Supporting Information

Synthesis of α-diazo-β-keto esters, phosphonates and sulfones via acylbenzotriazole-mediated acylation of diazomethyl anion

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Experimental Section

General experimental information

All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (Merck, 100-200 mesh). Melting points were recorded on a Precision melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer's RX I FTIR spectrophotometer. NMR spectra were recorded on a Brucker Avance spectrometer at 400 or 500 MHz (^{1}H), 100 or 125 MHz (^{13}C), and 162 MHz (^{31}P). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for ^{1}H and ^{13}C and phosphoric acid as the external standard for ^{31}P. The ^{13}C and ^{31}P spectra were proton decoupled and in case of ^{1}H NMR, the standard abbreviations such as s, d, t, q, m, dd referring to singlet, doublet, triplet, quartet, multiplet and doublet of doublet respectively, are used to describe spin multiplicity. The coupling constants (*J*) are given in Hz. The ESI-HRMS spectra were recorded on Agilent 6520- Q-TofLC/MS system.

Since diazo compounds are potentially hazardous (toxic and explosive), all the reactions were performed in fume hood with proper safety measures. All reactions were conducted in oven-dried glass wares under Nitrogen. THF was dried over sodium benzophenone ketyl. All other solvents and reagents were used as obtained from commercial sources. EDA, DAMP and diazomethylphenylsulfone were prepared according to the standard protocols.[1] Acyl benzotriazoles were prepared from corresponding carboxylic acids following the literature procedure.[2] The spectroscopic data for novel acyl benzotriazoles (**1i** & **1l**) is provided below.

General procedure for the DBU catalyzed acylation of diazo compounds with acyl benzotriazoles 1

To a stirred solution of acyl benzotriazole **1** (1.1 mmol) in dry MeCN (5 mL) was added the diazo substrate (1.0 mmol) followed by DBU (0.5 – 1.0 mmol, see tables 2, 3, 4) and the reaction mixture was stirred at room temperature for 10 min. to 2 hours (see Tables 2, 3, 4). Acetonitrile was distilled off under reduced pressure and crude residue was directly subjected to column chromatograpy on silica gel using hexane/ethyl acetate as eluent to afford the pure product **3**/**5**/**9**.

General procedure for the LDA catalyzed acylation of EDA 6 with acyl benzotriazoles 1

To diisopropylamine (1.5 mmol, 0.2 mL) in anhydrous THF (5 mL) was added n-BuLi (1.4 mmol, 0.9 mL, 1.6 M in hexane) dropwise at -78 ^{o}C to generate LDA. The

mixture was stirred for 30 minutes followed by dropwise addition of EDA **6** (1 mmol, 114 mg) dissolved in 1 mL of THF. After stirring for another 30 minutes the acyl benzotriazole **1**(1.1 mmol) dissolved in 1 mL THF was added into the reaction mixture in one portion. The reaction mixture was stirred at -78 ^{o}C for 1h before gradually warming it to the room temperature. The reaction was quenched by saturated solution of NH_4Cl (aq.) upon completion (TLC monitoring). The reaction mixture was extracted with ethyl acetate (15 mL x 3) and the combined organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude mixture was subjected to column chromatograpy on silica gel using hexane/ethyl acetate as eluent to afford the pure product **7**.

(1H-benzo[d][1,2,3]triazol-1-yl)(2-(phenylethynyl)phenyl)methanone (1i). Colourless solid (243 mg, 75%), Mp 118-120 °C. R_f 0.50 (30% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 – 8.32 (m, 2H), 8.01 – 8.04 (m, 2H), 7.67 – 7.69 (m, 2H), 7.58 – 7.64 (m, 2H), 7.39 – 7.52 (m, 2H), 7.07 – 7.11 (m, 2H), 6.99 – 7.03 (m, 2H), 6.83 – 6.86 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3 (CO), 146.2 (C_{Ar}), 135.2 (C_{Ar}), 132.8 ($C_{Ar}H$), 131.7 ($C_{Ar}H$), 131.6 (C_{Ar}), 131.4 ($C_{Ar}H$ x 2), 130.5 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 128.6 ($C_{Ar}H$), 128.1 ($C_{Ar}H$ x 2), 128.0 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 123.4 (C_{Ar}), 122.2 (C_{Ar}), 120.3 ($C_{Ar}H$), 114.3 ($C_{Ar}H$), 94.6 (C≡C), 86.2 (C≡C); **HRMS** for $C_{21}H_{13}N_3O$: calcd. ($M + Na^+$): 346.0951, found: 346.0957.

(1H-benzo[d][1,2,3]triazol-1-yl)(quinolin-2-yl)methanone (1l). Brown solid (219 mg, 80%), Mp 120-123 °C, R_f 0.50 (50% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 – 8.37 (m, 2H), 8.20 (d, J = 6.8 Hz, 1H), 8.12 (d, J = 6.6 Hz, 1H), 8.04 (d, J = 6.7 Hz, 1H), 7.89 (d, J = 6.5 Hz, 1H), 7.75 – 7.78 (m, 1H), 7.62 – 7.70 (m, 2H), 7.50 – 7.53 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7 (CO), 150.0 (C_{Ar}), 147.5 (C_{Ar}), 145.9 (C_{Ar}), 137.1 ($C_{Ar}H$), 132.1 (C_{Ar}), 130.7 ($C_{Ar}H$), 130.6 ($C_{Ar}H$), 130.5 ($C_{Ar}H$), 129.2 (C_{Ar}), 129.0 ($C_{Ar}H$), 127.7 ($C_{Ar}H$), 126.6 ($C_{Ar}H$), 121.6 ($C_{Ar}H$), 120.4 ($C_{Ar}H$), 114.6 ($C_{Ar}H$); **HRMS** for $C_{16}H_{10}N_4O$: calcd. (MH^+): 275.0927, found: 275.0930.

Dimethyl 1-diazo-2-oxo-2-phenylethylphosphonate (3a).[3] Yellow viscous liquid (219 mg, 86%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1039, 1216, 1279, 1390, 1636, 2117, 3016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.58 (m, 2H), 7.43 – 7.48 (m, 1H), 7.35 – 7.39 (m, 2H), 3.73 (d, $^{3}J_{H\text{-}P}$ = 11.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.4 (d, $^{2}J_{C\text{-}P}$ = 9.2 Hz, C_{Ar}), 136.7 (d, $^{3}J_{C\text{-}P}$ = 2.9 Hz, C_{Ar}), 132.5 ($C_{Ar}H$), 128.7 ($C_{Ar}H$ x 2), 127.3 ($C_{Ar}H$ x 2), 62.9 (d, $^{1}J_{C\text{-}P}$ = 217.4 Hz, CN_2), 54.0 (d, $^{2}J_{C\text{-}P}$ = 5.9 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 13.82; **HRMS** for $C_{10}H_{11}N_2O_4P$: calcd. (MH^+): 255.0529, found: 255.0522.

Dimethyl 1-diazo-2-(4-methoxyphenyl)-2-oxoethylphosphonate (3b). Yellow viscous liquid (244 mg, 86%). R_f 0.50 (70% EtOAc/hexane); **IR** (film, cm^{-1}): 1035, 1217, 1260, 1409, 1511, 1605, 2113, 3016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 3.78 (d, $^3J_{H\text{-}P}$ = 12.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.8 (d, $^2J_{C\text{-}P}$ = 9.3 Hz, CO), 163.1 ($C_{Ar}H$), 129.8 ($C_{Ar}H$ x 2), 129.3 (d, $^3J_{C\text{-}P}$ = 2.7 Hz, C_{Ar}), 113.8 ($C_{Ar}H$ x 2), 62.1 (d, $^1J_{C\text{-}P}$ = 217.1 Hz, CN_2), 55.5 (OCH_3), 54.0 (d, $^2J_{C\text{-}P}$ = 5.9 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 14.02; **HRMS** for $C_{11}H_{13}N_2O_5P$: calcd. (MH^+): 285.0635, found: 285.0632.

Dimethyl 1-diazo-2-(4-nitrophenyl)-2-oxoethylphosphonate (3c). Light yellow solid (260 mg, 87%), Mp 78-80 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1043, 1218, 1277, 1400, 1529, 1639, 2122; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.9 Hz, 2H), 7.77 (d, J = 8.9 Hz, 2H), 3.74 (d, $^3J_{H\text{-}P}$ = 11.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.6 (d, $^2J_{C\text{-}P}$ = 10.9 Hz, CO), 149.6 (C_{Ar}), 142.0 (C_{Ar}), 128.4 ($C_{Ar}H$ x 2), 123.6 ($C_{Ar}H$ x 2), 65.0 (d, $^1J_{C\text{-}P}$ = 217.6 Hz, CN_2), 54.0 (d, $J_{C\text{-}P}$ = 5.8 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 12.45; **HRMS** for $C_{10}H_{10}N_3O_6P$: calcd. (MH^+): 300.0380, found: 300.0379.

Dimethyl 2-(2-bromophenyl)1-diazo-2-oxoethylphosphonate (3d). Colorless solid (283 mg, 85%), Mp 78-80 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1039, 1216, 1297, 1389, 1643, 2125, 3016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.9 Hz, 1H), 7.22 – 7.33 (m, 3H), 3.75 (d, $^3J_{H\text{-}P}$ = 12.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.0 (d, $^2J_{C\text{-}P}$ = 9.4 Hz, CO), 138.8 (d, $^3J_{C\text{-}P}$ = 3.3 Hz, C_{Ar})133.2 ($C_{Ar}H$), 131.9 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 127.6 ($C_{Ar}H$), 118.5 (C_{Ar}), 54.1 (d, $^2J_{C\text{-}P}$ = 5.9 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 11.97; **HRMS** for $C_{10}H_{10}BrN_2O_4P$: calcd. (MH^+): 332.9634, found: 332.9634.

Dimethyl 2-(4-bromophenyl)-1-diazo-2-oxoethylphosphonate (3e). Yellow viscous liquid (293 mg, 88%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1039, 1216, 1395, 1590, 1634, 2117; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.54 (m, 4H), 3.74 (d, $^3J_{H\text{-}P}$ = 11.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.2 (d, $^2J_{C\text{-}P}$ = 9.9 Hz, CO), 135.5 (C_{Ar}), 131.9 ($C_{Ar}H$ x 2), 129.0 ($C_{Ar}H$ x 2), 127.3 (C_{Ar}), 63.6 (d, $^1J_{C\text{-}P}$ = 217.7 Hz, CN_2), 54.0 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 13.39; **HRMS** for $C_{10}H_{10}BrN_2O_4P$: calcd. (MH^+): 332.9634, found: 332.9624.

Dimethyl 2-(4-chlorophenyl)-1-diazo-2-oxoethylphosphonate (3f). Yellow viscous liquid (263 mg, 91%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1040, 1217, 1400, 1635, 2117; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.59 (m, 2H), 7.35 – 7.38 (m, 2H), 3.75 (d, $^3J_{H\text{-}P}$ = 11.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.0 (d, $^2J_{C\text{-}P}$ = 9.8 Hz, CO), 138.8 (C_{Ar}), 135.0 (C_{Ar}), 128.9 ($C_{Ar}H$ x 4), 63.5 (d, $^1J_{C\text{-}P}$ = 217.3 Hz, CN_2), 54.0 (d, $^2J_{C\text{-}P}$ = 5.9 Hz,

{PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 13.40; **HRMS** for $C_{10}H_{10}ClN_2O_4P$: calcd. (MH^+): 289.0139, found: 289.0139.

Dimethyl 1-diazo-2-(2-fluorophenyl)-2-oxoethylphosphonate (3g). Yellow viscous liquid (223 mg, 82%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1057, 1218, 1264, 1310, 1403, 1637, 2126; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.46 (m, 2H), 7.17 – 7.20 (m, 1H), 7.06 – 7.10 (m, 1H), 3.78 (d, $^3J_{H\text{-}P}$ = 12.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.7 (d, $^2J_{C\text{-}P}$ = 8.6 Hz, CO), 158.8 (d, $J_{C\text{-}F}$ = 248.6 Hz, C_{Ar}), 133.6 (d, $J_{C\text{-}F}$ = 8.3 Hz, $C_{Ar}H$), 129.6 ($C_{Ar}H$), 125.3 (d, $J_{C\text{-}F}$ = 12.7 Hz, C_{Ar}), 124.8 ($C_{Ar}H$), 116.1 (d, $J_{C\text{-}F}$ = 21.7 Hz, $C_{Ar}H$), 64.9 (d, $^1J_{C\text{-}P}$ = 217.2 Hz, CN_2), 54.0 (d, $J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 12.73; **HRMS** for $C_{10}H_{10}FN_2O_4P$: calcd. (MH^+): 273.0435, found: 273.0436.

Dimethyl 1-diazo-2-oxo-2-(4-(trifluoromethyl)phenyl)ethylphosphonate (3h). Yellow viscous liquid (245 mg, 76%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1059, 1217, 1280, 1323, 1407, 1639, 2120, 3018; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 3.75 (d, $^3J_{H\text{-}P}$ = 12.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.3 (d, $^2J_{C\text{-}P}$ = 10.6 Hz, CO), 139.8 (C_{Ar}), 133.9 (d, $^2J_{C\text{-}F}$ = 32.7 Hz, C_{Ar}), 125.7 (br q, CF_3), 127.8 ($C_{Ar}H$ x 4), 64.2 (d, $^1J_{C\text{-}P}$ = 219.7 Hz, CN_2), 54.1 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 12.99; **HRMS** for $C_{11}H_{10}F_3N_2O_4P$: calcd. (MH^+): 323.0403, found: 323.0405.

Dimethyl 1-diazo-2-oxo-2-(2-(phenylethynyl)phenyl)ethylphosphonate (3i). Yellow viscous liquid (291 mg, 82%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1059, 1219, 1380, 1639, 1718; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.54 (m, 9H), 3.74 (d, $^3J_{H\text{-}P}$ = 12.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.9 (CO), 139.7 (C_{Ar}, $^3J_{C\text{-}P}$ = 4.1 Hz), 132.7 ($C_{Ar}H$), 131.6 ($C_{Ar}H$ x 2), 130.8 ($C_{Ar}H$), 129.0 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.5 ($C_{Ar}H$ x 2), 127.3 ($C_{Ar}H$), 122.3 (C_{Ar}), 120.4 (C_{Ar}), 93.9 (C≡C), 85.8 (C≡C), 64.8 (d, $^1J_{C\text{-}P}$ = 213.4 Hz, CN_2), 54.1 (d, $^2J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 13.16; **HRMS** for $C_{18}H_{15}N_2O_4P$: calcd. (MH^+): 355.0842, found: 355.0843.

Dimethyl 1-diazo-2-(furan-2-yl)-2-oxoethylphosphonate (3j). Yellow viscous liquid (195 mg, 80%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1068, 1156, 1216, 1385, 1638, 2127; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 0.9 Hz, 1H), 7.18 (d, J = 3.7 Hz, 1H), 6.50 (dd, J = 3.6 Hz, J = 1.7 Hz, 1H), 3.79 (d, $^3J_{H\text{-}P}$ = 12.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3 (d, $^2J_{C\text{-}P}$ = 8.2 Hz, CO), 151.3 (d, $^3J_{C\text{-}P}$ = 5.1 Hz, C_{fur}), 145.3 ($C_{fur}H$), 117.3 ($C_{fur}H$), 112.5 ($C_{fur}H$), 60.7 (d, $^1J_{C\text{-}P}$ = 218.9 Hz, CN_2), 54.0 (d, $J_{C\text{-}P}$ = 5.9 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 14.24; **HRMS** for $C_8H_9N_2O_5P$: calcd. (MH^+): 245.0322, found: 245.0314.

Dimethyl 1-diazo-2-(1H-indol-2-yl)-2-oxoethylphosphonate (3k). Yellow solid (258 mg, 88%), Mp 140-142 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1035, 1155, 1217, 1387, 1617, 2118; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.05 – 7.37 (m, 4H), 3.81 (d, $^3J_{H\text{-}P}$ = 12.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.9 (d, $^2J_{C\text{-}P}$ = 10.5 Hz, CO), 136.8 (C_{Ar}), 132.6 (C_{Ar}), 127.5 (C_{Ar}), 126.5 ($C_{Ar}H$), 123.2 ($C_{Ar}H$), 121.2 ($C_{Ar}H$), 112.1 ($C_{Ar}H$), 108.7 ($C_{Ar}H$), 54.1 (d, $^2J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 14.20; **HRMS** for $C_{12}H_{12}N_3O_4P$: calcd. (MH^+): 294.0638, found: 294.0639.

Dimethyl 1-diazo-2-oxo-2-(quinolin-2-yl)ethylphosphonate (3l). Brown viscous liquid (250 mg, 82%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1039, 1149, 1216, 1332, 1388, 1634, 2130, 3016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.5 Hz, 1H), 7.99 – 8.04 (m, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.70 – 7.74 (m, 1H), 7.58 – 7.62 (m, 1H), 3.85 (d, $^3J_{H\text{-}P}$ = 12.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.3 (d, $^2J_{C\text{-}P}$ = 8.2 Hz, CO), 152.5 (d, $^3J_{C\text{-}P}$ = 5.5 Hz, C_{Ar}), 146.2 (C_{Ar}), 137.5 ($C_{Ar}H$), 130.4 ($C_{Ar}H$), 129.7 ($C_{Ar}H$), 129.6 (C_{Ar}), 128.9 ($C_{Ar}H$), 127.8 ($C_{Ar}H$), 118.4 ($C_{Ar}H$), 61.9 (d, $^1J_{C\text{-}P}$ = 219.2 Hz, CN_2), 54.1 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 12.99; **HRMS** for $C_{13}H_{12}N_3O_4P$: calcd. (MH^+): 306.0638, found: 306.0643.

Dimethyl 2-cyclohexyl-1-diazo-2-oxoethylphosphonate (3m). Yellow viscous liquid (206 mg, 79%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1034, 1216, 1264, 1393, 1648, 2118, 2935; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.77 (d, $^3J_{H\text{-}P}$ = 11.9 Hz, 6H), 2.58 – 2.64 (m, 1H), 1.61 – 1.79 (m, 5H), 1.34 – 1.43 (m, 2H), 1.13 – 1.26 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.1 (d, $^2J_{C\text{-}P}$ = 12.7 Hz, CO), 62.0 (d, $^1J_{C\text{-}P}$ = 222.7 Hz, CN_2), 53.6 (d, $^2J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 x 2), 47.3 (CH), 28.8 (CH_2 x 2), 25.5 (CH_2), 25.4 (CH_2 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 14.57; **HRMS** for $C_{10}H_{17}N_2O_4P$: calcd. (MH^+): 261.0999, found: 261.1001.

Dimethyl 1-diazo-2-oxo-3-phenylpropylphosphonate (3n). Light yellow viscous liquid (231 mg, 86%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1032, 1217, 1268, 1390, 1654, 2124, 3017; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.26 (m, 5H), 3.79 (s, 2H), 3.69 (d, $^3J_{H\text{-}P}$ = 11.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.2 (d, $^2J_{C\text{-}P}$ = 13.2 Hz, CO), 133.4 (C_{Ar}), 129.4 ($C_{Ar}H$ x 2), 128.6 ($C_{Ar}H$ x 2), 127.3 ($C_{Ar}H$), 63.5 (d, $^1J_{C\text{-}P}$ = 218.0 Hz, CN_2), 53.6 (d, $^2J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 x 2), 45.8 (CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 13.92; **HRMS** for $C_{11}H_{13}N_2O_4P$: calcd. (MH^+): 269.0686, found: 269.0691.

Dimethyl 1-diazo-3-(4-methoxyphenyl)-2-oxopropylphosphonate (3o). Yellow viscous liquid (248 mg, 83%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1033, 1218, 1402, 1640, 2125; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.7 Hz, 2H),

3.73 (s, 2H), 3.70 (d, $^{3}J_{H\text{-}P}$ = 12.0 Hz, 6H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.6 (d, $^{2}J_{C\text{-}P}$ = 13.3 Hz, CO), 158.8 (C_{Ar}), 130.5 ($C_{Ar}H$ x 2), 125.3 (C_{Ar}), 114.1 ($C_{Ar}H$ x 2), 63.2 (d, $^{1}J_{C\text{-}P}$ = 218.0 Hz, CN_2), 55.3 (CH_3), 53.6 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 x 2), 44.9 (CH_2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 14.02; **HRMS** for $C_{12}H_{15}N_2O_5P$: calcd. (MH^+): 299.0791, found: 299.0790.

2-Diazo-1-phenyl-2-(phenylsulfonyl)ethanone (5a).[4] Yellow solid (258 mg, 90%), Mp 128-130 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1025, 1069, 1156, 1215, 1385, 1645, 2109, 2400; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 8.00 (m, 2H), 7.57 – 7.61 (m, 1H), 7.47 – 7.51 (m, 5H), 7.35 – 7.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.6 (CO), 141.5 (C_{Ar}), 135.8 (C_{Ar}), 134.2 ($C_{Ar}H$), 133.1 ($C_{Ar}H$), 129.1 ($C_{Ar}H$ x 2), 128.9 ($C_{Ar}H$ x 2), 128.1 ($C_{Ar}H$ x 2), 127.5 ($C_{Ar}H$ x 2), 83.4 (CN_2); **HRMS** for $C_{14}H_{10}N_2O_3S$: calcd. (MH^+): 287.0485, found: 284.0476.

2-Diazo-1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (5b). Yellow solid (288 mg, 91%), Mp 85-87 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1075, 1159, 1216, 1261, 1338, 1406, 1602, 2106, 3022; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 8.00 (m, 2H), 7.56 – 7.60 (m, 1H), 7.46 – 7.52 (m, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.2 (CO), 163.6 (C_{Ar}), 141.7 (C_{Ar}), 134.1 ($C_{Ar}H$), 129.9 ($C_{Ar}H$ x 2), 129.1 ($C_{Ar}H$ x 2), 128.4 (C_{Ar}), 128.1 ($C_{Ar}H$ x 2), 114.1 ($C_{Ar}H$ x 2), 82.5 (CN_2), 55.6 (CH_3); **HRMS** for $C_{15}H_{12}N_2O_4S$: calcd. (MH^+): 317.0591, found: 317.0587.

2-Diazo-1-(4-nitrophenyl)-2-(phenylsulfonyl)ethanone (5c). Yellow solid (282 mg, 85%), Mp 148-150 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1083, 1152, 1216, 1340, 1404, 1586, 2116, 3022; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.51 (m, 2H), 7.59 – 7.63 (m, 3H), 7.88 (d, *J* = 7.6 Hz, 2H), 8.21 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.3 (CO), 150.1 (C_{Ar}), 141.2 (C_{Ar}), 140.8 (C_{Ar}), 134.5 ($C_{Ar}H$), 129.4 ($C_{Ar}H$ x 2), 128.7 ($C_{Ar}H$ x 2), 128.0 ($C_{Ar}H$ x 2), 124.0 ($C_{Ar}H$ x 2), 85.2 (CN_2); **HRMS** for $C_{14}H_9N_3O_5S$: calcd. (MH^+): 332.0336, found: 332.0333.

1-(4-Bromophenyl)-2-Diazo-2-(phenylsulfonyl)ethanone (5e). Yellow solid (340 mg, 93%), Mp 120-12 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1070, 1155, 1218, 1393, 1644, 2110; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.96 (m, 2H), 7.57 – 7.61 (m, 1H), 7.47 – 7.53 (m, 4H), 7.34 – 7.37 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.6 (CO), 141.4 (C_{Ar}), 134.5 (C_{Ar}), 134.3 ($C_{Ar}H$), 132.2 ($C_{Ar}H$ x 2), 129.2 ($C_{Ar}H$ x 2), 129.0 ($C_{Ar}H$ x 2), 128.1 ($C_{Ar}H$ x 2), 128.0 (C_{Ar}), 83.8 (CN_2); **HRMS** for $C_{14}H_9BrN_2O_3S$: calcd. (MH^+): 364.9590, found: 364.9589.

1-(4-Chlorophenyl)-2-Diazo-2-(phenylsulfonyl)ethanone (5f). Yellow solid (301 mg, 94%), Mp 125-128 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1083, 1155, 1216, 1327, 1642, 2111; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.57 – 7.61 (m, 1H), 7.43 – 7.51 (m, 4H), 7.33 – 7.35 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.5 (CO), 141.4 (C_{Ar}), 139.5 (C_{Ar}), 134.3 ($C_{Ar}H$), 134.1 (C_{Ar}), 129.2 ($C_{Ar}H$ x 4), 129.0 ($C_{Ar}H$ x 2), 128.1 ($C_{Ar}H$ x 2), 83.8 (CN_2); **HRMS** for $C_{14}H_9ClN_2O_3S$: calcd. (MH^+): 321.0095, found: 321.0096.

2-Diazo-1-(2-fluorophenyl)-2-(phenylsulfonyl)ethanone (5g). Yellow solid (253 mg, 83%), Mp 85-87 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1088, 1122, 1158, 1216, 1341, 1643, 2119, 2403; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.61 (m, 1H), 7.38 – 7.51 (m, 4H), 7.14 – 7.19 (m, 1H), 7.01 – 7.05 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.9 (CO), 159.0 (d, $J_{C\text{-}F}$ = 249.8 Hz, C_{Ar}), 141.3 (C_{Ar}), 134.4 (d, $J_{C\text{-}F}$ = 8.7 Hz, $C_{Ar}H$), 134.3 ($C_{Ar}H$), 130.3 ($C_{Ar}H$), 129.2 ($C_{Ar}H$ x 2), 128.1 ($C_{Ar}H$ x 2), 125.1 (d, $J_{C\text{-}F}$ = 3.4 Hz, $C_{Ar}H$), 124.4 (d, $J_{C\text{-}F}$ = 14.8 Hz, C_{Ar}), 116.3 (d, $J_{C\text{-}F}$ = 21.8 Hz, $C_{Ar}H$), 85.9 (CN_2); **HRMS** for $C_{14}H_9FN_2O_3S$: calcd. (MH^+): 305.0391, found: 305.0373.

2-Diazo-2-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethanone (5h). Light yellow solid (280 mg, 79%), Mp 110-113 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1064, 1216, 1325, 1645, 2115, 3021; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.93 (m, 2H), 7.57 – 7.64 (m, 5H), 7.47 – 7.50 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.8 (CO), 141.3 (C_{Ar}), 138.8 (C_{Ar}), 134.4 ($C_{Ar}H$), 134.3 (C_{Ar}), 129.3 ($C_{Ar}H$ x 4), 128.1 ($C_{Ar}H$ x 2), 127.9 ($C_{Ar}H$ x 2), 125.9 (q merged into d, CF_3); **HRMS** for $C_{15}H_9F_3N_2O_3S$: calcd. (MH^+): 355.0359, found: 355.0360.

2-Diazo-1-(furan-2-yl)-2-(phenylsulfonyl)ethanone (5j). Brown solid (218 mg, 79%), Mp 98-100 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1077, 1158, 1218, 1388, 1633, 2118, 3024; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.43 – 4.59 (m, 5H), 7.15 (d, *J* = 3.5 Hz, 1H), 6.48 (dd, *J* = 3.3 Hz, *J* = 1.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0 (CO), 151.0 (C_{Ar}), 145.3 ($C_{Ar}H$), 141.4 (C_{Ar}), 134.2 ($C_{Ar}H$), 129.1 ($C_{Ar}H$ x 2), 128.3 ($C_{Ar}H$ x 2), 118.0 ($C_{Ar}H$), 112.9 ($C_{Ar}H$), 81.7 (CN_2); **HRMS** for $C_{12}H_8N_2O_4S$: calcd. (MH^+): 277.0278, found: 277.0278.

2-Diazo-1-(1H-indol-2-yl)-2-(phenylsulfonyl)ethanone (5k). Yellow solid (283 mg, 87%), Mp 152-154 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1069, 1157, 1217, 1385, 1622, 2107; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.62 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.34 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.95 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6 (CO), 141.6 (C_{Ar}), 136.7 (C_{Ar}), 134.2 ($C_{Ar}H$),

131.9 (C_{Ar}), 129.2 ($C_{Ar}H$ x 2), 128.2 ($C_{Ar}H$ x 2), 127.3 (C_{Ar}), 126.9 ($C_{Ar}H$), 123.2 ($C_{Ar}H$), 121.6 ($C_{Ar}H$), 112.1 ($C_{Ar}H$), 108.3 ($C_{Ar}H$); **HRMS** for $C_{16}H_{11}N_3O_3S$: calcd. (MH^+): 326.0594, found: 326.0590.

2-Diazo-2-(phenylsulfonyl)-1-(quinolin-2-yl)ethanone (5l). Yellow solid (293 mg, 87%), Mp 150-152 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1073, 1156, 1216, 1335, 1387, 1643, 2125, 3023; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 7.4 Hz, 2H), 7.92 – 7.97 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.73 (m, 1H), 7.56 – 7.61 (m, 2H), 7.49 – 7.52 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8 (CO), 151.7 (C_{Ar}), 146.1 (C_{Ar}), 141.6 (C_{Ar}), 137.7 ($C_{Ar}H$), 134.0 ($C_{Ar}H$), 130.6 ($C_{Ar}H$), 129.7 (C_{Ar}), 129.5 ($C_{Ar}H$), 129.2 ($C_{Ar}H$), 129.0 ($C_{Ar}H$ x 2), 128.4 ($C_{Ar}H$ x 2), 127.9 ($C_{Ar}H$), 118.2 ($C_{Ar}H$), 83.1 (CN_2); **HRMS** for $C_{17}H_{11}N_3O_3S$: calcd. (MH^+): 338.0594, found: 338.0594.

1-Cyclohexyl-2-diazo-2-(phenylsulfonyl)ethanone (5m). Yellow solid (257 mg, 88%), Mp 80-82 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1099, 1156, 1216, 1383, 1662, 2110, 2858; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.93 (m, 2H), 7.57 – 7.61 (m, 1H), 7.48 – 7.52 (m, 2H), 2.59 – 2.66 (m, 1H), 1.48 – 1.68 (m, 5H), 1.06 – 1.31 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.8 (CO), 142.2 (C_{Ar}), 134.1 ($C_{Ar}H$), 129.4 ($C_{Ar}H$ x 2), 127.4 ($C_{Ar}H$ x 2), 84.2 (CN_2), 47.0 (CH), 28.5 (CH_2 x 2), 25.4 (CH_2 x 3); **HRMS** for $C_{14}H_{16}N_2O_3S$: calcd. (MH^+): 293.0954, found: 293.0938.

Ethyl 2-diazo-3-oxo-3-phenylpropanoate (7a).[5] Yellow oil (135 mg, 62%), R_f 0.50 (30% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.57 (m, 2H), 7.43 – 7.48 (m, 1H), 7.33 – 7.37 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); **HRMS** for $C_{11}H_{10}N_2O_3$: calcd. (MH^+): 219.0764, found: 219.0752.

Ethyl 2-diazo-3-(4-methoxyphenyl)-3-oxopropanoate (7b).[6] Yellow oil (188 mg, 76%), R_f 0.50 (30% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.61 (m, 2H), 6.83 – 6.86 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **HRMS** for $C_{12}H_{12}N_2O_4$: calcd. (MH^+): 249.0870, found: 249.0871.

Ethyl 3-(4-bromophenyl)-2-diazo-3-oxopropanoate (7e).[7] Yellow oil (196 mg, 66%), R_f 0.50 (30% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.51 (m, 2H), 7.42 – 7.45 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); **HRMS** for $C_{11}H_9BrN_2O_3$: calcd. (MH^+): 296.9869, found: 296.9868.

Ethyl 3-(4-chlorophenyl)-2-diazo-3-oxopropanoate (7f).[8] Yellow oil (173 mg, 69%), R_f 0.50 (30% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.51 (m, 2H), 7.42 – 7.45 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); **HRMS** for $C_{11}H_9ClN_2O_3$: calcd. (MH^+): 253.0374, found: 253.0374.

Ethyl 2-diazo-3-(furan-2-yl)-3-oxopropanoate (7j).[5] Yellow oil (124 mg, 60%), R_f 0.50 (30% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 0.6 Hz, *J* = 1.6 Hz, 1H), 7.43 (dd, *J* = 0.6 Hz, *J* = 3.6 Hz, 1H), 6.49 (dd, *J* = 1.7 Hz, *J* = 3.6 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **HRMS** for $C_9H_8N_2O_4$: calcd. (MH^+): 209.0557, found: 209.0558.

Dimethyl 5-chloro-2-(2-diazoacetyl)phenylphosphoramidate (9a). Colorless solid (176 mg, 58%), Mp 100-102 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1024, 1225, 1294, 1499, 1581, 2112, 3067; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (d, $^2J_{H\text{-}P}$ = 10.2 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 7.23 (dd, *J* = 1.6 Hz, *J* = 8.6 Hz, 1H), 6.84 (dd, *J* = 2.0 Hz, *J* = 8.6 Hz, 1H), 5.81 (s, 1H), 3.74 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.2 (CO), 143.6 (C_{Ar}), 140.4 (C_{Ar}), 129.3 ($C_{Ar}H$), 120.8 ($C_{Ar}H$), 118.7 (d, $^2J_{C\text{-}P}$ = 7.2 Hz, C_{Ar}), 118.6 ($C_{Ar}H$), 55.9 (CN_2), 53.7 (d, $^2J_{C\text{-}P}$ = 4.4 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 3.04; **HRMS** for $C_{10}H_{11}ClNO_4P$ (cyclised product after N_2 elimination): calcd. (MH^+): 276.0187, found: 276.0199.

Selected X-Ray Crystallographic data for **9a**, $C_{10}H_{11}ClN_3O_4P$: *M* = 303.64, Triclinic, *P*1, *a* = 5.927(5) Å, *b* = 8.999(5)Å, *c* = 13.598(5)Å, *V* = 685.6(7)Å^3, α = 106.549(5)°, β = 97.092(5)°, γ = 94.090(5)°, *Z* = 2, D_c = 1.471 g cm^{-3}, μ(Mo-Kα) = 0.408 mm^{-1}, *F*(000) = 312, Reflections Collected/unique = 8330/2555 observed = 1509 [*R*(int) = 0.050]. Final R indices [$I>2\sigma(I)$], *R*1 =0.0565, wR_2 = 0.1463 S = 1.04.

Dimethyl 2-(2-diazoacetyl)phenylphosphoramidate (9b). Brown solid (124 mg, 46%), Mp 90-92 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1042, 1299, 1359, 1586, 2111, 3020; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (d, $^2J_{H\text{-}P}$ = 10.6 Hz, 1H), 7.30 – 7.41 (m, 3H), 6.85 – 6.89 (m, 1H), 5.85 (s, 1H), 3.73 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.2 (CO), 142.2 (C_{Ar}), 134.3 ($C_{Ar}H$), 128.3 ($C_{Ar}H$), 120.5 ($C_{Ar}H$), 120.4 (C_{Ar}), 118.7 ($C_{Ar}H$), 55.8 (CN_2), 53.6 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 3.84; **HRMS** for $C_{10}H_{12}NO_4P$ (cyclised product after N_2 elimination): calcd. (MH^+): 242.0577, found: 242.2575.

Dimethyl 2-(2-diazoacetyl)-6-methylphenylphosphoramidate (9c). Brown solid (156 mg, 55%), Mp 112-115 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1046, 1216, 1353, 1406, 1599, 2109, 3019; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (br s, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.94 (t, *J* = 7.7 Hz, 1H), 5.74 (s, 1H), 3.70 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.1 (CO), 138.4 (C_{Ar}), 135.9 ($C_{Ar}H$), 134.2 (C_{Ar}), 128.4 (C_{Ar}), 125.7 ($C_{Ar}H$), 123.4 ($C_{Ar}H$), 56.6 (CN_2), 53.7 (d, $^2J_{C\text{-}P}$ = 6.0 Hz,

{PO}OCH_3 x 2), 19.4 (CH_3); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 3.04; **HRMS** for $C_{11}H_{14}NO_4P$ (cyclised product after N_2 elimination): calcd. (MH^+): 256.0733, found: 256.0725.

Dimethyl 2-(2-diazoacetyl)-4,5-dimethoxyphenylphosphoramidate (9d). Colorless solid (224 mg, 68%), Mp 130-132 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1039, 1156, 1215, 1272, 1378, 1524, 1627, 2109, 3020; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.14 (d, $^2J_{H\text{-}P}$ = 10.0 Hz, 1H), 7.09 (s, 1H), 6.70 (d, J = 1.0 Hz, 1H), 5.75 (s, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.72 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.7 (CO), 154.8 (C_{Ar}), 142.9 (C_{Ar}), 139.0 (C_{Ar}), 112.3 (d, $^2J_{C\text{-}P}$ = 8.9 Hz, C_{Ar}), 110.8 ($C_{Ar}H$), 101.7 ($C_{Ar}H$), 56.7 (OCH_3), 56.1 (OCH_3), 55.0 (CN_2), 53.7 (d, $^2J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 4.04; **HRMS** for $C_{12}H_{16}NO_6P$ (cyclised product after N_2 elimination): calcd. (MH^+): 302.0788, found: 302.0791.

Dimethyl 2,4-dibromo-6-(2-diazoacetyl)phenylphosphoramidate (9e). Colorless solid (278 mg, 65%), Mp 146-148 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1054, 1152, 1217, 1291, 1385, 1638, 1717, 3019; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 2.3 Hz, J = 0.5 Hz, 1H), 7.43 (dd, J = 2.2 Hz, J = 0.8 Hz, 1H), 6.91 (br s, 1H), 5.71 (s, 1H), 3.72 (d, $^3J_{H\text{-}P}$ = 11.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9 (CO), 138.8 (C_{Ar}), 130.2 ($C_{Ar}H$ x 2), 126.3 (C_{Ar}), 121.7 (C_{Ar}), 117.3 (C_{Ar}), 57.4 (CN_2), 54.0 (d, $^2J_{C\text{-}P}$ = 5.9 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 4.05; **HRMS** for $C_{10}H_{10}Br_2NO_4P$ (cyclised product after N_2 elimination): calcd. (MH^+): 397.8787, found: 397.8784.

Dimethyl 2-(2-diazoacetyl)-3-fluorophenylphosphoramidate (9f). Brown viscous liquid (135 mg, 47%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1047, 1218, 1399, 1638, 2112; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.92 (d, J = 9.5 Hz, 1H), 7.17 – 7.29 (m, 2H), 6.58 – 6.63 (m, 1H), 6.03 (s, 1H), 3.73 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.8 (CO), 162.4 (d, $^1J_{C\text{-}P}$ = 250.7 Hz, $C_{Ar}F$), 144.0 (C_{Ar}), 134.1 (d, $^3J_{C\text{-}P}$ = 12.2 Hz, $C_{Ar}H$), 114.4 ($C_{Ar}H$ merged with C_{Ar}), 108.0 (d, $^2J_{C\text{-}F}$ = 24.9 Hz, $C_{Ar}H$), 60.6 (d, $J_{C\text{-}F}$ = 23.9 Hz, CN_2), 53.7 (d, $^2J_{C\text{-}P}$ = 5.3 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 3.42; **HRMS** for $C_{10}H_{11}FNO_4P$ (cyclised product after N_2 elimination): calcd. (MH^+): 260.0482, found: 260.0480.

Dimethyl 1-diazo-2-(2-(methylamino)phenyl)-2-oxoethylphosphonate (9g). Yellow viscous liquid (232 mg, 82%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1067, 1218, 1403, 1639, 3671, 3849; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.9 Hz, J = 1.5 Hz, 1H), 7.28-7.32 (m, 1H), 7.08 (br s, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.52-6.57 (m, 1H), 3.79 (d, $^3J_{H\text{-}P}$ = 11.9 Hz, 6H), 2.79 (d, J = 3.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.0 (d, $^2J_{C\text{-}P}$ = 8.3 Hz, CO), 150.3 (C_{Ar}), 134.8 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 117.2 (d, $^3J_{C\text{-}P}$ = 3.8 Hz, C_{Ar}), 114.3

($C_{Ar}H$), 111.7 ($C_{Ar}H$), 61.2 (d, $^{1}J_{C\text{-}P}$ = 218.3 Hz, CN_2), 54.0 (d, $^{2}J_{C\text{-}P}$ = 5.8 Hz, {PO}OCH_3 x 2), 29.6 (CH_3); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 15.40; **HRMS** for $C_{11}H_{14}N_3O_4P$: calcd. (MH^+): 284.0795, found: 284.0786.

