Catalytic Imine-Imine Cross-Coupling Reactions

Masatoshi Matsumoto, Masashi Harada, Yasuhiro Yamashita, and Shū Kobayashi*

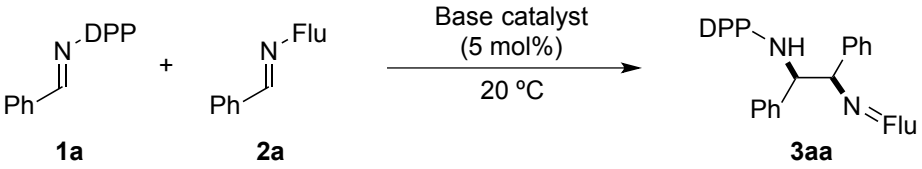
Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Electronic Supplementary Information

Contents

1. Supplementary tables and schemes

Table S1 Optimization of reaction conditions

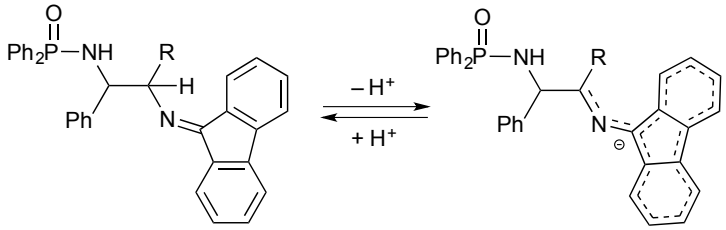


1a **2a** **3aa**

Entry	Base	Solvent	Time (h)	Yield (%)[a]	*syn*/*anti*[b]
1	KO^{t}Bu–18-crown-6	THF	24	60	60/40
2	KO^{t}Bu–18-crown-6	CH_2Cl_2	24	18	50/50
3	KO^{t}Bu–18-crown-6	Et_2O	24	39	67/33
4	KO^{t}Bu–18-crown-6	Et_2O/CH_2Cl_2 (4/1)	24	90	99/1
5	DBU	Et_2O/CH_2Cl_2 (4/1)	18	67	94/6
6	KOPh	Et_2O/CH_2Cl_2 (4/1)	18	86	94/6
7	$KOCH_2CF_3$	Et_2O/CH_2Cl_2 (4/1)	18	97	>99/1

[a] Isolated yield. [b] Determined by ^{1}H NMR analysis.

Scheme S1 Possible deprotonation



Scheme S2 Epimerization

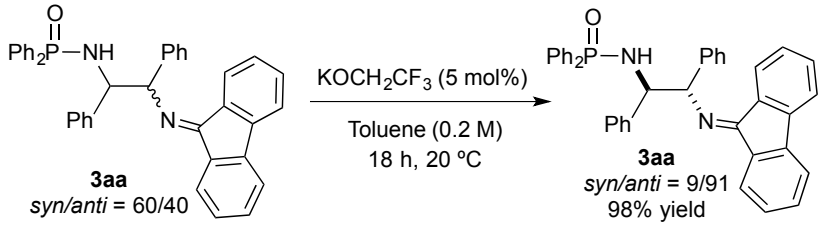
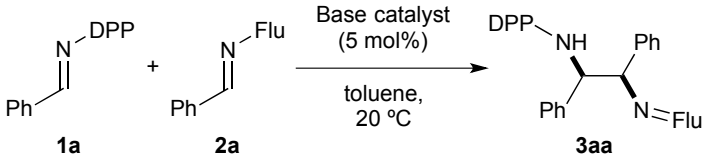


Table S2 Effect of bases on diastereoselectivity



Entry	Base	Time (h)	Yield (%)[a]	*syn*/*anti*[b]
1	KO^{t}Bu, 18-crown-6	18	80	7/93
2	KO^{t}Bu, 18-crown-6	0.5	73[c]	58/42
3	$KOCH_2CF_3$	18	92	3/97
4	KOPh	18	96	75/25
5	DBU	18	53[c]	94/6

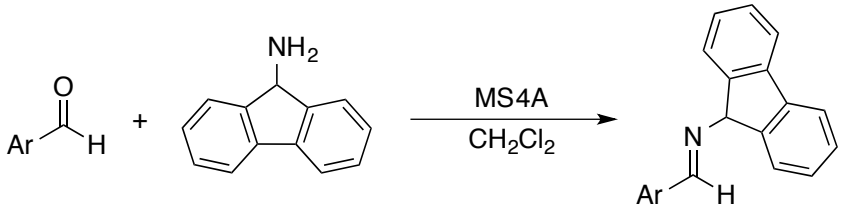
[a] Isolated yield. [b] Determined by ^{1}H NMR analysis. [c] NMR yield.

2. Experimental section

General:

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-ECX400, JNM-ECA500, and JNM-ECX600 spectrometers in $CDCl_3$ unless otherwise noted. $CDCl_3$ served as internal standard (δ = 7.24 for ^{1}H NMR, δ = 77.0 for ^{13}C NMR), H_3PO_4 served as external standard (δ = 0 for ^{31}P NMR). IR spectra were recorded with a JASCO FT/IR-4200 spectrometer. High-resolution mass spectrometry was recorded with a JEOL JMS-T100TD (DART®). Column chromatography was conducted on Silica gel 60N (spherical, neutral, Kanto Chem. Co., Inc.) or Iatrobeads 6RS-8060 (MITSUBISHI CHEMICAL MEDIENCE CORPORATION), and preparative thin-layer chromatography was carried out using a plate with Wakogel B-5F. Commercially available aldehydes were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and purified by distillation. Toluene, THF, CH_2Cl_2 and Et_2O were purchased from Wako Pure Chemical Industries, Ltd. as dry solvents, and dried further over molecular sieves or purified by distillation in the presence of benzophenone and sodium. KO^{t}Bu and 18-crown-6 were supplied from Wako Pure Chemical Industries, Ltd. 1,1,3,3-Tetramethylguanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Tokyo chemical industry co., Ltd. $KOCH_2CF_3$ was prepared from CF_3CH_2OH and KH (purchased from Kanto chemical co., Inc.). *tert*-Butylglyoxylate was prepared in the similar way to the literature method.[1] 9*H*-9-Fluorenylamine was prepared based on the reported method.[2]

General procedure for preparation of aromatic fluorenyl imines 2:

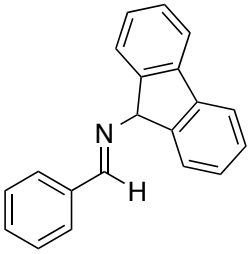


In a 100 mL flask, 9*H*-9-fluorenylamine (1.00 g, 5.52 mmol) and an aromatic aldehyde (5.80 mmol) were mixed in anhydrous CH_2Cl_2 (50 mL) in the presence of well dried MS 4A (5.0 g), and the mixture was stirred overnight at room temperature. The mixture was filtrated through Celite pad, and the remained solid was washed with

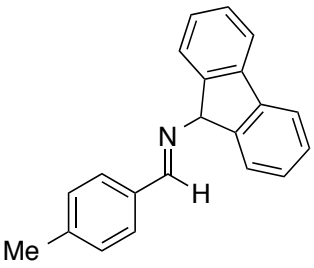
CH_2Cl_2 (20 mL). The filtrate was concentrated *in vacuo* to remove all volatile materials on a rotary evaporator. The crude mixture obtained was purified by recrystallization (toluene/CH_2Cl_2/hexane).

The following compounds were prepared as described above.

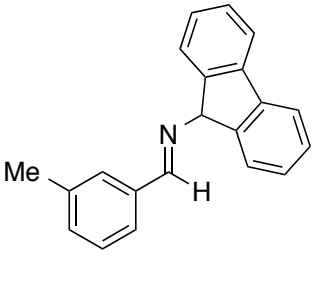
***N*-9-Fluorenylbenzaldehyde imine (2a):** m.p.: 139 ºC (dec.); IR (KBr): 3060, 3030, 2842, 1631, 1578, 1475, 1449, 1386, 1286, 1168, 1043, 845, 761, 742, 729, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 8.78 (s, 1H), 7.81 (dd, J = 7.8, 1.6 Hz, 2H), 7.76 (d, J = 7.4Hz, 2H), 7.41–7.28 (m, 9H), 5.43 (s, 1H); ^{13}C NMR ($CDCl_3$ 150.92 MHz): δ 163.4, 144.8, 141.1, 136.1, 131.0, 128.6, 128.5, 128.43, 127.42, 125.3, 120.1, 74.7; HRMS (ESI): Exact mass calcd for $C_{20}H_{16}N$ $[M+H]^+$ 270.12827, Found 270.12712.



***N*-9-Fluorenyl-*p*-tolaldehyde imine (2b):** m.p.: 123 ºC (dec.); IR (KBr): 3433, 3037, 3019, 2870, 2846, 1610, 1448, 1376, 1271, 1174, 1033, 843, 814, 738 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 8.75 (s, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.7 Hz, 2H), 7.42–7.22 (m, 8H), 5.40 (s, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 163.4, 144.9, 141.3, 141.0, 133.5, 129.3, 128.5, 128.4, 127.4, 125.2, 120.0, 74.7, 21.5; HRMS (ESI): Exact mass calcd for $C_{21}H_{18}N$ $[M+H]^+$ 284.14392, Found 284.14251.



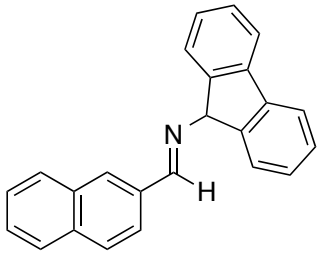
***N*-9-Fluorenyl-*m*-tolaldehyde imine (2c):** m.p.: 133 ºC (dec.); IR (KBr): 3042, 3021, 2915, 2864, 2829, 1634, 1604, 1582, 1450, 1374, 1278, 1166, 1046, 982, 797, 782 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 8.73 (s, 1H), 7.72 (d, J = 7.6 Hz, 2H), 7.66 (s, 1H), 7.54 (d, J =7.5 Hz, 1H), 7.39–7.21 (m, 8H), 5.37 (s, 1H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 163.8, 144.8, 141.0, 138.4, 135.9, 131.8, 128.6, 128.5, 128.42, 128.41, 126.2, 125.2, 120.1, 74.8, 21.2; HRMS (ESI): Exact mass calcd for $C_{21}H_{18}N$ $[M+H]^+$ 284.14392, Found 284.14466.



***N*-9-Fluorenyl-*o*-tolaldehyde imine (2d):** m.p.: 126–127 ºC; IR (KBr): 3017, 2963, 2883, 1626, 1598, 1476, 1449, 1395, 1379, 1370, 1285, 1228, 1043 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 9.08 (s, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 7.5 Hz, 2H),

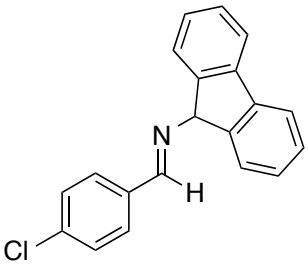
7.41–7.17 (m, 9H), 5.40 (s, 1H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 162.0, 144.8, 141.0, 137.6, 134.1, 130.7, 130.5, 128.4, 127.9, 127.4, 126.2, 125.2, 120.1, 75.2, 19.4; HRMS (ESI): Exact mass calcd for $C_{21}H_{18}N$ $[M+H]^+$ 284.14392, Found 284.14366.

***N*-9-Fluorenyl-2-naphthaldehyde imine (2e):** m.p.: 208 ºC (dec.); IR (KBr): 3046,



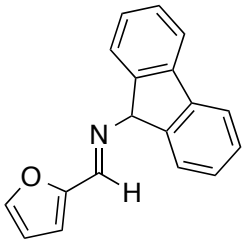
3022, 2868, 2832, 1956, 1630, 1596, 1343, 1303, 1274, 1174, 1121, 1042, 975, 958, 828, 782 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 8.93 (s, 1H), 8.16 (s, 1H), 8.02 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.90–7.82 (m, 3H), 7.77 (d, *J* =7.6 Hz, 2H), 7.53–7.29 (m, 8H), 5.49 (s, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 163.5, 144.8, 141.1, 134.9, 133.7, 133.1, 130.2, 128.7, 128.5, 128.2, 127.9, 127.5, 127.3, 126.5, 125.3, 124.3, 120.1, 74.8; HRMS (ESI): Exact mass calcd for $C_{24}H_{18}N$ $[M+H]^+$ 320.14392, Found 320.14393.

***N*-9-Fluorenyl-*p*-fluorobenzaldehyde imine (2f):** m.p.: 144 ºC (dec.); IR (KBr): 3067,

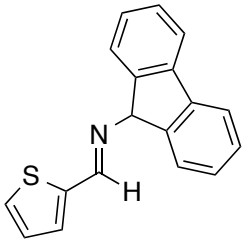


3023, 2871, 1637, 1594, 1572, 1489, 1449, 1377, 1274, 1082, 1045, 1011, 824, 766, 743 cm^{-1}; ^{1}H NMR ($CDCl_3$, 495.13 MHz): δ 8.72 (s, 1H), 7.76–7.73 (m, 4H), 7.42–7.24 (m, 8H), 5.42 (s, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 161.9, 144.5, 141.1, 137.0, 134.5, 129.7, 128.9, 128.5, 127.5, 125.2, 120.2, 74.5; HRMS (ESI): Exact mass calcd for $C_{20}H_{15}ClN$ $[M+H]^+$ 304.08930, Found 304.08997.

***N*-9-Fluorenyl-2-furanecarbaldehyde imine (2g):** m.p.: 121 ºC (dec.); IR (KBr): 3117,



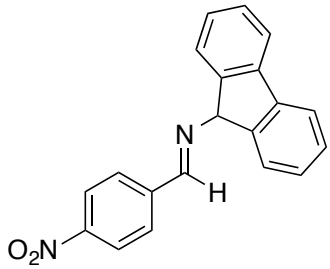
3078, 3017, 2885, 2853, 1958, 1923, 1639, 1478, 1447, 1393, 1363, 1300, 1272, 1155, 1050, 1021 cm^{-1}; ^{1}H NMR ($CDCl_3$, 495.13 MHz): δ 8.51 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.51 (s, 1H), 7.42–7.38 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 2H), 6.83 (d, *J* =3.5 Hz, 1H), 6.48 (m, 1H), 5.42 (s, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 151.4, 151.3, 144.9, 144.4, 141.0, 128.4, 127.3, 125.3, 119.9, 114.5, 111.7, 74.1; HRMS (ESI): Exact mass calcd for $C_{18}H_{14}NO$ $[M+H]^+$ 260.10754, Found 260.10639.



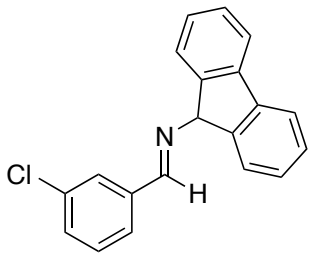
***N*-9-Fluorenyl-2-thiophenecarbaldehyde imine (2h):** m.p.: 139 ºC (dec.); IR (KBr): 3019, 2912, 2848, 1624, 1449, 1430, 1333, 1223, 1045, 1031 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 8.80 (s,

1H), 7.74 (d, J = 7.6Hz, 2H), 7.42–7.26 (m, 8H), 7.09–7.07 (m, 1H), 5.43 (s, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 156.2, 144.6, 142.2, 141.0, 130.9, 129.5, 128.4, 127.4, 127.3, 125.3, 120.1, 74.0; HRMS (ESI): Exact mass calcd for $C_{18}H_{14}NS$ $[M+H]^+$ 276.08470, Found 276.08497.

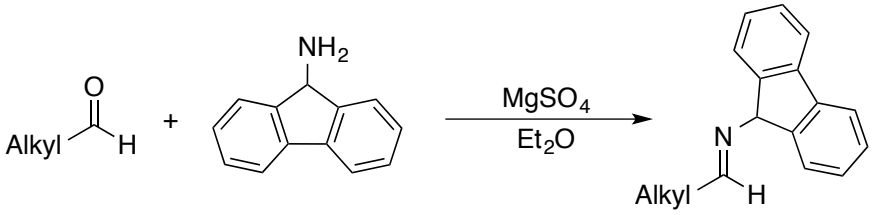
***N*-9-Fluorenyl-4-nitrobenzaldehyde imine (2n):** m.p.: 134 ºC (dec.); IR (KBr): 3437, 3035, 2831, 1639, 1600, 1519, 1449, 1340, 1279, 1048, 860, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$, 495.13 MHz): δ 8.82 (s, 1H), 8.25 (d, J =8.4 Hz, 2H), 7.96 (d, J = 8.3 Hz, 2H), 7.77 (d, J =7.6 Hz, 2H), 7.44–7.37 (m, 4H), 7.31 (td, J = 7.4, 0.8 Hz, 2 H), 5.51 (s, 1H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 160.7, 149.2, 144.0, 141.4, 141.1, 129.2, 128.7, 127.6, 125.2, 123.8, 120.3, 74.5; HRMS (ESI): Exact mass calcd for $C_{20}H_{15}N_2O_2$ $[M+H]^+$ 315.11335, Found 315.11186.



***N*-9-Fluorenyl-*m*-fluorobenzaldehyde imine (2o):** m.p.: 123–124 ºC; IR (KBr): 3069, 3040, 3016, 2865, 1634, 1567, 1475, 1449, 1363, 1272, 1217, 1181, 1098, 1072, 1035, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$, 495.13 MHz): δ 8.71 (s, 1H), 7.85 (s, 1H), 7.76 (d, J = 7.7 Hz, 2H), 7.65 (d, J = 7.5 Hz, 1H), 7.43–7.29 (m, 8H), 5.43 (s, 1H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 161.8, 144.4, 141.1, 137.8, 134.9, 130.9, 129.8, 128.6, 128.1, 127.5, 126.8, 125.2, 120.2, 74.5; HRMS (ESI): Exact mass calcd for $C_{20}H_{15}ClN$ $[M+H]^+$ 304.08930, Found 304.08855.



General procedure for preparation of aliphatic fluorenyl imines 2:

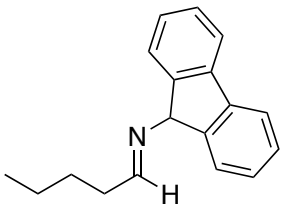


9*H*-9-fluorenylamine (0.700 g, 3.86 mmol) and well-dried anhydrous $MgSO_4$ (1.0 g) were placed in a flame dried 50 mL flask. Et_2O (20 mL) and an aliphatic aldehyde (4.63 mmol) were added to the flask via syringe, and the resulting mixture was stirred at room temperature for 30 min. Volatile materials were removed under reduced pressure, and then the residue was dissolved in Et_2O and passed through a short pad of Iatrobeads 6RS-8060 to remove remaining fluoreneamine. The crude mixture was

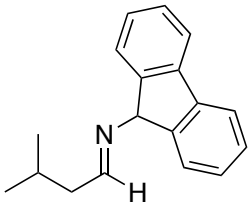
further purified by recrystallization (CH_2Cl_2/hexane).

The following compounds were prepared as described above unless otherwise noted. In the case of *N*-9-fluorenylisovaleraldehyde imine (**2j**), after filtration through a short pad of Iatrobeads 6RS-8060, the remaining solid was used for the reaction without further purification after complete removal of volatile solvent and aldehyde. In the case of *N*-9-fluorenylpentanealdehyde imine (**2i**), the 9-fluorenylamine (0.450 mmol (81.6 mg)) and pentanal (0.495 mmol (52.7 μL)) were used. After filtration through a pad of Celite and removal of all volatile materials under reduced pressure, the remaining oily product was used for the reaction immediately without further purification.

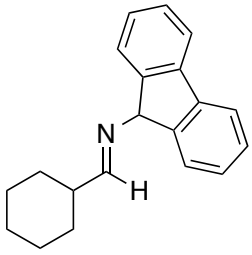
***N*-9-fluorenylpentanealdehyde imine (2i):** IR (KBr): 3066, 3041, 3020, 2956, 2928, 2858, 1659, 1450, 1377, 1302, 1100, 1030, 909 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 8.12 (t, *J* = 5.3 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.36–7.25 (m, 6H), 5.11 (s, 1H), 2.38 (td, *J* = 7.4, 5.3 Hz, 2H), 1.61–1.56 (m, 2H), 1.34–1.28 (qt, *J* = 7.4, 7.4 Hz, 2H), 0.93 (t, *J* =7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 168.2, 144.8, 141.0, 128.3, 127.3, 125.0, 120.0, 74.4, 35.9, 28.3, 22.4, 13.9; HRMS (ESI): Exact mass calcd for $C_{17}H_{18}N$ $[M+H]^+$ 250.15957, Found 250.15925.



***N*-9-fluorenylisovaleraldehyde imine (2j):** m.p.: 62–63 ºC; IR (KBr): 3064, 3040, 3018, 2952, 2929, 2865, 1655, 1464, 1448, 1382, 1305, 1154, 1018, 937 cm^{-1}; ^1H NMR ($CDCl_3$, 495.13 MHz): δ 8.18 (t, *J* = 5.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.39–7.26 (m, 6H), 5.16 (s, 1H), 2.3 (dd, *J* = 6.9, 5.3 Hz, 2H), 2.08–1.97 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 167.6, 144.7, 140.9, 128.2, 127.3, 124.9, 119.9, 74.5, 44.9, 26.4, 22.5; HRMS (ESI): Exact mass calcd for $C_{18}H_{20}N$ $[M+H]^+$ 250.15957, Found 250.15856.

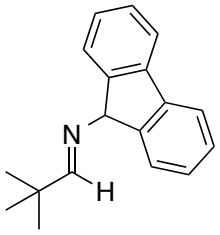


***N*-9-fluorenylcyclohexanecarbaldehyde imine (2k):** m.p.: 72–73 ºC; IR (KBr): 3064, 3040, 3020, 2925, 2852, 1654, 1447, 1374, 1303, 1280, 1099 cm^{-1}; ^1H NMR ($CDCl_3$, 495.13 MHz): δ 8.04 (d, *J* = 5.3 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.37 (td, *J* = 7.3, 1.1 Hz, 2H), 7.32–7.27 (m, 4H), 5.10 (s, 1H), 2.36–2.32 (m, 1H), 1.91–1.89 (m, 2H), 1.79–1.77 (m, 2H), 1.70–1.67 (m, 1H), 1.41–1.21 (m, 5H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 172.1, 144.9, 141.0, 128.2, 127.3, 124.9, 119.9, 74.4, 43.7, 29.9, 26.0,



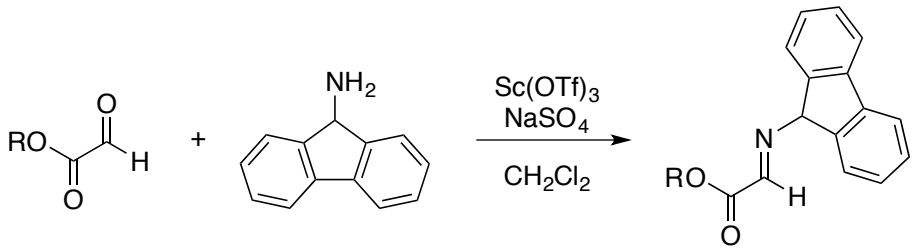
25.4; HRMS (ESI): Exact mass calcd for $C_{20}H_{22}N$ $[M+H]^+$ 276.17522, Found 276.17602.

***N*-9-fluorenylpivalaldehyde imine (2l):** m.p.: 142–143 ºC; IR (KBr): 3064, 3020, 2964,



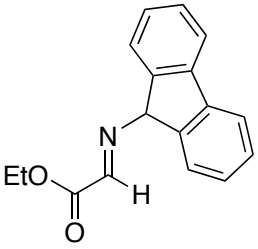
2928, 2867, 1957, 1919, 1655, 1475, 1448, 1397, 1373, 1363, 1301, 1102, 1057, 1031 cm^{-1}; ^1H NMR ($CDCl_3$, 600.13 MHz): δ 8.07 (s, 1H), 7.72 (d, J = 7.6 Hz, 2H), 7.39–7.36 (m, 2H), 7.30–7.28 (m, 4H), 5.11 (s, 1H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 175.5, 145.1, 141.0, 128.2, 127.3, 124.9, 120.0, 74.5, 36.5, 27.2; HRMS (ESI): Exact mass calcd for $C_{18}H_{20}N$ $[M+H]^+$ 250.15957, Found 250.15839.

General procedure for preparation of fluorenyl imines 2 derived from glyoxylate:



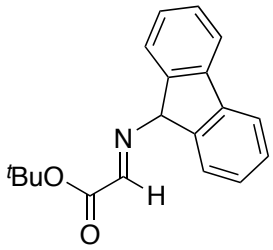
Under Ar atmosphere, 9*H*-9-fluorenylamine (1.00 g, 5.51 mmol), $Sc(OTf)_3$ (203mg 7.5 mol%) and Na_2SO_4 (400 mg) were measured in a well-dried 100 ml 2-neck round bottom flask. CH_2Cl_2 (30 ml) and glyoxylate (5.0 mmol) were added to the flask *via* syringe at room temperature, and the white suspension was immediately generated. The resulting solution was stirred at the same temperature for 1 h. The solution was diluted with another CH_2Cl_2 (30 ml) followed by filtration through filter paper, and the clear filtrate was collected. The solvent was removed under reduced pressure to obtain a crude mixture of the desired product. Recrystallization of the crude material using hexane/Et_2O was conducted to afford the pure desired product.

***N*-9-fluorenylethylglyoxylate imine (2m):** m.p.: 65 ºC (dec.). IR (neat) 3464,

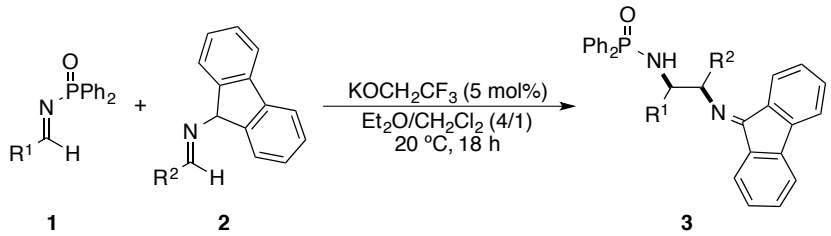


2975,1742, 1448,1184,1029: ^1H NMR ($CDCl_3$, 495.13 MHz): δ 8.04 (s, 1H), 7.72 (d, J = 7.4 Hz, 2H), 7.41–7.37 (m, 4H), 7.29 (t, J = 7.4 Hz, 2H), 5.58 (s, 1H), 4.33 (q, J = 6.9 Hz, 2H), 1.32 (t, J = 6.9 Hz, 3H);^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 163.2, 154.9, 142.71, 141.24, 128.9, 127.6, 125.5, 120.2, 73.4, 62.0, 14.1. HRMS (ESI): Exact mass calcd for $C_{18}H_{20}N$ $[M+H]^+$ 266.11756, Found 266.11810.

***N*-9-fluorenyl*tert*-butylglyoxylate imine (2p):** m.p.: 73 ºC (dec.). IR (neat): 3464, 2975, 1742, 1448, 1184, 1029: ^{1}H NMR ($CDCl_3$, 495.13 MHz): δ 7.92 (s, 1H), 7.72 (d, J = 7.4 Hz, 2H), 7.42–7.38 (m, 4H), 7.31 (t, J = 7.4 Hz, 2H), 5.60 (s, 1H), 1.52 (s, 9H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 162.1, 156.0, 142.9, 141.1, 128.8, 127.5, 125.6, 120.2, 82.8, 73.1, 27.9. HRMS (ESI): Exact mass calcd for $C_{18}H_{20}N$ $[M+H]^+$ 294.14886, Found 294.14940.



General procedure for catalytic imine–imine cross-coupling reaction:

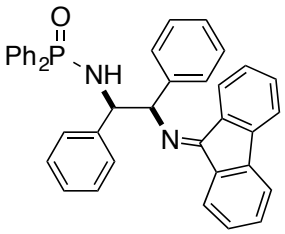


Under Ar atmosphere, fluorenyl substrate **2** (0.30 mmol) and $KOCH_2CF_3$ (0.015 mmol) were placed in a flame-dried test tube with a sleeve stopper. Dry Et_2O (1.2 mL) was added to the test tube via syringe, and the resulting mixture was stirred at room temperature for 10 min, and then kept at 20 ºC. DPP–imine **1** (0.36 mmol) in dichloromethane (0.3 mL) was added to the mixture at the same temperature, and the whole was stirred for another 18 hours under Ar. The reaction was quenched with a saturated aqueous NH_4Cl solution, and the mixture was extracted with dichloromethane (10 mL x 3). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was obtained. The crude product was purified by column chromatography on silica gel (hexane-acetone) to afford the desired adduct **3**.

The following compounds were prepared as described above unless otherwise noted. In the cases of using 18-crown-6 or phenol derivatives as additives, an additive and a base (0.015 mmol each) were combined in a flame dried test tube with a sleeve stopper. Dry Et_2O (0.5 mL) was added to the test tube via syringe, and the resulting mixture was stirred at room temperature for 10 min. The mixture was transferred to the test tube with suspension of the fluorenyl substrate (0.3 mmol) in Et_2O (0.5 mL) via cannula, and the test tube was washed with Et_2O (0.2 mL). After stirring at room

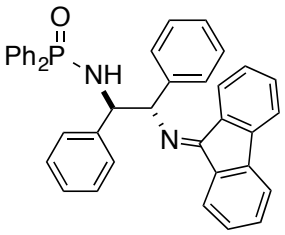
temperature for 10 min, DPP–imine (**1**) (0.36 mmol) in dichloromethane (0.3 mL) was added to the mixture at 20 ºC, and the whole was stirred for another 18 h under Ar.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1,2-diphenylethyl)-*P*,*P*-diphenylphosphinic amide (3aa-*syn*)[3]:** ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.87 (d, J = 7.4 Hz, 1H),



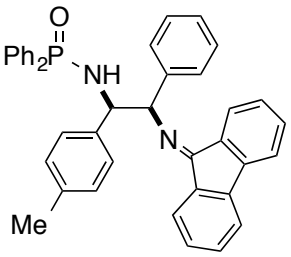
7.73–7.70 (m, 2 H), 7.51 (d, J = 7.6 Hz, 2H), 7.44–7.19 (m, 19H), 7.16 (t, J = 7.7 Hz, 2H), 7.09 (t, J = 7.3 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 5.71 (s, 1H), 5.07 (dd, J = 10.3, 8.0 Hz, 1H), 4.61 (ddd, J = 9.8, 7.5, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 165.2, 144.1 142.9, 141.9, 141.5, 138.4, 134.37, 133.50, 132.55, 132.46, 132.43, 132.36, 131.71, 131.7, 131.6, 131.5, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.7, 127.4, 127.2, 122.8, 120.4, 119.6, 70.3 (J_{PC} = 7.6 Hz), 62.8; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.7.

***N*-((1*RS*,2*SR*)-2-((9*H*-fluoren-9-ylidene)amino)-1,2-diphenylethyl)-*P*,*P*-diphenylphosphinic amide (3aa-*anti*):** m.p.: 160 ºC (dec.); IR (KBr): 3386, 3173, 3059, 3028,



2900, 1645, 1601, 1450, 1438, 1174, 1123, 1112 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.97 (d, J =7.4 Hz, 1H), 7.75 (dd, J =12.1, 7.6 Hz, 4H), 7.54–7.53 (m, 3H), 7.42–7.24 (m, 9H), 7.16–7.05 (m, 9H), 6.97–6.95 (m, 2H), 6.00 (d, J =3.8 Hz, 1H), 4.74 (ddd, J = 10.5, 10.5, 3.8 Hz, 1H), 4.14 (dd, J = 10.9, 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 165.6, 143.8, 141.3, 140.6, 139.9 (J_{PC} =5.6 Hz), 138.7, 133.4, 133.0, 132.5 (J_{PC} = 9.9 Hz), 132.1, 131.8 (J_{PC} = 9.6 Hz), 131.61, 131.56, 131.4, 131.2, 131.1, 128.33, 128.29 (J_{PC} = 88.3 Hz), 128.27, 128.25, 128.19, 128.13, 128.09, 127.3 (J_{PC} = 39.4 Hz), 126.9 (J_{PC} = 21.5 Hz), 122.6, 120.0, 199.3, 70.3 (J_{PC} = 2.8Hz), 61.7; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 24.1; HRMS (ESI): Exact mass calcd for $C_{39}H_{32}N_2OP$ $[M+H]^+$ 575.22523, Found 575.22781.

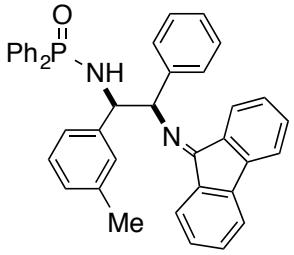
***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-2-phenyl-1-(*p*-tolyl)ethyl)-*P*,*P*-diphenylphosphinic amide (3ba-*syn*):** m.p.: 145–146 ºC; IR (KBr): 3356, 3058, 2917, 1650,



1600, 1513, 1492, 1449, 1439, 1394, 1304, 1235, 1189, 1121, 1028, 975, 905 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.87 (d, J = 7.2 Hz, 1H), 7.75–7.71 (m, 2H), 7.49 (d, J = 7.4 Hz, 2H), 7.43–7.19 (m, 17H), 7.15 (d, J = 7.7 Hz, 2H), 7.01 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 7.5 Hz, 2H), 5.70 (s, 1H), 5.02 (dd, J =

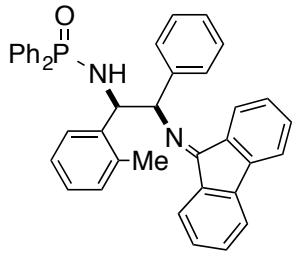
10.1, 7.8 Hz, 1H), 4.57 (dd, J = 10.2, 7.1 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.8, 143.9, 141.8, 141.3, 139.8, 138.7, 138.5, 138.2, 136.4, 134.3, 133.5, 132.6, 132.3 (J_{PC} = 9.2 Hz), 132.2 (J_{PC} = 9.3 Hz), 131.8, 131.40, 131.36, 131.3, 131.2, 128.4, 128.24, 128.16, 128.07, 128.0, 127.6, 127.5, 127.4, 127.1, 122.6, 120.1, 119.3, 70.2 (J_{PC} = 7.7 Hz), 62.4, 21.0; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.5; HRMS (ESI): Exact mass calcd for $C_{40}H_{34}N_2OP$ $[M+H]^+$ 589.24088, Found 589.23939.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-2-phenyl-1-(*m*-tolyl)ethyl)-*P*,*P*-diph enylphosphinic amide (3ca-*syn*):** m.p.: 160 ºC (dec.); IR (KBr): 3346, 3058, 3023,



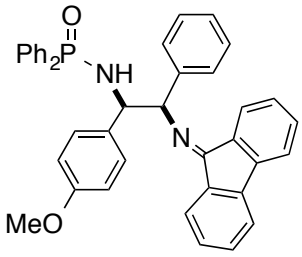
1656, 1606, 1491, 1449, 1440, 1398, 1306, 1236, 1214, 1157, 1121, 1027, 973 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.81 (d, J = 7.4 Hz, 1H), 7.64 (dd, J =11.9, 7.6 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.37–7.12 (m, 17H), 7.03–6.93 (m, 4H), 6.82 (d, J = 7.4 Hz, 1H), 5.61 (s, 1H), 4.99 (dd, J = 10.4, 8.1 Hz, 1H), 4.49 (ddd, J = 9.7, 7.7, 2.0 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.9, 143.9, 142.6, 141.7, 171.2, 138.2, 137.3, 134.1, 133.3, 132.5, 132.3 (J_{PC} = 9.6 Hz), 132.2 (J_{PC} = 9.6 Hz), 131.5, 131.4, 131.3, 131.2, 130.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.94, 127.89, 127.7, 127.6, 127.5, 127.4, 124.3, 122.6, 120.1, 119.4, 70.1 (J_{PC} = 8.0 Hz), 62.6, 21.4; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.9; HRMS (ESI): Exact mass calcd for $C_{40}H_{34}N_2OP$ $[M+H]^+$ 589.24088, Found 589.23885.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-2-phenyl-1-(*o*-tolyl)ethyl)-*P*,*P*-diph enylphosphinic amide (3da-*syn*):** m.p.: 74–76 ºC; IR (KBr): 3358, 3057, 1648, 1600,

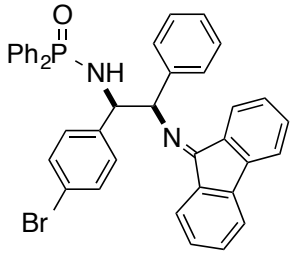


1491, 1449, 1438, 1406, 1303, 1195, 1122, 1073 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.88 (d, J = 7.5 Hz, 1H), 7.73–7.69 (m, 2H), 7.49 (d, J = 7.5 Hz, 2H), 7.42–7.19 (m, 17H), 7.09–6.99 (m, 4H), 6.88 (d, J = 7.3 Hz, 1H), 5.70 (s, 1H), 5.02 (dd, J =10.3, 8.0 Hz, 1H), 4.58 (ddd, J =10.1, 7.6, 2.0 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 165.0, 143.8, 141.7, 141.1, 140.6, 138.0, 133.8, 133.7, 133.0, 132.3, 132.2, 132.2, 132.1, 131.5, 131.4, 131.3, 131.2, 131.1, 129.7, 128.5, 128.3, 128.14, 128.06, 127.8, 127.7, 127.4, 127.3, 127.2, 126.7, 125.8, 122.5, 120.1, 119.3, 68.2 (J_{PC} = 7.1 Hz), 58.2, 19.1; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.9; HRMS (ESI): Exact mass calcd for $C_{40}H_{34}N_2OP$ $[M+H]^+$ 589.24088, Found 589.24321.

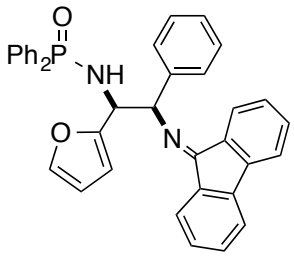
***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1-*p*-methoxyphenyl-2-phenylethyl)-*P*,*P*-diphenylphosphinic amide (3ea-*syn*):** m.p.: 98–100 ºC; IR (KBr): 3425, 1648, 1609, 1512, 1449, 1439, 1249, 1179, 1122 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.75–7.71 (m, 2H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.44–7.18 (m, 19H), 7.04–7.01 (m, 1H), 6.71–6.69 (m, 2H), 5.68 (s, 1H), 5.05–5.02 (m, 1H), 4.55 (ddd, *J* = 9.4, 7.0, 2.4 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.9, 158.5, 143.9, 141.7, 141.2, 138.1, 135.0, 134.2, 133.3, 132.3 (J_{PC} = 9.4 Hz), 312.2 (J_{PC} = 9.5 Hz), 131.5, 131.4, 131.3, 131.2, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 127.4, 122.6, 120.2, 119.4, 113.4, 112.6, 112.2, 70.2 (J_{PC} = 8.6 Hz), 62.0, 55.1; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.5; HRMS (ESI): Exact mass calcd for $C_{40}H_{34}N_2O_2P$ $[M+H]^+$ 605.23579, Found 605.23484.



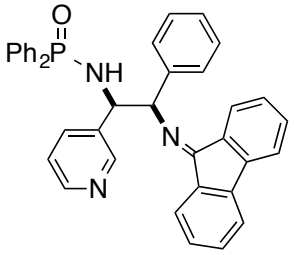
***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1-*p*-bromophenyl-2-phenylethyl)-*P*,*P*-diphenylphosphinic amide (3fa-*syn*)[3]:** ^1H NMR ($CDCl_3$, 600.17 MHz): δ 7.84 (d, *J* = 7.4 Hz, 1H), 7.74–7.71 (m, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.44–7.17 (m, 21H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.66 (s, 1H), 5.05 (dd, *J* = 10.2, 8.1 Hz, 1H), 4.57 (ddd, *J* = 9.8, 7.2, 2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 165.3, 143.9, 141.7, 141.2 (J_{PC} = 3.4 Hz), 137.9, 133.9, 133.1, 132.2 (J_{PC} = 9.8 Hz), 132.0 (J_{PC} = 9.4 Hz), 131.6, 131.4, 131.3, 131.0, 128.9, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 127.4, 122.4, 120.9, 120.2, 119.4, 69.8 (J_{PC} = 7.8 Hz), 62.0; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.7.



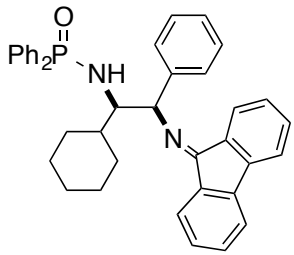
***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1-(2-furyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic amide (3ga-*syn*)[3]:** ^1H NMR ($CDCl_3$, 495.13 MHz): δ 7.82–7.76 (m, 3H), 7.53–7.15 (m, 20H), 7.06 (t, *J* = 7.7 Hz, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 6.16–6.15 (m, 1H), 6.02 (s, 1H), 4.83 (dd, *J* = 10.4, 7.4 Hz, 1H), 4.65–4.61 (m, 1H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 164.7, 155.0, 143.8, 141.2, 141.1, 141.1, 138.1, 134.0, 133.0, 132.3 (J_{PC} =9.5 Hz), 132.0 (J_{PC} = 8.5Hz), 131.5, 131.4, 131.3, 131.23, 131.17, 130.8, 138.5, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 122.6, 120.1, 119.3, 110.4, 108.2, 66.8 (J_{PC} = 7.0 Hz), 56.9; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.6.



***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-2-phenyl-1-(3-pyridyl)ethyl)-*P*,*P*-di phenylphosphinic amide (3ha-*syn*):** m.p.: 160 ºC (dec.); IR (KBr): 3309, 3056, 1647, 1599, 1450, 1439, 1402, 1308, 1196, 1120, 1028, 974, 914 cm^{-1}; ^{1}H NMR ($CDCl_3$, 399.78 MHz): δ 8.35 (s, 1H), 8.27 (d, J = 4.8 Hz, 1H), 7.76 (d, J = 7.4 Hz, 1H), 7.66–7.61 (m, 3H), 7.41–7.02 (m, 20H), 6.93 (t, J = 7.7 Hz, 1H), 5.61 (s, 1H), 4.96 (dd, J =10.2, 8.1 Hz, 1H), 4.57 (ddd, J = 9.6, 7.3, 2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 165.6, 148.5 (J_{PC} = 26.2 Hz), 143.9, 141.3, 140.8, 138.0, 137.9, 135.1, 133.7, 132.8, 132.1 (J_{PC} = 10.1 Hz), 132.0 (J_{PC} = 10.1 Hz), 131.7, 131.5, 131.0, 128.7, 128.42, 128.37, 128.32, 128.29, 128.24, 128.0, 127.8, 127.5, 127.5, 123.0, 122.5, 120.2, 119.4, 69.7 (J_{PC} = 7.4 Hz), 60.3; ^{31}P NMR ($CDCl_3$, 200.43 Hz): δ 21.9; HRMS (ESI): Exact mass calcd for $C_{38}H_{31}N_3OP$ $[M+H]^+$ 576.22047, Found 576.22167.

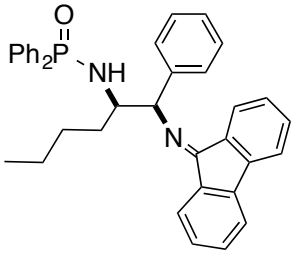


***N*-((1*R*,2*R*)-2-((9*H*-fluoren-9-ylidene)amino)-1-cyclohexyl-2-phenylethyl)-*P*,*P*-diphe nylphosphinic amide (3ia-*syn*)[3]:** ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.94–7.86 (m, 2H), .7.79 (d, J = 7.4 Hz, 1H), 7.61–7.57 (m, 2H), 7.46–7.28 (m, 13H), 7.23–7.13 (m, 4H), 7.09 (td, J = 7.7, 0.8 Hz, 1H), 5.75 (s, 1H), 4.87 (dd, J = 10.6 Hz, 1H), 3.31–3.28 (m, 1H), 1.93 (m, 1H), 1.77–1.53 (m, 5H), 1.21–1.02 (m, 5H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.0, 144.0, 143.2, 141.3, 138.2, 135.3, 134.4, 132.6 (J_{PC} = 9.4 Hz), 132.1 (J_{PC} = 9.4 Hz), 131.5, 131.4, 131.3, 130.9, 128.5, 128.3, 128.2, 128.0 (J_{PC} = 12.6 Hz), 127.4, 127.3, 127.0, 122.6, 120.3, 119.4, 64.8 (J_{PC} = 8.2 Hz), 64.0, 44.5, 30.3, 29.2, 26.7, 26.4; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 20.4.



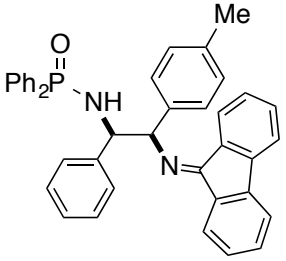
***N*-((1*RS*,2*RS*)-1-((9*H*-fluoren-9-ylidene)amino)-4-methyl-1-phenylpentan-2-yl)-*P*,*P*-diphenylphosphinic amide (3ja-*syn*)[3]:** ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.87–7.82 (m, 3H), 7.61–7.54 (m, 3H), 7.46–7.19 (m, 16H), 7.12 (t, J = 7.6 Hz, 1H), 5.64 (s, 1H), 4.32–4.29 (m, 1H), 3.47–3.41 (m, 1H), 1.81–1.67 (m, 3H), 0.83 (d, J = 6.3 Hz, 3H), 0.72 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.7, 143.9, 142.4, 141.2, 138.2, 134.6, 133.7, 132.5 (d, J_{PC} = 9.0 Hz), 132.2 (d, J_{PC} = 9.2 Hz), 131.5, 131.4, 131.3, 131.1, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 127.7, 127.5, 127.1, 122.6, 120.3, 119.4, 65.9 (d, J_{PC} = 8.1 Hz), 56.9, 45.5, 24.6, 23.1, 22.2; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 23.2.

***N*-((1*RS*,2*RS*)-1-((9*H*-fluoren-9-ylidene)amino)-1-phenylhexan-2-yl)-*P*,*P*-diphenylphosphinic amide (3ka-*syn*):** m.p.: 79 ºC (dec.); IR (KBr): 3058, 2954, 2927, 2869,



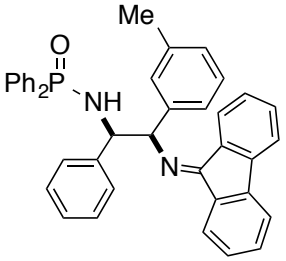
1648, 1601, 1450, 1439, 1401, 1304, 1193, 1122, 1110, 795 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 7.97–7.91 (m, 3H), 7.68–7.60 (m, 3H), 7.52–7.26 (m, 16H), 7.20–7.18 (m, 1H), 5.80 (s, 1H), 4.42 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.49–3.46 (m, 1H), 2.04–1.88 (m, 2H), 1.51–1.48 (m, 1H), 1.36–1.24 (m, 3H), 0.87 (t, *J* =7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.6, 143.6, 141.1, 138.1, 134.5, 133.7, 132.4 (J_{PC} = 9.2 Hz), 132.2, 131.9 (J_{PC} = 8.9 Hz), 131.3 (J_{PC} = 5.2 Hz), 131.14, 131.12, 131.0, 128.3, 128.2, 128.1 (J_{PC} = 5.7 Hz), 128.05, 128.02, 127.6, 127.4, 127.0, 122.5, 120.1, 119.3, 65.6 (J_{PC} = 8.1 Hz), 58.8, 35.8, 28.4, 22.4, 13.9; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 20.4; HRMS (ESI): Exact mass calcd for $C_{37}H_{36}N_2OP$ $[M+H]^+$ 555.25653, Found 555.25620.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1-phenyl-2-(*p*-tolyl)ethyl)-*P*,*P*-diphenylphosphinic amide (3ab-*syn*)[3]:** ^1H NMR ($CDCl_3$, 600.17 MHz): δ 7.88 (d, *J* = 7.4



Hz, 1H), 7.74 (dd, J = 11.8, 7.6 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.45–7.17 (m, 20 H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 5.65 (s, 1H), 5.16 (t, *J* = 9.5 Hz, 1H), 4.57 (ddd, *J* = 9.9, 7.7, 2.3 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.9, 143.8, 142.9, 141.0, 138.7, 138.1, 137.0, 134.0, 133.1, 132.3 (J_{PC} = 9.3 Hz), 132.1 (J_{PC} = 9.4 Hz), 131.6, 131.4, 131.3, 131.1, 129.2, 128.3 (J_{PC} = 7.9 Hz), 128.2 (J_{PC} = 6.4 Hz), 128.1, 128.00, 127.95, 127.5, 127.4, 127.2, 127.0, 122.5, 120.1, 119.4, 69.9 (J_{PC} = 8.1 Hz), 62.5, 21.2; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.9.

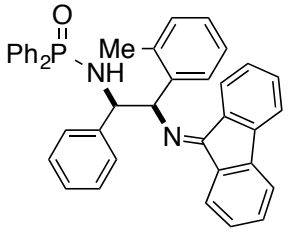
***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1-phenyl-2-(*m*-tolyl)ethyl)-*P*,*P*-diphenylphosphinic amide (3ac-*syn*):** m.p.: 164–166 ºC; IR (KBr): 3345, 3058, 1649, 1606,



1450, 1439, 1401, 1304, 1236, 1200, 1120, 1072 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 7.88–7.86 (m, 1H), 7.77–7.74 (m, 2H), 7.46–7.16 (m, 22H), 7.09–7.06 (m, 1H), 7.01–6.98 (m, 1H), 5.67 (s, 1H), 5.16–5.12 (m, 1H), 4.60–4.56 (m, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.8, 143.8, 142.8, 141.7, 141.2, 138.1, 134.2, 133.4, 132.3 (J_{PC} = 9.5 Hz), 132.1 (J_{PC} = 9.5 Hz), 131.4, 131.3, 131.2, 131.1, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.4, 127.1,

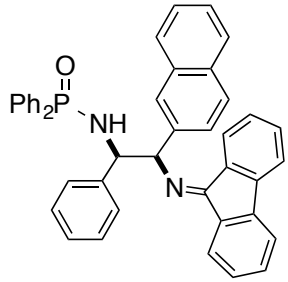
126.9, 124.6, 122.5, 120.1, 119.3, 70.1 (J_{PC} = 7.5 Hz), 62.6, 21.5; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.5; HRMS (ESI): Exact mass calcd for $C_{40}H_{34}N_2OP$ $[M+H]^+$ 589.24088, Found 589.24140.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1-phenyl-2-(*o*-tolyl)ethyl)-*P*,*P*-diph enylphosphinic amide (3ad-*syn*):** m.p.: 185 ºC (dec.); IR (KBr): 3355, 3058, 1648,



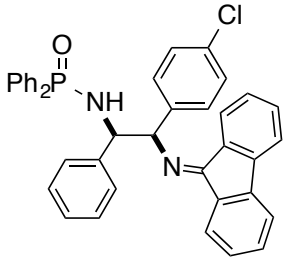
1603, 1450, 1439, 1402, 1304, 1244, 1199, 1120 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.89 (d, *J* = 7.4 Hz, 1H), 7.80–7.77 (m, 2H), 7.49–7.08 (m, 23H), 6.97 (t, *J* =7.8 Hz, 1H), 5.68 (s, 1H), 5.37 (dd, *J* = 10.8, 8.5 Hz, 1H), 4.50 (dd, *J* = 10.8, 6.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 164.9, 143.9, 143.5, 141.2, 140.2, 138.1, 134.6, 132.4 (J_{PC} = 9.8 Hz), 132.1 (J_{PC} = 9.7 Hz), 131.5, 131.4, 131.3, 131.2, 131.0, 128.4, 128.3, 128.22, 128.16, 128.08, 127.9, 127.8, 127.5, 127.0, 126.7, 126.5, 126.0, 122.5, 120.2, 119.4, 67.1 (J_{PC} = 8.3 Hz), 59.1, 19.3; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.2; HRMS (ESI): Exact mass calcd for $C_{40}H_{34}N_2OP$ $[M+H]^+$ 589.24088, Found 589.23918.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-2-(2-naphthyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic amide (3ae-*syn*):** m.p.: 114 ºC (dec.); IR (KBr): 3366, 3057, 1648,



1602, 1450, 1439, 1400, 1303, 1197, 1122, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.94 (d, *J* = 7.4 Hz, 1H), 7.89–7.60 (m, 4H), 7.68–7.64 (m, 2H), 7.56–7.10 (m, 20H), 6.97–6.92 (m, 3H), 5.86 (s, 1H), 5.15 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.69 (ddd, *J* = 9.6, 7.4, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 165.3, 143.9, 142.8, 141.3, 139.1, 138.1, 134.0, 133.4, 133.2, 132.9, 132.14, 132.12, 132.07, 131.5, 131.4, 131.1, 128.4 (J_{PC} = 7.2 Hz), 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.2, 127.0, 126.3, 126.0, 125.7, 122.7, 120.2, 119.4, 70.2 (J_{PC} = 8.0 Hz), 62.4; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 21.9; HRMS (ESI): Exact mass calcd for $C_{43}H_{34}N_2OP$ $[M+H]^+$ 625.24088, Found 625.24051.

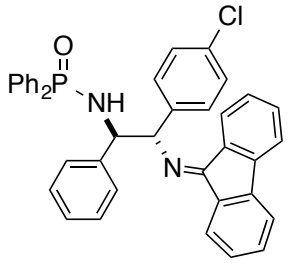
***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-2-(4-chlorophenyl)-1-phenylethyl)-**



***P*,*P*-diphenylphosphinic amide (3af-*syn*)[3]:** ^{1}H NMR ($CDCl_3$, 495.13 MHz): δ 7.99 (d, *J* = 7.4 Hz, 1H), 7.88–7.84 (m, 2H), 7.58–7.22 (m, 23H), 7.11 (t, *J* =7.7 Hz, 1H), 5.88 (s, 1H), 5.10 (dd, *J* = 10.4, 8.2 Hz, 1H), 4.77 (ddd, *J* = 10.0, 7.5, 2.6 Hz, 1H);

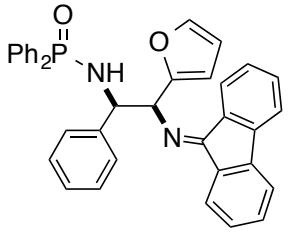
^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 165.0, 143.7, 142.0, 131.0, 139.7, 137.8, 133.6, 133.0, 132.5, 131.9, 131.8, 131.4, 131.3, 130.8, 128.8, 128.5, 128.19, 128.17, 128.1, 128.0, 127.9, 127.8, 127.2, 127.03, 126.97, 122.3, 120.1, 119.3, 69.1 (J_{PC} = 7.5 Hz), 62.1; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 24.4.

***N*-((1*RS*,2*SR*)-2-((9*H*-fluoren-9-ylidene)amino)-2-(4-chlorophenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic amide (3af-*anti*):** m.p.: 185 ºC (dec.); IR (KBr): 3176, 3059,



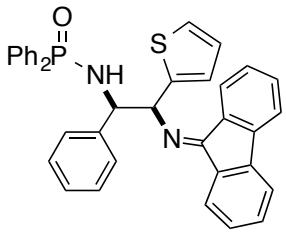
1644, 1606, 1489, 1449, 1438, 1178, 1124, 1110 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.86 (d, *J* = 7.4 Hz, 1h), 7.64 (dd, *J* = 12.1, 7.6 Hz, 4H), 7.45–6.93 (m, 20H), 6.81 (d, *J* = 8.2 Hz, 2H), 5.92 (d, *J* = 3.8 Hz, 1H), 4.61 (td, *J* = 10.7, 3.6 Hz, 1H), 4.06 (dd, *J* = 11.0, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 165.9, 143.8, 141.3, 139.4 (J_{PC} = 5.6 Hz), 138.5, 133.3, 132.6, 132.4, 132.4, 131.6, 131.6, 131.5, 131.3, 130.9, 128.7, 128.6, 128.32, 128.27, 128.23, 128.20, 128.15, 128.1, 128.0, 127.3, 127.0, 122.6, 120.1, 119.4, 69.4, 61.5; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 24.5; HRMS (ESI): Exact mass calcd for $C_{39}H_{31}ClN_2OP$ $[M+H]^+$ 609.18625, Found 609.18381.

***N*-((1*RS*,2*SR*)-2-((9*H*-fluoren-9-ylidene)amino)-2-(furan-2-yl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic amide (3ag-*syn*):** m.p.: 96 ºC (dec.); IR (KBr): 3365, 3058, 1713,



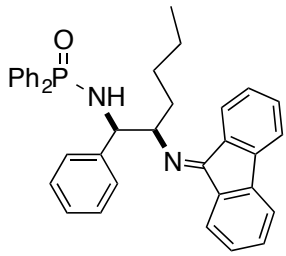
1647, 1600, 1450, 1439, 1406, 1305, 1194, 1123, 1071, 1007, 917 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.71–7.66 (m, 3H), 7.47 (dd, *J* = 12.1, 7.6 Hz, 2H), 7.49–6.96 (m, 18H), 6.88 (t, *J* = 7.8 Hz, 1H), 6.28 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 5.62 (s, 1H), 5.13 (dd, *J* = 10.2, 8.5 Hz, 1H), 4.79–4.75 (m, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 166.2, 152.5, 143.6, 142.3, 141.7, 141.1, 137.8, 133.8, 132.9, 132.6, 132.2, 132.12, 132.10, 132.06, 131.8, 131.6, 131.4, 131.3, 131.0, 128.22, 128.15, 128.1, 127.94, 127.88, 127.3, 127.0, 126.9, 122.5, 120.1, 199.3, 110.4, 107.9, 65.2 (d, J_{PC} = 6.9 Hz), 59.0; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 22.3; HRMS (ESI): Exact mass calcd for $C_{37}H_{30}N_2O_2P$ $[M+H]^+$ 565.20449, Found 565.20663.

***N*-((1*RS*,2*SR*)-2-((9*H*-fluoren-9-ylidene)amino)-1-phenyl-2-(thiophen-2-yl)ethyl)-*P*,*P*-diphenylphosphinic amide (3ah-*syn*):** m.p.: 117–118 ºC; IR (KBr): 3348, 3059, 1648, 1599, 1450, 1439, 1397, 1303, 1193, 1122, 1071 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.72–7.68 (m, 2H), 7.46–6.94 (m, 23H), 5.93 (s, 1H),



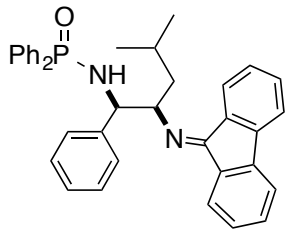
4.94 (dd, J = 10.3, 8.1 Hz, 1H), 4.59 (ddd, J = 10.2, 7.4, 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 143.9, 143.8, 141.9, 141.2, 138.0, 133.7, 132.9, 132.7, 132.3, 132.2, 132.1, 131.8, 131.6, 131.5, 131.4, 131.4, 131.2, 128.4, 128.3, 128.24, 128.19, 128.15, 128.1, 127.9, 127.5, 127.3, 127.1, 126.6, 124.7, 124.9, 124.3, 122.7, 120.2, 119.4, 66.3 (J_{PC} = 6.9 Hz), 62.7; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 22.3; HRMS (ESI): Exact mass calcd for $C_{37}H_{30}N_2OPS$ $[M+H]^+$ 581.18165, Found 581.17962.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1-phenylhexyl)-*P*,*P*-diphenylphosphinic amide (3ai-*syn*):** m.p.: 61–63 ºC (dec.); IR (KBr): 3347, 3058, 2954, 2928, 2858,



1647, 1602, 1449, 1439, 1402, 1304, 1199, 1122, 1110, 1069 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.97–7.93 (m, 2H), 7.79–7.73 (m, 3H), 7.52–7.02 (m, 18H), 5.24 (dd, J = 9.5, 8.4 Hz, 1H), 4.59–4.53 (m, 2H), 2.31–2.27 (m, 1H), 1.76–1.71 (m, 1H), 1.56–1.35 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 162.1, 144.0, 143.7, 140.7, 138.2, 134.2, 133.1, 132.5 (J_{PC} = 9.7 Hz), 132.1, 131.9 (J_{PC} = 9.3 Hz), 131.6, 131.5, 131.4, 131.1, 130.9, 128.8, 128.4 (J_{PC} = 12.6 Hz), 128.1 (J_{PC} = 11.5 Hz), 128.0, 127.8, 127.7, 126.7, 126.6 (J_{PC} = 3.7 Hz), 122.3, 120.2, 119.2, 66.5 (J_{PC} = 3.8 Hz), 57.2, 33.0, 28.8, 22.7, 14.1; ^{31}P NMR ($CDCl_3$, 200.43 Hz): δ 23.1; HRMS (ESI): Exact mass calcd for $C_{37}H_{36}N_2OP$ $[M+H]^+$ 555.25658, Found 555.25764.

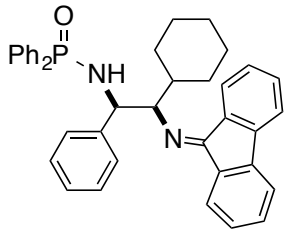
***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-4-methyl-1-phenylpentyl)-*P*,*P*-diphenylphosphinic amide (3aj-*syn*):** m.p.: 181 ºC (dec.); IR (KBr): 3259, 3060, 2954,



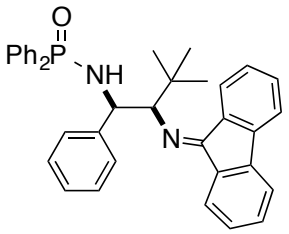
1656, 1606, 1450, 1439, 1403, 1302, 1123, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.95–7.92 (m, 2H), 7.74–7.71 (m, 3H), 7.58–7.24 (m, 12H), 7.15–7.04 (m, 6H), 5.20 (t, J =9.3 Hz, 1H), 4.77–4.75 (m, 1H), 4.55 (t, J = 10.2 Hz, 1H), 2.18–2.13 (m, 1H), 1.92–1.86 (m, 1H), 1.60–1.55 (m, 1H), 1.05 (d, J = 6.7 Hz, 3H), 0.98 (d, J = 6.5, 3H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 161.8, 144.1, 143.8, 140.8, 138.3, 134.2, 133.4, 133.1, 132.5 (J_{PC} = 8.2 Hz), 132.2, 131.9 (J_{PC} = 8.2 Hz), 131.61, 131.57, 131.4, 131.1, 130.9, 128.5 (J_{PC} = 11.4 Hz), 128.2, 128.1, 128.0, 127.8, 126.7, 126.6, 122.3, 120.2, 119.2, 64.0 (J_{PC} = 4.4 Hz), 57.1, 41.4, 24.9, 21.9; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 23.2; HRMS (ESI): Exact mass calcd for

$C_{37}H_{36}N_2OP$ $[M+H]^+$ 555.25658, Found 555.25661.

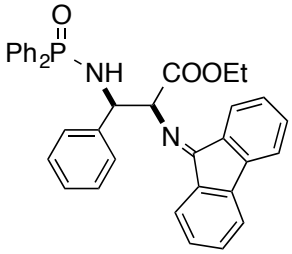
***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-2-cyclohexyl-1-phenylethyl)-*P*,*P*-di phenylphosphinic amide (3ak-*syn*):** m.p.: 82–84 ºC; IR (KBr): 3379, 3058, 2926, 2850, 1648, 1609, 1449, 1439, 1400, 1302, 1205, 1123, 1069 cm^{-1}; ^1H NMR (CDCl3, 600.17 MHz): δ 7.94–7.91 (m, 2H), 7.76–7.72 (m, 3H), 7.51–7.21 (m, 12H), 7.05–6.92 (m, 6H), 5.10 (dd, *J* = 9.1, 8.6 Hz, 1H), 4.75 (dd, *J* = 10.7, 9.4 Hz, 1H), 4.43 (d, *J* = 8.6 Hz, 1H), 2.28–2.19 (m, 2H), 1.84–0.84 (m, 9H); ^{13}C NMR ($CDCl_3$ 151.91 MHz): δ 162.6, 143.8, 143.7, 140.7, 138.2, 134.2, 133.3, 133.1, 132.4 (J_{PC} = 9.6 Hz), 132.2, 132.0 (J_{PC} = 9.3 Hz), 131.6, 131.4, 130.8 (J_{PC} = 13.8 Hz), 128.4 (J_{PC} = 12.6 Hz), 128.1 (J_{PC} = 8.7 Hz), 128.0, 127.8, 127.5, 126.6, 126.5, 126.5, 122.4, 120.0, 119.1, 71.1 (J_{PC} = 3.7 Hz), 56.2, 40.0, 30.5, 29.8, 26.4, 26.2, 26.1; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 23.0; HRMS (ESI): Exact mass calcd for $C_{39}H_{38}N_2OP$ $[M+H]^+$ 581.27218, Found 581.27127.



***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-3,3-dimethyl-1-phenylbutyl)-*P*,*P*-di phenylphosphinic amide (3al-*syn*):** m.p.: 82–84 ºC; IR (KBr): 3367, 3058, 2960, 2866, 1656, 1449, 1439, 1399, 1201, 1122, 1110, 1070 cm^{-1}; ^1H NMR ($CDCl_3$, 495.13 MHz): δ 7.71 (dd, *J* = 7.5, 5.4 Hz, 2H), 7.64–7.21 (m, 17H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.07–7.06 (m, 2H), 6.85 (d, *J* = 7.9 Hz, 1H), 4.68–4.59 (m, 2H), 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 170.2, 146.7, 145.2, 140.7, 140.4, 139.6, 133.4, 132.8, 132.3, 132.1 (d, J_{PC} = 9.6 Hz), 131.9 (J_{PC} = 9.6 Hz), 131.8, 131.3 (d, J_{PC} = 14.4 Hz), 129.2, 128.5, 128.1, 128.0, 127.9 (J_{PC} = 13.7 Hz), 127.0, 126.9, 126.8, 126.6, 125.9, 119.7 (J_{PC} = 35.2 Hz), 79.1 (J_{PC} = 8.8 Hz), 63.4, 36.7, 26.5; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 22.6; HRMS (ESI): Exact mass calcd for $C_{37}H_{36}N_2OP$ $[M+H]^+$ 555.25658, Found 555.25746.

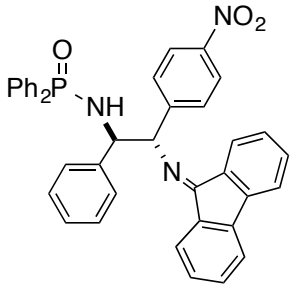


(2*SR*,3*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-3-((diphenylphosphoryl)amino)-3-phe nylpropanic acid ethyl ester (3am-*syn*): m.p.: 125 ºC; IR (neat.): 3339, 1729, 1660 1275,1201,1102, 919; ^1H NMR ($CDCl_3$, 495.13 MHz): δ. 7.84-7.78 (m, 4H), 7.55 (d, *J* = 5.9 Hz, 1H), 7.49-7.45 (m, 2H), 7.42-7.25 (m, 12H), 7.20-7.18 (m, *J* = 5.9 Hz, 2H), 7.15-7.11 (m, 2H), 5.25-5.21 (m, 2H), 5.04-5.00 (m, 1H), 4.33-4.29 (m,



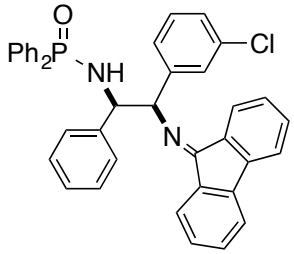
1H), 4.26-4.20 (m, 1H), 1.20 (t, J = 5.9 Hz, 3H); ^{13}C NMR ($CDCl_3$ 150.92 MHz): δ.169.6, 166.9, 144.0, 142.0, 141.3, 138.0, 134.7, 133.5, 133.2, 132.6, 132.5, 132.1, 132.0, 131.8, 131.6, 131.5, 129.1, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.2, 127.2, 126.8, 126.5, 124.3, 123.0, 120.5, 120.3, 119.4, 69.8 (J_{PC} = 4.9), 61.9, 57.8, 14.1; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ. 22.9; HRMS (ESI): Exact mass calcd for $C_{36}H_{32}N_2O_3P$ $[M+H]^+$ 571.21451, Found 571.21436.

***N*-((1*RS*,2*SR*)-2-((9*H*-fluoren-9-ylidene)amino)-2-(4-nitrophenyl)-1-phenylethyl)-*P*, *P*-diphenylphosphinic amide (3an-*anti*):** m.p.: 125 ºC (dec.); IR (KBr): 3367, 3059,



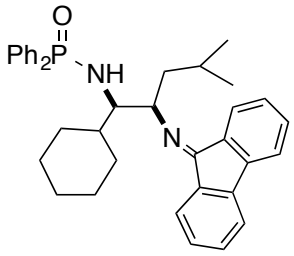
1648, 1601, 1520, 1450, 1438, 1344, 1190, 1123, 1108, 1069, 1029, 927 cm^{-1}; ^{1}H NMR ($CDCl_3$, 495.13 MHz): δ 7.97–7.91 (m, 3H), 7.73 (m, 4H), 7.60–7.07 (m, 20H), 6.20 (s, 1H), 4.78–4.72 (m, 1H), 4.20–4.16 (m, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 166.6, 148.3, 146.6, 143.9, 141.3, 138.7 (J_{PC} = 5.7 Hz), 138.2, 133.1, 132.4 (J_{PC} = 9.6 Hz), 131.80, 131.76, 131.7, 131.5, 131.5, 131.4, 130.7, 128.4, 128.3, 128.2, 128.1, 127.7, 127.4, 127.3, 123.2, 122.6, 120.2, 119.4, 69.3, 61.4; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 28.9; HRMS (ESI): Exact mass calcd for $C_{39}H_{31}N_3O_3P$ $[M+H]^+$ 620.21030, Found 620.20837.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-2-(3-chlorophenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic amide (3ao-*syn*):** m.p.: 175 ºC (dec.); IR (KBr): 3342, 3059,



1648, 1595, 1450, 1439, 1400, 1200, 1121 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.87 (d, J =7.4 Hz, 1H), 7.74 (dd, J = 11.3, 7.6 Hz, 2H), 7.52 (t, J = 6.8 Hz, 1H), 7.47–7.10 (m, 22H), 7.04 (t, J = 7.6 Hz, 1H), 5.69 (s, 1H), 5.02 (dd, J = 10.6, 7.7 Hz, 1H), 4.56–4.53 (m, 1H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 165.4, 144.0, 143.7, 142.4, 141.3, 137.9, 134.5, 132.23, 132.17, 132.1, 131.7, 131.5, 131.4, 131.1, 129.8, 128.4 (J_{PC} = 9.1 Hz), 128.3 (J_{PC} = 5.9 Hz), 128.2, 128.1, 128.0, 127.7, 127.1, 125.8, 122.7, 120.3, 119.5, 69.4 (J_{PC} = 7.3 Hz), 62.4; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 22.0; HRMS (ESI): Exact mass calcd for $C_{39}H_{31}ClN_2OP$ $[M+H]^+$ 609.18625, Found 609.18349.

