA	-	0/31	1/22
5	NaDA	120	TMEDA	-	0/0	0/0
6	KDA	120	TMEDA	-	0/0	0/0
7	$LiCH_2TMS$	120	TMEDA	-	0/30	1/22
8	KHMDS	120	TMEDA	18-crown-6	32/0	> 20/1
9	KHMDS	80	TMEDA	18-crown-6	46/0	> 20/1
10	KHMDS	30	TMEDA	18-crown-6	64/0	> 20/1
11[d]	KHMDS	30	TMEDA	18-crown-6	26/0	> 20/1
12[d]	KHMDS	30	THF	18-crown-6	48/0	> 20/1
13[d]	KHMDS	30	Et_2O	18-crown-6	60/0	> 20/1
14[d]	KHMDS	30	TBME	18-crown-6	60/0	> 20/1
15[d]	KHMDS	30	Benzene	18-crown-6	35/0	> 20/1
16[e]	KHMDS	30	TBME	18-crown-6	86(80)/0	> 20/1
17	LDA	100	TMEDA	-	0/44	1/28
18	LDA	90	TMEDA	-	0/49	1/29
19	LDA	80	TMEDA	-	0/50	1/39
20	LDA	75	TMEDA	-	0/63	1/35
21	LDA	70	TMEDA	-	0/60	1/33
22	LDA	65	TMEDA	-	0/40	1/27
23[f]	LDA	75	TMEDA	-	0/85(80)	< 1/20

[a]Conditions: 2-ethylthiophene (**1a**) (1.0 mmol), styrene (**2a**) (0.5 mmol), catalyst (20 mol%), solvent (0.2 mL), 24 h. [b]NMR yields based on styrene with 2-methoxynaphthalene as an internal standard. [c]Determined by GC analysis. [d]KHMDS (10 mol%), 18-crown-6 (10 mol%), solvent (0.5 mL); [e]2-ethylthiophene (**1a**) (2.0 mmol), styrene (**2a**) (0.5 mmol), KHMDS (10 mol%), 18-crown-6 (15 mol%), TBME (0.5 mL), 36 h, isolated yield in parentheses. [f]2-ethylthiophene (**1a**) (0.5 mmol), styrene (**2a**) (2.0 mmol), LDA (20 mol%), TMEDA (0.3 mL), 36 h, isolated yield in parentheses.

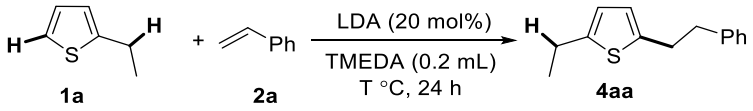
Table S2. Screening of solvents for LDA catalyzed 2-ethylthiophene sp^2 C-H alkylation reaction[a]



Entry	Solvent	Additive	**4aa** Yield (%)[b]
1	THF	-	21
2	Benzene	-	0
3	PMDTA	-	0
4	TMEDA	12-crown-4	0
5	TMEDA	-	31
6	-	-	0

[a]Conditions: 2-ethylthiophene (**1a**) (1.0 mmol), styrene (**2a**) (0.5 mmol), LDA (20 mol%), solvent (0.2 mL), 120 °C, 24 h. [b]NMR yields based on styrene with 2-methoxynaphthalene as an internal standard.

Table S3. Screening of temperature and ratio for LDA catalyzed 2-ethylthiophene sp^2 C-H alkylation reaction[a]



Entry	T (ºC)	Ratio (**1a**: **2a**)	**4aa** Yield (%)[b]
1	100	2: 1	44
2	90	2: 1	49
3	80	2: 1	50
4	75	2: 1	63
5	70	2: 1	60
6	65	2: 1	40
7	75	1: 1	54
8	75	1: 2	76
9	75	1: 3	79
10[c]	75	1: 3	81
11[c]	75	1: 4	82
12[c,d]	**75**	**1: 4**	**85(80)**

[a]Conditions: 2-ethylthiophene (**1a**) (0.5 mmol), LDA (20 mol%), TMEDA (0.2 mL), 24 h. [b]NMR yields based on styrene with 2-methoxynaphthale-ne as an internal standard, isolated yields in parentheses. [c]0.3 mL TMEDA. [d]36 h.

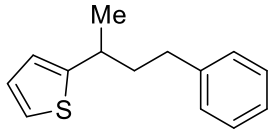
3. General Procedure and Analytical Data for Compounds 3 and 4

Typical procedure for KHMDS catalyzed benzylic sp^3 C-H Bond alkylation of alkylthiophene:

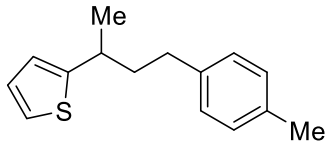
To a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added 2-ethylthiophene **1a** (2.0 mmol, 224.4 mg), 4-methylstyrene **2b** (0.5 mmol, 59.1 mg), KHMDS (10.0 mg, 0.05 mmol), 18-crown-6 (0.075 mmol, 19.8 mg), TBME (0.5 mL). The mixture was heated at 40 ℃ for 48 h and cooled to room temperature. The direct purification by silica gel column chromatography (hexane) afforded compound **3ab** as a colorless oil (81.1 mg, 70 %).

Typical procedure for LDA catalyzed sp^2 C-H bond alkylation of alkylthiophene:

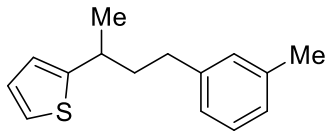
To a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added 2-ethylthiophene **1a** (0.5 mmol, 56.1 mg), 4-methylstyrene **2b** (2.0 mmol, 236.4 mg), LDA (11.3 mg, 0.10 mmol), TMEDA (0.30 mL). The mixture was heated at 80 ℃ for 60 h and cooled to room temperature. The direct purification by silica gel column chromatography (hexane) afforded compound **4ab** as a colorless oil (87.8 mg, 76% yield).



2-(4-phenylbutan-2-yl) thiophene (3aa).[5] Colorless oil, 86.0 mg (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 2H), 7.20-7.09 (m, 4H), 6.96-6.89 (m, 1H), 6.80 (d, *J* = 3.2 Hz, 1H), 3.11-3.00 (m, 1H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.01-1.87 (m, 2H), 1.34 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.69, 142.34, 128.54, 128.45, 126.59, 125.87, 122.93, 122.66, 41.13, 35.04, 33.75, 23.53.

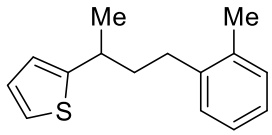


2-(4-(*p*-tolyl)butan-2-yl)thiophene (3ab). Colorless oil, 81.1 mg (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.13 (m, 1H), 7.10-7.04 (m, 4H), 6.96-6.90 (m, 1H), 6.85-6.79 (m, 1H), 3.09-3.01 (m, 1H), 2.55 (t, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 1.97-1.88 (m, 2H), 1.34 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 151.80, 139.25, 135.29, 129.14, 128.42, 126.58, 122.91, 122.63, 41.25, 35.01, 33.28, 23.54, 21.14. HRMS (EI, m/z): Calcd. for $C_{15}H_{18}S$ $[M]^+$ 230.1129, found 230.1125.

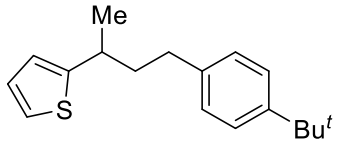


2-(4-(*m*-tolyl)butan-2-yl)thiophene (3ac). Colorless oil, 103.5 mg (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.16 (m, 2H), 7.07-6.97 (m, 4H), 6.91-6.83 (m, 1H), 3.16-3.06 (m, 1H), 2.61 (t, *J* = 8.0

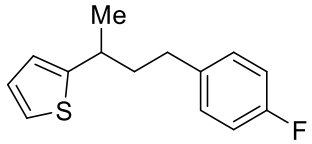
Hz, 2H), 2.37 (s, 3H), 2.04-1.92(m, 2H), 1.41 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.78, 142.30, 137.97, 129.36, 128.35, 126.61, 126.58, 125.55, 122.91, 122.64, 41.18, 35.10, 33.70, 23.53, 21.54. HRMS (EI, m/z): Calcd. for $C_{15}H_{18}S$ $[M]^+$ 230.1129, found 230.1124.



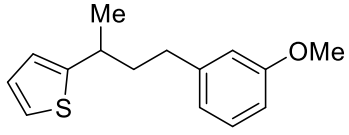
2-(4-(*o*-tolyl)butan-2-yl)thiophene (3ad). Colorless oil, 88.1 mg (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.04 (m, 5H), 7.01-6.95 (m, 1H), 6.91-6.84 (m, 1H), 3.21-3.10 (m, 1H), 2.62 (t, J = 8.0 Hz, 2H), 2.29 (s, 3H), 2.00-1.88 (m, 2H), 1.43 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.70, 140.59, 135.97, 130.30, 128.91, 126.59, 126.05, 126.01, 122.94, 122.68, 39.96, 35.59, 31.26, 23.54, 19.32. HRMS (EI, m/z): Calcd. for $C_{15}H_{18}S$ $[M]^+$ 230.1129, found 230.1123.



2-(4-(4-(tert-butyl)phenyl)butan-2-yl)thiophene (3ae). Colorless oil, 92.9 mg (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.18-7.15 (m, 1H), 7.14 - 7.10 (m, 2H), 6.98-6.91 (m, 1H), 6.88-6.81 (m, 1H), 3.14-3.05 (m, 1H), 2.59 (t, J = 8.0 Hz, 2H), 2.02-1.92 (m, 2H), 1.38-1.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.81, 148.61, 139.25, 128.17, 126.57, 125.33, 122.90, 122.63, 41.09, 35.10, 34.47, 33.18, 31.56, 23.55. HRMS (EI, m/z): Calcd. for $C_{18}H_{24}S$ $[M]^+$ 272.1599, found 272.1593.

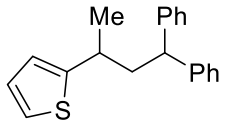


2-(4-(4-fluorophenyl)butan-2-yl)thiophene (3af). Colorless oil, 70.0 mg (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.04 (m, 3H), 7.03-6.91 (m, 3H), 6.88-6.79 (m, 1H), 3.12-3.02 (m, 1H), 2.58 (t, J = 8.0 Hz, 2H), 2.01-1.89 (m, 2H), 1.38 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.35 (d, J_{C-F} = 244.0 Hz), 151.52, 137.90 (d, J_{C-F} = 4.4 Hz), 129.83 (d, J_{C-F} = 7.9 Hz), 126.63, 122.98, 122.73, 115.16 (d, J_{C-F} = 21.2 Hz), 41.26, 34.98, 32.93, 23.53. HRMS (EI, m/z): Calcd. for $C_{14}H_{15}FS$ $[M]^+$ 234.0878, found 234.0875.

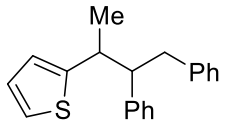


2-(4-(3-methoxyphenyl)butan-2-yl)thiophene (3ag). Colorless oil, 93.5 mg (76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 1H), 7.23-7.17 (m, 1H), 7.03-6.96 (m, 1H), 6.91-6.86 (m, 1H), 6.85-6.77

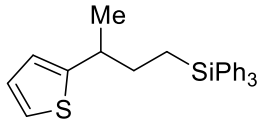
(m, 3H), 3.85 (s, 3H), 3.16-3.07 (m, 1H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.10-1.96 (m, 2H), 1.42 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.73, 151.65, 143.98, 129.38, 126.58, 122.93, 122.65, 120.95, 114.32, 111.13, 55.22, 40.97, 35.00, 33.78, 23.53. HRMS (EI, m/z): Calcd. for $C_{15}H_{18}OS$ $[M]^+$ 246.1078, found 246.1074.



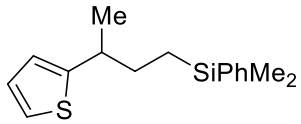
2-(4-(2-tolyl)butan-2-yl)thiophene (3ah). Colorless oil, 143.1 mg (98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.15 (m, 11H), 7.06-6.94 (m, 1H), 6.78 (d, *J* = 2.8 Hz, 1H), 3.95 (t, *J* = 8.0 Hz, 1H), 3.03-2.90 (m, 1H), 2.41 (t, *J* = 8.0 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.49, 145.05, 144.35, 128.65, 128.59, 128.29, 127.85, 126.60, 126.41, 126.25, 123.20, 122.80, 48.87, 45.51, 33.35, 24.11. HRMS (EI, m/z): Calcd. For $C_{20}H_{20}S$ $[M]^+$ 292.1286, found 292.1279.



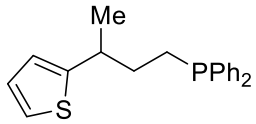
2-(3,4-diphenylbutan-2-yl)thiophene (3ai). Colorless oil, 118.5 mg (81% yield, d.r. = 1.5: 1 determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.13 (m, 5H), 7.13-7.10 (m, 2H), 7.08-7.04 (m, 2H), 7.03-6.98 (m, 2H), 6.91-6.85 (m, 1H), 6.65 (d, *J* = 3.2 Hz, 1H), 3.48-3.39 (m, 1H), 3.23-3.15 (m, 2H), 3.03-2.94 (m, 1H), 1.43 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.72, 141.99, 140.80, 129.18, 128.18, 127.77, 126.33, 126.29, 125.82, 124.31, 122.85, 54.99, 40.34, 38.07, 19.92. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.17 (m, 3H), 7.16-7.12 (m, 1H), 7.09-6.99 (m, 5H), 6.98-6.94 (m, 1H), 6.91-6.86 (m, 1H), 6.78 (d, *J* = 6.8 Hz, 2H), 3.40-3.31 (m, 1H), 2.98-2.86 (m, 2H), 2.74-2.62 (m, 1H), 1.1 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.80, 142.84, 140.81, 129.01, 128.63, 128.20, 127.95, 126.63, 126.38, 125.65, 124.05, 123.07, 57.08, 41.25, 41.21, 22.31. HRMS (EI, m/z): Calcd. for $C_{20}H_{20}S$ $[M]^+$ 292.1286, found 292.1280.



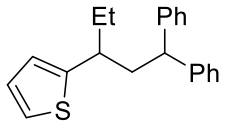
triphenyl(3-(thiophen-2-yl)butyl)silane (3aj). Colorless oil, 122.5 mg (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.46 (m, 6H), 7.44-7.35 (m, 8H), 7.30-7.27 (m, 1H), 7.21-7.06 (m, 1H), 6.98-6.89 (m, 1H), 6.78 (d, *J* = 3.6 Hz, 1H), 3.10-2.94 (m, 1H), 1.87-1.74 (m, 2H), 1.41-1.28 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.46, 135.76, 135.15, 129.53, 127.99, 126.56, 123.11, 122.66, 38.53, 33.63, 22.85, 10.83.



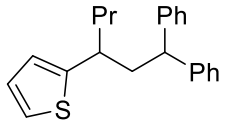
Dimethyl(phenyl)(3-(thiophen-2-yl)silane (3ak). Colorless oil, 78.2 mg (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.45 (m, 2H), 7.38-7.32 (m, 3H), 7.17-7.05 (m, 1H), 6.95-6.87 (m, 1H), 6.79-6.73 (m, 1H), 3.00-2.91 (m, 1H),1.67-1.58 (m, 2H), 1.29 (d, *J* = 6.8 Hz, 3H), 0.78-0.70 (m, 2H), 0.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.93, 139.38, 133.70, 128.97, 127.87, 127.84, 126.51, 122.51, 38.44, 33.72, 22.75, 13.37, -2.98.



Diphenyl(3-(thiophen-2-yl)butyl)phosphane (3al). Colorless oil, 75.4 mg (47% yield)； ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.33 (m, 10H), 7.18-7.10 (m, 1H), 6.96-6.88 (m, 1H), 6.82-6.74 (m, 1H), 3.22-3.13 (m, 1H), 2.22-2.09 (m, 2H), 1.89-1.72 (m, 2H), 1.34 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.94, 138.66 (d, $J_{C\text{-}P}$ = 12.1 Hz), 138.31(d, $J_{C\text{-}P}$ = 12.1 Hz), 132,96, 132.79 (d, $J_{C\text{-}P}$ = 1.4 Hz), 132.62, 128.66 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.53 (d, $J_{C\text{-}P}$ = 1.8 Hz), 128.46 (d, $J_{C\text{-}P}$ = 1.6 Hz), 126.56, 123.07, 122.74, 36.58 (d, $J_{C\text{-}P}$ = 13.5 Hz), 35.40 (d, $J_{C\text{-}P}$ = 16.8 Hz), 25.60 (d, $J_{C\text{-}P}$ = 10.8 Hz), 23.18. HRMS (EI, m/z): Calcd. for $C_{20}H_{21}PS$ $[M]^+$ 324.1102, found 324.1098.

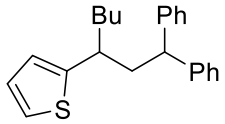


2-(1,1-diphenylpentan-3-yl)thiophene (3bh). Colorless oil, 145.4 mg (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.29-7.17 (m, 9H), 7.00-6.95 (m, 1H), 6.72 (d, *J* = 3.2 Hz, 1H), 3.88 (dd, *J* = 4.8 Hz, 6.0 Hz, 1H), 2.73-2.65 (m, 1H), 2.57-2.48 (m, 1H), 2.31-2.23 (m, 1H), 1.80-1.71 (m, 1H), 1.66-1.60 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.36, 145.60, 143.93, 128.62, 128.47, 127.72, 126.49, 126.41, 126.11, 124.50, 123.05, 48.65, 43.80, 40.86, 31.48, 11.95. HRMS (EI, m/z): Calcd. for $C_{21}H_{22}S$ $[M]^+$ 306.1442, found 306.1435.

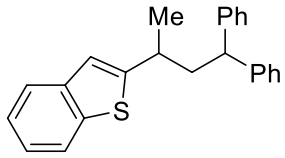


2-(1,1-diphenylhexan-3-yl)thiophene (3ch). Colorless oil, 136.8 mg (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.26-7.13 (m, 9H), 6.96-6.89 (m, 1H), 6.69-6.63 (m, 1H), 3.82 (dd, *J* = 4.4 Hz, 6.4 Hz, 1H), 2.79-2.68 (m, 1H), 2.53-2.42 (m, 1H), 2.27-2.15 (m, 1H), 1.64-1.54 (m, 2H), 1.23-1.10 (m, 2H), 0.79 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.74, 145.60, 143.87, 128.61, 128.47,

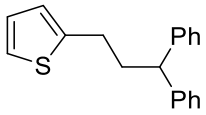
128.46, 127.71, 126.46, 126.40, 126.09, 124.34, 122.99, 48.61, 44.11, 40.93, 38.96, 20.57, 14.11. HRMS (EI, m/z): Calcd. for $C_{22}H_{24}S$ $[M]^+$ 320.1599, found 320.1594.



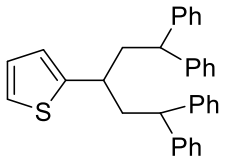
2-(1,1-diphenylheptan-3-yl)thiophene (3dh). Colorless oil, 147.1 mg (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 2H), 7.29-7.16 (m, 9H), 6.99-6.94 (m, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 3.86 (dd, *J* = 4.4 Hz, 6.4 Hz, 1H), 2.82-2.69 (m, 1H), 2.59-2.46 (m, 1H), 2.31-2.20 (m, 1H), 1.76-1.57 (m, 2H), 1.28-1.11 (m, 4H), 0.85-0.82 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.87, 145.65, 143.94, 128.63, 128.50, 127.75, 126.49, 126.42, 126.12, 124.34, 122.99, 48.67, 44.16, 39.21, 38.44, 29.60, 22.74, 14.09. HRMS (EI, m/z): Calcd. for $C_{23}H_{26}S$ $[M]^+$ 334.1755, found 334.1753.



2-(4,4-diphenylbutan-2-yl)benzo[b]thiophene (3eh). Colorless oil, 119.9 mg (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.37-7.23 (m, 11H), 7.22-7.17 (m, 1H), 6.98 (s, 1H), 3.98 (t, *J* = 8.0 Hz, 1H), 3.05-2.94 (m, 1H), 2.46 (t, *J* = 8.0 Hz, 2H), 1.42 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.29, 145.00, 144.12, 140.05, 139.06, 128.68, 128.59, 128.30, 127.79, 126.47, 126.28, 124.20, 123.62, 122.99, 122.47, 119.86, 48.83, 44.90, 34.23, 23.85. HRMS (EI, m/z): Calcd. for $C_{24}H_{22}S$ $[M]^+$ 342.1442, found 342.1440.

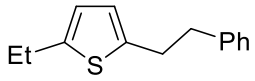


2-(3,3-diphenylpropyl)thiophene (3fh).[6] Colorless oil, 43.2 mg (31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 8H), 7.18 (t, *J* = 6.4 Hz, 2H), 7.12 (d, *J* = 4.8 Hz, 1H), 6.94-6.87 (m, 1H), 6.75 (d, *J* = 3.6 Hz,1H), 3.97 (t, *J* = 8.0 Hz, 1H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.44 (q, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.04, 144.62, 128.66, 128.05, 126.86, 126.41, 124.41, 123.17, 50.50, 37.64, 28.35. HRMS (EI, m/z): Calcd. for $C_{19}H_{18}S$ $[M]^+$ 278.1129, found 278.1125.

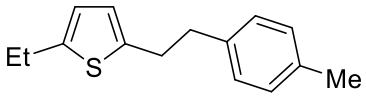


2-(1,1,5,5-tetraphenylpentan-3-yl)thiophene (3fh2). Colorless oil, 64.8 mg (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (m, 21H), 7.02 (dd, *J* = 3.6 Hz, 3.6 Hz, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 3.91 (dd,

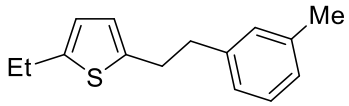
J = 5.6 Hz, 4.4 Hz, 2H), 2.93-2.84 (m, 1H), 2.66-2.55 (m, 2H), 2.44-2.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.10, 145.21, 143.53, 128.51, 128.49, 128.19, 127.78, 126.56, 126.26, 126.14, 124.83, 123.37, 48.63, 44.40, 36.91. HRMS (EI, m/z): Calcd. for $C_{33}H_{30}S$ $[M]^+$ 458.2068, found 458.2064.



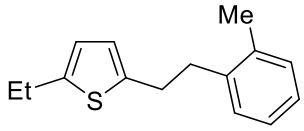
2-ethyl-5-phenethylthiophene (4aa). Colorless oil, 86.2 mg (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.18 (m, 3H), 6.60-6.53 (m, 2H), 3.09-3.03 (m, 2H), 2.98-2.92 (m, 2H), 2.81-2.78 (q, *J* = 8.0 Hz, 2H), 1.28 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.33, 142.02, 141.45, 128.54, 128.50, 126.19, 123.89, 122.84, 38.19, 32.23, 23.59, 16.11. HRMS (EI, m/z): Calcd. for $C_{14}H_{16}S$ $[M]^+$ 216.0973, found 216.0965.



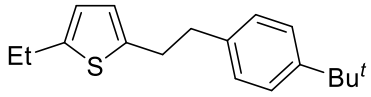
2-ethyl-5-(4-methylphenethyl)thiophene (4ab). Colorless oil, 87.8 mg (76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.28 (m, 2H), 7.13-7.12 (m, 2H), 6.66-6.56 (m, 2H), 3.09-3.03 (m, 2H), 2.98-2.90 (m, 2H), 2.82 (q, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 1.31 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.29, 142.19, 138.40, 135.65, 129.19, 128.40, 123.84, 122.83, 37.77, 32.38, 23.60, 21.18, 16.12. HRMS (EI, m/z): Calcd. for $C_{21}H_{22}S$ $[M]^+$ 230.1129, found 230.1120.



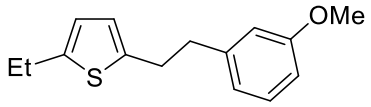
2-ethyl-5-(3-methylphenethyl)thiophene (4ac). Colorless oil, 78.6 mg (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 1H), 7.11-7.00 (m, 3H), 6.67-6.55 (m, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.82 (q, *J* = 8.0 Hz, 2H), 2.36 (s, 3H),1.32 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.29, 142.19, 141.42, 138.06, 129.35, 128.41, 126.93, 125.52, 123.83, 122.85, 38.19, 32.30, 23.60, 21.54, 16.13. HRMS (EI, m/z): Calcd. for $C_{15}H_{18}S$ $[M]^+$ 230.1129, found 230.1125.



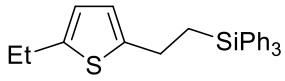
2-ethyl-5-(2-methylphenethyl)thiophene (4ad). Colorless oil, 84.0 mg (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.12 (m, 4H), 6.63-6.54 (m, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.80 (q, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.39, 142.22, 139.65, 136.09, 130.33, 128.86, 126.35, 126.15, 123.81, 122.91, 35.70, 31.02, 23.61, 19.40, 16.15. HRMS (EI, m/z): Calcd. for $C_{15}H_{18}S$ $[M]^+$ 230.1129, found 230.1121.



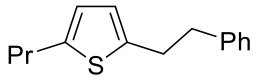
2-(4-(tert-butyl)phenethyl)-5-ethylthiophene (4ae). Colorless oil, 105.4 mg (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 2H), 7.19-7.13 (m, 2H), 6.63-6.56 (m, 2H), 3.06 (t, *J* = 8.8 Hz, 2H), 2.94 (t, *J* = 8.8 Hz, 2H), 2.80 (q, *J* = 8.0 Hz, 2H), 1.33-1.28 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.01, 145.28, 142.33, 138.45, 128.14, 125.41, 123.77, 122.86, 37.68, 34.52, 32.23, 31.55, 23.61, 16.13. HRMS (EI, m/z): Calcd. for $C_{18}H_{24}S$ $[M]^+$ 272.1599, found 272.1591.



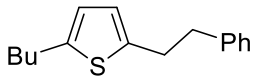
2-ethyl-5-(3-methoxyphenethyl)thiophene (4af). Colorless oil, 38.3 mg (31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 1H), 6.89-6.83 (m, 1H), 6.82-6.77 (m, 2H), 6.65-6.59 (m, 2H), 3.83 (s, 3H), 3.1 (t, *J* = 8.8 Hz, 2H), 2.98 (t, *J* = 8.8 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.75, 145.35, 143.06, 141.96, 129.46, 123.93, 122.85, 120.93, 114.24, 111.58, 55.26, 38.23, 32.12, 23.59, 16.12. HRMS (EI, m/z): Calcd. for $C_{15}H_{18}OS$ $[M]^+$ 246.1078, found 246.1073.



(2-(5-ethylthiophen-2-yl)ethyl)triphenylsilane (4ag). Colorless oil, 168.5 mg (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.55 (m, 6H), 7.47-7.36 (m, 9H), 6.66-6.52 (m, 2H), 2.99-2.88 (m, 2H), 2.80 (q, *J* = 8.8 Hz, 2H), 1.90-1.78 (m, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.89, 145.06, 135.76, 134.73, 129.70, 128.11, 122.80, 122.73, 24.82, 23.63, 16.16, 15.92. HRMS (EI, m/z): Calcd. for $C_{26}H_{26}SSi$ $[M]^+$ 398.1524, found 398.1521.

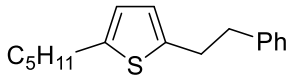


2-methyl-5-phenethylthiophene (4ba). Colorless oil, 86.1 mg (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.22-7.15 (m, 3H), 6.58-6.53 (m, 2H), 3.06 (t, *J* = 9.2 Hz, 2H), 2.95 (t, *J* = 8.4 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 1.72-1.62 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.53, 142.11, 141.47, 128.55, 128.49, 126.19, 123.87, 123.64, 38.19, 32.35, 32.25, 25.06, 13.83. HRMS (EI, m/z): Calcd. for $C_{15}H_{18}S$ $[M]^+$ 230.1129, found 230.1123.

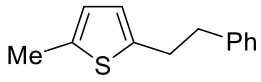


2-butyl-5-phenethylthiophene (4ca). Colorless oil, 80.5 mg (66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 2H), 7.25-7.18 (m, 3H), 6.64-6.51 (m, 2H), 3.07 (t, *J* = 7.2 Hz, 2H), 2.97 (t, *J* = 8.4 Hz,

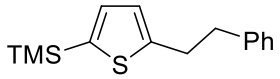
2H), 2.76 (t, *J* = 7.2 Hz, 2H), 1.71-1.58 (m, 2H), 1.47-1.34 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.77, 142.06, 141.47, 128.56, 128.50, 126.19, 123.86, 123.53, 38.20, 33.99, 32.26, 29.97, 22.34, 13.99. HRMS (EI, m/z): Calcd. for $C_{16}H_{20}S$ $[M]^+$ 244.1286, found 244.1280.



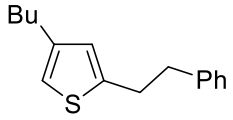
2-pentyl-5-phenethylthiophene (4da). Colorless oil, 84.9 mg (66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 2H), 7.34-7.23 (m, 3H), 6.74-6.56 (m, 2H), 3.17 (t, *J* = 8.8 Hz, 2H), 3.06 (t, *J* = 8.4 Hz, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 1.81-1.70 (m, 2H), 1.52-1.41 (m, 4H), 1.02 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.75, 142.02, 141.43, 128.53, 128.47, 126.16, 123.85, 123.50, 38.17, 32.24, 31.55, 31.43, 30.25, 22.57, 14.16. HRMS (EI, m/z): Calcd. for $C_{17}H_{22}S$ $[M]^+$ 258.1442, found 258.1432.



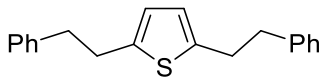
2-methyl-5-phenethylthiophene (4ea). Colorless oil, 41.1 mg (41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2H), 7.28-7.23 (m, 3H), 6.68-6.52 (m, 2H), 3.11 (t, *J* = 8.4 Hz, 2H), 3.00 (t, *J* = 8.4 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.41, 141.42, 137.56, 128.56, 128.50, 126.20, 124.75, 124.15, 38.20, 32.14, 15.41. HRMS (EI, m/z): Calcd. for $C_{13}H_{14}S$ $[M]^+$ 202.0816, found 202.0810.



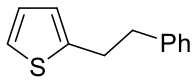
trimethyl(5-phenethylthiophen-2-yl)silane (4fa). Colorless oil, 64.5 mg (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 2H), 7.31-7.24 (m, 3H), 7.12 (d, *J* = 3.2 Hz, 1H), 6.91 (d, *J* = 3.2 Hz, 1H), 3.21 (t, *J* = 8.8 Hz, 2H), 3.05 (t, *J* = 9.2 Hz, 2H), 0.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.30, 141.42, 138.15, 134.13, 128.55, 128.52, 126.25, 125.92, 38.23, 32.07, 0.13. HRMS (EI, m/z): Calcd. for $C_{15}H_{20}SSi$ $[M]^+$ 260.1055, found 260.1047.



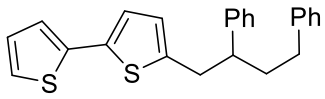
4-butyl-2-phenethylthiophene (4ga). Colorless oil, 74.0 mg (61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.29-7.23 (m, 3H), 6.74 (s, 1H), 6.65 (s, 1H), 3.13 (t, *J* = 8.8 Hz, 2H), 3.02 (t, *J* = 8.4 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.65-1.58 (m, 2H), 1.44-1.36 (m, 2H),0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.31, 143.02, 141.37, 128.56, 128.49, 126.20, 126.01, 117.60, 38.17, 32.72, 32.25, 30.36, 22.52, 14.07. HRMS (EI, m/z): Calcd. for $C_{16}H_{20}S$ $[M]^+$ 244.1286, found 244.1280.



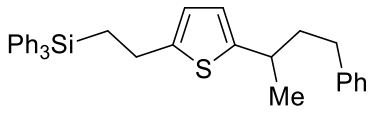
2,5-diphenethylthiophene (4ha). Colorless oil, 62.4 mg (43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 4H), 7.28-7.23 (m, 6H), 6.62-6.56 (m, 2H), 3.12 (t, *J* = 6.4 Hz, 4H), 3.00 (t, *J* = 8.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.43, 141.38, 128.57, 128.50, 126.21, 124.00, 38.18, 32.22. HRMS (EI, m/z): Calcd. for $C_{20}H_{20}S$ $[M]^+$ 292.1286, found 292.1280.



2-phenethylthiophene (4ha') Colorless oil, 14.0 mg (15% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.25-7.18 (m, 3H), 7.18-7.07 (m, 1H), 6.96-6.86 (m, 1H), 6.84-6.74 (m, 1H), 3.15 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.62, 141.26, 128.58, 128.53, 126.83, 126.26, 124.48, 123.21, 38.23, 31.97. HRMS (EI, m/z): Calcd. for $C_{12}H_{12}S$ $[M]^+$ 188.0660, found 188.0654.

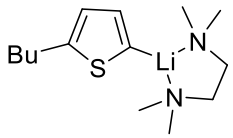


5-(2,4-diphenylbutyl)-2,2'-bithiophene (4ia). Colorless oil, 133.5 mg (71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 4H), 7.24-7.19 (m, 3H), 7.18-7.13 (m, 3H), 7.12-7.08 (m, 2H), 7.06-7.03 (m, 1H), 7.02-6.98 (m, 1H), 6.61 (d, *J* = 3.6 Hz, 1H), 3.21-3.13 (m, 1H), 3.03-2.96 (m, 2H), 2.77-2.67 (m, 1H), 2.61-2.52 (m, 1H), 2.17-2.07 (m, 1H), 2.02-1.92 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.25, 141.03, 138.91, 137.09, 134.16, 128.21, 127.56, 127.46, 127.32, 126.85, 125.24, 124.93, 124.32, 122.95, 122.23, 122.18, 43.73, 42.25, 37.47, 32.65. HRMS (EI, m/z): Calcd. for $C_{24}H_{22}S_2$ $[M]^+$ 374.1163, found 374.1158.

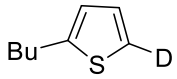


Triphenyl(2-(5-(4-phenylbutan-2-yl)thiophen-2-yl)silane (5). 2-Ethylthiophene **1a** (2.0 mmol, 224.4 mg), styrene **2b** (0.5 mmol, mg), KHMDS (10.0 mg, 0.05 mmol), 18-crown-6 (0.075 mmol, 19.8 mg), TBME (0.5 mL). The tube was sealed, removed from the glovebox and heated at 30 ℃ for 36 h. The mixture was cooled to room temperature and purified directly by silica gel column chromatography (hexane) to afford compound **3aa** as a colorless oil (88.1 mg, 82%). 2-(4-phenylbutan-2-yl)thiophene (**3aa**) (0.5 mmol, 108.1 mg), triphenylvinylsilan **2g** (2.0 mmol, 572.9 mg), LDA (11.3 mg, 0.10 mmol), TMEDA (0.30 mL). The tube was sealed, removed from the glovebox and heated at 70 ℃ for 60 h. The mixture was cooled to room temperature and purified directly by silica gel column chromatography (hexane) to afford compound **5** as a colorless oil (193.3mg, 77% yield). Therefore, the total yield of the two steps is 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 5H), 7.48-7.37 (m, 10H), 7.32-7.27

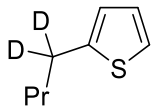
(m, 3H), 7.20-7.17 (m, 2H), 6.70-6.53 (m, 2H), 3.04-2.91 (m, 3H), 2.67-2.55 (m, 2H), 1.99-1.81 (m, 4H), 1.34 (d, J = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.03, 145.59, 142.35, 135.73, 134.67, 129.68, 128.51, 128.39, 128.09, 125.80, 122.52, 122.42, 40.98, 35.22, 33.74, 24.89, 23.49, 15.79. HRMS (EI, m/z): Calcd. for $C_{34}H_{34}SSi$ $[M]^+$ 502.2150, found 502.2147.



