Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For the article entitled

Stereo-selective synthesis of complex dienes and eneynes by sequential hydroarylation and olefinic C−H functionalization

Yuhang Zhu, Xiaoli Li, Cheng Zhang, Xiuying Liu, Linzhi Huang, Yongbo Zhang,

Chao Shen,* Liyuan Ding, Guofu Zhong,* and Jian Zhang*

shenchaozju@zjsru.edu.cn; gzhong@eitech.edu.cn; zhangjian@hznu.edu.cn

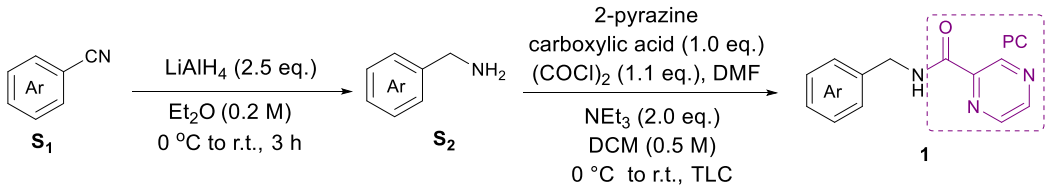
Table of Contents

1. General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent), and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartets), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). $Pd(OAc)_2$ and $[Rh(cod)Cl]_2$ were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification. The corresponding alkenes were prepared from the bromides by the reported methods.

2. General Procedure for Substrate Synthesis

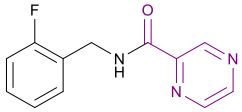
2.1 General Procedure A for Substrate Synthesis



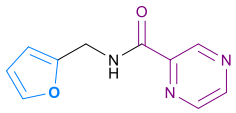
General Procedure for Benzonitrile Reduction[1]: To a solution of substituted benzonitrile **(S_1)** in Et_2O (0.2 M) was added $LiAlH_4$ (2.5 equiv, 2.5 M in Et_2O) dropwisely over 30 min at 0°C and stirred for 3 h at room temperature. After the reaction was completed (monitored by TLC), NaOH (2 N, aq.) was added slowly until a clear solution was obtained. The Et_2O layer was separated and the aqueous phase was extracted with Et_2O (20 mL × 3). The organic layer was combined and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the resulting benzylamine **(S_2)** was used in the next step without further purification.

General Procedure for Amide Preparation[2]. A 50 mL round-bottomed flask immersed in a 0 °C bath (ice and water) was charged with 2-pyrazinecarboxylic acid (5.0 mmol, 1.0 equiv) and CH_2Cl_2 (10 mL). The stirred suspension was added oxalyl chloride (5.50 mmol, 1.10 equiv, 2.0 mol/L in DCM) dropwisely over a 15 minute period followed by the addition of DMF (0.1 mL, catalytic amount) in one portion, producing a yellow solution with gas evolution. The mixture was kept in the cooling bath for 1 h and then allowed to warm to room temperature. After gas evolution ceased, the mixture was again cooled to 0°C and NEt_3 (10.0 mmol, 2.0 equiv) was added dropwisely over a 15 minute period followed by dropwise addition of benzylamine **(S_2)** (5.50 mmol, 1.10 equiv) over a 15 minute period. The brown mixture was kept in a cooling bath for 30 minutes and then allowed to warm to room temperature. Stirring was continued at room temperature for 6-8 h. The reaction mixture was quenched with water and extracted with CH_2Cl_2 (10 mL× 3).. The organic phase was combined and dried over anhydrous Na_2SO_4 and filtered. The solvent was

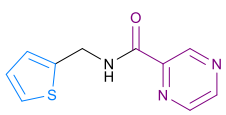
removed in vacuo, and the resulting residue was purified by silica gel column chromatography (PE/EA mixtures) to obtain the corresponding amide **1**.



***N*-(2-Fluorobenzyl) pyrazine-2-carboxamide (1a)** Following **the general procedure A** from 2-Fluorobenzylamine, **1a** was obtained as a white solid (89% yield, m.p. = 105.2 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.82 – 8.68 (m, 1H), 8.51 (s, 1H), 8.20 (s, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 19.2 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 9.2 Hz, 1H), 4.73 (d, *J* = 6.1 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.93, 161.02, 159.06, 146.32, 143.38 (d, J_{CF} = 21.9 Hz), 141.52, 129.25 (d, J_{CF} = 4.1 Hz), 128.50 (d, J_{CF} = 8.1 Hz), 123.72 (d, J_{CF} = 14.8 Hz), 123.34 (d, J_{CF} = 3.6 Hz), 114.45 (d, J_{CF} = 21.2 Hz), 36.46 (d, J_{CF}= 4.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.74. **HRMS (ESI)** calcd for $C_{12}H_{10}FN_3ONa$ $[M+Na]^+$: 254.0700, found: 254.0703. **FTIR** (KBr, cm^{-1}) 2965.42, 2836.45, 2710.28, 1605.61, 1358.88, 1070.09, 775.70.

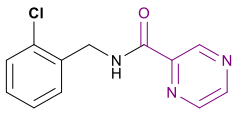


***N*-(Furan-2-ylmethyl)pyrazine-2-carboxamide (1j)** Following **the general procedure A** from 2-Furfurylamine, **1j** was obtained as a white solid (68% yield, m.p. = 116.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.75 (d, *J* = 2.4 Hz, 1H), 8.60 – 8.50 (m, 1H), 8.13 (s, 1H), 7.38 (s, 1H), 6.38 – 6.23 (m, 2H), 4.68 (d, *J* = 5.9 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.77, 149.71, 146.35, 143.49, 143.25, 141.53, 141.41, 109.47, 106.78, 35.37. **HRMS (ESI)** calcd for $C_{10}H_9N_3O_2Na$ $[M+Na]^+$: 226.0587, found: 226.0596. **FTIR** (KBr, cm^{-1}) 2968.22, 271308, 1602.80, 1361.68, 1078.50, 778.50.

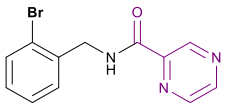


***N*-(Thiophen-2-ylmethyl)pyrazine-2-carboxamide (1k)** Following **the general procedure A** from 2-Thiophenemethylamine, **1k** was obtained as a white solid (89% yield, m.p. = 114.8 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.48 – 9.38 (m, 1H), 8.75 (d, *J* = 2.3 Hz, 1H), 8.60 – 8.47 (m, 1H), 8.17 (s, 1H), 7.27 – 7.22 (m, 1H), 7.07 (d, *J* = 2.9

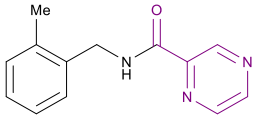
Hz, 1H), 6.98 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.85 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.70, 147.42, 144.53, 144.22, 142.59, 140.16, 127.01, 126.42, 125.49, 38.17. **HRMS (ESI)** calcd for $C_{10}H_9N_3OSNa$ $[M+Na]^+$: 242.0359, found: 242.0367. **FTIR** (KBr, cm^{-1}) 2954.21, 2833.64, 2713.08, 1597.20, 1361.68, 1081.31, 775.70.



***N*-(2-Chlorobenzyl)pyrazine-2-carboxamide (1l)** Following **the general procedure A** from 2-Chlorobenzylamine, **1l** was obtained as a white solid (88% yield, m.p. = 103.3 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.75 (s, 1H), 8.52 (s, 1H), 8.27 (s, 1H), 7.43 (d, *J* = 33.8 Hz, 2H), 7.30 – 7.15 (m, 2H), 4.77 (d, *J* = 5.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.93, 146.34, 143.48, 143.30, 141.55, 134.16, 132.74, 129.19, 128.60, 128.12, 126.13, 40.42. **HRMS (ESI)** calcd for $C_{12}H_{10}ClN_3ONa$ $[M+Na]^+$: 270.0405, found: 270.0408. **FTIR** (KBr, cm^{-1}) 2830.84, 2713.08, 1597.20, 1361.68, 1067.29, 775.70.

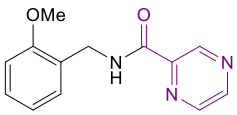


***N*-(2-Bromobenzyl)pyrazine-2-carboxamide (1m)** Following **the general procedure A** from 2-Bromobenzylamine, **1m** was obtained as a white solid (86% yield, m.p. = 104.5 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 1.4 Hz, 1H), 8.75 (d, *J* = 2.4 Hz, 1H), 8.55 – 8.50 (m, 1H), 8.30 (s, 1H), 7.61 – 7.53 (m, 1H), 7.46 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.20 – 7.12 (m, 1H), 4.76 (d, *J* = 6.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.90, 146.34, 143.48, 143.29, 141.56, 135.81, 131.88, 129.34, 128.35, 126.77, 122.82, 42.75. **HRMS (ESI)** calcd for $C_{12}H_{10}BrN_3ONa$ $[M+Na]^+$: 313.9899, found: 313.9902. **FTIR** (KBr, cm^{-1}) 2954.21, 2833.64, 2724.30, 2354.21, 1605.61, 1364.49, 1072.90, 772.90.

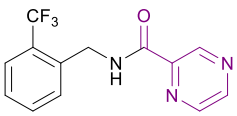


***N*-(2-Methylbenzyl)pyrazine-2-carboxamide (1n)** Following **the general procedure A** from 2-Methylbenzylamine, **1n** was

obtained as a white solid (64% yield, m.p. = 102.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (d, *J* = 1.4 Hz, 1H), 8.66 (d, *J* = 2.4 Hz, 1H), 8.44 – 8.39 (m, 1H), 7.89 (s, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.17 – 7.09 (m, 3H), 4.60 (d, *J* = 5.8 Hz, 2H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.68, 146.28, 143.47, 143.35, 141.48, 135.46, 134.34, 129.59, 127.59, 126.92, 125.27, 40.65, 18.07. **HRMS (ESI)** calcd for $C_{13}H_{13}N_3ONa$ $[M+Na]^+$: 250.0951, found: 250.0956. **FTIR** (KBr, cm^{-1}) 2965.42, 2833.64, 2713.08, 2357.01, 1611.21, 1364.49, 1067.29, 775.70, 565.42.

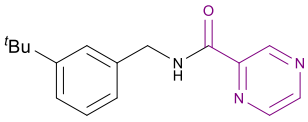


***N*-(2-Methoxybenzyl)pyrazine-2-carboxamide (1o)** Following **the general procedure A** from 2-Methoxybenzylamine, **1o** was obtained as a white solid (73% yield, m.p. = 114.8 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.41 (d, *J* = 1.4 Hz, 1H), 8.71 (d, *J* = 2.4 Hz, 1H), 8.51 – 8.46 (m, 1H), 8.26 (s, 1H), 7.34 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.98 – 6.87 (m, 2H), 4.68 (d, *J* = 6.2 Hz, 2H), 3.89 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.64, 156.61, 146.04, 143.73, 143.47, 141.48, 128.71, 128.02, 124.76, 119.65, 109.38, 54.39, 38.22. **HRMS (ESI)** calcd for $C_{13}H_{13}N_3O_2Na$ $[M+Na]^+$: 266.0900, found: 266.0892. **FTIR** (KBr, cm^{-1}) 2965.42, 2828.04, 2718.69, 1591.59, 1367.29, 1067.29, 775.70, 559.81.

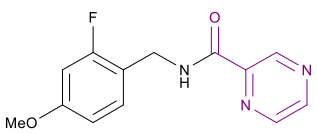


***N*-(2-(Trifluoromethyl)benzyl)pyrazine-2-carboxamide (1p)** Following **the general procedure A** from 2-(Trifluoromethyl)benzylamine, **1p** was obtained as a white solid (71% yield, m.p. = 117.8 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.44 (d, *J* = 1.4 Hz, 1H), 8.76 (d, *J* = 2.4 Hz, 1H), 8.52 (dd, *J* = 2.3, 1.5 Hz, 1H), 8.22 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 4.87 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.98, 147.45, 144.52, 144.20, 142.62, 136.10 (d, J_{CF} = 1.5 Hz), 132.42, 130.76, 128.30 (d, J_{CF} = 30.5 Hz), 127.84, 126.11 (q, J_{CF} = 5.6 Hz),124.43 (d, J_{CF} = 271.4 Hz), 40.07 (d, J_{CF} = 2.2 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -59.47. **HRMS (ESI)** calcd for $C_{13}H_{10}F_3N_3ONa$

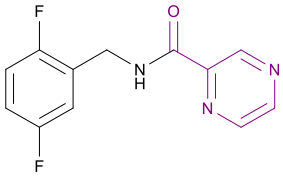
[M+Na]$^+$: 304.0668, found: 304.0672. **FTIR** (KBr, cm^{-1}) 2959.81, 2830.84, 2721.50, 1591.59, 1361.68, 1078.50, 775.70.



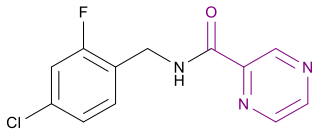
***N*-(3-(Tert-butyl)benzyl)pyrazine-2-carboxamide (1r)** Following **the general procedure A** 3-(tert-butyl)benzonitrile, **1r** was obtained as a white solid (62% yield for two steps, m.p. = 106.4 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.46 (d, *J* = 1.1 Hz, 1H), 8.74 (d, *J* = 2.4 Hz, 1H), 8.50 (s, 1H), 8.11 (s, 1H), 7.42 – 7.25 (m, 3H), 7.19 (d, *J* = 7.3 Hz, 1H), 4.68 (d, *J* = 6.0 Hz, 2H), 1.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.77, 150.75, 146.24, 143.49, 143.42, 141.50, 136.24, 127.53, 124.00, 123.72, 42.82, 33.66, 30.30. **HRMS (ESI)** calcd for $C_{16}H_{19}N_3ONa$ [M+Na]$^+$: 292.1420, found: 292.1422. **FTIR** (KBr, cm^{-1}) 2959.81, 2830.84, 2713.08, 2351.40, 1597.20, 1358.88, 1070.09, 778.50.



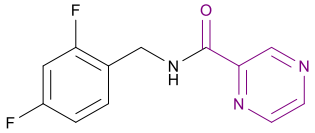
***N*-(2-Fluoro-4-methoxybenzyl)pyrazine-2-carboxamide (1s)** Following **the general procedure A** from 2-fluoro-4-methoxybenzonitrile, **1s** was obtained as a white solid (65% yield for two steps, m.p. = 110.8 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.74 (d, *J* = 2.3 Hz, 1H), 8.52 – 8.46 (m, 1H), 8.12 (s, 1H), 7.32 (t, *J* = 8.6 Hz, 1H), 6.71 – 6.60 (m, 2H), 4.65 (d, *J* = 6.1 Hz, 2H), 3.79 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.85, 161.62 (d, J_{CF} = 259.5 Hz), 160.68 (d, J_{CF} = 2.3 Hz), 147.28, 144.46, 144.40, 142.53, 131.01 (d, J_{CF} = 6.2 Hz), 116.64 (d, J_{CF} = 15.5 Hz), 109.90 (d, J_{CF} = 3.1 Hz), 101.80 (d, J_{CF} = 25.0 Hz), 55.59, 37.13 (d, J_{CF} = 3.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.65. **HRMS (ESI)** calcd for $C_{13}H_{12}FN_3O_2Na$ [M+Na]$^+$: 284.0806, found: 284.0808. **FTIR** (KBr, cm^{-1}) 2962.62, 2830.84, 2710.28, 1600.00, 1367.29, 1070.09, 781.31.



***N*-(2,5-Difluorobenzyl)pyrazine-2-carboxamide (1t)** Following **the general procedure A** from 2,5-difluorobenzonitrile, **1t** was obtained as a white solid (60% yield for two steps, m.p. = 132.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.77 (d, *J* = 2.4 Hz, 1H), 8.58 – 8.51 (m, 1H), 8.22 (s, 1H), 7.16 – 7.09 (m, 1H), 7.07 – 7.00 (m, 1H), 7.00 – 6.91 (m, 1H), 4.71 (d, *J* = 6.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.11, 157.69 (dd, J_{CF} = 230.1, 2.4 Hz), 155.76 (dd, J_{CF} = 229.2, 2.4 Hz), 146.50, 143.51, 143.09, 141.57, 125.49 (dd, J_{CF} = 17.5, 7.5 Hz), 115.46 (dd, J_{CF} = 24.4, 14.4 Hz), 115.44 (dd, J_{CF} = 24.4, 1.0 Hz), 114.67 (dd, J_{CF} = 24.1, 8.6 Hz), 36.14 (d, J_{CF} = 3.2 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.31 (d, J_{FF} = 17.8 Hz), -124.84 (d, J_{FF} = 17.8 Hz). **HRMS (ESI)** calcd for $C_{12}H_9F_2N_3ONa$ $[M+Na]^+$: 272.0606, found: 272.0599. **FTIR** (KBr, cm^{-1}) 2957.01, 2828.04, 2718.69, 2357.01, 1597.20, 1361.68, 1070.09, 781.31.

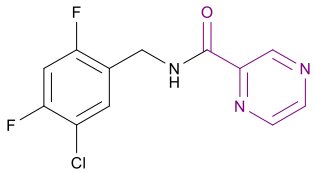


***N*-(4-Chloro-2-fluorobenzyl)pyrazine-2-carboxamide (1u)** Following **the general procedure A** from (4-chloro-2-fluorophenyl)methanamine, **1u** was obtained as a white solid (89% yield, m.p. = 128.6 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.76 (d, *J* = 2.3 Hz, 1H), 8.52 (s, 1H), 8.19 (s, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.16 – 7.07 (m, 2H), 4.69 (d, *J* = 6.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.08, 160.76 (d, J_{CF} = 250.1 Hz), 147.48, 144.50, 144.16, 142.58, 134.42 (d, J_{CF} = 10.3 Hz), 131.06 (d, J_{CF} = 5.1 Hz), 124.75 (d, J_{CF} = 3.6 Hz), 123.56 (d, J_{CF} = 15.0 Hz), 116.33 (d, J_{CF} = 24.8 Hz), 36.99 (d, J_{CF} = 3.6 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.10. **HRMS (ESI)** calcd for $C_{12}H_9ClFN_3ONa$ $[M+Na]^+$: 288.0310, found: 288.0303. **FTIR** (KBr, cm^{-1}) 2965.55, 2833.78, 2721.63, 1605.75, 1361.83, 1067.44, 773.05.

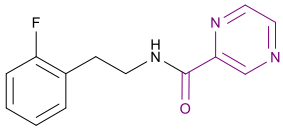


***N*-(2,4-Difluorobenzyl)pyrazine-2-carboxamide (1v)** Following **the general procedure A** from

2,4-difluorobenzonitrile, **1v** was obtained as a white solid (63% yield for two steps, m.p. = 131.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 9.42 (d, *J* = 1.4 Hz, 1H), 8.76 (d, *J* = 2.3 Hz, 1H), 8.57 – 8.47 (m, 1H), 8.18 (s, 1H), 7.41 (q, *J* = 8.3 Hz, 1H), 6.91 – 6.74 (m, 2H), 4.69 (d, *J* = 6.2 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) 162.00, 161.52 (dd, J_{CF} = 249.0, 12.0 Hz), 160.04 (dd, J_{CF} = 249.1, 12.0 Hz), 146.42, 143.47, 143.18, 141.54, 130.21 (dd, J_{CF} = 9.7, 5.8 Hz), 119.81 (dd, J_{CF} = 15.1, 3.8 Hz), 110.43 (dd, J_{CF} = 21.2, 3.7 Hz), 102.98 (t, J_{CF} = 25.4 Hz), 35.95 (d, J_{CF} = 3.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.42 (d, J_{FF} = 7.4 Hz), -114.52 (d, J_{FF} = 7.4 Hz). **HRMS (ESI)** calcd for $C_{12}H_9F_2N_3ONa$ $[M+Na]^+$: 272.0606, found: 272.0611. **FTIR** (KBr, cm^{-1}) 2959.81, 2833.64, 2713.08, 2357.01, 1608.41, 1370.09, 1075.70, 778.50.

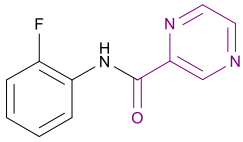


***N*-(5-Chloro-2,4-difluorobenzyl)pyrazine-2-carboxamide (1w)** Following **the general procedure A** from (5-chloro-2,4-difluorophenyl)methanamine, **1w** was obtained as a white solid (92% yield, m.p. = 142.1 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.78 (d, *J* = 2.4 Hz, 1H), 8.62 – 8.48 (m, 1H), 8.21 (s, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 9.1 Hz, 1H), 4.67 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.14, 158.15 (dd, J_{CF} = 249.5, 10.4 Hz), 156.49 (dd, J_{CF} = 251.5, 12.3 Hz), 146.57, 143.50, 142.98, 141.58, 130.21 (d, J_{CF} = 5.4 Hz), 121.19 (dd, J_{CF} = 16.4, 4.2 Hz), 115.61 (dd, J_{CF} = 17.8, 4.2 Hz), 104.18 (dd, J_{CF} = 26.8, 25.0 Hz), 35.57 (d, J_{CF} = 3.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -111.44 (d, J_{FF} = 7.2 Hz), -116.07 (d, J_{FF} = 7.4 Hz). **HRMS (ESI)** calcd for $C_{12}H_8ClF_2N_3ONa$ $[M+Na]^+$: 287.0232, found: 287.0240. **FTIR** (KBr, cm^{-1}) 2962.75, 2830.97, 2716.02, 1602.95, 1361.83, 1064.64, 773.05.

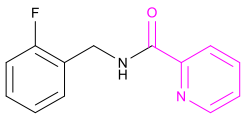


***N*-(2-Fluorophenethyl)pyrazine-2-carboxamide (1x)** Following **the general procedure A** from 2-Fluorophenethylamine, **1x** was obtained as a white solid (84% yield, m.p. = 99.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.40 (d, *J* = 1.4 Hz, 1H),

8.73 (d, J = 2.4 Hz, 1H), 8.49 (dd, J = 2.4, 1.5 Hz, 1H), 7.94 (s, 1H), 7.27 – 7.19 (m, 2H), 7.12 – 6.99 (m, 2H), 3.76 (q, J = 6.9 Hz, 2H), 3.00 (t, J = 7.1 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.01, 160.26 (d, J_{CF} = 245.1 Hz), 146.20, 143.40, 143.33, 141.50, 130.03 (d, J_{CF} = 4.8 Hz), 127.41 (d, J_{CF} = 8.1 Hz), 124.53 (d, J_{CF} = 15.9 Hz), 123.21 (d, J_{CF} = 3.6 Hz), 114.38 (d, J_{CF} = 22.0 Hz), 38.51, 28.23 (d, J_{CF} = 1.7 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.51. **HRMS (ESI)** calcd for $C_{13}H_{12}FN_3ONa$ $[M+Na]^+$: 268.0852, found: 268.0857. **FTIR** (KBr, cm^{-1}) 2957.01, 2833.64, 2718.69, 1602.80, 1367.29, 1078.50, 770.09.

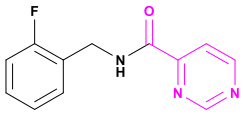


***N*-(2-Fluorophenyl)pyrazine-2-carboxamide** Following **the general procedure A** from 2-fluoroaniline, **N-(2-Fluorophenyl)pyrazine-2-carboxamide** was obtained as a white solid (71% yield, m.p. = 104.8 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 9.51 (s, 1H), 8.82 (d, J = 2.2 Hz, 1H), 8.62 (s, 1H), 8.54 (t, J = 7.9 Hz, 1H), 7.24 – 7.05 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.72, 151.79 (d, J_{CF} = 244.6 Hz), 146.68, 143.58, 143.15, 141.53, 124.88, 123.89 (d, J_{CF} = 7.6 Hz), 123.68 (d, J_{CF} = 3.7 Hz), 120.36, 113.99 (d, J_{CF} = 19.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -130.70. **HRMS (ESI)** calcd for $C_{11}H_8FN_3ONa$ $[M+Na]^+$: 254.0700, found: 254.0705. **FTIR** (KBr, cm^{-1}) 2957.01, 2828.04, 2721.50, 1591.59, 1364.49, 1078.50, 772.90.



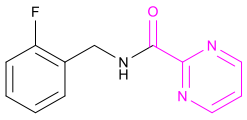
***N*-(2-Fluorobenzyl)picolinamide (1aa)** Following **the general procedure A** from 2-Fluorobenzylamine and 1-picolinic acid, **1aa** was obtained as a white solid (87% yield, m.p. = 75.8 °C). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.53 (d, J = 4.2 Hz, 1H), 8.42 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.88 – 7.80 (m, 1H), 7.42 (t, J = 6.7 Hz, 2H), 7.30 – 7.22 (m, 1H), 7.14 – 7.03 (m, 2H), 4.73 (d, J = 6.2 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.28, 160.00 (d, J_{CF} = 246.4 Hz), 148.70, 147.07, 136.31, 129.14 (d, J_{CF} = 4.3 Hz), 128.22 (d, J_{CF} = 8.1 Hz), 125.21, 124.18 (d, J_{CF} = 14.8 Hz), 123.25 (d, J_{CF} = 3.6 Hz), 121.30, 114.36 (d, J_{CF} = 21.3 Hz), 36.32 (d, J_{CF} = 4.2 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.80.

HRMS (ESI) calcd for $C_{13}H_{11}FN_2ONa$ $[M+Na]^+$: 253.0748, found: 253.0739. **FTIR** (KBr, cm^{-1}) 2951.40, 2836.45, 2721.50, 1594.39, 1367.29, 1064.49, 781.31.



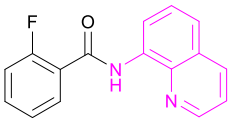
***N*-(2-Fluorobenzyl)pyrimidine-4-carboxamide (1bb)**

Following **the general procedure A** from 2-Fluorobenzylamine and 1-pyrimidine-4-carboxylic acid, **1bb** was obtained as a yellow solid (70% yield, m.p. = 96.8 ^oC). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 1.1 Hz, 1H), 8.90 (d, *J* = 5.0 Hz, 1H), 8.30 (s, 1H), 8.06 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.26 – 7.17 (m, 1H), 7.10 – 6.95 (m, 2H), 4.65 (d, *J* = 6.2 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.60, 161.06 (d, J_{CF} = 246.6 Hz), 159.25, 157.78, 156.07, 130.25 (d, J_{CF} = 4.1 Hz), 129.61 (d, J_{CF} = 8.2 Hz), 124.51 (d, J_{CF} = 14.9 Hz), 124.38 (d, J_{CF} = 3.6 Hz), 118.61, 115.53 (d, J_{CF} = 21.2 Hz), 37.65 (d, J_{CF} = 4.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.63. **HRMS (ESI)** calcd for $C_{12}H_{10}FN_3ONa$ $[M+Na]^+$: 254.0700, found: 254.0705. **FTIR** (KBr, cm^{-1}) 2948.60, 2715.89, 1597.20, 1361.68, 1070.09, 772.90.



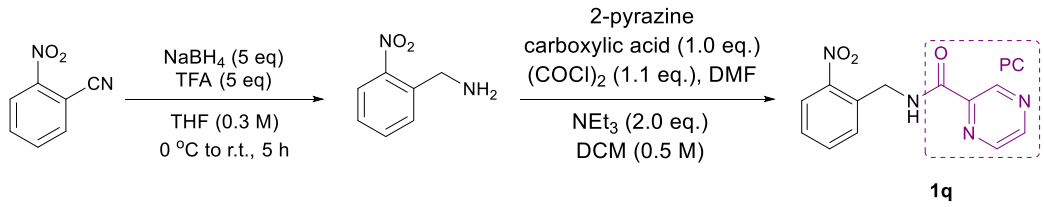
***N*-(2-Fluorobenzyl)pyrimidine-2-carboxamide (1cc)**

Following **the general procedure A** from 2-Fluorobenzylamine and 1-pyrimidine-2-carboxylic acid, **1cc** was obtained as a yellow liquid (27% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.7 Hz, 2H), 8.30 (s, 1H), 7.37 (q, *J* = 8.6, 6.7 Hz, 2H), 7.20 (q, *J* = 6.4 Hz, 1H), 7.08 – 6.93 (m, 2H), 4.69 (d, *J* = 6.1 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.17, 161.03 (d, J_{CF} = 246.4 Hz), 157.48, 130.36 (d, J_{CF} = 4.1 Hz), 129.47 (d, J_{CF} = 8.1 Hz), 124.81, 124.66, 124.37 (d, J_{CF} = 3.6 Hz), 122.63, 115.41 (d, J_{CF} = 21.2 Hz), 37.77 (d, J_{CF} = 4.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.75. **HRMS (ESI)** calcd for $C_{12}H_{10}FN_3O$ $[M+ H]^+$: 232.0886, found: 232.0889. **FTIR** (KBr, cm^{-1}) 2953.62, 2720.83, 1600.41, 1373.65, 1063.52, 773.91.



2-Fluoro-*N*-(quinolin-8-yl)benzamide (1dd) was performed according to previous literature[3] with 90% yield and the NMR data is consistent with the literature reports.

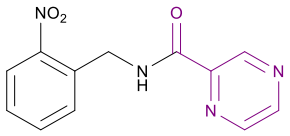
2.2 Procedure for the Synthesis of 1q



1q

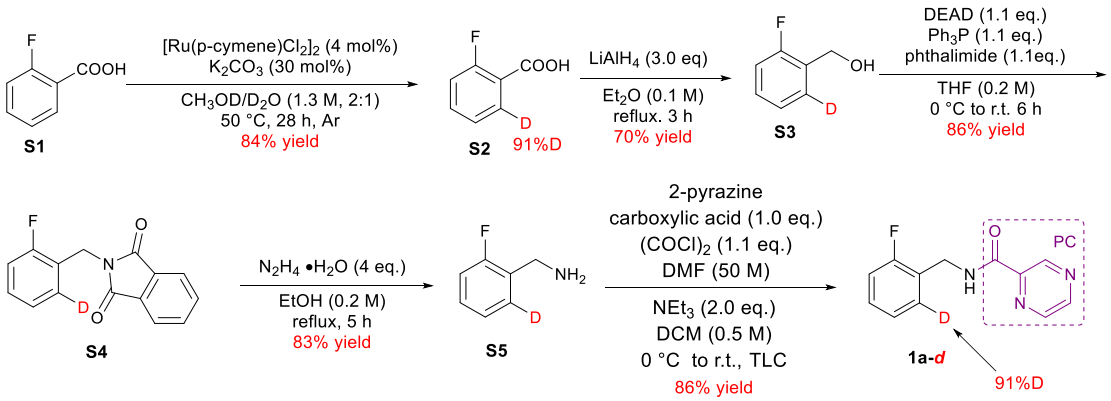
Benzonitrile Reduction[4]: A round bottom flask equipped with a stirring bar was charged with $NaBH_4$ (25.0 mmol, 5 equiv) and anhydrous THF (12.5 mL) was added via a syringe. The flask was submerged into an ice/water bath and cooled to 0 ºC. The suspension was slowly added trifluoroacetic acid (25 mmol, 5.0 equiv) (Caution: gas evolution observed). A solution of 2-nitrobenzonitrile (5 mmol, 1 equiv) in THF (4 mL) was added. The ice bath was removed and the reaction mixture was stirred at room temperature overnight. After the reaction completed (monitored by TLC), the reaction mixture was poured into an aqueous solution of 1N sodium hydroxide (35 mL), then EtOAc (25 mL) was added and the biphasic mixture was stirred for 1.5 h. The layers were separated and the aqueous layer was extracted with EtOAc (12.5 mL×3). The organic layers were combined and washed with saturated brine. Then, the organic layers were dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure, and the resulting residue was flushed through a short silica pad, eluting with CH_2Cl_2: MeOH (10:1, *v/v*) to obtain the corresponding crude benzylamine which was used in the next step without further purification.

Amide Preparation was performed following **the general procedure A**



***N*-(2-Nitrobenzyl)pyrazine-2-carboxamide (1q)** Following **the general procedure B, 1q** was obtained as a yellow solid (41% yield for two steps, m.p. = 125.5 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.39 (d, *J* = 1.2 Hz, 1H), 8.76 (d, *J* = 2.4 Hz, 1H), 8.62 (s, 1H), 8.58 – 8.49 (m, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 6.9 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.4 Hz, 1H), 4.95 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.23, 148.30, 147.47, 144.43, 144.19, 142.73, 134.21, 133.15, 132.27, 128.98, 125.28, 41.21. **HRMS (ESI)** calcd for $C_{12}H_{10}N_4O_3Na$ $[M+Na]^+$: 281.0645, found: 281.0640. **FTIR** (KBr, cm^{-1}) 2951.40, 2833.64, 2718.69, 1605.61, 1367.29, 1070.09, 778.50.

2.3 Procedure for the Synthesis of 1a-*d*



Preparation of deuterobenzoic acid[5]: A oven-dried Schlenk tube was sequentially added 2-fluorobenzoic acid (2.80 g, 20 mmol, 1 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (490.0 mg, 0.8 mmol, 0.04 equiv), and K_2CO_3 (829.2 mg, 6 mmol, 0.03 equiv) in an open air. After being evacuated and backfilled with nitrogen three times, CH_3OD (10 mL) and D_2O (5 mL) were added. Then, the reaction tube was heated to 50 °C with stirring for 28 hours. After 28 hours, 2 N HCl (10 mL) was added, and extracted with ethyl acetate (20 mL × 3). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration and concentration in vacuo, the crude residue was purified by chromatography on silica gel (eluent: PE/EA= 10/1 to 5/1) to obtain deuterated

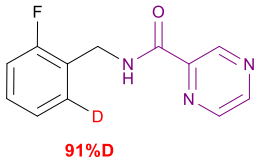
benzoic acid **S2** as a white solid (2.36 g, 84% yield, 91% deuterium).

Carboxyl reduction[6]: To a solution of substituted deuterated benzoic acid **S2** in Et_2O (0.1 M) was added dropwise $LiAlH_4$ (3.0 equiv, 2.5 M in Et_2O) over 30 min at 0°C and then the solvent was heated to reflux with stirring for 3h. After the reaction was completed (monitored by TLC), 1N HCl was added slowly under 0°C until a clear solution was obtained. The Et_2O layer was separated and the aqueous phase was extracted with Et_2O (20 mL × 3). The organic layers were combined and dried over Na_2SO_4. After filtrating and removing the solvent under reduced pressure, the crude residual was purified by chromatography on silica gel (eluent: PE/EA= 50/1 to 20/1) to obtain alcohol **S3** as a colorless liquid (70% yield, 91% deuterium).

Mitsunobu reaction[7]: Alcohol **(S3)** (1.0 equiv) and diethyl azodicarboxylate (DEAD, 1.1 equiv) were added to a solution of triphenylphosphine (1.1 equiv) and phthalimide (1.1 equiv) in dry THF (0.2 M) at 0 °C under a nitrogen atmosphere. The solution was stirred at 0 °C for 10 min and then at room temperature for an additional 6 h. After filtrating and removing the solvent under reduced pressure, the crude residue was purified by silica gel chromatography (eluent: PE/EA = 100:1) to obtain the product **(S4)** as a white solid (86% yield, 91% deuterium).

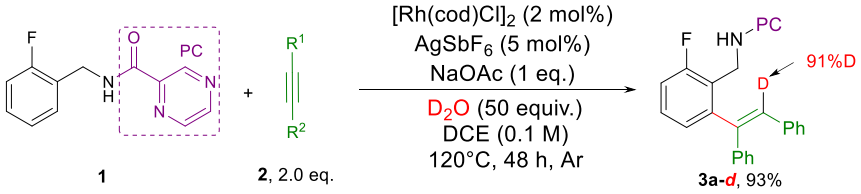
Hydrazinolysis[7]: A solution of **S4** (1.0 equiv) and $N_2H_4 \cdot H_2O$ (4.0 equiv) in EtOH (0.2 M) was heated to reflux with stirring for 3 h. The reaction was acidified with 1N HCl to pH = 3 and washed with Et_2O (10 mL × 3). The aqueous phase was treated with 1 N NaOH solution to pH = 12 and extracted with DCM (10 mL × 3). The organic layers were combined and dried over Na_2SO_4, and the following filteration and concentration gave the product benzylamine **(S5)** as a yellow liquid (83% yield, 91% deuterium), which was used in the next step without further purification.

Amide preparation was performed following **the general procedure A** to obtained amide product **1a-*d*** as a white solid (86% yield, 91% deuterium).

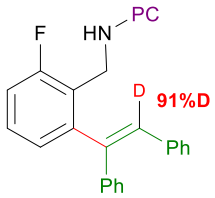


N*-((2-Fluorocyclohexa-1,3-dien-1-yl-6-d)methyl)pyrazine-2-carboxamide (1a-*d*)** Following **the procedure C**, **1a-*d was obtained as a white solid (36% yield for four steps, 91% deuterium). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.43 (d, *J* = 1.4 Hz, 1H), 8.75 (d, *J* = 2.4 Hz, 1H), 8.52 (dd, *J* = 2.4, 1.5 Hz, 1H), 8.17 (s, 1H), 7.33 – 7.27 (m, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.10 – 7.05 (m, 1H), 4.74 (d, *J* = 6.2 Hz, 2H).

2.4 Procedure for the Synthesis of 3a-*d*



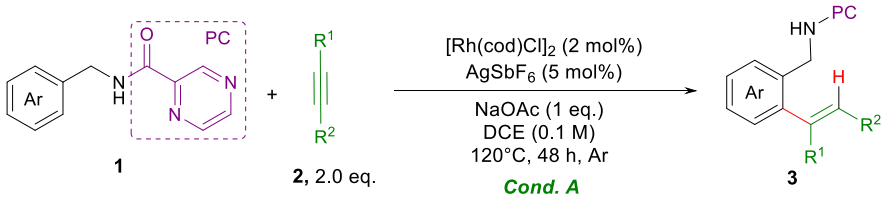
A screw-cap vial was charged with $[Rh(cod)Cl]_2$ (1.5 mg, 0.003 mmol, 2 mol%), $AgSbF_6$ (2.6 mg, 0.0075 mmol, 0.05 equiv), NaOAc (12.3 mg, 0.15 mmol, 1.00 equiv), amide **1** (0.15 mmol, 1.0 equiv), diphenylacetylene **2** (53.3 mg, 0.30 mmol, 2.00 equiv), DCE (1.5 mL) and D_2O (7.5 mmol, 50 equiv) in sequence. The vial was sealed under argon and heated to 120 °C with stirring for 48 h. After cooling down, the mixture was concentrated and directly applied to a flash column chromatography (PE/EA mixtures) to obtain the corresponding product **3a-*d*** as a white solid (93% yield, 91% deuterium).



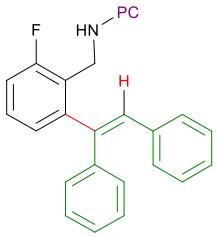
(*E*)-*N*-(2-(1,2-Diphenylvinyl-2-d)-6-fluorobenzyl)pyrazine-2-carboxamide (3a-*d*) Following **the procedure D**, **3a-*d*** was obtained as a white solid (93% yield, 91% deuterium). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.24 (d, *J* = 1.4 Hz, 1H), 8.62 (d, *J* = 2.4 Hz, 1H), 8.34 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.48 (s, 1H), 7.29 – 7.21 (m, 1H), 7.15 – 7.07 (m, 8H), 7.07 – 6.98 (m, 4H), 4.50 (d, *J* = 6.6 Hz, 2H).

3. General Procedure for C−H Functionalization

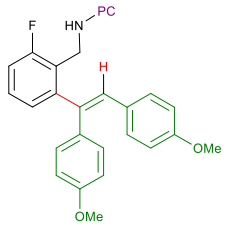
3.1 General Procedure 1 for Hydroarylation



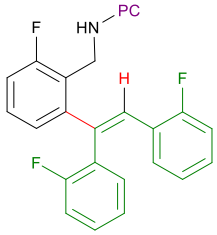
A screw-cap vial was charged with $[Rh(cod)Cl]_2$ (1.5 mg, 0.003 mmol, 2 mol%), $AgSbF_6$ (2.6 mg, 0.0075 mmol, 0.05 equiv), NaOAc (12.3 mg, 0.15 mmol, 1.0 equiv), amide **1** (1.0 equiv, 0.15 mmol), diphenylacetylene **2** (53.3 mg, 0.30 mmol, 2.0 equiv) and DCE (1.5 mL) in sequence. The vial was sealed under argon and heated to 120 °C with stirring for 48 h. After cooling down, the mixture was concentrated and directly applied to a flash column chromatography (PE/EA mixtures) to obtain product **3**.



(*E*)-*N*-(2-(2-(Cyclohexa-1,3-dien-1-yl)-1-phenylvinyl)-6-fluorobenzyl)pyrazine-2-carboxamide (3a) Following **the general procedure 1**, **3a** was obtained as a white solid (58.3 mg, 95% yield, m.p. = 111.1 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.32 (d, *J* = 1.3 Hz, 1H), 8.69 (d, *J* = 2.4 Hz, 1H), 8.45 – 8.38 (m, 1H), 7.56 (s, 1H), 7.36 – 7.29 (m, 1H), 7.23 – 7.15 (m, 8H), 7.14 – 7.05 (m, 4H), 6.71 (s, 1H), 4.58 (d, *J* = 5.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.04, 161.82 (d, J_{CF} = 248.0 Hz), 147.01, 146.79 (d, J_{CF} = 3.4 Hz), 144.44, 144.34, 142.28, 140.54 (d, J_{CF} = 2.6 Hz), 139.57, 136.61, 131.68, 129.74, 129.42, 129.23 (d, J_{CF} = 9.4 Hz), 128.61, 128.13, 127.66, 127.31, 126.54 (d, J_{CF} = 2.9 Hz), 122.77 (d, J_{CF} = 14.9 Hz), 114.98 (d, J_{CF} = 22.7 Hz), 35.04 (d, J_{CF} = 4.8 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.69. **HRMS (ESI)** calcd for $C_{26}H_{20}FN_3ONa$ $[M+Na]^+$: 432.1483, found: 432.1482. **FTIR** (KBr, cm^{-1}) 2962.62, 2830.84, 2718.69, 2348.60, 1605.61, 1361.68, 1067.29, 772.90.

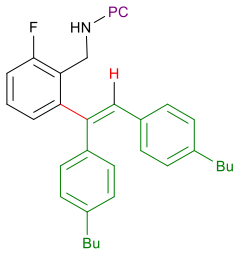


(*E*)-*N*-(2-(1,2-Bis(4-methoxyphenyl)vinyl)-6-fluorobenzyl)pyrazine-2-carboxamide (3b) Following **the general procedure 1** at the conditions of 140°C, **3b** was obtained as a yellow liquid (53.5 mg, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31 (d, *J* = 1.3 Hz, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.41 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.43 (s, 1H), 7.35 – 7.28 (m, 1H), 7.18 (d, *J* = 6.8 Hz, 1H), 7.10 (dd, *J* = 11.9, 8.7 Hz, 4H), 7.08 – 7.02 (m, 1H), 6.76 – 6.69 (m, 4H), 6.57 (s, 4H), 4.55 (d, *J* = 6.5 Hz, 2H), 3.77 (s, 3H), 3.66 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.02, 161.77 (d, J_{CF} = 247.9 Hz), 158.90, 158.66, 147.42 (d, J_{CF} = 3.3 Hz), 146.95, 144.44, 144.26, 142.34, 138.43 (d, J_{CF} = 2.6 Hz), 132.23, 130.98, 130.62, 130.18, 129.41, 129.20 (d, J_{CF} = 9.5 Hz), 126.51 (d, J_{CF} = 2.8 Hz), 122.60 (d, J_{CF} = 14.8 Hz), 114.78 (d, J_{CF} = 22.7 Hz), 114.06, 113.55, 55.19, 55.03, 35.04 (d, J_{CF} = 4.9 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.84. **HRMS (ESI)** calcd for $C_{28}H_{24}FN_3O_3Na$ $[M+Na]^+$: 492.1694, found: 492.1680. **FTIR** (KBr, cm^{-1}) 2962.62, 2828.04, 2724.30, 1611.21, 1361.68, 1067.29, 775.70.

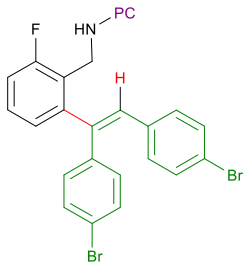


(*Z*)-*N*-(2-(1,2-Bis(2-fluorophenyl)vinyl)-6-fluorobenzyl)pyrazine-2-carboxamide (3c) Following **the general procedure 1** at the conditions of 140°C, **3c** was obtained as a white solid (34.7 mg, 52% yield, m.p. = 143.9 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (d, *J* = 1.2 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.51 – 8.39 (m, 1H), 7.75 (s, 1H), 7.35 – 7.28 (m, 1H), 7.21 – 7.14 (m, 4H), 7.09 (t, *J* = 8.9 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.97 – 6.91 (m, 2H), 6.89 (s, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 4.71 (d, *J* = 6.2 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) 162.16, 161.86 (d, J_{CF} = 247.9 Hz), 160.59 (d, J_{CF} = 249.0 Hz), 159.65 (d, J_{CF} = 249.1 Hz), 147.05, 145.44 (d, *J* = 3.4 Hz), 144.42, 144.30, 142.39, 135.89, 131.57 (d, J_{CF} = 3.3 Hz), 129.96 (d, J_{CF} = 8.2 Hz), 129.52 (d, J_{CF} = 3.0 Hz), 129.32 (dd, J_{CF} = 22.8, 8.9 Hz), 127.29 (d, J_{CF} = 14.6 Hz), 127.28 (d, J_{CF} = 4.1 Hz), 126.22 (d, J_{CF} = 3.0 Hz), 124.48, 124.45, 124.36, 123.57 (d, J_{CF} = 3.5 Hz), 122.61 (d, J_{CF} = 15.1 Hz), 116.26 (d, J_{CF} = 22.0 Hz), 115.43 (d, J_{CF} = 21.9 Hz), 115.09 (d, J_{CF} = 22.6 Hz), 35.00 (d, J_{CF} = 4.7 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ

-111.98, -115.24, -115.46. **HRMS (ESI)** calcd for $C_{26}H_{18}F_3N_3ONa$ $[M+Na]^+$: 468.1294, found: 468.1301. **FTIR** (KBr, cm^{-1}) 2959.81, 2828.04, 271308, 1602.80, 1364.49, 1070.09, 778.50.

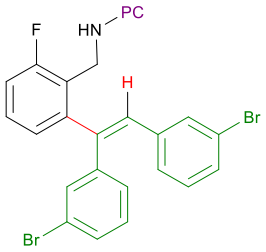


(*E*)-*N*-(2-(1,2-Bis(4-butylphenyl)vinyl)-6-fluorobenzyl)pyrazine-2-carboxamide (3d) Following **the general procedure 1**, **3d** was obtained as a yellow liquid (69.6 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 – 9.27 (m, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.47 – 8.34 (m, 1H), 7.55 (s, 1H), 7.34 – 7.28 (m, 1H), 7.19 (d, *J* = 6.9 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.08 – 7.02 (m, 3H), 6.99 (dd, *J* = 8.1, 4.4 Hz, 4H), 6.63 (s, 1H), 4.56 (d, *J* = 4.9 Hz, 2H), 2.55 (t, 2H), 2.44 (t, 2H), 1.60 – 1.52 (m, 2H), 1.49 – 1.41 (m, 2H), 1.38 – 1.31 (m, 2H), 1.30 – 1.22 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.99, 161.77 (d, J_{CF} = 247.9 Hz), 147.26 (d, J_{CF} = 3.3 Hz), 146.94, 144.52, 144.43, 142.43, 142.28, 142.13, 139.72 (d, J_{CF} = 2.5 Hz), 137.00, 134.08, 131.21, 129.54, 129.29, 129.13 (d, J_{CF} = 9.3 Hz), 128.57, 128.14, 126.51 (d, J_{CF} = 2.9 Hz), 122.76 (d, J_{CF} = 14.7 Hz), 114.77 (d, J_{CF} = 22.7 Hz), 35.39, 35.30, 35.03 (d, J_{CF} = 4.7 Hz), 33.44, 33.25, 22.37, 22.37, 13.96, 13.94. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.89. **HRMS (ESI)** calcd for $C_{34}H_{36}FN_3ONa$ $[M+Na]^+$:544.2735, found: 544.2732. **FTIR** (KBr, cm^{-1}) 2965.42, 2833.64, 2715.89, 1597.20, 1364.49, 1064.49, 772.90.

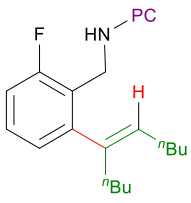


(*E*)-*N*-(2-(1,2-bis(4-bromophenyl)vinyl)-6-fluorobenzyl)pyrazine-2-carboxamide (3e) Following **the general procedure 1**, **3e** was obtained as a white solid (64.4 mg, 76% yield, m.p. = 155.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.71 (s, 1H), 8.47 (s, 1H), 7.39 (s, 1H), 7.36 – 7.26 (m, 5H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 8.9 Hz, 1H), 7.06 – 7.01 (m, 2H), 7.02 – 6.96 (m, 2H), 6.64 (s, 1H), 4.56 (d, *J* = 4.7 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.02, 162.02 (d, J_{CF} = 248.6 Hz), 147.18, 146.03 (d, J_{CF} = 3.5 Hz), 144.35, 144.14, 142.49, 140.14 (d,

J_{CF} = 2.4 Hz), 138.37, 135.17, 131.99, 131.51, 131.39, 130.91, 130.87, 129.50 (d, J_{CF} = 9.2 Hz), 126.41 (d, J_{CF} = 2.7 Hz), 122.67 (d, J_{CF} = 15.1 Hz), 122.16, 121.54, 115.40 (d, J_{CF} = 22.5 Hz), 35.15 (d, J_{CF} = 4.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.29. **HRMS (ESI)** calcd for $C_{26}H_{18}Br_2FN_3ONa$ $[M+Na]^+$: 587.9693, found: 587.9701. **FTIR** (KBr, cm^{-1}) 2965.55, 2830.97, 2713.22, 2357.15, 1611.36, 1361.83, 1070.24, 775.85.

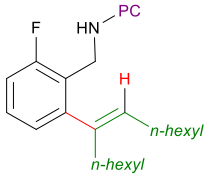


(*E*)-N-(2-(1,2-Bis (3-bromophenyl)vinyl)-6-fluorobenzyl) pyrazine-2-carboxamide (3f) Following **the general procedure 1** at the conditions of 140°C, **3f** was obtained as a yellow solid (72.0 mg, 85% yield, m.p. = 48.3 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.77 – 8.65 (m, 1H), 8.49 (s, 1H), 7.59 (s, 1H), 7.38 – 7.29 (m, 2H), 7.27 (s, 1H), 7.24 (d, J = 7.1 Hz, 2H), 7.17 – 7.09 (m, 3H), 7.08 – 6.98 (m, 3H), 6.66 (s, 1H), 4.59 (d, J = 5.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.03, 161.91 (d, J_{CF} = 248.4 Hz), 147.21, 145.43 (d, J_{CF} = 3.3 Hz), 144.33, 144.19, 142.41, 141.16, 140.44 (d, J_{CF} = 2.6 Hz), 138.19, 132.33 (d, J_{CF} = 2.3 Hz), 131.11, 131.02, 130.57, 130.12, 129.76, 129.57, 129.49, 128.51, 127.84, 126.44 (d, J_{CF} = 3.0 Hz), 122.83, 122.71, 122.30, 115.52 (d, J_{CF} = 22.6 Hz), 34.97 (d, J_{CF} = 4.8 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.30. **HRMS (ESI)** calcd for $C_{26}H_{18}Br_2FN_3ONa$ $[M+Na]^+$: 587.9693, found: 587.9700. **FTIR** (KBr, cm^{-1}) 2965.42, 2828.04, 2713.08, 1600.00, 1370.09, 1075.70, 781.31.

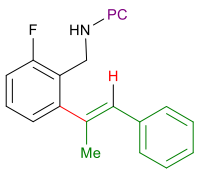


(*E*)-N-(2-(Dec-5-en-5-yl)-6-fluorobenzyl)pyrazine-2-carboxamide (3g) Following **the general procedure 1** with the $[Rh(cod)Cl]_2$ (4 mol %), $AgSbF_6$ (10 mol %) under O_2 at 140 °C for 48 h, **3g** was obtained as a yellow liquid (37.1 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.72 (d, J = 2.4 Hz, 1H), 8.47 (dd, J = 2.3, 1.5 Hz, 1H), 7.91 (s, 1H), 7.26 – 7.20 (m, 1H), 6.99 (t, J = 8.6 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 5.32 (t, J = 7.2 Hz, 1H), 4.71 (d, J = 6.3 Hz, 2H), 2.40 – 2.34 (m, 2H), 2.19 (q, J = 7.2

Hz, 2H), 1.41 – 1.30 (m, 4H), 1.30 – 1.21 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.15, 161.91 (d, J_{CF} = 247.1 Hz), 147.54, 147.12, 144.54, 144.43, 142.45, 138.29 (d, J_{CF} = 2.2 Hz), 131.93, 128.77 (d, J_{CF} = 9.3 Hz), 125.22 (d, J_{CF} = 2.9 Hz), 121.97 (d, J_{CF} = 14.3 Hz), 113.59 (d, J_{CF} = 22.2 Hz), 35.49 (d, J_{CF} = 3.9 Hz), 32.06, 31.84, 30.35, 27.85, 22.78, 22.44, 13.97, 13.89. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.21. **HRMS (ESI)** calcd for $C_{22}H_{28}FN_3ONa$ $[M+Na]^+$: 392.2109, found: 392.2114. **FTIR** (KBr, cm^{-1}) 2951.40, 2836.45, 2715.89, 1588.79, 1364.49, 1072.90, 781.31.

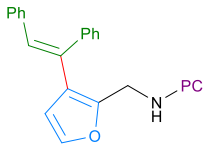


(*E*)-*N*-(2-fluoro-6-(tetradec-7-en-7-yl)benzyl)pyrazine-2-carboxamide (3h) Following **the general procedure 1** with the $[Rh(cod)Cl]_2$ (4 mol %), $AgSbF_6$ (10 mol %) under O_2 at 140 °C for 48 h,, **3h** was obtained as a yellow liquid (48.4 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.45 – 9.40 (m, 1H), 8.74 – 8.70 (m, 1H), 8.47 (dd, *J* = 2.3, 1.5 Hz, 1H), 7.91 (s, 1H), 7.26 – 7.20 (m, 1H), 6.99 (t, *J* = 9.0 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.32 (t, *J* = 7.2 Hz, 1H), 4.71 (d, *J* = 4.8 Hz, 2H), 2.37 (t, *J* = 7.1 Hz, 2H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.43 – 1.36 (m, 2H), 1.35 – 1.29 (m, 2H), 1.28 – 1.15 (m, 12H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.13, 161.91 (d, J_{CF} = 247.1 Hz), 147.52 (d, J_{CF} = 3.3 Hz), 147.12, 144.53, 144.44, 142.43, 138.30 (d, J_{CF} = 2.1 Hz), 131.96, 128.76 (d, J_{CF} = 9.4 Hz), 125.21 (d, J_{CF} = 2.9 Hz), 121.97 (d, J_{CF} = 14.2 Hz), 113.58 (d, J_{CF} = 22.2 Hz), 35.48 (d, J_{CF} = 3.9 Hz), 32.32, 31.73, 31.64, 29.64, 29.37, 29.07, 28.16, 28.13, 22.60, 22.56, 14.07, 14.02. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.19. **HRMS (ESI)** calcd for $C_{26}H_{36}FN_3ONa$ $[M+Na]^+$: 448.2735, found: 448.2736. **FTIR** (KBr, cm^{-1}) 2962.62, 2828.04, 2713.08, 1594.39, 1375.70, 1084.11, 778.50.

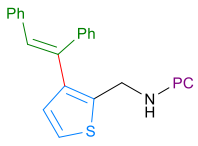


(*E*)-*N*-(2-Fluoro-6-(1-phenylprop-1-en-2-yl)benzyl)pyrazine-2-carboxamide (3i) Following **the general procedure 1** at the conditions of 140°C, **3i** was obtained as a yellow solid (27.1 mg, 52%

yield, m.p. = 79.6 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.41 – 9.37 (m, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.45 (d, *J* = 2.3 Hz, 1H), 8.10 (s, 1H), 7.42 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 7.27 – 7.23 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 9.1 Hz, 1H), 6.43 (s, 1H), 4.83 (d, *J* = 5.1 Hz, 2H), 2.24 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.31, 161.90 (d, J_{CF} = 247.1 Hz), 148.36 (d, J_{CF} = 3.5 Hz), 147.18, 144.46, 144.42, 142.49, 137.20, 136.56 (d, J_{CF} = 2.3 Hz), 130.81, 129.24 (d, J_{CF} = 9.4 Hz), 128.99, 128.27, 126.88, 124.42 (d, J_{CF} = 3.0 Hz), 121.80 (d, J_{CF} = 14.4 Hz), 114.06 (d, J_{CF} = 22.3 Hz), 35.32 (d, J_{CF} = 4.1 Hz), 20.49. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.12. **HRMS (ESI)** calcd for $C_{21}H_{18}FN_3ONa$ $[M+Na]^+$: 370.1326, found: 370.1335. **FTIR** (KBr, cm^{-1}) 2959.81, 2833.64, 2715.89, 1597.20, 1364.49, 1072.90, 781.31.

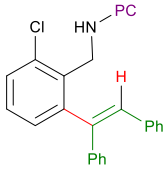


(*E*)-*N*-((3-(1,2-Diphenylvinyl)furan-2-yl)methyl)pyrazine-2-carboxamide (3j) Following **the general procedure 1**, 3j was obtained as a yellow solid (30.3 mg, 53% yield, m.p. = 143.2 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (d, *J* = 1.1 Hz, 1H), 8.72 (d, *J* = 2.4 Hz, 1H), 8.53 – 8.47 (m, 1H), 7.78 (s, 1H), 7.36 (d, *J* = 1.9 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.29 – 7.26 (m, 2H), 7.14 – 7.08 (m, 3H), 7.03 – 7.00 (m, 2H), 6.80 (s, 1H), 6.41 (d, *J* = 1.9 Hz, 1H), 4.31 (d, *J* = 5.8 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.49, 147.39, 147.25, 144.51, 144.33, 142.49, 141.75, 139.85, 136.73, 133.85, 129.67, 129.38, 128.88, 128.78, 128.00, 127.88, 126.87, 126.37, 111.45, 35.55. **HRMS (ESI)** calcd for $C_{24}H_{19}N_3O_2Na$ $[M+Na]^+$: 404.1369, found: 404.1366. **FTIR** (KBr, cm^{-1}) 2957.01, 2830.84, 2718.69, 1602.80, 1367.29, 1070.09, 784.11.

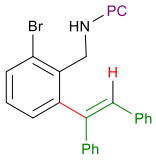


(*E*)-*N*-((3-(1,2-Diphenylvinyl) thiophen-2-yl) methyl) pyrazine-2-carboxamide (3k) Following **the general procedure 1**, **3k** was obtained as a yellow solid (48.8 mg, 82% yield, m.p. = 50.3 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (d, *J* = 1.4 Hz, 1H), 8.73 (d, *J* = 2.4 Hz, 1H), 8.50 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.85 (s, 1H), 7.32 – 7.26 (m, 3H), 7.25 – 7.21 (m, 2H), 7.19 – 7.12 (m, 4H), 7.07 (dd, *J* = 7.3, 2.0 Hz, 2H), 6.90 (d, *J* = 5.2 Hz, 1H), 6.75 (s,

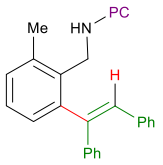
1H), 4.64 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.53, 147.30, 144.48, 144.25, 142.74, 142.51, 140.24, 136.82, 136.71, 136.23, 130.59, 129.77, 129.44, 128.72, 128.08, 127.71, 127.05, 123.64, 36.93. **HRMS (ESI)** calcd for $C_{24}H_{19}N_3OSNa$ $[M+Na]^+$: 420.1141, found: 420.1145. **FTIR** (KBr, cm^{-1}) 2951.40, 2825.23, 2718.69, 1602.80, 1372.90, 1199.07, 1075.70, 778.50, 551.40.



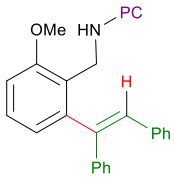
(*E*)-*N*-(2-Chloro-6-(1,2-diphenylvinyl)benzyl)pyrazine-2-carboxamide (3l) Following **the general procedure 1**, **3l** was obtained as a white solid (47.2 mg, 74% yield, m.p. = 151.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.67 (d, *J* = 2.1 Hz, 1H), 8.40 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.37 (s, 1H), 7.36 – 7.28 (m, 2H), 7.20 – 7.10 (m, 9H), 7.03 (t, *J* = 7.1 Hz, 1H), 6.69 (s, 1H), 4.70 (d, *J* = 5.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.99, 147.24, 147.00, 144.37, 144.30, 142.23, 141.03, 139.61, 136.59, 136.03, 132.96, 131.60, 129.76, 129.56, 129.40, 129.29, 129.08, 128.59, 128.15, 127.60, 127.33, 39.33. **HRMS (ESI)** calcd for $C_{26}H_{20}ClN_3ONa$ $[M+Na]^+$: 448.1187, found: 448.1190. **FTIR** (KBr, cm^{-1}) 2959.95, 2830.97, 2716.02, 1605.75, 1359.03, 1078.65, 778.66.



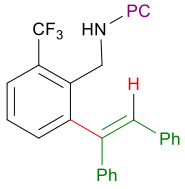
(*E*)-*N*-(2-Bromo-6-(1,2-diphenylvinyl)benzyl)pyrazine-2-carboxamide (3m) Following **the general procedure 1**, **3m** was obtained as a white solid (35.2 mg, 50% yield, m.p. = 143.6°C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.45 – 8.34 (m, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.34 (s, 1H), 7.25 – 7.21 (m, 1H), 7.19 – 7.09 (m, 9H), 7.01 (t, *J* = 7.1 Hz, 1H), 6.67 (s, 1H), 4.70 (d, *J* = 5.2 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.95, 147.42, 146.99, 144.34, 144.29, 142.22, 141.17, 139.56, 136.55, 134.49, 132.71, 131.57, 130.23, 129.75, 129.41, 129.38, 128.56, 128.14, 127.57, 127.33, 126.52, 41.94. **HRMS (ESI)** calcd for $C_{26}H_20BrN_3ONa$ $[M+Na]^+$: 492.0682, found: 492.0700. **FTIR** (KBr, cm^{-1}) 2959.95, 2830.97, 2716.02, 1605.75, 1359.03, 1078.65, 778.66.



(*E*)-*N*-(2-(1,2-Diphenylvinyl)-6-methylbenzyl)pyrazine-2-carboxamide (3n) Following **the general procedure 1**, **3n** was obtained as a white solid (35.9 mg, 59% yield, m.p. = 154.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.67 (d, *J* = 2.4 Hz, 1H), 8.37 (dd, *J* = 2.3, 1.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.23 – 7.09 (m, 11H), 7.04 – 6.99 (m, 1H), 6.70 (s, 1H), 4.56 (d, *J* = 5.4 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.08, 146.95, 145.67, 144.35, 144.20, 142.47, 142.17, 140.31, 138.59, 136.96, 133.15, 130.73, 130.33, 129.71, 129.37, 128.79, 128.55, 128.09, 127.99, 127.37, 127.08, 38.94, 19.60. **HRMS (ESI)** calcd for $C_{27}H_{23}N_3ONa$ $[M+Na]^+$: 428.1733, found: 428.1732. **FTIR** (KBr, cm^{-1}) 2954.21, 2828.04, 2713.08, 1611.21, 1370.09, 1075.70, 778.50.

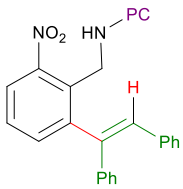


(*E*)-*N*-(2-(1,2-diphenylvinyl)-6-methoxybenzyl)pyrazine-2-carboxamide (3o) Following **the general procedure 1**, **3o** was obtained as a yellow solid (53.7 mg, 85% yield, m.p. = 123.9 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31 (d, *J* = 1.3 Hz, 1H), 8.67 (d, *J* = 2.4 Hz, 1H), 8.45 – 8.38 (m, 1H), 7.62 (s, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 3H), 7.13 (t, *J* = 8.1 Hz, 6H), 7.03 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.66 (s, 1H), 4.64 (d, *J* = 5.4 Hz, 2H), 3.87 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.90, 158.56, 146.74, 146.27, 144.88, 144.31, 142.25, 141.36, 140.14, 136.97, 131.07, 129.77, 129.41, 128.69, 128.37, 128.04, 127.25, 127.01, 123.55, 123.07, 109.93, 55.80, 36.32. **HRMS (ESI)** calcd for $C_{27}H_{23}N_3O_2Na$ $[M+Na]^+$: 444.1682, found: 444.1688. **FTIR** (KBr, cm^{-1}) 2954.21, 2828.04, 2713.08, 1602.80, 1370.09, 1070.09, 775.70.

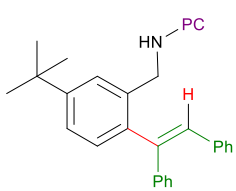


(*E*)-*N*-(2-(1,2-Diphenylvinyl)-6-(trifluoromethyl)benzyl)pyrazine-2-carboxamide (3p) Following **the general procedure 1**, **3p** was obtained as a yellow solid (28.9 mg, 42% yield, m.p. = 121.1°C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.28 (d, *J* = 1.2 Hz, 1H), 8.69 (d, *J* = 2.4

Hz, 1H), 8.39 (dd, *J* = 2.3, 1.5 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.18 – 7.13 (m, 5H), 7.12 – 7.04 (m, 4H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.66 (s, 1H), 4.72 (d, *J* = 5.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.68, 147.51, 147.03, 144.27, 142.24, 140.50, 138.78, 136.41, 134.98, 133.14, 132.08, 130.56 (q, J_{CF} = 30.1 Hz), 129.59, 129.30, 128.46, 128.27, 128.14, 127.62, 127.41, 125.86 (q, J_{CF} = 5.9 Hz), 124.21 (d, J_{CF} = 274.3 Hz), 38.11. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -58.66. **HRMS (ESI)** calcd for $C_{27}H_{20}F_3N_3ONa$ $[M+Na]^+$: 482.1451, found: 482.1457. **FTIR** (KBr, cm^{-1}) 2963.28,2831.62, 2725.18, 1601.88, 1360.98, 1192.91, 1078.05, 775.52, 565.43.

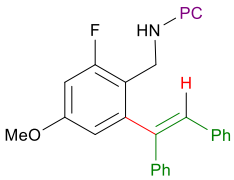


(*E*)-*N*-(2-(1,2-Diphenylvinyl)-6-nitrobenzyl)pyrazine-2-carboxamide (3q) Following **the general procedure 1**, **3q** was obtained as a yellow solid (28.1 mg, 43% yield, m.p. = 80.6 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.29 (d, *J* = 1.3 Hz, 1H), 8.71 (d, *J* = 2.4 Hz, 1H), 8.52 – 8.43 (m, 1H), 8.05 (s, 1H), 7.85 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.21 – 7.15 (m, 5H), 7.15 – 7.08 (m, 3H), 6.66 (s, 1H), 4.80 (d, *J* = 5.8 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.21, 151.33, 147.68, 147.19, 144.29, 144.21, 142.51, 139.38, 138.91, 136.26, 135.45, 133.02, 130.03, 129.82, 129.41, 128.60, 128.52, 128.20, 127.85, 127.58, 123.86, 37.96. **HRMS (ESI)** calcd for $C_{26}H_{20}N_4O_3Na$ $[M+Na]^+$: 459.1428, found: 459.1426. **FTIR** (KBr, cm^{-1}) 2954.21, 2833.64, 2715.89, 1600.00, 1361.8, 1081.31, 775.70, 573.83.

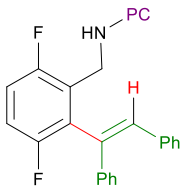


(*E*)-*N*-(5-(Tert-butyl)-2-(1,2-diphenylvinyl)benzyl)pyrazine-2-carboxamide (3r) Following **the general procedure 1** at the conditions of 140°C, **3r** was obtained as a white solid (61.0 mg, 91% yield, m.p. = 138.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.72 – 8.65 (m, 1H), 8.43 (s, 1H), 7.69 (s, 1H), 7.40 (s, 1H), 7.34 (q, *J* = 8.2 Hz, 2H), 7.22 – 7.13 (m, 8H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.71 (s, 1H), 4.44 (d, *J* = 5.8

Hz, 2H), 1.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.30, 151.22, 147.02, 144.61, 144.38, 142.31, 141.88, 141.14, 139.95, 137.08, 134.96, 130.92, 130.63, 129.78, 129.41, 128.51, 128.06, 127.49, 127.07, 127.01, 124.81, 42.19, 34.60, 31.36. **HRMS (ESI)** calcd for $C_{30}H_{29}N_3ONa$ $[M+Na]^+$: 470.2203, found: 470.2196. **FTIR** (KBr, cm^{-1}) 2965.42, 2836.45, 2721.50, 1591.59, 1364.49, 1070.09, 775.70.

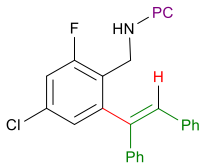


(*E*)-*N*-(2-(1,2-Diphenylvinyl)-6-fluoro-4-methoxybenzyl)pyrazine-2-carboxamide (3s) Following **the general procedure 1** at the conditions of 140°C, **3s** was obtained as a white solid (42.2 mg, 65% yield, m.p. = 152.9 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.44 – 8.37 (m, 1H), 7.44 (s, 1H), 7.23 – 7.14 (m, 7H), 7.14 – 7.06 (m, 3H), 6.78 (d, *J* = 2.0 Hz, 1H), 6.72 (s, 1H), 6.65 (dd, *J* = 11.4, 2.5 Hz, 1H), 4.49 (d, *J* = 4.5 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.44 (d, J_{CF} = 247.2 Hz), 161.97, 160.04 (d, J_{CF} = 12.4 Hz), 147.26 (d, J_{CF} = 5.3 Hz), 146.95, 144.48, 144.28, 142.26, 140.75 (d, J_{CF} = 3.0 Hz), 139.35, 136.54, 131.46, 129.68, 129.41, 128.61, 128.13, 127.67, 127.33, 114.74 (d, J_{CF} = 15.6 Hz), 112.51 (d, J_{CF} = 2.4 Hz), 100.95 (d, J_{CF} = 26.5 Hz), 55.67, 34.68 (d, J_{CF} = 4.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.59. **HRMS (ESI)** calcd for $C_{27}H_{22}FN_3O_2Na$ $[M+Na]^+$: 462.1588, found: 462.1585. **FTIR** (KBr, cm^{-1}) 2954.21, 2828.04, 2718.69, 1600.00, 1364.49, 1072.90, 775.70.

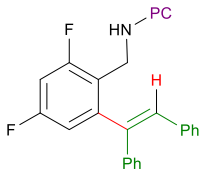


(*E*)-*N*-(2-(1,2-Diphenylvinyl)-3,6-difluorobenzyl)pyrazine-2-carboxamide (3t) Following **the general procedure 1** at the conditions of 140°C, **3t** was obtained as a white solid (59.6 mg, 93% yield, m.p. = 125.1 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 1.3 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.41 (dd, *J* = 2.3, 1.6 Hz, 1H), 7.71 (s, 1H), 7.24 – 7.21 (m, 2H), 7.20 – 7.11 (m, 8H), 7.11 – 7.03 (m, 2H), 6.71 (s, 1H), 4.69 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.13, 157.60 (dd, J_{CF} = 244.4, 2.4 Hz), 156.29 (dd, J_{CF} = 241.5, 2.3 Hz), 147.17, 144.40, 144.29, 142.30, 138.63, 136.10, 133.73, 133.45 (dd,

J_{CF} = 19.0, 3.5 Hz), 133.02 (d, J_{CF} = 1.6 Hz), 129.43, 129.36, 128.54, 128.17, 127.69, 127.57, 124.65 (dd, J_{CF} = 16.7, 2.2 Hz), 116.30 (dd, J_{CF} = 26.0, 9.3 Hz), 115.67 (dd, J_{CF} = 25.2, 8.7 Hz), 35.02 (d, J_{CF} = 5.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.83 (d, J_{FF} = 17.5 Hz), -120.62 (d, J_{FF} = 17.5 Hz). **HRMS (ESI)** calcd for $C_{26}H_{19}F_2N_3ONa$ $[M+Na]^+$: 450.1388, found: 450.1381. **FTIR** (KBr, cm^{-1}) 2957.01, 2839.25, 2715.89, 1608.41, 1358.88, 1078.50, 775.70.

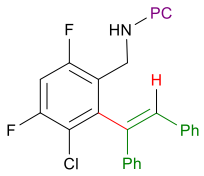


(*E*)-*N*-(4-Chloro-2-(1,2-diphenylvinyl)-6-fluorobenzyl)pyrazine-2-carboxamide (3u) Following **the general procedure 1** at the conditions of 140°C, **3u** was obtained as a white solid (54.5 mg, 82% yield, m.p. = 224.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.70 (d, J = 2.4 Hz, 1H), 8.45 – 8.40 (m, 1H), 7.52 (s, 1H), 7.24 – 7.17 (m, 8H), 7.16 – 7.09 (m, 4H), 6.71 (s, 1H), 4.52 (d, J = 5.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.08, 161.61 (d, J_{CF} = 251.4 Hz), 147.68 (d, J_{CF} = 4.2 Hz), 147.14, 144.36, 144.27, 142.27, 139.46 (d, J_{CF} = 2.7 Hz), 138.92, 136.20, 134.26 (d, J_{CF} = 12.0 Hz), 132.35, 129.69, 129.43, 128.77, 128.19, 127.94, 127.58, 126.69 (d, J_{CF} = 3.1 Hz), 121.69 (d, J_{CF} = 15.0 Hz), 115.67 (d, J_{CF} = 26.4 Hz), 34.61 (d, J_{CF} = 4.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.92. **HRMS (ESI)** calcd for $C_{26}H_{19}ClFN_3ONa$ $[M+Na]^+$: 466.1093, found: 466.1088. **FTIR** (KBr, cm^{-1}) 2968.22, 2830.84, 2715.89, 1594.39, 1367.29, 1081.31, 778.50.

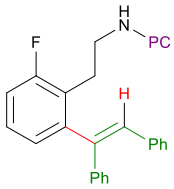


(*E*)-*N*-(2-(1,2-Diphenylvinyl)-4,6-difluorobenzyl)pyrazine-2-carboxamide (3v) Following **the general procedure 1** at the conditions of 140°C, **3v** was obtained as a white solid (46.1 mg, 72% yield, m.p. = 139.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.70 (d, J = 2.3 Hz, 1H), 8.42 (s, 1H), 7.51 (s, 1H), 7.22 – 7.16 (m, 7H), 7.15 – 7.09 (m, 3H), 6.96 (d, J = 8.8 Hz, 1H), 6.87 – 6.81 (m, 1H), 6.71 (s, 1H), 4.53 (d, J = 5.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) 162.05, 162.03 (dd, J_{CF} = 250.1, 8.0 Hz), 161.92 (dd, J_{CF} = 250.1, 7.0 Hz), 147.86 (dd, J_{CF} = 9.1, 4.9 Hz), 147.09, 144.35, 144.30,

142.25, 139.69, 138.97, 136.19, 132.20, 129.65, 129.41, 128.73, 128.17, 127.90, 127.55, 119.00 (dd, J_{CF} = 15.1, 3.9 Hz), 113.68 (dd, J_{CF} = 21.3, 3.2 Hz), 103.29 (dd, J_{CF} = 26.5, 25.4 Hz), 34.56 (d, J_{CF} = 4.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.38 (d, J_{FF} = 8.2 Hz), -111.18 (d, J_{FF} = 8.1 Hz). **HRMS (ESI)** calcd for $C_{26}H_{19}F_2N_3ONa$ $[M+Na]^+$: 450.1388, found: 450.1381. **FTIR** (KBr, cm^{-1}) 2965.42, 2828.04, 2713.08, 1600.00, 1361.68, 1075.70, 772.90.

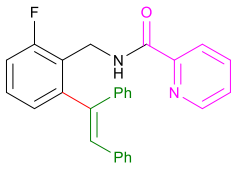


(*E*)-*N*-(3-chloro-2-(1,2-diphenylvinyl)-4,6-difluorobenzyl)pyrazine-2-carboxamide (3w) Following **the general procedure 1** at the conditions of 140°C, **3w** was obtained as a white solid (48.4 mg, 70% yield, m.p. = 161.1 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.32 (d, J = 1.2 Hz, 1H), 8.70 (d, J = 2.4 Hz, 1H), 8.45 – 8.33 (m, 1H), 7.61 (s, 1H), 7.24 – 7.18 (m, 7H), 7.18 – 7.10 (m, 3H), 6.99 (t, J = 8.9 Hz, 1H), 6.68 (s, 1H), 4.73 – 4.59 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.10, 159.92 (dd, J_{CF} = 236.0, 11.9 Hz), 157.92 (dd, J_{CF} = 238.0, 12.8 Hz), 147.20, 145.99 (d, J_{CF} = 4.6 Hz), 144.34, 144.17, 142.28, 137.43, 135.99, 135.58 (t, J_{CF} = 2.1 Hz), 133.79, 129.42, 129.38, 128.55, 128.30, 127.94, 127.78, 120.76 (dd, J_{CF} = 15.7, 4.1 Hz), 117.67 (dd, J_{CF} = 16.9, 4.2 Hz), 104.35 (dd, J_{CF} = 27.8, 25.4 Hz), 35.00 (d, J_{CF} = 3.7 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -107.72 (d, J_{FF} = 8.0 Hz), -112.71 (d, J_{FF} = 8.0 Hz). **HRMS (ESI)** calcd for $C_{26}H_{18}ClF_2N_3ONa$ $[M+Na]^+$: 484.0999, found: 484.0992. **FTIR** (KBr, cm^{-1}) 2957.01, 2828.04, 2724.30, 1608.41, 1370.09, 1207.48, 1070.09, 772.90, 565.42.

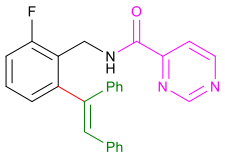


(*E*)-*N*-(2-(1,2-Diphenyl vinyl)-6-fluoro phenethyl) pyrazine-2-carboxamide (3x) Following **the general procedure 1** at the conditions of 140°C, **3x** was obtained as a yellow liquid (17.1 mg, 27% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.71 (d, J = 2.3 Hz, 1H), 8.48 (s, 1H), 7.67 (s, 1H), 7.28 – 7.20 (m, 4H), 7.20 – 7.13 (m, 6H), 7.09 – 7.00 (m, 3H), 6.65 (s, 1H), 3.38 (q, J = 6.8 Hz, 2H), 2.87 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.71, 161.84 (d, J_{CF} = 245.2 Hz), 147.06, 146.53 (d, J_{CF}

= 4.1 Hz), 144.53, 144.37, 142.47, 141.33 (d, J_{CF} = 2.5 Hz), 139.79, 136.72, 131.20, 129.80, 129.38, 128.47, 128.11, 127.80 (d, J_{CF} = 9.2 Hz), 127.69, 127.16, 126.54 (d, J_{CF} = 2.9 Hz), 124.36 (d, J_{CF} = 15.5 Hz), 114.66 (d, J_{CF} = 23.1 Hz), 38.94, 26.62 (d, J_{CF} = 2.1 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.34. **HRMS (ESI)** calcd for $C_{27}H_{22}FN_3ONa$ $[M+Na]^+$: 446.1639, found: 446.1634. **FTIR** (KBr, cm^{-1}) 2959.81, 2833.64, 2724.30,1600.00, 1370.09, 1070.09, 775.70.

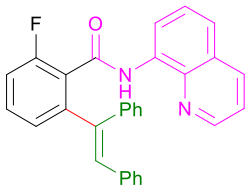


(*E*)-*N*-(2-(1,2-Diphenylvinyl)-6-fluorobenzyl) picolinamide (3aa) Following **the general procedure 1**, **3aa** was obtained as a yellow solid (59.4 mg, 97% yield, m.p. = 45.3 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (d, J = 4.1 Hz, 1H), 8.12 (d, J = 7.3 Hz, 1H), 7.93 (s, 1H), 7.76 (t, J = 7.7 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.32 – 7.26 (m, 1H), 7.24 – 7.10 (m, 11H), 7.05 (t, J = 8.9 Hz, 1H), 6.71 (s, 1H), 4.58 (d, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.46, 161.83 (d, J_{CF} = 247.9 Hz), 149.87, 147.85, 146.76 (d, J_{CF} = 3.4 Hz), 140.67 (d, J_{CF} = 2.5 Hz), 139.55, 137.16, 136.77, 131.62, 129.78, 129.49, 128.99 (d, J_{CF} = 9.3 Hz), 128.58, 128.09, 127.65, 127.20, 126.48 (d, J_{CF} = 2.9 Hz), 125.97, 123.29 (d, J_{CF} = 14.8 Hz), 122.16, 114.91 (d, J_{CF} = 22.8 Hz), 34.95 (d, J_{CF} = 4.8 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.60. **HRMS (ESI)** calcd for $C_{27}H_{21}FN_2ONa$ $[M+Na]^+$: 431.1530, found: 431.1531. **FTIR** (KBr, cm^{-1}) 2957.01, 2828.04, 2718.69, 1600.00, 1364.49, 1210.28, 1078.50, 778.50, 576.64.



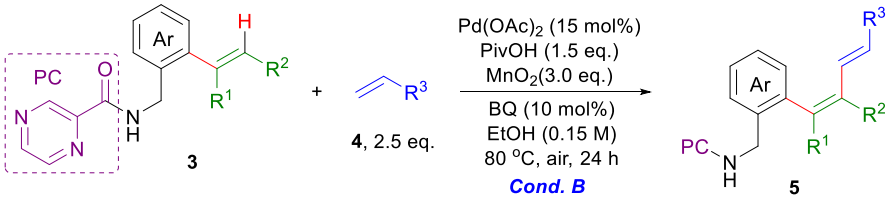
(*E*)-*N*-(2-(1,2-Diphenylvinyl)-6-fluorobenzyl)pyrimidine-4-carb oxamide (3bb) Following **the general procedure 1**, **3bb** was obtained as a yellow liquid (54.6 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.06 – 9.01 (m, 1H), 8.81 (d, J = 5.0 Hz, 1H), 7.94 (dd, J = 5.0, 1.4 Hz, 1H), 7.68 (s, 1H), 7.27 – 7.19 (m, 1H), 7.13 – 7.09 (m, 5H), 7.09 – 7.06 (m, 3H), 7.05 – 7.02 (m, 3H), 6.99 (t, J = 8.9 Hz, 1H), 6.62 (s, 1H), 4.48 (d, J = 6.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.78 (d, J_{CF} = 248.1 Hz), 161.68, 159.05, 157.52, 156.15, 146.78 (d, J_{CF} = 3.3 Hz), 140.52 (d, J_{CF} = 2.6 Hz), 139.52, 136.60, 131.73,

129.73, 129.44, 129.31 (d, J_{CF} = 9.4 Hz), 128.66, 128.15, 127.76, 127.34, 126.58 (d, J_{CF} = 3.0 Hz), 122.58 (d, J_{CF} = 14.8 Hz), 118.49, 115.00 (d, J_{CF} = 22.7 Hz), 35.12 (d, J_{CF} = 4.9 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.66. **HRMS (ESI)** calcd for $C_{26}H_{20}FN_3ONa$ $[M+Na]^+$: 432.1483, found: 432.1480. **FTIR** (KBr, cm^{-1}) 2962.62, 2828.04, 2721.50, 1600.00, 1370.09, 1075.70, 772.90.



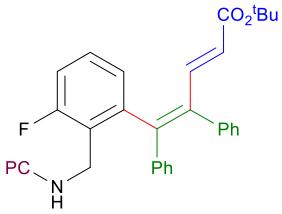
(*E*)-2-(1,2-diphenylvinyl)-6-fluoro-*N*-(quinolin-8-yl)benzamide (3dd) Following **the general procedure 1**, **3dd** was obtained as a white solid (40.3 mg, 91% yield, m.p. = 89.4 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.74 (dd, J = 4.2, 1.7 Hz, 1H), 8.60 (dd, J = 6.2, 2.7 Hz, 1H), 8.12 (dd, J = 8.3, 1.7 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.25 (d, J = 1.0 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.15 – 7.08 (m, 2H), 7.04 – 6.96 (m, 7H), 6.94 – 6.89 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.81, 159.66 (d, J_{CF} = 249.6 Hz), 147.99, 144.95 (d, J_{CF} = 2.9 Hz), 140.47 (d, J_{CF} = 2.2 Hz), 139.14, 138.31, 136.88, 136.19, 134.27, 131.54, 130.68 (d, J_{CF} = 8.9 Hz), 130.45, 129.36, 128.07, 127.80, 127.76, 127.27, 126.96, 126.21 (d, J_{CF} = 3.0 Hz), 125.53, 125.40, 121.67, 121.49, 116.66, 115.20 (d, J_{CF} = 22.2 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.37. **HRMS (ESI)** calcd for $C_{30}H_{21}FN_2ONa$ $[M+Na]^+$: 467.1530, found: 467.1531. **FTIR** (KBr, cm^{-1}) 3453.27, 2954.21, 2833.64, 2713.08, 2345.79, 1605.61, 1347.66, 1067.29, 772.90.

3.2 General Procedure 2 for Olefinic C-H Alkenylation

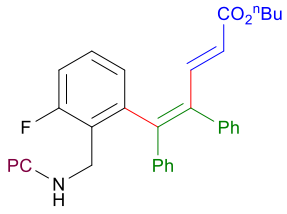


A screw-cap vial was charged with $Pd(OAc)_2$ (5.1 mg, 0.0225 mmol, 15 mol%), MnO_2 (39.1 mg, 0.45 mmol, 3.0 equiv), BQ (1.6 mg, 0.015 mmol, 10 mol%), amide **3** (0.15 mmol, 1.0 equiv), EtOH (1.0 mL). Then, pivalic acid (23.0 mg, 0.18 mmol, 1.5

equiv), and olefin **2** (48.1 mg, 0.375 mmol, 2.5 equiv) were added into the solution in sequence. The vial was sealed under air and heated to 80 ºC with stirring for 24 h. After cooling down, the mixture was concentrated and directly applied to a flash column chromatography (PE/EA mixtures) to obtain the diene product **5**.

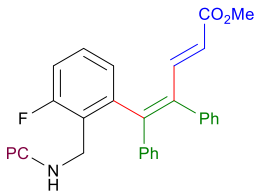


Tert-butyl(2*E*,4*E*)-5-(3-fluoro-2-((pyrazine-2-carboxamido) methyl)phenyl)-4,5-diphenylpenta-2,4-dienoate (5a) Following **the general procedure 2**, **5a** was obtained as a white solid (73.9 mg, 92% yield, *E/Z* > 99:1, m.p. = 81.3 ºC). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 1.3 Hz, 1H), 8.67 (d, *J* = 2.4 Hz, 1H), 8.42 – 8.37 (m, 1H), 7.59 (s, 1H), 7.44 – 7.38 (m, 1H), 7.28 (d, *J* = 5.7 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.20 – 7.14 (m, 4H), 7.00 – 6.91 (m, 5H), 5.47 (d, *J* = 15.5 Hz, 1H), 4.68 – 4.54 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.24, 162.18 (d, J_{CF} = 248.6 Hz), 162.05, 146.98, 145.11 (d, J_{CF} = 2.3 Hz), 144.36, 144.26, 143.83, 143.33 (d, J_{CF} = 3.6 Hz), 142.29, 140.02, 139.22, 138.02, 130.84, 130.35, 129.55 (d, J_{CF} = 9.3 Hz), 128.40, 127.72, 127.42, 127.34, 127.21 (d, J_{CF} = 3.0 Hz), 124.49, 123.43 (d, J_{CF} = 15.1 Hz), 115.60 (d, J_{CF} = 22.3 Hz), 80.21, 35.00 (d, J_{CF} = 4.1 Hz), 28.04. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.70. **HRMS (ESI)** calcd for $C_{33}H_{30}FN_3O_3Na$ $[M+Na]^+$: 558.2163, found: 558.2164. **FTIR** (KBr, cm^{-1}) 2957.01, 2825.23, 2713.08, 1605.61, 1364.49, 1067.29, 778.50.

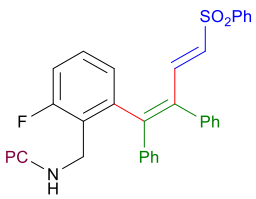


Butyl (2*E*,4*E*)-5-(3-fluoro-2-((pyrazine-2-carboxamido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5b) Following **the general procedure 2**, **5b** was obtained as a yellow solid (70.6 mg, 88% yield, *E/Z* > 99:1, m.p. = 63.9 ºC). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.70 – 8.63 (m, 1H), 8.39 (s, 1H), 7.61 (s, 1H), 7.43 – 7.38 (m, 1H), 7.35 (d, *J* = 15.5 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.21 – 7.13 (m, 4H), 7.01 – 6.94 (m, 3H), 6.94 – 6.91 (m, 2H), 5.55 (d, *J* = 15.6 Hz, 1H), 4.62 (d, *J* = 5.6 Hz, 2H), 4.01 – 3.91 (m, 2H), 1.53 – 1.44 (m, 2H), 1.30 – 1.20 (m, 2H), 0.86 (t,

J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.89, 161.15 (d, J_{CF} = 248.8 Hz), 161.02, 145.96, 144.51 (d, J_{CF} = 2.2 Hz), 143.78, 143.28, 143.23, 142.24 (d, J_{CF} = 3.6 Hz), 141.22, 138.87, 138.13, 136.82, 129.79, 129.32, 128.54 (d, J_{CF} = 9.3 Hz), 127.42, 126.72, 126.49, 126.45, 126.14 (d, J_{CF} = 3.0 Hz), 122.47 (d, J_{CF} = 15.2 Hz), 121.61, 114.60 (d, J_{CF} = 22.4 Hz), 63.10, 33.98 (d, J_{CF} = 4.1 Hz), 29.52, 18.06, 12.63. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.54. **HRMS (ESI)** calcd for $C_{33}H_{30}FN_3O_3Na$ $[M+Na]^+$: 558.2163, found: 558.2169. **FTIR** (KBr, cm^{-1}) 2968.22, 2830.84, 2718.69, 1585.98, 1356.07, 1070.09, 784.11.

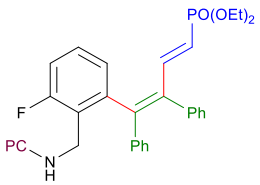


Methyl (2*E*,4*E*)-5-(3-fluoro-2-((pyrazine-2-carboxamido) methyl)phenyl)-4,5-diphenylpenta-2,4-dienoate (5c) Following **the general procedure 2**, **5c** was obtained as a white solid (66.6 mg, 90% yield, *E/Z*=97:3, m.p. = 57.1 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.25 (d, J = 1.3 Hz, 1H), 8.60 (d, J = 2.4 Hz, 1H), 8.33 – 8.30 (m, 1H), 7.52 (s, 1H), 7.38 – 7.30 (m, 1H), 7.26 (d, J = 15.6 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.19 – 7.15 (m, 2H), 7.13 – 7.08 (m, 3H), 7.06 (d, J = 7.4 Hz, 1H), 6.94 – 6.87 (m, 3H), 6.86 – 6.82 (m, 2H), 5.47 (d, J = 15.6 Hz, 1H), 4.59 – 4.47 (m, 2H), 3.48 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.25, 161.16 (d, J_{CF} = 248.8 Hz), 161.02, 145.97, 144.66 (d, J_{CF} = 2.3 Hz), 143.93, 143.29, 143.26, 142.15 (d, J_{CF} = 3.5 Hz), 141.20, 138.91, 138.13, 136.85, 129.81, 129.31, 128.59 (d, J_{CF} = 9.3 Hz), 127.41, 126.73, 126.51, 126.46, 126.18 (d, J_{CF} = 3.1 Hz), 122.48 (d, J_{CF} = 15.2 Hz), 121.33, 114.71 (d, J_{CF} = 22.3 Hz), 50.40, 33.97 (d, J_{CF} = 4.2 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.47. **HRMS (ESI)** calcd for $C_{30}H_{24}FN_3O_3Na$ $[M+Na]^+$: 516.1694, found: 516.1704. **FTIR** (KBr, cm^{-1}) 2954.34, 2836.58, 2718.83, 1600.15, 1373.04, 1073.05, 778.66.



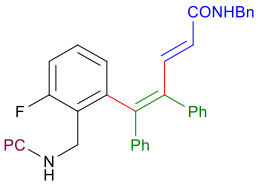
***N*-(2-((1*E*,3*E*)-1,2-Diphenyl-4-(phenylsulfonyl)buta-1,3-dien-1-yl)-6-fluorobenzyl)pyrazine-2-carboxamide (5d)** Following **the general procedure 1**, **5d** was obtained as a white solid

(64.7 mg, 75% yield, *E/Z*=99:1, m.p. = 62.3 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.71 (d, *J* = 2.4 Hz, 1H), 8.51 – 8.42 (m, 1H), 7.67 (d, *J* = 7.3 Hz, 3H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.25 (dd, *J* = 12.1, 2.3 Hz, 3H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.13 – 7.08 (m, 3H), 6.98 (d, *J* = 7.1 Hz, 3H), 6.93 – 6.87 (m, 2H), 6.05 (d, *J* = 15.0 Hz, 1H), 4.55 – 4.46 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.20 (d, J_{CF} = 249.1 Hz), 161.11, 146.93 (d, J_{CF} = 2.3 Hz), 146.22, 143.21, 143.14, 141.70, 141.53 (d, J_{CF} = 3.6 Hz), 141.47, 139.46, 138.38, 136.11 (d, J_{CF} = 6.5 Hz), 132.23, 130.46, 129.63, 129.35, 128.60 (d, J_{CF} = 9.2 Hz), 128.16, 127.65, 126.88 (d, J_{CF} = 3.7 Hz), 126.81, 126.44, 126.21 (d, J_{CF} = 3.0 Hz), 122.66 (d, J_{CF} = 15.2 Hz), 115.19 (d, J_{CF} = 22.4 Hz), 33.79 (d, J_{CF} = 4.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.15. **HRMS (ESI)** calcd for $C_{34}H_{26}FN_3O_3SNa$ $[M+Na]^+$: 598.1571, found: 598.1561. **FTIR** (KBr, cm^{-1}) 2954.21, 2833.64, 2721.50, 1597.20, 1370.09, 1072.90, 772.90.

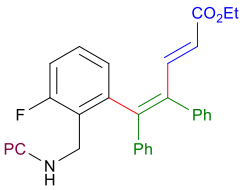


Diethyl((1*E*,3*E*)-4-(3-fluoro-2-((pyrazine-2-carboxamido)methyl) phenyl)-3,4-diphenyl buta-1,3-dien-1-yl) phosphonate (5e) Following **the general procedure 2**, **5e** was obtained as a yellow liquid (43.7 mg, 51% yield, *E/Z* > 99:1,). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.69 (d, *J* = 2.4 Hz, 1H), 8.48 – 8.41 (m, 1H), 7.59 (s, 1H), 7.44 – 7.38 (m, 1H), 7.31 – 7.27 (m, 1H), 7.27 – 7.21 (m, 2H), 7.19 – 7.14 (m, 4H), 7.09 (dd, *J* = 21.8, 17.1 Hz, 1H), 7.01 – 6.88 (m, 5H), 5.47 (dd, *J* = 19.7, 17.1 Hz, 1H), 4.56 (d, *J* = 5.6 Hz, 2H), 3.96 – 3.85 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.21 (d, J_{CF} = 248.9 Hz), 162.07, 147.64 (d, J_{CP} = 8.1 Hz), 147.08, 144.87, 144.27, 144.23, 143.11 (d, J_{CF} = 3.5 Hz), 142.39, 139.90 (d, J_{CF} = 2.0 Hz), 139.53 (d, J_{CP} = 24.5 Hz), 137.58, 130.95, 130.32, 129.49 (d, J_{CF} = 9.3 Hz), 128.47, 127.77, 127.52 (d, J_{CF} = 17.2 Hz), 127.42, 127.40, 123.57 (d, J_{CF} = 15.1 Hz), 119.05 (d, J_{CP} = 190.2 Hz), 115.70 (d, J_{CF} = 22.4 Hz), 61.70 (t, J_{CP} = 6.2 Hz), 34.93 (d, J_{CF} = 4.1 Hz), 16.24 (dd, J_{CP} = 6.4, 3.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.38. **^{31}P NMR** (202 MHz, $CDCl_3$) δ 19.29. **HRMS (ESI)** calcd for $C_{32}H_{31}FN_3O_4PNa$ $[M+Na]^+$: 594.1928, found: 594.1924. **FTIR** (KBr, cm^{-1}) 2968.22,

2833.64, 2724.30, 1602.80, 1361.68, 1086.92, 775.70.

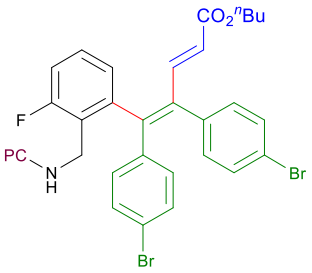


_N_-(2-((1*E*,3*E*)-5-(Benzylamino)-5-oxo-1,2-diphenylpenta-1,3-dien-1-yl)-6-fluorobenzyl)pyrazine-2-carboxamide (5f) Following **the general procedure 2** use methanol instead of ethanol, **5f** was obtained as a white solid (77.6 mg, 91% yield, *E*/*Z*=96:4, m.p. = 81.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.26 (d, *J* = 1.2 Hz, 1H), 8.57 (d, *J* = 2.4 Hz, 1H), 8.35 – 8.27 (m, 1H), 7.63 (s, 1H), 7.42 – 7.37 (m, 1H), 7.35 (d, *J* = 15.1 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.26 – 7.20 (m, 4H), 7.20 – 7.11 (m, 6H), 6.99 – 6.88 (m, 5H), 5.67 (s, 1H), 5.46 (d, *J* = 15.1 Hz, 1H), 4.67 (dd, *J* = 14.3, 6.3 Hz, 1H), 4.55 (dd, *J* = 14.4, 4.6 Hz, 1H), 4.37 – 4.27 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.46, 162.25 (d, J_{CF} = 248.5 Hz), 162.10, 146.88, 144.60 (d, J_{CF} = 2.1 Hz), 144.38, 144.10, 143.28 (d, J_{CF} = 3.6 Hz), 142.37, 141.74, 140.21, 139.10, 138.42, 138.09, 130.88, 130.31, 129.67 (d, J_{CF} = 9.3 Hz), 128.68, 128.35, 127.95, 127.68, 127.28 (d, J_{CF} = 14.5 Hz), 127.20, 127.17, 124.98, 123.37 (d, J_{CF} = 15.0 Hz), 115.59 (d, J_{CF} = 22.3 Hz), 43.68, 35.15 (d, J_{CF} = 3.8 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.65. **HRMS (ESI)** calcd for $C_{36}H_{29}FN_4O_2Na$ $[M+Na]^+$: 591.2167, found: 591.2165. **FTIR** (KBr, cm^{-1}) 2954.21, 2830.84, 2715.89, 1600.00, 1361.68, 1075.70, 778.50.

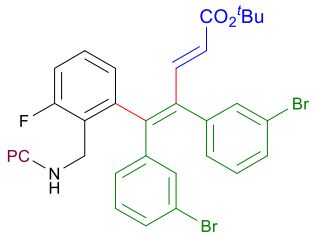


Ethyl (2*E*,4*E*)-5-(3-fluoro-2-((pyrazine-2-carboxamido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5g) Following **the general procedure 2**, **5g** was obtained as a yellow liquid (54.0 mg, 71% yield, *E*/*Z*=98:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.67 (d, *J* = 2.3 Hz, 1H), 8.42 – 8.37 (m, 1H), 7.61 (s, 1H), 7.44 – 7.38 (m, 1H), 7.35 (d, *J* = 15.5 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.21 – 7.13 (m, 4H), 7.01 – 6.90 (m, 5H), 5.55 (d, *J* = 15.5 Hz, 1H), 4.68 – 4.55 (m, 2H), 4.07 – 3.95 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.90, 162.19 (d, J_{CF} = 248.7 Hz), 162.06, 146.97, 145.57 (d, J_{CF} = 2.3 Hz), 144.81, 144.33,

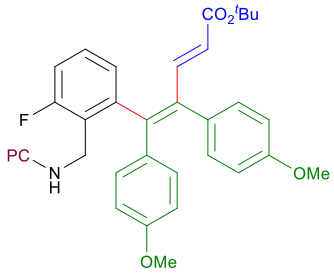
144.24, 143.21 (d, J_{CF} = 3.5 Hz), 142.27, 139.96, 139.18, 137.92, 130.83, 130.35, 129.59 (d, J_{CF} = 9.3 Hz), 128.44, 127.75, 127.51, 127.46, 127.22 (d, J_{CF} = 3.0 Hz), 123.48 (d, J_{CF} = 15.2 Hz), 122.69, 115.69 (d, J_{CF} = 22.3 Hz), 60.24, 53.45, 35.02 (d, J_{CF} = 4.1 Hz), 14.13. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.54. **HRMS (ESI)** calcd for $C_{31}H_{26}FN_3O_3Na$ $[M+Na]^+$: 530.1850, found: 530.1856. **FTIR** (KBr, cm^{-1}) 2965.42, 2830.84, 2724.30, 2351.40, 1608.41, 1372.90, 1061.68, 770.09, 568.22.



Butyl(2*E*,4*E*)-4,5-bis(4-bromophenyl)-5-(3-fluoro-2-(((phosphaneylmethyl)amino)methyl)phenyl)penta-2,4-dienoate (5h) Following **the general procedure 2** at the conditions of 110 °C, **5h** was obtained as a white solid (71.5 mg, 69% yield, *E*/*Z*=96:4, m.p. = 58.3 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.69 (d, *J* = 2.4 Hz, 1H), 8.46 – 8.39 (m, 1H), 7.52 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.28 (d, *J* = 15.6 Hz, 1H), 7.19 (t, *J* = 8.9 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 3H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.51 (d, *J* = 15.6 Hz, 1H), 4.65 (dd, *J* = 14.3, 6.3 Hz, 1H), 4.50 (dd, *J* = 14.4, 4.9 Hz, 1H), 4.01 – 3.92 (m, 2H), 1.54 – 1.46 (m, 2H), 1.31 – 1.22 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.65, 162.32 (d, J_{CF} = 249.1 Hz), 162.04, 147.16, 144.62 (d, J_{CF} = 2.2 Hz), 144.16 (d, J_{CF} = 14.9 Hz), 144.06, 142.53, 142.48, 138.72, 138.41, 136.52, 132.44, 131.94, 131.91, 131.21, 129.81 (d, J_{CF} = 9.3 Hz), 127.09 (d, J_{CF} = 2.9 Hz), 123.49 (d, J_{CF} = 15.3 Hz), 123.15, 122.11 (d, J_{CF} = 22.6 Hz), 116.02 (d, J_{CF} = 22.3 Hz), 64.31, 34.95 (d, J_{CF} = 3.8 Hz), 30.53, 19.09, 13.66. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.19. **HRMS (ESI)** calcd for $C_{33}H_{28}Br_2FN_3O_3$ $[M+Na]^+$: 714.0374, found: 714.0371. **FTIR** (KBr, cm^{-1}) 2948.60, 2828.04, 2718.69, 2357.01, 1597.20, 1361.68, 1084.11, 784.11.

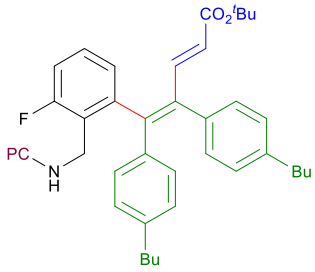


Ttert-butyl(2*E*,4*E*)-4,5-bis(3-bromophenyl)-5-(3-fluoro-2-((pyrazine-2-carboxamido)methyl)phenyl)penta-2,4-dienoate (5i) Following **the general procedure 2** at the conditions of 110 °C, **5i** was obtained as a white solid (78.8 mg, 76% yield, *E*/*Z*=93:7, m.p. = 56.5 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.69 (d, *J* = 2.3 Hz, 1H), 8.46 – 8.43 (m, 1H), 7.64 (s, 1H), 7.45 – 7.40 (m, 2H), 7.36 (s, 1H), 7.22 – 7.13 (m, 4H), 7.10 (d, *J* = 7.0 Hz, 1H), 7.09 – 7.06 (m, 1H), 7.03 (t, *J* = 1.7 Hz, 1H), 6.91 – 6.87 (m, 1H), 6.84 (t, *J* = 7.8 Hz, 1H), 5.45 (d, *J* = 15.6 Hz, 1H), 4.67 – 4.51 (m, 2H), 1.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.81, 162.22 (d, J_{CF} = 249.0 Hz), 162.04, 147.14, 144.26, 144.14, 144.03 (d, J_{CF} = 2.2 Hz), 142.81, 142.38, 142.05 (d, J_{CF} = 3.5 Hz), 141.67, 139.73, 138.74, 133.38, 132.95, 130.90, 130.64, 130.16, 129.86 (d, J_{CF} = 9.3 Hz), 129.53, 129.30, 128.97, 127.09 (d, J_{CF} = 3.2 Hz), 125.42, 123.48 (d, J_{CF} = 15.3 Hz), 122.44, 122.06, 116.09 (d, J_{CF} = 22.4 Hz), 80.58, 34.82 (d, J_{CF}= 4.3 Hz), 28.01. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.36. **HRMS (ESI)** calcd for $C_{33}H_{28}Br_2FN_3O_3Na$ $[M+Na]^+$: 714.0374, found: 714.0373. **FTIR** (KBr, cm^{-1}) 2965.42, 2833.64, 2715.89, 1602.80, 1356.07, 1072.90, 781.31.

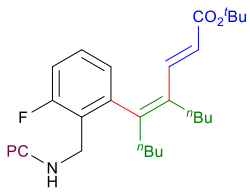


Tert-butyl(2*E*,4*E*)-5-(3-fluoro-2-((pyrazine-2-carboxamido) methyl) phenyl)-4,5-bis(4-methoxyphenyl) penta-2,4-dienoate (5j) Following **the general procedure 2** at the conditions of 110°C, **5j** was obtained as a white solid (59.8 mg, 67% yield, *E*/*Z*=98:2, m.p. = 116.6 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.66 (d, *J* = 2.3 Hz, 1H), 8.40 – 8.37 (m, 1H), 7.45 (s, 1H), 7.42 – 7.37 (m, 1H), 7.25 (d, *J* = 15.4 Hz, 1H), 7.14 – 7.08 (m, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 8.9 Hz, 2H), 5.48 (d, *J* = 15.4 Hz, 1H), 4.62 (dd, *J* = 14.3, 6.2 Hz, 1H), 4.51 (dd, *J* = 13.7, 4.6 Hz, 1H), 3.81 (s, 3H), 3.59 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.45, 162.15 (d, J_{CF} = 248.8 Hz), 161.99, 158.71 (d, J_{CF} = 12.3 Hz), 146.90, 144.53,

144.37, 144.21, 143.91 (d, J_{CF} = 3.5 Hz), 142.31, 137.50, 132.65, 131.97, 131.87, 130.97, 130.61, 130.50, 129.50 (d, J_{CF} = 9.2 Hz), 127.24 (d, J_{CF} = 3.0 Hz), 123.53, 123.31 (d, J_{CF} = 15.1 Hz), 115.48 (d, J_{CF} = 22.4 Hz), 113.98, 113.22, 80.06, 55.19, 54.95, 34.98 (d, J = 4.1 Hz), 28.05. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.71. **HRMS (ESI)** calcd for $C_{35}H_{34}FN_3O_5Na$ $[M+Na]^+$: 618.2375, found: 618.2382. **FTIR** (KBr, cm^{-1}) 2957.14, 2828.17, 2718.83, 1600.15, 1359.03, 1078.65, 778.66, 568.38.

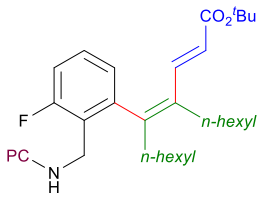


Tert-butyl(2*E*,4*E*)-4,5-bis(4-butylphenyl)-5-(3-fluoro-2-((pyrazine-2-carboxamido)methyl)phenyl)penta-2,4-dienoate (5k) Following **the general procedure 2** at the conditions of 110°C, **5k** was obtained as a yellow liquid (54.4 mg, 56% yield, *E*/*Z*=98:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.66 (d, J = 2.1 Hz, 1H), 8.39 (s, 1H), 7.58 (s, 1H), 7.43 – 7.37 (m, 1H), 7.26 (d, J = 15.4 Hz, 1H), 7.15 (t, J = 7.5 Hz, 2H), 7.10 – 7.03 (m, 4H), 6.77 (s, 4H), 5.50 (d, J = 15.5 Hz, 1H), 4.57 (d, J = 5.4 Hz, 2H), 2.59 (t, J = 7.6 Hz, 2H), 2.37 – 2.31 (m, 2H), 1.59 (p, J = 7.6 Hz, 2H), 1.41 – 1.34 (m, 3H), 1.33 (s, 9H), 1.24 – 1.16 (m, 3H), 0.92 (t, J = 7.4 Hz, 3H), 0.83 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.41, 162.12 (d, J_{CF} = 248.5 Hz), 162.02, 146.91, 145.00 (d, J_{CF} = 2.3 Hz), 144.42, 144.31, 144.22, 143.71 (d, J_{CF} = 3.4 Hz), 142.30, 142.23, 141.99, 138.64, 137.34, 135.33, 130.63, 130.29, 129.45 (d, J_{CF} = 9.3 Hz), 128.45, 127.61, 127.24 (d, J_{CF} = 3.0 Hz), 123.91, 123.39 (d, J_{CF} = 15.0 Hz), 115.43 (d, J_{CF} = 22.3 Hz), 80.06, 35.33, 35.14, 35.03 (d, J_{CF} = 4.0 Hz), 33.43, 33.06, 28.04, 22.24, 22.17, 13.98, 13.88. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.86. **HRMS (ESI)** calcd for $C_{41}H_{46}FN_3O_3Na$ $[M+Na]^+$: 670.3415, found: 670.3419. **FTIR** (KBr, cm^{-1}) 2954.21, 2825.23, 2729.91, 1594.39, 1364.49, 1078.50, 778.50.



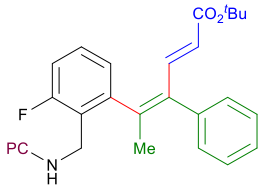
Tert-butyl(2*E*,4*Z*)-4-butyl-5-(3-fluoro-2-((pyrazine-2-carboxamido)methyl) phenyl)nona-2,4-dienoate (5l) Following **the general procedure 2** at the conditions of 110°C, **5l** was obtained

as a yellow liquid (41.6 mg, 56% yield, *E*/*Z*=96:4). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.69 (d, *J* = 2.1 Hz, 1H), 8.44 (s, 1H), 7.86 (s, 1H), 7.33 – 7.28 (m, 1H), 7.07 (t, *J* = 9.0 Hz, 1H), 6.88 – 6.82 (m, 2H), 5.69 (d, *J* = 15.8 Hz, 1H), 4.72 (dd, *J* = 14.2, 6.0 Hz, 1H), 4.43 (dd, *J* = 14.2, 4.9 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.43 – 2.30 (m, 3H), 1.56 – 1.39 (m, 5H), 1.38 – 1.19 (m, 12H), 0.96 (t, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.51, 162.16, 162.04 (d, J_{CF} = 248.0 Hz), 147.01, 146.21 (d, J_{CF} = 1.8 Hz), 144.43, 144.29, 143.90 (d, J_{CF} = 3.4 Hz), 142.52 (d, J_{CF} = 10.7 Hz), 135.39, 129.22 (d, J_{CF} = 9.3 Hz), 125.37 (d, J_{CF} = 3.0 Hz), 122.34 (d, J_{CF} = 14.6 Hz), 119.09, 114.54 (d, J_{CF} = 22.1 Hz), 79.88, 35.21 (d, J_{CF} = 3.4 Hz), 35.09, 31.37, 30.15, 28.04, 27.67, 23.16, 23.01, 13.95, 13.83. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.96. **HRMS (ESI)** calcd for $C_{29}H_{38}FN_3O_3Na$ $[M+Na]^+$: 518.2789, found: 518.2795. **FTIR** (KBr, cm^{-1}) 2965.42, 2830.84, 2715.89, 2365.42, 1311.21, 1367.29, 1086.92, 786.92, 565.42.

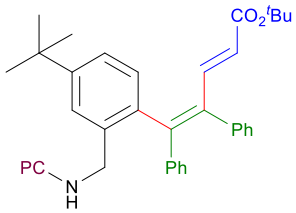


Tert-butyl (2*E*,4*Z*)-5-(3-fluoro-2-((pyrazine-2-carboxamido) methyl)phenyl)-4-hexylundeca-2,4-dienoate (5m) Following **the general procedure 2** at the conditions of 110°C, **5m** was obtained as a yellow liquid (49.2 mg, 54% yield, *E*/*Z*=97:3). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.69 (s, 1H), 8.44 (s, 1H), 7.84 (s, 1H), 7.33 – 7.25 (m, 1H), 7.06 (t, *J* = 9.0 Hz, 1H), 6.91 – 6.82 (m, 2H), 5.69 (d, *J* = 15.8 Hz, 1H), 4.72 (dd, *J* = 14.2, 6.1 Hz, 1H), 4.42 (dd, *J* = 14.5, 4.7 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.38 (t, *J* = 7.9 Hz, 2H), 2.35 – 2.28 (m, 1H), 1.53 – 1.36 (m, 5H), 1.33 (s, 9H), 1.30 – 1.10 (m, 11H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.50, 162.14, 162.03 (d, J_{CF} = 248.0 Hz), 147.01, 146.23 (d, J_{CF} = 1.8 Hz), 144.44, 144.31, 143.91 (d, J_{CF} = 3.4 Hz), 142.56, 142.46, 135.43, 129.21 (d, J_{CF} = 9.4 Hz), 125.35 (d, J_{CF} = 2.9 Hz), 122.35 (d, J_{CF} = 14.7 Hz), 119.11, 114.53 (d, J_{CF} = 22.1 Hz), 79.87, 35.36, 35.19 (d, J_{CF} = 3.4 Hz), 31.62, 31.57, 29.76, 29.58, 29.21, 28.04, 27.97, 27.11, 22.65, 22.52, 14.08, 14.00. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.96. **HRMS (ESI)** calcd for $C_{33}H_{46}FN_3O_3Na$ $[M+Na]^+$: 574.3415,

found: 574.3418. **FTIR** (KBr, cm^{-1}) 2959.81, 2836.45, 2721.50, 2351.40, 1614.02, 1358.88, 1084.11, 770.09.

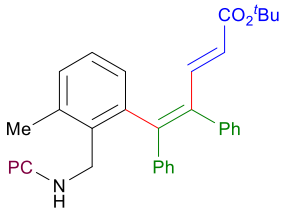


Tert-butyl (2*E*,4*E*)-5-(3-fluoro-2-((pyrazine-2-carboxamido) methyl)phenyl)-4-phenylhexa-2,4-dienoate (5n) Following **the general procedure 2** at the conditions of 110°C, **5n** was obtained as a white solid (59.6 mg, 84% yield, *E*/*Z*>99:1, m.p. = 59.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.68 (s, 1H), 8.45 (s, 1H), 8.06 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.30 (d, *J* = 6.9 Hz, 2H), 7.14 – 7.08 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 5.16 (d, *J* = 15.4 Hz, 1H), 4.85 (dd, *J* = 14.4, 6.1 Hz, 1H), 4.63 (dd, *J* = 14.2, 5.6 Hz, 1H), 1.93 (s, 3H), 1.29 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.35, 162.27, 162.07 (d, J_{CF} = 247.7 Hz), 147.11, 144.38, 144.33, 144.29, 142.84 (d, J_{CF} = 2.1 Hz), 142.72, 142.52, 138.32, 137.81, 129.84 (d, J_{CF} = 9.4 Hz), 129.58, 128.66, 127.39, 124.49 (d, J_{CF} = 3.1 Hz), 122.80, 122.28 (d, J_{CF} = 14.8 Hz), 114.81 (d, J_{CF} = 22.1 Hz), 79.98, 34.95 (d, J_{CF} = 3.5 Hz), 28.01, 24.08. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.16. **HRMS (ESI)** calcd for $C_{28}H_{28}FN_3O_3Na$ $[M+Na]^+$: 496.2007, found: 496.2006. **FTIR** (KBr, cm^{-1}) 2945.79, 2833.64, 2713.08, 1594.39, 1361.68, 1067.29, 778.50.

