Nickel-Catalyzed Manipulation on Tertiary Phosphines via Highly Selective C-P Bond Cleavage

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‡ Prof. Huang passed away on March 6, 2010. He had been fully in charge of this project. At this moment, Prof. Luling Wu is helping him to finish all the projects with the help from Prof. Shengming Ma

Supporting Information

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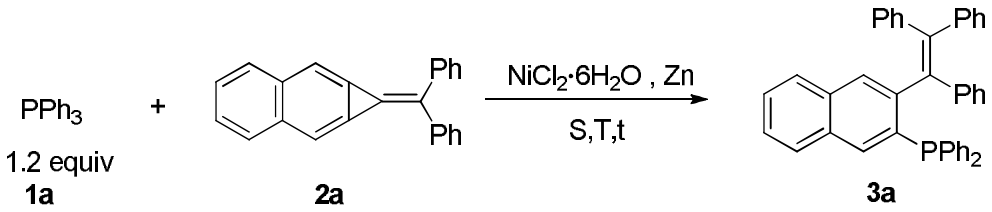
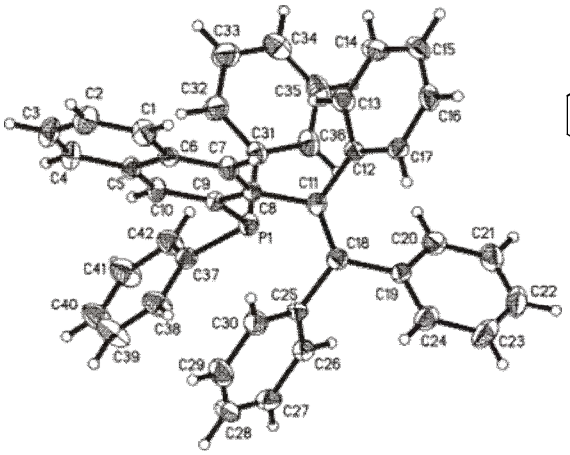
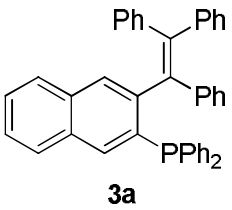
Table S1. Optimization of reaction conditions for the nickel-catalyzed ring-opening coupling of triphenylphosphine (**1a**).with 1-(diphenylmethylene)-1H-cyclopropa[*b*]naphthalene (**2a**) [a]



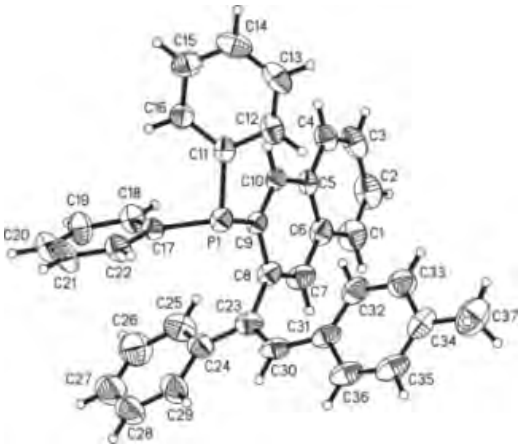
entry	$NiCl_2·6H_2O$ / Zn (%)	solvent / concentration	T(℃)	time (h)	yield of **3a** (%)
1	no	dioxane /0.1M	110	24	N.R.
2	10/30	dioxane /0.1M	110	2	96
3	5/15	dioxane /0.1M	110	5	96
4	2/6	dioxane /0.1M	110	10	96
5	**2/6**	**dioxane /0.2M**	**110**	**0.5**	**96**
6	2/6	dioxane /0.4M	110	0.5	92
7	2/6	toluene/0.2M	110	17	96
8	2/6	$CHCl_3$/0.2M	70	24	<10[c]
8	2/6	THF/0.2M	70	2	93
10	2/6	acetone/0.2M	70	24	30[d]
11	2/6	DMF/0.2M	110	1	94
12	2/6	DMSO/0.2M	110	4	90

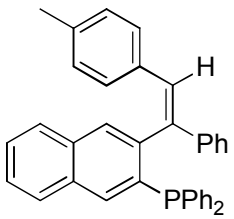
[a] The reaction was conducted with 0.24 mmol of **1a**, 0.2 mmol of **2a**, and corresponding of $NiCl_2·6H_2O$, Zn and solvent. [b] Isolated yield. [c] 80% of **2a** was recovered. [d] 60% of **2a** was recovered.



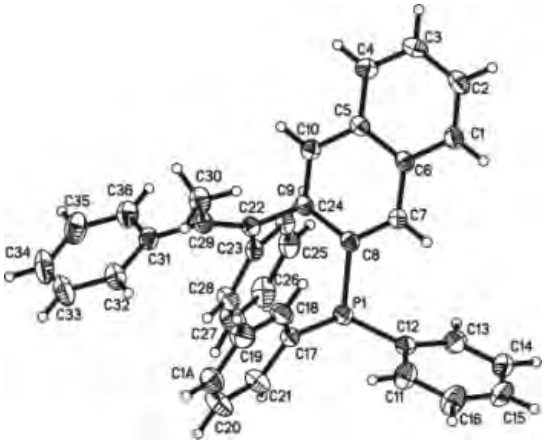


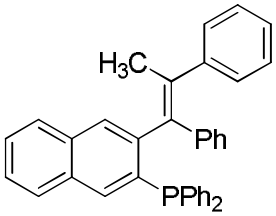
3a





3k





3l

Figure 1. ORTEP representation of **3a**, **3k** and **3l**.

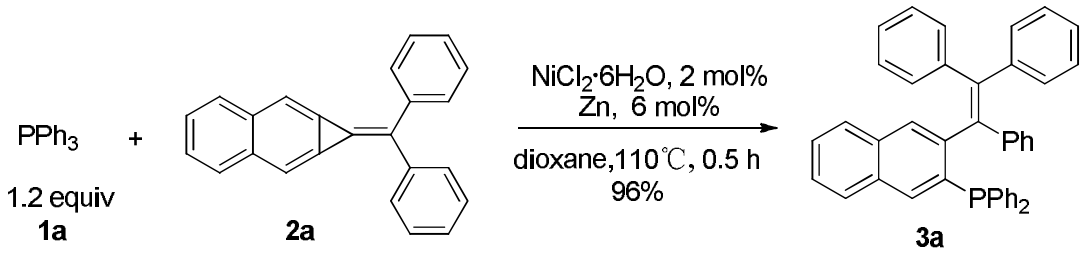
a)X-ray crystal data for **3a**: $C_{42}H_{31}P$; *M*=566.64; crystal system: monoclinic; space group: *P 21/c*; final *R* indices [$I > 2\sigma(I)$] *R*1= 0.0494, *wR*2= 0.1149, R indices (all data) *R*1= 0.0670, *wR*2= 0.1249; *a*= 10.0368(3) Å, *b*= 30.8934(8) Å, *c*= 10.8177(4) Å; *α*= 90.00, *β*= 109.139(4), *γ*= 90.00, *V*= 3168.85(17) $Å^3$, *T*=293(2) K, *Z*=4; F(000) 1192; reflections collected/unique: 13835/5789 [*R*(int)= 0.0260]; number of observations [$I > 2\sigma(I)$]: 4487; parameters: 388. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 903816. b)X-ray crystal data for **3k**: $C_{37}H_{29}P$; *M*=504.57; crystal system: monoclinic; space group: *P 21/c*; final *R* indices [$I > 2\sigma(I)$] *R*1= 0.0797, *wR*2= 0.1938, R indices (all data) *R*1= 0.1220, *wR*2= 0.2221; *a*= 9.8232(11) Å, *b*= 30.276(2) Å, *c*= 10.9053(19) Å; *α*= 90.00, *β*= 120.527(9), *γ*= 90.00, *V*= 2793.8(6) $Å^3$, *T*=293(2) K, *Z*=4; F(000) 1064; reflections collected/unique: 11860/5090 [*R*(int)= 0.0378]; number of observations [$I > 2\sigma(I)$]: 3274; parameters: 344. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 917493. c) X-ray crystal data for **3l**: $C_{37}H_{29}P$; *M*=504.57; crystal system: monoclinic; space group: *P 21/c*; final *R* indices [$I > 2\sigma(I)$] *R*1= 0.0458, *wR*2= 0.0982, R indices (all data) *R*1= 0.0705, *wR*2= 0.1100; *a*= 9.8506(5) Å, *b* = 9.3011(4) Å, *c*= 29.8411(11) Å; *α*= 90.00, *β*= 93.387(3), *γ*= 90.00, *V*= 2729.3(2) $Å^3$, *T*=293(2) K, *Z*=4; F(000) 1064; reflections collected/unique: 15308 / 4992 [*R*(int)= 0.0358]; number of observations [$I > 2\sigma(I)$]: 3621; parameters: 344. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 917494.

General Experimental Procedures:

1,4-Dioxane, PhMe and THF were distilled from Na/benzophenone immediately prior to use. Petroleum ether refers to the fraction with the boiling point in the range 60℃-90℃. All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in $CDCl_3$ with TMS as the internal standard unless noted otherwise. Chemical shifts are expressed in ppm, and *J* values are given in Hz. The other commercially available chemicals were purchased and used without further purification unless noted otherwise.

General Experimental Procedures:

(1) Diphenyl[3-(1,2,2-triphenylvinyl)naphthalen-2-yl]phosphine (3a)

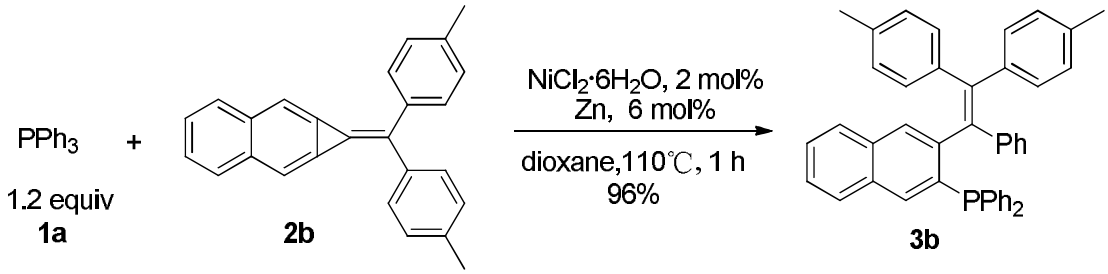


Typical procedure: A rubber-capped Schlenk vessel containing $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (**2a**, 61 mg, 0.2 mmol) was degassed and backfilled with nitrogen for three times, then dioxane (1 mL) was added to the Schlenk vessel. The resulting mixture was then allowed to stir at 110 °C. After the reaction was completed as monitored by TLC, The reaction mixture was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/CH_2Cl_2 = 10:1) to afford **3a** (109 mg, 96%) as a white solid: m.p. 220-222 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):

δ = 7.68-7.61 (m, 2H), 7.54 (d, J = 7.2Hz, 2H), 7.37-7.28 (m, 2H), 7.24-7.04 (m, 15H), 6.96-6.88 (m, 5H), 6.82-6.76 (m, 5H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.80 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.6 (d, J = 31.5Hz), 143.72, 143.69 142.8, 142.3, 142.3, 140.5 (d, J = 4.6Hz), 138.9 (d, J = 13.7Hz), 136.9 (d, J = 13.7Hz), 136.7, 136.2, 136.1 (d, J = 14.1Hz), 134.0 (d, J = 20.0Hz). 133.5, 133.0 (d, J = 17.5Hz), 132.2, 131.6, 131.5, 131.4, 130.9 (d, J = 7.3Hz), 128.2 (d, J = 12.9Hz), 128.14, 128.12, 128.0, 127.9, 127.7, 127.5, 127.4, 127.2, 126.6 (d, J = 17.8Hz), 126.2 (d, J = 18.3Hz), 125.7 ppm; MS(EI): m/z (%) = 566 (M^+, 25.0); IR (neat): 3056, 1583, 1492, 1436, 1264, 1195, 1115, 1029 cm^{-1}; HRMS calcd. for $C_{42}H_{32}P$ ($(M+1)^+$): 567.2236; found: 567.2246.

The following compounds were prepared according to this procedure.

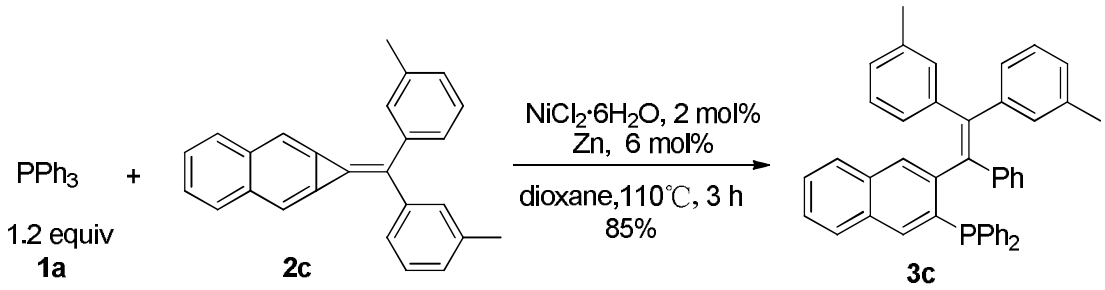
(2) Diphenyl[3-(1-phenyl-2,2-di-*p*-tolylvinyl)naphthalen-2-yl]phosphine (3b)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2b** (66 mg, 0.2 mmol) in dioxane (1 mL) afforded **3b** (114 mg, 96%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 219-221 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68-7.61 (m, 2H), 7.57-7.53 (m, 2H), 7.37-7.28 (m, 2H), 7.24-6.98 (m, 12H), 6.96-6.88 (m, 4H), 6.84-6.77 (m, 5H), 6.73 (d, J = 7.2Hz, 2H), 2.25 (s, 3H), 2.14 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.87 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.0 (d, J = 31.3Hz), 143.3, 142.2, 140.90,

140.88, 139.4 (d, J = 5.5Hz), 139.0 (d, J = 14.1Hz), 137.2 (d, J = 13.9Hz), 136.79, 136.77, 136.1 (d, J = 13.8Hz), 135.9 (d, J = 28.2Hz), 133.9 (d, J = 21.6Hz), 133.5, 132.9 (d, J = 18.4Hz), 132.2, 131.6, 131.43, 131.38, 130.9 (d, J = 6.9Hz), 128.4, 128.2, 128.1, 128.0(broad peak, 2C), 127.9, 127.6, 127.5, 127.2, 126.6, 125.8, 125.6, 21.2, 21.1 ppm; MS(EI): m/z (%) = 594 (M^+, 79.0), 503 (100); IR (neat): 3050, 1636, 1558, 1541, 1508, 1489, 1457, 1435, 1276, 1261, 1182, 1114, 1025 cm^{-1}; HRMS calcd. for $C_{44}H_{36}P$ ($(M+1)^+$): 595.2549; found: 595.2561.

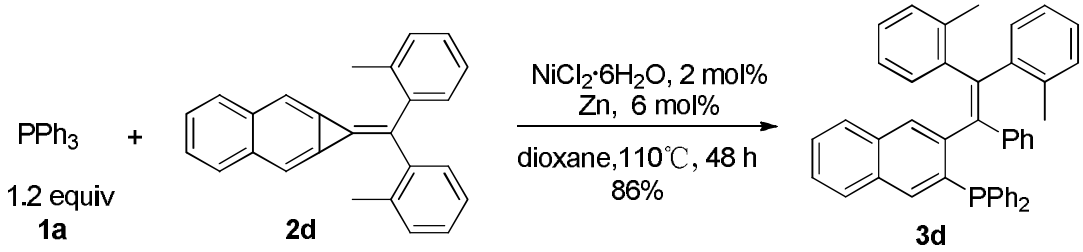
(3) Diphenyl[3-(1-phenyl-2,2-di-*m*-tolylvinyl)naphthalen-2-yl]phosphine (3c)



The reaction of $NiCl_2·6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2c** (66 mg, 0.2 mmol) in dioxane (1 mL) afforded **3c** (101 mg, 85%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 190-192 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.66 (d, J = 5.2Hz, 2H), 7.59-7.53 (m, 2H), 7.41-7.28 (m, 2H), 7.25-7.07 (m, 6H), 7.07-6.91 (m, 10H), 6.89-6.75 (m, 7H), 2.17 (s, 3H), 2.01 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.97 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.7 (d, J = 33.2Hz), 143.7, 143.5, 142.7, 142.4, 140.3(d, J = 5.5Hz), 139.2 (d, J = 13.3Hz), 137.0, 136.9, 136.7, 136.1 (d, J = 13.9Hz), 133.9 (d, J = 20.8Hz), 133.5, 132.9 (d, J = 18.1Hz), 132.2, 132.1, 131.8, 131.6, 130.8 (d, J = 6.5Hz), 128.6, 128.4, 128.2, 128.15, 128.09, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.23, 127.18, 127.1,

126.6, 126.0, 125.6, 21.3, 21.2 ppm; MS(EI): *m*/*z* (%) = 594 (M^+, 32.0), 503 (100); IR (neat): 3051, 1600, 1484, 1436, 1266, 1197, 1116, 1094, 1028 cm^{-1}; HRMS calcd. for $C_{44}H_{36}P$ $((M+1)^+)$: 595.2549; found: 595.2561.

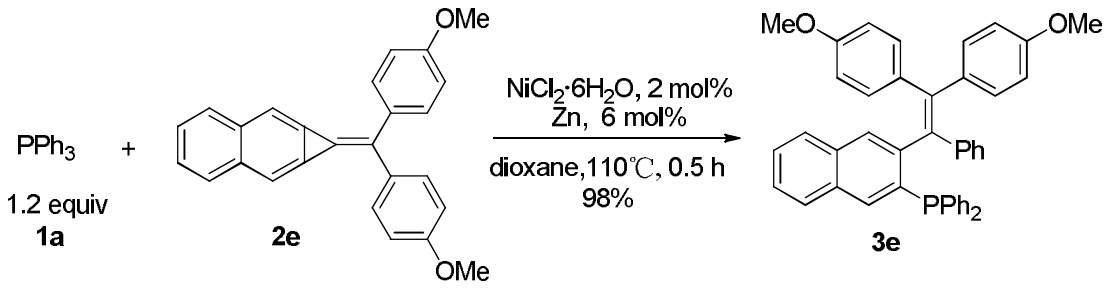
(4) Diphenyl[3-(1-phenyl-2,2-di-*o*-tolylvinyl)naphthalen-2-yl]phosphine (3d)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2d (**66 mg, 0.2 mmol) in dioxane (1 mL) afforded **3d** (102 mg, 86%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 132-134 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO-D_6, 80 °C): δ = 7.79-7.73 (m, 2H), 7.63-7.57 (m, 2H), 7.46-7.33 (m, 6H), 7.20-6.99 (m, 9H), 6.93-6.88 (m, 4H), 6.82-6.75 (m, 6H), 2.18 (s, 3H), 2.10 (s, 3H) ppm; ^{31}P NMR (162 MHz, DMSO-D_6, 80 °C): δ= -13.94 ppm; ^{13}C NMR (100 MHz, DMSO-D_6, 80 °C): δ = 145.3 (d, *J* = 33.4Hz), 142.3, 141.4, 140.3, 138.2, 138.1, 136.2, 136.1, 135.9, 135.8, 135.0, 134.8, 132.7, 132.5, 132.3, 132.1, 131.3 (broad peak, 2C), 131.0, 130.3, 129.7 (broad peak, 2C), 129.3, 127.9 (d, *J* = 4.6Hz), 127.7, 127.5 (d, *J* = 6.1Hz), 127.4, 127.0 (d, *J* = 14.4Hz), 126.6, 126.4, 126.3, 126.1, 125.7, 125.6, 124.6, 124.2, 19.8, 19.7 ppm; MS(EI): *m*/*z* (%) = 594 (M^+, 20.0), 57 (100); IR (neat): 2984, 1651, 1558, 1540, 1513, 1490, 1456, 1436, 1396, 1338, 1273, 1196, 1114, 1046 cm^{-1}; HRMS calcd. for $C_{44}H_{36}P$ $((M+1)^+)$: 595.2549; found: 595.2561; anal. calcd. for $C_{44}H_{35}P$: C 88.86, H 5.93; found: C 88.98, H 6.044.

(5) {3-[2,2-Bis(4-methoxyphenyl)-1-phenylvinyl]naphthalen-2-yl}diphenylphosphine

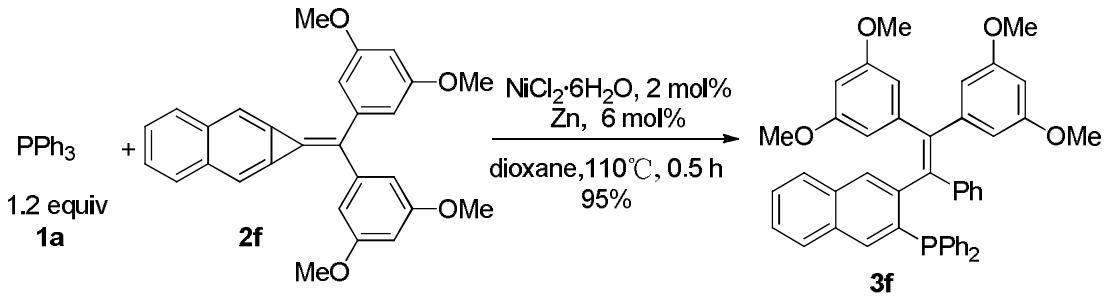
(3e)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2e** (73 mg, 0.2 mmol) in dioxane (1 mL) afforded **3e** (123 mg, 98%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 5:1): m.p. 215-217 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68-7.61 (m, 2H), 7.56 (d, J = 6.0Hz, 2H), 7.40-7.28 (m, 2H), 7.24-7.00 (m, 12H), 6.93-6.86 (m, 2H), 6.83-6.79 (m, 5H), 6.68 (d, J = 8.8Hz, 2H), 6.46 (d, J = 8.8Hz, 2H), 3.71 (s, 3H), 3.63 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ= -13.69 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.2, 157.9, 147 (d, J = 32.2Hz), 141.7 (d, J = 1.2Hz), 143.6, 139.0 (d, J = 13.6 Hz), 138.6 (d, J = 4.7Hz), 137.5 (d, J = 14.2Hz), 136.7 (d, J = 2.3Hz), 136.4, 136.3, 136.2 (d, J = 13.0Hz), 134.0 (d, J = 20.8Hz), 133.6, 133.0, 132.8 (d, J =15.0 Hz), 132.8, 132.2, 131.5, 130.9 (d, J = 6.4Hz), 128.1, 128.13, 128.09, 128.07, 128.05, 127.9, 127.6 (d, J = 10.2Hz), 127.2, 126.2, 125.6 (d, J = 13.9Hz), 113.1, 112.7, 55.05, 54.96 ppm; MS(EI): m/z (%) = 626 (M^+, 59.0), 549 (100); IR (neat): 3051, 1603, 1576, 1506, 1483, 1461, 1437, 1244, 1175, 1109, 1033 cm^{-1}; HRMS calcd. for $C_{44}H_{36}O_2P$ ($(M+1)^+$): 627.2447; found: 627.2453.

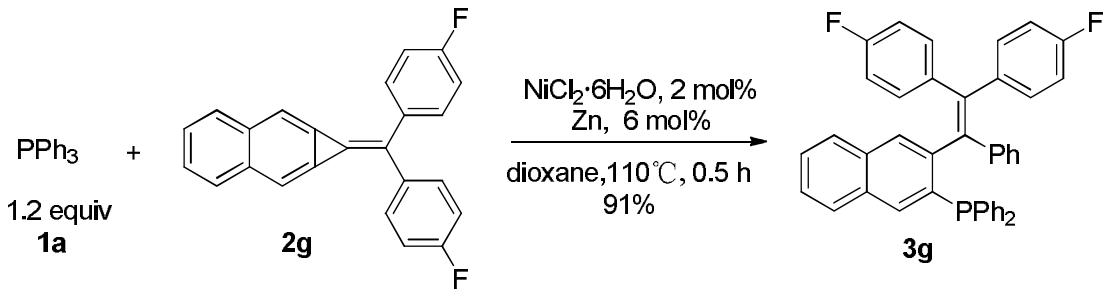
(6) {3-[2,2-Bis(3,5-dimethoxyphenyl)-1-phenylvinyl]naphthalen-2-yl}diphenylphosphine

(3f)



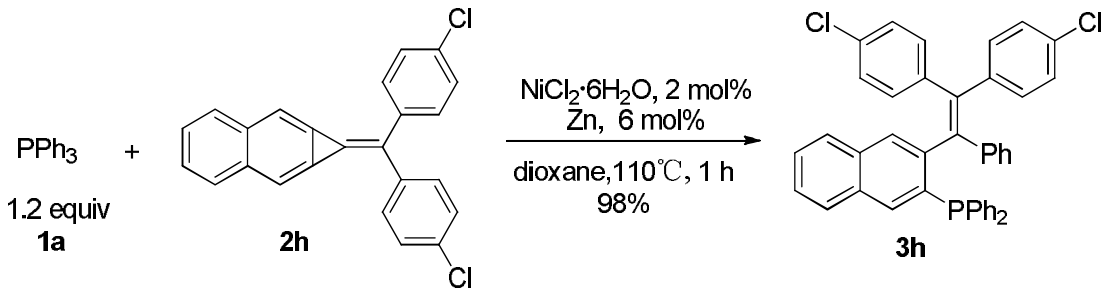
The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2f (**85 mg, 0.2 mmol) in dioxane (1 mL) afforded **3b** (130 mg, 96%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 3:1): m.p. 198-200 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.72-7.64 (m, 2H), 7.60-7.54 (m, 2H), 7.44-7.30 (m, 2H), 7.25-7.18 (m, 4H), 7.18-7.08 (m, 4H), 6.99-6.92 (m, 2H), 6.83-6.75 (m, 5H), 6.39-6.33 (m, 4H), 6.25 (s, 1H), 6.11 (s, 1H), 3.57 (s, 6H), 3.36 (s, 6H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ= -13.85 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.0, 159.6, 146.3 (d, J = 31.5Hz), 145.0 (d, J = 10.7Hz), 142.8, 142.1, 140.5 (d, J = 3.7Hz), 138.9 (d, J = 14.0Hz), 137.1 (d, J = 13.5Hz), 136.5, 136.0 (d, J = 13.6Hz), 134.1 (d, J = 21.6Hz),133.4, 132.9 (d, J = 18.2Hz), 132.2, 131.2, 130.4 (d, J = 5.8Hz), 128.4, 128.12, 128.07, 128.0, 127.9, 127.7, 127.4, 127.2, 126.8, 126.2, 125.7, 109.7, 109.6, 99.5, 99.3, 55.2, 55.0 ppm; MS(EI): m/z (%) = 686 (M^+, 40.0), 549 (100); IR (neat): 3052, 2999, 1589, 1456, 1422, 1344, 1267, 1201, 1152, 1118, 1065cm^{-1}; HRMS calcd. for $C_{46}H_{40}O_4P$ ($(M+1)^+$): 687.2659; found: 687.2669.

(7) {3-[2,2-Bis(4-fluorophenyl)-1-phenylvinyl]naphthalen-2-yl}diphenylphosphine (3g)



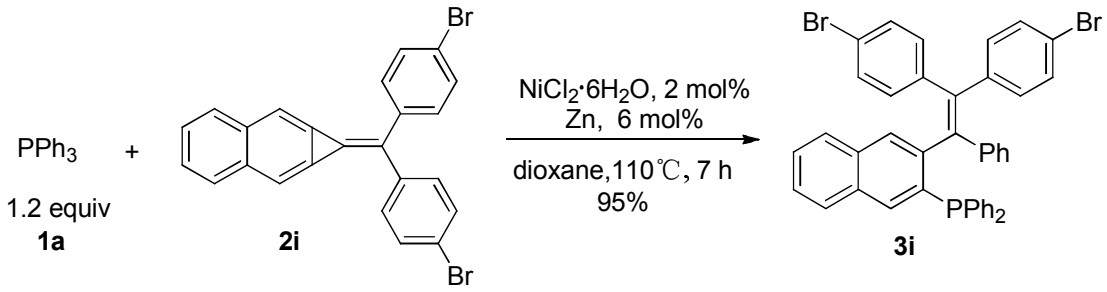
The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2g (**68 mg, 0.2 mmol) in dioxane (1 mL) afforded **3g** (110 mg, 91%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 230-232 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.67-7.63 (m, 2H), 7.59-7.54 (m, 2H), 7.41-7.28 (m, 2H), 7.25-7.03 (m, 12H), 6.96-6.90 (m, 2H), 6.86-6.78 (m, 7H), 6.64-6.56 (m, 2H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.76 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 161.6 (d, $J_{C\text{-}F}$ = 246.0Hz), 163.3 (d, $J_{C\text{-}F}$ = 243.6Hz), 146.2 (d, J = 32.6Hz), 142.7, 140.8, 140.2, 139.5, 139.4 (d, J = 11.4Hz), 138.4 (d, J = 14.3Hz), 136.9, 135.7 (d, J = 13.8Hz), 133.9 (d, J = 20.8Hz), 133.5, 133.0 (broad peak, 2C), 132.9, 132.3, 131.4, 130.9, (d, J = 6.5Hz), 128.4 (d, J = 10.4Hz), 128.3, 128.23, 128.16, 127.95, 127.92, 127.5, 127.4, 126.9, 126.3, 125.9, 114.8 (d, $J_{C\text{-}F}$ = 21.2Hz), 114.4 (d, $J_{C\text{-}F}$ = 21.2Hz) ppm; MS(EI): m/z (%) = 602 (M^+, 45.0), 507 (100); IR (neat): 3058, 2986, 1602, 1558, 1540, 1509, 1456, 1437, 1395, 1339, 1262, 1226, 1198, 1159, 1117 cm^{-1}; HRMS calcd. for $C_{42}H_{30}F_2P$ ($(M+1)^+$): 603.2048; found: 603.2060.

(8) {3-[2,2-Bis(4-chlorophenyl)-1-phenylvinyl]naphthalen-2-yl}diphenylphosphine (3h)



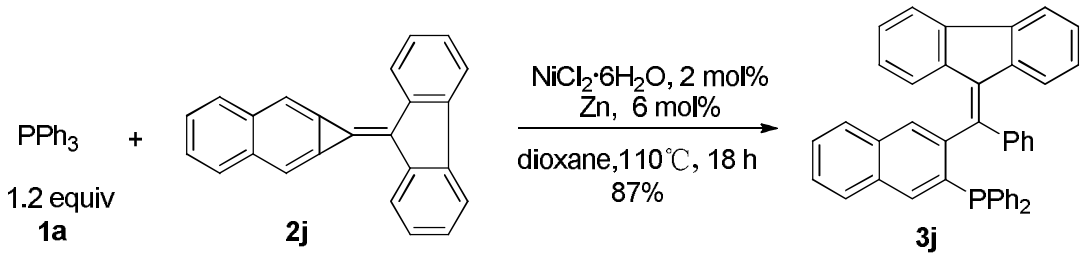
The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2h (**75 mg, 0.2 mmol) in dioxane (1 mL) afforded **3h** (124 mg, 98%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 249-251 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.70-7.55 (m, 4H), 7.46-7.30 (m, 2H), 7.25-7.06 (m, 12H), 7.02-6.96 (m, 2H), 6.91-6.80 (m, 9H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.90 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.9 (d, J = 22.6Hz), 142.4, 141.8, 141.6 (broad peak, 2C), 139.8, 138.1 (d, J = 13.1Hz), 137.1 (d, J = 12.5Hz), 135.5 (d, J = 13.7Hz), 133.9 (d, J = 20.9Hz), 133.7 (d, J = 19.2Hz), 133.4, 132.9 (d, J = 14.2Hz), 132.8 (broad peak, 2C), 132.7, 132.6, 132.3, 131.4, 130.8 (d, J = 5.5Hz), 128.6 (d, J = 18.9Hz), 128.4 (d, J = 10.3Hz), 128.3 (d, J = 4.1Hz), 128.16, 128.12, 127.9 (d, J = 6.1Hz), 127.7, 127.53, 127.48, 126.97, 126.5, 126.0 ppm; MS(EI): m/z (%) = 634(M^+(^{35,35}Cl), 36.0), 636 (M^+(^{35,37}Cl), 27.0), 638 (M^+(^{37,37}Cl), 4.0), 523 (100); IR (neat): 3053, 1585, 1541, 1488, 1436, 1397, 1266, 1197, 1090, 1016 cm^{-1}; HRMS calcd. for $C_{42}H_{30}{}^{35,35}Cl_2P$ ($(M+1)^+$): 635.1457; found: 635.1446.

(9) {3-[2,2-Bis(4-bromophenyl)-1-phenylvinyl]naphthalen-2-yl}diphenylphosphine (3i)



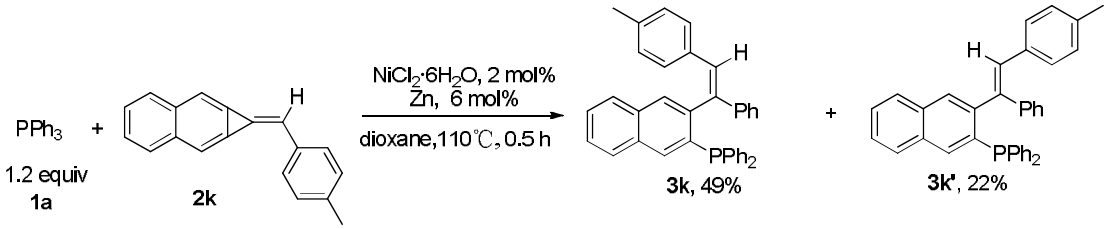
The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2i (**92 mg, 0.2 mmol) in dioxane (1 mL) afforded **3i** (138 mg, 95%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 192-194 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68 (d, J = 8.0Hz, 1H), 7.63 (d, J = 4.0Hz, 1H), 7.7.60 (d, J = 8.4Hz, 1H), 7.57 (d, J = 4.0Hz, 1H), 7.44-7.36 (m, 2H), 7.30-7.14 (m, 8H), 7.11-7.06 (m, 2H), 7.05-6.99 (m, 4H), 6.94-6.79 (m, 9H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.85 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.9 (d, J = 31.8Hz), 142.4, 142.2, 141.9, 141.5 (d, J = 5.3Hz), 139.9, 138.1 (d, J = 12.3Hz), 137.1, 137.0 (broad peak, 2C), 135.4 (d, J = 13.7Hz), 133.9 (d, J = 20.2Hz), 133.4, 133.2, 133.1, 132.8 (d, J = 18.4Hz), 132.4, 131.3, 131.1, 130.8 (d, J = 5.5Hz), 130.6, 128.4 (d, J = 9.1Hz), 128.3, 128.2 (d, J = 6.7Hz), 127.9 (d, J = 7.8Hz), 127.54, 127.49, 127.0, 126.4, 126.0, 120.9, 120.7 ppm; MS(EI): m/z (%) = 722(M^+(^{79,79}Br), 14.0), 724 (M^+(^{79,81}Br), 29.0), 726 (M^+(^{81,81}Br), 15.0), 57 (100);IR (neat): 3053, 1541, 1512, 1486, 1435, 1394, 1339, 1266, 1195, 1071, 1011 cm^{-1}; HRMS calcd. for $C_{42}H_{30}{}^{79,79}Br_2P$ ($(M+1)^+$): 723.0446; found: 723.0452.

(10) {3-[(9H-fluoren-9-ylidene)(phenyl)methyl]naphthalen-2-yl}diphenylphosphine (3j)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2j** (60 mg, 0.2 mmol) in dioxane (1 mL) afforded **3j** (98 mg, 87%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 161-163 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.89 (d, J = 4.0Hz, 1H), 7.78 (d, J = 7.8Hz, 1H), 7.73 (d, J = 4.0Hz, 1H), 7.71-7.63 (m, 3H), 7.49-7.42 (m, 3H), 7.28 (d, J = 8.0Hz, 1H), 7.25-7.05 (m, 12H), 7.01-6.88 (m, 4H), 6.85 (d, J = 8.0Hz, 1H), 6.75-6.71 (m, 1H), 6.26 (d, J = 8.0Hz, 1H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.64 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.7 (d, J = 33.7Hz), 144.59, 144.55, 141.4, 140.8, 140.4, 139.2, 138.5, 137.6 (d, J = 13.3Hz), 136.9 (d, J = 2.0Hz), 136.7 (d, J = 11.5Hz), 135.7 (d, J = 3.1Hz), 135.5 (d, J = 14.6Hz), 133.9, 133.8 (d, J = 20.1Hz), 133.4 (d, J = 18.9Hz), 132.9, 131.9, 131.8, 129.6, 128.4, 128.4, 128.3, 128.2, 128.1, 128.03, 127.96, 127.9 (d, J = 4.1Hz), 127.7, 127.5, 127.1, 126.5, 126.4 (d, J = 8.6Hz), 125.1 (d, J = 10.7Hz), 119.2, 119.1 ppm; MS(EI): m/z (%) = 564 (M^+, 14.0), 487 (100); IR (neat): 3056, 1541, 1513, 1489, 1440, 1273, 1195, 1118 cm^{-1}; HRMS calcd. for $C_{42}H_{30}P$ ($(M+1)^+$): 565.2080; found: 565.2066.

(11) (Z)-Diphenyl[3-(1-phenyl-2-(*p*-tolyl)vinyl)naphthalen-2-yl]phosphine (3k) and (E)-diphenyl{3-[1-phenyl-2-(*p*-tolyl)vinyl]naphthalen-2-yl}phosphine (3k')

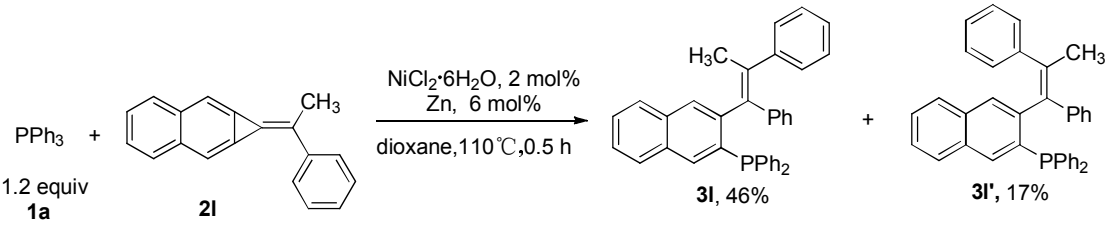


The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2k (**48 mg, 0.2 mmol) in dioxane (1 mL) afforded **3k** (49 mg, 49%) and **3k'** (22 mg, 22%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1). **3k**: m.p. 150-152 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.77-7.71 (m, 4H), 7.49-7.44 (m, 2H), 7.22-7.01 (m, 16H), 6.85-6.77 (m, 4H), 2.20 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -14.19 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.0 (d, J = 33.2Hz), 142.8, 140.7 (d, J = 6.0Hz), 137.6 (d, J = 12.7Hz), 136.8 (d, J = 11.9Hz), 136.5 (broad peak, 2C), 136.2 (d, J = 14.6Hz), 134.5, 133.9, 133.8, 133.7, 133.6, 133.5, 132.7, 129.7, 129.6, 129.5, 128.7, 128.2, 128.1, 128.02, 127.96, 127.9, 127.8, 127.2, 126.9 (d, J = 11.8Hz), 126.0, 21.1ppm; MS(EI): m/z (%) = 504 (M^+, 40.0), 314 (100); IR (neat): 3056, 3009, 1651, 1512, 1487, 1436, 1274, 1192, 1115 cm^{-1}; HRMS calcd. for $C_{37}H_{30}P$ ($(M+1)^+$): 505.2080; found: 505.2072.

3k': m.p. 70-72 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.77-7.71 (m, 2H), 7.58 (d, J = 8.0Hz, 1H), 7.48 (d, J = 4.0Hz, 1H), 7.43-7.35 (m, 2H), 7.30-7.23 (m, 10H), 7.20-7.15 (m, 2H), 7.12-7.09 (m, 3H), 6.90 (d, J = 8.0Hz, 2H), 6.77 (d, J = 8.0Hz, 2H), 6.33(s, 1H), 2.24 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -12.07 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.6 (d, J = 28.1Hz), 140.9 (d, J = 5.9Hz), 140.2, 137.5 (d, J = 12.3Hz), 136.4, 136.0, 135.8, 134.7, 134.2, 134.1, 134.0, 133.2, 132.7 (d, J = 4.4Hz), 132.3, 130.4, 130.4, 129.2, 129.1 (d, J = 4.7Hz), 128.5, 128.4, 128.3, 128.2,

127.84, 127.82, 127.5, 127.1, 126.7, 125.9, 21.2 ppm; MS(EI): *m/z* (%) = 504 (M^+, 18.0), 57 (100); IR (neat): 3050, 2922, 1578, 1510, 1483, 1436, 1310, 1270, 1186, 1094, 1024 cm^{-1}; HRMS calcd. for $C_{37}H_{30}P$ ($(M+1)^+$): 505.2080; found: 505.2073.

(12) (E)-[3-(1,2-diphenylprop-1-en-1-yl)naphthalen-2-yl]diphenylphosphine (3l) and (Z)-[3-(1,2-diphenylprop-1-en-1-yl)naphthalen-2-yl]diphenylphosphine (3l')

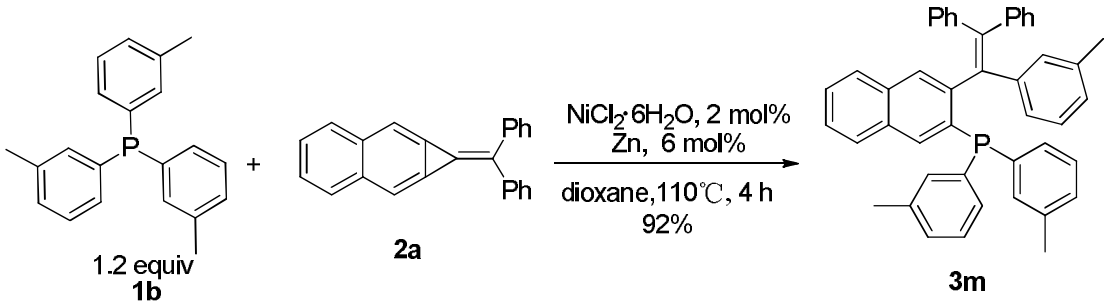


The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), PPh_3 (**1a**, 63 mg 0.24 mmol) and **2l** (48 mg, 0.2 mmol) in dioxane (1 mL) afforded **3l** (46 mg, 46%) and **3l'** (17 mg, 17%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1). **3l**: m.p. 194-196 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, *J* = 8.0Hz, 1H), 7.80 (d, *J* = 7.6Hz, 1H), 7.66 (d, *J* = 8.4Hz, 1H), 7.61 (d, *J* = 4.0Hz, 1H), 7.51-7.45 (m, 1H), 7.44-7.38 (m, 3H), 7.36-7.33 (m, 3H), 7.22-7.06 (m, 10H), 6.95-6.85 (m, 5H), 1.60 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.22 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.3 (d, *J* = 31.3Hz), 143.8, 141.2, 138.0 (d, *J* = 5.2Hz), 137.8, 137.3 (d, *J* = 12.5Hz), 137.0 (d, *J* = 12.9Hz), 136.5 (d, *J* = 13.9Hz), 135.0, 134.6 (d, *J* = 21.7Hz), 133.6, 133.5 (d, *J* = 19.2Hz), 132.3, 131.1 (d, *J* = 2.4Hz), 129.1, 128.84, 128.75 (broad peak, 2C), 128.4 (d, *J* = 6.9Hz), 128.2 (d, *J* = 6.5Hz), 128.0 (d, *J* = 12.3Hz), 127.8, 127.5, 126.9, 126.7, 126.2, 125.8, 125.6, 23.8 ppm; MS(EI): *m/z* (%) = 504 (M^+, 62.0), 489 (100); IR (neat): 3056, 3009, 1488, 1436, 1272, 1089, 1028cm^{-1}; HRMS calcd. for $C_{37}H_{30}P$

((M+1)$^+$): 505.2080; found: 505.2080. anal. calcd. for $C_{37}H_{29}P$: C 88.07, H 5.79; found: C 88.24, H 5.801.

3l': m.p. 160-162 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.65 (d, J = 8.0Hz, 1H), 7.58 (d, J = 8.4Hz, 1H), 7.51 (d, J = 8.0Hz, 1H), 7.43 (d, J = 8.0Hz, 1H), 7.39-7.34 (m, 1H), 7.33-7.22 (m, 6H), 7.20-7.11 (m, 3H), 7.10-6.94 (m, 10H), 6.91-6.86 (m, 2H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -14.09 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.2 (d, J = 33.8Hz), 144.3, 142.0, 139.2 (d, J = 15.2Hz), 138.8 (d, J = 13.6Hz), 137.1, 137.0, 136.8, 135.6 (d, J = 13.1Hz), 133.5, 133.3, 133.3 (d, J = 6.6Hz), 133.0, 132.0, 130.8, 130.7, 130.6 (d, J = 6.8Hz), 129.1, 128.2 (d, J = 5.5Hz), 127.9, 127.8, 127.8 (d, J = 4.1Hz), 127.6, 127.4, 126.6, 126.2, 126.0, 125.5, 23.0ppm; MS(EI): m/z (%) = 504 (M$^+$, 2.0), 85 (100); IR (neat): 3055, 2926, 1578, 1489, 1437, 1378, 1274, 1187, 1116, 1028 cm^{-1}; HRMS calcd. for $C_{37}H_{30}P$ ((M+1)$^+$): 505.2080; found: 505.2088.

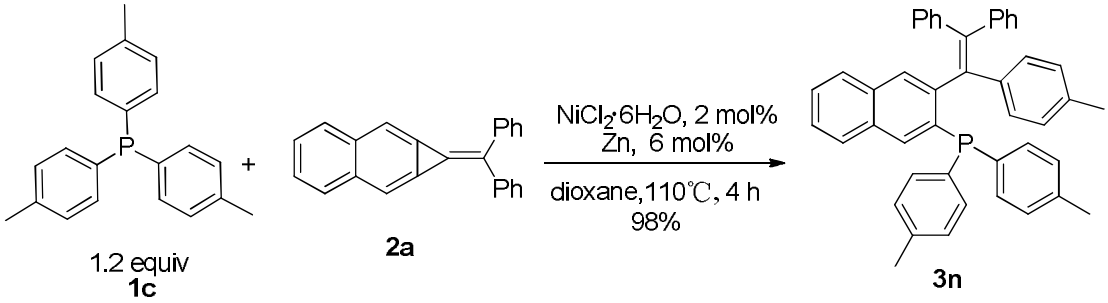
(13) 3-[2,2-Diphenyl-1-(m-tolyl)vinyl)naphthalen-2-yl]di-m-tolylphosphine (3m)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1b** (73 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3m** (112 mg, 92%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 130-132 °C (petroleum

ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.69-7.63 (m, 2H), 7.60 (d, J = 8.0Hz, 1H), 7.56 (d, J = 4.0Hz, 1H), 7.41-7.33 (m, 2H), 7.19-7.09 (m, 8H), 7.09-7.01 (m, 3H), 6.96-6.93 (m, 4H), 6.87 (d, J = 8.8Hz, 1H), 6.72-6.68 (m, 4H), 6.62-6.58 (m, 1H), 6.48 (s, 1H), 2.23 (s, 3H), 2.19 (s, 3H), 1.85 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -13.67 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.7 (d, J = 31.9Hz), 143.9, 143.8, 142.7, 141.9, 140.6 (d, J = 15.4Hz), 139.1 (d, J = 13.0Hz), 137.5 (d, J = 6.0Hz), 137.3 (d, J = 8.6Hz), 136.7, 136.6 (d, J = 11.5Hz), 136.4 (d, J = 14.1Hz), 135.1, 134.8, 133.5 (d, J = 9.6Hz), 133.3, 132.2, 131.5 (broad peak, 3C), 131.0 (d, J = 17.8Hz), 130.7 (d, J = 5.9Hz), 129.8 (d, J = 16.3Hz), 129.2, 128.9, 128.4, 128.0 (broad peak, 2C), 127.8 (d, J = 7.3Hz), 127.62, 127.55, 127.3, 126.80, 126.76, 126.5, 126.4, 126.2, 125.5, 21.5, 21.4, 21.1 ppm; MS(EI): m/z (%) = 608 (M^+, 10.0), 43 (100); IR (neat): 3050, 3023, 1594, 1489, 1269, 1190, 1108, 1034cm^{-1}; HRMS calcd. for $C_{45}H_{38}P$ ($(M+1)^+$): 609.2706; found: 609.2718.

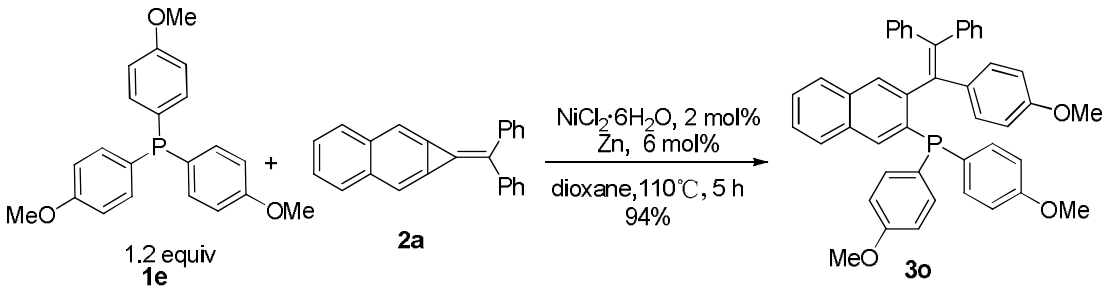
(14) {3-[2,2-Diphenyl-1-(p-tolyl)vinyl]naphthalen-2-yl}di-p-tolylphosphine (3n)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1c** (73 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3n** (119 mg, 98%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 223-225 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.66-7.61 (m, 2H), 7.58-7.52 (m, 2H),

7.36-7.29 (m, 2H), 7.19-7.10 (m, 7H), 7.04 (d, J = 7.2Hz, 2H), 6.97-6.91 (m, 7H), 6.88-6.81 (m, 2H), 6.66 (d, J = 8.0Hz, 2H), 6.54 (d, J = 8.0Hz, 2H) ,2.31 (s, 3H), 2.28 (s, 3H), 2.04 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -15.50 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.7 (d, J = 32.0Hz), 144.0 (d, J = 9.2Hz), 141.4, 140.6 (d, J = 5.7Hz), 139.8, 137.9, 137.4, 136.7 (d, J = 13.9Hz), 136.4 (broad peak, 2C), 135.7, 135.6, 134.1 (d, J = 20.9Hz), 133.4, 133.2, 133.0 (d, J = 18.9Hz), 132.2, 131.6, 131.5, 131.3 (d, J = 2.5Hz), 130.7 (d, J = 7.0Hz), 129.0 (d, J = 5.5Hz), 128.7 (d, J = 7.7Hz), 127.9, 127.8, 127.7, 127.5, 127.3, 126.5, 126.4, 126.1, 125.5, 21.26, 21.23, 21.0 ppm; MS(EI): m/z (%) = 608 (M^+, 40.0), 531 (100); IR (neat): 3020, 1651, 1599, 1492, 1443, 1397, 1272, 1187, 1115, 1023 cm^{-1}; HRMS calcd. for $C_{45}H_{38}P$ ($(M+1)^+$): 609.2706; found: 609.2694.

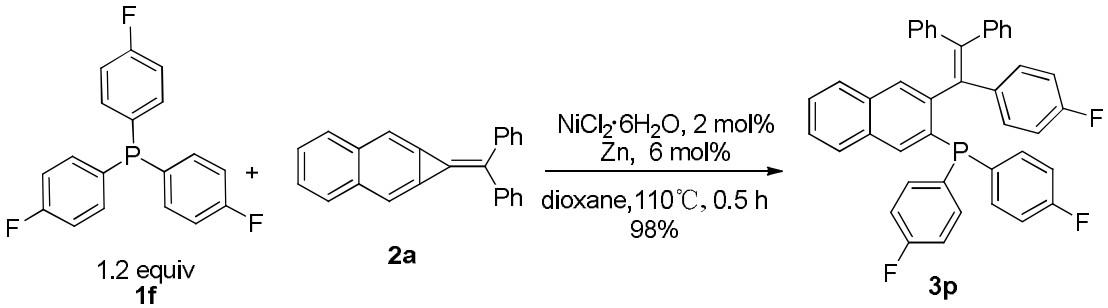
(15) Bis(4-methoxyphenyl){3-[1-(4-methoxyphenyl)-2,2-diphenylvinyl]naphthalen-2-yl}phosphine (3o)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1e** (84 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3m** (121 mg, 92%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 166-168 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.65-7.55 (m, 3H), 7.50 (d, J = 4.0Hz, 1H), 7.37-7.31 (m, 2H), 7.21-7.12 (m, 7H), 7.01-6.88 (m, 7H), 6.81 (d, J = 8.8Hz, 2H), 6.67

(d, J = 8.4Hz, 4H), 6.25 (d, J = 8.0Hz, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 3.55 (s, 3H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -16.75 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 159.7, 159.5, 157.6, 146.4 (d, J = 31.3Hz), 144.0 (d, J = 16.4Hz), 140.8, 140.3 (d, J = 5.3Hz), 137.3 (d, J = 13.7Hz), 136.0, 135.5 (d, J = 12.9Hz), 135.00, 134.99, 134.3 (d, J = 19.6Hz), 133.3, 132.9, 132.2, 131.5, 131.2 (d, J = 2.0Hz), 130.7 (d, J = 5.9Hz), 130.0 (d, J = 9.9Hz), 127.8, 127.7, 127.44, 127.39, 127.3, 126.5, 126.3, 126.0, 125.6, 114.0 (d, J = 5.8Hz), 113.5 (d, J = 8.7Hz), 112.5, 55.1, 55.0, 54.7 ppm; MS(EI): m/z (%) = 656 (M^+, 41.0), 579 (100); IR (neat): 3007, 2836, 1652, 1596, 1504, 1458, 1256, 1178, 1116, 1029 cm^{-1}; HRMS calcd. for $C_{45}H_{38}O_3P$ ($(M+1)^+$): 657.2553; found: 657.2566.

