Supporting Information
For

Visible Light Catalyzed Mannich Reaction between *tert*-Amines and Silyl Diazoenolates

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1. General Information

All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. 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) and 100 MHz (^{13}C). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard. To describe spin multiplicity, standard abbreviations such as s, d, t, q, m, dd referring to singlet, doublet, triplet, quartet, multiplet and doublet of doublet respectively, are used. The ESI-HRMS spectra were recorded on Agilent 6520- Q-TofLC/MS system.

The 2-Aryl-1,2,3,4-tetrahydroisoquinolines **1** were synthesized following literature protocol as described below.[1] The ethyl 3-((tert-butyldimethylsilyl)oxy)-2-diazobut-3-enolate **2** was synthesized as reported earlier.[2] All other chemicals including catalysts and solvents were purchased from commercial sources and used as received except DCM used in the ylide formation reaction which was freshly dried by distillation over CaH_2. The data for 2-Aryl-1,2,3,4-tetrahydroisoquinolines **1a,b,d,g,i,o** was matched with their reported data[3] and the characterization data for remaining 1,2,3,4-tetrahydroisoquinolines has been reported here.

2. General Procedures

General Procedure for the Synthesis of 2-Aryl-1,2,3,4-Tetrahydroisoquinoline 1

CuI (19.0 mg, 0.1 mmol) and K_3PO_4 (424.0 mg, 2.0 mmol) were taken in a two-necked RB flask under nitrogen at room temperature. Subsequently isopropanol (2.0 mL), ethylene glycol (0.1 mL, 2.0 mmol), 1,2,3,4-tetrahydroisoquinoline (0.2 mL, 1.5 mmol) and aryl iodide (1.0 mmol) were added. The reaction mixture was heated at 90 ^{o}C for 24 h. After cooling the suspension to room temperature diethyl ether (5 mL) and water (5 mL) were added to the reaction mixture. The organic layer was extracted with diethyl ether (2 × 10 mL) and combined organic phases were washed with brine. The residue obtained after drying (Na_2SO_4) and solvent evaporation was purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

General Procedure for VLPC Mannich Reaction

In a 10 mL snap vial equipped with magnetic stirring bar, 2-aryl-1,2,3,4-tetrahydroisoquinoline **1** (0.5 mmol), ethyl 3-((tert-butyldimethylsilyl)oxy)-2-diazobut-3-enolate **2** (337.0 mg, 1.25 mmol) and photocatalyst Rose Bengal (2.5 mg, 0.5 mol%) were dissolved in methanol (2.0 mL) under open air condition. The vial was irradiated using 530

nm green LEDs with a cooling device maintaining a temperature around 25 °C. After 3-12h of irradiation (TLC monitoring), the solvent was evaporated and the crude mixture was subjected to column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the pure product **3**.

General Procedure for Rh-Carbenoid Mediated Ammonium Ylide Formation

To a stirred solution of ethyl 2-diazo-3-oxo-4-(2-aryl-1,2,3,4-tetrahydroisoquinolin-1-yl)butanoate **3** (0.05 mmol) in dry dichloromethane (1.0 mL) was added the catalyst $Rh_2(OAc)_4$ (0.2 mg, 1.0 mol%). The reaction mixture was stirred at room temperature under nitrogen atmosphere till consumption of the starting material (TLC monitoring). Dichloromethane was distilled off under reduced pressure and crude product was recrystallized with dichloromethane-hexane (1:3) to get the solid pure product **4**.

3. X-Ray Data Collection and Structure Refinement Details

A good quality single crystal of size 0.30 x 0.18 x 0.10 mm was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **4a** were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the monochromated Mo-Kα radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics.

Data collection was performed using ω-scans of 0.5^{o} steps at 293(2) K. Cell determination, data collection and data reduction was performed using the Rigaku CrystalClear-SM Expert 2.1 b24 software.[1] Structure solution and refinement were performed by using SHELX-97.[2] Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

In X-Ray structural analysis it was noticed that bond lengths of C11-C12 and C12-C13 are found 1.412(5) Å and 1.414(5) Å, respectively. These bond lengths deviate significantly from the generally accepted value which is 1.52Å, between carbon-carbon atoms with one carbon atom with 4 bonds and another with 3 bonds.[3] The reason of deviation of these bond lengths may be the delocalized electrons in the molecule. This can be substantiated by residual densities on C-C bonds in difference density map.

4. Crystallographic Data

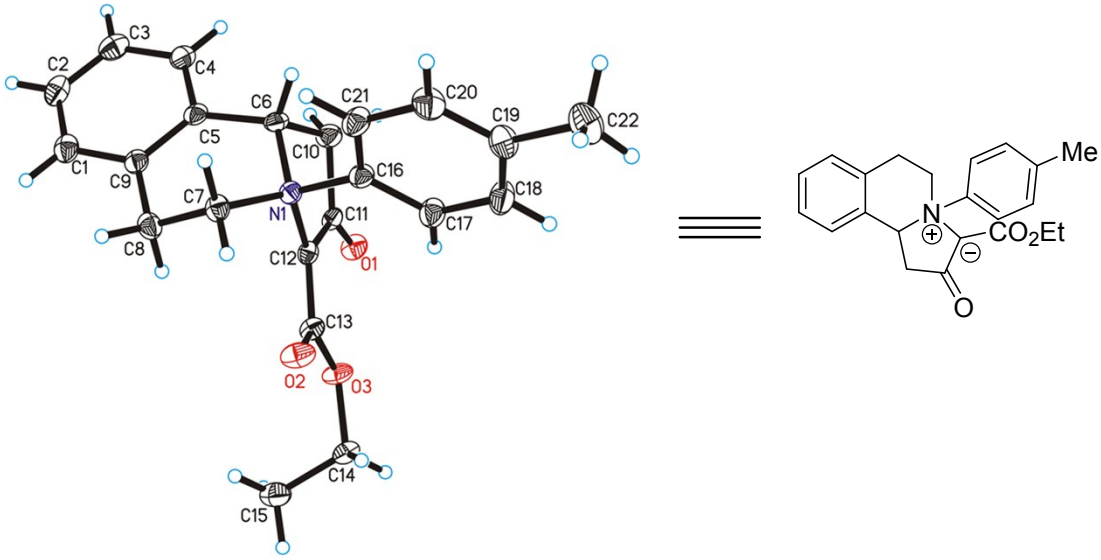

Figure 1. ORTEP diagram drawn with 20% ellipsoid probability for non-H atoms of the crystal structure of compound 4a determined at 293 K

Table 1 Crystal data and structure refinement details for **4a**

Compound	**4a**
Empirical formula	$C_{22}H_{23}NO_3$
Formula weight	349.41
Crystal System	Monoclinic
Space group	$P\,2_1/c$
a (Å)	14.557(8)
b (Å)	7.392(4)
c (Å)	18.717(8)
α (°)	90.00
β (°)	113.45(3)
γ (°)	90.00
V (Å^3)	1847.7(16)
Z	4
D_c (g/cm^3)	1.256
F_{000}	744
μ (mm^{-1})	0.083
θ_{max} (°)	25.33
Total reflections	9815
Unique reflections	3236
Reflections [$I > 2\sigma(I)$]	1507
Parameters	237
R_{int}	0.0881
Goodness-of-fit	0.961
R [$F^2 > 2\sigma(F^2)$]	0.0750
wR (F^2, all data)	0.2001
CCDC No.	1539489

5. Compound Characterization

2-(4-butylphenyl)-1,2,3,4-tetrahydroisoquinoline (1c)

Brown viscous liquid; isolated yield 71% (200 mg). R_f 0.50 (10% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 – 7.13 (m, 4H), 7.06 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 4.32 (s, 2H), 3.47 (t, J = 5.8 Hz, 2H), 2.93 (t, J = 5.7 Hz, 2H), 2.50 (t, J = 7.8 Hz, 2H), 1.50 – 1.57 (m, 2H), 1.26 – 1.35 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 134.8, 134.7, 133.5, 129.1, 128.6, 126.6, 126.3, 126.0, 115.6, 51.4, 47.1, 34.7, 33.9, 29.2, 22.4, 14.0; **HRMS** for $C_{19}H_{23}N$: calcd. (MH^+): 266.1903, found: 266.1903

2-(3,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (1e)

Brown solid; isolated yield 57% (135 mg). R_f 0.50 (10% EtOAc/hexane); Mp 69-72 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 – 7.10 (m, 4H), 6.98 (d, J = 8.2 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 6.69 (dd, J = 8.2 Hz, 2.6 Hz, 1H), 4.28 (s, 2H), 3.43 (t, J = 5.8 Hz, 2H), 2.92 (t, J = 5.8 Hz, 2H), 2.19 (s, 3H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 137.2, 134.8, 134.7, 130.2, 128.6, 127.2, 126.5, 126.2, 125.9, 117.5, 113.3, 51.6, 47.3, 29.2, 20.3, 18.7; **HRMS** for $C_{17}H_{19}N$: calcd. (MH^+): 238.1590, found: 238.1594

2-(3-bromo-4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1f)

Colorless solid; isolated yield 63% (201 mg). R_f 0.50 (15% EtOAc/hexane); Mp 72-73 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, J = 2.8 Hz, 1H), 7.06 – 7.12 (m, 4H), 6.84 (dd, J = 8.9 Hz, 2.7 Hz, 1H), 6.79 (d, J = 8.9 Hz, 1H), 4.23 (s, 2H), 3.77 (s, 3H), 3.38 (t, J = 5.8 Hz, 2H), 2.91 (t, J = 5.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5, 146.1, 134.5, 134.2, 128.6, 126.5, 126.4, 126.1, 121.3, 116.1, 113.2, 112.4, 56.9, 51.9, 47.8, 29.1; **HRMS** for $C_{16}H_{16}BrNO$: calcd. (MH^+): 318.0488, found: 318.0478

2-(3-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (1h)

Yellow solid; isolated yield 48% (151 mg). R_f 0.50 (30% EtOAc/hexane); Mp 71-73 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (t, J = 2.3 Hz, 1H), 7.52 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.31 (t, J = 8.2 Hz, 1H), 7.11 – 7.17 (m, 5H),4.41 (s, 2H), 3.56 (t, J = 5.9 Hz, 2H), 2.94 (t, J = 5.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 149.4, 134.7, 133.5, 129.7, 128.4, 126.8, 126.6, 126.4, 119.5, 112.2, 108.0, 49.7, 45.6, 29.0; **HRMS** for $C_{15}H_{14}N_2O_2$: calcd. (MH^+): 255.1128, found: 255.1126

6,7-dimethoxy-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (1j)

Yellow solid; isolated yield 60% (180 mg). R_f 0.50 (25% EtOAc/hexane); Mp 85-88 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.55, 6.56 (two s merged, 2H), 4.20 (s, 2H), 3.79, 3.78 (two s merged, 6H), 3.42 (t, J = 5.8 Hz, 2H), 2.81 (t, J = 5.7 Hz, 2H), 2.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.7, 147.6, 147.5, 129.7, 128.5, 126.6, 126.4, 116.0, 111.5, 109.4, 56.0, 55.9, 51.2, 47.5, 28.5, 20.4; **HRMS** for $C_{18}H_{21}NO_2$: calcd. (MH^+): 284.1645, found: 284.1651

2-(4-butylphenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (1k)

Brown solid; isolated yield 49% (158 mg). R_f 0.50 (25% EtOAc/hexane); Mp 81-84 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.03 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 6.57 (br s, 2H), 4.22 (s, 2H), 3.80, 3.79 (two s merged, 6H), 3.43 (t, J = 5.6 Hz, 2H), 2.82 (t, J = 5.2 Hz, 2H), 2.47 (t, J = 7.7 Hz, 2H), 1.47 – 1.53 (m, 2H), 1.23 – 1.30 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 147.6, 147.5, 133.5, 129.1, 126.7, 126.4, 115.8, 111.5, 109.5, 56.0, 55.9, 51.1, 47.3, 34.7, 33.9, 28.6, 22.4, 14.0; **HRMS** for $C_{21}H_{27}NO_2$: calcd. (MH^+): 326.2115, found: 326.2108

6,7-dimethoxy-2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1l)

Brown solid; isolated yield 78% (232 mg). R_f 0.50 (30% EtOAc/hexane); Mp 72-74 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (t, J = 8.2 Hz, 1H), 6.57 (d, J = 2.1 Hz, 2H), 6.52 (dd, J = 8.2 Hz, 2.1 Hz, 1H), 6.44 (t, J = 2.3 Hz, 1H), 6.31 (dd, J = 8.0 Hz, 2.2 Hz, 1H), 4.25 (s, 2H), 3.79, 3.78 (two s merged, 6H), 3.76 (s, 3H), 3.46 (t, J = 5.8 Hz, 2H), 2.81 (t, J = 5.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 151.9, 147.6, 147.5, 129.8, 126.7, 126.2, 111.4, 109.5, 108.1, 103.4, 101.7, 56.0, 55.9, 55.2, 50.4, 46.6, 28.5; **HRMS** for $C_{18}H_{21}NO_3$: calcd. (MH^+): 300.1594, found: 300.1594

6,7-dimethoxy-2-(3-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (1m)

Yellow solid; isolated yield 48% (151 mg). R_f 0.50 (30% EtOAc/hexane); Mp 71-74 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (t, J = 2.2 Hz, 1H), 7.53 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.31 (t, J = 8.2 Hz, 1H), 7.13 (dd, J = 8.2 Hz, 2.2 Hz, 1H), 6.61 (d, J = 8.0 Hz, 2H), 4.35 (s, 2H), 3.81, 3.82 (two s merged, 6H), 3.56 (t, J = 5.8 Hz, 2H), 2.86 (t, J = 5.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 149.4, 147.9, 147.8, 129.7, 126.5, 125.2, 119.7, 112.4, 111.3, 109.4, 108.2, 56.0, 55.9, 49.6, 45.8, 28.4; **HRMS** for $C_{17}H_{18}N_2O_4$: calcd. (MH^+): 315.1339, found: 315.1340

7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline (1n)

Brown viscous liquid; isolated yield 49% (141 mg). R_f 0.50 (5% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.23 (m, 4H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 4.29 (s, 2H), 3.48 (t, *J* = 5.5 Hz, 2H), 2.84 (t, *J* = 5.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.2, 136.7, 133.8, 130.3, 129.4, 129.3, 129.2, 119.5, 119.1, 115.4, 50.5, 46.6, 28.4; **HRMS** for $C_{15}H_{14}BrN$: calcd. (MH^+): 288.0382, found: 288.0379

Ethyl 2-diazo-3-oxo-4-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)butanoate (3a)

Yellow viscous liquid; isolated yield 78% (141 mg). R_f 0.50 (5% EtOAc/hexane); **IR** (Film, cm^{-1}): 1385, 1619; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 7.17 (m, 3H), 7.02 – 7.08 (m, 3H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 5.46 (t, *J* = 6.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.57 (dd, *J* = 7.6 Hz, 4.8 Hz, 2H), 3.52 (dd, *J* = 15.6 Hz, 7.2 Hz, 1H), 3.19 (dd, *J* = 15.6 Hz, 6.2 Hz, 1H), 2.95 – 3.02 (m, 1H), 2.78 (dt, *J* = 16.2 Hz, 4.7 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.9, 161.1, 149.0, 138.0, 134.8, 129.2, 128.7, 127.0, 126.8, 126.1, 118.1, 114.7, 61.4, 55.7, 46.0, 41.5, 27.0, 14.3; **HRMS** for $C_{21}H_{21}N_3O_3$: calcd. (MH^+): 364.1656, found: 364.1658

Ethyl 2-diazo-3-oxo-4-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)butanoate (3b)

Yellow viscous liquid; isolated yield 65% (122 mg). R_f 0.50 (5% EtOAc/hexane);**IR** (Film, cm^{-1}): 1387, 1647, 1717, 2135; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.16 (m, 1H), 7.01 – 7.08 (m, 3H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.42 (t, *J* = 6.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.50 – 3.56 (m, 3H), 3.14 (dd, *J* = 15.4 Hz, 5.9 Hz, 1H), 2.94 – 3.02 (m, 1H), 2.73 (dt, *J* = 16.2 Hz, 4.3 Hz, 1H), 2.16 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.9, 161.2, 147.0, 138.0, 134.8, 129.7, 128.8, 127.7, 127.0, 126.7, 126.0, 115.6, 61.3, 56.2, 45.9, 41.6, 26.8, 20.3, 14.3; **HRMS** for $C_{22}H_{23}N_3O_3$: calcd. (MH^+): 378.1812, found: 378.1814

Ethyl 4-(2-(4-butylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazo-3-oxobutanoate (3c)

Yellow viscous liquid; isolated yield 69% (144 mg). R_f 0.50 (5% EtOAc/hexane); **IR** (Film, cm^{-1}): 1647, 1715, 2135; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.15 (m, 1H), 7.01 – 7.07 (m, 3H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.43 (t, *J* = 6.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.51 – 3.57 (m, 3H), 3.12 (dd, *J* = 15.4 Hz, 5.8 Hz, 1H), 2.94 – 3.02 (m, 1H), 2.74 (dt, *J* = 16.2 Hz, 4.2 Hz, 1H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.42 – 1.50 (m, 2H), 1.18 – 1.28 (m, 5H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.0, 161.2, 147.1, 138.1,

134.8, 132.8, 129.0, 128.8, 127.0, 126.7, 126.0, 115.4, 61.3, 56.3, 45.9, 41.5, 34.6, 33.9, 26.9, 22.4, 14.3, 14.0; **HRMS** for $C_{25}H_{29}N_3O_3$: calcd. (MH^+): 420.2282, found: 420.2279

Ethyl 2-diazo-4-(2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxobutanoate (3d)

Brown viscous liquid; isolated yield 61% (119 mg). R_f 0.50 (10% EtOAc/hexane); **IR** (Film, cm^{-1}): 1046, 1645, 1713, 2139; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.15 (m, 1H), 7.04 – 7.09 (m, 4H), 6.49 (dd, *J* = 8.3 Hz, 2.3 Hz, 1H), 6.44 (t, *J* = 2.3 Hz, 1H), 6.24 (dd, *J* = 8.1 Hz, 2.2 Hz, 1H), 5.45 (t, *J* = 6.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 3.49 – 3.57 (m, 3H), 3.20 (dd, *J* = 15.6 Hz, 6.3 Hz, 1H), 2.96– 3.03 (m, 1H), 2.79 (dt, *J* = 11.3 Hz, 4.8 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.8, 161.1, 160.8, 150.4, 137.9, 134.8, 129.9, 128.6, 127.0, 126.8, 126.1, 107.4, 103.0, 100.9, 61.4, 55.8, 55.1, 46.0, 41.7, 27.0, 14.3; **HRMS** for $C_{22}H_{23}N_3O_4$: calcd. (MH^+): 394.1761, found: 394.1761

Ethyl 2-diazo-4-(2-(3,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxobutanoate (3e)

Brown viscous liquid; isolated yield 67% (130 mg). R_f 0.50 (5% EtOAc/hexane); **IR** (Film, cm^{-1}): 1646, 1713, 2141; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.16 (m, 1H), 7.01 – 7.07 (m, 3H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 2.3 Hz, 1H), 6.62 (dd, *J* = 8.3 Hz, 2.6 Hz, 1H), 5.41 (t, *J* = 6.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.56 (m, 3H), 3.13 (dd, *J* = 15.3 Hz, 5.8 Hz, 1H), 2.93 – 3.01 (m, 1H), 2.72 (dt, *J* = 16.2 Hz, 4.1 Hz, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.9, 161.2, 147.4, 138.1, 137.1, 134.8, 130.2, 128.8, 127.0, 126.7, 126.5, 125.9, 117.2, 113.1, 61.3, 56.3, 45.9, 41.5, 26.9, 20.3, 18.6, 14.3; **HRMS** for $C_{23}H_{25}N_3O_3$: calcd. (MH^+): 392.1969, found: 392.1976

Ethyl 4-(2-(3-bromo-4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazo-3-oxobutanoate (3f)

Brown solid; isolated yield 54% (127 mg). R_f 0.50 (15% EtOAc/hexane); Mp 70-72 ^{o}C; **IR** (KBr, cm^{-1}): 757, 1052, 1646, 1713, 2139; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.15 (m, 1H), 7.03 – 7.09 (m, 4H), 6.81 (dd, *J* = 9.0 Hz, 2.8 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 1H), 5.32 (t, *J* = 7.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.47 – 3.57 (m, 3H), 3.07 (dd, *J* = 15.5 Hz, 5.4 Hz, 1H), 2.91 – 2.99 (m, 1H), 2.71 (dt, *J* = 16.4 Hz, 3.8 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.7, 161.2, 149.1, 144.6, 137.6, 134.4, 128.9, 127.0, 126.8, 126.1, 121.2, 116.4, 113.3, 112.3, 61.5, 56.9, 56.6, 45.8, 41.9, 26.6, 14.3; **HRMS** for $C_{22}H_{22}BrN_3O_4$: calcd. (MH^+): 472.0866, found: 472.0862

Ethyl 4-(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazo-3-oxobutanoate (3g)