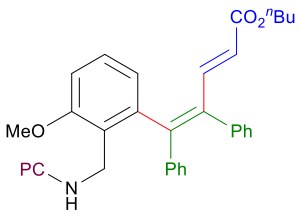


Tert-butyl (2*E*,4*E*)-5-(4-(tert-butyl)-2-(((phosphaneyl methyl) amino) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5o) Following **the general procedure 2** at the conditions of 140°C, **5o** was obtained as a yellow solid (65.4 mg, 76% yield, *E*/*Z*=96:4, m.p. = 131.5 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.43 – 8.38 (m, 1H), 7.63 (s, 1H), 7.46 (d, *J* = 1.9 Hz, 1H), 7.42 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.37 (d, *J* = 15.6 Hz, 1H), 7.28 – 7.22 (m, 4H), 7.13 (d, *J* = 6.4 Hz, 2H), 7.00 – 6.95 (m, 3H), 6.91 (dd, *J* = 7.5, 2.1 Hz, 2H), 5.47 (d, *J* = 15.6 Hz, 1H), 4.51 – 4.42 (m, 2H), 1.36 (s, 9H), 1.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.46, 162.30, 151.83, 147.10, 146.98, 144.52,

144.49, 144.28, 142.32, 140.54, 138.62, 138.45, 137.65, 135.39, 131.37, 130.90, 130.41, 128.30, 127.60, 127.21, 127.18, 127.17, 124.94, 123.88, 80.01, 42.06, 34.71, 31.34, 28.06. **HRMS (ESI)** calcd for $C_{37}H_{39}N_3O_3Na$ $[M+Na]^+$: 596.2884, found: 296.2875. **FTIR** (KBr, cm^{-1}) 2645.79, 2836.45, 2718.69, 2368.22, 1597.20, 1386.92, 1199.07, 1075.70, 767.29, 599.07.

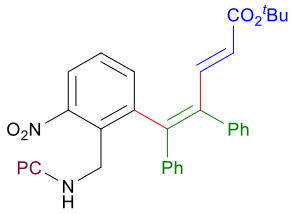


Tert-butyl(2*E*,4*E*)-5-(3-methyl-2-((pyrazine-2-carboxamido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5p) Following **the general procedure 2** at the conditions of 110°C, **5p** was obtained as a Orange solid (36.7 mg, 46% yield, *E*/*Z*=93:7, m.p. = 130.6 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.29 (d, *J* = 1.4 Hz, 1H), 8.63 (d, *J* = 2.4 Hz, 1H), 8.31 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.28 – 7.22 (m, 5H), 7.14 (d, *J* = 6.5 Hz, 2H), 7.08 (s, 1H), 6.97 – 6.92 (m, 2H), 6.92 – 6.85 (m, 3H), 5.48 (d, *J* = 15.5 Hz, 1H), 4.62 (dd, *J* = 14.2, 6.4 Hz, 1H), 4.48 (dd, *J* = 14.2, 4.3 Hz, 1H), 2.40 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.45, 162.12, 147.52, 146.89, 144.45, 144.26, 144.10, 142.15, 141.98, 140.68, 138.92, 138.49, 138.31, 133.47, 130.94, 130.86, 130.35, 129.42, 128.36, 128.11, 127.69, 127.29, 127.12, 123.81, 80.10, 39.00, 28.07, 19.55. **HRMS (ESI)** calcd for $C_{34}H_{33}N_3O_3Na$ $[M+Na]^+$: 554.2414, found: 554.2407. **FTIR** (KBr, cm^{-1}) 2951.40, 2836.45, 2718.69, 2368.22, 1597.2, 1358.88, 1199.07, 1070.09, 778.50, 756.64.

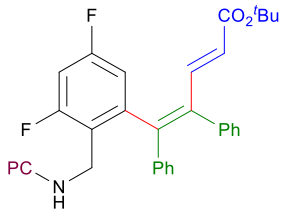


Butyl (2*E*,4*E*)-5-(3-methoxy-2-(((phosphaneylmethyl)amino)methyl)phenyl)-4,5-diphenylpenta-2,4-dienoate (5q) Following **the general procedure 2** at the conditions of 110°C, **5q** was obtained as a yellow solid (64.8 mg, 79% yield, *E*/*Z*>99:1, m.p. = 103.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.65 (s, 1H), 8.39 (s, 1H), 7.73 (s, 1H), 7.40 – 7.34 (m, 2H), 7.30 – 7.20 (m, 5H), 7.00 – 6.88 (m, 7H), 5.51 (d, *J* = 15.6 Hz, 1H), 4.70 – 4.58 (m, 2H), 3.98 – 3.85 (m, 5H), 1.51 – 1.42 (m, 2H), 1.29 – 1.20 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR**

(125 MHz, $CDCl_3$) δ 166.13, 160.88, 157.69, 145.84, 145.67, 144.33, 143.77, 143.23, 141.41, 141.22, 139.38, 137.60, 137.16, 129.90, 129.32, 128.01, 127.32, 126.50, 126.25, 126.09, 123.15, 122.29, 120.82, 109.34, 62.93, 54.68, 35.20, 29.53, 18.05, 12.65. **HRMS (ESI)** calcd for $C_{34}H_{33}N_3O_3Na$ $[M+Na]^+$: 570.2363, found: 570.2362. **FTIR** (KBr, cm^{-1}) 2959.81, 2836.45, 2365.42, 1316.82, 1358.88, 1207.48, 1081.31, 778.50.



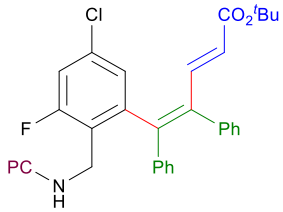
Tert-butyl (2*E*,4*E*)-5-(3-nitro-2-((pyrazine-2-carboxamido) methyl)phenyl)-4,5-diphenylpenta-2,4-dienoate (5r) Following **the general procedure 2** at the conditions of 110°C, **5r** was obtained as a yellow solid (64.1 mg, 76% yield, *E*/*Z*>99:1, m.p. = 147.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.49 – 8.43 (m, 1H), 8.25 (dd, *J* = 7.3, 3.7 Hz, 1H), 7.99 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.34 – 7.22 (m, 5H), 7.10 (d, *J* = 15.4 Hz, 1H), 7.03 – 6.96 (m, 5H), 5.40 (d, *J* = 15.4 Hz, 1H), 4.99 (dd, *J* = 14.1, 7.8 Hz, 1H), 4.48 (dd, *J* = 14.1, 4.0 Hz, 1H), 1.27 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.86, 162.05, 151.51, 147.02, 144.39, 144.34, 144.20, 143.92, 143.24, 142.57, 140.33, 139.23, 137.65, 136.16, 130.87, 130.50, 130.43, 129.01, 128.40, 127.76, 127.56, 127.53, 124.92, 124.54, 80.24, 37.51, 27.96. **HRMS (ESI)** calcd for $C_{33}H_{30}N_4O_5Na$ $[M+Na]^+$: 585.2108, found: 585.2110. **FTIR** (KBr, cm^{-1}) 2957.01, 2825.23, 2715.89, 2359.81, 1602.80, 1364.49, 1210.28, 1072.90, 778.50, 576.64.



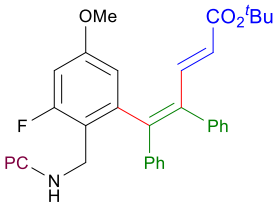
Tert-butyl(2*E*,4*E*)-5-(3,5-difluoro-2-((pyrazine-2-carboxa mido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5s) Following **the general procedure 2**, **5s** was obtained as a yellow solid (59.7 mg, 72% yield, *E*/*Z*=96:4, m.p. = 60.1 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.43 – 8.37 (m, 1H), 7.59 (s, 1H), 7.31 – 7.26 (m, 3H), 7.23 (d, *J* = 15.5 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.03 – 6.96 (m, 3H), 6.95 – 6.90 (m, 4H), 5.49 (d, *J* = 15.5 Hz, 1H), 4.65 – 4.51 (m,

2H), 1.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.05, 162.35 (dd, J_{CF} = 251.2, 12.8 Hz), 162.16 (dd, J_{CF} = 251.4, 13.6 Hz), 162.08, 147.06, 144.50 (dd, J_{CF} = 9.1, 4.9 Hz), 144.26, 144.25, 143.83, 143.24, 142.31, 139.56, 139.36, 137.66, 130.75, 130.24, 128.46, 127.85, 127.59, 127.58, 125.17, 119.74 (dd, J_{CF} = 15.4, 3.9 Hz), 114.26 (dd, J_{CF} = 21.1, 3.4 Hz), 104.05 (t, J_{CF} = 25.2 Hz), 80.39, 34.51 (d, J_{CF} = 3.6 Hz), 28.02.

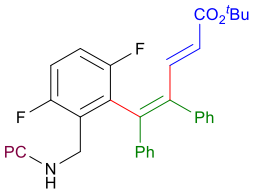
^{19}F NMR (471 MHz, $CDCl_3$) δ -109.40 (d, J_{FF} = 8.5 Hz), -111.03 (d, J_{FF} = 8.6 Hz). **HRMS (ESI)** calcd for $C_{33}H_{29}F_2N_3O_3$ $[M+Na]^+$: 576.2069, found: 576.2065. **FTIR** (KBr, cm^{-1}) 2962.75, 2833.78, 2721.63, 2357.15, 1616.97, 1375.85, 1196.41, 1064.64, 781.46, 562.77.



Tert-butyl(2*E*,4*E*)-5-(5-chloro-3-fluoro-2-((pyrazine-2-carboxamido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5t) Following **the general procedure 2** at the conditions of 110°C, **5t** was obtained as a yellow solid (64.9 mg, 76% yield, *E*/*Z*=96:4, m.p. = 105.5 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.41 (dd, *J* = 2.3, 1.5 Hz, 1H), 7.63 (s, 1H), 7.31 – 7.25 (m, 3H), 7.24 – 7.15 (m, 5H), 7.02 – 6.96 (m, 3H), 6.94 – 6.90 (m, 2H), 5.50 (d, *J* = 15.5 Hz, 1H), 4.65 – 4.54 (m, 2H), 1.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.04, 162.10, 161.97 (d, J_{CF} = 252.1 Hz), 147.09, 144.34 (d, J_{CF} = 4.4 Hz), 144.27, 144.21, 143.56 (d, J_{CF} = 2.3 Hz), 143.21, 142.34, 139.73, 139.37, 137.66, 134.70 (d, J_{CF} = 11.8 Hz), 130.75, 130.29, 128.46, 127.86, 127.60, 127.07 (d, J_{CF} = 3.2 Hz), 125.26, 122.40 (d, J_{CF} = 15.2 Hz), 116.33 (d, J_{CF} = 25.9 Hz), 80.40, 34.58 (d, J_{CF} = 3.5 Hz), 28.02. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.84. **HRMS (ESI)** calcd for $C_{33}H_{29}ClF_2N_3O_3Na$ $[M+Na]^+$: 592.1774, found: 592.1768. **FTIR** (KBr, cm^{-1}) 2959.81, 2836.45, 2365.42, 1616.82, 1358.88, 1207.48, 1081.31, 778.50.

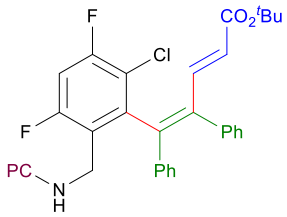


Tert-butyl(2*E*,4*E*)-5-(3-fluoro-5-methoxy-2-((pyrazine-2-carboxamido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5u) Following **the general procedure 2** at the conditions of 110ºC, **5u** was obtained as a yellow solid (55.4 mg, 68% yield, *E/Z* = 94:6, m.p. = 50.9 ºC). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.66 (d, *J* = 2.0 Hz, 1H), 8.41 – 8.35 (m, 1H), 7.52 (s, 1H), 7.32 (d, *J* = 15.5 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.18 (d, *J* = 6.7 Hz, 2H), 6.95 (q, *J* = 5.3 Hz, 5H), 6.74 – 6.68 (m, 2H), 5.47 (d, *J* = 15.5 Hz, 1H), 4.63 – 4.45 (m, 2H), 3.83 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.25, 162.83 (d, J_{CF} = 247.8 Hz), 161.97, 160.21 (d, J_{CF} = 12.2 Hz), 146.92, 145.13 (d, J_{CF} = 2.7 Hz), 144.39, 144.19, 143.86, 143.73 (d, J_{CF} = 5.4 Hz), 142.31, 139.70, 139.04, 137.95, 130.82, 130.27, 128.40, 127.71, 127.39 (d, J_{CF} = 7.0 Hz), 124.43, 115.33 (d, J_{CF} = 15.8 Hz), 113.17 (d, J_{CF} = 2.5 Hz), 101.39 (d, J_{CF} = 26.2 Hz), 80.20, 55.75, 34.61 (d, J_{CF} = 3.6 Hz), 28.05. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.54. **HRMS (ESI)** calcd for $C_{34}H_{32}FN_3O_4Na$ $[M+H]^+$: 566.2455, found: 566.2452.

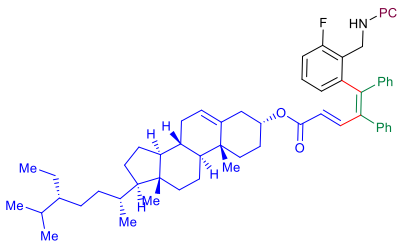


Tert-butyl(2*E*,4*E*)-5-(3,6-difluoro-2-((pyrazine-2-carboxamido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5v) Following **the general procedure 2** at the conditions of 110ºC, **5v** was obtained as a yellow solid (52.3 mg, 63% yield, *E/Z*=93:7, m.p. = 145.6 ºC). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.67 (d, *J* = 2.3 Hz, 1H), 8.40 (s, 1H), 7.68 (s, 1H), 7.33 – 7.26 (m, 3H), 7.23 – 7.20 (m, 2H), 7.20 – 7.12 (m, 3H), 7.02 – 6.94 (m, 5H), 5.48 (d, *J* = 15.4 Hz, 1H), 4.70 (dd, *J* = 14.2, 7.9 Hz, 1H), 4.57 (dd, *J* = 14.2, 4.5 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.03, 162.09, 157.93 (dd, J_{CF} = 245.1, 2.3 Hz), 155.83 (dd, J_{CF} = 242.2, 2.1 Hz), 147.08, 144.26, 144.22, 142.85, 142.34, 141.15, 139.02, 138.01 (d, J_{CF} = 1.3 Hz), 137.56, 130.75, 130.25 (dd, J_{CF} = 19.7, 3.6 Hz), 129.95, 128.40, 127.80, 127.56, 127.46, 125.36, 124.77 (dd, J_{CF} = 17.1, 2.1 Hz), 116.69 (dd, *J* = 25.3, 16.6 Hz), 116.69 (d, *J* = 25.1 Hz), 80.29, 34.80, 28.01. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.18

(d, J_{FF} = 17.6 Hz), -120.73 (d, J_{FF} = 17.6 Hz). **HRMS (ESI)** calcd for $C_{33}H_{29}F_2N_3O_3Na$ $[M+Na]^+$: 576.2069, found: 576.2065. **FTIR** (KBr, cm^{-1}) 2951.40, 2836.45, 2718.69, 2368.22, 1597.20, 1358.88, 1199.07, 1070.09, 778.50, 576.64.

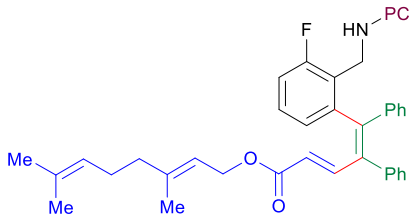


Tert-butyl(2*E*,4*E*)-5-(2-chloro-3,5-difluoro-6-((pyrazine-2-carboxamido)methyl)phenyl)-4,5-diphenylpenta-2,4-dienoate (5w) Following **the general procedure 2** at the conditions of 110°C, **5w** was obtained as a yellow solid (65.2 mg, 74% yield, *E*/*Z*=95:5, m.p. = 103.3 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.67 (d, *J* = 2.4 Hz, 1H), 8.38 (dd, *J* = 2.4, 1.5 Hz, 1H), 7.60 (s, 1H), 7.34 – 7.28 (m, 3H), 7.27 – 7.23 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 15.4 Hz, 1H), 7.02 – 6.98 (m, 3H), 6.97 – 6.94 (m, 2H), 5.48 (d, *J* = 15.4 Hz, 1H), 4.70 (dd, *J* = 14.4, 6.9 Hz, 1H), 4.53 (dd, *J* = 14.9, 5.1 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.88, 162.05, 160.19 (dd, J_{CF} = 252.8, 12.7 Hz), 158.18 (dd, J_{CF} = 253.7, 13.6 Hz), 147.09, 144.21, 144.11, 143.10 (d, J_{CF} = 4.7 Hz), 142.31, 140.68, 139.98, 137.80, 137.48, 130.64, 130.01, 128.54, 127.91, 127.78, 127.75, 125.90, 120.83 (dd, J_{CF} = 16.1, 4.1 Hz), 117.74 (dd, J_{CF} = 17.1, 4.0 Hz), 105.10 (dd, J_{CF} = 27.6, 25.3 Hz), 80.43, 34.77 (d, J_{CF} = 3.4 Hz), 28.01. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -107.19 (d, J_{FF} = 8.4 Hz), -112.61 (d, J_{FF} = 8.3 Hz). **HRMS (ESI)** calcd for $C_{33}H_{28}ClF_2N_3O_3Na$ $[M+Na]^+$: 610.1679, found: 610.1684. **FTIR** (KBr, cm^{-1}) 2951.53, 2836.58, 2713.22, 2354.34, 1594.54, 1364.63, 1207.63, 1070.24, 784.27, 487.07.



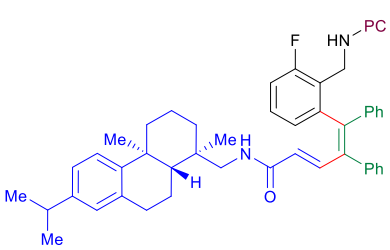
(3*S*,8*R*,9*R*,10*S*,13*S*,14*R*,17*S*)-17-((2*S*,5*S*)-5-ethyl-6-methylheptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl(2*E*,4*E*)-5-(3-fluoro-2-((pyrazine-2-carboxamido)methyl)phenyl)-4,5-diphenylpenta-2,4-dienoate (5x) Following **the general procedure 2** at 110 °C, **5x** was obtained as a yellow solid (68.3 mg, 52% yield, *E*/*Z* > 99:1, m.p. = 72.1 °C). **^{1}H NMR**

(500 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.66 (s, 1H), 8.39 (s, 1H), 7.60 (s, 1H), 7.43 – 7.38 (m, 1H), 7.35 (d, *J* = 15.5 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.21 – 7.12 (m, 4H), 7.01 – 6.86 (m, 5H), 5.53 (d, *J* = 15.5 Hz, 1H), 5.33 (d, *J* = 18.7 Hz, 1H), 4.71 – 4.54 (m, 2H), 4.47 (tt, *J* = 10.1, 4.3 Hz, 1H), 2.26 – 2.11 (m, 2H), 2.08 – 1.90 (m, 3H), 1.89 – 1.78 (m, 2H), 1.77 – 1.62 (m, 2H), 1.61 – 1.38 (m, 7H), 10.9, 10.5, 4.9 Hz, 7H), 1.37 – 0.89 (m, 20H), 0.88 – 0.75 (m, 8H), 0.68 (d, *J* = 9.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.35, 162.20 (d, J_{CF} = 248.8 Hz), 162.05, 146.97 (d, J_{CF} = 3.6 Hz), 145.53, 144.75 (d, J_{CF} = 3.7 Hz), 144.34, 144.25, 143.23 (d, J_{CF} = 3.1 Hz), 142.28, 139.99 (d, J_{CF} = 3.0 Hz), 139.62 (d, J_{CF} = 6.4 Hz), 139.21, 137.95 (d, J_{CF} = 1.4 Hz), 130.84, 130.36, 129.57 (d, J_{CF} = 8.5 Hz), 128.44, 127.74, 127.49, 127.44, 127.24 (d, J_{CF} = 2.9 Hz), 123.49 (d, J_{CF} = 15.2 Hz), 122.98 (d, J_{CF} = 6.1 Hz), 122.62, 115.67 (d, J_{CF} = 22.3 Hz), 73.99, 56.69, 56.04, 49.99, 45.84, 42.31, 39.72, 38.05 (d, J_{CF} = 5.3 Hz), 36.95 (d, J_{CF} = 3.2 Hz), 36.58, 36.15, 35.04, 33.95, 31.87 (d, J_{CF} = 5.9 Hz), 29.16, 28.25, 27.70 (d, J_{CF} = 2.6 Hz), 26.08, 24.30, 23.08, 21.02, 19.84, 19.27, 19.06, 18.79, 18.28, 12.00, 11.86. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.56. **HRMS (ESI)** calcd for $C_{58}H_{70}FN_3O_3Na$ $[M+Na]^+$: 898.2593, found: 898.2595.

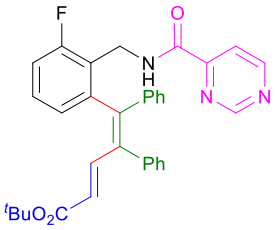


(*E*)-3,7-dimethylocta-2,6-dien-1-yl (2*E*,4*E*)-5-(3-fluoro -2-((pyrazine-2-carboxamido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5y) Following **the general procedure 2** at 110 °C, **5y** was obtained as a yellow liquid (69.7 mg, 53% yield, *E*/*Z* = 96:4). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.32 (d, *J* = 1.3 Hz, 1H), 8.67 – 8.64 (m, 1H), 8.41 – 8.35 (m, 1H), 7.58 (t, *J* = 5.2 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.36 (d, *J* = 15.5 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.16 (dd, *J* = 15.2, 7.5 Hz, 4H), 7.00 – 6.89 (m, 5H), 5.57 (d, *J* = 15.5 Hz, 1H), 5.23 (t, *J* = 7.0 Hz, 1H), 5.05 (t, *J* = 6.8 Hz, 1H), 4.66 – 4.56 (m, 2H), 4.55 – 4.44 (m, 2H), 2.10 – 2.03 (m, 2H), 2.03 – 1.97 (m, 2H), 1.66 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.93, 162.19 (d, J_{CF} = 248.8 Hz), 162.05, 146.97, 145.58 (d, J_{CF} = 2.3 Hz), 144.89, 144.32, 144.27, 143.24 (d, *J* = 3.5

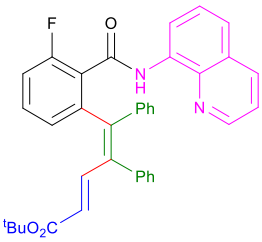
Hz), 142.41, 142.26, 139.97, 139.21, 137.92, 131.84, 130.82, 130.35, 129.59 (d, J_{CF} = 9.3 Hz), 128.43, 127.74, 127.50, 127.45, 127.23 (d, J_{CF} = 3.1 Hz), 123.69, 123.48 (d, J_{CF} = 15.1 Hz), 122.70, 118.09, 115.69 (d, J_{CF} = 22.2 Hz), 61.18, 39.51, 35.03 (d, J_{CF} = 4.0 Hz), 26.28, 25.68, 17.69, 16.45. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.49. **HRMS (ESI)** calcd for $C_{39}H_{38}FN_3O_3Na$ $[M+Na]^+$: 638.2789, found: 638.2788.



***N*-(2-fluoro-6-((1*E*,3*E*)-5-((((1*S*,4a*R*,10a*S*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)amino)-5-oxo-1,2-diphenylpenta-1,3-dien-1-yl)benzyl)pyrazine-2-carboxamide (5z)** Following **the general procedure 2** at 110 °C, **5z** was obtained as a yellow solid (79.6 mg, 71% yield, *E/Z* > 99:1, m.p. = 193.9 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.61 (d, *J* = 12.6 Hz, 1H), 8.37 (d, *J* = 14.9 Hz, 1H), 7.66 – 7.53 (m, 1H), 7.41 – 7.05 (m, 10H), 7.02 – 6.85 (m, 7H), 5.45 (dd, *J* = 15.1, 10.6 Hz, 1H), 5.38 – 5.31 (m, 1H), 4.64 (dd, *J* = 14.1, 5.8 Hz, 1H), 4.57 – 4.49 (m, 1H), 3.18 – 2.95 (m, 2H), 2.93 – 2.69 (m, 3H), 2.24 (d, *J* = 12.6 Hz, 1H), 1.86 – 1.75 (m, 1H), 1.73 – 1.52 (m, 3H), 1.35 – 1.11 (m, 13H), 0.86 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.00, 165.85, 162.24 (dd, J_{CF} = 248.4, 2.4 Hz), 162.09, 147.15, 146.90, 145.69 (d, J_{CF} = 9.2 Hz), 144.42, 144.15, 143.30, 142.35, 141.38 (d, J_{CF} = 18.7 Hz), 140.33, 139.15 (d, J_{CF} = 5.0 Hz), 138.41 (d, J_{CF} = 3.9 Hz), 134.82 (d, J_{CF} = 10.8 Hz), 130.94, 130.34 (d, J_{CF} = 2.1 Hz), 129.56 (t, J_{CF} = 9.4 Hz), 128.40, 127.68, 127.33 (d, J_{CF} = 2.8 Hz), 127.26 (d, J_{CF}= 2.9 Hz), 127.16, 126.93 (d, J_{CF} = 3.5 Hz), 125.39 (d, J_{CF} = 16.2 Hz), 124.16, 123.87, 123.39 (d, J_{CF} = 15.0 Hz), 115.56 (dd, J_{CF} = 22.2, 2.7 Hz), 49.76 (d, J_{CF} = 3.1 Hz), 45.03 (d, J_{CF} = 15.5 Hz), 38.22 (d, J_{CF} = 3.2 Hz), 37.50 (d, J_{CF} = 19.4 Hz), 36.10, 35.20 (dd, J_{CF} = 6.1, 4.4 Hz), 33.45, 29.91 (d, J_{CF} = 47.9 Hz), 29.53 (d, J_{CF} = 37.5 Hz), 25.30 (d, J_{CF} = 6.9 Hz), 24.02, 18.89 (d, J_{CF} = 4.2 Hz), 18.80 (d, J_{CF} = 1.7 Hz), 18.55. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.64. **HRMS (ESI)** calcd for $C_{49}H_{51}FN_4O_2Na$ $[M+Na]^+$: 769.3888, found: 769.3890.



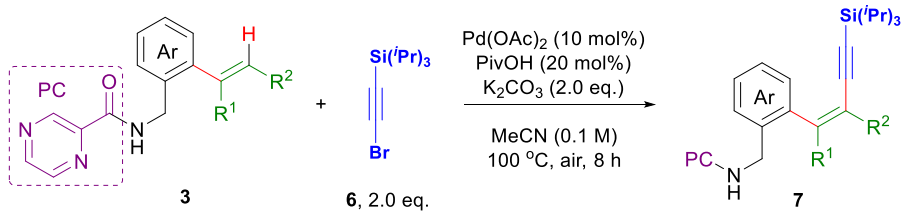
Tert-butyl(2*E*,4*E*)-5-(3-fluoro-2-((pyrimidine-4-carboxamido) methyl) phenyl)-4,5-diphenylpenta-2,4-dienoate (5bb) Following **the general procedure 2** at the conditions of 110°C, **5bb** was obtained as a yellow solid (61.0 mg, 76% yield, *E*/*Z*=96:4, m.p. = 63.8 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.90 (d, *J* = 5.0 Hz, 1H), 8.05 (d, *J* = 6.1 Hz, 1H), 7.78 (s, 1H), 7.45 – 7.38 (m, 1H), 7.31 – 7.23 (m, 4H), 7.21 – 7.14 (m, 4H), 7.01 – 6.94 (m, 3H), 6.94 – 6.90 (m, 2H), 5.49 (d, *J* = 15.5 Hz, 1H), 4.66 – 4.54 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.23, 162.15 (d, J_{CF} = 248.8 Hz), 161.69, 158.95, 157.49, 156.07, 145.07 (d, J_{CF} = 2.2 Hz), 143.80, 143.31 (d, J_{CF} = 3.4 Hz), 139.99, 139.24, 138.03, 131.98, 130.84, 130.32, 129.63 (d, J_{CF} = 9.3 Hz), 128.39, 127.76, 127.43, 127.25 (d, J_{CF} = 3.1 Hz), 124.55, 123.20 (d, J_{CF} = 15.1 Hz), 118.43, 115.64 (d, J_{CF} = 22.4 Hz), 80.28, 35.13 (d, J_{CF} = 4.2 Hz), 28.03. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.59. **HRMS (ESI)** calcd for $C_{33}H_{30}FN_3O_3Na$ $[M+Na]^+$: 558.2163, found: 558.2162. **FTIR** (KBr, cm^{-1}) 2948.60, 2833.64, 2713.08, 2348.60, 1616.82, 1367.29, 1204.67, 1078.50, 778.50, 565.42.



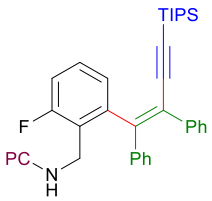
Tert-butyl(2*E*,4*E*)-5-(3-fluoro-2-(quinolin-8-ylcarbamoyl)phenyl)-4,5-diphenylpenta-2,4-dienoate (5dd) Following **the general procedure 2**, **5dd** was obtained as a colorless liquid (26.6 mg, 47% yield, *E*/*Z* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.68 (dd, *J* = 5.2, 3.8 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.61 (d, *J* = 15.5 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.12 (m, 3H), 7.11 – 7.07 (m, 2H), 6.95 – 6.81 (m, 5H), 5.44 (d, *J* = 15.5 Hz, 1H), 1.23 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.36, 161.89, 159.52 (d, J_{CF} = 250.1 Hz), 148.12, 146.03 (d, J_{CF} = 1.9 Hz), 143.92, 142.70 (d, J_{CF} = 2.7 Hz), 140.61, 138.68, 138.36, 138.05, 136.07, 134.47, 131.00 (d, J_{CF} = 10.7 Hz), 130.90 (d, J_{CF} =

15.1 Hz), 128.04, 127.78, 127.61 (d, J_{CF} = 3.0 Hz), 127.32, 127.30, 127.07, 127.04, 126.52, 126.39, 124.04, 121.72, 121.50, 116.53, 115.97 (d, J_{CF} = 22.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.03. **HRMS (ESI)** calcd for $C_{37}H_{31}FN_2O_3Na$ $[M+Na]^+$: 593.2211 found: 593.2214. **FTIR** (KBr, cm^{-1}) 3450.47, 2962.62, 2830.84, 2721.50, 2348.60, 1605.61, 1356.07, 1058.88, 767.29.

3.3 General Procedure 3 for Olefinic C-H Alkynylation

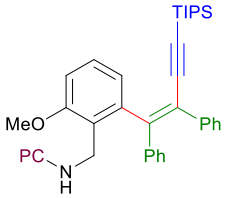


A screw-cap vial was charged with $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 10 mol%), K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv), amide **3** (0.1 mmol, 1.0 equiv), MeCN (1.0 mL). Then, pivalic acid (2.1 mg, 0.02 mmol, 20 mol%), and alkyne **6** (52.3 mg, 0.2 mmol, 2.0 equiv) were added into the solution in sequence. The vial was sealed under air and heated to 100 °C with stirring for 8 h. After cooling down, the mixture was concentrated and directly applied to a flash column chromatography (PE/EA mixtures) for separation to obtain the diene product **7**.

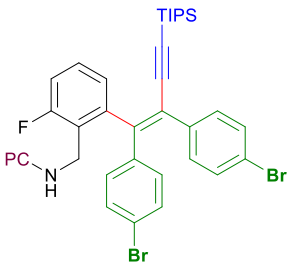


(*Z*)-*N*-(2-(1,2-diphenyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)-6-fluorobenzyl)pyrazine-2-carboxamide (7a) Following **the general procedure 3**, **7a** was obtained as a yellow oil (42.5 mg, 72% yield, *Z*/*E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.70 (d, *J* = 2.3 Hz, 1H), 8.42 (s, 1H), 7.71 (s, 1H), 7.38 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.19 (m, 3H), 7.09 – 7.04 (m, 1H), 7.06 – 6.97 (m, 5H), 4.83 (dd, *J* = 14.3, 5.5 Hz, 1H), 4.56 (dd, *J* = 14.2, 4.7 Hz, 1H), 0.92 – 0.83 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.13, 162.07 (d, J_{CF} = 247.4 Hz), 146.95, 146.18 (d, J_{CF} = 2.1 Hz), 145.54 (d, J_{CF} = 3.6 Hz), 144.56, 144.40, 142.22, 139.41, 138.08, 130.28, 129.95, 129.36, 129.28, 128.00, 127.55 (d, J_{CF} = 5.3

Hz), 126.73 (d, J_{CF} = 2.9 Hz), 124.85, 123.13, 123.02, 114.86 (d, J_{CF} = 22.5 Hz), 107.71, 97.67, 35.05 (d, J_{CF} = 4.5 Hz), 18.47, 11.15. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.52. **HRMS (ESI)** calcd for $C_{37}H_{40}FN_3OSiNa$ $[M+Na]^+$: 612.2817, found: 612.2819.

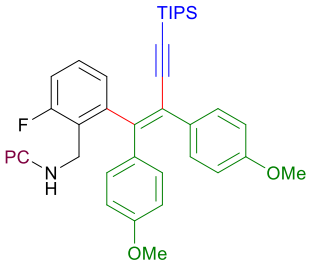


(*Z*)-*N*-(2-(1,2-diphenyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl) -6-methoxybenzyl)pyrazine-2-carboxamide (7b) Following **the general procedure 3** at 110 °C for 12 h, **7b** was obtained as a yellow oil (18.7 mg, 31% yield, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.67 (d, *J* = 2.3 Hz, 1H), 8.41 (s, 1H), 7.84 (s, 1H), 7.42 – 7.38 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.19 (q, *J* = 5.8 Hz, 3H), 7.02 – 6.93 (m, 6H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.92 (dd, *J* = 14.0, 6.3 Hz, 1H), 4.56 (dd, *J* = 14.0, 4.8 Hz, 1H), 3.88 (s, 3H), 0.86 (d, *J* = 3.1 Hz, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.96, 158.63, 147.46, 146.68, 145.06, 144.82, 144.41, 142.22, 139.93, 138.40, 130.31, 130.02, 128.81, 127.92, 127.79, 127.29, 127.18, 124.32, 123.87, 122.91, 109.84, 108.03, 96.62, 55.67, 36.27, 18.49, 11.18. **HRMS (ESI)** calcd for $C_{38}H_{44}N_3O_2Si$ $[M+H]^+$: 602.3197, found: 602.3194.

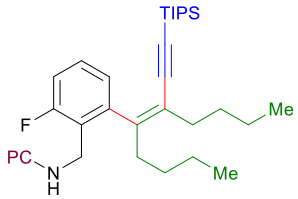


(*Z*)-*N*-(2-(1,2-bis (4-bromophenyl)-4-(triisopropylsilyl) but-1-en-3-yn-1-yl)-6-fluorobenzyl)pyrazine-2-carboxamid e (7c) Following **the general procedure 3** at 110 °C for 12 h, **7c** was obtained as a yellow oil (24.6 mg, 33% yield, *Z/E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 – 9.32 (m, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.44 (dd, *J* = 2.3, 1.5 Hz, 1H), 7.59 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.25 (d, *J* = 9.4 Hz, 2H), 7.20 – 7.15 (m, 3H), 7.08 (t, *J* = 8.7 Hz, 1H), 6.87 (s, 2H), 4.75 (dd, *J* = 14.5, 5.7 Hz, 1H), 4.59 (dd, *J* = 14.3, 5.3 Hz, 1H), 0.87 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.22 (d, J_{CF} = 247.4 Hz), 162.09, 147.16, 145.27 (d, J_{CF} = 2.3 Hz), 144.81 (d, J_{CF} = 3.7 Hz), 144.34, 144.27, 142.43, 138.23, 136.81, 131.86, 131.50, 131.45, 131.43, 129.54 (d, J_{CF} = 9.2 Hz), 126.52 (d,

J_{CF} = 2.9 Hz), 124.28, 123.15 (d, J_{CF} = 15.3 Hz), 122.18, 121.99, 115.21 (d, J_{CF} = 22.2 Hz), 106.91, 98.75, 35.04 (d, J_{CF} = 4.2 Hz), 18.45, 11.09. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.16. **HRMS (ESI)** calcd for $C_{37}H_{39}Br_2FN_3OSi$ $[M+H]^+$: 746.1208, found: 746.1207.

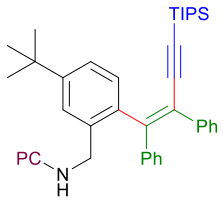


(*Z*)-*N*-(2-(1,2-bis (4-methoxyphenyl)-4-(triisopropylsilyl) but-1-en-3-yn-1-yl)-6-fluorobenzyl)pyrazine-2-carboxamide (7d) Following **the general procedure 3**, **7d** was obtained as a yellow oil (37.0 mg, 57% yield, *Z*/*E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 1.2 Hz, 1H), 8.67 (d, *J* = 2.4 Hz, 1H), 8.41 – 8.37 (m, 1H), 7.58 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.04 (t, *J* = 8.7 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.9 Hz, 2H), 4.74 (dd, *J* = 14.4, 5.5 Hz, 1H), 4.56 (dd, *J* = 14.3, 5.4 Hz, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 0.87 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.08, 162.04 (d, J_{CF} = 247.4 Hz), 158.86 (d, J_{CF} = 3.2 Hz), 146.89, 146.08 (d, J_{CF} = 3.4 Hz), 144.64 (d, J_{CF} = 2.2 Hz), 144.56, 144.33, 142.24, 132.08, 131.61, 131.14, 130.61, 129.27 (d, J_{CF} = 9.2 Hz), 126.78 (d, J_{CF} = 2.9 Hz), 123.01, 122.89, 122.85, 114.69 (d, J_{CF} = 22.5 Hz), 113.50, 113.43, 108.18, 96.69, 55.18, 54.99, 35.03 (d, J_{CF} = 4.5 Hz), 18.50, 11.16. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.60. **HRMS (ESI)** calcd for $C_{39}H_{44}FN_3O_3SiNa$ $[M+Na]^+$: 640.3130, found: 640.3131.



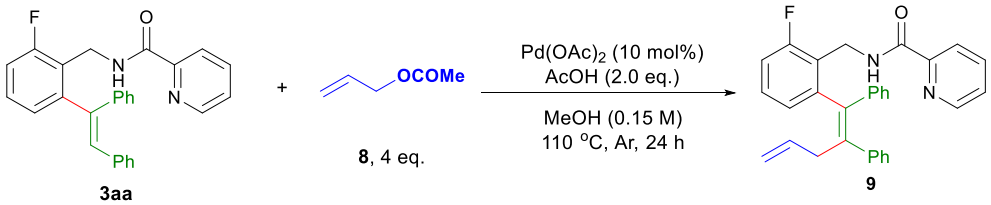
(*Z*)-*N*-(2-fluoro-6-(6-((triisopropylsilyl)ethynyl)dec-5-en-5-yl)benzyl)pyrazine-2-carboxamide (7e) Following **the general procedure 3**, **7e** was obtained as a yellow oil (35.7 mg, 65% yield, *Z*/*E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.40 (s, 1H), 8.70 (d, *J* = 2.3 Hz, 1H), 8.44 (s, 1H), 7.93 (s, 1H), 7.25 – 7.19 (m, 1H), 6.96 (t, *J* = 9.0 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 4.87 (dd, *J* = 14.4, 6.7 Hz, 1H), 4.48 (dd, *J* = 14.4, 4.1 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.38 – 2.20 (m, 3H), 1.65 – 1.57 (m,

2H), 1.44 – 1.36 (m, 2H), 1.31 – 1.22 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H), 0.87 – 0.78 (m, 24H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.26, 162.12 (d, J_{CF} = 246.7 Hz), 147.01, 146.07 (d, J_{CF} = 2.1 Hz), 145.94 (d, J_{CF} = 3.6 Hz), 144.67, 144.48, 142.38, 128.97 (d, J_{CF} = 9.4 Hz), 125.23 (d, J_{CF} = 2.9 Hz), 123.67, 121.99 (d, J_{CF} = 14.4 Hz), 113.86 (d, J_{CF} = 22.1 Hz), 107.10, 93.85, 35.43 (d, J_{CF} = 3.5 Hz), 33.76, 31.37, 30.77, 30.20, 22.88, 22.38, 18.42 (d, J = 3.9 Hz), 14.02, 13.85, 11.11. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.86. **HRMS (ESI)** calcd for $C_{33}H_{48}FN_3OSiNa$ $[M+Na]^+$: 572.3443, found: 572.3443.



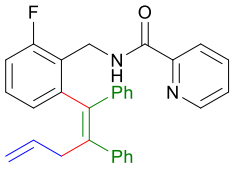
(*Z*)-*N*-(5-(tert-butyl)-2-(1,2-diphenyl-4-(triisopropylsilyl)but-1-en-3-yn-1-yl)benzyl)pyrazine-2-carboxamide (7f) Following **the general procedure 3** for 12 h, **7f** was obtained as a yellow oil (32.7 mg, 52% yield, *Z*/*E* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.73 – 8.66 (m, 1H), 8.48 – 8.39 (m, 1H), 7.76 (s, 1H), 7.42 – 7.38 (m, 2H), 7.37 – 7.34 (m, 3H), 7.20 – 7.16 (m, 3H), 7.05 – 7.02 (m, 3H), 7.01 – 6.98 (m, 2H), 4.61 (s, 1H), 4.41 (s, 1H), 1.32 (s, 9H), 0.87 (d, J = 4.0 Hz, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.34, 151.04, 148.06, 146.92, 144.73, 144.38, 142.26, 139.99, 139.76, 138.43, 134.72, 130.88, 130.27, 130.00, 127.95, 127.90, 127.39, 127.33, 126.94, 124.96, 124.02, 108.23, 96.73, 42.32, 34.58, 31.36, 18.57, 11.19. **HRMS (ESI)** calcd for $C_{41}H_{49}N_3OSiNa$ $[M+Na]^+$: 650.3537, found: 650.3538.

3.4 General Procedure 4 for Olefinic C-H Allylation



A screw-cap vial was charged with $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 10 mol%), amide **3aa** (0.1 mmol, 1.0 equiv), MeOH (0.7 mL). Then, AcOH (12.0 mg, 0.2 mmol, 2.0 equiv), and Allyl acetate **8** (40.0 mg, 0.4 mmol, 4.0 equiv) were added into the

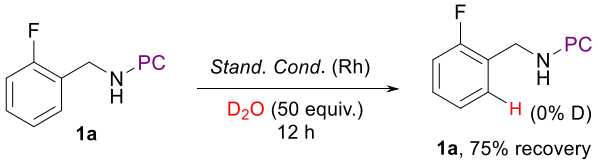
solution in sequence. The vial was sealed under argon and heated to 110°C with stirring for 24 h. After cooling down, the mixture was concentrated and directly applied to a flash column chromatography (PE/EA mixtures) to obtain the diene product **9**.



(*E*)-*N*-(2-(1,2-diphenylpenta-1,4-dien-1-yl)-6-fluorobenzyl)picolinamide (9) Following the **general procedure 4**, **9** was obtained as a yellow oil (19.7 mg, 44% yield, *E*/*Z* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.4 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.92 (s, 1H), 7.88 – 7.79 (m, 1H), 7.43 – 7.35 (m, 2H), 7.27 (d, *J* = 6.7 Hz, 2H), 7.21 – 7.14 (m, 4H), 7.10 (t, *J* = 8.9 Hz, 1H), 7.02 – 6.91 (m, 5H), 5.66 – 5.54 (m, 1H), 4.88 – 4.77 (m, 2H), 4.61 (dd, *J* = 14.1, 5.1 Hz, 1H), 4.48 (dd, *J* = 14.2, 7.5 Hz, 1H), 3.14 (dd, *J* = 14.9, 6.4 Hz, 1H), 3.00 (dd, *J* = 14.9, 6.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.07, 162.26 (d, J_{CF} = 292.1 Hz), 149.92, 147.83, 144.79 (d, J_{CF} = 3.4 Hz), 141.18, 140.50, 140.32, 137.23, 137.14 (d, J_{CF} = 2.4 Hz), 135.28, 130.25, 129.76, 128.98 (d, J_{CF} = 9.2 Hz), 127.96, 127.68, 126.67, 126.35, 126.32, 126.02, 123.35 (d, J_{CF} = 14.8 Hz), 122.20, 116.08, 114.74 (d, J_{CF} = 22.6 Hz), 41.12, 34.74 (d, J_{CF} = 4.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.90. **HRMS (ESI)** calcd for $C_{30}H_{25}FN_2ONa$ $[M+Na]^+$: 471.1843, found: 471.1843.

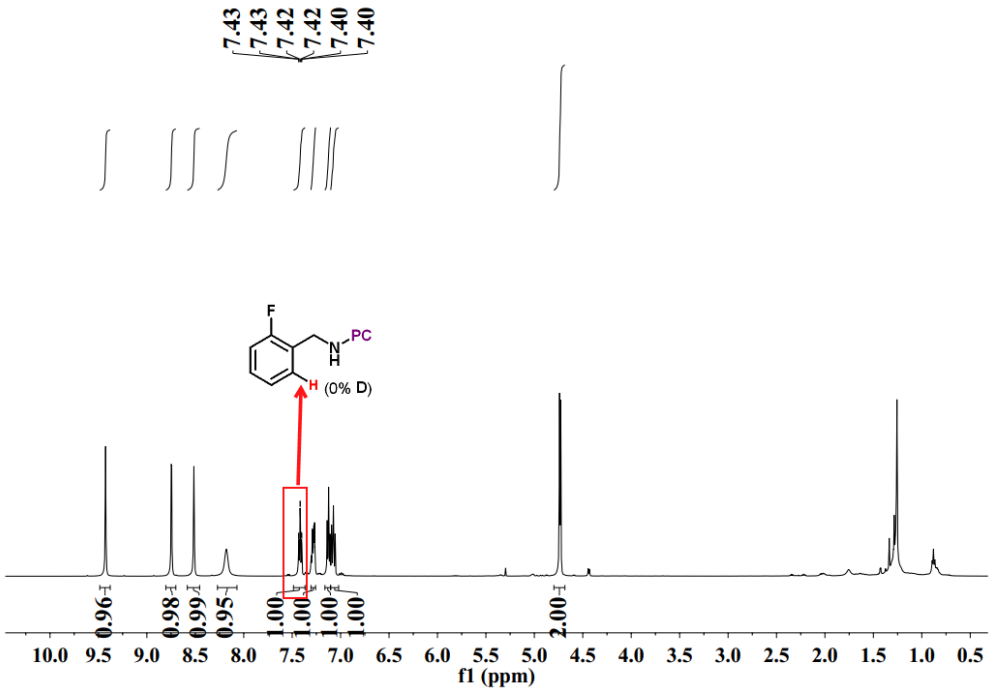
4. Deuterium-Labelled Experiments

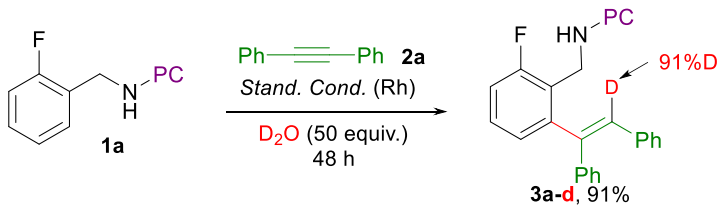
4.1 Rh-Catalyzed H/D Exchange in Hydroarylation



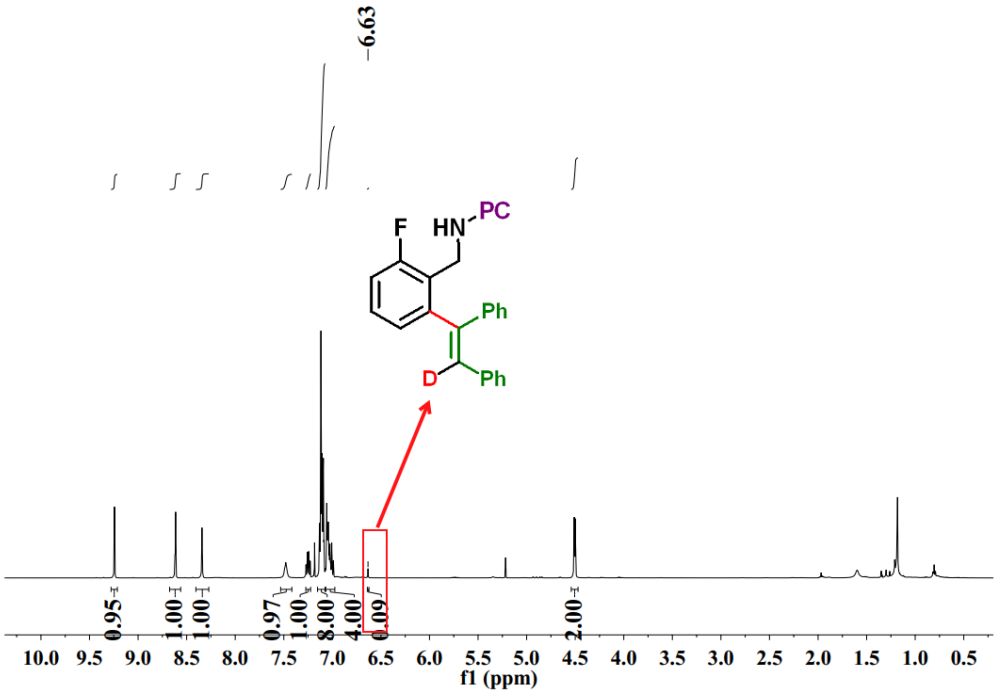
A screw-cap vial was charged with $[Rh(cod)Cl]_2$ (1.0 mg, 0.002 mmol, 2 mol%), $AgSbF_6$ (1.7 mg, 0.0050 mmol, 0.05 equiv), NaOAc (8.2 mg, 0.10 mmol, 1.0 equiv),

amide **1a** (23.1 mg, 0.10 mmol, 1.0 equiv), DCE (1.0 mL) and D_2O (5 mmol, 50.0 equiv) in sequence. The vial was sealed under argon and heated to 120 °C with stirring for 12 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) to obtain **1a** and **1a-*d***. Deuterium incorporation was determined by ^{1}H NMR analysis.



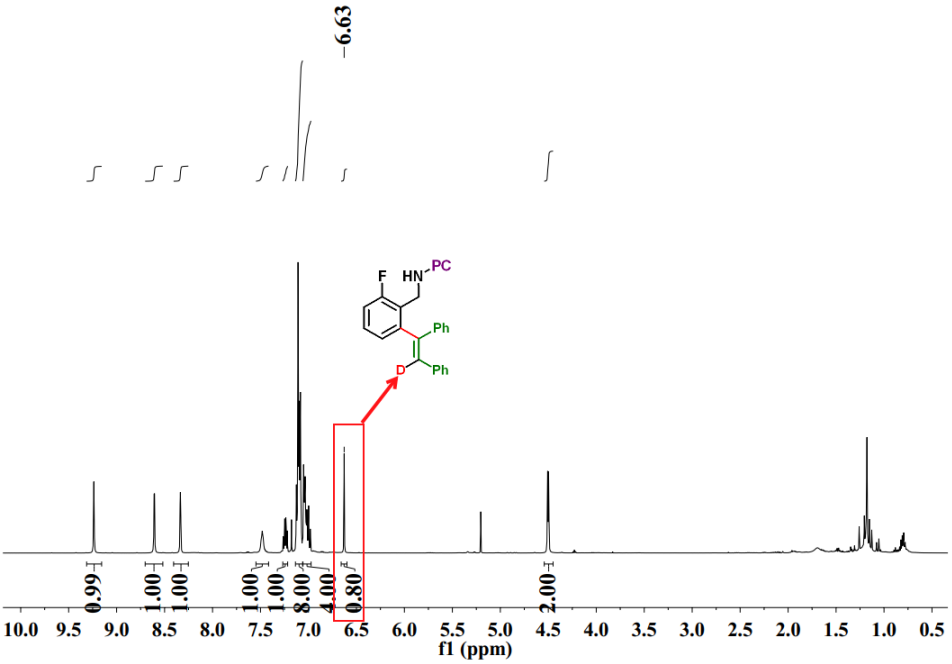


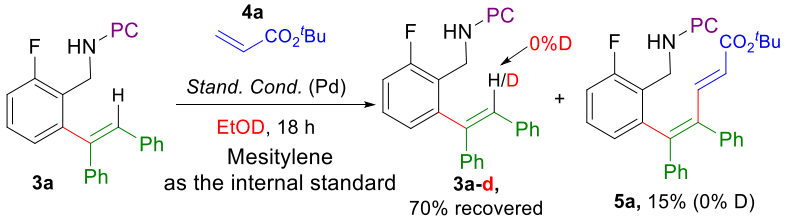
A screw-cap vial was charged with $[Rh(cod)Cl]_2$ (1.5 mg, 0.003 mmol, 2 mol%), $AgSbF_6$ (2.6 mg, 0.0075 mmol, 0.05 equiv), NaOAc (12.3 mg, 0.15 mmol, 1.00 equiv), amide **1**a (0.15 mmol, 1.0 equiv), **2a** (53.3 mg, 0.30 mmol, 2.00 equiv), DCE (1.5 mL) and D_2O (7.5 mmol, 50.0 equiv) in sequence. The vial was sealed under Argon and heated to 120 °C with stirring for 48 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) to obtain the corresponding product **3a** and **3a-*d***. Deuterium incorporation was determined by ^{1}H NMR analysis.



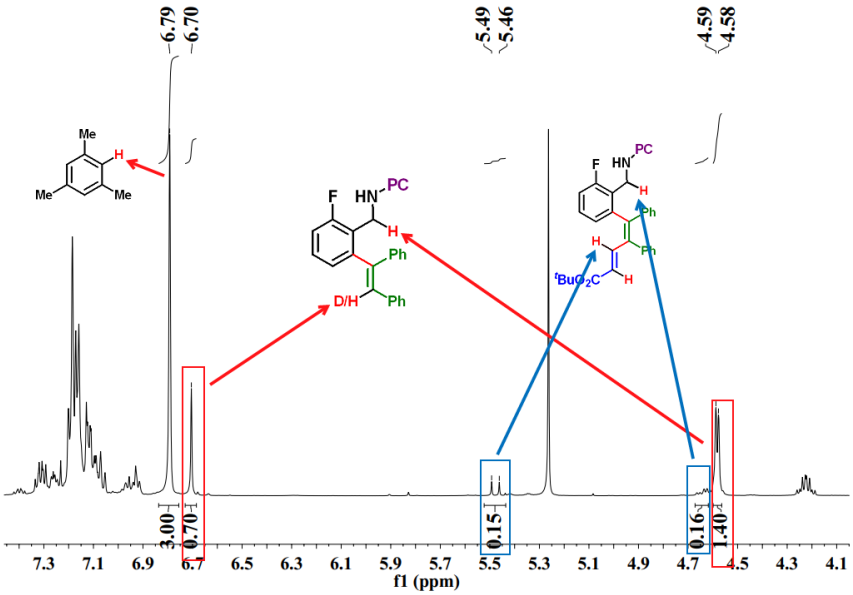
4.2 Pd-Catalyzed H/D Exchange

A screw-cap vial was charged with $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 15 mol%), MnO_2 (26.1 mg, 0.3 mmol, 3.0 equiv), BQ (1.1 mg, 0.01 mmol, 10 mol%), amide **3a** (40.9 mg, 0.10 mmol, 1.0 equiv), and EtOD (0.7 mL) was added. Then, pivalic acid (15.3 mg, 0.15 mmo l, 1.5 equiv) were added into the solution in sequence. The vial was sealed under air and heated to 80 °C with stirring for 6 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) to obtain the mixture **3a** and **3a-d**. Deuterium incorporation was determined by ^1H NMR analysis.



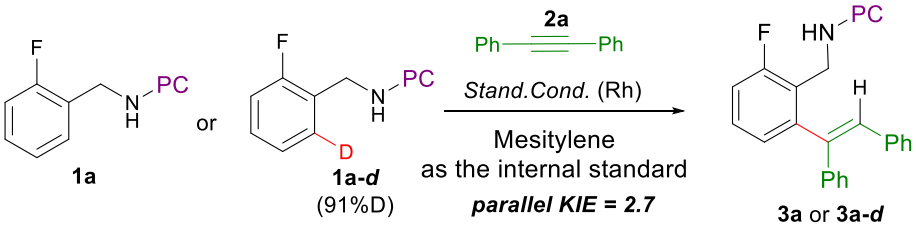


A screw-cap vial was charged with $Pd(OAc)_2$ (3.4 mg, 15 mol%, 0.015 mmol), MnO_2 (26.1 mg, 0.3 mmol, 3.0 equiv), BQ (1.1 mg, 0.01 mmol, 10 mol%), amide **3a** (40.9 mg, 0.10 mmol, 1.0 equiv) and EtOD (0.7 mL) was added. Then, pivalic acid (15.3 mg, 0.15 mmol, 1.5 equiv), and t-butyl acrylate **4a** (32.0 mg, 0.25 mmol, 2.5 equiv) were added into the solution in sequence. The vial was sealed under air and heated to 80 ºC with stirring for 18 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) to obtain the mixture **3a-*d*** and **5a**. To the reaction residue was added mesitylene (0.1 mmol, 13.5 μL, 12.0 mg) as the internal standard. The yield and deuterium incorporation of **3a-*d*** and **5a** were analyzed with ^{1}H NMR.



5. KIE Experiments

5.1 Parallel KIE experiments with 1a or 1a-*d*

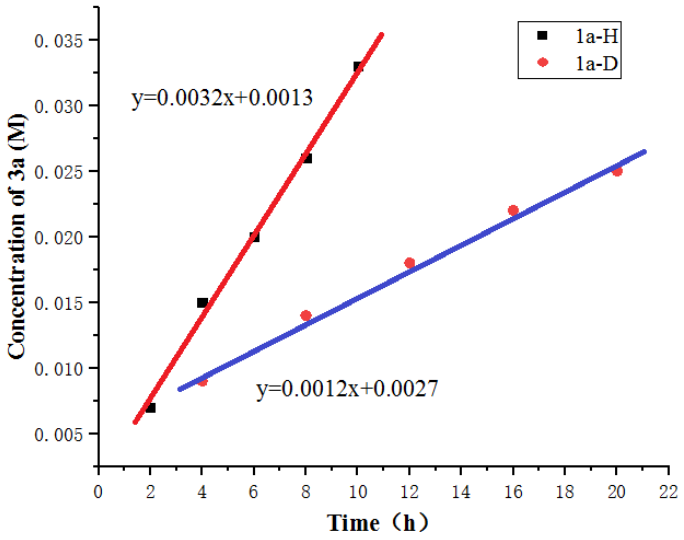


A screw-cap vial was charged with $[Rh(cod)Cl]_2$ (1.0 mg, 0.002 mmol, 2 mol%), $AgSbF_6$ (1.7 mg, 0.0050 mmol, 0.05 equiv), NaOAc (8.2 mg, 0.10 mmol, 1.00 equiv), amide **1a** (23.1 mg, 0.10 mmol, 1.0 equiv) or **1a-d** (23.2 mg, 0.10 mmol, 1.0 equiv), **2a** (35.6 mg, 0.20 mmol, 2.0 equiv) and DCE (1.0 mL) in sequence. The vial was sealed under argon and heated to 120 °C with stirring for corresponding reaction time. After cooling down, the reaction mixture was filtrated through a short column of silica gel eluted with PE/EA mixtures and concentration in vacuo. To the reaction residue was added mesitylene (0.1 mmol, 13.5 μL, 12.0 mg) as the internal standard and the yield of **3a** or **3a-*d*** was analyzed with ^1H NMR measurement. Yields and concentrations of **3a** or **3a-*d*** were used to obtain reaction rate profiles. A KIE value was determined to be 2.7.

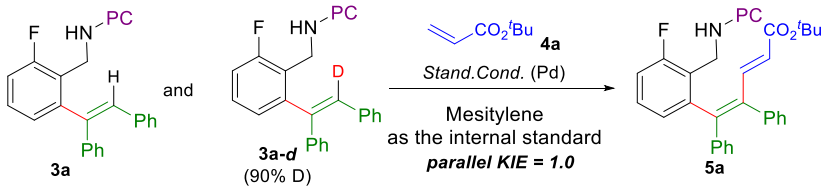
The relevant data are listed below:

Parallel KIE in Rh-catalysed cross coupling

1a-*d*			**1a**		
Time(h)	**5a** yield (%)	Concentration [M]	Time(h)	**5a** yield (%)	Concentration [M]
4	9	0.009	2	7	0.007
8	14	0.014	4	15	0.015
12	18	0.018	6	20	0.02
16	21	0.021	8	26	0.026
20	25	0.025	10	33	0.033
（M/h）	0.0012		**（M/h）**	0.0032	
k_H/k_D	**2.7**				



5.2 Parallel KIE experiments with 3a and 3a-*d*

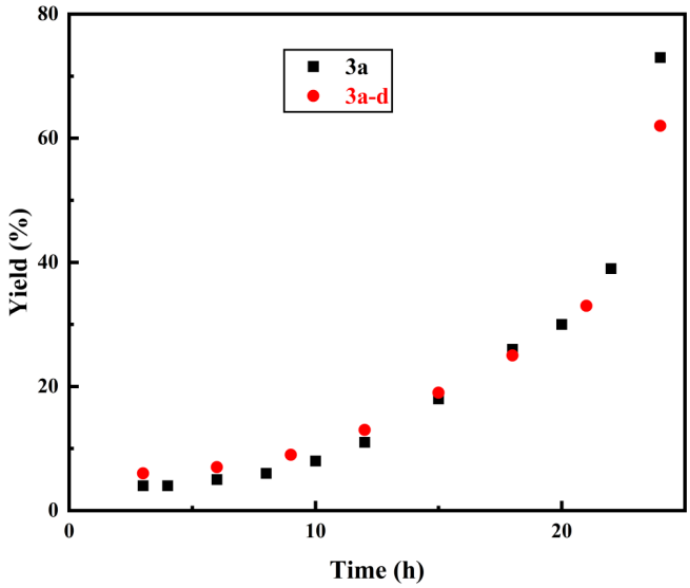


A screw-cap vial was charged with $Pd(OAc)_2$ (3.4 mg, 15 mol%, 0.015 mmol), MnO_2 (26.1 mg, 0.3 mmol, 3.0 equiv), BQ (1.1 mg, 0.01 mmol, 10 mol%), amide **3a**

(40.9 mg, 0.10 mmol, 1.0 equiv) or **3a-*d*** (40.9 mg, 0.10 mmol, 1.0 equiv) and EtOH (0.7 mL) was added. Then, pivalic acid (15.3 mg, 0.15 mmol, 1.5 equiv), and tert-butyl acrylate **4a** (32.0 mg, 0.25 mmol, 2.5 equiv) were added into the solution in sequence. The vial was sealed under air and heated to 80 °C with stirring for corresponding reaction time. After cooling down, the reaction mixture was filtrated through a short column of silica gel eluted with PE/EA mixtures and concentration in vacuo. To the reaction residue was added mesitylene (0.1 mmol, 13.5 μL, 12.0 mg) as the internal standard and the yield of **5a** was analyzed with ^{1}H NMR measurement. Yields and concentrations of **5a** were used to obtain reaction rate profiles. A KIE value was determined to be **1.0**.

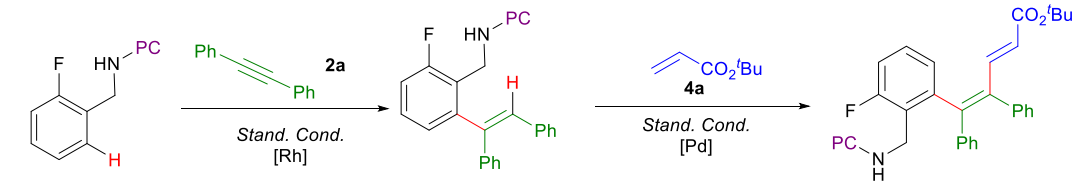
The relevant data are listed below:

Parallel KIE in Pd-catalysed cross coupling		
	3a	**3a-*d***
Time (h)	**5a** yield (%)	
3	4	6
4	4	-
6	5	7
8	6	-
9	-	9
10	8	-
12	11	13
15	18	19
18	26	25
20	30	-
21	-	33
22	39	-
24	73	62
k_H/k_D	**1.0**	



6. Synthetic Applications

6.1 Scaled-up Preparation



1a, 0.46g ,2 mmol

3a, 0.71 g, 85% yield

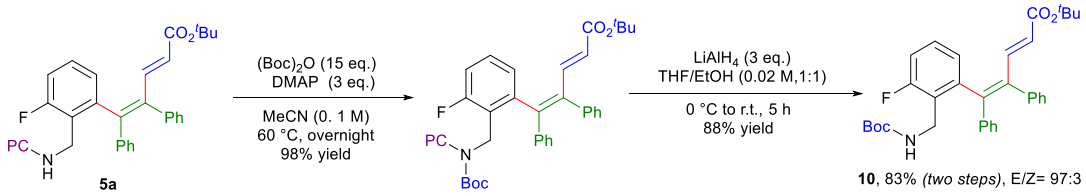
5a, 0.74 g, 80% , *E*/*Z*> 99:1

A screw-cap vial was charged with $[Rh(cod)Cl]_2$ (19.9 mg, 0.04 mmol, 2 mol%), $AgSbF_6$ (34.4 mg, 0.10 mmol, 0.05 equiv), NaOAc (164.1 mg, 2 mmol, 1.0 equiv), amide **1a** (0.46 g, 2.0 mmol, 1.0 equiv), diphenylacetylene (0.71 g, 4 mmol, 2.00 equiv) and DCE (20 mL) in sequence. The vial was sealed under Argon and heated to 120 ºC with stirring for 48 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) to obtain the corresponding product **3a** (0.71 g, 85% yield).

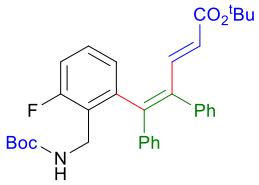
A screw-cap vial was charged with $Pd(OAc)_2$ (38.8 mg, 10 mol%), MnO_2 (270.6 mg, 3.0 equiv), BQ (11.1 mg, 10 mol%), amide **3a** (0.71 g, 1.73 mmol, 1.0 equiv), EtOH (11 mL). Then, pivalic acid (265.4 mg, 1.5 equiv), and olefin **4a** (332.5 mg, 2.5

equiv) were added into the solution in sequence. The vial was sealed under air and heated to 80 °C with stirring for 24 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE/EA mixtures) to obtain the corresponding product **5a** (0.74 g, 80% yield, *E/Z* > 99:1).

6.2 DG Removal



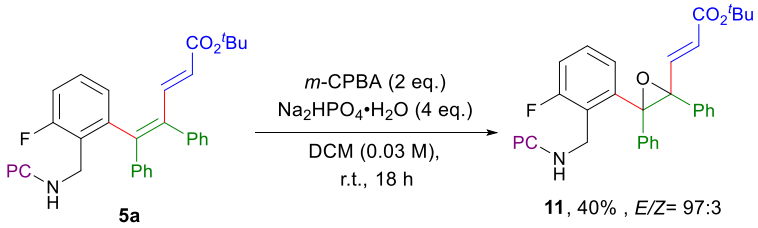
DG removal experiment was performed according to previous literature[8]. Boc-anhydride (327.4 mg, 15.0 equiv, 1.5 mmol) was added to a solution of **5a** (53.5 mg, 0.1 mmol, 1.0 equiv) and DMAP (43.3 mg, 0.3 mmol, 3.0 equiv) in MeCN (1 mL) and the rection mixture was heated to 60 °C and stirred overnight until the reaction is completed. The reaction mixture was quenched with NH_4Cl (10 mL, sat. aq.) and extracted with CH_2Cl_2 (20 mL × 3). The organic layers were combined and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude residue was purified by chromatography on silica gel (SiO_2, PE / EA = 40:1 to 20: 1) to give N-Boc-amide as a pale yellow solid (110.9 mg, 76% yield, *E/Z* = 95:5). Then to a solution of N-Boc-amide in THF/EtOH (0.02 M, *v:v*=1:1) was added $LiAlH_4$ (3.0 equiv，2.5 M in Et_2O) in dropwise over 30 min at 0°C and stirred at room temperature for 5 h, and 2 N NaOH was added slowly at 0°C until a clear solution was obtained. The organic layer was separated and the aqueous phase was extracted with Et_2O (20 mL × 3). The organic layers were combined and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude residue was purified by chromatography on silica gel with PE/EA to result N-boc benzylamine **10** as a white solid (44.0 mg, 88% yield, *E/Z* = 97:3, 83% yield for two steps, m.p. = 73.9 °C).



Tert-Butyl (2*E*,4*E*)-5-(2-(((tert-butoxycarbonyl) amino) methyl)-3-fluorophenyl)-4,5-diphenylpenta-2,4-dienoate (10)

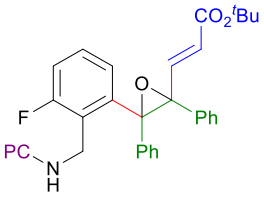
According to previous literature reports, **10** was obtained as a white solid (44.0 mg, 88% yield, *E/Z* = 97:3, 83% yield for two steps, m.p. = 73.9 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 7H), 7.05 – 6.98 (m, 2H), 6.97 – 6.91 (m, 3H), 6.85 – 6.78 (m, 2H), 5.44 (d, *J* = 15.5 Hz, 1H), 4.38 (s, 1H), 4.21 (d, *J* = 5.1 Hz, 2H), 1.31 (s, 9H), 1.30 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.48, 162.21 (d, J_{CF} = 248.1 Hz), 155.15, 145.23 (d, J_{CF} = 2.4 Hz), 144.07, 142.90 (d, J_{CF} = 2.6 Hz), 140.28, 138.86, 138.12, 130.87, 130.35, 129.16 (d, J_{CF} = 9.5 Hz), 128.34, 127.68, 127.34 (d, *J* = 2.6 Hz), 126.86, 124.68, 124.53, 124.23, 115.35 (d, J_{CF} = 21.5 Hz), 80.28, 79.12, 36.39 (d, J_{CF} = 2.8 Hz), 28.37, 28.09. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.04. **HRMS (ESI)** calcd for $C_{33}H_2FNO_4Na$ $[M+Na]^+$: 552.2521, found: 552.2527. **FTIR** (KBr, cm^{-1}) 2959.81, 2830.84, 2718.69, 2348.60, 1608.41, 1210.28, 1064.49, 775.70, 568.22.

6.3 Epoxidation Reaction



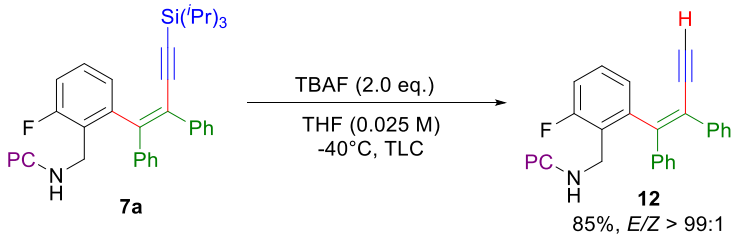
Epoxidation experiment was performed according to previous literature[9]. A solution of **5a** (53.6mg, 0.1 mmol, 1.0 equiv) in CH_2Cl_2 (3.3 mL, 0.03 M) at 0 °C was added *m*-CPBA (49.3 mg, 0.2 mmol, 2.0 equiv, 30% water) and $Na_2HPO_4{\cdot}2H_2O$ (71.2 mg, 0.4 mmol, 4.0 equiv). The mixture was stirred for 18 h at room temperature. After the reaction was completed (monitored by TLC), the mixture was extracted with CH_2Cl_2 (30 mL) for three times. The organic layers were combined and washed with Na_2SO_4 (20 mL, 10% aq.), $NaHCO_3$ (20 mL, sat. aq) and NaCl (20 mL, sat. aq), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give epoxy compound **11** as

a colorless liquid (22.0 mg, 40% yield, *E*/*Z* = 97:3).

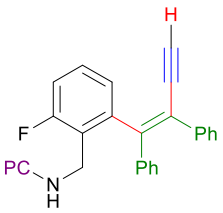


Tert-butyl(*E*)-3-((2R,3R)-3-(3-fluoro-2-((pyrazine-2-carbox amido) methyl) phenyl)-2,3-diphenyloxiran-2-yl)acrylate (11) According to previous literature reports, **11** was obtained as a colorless liquid (22.0 mg, 40 % yield, *E*/*Z* = 97:3). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.26 (d, *J* = 4.0 Hz, 1H), 8.11 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.54 (s, 1H), 7.46 – 7.40 (m, 1H), 7.32 – 7.23 (m, 4H), 7.21 – 7.13 (m, 4H), 7.03 – 6.95 (m, 3H), 6.93 – 6.87 (m, 2H), 5.49 (d, *J* = 15.5 Hz, 1H), 4.68 – 4.49 (m, 2H), 1.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.31, 162.16 (d, J_{CF} = 248.8 Hz), 160.06, 149.35, 145.43, 144.98 (d, J_{CF} = 2.1 Hz), 143.80, 143.30 (d, J_{CF} = 3.6 Hz), 140.00, 139.30, 137.93, 135.27, 133.57, 130.81, 130.34, 129.81, 128.45, 127.77, 127.45 (d, J_{CF} = 11.1 Hz), 127.28 (d, J_{CF} = 3.0 Hz), 124.58, 122.98 (d, J_{CF} = 15.1 Hz), 115.65 (d, J_{CF}= 22.3 Hz), 80.33, 53.47, 35.21 (d, J_{CF} = 4.1 Hz), 29.72, 28.02. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.69. **HRMS (ESI)** calcd for $C_{33}H_{30}FN_3O_4Na$ $[M+Na]^+$: 574.2113, found: 574.2118.

6.4 Desilylated Reaction



To an oven-dried 25 mL flask was added **7a** (28.9mg, 0.05 mmol), a solution of TBAF (2.0 eq.) in THF (0.025M),. The reaction was stir at -40°C under Ar. After the reaction was completed (monitored by TLC), the reaction was quenched by saturated $NaHCO_3$ solution (4 mL), extracted by DCM (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The residue was purified by column chromatography on silica gel (PE/EA) to afford the product **12** as colorless liquid (18.4 mg, 85% yield, *E*/*Z* > 99:1).

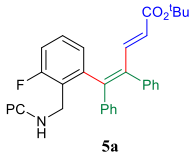
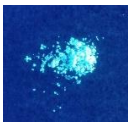
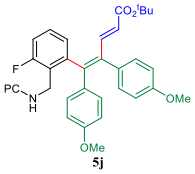
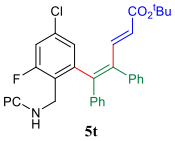
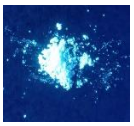
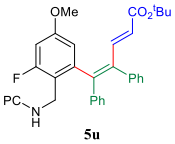
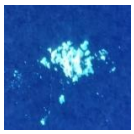


(*E*)-*N*-(2-(1,2-diphenyl but-1-en-3-yn-1-yl)-6-fluorobenzyl) pyrazine-2-carboxamide (12) According to previous literature reports, **12** was obtained as a colorless liquid (18.4 mg, 85 % yield, *E/Z* > 99:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.38 (d, *J* = 1.2 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 8.48 – 8.40 (m, 1H), 7.86 (s, 1H), 7.40 – 7.34 (m, 1H), 7.34 – 7.29 (m, 2H), 7.23 – 7.18 (m, 4H), 7.11 (t, *J* = 9.0 Hz, 1H), 7.08 – 7.03 (m, 3H), 7.01 – 6.95 (m, 2H), 4.91 (dd, *J* = 14.0, 5.9 Hz, 1H), 4.52 (dd, *J* = 13.8, 3.7 Hz, 1H), 3.06 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.20, 161.98 (d, J_{CF} = 248.0 Hz), 147.37 (d, J_{CF} = 2.3 Hz), 147.02, 144.92 (d, J_{CF} = 3.8 Hz), 144.57, 144.43, 142.30, 139.08, 137.77, 130.19, 129.77, 129.45 (d, J_{CF} = 9.2 Hz), 128.21, 128.08, 127.79, 126.17 (d, J_{CF} = 3.2 Hz), 123.46, 123.11, 122.99, 115.16 (d, J_{CF} = 22.3 Hz), 84.78, 83.25, 35.28 (d, J_{CF} = 4.2 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.72. **HRMS (ESI)** calcd for $C_{28}H_{20}FN_3ONa$ $[M+Na]^+$: 456.1488, found: 456.1489.

7. Photophysical properties of products

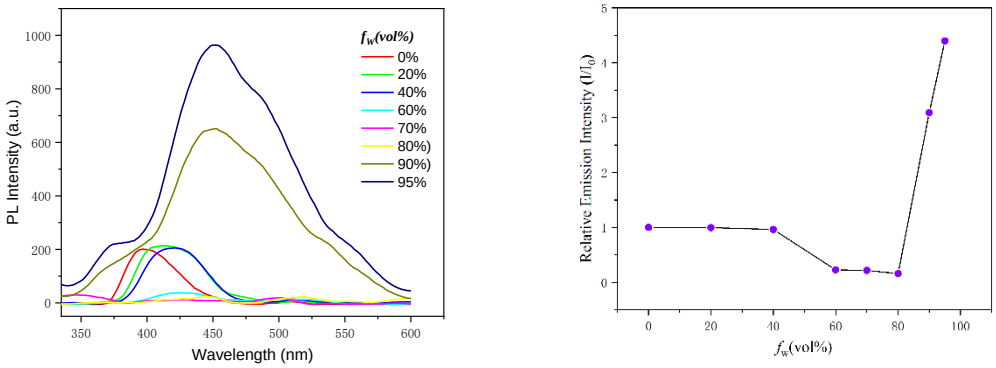
After developing a method for the synthesis of tetra-substituted olefins, we investigated their AIE performance, the corresponding results are shown in **Figure S1**. The photophysical properties of representative compounds are summarized in **Table S1** and the corresponding spectra are given.

Supplementary Table 1. Photophysical data of representative AIE-gens[a]

Compound	Solution [nm]			Photo imagesc
	λabs	*λem*	Stoke's shift	
 **5a**	319	449	130	
 **5j**	265	459	194	
 **5t**	260	452	192	
 **5u**	260	434	174	

[a] λabs and λem refer to optimal absorption wavelength and photoluminescence (PL) peak, respectively. [b] Photo images of the solid under UV light (λex = 365 nm).

Fluorescence Behaviour of Compounds 5a in 1,4-dioxane/H_2O Mixture



Supplementary Figure S1. (a) Emission spectra and (b) emission profile of compound 5a in 1,4-dioxane /H_2O mixture with increasing f_w to 95% (c = 150 μM, λex = 319 nm).

8. References

[1] Chreib, B. S.; Carreira, E. M. *J. Am. Chem. Soc*. **2019**, *141*, 8758–8763.

[2] Martínez, A. M.; Echavarren, J.; Alonso, I.; Rodríguez, N.; Arrayás, R. G.; Carretero, J. C. *Chem. Sci*. **2015**, *6*, 5802–5814.

[3] Wang, J.; Hu, D,; Sun, X.; Hong, H.; Shi, Y. *Org. Lett.* **2023**, *25*, 2006–2011.

[4] Ye, Y.; Kevlishvili, I.; Feng, S.; Liu, P.; Buchwald. S. L. *J. Am. Chem. Soc*. **2020**, 142, 10550–10556.

[5] Wu, X.; Fan, J.; Fu, C.; Ma. S. *Chem. Sci*. **2019**, *10*, 6316–6321.

[6] Moghaddam, F. M.; Farimani, M. M.; *Tetrahedron Lett*. **2010**, **51**, 540–542.

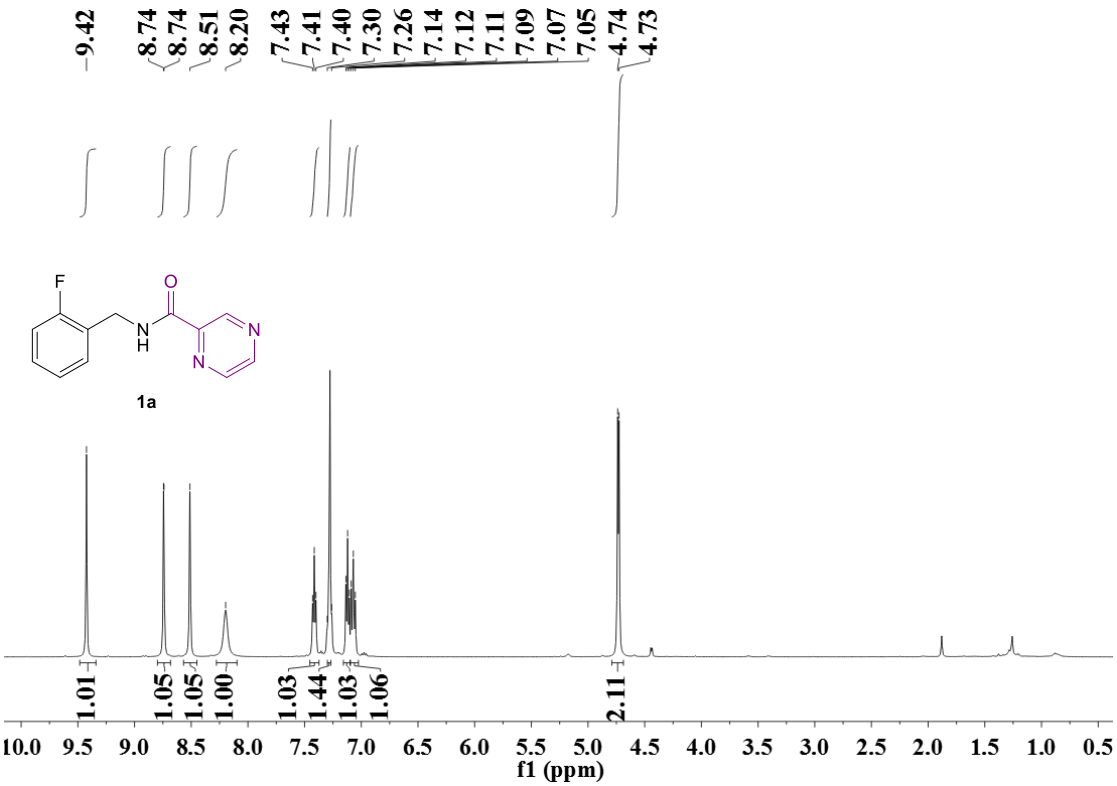
[7] Wei, W.; Liao, L.; Qin, T.; Zhao, X. *Org. Lett*. **2019**, **21**, 7846–7850.

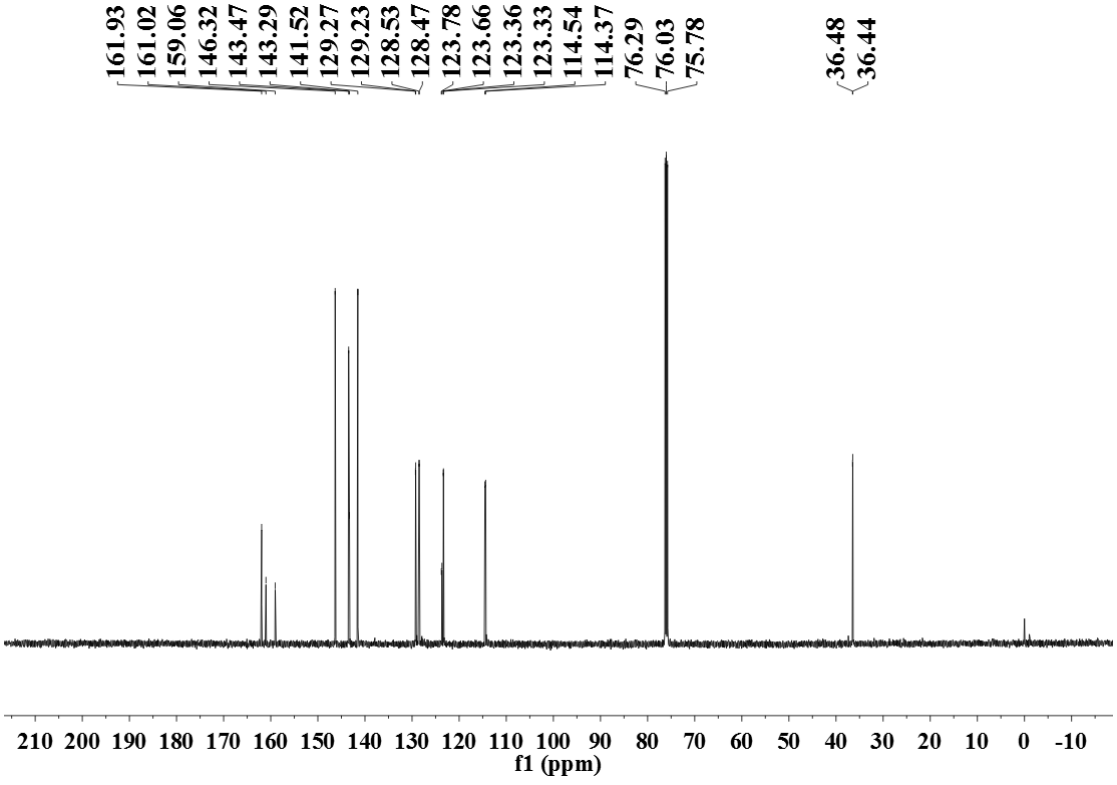
[8] Shen, Cong.; Zhu, Y.; Jin, S.; Xu, K.; Luo, S.; Xu, L.; Zhong, G.; Zhong, Li.; Zhang, J. *Org. Chem. Front*. **2022**, *9*, 989–994.

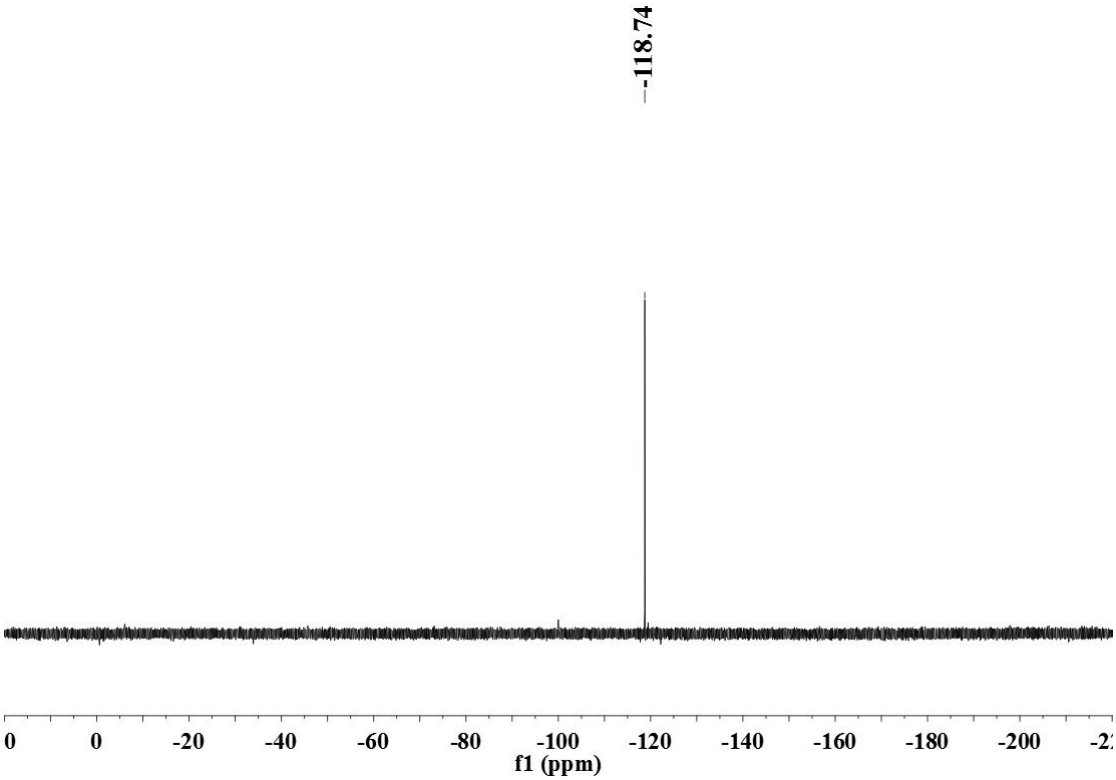
[9] Zezschwitz, P.; Voigt, K.; Lansky, A.; Noltemeyer, M.; Meijere. A. *J. Org. Chem*. **1999**, *64*, 3806–3812.

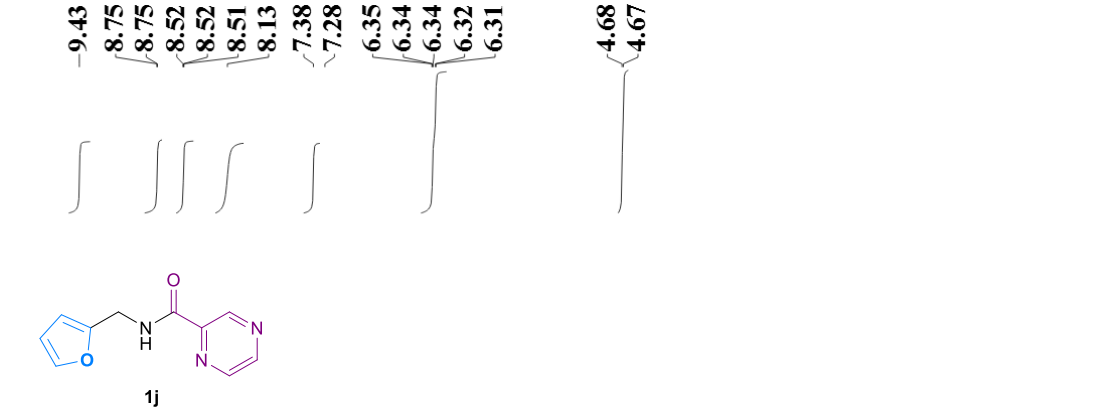
9. NMR Spectra

9.1 NMR Spectra of Substrates 1

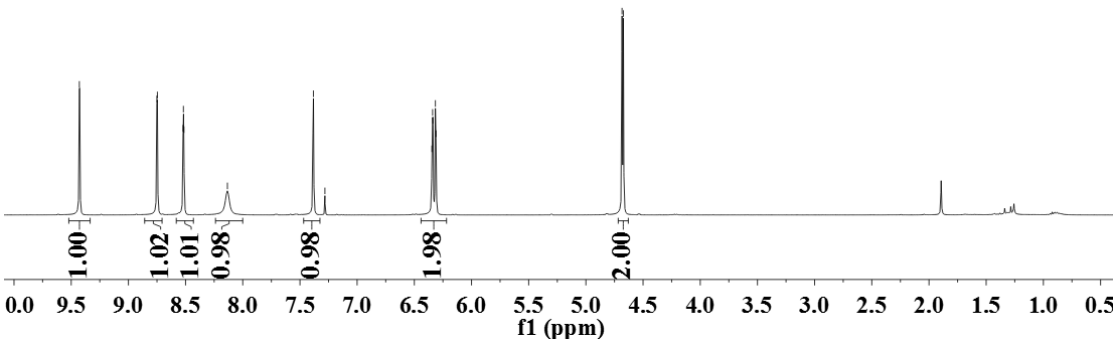


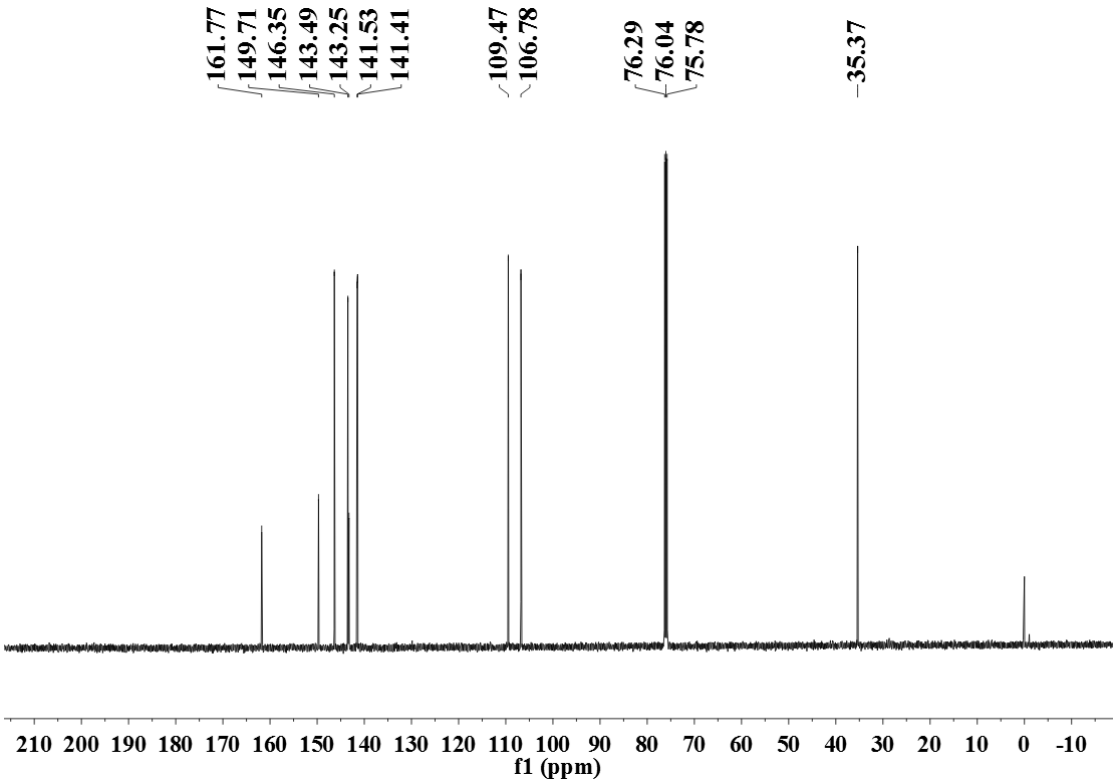


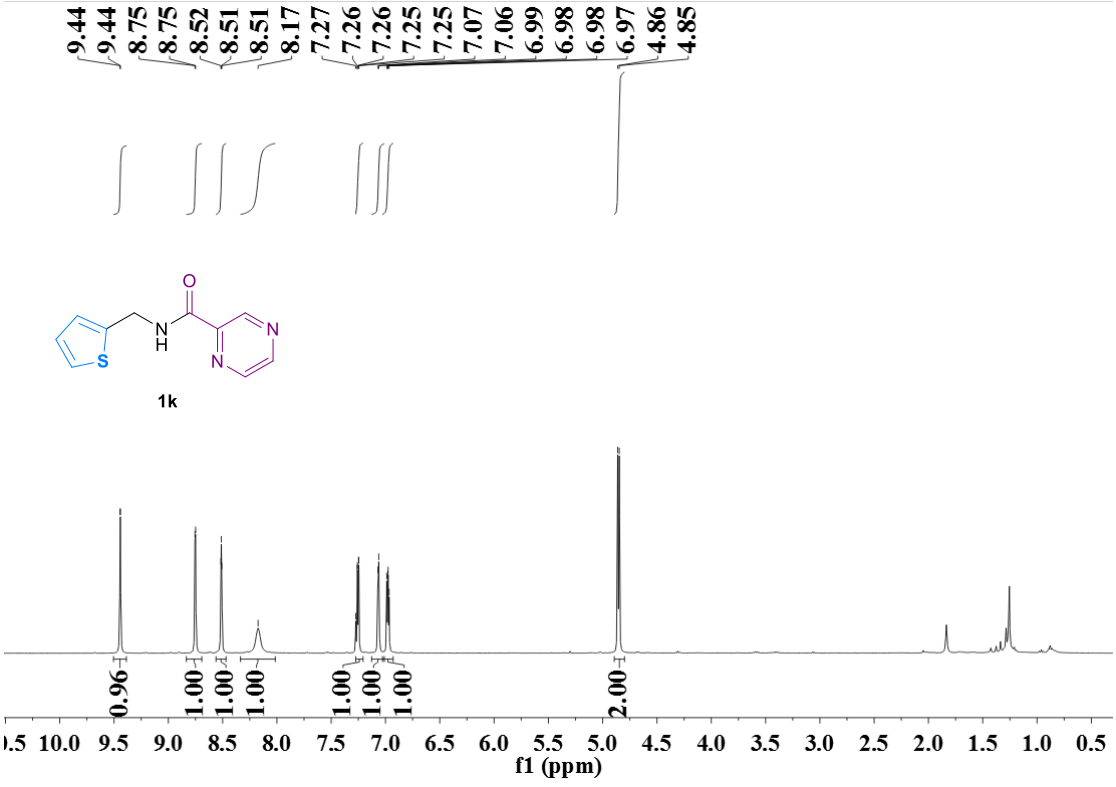

-118.74
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

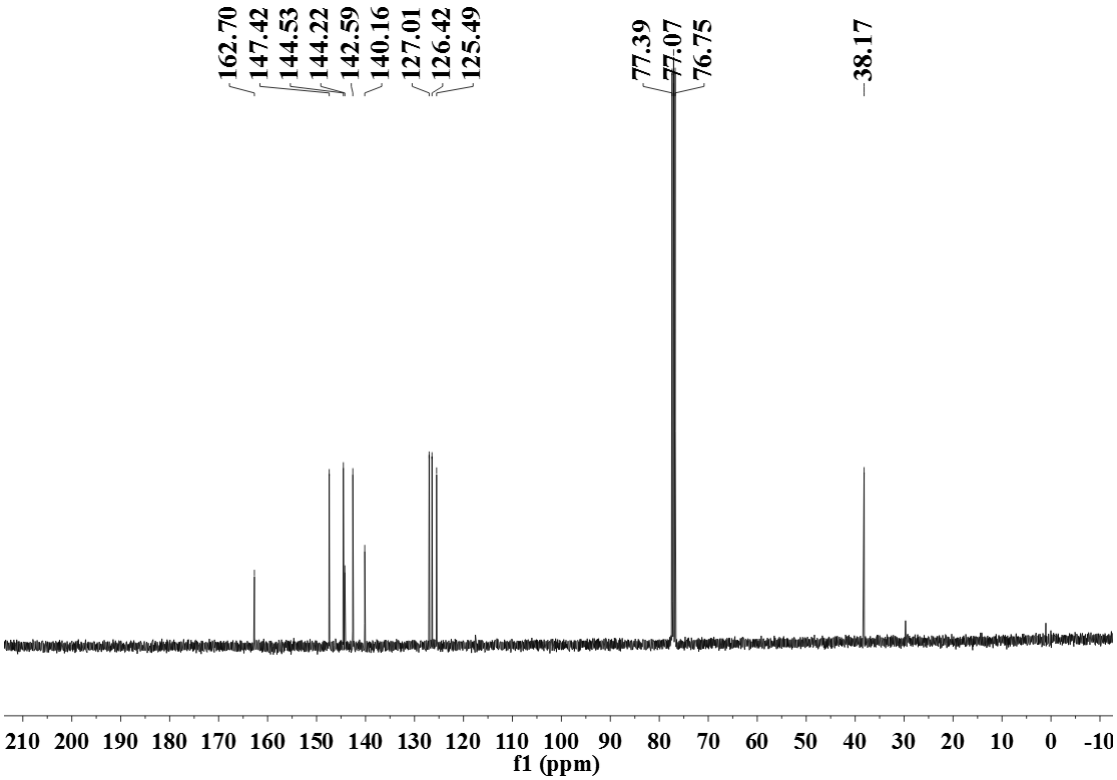

9.43
8.75
8.75
8.52
8.52
8.51
8.13
7.38
7.28
6.35
6.34
6.34
6.32
6.31
4.68
4.67
O
N
H
N
O
N

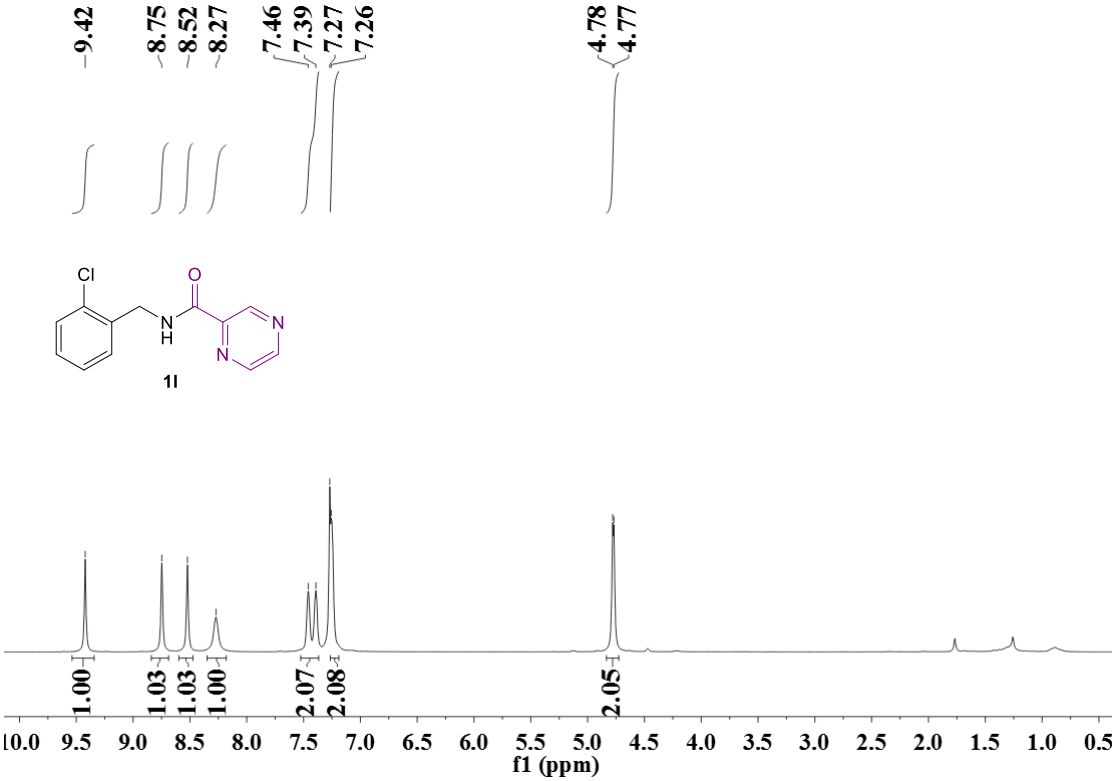
1j

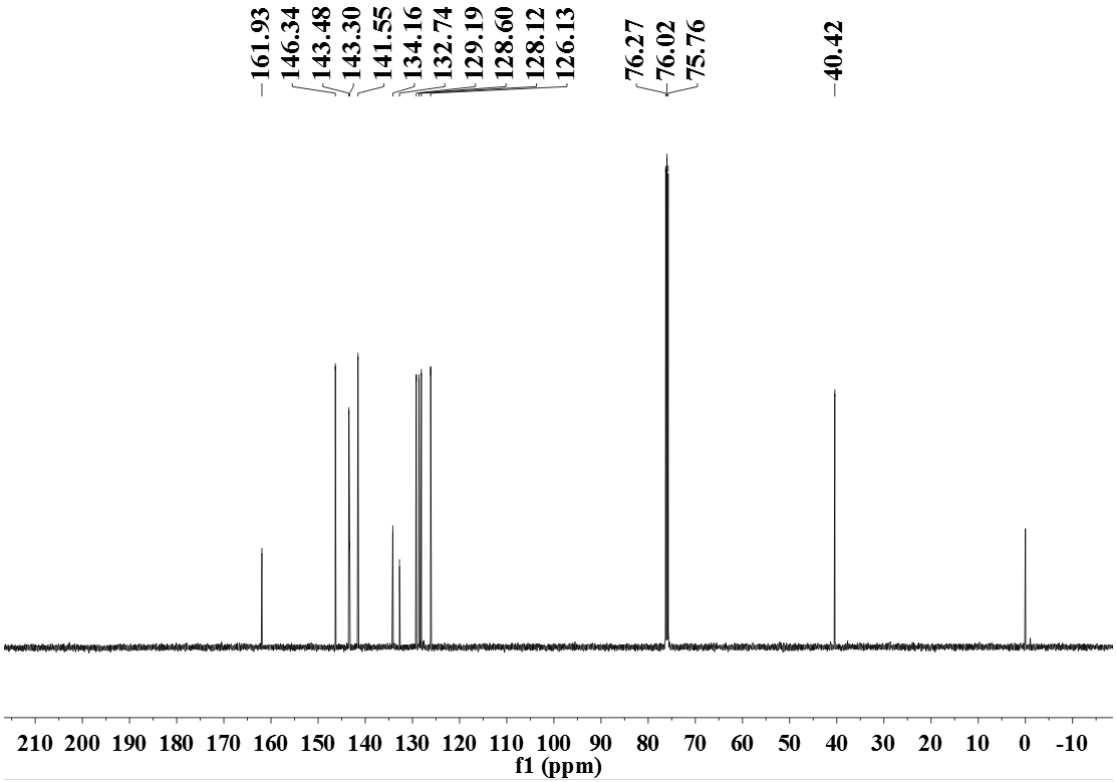

1.00
1.02
1.01
0.98
0.98
1.98
2.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

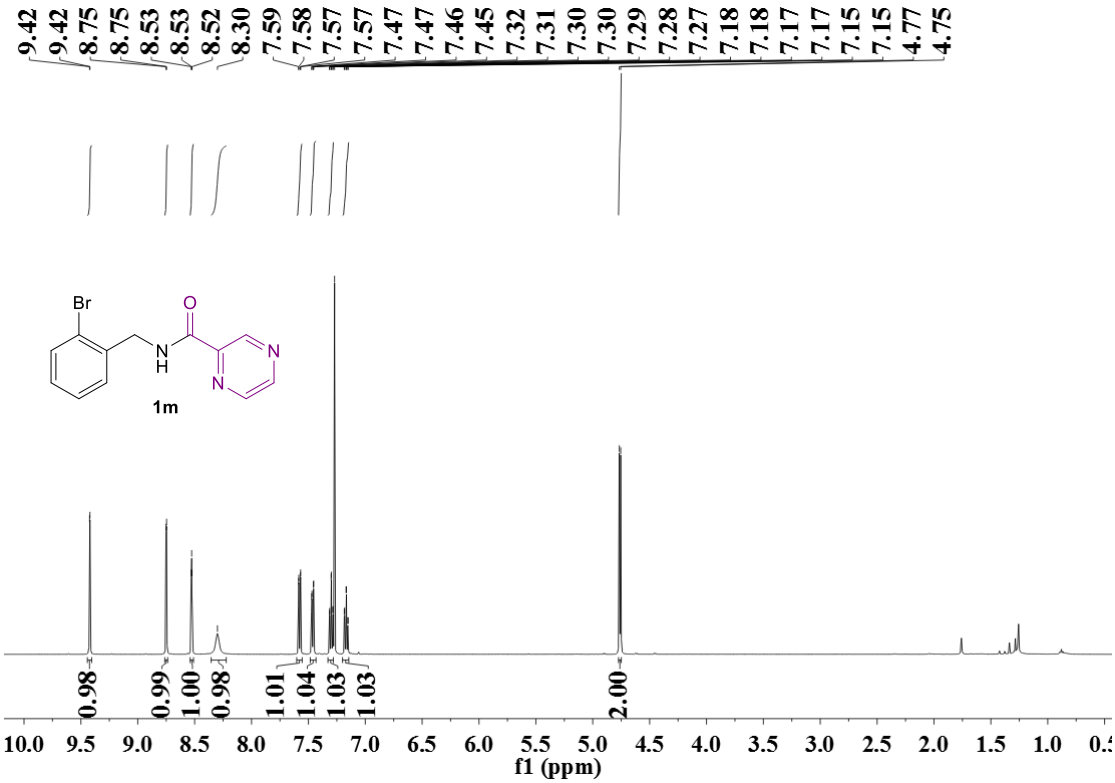

161.77
149.71
146.35
143.49
143.25
141.53
141.41
109.47
106.78
76.29
76.04
75.78
35.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

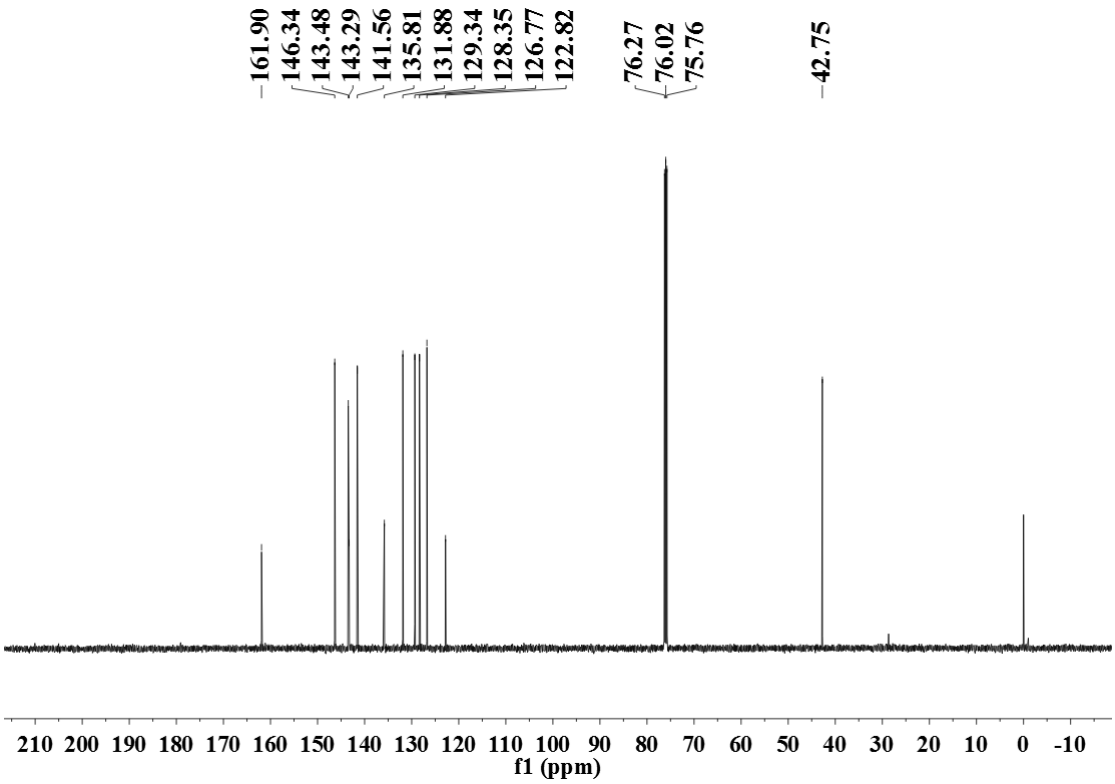

9.44
9.44
8.75
8.75
8.52
8.51
8.51
8.17
7.27
7.26
7.26
7.25
7.25
7.07
7.06
6.99
6.98
6.98
6.97
4.86
4.85
O
N
H
S
N
N
1k
0.96
1.00
1.00
1.00
1.00
1.00
1.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

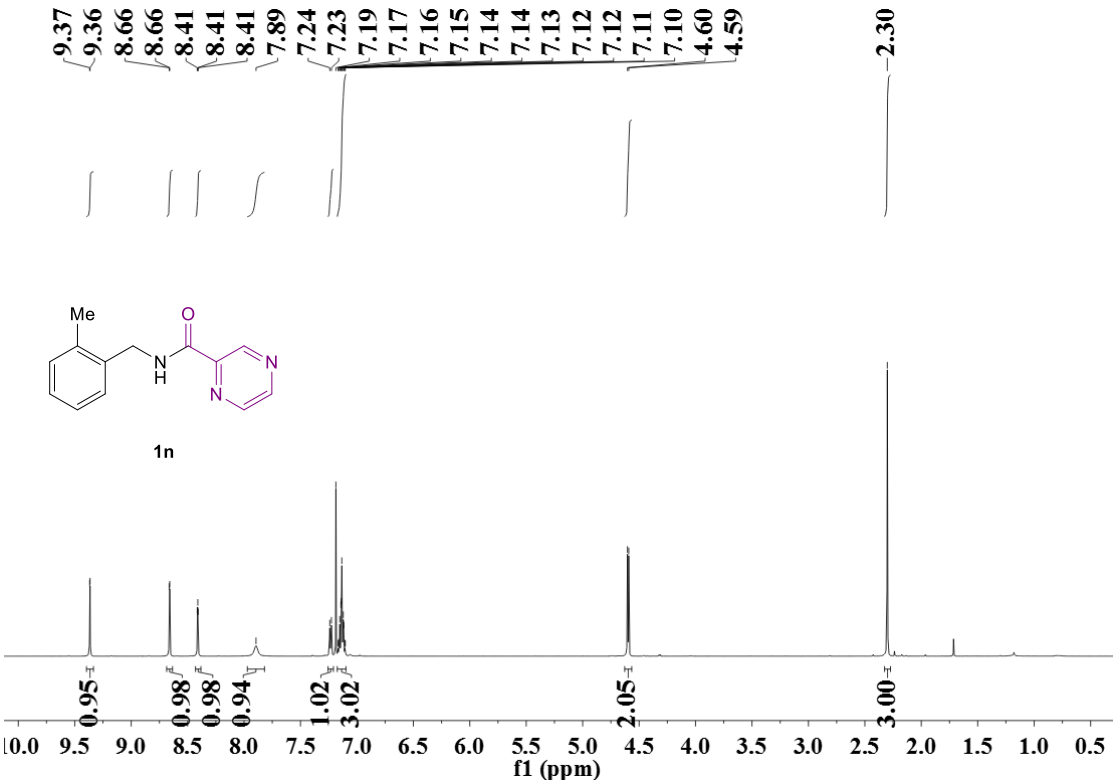

162.70
147.42
144.53
144.22
142.59
140.16
127.01
126.42
125.49
77.39
77.07
76.75
38.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

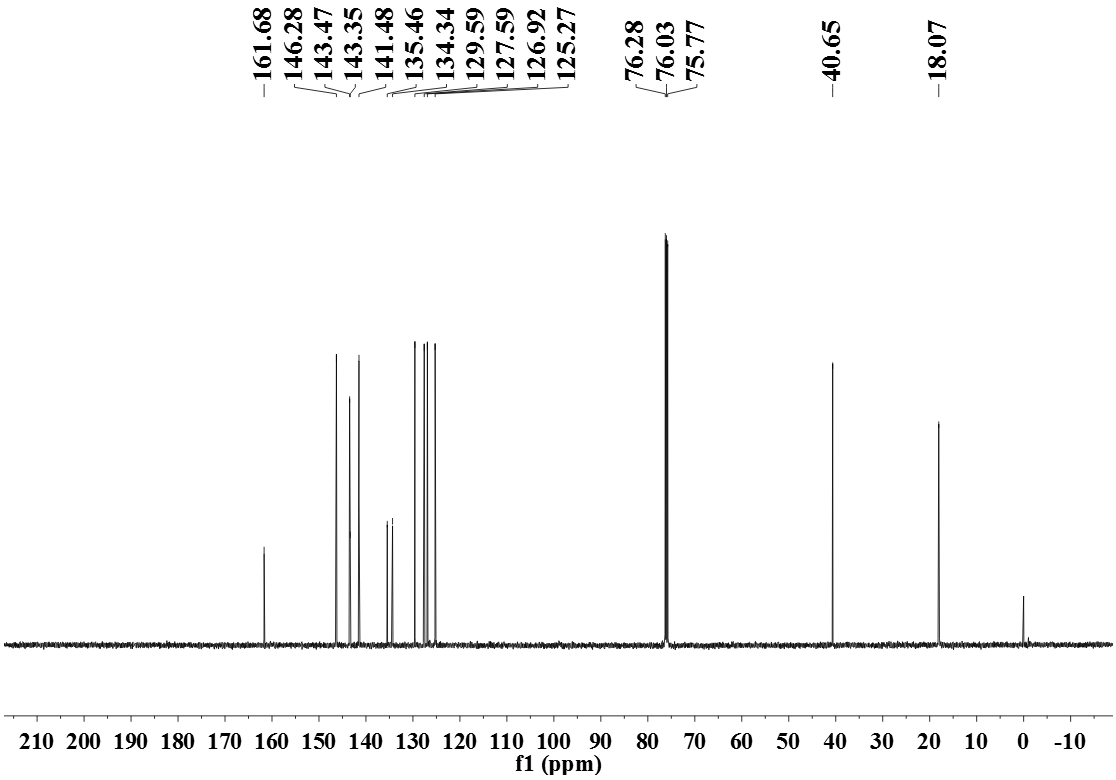

9.42
8.75
8.52
8.27
7.46
7.39
7.27
7.26
4.78
4.77
Cl
O
N
H
N
N
1l
1.00
1.03
1.03
1.00
2.07
2.08
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