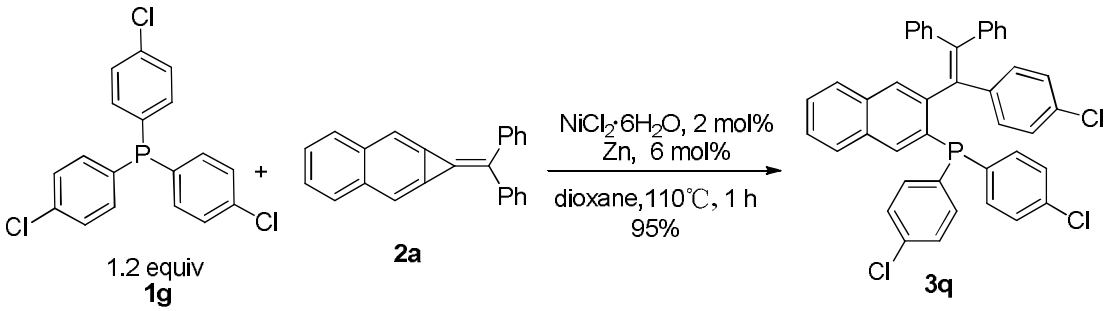
(16) Bis(4-fluorophenyl){3-[1-(4-fluorophenyl)-2,2-diphenylvinyl]naphthalen-2-yl}phosphine (3p)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1f** (76 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3p** (122 mg, 98%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 202-204 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68-7.63 (m, 2H), 7.59 (d, J = 8.4Hz, 1H), 7.46 (d, J = 8.0Hz, 1H), 7.42-7.21 (m, 2H), 7.19-7.10 (m, 7H), 7.06-6.83 (m, 11H), 6.77-6.71 (m, 2H), 6.49-6.40 (m, 2H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -16.08 ppm; ^{13}C NMR (100

MHz, $CDCl_3$, 25 °C): δ = 163.2 (d, $J_{C\text{-}F}$ = 246.9Hz), 162.9 (d, $J_{C\text{-}F}$ = 247.4Hz), 161.0 (d, J = 245.5Hz), 145.9 (d, $J_{C\text{-}F}$ = 21.8Hz), 143.5, 143.3, 142.5, 139.2 (d, $J_{C\text{-}F}$ = 6.1Hz), 138.5, 136.4 (broad peak, 2C), 135.8 (dd, $J_{C\text{-}F}$ = 7.3Hz, J = 22.1Hz), 135.7 (dd, $J_{C\text{-}F}$ = 8.2Hz, J = 19.8Hz), 133.9 (dd, $J_{C\text{-}F}$ = 2.8Hz, J = 13.2Hz), 133.5, 133.2 (d, $J_{C\text{-}F}$ = 7.6Hz), 132.2, 131.6 (dd, $J_{C\text{-}F}$ = 3.3Hz, J = 12.8Hz), 131.4, 131.1 (broad peak, 2C), 127.9, 127.8, 127.5, 127.4, 127.0, 126.8, 126.4, 126.0, 115.6(dd, $J_{C\text{-}F}$ = 21.2Hz, J = 6.4Hz), 115.3 (dd, $J_{C\text{-}F}$ = 20.9Hz, J = 8.4Hz), 114.2 (d, J = 21.0Hz) ppm; MS(EI): m/z (%) = 656 (M^+, 58.0), 543 (100); IR (neat): 3055, 1651, 1588, 1493, 1394, 1263, 1228, 1159, 1092, 1015 cm^{-1}; HRMS calcd. for $C_{42}H_{29}F_3P$ ($(M+1)^+$): 621.1954; found: 621.1939.

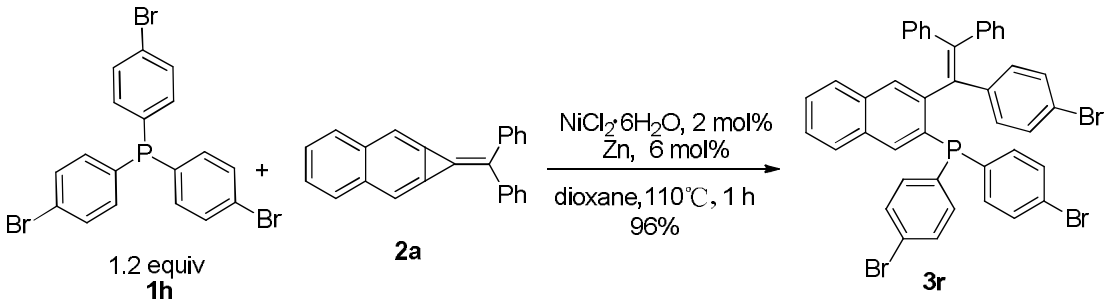
(17) Bis(4-chlorophenyl){3-[1-(4-chlorophenyl)-2,2-diphenylvinyl]naphthalen-2-yl}phosphine (3q)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1g** (88 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3q** (127 mg, 95%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 218-220 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68-7.63 (m, 2H), 7.60 (d, J = 8.0Hz, 1H), 7.47 (d, J = 8.4Hz, 1H), 7.42-7.36 (m, 2H), 7.23 (d, J = 8.0Hz, 2H), 7.18-7.12 (m, 9H), 6.99-6.87 (m, 5H), 6.87-6.83 (m, 2H), 6.72-6.68 (m, 4H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$,

25 °C): δ = -15.48 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.8 (d, J = 33.4Hz), 143.4, 143.0, 140.9, 139.1 (d, J = 4.8Hz), 137.0 (d, J = 14.1Hz), 136.7, 135.2, 135.14, 135.05, 135.0, 134.4, 134.2, 134.2, 134.0, 133.6, 132.9, 132.28, 132.25, 131.4, 131.2 (d, J = 6.9Hz), 131.0, 128.6 (d, J = 6.2Hz), 128.5 (d, J = 7.7Hz), 128.0, 127.9, 127.5 (broad peak, 2C), 127.2, 126.9, 126.6, 126.1 ppm; MS(EI): m/z (%) = 668(M^+(^{35,35,35}Cl), 40.0), 670 (M^+(^{35,35,37}Cl), 41.0), 672 (M^+(^{35,37,37}Cl), 16.0), 674 (M^+(^{37,37,37}Cl), 2.0), 523 (100); IR (neat): 3053, 1651, 1575, 1482, 1442, 1389, 1263, 1182, 1092, 1014 cm^{-1}; HRMS calcd. for $C_{42}H_{29}{}^{35,35,35}Cl_3P$ ($(M+1)^+$): 669.1067; found: 669.1073.

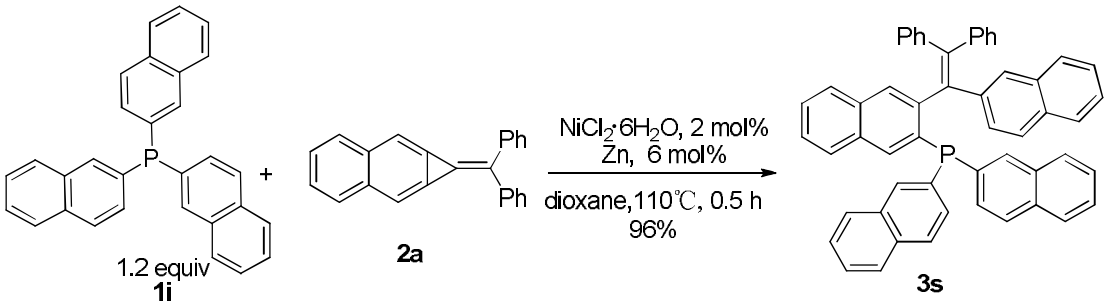
(18) Bis(4-bromophenyl){3-[1-(4-bromophenyl)-2,2-diphenylvinyl]naphthalen-2-yl}phos phine (3r)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1h** (120 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3r** (154 mg, 96%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 250-252 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68-7.59 (m, 3H), 7.47 (d, J = 8.0Hz, 1H), 7.43-7.36 (m, 4H), 7.32-7.28 (m, 2H), 7.18-7.12 (m, 7H), 7.00-6.97 (m, 3H), 6.88-6.76 (m, 6H), 6.64 (d, J = 8.4Hz, 2H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -15.51 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.8 (d, J = 32.5Hz), 143.4, 143.0, 142.9, 141.3,

139.1 (d, J = 6.1Hz), 137.5 (d, J = 13.1Hz), 136.7, 135.3 (d, J = 21.1Hz), 134.7 (d, J = 12.6Hz), 134.4 (d, J = 13.1Hz), 134.3 (d, J = 18.7Hz), 133.6, 133.2, 132.2, 131.5, 131.5 (d, J = 3.5Hz), 131.4, 131.3, 131.2 (d, J = 7.2Hz), 131.0, 130.4, 128.0, 127.8, 127.5, 127.2, 127.0, 126.6, 126.2, 123.5, 122.7, 120.7 ppm; MS(EI): m/z (%) = 800 (M^+(^{79,79,79}Br), 10.0), 802 (M^+(^{79,79,81}Br), 29.0), 804 (M^+(^{79,81,81}Br), 29.0), 806 (M^+(^{81,81,81}Br), 10.0), 647 (100); IR (neat): 3009, 1651, 1541, 1513, 1480, 1381, 1274, 1069 cm^{-1}; HRMS calcd. for $C_{42}H_{29}{}^{79,79,79}Br_3P$ ($(M+1)^+$): 800.9552; found: 800.9534; anal. calcd. for $C_{42}H_{28}Br_3P$: C 62.79, H 3.51; found: C 63.13, H 3.315.

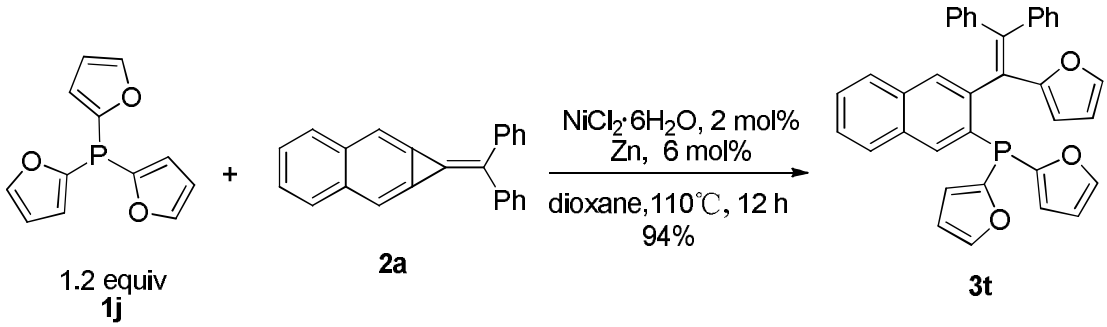
(19) Di(naphthalen-2-yl){3-[1-(naphthalen-2-yl)-2,2-diphenylvinyl]naphthalen-2-yl}phosphine (3s)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1i** (82 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3m** (137 mg, 92%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 200-202 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.78-7.73 (m, 2H), 7.72-7.64 (m, 3H), 7.55-7.51 (m, 3H), 7.41-7.09 (m, 22H), 7.03-6.99 (m, 7H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -12.09 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.0 (d, J = 32.8Hz), 144.0, 143.4, 142.5, 140.7 (d, J = 4.9Hz), 140.2, 137.0, 136.9 (d, J = 12.7Hz), 136.0 (d, J = 12.2Hz), 134.8,

134.6, 133.6, 133.3 (d, J = 4.0Hz), 133.0, 132.9, 132.7, 132.6, 132.5, 132.3, 131.7 (broad peak, 2C), 131.5, 131.3, 131.22, 131.18, 130.0, 129.8, 129.6, 129.5, 128.0, 127.94, 127.87, 127.82, 127.6 (broad peak, 2C), 127.5, 127.4, 127.2 (d, J = 6.4Hz), 126.78, 126.75, 126.7, 126.44, 126.38, 126.2, 126.13, 126.06, 125.8, 125.7, 125.5, 125.0 ppm; MS(EI): m/z (%) = 716 (M^+, 18.0), 44 (100); IR (neat): 3008, 1651, 1541, 1512, 1274 cm^{-1}; HRMS calcd. for $C_{54}H_{38}P$ ($(M+1)^+$): 717.2706; found: 717.2698.

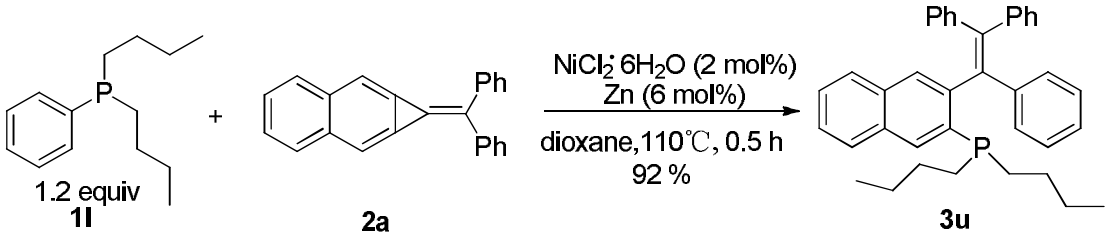
(20) Di(furan-2-yl){3-[1-(furan-2-yl)-2,2-diphenylvinyl]naphthalen-2-yl}phosphine (3t)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1j** (55 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3t** (100 mg, 94%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 144-146 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.99-7.96 (m, 1H), 7.72-7.69 (m, 1H), 7.67-7.59 (m, 3H), 7.57 (s, 1H), 7.39-7.34 (m, 2H), 7.34-7.25 (m, 5H), 7.02 (s, 1H), 6.96-6.93 (m, 2H), 6.89-6.86 (m, 3H), 6.58 (s, 1H), 6.52 (s, 1H), 6.39-6.37 (m, 1H), 6.31-6.29 (m, 1H), 6.10-6.08 (m, 1H), 5.50-5.47 (m, 1H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -57.73 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 154.8, 151.2 (d, J = 11.3Hz), 150.5 (d, J = 12.3Hz), 147.2, 147.1, 143.7, 142.3, 141.8, 141.5, 141.2, 135.2, 133.4, 133.2 (d, J = 3.4Hz), 132.4, 131.0 (d, J = 6.1Hz), 130.7, 130.1, 129.4 (d, J = 6.6Hz), 128.2, 128.0, 127.5, 127.3, 126.9,

126.7, 126.3, 126.0, 121.2 (d, J = 15.2Hz), 121.0 (d, J = 12.9Hz), 112.4, 111.0, 110.8 (d, J = 5.4Hz), 110.6 (d, J = 6.2Hz) ppm; MS(EI): m/z (%) = 536 (M^+, 19.0), 43 (100); IR (neat): 3053, 1555, 1489, 1453, 1367, 1265, 1155, 1008 cm^{-1}; HRMS calcd. for $C_{36}H_{26}O_3P$ ($(M+1)^+$): 537.1614; found: 537.1623. ; anal. calcd. for $C_{36}H_{25}O_3P$: C 80.59, H 4.70; found: C 80.41, H 4.634.

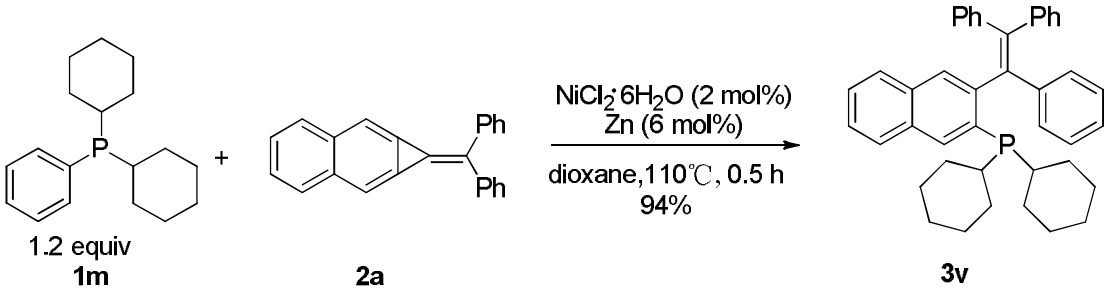
(21) Dibutyl[3-(1,2,2-triphenylvinyl)naphthalen-2-yl]phosphine (3u)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1l** (53 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3u** (97 mg, 92%) as a colorless oil (eluent: petroleum ether/CH_2Cl_2 = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.88 (m, 1H), 7.76 (d, J = 6.8Hz, 1H), 7.66-7.62 (m, 1H), 7.60 (d, J = 2.8Hz, 1H), 7.40-7.36 (m, 2H), 7.18-7.11 (m, 7H), 7.04-6.90 (m, 8H) 1.64-1.60 (m, 2H), 1.45-1.38 (m, 4H), 1.07-0.89 (m, 8H), 0.72-0.66 (m, 4H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -34.82 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.9 (d, J = 30.4Hz), 143.7, 143.4, 143.2, 141.2, 137.1, 133.3, 132.2, 131.8, 131.5 (broad peak, 2C), 131.3, 130.9, 130.2, 128.8, 127.6, 127.5, 127.3 (broad peak, 2C), 126.5, 126.2 (broad peak, 2C), 125.6, 29.7, 28.7 (d, J = 16.6Hz), 28.0 (d, J = 12.7Hz), 27.5 (d, J = 11.3Hz), 24.8 (d, J = 12.4Hz), 24.3 (d, J = 11.3Hz), 14.0, 13.7 ppm; MS(EI): m/z (%) = 526 (M^+, 16.0), 149 (100); IR (neat): 3053, 2957, 2927, 2868, 1597, 1490, 1443, 1379, 1274, 1171, 1075, 1031 cm^{-1}; HRMS calcd. for $C_{38}H_{40}P$ ($(M+1)^+$): 527.2862;

found: 527.2865.

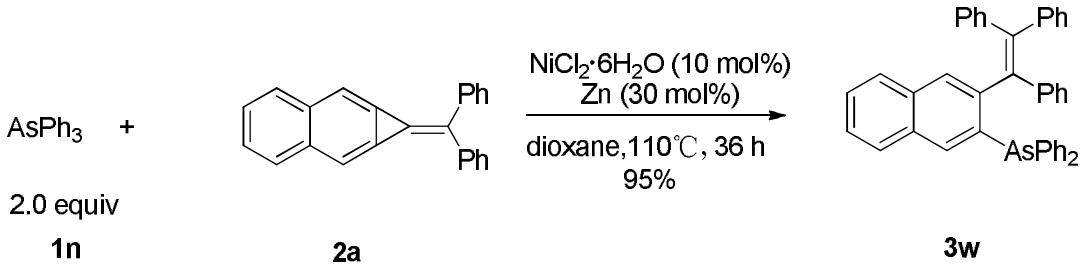
(22) Dicyclohexyl[3-(1,2,2-triphenylvinyl)naphthalen-2-yl]phosphine (3v)



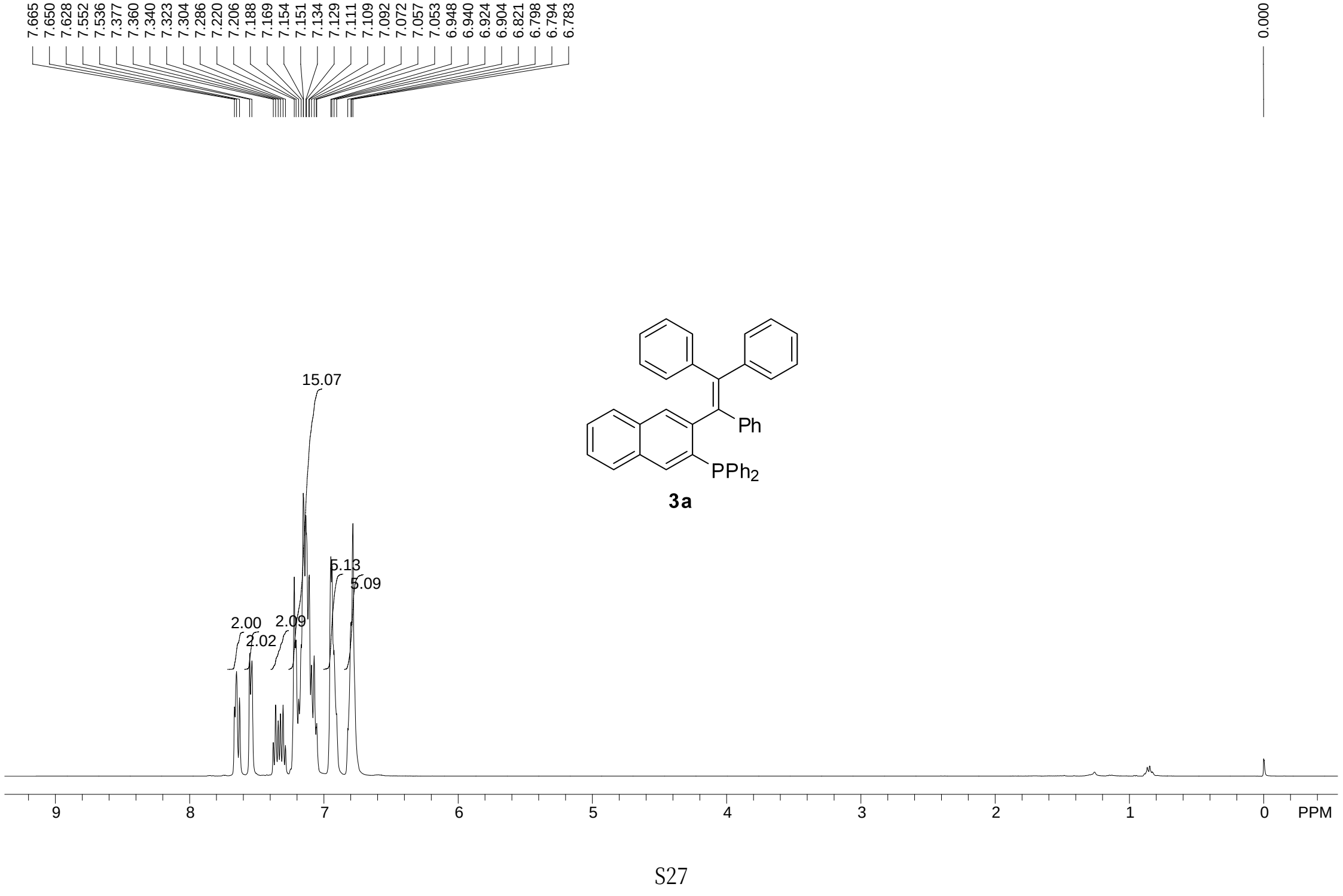
1.2 equiv **1m** **2a** **3v**

The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1m** (66 mg 0.24 mmol) and **2a** (61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3v** (109 mg, 94%) as a colorless oil (eluent: petroleum ether/CH_2Cl_2 = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.87 (s, 1H), 7.77 (d, J = 7.2Hz, 1H), 7.65-7.58 (m, 2H), 7.41-7.33 (m, 2H), 7.24 (d, J = 7.6Hz, 2H), 7.13-7.08 (m, 5H), 7.08-6.96 (m, 5H), 6.96-6.85 (m, 3H), 2.2 (s, 1H), 1.96-1.81 (m, 2H), 1.74-1.62 (m, 4H), 1.55-1.25 (m, 9H), 1.01-0.83 (m, 3H), 0.71-0.59 (m, 2H), 0.27 (t, J = 11.8 Hz, 1H) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = -8.52 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 147.4 (d, J = 31.0Hz), 143.8, 143.2, 142.9, 142.0 (d, J = 4.4Hz), 141.0, 135.3 (d, J = 18.3Hz), 133.1, 133.0, 131.8, 131.7, 131.6, 131.5, 130.7 (broad peak, 2C), 127.6, 127.5 (broad peak, 2C), 127.4, 127.2, 126.4, 126.1, 126.0, 125.5, 35.4 (d, J = 15.4Hz), 33.5 (d, J = 14.3Hz), 32.4 (d, J = 20.4Hz), 30.4 (d, J = 15.9Hz), 27.5 (d, J = 4.5Hz), 27.4 (d, J = 6.4Hz), 27.3, 27.0 (d, J = 10.4Hz), 26.4, 26.2 ppm; MS(EI): m/z (%) = 578 (M^+, 17.0), 501 (100); IR (neat): 2930, 2853, 1541, 1491, 1450, 1274, 1175 cm^{-1}; HRMS calcd. for $C_{42}H_{44}P$ $((M+1)^+)$: 579.3175; found: 579.3172.

(23) Diphenyl[3-(1,2,2-triphenylvinyl)naphthalen-2-yl]arsine (3w)



The reaction of $NiCl_2 \cdot 6H_2O$ (1 mg, 0.004 mmol), Zn (1 mg, 0.012 mmol), **1n** (73 mg 0.24 mmol) and **2a (**61 mg, 0.2 mmol) in dioxane (1 mL) afforded **3w** (116 mg, 95%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1): m.p. 212-214 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68-7.63 (m, 2H), 7.57-7.53 (m, 2H), 7.38-7.31 (m, 2H), 7.25-6.10 (m, 15H), 6.98-6.82 (m, 5H), 6.86-6.81 (m, 5H)) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.4, 143.6, 143.5, 143.0, 142.5, 141.1, 140.8, 140.1, 139.3, 136.1, 133.7, 133.3 (broad peak, 2C), 132.5, 131.6, 131.55, 131.49, 130.5, 128.4, 128.3, 128.1, 127.77 (broad peak, 2C), 127.75, 127.6, 127.4, 127.3, 126.6, 126.41, 126.37, 126.2, 125.6 ppm; MS(EI): *m*/*z* (%) = 610 (M^+, 27.0), 381 (100); IR (neat): 3053, 1578, 1558, 1541, 1491, 1438, 1264, 1182, 1137, 1085, 1030 cm^{-1}; HRMS calcd. for $C_{42}H_{32}{}^{74}As$ ($(M+1)^+$): 611.1709; found: 611.1699.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7.072
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6.821
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6.783
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5.09
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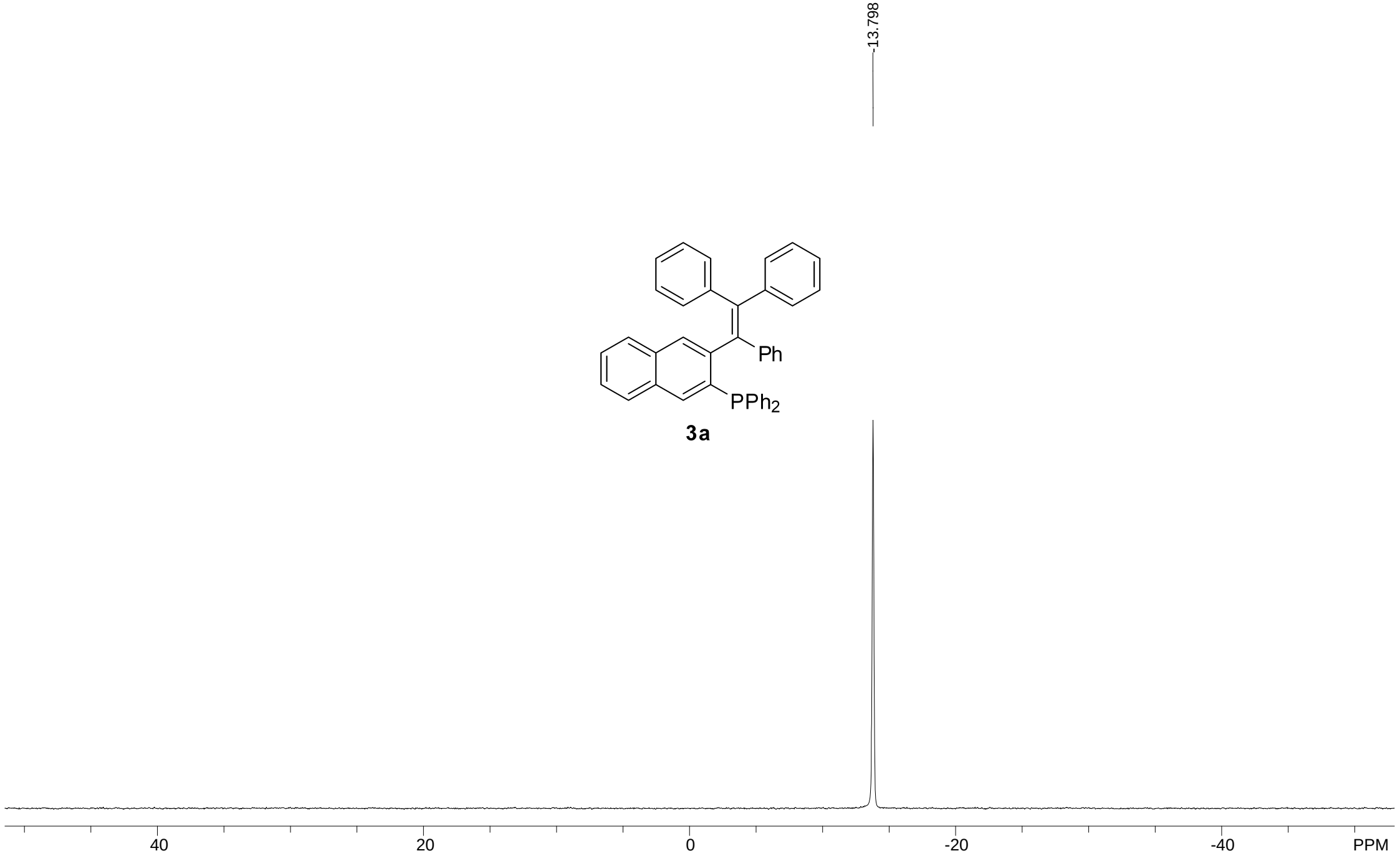
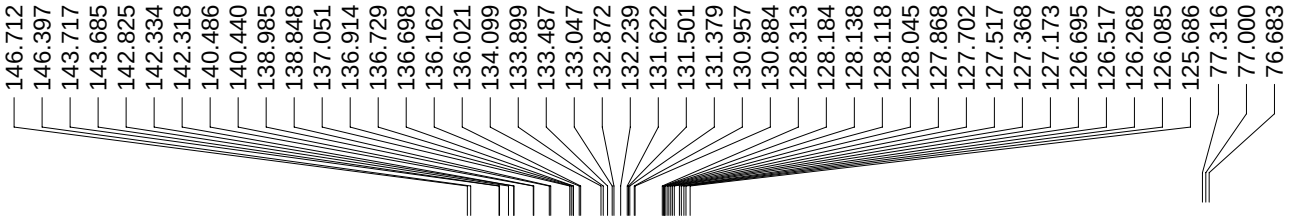


3a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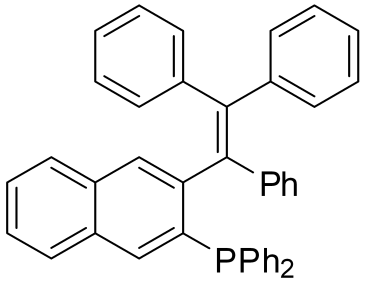
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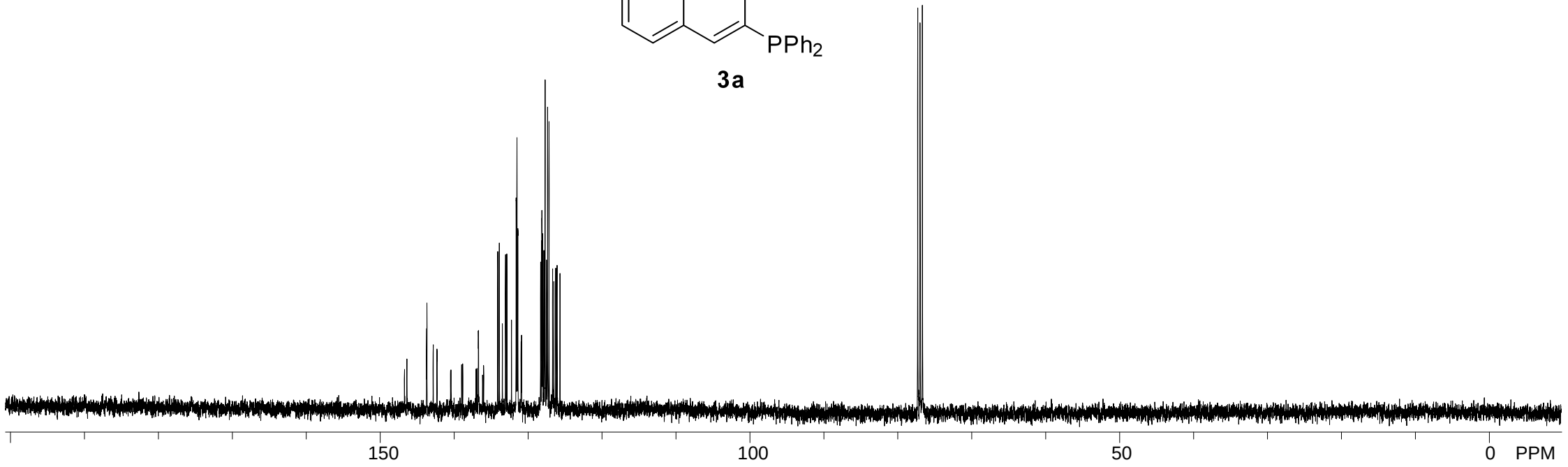
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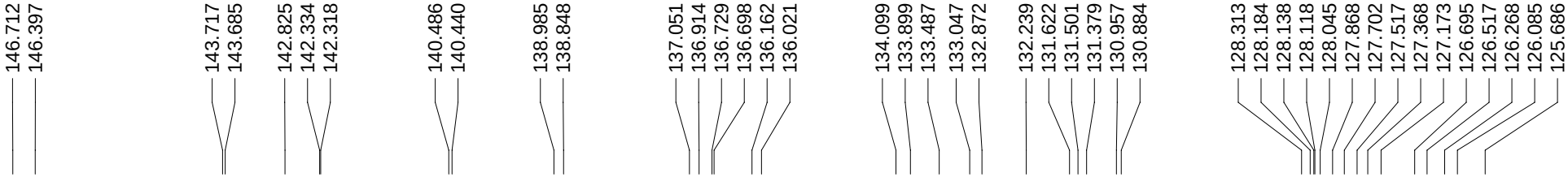
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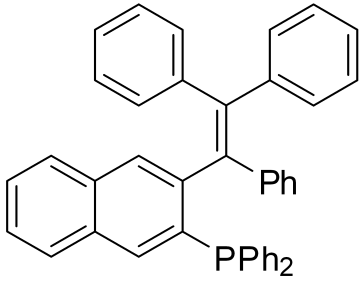
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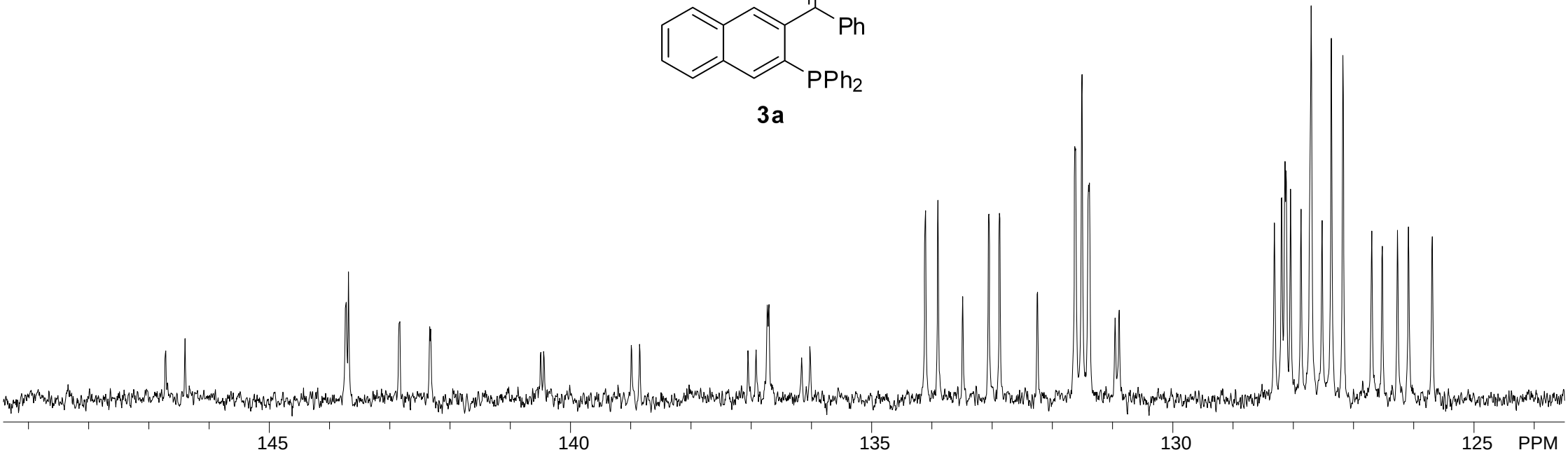
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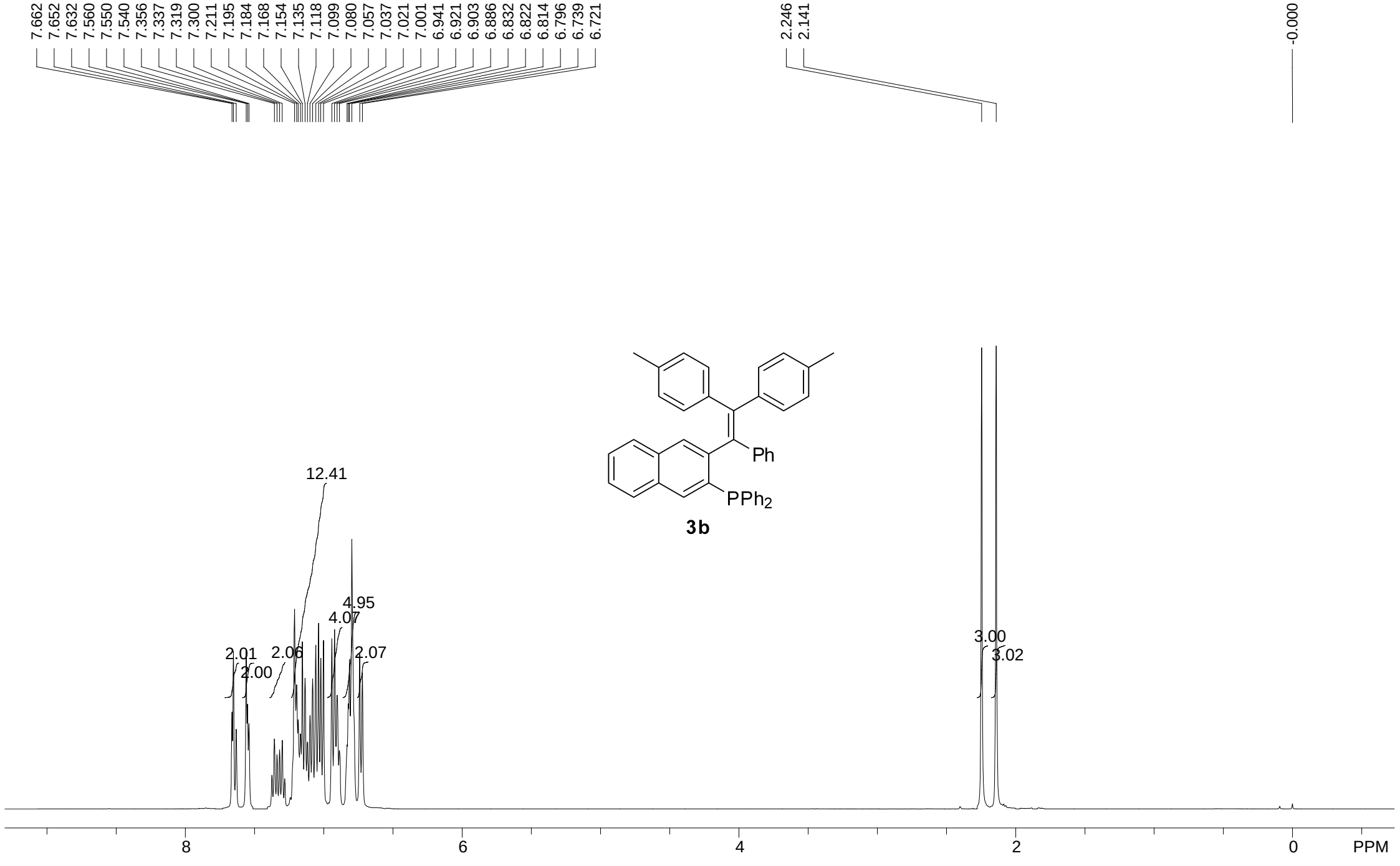
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PPh2
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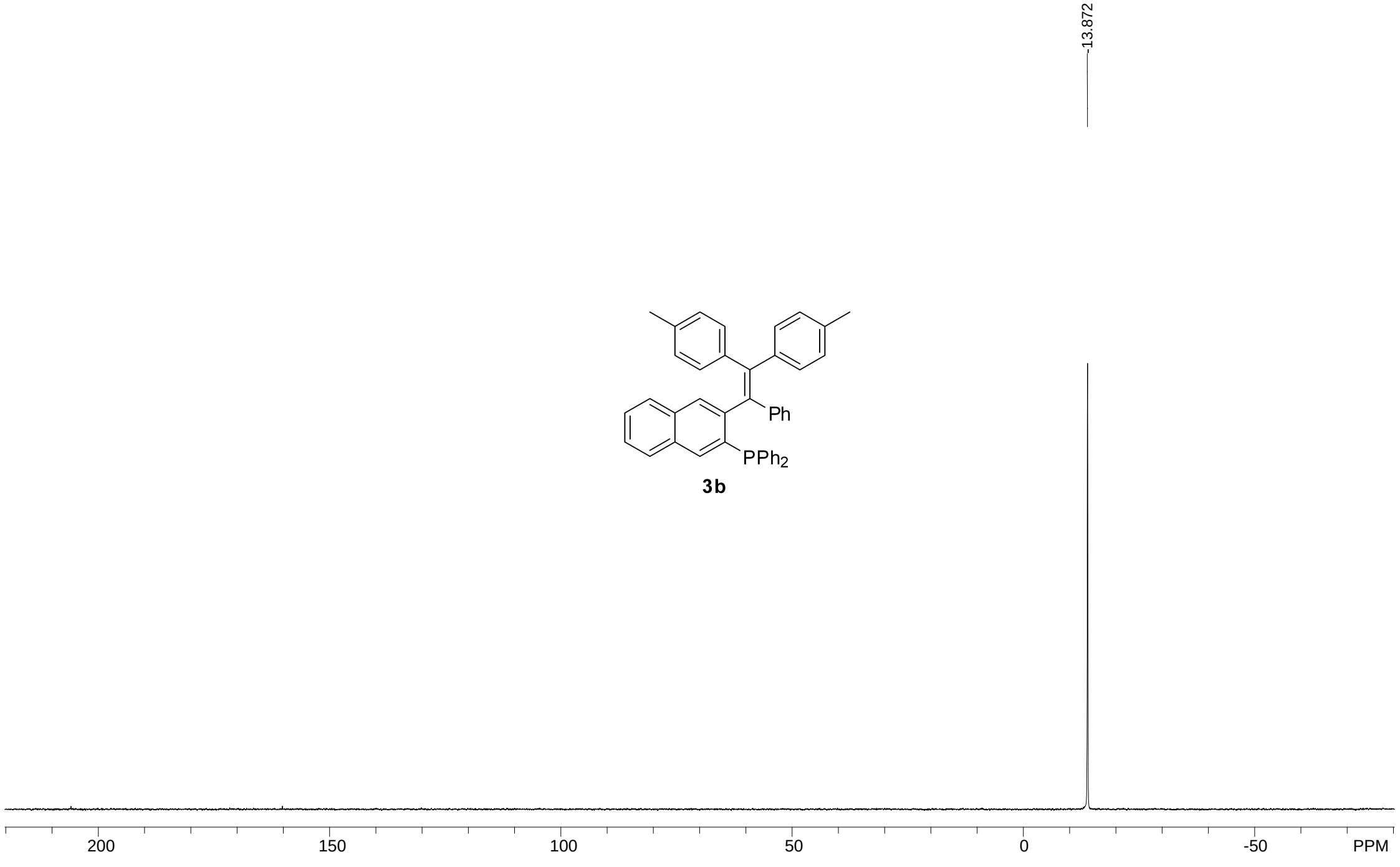

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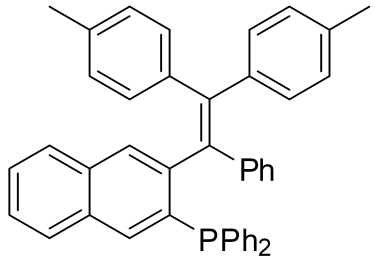

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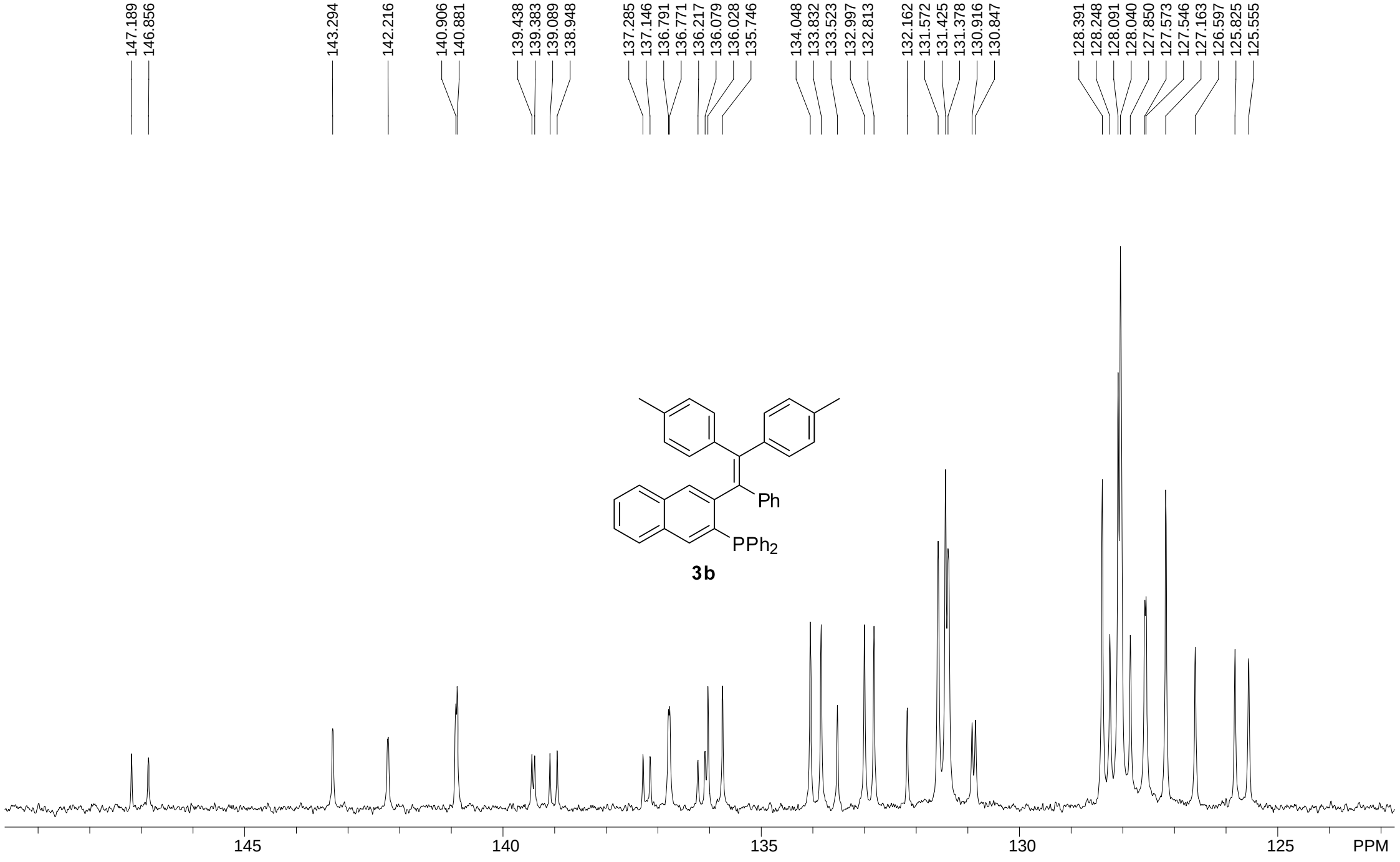

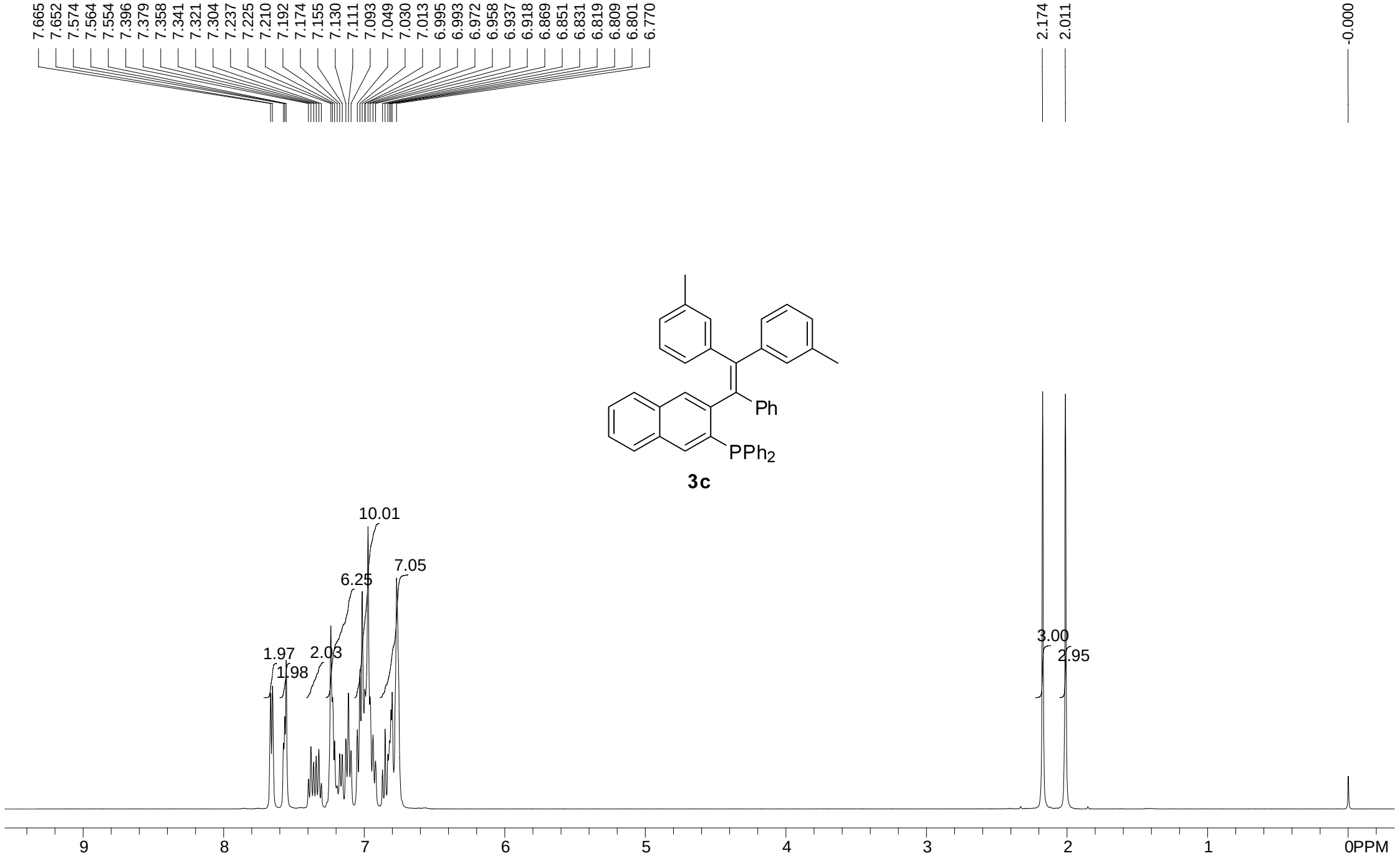
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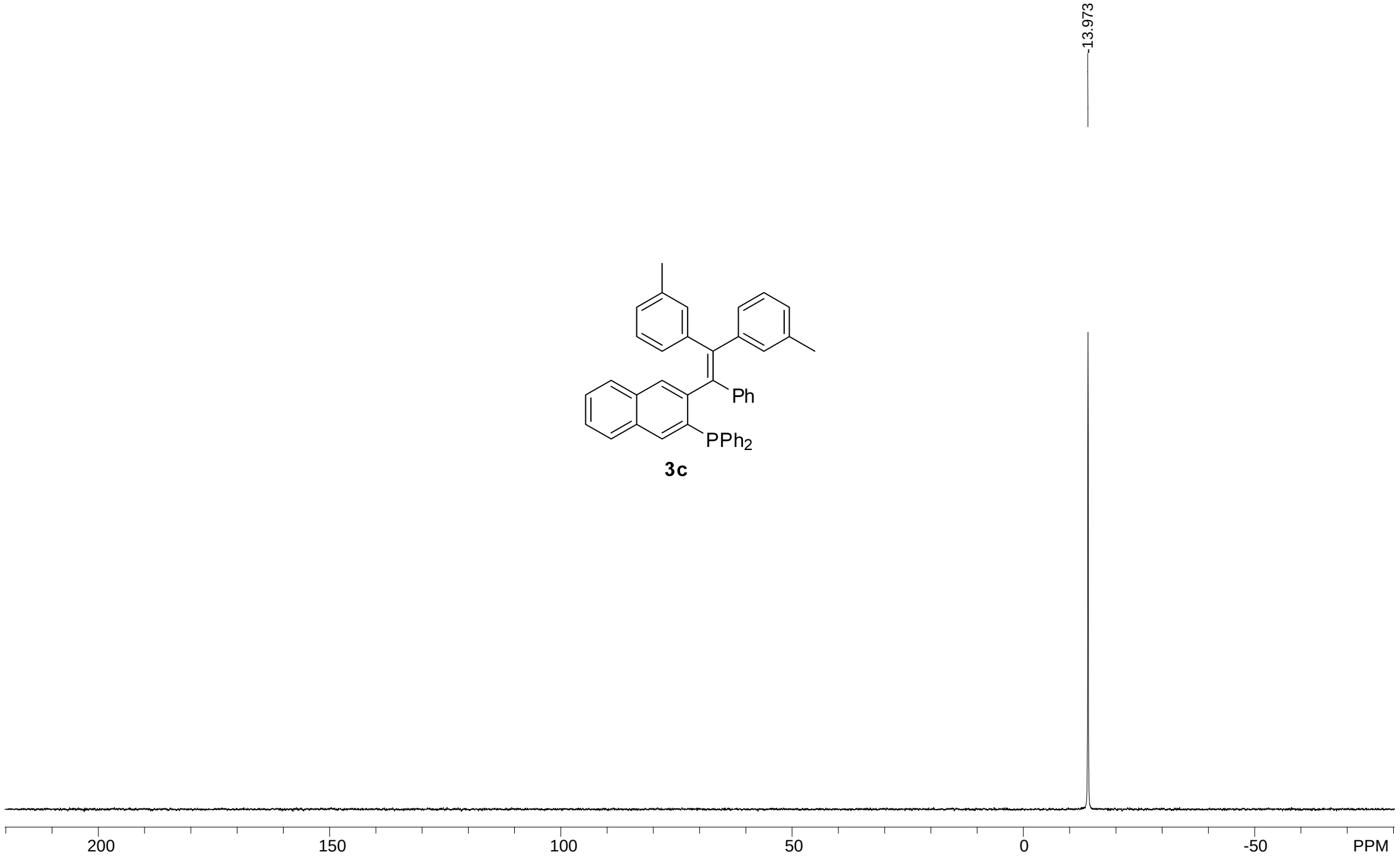