Colorless solid; isolated yield 82% (162 mg). R_f 0.50 (5% EtOAc/hexane); Mp 98-100 ^oC; **IR** (KBr, cm^{-1}): 757, 1385, 1645, 1713, 2141; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 – 7.13 (m, 1H), 7.02 – 7.08 (m, 5H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.39 (t, *J* = 6.7 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.46 – 3.54 (m, 3H), 3.17 (dd, *J* = 15.7 Hz, 6.2 Hz, 1H), 2.91 – 2.99 (m, 1H), 2.77 (dt, *J* = 16.2 Hz, 4.8 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.7, 161.0, 147.6, 137.6, 134.5, 129.0, 128.7, 126.9, 126.1, 122.7, 115.8, 76.6, 61.4, 55.7, 45.8, 41.7, 26.8, 14.3; **HRMS** for $C_{21}H_{20}ClN_3O_3$: calcd. (MH^+): 398.1266, found: 398.1266

Ethyl 2-diazo-4-(2-(3-nitrophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxobutanoate (3h)

Yellow viscous liquid; isolated yield 55% (112 mg). R_f 0.50 (15% EtOAc/hexane); **IR** (Film, cm^{-1}): 1311, 1645, 1712, 2142; **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.66 (t, *J* = 2.2 Hz, 1H), 7.47 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H), 7.27 (t, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 2.8 Hz, 2H), 7.07 – 7.12 (m, 3H), 5.51 (t, *J* = 6.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.63 – 3.66 (m, 2H), 3.51 (dd, *J* = 15.8 Hz, 7.5 Hz, 1H), 3.28 (dd, *J* = 15.7 Hz, 6.2 Hz, 1H), 2.99 – 3.07 (m, 1H), 2.88 (dt, *J* = 16.2 Hz, 5.1 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.3, 161.2, 149.5, 137.1, 134.4, 129.9, 128.7, 127.2, 127.0, 126.4, 119.3, 112.0, 107.8, 61.6, 55.5, 46.0, 41.7, 26.7, 14.3; **HRMS** for $C_{21}H_{20}N_4O_5$: calcd. (MH^+): 409.1506, found: 409.1509

Ethyl 2-diazo-4-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxobutanoate (3i)

Yellow viscous liquid; isolated yield 52% (100 mg). R_f 0.50 (25% EtOAc/hexane); **IR** (Film, cm^{-1}): 1066, 1645; **^{1}H NMR** (400 MHz, $CDCl_3$) δ.12 – 7.18 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.65 - 6.69 (m, 2H), 6.52 (s, 1H), 5.37 (t, *J* = 6.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.50 – 3.62 (m, 3H), 3.15 (dd, *J* = 15.5 Hz, 6.0 Hz, 1H), 2.87 – 2.95 (m, 1H), 2.65 (dt, *J* = 16.0 Hz, 4.3 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.2, 161.1, 149.2, 147.9, 147.3, 129.9, 129.2, 126.8, 118.2, 115.1, 111.4, 110.0, 61.4, 56.1, 55.9, 55.7, 45.8, 41.4, 26.4, 14.3; **HRMS** for $C_{23}H_{25}N_3O_5$: calcd. (MH^+): 424.1867, found: 424.1860

Ethyl 2-diazo-4-(6,7-dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxobutanoate (3j)

Yellow viscous liquid; isolated yield 59% (129 mg). R_f 0.50 (25% EtOAc/hexane); **IR** (Film, cm^{-1}): 1065, 1646, 1714, 2135; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.67 (s, 1H), 6.50 (s, 1H), 5.31 (t, *J* = 7.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.49 – 3.57 (m, 3H), 3.10 (dd, *J* = 15.4 Hz, 5.6 Hz, 1H), 2.86 – 2.94 (m, 1H), 2.60 (dt, *J* = 16.0 Hz, 3.8 Hz, 1H), 2.15 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.2, 161.1, 147.8, 147.3, 147.2, 129.9, 129.6, 127.9, 126.7, 116.0, 111.4, 110.0, 61.3, 56.2, 56.0, 55.9, 45.7, 41.5, 26.2, 20.3, 14.3; **HRMS** for $C_{24}H_{27}N_3O_5$: calcd. (MH^+): 438.2023, found: 438.2024

Ethyl 4-(2-(4-(tert-butyl)phenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazo-3-oxobutanoate (3k)

Yellow viscous liquid; isolated yield 55% (131 mg). R_f 0.50 (25% EtOAc/hexane); **IR** (Film, cm^{-1}): 1070, 1644, 1714, 2140; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.66 (s, 1H), 6.51 (s, 1H), 5.33 (dd, *J* = 7.3 Hz, 6.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.50 – 3.59 (m, 3H), 3.08 (dd, *J* = 15.3 Hz, 5.6 Hz, 1H), 2.86 – 2.94 (m, 1H), 2.61 (dt, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.42 (t, *J* = 7.8 Hz, 2H), 1.42 – 1.50 (m, 1H), 1.18 – 1.28 (m, 5H), 0.83 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.2, 161.1, 147.8, 147.3, 147.2, 133.0, 130.0, 129.0, 126.8, 115.7, 111.4, 110.0, 61.3, 56.2, 56.0, 55.9, 45.7, 41.4, 34.6, 33.8, 26.3, 22.4, 14.3, 14.0; **HRMS** for $C_{27}H_{33}N_3O_5$: calcd. (MH^+): 480.2493, found: 480.2487

Ethyl 2-diazo-4-(6,7-dimethoxy-2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxobutanoate (3l)

Yellow viscous liquid; isolated yield 58% (131 mg). R_f 0.50 (30% EtOAc/hexane); **IR** (Film, cm^{-1}): 1040, 1115, 1607, 1713, 2141; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.04 (t, *J* = 8.2 Hz, 1H), 6.66 (s, 1H), 6.52 (s, 1H), 6.48 (d, *J* = 8.3 Hz, 1H), 6.43 (s, 1H), 6.24 (dd, *J* = 8.1 Hz, 1.4 Hz, 1H), 5.35 (t, *J* = 6.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 6H), 3.70 (s, 3H), 3.52 – 3.56 (m, 3H), 3.16 (dd, *J* = 15.5 Hz, 6.0 Hz, 1H), 2.88 – 2.95 (m, 1H), 2.65 (dt, *J* = 16.0 Hz, 4.1 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1, 161.1, 160.7, 150.5, 147.9, 147.3, 129.9, 129.8, 126.8, 111.4, 110.0, 107.7, 103.2, 101.3, 61.4, 56.0, 55.9, 55.8, 55.1, 45.9, 41.5, 26.4, 14.3; **HRMS** for $C_{24}H_{27}N_3O_6$: calcd. (MH^+): 454.1973, found: 454.1967

Ethyl 2-diazo-4-(6,7-dimethoxy-2-(3-nitrophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-3-oxobutanoate (3m)

Brown viscous liquid; isolated yield 63% (147 mg). R_f 0.50 (30% EtOAc/hexane); **IR** (Film, cm^{-1}): 1027, 1350, 1526, 1619, 1712, 2142; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 2.3 Hz, 1H), 7.46 – 7.48 (m, 1H), 7.26 (t, *J* = 8.3 Hz, 1H), 7.16 - 7.19 (m, 1H), 6.69 (s, 1H), 6.55 (s, 1H), 5.43 (t, *J* = 7.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.78, 3.79 (2s, 6H), 3.62 – 3.65 (m, 2H), 3.54 (dd, *J* = 15.7 Hz, 7.8 Hz, 1H), 3.24 (dd, *J* = 15.7 Hz, 5.8 Hz, 1H), 2.91– 2.99 (m, 1H), 2.74 (dt, *J* = 16.0 Hz, 4.7 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.5, 161.1, 149.6, 149.5, 148.2, 147.6, 129.8, 129.0, 126.4, 119.6, 112.1, 111.5, 110.0, 108.2, 61.6, 56.1, 55.9, 55.4, 46.0, 41.5, 26.1, 14.3; **HRMS** for $C_{23}H_{24}N_4O_7$: calcd. (MH^+): 469.1718, found: 469.1710

Ethyl 4-(7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazo-3-oxobutanoate (3n)

Brown viscous liquid; isolated yield 35% (77 mg). R_f 0.50 (5% EtOAc/hexane); **IR** (Film, cm^{-1}): 670, 1068, 1646, 1714, 2141; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 2.0 Hz, 1H), 7.12 – 7.21 (m, 3H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 5.43 (t, *J* = 6.6 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.49 – 3.64 (m, 3H), 3.14 (dd, *J* = 15.8 Hz, 6.0 Hz, 1H), 2.87 – 2.95 (m, 1H), 2.68 (dt, *J* = 16.4 Hz, 4.3 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.4, 161.2, 148.8, 140.2, 133.7, 130.5, 129.9, 129.8, 129.3, 119.5, 118.6, 115.2, 61.4, 55.2, 45.9, 41.2, 26.2, 14.3; **HRMS** for $C_{21}H_{20}BrN_3O_3$: calcd. (MH^+): 442.0761, found: 442.0757

Ethyl 2-diazo-3-oxo-4-(1-phenylpyrrolidin-2-yl)butanoate (3o)

Brown viscous liquid; isolated yield 39% (59 mg). R_f 0.50 (5% EtOAc/hexane); **IR** (Film, cm^{-1}):1599, 2139; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 2H), 6.53 – 6.60 (m, 3H), 4.26 – 4.30 (m, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.34 (t, *J* = 7.1 Hz, 1H), 3.06 – 3.14 (m, 2H), 2.96 (dd, *J* = 16.4 Hz, 9.8 Hz, 1H), 1.93 – 2.01 (m, 3H), 1.68 – 1.76 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.8, 161.2, 146.5, 129.3, 115.7, 111.9, 61.5, 54.8, 47.7, 42.6, 31.3, 23.1, 14.3; **HRMS** for $C_{16}H_{19}N_3O_3$: calcd. (MH^+): 302.1499, found: 302.1496

3-(ethoxycarbonyl)-2-oxo-4-(p-tolyl)-2,3,4,5,6,10b-hexahydro-1H-pyrrolo[2,1-a]isoquinolin-4-ium-3-ide (4a)

Colorless solid; isolated yield 79% (14 mg). Mp 174-176 ^{o}C; **IR** (KBr, cm^{-1}): 1068, 1646; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.20 (m, 2H), 7.10 – 7.13 (m, 1H), 6.93 – 6.95 (m, 1H), 5.10 (d, *J* = 7.6 Hz, 1H), 4.94 - 4.98 (m, 1H), 4.15 – 4.23 (m, 2H), 3.98 – 4.05 (m, 1H), 3.32 – 3.40 (m, 1H), 2.88 (dd, *J* = 15.8 Hz, 7.8 Hz, 1H), 2.81 (d, *J* = 17.4 Hz, 1H), 2.44 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.6, 163.1, 146.0, 140.2, 133.4, 131.9, 130.6, 128.5, 127.8, 127.5, 126.3, 121.0, 98.9, 75.1, 59.3, 59.1, 41.9, 25.6, 20.7, 14.7; **HRMS** for $C_{22}H_{23}NO_3$: calcd. (MH^+): 350.1751, found: 350.1754

Selected X-Ray Crystallographic data for 4a, $C_{22}H_{23}NO_3$: *M* = 349.41, Monolinic, *P* $2_{1/c}$, *a* = 14.557(8) Å, *b* = 7.392(4) Å, *c* = 18.717(8) Å, *V* = 1847.7(16)Å^3, α = 90.00°, *β* = 113.45(3)°, γ = 90.00°, *Z* = 4, D_c = 1.256 g cm^{-3}, μ(Mo-Kα) = 0.083 mm^{-1}, *F*(000) = 744, Reflections Collected: unique 9815/3236 [*R*(int) = 0.0881]. Final R indices [*I* > 2s(*I*)], *R*1 = 0.0750, wR_2 = 0.2001.

4-(4-butylphenyl)-3-(ethoxycarbonyl)-2-oxo-2,3,4,5,6,10b-hexahydro-1H-pyrrolo[2,1-a]isoquinolin-4-ium-3-ide (4b)

Colorless solid; isolated yield 61% (12 mg). Mp 128-130 ^{o}C; **IR** (KBr, cm^{-1}): 1026, 1607; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.12 – 7.19 (m, 3H), 6.94 (br s, 1H), 5.12 (d, *J* = 7.2 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H),7.16 – 7.23 (m, 2H), 4.01 (t, *J* = 11.1 Hz, 1H), 3.36 (t, *J* = 14.1 Hz, 1H), 2.78 – 2.91 (m, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 2.44 (d, *J* = 15.6 Hz, 1H), 1.50 – 1.58 (m, 2H), 1.27 – 1.31 (m appearing as t, *J* = 7.0 Hz, 5H), 0.87 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.5, 163.1, 146.0, 145.1, 133.4, 131.9, 130.0, 128.6, 127.7, 127.5, 126.3, 121.0, 98.6, 75.0, 59.3, 59.1, 41.9, 34.8, 33.2, 25.6, 22.3, 14.8, 13.9; **HRMS** for $C_{25}H_{29}NO_3$: calcd. (MH^+): 392.2220, found: 392.2219

3-(ethoxycarbonyl)-4-(3-methoxyphenyl)-2-oxo-2,3,4,5,6,10b-hexahydro-1H-pyrrolo[2,1-a]isoquinolin-4-ium-3-ide (4c)

Colorless solid; isolated yield 72% (13 mg). Mp 175-177 ^{o}C; **IR** (KBr, cm^{-1}):1100, 1254, 1612; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 8.3 Hz, 1H), 7.10 – 7.20 (m, 5H), 6.91 – 6.95 (m, 2H), 5.15 (d, *J* = 7.6 Hz, 1H), 4.97 – 5.01 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.97 – 4.03 (m, 1H), 3.76 (s, 3H), 3.32 – 3.40 (m, 1H), 2.89 (dd, *J* = 15.7 Hz, 7.8 Hz, 1H), 2.81 (d, *J* = 17.4 Hz, 1H), 2.43 (d, *J* = 15.6 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 179.5, 163.1, 160.9, 149.8, 133.4, 132.0, 130.9, 128.6, 127.8, 127.5, 126.3, 114.6, 113.1, 108.2, 98.6, 75.0, 59.3, 59.2, 55.7, 42.1, 25.6, 14.8; **HRMS** for $C_{22}H_{23}NO_4$: calcd. (MH^+): 366.1700, found: 366.1694

4-(3,4-dimethylphenyl)-3-(ethoxycarbonyl)-2-oxo-2,3,4,5,6,10b-hexahydro-1H-pyrrolo[2,1-a]isoquinolin-4-ium-3-ide (4d)

Colorless solid; isolated yield 59% (11 mg). Mp 195-197 ^oC; **IR** (KBr, cm^{-1}): 1216, 1608; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.35 (m, 2H), 7.16 – 7.19 (m, 3H), 7.10 – 7.12 (m, 1H), 6.92 – 6.94 (m, 1H), 5.11 (d, *J* = 7.5 Hz, 1H), 4.93 – 4.97 (m, 1H), 4.15 – 4.22 (m, 2H), 3.98 – 4.05 (m, 1H), 3.31 – 3.39 (m, 1H), 2.90 (dd, *J* = 15.8 Hz, 7.8 Hz, 1H), 2.80 (d, *J* = 17.6 Hz, 1H), 2.43 (d, *J* = 15.8 Hz, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.5, 163.1, 146.1, 138.9, 138.8, 133.5, 132.0, 128.5, 127.7, 127.5, 126.3, 121.8, 118.3, 98.8, 75.0, 59.3, 59.0, 42.0, 25.6, 20.4, 19.2, 14.7; **HRMS** for $C_{23}H_{25}NO_3$: calcd. (MH^+): 364.1907, found: 364.1914

4-(3-bromo-4-methoxyphenyl)-3-(ethoxycarbonyl)-2-oxo-2,3,4,5,6,10b-hexahydro-1H-pyrrolo[2,1-a]isoquinolin-4-ium-3-ide (4e)

Colorless solid; isolated yield 69% (15 mg). Mp 135-137 ^oC; **IR** (KBr, cm^{-1}): 669, 1068, 1216, 1646; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 3.0 Hz, 1H), 7.57 (dd, *J* = 9.2 Hz, 3.1 Hz, 1H), 7.19 – 7.21 (m, 2H), 7.10 – 7.12 (m, 1H), 6.94 – 6.96 (m, 1H), 6.88 (d, *J* = 9.2 Hz, 1H), 5.09 (d, *J* = 7.4 Hz, 1H), 4.94 – 4.97 (m, 1H), 4.15 – 4.23 (m, 2H), 3.93 – 4.00 (m, 1H), 3.87 (s, 3H), 3.29 – 3.38 (m, 1H), 2.89 (dd, *J* = 15.8 Hz, 7.8 Hz, 1H), 2.81 (d, *J* = 17.6 Hz, 1H), 2.45 (d, *J* = 15.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.2, 163.0, 156.8, 141.2, 133.0, 131.7, 128.6, 127.9, 127.6, 126.3, 126.1, 121.9, 112.9, 111.7, 98.9, 75.5, 59.5, 59.4, 56.7, 41.9, 25.6, 14.8; **HRMS** for $C_{22}H_{22}BrNO_4$: calcd. (MH^+): 444.0805, found: 444.0811

4-(4-chlorophenyl)-3-(ethoxycarbonyl)-2-oxo-2,3,4,5,6,10b-hexahydro-1H-pyrrolo[2,1-a]isoquinolin-4-ium-3-ide (4f)

Colorless solid; isolated yield 67% (12 mg).Mp 172-174 ^oC; **IR** (KBr, cm^{-1}): 759, 1103, 1610; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 9.0 Hz, 2H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.19 – 7.21 (m, 2H), 7.11 – 7.13 (m, 1H), 6.92 – 6.95 (m, 1H), 5.08 (d, *J* = 7.3 Hz, 1H), 4.95 – 4.98 (m, 1H), 4.12 – 4.24 (m, 2H), 3.98 – 4.04 (m, 1H), 3.32 – 3.40 (m, 1H), 2.81 – 2.91 (m, 2H), 2.48 (d, *J* = 15.9 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 163.0, 147.0, 136.0, 133.0, 131.7, 130.2, 128.6, 128.0, 127.7, 126.3, 122.8, 99.0, 75.4,

59.4 (two peaks merged), 42.0, 25.6, 14.7; **HRMS** for $C_{21}H_{20}ClNO_3$: calcd. (MH^+): 370.1204, found: 370.1193

3-(ethoxycarbonyl)-4-(3-nitrophenyl)-2-oxo-2,3,4,5,6,10b-hexahydro-1H-pyrrolo[2,1-a]isoquinolin-4-ium-3-ide (4g)

Colorless solid; isolated yield 74% (14 mg). Mp 165-167 ^oC; **IR** (KBr, cm^{-1}): 1067, 1216, 1388, 1645; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 6.4 Hz, 1H), 7.68 (t, *J* = 8.3 Hz, 1H), 6.16 – 6.25 (m, 3H), 6.95 – 6.98 (m, 1H), 5.18 (d, *J* = 7.2 Hz, 1H), 4.99 (d, *J* = 11.4 Hz, 1H), 4.12 – 4.22 (m, 3H), 3.35 – 3.43 (m, 1H), 2.87 – 2.94 (m, 2H), 2.53 (d, *J* = 16.1 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.7, 162.9, 149.8, 149.1, 132.4, 131.4, 131.2, 128.7, 128.3, 127.9, 127.7, 126.3, 124.9, 117.1, 100.0, 75.9, 60.0, 59.6, 42.0, 25.6, 14.7; **HRMS** for $C_{21}H_{20}N_2O_5$: calcd. (MH^+): 381.1445, found: 381.1438

6. References

[1] J.-J. Zhong, Q.-Y. Meng, B. Liu, X.-B. Li, X.-W. Gao, T. Lei, C.-J. Wu, Z.-J. Li, C.-H. Tung, L.-Z. Wu, *Org. Lett*. **2014**, *16*, 1988.

[2] C. Zhu, G. Xu, J. Sun, *Angew. Chem., Int. Ed*. **2016**, *55*, 11867.

[3] (a) A. M. Nauth, N. Otto, T. Opatz, *Adv. Synth. Catal.* **2015**, *357*, 3424; (b) W. Zhang, S. Yang, Z. Shen, *Adv. Synth. Catal.* **2016**, *358*, 2392.