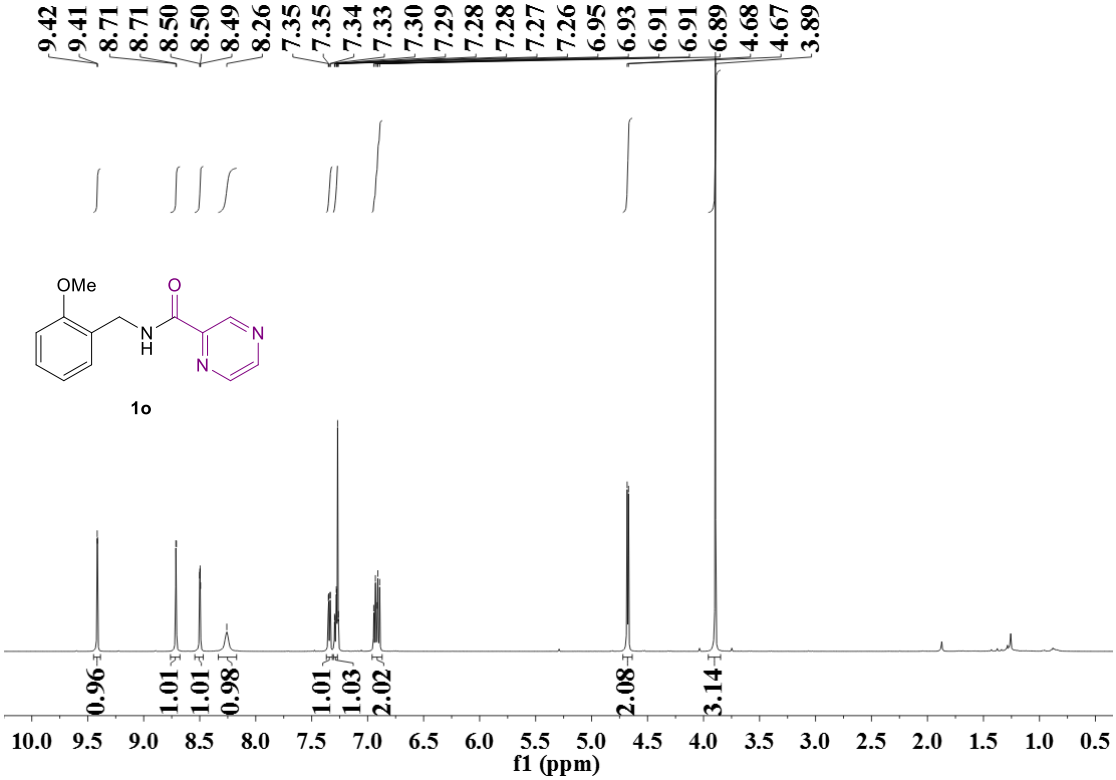

161.93
146.34
143.48
143.30
141.55
134.16
132.74
129.19
128.60
128.12
126.13
76.27
76.02
75.76
40.42
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

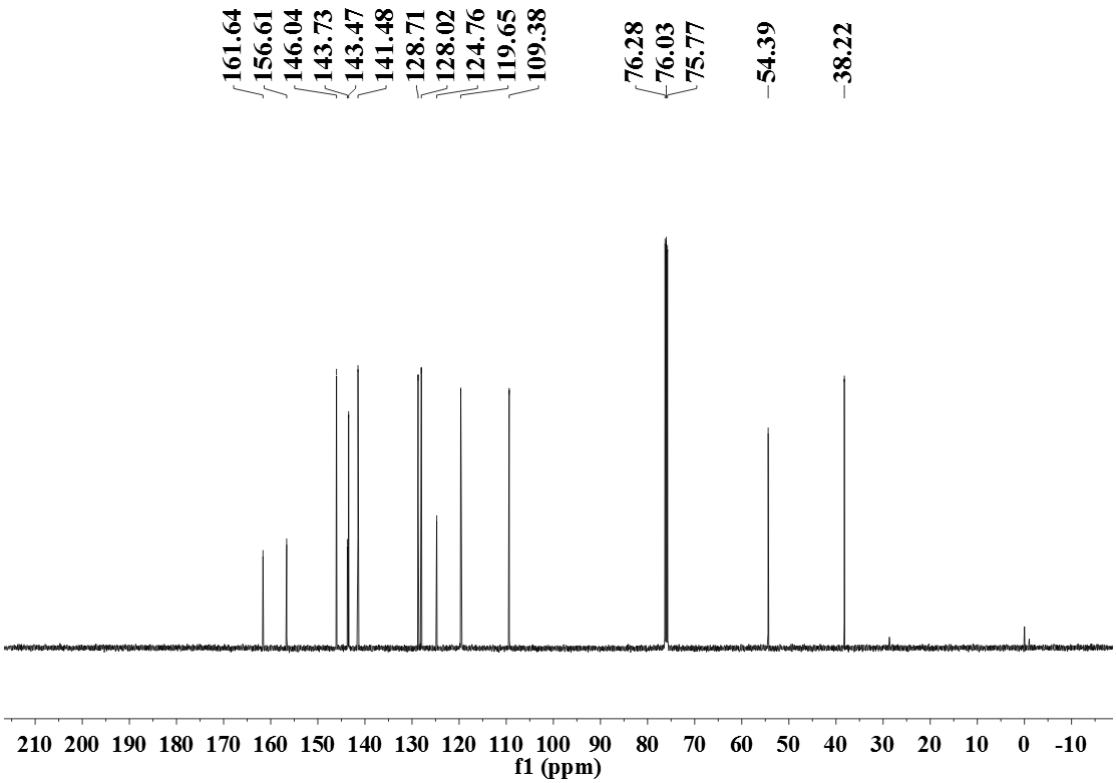

9.42
9.42
8.75
8.75
8.53
8.53
8.52
8.30
7.59
7.58
7.57
7.57
7.47
7.47
7.46
7.45
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.18
7.18
7.17
7.17
7.15
7.15
4.77
4.75
Br
O
N
H
N
N
1m
0.98
0.99
1.00
0.98
1.01
1.04
1.03
1.03
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

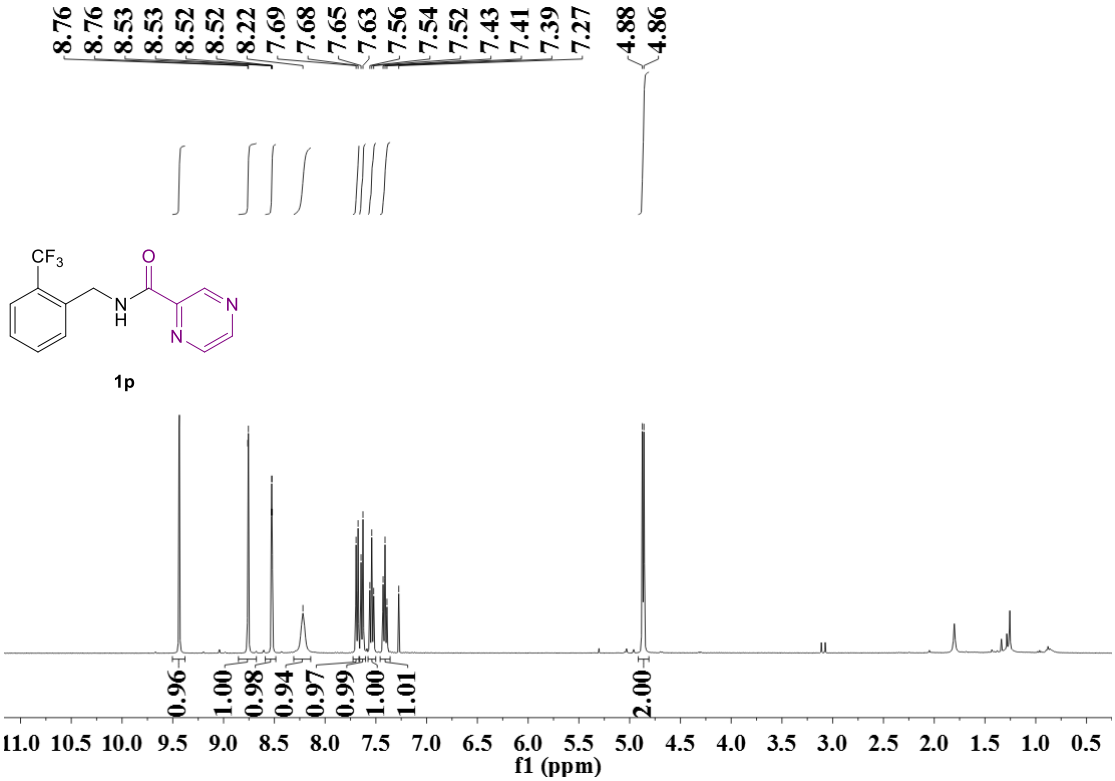

161.90
146.34
143.48
143.29
141.56
135.81
131.88
129.34
128.35
126.77
122.82
76.27
76.02
75.76
42.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

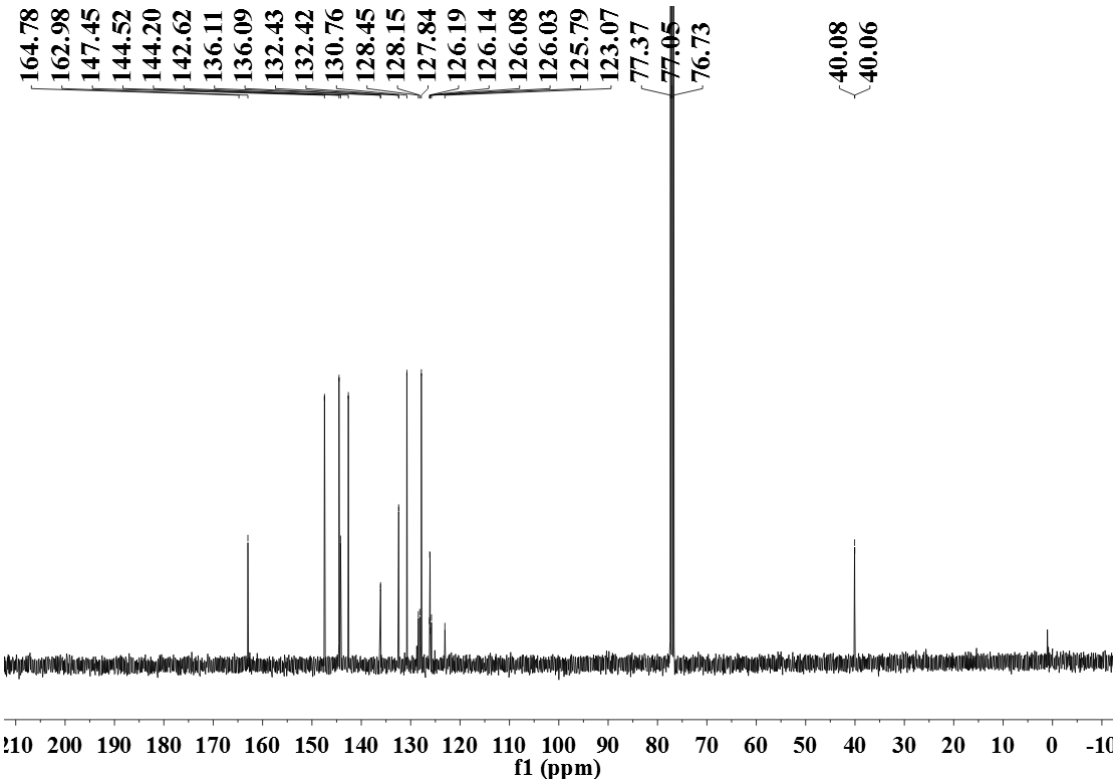

9.37
9.36
8.66
8.66
8.41
8.41
8.41
7.89
7.24
7.23
7.19
7.17
7.16
7.15
7.14
7.14
7.13
7.12
7.12
7.11
7.10
4.60
4.59
2.30
Me
O
N
H
N
N
1n
0.95
0.98
0.98
0.94
1.02
3.02
2.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

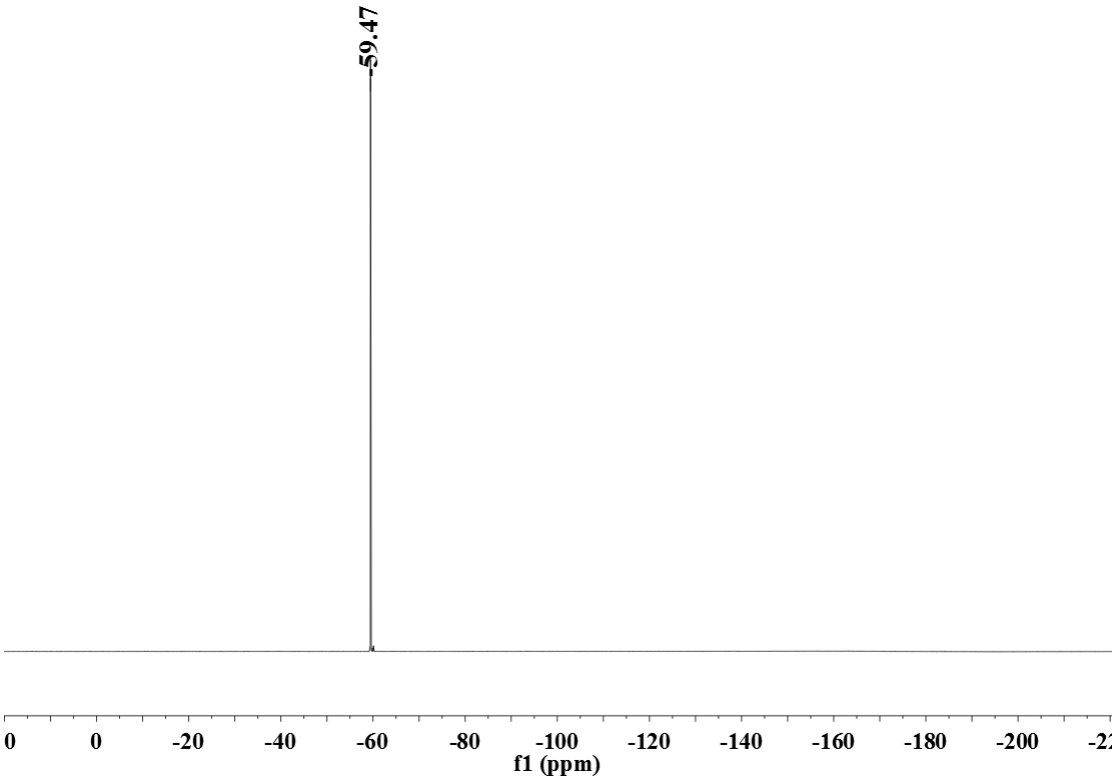

161.68
146.28
143.47
143.35
141.48
135.46
134.34
129.59
127.59
126.92
125.27
76.28
76.03
75.77
40.65
18.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

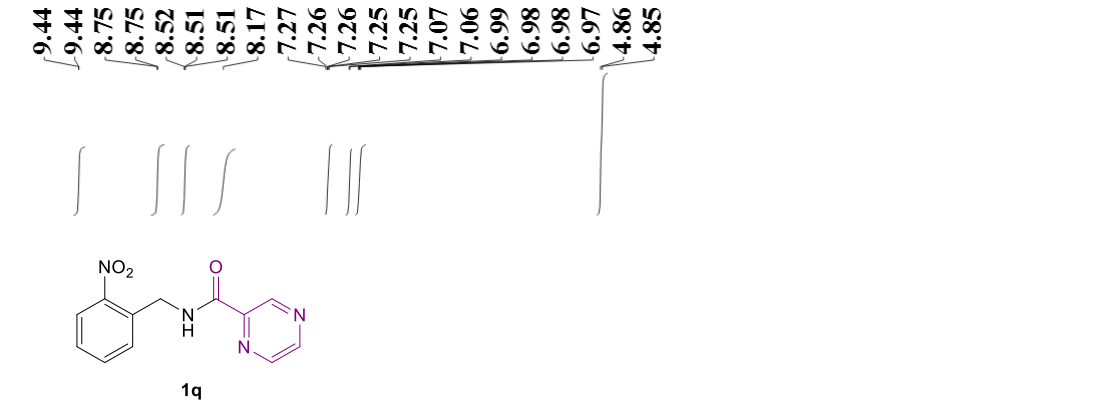

9.42
9.41
8.71
8.71
8.50
8.50
8.49
8.26
7.35
7.35
7.34
7.33
7.30
7.29
7.28
7.28
7.27
7.26
6.95
6.93
6.91
6.91
6.89
4.68
4.67
3.89
OMe
O
N
H
N
N
1o
0.96
1.01
1.01
0.98
1.01
1.03
2.02
2.08
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


161.64
156.61
146.04
143.73
143.47
141.48
128.71
128.02
124.76
119.65
109.38
76.28
76.03
75.77
54.39
38.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

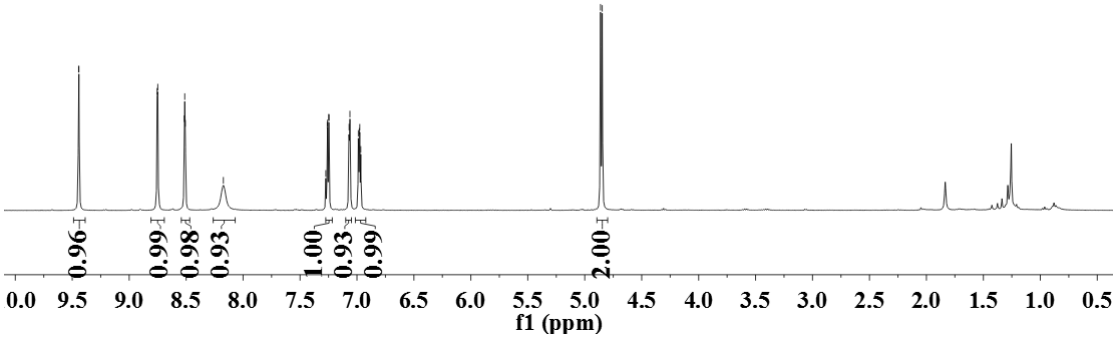

8.76
8.76
8.53
8.53
8.52
8.52
8.22
7.69
7.68
7.65
7.63
7.56
7.54
7.52
7.43
7.41
7.39
7.27
4.88
4.86
CF3
O
N
H
N
N
1p
0.96
1.00
0.98
0.94
0.97
0.99
1.00
1.01
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

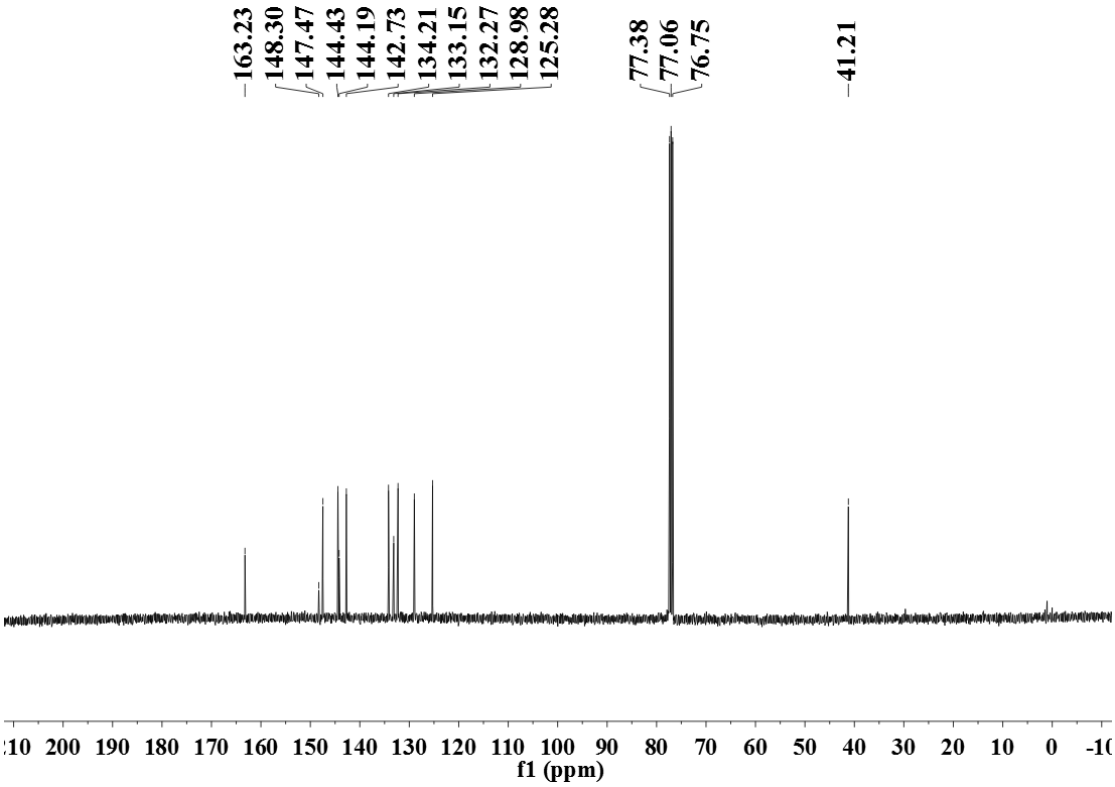

164.78
162.98
147.45
144.52
144.20
142.62
136.11
136.09
132.43
132.42
130.76
128.45
128.15
127.84
126.19
126.14
126.08
126.03
125.79
123.07
77.37
77.05
76.73
40.08
40.06
f1 (ppm)

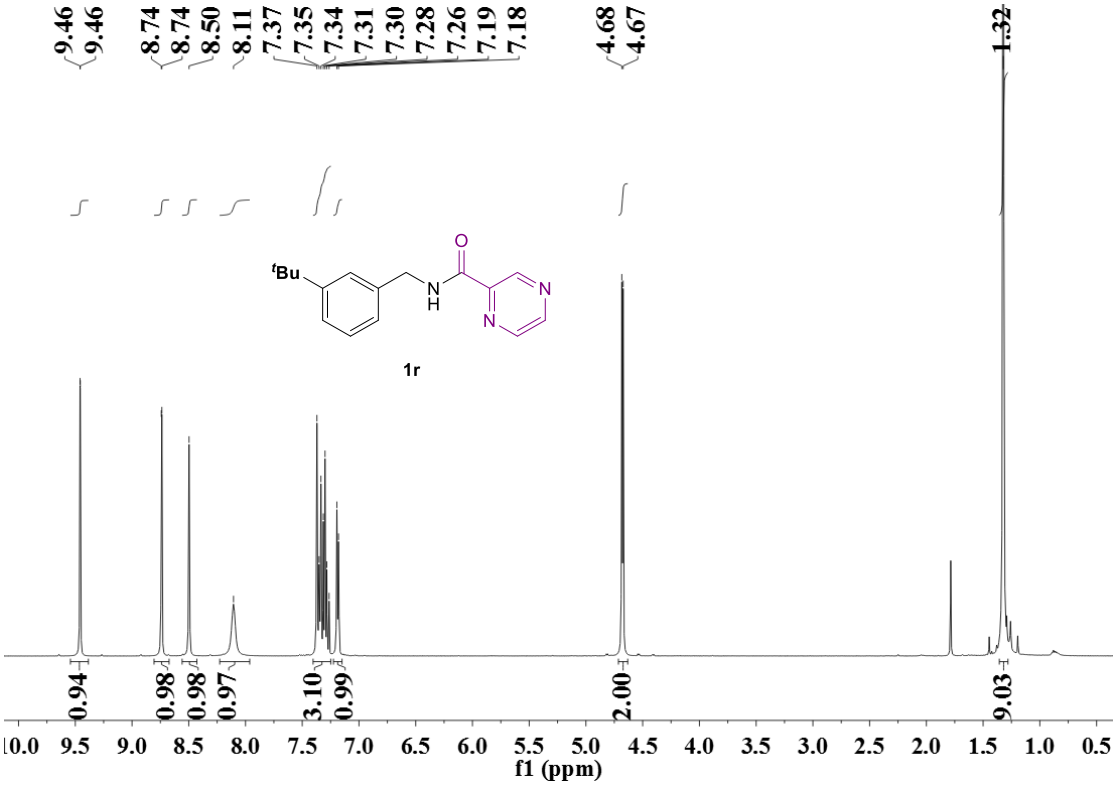

59.47
f1 (ppm)

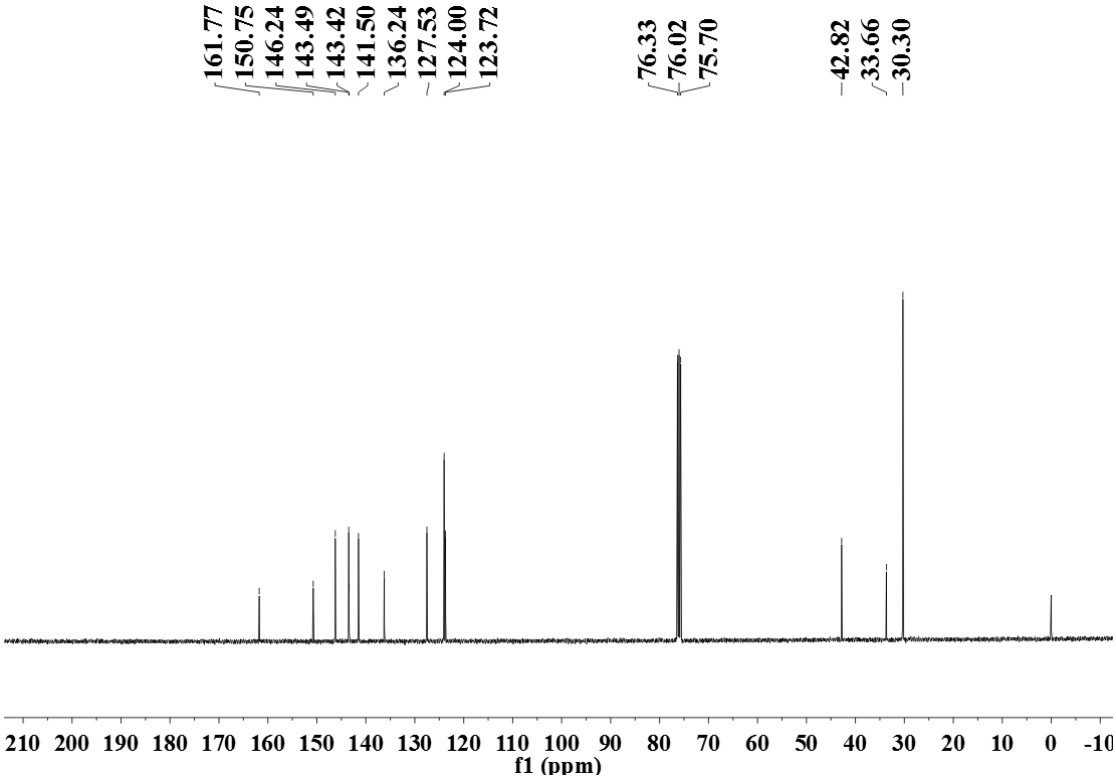

9.44
9.44
8.75
8.75
8.52
8.51
8.51
8.17
7.27
7.26
7.26
7.25
7.25
7.07
7.06
6.99
6.98
6.98
6.97
4.86
4.85
NO2
O
N
H
N
N

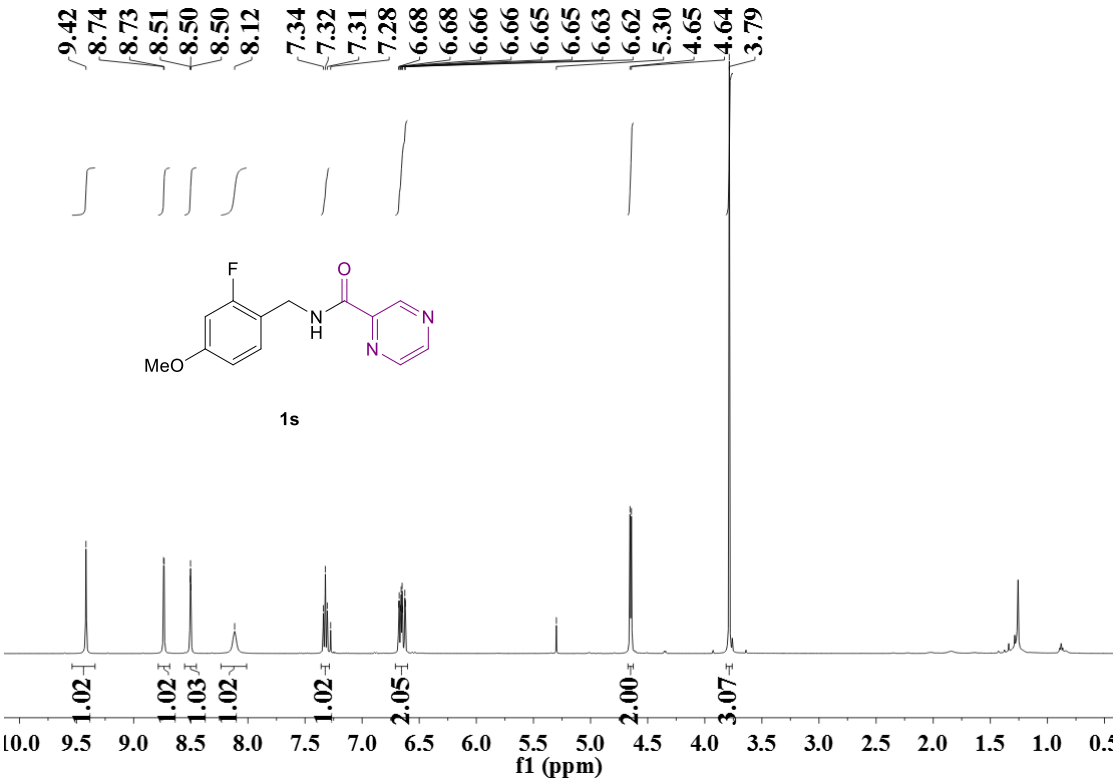
1q

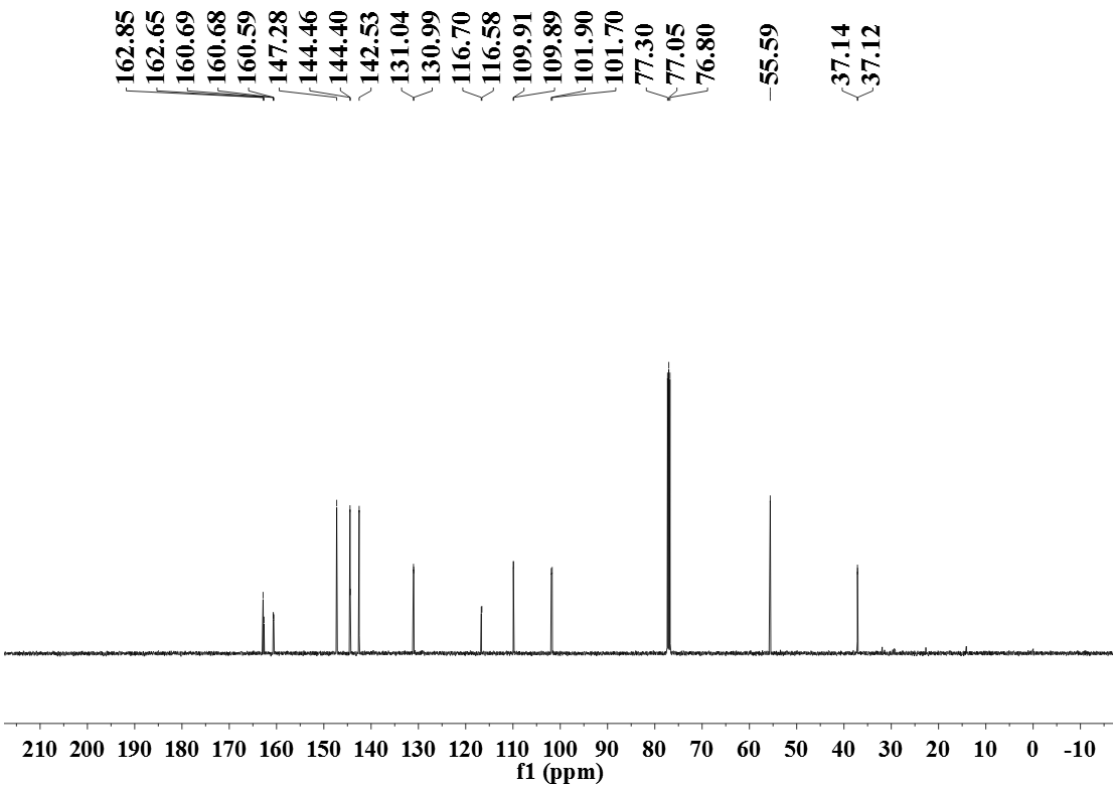

0.96
0.99
0.98
0.93
1.00
0.93
0.99
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

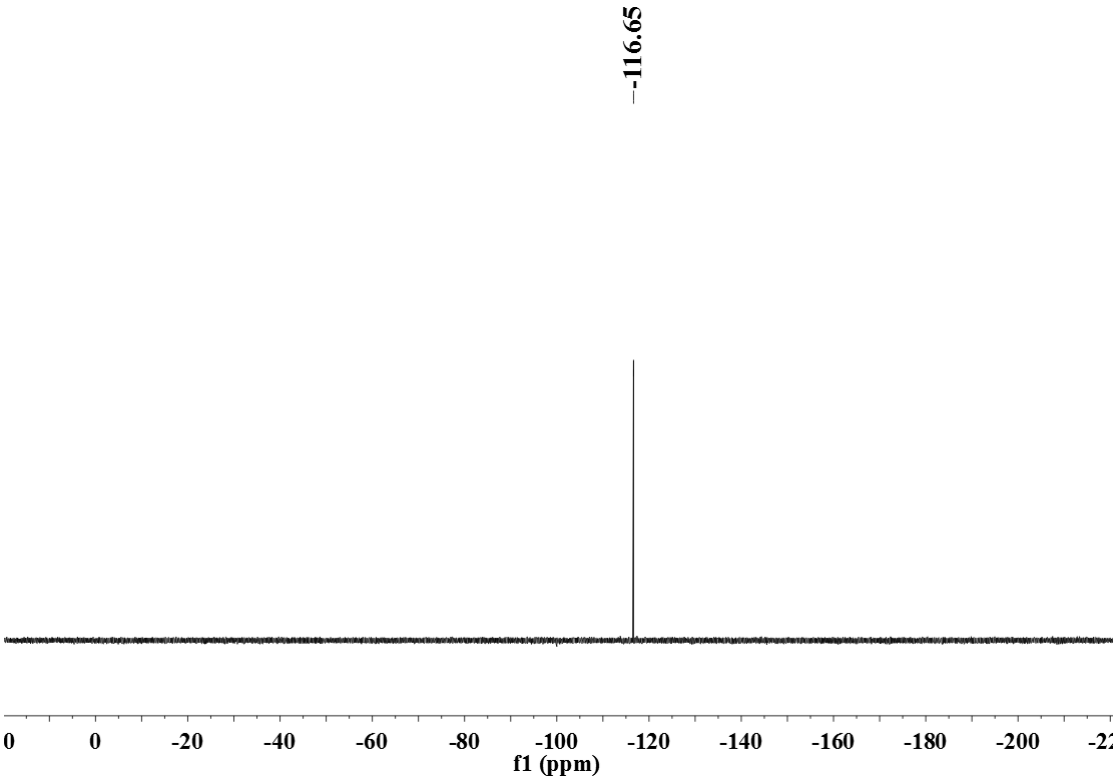

163.23
148.30
147.47
144.43
144.19
142.73
134.21
133.15
132.27
128.98
125.28
77.38
77.06
76.75
41.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

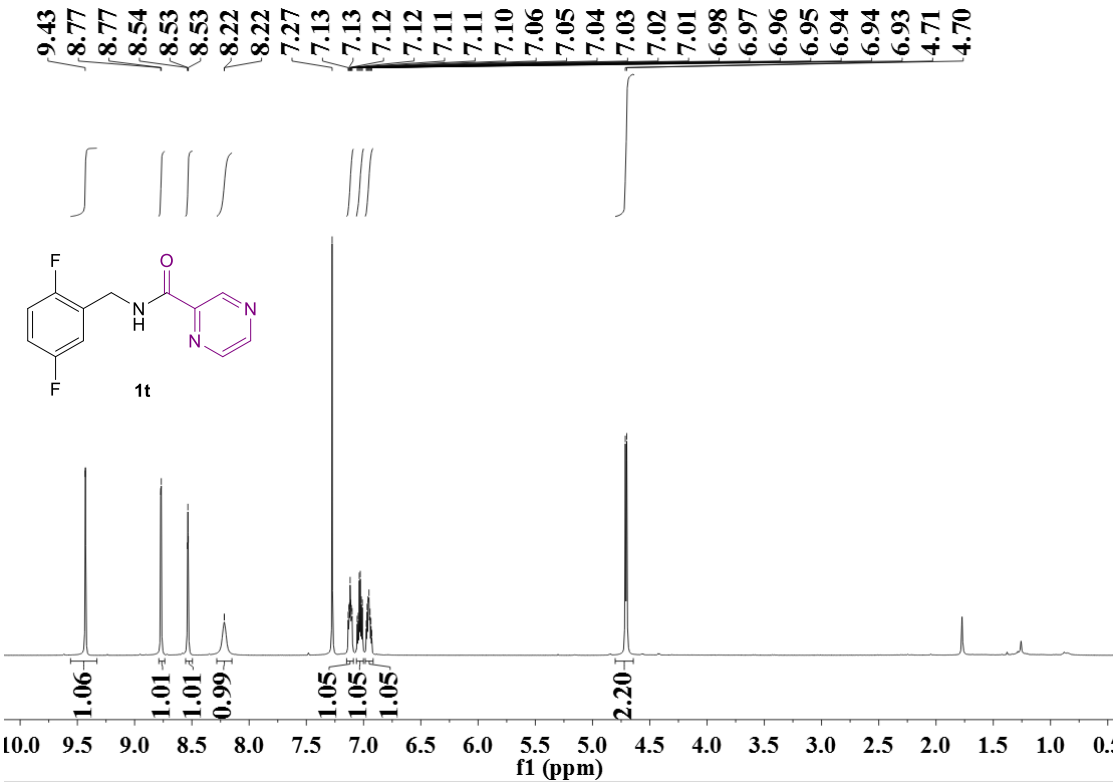

9.46
9.46
8.74
8.74
8.50
8.11
7.37
7.35
7.34
7.31
7.30
7.28
7.26
7.19
7.18
4.68
4.67
1.32
tBu
N
H
O
N
N
1r
0.94
0.98
0.98
0.97
3.10
0.99
2.00
9.03
f1 (ppm)

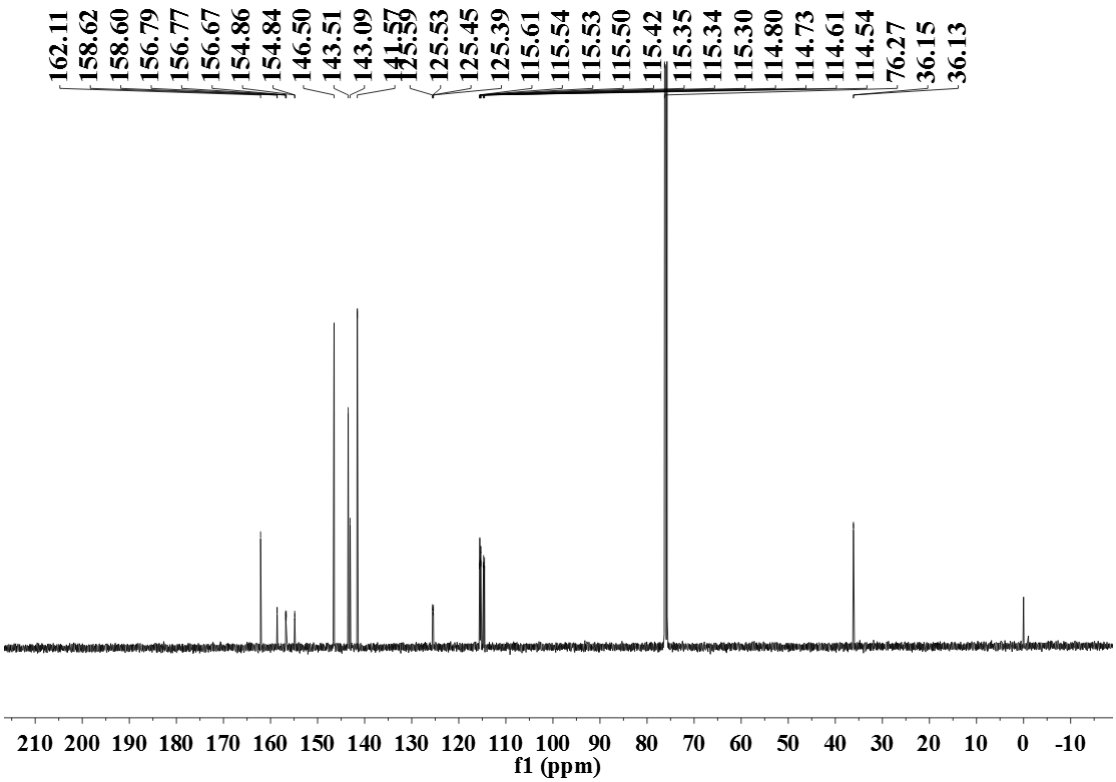

161.77
150.75
146.24
143.49
143.42
141.50
136.24
127.53
124.00
123.72
76.33
76.02
75.70
42.82
33.66
30.30
f1 (ppm)

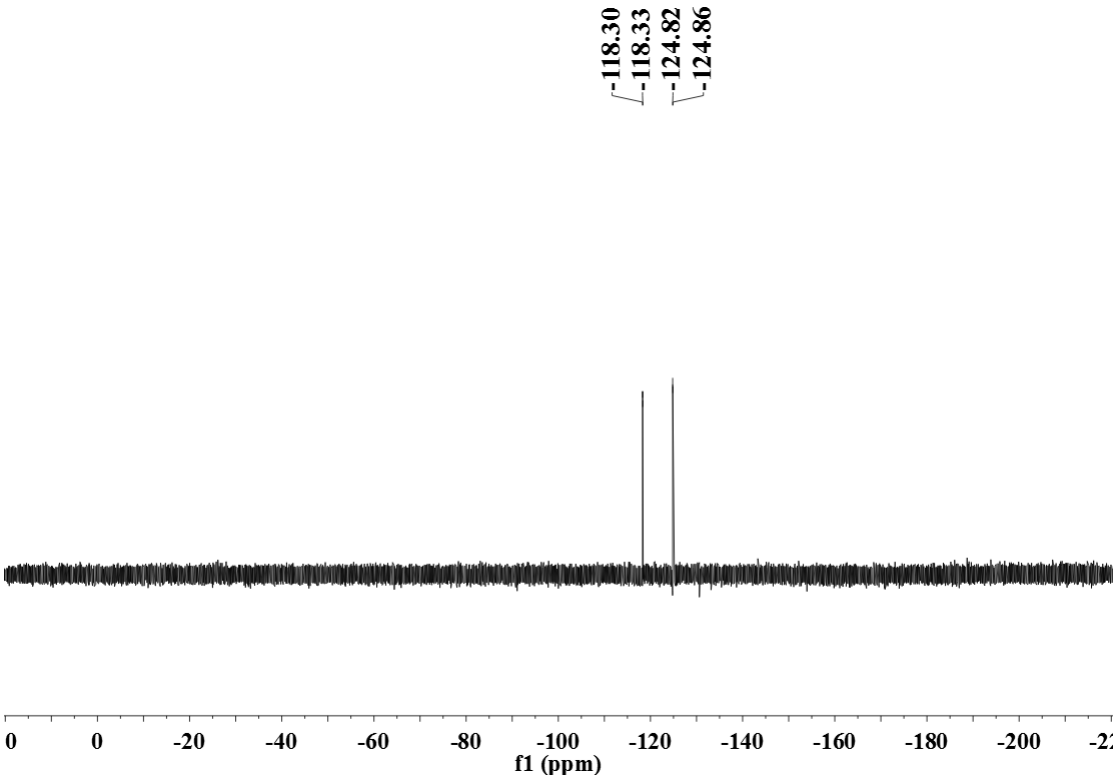

9.42
8.74
8.73
8.51
8.50
8.50
8.12
7.34
7.32
7.31
7.28
6.68
6.68
6.66
6.66
6.65
6.65
6.63
6.62
5.30
4.65
4.64
3.79
F
O
N
H
N
N
MeO
1s
1.02
1.02
1.03
1.02
1.02
2.05
2.00
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

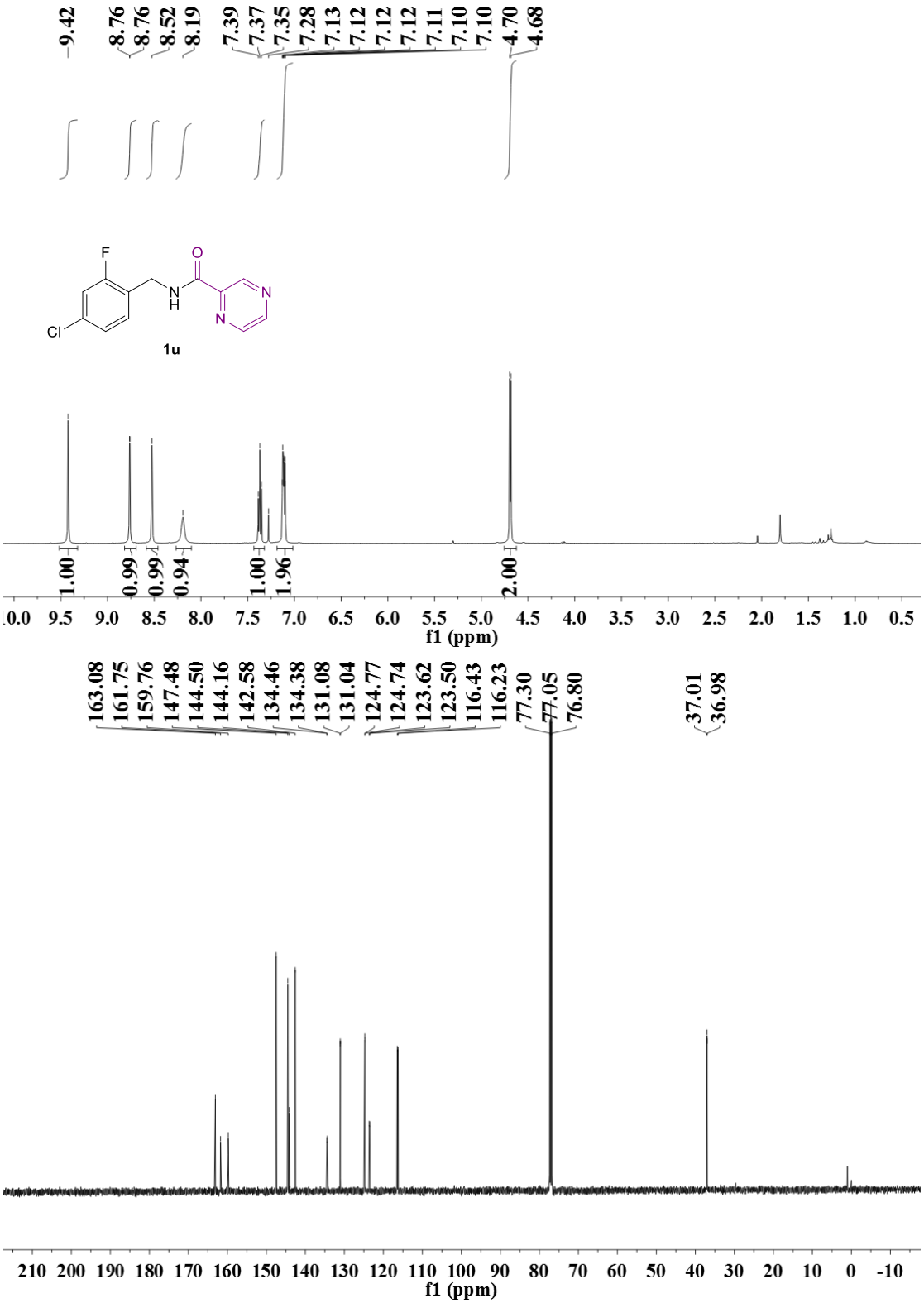

162.85
162.65
160.69
160.68
160.59
147.28
144.46
144.40
142.53
131.04
130.99
116.70
116.58
109.91
109.89
101.90
101.70
77.30
77.05
76.80
55.59
37.14
37.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

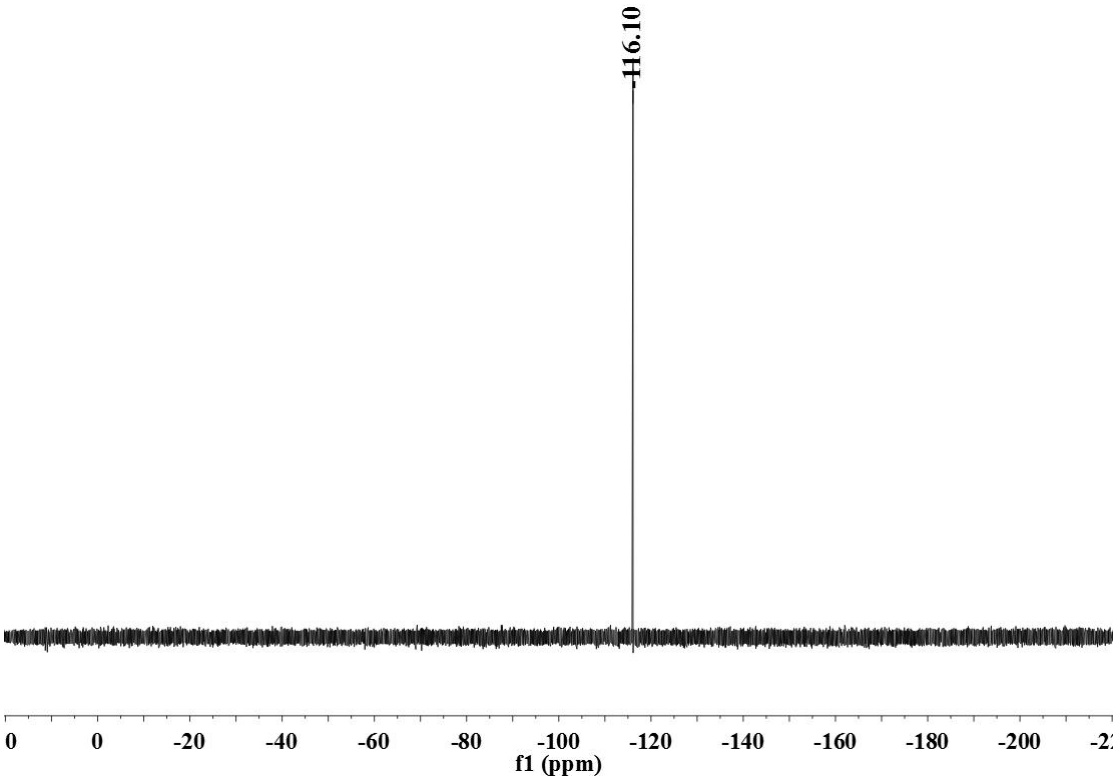

-116.65
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

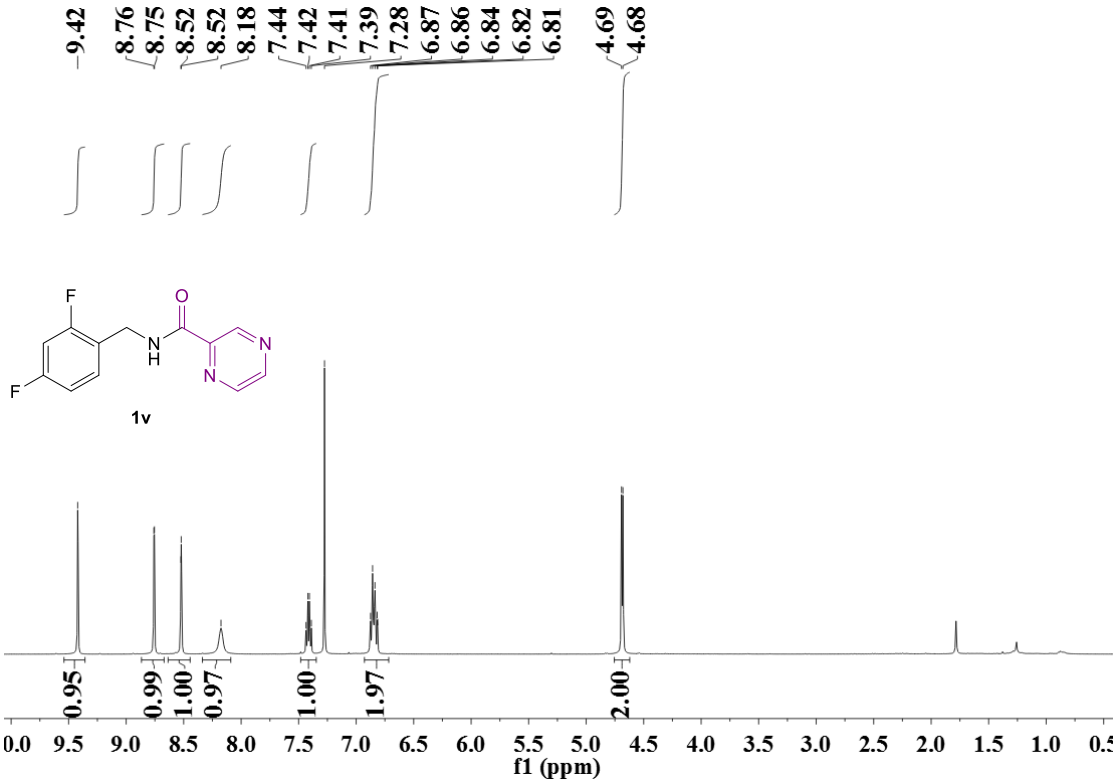

9.43
8.77
8.77
8.54
8.53
8.53
8.22
8.22
7.27
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.06
7.05
7.04
7.03
7.02
7.01
6.98
6.97
6.96
6.95
6.94
6.94
6.93
4.71
4.70
F
O
N
H
N
N
F
1t
1.06
1.01
1.01
0.99
1.05
1.05
1.05
2.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

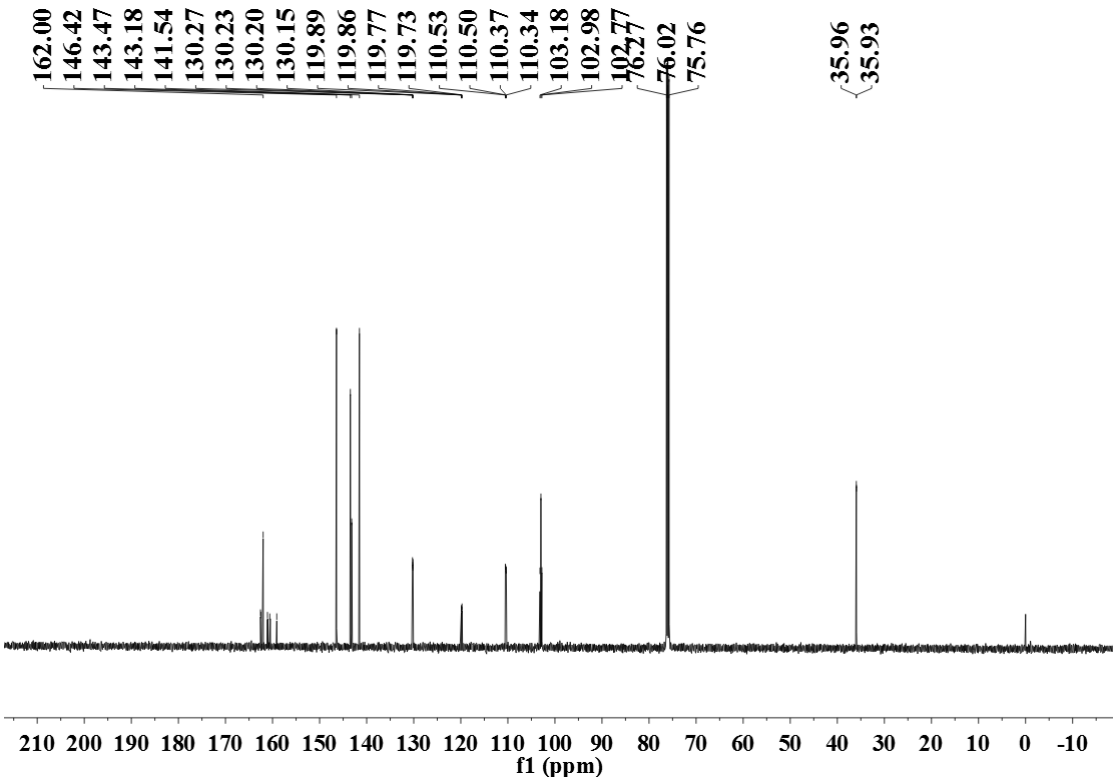

162.11
158.62
158.60
156.79
156.77
156.67
154.86
154.84
146.50
143.51
143.09
125.53
125.45
125.39
115.61
115.54
115.53
115.50
115.42
115.35
115.34
115.30
114.80
114.73
114.61
114.54
76.27
36.15
36.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

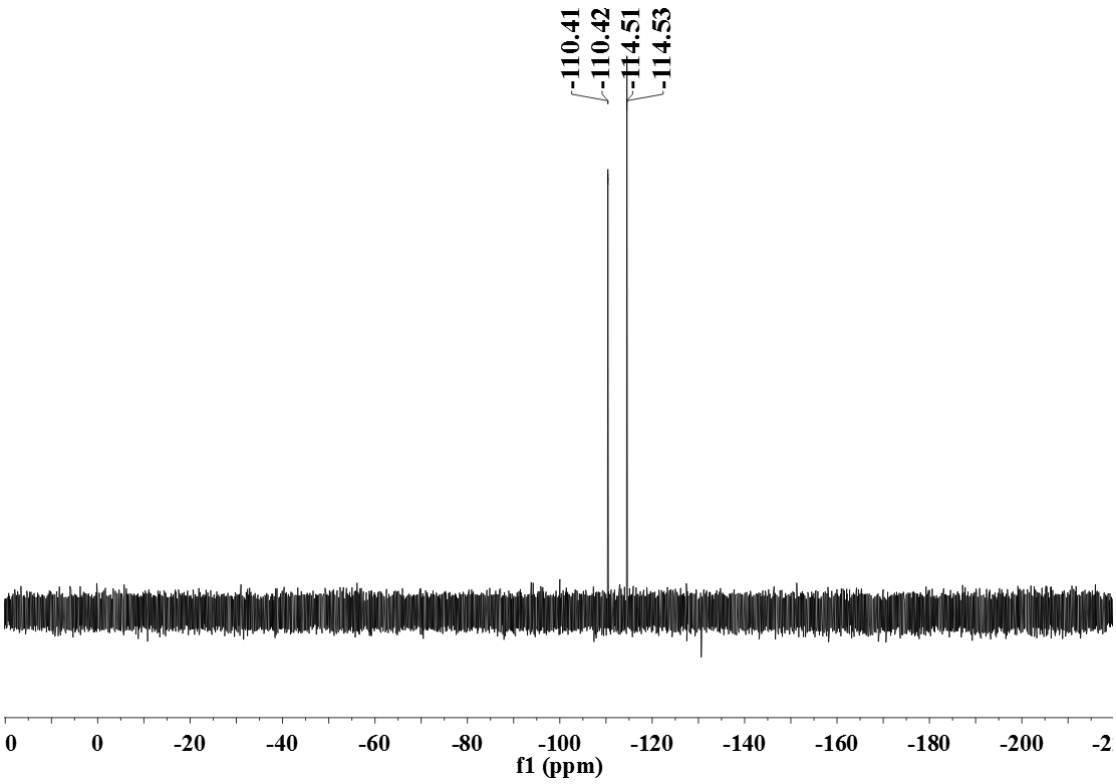

-118.30
-118.33
-124.82
-124.86
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

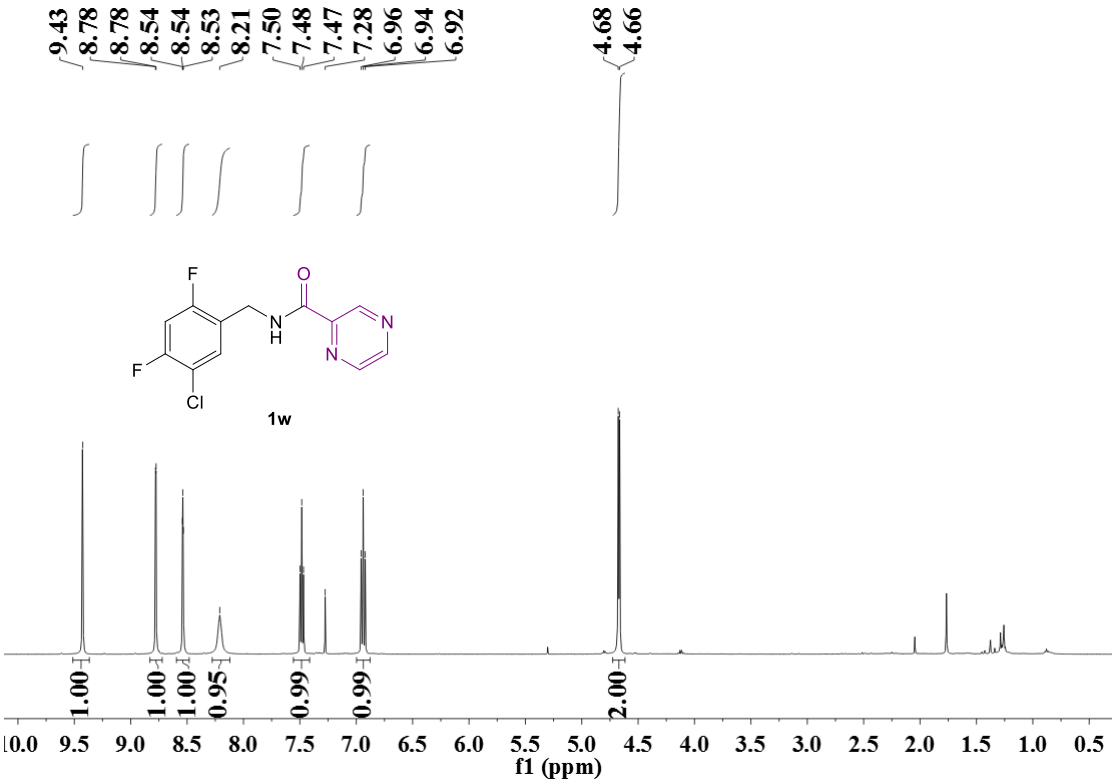

9.42
8.76
8.76
8.52
8.19
7.39
7.37
7.35
7.28
7.13
7.12
7.12
7.12
7.11
7.10
7.10
4.70
4.68
F
O
N
H
N
N
Cl
1u
1.00
0.99
0.99
0.94
1.00
1.96
2.00
f1 (ppm)
163.08
161.75
159.76
147.48
144.50
144.16
142.58
134.46
134.38
131.08
131.04
124.77
124.74
123.62
123.50
116.43
116.23
77.30
77.05
76.80
37.01
36.98
f1 (ppm)

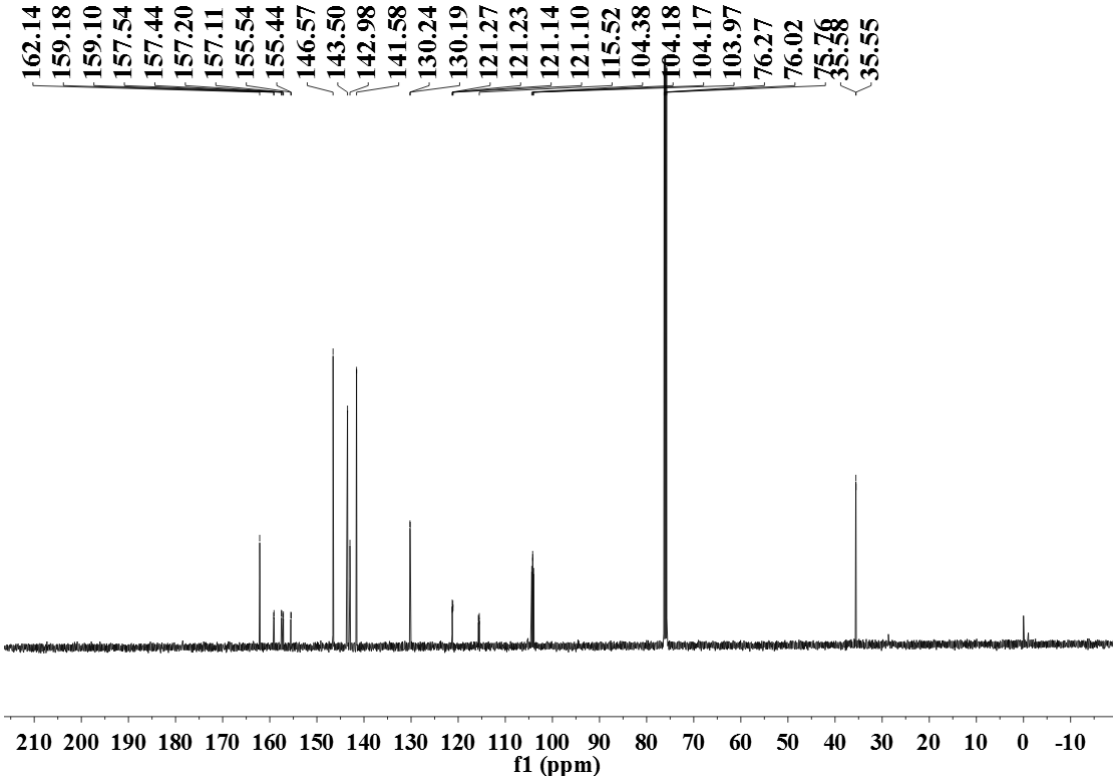

-116.10
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

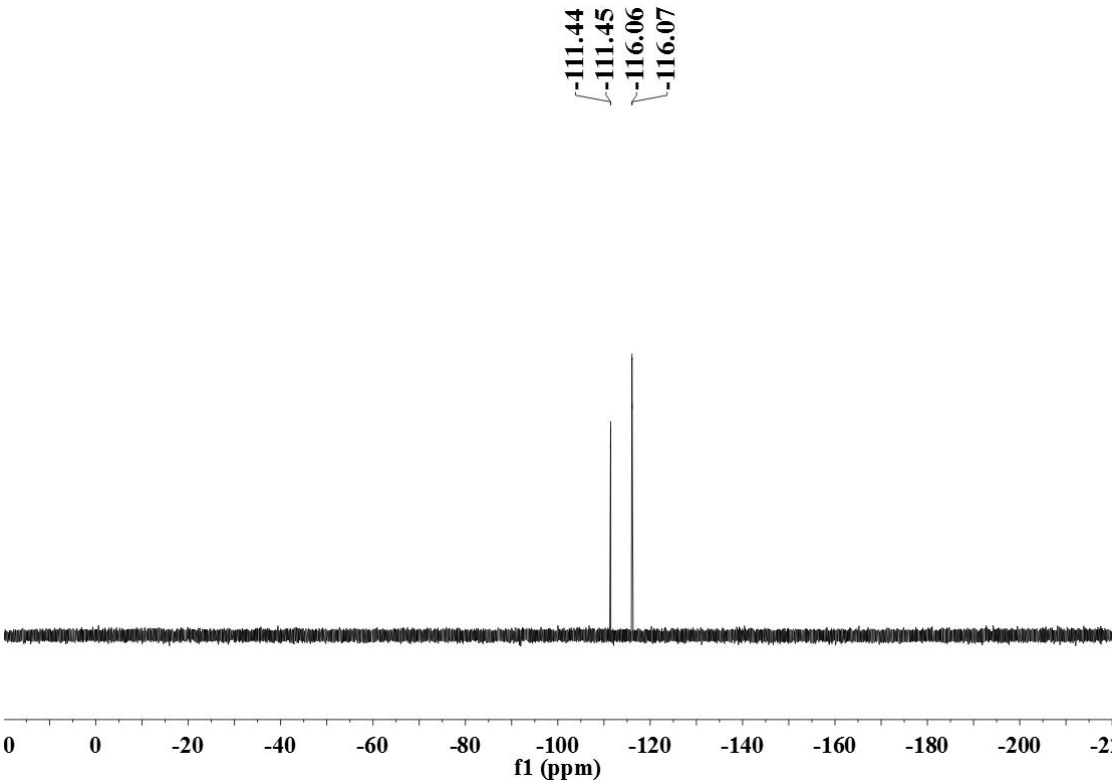

9.42
8.76
8.75
8.52
8.52
8.18
7.44
7.42
7.41
7.39
7.28
6.87
6.86
6.84
6.82
6.81
4.69
4.68
F
O
N
H
N
F
1v
0.95
0.99
1.00
0.97
1.00
1.97
2.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

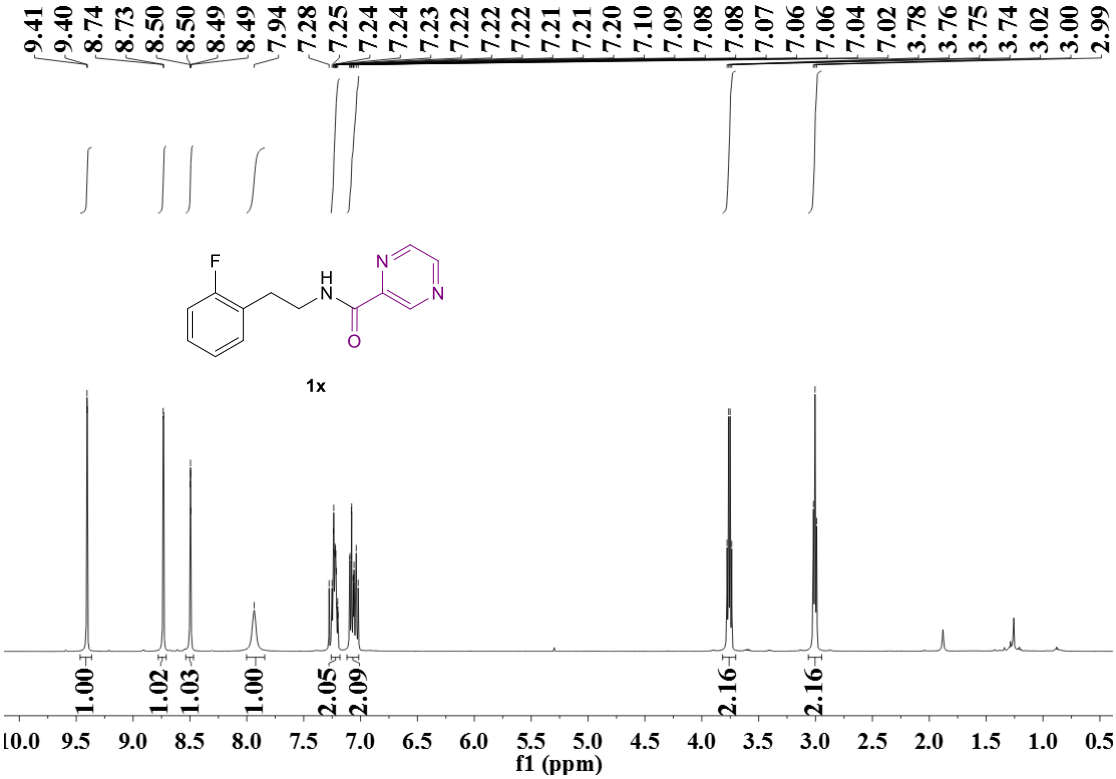

162.00
146.42
143.47
143.18
141.54
130.27
130.23
130.20
130.15
119.89
119.86
119.77
119.73
110.53
110.50
110.37
110.34
103.18
102.98
102.77
76.27
76.02
75.76
35.96
35.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

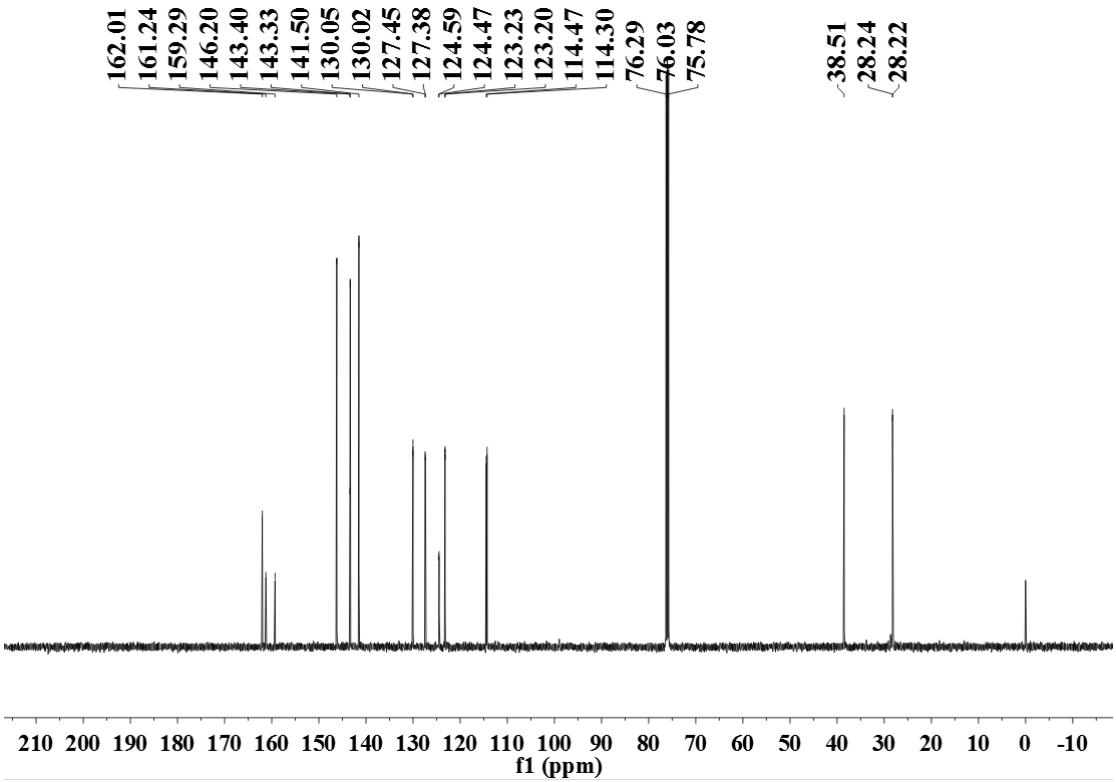

-110.41
-110.42
-114.51
-114.53
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

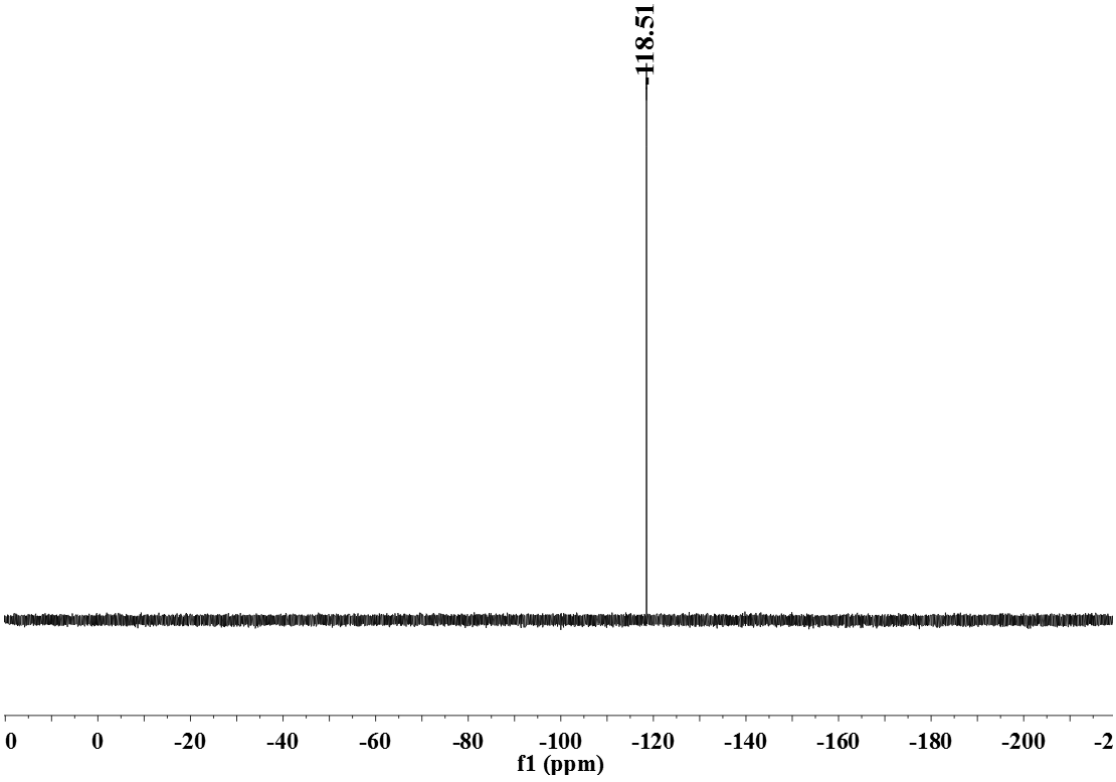

9.43
8.78
8.78
8.54
8.54
8.53
8.21
7.50
7.48
7.47
7.28
6.96
6.94
6.92
4.68
4.66
F
O
N
H
N
N
F
Cl
1w
1.00
1.00
1.00
0.95
0.99
0.99
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

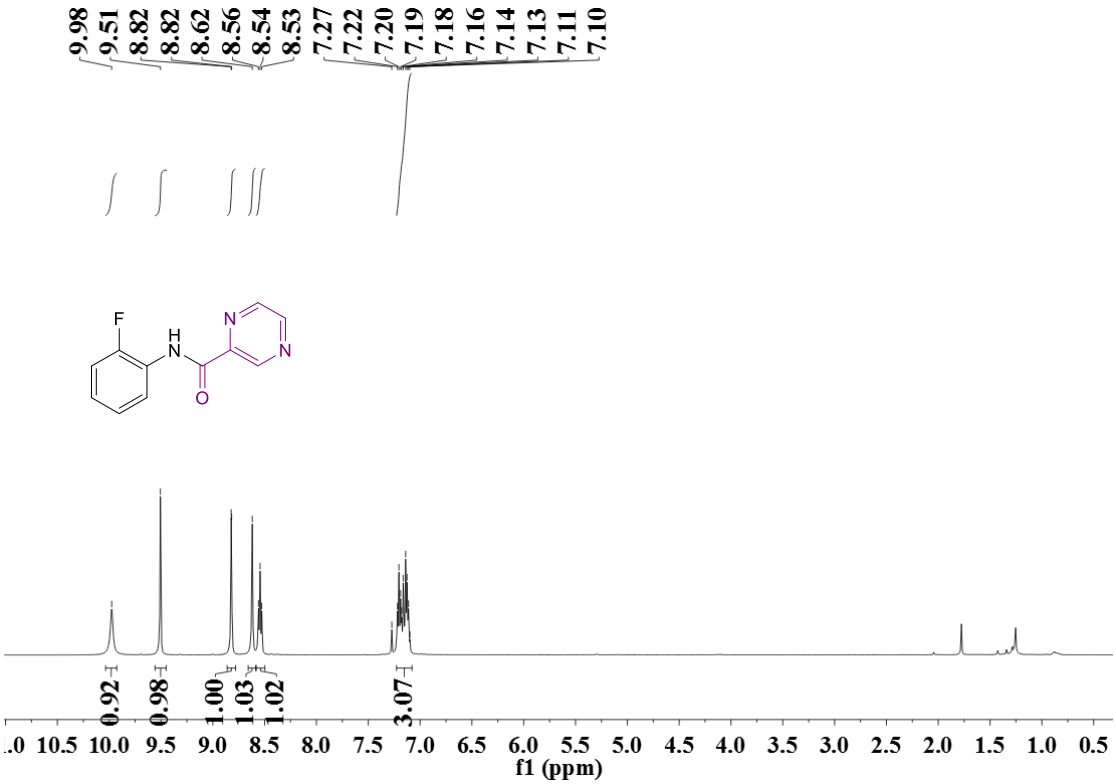

162.14
159.18
159.10
157.54
157.44
157.20
157.11
155.54
155.44
146.57
143.50
142.98
141.58
130.24
130.19
121.27
121.23
121.14
121.10
115.52
104.38
104.18
104.17
103.97
76.27
76.02
75.76
35.58
35.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

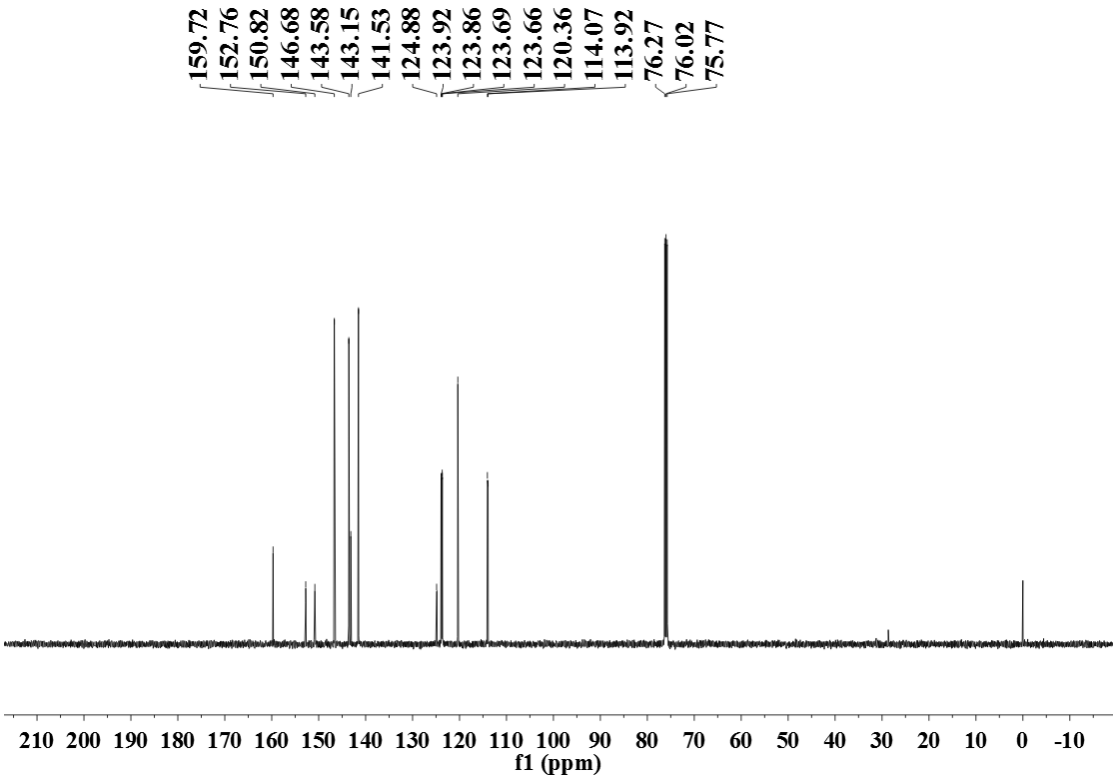

-111.44
-111.45
-116.06
-116.07
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

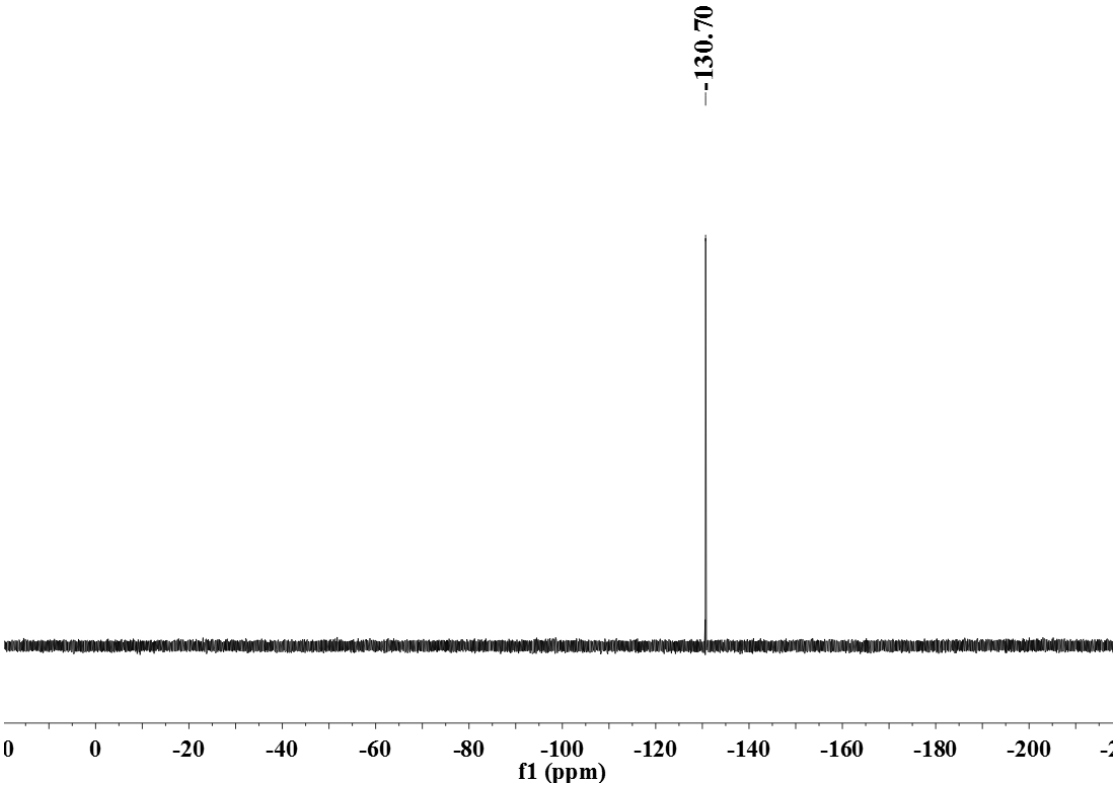

9.41
9.40
8.74
8.73
8.50
8.50
8.49
8.49
7.94
7.28
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.10
7.09
7.08
7.08
7.07
7.06
7.06
7.04
7.02
3.78
3.76
3.75
3.74
3.02
3.00
2.99
F
H
N
N
N
O
1x
1.00
1.02
1.03
1.00
2.05
2.09
2.16
2.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

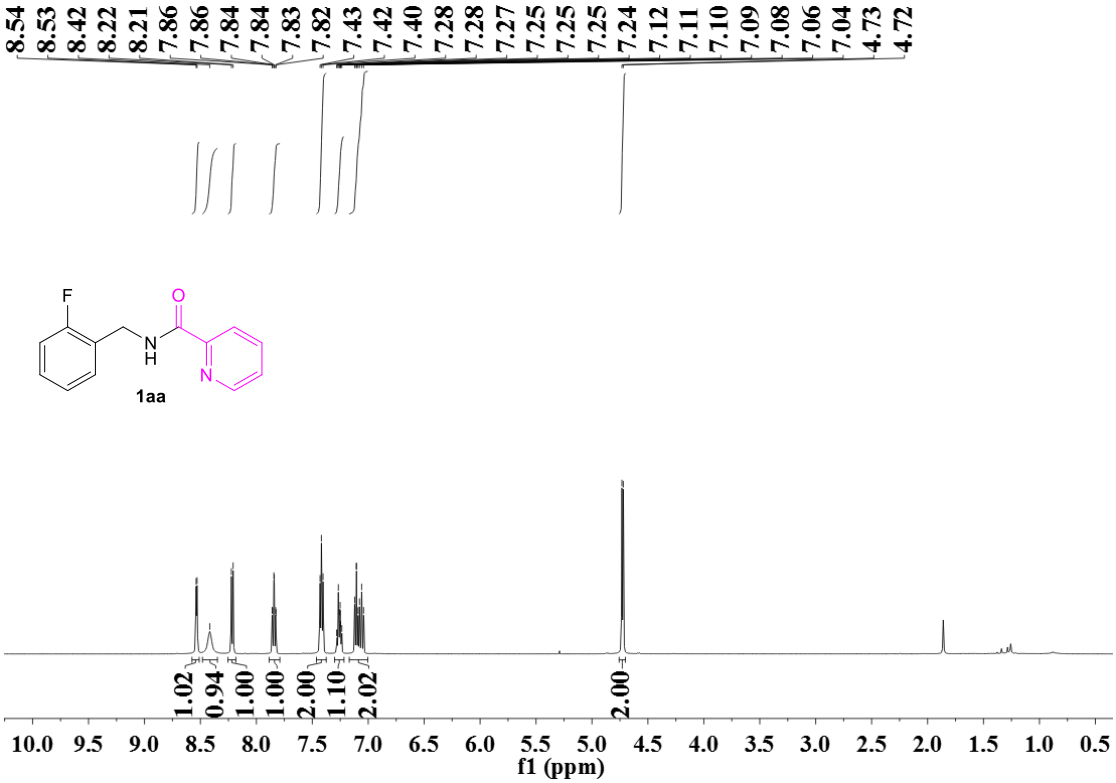

162.01
161.24
159.29
146.20
143.40
143.33
141.50
130.05
130.02
127.45
127.38
124.59
124.47
123.23
123.20
114.47
114.30
76.29
76.03
75.78
38.51
28.24
28.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

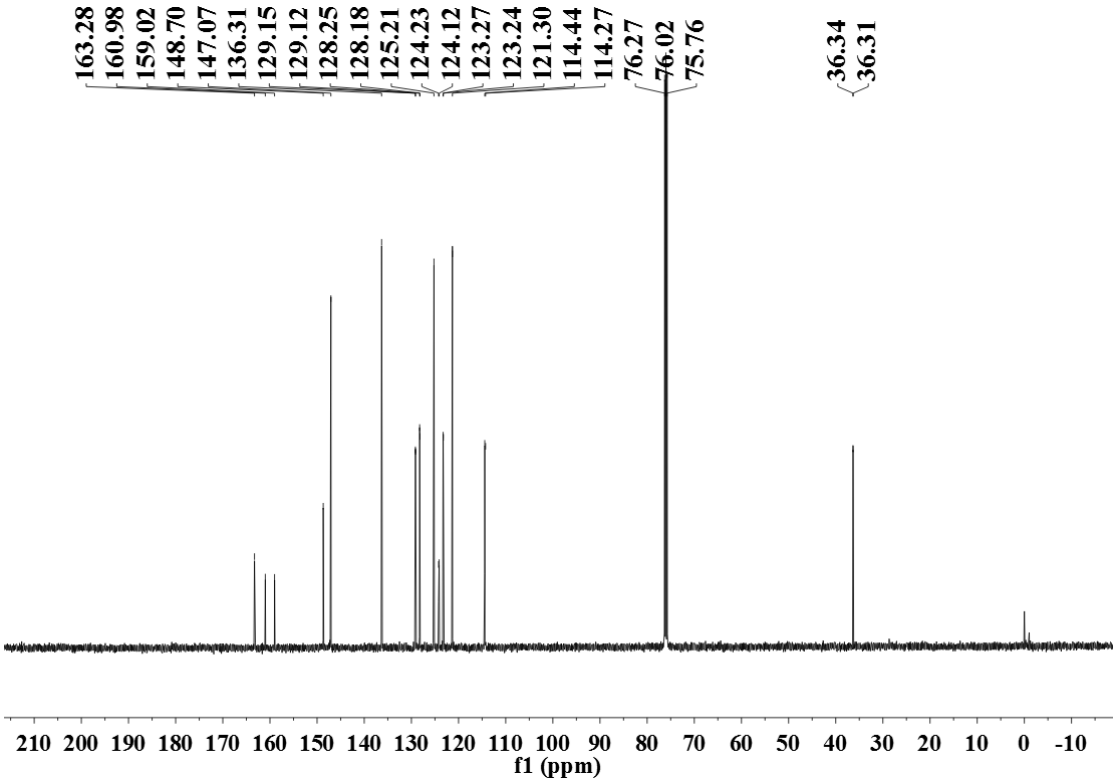

-118.51
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

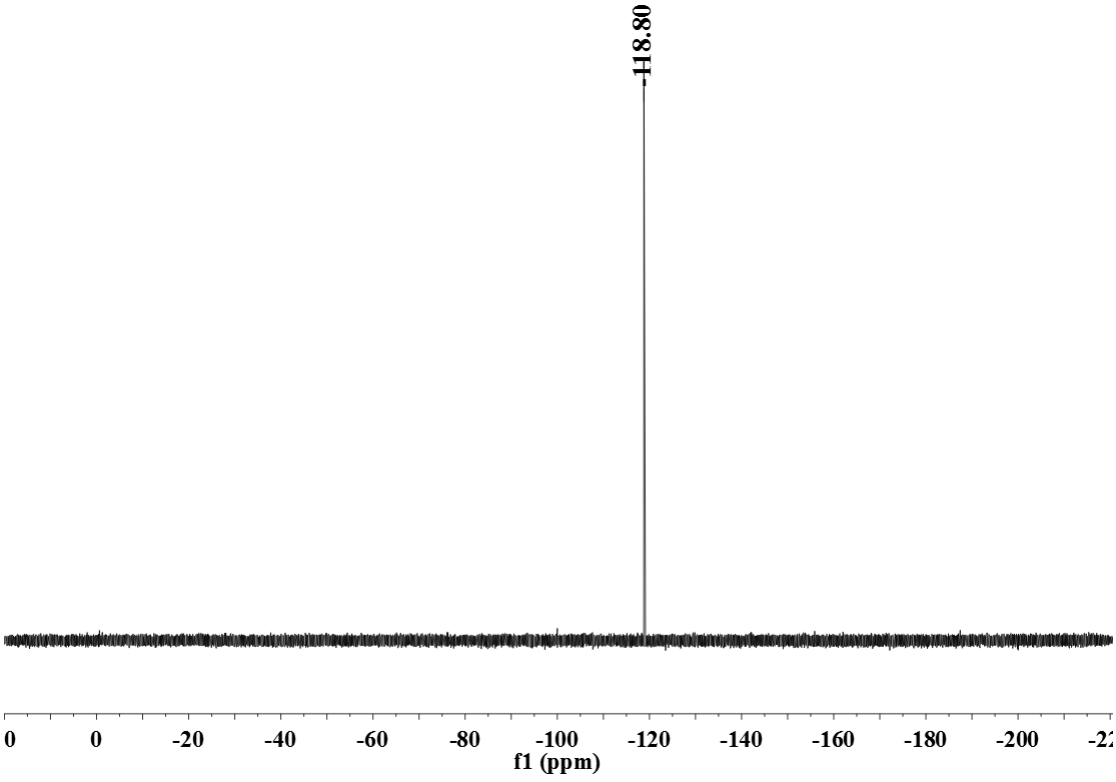

9.98
9.51
8.82
8.82
8.62
8.56
8.54
8.53
7.27
7.22
7.20
7.19
7.18
7.16
7.14
7.13
7.11
7.10
F
H
N
N
N
O
0.92
0.98
1.00
1.03
1.02
3.07
f1 (ppm)

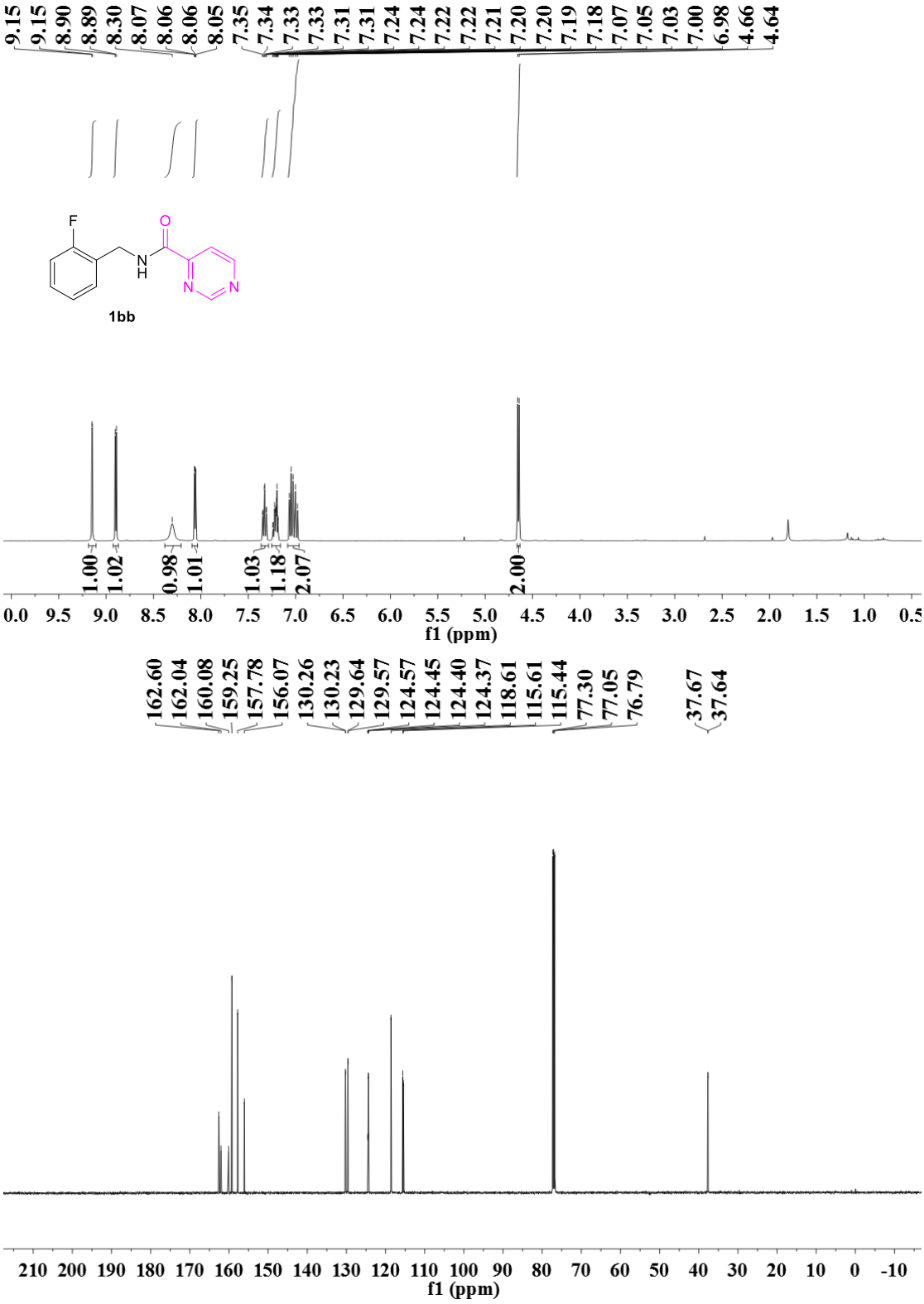

159.72
152.76
150.82
146.68
143.58
143.15
141.53
124.88
123.92
123.86
123.69
123.66
120.36
114.07
113.92
76.27
76.02
75.77
f1 (ppm)

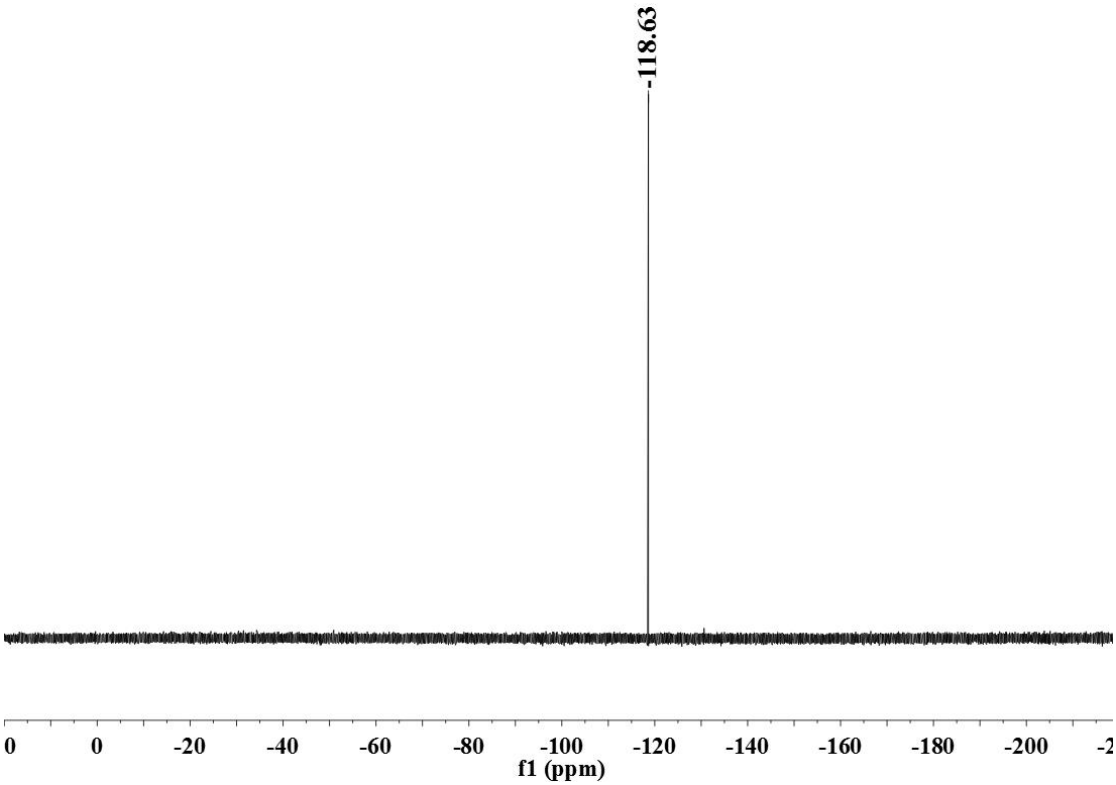

-130.70
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

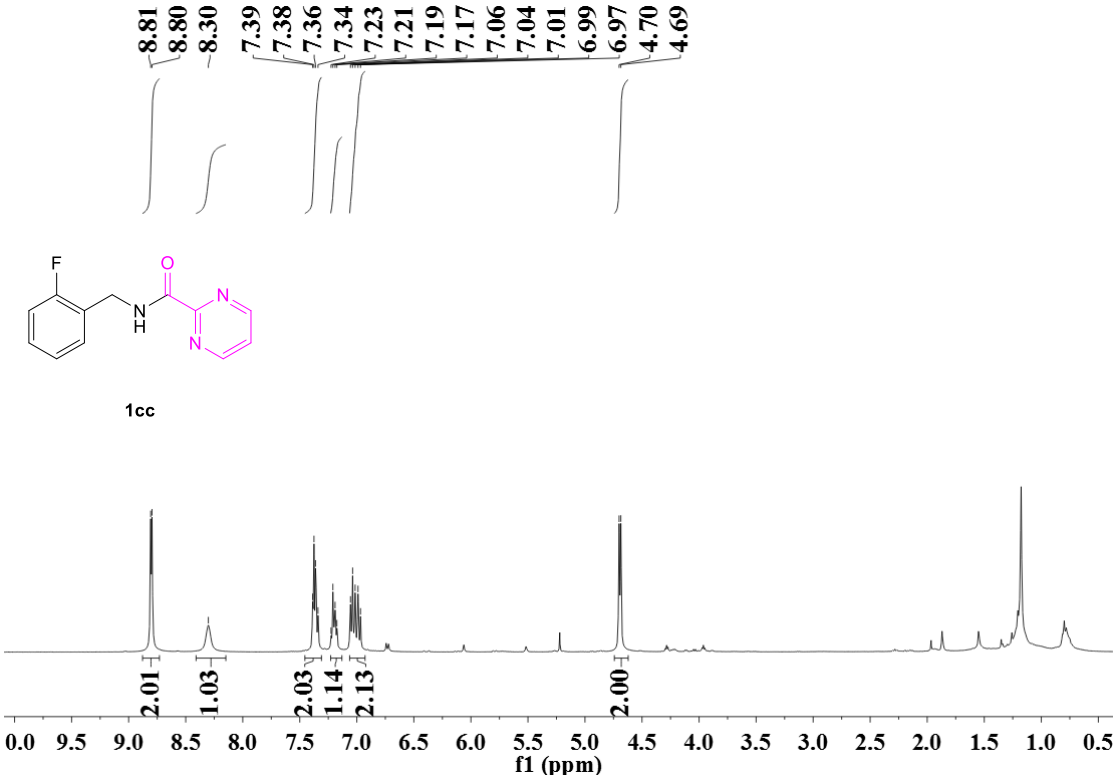

8.54
8.53
8.42
8.22
8.21
7.86
7.86
7.84
7.84
7.83
7.82
7.43
7.42
7.40
7.28
7.28
7.27
7.25
7.25
7.25
7.24
7.12
7.11
7.10
7.09
7.08
7.06
7.04
4.73
4.72
F
O
N
H
N
1aa
1.02
0.94
1.00
1.00
2.00
1.10
2.02
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

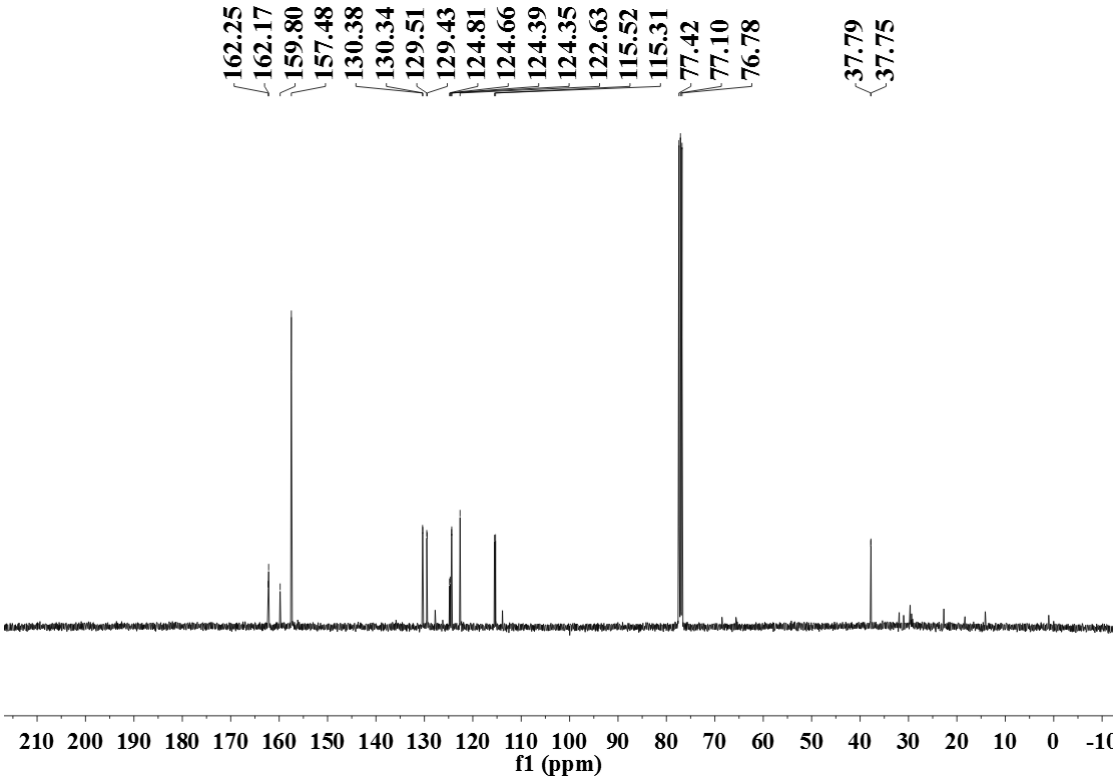

163.28
160.98
159.02
148.70
147.07
136.31
129.15
129.12
128.25
128.18
125.21
124.23
124.12
123.27
123.24
121.30
114.44
114.27
76.27
76.02
75.76
36.34
36.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

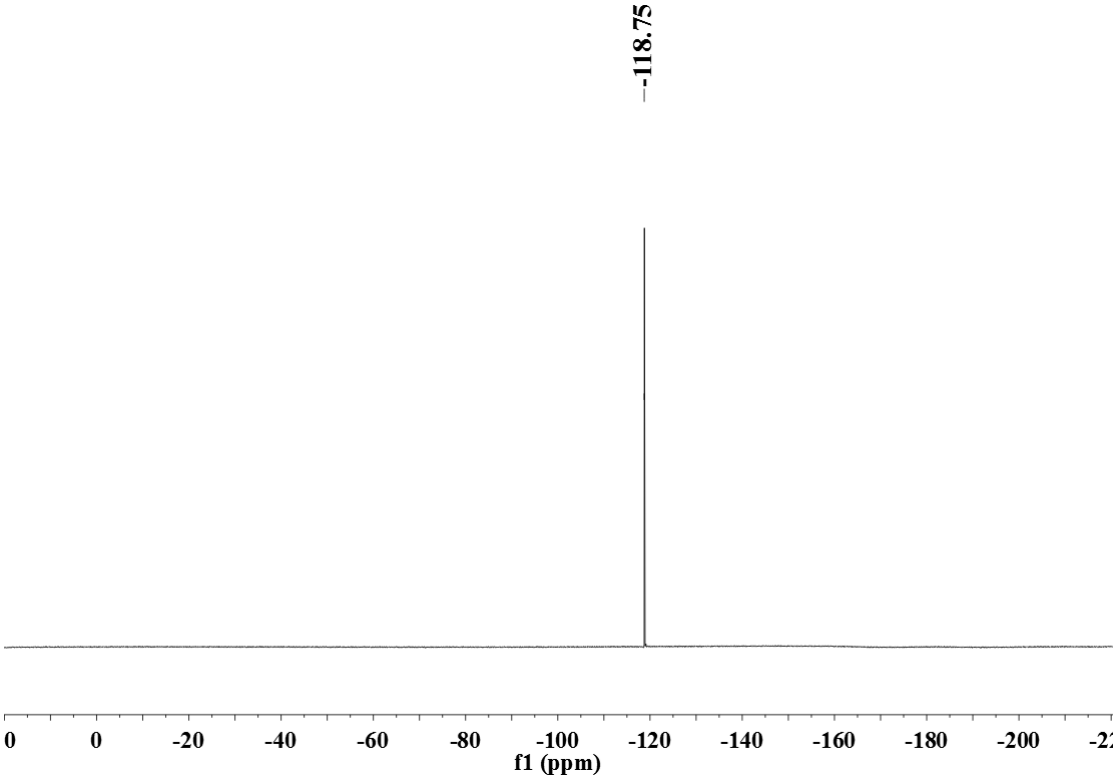

-118.80
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -22
f1 (ppm)

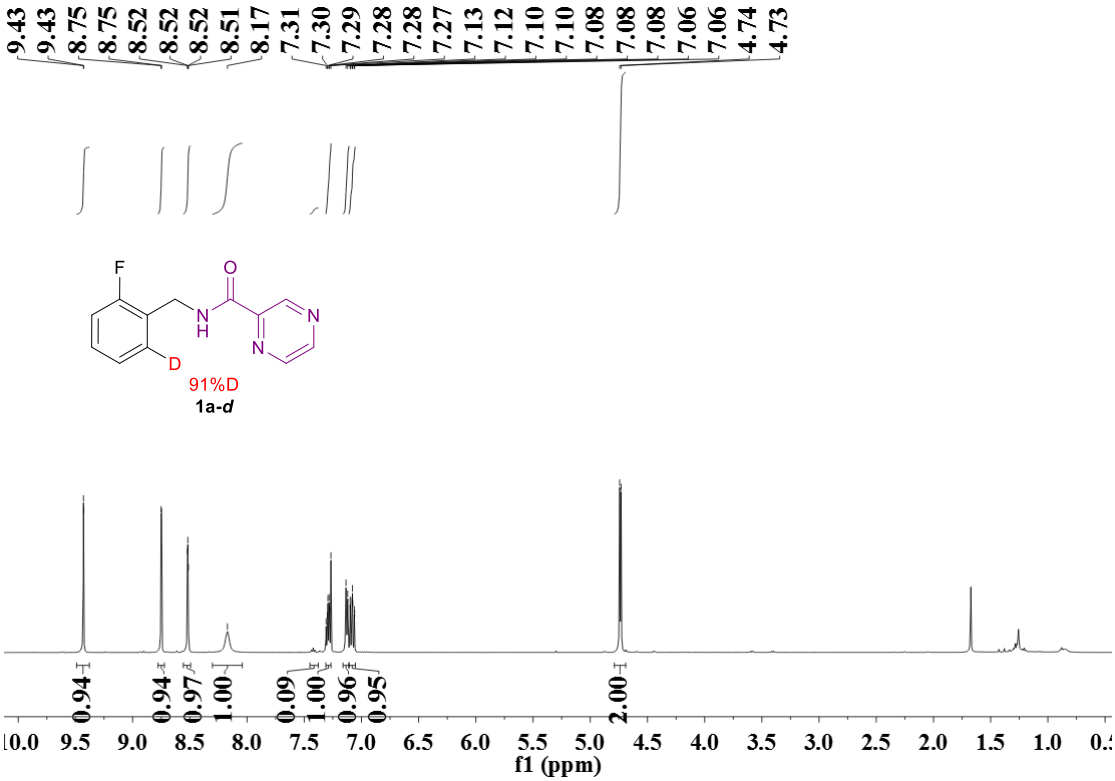

9.15
9.15
8.90
8.89
8.30
8.07
8.06
8.06
8.05
7.35
7.34
7.33
7.33
7.31
7.31
7.24
7.24
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.07
7.05
7.03
7.00
6.98
4.66
4.64
F
O
N
H
N
N
1bb
1.00
1.02
0.98
1.01
1.03
1.18
2.07
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
162.60
162.04
160.08
159.25
157.78
156.07
130.26
130.23
129.64
129.57
124.57
124.45
124.40
124.37
118.61
115.61
115.44
77.30
77.05
76.79
37.67
37.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-118.63
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