***N*-((1*RS*,2*RS*)-2-((9*H*-fluoren-9-ylidene)amino)-1-cyclohexyl-4-methylpentyl)-*P*,*P*-diphenylphosphinic amide (3ij-*syn*):** m.p.: 76–79 ºC; IR (KBr): 3348, 3058, 2926, 2850, 1716, 1647, 1606, 1448, 1404, 1302, 1203 1122 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 8.00–7.93 (m, 4H), 7.90 (d. J = 7.8 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 7.5

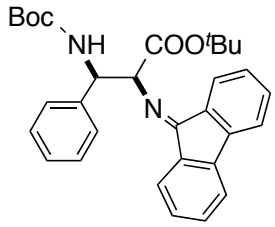


Hz, 1H), 7.59 (d, J = 7.4 Hz, 1H), 7.52–7.25 (m, 10H), 4.99 (t, J = 10.5 Hz, 1H), 4.82 (dd, J = 10.3, 4.5 Hz, 1H), 3.37–3.33 (m, 1H), 2.00 (ddd, J = 14.1, 10.4, 3.8 Hz, 1H), 1.74–1.50 (m, 7H), 1.20–0.81 (m, 12H); ^{13}C NMR ($CDCl_3$ 150.91 MHz): δ 160.2, 143.9, 140.7, 138.5, 134.8, 134.4, 133.9, 133.6, 132.14, 132.08, 132.0, 131.6, 131.4, 131.3, 131.2, 130.8, 128.3, 128.2, 128.1, 126.7, 122.2, 120.4, 119.0, 58.1 (J_{PC} = 4.6 Hz), 56.4, 44.4, 41.3, 30.5, 28.9, 26.5, 26.6, 23.7, 21.2; ^{31}P NMR ($CDCl_3$, 242.95 Hz): δ 22.3; HRMS (ESI): Exact mass calcd for $C_{37}H_{42}N_2OP$ $[M+H]^+$ 561.30348, Found 561.30184.

General procedure for catalytic asymmetric imine-imine cross-coupling reactions of fluorenyl glyoxylate imines with Boc-imines:

Under Ar atmosphere, the fluorenyl ^{t}Bu-glyoxylate imine **2p** (58.6 mg, 0.200 mmol) was dissolved in anhydrous toluene (2 mL) in a well-dried 10 mL reaction tube, and the reaction tube was cooled at -60 °C. A chiral guanidine (8.0 mg, 0.020 mmol, 10 mol%) in toluene (1.0 mL) was then added dropwise, and the mixture was stirred at -60 ºC. A solution Boc-imine (49.2 mg, 0.240 mmol, 1.2 eq.) in toluene (1.0 mL) was added to the mixture, and the whole was stirred at –60 ºC for 18 h. The reaction was quenched by a sat. NH_4Cl aqueous solution (1.0 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 5.0 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. Finally, the crude material was purified by column chromatography on silica gel using a mixed solvent (hexane/Et_2O) to give the corresponding cross-coupling product **6**.

(2*S*,3*R*)-3-*tert*-Butoxycarbonylamino-2-(fluoren-9-ylideneamino)-3-phenyl-propionic acid *tert*-butyl ester (6)[4]: m.p.: 181-182 ºC; IR (neat): 3322, 2974, 2885, 2542,



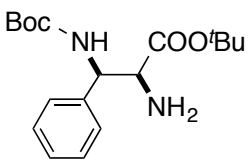
2256, 1926, 1759, 1660, 1451, 1381, 1328, 1274, 1090, 1050, 881, 803, 686; ^{1}H NMR ($CDCl_3$, 495.13 MHz): δ 7.88 (d, J = 7.4 Hz, 1H), 7.57 (d, J = 7.4 Hz, 1H), 7.50–7.27 (m, 7H), 7.24-7.20 (m, 2H), 7.18-7.11 (m, 2H), 6.36 (d, J = 7.9 Hz, 1H), 5.63 (d, J = 7.9 Hz, 1H), 5.19 (s, 1H), 1.37 (s, 9H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$ 124.51 MHz): δ 168.3, 166. 8, 155.2, 144.0, 141.1, 138.0, 131.7, 131.7, 131.4, 128.6, 128.4, 128.2, 127.8, 127.1, 127.0, 126.5, 123.1, 120.4, 119.3, 82.7, 79.3, 68.9, 56.7, 28.37, 27.89; HRMS (ESI): Exact mass calcd for $C_{31}H_{34}N_2O_4$ $[M+H]^+$

499.25968, Found 499.25780; HPLC Column AD–H, eluent Hex/IPA = 4/1, flow rate 1.0 mL/min; rac 5.5 min. 28.8 min. (major), 7.2 min. 11.0 min. (minor). $[\alpha]_D^{24} = -139$ (c 0.200, CH_2Cl_2).

Hydrolysis of compound 6

The coupling product **6** (1.12 g, 2.24 mmol) was added to a solution of 1.0 M aq. HCl and Et_2O (4/1). The mixture was stirred for 30 min at room temperature and then diluted with water. The aqueous phase was washed with Et_2O three times and basicified with sat. $NaHCO_3$, and the aqueous phase was extracted with Et_2O. The organic layers were combined and dried over Na_2SO_4. Filtration and evaporation under reduced pressure afforded free amine **7** (0.487 g, 1.45 mmol, 65% yield).

***Syn*-2-amino-3-*tert*-Butoxycarbonylamino propanoic acid *tert*-butyl ester (7)**

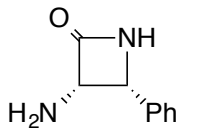


IR (neat): 3428, 2975, 1711, 1640, 1492, 1367, 1251, 1162, ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.28-7.19 (d, J = 7.2 Hz, 1H), 5.66 (s, 1H), 5.11 (s, 1H), 3.71 (s, 1H), 1.38 (s, 9H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$ 150.92 MHz): δ 171.5, 155.1, 140.4, 128.5, 127.3, 126.5, 82.1, 79.3, 58.9, 56.2, 28.3, 27.9; HRMS (ESI): Exact mass calcd for $C_{18}H_{30}N_2O_4$ $[M+H]^+$ 337.21273, Found 337.21106.

Synthesis of monobactam

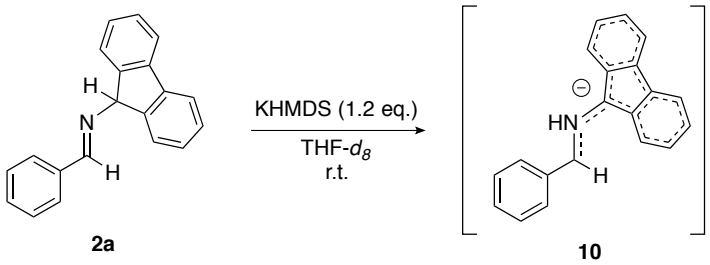
A solution of **7** (250 mg, 0.740 mmol) in MeOH (4 mL) and conc. HCl (1 mL) was stirred at room temperature for 2 h, then diluted with H_2O (10 mL), and the aqueous phase was washed with Et_2O (10 mL × 3). The aqueous layers were combined, and evaporated under reduced pressure to afford the corresponding hydrochloric acid salt **8** (178 mg, quantitative yield). The diamine HCl salt **8** (70.0 mg, 0.230 mmol) was directly dissolved in THF, and the solution was kept at –60 ºC. LDA in THF was added to this solution dropwise at the same temperature. After 24 h stirring, the reaction was quenched by a sat. $NaHCO_3$ aqueous solution. The crude mixture was extracted with CH_2Cl_2, then dried with Na_2SO_4. The residue was isolated by column chromatography on silica gel using a mixture of CH_2Cl_2/Et_2O to give the corresponding cyclized product **9** (27.2 mg, 0.167 mmol, 75% yield).

(3*S*,4*R*)-3-amino-4-phenylazetidin-2-one (9): m.p.: 172-175 ºC; IR (neat): 3347, 2974, 1275, 1090, 1050, 881; ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.50 (m, 5H), 6.25 (br, 1H), 4.62 (d, *J* = 5.4, 1H), 4.05 (d, *J* = 5.5, 1H), 1.60 (br, 2H); ^{13}C NMR ($CDCl_3$ 150.92 MHz): δ 176.5, 128.8. 127.8, 126.8, 125.7, 84.9, 75.0; HRMS (ESI): Exact mass calcd for $C_9H_{10}N_2O$ $[M+H]^+$ 163.08714, Found 163.08700; $[\alpha]_D^{24} = -45.1$ (c 0.200, CH_2Cl_2).



Mechanism

NMR study of the anion formation from 2a



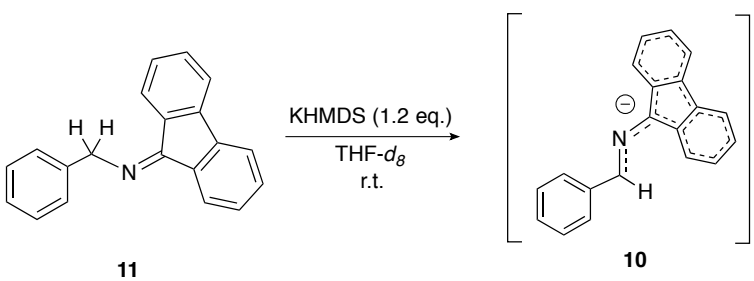
2a **10**

N-Fluorenyl imine **2a** (5.00 mg, 0.019 mmol) and KHMDS (4.00 mg, 0.020 mmol) were placed in a NMR tube (WILMAD screw-cap NMR tube). THF-d_8 (0.500 mL) was then added via a syringe at ambient temperature, and the resulting mixture was examined by ^{1}H NMR analysis (JEOL JNM-ECX600 spectrometers). The spectrum of **10** was obtained.

Anion 10:

^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 8.54 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 4H) 7.67 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 7.2 Hz, 2H),.

NMR study of the anion formation from 11

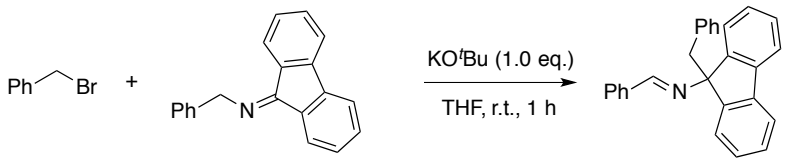


11 **10**

Aminoalkane substrate **11** (5.00 mg, 0.019 mmol) and KHMDS (4.00 mg, 0.020

mmol) were placed in a NMR tube (WILMAD screw-cap NMR tube). THF-d_8 (0.500 mL) was then added via a syringe at ambient temperature, and the resulting mixture was examined by ^{1}H NMR analysis (JEOL JNM-ECX600 spectrometers). The spectrum of **10** was obtained.

Benzylation of 11

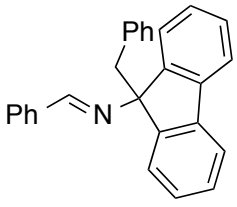


11 **12**

88% yield

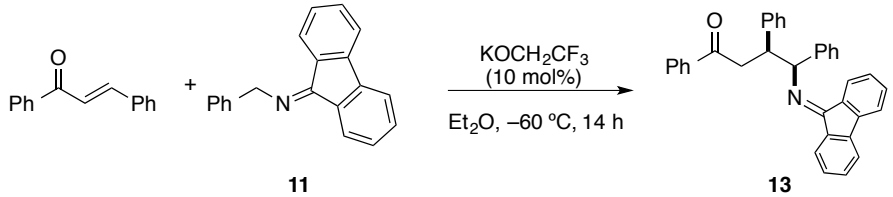
Under Ar atmosphere, aminoalkane **11** (53.9 mg, 0.200 mmol) and KO^{t}Bu (22.4 mg, 0.020 mmol) were placed in a flame-dried test tube with a sleeve stopper. To the test tube was added anhydrous THF (1.00 mL) and benzyl bromide (28.7 μL, 0.240 mmol) via a syringe. The resulting mixture was stirred at room temperature for 1 hour. The reaction was quenched with saturated aqueous NH_4Cl solution, and the mixture was extracted with dichloromethane (10 mL x 3). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was obtained. The crude product was then recrystallized from toluene to afford the product **12** (63.3 mg) in 88% yield.

***E*-9-benzylideneamino-9-benzylfluorene (12):**



m.p.: 96-99 ºC; IR (KBr): 3130, 2769, 1632, 1324, 1197,1170, 984: ^{1}H NMR ($CDCl_3$, 600.17 MHz): δ 7.93 (s, 1H), 7.70 (d, J = 4.8 Hz, 2H) 7.60 (d, J = 7.2 Hz, 2H), 7.37–7.30 (5H, m), 7.25–7.21 (4H, m), 7.09–7.03 (3H, m), 6.95 (d, J = 7.2 Hz, 2H), 3.52 (s, 2H); ^{13}C NMR ($CDCl_3$ 150.92 MHz): δ157.5, 147.4, 140.0, 137.2, 136.6, 130.9, 130.5, 128.4, 128.3, 128.0, 127.2, 127.0, 126.1, 125.6, 120.0, 77.4, 47.1. HRMS (DART): Exact mass calcd for $C_{27}H_{22}N$ [M+H]: 360.17522, Found: 360.17561.

Catalytic 1,4-addition reaction of 11 with Chalcone

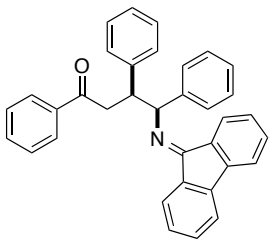


11 **13**

99% yield, *syn*/*anti* = >99/1

Under Ar atmosphere, chalcone (50.0 mg, 0.240 mmol), aminoalkane **11** (53.9 mg, 0.20 mmol) and $KOCH_2CF_3$ (2.76 mg, 0.0200 mmol) were placed in a flame-dried test tube with a sleeve stopper. To the test tube was added anhydrous Et_2O (1.50 mL) via a syringe, and the resulting mixture was stirred at –60 ºC for 14 hours. The reaction was quenched with saturated aqueous NH_4Cl solution, and the mixture was extracted with dichloromethane (10 mL x 3). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was obtained. The crude product was purified by column chromatography on silica gel (hexane/acetone=4/1) to afford the desired 1,4-adduct (94.6 mg) in 99% yield with >99/1 *syn*/*anti* selectivity.

(3*RS*,4*RS*)-4-((9*H*-fluoren-9-ylidene)amino)-1,3,4-triphenylbutan-1-one (13):



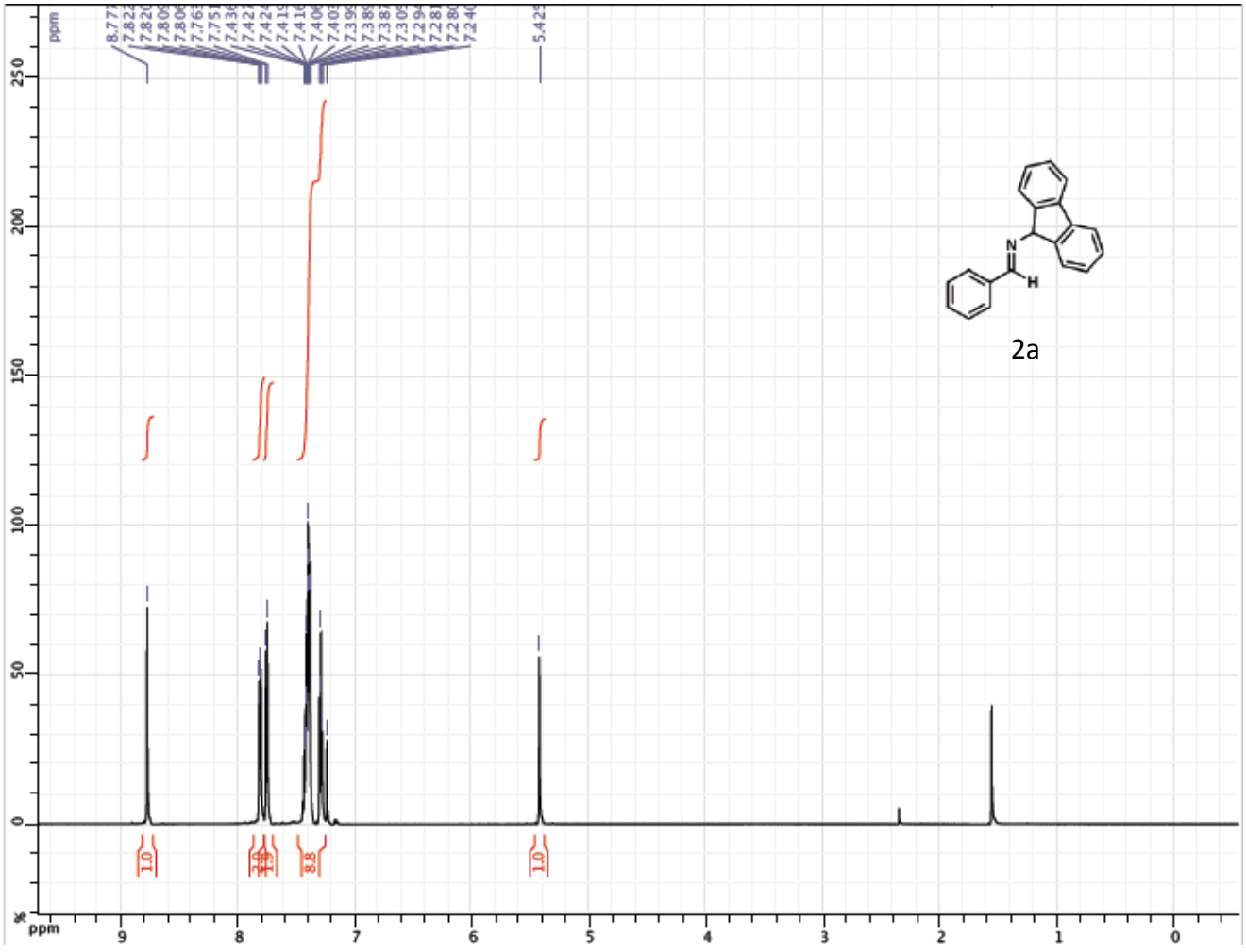
m.p.: 59–61 ºC; IR (KBr): 1102, 1180, 1266, 1303, 1339, 1371, 1449, 1493, 1599, 1647, 1683, 3028, 3061 cm^{-1}; ^1H NMR ($CDCl_3$, 600.17 MHz): δ 7.67 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 2H) 7.33 (d, *J* = 7.8 Hz, 1H,), 7.18–6.74 (19H, m), 5.44 (d, *J* = 6.6 Hz, 1H), 3.90–3.87 (m, 1H), 3.45–3.34 (m, 2H); ^{13}C NMR ($CDCl_3$ 150.92 MHz): δ 199.0, 163.0, 143.8, 142.4, 142.2, 140.9, 140.8, 138.6, 137.1, 132.5, 131.3, 131.0, 130.8, 128.8, 128.6, 128.23, 128.16, 128.04, 127.97, 127.8, 127.5, 127.4, 126.8, 126.4, 122.6, 120.1, 119.2, 69.5, 50.9, 40.4; HRMS (DART): Exact mass calcd for $C_{35}H_{28}NO$ [M+H]: 478.21709 , Found: 478.21485.

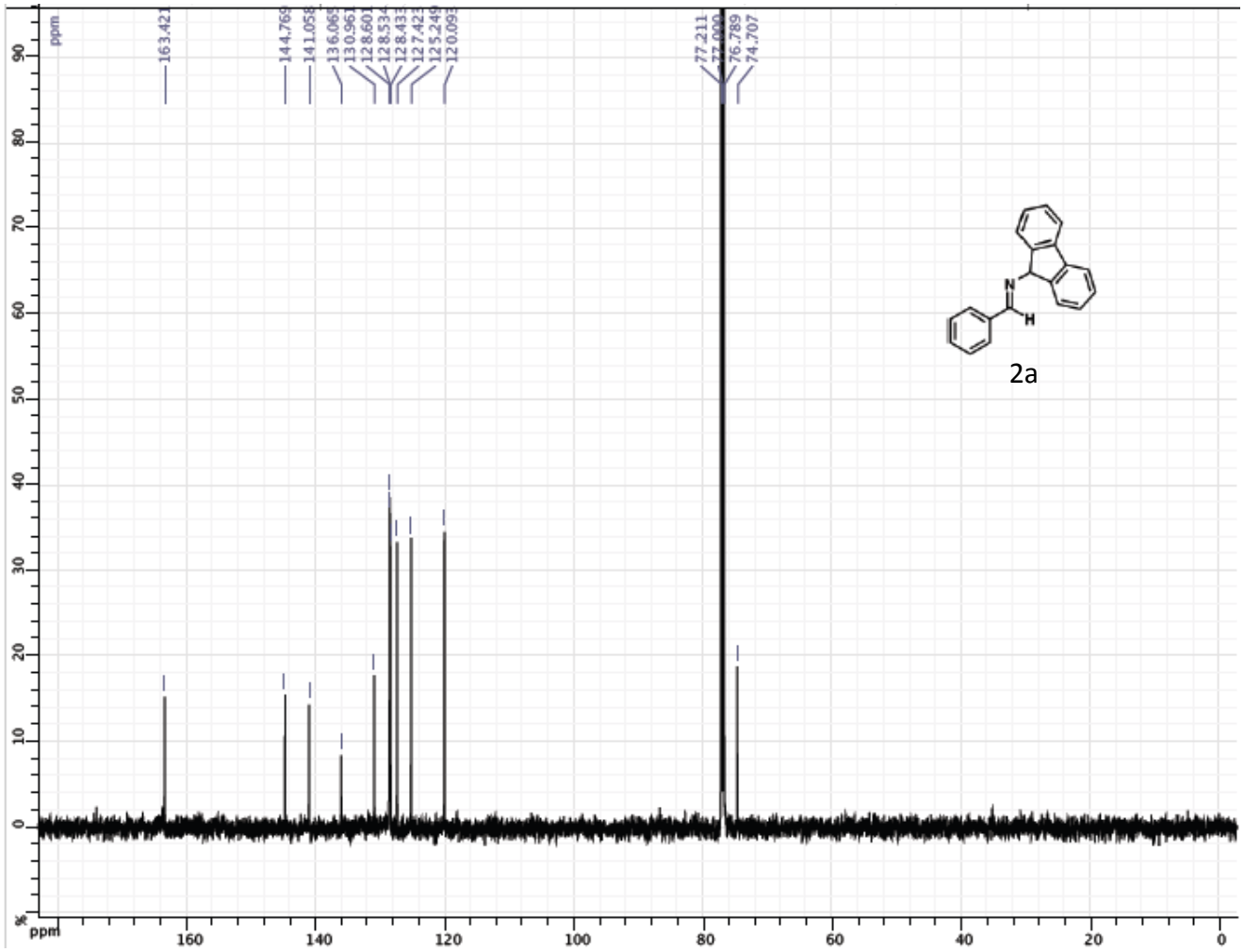
[1] Fukuyama, T.; Nunes, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 5196.

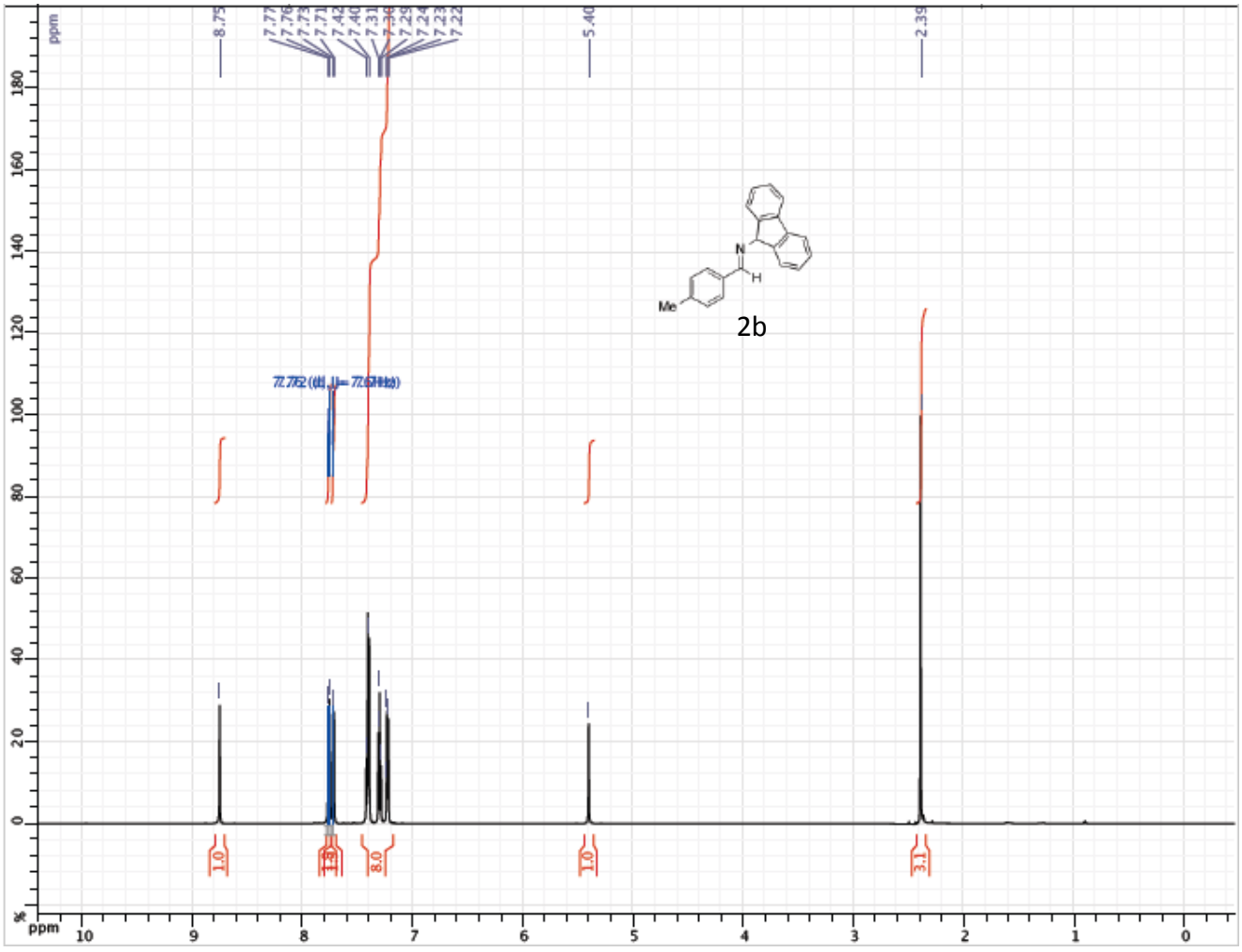
[2] [a] Zhang, Y.; Lu, Z.; Desai, A.; Wulff, W. D. *Org. Lett.* 2008, *10*, 5429. [b] Takamura, M.; Hamashima, Y.; Usuda, H.; Kanai, M.; Shibasaki, M. *Angew. Chem. Int. Ed.* **2000**, *39*, 1650.

[3] Chen, Y. J.; Seki, K.; Yamashita, Y.; Kobayashi, S. *J. Am. Chem. Soc.* **2010**, *132*, 3244.

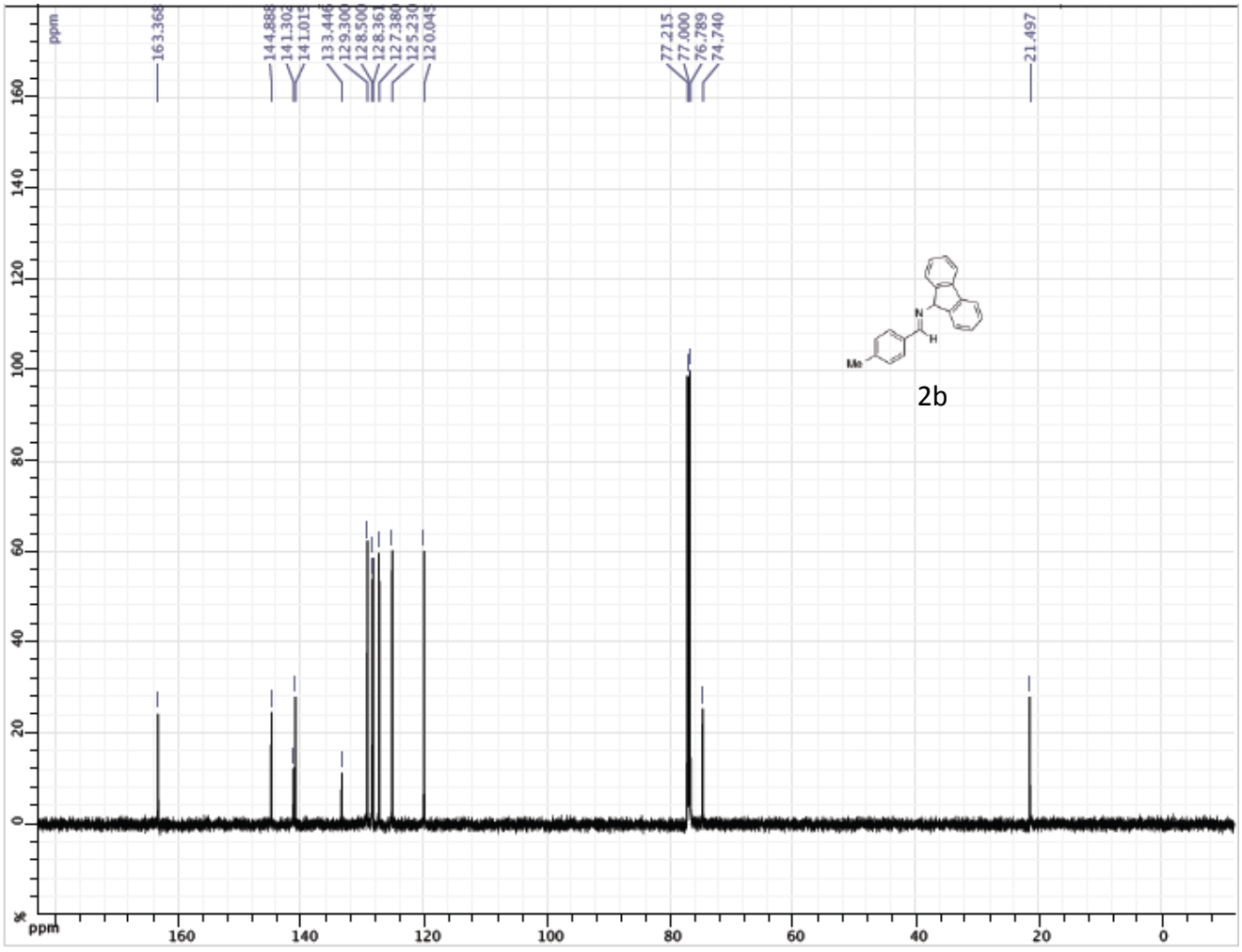
[4] Kobayashi, S.; Yazaki, R.; Seki, K.; Yamashita, Y. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 5613.


ppm
8.77
7.82
7.80
7.76
7.75
7.43
7.42
7.41
7.40
7.39
7.38
7.30
7.29
7.28
7.24
5.42
1.0
2.0
1.9
8.8
1.0
ppm
2a

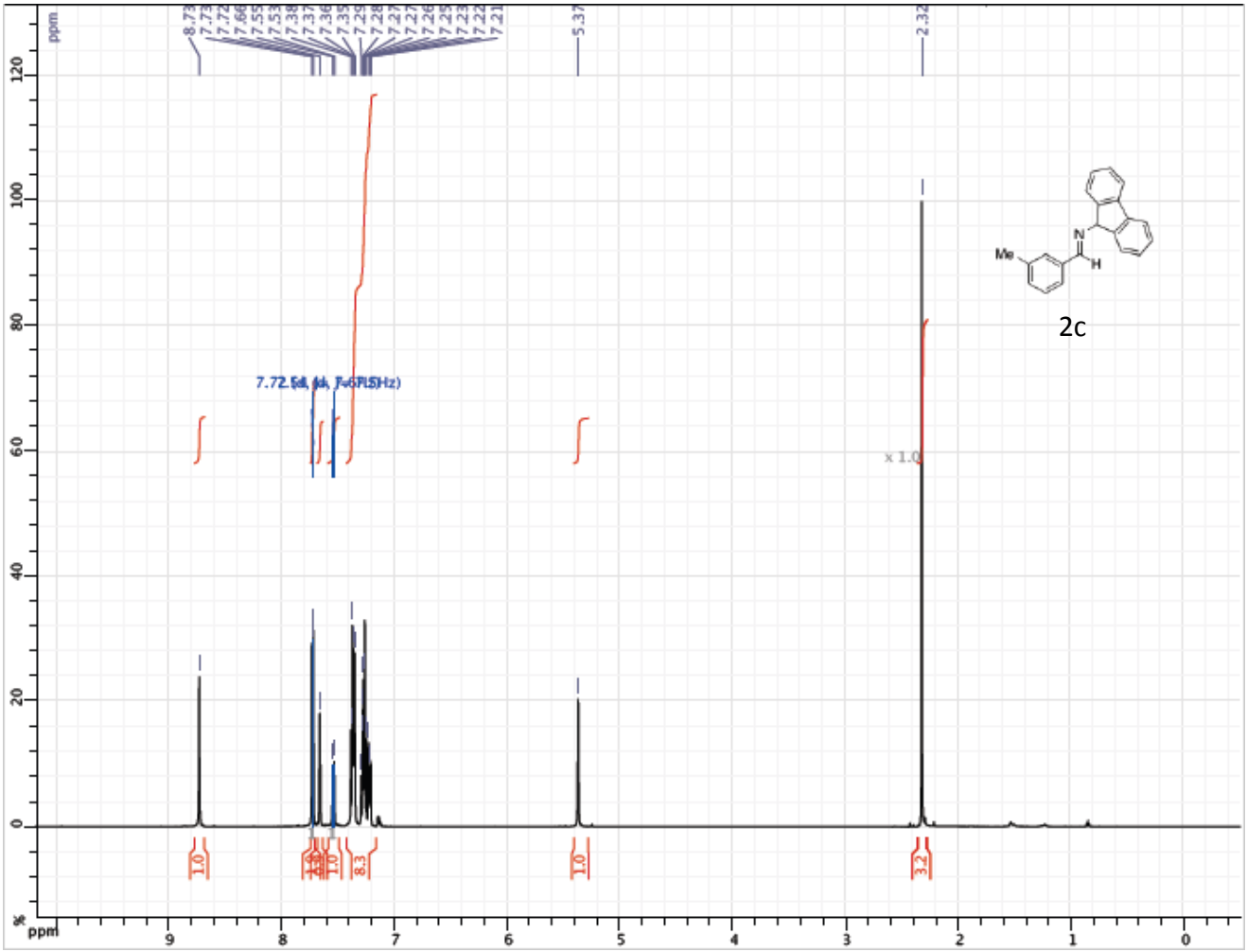

ppm
163.42
144.76
141.05
136.06
130.96
128.60
128.53
128.43
127.42
125.24
120.09
77.21
77.00
76.78
74.70
ppm
2a

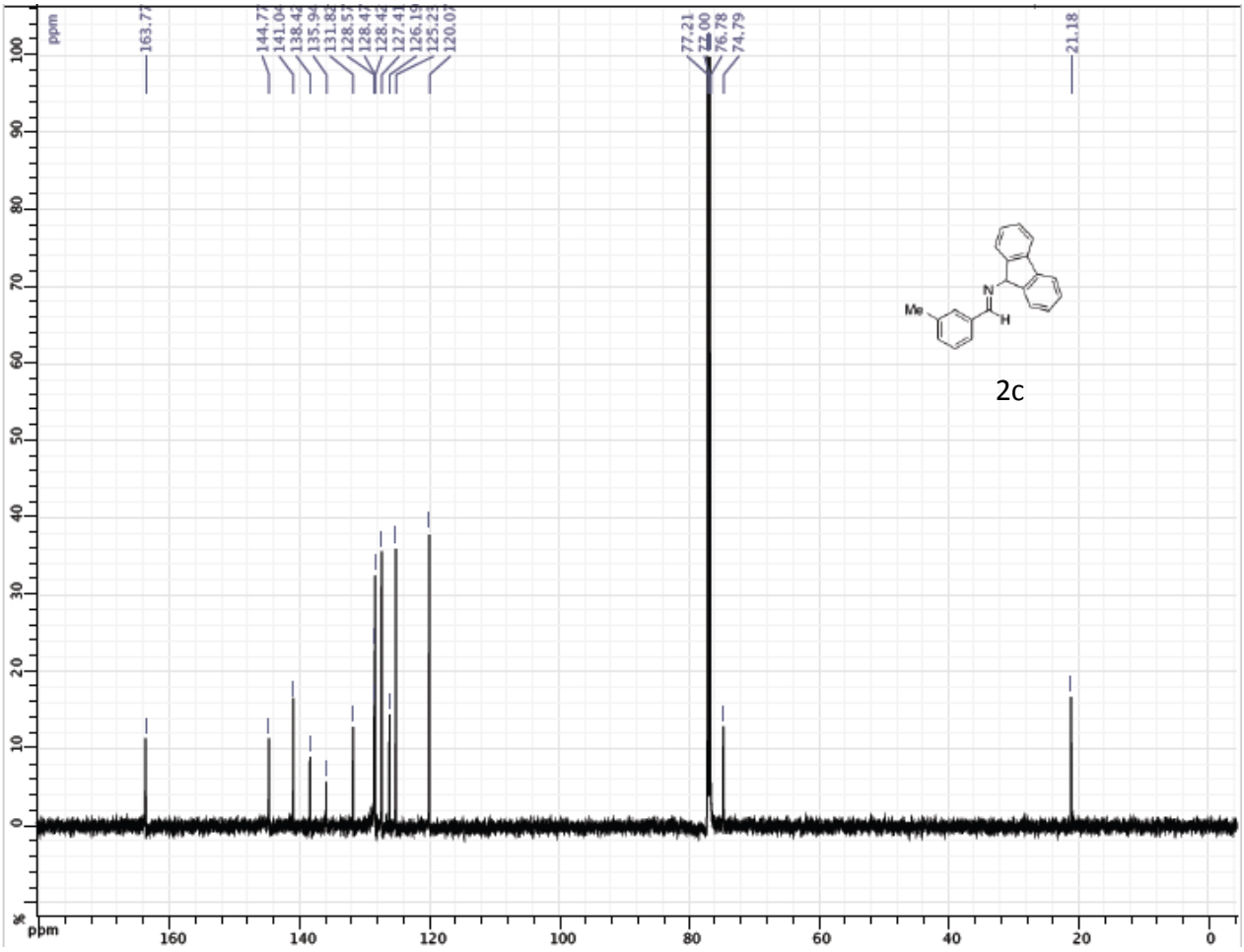

8.75
7.77
7.76
7.73
7.71
7.42
7.40
7.31
7.29
7.24
7.23
7.22
5.40
2.39
N
H
Me
1.0
1.0
8.0
1.0
3.1
ppm

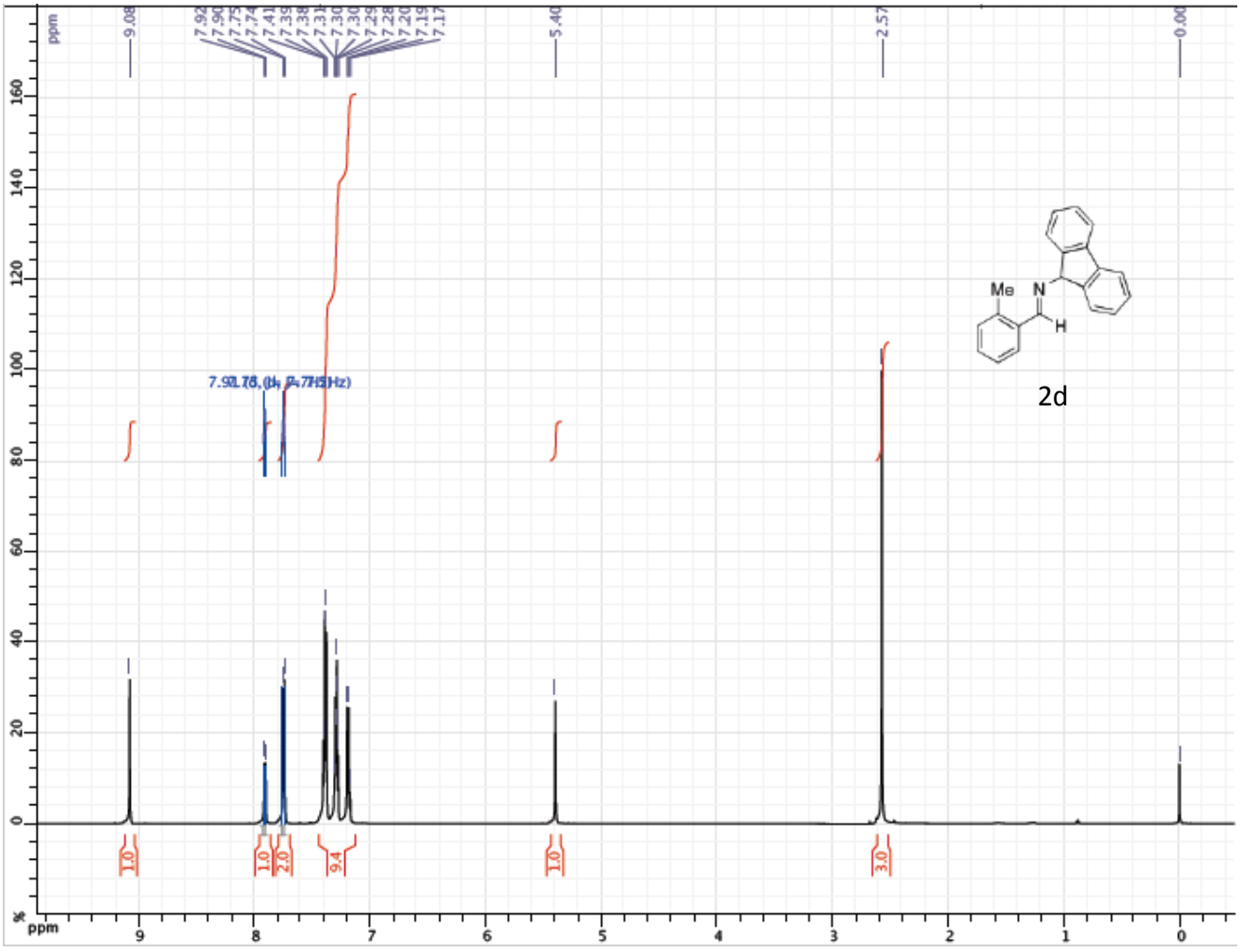
2b

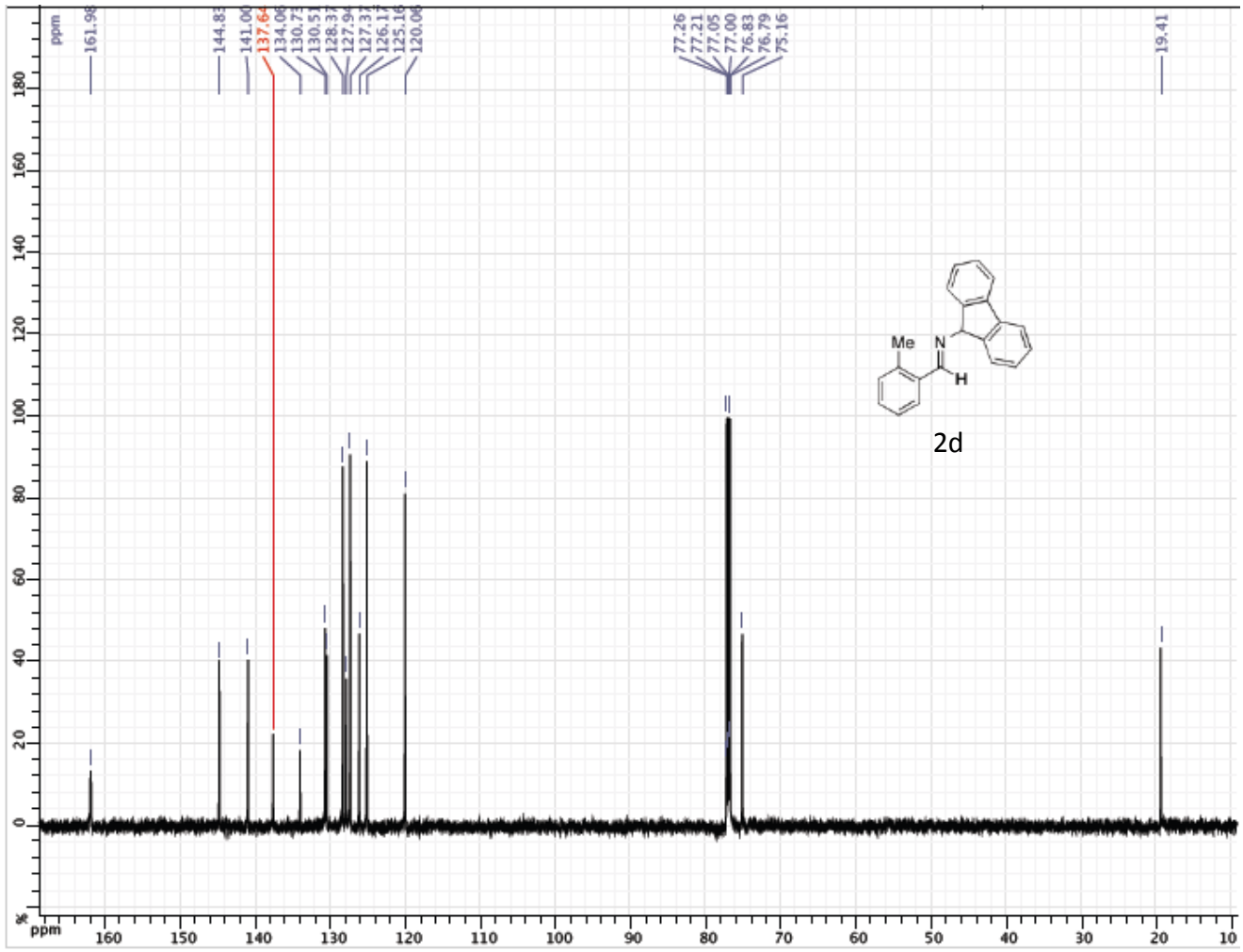

163.368
144.888
141.302
141.015
133.446
129.300
128.500
128.361
127.380
125.230
120.045
77.215
77.000
76.789
74.740
21.497
N
H
Me
ppm

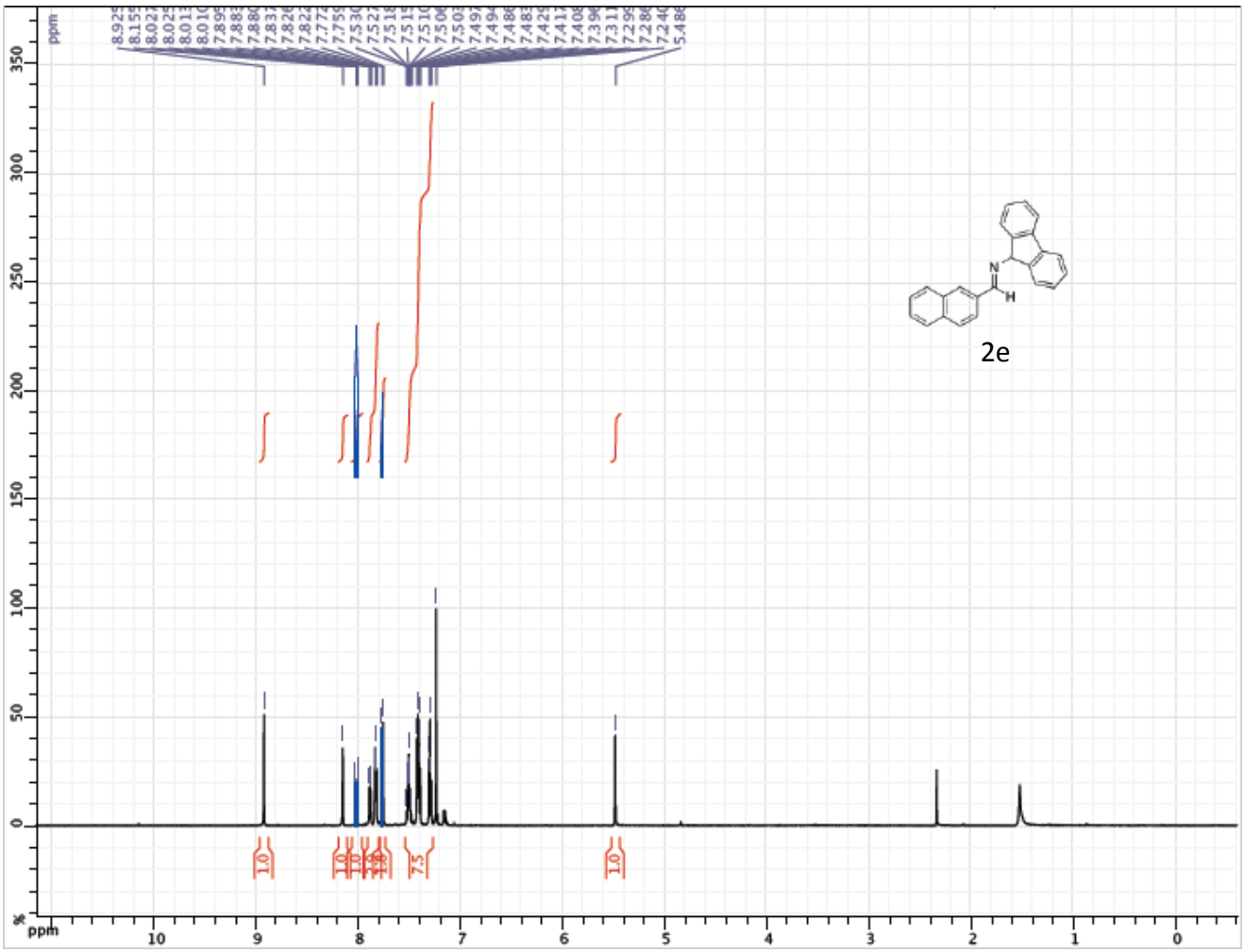
2b

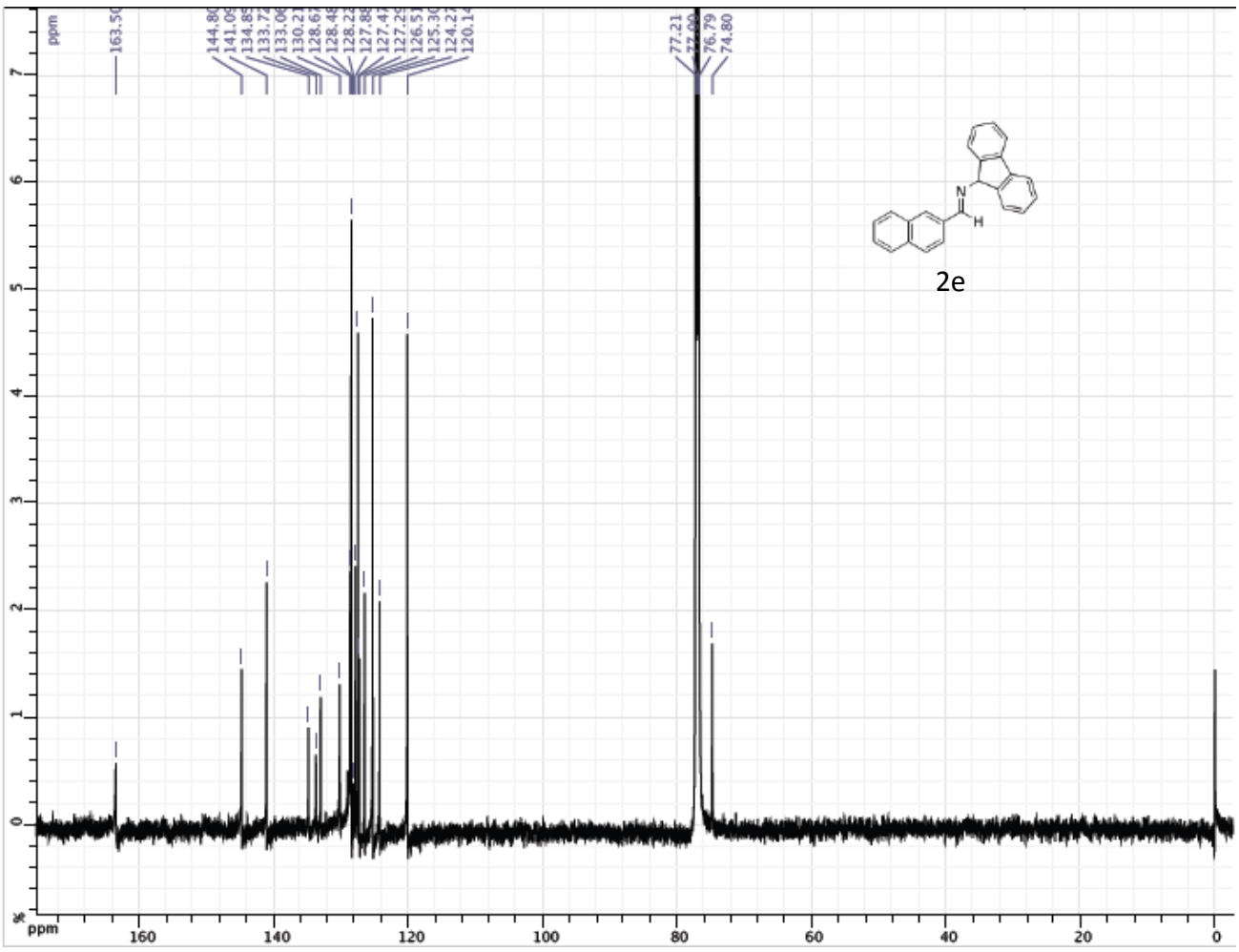

Me
N
H
2c

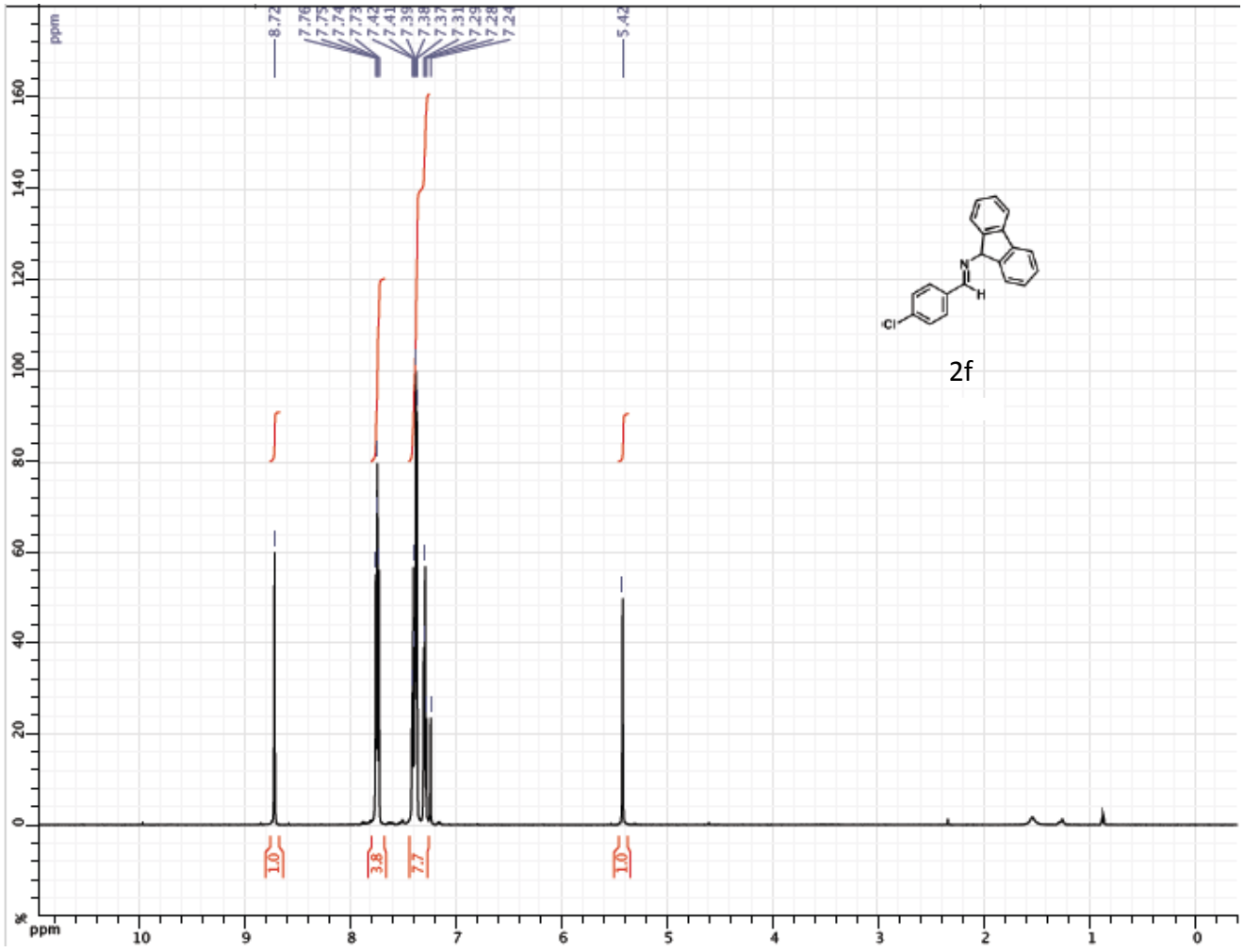

Me
N
H
2c


Me
N
H
2d

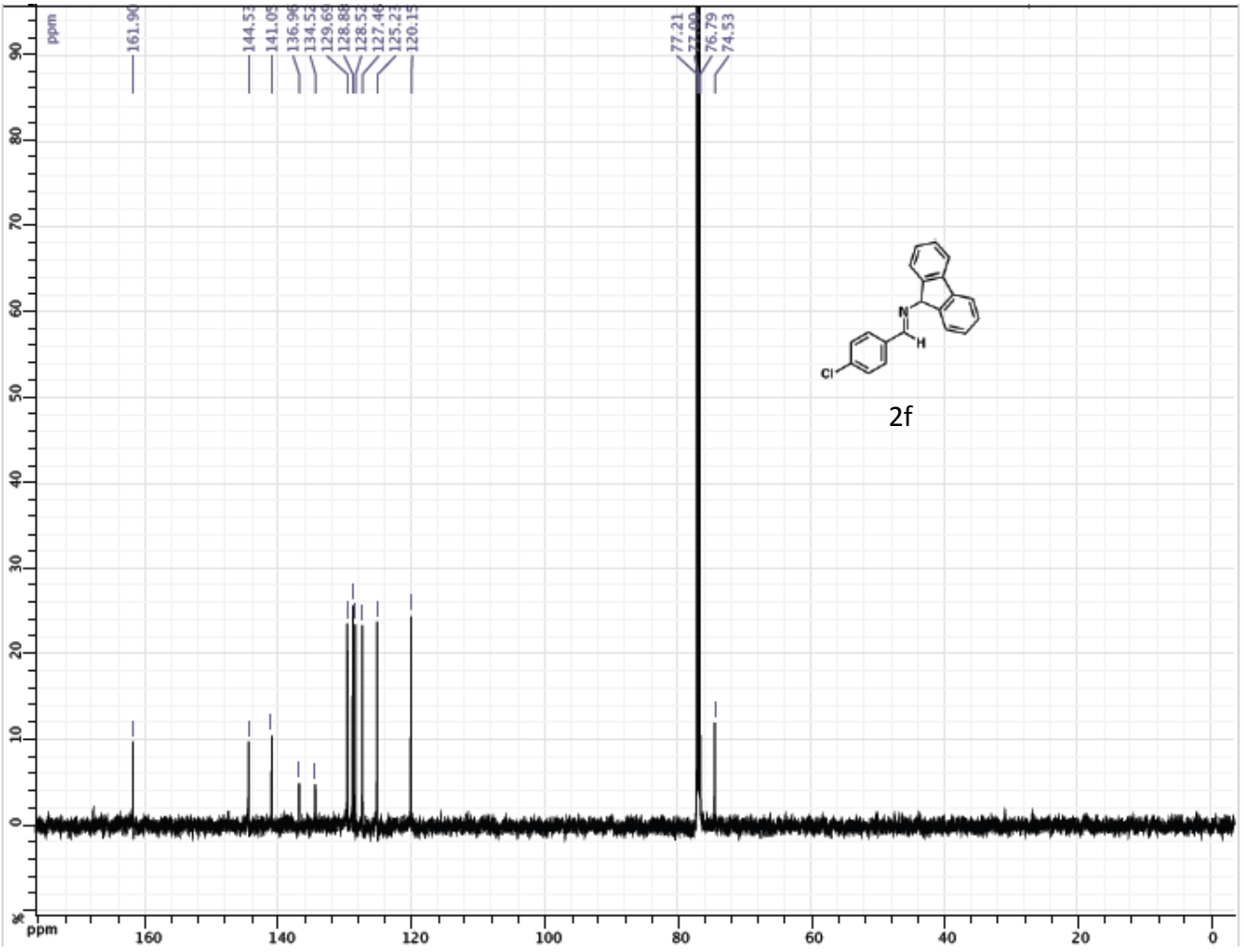

Me
N
H
2d


2e

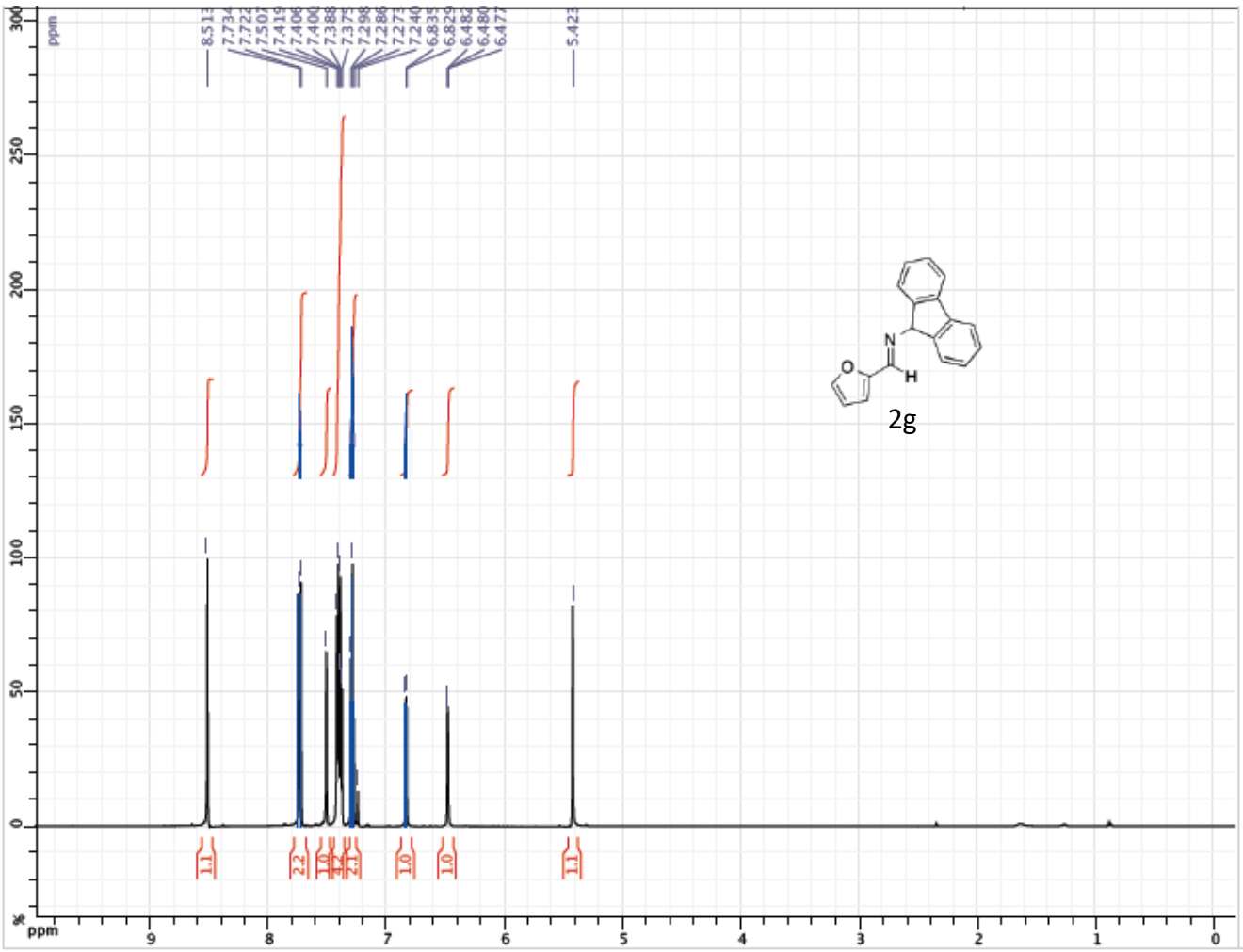

2e


ppm
8.72
7.76
7.75
7.74
7.73
7.42
7.41
7.39
7.38
7.37
7.31
7.29
7.28
7.24
5.42
1.0
3.8
7.7
1.0
ppm
10
9
8
7
6
5
4
3
2
1
0
Cl
N
H

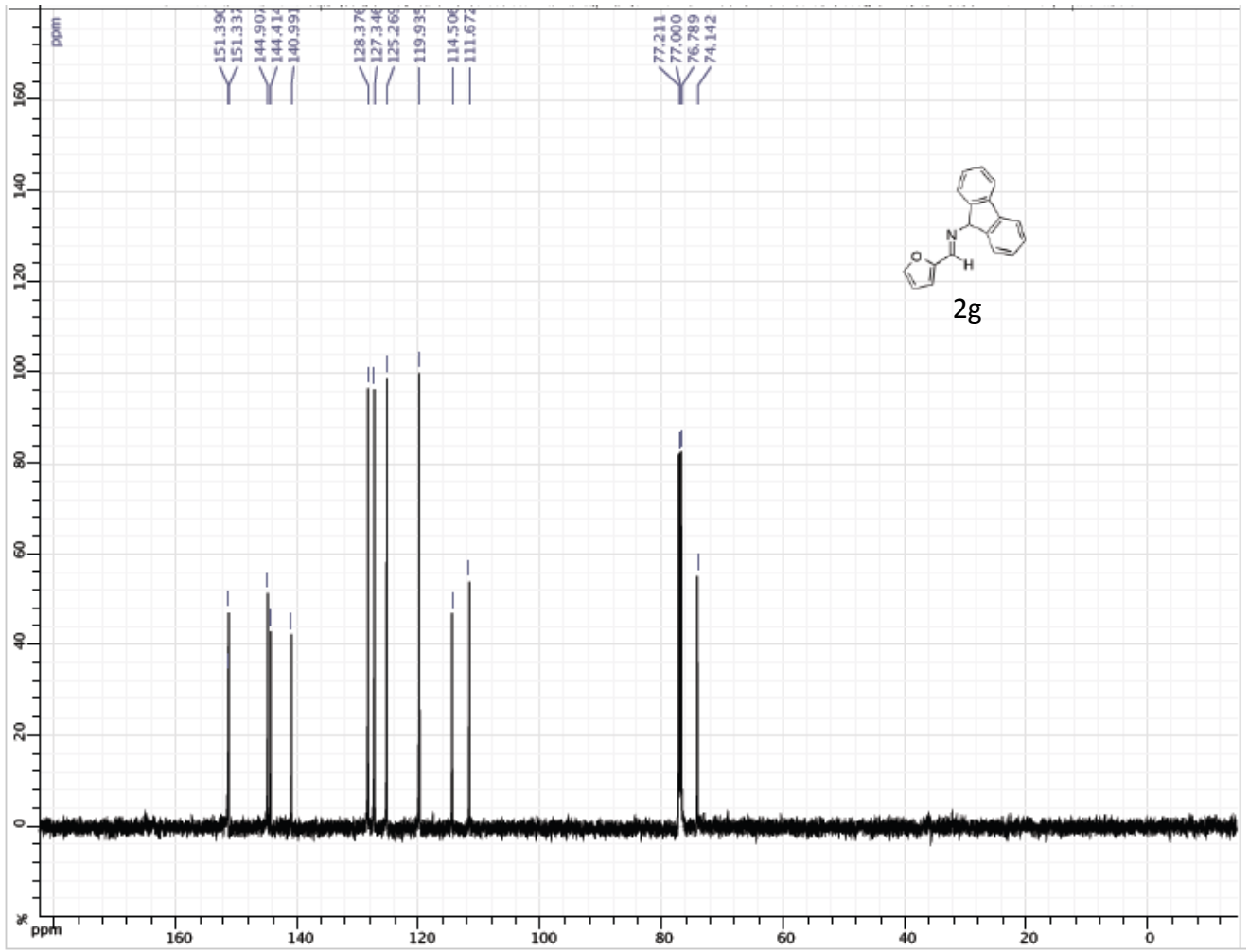
2f


ppm
161.90
144.53
141.05
136.96
134.52
129.69
128.88
128.52
127.46
125.23
120.15
77.21
77.00
76.79
74.53
ppm
160
140
120
100
80
60
40
20
0
Cl
N
H