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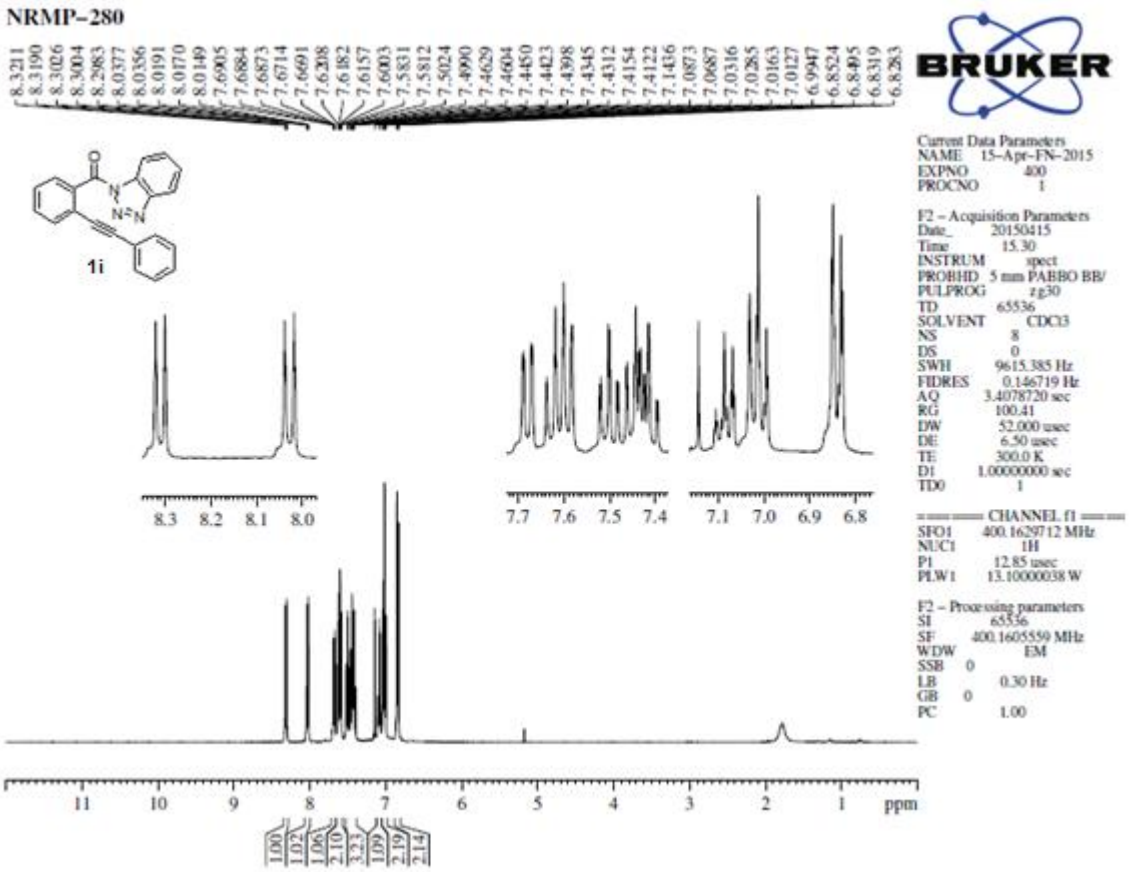