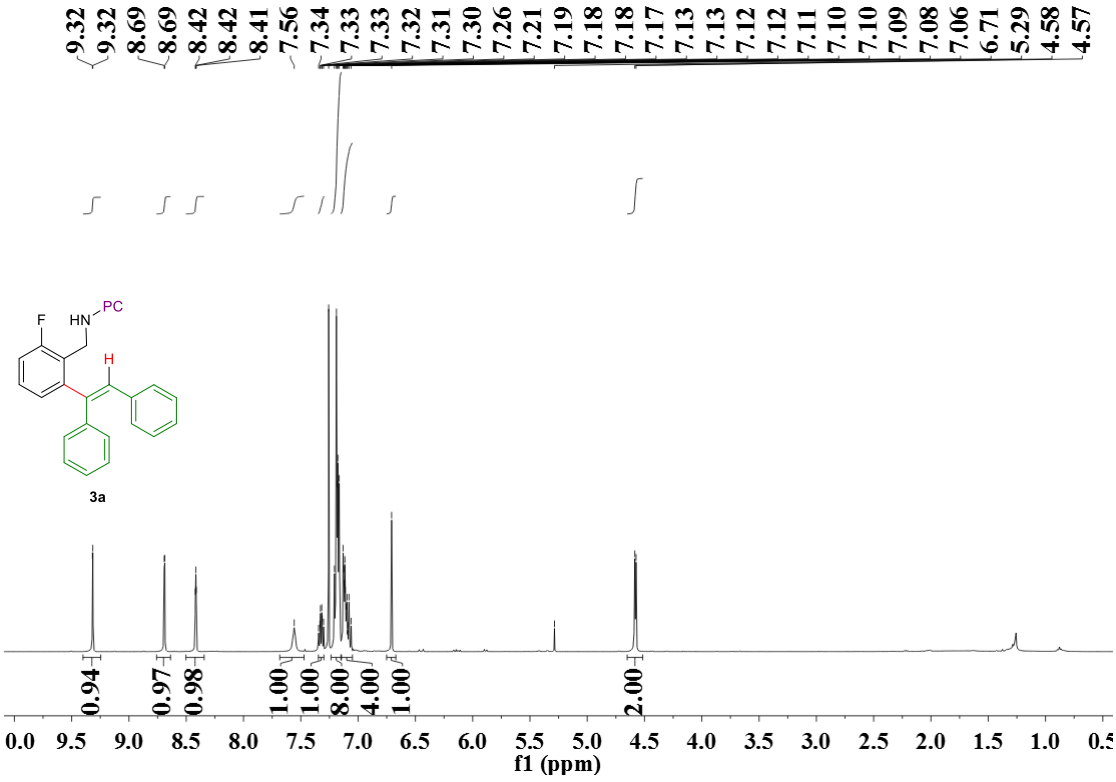

8.81
8.80
8.30
7.39
7.38
7.36
7.34
7.23
7.21
7.19
7.17
7.06
7.04
7.01
6.99
6.97
4.70
4.69
F
O
N
H
N
N
1cc
2.01
1.03
2.03
1.14
2.13
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

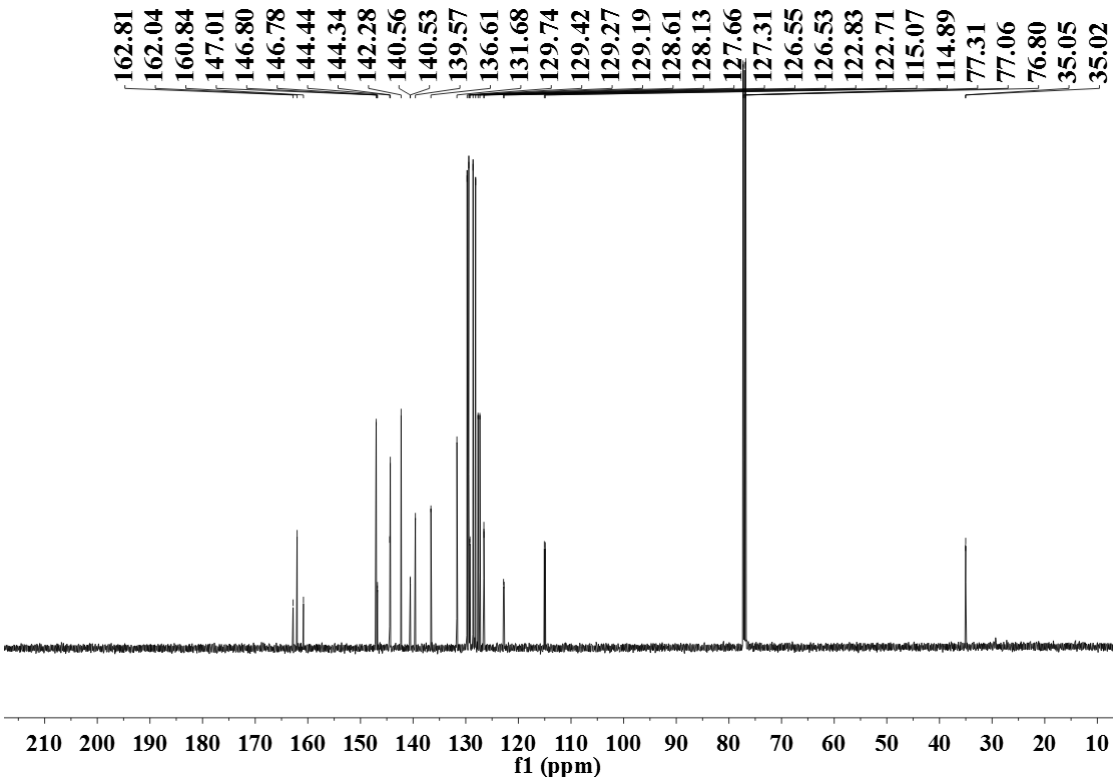

162.25
162.17
159.80
157.48
130.38
130.34
129.51
129.43
124.81
124.66
124.39
124.35
122.63
115.52
115.31
77.42
77.10
76.78
37.79
37.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

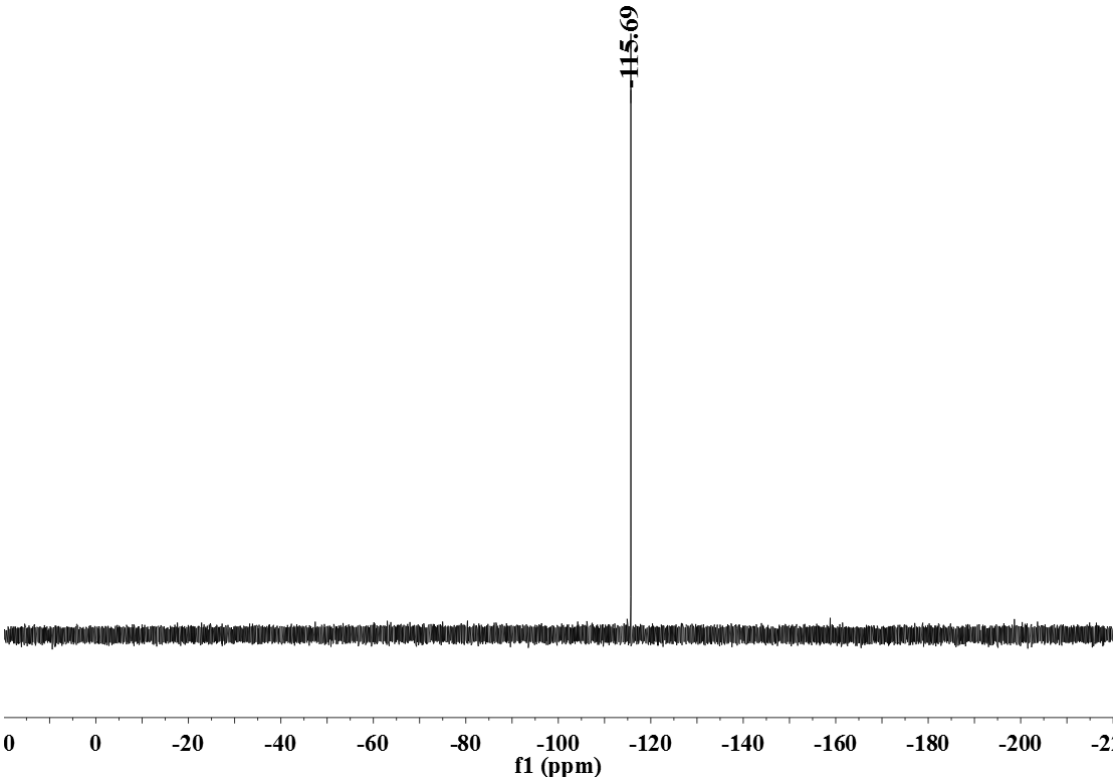

-118.75
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -22
f1 (ppm)

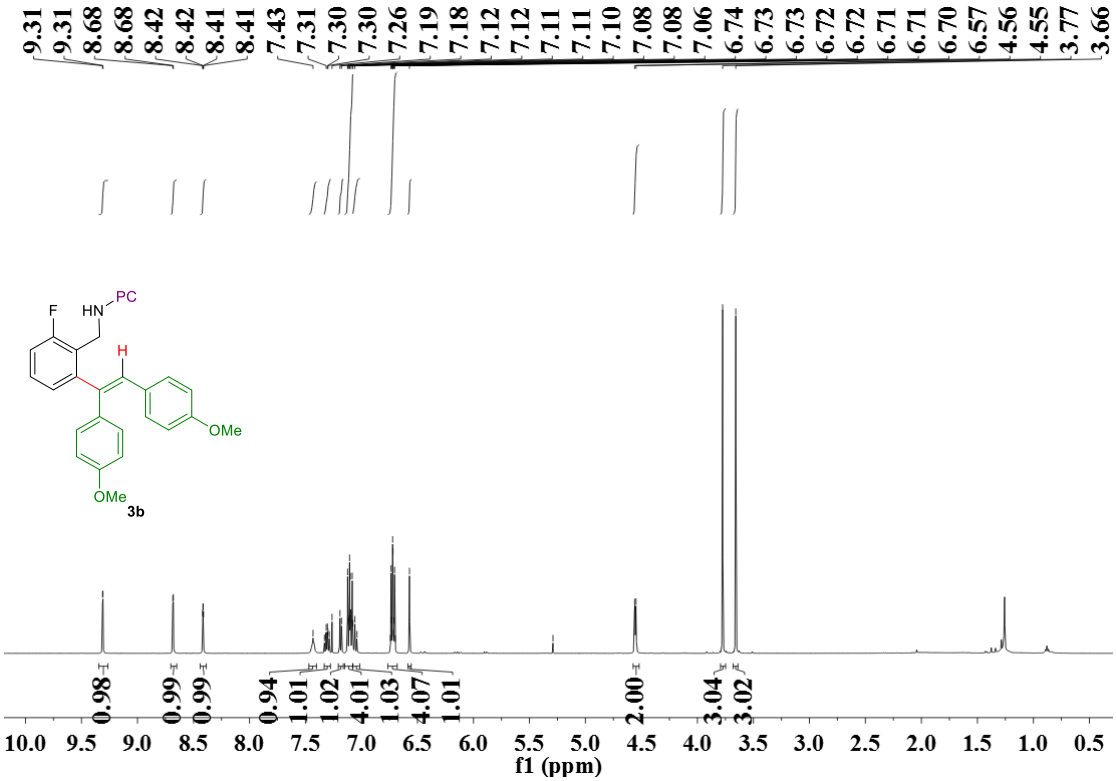


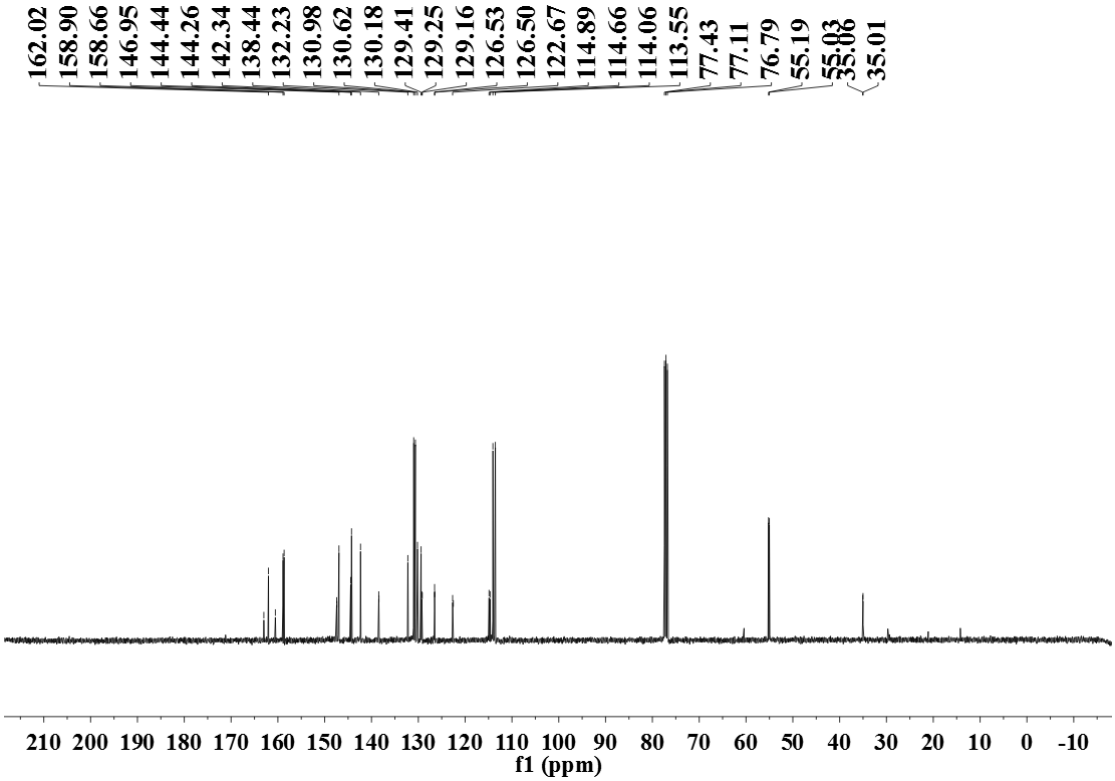
9.2 NMR Spectra of 3

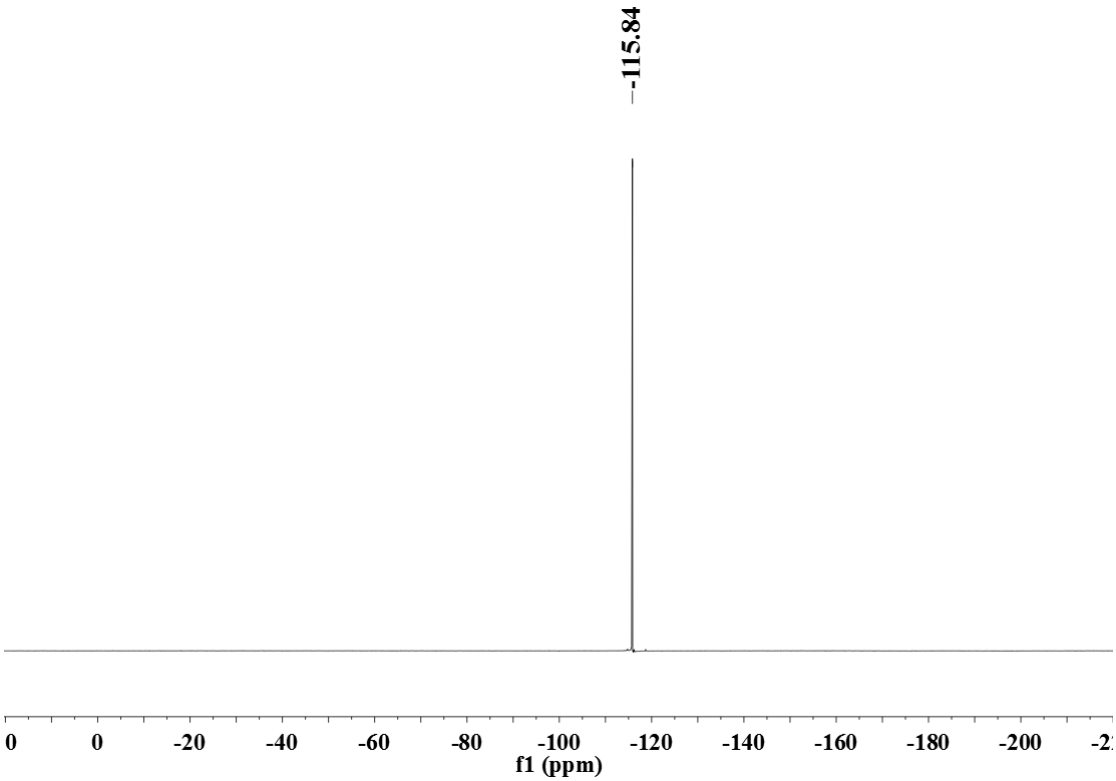


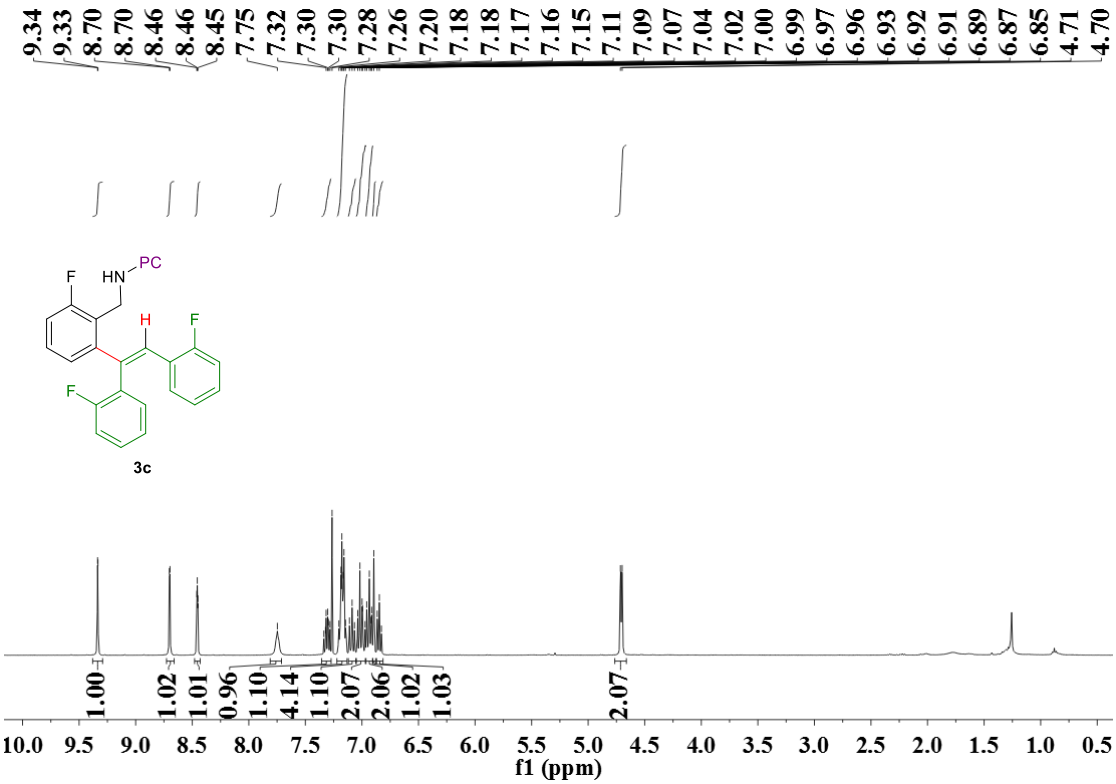

162.81
162.04
160.84
147.01
146.80
146.78
144.44
144.34
142.28
140.56
140.53
139.57
136.61
131.68
129.74
129.42
129.27
129.19
128.61
128.13
127.66
127.31
126.55
126.53
122.83
122.71
115.07
114.89
77.31
77.06
76.80
35.05
35.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

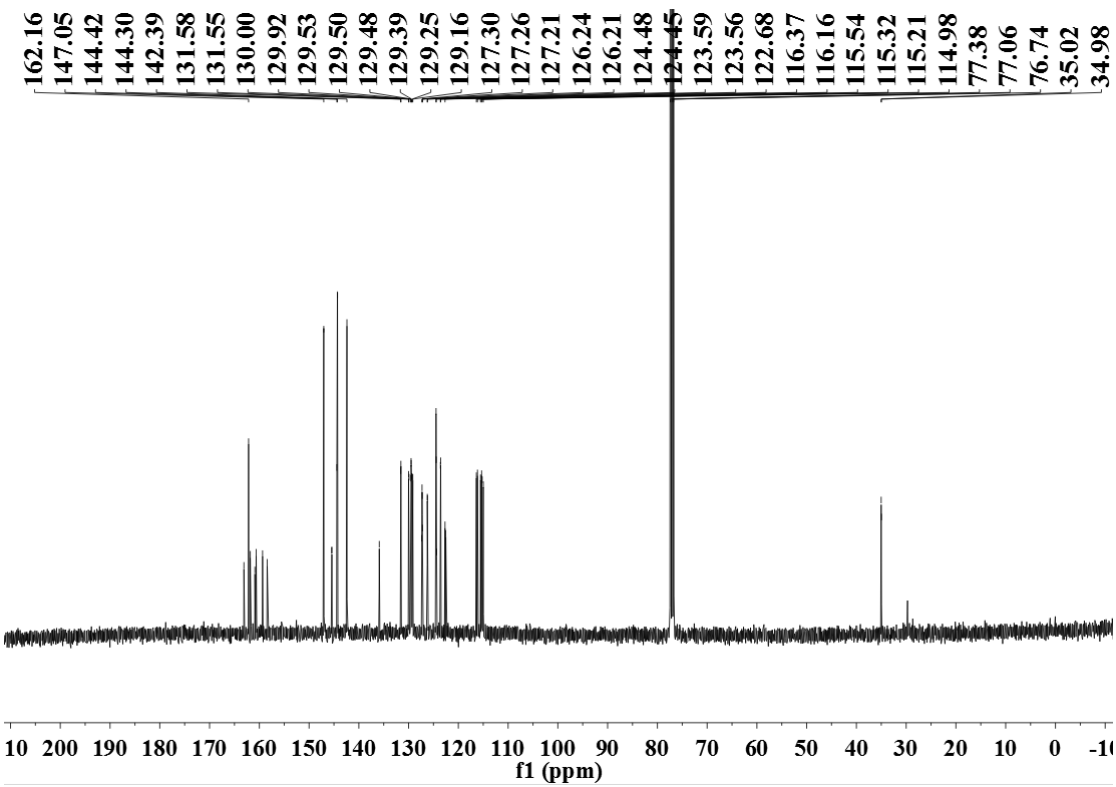

-115.69
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

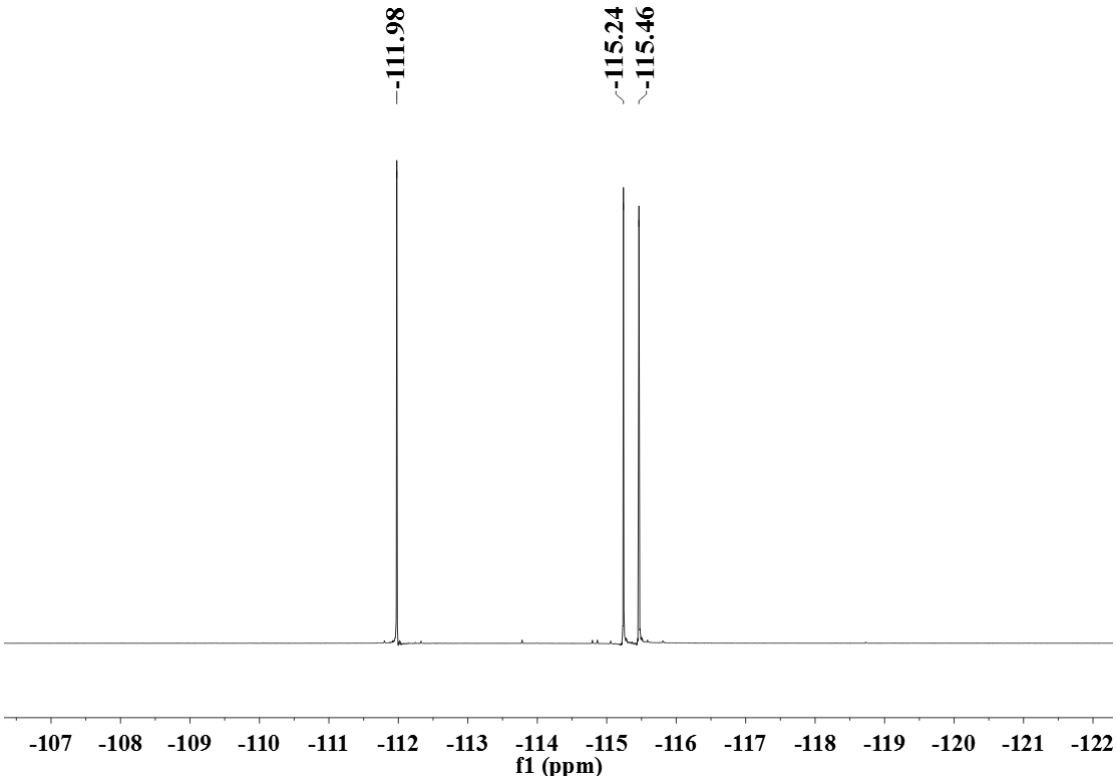

9.31 9.31 8.68 8.68 8.42 8.42 8.41 8.41 7.43 7.31 7.30 7.30 7.26 7.19 7.18 7.12 7.12 7.11 7.11 7.10 7.08 7.08 7.06 6.74 6.73 6.73 6.72 6.72 6.71 6.71 6.70 6.57 4.56 4.55 3.77 3.66
F
HN
PC
H
OMe
OMe
3b
0.98 0.99 0.99 0.94 1.01 1.02 4.01 1.03 4.07 1.01 2.00 3.04 3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

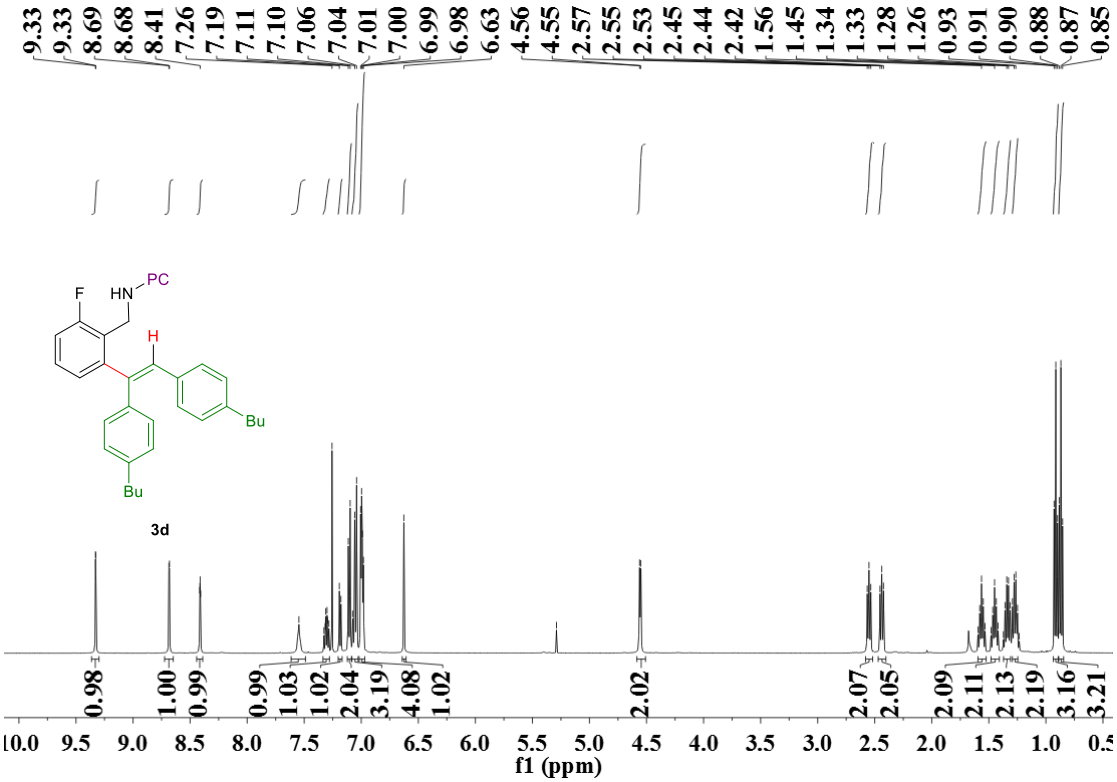

162.02 158.90 158.66 146.95 144.44 144.26 142.34 138.44 132.23 130.98 130.62 130.18 129.41 129.25 129.16 126.53 126.50 122.67 114.89 114.66 114.06 113.55 77.43 77.11 76.79 55.19 55.03 35.06 35.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

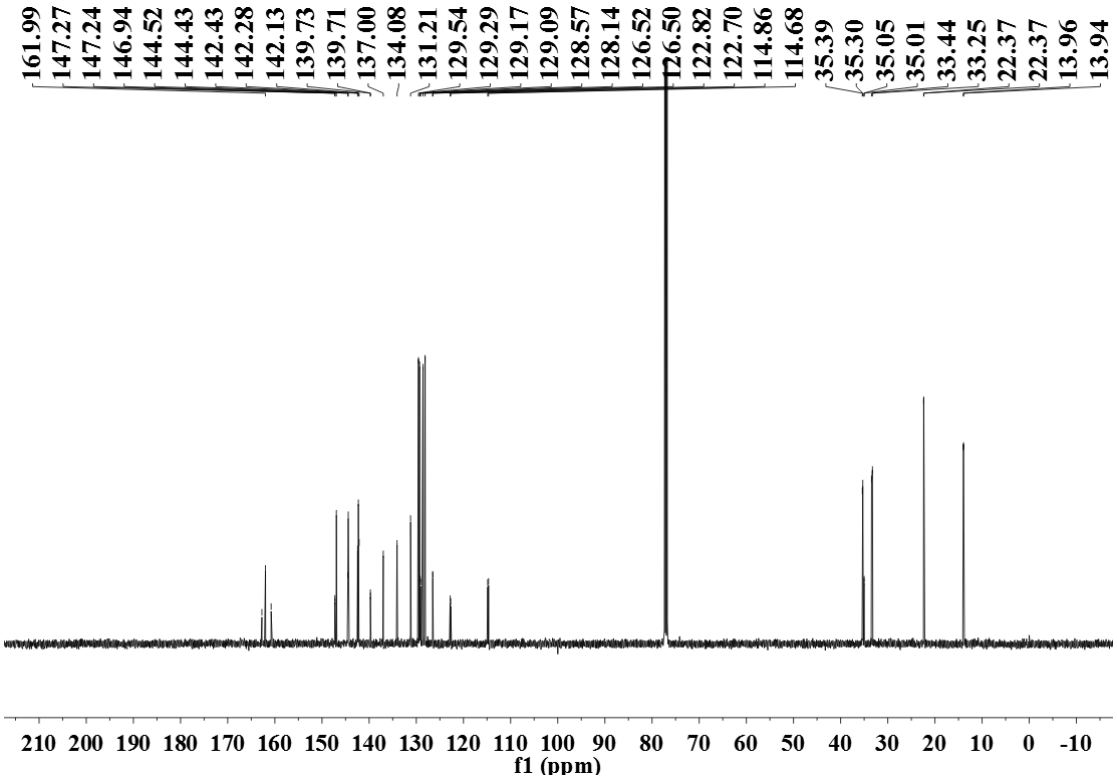

-115.84
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

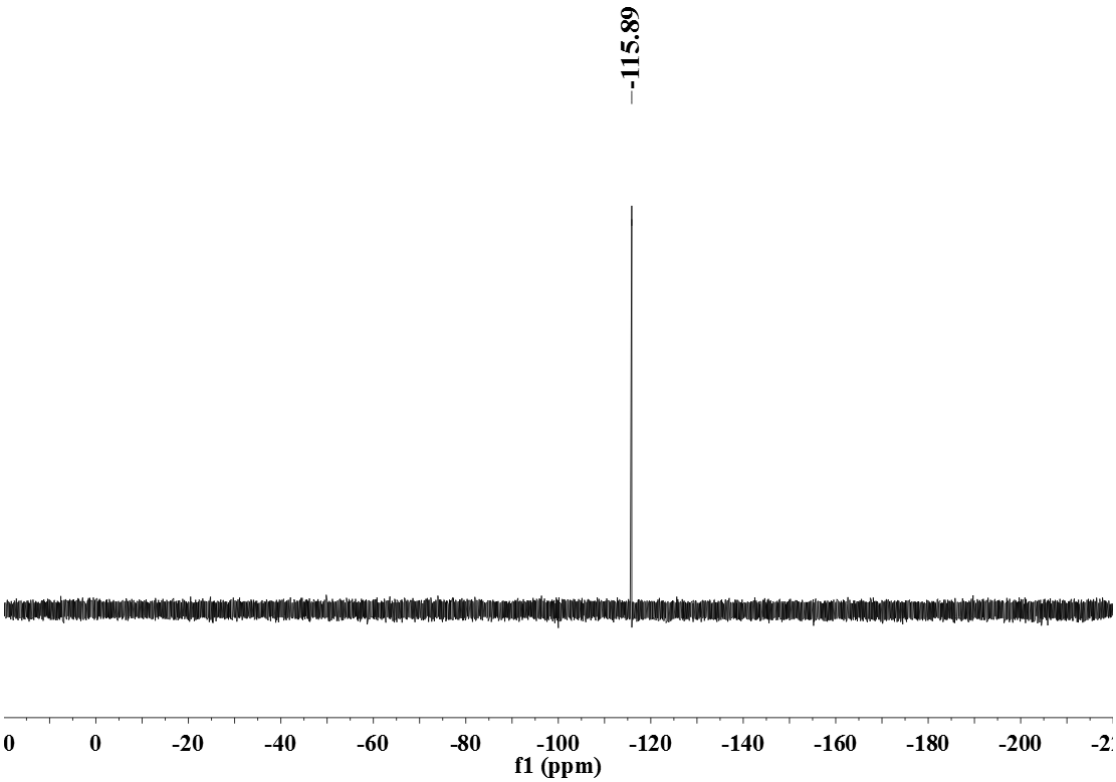

9.34
9.33
8.70
8.70
8.46
8.46
8.45
7.75
7.32
7.30
7.30
7.28
7.26
7.20
7.18
7.18
7.17
7.16
7.15
7.11
7.09
7.07
7.04
7.02
7.00
6.99
6.97
6.96
6.93
6.92
6.91
6.89
6.87
6.85
4.71
4.70
F
HN
PC
H
F
F
3c
1.00
1.02
1.01
0.96
1.10
4.14
1.10
2.07
2.06
1.02
1.03
2.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

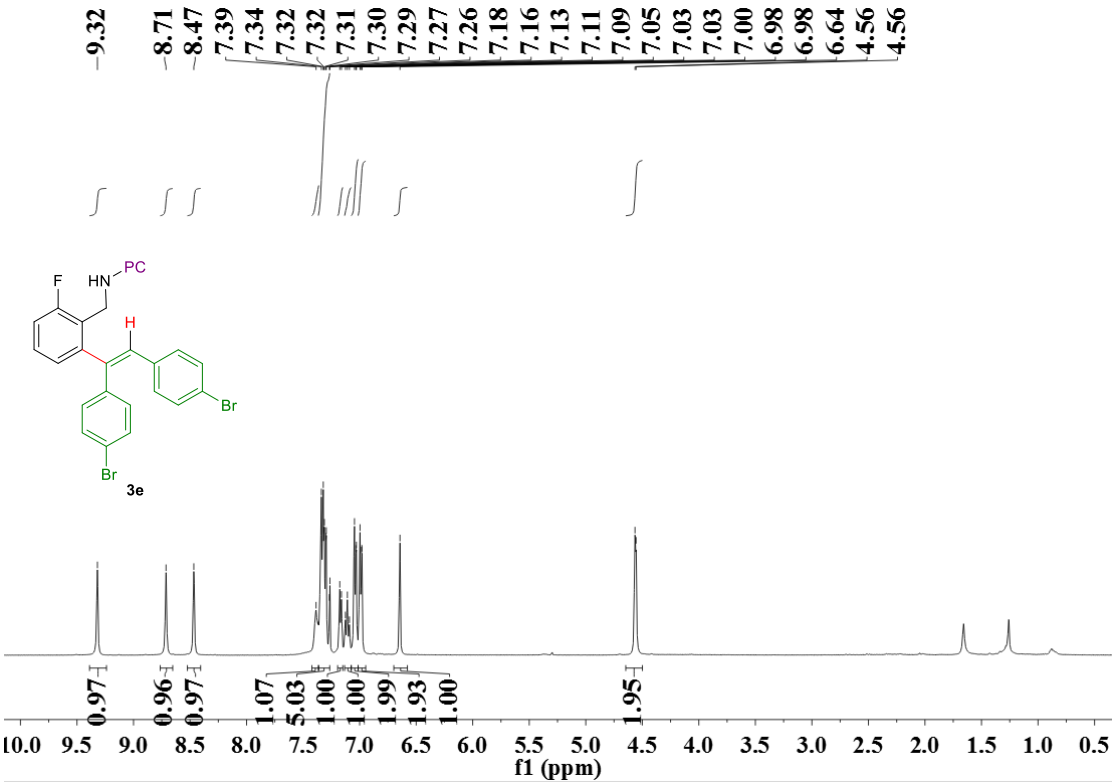

162.16
147.05
144.42
144.30
142.39
131.58
131.55
130.00
129.92
129.53
129.50
129.48
129.39
129.25
129.16
127.30
127.26
127.21
126.24
126.21
124.48
124.45
123.59
123.56
122.68
116.37
116.16
115.54
115.32
115.21
114.98
77.38
77.06
76.74
35.02
34.98
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

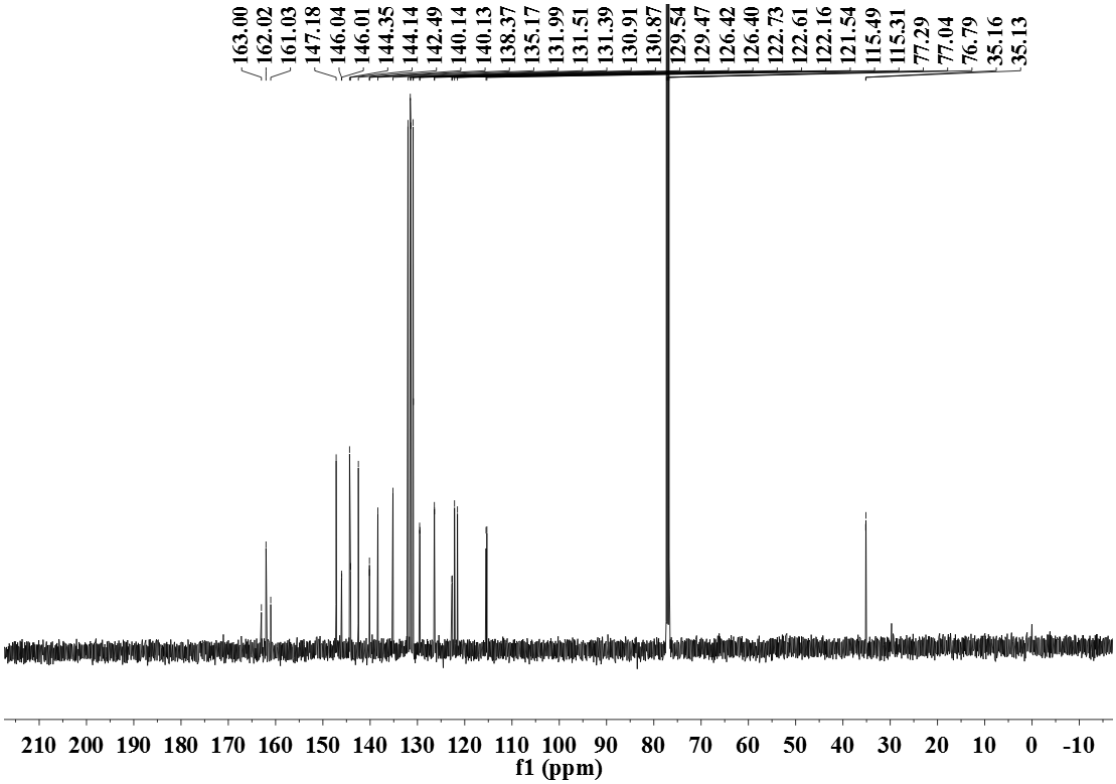

-111.98
-115.24
-115.46
-107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122
f1 (ppm)

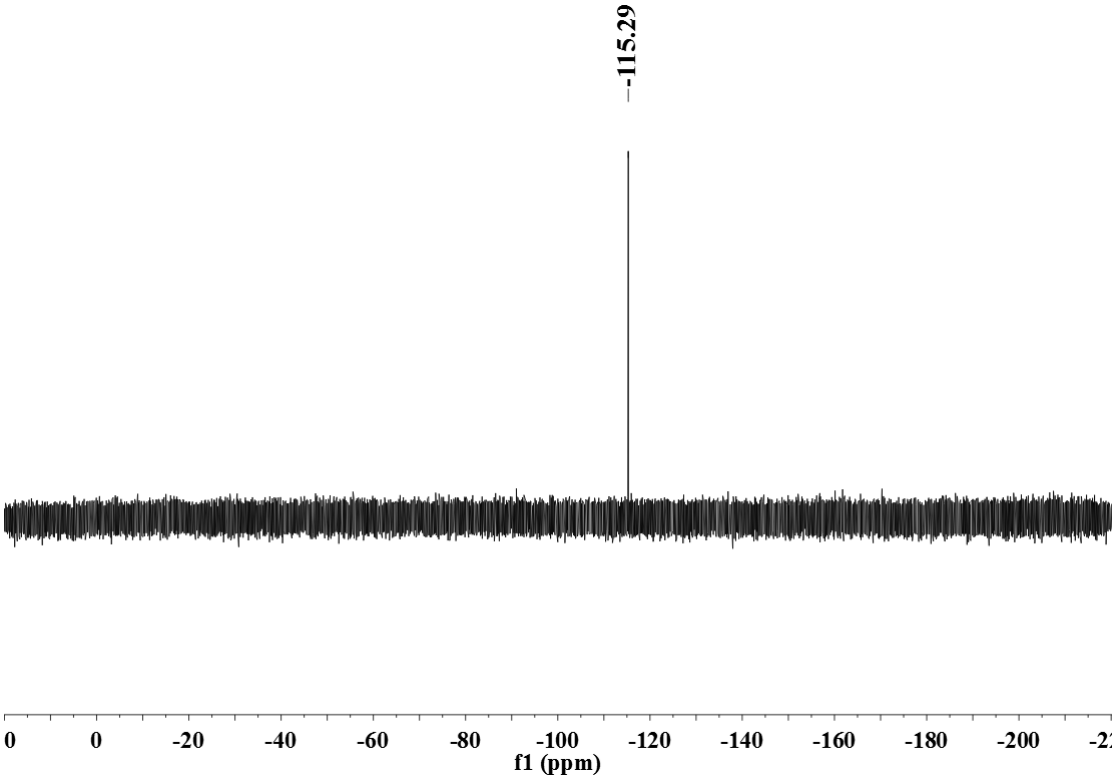

9.33 9.33 8.69 8.68 8.41 7.26 7.19 7.11 7.10 7.06 7.04 7.01 7.00 6.99 6.98 6.63 4.56 4.55 2.57 2.55 2.53 2.45 2.44 2.42 1.56 1.45 1.34 1.33 1.28 1.26 0.93 0.91 0.90 0.88 0.87 0.85
F
HN
PC
H
Bu
Bu
3d
0.98 1.00 0.99 0.99 1.03 1.02 2.04 3.19 4.08 1.02 2.02 2.07 2.05 2.09 2.11 2.13 2.19 3.16 3.21
f1 (ppm)

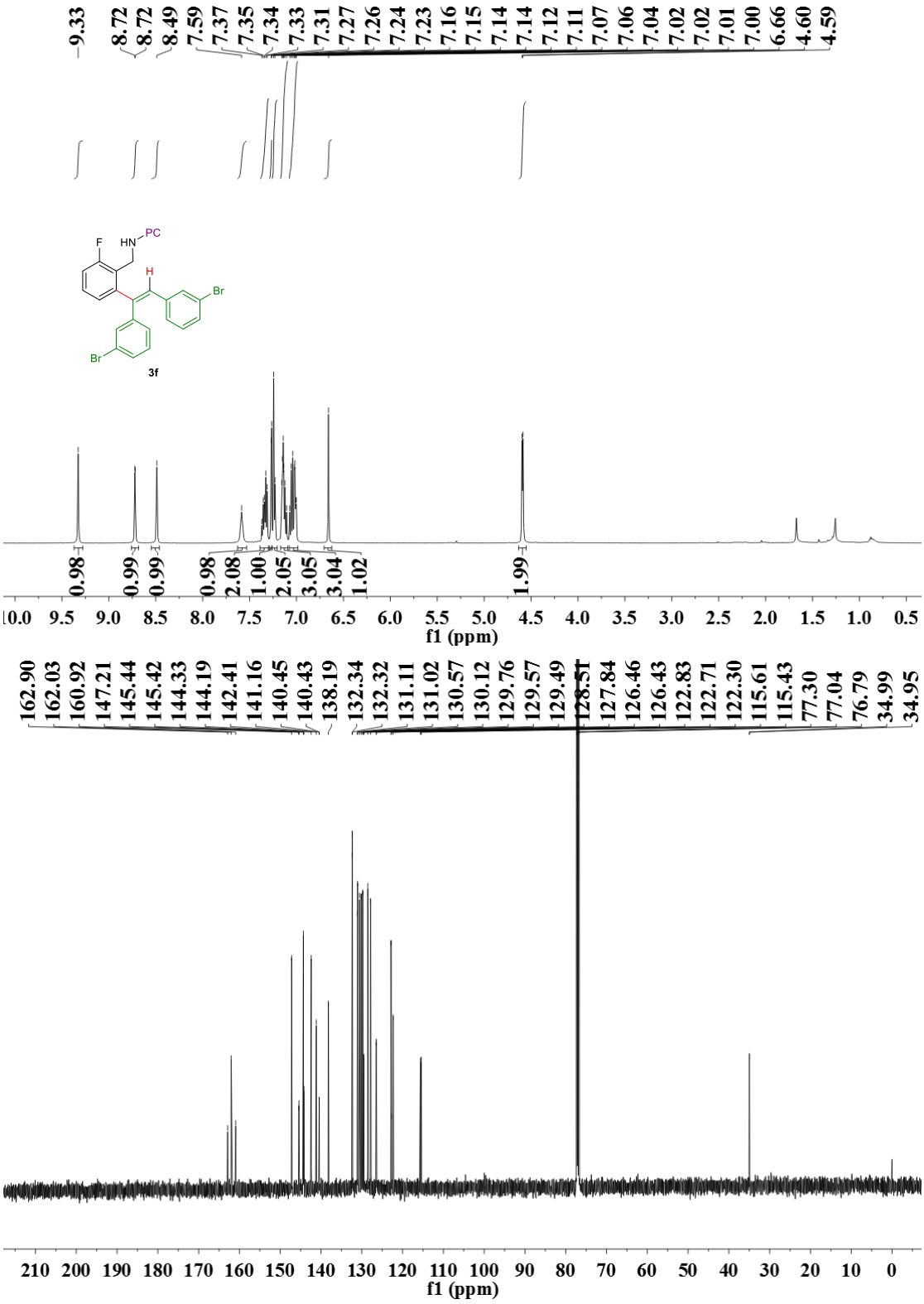

161.99 147.27 147.24 146.94 144.52 144.43 142.43 142.28 142.13 139.73 139.71 137.00 134.08 131.21 129.54 129.29 129.17 129.09 128.57 128.14 126.52 126.50 122.82 122.70 114.86 114.68 35.39 35.30 35.05 35.01 33.44 33.25 22.37 22.37 13.96 13.94
f1 (ppm)

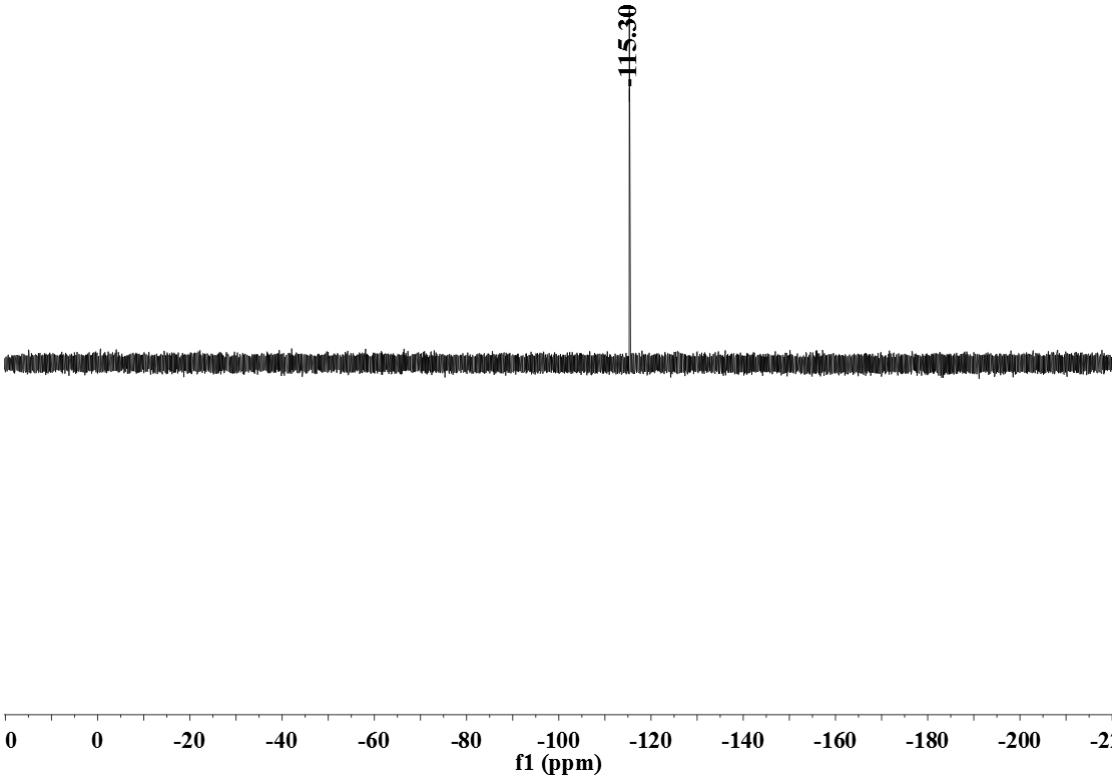

-115.89
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

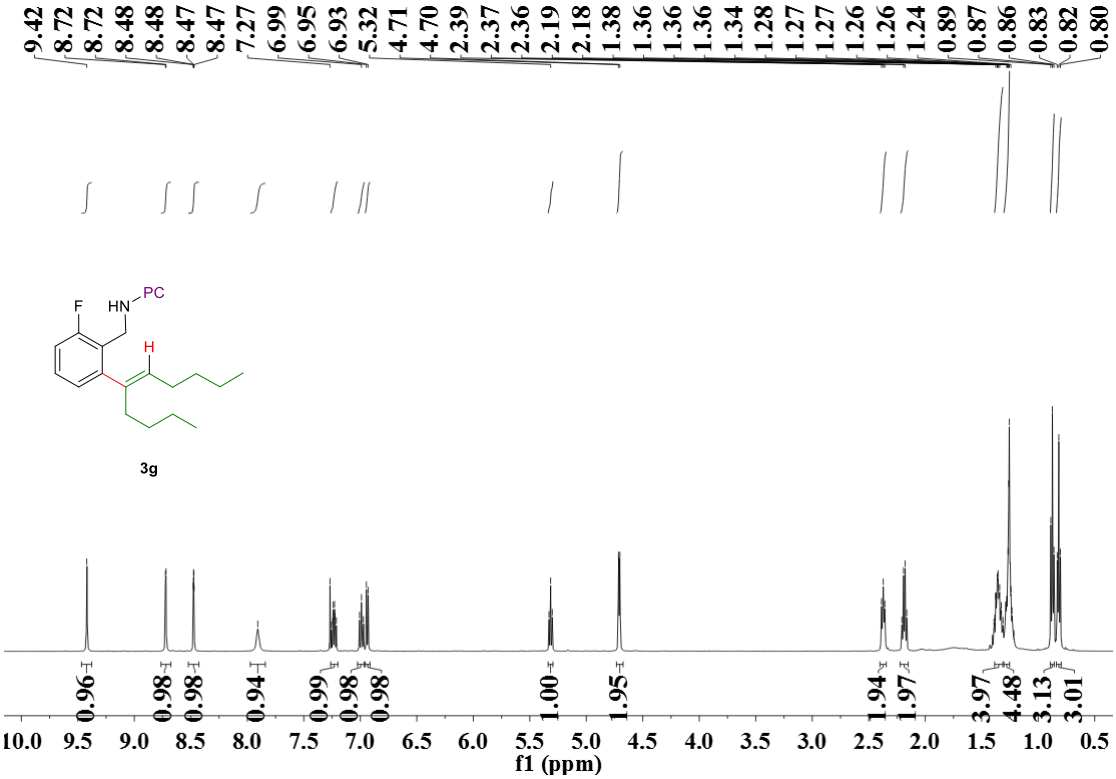

9.32
8.71
8.47
7.39
7.34
7.32
7.32
7.31
7.30
7.29
7.27
7.26
7.18
7.16
7.13
7.11
7.09
7.05
7.03
7.03
7.00
6.98
6.98
6.64
4.56
4.56
F
HN
PC
H
Br
Br
3e
0.97
0.96
0.97
1.07
5.03
1.00
1.00
1.99
1.93
1.00
1.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

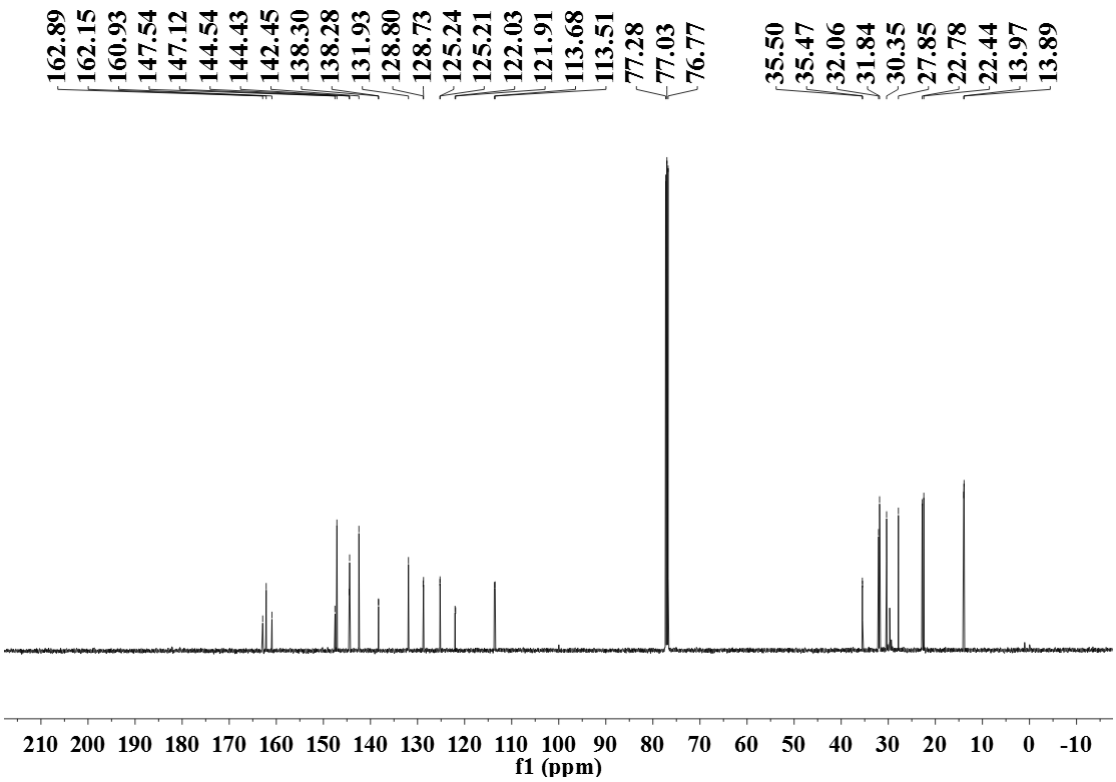

163.00
162.02
161.03
147.18
146.04
146.01
144.35
144.14
142.49
140.14
140.13
138.37
135.17
131.99
131.51
131.39
130.91
130.87
129.54
129.47
126.42
126.40
122.73
122.61
122.16
121.54
115.49
115.31
77.29
77.04
76.79
35.16
35.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

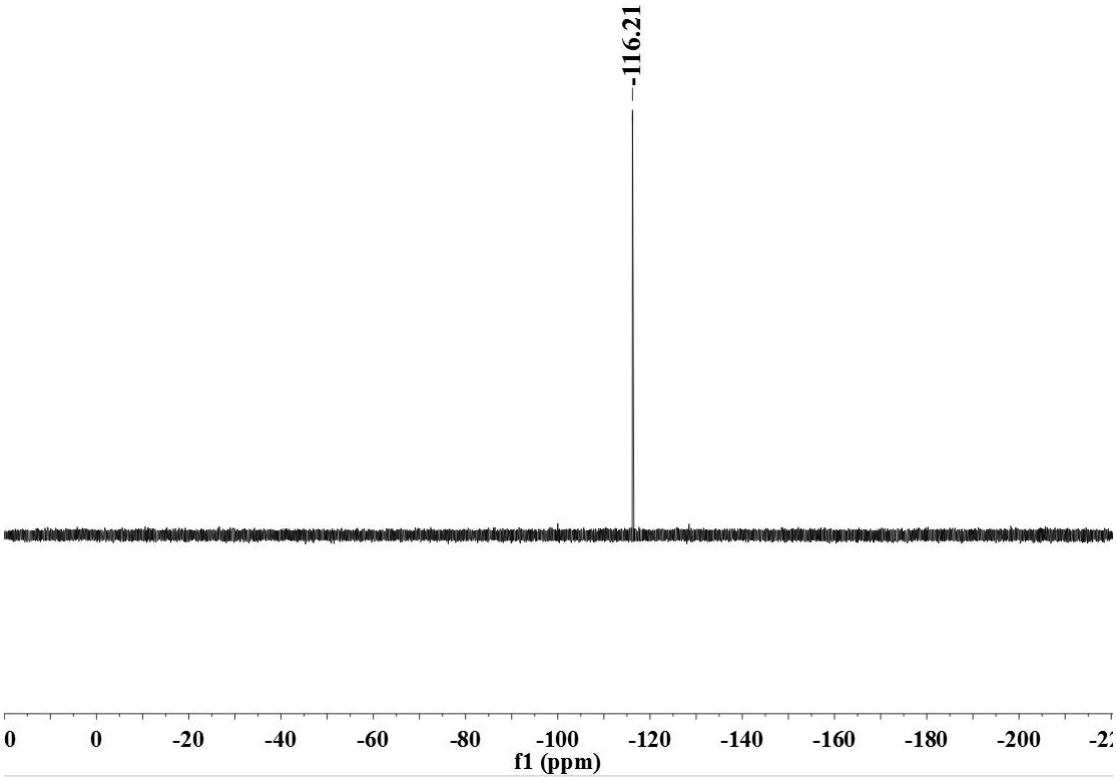

-115.29
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

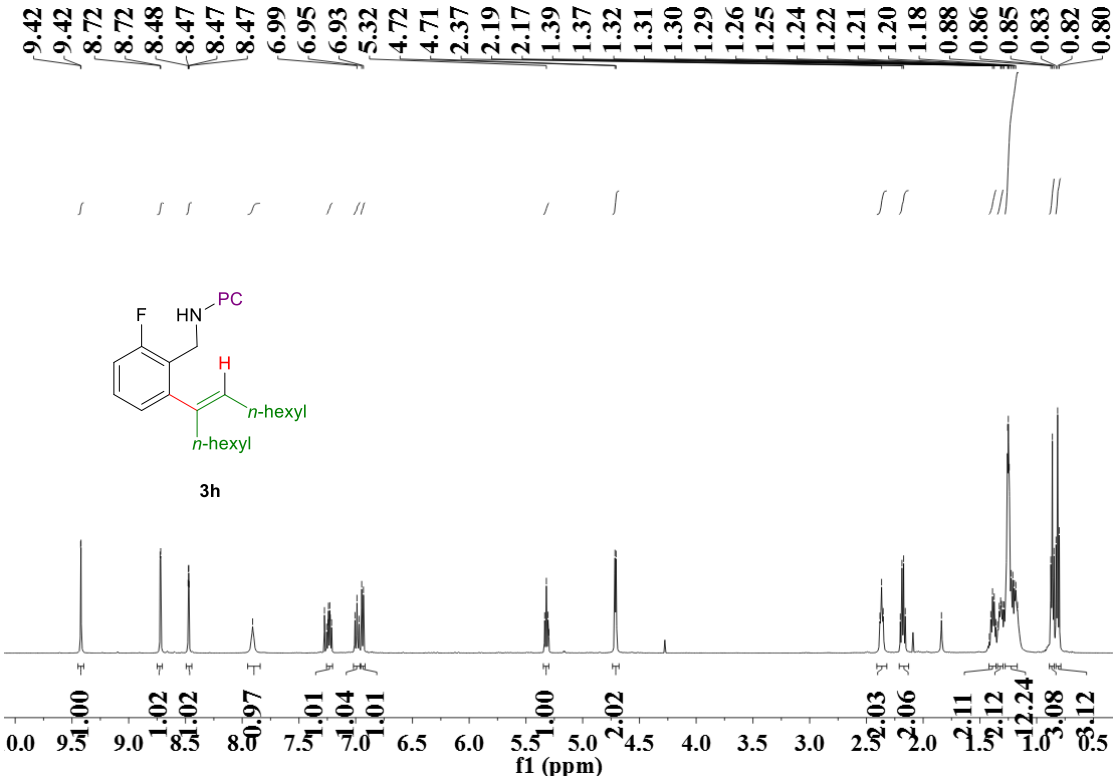

9.33
8.72
8.72
8.49
7.59
7.37
7.35
7.34
7.33
7.31
7.27
7.26
7.24
7.23
7.16
7.15
7.14
7.14
7.12
7.11
7.07
7.06
7.04
7.02
7.02
7.01
7.00
6.66
4.60
4.59
F
HN
PC
H
Br
Br
3f
0.98
0.99
0.99
0.98
2.08
1.00
2.05
3.05
3.04
1.02
1.99
f1 (ppm)
162.90
162.03
160.92
147.21
145.44
145.42
144.33
144.19
142.41
141.16
140.45
140.43
138.19
132.34
132.32
131.11
131.02
130.57
130.12
129.76
129.57
129.49
128.51
127.84
126.46
126.43
122.83
122.71
122.30
115.61
115.43
77.30
77.04
76.79
34.99
34.95
f1 (ppm)

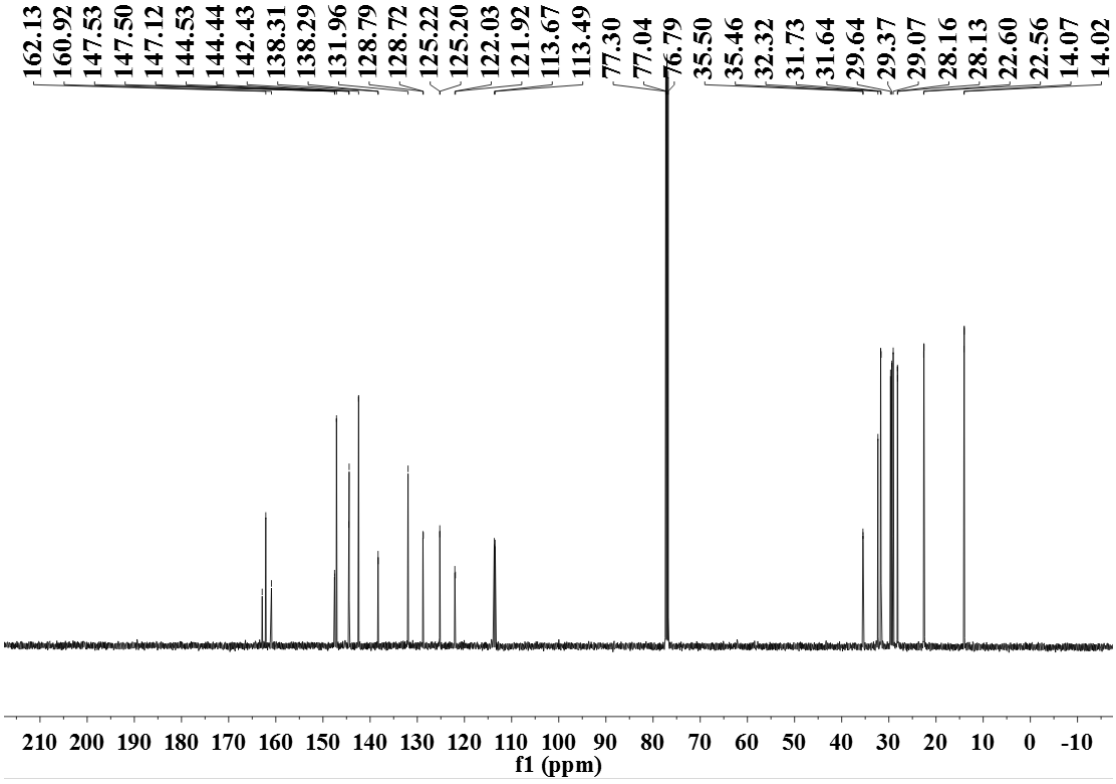

-115.30
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

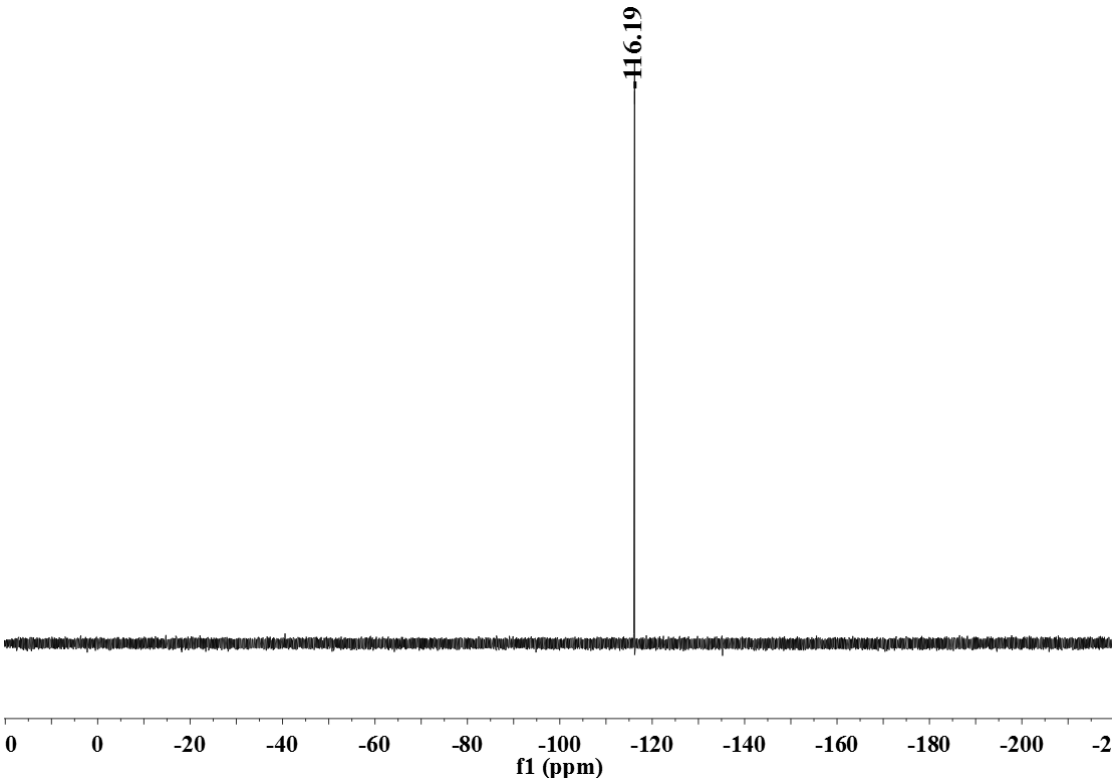

9.42
8.72
8.72
8.48
8.48
8.47
8.47
7.27
6.99
6.95
6.93
5.32
4.71
4.70
2.39
2.37
2.36
2.19
2.18
1.38
1.36
1.36
1.36
1.34
1.28
1.27
1.27
1.26
1.26
1.24
0.89
0.87
0.86
0.83
0.82
0.80
F
HN
PC
H
3g
0.96
0.98
0.98
0.94
0.99
0.98
0.98
1.00
1.95
1.94
1.97
3.97
4.48
3.13
3.01
f1 (ppm)

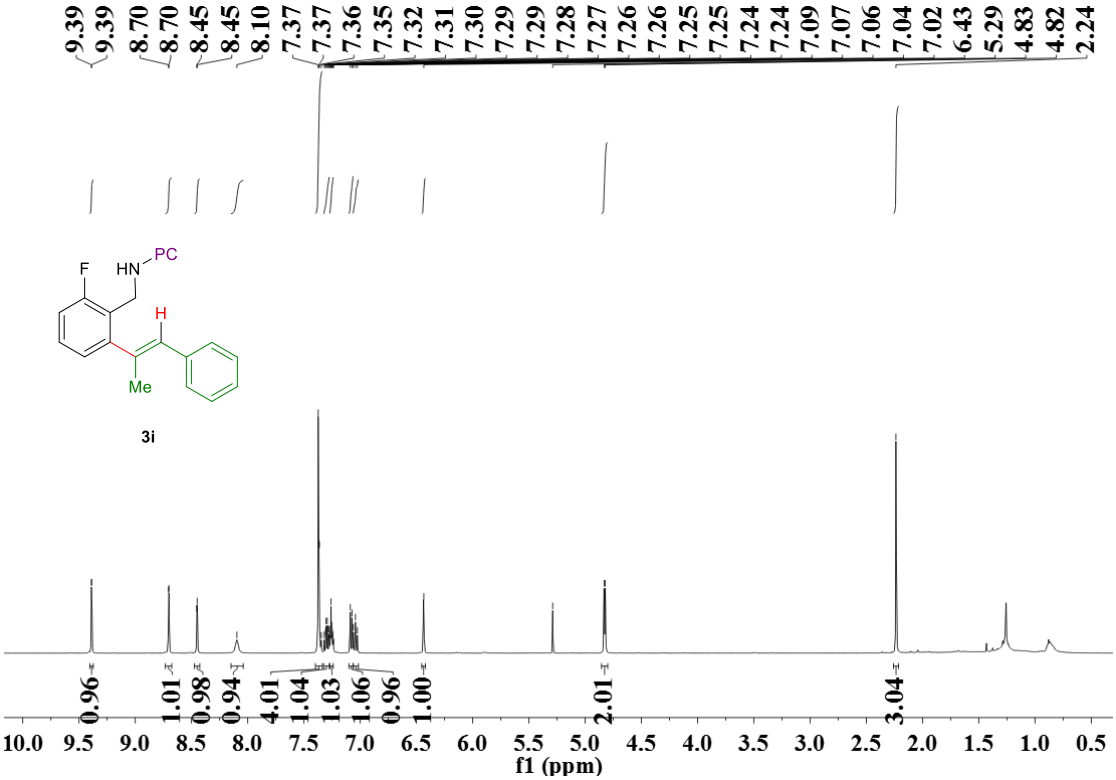

162.89
162.15
160.93
147.54
147.12
144.54
144.43
142.45
138.30
138.28
131.93
128.80
128.73
125.24
125.21
122.03
121.91
113.68
113.51
77.28
77.03
76.77
35.50
35.47
32.06
31.84
30.35
27.85
22.78
22.44
13.97
13.89
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

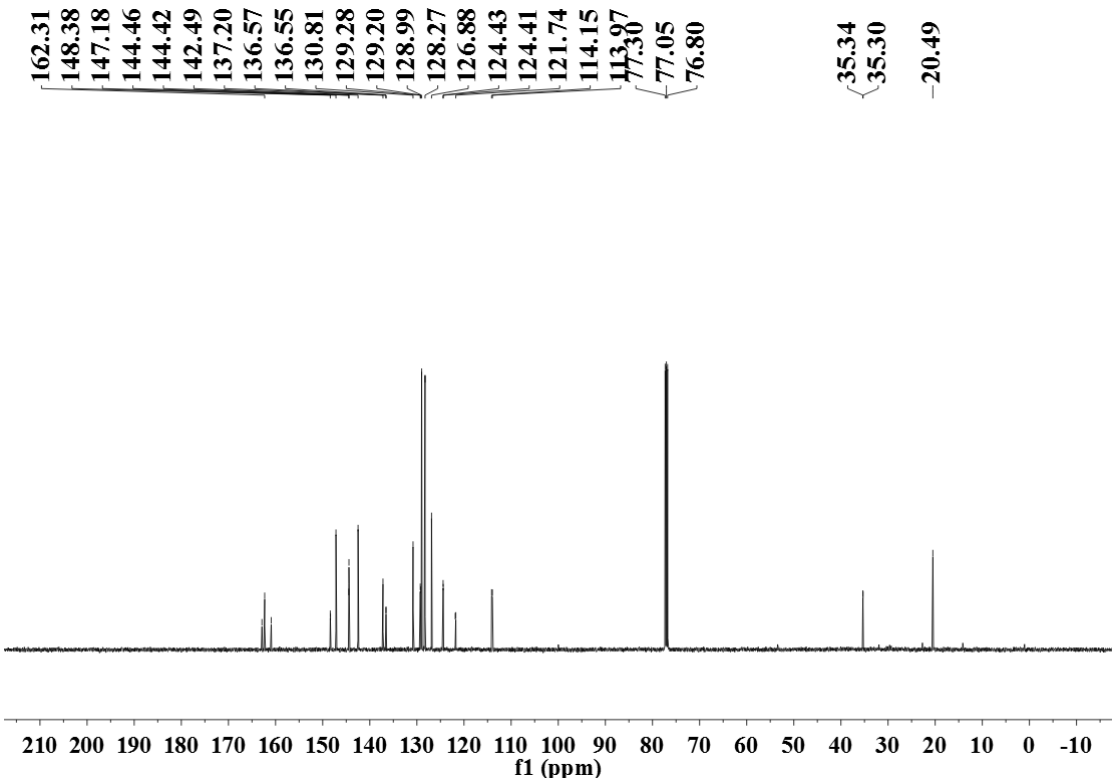

-116.21
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

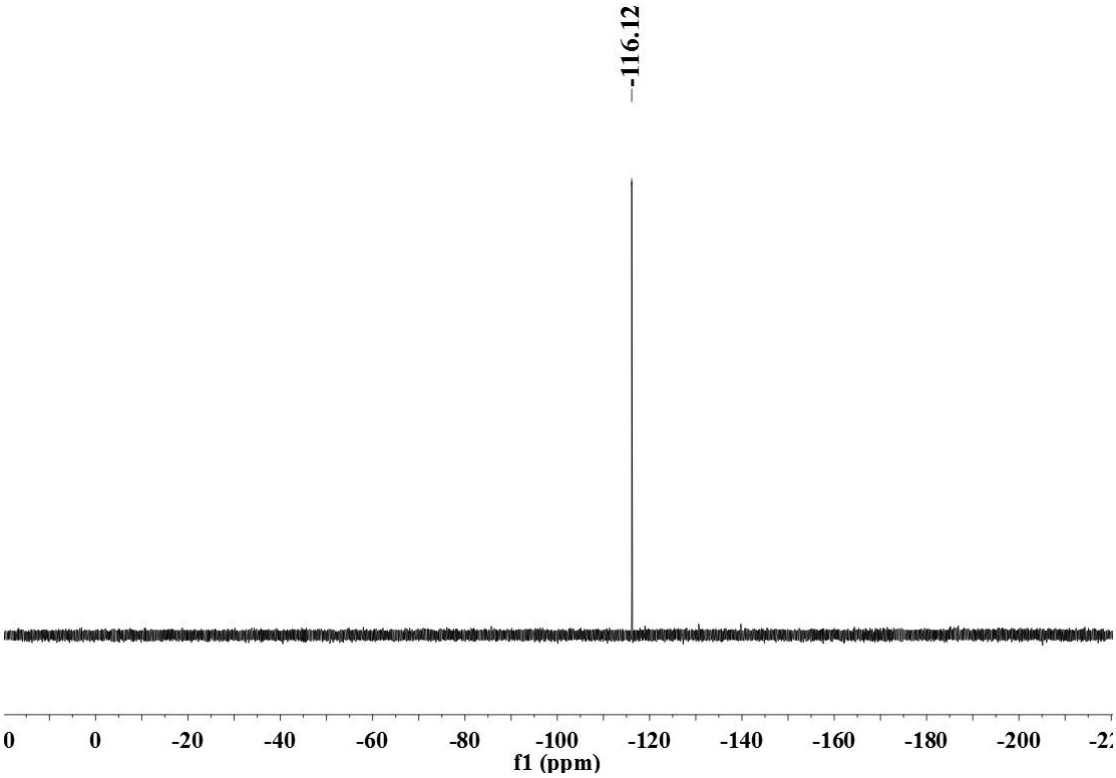

9.42 9.42 8.72 8.72 8.48 8.47 8.47 8.47 6.99 6.95 6.93 5.32 4.72 4.71 2.37 2.19 2.17 1.39 1.37 1.32 1.31 1.30 1.29 1.26 1.25 1.24 1.22 1.21 1.20 1.18 0.88 0.86 0.85 0.83 0.82 0.80
F
HN
PC
H
n-hexyl
n-hexyl
3h
1.00 1.02 1.02 0.97 1.01 1.04 1.01 1.00 2.02 2.03 2.06 2.11 2.12 12.24 3.08 3.12
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

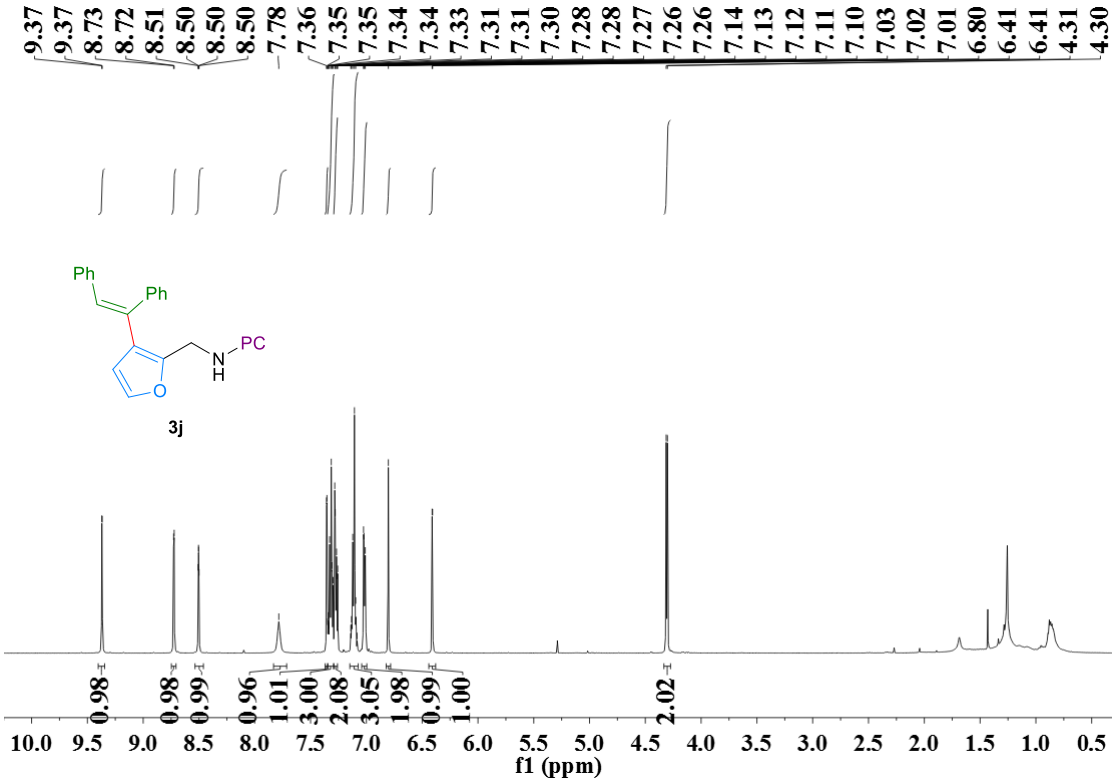

162.13 160.92 147.53 147.50 147.12 144.53 144.44 142.43 138.31 138.29 131.96 128.79 128.72 125.22 125.20 122.03 121.92 113.67 113.49 77.30 77.04 76.79 35.50 35.46 32.32 31.73 31.64 29.64 29.37 29.07 28.16 28.13 22.60 22.56 14.07 14.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

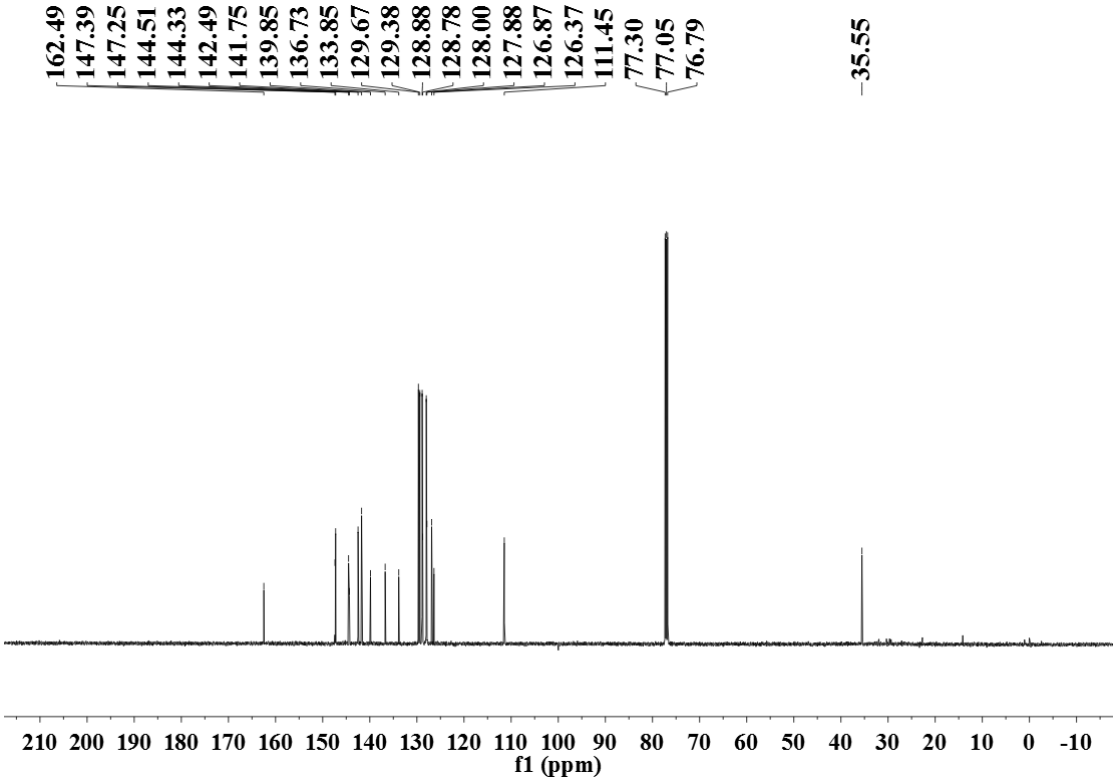

-116.19
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)

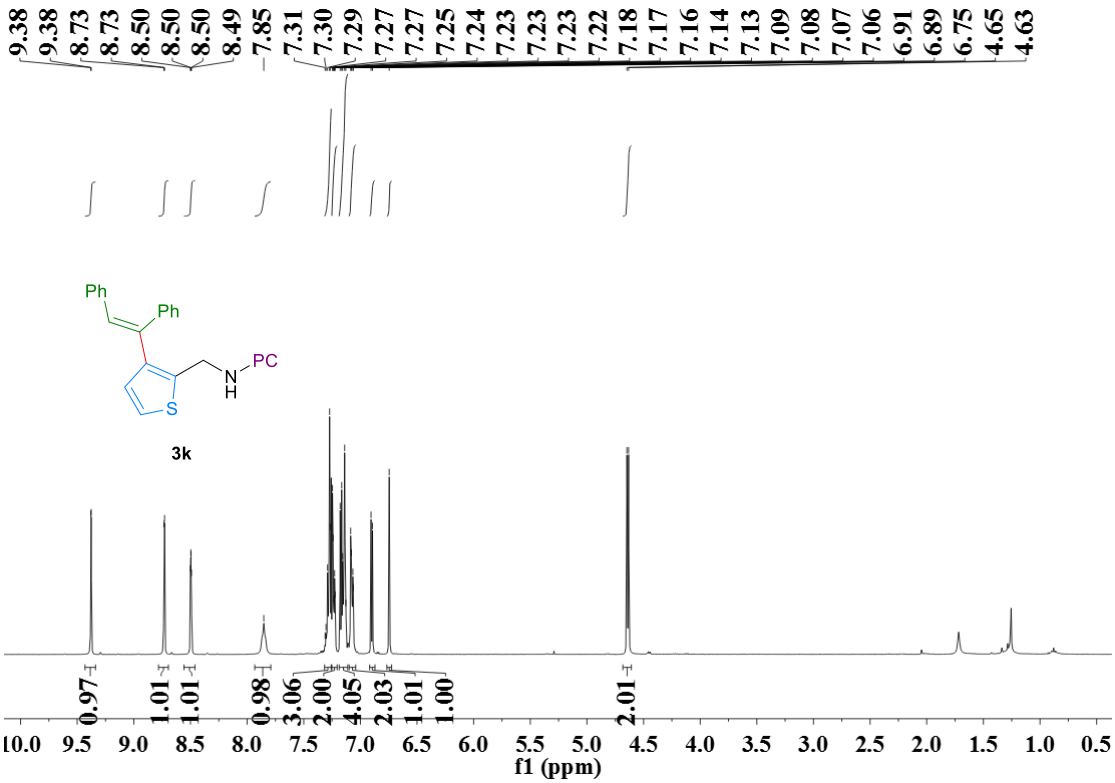

9.39
9.39
8.70
8.70
8.45
8.45
8.10
7.37
7.37
7.36
7.35
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.09
7.07
7.06
7.04
7.02
6.43
5.29
4.83
4.82
2.24
F
HN
PC
H
Me
3i
0.96
1.01
0.98
0.94
4.01
1.04
1.03
1.06
0.96
1.00
2.01
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

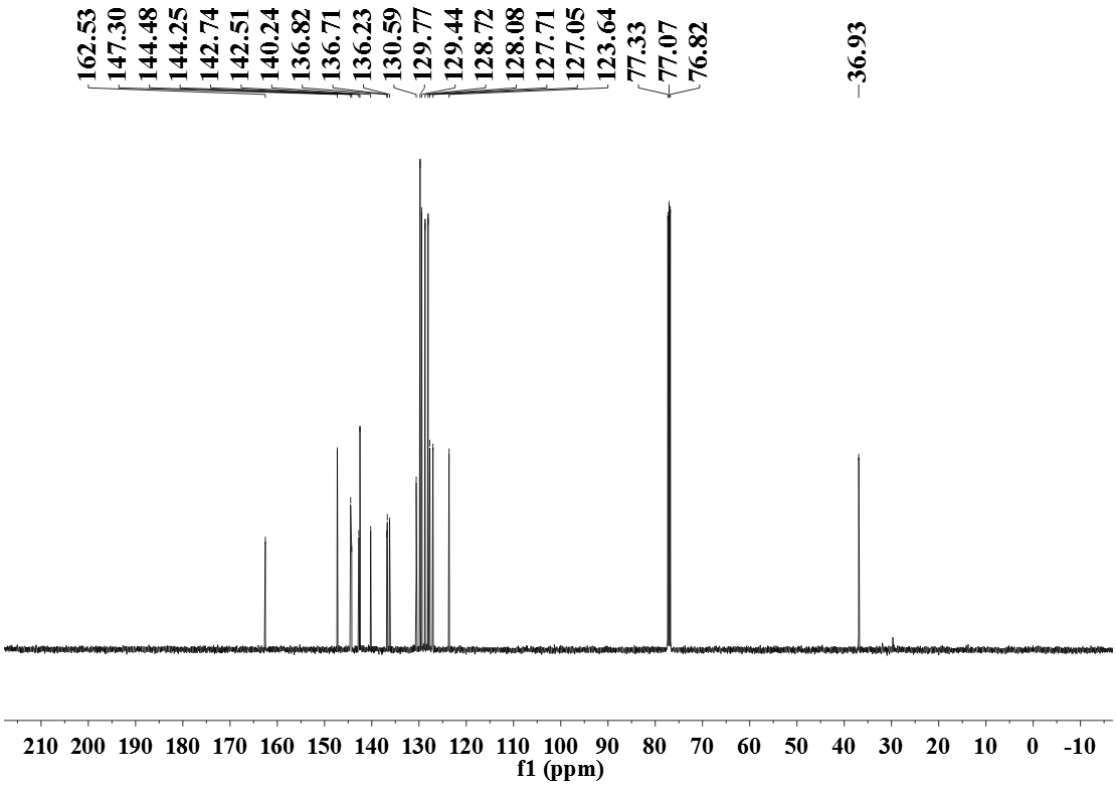

162.31
148.38
147.18
144.46
144.42
142.49
137.20
136.57
136.55
130.81
129.28
129.20
128.99
128.27
126.88
124.43
124.41
121.74
114.15
113.97
77.30
77.05
76.80
35.34
35.30
20.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

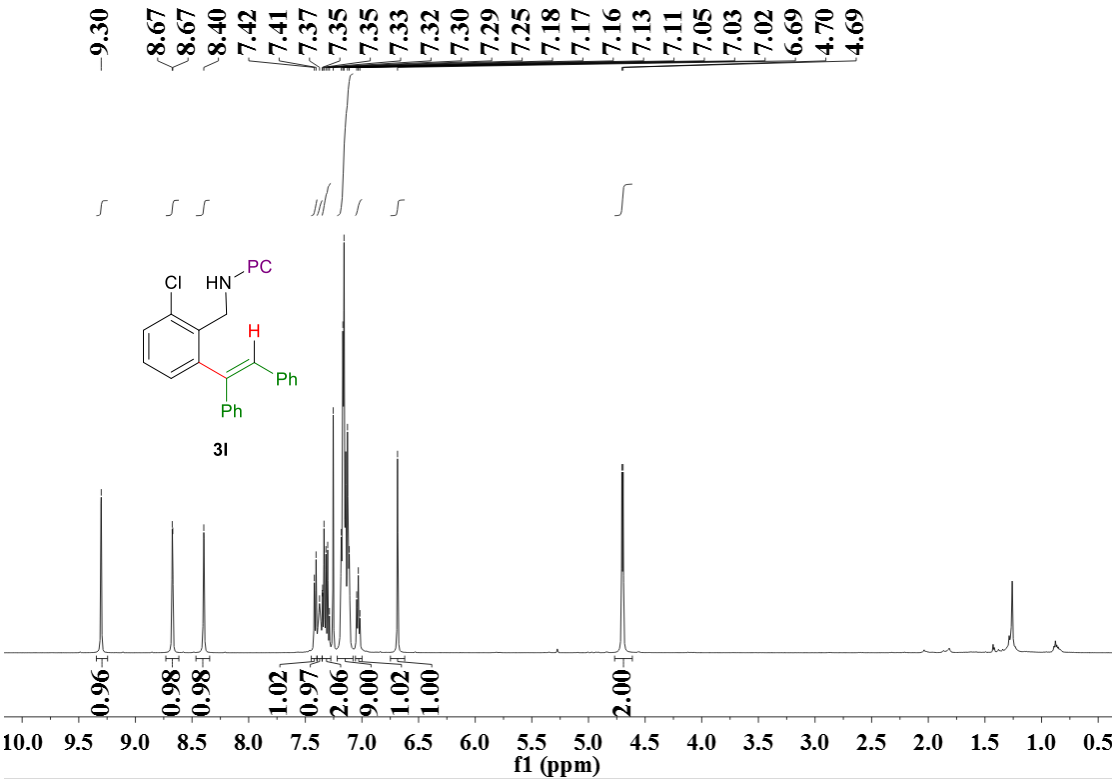

-116.12
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

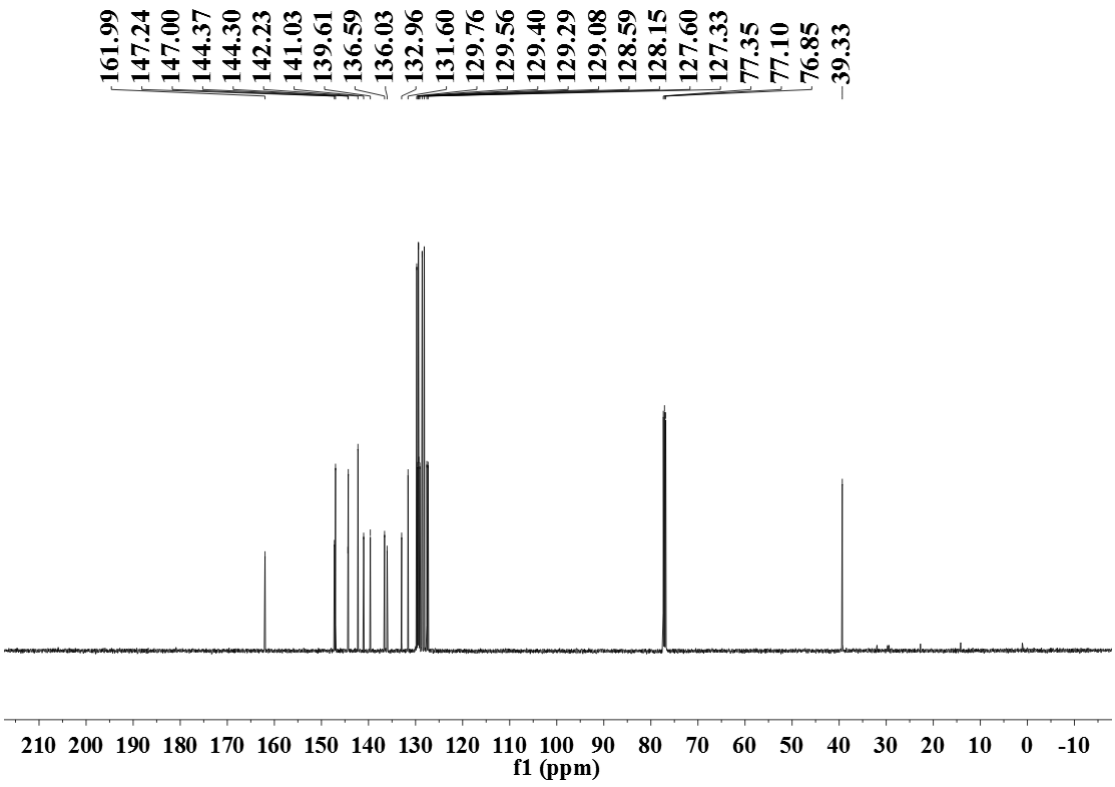

9.37 9.37 8.73 8.72 8.51 8.50 8.50 8.50 7.78 7.36 7.35 7.35 7.34 7.34 7.33 7.31 7.31 7.30 7.28 7.28 7.27 7.26 7.26 7.14 7.13 7.12 7.11 7.10 7.03 7.02 7.01 6.80 6.41 6.41 4.31 4.30
Ph
Ph
PC
N
H
O
3j
0.98 0.98 0.99 0.96 1.01 3.00 2.08 3.05 1.98 0.99 1.00 2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

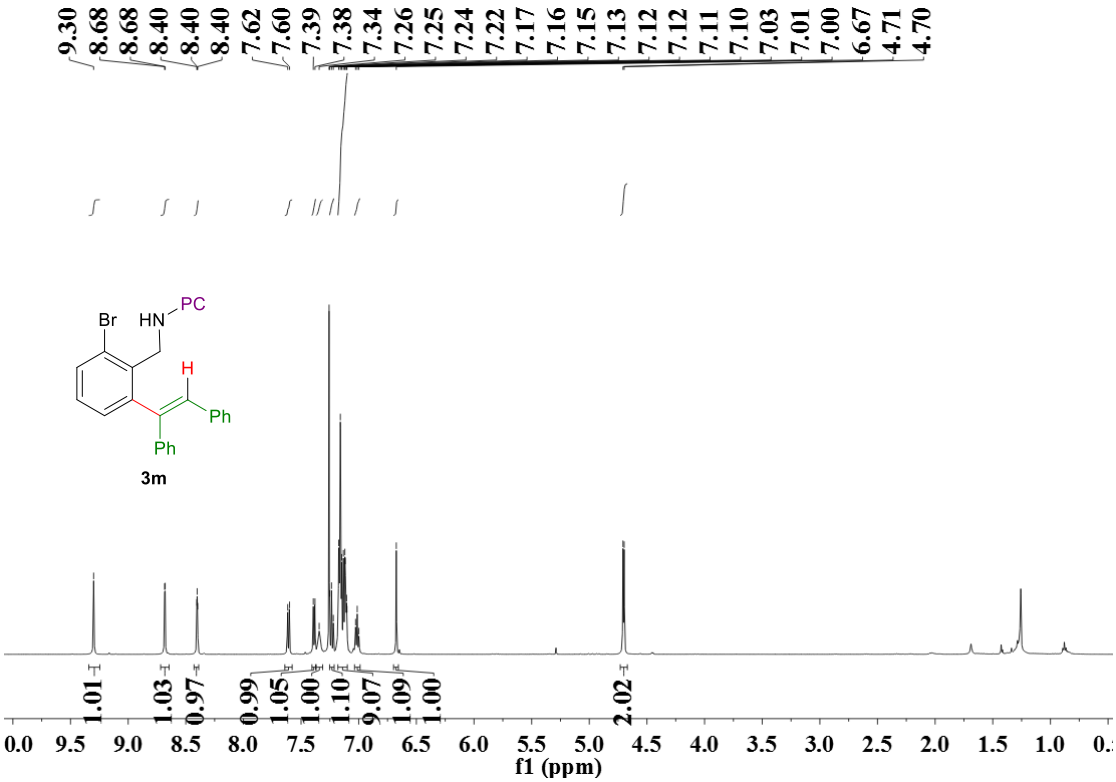

162.49 147.39 147.25 144.51 144.33 142.49 141.75 139.85 136.73 133.85 129.67 129.38 128.88 128.78 128.00 127.88 126.87 126.37 111.45 77.30 77.05 76.79 35.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

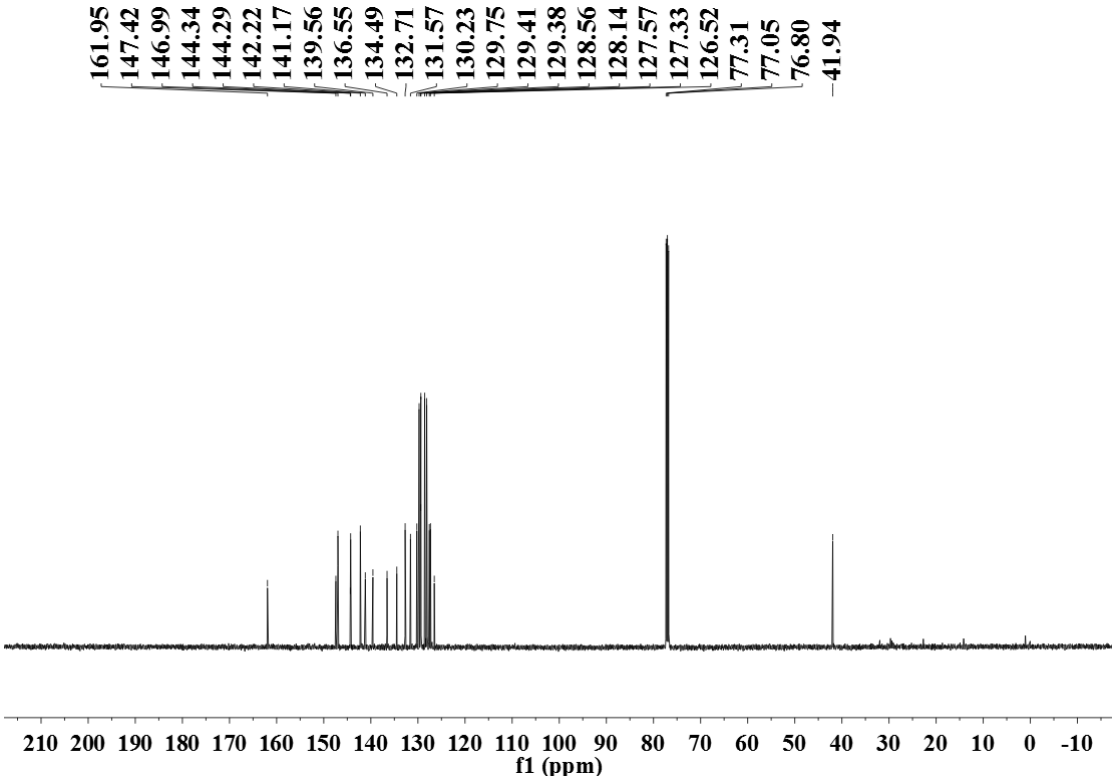

9.38
9.38
8.73
8.73
8.50
8.50
8.50
8.49
7.85
7.31
7.30
7.29
7.27
7.27
7.25
7.24
7.23
7.23
7.23
7.22
7.18
7.17
7.16
7.14
7.13
7.09
7.08
7.07
7.06
6.91
6.89
6.75
4.65
4.63
Ph
Ph
PC
N
H
S
3k
0.97
1.01
1.01
0.98
3.06
2.00
4.05
2.03
1.01
1.00
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

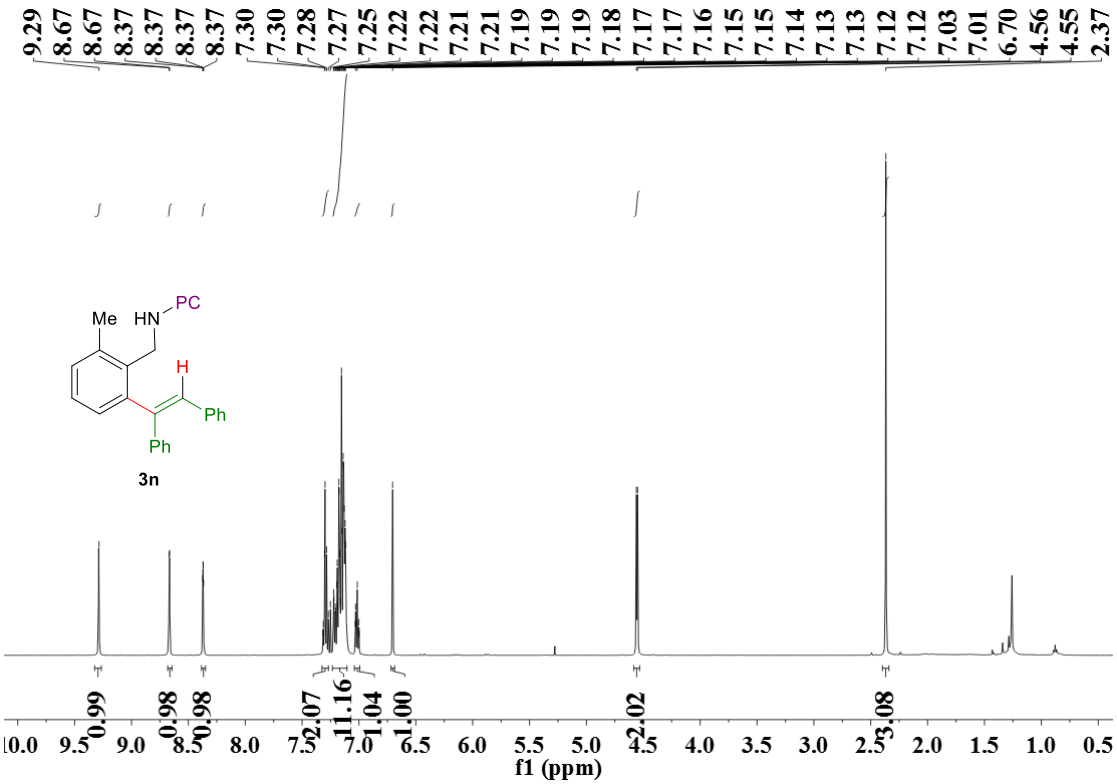

162.53
147.30
144.48
144.25
142.74
142.51
140.24
136.82
136.71
136.23
130.59
129.77
129.44
128.72
128.08
127.71
127.05
123.64
77.33
77.07
76.82
36.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

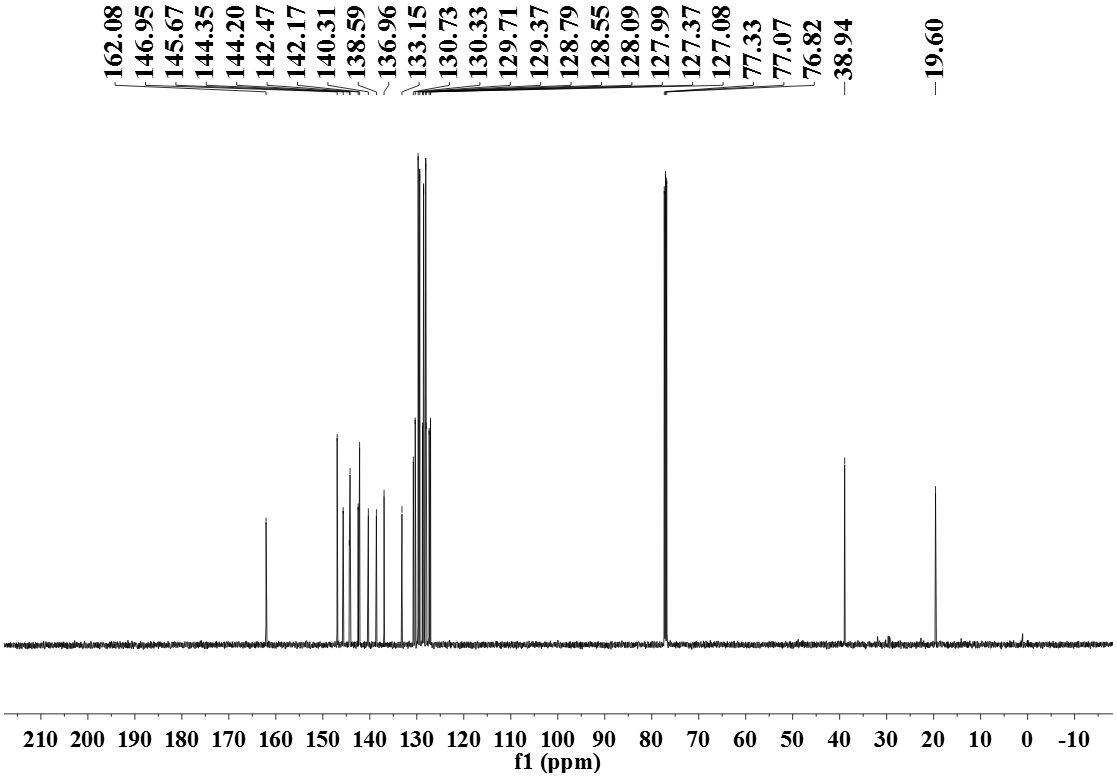

9.30
8.67
8.67
8.40
7.42
7.41
7.37
7.35
7.35
7.33
7.32
7.30
7.29
7.25
7.18
7.17
7.16
7.13
7.11
7.05
7.03
7.02
6.69
4.70
4.69
Cl
HN
PC
H
Ph
Ph
3l
0.96
0.98
0.98
1.02
0.97
2.06
9.00
1.02
1.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

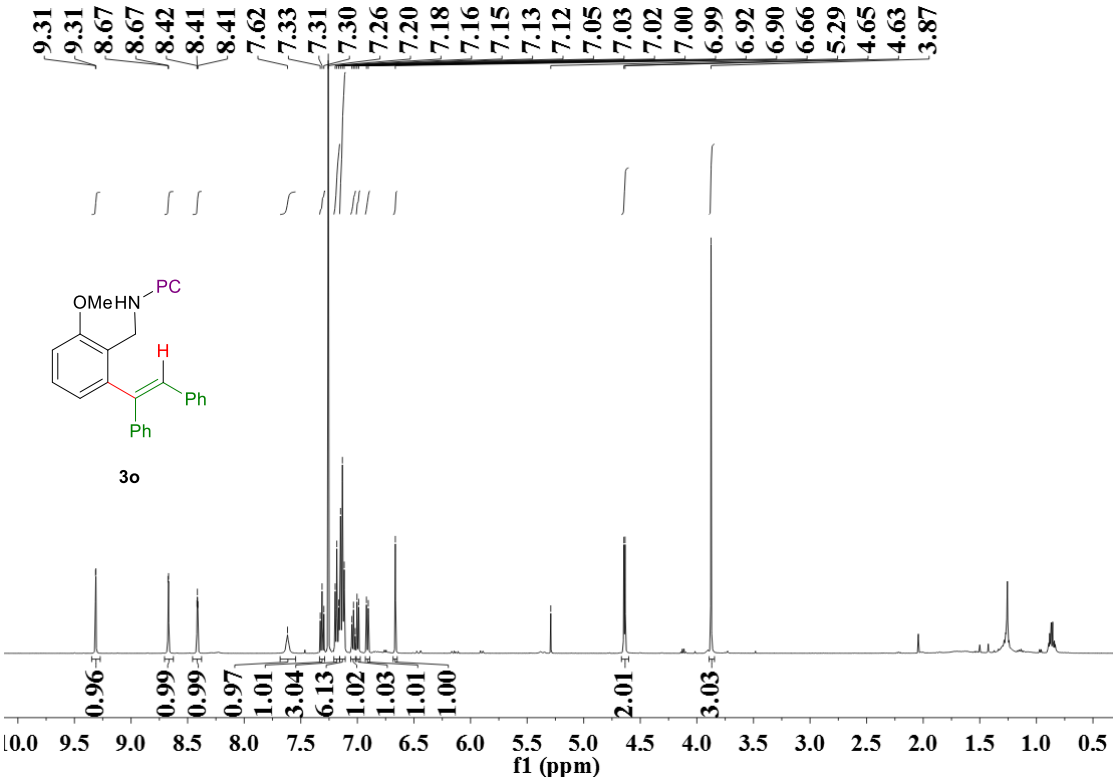

161.99
147.24
147.00
144.37
144.30
142.23
141.03
139.61
136.59
136.03
132.96
131.60
129.76
129.56
129.40
129.29
129.08
128.59
128.15
127.60
127.33
77.35
77.10
76.85
39.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

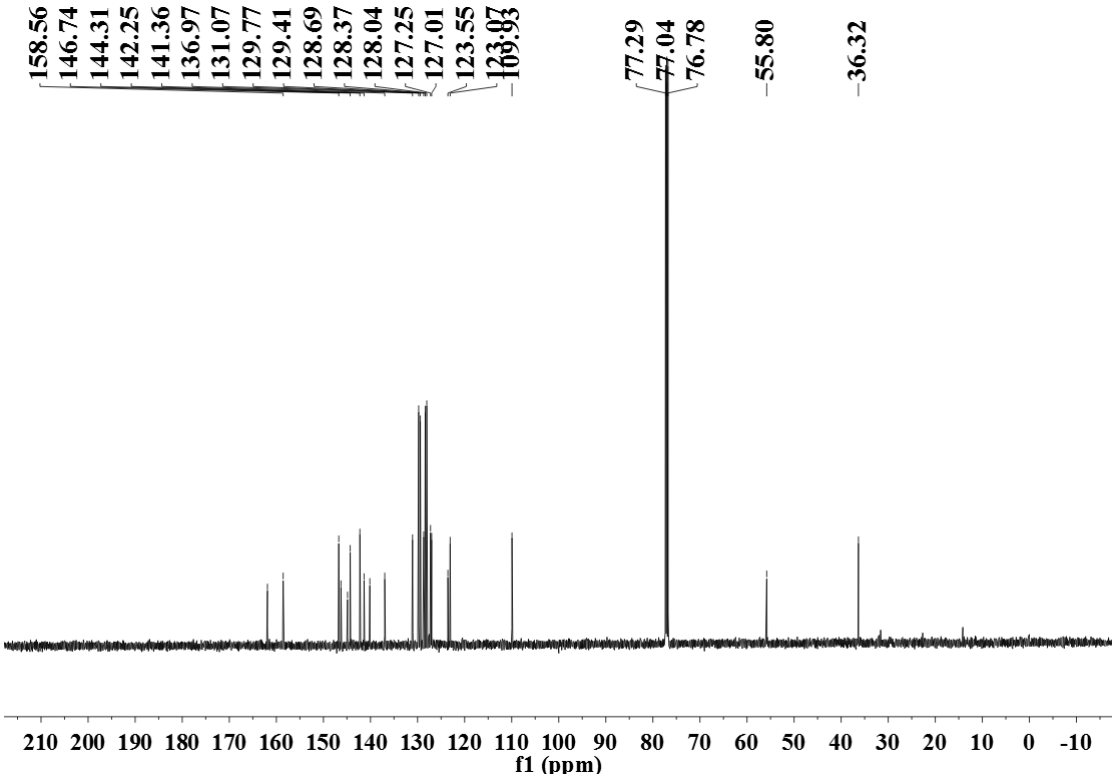

9.30 8.68 8.68 8.40 8.40 8.40 7.62 7.60 7.39 7.38 7.34 7.26 7.25 7.24 7.22 7.17 7.16 7.15 7.13 7.12 7.12 7.11 7.10 7.03 7.01 7.00 6.67 4.71 4.70
Br HN PC H Ph Ph
3m
1.01 1.03 0.97 0.99 1.05 1.00 1.10 9.07 1.09 1.00 2.02
f1 (ppm)

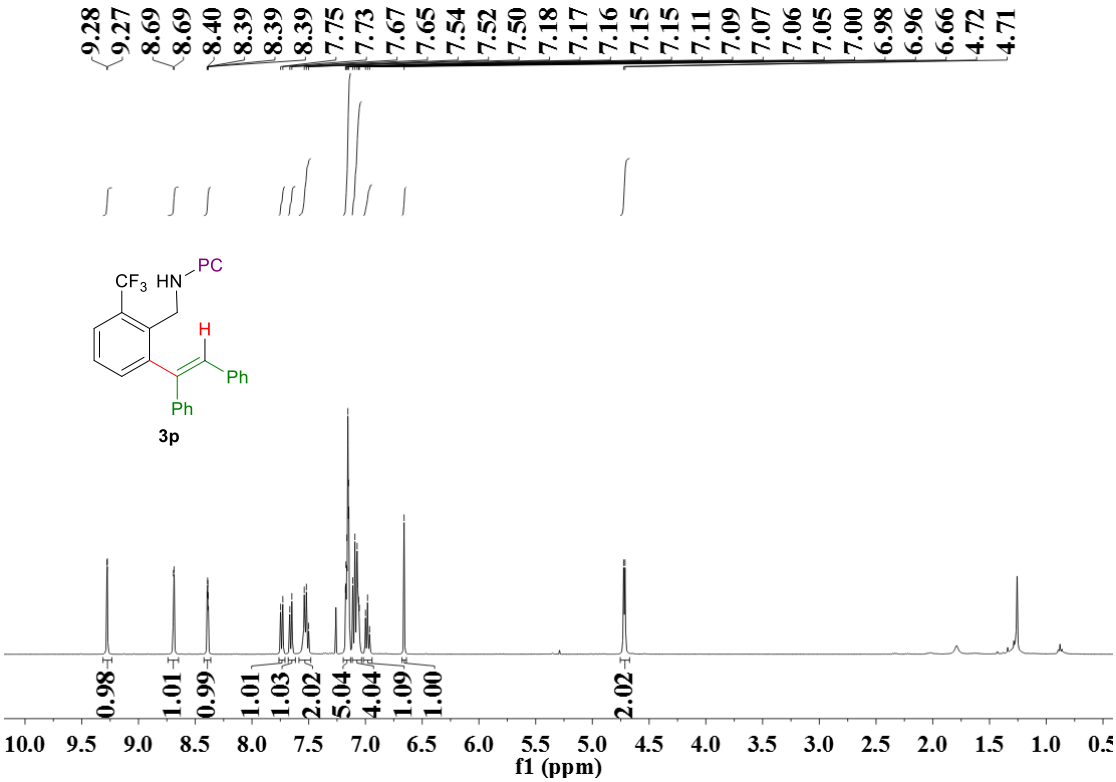

161.95 147.42 146.99 144.34 144.29 142.22 141.17 139.56 136.55 134.49 132.71 131.57 130.23 129.75 129.41 129.38 128.56 128.14 127.57 127.33 126.52 77.31 77.05 76.80 41.94
f1 (ppm)