7. Copies of 1H and 13C NMR Spectra

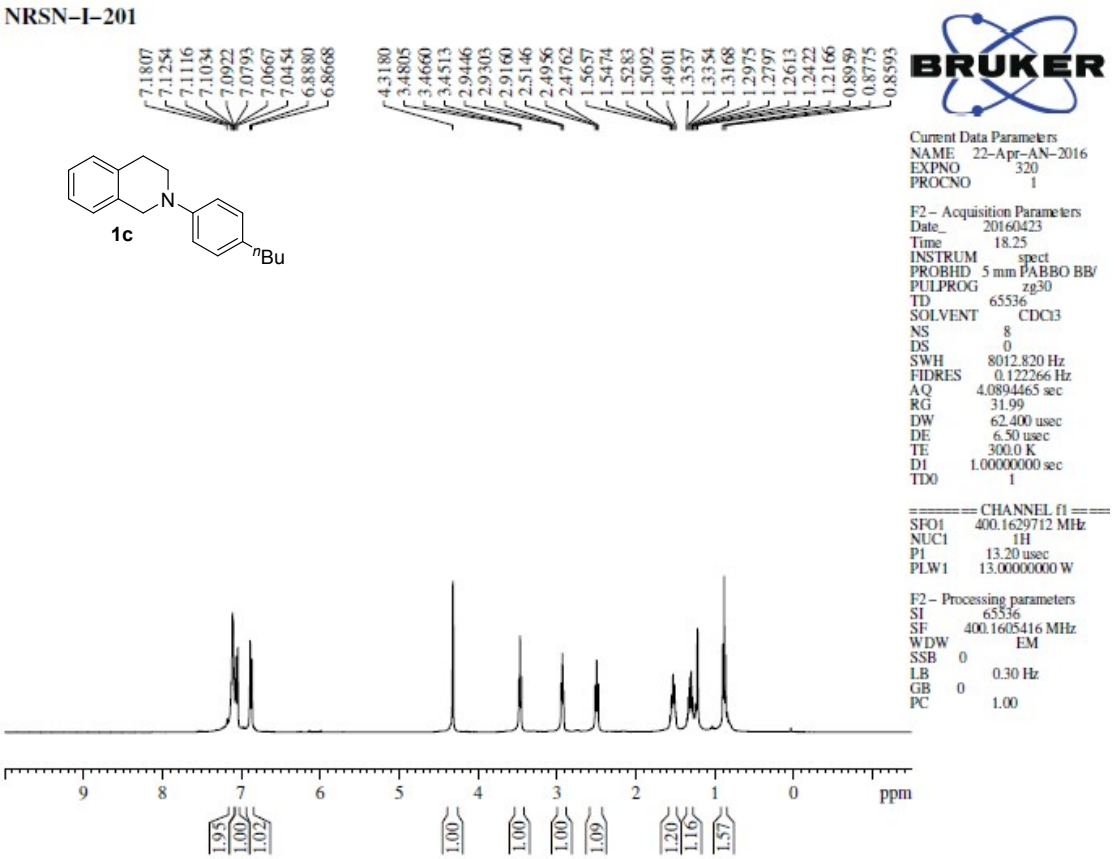

Figure 2. ^{1}H NMR spectra of 1c

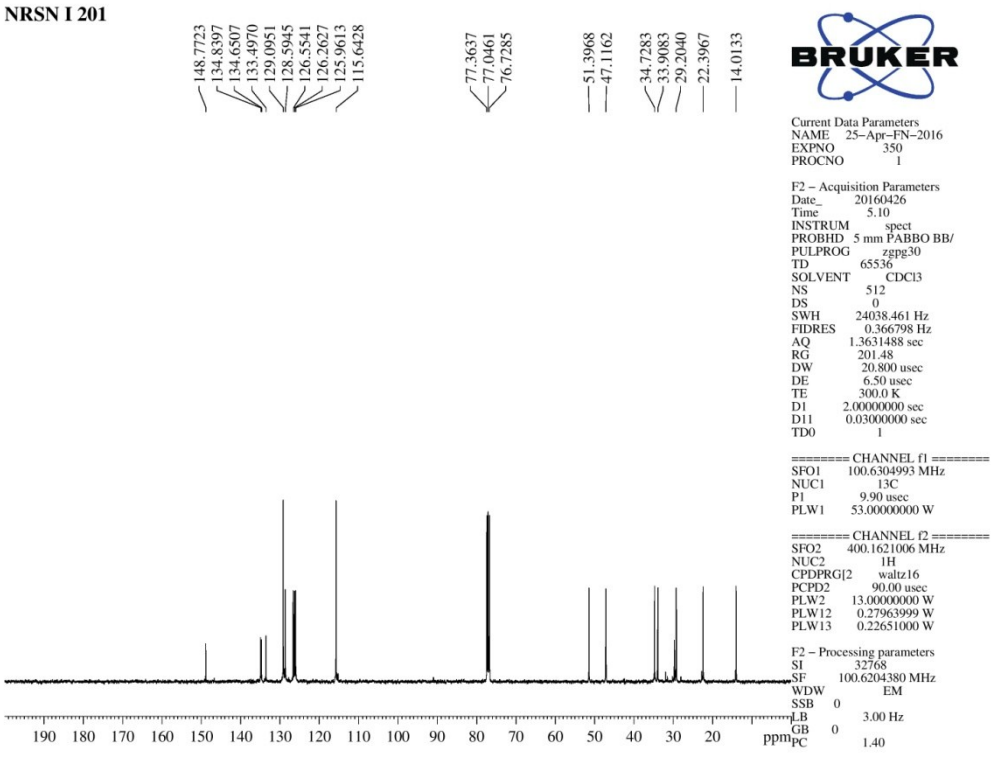

Figure 3. ^{13}C NMR spectra of 1c

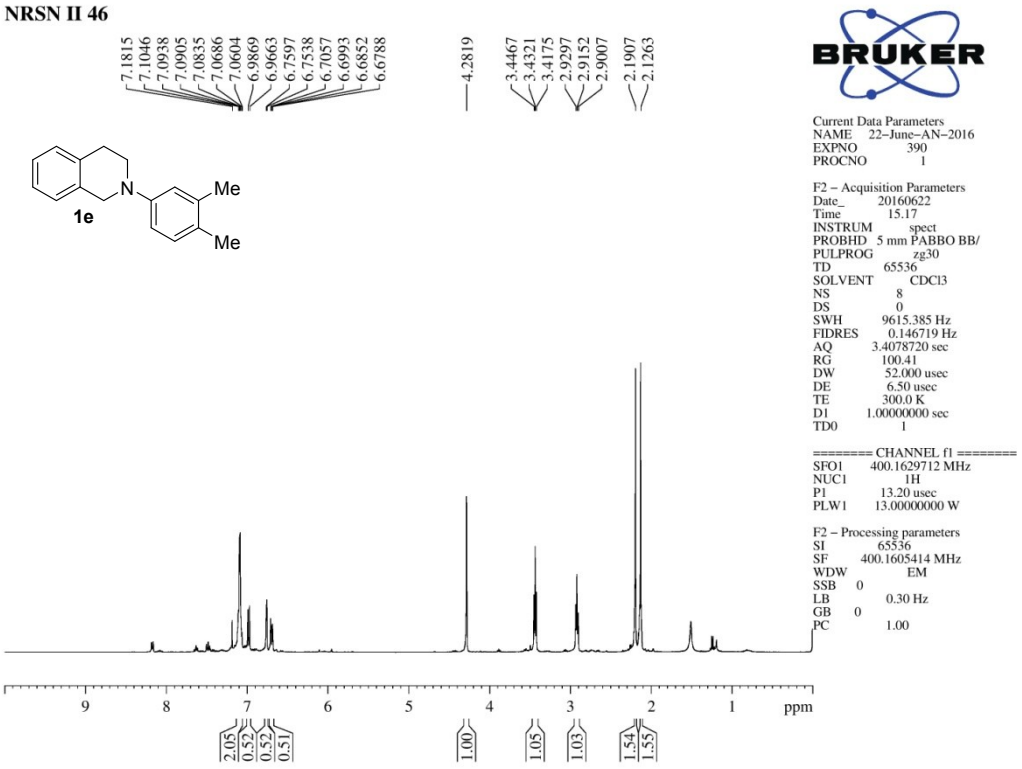

Figure 4. ^{1}H NMR spectra of 1e

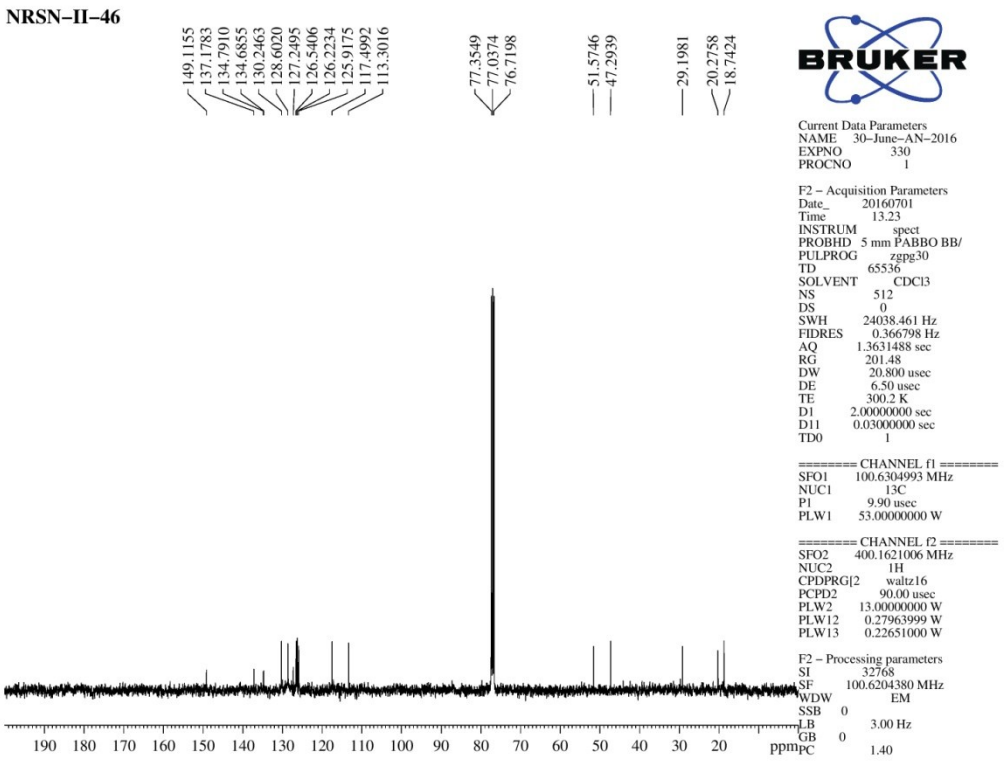

Figure 5. ^{13}C NMR spectra of 1e

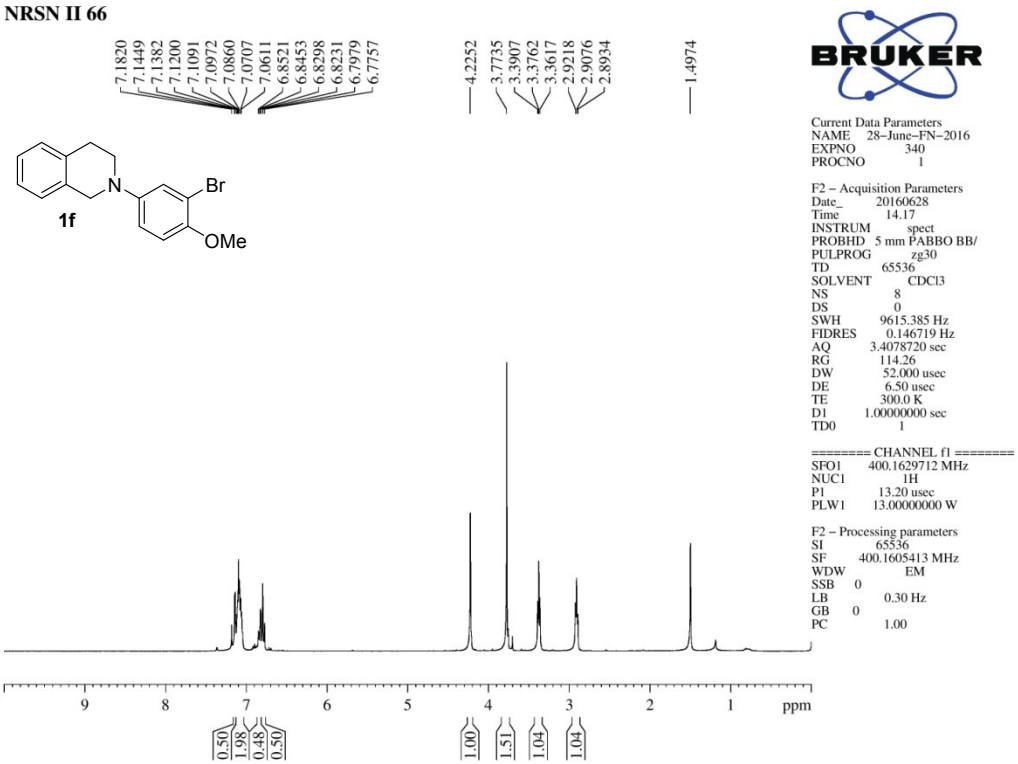

Figure 6. ^{1}H NMR spectra of 1f

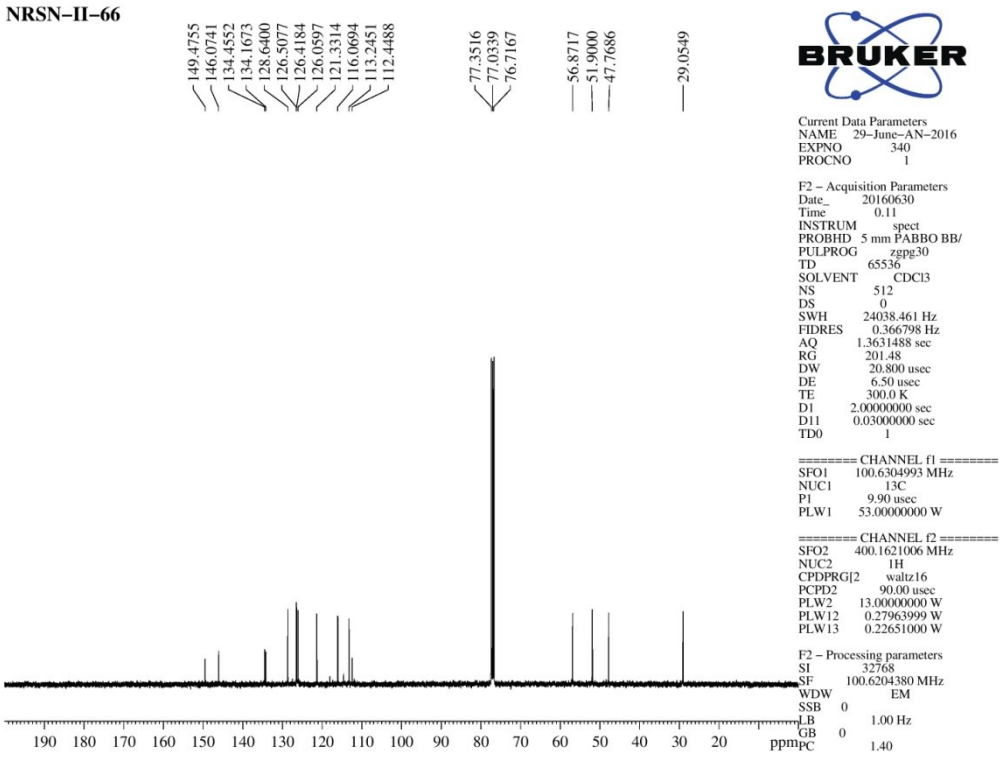

Figure 7. ^{13}C NMR spectra of 1f

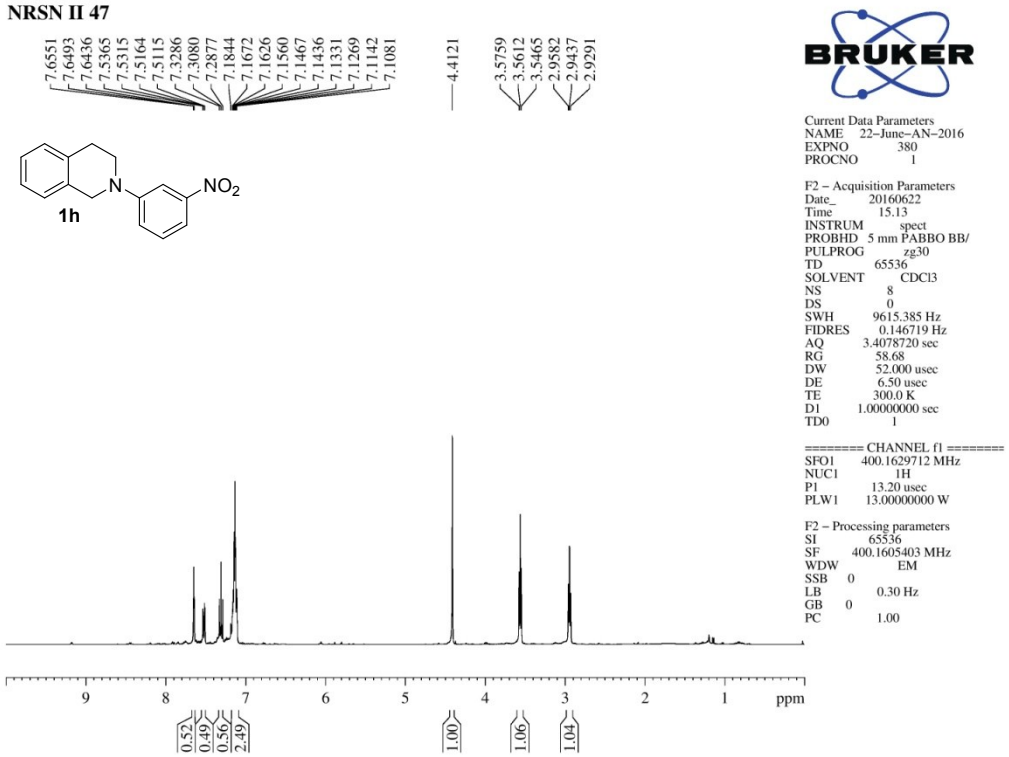

Figure 8. ^{1}H NMR spectra of 1h

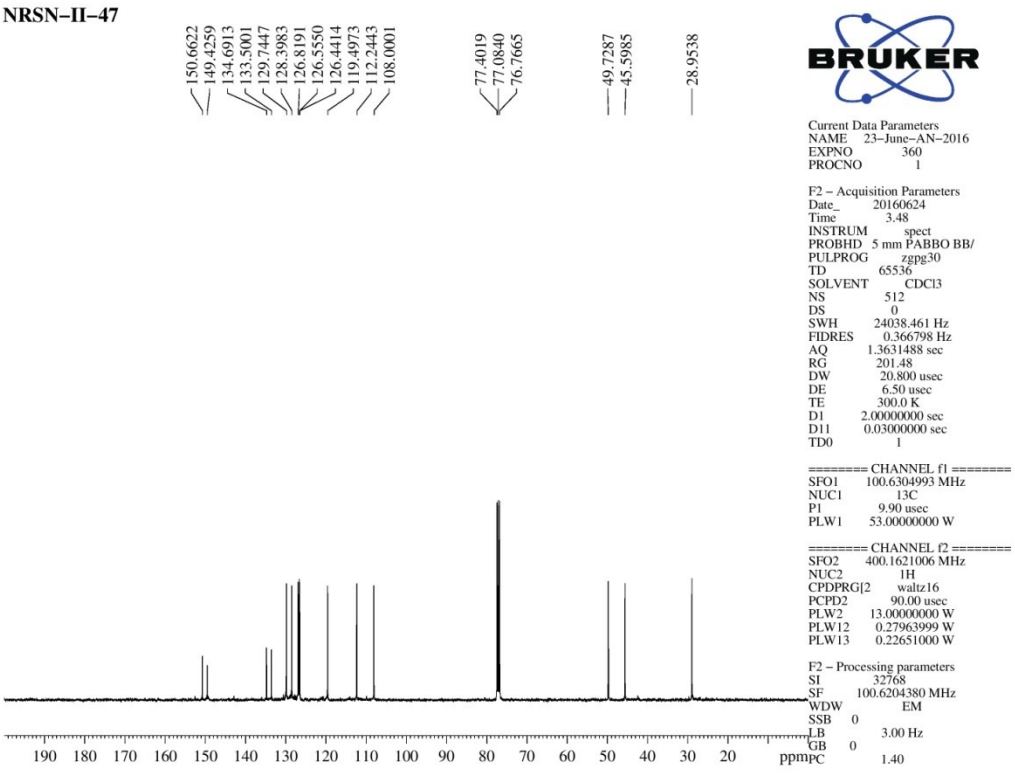

Figure 9. ^{13}C NMR spectra of 1h