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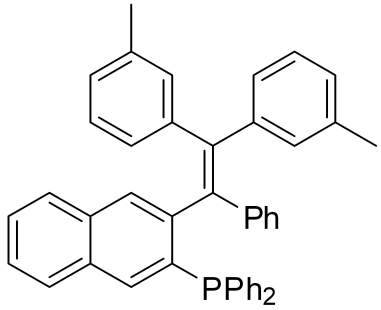

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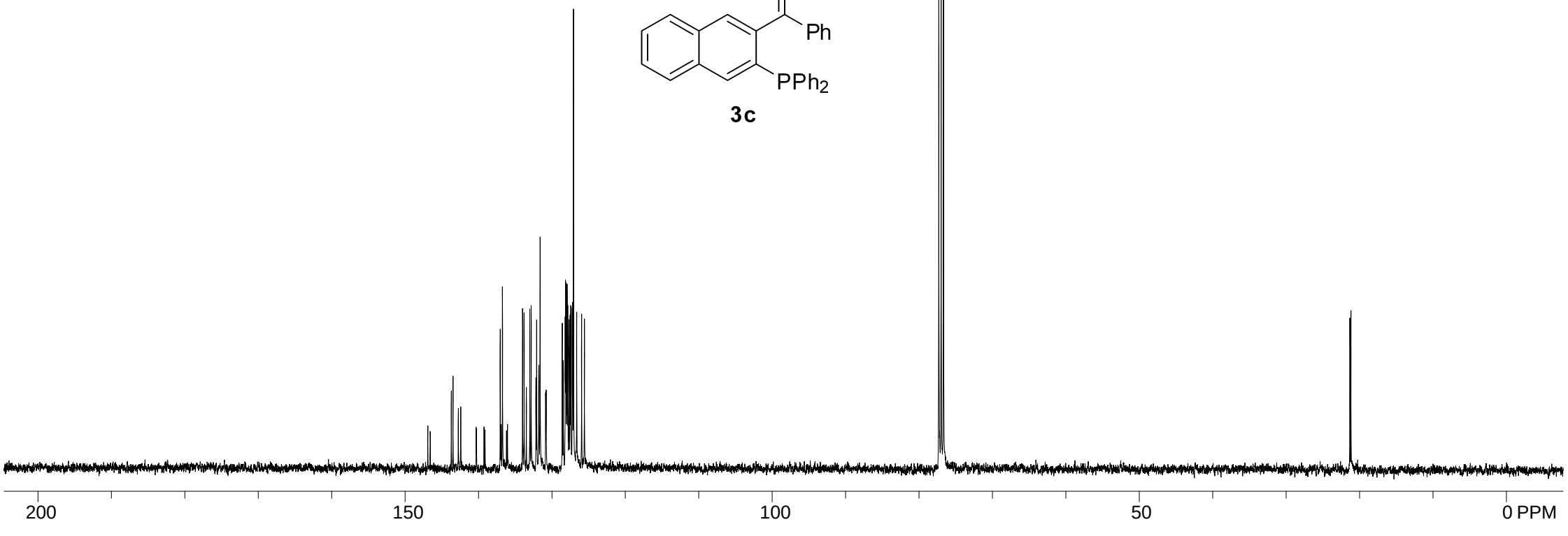

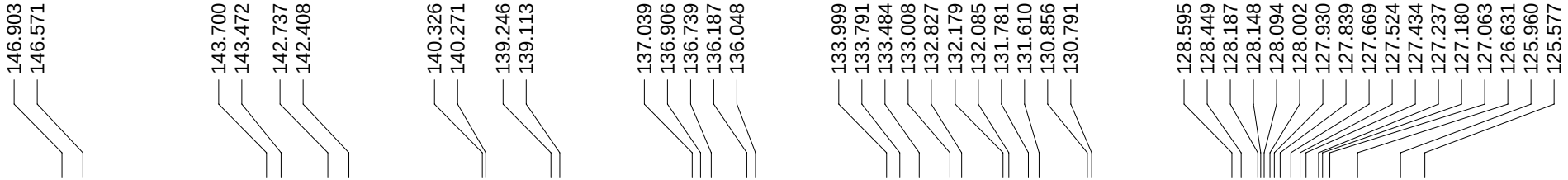
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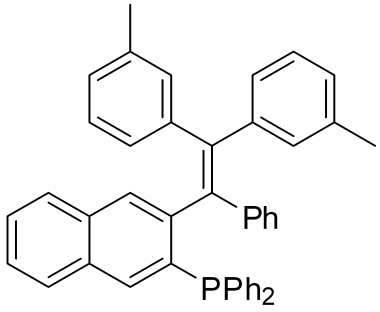
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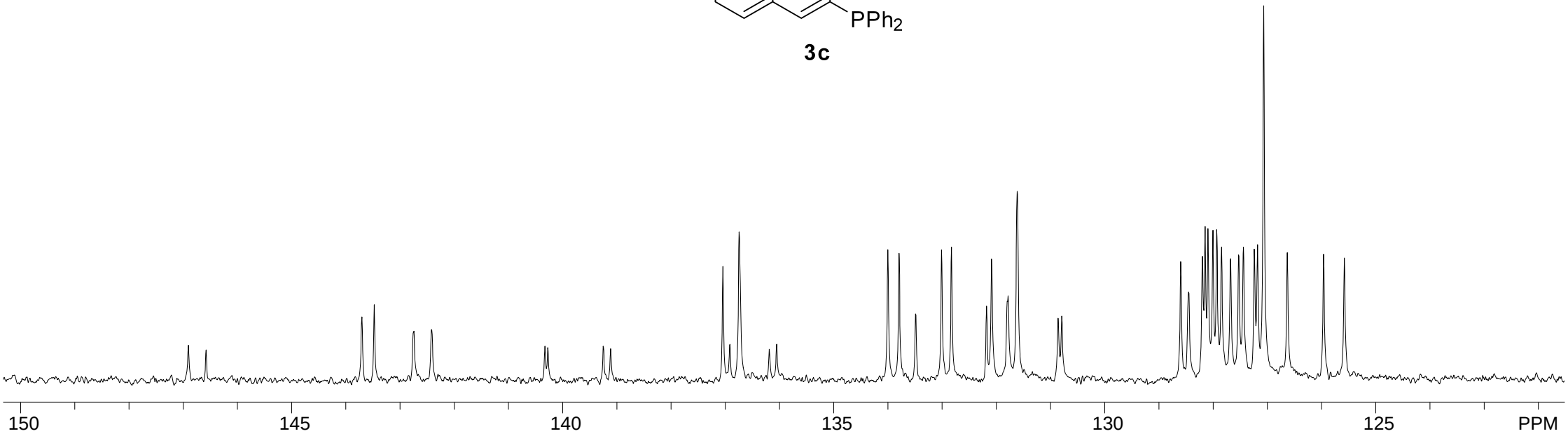
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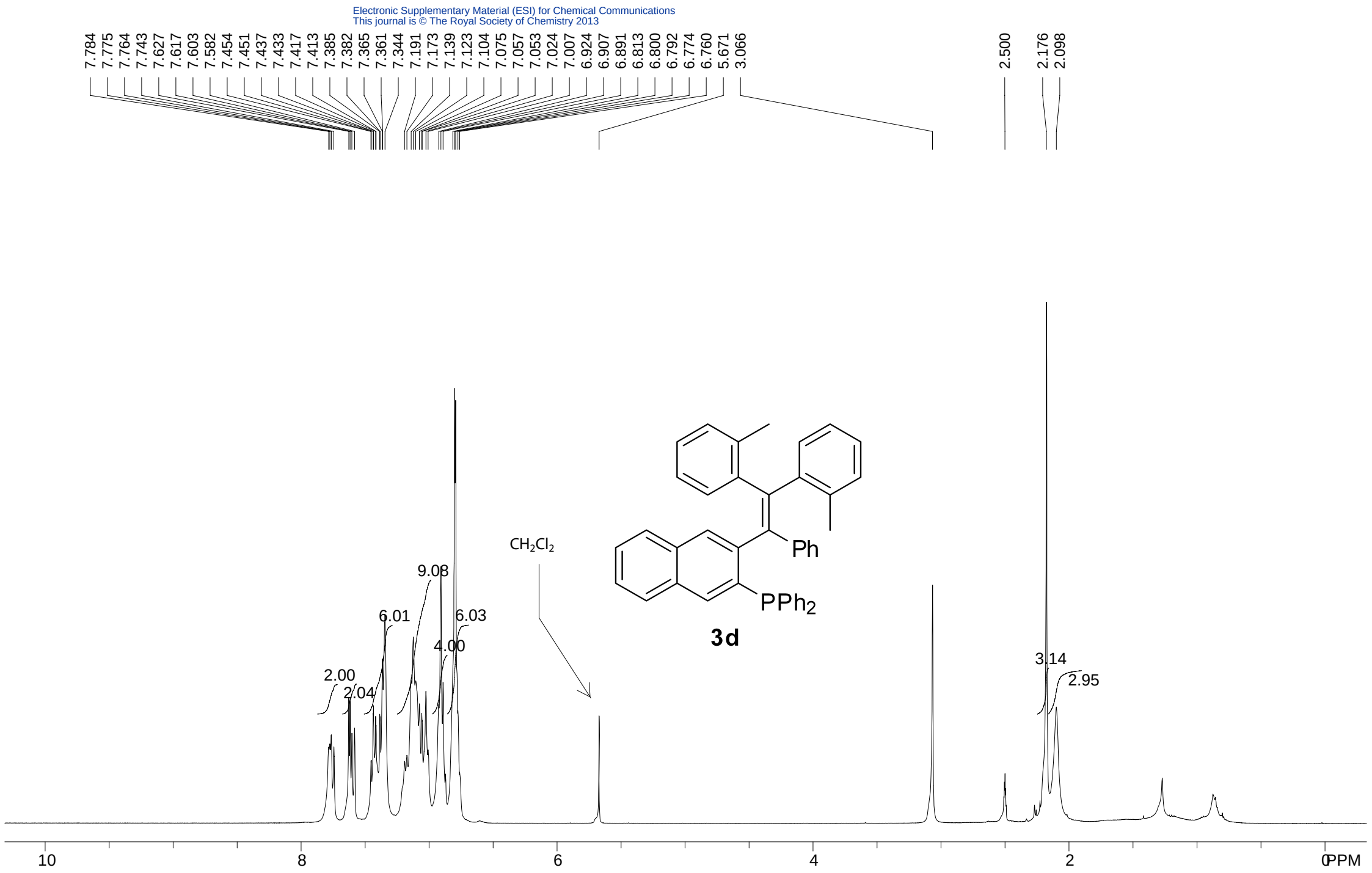
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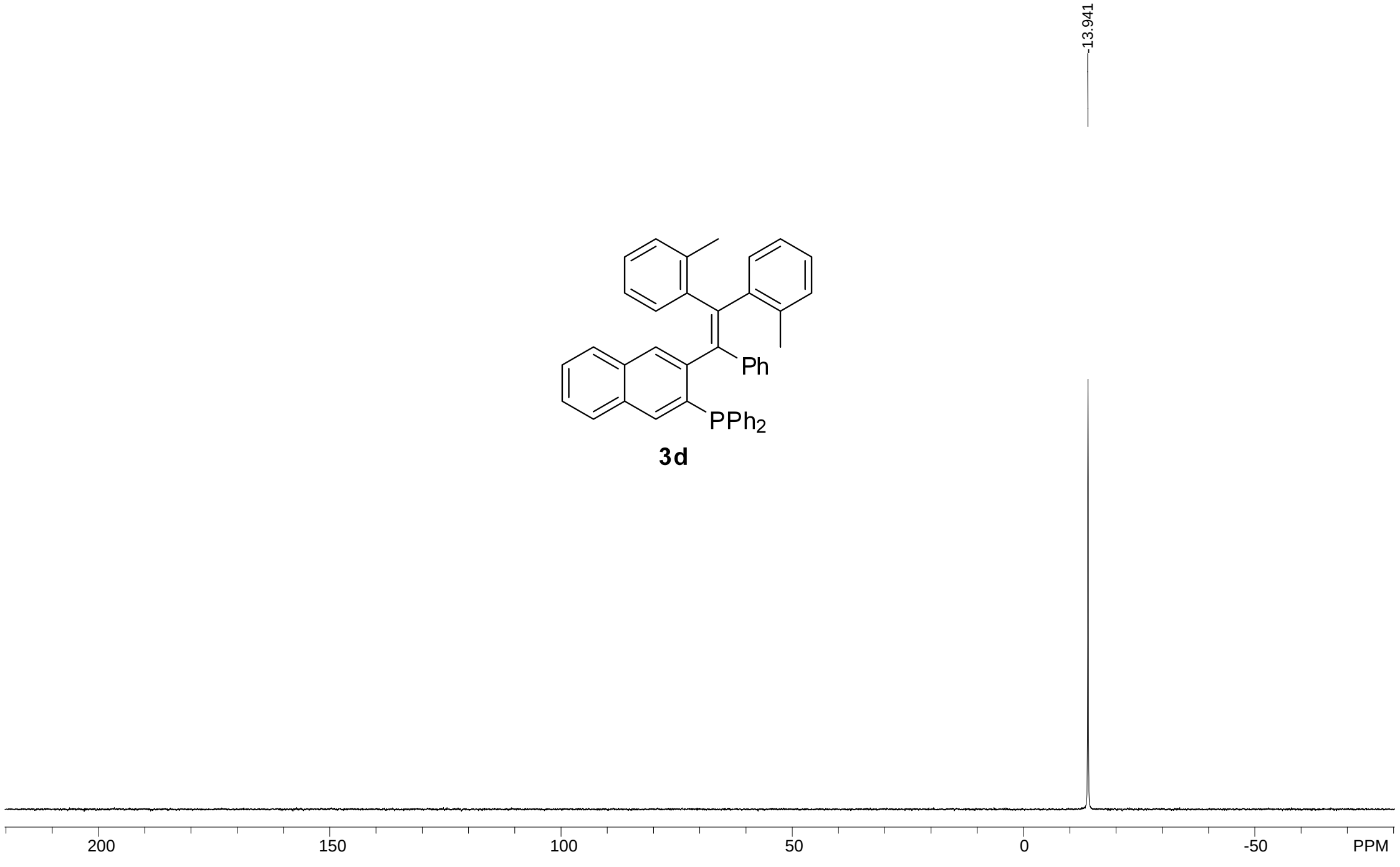

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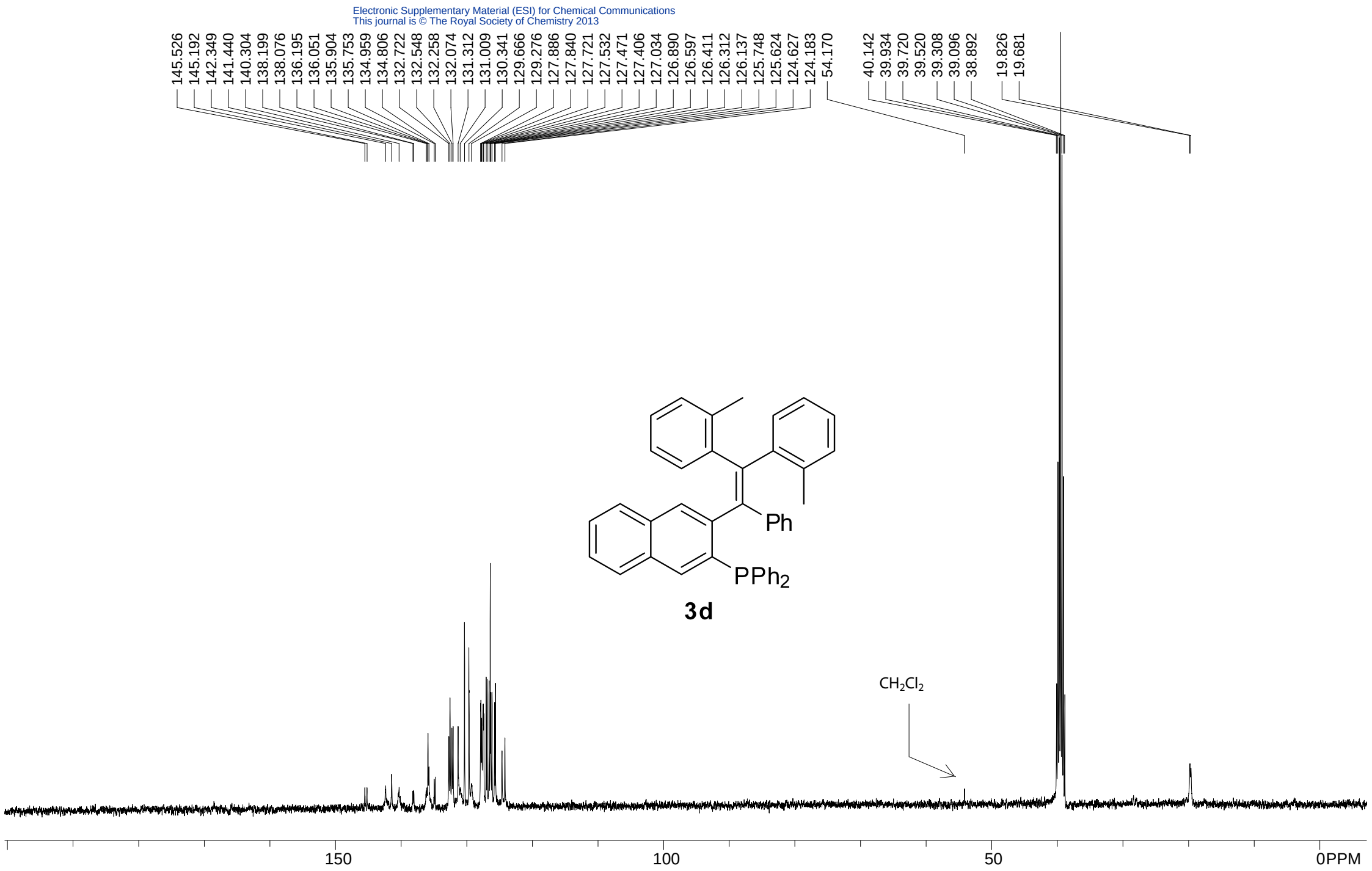

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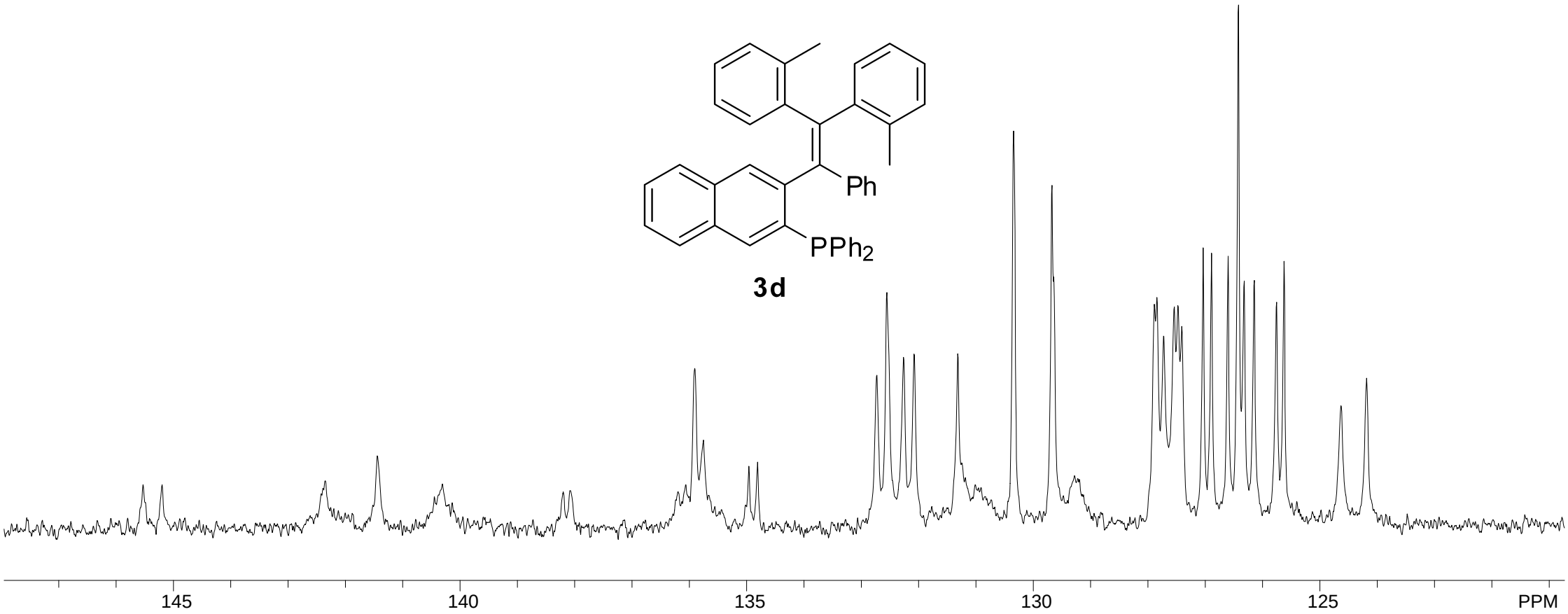

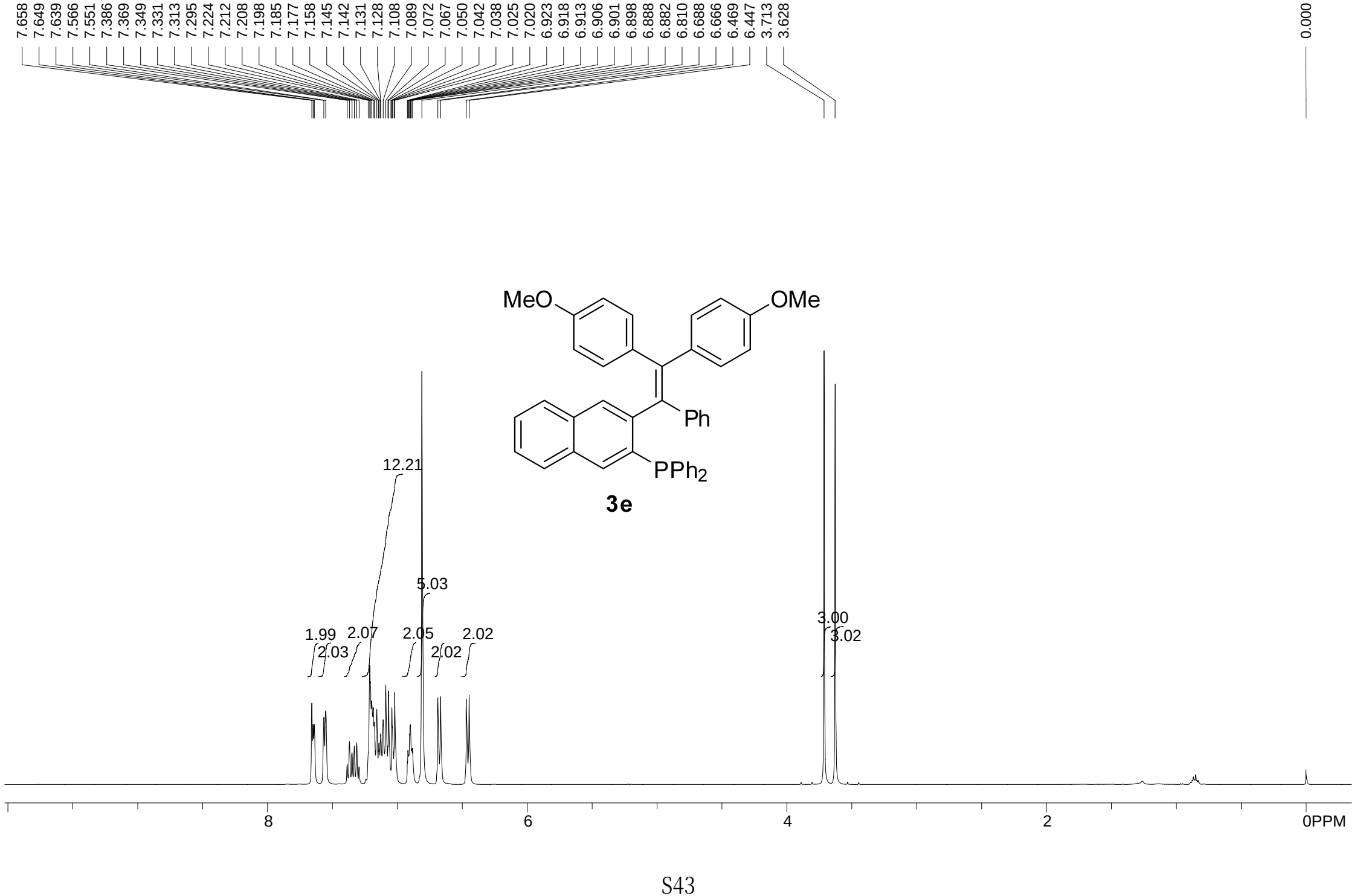

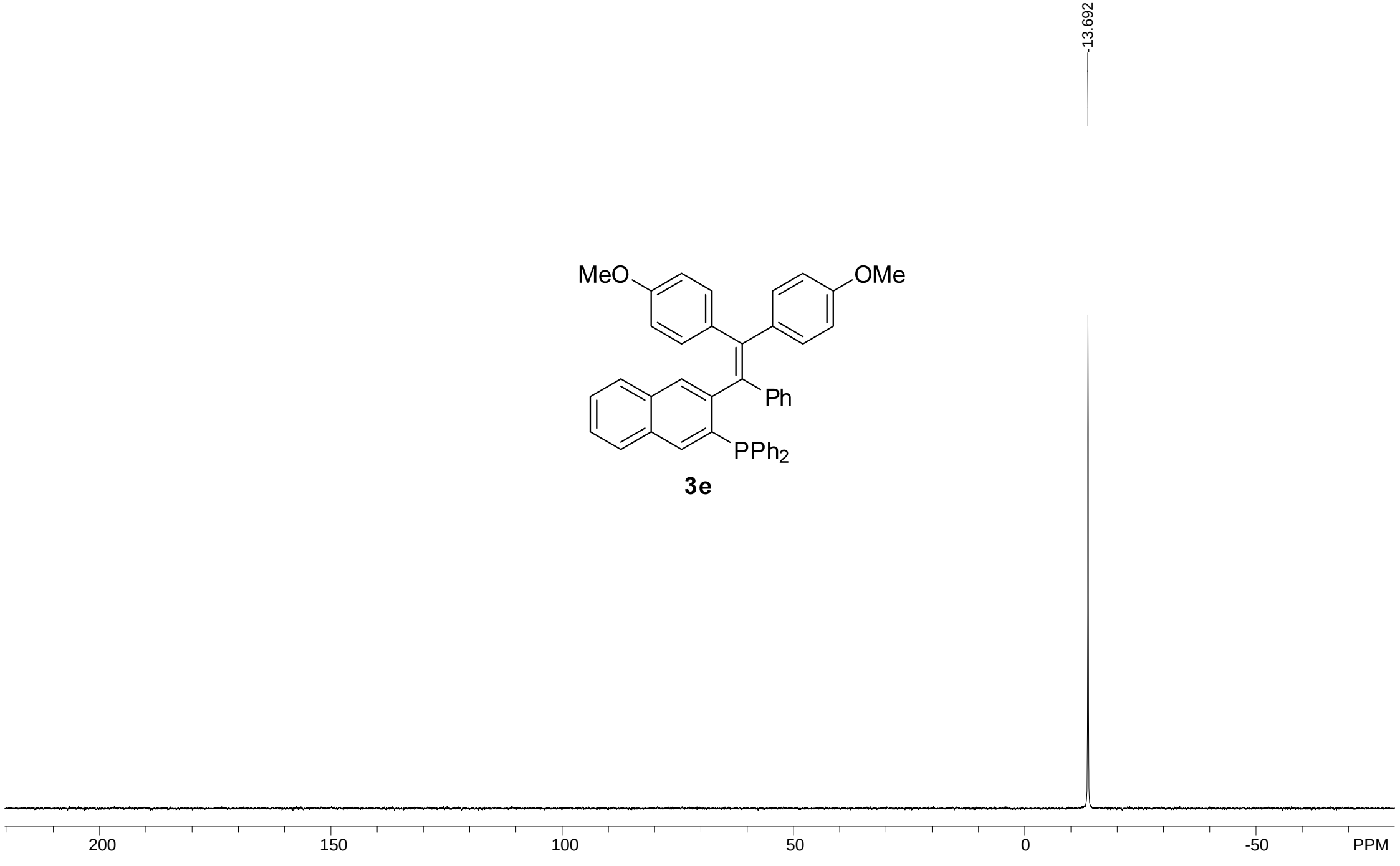

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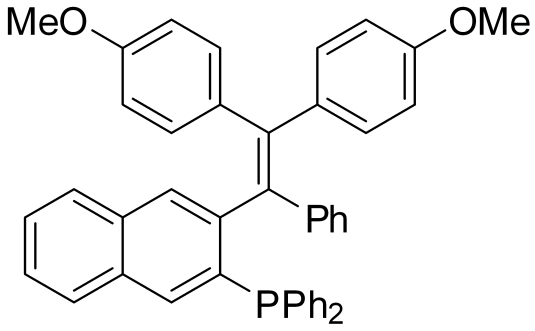

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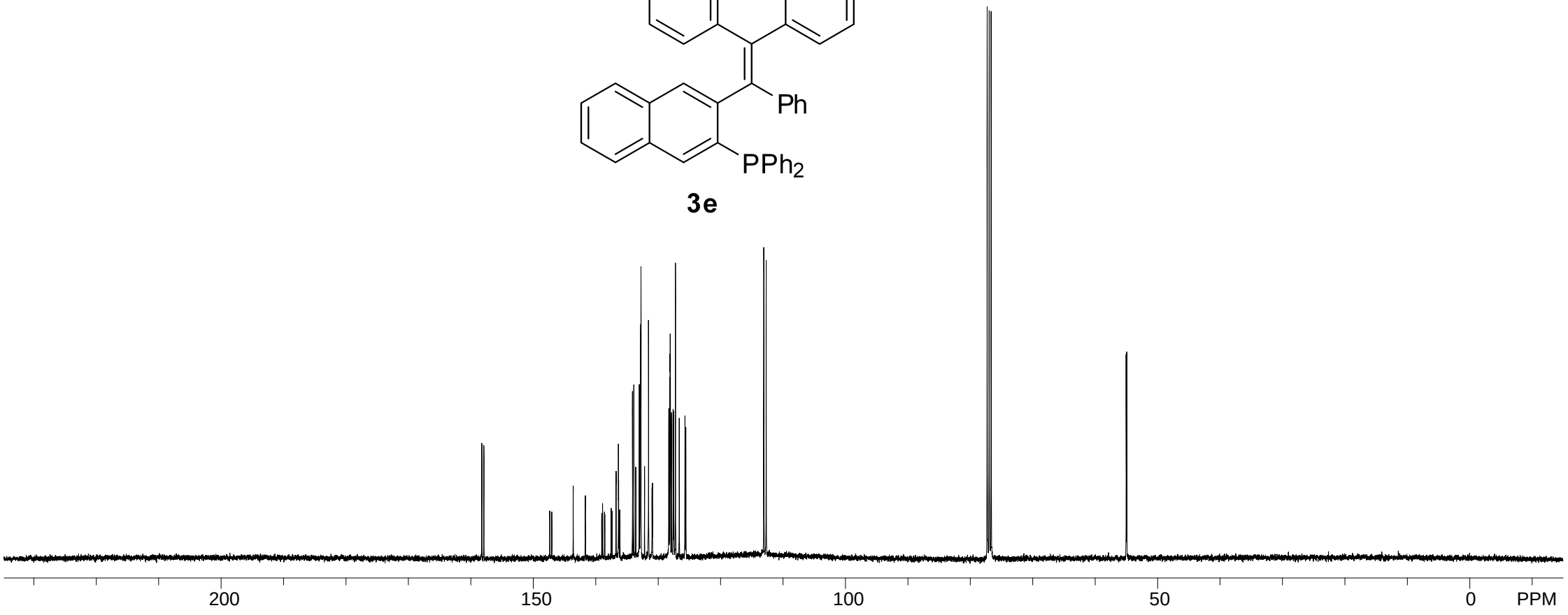

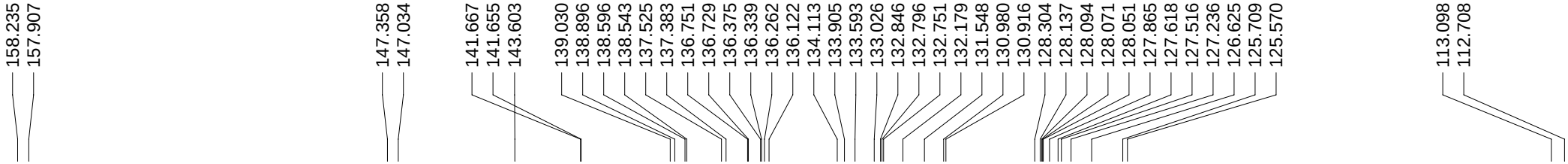
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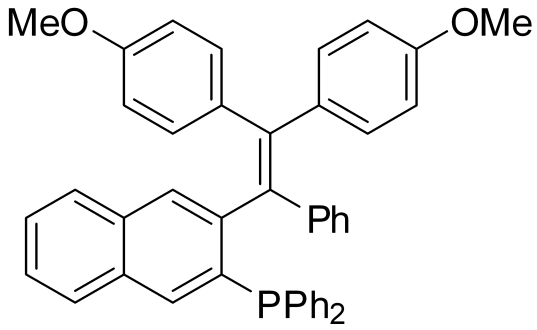
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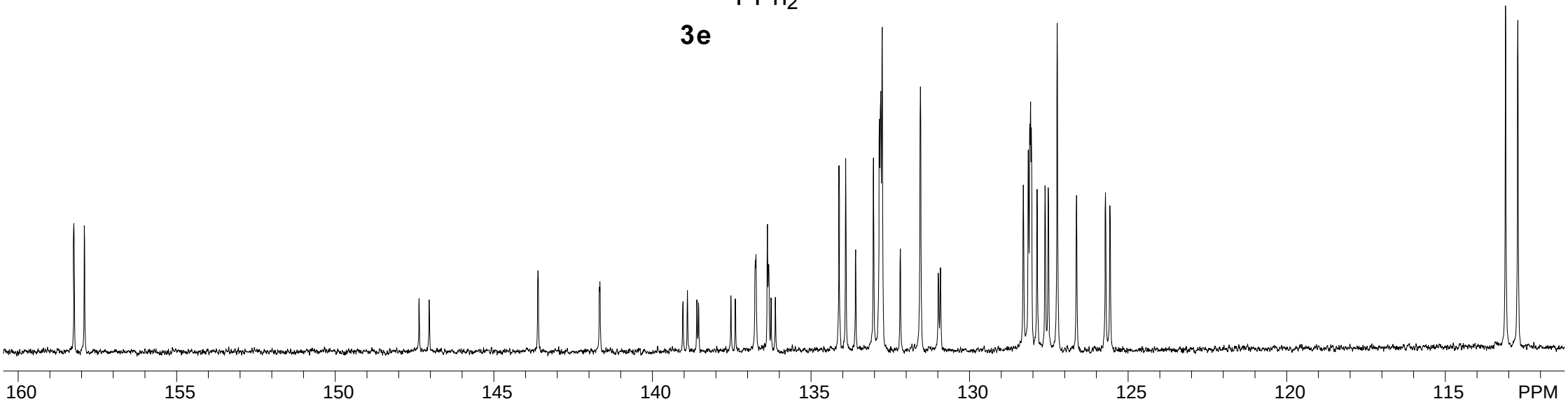
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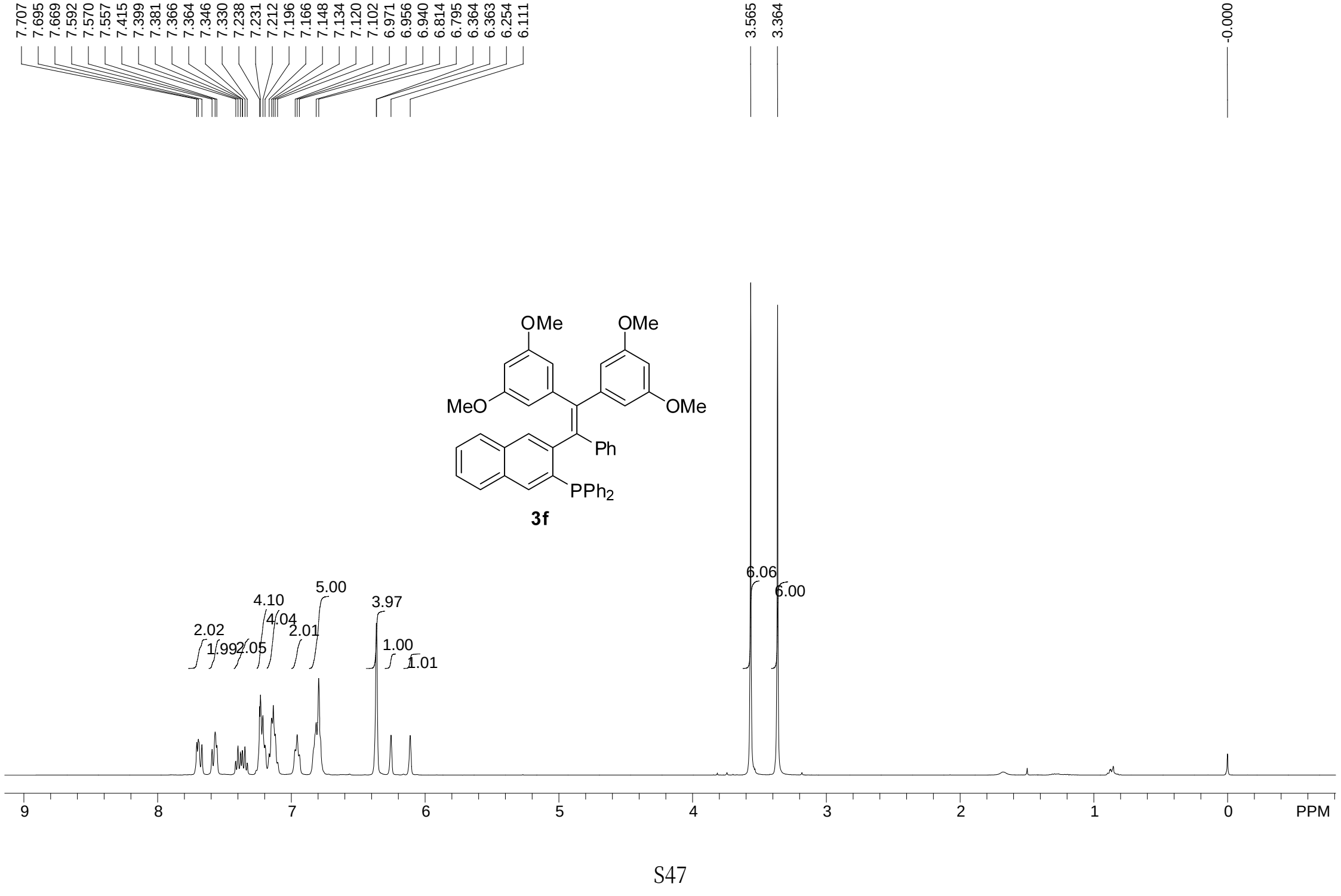

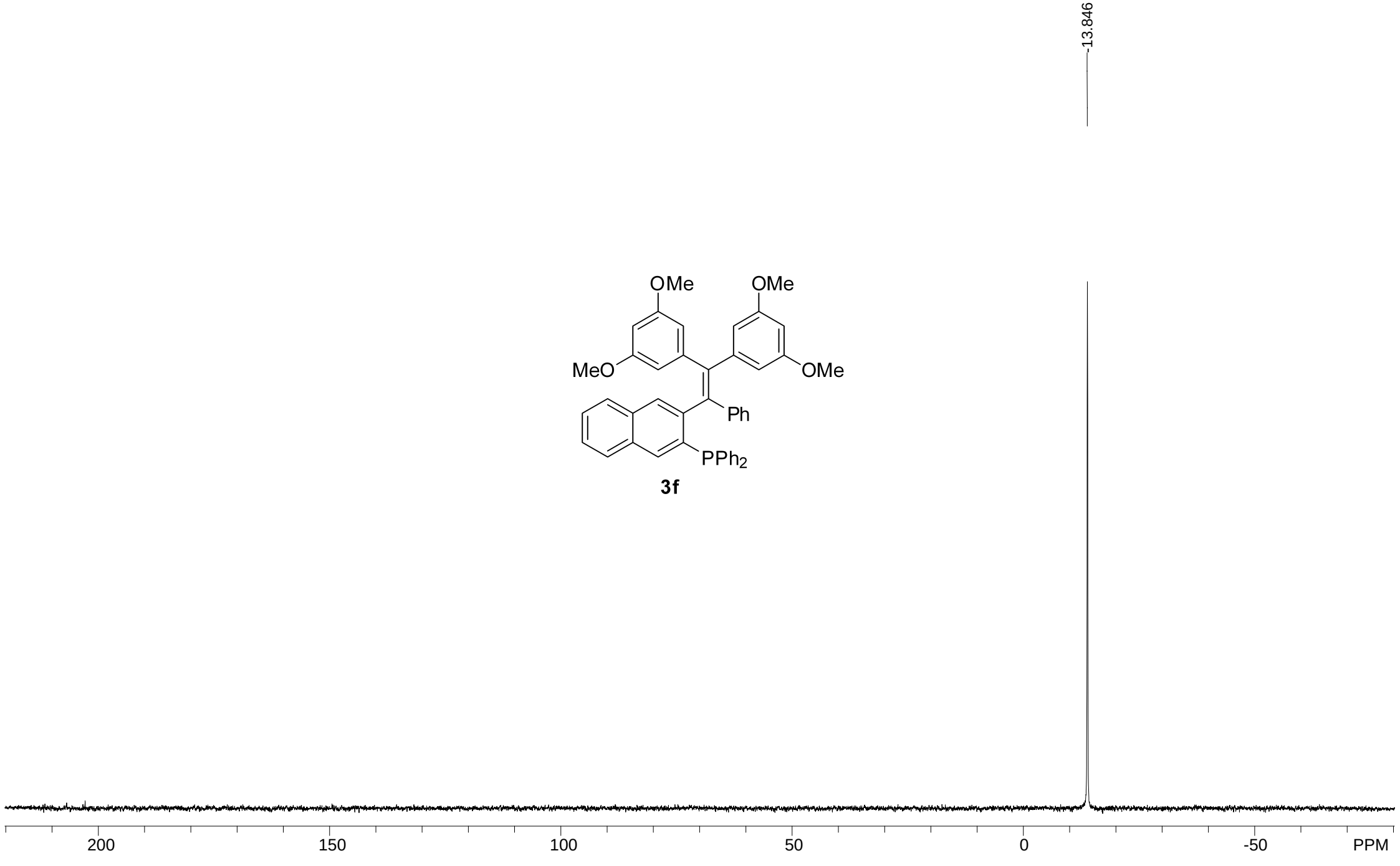

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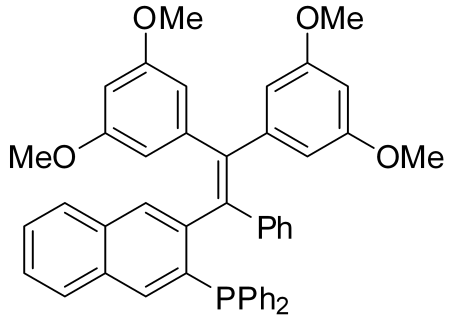

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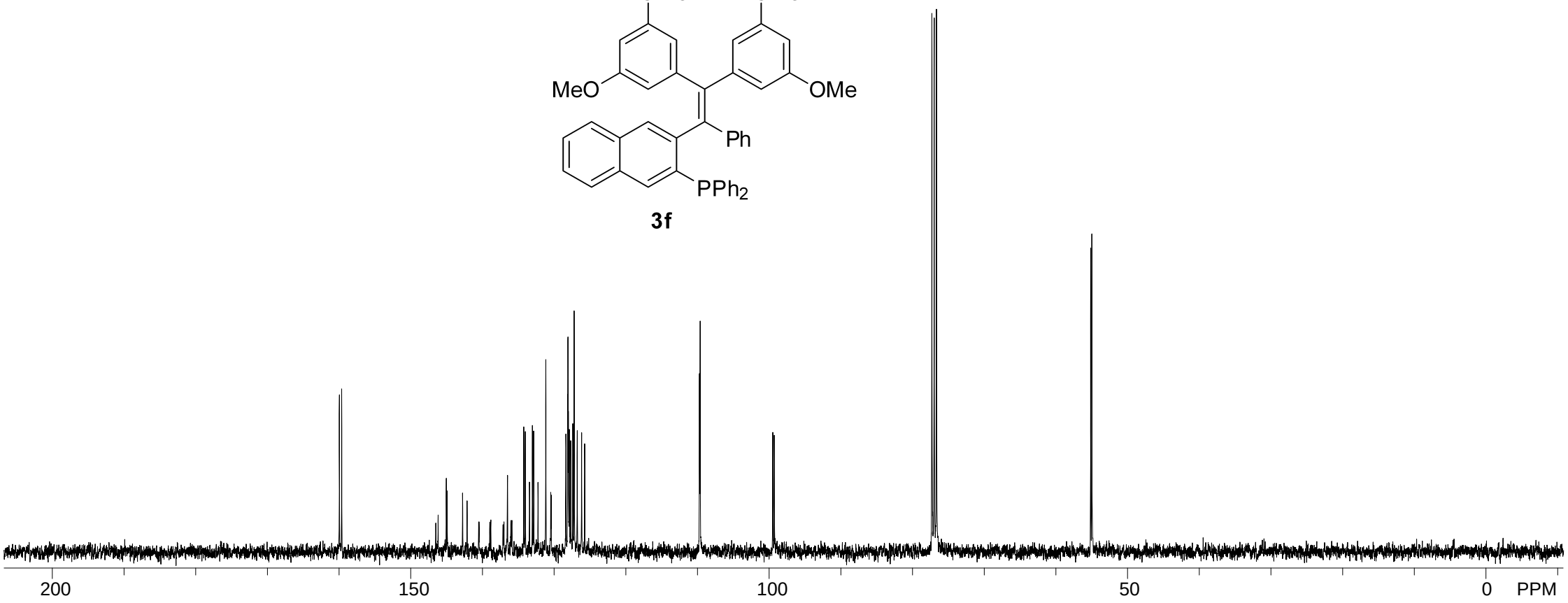

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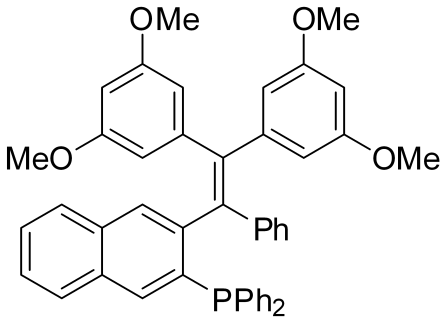

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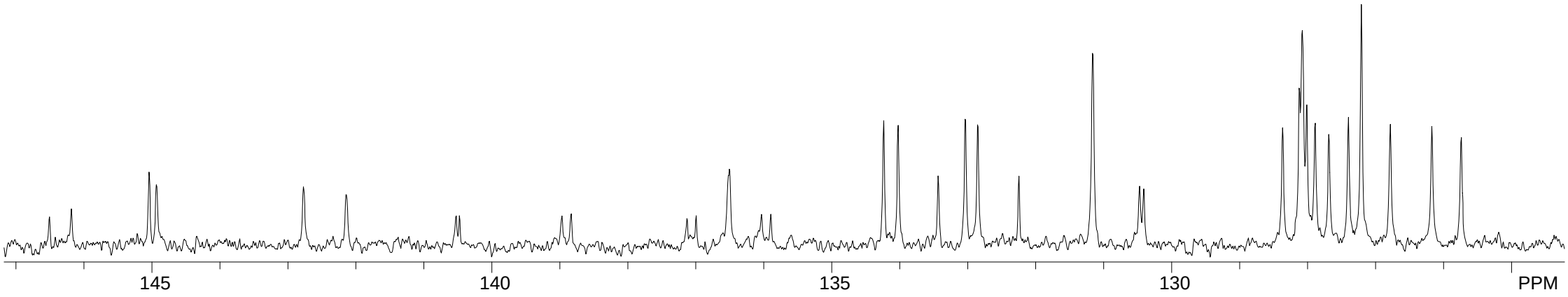