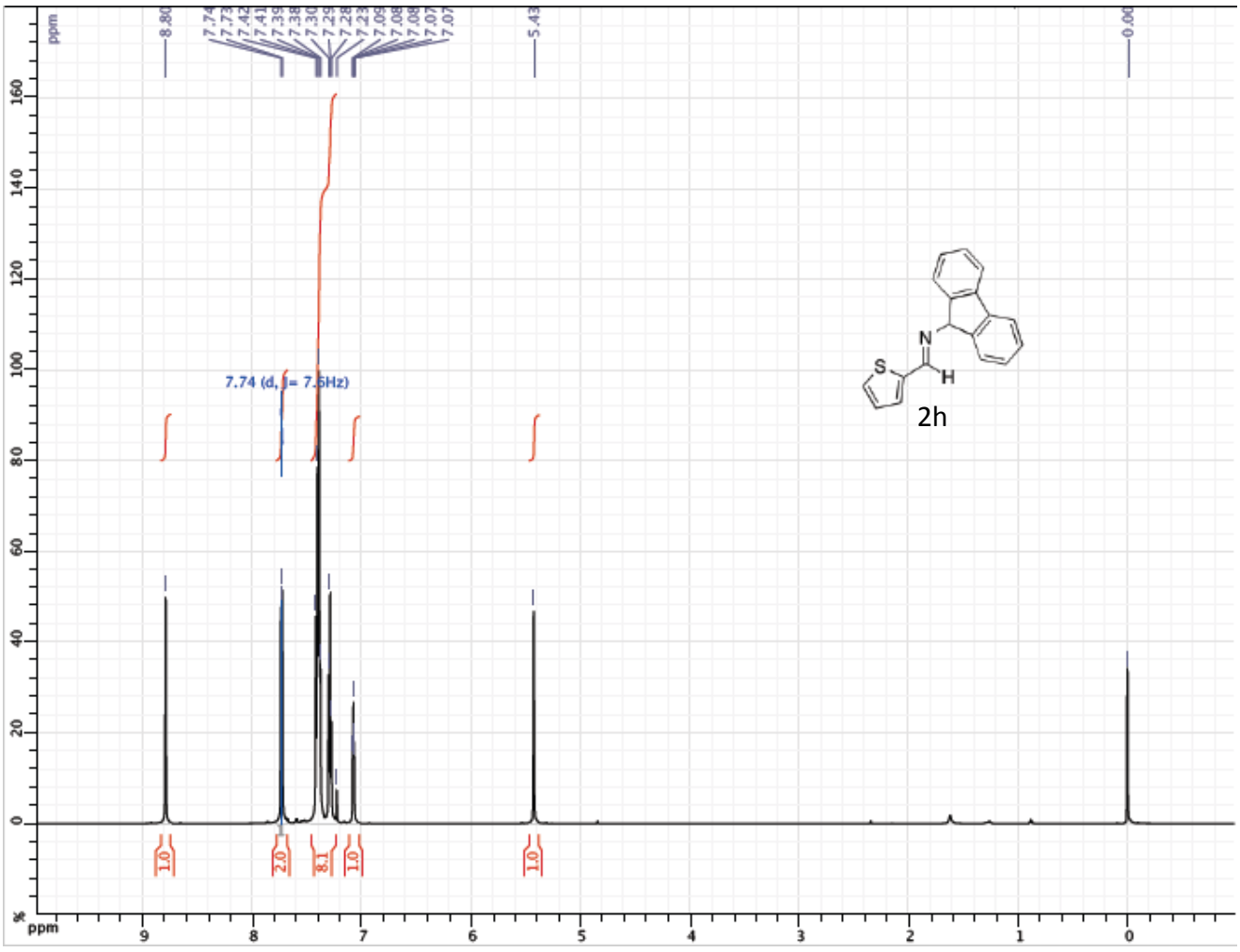
2f

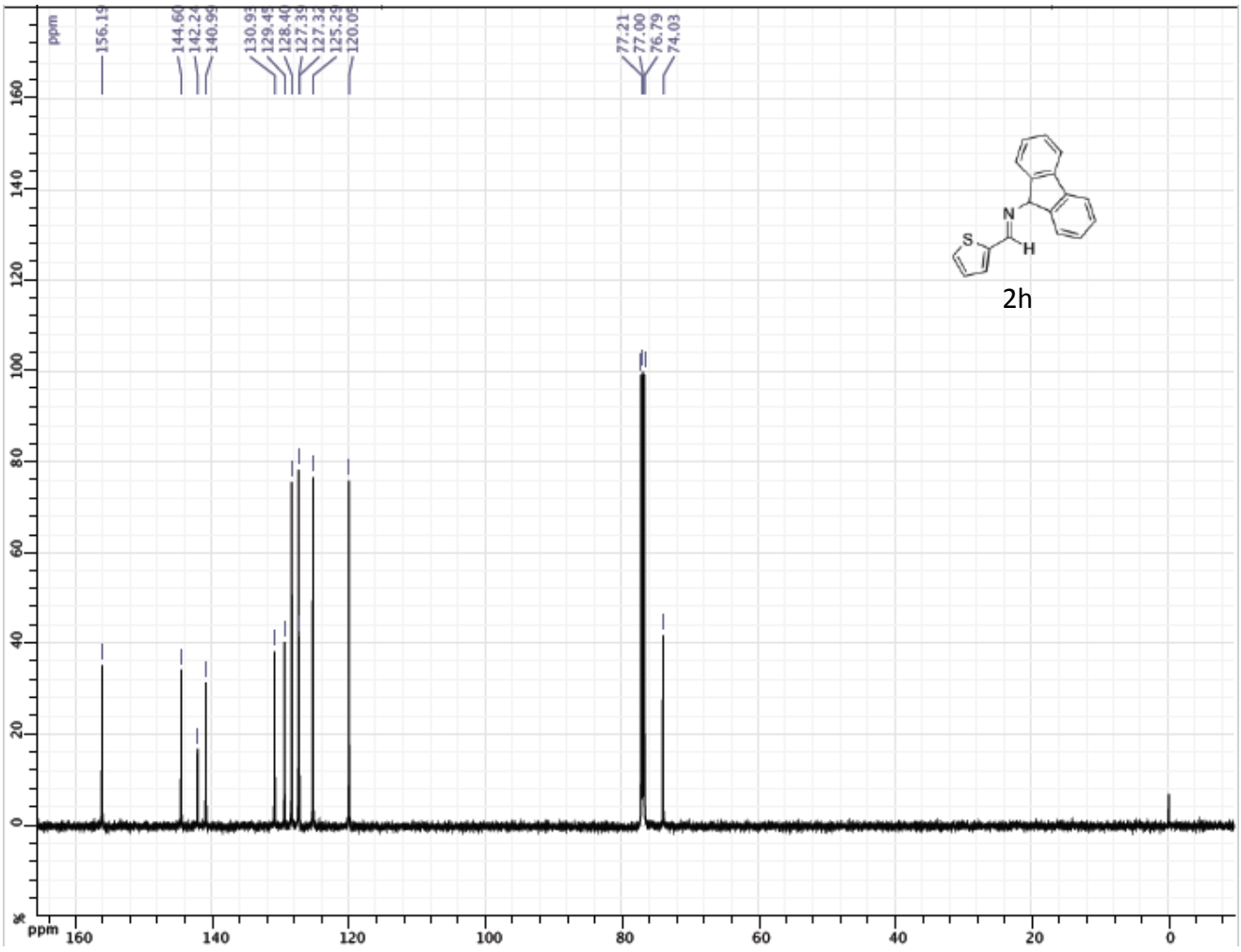

8.513
7.734
7.722
7.507
7.419
7.406
7.400
7.388
7.375
7.298
7.286
7.273
7.240
6.835
6.829
6.482
6.480
6.477
5.423
ppm
1.1
2.2
1.0
4.2
2.1
1.0
1.0
1.1
N
O
H

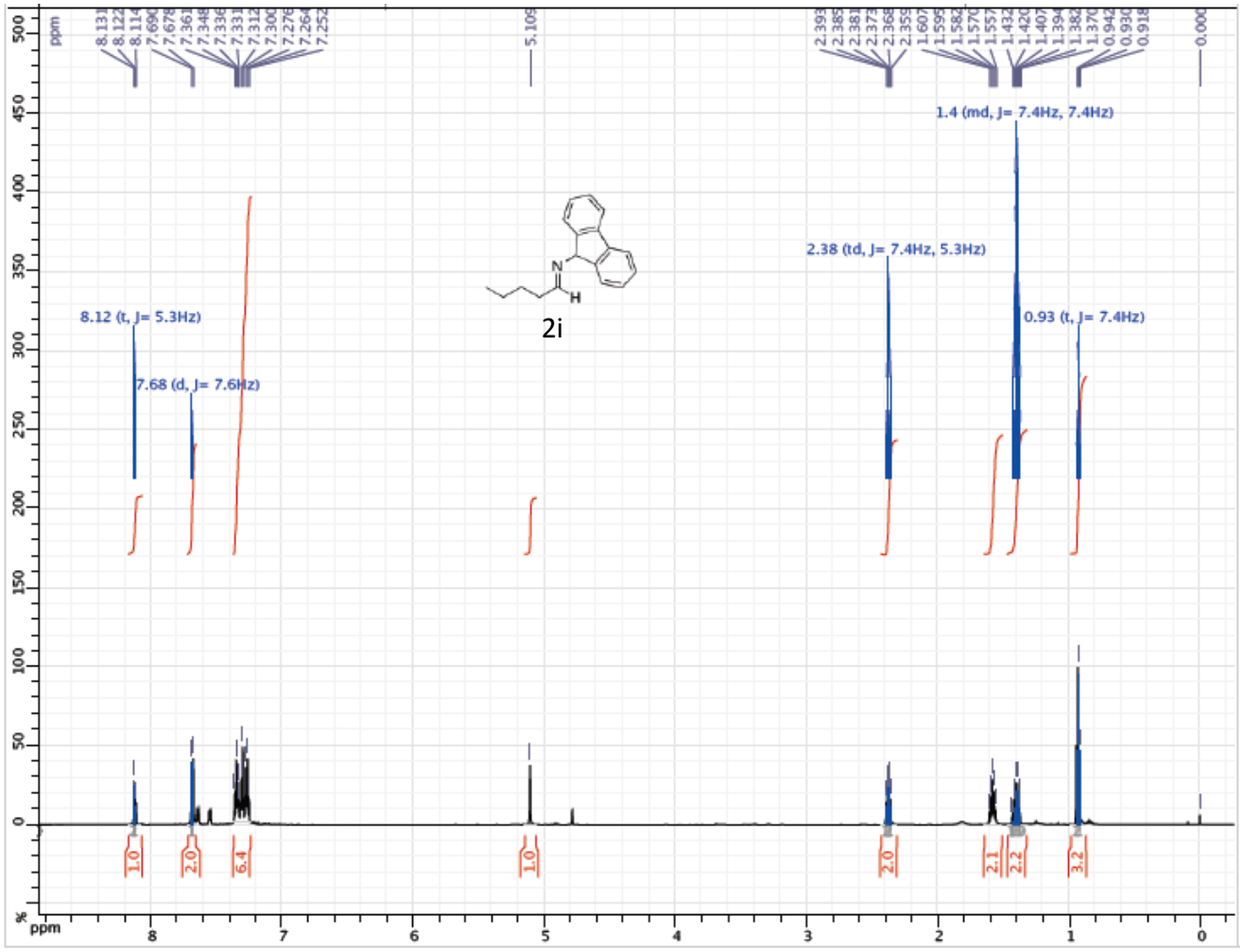
2g

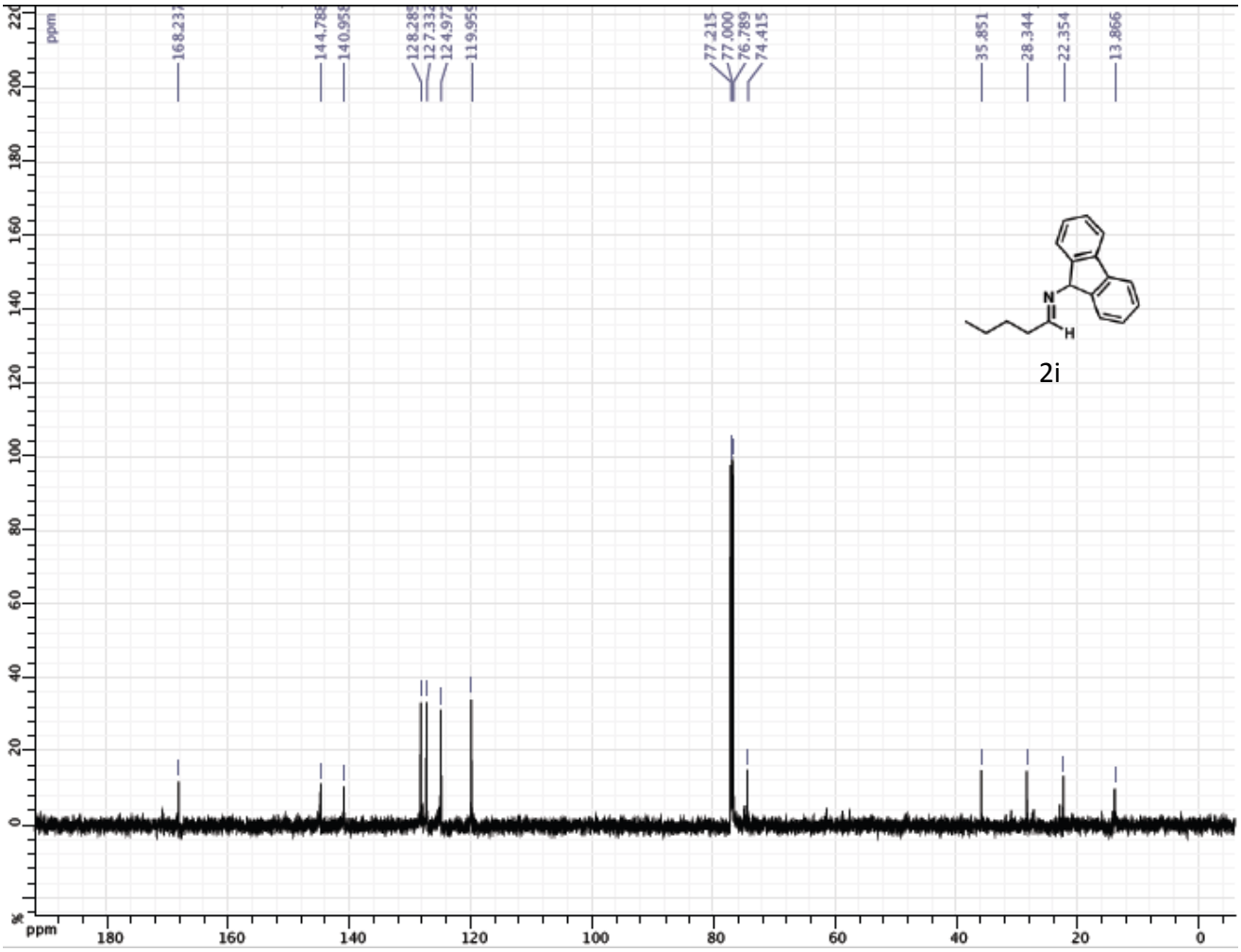

151.396
151.332
144.907
144.414
140.994
128.376
127.346
125.266
119.935
114.506
111.672
77.211
77.000
76.789
74.142
ppm
N
O
H

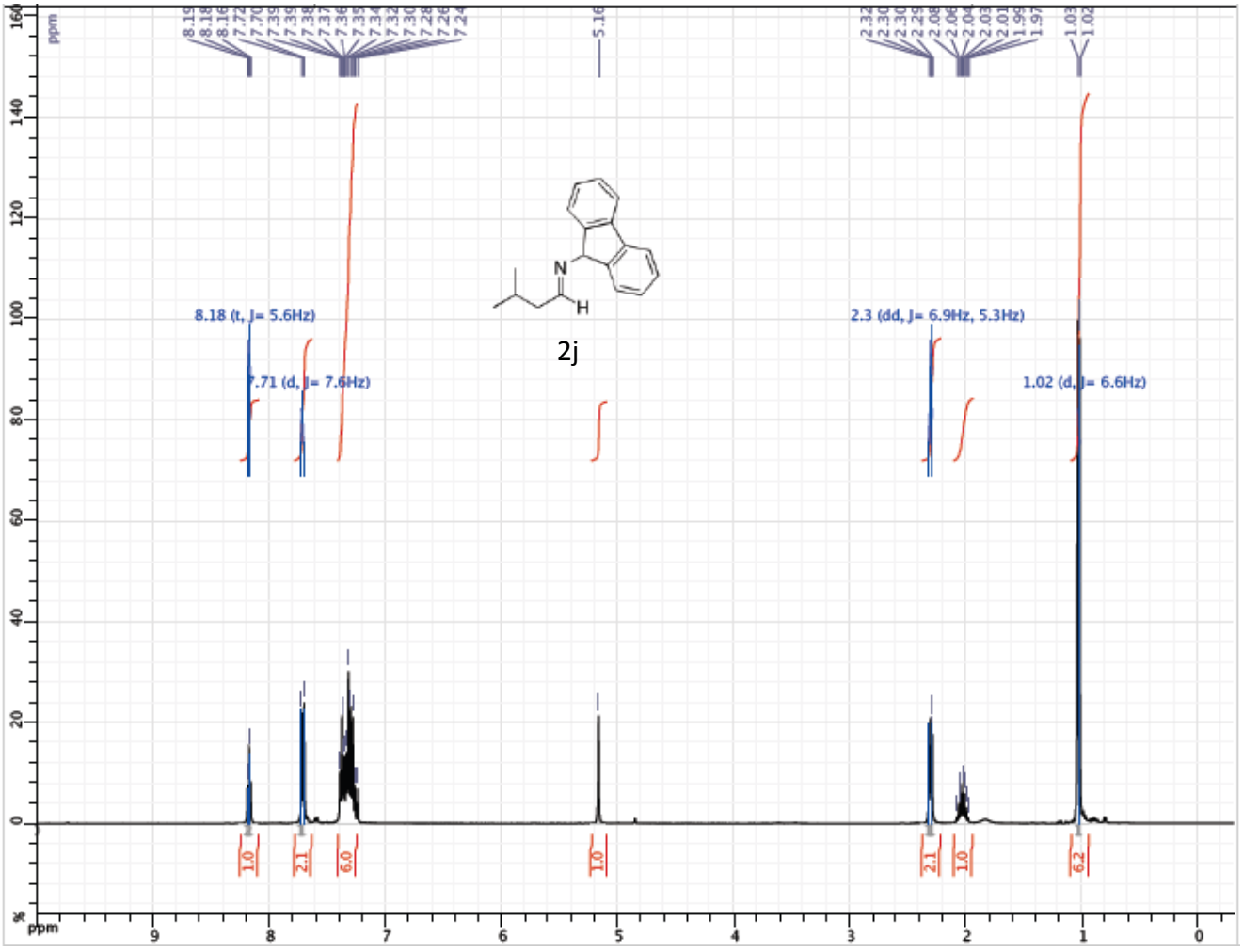
2g

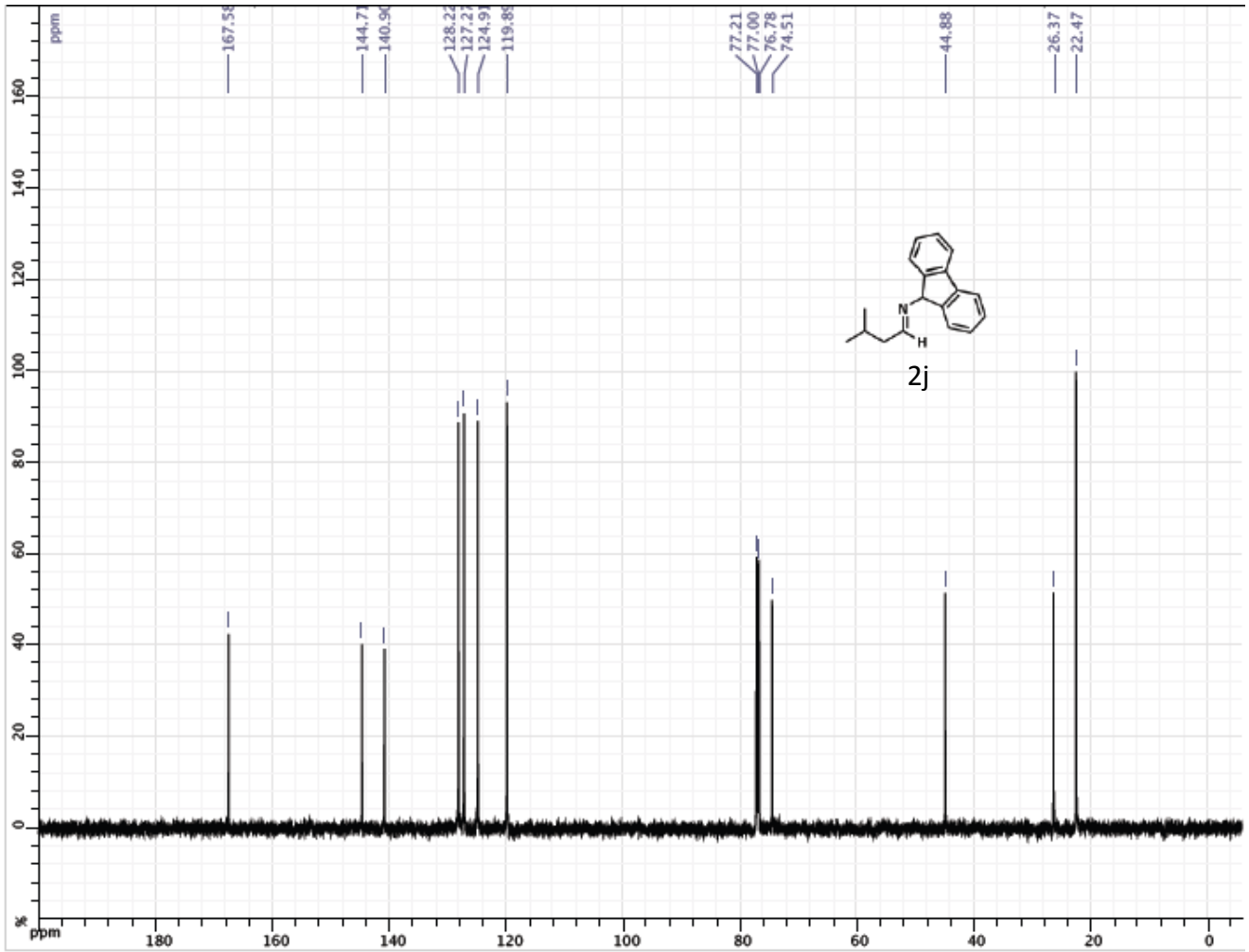

7.74 (d, J= 7.6Hz)
2h

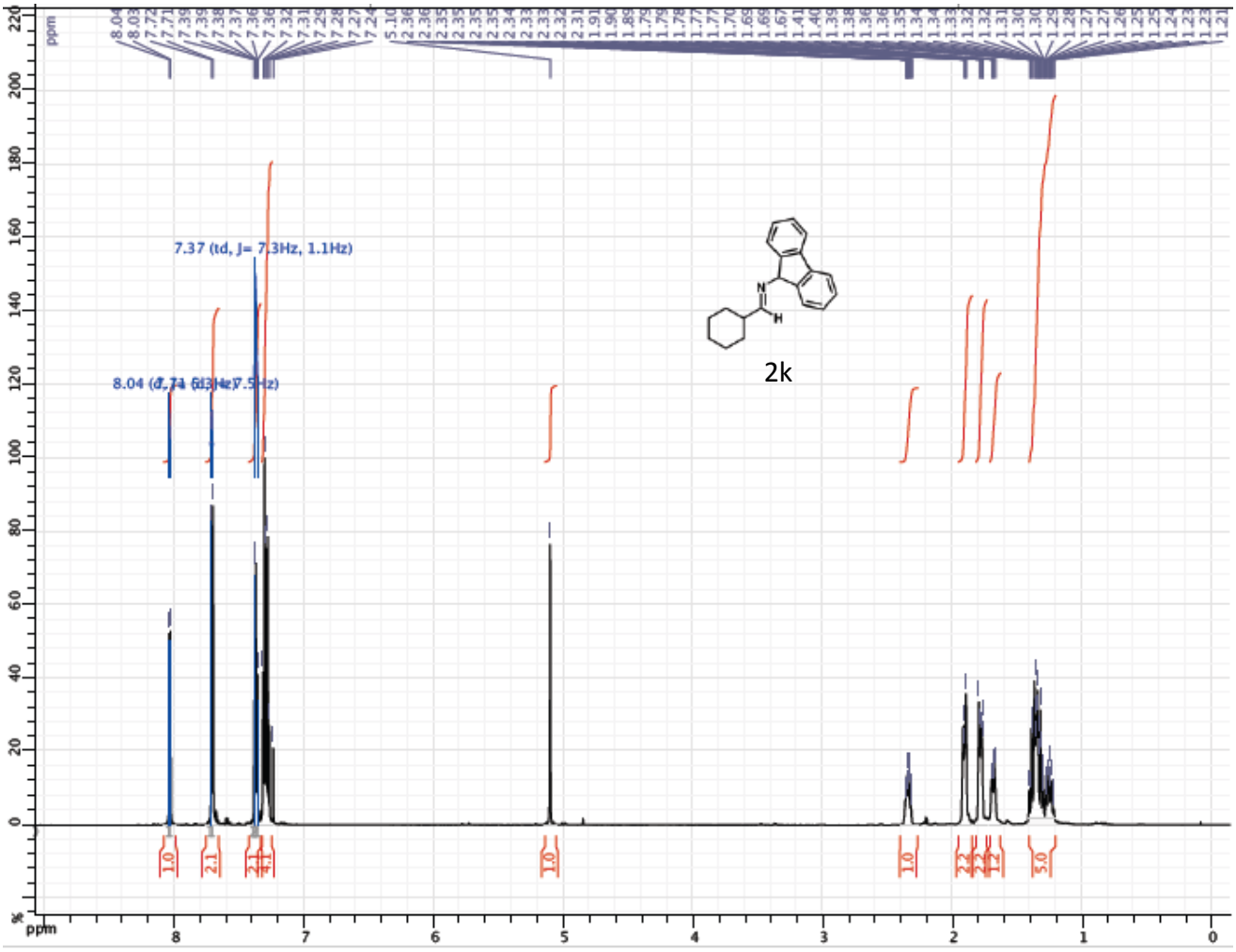

2h

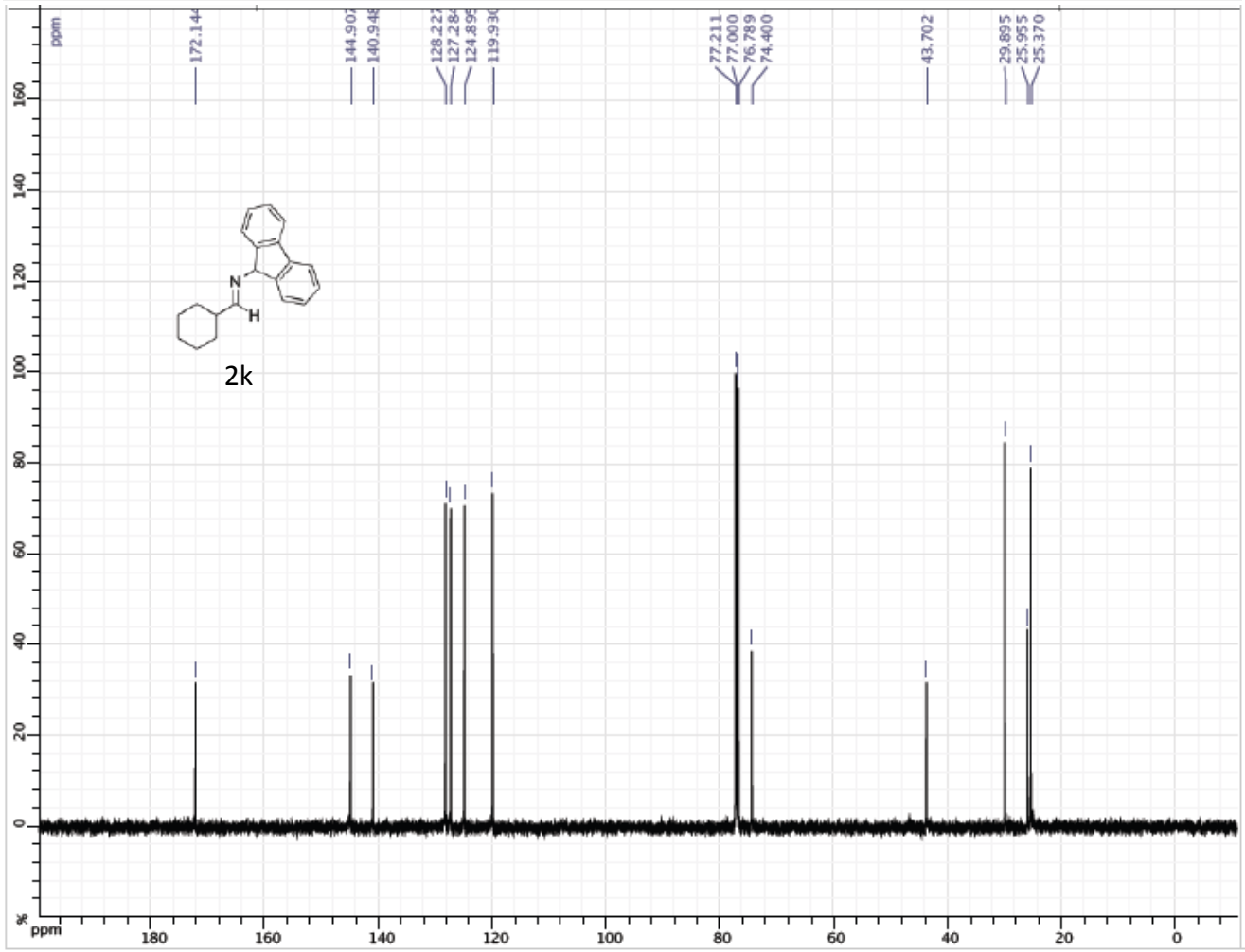

8.12 (t, J= 5.3Hz)
7.68 (d, J= 7.6Hz)
2.38 (td, J= 7.4Hz, 5.3Hz)
1.4 (md, J= 7.4Hz, 7.4Hz)
0.93 (t, J= 7.4Hz)
2i

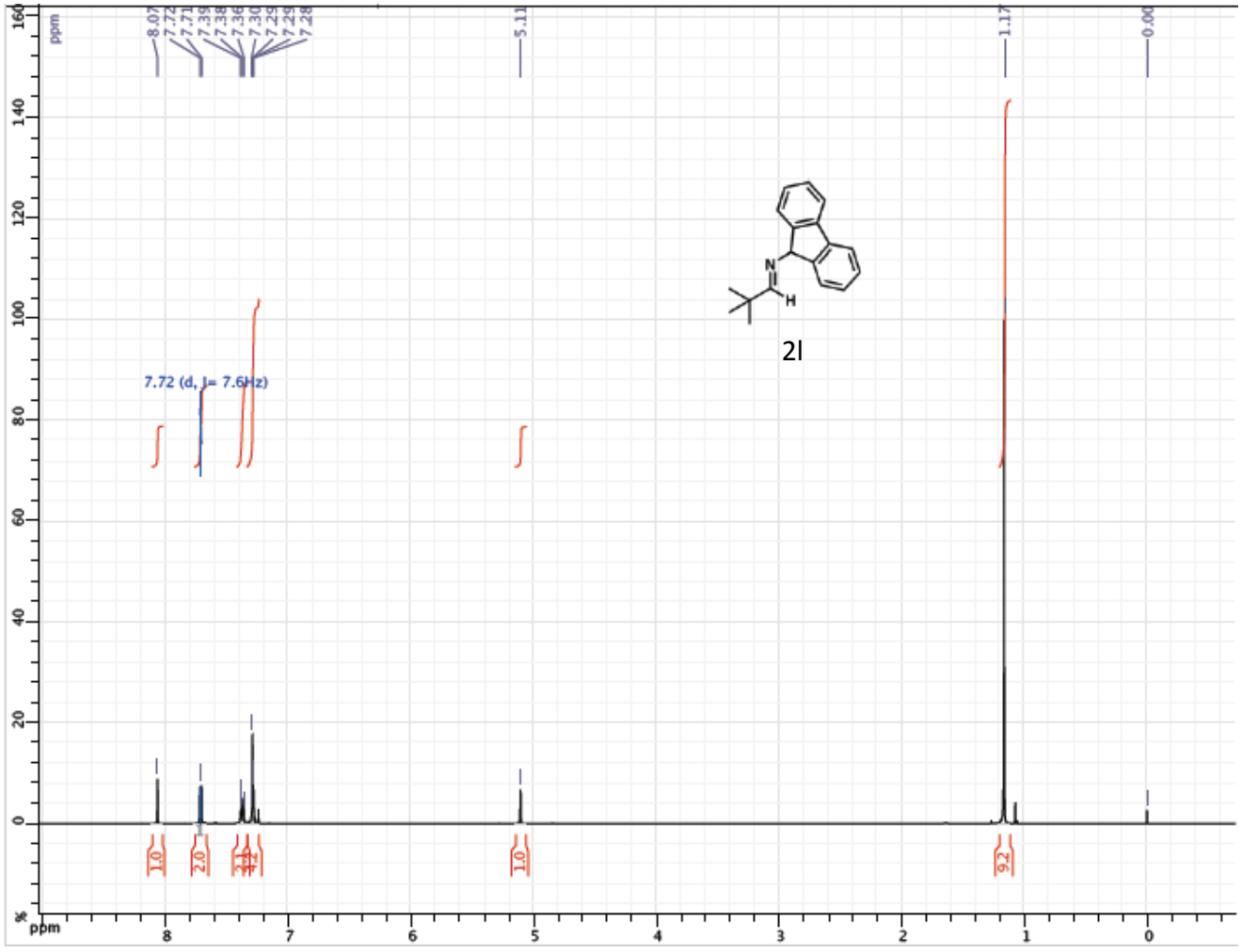

2i

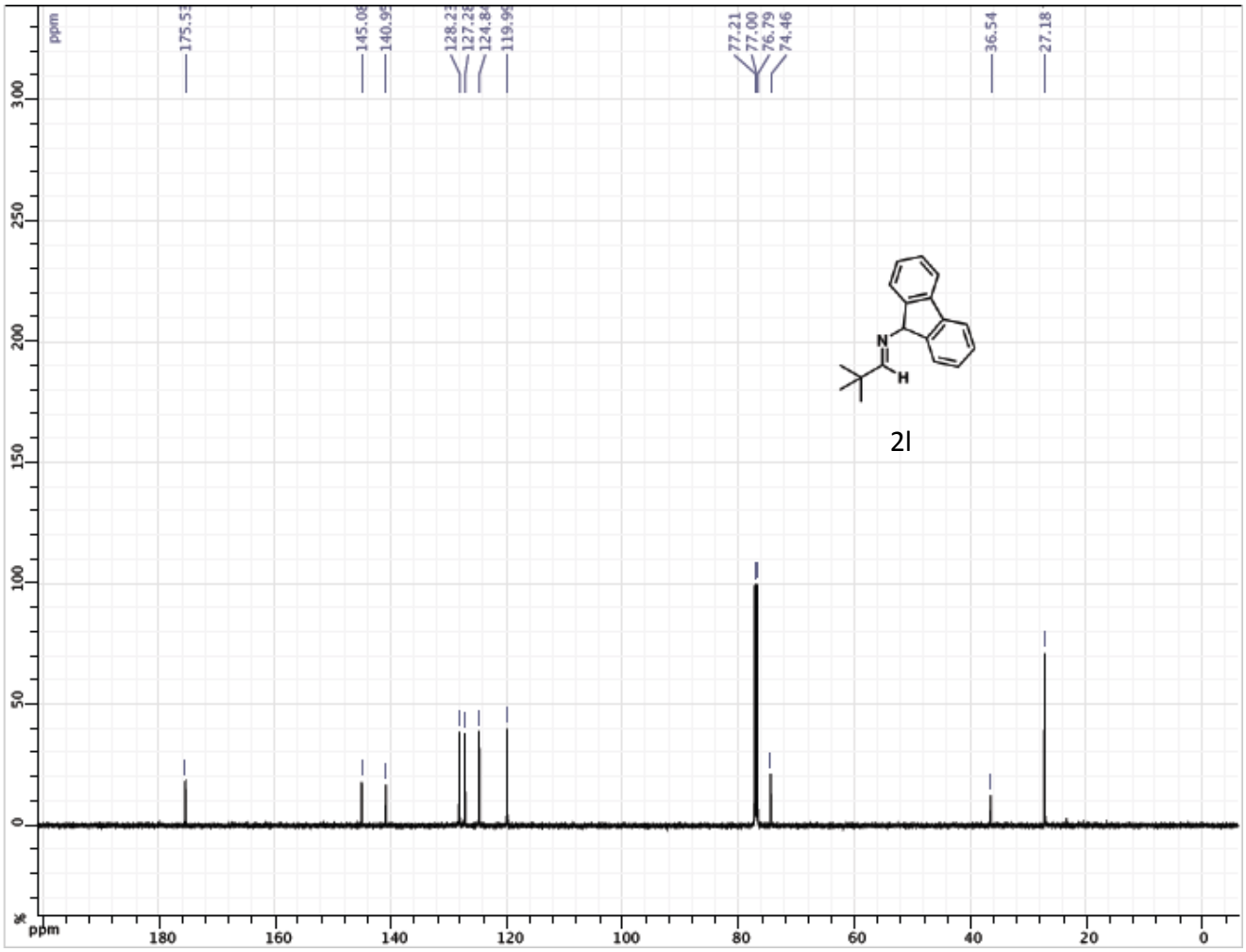

8.18 (t, J= 5.6Hz)
7.71 (d, J= 7.6Hz)
2.3 (dd, J= 6.9Hz, 5.3Hz)
1.02 (d, J= 6.6Hz)
2j

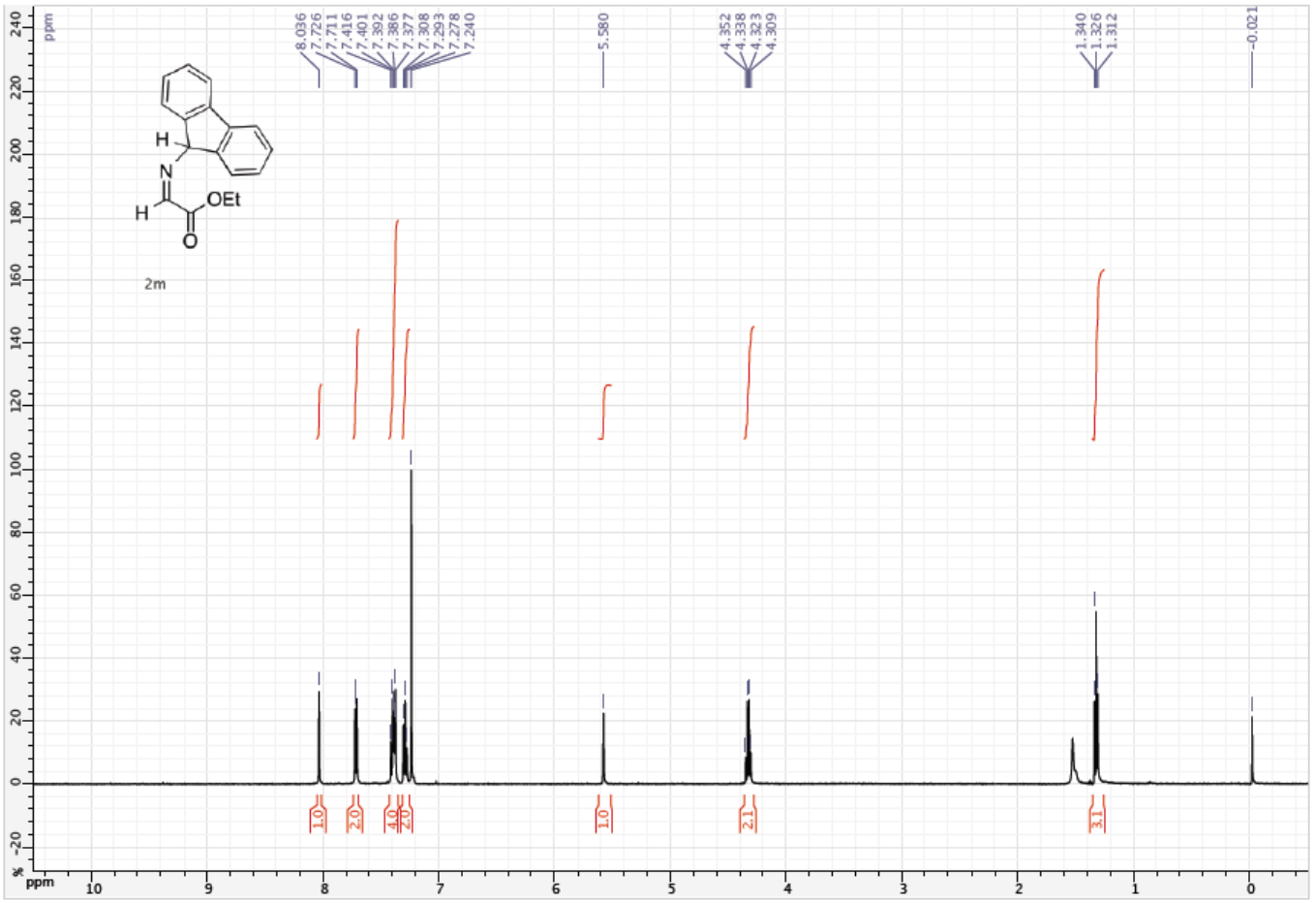

2j

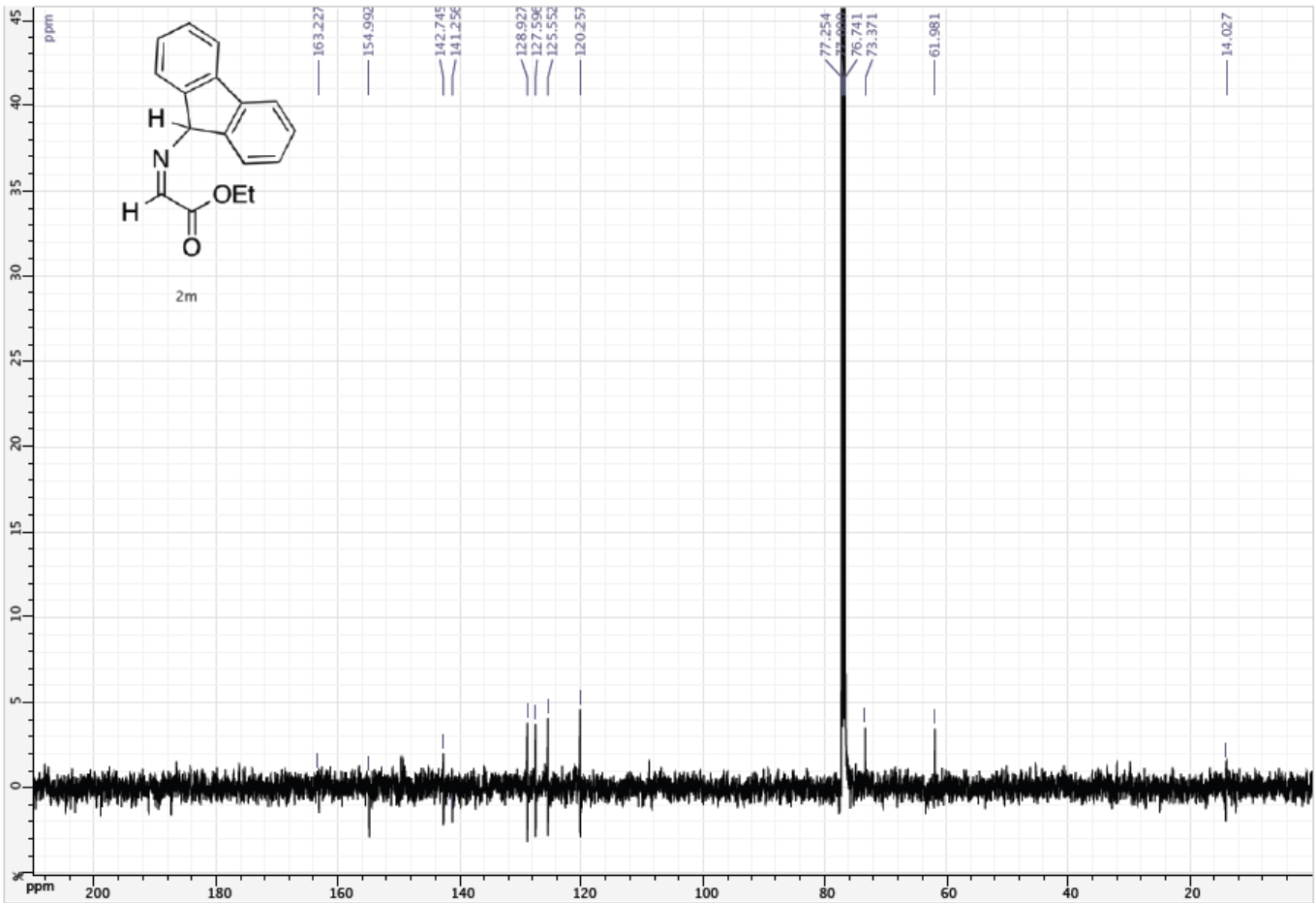

7.37 (td, J= 7.3Hz, 1.1Hz)
8.04 (d, J= 7.5Hz)
2k

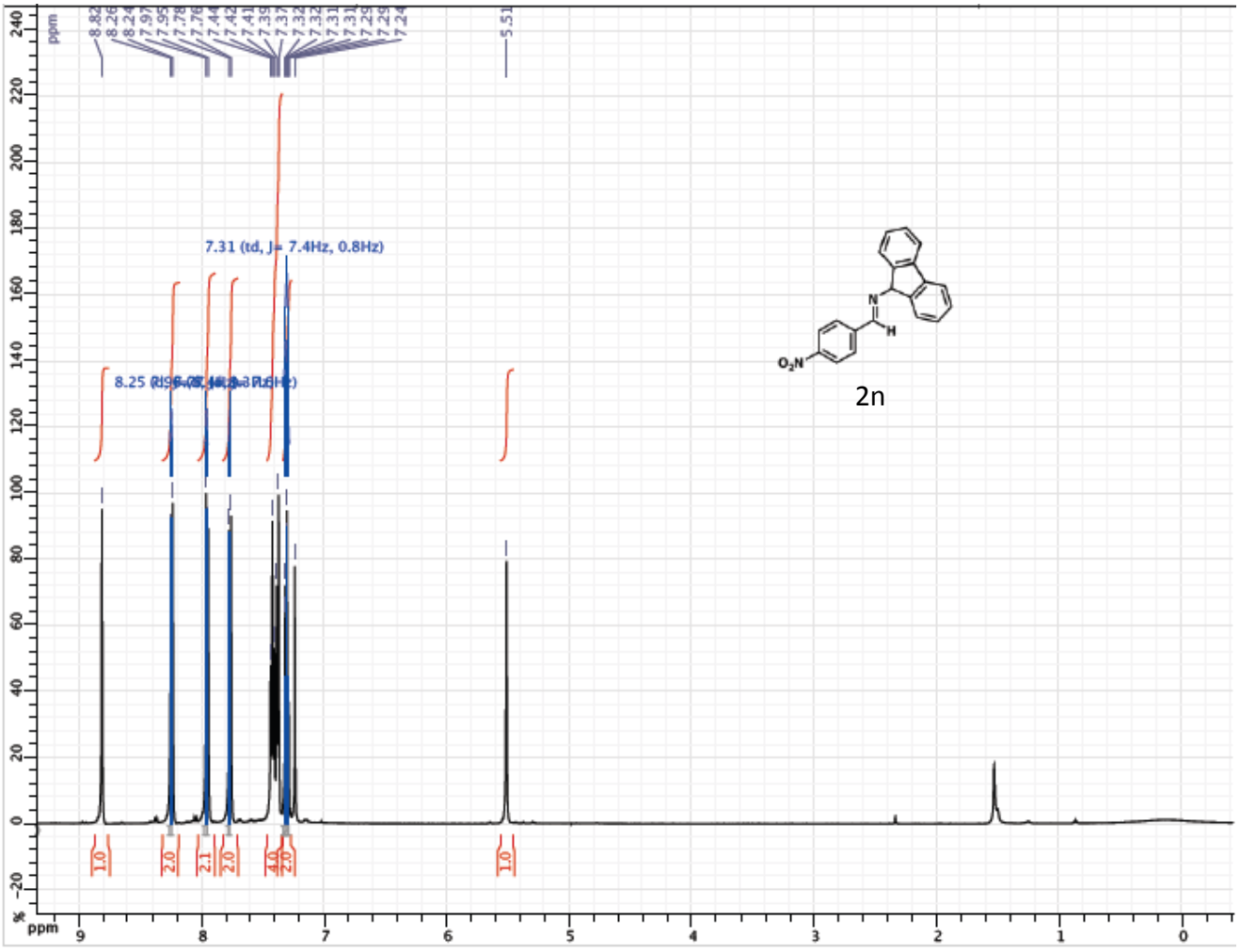

172.144
144.907
140.948
128.227
127.284
124.895
119.936
77.211
77.000
76.789
74.400
43.702
29.895
25.955
25.370
2k


7.72 (d, J= 7.6Hz)
2l

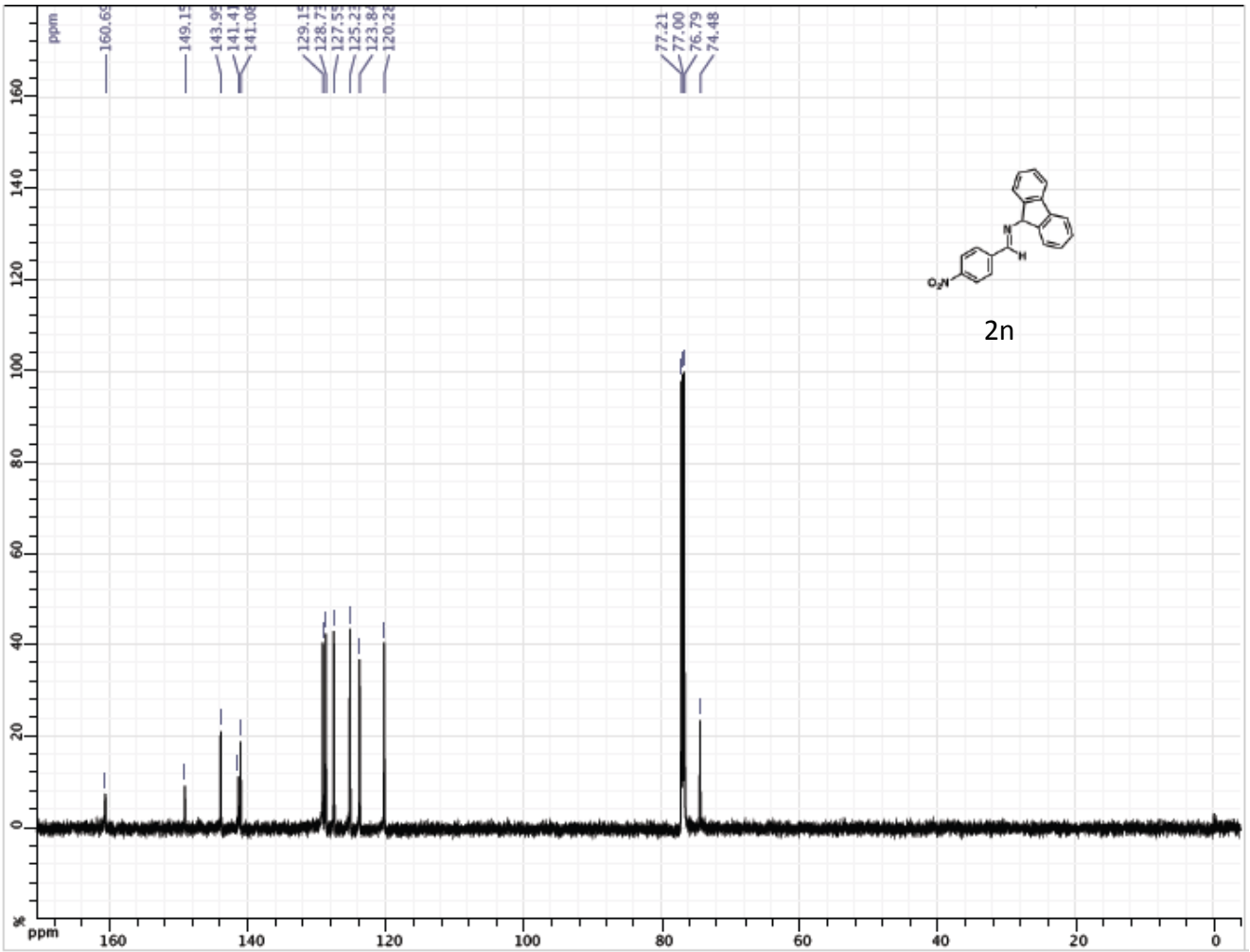

2l


ppm
8.036
7.726
7.711
7.416
7.401
7.392
7.386
7.377
7.308
7.293
7.278
7.240
5.580
4.352
4.338
4.323
4.309
1.340
1.326
1.312
-0.021
H
N
H
OEt
O
2m
1.0
2.0
4.0
2.0
1.0
2.1
3.1

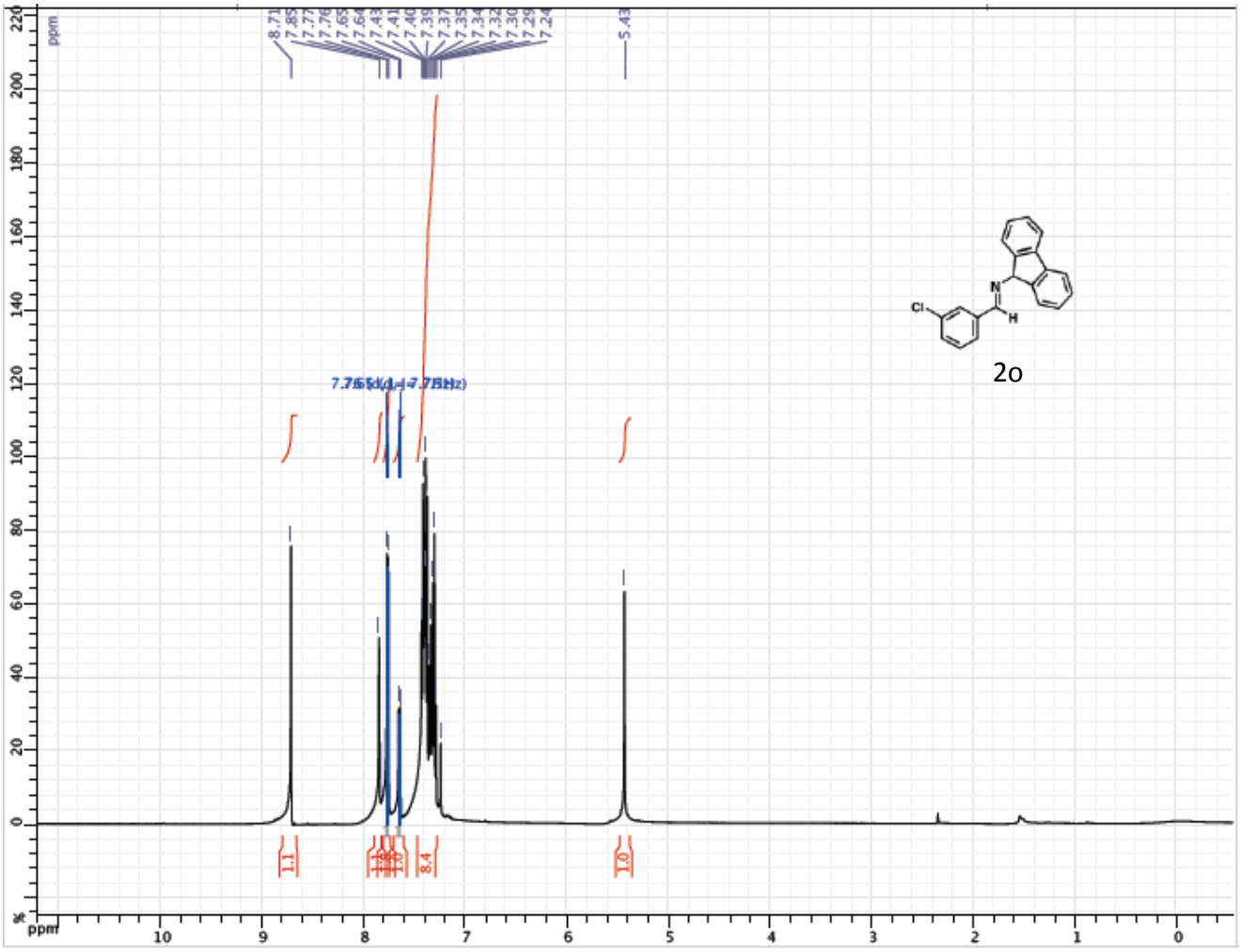

ppm
163.227
154.992
142.745
141.256
128.927
127.596
125.552
120.257
77.254
76.741
73.371
61.981
14.027
H
N
H
OEt
O
2m


7.31 (td, J= 7.4Hz, 0.8Hz)
8.25
5.51
1.0
2.0
2.1
2.0
4.0
2.0
1.0
ppm

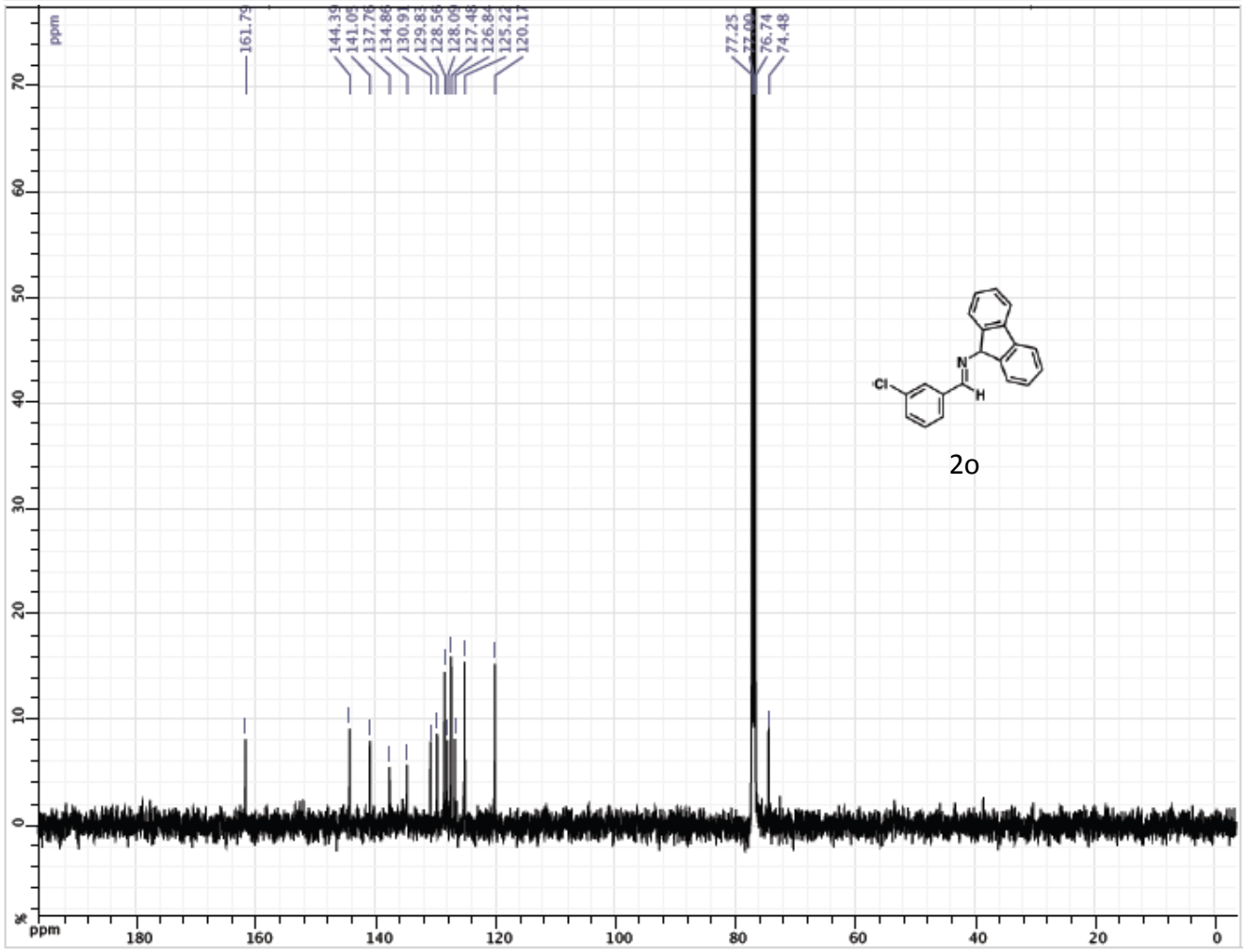
2n


160.69
149.15
143.99
141.41
141.08
129.15
128.73
127.55
125.23
123.84
120.28
77.21
77.00
76.79
74.48
ppm

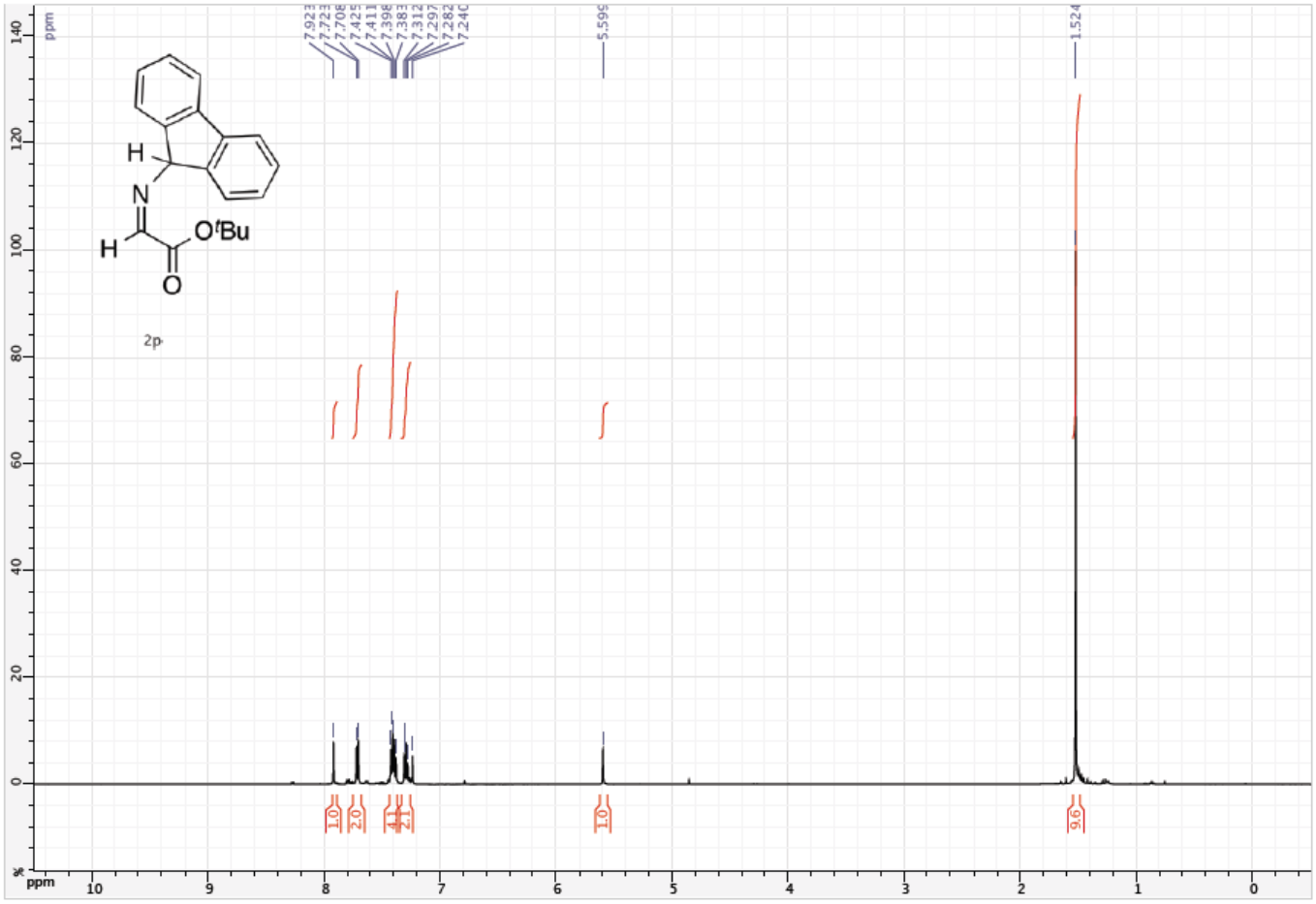
2n

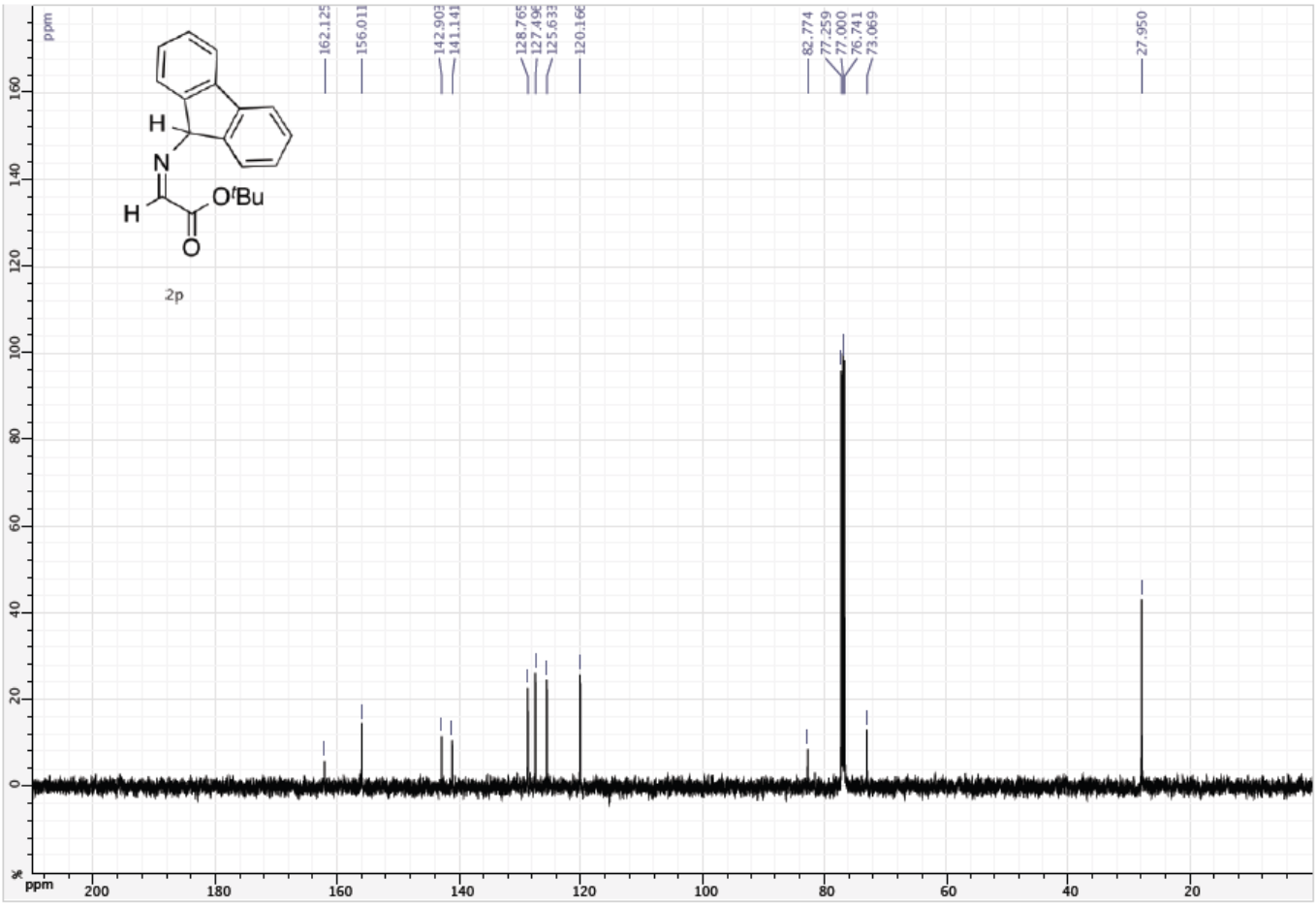

8.71
7.85
7.77
7.76
7.65
7.64
7.43
7.41
7.40
7.39
7.37
7.35
7.34
7.32
7.30
7.29
7.24
5.43
1.1
8.4
1.0
Cl
N
H

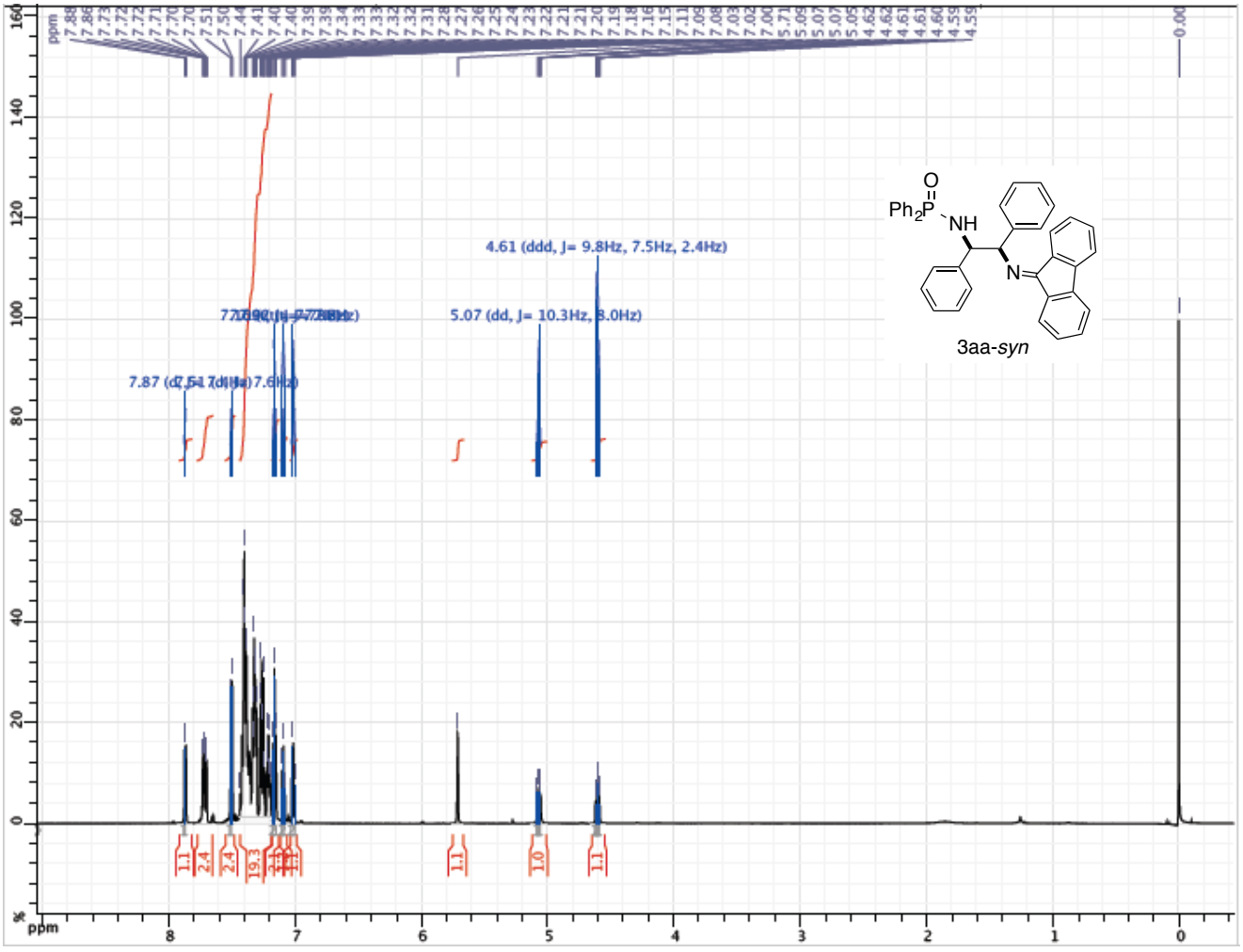
2o

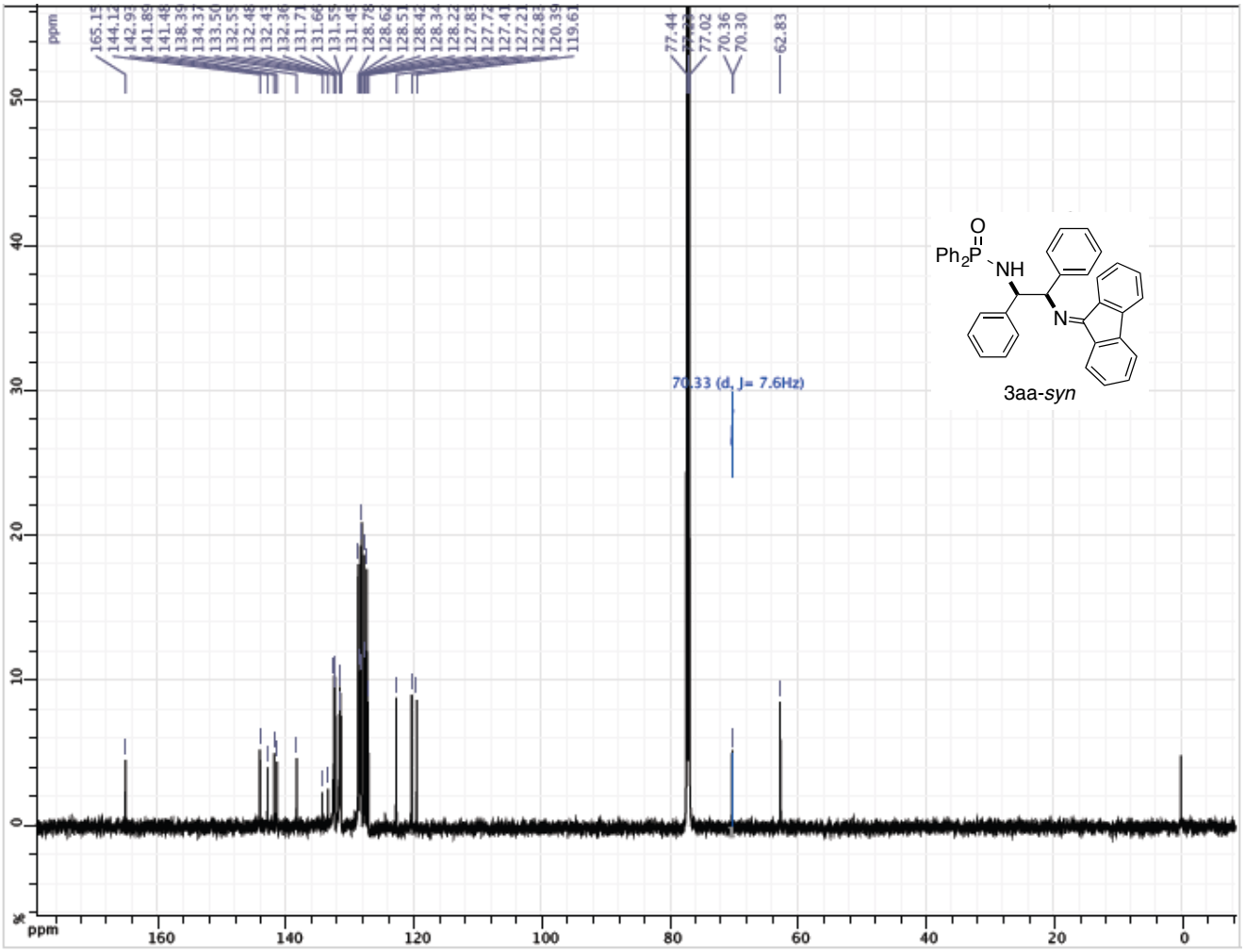

161.79
144.39
141.05
137.76
134.86
130.91
129.83
128.56
128.09
127.48
126.84
125.22
120.17
77.25
77.00
76.74
74.48
Cl
N
H