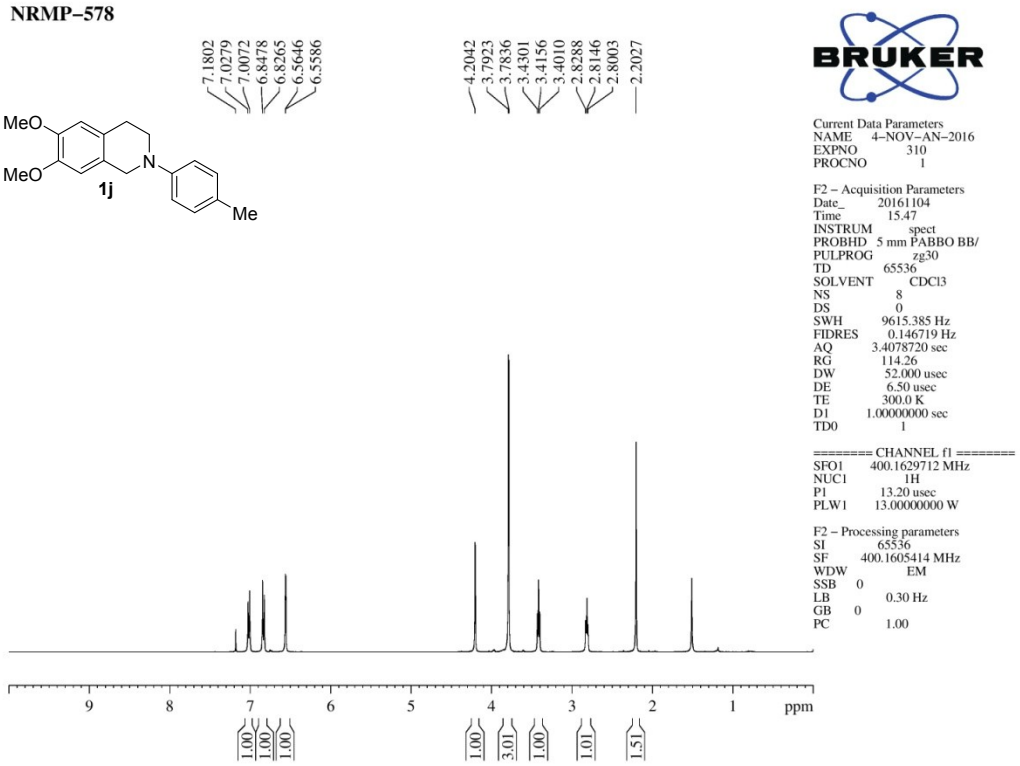

Figure 10. ^{1}H NMR spectra of 1j

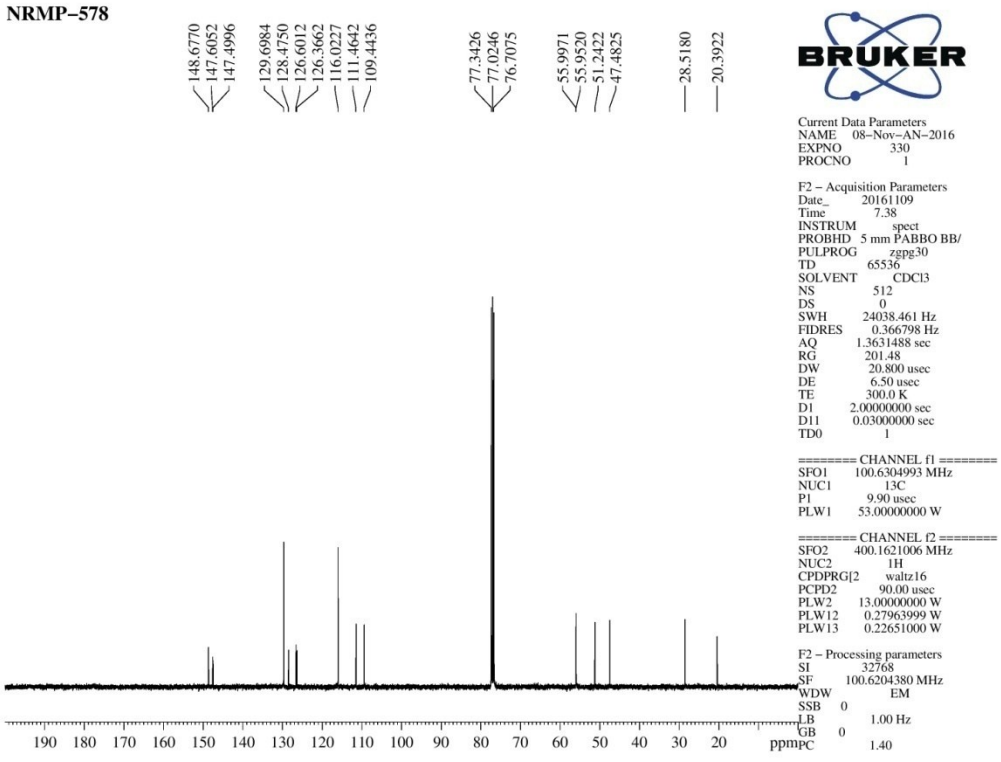

Figure 11. ^{13}C NMR spectra of 1j

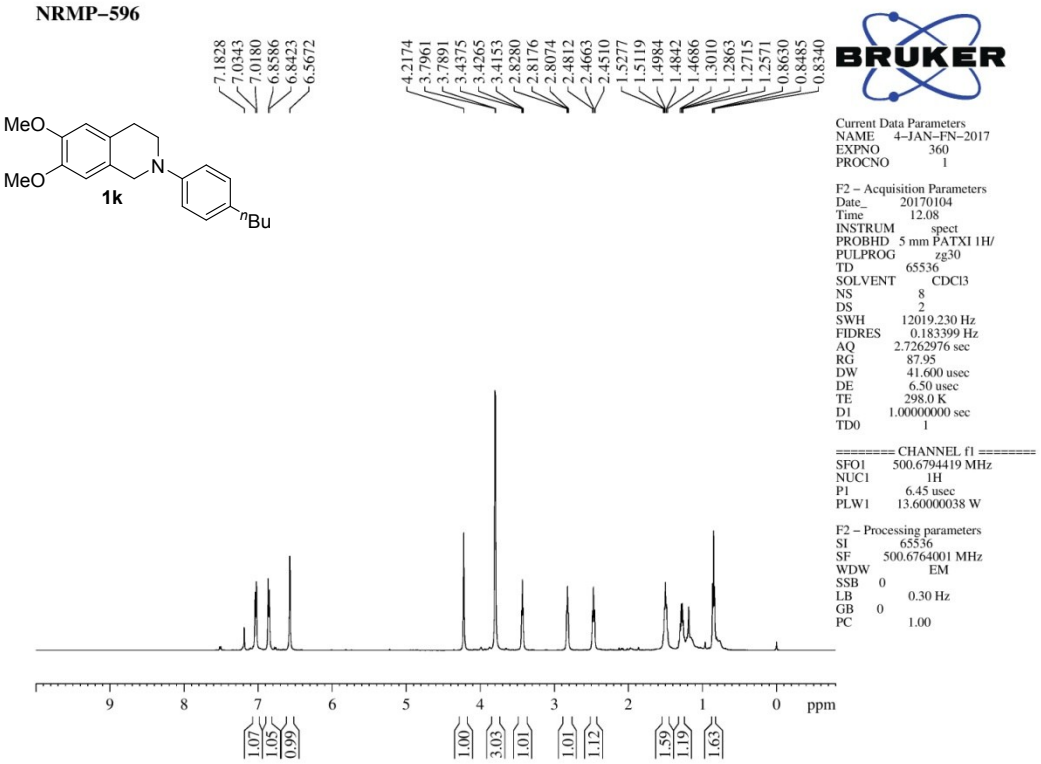

Figure 12. ^{1}H NMR spectra of 1k

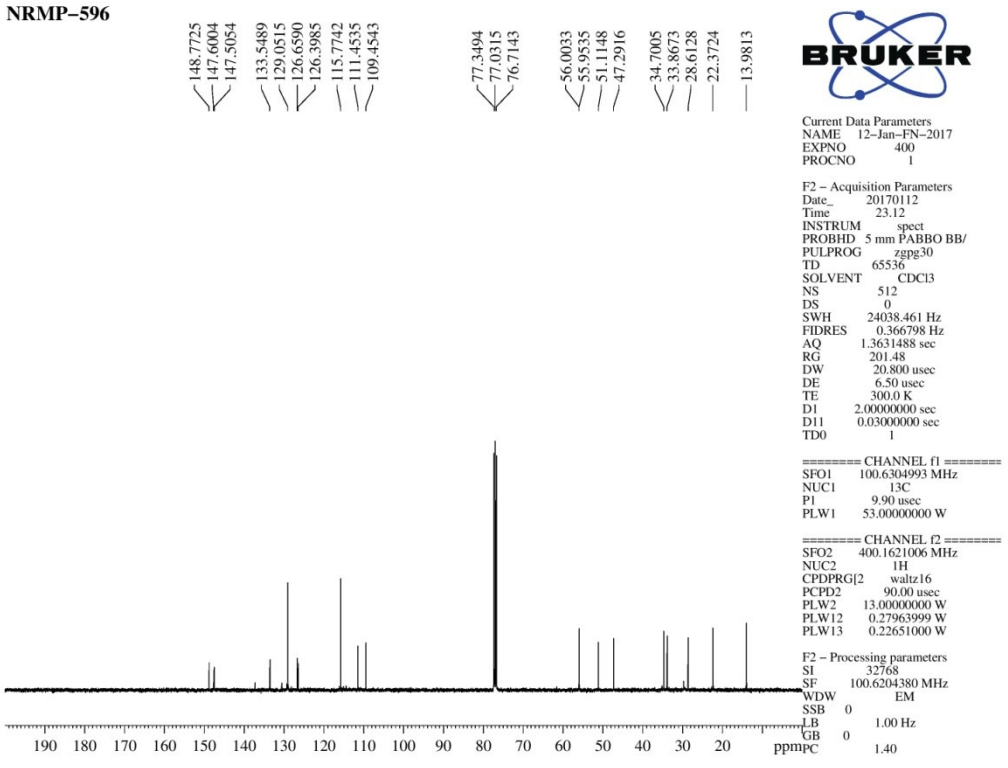

Figure 13. ^{13}C NMR spectra of 1k

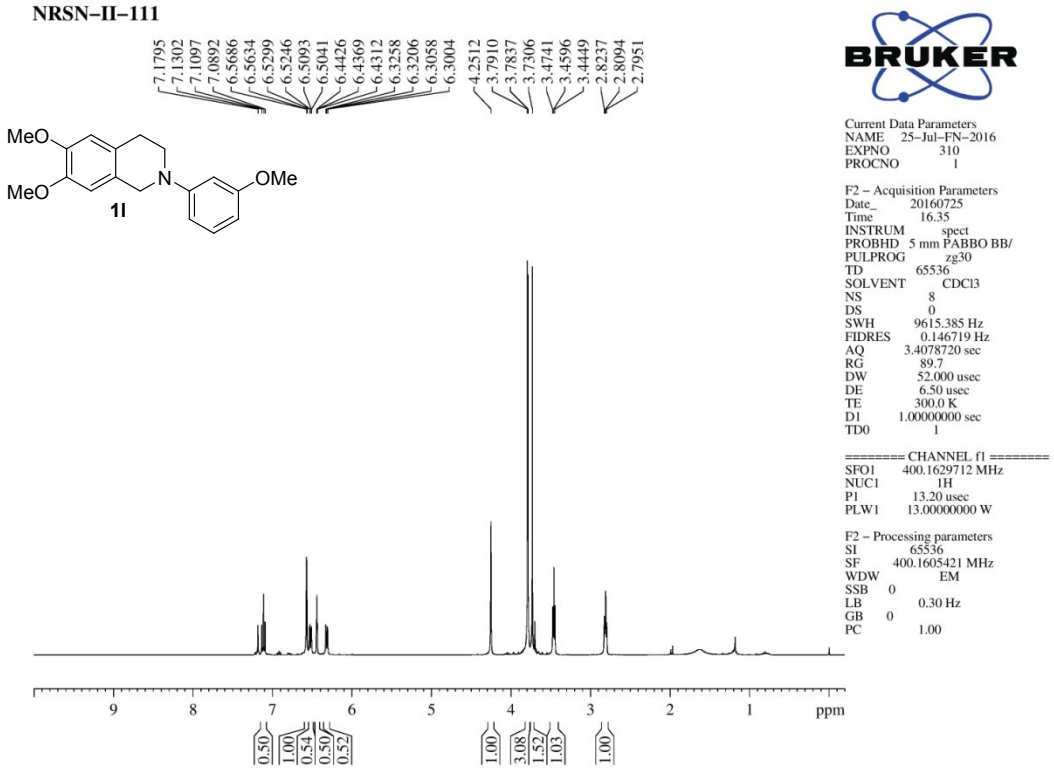

Figure 14. ^{1}H NMR spectra of 1l

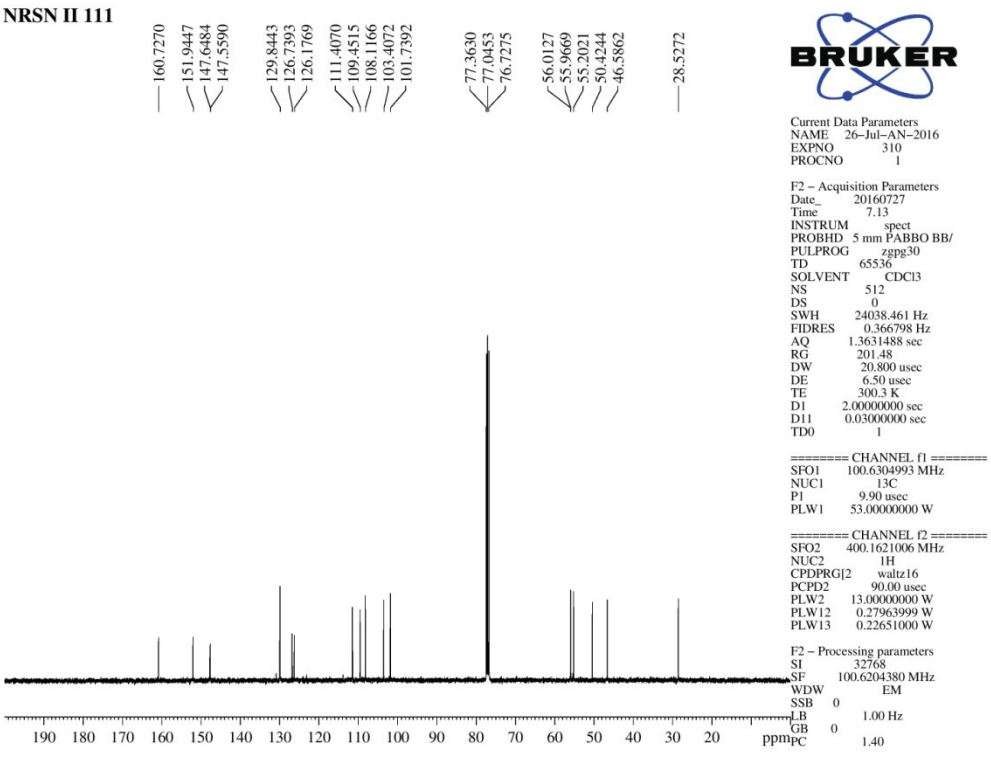

Figure 15. ^{13}C NMR spectra of 1l

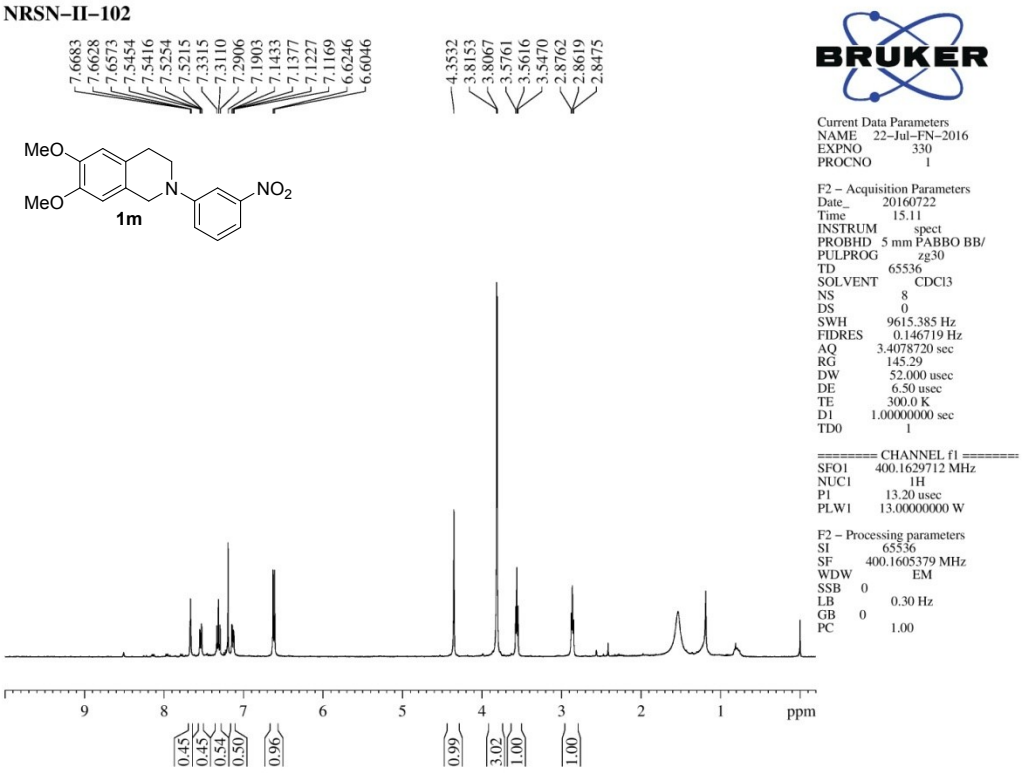

Figure 16. ^{1}H NMR spectra of 1m

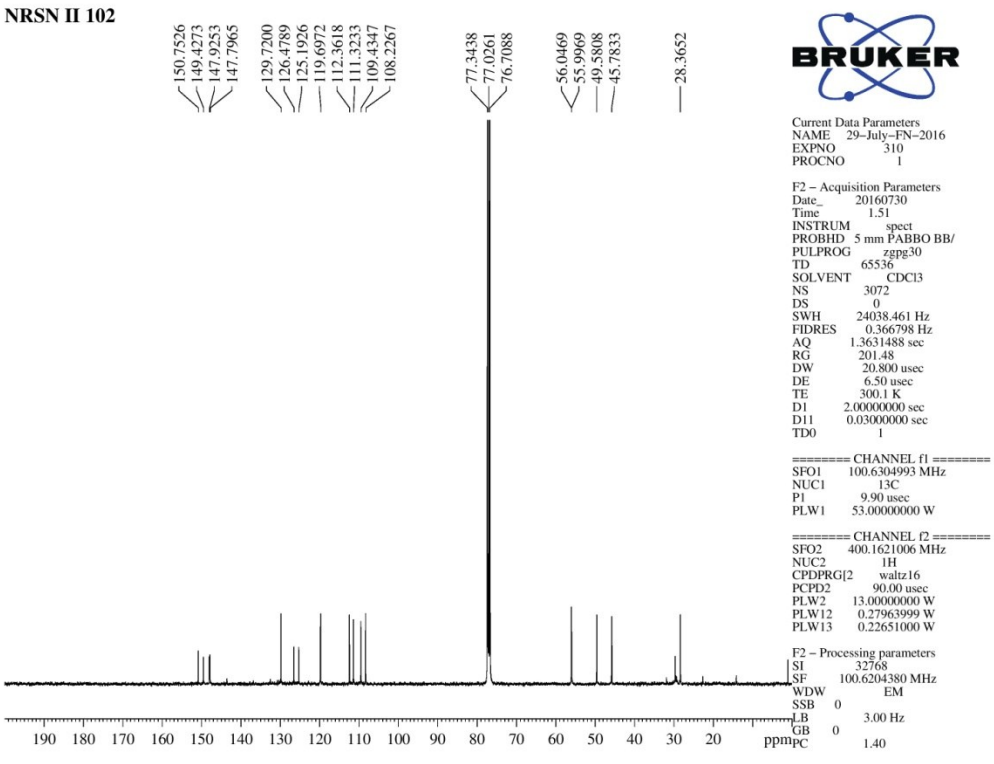

Figure 17. ^{13}C NMR spectra of 1m

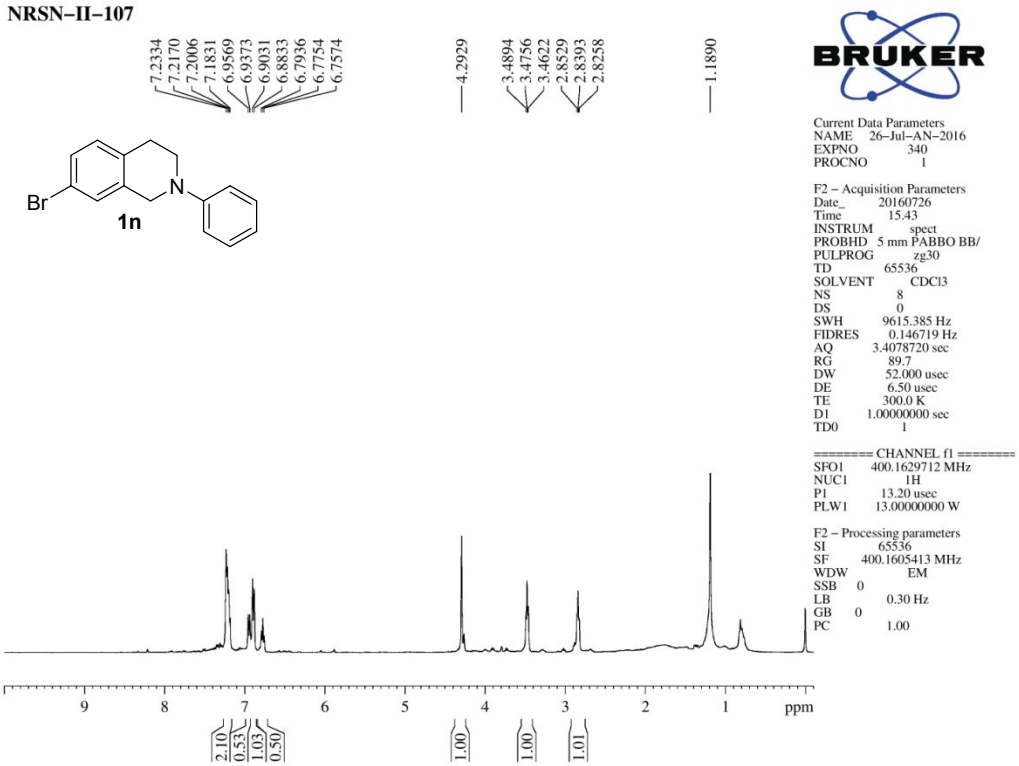