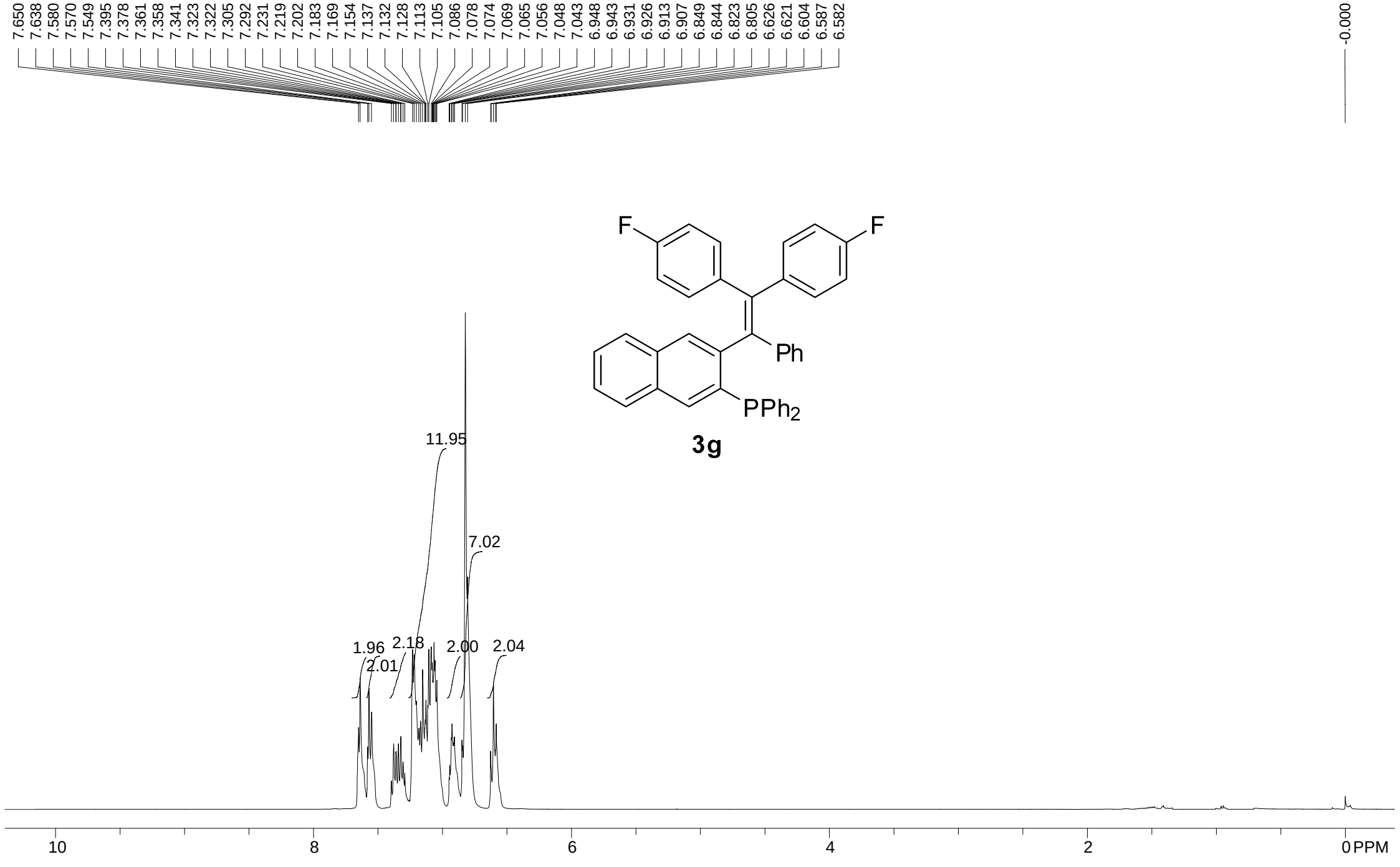
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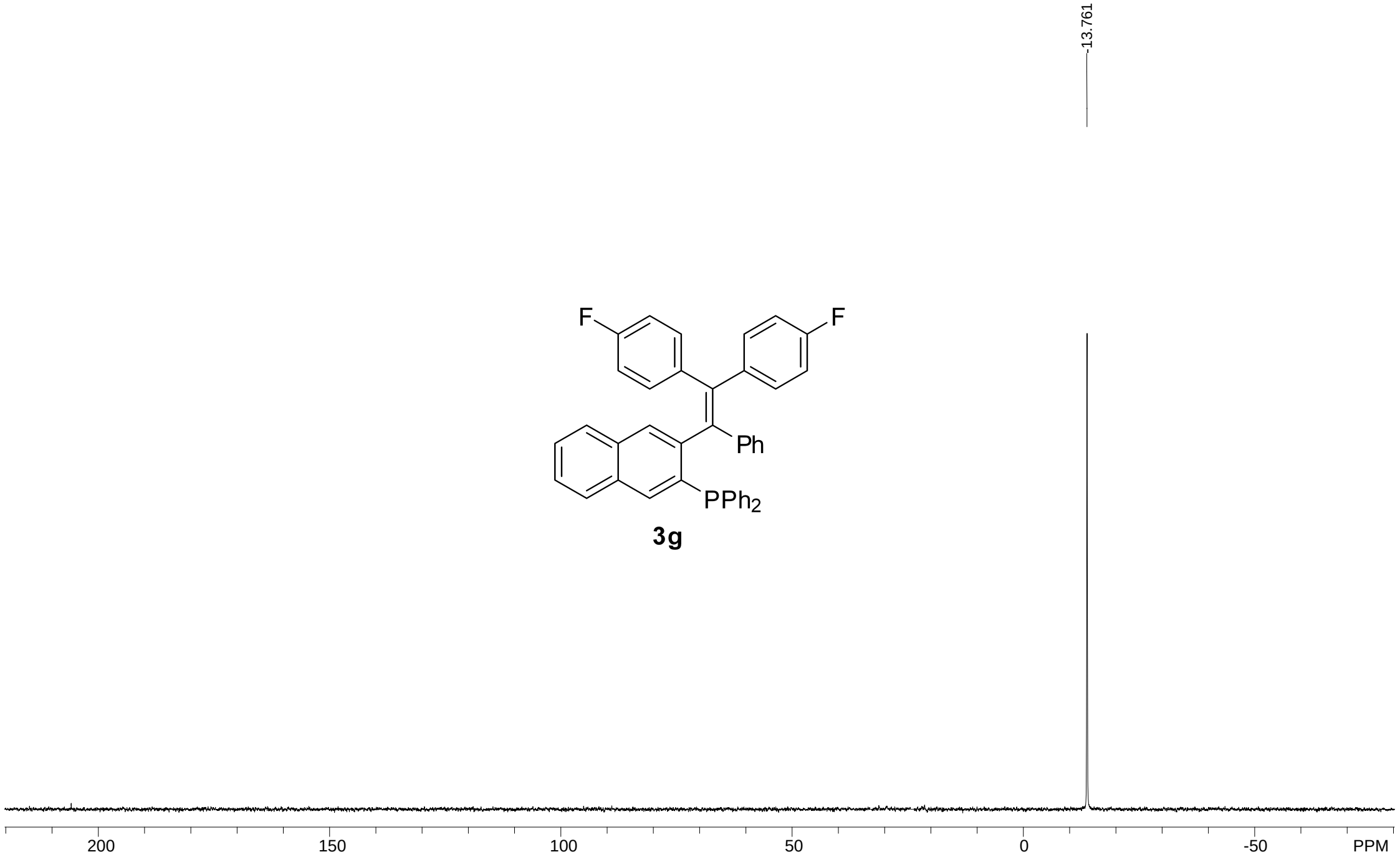

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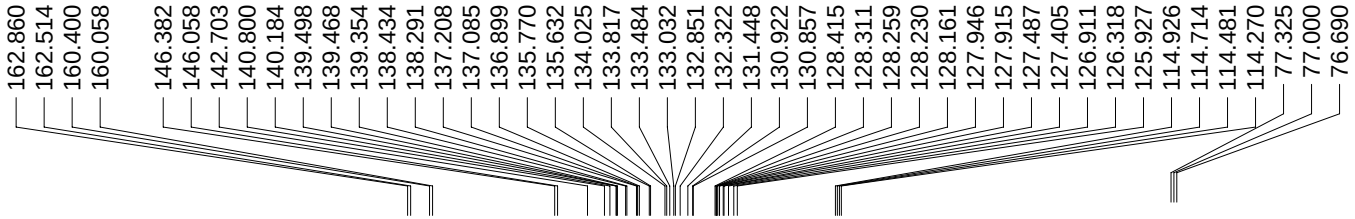
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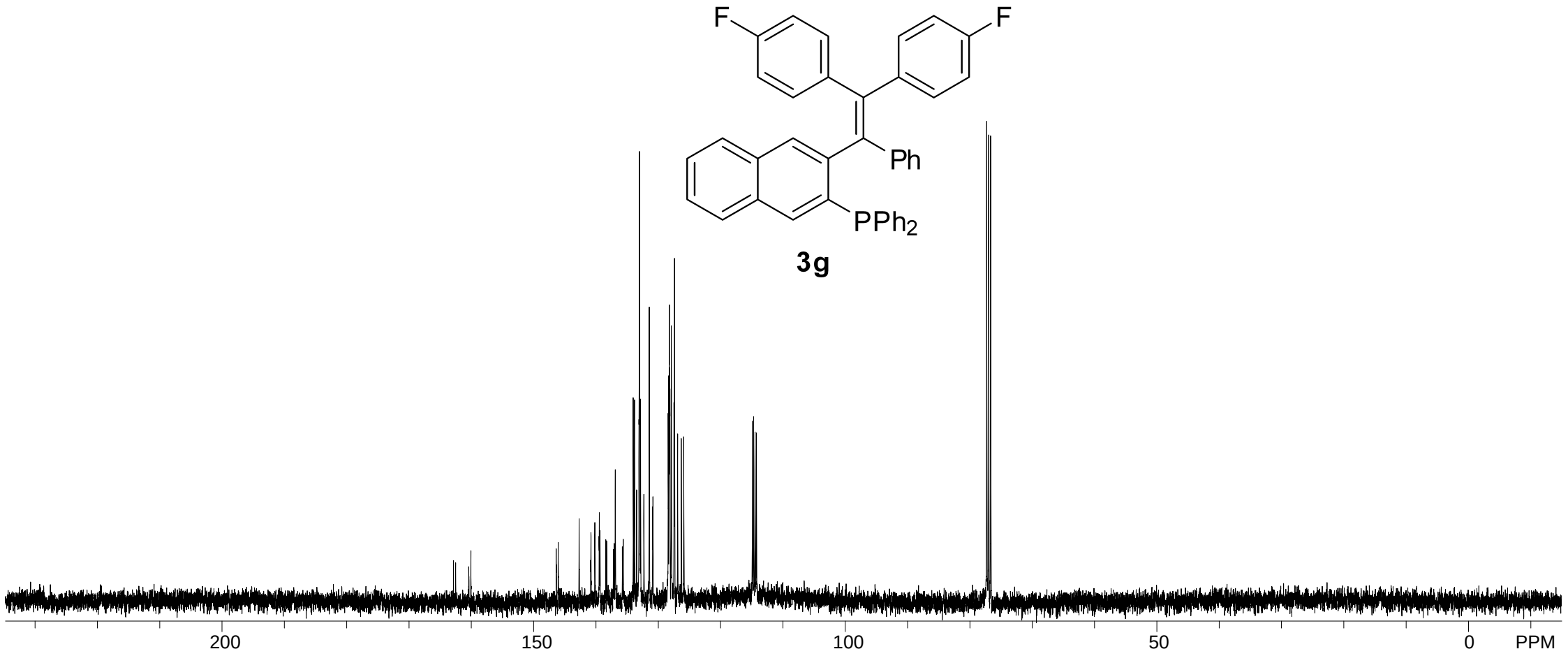
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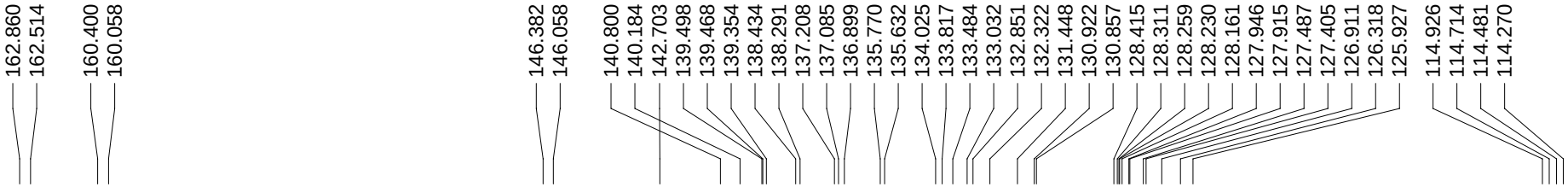
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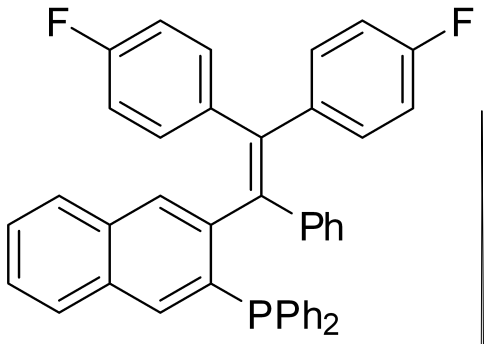
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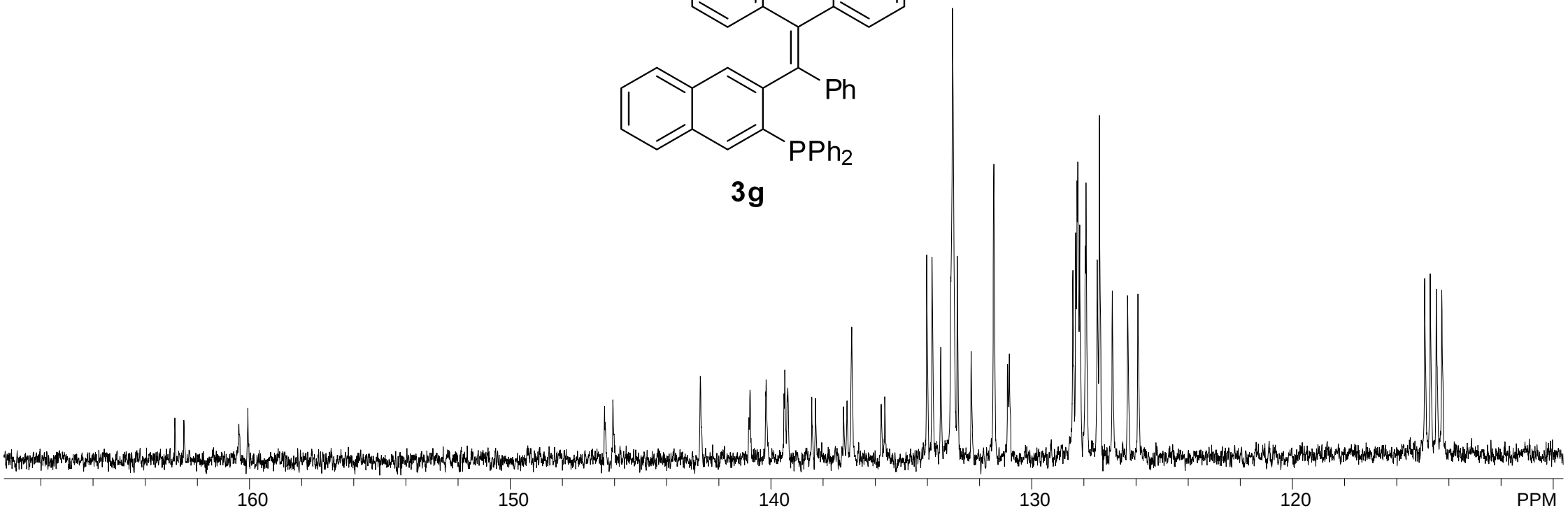
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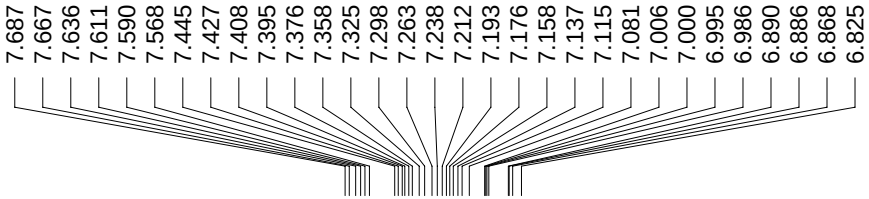

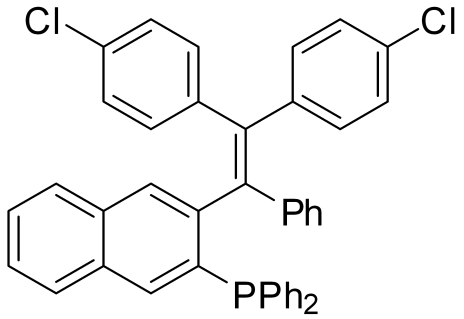

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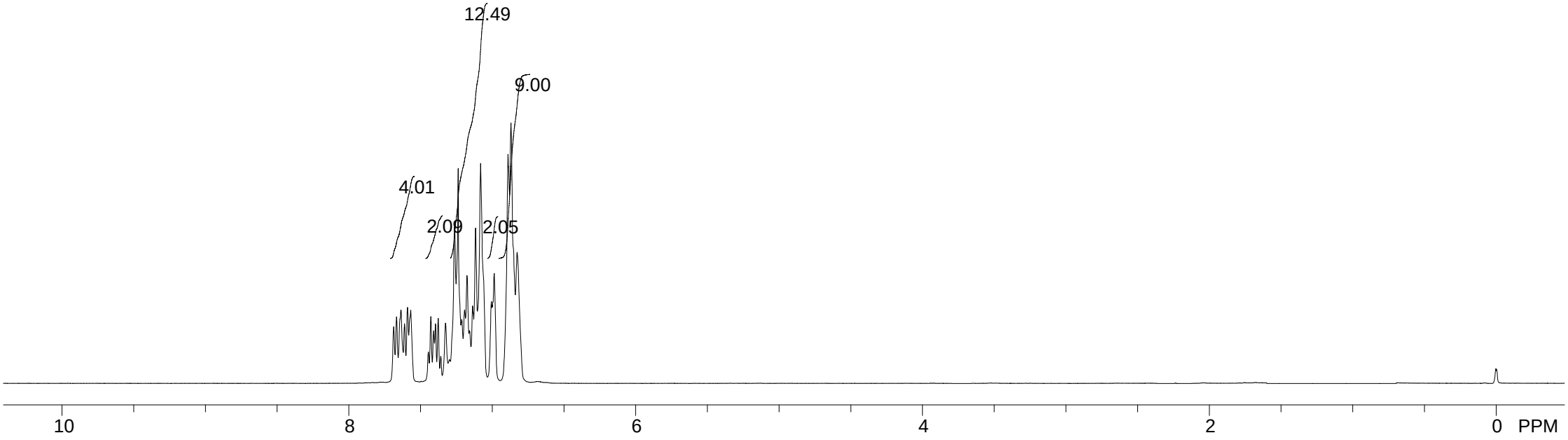

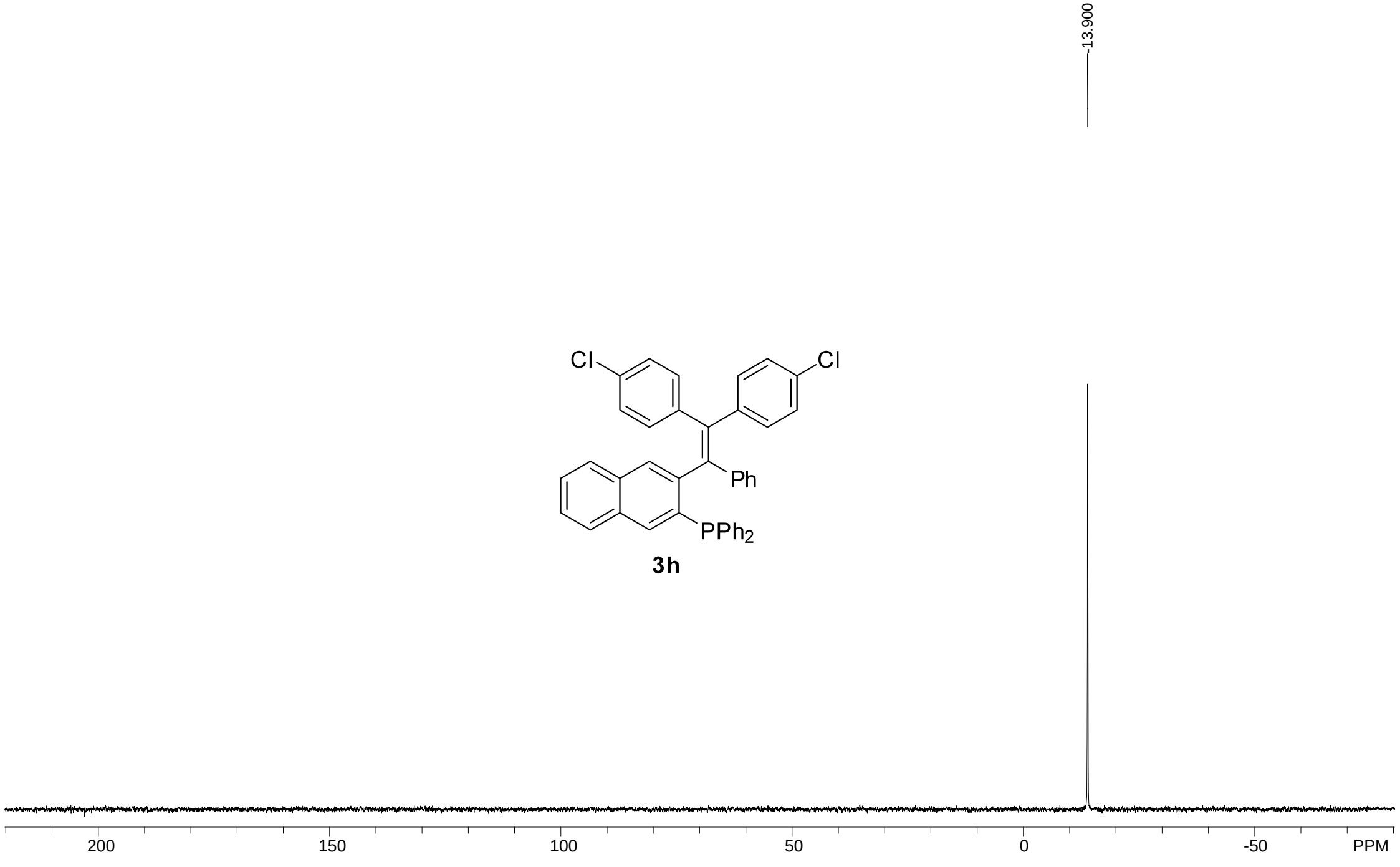

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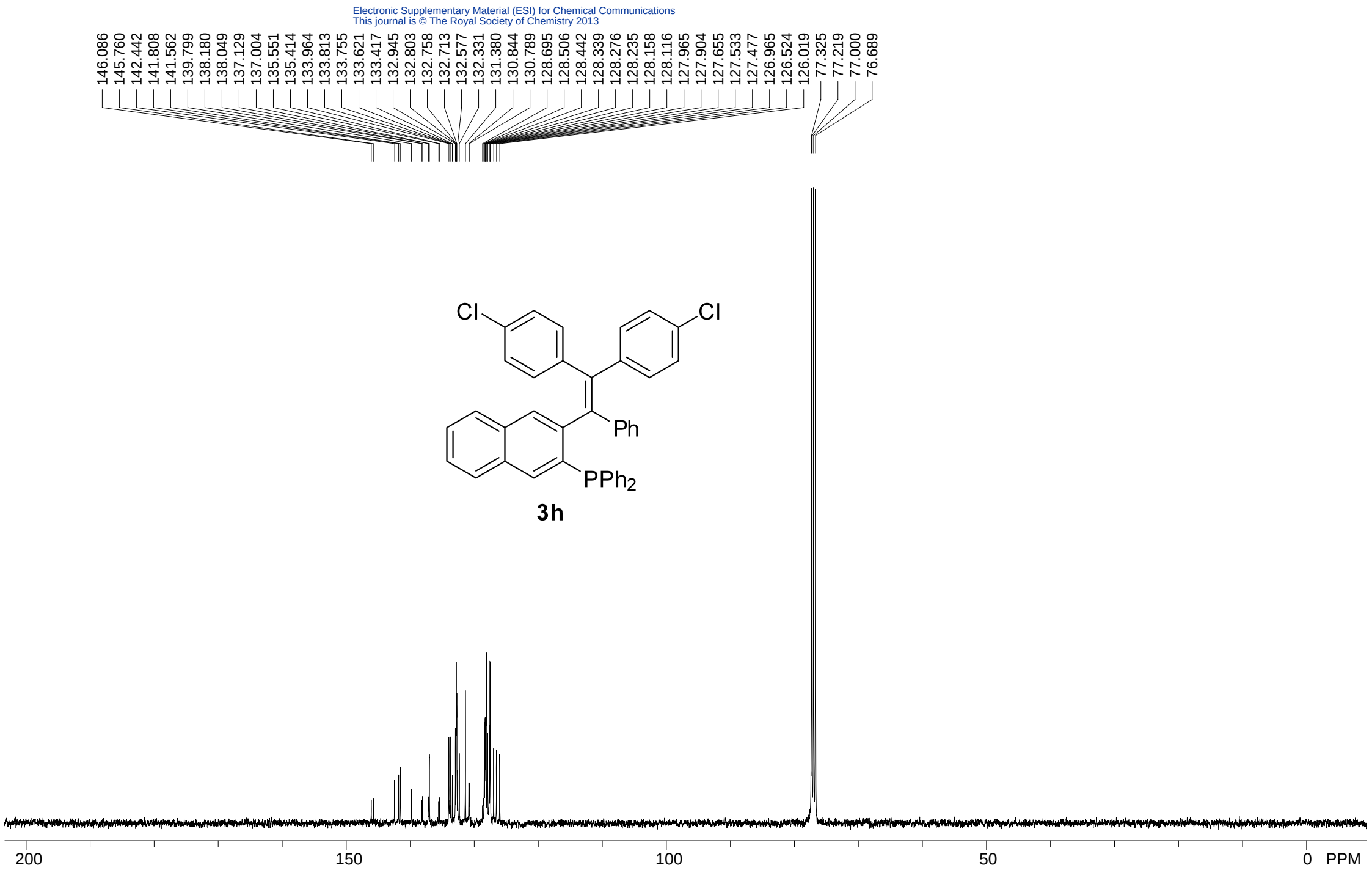

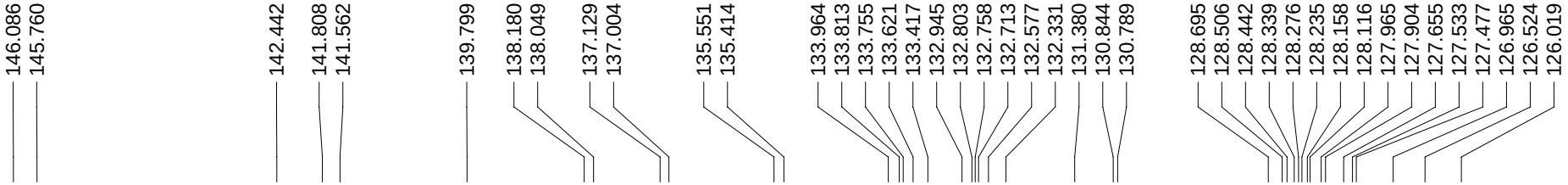
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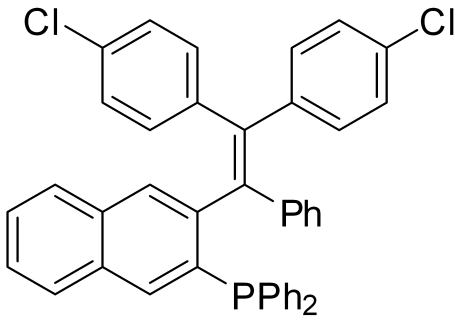
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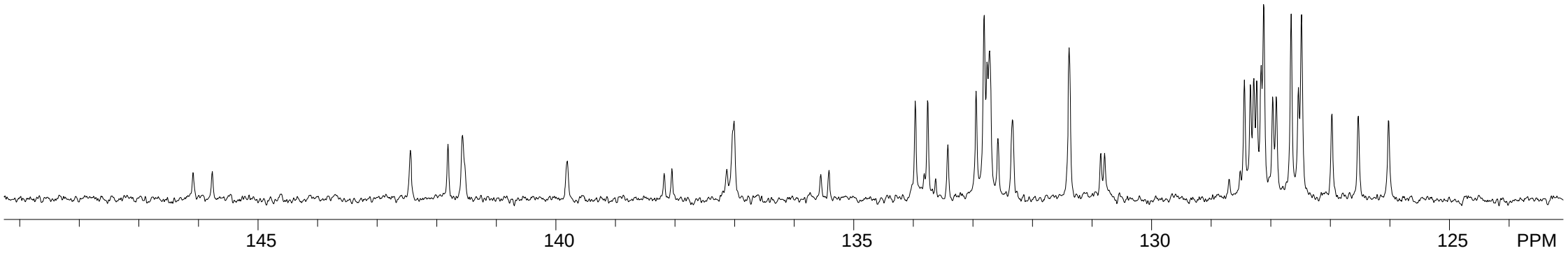
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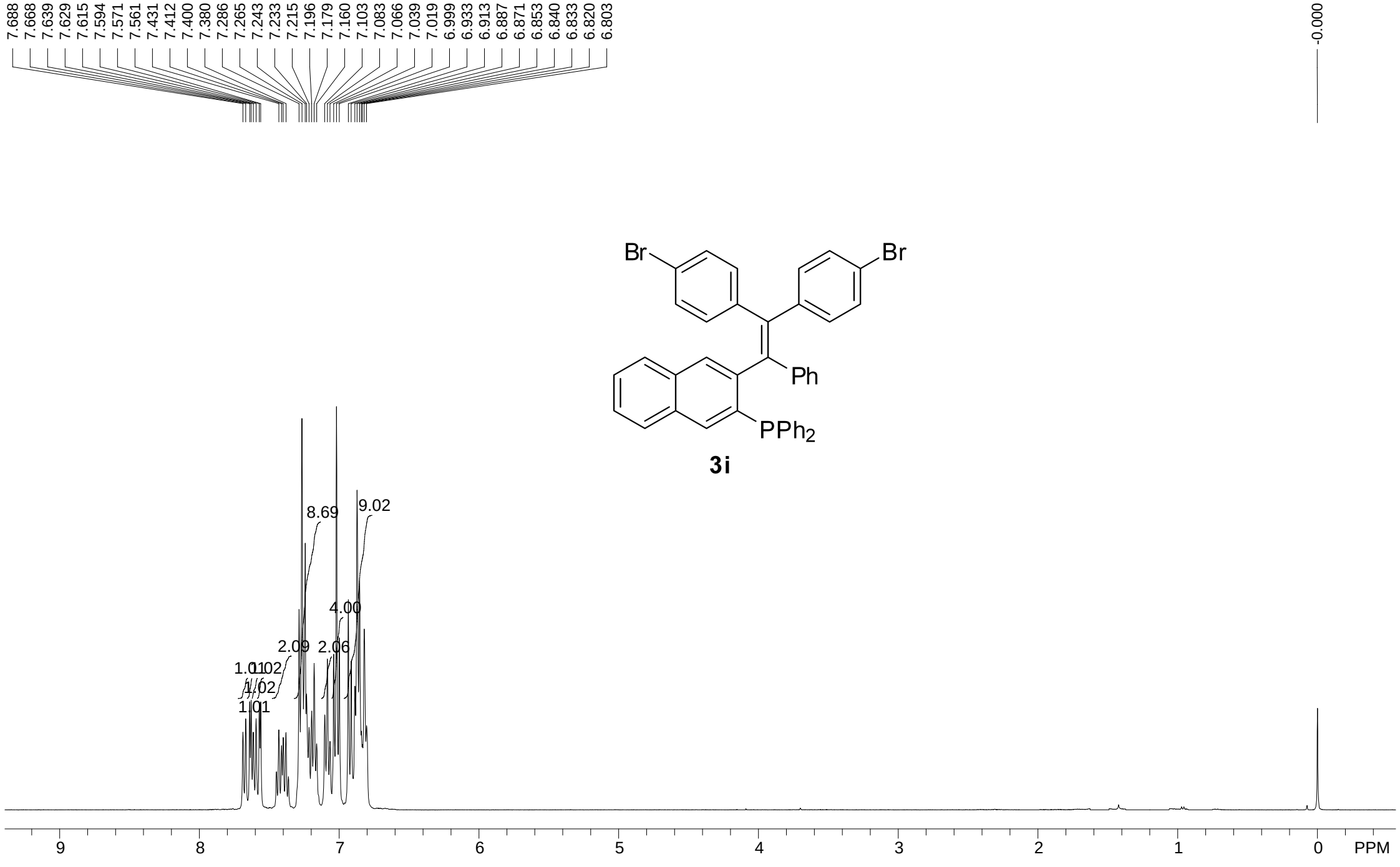
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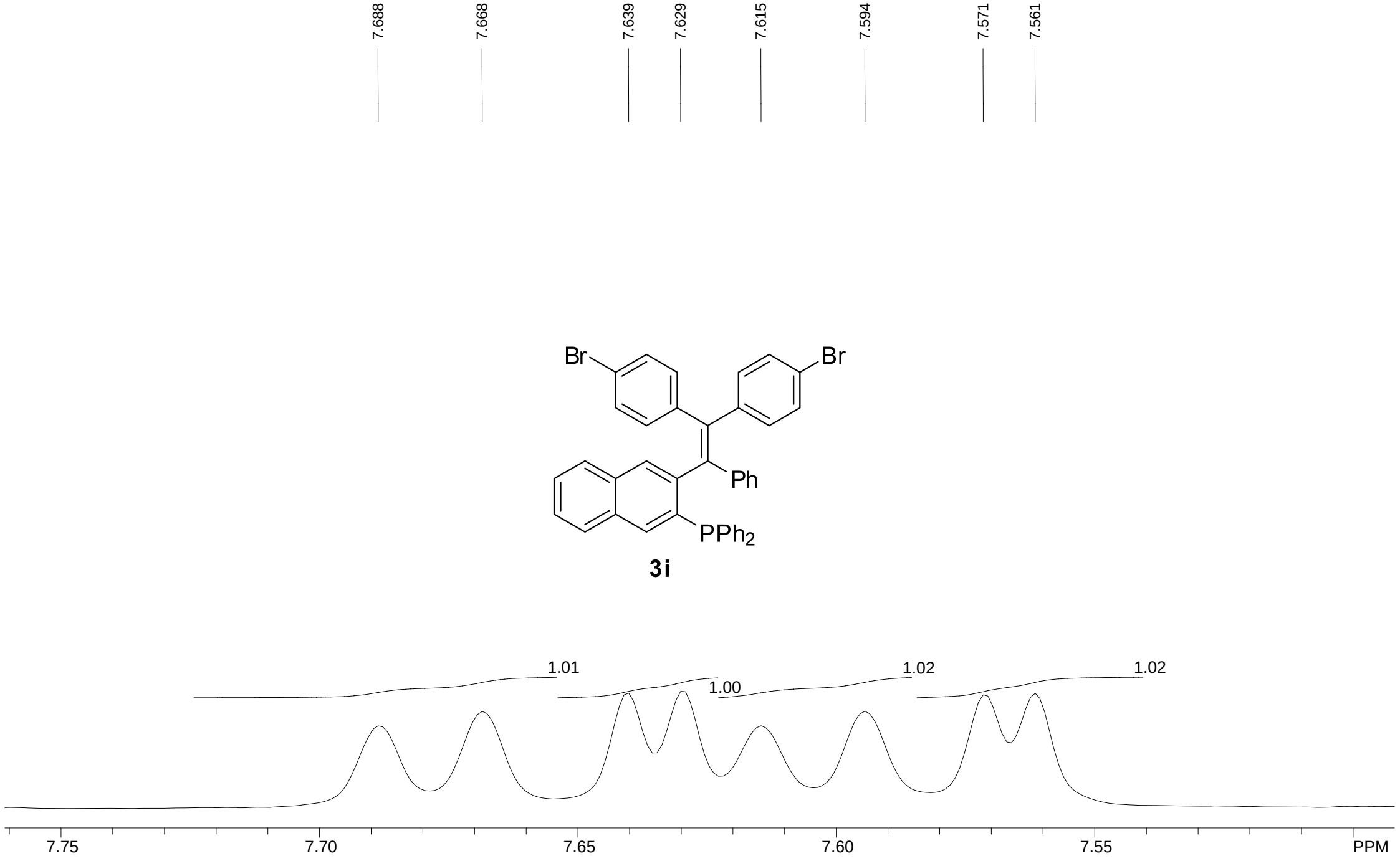
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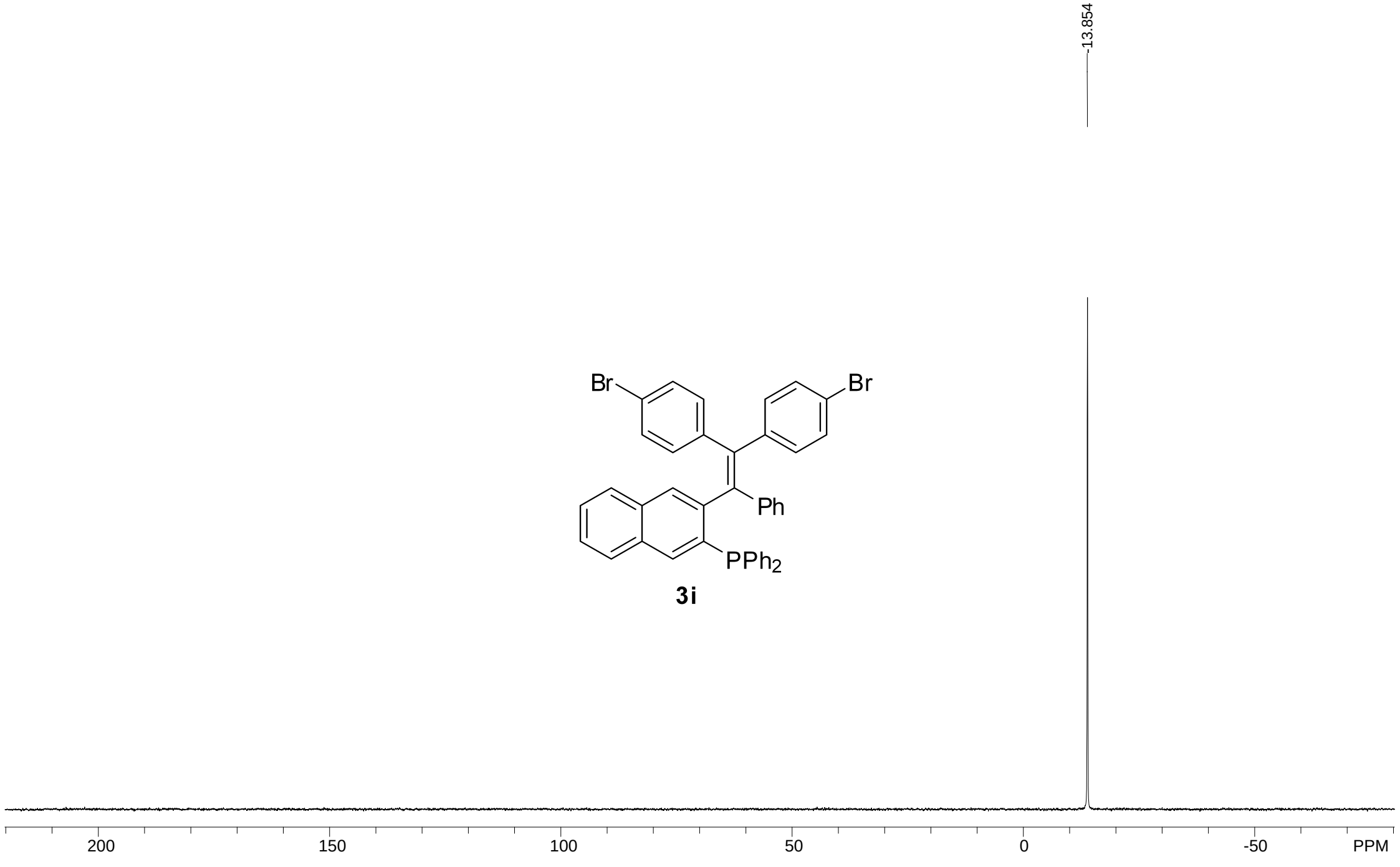

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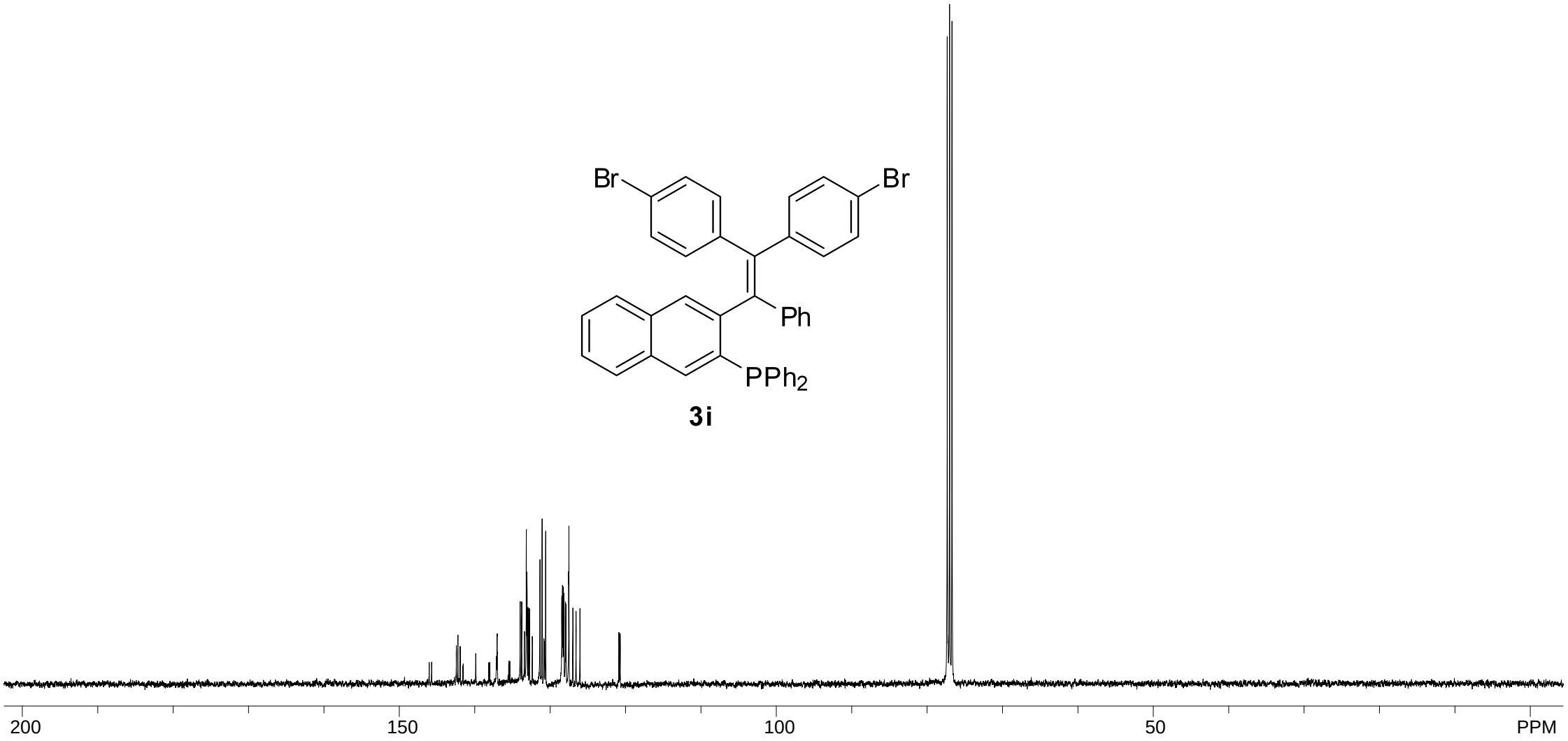

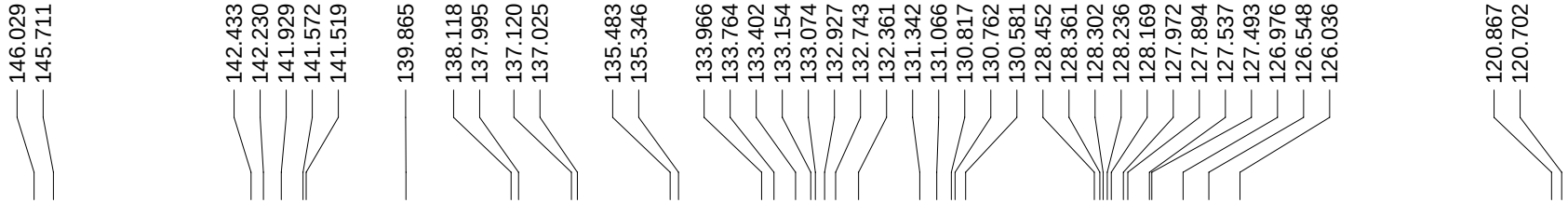
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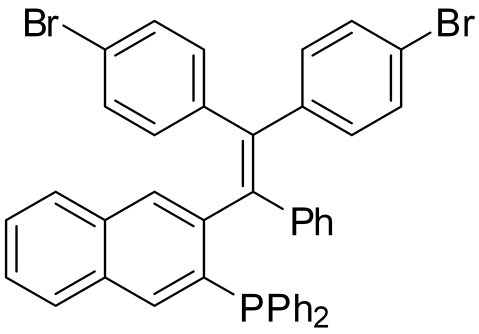
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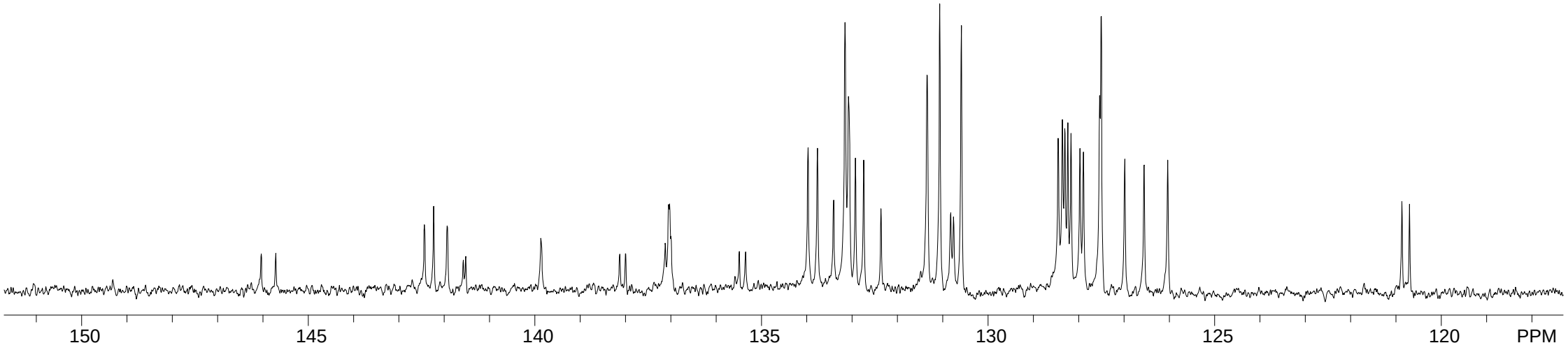
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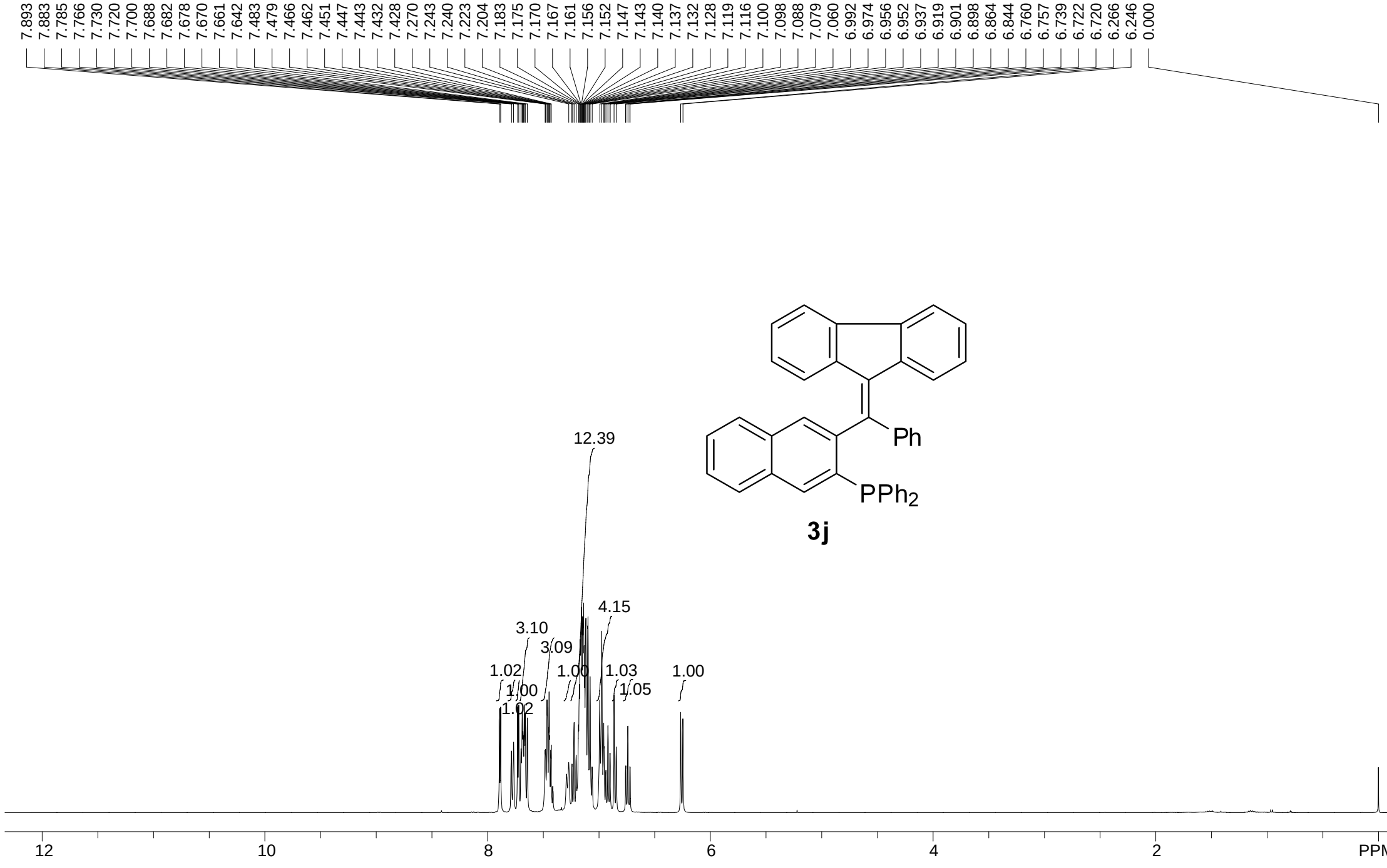
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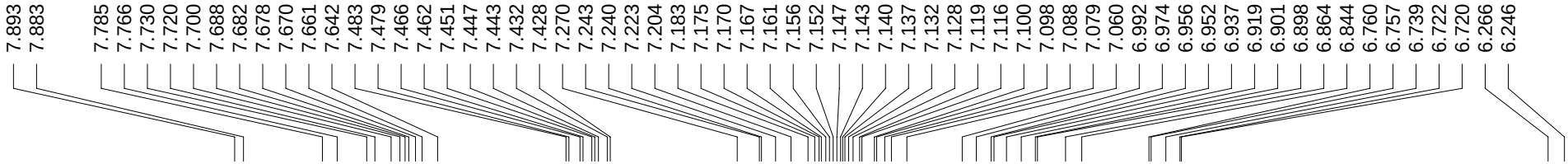

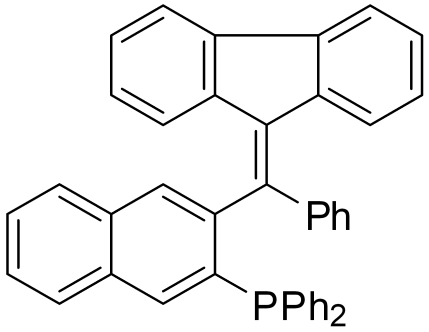

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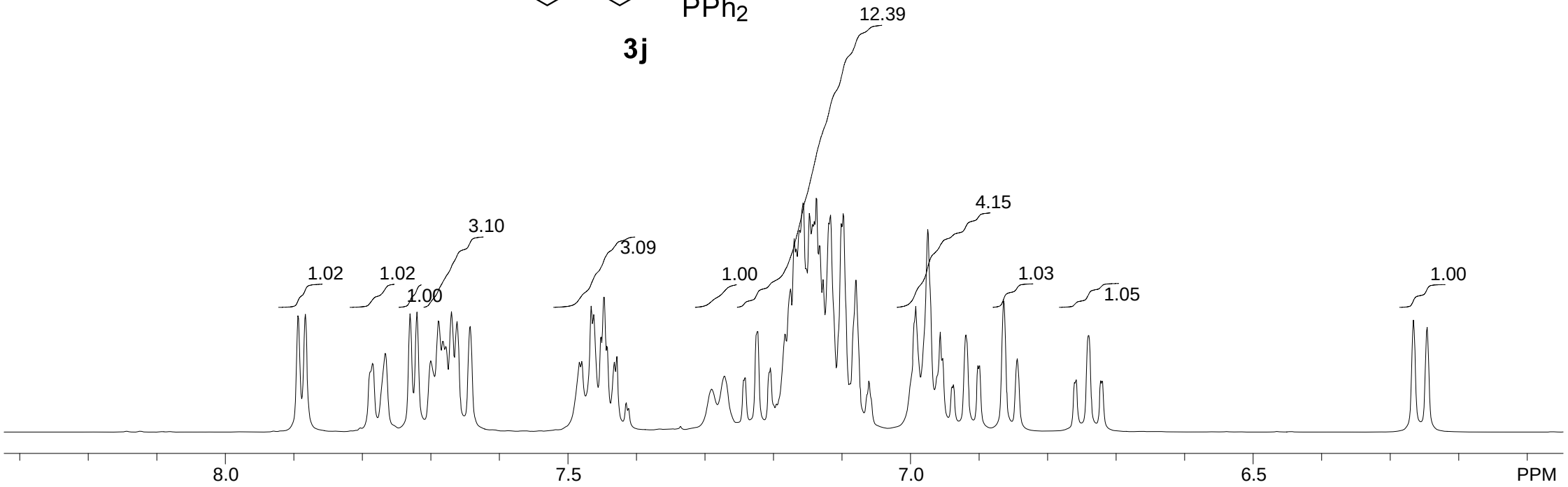

