

Advanced
**Synthesis &
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Supporting Information

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Supporting Information

Palladium/Phosphite or Phosphate Catalyzed Oxidative Coupling of Arylboronic Acids with Alkynes to Produce 1,4-Diaryl-1,3-Butadienes

Hakaru Horiguchi, Hayato Tsurugi, Tetsuya Satoh,* and Masahiro Miura*

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita,
Osaka 565-0871, Japan*

e-mail: satoh@chem.eng.osaka-u.ac.jp; miura@chem.eng.osaka-u.ac.jp

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Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, or 270 MHz and 68 MHz, respectively, for CDCl_3 solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm x 25 m). The structures of all products listed below were unambiguously determined by ^1H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Diarylacetylenes **5b-d** were prepared according to published procedures.^[17] Other starting materials were commercially available.

The following experimental procedures may be regarded as typical in methodology and scale.

Pd-Catalyzed Reaction of Phenylboronic Acid (1a) with 4-Octyne (2a) (entry 11 in Table 1): A mixture of phenylboronic acid (**1a**) (4 mmol, 488 mg), 4-octyne (**2a**) (2 mmol, 220 mg), $\text{Pd}(\text{OAc})_2$ (0.05 mmol, 11 mg), $[(4\text{-MeC}_6\text{H}_4)\text{O}]_3\text{P}$ (0.05 mmol, 18 mg), Ag_2CO_3 (2 mmol, 551 mg), and 1-methylnaphthalene (ca. 60 mg) as internal standard was stirred in DMF/ H_2O (5 mL, 9:1) under nitrogen at 140 °C. After 3 h, the reaction mixture was cooled to room temperature, Et_2O (100 mL) and water (100 mL) were added, and insoluble materials were removed by filtration through filter paper. Then the organic layer was washed by water (100 mL, three times) and dried over sodium sulfate. GC and GC-MS analyses confirmed the formation of (4Z,6Z)-4,7-Diphenyl-5,6-dipropyl-4,6-decadiene (**3a**) (0.85 mmol, 85%) and biphenyl (**4a**) (0.52 mmol). The product **3a** (279 mg, 75%) was isolated by column chromatography on silica gel using hexane as eluant and subsequent Kugelrohr distillation to remove hydrocarbon impurities such as the internal standard.

Characterization Data of Products.

4,7-Diphenyl-5,6-dipropyl-4,6-decadiene (3a) (entry 11 in Table 1): mp 83-85 °C (lit.^[6] mp 88 °C); ^1H NMR (270 MHz, CDCl_3) δ 0.77 (t, J = 6.9 Hz, 6H), 0.82 (t, J = 6.9 Hz, 6H), 1.13-1.22 (m, 4H), 1.24-1.44 (m, 4H), 1.56-1.67 (m, 2H), 2.00-2.12 (m, 2H), 2.17-2.29 (m, 4H), 7.06-7.20 (m, 10H); ^{13}C NMR (68 MHz, CDCl_3) δ 14.2, 14.9, 21.5, 22.8, 36.1, 36.5, 125.5, 127.2, 128.6, 136.6, 139.1, 143.8; HRMS m/z calcd for $\text{C}_{28}\text{H}_{38}$ (M^+) 374.2973, found 374.2971.

5,8-Diphenyl-6,7-dibutyl-5,7-dodecadiene (3b) (entry 1 in Table 2): oil; ^1H NMR (270 MHz, CDCl_3) δ 0.79 (t, $J = 6.9$ Hz, 6H), 0.85 (t, $J = 6.9$ Hz, 6H), 1.14-1.37 (m, 16H), 1.58-1.69 (m, 2H), 2.02-2.13 (m, 2H), 2.18-2.29 (m, 4H), 7.06-7.20 (m, 10H); ^{13}C NMR (68 MHz, CDCl_3) δ 14.05, 14.08, 22.8, 23.5, 30.5, 31.7, 33.8, 33.9, 125.5, 127.2, 128.6, 136.5, 140.0, 143.9; HRMS m/z calcd for $\text{C}_{32}\text{H}_{46}$ (M^+) 430.3600, found 430.3602.

8,11-Diphenyl-9,10-diheptyl-8,10-nonadecadiene (3c) (entry 3 in Table 2): oil; ^1H NMR (270 MHz, CDCl_3) δ 0.84 (t, $J = 6.4$ Hz, 6H), 0.88 (t, $J = 6.4$ Hz, 6H), 1.16-1.32 (m, 40H), 1.58-1.68 (m, 2H), 2.00-2.11 (m, 2H), 2.16-2.29 (m, 4H), 7.05-7.19 (m, 10H); ^{13}C NMR (68 MHz, CDCl_3) δ 14.19, 14.22, 22.75, 22.80, 28.4, 29.2, 29.3, 29.5, 29.7, 30.4, 31.9, 32.0, 34.0, 34.3, 125.5, 127.2, 128.5, 136.5, 139.1, 143.9; HRMS m/z calcd for $\text{C}_{44}\text{H}_{70}$ (M^+) 598.5477, found 598.5482.

5,8-Diphenyl-6,7-diisopentyl-2,11-dimethyl-5,7-dodecadiene (3d) (entry 5 in Table 2): oil; ^1H NMR (270 MHz, CDCl_3) δ 0.76-0.89 (m, 24H), 0.96-1.09 (m, 4H), 1.14-1.47 (m, 8H), 1.62-1.73 (m, 2H), 2.05-2.14 (m, 2H), 2.18-2.25 (m, 4H), 7.00-7.20 (m, 10H); ^{13}C NMR (68 MHz, CDCl_3) δ 22.56, 22.58, 22.66, 22.68, 28.3, 29.0, 31.9, 32.2, 37.5, 38.7, 125.5, 127.2, 128.5, 136.6, 139.0, 143.9; HRMS m/z calcd for $\text{C}_{36}\text{H}_{54}$ (M^+) 486.4226, found 486.4229.

4,7-Bis(4-chlorophenyl)-5,6-dipropyl-4,6-decadiene (3e) (entry 7 in Table 2): mp 99-101 $^\circ\text{C}$; ^1H NMR (270 MHz, CDCl_3) δ 0.76 (t, $J = 7.3$ Hz, 6H), 0.89 (t, $J = 7.3$ Hz, 6H), 1.05-1.16 (m, 4H), 1.31-1.48 (m, 4H), 1.71-1.83 (m, 2H), 2.08-2.20 (m, 6H), 6.85 (d, $J = 8.2$ Hz, 4H), 7.12 (d, $J = 8.2$ Hz, 4H); ^{13}C NMR (68 MHz, CDCl_3) δ 14.2, 15.0, 21.5, 22.9, 35.8, 36.5, 127.4, 129.8, 131.2, 136.0, 139.2, 141.8; HRMS m/z calcd for $\text{C}_{28}\text{H}_{36}\text{Cl}_2$ (M^+) 442.2194, found 442.2199.

4,7-Bis[4-(methoxycarbonyl)phenyl]-5,6-dipropyl-4,6-decadiene (3f) (entry 8 in Table 2): $^{[7b]}$ oil; ^1H NMR (270 MHz, CDCl_3) δ 0.75 (t, $J = 7.4$ Hz, 6H), 0.91 (t, $J = 7.4$ Hz, 6H), 1.05-1.14 (m, 4H), 1.40-1.52 (m, 4H), 1.77-1.88 (m, 2H), 2.11-2.25 (m, 6H), 3.92 (s, 6H), 6.93 (d, $J = 8.4$ Hz, 4H), 7.82 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (68 MHz, CDCl_3) δ 14.1, 15.0, 21.5, 23.0, 35.7, 36.7, 52.0, 127.2, 128.5, 128.6, 136.8, 139.8, 148.5, 167.1; HRMS m/z calcd for $\text{C}_{32}\text{H}_{42}\text{O}_4$ (M^+) 490.3083, found 490.3076.

4,7-Bis(4-methylphenyl)-5,6-dipropyl-4,6-decadiene (3g) (entry 9 in Table 2): $^{[7b]}$ oil; ^1H NMR (400 MHz, CDCl_3) δ 0.78 (t, $J = 7.3$ Hz, 12H), 1.14-1.28 (m, 6H), 1.33-1.42 (m, 2H), 1.49-1.57 (m, 2H), 1.96-2.04 (m, 2H), 2.16-2.26 (m, 4H), 2.33 (s,

6H), 7.01 (d, $J = 8.0$ Hz, 4H), 7.09 (d, $J = 8.0$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 14.8, 21.2, 21.4, 22.7, 36.0, 36.4, 128.1, 128.4, 135.1, 136.2, 139.2, 140.9; HRMS m/z calcd for $\text{C}_{30}\text{H}_{42}$ (M^+) 402.3286, found 402.3291.

4,7-Bis(4-methoxyphenyl)-5,6-dipropyl-4,6-decadiene (3h) (entry 10 in Table 2):^[7b] oil; ^1H NMR (400 MHz, CDCl_3) δ 0.79 (t, $J = 6.9$ Hz, 6H), 0.80 (t, $J = 6.9$ Hz, 6H), 1.17-1.40 (m, 8H), 1.53-1.61 (m, 2H), 1.98-2.06 (m, 2H), 2.15-2.31 (m, 4H), 3.81 (s, 6H), 6.75 (d, $J = 8.7$ Hz, 4H), 7.08 (d, $J = 8.7$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 14.8, 21.4, 22.7, 36.0, 36.3, 55.1, 112.7, 129.6, 135.9, 136.3, 139.0, 157.5; HRMS m/z calcd for $\text{C}_{30}\text{H}_{42}\text{O}_2$ (M^+) 434.3185, found 434.3188.

1,1,2,3,4,4-Hexaphenyl-1,3-butadiene (6a) (entry 5 in Table 3): mp 218-219 °C (lit.^[18] 221 °C); ^1H -NMR (400 MHz, CDCl_3) δ 6.86 (t, $J = 7.3$ Hz, 2H), 6.90-6.94 (m, 12H), 7.04-7.06 (m, 12H), 7.18 (d, $J = 7.0$ Hz, 4H); ^{13}C -NMR (100 MHz, CDCl_3) δ 125.9, 126.4, 126.6, 127.2, 127.3, 127.5, 129.9, 131.3, 131.4, 140.5, 141.5, 143.0, 143.8, 144.0; HRMS m/z calcd for $\text{C}_{40}\text{H}_{30}$ (M^+) 510.2348, found 510.2345.

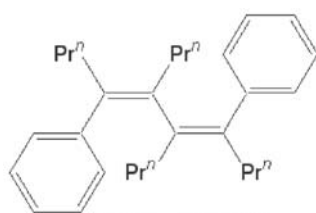
1,1,2,3,4,4-Hexakis(4-methylphenyl)-1,3-butadiene (6b) (Scheme 2): mp 224.5-226 °C (lit.^[6] 247-248 °C); ^1H -NMR (400 MHz, CDCl_3) δ 2.12 (s, 6H), 2.21 (s, 6H), 2.23 (s, 6H), 6.72-6.87 (m, 20H), 7.07 (d, $J = 7.1$ Hz, 4H); ^{13}C -NMR (100 MHz, CDCl_3) δ 21.1, 21.2 (overlapped), 127.7, 127.9, 128.1, 129.8, 131.1, 131.2, 135.0, 135.6, 135.7, 138.6, 139.6, 141.4, 141.6, 141.7; HRMS m/z calcd for $\text{C}_{46}\text{H}_{42}$ (M^+) 594.3287, found 594.3292.