Figure 1: ^{1}H NMR spectrum of 1i

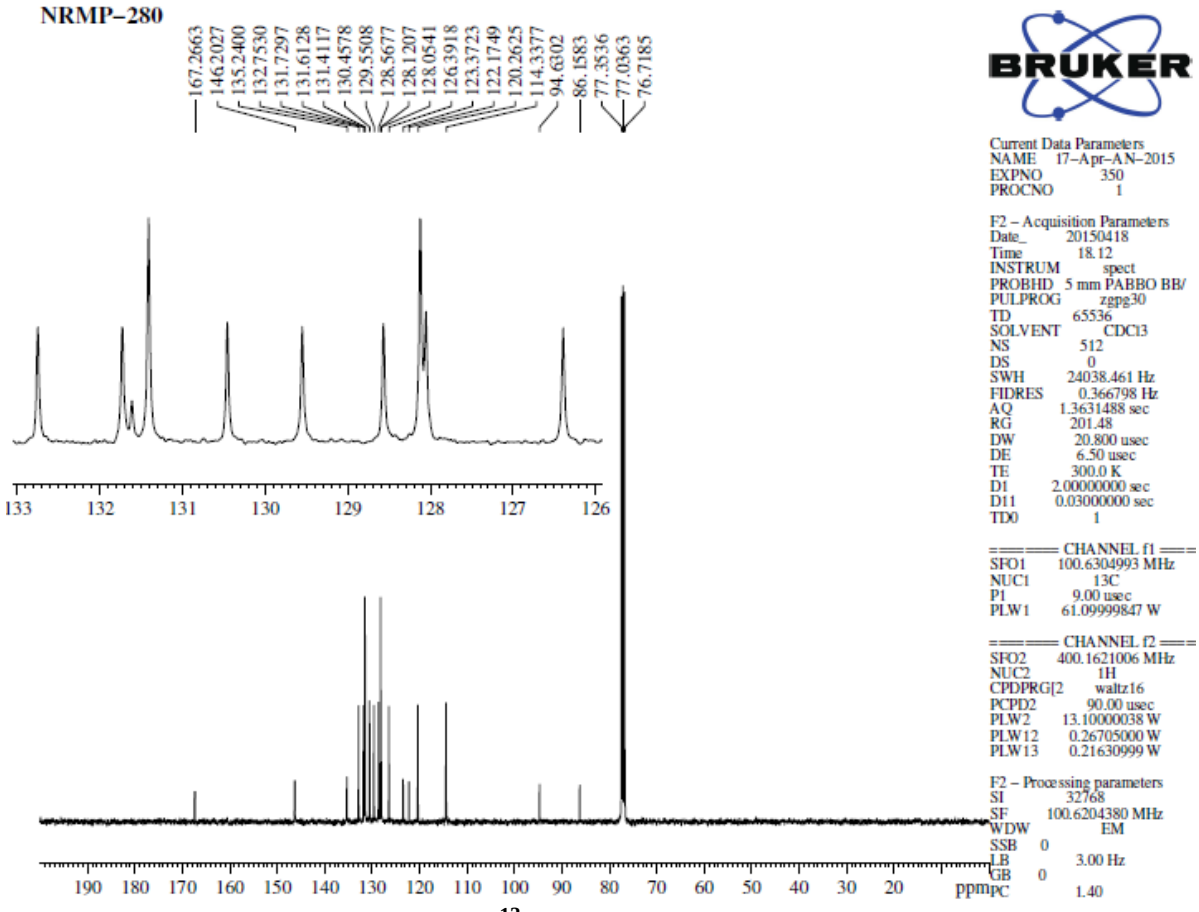

Figure 2: ^{13}C NMR spectrum of 1i

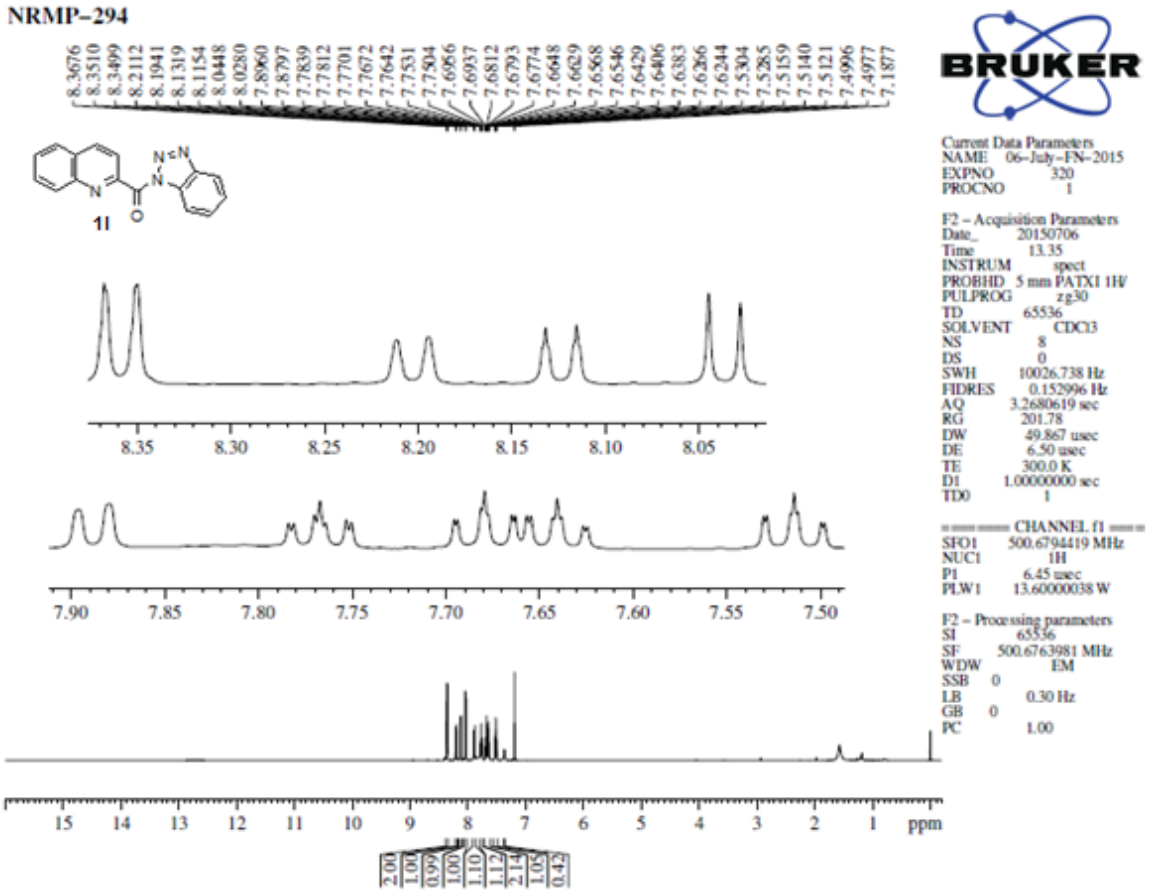

Figure 3: ^{1}H NMR spectrum of 1l

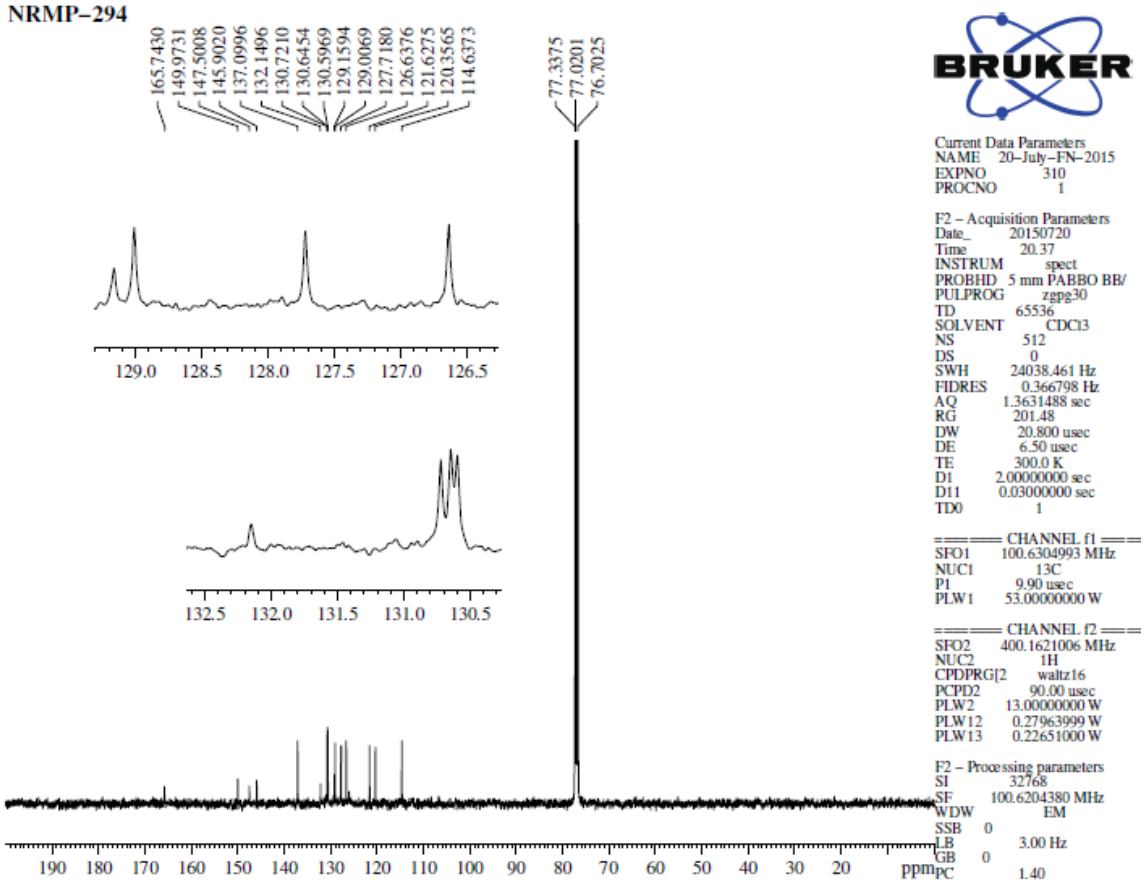

Figure 4: ^{13}C NMR spectrum of 1l

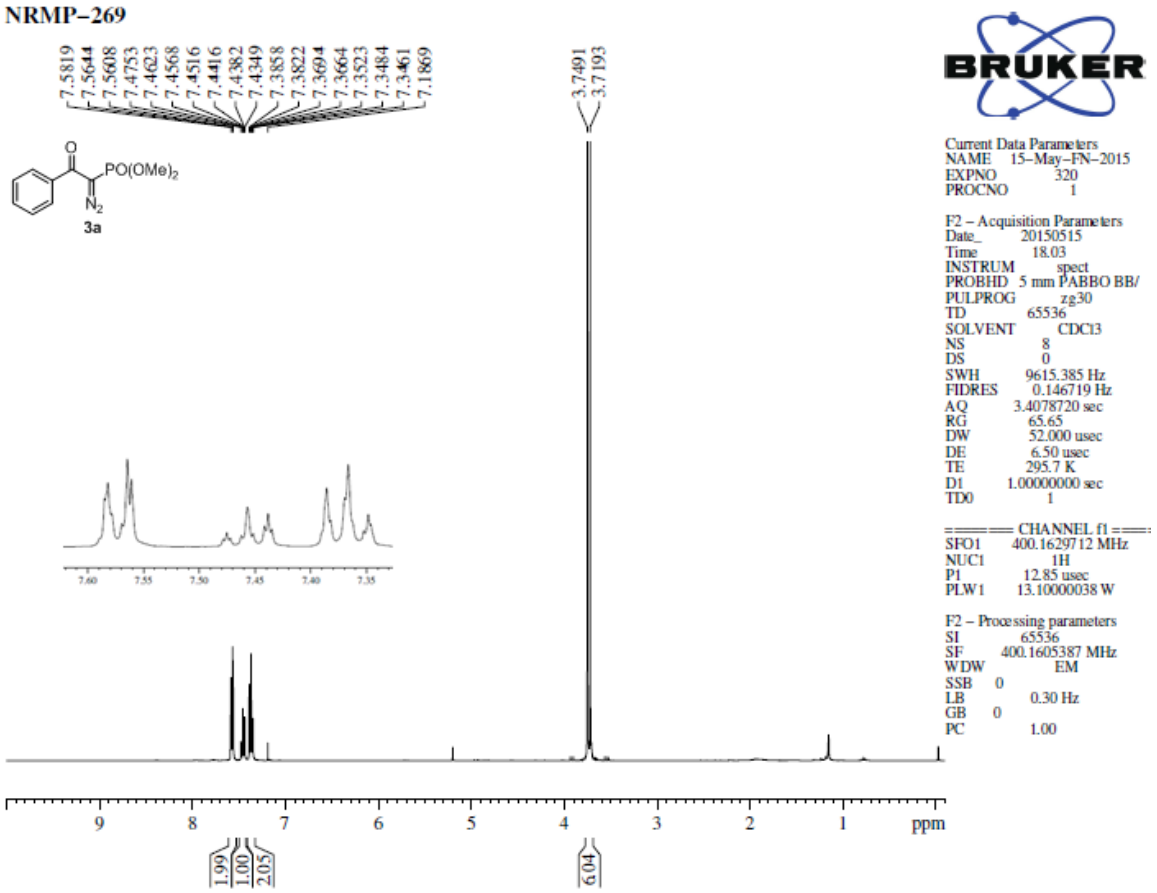

Figure 5: ^{1}H NMR spectrum of 3a

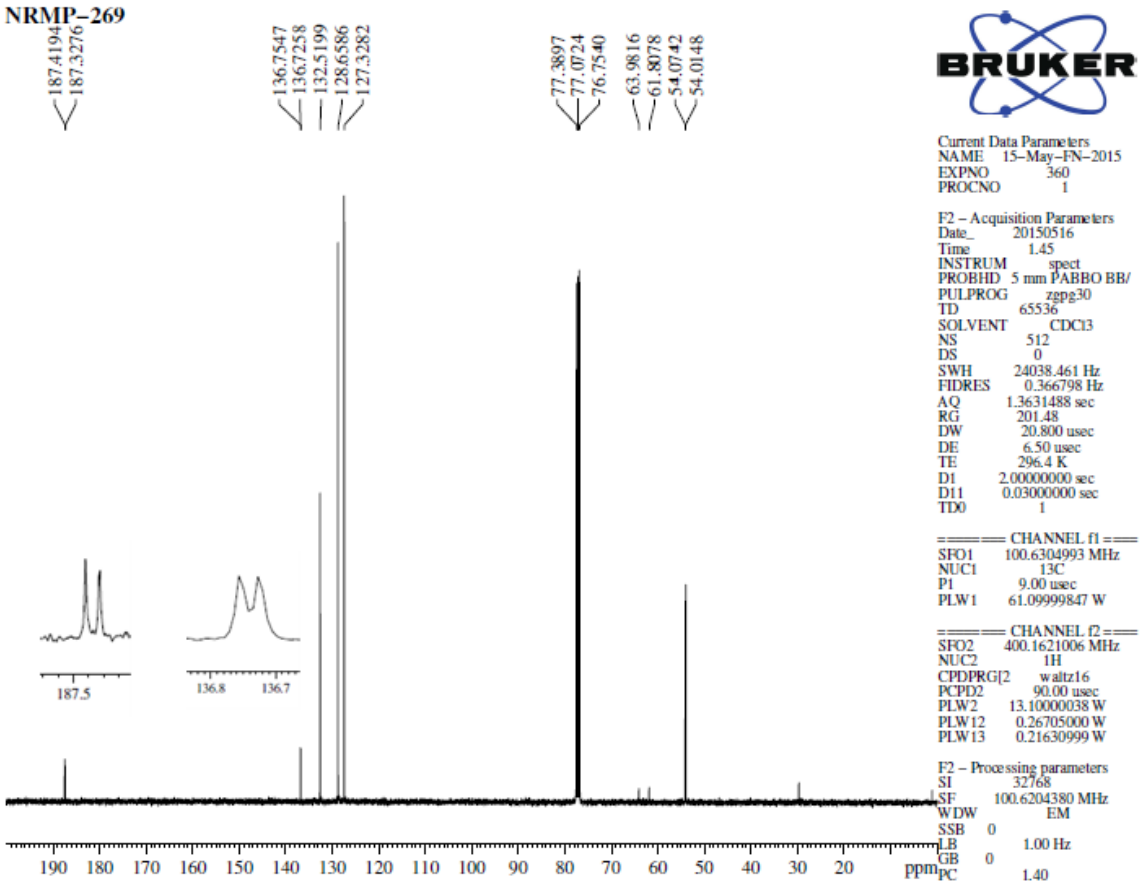

Figure 6: ^{13}C NMR spectrum of 3a

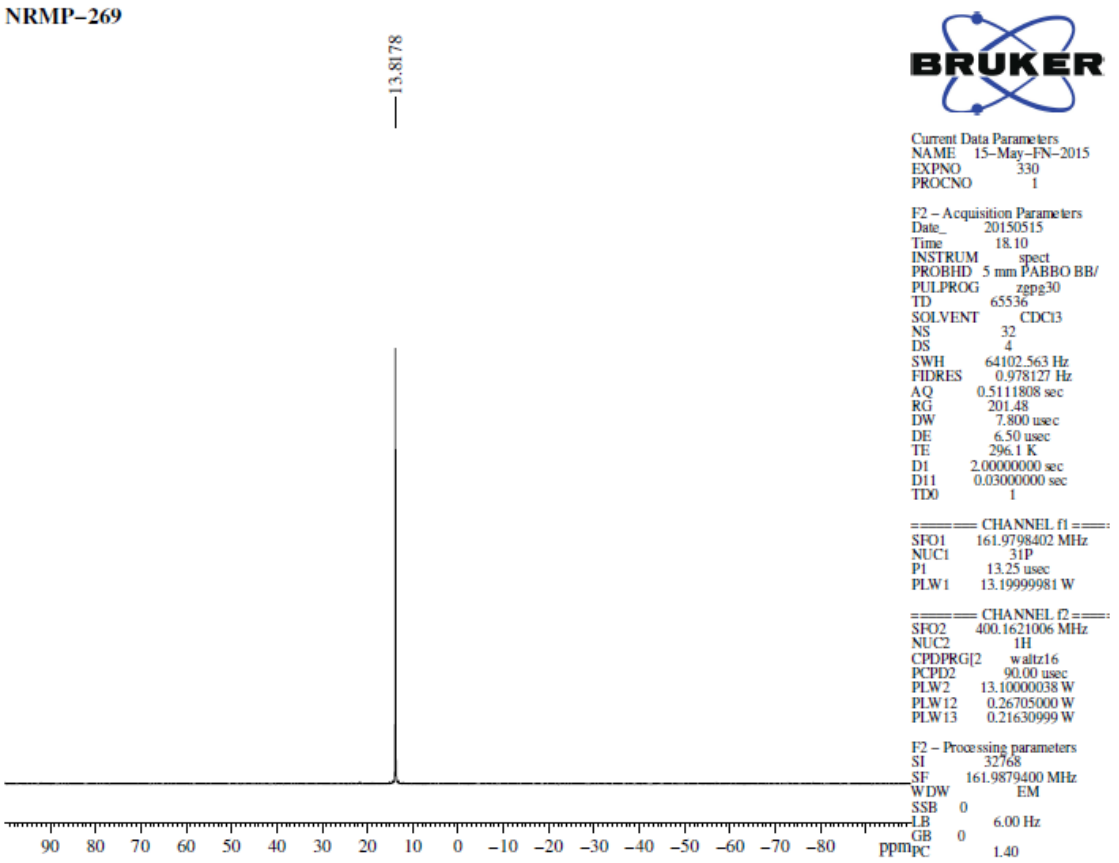

Figure 7: ^{31}P NMR spectrum of 3a

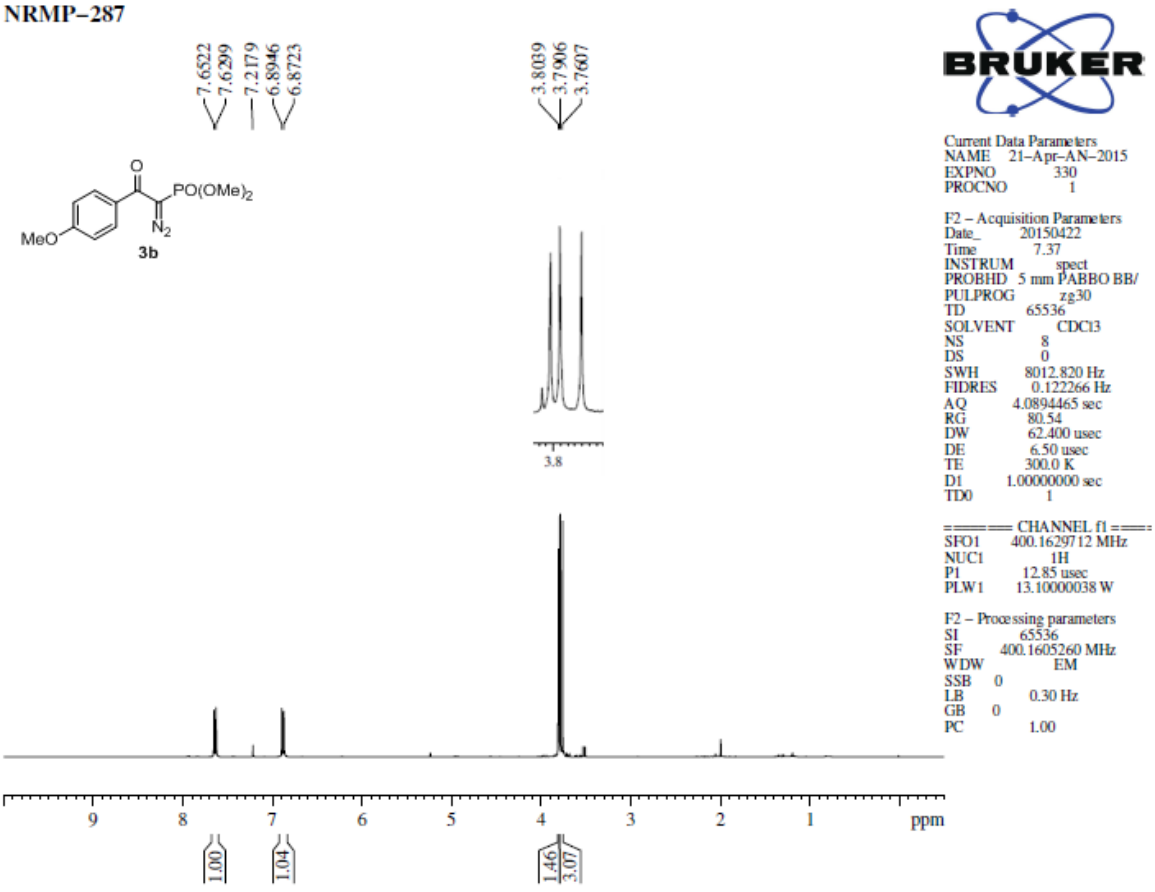

Figure 8: ^{1}H NMR spectrum of 3b

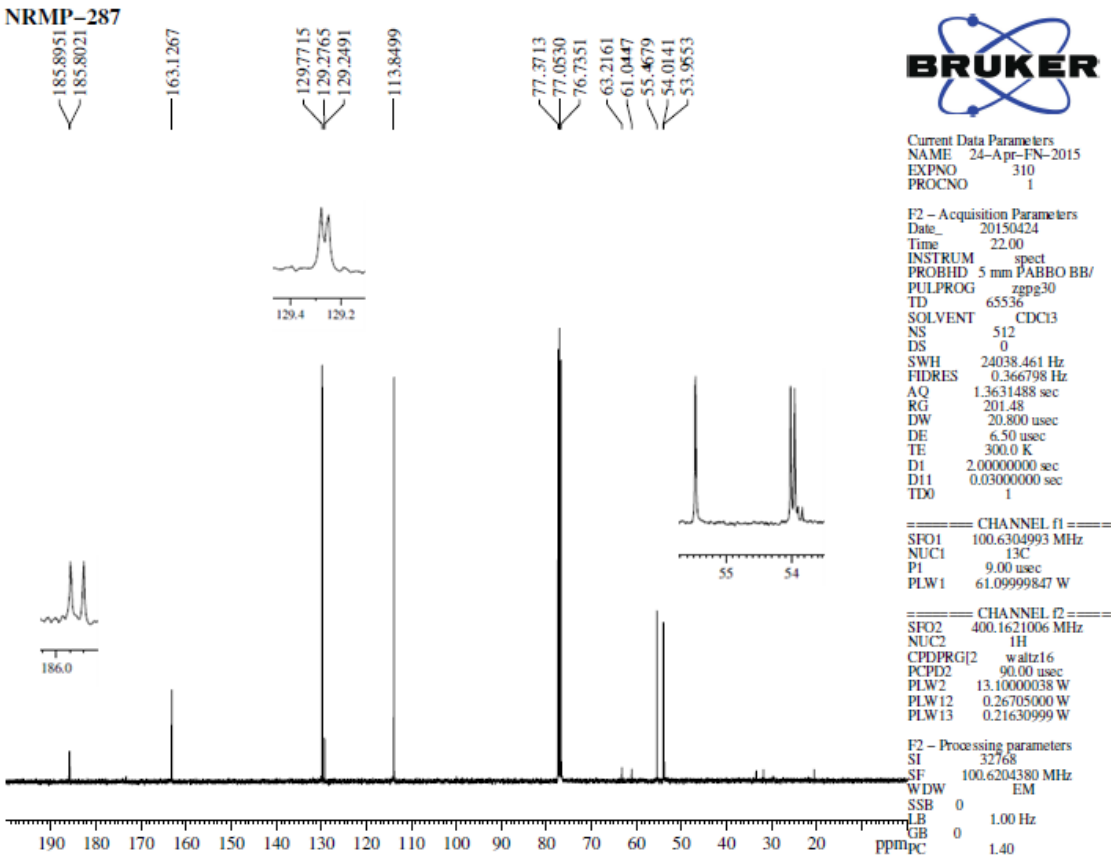

Figure 9: ^{13}C NMR spectrum of 3b

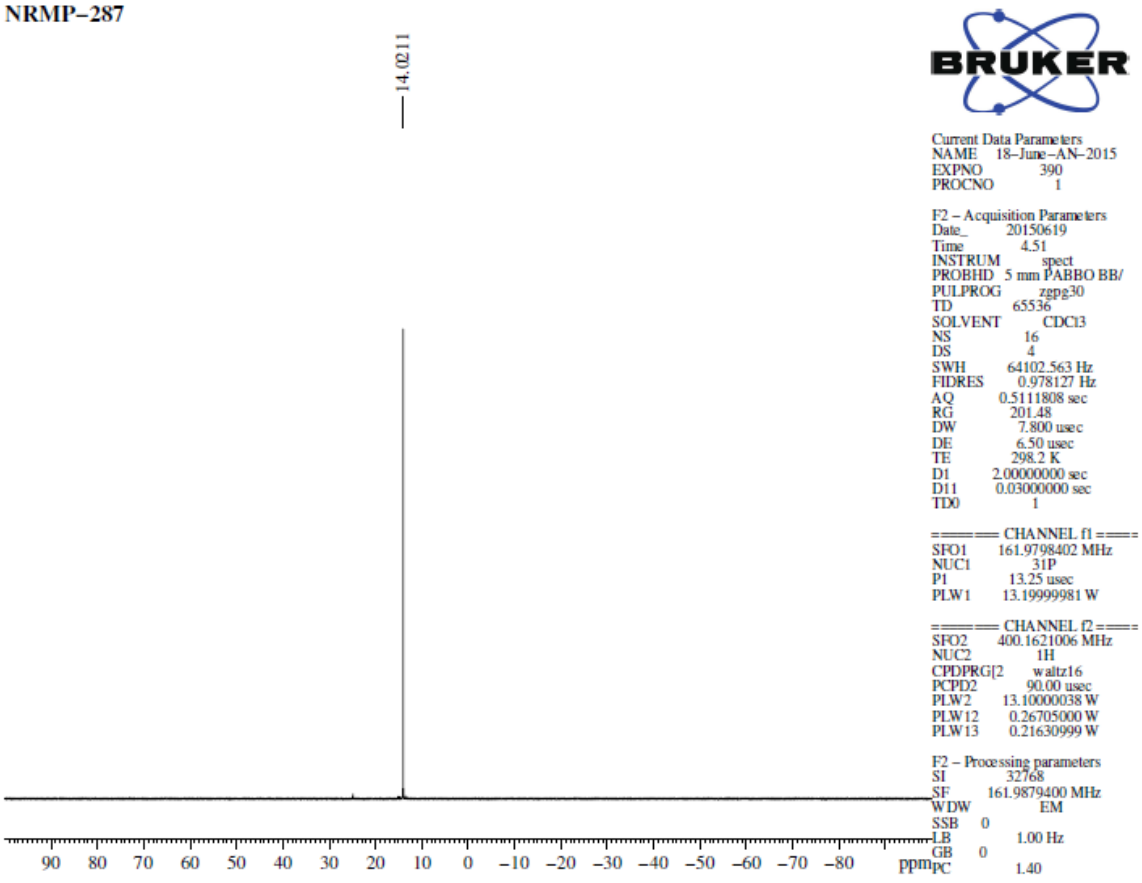

Figure 10: ^{31}P NMR spectrum of 3b

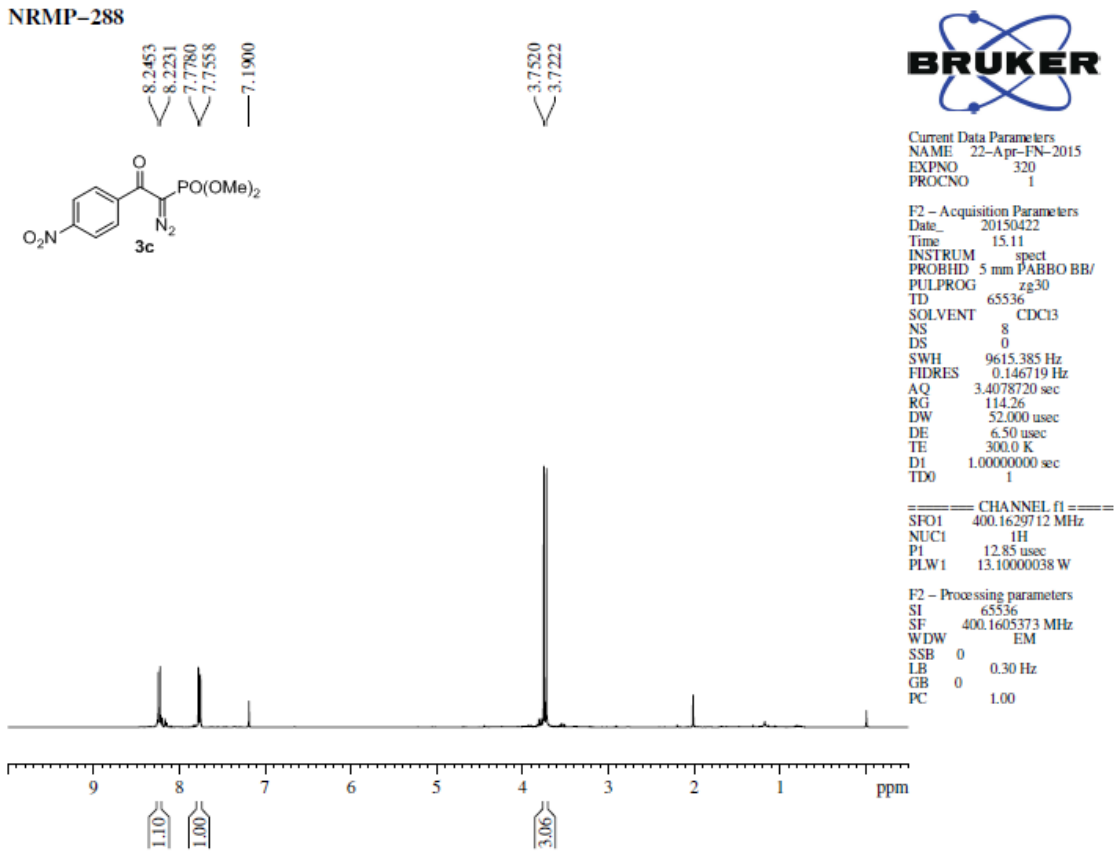

Figure 11: ^{1}H NMR spectrum of 3c

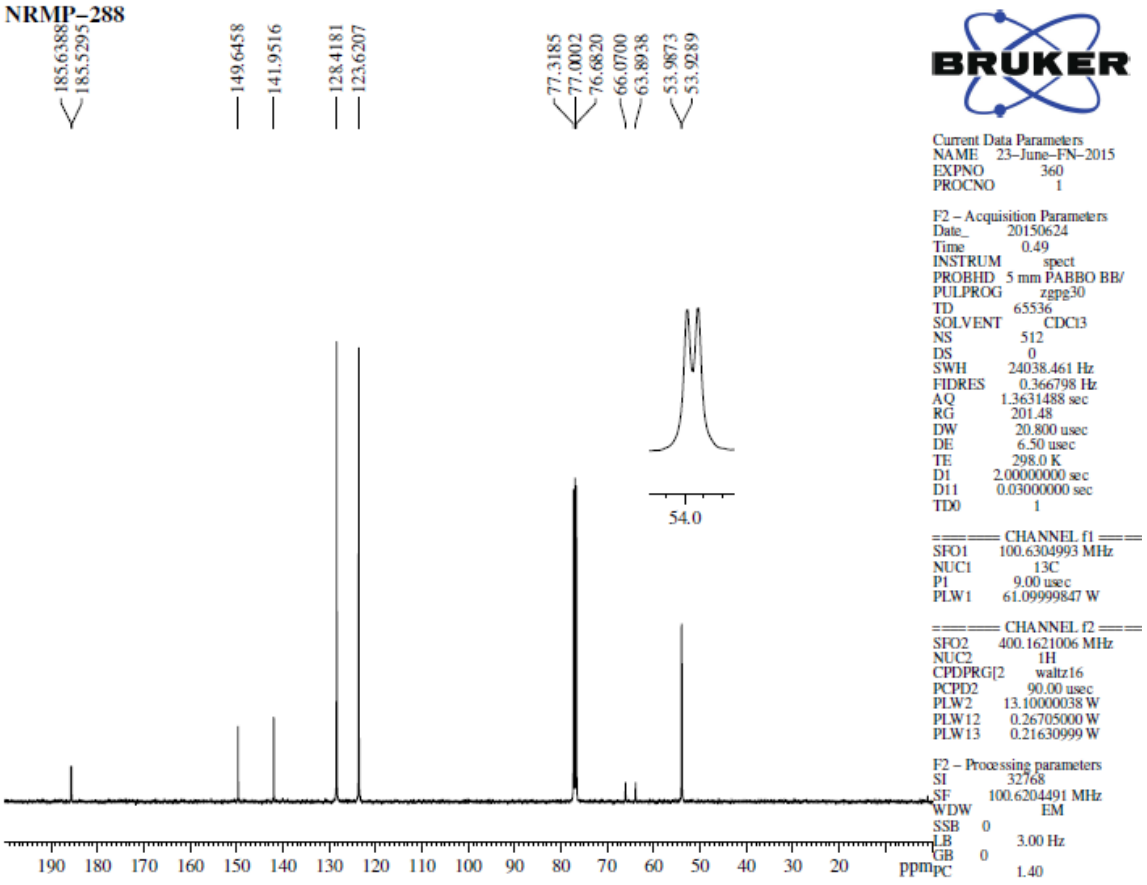

Figure 12: ^{13}C NMR spectrum of 3c

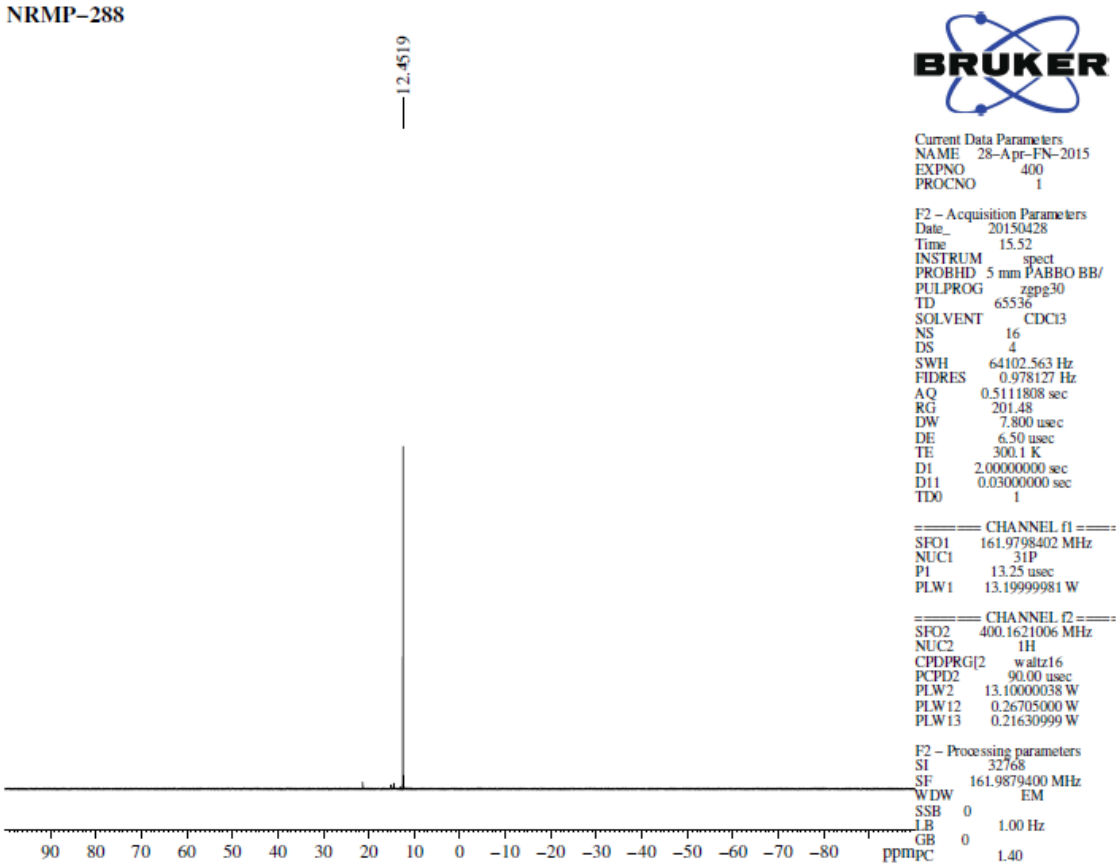

Figure 13: ^{31}P NMR spectrum of 3c

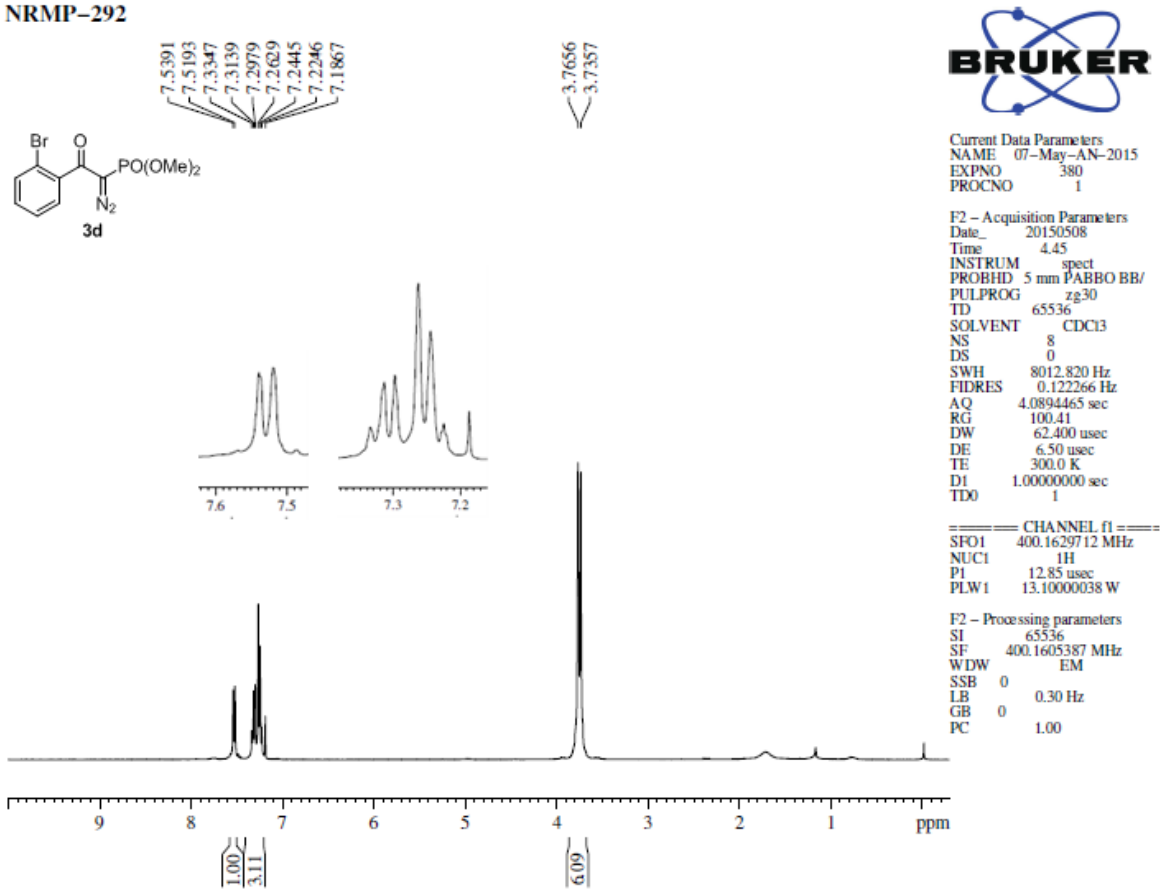

Figure 14: ^{1}H NMR spectrum of 3d

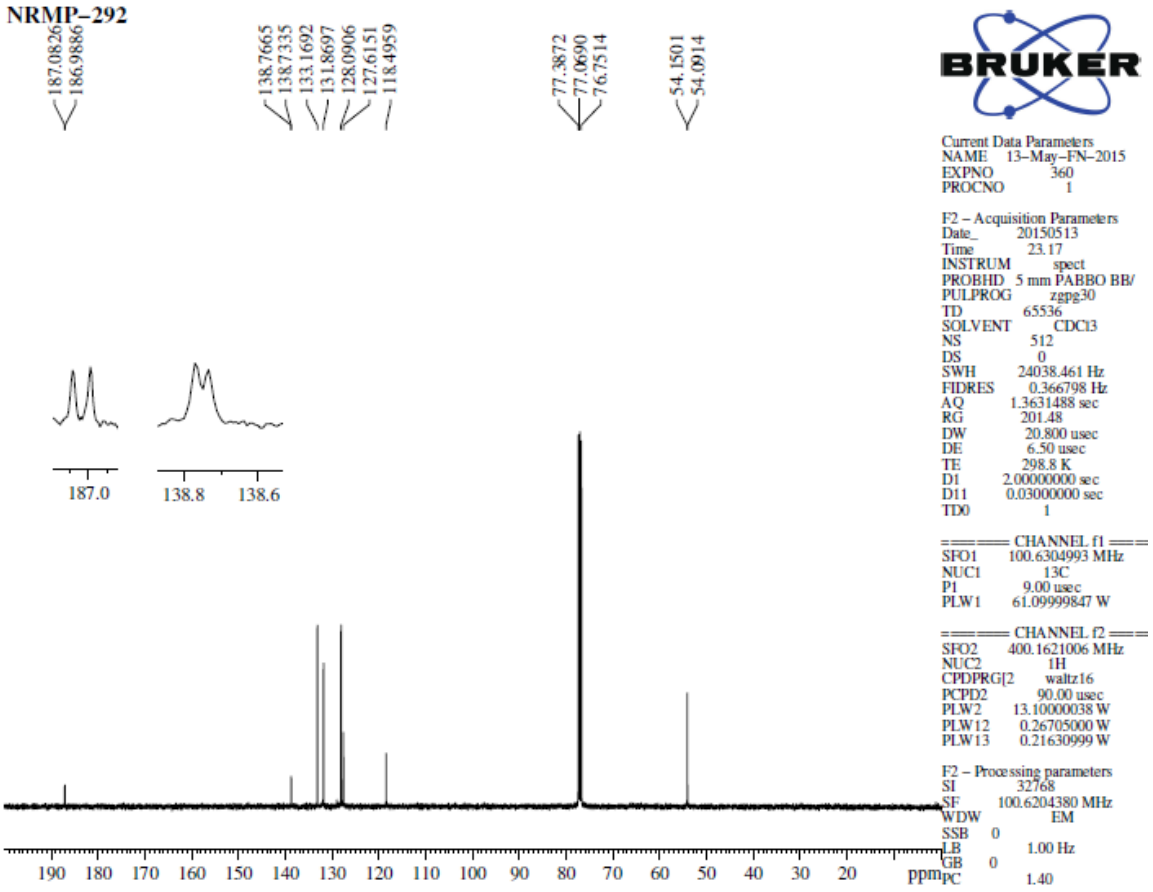

Figure 15: ^{13}C NMR spectrum of 3d

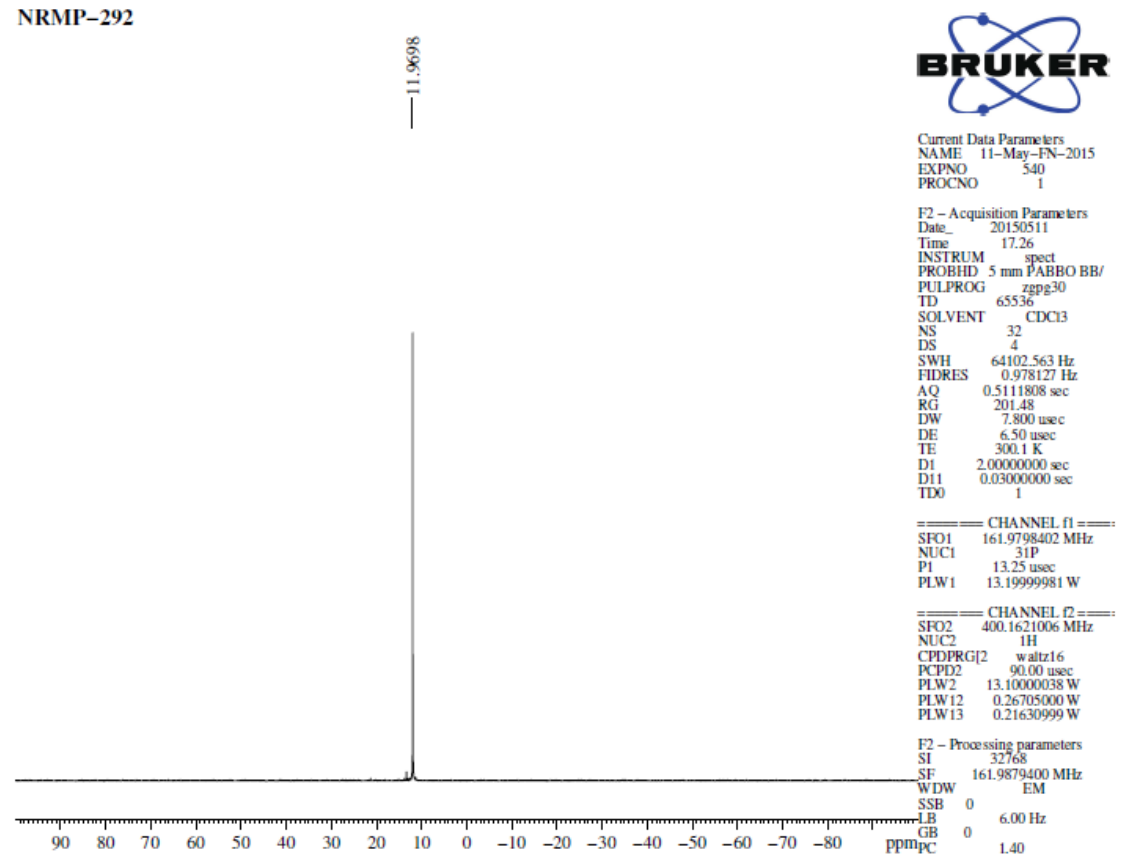

Figure 16: ^{31}P NMR spectrum of 3d

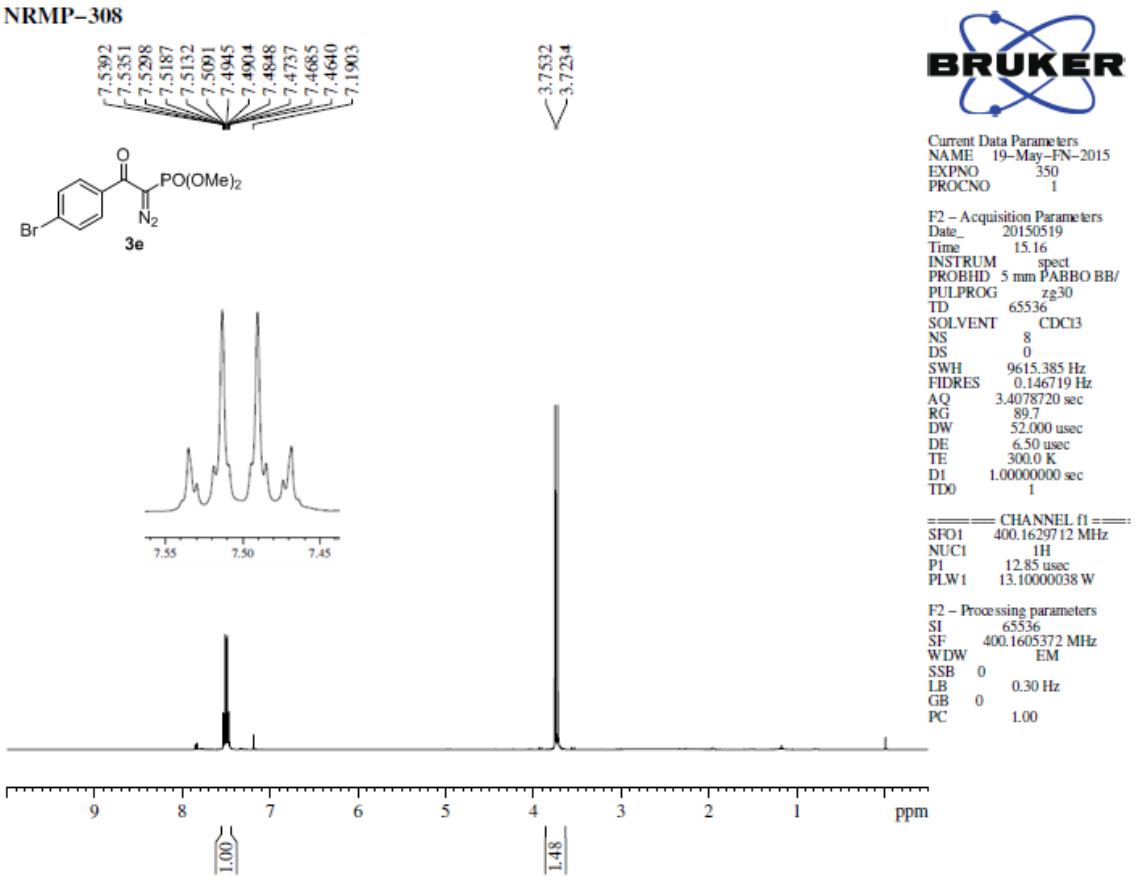