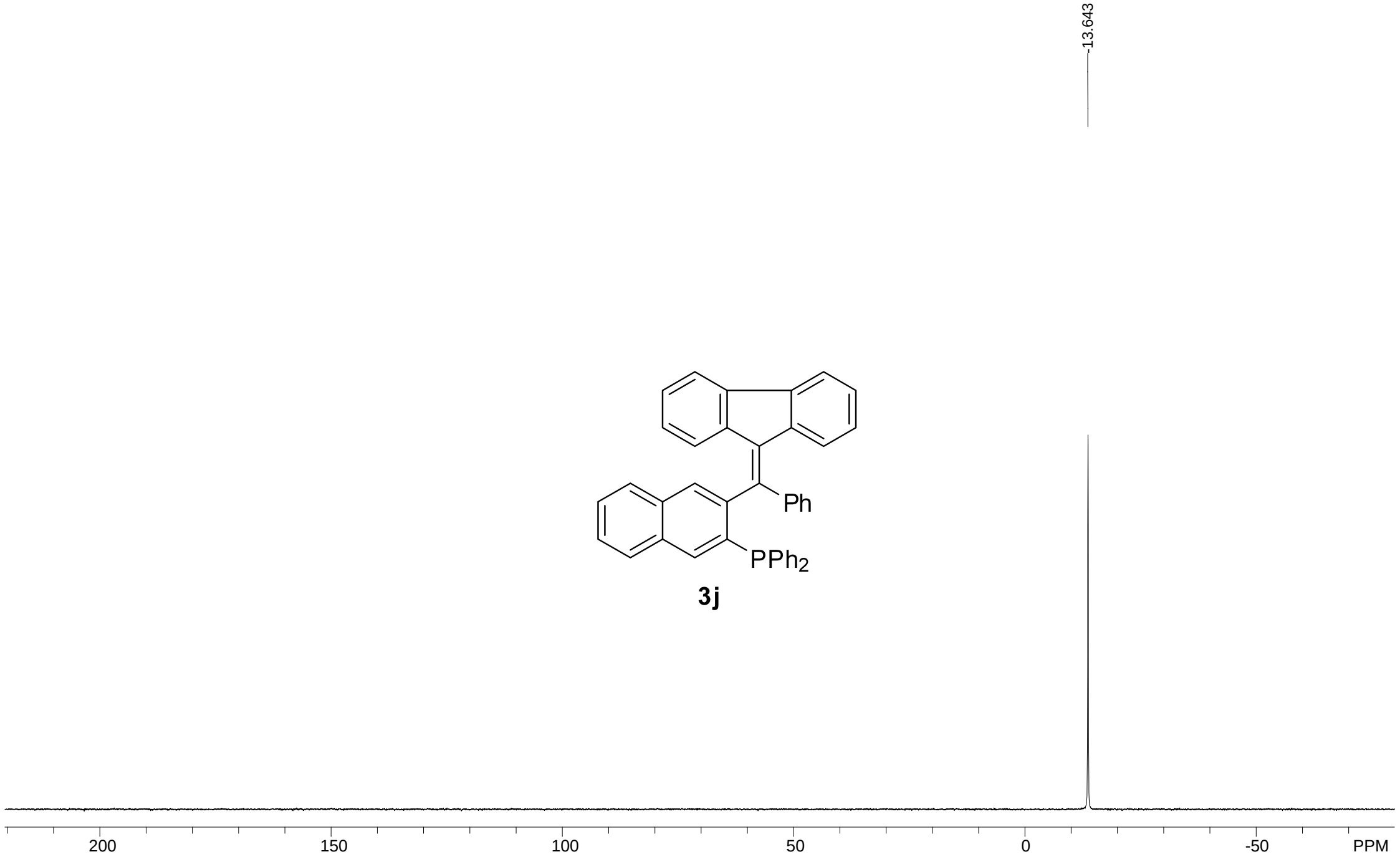

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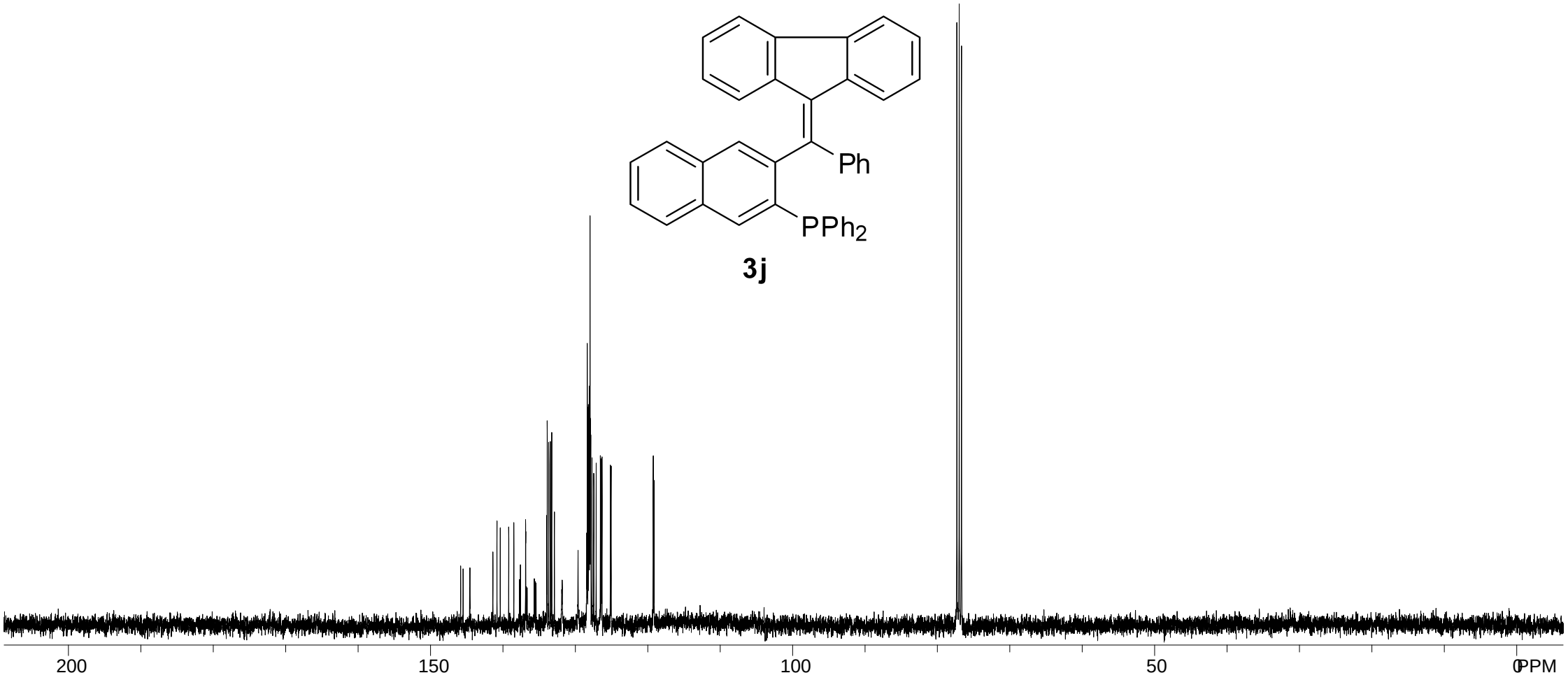

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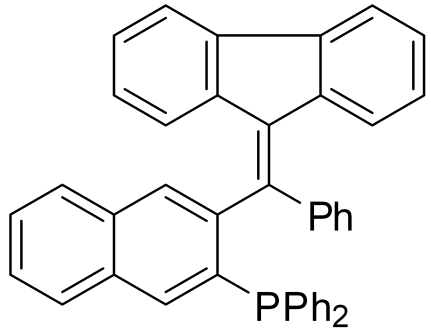

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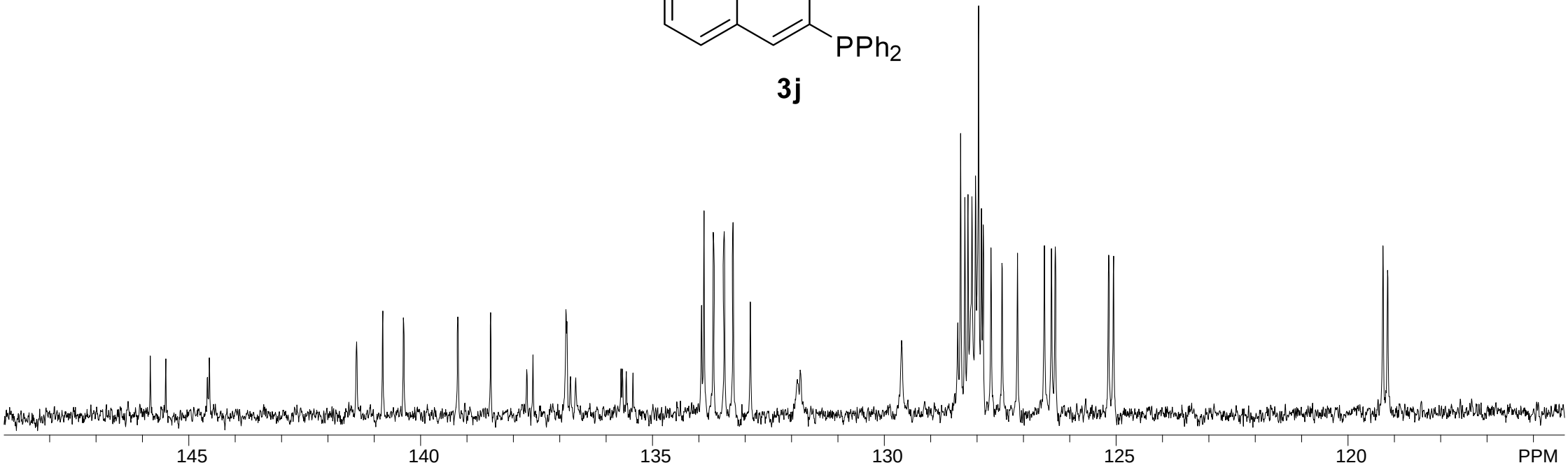

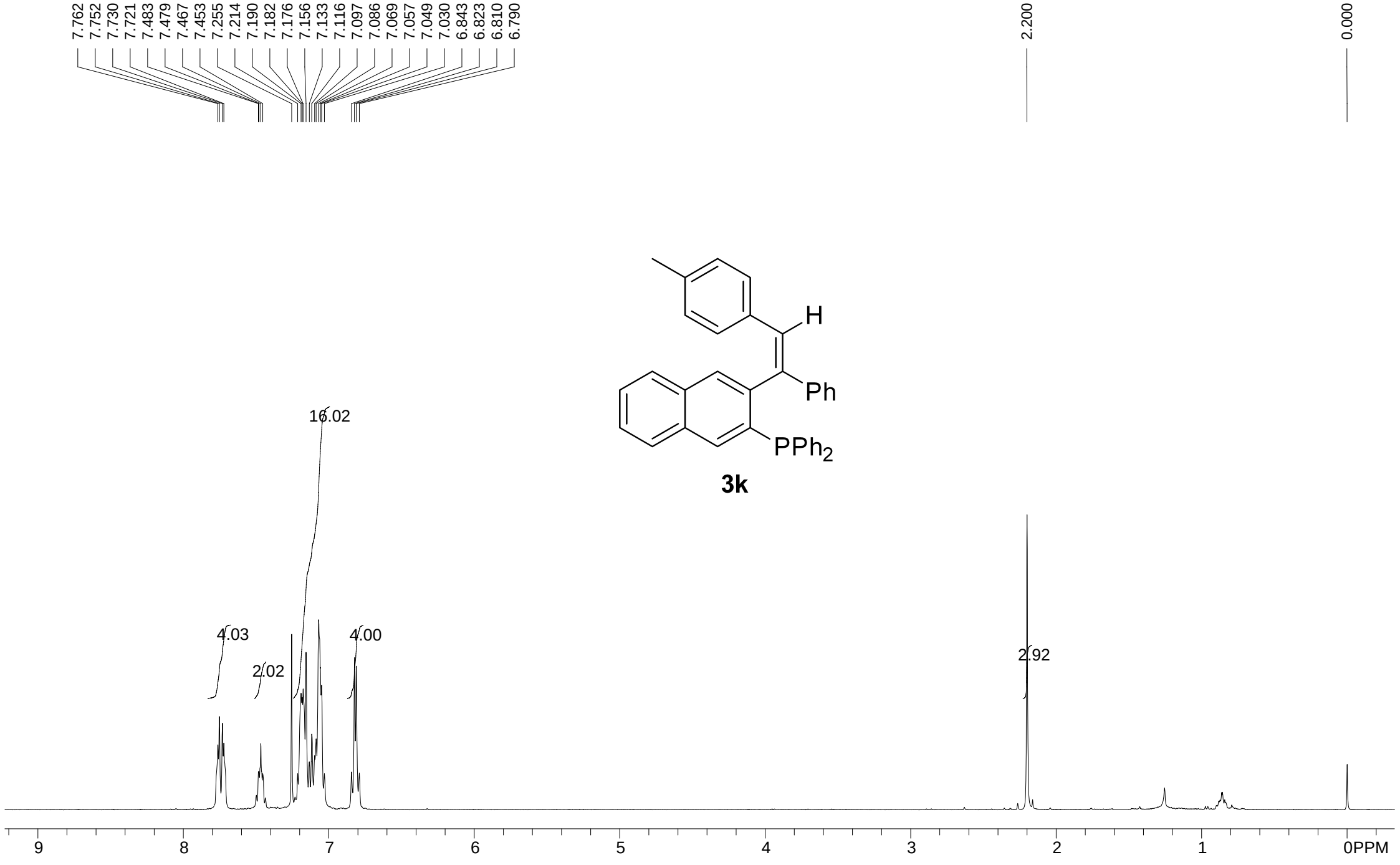
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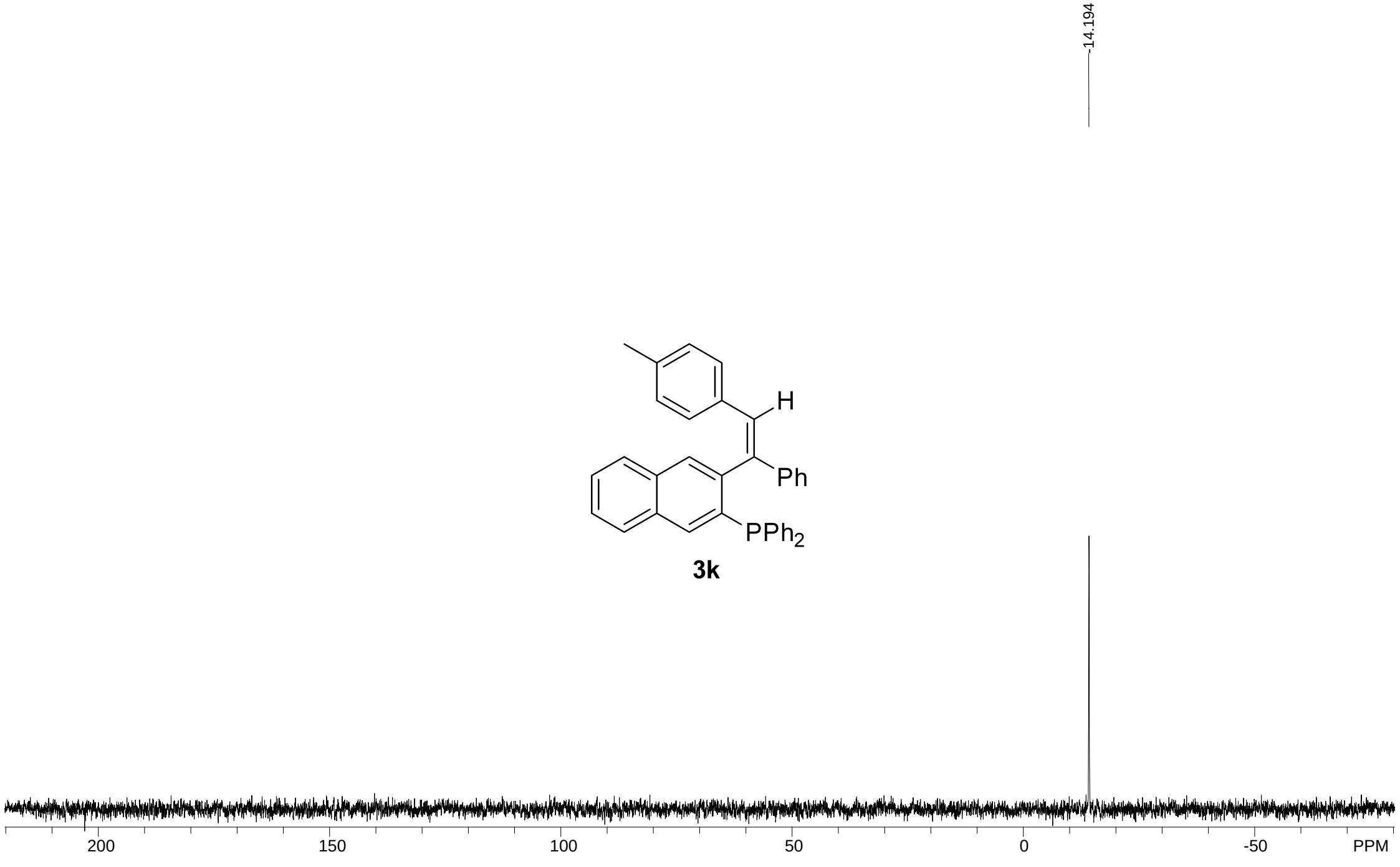

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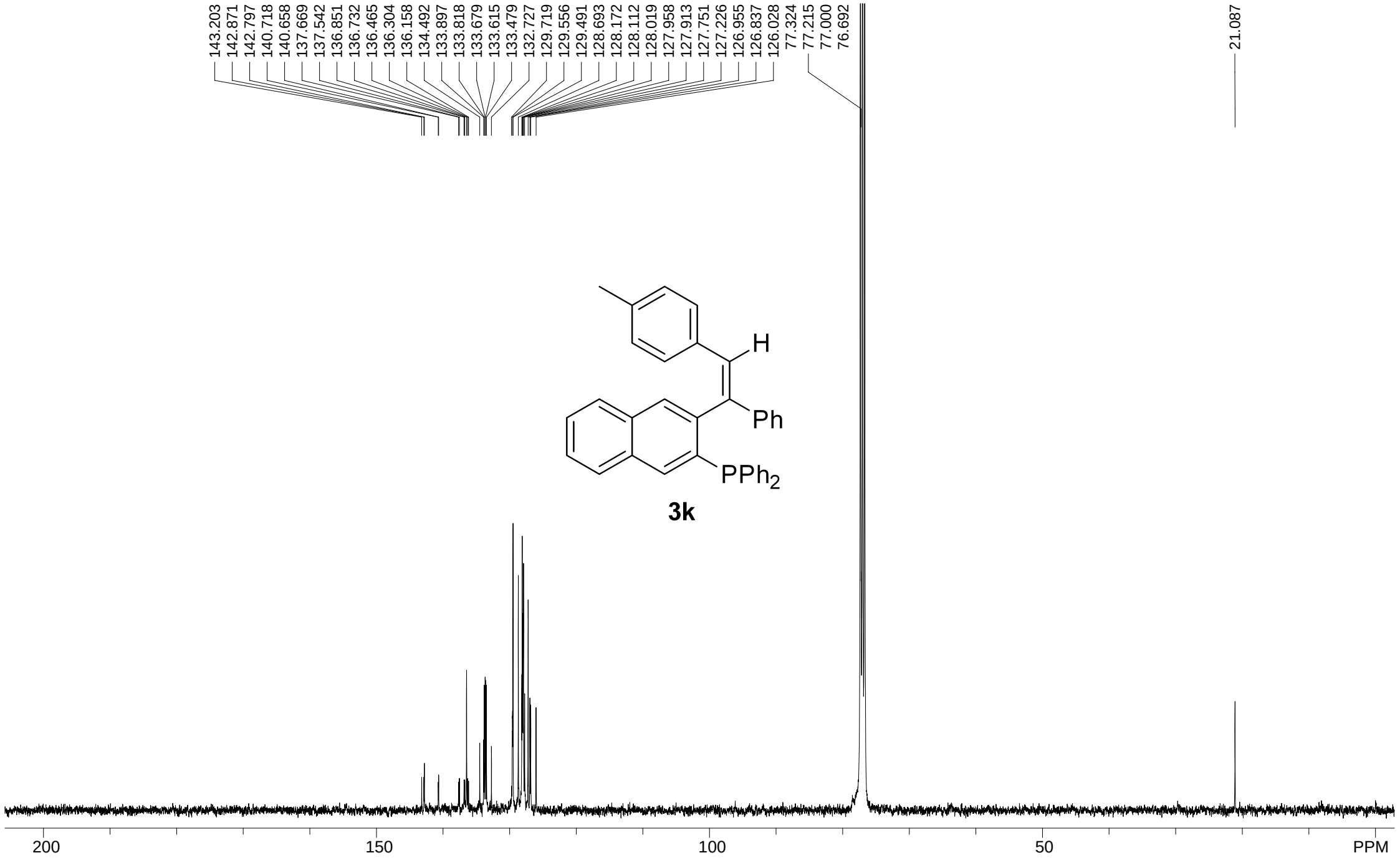
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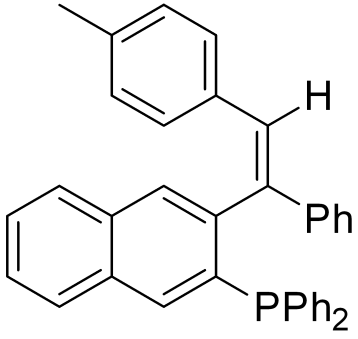

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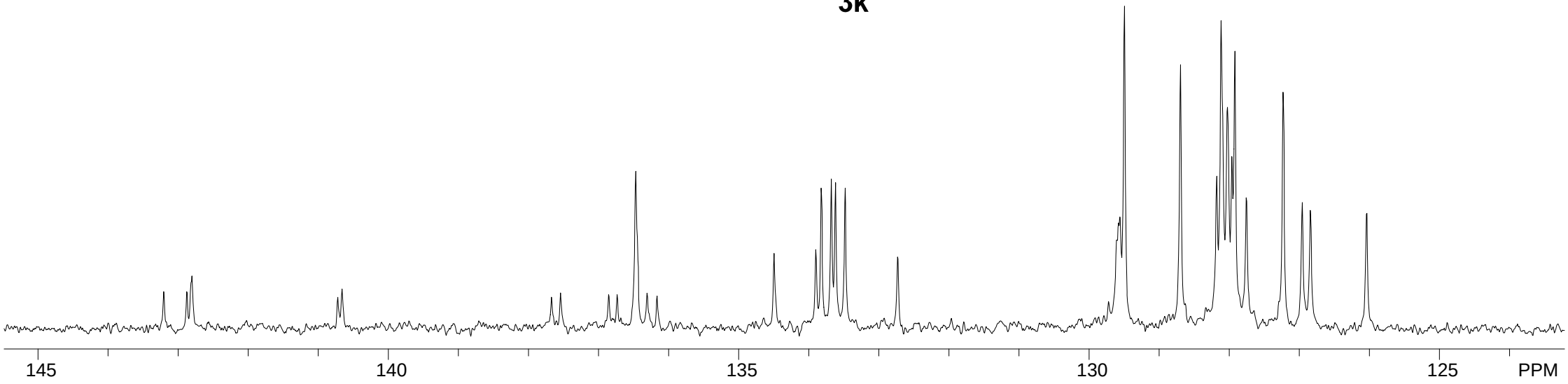

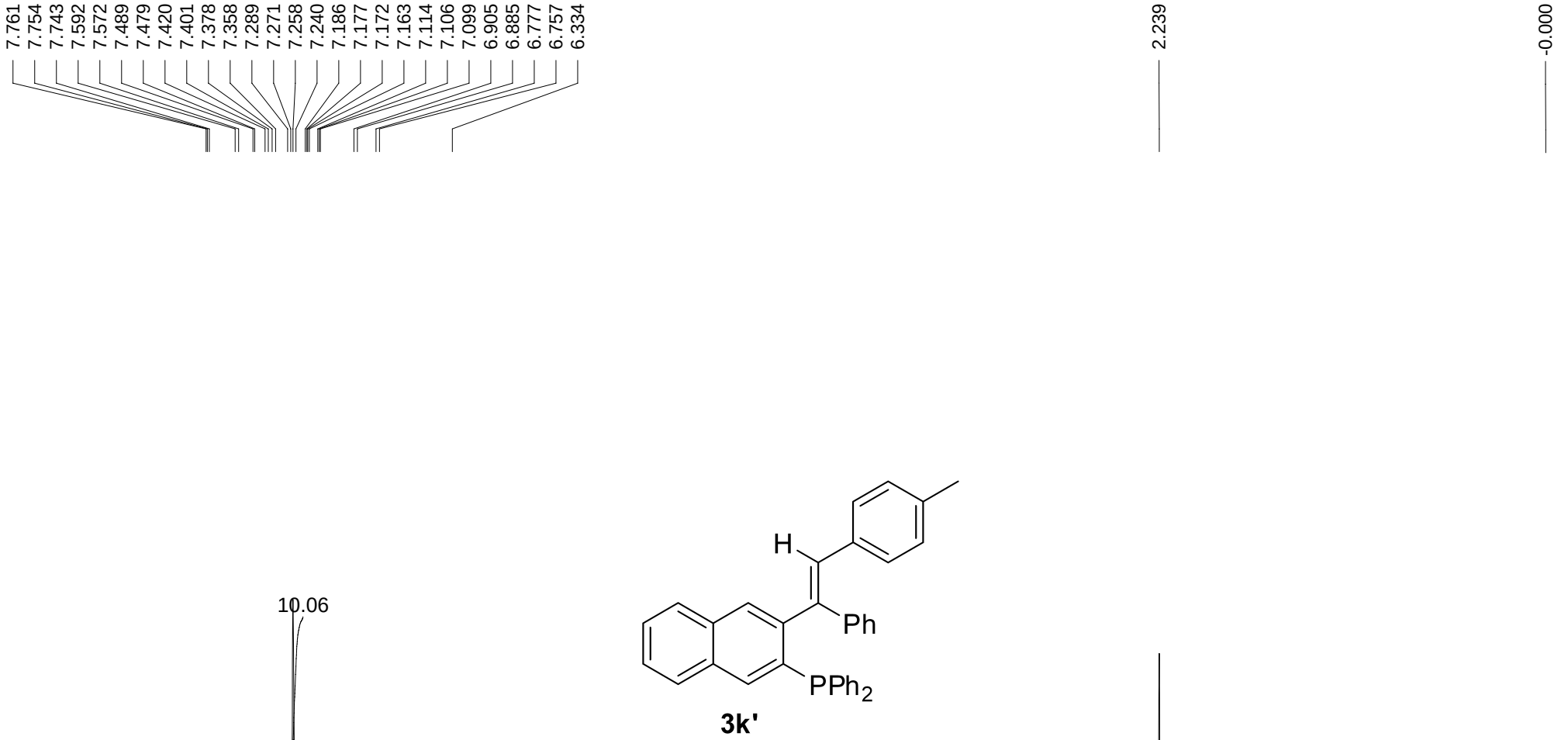
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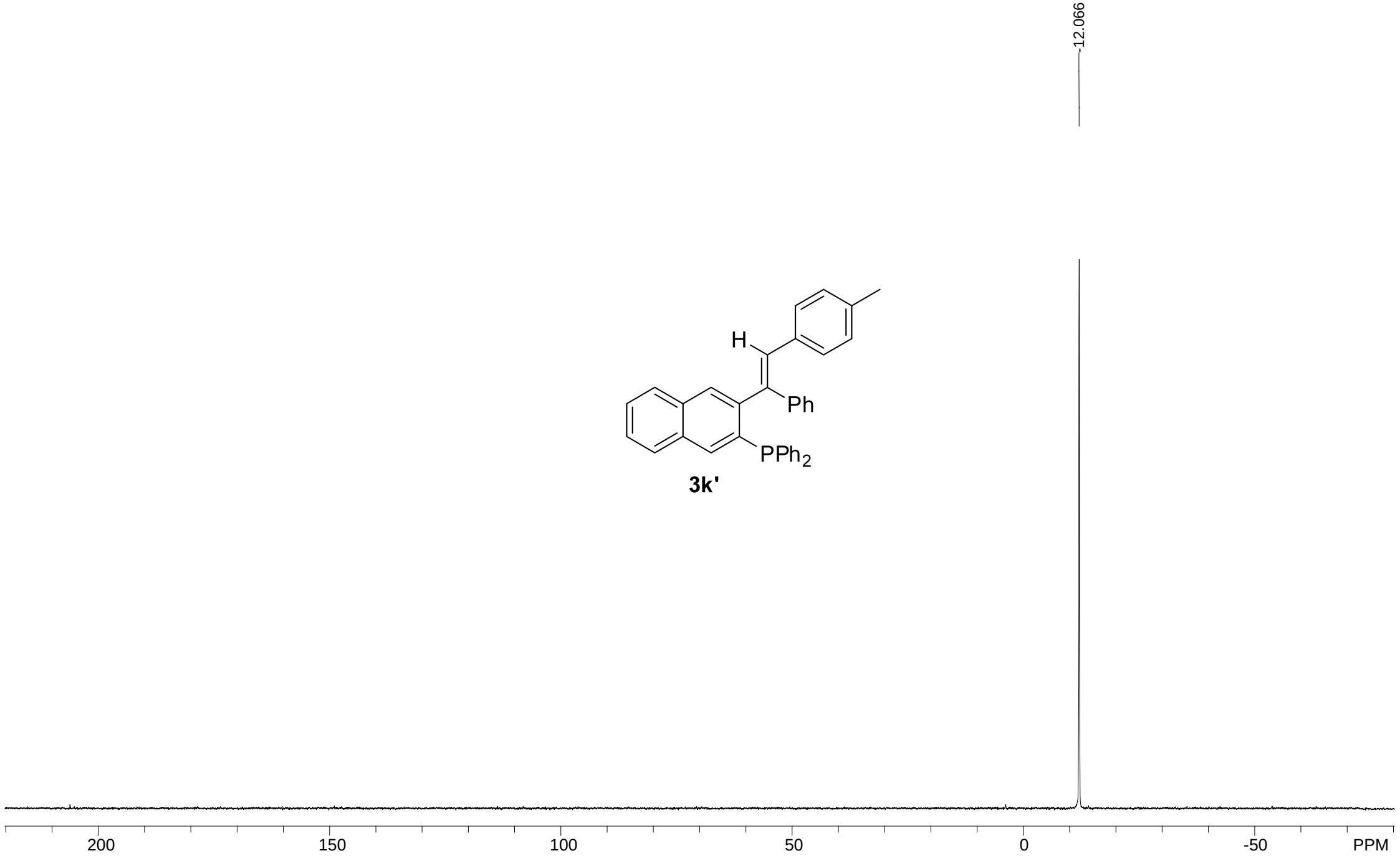

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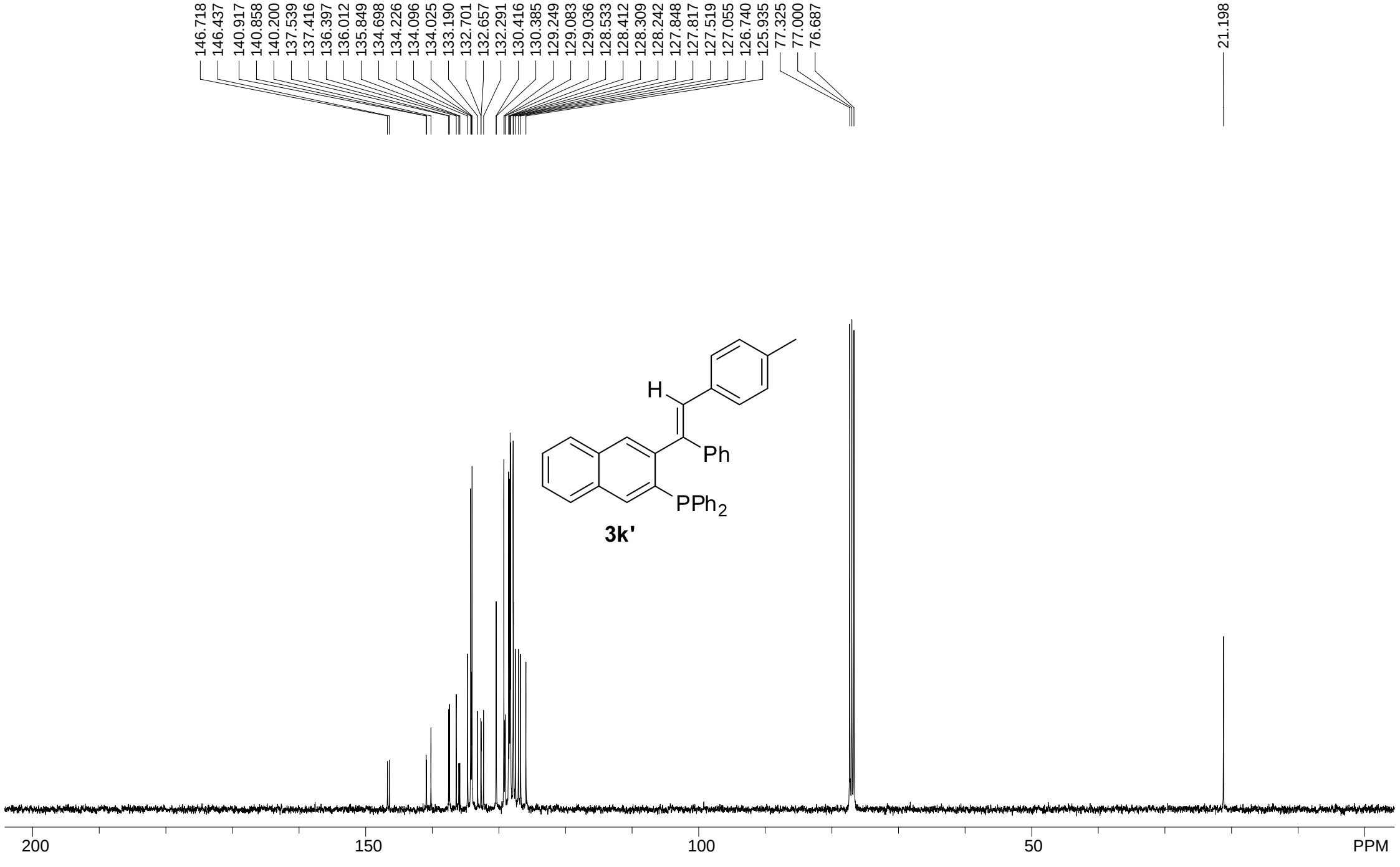

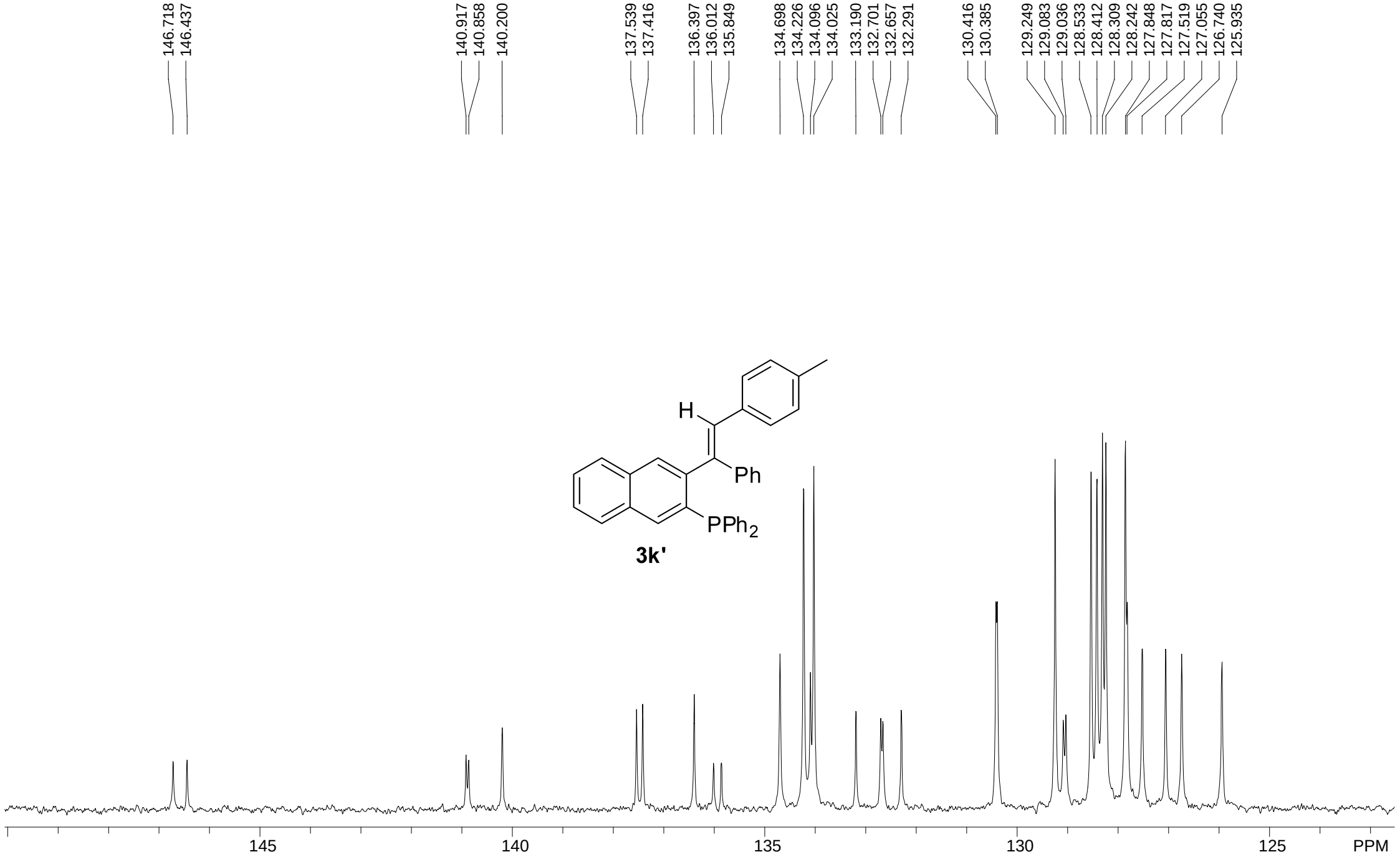

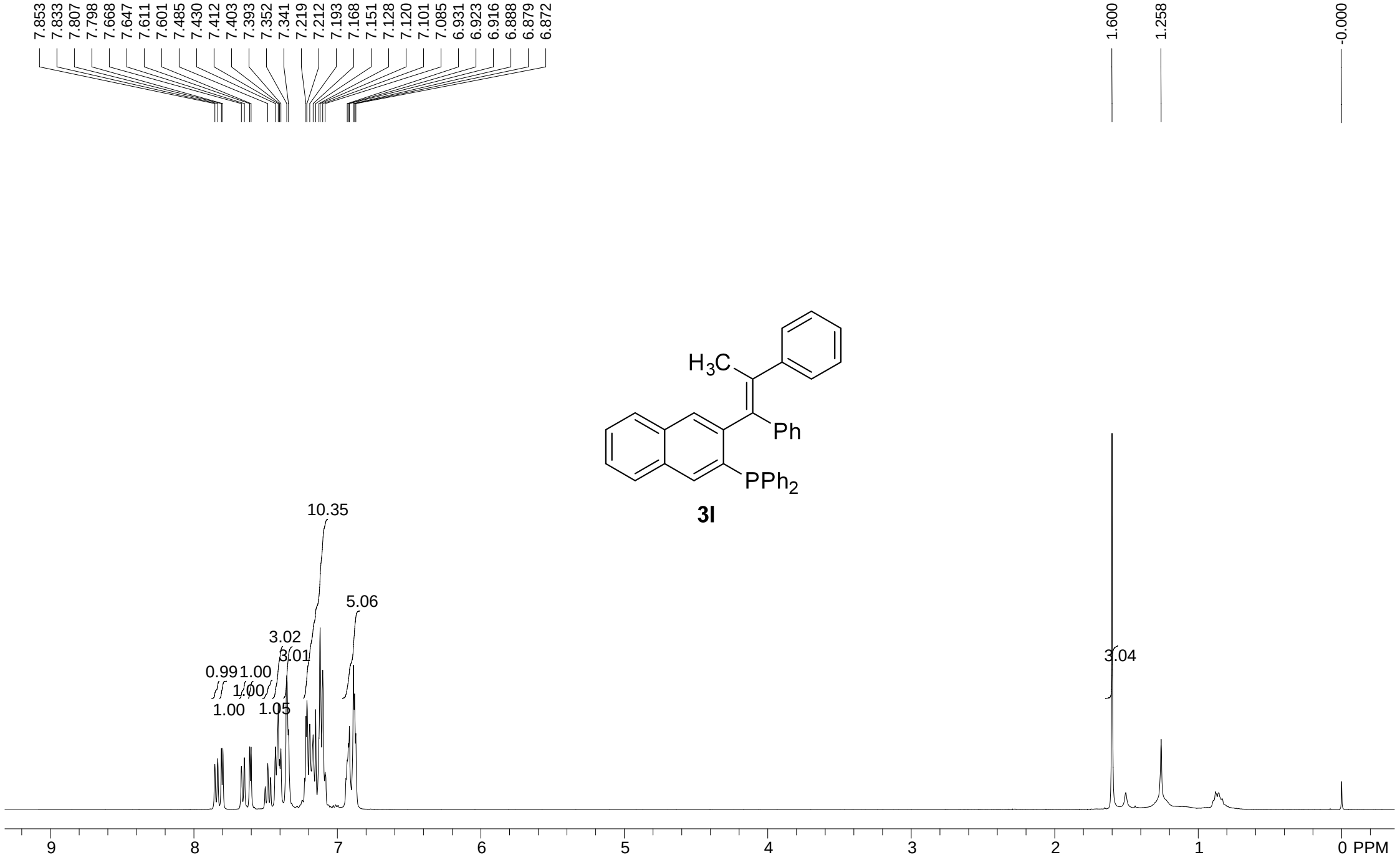
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PPh2
3l
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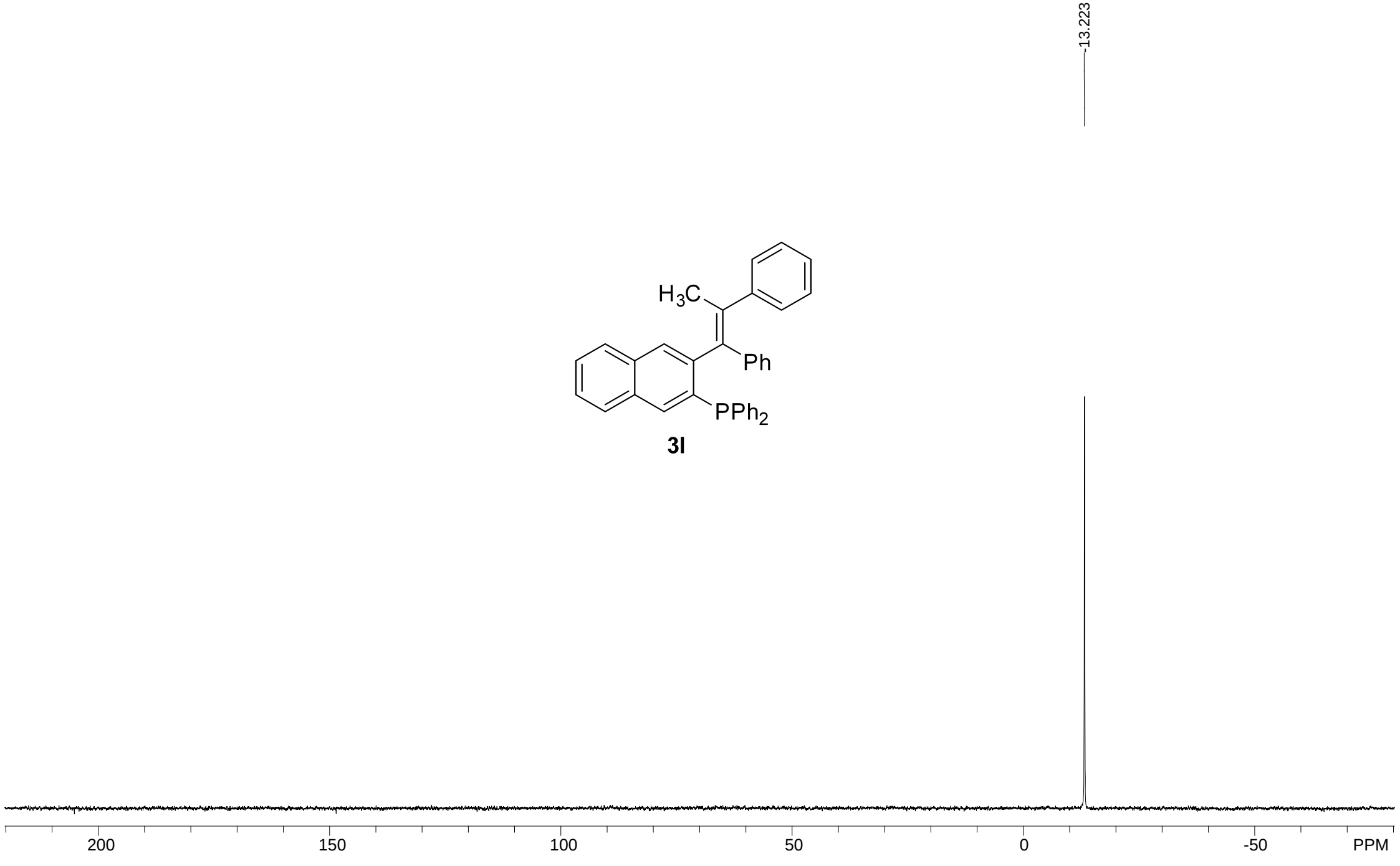

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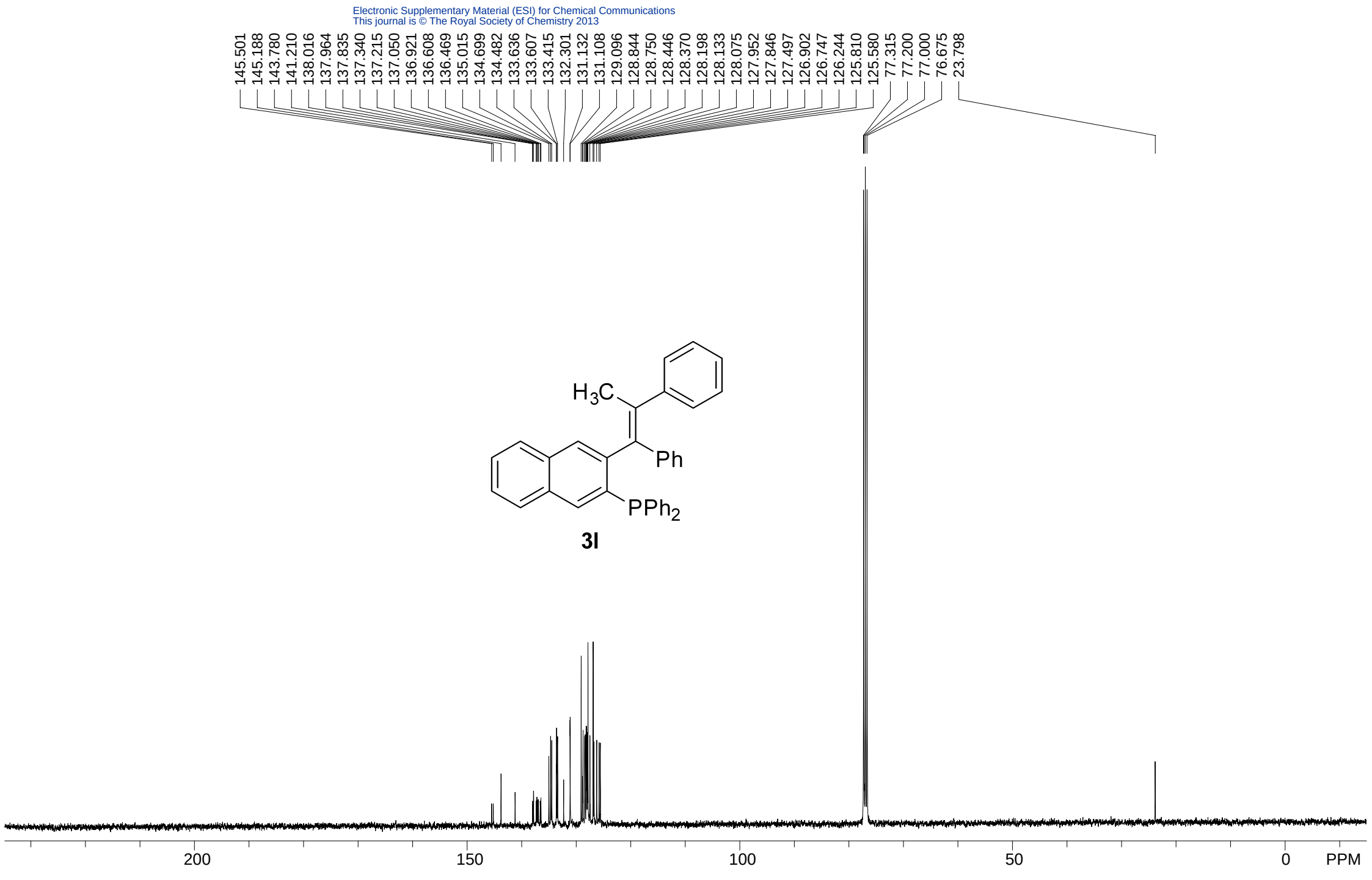
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Ph
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3l

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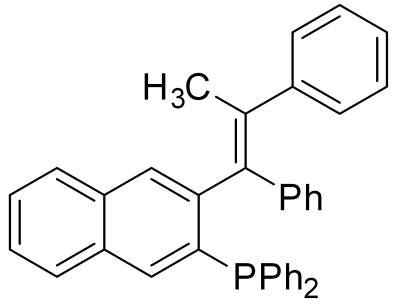

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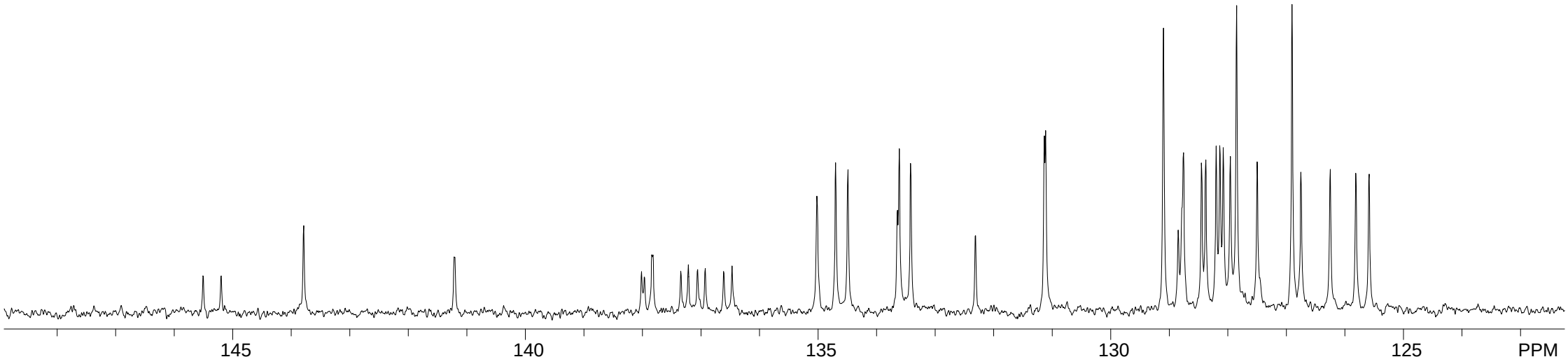