1,2-Dihydro-7-methoxy-1,1,2,3,4-pentakis(4-methoxyphenyl)naphthalene (7) (Scheme 3): mp 234-235.2 °C; ^1H -NMR (400 MHz, CDCl_3) δ 3.67 (s, 3H), 3.71 (s, 6H), 3.73 (s, 3H), 3.75 (s, 3H), 3.79 (s, 3H), 4.15 (s, 1H), 6.49-6.91 (m, 21H), 7.15-7.25 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ 54.94, 55.06, 55.07, 55.13 (overlapped), 55.2, 57.0, 58.7, 110.5, 111.6, 112.5, 112.8, 113.2, 113.3, 116.5, 128.3, 129.0, 129.7, 130.4, 131.6, 131.8, 132.1, 132.2, 132.3, 134.9, 135.4, 135.8, 136.8, 138.0, 142.1, 157.4, 157.5, 157.6, 158.0, 158.1, 158.5; HRMS m/z calcd for $\text{C}_{46}\text{H}_{42}\text{O}_6$ (M^+) 690.2981, found 690.2986.

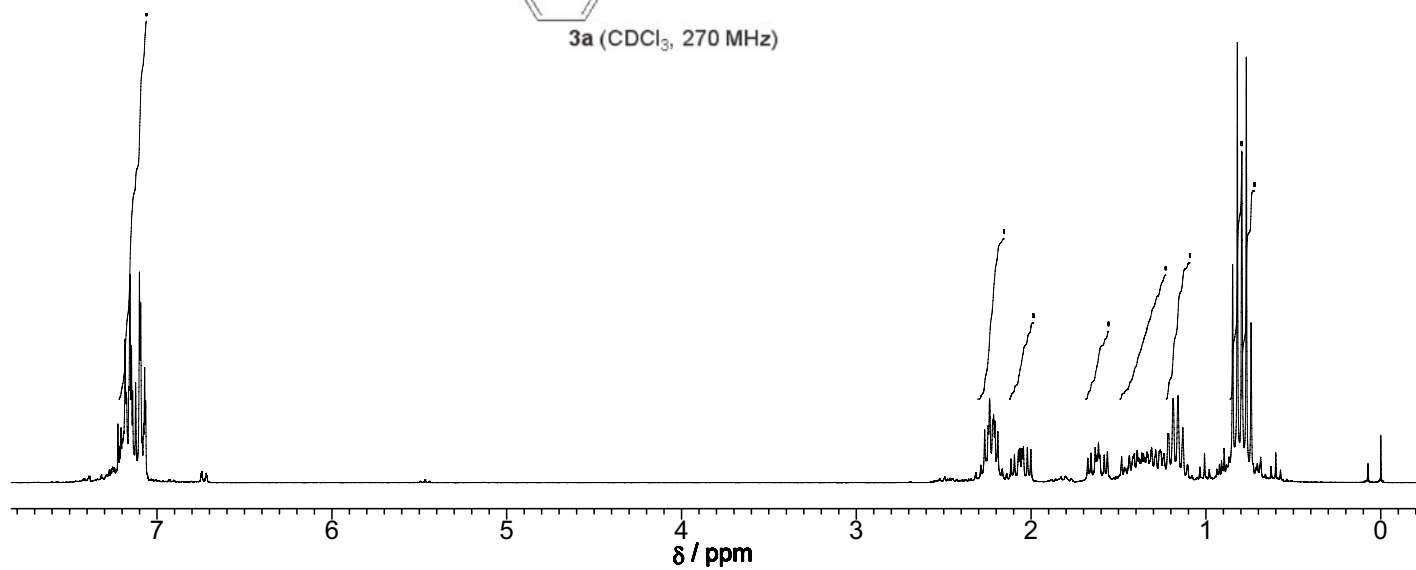
1,1,2,2-Tetrakis(4-chlorophenyl)ethane (8) (Scheme 4): mp 215-216.5 °C (lit.^[19] 216-217 °C); ^1H -NMR (400 MHz, CDCl_3) δ 6.91 (d, $J = 8.4$ Hz, 8H), 7.10 (d, $J = 8.4$ Hz, 8H); ^{13}C -NMR (100 MHz, CDCl_3) δ 128.3, 132.4, 133.0, 139.6, 141.1; HRMS m/z calcd for $\text{C}_{26}\text{H}_{16}\text{Cl}_4$ (M^+) 468.0006, found 467.9998.

References

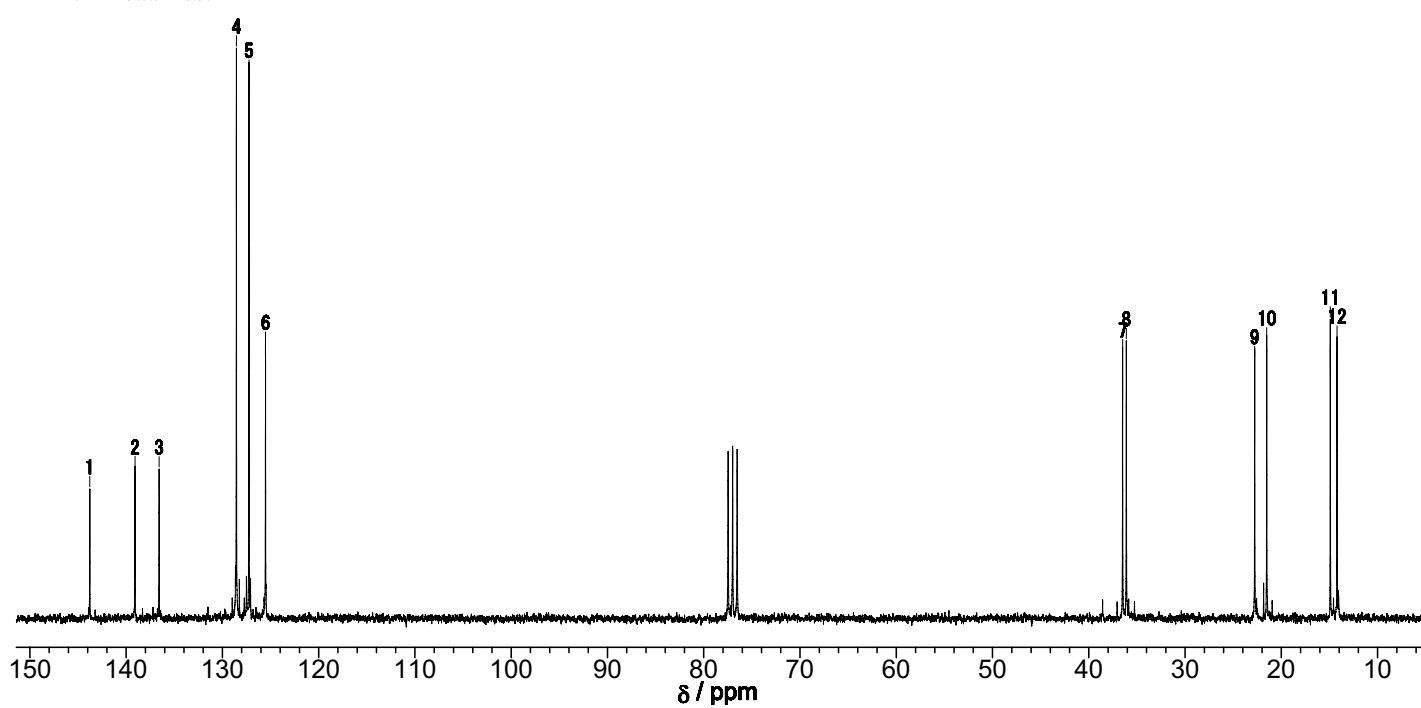
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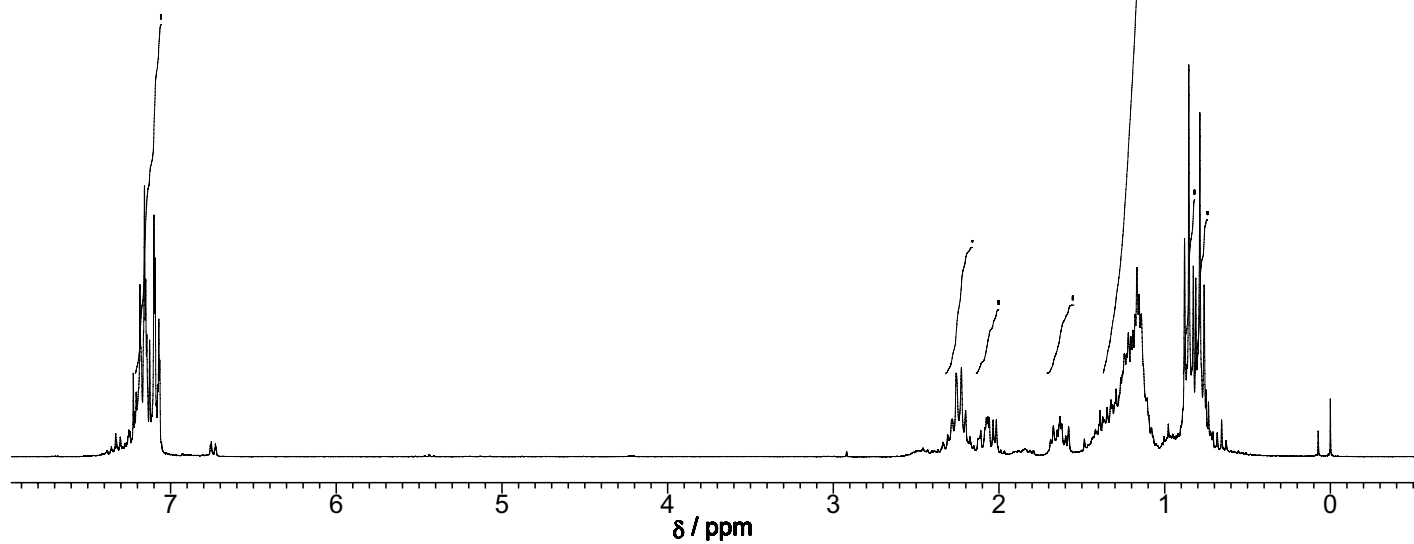
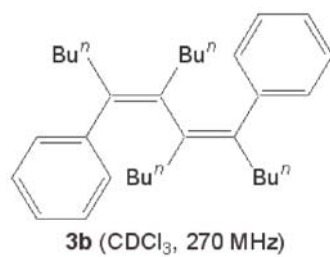


3a (CDCl_3 , 270 MHz)