2-butylthiophene lithium (1c-Li). ^{1}H NMR (400 MHz, C_6D_6) δ 7.63-7.50 (m, 1H), 7.32-7.22 (m, 1H), 3.15 (t, J = 7.6 Hz, 2H), 2.00 (s, 12 H), 1.90-1.82 (m, 2H), 1.72 (s, 4 H), 1.50-1.40 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 173.94, 150.94, 137.41, 125.77, 56.92, 46.42, 35.47, 30.53, 22.84, 14.30.



5-d-2-butylthiophene (1c-D). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J = 3.2 Hz, 1H), 6.85-6.75 (m, 1H), 2.85 (t, J = 7.6 Hz, 2H), 1.72-1.64 (m, 2H), 1.45-1.37 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.86, 126.60, 124.01, 122.93-122.65 (t, 1C, J_{CD} = 28.6 Hz), 34.07, 29.74, 22.35, 13.97.

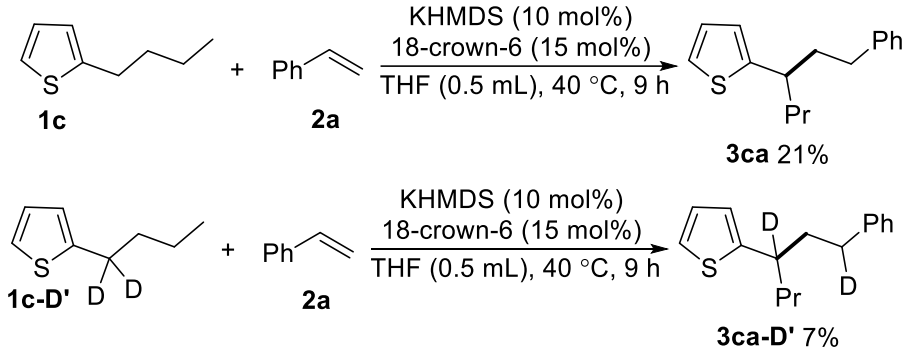


2-(butyl-1,1-d^2)thiophene(1c-D'). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 5.2 Hz, 1H), 6.97-6.91 (m, 1H), 6.83-6.78 (m, 1H), 1.68 (t, J = 7.6 Hz, 2H), 1.45-1.37 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83, 126.75, 124.02, 122.83, 33.87, 29.21-28.85 (m, 1C), 22.29, 13.96.

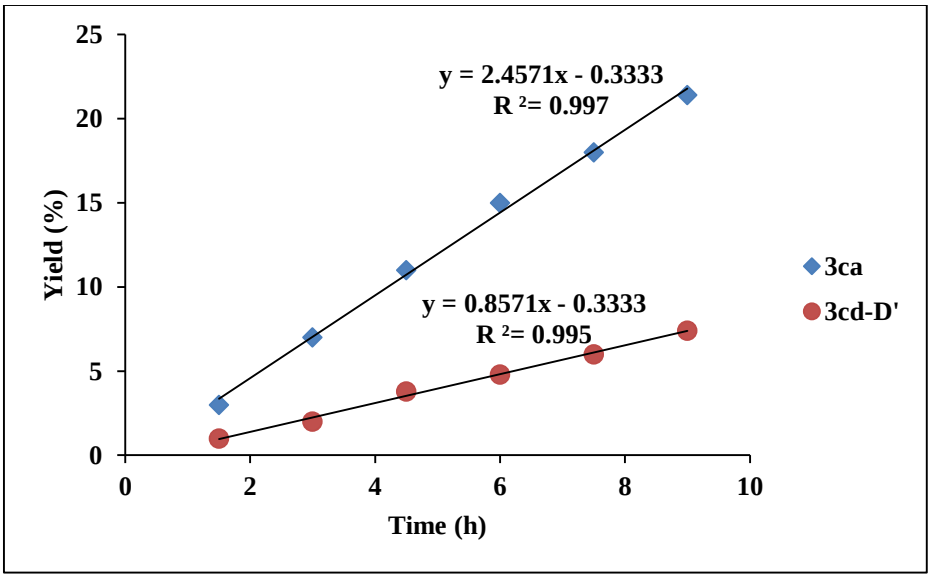
4. Kinetic Isotope Effect Experiments

4.1 Kinetic isotope effect in KHMDS catalyzed benzylic sp^3 C-H Bond alkylation of 2-butylthiophene:

To a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added 2-butylthiophene **1c** (1.0 mmol, 140.3 mg), styrene **2a** (0.25 mmol, 26.0 mg), KHMDS (5.0 mg, 0.025 mmol), 18-crown-6 (0.038 mmol, 10.0 mg), THF (0.5 mL). The mixture was heated at 40 ℃ and monitored by GC analysis every 1.5 hours. The reaction of deuterated 2-butylthiophene **1c-D'** was carried out and monitored under exact same conditions. The kinetic isotope effect was proved to be 2.9.

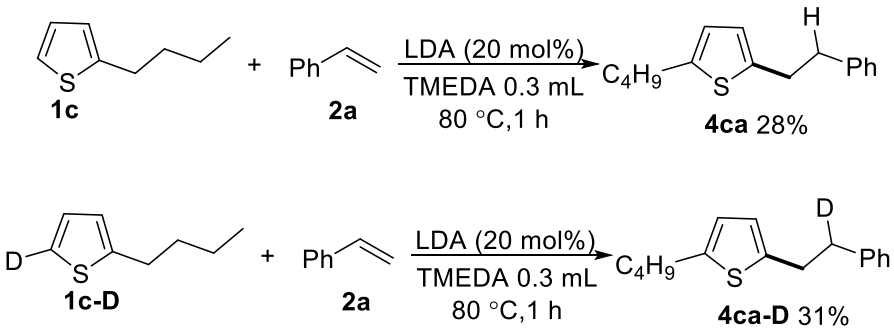


K_H / K_D = 2.4571/ 0.8571 = 2.9

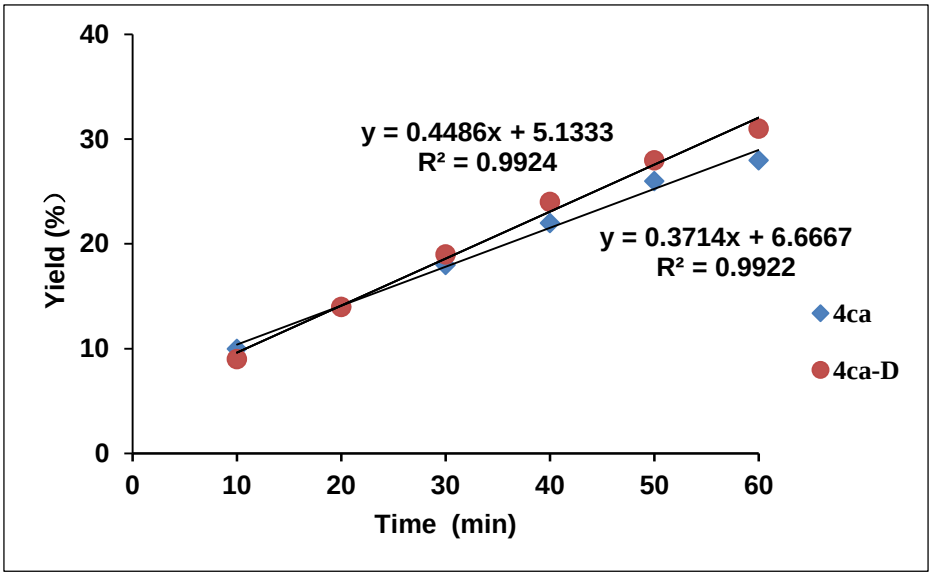


4.2 Kinetic isotope effect in LDA catalyzed sp^2 C-H Bond alkylation of 2-butylthiophene:

To a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added 2-butylthiophene **1c** (0.25 mmol, 35.1 mg), styrene **2a** (1.00 mmol, 104.2 mg), LDA (5.7 mg, 0.025 mmol), TMEDA (0.3 mL). The mixture was heated at 80 ℃ and monitored by ^{1}H NMR once every 10 minters. The reaction of deuterated 2-butylthiophene **1c-D** was carried out and monitored under exact same conditions. The kinetic isotope effect was proved to be 0.83. The ^{1}H NMR yields of **4ca** and **4ca-D** were determined by integral of C-H group (δ: 6.56 ppm) of alkylation products using the C-H group (2-butylthiophene plus product) as an internal standard.



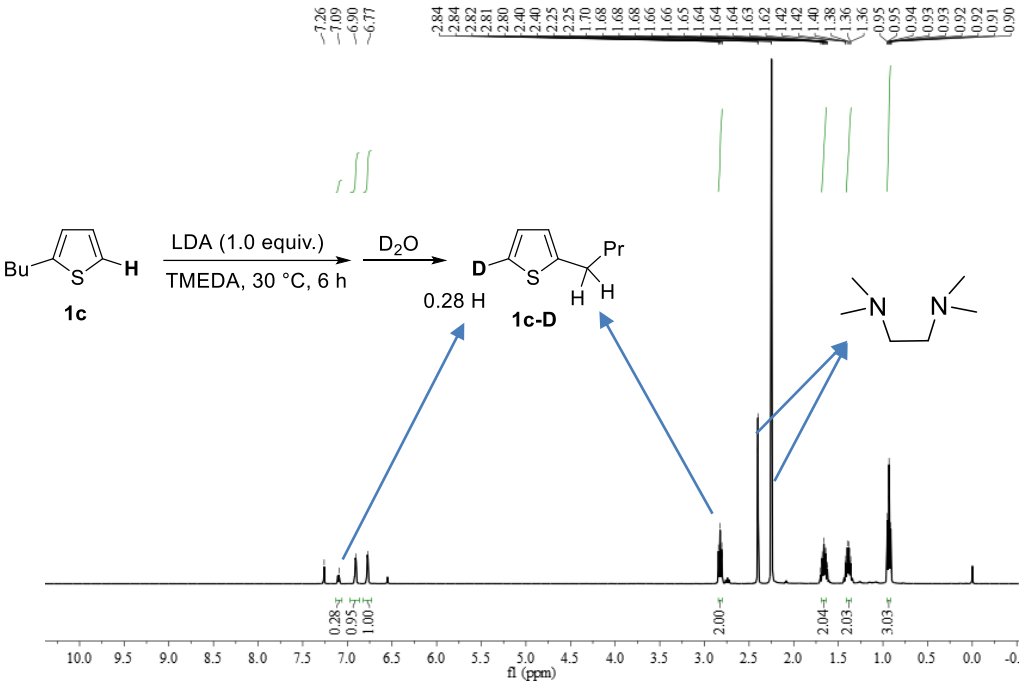
K_H / K_D = 0.3714/0.4486 = 0.83

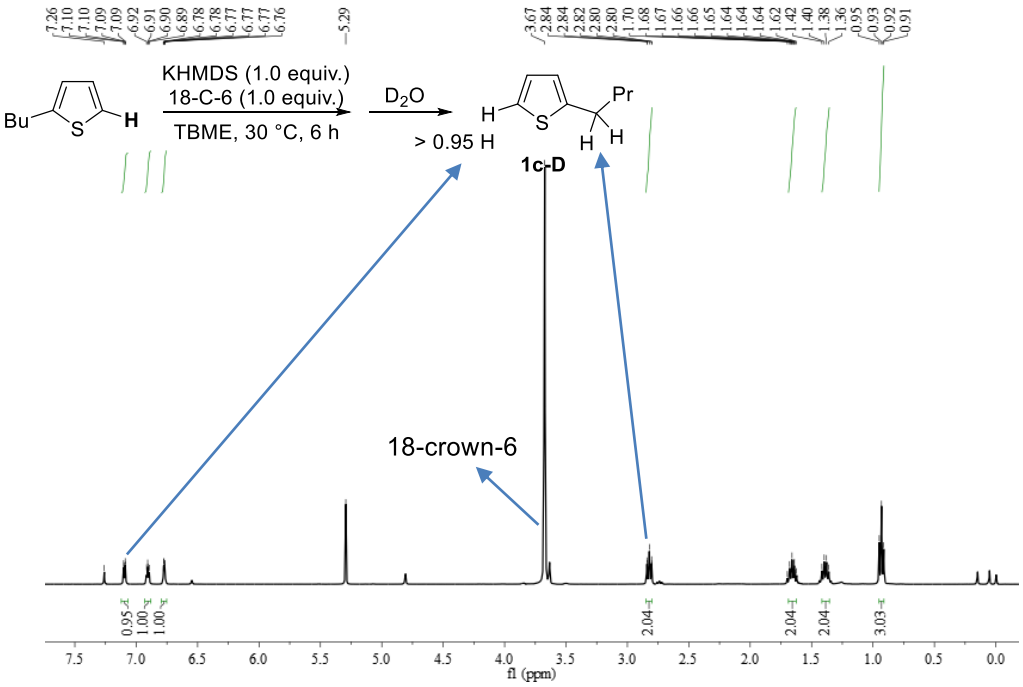


5. Deprotonation Experiments

5.1 Deprotonation with LDA or KHMDS

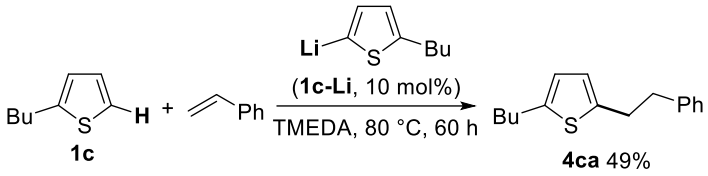
In a glovebox, to a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added 2-butylthiophene **1c** (0.5 mmol, 70.2 mg), LDA (56.5mg, 0.5 mmol), TMEDA (0.3 mL). The mixture was heated at 30 ℃ for 6 h and quenched with deuterium water. The solvent was removed under vacuum to afford the crude product, which was characterized by ^{1}HNMR. The deprotonation reaction with KHMDS/18-C-6 was carried out under the same conditions in TBME.





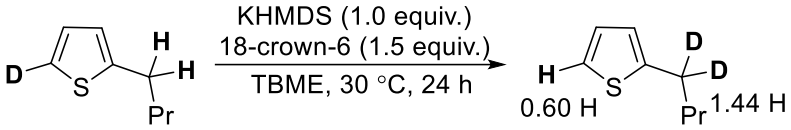
5.2 Catalytic alkylation of 2-butylthiophene with 1c-Li as catalyst.

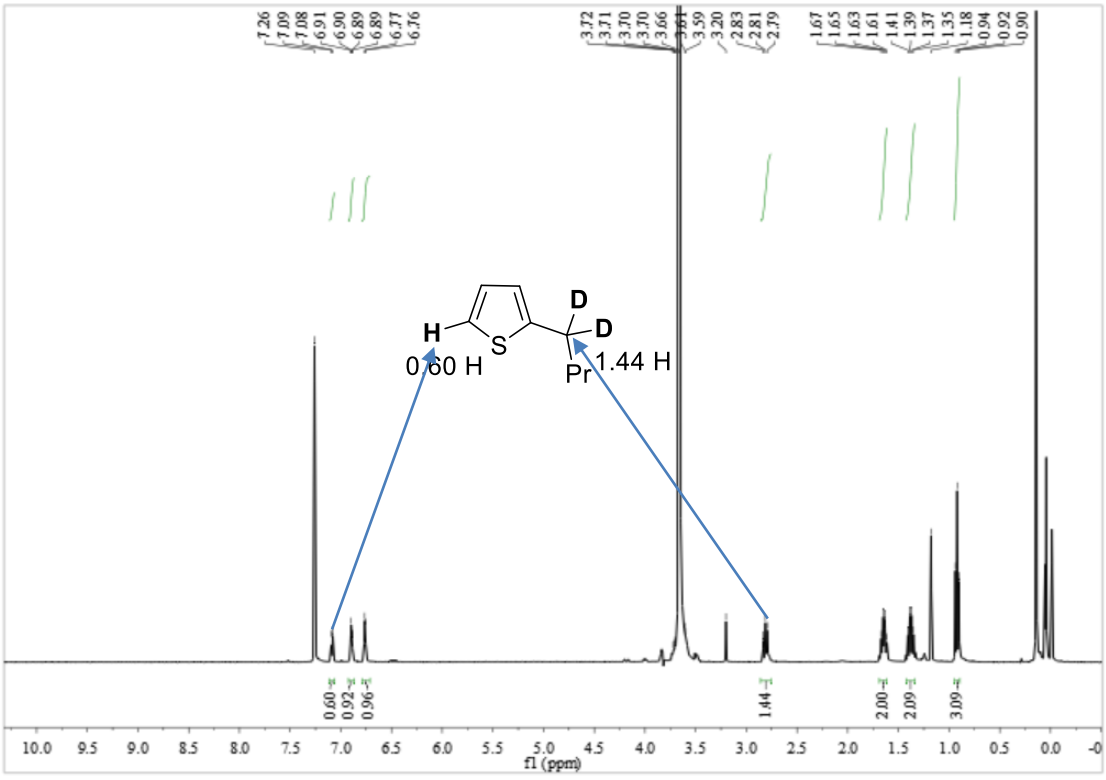
To a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added 2-butylthiophene **1c** (0.5 mmol, 70.1 mg), styrene **2a** (2.0 mmol, 208.4 mg), 2-butylthiophene lithium **1c-Li** (13.8 mg, 0.05 mmol), TMEDA (0.30 mL). The mixture was heated at 80 ℃ for 60 h, and then cooled to room temperature. The direct purification by silica gel column chromatography (hexane) afforded compound **4ca** as a colorless oil (65.7 mg, 49% yield).



5.3 H-D exchange between 1e and 1c-D'

(1) To a 25-mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added deuterated 2-butylthiophene **1c-D** (0.20 mmol, 28.2 mg), KHMDS (0.20 mmol, 39.9 mg), 18-crown-6 (0.30 mmol, 79.3 mg), TBME (0.5 mL). The mixture was heated at 30 ℃ for 24 h. After that, the mixture was characterized in $CDCl_3$ by ^{1}HNMR (shown below).





6. References

[1] Barr, D.; Dawson, A. J.; Wakefield, B. J. *J. Chem. Soc., Chem. Commun*. **1992**, 204-204.

[2] Ai, Q.; Pang, S.; Ahn, K. *Chem. Eur.J.* **2016**, 22, 656-662.

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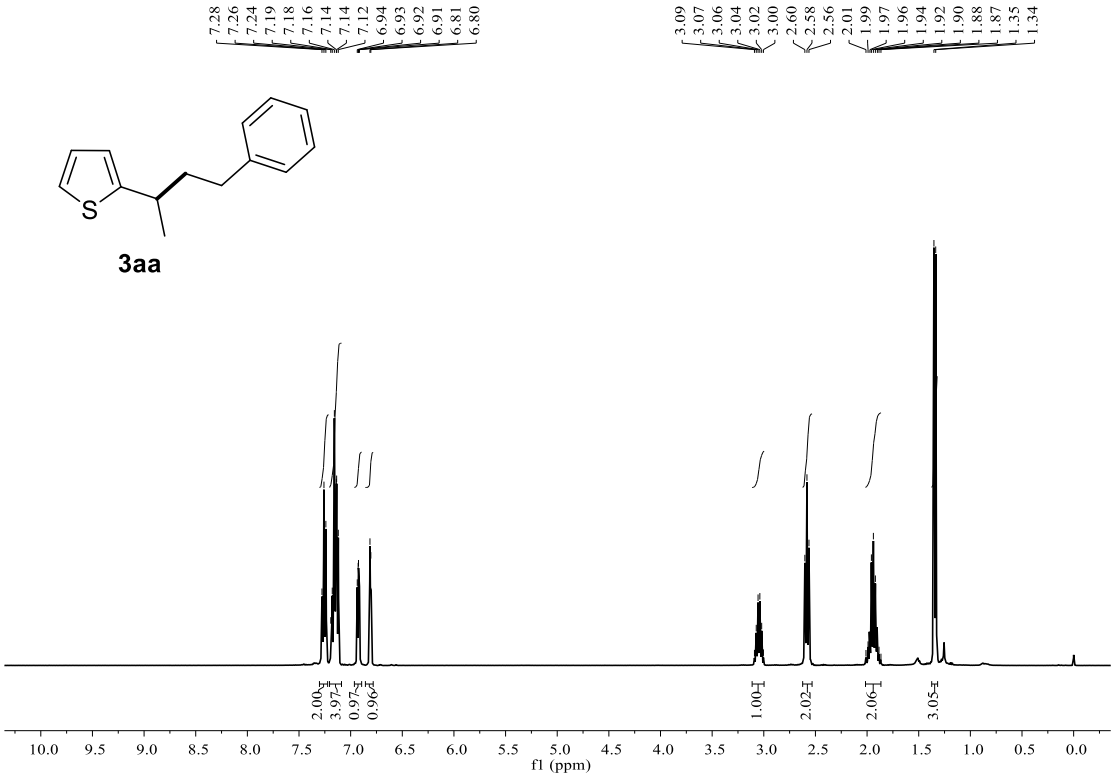
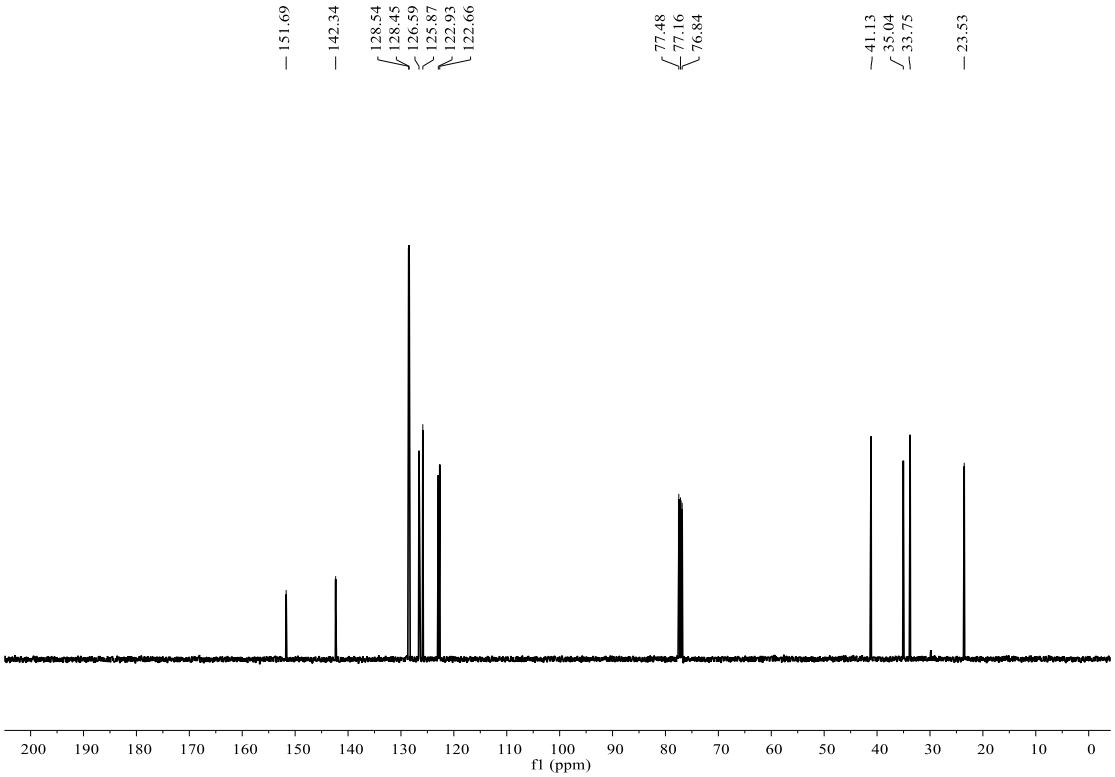
[4] Shoji H.; Kobatake S. *Chem. Commun*. **2013**, 49, 2362-2364.

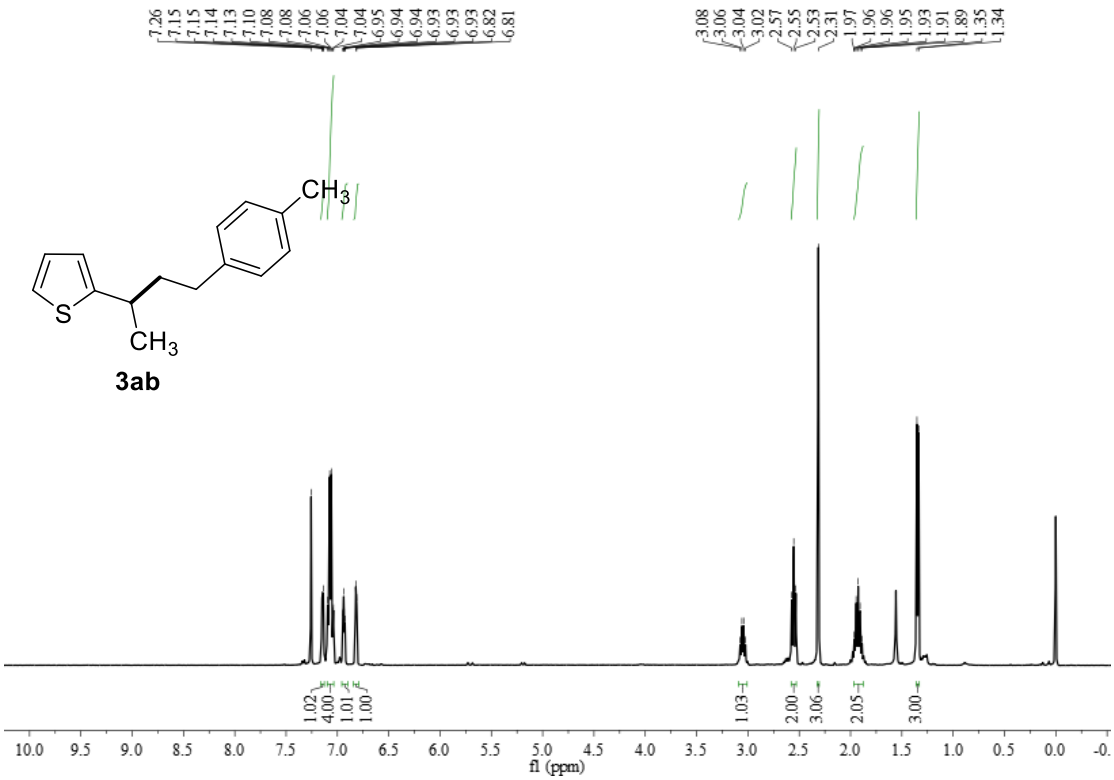
[5] Odachowski M, Bonet A, Essafi S, Conti-Ramsden P, Harvey J N, Leonori D, and Aggarwal V K.. *J. Am. Chem. Soc.* **2016**, 138, 9521-9532.

[6] Gu F.; Huang W.; Liu X.; Chen W.; Cheng X. *Adv. Synth. Catal.* **2018**, 360, 925-931.