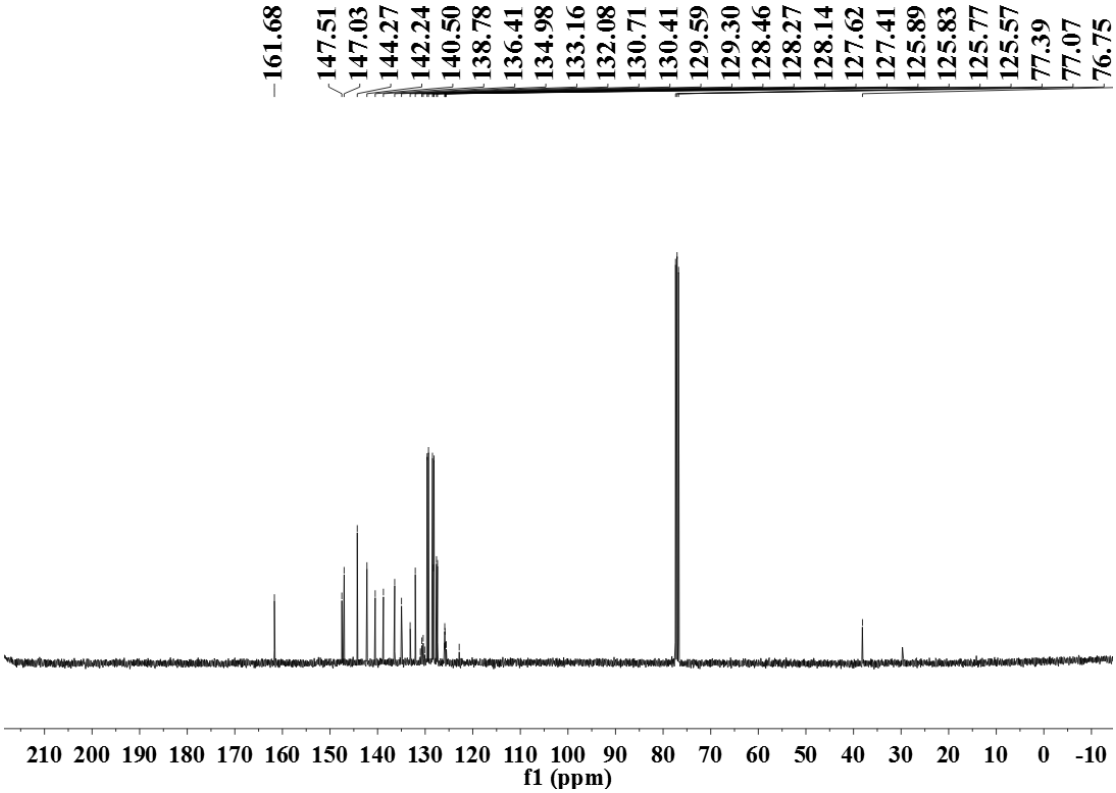

9.29
8.67
8.67
8.37
8.37
8.37
8.37
7.30
7.30
7.28
7.27
7.25
7.22
7.22
7.21
7.21
7.19
7.19
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.03
7.01
6.70
4.56
4.55
2.37
Me
HN
PC
H
Ph
Ph
3n
0.99
0.98
0.98
2.07
11.16
1.04
1.00
2.02
3.08
f1 (ppm)

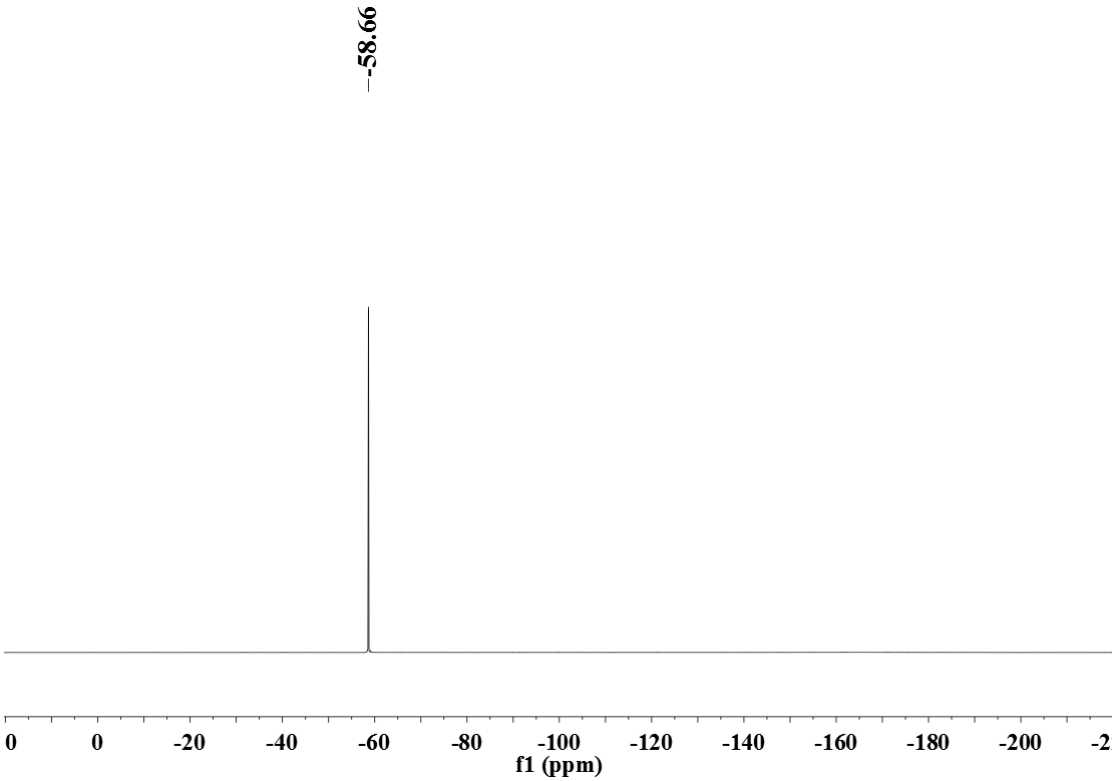

162.08
146.95
145.67
144.35
144.20
142.47
142.17
140.31
138.59
136.96
133.15
130.73
130.33
129.71
129.37
128.79
128.55
128.09
127.99
127.37
127.08
77.33
77.07
76.82
38.94
19.60
f1 (ppm)

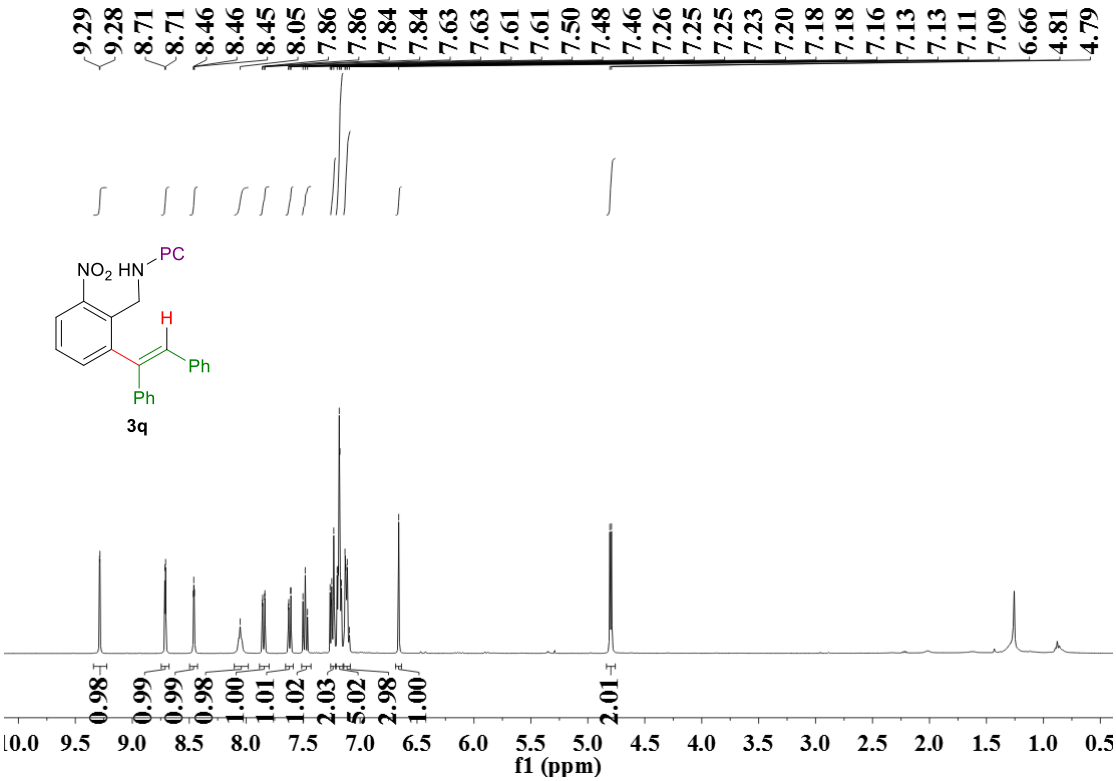

9.31 9.31 8.67 8.67 8.42 8.41 8.41 7.62 7.33 7.31 7.30 7.26 7.20 7.18 7.16 7.15 7.13 7.12 7.05 7.03 7.02 7.00 6.99 6.92 6.90 6.66 5.29 4.65 4.63 3.87
OMeHN
PC
H
Ph
Ph
3o
0.96 0.99 0.99 0.97 1.01 3.04 6.13 1.02 1.03 1.01 1.00 2.01 3.03
f1 (ppm)

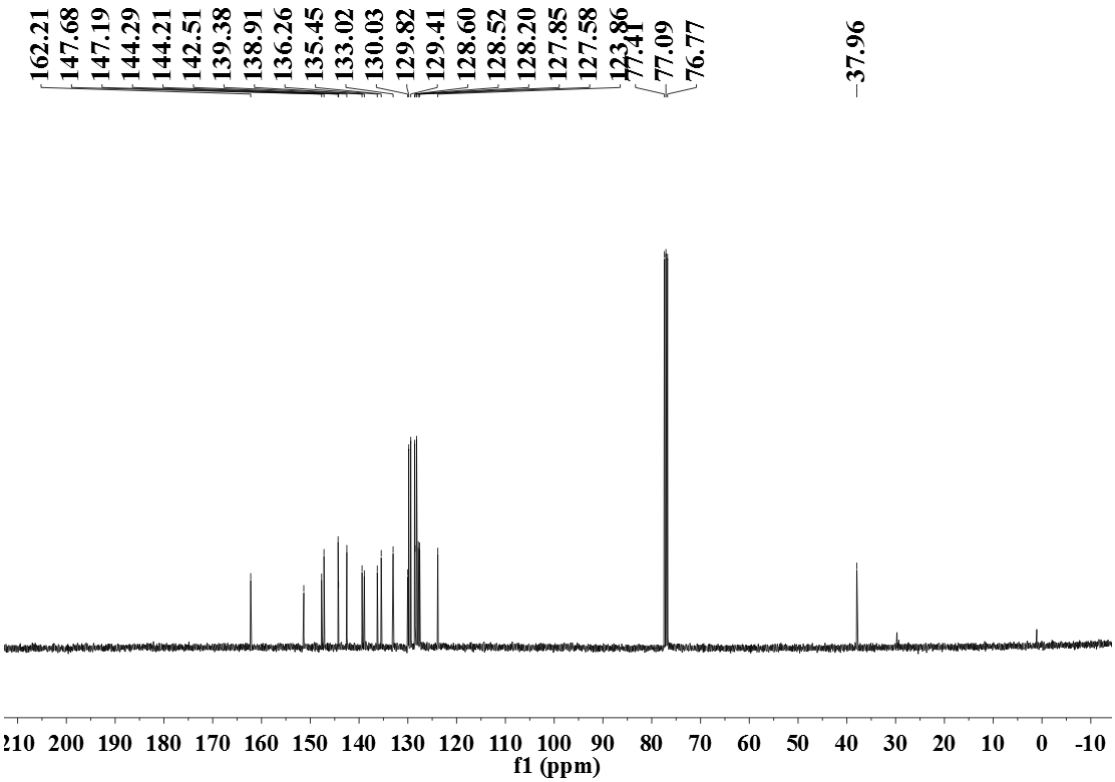

158.56 146.74 144.31 142.25 141.36 136.97 131.07 129.77 129.41 128.69 128.37 128.04 127.25 127.01 123.55
77.29 77.04 76.78 55.80 36.32
f1 (ppm)

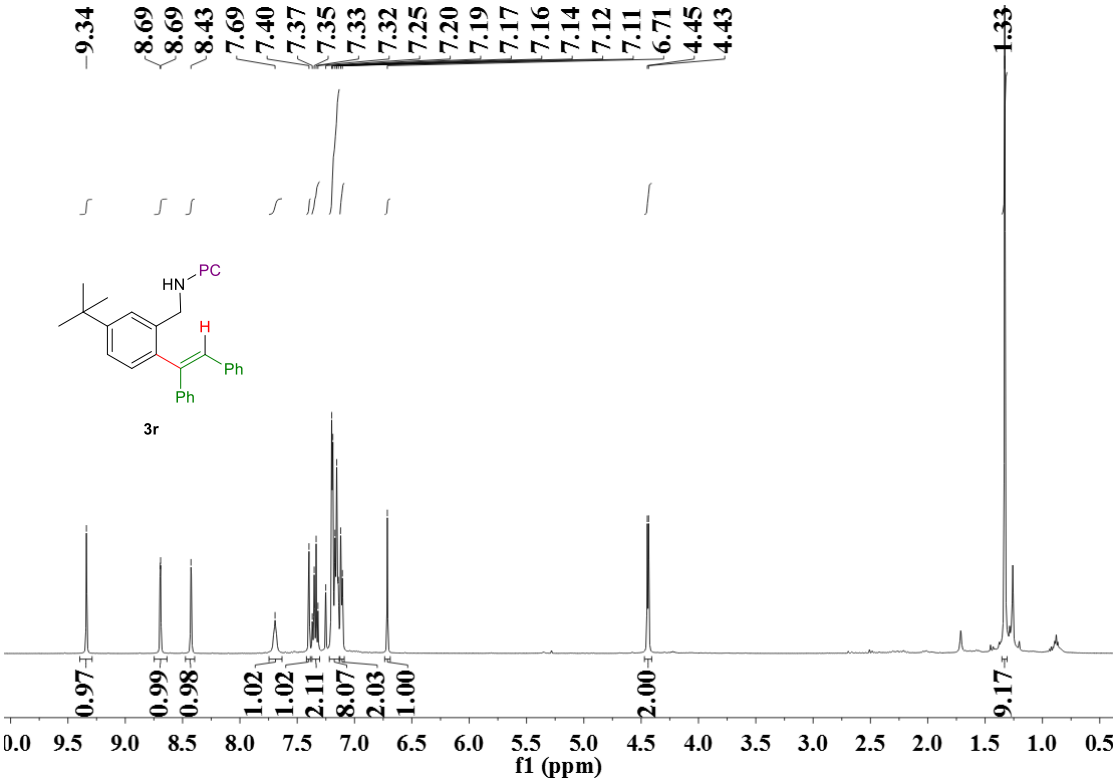

9.28
9.27
8.69
8.69
8.40
8.39
8.39
8.39
7.75
7.73
7.67
7.65
7.54
7.52
7.50
7.18
7.17
7.16
7.15
7.15
7.11
7.09
7.07
7.06
7.05
7.00
6.98
6.96
6.66
4.72
4.71
CF3 HN PC
H
Ph
Ph
3p
0.98
1.01
0.99
1.01
1.03
2.02
5.04
4.04
1.09
1.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

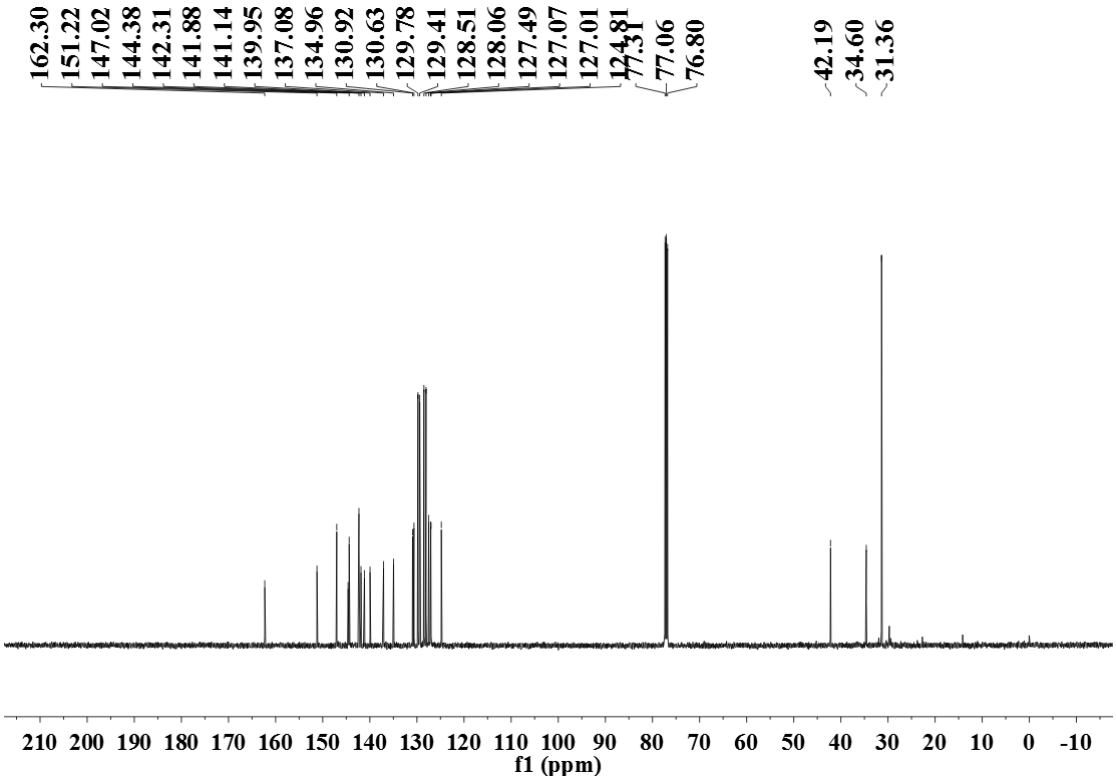

161.68
147.51
147.03
144.27
142.24
140.50
138.78
136.41
134.98
133.16
132.08
130.71
130.41
129.59
129.30
128.46
128.27
128.14
127.62
127.41
125.89
125.83
125.77
125.57
77.39
77.07
76.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

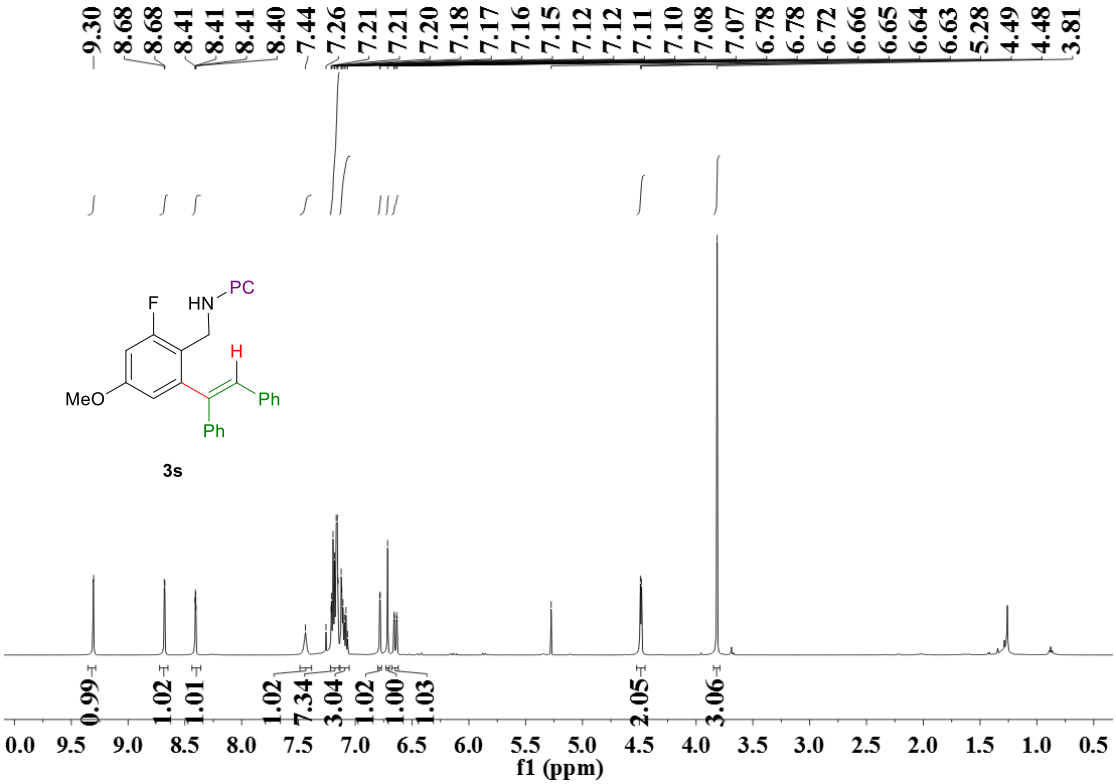

-58.66
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

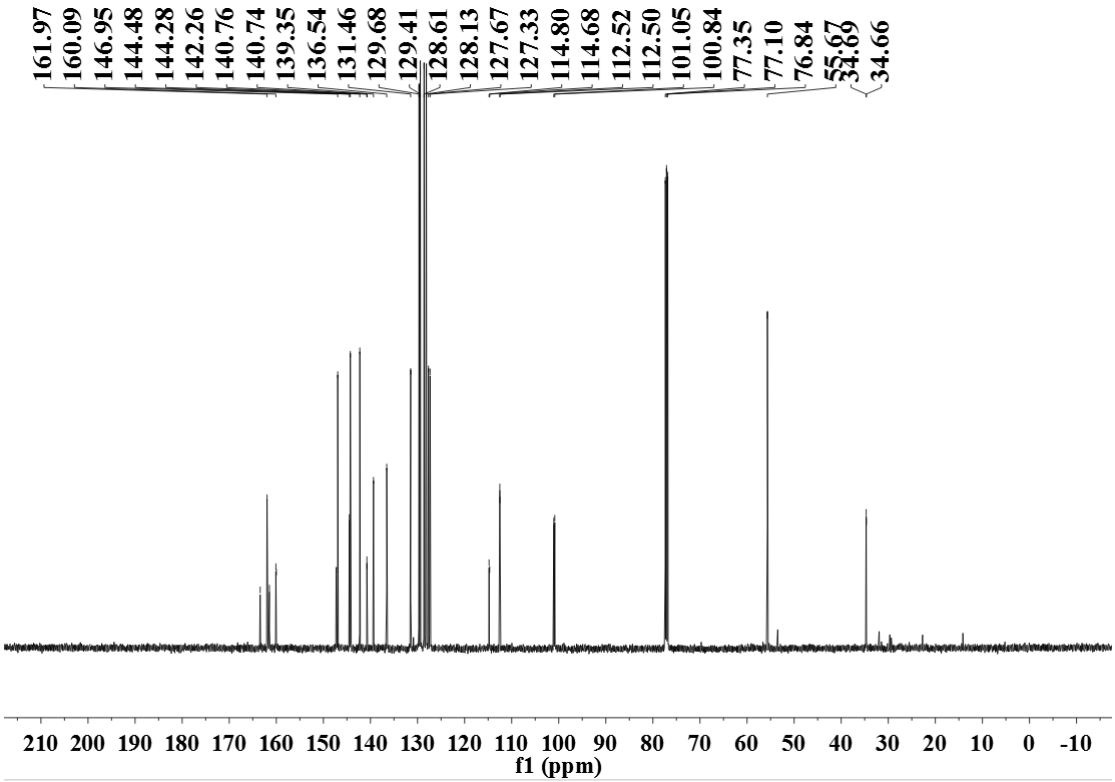

9.29
9.28
8.71
8.71
8.46
8.46
8.45
8.05
7.86
7.86
7.84
7.84
7.63
7.63
7.61
7.61
7.50
7.48
7.46
7.26
7.25
7.25
7.23
7.20
7.18
7.18
7.16
7.13
7.13
7.11
7.09
6.66
4.81
4.79
NO2 HN
PC
H
Ph
Ph
3q
0.98
0.99
0.99
0.98
1.00
1.01
1.02
2.03
5.02
2.98
1.00
2.01
f1 (ppm)

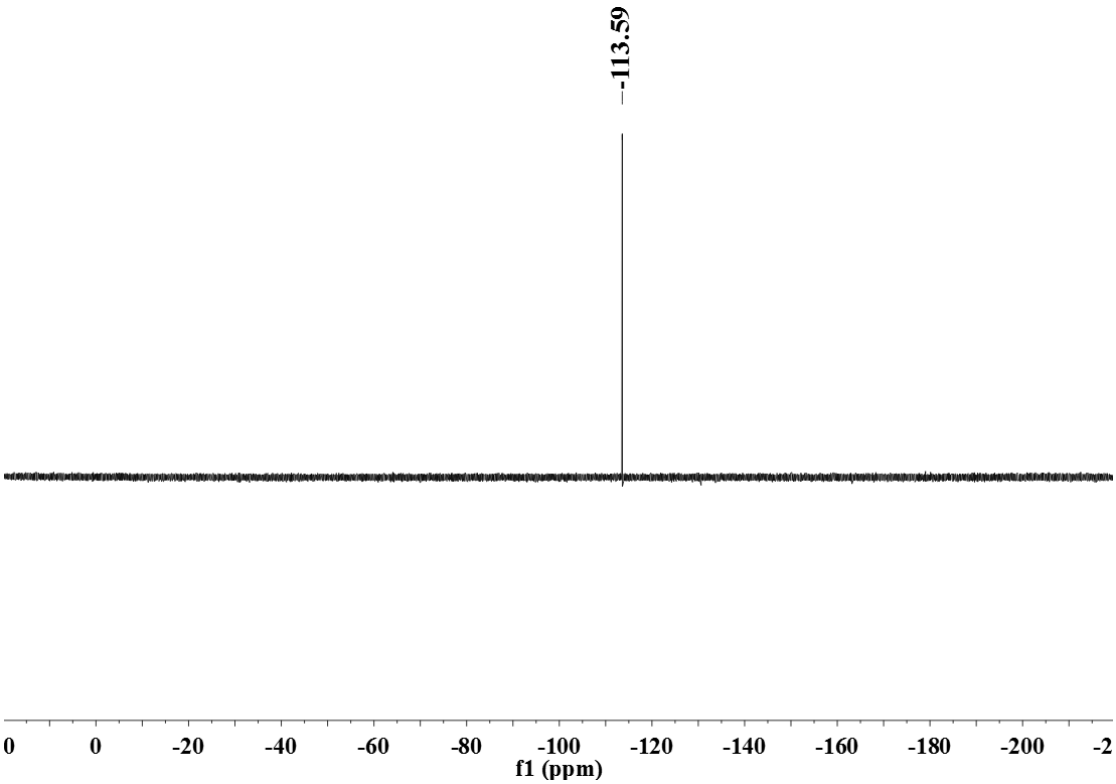

162.21
147.68
147.19
144.29
144.21
142.51
139.38
138.91
136.26
135.45
133.02
130.03
129.82
129.41
128.60
128.52
128.20
127.85
127.58
123.86
77.41
77.09
76.77
37.96
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

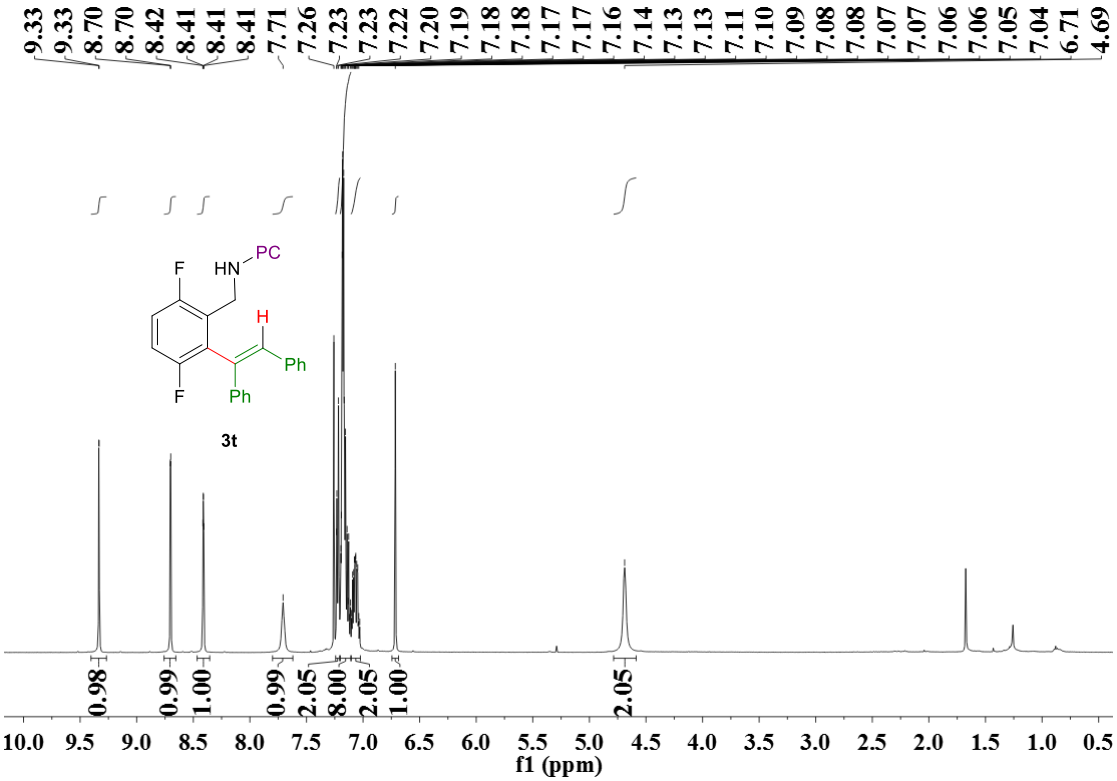

9.34
8.69
8.69
8.43
7.69
7.40
7.37
7.35
7.33
7.32
7.25
7.20
7.19
7.17
7.16
7.14
7.12
7.11
6.71
4.45
4.43
1.33
HN
PC
H
Ph
Ph
3r
0.97
0.99
0.98
1.02
1.02
2.11
8.07
2.03
1.00
2.00
9.17
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

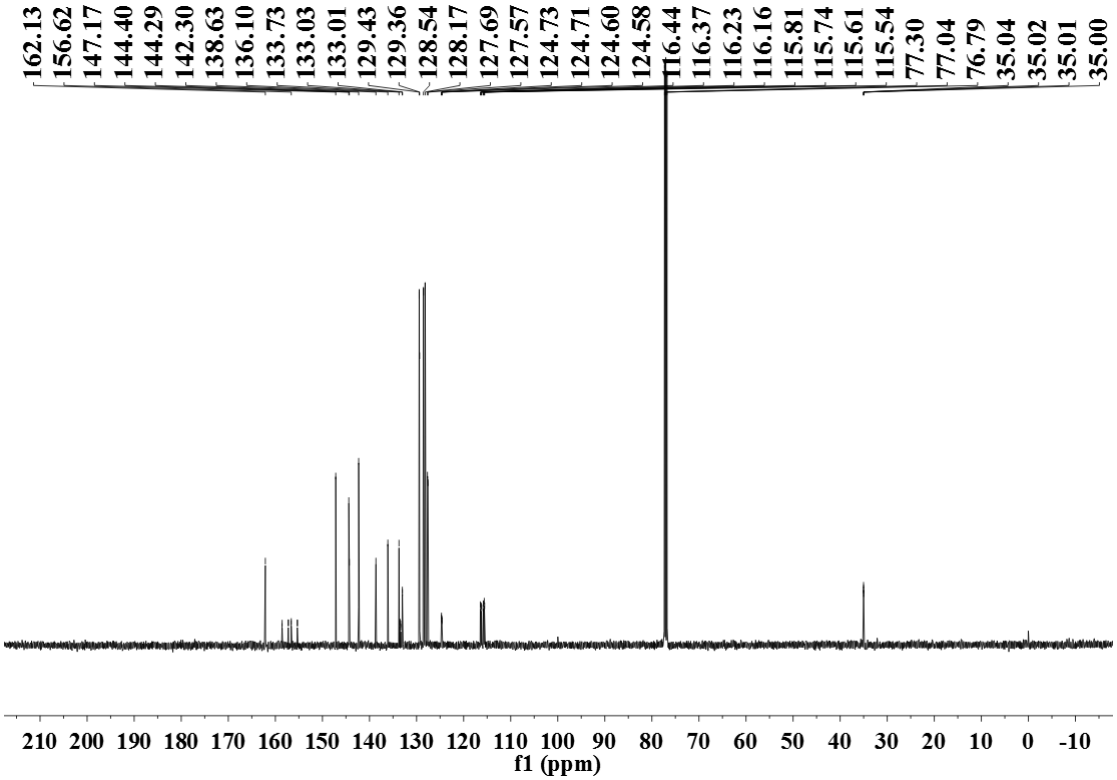

162.30
151.22
147.02
144.38
142.31
141.88
141.14
139.95
137.08
134.96
130.92
130.63
129.78
129.41
128.51
128.06
127.49
127.07
127.01
124.81
77.31
77.06
76.80
42.19
34.60
31.36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

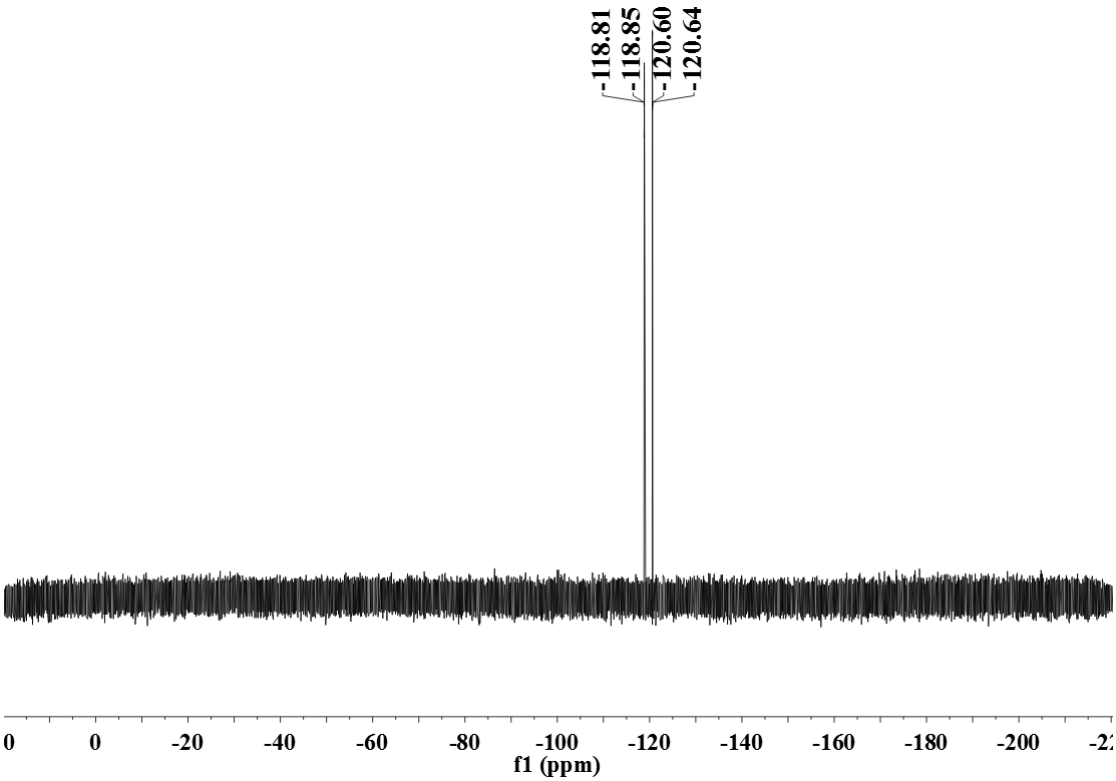

9.30
8.68
8.68
8.41
8.41
8.41
8.40
7.44
7.26
7.21
7.21
7.20
7.18
7.17
7.16
7.15
7.12
7.12
7.11
7.10
7.08
7.07
6.78
6.78
6.72
6.66
6.65
6.64
6.63
5.28
4.49
4.48
3.81
F
HN
PC
H
MeO
Ph
Ph
3s
0.99
1.02
1.01
1.02
7.34
3.04
1.02
1.00
1.03
2.05
3.06
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

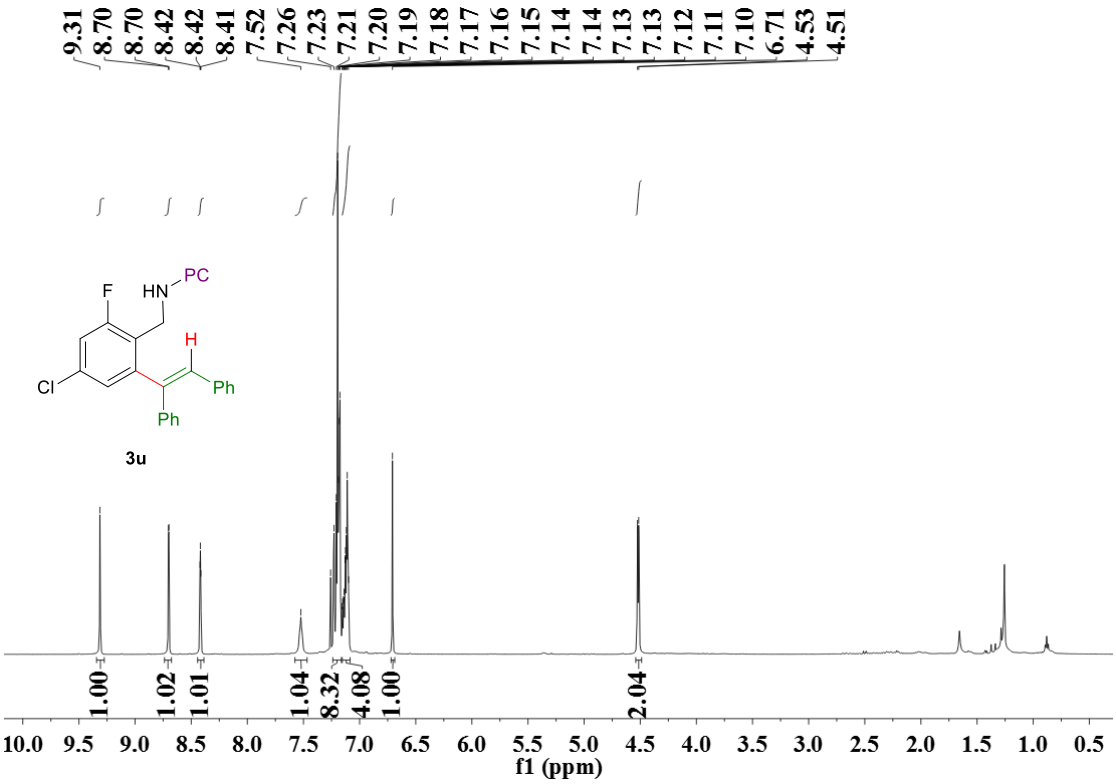

161.97
160.09
146.95
144.48
144.28
142.26
140.76
140.74
139.35
136.54
131.46
129.68
129.41
128.61
128.13
127.67
127.33
114.80
114.68
112.52
112.50
101.05
100.84
77.35
77.10
76.84
55.67
34.69
34.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

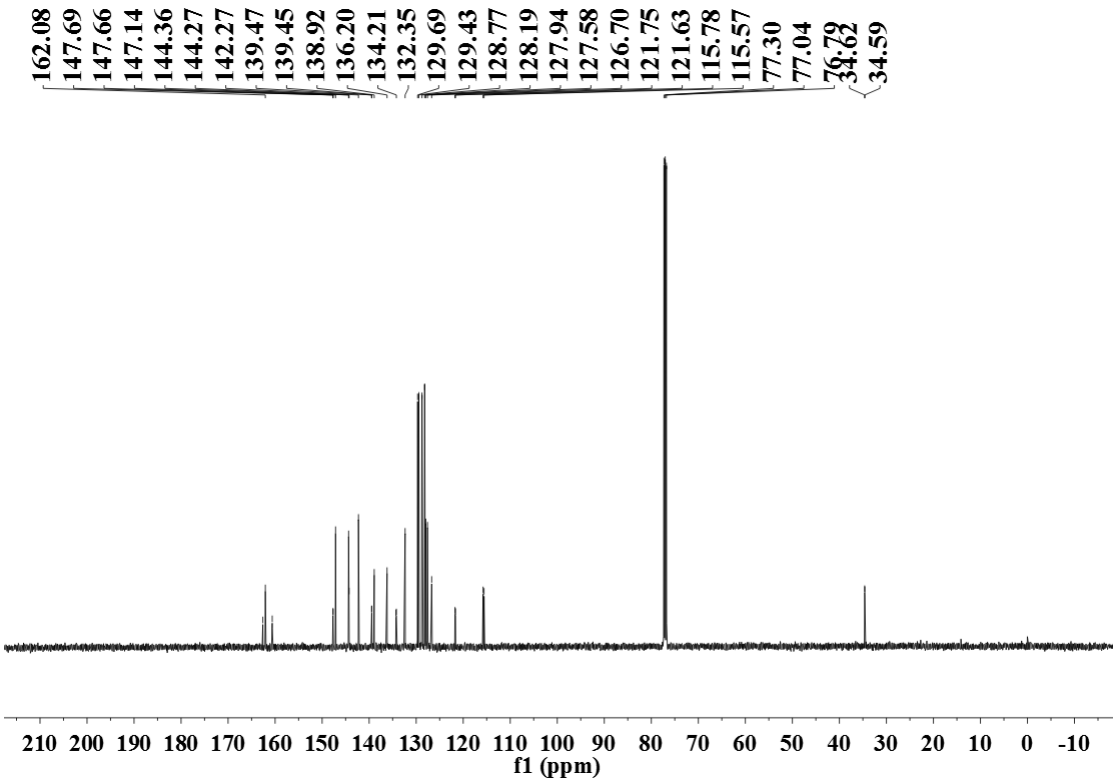

-113.59
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

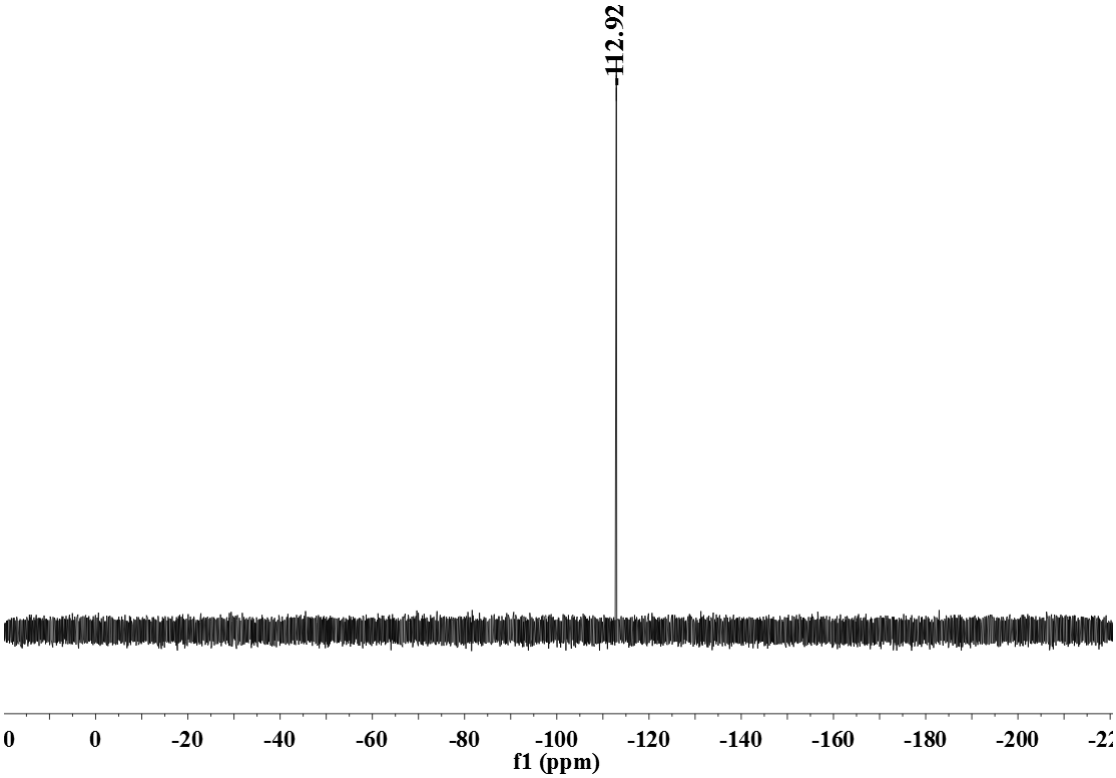

9.33 9.33 8.70 8.70 8.42 8.41 8.41 8.41 7.71 7.26 7.23 7.23 7.22 7.20 7.19 7.18 7.18 7.17 7.17 7.16 7.14 7.13 7.13 7.11 7.10 7.09 7.08 7.08 7.07 7.07 7.06 7.06 7.05 7.04 6.71 4.69
F
HN
PC
H
Ph
F
Ph
3t
0.98 0.99 1.00 0.99 2.05 8.00 2.05 1.00 2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

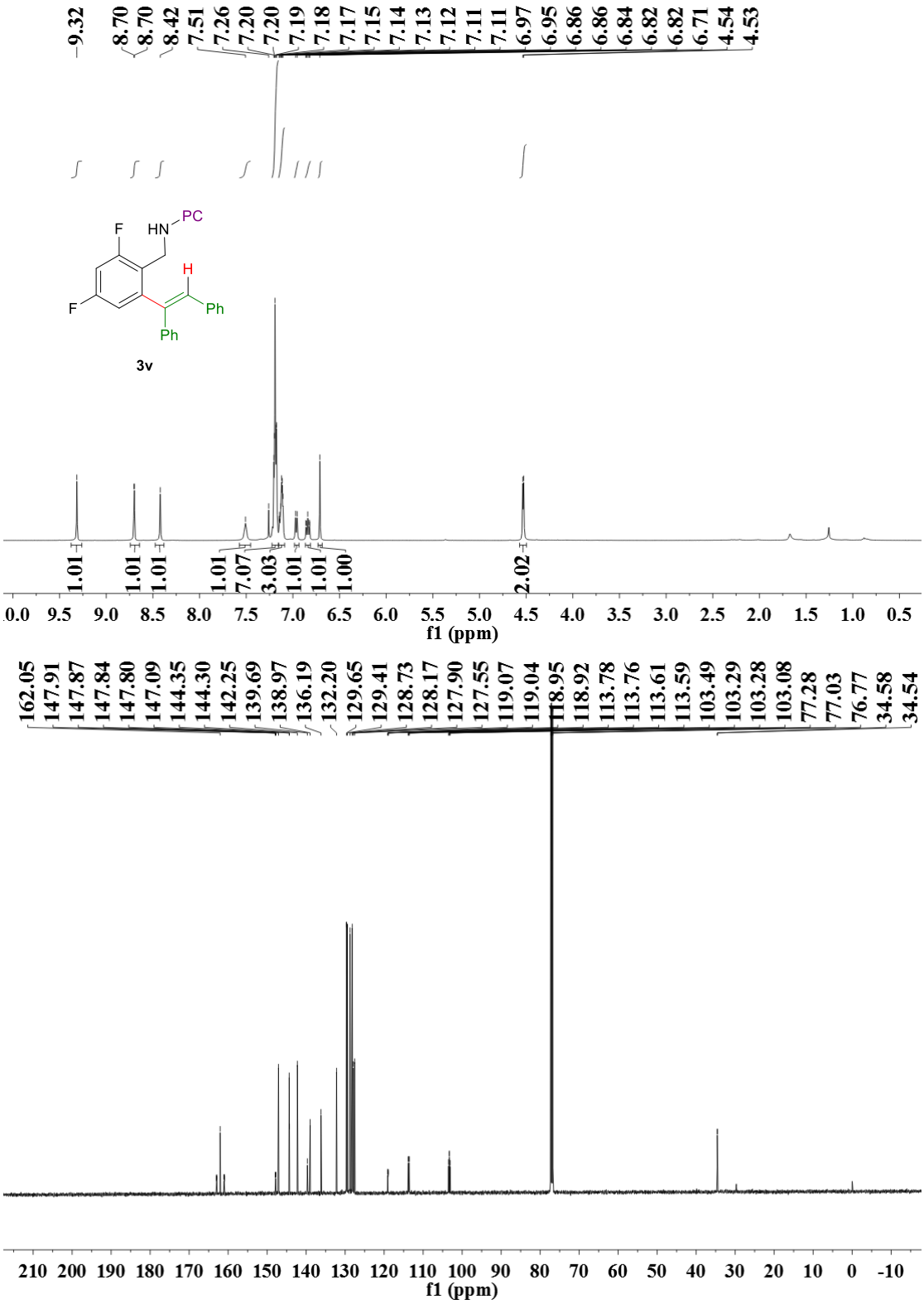

162.13 156.62 147.17 144.40 144.29 142.30 138.63 136.10 133.73 133.03 133.01 129.43 129.36 128.54 128.17 127.69 127.57 124.73 124.71 124.60 124.58 116.44 116.37 116.23 116.16 115.81 115.74 115.61 115.54 77.30 77.04 76.79 35.04 35.02 35.01 35.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

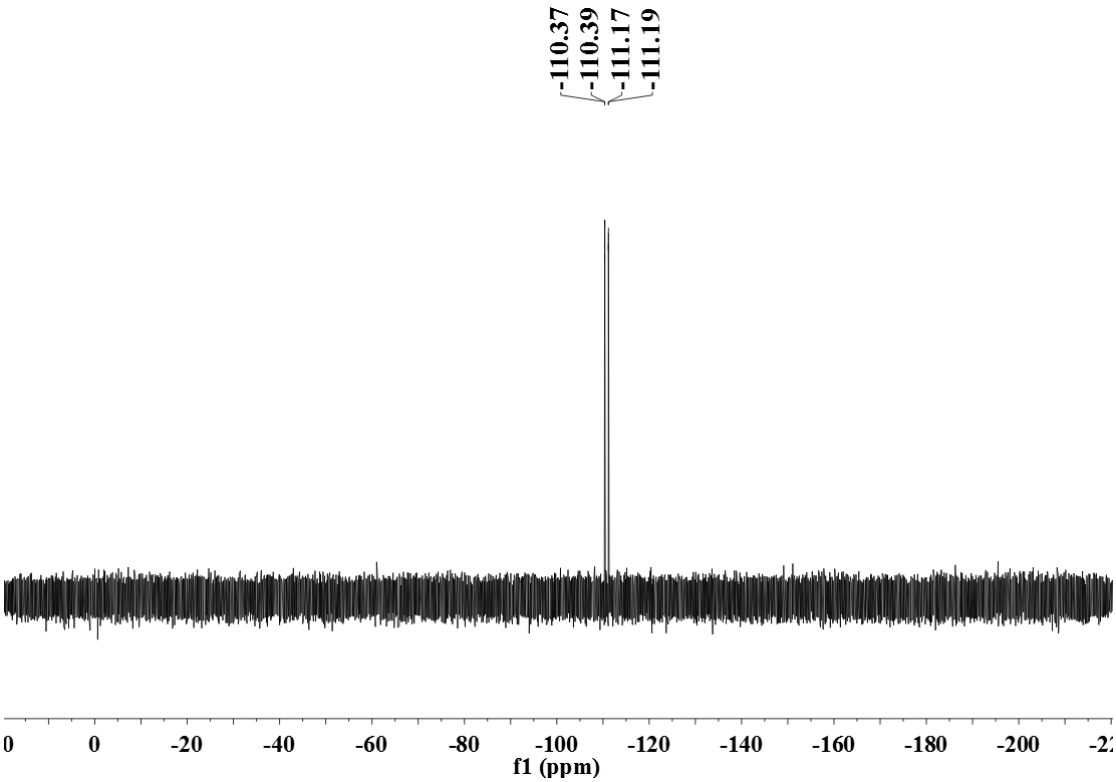

-118.81
-118.85
-120.60
-120.64
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

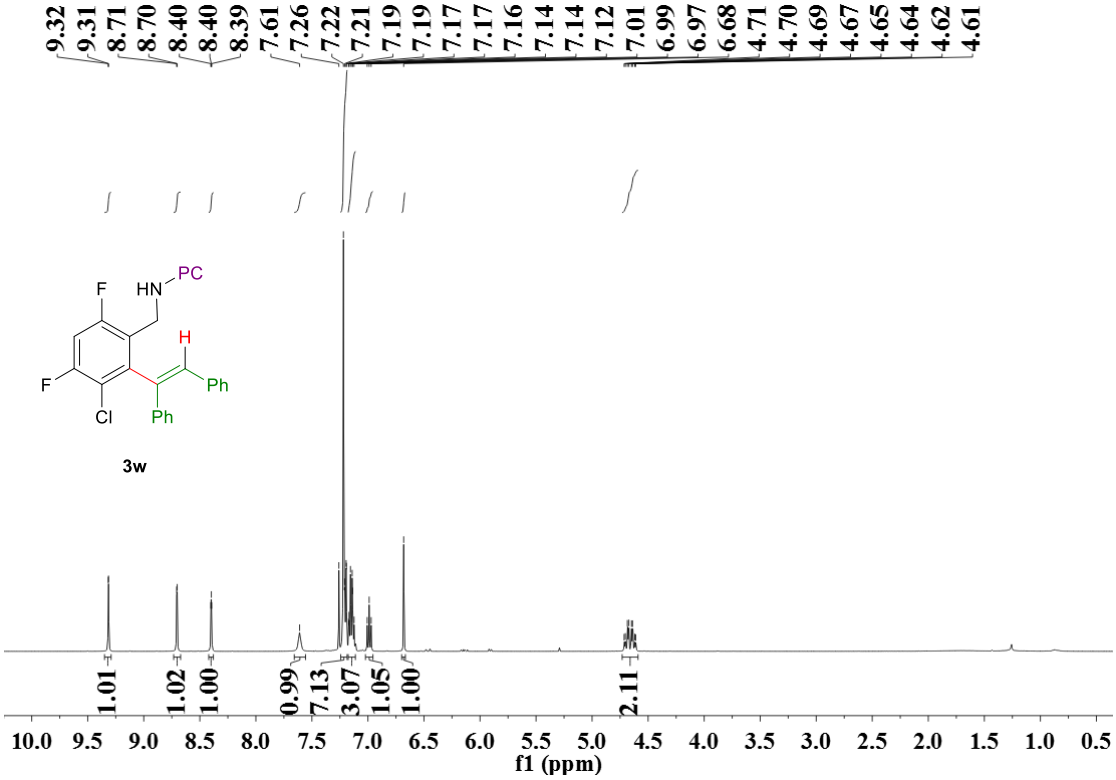

9.31
8.70
8.70
8.42
8.42
8.41
7.52
7.26
7.23
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.11
7.10
6.71
4.53
4.51
F
HN
PC
H
Cl
Ph
Ph
3u
1.00
1.02
1.01
1.04
8.32
4.08
1.00
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

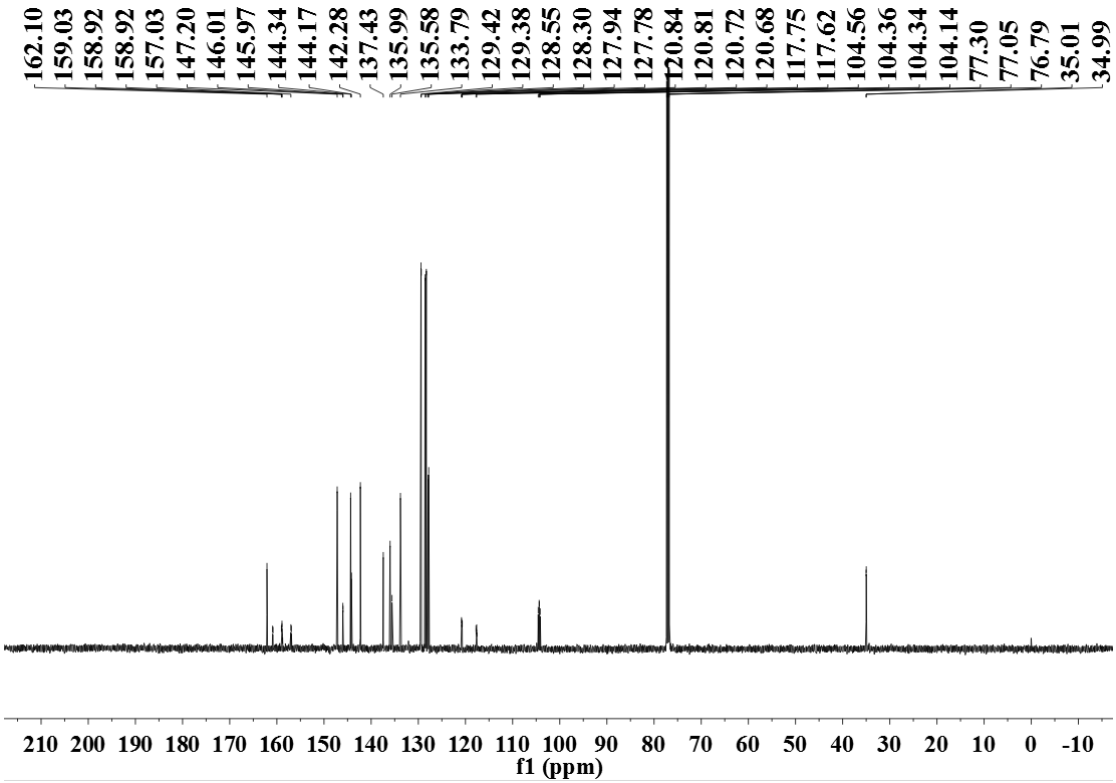

162.08
147.69
147.66
147.14
144.36
144.27
142.27
139.47
139.45
138.92
136.20
134.21
132.35
129.69
129.43
128.77
128.19
127.94
127.58
126.70
121.75
121.63
115.78
115.57
77.30
77.04
76.79
34.62
34.59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

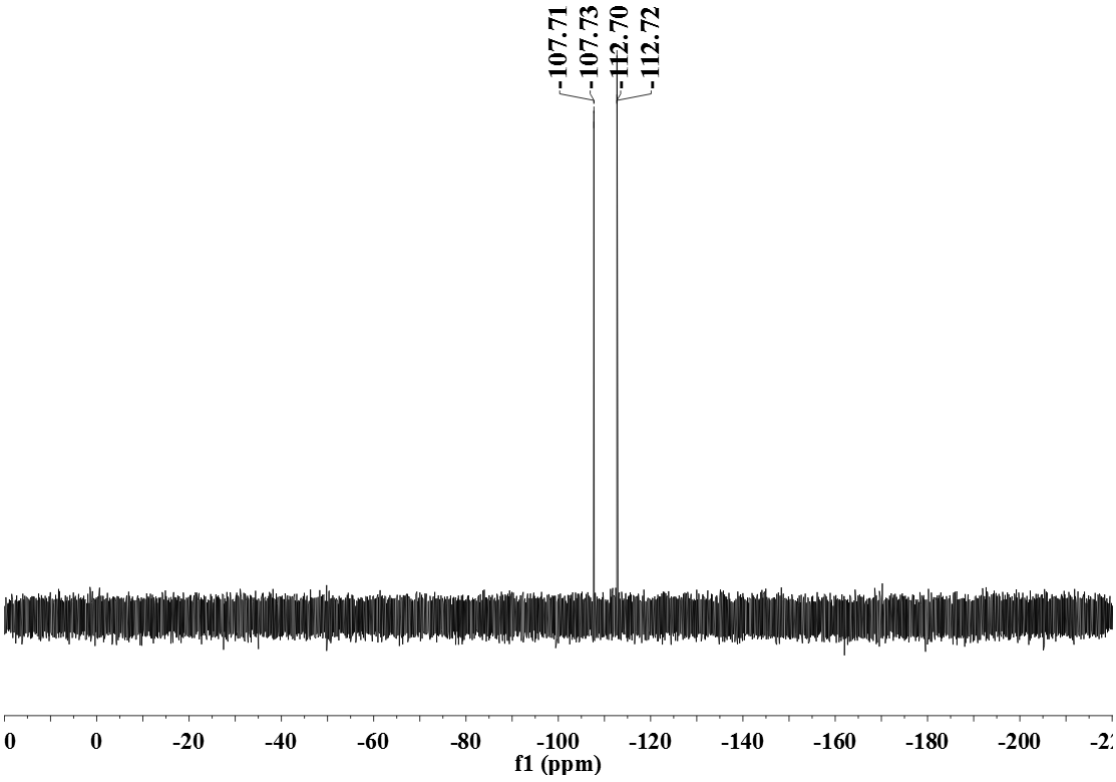

-112.92
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -22
f1 (ppm)

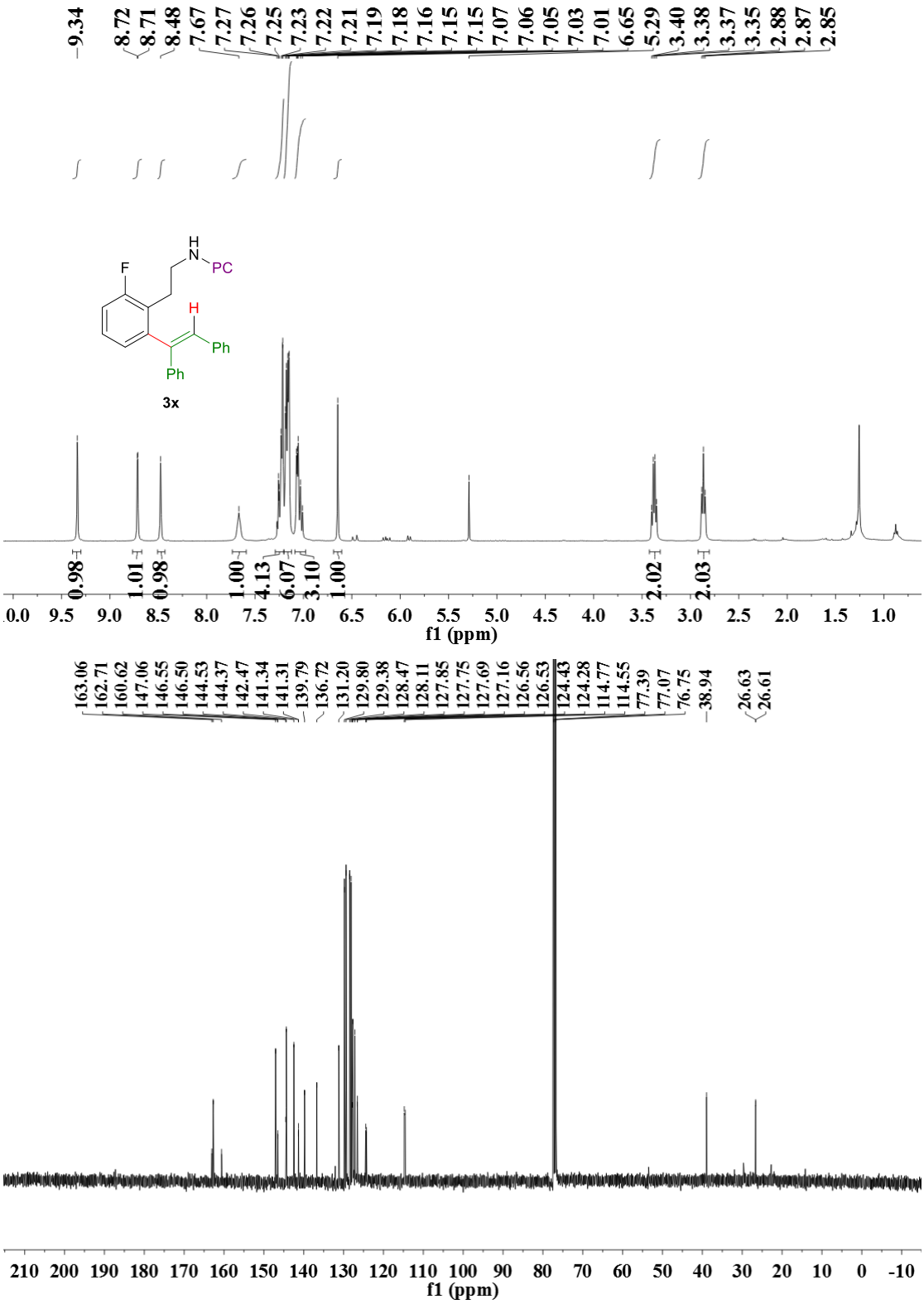

9.32
8.70
8.70
8.42
7.51
7.26
7.20
7.20
7.19
7.18
7.17
7.15
7.14
7.13
7.12
7.11
7.11
6.97
6.95
6.86
6.86
6.84
6.82
6.82
6.71
4.54
4.53
F
HN
PC
H
F
Ph
Ph
3v
1.01
1.01
1.01
1.01
7.07
3.03
1.01
1.01
1.00
2.02
f1 (ppm)
162.05
147.91
147.87
147.84
147.80
147.09
144.35
144.30
142.25
139.69
138.97
136.19
132.20
129.65
129.41
128.73
128.17
127.90
127.55
119.07
119.04
118.95
118.92
113.78
113.76
113.61
113.59
103.49
103.29
103.28
103.08
77.28
77.03
76.77
34.58
34.54
f1 (ppm)

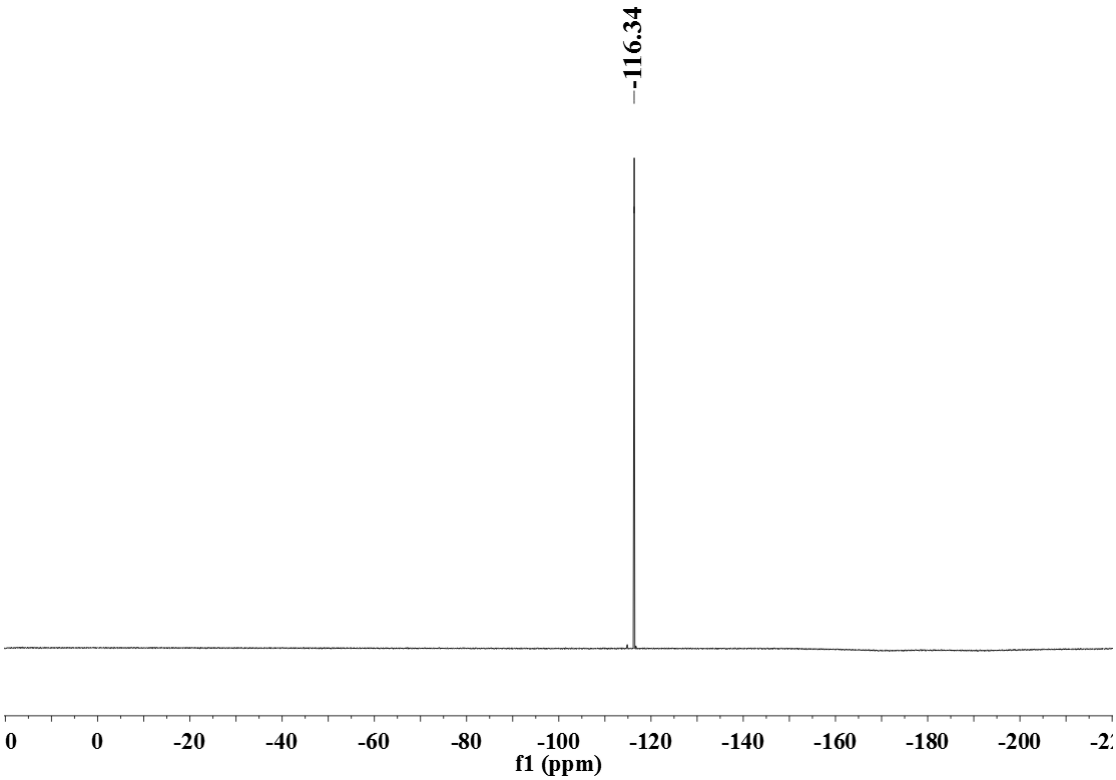

-110.37
-110.39
-111.17
-111.19
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

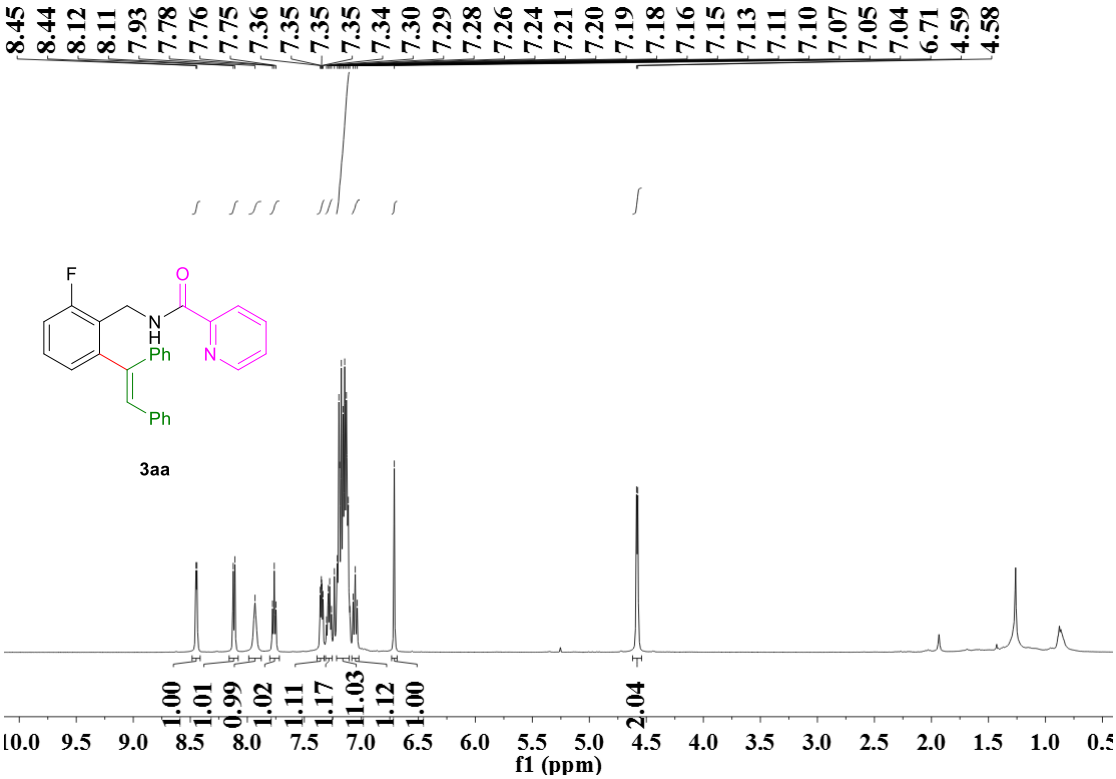

9.32
9.31
8.71
8.70
8.40
8.40
8.39
7.61
7.26
7.22
7.21
7.19
7.19
7.17
7.17
7.16
7.14
7.14
7.12
7.01
6.99
6.97
6.68
4.71
4.70
4.69
4.67
4.65
4.64
4.62
4.61
F
HN
PC
H
F
Ph
Cl
Ph
3w
1.01
1.02
1.00
0.99
7.13
3.07
1.05
1.00
2.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

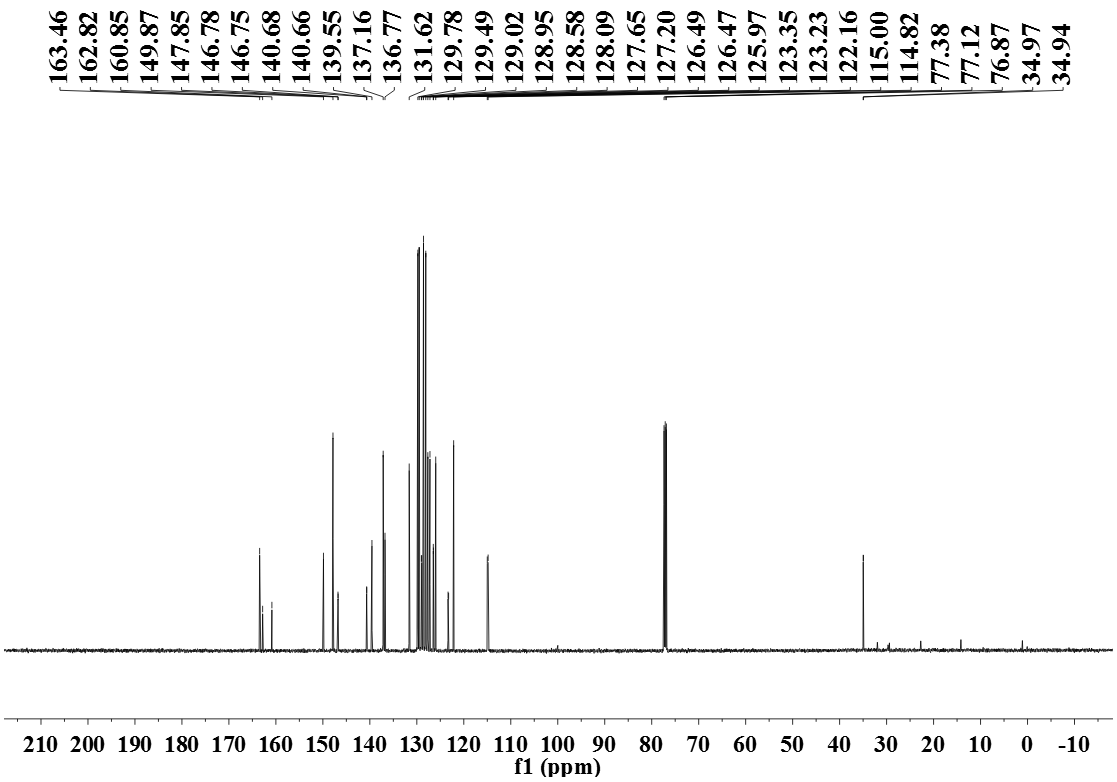

162.10
159.03
158.92
158.92
157.03
147.20
146.01
145.97
144.34
144.17
142.28
137.43
135.99
135.58
133.79
129.42
129.38
128.55
128.30
127.94
127.78
120.84
120.81
120.72
120.68
117.75
117.62
104.56
104.36
104.34
104.14
77.30
77.05
76.79
35.01
34.99
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

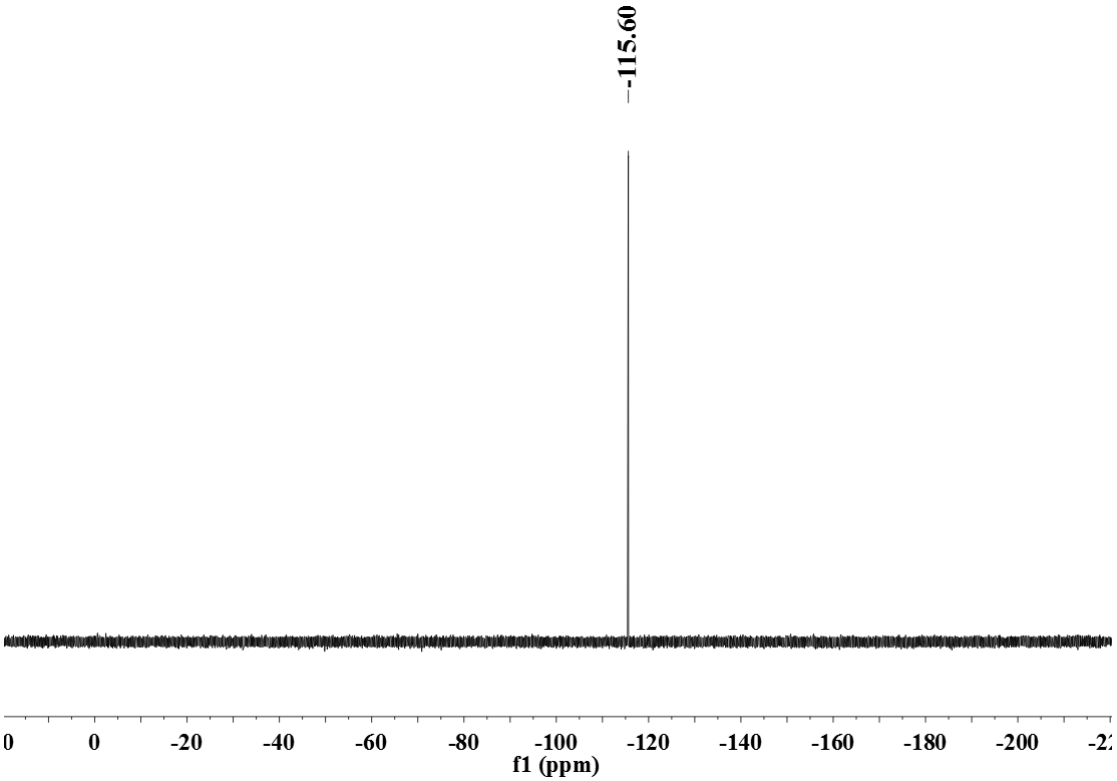

-107.71
-107.73
-112.70
-112.72
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

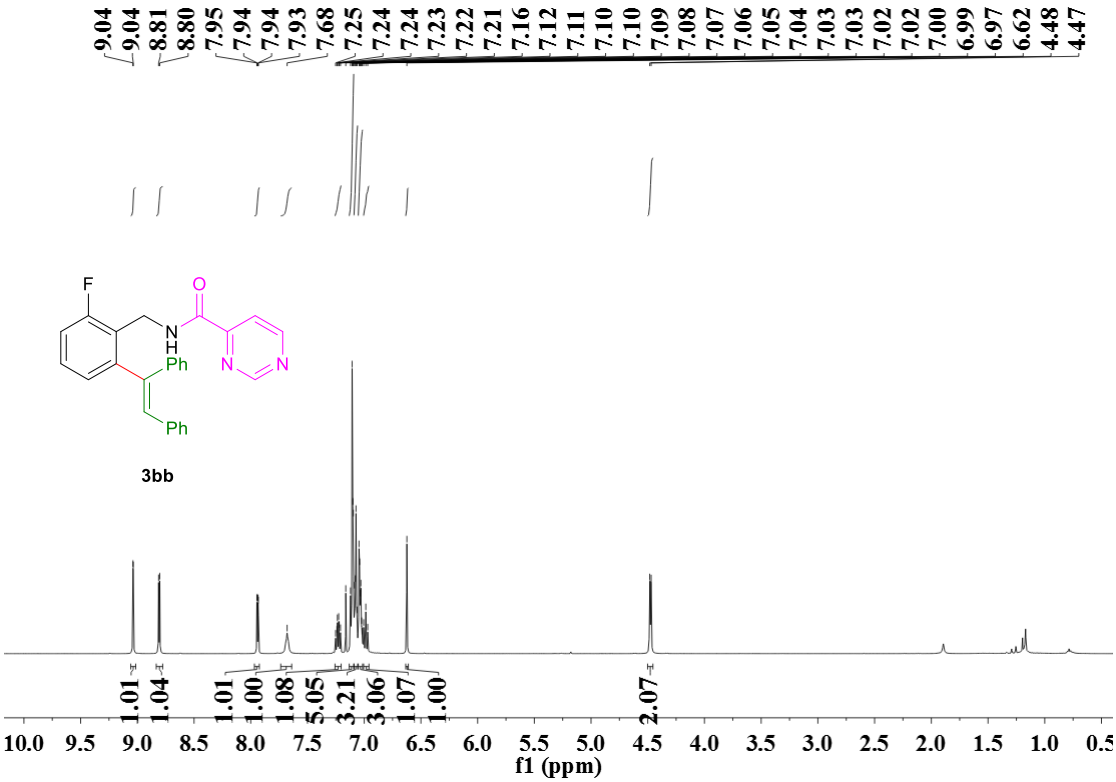

9.34
8.72
8.71
8.48
7.67
7.27
7.26
7.25
7.23
7.22
7.21
7.19
7.18
7.16
7.15
7.15
7.07
7.06
7.05
7.03
7.01
6.65
5.29
3.40
3.38
3.37
3.35
2.88
2.87
2.85
F
H
N
PC
H
Ph
Ph
3x
0.98
1.01
0.98
1.00
4.13
6.07
3.10
1.00
2.02
2.03
f1 (ppm)
163.06
162.71
160.62
147.06
146.55
146.50
144.53
144.37
142.47
141.34
141.31
139.79
136.72
131.20
129.80
129.38
128.47
128.11
127.85
127.75
127.69
127.16
126.56
126.53
124.43
124.28
114.77
114.55
77.39
77.07
76.75
38.94
26.63
26.61
f1 (ppm)

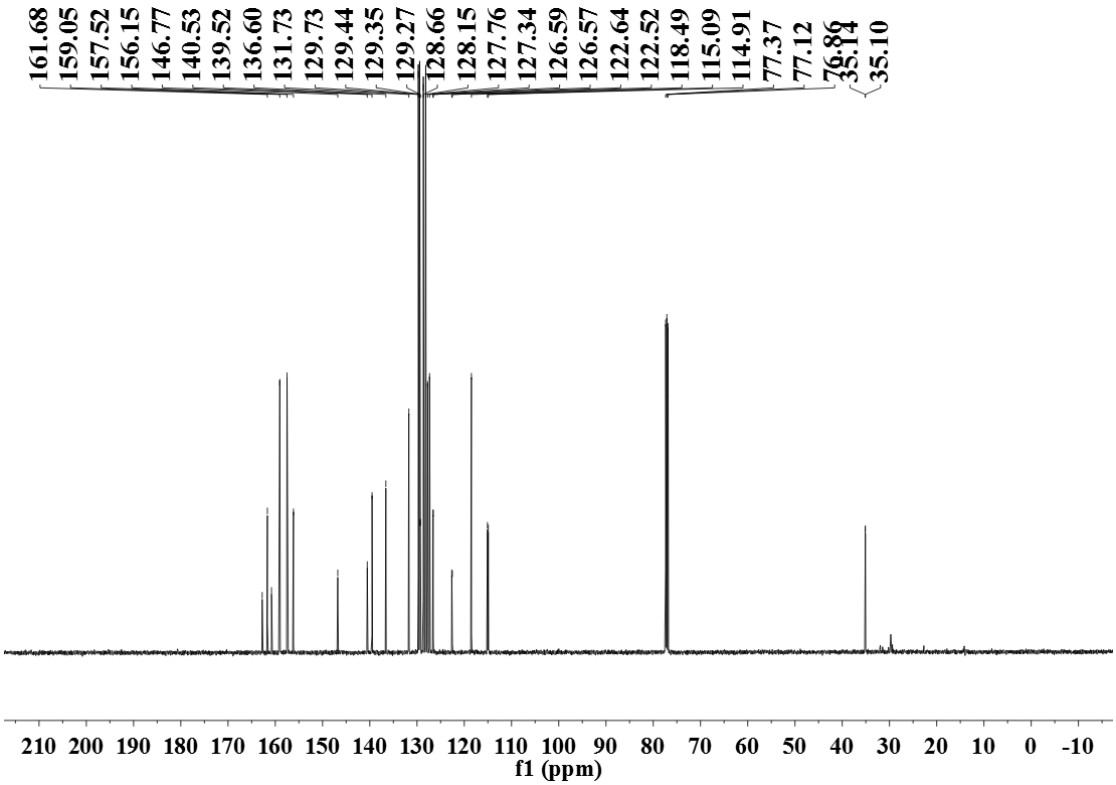

-116.34
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

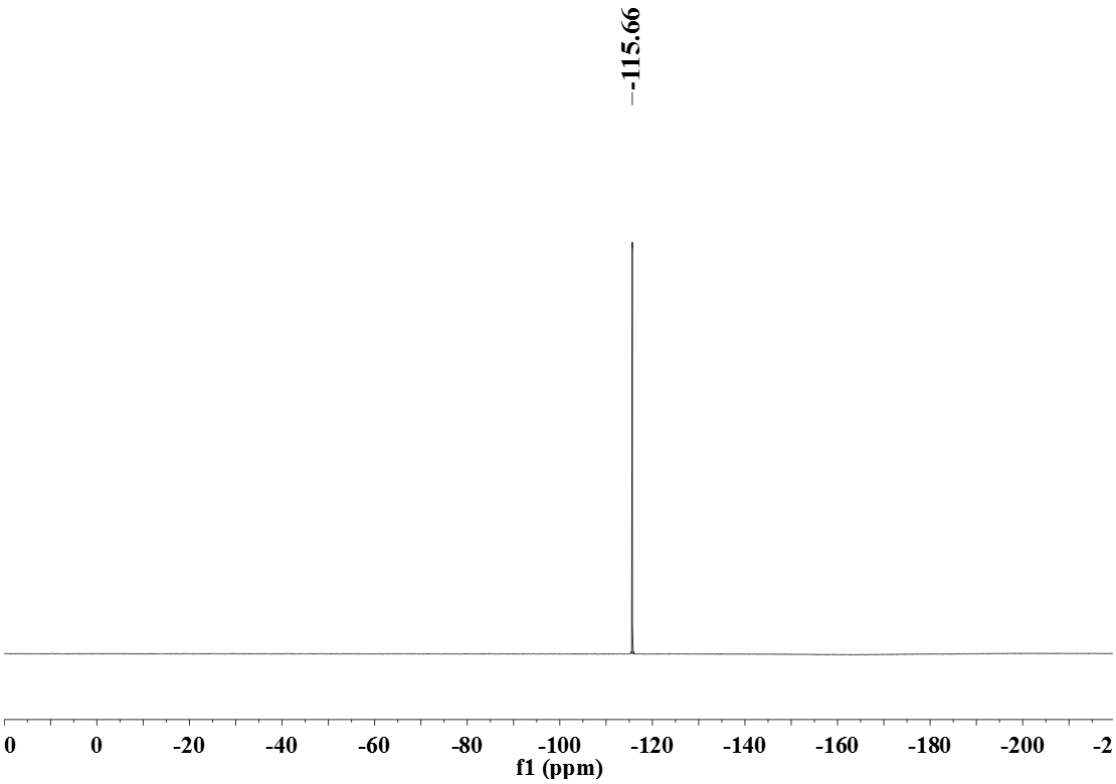

8.45
8.44
8.12
8.11
7.93
7.78
7.76
7.75
7.36
7.35
7.35
7.35
7.34
7.30
7.29
7.28
7.26
7.24
7.21
7.20
7.19
7.18
7.16
7.15
7.13
7.11
7.10
7.07
7.05
7.04
6.71
4.59
4.58
F
O
N
H
Ph
N
Ph
3aa
1.00
1.01
0.99
1.02
1.11
1.17
11.03
1.12
1.00
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

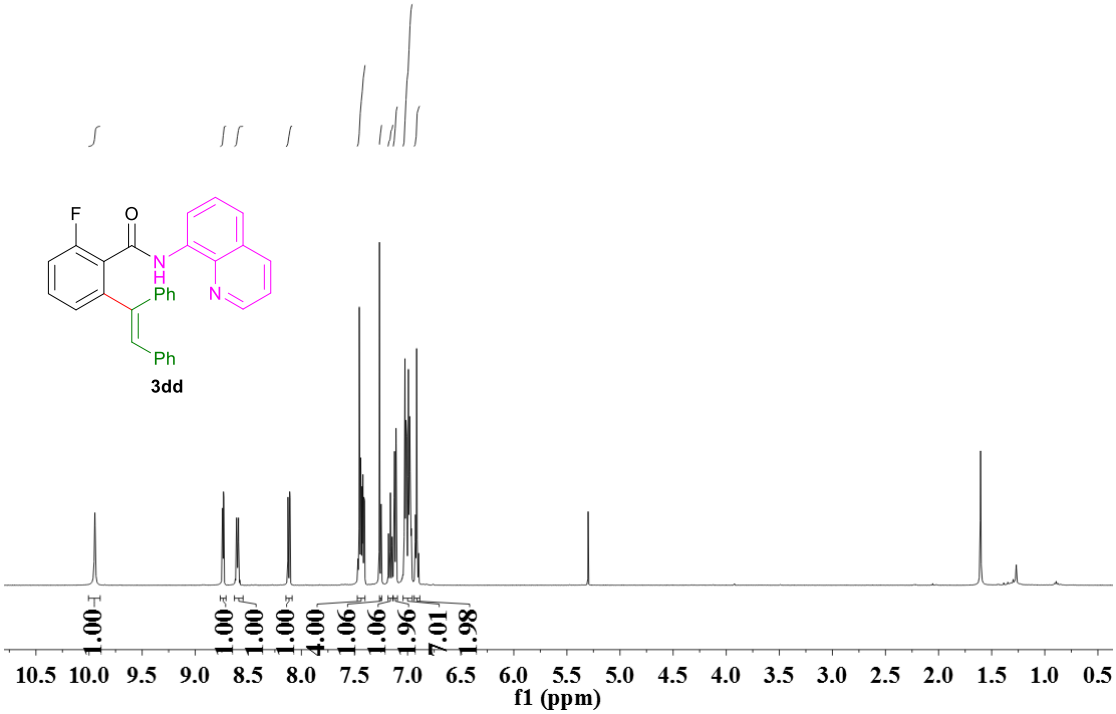

163.46
162.82
160.85
149.87
147.85
146.78
146.75
140.68
140.66
139.55
137.16
136.77
131.62
129.78
129.49
129.02
128.95
128.58
128.09
127.65
127.20
126.49
126.47
125.97
123.35
123.23
122.16
115.00
114.82
77.38
77.12
76.87
34.97
34.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

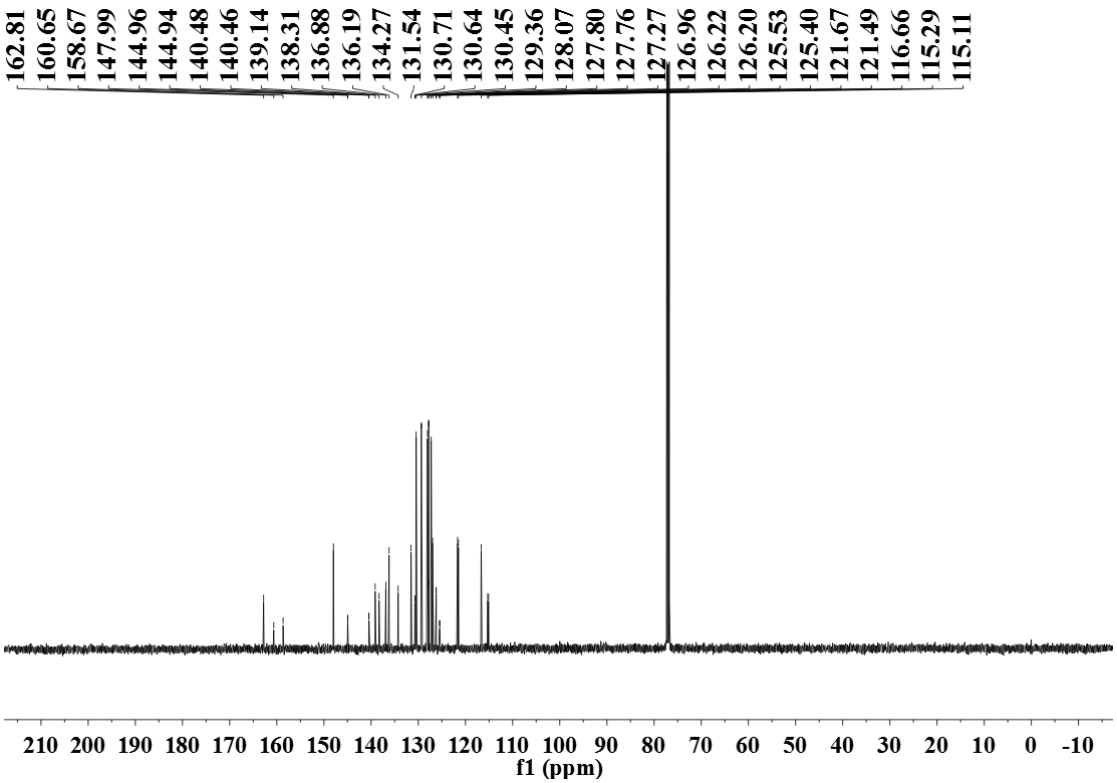

-115.60
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

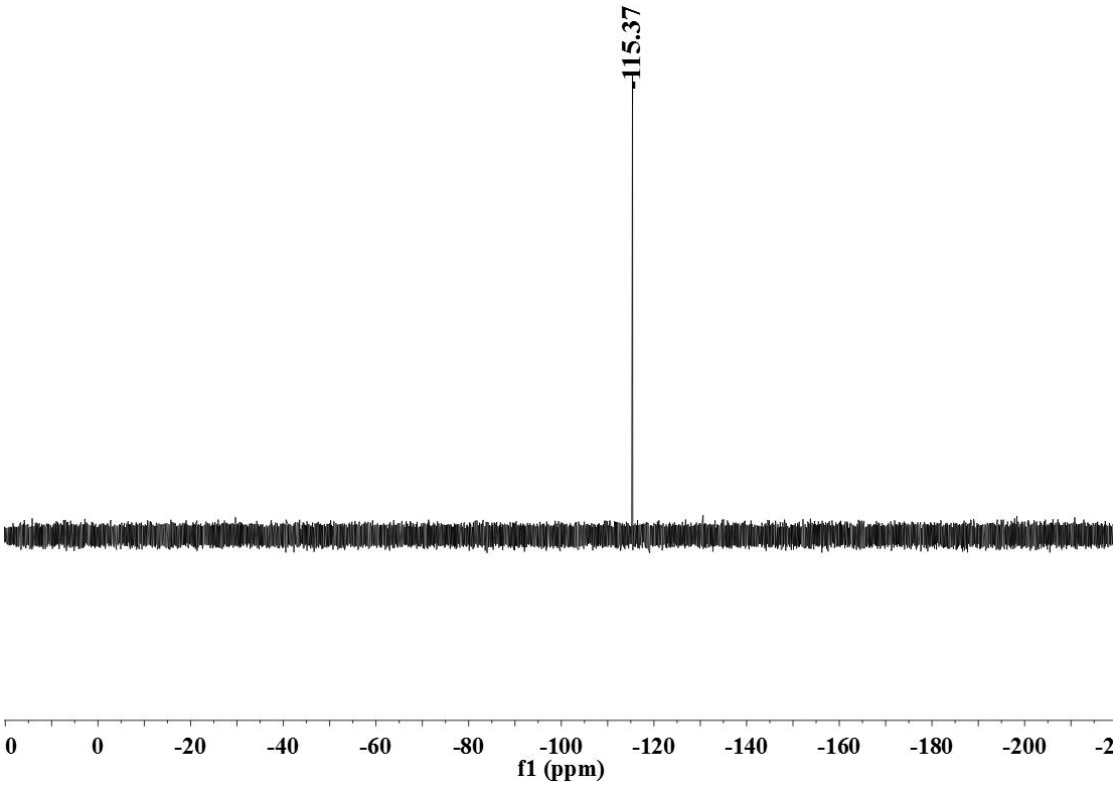

9.04 9.04 8.81 8.80 7.95 7.94 7.94 7.93 7.68 7.25 7.24 7.24 7.23 7.22 7.21 7.16 7.12 7.11 7.10 7.10 7.09 7.08 7.07 7.06 7.05 7.04 7.03 7.03 7.02 7.02 7.00 6.99 6.97 6.62 4.48 4.47
F
O
N
H
Ph
N
N
Ph
3bb
1.01 1.04 1.01 1.00 1.08 5.05 3.21 3.06 1.07 1.00 2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

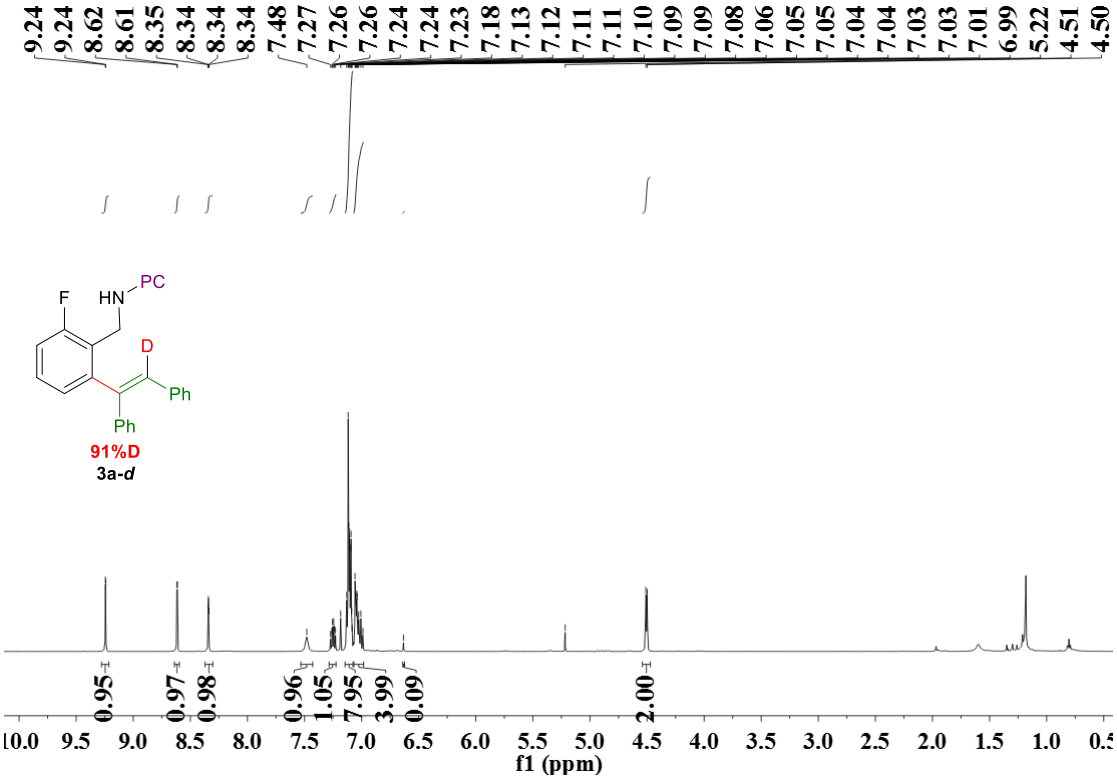

161.68 159.05 157.52 156.15 146.77 140.53 139.52 136.60 131.73 129.73 129.44 129.35 129.27 128.66 128.15 127.76 127.34 126.59 126.57 122.64 122.52 118.49 115.09 114.91 77.37 77.12 76.86 35.14 35.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-115.66
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-2
f1 (ppm)

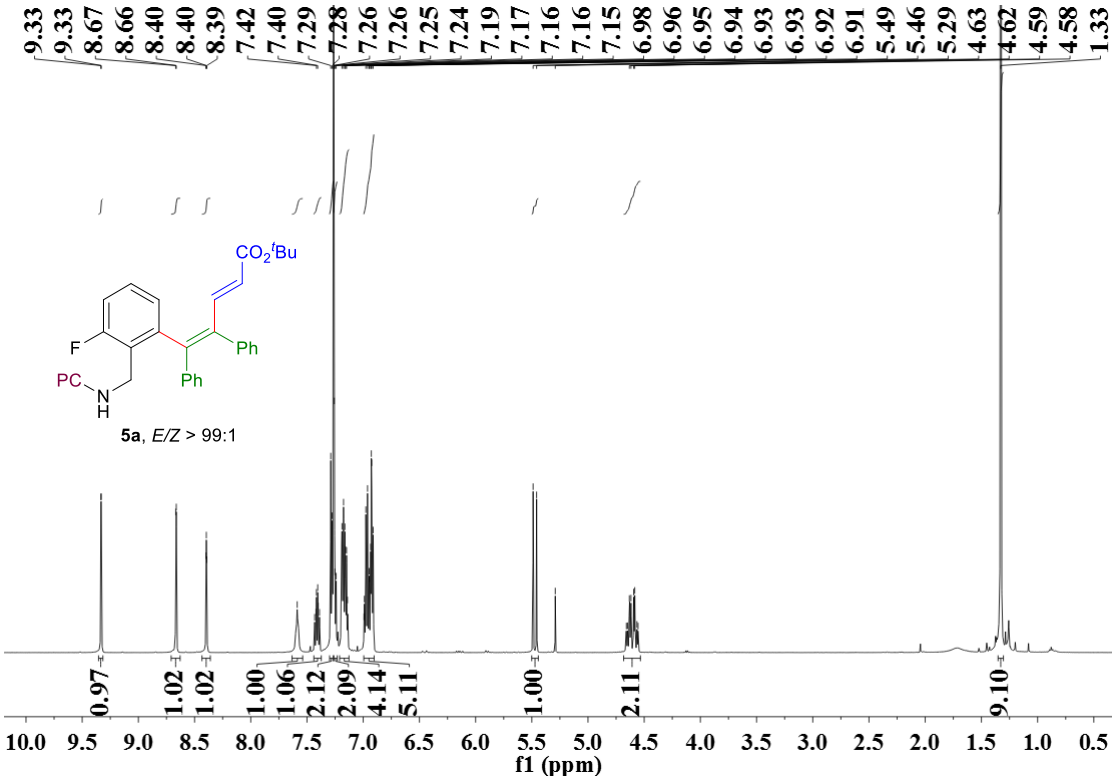

F
O
N
H
Ph
N
Ph
3dd
1.00
1.00
1.00
1.00
4.00
1.06
1.06
1.96
7.01
1.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

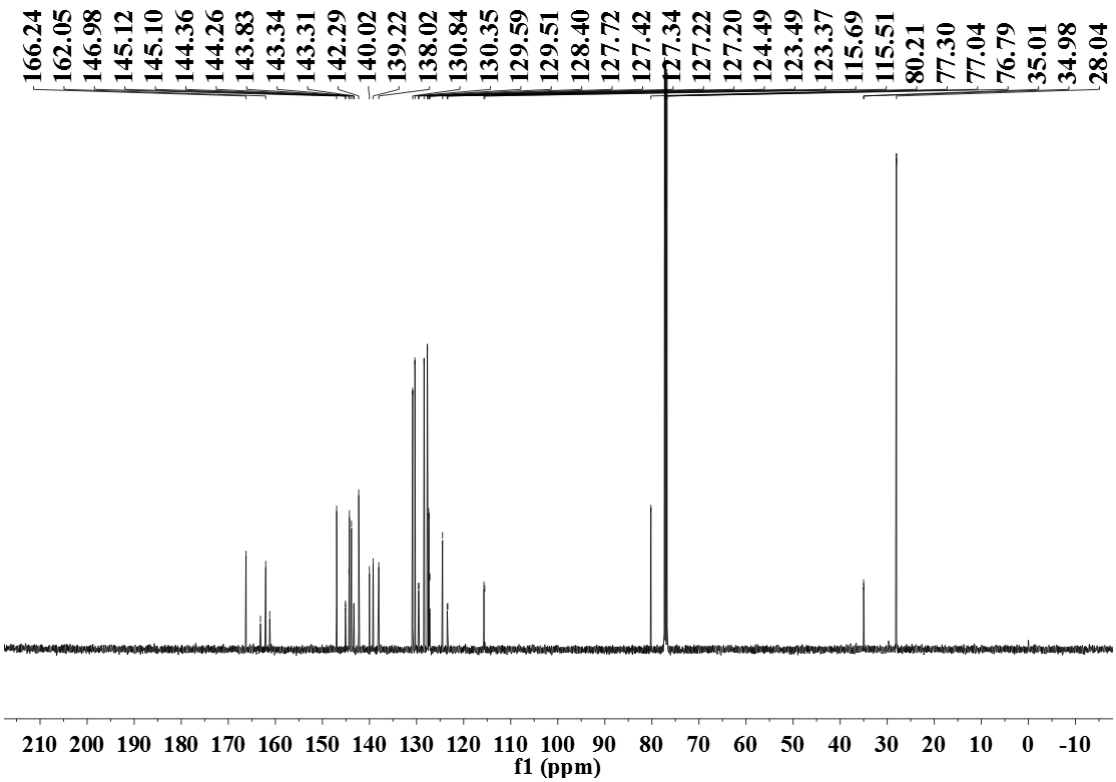

162.81
160.65
158.67
147.99
144.96
144.94
140.48
140.46
139.14
138.31
136.88
136.19
134.27
131.54
130.71
130.64
130.45
129.36
128.07
127.80
127.76
127.27
126.96
126.22
126.20
125.53
125.40
121.67
121.49
116.66
115.29
115.11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

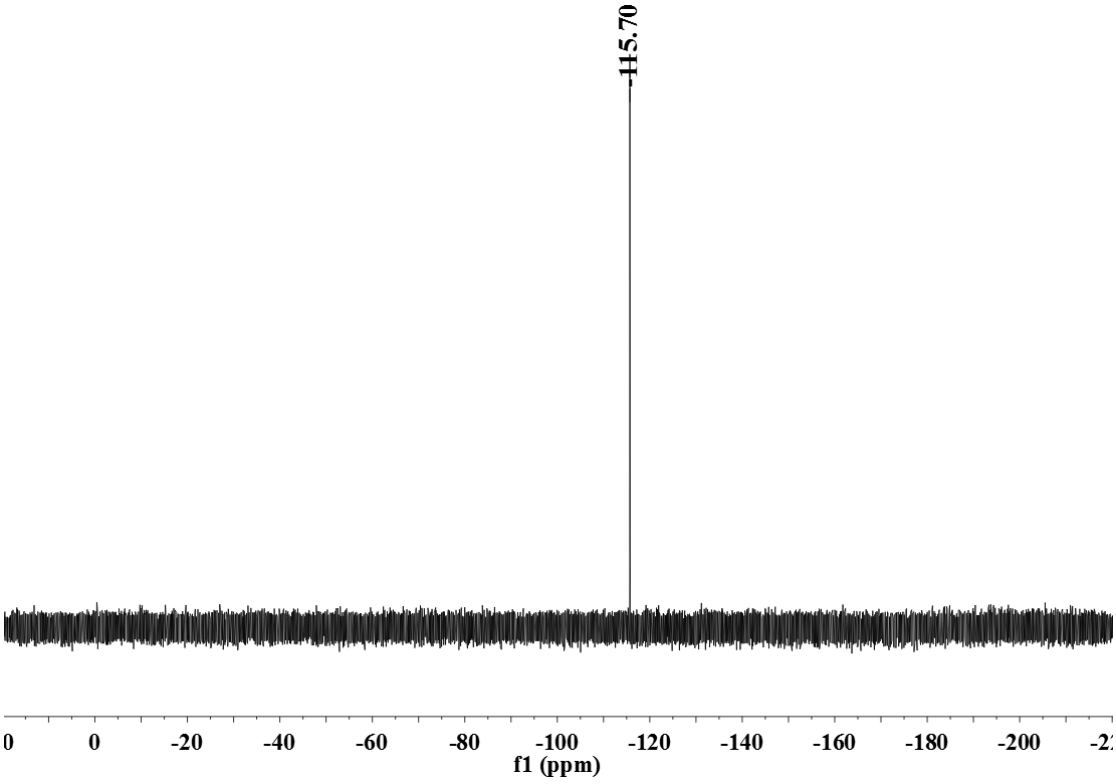

-115.37
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

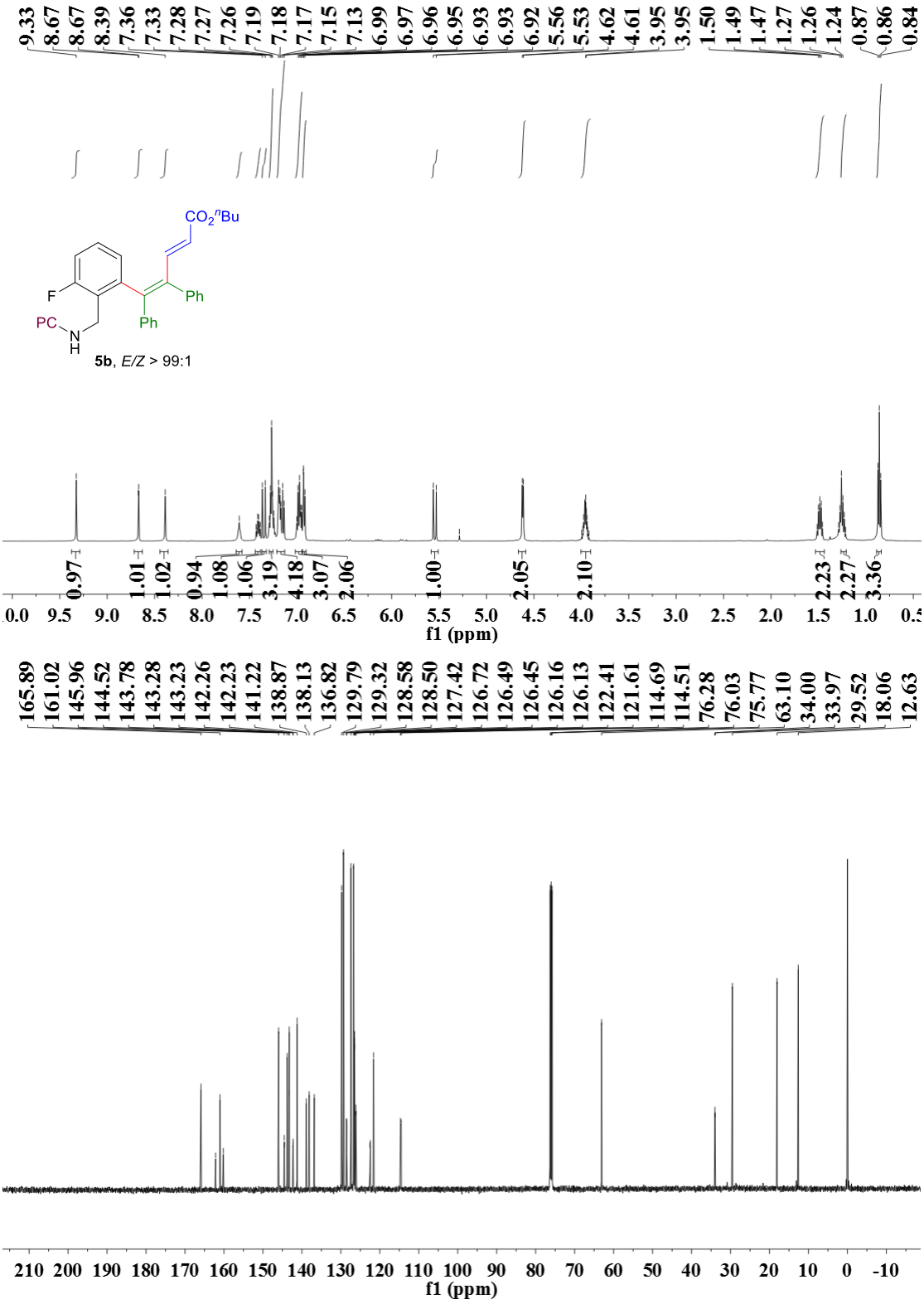


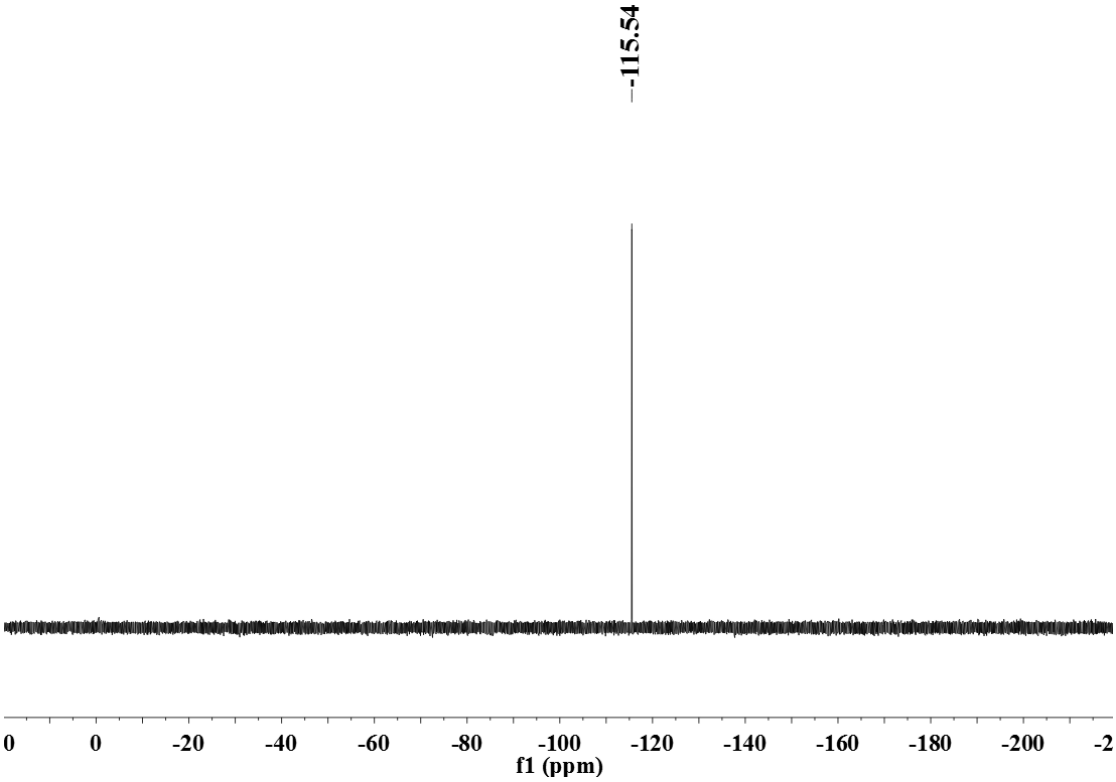
9.3 NMR Spectra of 5

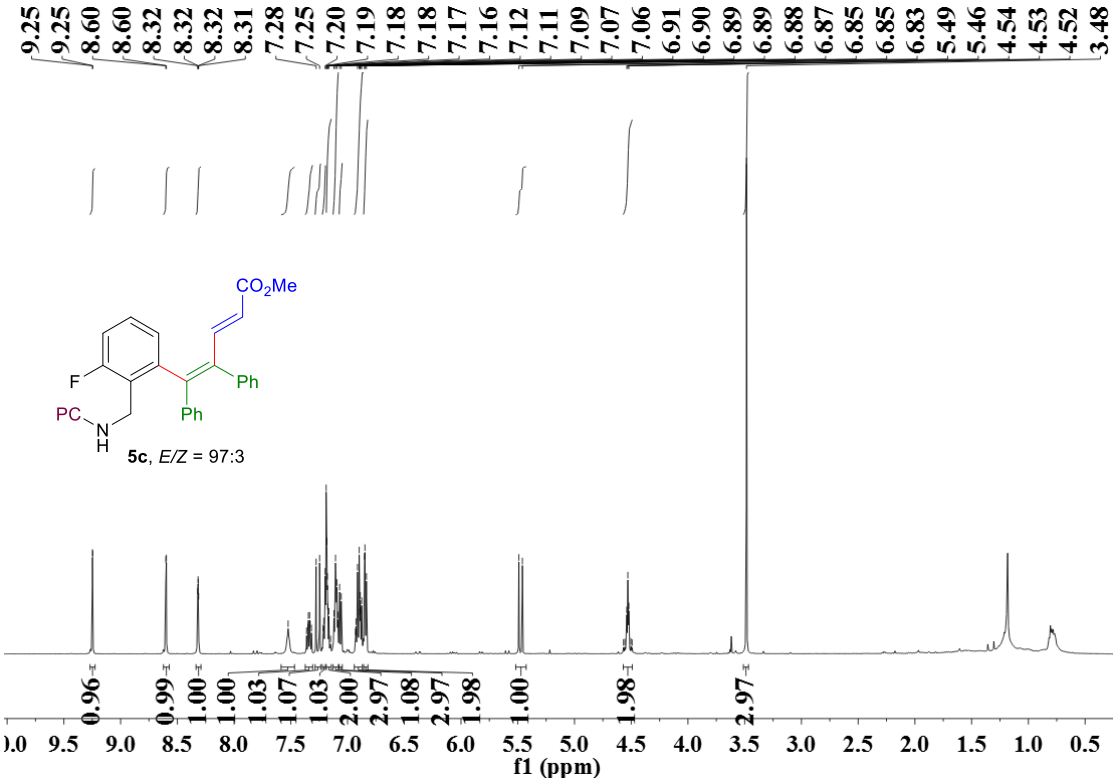


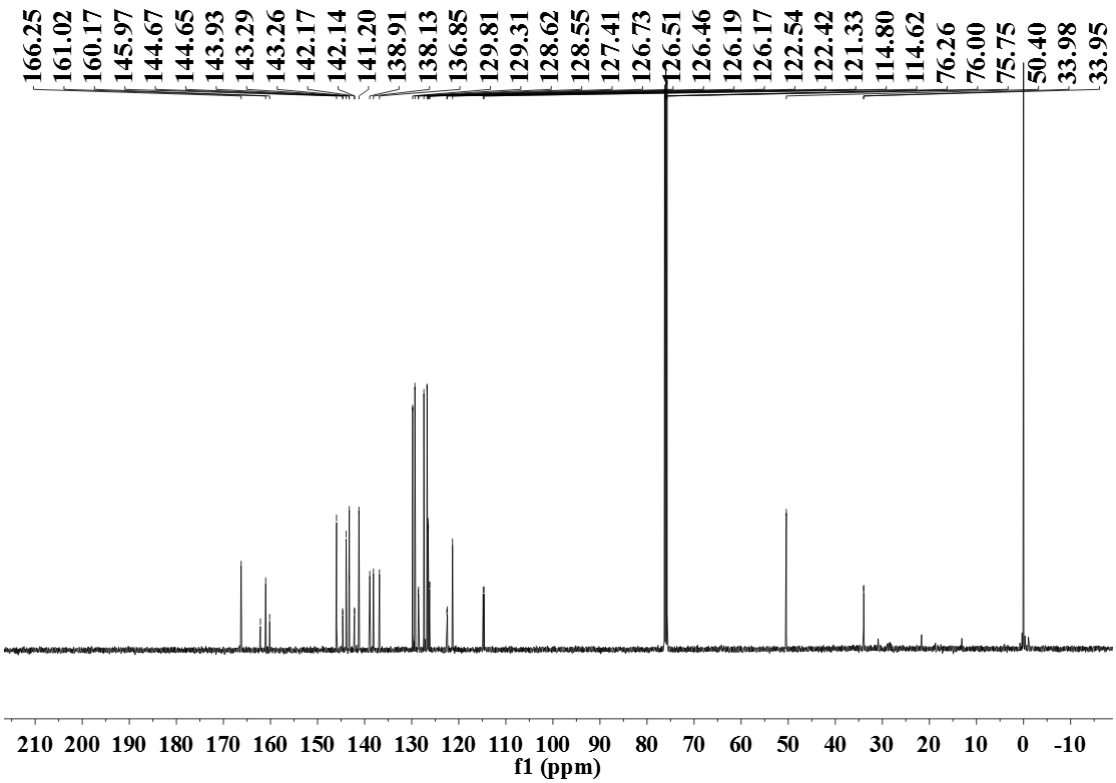

166.24
162.05
146.98
145.12
145.10
144.36
144.26
143.83
143.34
143.31
142.29
140.02
139.22
138.02
130.84
130.35
129.59
129.51
128.40
127.72
127.42
127.34
127.22
127.20
124.49
123.49
123.37
115.69
115.51
80.21
77.30
77.04
76.79
35.01
34.98
28.04
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