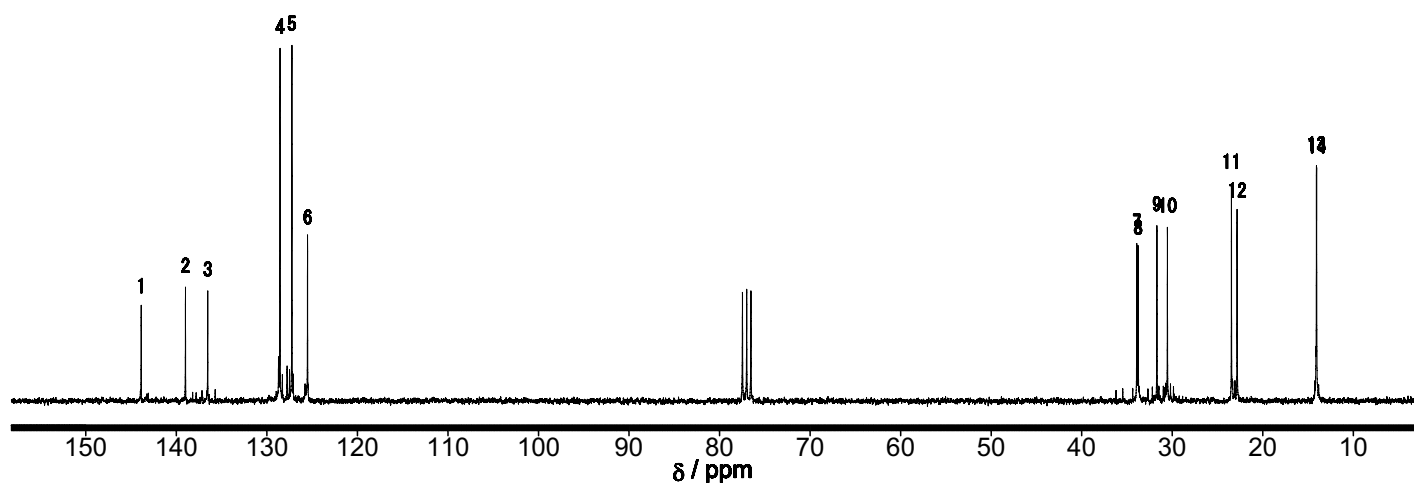


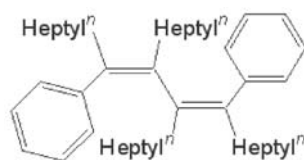
No.	ppm	Hz	Height
1	143.78	9767.1	23.09
2	139.08	9448.0	26.59
3	136.58	9278.1	26.55
4	128.55	8732.6	100
5	127.24	8643.7	95.77
6	125.53	8527.4	48.30
7	36.49	2478.7	47.00
8	36.10	2452.4	48.95
9	22.77	1547.0	45.80
10	21.52	1462.0	49.07
11	14.91	1013.2	52.70
12	14.22	965.7	49.38



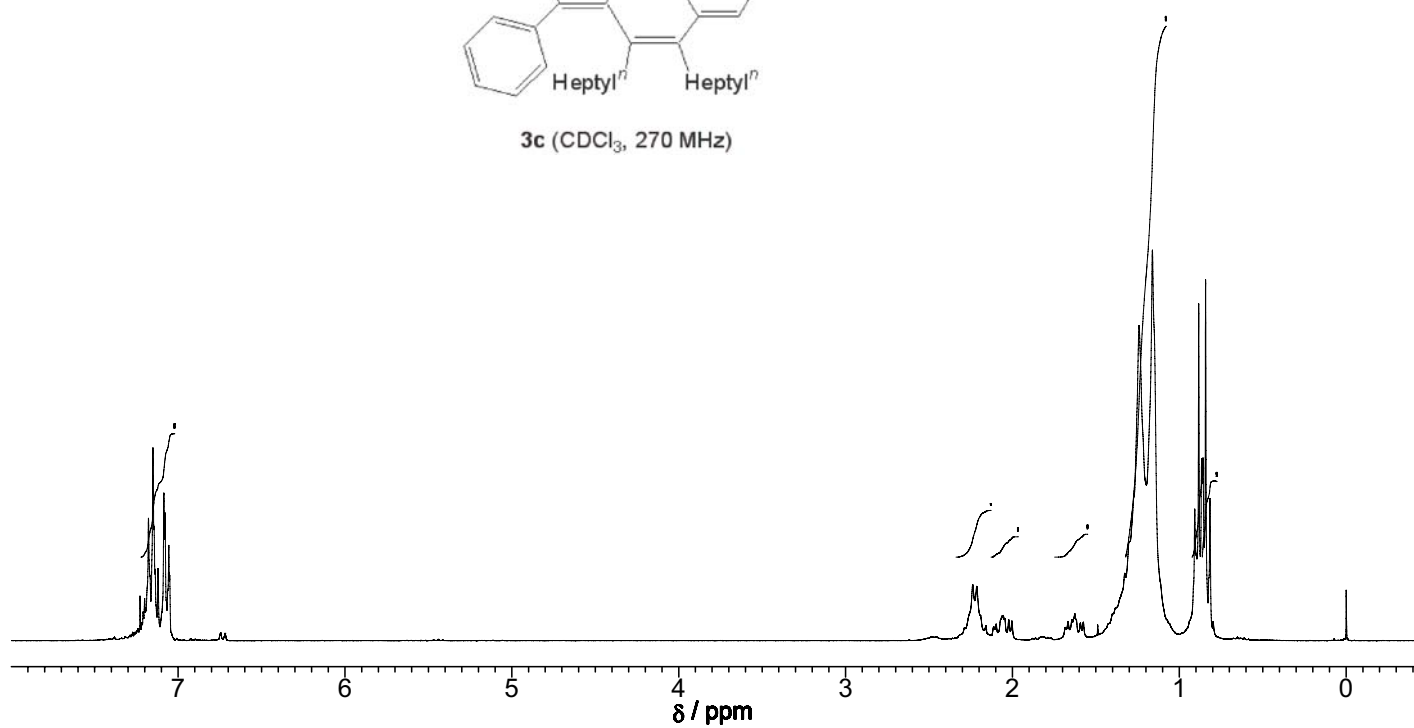


No.	ppm	Hz	Height
1	143.87	9773.8	25.87
2	138.99	9441.8	31.64
3	136.53	9274.7	30.60
4	128.55	8732.6	99.13
5	127.23	8643.1	99.97
6	125.50	8525.8	45.28
7	33.91	2303.8	44.00
8	33.77	2294.3	42.38
9	31.69	2152.8	49.03
10	30.53	2074.0	48.57
11	23.46	1593.9	60.98
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13	14.08	956.2	65.97
14	14.05	954.5	65.44

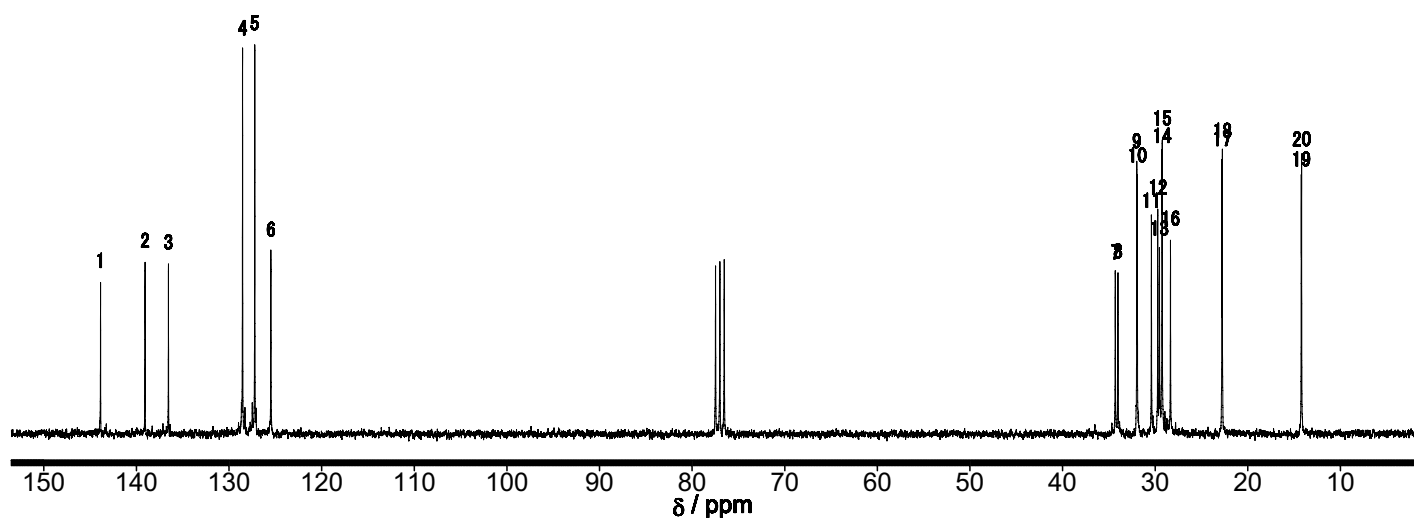


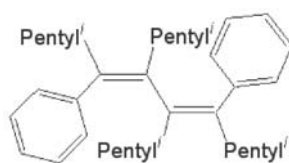


3c (CDCl₃, 270 MHz)

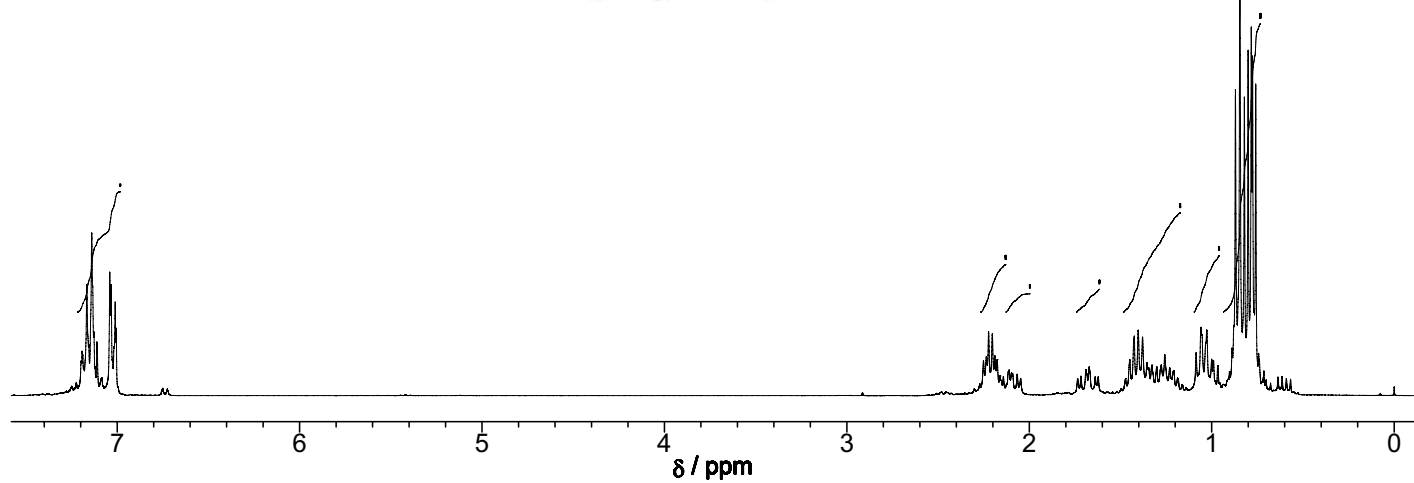


No.	ppm	Hz	Height
1	143.87	9773.8	38.93
2	139.07	9447.4	44.07
3	136.54	9275.8	43.64
4	128.54	8732.0	98.59
5	127.22	8642.6	99.82
6	125.49	8524.6	46.91
7	34.31	2330.6	41.15
8	34.02	2311.0	41.39
9	31.99	2173.0	69.61
10	31.93	2169.1	65.94
11	30.41	2065.7	54.32
12	29.72	2019.3	57.73
13	29.54	2007.0	47.22
14	29.27	1988.5	70.96
15	29.24	1986.3	75.44
16	28.35	1925.9	49.73
17	22.80	1548.6	70.17
18	22.75	1545.3	72.26
19	14.22	966.2	64.93
20	14.19	964.0	70.10