7. ^{1}H and ^{13}C NMR Spectral Charts



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7.08
7.06
7.06
7.04
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6.93
6.93
6.93
6.82
6.81
3.08
3.06
3.04
3.02
2.57
2.55
2.53
2.31
1.97
1.96
1.96
1.95
1.93
1.91
1.89
1.35
1.34
CH3
S
CH3
3ab
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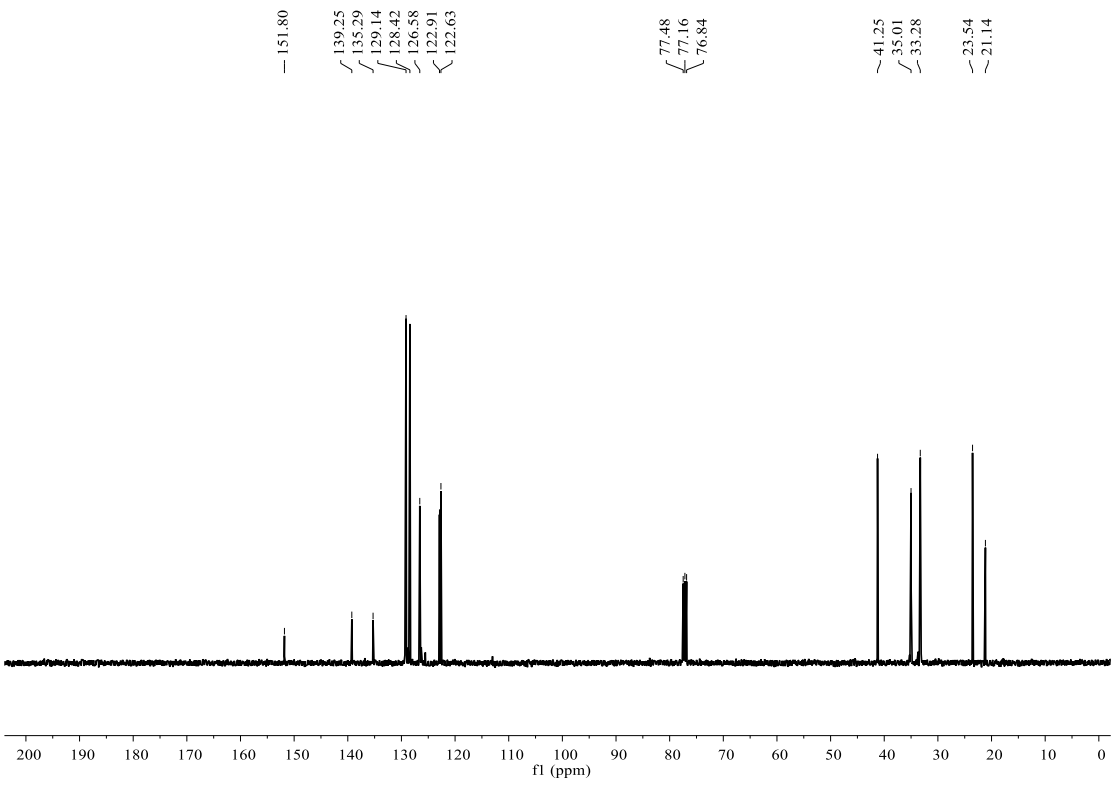
2.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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21.14
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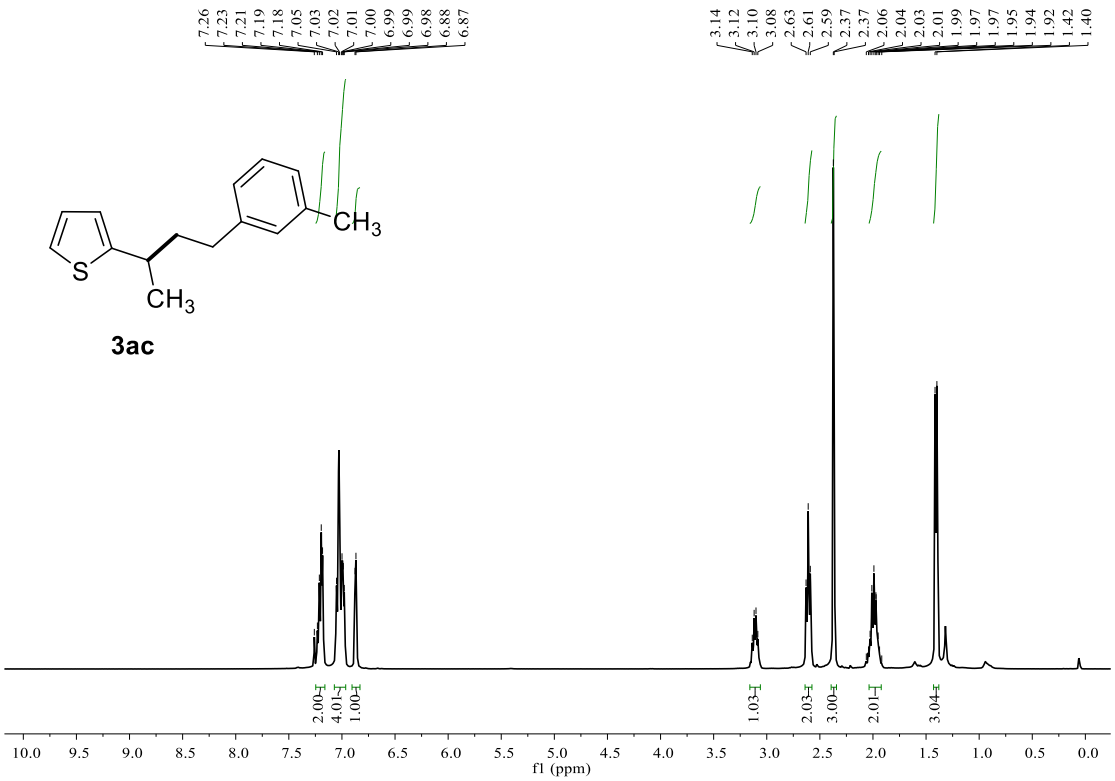
f1 (ppm)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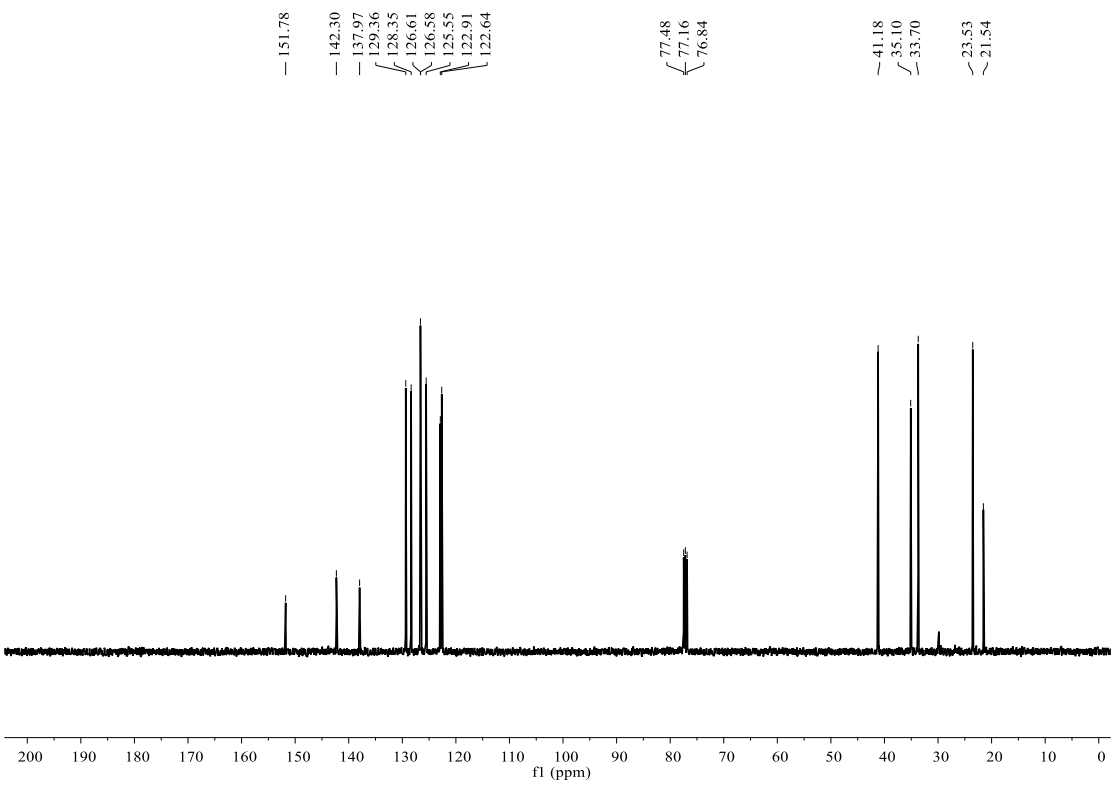
3.04
f1 (ppm)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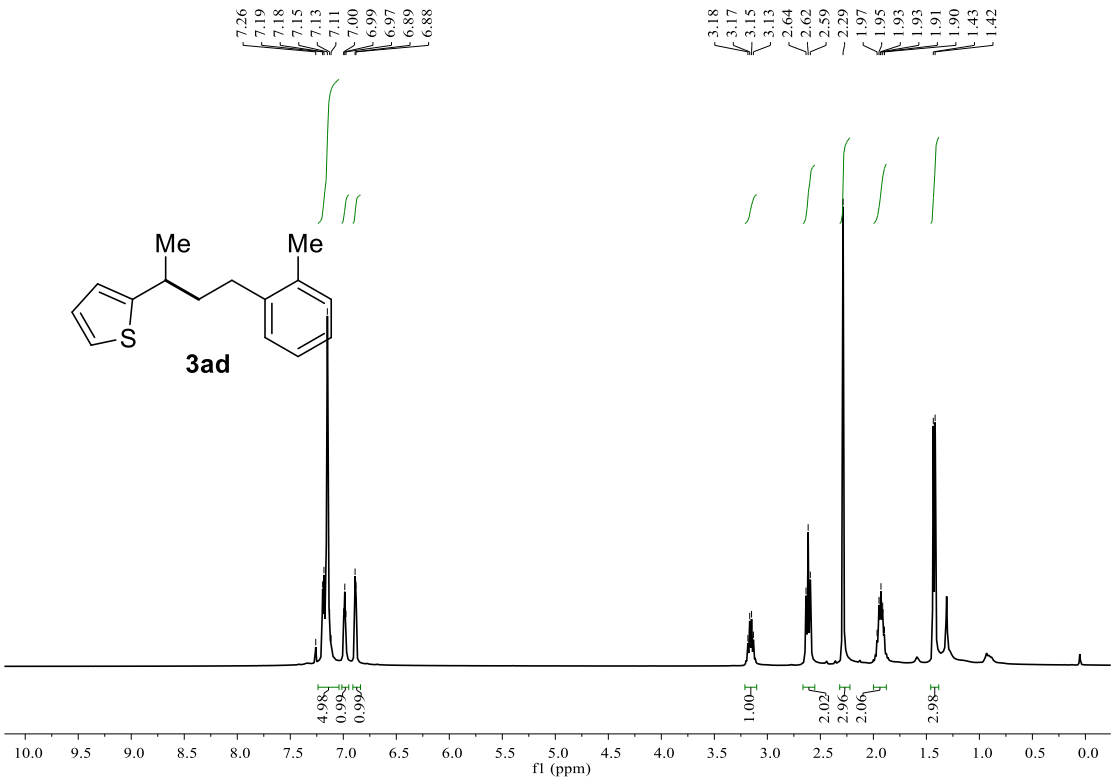
21.54
f1 (ppm)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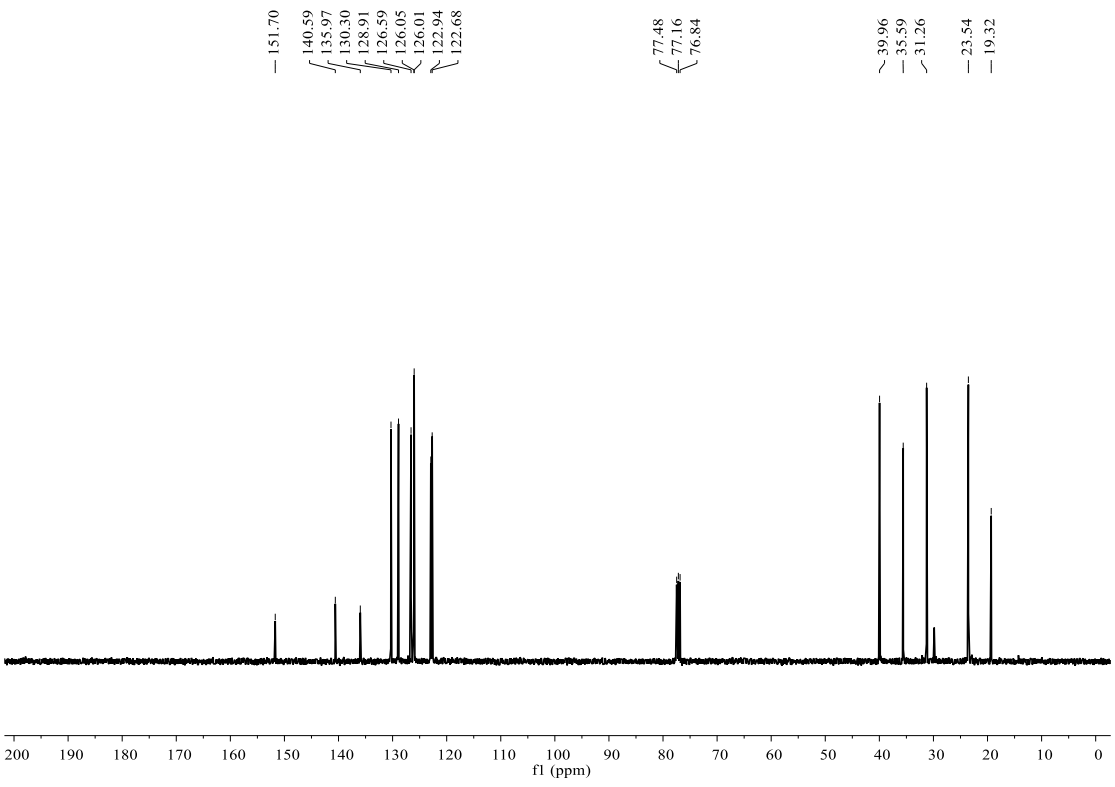
1.42
Me
Me
S
3ad
4.98
0.99
0.99
1.00
2.02
2.96
2.06
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.59
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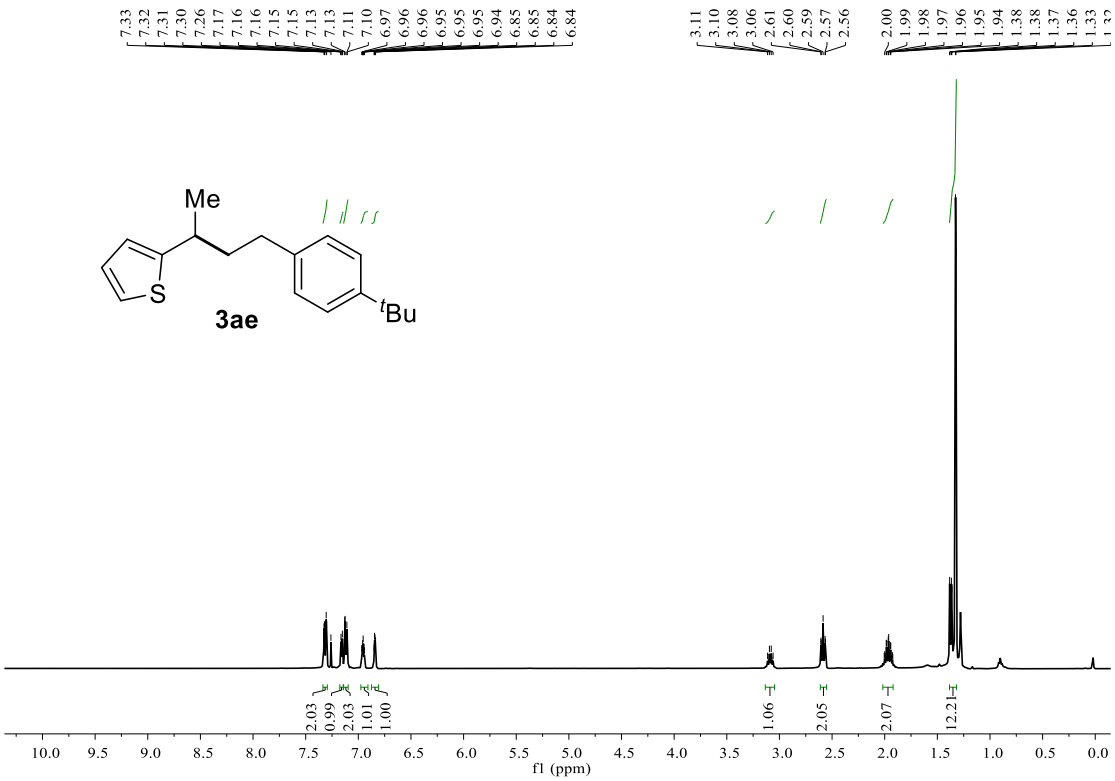
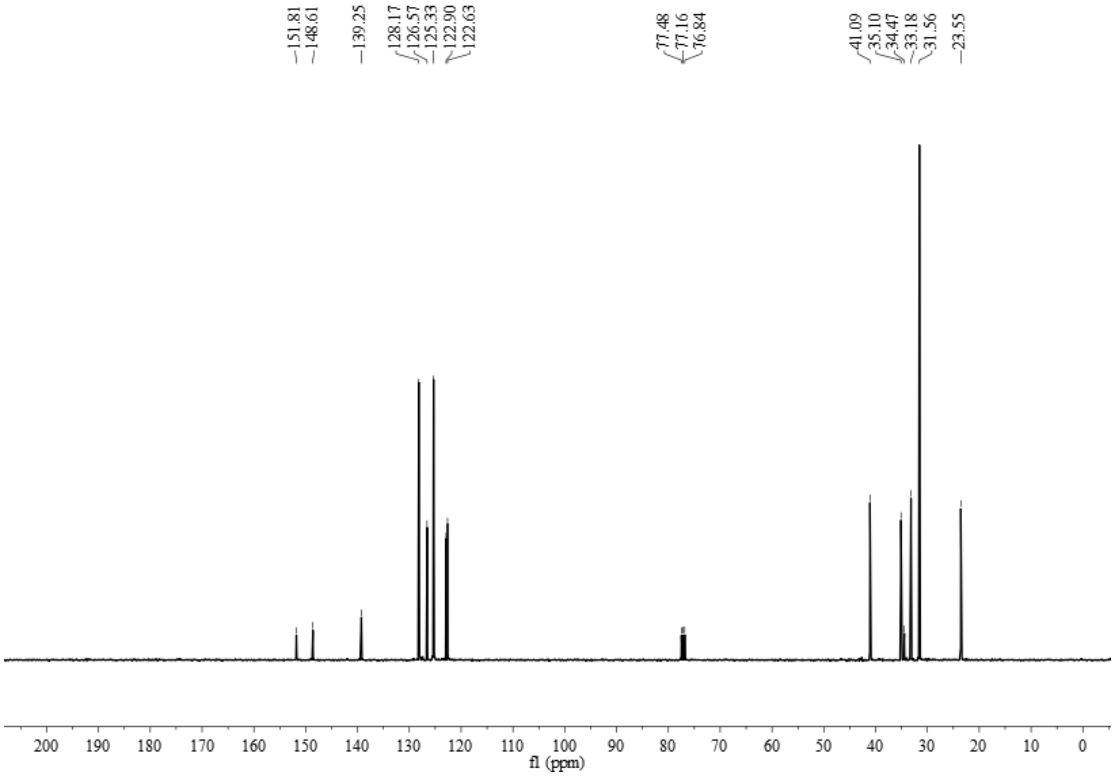
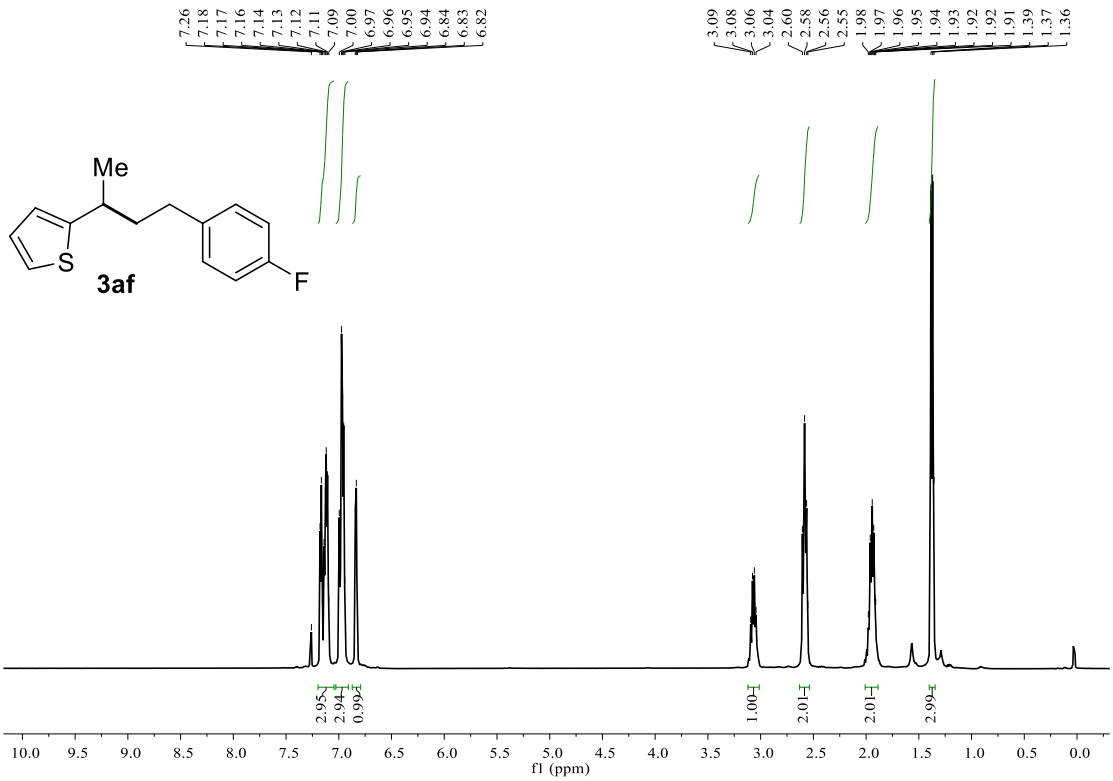
130.30
128.91
126.59
126.05
126.01
122.94
122.68
77.48
77.16
76.84
39.96
35.59
31.26
23.54
19.32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
S
3ae
tBu
fl (ppm)


fl (ppm)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7.00
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6.96
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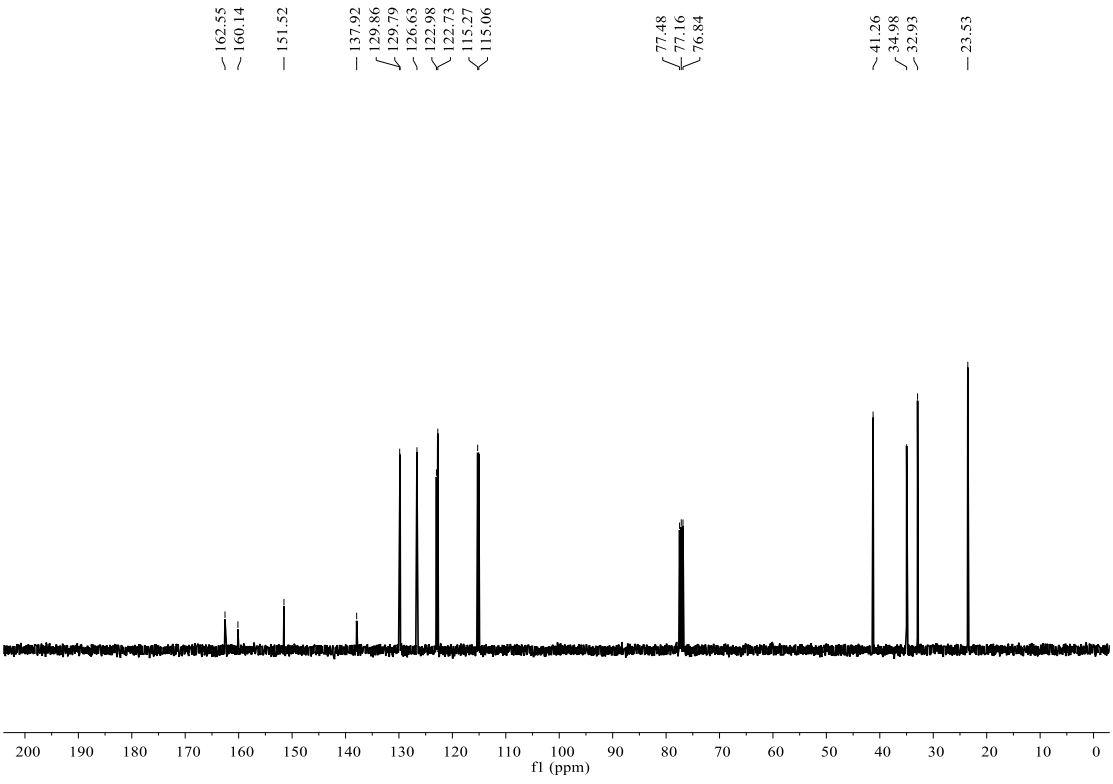
6.94
6.84
6.83
6.82
3.09
3.08
3.06
3.04
2.60
2.58
2.56
2.55
1.98
1.97
1.96
1.95
1.94
1.93
1.92
1.92
1.91
1.39
1.37
1.36
Me
S
F
3af
2.95
2.94
0.99
1.00
2.01
2.01
2.99
f1 (ppm)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160.14
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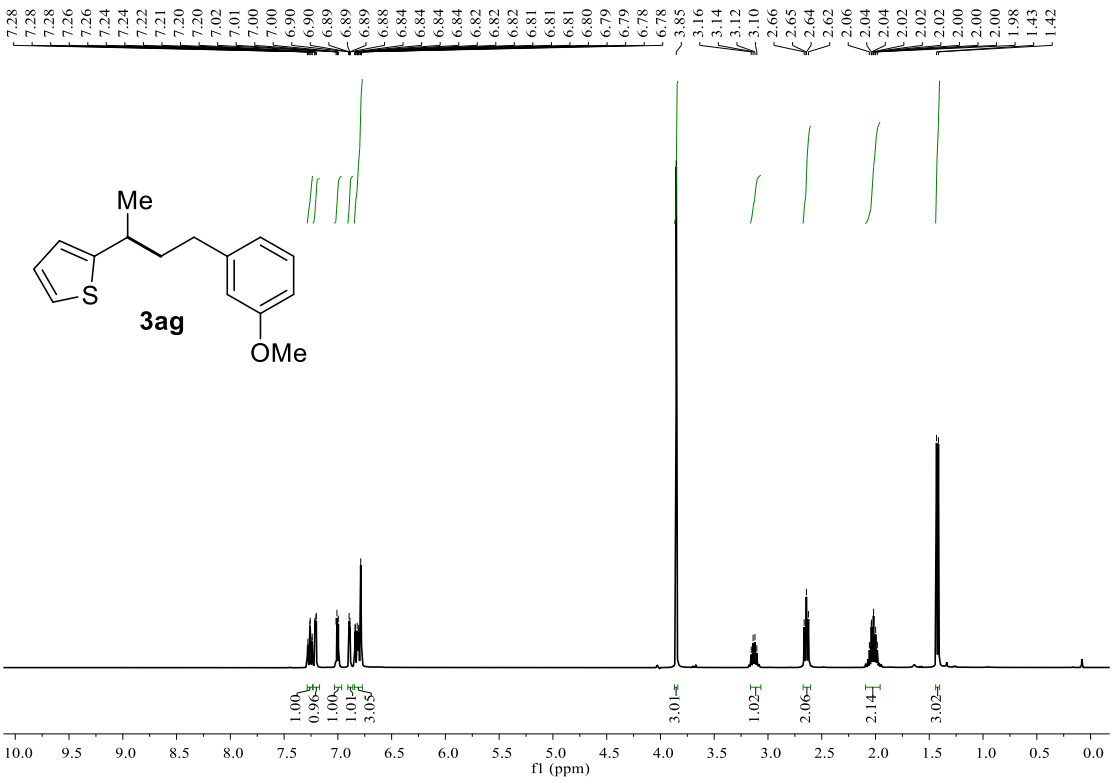
137.92
129.86
129.79
126.63
122.98
122.73
115.27
115.06
77.48
77.16
76.84
41.26
34.98
32.93
23.53
f1 (ppm)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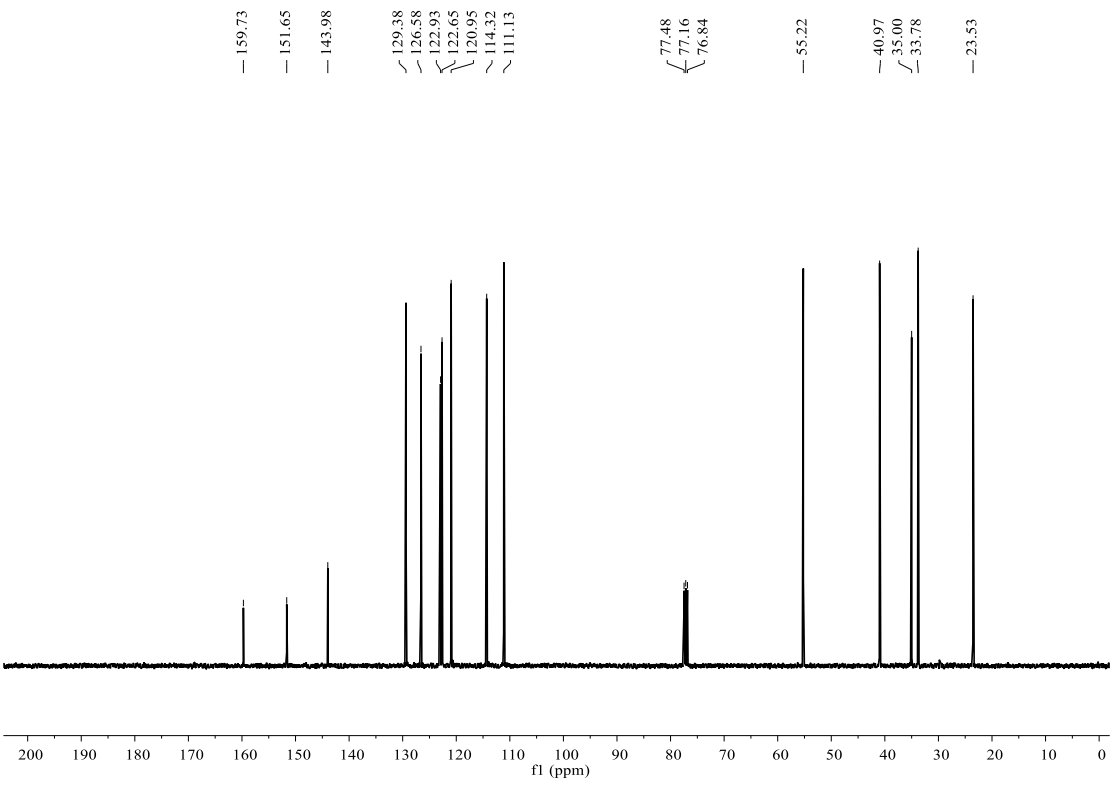
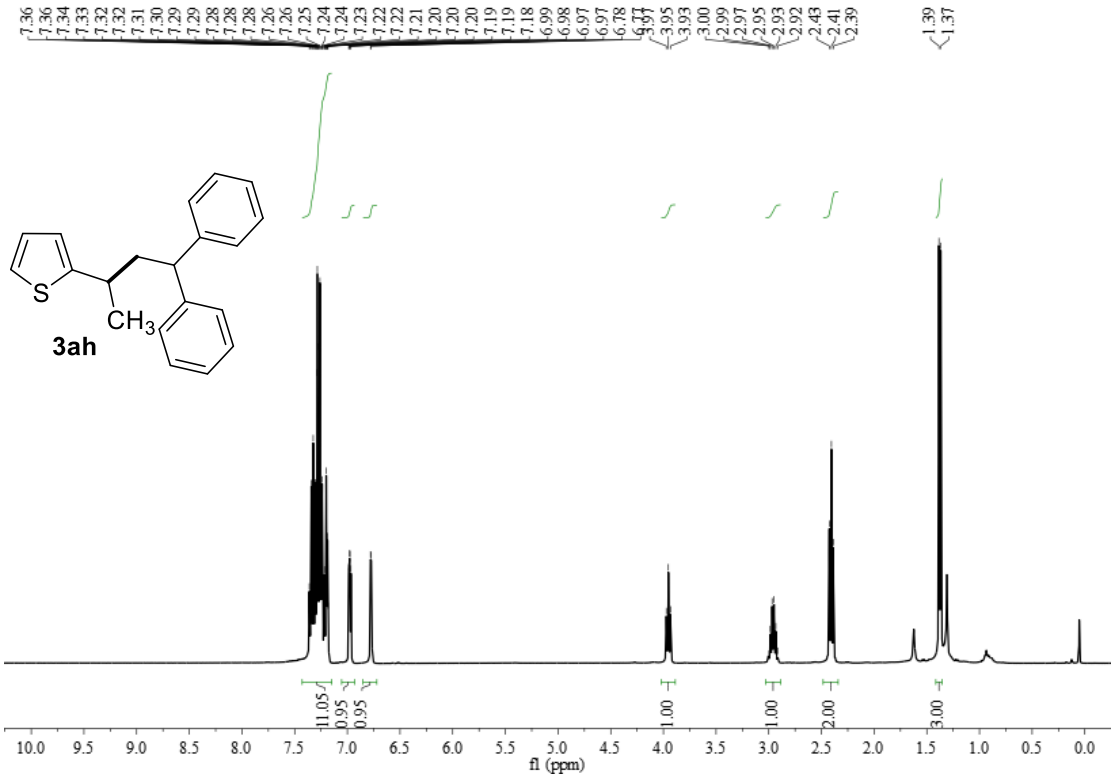
S
3ag
OMe
f1 (ppm)


f1 (ppm)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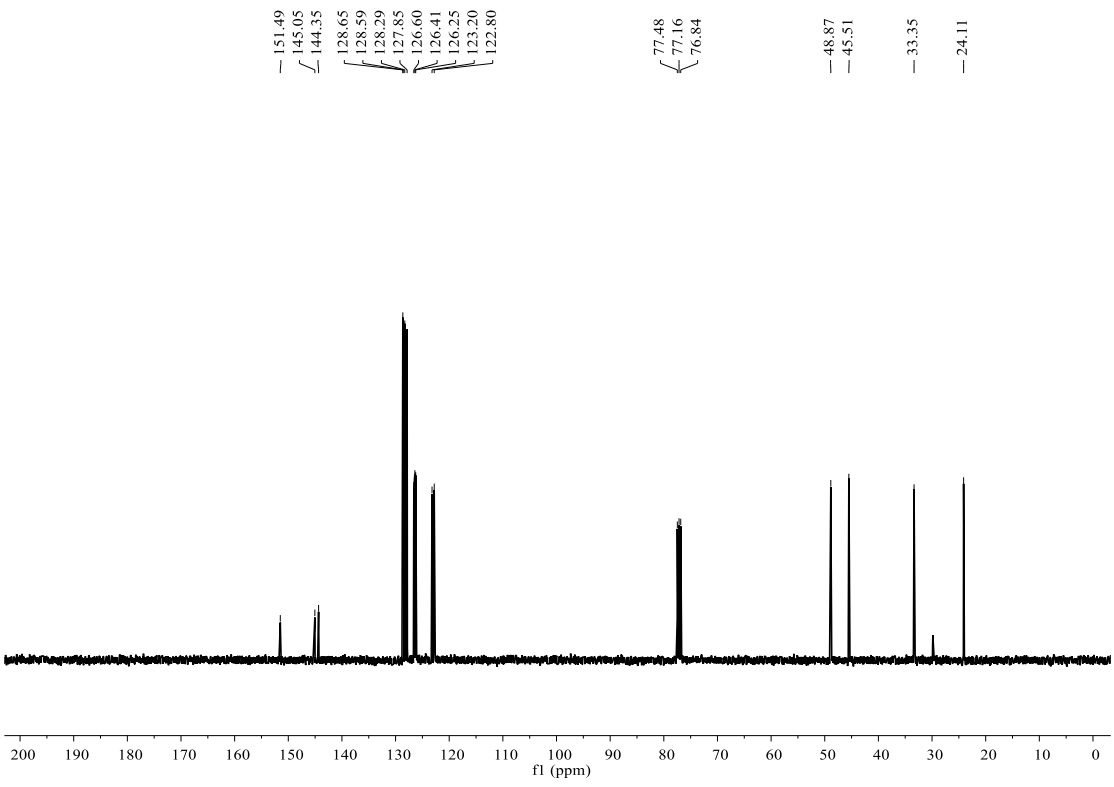
7.36
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.28
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.20
7.19
7.19
7.18
6.99
6.98
6.97
6.97
6.78
3.95
3.93
3.00
2.99
2.97
2.95
2.93
2.92
2.43
2.41
2.39
1.39
1.37
S
CH3
3ah
11.05
0.95
0.95
1.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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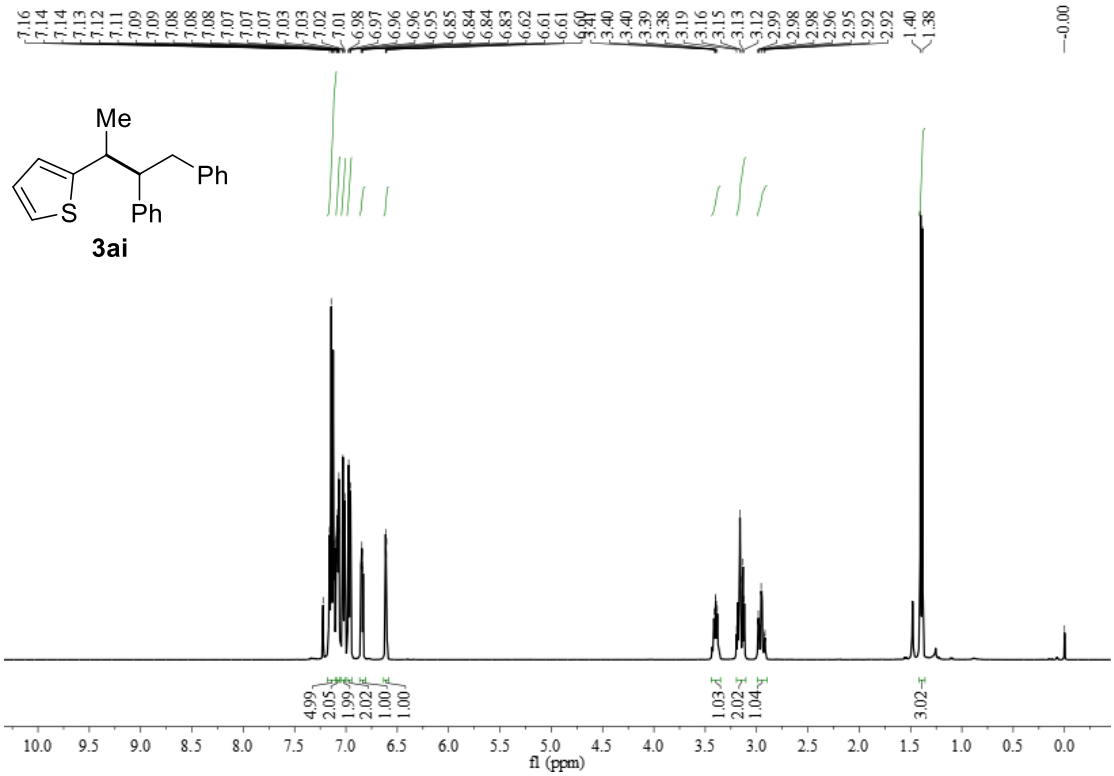
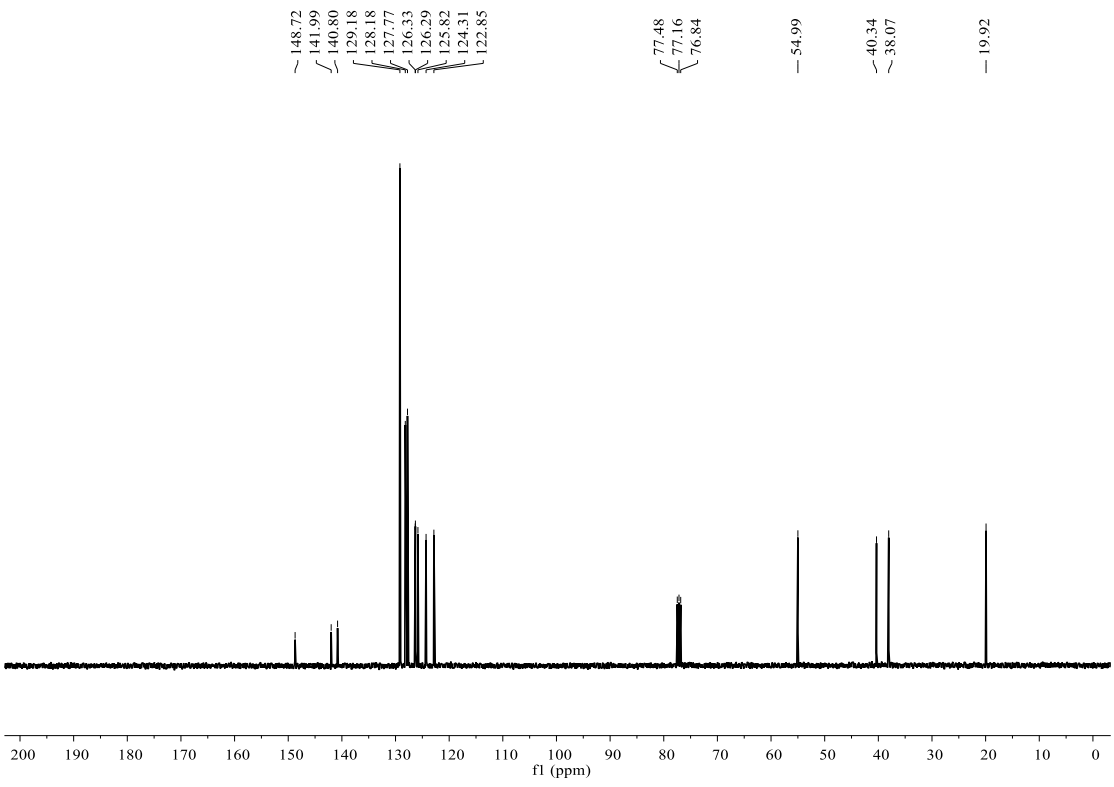
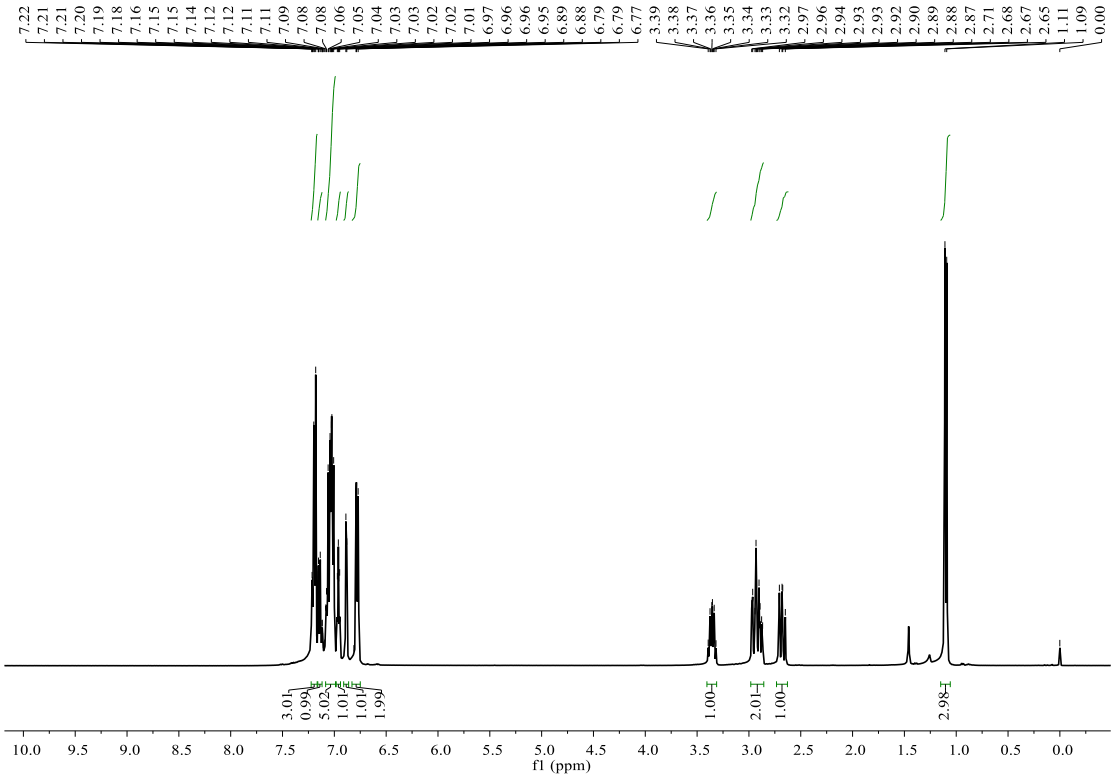
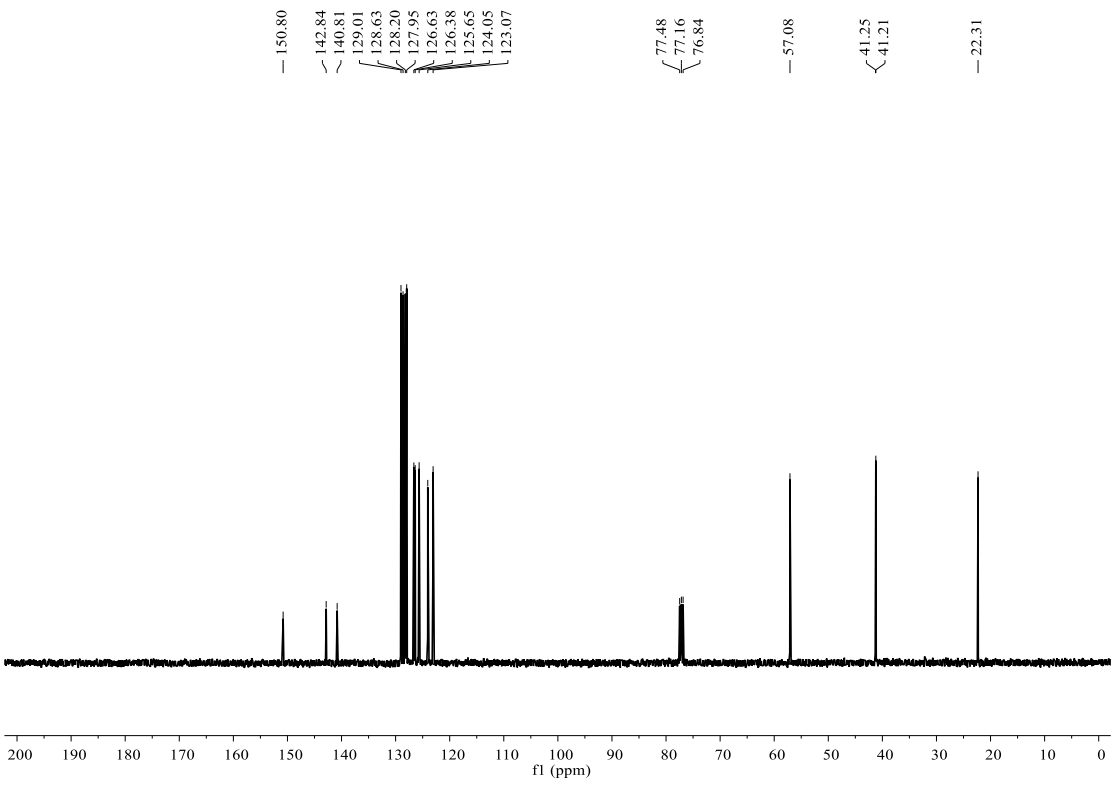
145.05
144.35
128.65
128.59
128.29
127.85
126.60
126.41
126.25
123.20
122.80
77.48
77.16
76.84
48.87
45.51
33.35
24.11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Ph
S
Ph
3ai
fl (ppm)