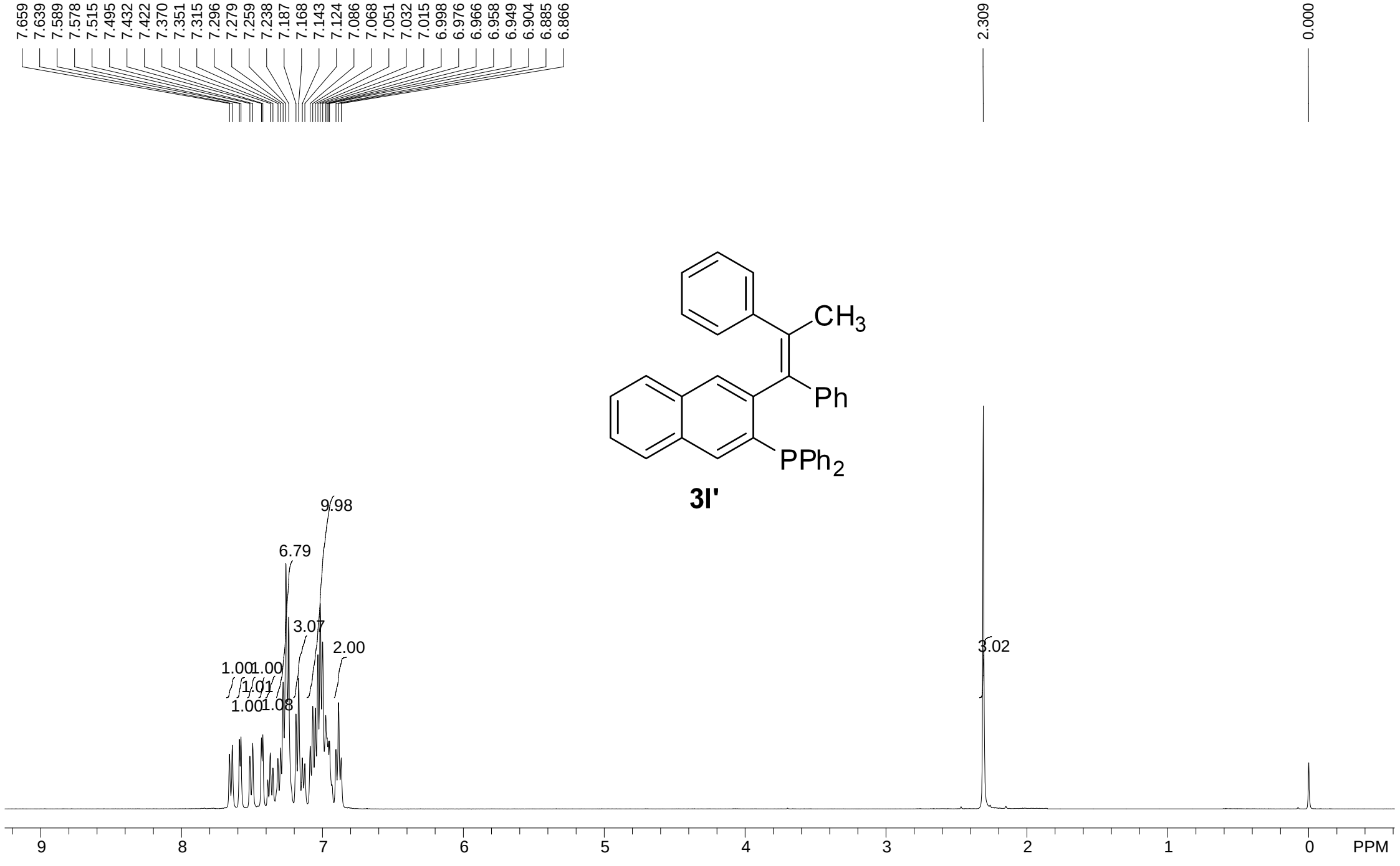
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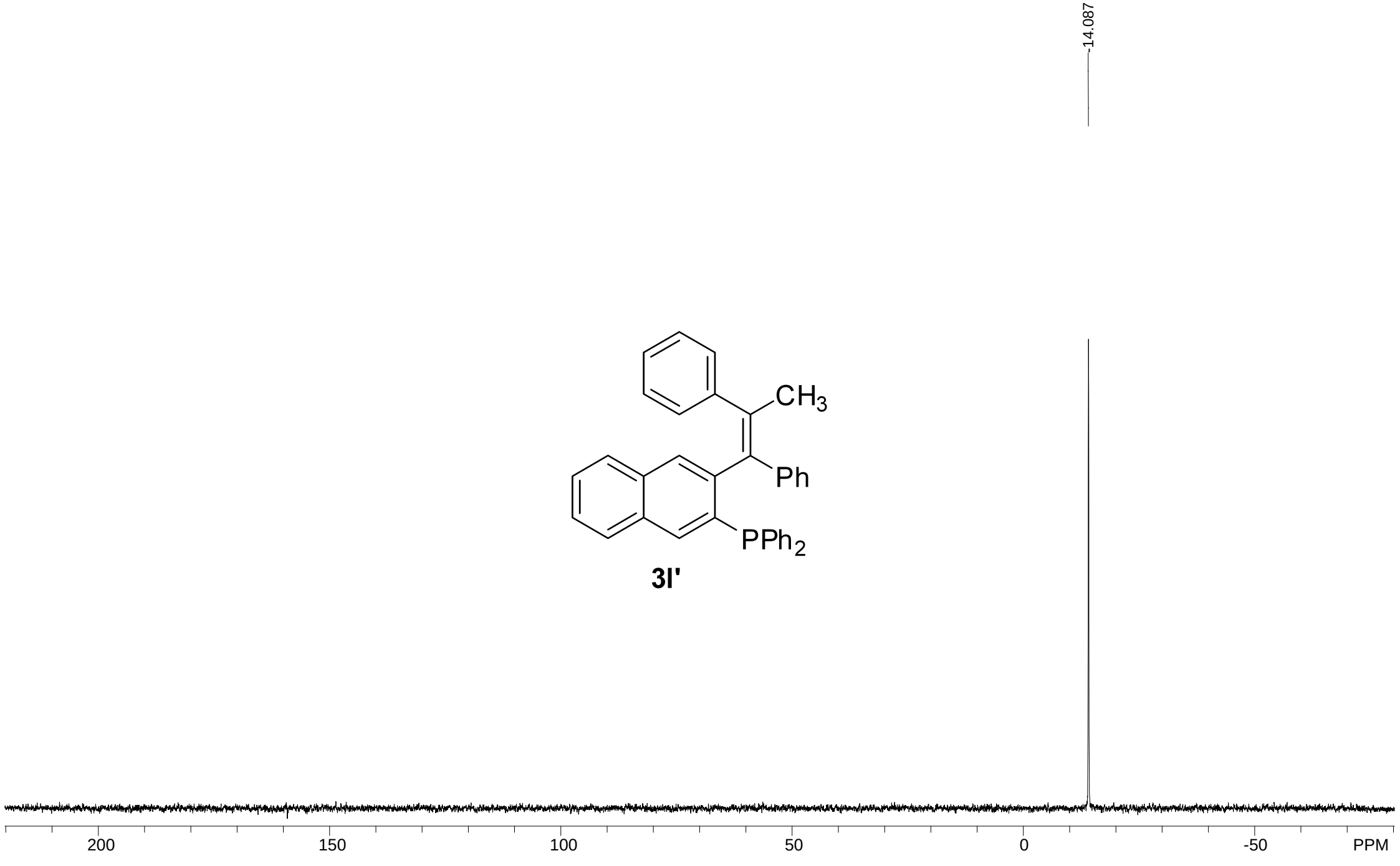

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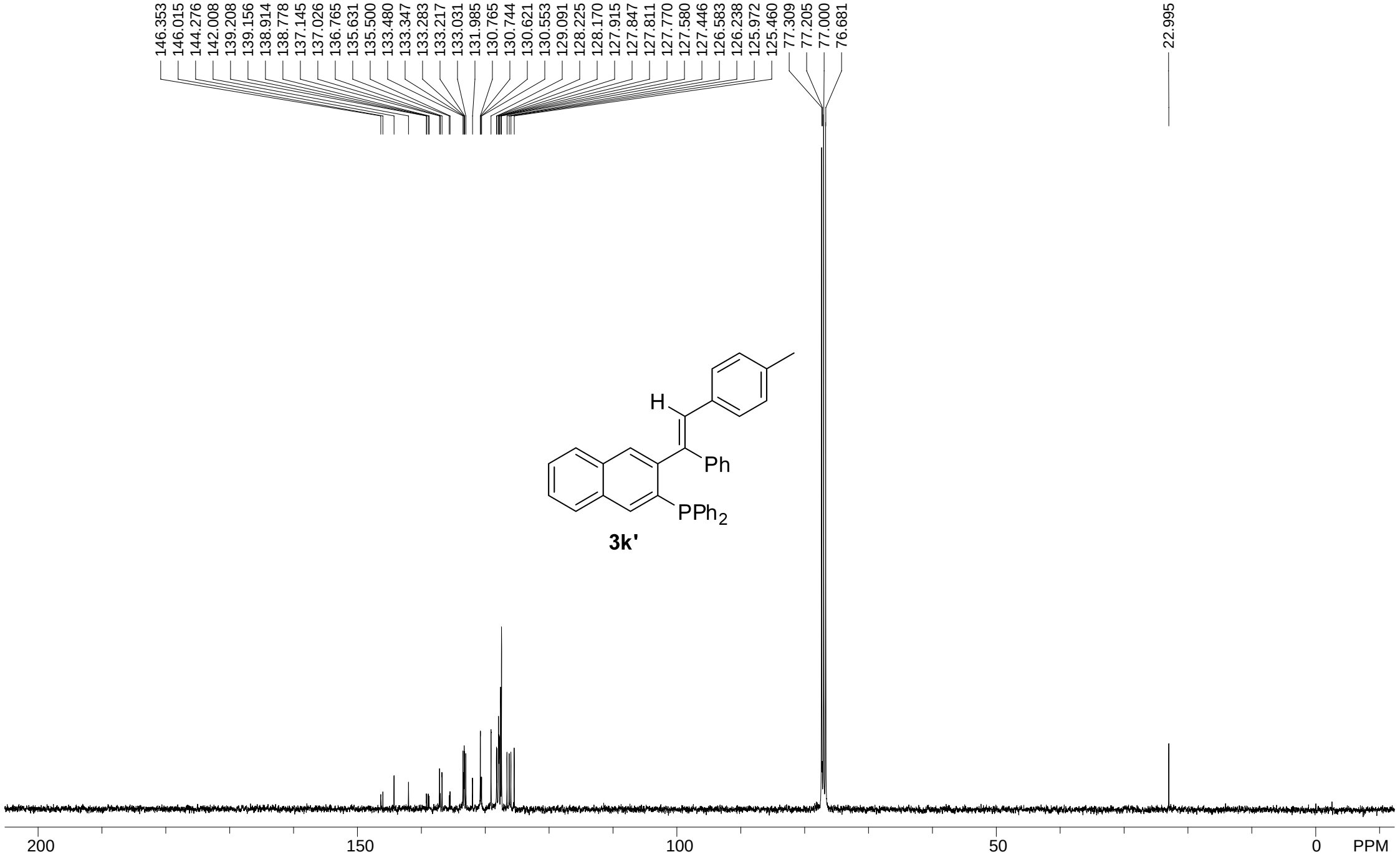

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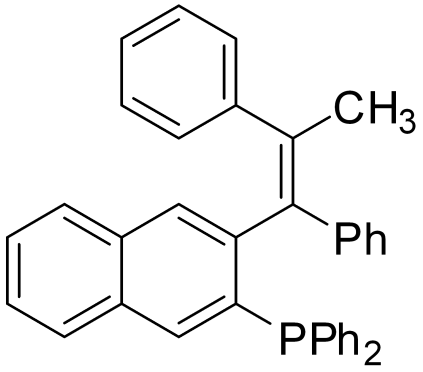

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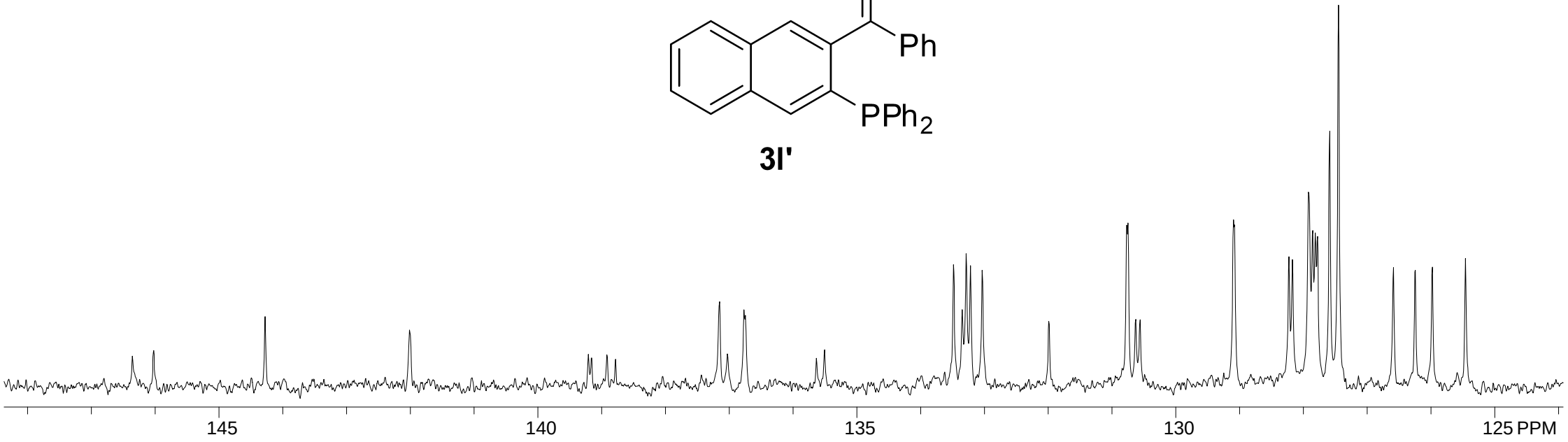

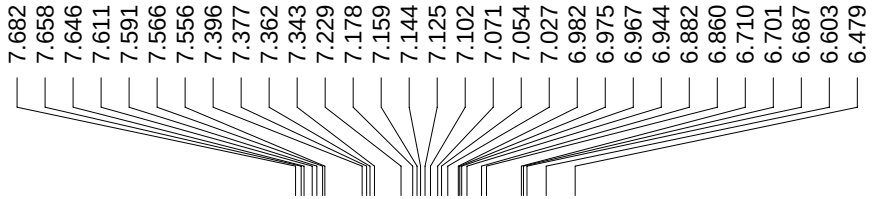
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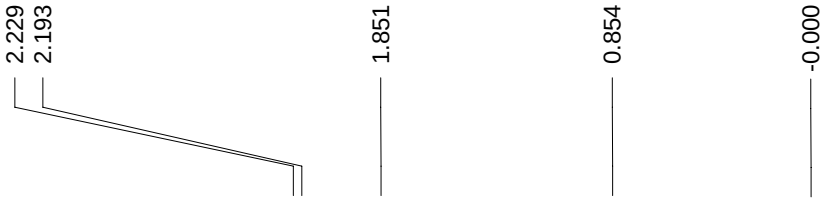
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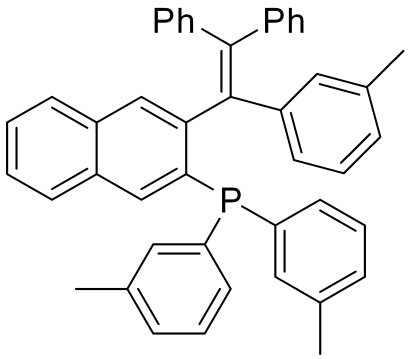
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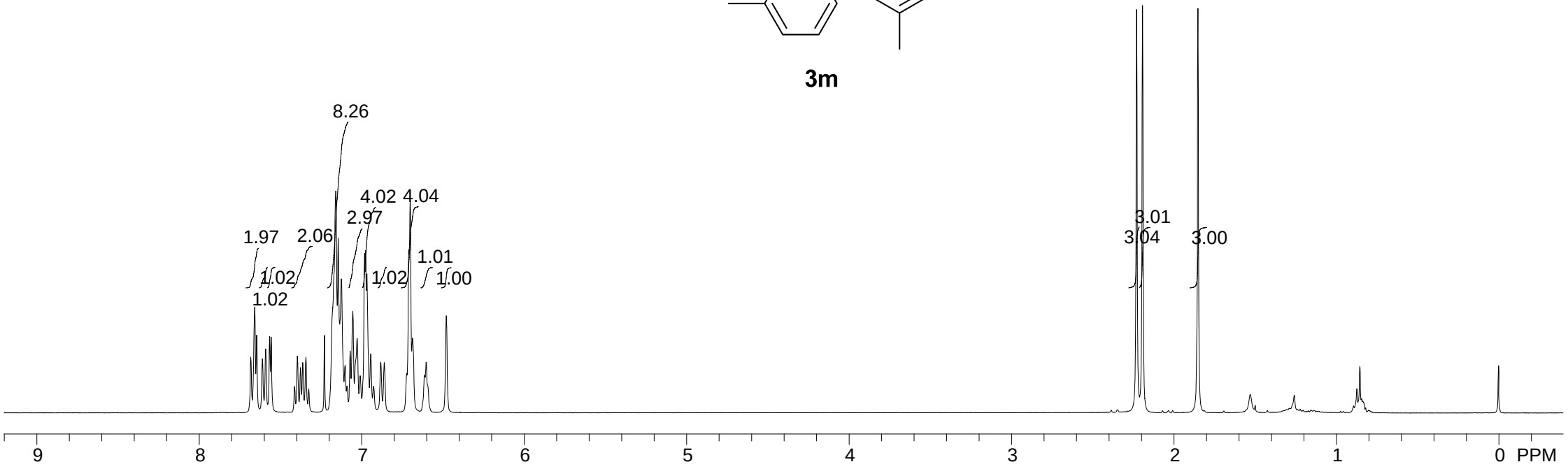
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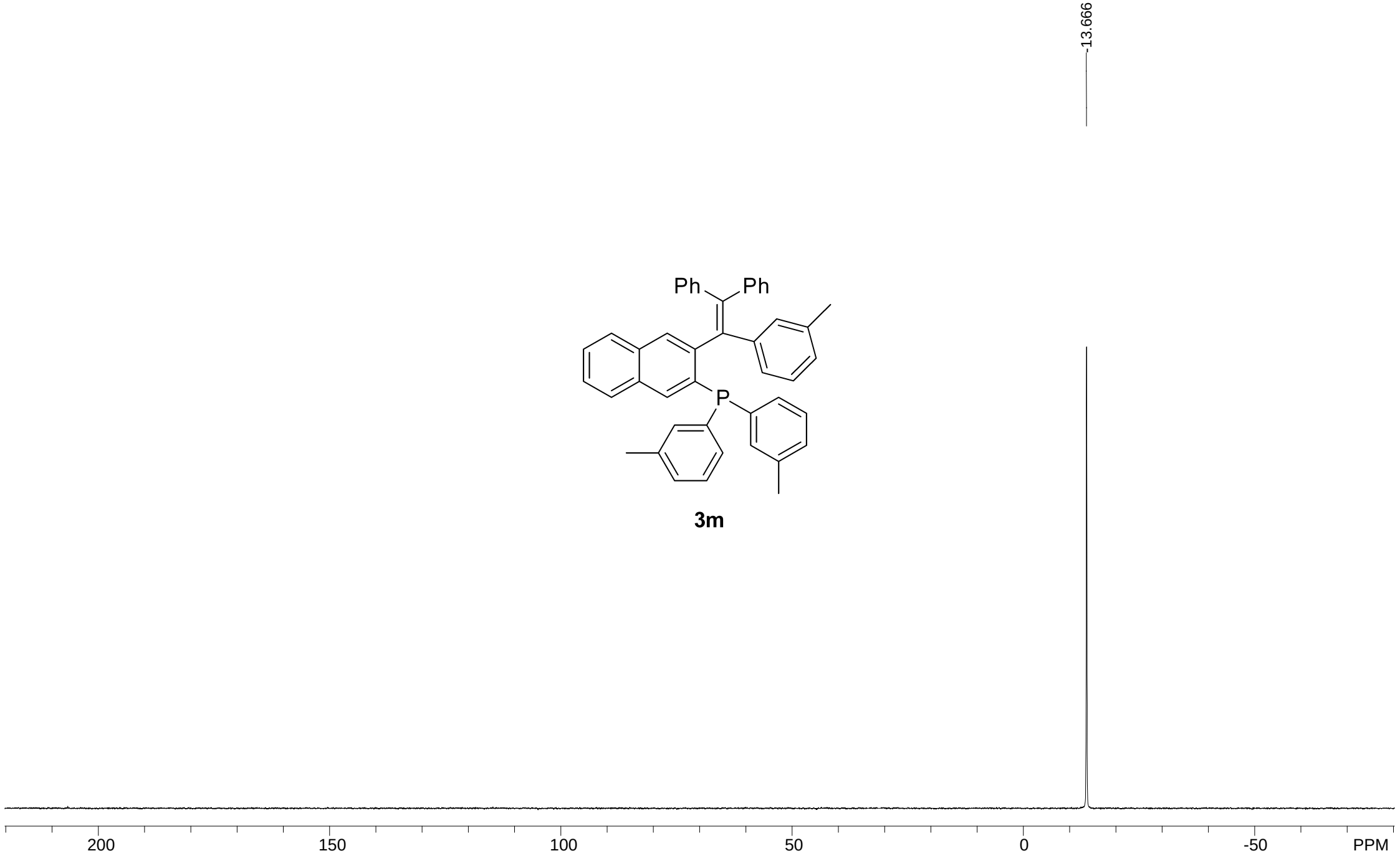

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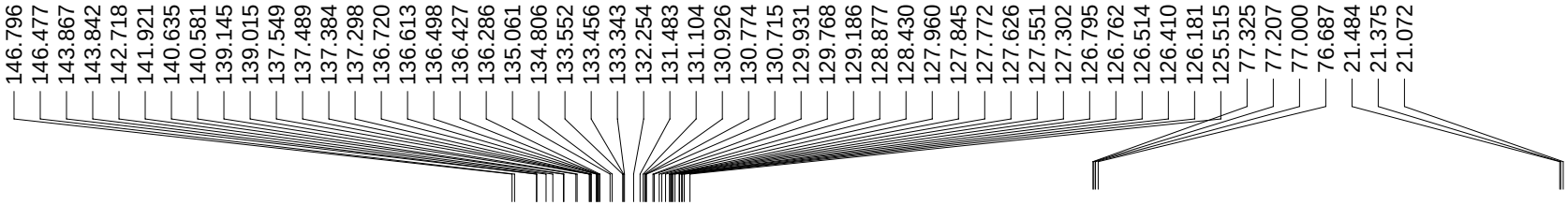
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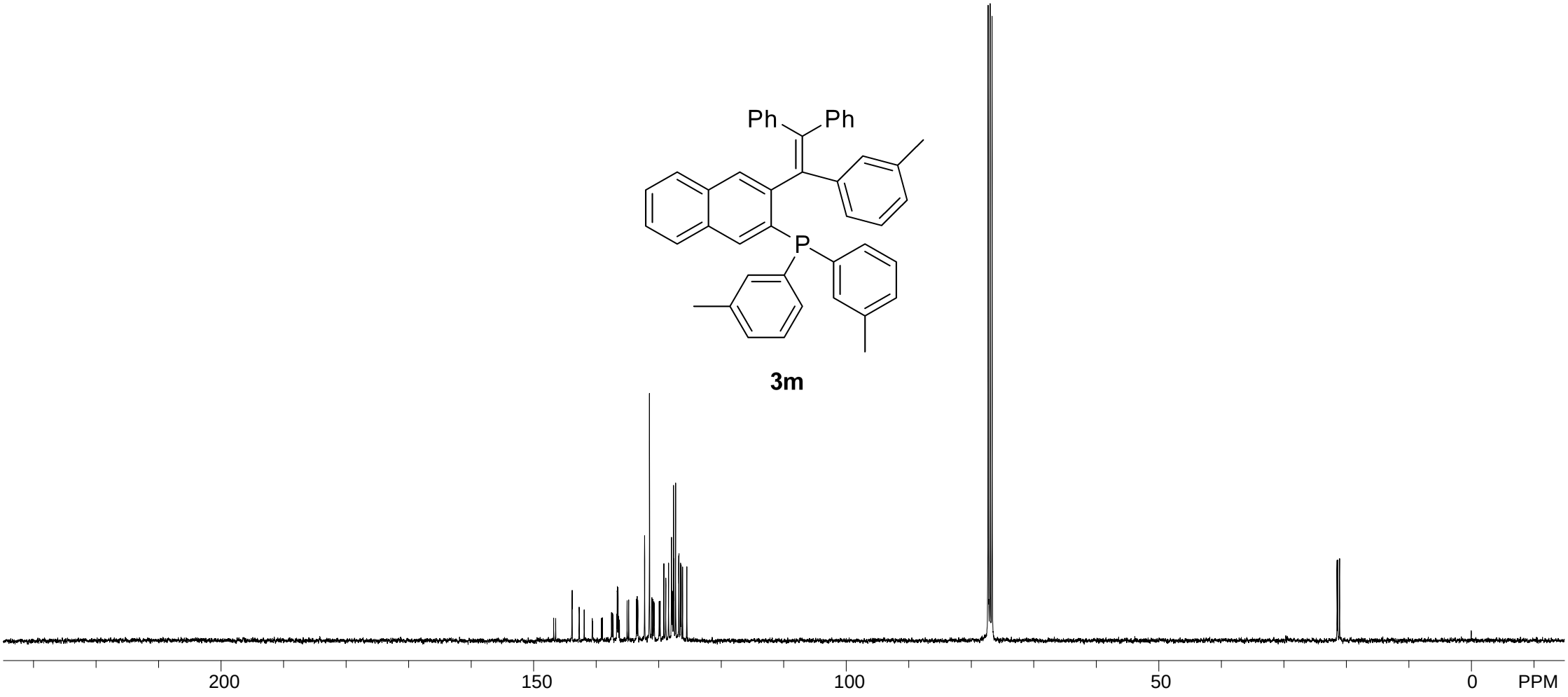
3m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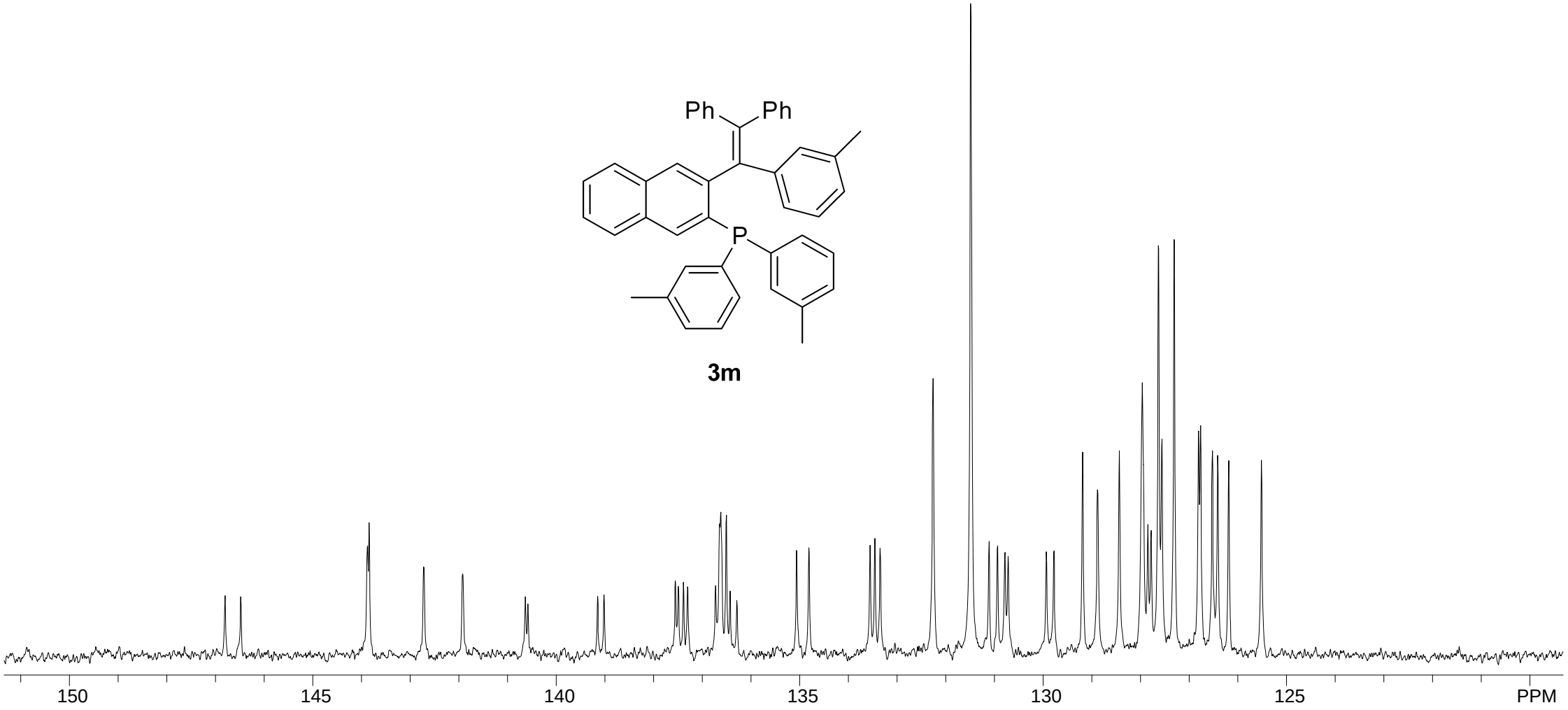

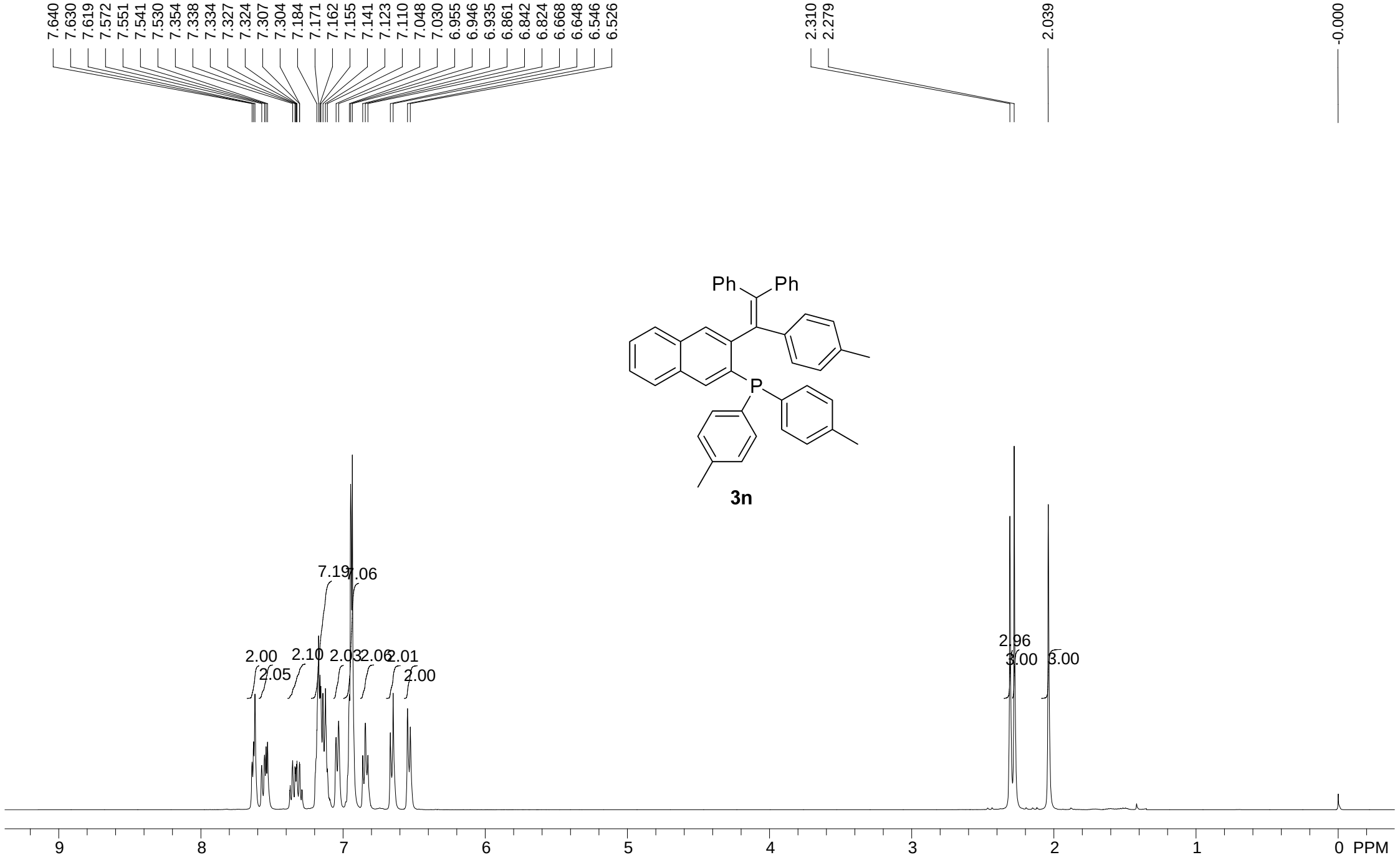
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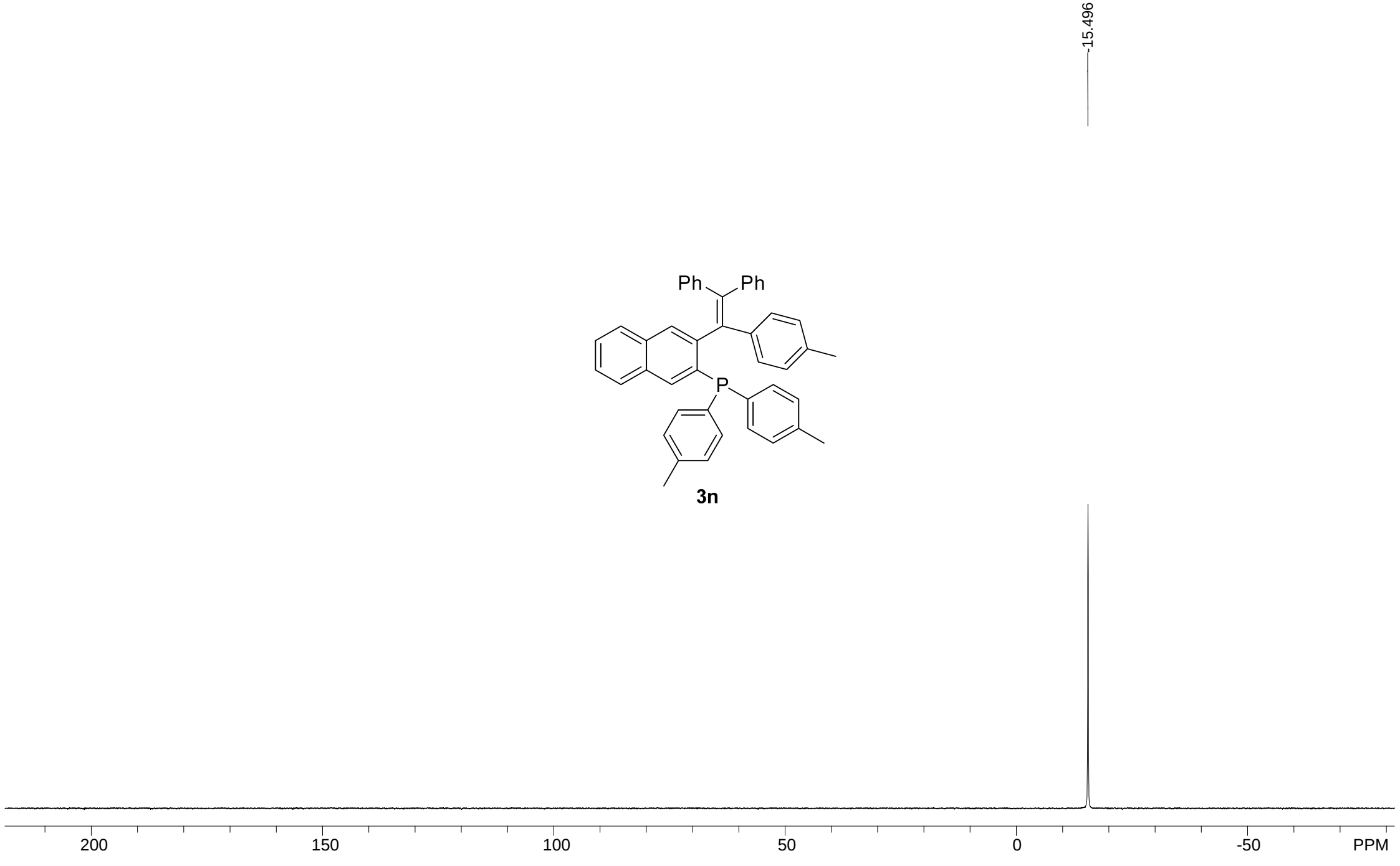

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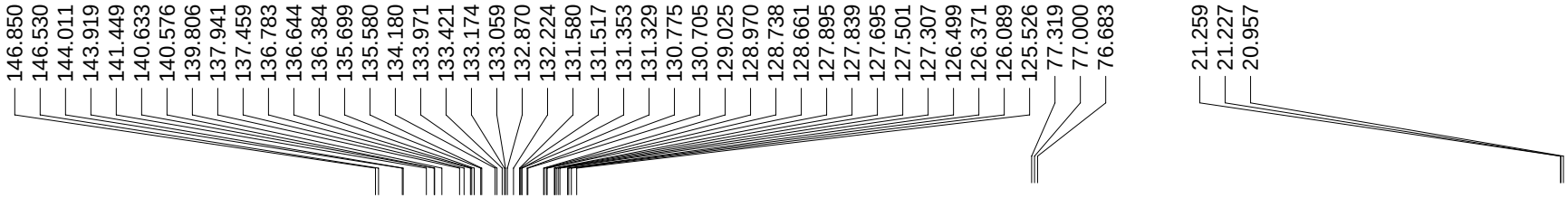
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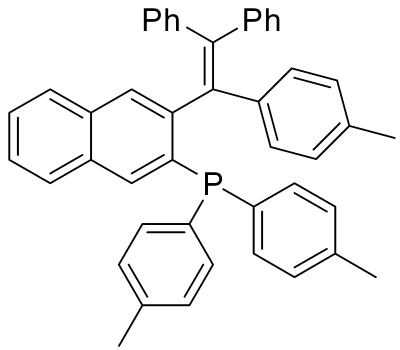
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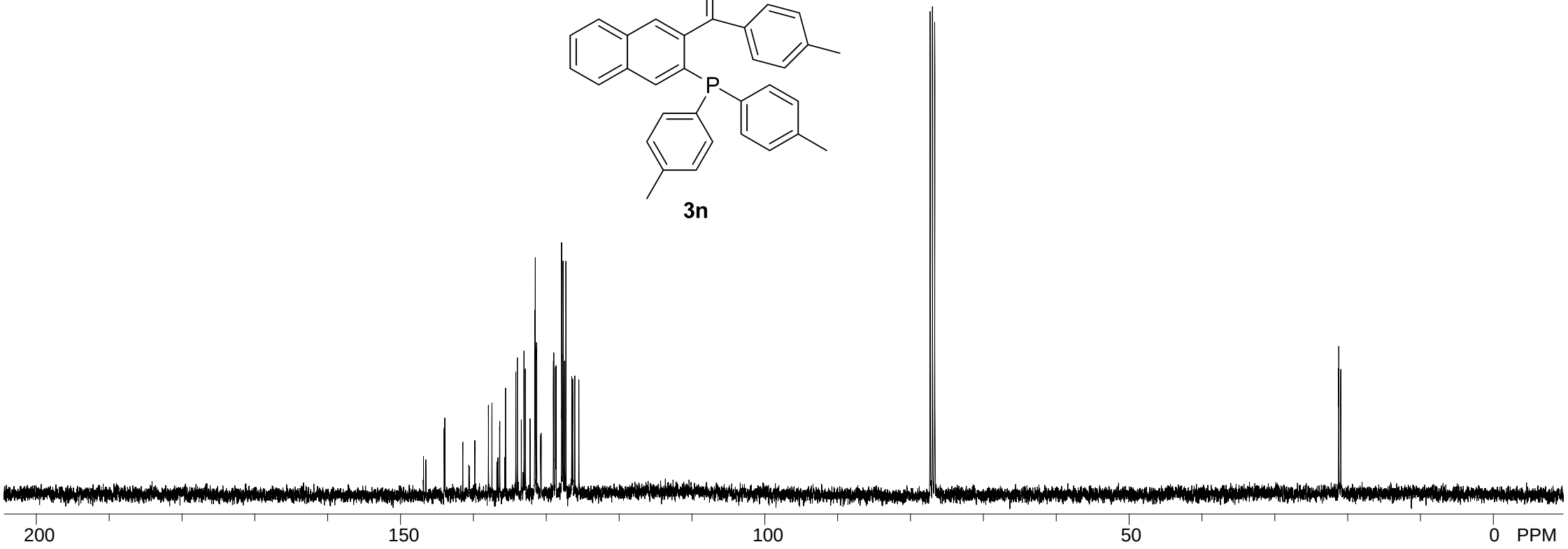
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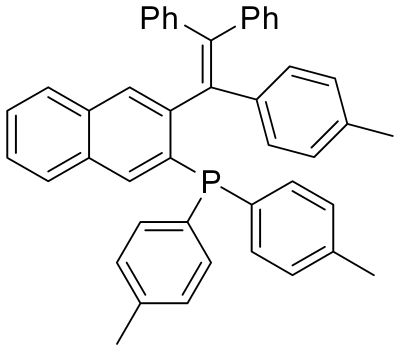

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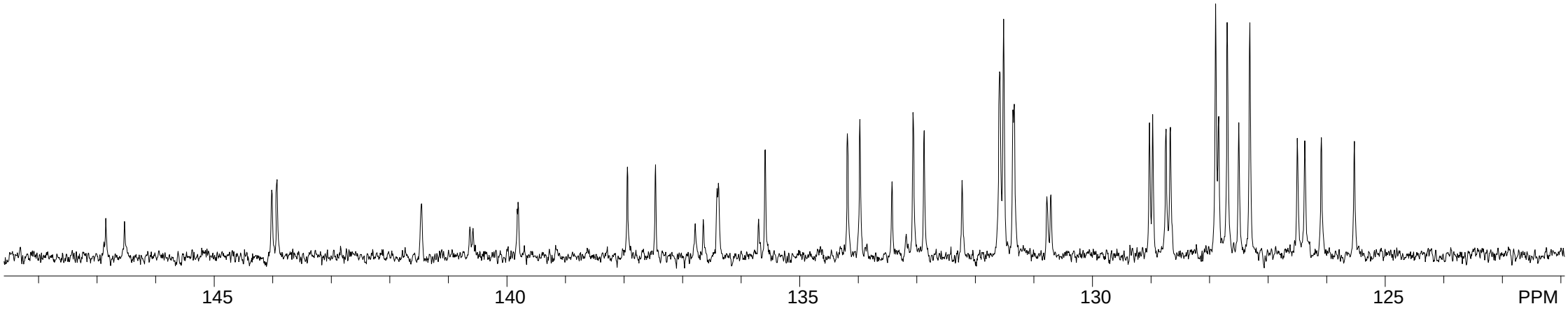

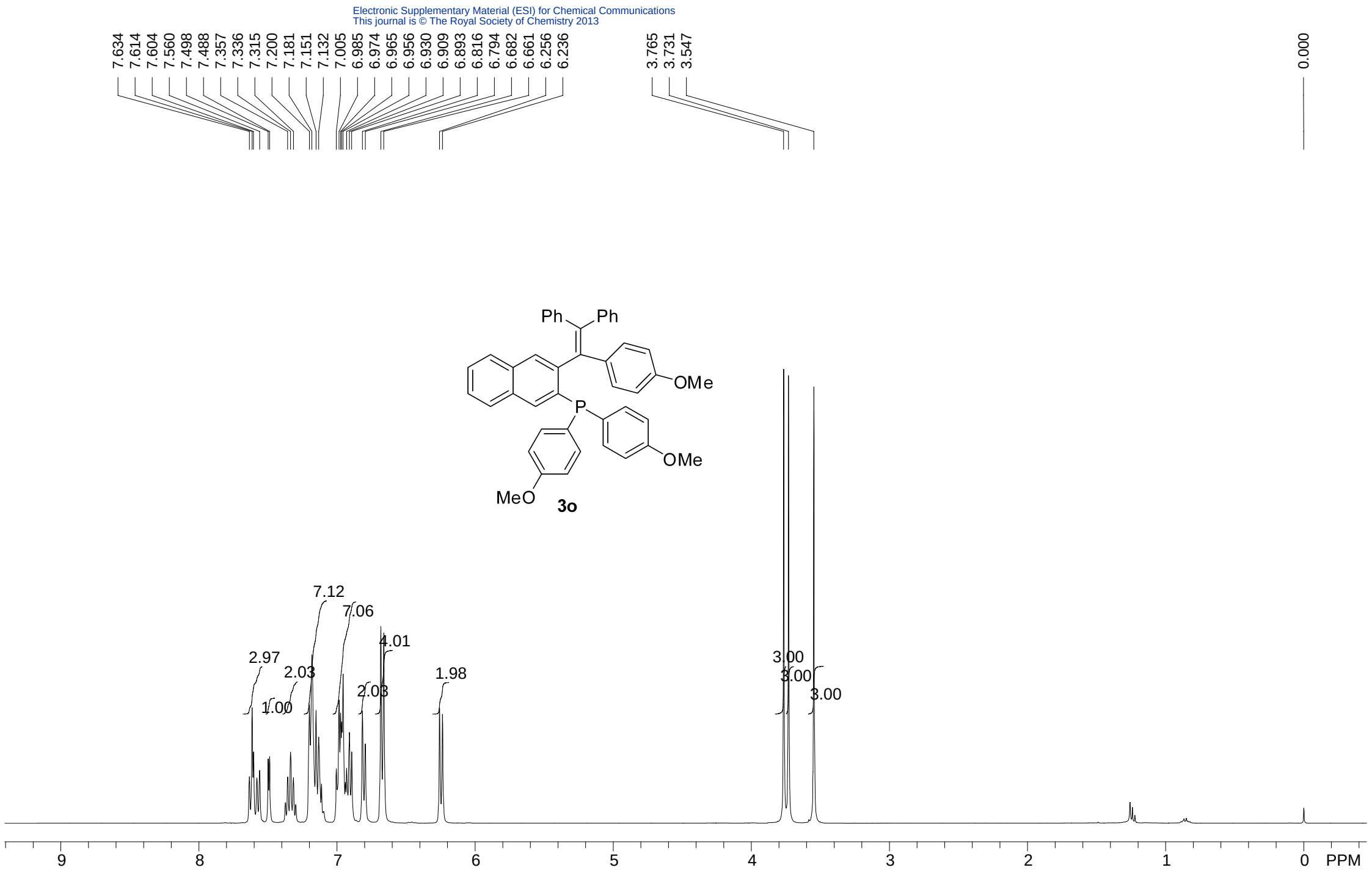
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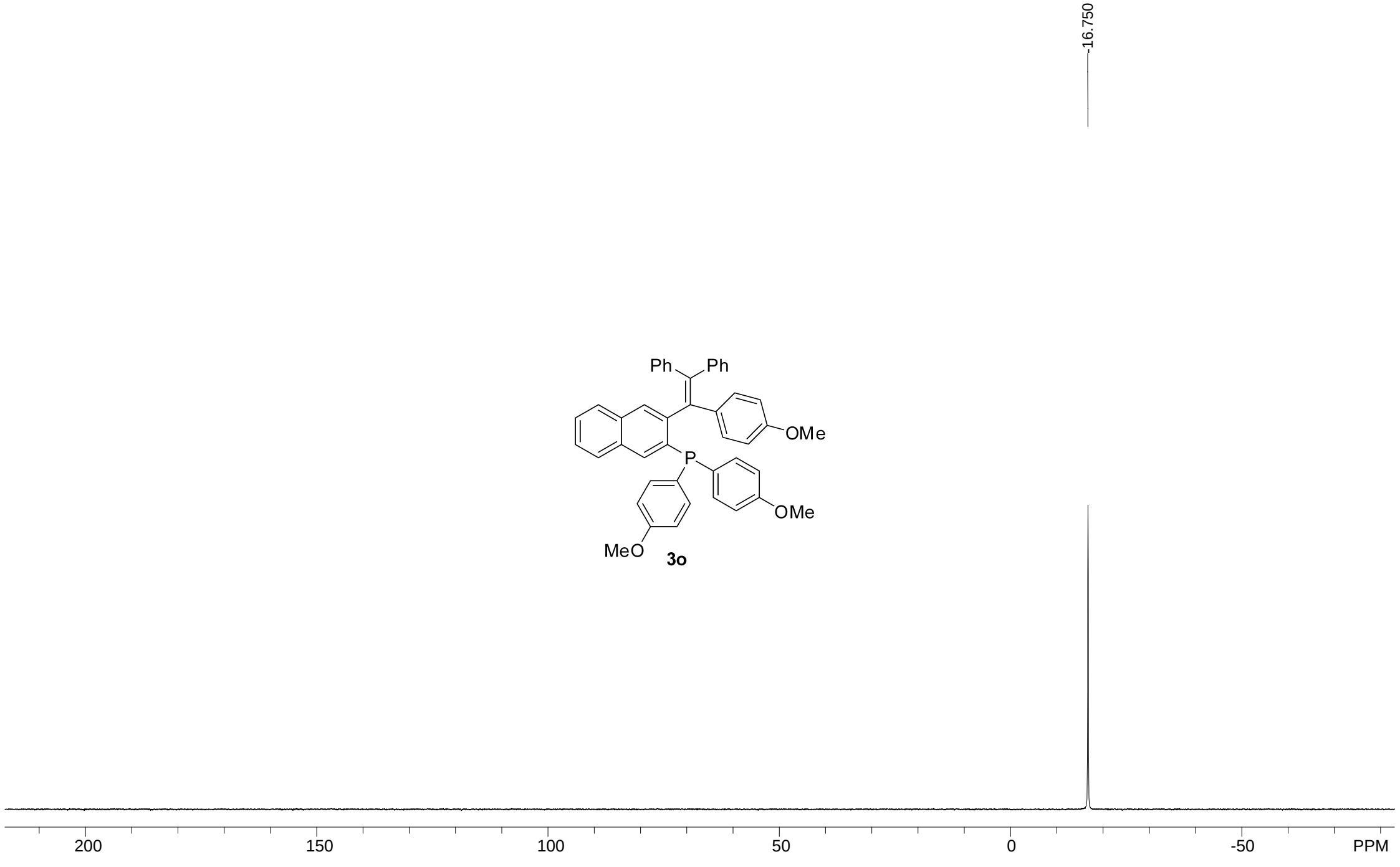

3o

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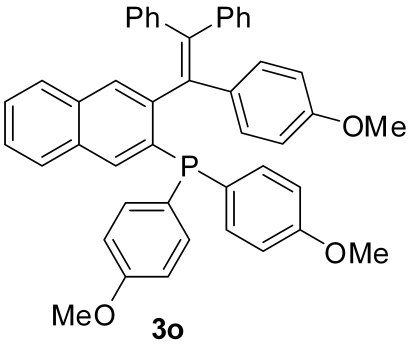

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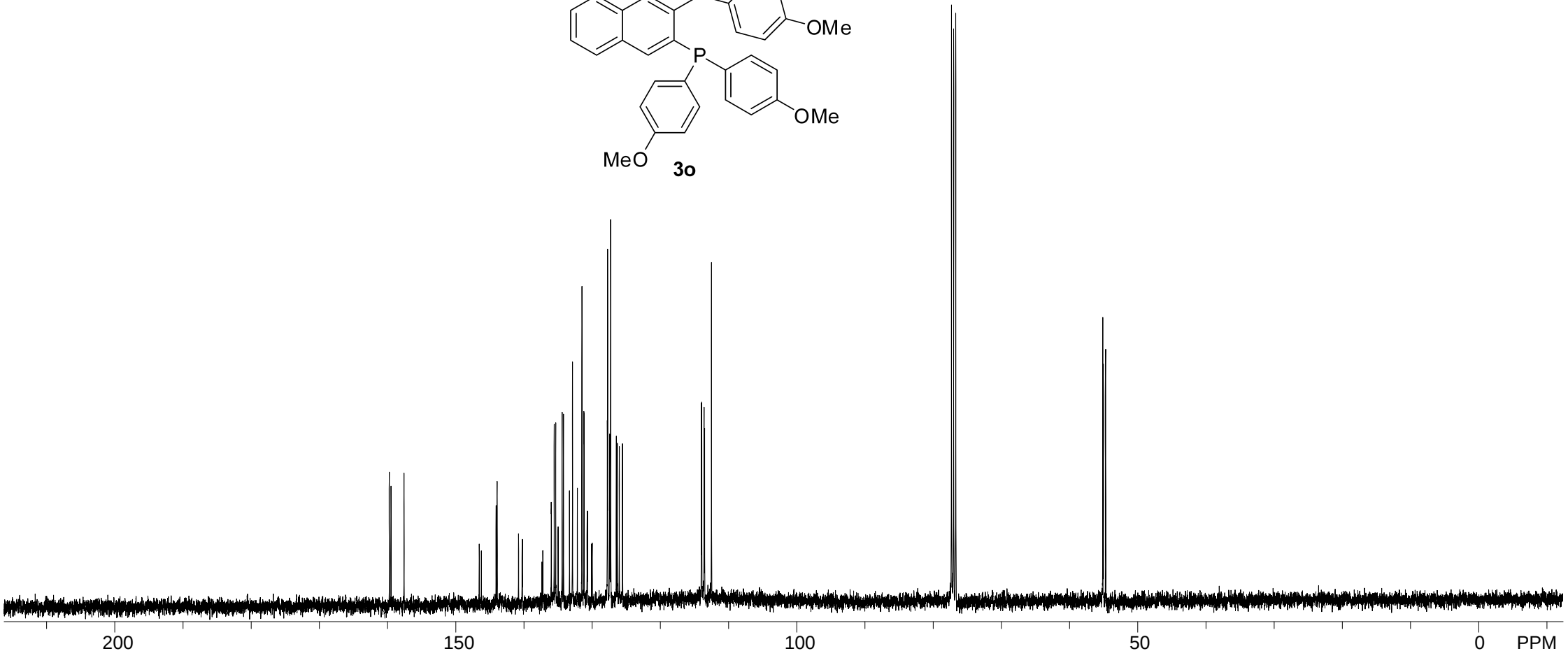