Figure 17: ^{1}H NMR spectrum of 3e

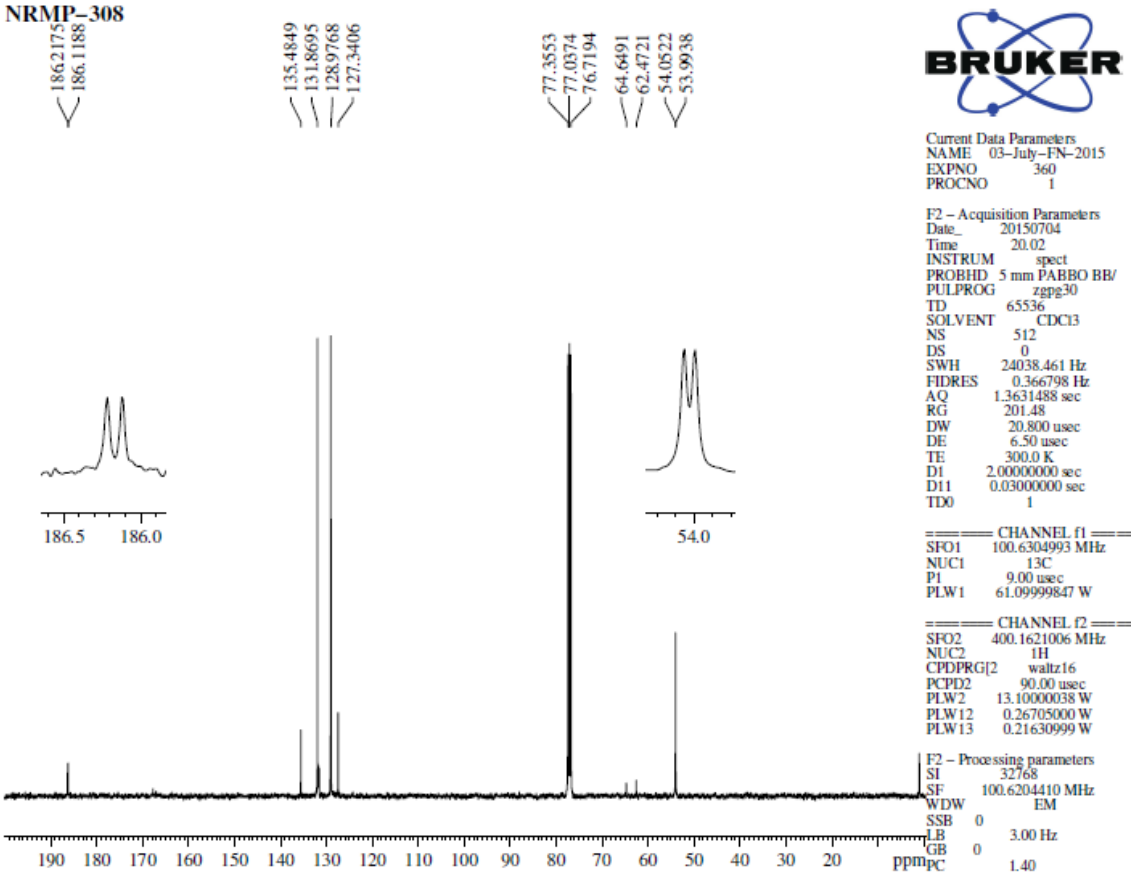

Figure 18: ^{13}C NMR spectrum of 3e

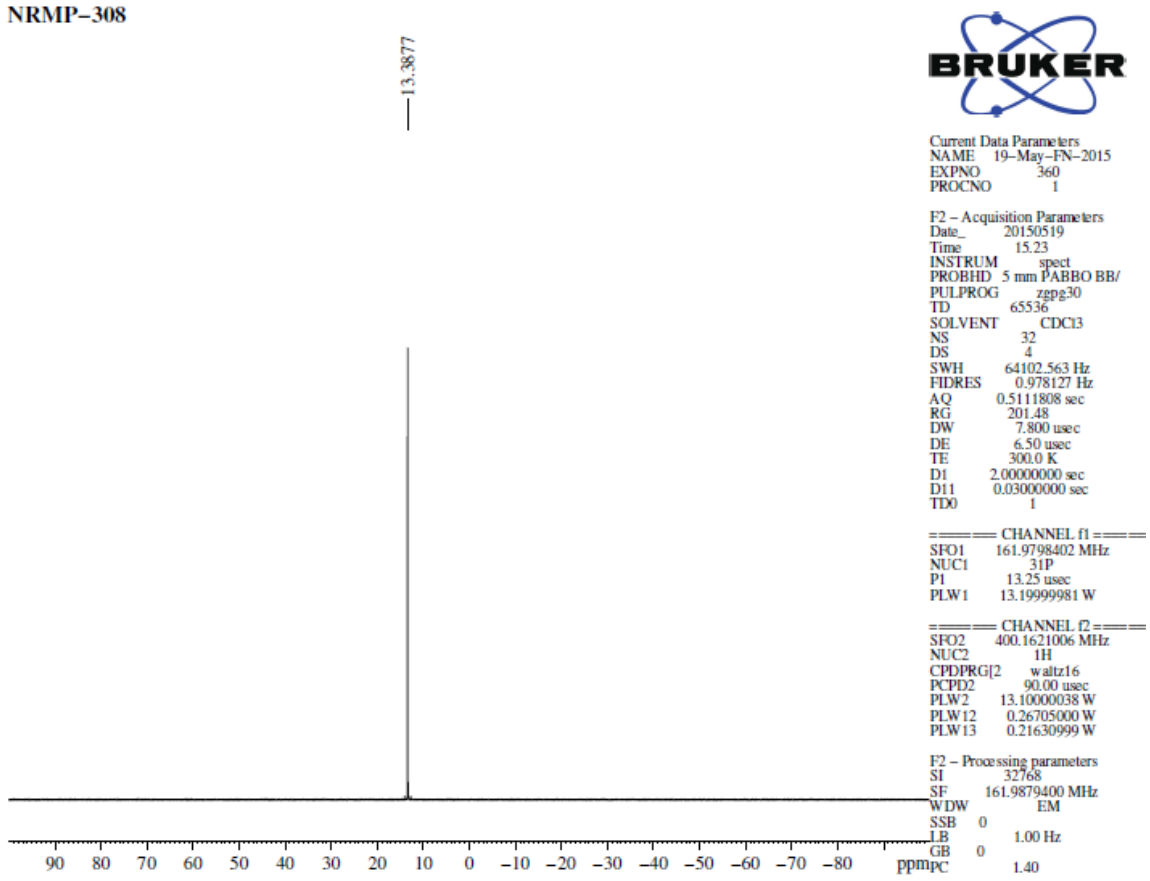

Figure 19: ^{31}P NMR spectrum of 3e

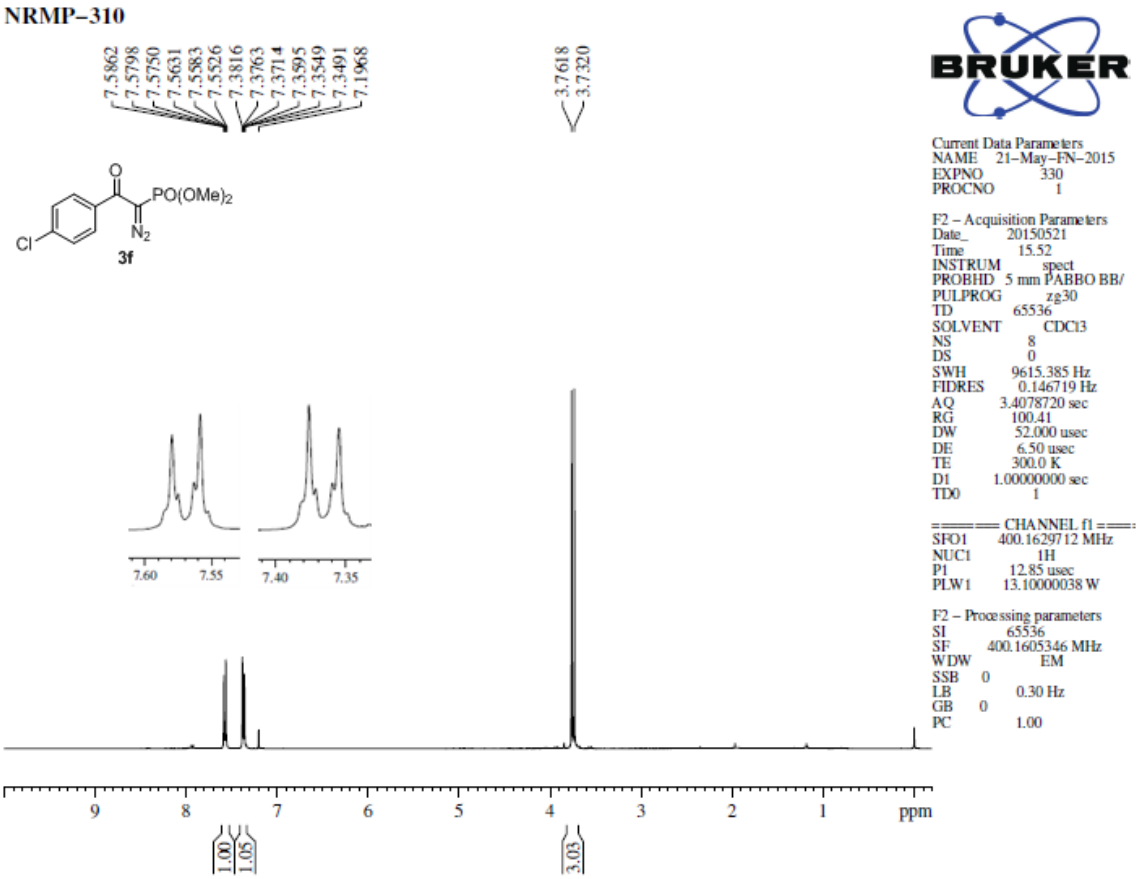

Figure 20: ^{1}H NMR spectrum of 3f

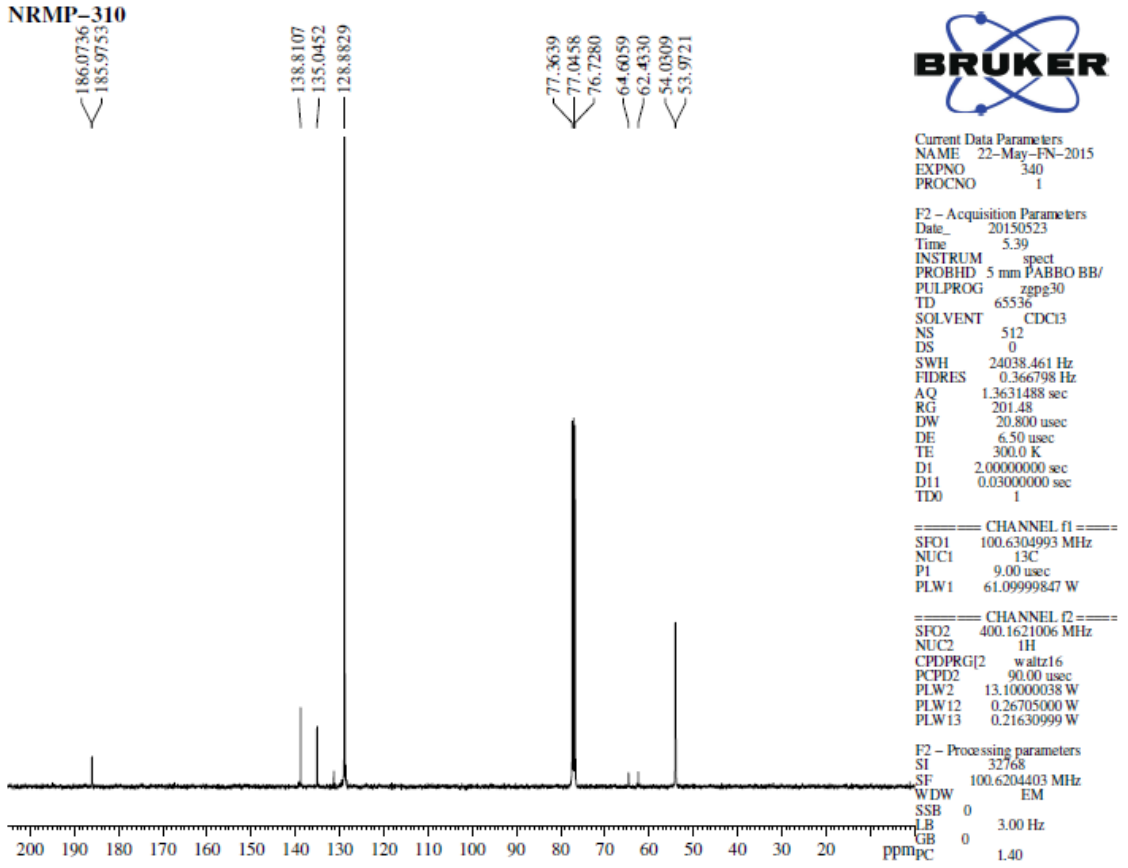

Figure 21: ^{13}C NMR spectrum of 3f

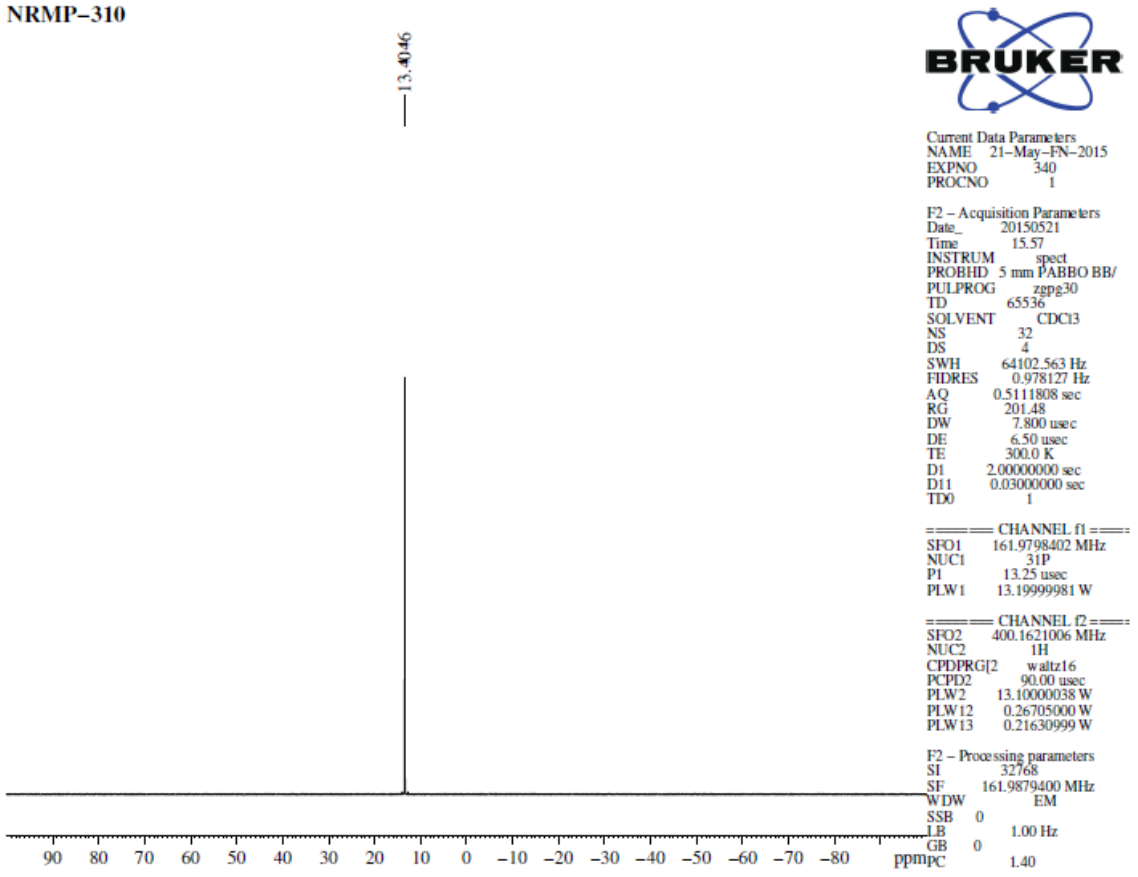

Figure 22: ^{31}P NMR spectrum of 3f

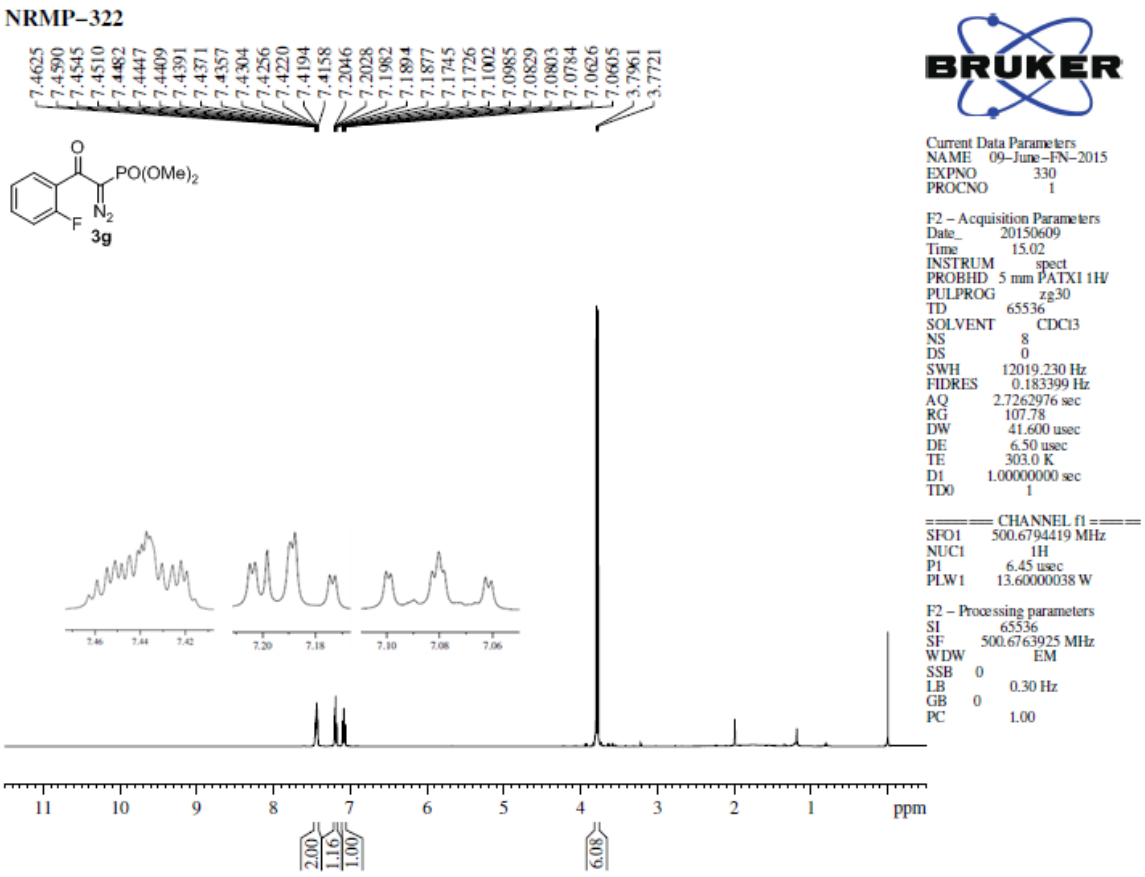

Figure 23: ^{1}H NMR spectrum of 3g

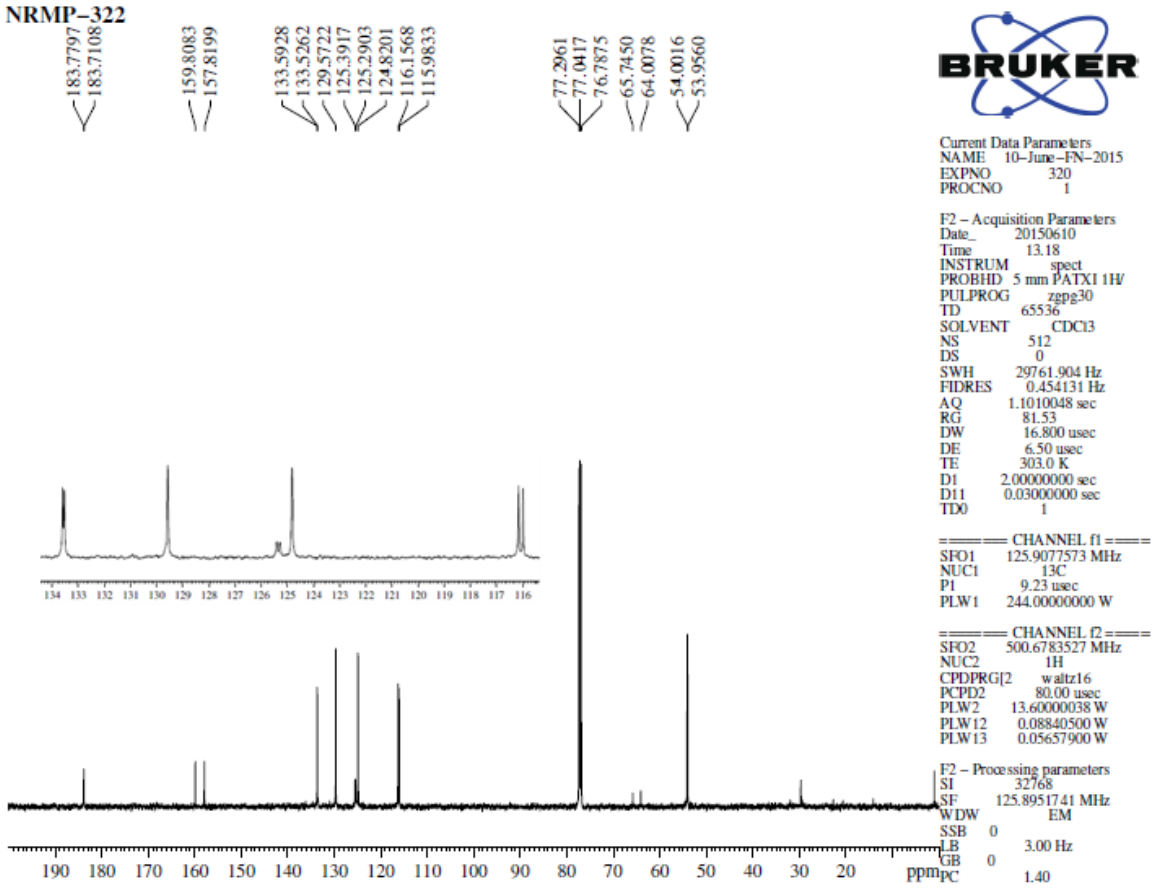

Figure 24: ^{13}C NMR spectrum of 3g

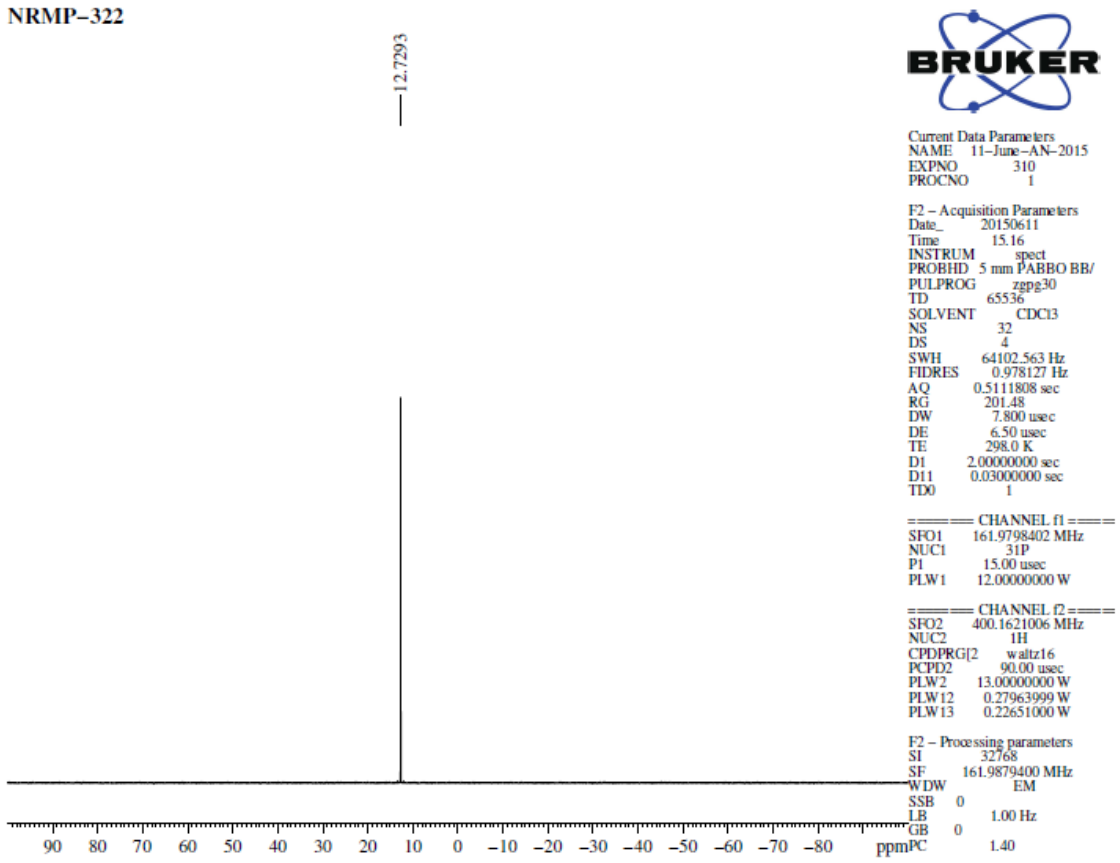

Figure 25: ^{31}P NMR spectrum of 3g

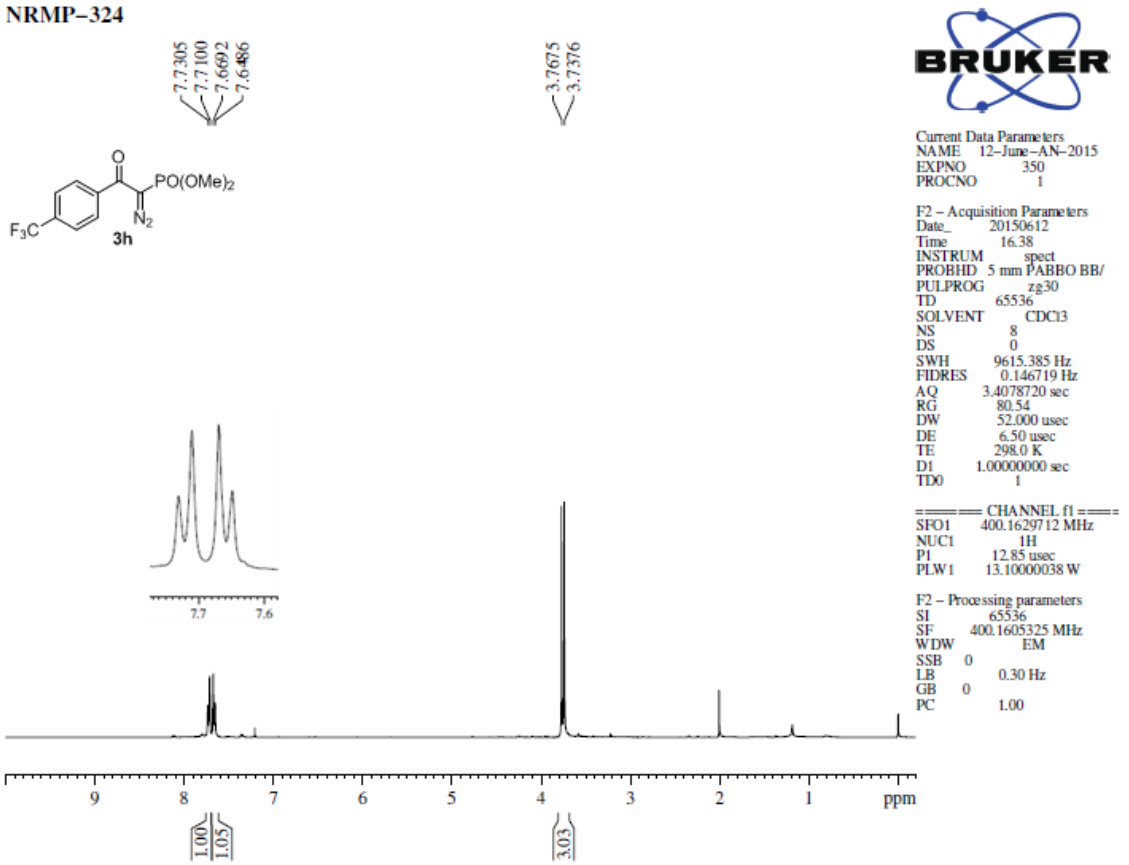

Figure 26: ^{1}H NMR spectrum of 3h

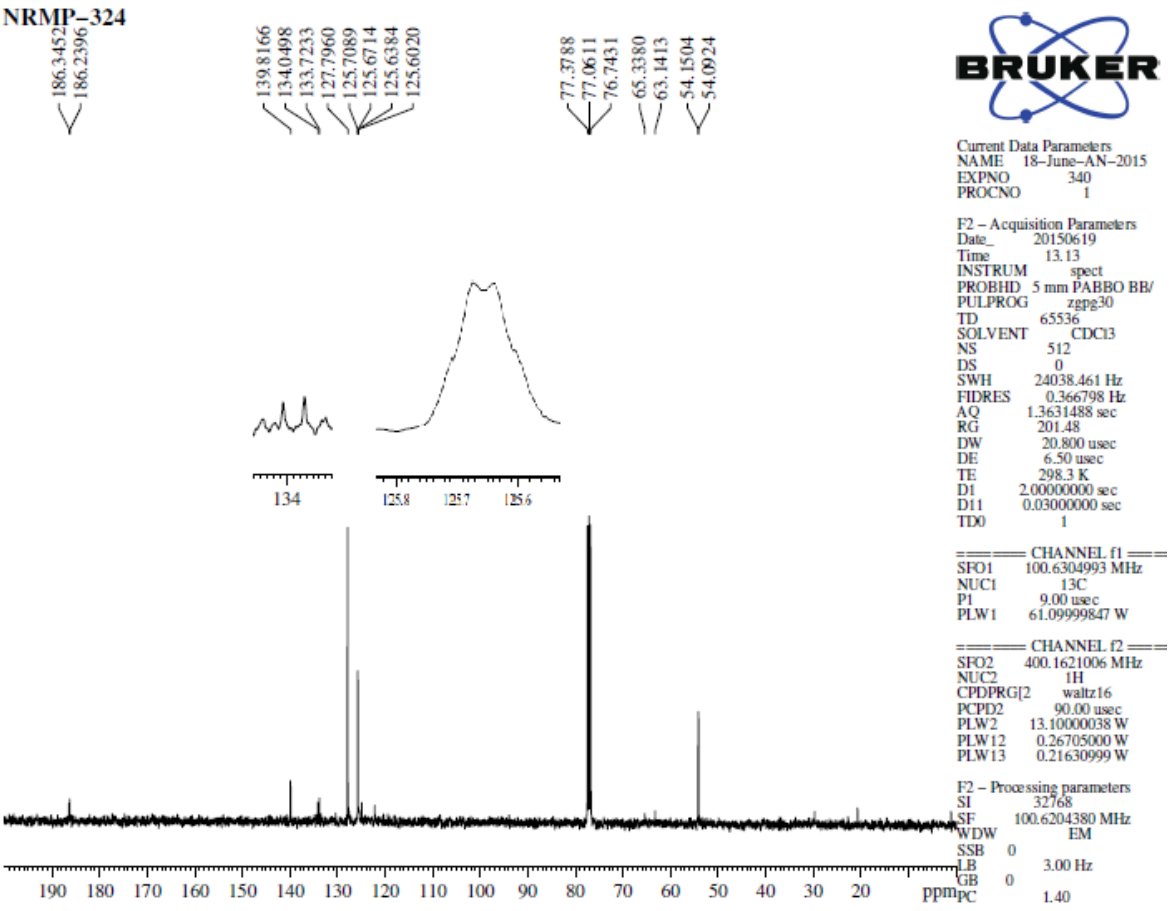

Figure 27: ^{13}C NMR spectrum of 3h

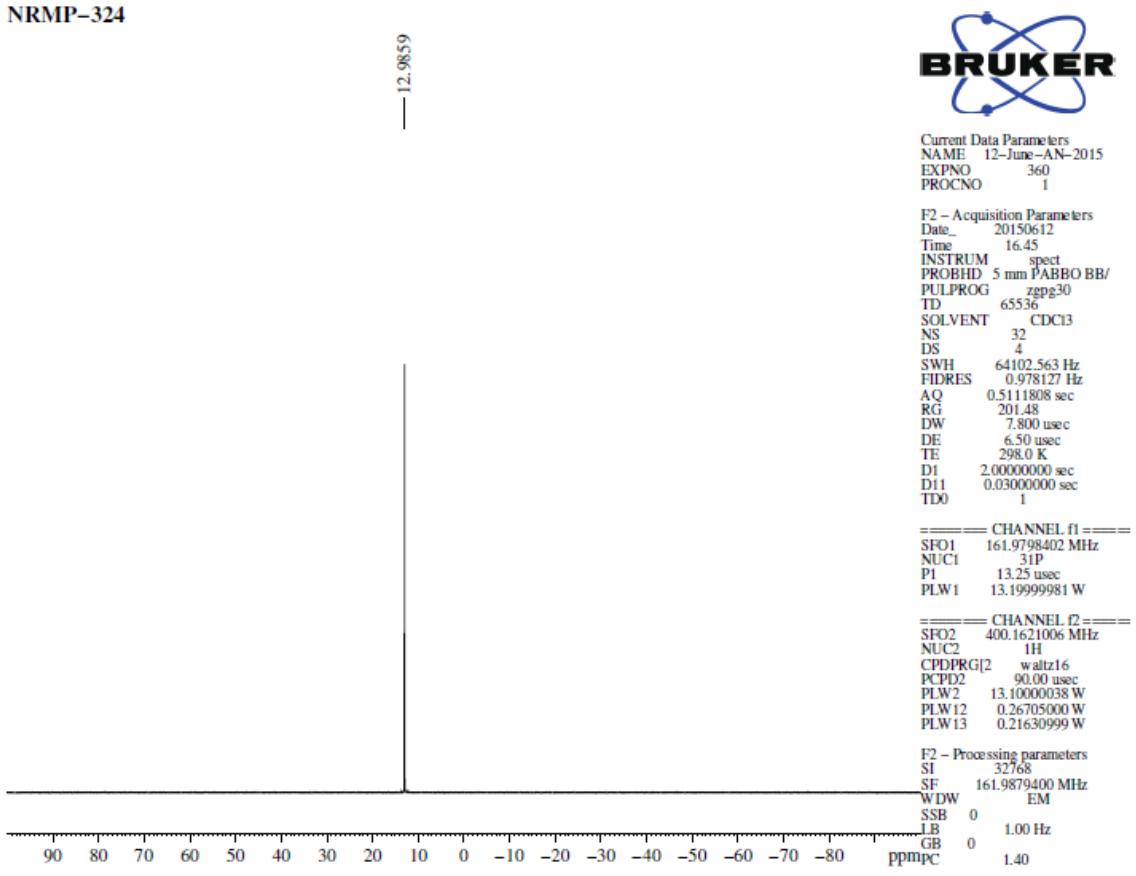

Figure 28: ^{31}P NMR spectrum of 3h

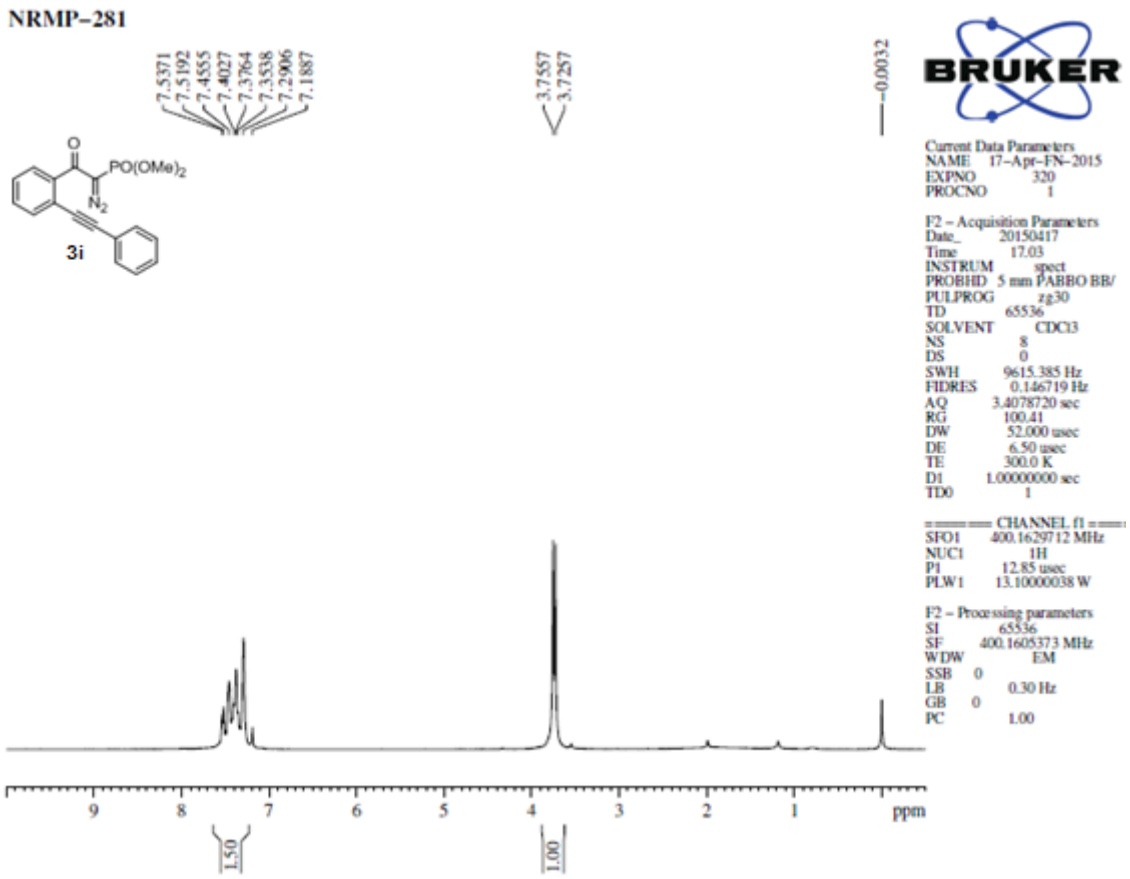

Figure 29: ^{1}H NMR spectrum of 3i

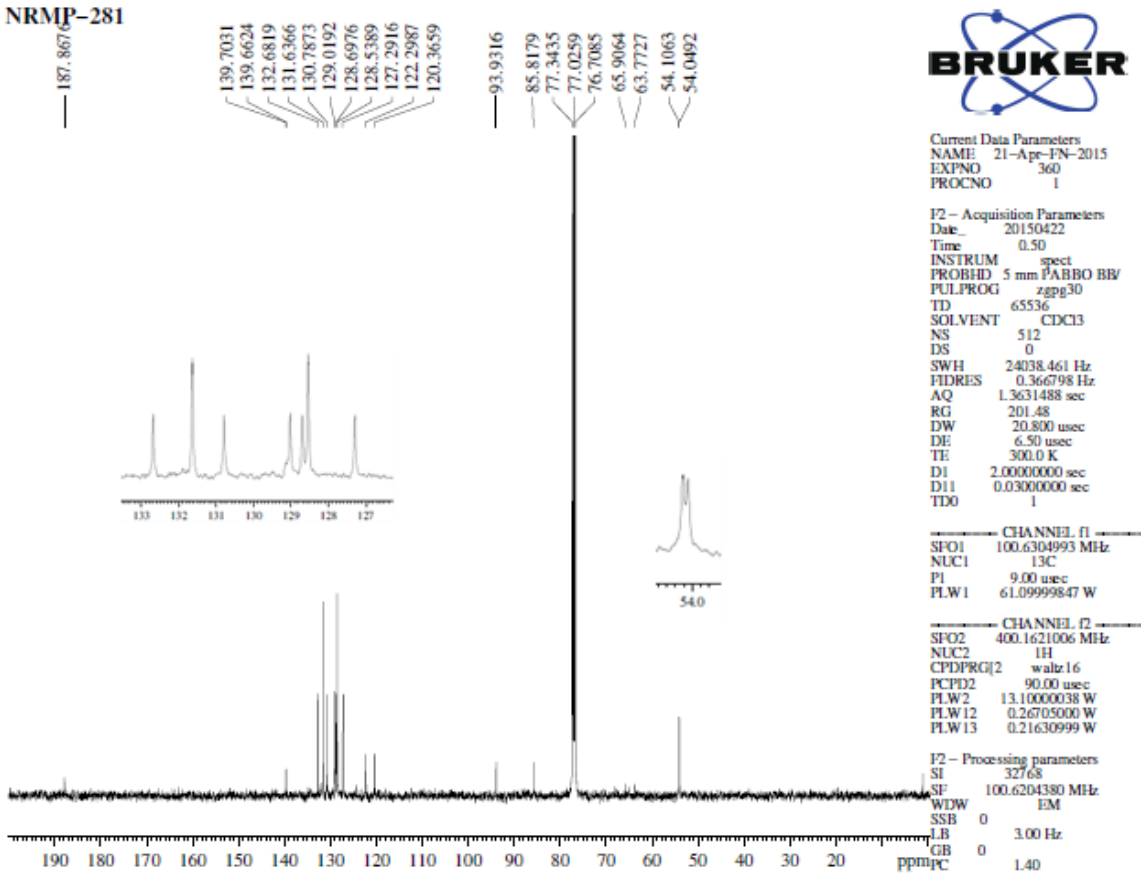

Figure 30: ^{13}C NMR spectrum of 3i

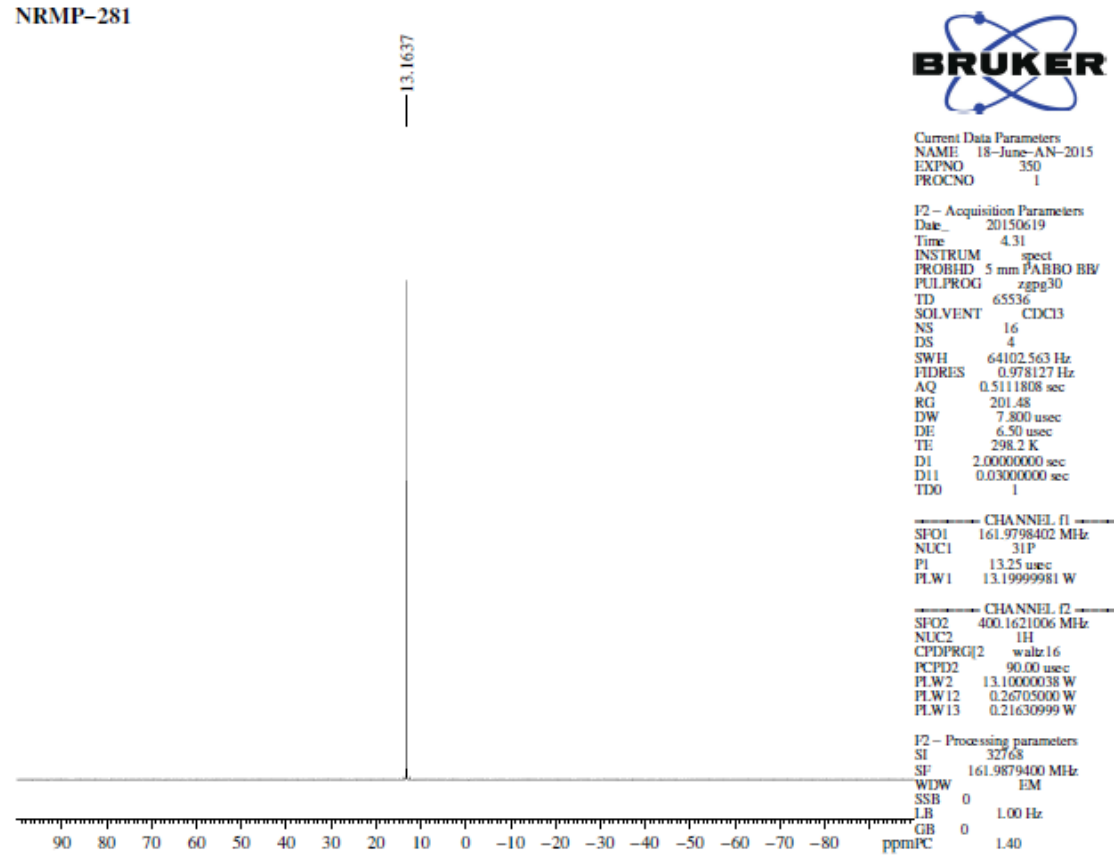

Figure 31: ^{31}P NMR spectrum of 3i

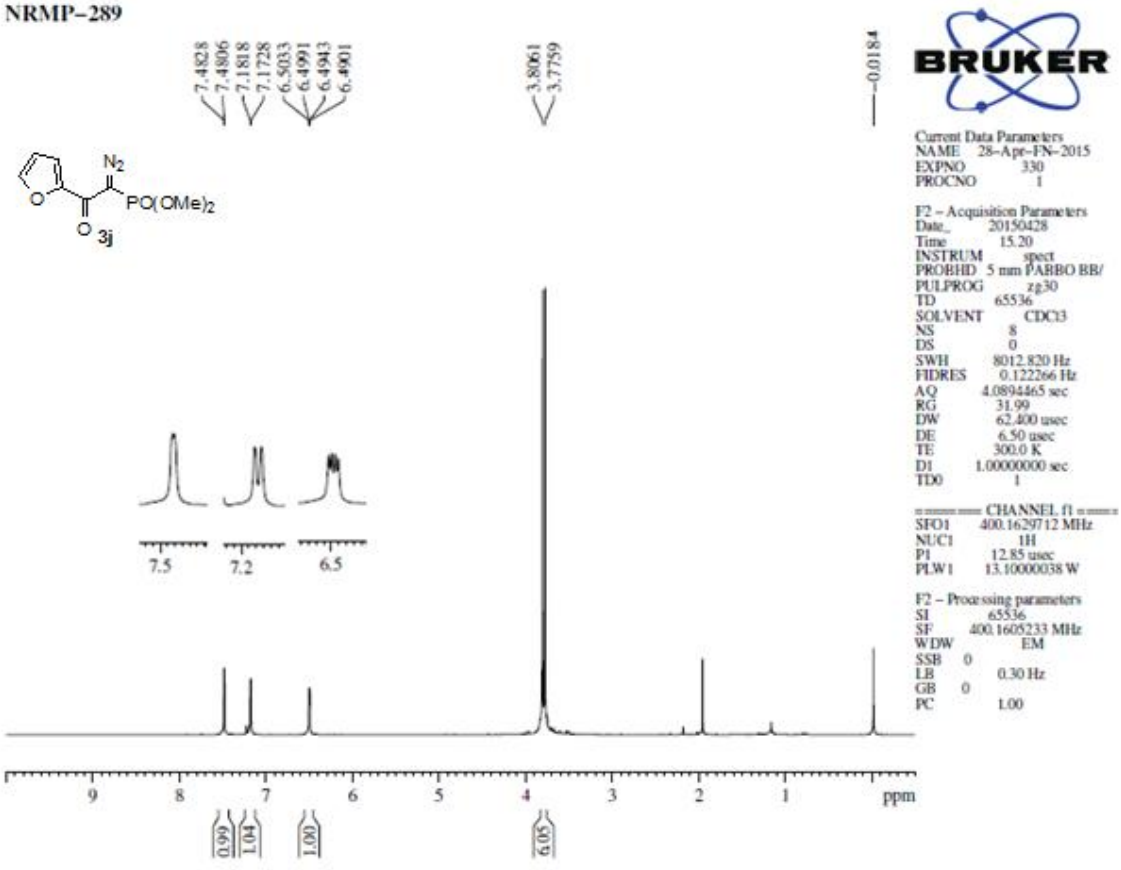

Figure 32: ^{1}H NMR spectrum of 3j

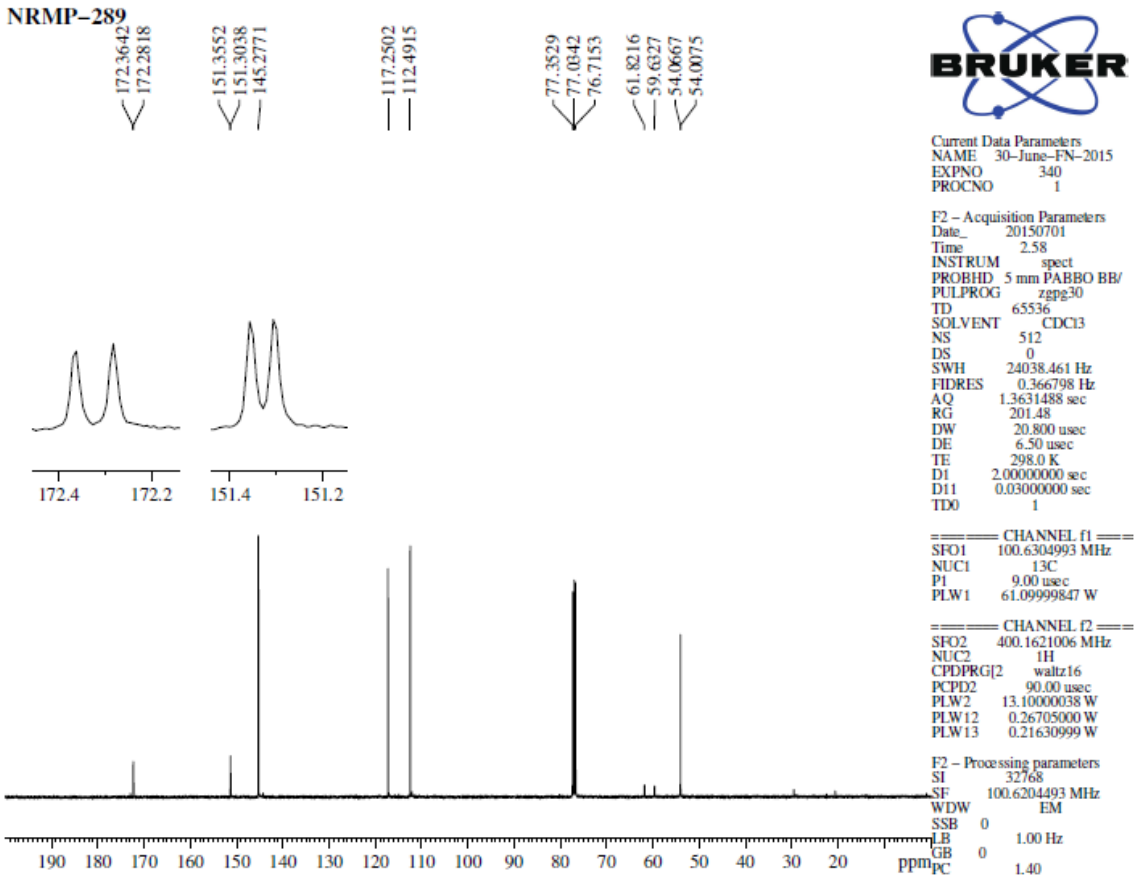