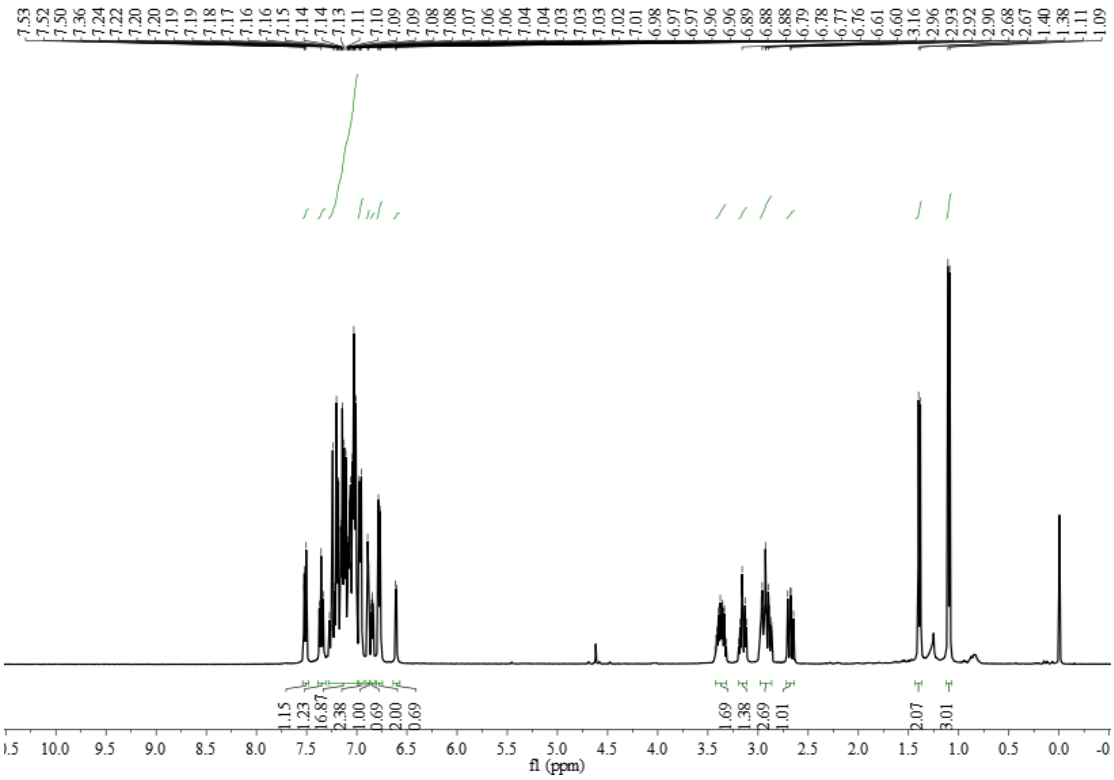

fl (ppm)

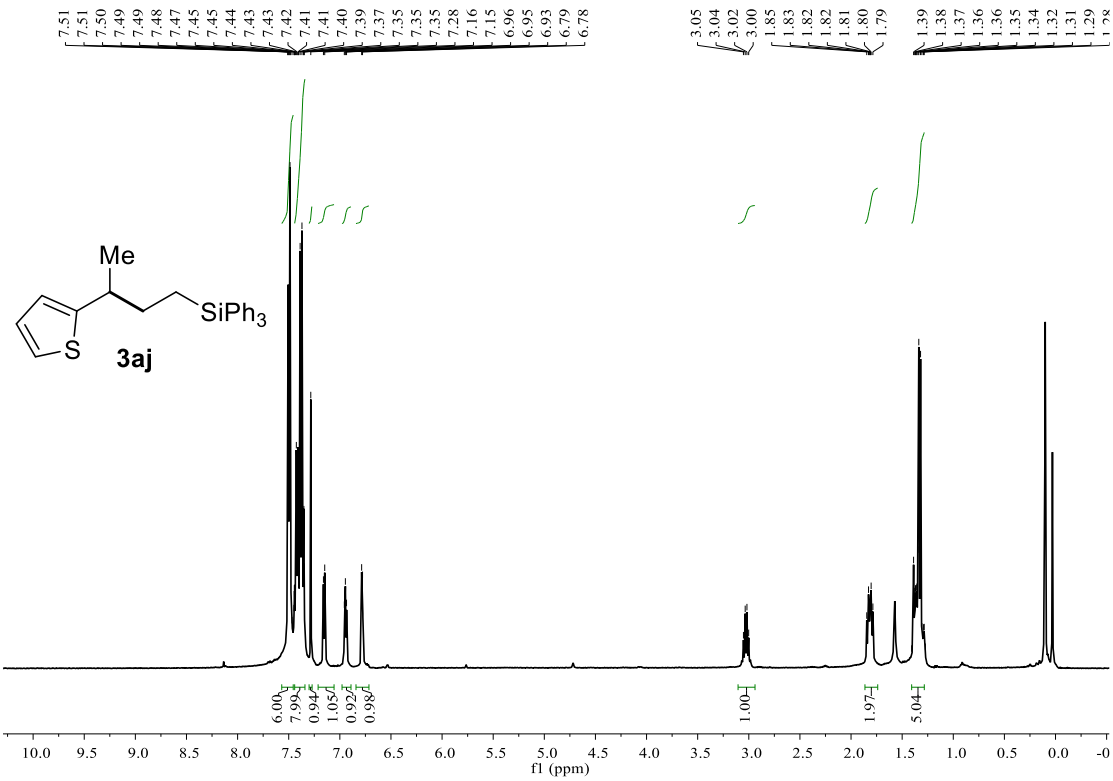
3ai'

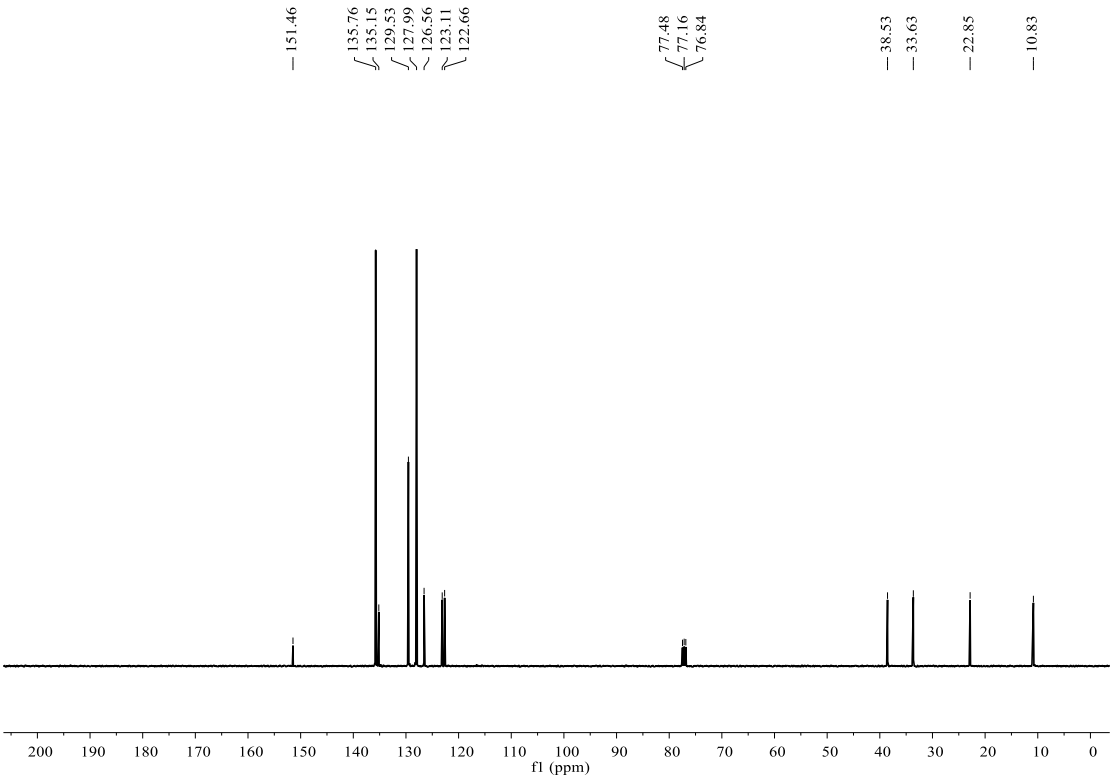

7.22 7.21 7.21 7.20 7.19 7.18 7.16 7.15 7.15 7.14 7.12 7.12 7.11 7.11 7.09 7.08 7.08 7.06 7.05 7.04 7.03 7.03 7.02 7.02 7.01 6.97 6.96 6.96 6.95 6.89 6.88 6.79 6.79 6.77 3.39 3.38 3.37 3.36 3.35 3.34 3.33 3.32 2.97 2.96 2.94 2.93 2.93 2.92 2.90 2.89 2.88 2.87 2.71 2.68 2.67 2.65 1.11 1.09 0.00
3.01 0.99 5.02 1.01 1.01 1.99 1.00 2.01 1.00 2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

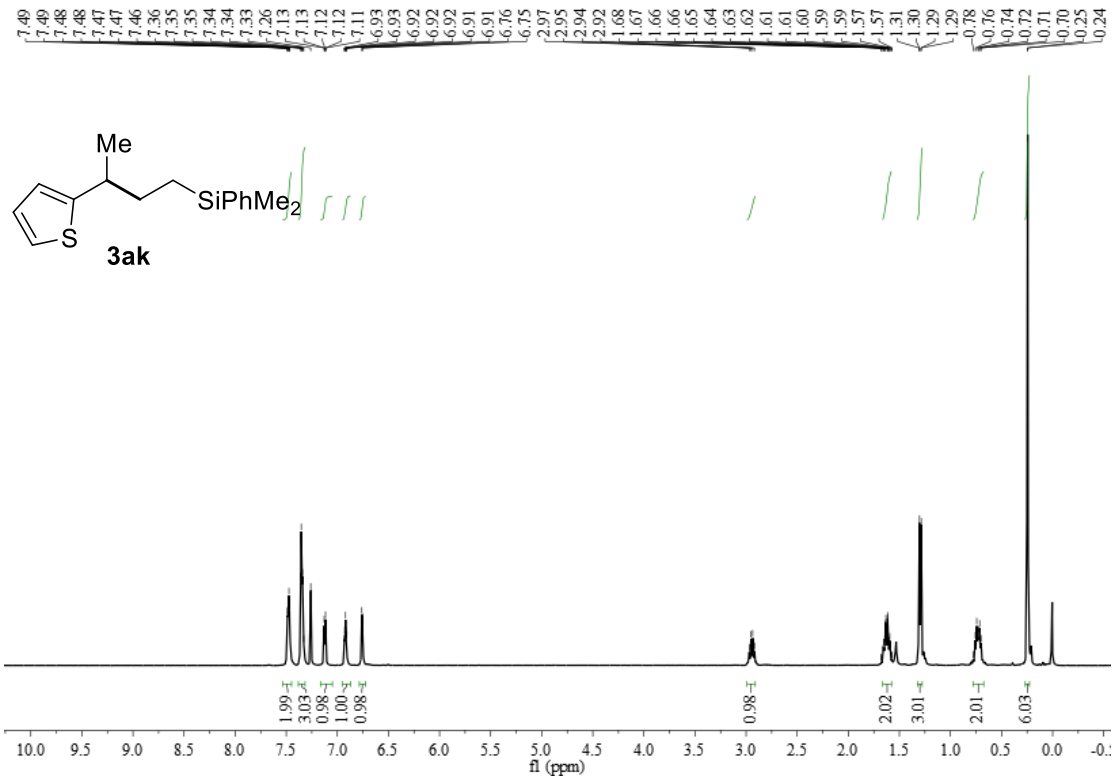

150.80 142.84 140.81 129.01 128.63 128.20 127.95 126.63 126.38 125.65 124.05 123.07 77.48 77.16 76.84 57.08 41.25 41.21 22.31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

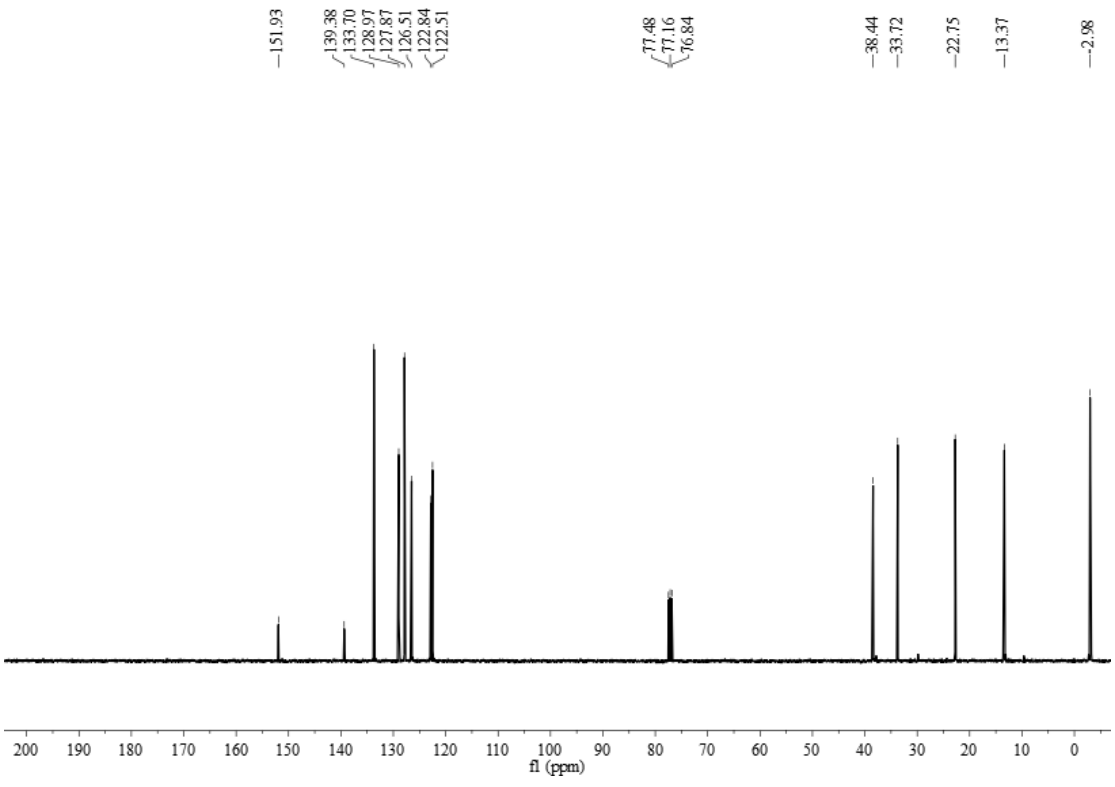
3ai+3ai'

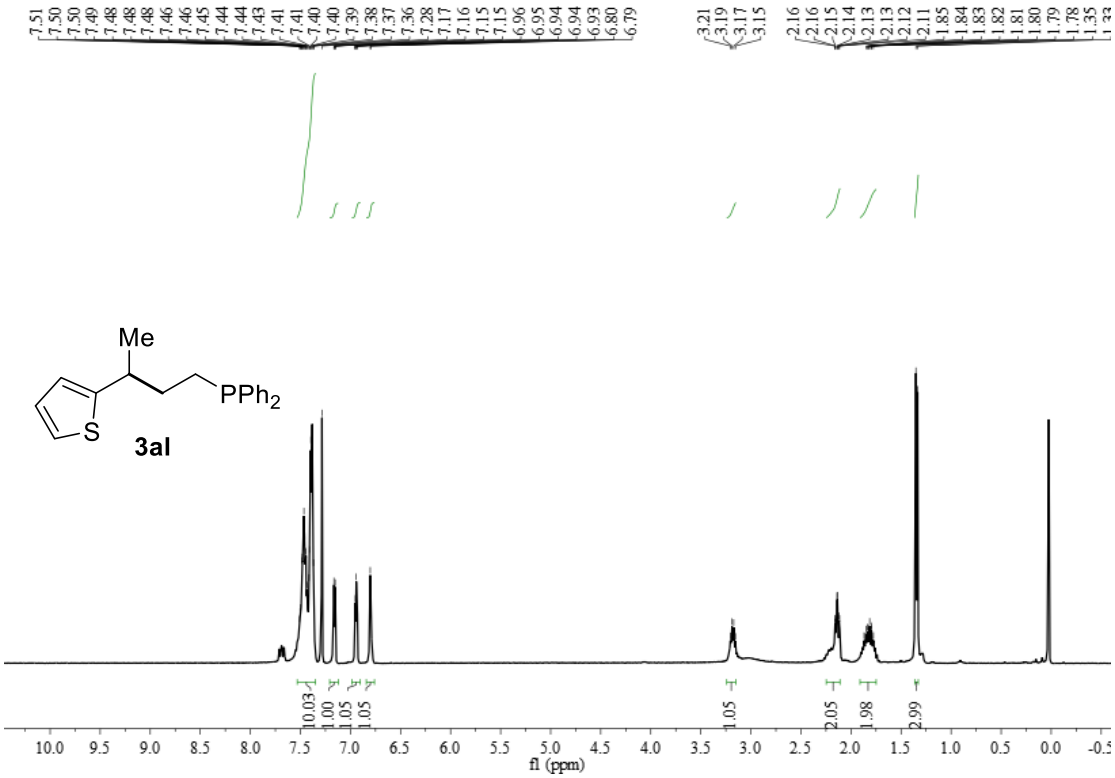

7.53 7.52 7.50 7.36 7.24 7.22 7.20 7.20 7.19 7.19 7.18 7.17 7.16 7.16 7.15 7.14 7.14 7.13 7.11 7.10 7.09 7.09 7.08 7.08 7.07 7.06 7.06 7.04 7.04 7.03 7.03 7.03 7.02 7.01 6.98 6.97 6.96 6.96 6.89 6.88 6.88 6.79 6.78 6.77 6.76 6.61 6.60 3.16 2.96 2.93 2.92 2.90 2.68 2.67 1.40 1.38 1.11 1.09
1.15 1.23 16.87 2.38 1.00 0.69 2.00 0.69 1.69 1.38 2.69 1.01 2.07 3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

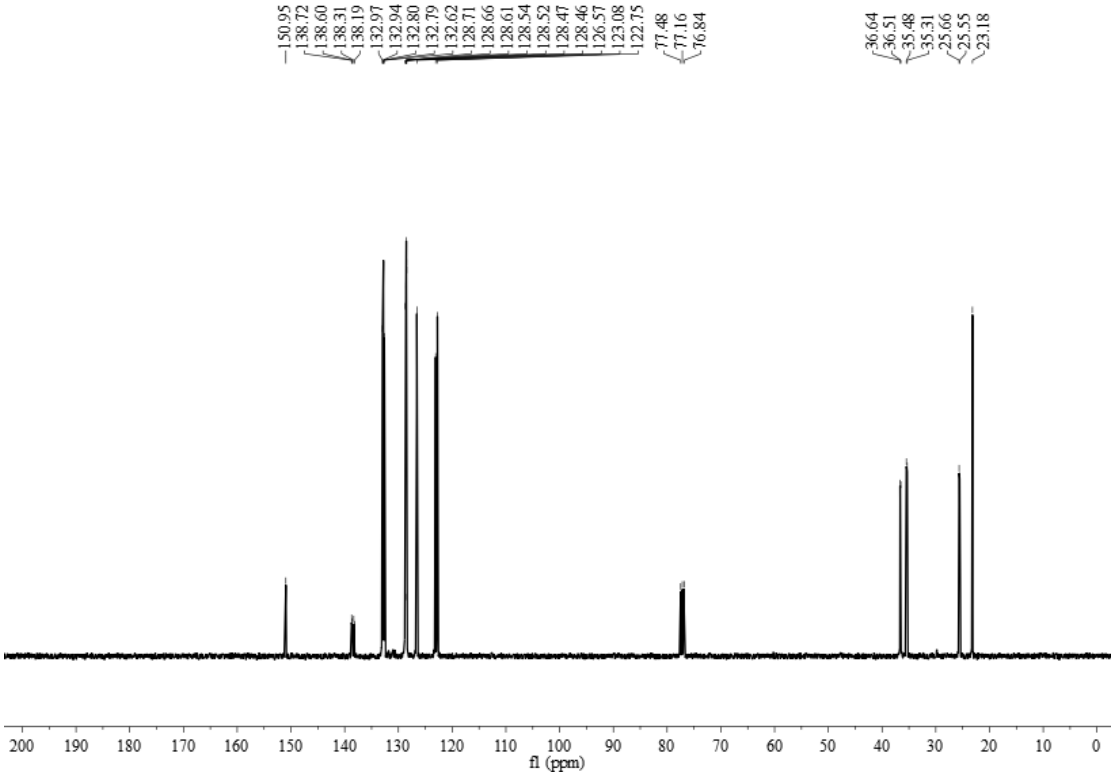

Me
SiPh3
S
3aj
f1 (ppm)

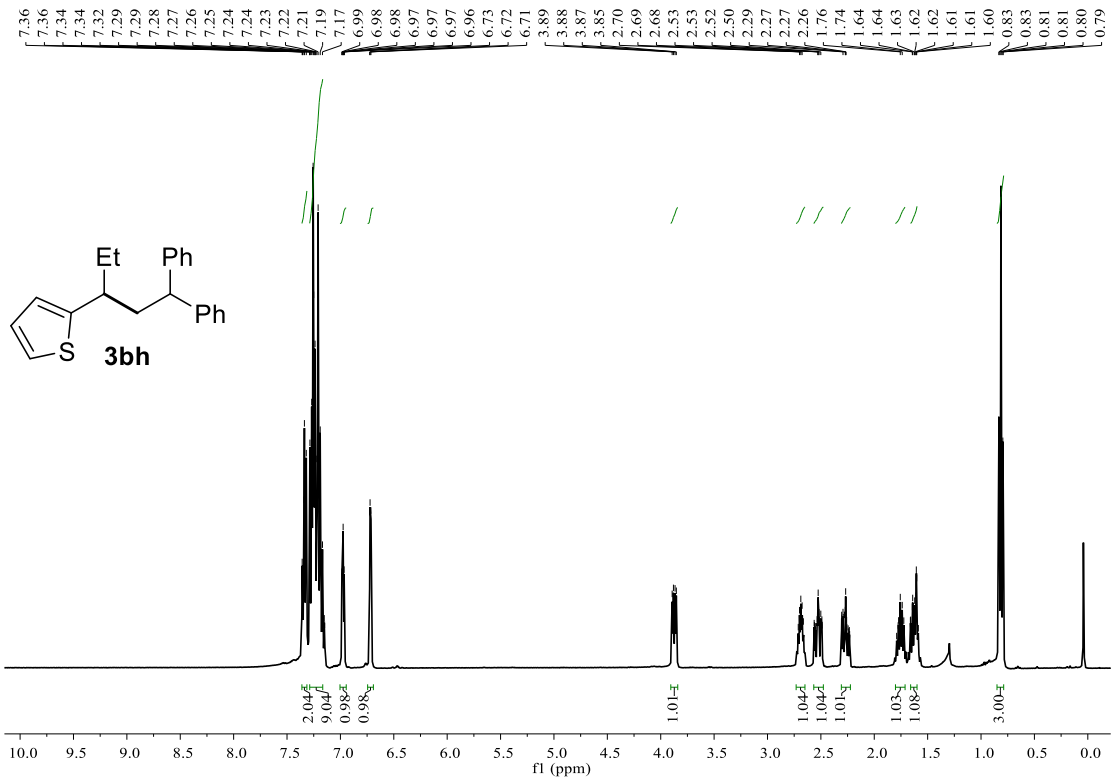

f1 (ppm)

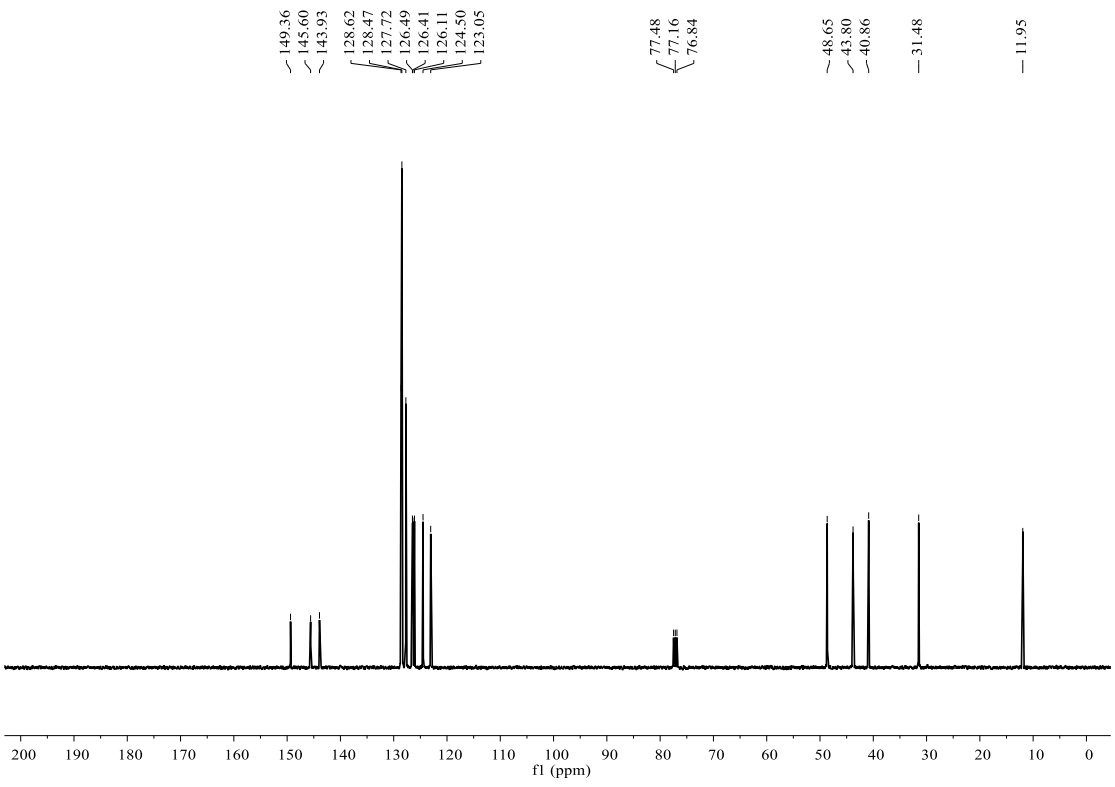

Me
SiPhMe2
S
3ak
fl (ppm)

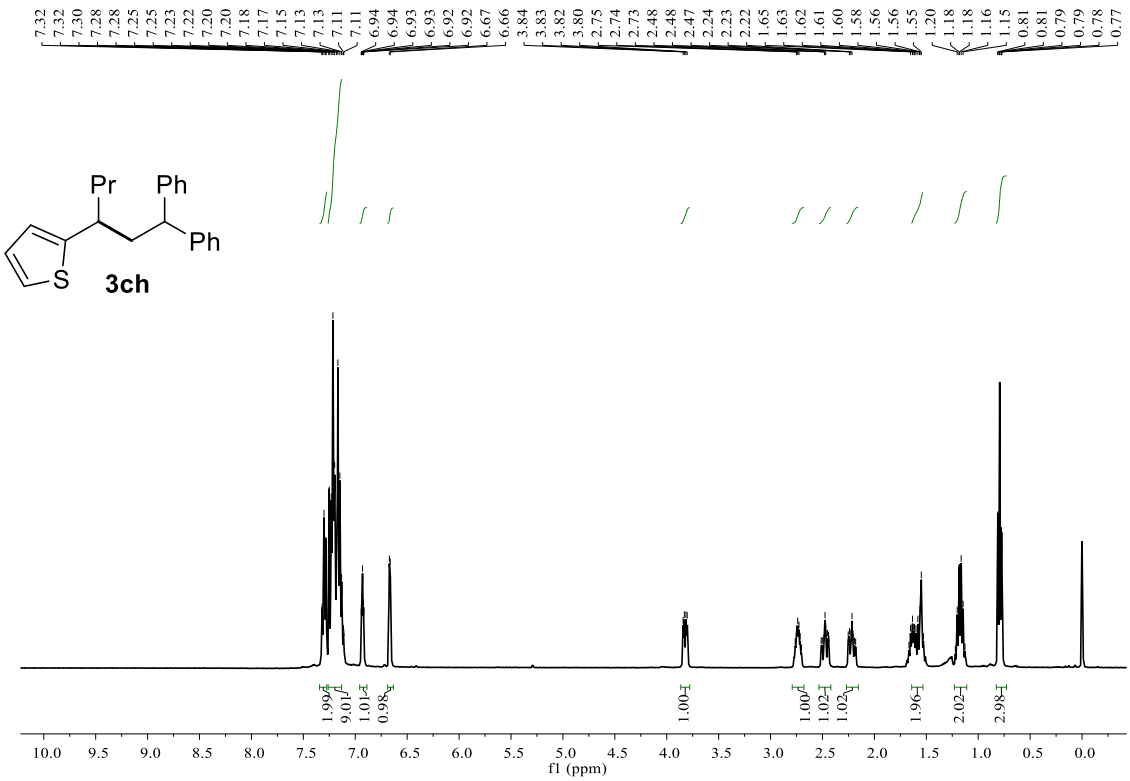

fl (ppm)