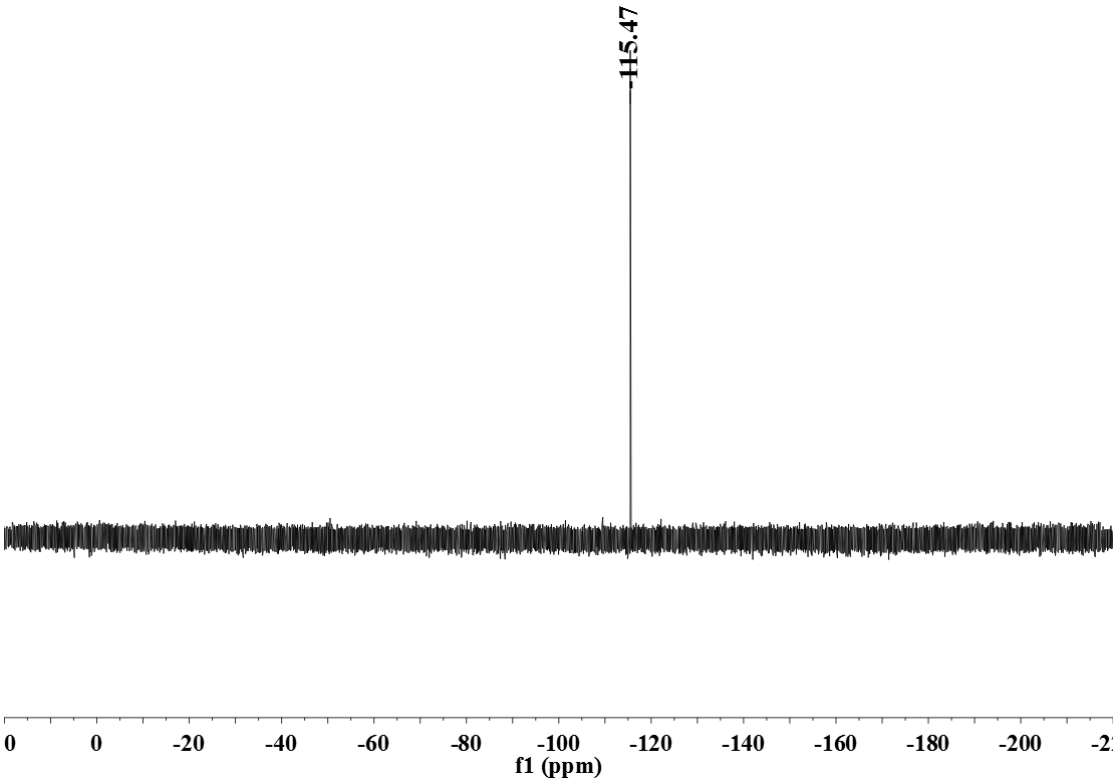

-115.70
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

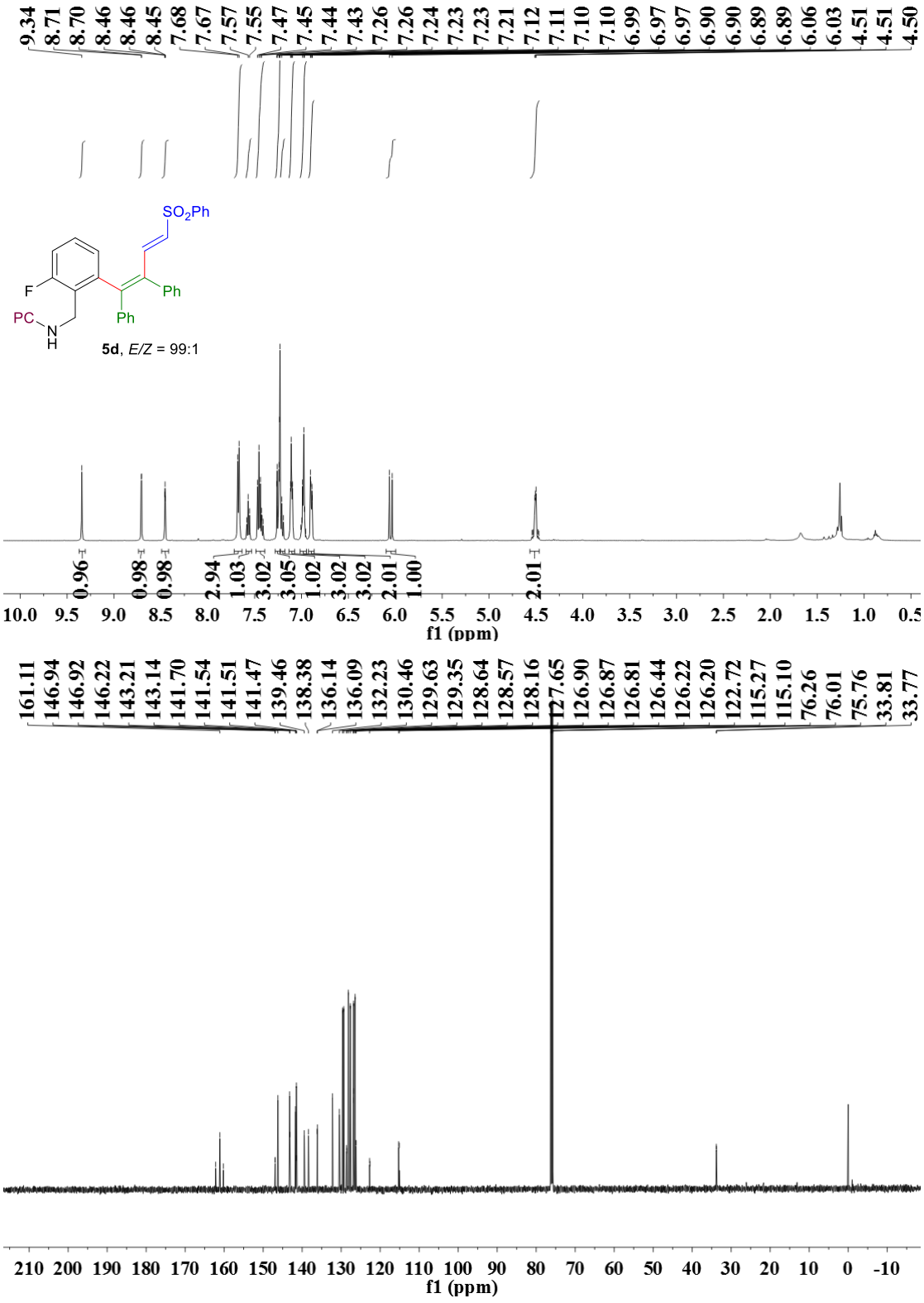

9.33 8.67 8.67 8.39 7.36 7.33 7.28 7.27 7.26 7.19 7.18 7.17 7.15 7.13 6.99 6.97 6.96 6.95 6.93 6.93 6.92 5.56 5.53 4.62 4.61 3.95 3.95 1.50 1.49 1.47 1.27 1.26 1.24 0.87 0.86 0.84
CO2nBu
F
Ph
PC
N
H
Ph
5b, E/Z > 99:1
0.97 1.01 1.02 0.94 1.08 1.06 3.19 4.18 3.07 2.06 1.00 2.05 2.10 2.23 2.27 3.36
f1 (ppm)
165.89 161.02 145.96 144.52 143.78 143.28 143.23 142.26 142.23 141.22 138.87 138.13 136.82 129.79 129.32 128.58 128.50 127.42 126.72 126.49 126.45 126.16 126.13 122.41 121.61 114.69 114.51 76.28 76.03 75.77 63.10 34.00 33.97 29.52 18.06 12.63
f1 (ppm)

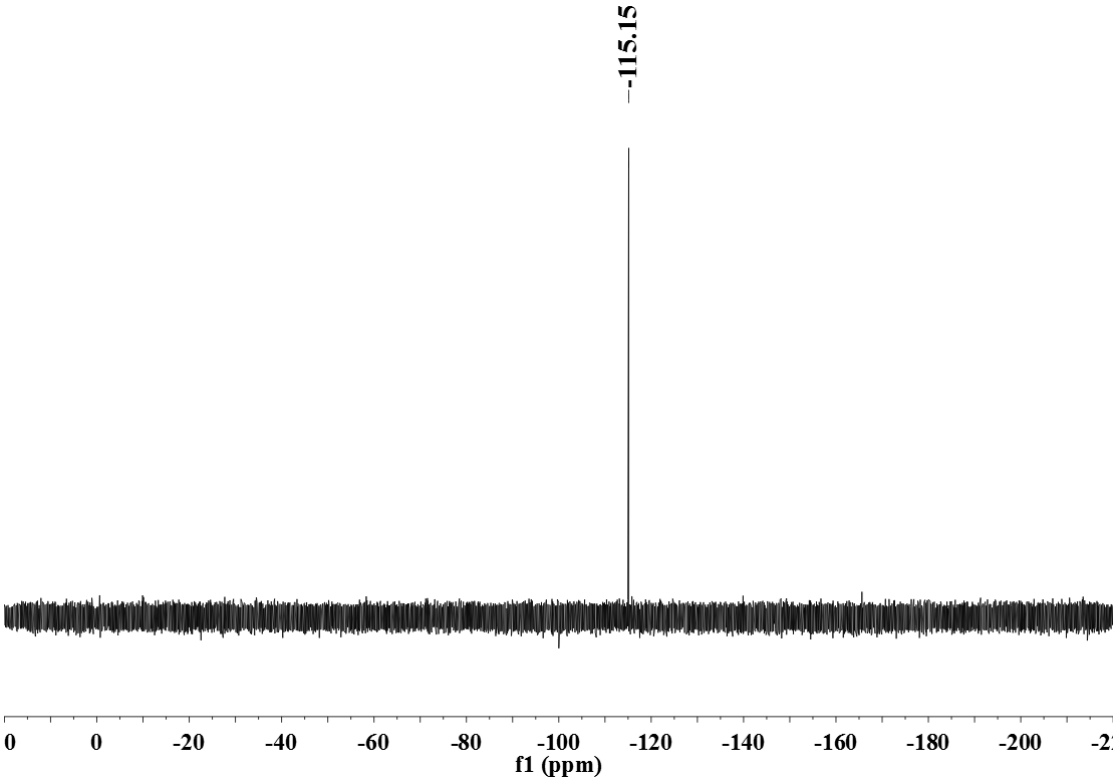

-115.54
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

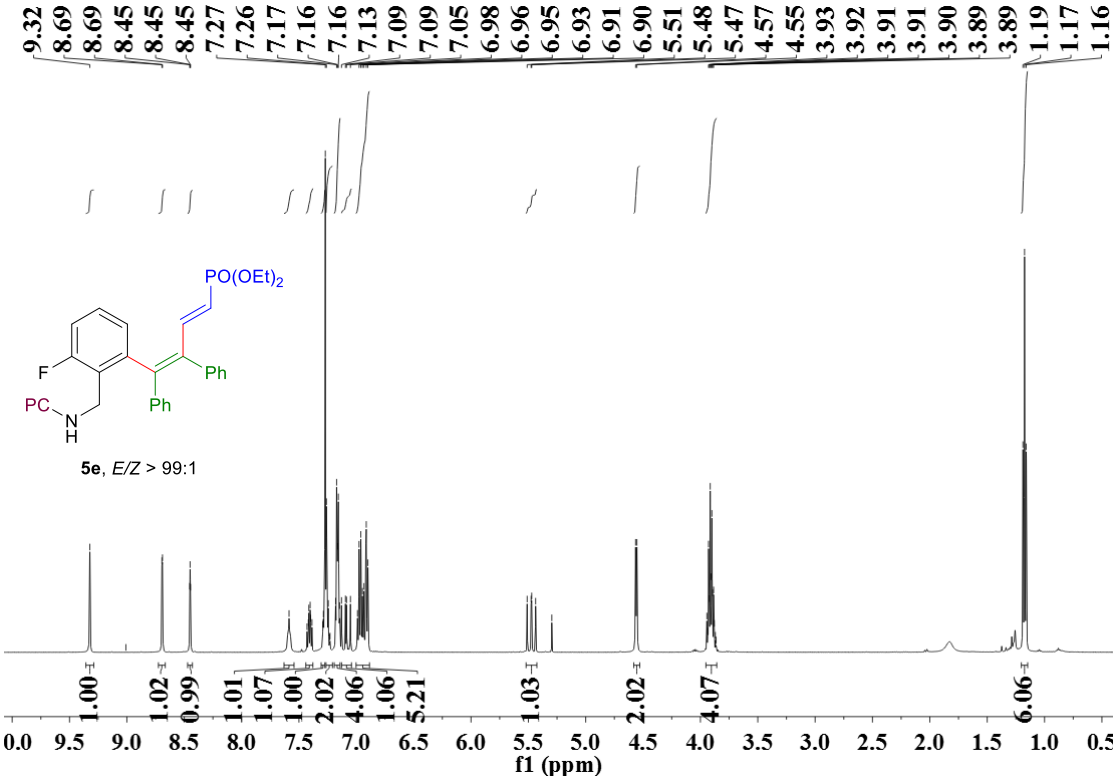

9.25
9.25
8.60
8.60
8.32
8.32
8.32
8.31
7.28
7.25
7.20
7.19
7.18
7.18
7.17
7.16
7.12
7.11
7.09
7.07
7.06
6.91
6.90
6.89
6.89
6.88
6.87
6.85
6.85
6.83
5.49
5.46
4.54
4.53
4.52
3.48
CO2Me
F
Ph
PC
N
H
Ph
5c, E/Z = 97:3
0.96
0.99
1.00
1.00
1.03
1.07
1.03
2.00
2.97
1.08
2.97
1.98
1.00
1.98
2.97
f1 (ppm)

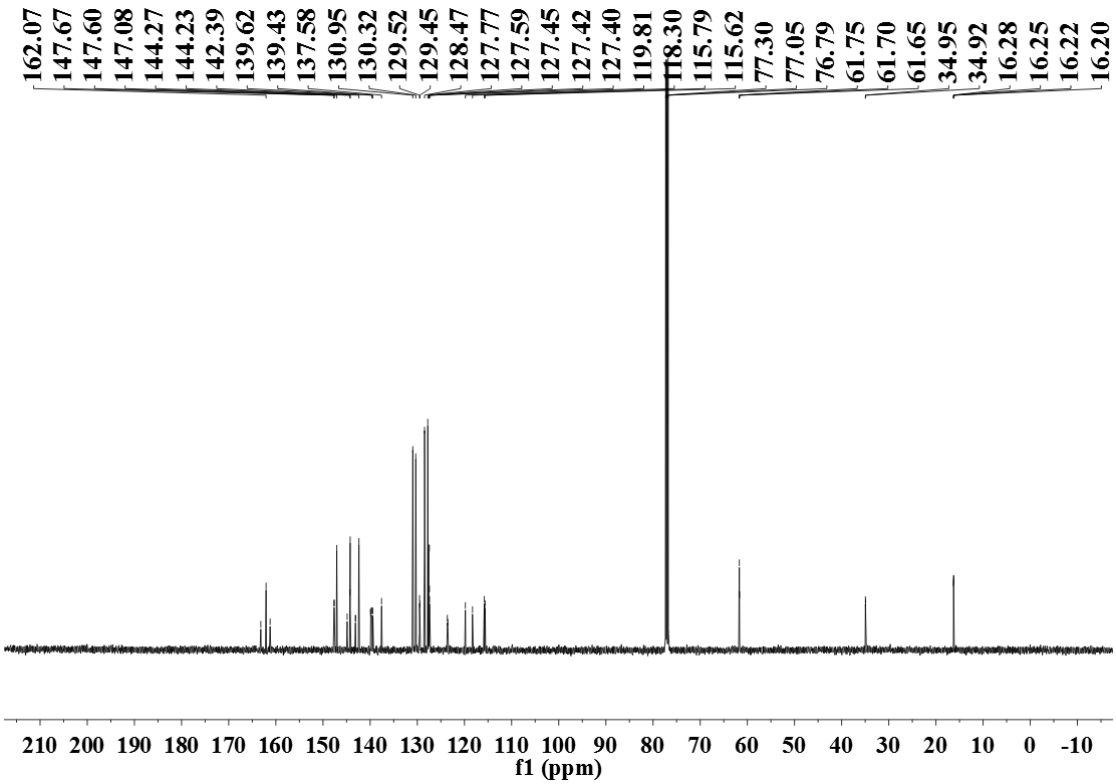

166.25
161.02
160.17
145.97
144.67
144.65
143.93
143.29
143.26
142.17
142.14
141.20
138.91
138.13
136.85
129.81
129.31
128.62
128.55
127.41
126.73
126.51
126.46
126.19
126.17
122.54
122.42
121.33
114.80
114.62
76.26
76.00
75.75
50.40
33.98
33.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

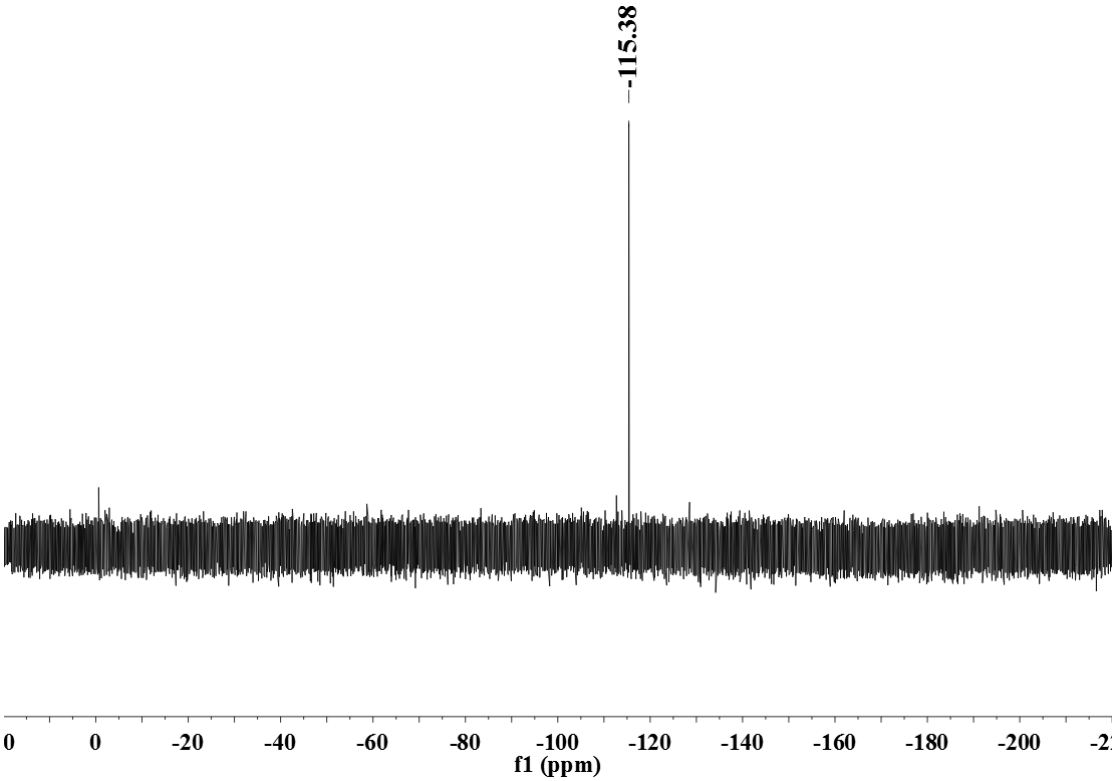

-115.47
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

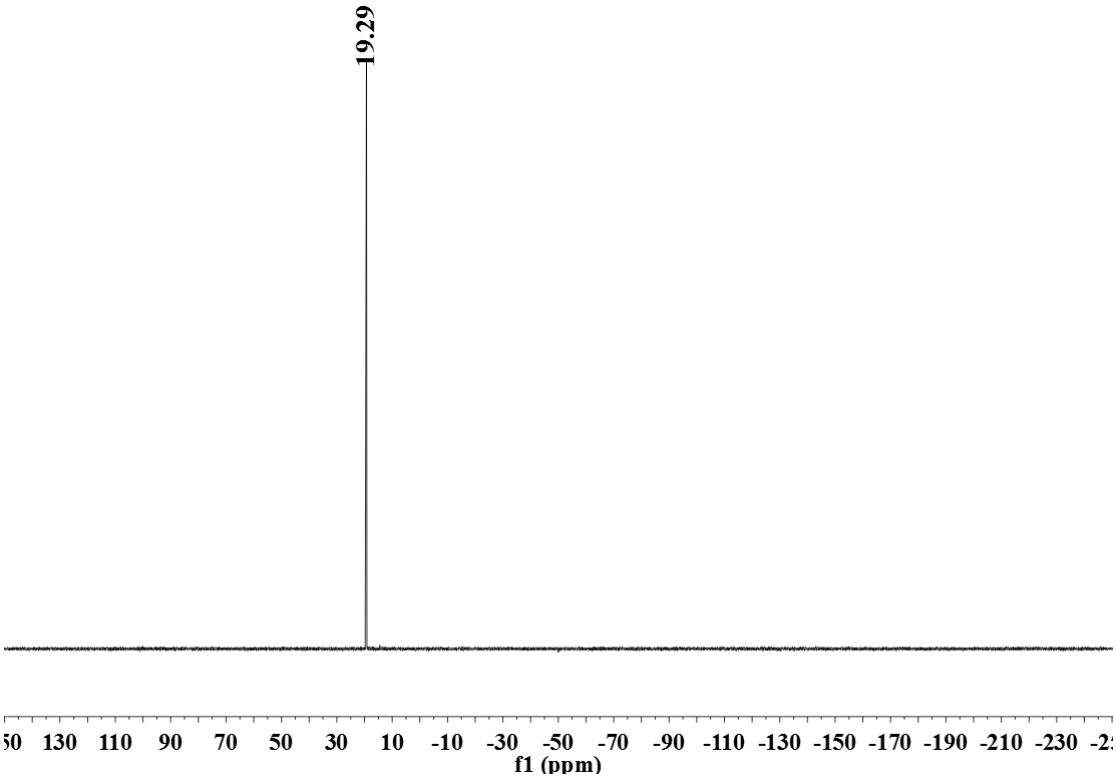

9.34 8.71 8.70 8.46 8.46 8.45 7.68 7.67 7.57 7.55 7.47 7.45 7.44 7.43 7.26 7.26 7.24 7.23 7.23 7.21 7.12 7.11 7.10 7.10 6.99 6.97 6.97 6.90 6.90 6.89 6.89 6.06 6.03 4.51 4.51 4.50
SO2Ph
F
Ph
PC
N
H
Ph
5d, E/Z = 99:1
0.96 0.98 0.98 2.94 1.03 3.02 3.05 1.02 3.02 3.02 2.01 1.00 2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
161.11 146.94 146.92 146.22 143.21 143.14 141.70 141.54 141.51 141.47 139.46 138.38 136.14 136.09 132.23 130.46 129.63 129.35 128.64 128.57 128.16 127.65 126.90 126.87 126.81 126.44 126.22 126.20 122.72 115.27 115.10 76.26 76.01 75.76 33.81 33.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

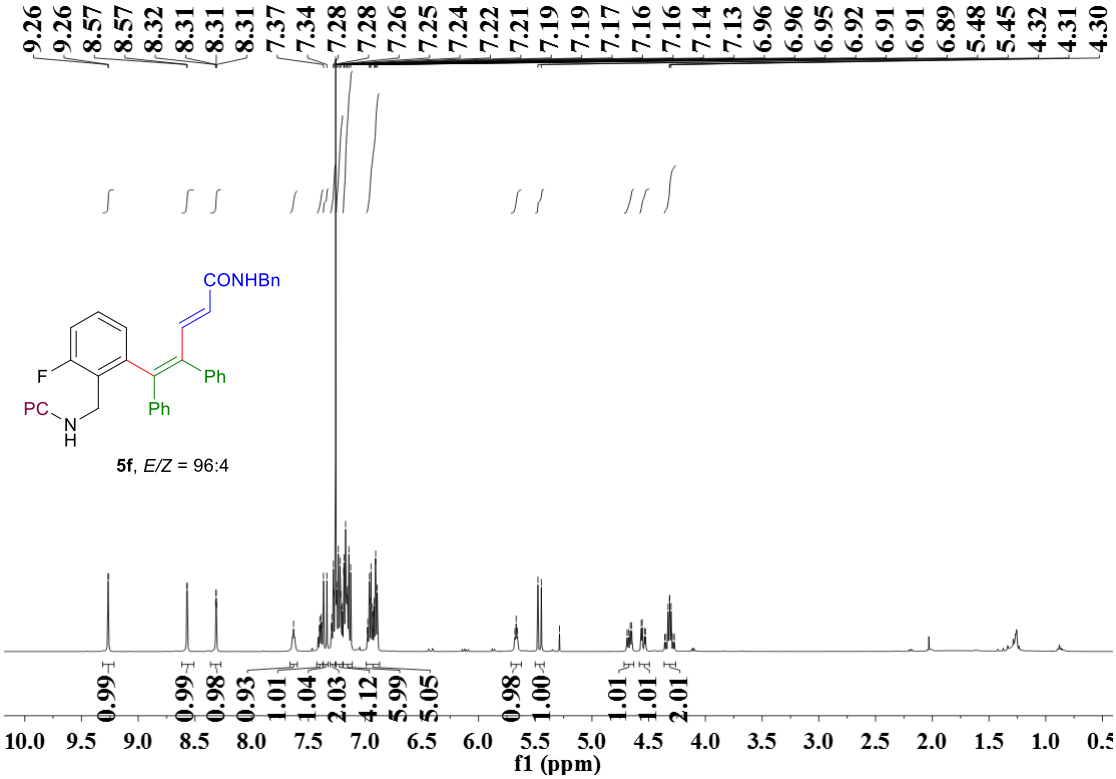

-115.15
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

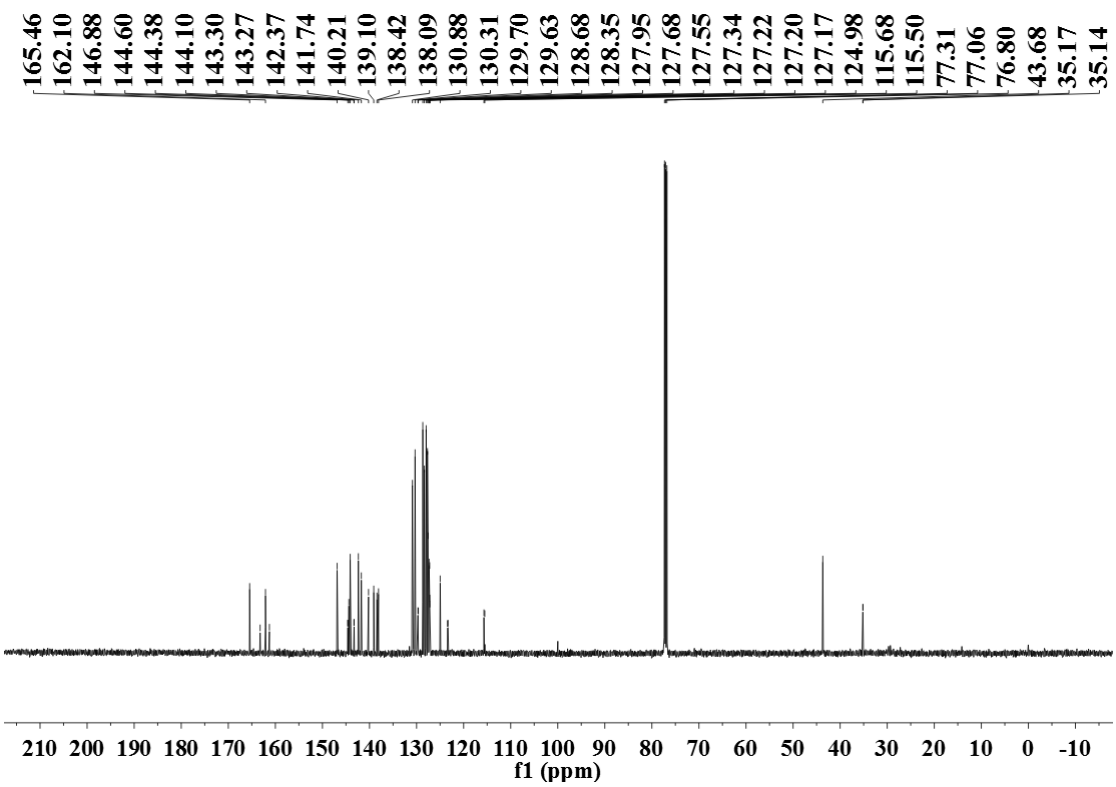

9.32
8.69
8.69
8.45
8.45
8.45
7.27
7.26
7.17
7.16
7.16
7.13
7.09
7.09
7.05
6.98
6.96
6.95
6.93
6.91
6.90
5.51
5.48
5.47
4.57
4.55
3.93
3.92
3.91
3.91
3.90
3.89
3.89
1.19
1.17
1.16
PO(OEt)2
F
Ph
PC
N
H
Ph
5e, E/Z > 99:1
1.00
1.02
0.99
1.01
1.07
1.00
2.02
4.06
1.06
5.21
1.03
2.02
4.07
6.06
f1 (ppm)

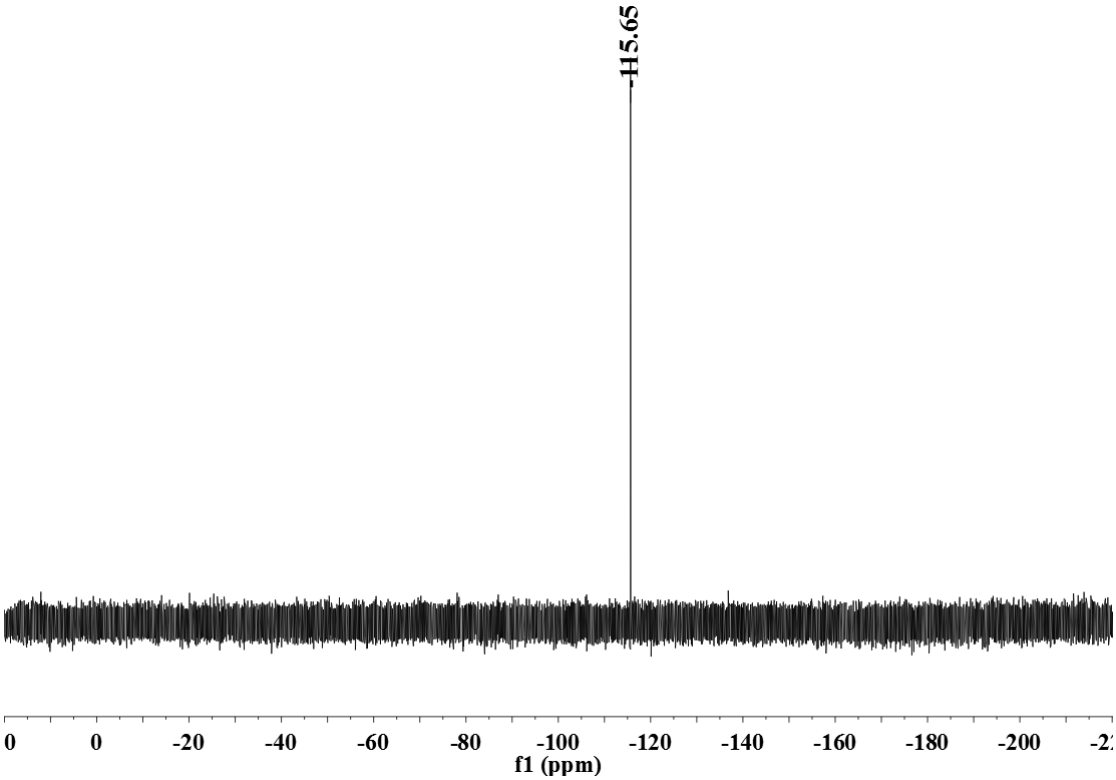

162.07
147.67
147.60
147.08
144.27
144.23
142.39
139.62
139.43
137.58
130.95
130.32
129.52
129.45
128.47
127.77
127.59
127.45
127.42
127.40
119.81
118.30
115.79
115.62
77.30
77.05
76.79
61.75
61.70
61.65
34.95
34.92
16.28
16.25
16.22
16.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

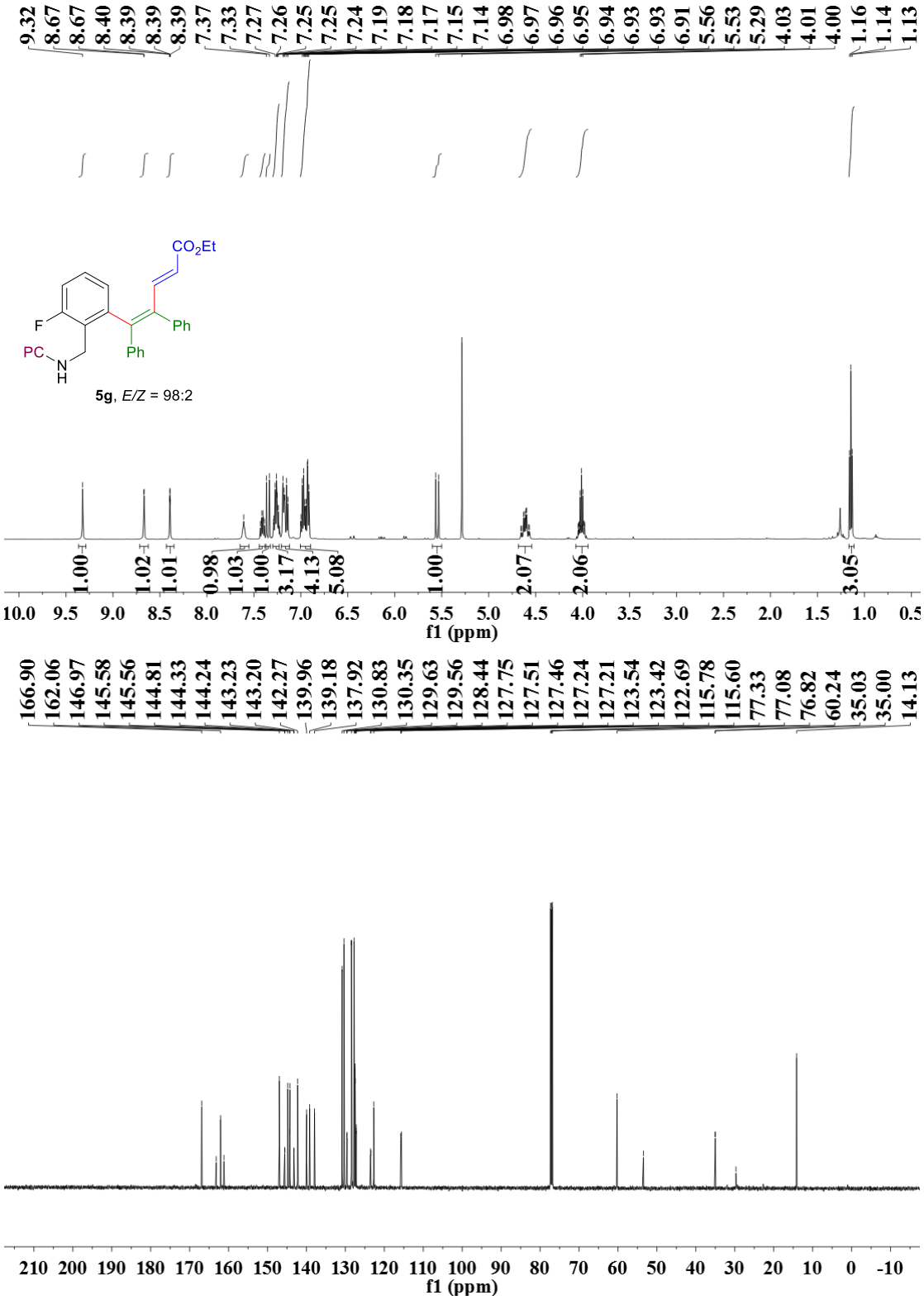

-115.38
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

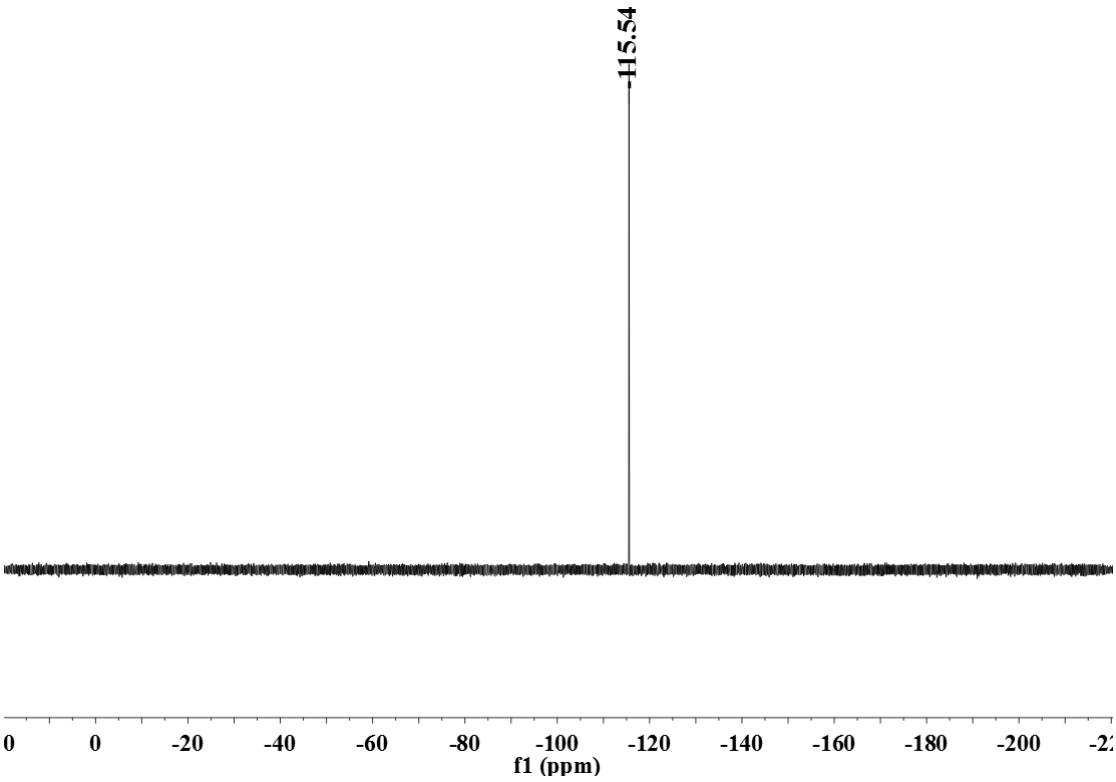

19.29
f1 (ppm)

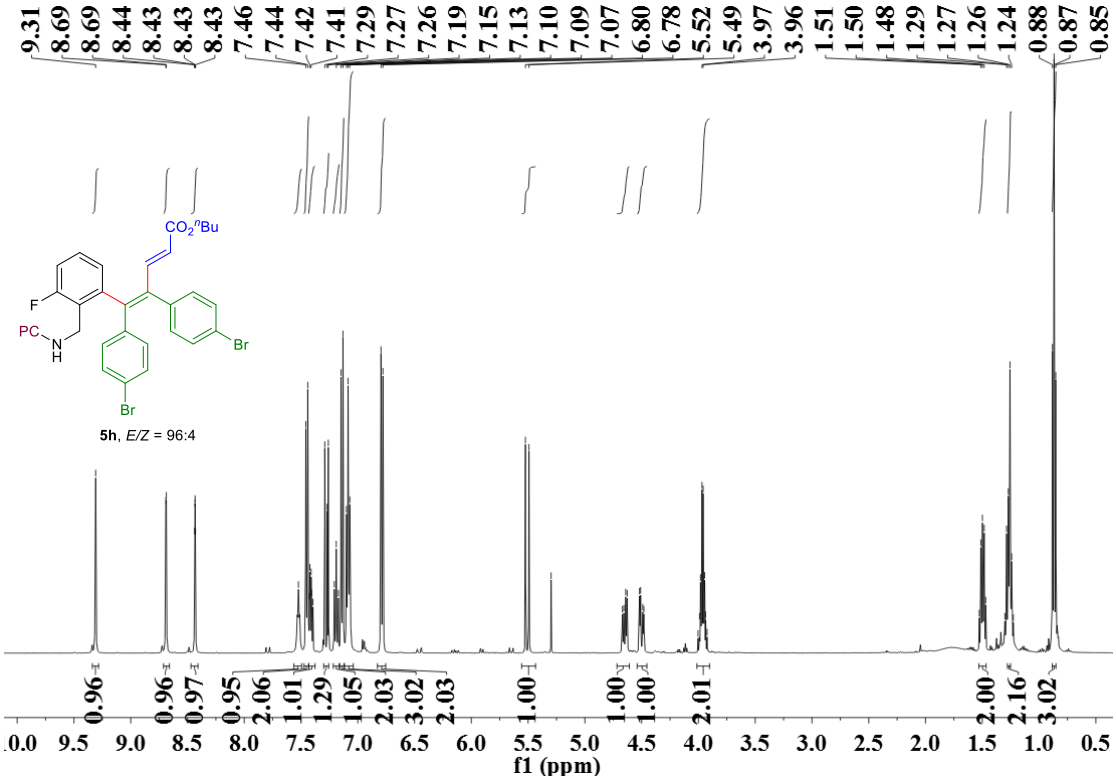

9.26
9.26
8.57
8.57
8.32
8.31
8.31
8.31
7.37
7.34
7.28
7.28
7.26
7.25
7.24
7.22
7.21
7.19
7.19
7.17
7.16
7.16
7.14
7.13
6.96
6.96
6.95
6.92
6.91
6.91
6.89
5.48
5.45
4.32
4.31
4.30
CONHBn
F
Ph
Ph
PC
N
H
5f, E/Z = 96:4
0.99
0.99
0.98
0.93
1.01
1.04
2.03
4.12
5.99
5.05
0.98
1.00
1.01
1.01
2.01
f1 (ppm)

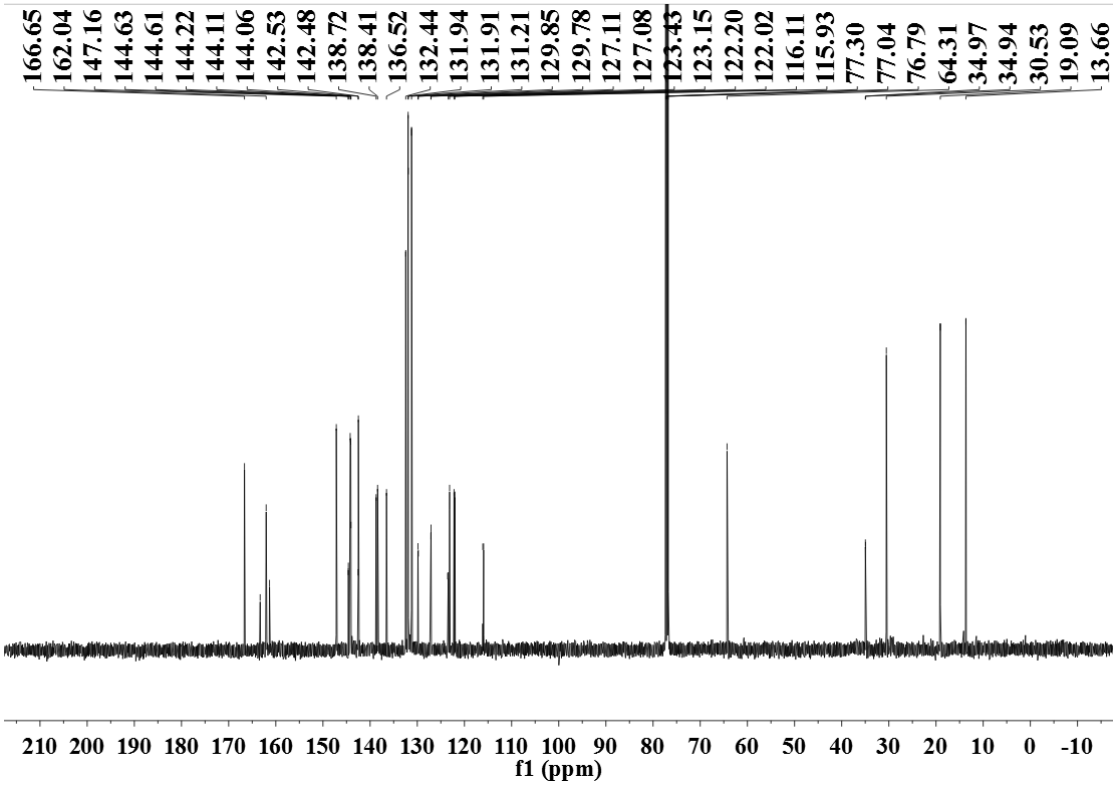

165.46
162.10
146.88
144.60
144.38
144.10
143.30
143.27
142.37
141.74
140.21
139.10
138.42
138.09
130.88
130.31
129.70
129.63
128.68
128.35
127.95
127.68
127.55
127.34
127.22
127.20
127.17
124.98
115.68
115.50
77.31
77.06
76.80
43.68
35.17
35.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

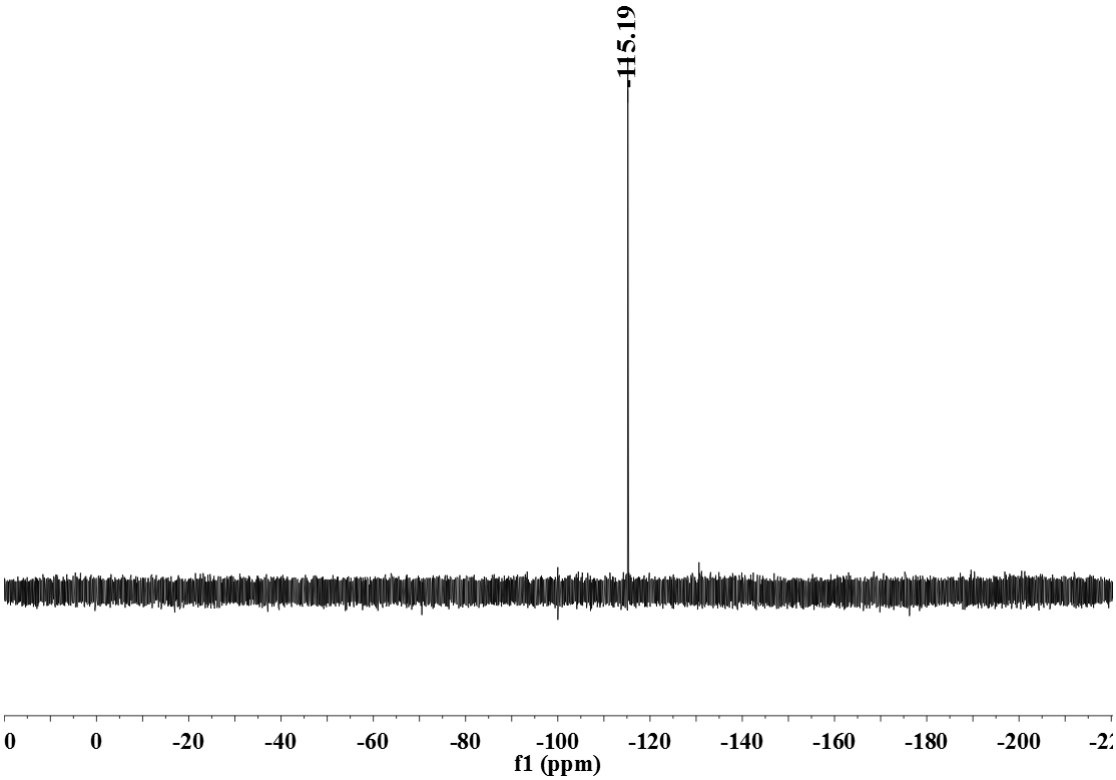

-115.65
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

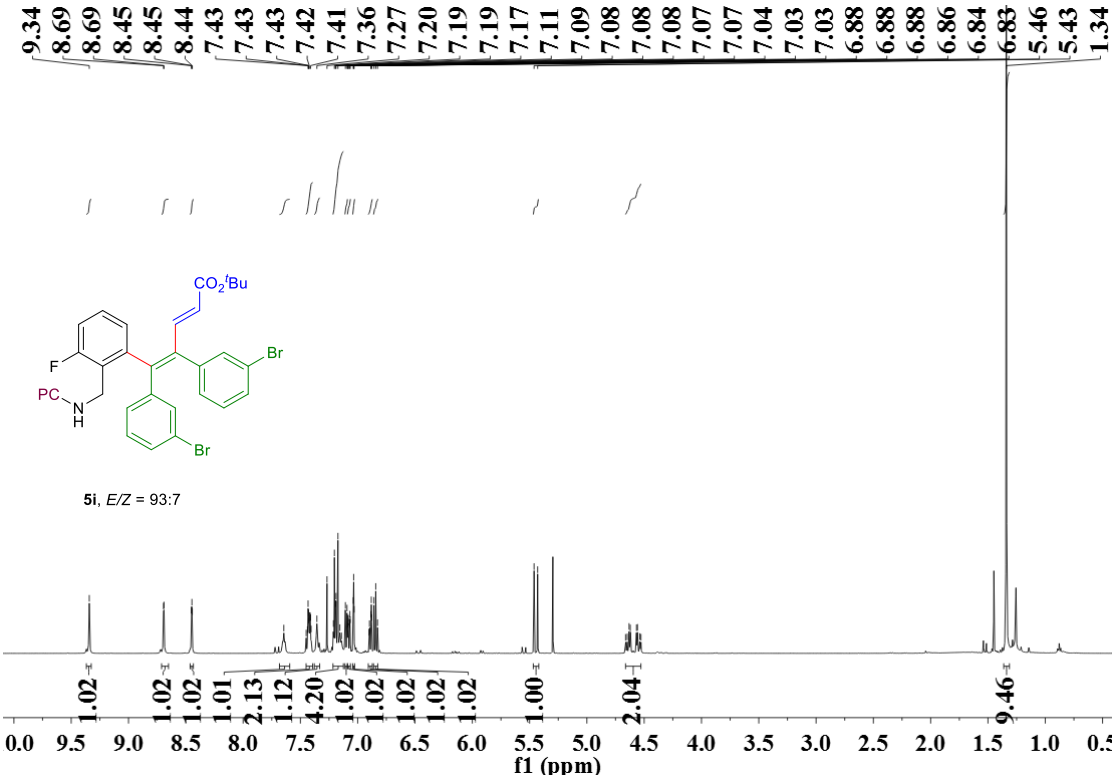

9.32 8.67 8.67 8.40 8.39 8.39 8.39 7.37 7.33 7.27 7.26 7.25 7.25 7.24 7.19 7.18 7.17 7.15 7.14 6.98 6.97 6.96 6.95 6.94 6.93 6.93 6.91 5.56 5.53 5.29 4.03 4.01 4.00 1.16 1.14 1.13
CO2Et
F
Ph
Ph
PC
N
H
5g, E/Z = 98:2
1.00 1.02 1.01 0.98 1.03 1.00 3.17 4.13 5.08 1.00 2.07 2.06 3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
166.90 162.06 146.97 145.58 145.56 144.81 144.33 144.24 143.23 143.20 142.27 139.96 139.18 137.92 130.83 130.35 129.63 129.56 128.44 127.75 127.51 127.46 127.24 127.21 123.54 123.42 122.69 115.78 115.60 77.33 77.08 76.82 60.24 35.03 35.00 14.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

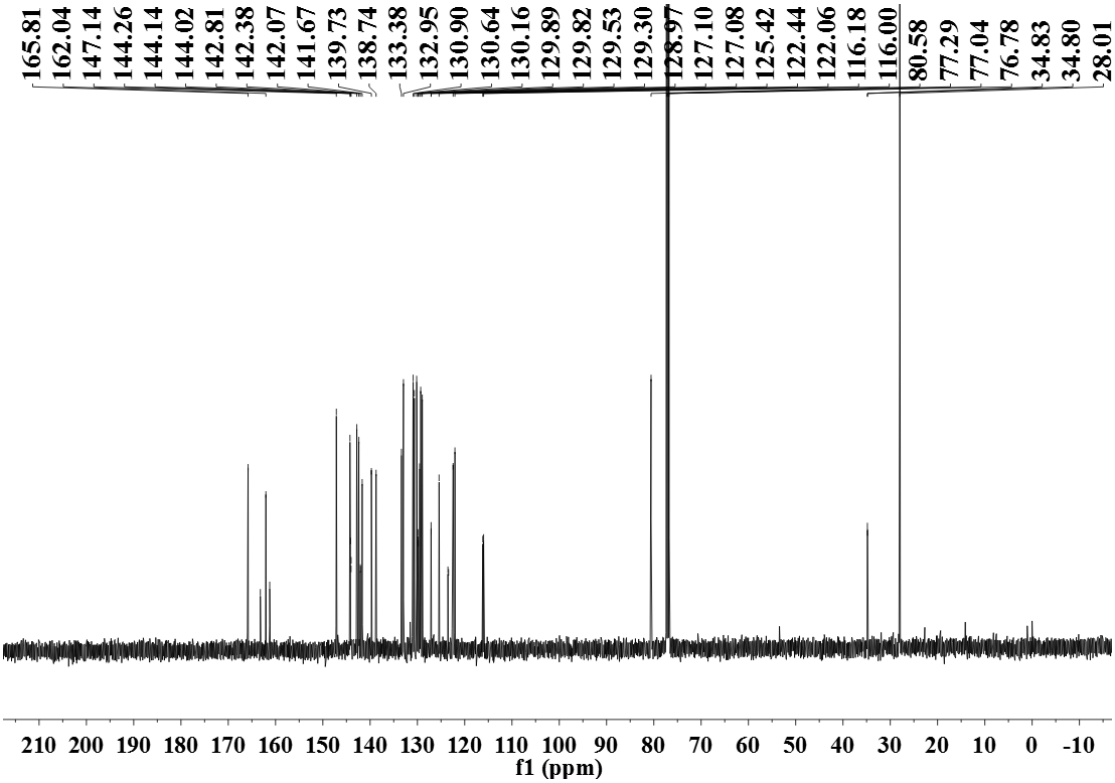

-115.54
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

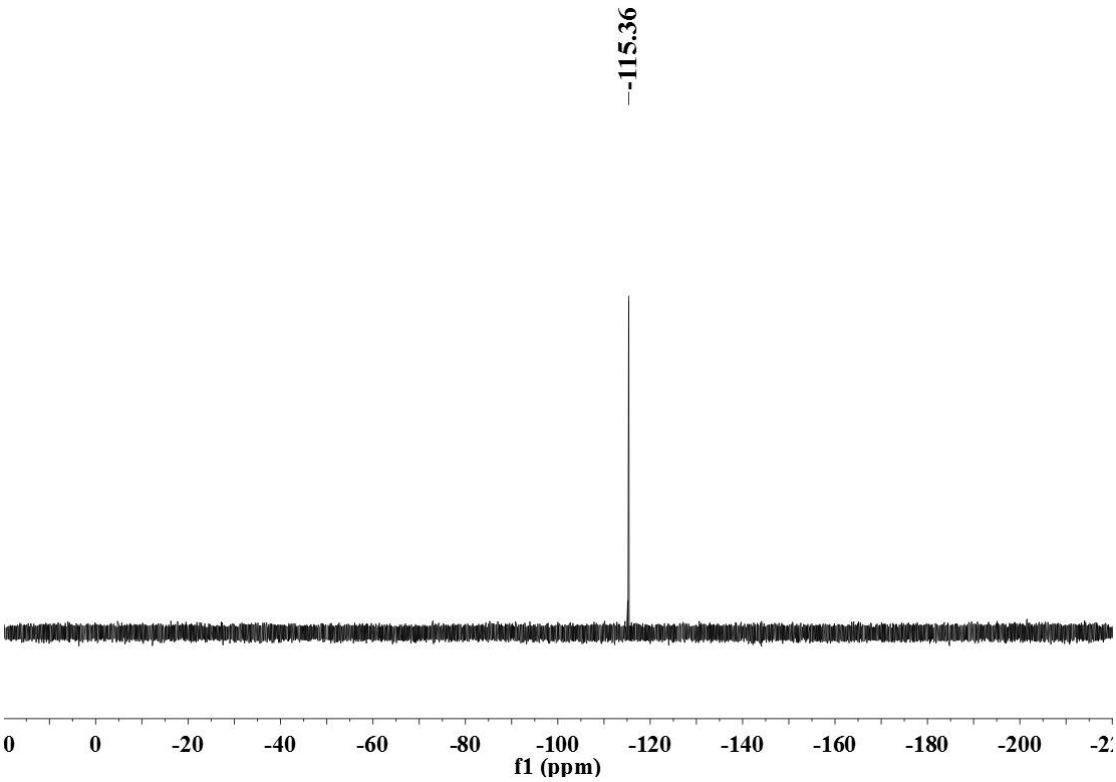

9.31
8.69
8.69
8.44
8.43
8.43
8.43
7.46
7.44
7.42
7.41
7.29
7.27
7.26
7.19
7.15
7.13
7.10
7.09
7.07
6.80
6.78
5.52
5.49
3.97
3.96
1.51
1.50
1.48
1.29
1.27
1.26
1.24
0.88
0.87
0.85
CO2nBu
F
PC
N
H
Br
Br
5h, E/Z = 96:4
0.96
0.96
0.97
0.95
2.06
1.01
1.29
1.05
2.03
3.02
2.03
1.00
1.00
1.00
2.01
2.00
2.16
3.02
f1 (ppm)

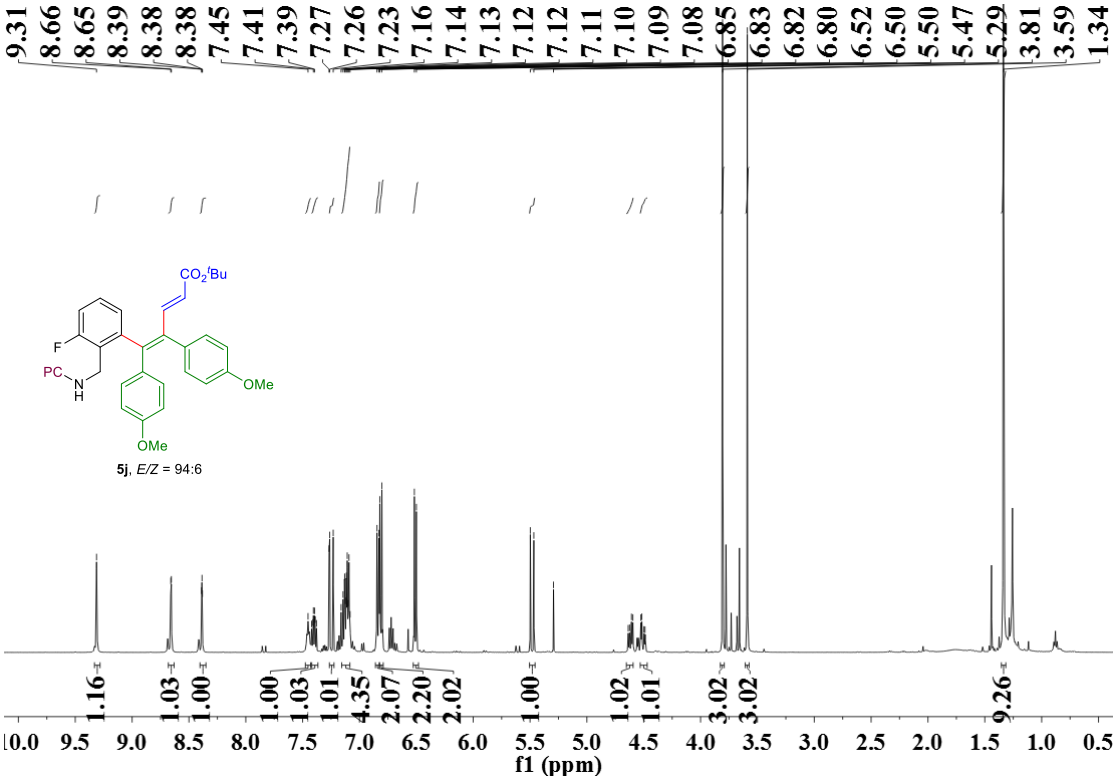

166.65
162.04
147.16
144.63
144.61
144.22
144.11
144.06
142.53
142.48
138.72
138.41
136.52
132.44
131.94
131.91
131.21
129.85
129.78
127.11
127.08
123.43
123.15
122.20
122.02
116.11
115.93
77.30
77.04
76.79
64.31
34.97
34.94
30.53
19.09
13.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

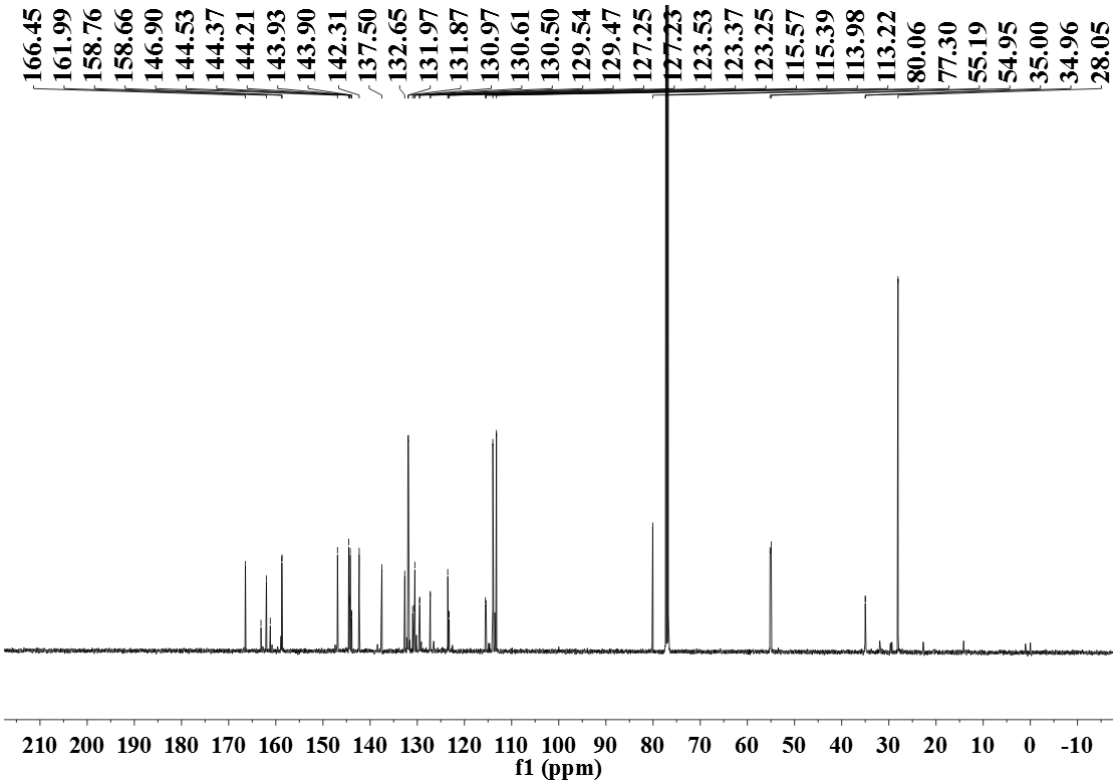

-115.19
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

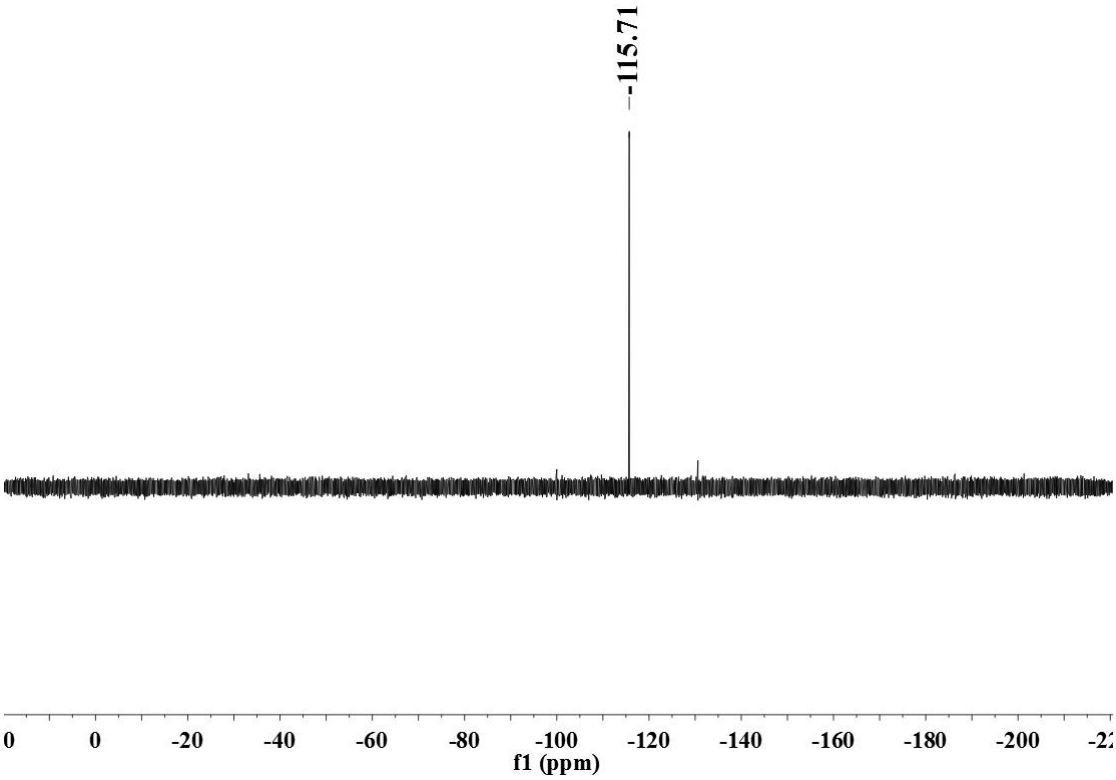

9.34
8.69
8.69
8.45
8.45
8.44
7.43
7.43
7.43
7.42
7.41
7.36
7.27
7.20
7.19
7.19
7.17
7.11
7.09
7.08
7.08
7.08
7.07
7.07
7.04
7.03
7.03
6.88
6.88
6.88
6.86
6.84
6.83
5.46
5.43
1.34
CO2tBu
F
PC
N
H
Br
Br
5i, E/Z = 93:7
1.02
1.02
1.02
1.01
2.13
1.12
4.20
1.02
1.02
1.02
1.02
1.02
1.00
2.04
9.46
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

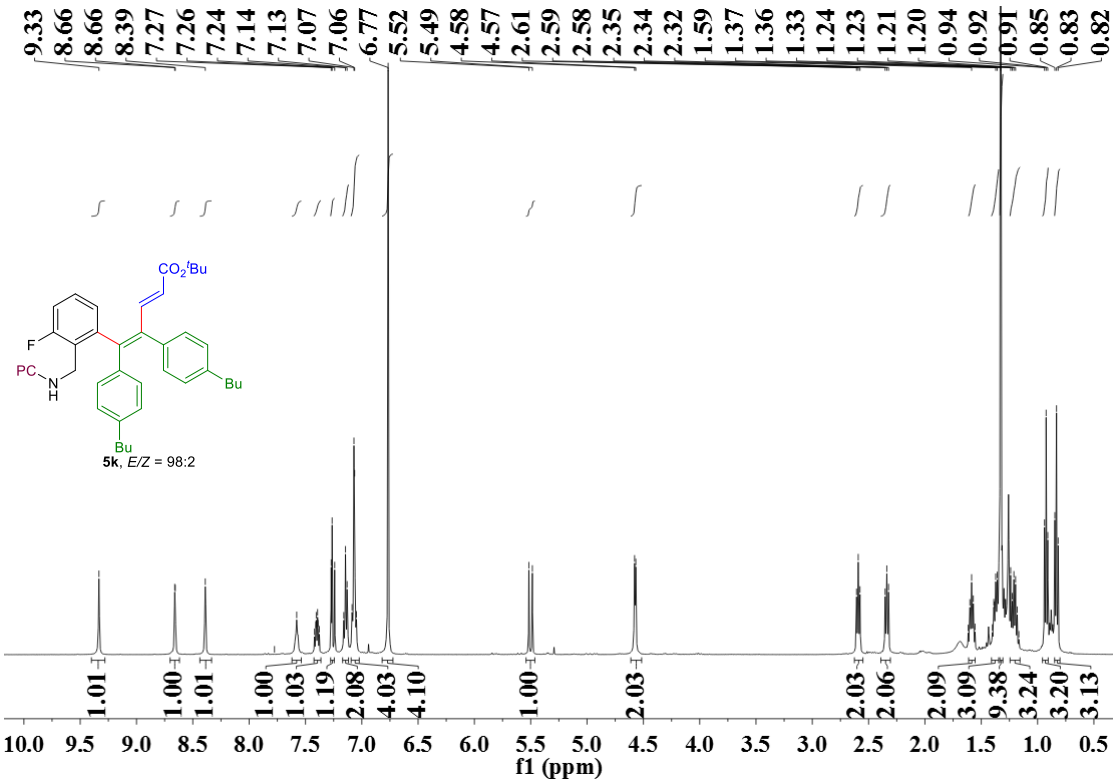

165.81
162.04
147.14
144.26
144.14
144.02
142.81
142.38
142.07
141.67
139.73
138.74
133.38
132.95
130.90
130.64
130.16
129.89
129.82
129.53
129.30
128.97
127.10
127.08
125.42
122.44
122.06
116.18
116.00
80.58
77.29
77.04
76.78
34.83
34.80
28.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

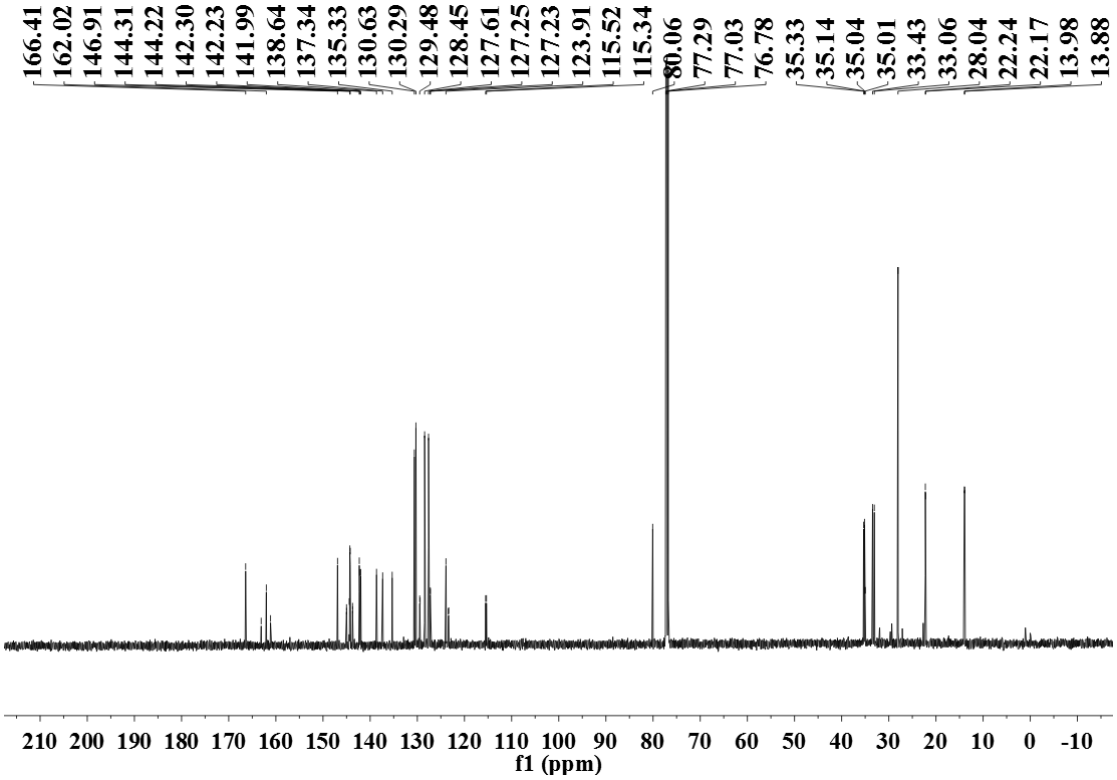

-115.36
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

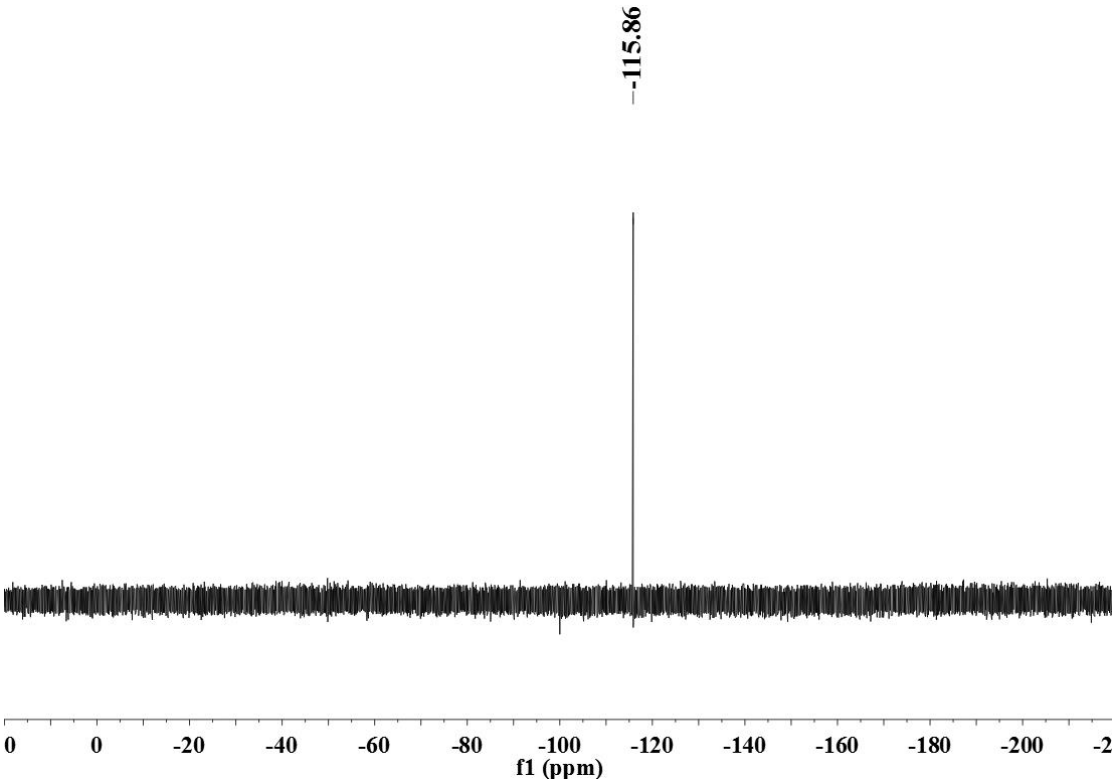

9.31
8.66
8.65
8.39
8.38
8.38
7.45
7.41
7.39
7.27
7.26
7.23
7.16
7.14
7.13
7.12
7.12
7.11
7.10
7.09
7.08
6.85
6.83
6.82
6.80
6.52
6.50
5.50
5.47
5.29
3.81
3.59
1.34
CO2tBu
F
PC
N
H
OMe
OMe
5j, E/Z = 94:6
1.16
1.03
1.00
1.00
1.03
1.01
4.35
2.07
2.20
2.02
1.00
1.02
1.01
3.02
3.02
9.26
f1 (ppm)

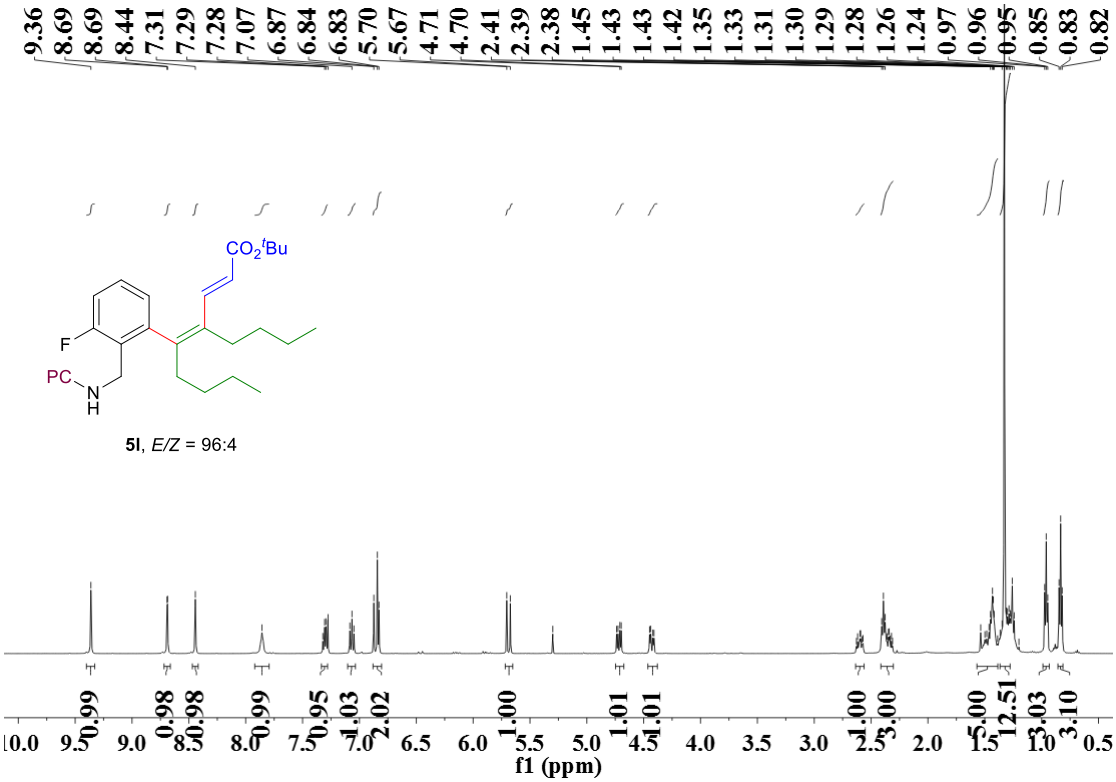

166.45
161.99
158.76
158.66
146.90
144.53
144.37
144.21
143.93
143.90
142.31
137.50
132.65
131.97
131.87
130.97
130.61
130.50
129.54
129.47
127.25
127.23
123.53
123.37
123.25
115.57
115.39
113.98
113.22
80.06
77.30
55.19
54.95
35.00
34.96
28.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-115.71
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -22
f1 (ppm)

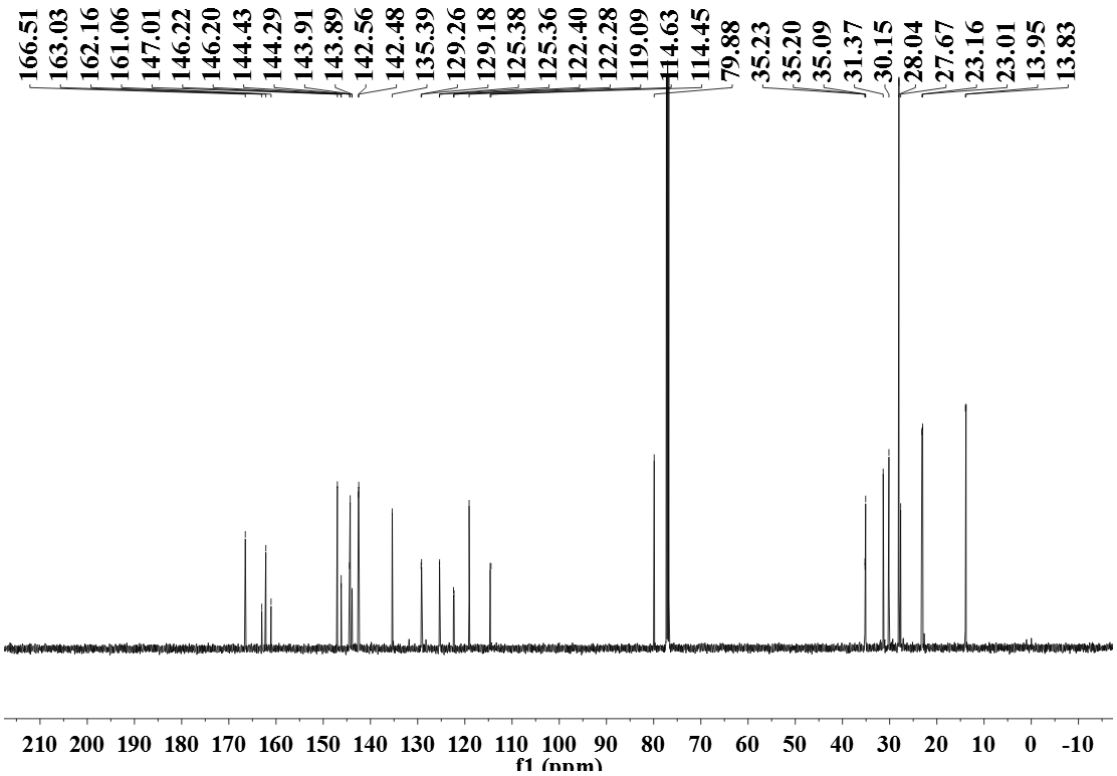

9.33 8.66 8.66 8.39 7.27 7.26 7.24 7.14 7.13 7.07 7.06 6.77 5.52 5.49 4.58 4.57 2.61 2.59 2.58 2.35 2.34 2.32 1.59 1.37 1.36 1.33 1.24 1.23 1.21 1.20 0.94 0.92 0.91 0.85 0.83 0.82
CO2tBu
F
PC
N
H
Bu
Bu
5k, E/Z = 98:2
1.01 1.00 1.01 1.00 1.03 1.19 2.08 4.03 4.10 1.00 2.03 2.03 2.06 2.09 3.09 9.38 3.24 3.20 3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

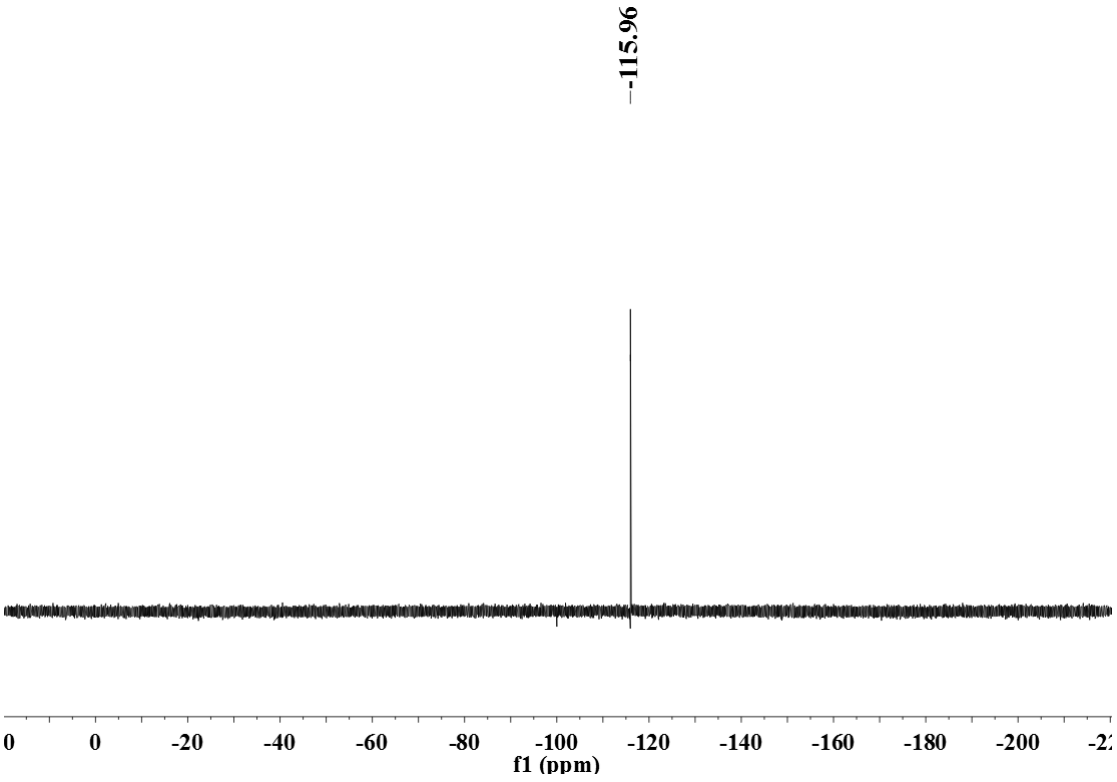

166.41 162.02 146.91 144.31 144.22 142.30 142.23 141.99 138.64 137.34 135.33 130.63 130.29 129.48 128.45 127.61 127.25 127.23 123.91 115.52 115.34 80.06 77.29 77.03 76.78 35.33 35.14 35.04 35.01 33.43 33.06 28.04 22.24 22.17 13.98 13.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

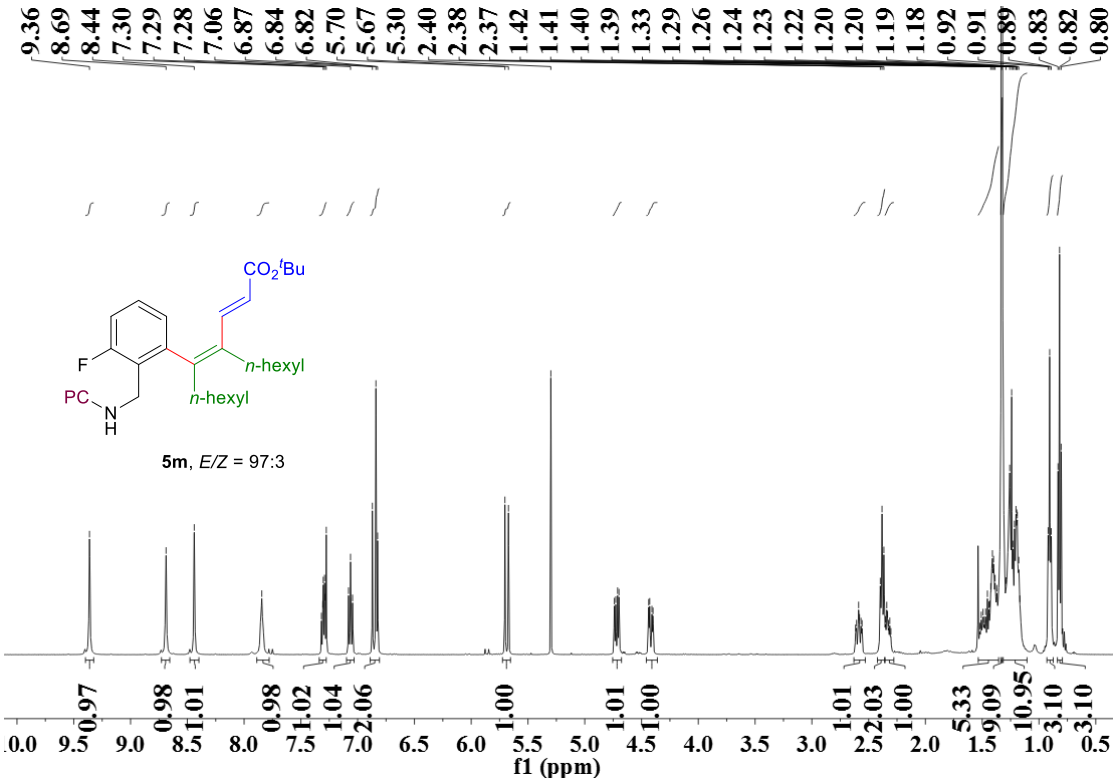

-115.86
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

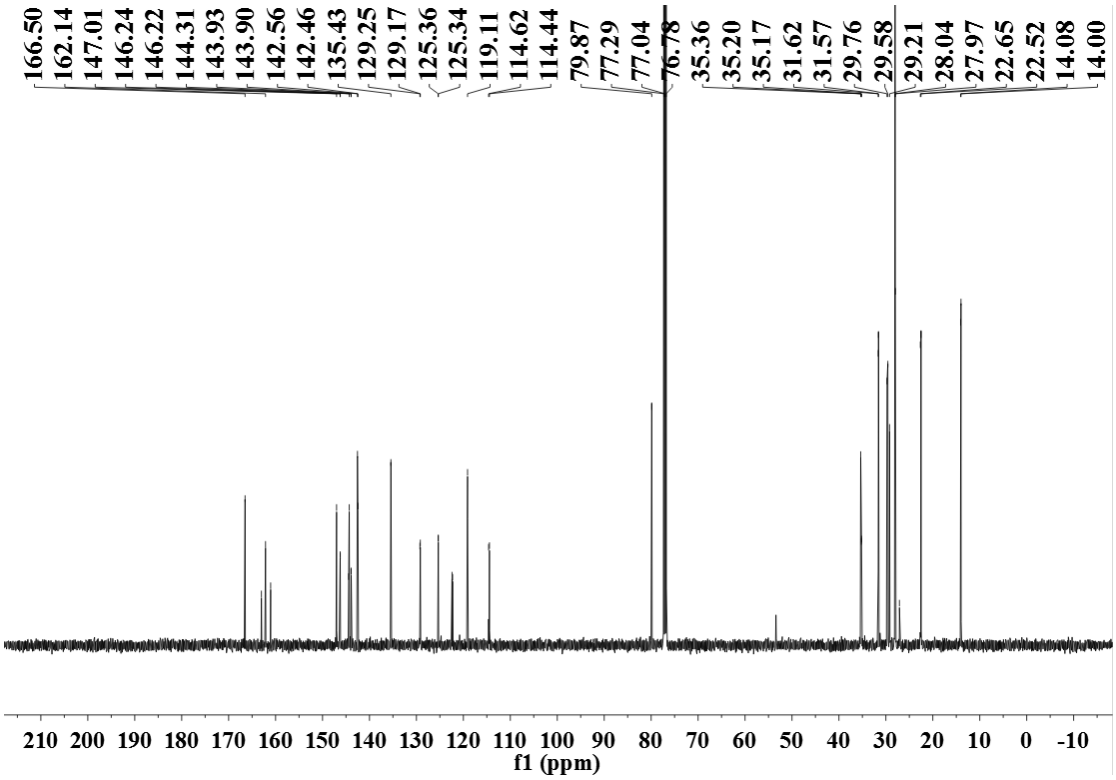

9.36
8.69
8.69
8.44
7.31
7.29
7.28
7.07
6.87
6.84
6.83
5.70
5.67
4.71
4.70
2.41
2.39
2.38
1.45
1.43
1.43
1.42
1.35
1.33
1.31
1.30
1.29
1.28
1.26
1.24
0.97
0.96
0.95
0.85
0.83
0.82
CO2tBu
F
PC
N
H
0.99
0.98
0.98
0.99
0.95
1.03
2.02
1.00
1.01
1.01
1.00
3.00
5.00
12.51
3.03
3.10
f1 (ppm)

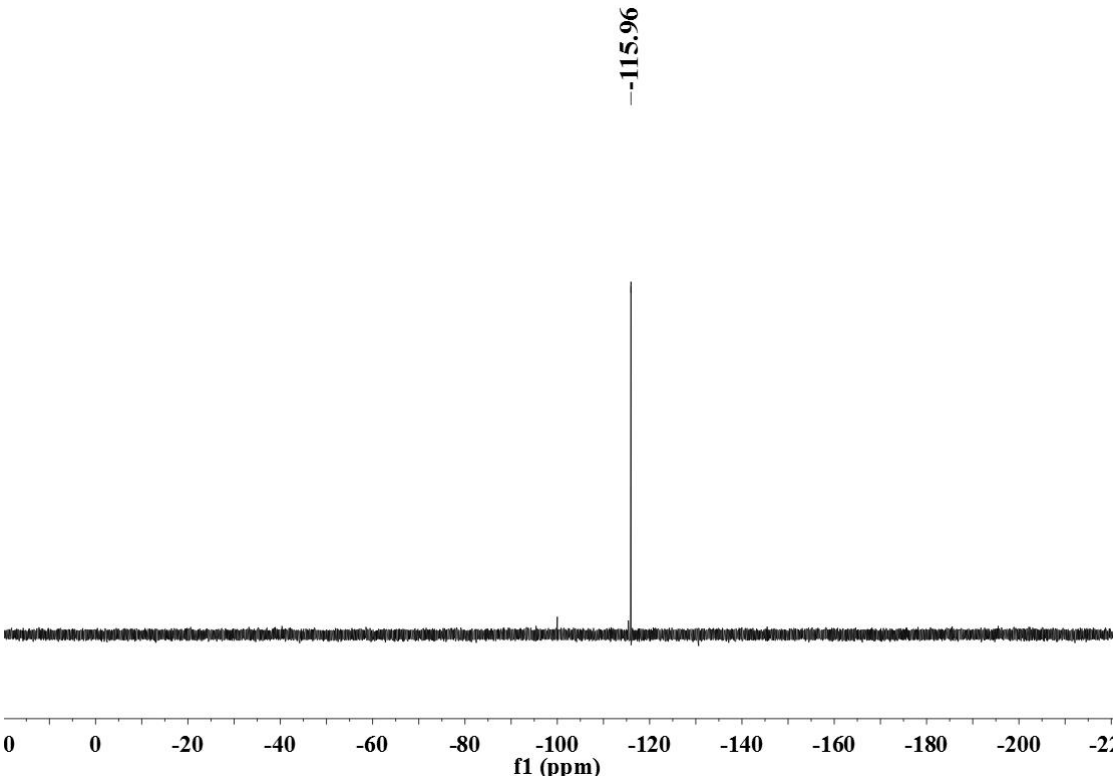
5l, *E*/*Z* = 96:4

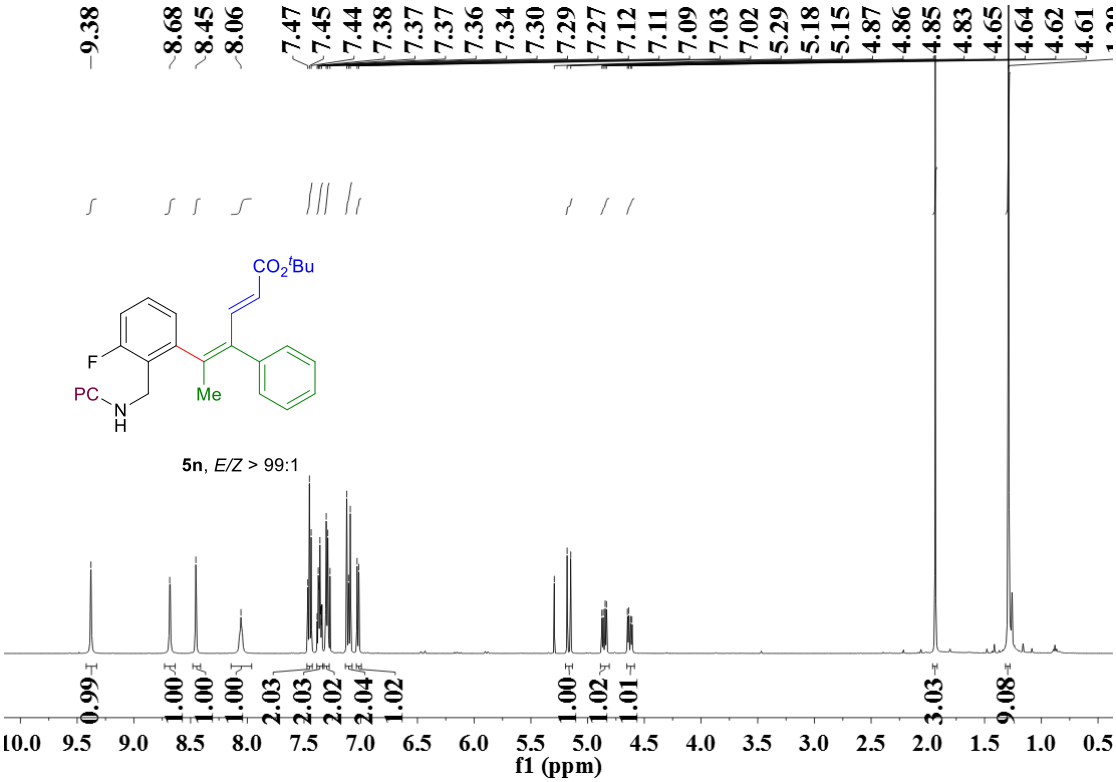

166.51
163.03
162.16
161.06
147.01
146.22
146.20
144.43
144.29
143.91
143.89
142.56
142.48
135.39
129.26
129.18
125.38
125.36
122.40
122.28
119.09
114.63
114.45
79.88
35.23
35.20
35.09
31.37
30.15
28.04
27.67
23.16
23.01
13.95
13.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

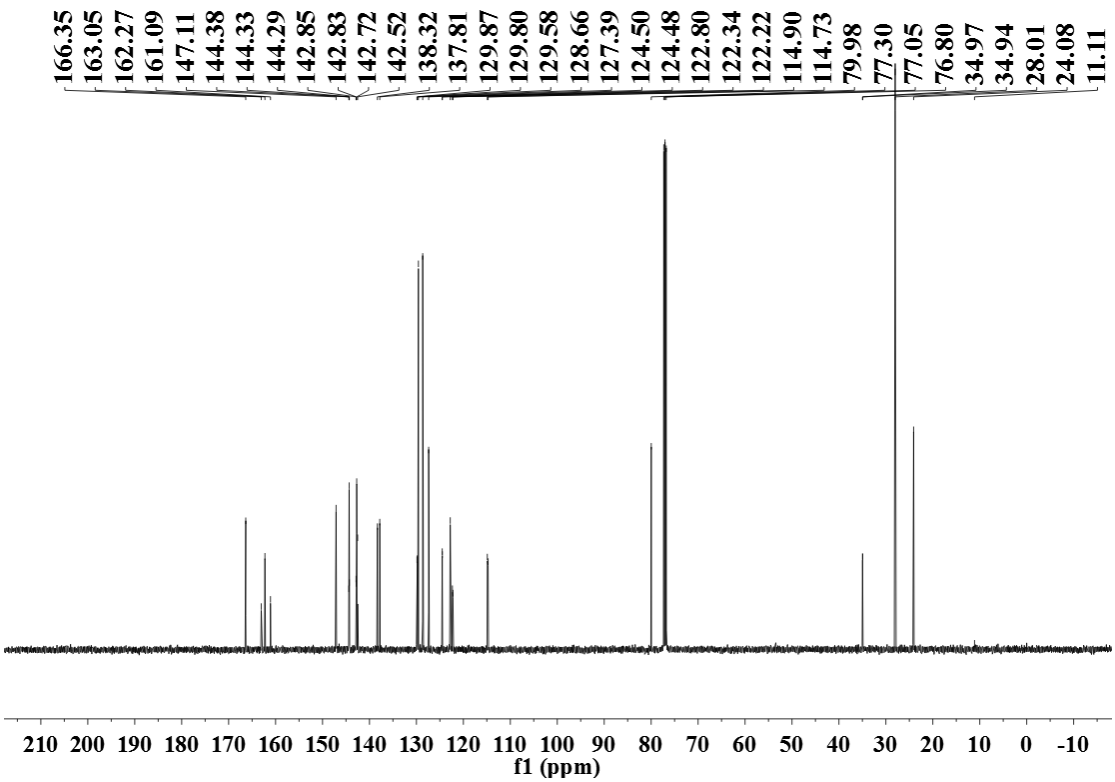

-115.96
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

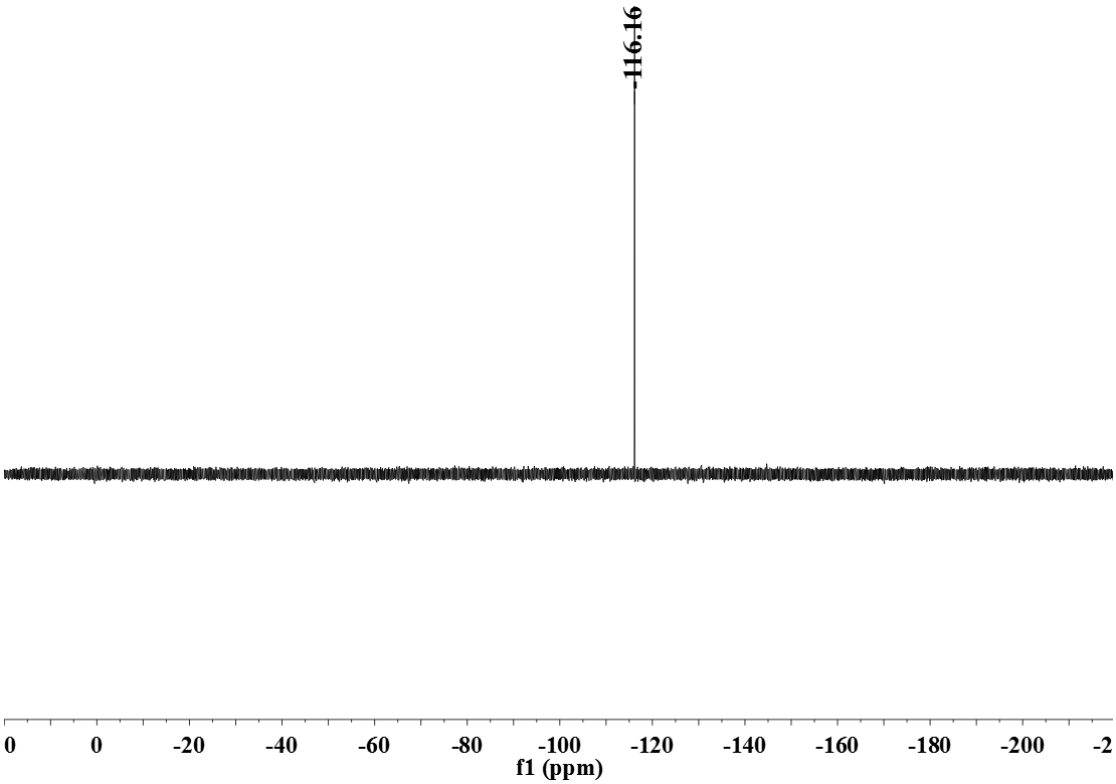

9.36 8.69 8.44 7.30 7.29 7.28 7.06 6.87 6.84 6.82 5.70 5.67 5.30 2.40 2.38 2.37 1.42 1.41 1.40 1.39 1.33 1.29 1.26 1.24 1.23 1.22 1.20 1.20 1.19 1.18 0.92 0.91 0.89 0.83 0.82 0.80
CO2tBu
F
n-hexyl
PC
N
H
n-hexyl
5m, E/Z = 97:3
0.97 0.98 1.01 0.98 1.02 1.04 2.06 1.00 1.01 1.00 1.01 2.03 1.00 5.33 9.09 10.95 3.10 3.10
f1 (ppm)

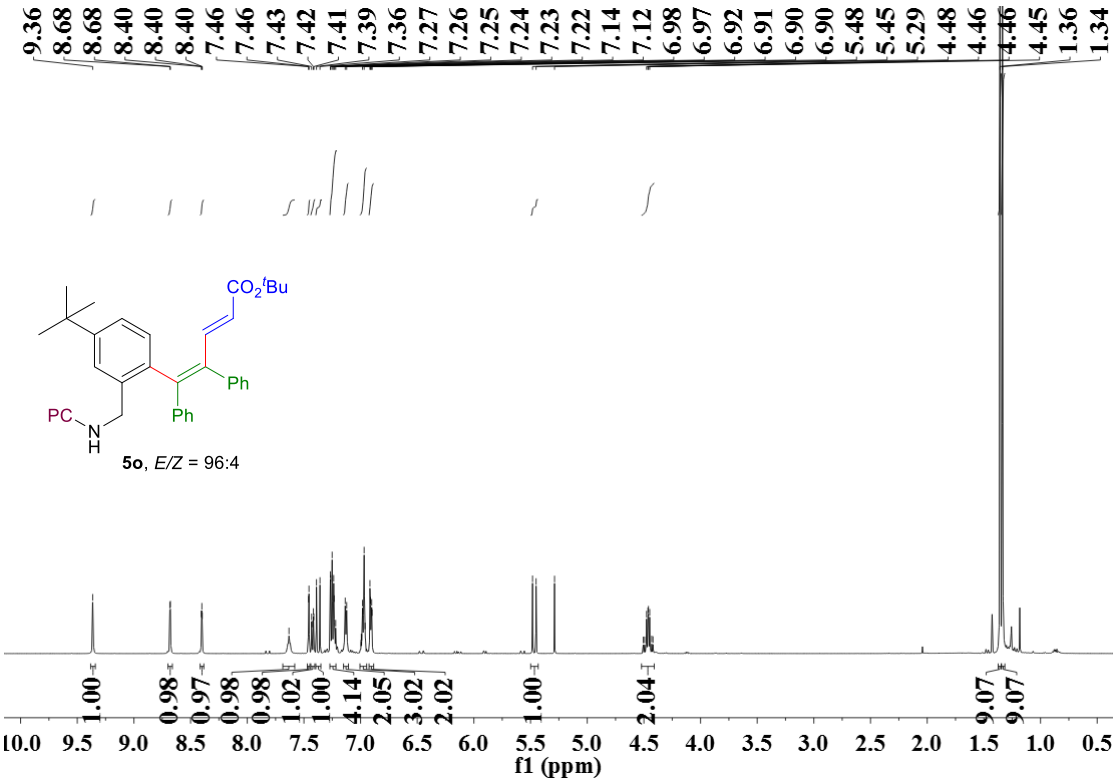

166.50 162.14 147.01 146.24 146.22 144.31 143.93 143.90 142.56 142.46 135.43 129.25 129.17 125.36 125.34 119.11 114.62 114.44 79.87 77.29 77.04 76.78 35.36 35.20 35.17 31.62 31.57 29.76 29.58 29.21 28.04 27.97 22.65 22.52 14.08 14.00
f1 (ppm)

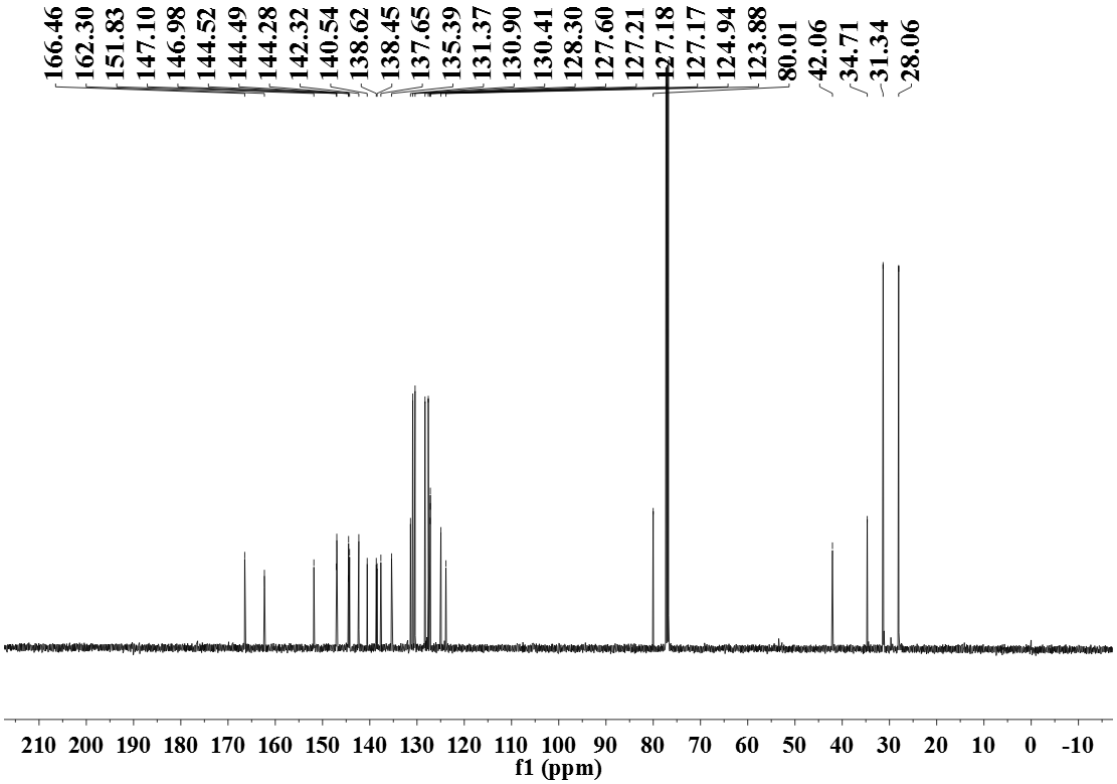

-115.96
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

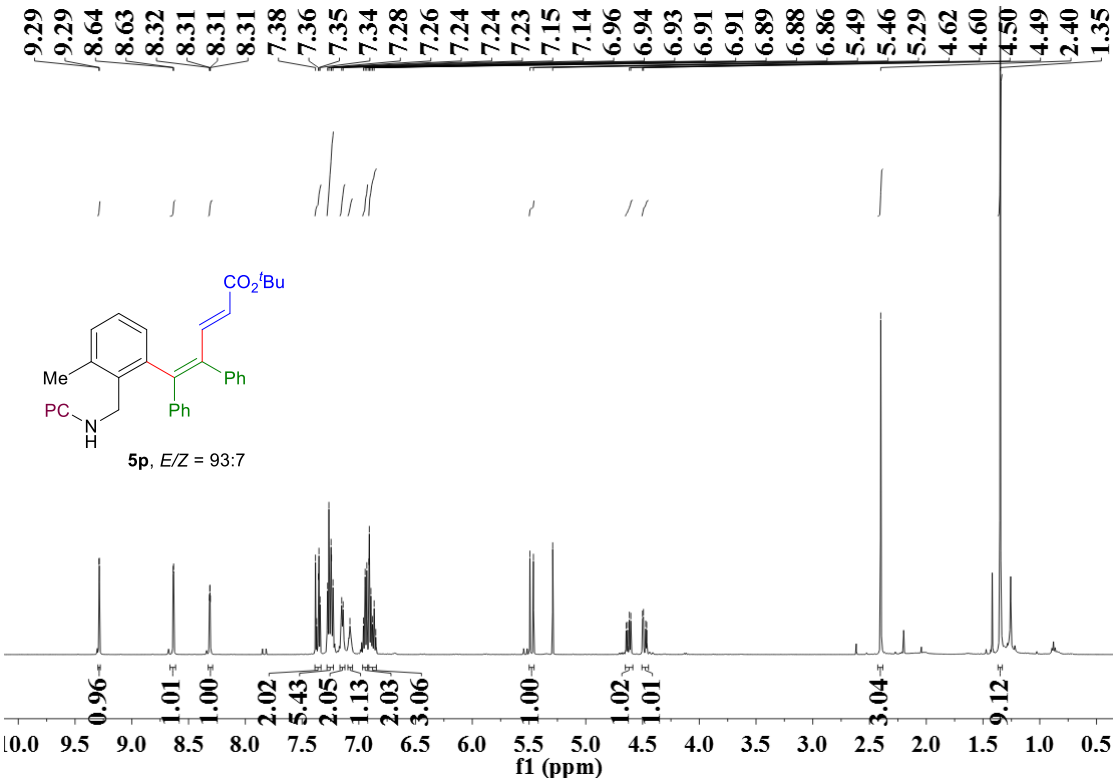

9.38
8.68
8.45
8.06
7.47
7.45
7.44
7.38
7.37
7.37
7.36
7.34
7.30
7.29
7.27
7.12
7.11
7.09
7.03
7.02
5.29
5.18
5.15
4.87
4.86
4.85
4.83
4.65
4.64
4.62
4.61
CO2tBu
F
PC
N
H
Me
5n, E/Z > 99:1
0.99
1.00
1.00
1.00
2.03
2.03
2.02
2.04
1.02
1.00
1.02
1.01
3.03
9.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