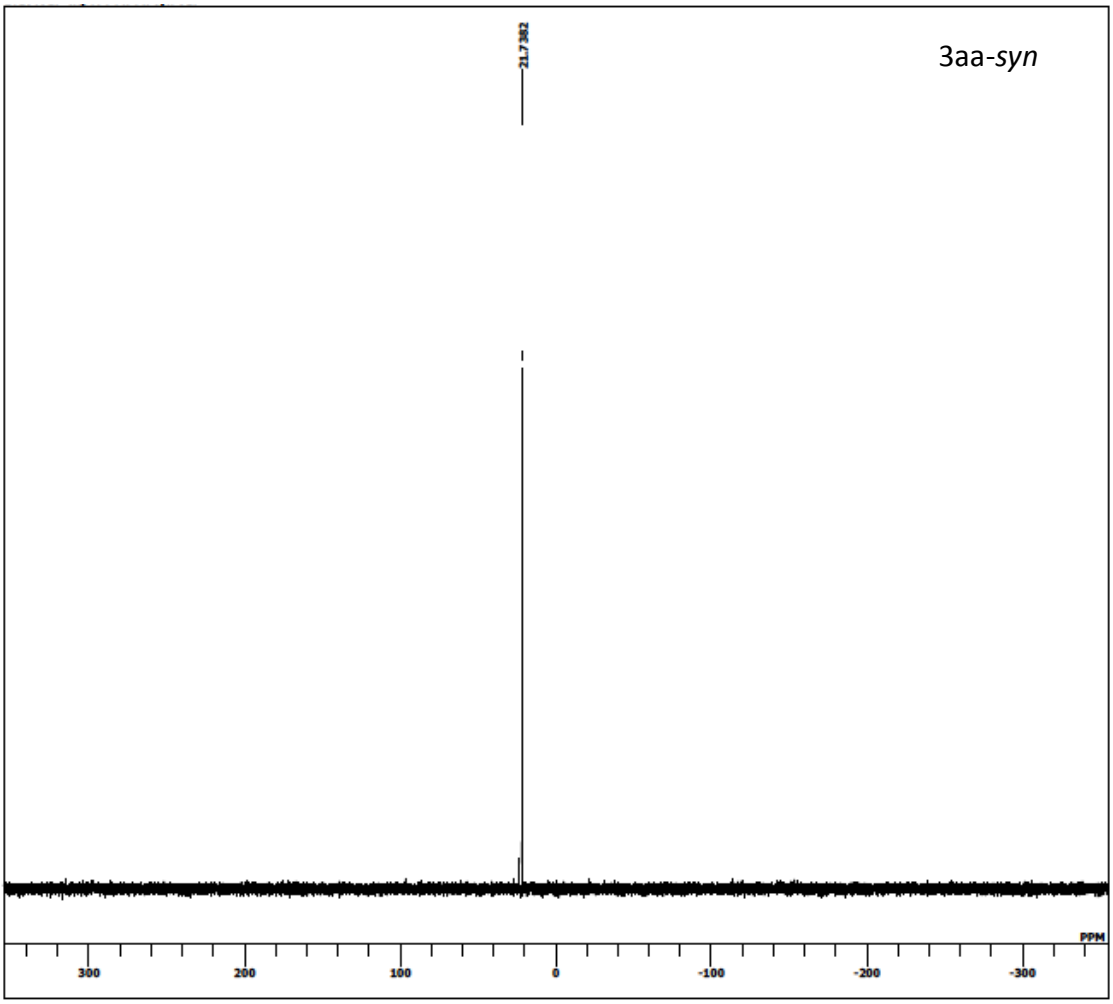
2o

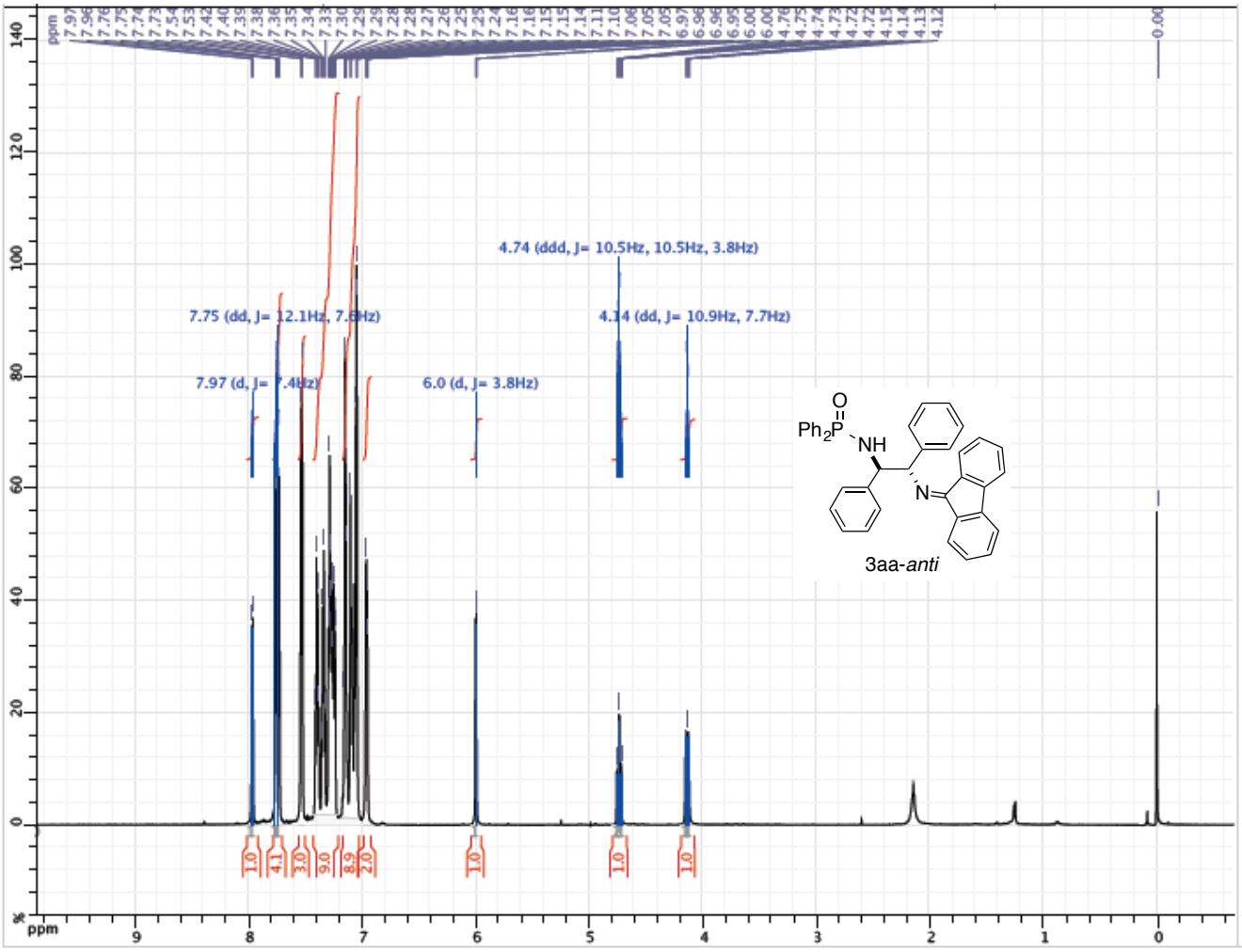

7.923
7.723
7.708
7.425
7.411
7.398
7.383
7.312
7.297
7.282
7.240
5.595
1.524
H
N
H
O
O^{t}Bu
2p
1.0
2.0
4.1
2.1
1.0
9.6
ppm

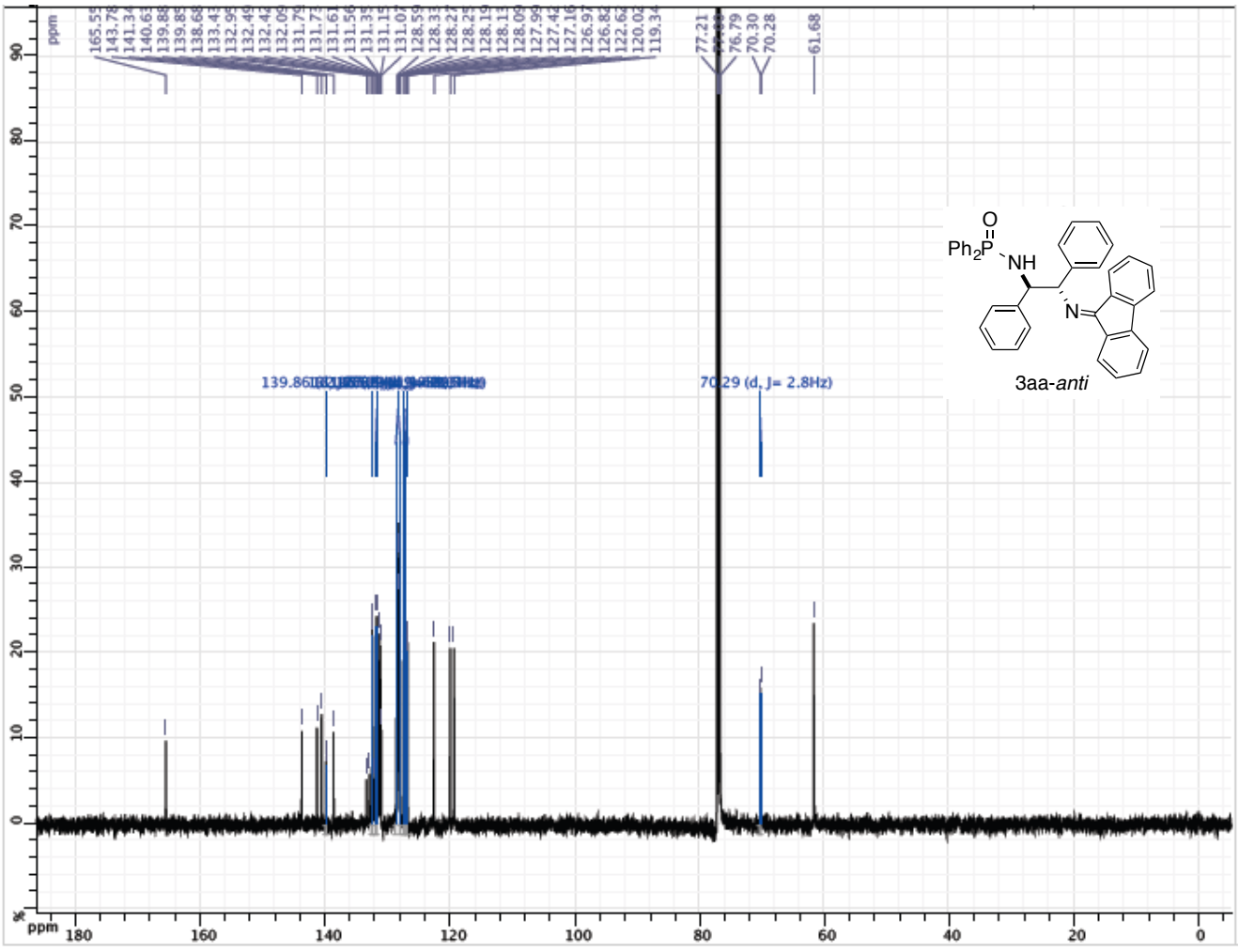

162.125
156.011
142.903
141.141
128.765
127.496
125.633
120.166
82.774
77.259
77.000
76.741
73.069
27.950
H
N
H
O
O^{t}Bu
2p
ppm

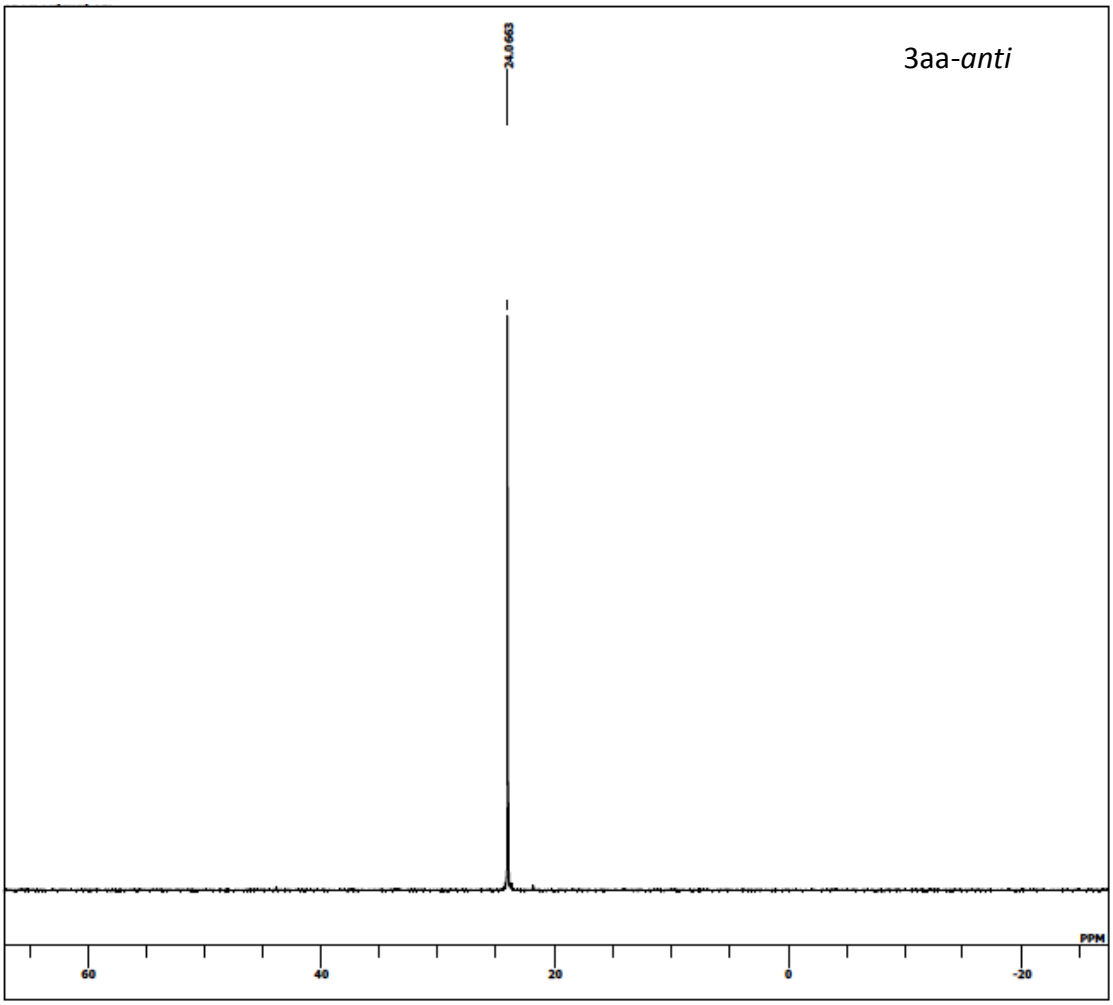

4.61 (ddd, J= 9.8Hz, 7.5Hz, 2.4Hz)
5.07 (dd, J= 10.3Hz, 8.0Hz)
3aa-syn

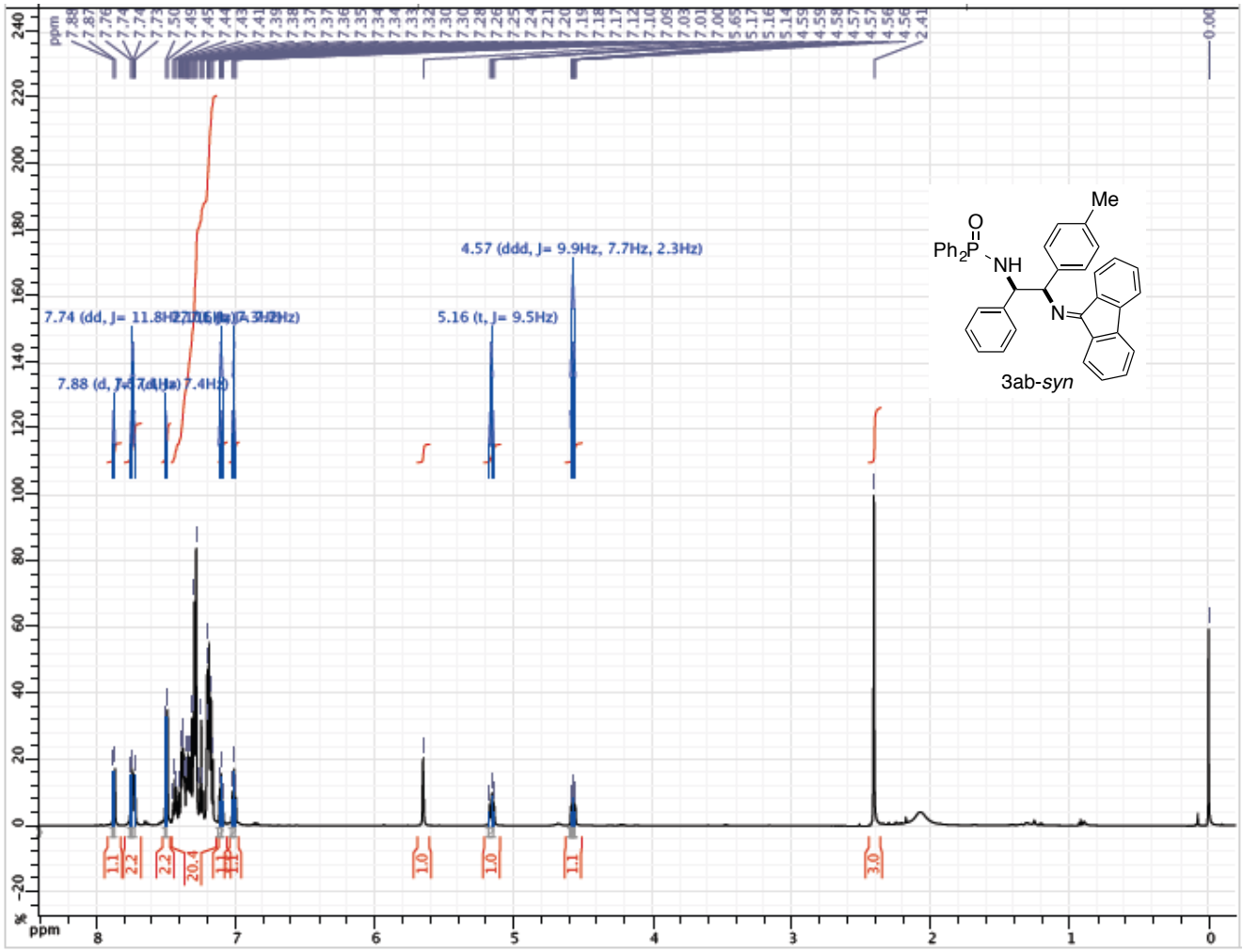

70.33 (d, J= 7.6Hz)
3aa-syn

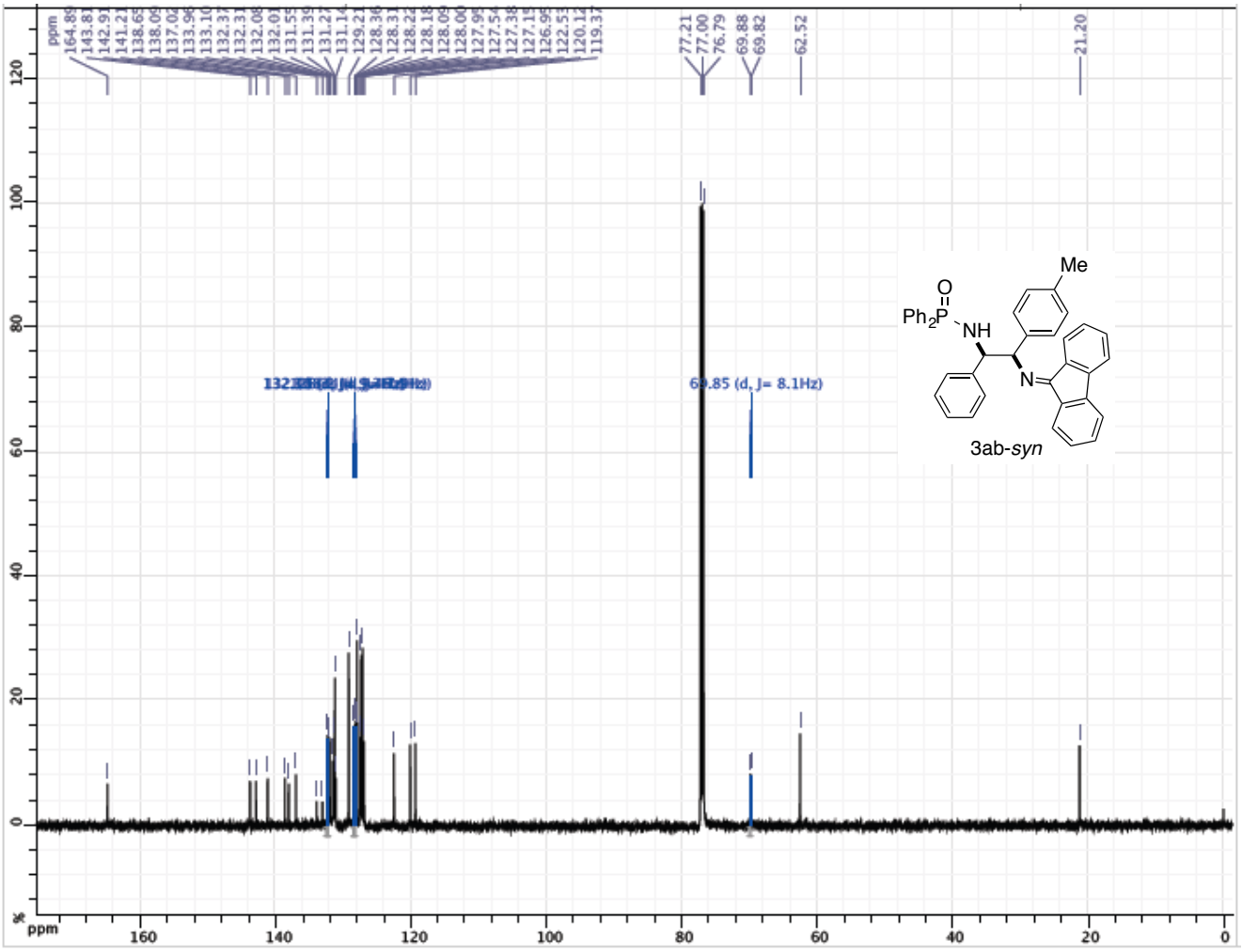

3aa-*syn*
PPM
300
200
100
0
-100
-200
-300

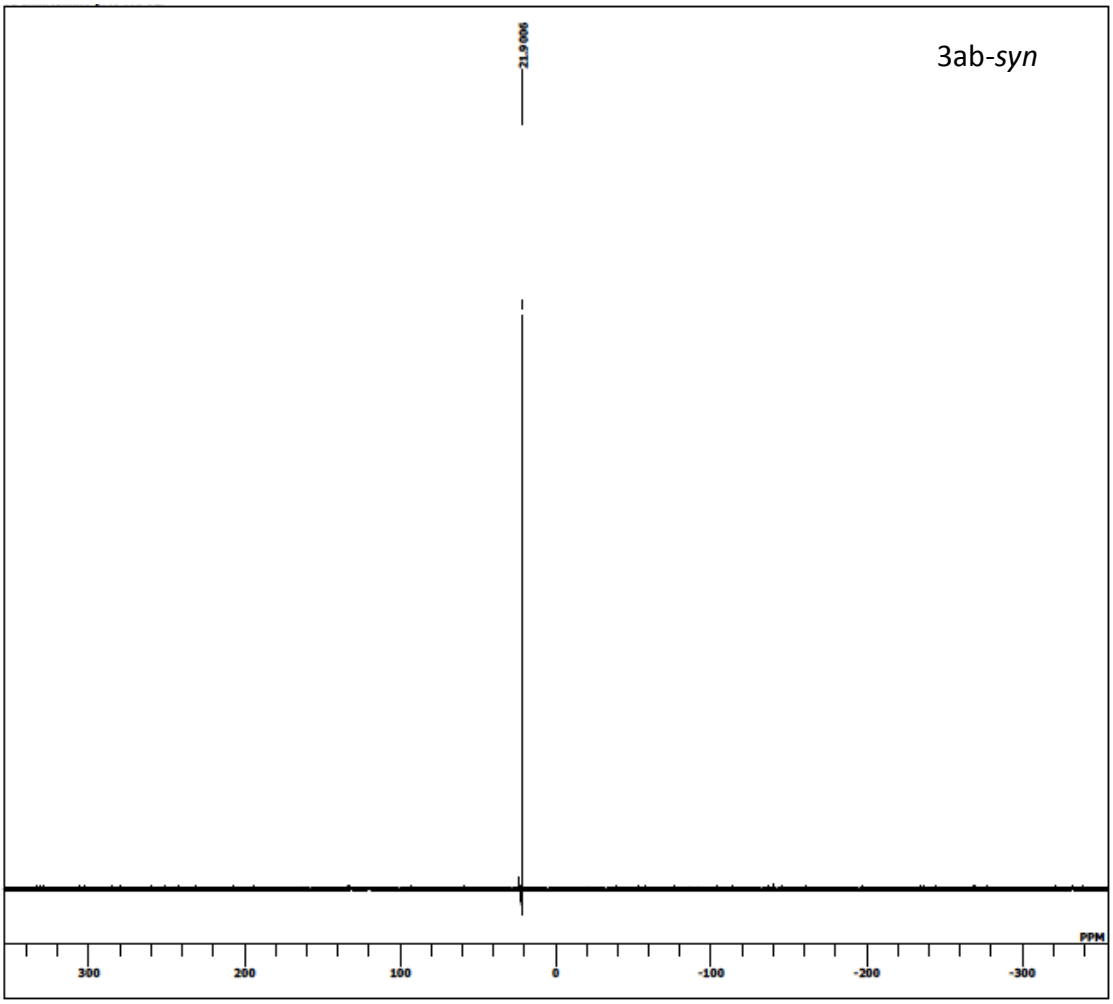

4.74 (ddd, J= 10.5Hz, 10.5Hz, 3.8Hz)
7.75 (dd, J= 12.1Hz, 7.6Hz)
4.14 (dd, J= 10.9Hz, 7.7Hz)
7.97 (d, J= 7.4Hz)
6.0 (d, J= 3.8Hz)
Ph2P
O
NH
N
3aa-*anti*
ppm

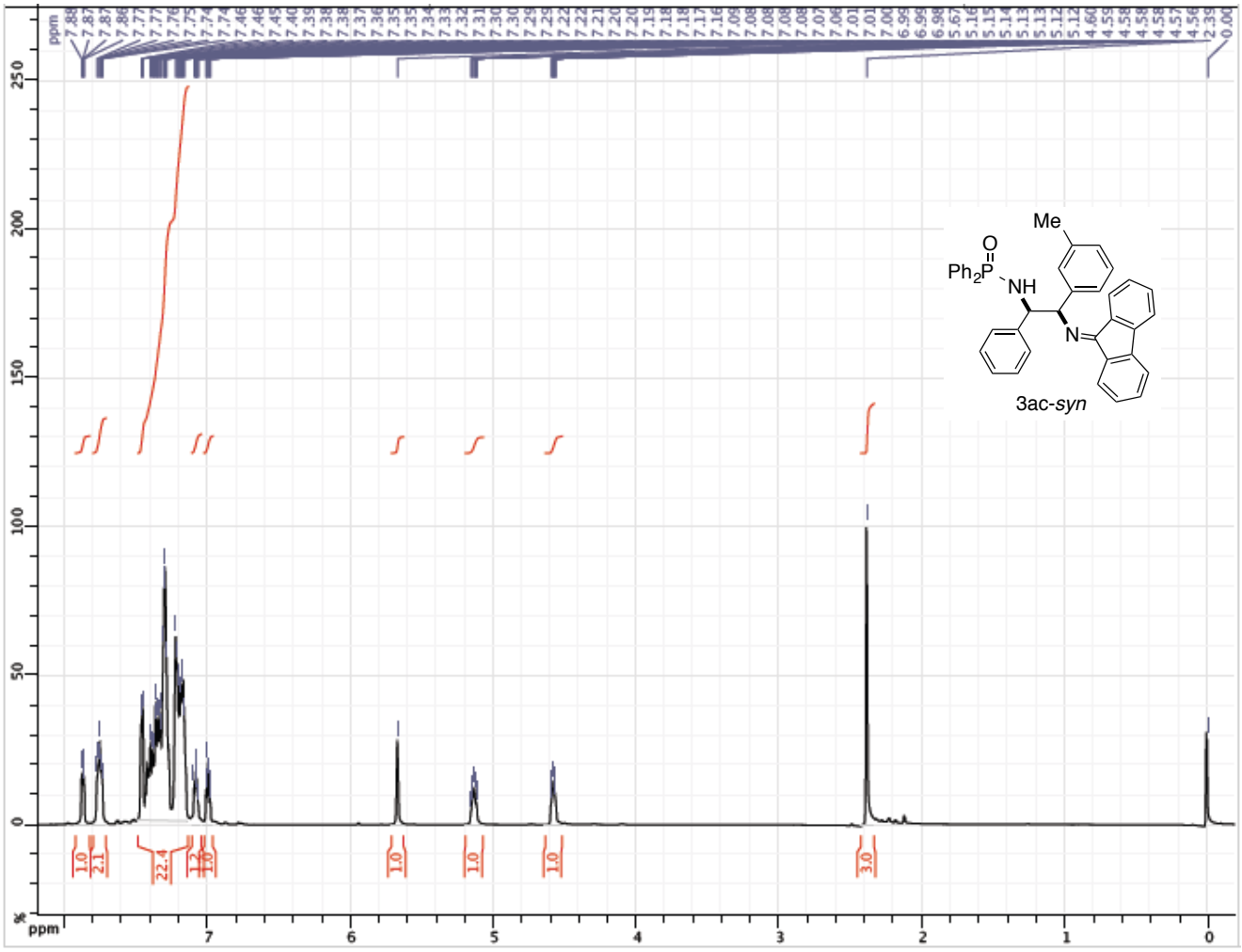

ppm
165.55
143.78
141.34
140.63
139.88
139.85
138.68
133.43
132.95
132.49
132.42
132.06
131.79
131.73
131.61
131.56
131.35
131.15
131.07
128.59
128.33
128.27
128.25
128.19
128.13
128.09
127.99
127.42
127.16
126.97
126.82
122.62
120.02
119.34
77.21
76.79
70.30
70.28
61.68
139.86
70.29 (d, J= 2.8Hz)
Ph2P
O
NH
N
3aa-anti
ppm
180
160
140
120
100
80
60
40
20
0

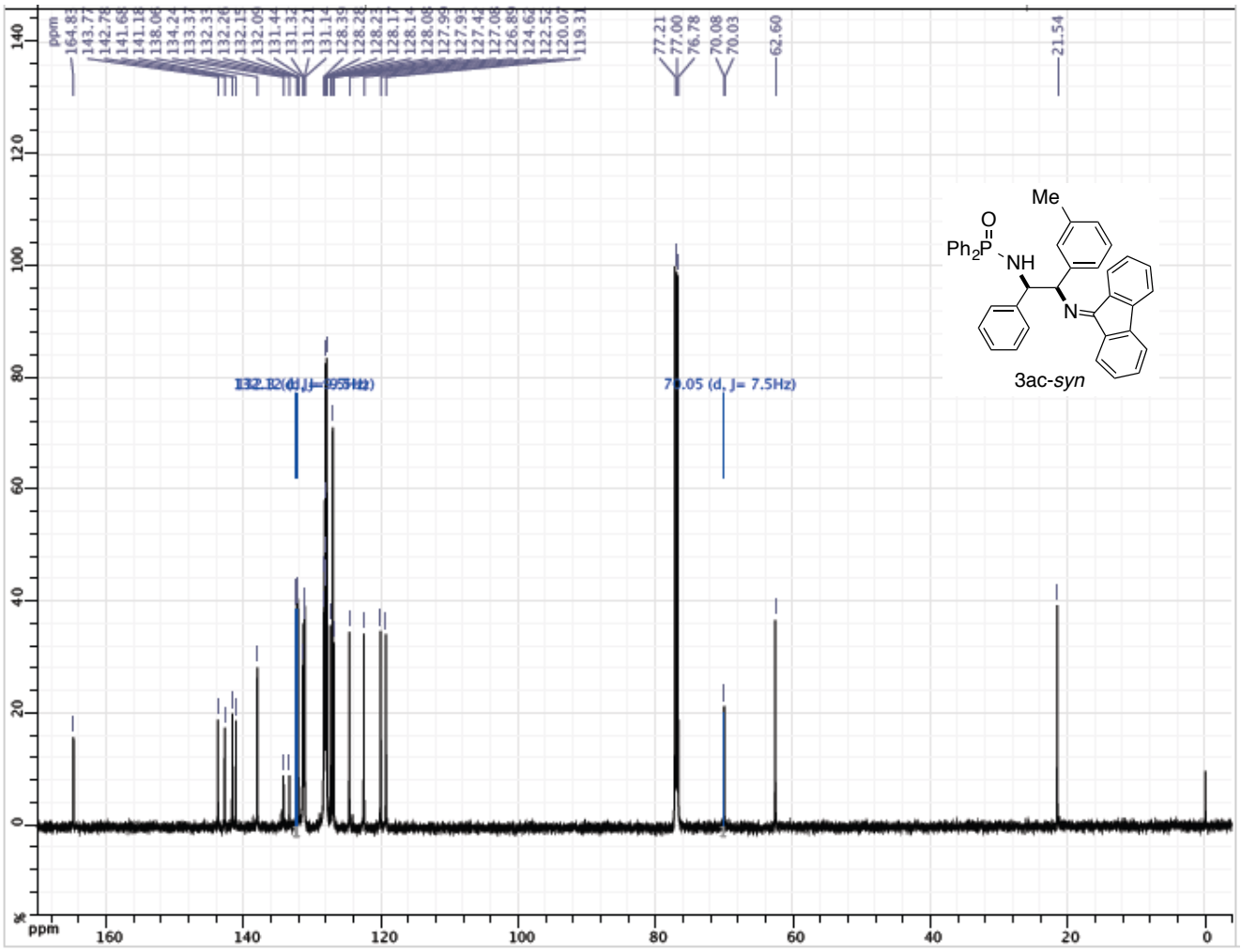

24.0 663
3aa-anti
PPM
60
40
20
0
-20

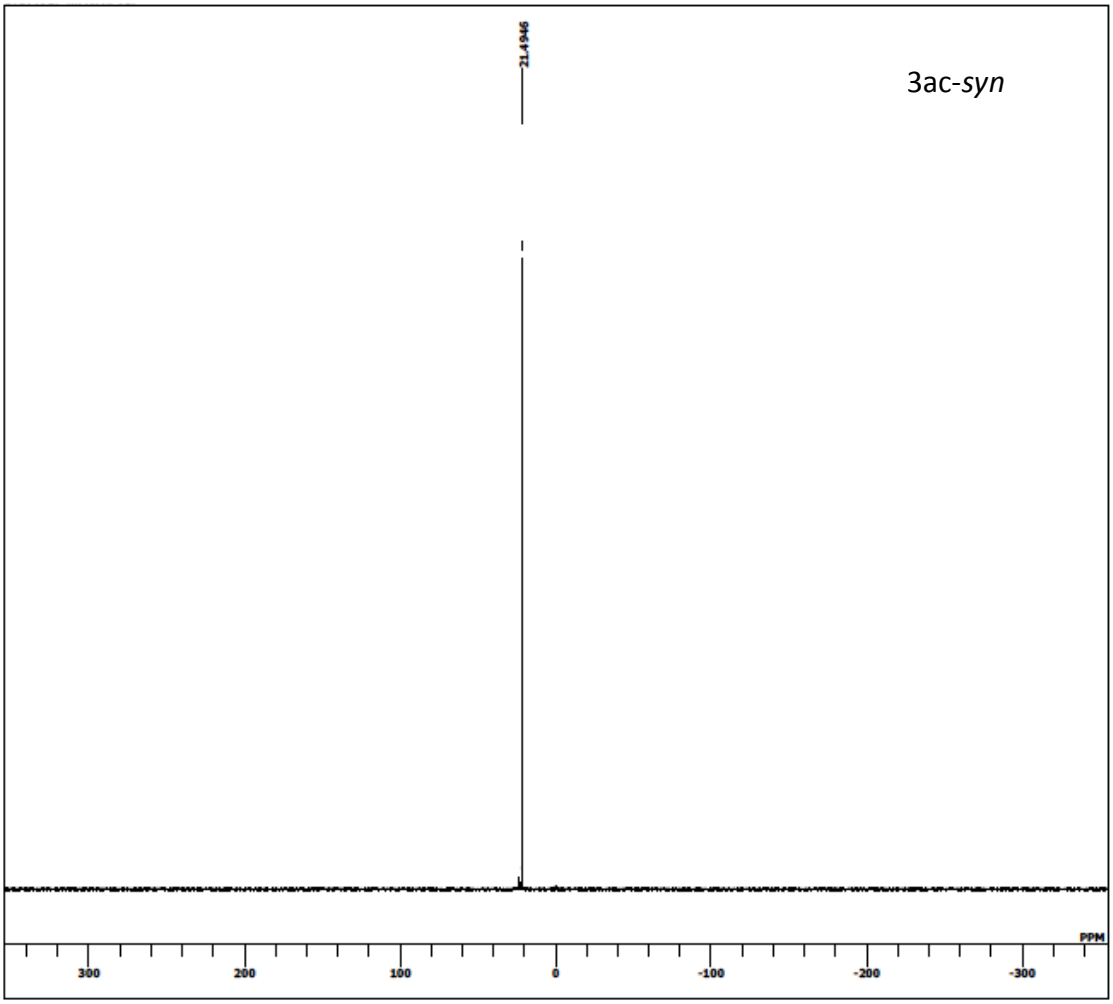

4.57 (ddd, J= 9.9Hz, 7.7Hz, 2.3Hz)
5.16 (t, J= 9.5Hz)
7.74 (dd, J= 11.8Hz
7.88 (d, J= 7.4Hz)
Me
O
Ph2P
NH
N
3ab-syn

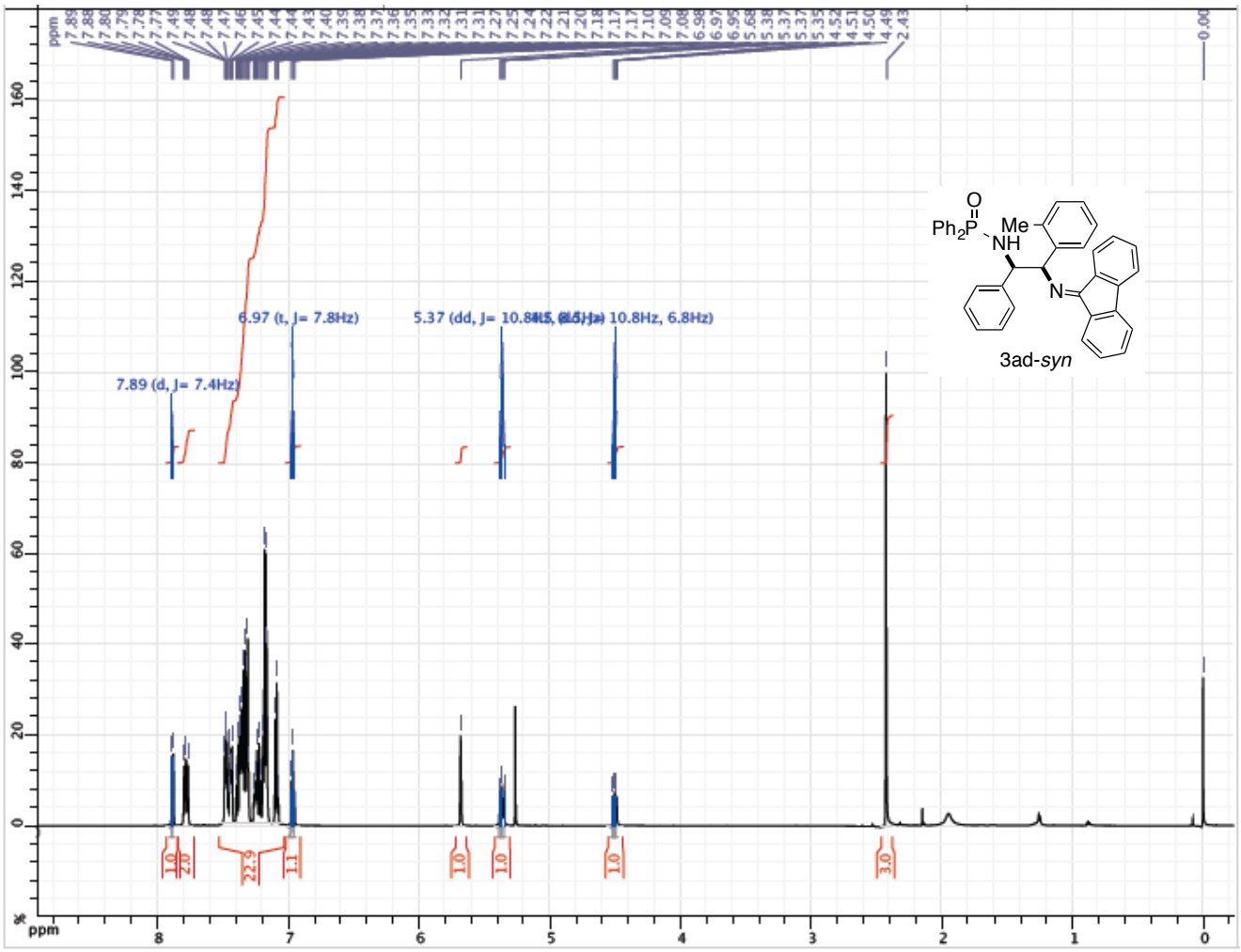

69.85 (d, J= 8.1Hz)
Me
O
Ph2P
NH
N
3ab-syn

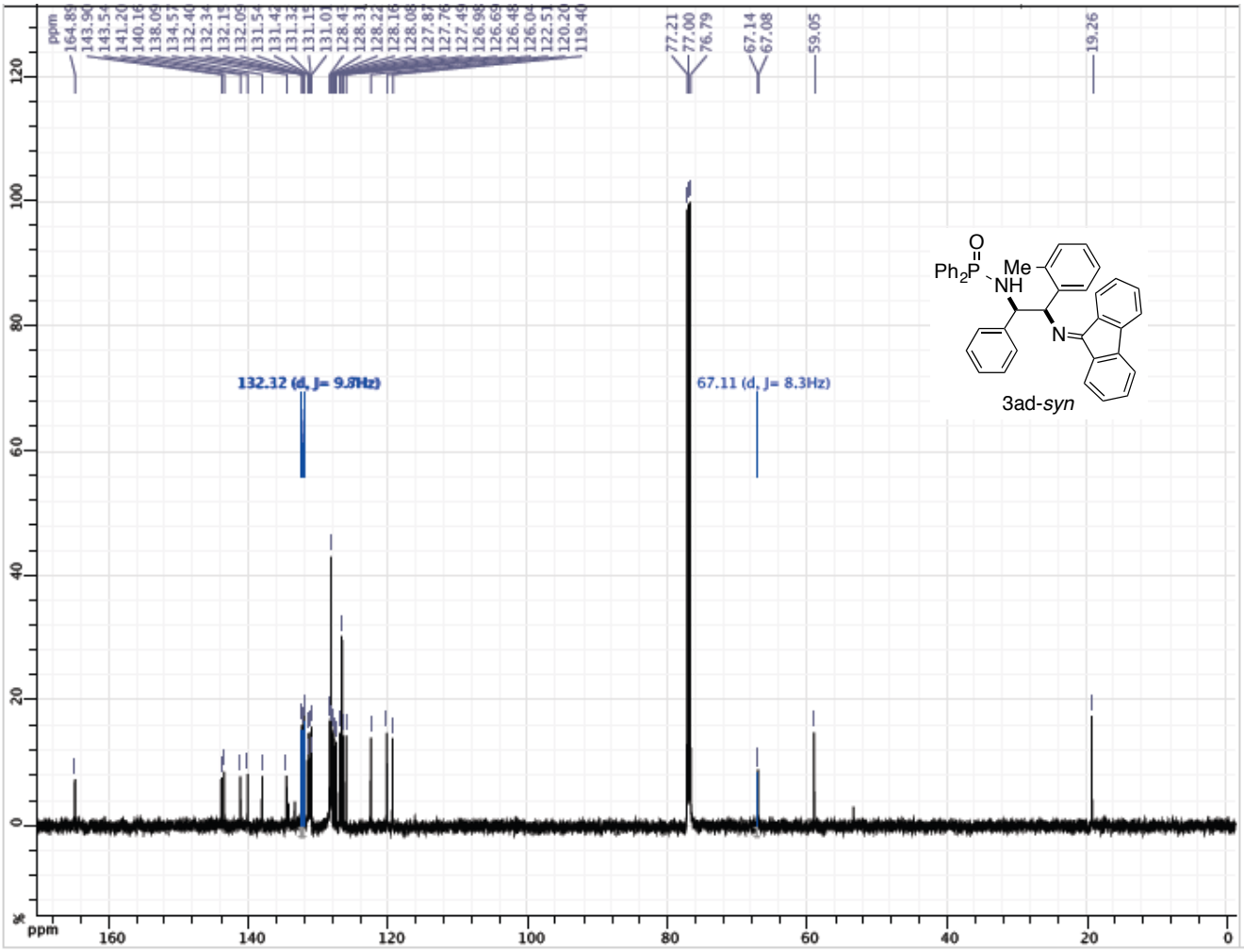

21.9006
3ab-*syn*
PPM
300
200
100
0
-100
-200
-300

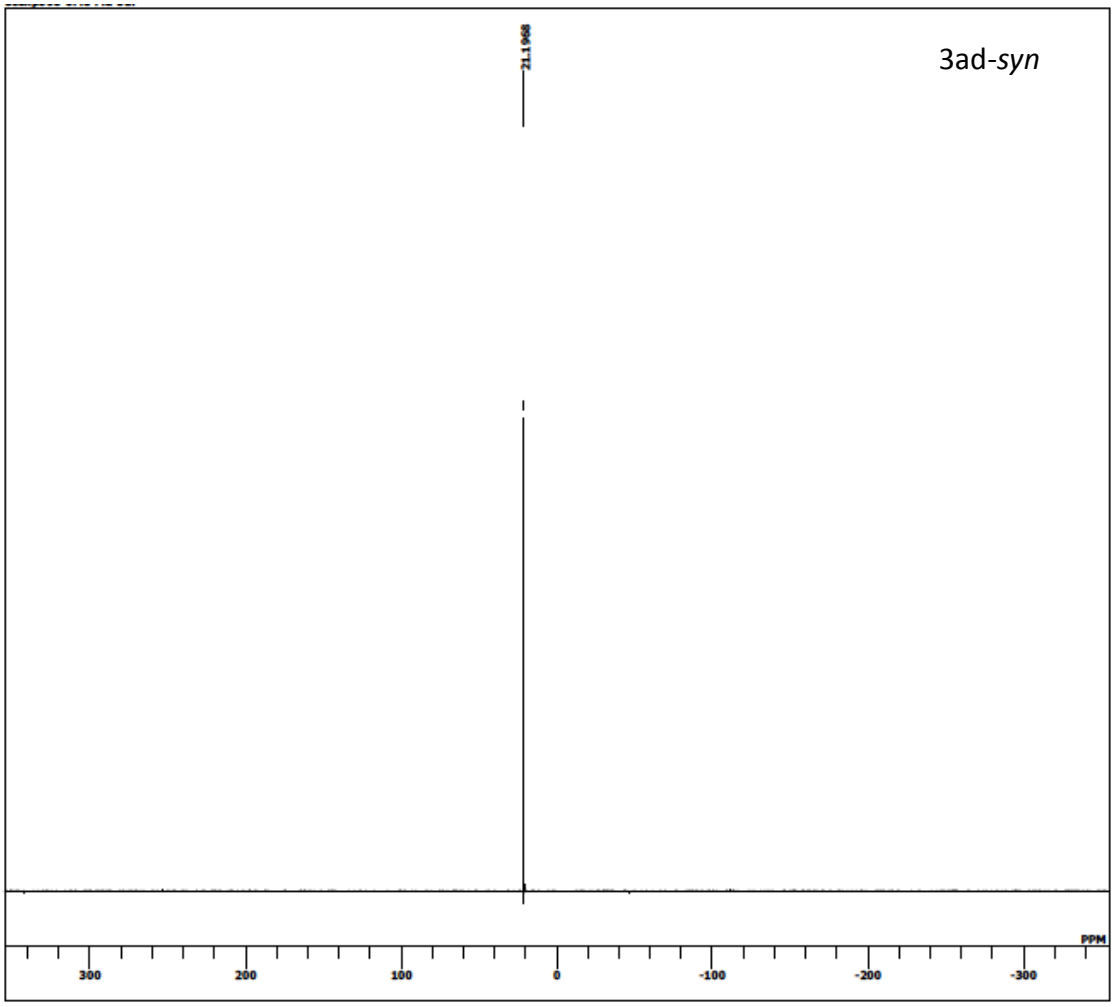

Me
O
Ph2P
NH
N
3ac-*syn*
ppm
7
6
5
4
3
2
1
0
250
200
150
100
50
0
%
1.0
2.1
22.4
1.0
1.0
1.0
3.0

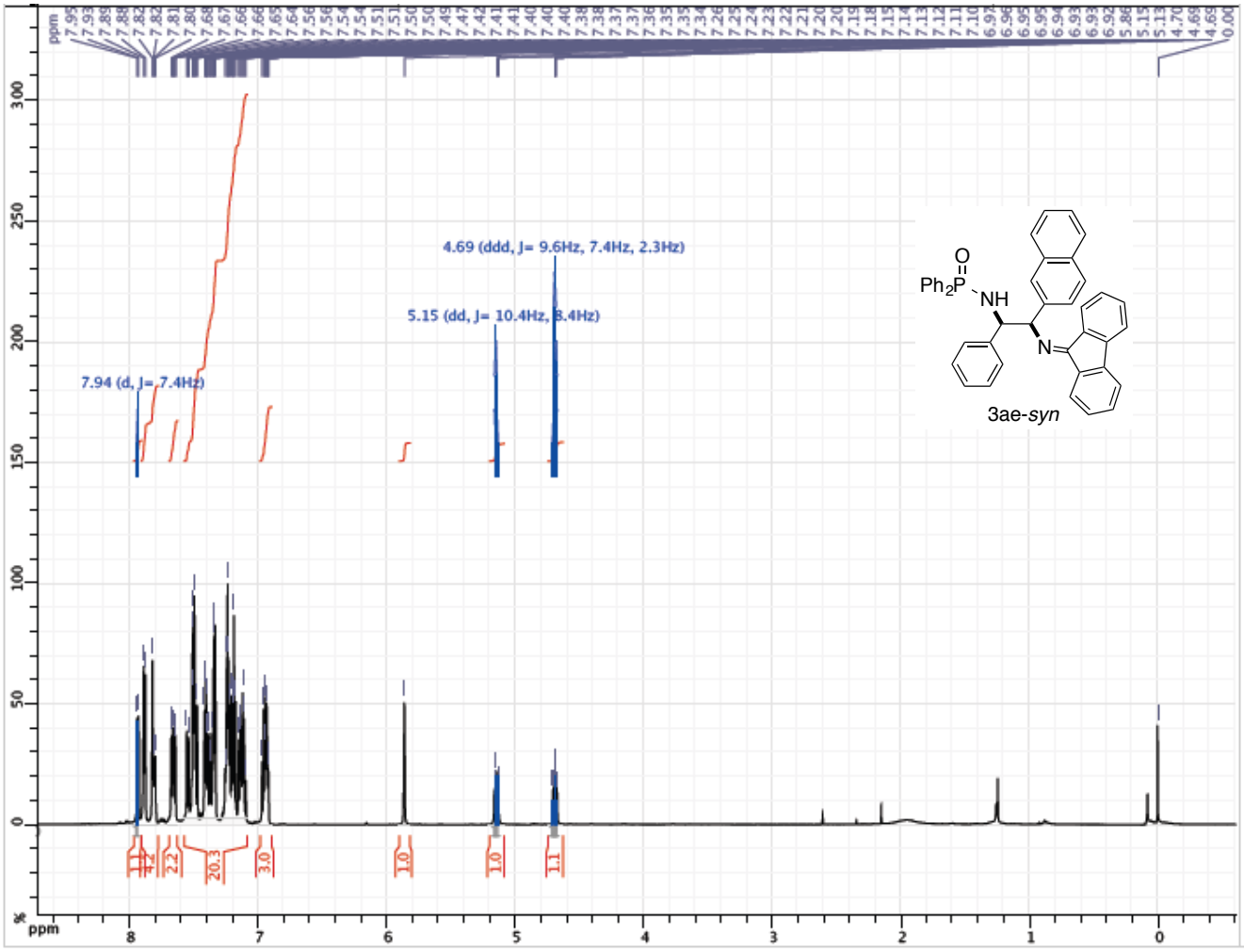

Me
O
Ph2P
NH
N
3ac-syn
79.05 (d, J= 7.5Hz)
ppm

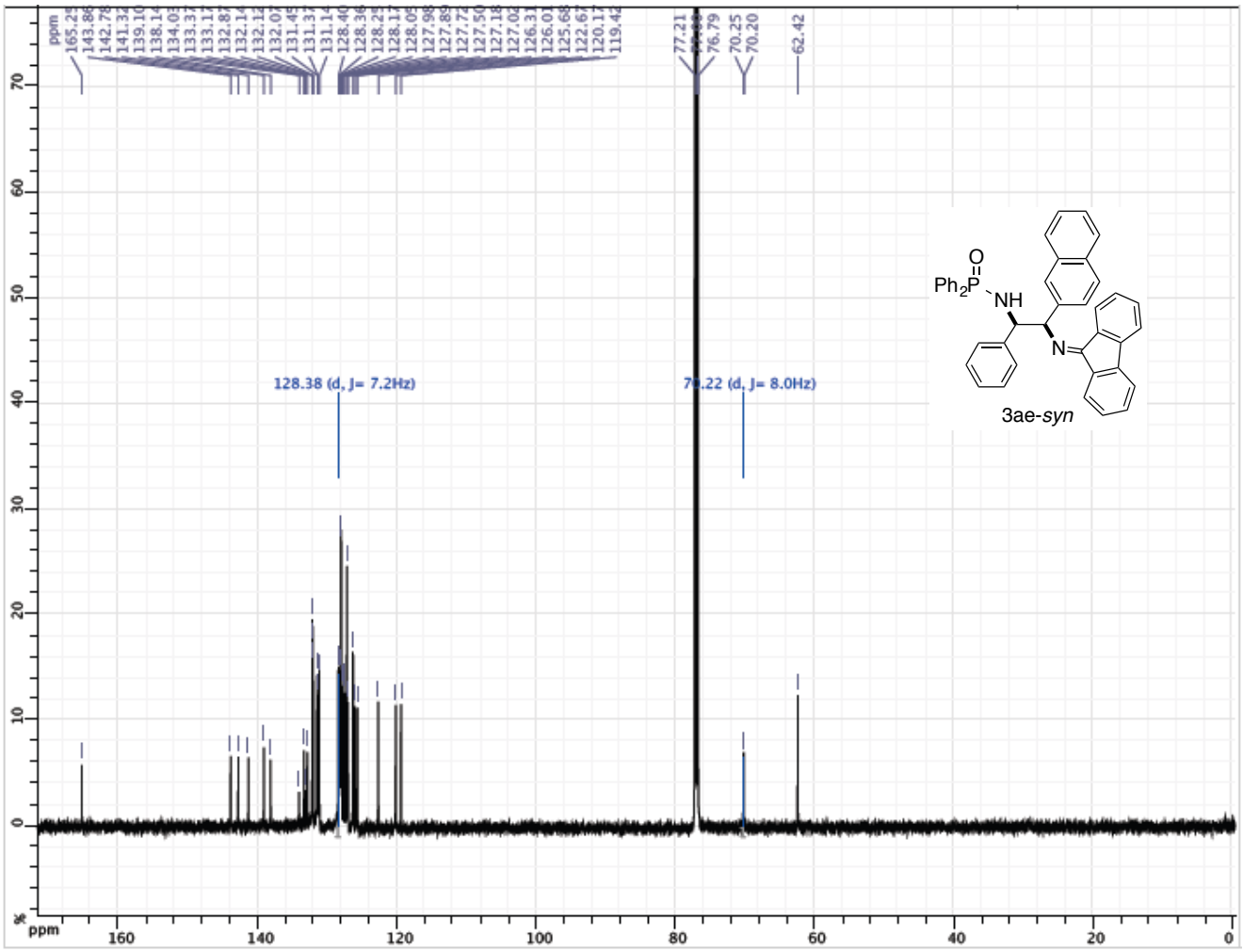

3ac-syn
PPM

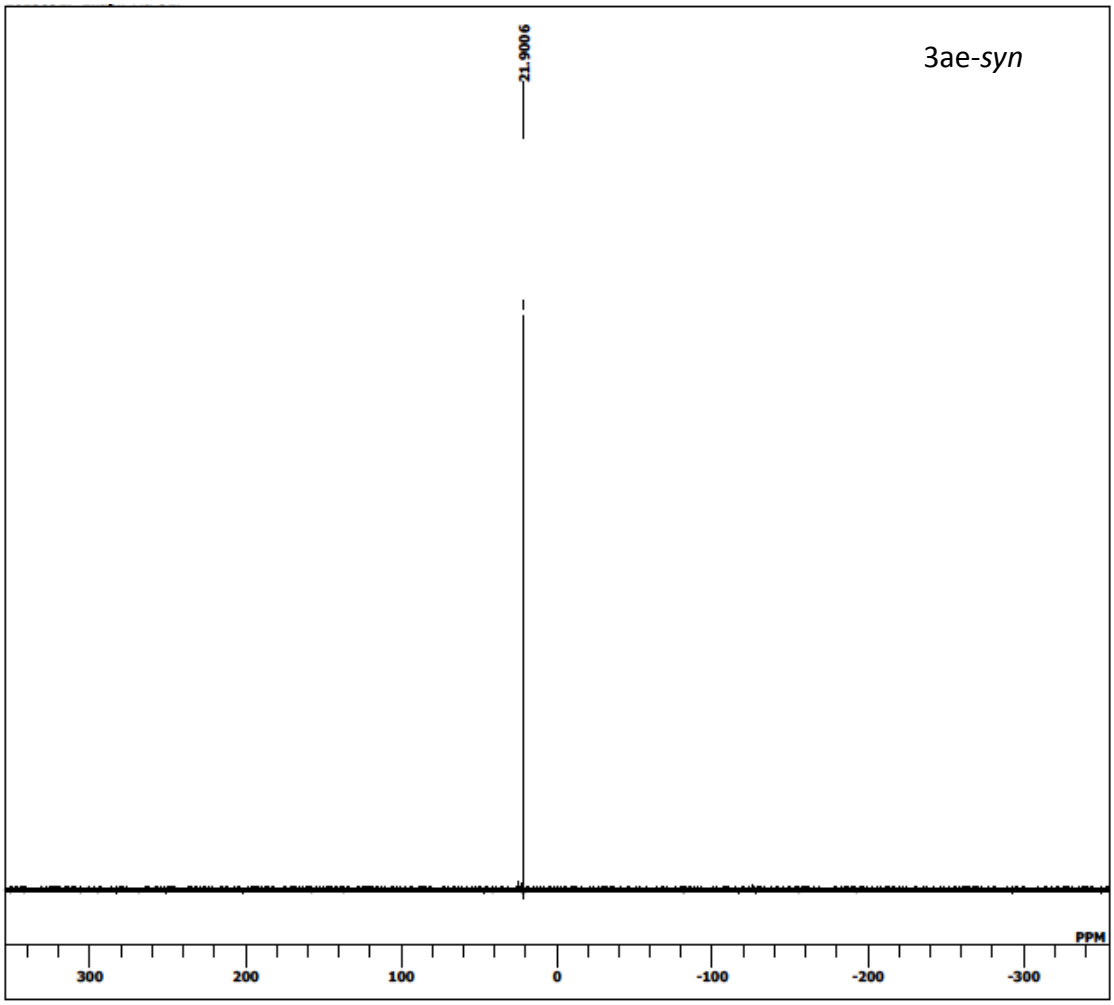

6.97 (t, J= 7.8Hz)
5.37 (dd, J= 10.8Hz, 6.8Hz)
7.89 (d, J= 7.4Hz)
3ad-syn

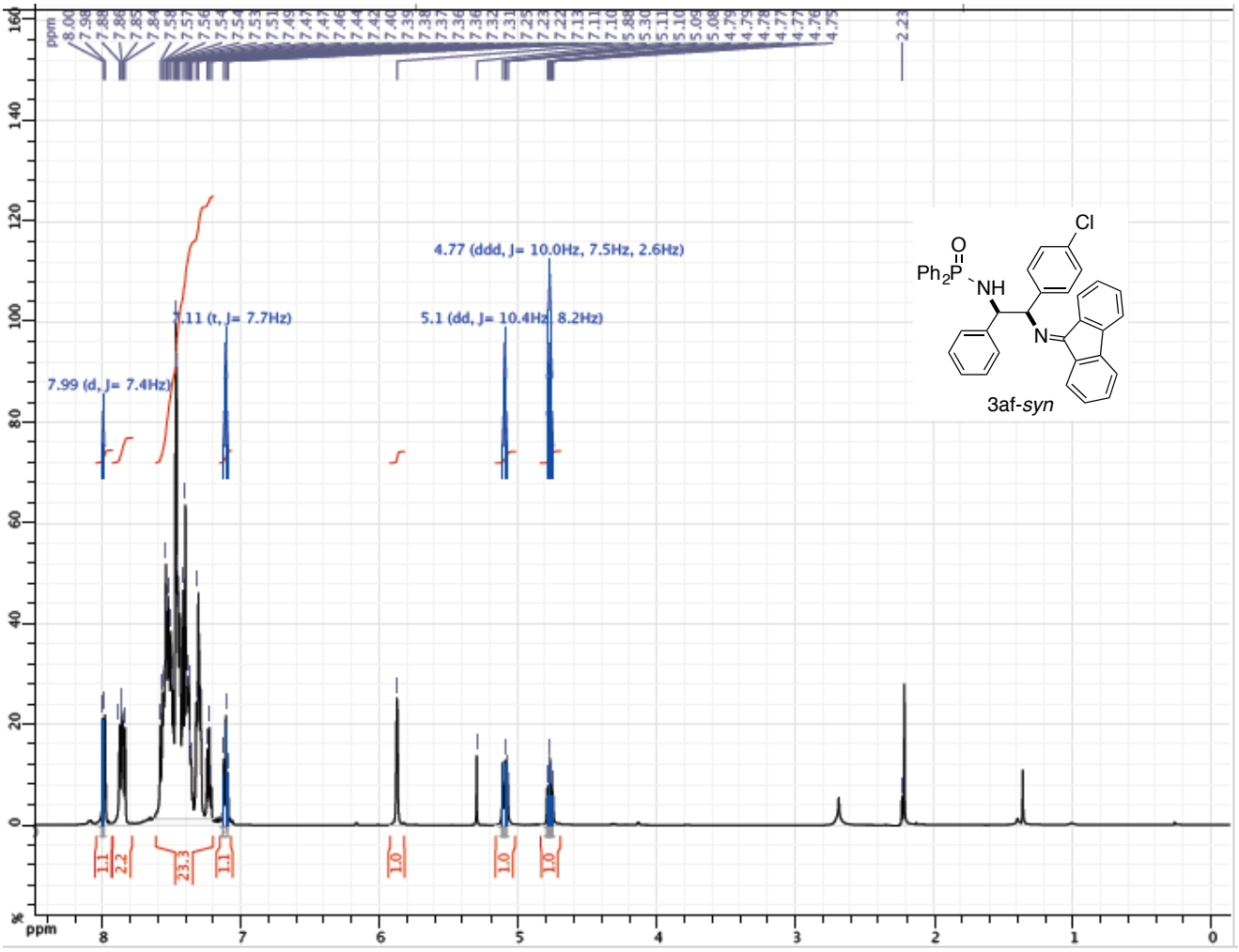

132.32 (d, J= 9.8Hz)
67.11 (d, J= 8.3Hz)
3ad-syn

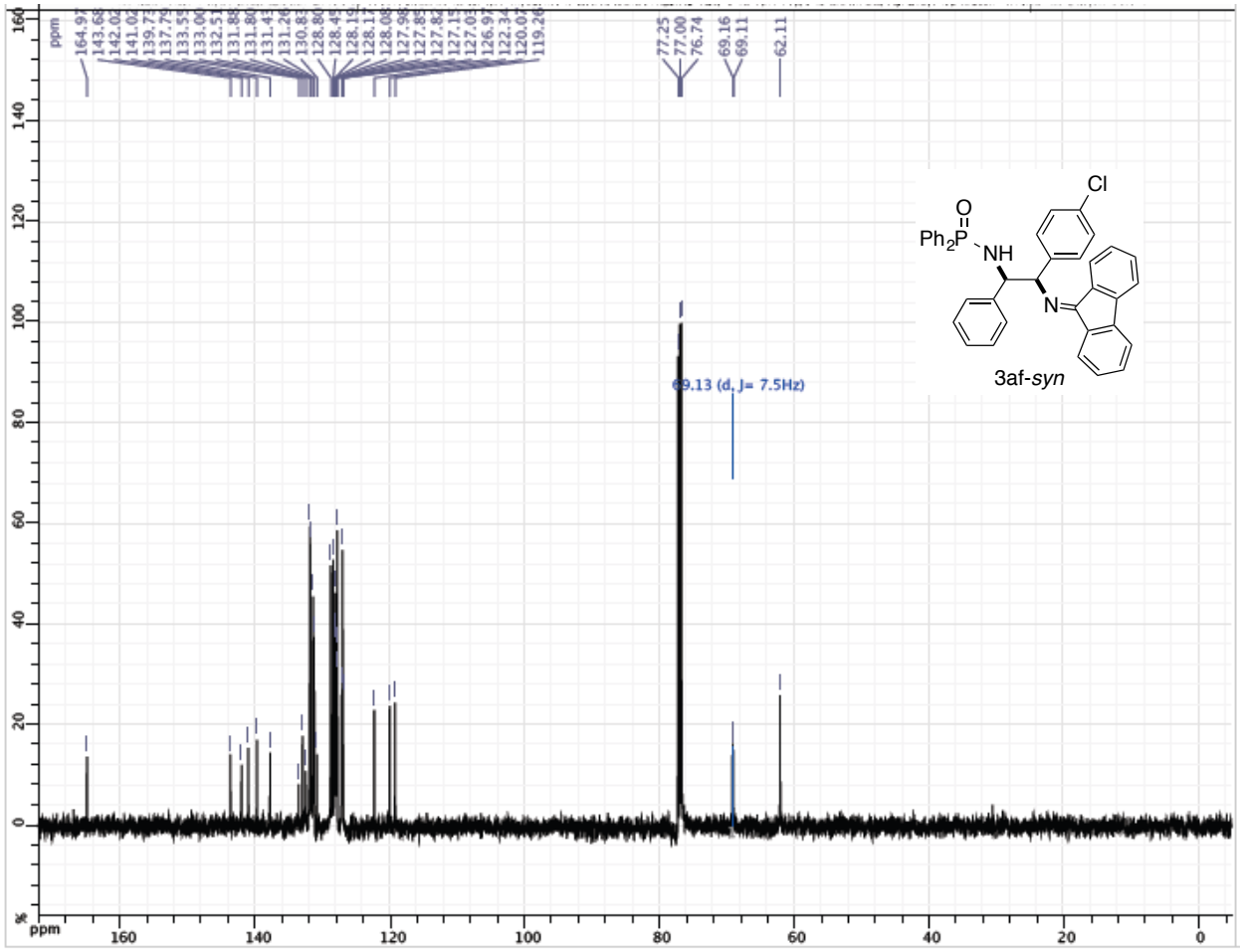

3ad-*syn*
21.1968
PPM
300
200
100
0
-100
-200
-300

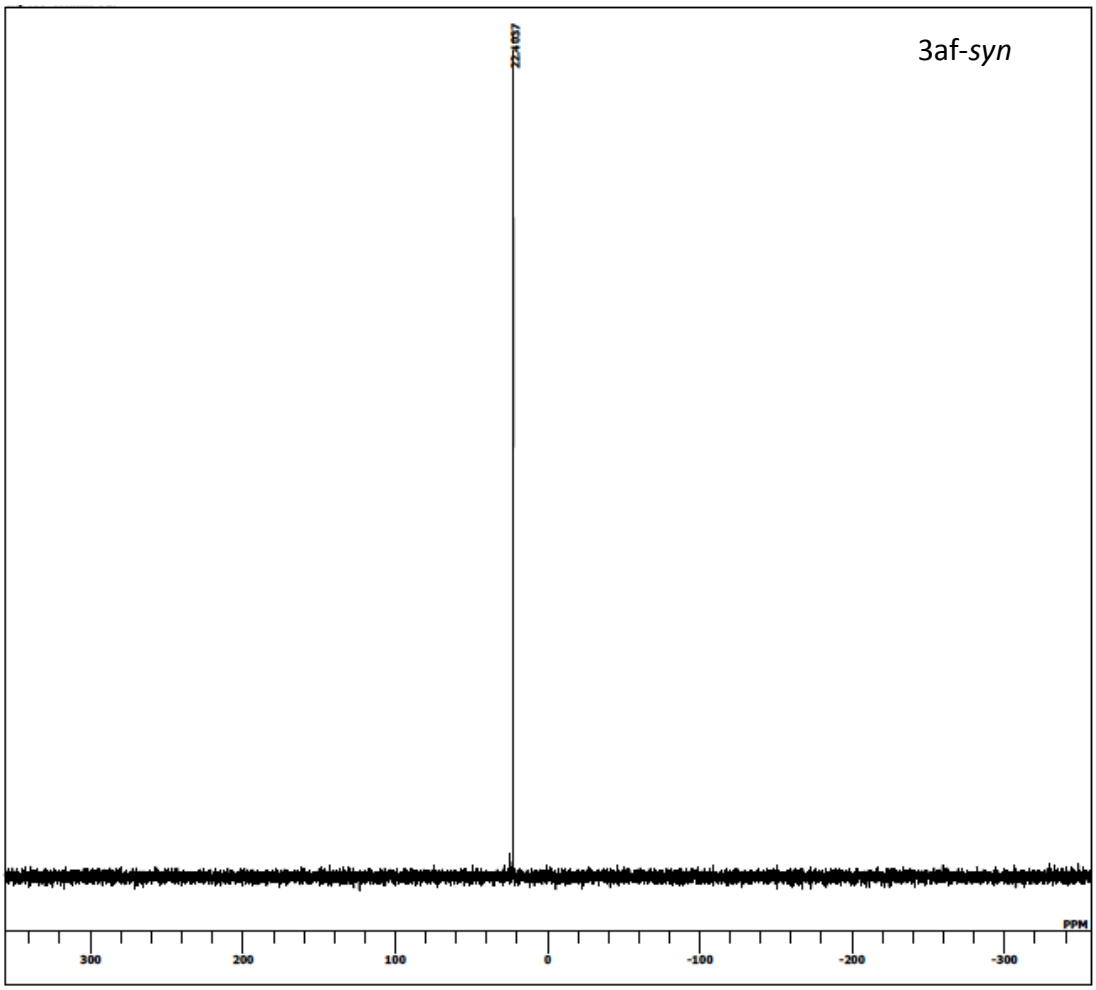

4.69 (ddd, J= 9.6Hz, 7.4Hz, 2.3Hz)
5.15 (dd, J= 10.4Hz, 3.4Hz)
7.94 (d, J= 7.4Hz)
Ph2P
O
NH
N
3ae-*syn*
ppm