Figure 18. ^{1}H NMR spectra of 1n

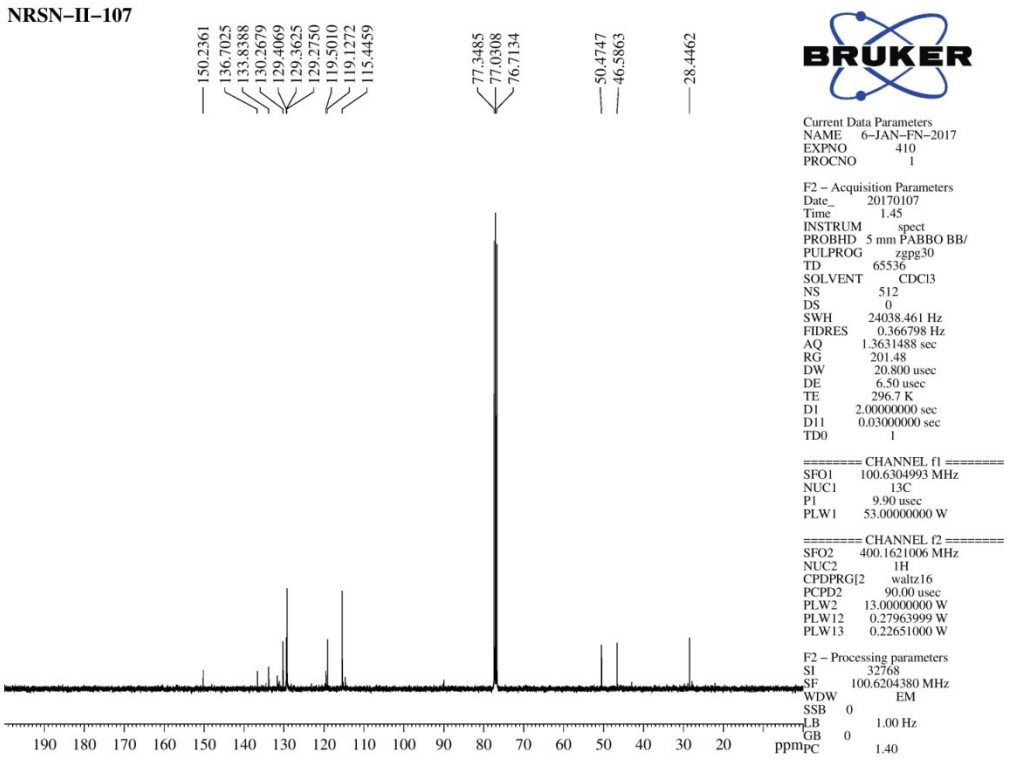

Figure 19. ^{13}C NMR spectra of 1n

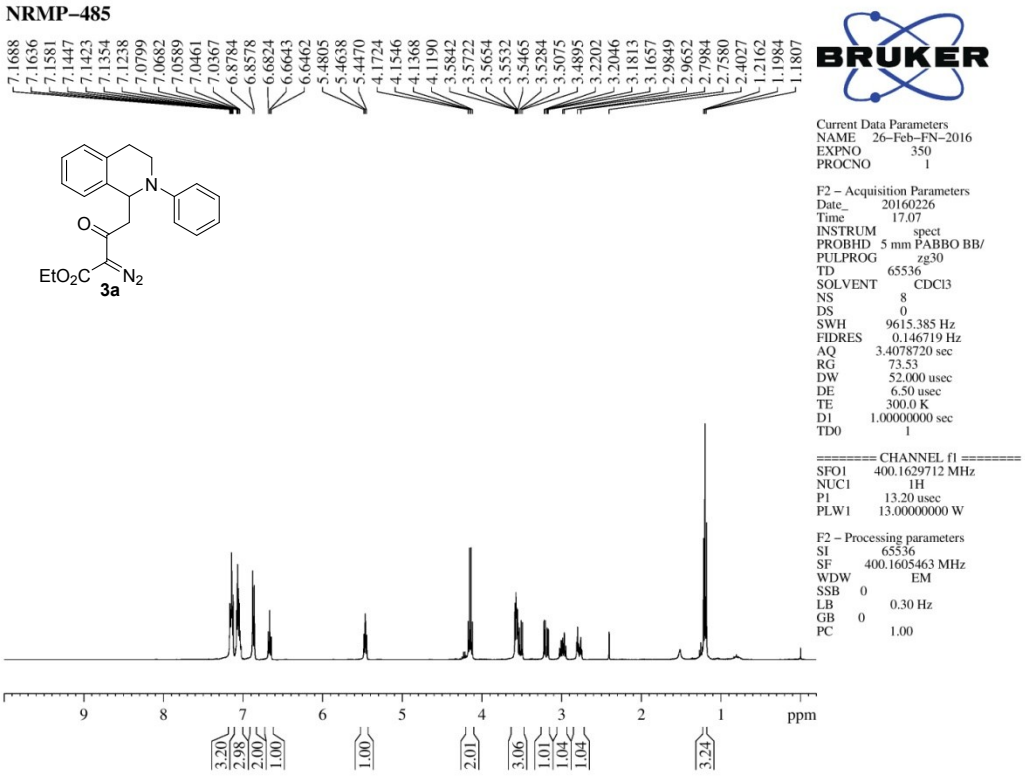

Figure 20. ^{1}H NMR spectra of 3a

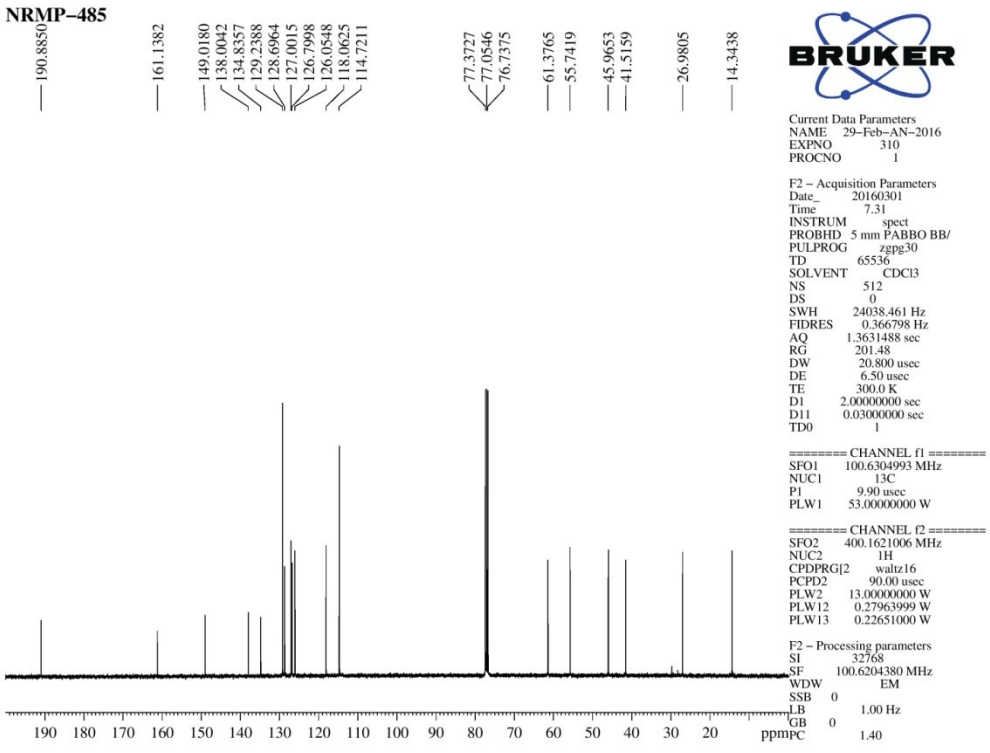

Figure 21. ^{13}C NMR spectra of 3a

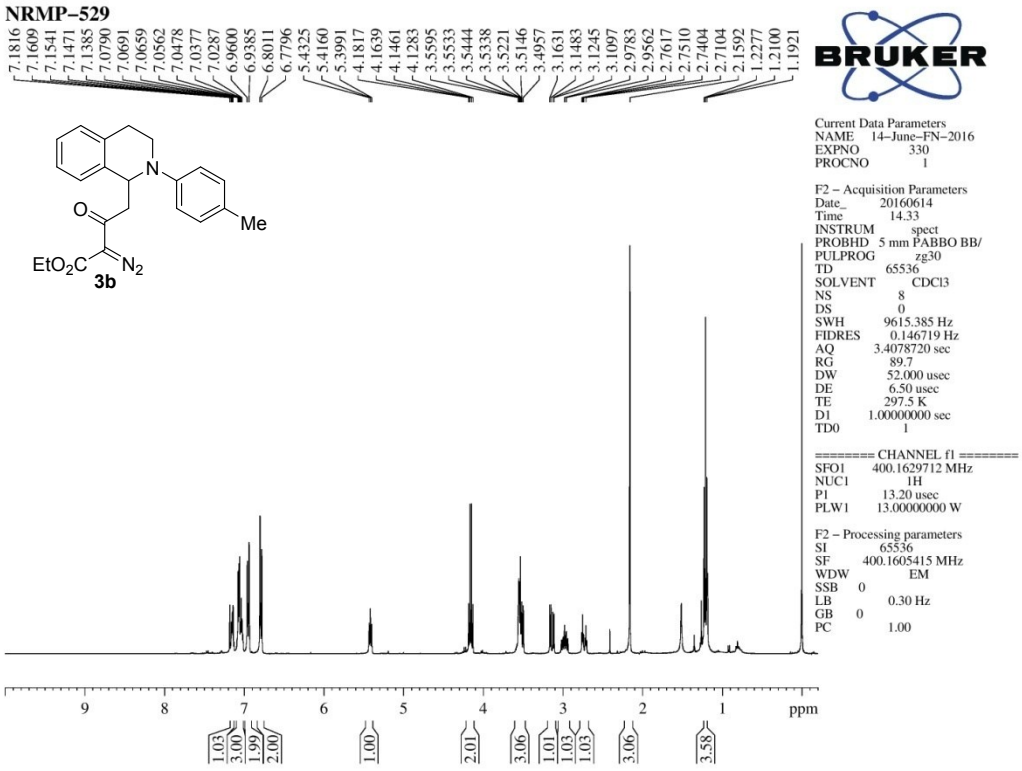

Figure 22. ^{1}H NMR spectra of 3b

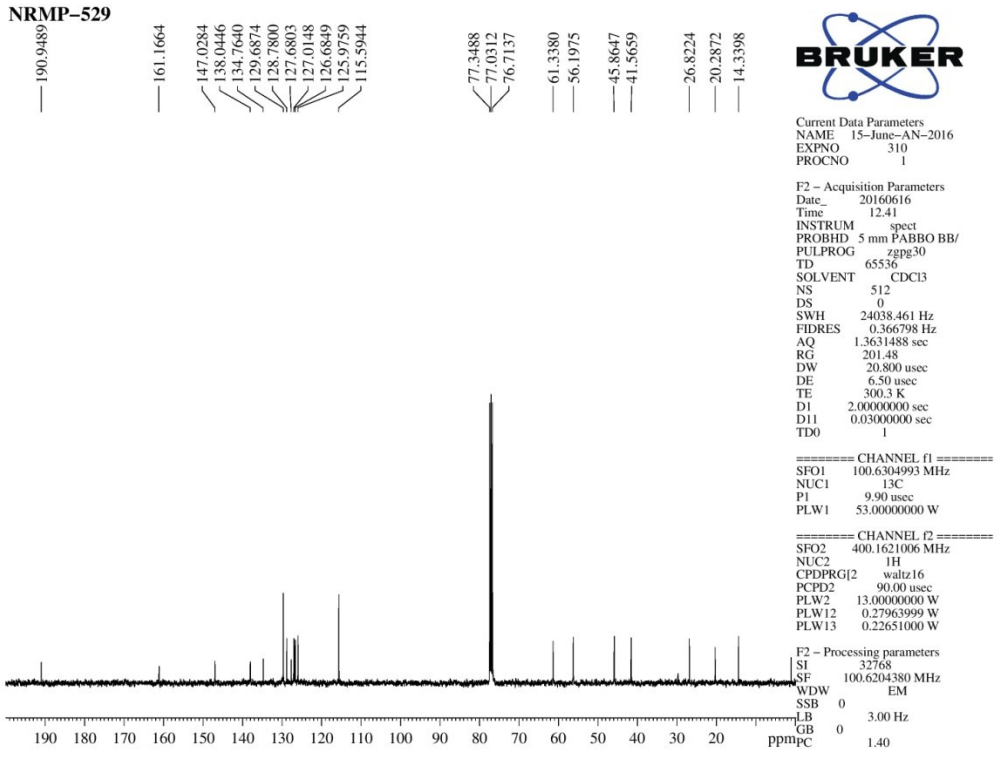

Figure 23. ^{13}C NMR spectra of 3b

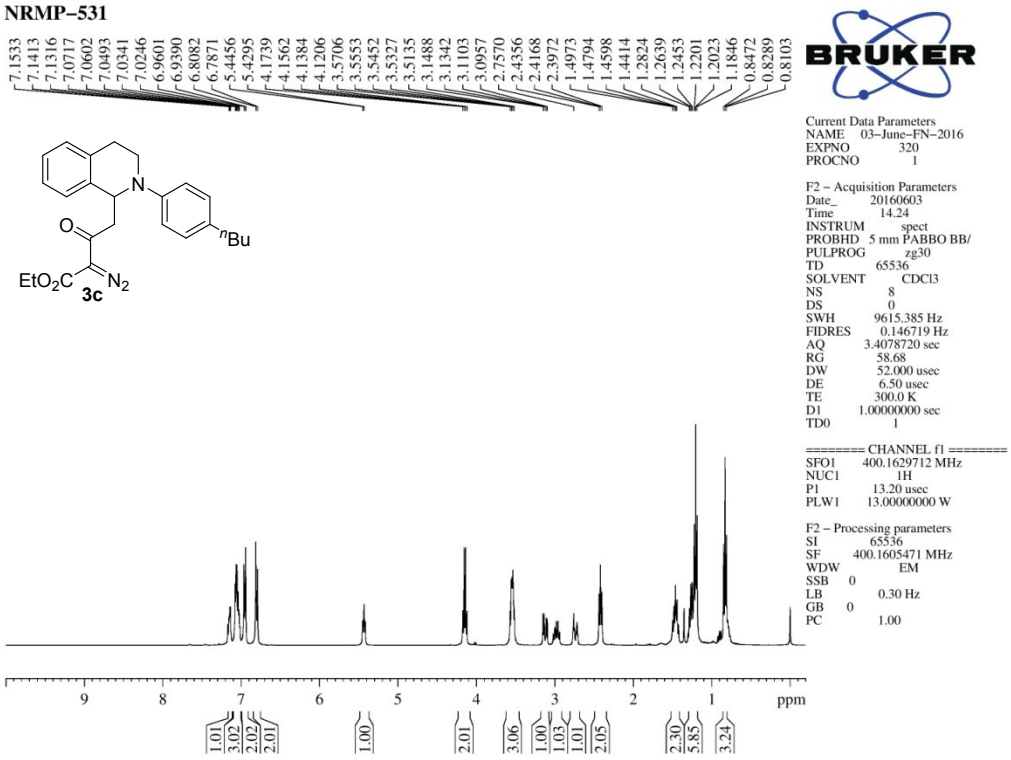

Figure 24. ^{1}H NMR spectra of 3c

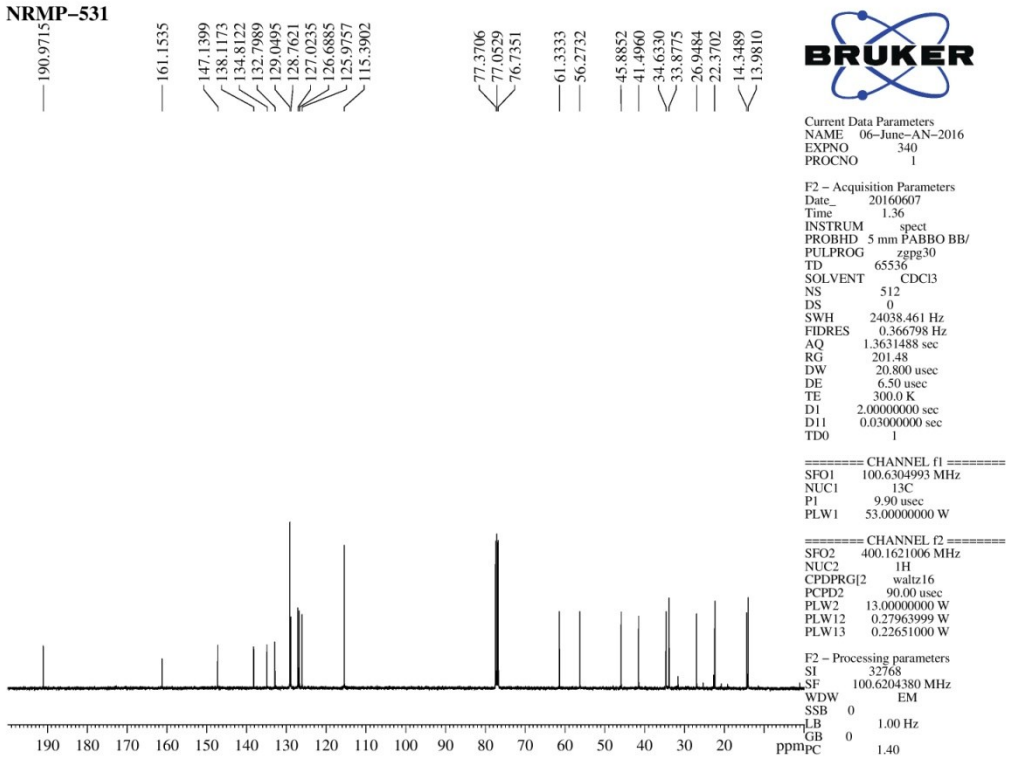

Figure 25. ^{13}C NMR spectra of 3c

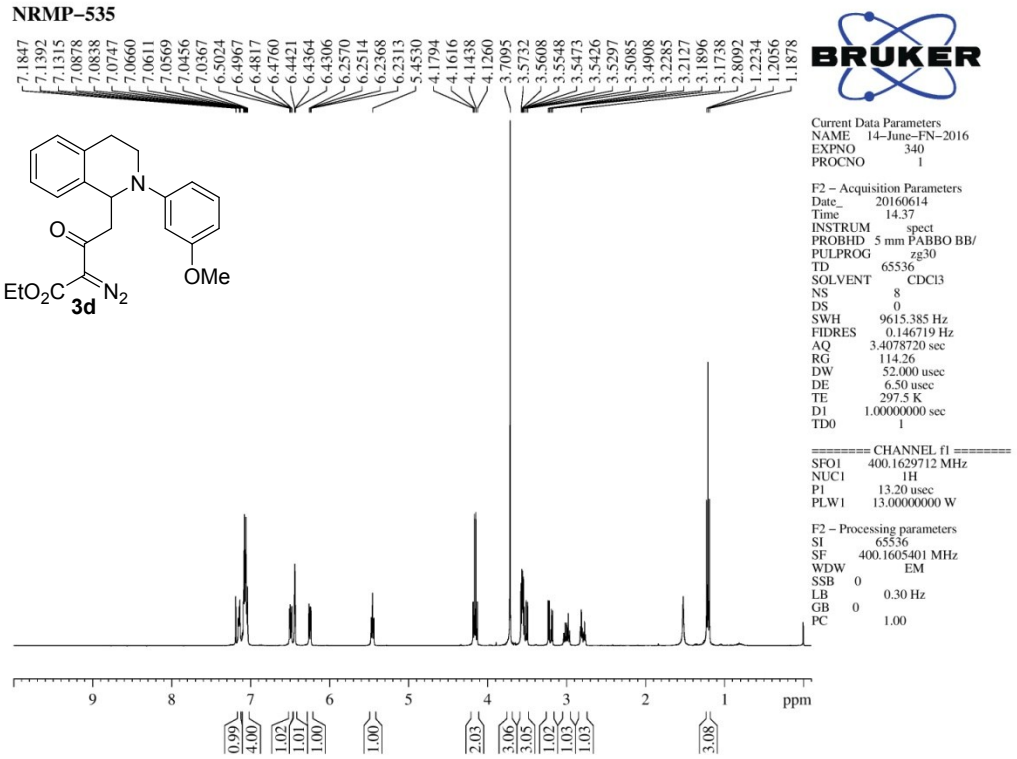

Figure 26. ^{1}H NMR spectra of 3d