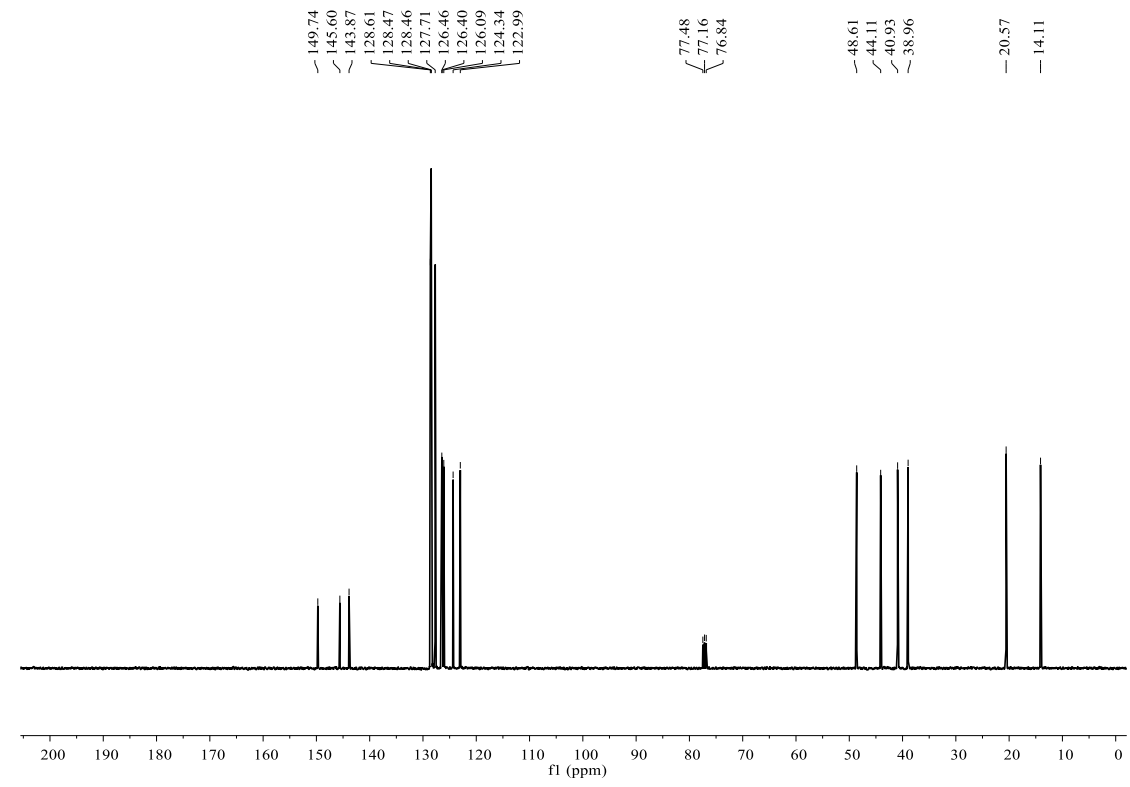

Me
PPh2
S
3al
fl (ppm)

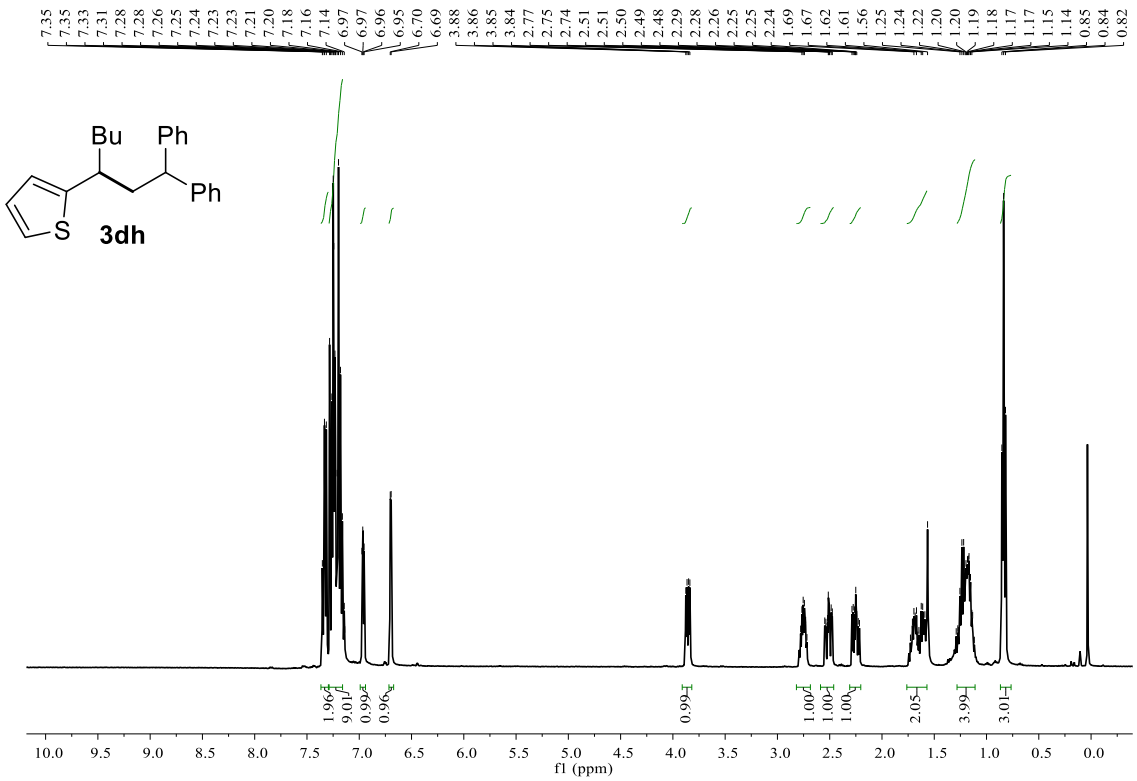

fl (ppm)

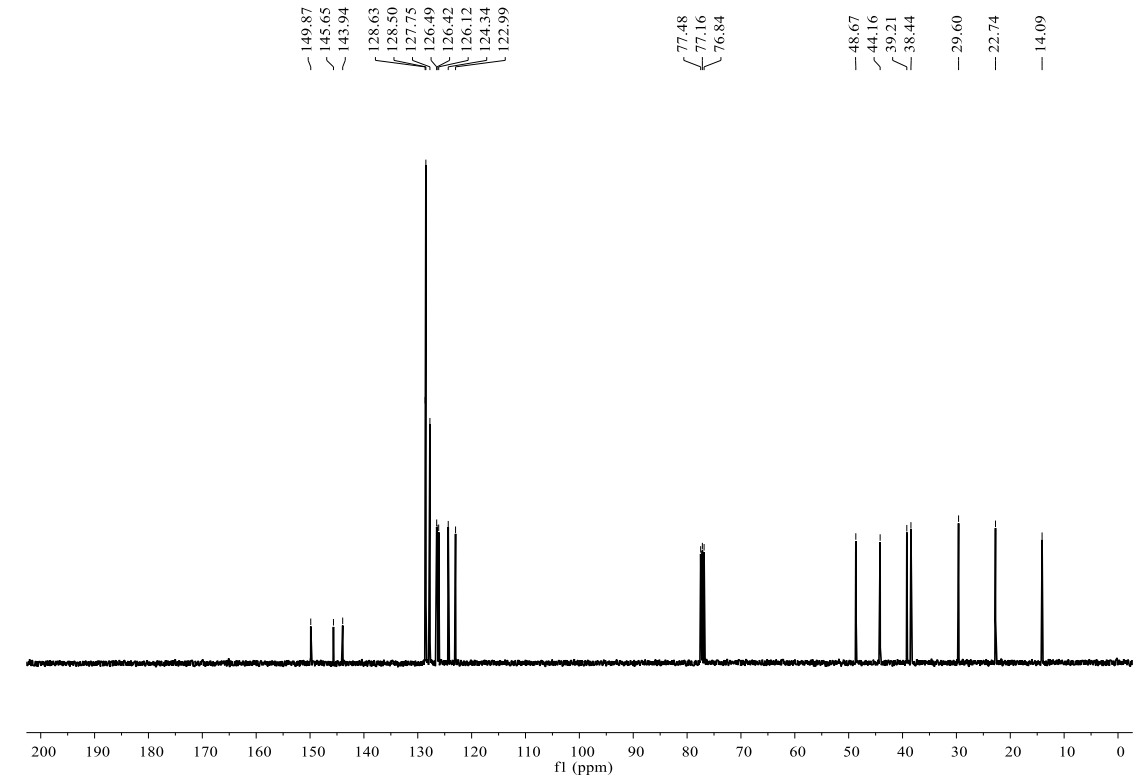

Et
Ph
Ph
S
3bh
f1 (ppm)

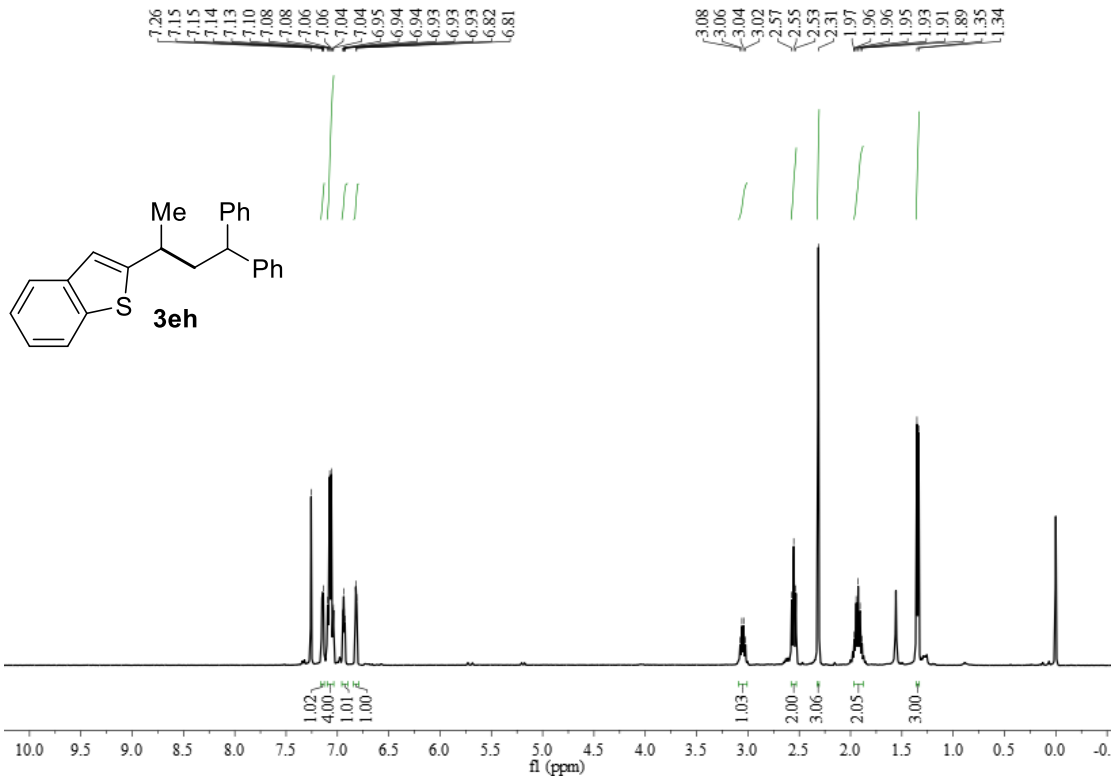

f1 (ppm)


Pr
Ph
Ph
S
3ch
f1 (ppm)


f1 (ppm)


7.35 7.35 7.33 7.31 7.28 7.28 7.26 7.25 7.24 7.23 7.23 7.21 7.20 7.18 7.16 7.14 6.97 6.97 6.96 6.95 6.70 6.69
3.88 3.86 3.85 3.84 2.77 2.75 2.74 2.51 2.51 2.50 2.49 2.48 2.29 2.28 2.26 2.25 2.25 2.24 1.69 1.67 1.62 1.61 1.56 1.25 1.24 1.22 1.20 1.20 1.19 1.18 1.17 1.17 1.15 1.14 0.85 0.84 0.82
Bu
Ph
Ph
S
3dh
1.96 9.01 0.99 0.96 0.99 1.00 1.00 1.00 2.05 3.99 3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.87 145.65 143.94 128.63 128.50 127.75 126.49 126.42 126.12 124.34 122.99
77.48 77.16 76.84
48.67 44.16 39.21 38.44 29.60 22.74 14.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.10
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7.06
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7.04
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6.94
6.94
6.93
6.93
6.93
6.82
6.81
3.08
3.06
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2.57
2.55
2.53
2.31
1.97
1.96
1.96
1.95
1.93
1.91
1.89
1.35
1.34
Me
Ph
Ph
S
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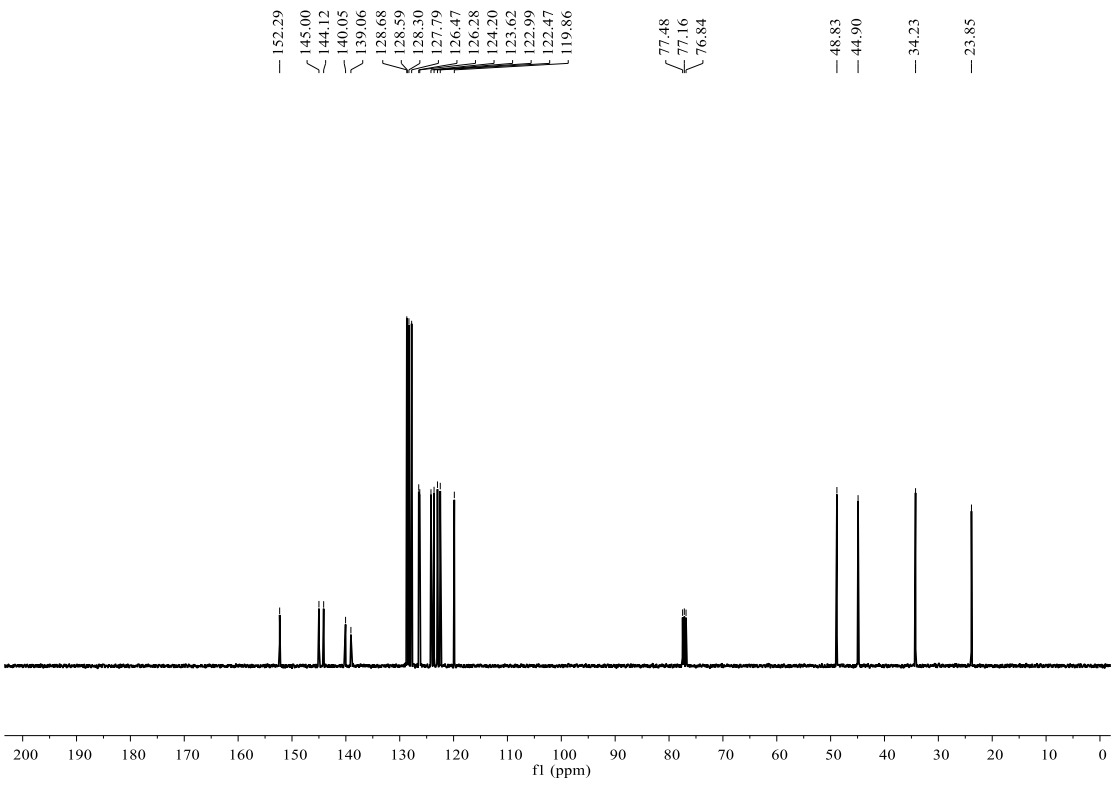
4.00
1.01
1.00
1.03
2.00
3.06
2.05
3.00
fl (ppm)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126.47
126.28
124.20
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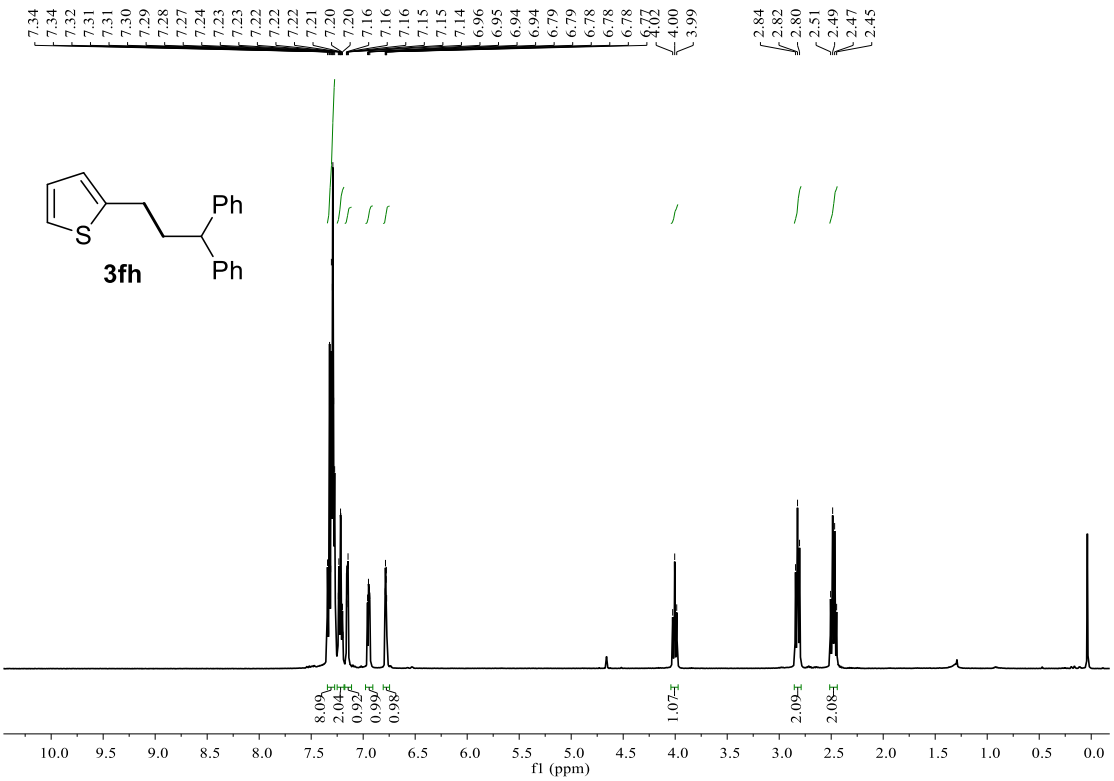
122.99
122.47
119.86
77.48
77.16
76.84
48.83
44.90
34.23
23.85
fl (ppm)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7.34
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7.24
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7.23
7.22
7.22
7.22
7.21
7.20
7.20
7.16
7.16
7.16
7.15
7.15
7.14
6.96
6.95
6.94
6.94
6.79
6.79
6.78
6.78
6.78
6.77
4.02
4.00
3.99
2.84
2.82
2.80
2.51
2.49
2.47
2.45
Ph
Ph
S
3fh
8.09
2.04
0.92
0.99
0.98
1.07
2.09
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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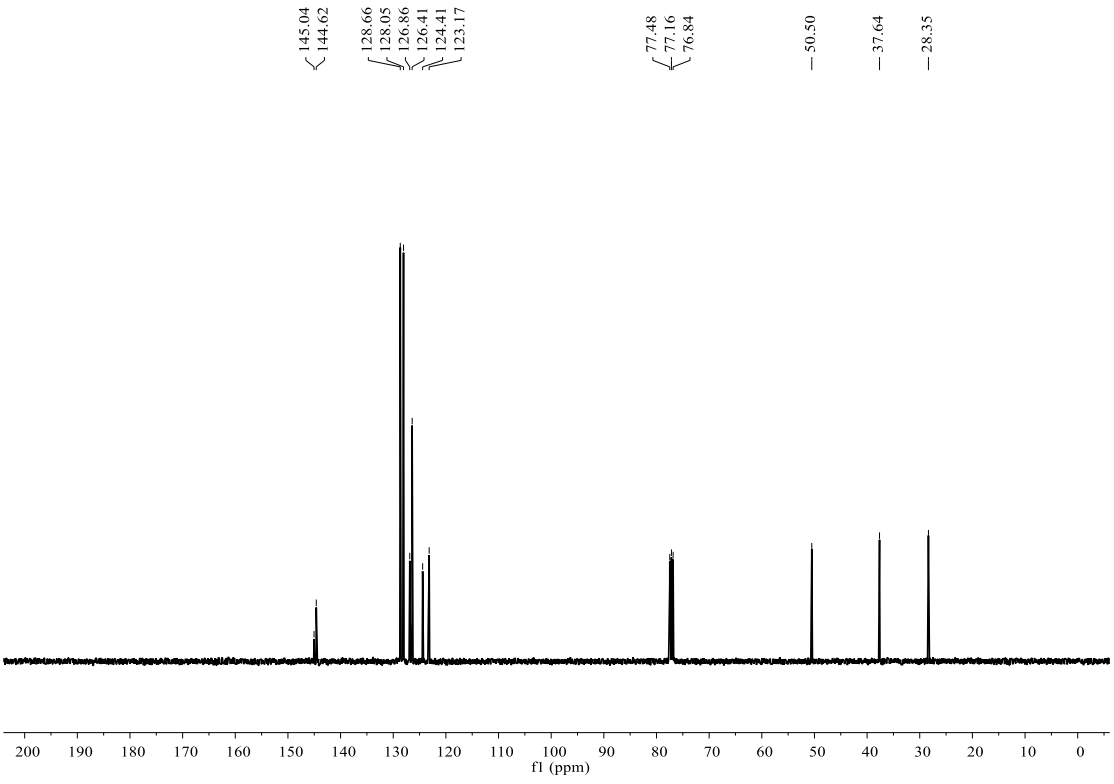
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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123.17
77.48
77.16
76.84
50.50
37.64
28.35
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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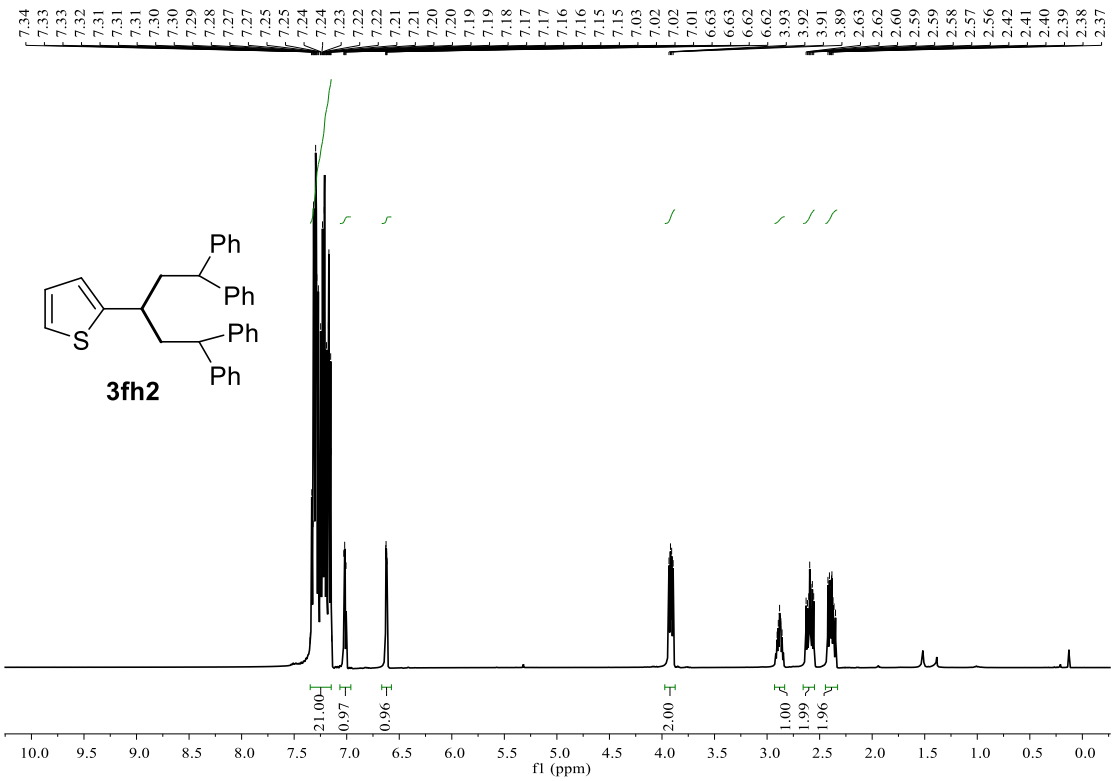
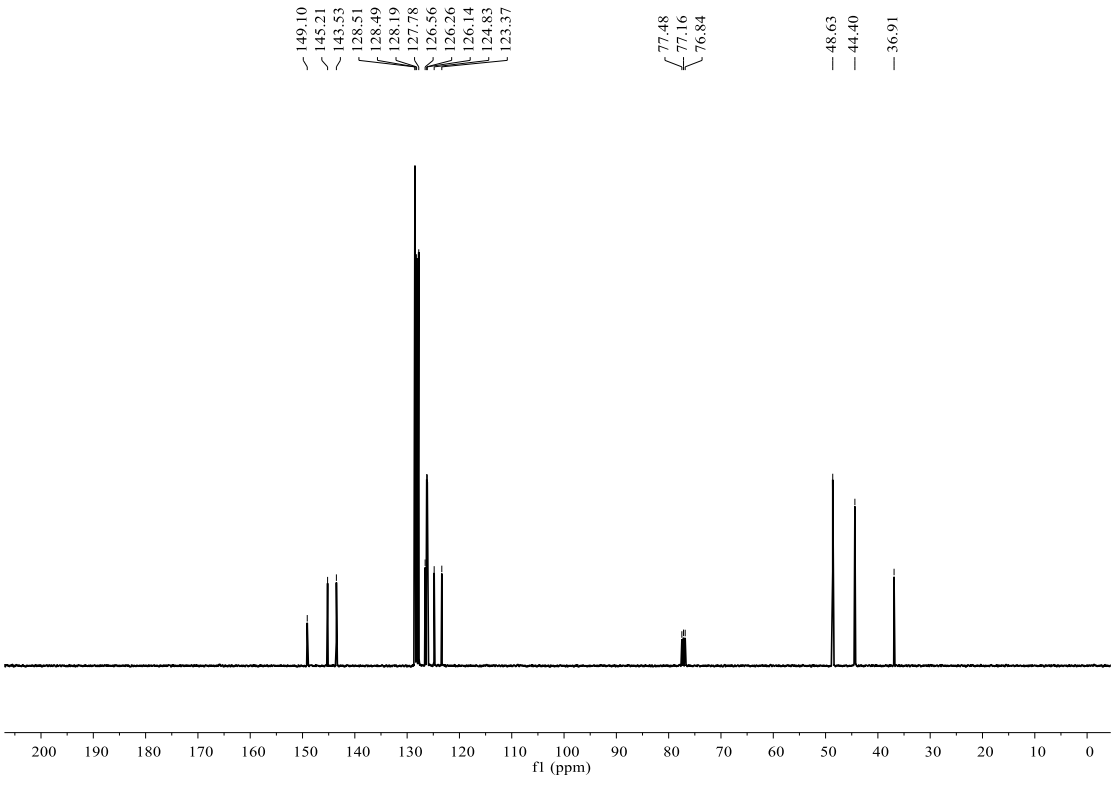
50
40
30
20
10
0
f1 (ppm)