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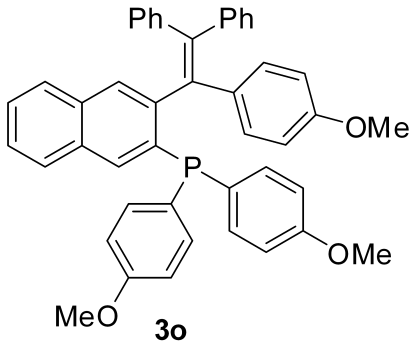

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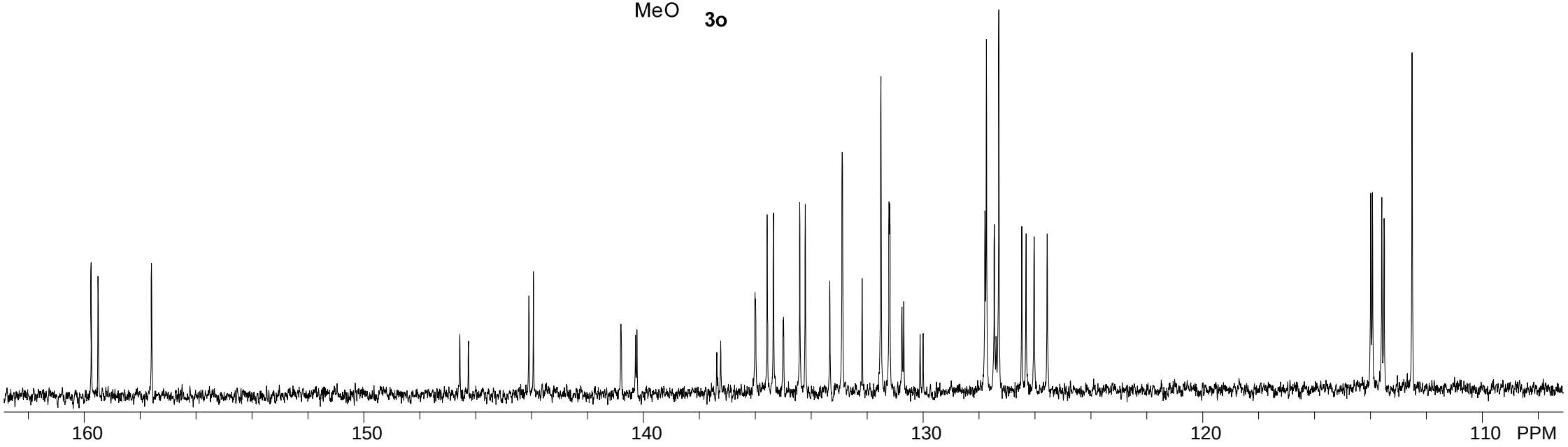

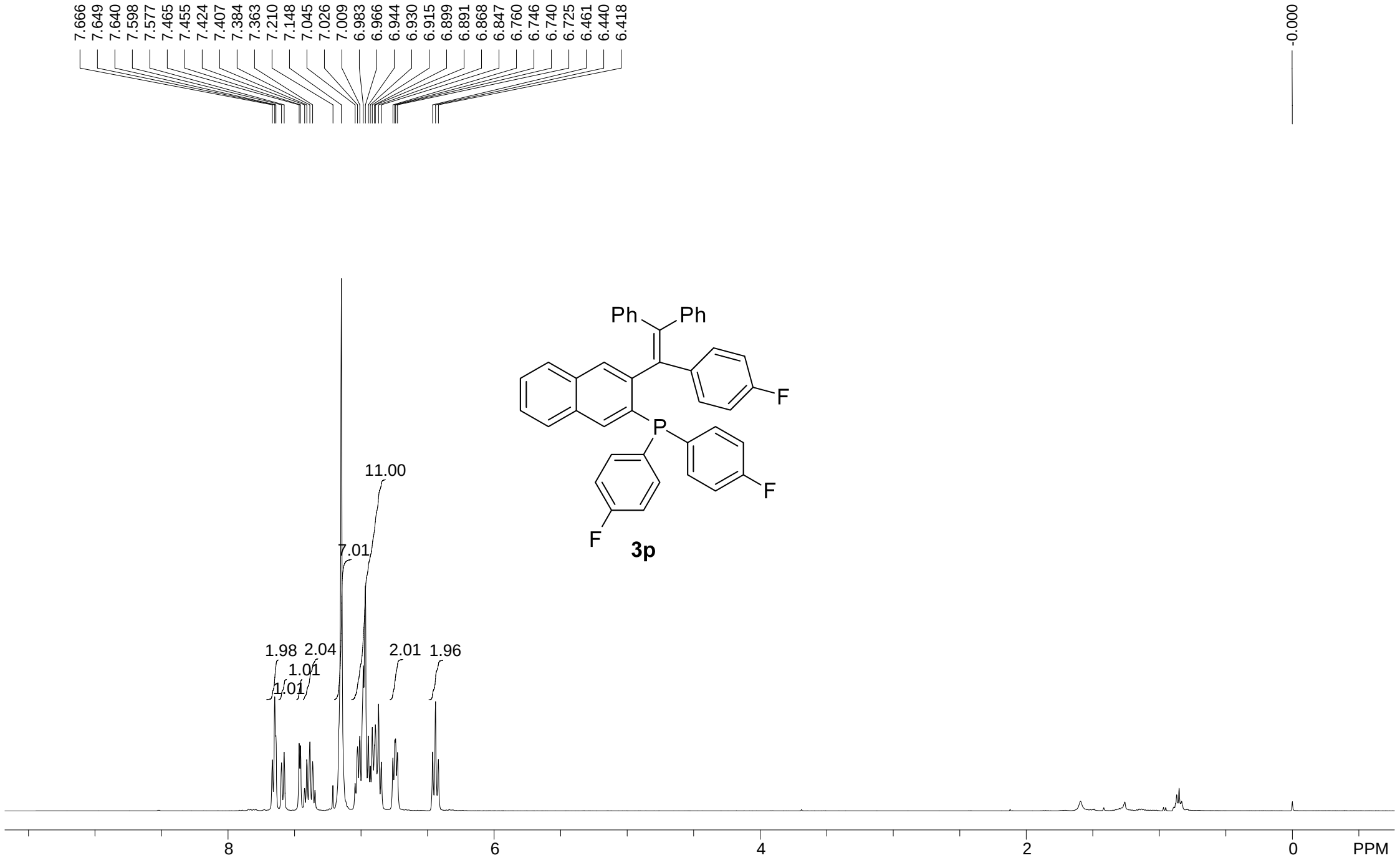
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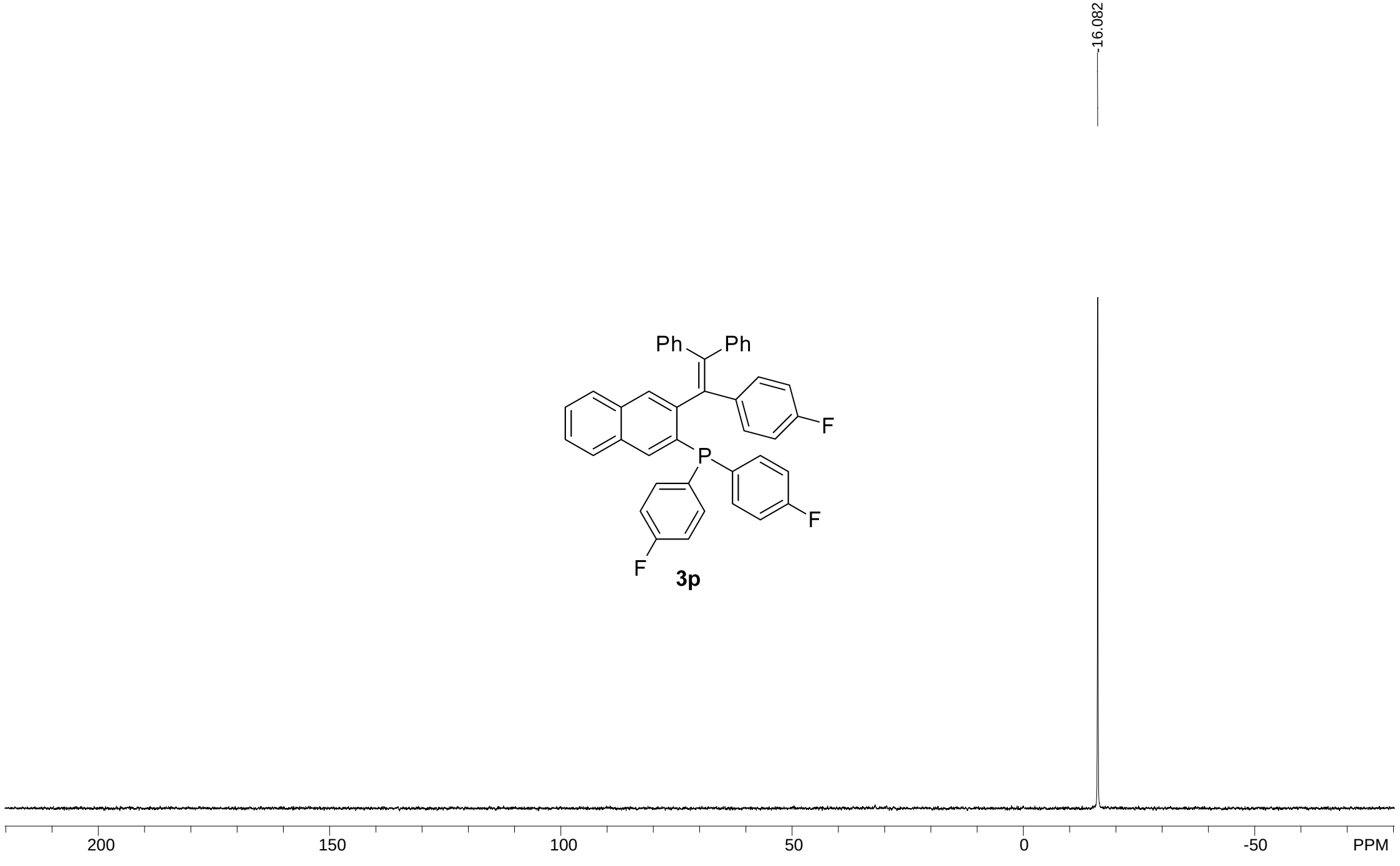

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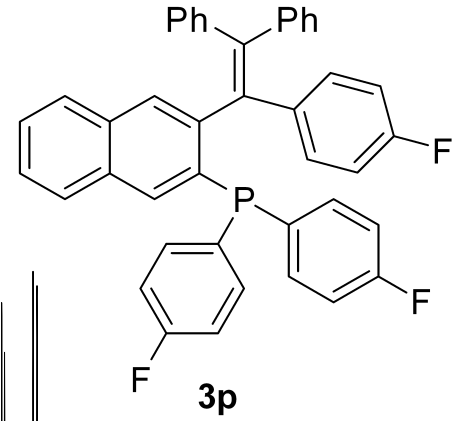

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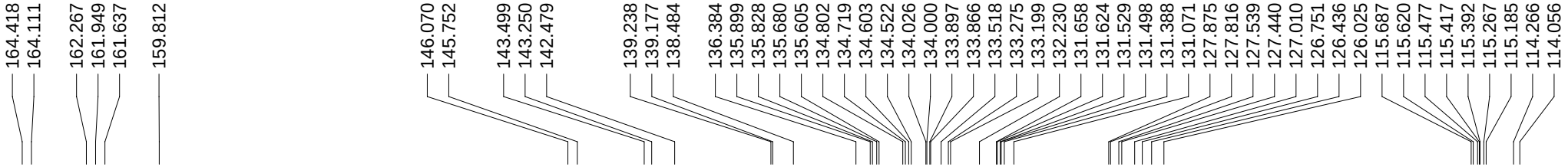
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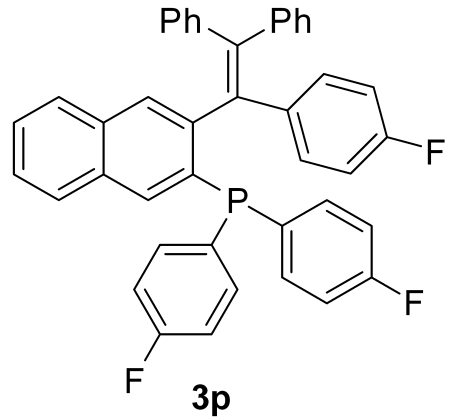
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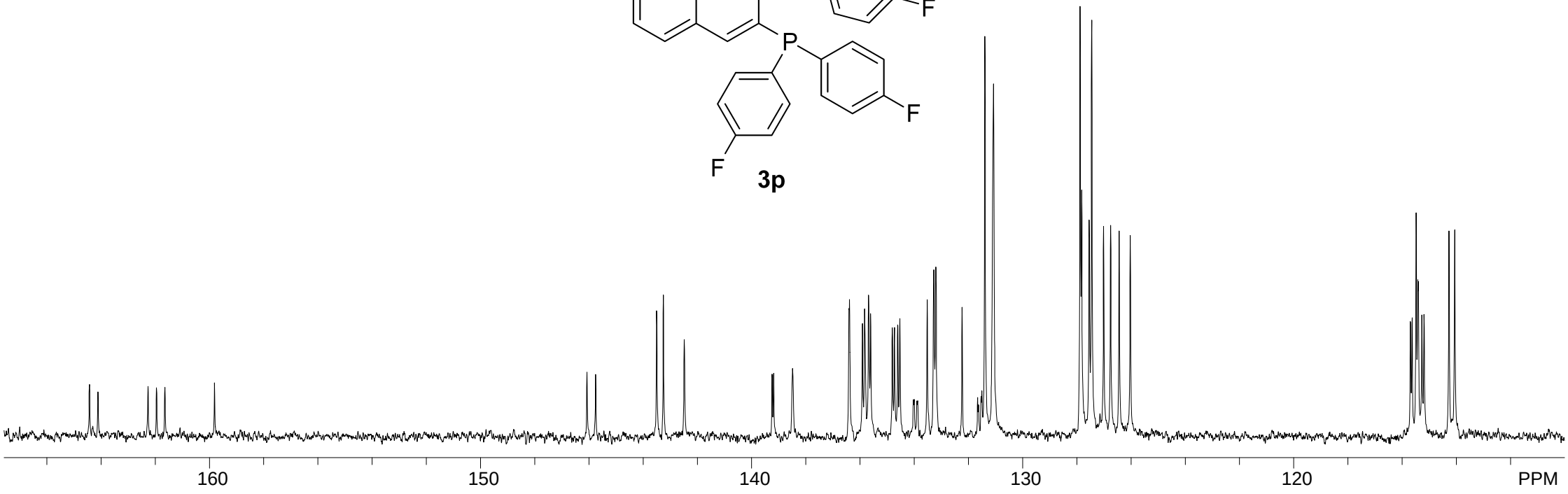
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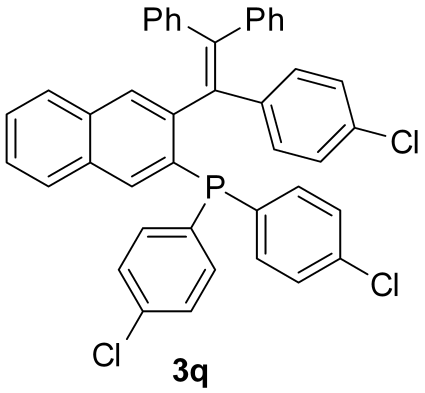
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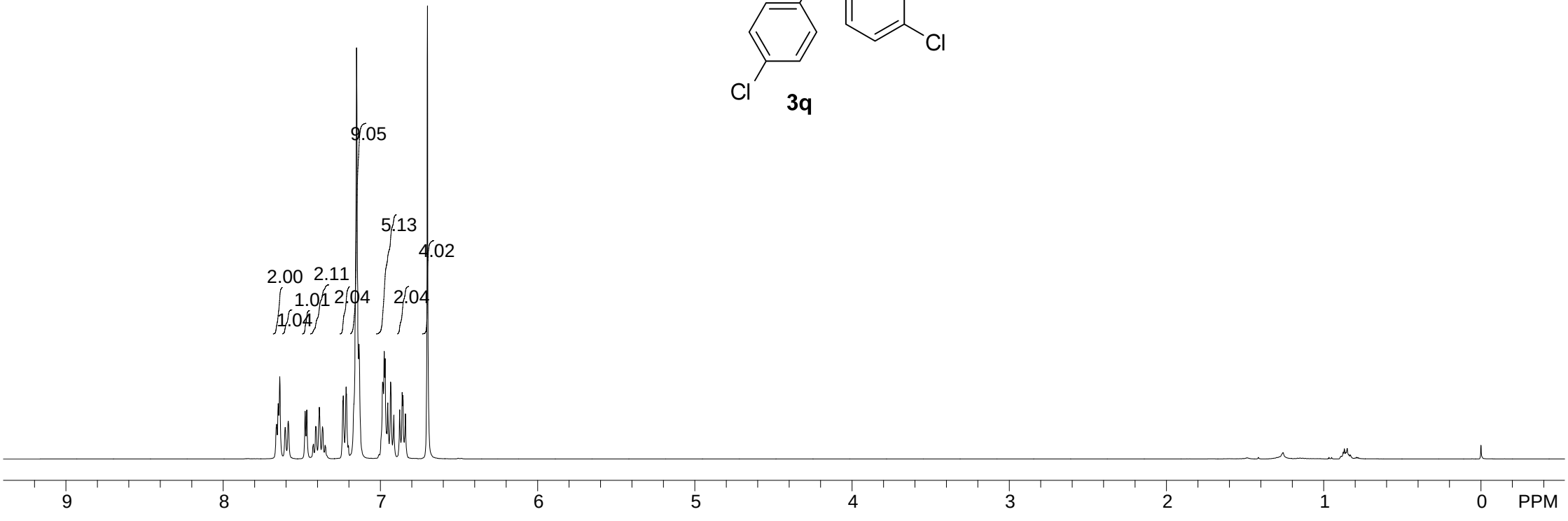
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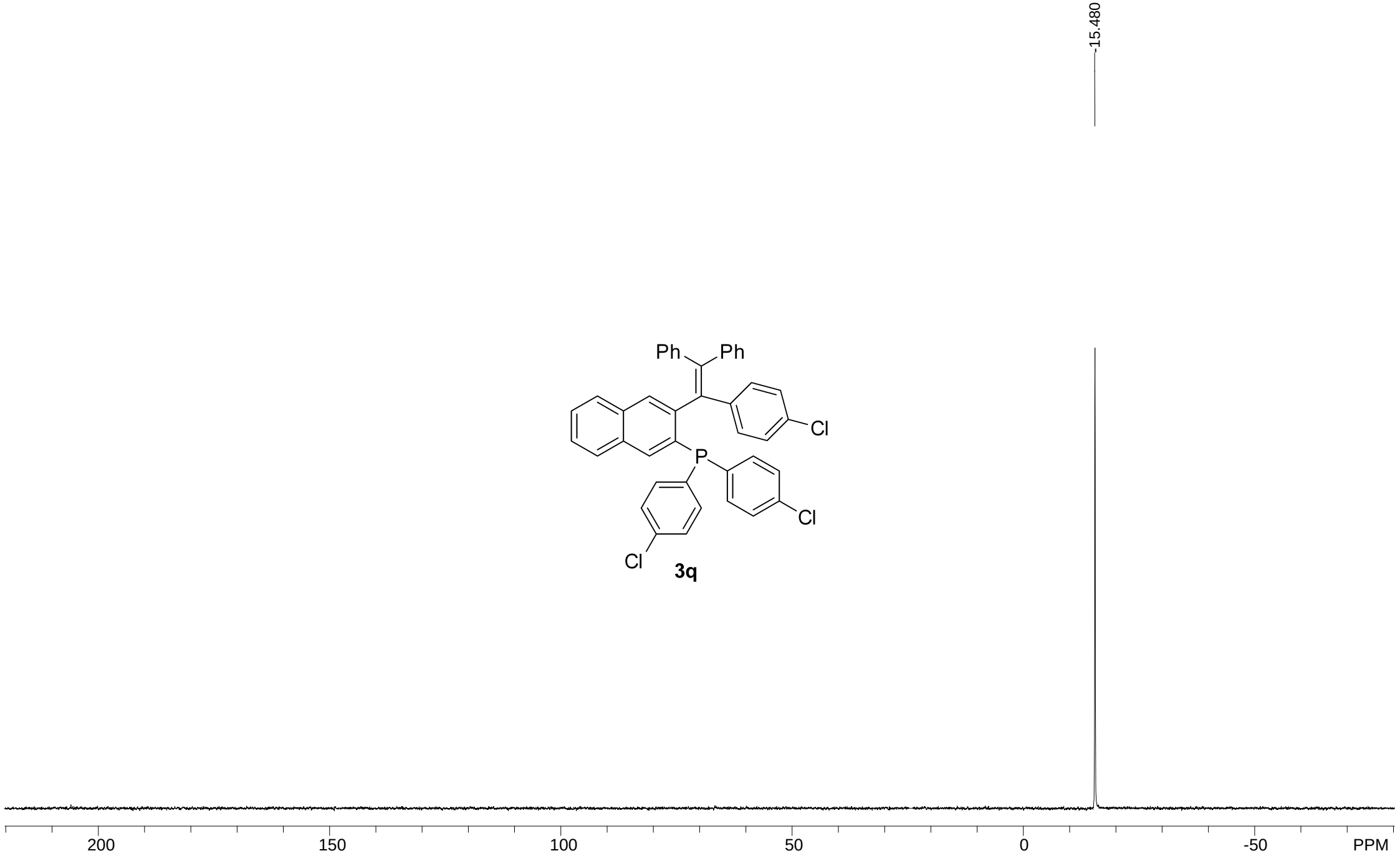

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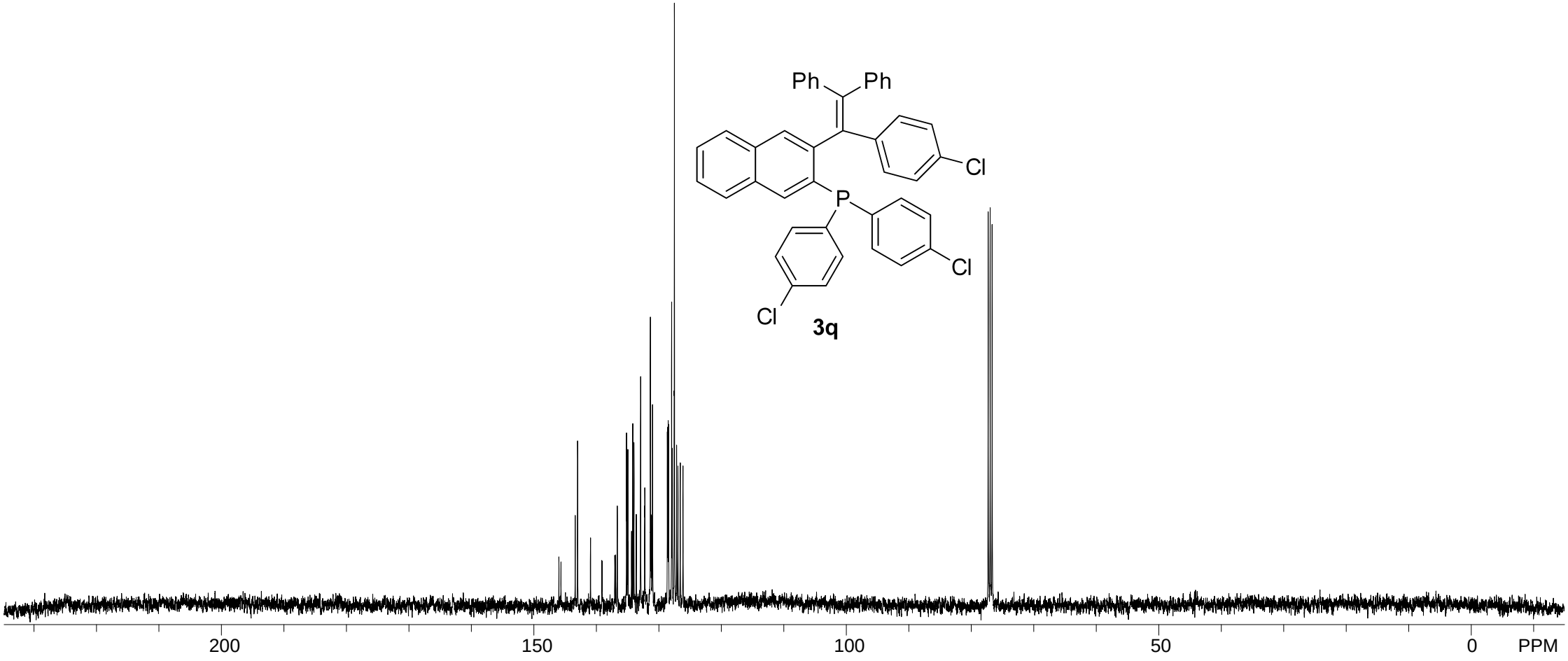

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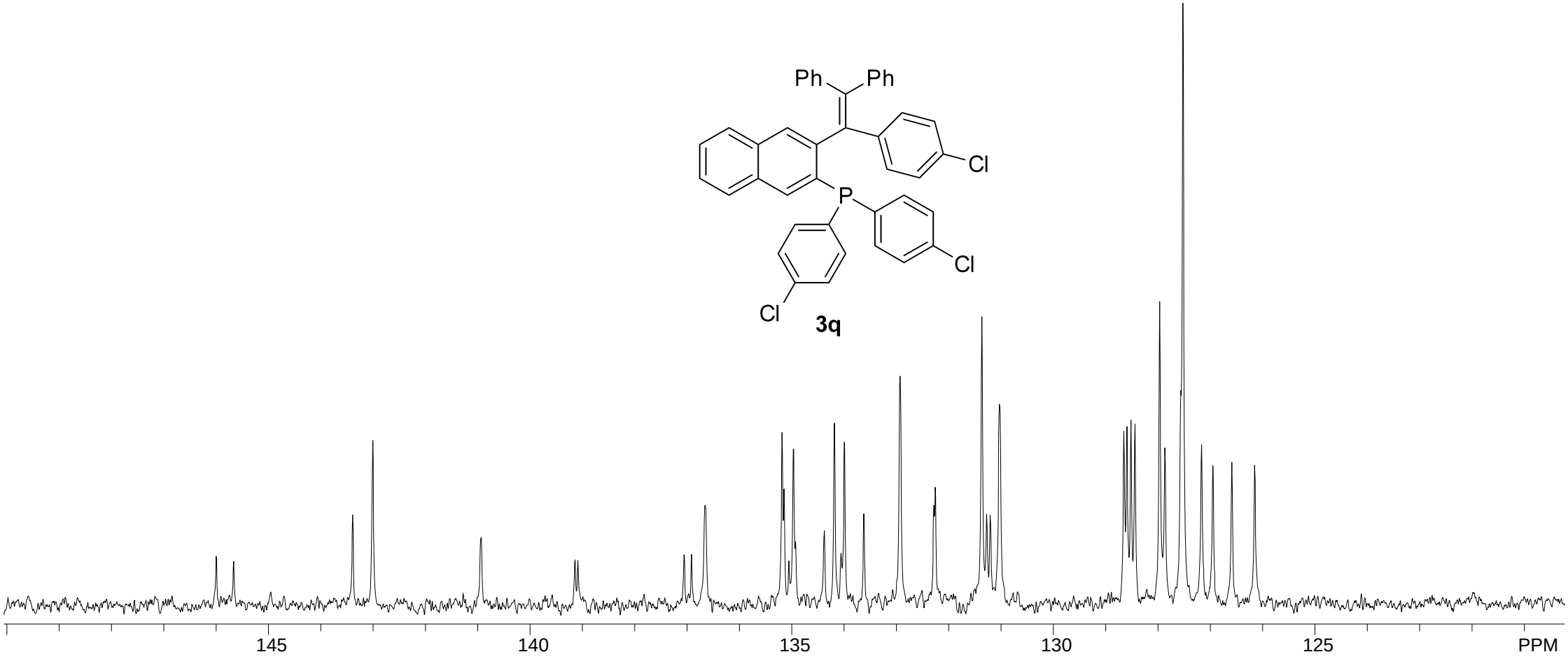

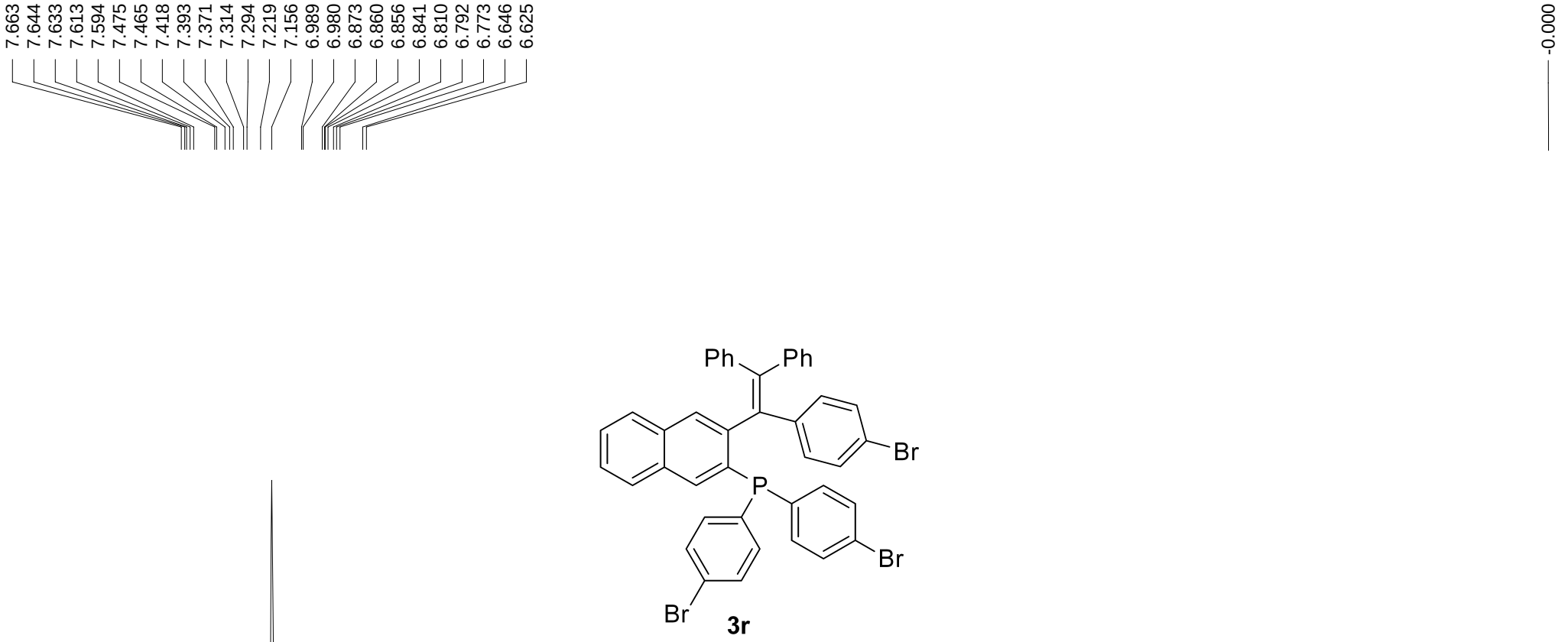
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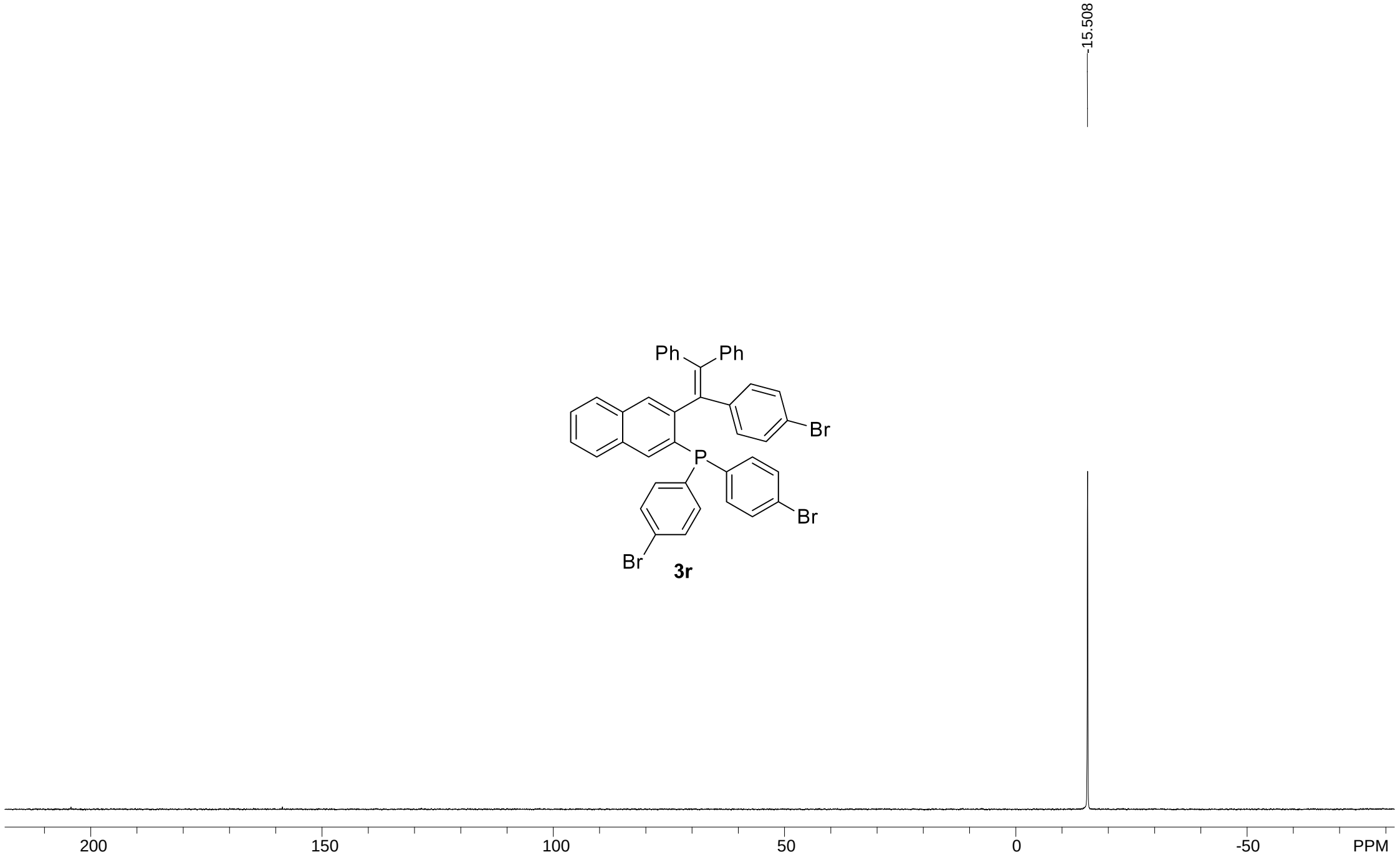

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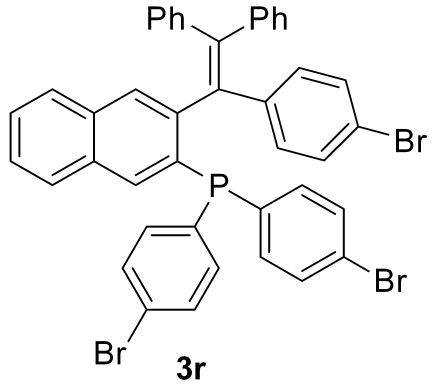

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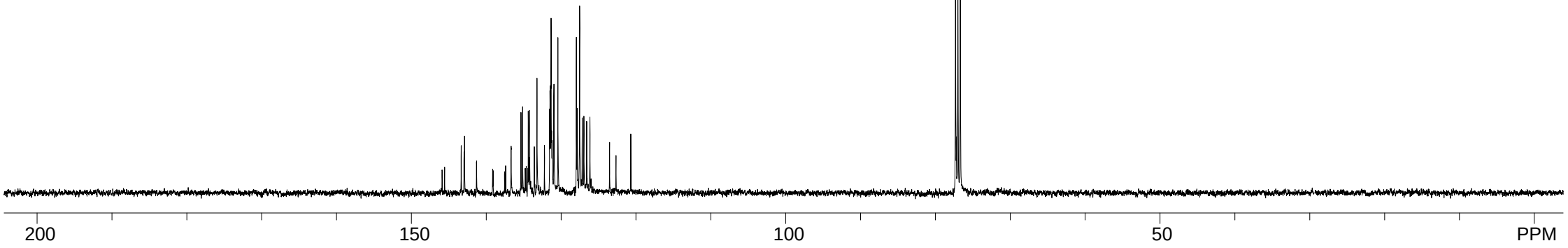

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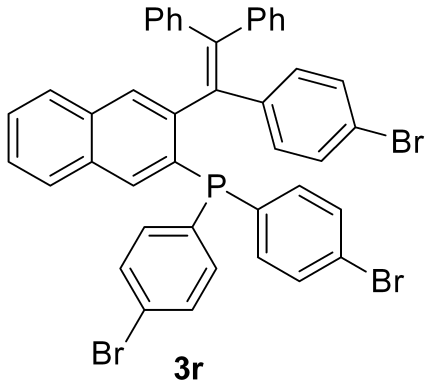

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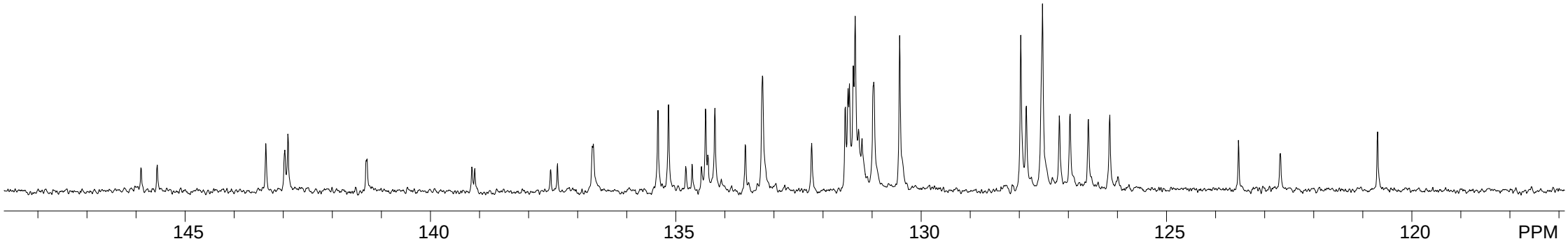

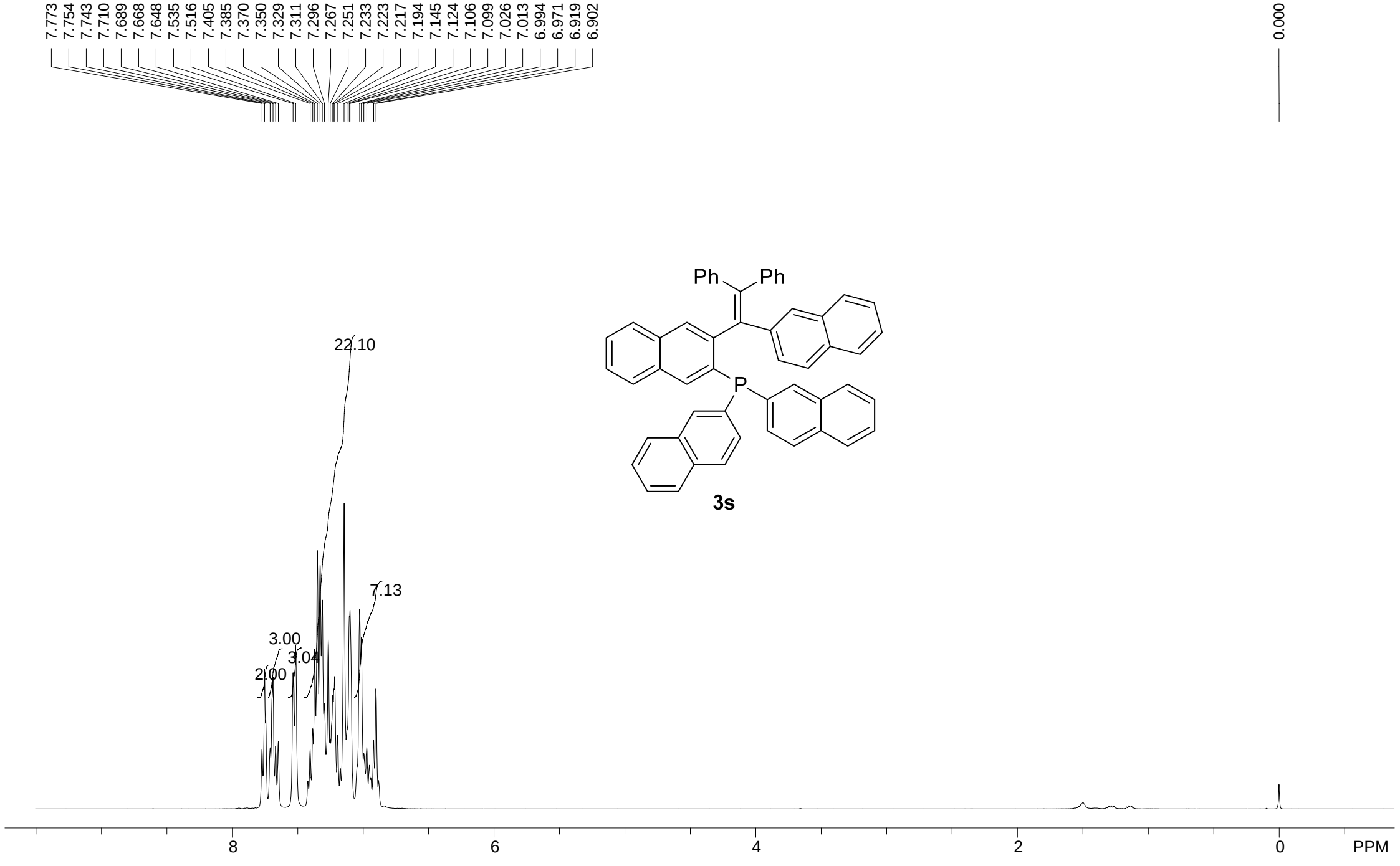
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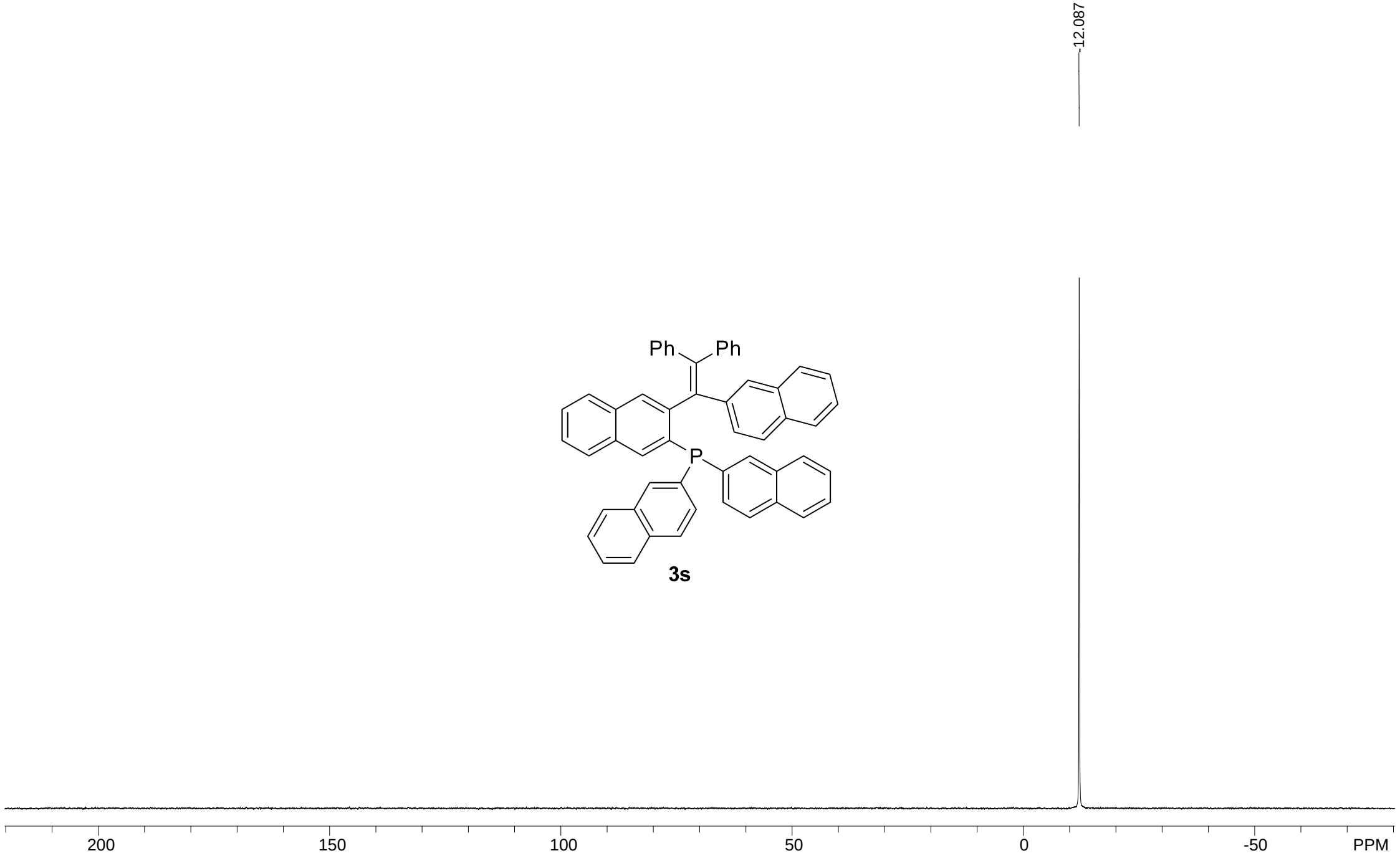

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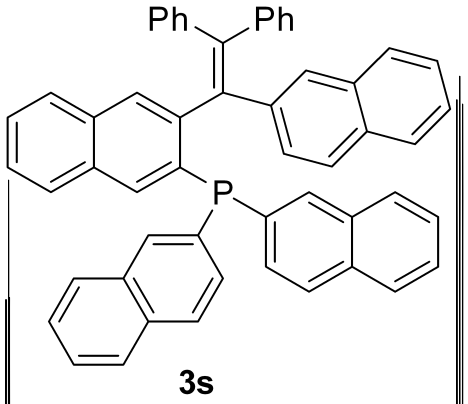

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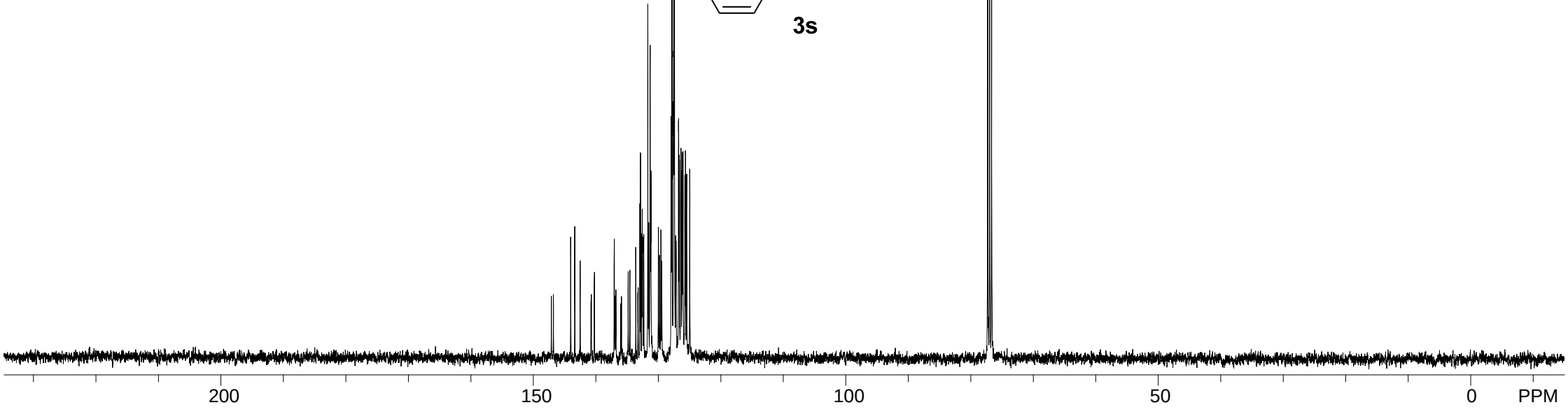

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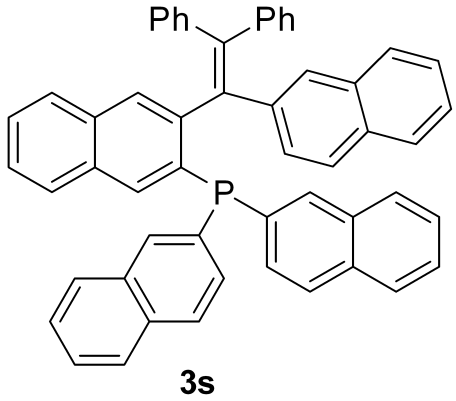

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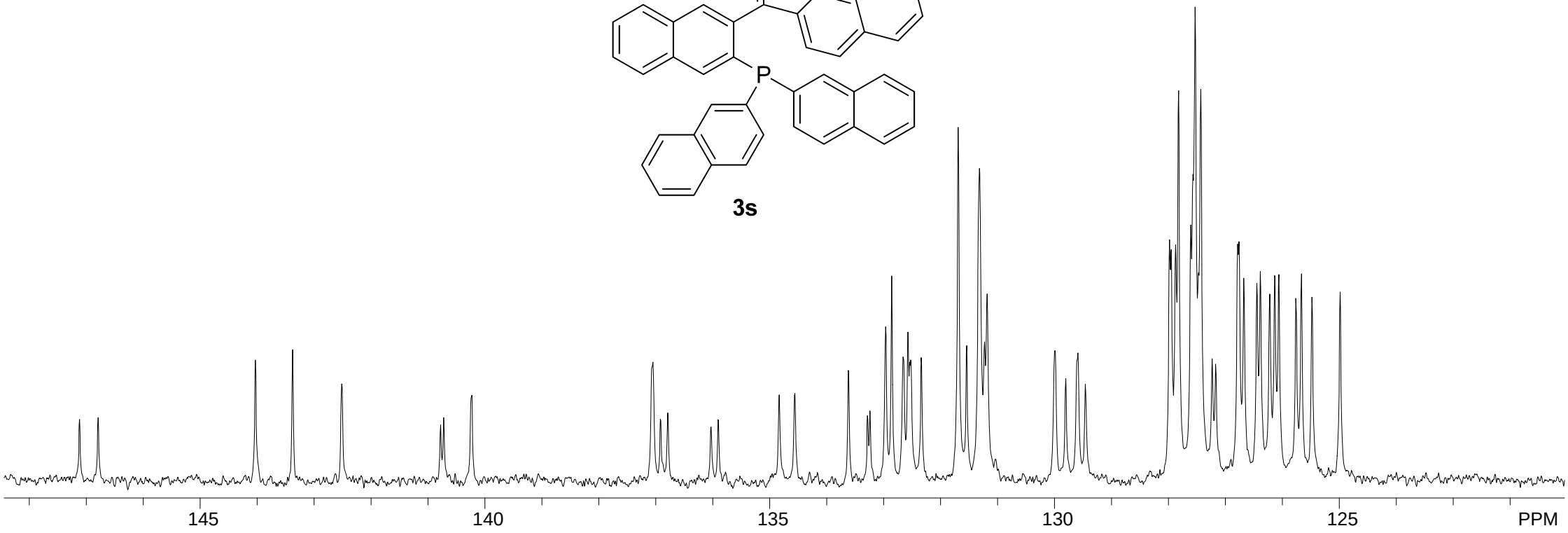