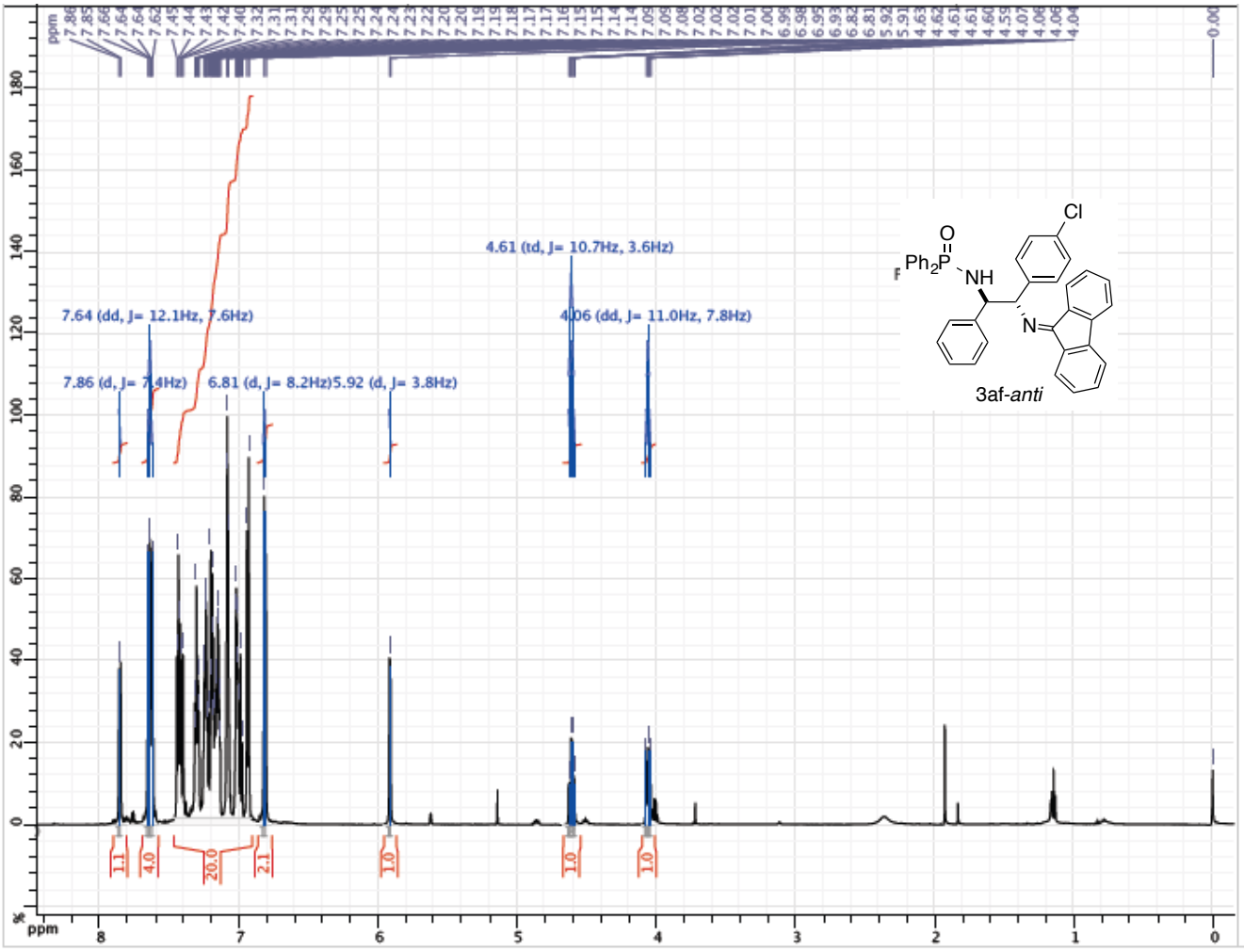

128.38 (d, J= 7.2Hz)
79.22 (d, J= 8.0Hz)
3ae-syn

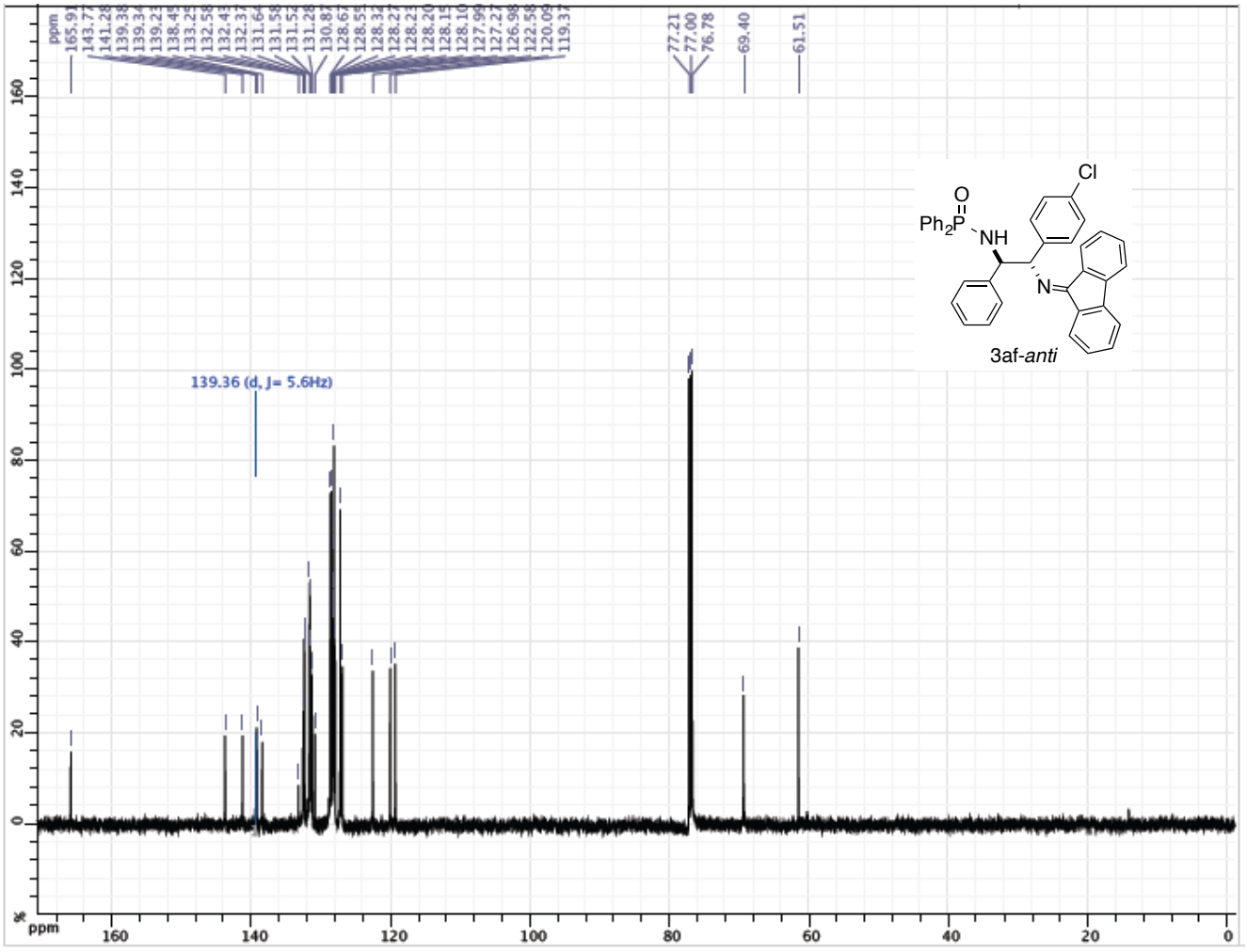

21.9006
3ae-syn
PPM

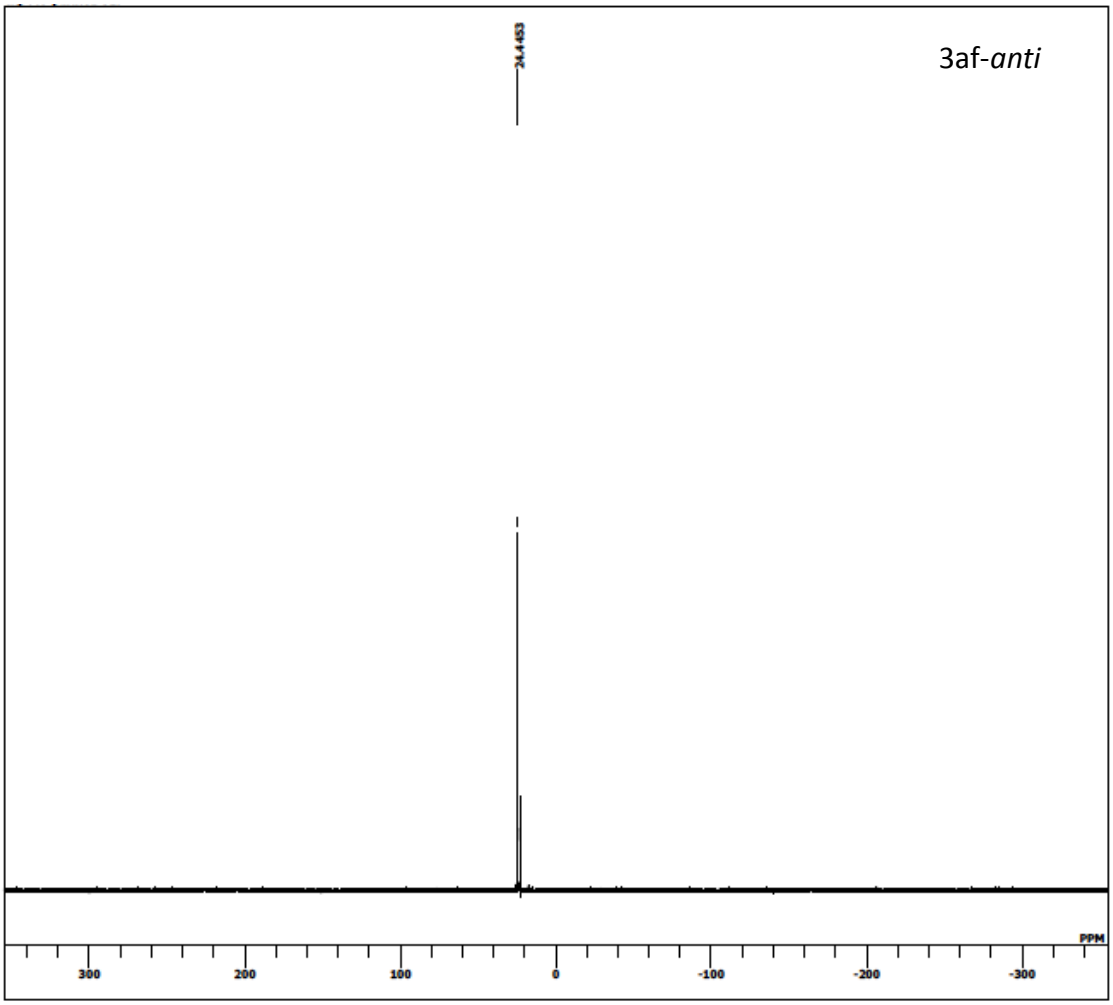

4.77 (ddd, J= 10.0Hz, 7.5Hz, 2.6Hz)
7.11 (t, J= 7.7Hz)
5.1 (dd, J= 10.4Hz, 8.2Hz)
7.99 (d, J= 7.4Hz)
Cl
O
Ph2P
NH
N
3af-syn

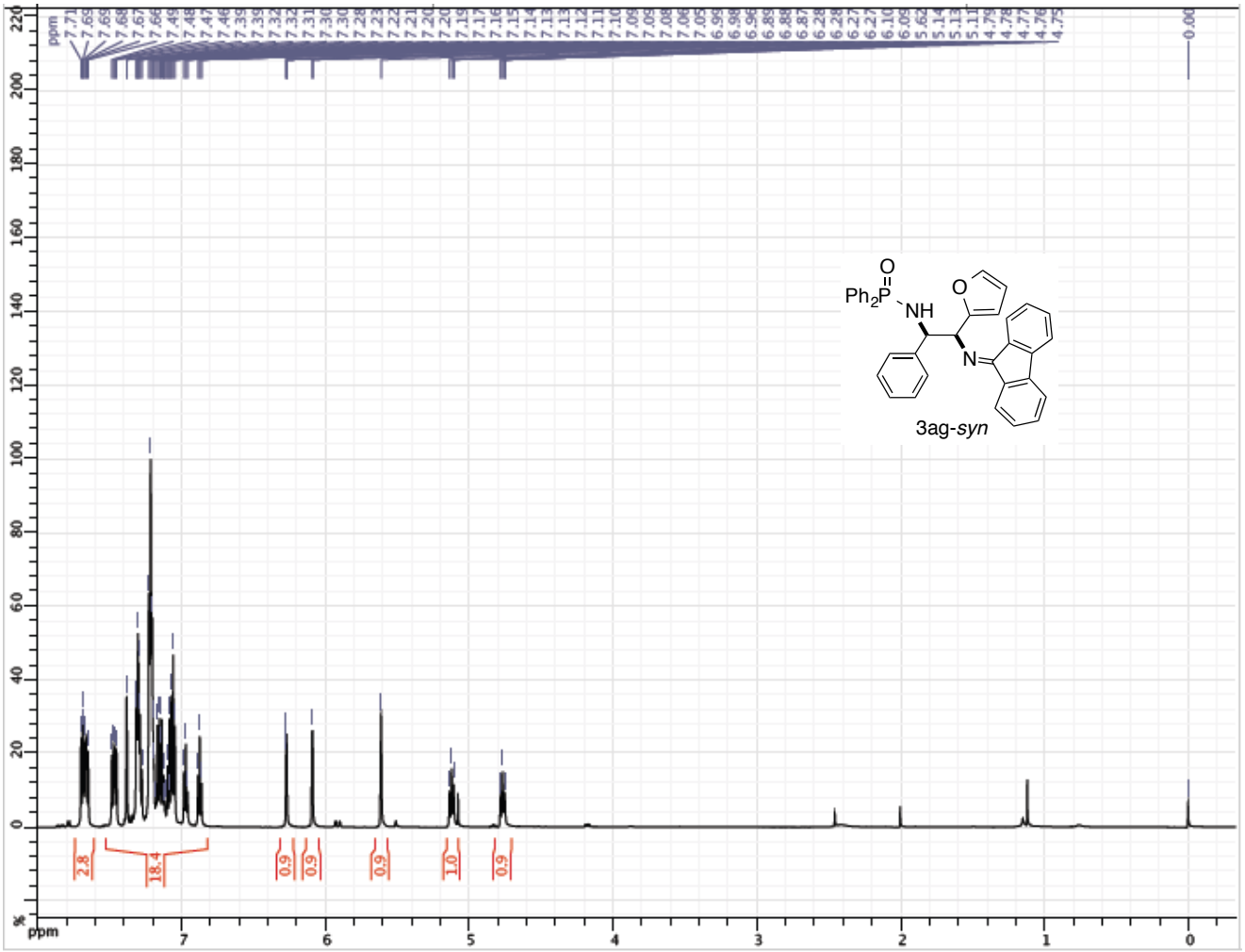

69.13 (d, J= 7.5Hz)
Cl
O
Ph2P
NH
N
3af-syn

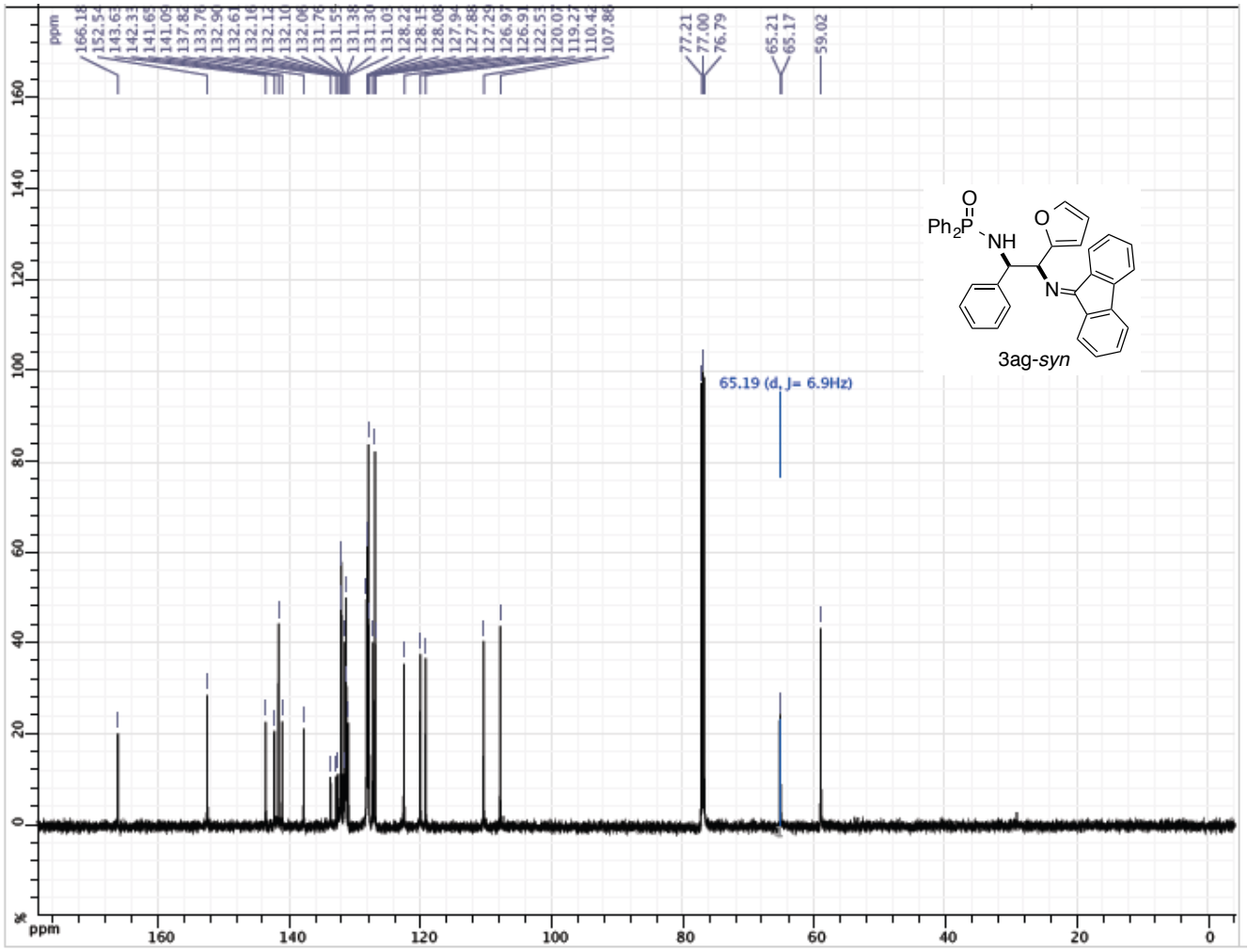

3af-*syn*
PPM
300
200
100
0
-100
-200
-300

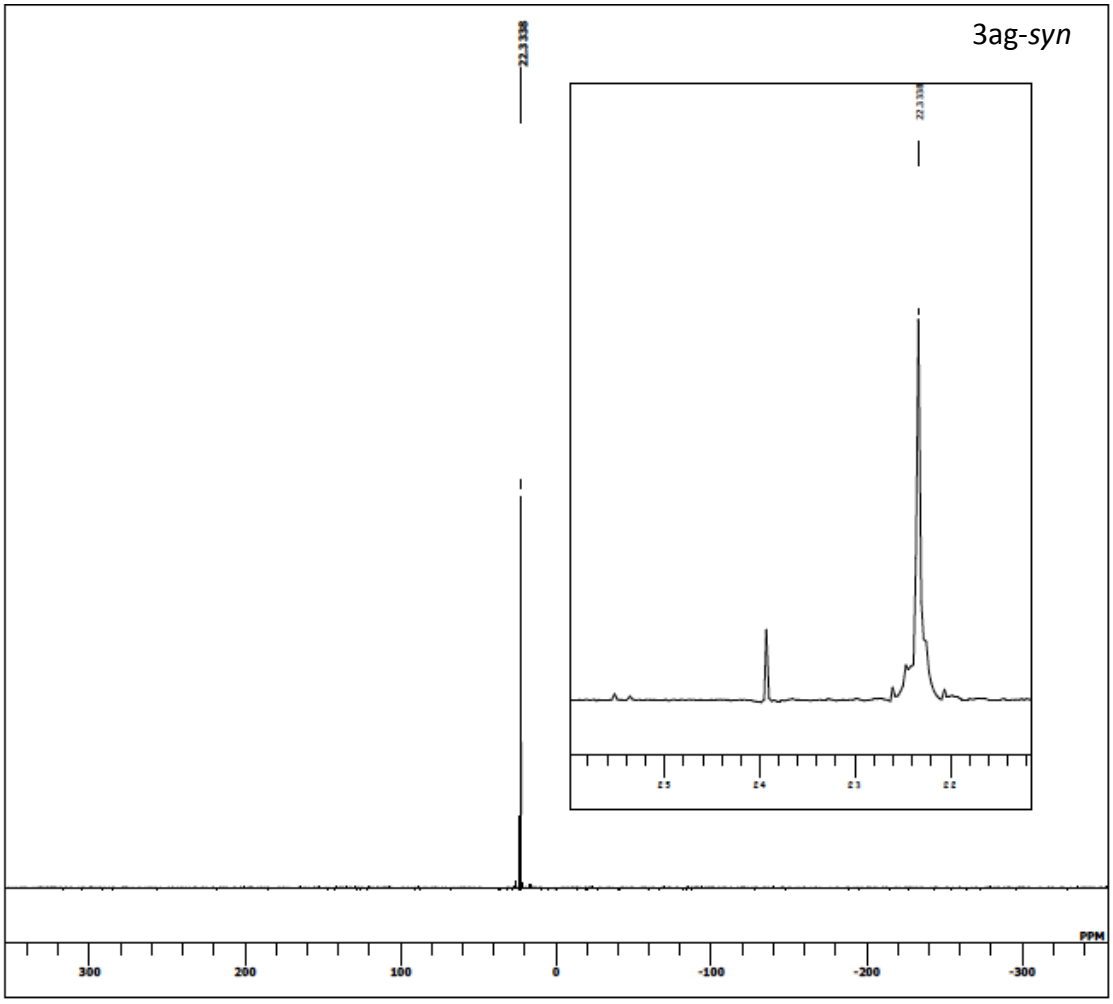

7.64 (dd, J= 12.1Hz, 7.6Hz)
7.86 (d, J= 7.4Hz)
6.81 (d, J= 8.2Hz)
5.92 (d, J= 3.8Hz)
4.61 (td, J= 10.7Hz, 3.6Hz)
4.06 (dd, J= 11.0Hz, 7.8Hz)
Cl
O
Ph2P
NH
N
3af-*anti*
1.1
4.0
20.0
2.1
1.0
1.0
1.0
ppm

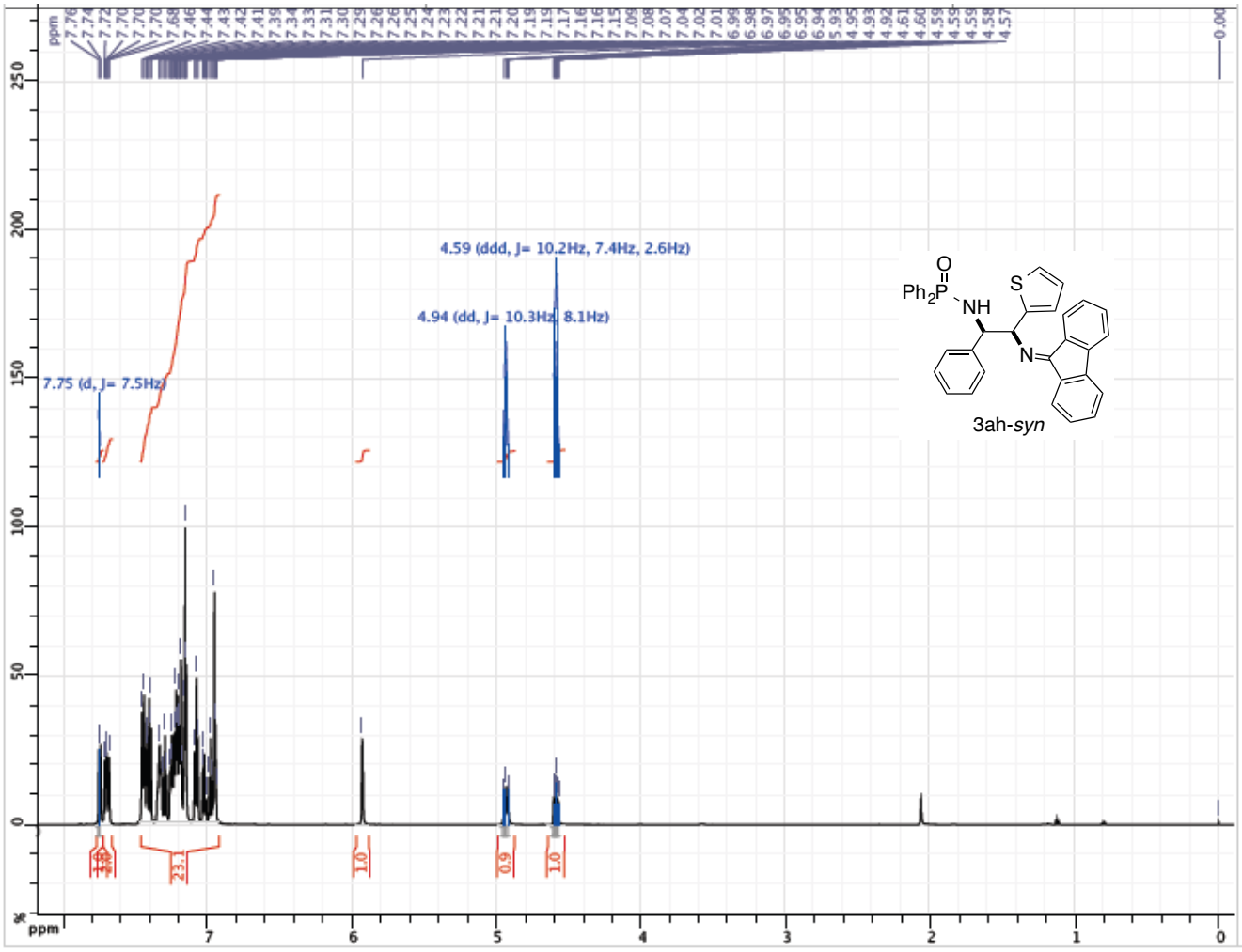

ppm
165.91
143.77
141.28
139.38
139.34
139.23
138.45
133.25
132.58
132.43
132.37
131.64
131.58
131.52
131.28
130.87
128.67
128.58
128.32
128.27
128.23
128.20
128.15
128.10
127.99
127.27
126.98
122.58
120.09
119.37
77.21
77.00
76.78
69.40
61.51
139.36 (d, J= 5.6Hz)
Cl
O
Ph2P
NH
N
3af-anti
%
ppm
160
140
120
100
80
60
40
20
0

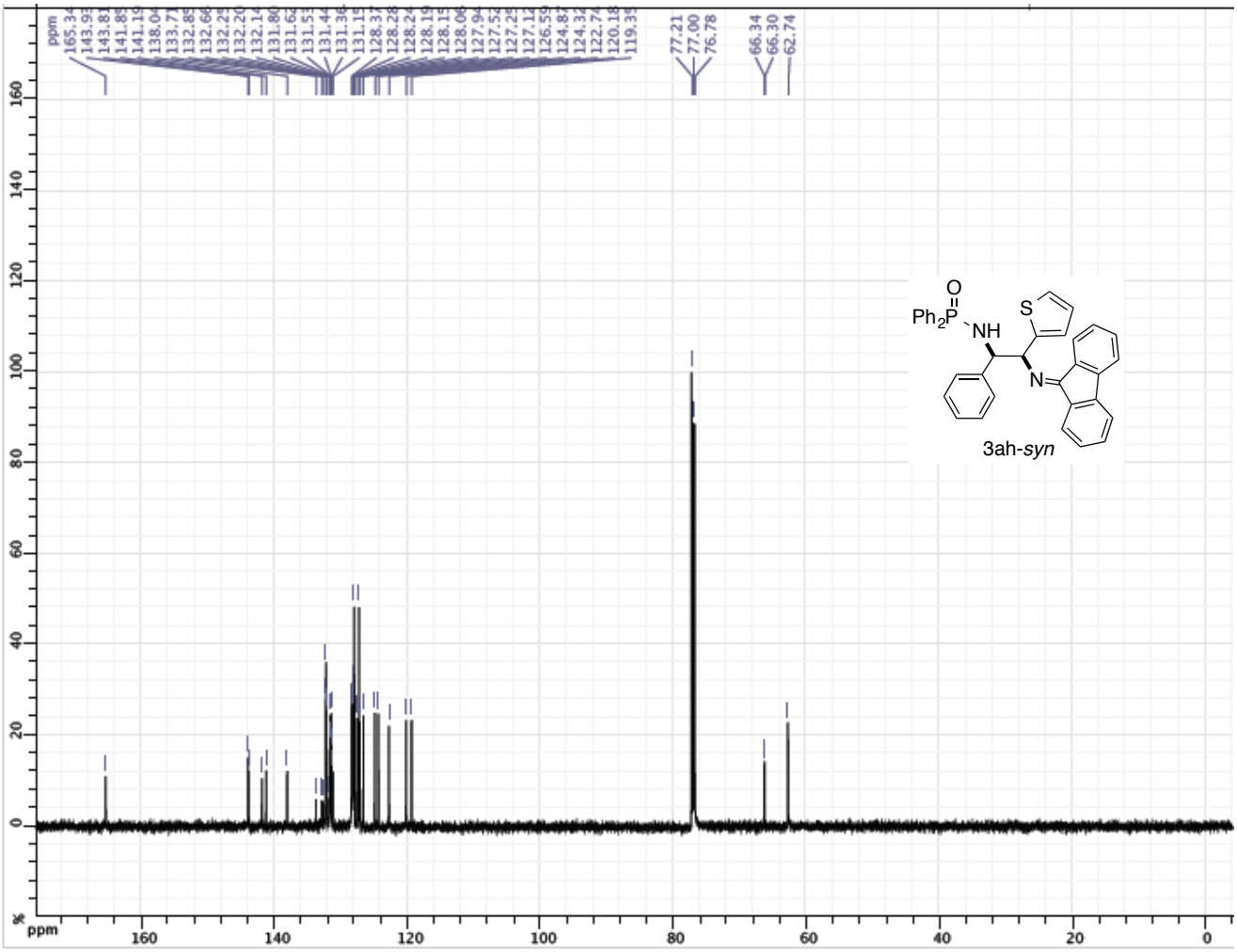

24.463
3af-anti
PPM
300
200
100
0
-100
-200
-300

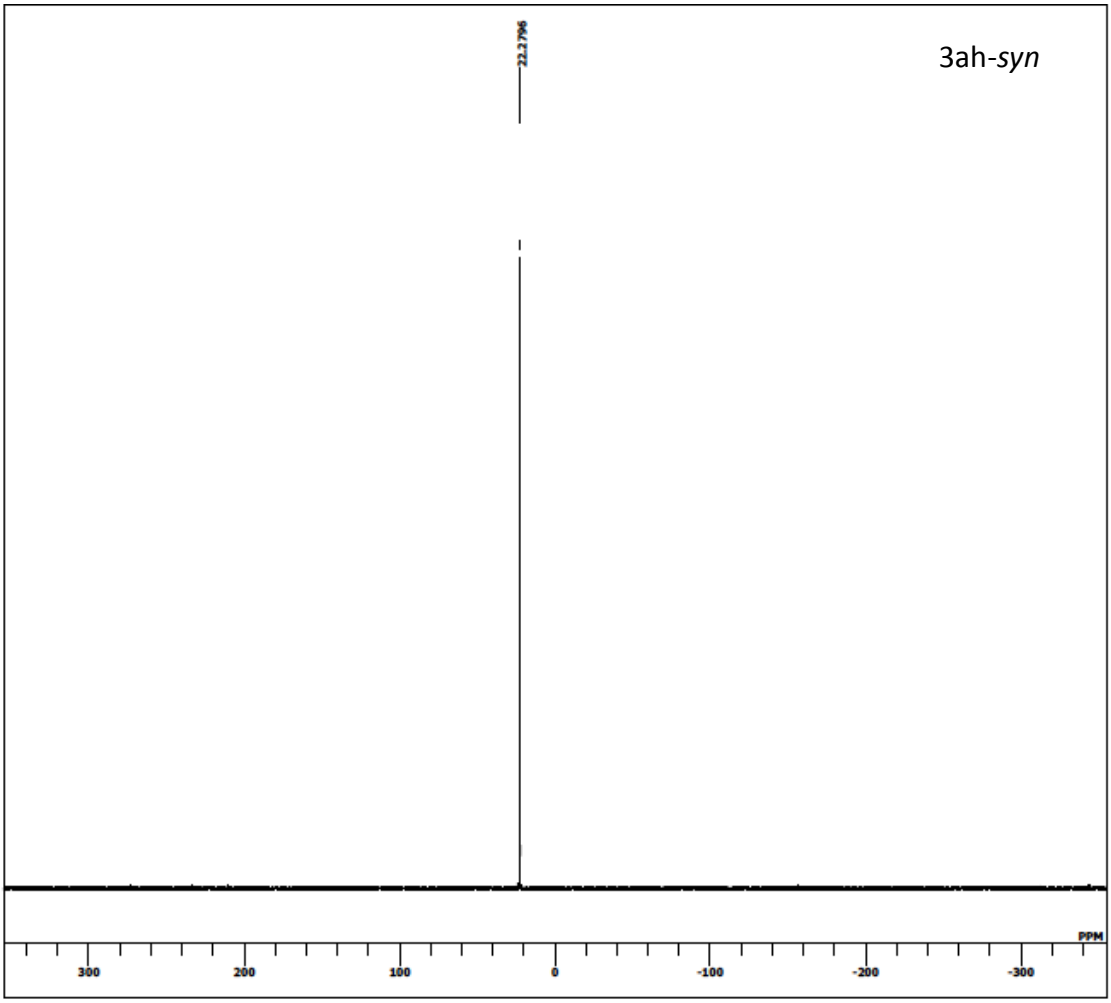

3ag-*syn*

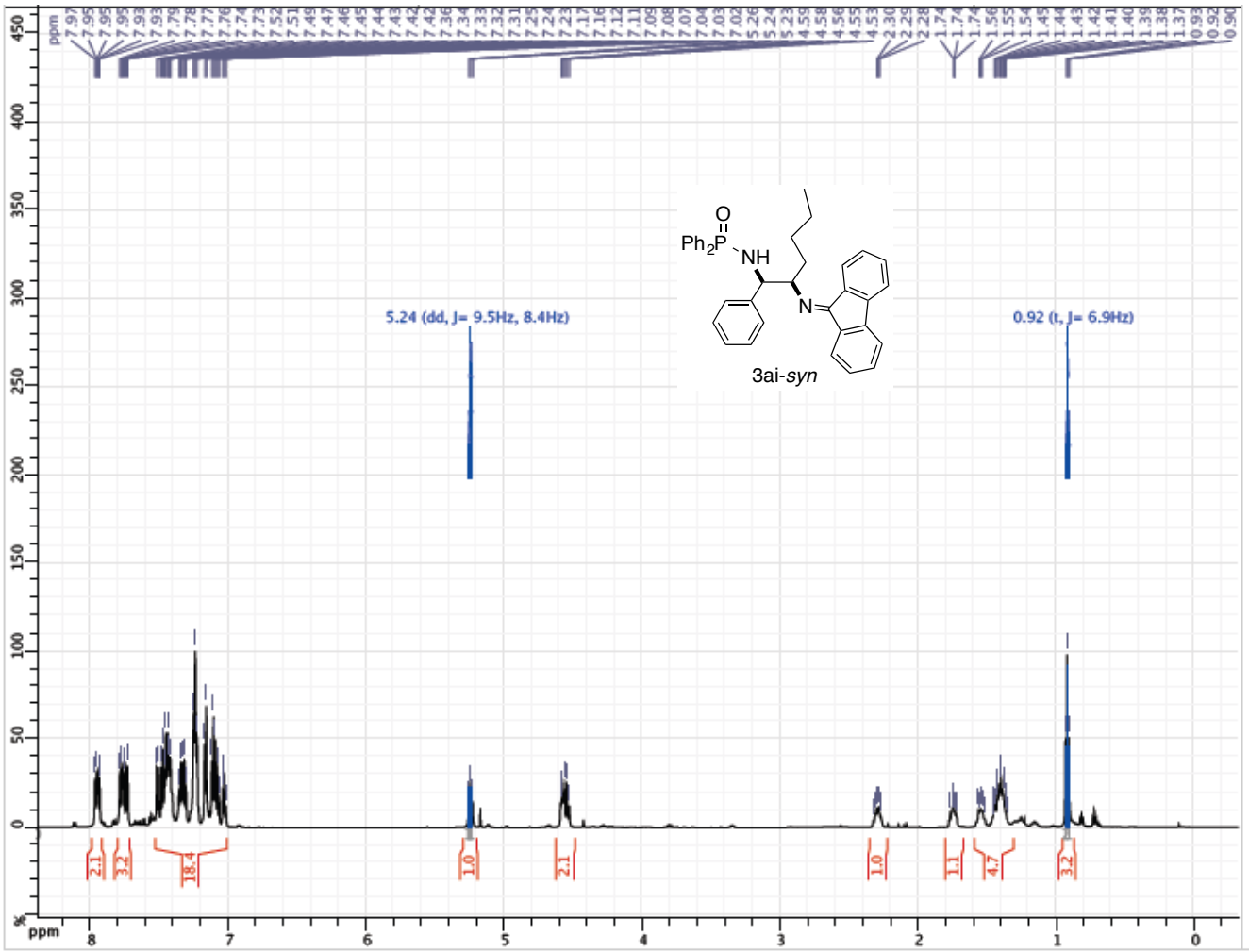

65.19 (d, J= 6.9Hz)
3ag-*syn*

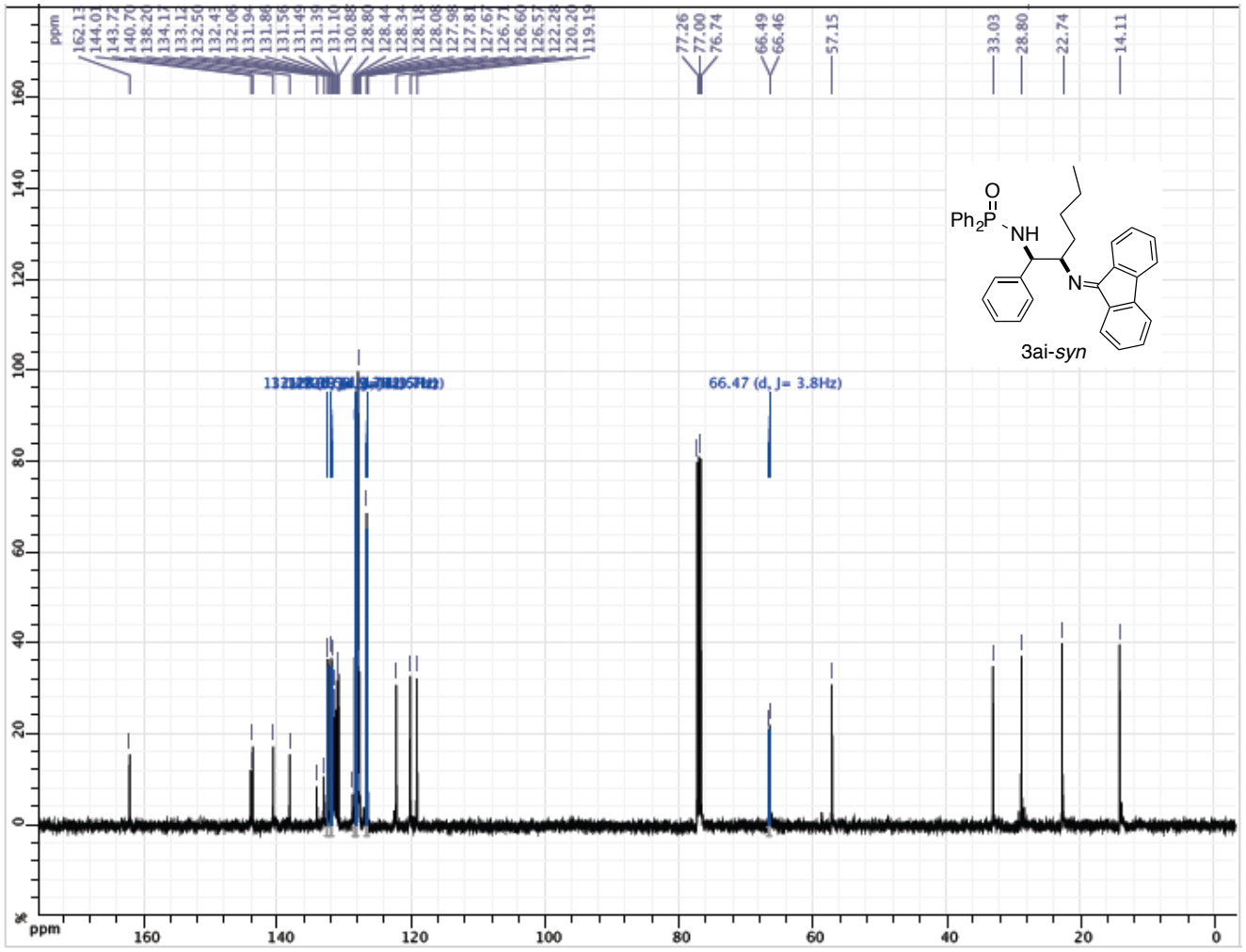

3ag-syn
PPM
300
200
100
0
-100
-200
-300

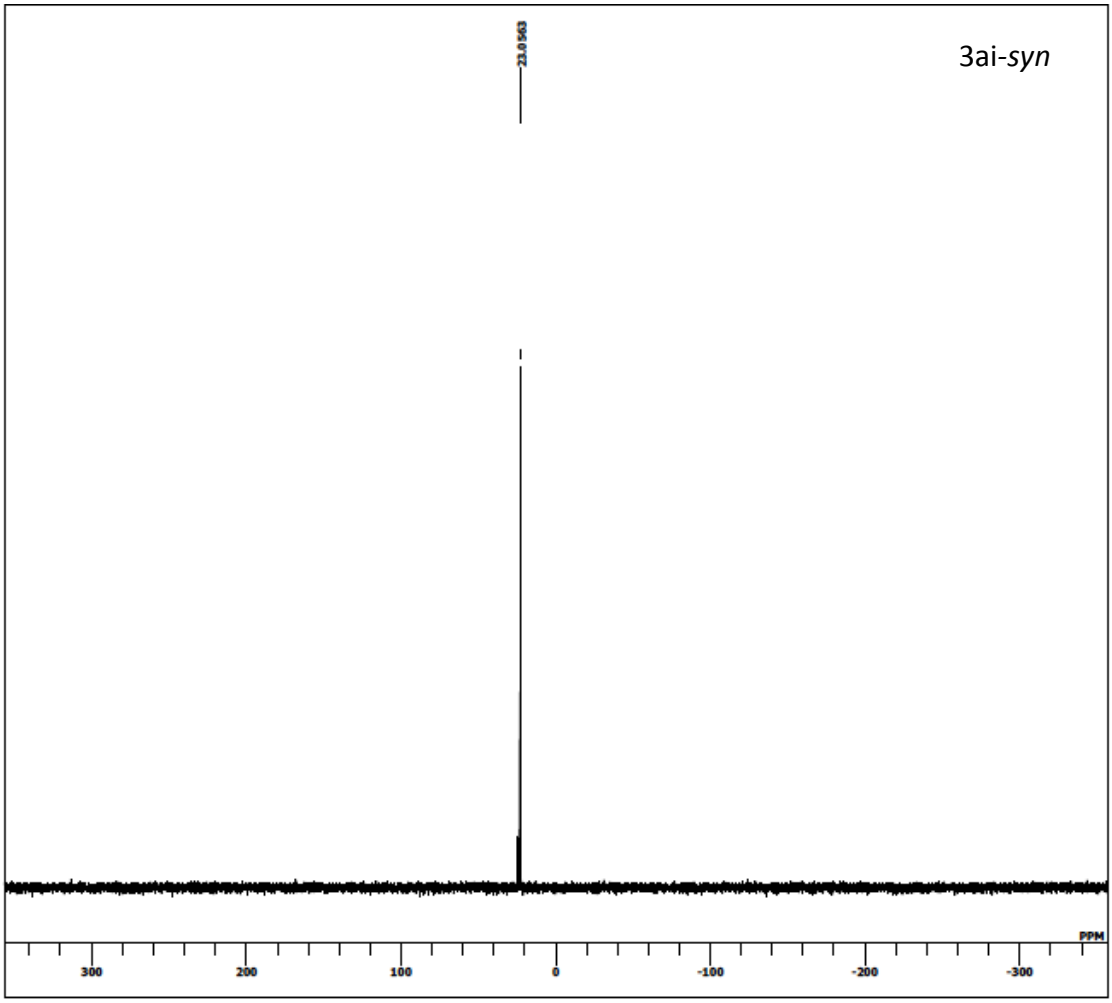

4.59 (ddd, J= 10.2Hz, 7.4Hz, 2.6Hz)
4.94 (dd, J= 10.3Hz, 8.1Hz)
7.75 (d, J= 7.5Hz)
Ph2P
O
NH
S
N
3ah-syn
ppm