7.34 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.28 7.27 7.27 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.15 7.03 7.02 7.02 7.01 6.63 6.63 6.62 6.62 3.93 3.92 3.91 3.89 2.63 2.62 2.60 2.59 2.59 2.58 2.57 2.56 2.42 2.41 2.40 2.39 2.38 2.37
Ph
Ph
Ph
Ph
S
3fh2
21.00
0.97
0.96
2.00
1.00
1.99
1.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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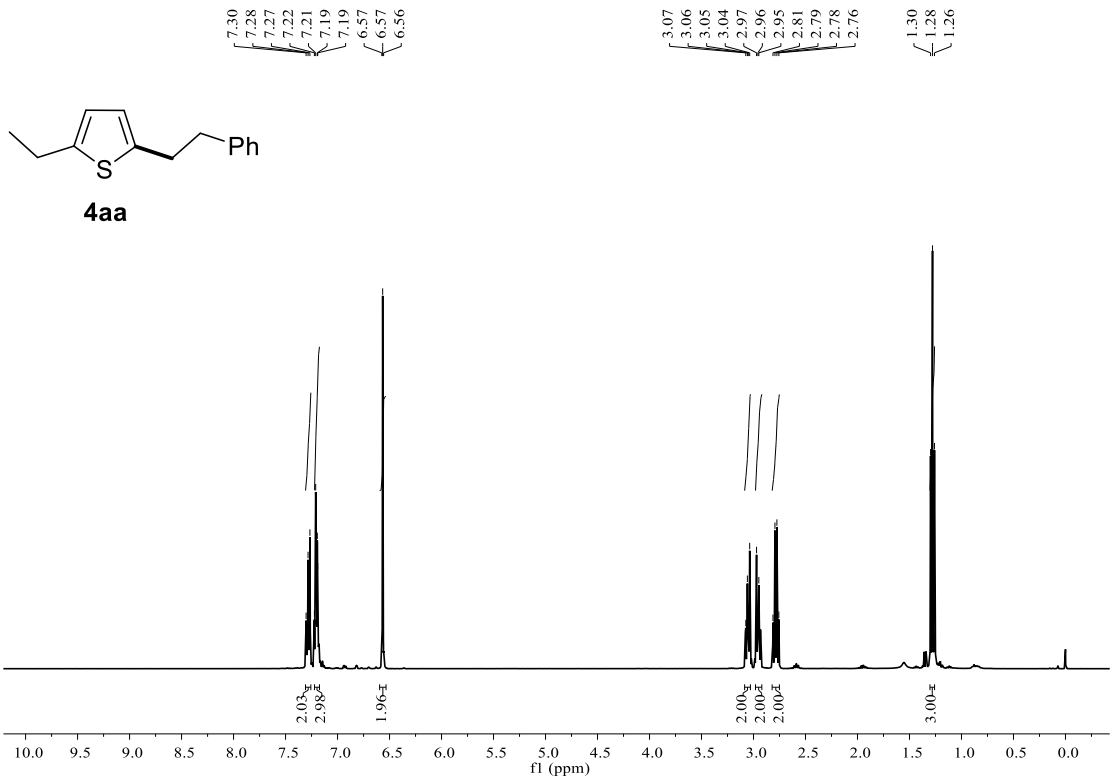
126.14
124.83
123.37
77.48
77.16
76.84
48.63
44.40
36.91
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.22
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7.19
7.19
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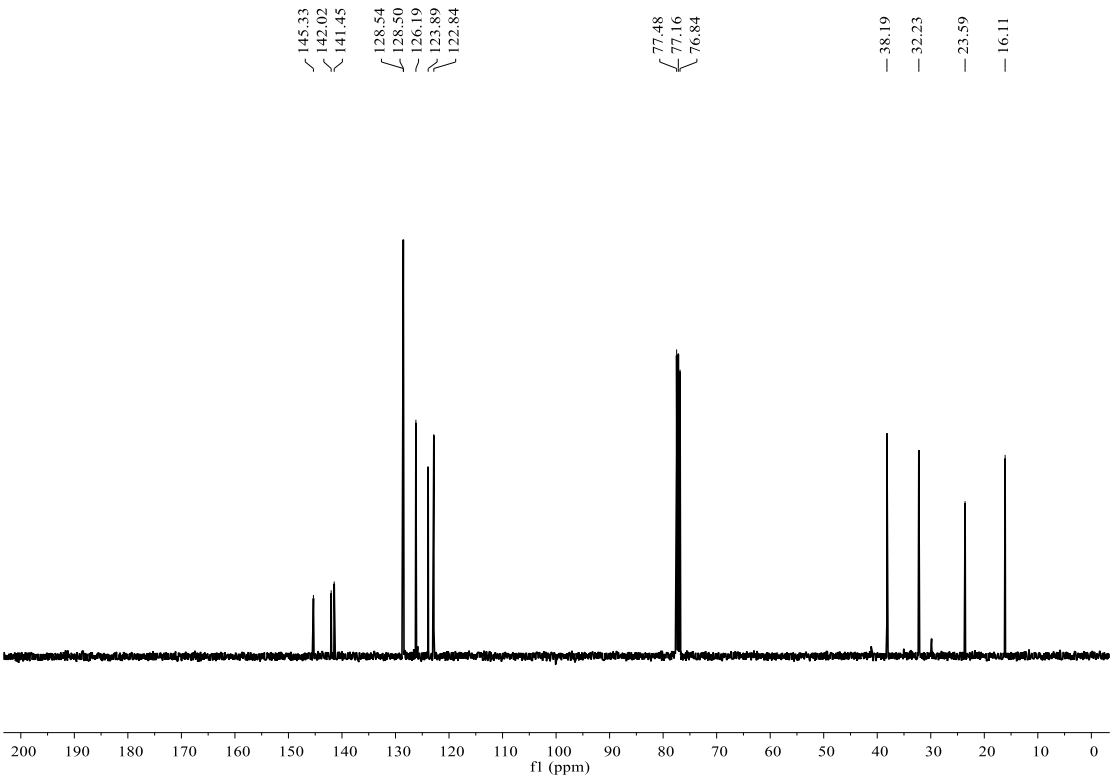
6.56
3.07
3.06
3.05
3.04
2.97
2.96
2.95
2.81
2.79
2.78
2.76
1.30
1.28
1.26
Ph
S
4aa
2.03
2.98
1.96
2.00
2.00
2.00
3.00
f1 (ppm)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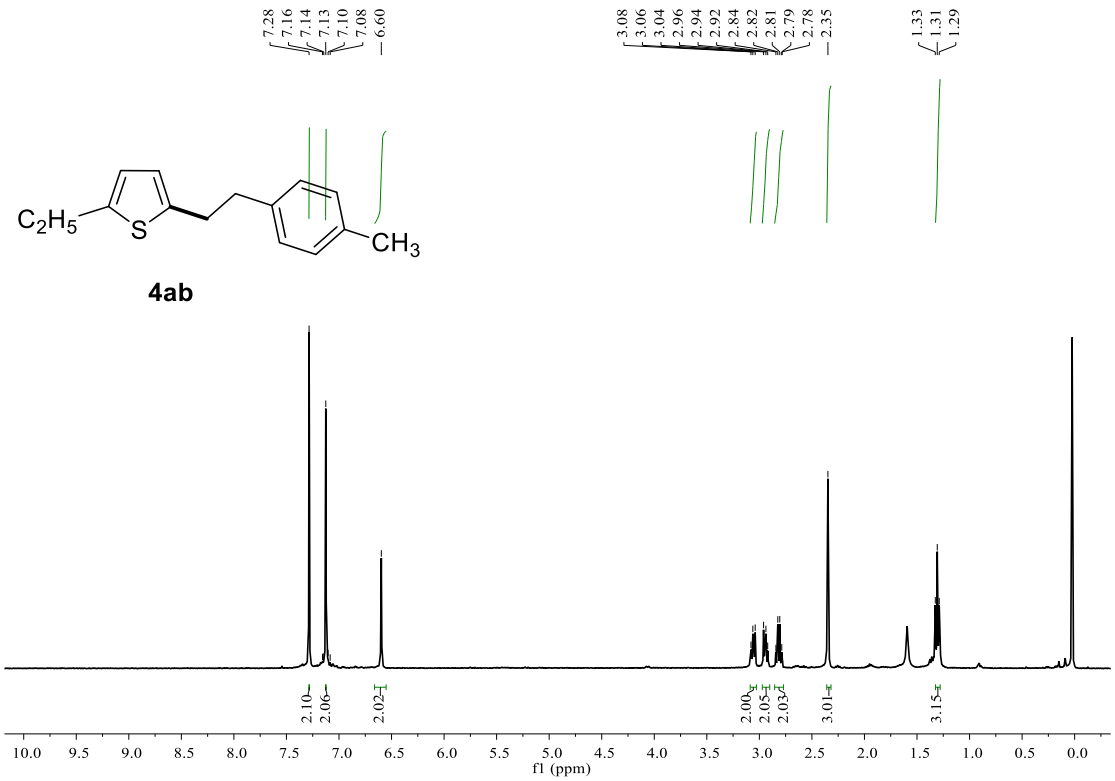
76.84
38.19
32.23
23.59
16.11
f1 (ppm)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7.14
7.13
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7.08
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3.08
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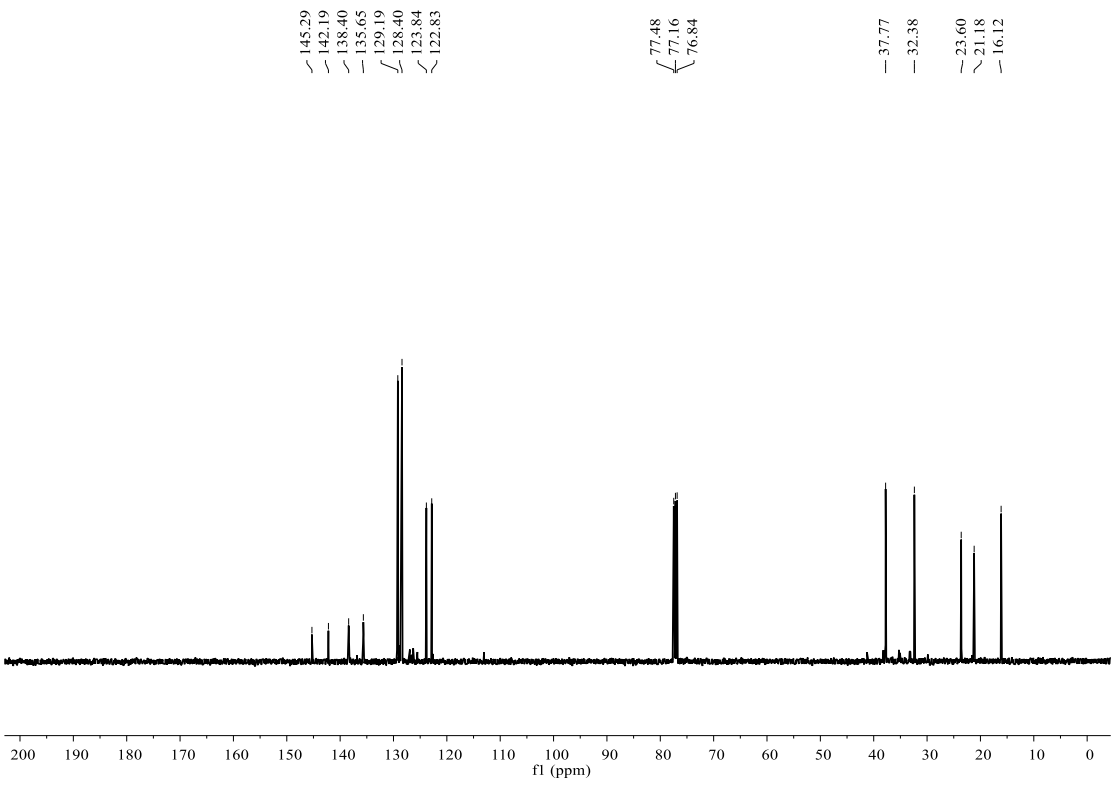
3.04
2.96
2.94
2.92
2.84
2.82
2.81
2.79
2.78
2.35
1.33
1.31
1.29
C2H5
S
CH3
2.10
2.06
2.02
2.00
2.05
2.03
3.01
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4ab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122.83
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77.16
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23.60
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16.12
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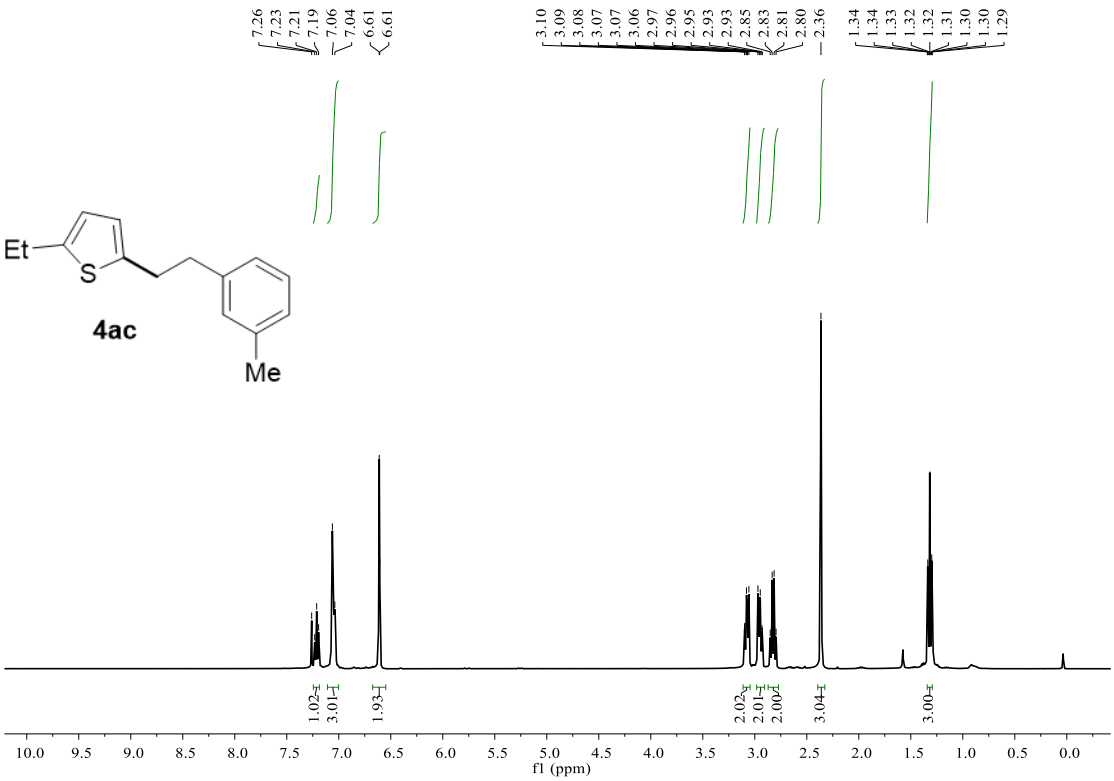
f1 (ppm)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3.09
3.08
3.07
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2.85
2.83
2.81
2.80
2.36
1.34
1.34
1.33
1.32
1.32
1.31
1.30
1.30
1.29
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S
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Me
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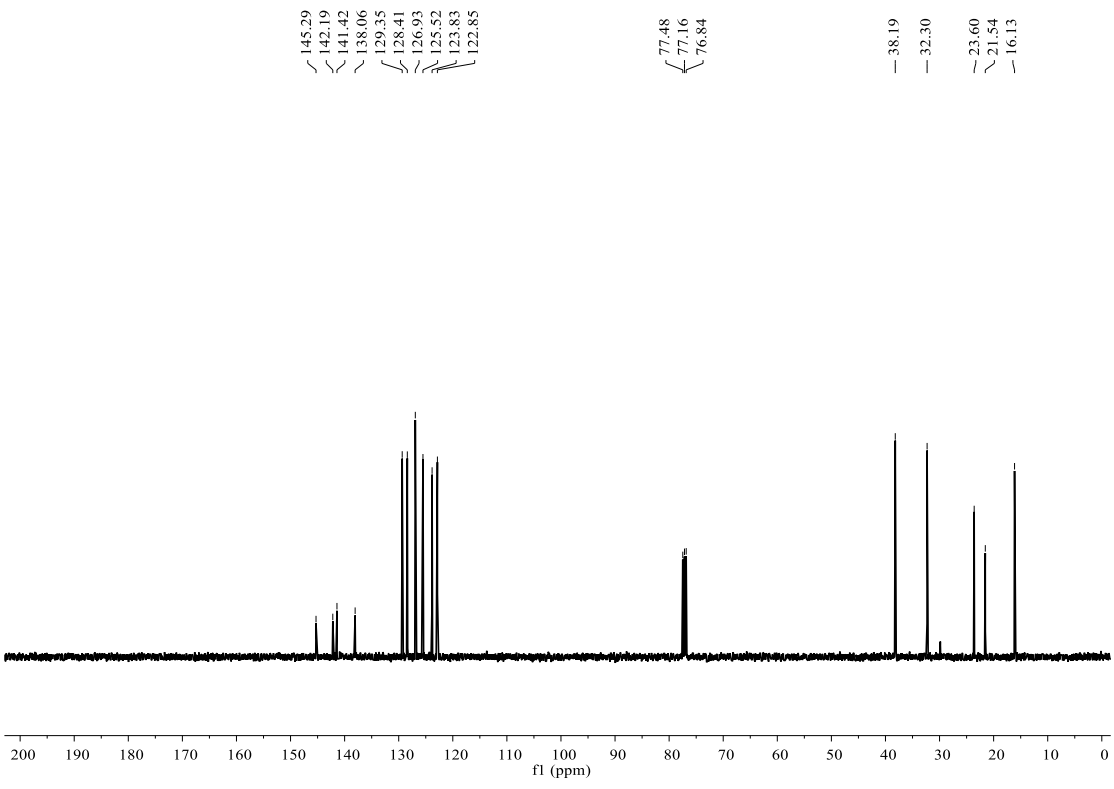
3.01
1.93
2.02
2.01
2.00
3.04
3.00
f1 (ppm)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77.16
76.84
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23.60
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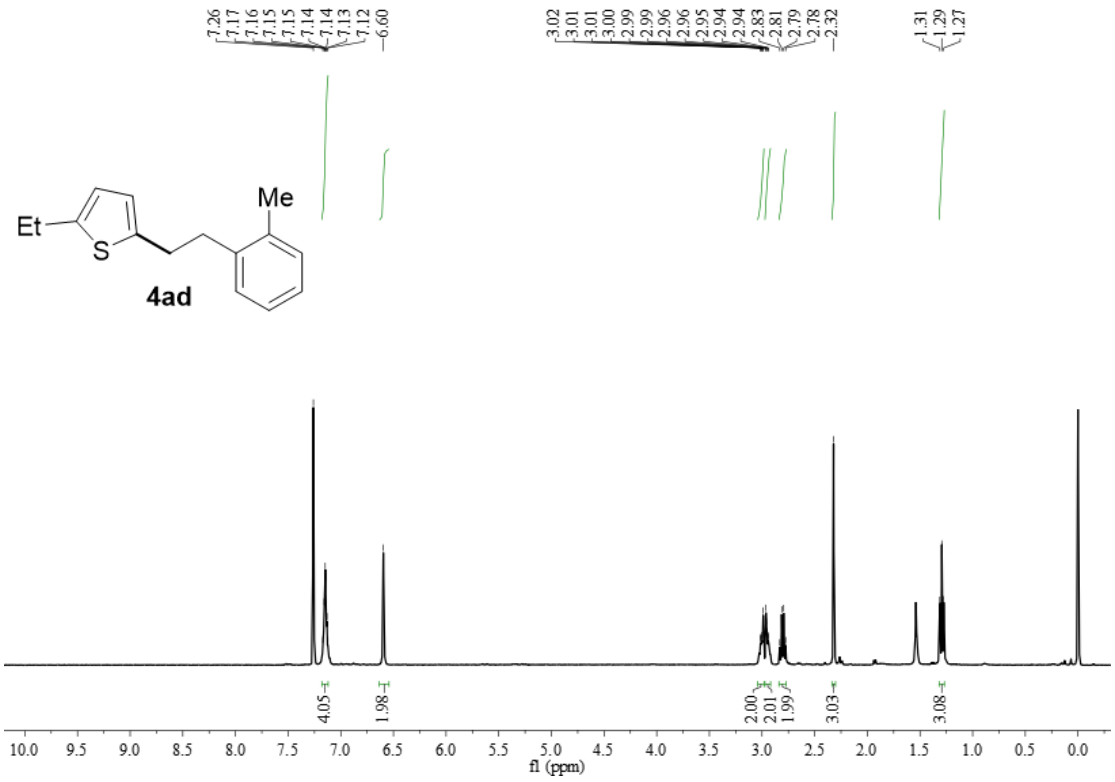
16.13
f1 (ppm)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3.01
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3.00
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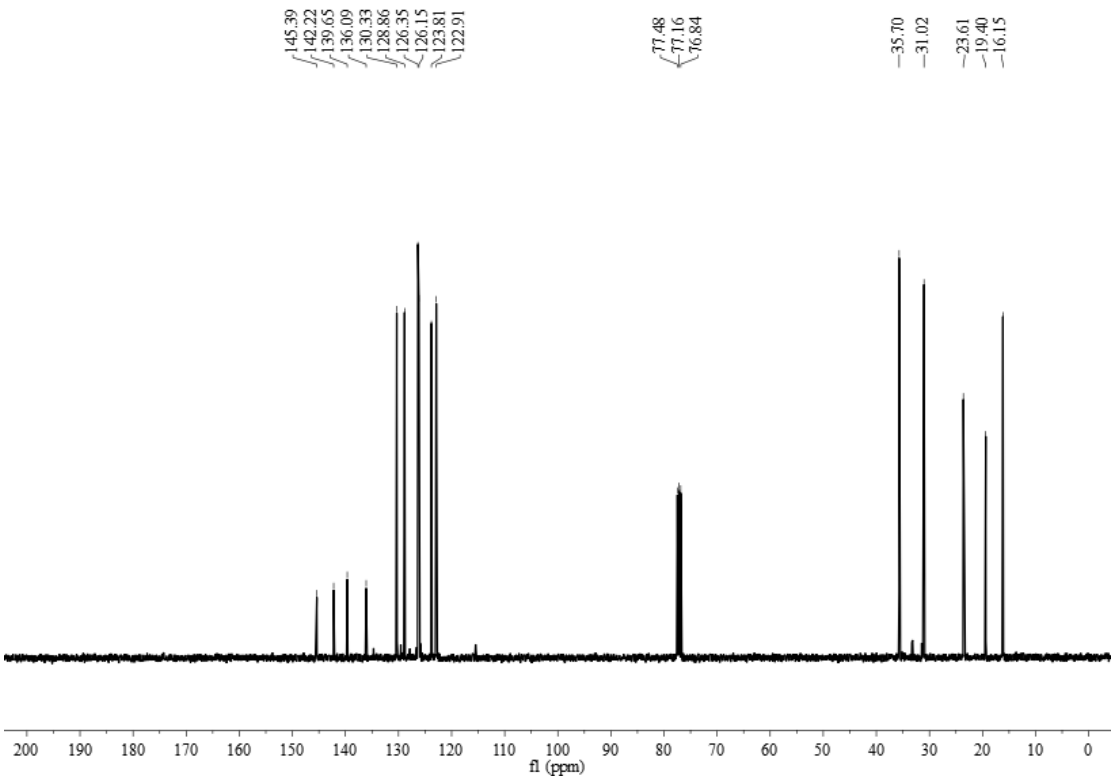
2.96
2.96
2.95
2.94
2.94
2.83
2.81
2.79
2.78
2.32
1.31
1.29
1.27
Et
S
Me
4ad
4.05
1.98
2.00
2.01
1.99
3.03
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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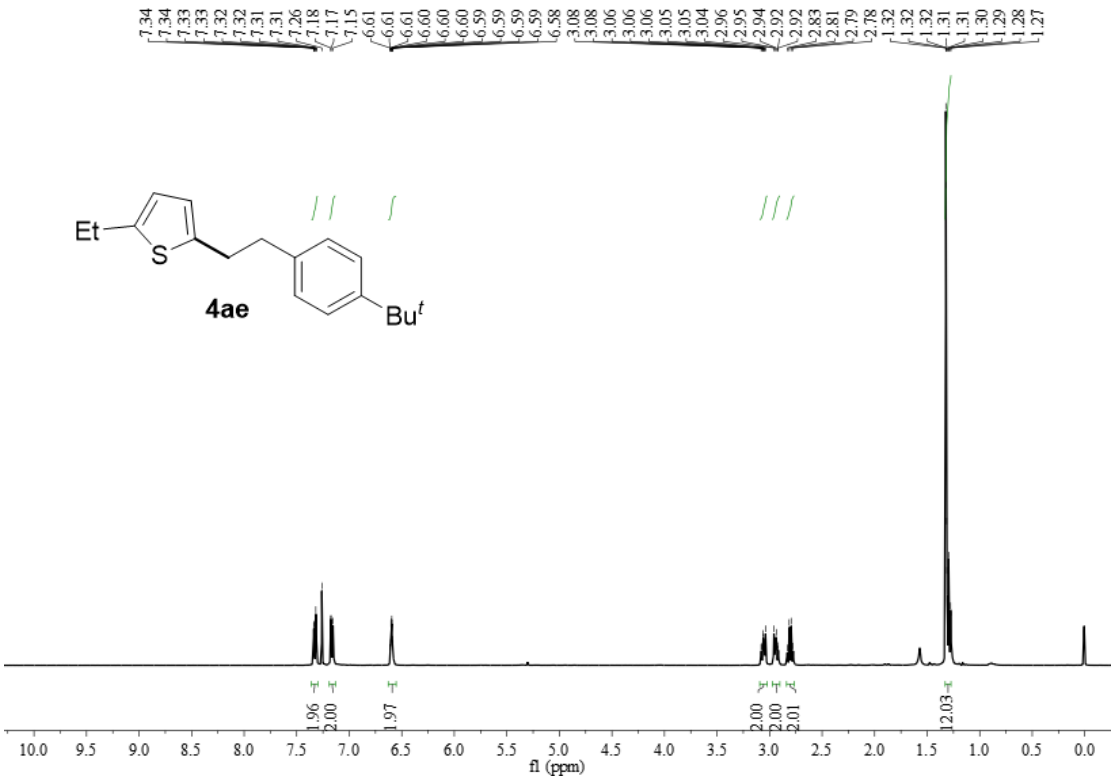
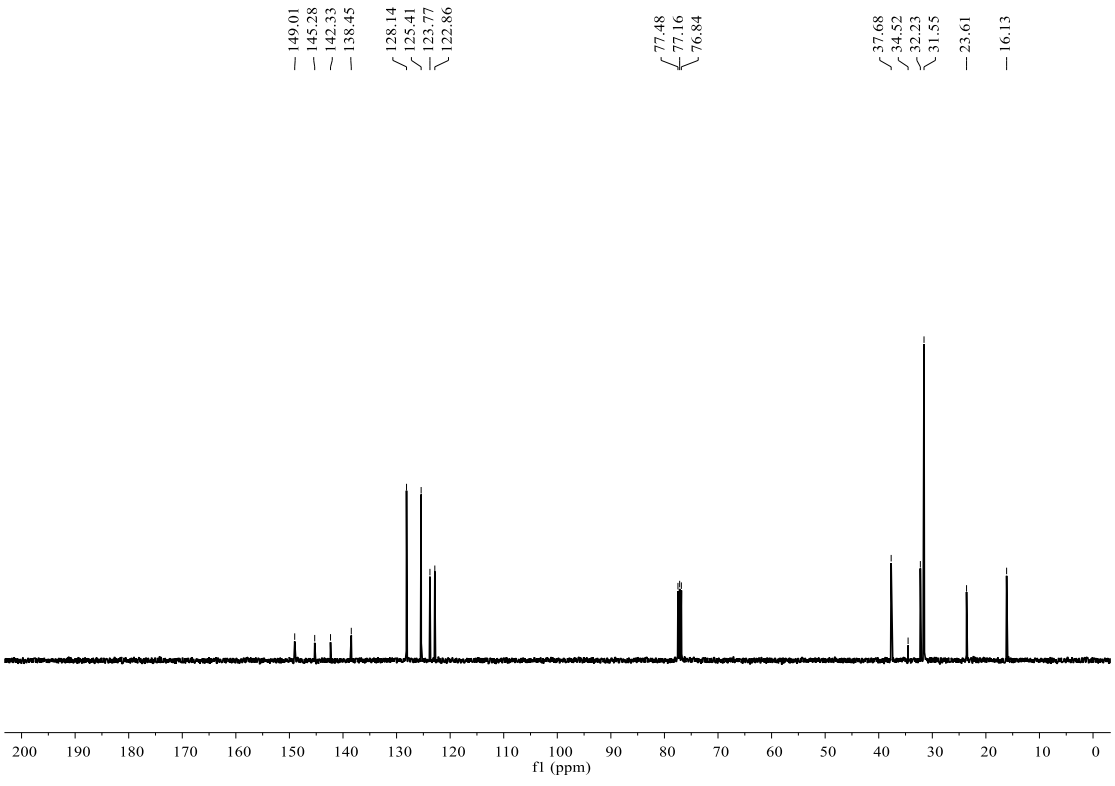
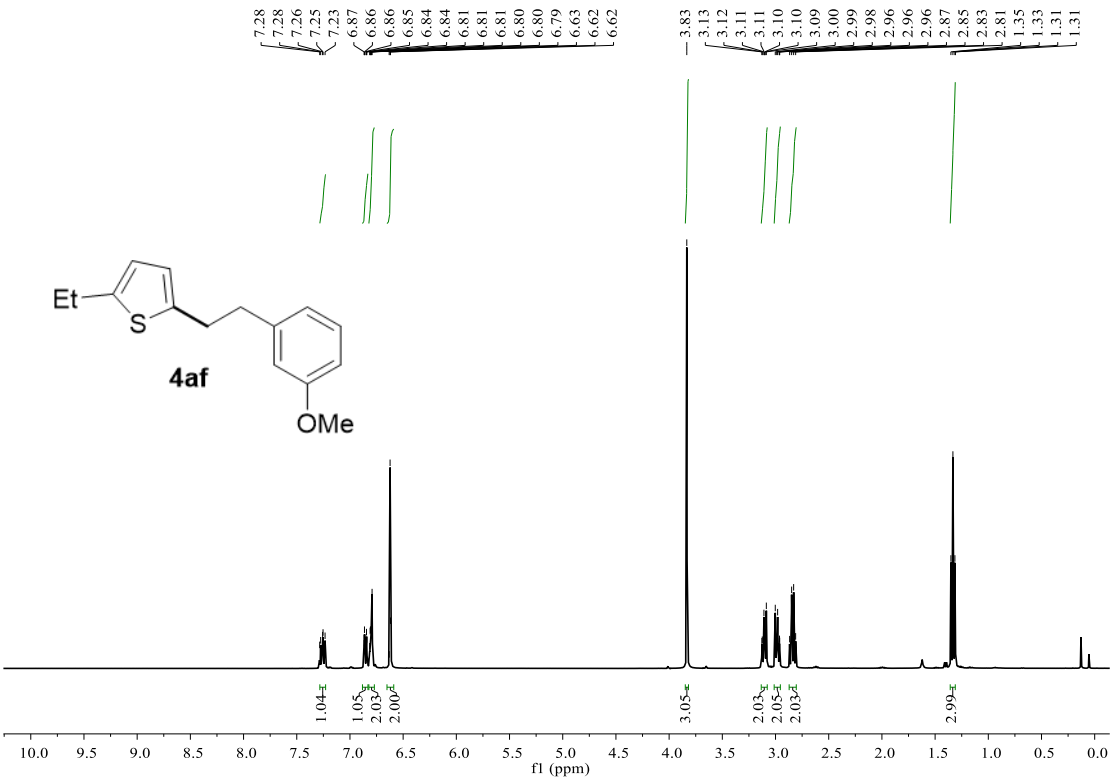
128.86
126.35
126.15
123.81
122.91
77.48
77.16
76.84
35.70
31.02
23.61
19.40
16.15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Et
S
4ae
Bu^t
fl (ppm)