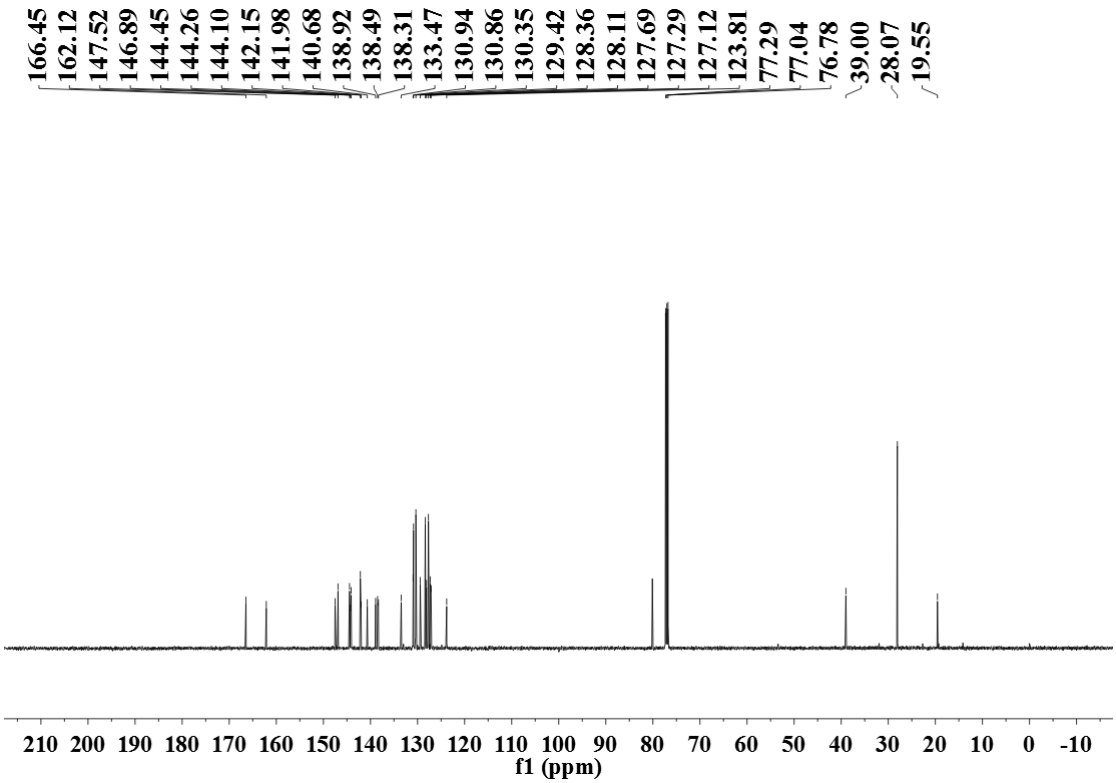

166.35
163.05
162.27
161.09
147.11
144.38
144.33
144.29
142.85
142.83
142.72
142.52
138.32
137.81
129.87
129.80
129.58
128.66
127.39
124.50
124.48
122.80
122.34
122.22
114.90
114.73
79.98
77.30
77.05
76.80
34.97
34.94
28.01
24.08
11.11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

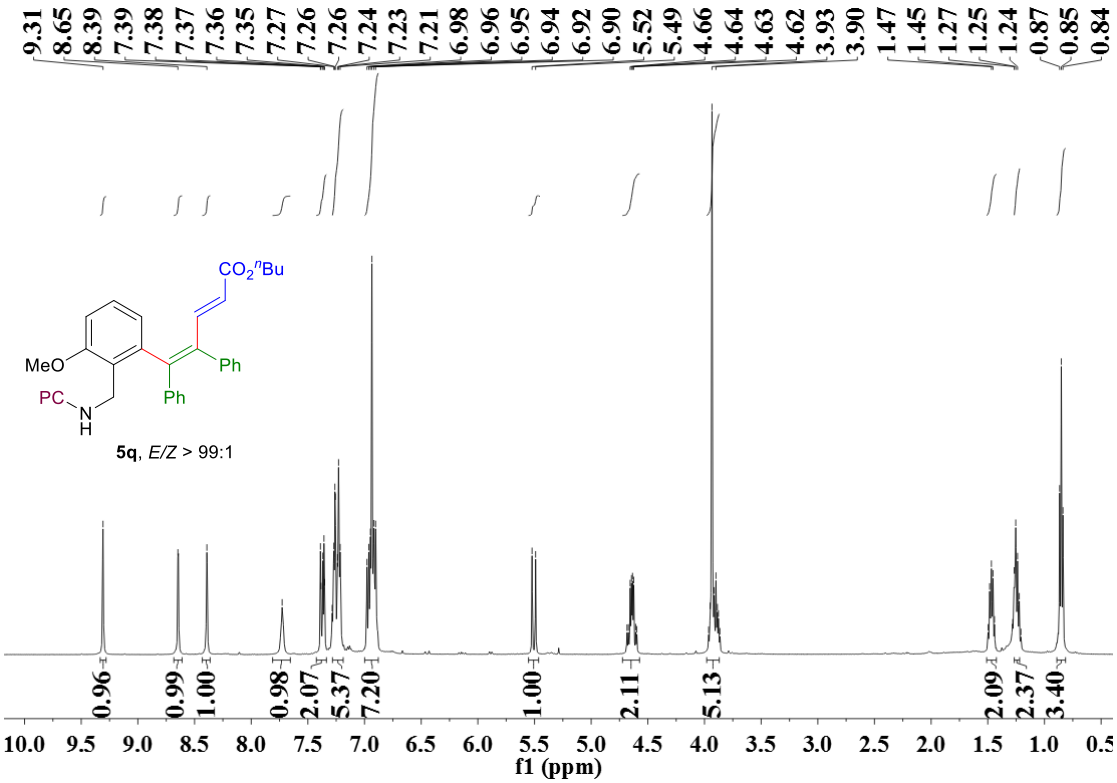

-116.16
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

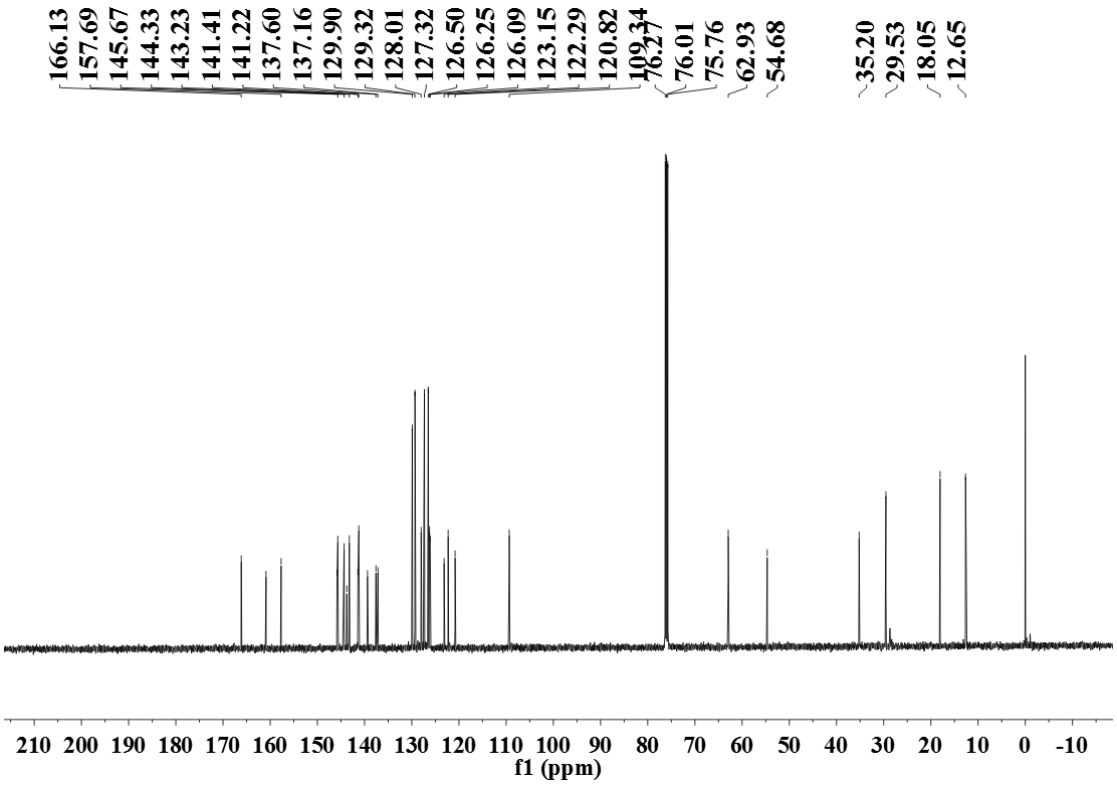

9.36 8.68 8.68 8.40 8.40 8.40 7.46 7.46 7.43 7.42 7.41 7.39 7.36 7.27 7.26 7.25 7.24 7.23 7.22 7.14 7.12 6.98 6.97 6.92 6.91 6.90 6.90 5.48 5.45 5.29 4.48 4.46 4.46 4.45 1.36 1.34
CO2tBu
Ph
Ph
PC
N
H
5o, E/Z = 96:4
1.00 0.98 0.97 0.98 0.98 1.02 1.00 4.14 2.05 3.02 2.02 1.00 2.04 9.07 9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

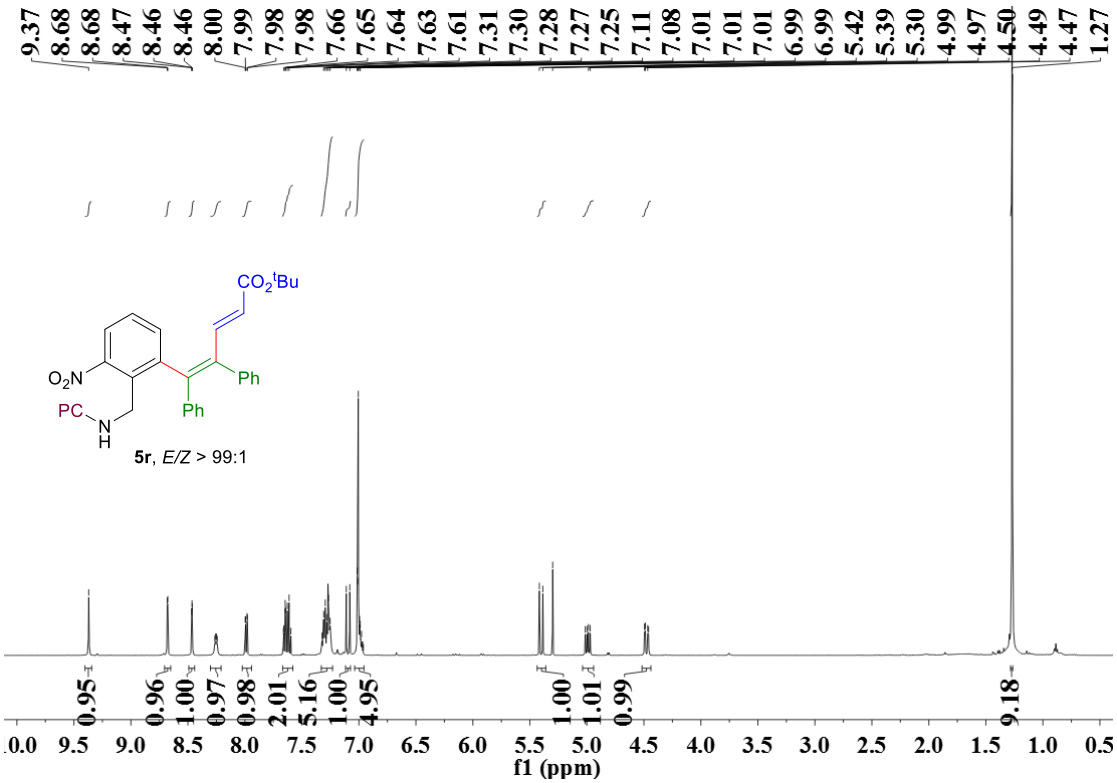

166.46 162.30 151.83 147.10 146.98 144.52 144.49 144.28 142.32 140.54 138.62 138.45 137.65 135.39 131.37 130.90 130.41 128.30 127.60 127.21 127.18 127.17 124.94 123.88 80.01 42.06 34.71 31.34 28.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

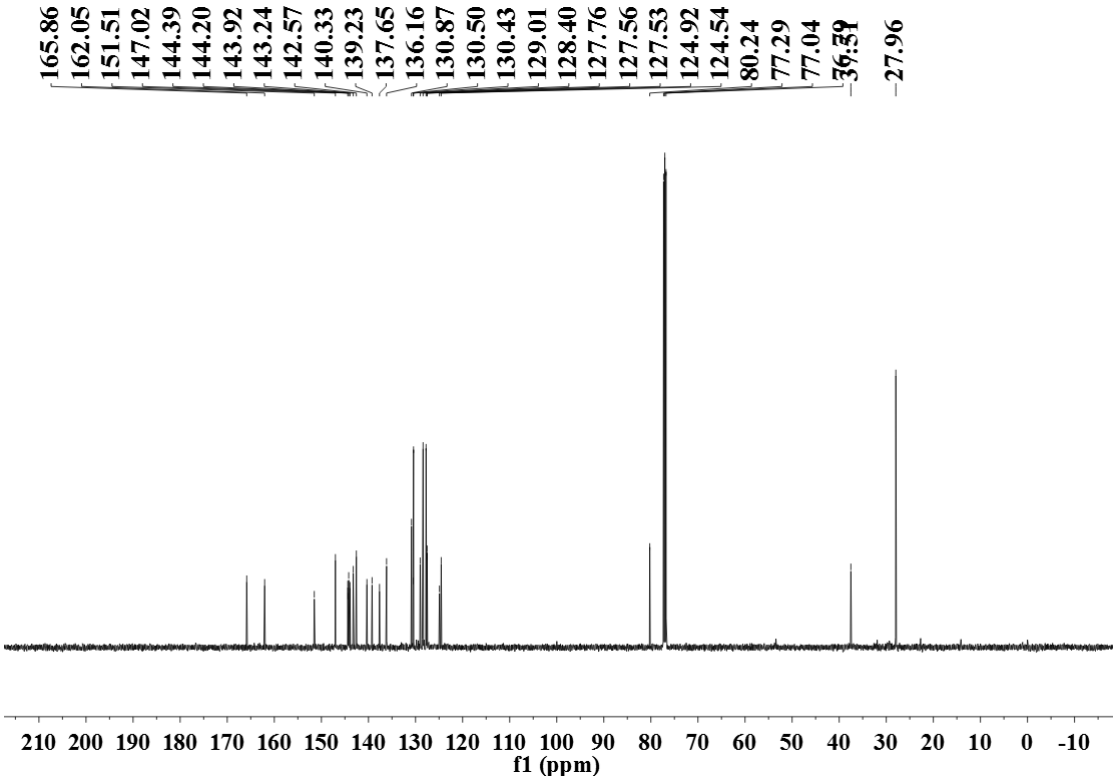

9.29 9.29 8.64 8.63 8.32 8.31 8.31 8.31 7.38 7.36 7.35 7.34 7.28 7.26 7.24 7.24 7.23 7.15 7.14 6.96 6.94 6.93 6.91 6.91 6.89 6.88 6.86 5.49 5.46 5.29 4.62 4.60 4.50 4.49 2.40 1.35
CO2tBu
Me
Ph
PC
N
H
Ph
5p, E/Z = 93:7
0.96 1.01 1.00 2.02 5.43 2.05 1.13 2.03 3.06 1.00 1.02 1.01 3.04 9.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

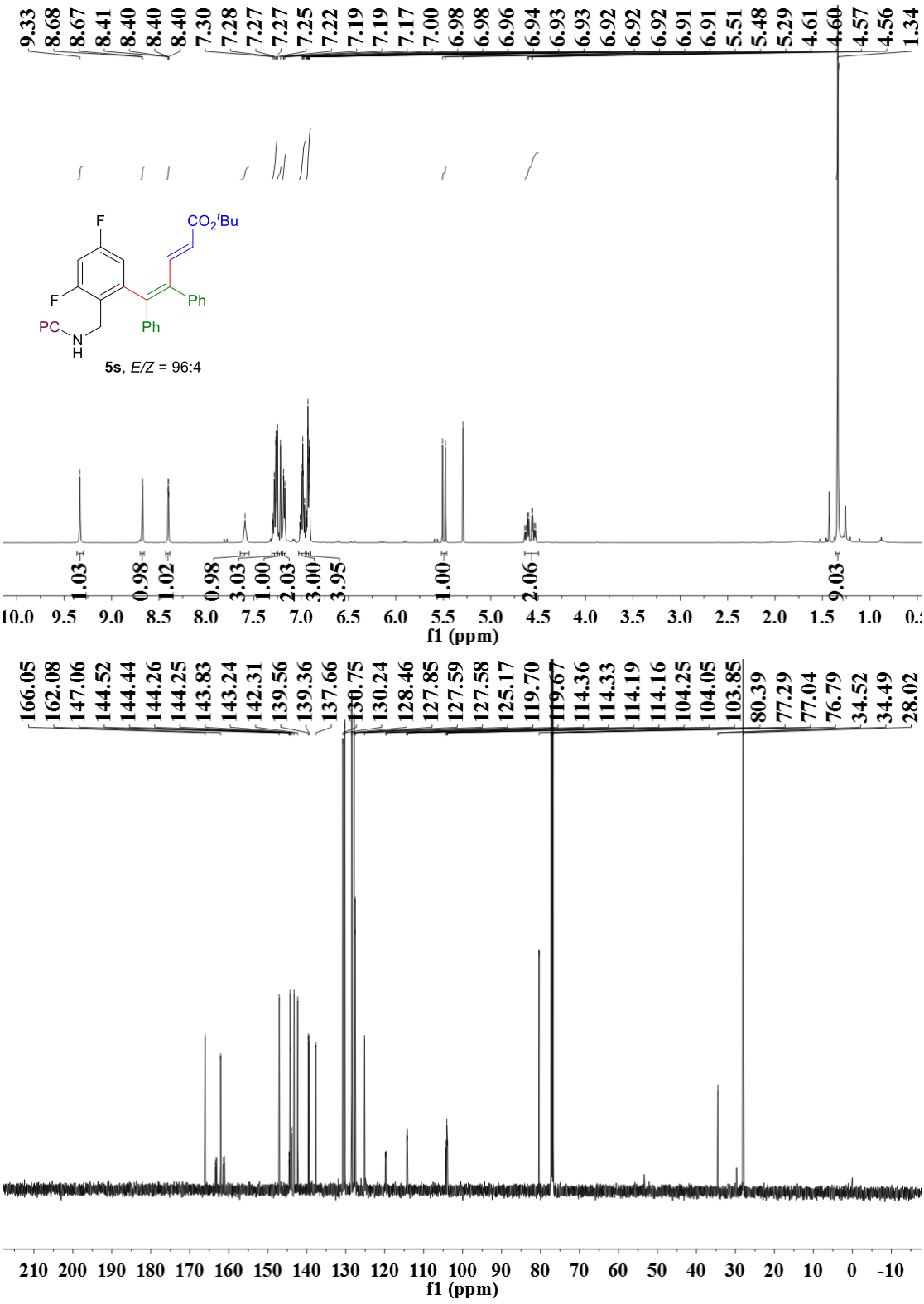

166.45 162.12 147.52 146.89 144.45 144.26 144.10 142.15 141.98 140.68 138.92 138.49 138.31 133.47 130.94 130.86 130.35 129.42 128.36 128.11 127.69 127.29 127.12 123.81 77.29 77.04 76.78 39.00 28.07 19.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

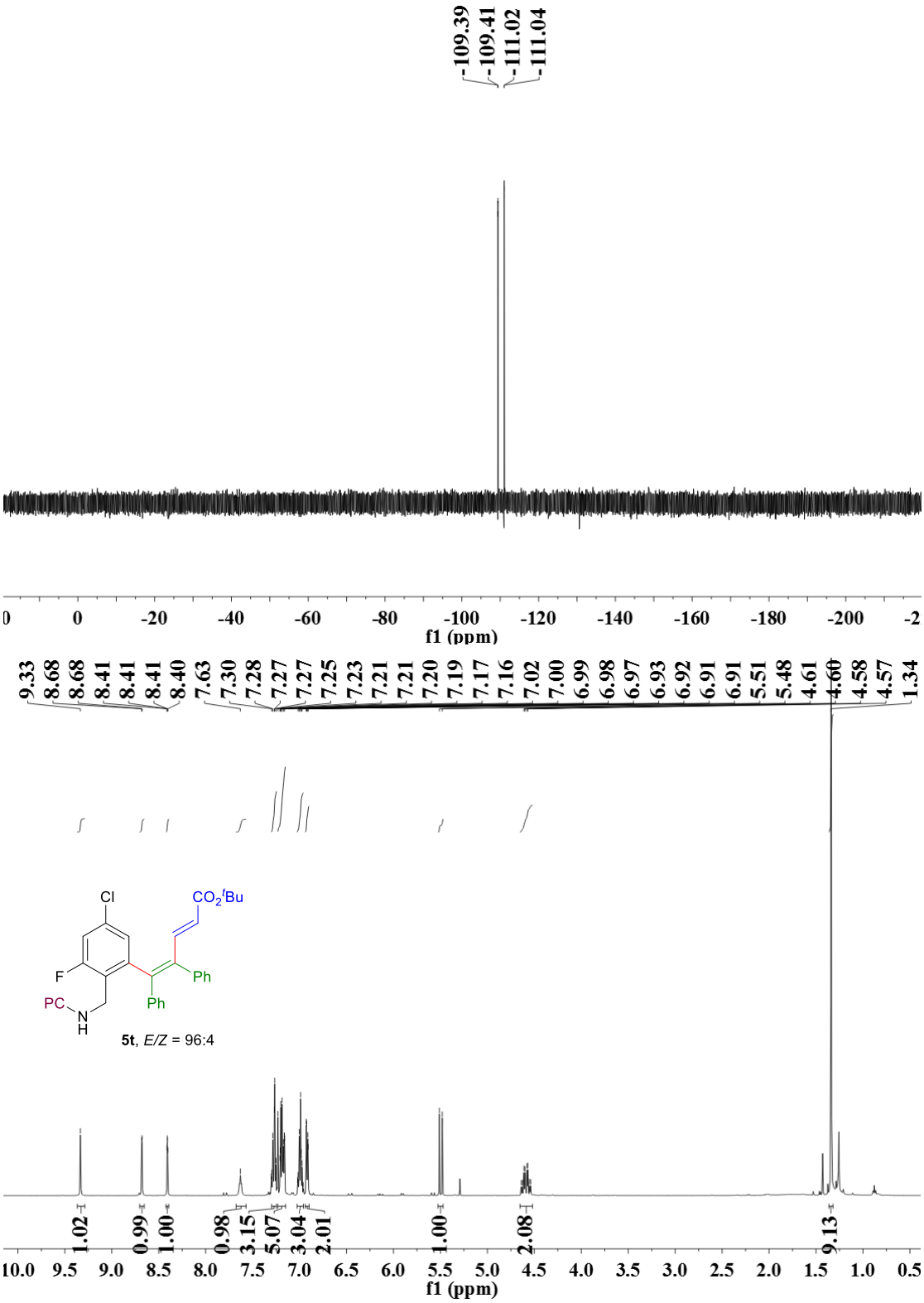

9.31 8.65 8.39 7.39 7.38 7.37 7.36 7.35 7.27 7.26 7.26 7.24 7.23 7.21 6.98 6.96 6.95 6.94 6.92 6.90 5.52 5.49 4.66 4.64 4.63 4.62 3.93 3.90 1.47 1.45 1.27 1.25 1.24 0.87 0.85 0.84
CO2nBu
MeO
Ph
PC
N
H
Ph
5q, E/Z > 99:1
0.96 0.99 1.00 0.98 2.07 5.37 7.20 1.00 2.11 5.13 2.09 2.37 3.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

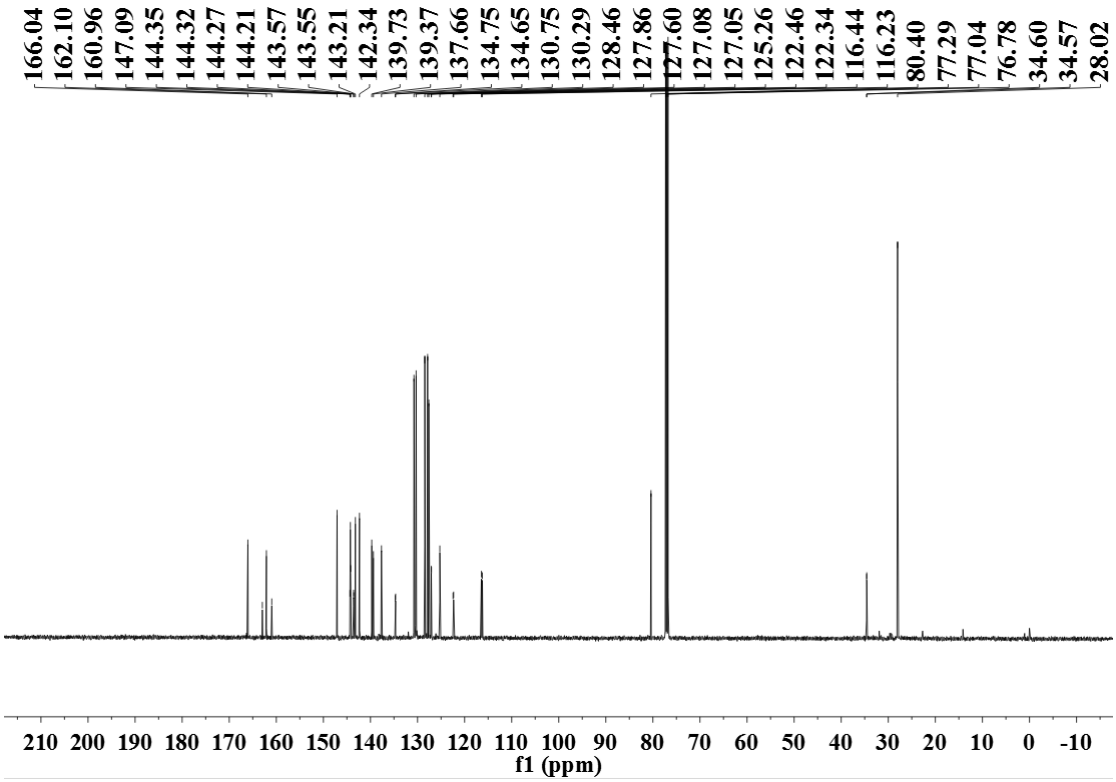

166.13 157.69 145.67 144.33 143.23 141.41 141.22 137.60 137.16 129.90 129.32 128.01 127.32 126.50 126.25 126.09 123.15 122.29 120.82 109.34 76.27 76.01 75.76 62.93 54.68 35.20 29.53 18.05 12.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

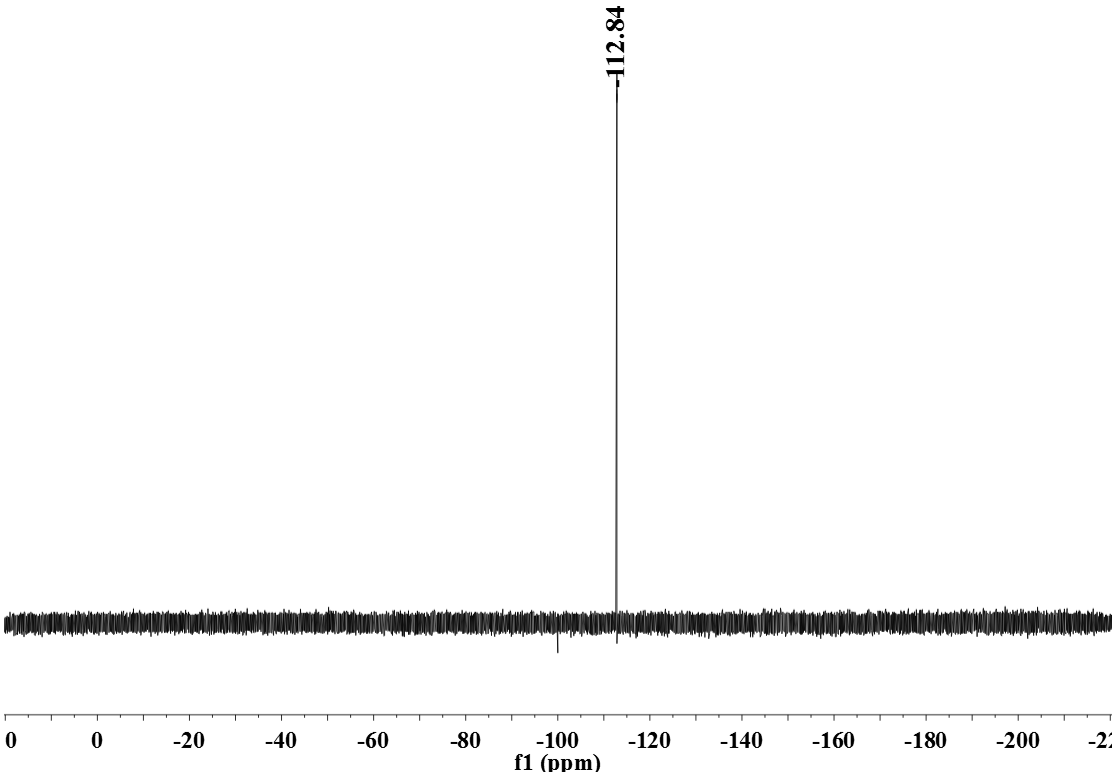

9.37 8.68 8.68 8.47 8.46 8.46 8.00 7.99 7.98 7.98 7.66 7.65 7.64 7.63 7.61 7.31 7.30 7.28 7.27 7.25 7.11 7.08 7.01 7.01 7.01 6.99 6.99 5.42 5.39 5.30 4.99 4.97 4.50 4.49 4.47 1.27
CO2tBu
O2N
PC
N
H
Ph
Ph
5r, E/Z > 99:1
0.95 0.96 1.00 0.97 0.98 2.01 5.16 1.00 4.95 1.00 1.01 0.99 9.18
f1 (ppm)

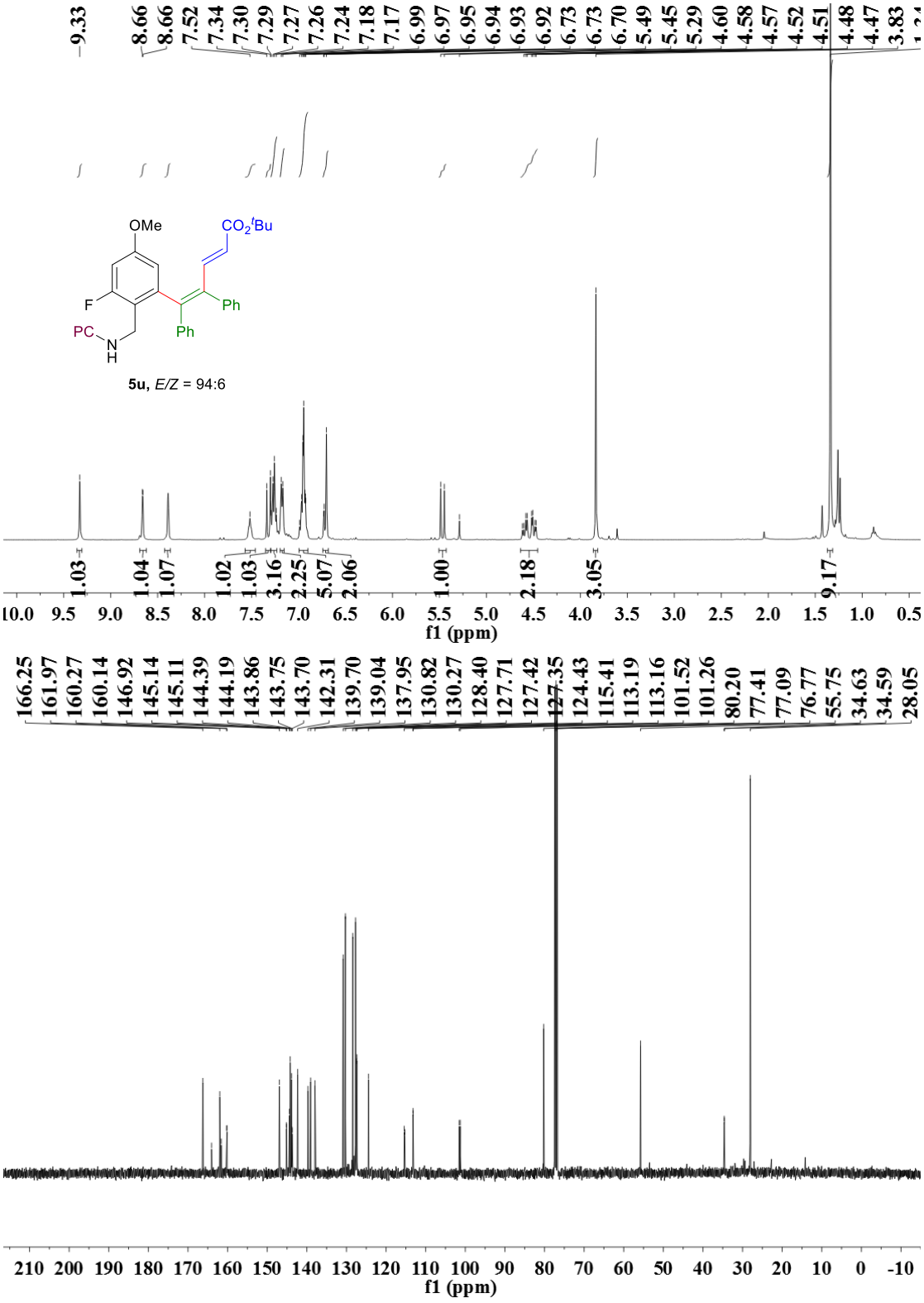

165.86 162.05 151.51 147.02 144.39 144.20 143.92 143.24 142.57 140.33 139.23 137.65 136.16 130.87 130.50 130.43 129.01 128.40 127.76 127.56 127.53 124.92 124.54 80.24 77.29 77.04 27.96
f1 (ppm)

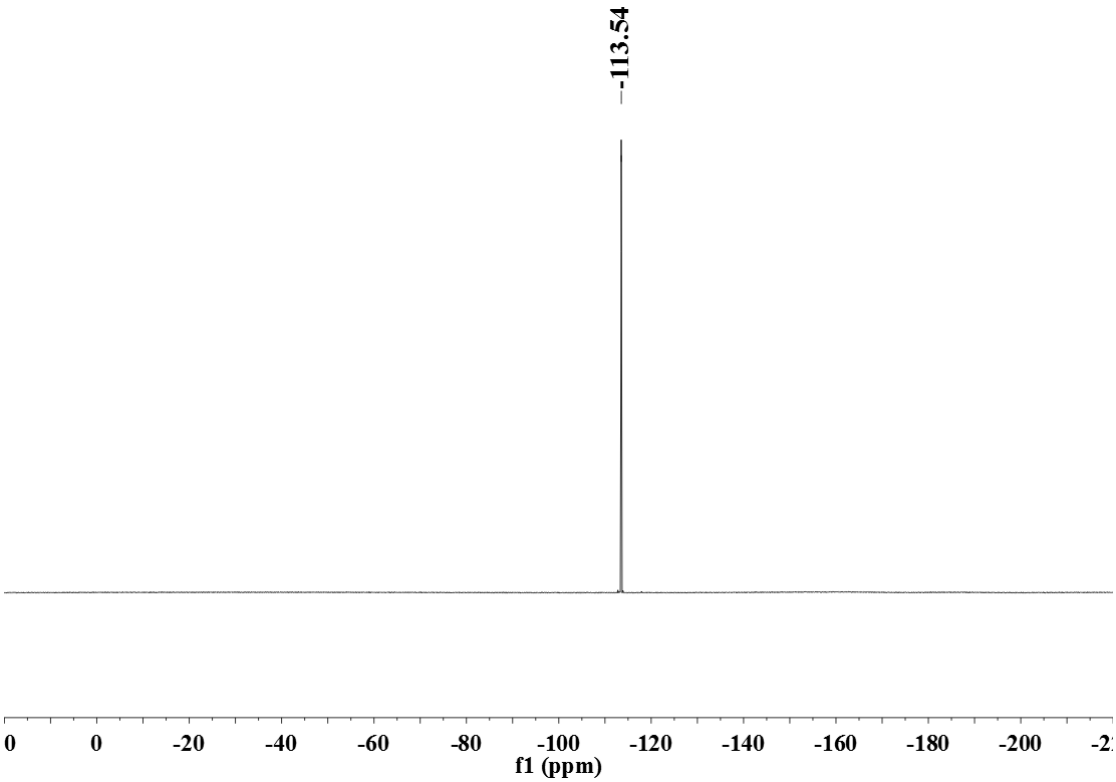

9.33 8.68 8.67 8.41 8.40 8.40 8.40 7.30 7.28 7.27 7.27 7.25 7.22 7.19 7.19 7.17 7.00 6.98 6.98 6.96 6.94 6.93 6.93 6.92 6.92 6.92 6.91 6.91 5.51 5.48 5.29 4.61 4.60 4.57 4.56 1.34
F
CO2tBu
F
Ph
PC
N
H
Ph
5s, E/Z = 96:4
1.03 0.98 1.02 0.98 3.03 1.00 2.03 3.00 3.95 1.00 2.06 9.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)
166.05 162.08 147.06 144.52 144.44 144.26 144.25 143.83 143.24 142.31 139.56 139.36 137.66 130.75 130.24 128.46 127.85 127.59 127.58 125.17 119.70 119.67 114.36 114.33 114.19 114.16 104.25 104.05 103.85 80.39 77.29 77.04 76.79 34.52 34.49 28.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

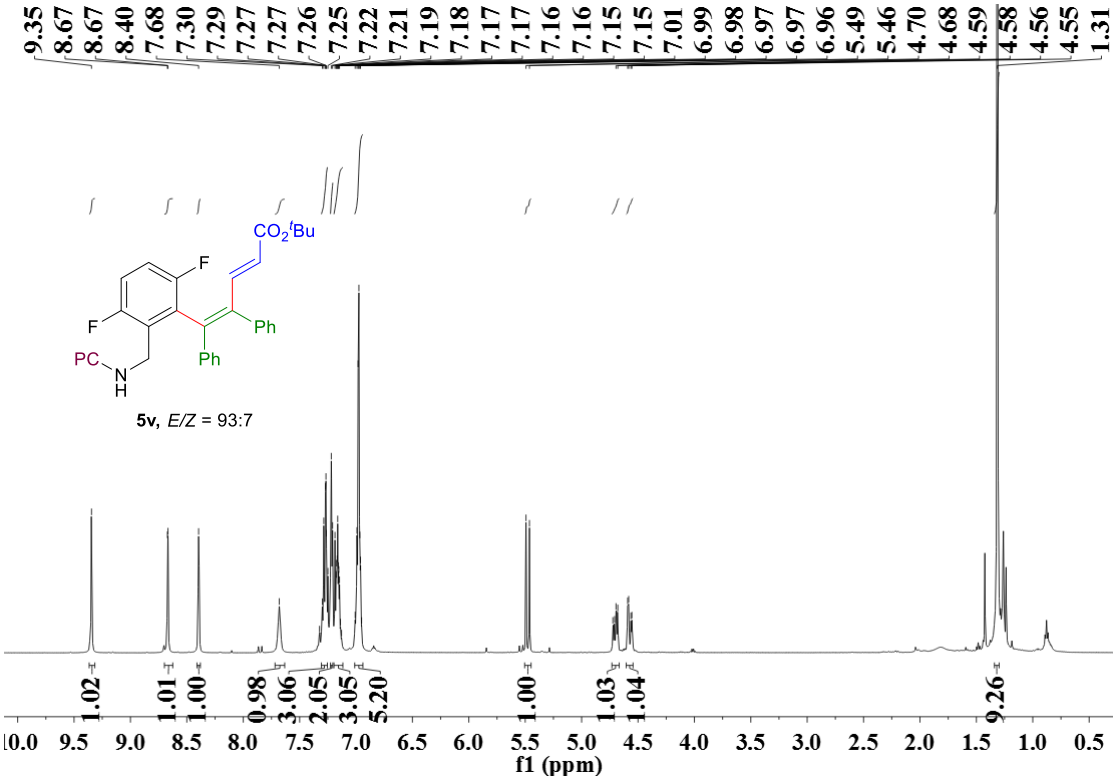

-109.39
-109.41
-111.02
-111.04
f1 (ppm)
9.33
8.68
8.68
8.41
8.41
8.41
8.40
7.63
7.30
7.28
7.27
7.27
7.25
7.23
7.21
7.21
7.20
7.19
7.17
7.16
7.02
7.00
6.99
6.98
6.97
6.93
6.92
6.91
6.91
5.51
5.48
4.61
4.60
4.58
4.57
1.34
Cl
CO2tBu
F
Ph
PC
N
H
Ph
5t, E/Z = 96:4
1.02
0.99
1.00
0.98
3.15
5.07
3.04
2.01
1.00
2.08
9.13
f1 (ppm)

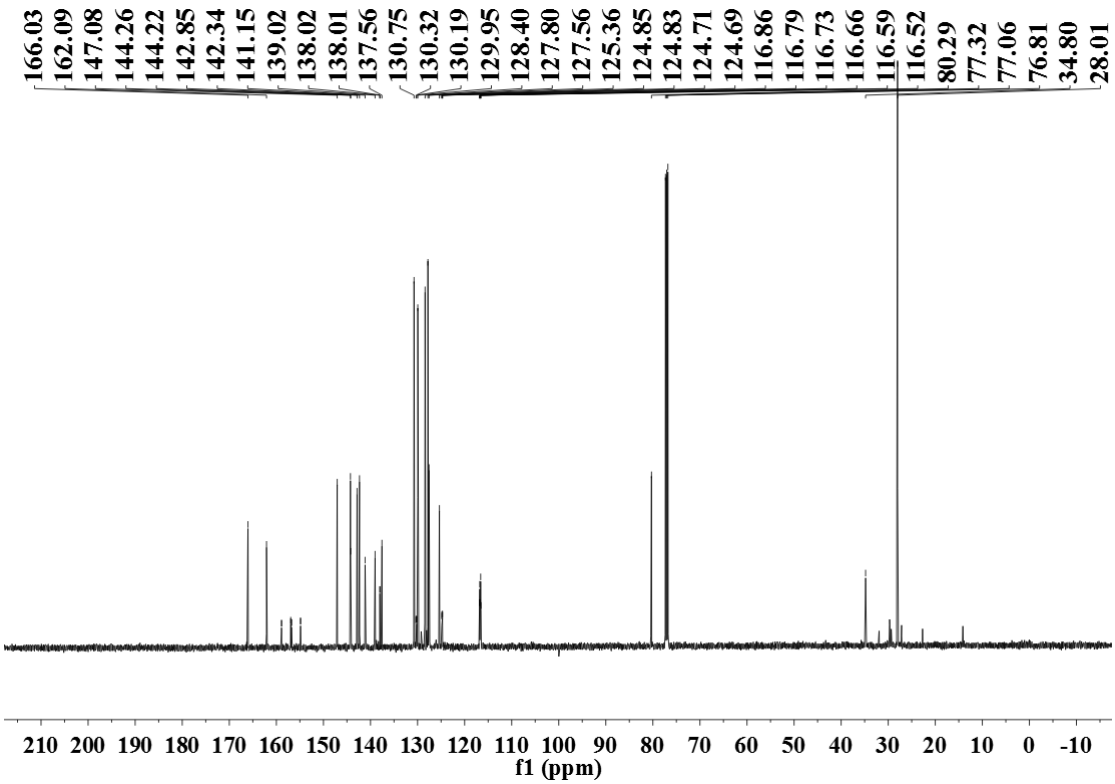

166.04
162.10
160.96
147.09
144.35
144.32
144.27
144.21
143.57
143.55
143.21
142.34
139.73
139.37
137.66
134.75
134.65
130.75
130.29
128.46
127.86
127.60
127.08
127.05
125.26
122.46
122.34
116.44
116.23
80.40
77.29
77.04
76.78
34.60
34.57
28.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

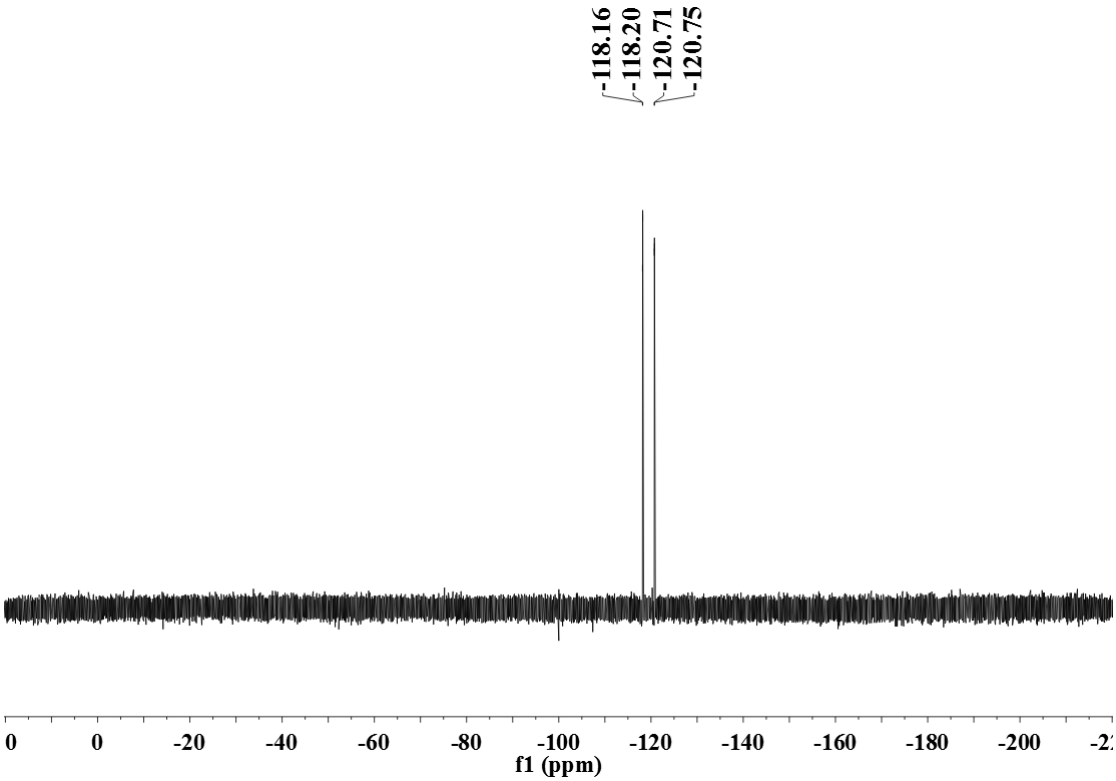

-112.84
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

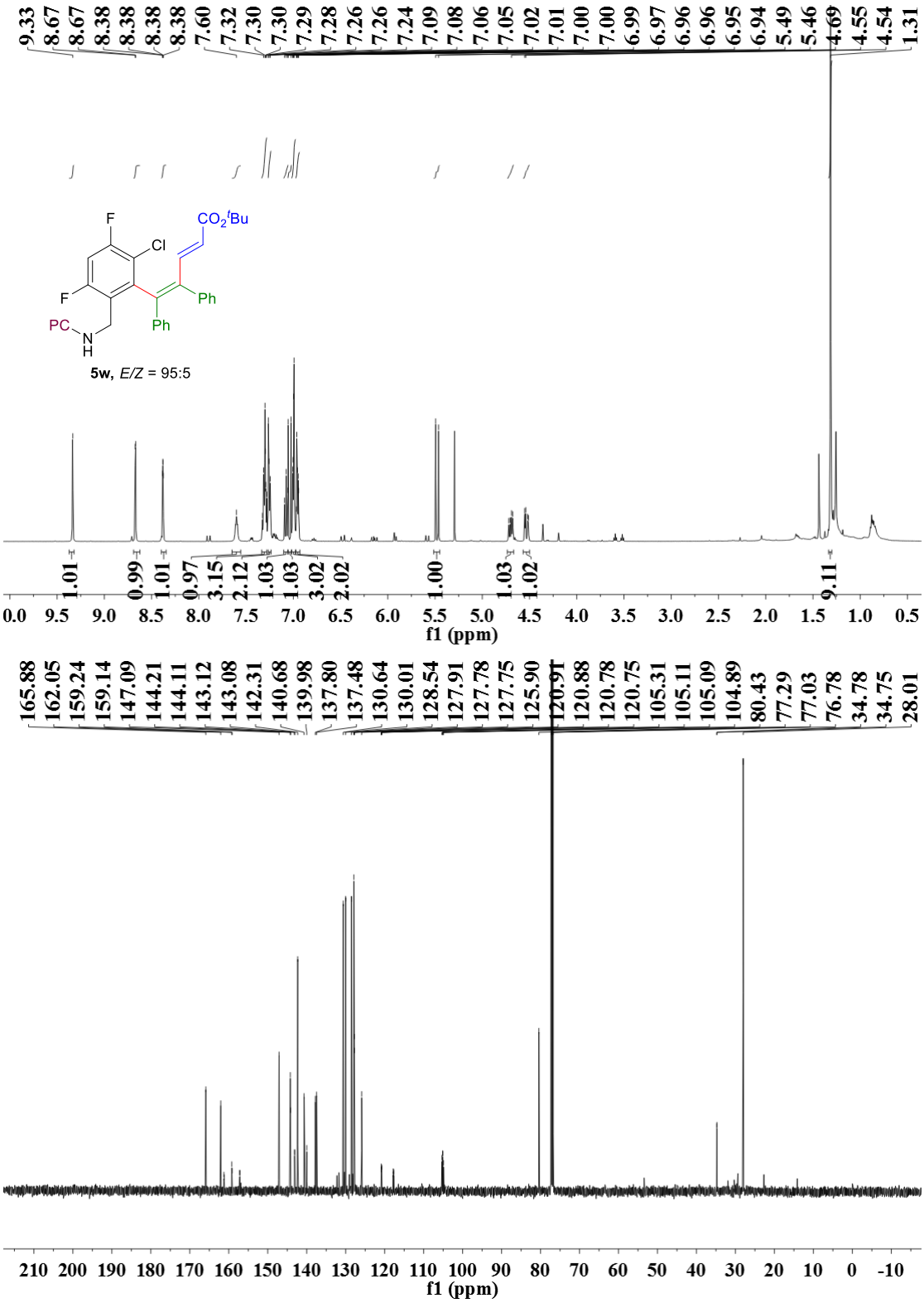

OMe
CO2tBu
F
Ph
PC
N
H
Ph
5u, E/Z = 94:6
f1 (ppm)
f1 (ppm)

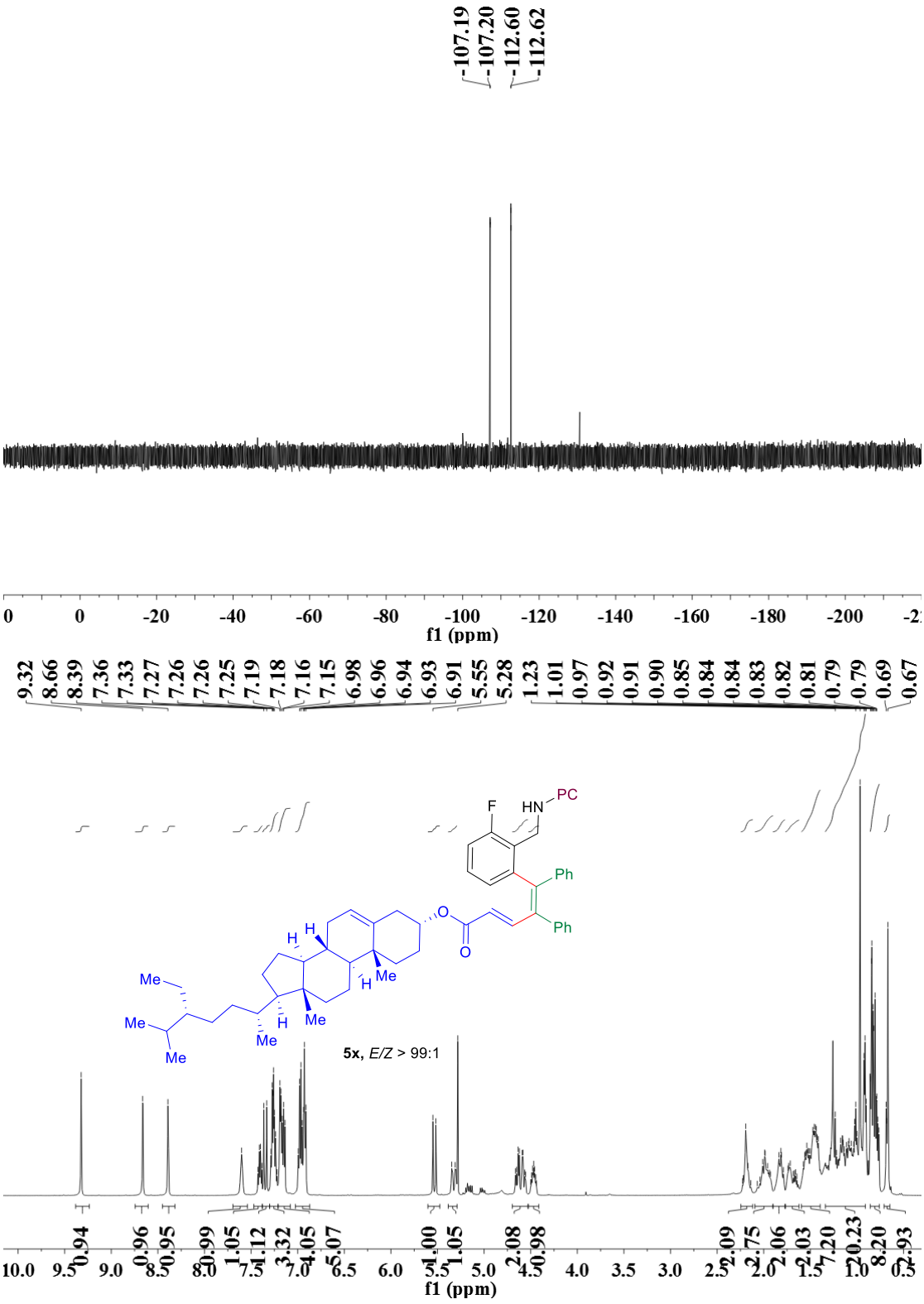

-113.54
0
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

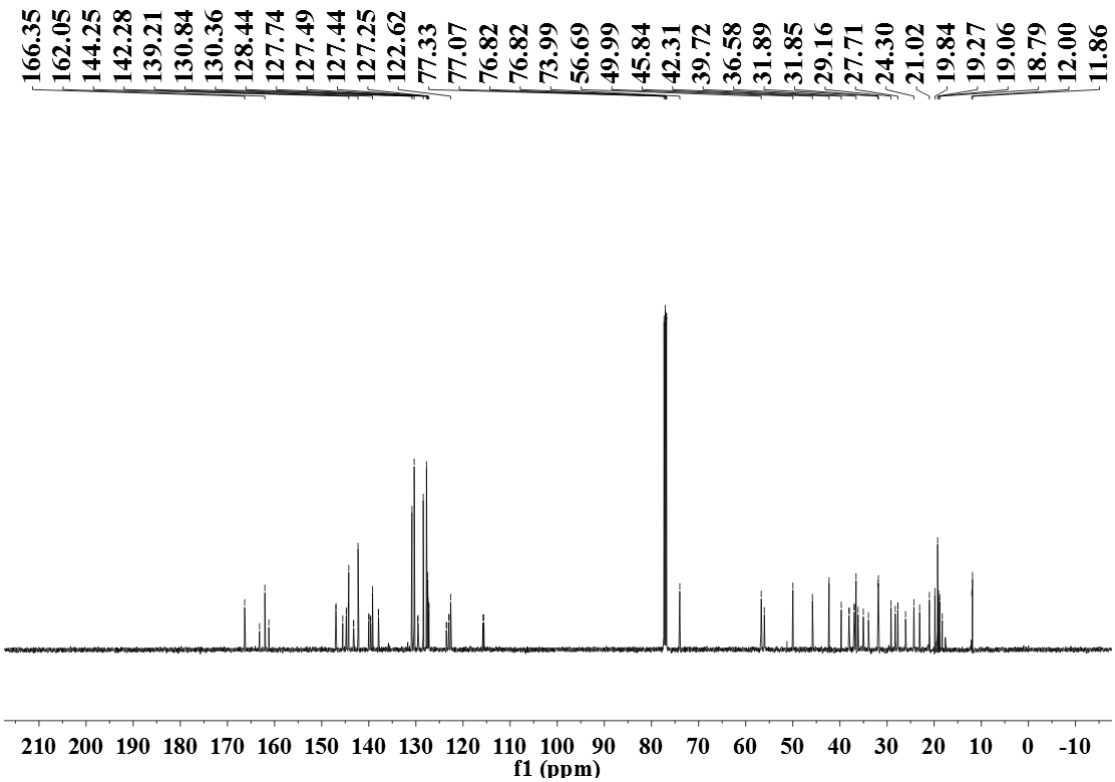

9.35
8.67
8.67
8.40
7.68
7.30
7.29
7.27
7.27
7.26
7.25
7.22
7.21
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.01
6.99
6.98
6.97
6.97
6.96
5.49
5.46
4.70
4.68
4.59
4.58
4.56
4.55
1.31
CO2tBu
F
F
Ph
Ph
PC
N
H
5v, E/Z = 93:7
1.02
1.01
1.00
0.98
3.06
2.05
3.05
5.20
1.00
1.03
1.04
9.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

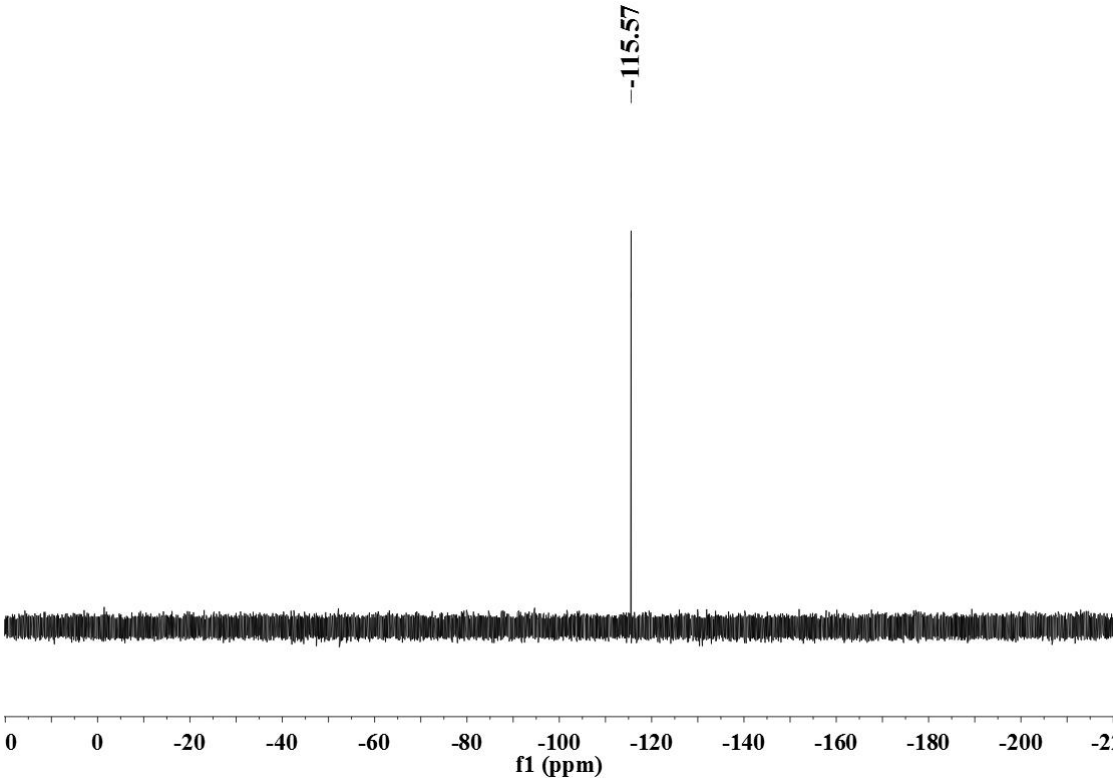

166.03
162.09
147.08
144.26
144.22
142.85
142.34
141.15
139.02
138.02
138.01
137.56
130.75
130.32
130.19
129.95
128.40
127.80
127.56
125.36
124.85
124.83
124.71
124.69
116.86
116.79
116.73
116.66
116.59
116.52
80.29
77.32
77.06
76.81
34.80
28.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

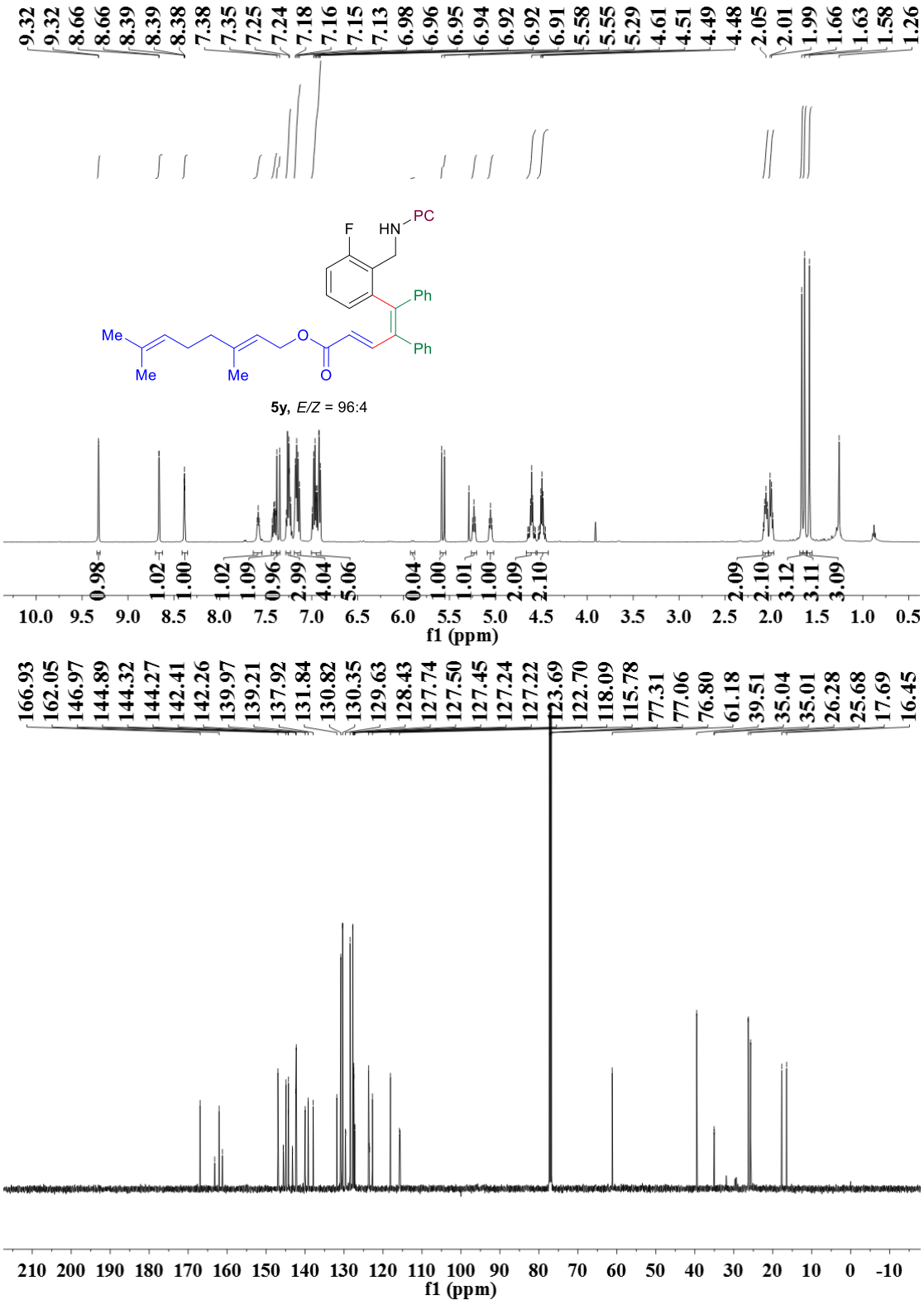

-118.16
-118.20
-120.71
-120.75
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

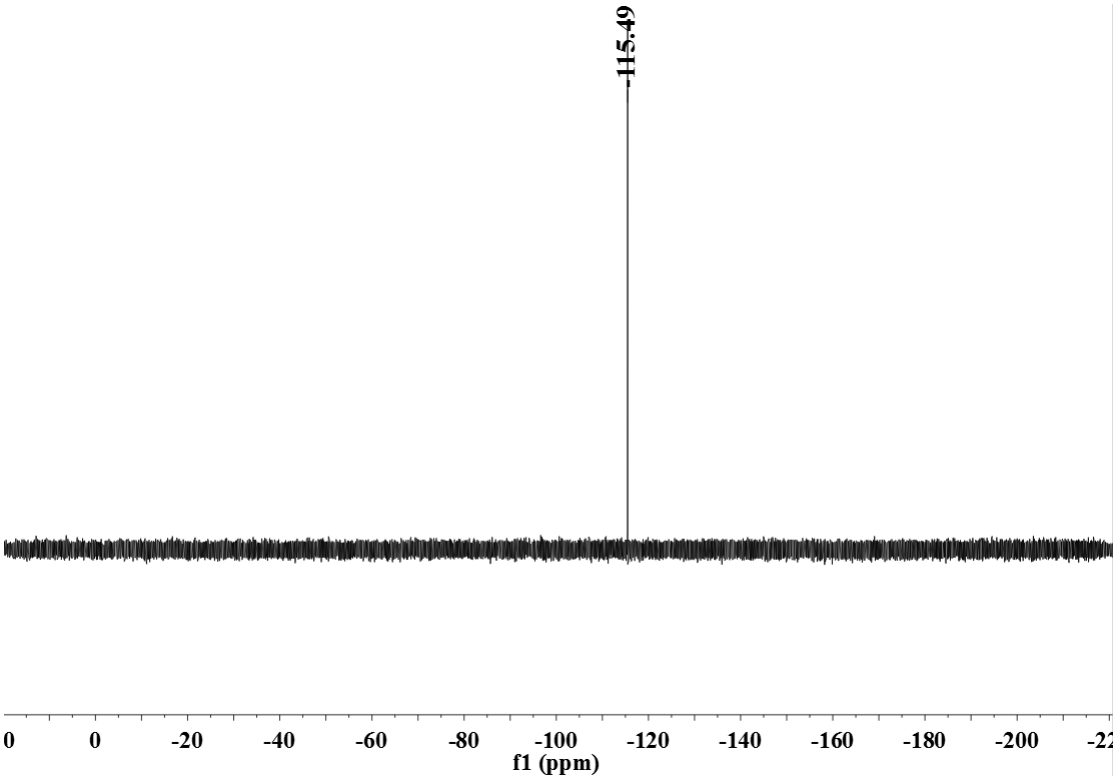

9.33 8.67 8.67 8.38 8.38 8.38 8.38 7.60 7.32 7.30 7.30 7.29 7.28 7.26 7.26 7.24 7.09 7.08 7.06 7.05 7.02 7.01 7.00 7.00 6.99 6.97 6.96 6.96 6.95 6.94 5.49 5.46 4.69 4.55 4.54 1.31
F
Cl
F
CO2tBu
Ph
Ph
PC
N
H
5w, E/Z = 95:5
1.01 0.99 1.01 0.97 3.15 2.12 1.03 1.03 3.02 2.02 1.00 1.03 1.02 9.11
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
165.88 162.05 159.24 159.14 147.09 144.21 144.11 143.12 143.08 142.31 140.68 139.98 137.80 137.48 130.64 130.01 128.54 127.91 127.78 127.75 125.90 120.91 120.88 120.78 120.75 105.31 105.11 105.09 104.89 80.43 77.29 77.03 76.78 34.78 34.75 28.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

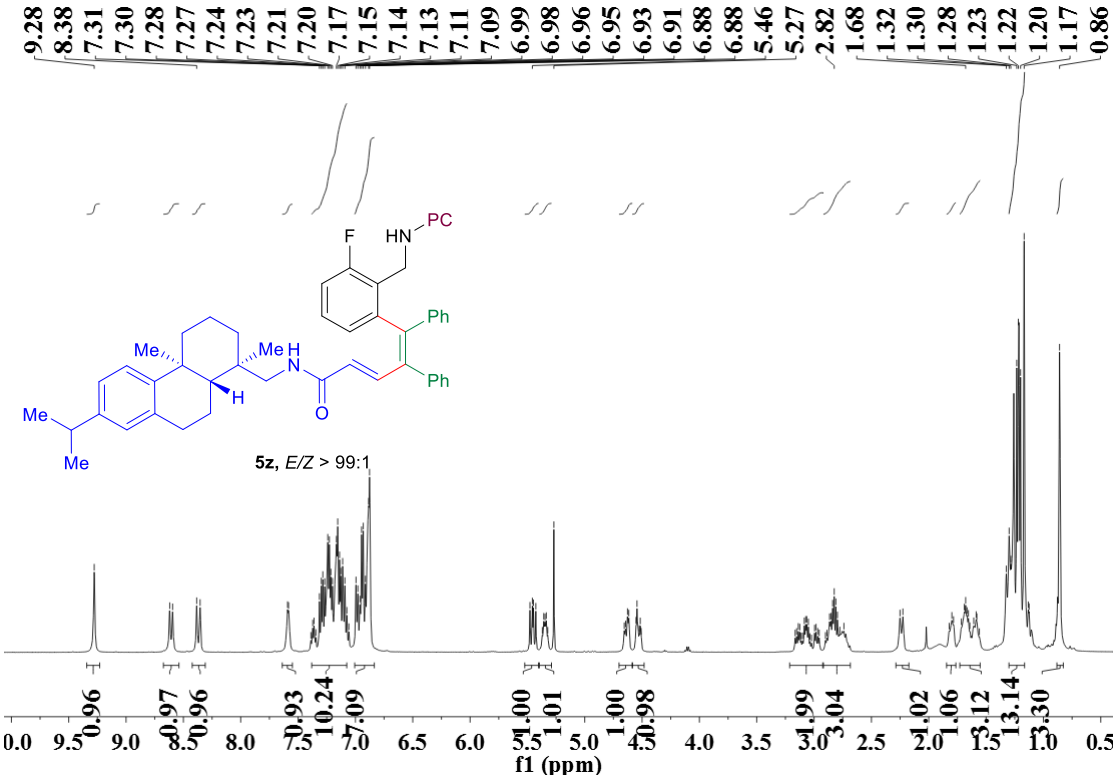

-107.19
-107.20
-112.60
-112.62
f1 (ppm)
9.32 8.66 8.39 7.36 7.33 7.27 7.26 7.26 7.25 7.19 7.18 7.16 7.15 6.98 6.96 6.94 6.93 6.91 5.55 5.28 1.23 1.01 0.97 0.92 0.91 0.90 0.85 0.84 0.84 0.83 0.82 0.81 0.79 0.79 0.69 0.67
F
HN
PC
Ph
Ph
O
O
H
H
H
Me
Me
Me
Me
Me
Me
5x, E/Z > 99:1
0.94 0.96 0.95 0.99 1.05 1.12 3.32 4.05 5.07 1.00 1.05 2.08 0.98 2.09 2.75 2.06 2.03 7.20 0.23 8.20 2.93
f1 (ppm)

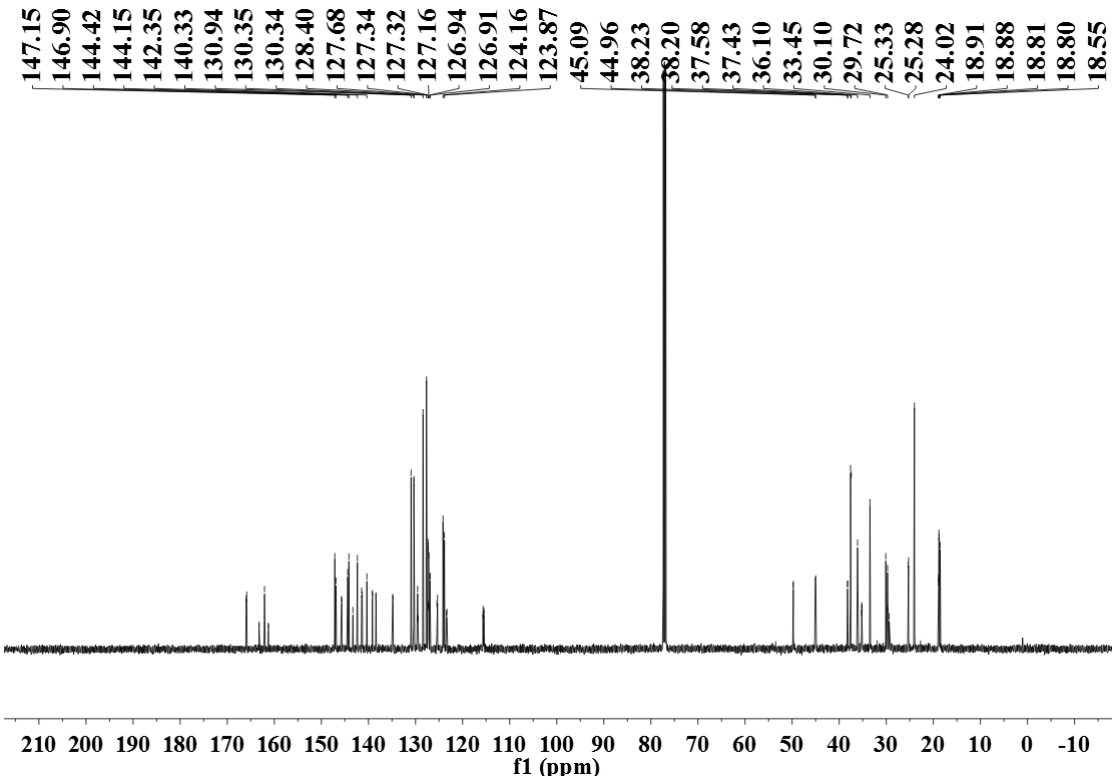

166.35
162.05
144.25
142.28
139.21
130.84
130.36
128.44
127.74
127.49
127.44
127.25
122.62
77.33
77.07
76.82
76.82
73.99
56.69
49.99
45.84
42.31
39.72
36.58
31.89
31.85
29.16
27.71
24.30
21.02
19.84
19.27
19.06
18.79
12.00
11.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

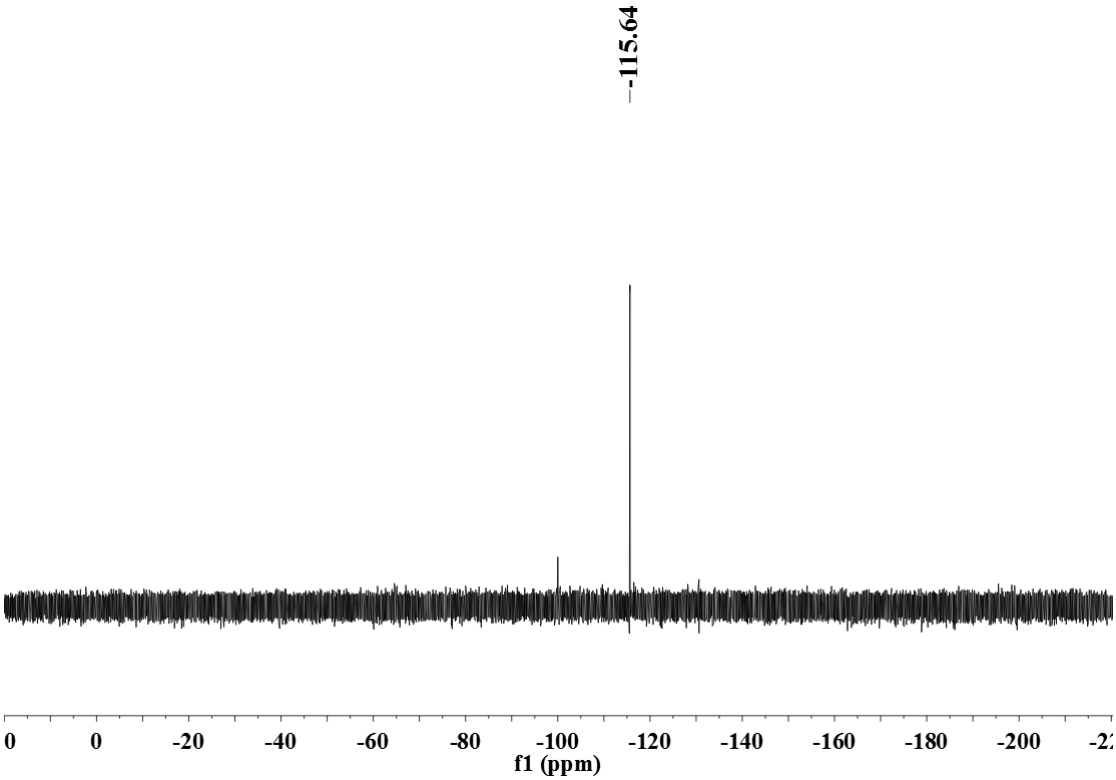

-115.57
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

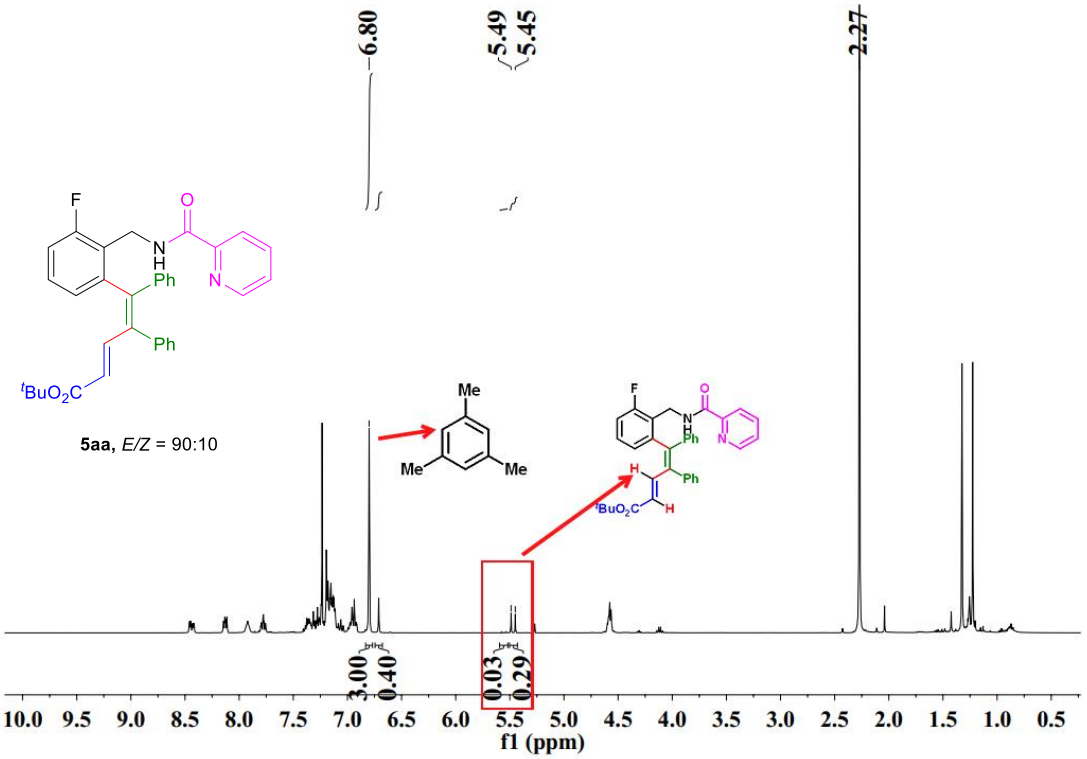

9.32 9.32 8.66 8.66 8.39 8.39 8.38 7.38 7.35 7.25 7.24 7.18 7.16 7.15 7.13 6.98 6.96 6.95 6.94 6.92 6.92 6.91 5.58 5.55 5.29 4.61 4.51 4.49 4.48 2.05 2.01 1.99 1.66 1.63 1.58 1.26
F
HN
PC
Ph
Ph
Me
Me
Me
O
O
5y, E/Z = 96:4
0.98 1.02 1.00 1.02 1.09 0.96 2.99 4.04 5.06 0.04 1.00 1.01 1.00 2.09 2.10 2.09 2.10 3.12 3.11 3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
166.93 162.05 146.97 144.89 144.32 144.27 142.41 142.26 139.97 139.21 137.92 131.84 130.82 130.35 129.63 128.43 127.74 127.50 127.45 127.24 127.22 123.69 122.70 118.09 115.78 77.31 77.06 76.80 61.18 39.51 35.04 35.01 26.28 25.68 17.69 16.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

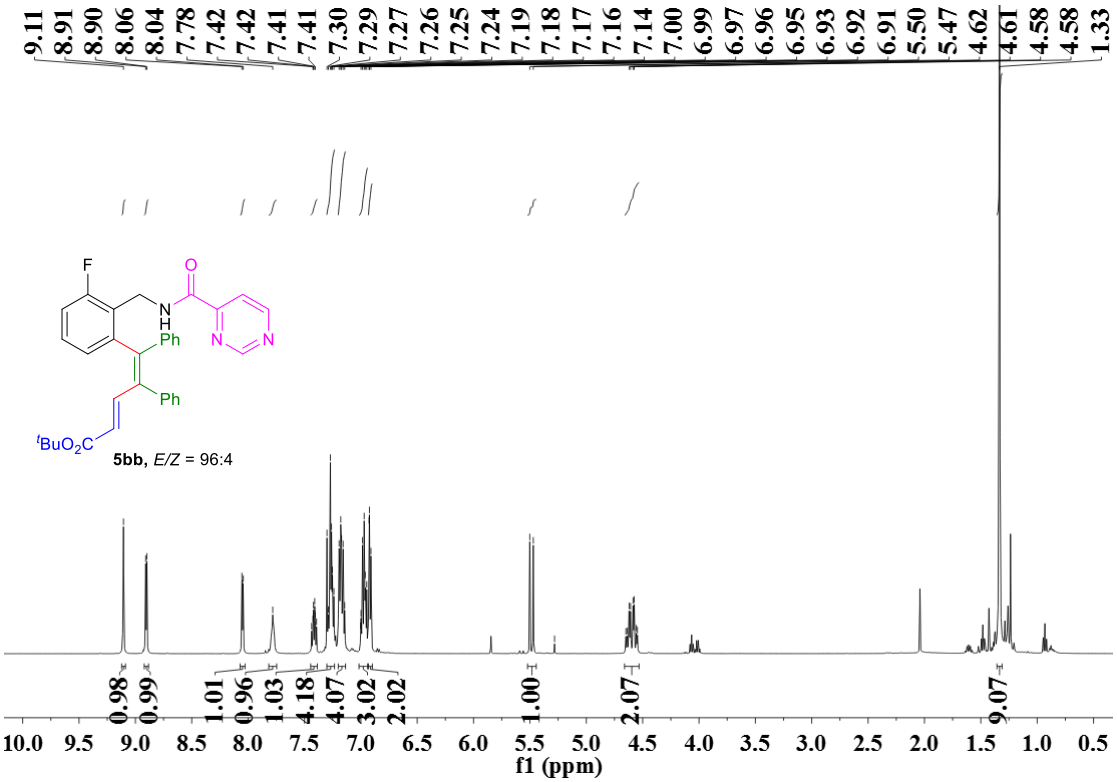

-115.49
f1 (ppm)

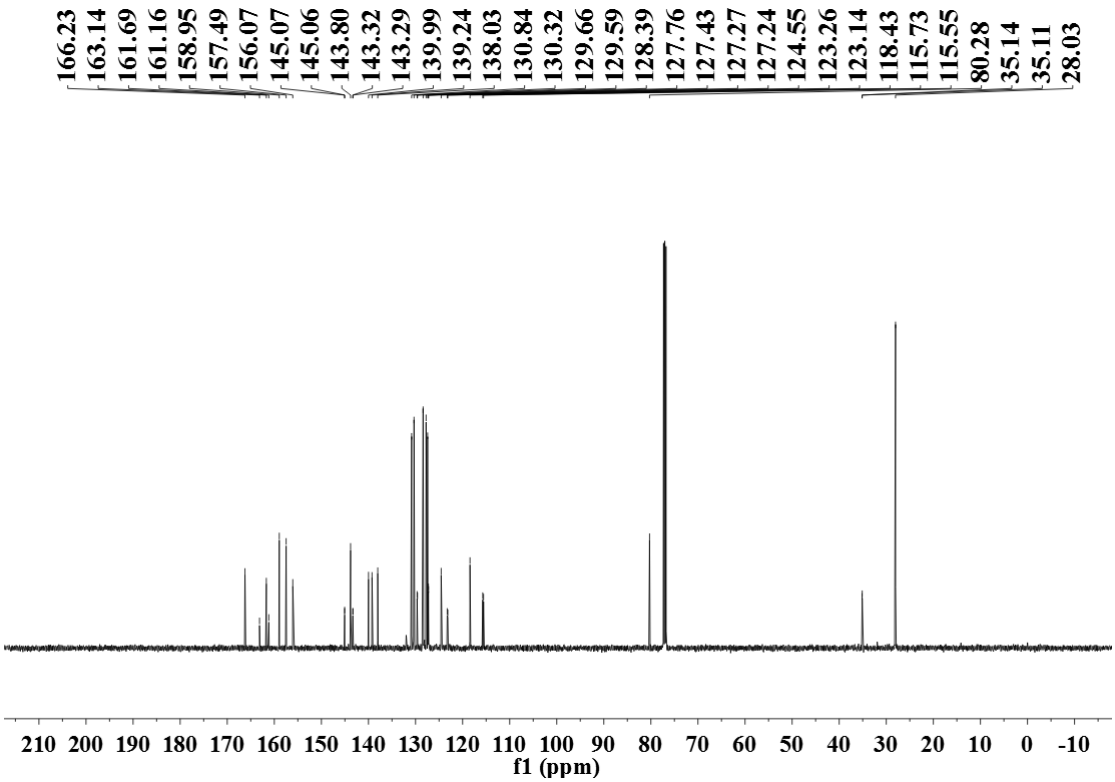

9.28
8.38
7.31
7.30
7.28
7.27
7.24
7.23
7.21
7.20
7.17
7.15
7.14
7.13
7.11
7.09
6.99
6.98
6.96
6.95
6.93
6.91
6.88
6.88
5.46
5.27
2.82
1.68
1.32
1.30
1.28
1.23
1.22
1.20
1.17
0.86
F
HN
PC
Ph
Ph
Me
Me
H
N
H
O
Me
Me
5z, E/Z > 99:1
0.96
0.97
0.96
0.93
10.24
7.09
1.00
1.01
1.00
0.98
1.99
3.04
1.02
1.06
3.12
13.14
3.30
f1 (ppm)

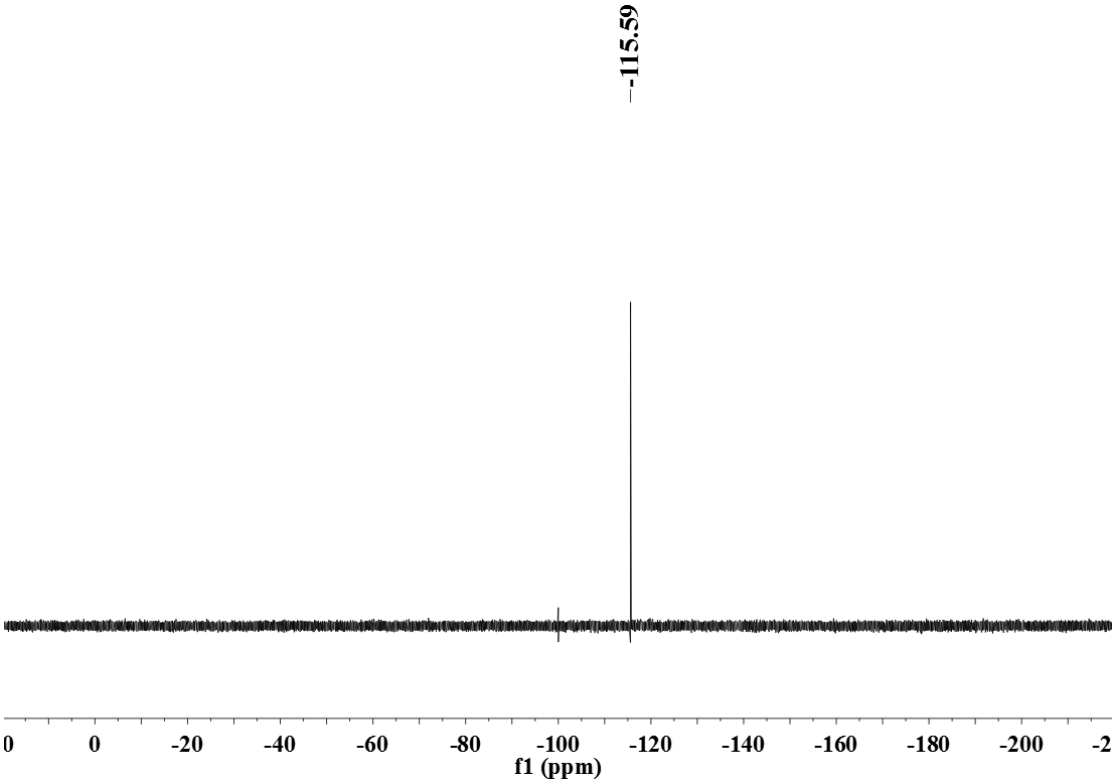

147.15
146.90
144.42
144.15
142.35
140.33
130.94
130.35
130.34
128.40
127.68
127.34
127.32
127.16
126.94
126.91
124.16
123.87
45.09
44.96
38.23
38.20
37.58
37.43
36.10
33.45
30.10
29.72
25.33
25.28
24.02
18.91
18.88
18.81
18.80
18.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

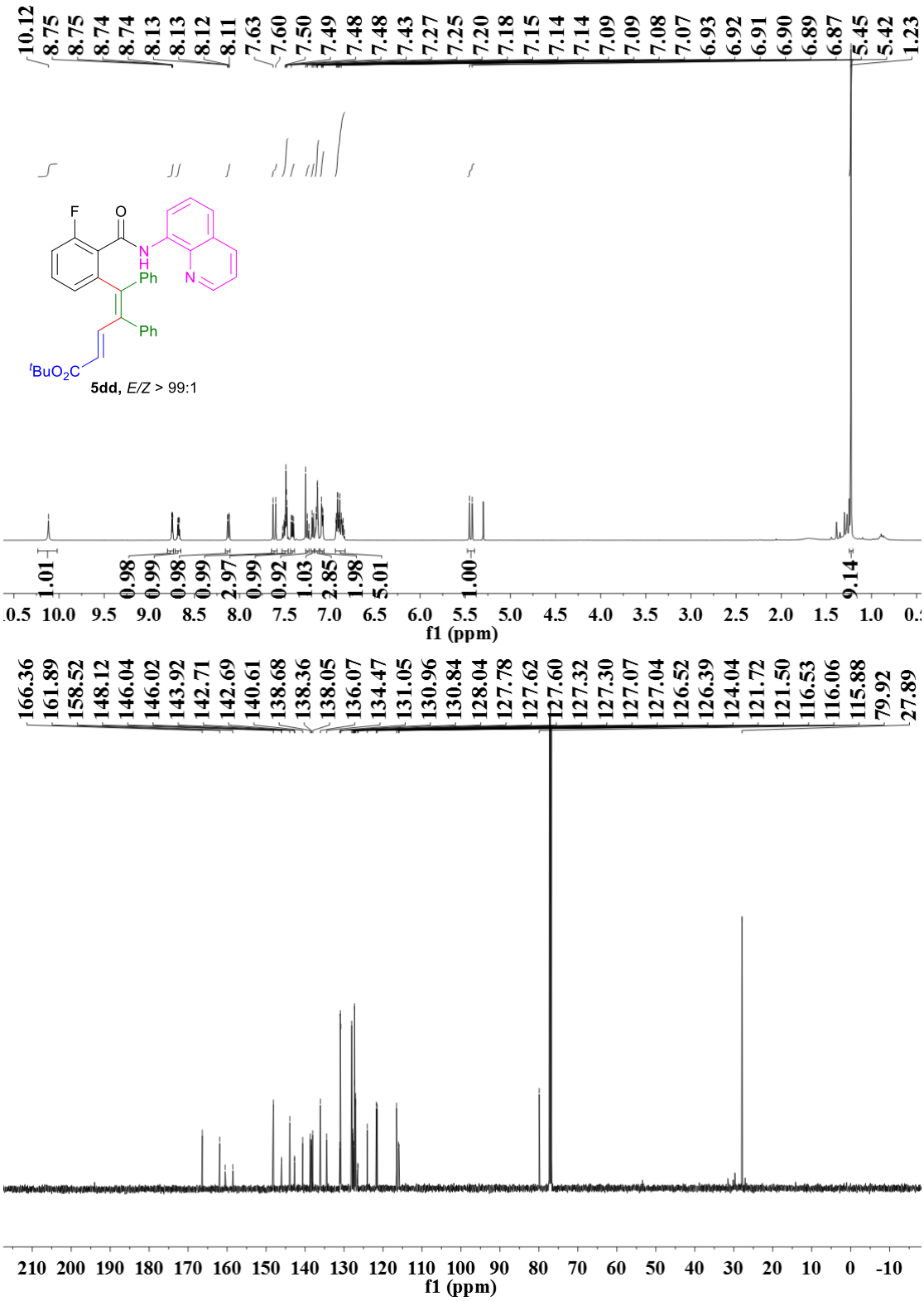

-115.64
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

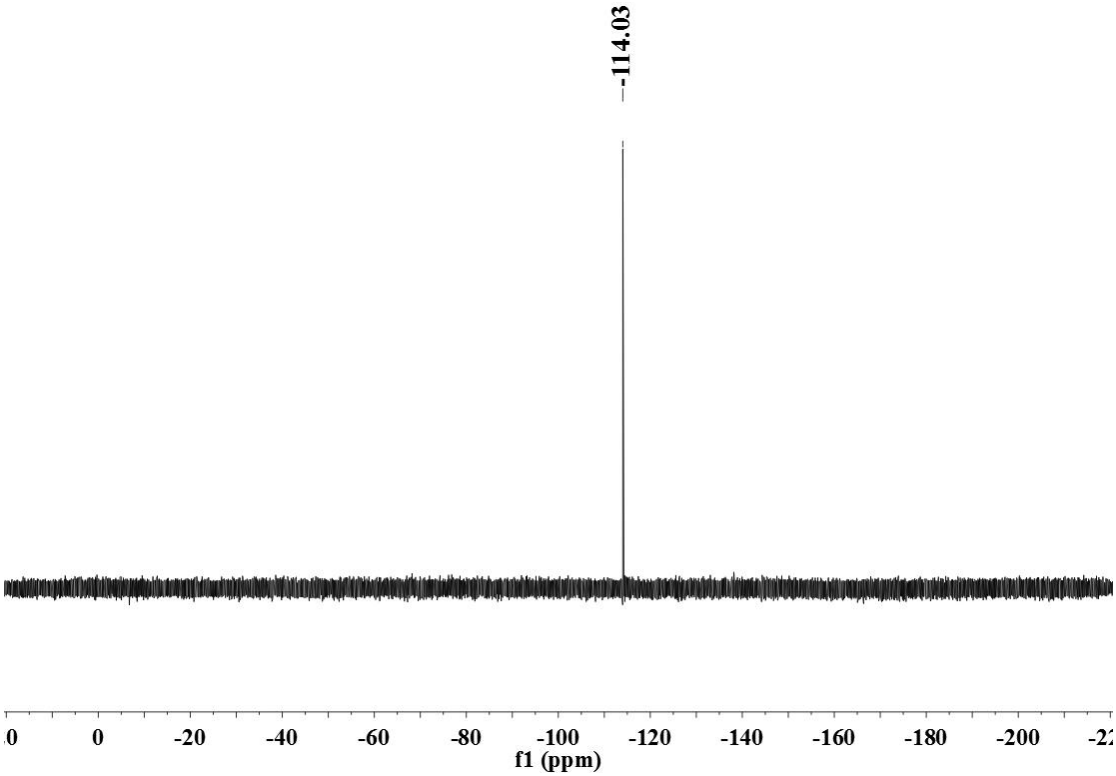

6.80
5.49
5.45
2.27
F
O
N
H
Ph
N
Ph
tBuO2C
5aa, E/Z = 90:10
Me
Me
Me
F
O
N
H
Ph
N
Ph
H
tBuO2C
H
3.00
0.40
0.03
0.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


9.11
8.91
8.90
8.06
8.04
7.78
7.42
7.42
7.41
7.41
7.30
7.29
7.27
7.26
7.25
7.24
7.19
7.18
7.17
7.16
7.14
7.00
6.99
6.97
6.96
6.95
6.93
6.92
6.91
5.50
5.47
4.62
4.61
4.58
4.58
1.33
F
O
N
H
Ph
N
N
Ph
tBuO2C
5bb, E/Z = 96:4
0.98
0.99
1.01
0.96
1.03
4.18
4.07
3.02
2.02
1.00
2.07
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

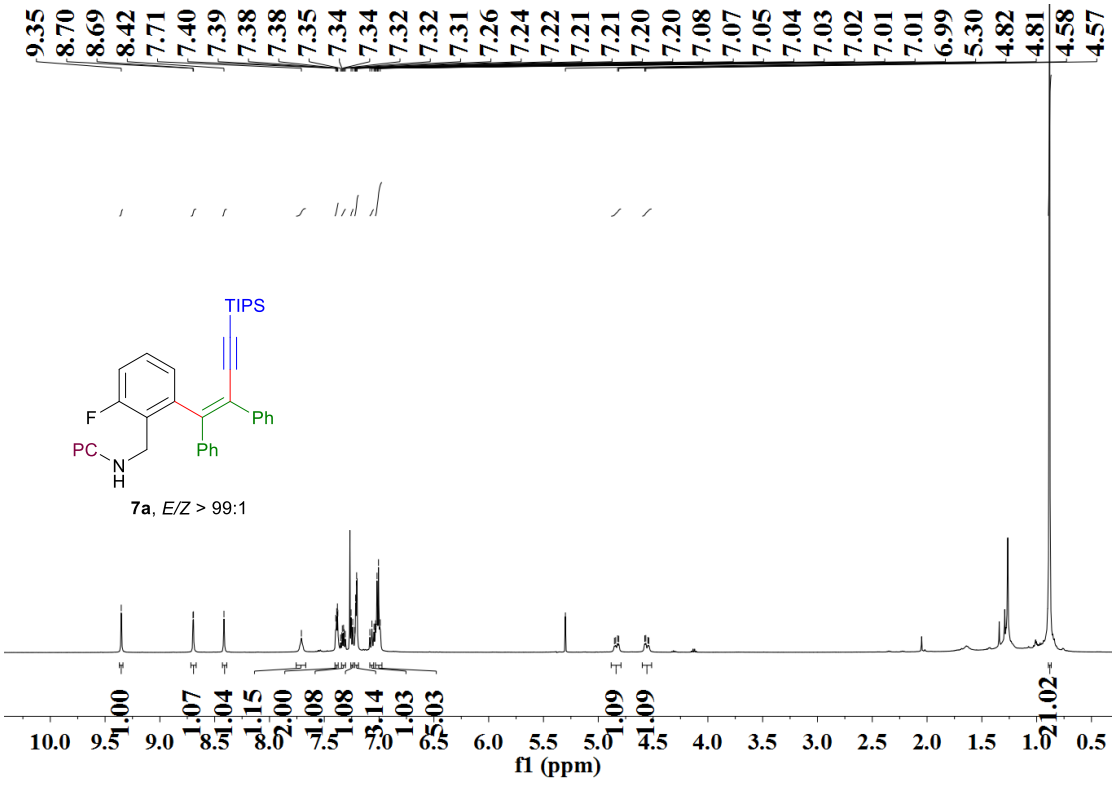

166.23
163.14
161.69
161.16
158.95
157.49
156.07
145.07
145.06
143.80
143.32
143.29
139.99
139.24
138.03
130.84
130.32
129.66
129.59
128.39
127.76
127.43
127.27
127.24
124.55
123.26
123.14
118.43
115.73
115.55
80.28
35.14
35.11
28.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

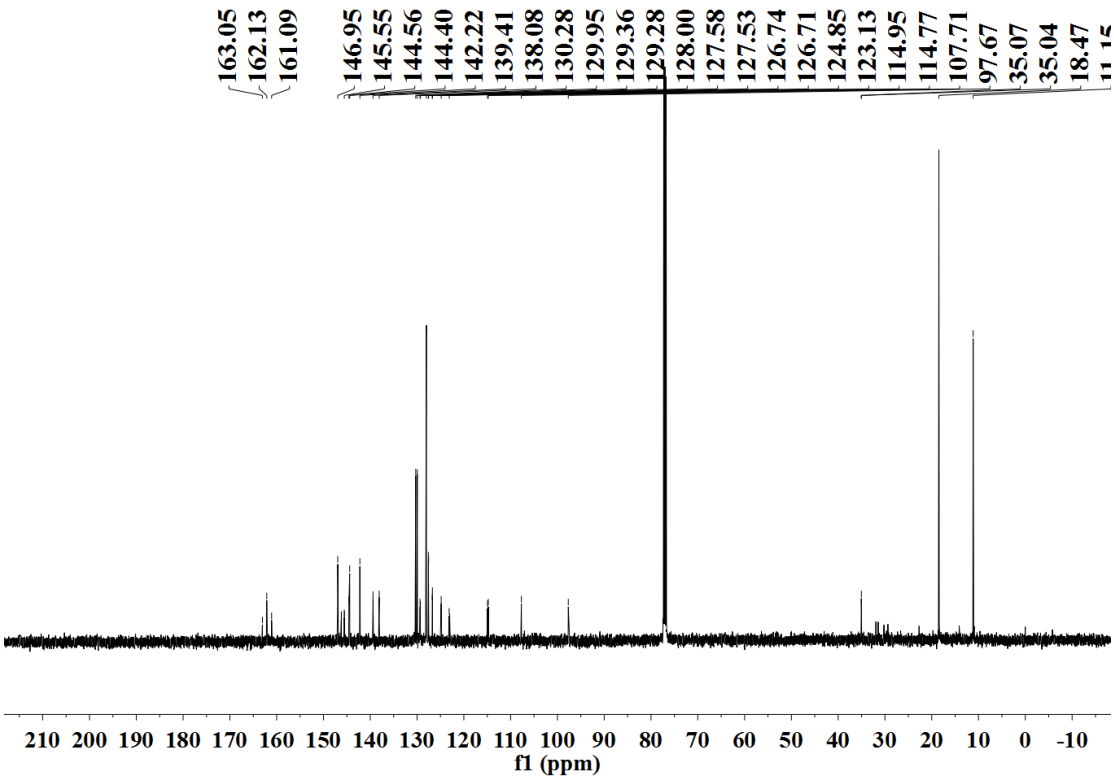

-115.59
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

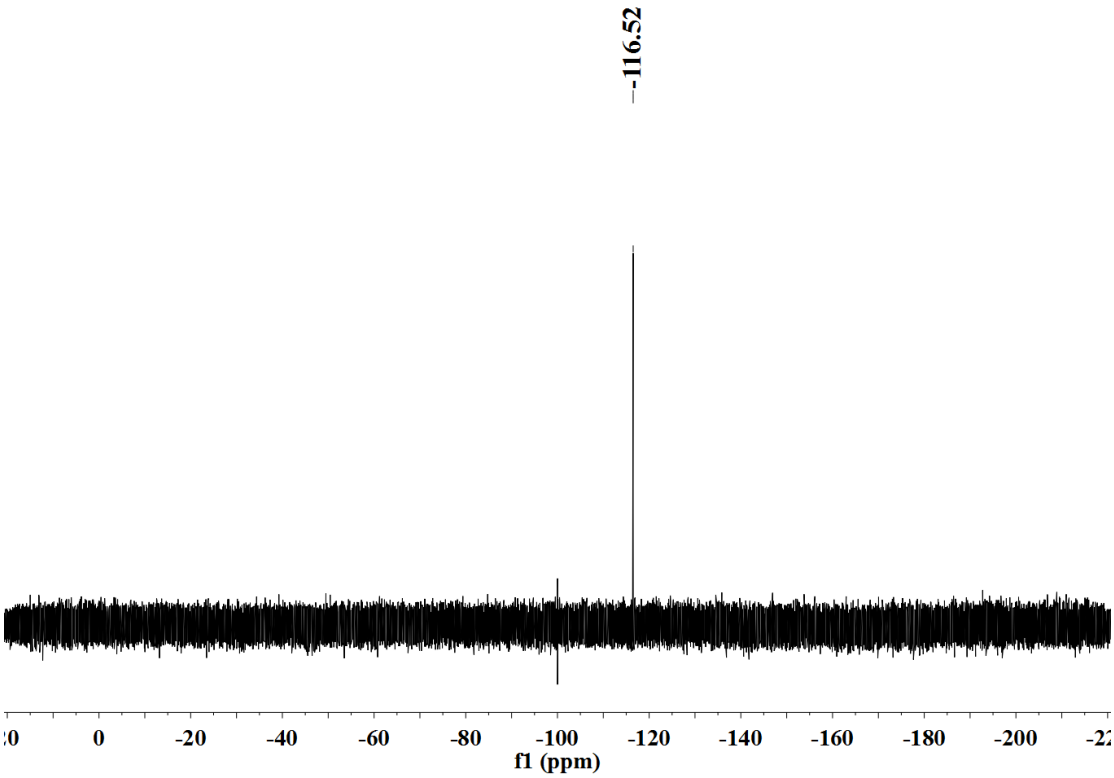

10.12
8.75
8.75
8.74
8.74
8.13
8.13
8.12
8.11
7.63
7.60
7.50
7.49
7.48
7.48
7.43
7.27
7.25
7.20
7.18
7.15
7.14
7.14
7.09
7.09
7.08
7.07
6.93
6.92
6.91
6.90
6.89
6.87
5.45
5.42
1.23
F
O
N
H
Ph
N
Ph
tBuO2C
5dd, E/Z > 99:1
1.01
0.98
0.99
0.98
0.99
2.97
0.99
0.92
1.03
2.85
1.98
5.01
1.00
9.14
f1 (ppm)
166.36
161.89
158.52
148.12
146.04
146.02
143.92
142.71
142.69
140.61
138.68
138.36
138.05
136.07
134.47
131.05
130.96
130.84
128.04
127.78
127.62
127.60
127.32
127.30
127.07
127.04
126.52
126.39
124.04
121.72
121.50
116.53
116.06
115.88
79.92
27.89
f1 (ppm)

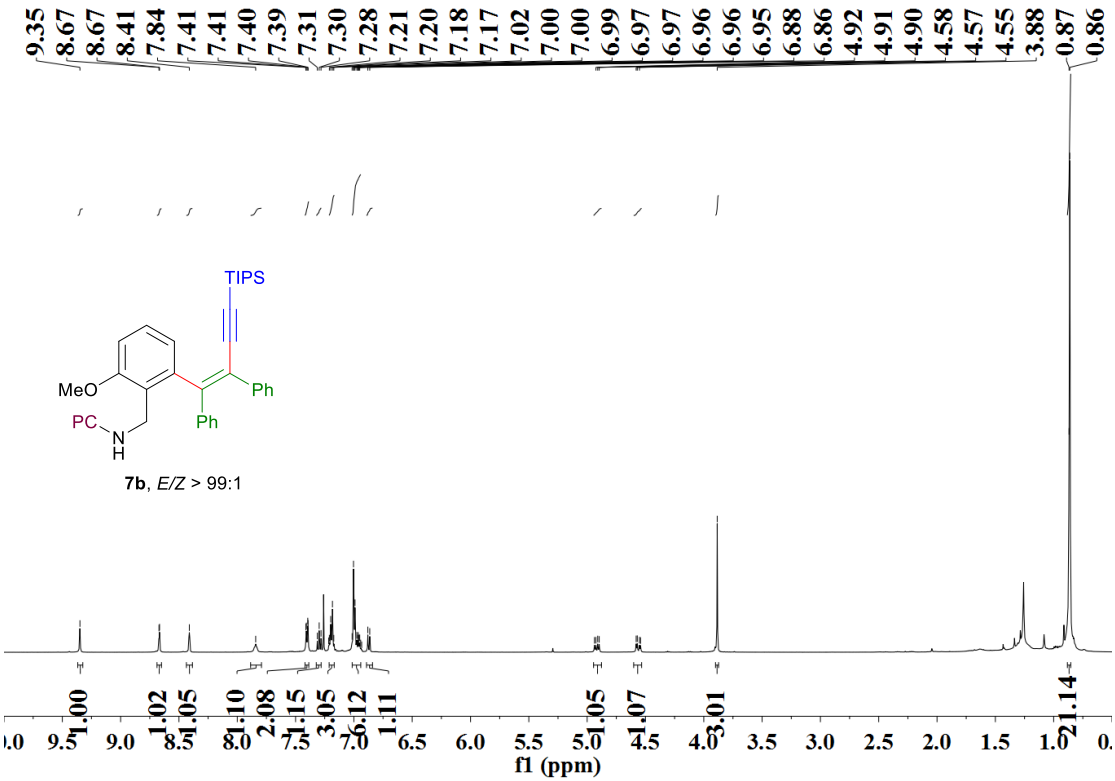


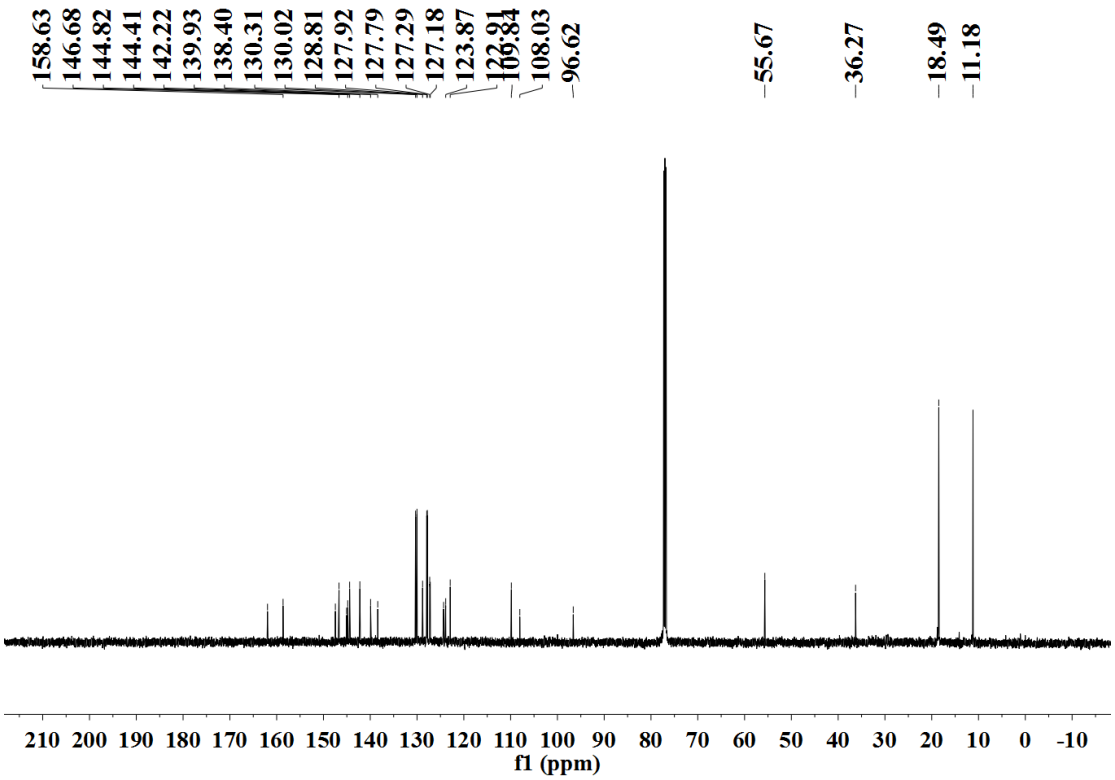
9.4 NMR Spectra of 7

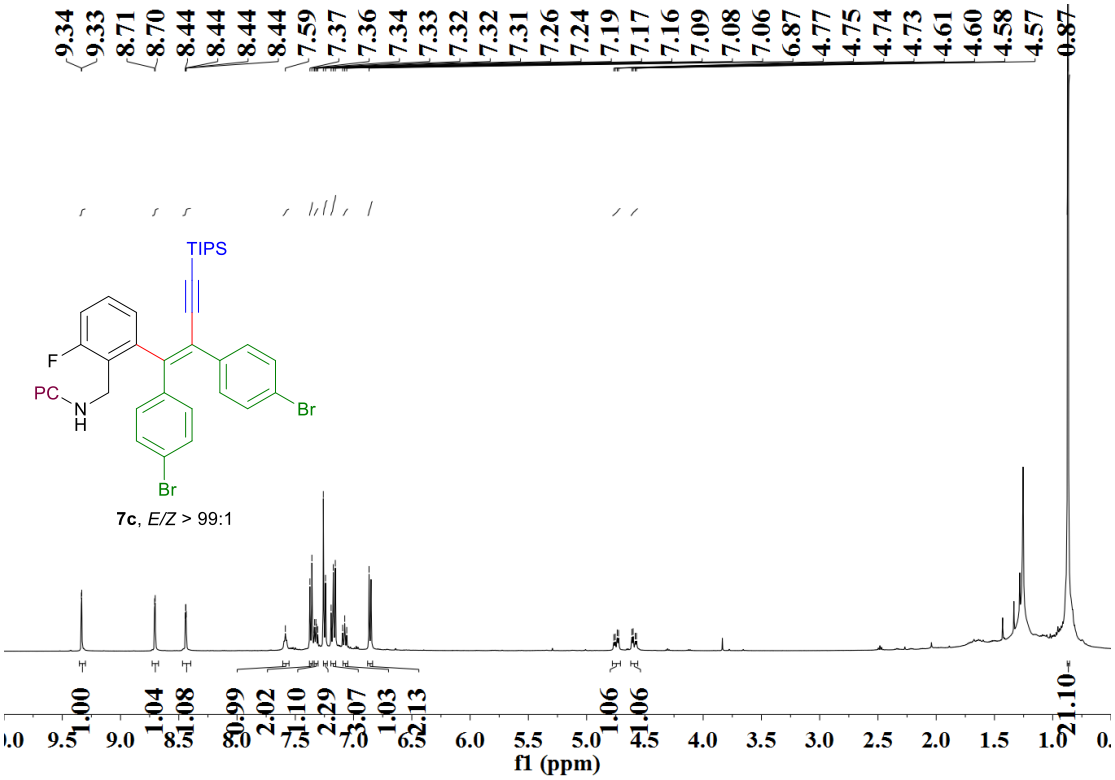


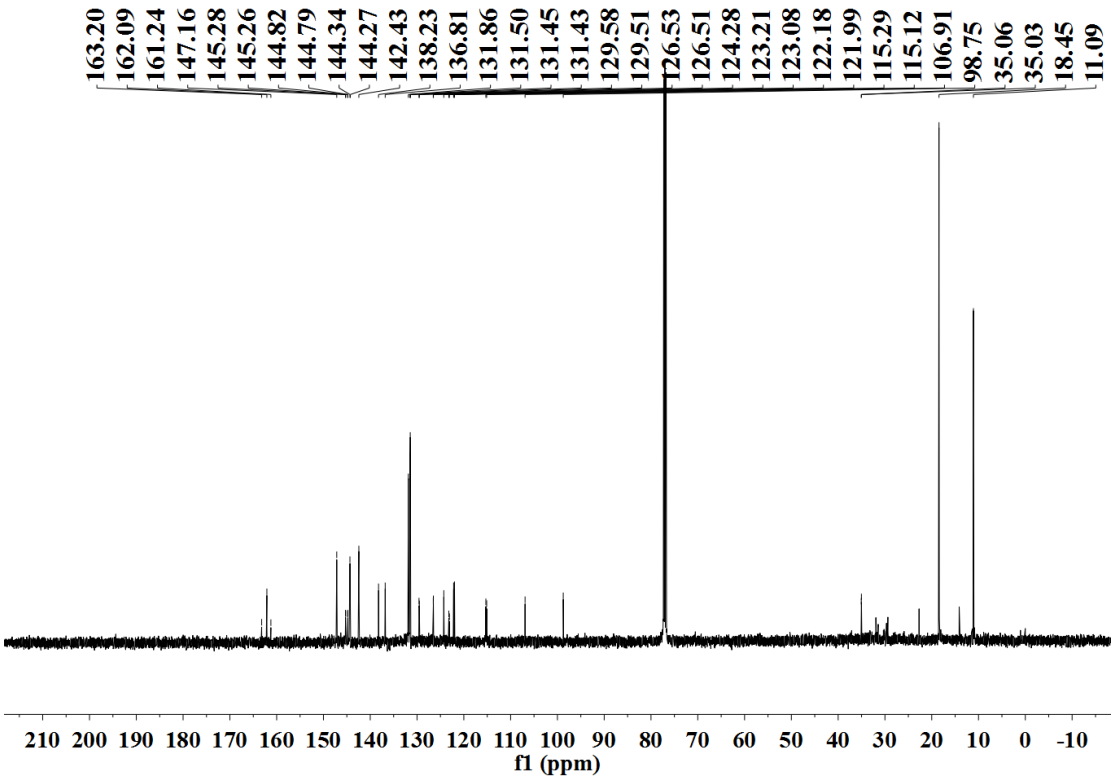

163.05
162.13
161.09
146.95
145.55
144.56
144.40
142.22
139.41
138.08
130.28
129.95
129.36
129.28
128.00
127.58
127.53
126.74
126.71
124.85
123.13
114.95
114.77
107.71
97.67
35.07
35.04
18.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