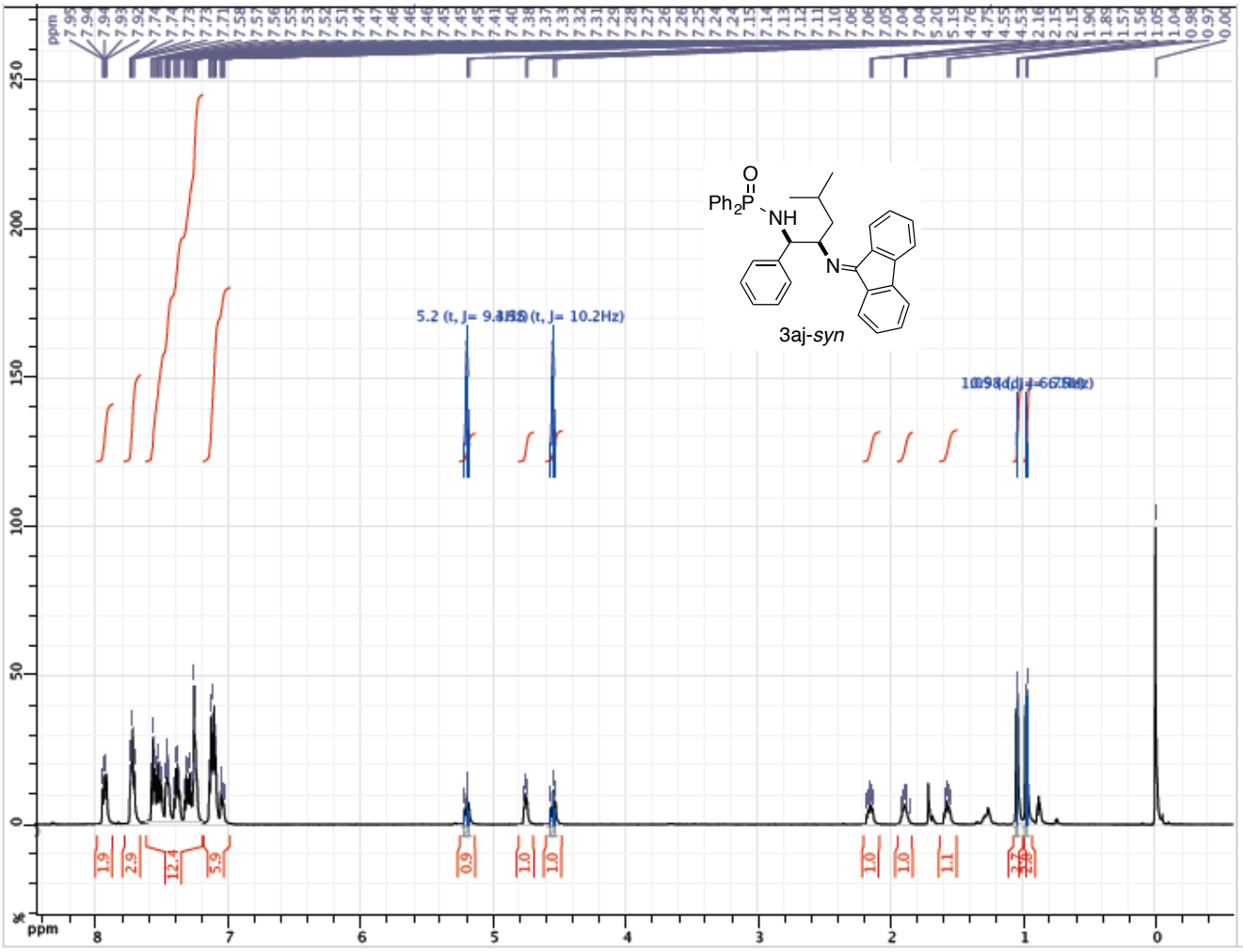

3ah-*syn*

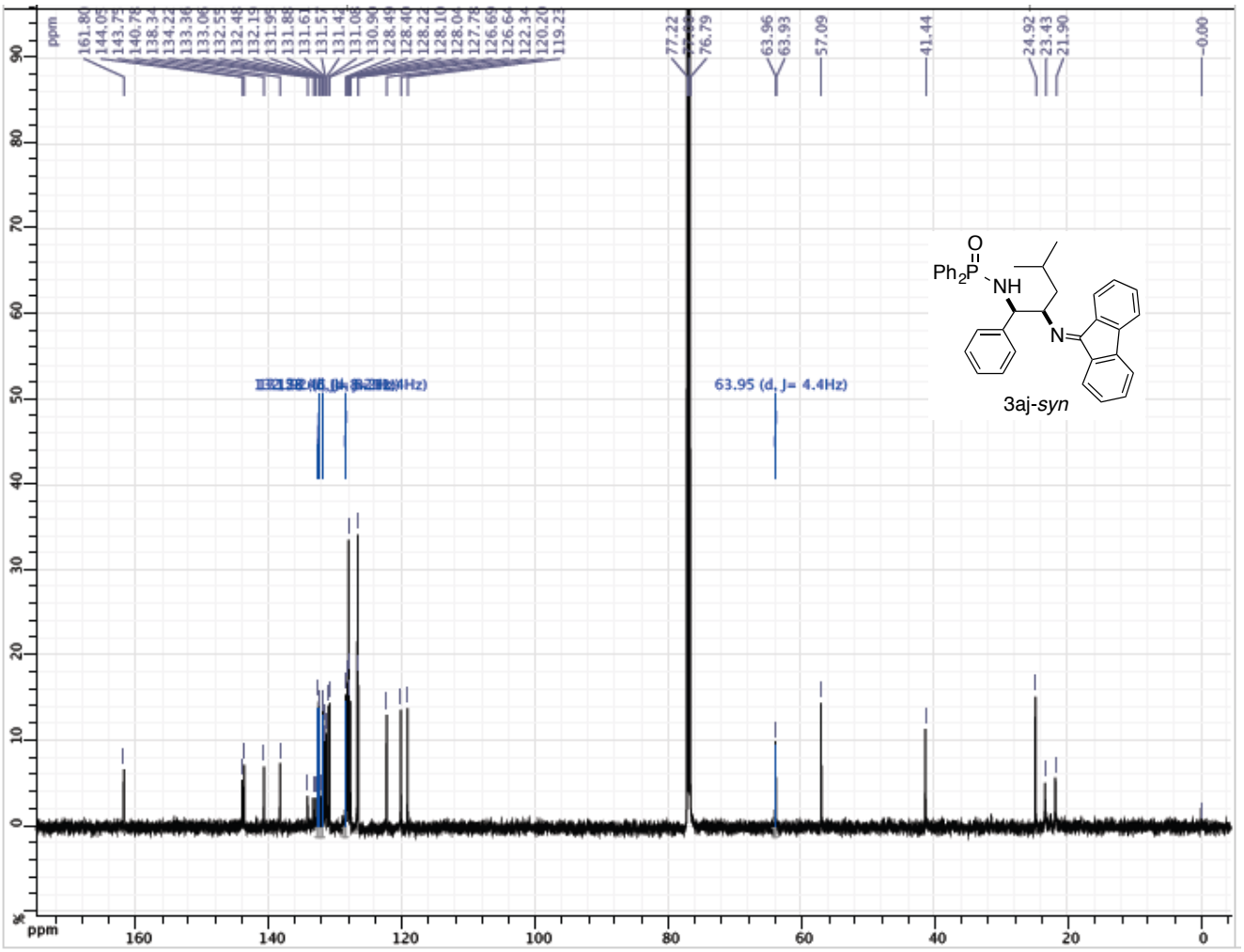

3ah-*syn*

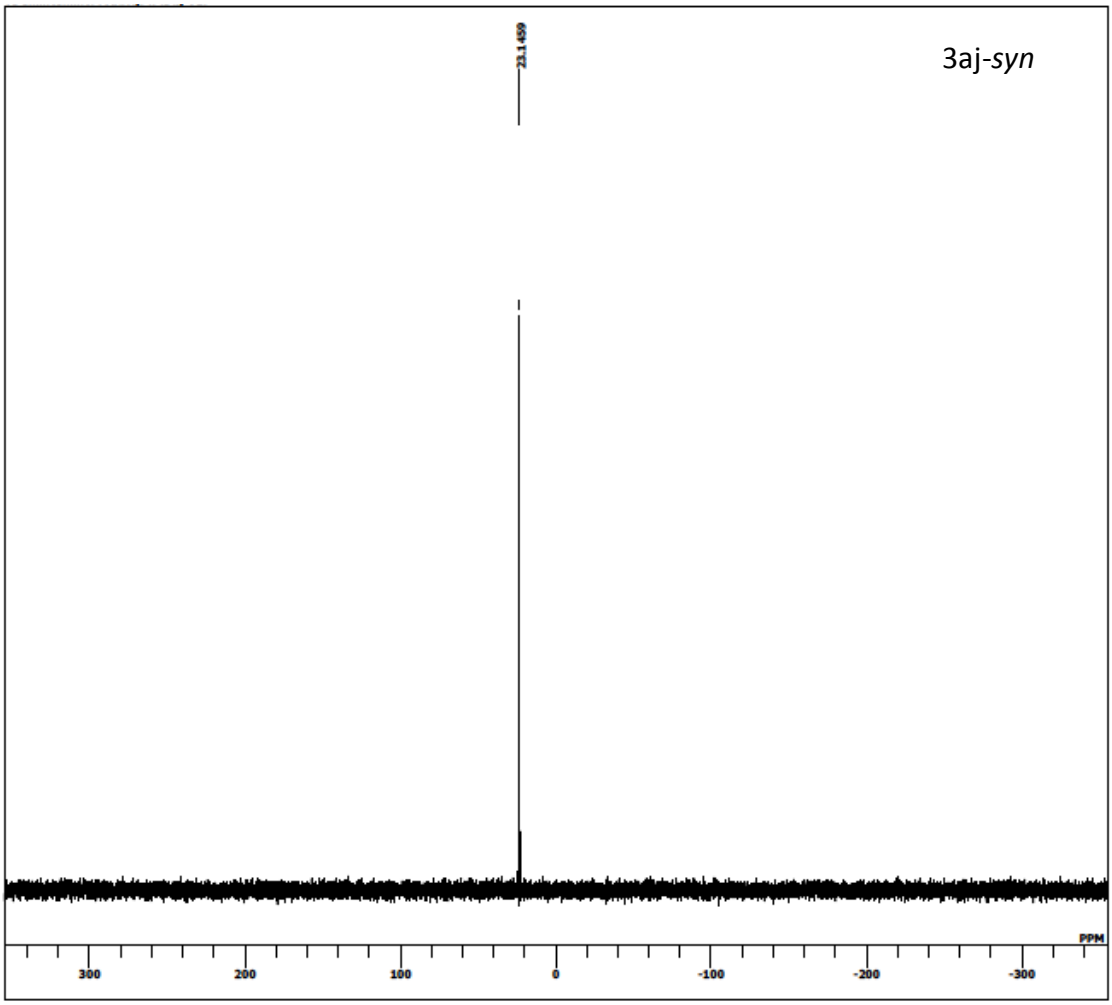

5.24 (dd, J= 9.5Hz, 8.4Hz)
0.92 (t, J= 6.9Hz)
3ai-syn

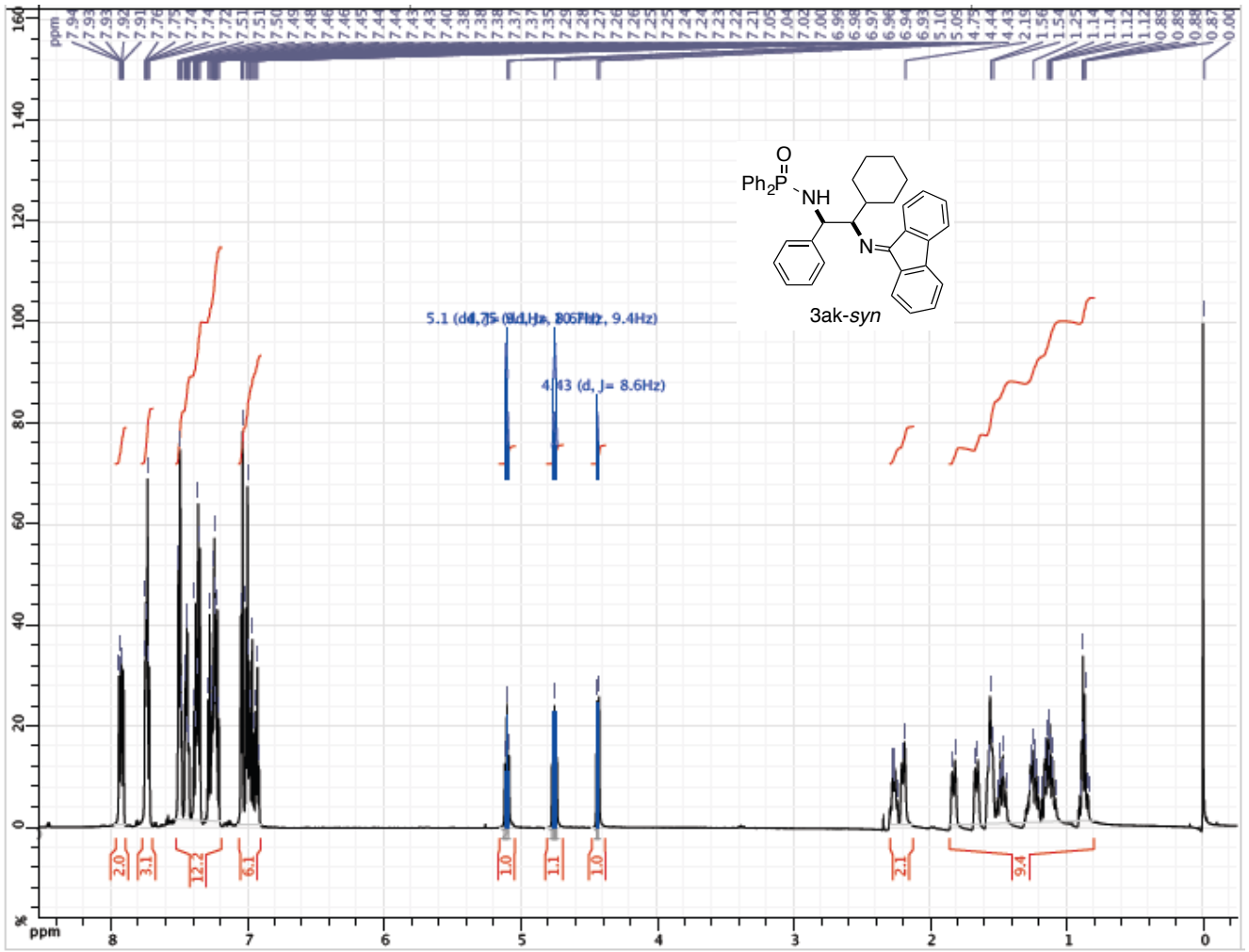

66.47 (d, J= 3.8Hz)
3ai-syn

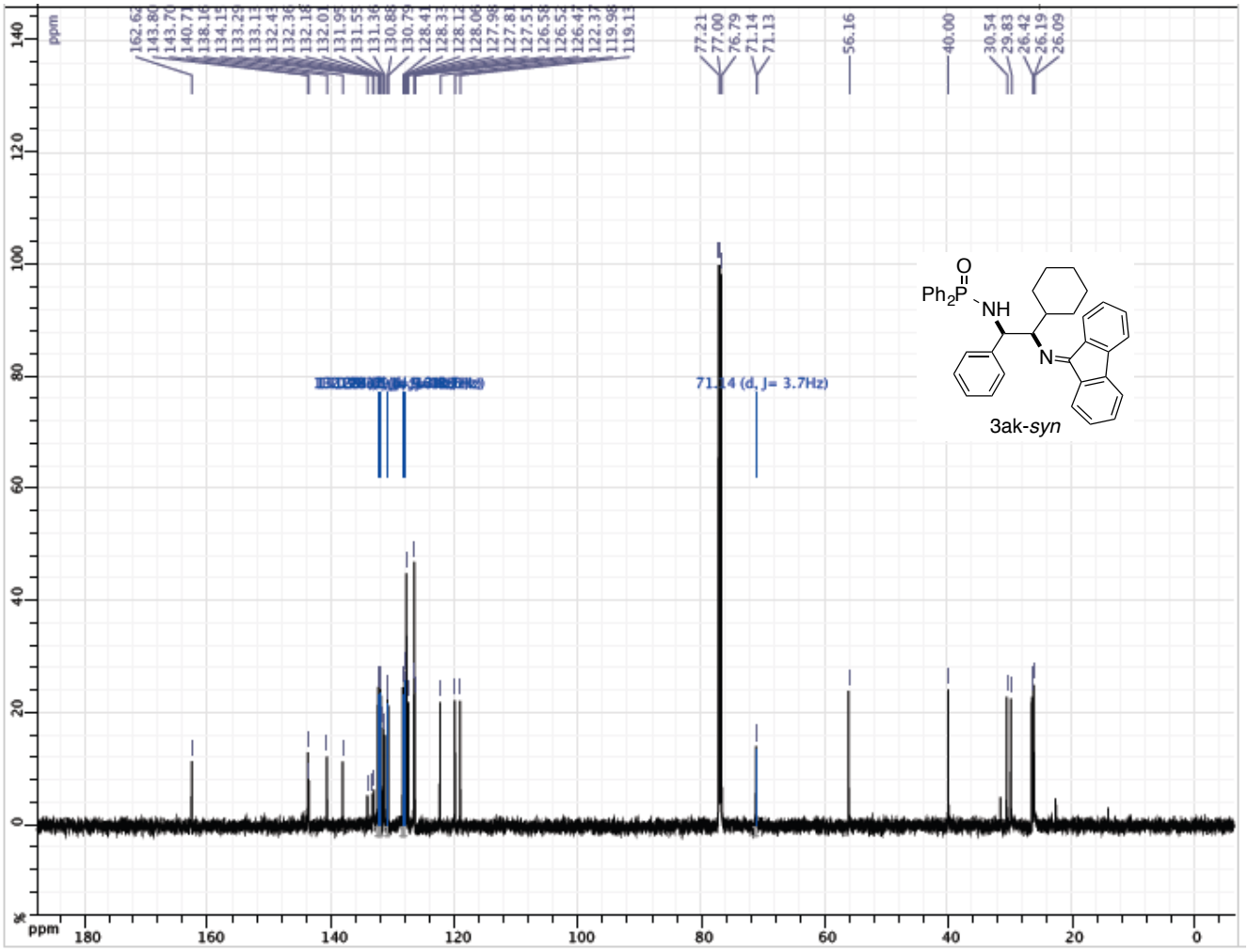

3ai-*syn*
PPM
300
200
100
0
-100
-200
-300

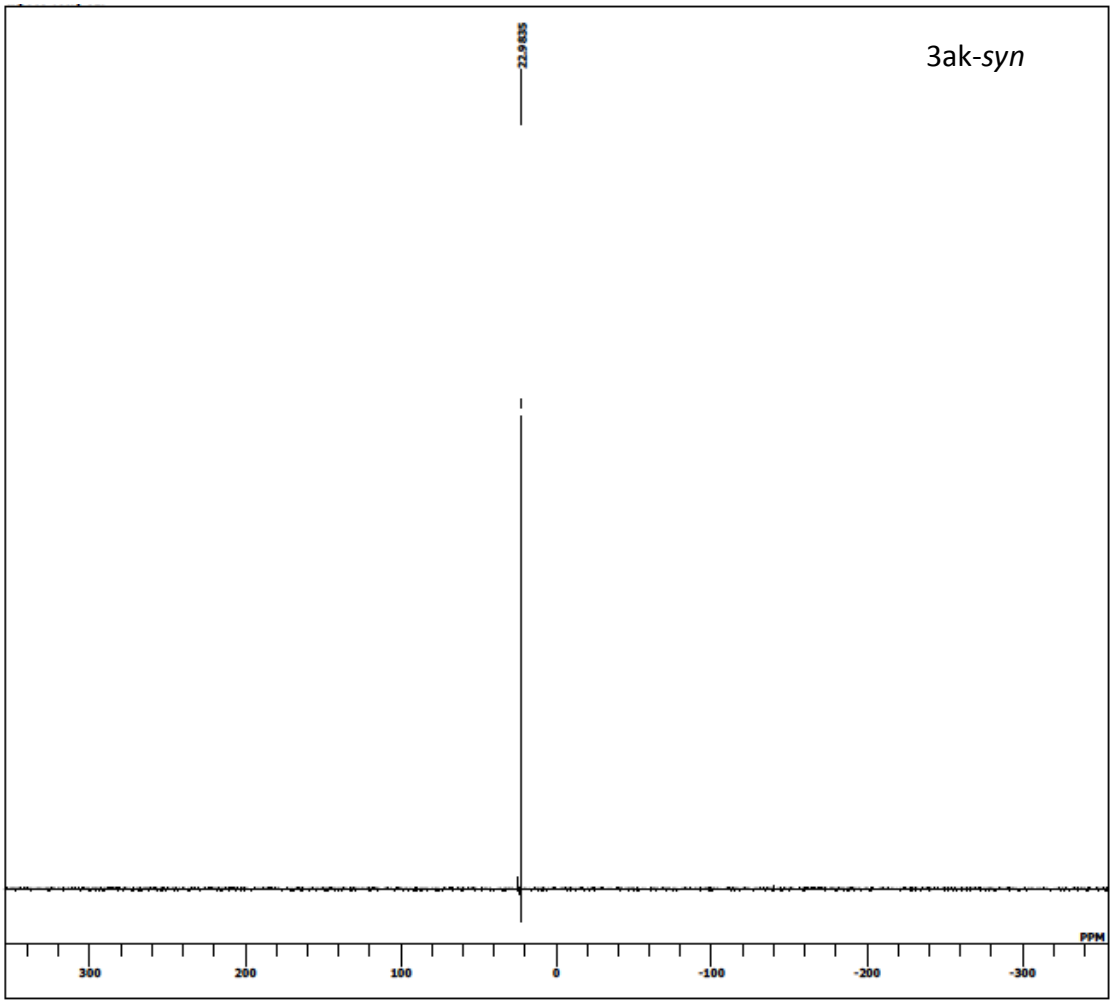

3aj-*syn*
ppm
8
7
6
5
4
3
2
1
0

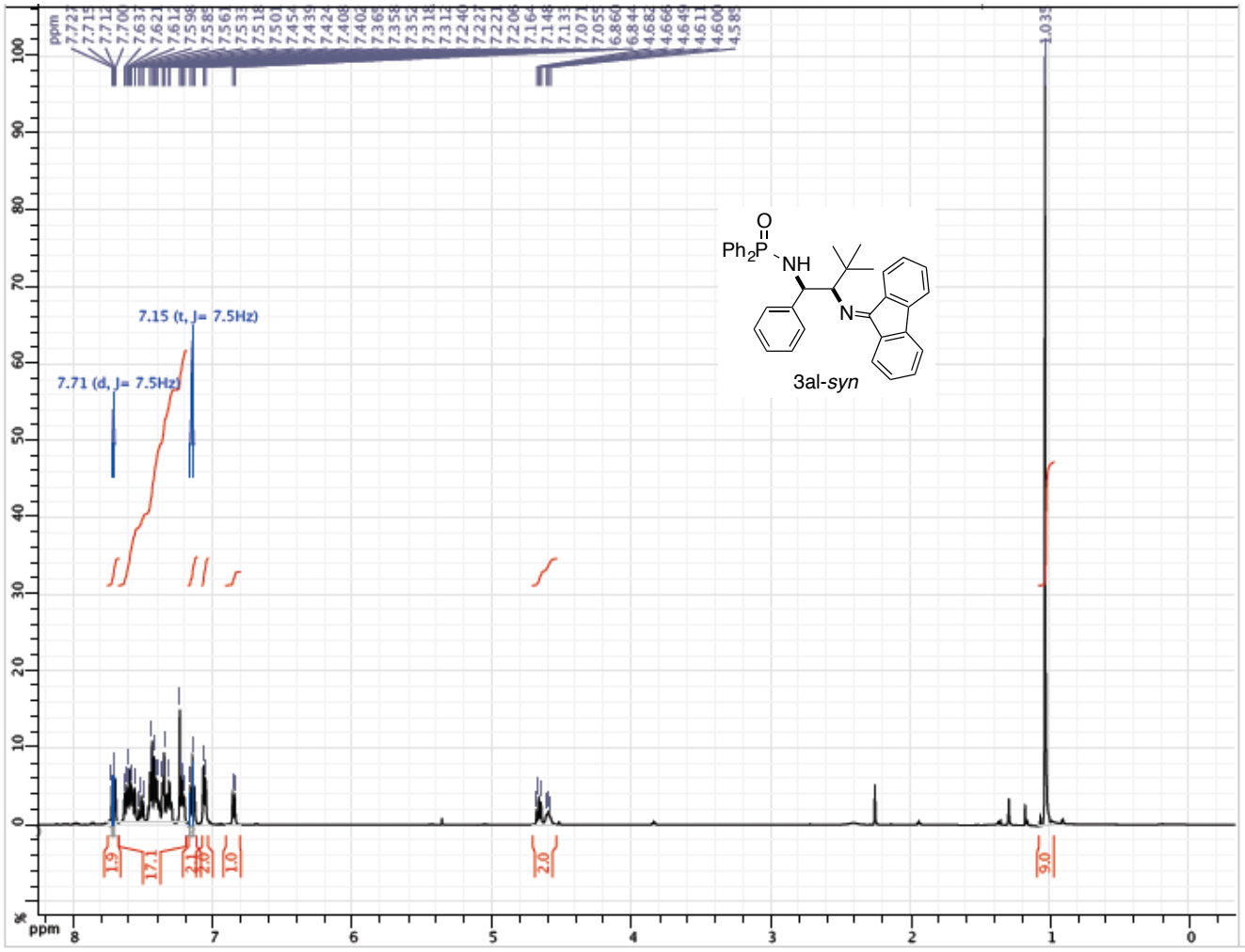

63.95 (d, J= 4.4Hz)
3aj-*syn*

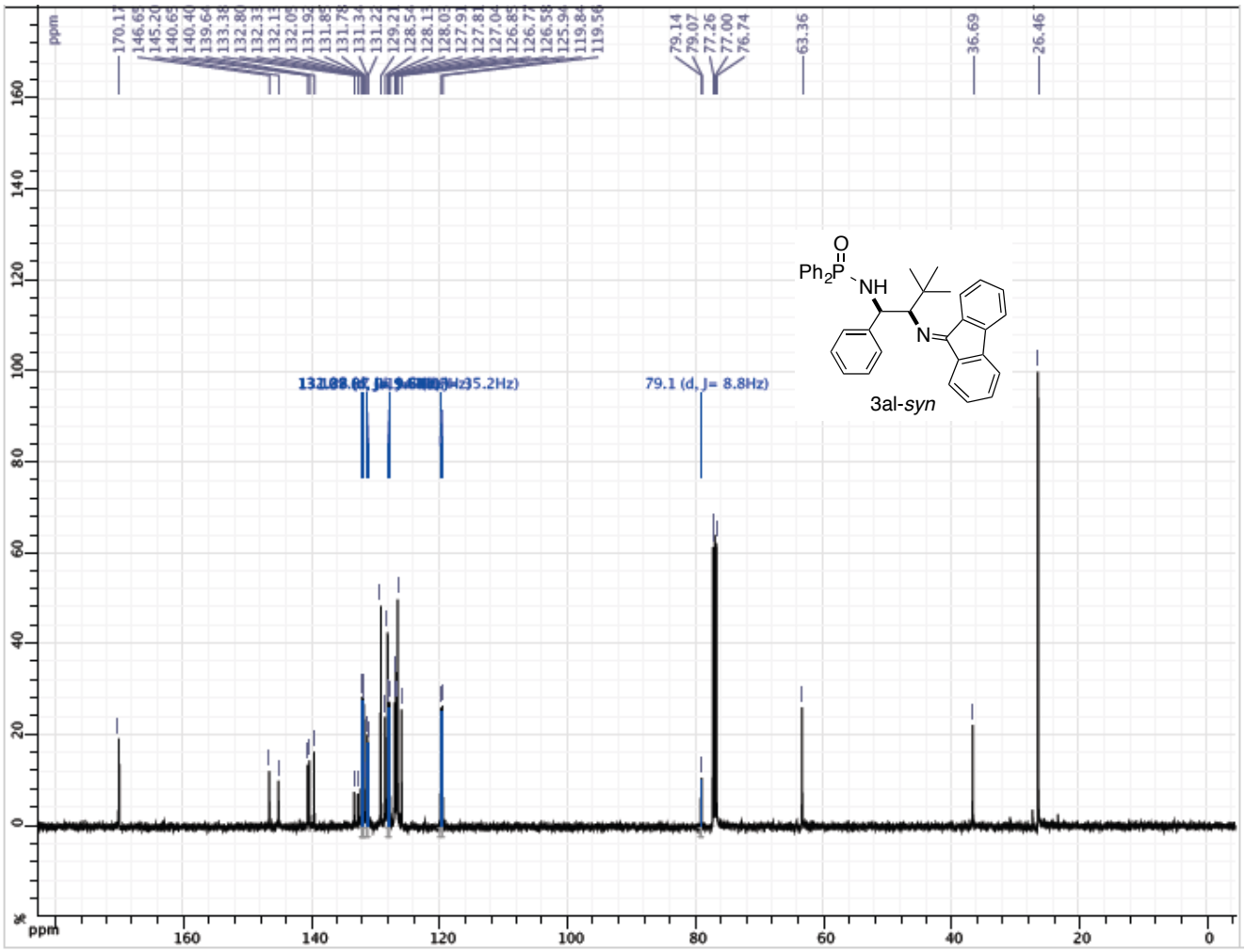

3aj-*syn*

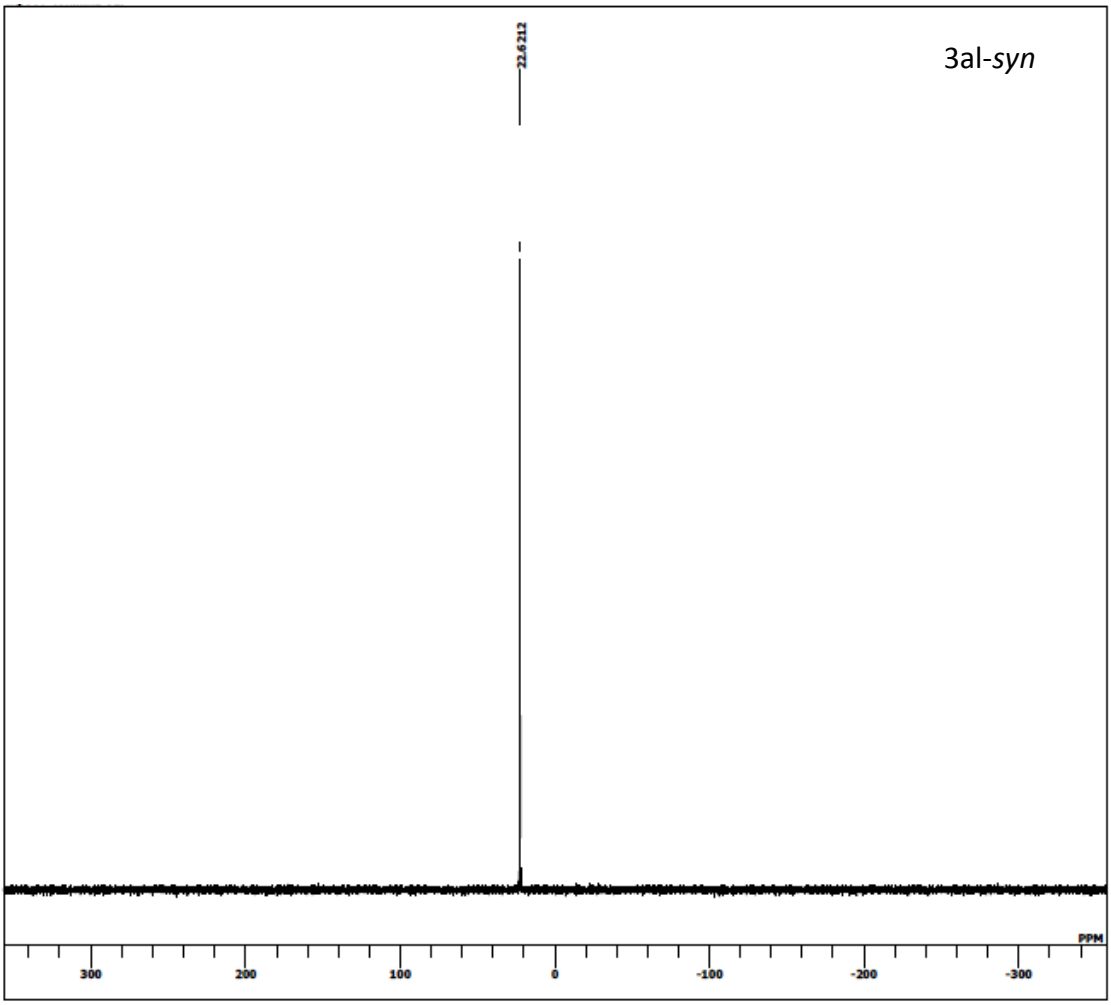

3ak-syn

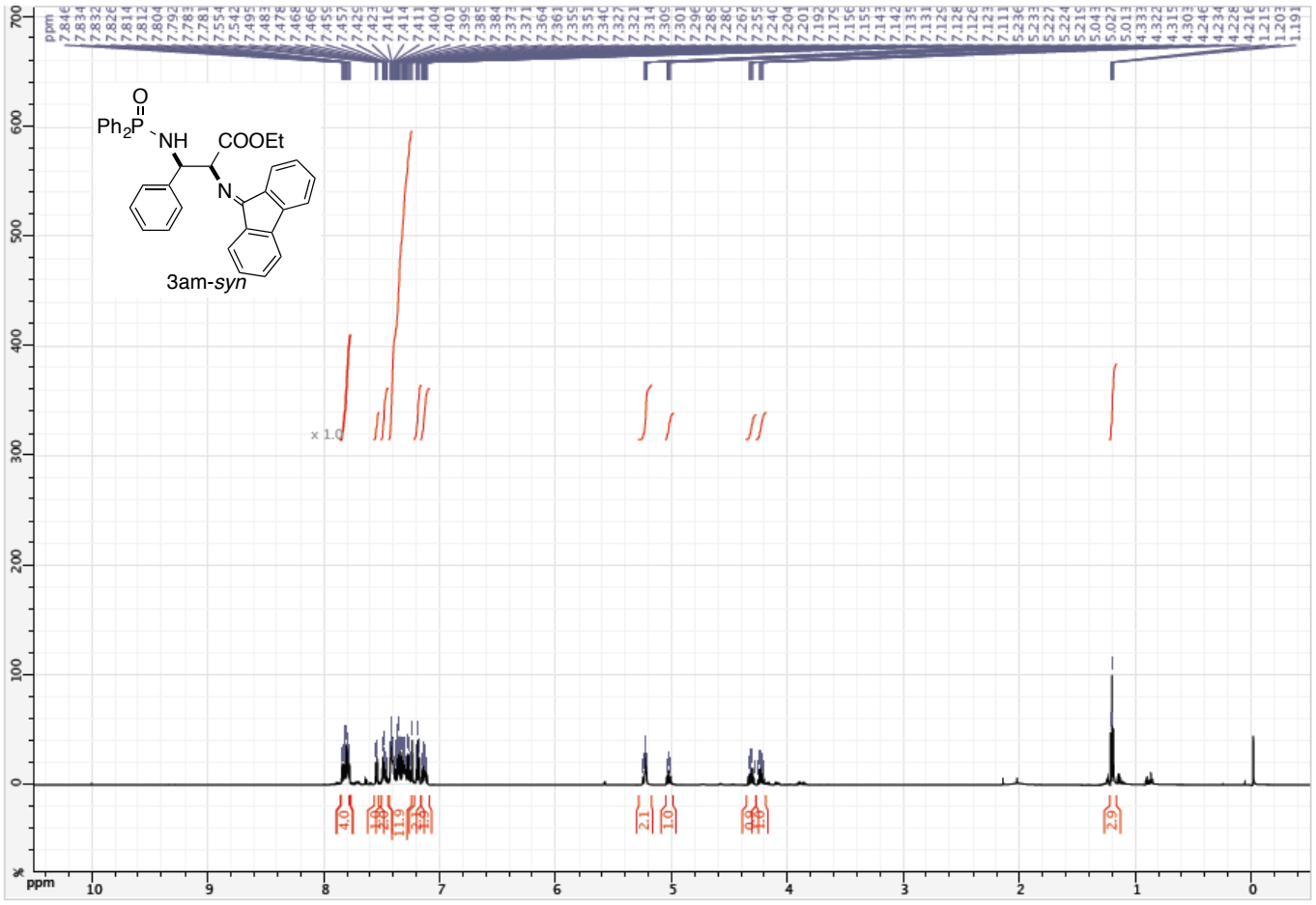

3ak-syn

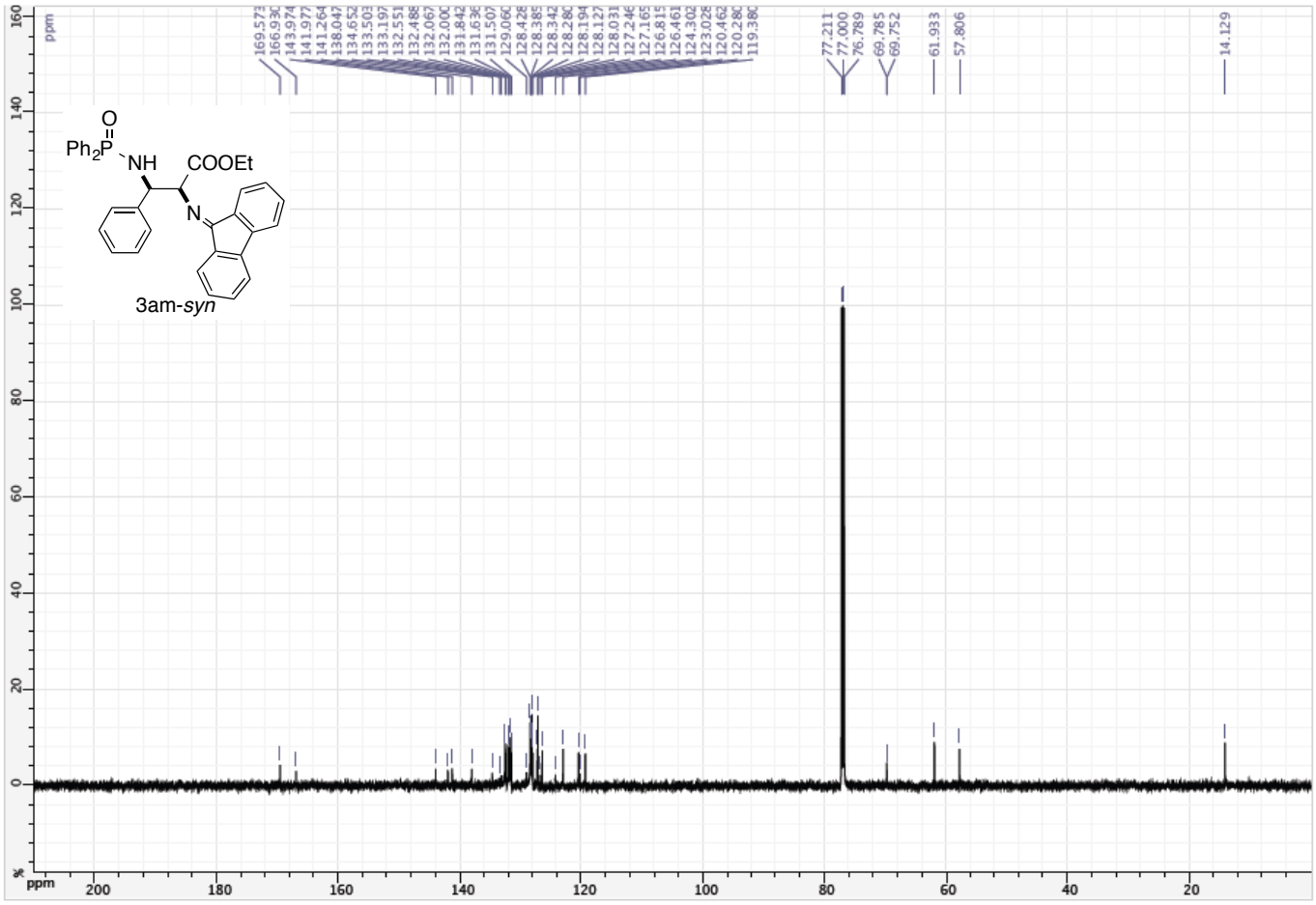

3ak-*syn*
22.9835
PPM
300
200
100
0
-100
-200
-300

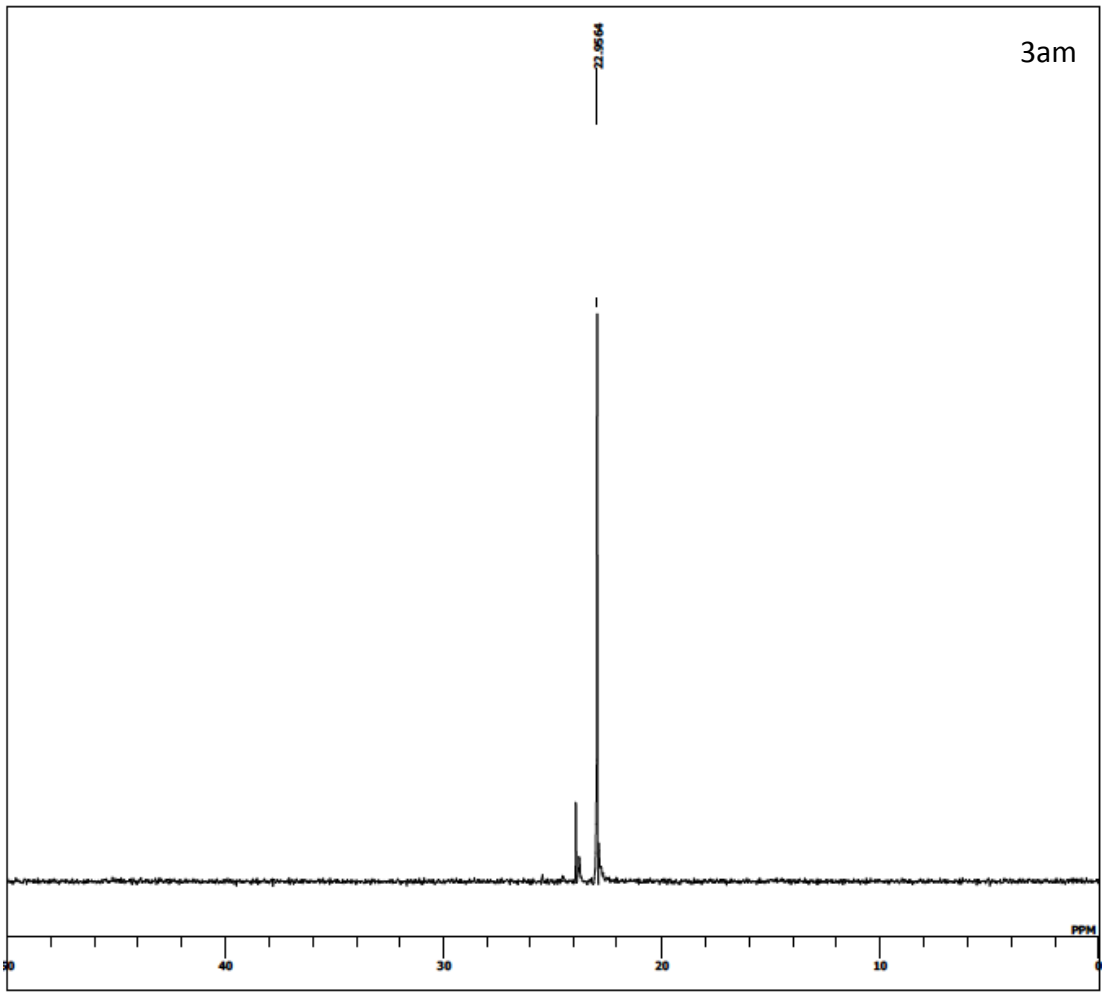

7.15 (t, J= 7.5Hz)
7.71 (d, J= 7.5Hz)
3al-*syn*
ppm

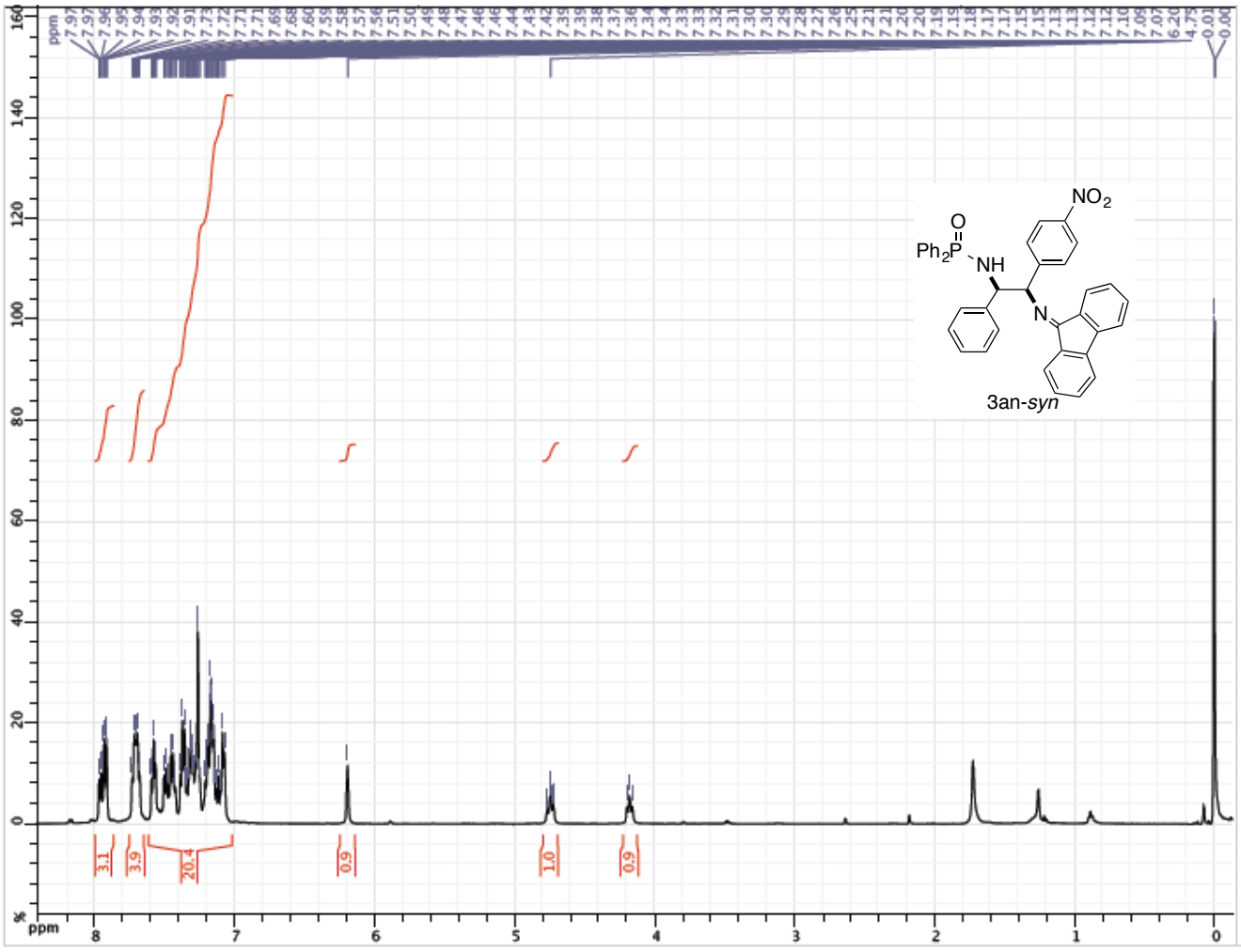

ppm
170.17
146.65
145.20
140.65
140.40
139.64
133.38
132.80
132.33
132.13
132.05
131.92
131.85
131.78
131.34
131.22
129.21
128.54
128.13
128.03
127.91
127.81
127.04
126.85
126.77
126.58
125.94
119.84
119.56
79.14
79.07
77.26
77.00
76.74
63.36
36.69
26.46
79.1 (d, J= 8.8Hz)
O
Ph2P
NH
N
3al-syn

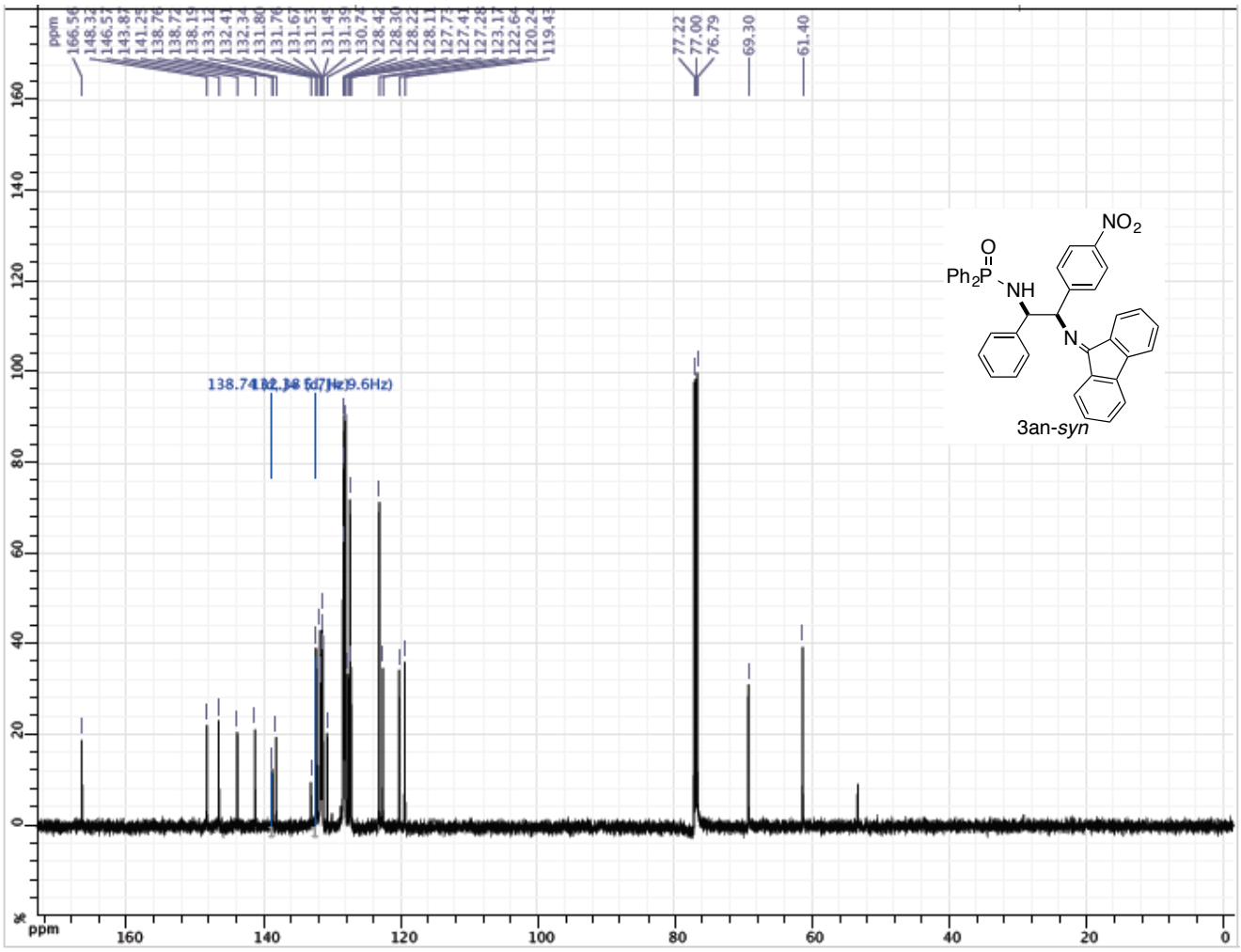

226.212
3al-syn
PPM

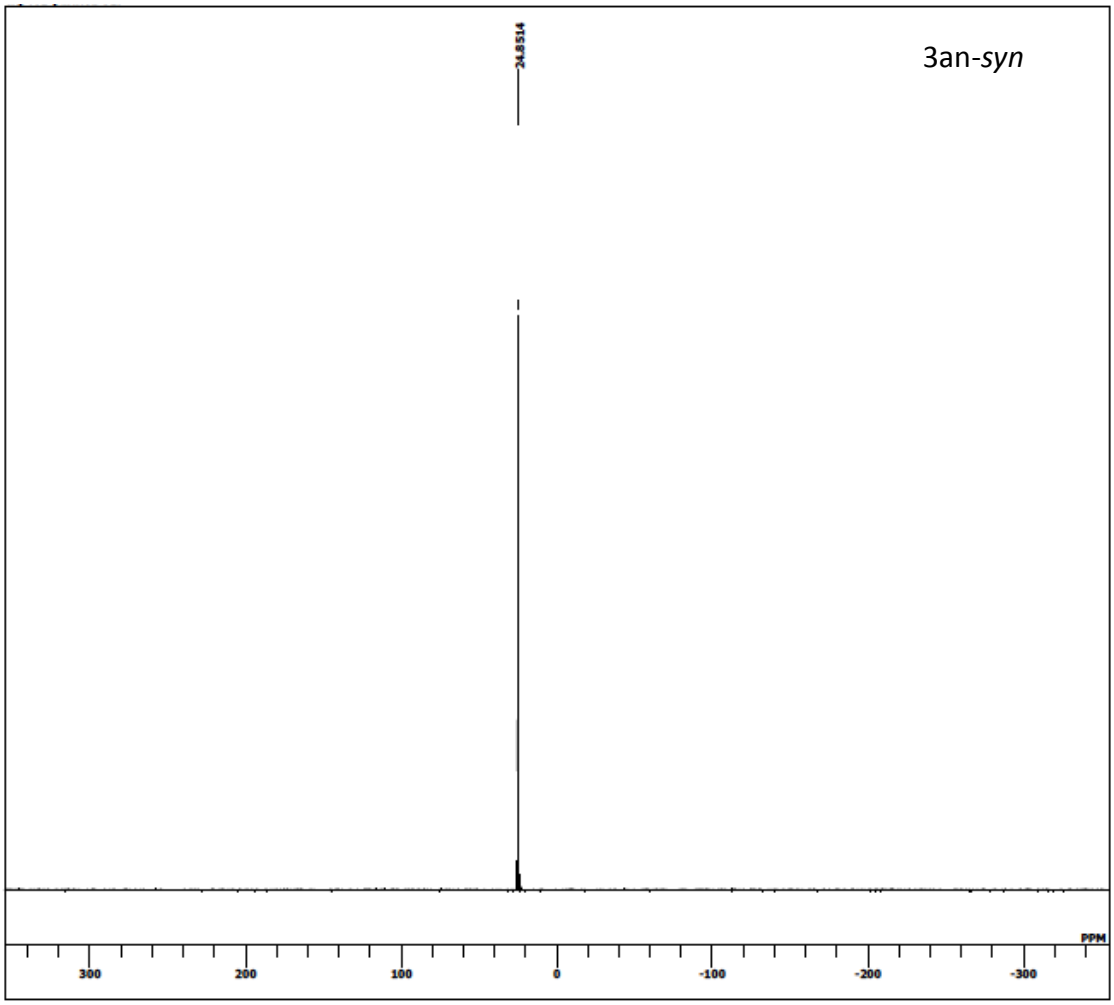

O
Ph2P
NH
COOEt
N
3am-syn

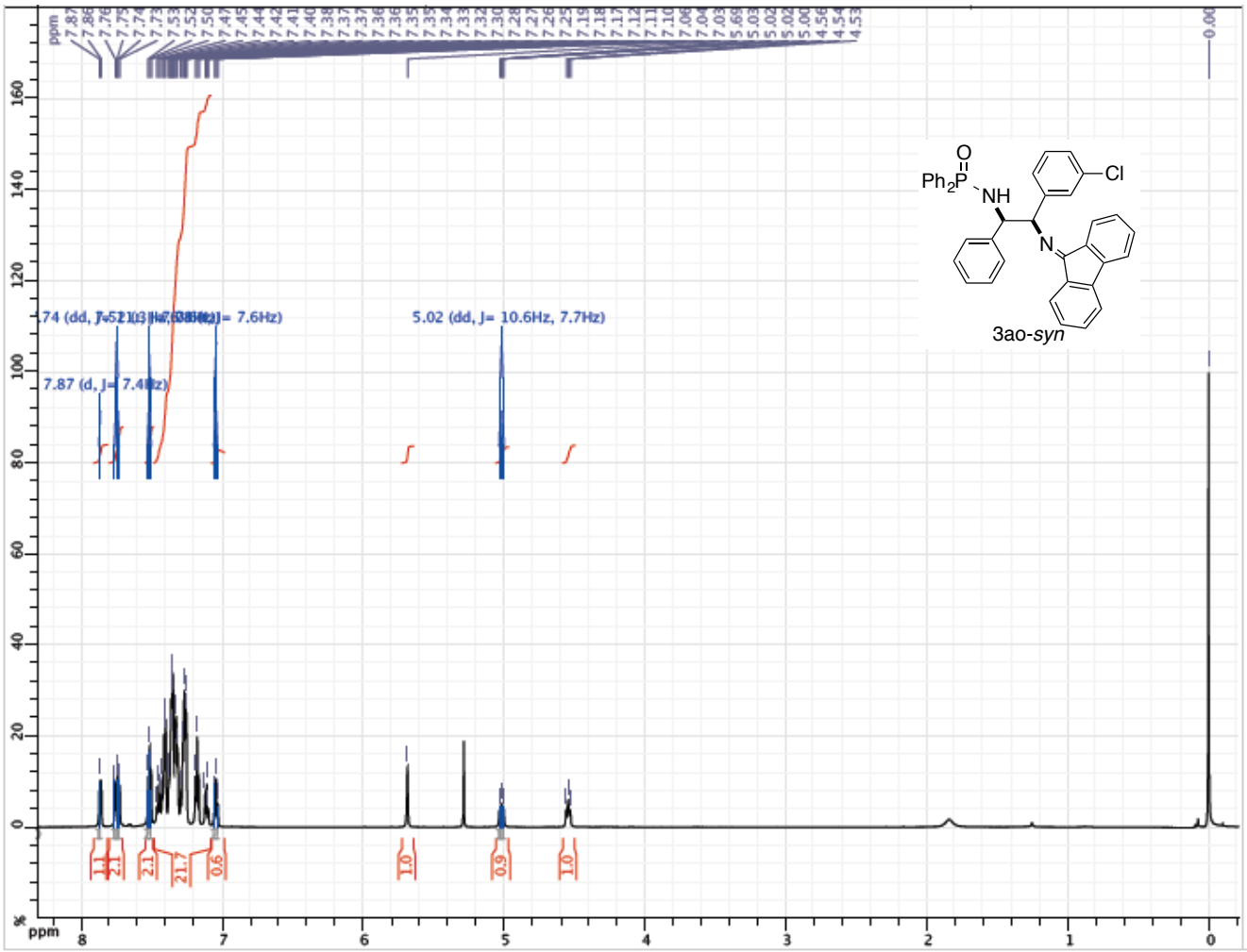

O
Ph2P
NH
COOEt
N
3am-syn

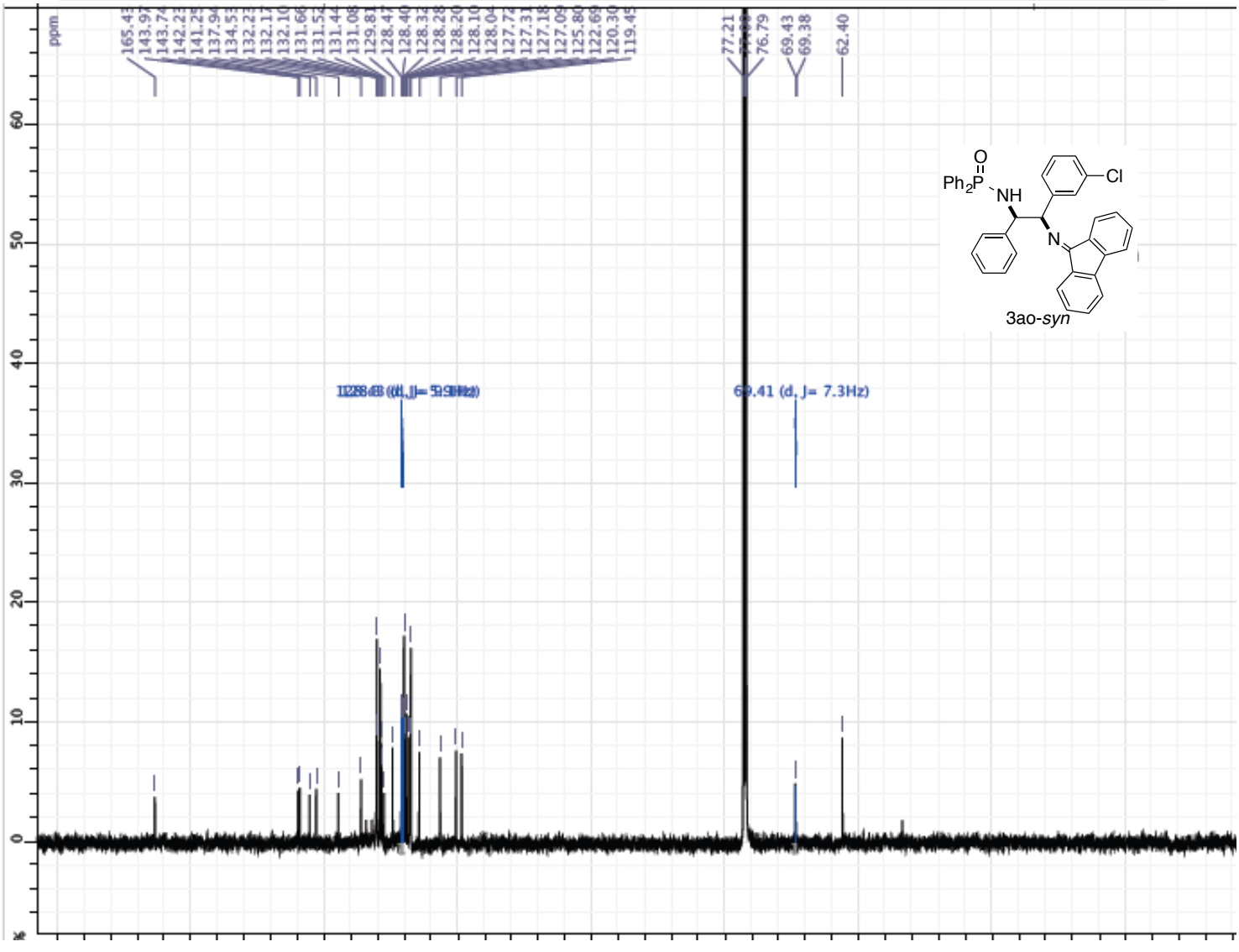

3am
22.9564
PPM
50
40
30
20
10
0

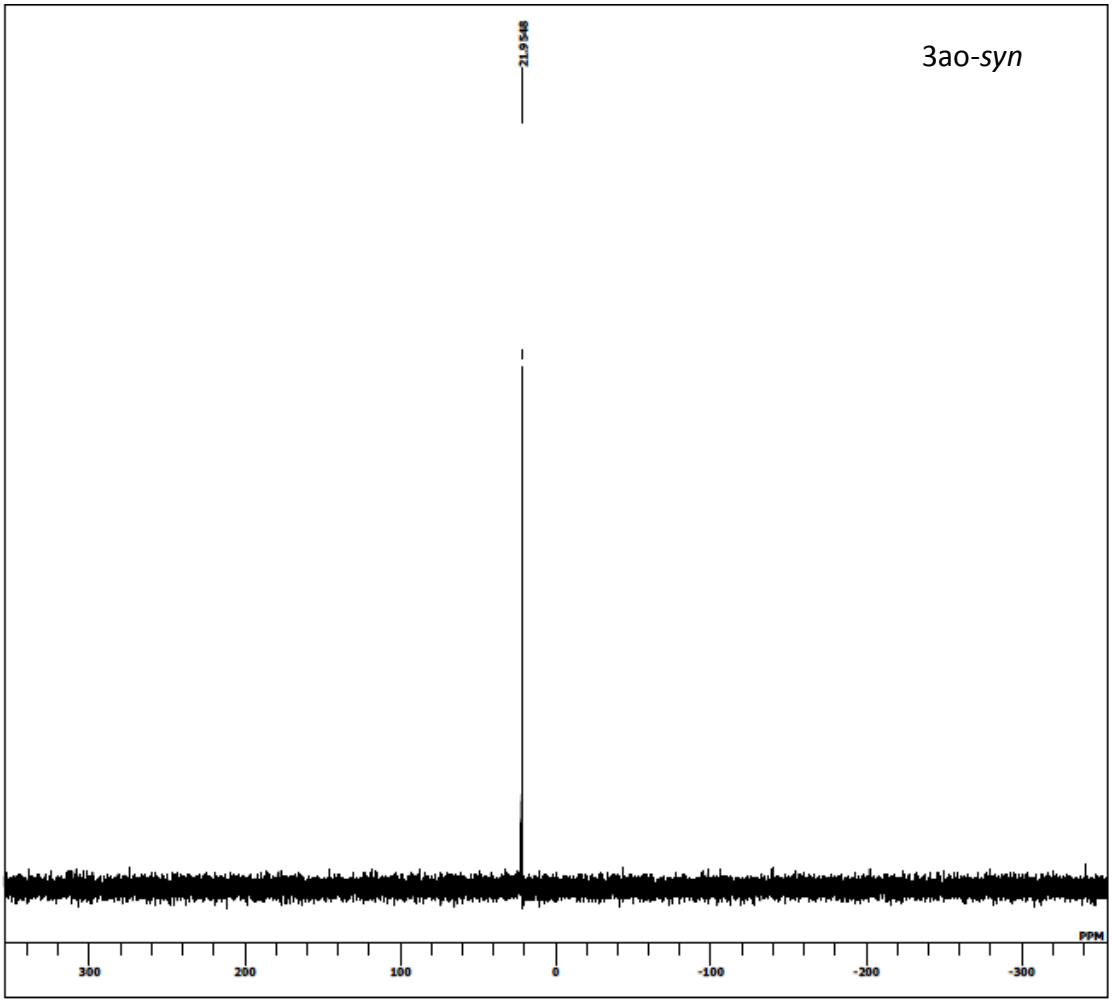

ppm
NO2
O
Ph2P
NH
N
3an-syn
3.1
3.9
20.4
0.9
1.0
0.9

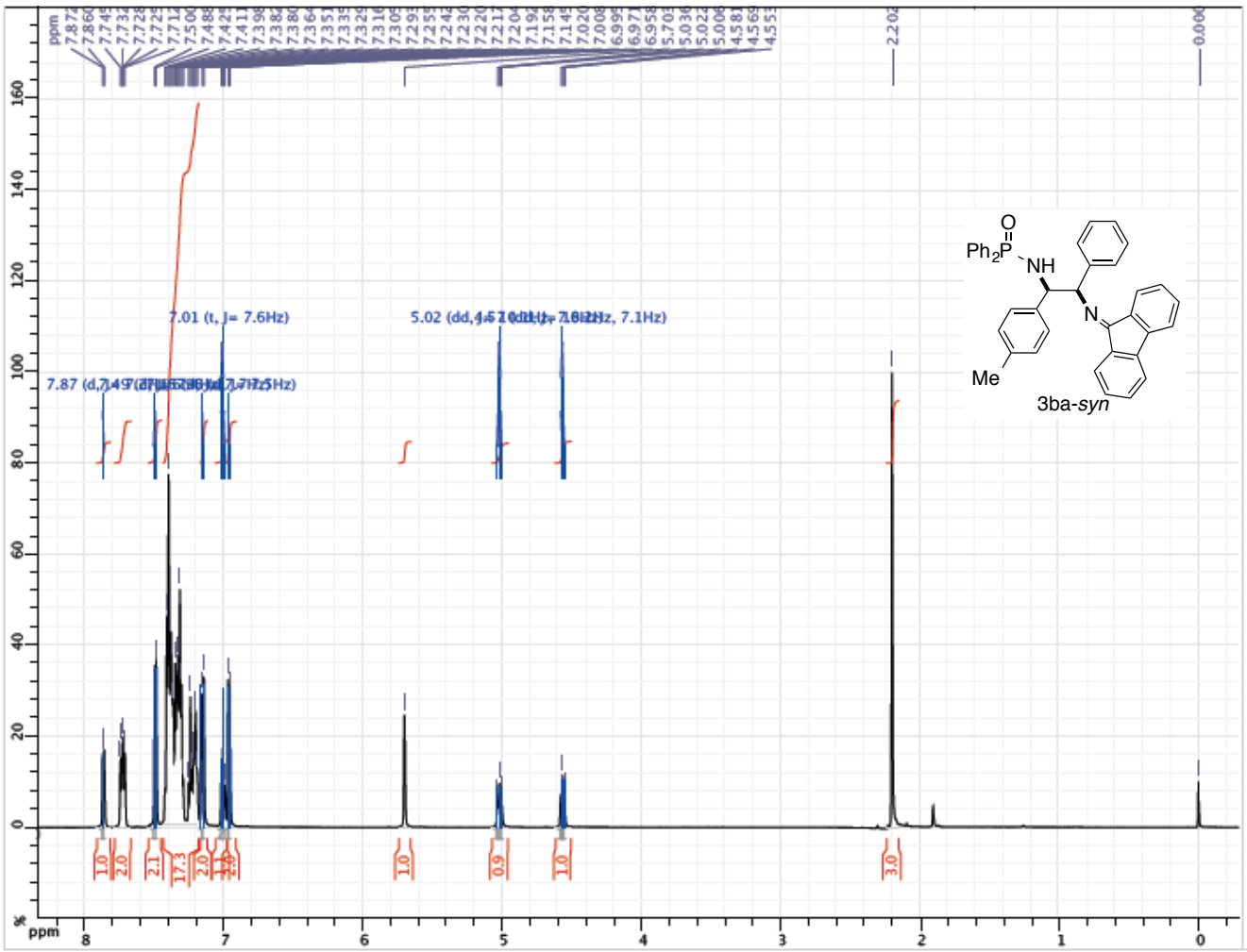

NO2
O
Ph2P
NH
N
3an-syn

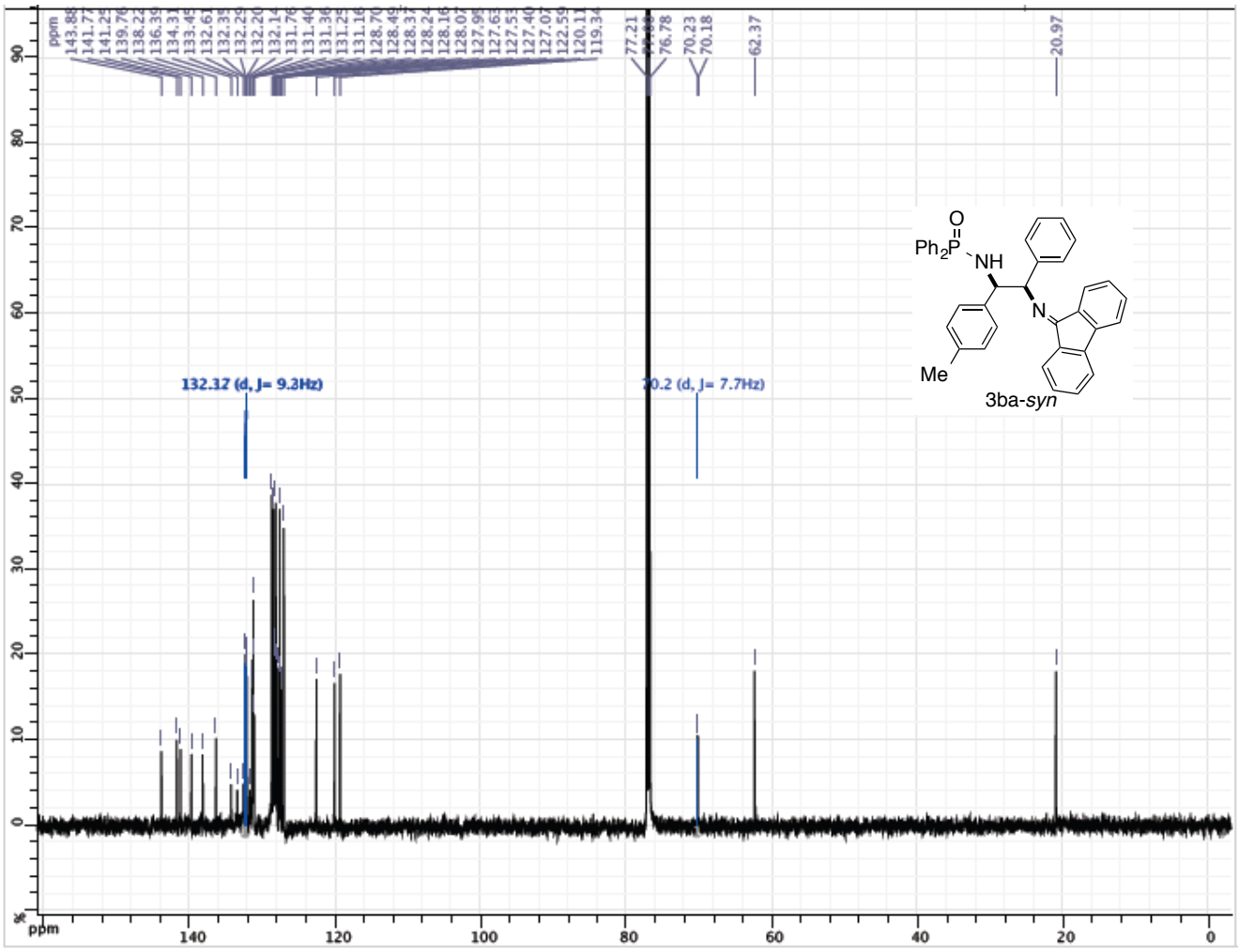

3an-syn

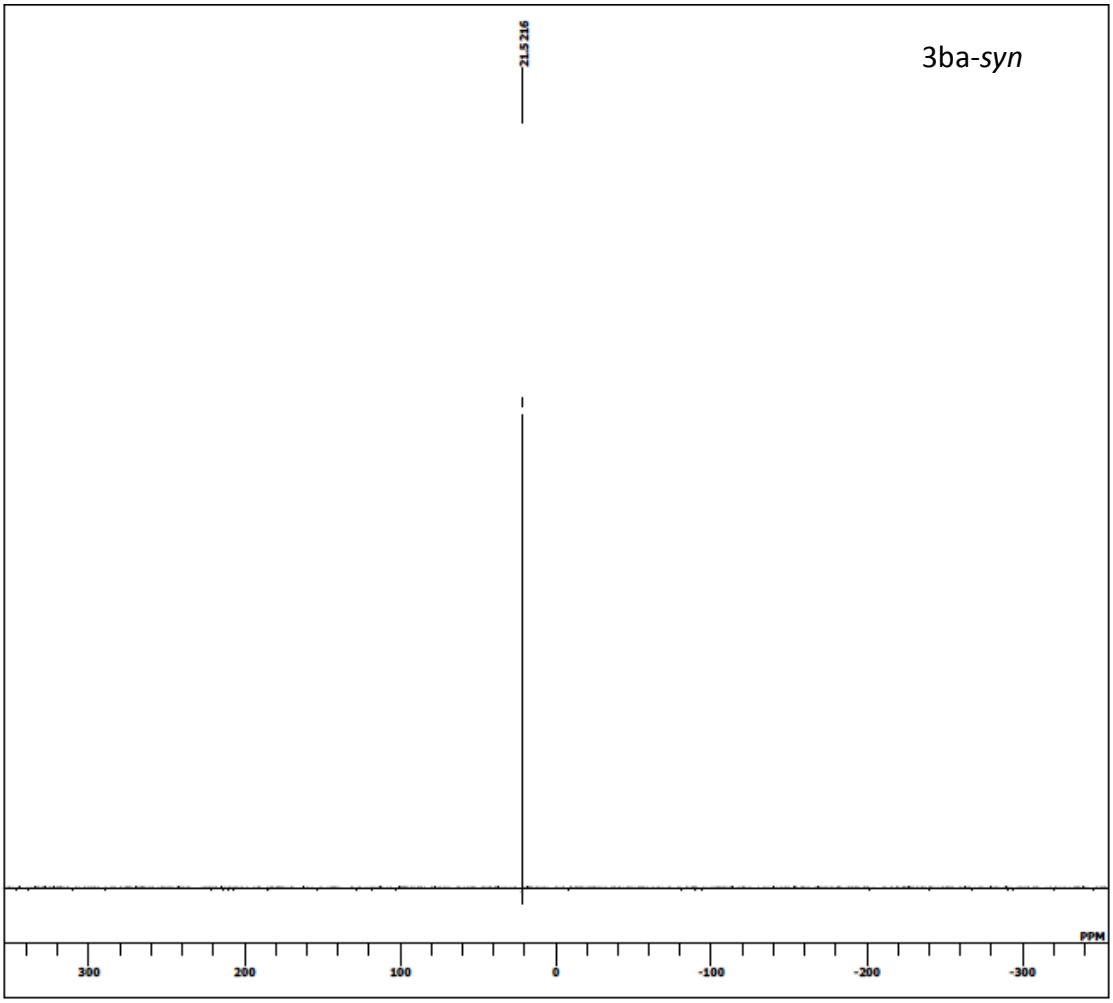

5.02 (dd, J= 10.6Hz, 7.7Hz)
7.87 (d, J= 7.4Hz)
Cl
NH
N
3ao-syn

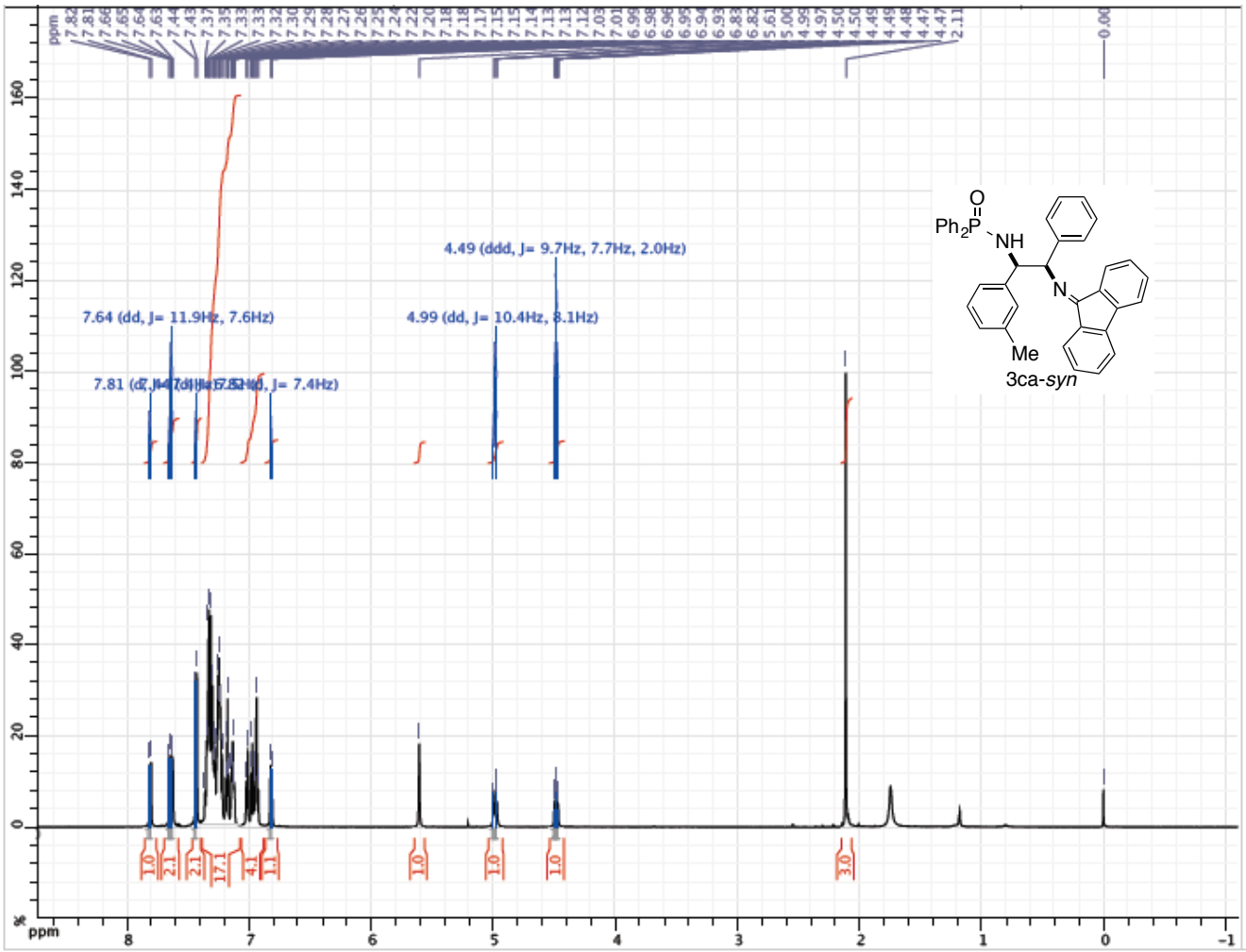

69.41 (d, J= 7.3Hz)
Cl
NH
N
3ao-syn

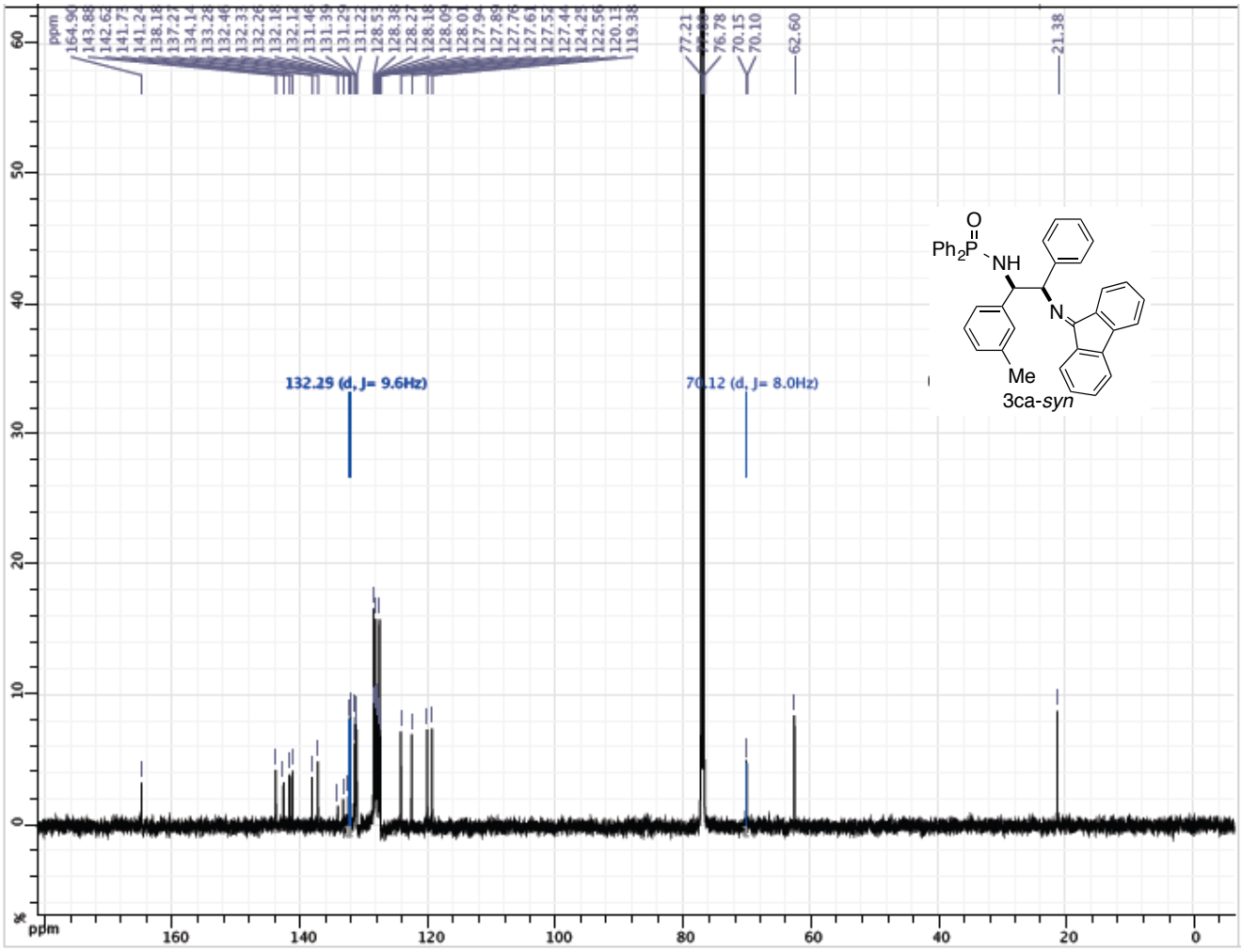

3ao-*syn*
21.9548
PPM
300
200
100
0
-100
-200
-300

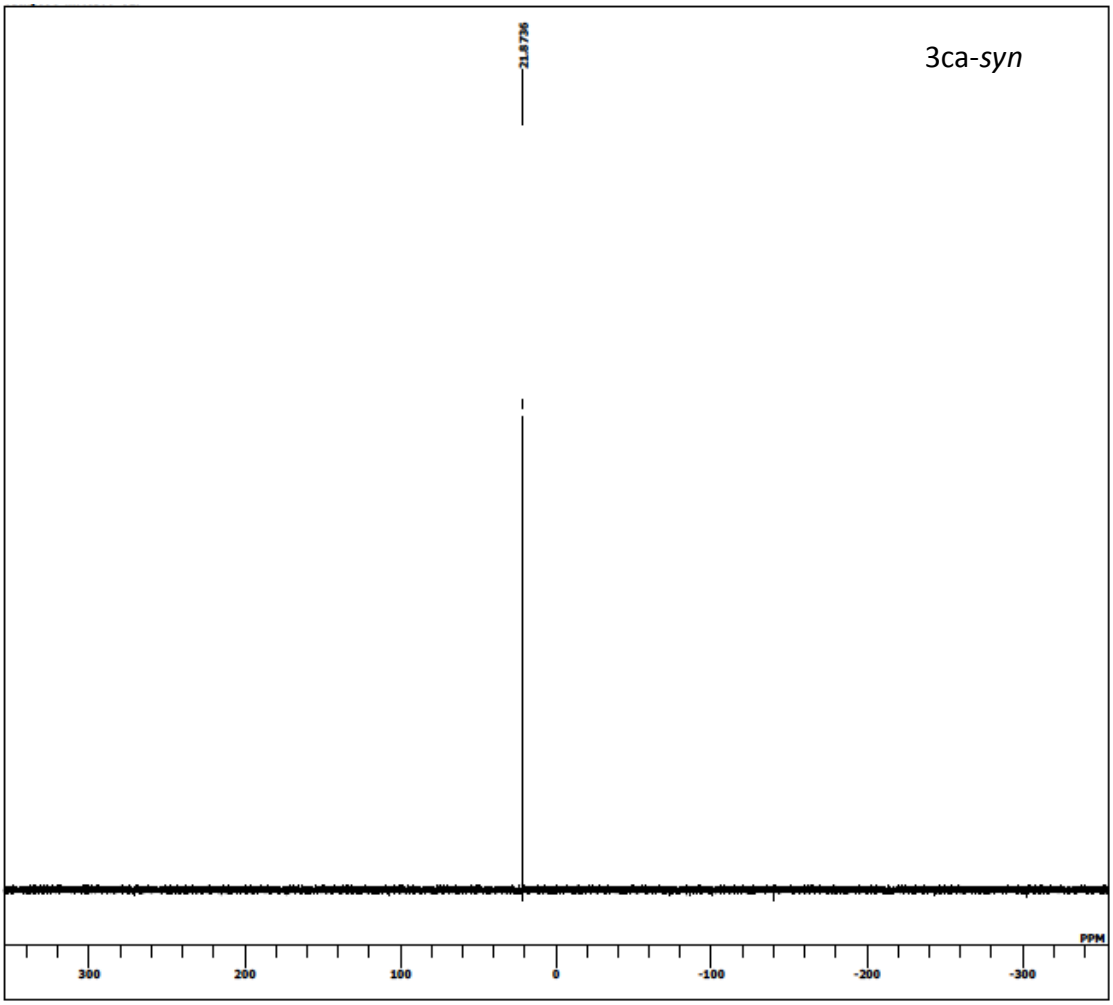

7.01 (t, J= 7.6Hz)
5.02 (dd, J= 7.6Hz, 7.1Hz)
7.87 (d, J= 7.7Hz)
2.202
0.000
Ph2P
O
NH
N
Me
3ba-*syn*
ppm

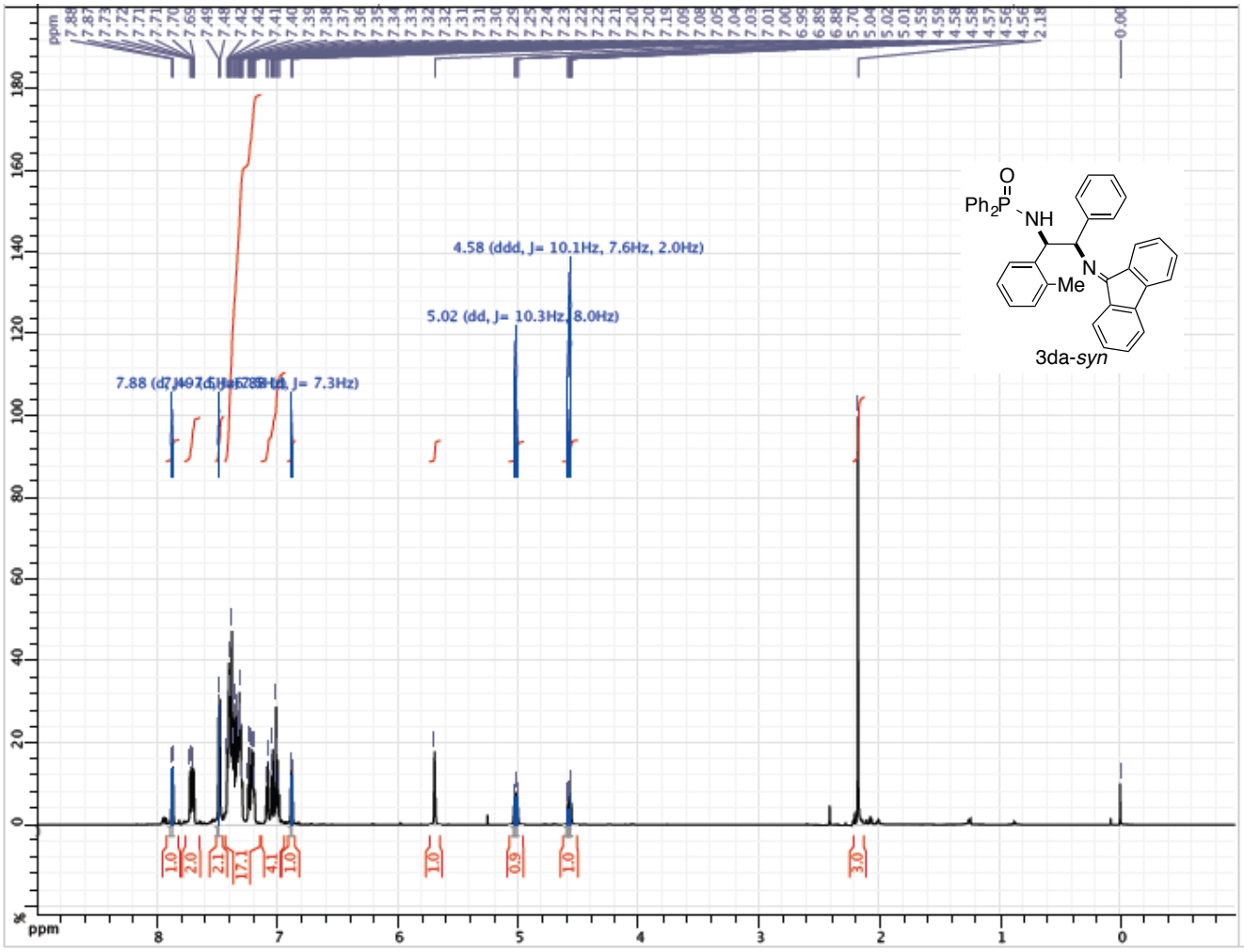

132.12 (d, J= 9.3Hz)
70.2 (d, J= 7.7Hz)
Me
3ba-*syn*

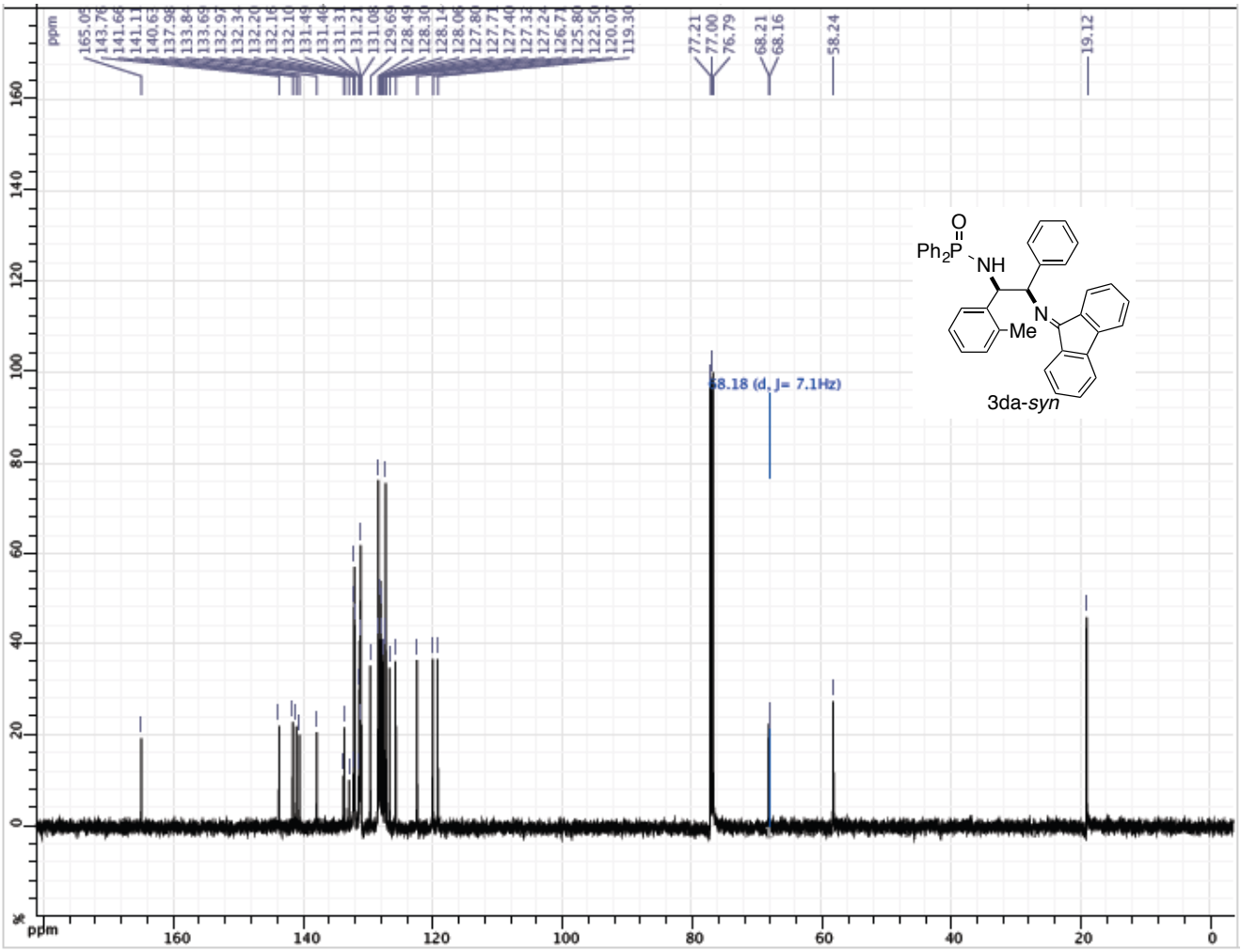

3ba-*syn*
PPM

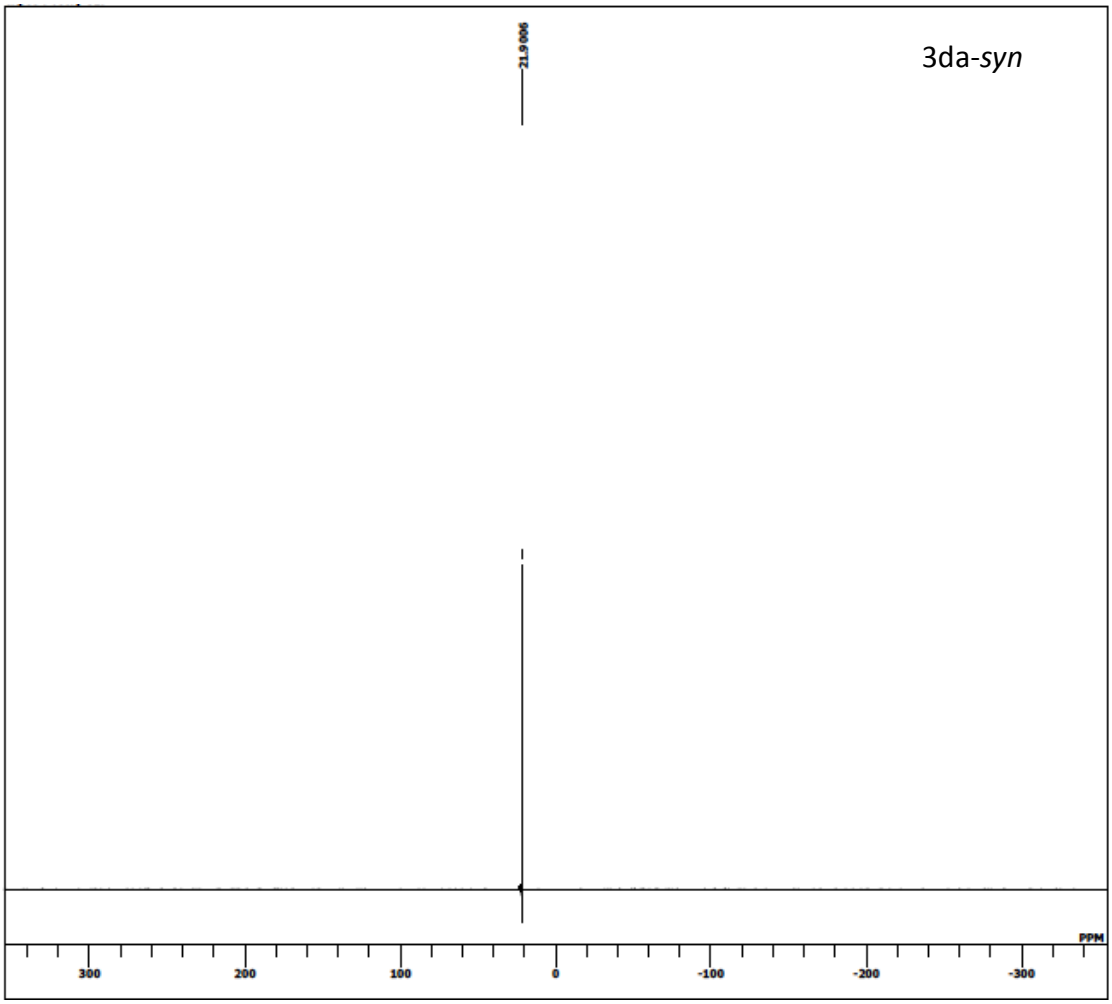

4.49 (ddd, J= 9.7Hz, 7.7Hz, 2.0Hz)
7.64 (dd, J= 11.9Hz, 7.6Hz)
4.99 (dd, J= 10.4Hz, 8.1Hz)
7.81 (d, J= 7.4Hz)
Ph2P
O
NH
N
Me
3ca-syn
ppm