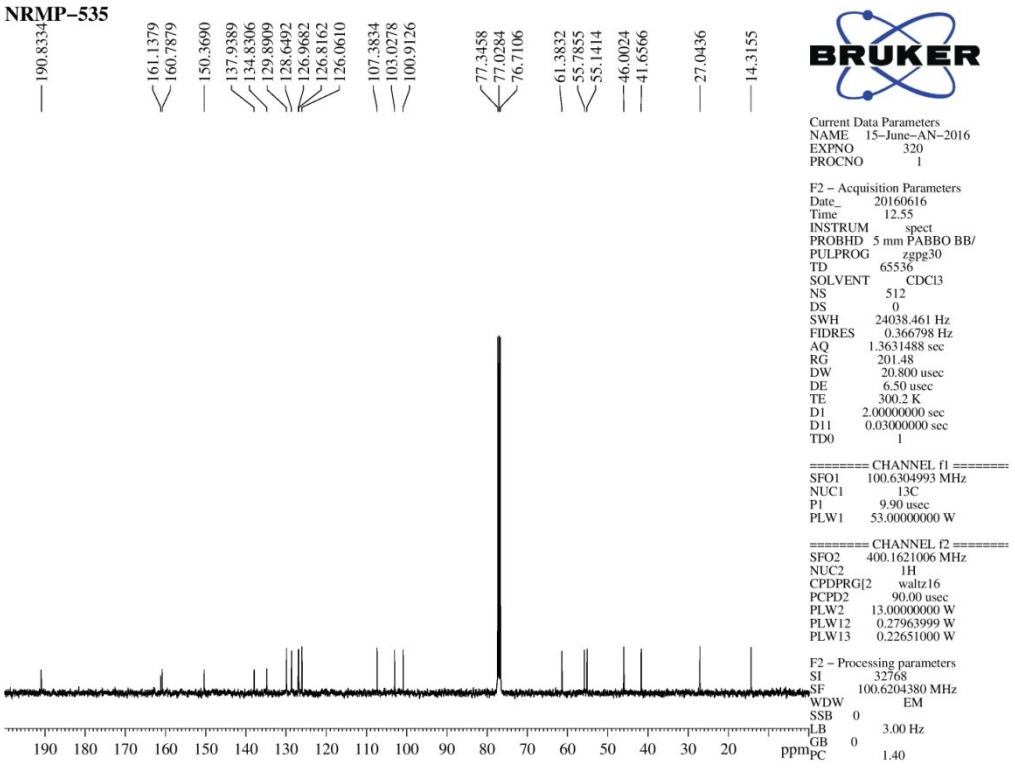

Figure 27. ^{13}C NMR spectra of 3d

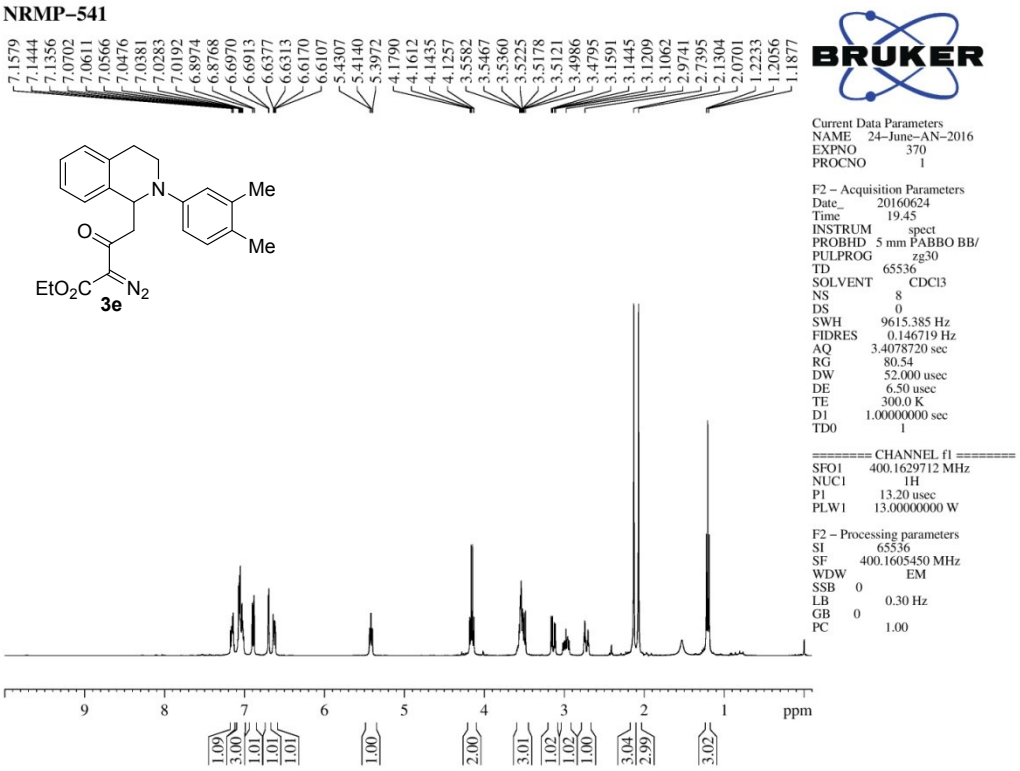

Figure 28. ^{1}H NMR spectra of 3e

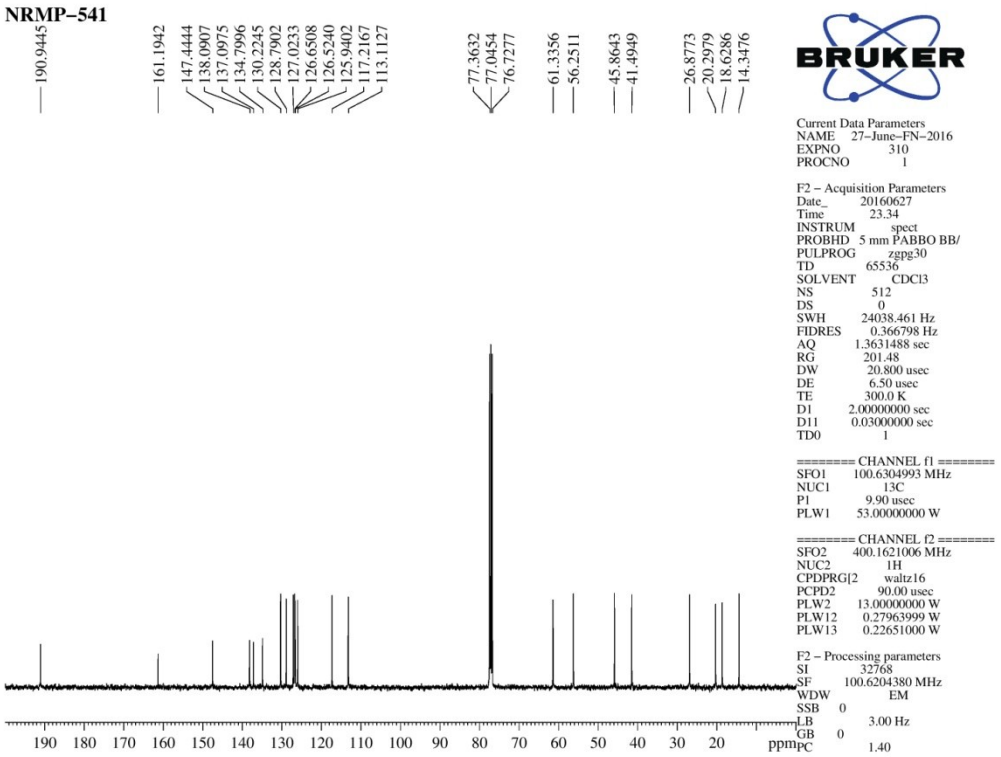

Figure 29. ^{13}C NMR spectra of 3e

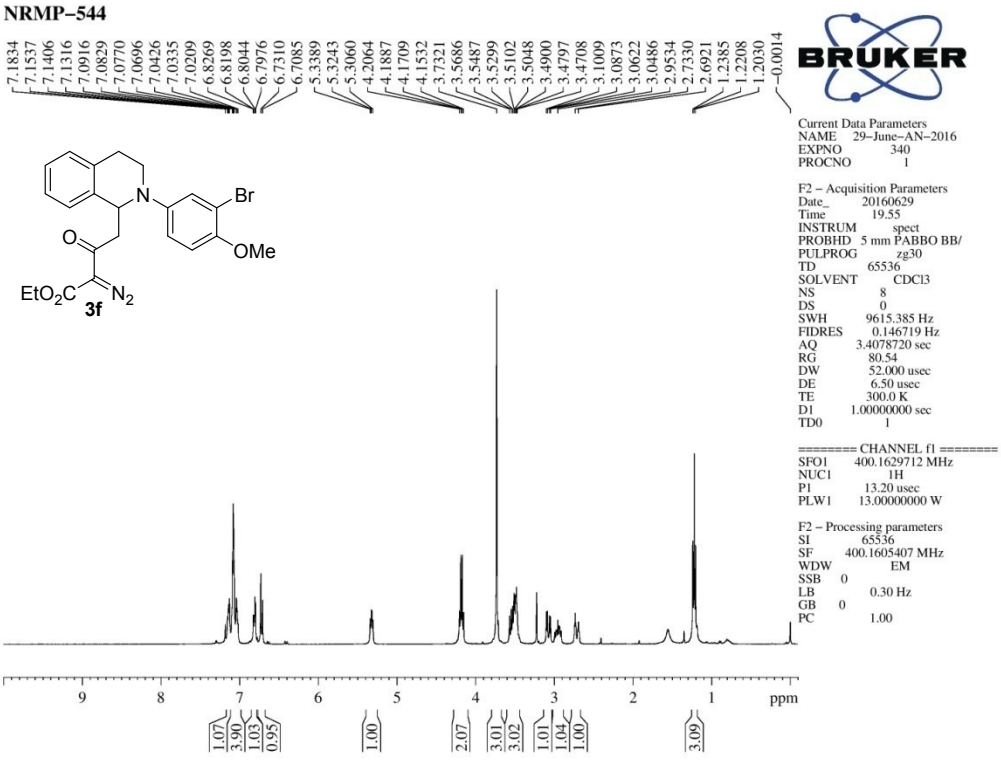

Figure 30. ^{1}H NMR spectra of 3f

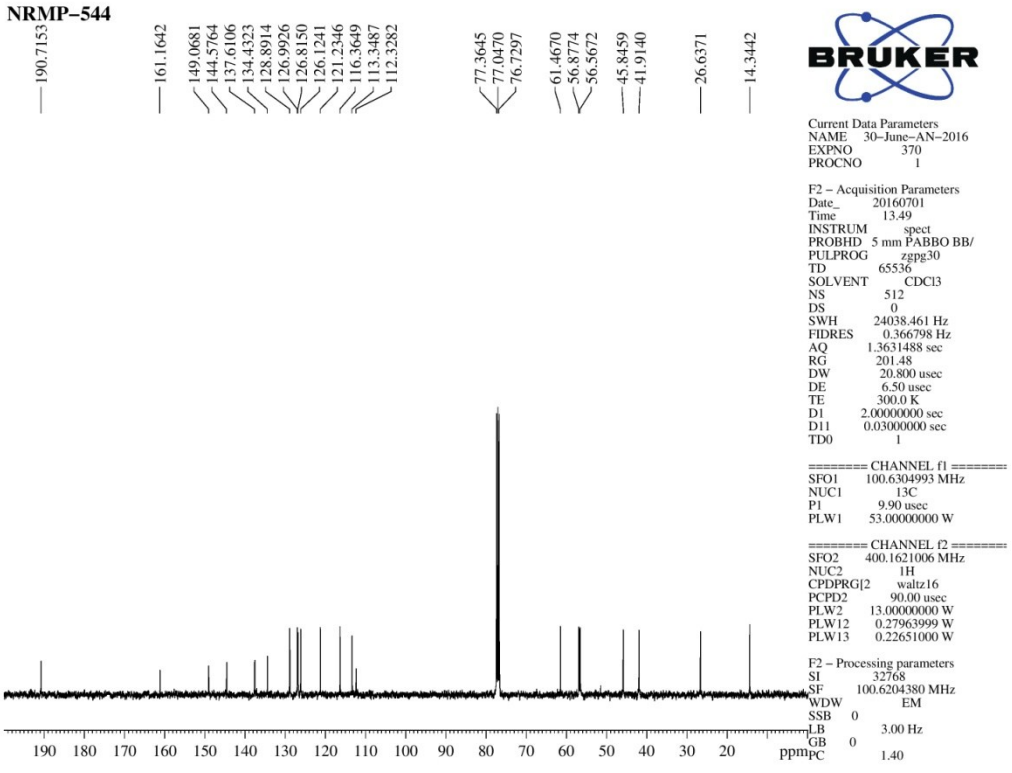

Figure 31. ^{13}C NMR spectra of 3f

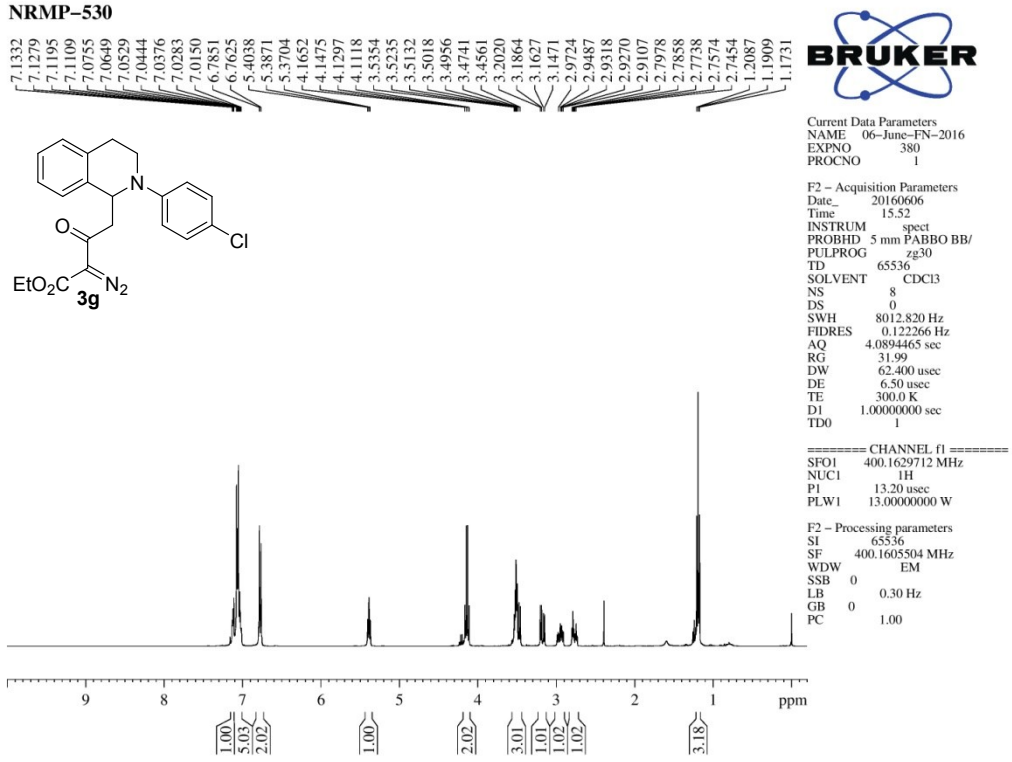

Figure 32. ^{1}H NMR spectra of 3g

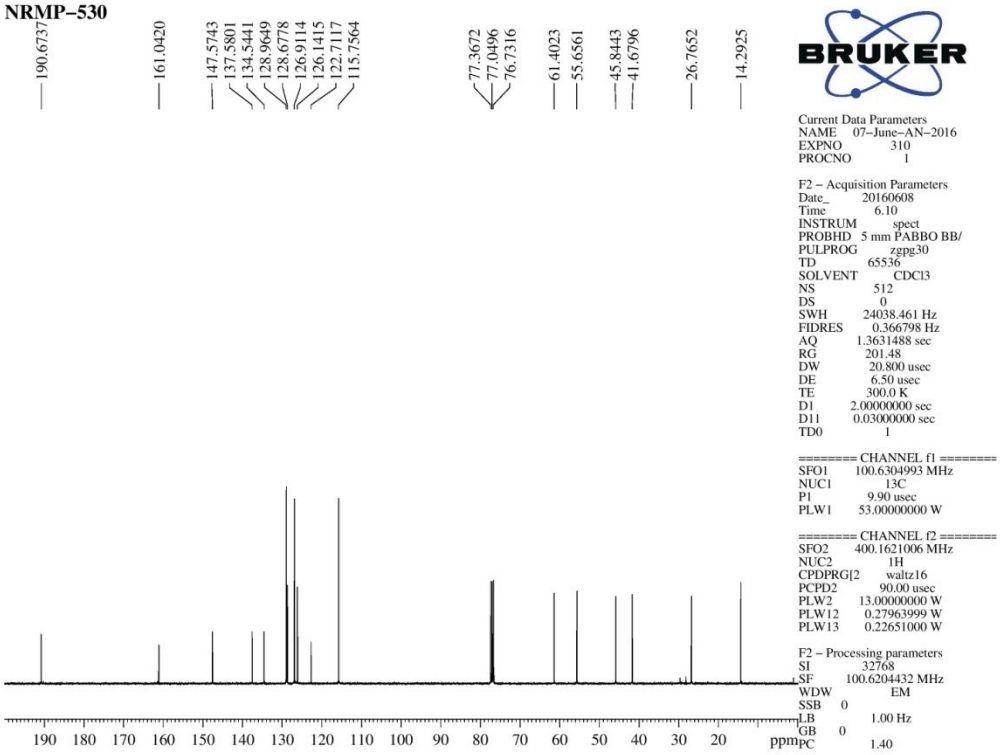

Figure 33. ^{13}C NMR spectra of 3g

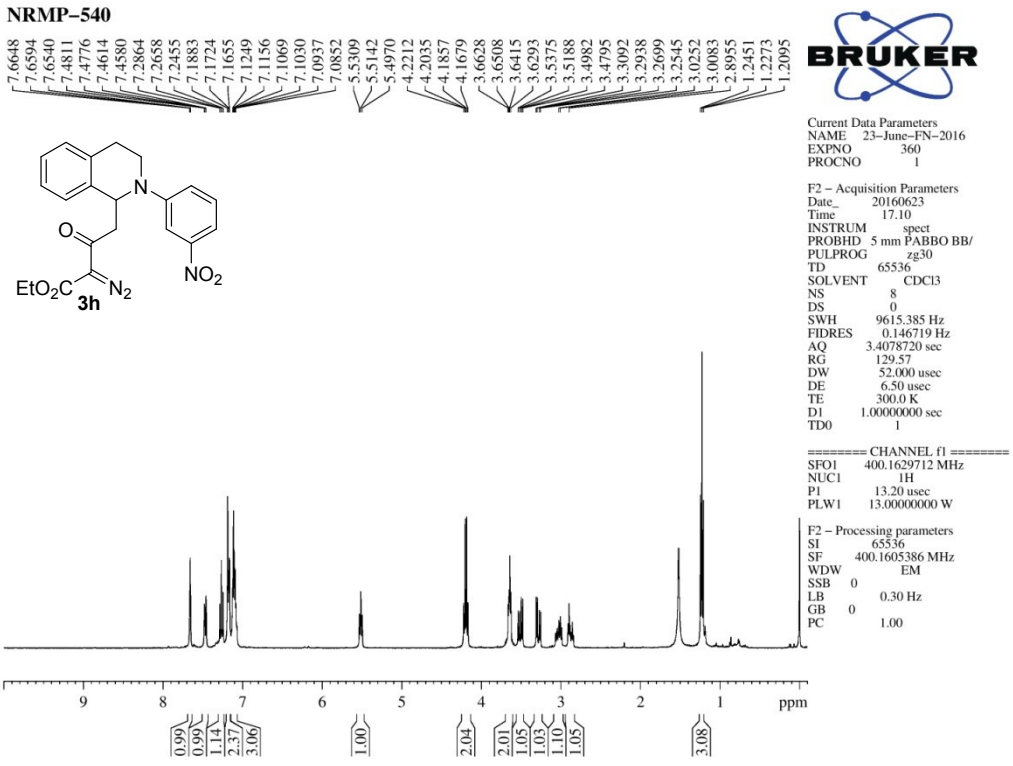

Figure 34. ^{1}H NMR spectra of 3h