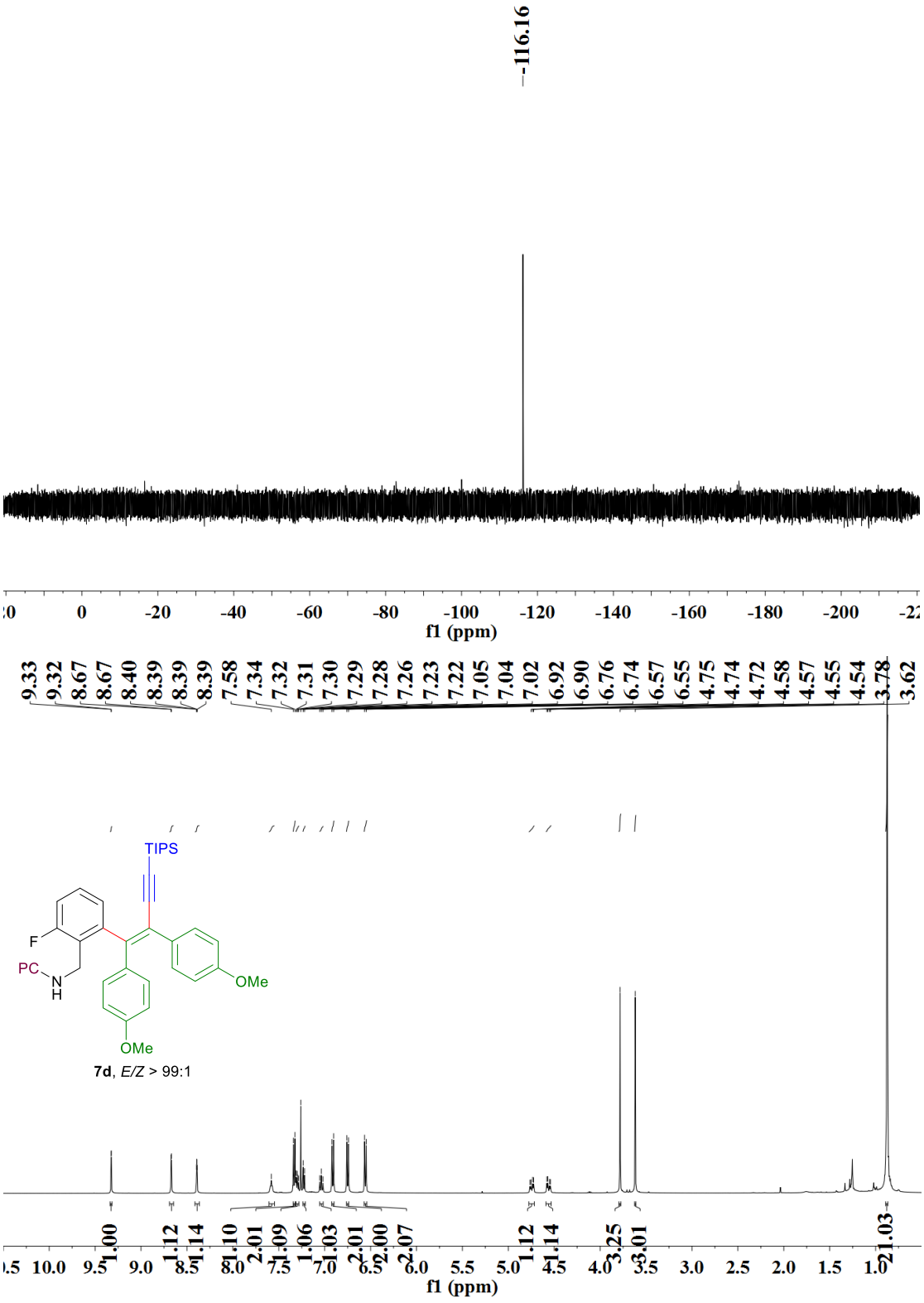

-116.52
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

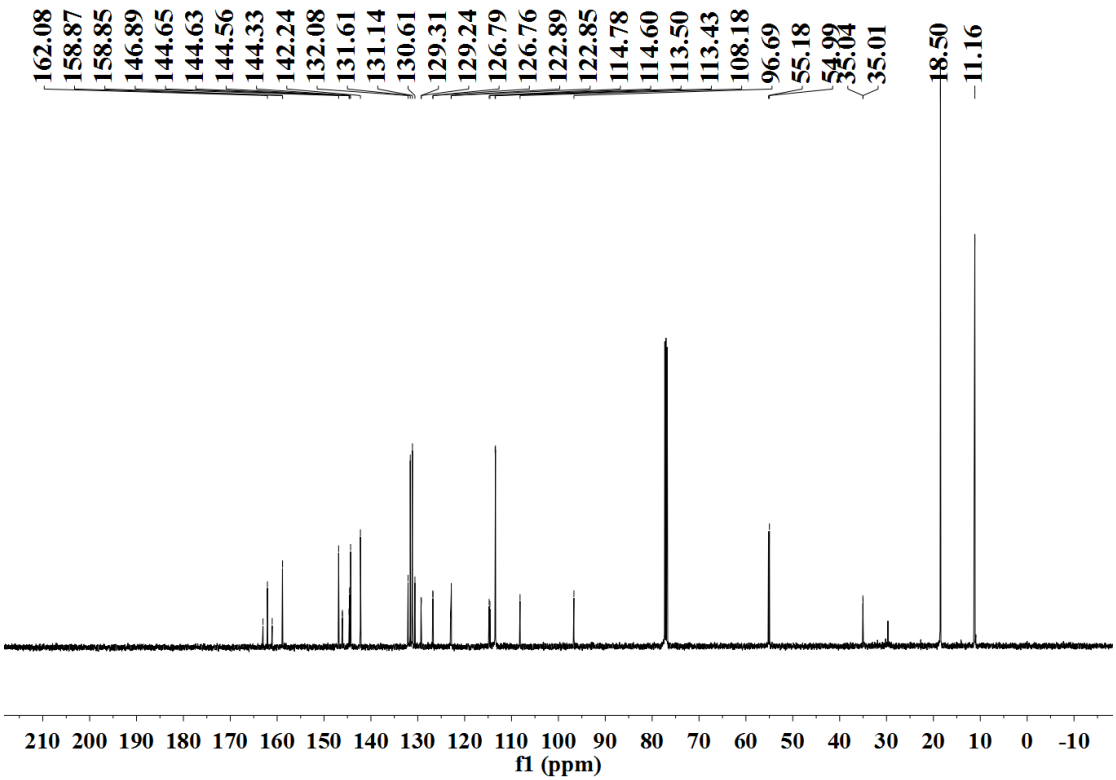

9.35
8.67
8.67
8.41
7.84
7.41
7.41
7.40
7.39
7.31
7.30
7.28
7.21
7.20
7.18
7.17
7.02
7.00
7.00
6.99
6.97
6.97
6.96
6.96
6.95
6.88
6.86
4.92
4.91
4.90
4.58
4.57
4.55
3.88
0.87
0.86
TIPS
MeO
Ph
PC
N
H
Ph
7b, E/Z > 99:1
1.00
1.02
1.05
1.10
2.08
1.15
3.05
6.12
1.11
1.05
1.07
3.01
21.14
f1 (ppm)

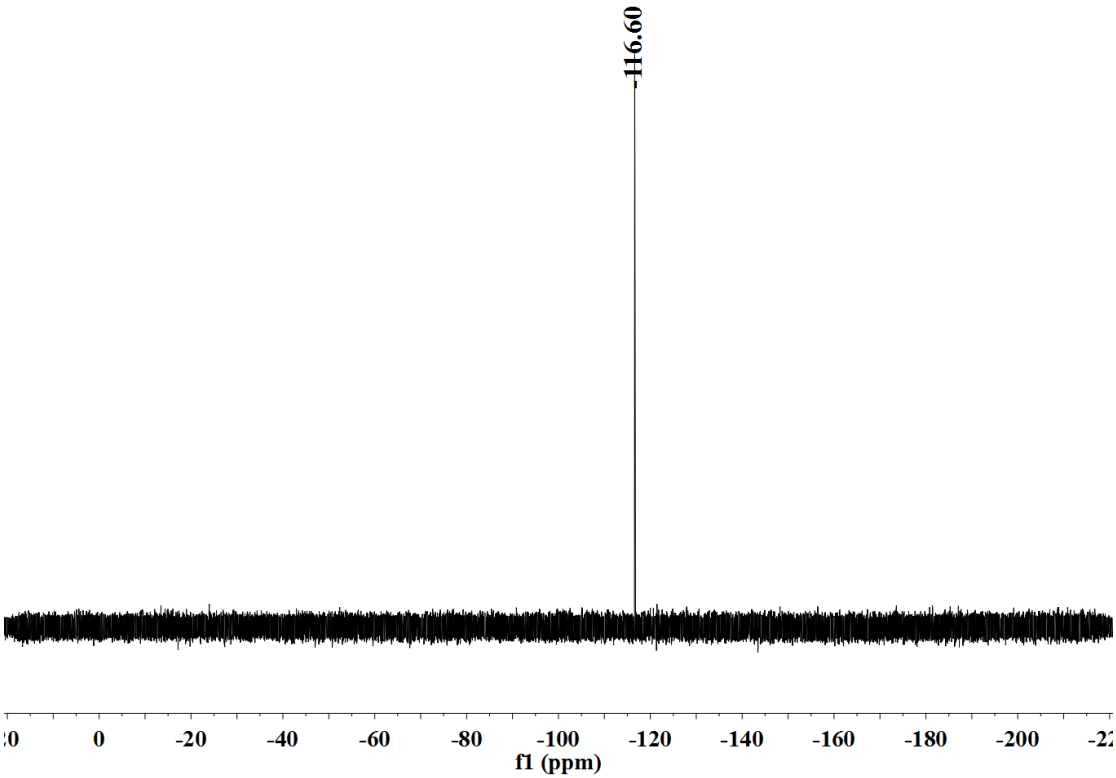

158.63
146.68
144.82
144.41
142.22
139.93
138.40
130.31
130.02
128.81
127.92
127.79
127.29
127.18
123.87
108.03
96.62
55.67
36.27
18.49
11.18
f1 (ppm)

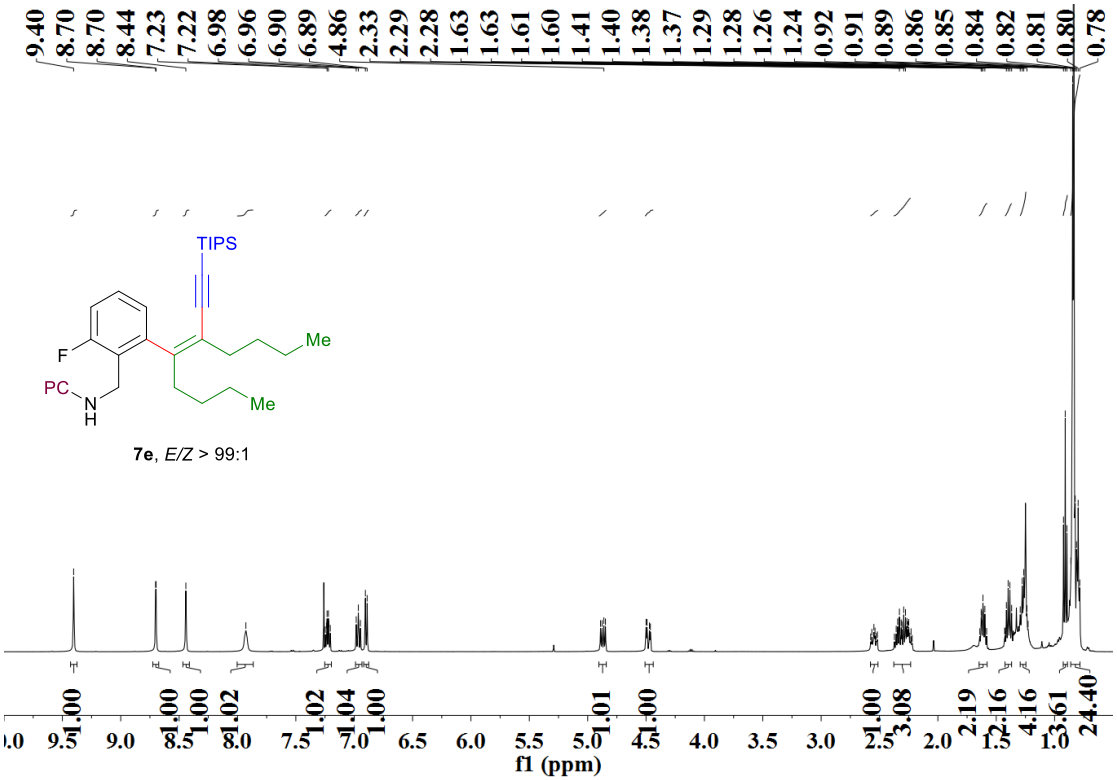

9.34
9.33
8.71
8.70
8.44
8.44
8.44
8.44
7.59
7.37
7.36
7.34
7.33
7.32
7.32
7.31
7.26
7.24
7.19
7.17
7.16
7.09
7.08
7.06
6.87
4.77
4.75
4.74
4.73
4.61
4.60
4.58
4.57
0.87
TIPS
F
PC
N
H
Br
Br
7c, E/Z > 99:1
1.00
1.04
1.08
0.99
2.02
1.10
2.29
3.07
1.03
2.13
1.06
1.06
21.10
f1 (ppm)


163.20
162.09
161.24
147.16
145.28
145.26
144.82
144.79
144.34
144.27
142.43
138.23
136.81
131.86
131.50
131.45
131.43
129.58
129.51
126.53
126.51
124.28
123.21
123.08
122.18
121.99
115.29
115.12
106.91
98.75
35.06
35.03
18.45
11.09
f1 (ppm)

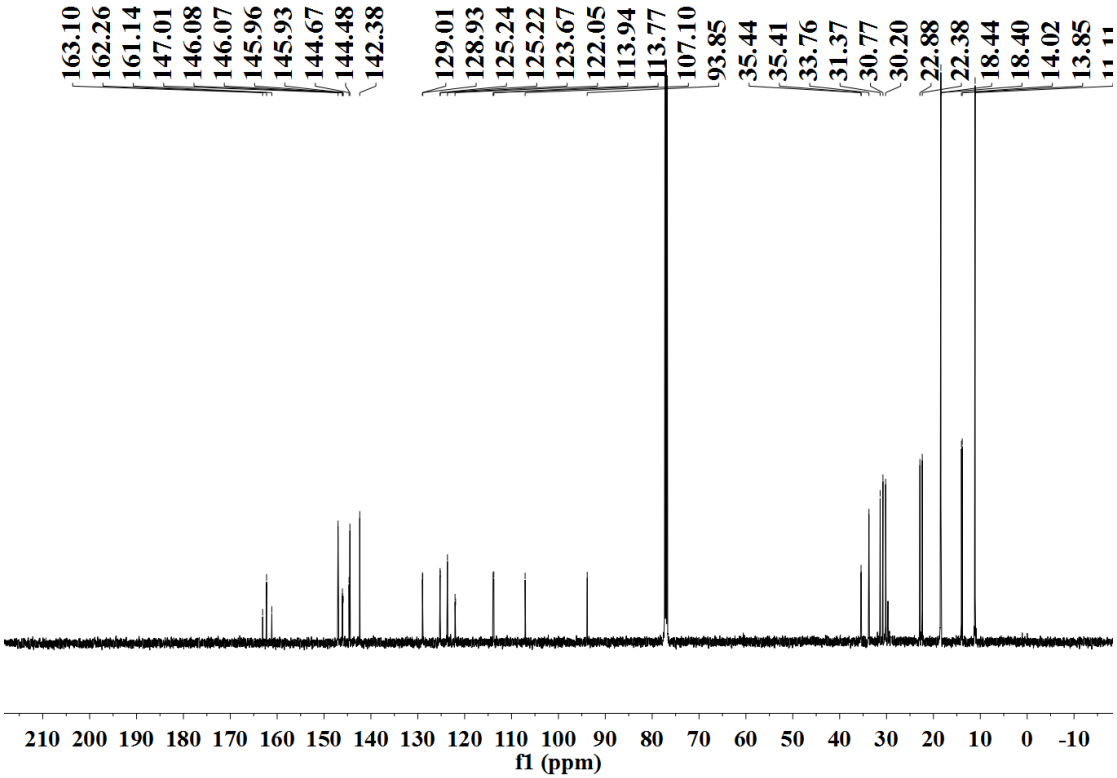

-116.16
f1 (ppm)
9.33 9.32 8.67 8.67 8.40 8.39 8.39 8.39 7.58 7.34 7.32 7.31 7.30 7.29 7.28 7.26 7.23 7.22 7.05 7.04 7.02 6.92 6.90 6.76 6.74 6.57 6.55 4.75 4.74 4.72 4.58 4.57 4.55 4.54 3.78 3.62
TIPS
F
PC
N
H
OMe
OMe
7d, E/Z > 99:1
1.00 1.12 1.14 1.10 2.01 1.09 1.06 1.03 2.01 2.00 2.07 1.12 1.14 3.25 3.01 21.03
f1 (ppm)

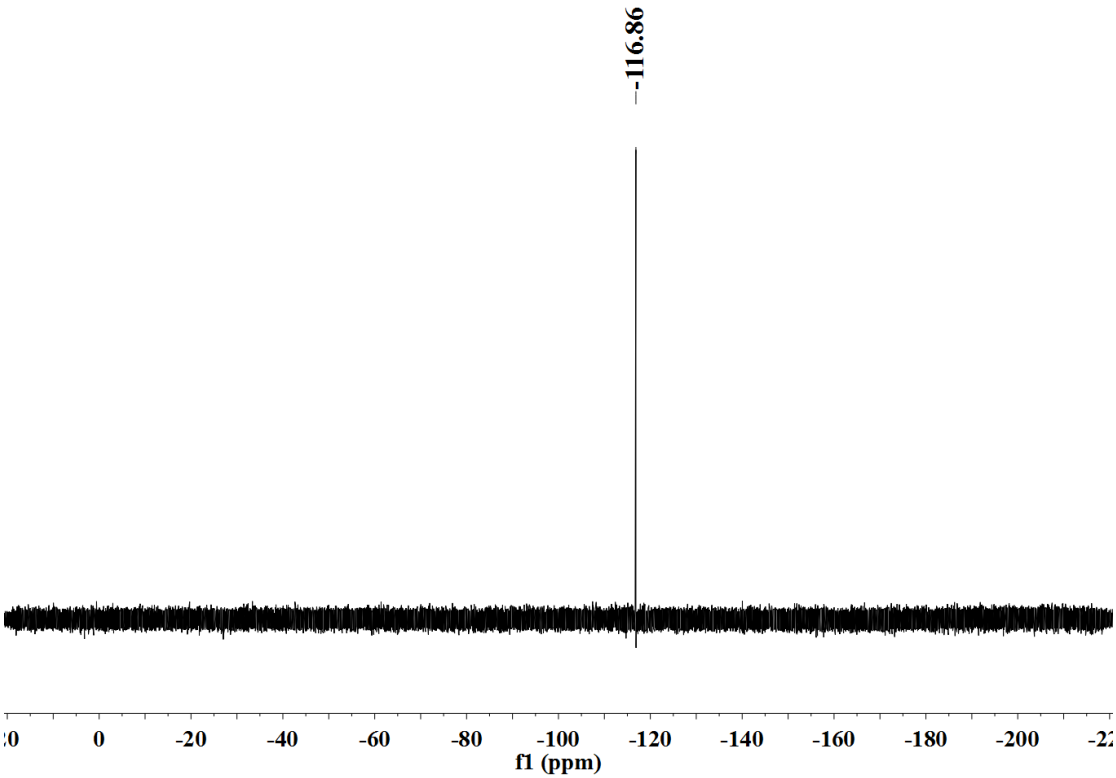

162.08
158.87
158.85
146.89
144.65
144.63
144.56
144.33
142.24
132.08
131.61
131.14
130.61
129.31
129.24
126.79
126.76
122.89
122.85
114.78
114.60
113.50
113.43
108.18
96.69
55.18
54.99
35.04
35.01
18.50
11.16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

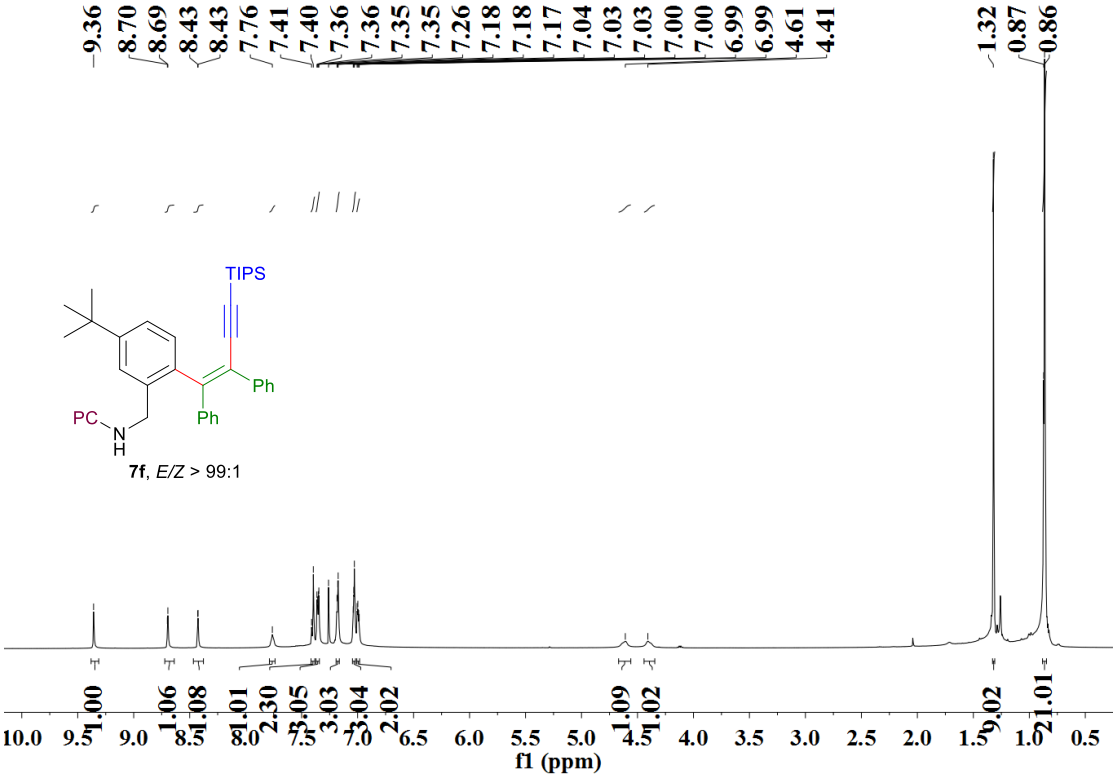

-116.60
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)



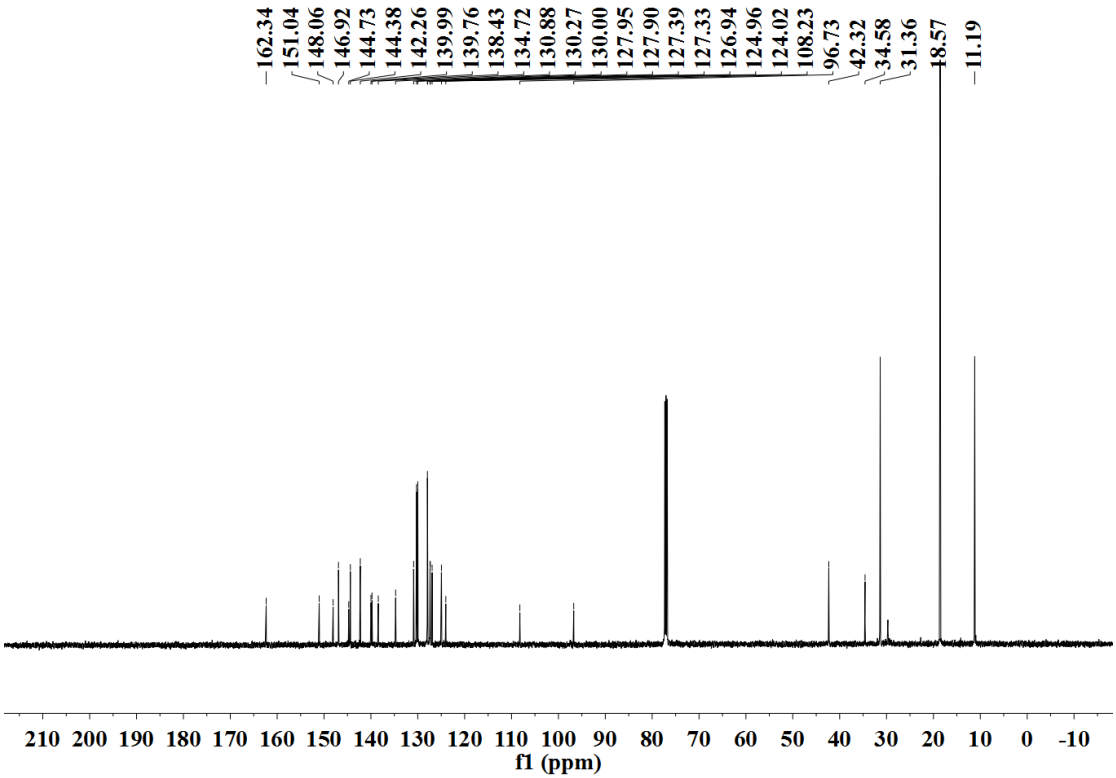
7e, *E*/*Z* > 99:1



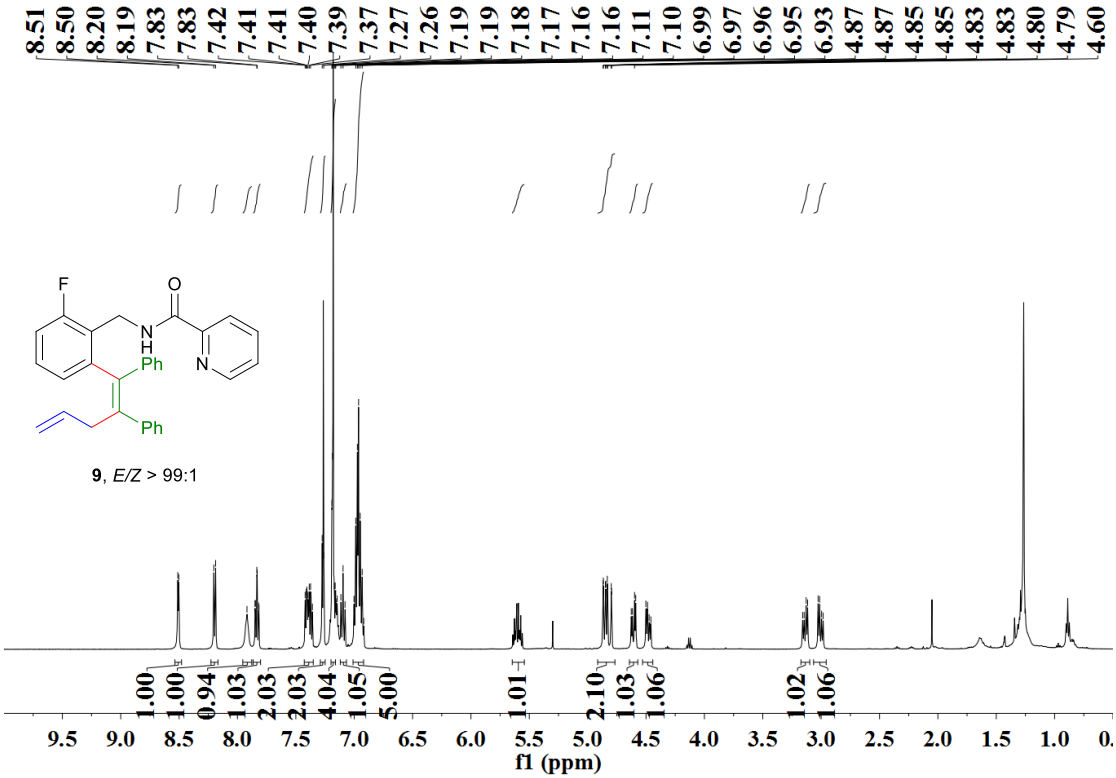

-116.86
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

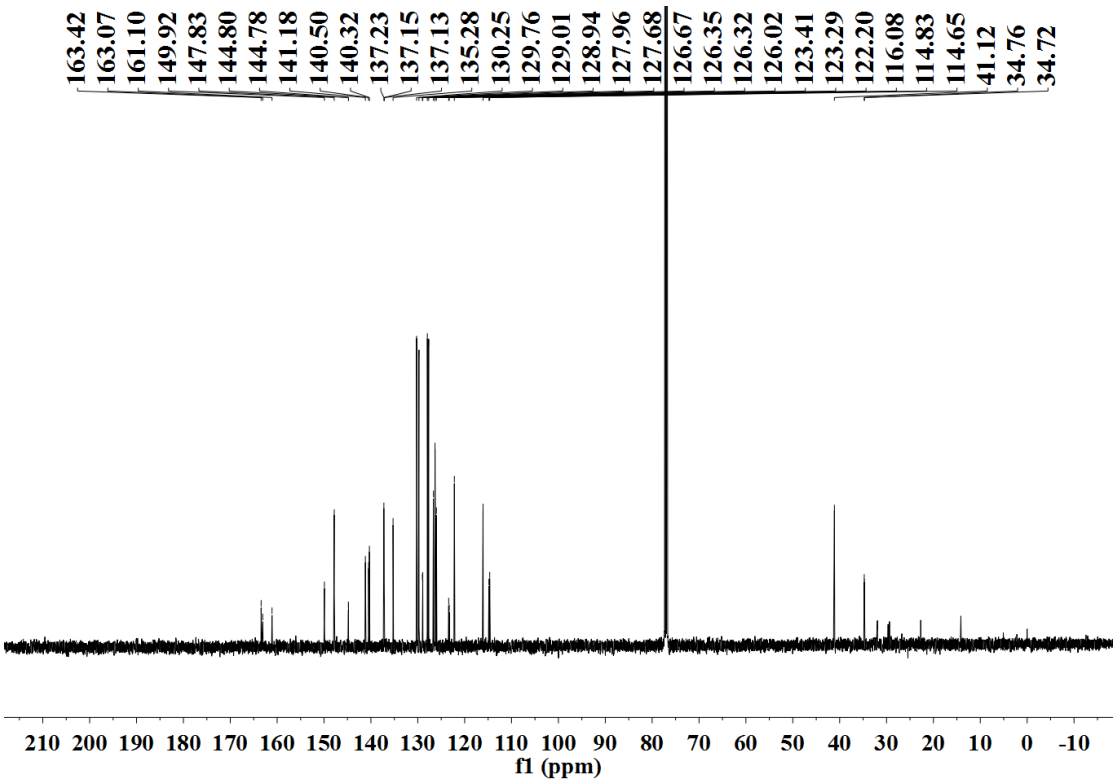

9.36
8.70
8.69
8.43
8.43
7.76
7.41
7.40
7.36
7.36
7.35
7.35
7.26
7.18
7.18
7.17
7.04
7.03
7.03
7.00
7.00
6.99
6.99
4.61
4.41
1.32
0.87
0.86
TIPS
Ph
Ph
PC
N
H
1.00
1.06
1.08
1.01
2.30
3.05
3.03
3.04
2.02
1.09
1.02
9.02
21.01
f1 (ppm)

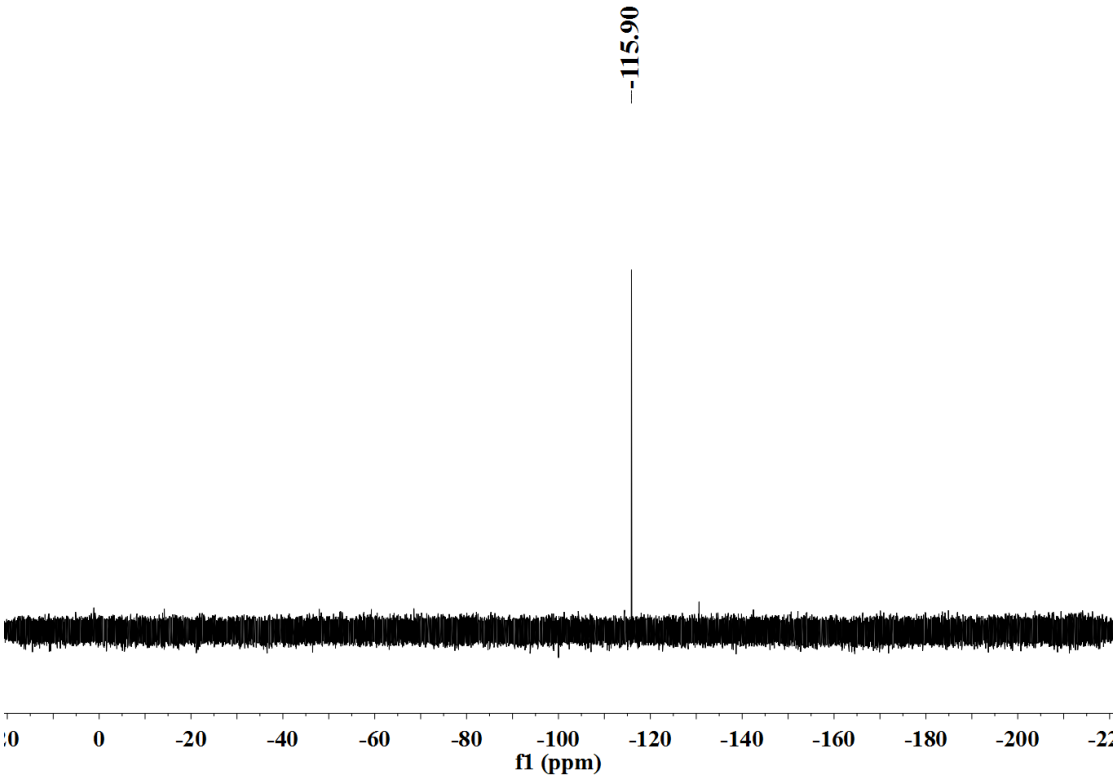
7f, *E*/*Z* > 99:1



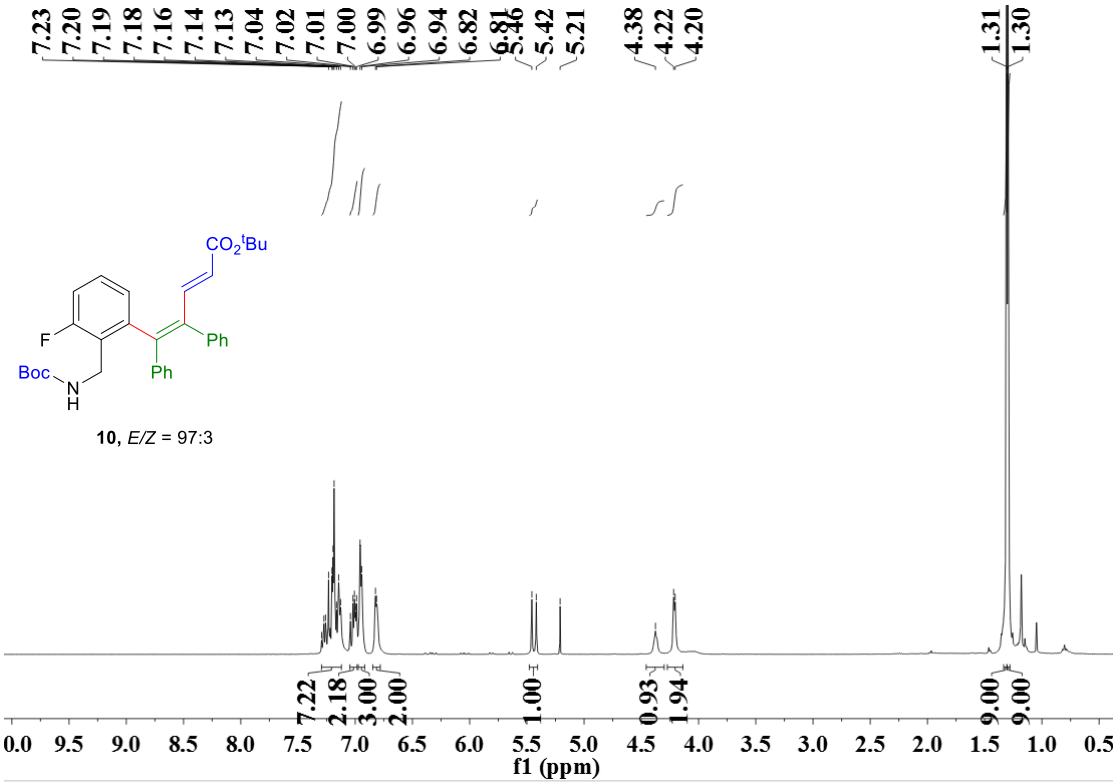
9.5 NMR Spectra of 9

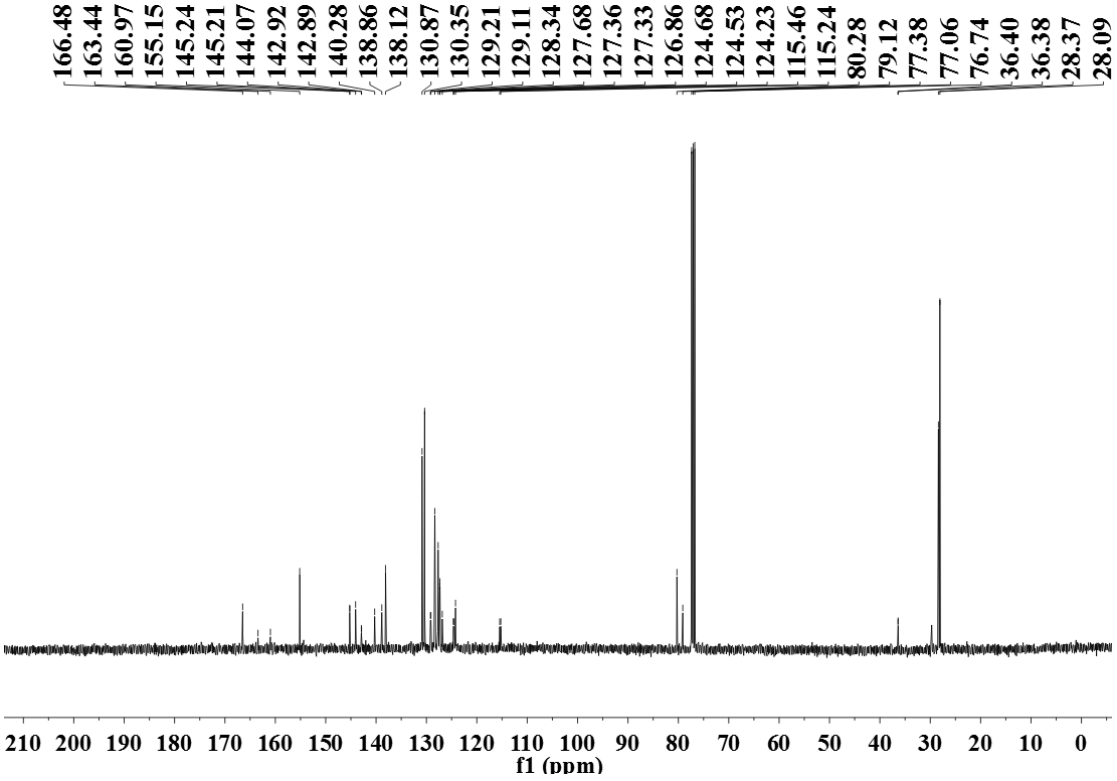


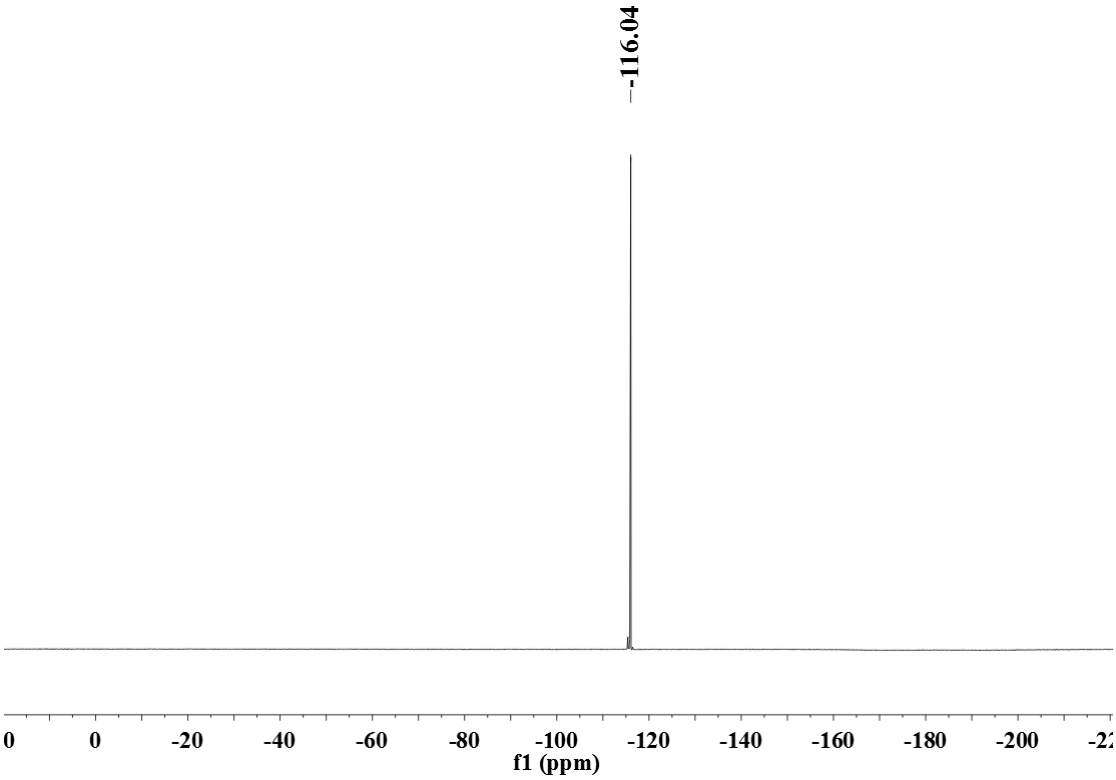

163.42
163.07
161.10
149.92
147.83
144.80
144.78
141.18
140.50
140.32
137.23
137.15
137.13
135.28
130.25
129.76
129.01
128.94
127.96
127.68
126.67
126.35
126.32
126.02
123.41
123.29
122.20
116.08
114.83
114.65
41.12
34.76
34.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

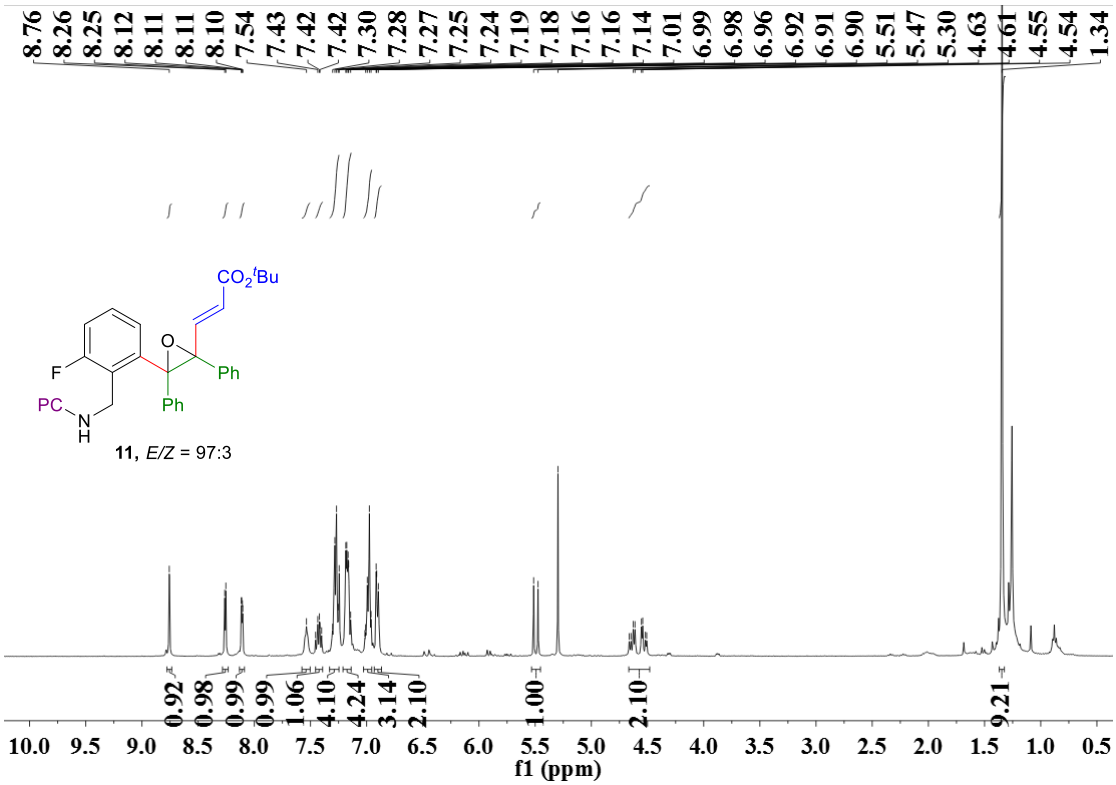

-115.90
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

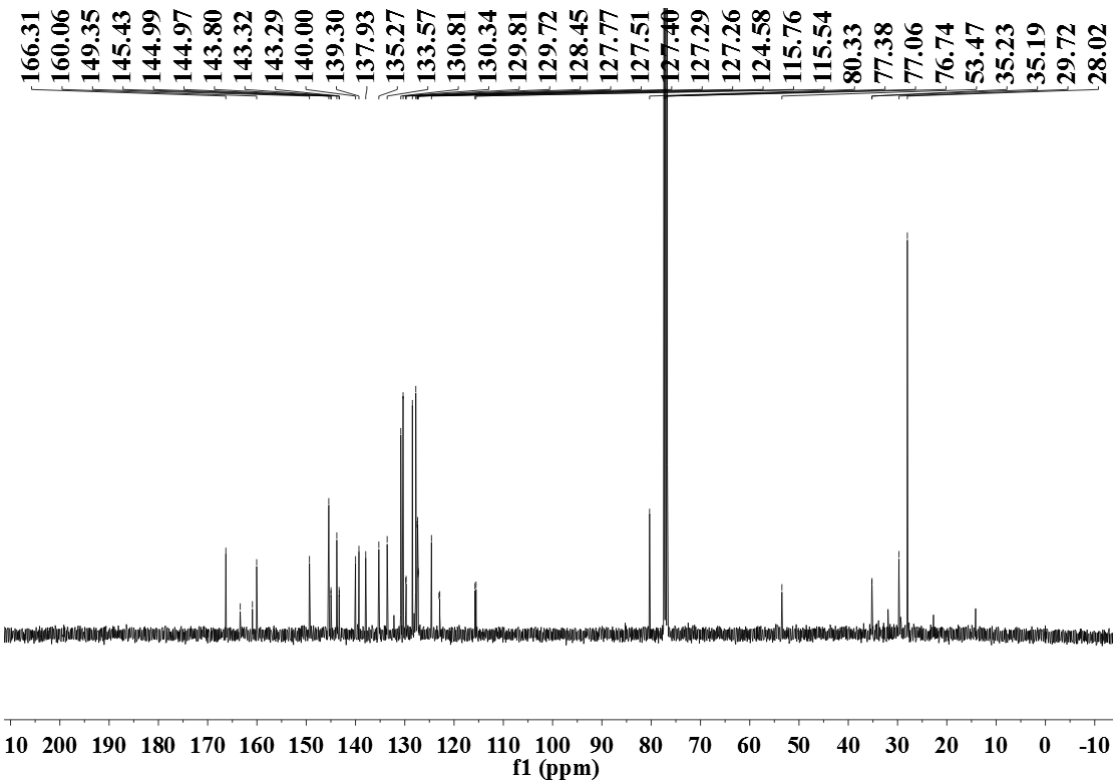
9.6 NMR Spectra of Synthetic Applications

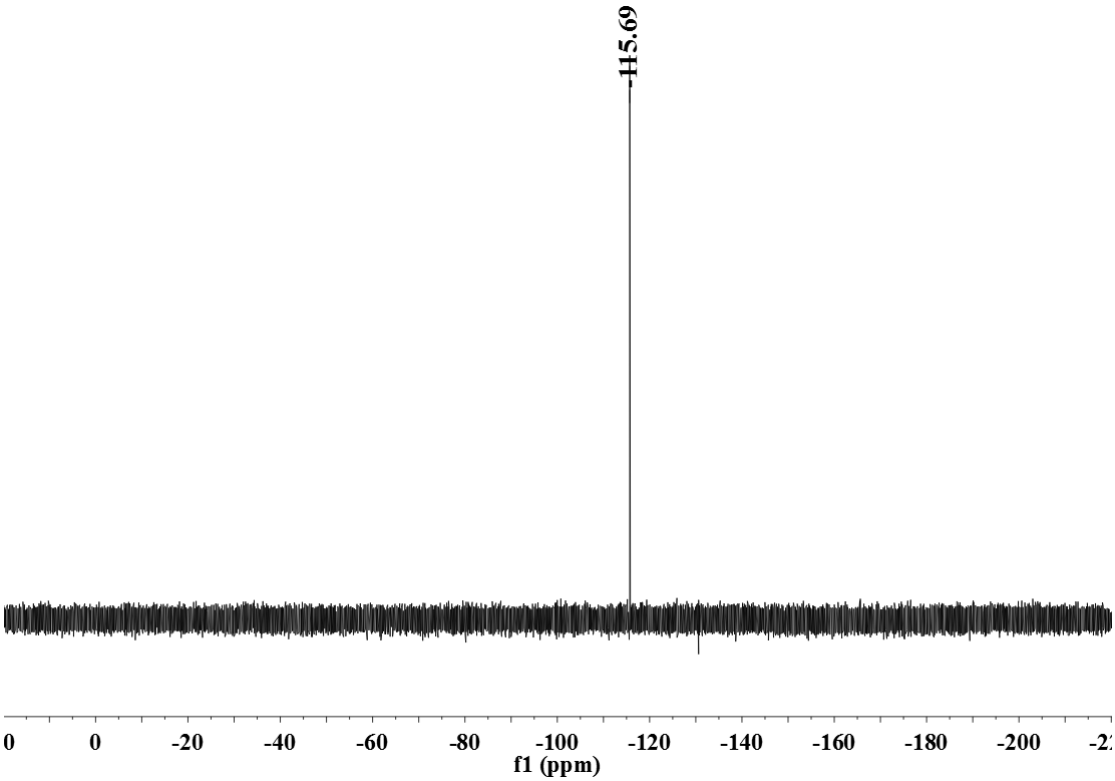


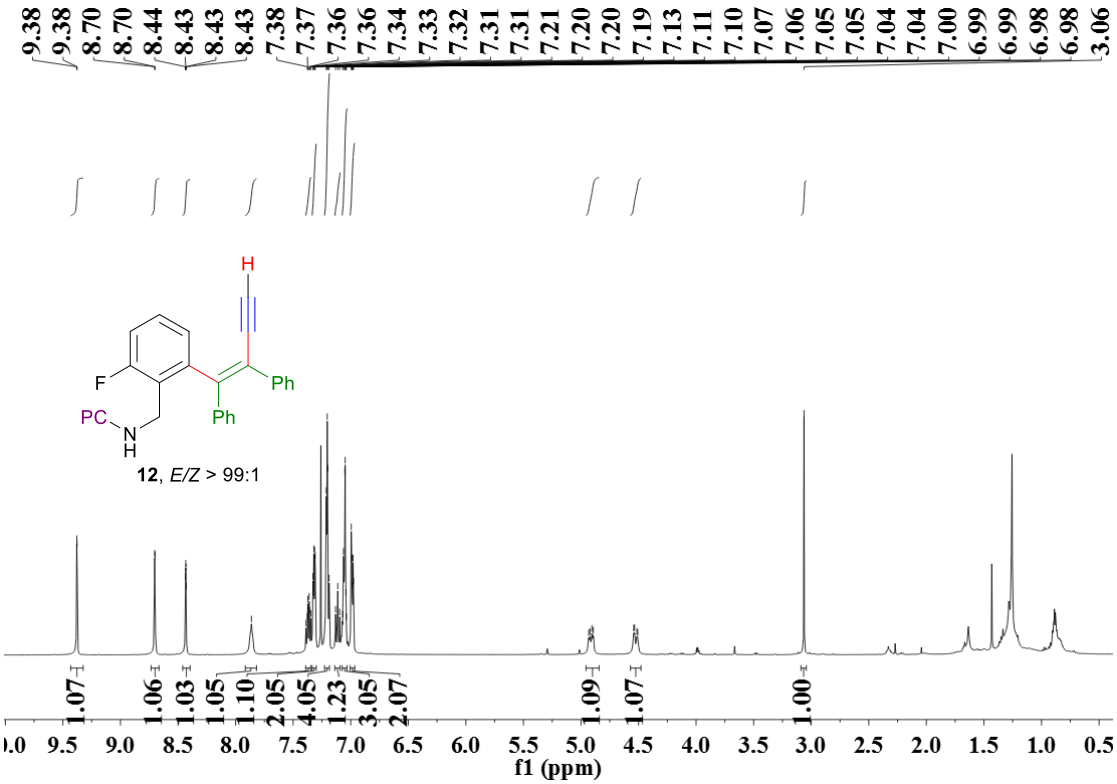


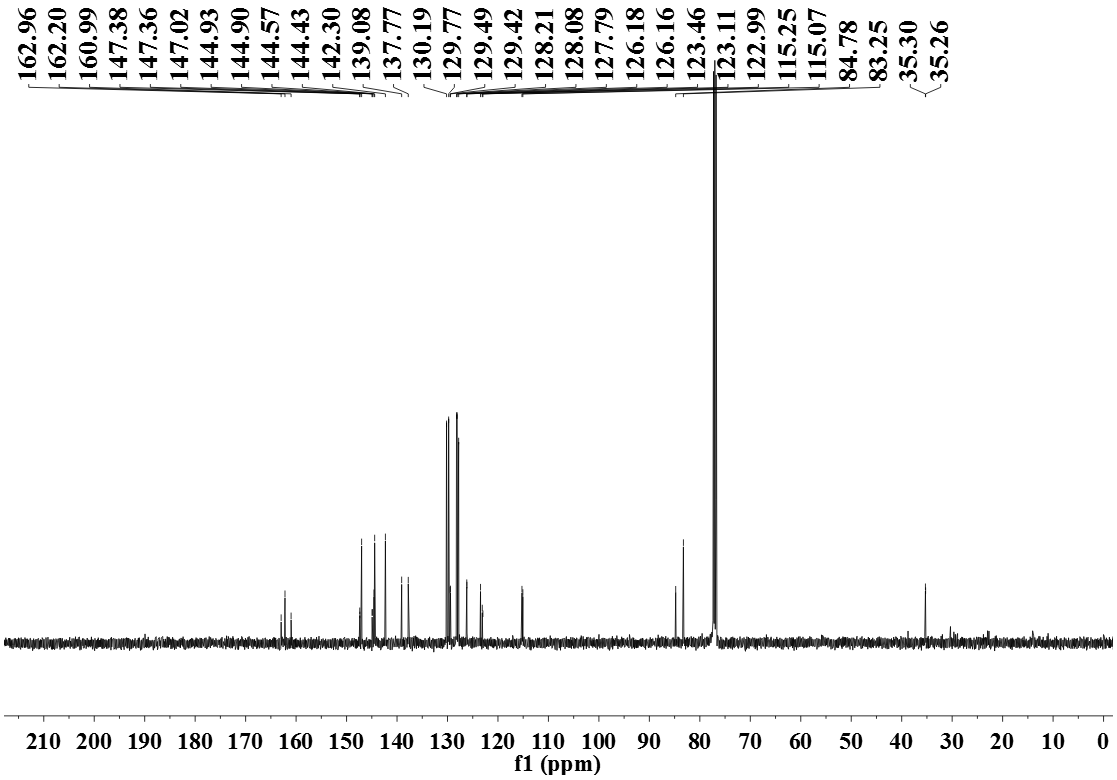

-116.04
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

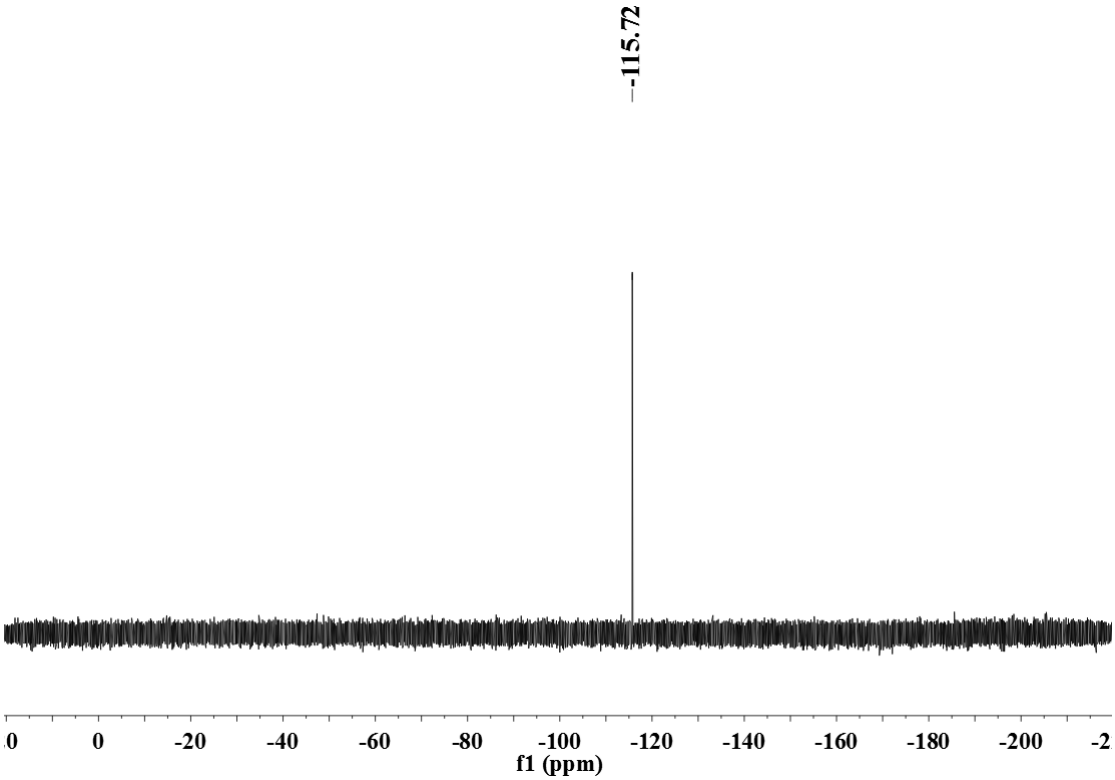

8.76
8.26
8.25
8.12
8.11
8.11
8.10
7.54
7.43
7.42
7.42
7.30
7.28
7.27
7.25
7.24
7.19
7.18
7.16
7.16
7.14
7.01
6.99
6.98
6.96
6.92
6.91
6.90
5.51
5.47
5.30
4.63
4.61
4.55
4.54
1.34
CO2tBu
O
F
Ph
PC
N
H
Ph
11, E/Z = 97:3
0.92
0.98
0.99
0.99
1.06
4.10
4.24
3.14
2.10
1.00
2.10
9.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.31
160.06
149.35
145.43
144.99
144.97
143.80
143.32
143.29
140.00
139.30
137.93
135.27
133.57
130.81
130.34
129.81
129.72
128.45
127.77
127.51
127.40
127.29
127.26
124.58
115.76
115.54
80.33
77.38
77.06
76.74
53.47
35.23
35.19
29.72
28.02
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

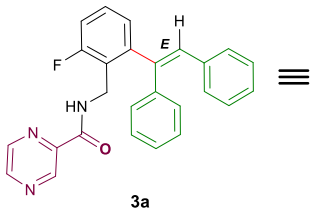

-115.69
0 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

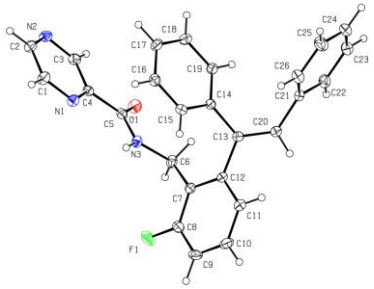

9.38 9.38 8.70 8.70 8.44 8.43 8.43 8.43 7.38 7.37 7.36 7.36 7.34 7.33 7.32 7.31 7.31 7.21 7.20 7.20 7.19 7.13 7.11 7.10 7.07 7.06 7.05 7.05 7.04 7.04 7.00 6.99 6.99 6.98 6.98 3.06
H
F
Ph
Ph
PC
N
H
12, E/Z > 99:1
1.07 1.06 1.03 1.05 1.10 2.05 4.05 1.23 3.05 2.07 1.09 1.07 1.00
f1 (ppm)


162.96 162.20 160.99 147.38 147.36 147.02 144.93 144.90 144.57 144.43 142.30 139.08 137.77 130.19 129.77 129.49 129.42 128.21 128.08 127.79 126.18 126.16 123.46 123.11 122.99 115.25 115.07 84.78 83.25 35.30 35.26
f1 (ppm)



10. X-Ray Crystal Data





230103_ZJ_ZYH_3aa_0m

Table 1 Crystal data and structure refinement for 230103_ZJ_ZYH_3aa_0m.

Identification code	230103_ZJ_ZYH_3aa_0m
Empirical formula	$C_{26}H_{20}FN_3O$
Formula weight	409.45
Temperature/K	170.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.4685(11)
b/Å	5.7414(7)
c/Å	37.581(4)
α/°	90

β/°	97.187(3)
γ/°	90
Volume/Å^3	2027.0(4)
Z	4
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	0.461
F(000)	856.0
Crystal size/mm^3	0.32 × 0.08 × 0.06
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	4.124 to 121.382
Index ranges	-12 ≤ h ≤ 12, -7 ≤ k ≤ 7, -48 ≤ l ≤ 48
Reflections collected	34858
Independent reflections	4663 [R_{int} = 0.0665, R_{sigma} = 0.0654]
Data/restraints/parameters	4663/0/280
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0489, wR_2 = 0.1157
Final R indexes [all data]	R_1 = 0.0520, wR_2 = 0.1178
Largest diff. peak/hole / e Å^{-3}	0.25/-0.28

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 230103_ZJ_ZYH_3aa_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	752.3(9)	4742.6(18)	5470.6(2)	44.4(2)
O1	4314.4(10)	-1377.5(16)	5620.9(3)	33.5(2)
N1	6338.4(11)	3230.5(18)	5302.3(3)	26.1(2)
N2	8010.0(12)	-616.6(18)	5156.0(3)	28.6(2)
N3	3998.5(11)	2507.7(19)	5662.4(3)	24.8(2)
C1	7521.2(14)	3453(2)	5144.6(4)	29.3(3)
C2	8354.3(13)	1553(2)	5075.8(4)	27.5(3)
C3	6805.7(13)	-847(2)	5305.3(3)	26.4(3)
C4	5990.6(12)	1053(2)	5380.8(3)	21.7(2)
C5	4690.4(13)	628(2)	5563.4(3)	23.8(2)
C6	2813.8(13)	2107(2)	5869.4(3)	27.6(3)
C7	2220.8(12)	4290(2)	6016.5(3)	24.9(3)
C8	1150.2(13)	5510(3)	5809.7(3)	30.3(3)
C9	443.7(13)	7406(3)	5928.8(4)	36.0(3)
C10	828.0(15)	8132(3)	6276.8(4)	36.9(3)
C11	1892.7(14)	6978(3)	6495.6(4)	32.5(3)
C12	2596.8(12)	5062(2)	6370.4(3)	25.2(3)
C13	3734.1(12)	3900(2)	6621.5(3)	24.6(3)

Table 2 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for 230103_ZJ_ZYH_3aa_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C14	5171.1(12)	3696(2)	6501.9(3)	22.3(2)
C15	5699.7(13)	5471(2)	6301.6(3)	25.2(3)
C16	7018.0(13)	5251(2)	6178.9(3)	28.4(3)
C17	7823.8(13)	3256(2)	6251.3(4)	30.6(3)
C18	7305.7(14)	1473(2)	6446.8(4)	31.2(3)
C19	5990.0(13)	1685(2)	6571.7(3)	26.3(3)
C20	3413.4(13)	3188(3)	6941.7(3)	29.8(3)
C21	4417.0(13)	2444(2)	7256.1(3)	28.5(3)
C22	4196.6(15)	415(3)	7445.5(4)	36.4(3)
C23	5124.0(16)	-195(3)	7746.3(4)	40.6(3)
C24	6258.1(16)	1232(3)	7867.4(4)	40.9(4)
C25	6478.8(17)	3259(3)	7684.3(4)	42.0(4)
C26	5565.1(15)	3858(3)	7379.7(4)	34.3(3)

Table 3 Anisotropic Displacement Parameters ($Å^2\times10^3$) for 230103_ZJ_ZYH_3aa_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	36.6(5)	63.2(6)	30.0(4)	9.1(4)	-8.8(3)	-8.5(4)
O1	33.9(5)	26.2(5)	41.5(5)	5.3(4)	9.0(4)	-3.5(4)
N1	29.0(5)	18.9(5)	31.2(5)	-0.4(4)	7.7(4)	1.5(4)
N2	27.9(5)	21.3(5)	37.2(6)	1.9(4)	5.7(4)	4.7(4)
N3	23.6(5)	26.6(5)	25.1(5)	-0.3(4)	6.4(4)	-3.0(4)
C1	32.5(6)	18.2(5)	39.1(7)	0.1(5)	12.6(5)	-1.3(5)
C2	26.1(6)	23.1(6)	34.4(6)	-0.4(5)	7.6(5)	0.1(5)
C3	28.5(6)	17.9(5)	32.5(6)	2.5(5)	3.2(5)	0.5(5)
C4	22.6(5)	21.5(5)	20.2(5)	-0.2(4)	-0.5(4)	0.0(4)
C5	23.5(5)	25.9(6)	21.1(5)	2.2(4)	-0.3(4)	-1.3(5)
C6	24.7(6)	32.7(6)	26.2(6)	-1.0(5)	6.6(5)	-6.3(5)
C7	17.4(5)	32.3(6)	25.6(6)	4.4(5)	5.1(4)	-2.9(5)
C8	19.7(5)	42.2(7)	28.5(6)	10.2(5)	0.9(5)	-6.5(5)
C9	18.0(6)	43.6(8)	46.4(8)	20.6(6)	3.7(5)	3.0(5)
C10	26.9(6)	37.1(7)	49.1(8)	10.2(6)	13.6(6)	10.6(6)
C11	28.1(6)	38.0(7)	32.4(6)	1.0(5)	8.2(5)	7.3(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 230103_ZJ_ZYH_3aa_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12	18.8(5)	31.8(6)	25.6(6)	3.2(5)	5.4(4)	3.2(5)
C13	21.8(5)	27.4(6)	24.5(6)	0.1(5)	1.9(4)	3.2(5)
C14	21.0(5)	25.8(6)	19.9(5)	-1.1(4)	1.4(4)	1.1(4)
C15	24.4(6)	25.1(6)	25.3(6)	1.7(5)	-0.5(4)	1.2(5)
C16	26.4(6)	31.8(6)	27.2(6)	2.4(5)	3.7(5)	-5.5(5)
C17	22.0(6)	39.2(7)	31.5(6)	-2.7(5)	6.8(5)	1.1(5)
C18	27.6(6)	31.0(7)	35.6(7)	0.6(5)	6.2(5)	7.7(5)
C19	27.0(6)	25.2(6)	27.2(6)	2.7(5)	5.7(5)	2.7(5)
C20	21.5(6)	41.6(7)	26.7(6)	2.8(5)	4.4(5)	3.8(5)
C21	25.6(6)	39.3(7)	21.4(6)	1.8(5)	6.2(4)	5.2(5)
C22	30.8(7)	48.0(8)	31.2(7)	7.9(6)	6.6(5)	-3.1(6)
C23	38.0(7)	51.5(9)	33.6(7)	15.6(6)	9.3(6)	6.0(7)
C24	35.9(7)	59.8(10)	26.2(6)	7.8(6)	0.4(5)	9.5(7)
C25	40.2(8)	51.4(9)	32.0(7)	-0.3(6)	-4.6(6)	-3.4(7)
C26	37.7(7)	36.1(7)	28.5(6)	1.9(5)	1.2(5)	-0.2(6)

Table 4 Bond Lengths for 230103_ZJ_ZYH_3aa_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C8	1.3567(16)	C11	C12	1.3977(18)
O1	C5	1.2325(15)	C12	C13	1.4972(16)
N1	C1	1.3371(16)	C13	C14	1.4900(16)
N1	C4	1.3352(16)	C13	C20	1.3413(18)
N2	C2	1.3315(17)	C14	C15	1.3964(17)
N2	C3	1.3389(17)	C14	C19	1.3974(17)
N3	C5	1.3389(16)	C15	C16	1.3895(18)
N3	C6	1.4611(15)	C16	C17	1.3842(19)
C1	C2	1.3893(17)	C17	C18	1.385(2)
C3	C4	1.3859(17)	C18	C19	1.3904(18)
C4	C5	1.5024(17)	C20	C21	1.4833(17)
C6	C7	1.5067(18)	C21	C22	1.394(2)
C7	C8	1.3871(18)	C21	C26	1.389(2)
C7	C12	1.4049(18)	C22	C23	1.387(2)
C8	C9	1.382(2)	C23	C24	1.382(2)
C9	C10	1.377(2)	C24	C25	1.381(2)
C10	C11	1.3874(19)	C25	C26	1.389(2)

Table 5 Bond Angles for 230103_ZJ_ZYH_3aa_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	N1	C1	115.51(10)	C11	C12	C7	119.47(11)
C2	N2	C3	115.63(11)	C11	C12	C13	118.29(11)
C5	N3	C6	117.12(10)	C14	C13	C12	117.18(10)
N1	C1	C2	122.29(11)	C20	C13	C12	118.41(11)
N2	C2	C1	122.11(11)	C20	C13	C14	124.37(11)
N2	C3	C4	122.24(11)	C15	C14	C13	120.51(11)
N1	C4	C3	122.18(11)	C15	C14	C19	118.45(11)
N1	C4	C5	119.46(10)	C19	C14	C13	120.97(11)
C3	C4	C5	118.36(11)	C16	C15	C14	120.66(11)
O1	C5	N3	122.84(11)	C17	C16	C15	120.40(12)
O1	C5	C4	120.19(11)	C16	C17	C18	119.52(12)
N3	C5	C4	116.96(10)	C17	C18	C19	120.40(12)
N3	C6	C7	114.23(10)	C18	C19	C14	120.57(12)
C8	C7	C6	119.61(12)	C13	C20	C21	127.44(11)
C8	C7	C12	116.87(12)	C22	C21	C20	121.69(13)
C12	C7	C6	123.23(11)	C26	C21	C20	119.64(12)
F1	C8	C7	117.39(13)	C26	C21	C22	118.57(12)
F1	C8	C9	118.12(12)	C23	C22	C21	120.46(14)
C9	C8	C7	124.47(13)	C24	C23	C22	120.38(14)
C10	C9	C8	117.71(12)	C25	C24	C23	119.68(13)
C9	C10	C11	120.28(13)	C24	C25	C26	120.11(15)
C10	C11	C12	121.21(13)	C25	C26	C21	120.78(14)
C7	C12	C13	122.23(11)				

Table 6 Torsion Angles for 230103_ZJ_ZYH_3aa_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C8	C9	C10	178.23(12)	C10	C11	C12	C13	-179.96(12)
N1	C1	C2	N2	1.4(2)	C11	C12	C13	C14	-124.09(13)
N1	C4	C5	O1	176.24(11)	C11	C12	C13	C20	53.66(17)
N1	C4	C5	N3	-4.82(16)	C12	C7	C8	F1	-178.32(11)
N2	C3	C4	N1	1.50(19)	C12	C7	C8	C9	0.05(19)
N2	C3	C4	C5	-177.34(11)	C12	C13	C14	C15	36.13(16)
N3	C6	C7	C8	88.23(14)	C12	C13	C14	C19	-140.67(12)
N3	C6	C7	C12	-98.21(14)	C12	C13	C20	C21	-166.77(13)
C1	N1	C4	C3	0.28(18)	C13	C14	C15	C16	-177.73(11)
C1	N1	C4	C5	179.11(11)	C13	C14	C19	C18	177.46(12)

Table 6 Torsion Angles for 230103_ZJ_ZYH_3aa_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	N2	C3	C4	-1.75(18)	C13	C20	C21	C22	-132.74(16)
C3	N2	C2	C1	0.36(19)	C13	C20	C21	C26	51.0(2)
C3	C4	C5	O1	-4.88(17)	C14	C13	C20	C21	10.8(2)
C3	C4	C5	N3	174.06(11)	C14	C15	C16	C17	0.50(19)
C4	N1	C1	C2	-1.67(19)	C15	C14	C19	C18	0.60(18)
C5	N3	C6	C7	171.68(10)	C15	C16	C17	C18	0.1(2)
C6	N3	C5	O1	4.46(17)	C16	C17	C18	C19	-0.4(2)
C6	N3	C5	C4	-174.45(10)	C17	C18	C19	C14	0.0(2)
C6	C7	C8	F1	-4.36(17)	C19	C14	C15	C16	-0.85(18)
C6	C7	C8	C9	174.01(12)	C20	C13	C14	C15	-141.47(14)
C6	C7	C12	C11	-173.71(11)	C20	C13	C14	C19	41.73(19)
C6	C7	C12	C13	6.25(18)	C20	C21	C22	C23	-177.62(13)
C7	C8	C9	C10	-0.1(2)	C20	C21	C26	C25	176.70(13)
C7	C12	C13	C14	55.96(16)	C21	C22	C23	C24	1.6(2)
C7	C12	C13	C20	-126.29(14)	C22	C21	C26	C25	0.3(2)
C8	C7	C12	C11	0.02(18)	C22	C23	C24	C25	-0.9(2)
C8	C7	C12	C13	179.97(11)	C23	C24	C25	C26	-0.1(2)
C8	C9	C10	C11	0.1(2)	C24	C25	C26	C21	0.4(2)
C9	C10	C11	C12	-0.1(2)	C26	C21	C22	C23	-1.3(2)
C10	C11	C12	C7	0.0(2)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230103_ZJ_ZYH_3aa_0m.

Atom	*x*	*y*	*z*	U(eq)
H3	4246.67	3923.2	5605.25	30
H1	7801.74	4962.22	5077.32	35
H2	9196.53	1809.49	4968.04	33
H3A	6499.48	-2363.82	5361.34	32
H6A	3137.55	1052.97	6071.71	33
H6B	2040.64	1305.24	5714.44	33
H9	-282.05	8183.31	5775.91	43
H10	362.03	9429.43	6367.3	44
H11	2147.79	7497.88	6734.98	39
H15	5152.43	6842.95	6248.65	30
H16	7368.3	6477.08	6044.48	34
H17	8725.53	3111.07	6167.42	37

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230103_ZJ_ZYH_3aa_0m.

Atom	*x*	*y*	*z*	U(eq)
H18	7852.82	97.33	6495.96	37
H19	5644.82	451.74	6705.56	32
H20	2430.91	3156.33	6970.49	36
H22	3405.59	-556.71	7367.91	44
H23	4978.7	-1601.12	7869.81	49
H24	6882.99	821.42	8075.71	49
H25	7256.85	4245.78	7766.81	50
H26	5727.29	5250.05	7254.35	41

Experimental

Single crystals of $C_{26}H_{20}FN_3O$ **[230103_ZJ_ZYH_3aa_0m]** were **[]**. A suitable crystal was selected and **[]** on a diffractometer. The crystal was kept at 170.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [230103_ZJ_ZYH_3aa_0m]

Crystal Data for $C_{26}H_{20}FN_3O$ (M =409.45 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 9.4685(11) Å, b = 5.7414(7) Å, c = 37.581(4) Å, β = 97.187(3)°, V = 2027.0(4) Å^3, Z = 4, T = 170.00 K, μ(GaKα) = 0.461 mm^{-1}, *Dcalc* = 1.342 g/cm^3, 34858 reflections measured (4.124° ≤ 2Θ ≤ 121.382°), 4663 unique (R_{int} = 0.0665, R_{sigma} = 0.0654) which were used in all calculations. The final R_1 was 0.0489 (I > 2σ(I)) and wR_2 was 0.1178 (all data).

Refinement model description

Number of restraints0, number of constraintsunknown.

Details:

1. Fixed Uiso

At 1.2 times of:

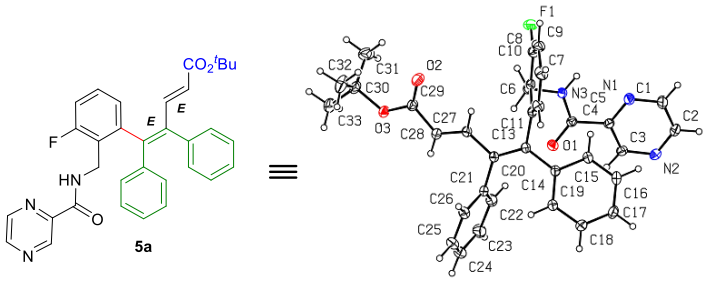
All C(H) groups, All C(H,H) groups, All N(H) groups

2.a Secondary CH2 refined with riding coordinates:

C6(H6A,H6B)

2.b Aromatic/amide H refined with riding coordinates:

N3(H3), C1(H1), C2(H2), C3(H3A), C9(H9), C10(H10), C11(H11), C15(H15), C16(H16), C17(H17), C18(H18), C19(H19), C20(H20), C22(H22), C23(H23), C24(H24), C25(H25), C26(H26)



230103_ZJ_ZYH_5aa_tBu_0m

Table 1 Crystal data and structure refinement for 230103_ZJ_ZYH_5aa_tBu_0m.

Identification code	230103_ZJ_ZYH_5aa_tBu_0m
Empirical formula	$C_{33}H_{30}FN_3O_3$
Formula weight	535.60
Temperature/K	170.00
Crystal system	triclinic
Space group	P-1
a/Å	10.3014(13)
b/Å	15.605(2)
c/Å	18.244(2)
α/°	82.729(4)
β/°	80.543(4)
γ/°	81.413(4)
Volume/Å^3	2844.7(6)
Z	4
ρ_{calc}g/cm^3	1.251
μ/mm^{-1}	0.440
F(000)	1128.0
Crystal size/mm^3	0.08 × 0.05 × 0.04
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	4.296 to 121.18
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23
Reflections collected	54150
Independent reflections	12693 [R_{int} = 0.0596, R_{sigma} = 0.0665]
Data/restraints/parameters	12693/0/727
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0502, wR_2 = 0.1294
Final R indexes [all data]	R_1 = 0.0549, wR_2 = 0.1329
Largest diff. peak/hole / e Å^{-3}	0.26/-0.29

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 230103_ZJ_ZYH_5aa_tBu_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	11077.9(7)	4637.6(5)	7779.0(5)	45.3(2)
O1	7167.0(9)	2934.7(6)	7109.2(5)	35.64(19)
O2	8866.3(10)	6938.8(7)	6099.4(5)	46.7(2)
O3	7963.0(9)	6975.3(6)	5041.1(4)	34.63(19)
N1	8831.9(12)	1710.3(7)	8536.9(7)	41.2(3)
N2	7077.5(11)	546.5(7)	8424.5(6)	36.4(2)
N3	8940.4(9)	3196.2(6)	7608.0(6)	28.6(2)
C1	8777.0(16)	965.2(10)	8981.9(9)	49.3(4)
C2	7894.5(14)	400.3(9)	8931.1(8)	39.6(3)
C3	7161.2(11)	1278.6(8)	7957.4(7)	30.8(2)
C4	8014.9(11)	1864.5(7)	8023.4(6)	27.7(2)
C5	8001.0(11)	2714.8(7)	7531.2(6)	27.0(2)
C6	8962.1(12)	4091.2(7)	7265.1(6)	29.4(2)
C7	8758.4(11)	4701.6(7)	7867.9(6)	27.8(2)
C8	9848.6(12)	4920.9(8)	8126.8(7)	34.0(3)
C9	9766.5(14)	5413.6(9)	8710.8(8)	41.4(3)
C10	8519.8(15)	5700.0(9)	9068.9(8)	42.3(3)
C11	7391.9(13)	5513.6(8)	8828.5(7)	35.8(3)
C12	7495.7(11)	5034.6(7)	8217.7(6)	27.6(2)
C13	6241.6(11)	4929.5(7)	7939.0(6)	27.1(2)
C14	5355.9(11)	4377.2(7)	8450.3(6)	27.6(2)
C15	5922.7(12)	3669.0(8)	8897.2(7)	32.6(2)
C16	5135.1(14)	3131.8(8)	9381.3(7)	37.9(3)
C17	3766.2(14)	3301.8(9)	9441.7(7)	39.7(3)
C18	3190.3(13)	4013.2(9)	9020.9(7)	39.6(3)
C19	3971.9(12)	4546.9(8)	8526.4(7)	33.6(3)
C20	5996.1(11)	5343.6(7)	7262.2(6)	27.6(2)
C21	4827.6(11)	5271.6(8)	6890.8(6)	30.2(2)
C22	4790.7(14)	4549.4(9)	6526.8(7)	38.6(3)
C23	3748.5(16)	4530.0(11)	6129.4(9)	49.5(3)
C24	2743.8(16)	5217.5(11)	6101.3(9)	51.7(4)
C25	2767.1(15)	5936.4(10)	6467.7(9)	49.3(4)
C26	3809.2(13)	5966.8(9)	6855.3(8)	39.8(3)
C27	6947.9(11)	5888.4(7)	6828.6(6)	28.8(2)
C28	6998.9(12)	6199.6(8)	6108.4(7)	31.9(2)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 230103_ZJ_ZYH_5aa_tBu_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C29	8051.5(12)	6739.5(8)	5767.5(7)	33.2(2)
C30	8875.0(14)	7546.4(10)	4577.6(7)	41.7(3)
C31	10290.3(16)	7101.8(16)	4539.5(9)	65.0(5)
C32	8657(2)	8430.6(12)	4880.3(10)	62.1(5)
C33	8404.3(16)	7627.1(11)	3820.6(8)	49.6(4)
F2	2872.1(7)	11449.1(5)	417.1(4)	36.50(17)
O4	7986.9(8)	9792.8(6)	641.4(5)	37.1(2)
O5	3834.4(10)	9336.9(7)	3451.6(5)	47.4(2)
O6	4982.4(9)	8942.0(6)	4426.0(5)	36.0(2)
N4	5869.6(10)	8442.8(7)	1838.8(6)	34.1(2)
N5	8297.9(10)	7364.5(7)	1854.9(7)	38.0(2)
N6	5738.8(9)	9993.7(6)	956.4(5)	26.90(19)
C34	5974.3(13)	7674.2(8)	2251.8(8)	38.0(3)
C35	7179.0(13)	7146.7(8)	2263.5(7)	36.1(3)
C36	8183.0(12)	8127.5(8)	1428.4(7)	33.9(3)
C37	6986.4(11)	8668.9(7)	1429.8(6)	26.9(2)
C38	6950.3(11)	9540.7(7)	969.5(6)	27.3(2)
C39	5543.1(11)	10881.2(7)	588.0(6)	27.1(2)
C40	4615.9(11)	11458.4(7)	1105.6(6)	25.4(2)
C41	3286.5(11)	11677.1(7)	1030.8(7)	28.9(2)
C42	2350.8(12)	12101.8(8)	1538.4(8)	35.8(3)
C43	2764.9(13)	12337.3(8)	2157.0(8)	38.6(3)
C44	4092.0(12)	12159.2(8)	2249.3(7)	34.5(3)
C45	5022.2(11)	11722.5(7)	1730.5(6)	27.4(2)
C46	6446.1(11)	11541.9(7)	1848.9(6)	28.1(2)
C47	7360.5(12)	12068.9(8)	1320.9(6)	31.0(2)
C48	6922.7(14)	12930.7(9)	1067.5(7)	39.0(3)
C49	7721.1(17)	13409.5(10)	530.7(8)	49.5(4)
C50	8968.9(16)	13030.1(12)	228.8(8)	51.4(4)
C51	9416.3(14)	12181.2(11)	475.8(8)	46.7(3)
C52	8626.7(13)	11698.0(9)	1018.6(7)	37.0(3)
C53	6804.2(11)	10936.5(8)	2409.8(6)	28.9(2)
C54	8126.5(11)	10839.7(8)	2666.9(6)	29.4(2)
C55	8578.1(12)	11564.4(9)	2867.8(7)	33.5(3)
C56	9787.1(13)	11486.6(10)	3131.9(7)	42.1(3)
C57	10562.3(13)	10683.3(12)	3194.1(8)	47.5(3)
C58	10124.3(14)	9959.9(11)	2998.7(8)	45.6(3)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 230103_ZJ_ZYH_5aa_tBu_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C59	8916.3(13)	10035.5(9)	2735.6(7)	37.6(3)
C60	5834.2(12)	10374.6(8)	2799.1(6)	31.0(2)
C61	5909.4(13)	9850.9(8)	3434.6(7)	33.7(3)
C62	4789.5(13)	9356.0(8)	3752.7(7)	34.1(3)
C63	3994.0(13)	8408.2(9)	4861.7(7)	37.6(3)
C64	3943(2)	7631.9(11)	4447.2(10)	58.9(4)
C65	2653.8(16)	8953.6(13)	5017.9(9)	56.2(4)
C66	4583.8(16)	8119.2(10)	5580.5(8)	49.2(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 230103_ZJ_ZYH_5aa_tBu_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	28.5(4)	43.5(4)	64.6(5)	-6.3(4)	-8.5(3)	-4.5(3)
O1	35.5(4)	33.9(4)	40.1(5)	2.0(4)	-14.6(4)	-7.9(3)
O2	50.4(6)	62.0(6)	33.1(5)	3.5(4)	-8.8(4)	-28.8(5)
O3	36.1(4)	41.1(5)	26.6(4)	3.0(3)	-2.9(3)	-12.0(4)
N1	44.3(6)	37.9(6)	46.4(6)	10.7(5)	-20.9(5)	-18.9(5)
N2	33.6(5)	34.4(5)	42.2(6)	0.9(4)	-5.0(4)	-12.7(4)
N3	27.1(5)	22.5(4)	36.7(5)	0.7(4)	-8.2(4)	-4.2(3)
C1	56.2(9)	46.3(8)	51.7(8)	17.2(6)	-27.2(7)	-24.4(7)
C2	43.2(7)	35.4(6)	40.5(7)	8.0(5)	-8.0(5)	-14.7(5)
C3	27.7(5)	30.1(6)	35.5(6)	-2.5(5)	-5.1(4)	-6.9(4)
C4	25.3(5)	27.4(5)	30.4(5)	-2.5(4)	-3.1(4)	-5.5(4)
C5	25.5(5)	25.8(5)	29.4(5)	-3.5(4)	-2.4(4)	-3.5(4)
C6	31.0(5)	23.7(5)	32.7(6)	0.1(4)	-3.3(4)	-4.8(4)
C7	31.0(6)	21.4(5)	31.5(5)	2.7(4)	-8.0(4)	-5.6(4)
C8	30.5(6)	27.2(5)	44.6(7)	1.5(5)	-10.6(5)	-3.5(4)
C9	41.9(7)	35.4(6)	53.0(8)	-4.5(6)	-22.8(6)	-7.4(5)
C10	51.6(8)	39.3(7)	40.9(7)	-9.8(5)	-17.3(6)	-5.1(6)
C11	39.5(6)	34.7(6)	33.9(6)	-5.6(5)	-8.0(5)	-2.2(5)
C12	31.8(6)	23.2(5)	27.7(5)	2.9(4)	-7.2(4)	-4.8(4)
C13	28.7(5)	23.4(5)	28.6(5)	-0.8(4)	-4.9(4)	-2.4(4)
C14	31.0(5)	26.6(5)	24.9(5)	-0.3(4)	-4.9(4)	-4.7(4)
C15	33.9(6)	31.2(6)	31.2(6)	2.8(5)	-7.1(5)	-2.3(5)
C16	47.0(7)	31.3(6)	32.9(6)	7.5(5)	-6.8(5)	-5.0(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 230103_ZJ_ZYH_5aa_tBu_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C17	45.0(7)	40.5(7)	32.8(6)	6.8(5)	-2.5(5)	-15.4(6)
C18	32.8(6)	47.4(7)	36.9(6)	4.9(5)	-3.0(5)	-9.5(5)
C19	31.5(6)	35.4(6)	31.8(6)	5.2(5)	-5.8(5)	-3.5(5)
C20	29.4(5)	24.2(5)	28.6(5)	0.7(4)	-5.4(4)	-3.4(4)
C21	30.6(6)	31.1(6)	27.9(5)	7.6(4)	-6.0(4)	-8.0(4)
C22	41.7(7)	35.7(6)	39.7(6)	0.9(5)	-12.0(5)	-7.0(5)
C23	55.0(9)	49.9(8)	50.3(8)	-2.4(6)	-21.4(7)	-15.8(7)
C24	46.0(8)	59.5(9)	54.3(8)	10.8(7)	-26.1(7)	-16.1(7)
C25	37.8(7)	49.0(8)	60.2(9)	9.6(7)	-19.6(6)	-2.7(6)
C26	38.0(7)	35.4(6)	45.7(7)	4.3(5)	-12.6(5)	-3.4(5)
C27	30.5(5)	24.4(5)	31.4(5)	0.3(4)	-6.1(4)	-4.1(4)
C28	33.0(6)	32.5(6)	30.3(6)	2.2(4)	-5.7(4)	-8.3(5)
C29	36.2(6)	36.0(6)	27.3(5)	0.1(5)	-3.0(5)	-8.9(5)
C30	42.8(7)	52.6(8)	29.4(6)	5.0(5)	0.6(5)	-19.8(6)
C31	38.1(8)	110.3(16)	43.5(8)	1.6(9)	1.5(6)	-16.1(9)
C32	92.0(13)	52.1(9)	46.0(8)	4.6(7)	-3.9(8)	-36.8(9)
C33	53.9(8)	62.8(9)	30.2(6)	6.5(6)	-2.1(6)	-15.4(7)
F2	37.8(4)	34.9(4)	41.3(4)	-0.6(3)	-19.1(3)	-7.6(3)
O4	28.5(4)	37.5(5)	42.9(5)	7.4(4)	-4.1(4)	-8.1(3)
O5	49.0(6)	63.2(6)	36.3(5)	4.9(4)	-12.8(4)	-29.4(5)
O6	42.2(5)	35.1(4)	31.7(4)	4.8(3)	-6.8(4)	-13.8(4)
N4	30.0(5)	29.8(5)	39.3(5)	2.5(4)	-0.8(4)	-3.3(4)
N5	30.8(5)	34.0(5)	47.8(6)	6.3(5)	-10.5(4)	-3.5(4)
N6	27.0(4)	22.9(4)	31.2(5)	0.0(4)	-4.8(4)	-6.2(3)
C34	34.9(6)	33.2(6)	41.9(7)	5.0(5)	0.7(5)	-6.2(5)
C35	38.0(6)	30.8(6)	39.0(6)	5.6(5)	-9.3(5)	-6.3(5)
C36	26.9(5)	34.4(6)	39.3(6)	3.3(5)	-6.3(5)	-4.9(5)
C37	27.4(5)	27.2(5)	27.3(5)	-1.9(4)	-6.3(4)	-5.3(4)
C38	28.2(5)	28.0(5)	27.0(5)	-0.9(4)	-6.9(4)	-6.7(4)
C39	30.6(5)	24.8(5)	26.4(5)	1.6(4)	-6.7(4)	-6.0(4)
C40	28.6(5)	20.7(5)	27.3(5)	3.5(4)	-6.3(4)	-7.1(4)
C41	31.7(6)	22.1(5)	34.9(6)	3.1(4)	-11.7(4)	-8.0(4)
C42	27.1(6)	29.8(6)	50.8(7)	-1.3(5)	-7.6(5)	-4.9(4)
C43	33.4(6)	34.3(6)	47.2(7)	-10.2(5)	1.9(5)	-5.4(5)
C44	35.1(6)	35.3(6)	35.2(6)	-7.7(5)	-3.7(5)	-9.4(5)
C45	29.5(5)	25.5(5)	28.1(5)	1.0(4)	-5.3(4)	-9.0(4)
C46	29.6(5)	30.6(5)	26.4(5)	-3.2(4)	-5.7(4)	-9.3(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 230103_ZJ_ZYH_5aa_tBu_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C47	32.8(6)	38.0(6)	26.6(5)	0.8(4)	-10.0(4)	-15.7(5)
C48	42.6(7)	39.2(7)	38.8(6)	4.5(5)	-13.8(5)	-16.2(5)
C49	63.1(9)	47.2(8)	44.8(7)	12.8(6)	-20.4(7)	-30.4(7)
C50	54.7(9)	72.2(10)	34.9(7)	9.7(7)	-10.7(6)	-41.4(8)
C51	37.6(7)	74.4(10)	32.7(6)	-2.4(6)	-4.4(5)	-25.9(7)
C52	33.8(6)	49.6(7)	30.2(6)	-0.9(5)	-6.9(5)	-14.4(5)
C53	31.2(6)	30.6(5)	27.1(5)	-3.2(4)	-6.8(4)	-8.5(4)
C54	28.9(5)	35.8(6)	24.1(5)	0.5(4)	-5.1(4)	-8.3(4)
C55	33.4(6)	39.9(6)	29.5(5)	-1.7(5)	-6.4(5)	-12.0(5)
C56	36.3(7)	59.8(8)	35.3(6)	-4.7(6)	-7.4(5)	-20.7(6)
C57	28.5(6)	75.3(10)	39.1(7)	0.8(7)	-8.2(5)	-10.1(6)
C58	34.0(7)	55.8(8)	42.2(7)	0.1(6)	-3.8(5)	3.3(6)
C59	36.5(6)	39.4(7)	36.1(6)	-2.8(5)	-4.5(5)	-4.8(5)
C60	33.8(6)	32.9(6)	28.9(5)	-2.4(4)	-7.1(4)	-10.4(5)
C61	37.7(6)	34.9(6)	31.4(6)	-0.1(5)	-9.2(5)	-12.7(5)
C62	42.0(7)	34.1(6)	28.7(5)	-1.1(5)	-7.0(5)	-12.9(5)
C63	41.9(7)	36.6(6)	32.2(6)	1.7(5)	2.5(5)	-11.7(5)
C64	76.7(11)	45.1(8)	57.2(9)	-6.5(7)	4.6(8)	-30.3(8)
C65	46.4(8)	72.4(11)	42.4(8)	1.7(7)	1.3(6)	0.8(7)
C66	54.7(9)	47.9(8)	38.7(7)	10.5(6)	-2.2(6)	-4.4(6)

Table 4 Bond Lengths for 230103_ZJ_ZYH_5aa_tBu_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C8	1.3571(15)	F2	C41	1.3658(13)
O1	C5	1.2292(14)	O4	C38	1.2285(14)
O2	C29	1.2084(16)	O5	C62	1.2088(16)
O3	C29	1.3440(14)	O6	C62	1.3441(15)
O3	C30	1.4800(15)	O6	C63	1.4773(14)
N1	C1	1.3341(17)	N4	C34	1.3330(16)
N1	C4	1.3362(15)	N4	C37	1.3331(15)
N2	C2	1.3264(17)	N5	C35	1.3305(17)
N2	C3	1.3408(16)	N5	C36	1.3382(16)
N3	C5	1.3449(15)	N6	C38	1.3416(15)
N3	C6	1.4581(14)	N6	C39	1.4616(14)
C1	C2	1.3784(19)	C34	C35	1.3847(18)

Table 4 Bond Lengths for 230103_ZJ_ZYH_5aa_tBu_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C3	C4	1.3879(16)	C36	C37	1.3863(16)
C4	C5	1.5047(15)	C37	C38	1.5044(15)
C6	C7	1.5134(16)	C39	C40	1.5091(16)
C7	C8	1.3898(16)	C40	C41	1.3859(16)
C7	C12	1.4067(16)	C40	C45	1.4041(15)
C8	C9	1.3755(19)	C41	C42	1.3774(18)
C9	C10	1.379(2)	C42	C43	1.3787(19)
C10	C11	1.3884(19)	C43	C44	1.3874(18)
C11	C12	1.3998(17)	C44	C45	1.3960(17)
C12	C13	1.5016(16)	C45	C46	1.4977(16)
C13	C14	1.4822(15)	C46	C47	1.4913(16)
C13	C20	1.3630(15)	C46	C53	1.3605(16)
C14	C15	1.4010(16)	C47	C48	1.3986(18)
C14	C19	1.3977(17)	C47	C52	1.3997(19)
C15	C16	1.3862(17)	C48	C49	1.3882(19)
C16	C17	1.384(2)	C49	C50	1.389(3)
C17	C18	1.3823(19)	C50	C51	1.380(2)
C18	C19	1.3881(17)	C51	C52	1.3929(18)
C20	C21	1.4993(16)	C53	C54	1.4929(16)
C20	C27	1.4607(16)	C53	C60	1.4637(16)
C21	C22	1.3869(18)	C54	C55	1.3957(17)
C21	C26	1.3950(18)	C54	C59	1.3933(18)
C22	C23	1.3965(19)	C55	C56	1.3911(17)
C23	C24	1.377(2)	C56	C57	1.385(2)
C24	C25	1.382(2)	C57	C58	1.383(2)
C25	C26	1.3885(19)	C58	C59	1.3895(19)
C27	C28	1.3373(16)	C60	C61	1.3374(17)
C28	C29	1.4801(16)	C61	C62	1.4822(17)
C30	C31	1.513(2)	C63	C64	1.519(2)
C30	C32	1.523(2)	C63	C65	1.514(2)
C30	C33	1.522(2)	C63	C66	1.524(2)

Table 5 Bond Angles for 230103_ZJ_ZYH_5aa_tBu_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C29	O3	C30	120.91(10)	C62	O6	C63	120.63(10)
C1	N1	C4	116.30(11)	C34	N4	C37	116.24(10)

Table 5 Bond Angles for 230103_ZJ_ZYH_5aa_tBu_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	N2	C3	116.07(11)	C35	N5	C36	115.57(11)
C5	N3	C6	122.50(10)	C38	N6	C39	122.09(9)
N1	C1	C2	121.80(13)	N4	C34	C35	121.85(12)
N2	C2	C1	122.44(12)	N5	C35	C34	122.38(11)
N2	C3	C4	121.66(11)	N5	C36	C37	122.27(11)
N1	C4	C3	121.64(11)	N4	C37	C36	121.65(11)
N1	C4	C5	118.10(10)	N4	C37	C38	119.10(10)
C3	C4	C5	120.21(10)	C36	C37	C38	119.24(10)
O1	C5	N3	124.55(10)	O4	C38	N6	124.65(10)
O1	C5	C4	120.85(10)	O4	C38	C37	120.01(10)
N3	C5	C4	114.59(10)	N6	C38	C37	115.33(10)
N3	C6	C7	109.64(9)	N6	C39	C40	109.70(9)
C8	C7	C6	119.95(11)	C41	C40	C39	121.33(10)
C8	C7	C12	116.93(11)	C41	C40	C45	116.72(10)
C12	C7	C6	123.04(10)	C45	C40	C39	121.61(10)
F1	C8	C7	118.13(11)	F2	C41	C40	117.92(10)
F1	C8	C9	117.54(11)	F2	C41	C42	117.73(10)
C9	C8	C7	124.33(12)	C42	C41	C40	124.34(11)
C8	C9	C10	117.81(12)	C41	C42	C43	117.98(11)
C9	C10	C11	120.53(12)	C42	C43	C44	120.19(12)
C10	C11	C12	120.77(12)	C43	C44	C45	120.87(12)
C7	C12	C13	122.30(10)	C40	C45	C46	120.80(10)
C11	C12	C7	119.50(11)	C44	C45	C40	119.86(11)
C11	C12	C13	118.15(10)	C44	C45	C46	119.34(10)
C14	C13	C12	115.23(9)	C47	C46	C45	114.90(10)
C20	C13	C12	119.17(10)	C53	C46	C45	119.50(10)
C20	C13	C14	125.60(10)	C53	C46	C47	125.60(10)
C15	C14	C13	118.90(10)	C48	C47	C46	120.16(11)
C19	C14	C13	122.94(10)	C48	C47	C52	118.33(11)
C19	C14	C15	118.13(11)	C52	C47	C46	121.29(11)
C16	C15	C14	120.98(11)	C49	C48	C47	121.04(14)
C17	C16	C15	120.09(11)	C48	C49	C50	120.04(14)
C18	C17	C16	119.64(12)	C51	C50	C49	119.55(13)
C17	C18	C19	120.63(12)	C50	C51	C52	120.82(14)
C18	C19	C14	120.48(11)	C51	C52	C47	120.21(14)
C13	C20	C21	125.64(10)	C46	C53	C54	123.01(10)
C13	C20	C27	119.39(10)	C46	C53	C60	118.68(10)
C27	C20	C21	114.93(9)	C60	C53	C54	118.27(10)

Table 5 Bond Angles for 230103_ZJ_ZYH_5aa_tBu_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C22	C21	C20	120.88(11)	C55	C54	C53	119.70(11)
C22	C21	C26	118.94(12)	C59	C54	C53	121.83(11)
C26	C21	C20	119.98(11)	C59	C54	C55	118.44(11)
C21	C22	C23	119.88(13)	C56	C55	C54	120.85(13)
C24	C23	C22	120.73(14)	C57	C56	C55	119.98(13)
C23	C24	C25	119.76(13)	C58	C57	C56	119.72(12)
C24	C25	C26	119.91(14)	C57	C58	C59	120.43(14)
C25	C26	C21	120.77(13)	C58	C59	C54	120.58(13)
C28	C27	C20	126.91(11)	C61	C60	C53	127.47(11)
C27	C28	C29	118.70(11)	C60	C61	C62	118.99(11)
O2	C29	O3	125.29(11)	O5	C62	O6	125.06(11)
O2	C29	C28	124.53(11)	O5	C62	C61	124.69(11)
O3	C29	C28	110.18(10)	O6	C62	C61	110.24(10)
O3	C30	C31	109.84(12)	O6	C63	C64	108.97(11)
O3	C30	C32	109.35(11)	O6	C63	C65	110.77(11)
O3	C30	C33	101.85(11)	O6	C63	C66	102.02(11)
C31	C30	C32	113.67(15)	C64	C63	C66	110.97(13)
C31	C30	C33	111.02(13)	C65	C63	C64	112.71(14)
C33	C30	C32	110.45(14)	C65	C63	C66	110.89(12)

Table 6 Torsion Angles for 230103_ZJ_ZYH_5aa_tBu_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C8	C9	C10	-179.70(12)	F2	C41	C42	C43	-179.68(10)
N1	C1	C2	N2	2.2(3)	N4	C34	C35	N5	-1.3(2)
N1	C4	C5	O1	-171.66(11)	N4	C37	C38	O4	173.61(11)
N1	C4	C5	N3	7.19(15)	N4	C37	C38	N6	-6.08(15)
N2	C3	C4	N1	2.69(19)	N5	C36	C37	N4	-2.42(19)
N2	C3	C4	C5	-174.87(11)	N5	C36	C37	C38	176.43(11)
N3	C6	C7	C8	91.58(12)	N6	C39	C40	C41	-100.42(11)
N3	C6	C7	C12	-85.03(13)	N6	C39	C40	C45	72.75(13)
C1	N1	C4	C3	-0.2(2)	C34	N4	C37	C36	0.84(18)
C1	N1	C4	C5	177.41(13)	C34	N4	C37	C38	-178.02(11)
C2	N2	C3	C4	-2.62(18)	C35	N5	C36	C37	1.99(19)
C3	N2	C2	C1	0.3(2)	C36	N5	C35	C34	-0.2(2)
C3	C4	C5	O1	5.98(17)	C36	C37	C38	O4	-5.27(16)
C3	C4	C5	N3	-175.17(10)	C36	C37	C38	N6	175.03(11)

Table 6 Torsion Angles for 230103_ZJ_ZYH_5aa_tBu_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	N1	C1	C2	-2.1(2)	C37	N4	C34	C35	0.93(19)
C5	N3	C6	C7	115.84(12)	C38	N6	C39	C40	-131.34(11)
C6	N3	C5	O1	8.22(18)	C39	N6	C38	O4	-4.94(17)
C6	N3	C5	C4	-170.59(10)	C39	N6	C38	C37	174.74(9)
C6	C7	C8	F1	5.82(16)	C39	C40	C41	F2	-8.27(15)
C6	C7	C8	C9	-174.71(11)	C39	C40	C41	C42	171.04(11)
C6	C7	C12	C11	172.66(10)	C39	C40	C45	C44	-171.60(10)
C6	C7	C12	C13	-10.09(16)	C39	C40	C45	C46	8.43(15)
C7	C8	C9	C10	0.8(2)	C40	C41	C42	C43	1.01(18)
C7	C12	C13	C14	114.17(12)	C40	C45	C46	C47	71.09(13)
C7	C12	C13	C20	-66.72(15)	C40	C45	C46	C53	-109.22(13)
C8	C7	C12	C11	-4.04(16)	C41	C40	C45	C44	1.87(15)
C8	C7	C12	C13	173.21(10)	C41	C40	C45	C46	-178.10(10)
C8	C9	C10	C11	-1.8(2)	C41	C42	C43	C44	1.04(19)
C9	C10	C11	C12	-0.2(2)	C42	C43	C44	C45	-1.53(19)
C10	C11	C12	C7	3.23(18)	C43	C44	C45	C40	0.01(18)
C10	C11	C12	C13	-174.13(11)	C43	C44	C45	C46	179.99(11)
C11	C12	C13	C14	-68.54(13)	C44	C45	C46	C47	-108.88(12)
C11	C12	C13	C20	110.56(13)	C44	C45	C46	C53	70.80(15)
C12	C7	C8	F1	-177.38(10)	C45	C40	C41	F2	178.23(9)
C12	C7	C8	C9	2.09(18)	C45	C40	C41	C42	-2.45(16)
C12	C13	C14	C15	-33.47(15)	C45	C46	C47	C48	35.08(15)
C12	C13	C14	C19	144.36(11)	C45	C46	C47	C52	-139.44(11)
C12	C13	C20	C21	176.96(10)	C45	C46	C53	C54	-167.35(10)
C12	C13	C20	C27	-0.79(16)	C45	C46	C53	C60	10.31(16)
C13	C14	C15	C16	-179.70(11)	C46	C47	C48	C49	-174.78(11)
C13	C14	C19	C18	-179.22(12)	C46	C47	C52	C51	174.19(11)
C13	C20	C21	C22	-78.27(16)	C46	C53	C54	C55	52.89(16)
C13	C20	C21	C26	107.00(14)	C46	C53	C54	C59	-129.12(13)
C13	C20	C27	C28	166.14(12)	C46	C53	C60	C61	-167.87(13)
C14	C13	C20	C21	-4.03(19)	C47	C46	C53	C54	12.30(18)
C14	C13	C20	C27	178.21(10)	C47	C46	C53	C60	-170.04(11)
C14	C15	C16	C17	-1.5(2)	C47	C48	C49	C50	0.9(2)
C15	C14	C19	C18	-1.38(18)	C48	C47	C52	C51	-0.43(17)
C15	C16	C17	C18	-0.5(2)	C48	C49	C50	C51	-1.1(2)
C16	C17	C18	C19	1.4(2)	C49	C50	C51	C52	0.6(2)
C17	C18	C19	C14	-0.5(2)	C50	C51	C52	C47	0.2(2)
C19	C14	C15	C16	2.36(18)	C52	C47	C48	C49	-0.10(18)

Table 6 Torsion Angles for 230103_ZJ_ZYH_5aa_tBu_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C20	C13	C14	C15	147.49(12)	C53	C46	C47	C48	-144.58(12)
C20	C13	C14	C19	-34.68(18)	C53	C46	C47	C52	40.90(17)
C20	C21	C22	C23	-174.40(12)	C53	C54	C55	C56	177.93(11)
C20	C21	C26	C25	175.37(12)	C53	C54	C59	C58	-177.97(11)
C20	C27	C28	C29	-179.65(11)	C53	C60	C61	C62	177.81(11)
C21	C20	C27	C28	-11.85(17)	C54	C53	C60	C61	9.91(19)
C21	C22	C23	C24	-0.8(2)	C54	C55	C56	C57	0.36(19)
C22	C21	C26	C25	0.54(19)	C55	C54	C59	C58	0.04(18)
C22	C23	C24	C25	0.2(2)	C55	C56	C57	C58	-0.5(2)
C23	C24	C25	C26	0.7(2)	C56	C57	C58	C59	0.4(2)
C24	C25	C26	C21	-1.1(2)	C57	C58	C59	C54	-0.2(2)
C26	C21	C22	C23	0.39(19)	C59	C54	C55	C56	-0.12(18)
C27	C20	C21	C22	99.57(13)	C60	C53	C54	C55	-124.78(12)
C27	C20	C21	C26	-75.16(14)	C60	C53	C54	C59	53.21(16)
C27	C28	C29	O2	-1.6(2)	C60	C61	C62	O5	5.7(2)
C27	C28	C29	O3	178.64(11)	C60	C61	C62	O6	-173.50(11)
C29	O3	C30	C31	62.24(16)	C62	O6	C63	C64	65.55(16)
C29	O3	C30	C32	-63.15(16)	C62	O6	C63	C65	-58.99(15)
C29	O3	C30	C33	179.97(12)	C62	O6	C63	C66	-177.06(11)
C30	O3	C29	O2	-2.0(2)	C63	O6	C62	O5	0.2(2)
C30	O3	C29	C28	177.77(11)	C63	O6	C62	C61	179.49(10)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230103_ZJ_ZYH_5aa_tBu_0m.

Atom	*x*	*y*	*z*	U(eq)
H3	9565.73	2962.15	7875.5	34
H1	9362.22	819.97	9343.72	59
H2	7870.41	-112.86	9271.53	48
H3A	6622.62	1399.44	7571.53	37
H6A	8250.25	4248.75	6948.96	35
H6B	9824.55	4145.62	6943.07	35
H9	10542.86	5552.12	8862.54	50
H10	8432.27	6027.53	9483.26	51
H11	6539.7	5713.33	9081.58	43
H15	6860.78	3555.31	8868.05	39
H16	5535.38	2646.15	9672.07	46

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230103_ZJ_ZYH_5aa_tBu_0m.

Atom	*x*	*y*	*z*	U(eq)
H17	3225.33	2931.7	9770.5	48
H18	2250.63	4138.1	9070.59	48
H19	3563.1	5030.91	8237.71	40
H22	5473.18	4068.64	6547.7	46
H23	3732.32	4037.18	5875.68	59
H24	2037.36	5197.56	5830.92	62
H25	2070.97	6409.27	6454.51	59
H26	3828.97	6466.72	7099.14	48
H27	7599.91	6037.39	7085.47	35
H28	6371.74	6076.64	5821.2	38
H31A	10336.73	6507.4	4407.24	98
H31B	10583.27	7080.82	5026.81	98
H31C	10867.77	7429.07	4159.75	98
H32A	8973.6	8369.03	5364.72	93
H32B	7708.61	8652.64	4941.79	93
H32C	9149.5	8839.09	4529.05	93
H33A	7469.73	7883	3866.79	74
H33B	8499.34	7048.29	3647.83	74
H33C	8940.6	8002.08	3459.83	74
H6	5039.78	9748.62	1176.69	32
H34	5200.68	7483.04	2546.26	46
H35	7207.6	6609.86	2574.57	43
H36	8947.86	8304.31	1113.89	41
H39A	5163.06	10880.36	123.68	33
H39B	6407.51	11108.77	452.18	33
H42	1447.57	12228.51	1464.51	43
H43	2139.71	12622.38	2521.08	46
H44	4371.36	12336.72	2671.2	41
H48	6065.47	13192.71	1265.81	47
H49	7413.74	13996.9	369.74	59
H50	9510.95	13352.7	-145.16	62
H51	10273.29	11923.29	273.08	56
H52	8948.63	11114.9	1184.28	44
H55	8053.05	12118.05	2823.65	40
H56	10080.66	11984.48	3269.39	51
H57	11391.7	10629.3	3370.45	57
H58	10652.6	9407.68	3044.5	55

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 230103_ZJ_ZYH_5aa_tBu_0m.

Atom	*x*	*y*	*z*	U(eq)
H59	8626.45	9534.45	2601.5	45
H60	5062.51	10382.9	2574.6	37
H61	6669.14	9796.89	3678.33	40
H64A	3526.33	7830.7	3999.15	88
H64B	3423.94	7217.14	4773.22	88
H64C	4847.33	7346.82	4301.67	88
H65A	2762.39	9489.82	5215.63	84
H65B	2062.09	8622.3	5385.44	84
H65C	2269.48	9101.65	4553.8	84
H66A	5457.72	7778.7	5464.86	74
H66B	3995.88	7759.82	5923.23	74
H66C	4677.12	8633.19	5815.74	74

Experimental

Single crystals of $C_{33}H_{30}FN_3O_3$ **[230103_ZJ_ZYH_5aa_tBu_0m]** were **[]**. A suitable crystal was selected and **[]** on a diffractometer. The crystal was kept at 170.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [230103_ZJ_ZYH_5aa_tBu_0m]

Crystal Data for $C_{33}H_{30}FN_3O_3$ (M =535.60 g/mol): triclinic, space group P-1 (no. 2), a = 10.3014(13) Å, b = 15.605(2) Å, c = 18.244(2) Å, α = 82.729(4)°, β = 80.543(4)°, γ = 81.413(4)°, V = 2844.7(6) Å^3, Z = 4, T = 170.00 K, μ(GaKα) = 0.440 mm^{-1}, *Dcalc* = 1.251 g/cm^3, 54150 reflections measured (4.296° ≤ 2Θ ≤ 121.18°), 12693 unique (R_{int} = 0.0596, R_{sigma} = 0.0665) which were used in all calculations. The final R_1 was 0.0502 (I > 2σ(I)) and wR_2 was 0.1329 (all data).

Refinement model description

Number of restraints0, number of constraintsunknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All N(H) groups

At 1.5 times of:

All C(H,H,H) groups

2.a Secondary CH2 refined with riding coordinates:

C6(H6A,H6B), C39(H39A,H39B)

2.b Aromatic/amide H refined with riding coordinates:

N3(H3), C1(H1), C2(H2), C3(H3A), C9(H9), C10(H10), C11(H11), C15(H15), C16(H16), C17(H17), C18(H18), C19(H19), C22(H22), C23(H23), C24(H24), C25(H25), C26(H26), C27(H27), C28(H28), N6(H6), C34(H34), C35(H35), C36(H36), C42(H42), C43(H43), C44(H44), C48(H48), C49(H49), C50(H50), C51(H51), C52(H52), C55(H55), C56(H56), C57(H57), C58(H58), C59(H59), C60(H60), C61(H61)

2.c Idealised Me refined as rotating group:

C31(H31A,H31B,H31C), C32(H32A,H32B,H32C), C33(H33A,H33B,H33C), C64(H64A,H64B, H64C), C65(H65A,H65B,H65C), C66(H66A,H66B,H66C)