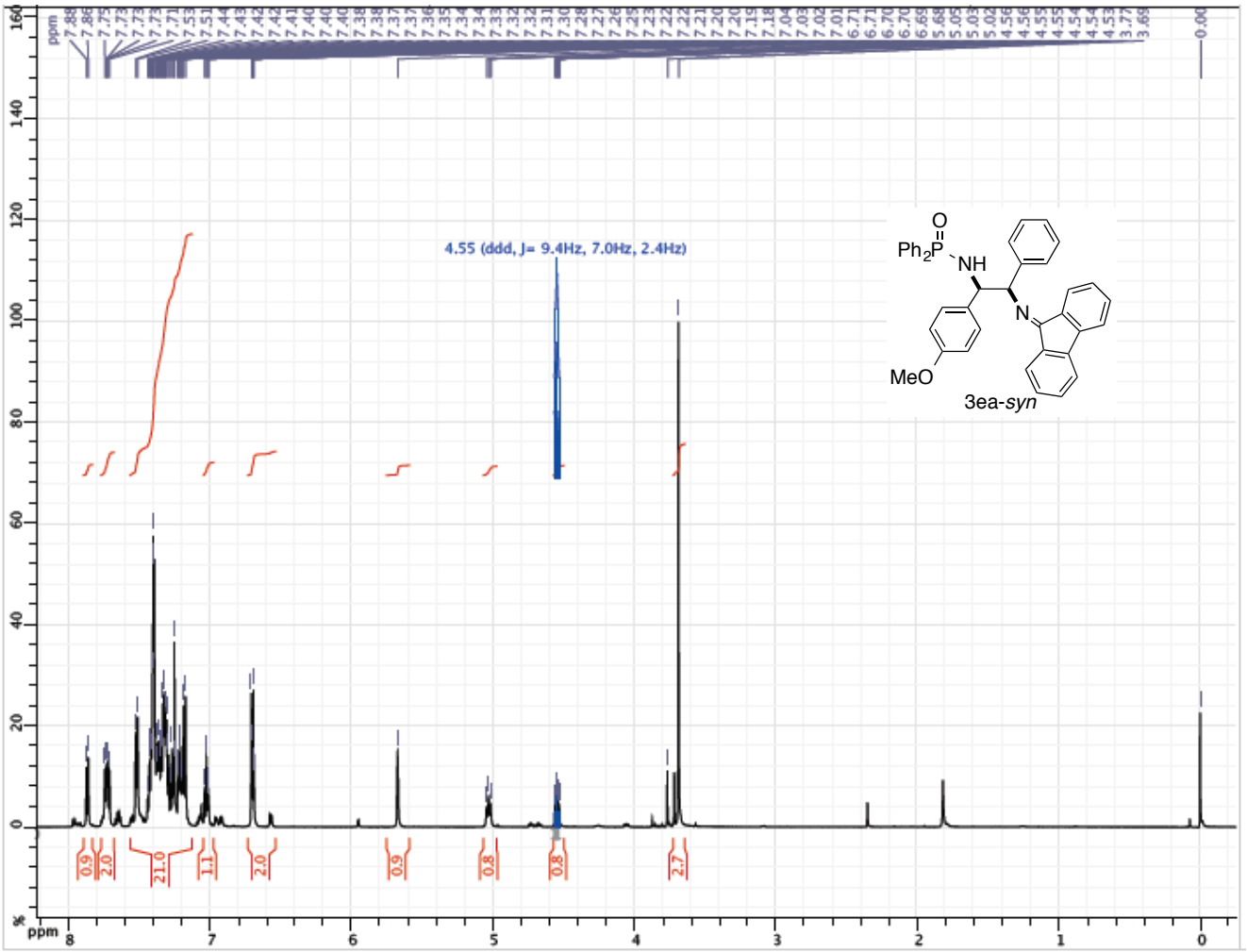

132.29 (d, J= 9.6Hz)
70.12 (d, J= 8.0Hz)
Ph2P
O
NH
N
Me
3ca-syn
ppm

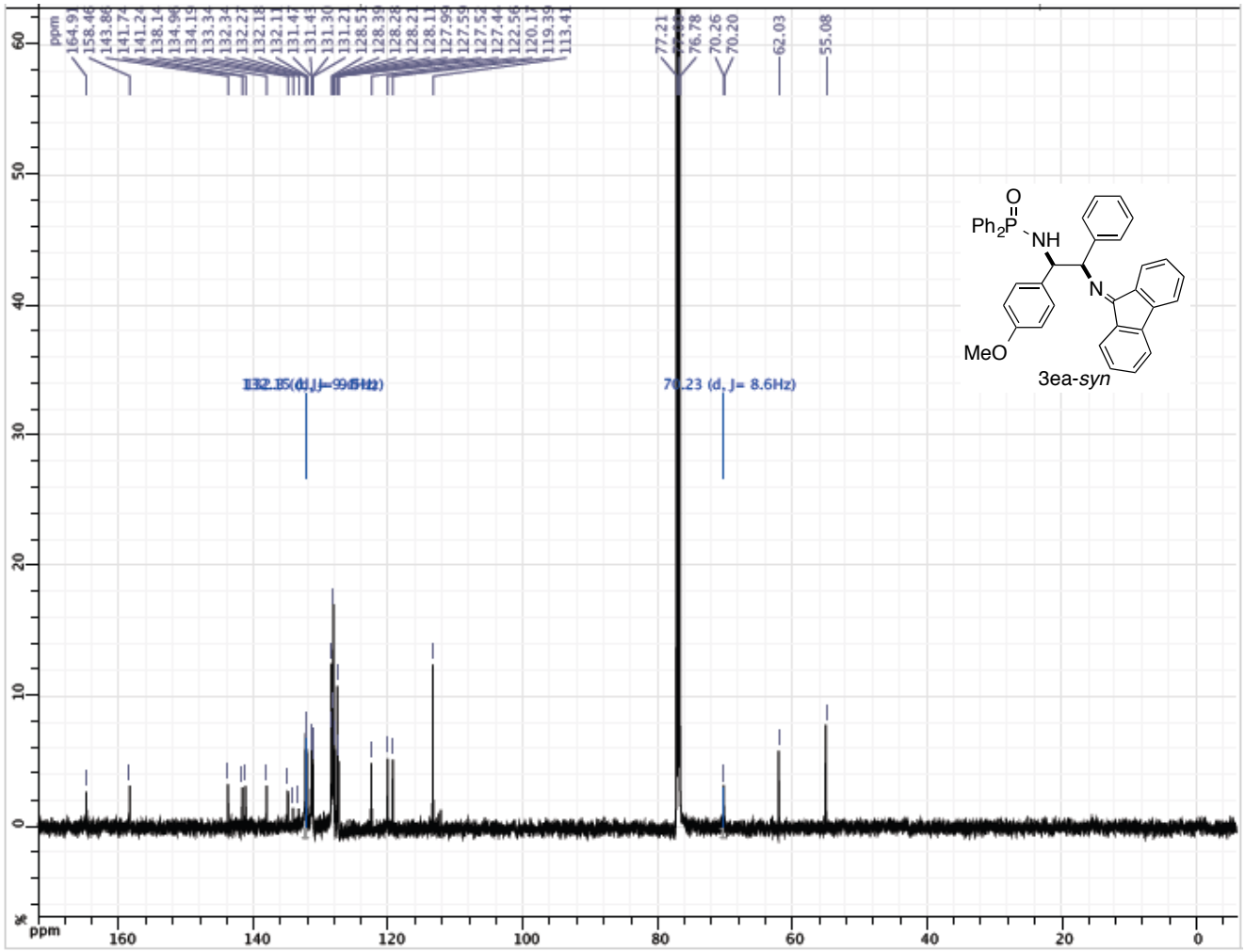

3ca-*syn*
PPM
300
200
100
0
-100
-200
-300

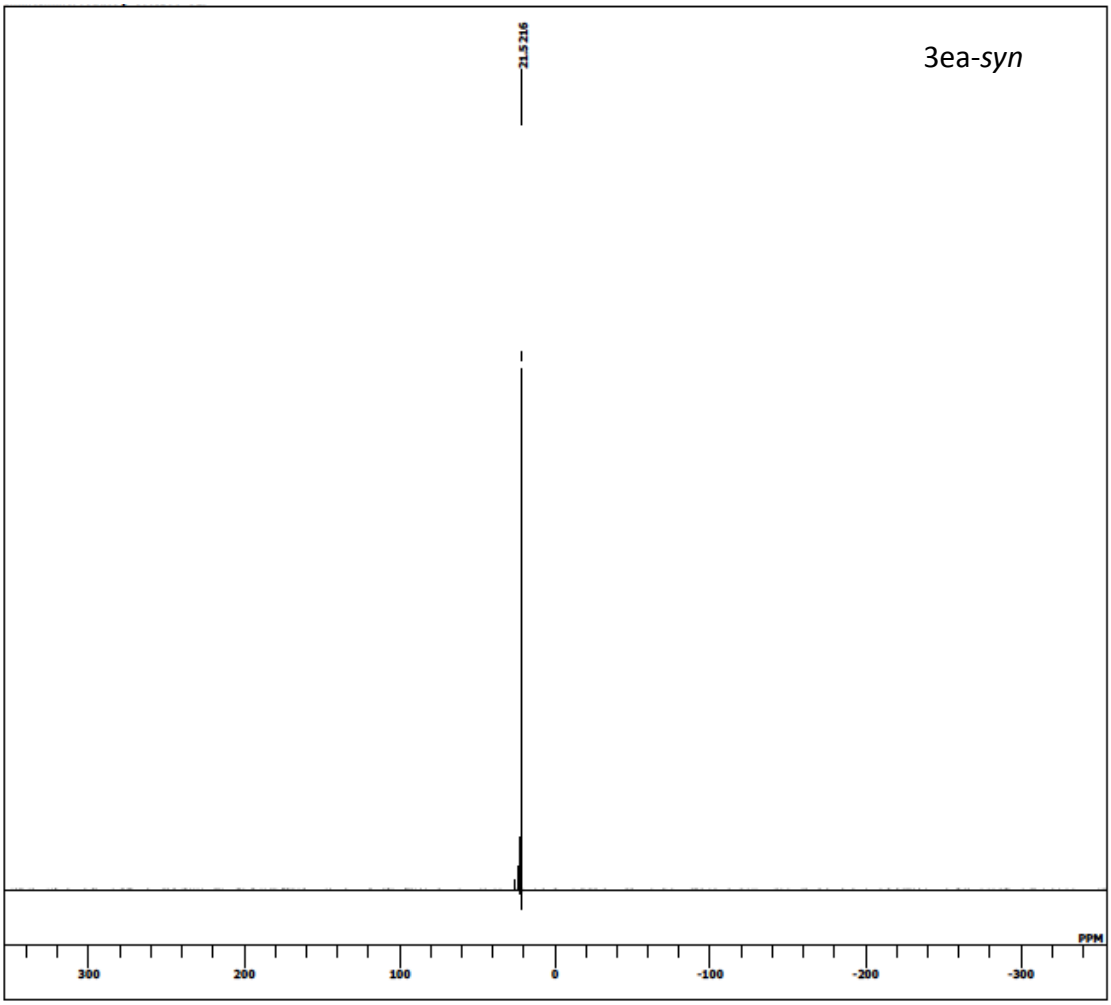

4.58 (ddd, J= 10.1Hz, 7.6Hz, 2.0Hz)
5.02 (dd, J= 10.3Hz, 8.0Hz)
7.88 (d, J= 7.3Hz)
Ph2P
O
NH
N
Me
3da-*syn*
ppm

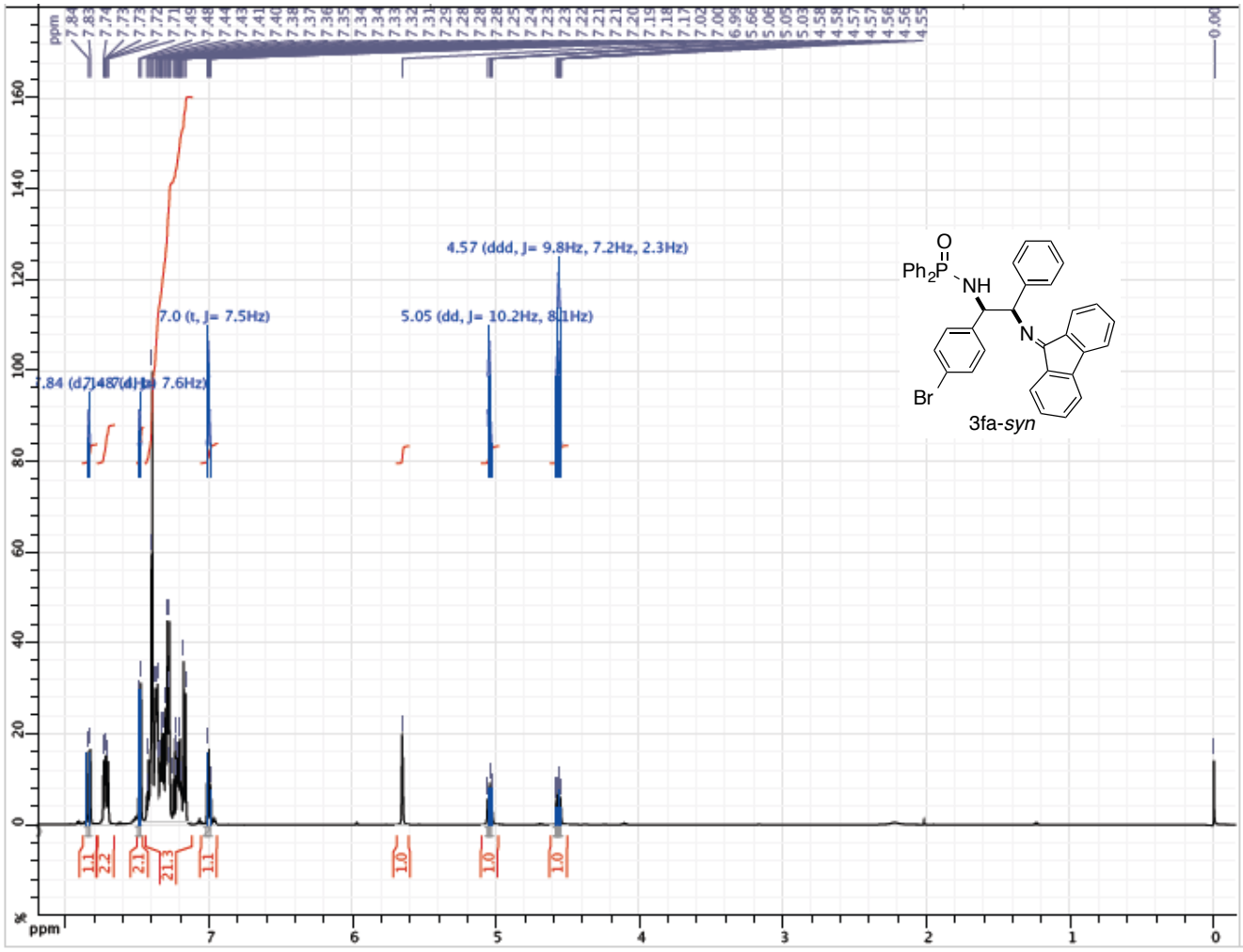

ppm
165.05
143.76
141.66
141.11
140.63
137.98
133.84
133.69
132.97
132.34
132.20
132.16
132.10
131.49
131.46
131.31
131.21
131.08
129.69
128.49
128.30
128.14
128.06
127.80
127.71
127.40
127.32
127.24
126.71
125.80
122.50
120.07
119.30
77.21
77.00
76.79
68.21
68.16
58.24
19.12
68.18 (d, J= 7.1Hz)
Ph2P
O
NH
N
Me
3da-syn
%
ppm
160
140
120
100
80
60
40
20
0

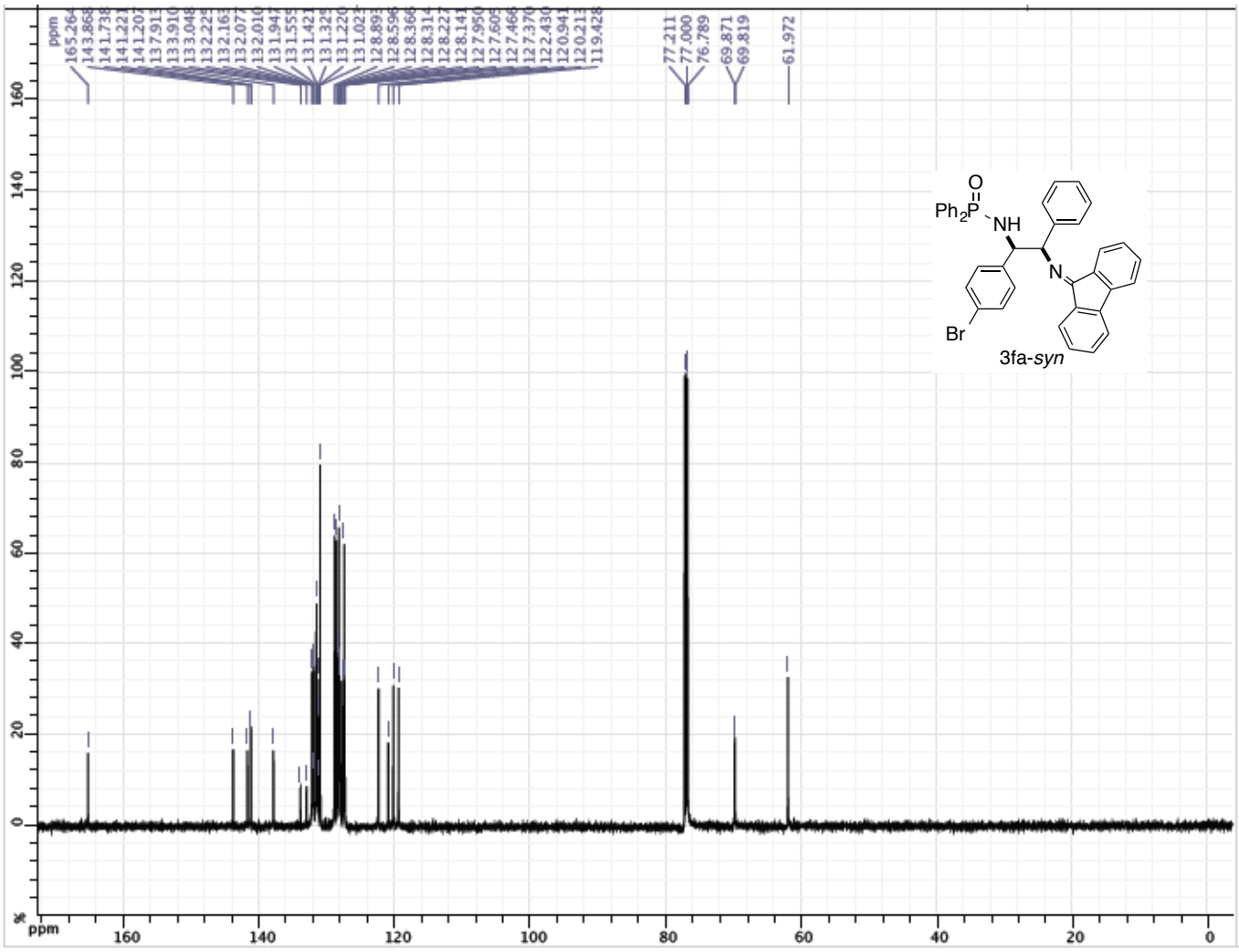

21.9006
3da-syn
PPM
300
200
100
0
-100
-200
-300

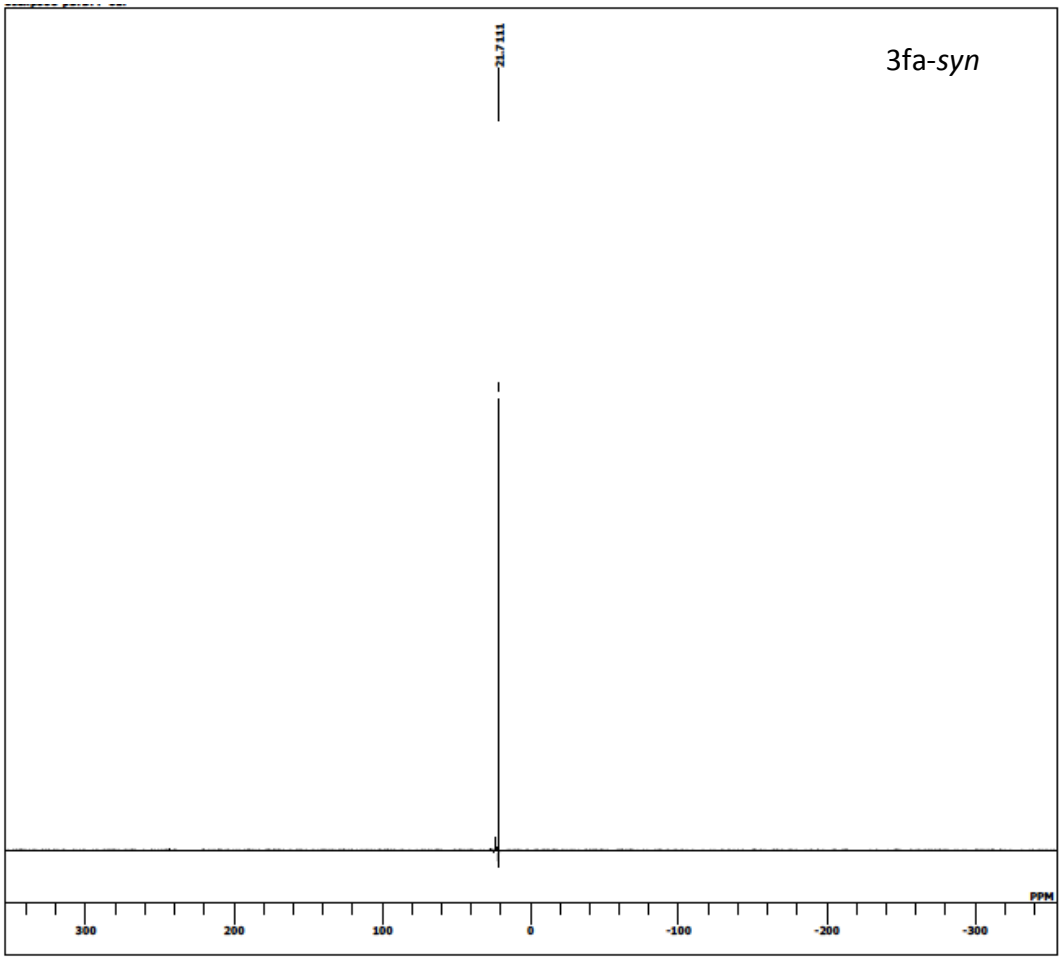

4.55 (ddd, J= 9.4Hz, 7.0Hz, 2.4Hz)
O
Ph2P
NH
N
MeO
3ea-syn

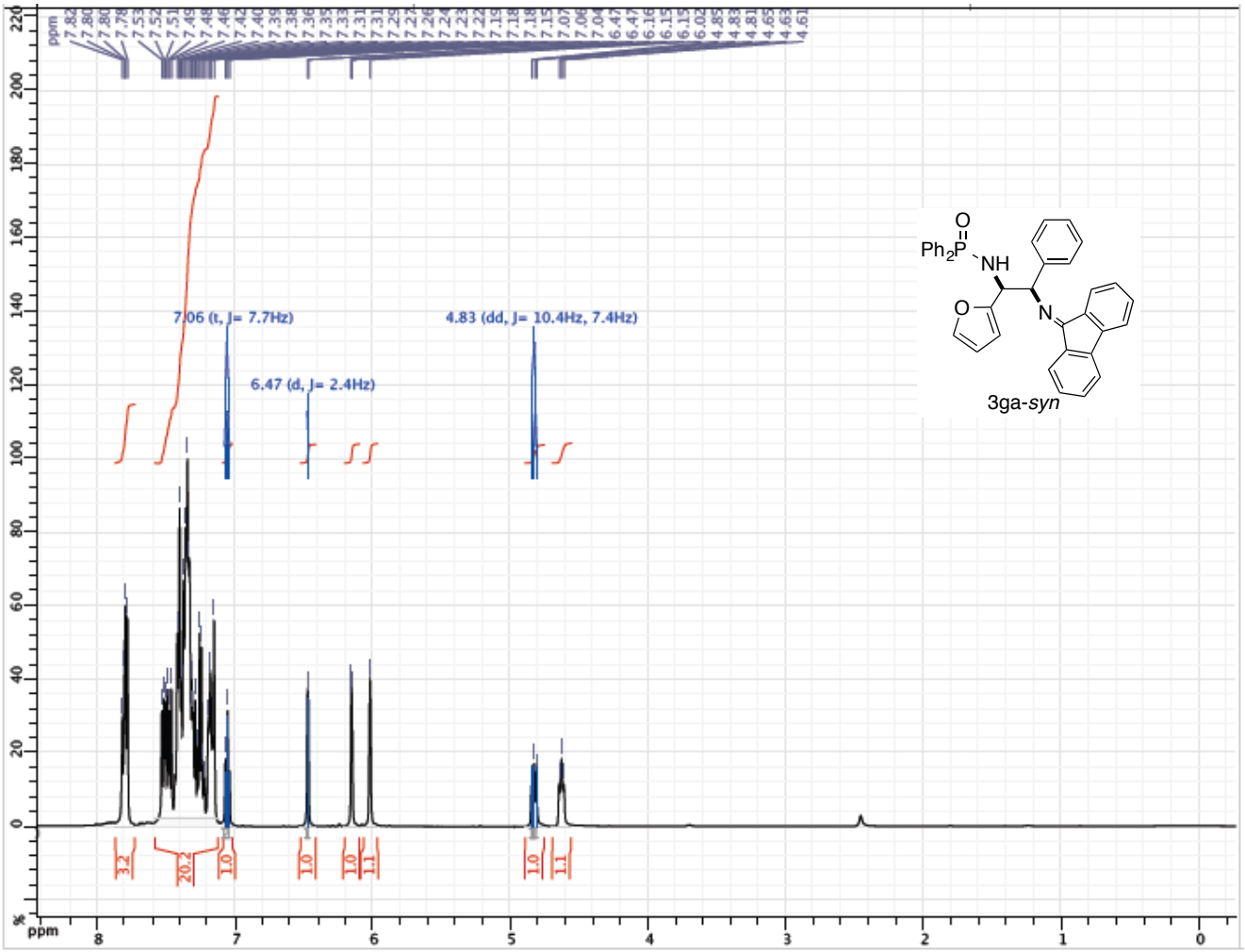

O
Ph2P
NH
N
MeO
3ea-syn

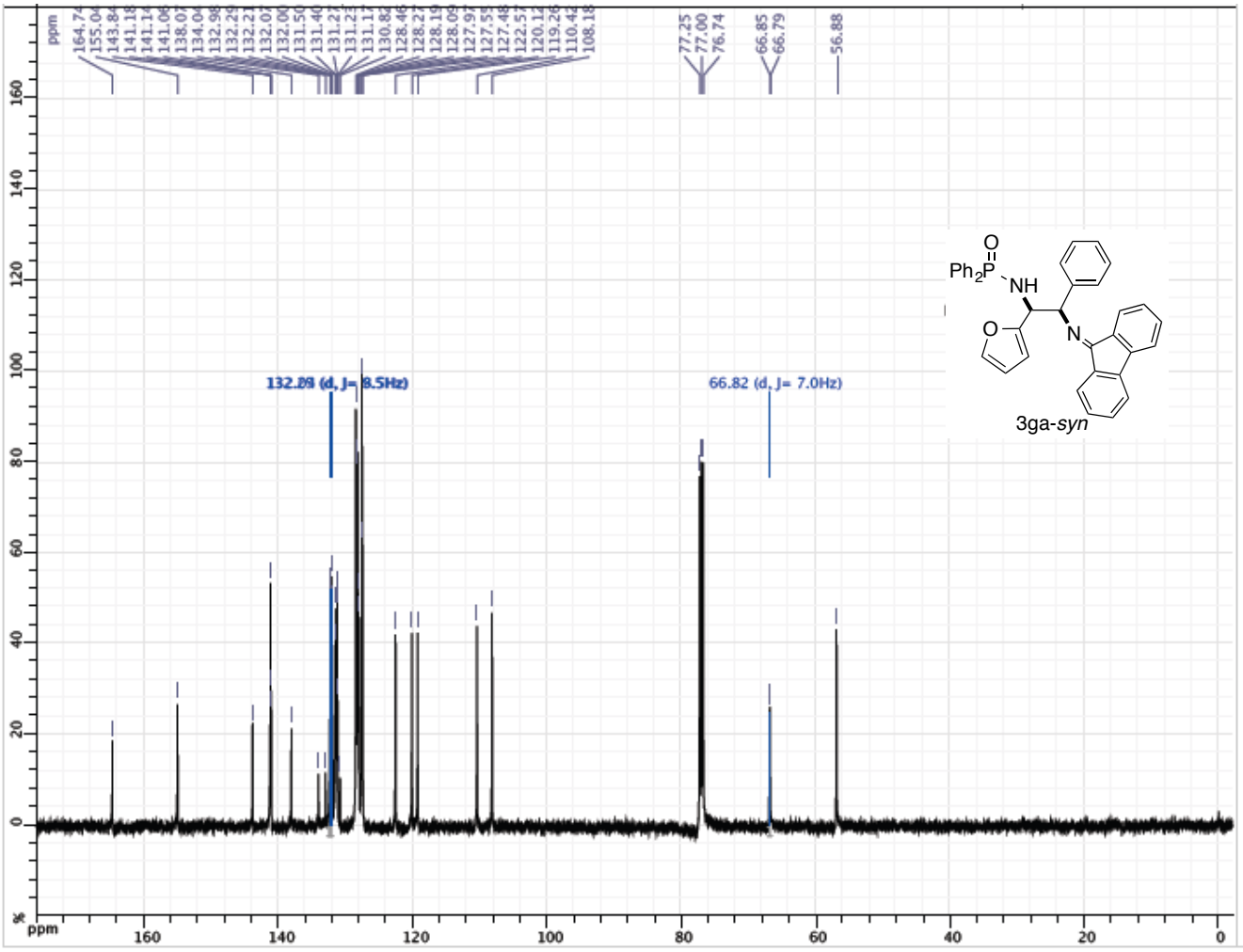

3ea-*syn*
21.5216
PPM
300
200
100
0
-100
-200
-300

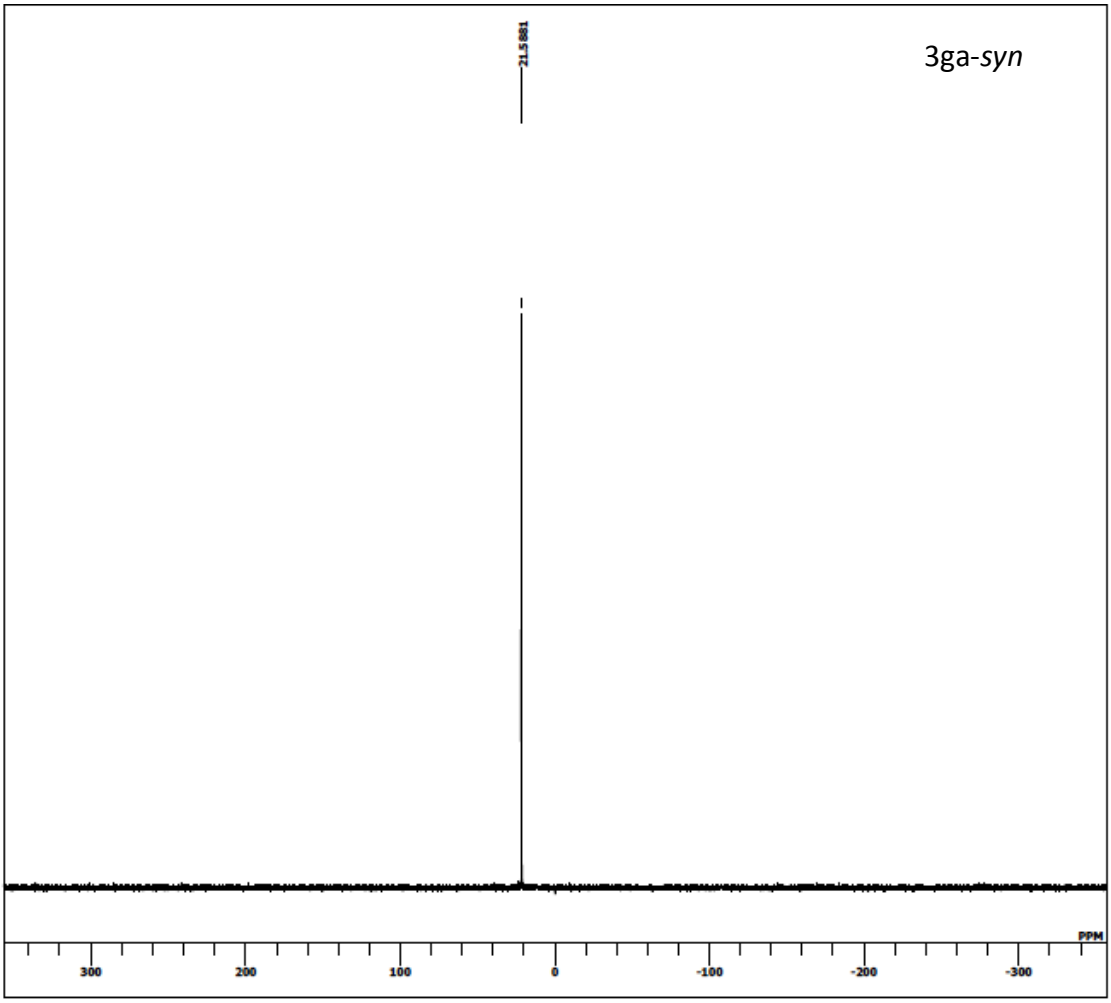

4.57 (ddd, J= 9.8Hz, 7.2Hz, 2.3Hz)
7.0 (t, J= 7.5Hz)
5.05 (dd, J= 10.2Hz, 8.1Hz)
7.6Hz)
Ph2P
O
NH
N
Br
3fa-*syn*
ppm

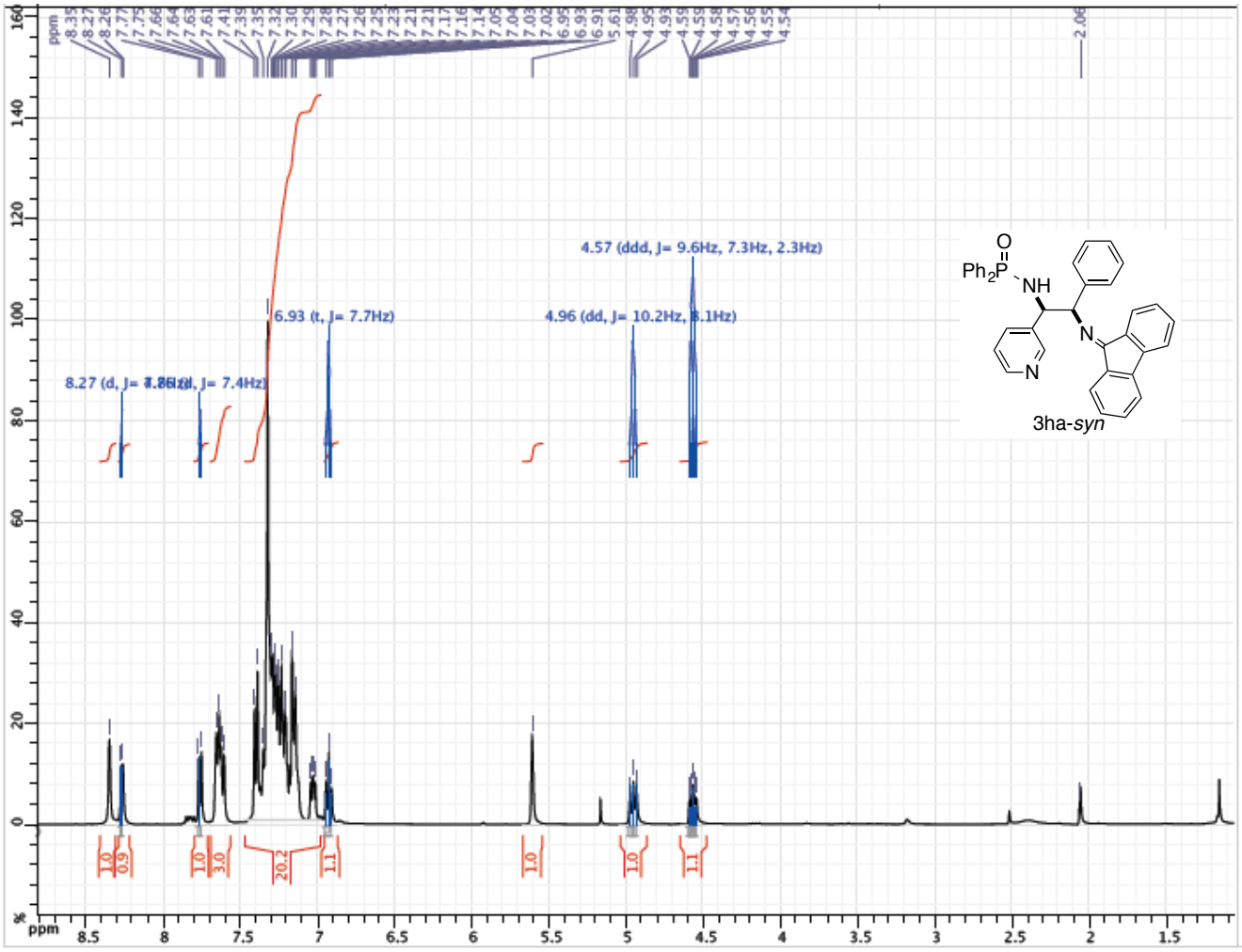

ppm
77.211
77.000
76.789
69.871
69.819
61.972
O
Ph2P
NH
N
Br
3fa-syn
ppm
160
140
120
100
80
60
40
20
0

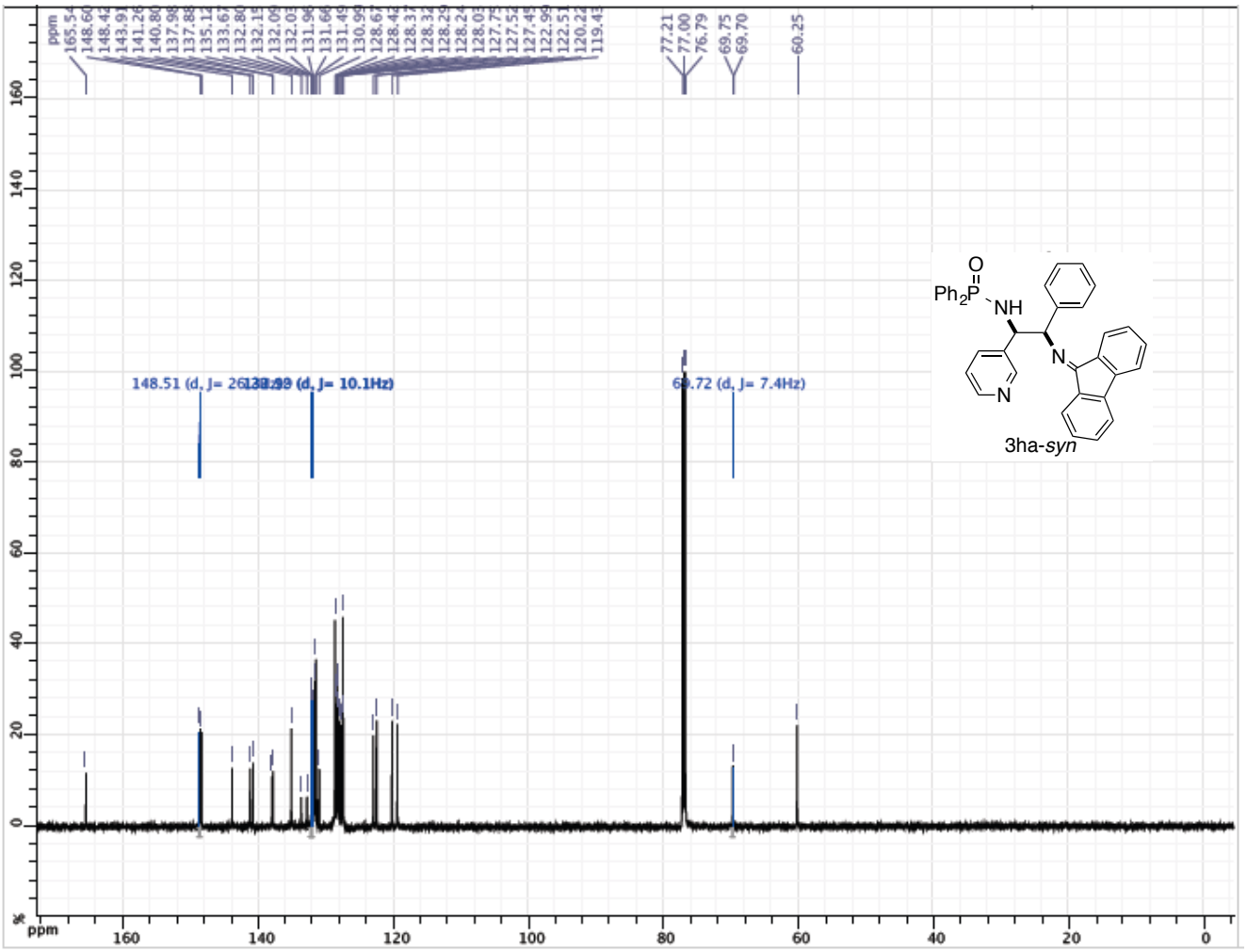

3fa-syn
21.711
PPM
300
200
100
0
-100
-200
-300

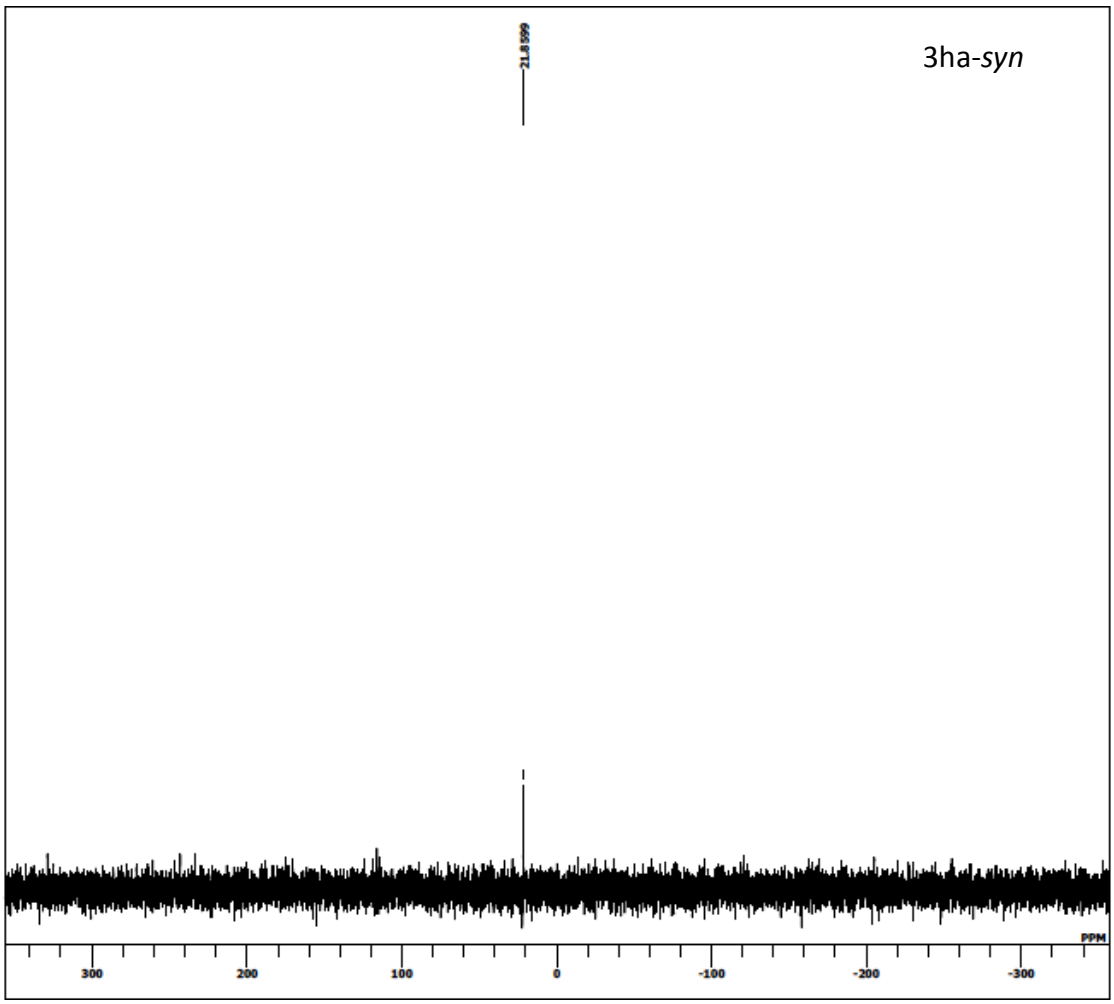

7.06 (t, J= 7.7Hz)
6.47 (d, J= 2.4Hz)
4.83 (dd, J= 10.4Hz, 7.4Hz)
3ga-syn

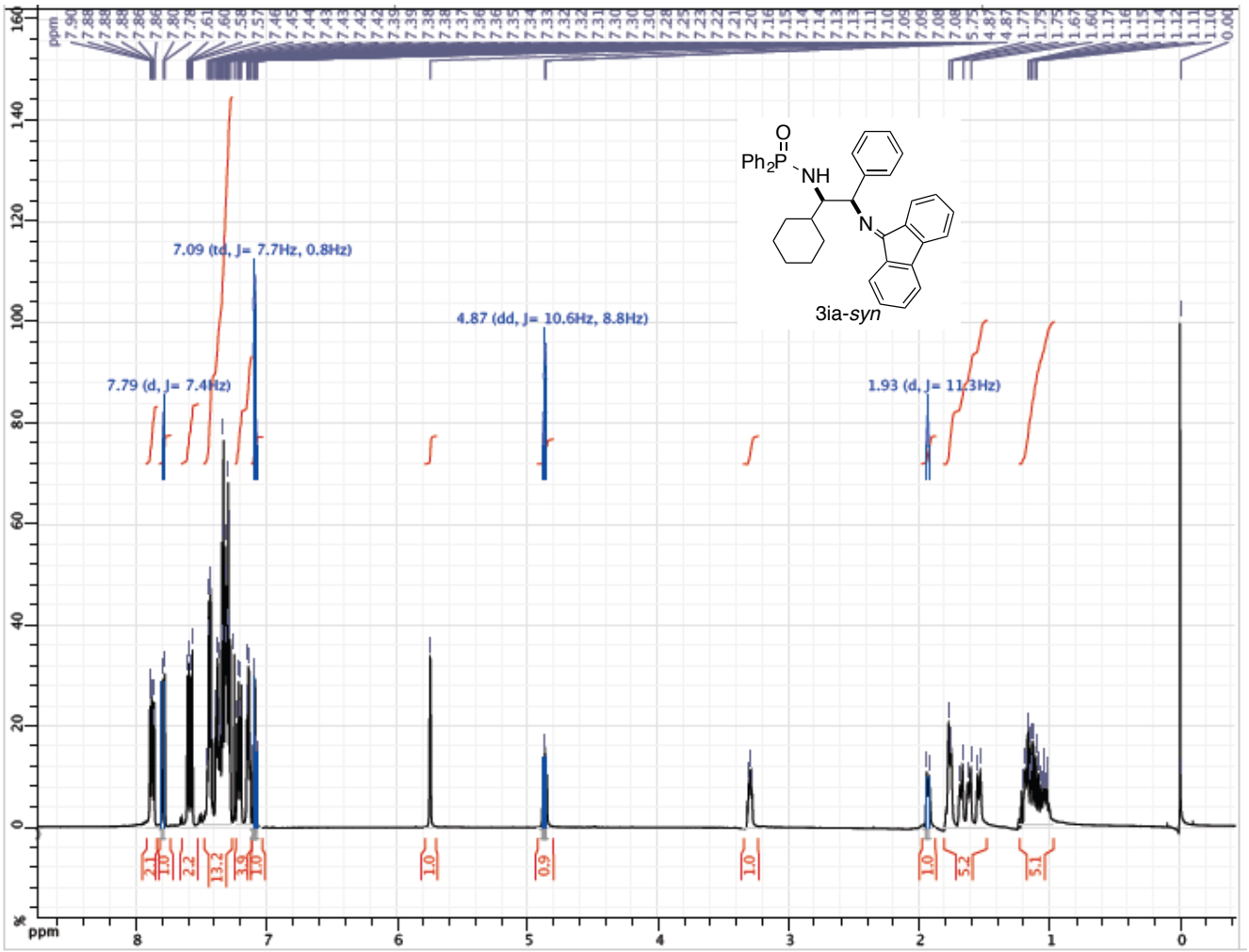

66.82 (d, J= 7.0Hz)
3ga-syn

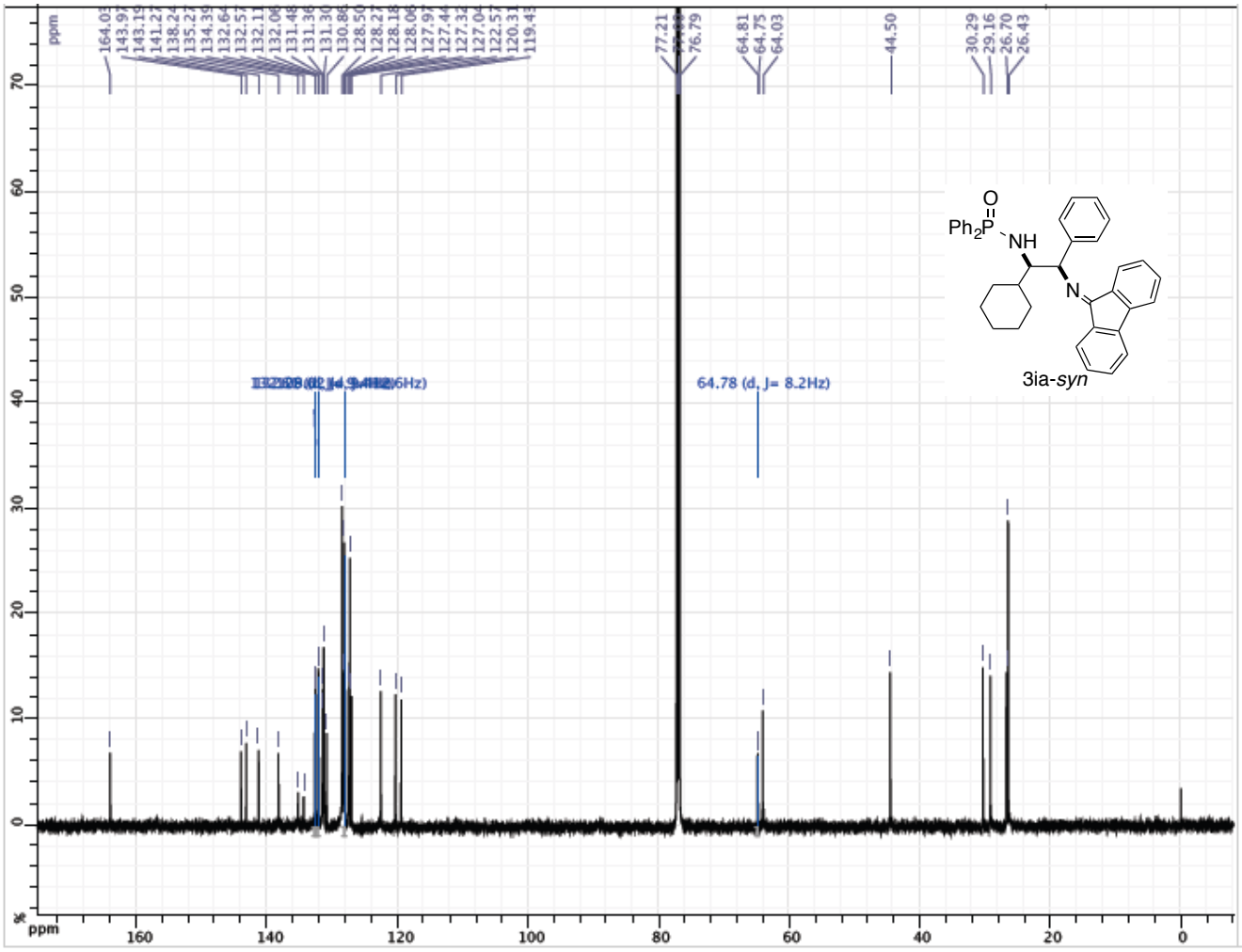

3ga-*syn*
PPM

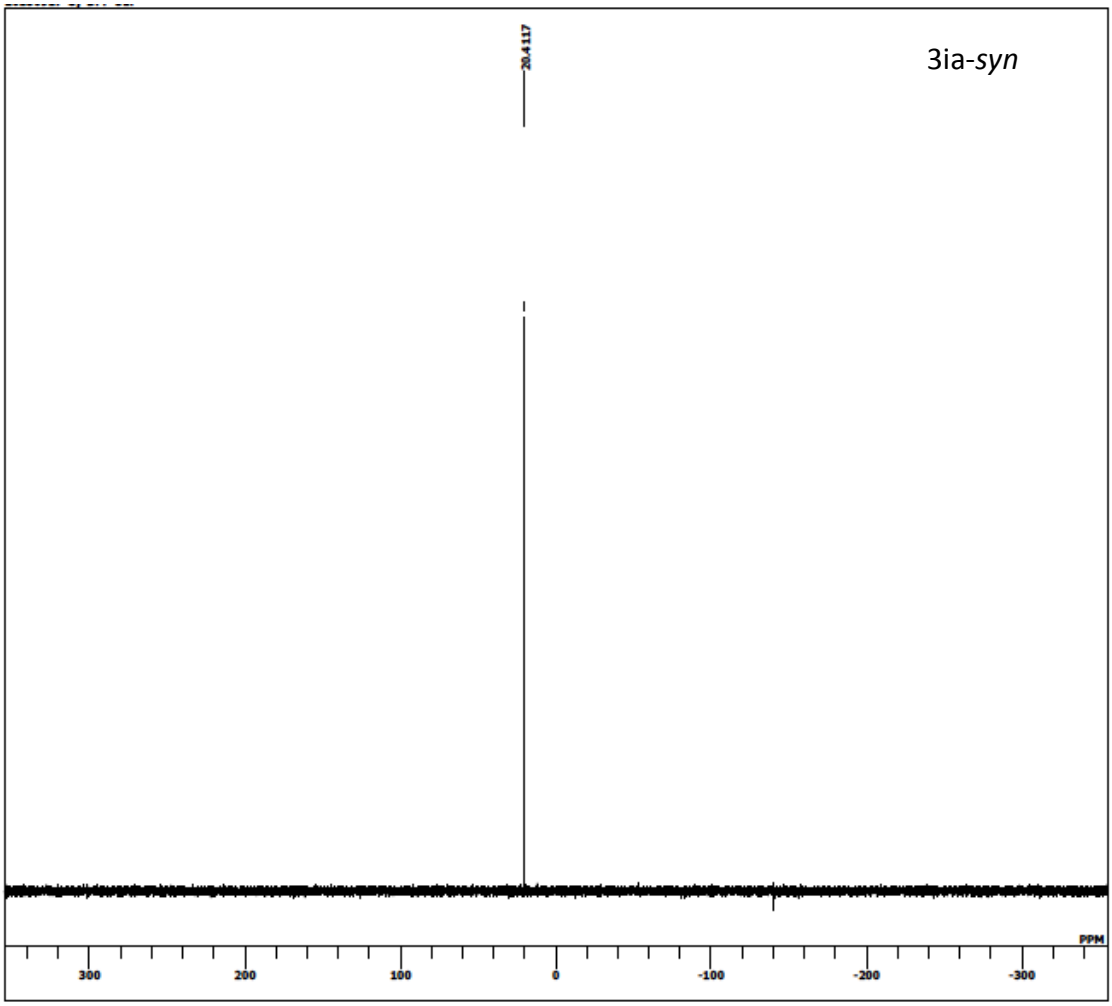

4.57 (ddd, J= 9.6Hz, 7.3Hz, 2.3Hz)
6.93 (t, J= 7.7Hz)
4.96 (dd, J= 10.2Hz, 8.1Hz)
8.27 (d, J= 7.4Hz)
3ha-*syn*
ppm

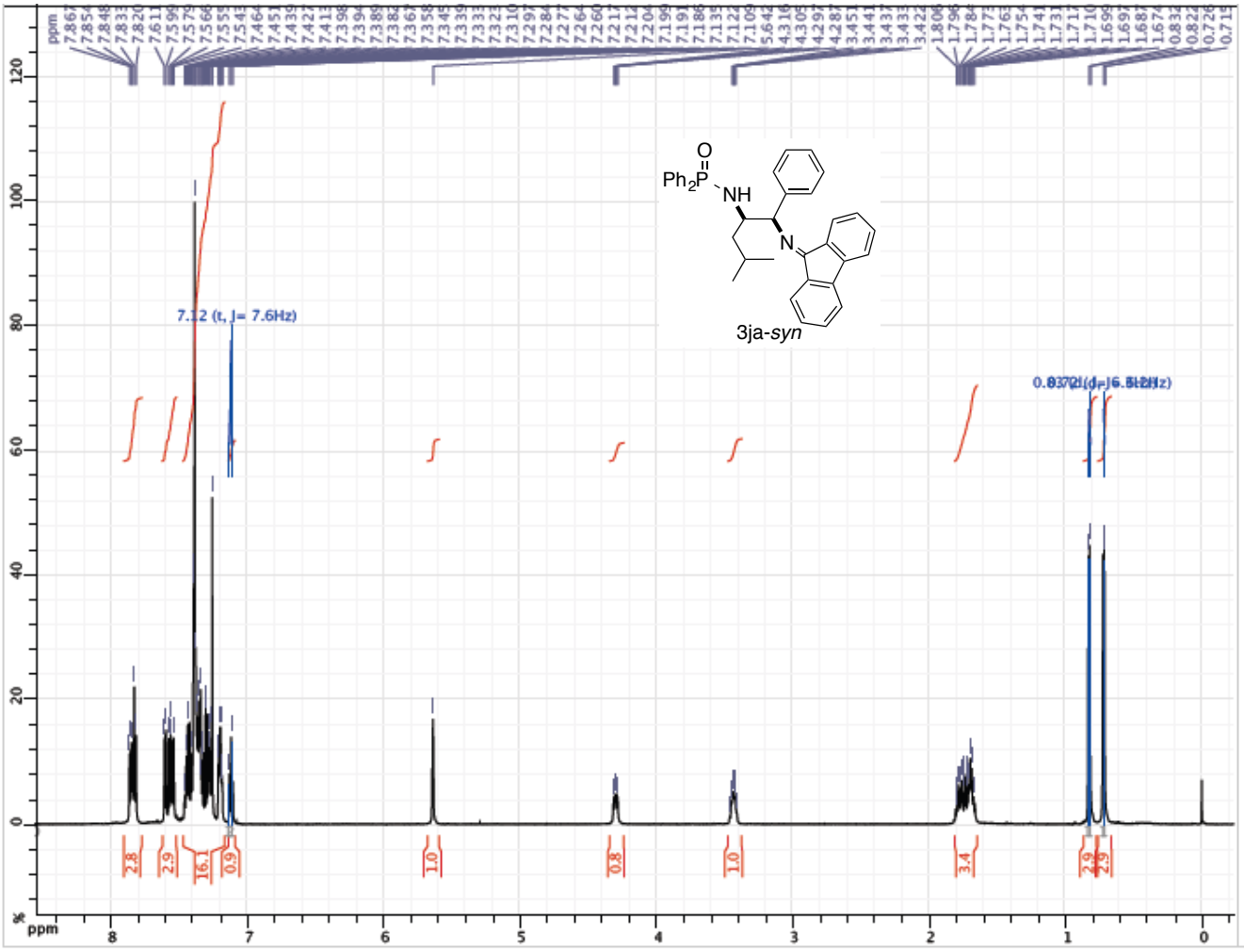

148.51 (d, J= 26
69.72 (d, J= 7.4Hz)
3ha-syn

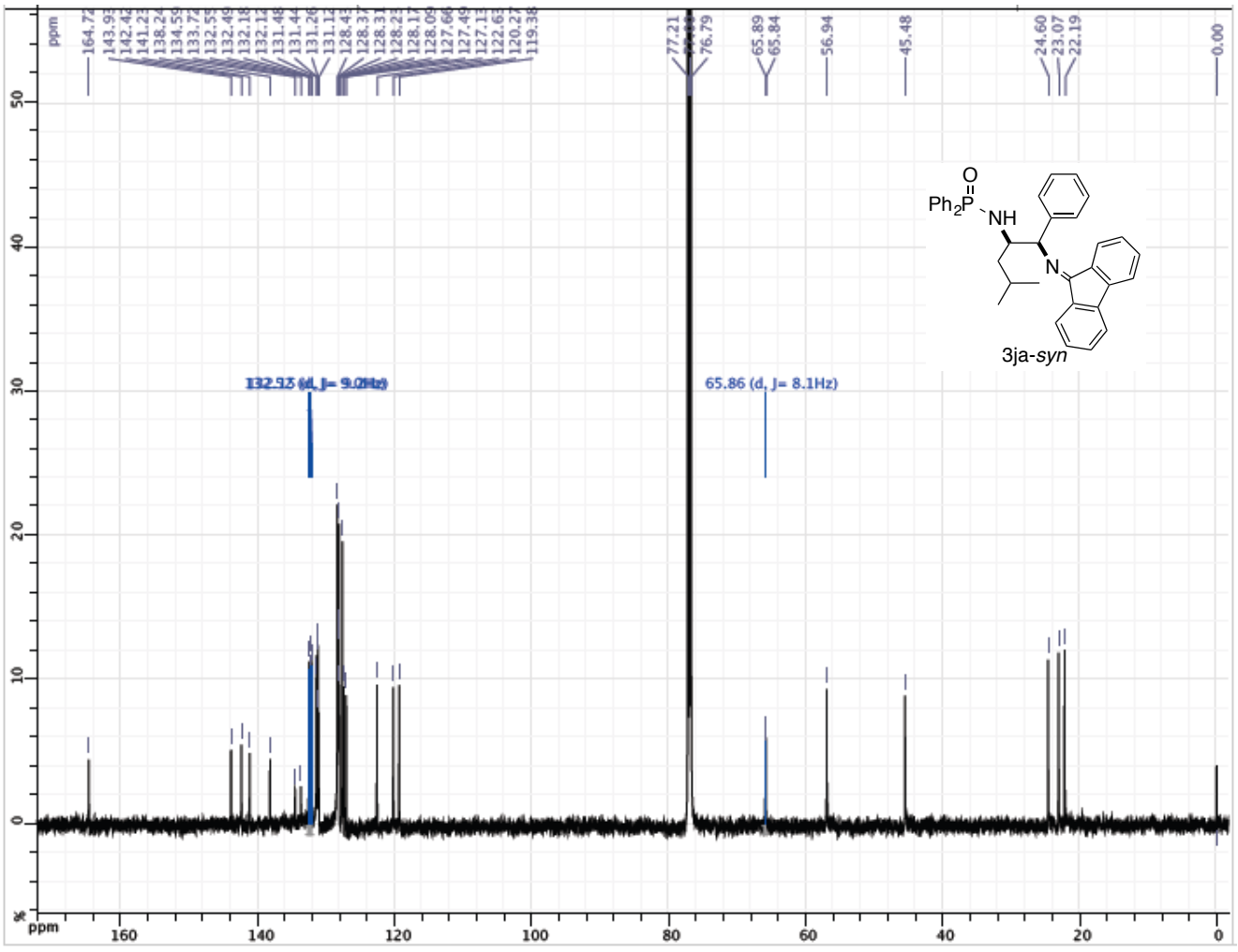

3ha-syn

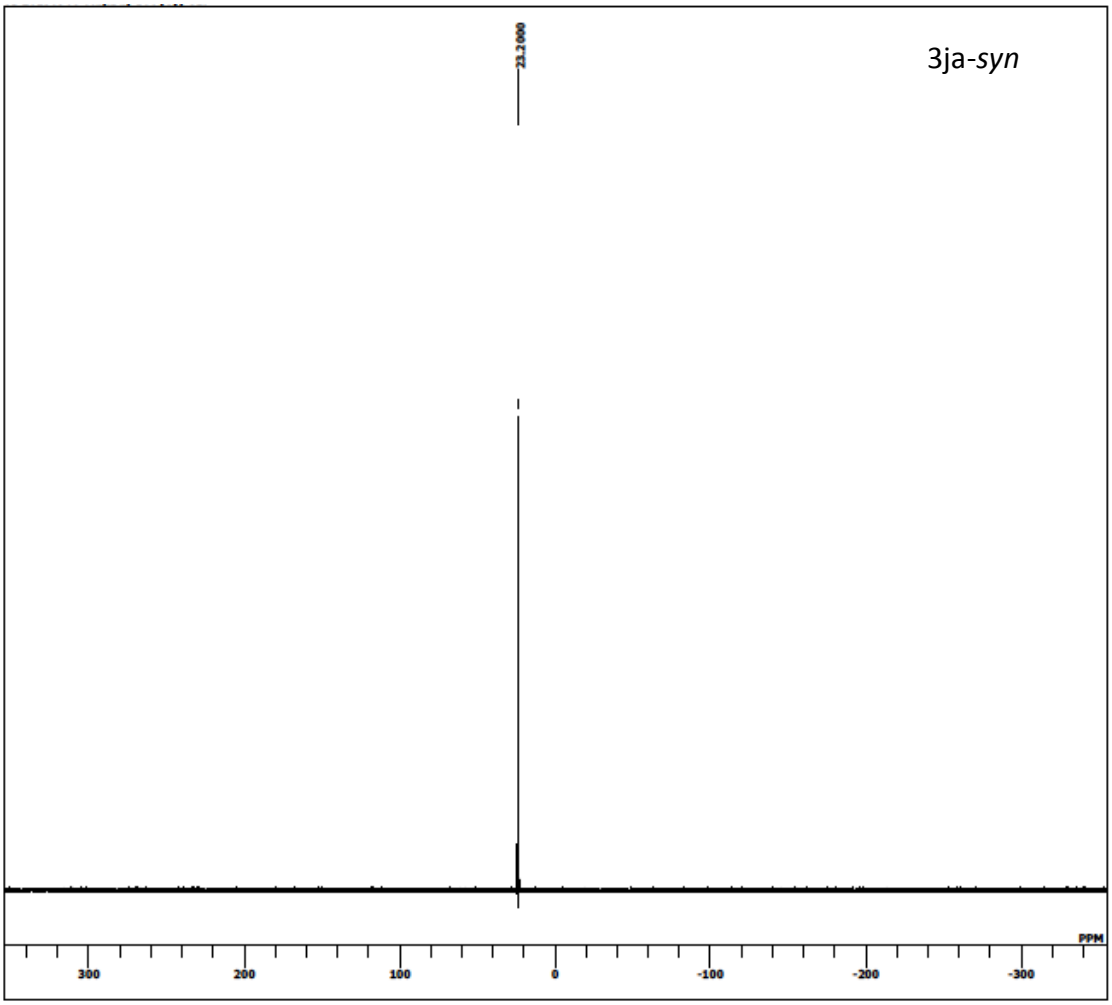

7.09 (td, J= 7.7Hz, 0.8Hz)
4.87 (dd, J= 10.6Hz, 8.8Hz)
7.79 (d, J= 7.4Hz)
1.93 (d, J= 11.3Hz)
3ia-syn