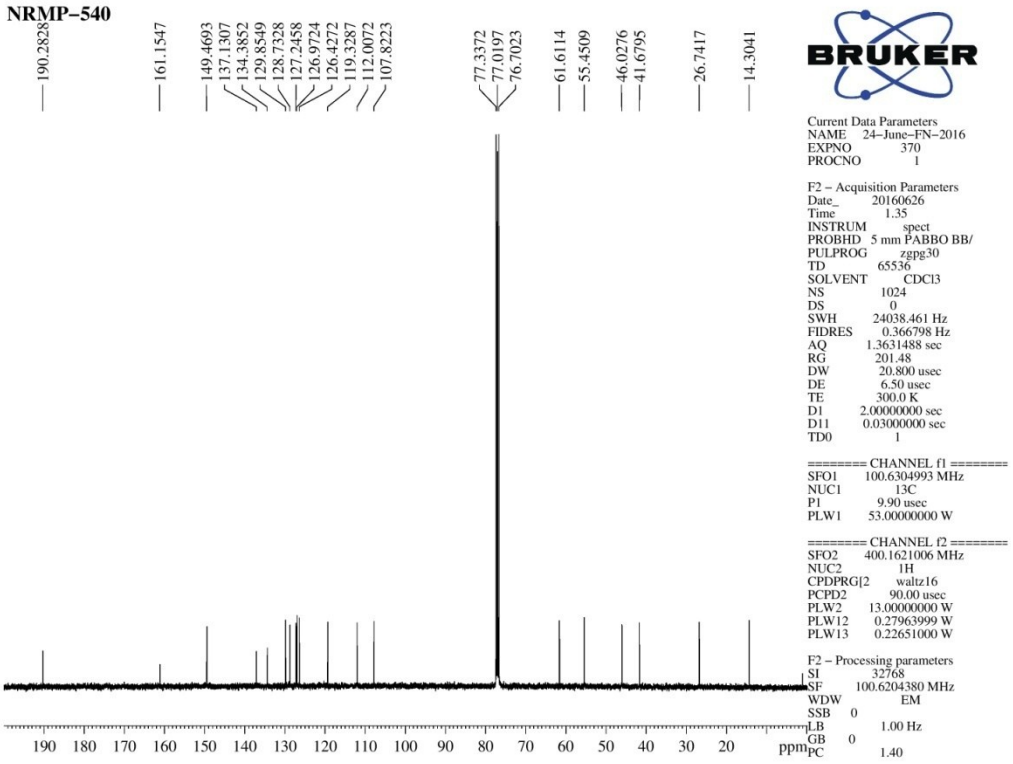

Figure 35. ^{13}C NMR spectra of 3h

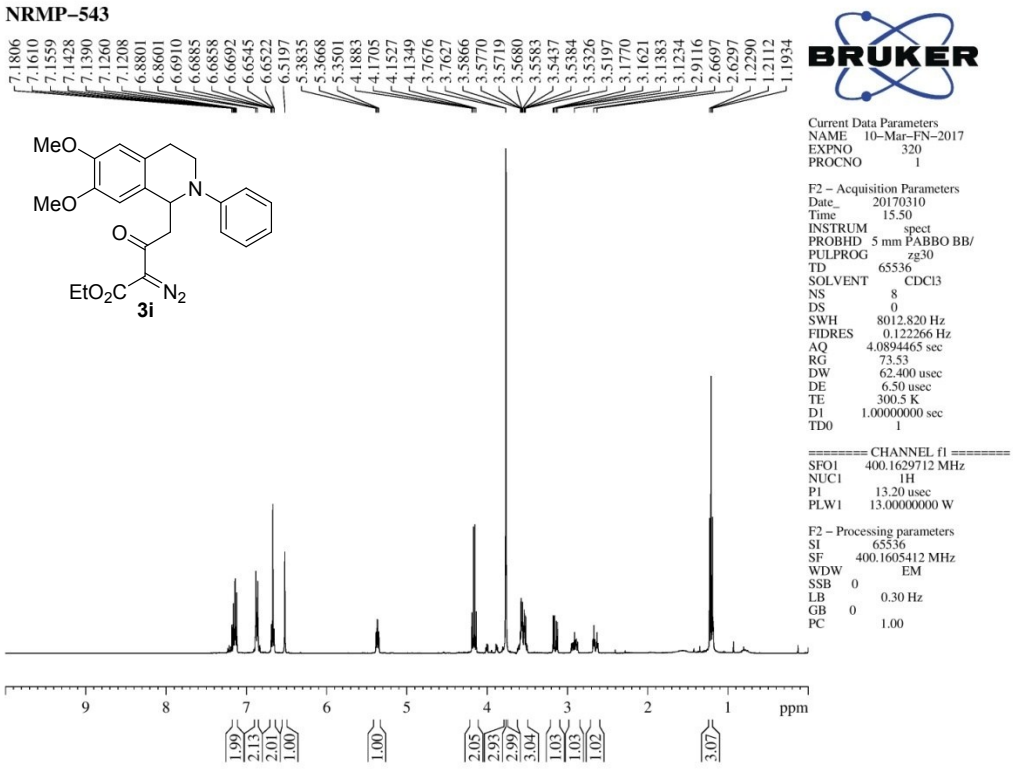

Figure 36. ^{1}H NMR spectra of 3i

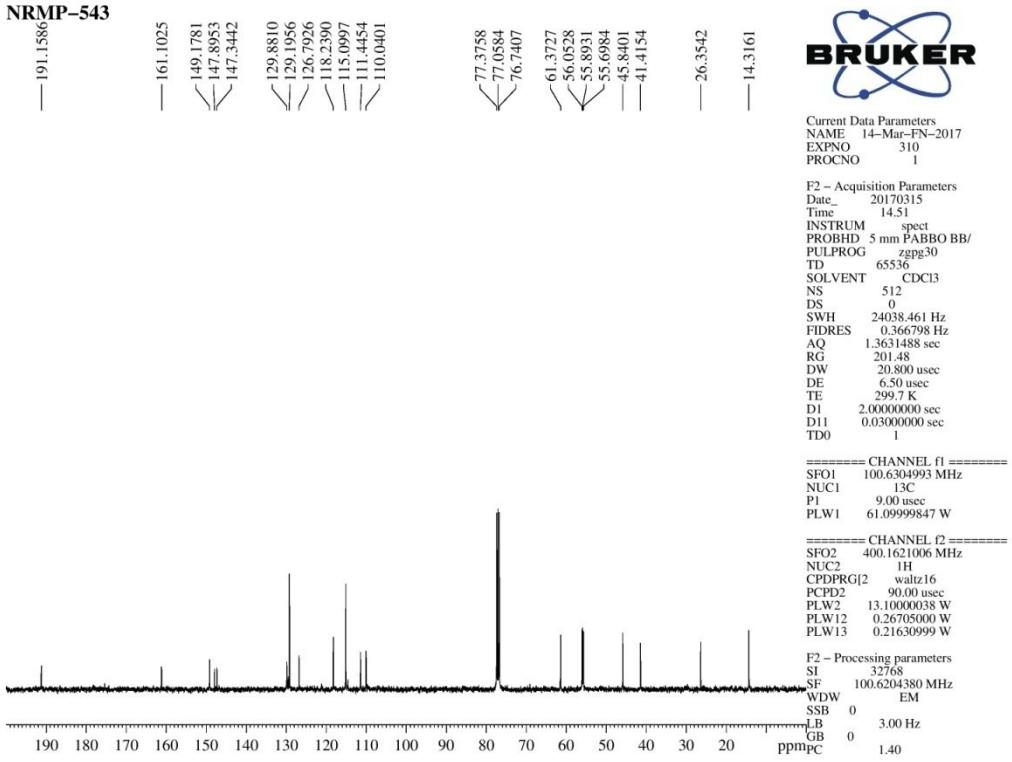

Figure 37. ^{13}C NMR spectra of 3i

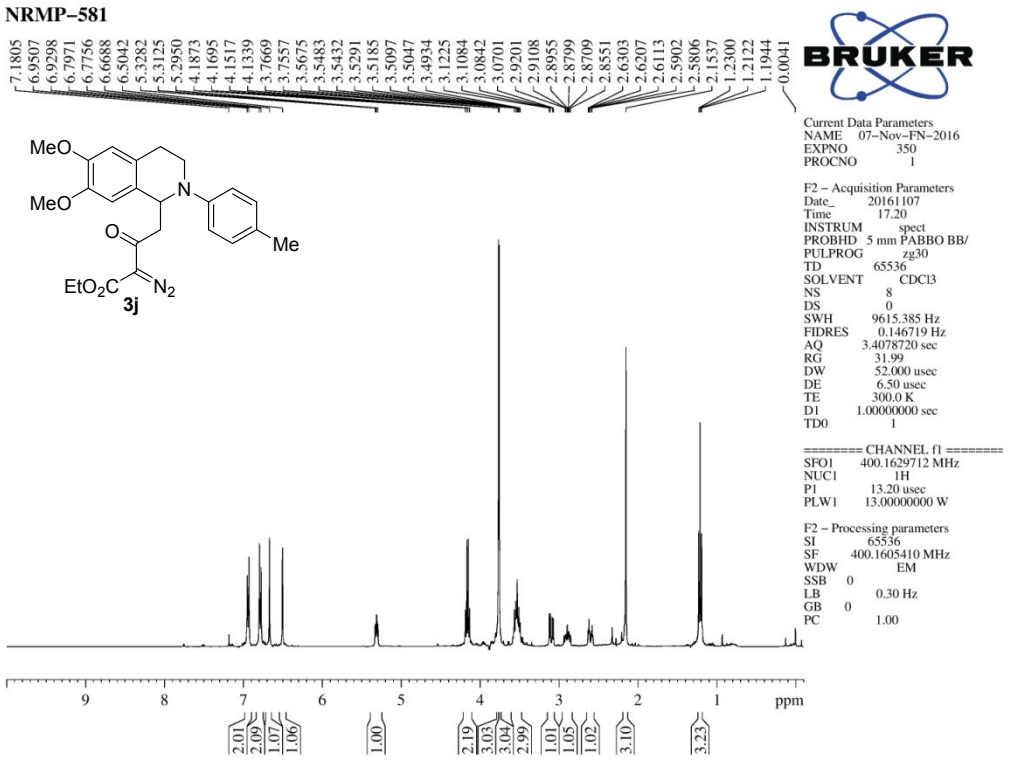

Figure 38. ^{1}H NMR spectra of 3j

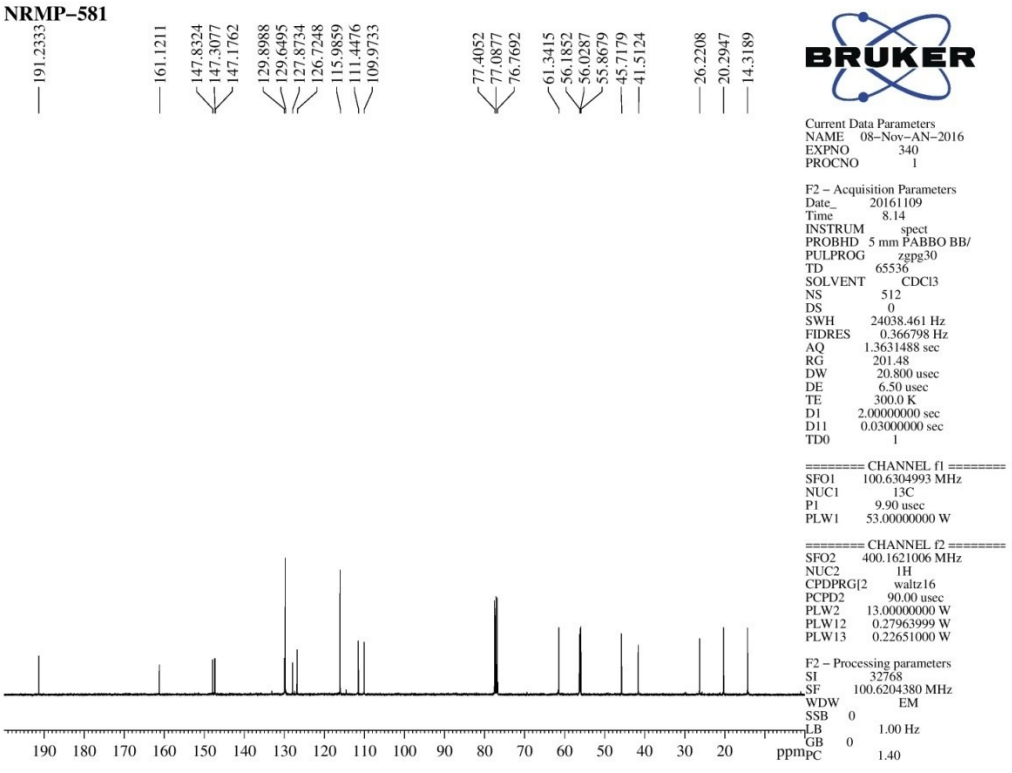

Figure 39. ^{13}C NMR spectra of 3j

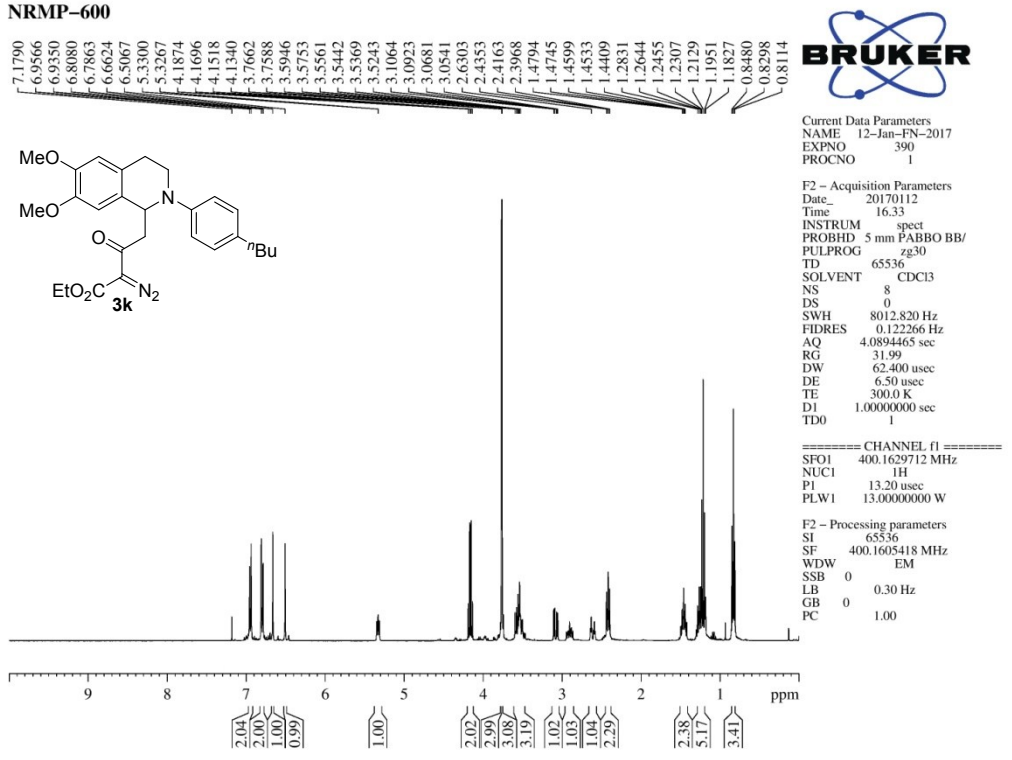

Figure 40. ^{1}H NMR spectra of 3k

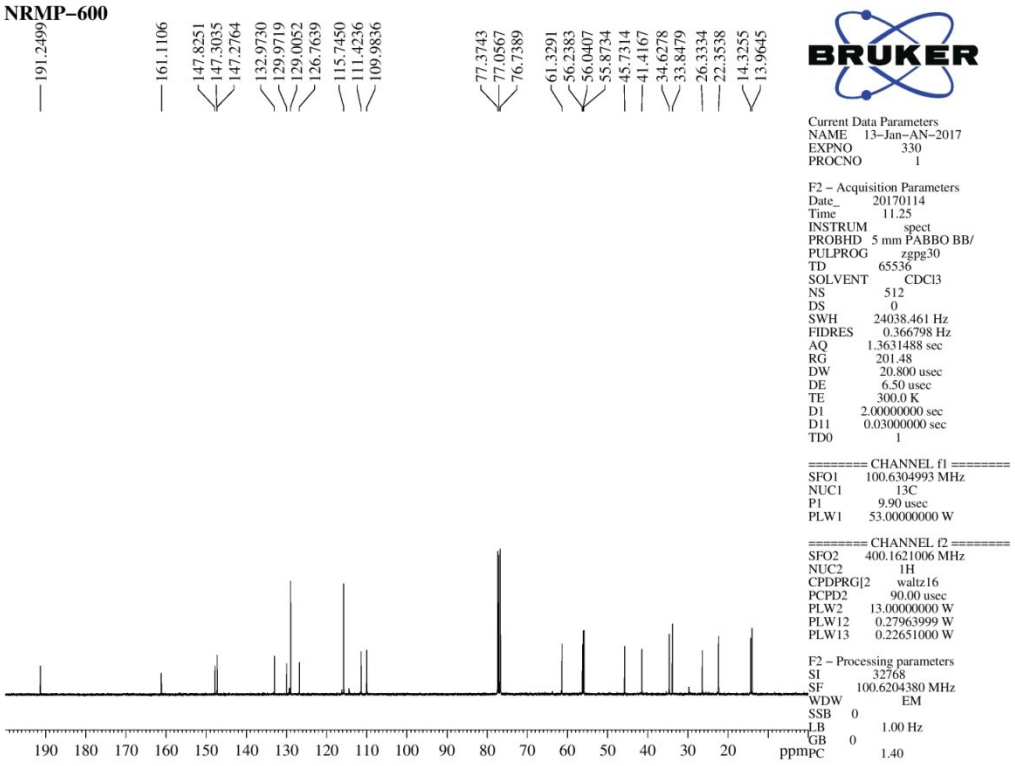

Figure 41. ^{13}C NMR spectra of 3k

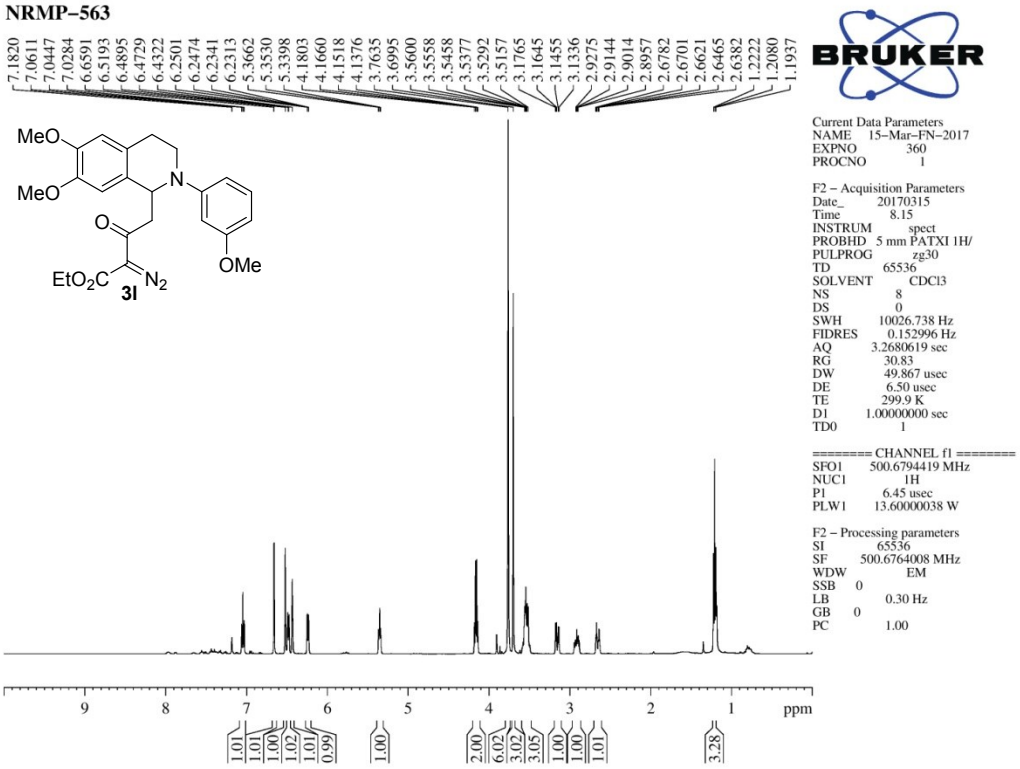

Figure 42. ^{1}H NMR spectra of 3l

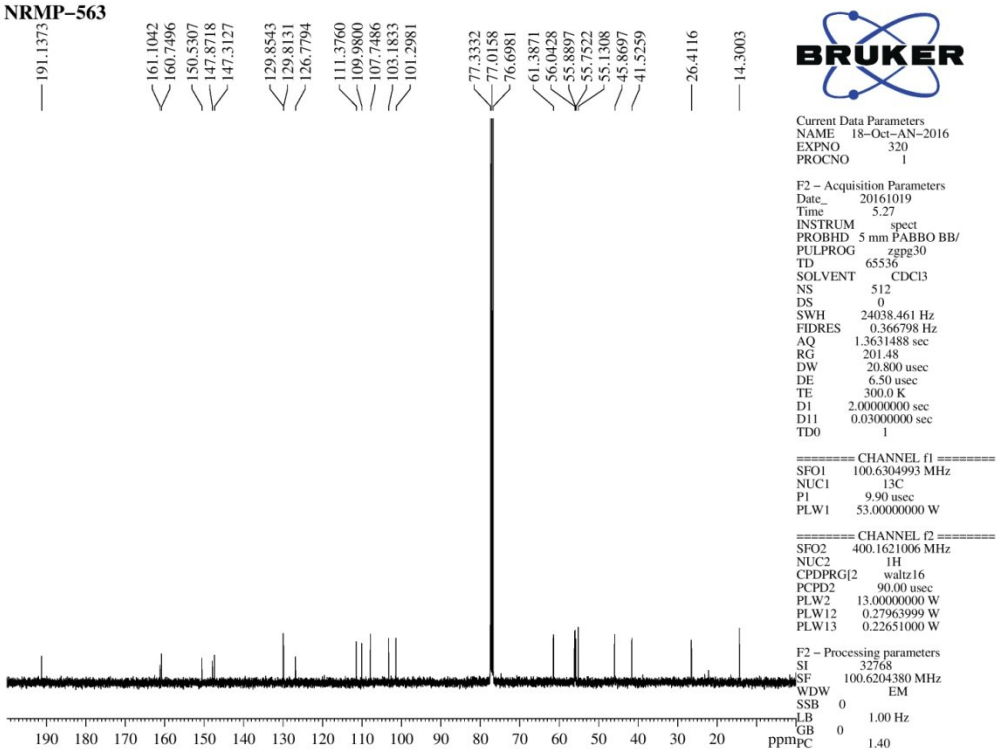