Figure 33: ^{13}C NMR spectrum of 3j

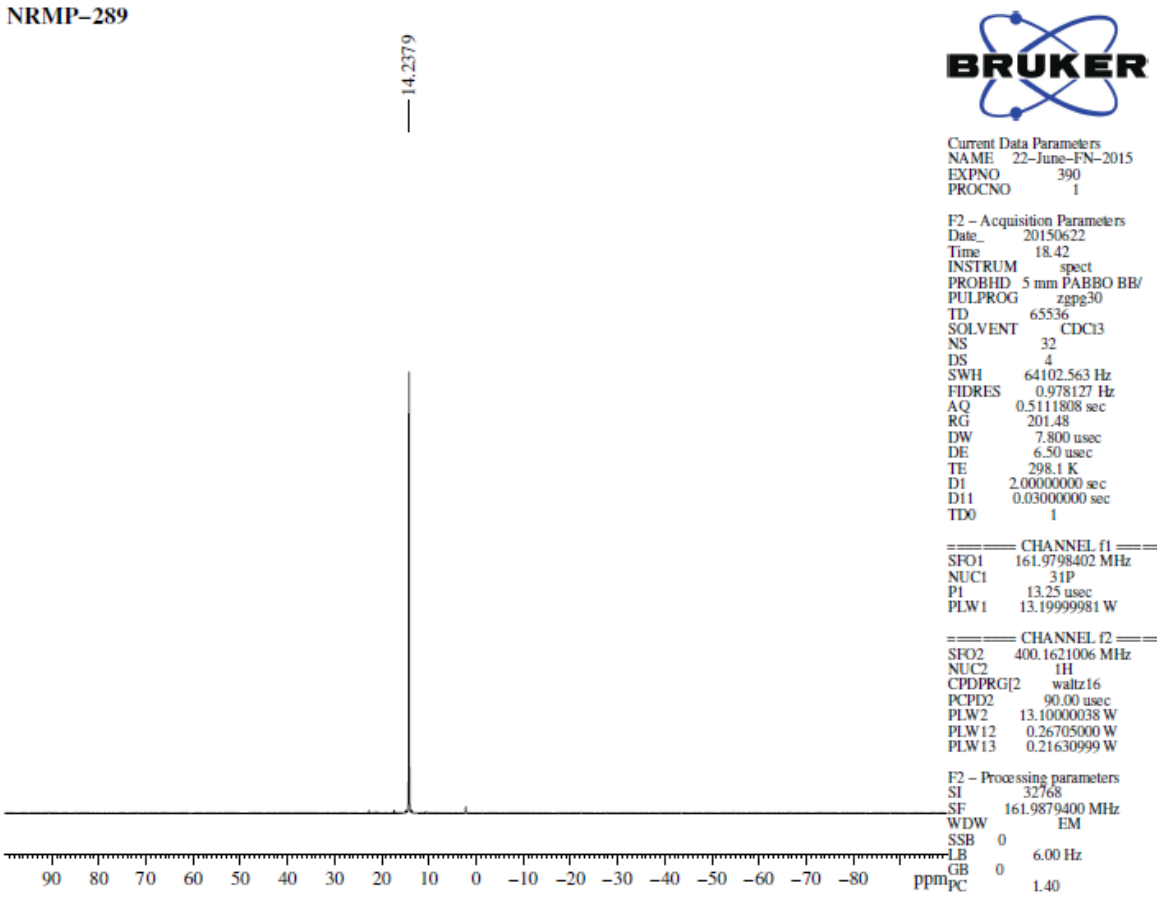

Figure 34: ^{31}P NMR spectrum of 3j

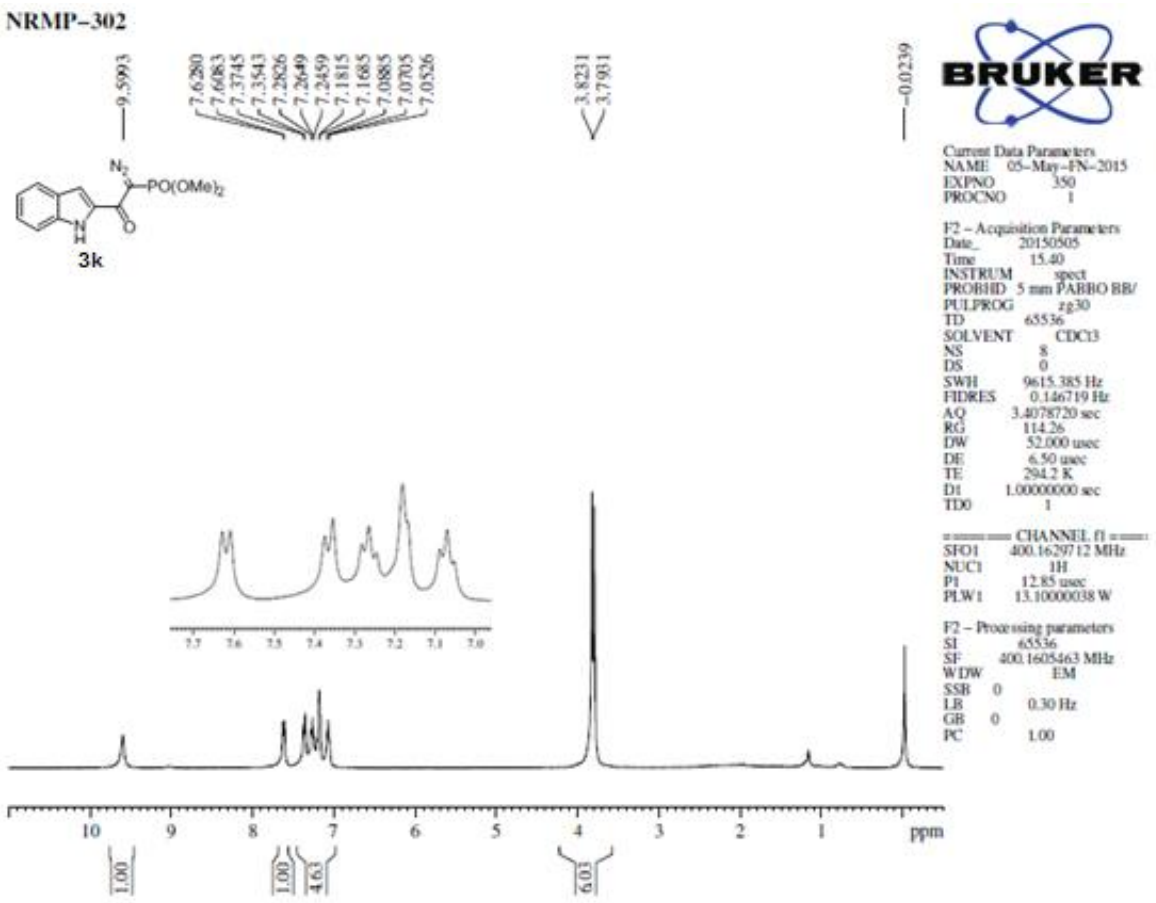

Figure 35: ^{1}H NMR spectrum of 3k

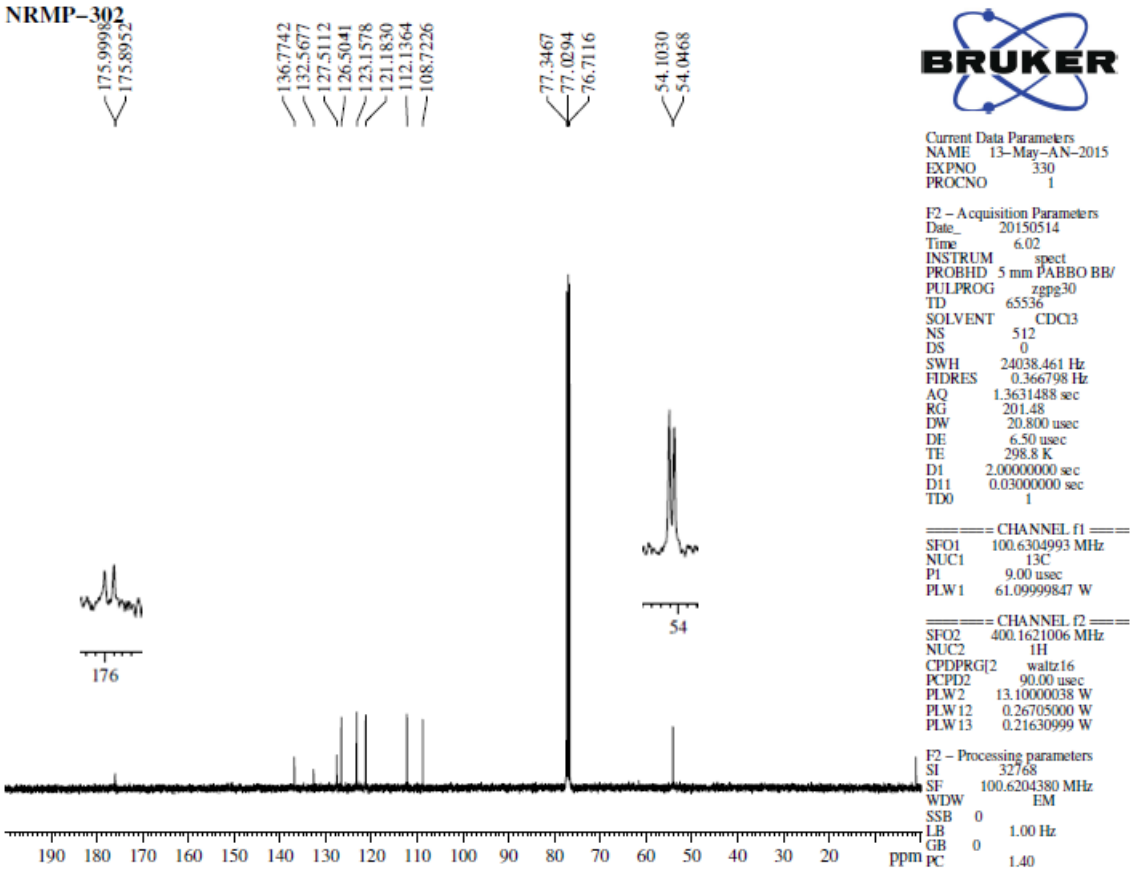

Figure 36: ^{13}C NMR spectrum of 3k

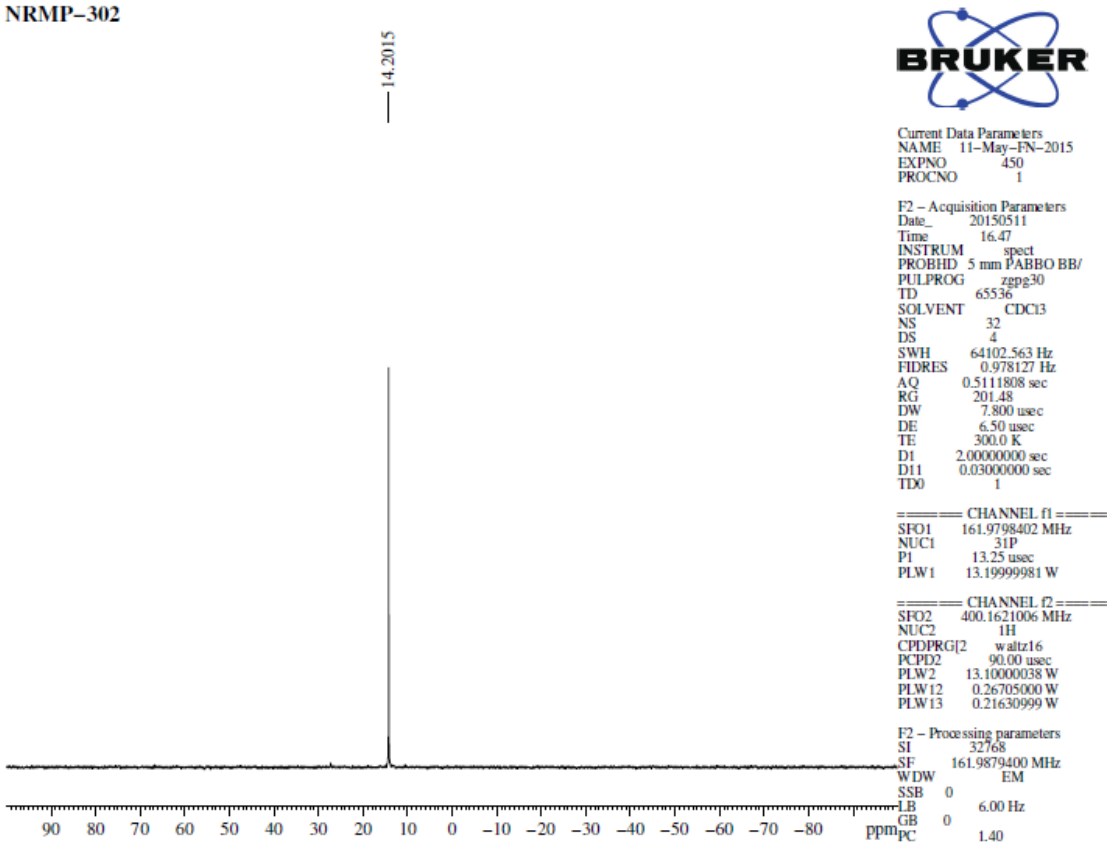

Figure 37: ^{31}P NMR spectrum of 3k

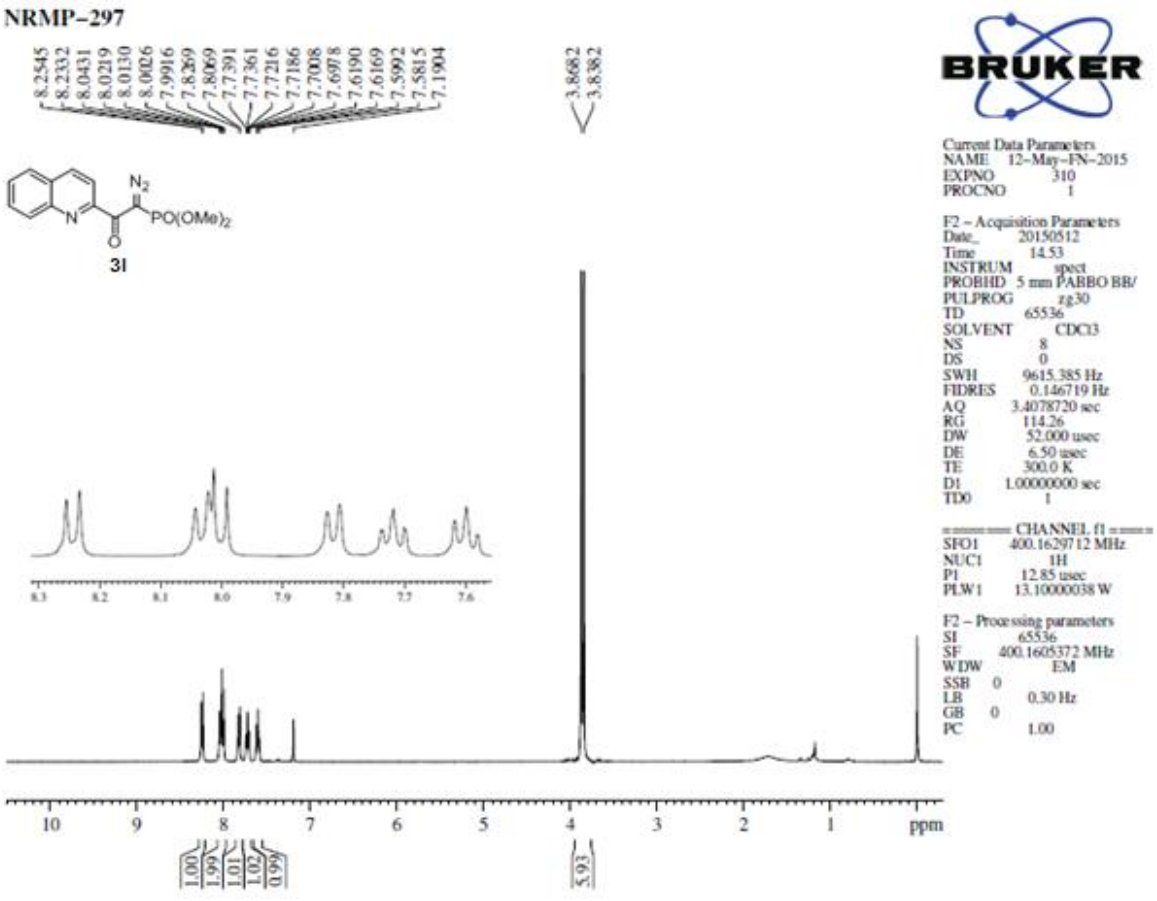

Figure 38: ^{1}H NMR spectrum of 3l

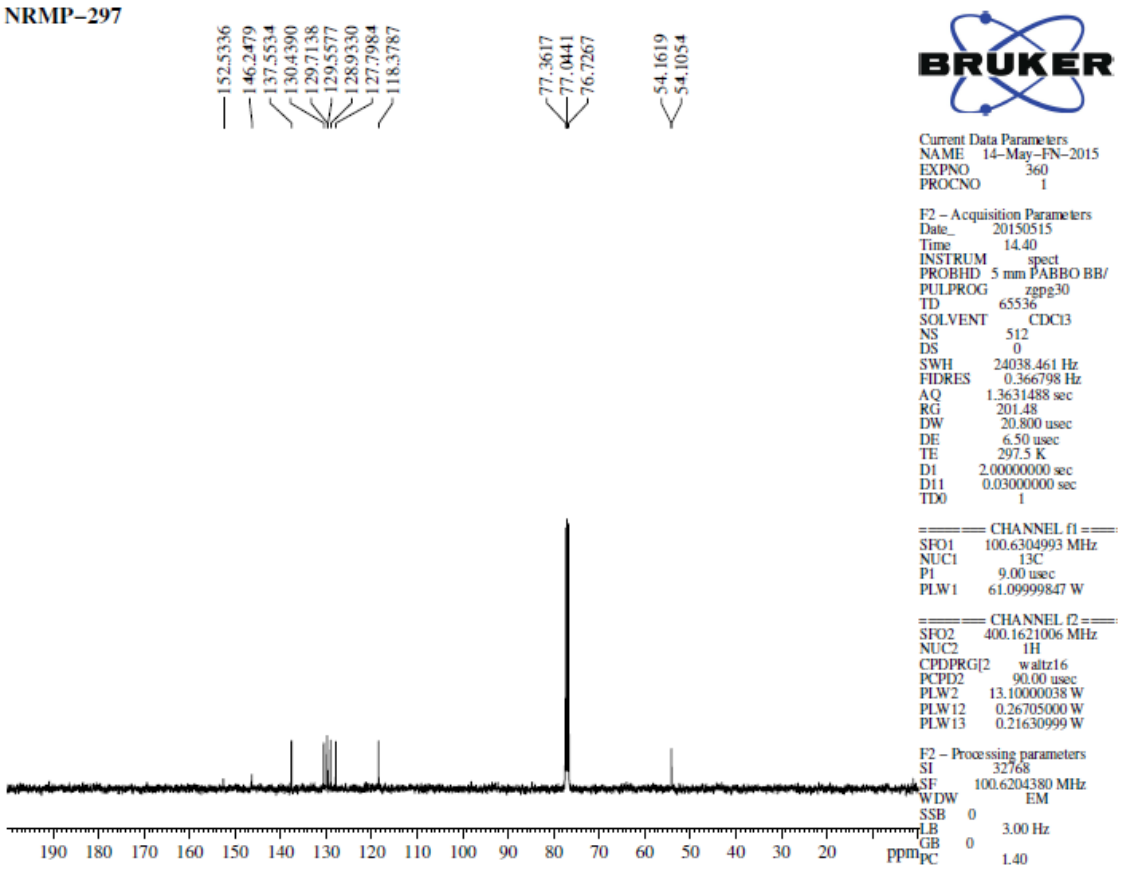

Figure 39: ^{13}C NMR spectrum of 3l

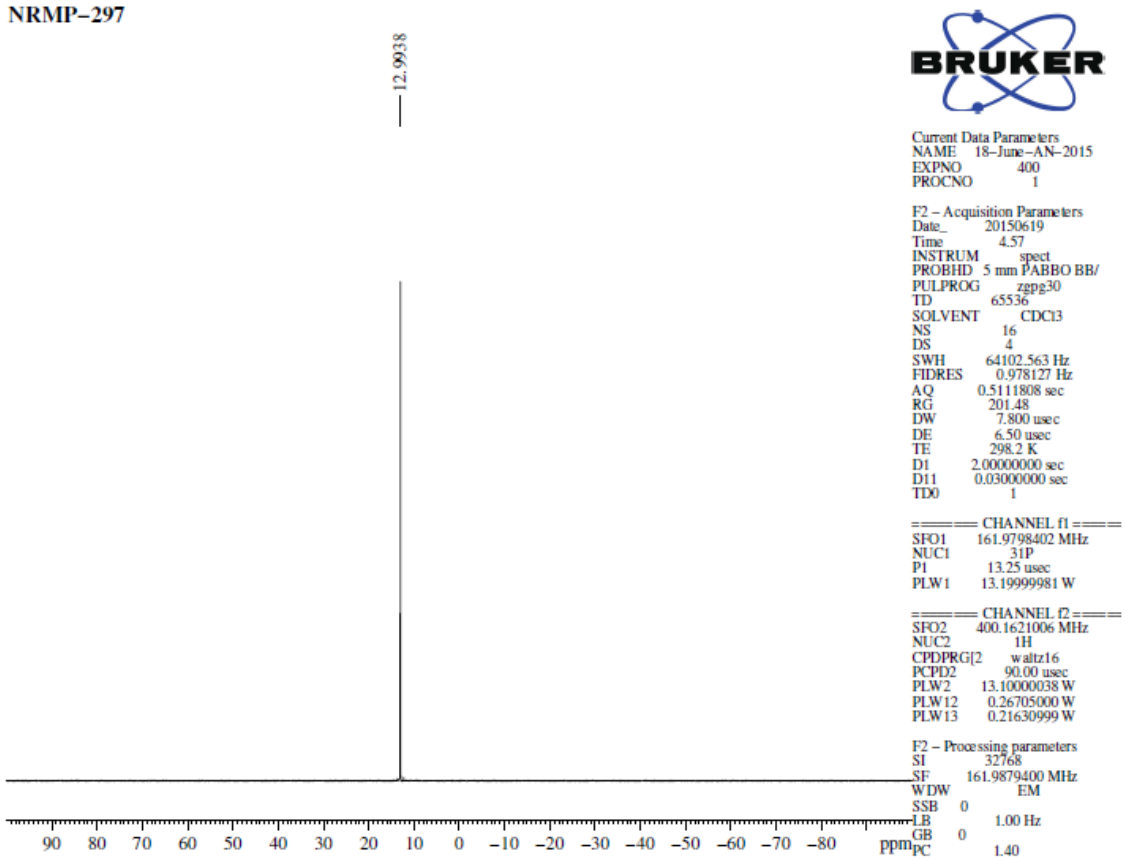

Figure 40: ^{31}P NMR spectrum of 3l

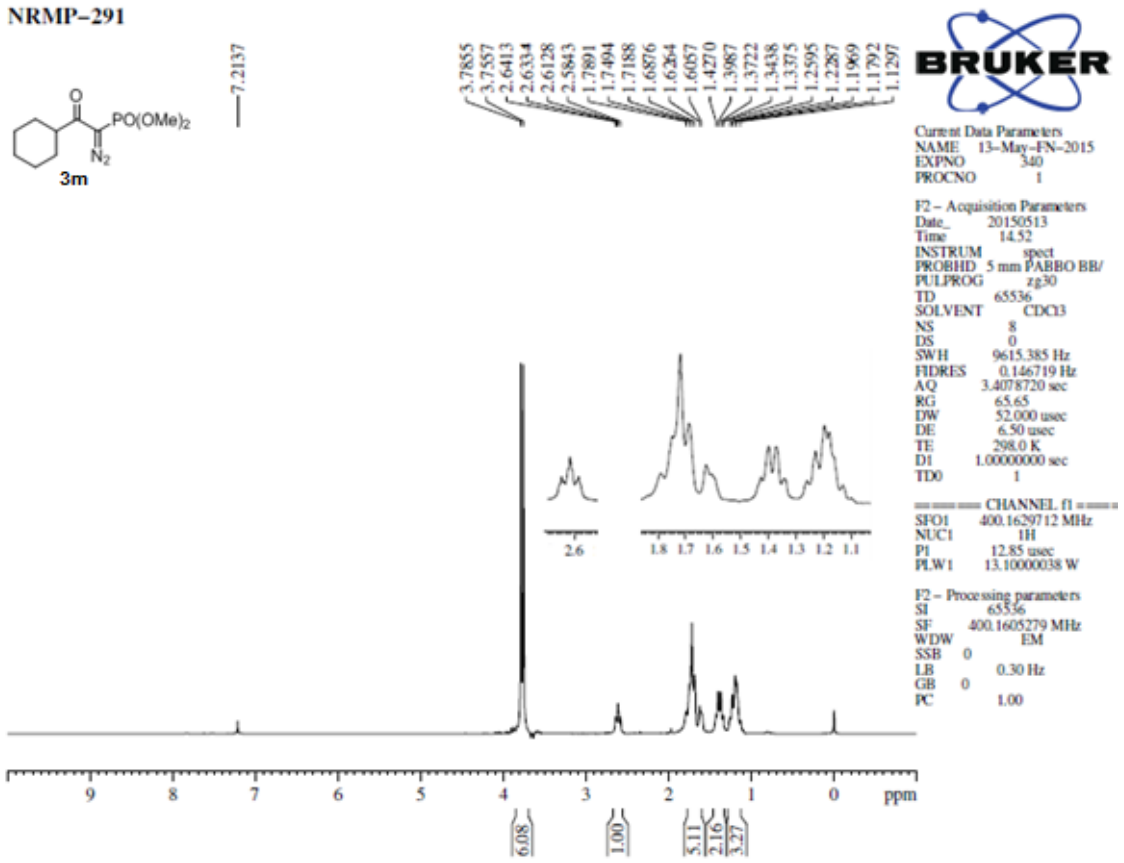

Figure 41: ^{1}H NMR spectrum of 3m

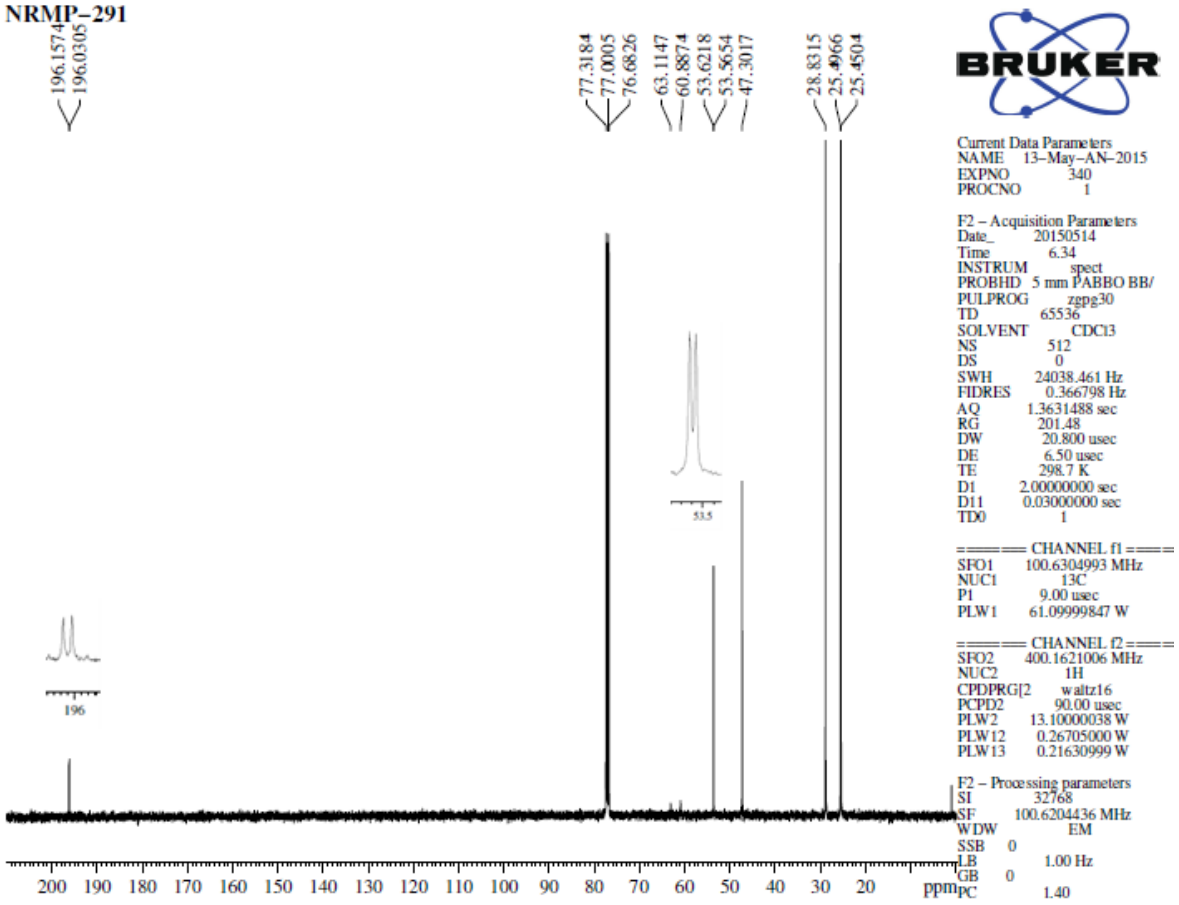

Figure 42: ^{13}C NMR spectrum of 3m

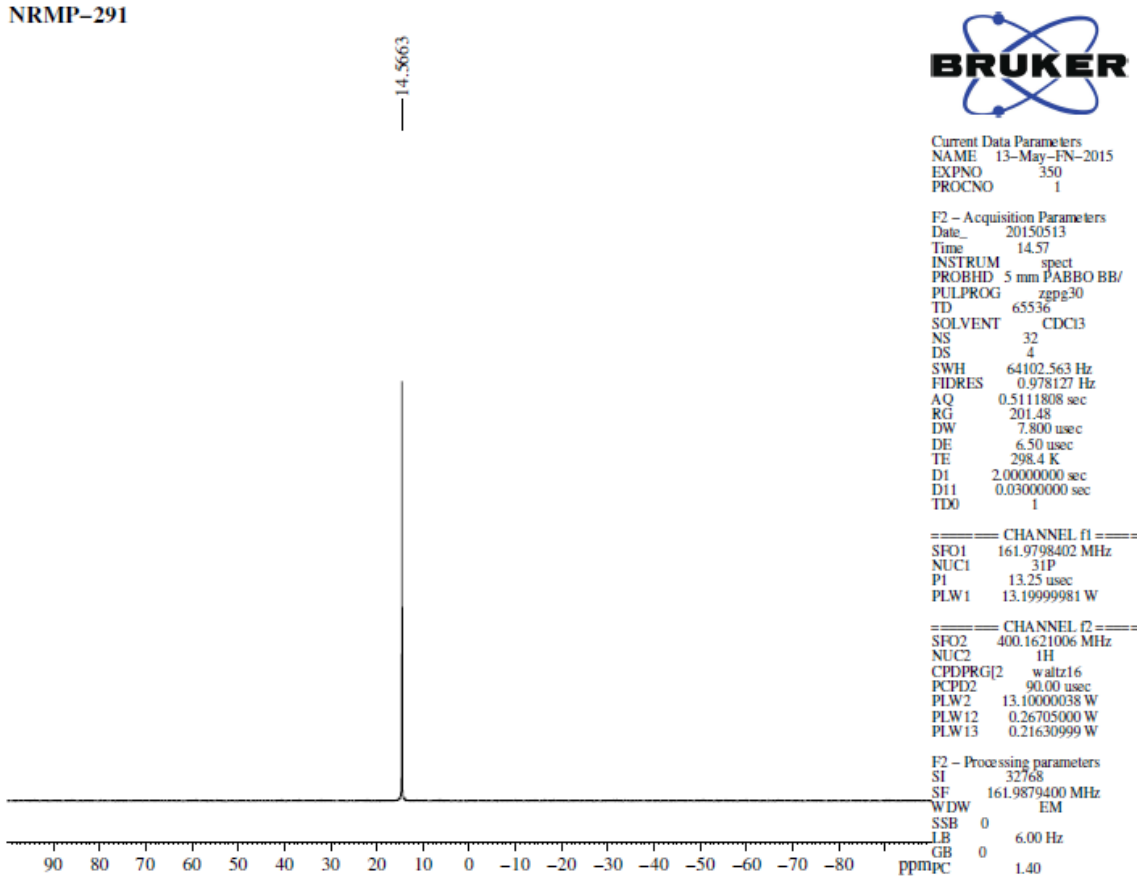

Figure 43: ^{31}P NMR spectrum of 3m

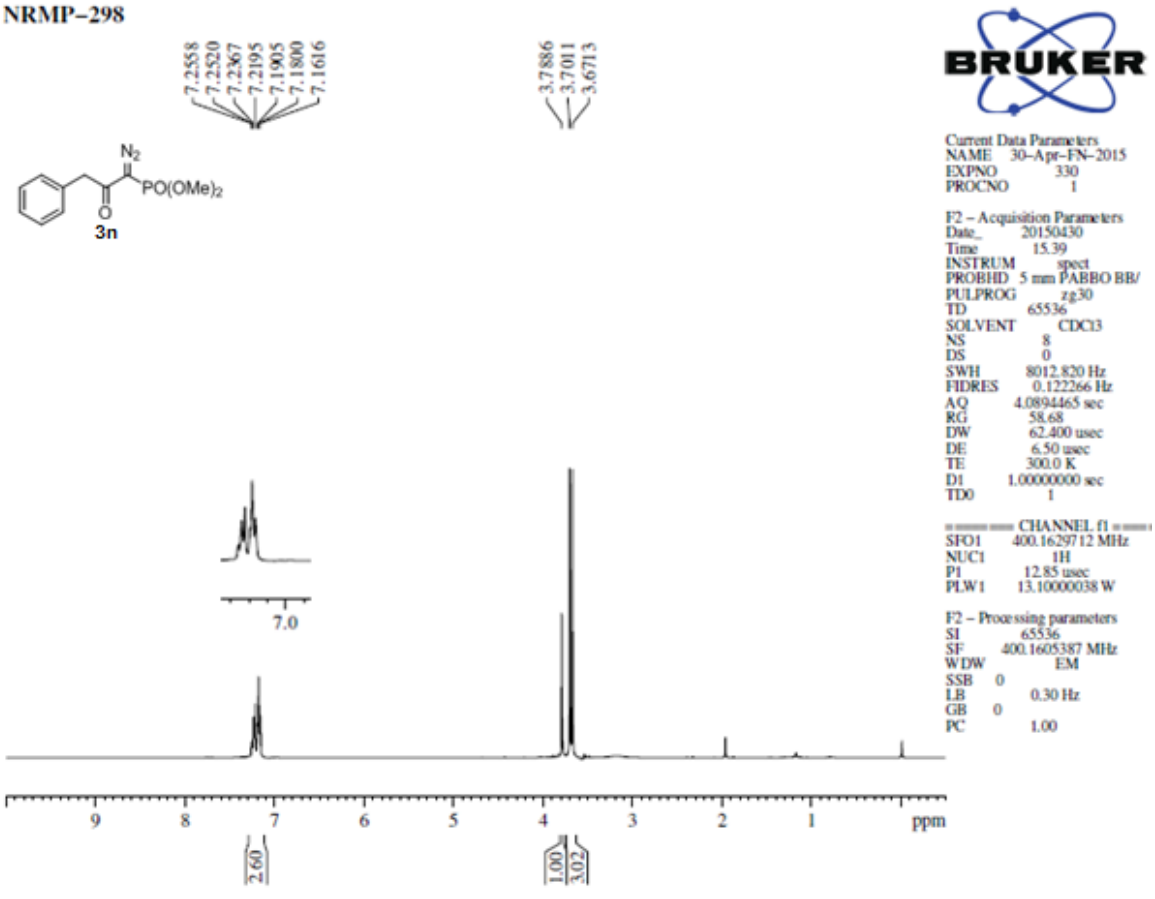

Figure 44: ^{1}H NMR spectrum of 3n

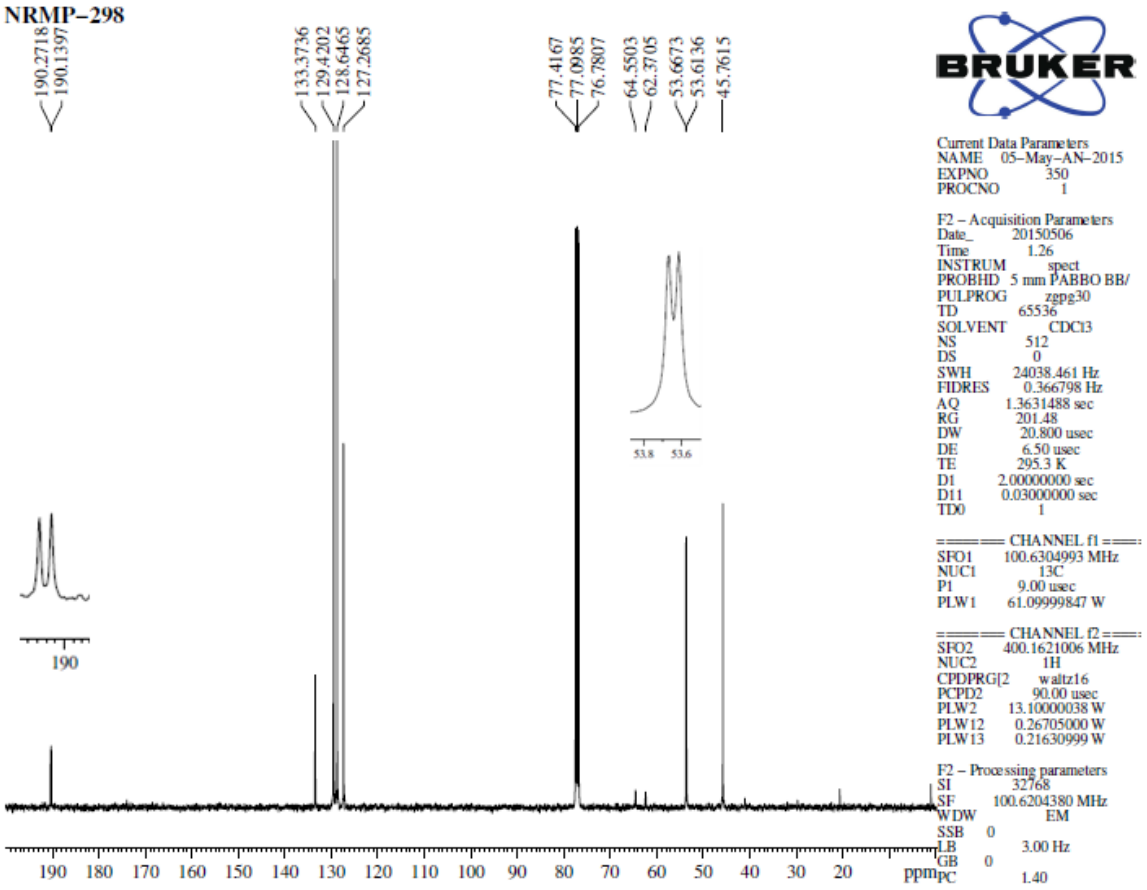

Figure 45: ^{13}C NMR spectrum of 3n

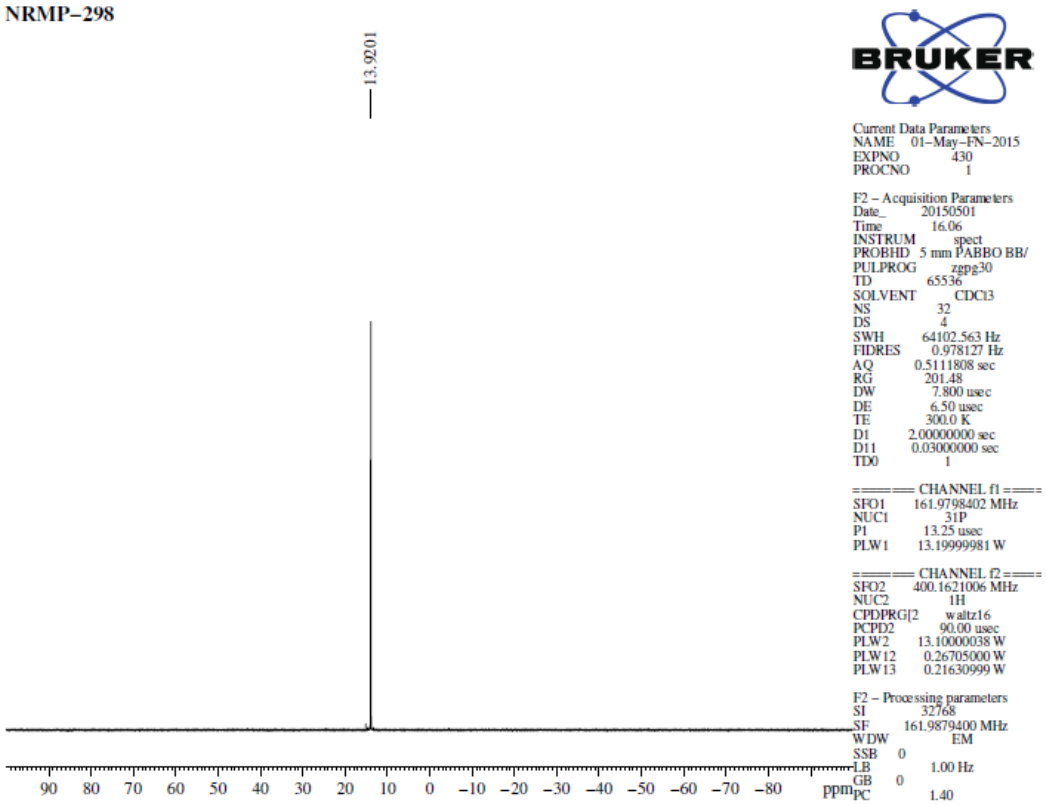

Figure 46: ^{31}P NMR spectrum of 3n

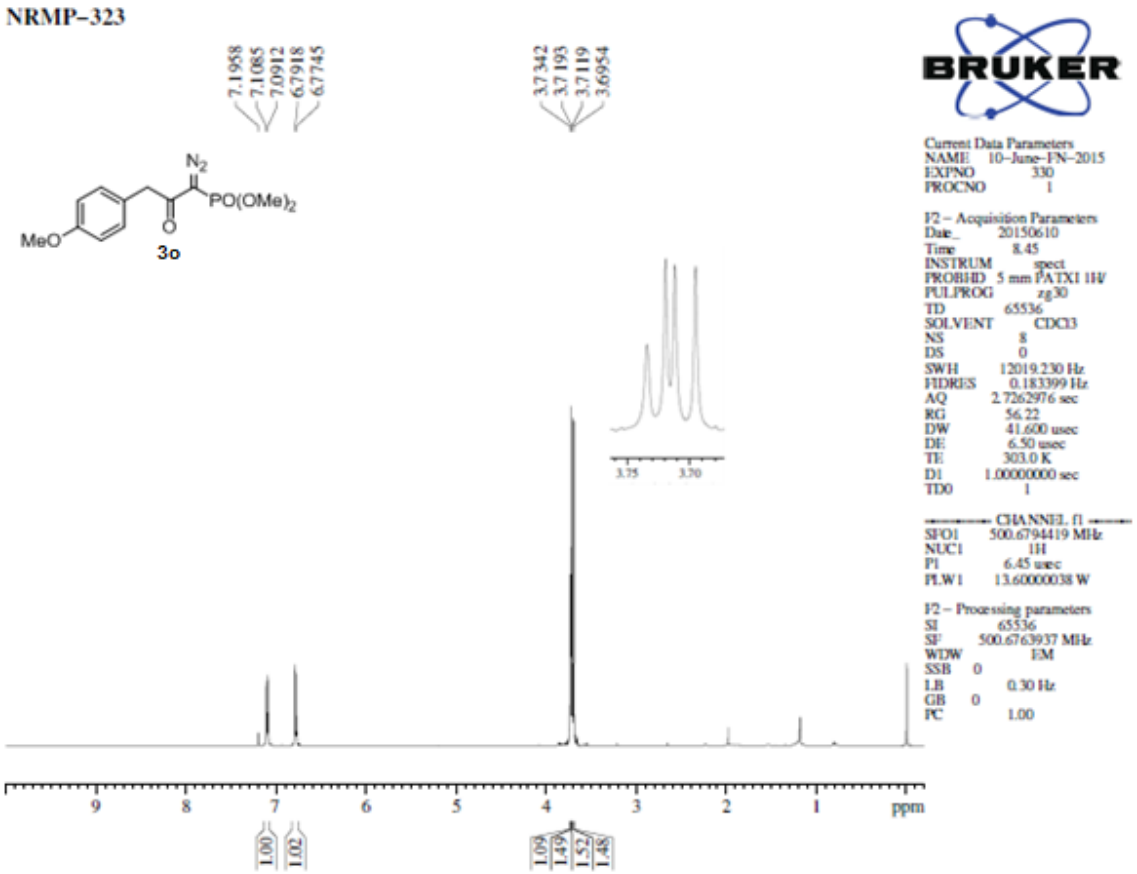

Figure 47: ^{1}H NMR spectrum of 3o

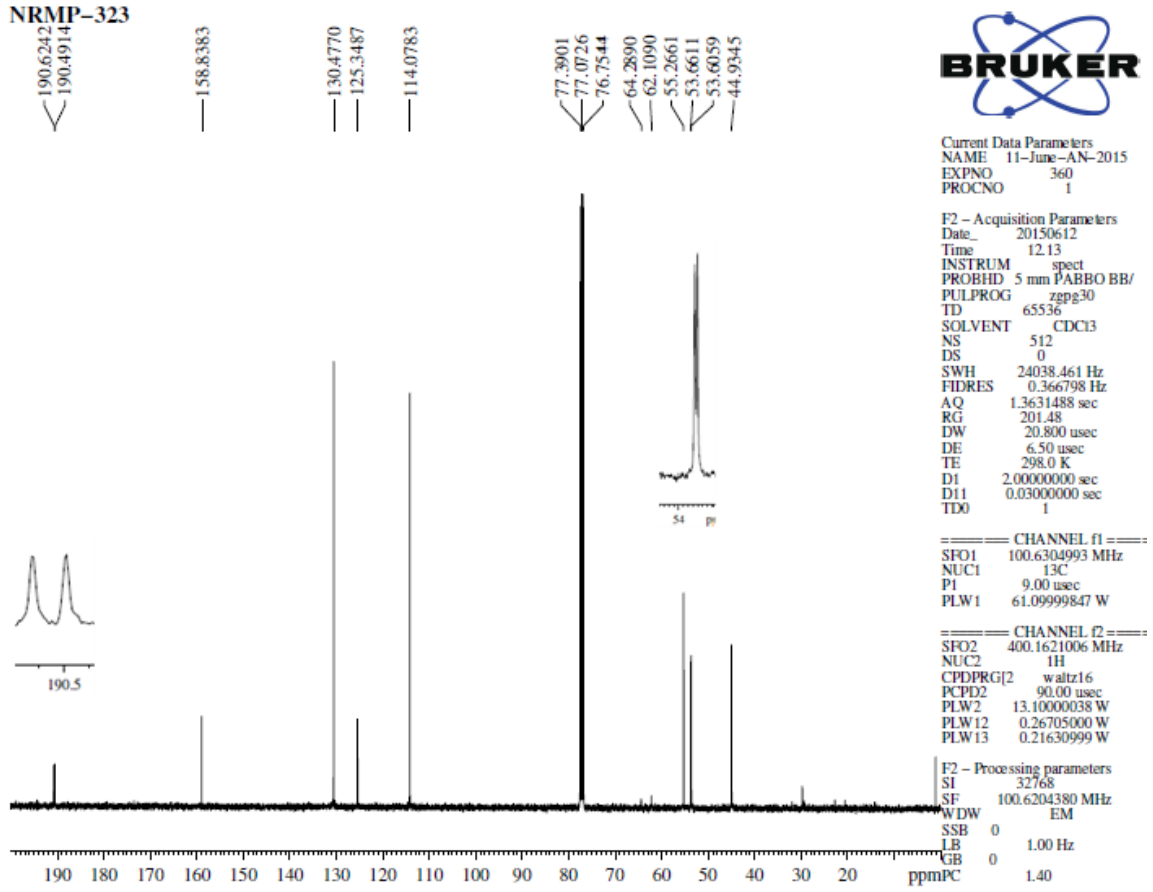

Figure 48: ^{13}C NMR spectrum of 3o

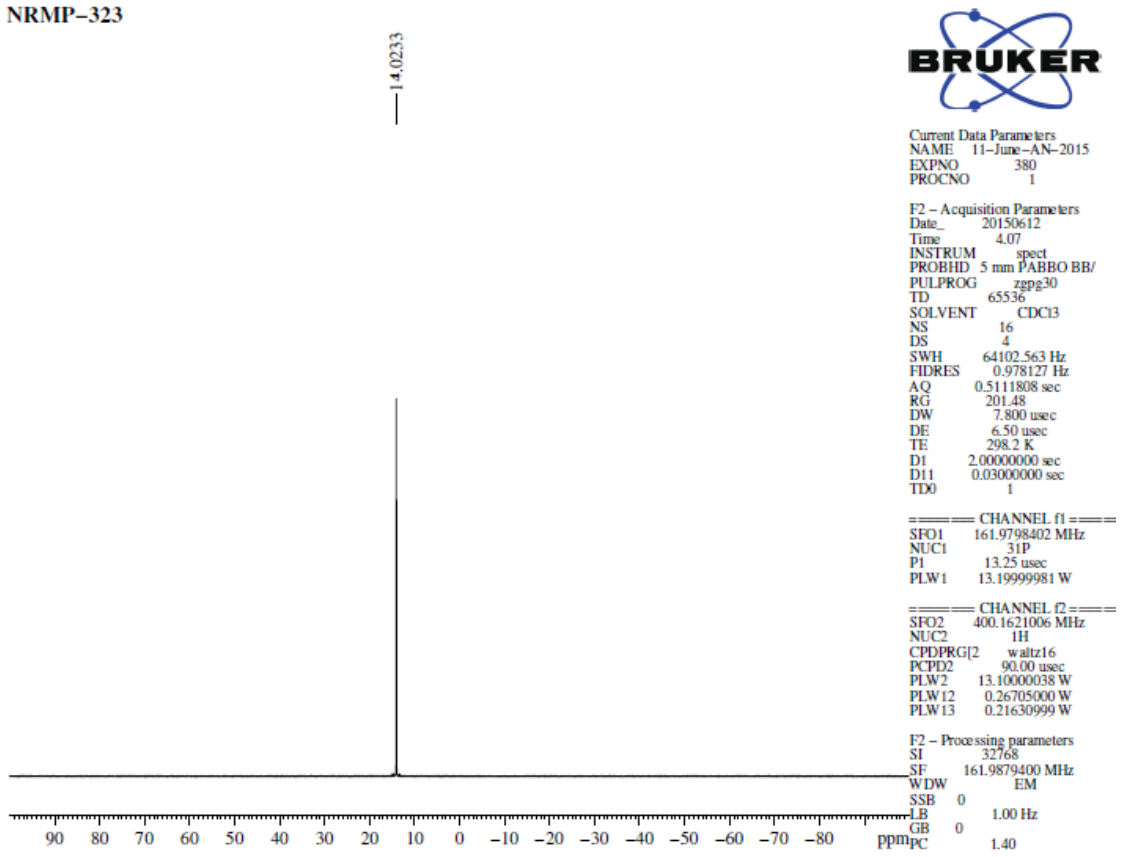