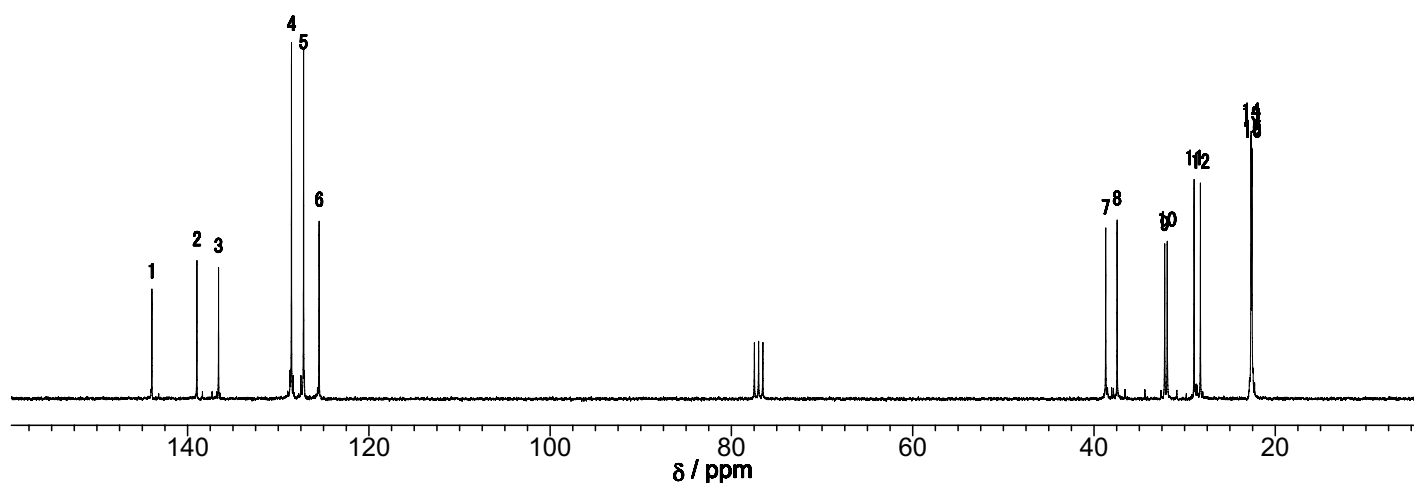


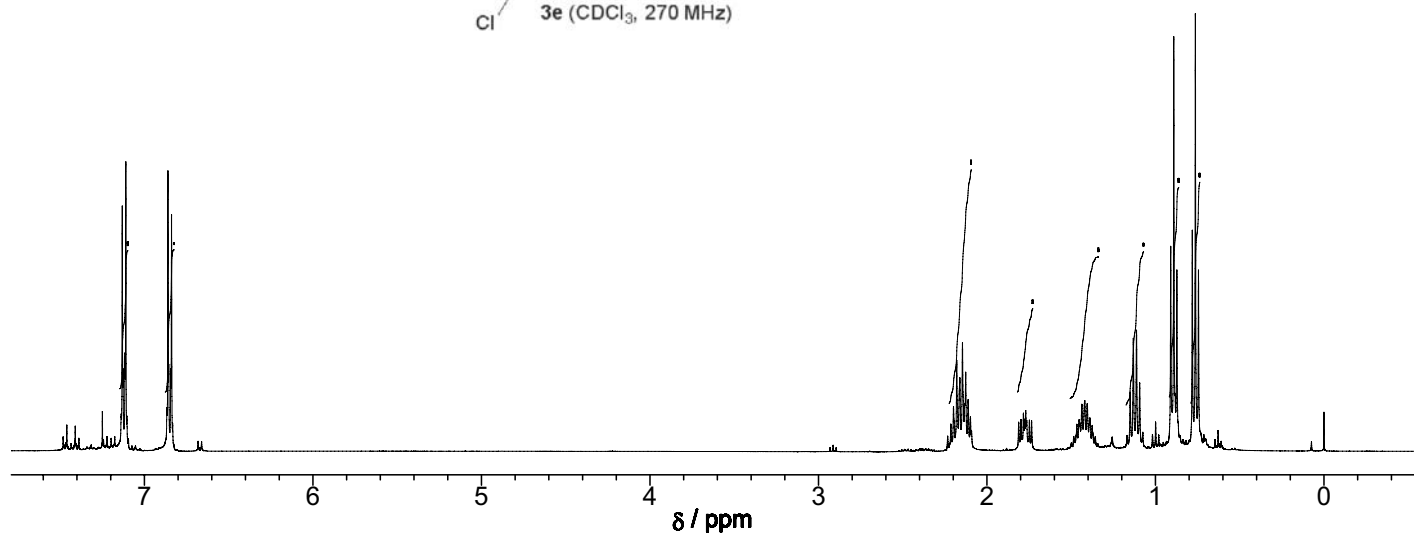
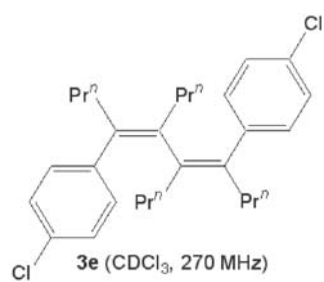


3d (CDCl₃, 270 MHz)