fl (ppm)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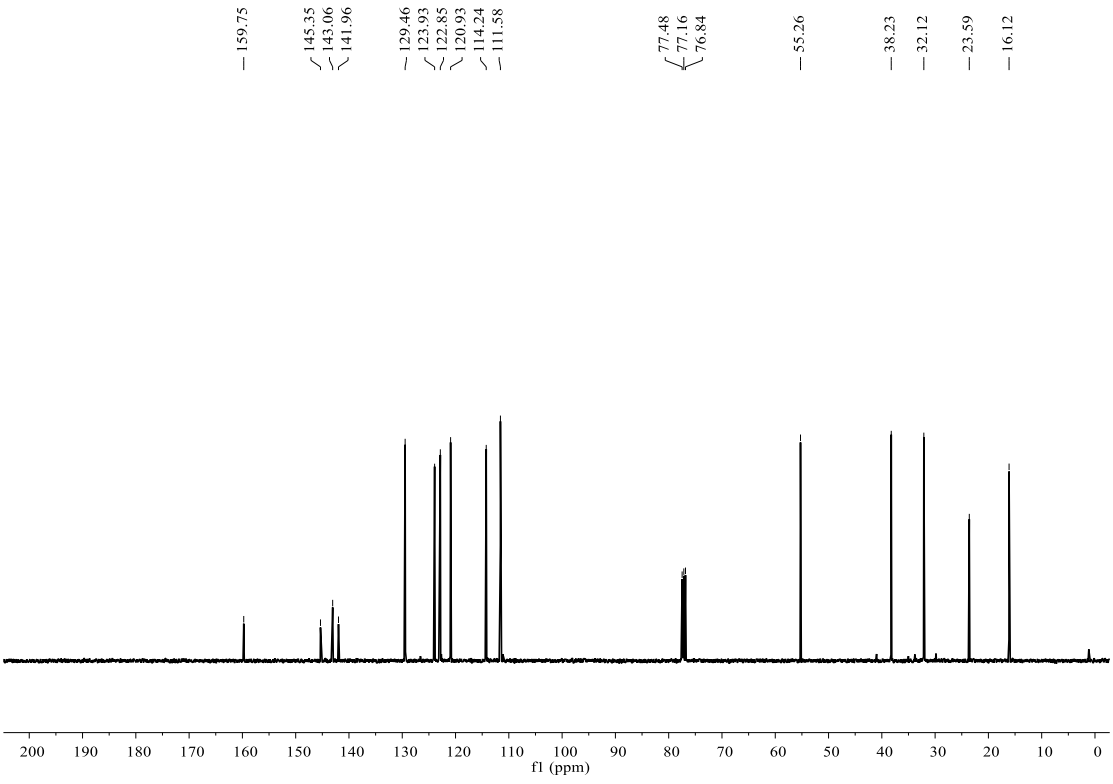
6.81
6.81
6.80
6.80
6.79
6.63
6.62
6.62
3.83
3.13
3.12
3.11
3.11
3.10
3.10
3.09
3.00
2.99
2.98
2.96
2.96
2.96
2.87
2.85
2.83
2.81
1.35
1.33
1.31
1.31
Et
S
4af
OMe
1.04
1.05
2.03
2.00
3.05
2.03
2.05
2.03
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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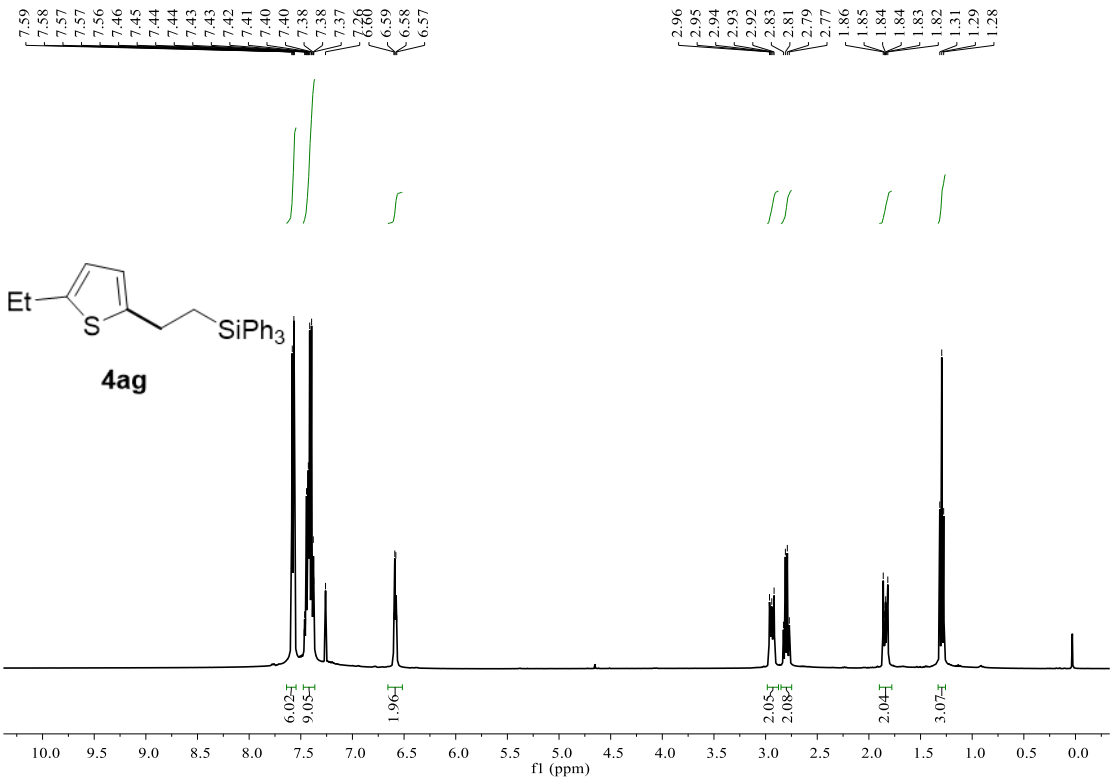
122.85
120.93
114.24
111.58
77.48
77.16
76.84
55.26
38.23
32.12
23.59
16.12
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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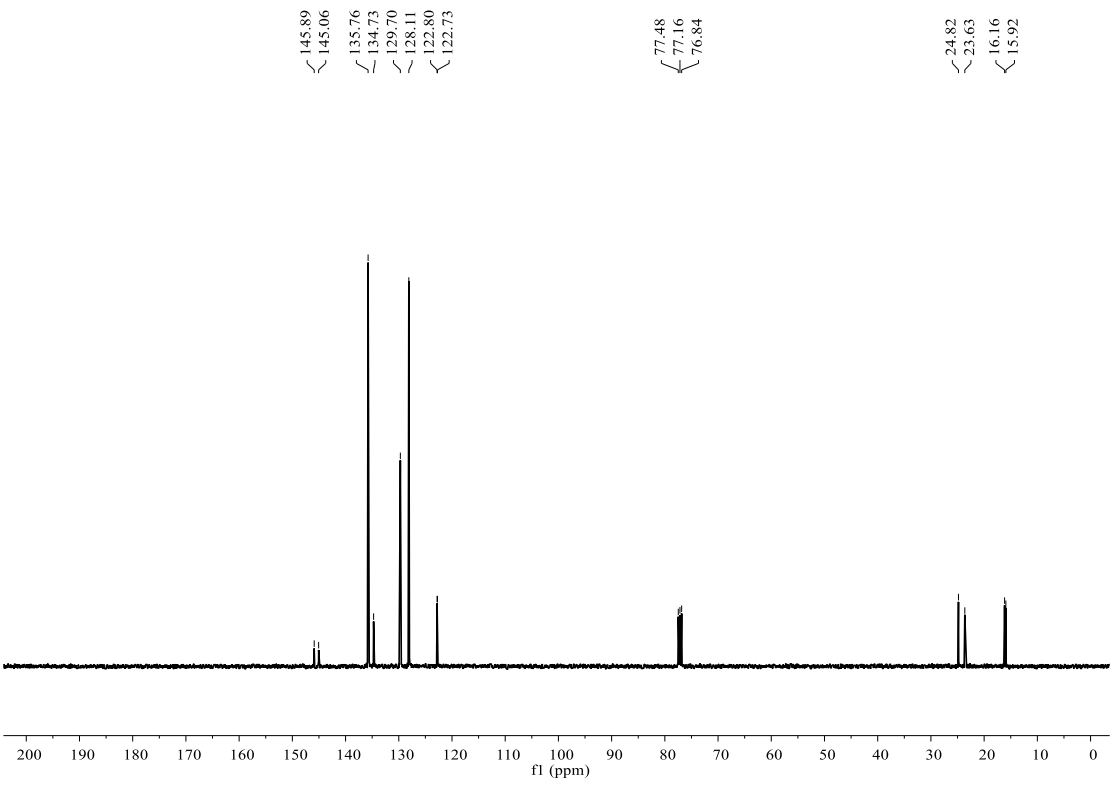
2.83
2.81
2.79
2.77
1.86
1.85
1.84
1.84
1.83
1.82
1.31
1.29
1.28
Et
S
SiPh3
4ag
6.02
9.05
1.96
2.05
2.08
2.04
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.70
128.11
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122.73
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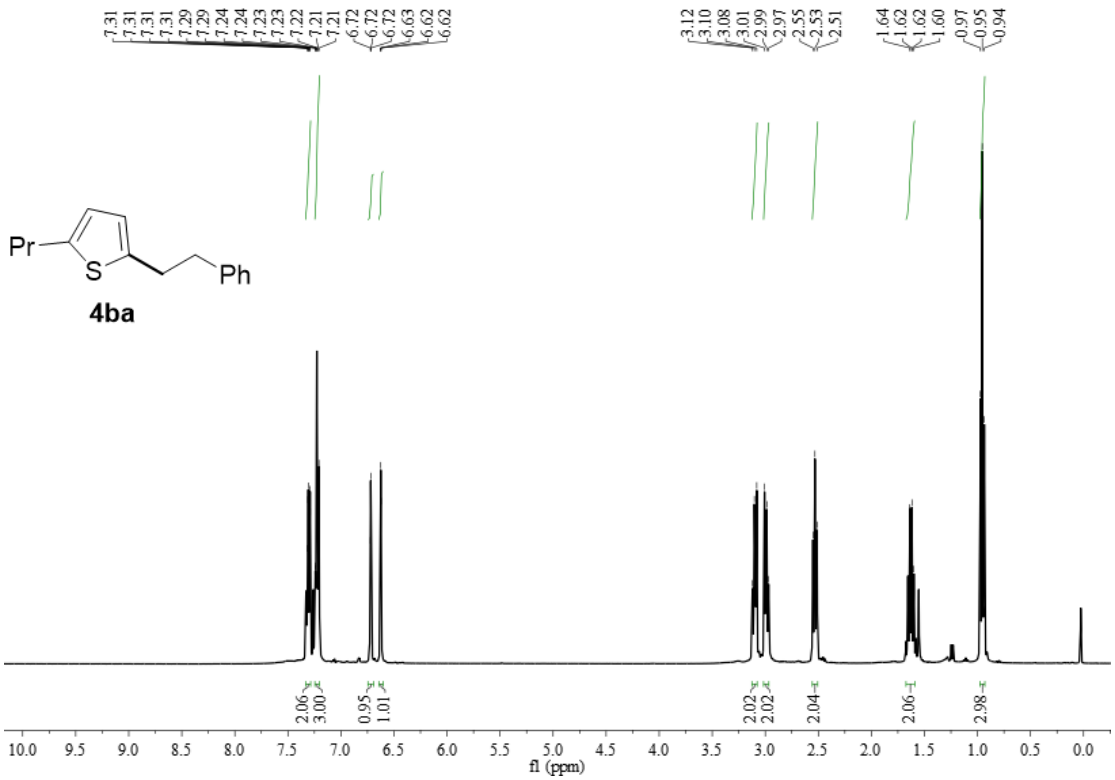
77.16
76.84
24.82
23.63
16.16
15.92
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.23
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7.21
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6.62
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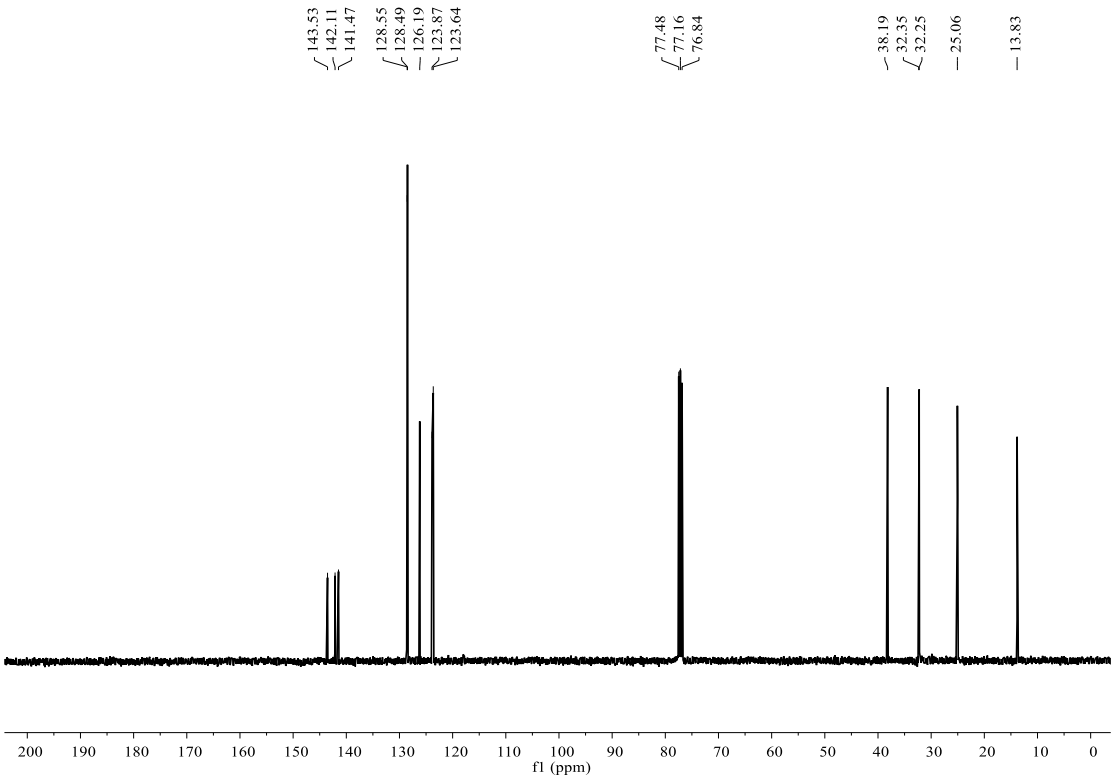
3.10
3.08
3.01
2.99
2.97
2.55
2.53
2.51
1.64
1.62
1.62
1.60
0.97
0.95
0.94
Pr
S
Ph
4ba
2.06
3.00
0.95
1.01
2.02
2.02
2.04
2.06
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.16
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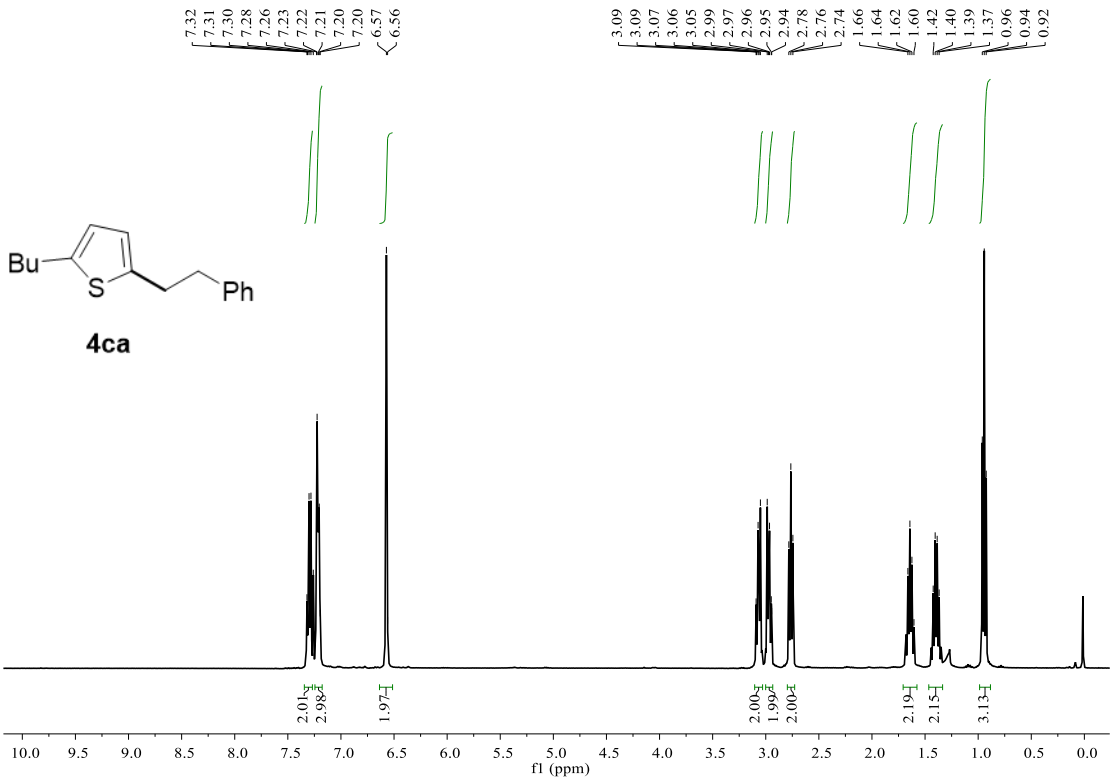
32.25
25.06
13.83
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.20
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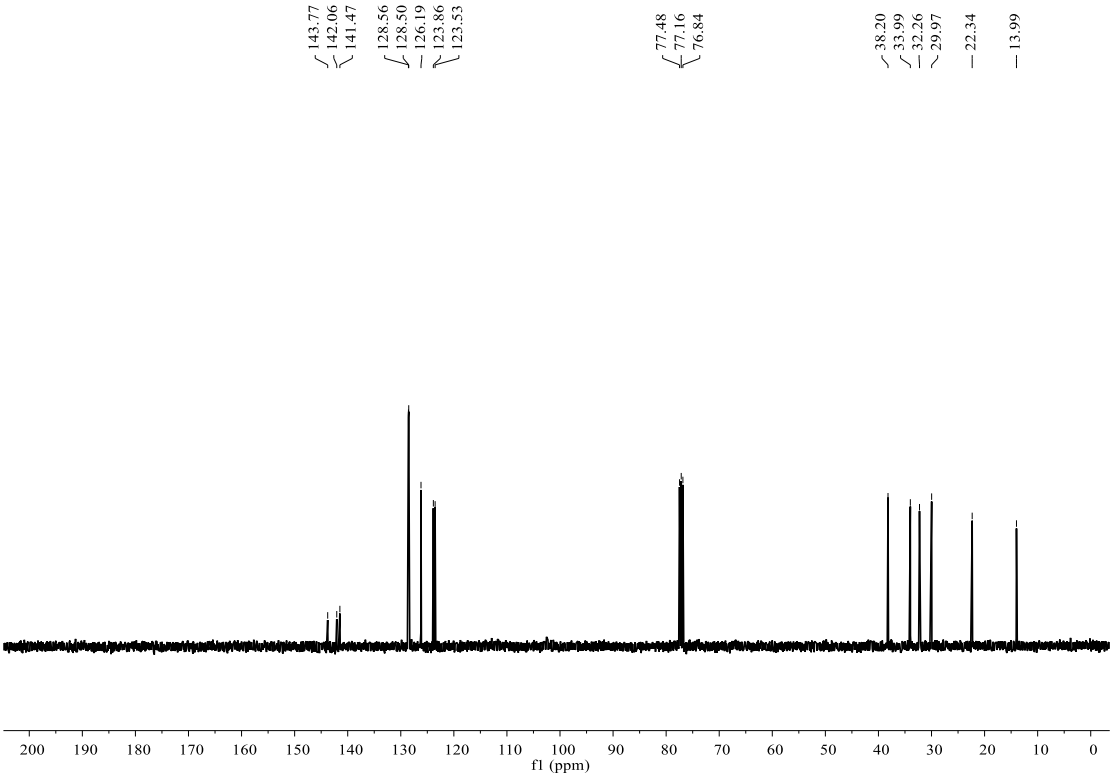
6.56
3.09
3.09
3.07
3.06
3.05
2.99
2.97
2.96
2.95
2.94
2.78
2.76
2.74
1.66
1.64
1.62
1.60
1.42
1.40
1.39
1.37
0.96
0.94
0.92
Bu
S
Ph
4ca
2.01
2.98
1.97
2.00
1.99
2.00
2.19
2.15
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.16
76.84
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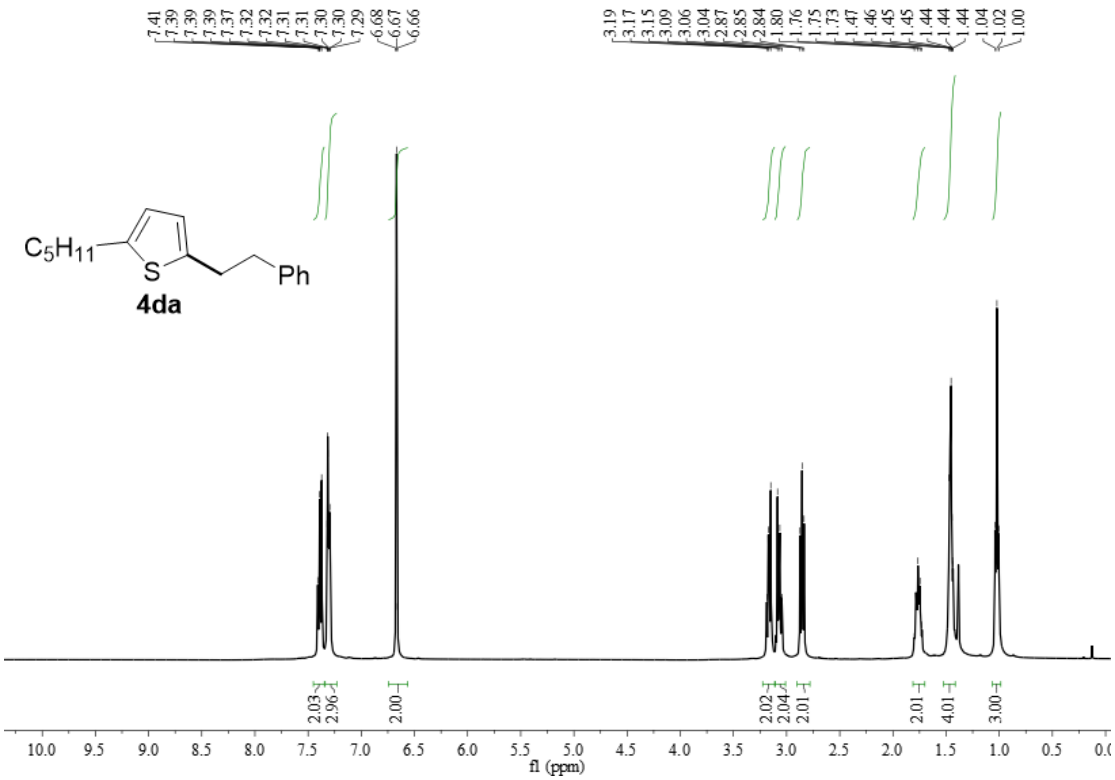
32.26
29.97
22.34
13.99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.66
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3.17
3.15
3.09
3.06
3.04
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2.85
2.84
1.80
1.76
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1.73
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1.46
1.45
1.45
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1.44
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1.02
1.00
C5H11
S
Ph
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2.03
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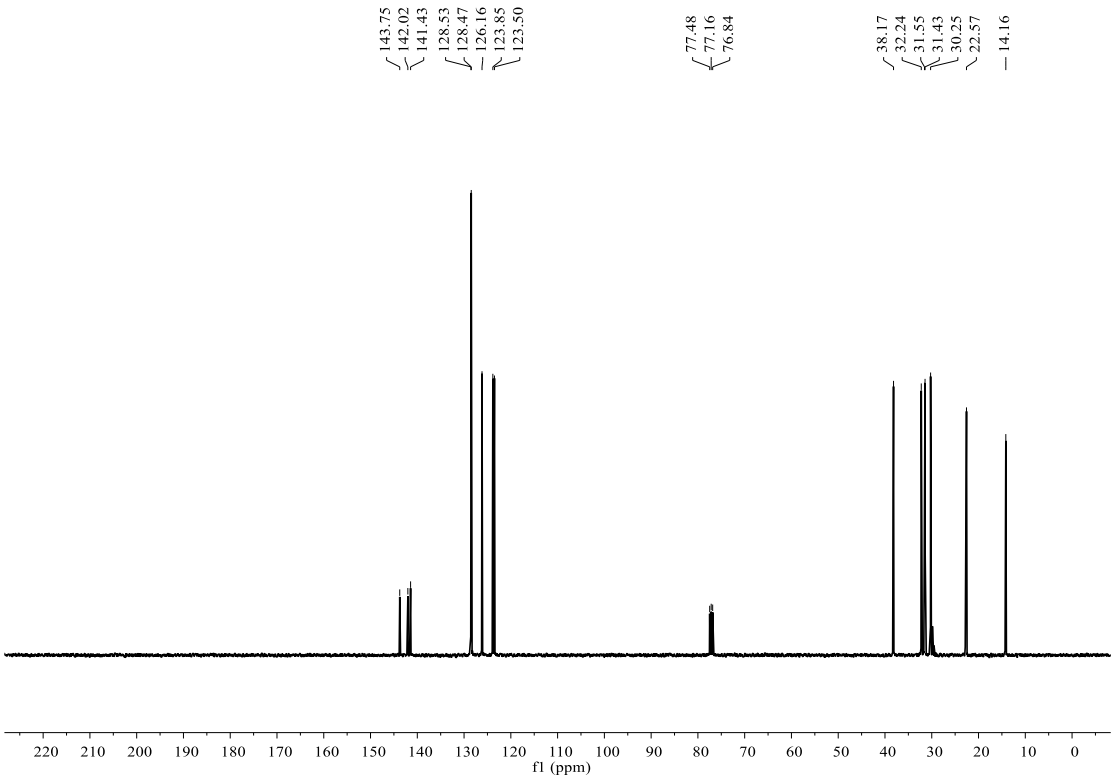
2.00
2.02
2.04
2.01
2.01
4.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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126.16
123.85
123.50
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77.16
76.84
38.17
32.24
31.55
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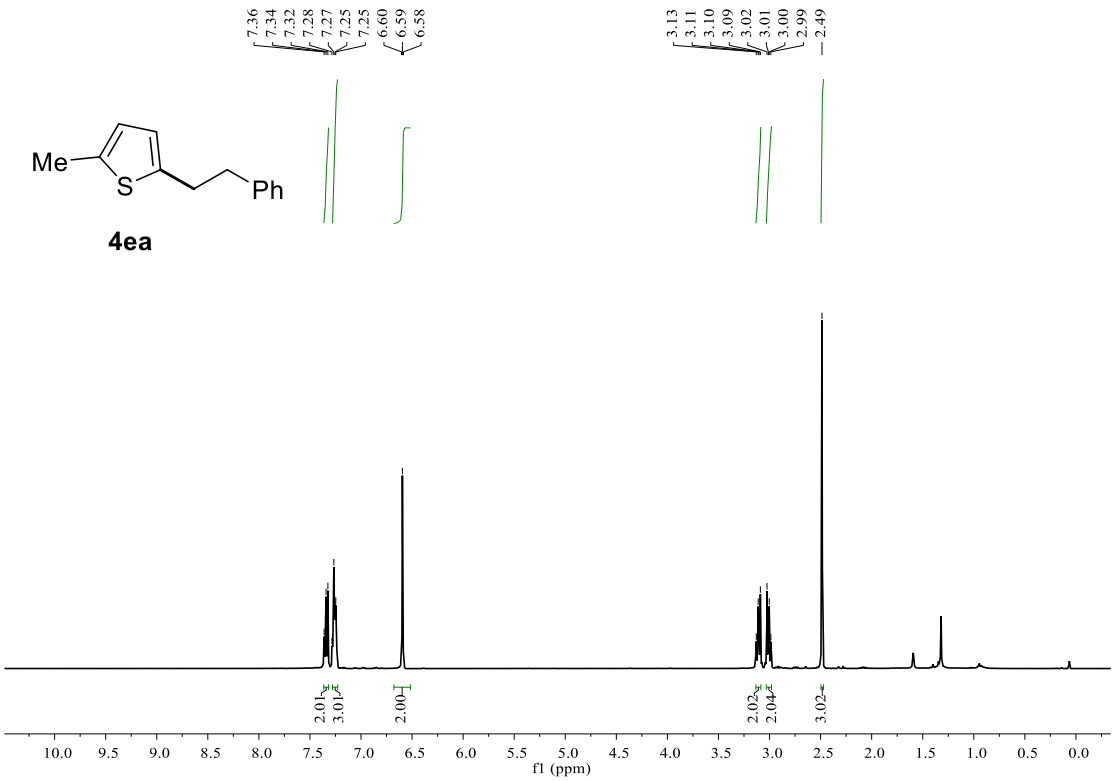
30.25
22.57
14.16
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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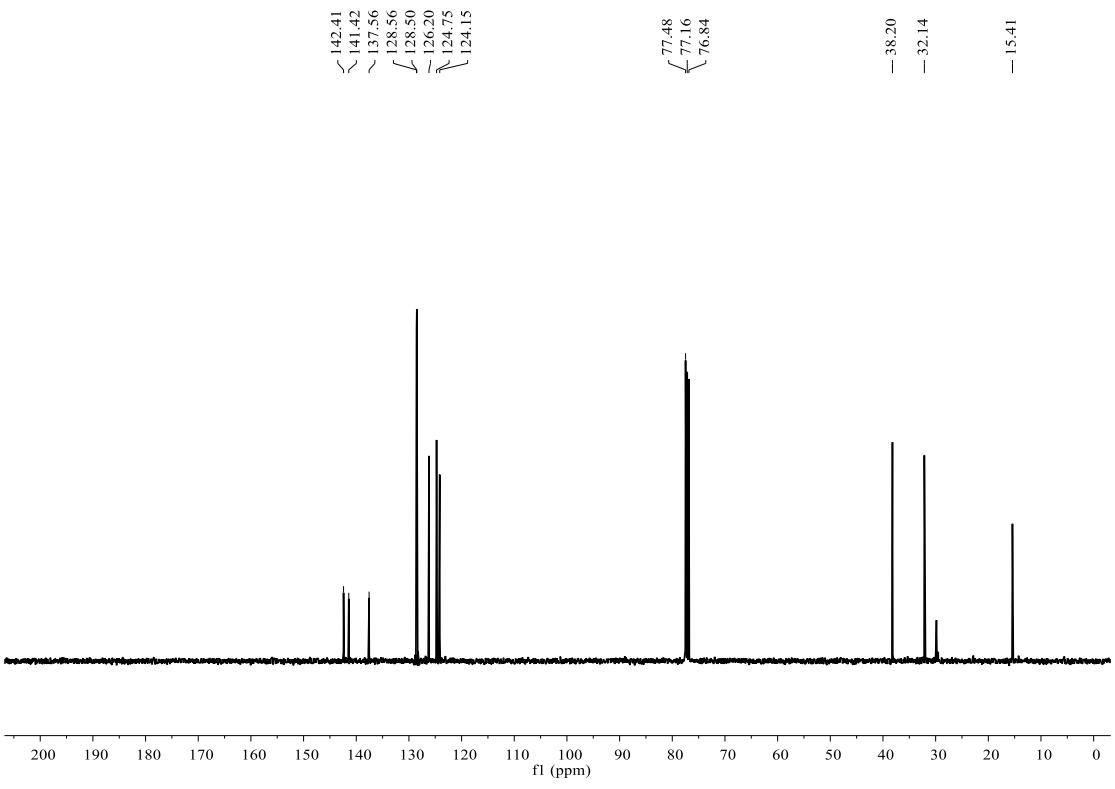
6.58
3.13
3.11
3.10
3.09
3.02
3.01
3.00
2.99
2.49
Me
S
Ph
4ea
2.01
3.01
2.00
2.02
2.04
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.15
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76.84
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32.14
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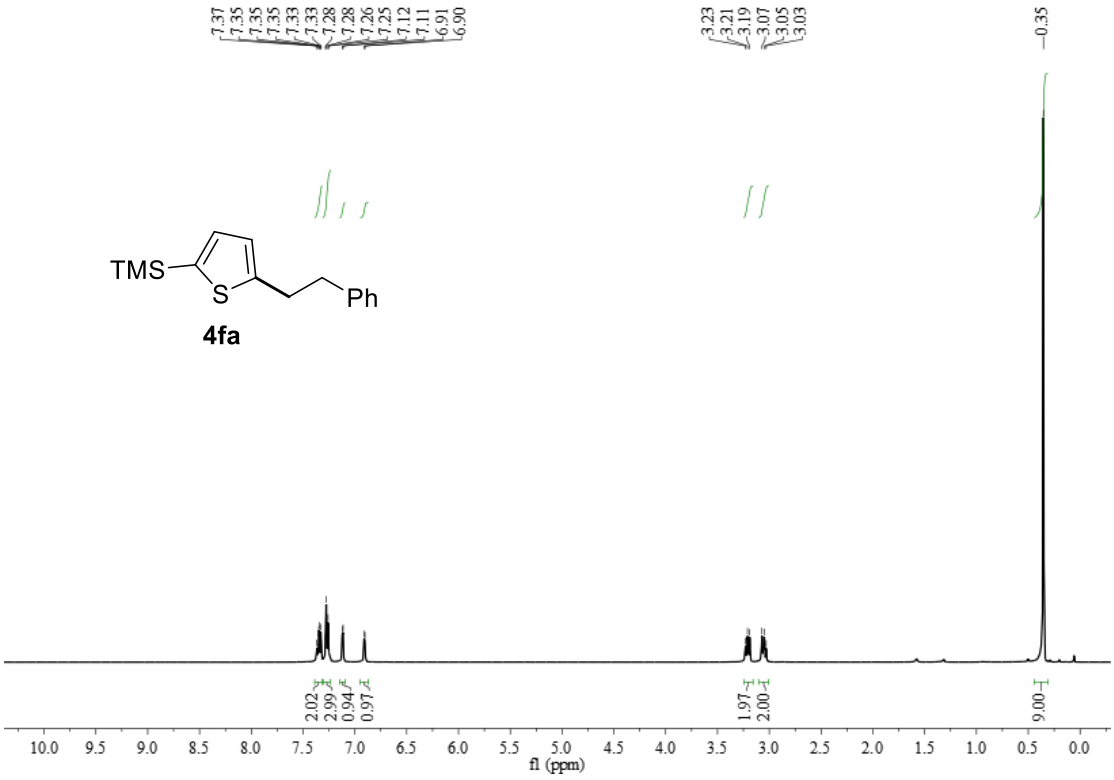
f1 (ppm)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7.11
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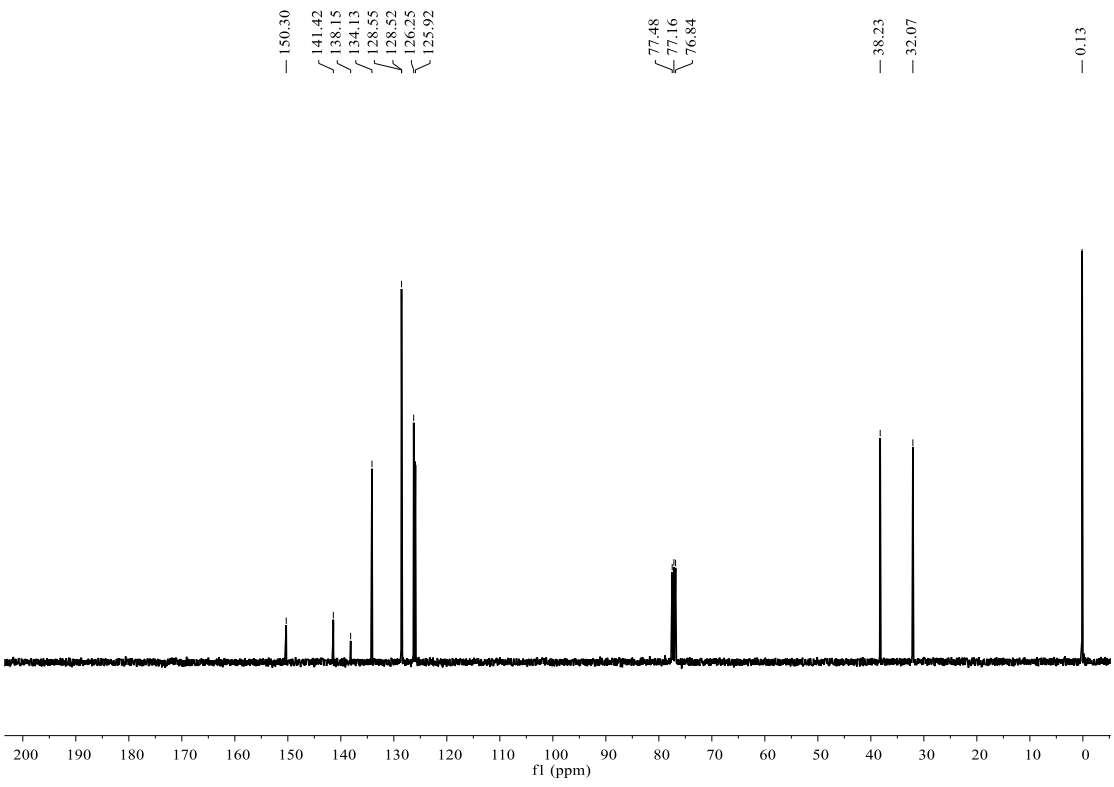
6.90
3.23
3.21
3.19
3.07
3.05
3.03
0.35
TMS
S
Ph
4fa
2.02
2.99
0.94
0.97
1.97
2.00
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.13
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128.52
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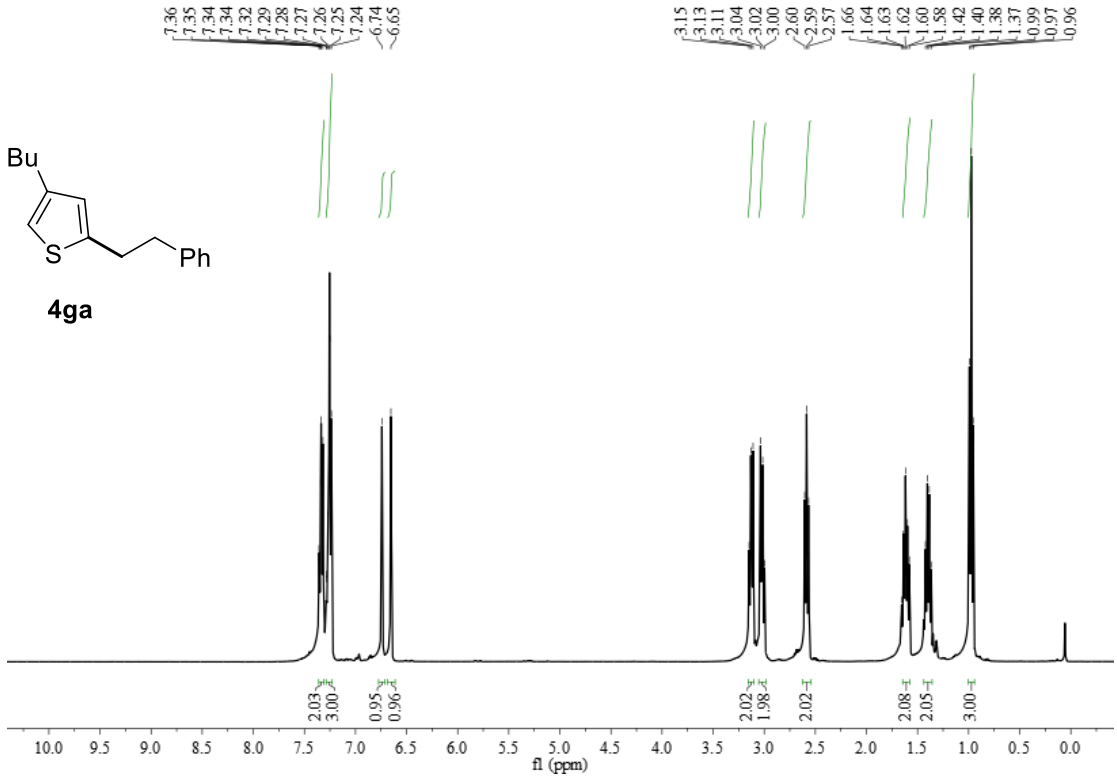
125.92
77.48
77.16
76.84
38.23
32.07
0.13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Bu
S
Ph
4ga
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7.32
7.29
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7.27
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7.25
7.24
6.74
6.65
3.15
3.13
3.11
3.04
3.02
3.00
2.60
2.59
2.57
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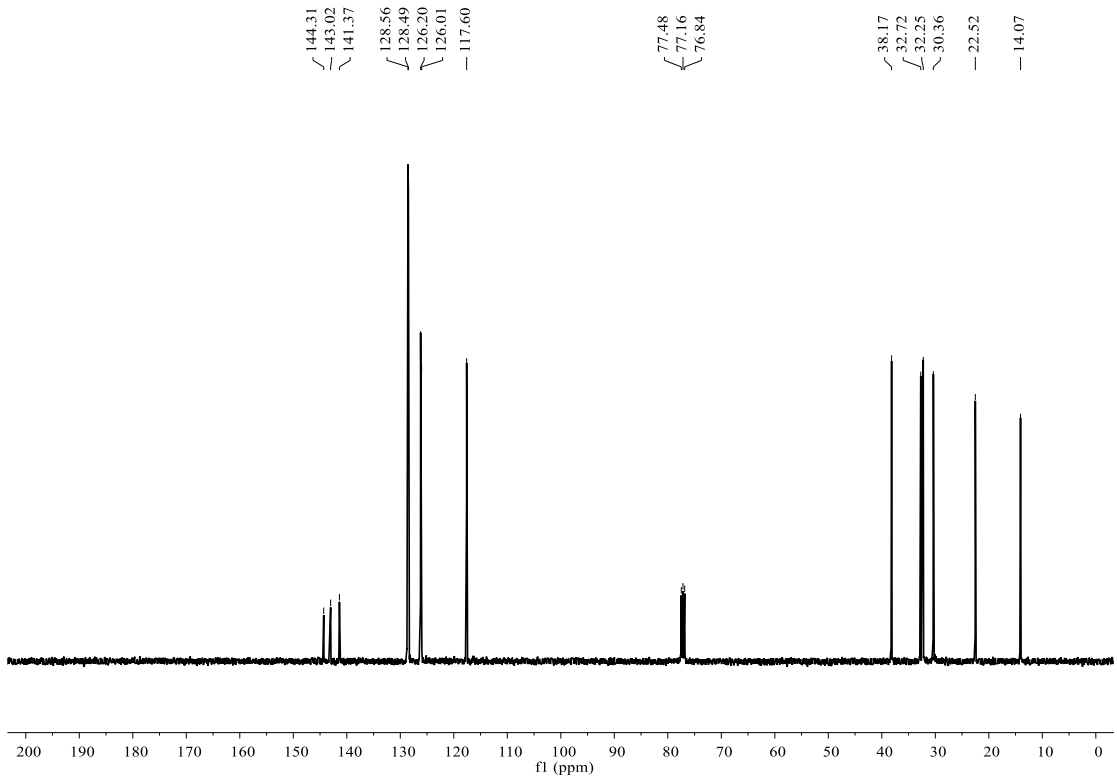
1.63
1.62
1.60
1.58
1.42
1.40
1.38
1.37
0.99
0.97
0.96
2.03
3.00
0.95
0.96
2.02
1.98
2.02
2.08
2.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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126.20
126.01
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77.48
77.16
76.84
38.17
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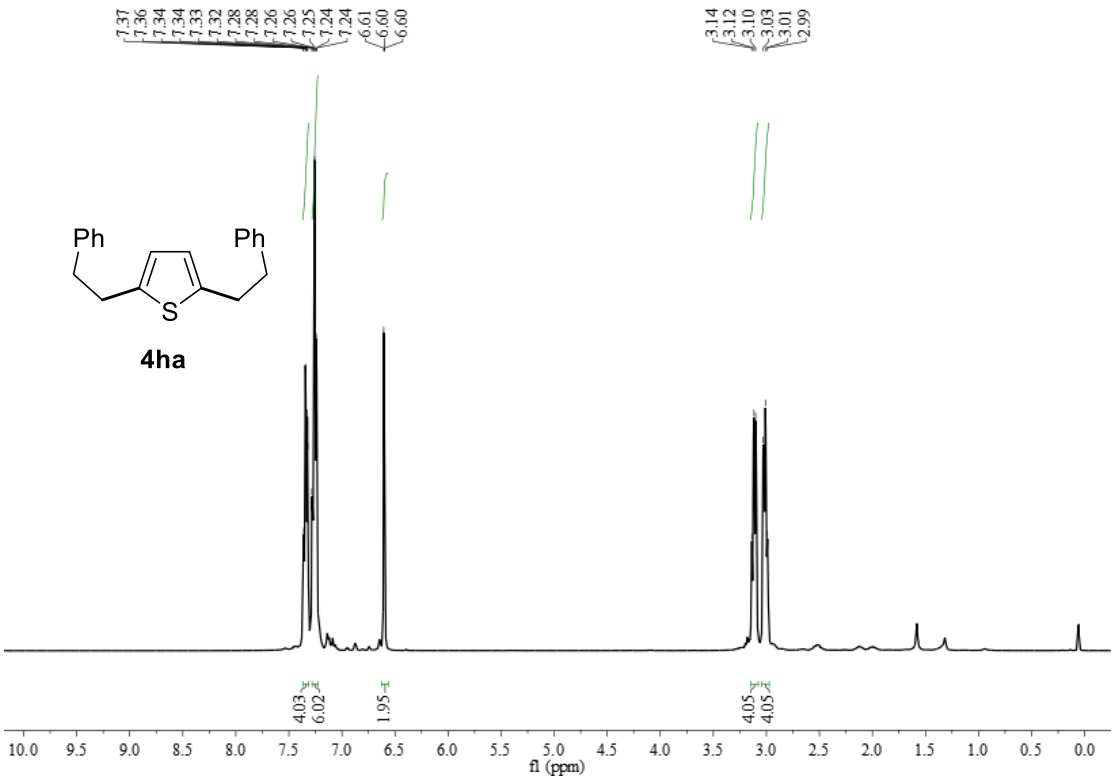
32.25
30.36
22.52
14.07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.60
6.60
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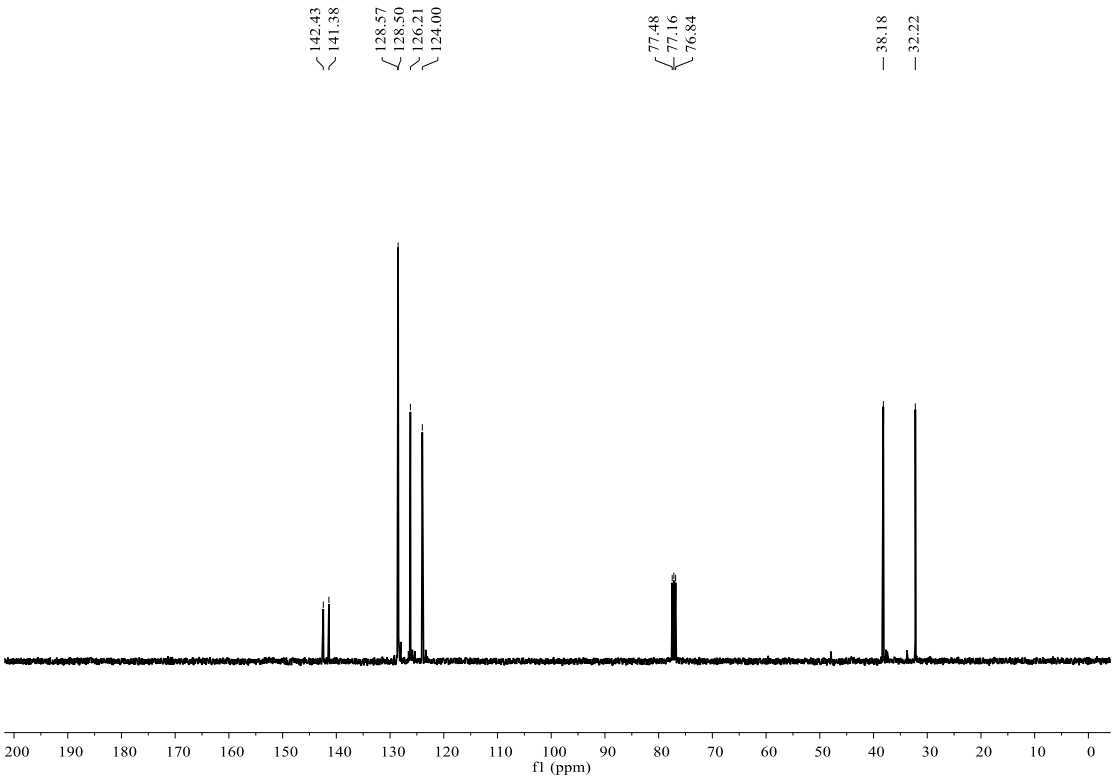
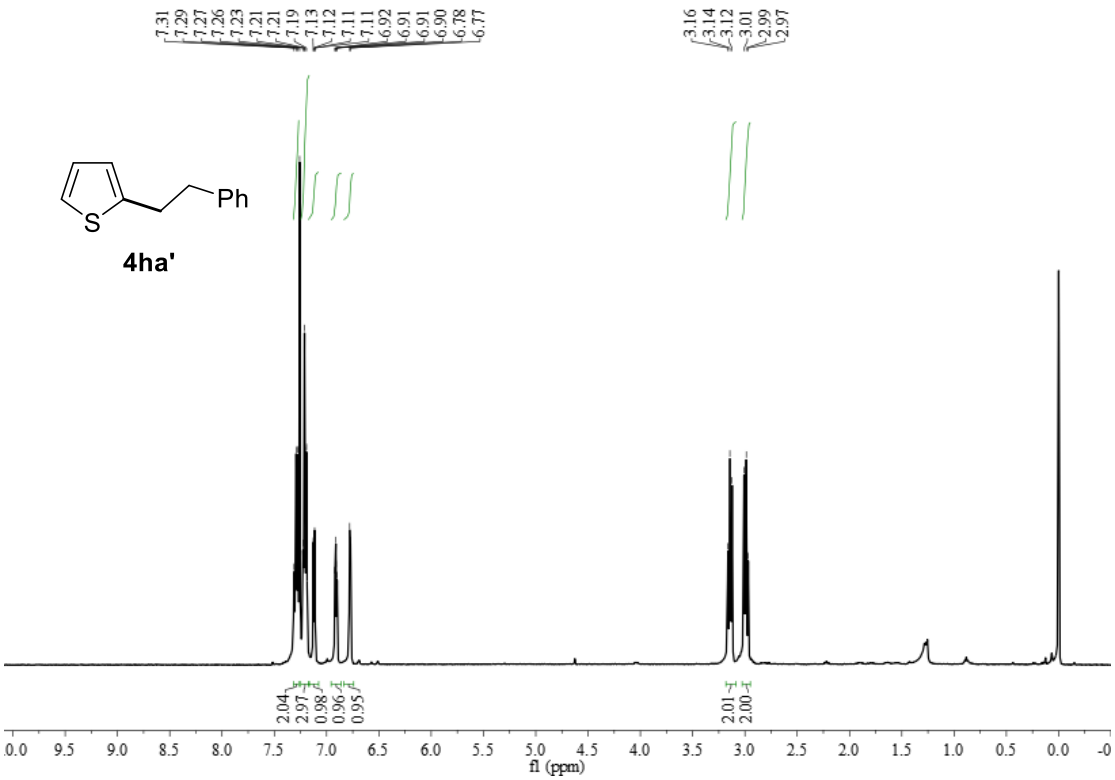
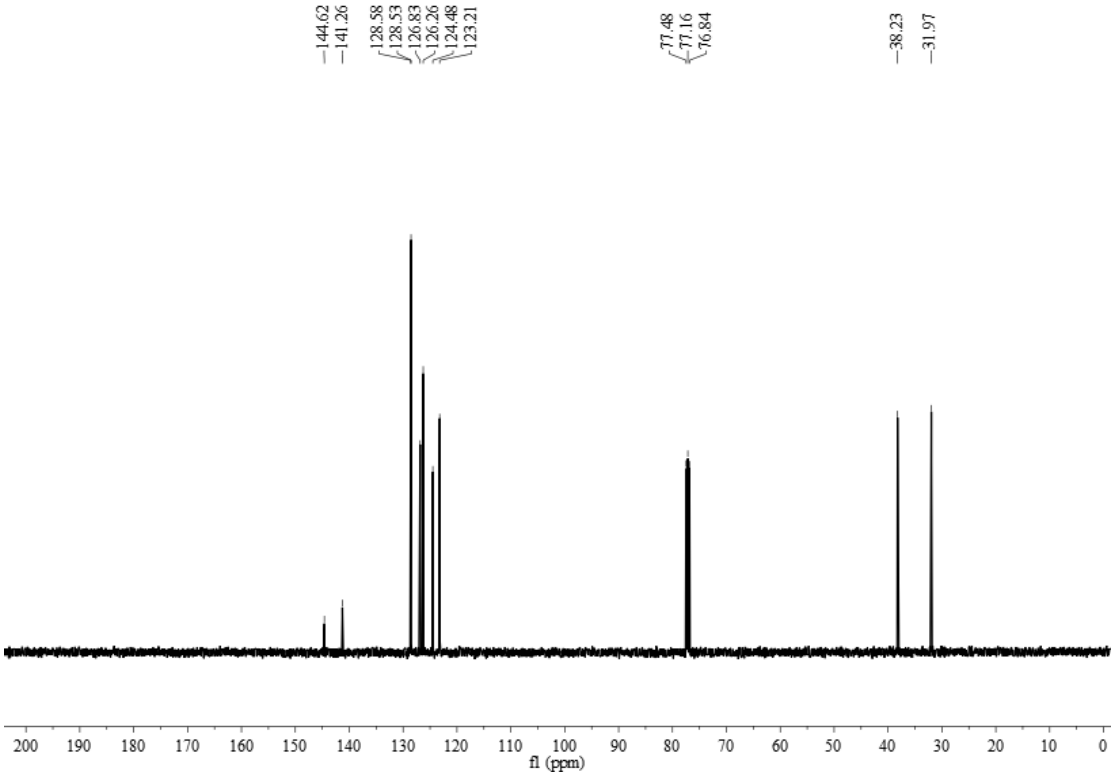
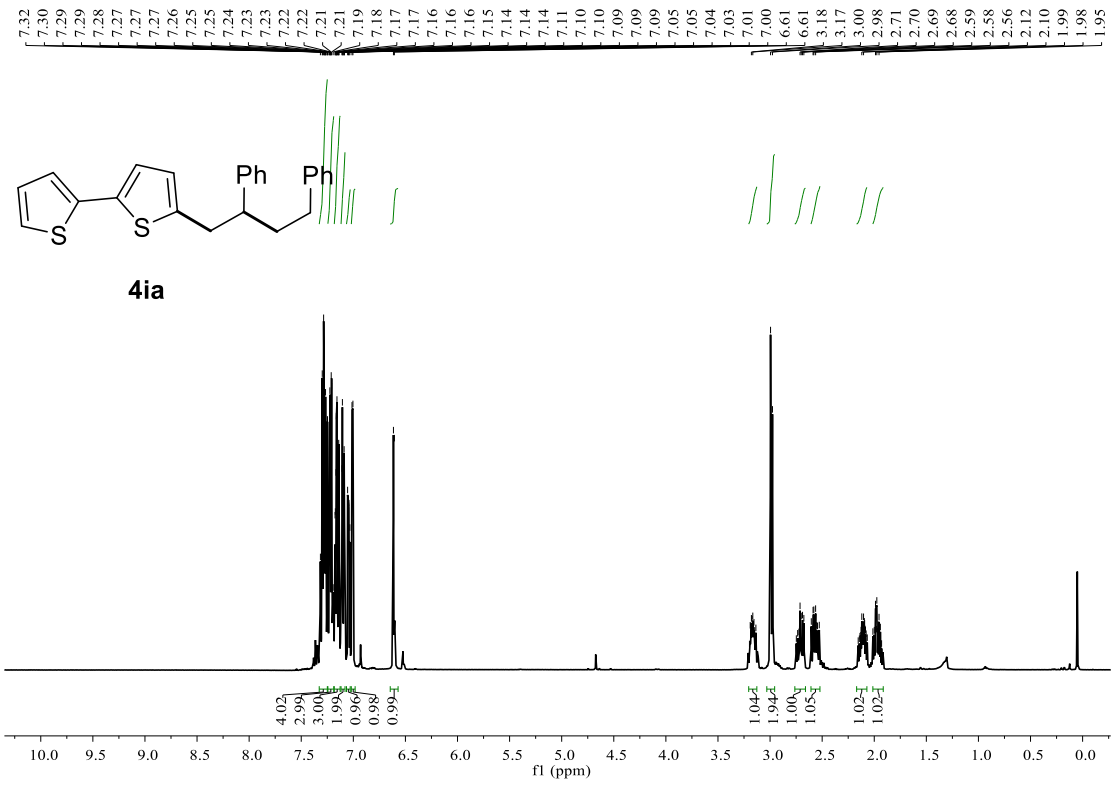
3.12
3.10
3.03
3.01
2.99
Ph
Ph
S
4ha
4.03
6.02
1.95
4.05
4.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