Figure 49: ^{31}P NMR spectrum of 3o

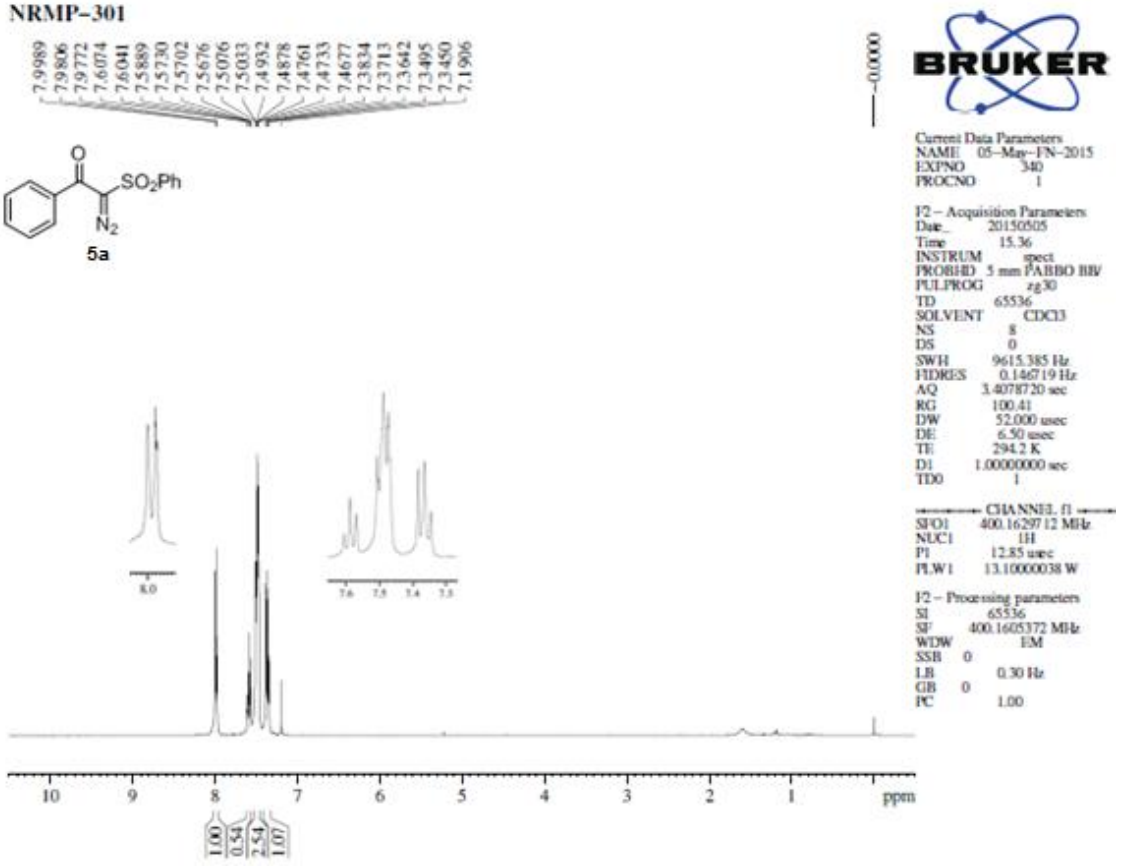

Figure 50: ^{1}H NMR spectrum of 5a

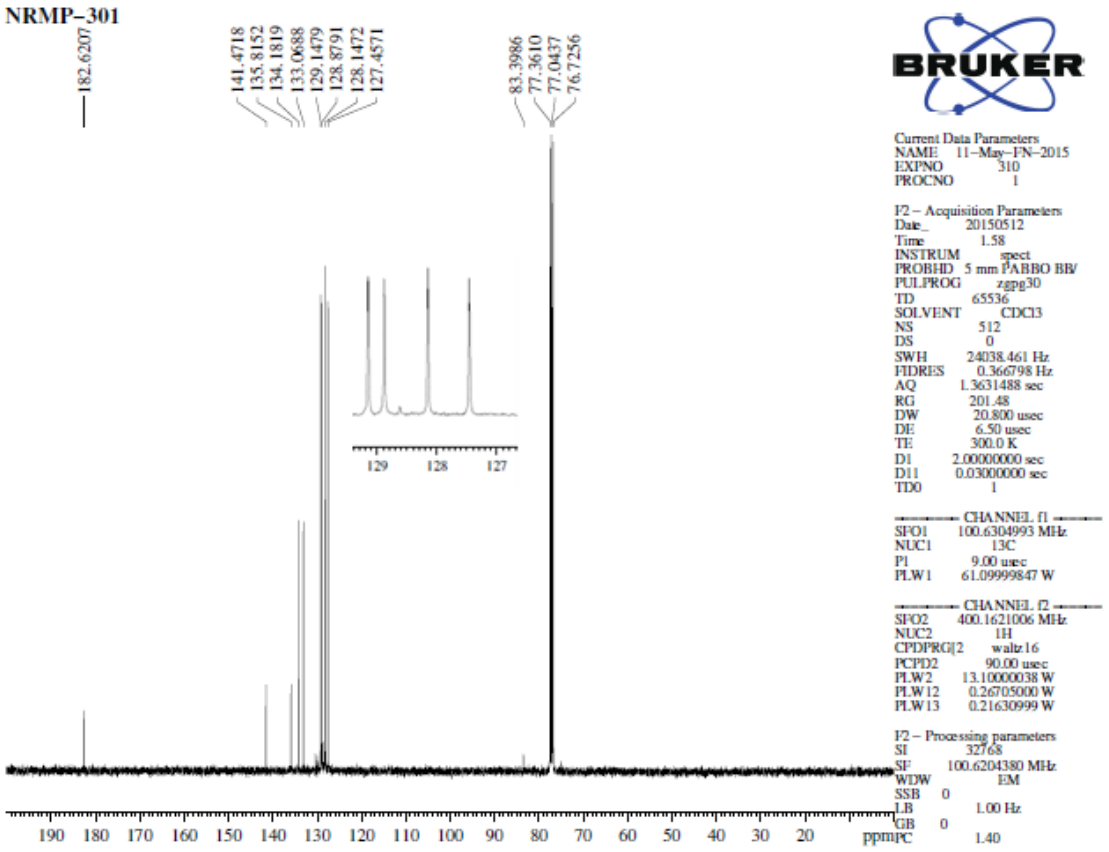

Figure 51: ^{13}C NMR spectrum of 5a

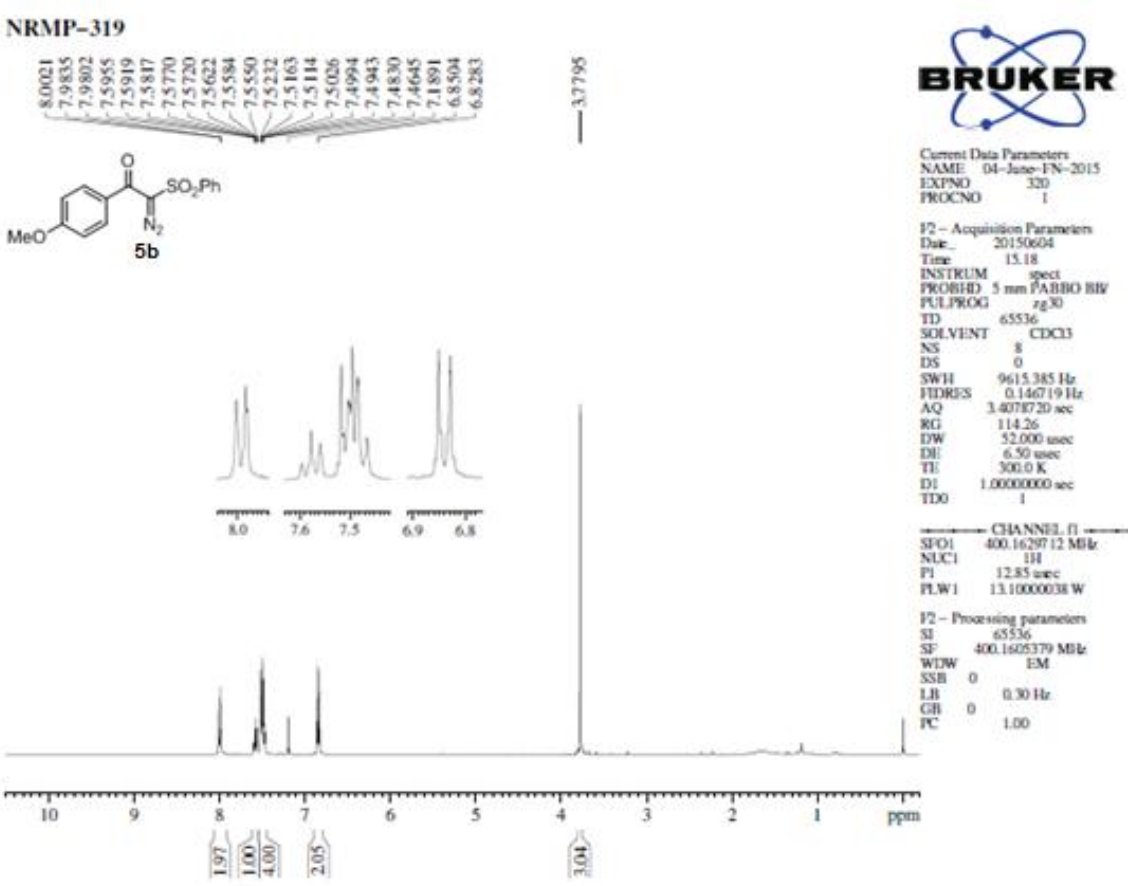

Figure 52: ^{1}H NMR spectrum of 5b

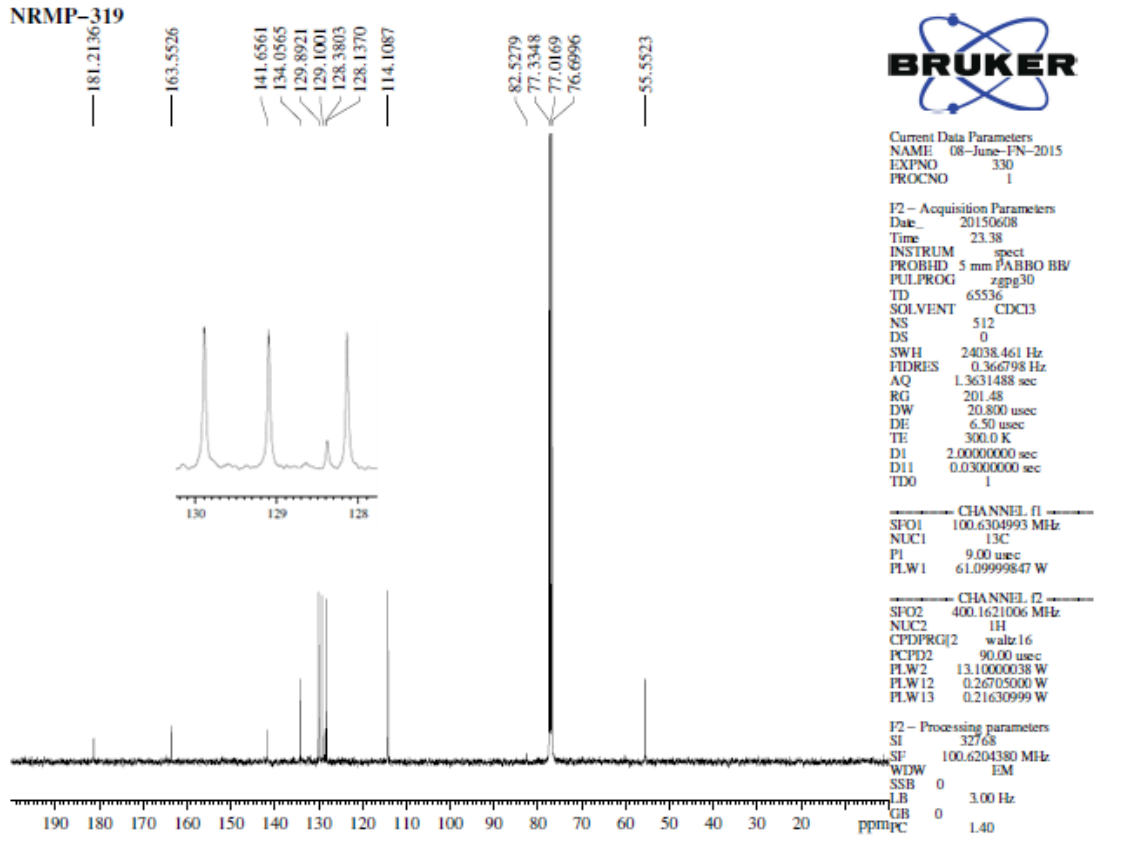

Figure 53: ^{13}C NMR spectrum of 5b

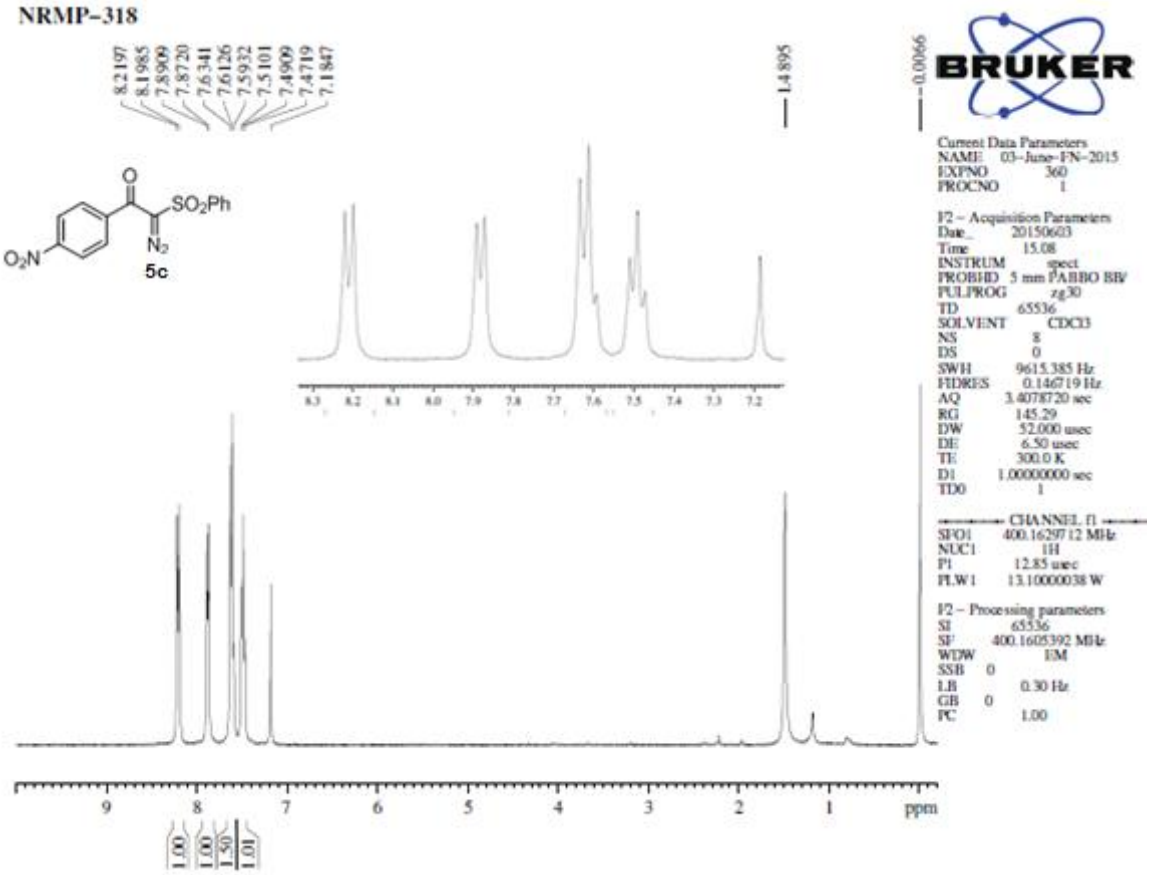

Figure 54: ^{1}H NMR spectrum of 5c

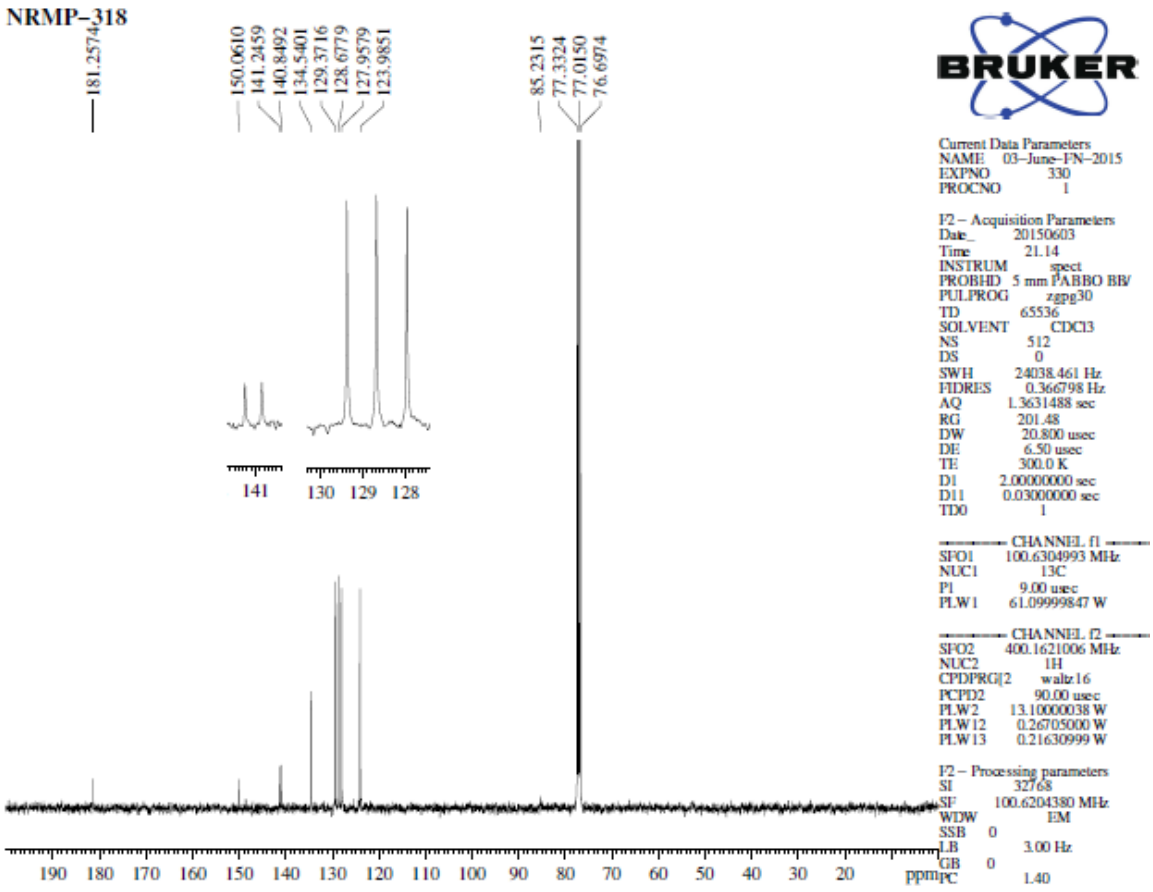

Figure 55: ^{13}C NMR spectrum of 5c

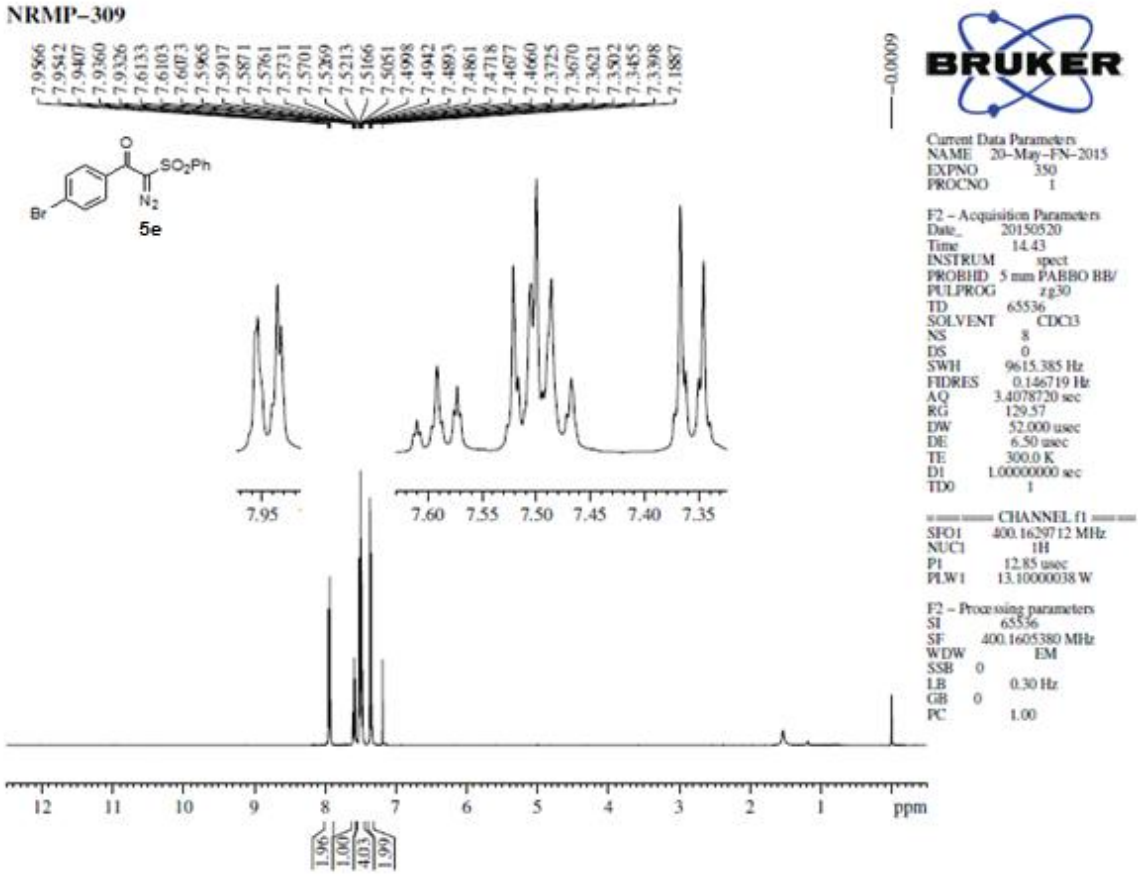

Figure 56: ^{1}H NMR spectrum of 5e

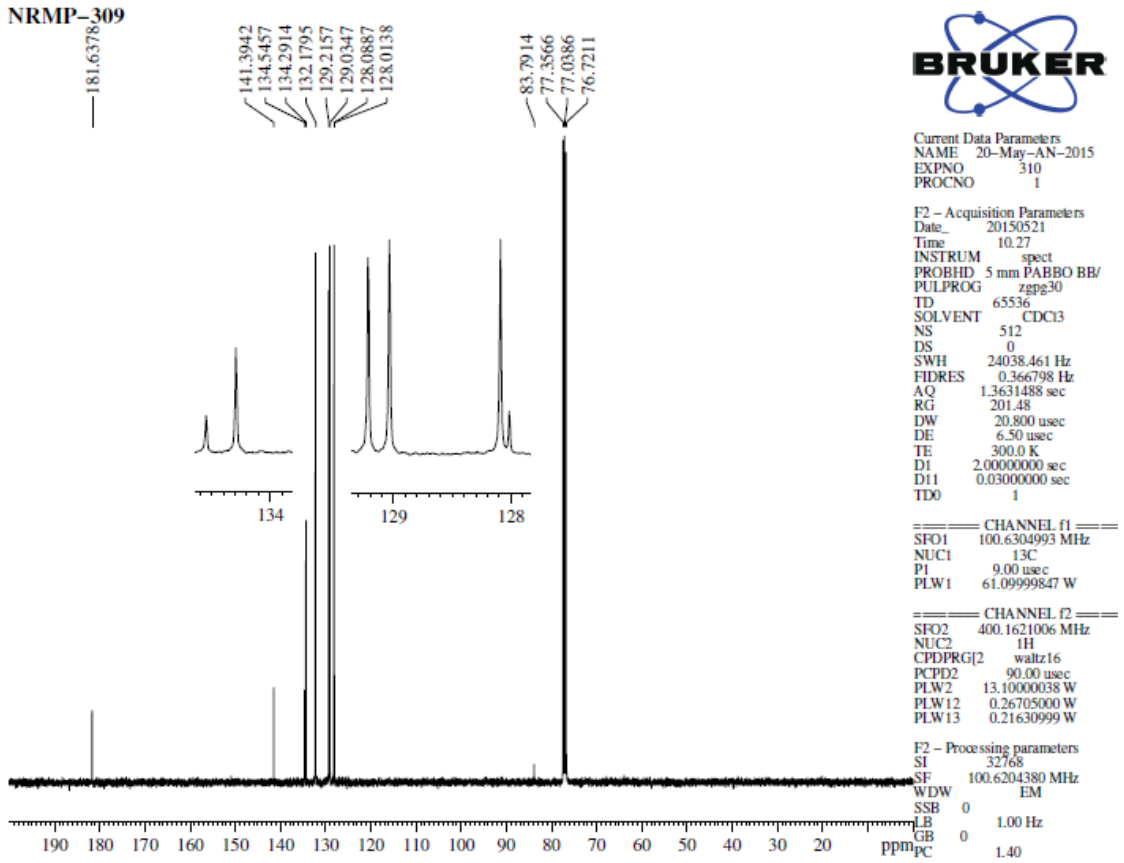

Figure 57: ^{13}C NMR spectrum of 5e

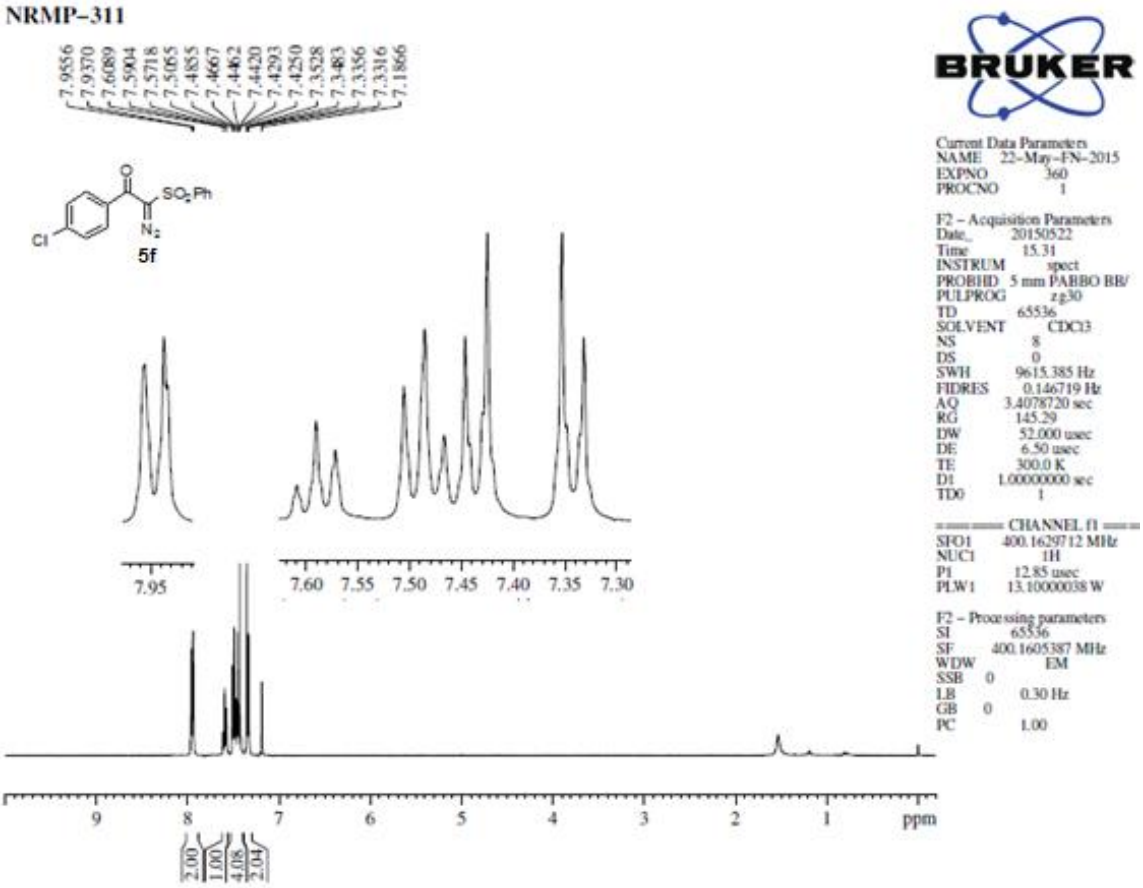

Figure 58: ^{1}H NMR spectrum of 5f

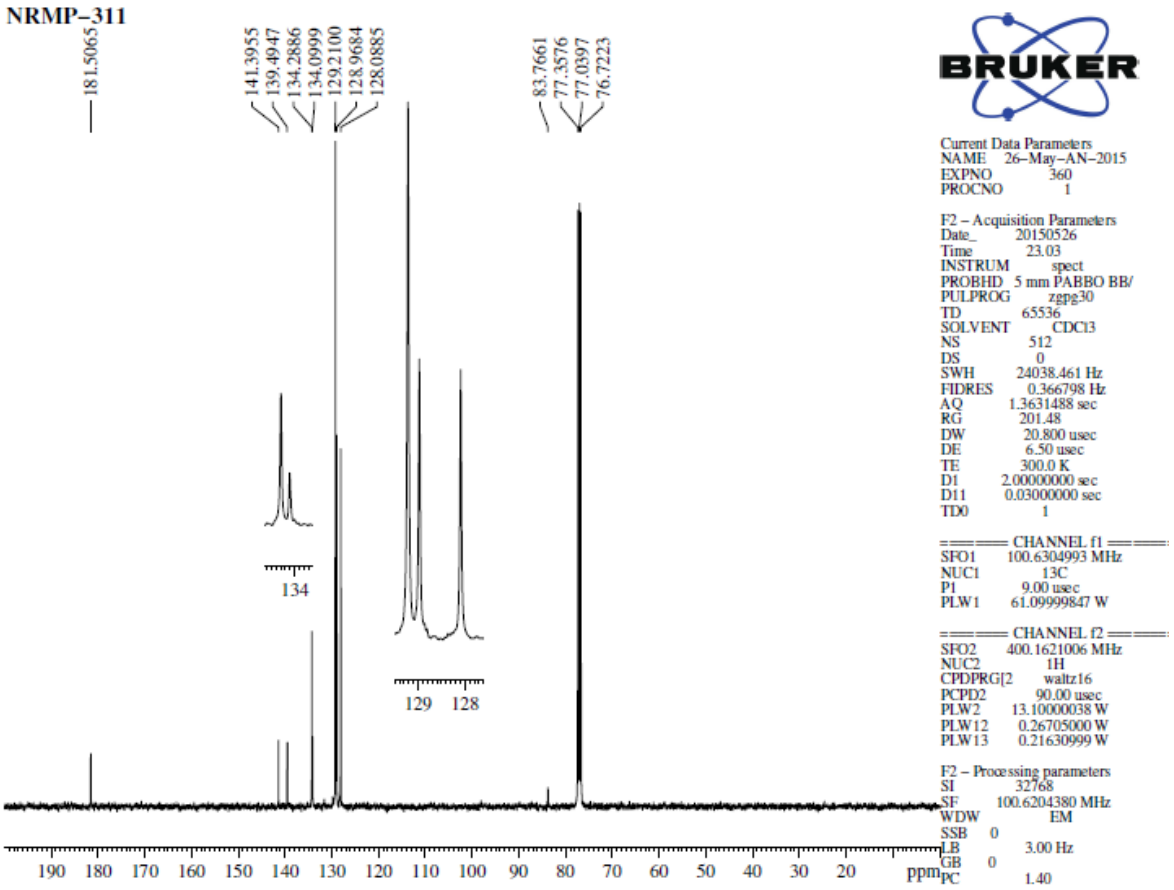

Figure 59: ^{13}C NMR spectrum of 5f

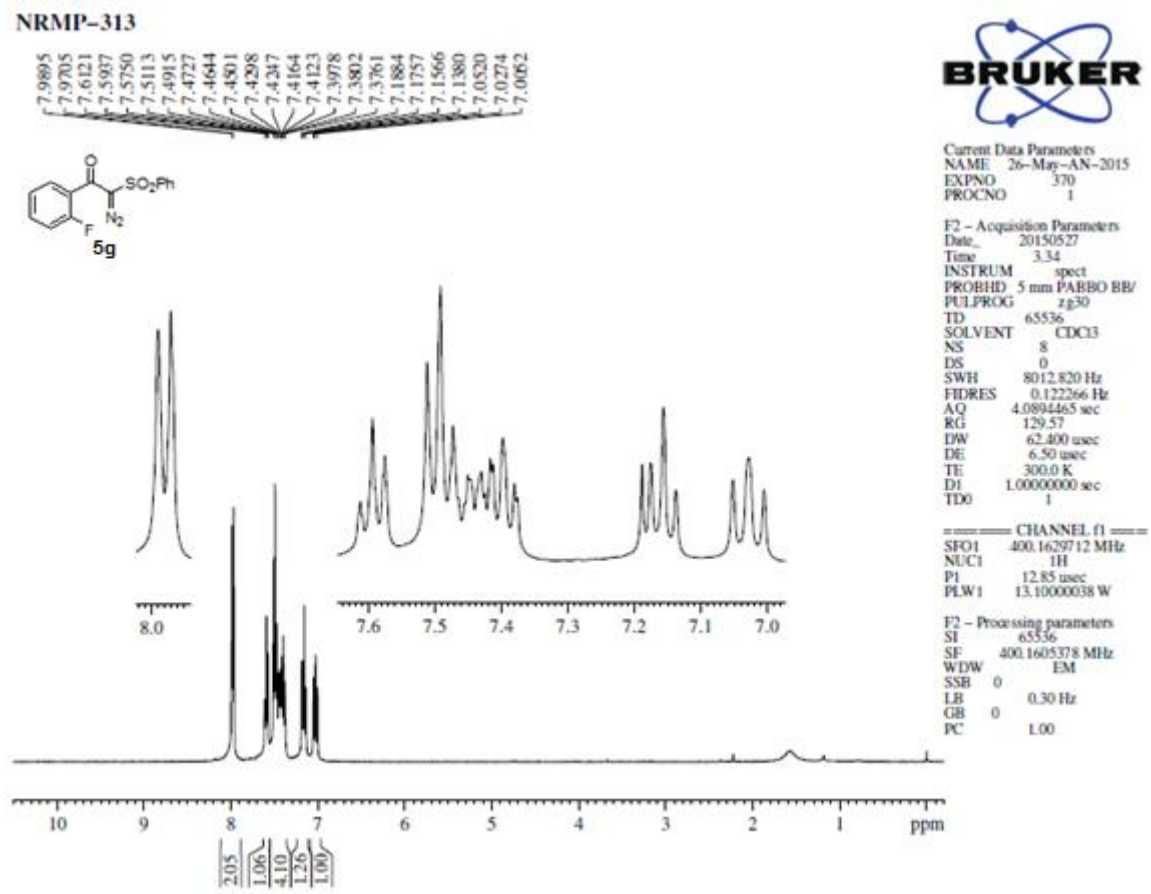

Figure 60: ^{1}H NMR spectrum of 5g

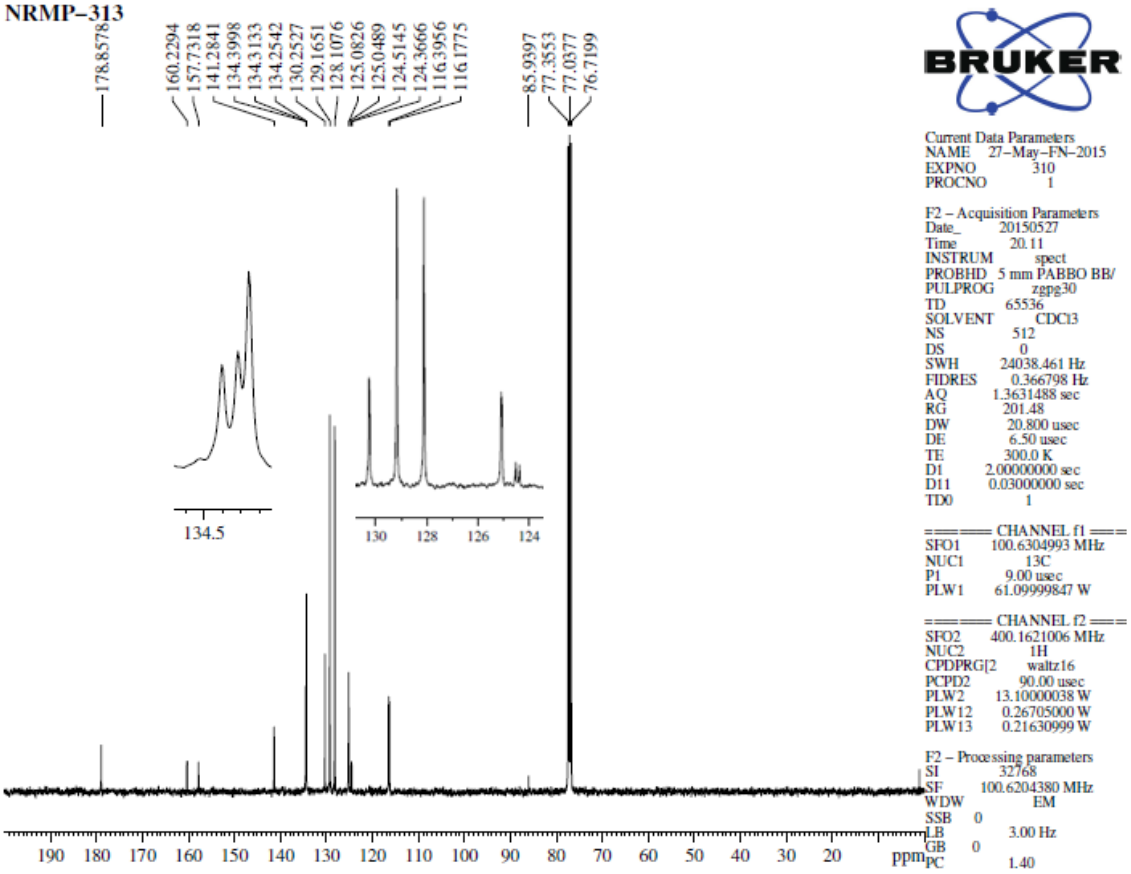

Figure 61: ^{13}CNMR spectrum of 5g

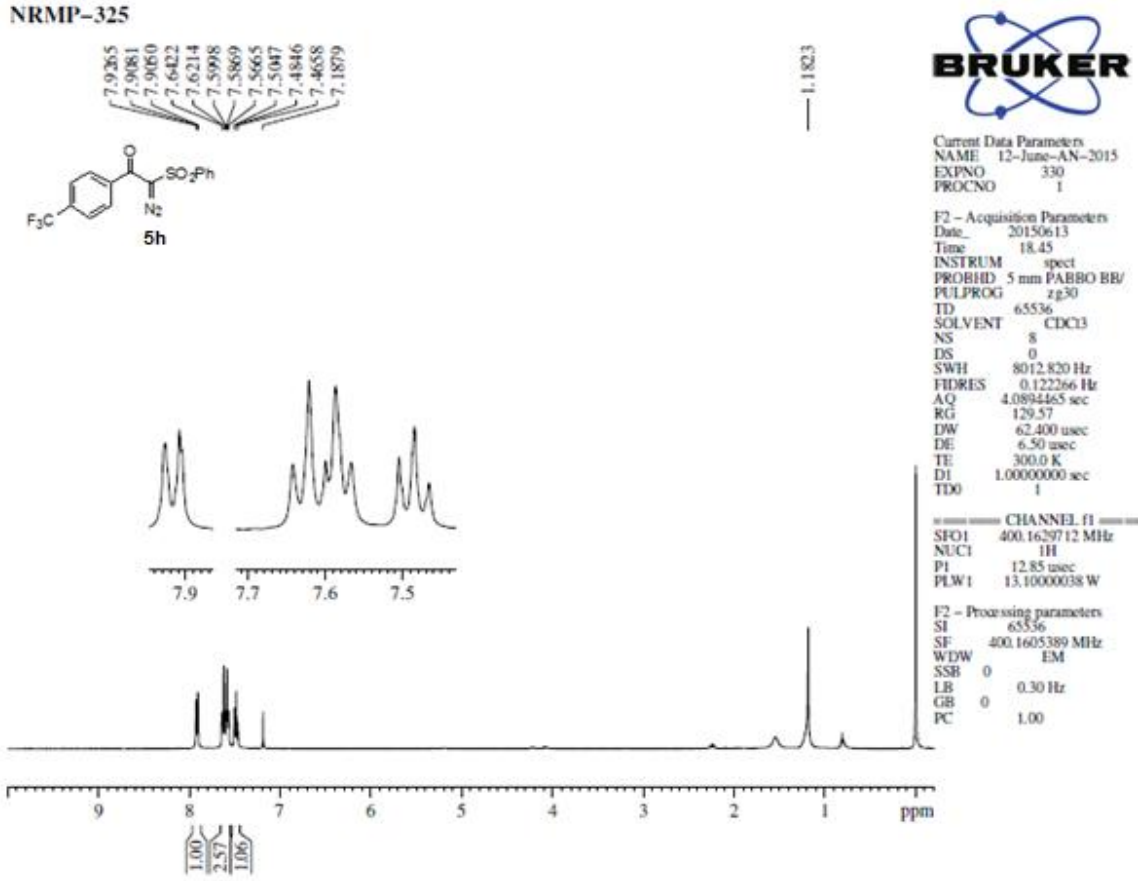

Figure 62: ^{1}H NMR spectrum of 5h

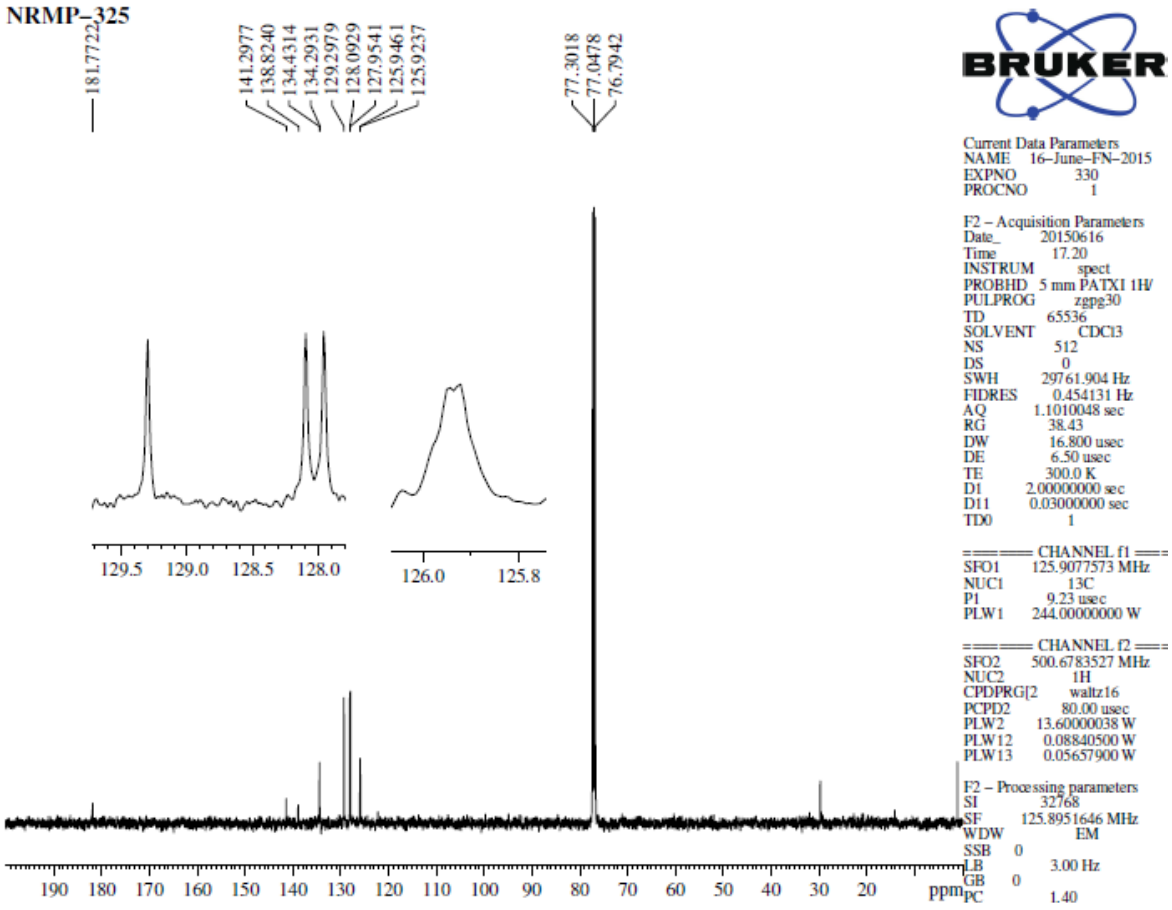

Figure 63: ^{13}C NMR spectrum of 5h

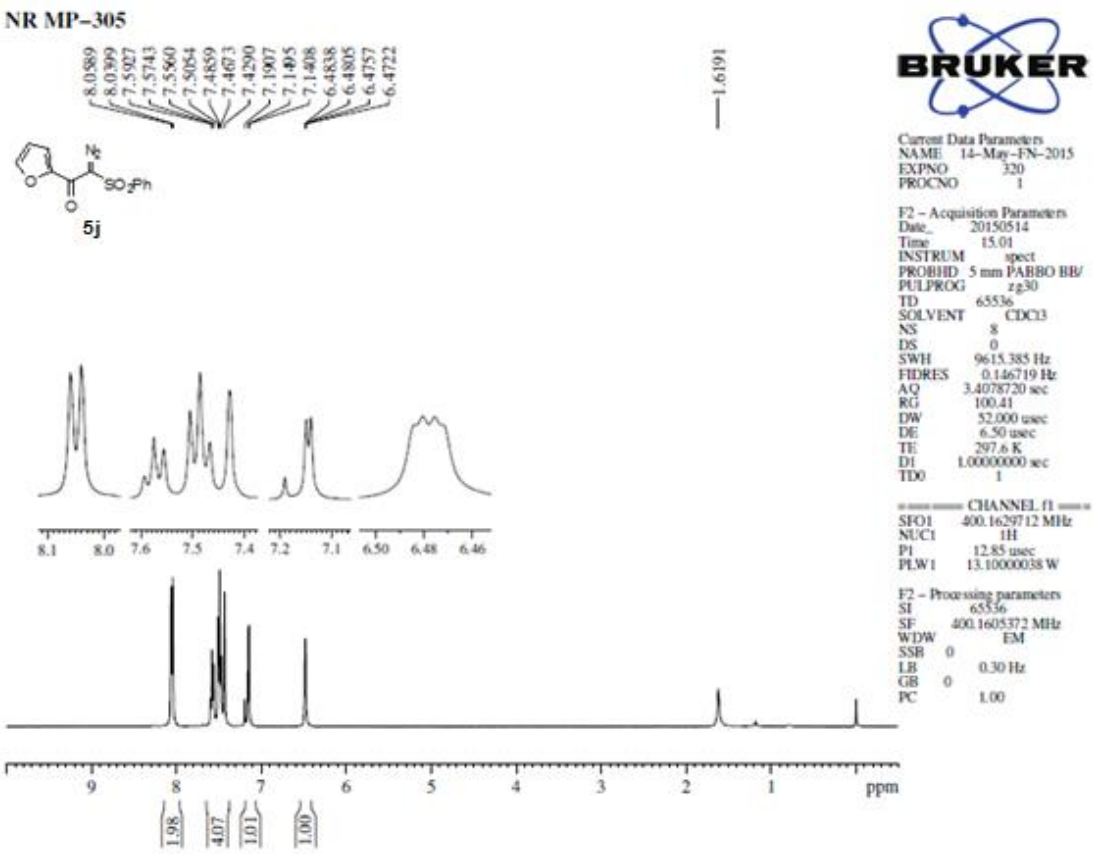

Figure 64: ^{1}H NMR spectrum of 5j

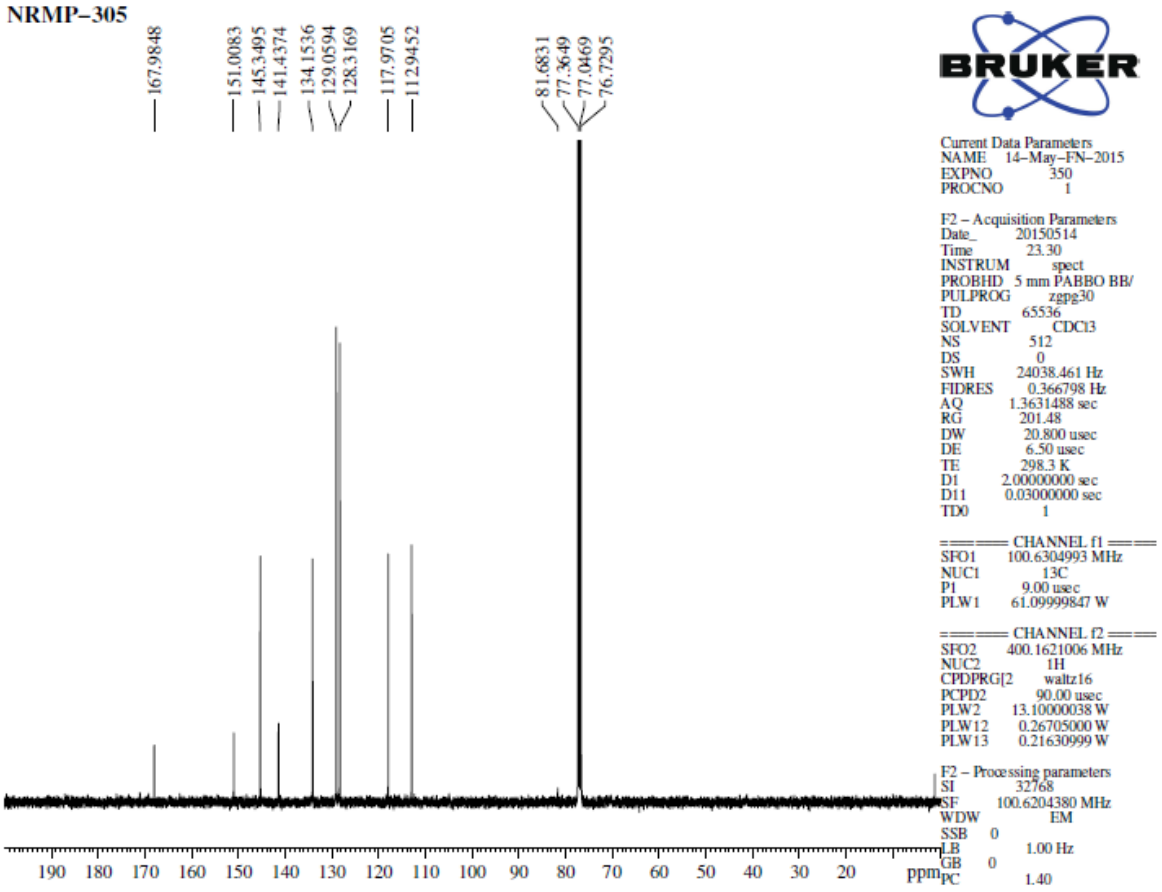

Figure 65: ^{13}C NMR spectrum of 5j