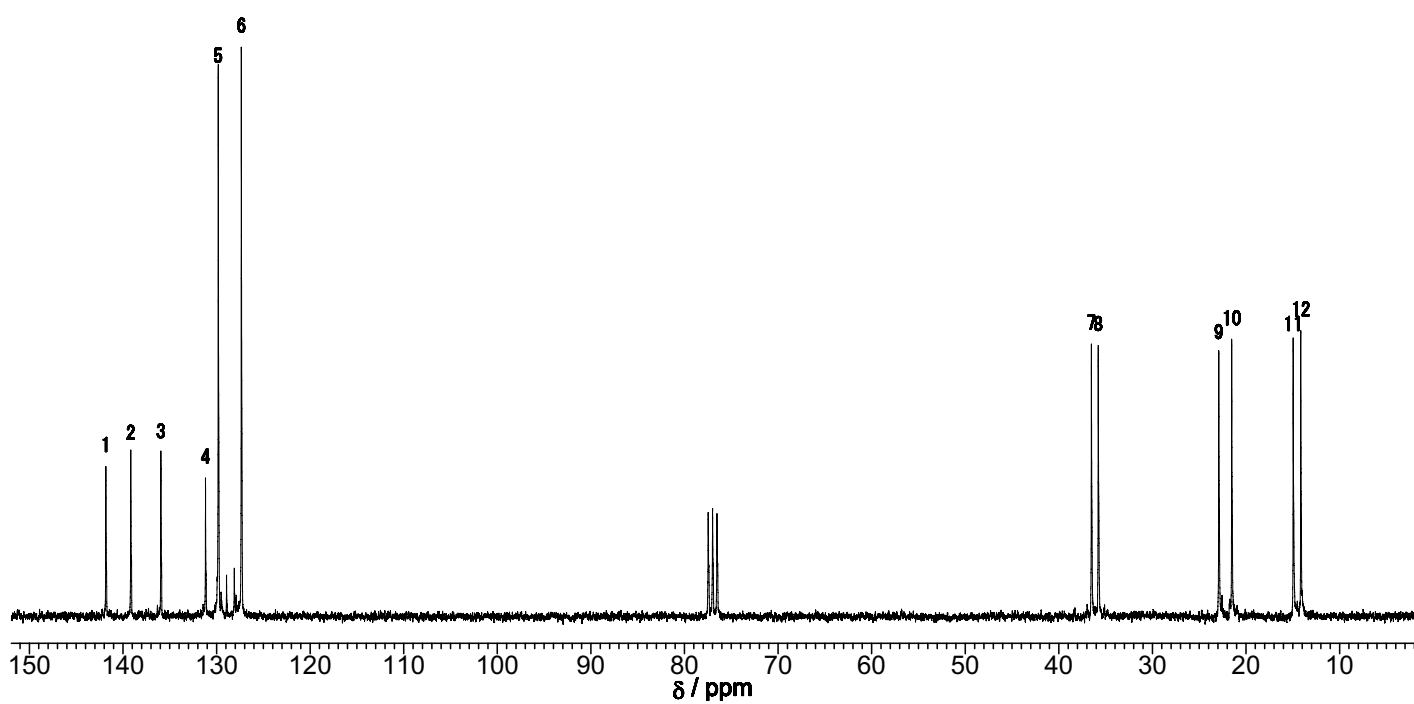


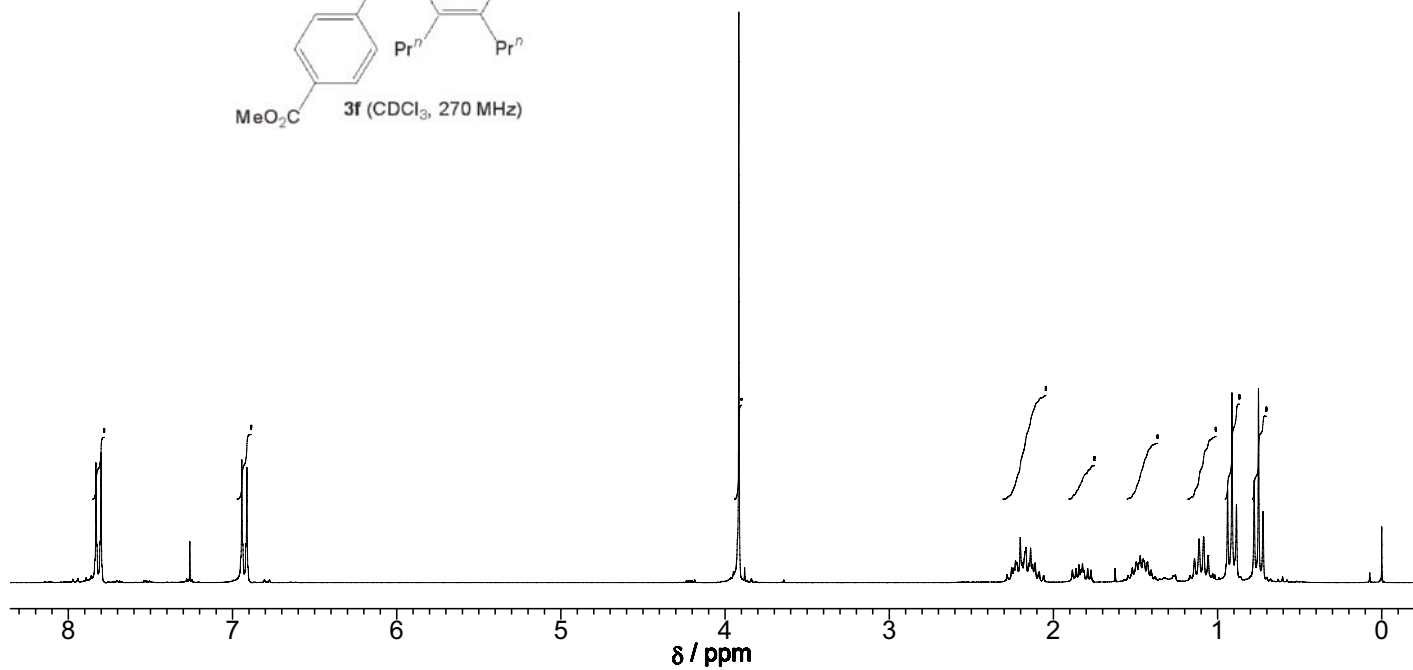
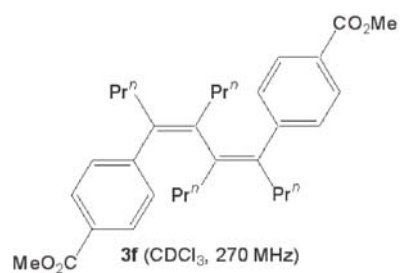
No.	ppm	Hz	Height
1	143.93	9777.8	29.45
2	138.97	9440.7	38.38
3	136.58	9278.6	36.48
4	128.54	8732.0	97.96
5	127.20	8641.5	92.83
6	125.49	8525.2	49.26
7	38.71	2629.6	47.18
8	37.45	2544.1	49.60
9	32.20	2187.5	42.55
10	31.92	2168.5	43.73
11	28.96	1967.3	60.81
12	28.26	1919.8	59.82
13	22.68	1540.8	72.94
14	22.66	1539.7	73.81
15	22.58	1534.1	69.09
16	22.56	1532.4	68.39



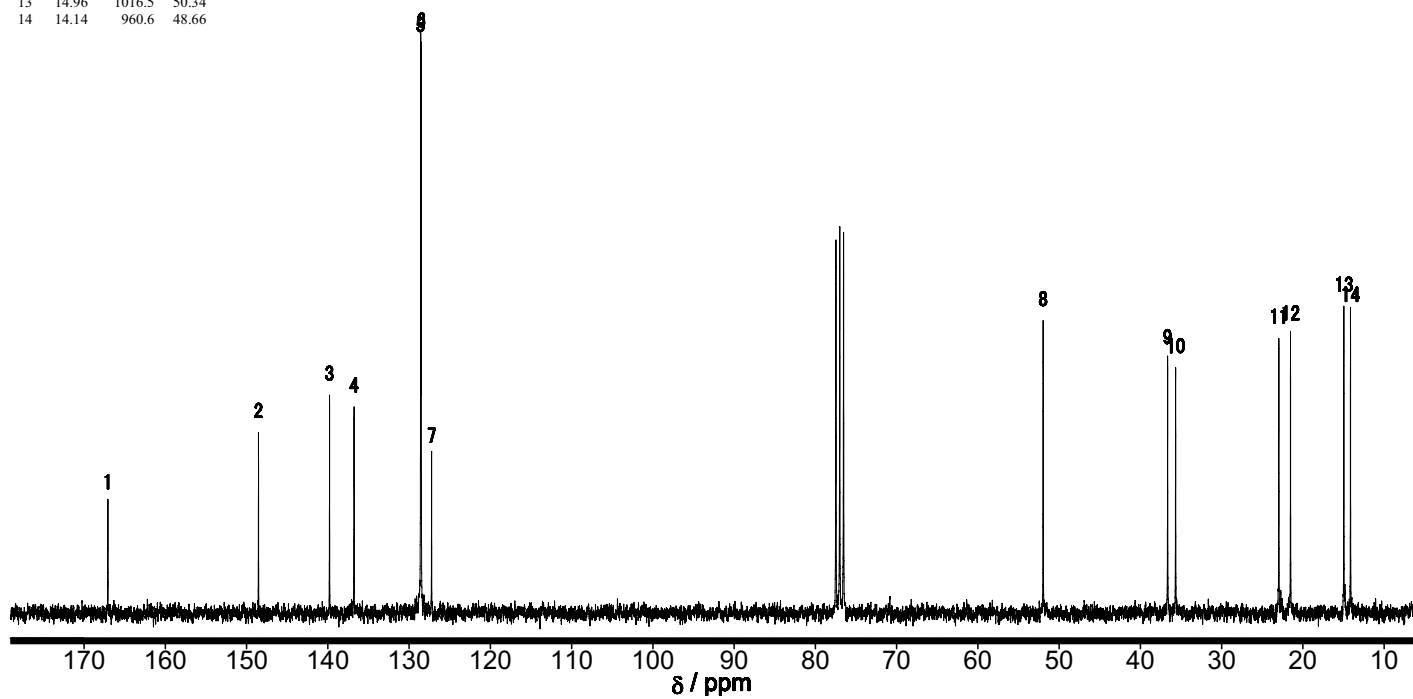


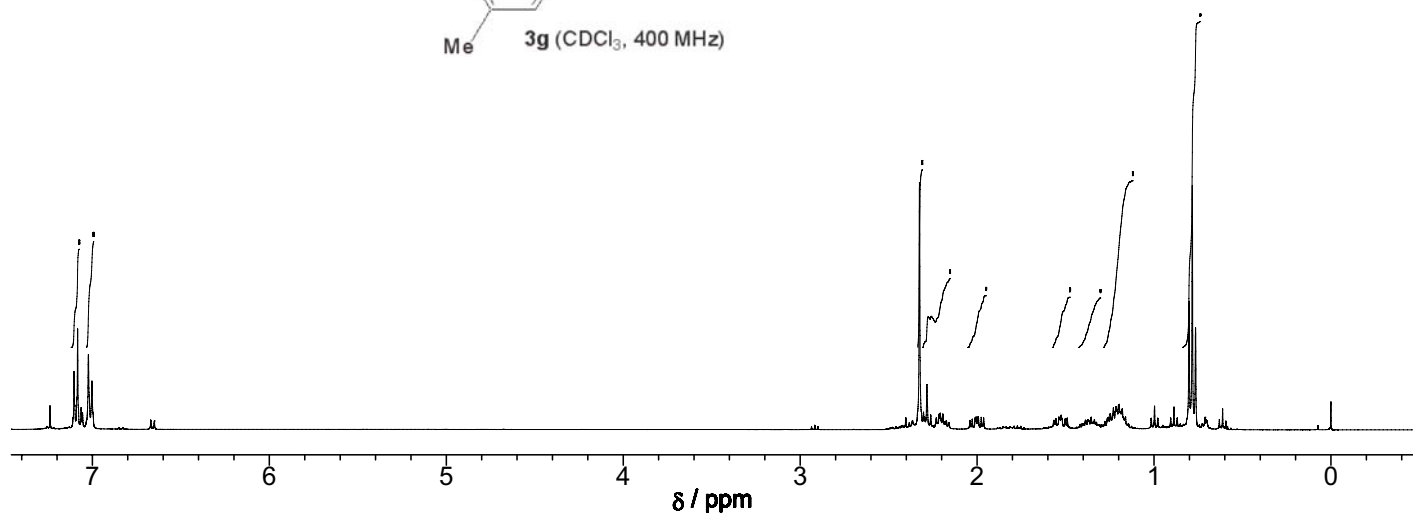
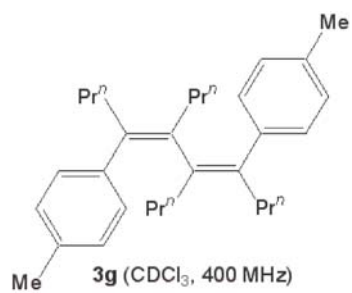
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3	135.95	9235.6	28.29
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5	129.82	8819.2	92.92
6	127.35	8651.5	98.12
7	36.52	2480.9	47.01
8	35.79	2431.2	46.77
9	22.91	1556.5	45.38
10	21.53	1462.6	47.76
11	14.96	1016.5	46.77
12	14.15	961.2	49.32