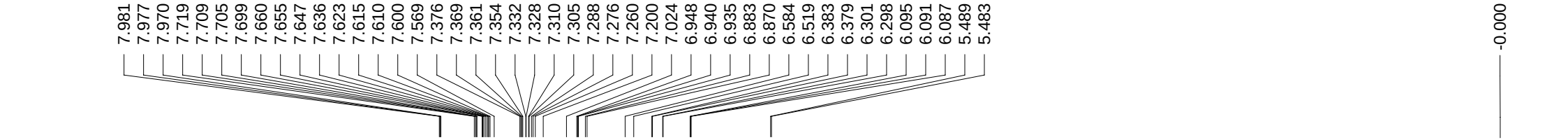

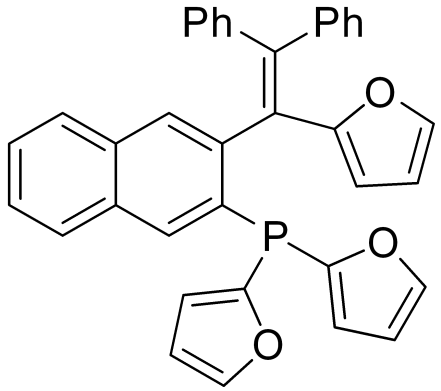

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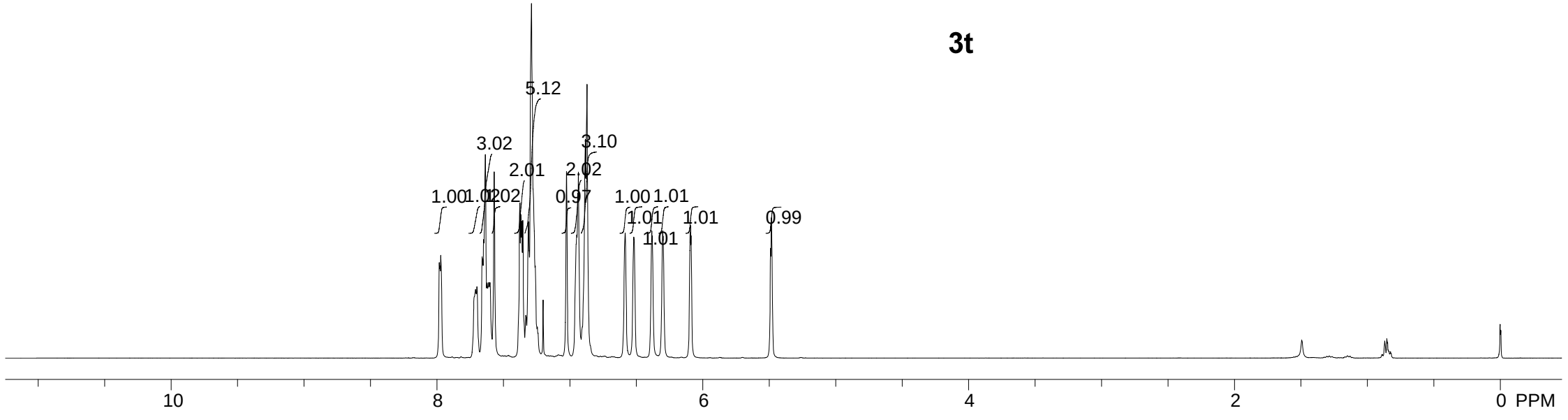

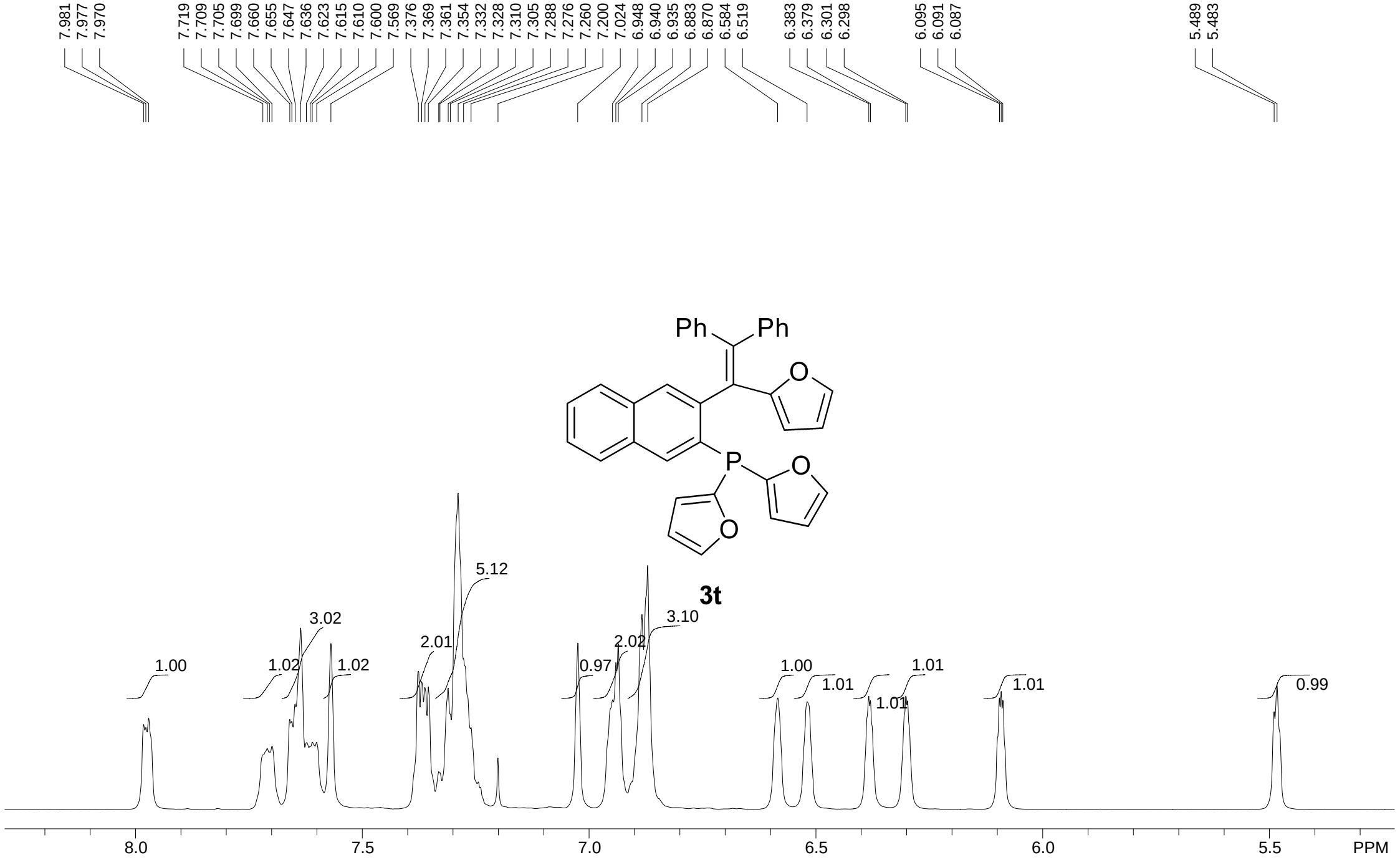
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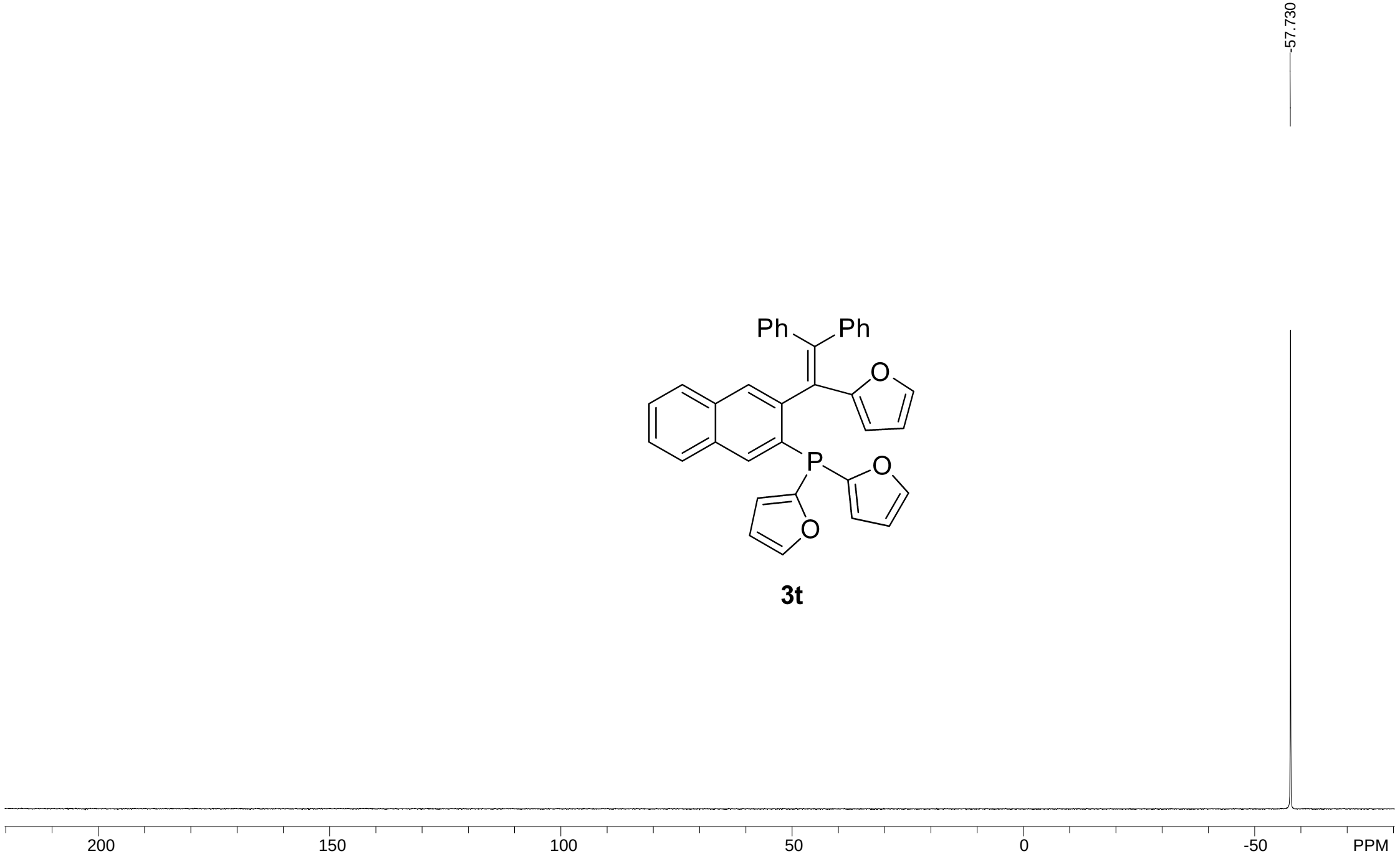

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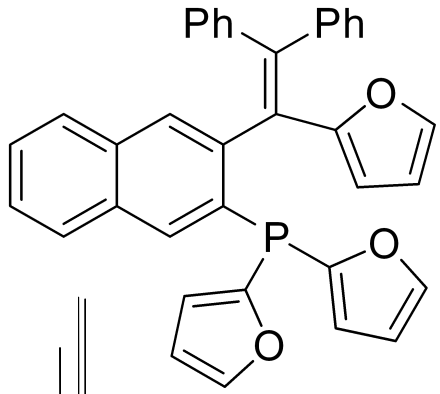

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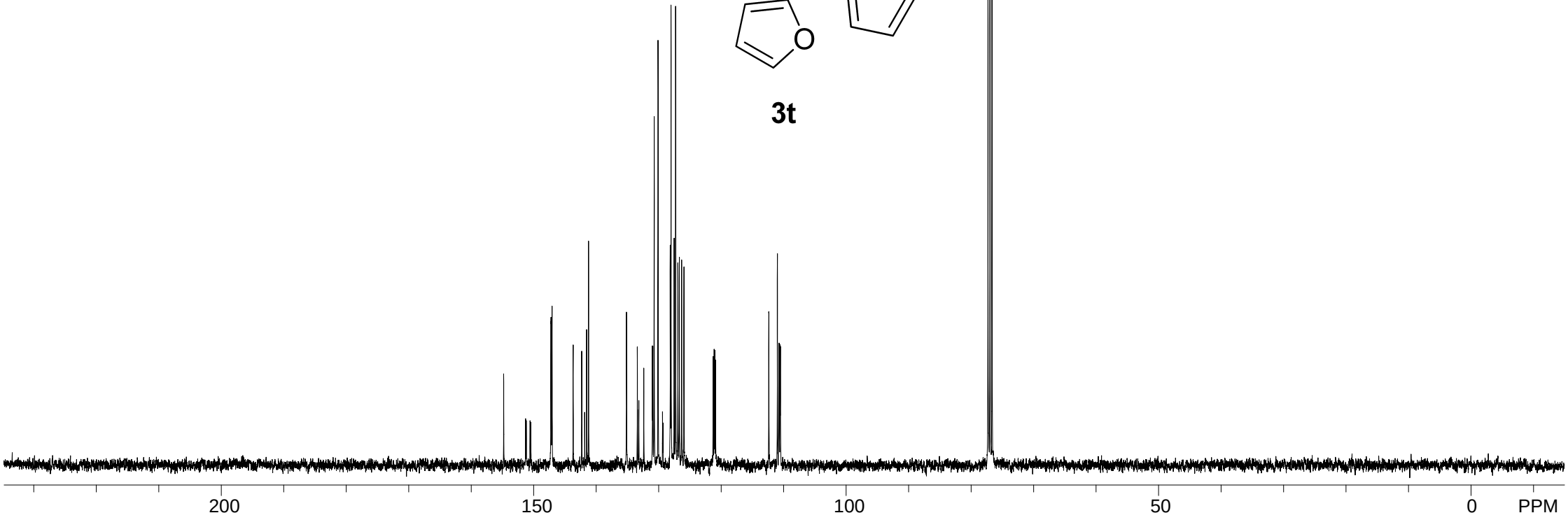

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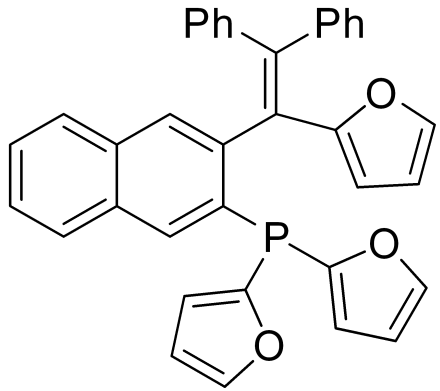

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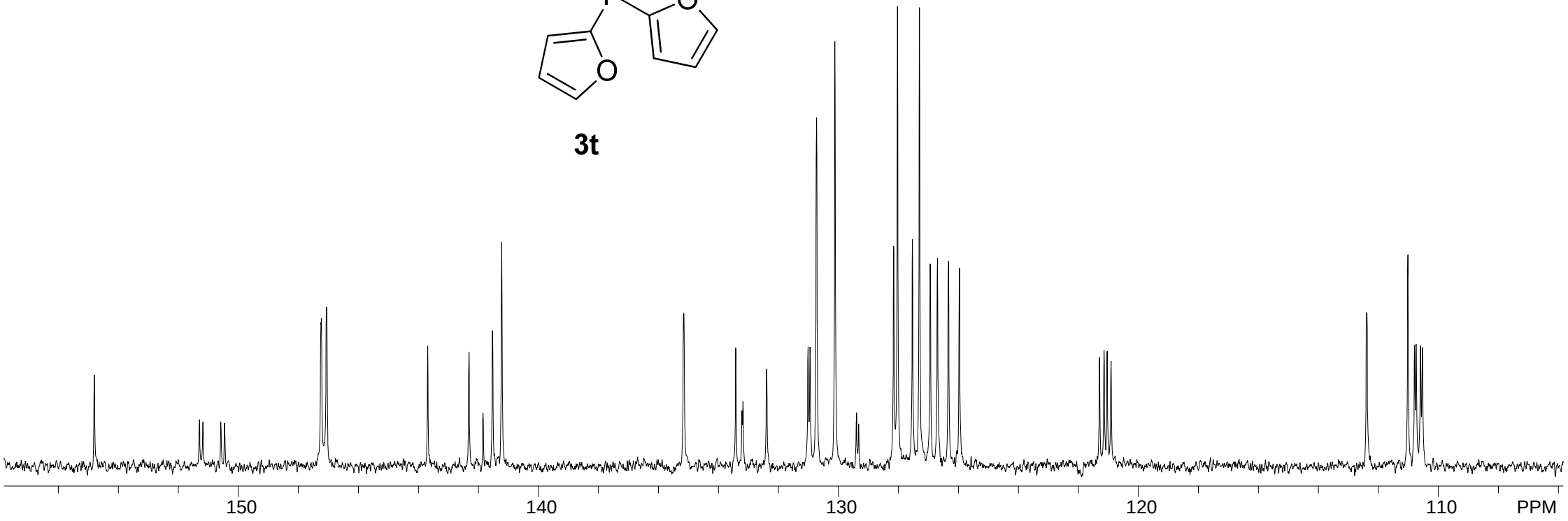

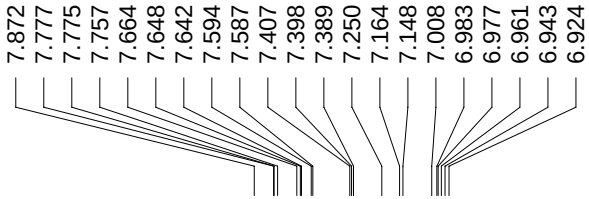
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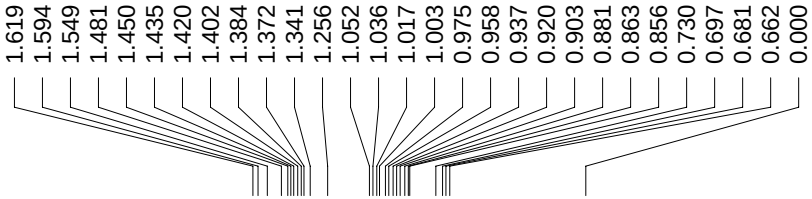
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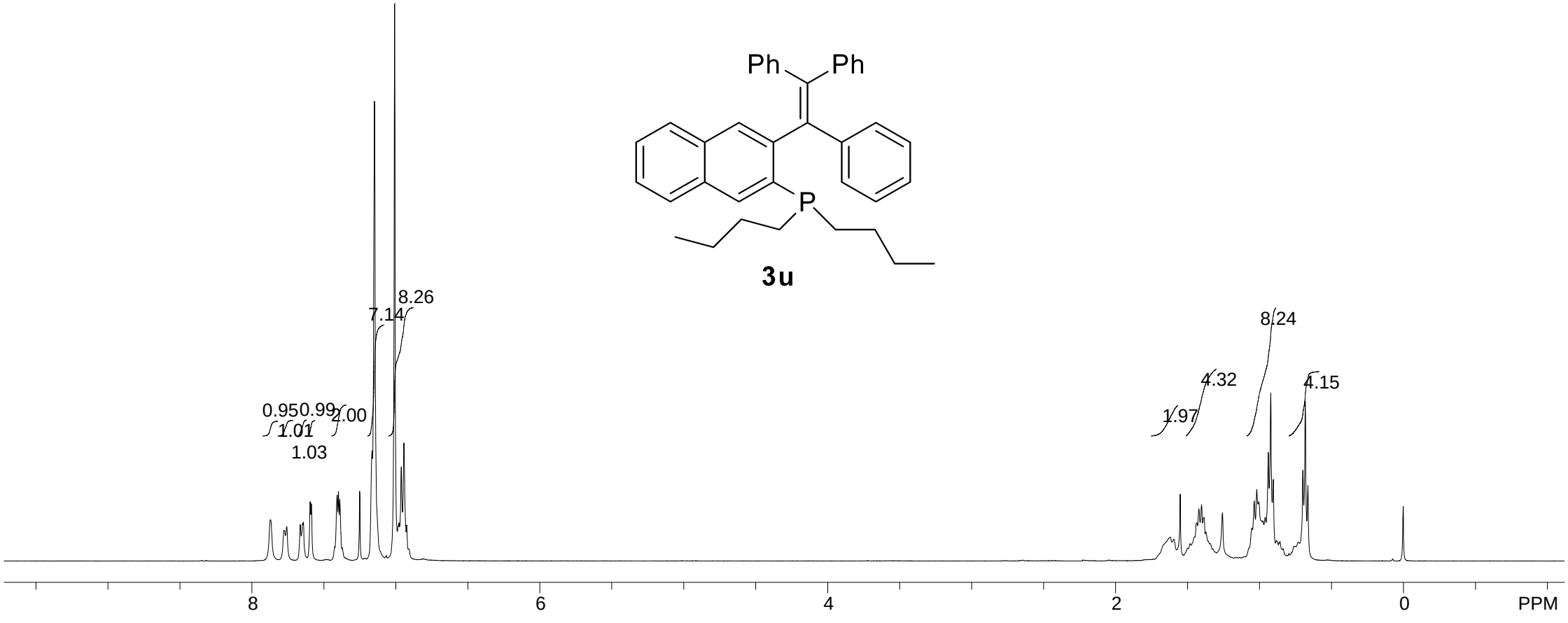
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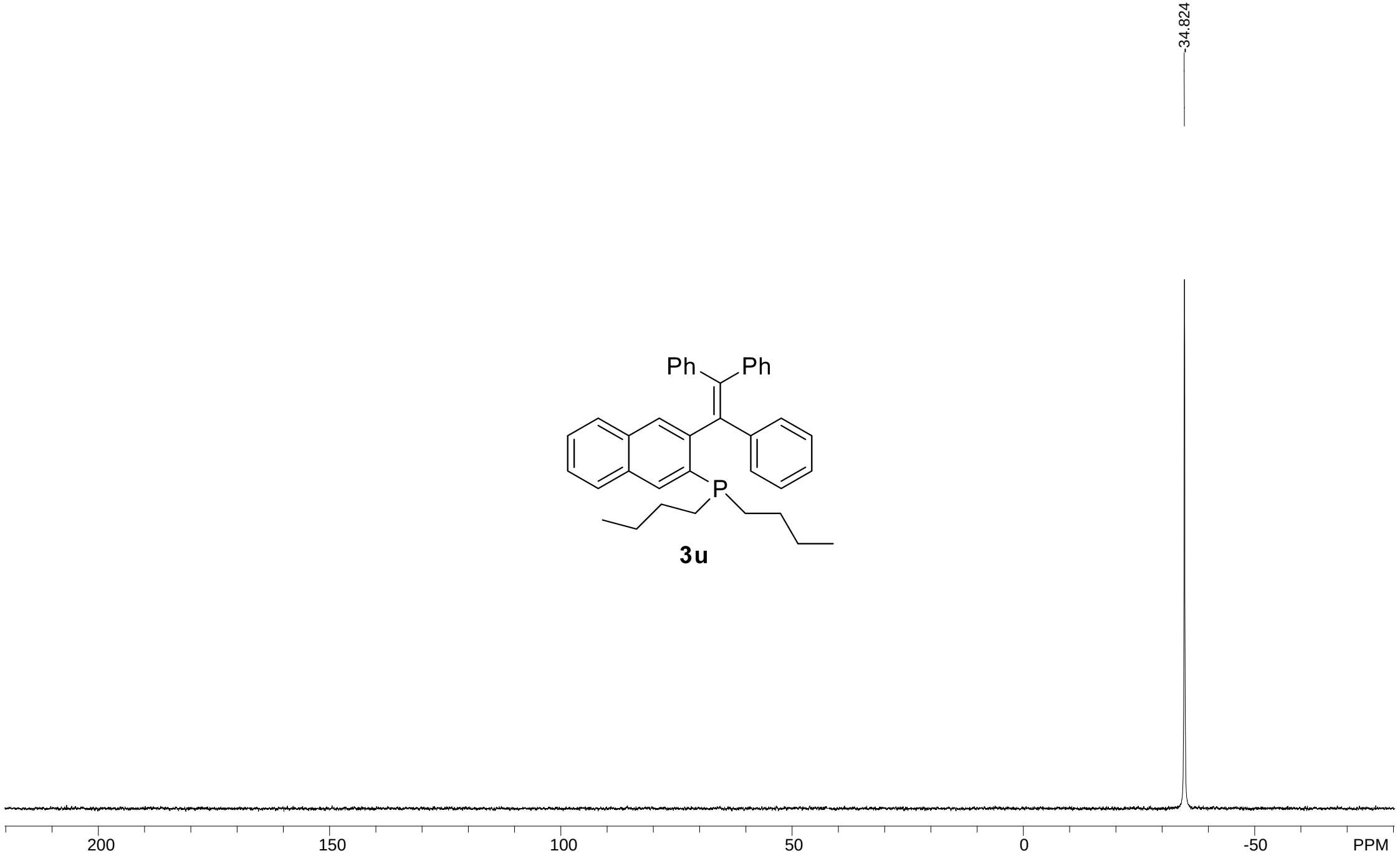

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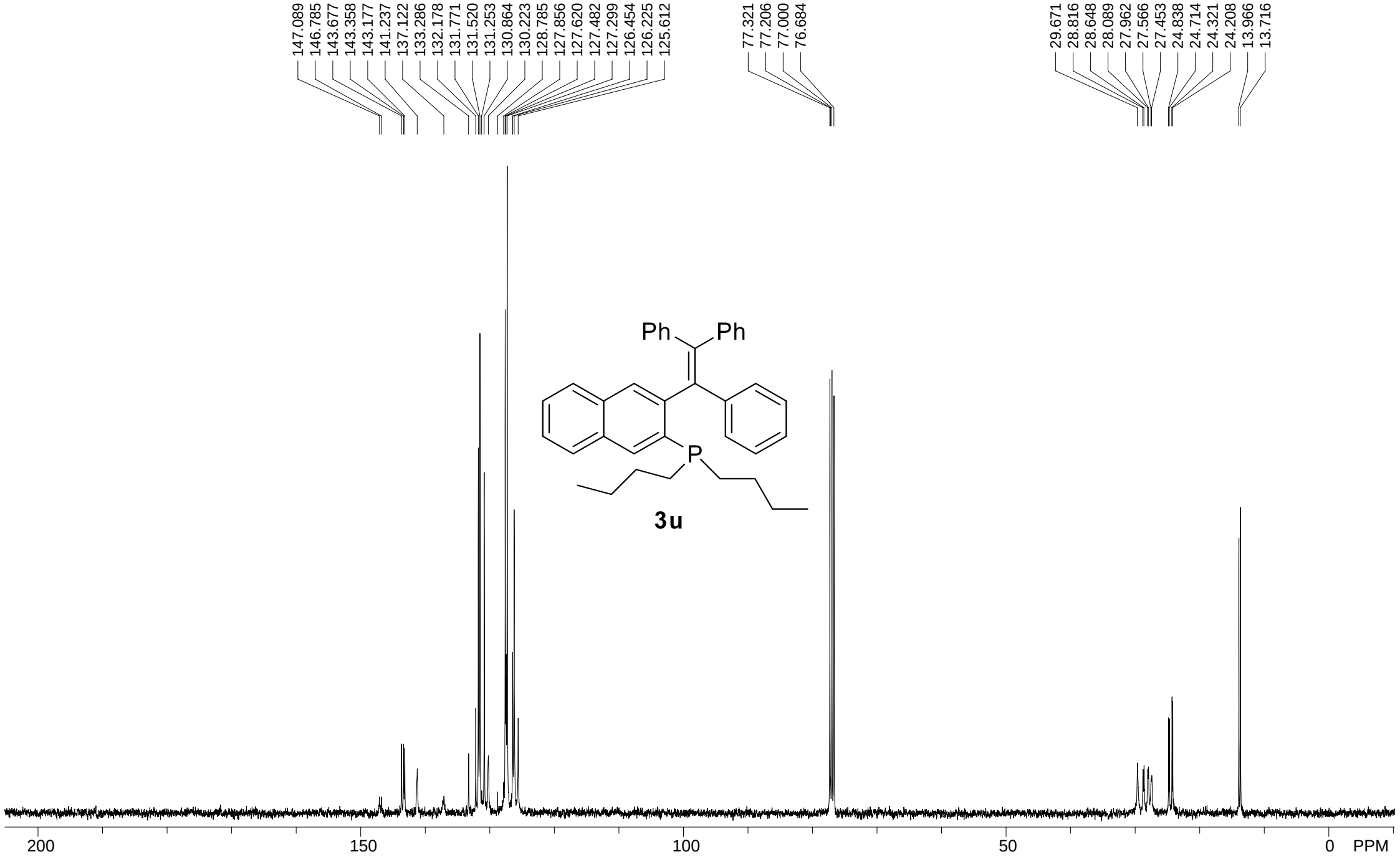
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13.716
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Ph
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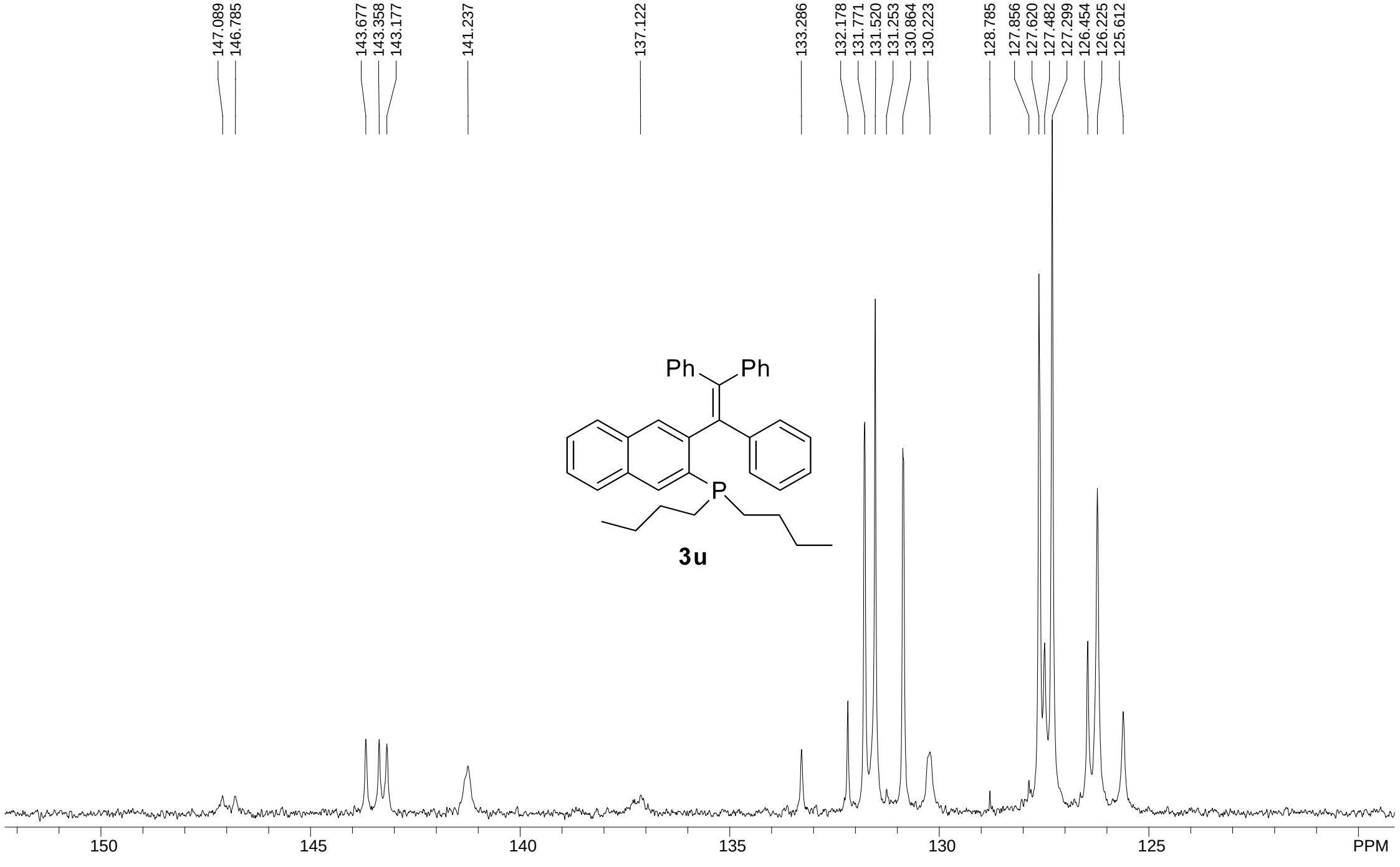
PPM



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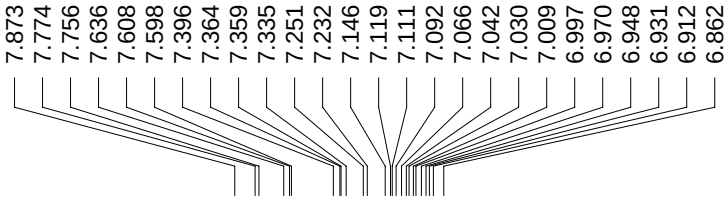
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7.232
7.146
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7.042
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7.009
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6.948
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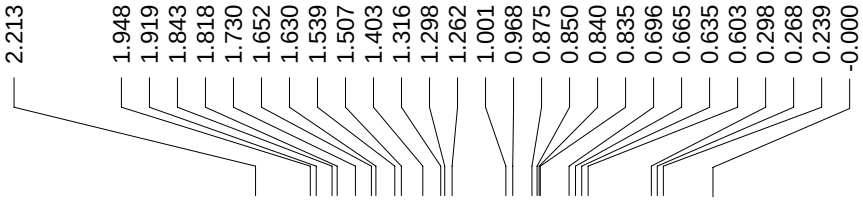
6.912
6.862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1.630
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1.507
1.403
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1.298
1.262
1.001
0.968
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0.298
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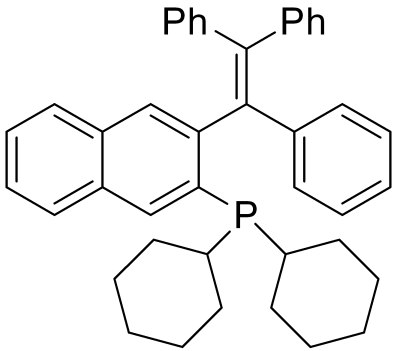
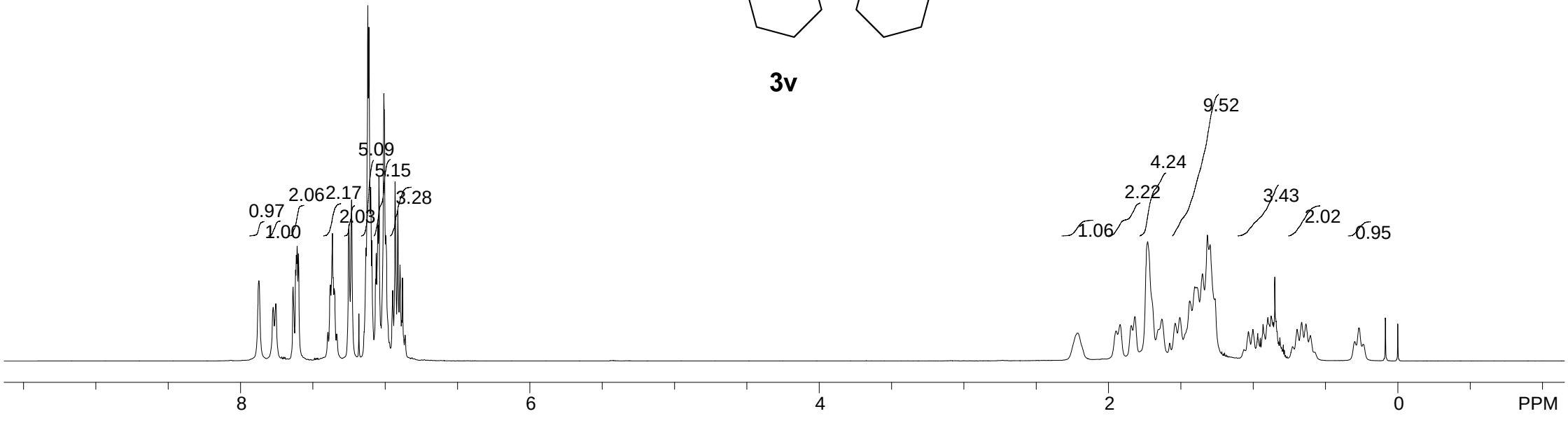
-0.000


Ph
Ph
P

3v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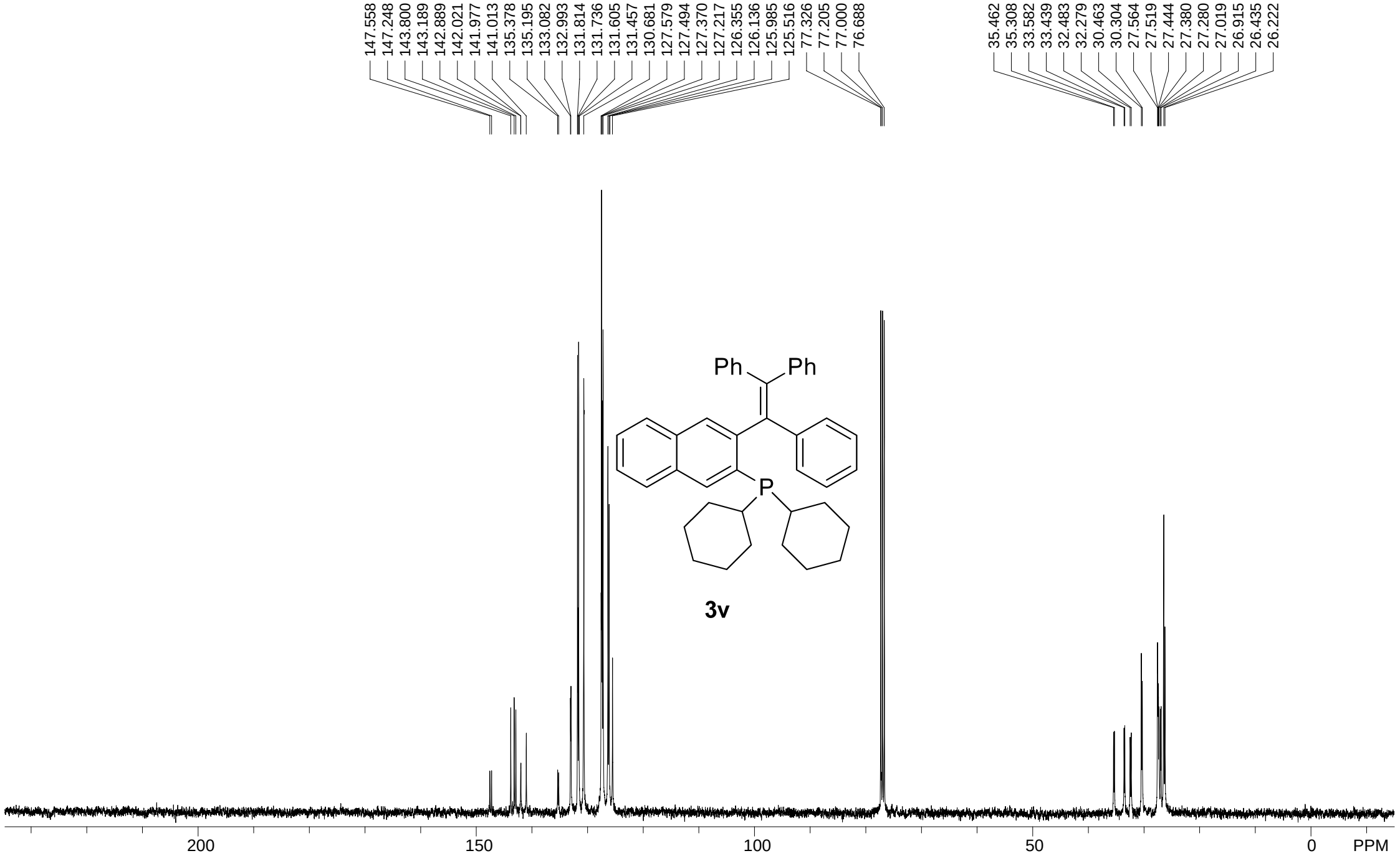
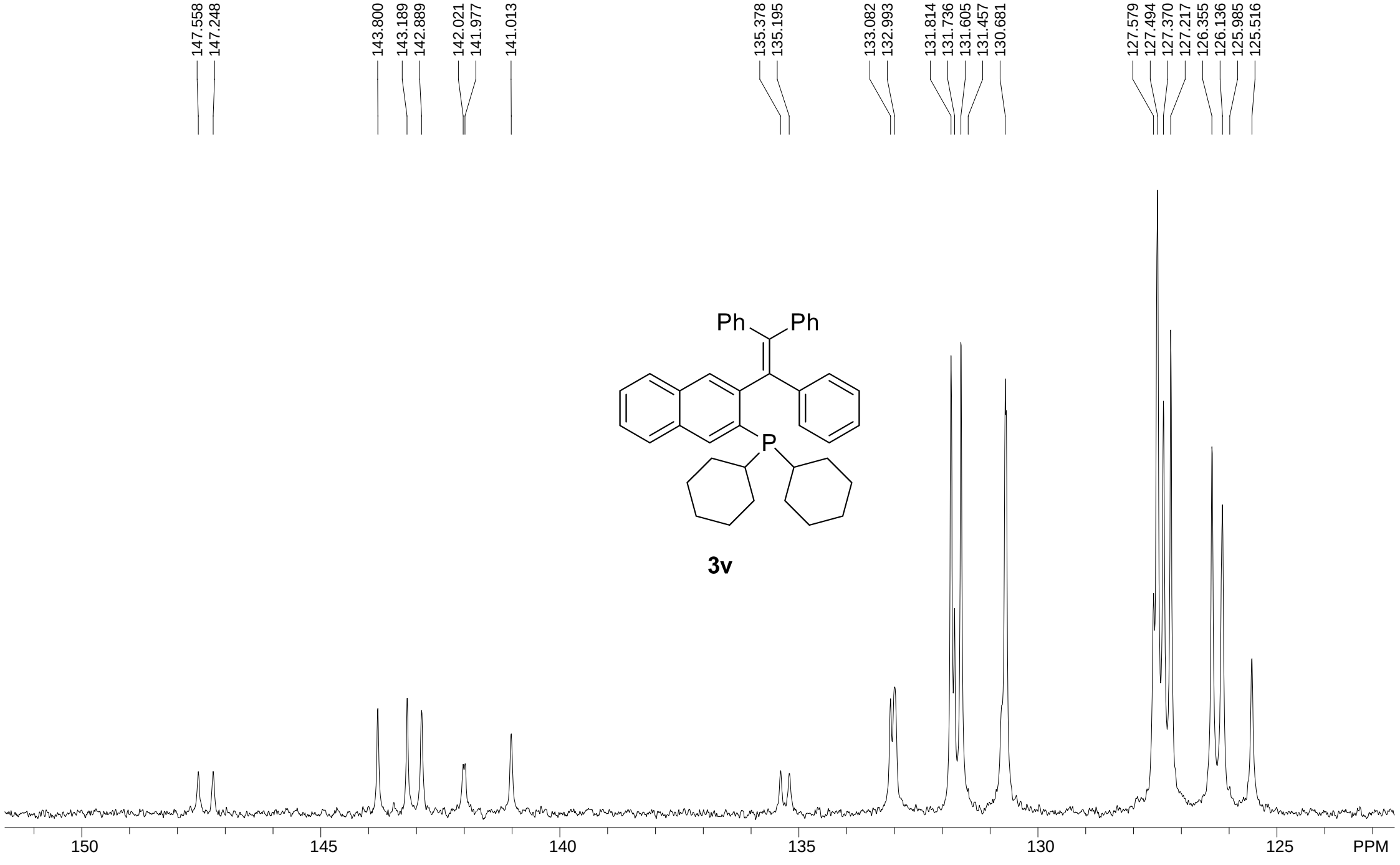
8
6
4
2
0
PPM

3v





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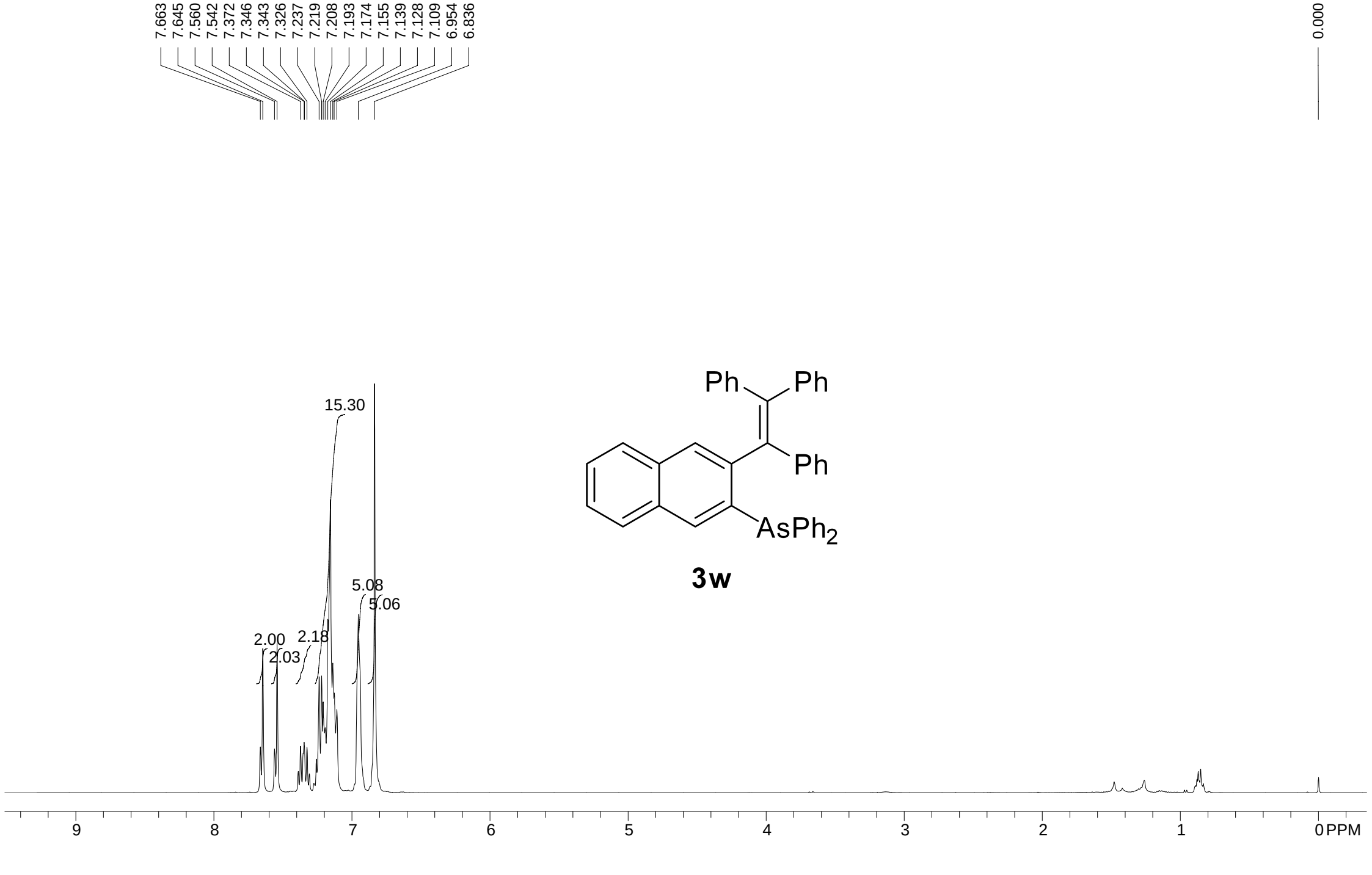
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7.155
7.139
7.128
7.109
6.954
6.836
0.000
15.30
5.08
5.06
2.00
2.03
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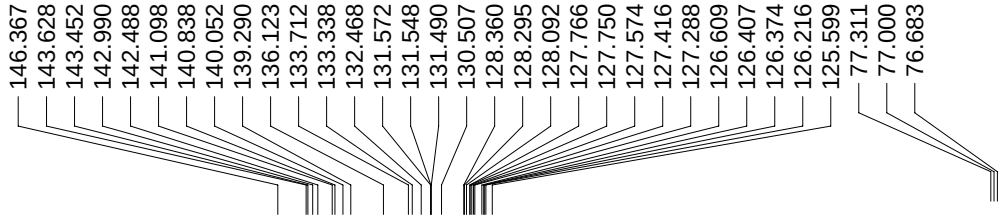
Ph
Ph
Ph
AsPh2
3w
9
8
7
6
5
4
3
2
1
0 PPM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133.712
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132.468
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128.360
128.295
128.092
127.766
127.750
127.574
127.416
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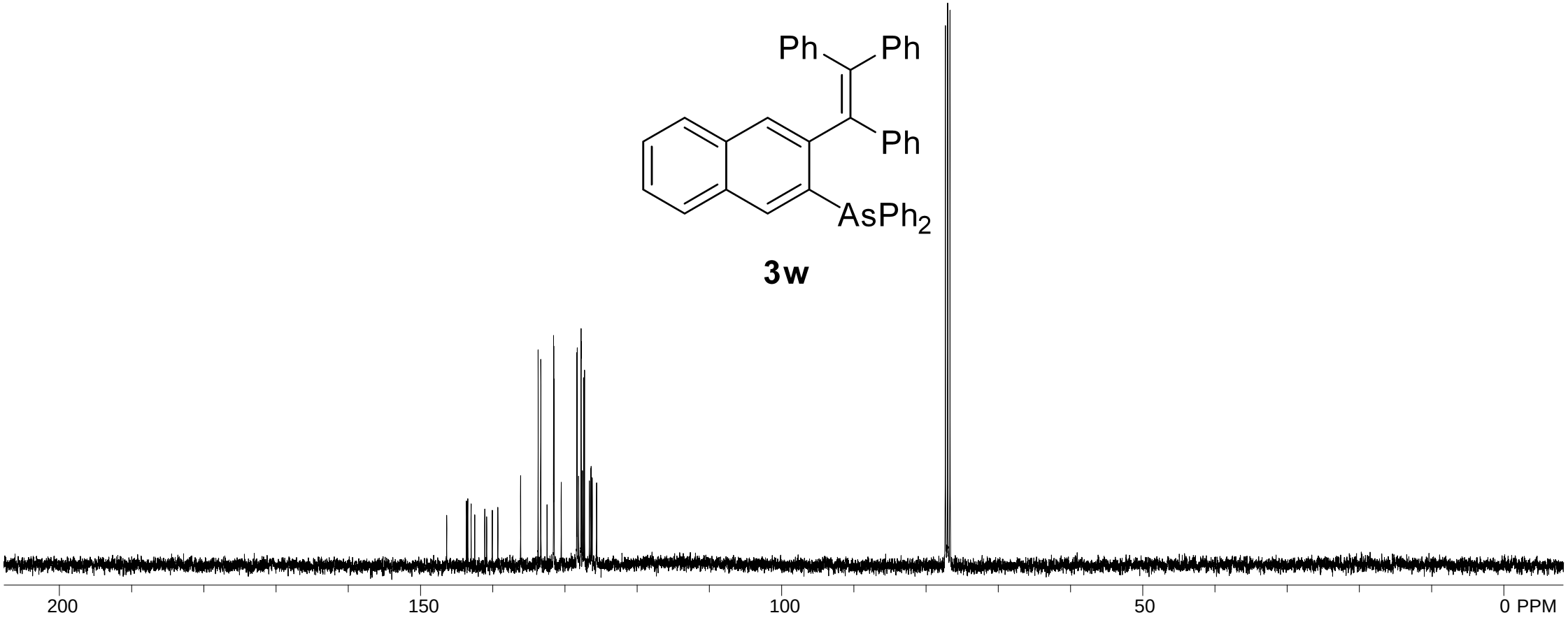
76.683

Ph
Ph
Ph
AsPh2

3w


200
150
100
50
0 PPM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142.990
142.488
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132.468
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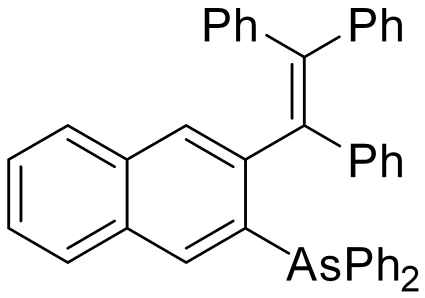
Ph
Ph
Ph
AsPh2

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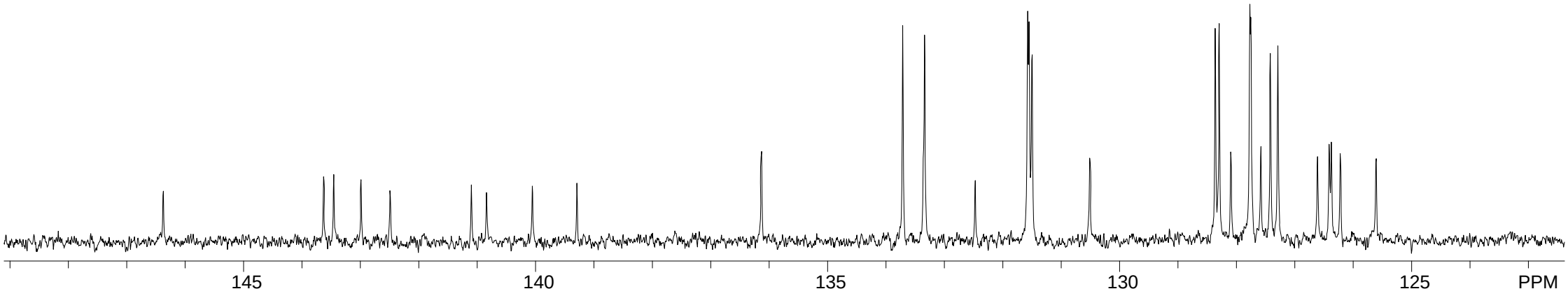
145
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135
130
125
PPM