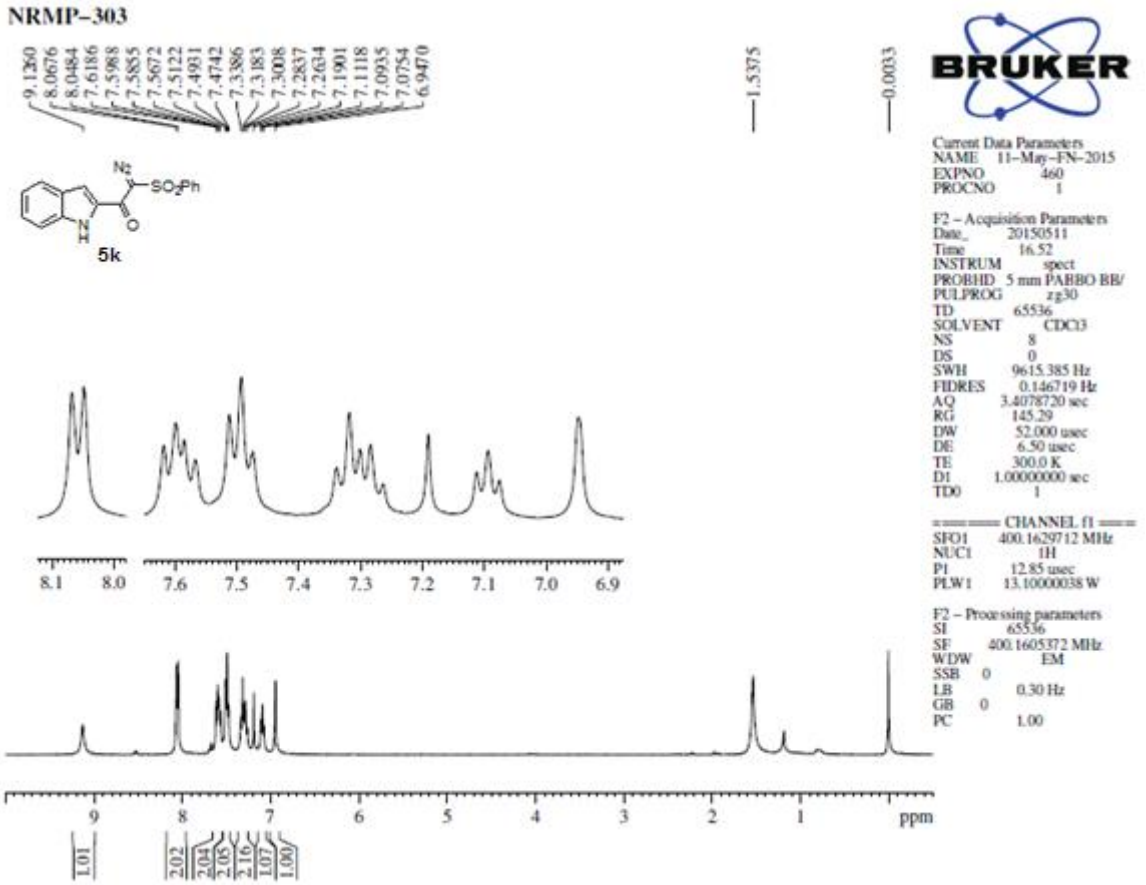

Figure 66: ^{1}H NMR spectrum of 5k

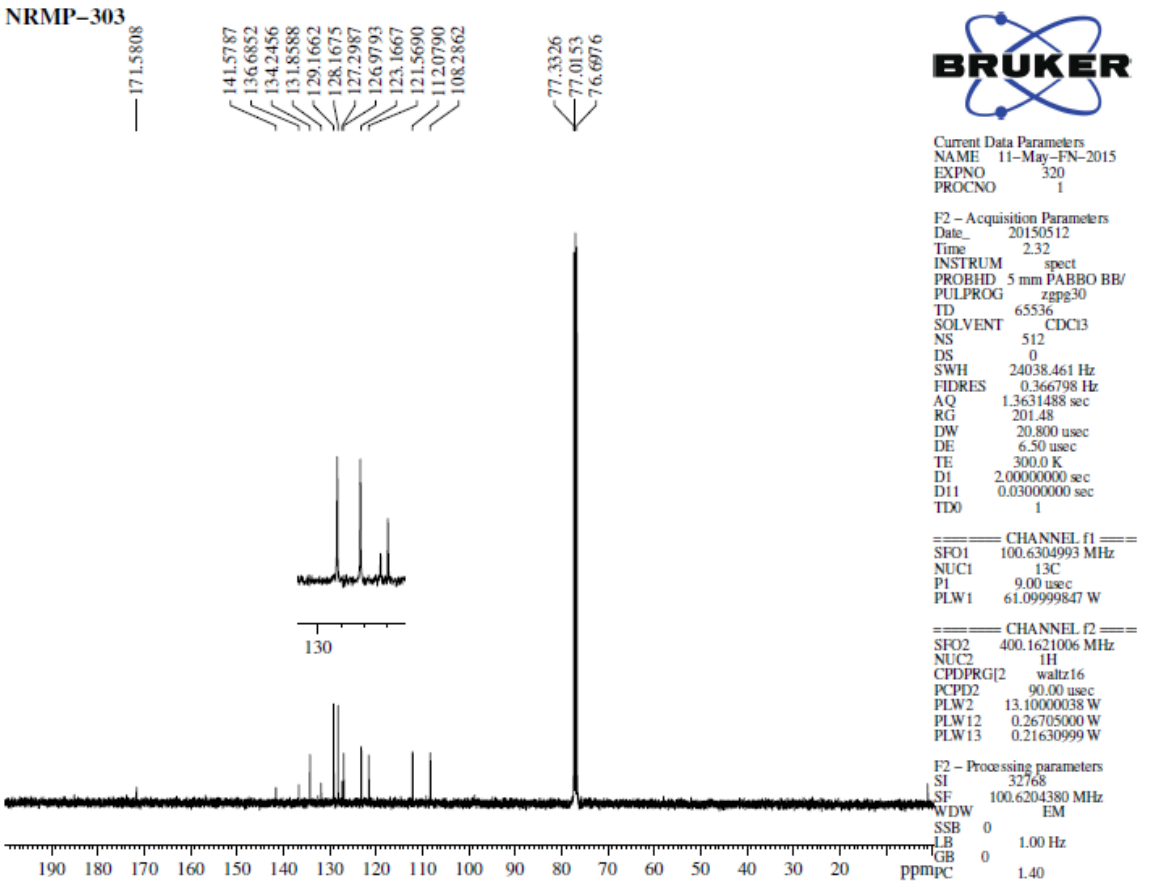

Figure 67: ^{13}C NMR spectrum of 5k

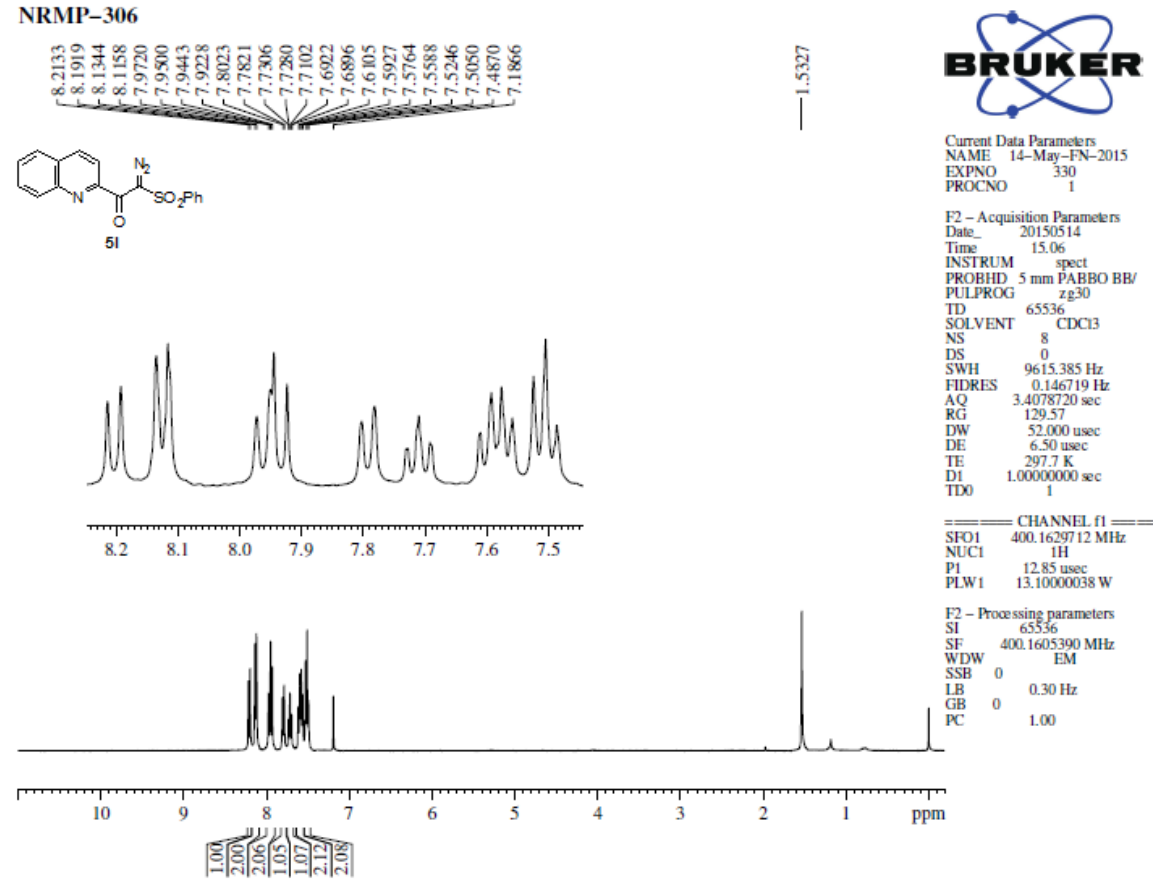

Figure 68: ^{1}H NMR spectrum of 5l

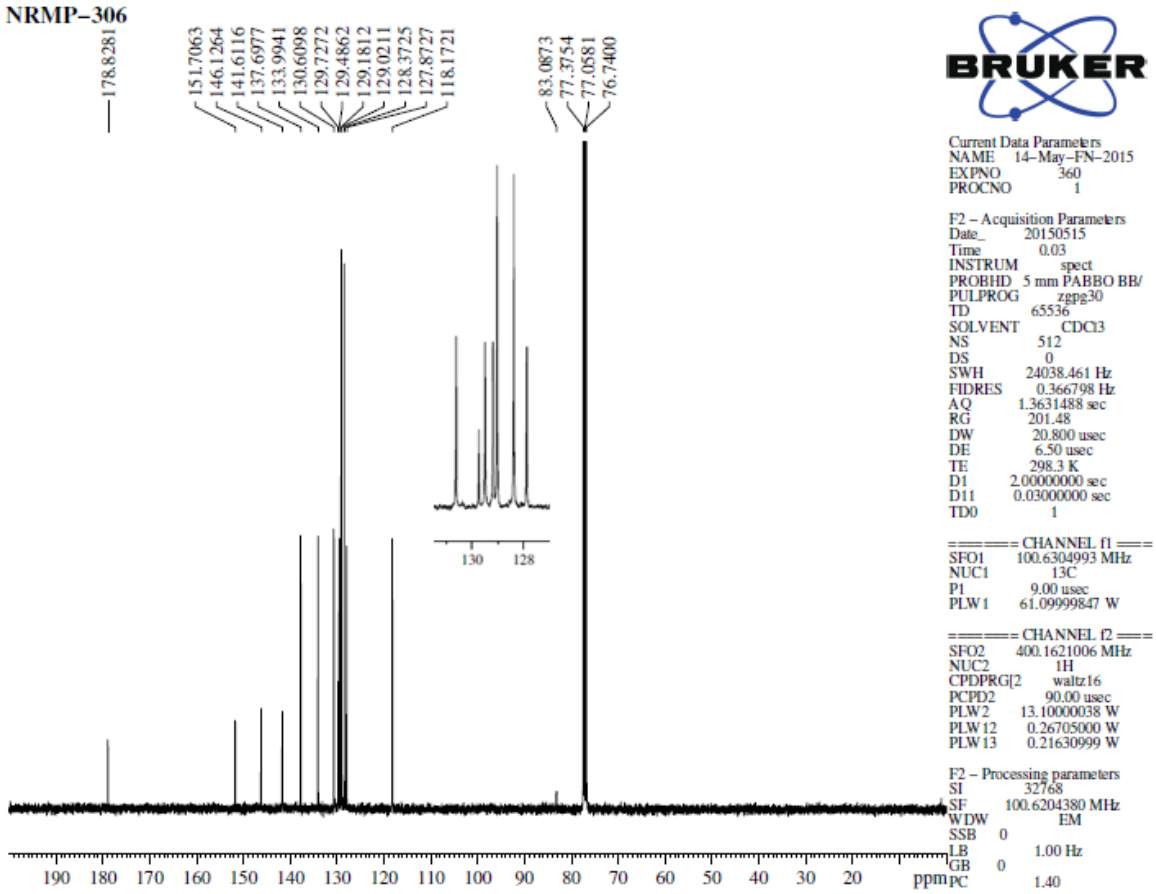

Figure 69: ^{13}C NMR spectrum of 5l

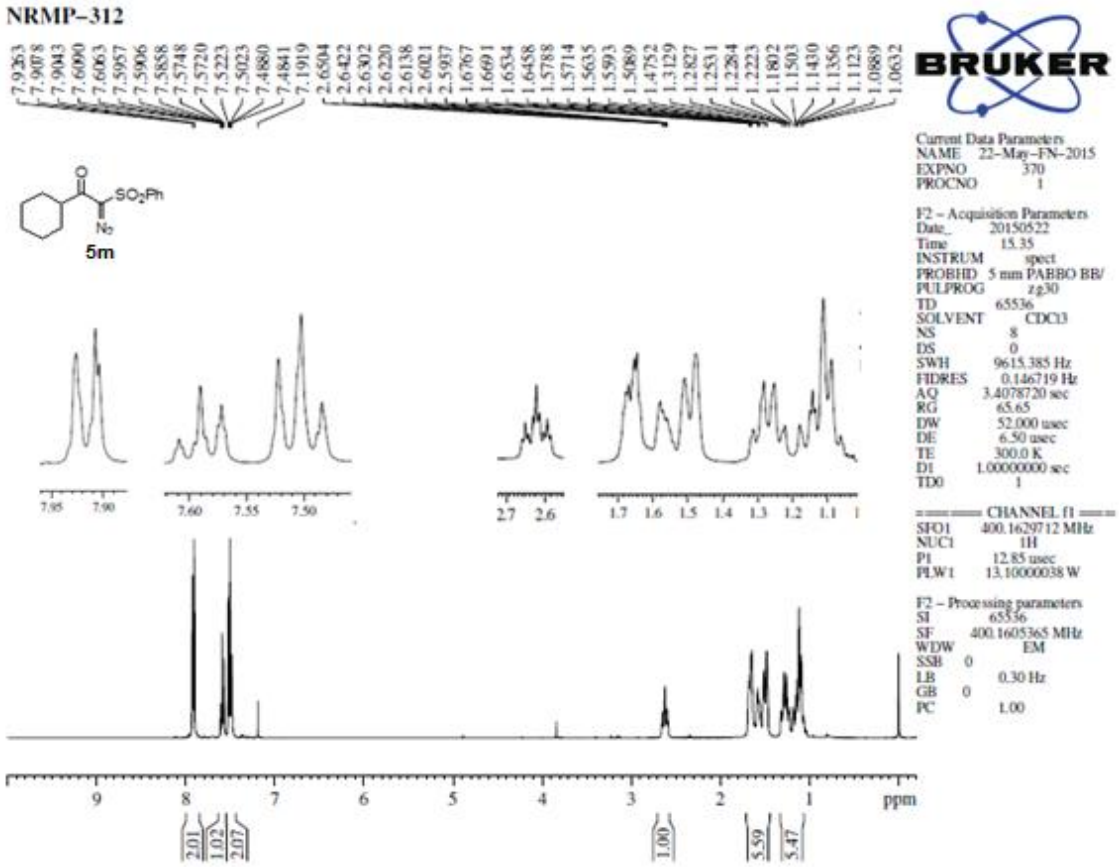

Figure 70: ^{1}H NMR spectrum of 5m

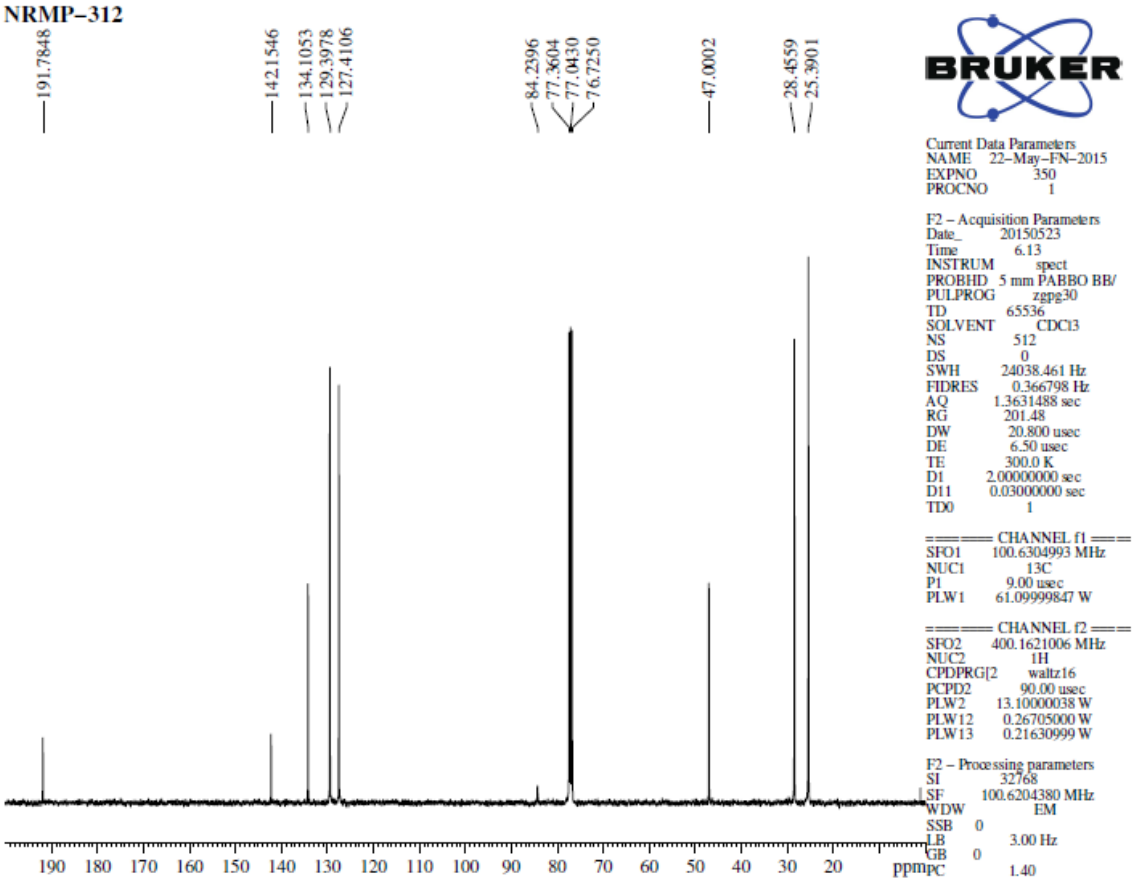

Figure 71: ^{13}C NMR spectrum of 5m

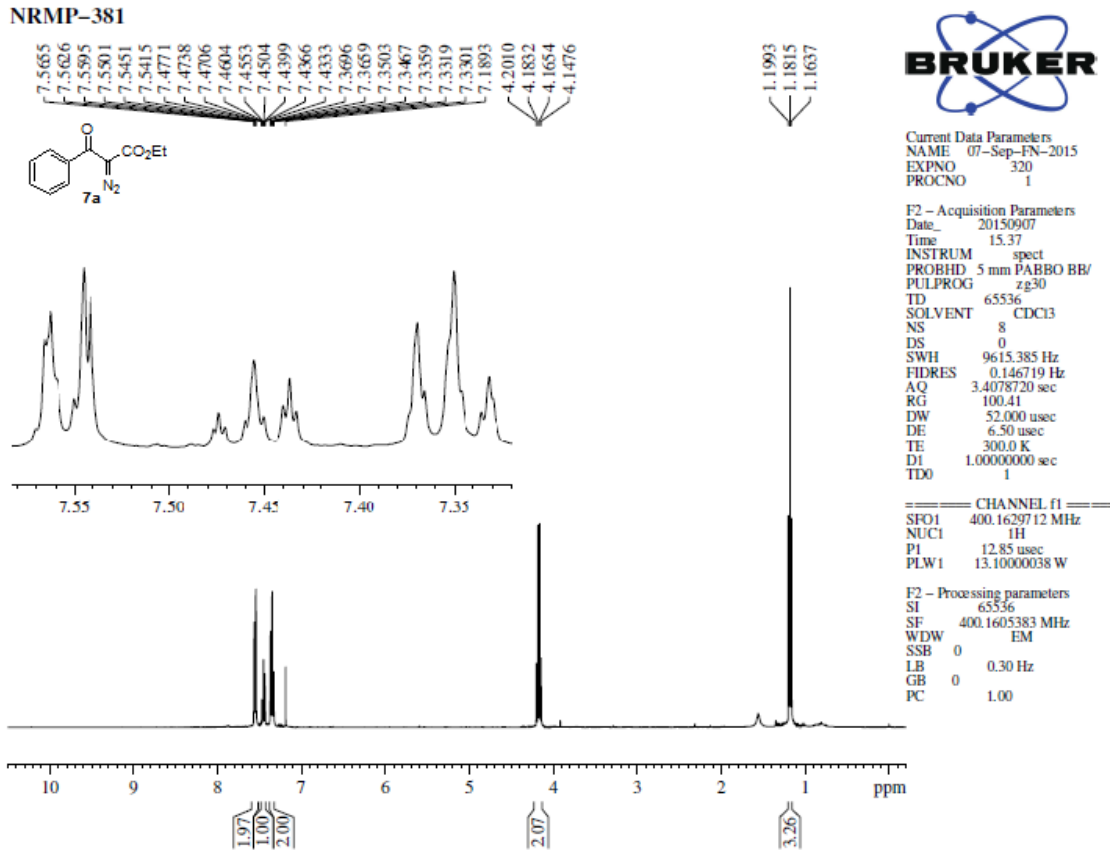

Figure 72: ^{1}H NMR spectrum of 7a

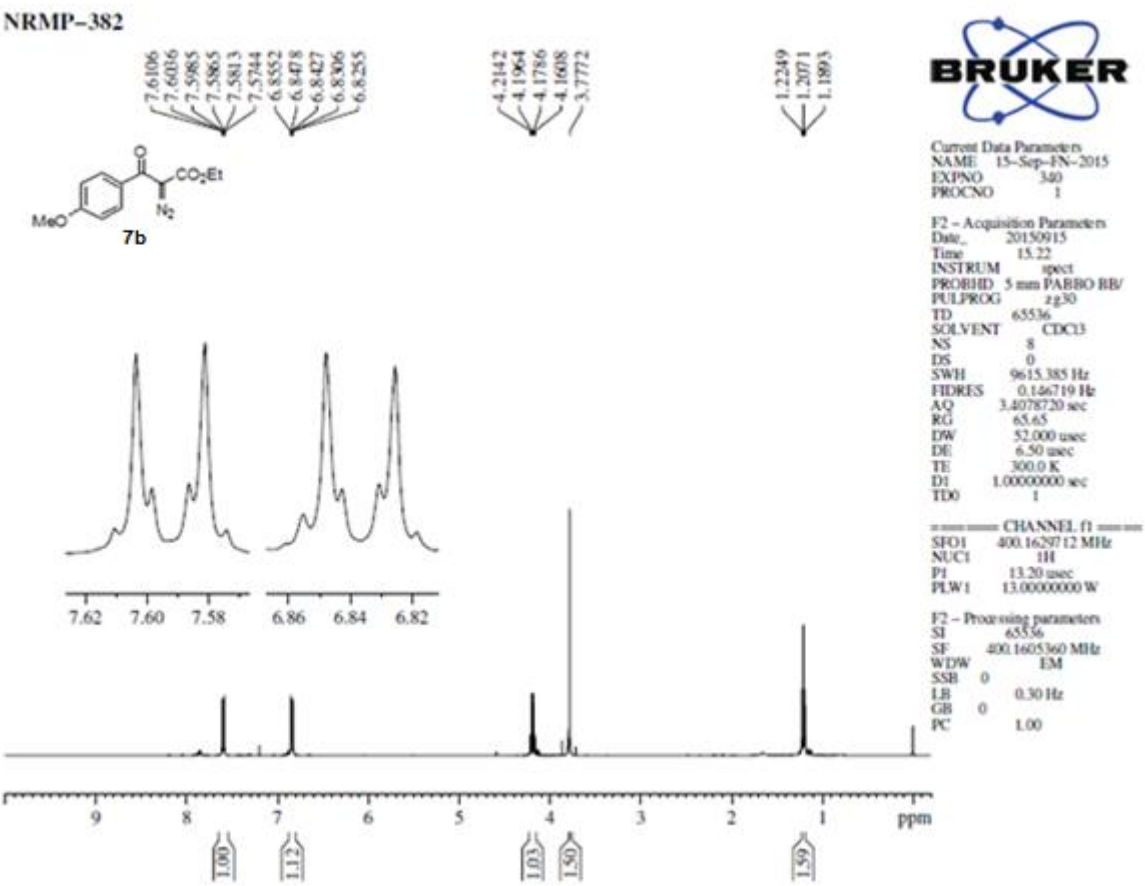

Figure 73: ^{1}H NMR spectrum of 7b

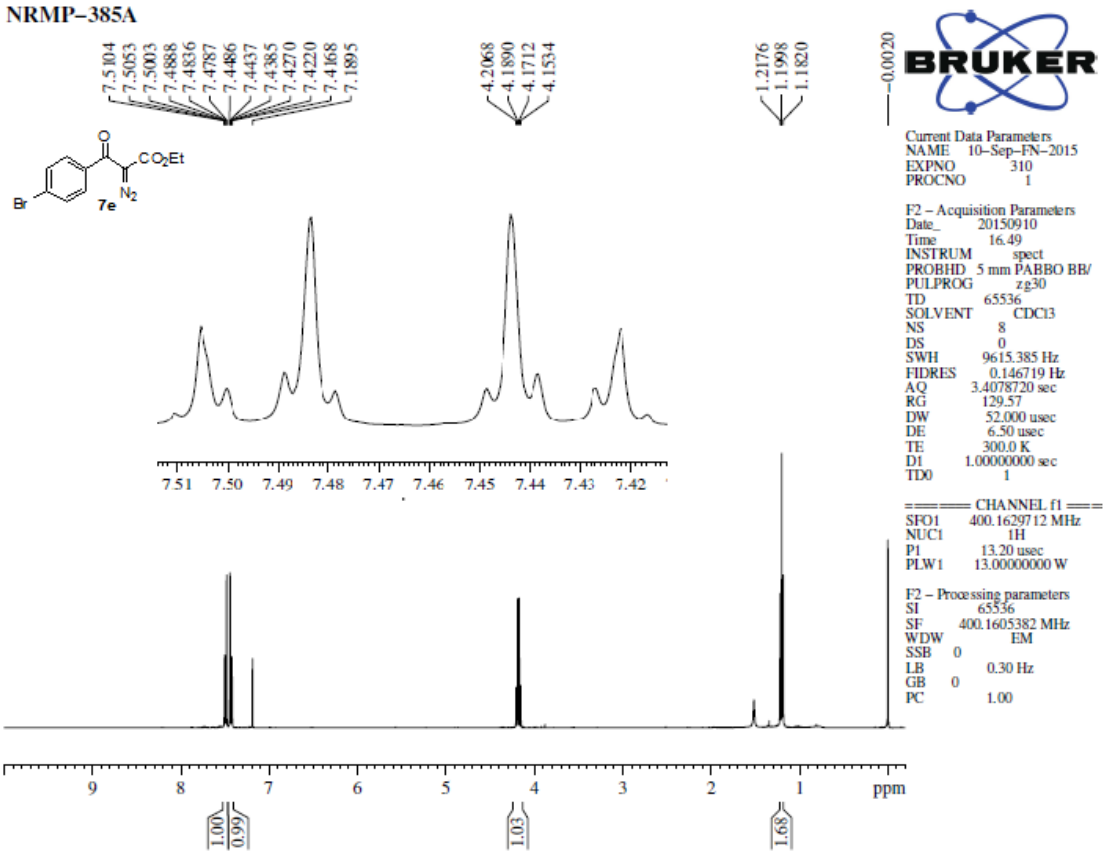

Figure 74: ^{1}H NMR spectrum of 7e

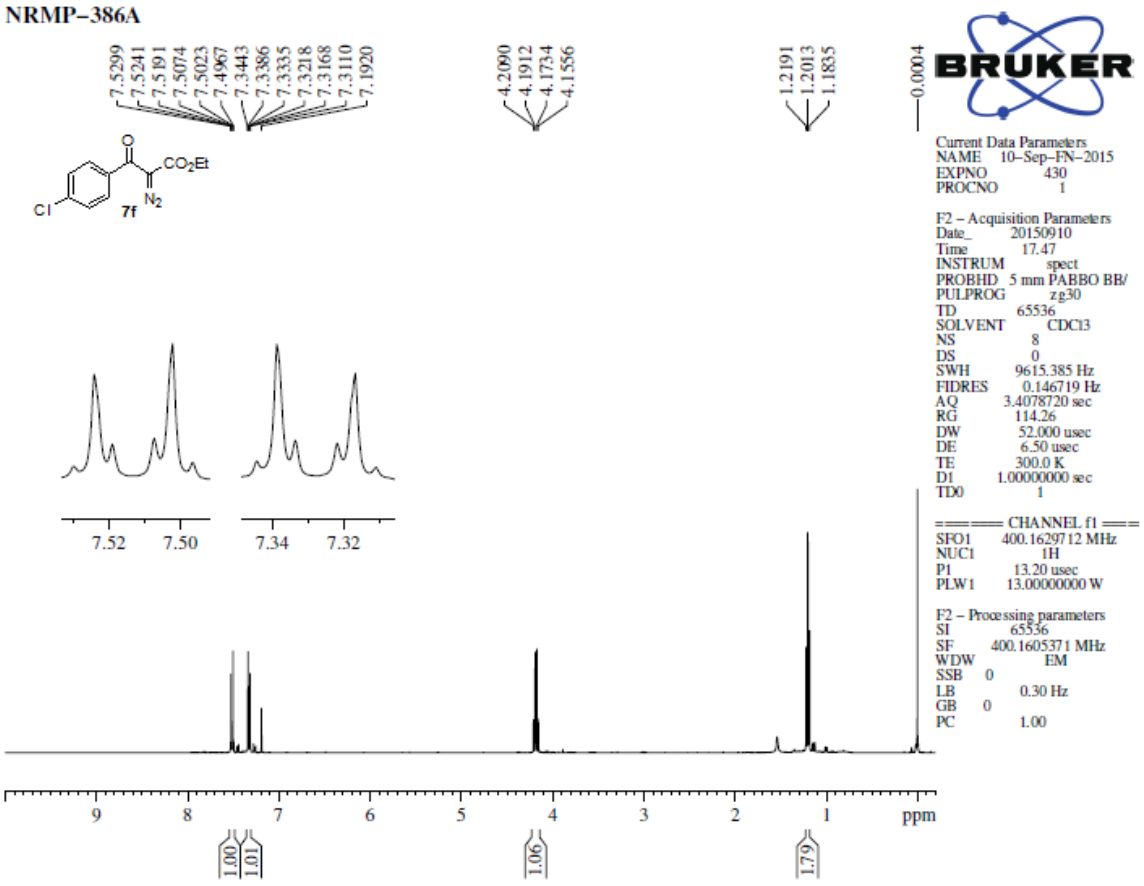

Figure 75: ^{1}H NMR spectrum of 7f

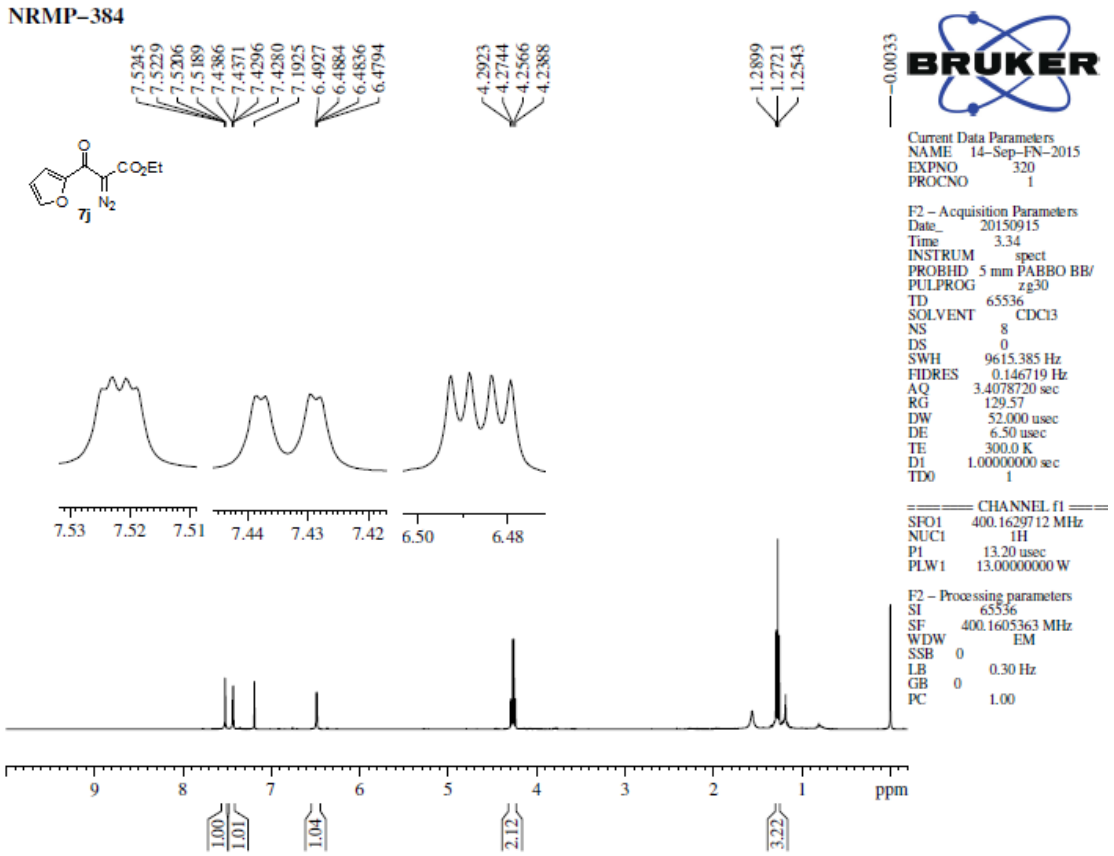

Figure 76: ^{1}H NMR spectrum of 7j

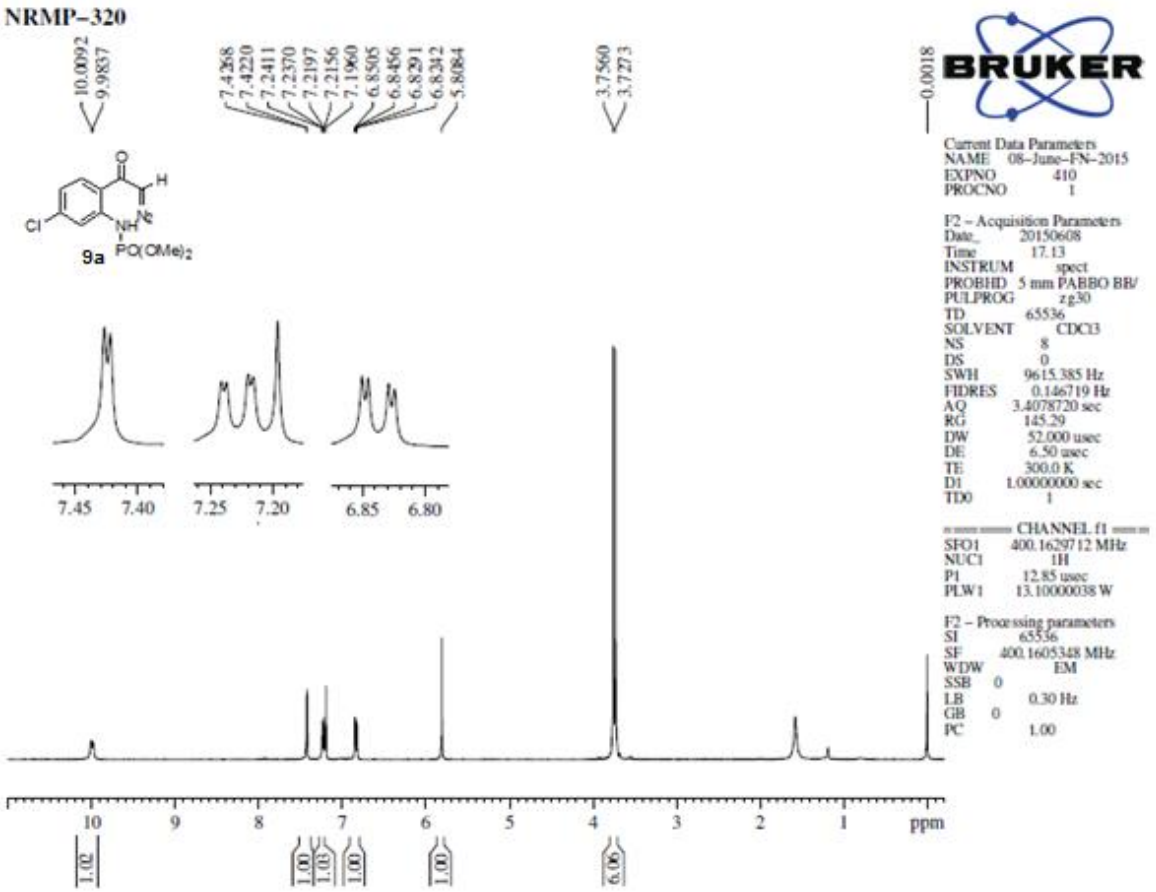

Figure 77: ^{1}H NMR spectrum of 9a

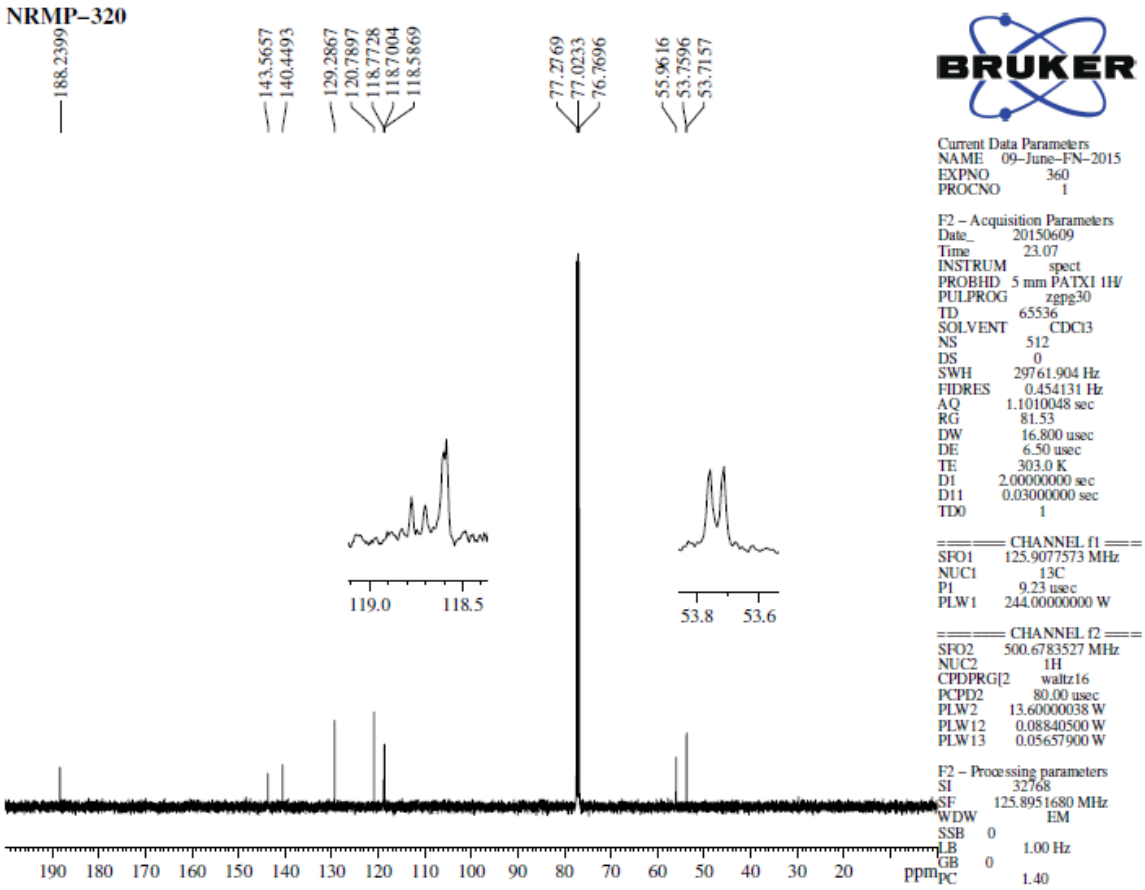

Figure 78: ^{13}C NMR spectrum of 9a

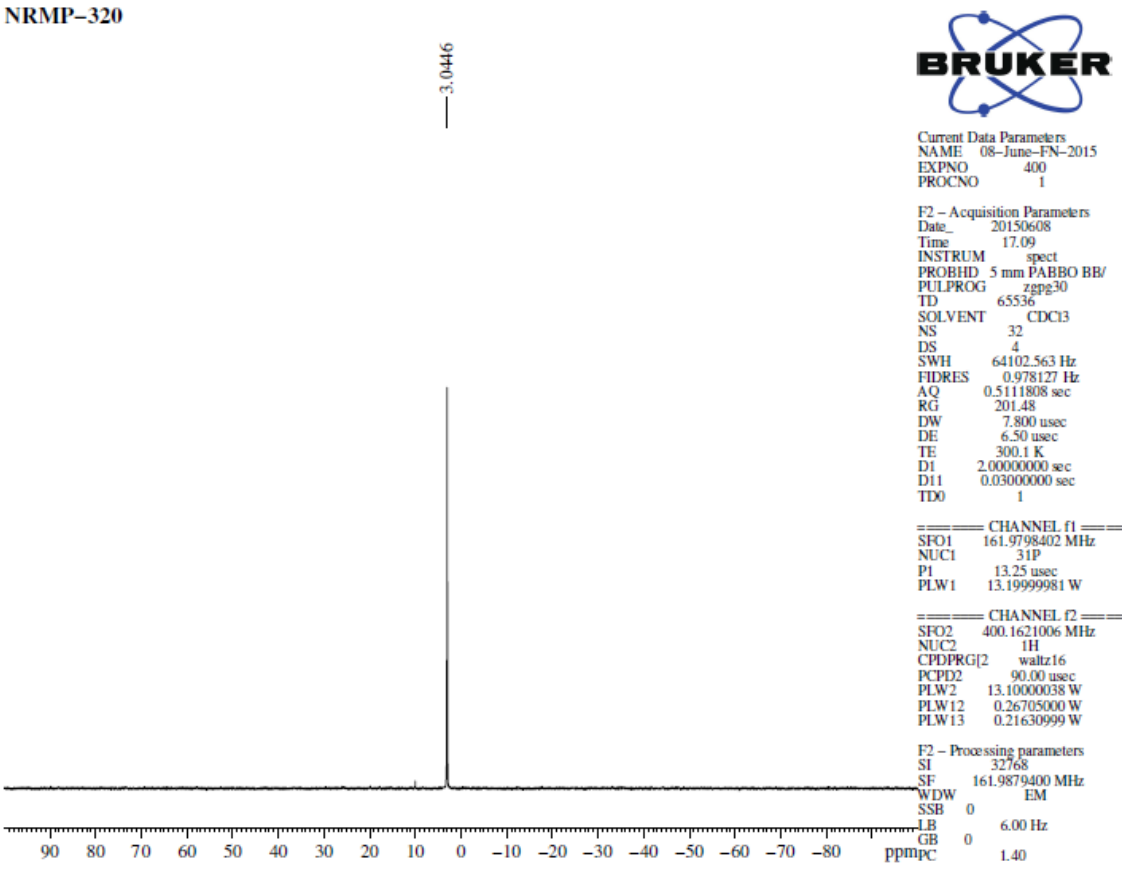

Figure 79: ^{31}P NMR spectrum of 9a

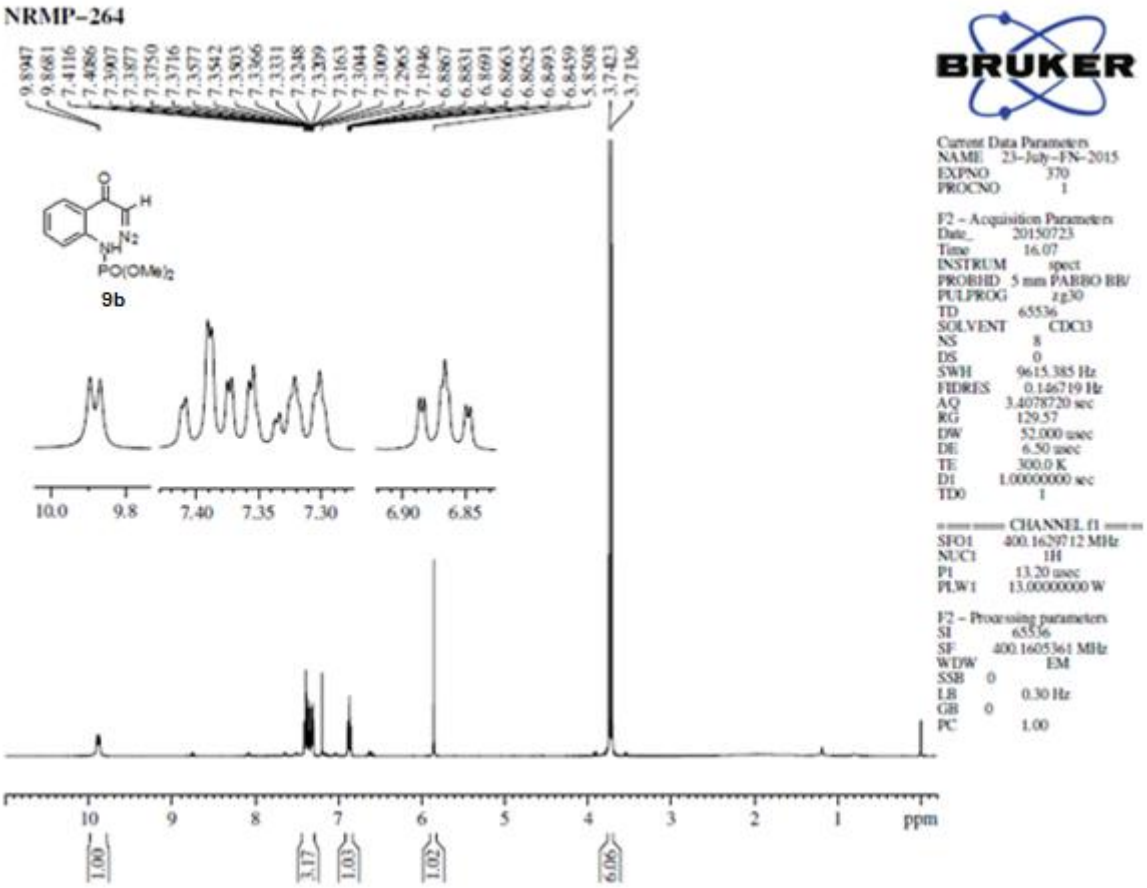

Figure 80: ^{1}H NMR spectrum of 9b

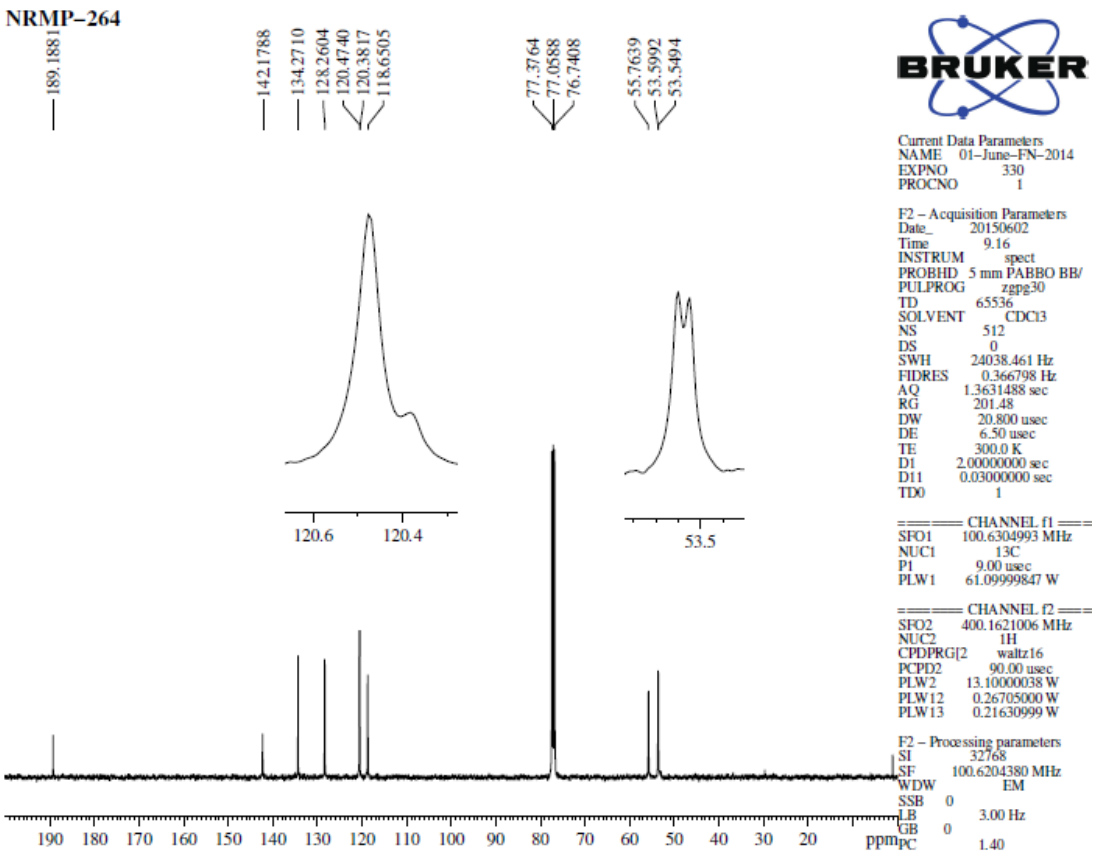

Figure 81: ^{13}C NMR spectrum of 9b