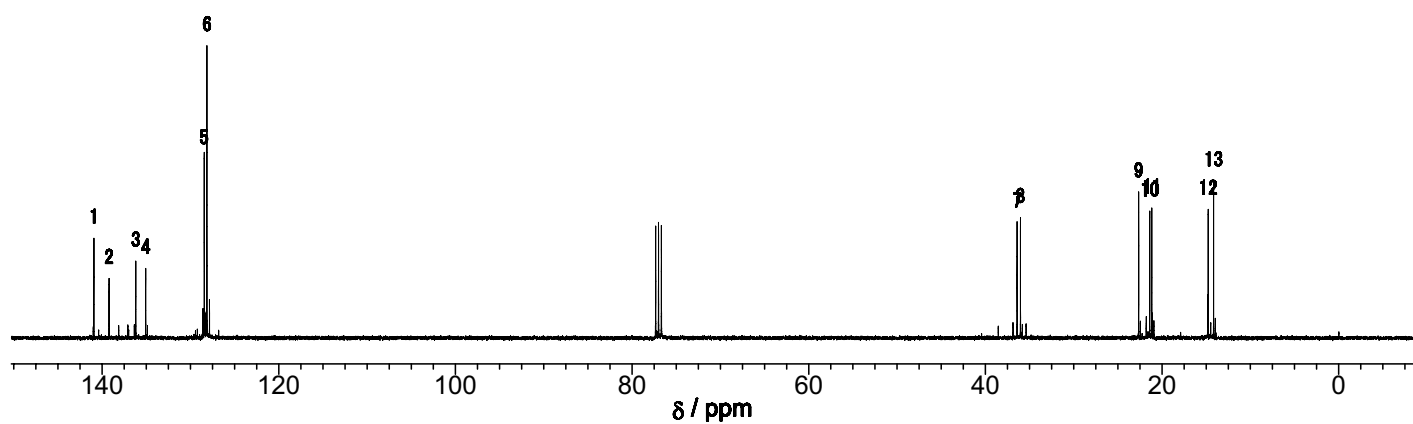


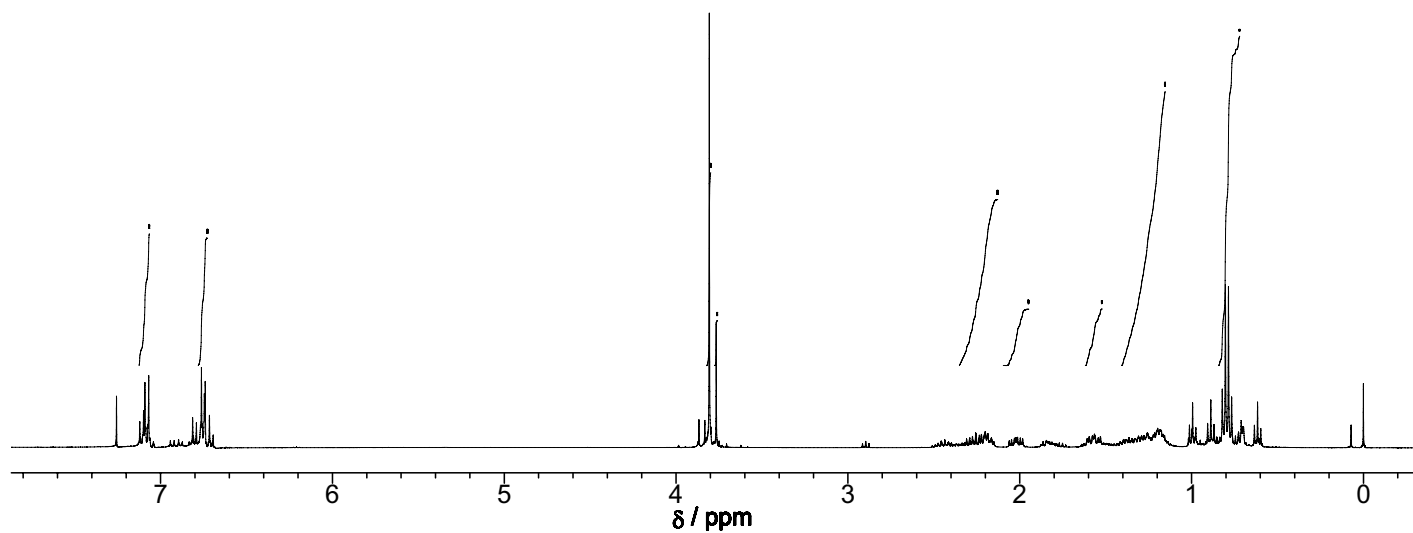
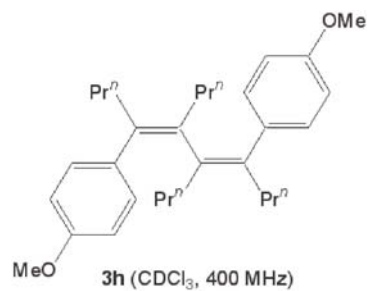
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4	136.77	9291.5	33.78
5	128.58	8734.8	93.05
6	128.51	8730.3	93.78
7	127.23	8643.1	25.49
8	51.97	3530.6	47.97
9	36.65	2489.9	41.71
10	35.66	2422.8	40.23
11	22.96	1559.8	45.06
12	21.53	1462.6	45.64
13	14.96	1016.5	50.34
14	14.14	960.6	48.66



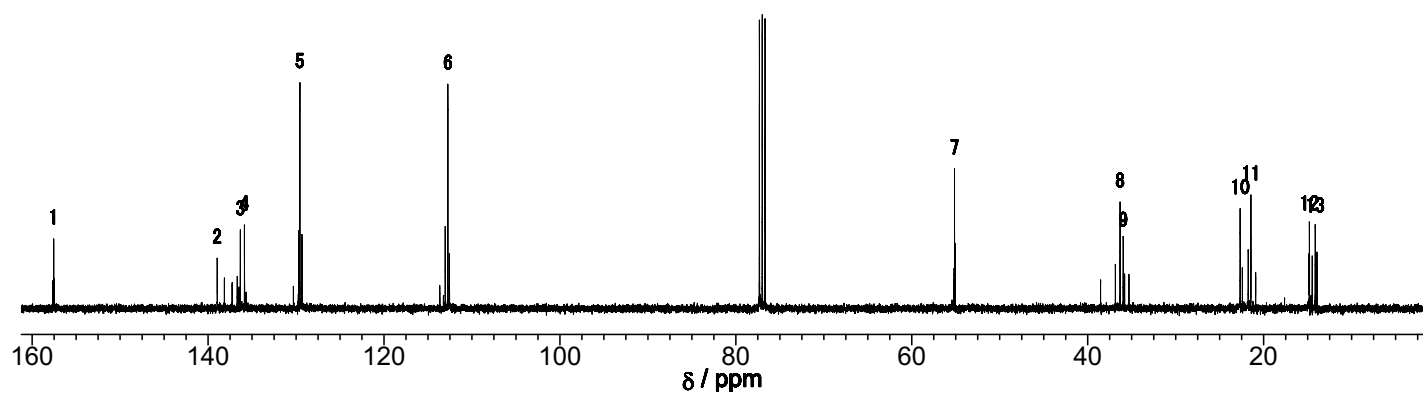


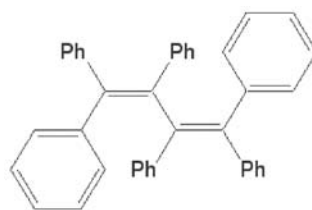
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3	136.19	13555.4	25.82
4	135.06	13443.5	23.35
5	128.44	12784.4	60.26
6	128.14	12754.0	98.30
7	36.42	3624.6	39.06
8	36.03	3586.5	40.48
9	22.65	2254.0	49.11
10	21.39	2129.2	42.62
11	21.16	2106.3	43.70
12	14.78	1470.9	43.24
13	14.17	1410.0	52.83



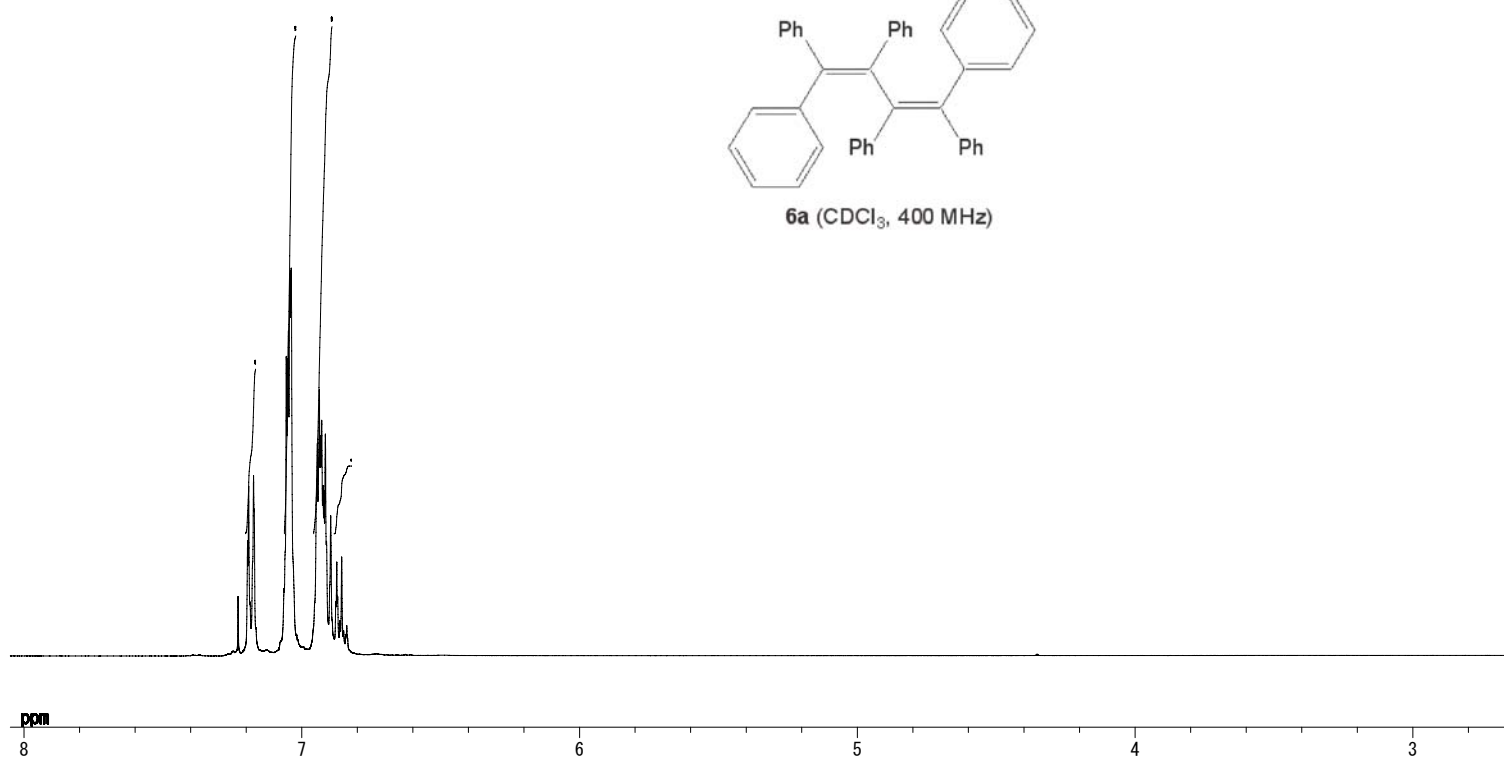


No.	ppm	Hz	Height
1	157.54	15680.9	23.37
2	138.96	13831.6	16.86
3	136.33	13569.8	26.41
4	135.87	13523.4	28.05
5	129.56	12895.5	75.92
6	112.74	11221.3	75.41
7	55.14	5488.4	46.95
8	36.32	3615.5	35.75
9	35.96	3579.7	22.49
10	22.68	2257.0	33.53
11	21.44	2134.5	38.13
12	14.80	1473.1	28.07
13	14.14	1406.9	27.38