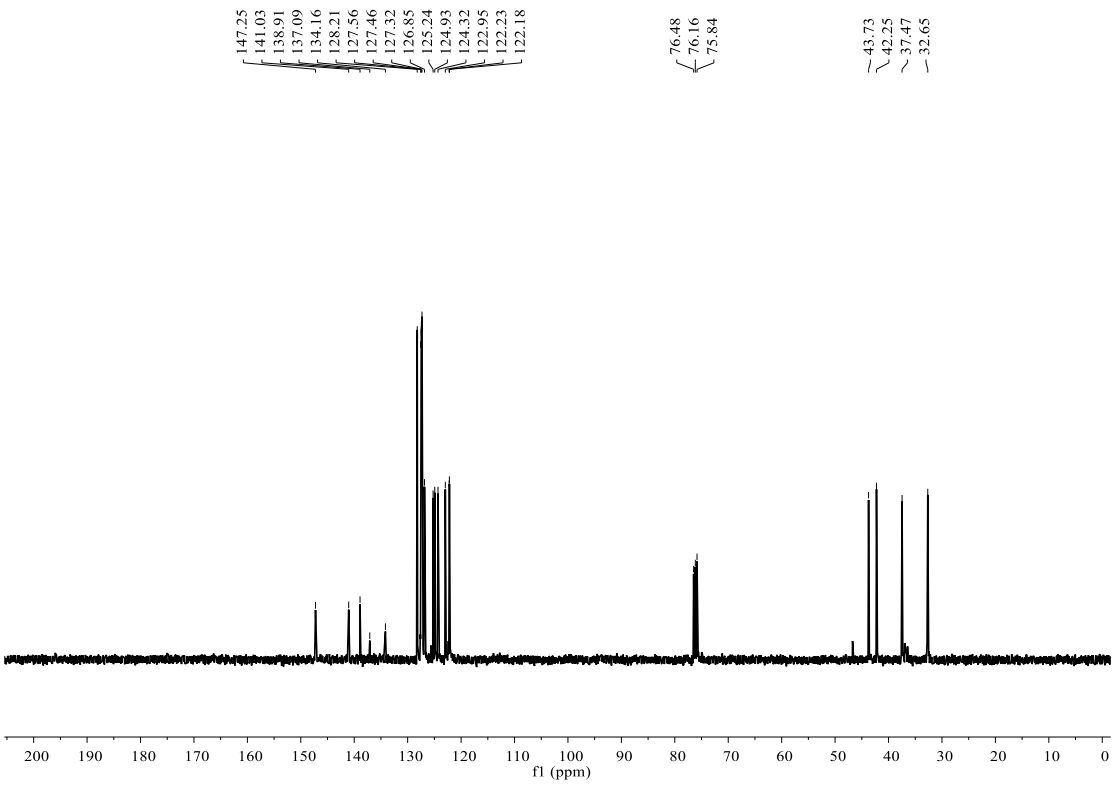

142.43
141.38
128.57
128.50
126.21
124.00
77.48
77.16
76.84
38.18
32.22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

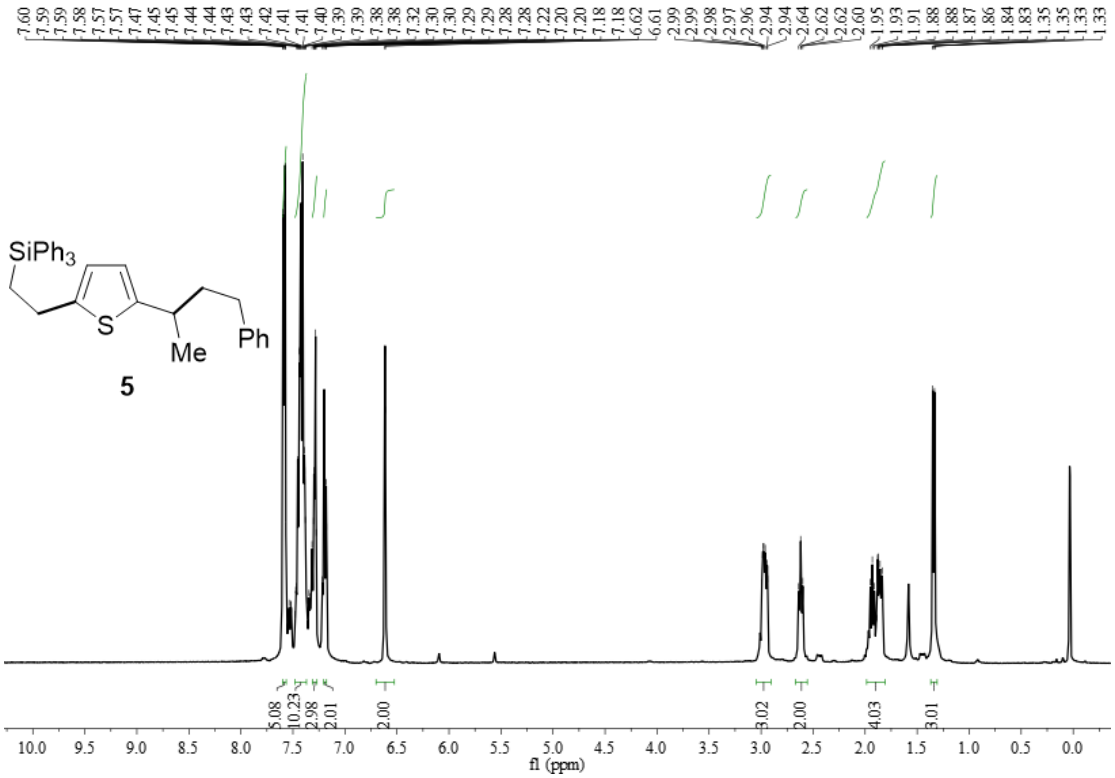

7.31
7.29
7.27
7.26
7.23
7.21
7.21
7.19
7.13
7.12
7.11
7.11
6.92
6.91
6.91
6.90
6.78
6.77
3.16
3.14
3.12
3.01
2.99
2.97
Ph
S
4ha'
2.04
2.97
0.98
0.96
0.95
2.01
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

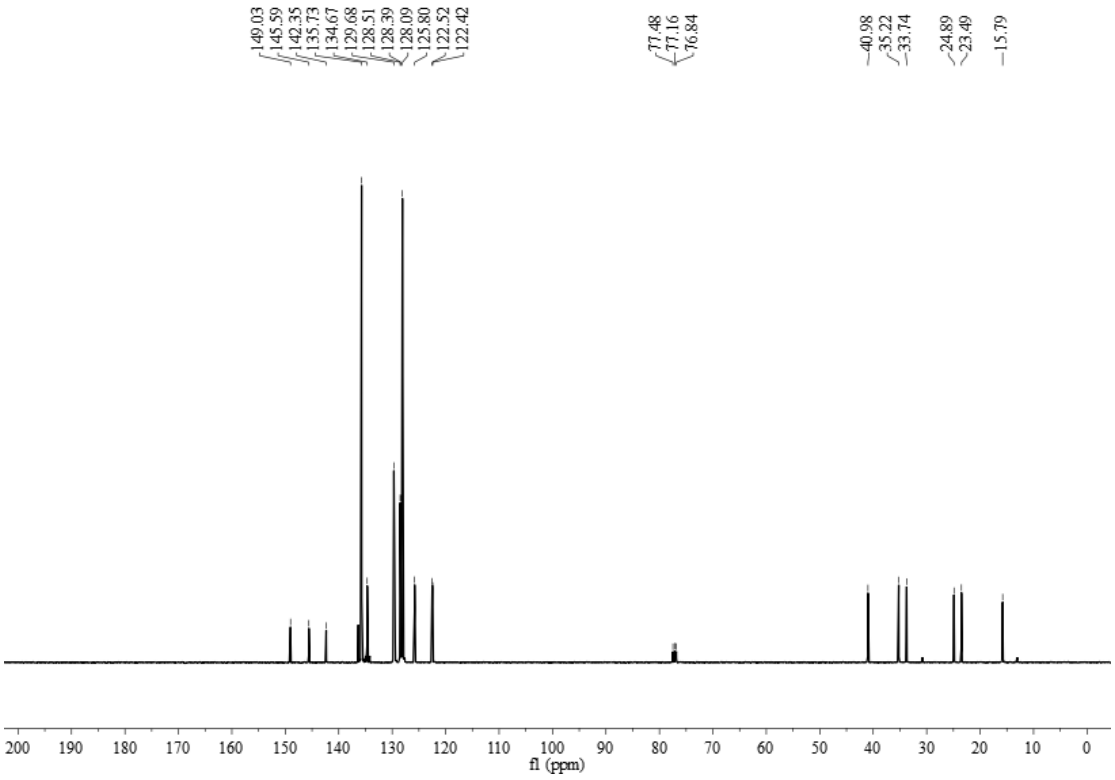

144.62
141.26
128.58
128.53
126.83
126.26
124.48
123.21
77.48
77.16
76.84
38.23
31.97
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

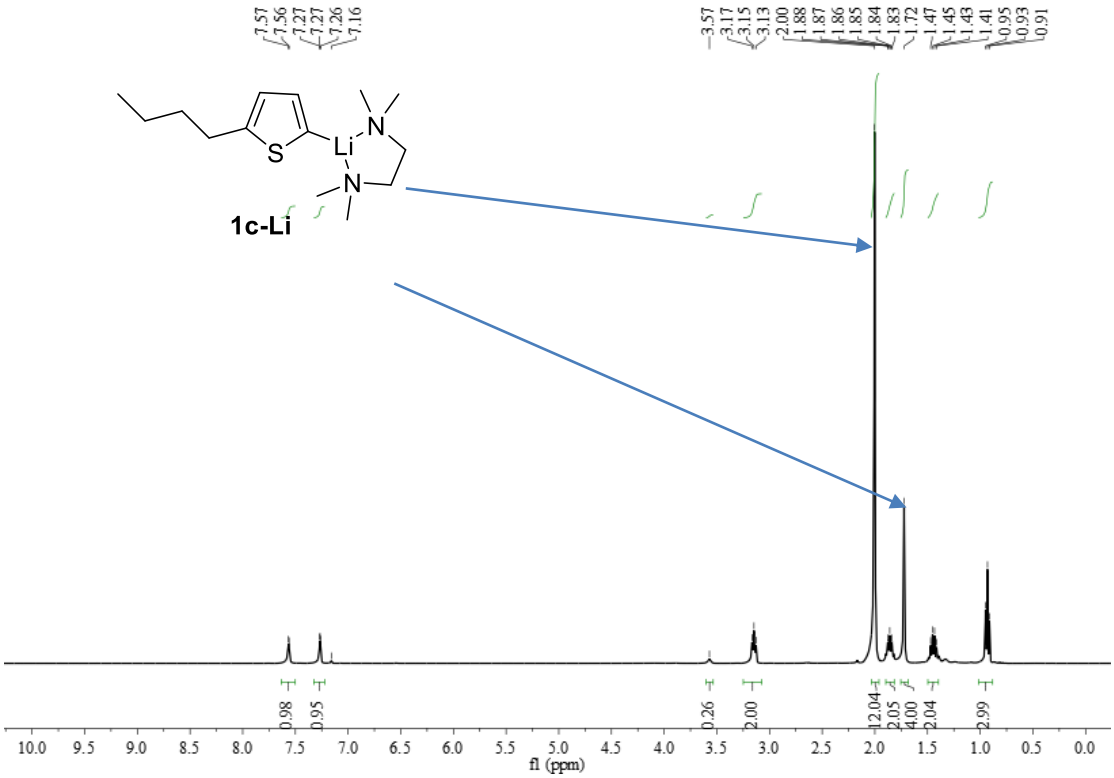


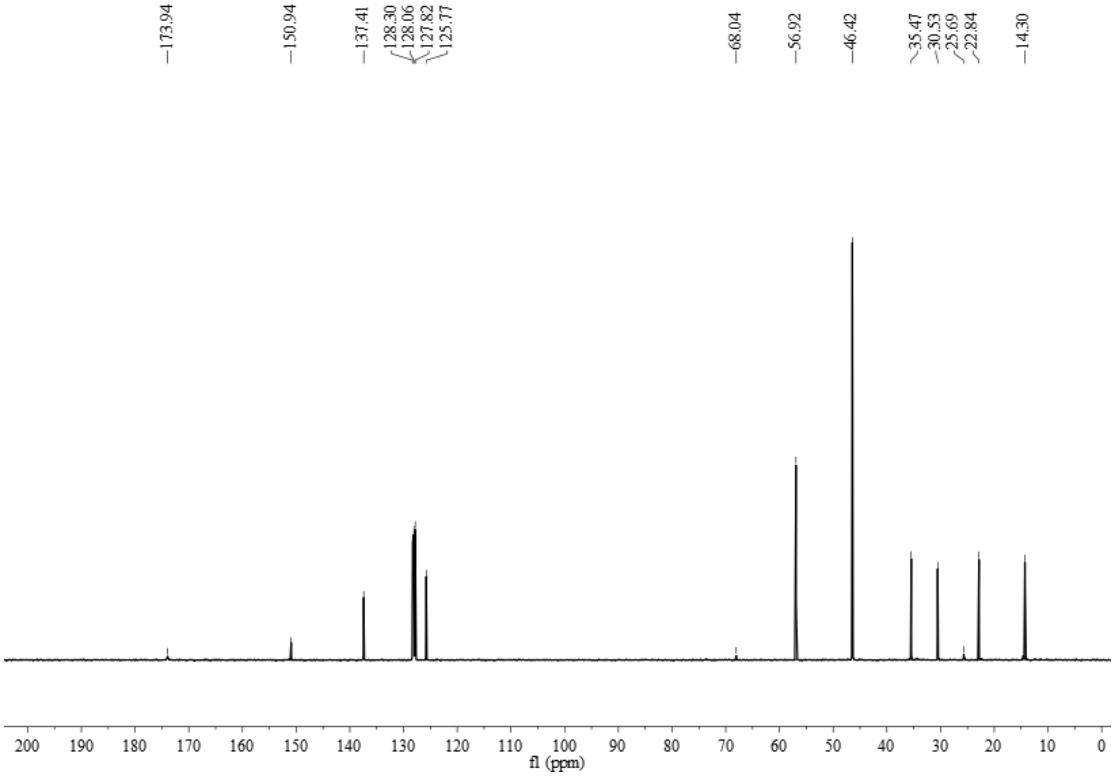
4ia

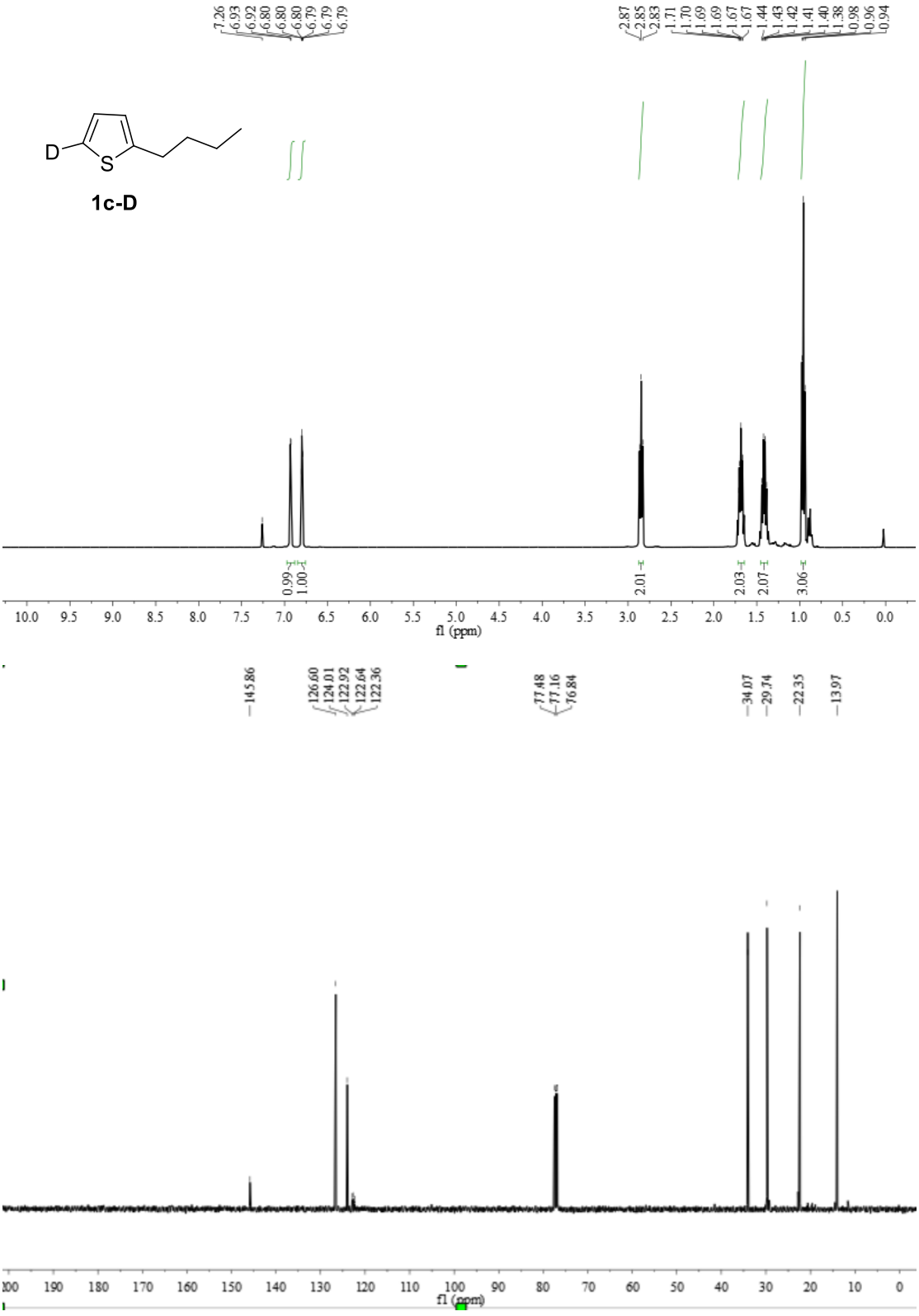


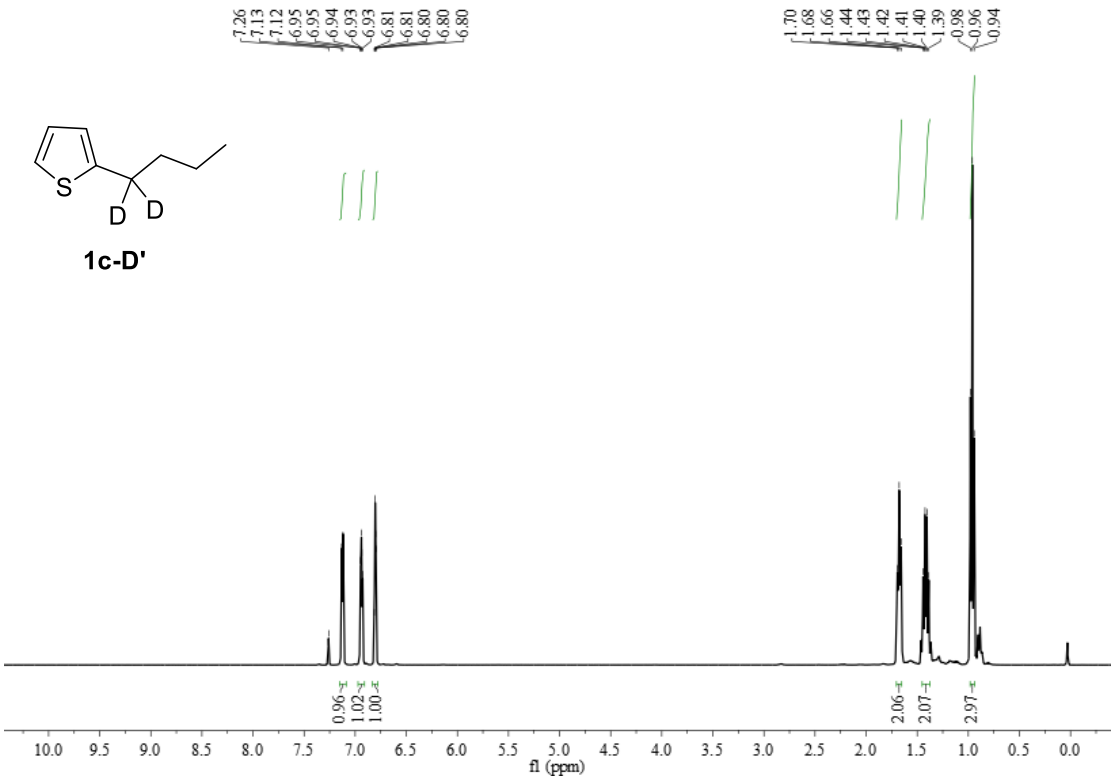

SiPh3
S
Me
Ph
5
fl (ppm)


fl (ppm)

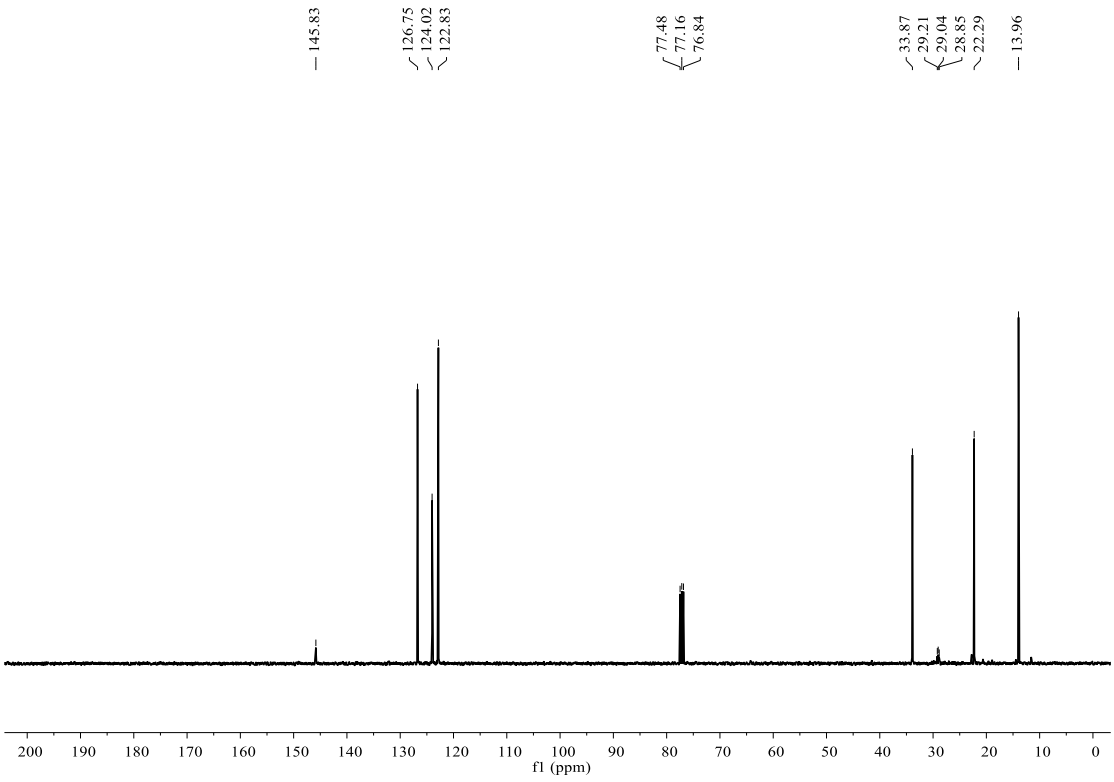

7.57
7.56
7.27
7.27
7.26
7.16
3.57
3.17
3.15
3.13
2.00
1.88
1.87
1.86
1.85
1.84
1.83
1.72
1.47
1.45
1.43
1.41
0.95
0.93
0.91
S
Li
N
N
1c-Li
0.98
0.95
0.26
2.00
12.04
2.05
4.00
2.04
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.94
150.94
137.41
128.30
128.06
127.82
125.77
68.04
56.92
46.42
35.47
30.53
25.69
22.84
14.30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
6.93
6.92
6.80
6.80
6.80
6.79
6.79
6.79
2.87
2.85
2.83
1.71
1.70
1.69
1.69
1.67
1.67
1.44
1.43
1.42
1.41
1.40
1.38
0.98
0.96
0.94
D
S
1c-D
0.99
1.00
2.01
2.03
2.07
3.06
fl (ppm)
145.86
126.60
124.01
122.92
122.64
122.36
77.48
77.16
76.84
34.07
29.74
22.35
13.97
fl (ppm)


7.26
7.13
7.12
6.95
6.95
6.94
6.93
6.93
6.81
6.81
6.80
6.80
6.80
1.70
1.68
1.66
1.44
1.43
1.42
1.41
1.40
1.39
0.98
0.96
0.94
S
D
D
0.96
1.02
1.00
2.06
2.07
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

1c-D'


145.83
126.75
124.02
122.83
77.48
77.16
76.84
33.87
29.21
29.04
28.85
22.29
13.96
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)