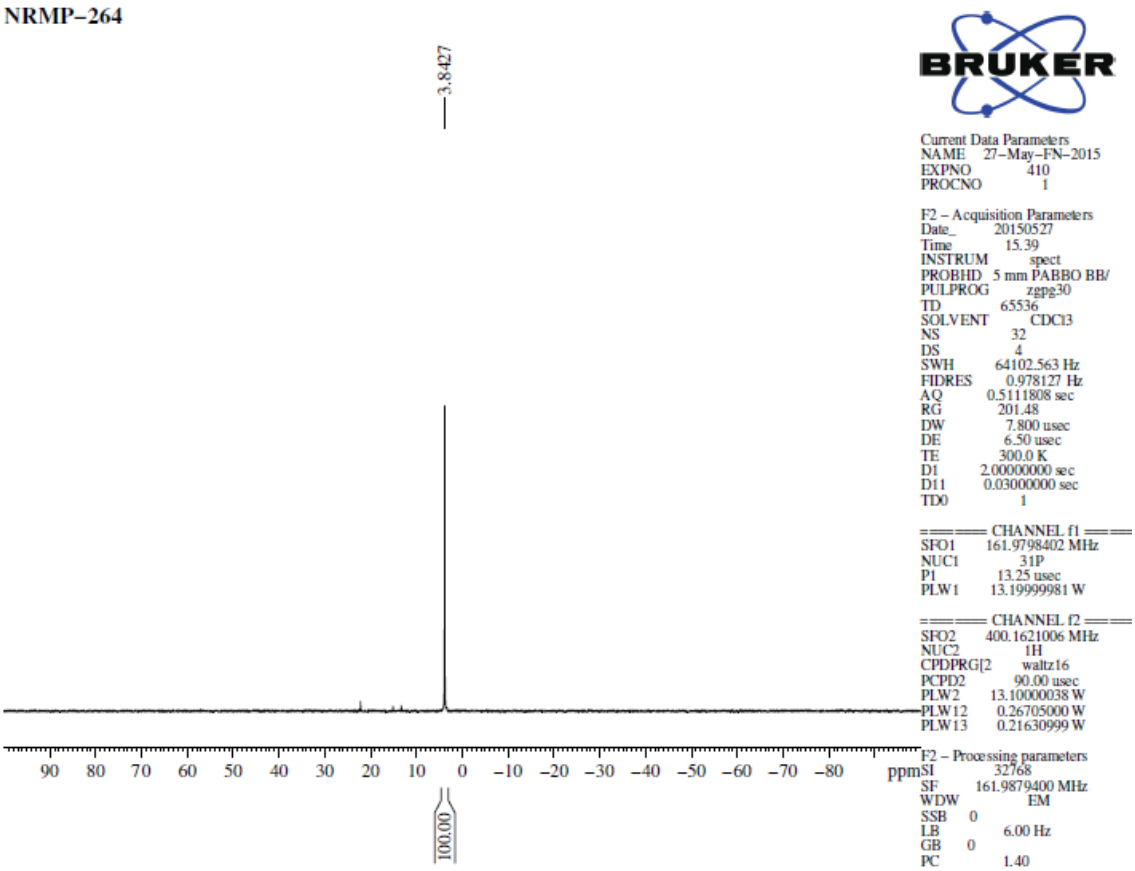

Figure 82: ^{31}P NMR spectrum of 9b

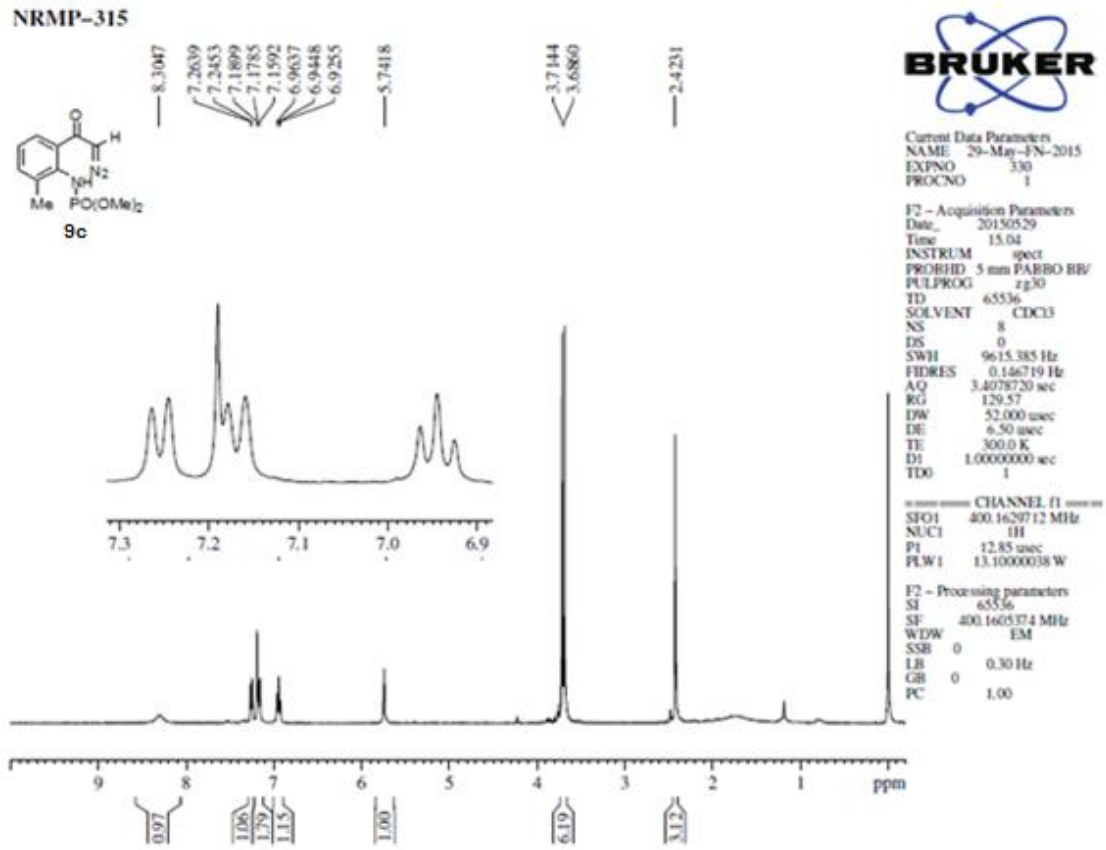

Figure 83: ^{1}H NMR spectrum of 9c

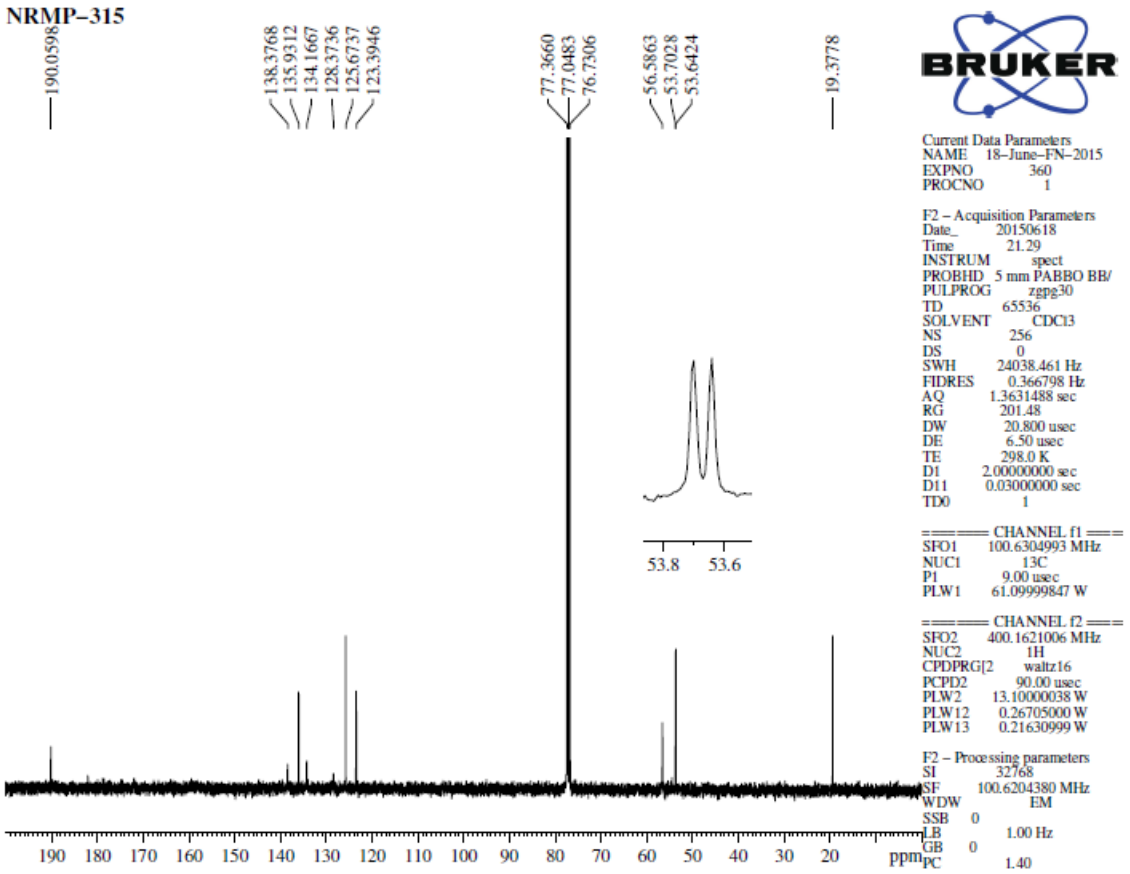

Figure 84: ^{13}C NMR spectrum of 9c

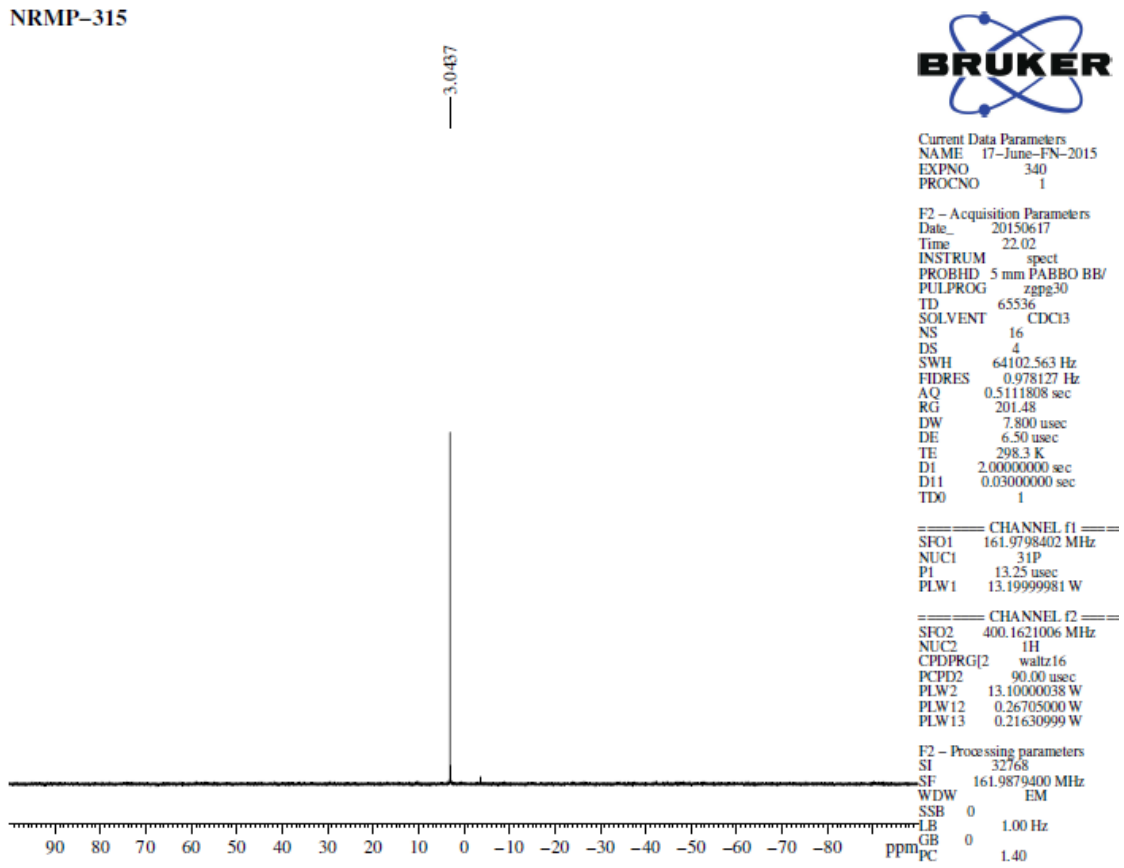

Figure 85: ^{31}P NMR spectrum of 9c

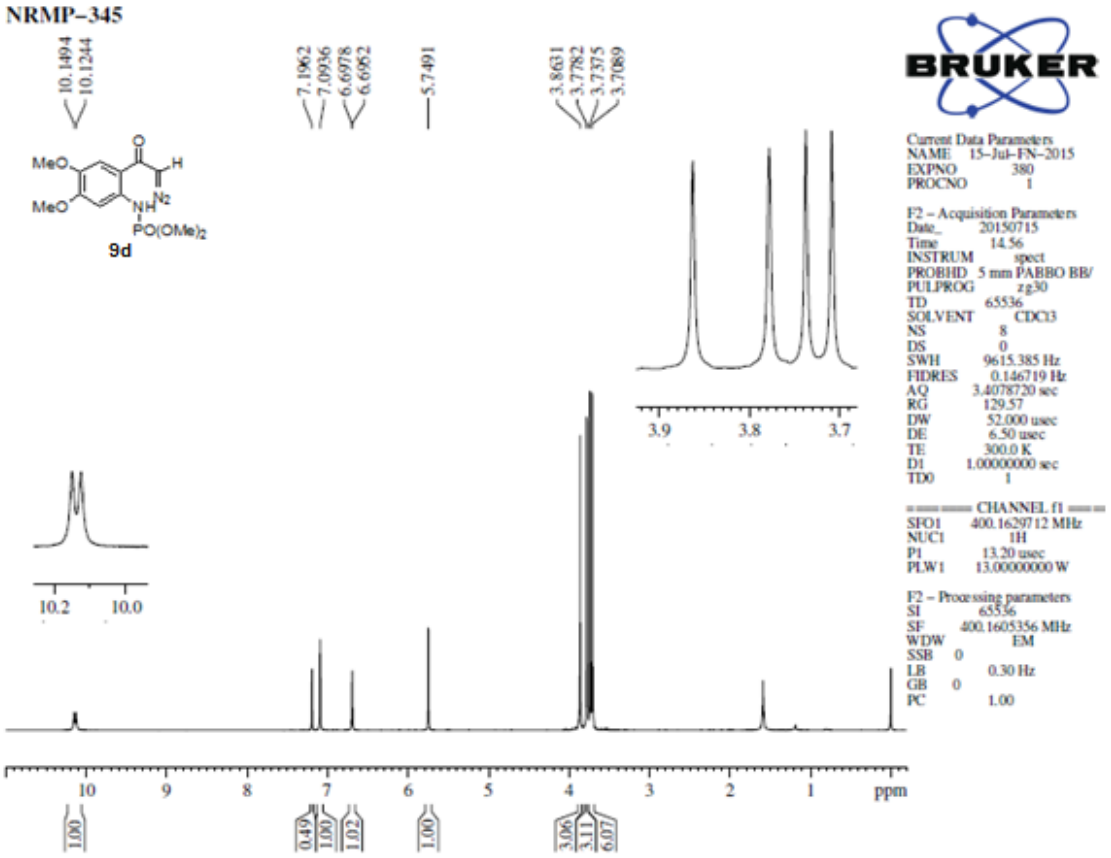

Figure 86: ^{1}H NMR spectrum of 9d

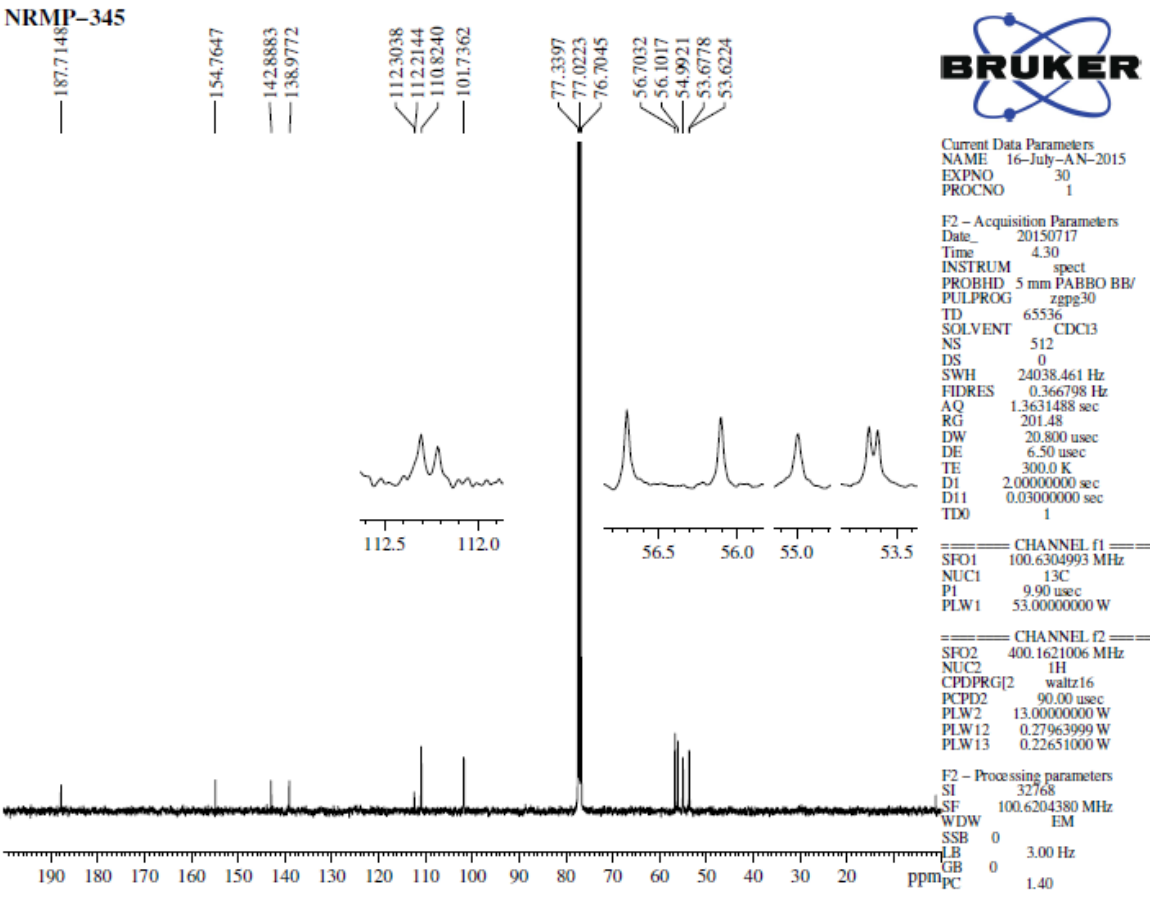

Figure 87: ^{13}C NMR spectrum of 9d

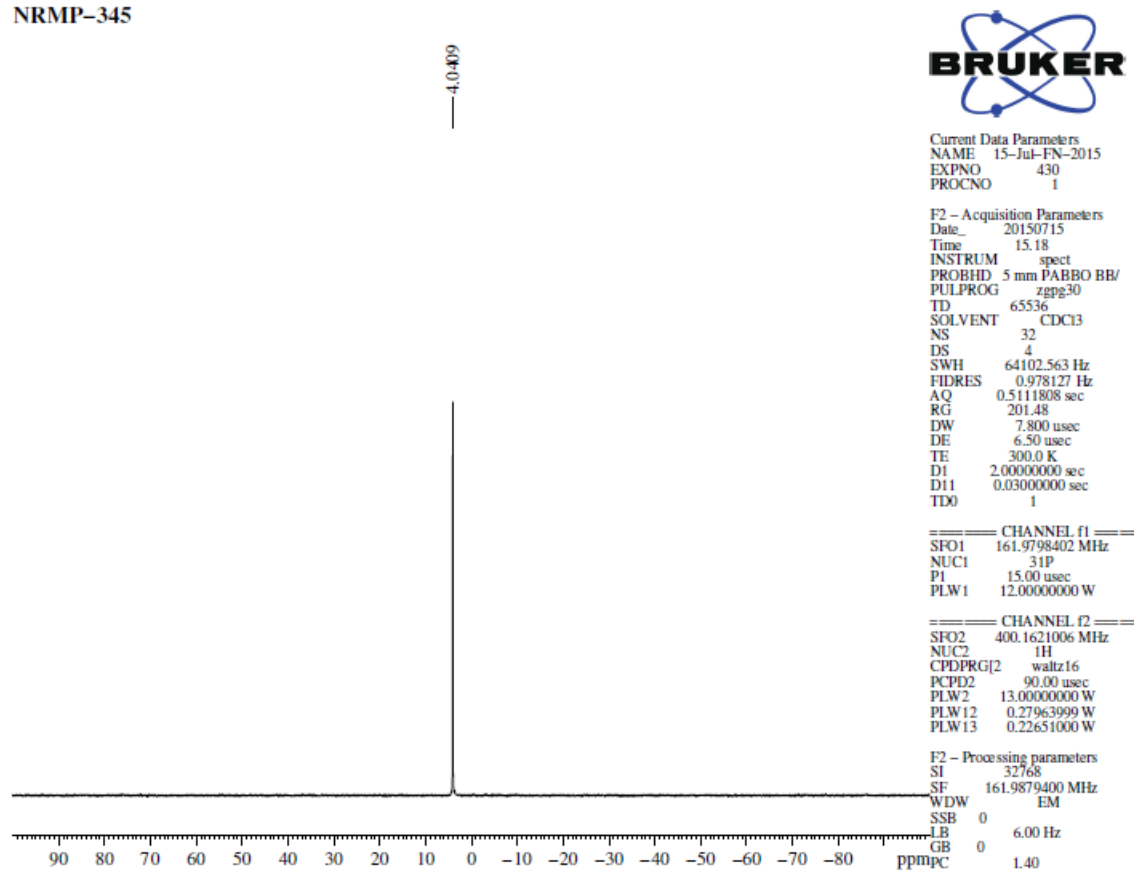

Figure 88: ^{31}P NMR spectrum of 9d

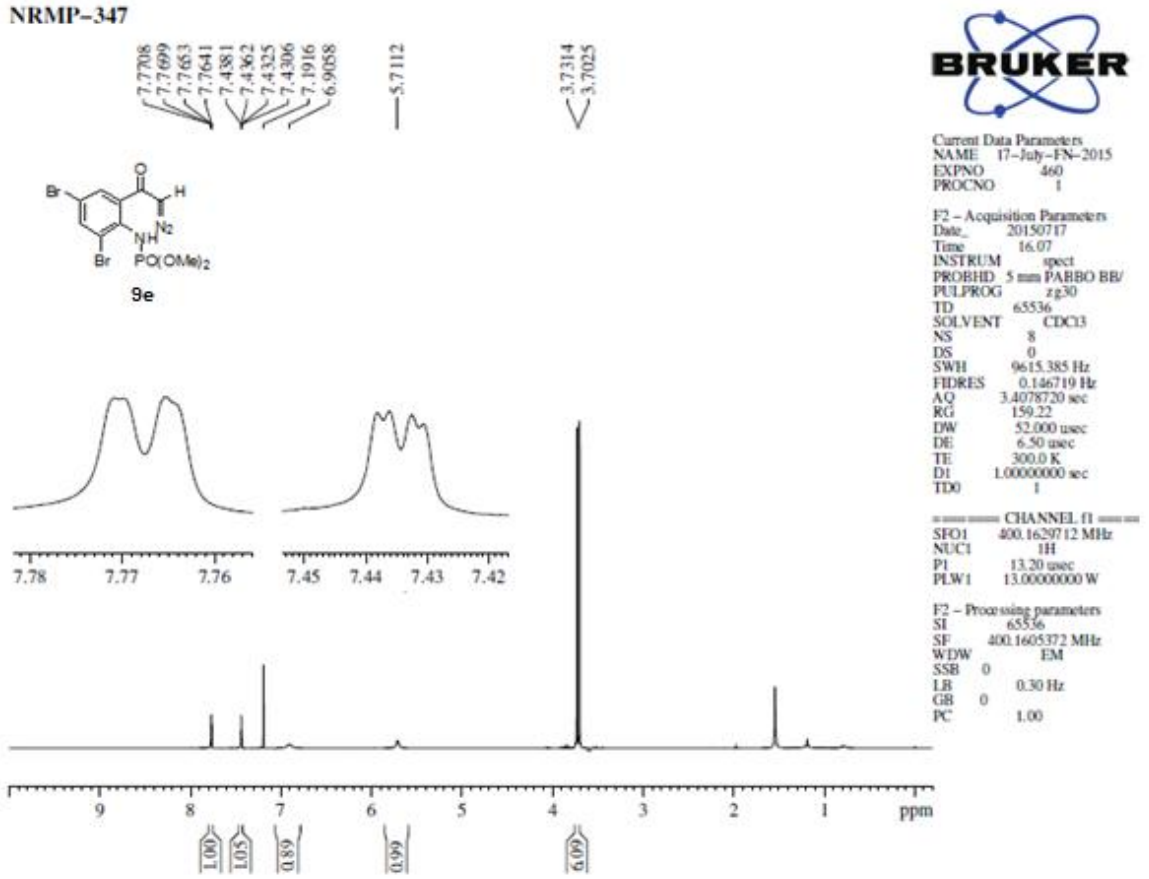

Figure 89: ^{1}H NMR spectrum of 9e

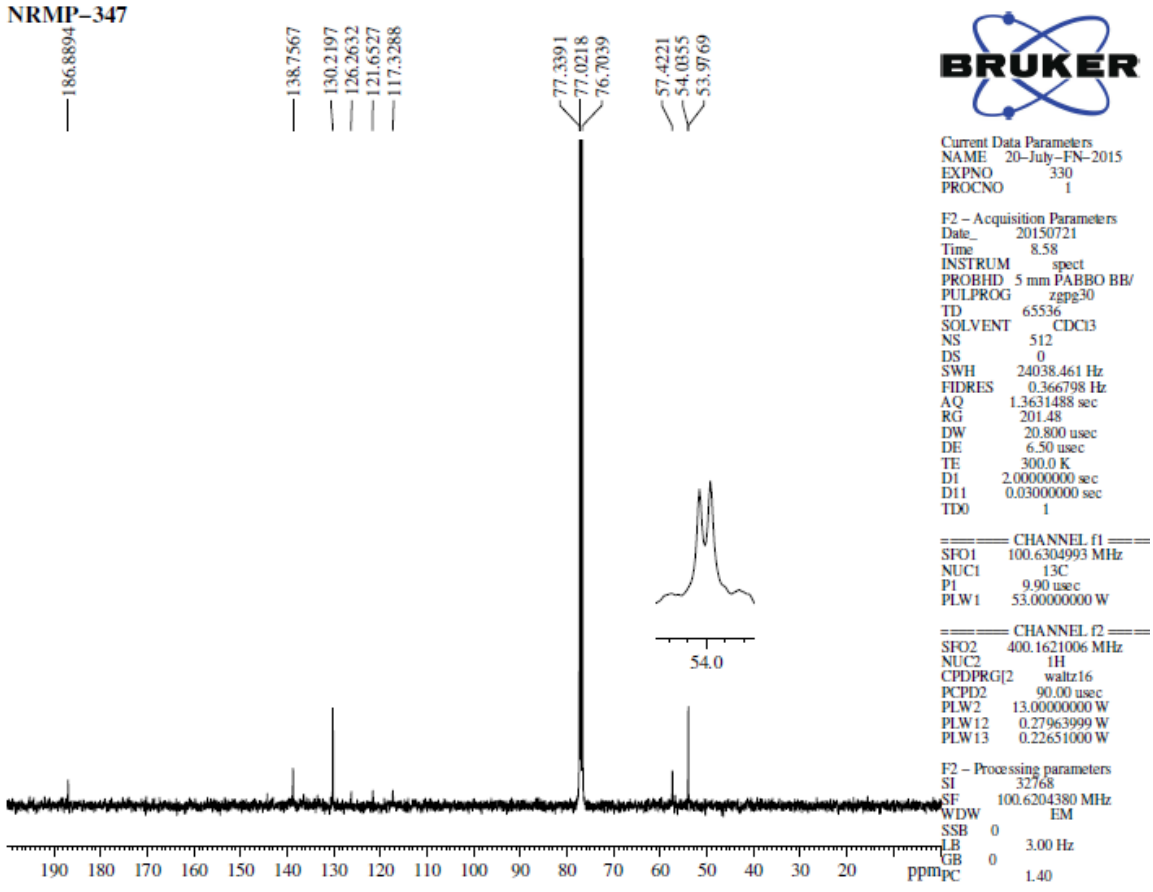

Figure 90: ^{13}C NMR spectrum of 9e

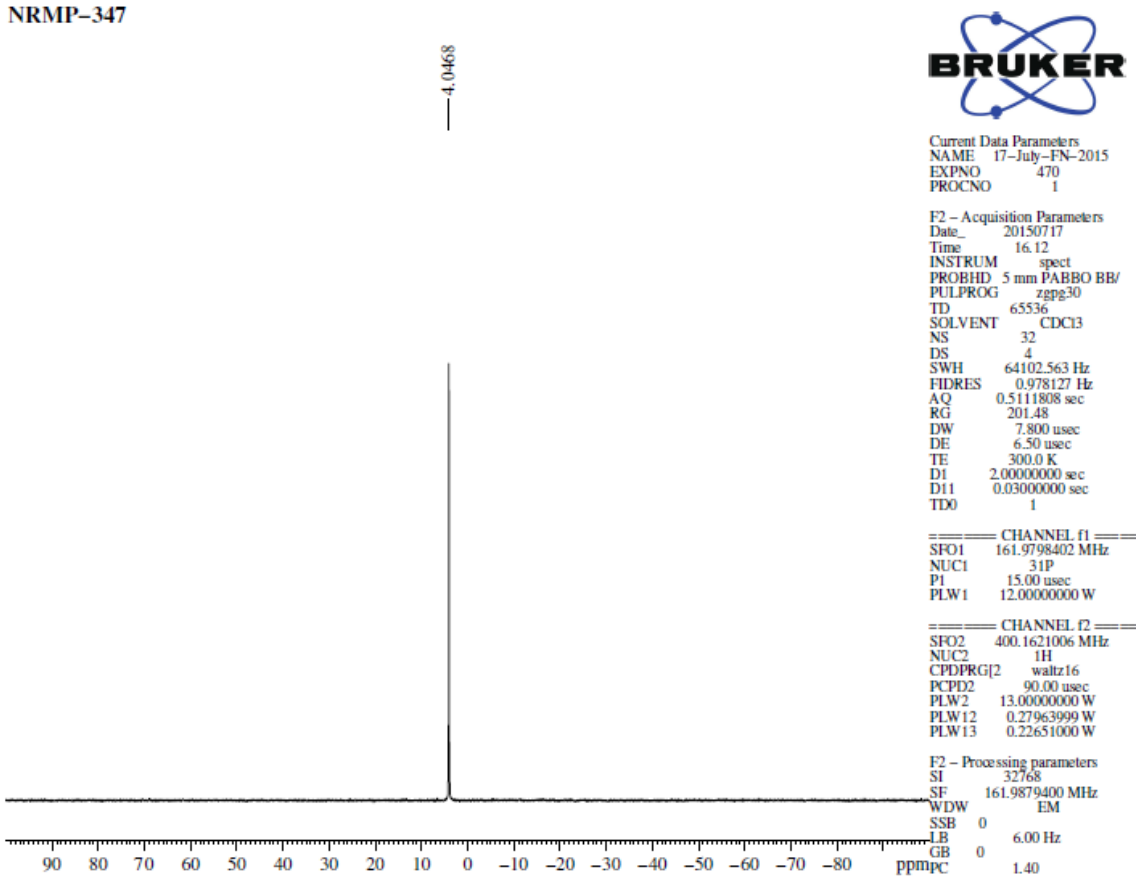

Figure 91: ^{31}P NMR spectrum of 9e

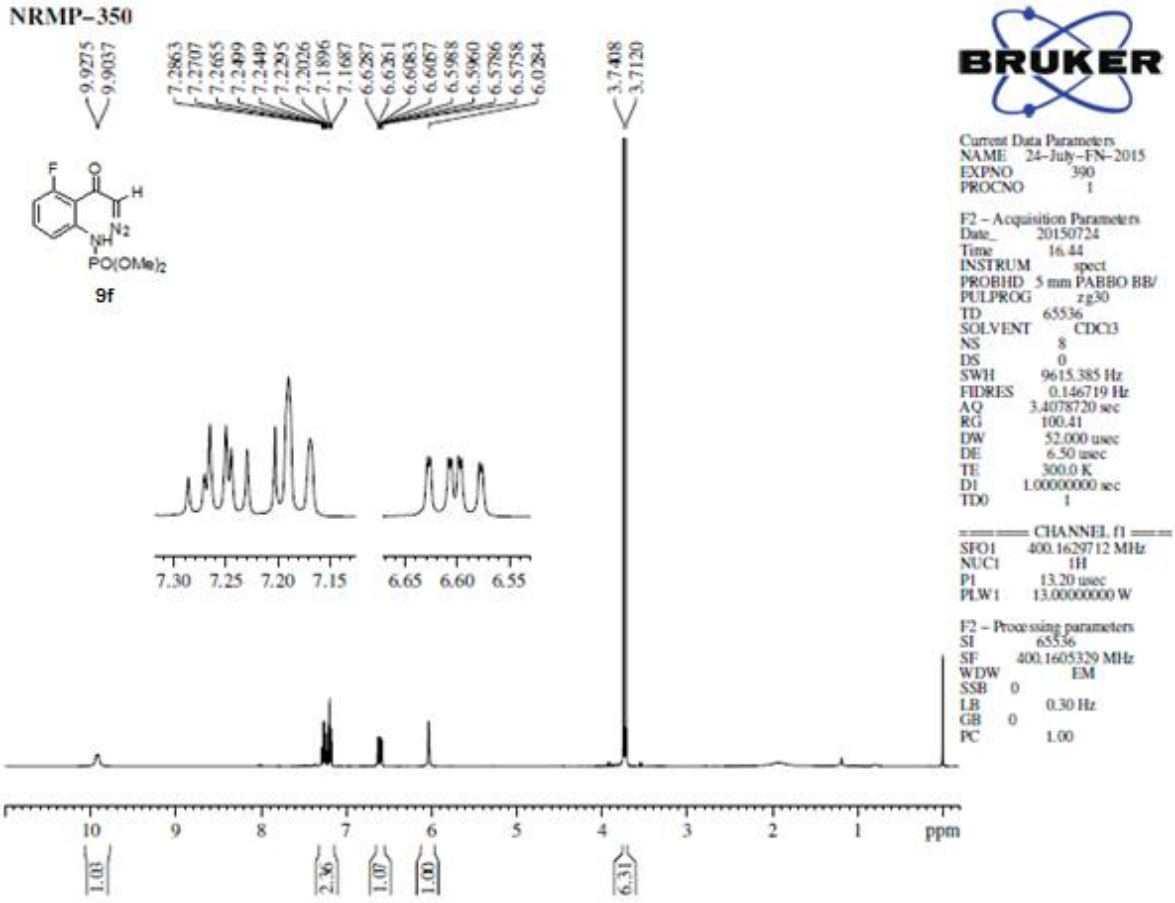

Figure 92: ^{1}H NMR spectrum of 9f

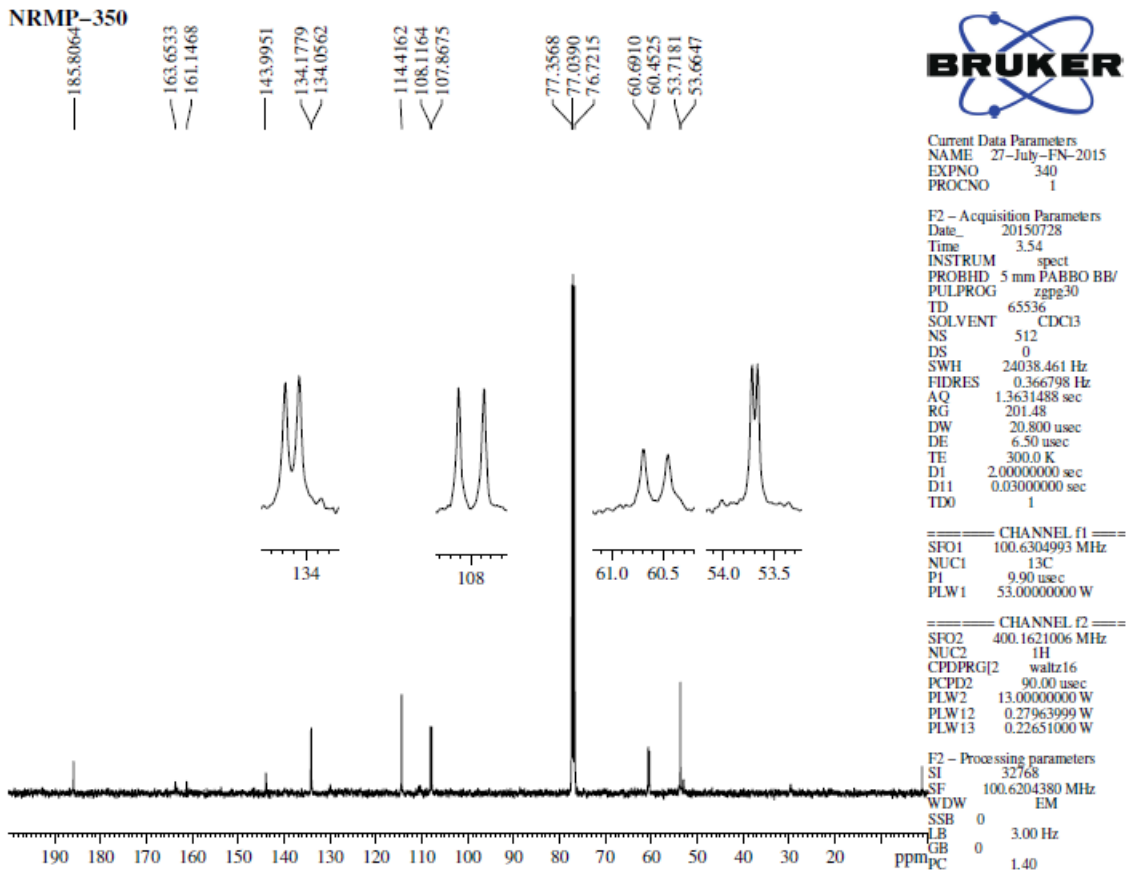

Figure 93: ^{13}C NMR spectrum of 9f

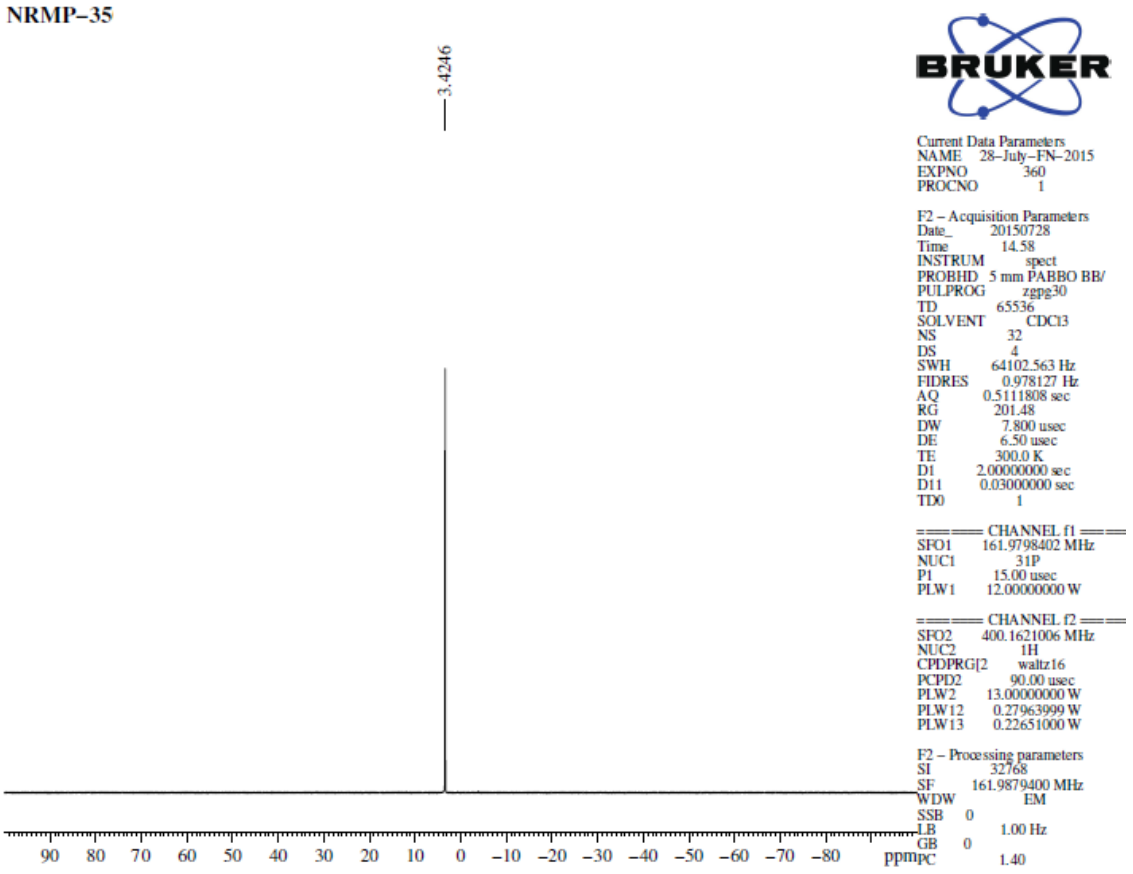

Figure 94: ^{31}P NMR spectrum of 9f

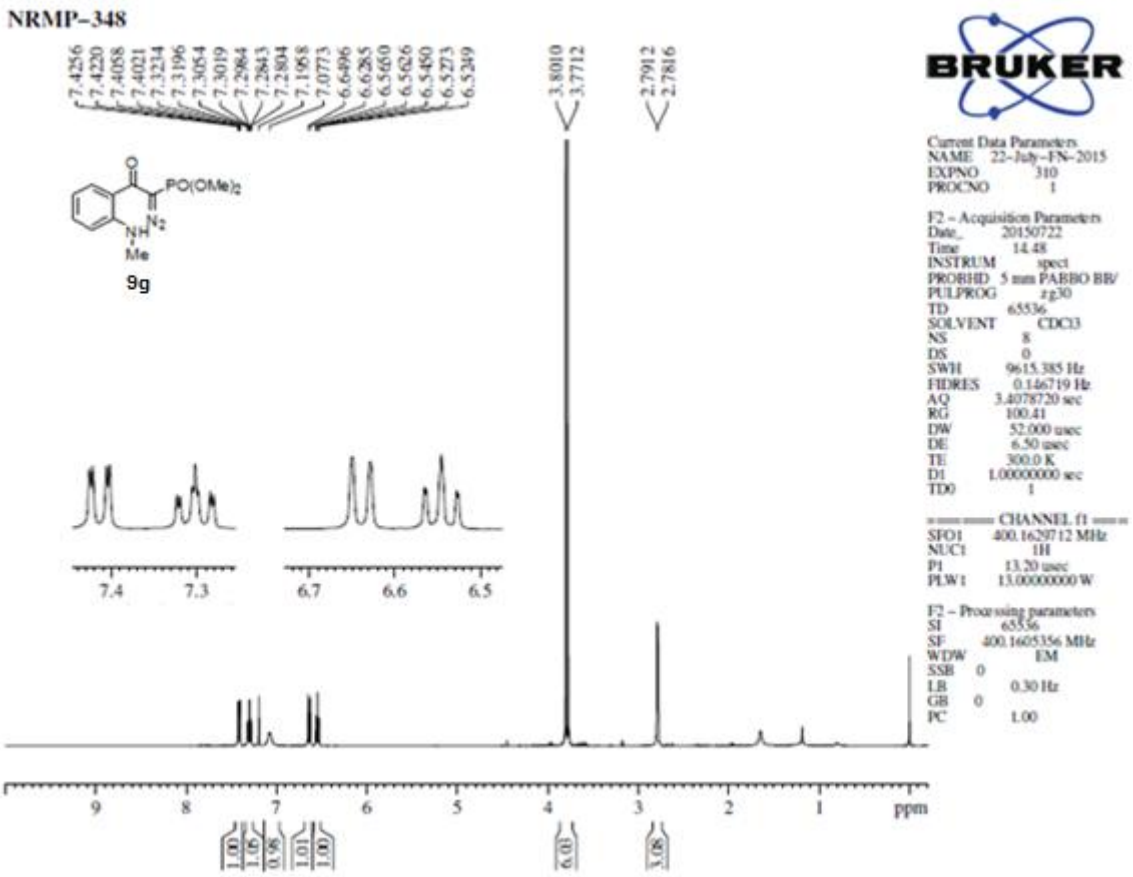

Figure 95: ^{1}H NMR spectrum of 9g

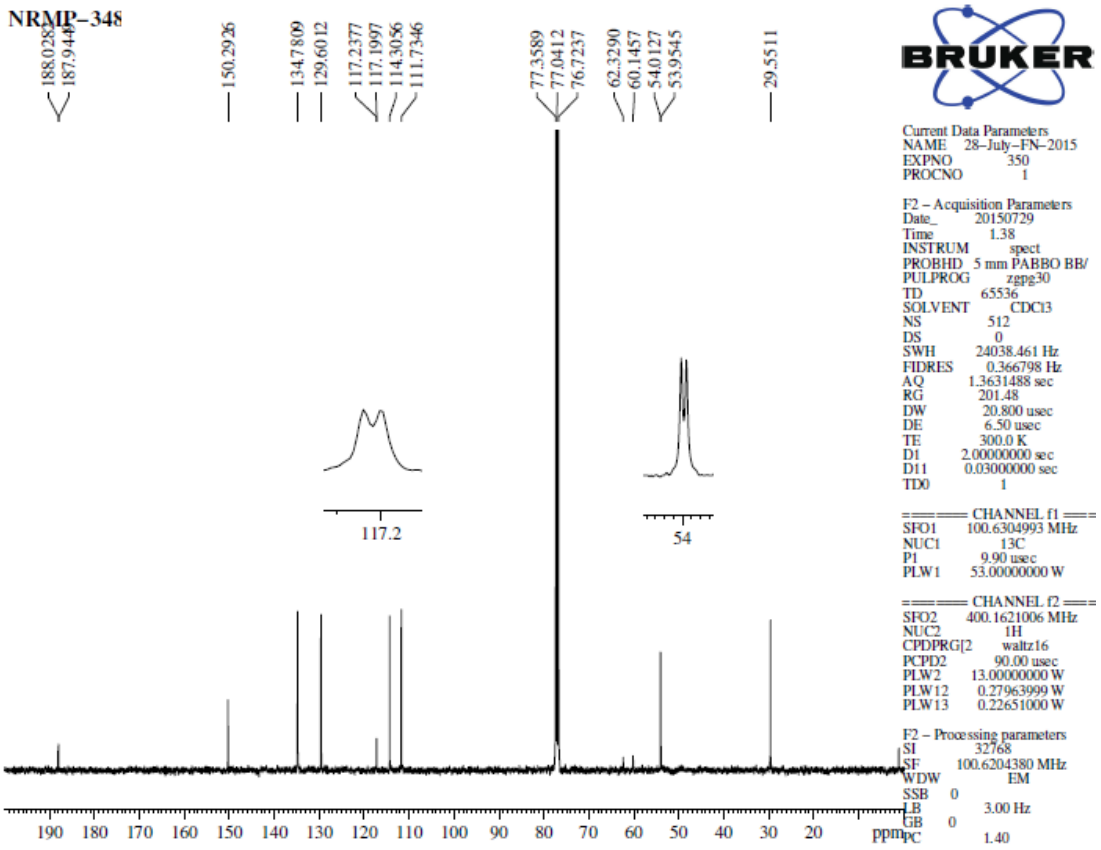

Figure 96: ^{13}C NMR spectrum of 9g

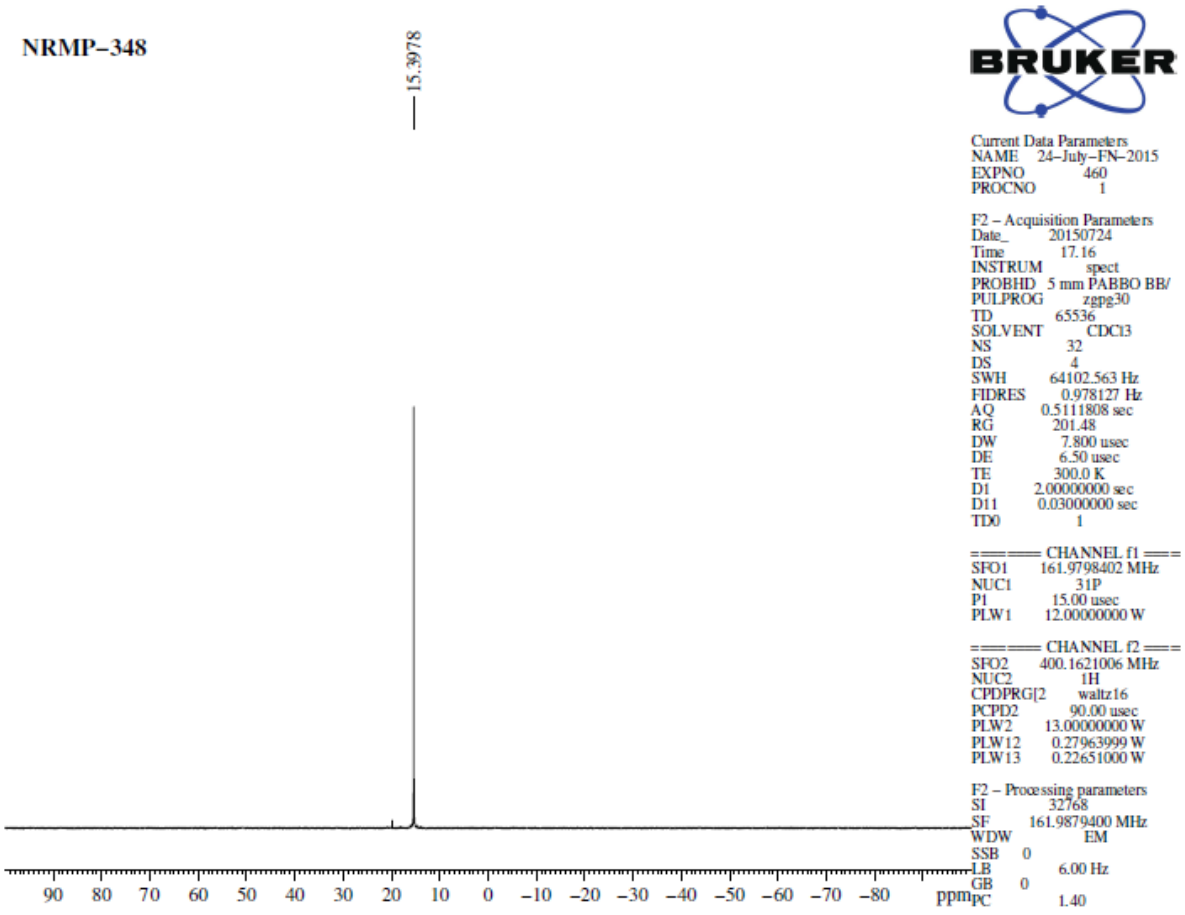

Figure 97: ^{31}P NMR spectrum of 9g