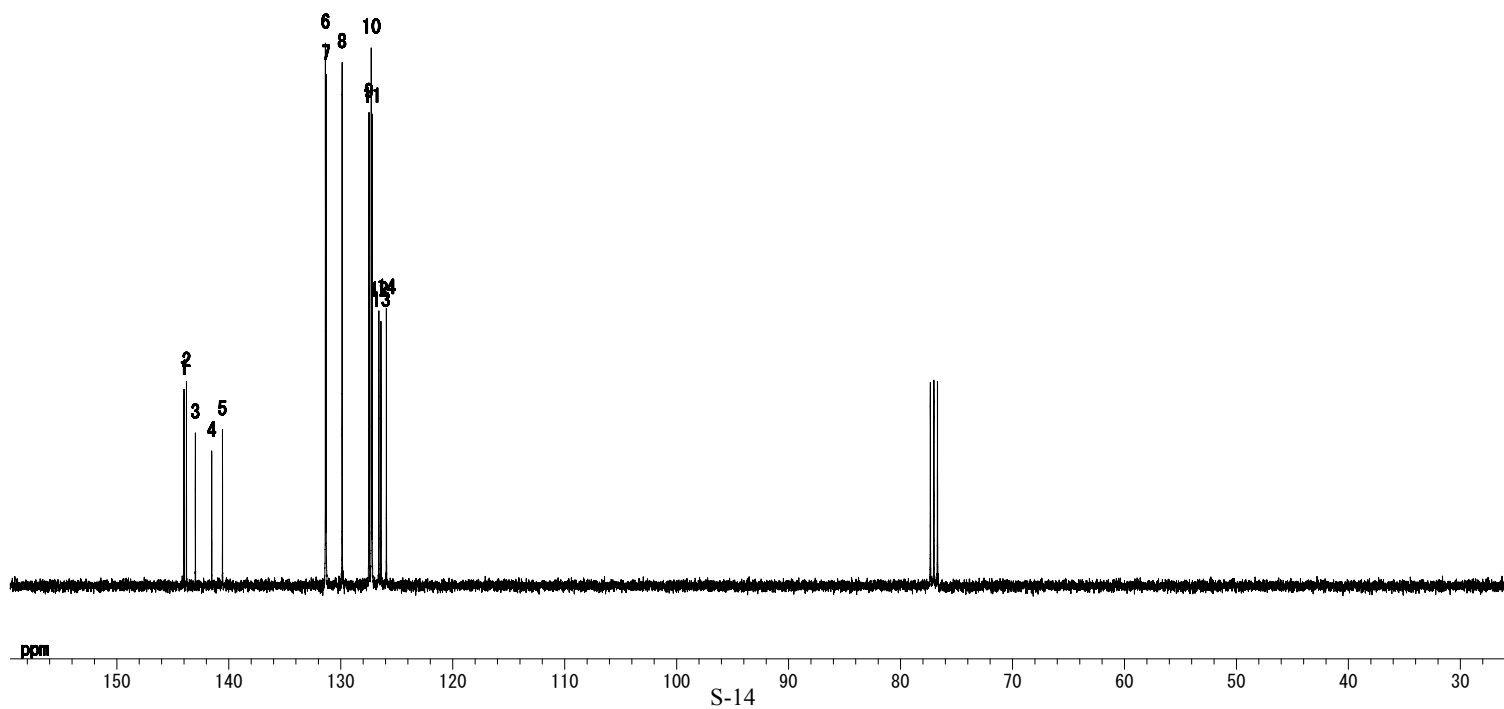


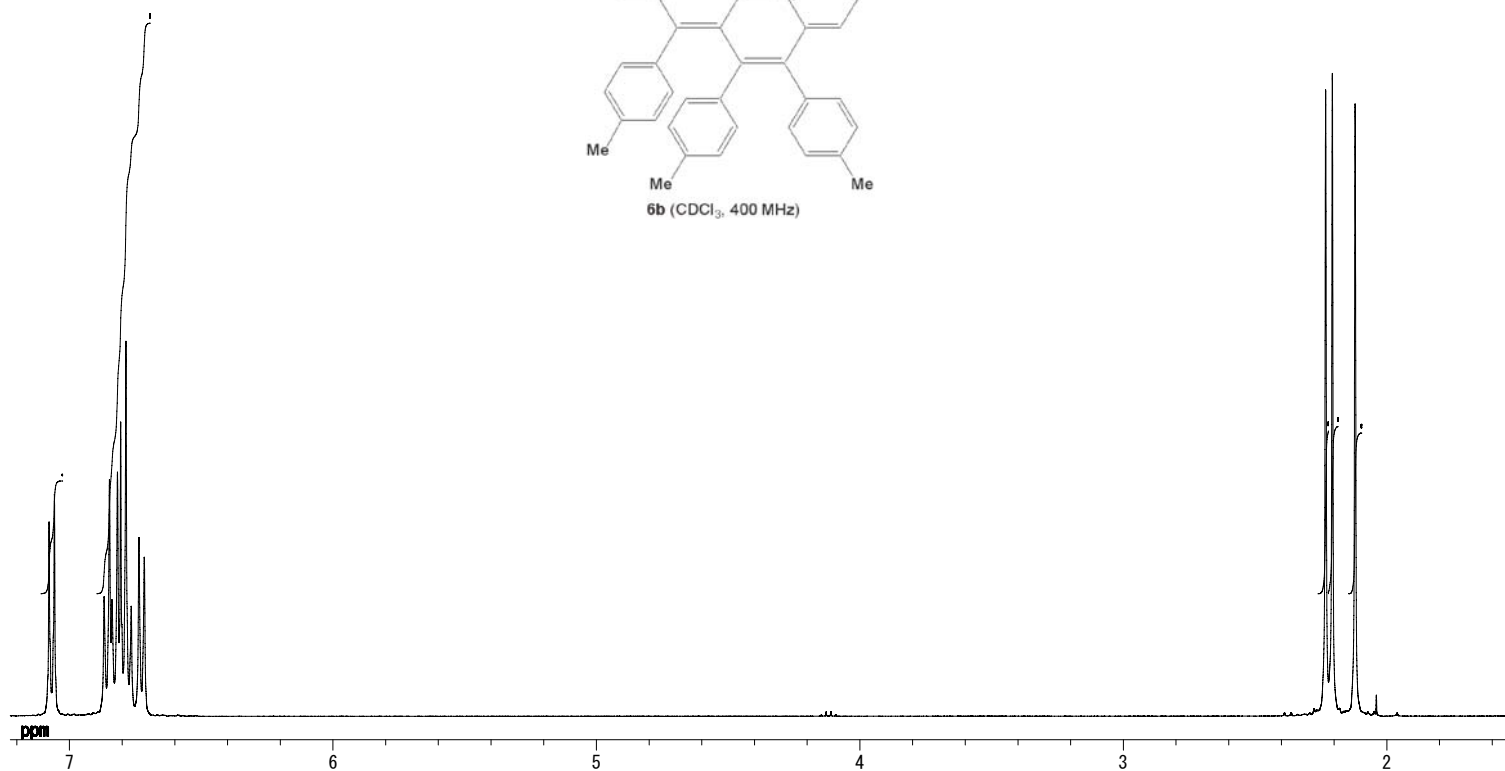
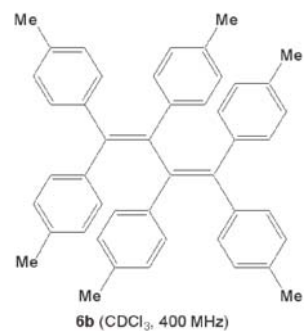


6a (CDCl₃, 400 MHz)

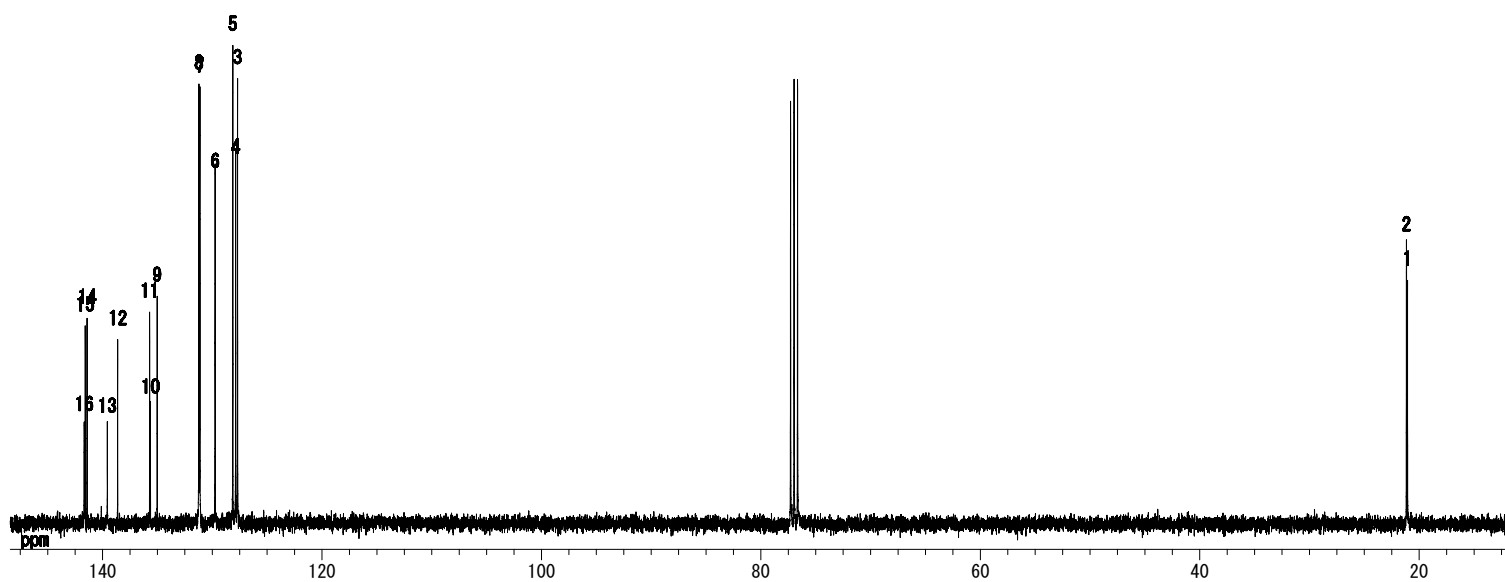


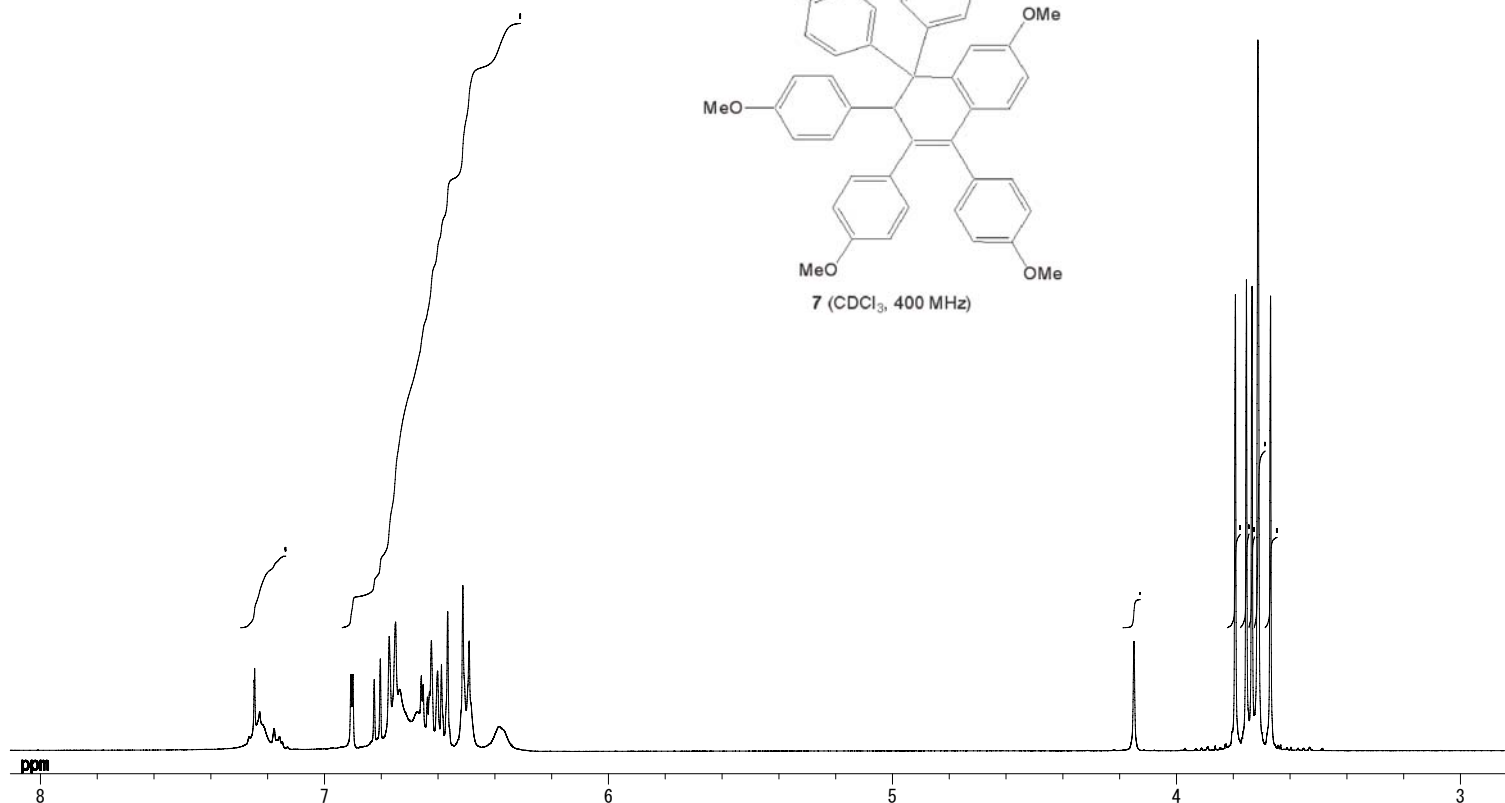
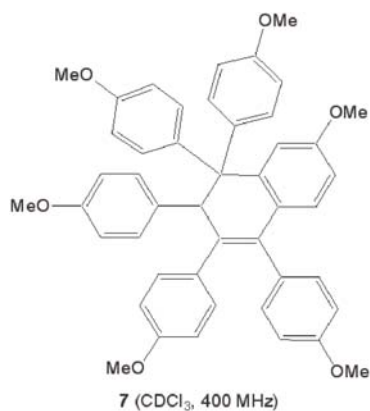
No.	ppm	Hz	Amp.	Height
1	144.00	14475.7	201638500	33.51
2	143.78	14453.6	209893500	34.88
3	142.98	14373.5	156717000	26.04
4	141.53	14227.0	138151500	22.96
5	140.56	14130.1	159939600	26.58
6	131.37	13206.2	557837700	92.70
7	131.31	13200.1	525681300	87.35
8	129.88	13055.9	537888400	89.38
9	127.48	12814.8	486519300	80.85
10	127.27	12794.2	552852500	91.87
11	127.20	12787.3	481784300	80.06
12	126.60	12726.3	282387000	46.92
13	126.41	12707.2	271594200	45.13
14	125.92	12658.4	284854100	47.33