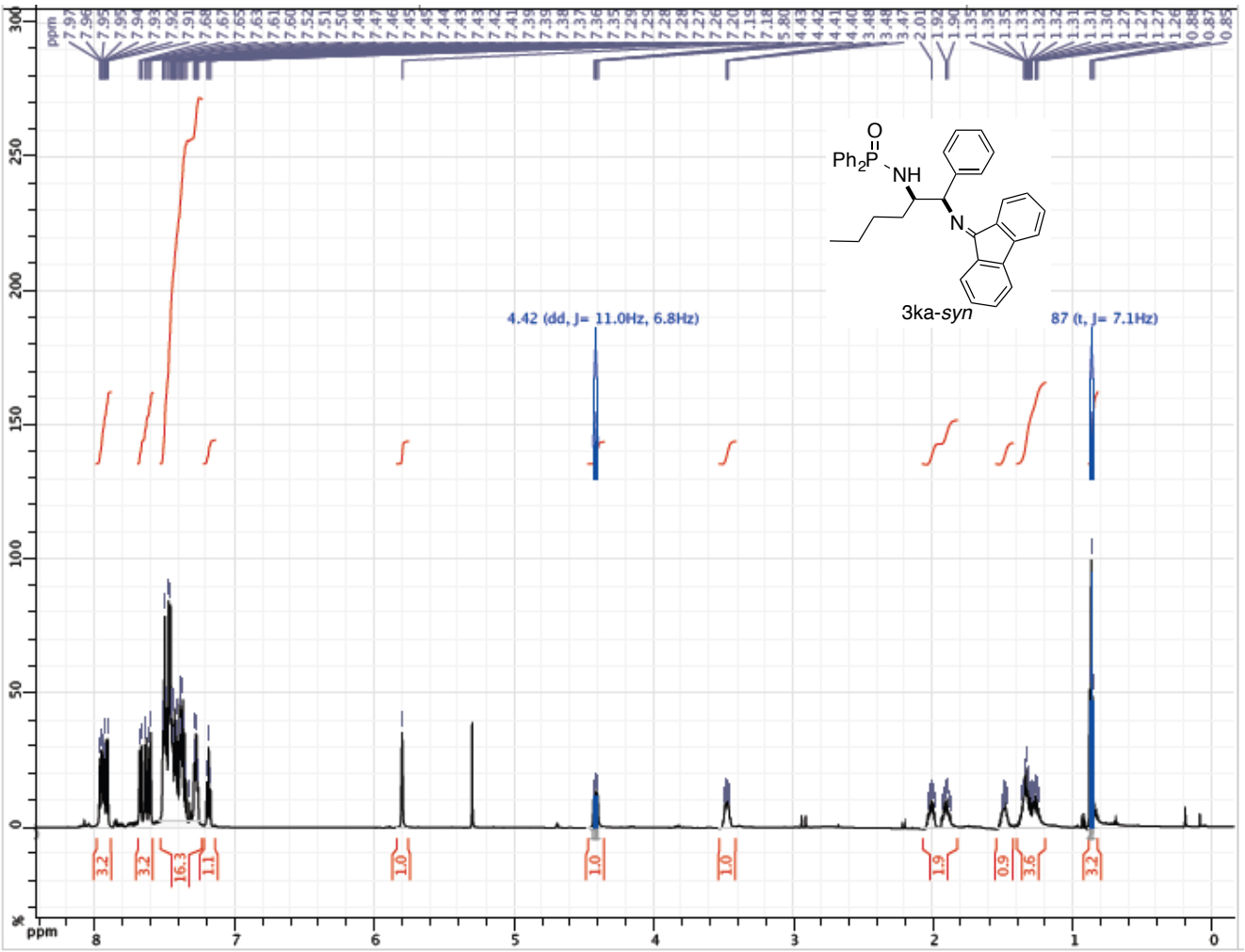

64.78 (d, J= 8.2Hz)
3ia-syn

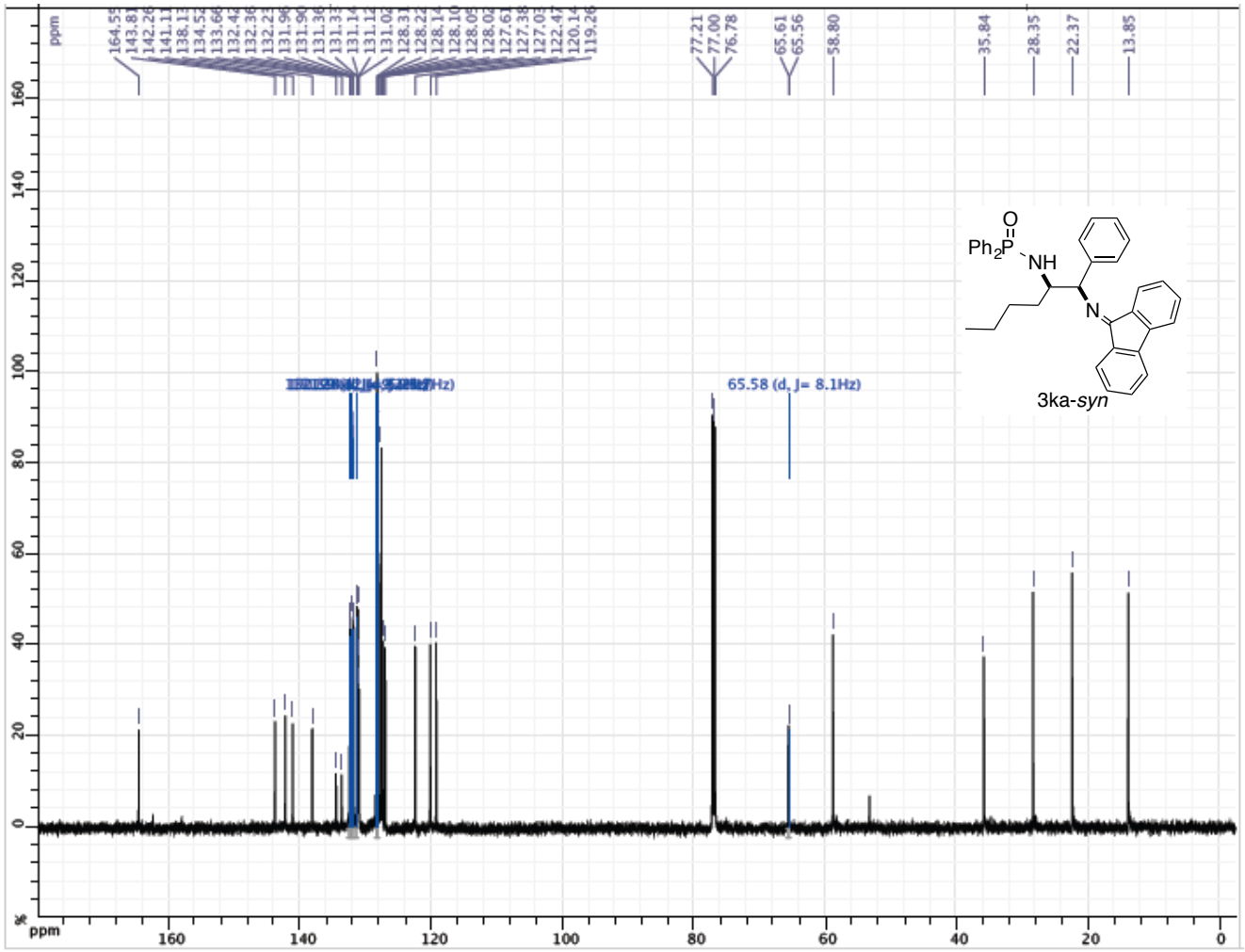

3ia-*syn*
PPM
300
200
100
0
-100
-200
-300

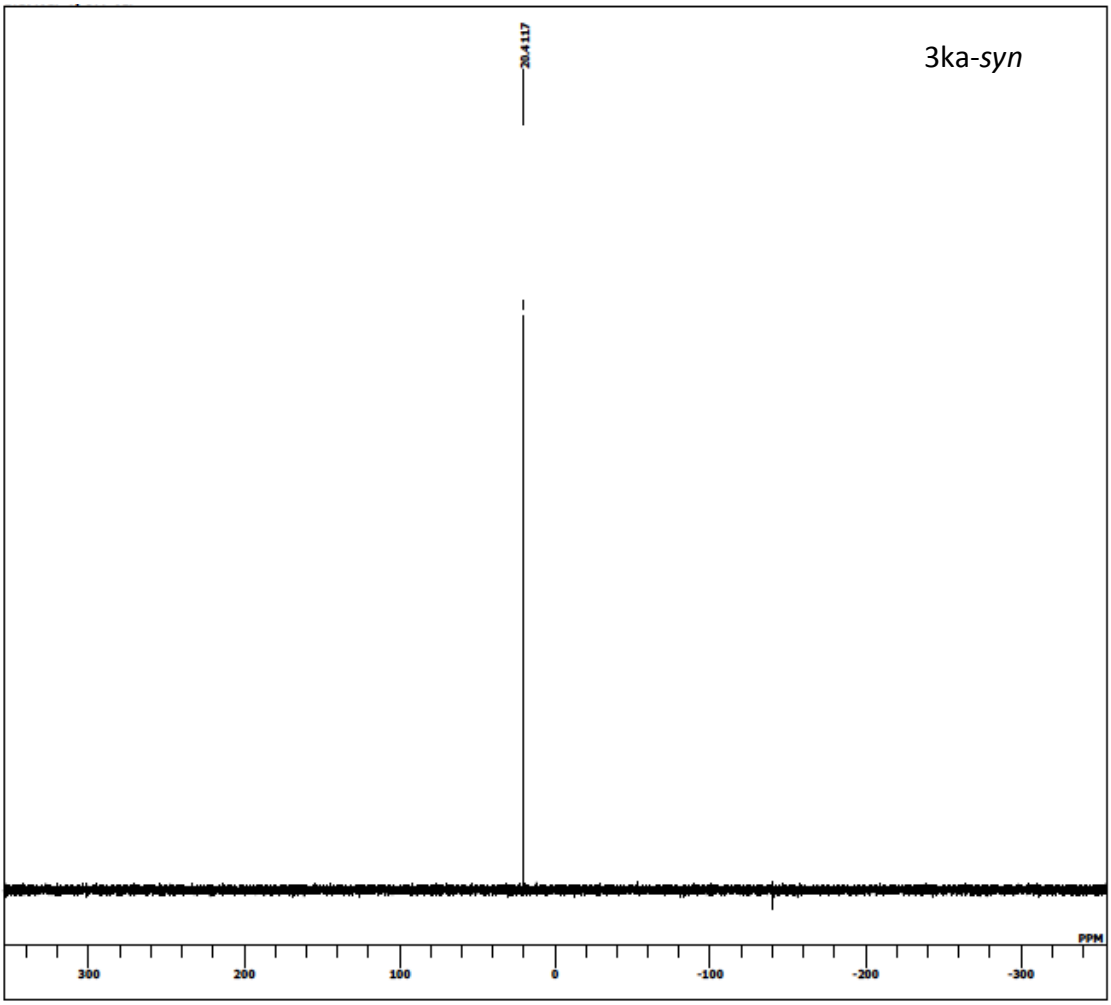

ppm
7.12 (t, J= 7.6Hz)
3ja-*syn*
O
Ph2P
NH
N
ppm
8
7
6
5
4
3
2
1
0

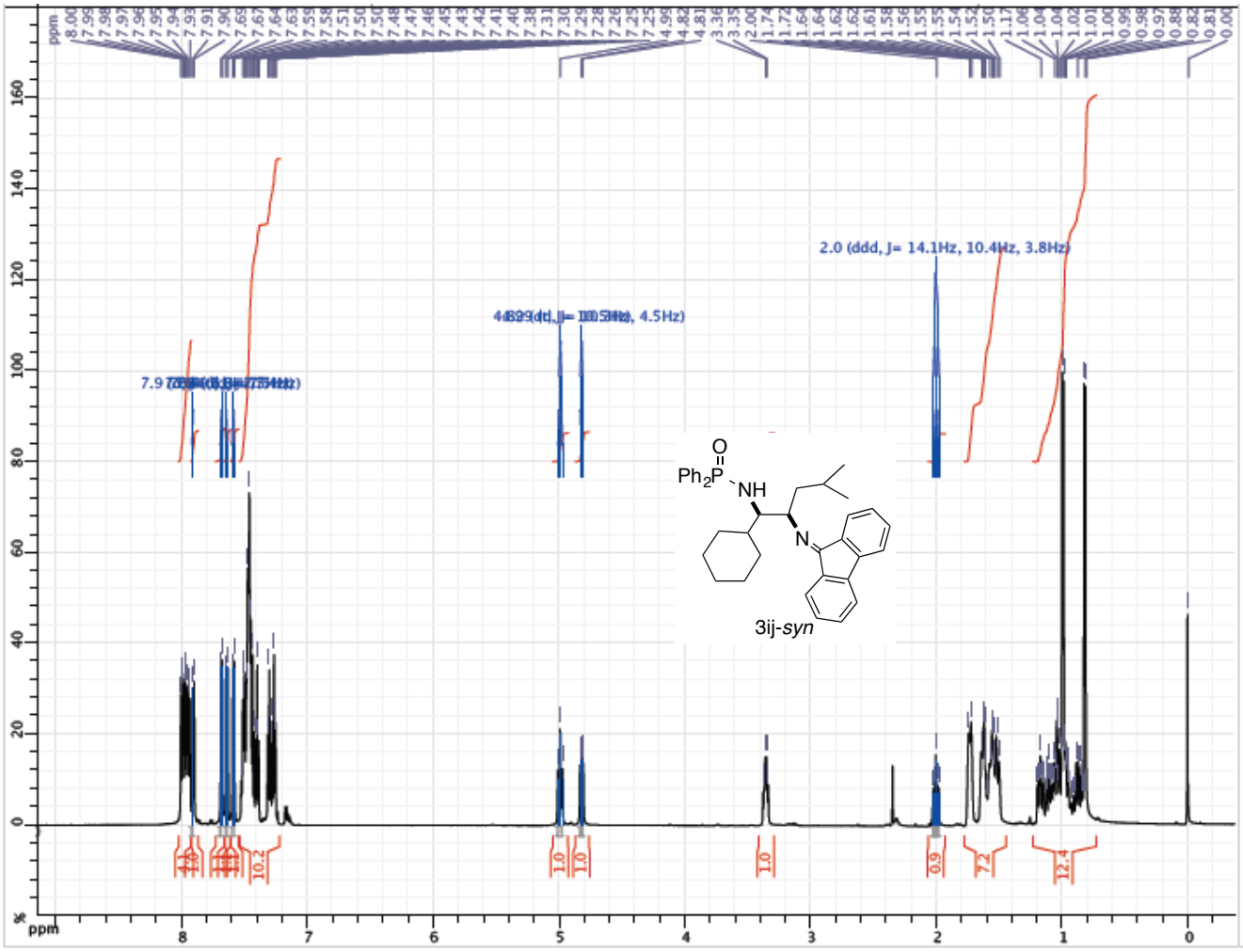

ppm
164.72
143.93
142.42
141.23
138.24
134.59
133.72
132.55
132.49
132.18
132.12
131.48
131.44
131.26
131.12
128.43
128.37
128.31
128.23
128.17
128.09
127.66
127.49
127.13
122.63
120.27
119.38
77.21
76.79
65.89
65.84
56.94
45.48
24.60
23.07
22.19
0.00
132.93 (d, J= 9.0Hz)
65.86 (d, J= 8.1Hz)
O
Ph2P
NH
N
3ja-syn
%
ppm
160
140
120
100
80
60
40
20
0

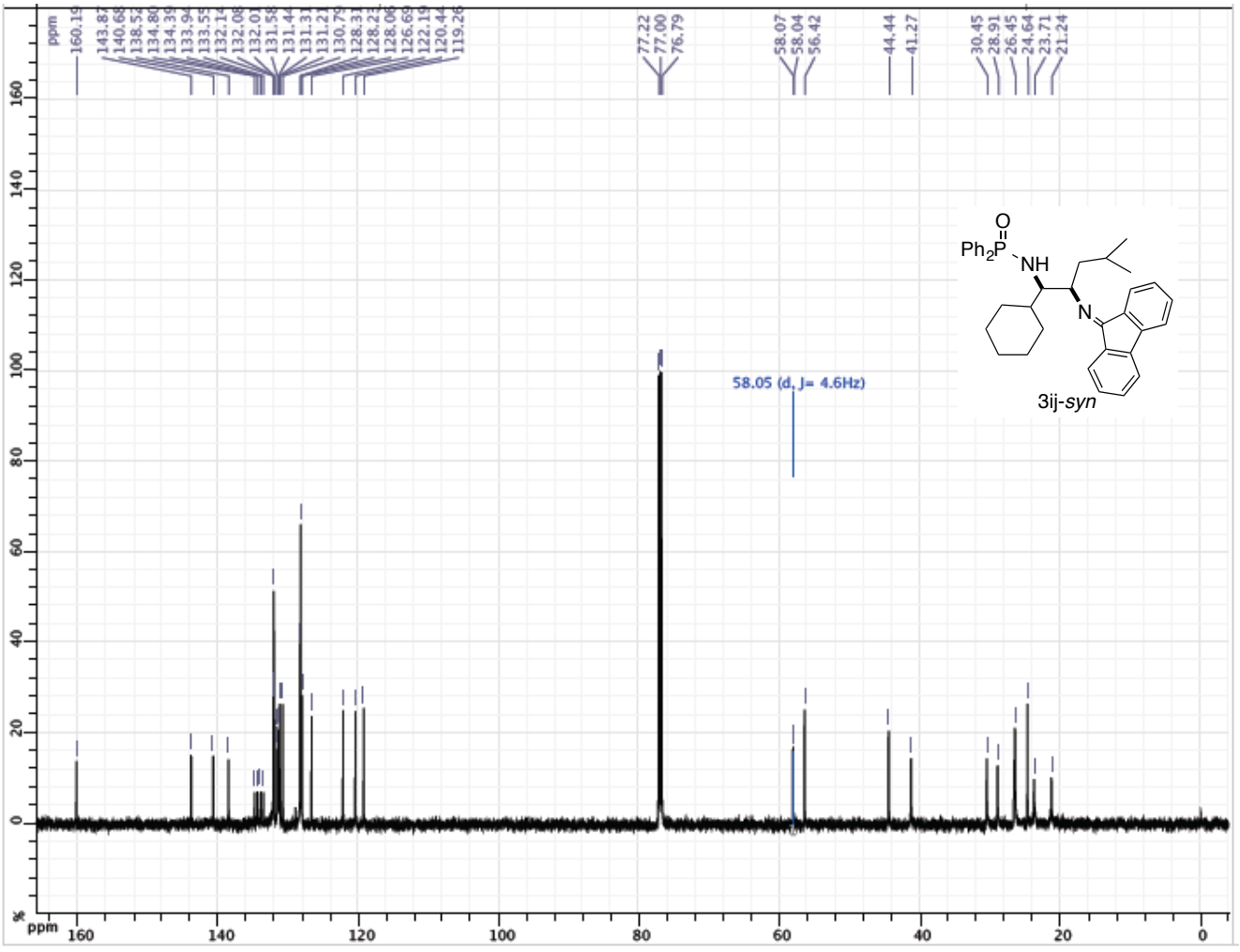

23.1000
3ja-syn
PPM
300
200
100
0
-100
-200
-300

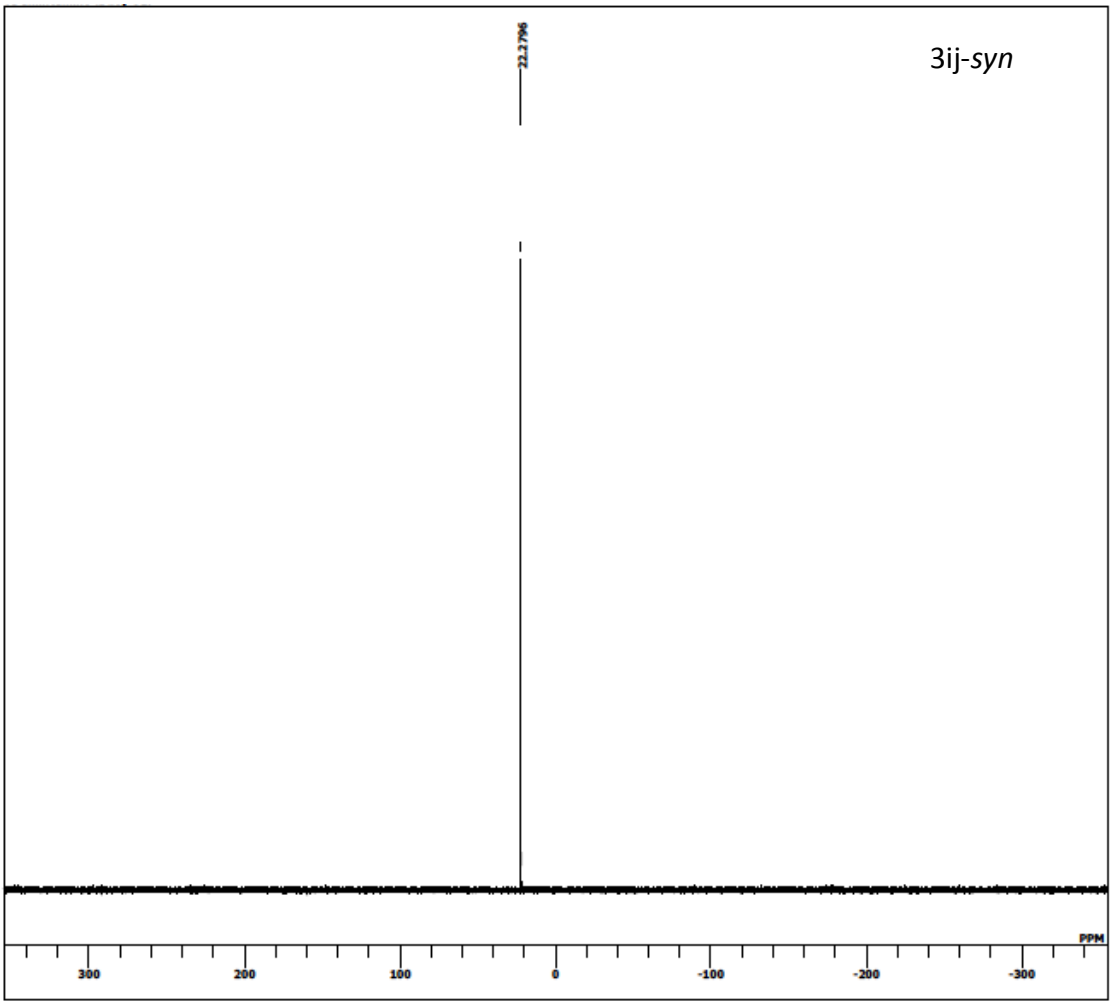

4.42 (dd, J= 11.0Hz, 6.8Hz)
87 (t, J= 7.1Hz)
3ka-syn

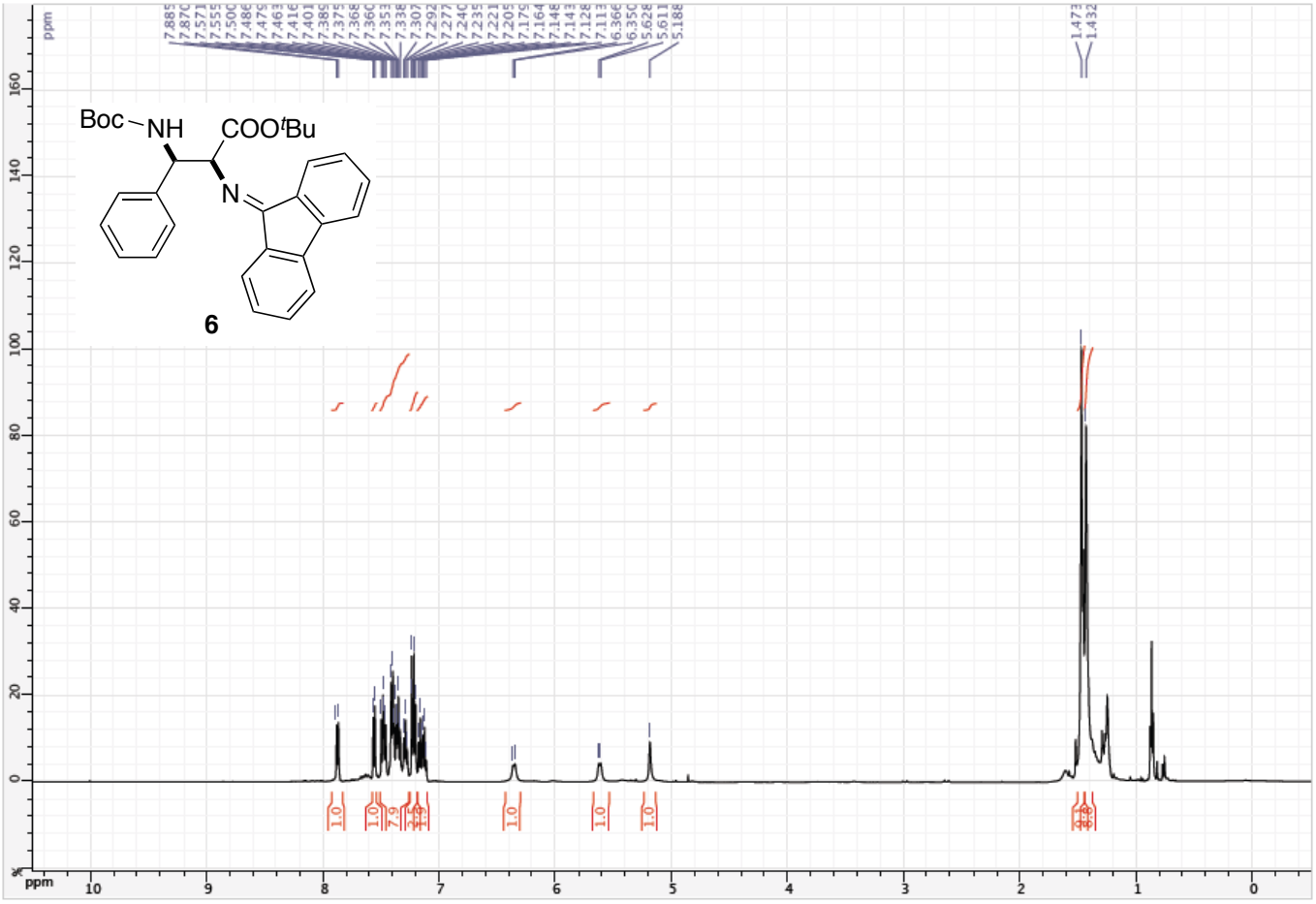

65.58 (d, J= 8.1Hz)
3ka-syn

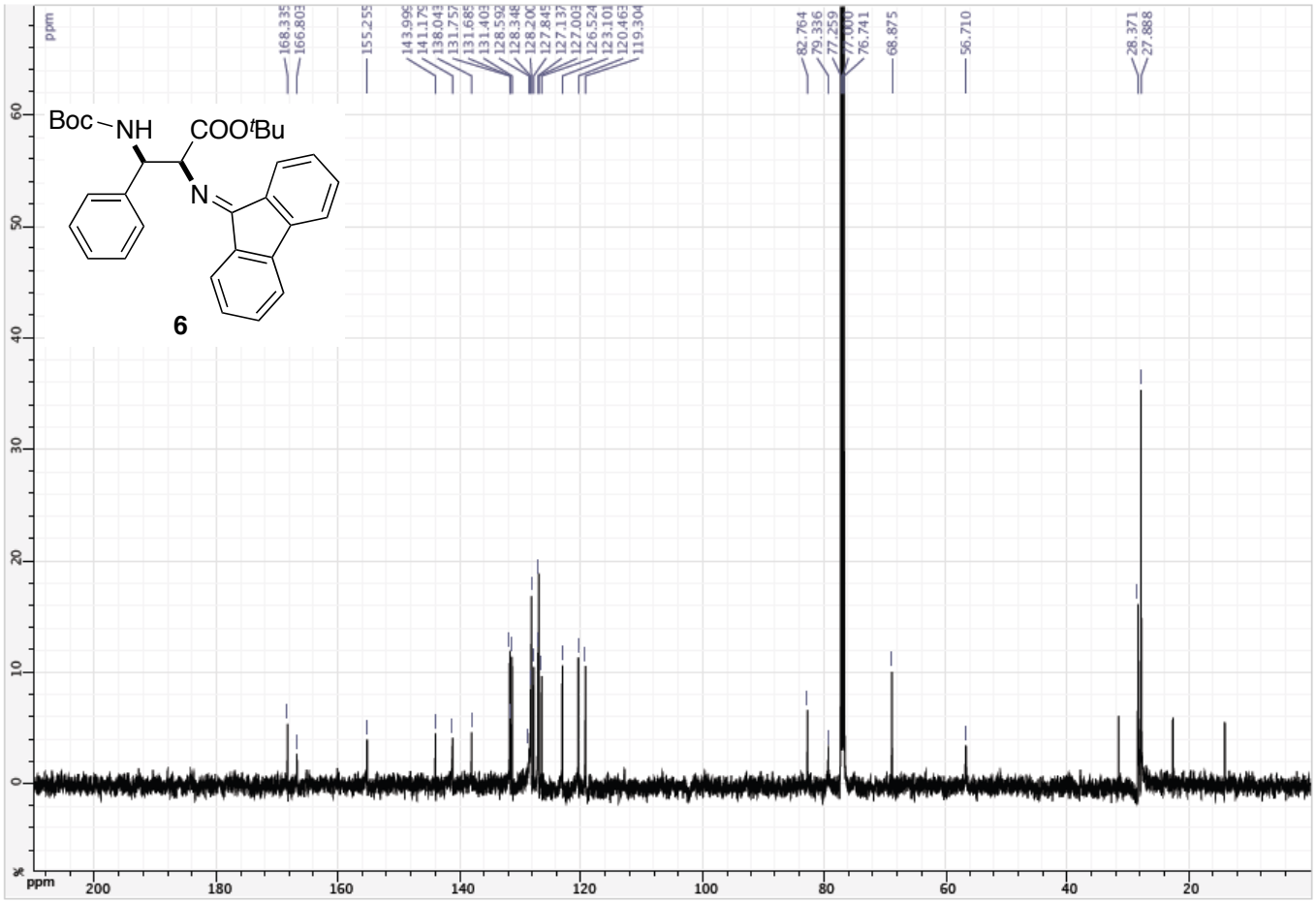

3ka-*syn*
20.4117
PPM
300
200
100
0
-100
-200
-300


2.0 (ddd, J= 14.1Hz, 10.4Hz, 3.8Hz)
4.5Hz)
Ph2P
O
NH
N
3ij-*syn*
ppm

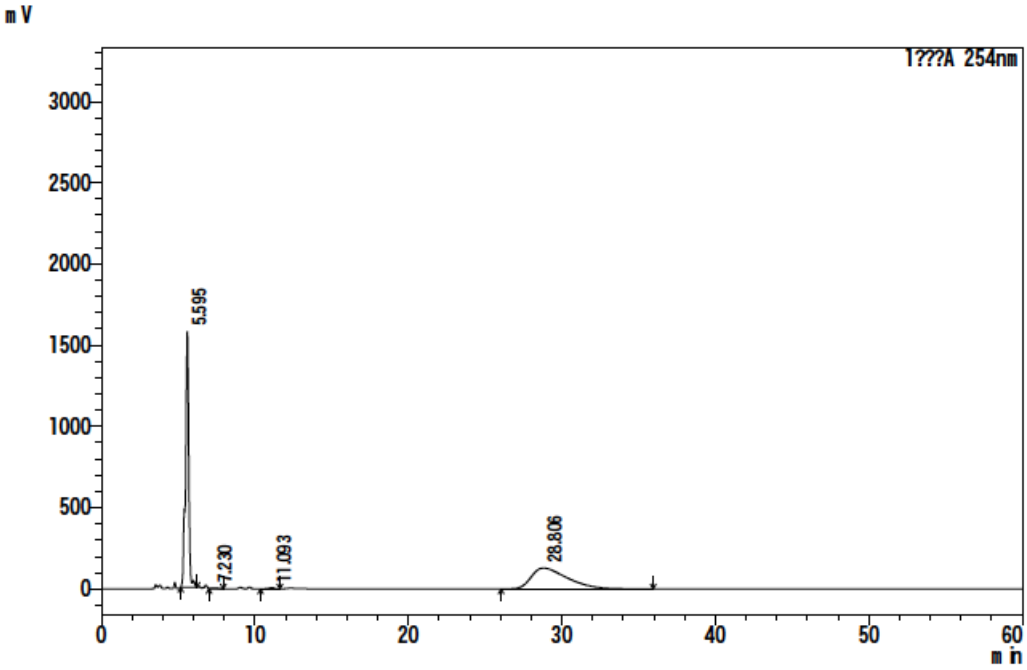

58.05 (d, J= 4.6Hz)
3ij-*syn*


3ij-*syn*


Boc
NH
COO^{t}Bu
N
6


Boc
NH
COO^{t}Bu
N
6

Racemic (6)

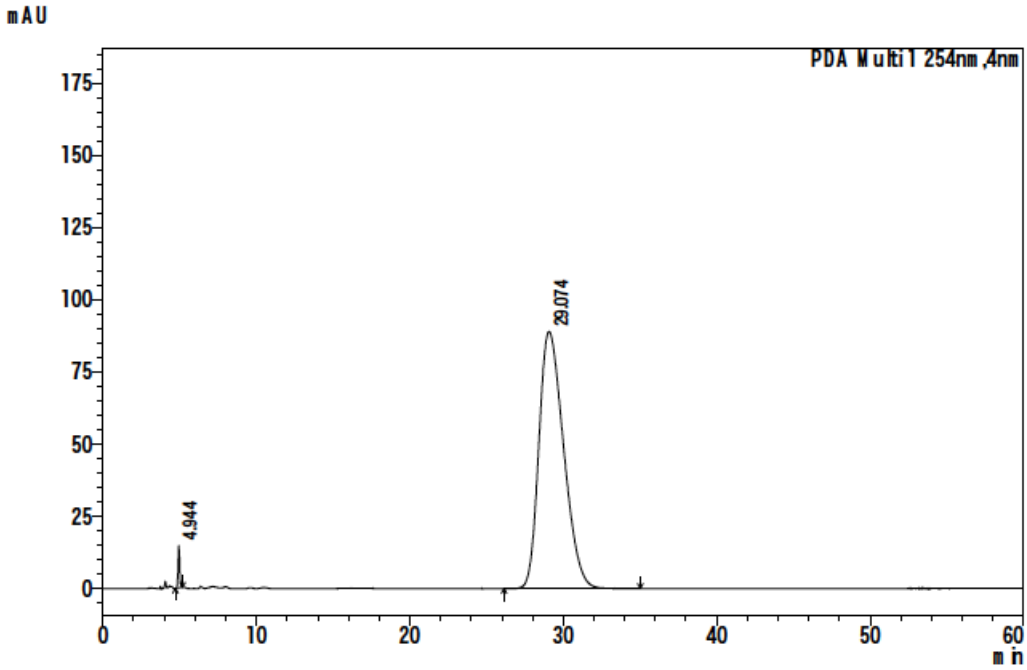


Peak Table

???A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.595	23171576	1575599	51.894
2	7.230	141550	5049	0.317
3	11.093	204580	8534	0.458
4	28.806	21134435	129290	47.331
Total		44652142	1718472	100.000

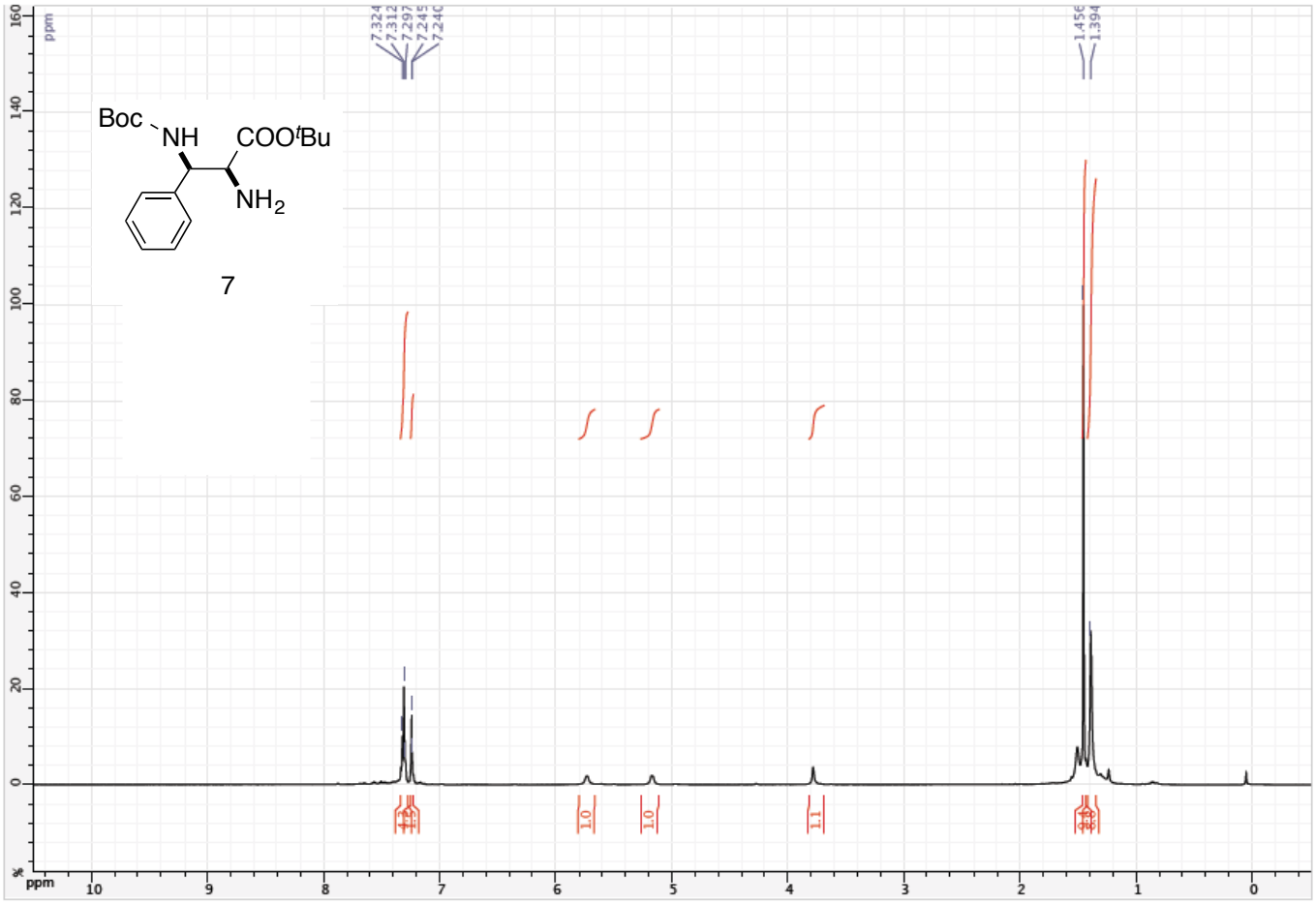
Non-racemic (6)

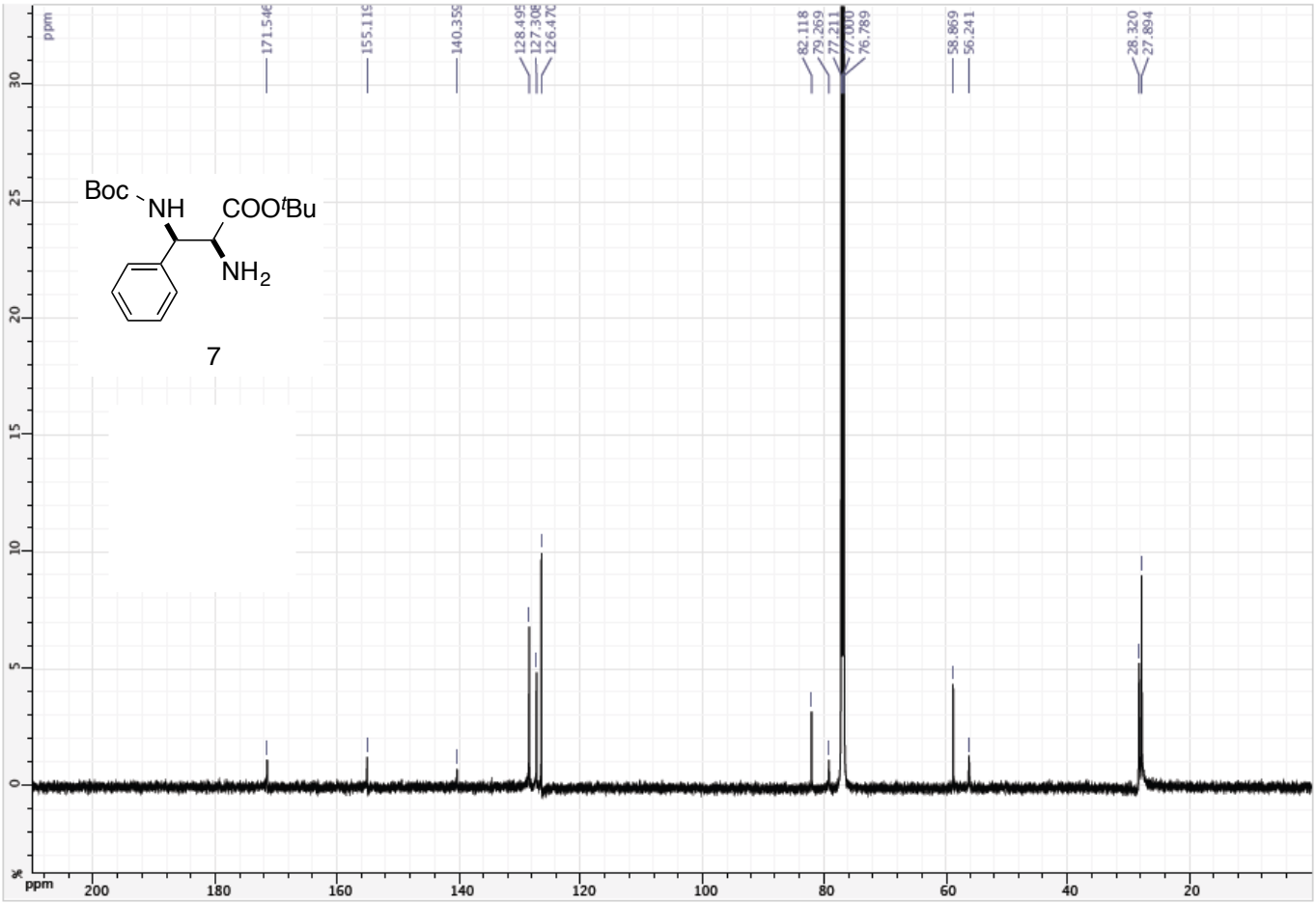


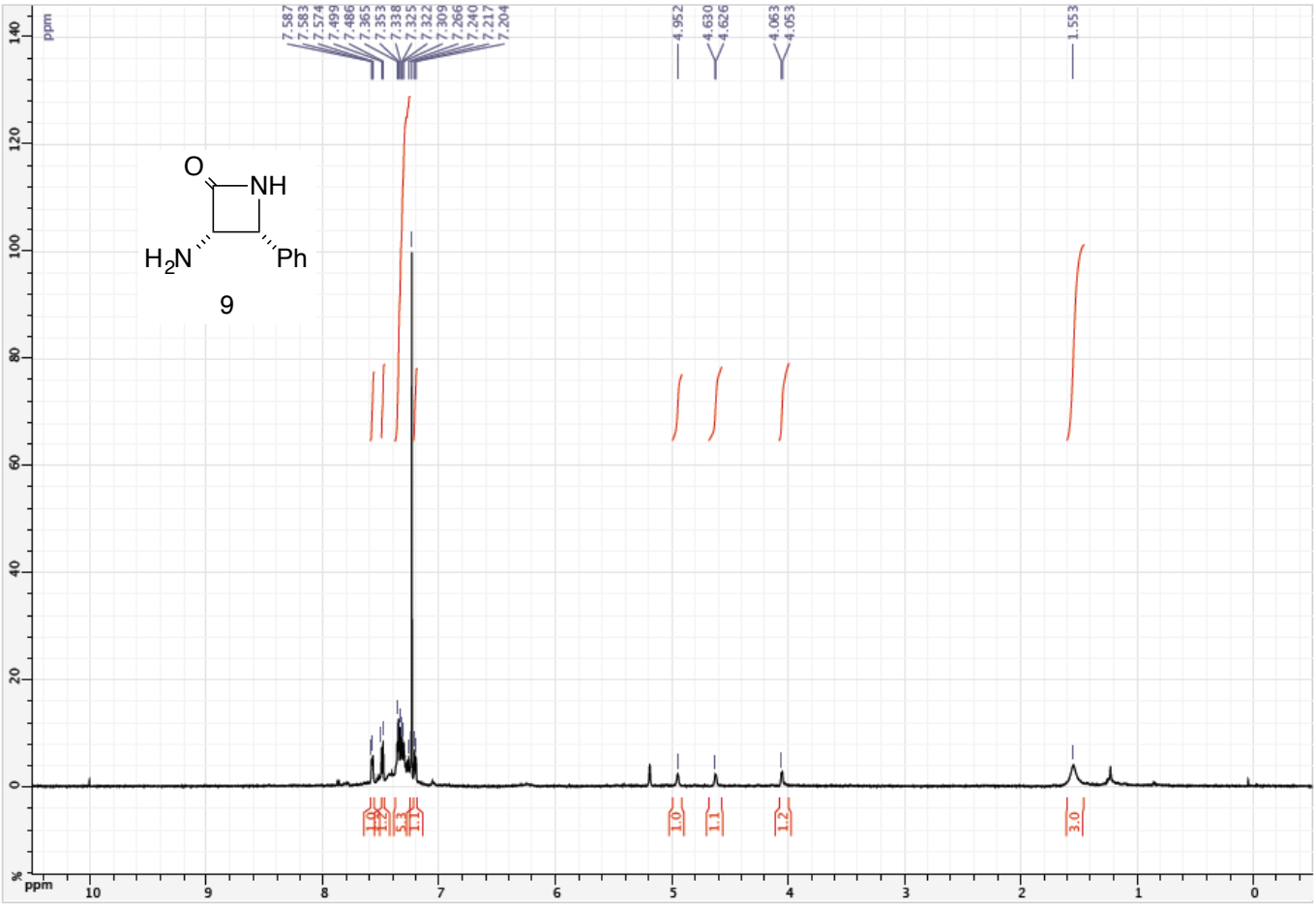
Peak Table

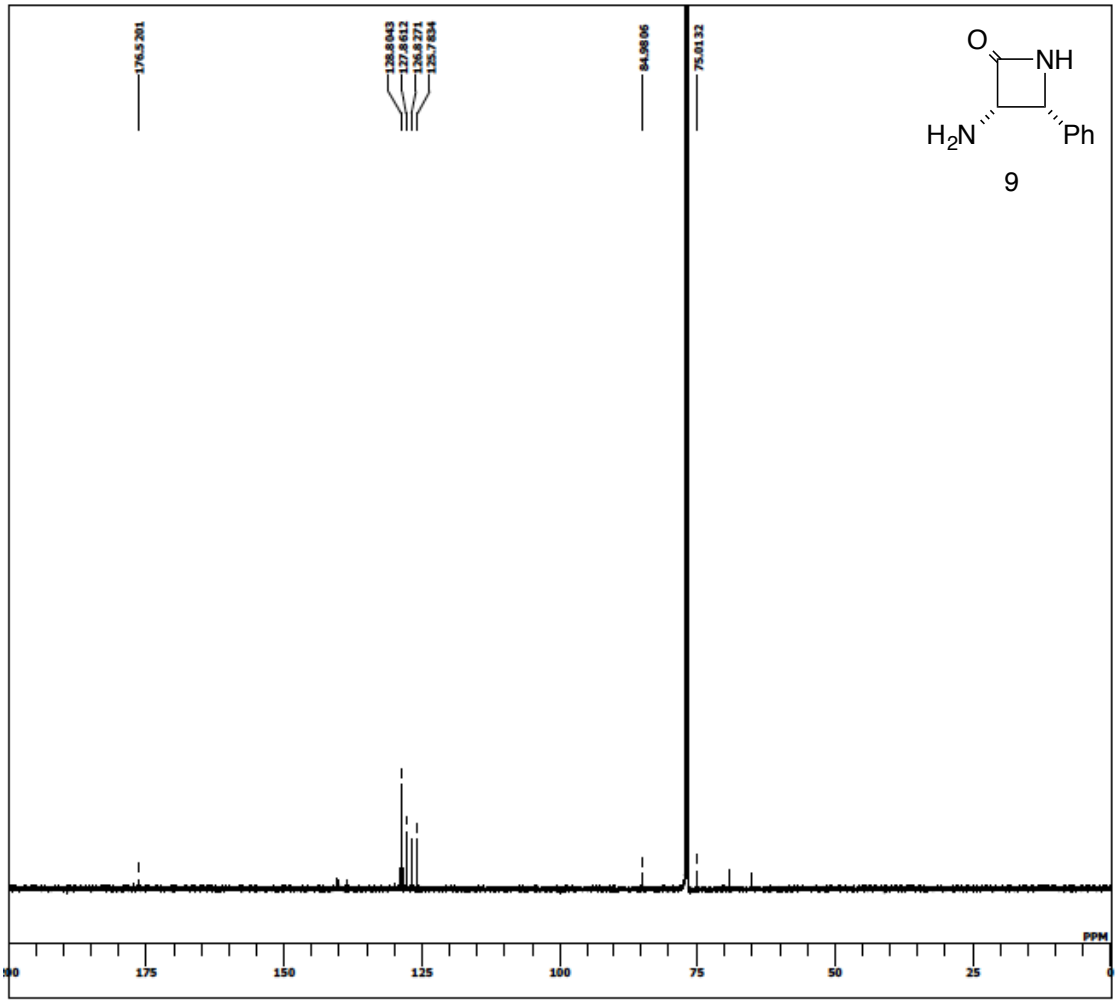
SPD-M20A Ch1 254nm

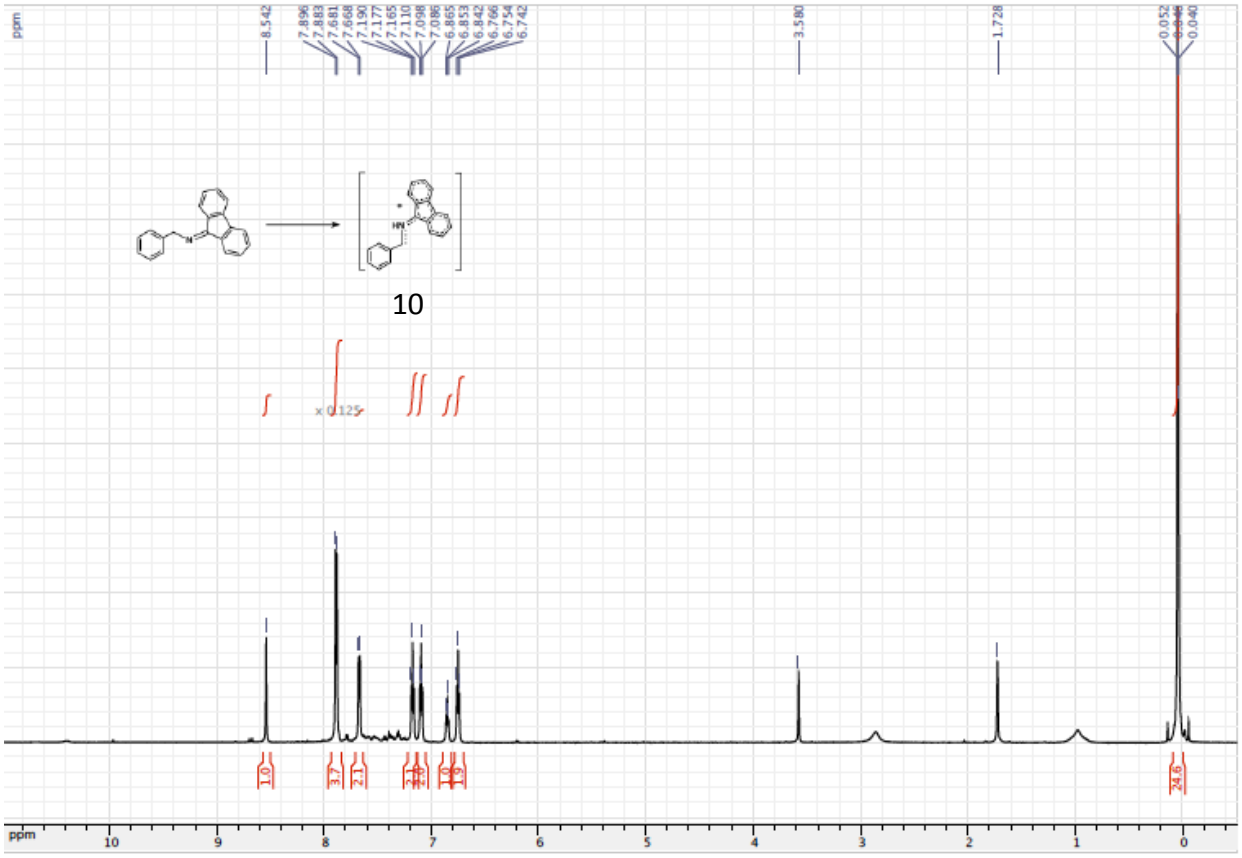
Peak#	Ret. Time	Area	Height	Area%
1	4.944	107804	14482	1.069
2	29.074	9973886	89047	98.931
Total		10081691	103530	100.000


Boc
NH
COO^{t}Bu
NH$_2$
7
ppm

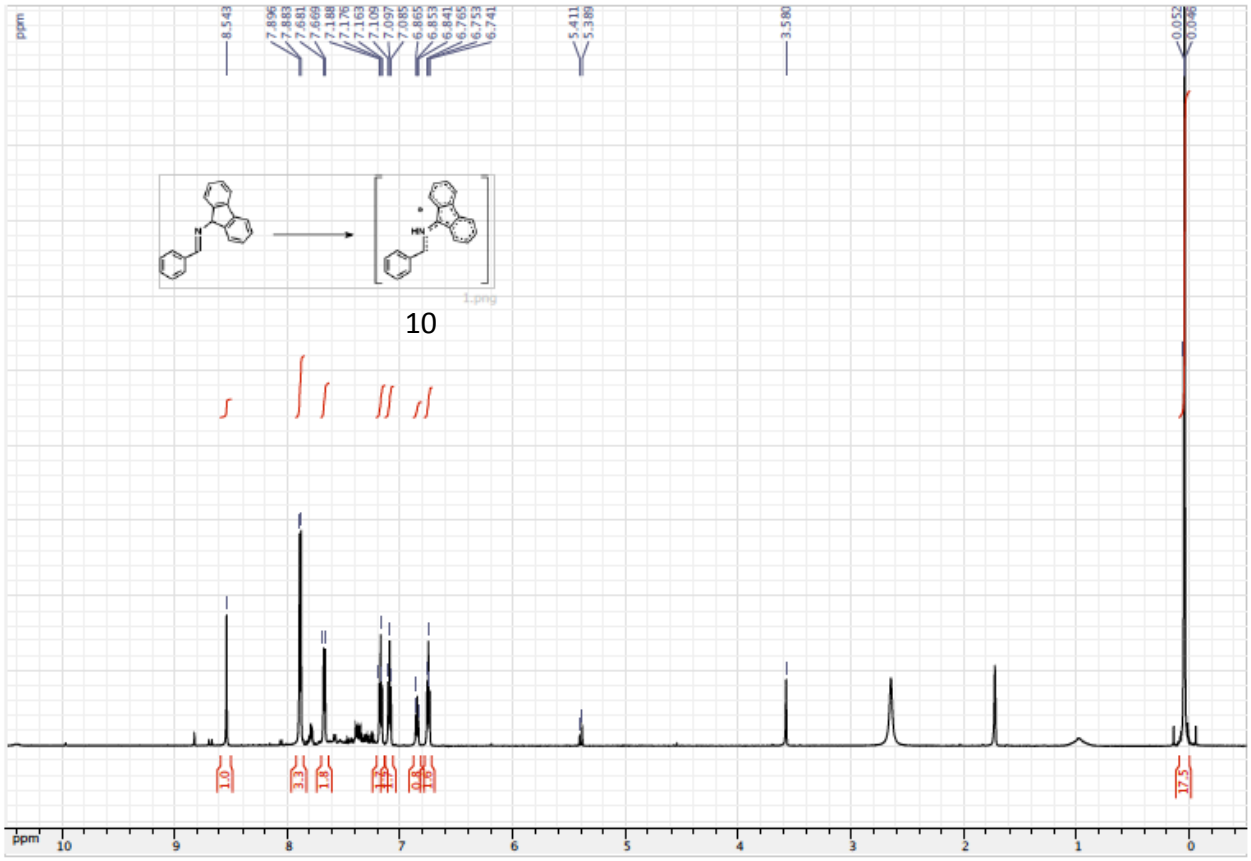

Boc
NH
COO^{t}Bu
NH$_2$
7
ppm


7.587
7.583
7.574
7.499
7.486
7.365
7.353
7.338
7.325
7.322
7.309
7.266
7.240
7.217
7.204
4.952
4.630
4.626
4.063
4.053
1.553
O
NH
H2N
Ph
9
ppm

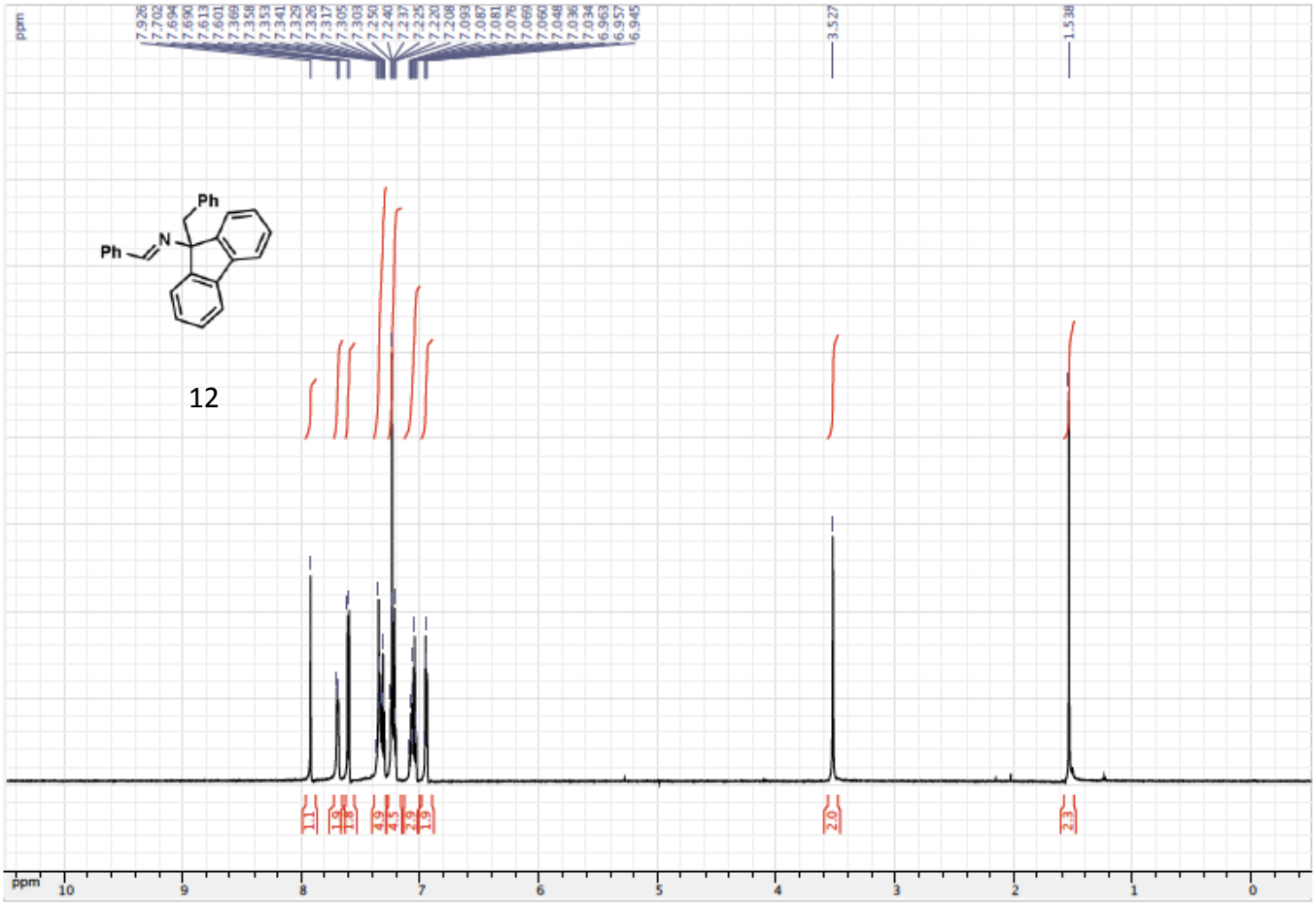

176.5201
128.8043
127.8612
126.9271
125.7834
84.9806
75.0132
O
NH
H2N
Ph
9
PPM

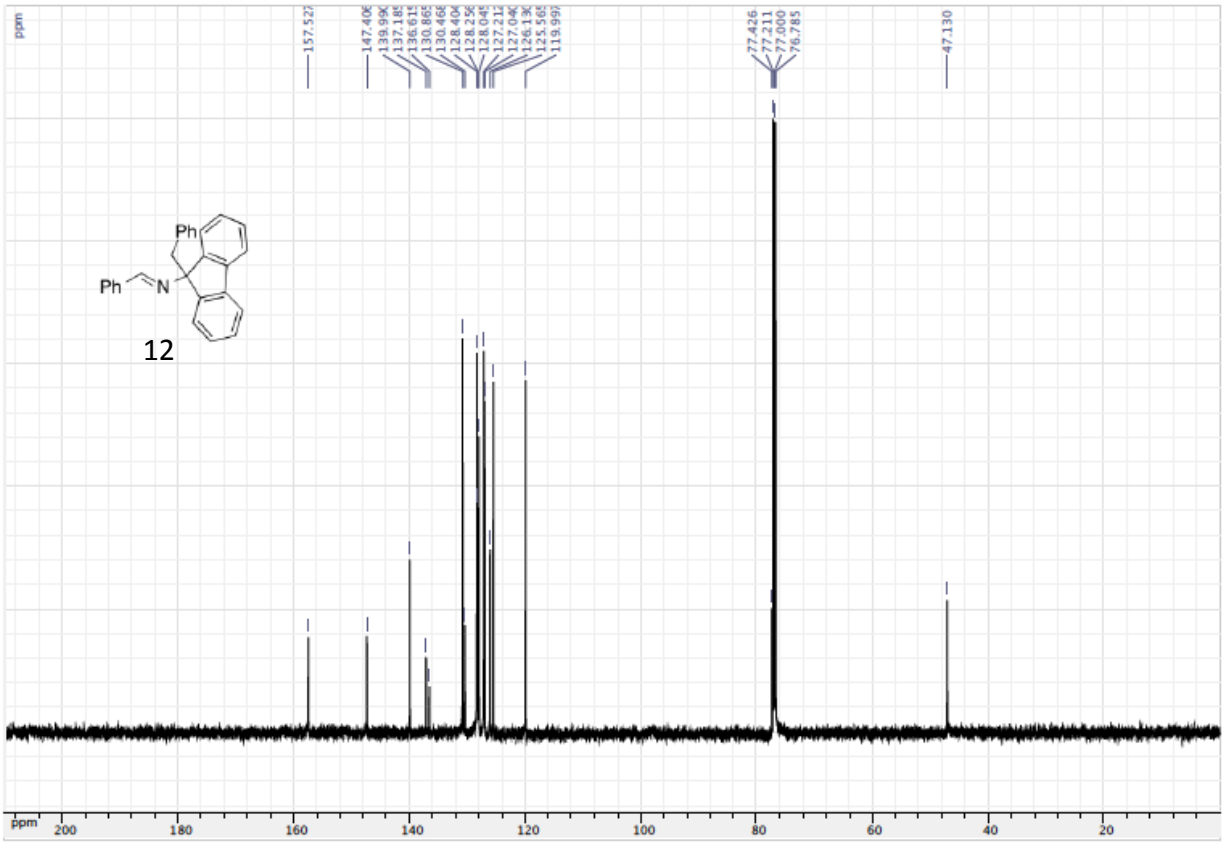


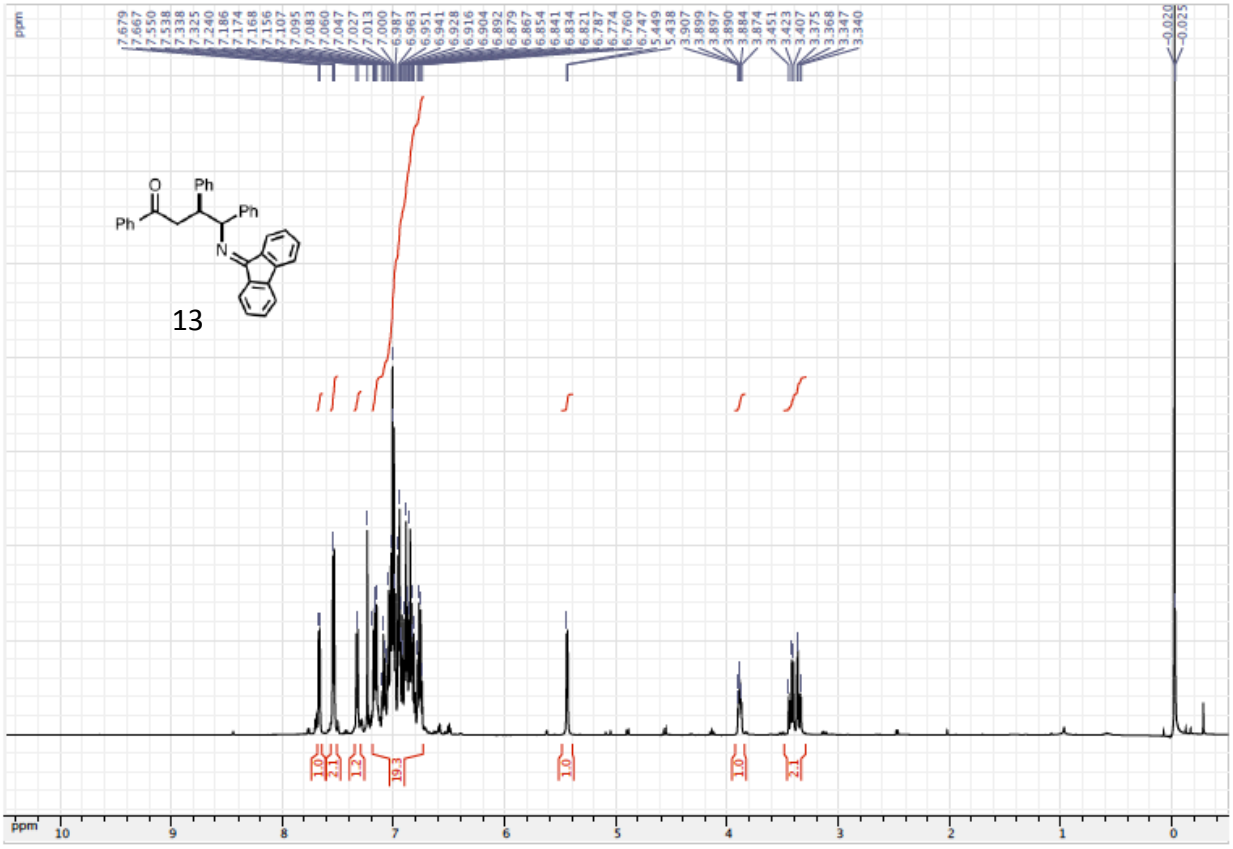
10

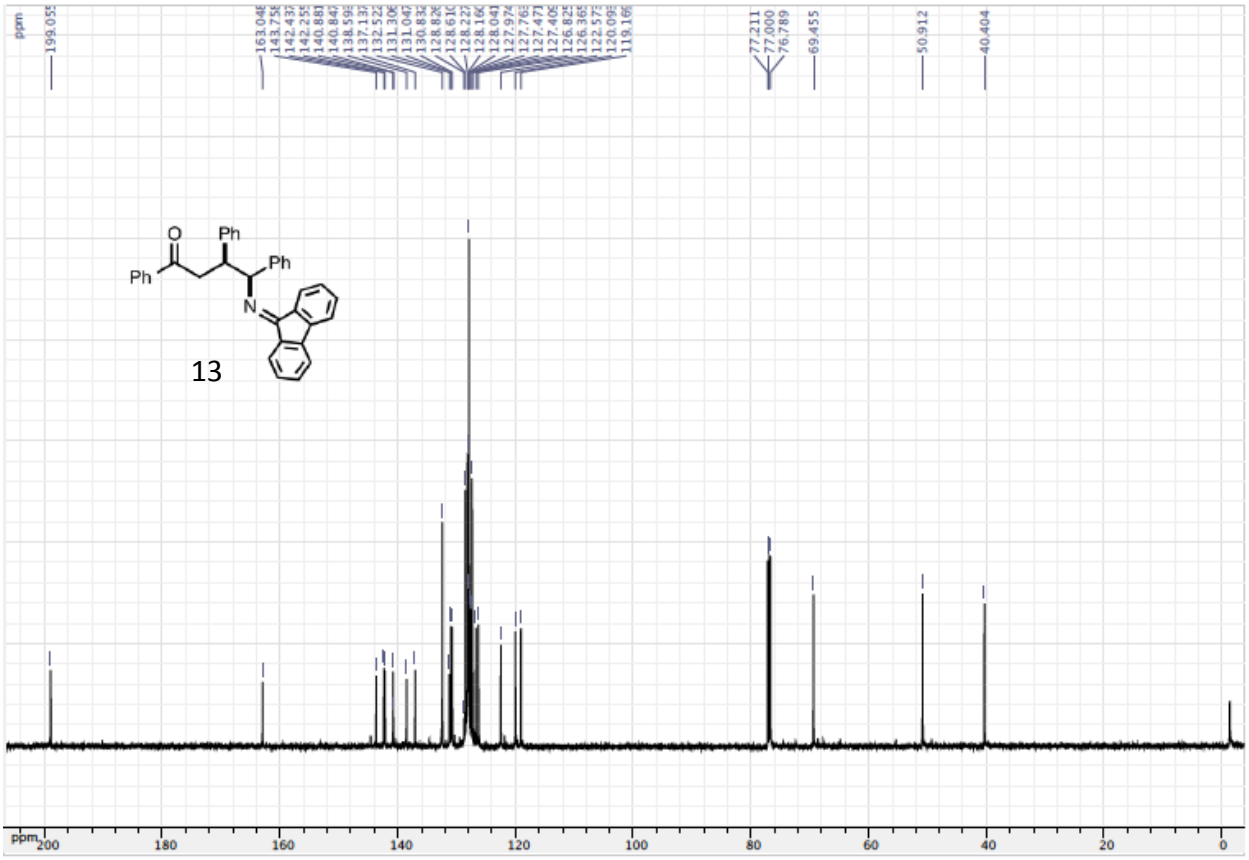


10


Ph
Ph
N
12


Ph
Ph
N
12


O
Ph
Ph
Ph
N
13


O
Ph
Ph
Ph
N
13