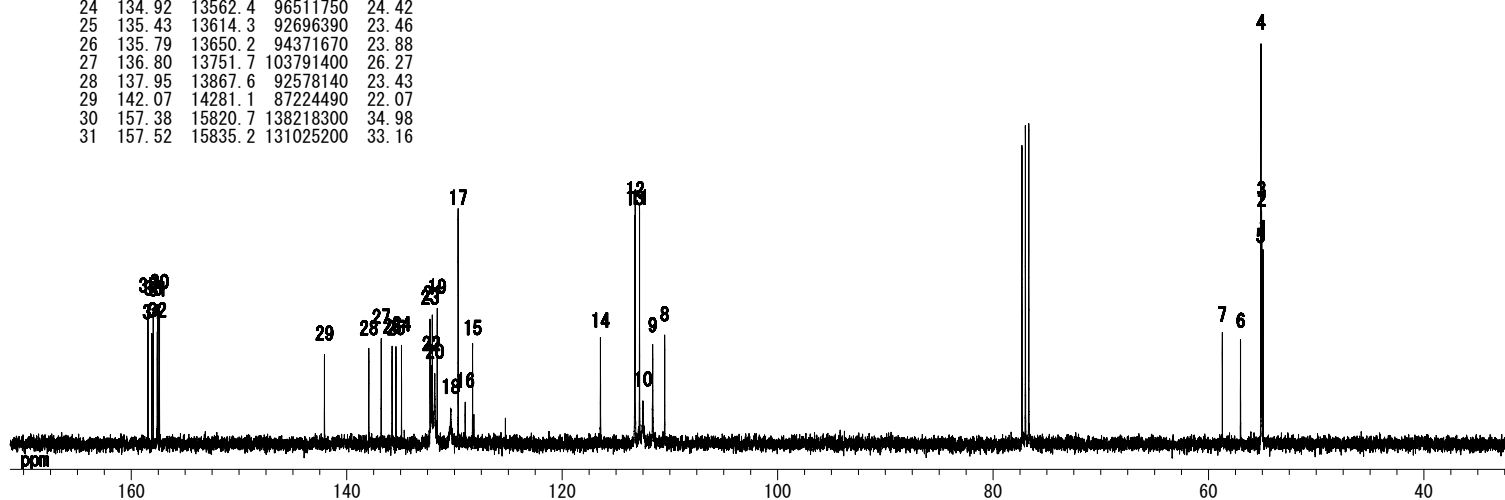


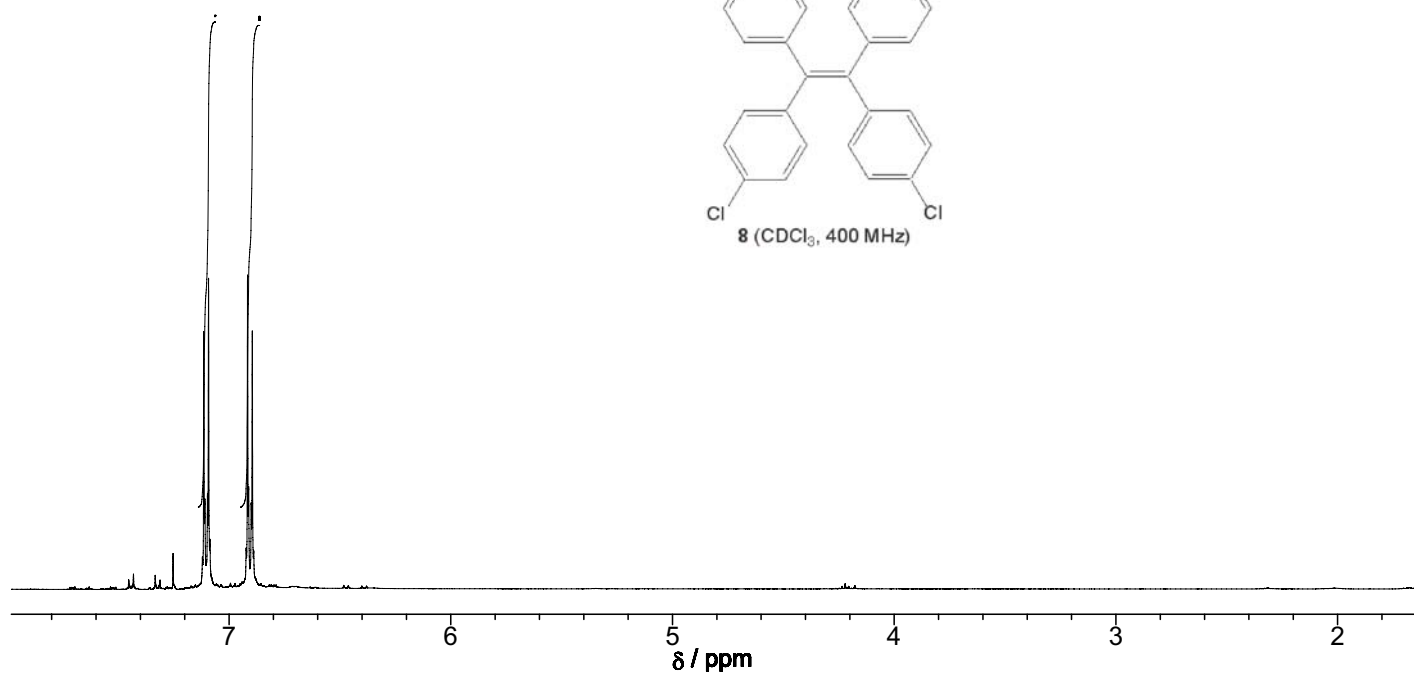
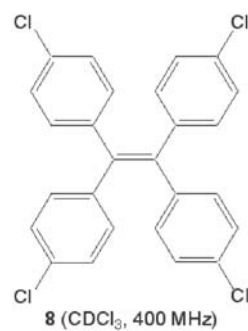
No.	ppm	Hz	Amp.	Height
1	21.07	2117.6	333306300	50.25
2	21.16	2127.5	381025800	57.44
3	127.70	12836.9	610334300	92.02
4	127.87	12853.7	487290000	73.46
5	128.13	12880.4	655678300	98.85
6	129.75	13042.9	467746600	70.52
7	131.13	13181.7	598907600	90.29
8	131.22	13190.9	602658000	90.86
9	135.02	13573.1	311538500	46.97
10	135.64	13634.9	158119400	23.84
11	135.71	13642.6	289638200	43.67
12	138.63	13935.5	252138400	38.01
13	139.57	14030.1	131876200	19.88
14	141.41	14215.5	281163600	42.39
15	141.58	14232.3	270987800	40.85
16	141.67	14241.5	134269600	20.24





No.	ppm	Hz	Amp.	Height	No.	ppm	Hz	Amp.	Height
1	54.94	5522.6	191520000	48.47	32	157.59	15841.3	110334500	27.92
2	55.06	5534.8	219864700	55.64	33	157.97	15879.5	131957500	33.39
3	55.07	5536.3	230072400	58.23	34	158.10	15893.2	108463000	27.45
4	55.13	5541.7	395143100	100	35	158.45	15928.3	134652100	34.08
5	55.15	5544.0	183702600	46.49					
6	57.02	5732.4	99809740	25.26					
7	58.72	5902.5	106311200	26.90					
8	110.49	11106.5	106425400	26.93					
9	111.59	11217.9	95484540	24.16					
10	112.50	11309.5	41933520	10.61					
11	112.82	11341.5	221572900	56.07					
12	113.22	11381.2	230021800	58.21					
13	113.26	11385.8	221310500	56.01					
14	116.45	11706.2	100164400	25.35					
15	128.31	12898.7	92762260	23.48					
16	129.00	12968.1	40656370	10.29					
17	129.66	13034.5	221523900	56.06					
18	130.35	13103.9	34533730	8.74					
19	131.60	13229.0	133510100	33.79					
20	131.83	13251.9	69112560	17.49					
21	132.05	13274.8	126893700	32.11					
22	132.15	13284.7	76982220	19.48					
23	132.27	13296.2	122810700	31.08					
24	134.92	13562.4	96511750	24.42					
25	135.43	13614.3	92696390	23.46					
26	135.79	13650.2	94371670	23.88					
27	136.80	13751.7	103791400	26.27					
28	137.95	13867.6	92578140	23.43					
29	142.07	14281.1	87224490	22.07					
30	157.38	15820.7	138218300	34.98					
31	157.52	15835.2	131025200	33.16					





No.	ppm	Hz	Amp.	Height
1	128.31	12898.7	1980620000	74.64
2	132.43	13312.2	2478706000	93.41
3	132.97	13366.4	474966800	17.90
4	139.55	14027.8	242724500	9.15
5	141.09	14183.5	873471100	32.92