Figure 43. ^{13}C NMR spectra of 3l

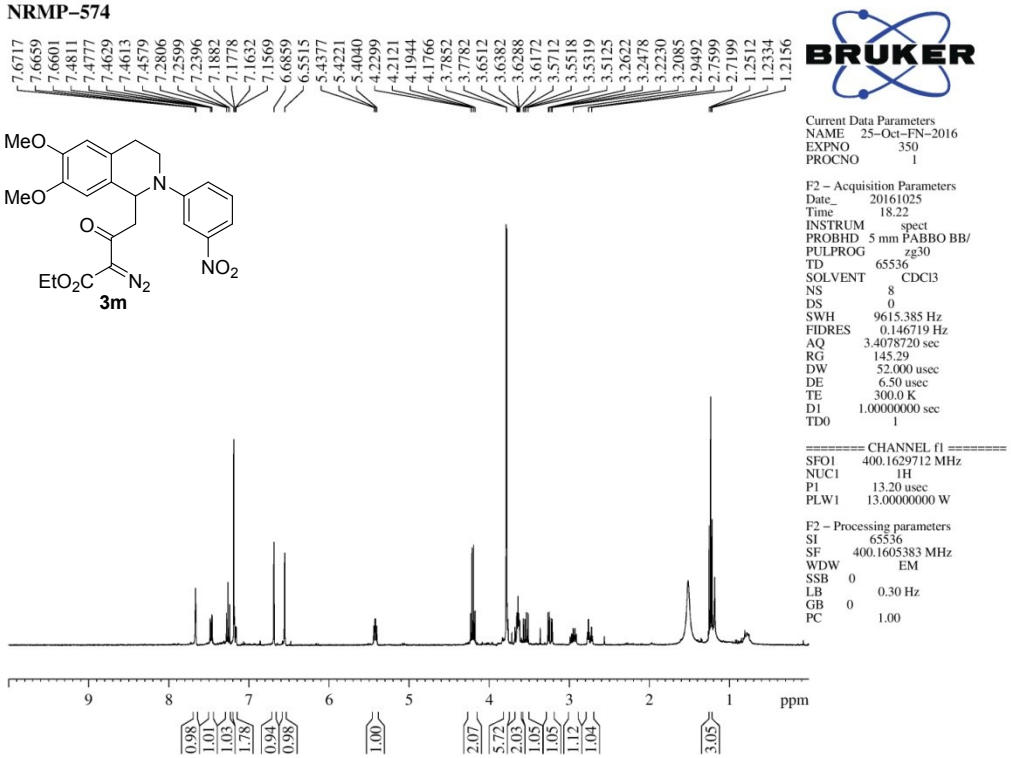

Figure 44. ^{1}H NMR spectra of 3m

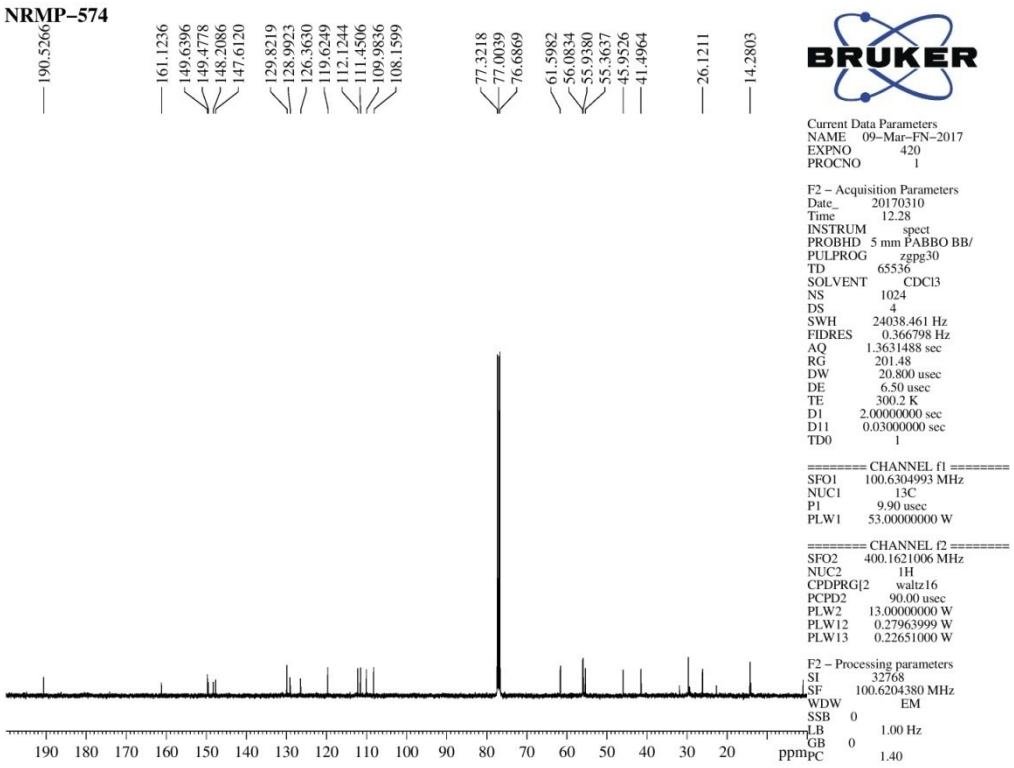

Figure 45. ^{13}C NMR spectra of 3m

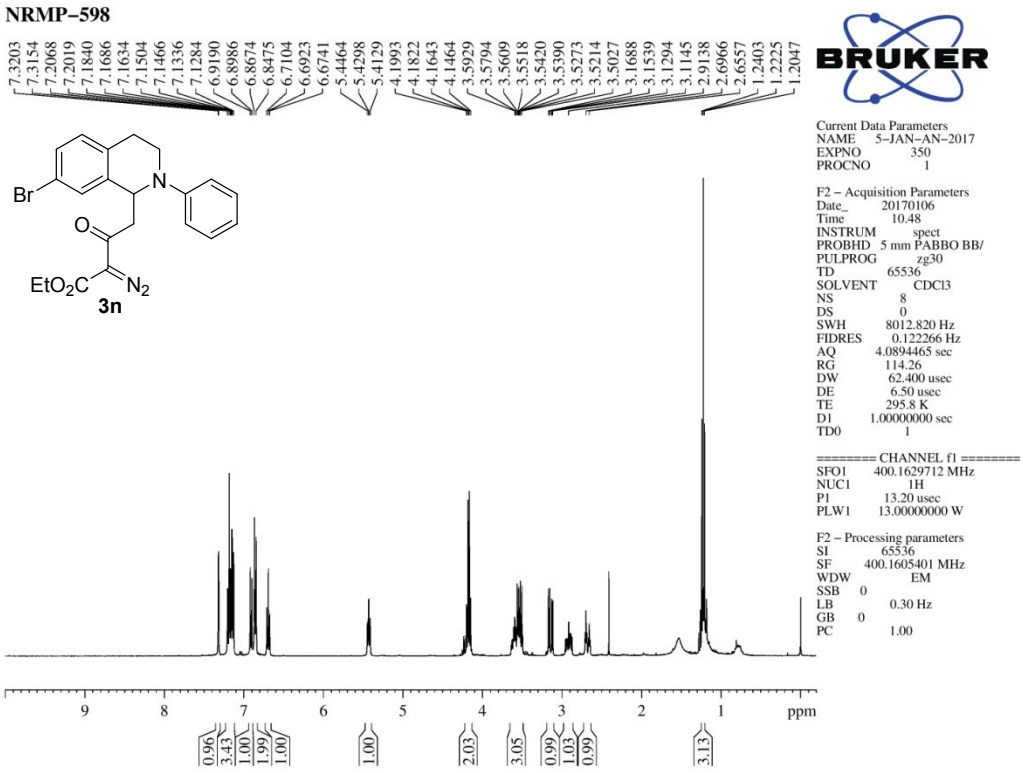

Figure 46. ^{1}H NMR spectra of 3n

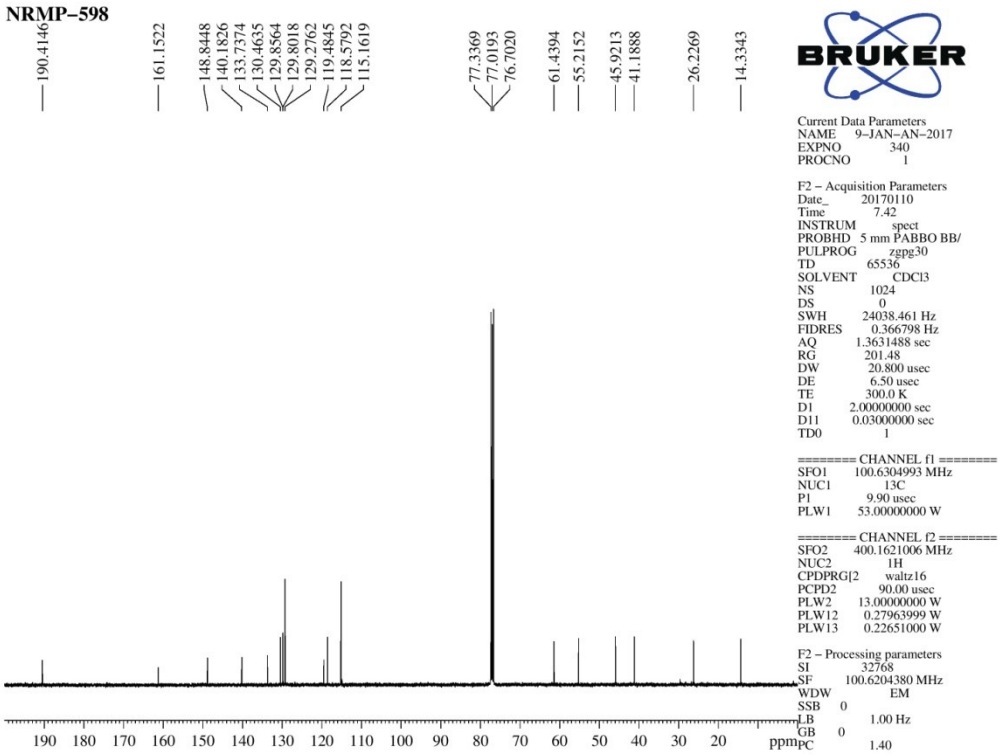

Figure 47. ^{13}C NMR spectra of 3n

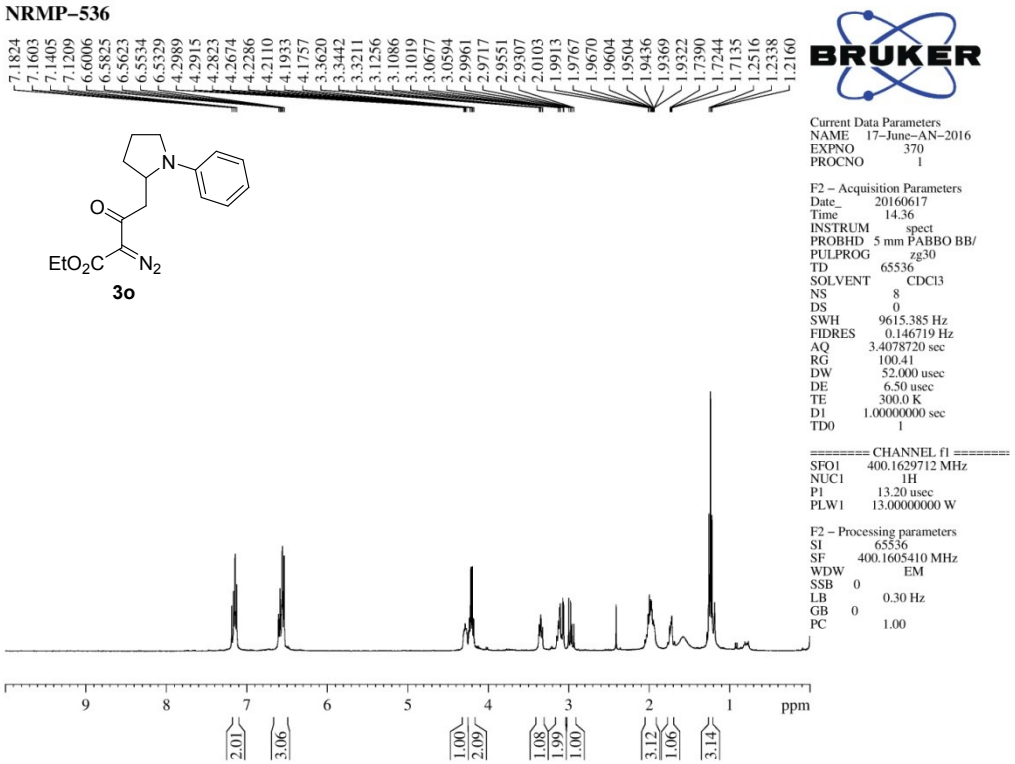

Figure 48. ^{1}H NMR spectra of 3o

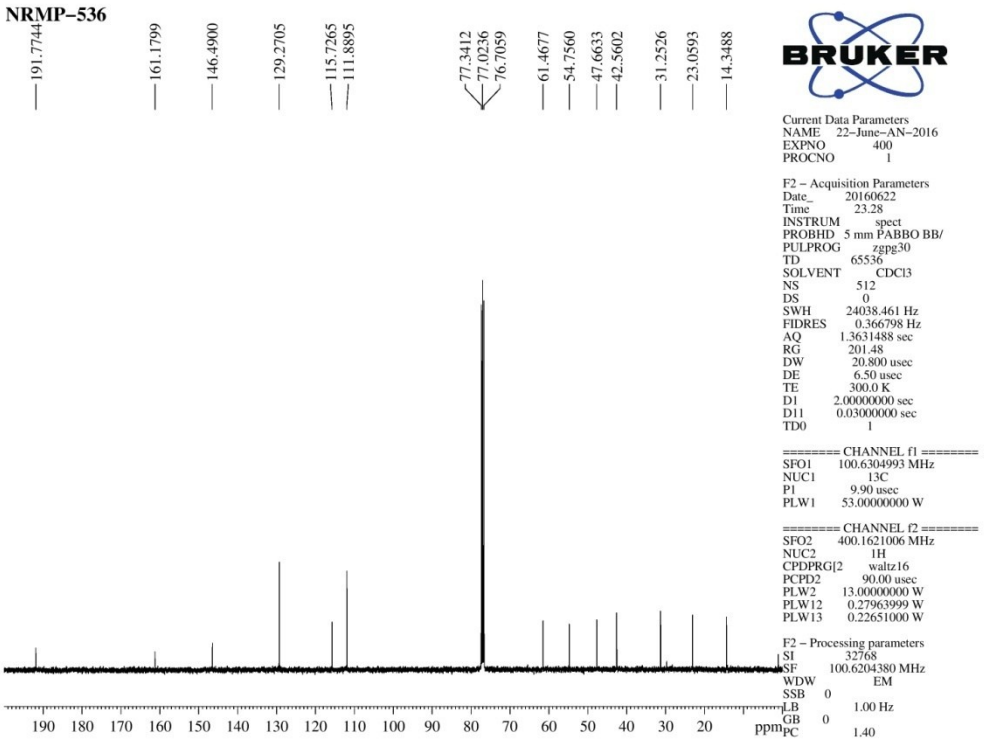

Figure 49. ^{13}C NMR spectra of 3o

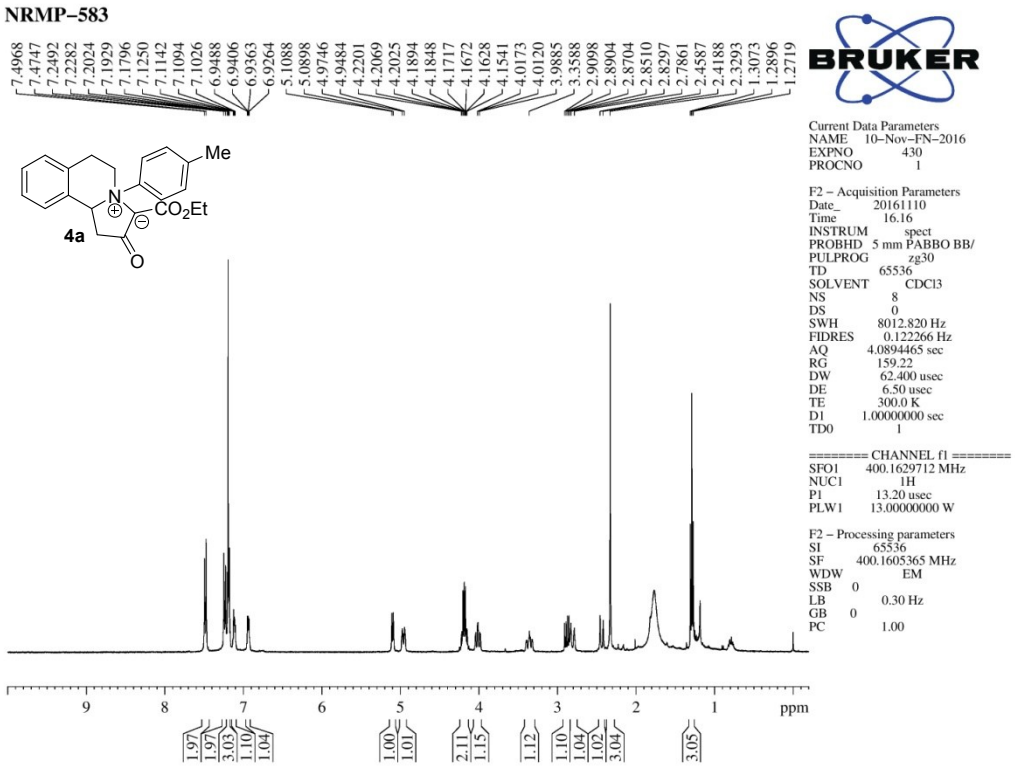

Figure 50. ^{1}H NMR spectra of 4a

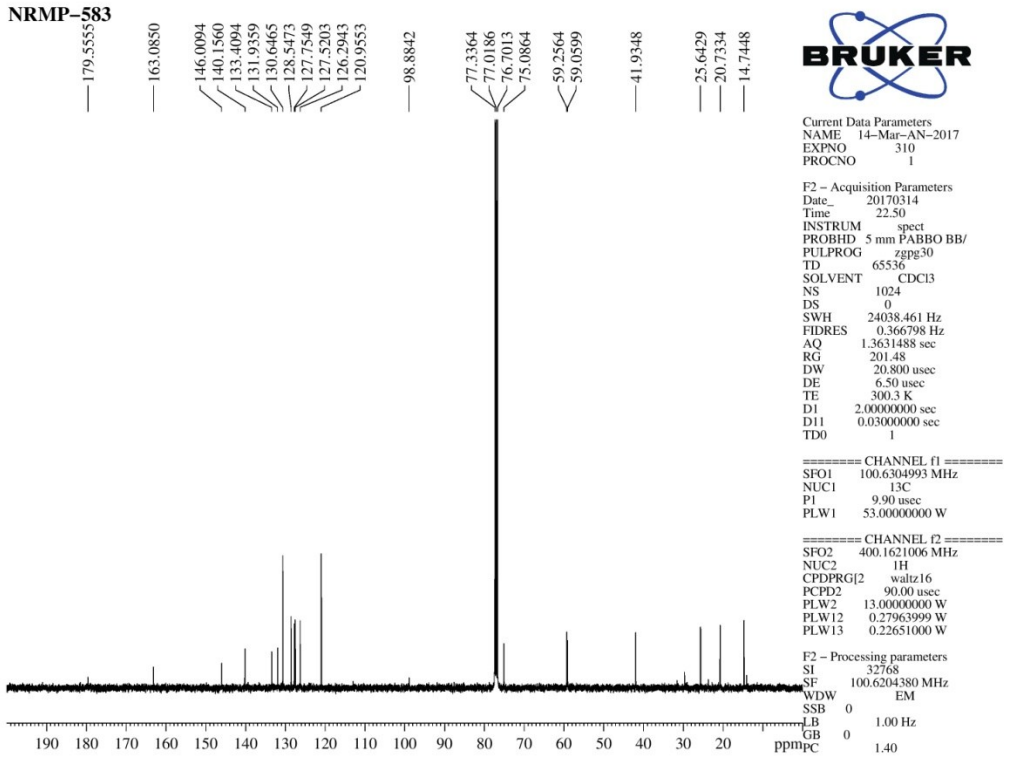

Figure 51. ^{13}C NMR spectra of 4a

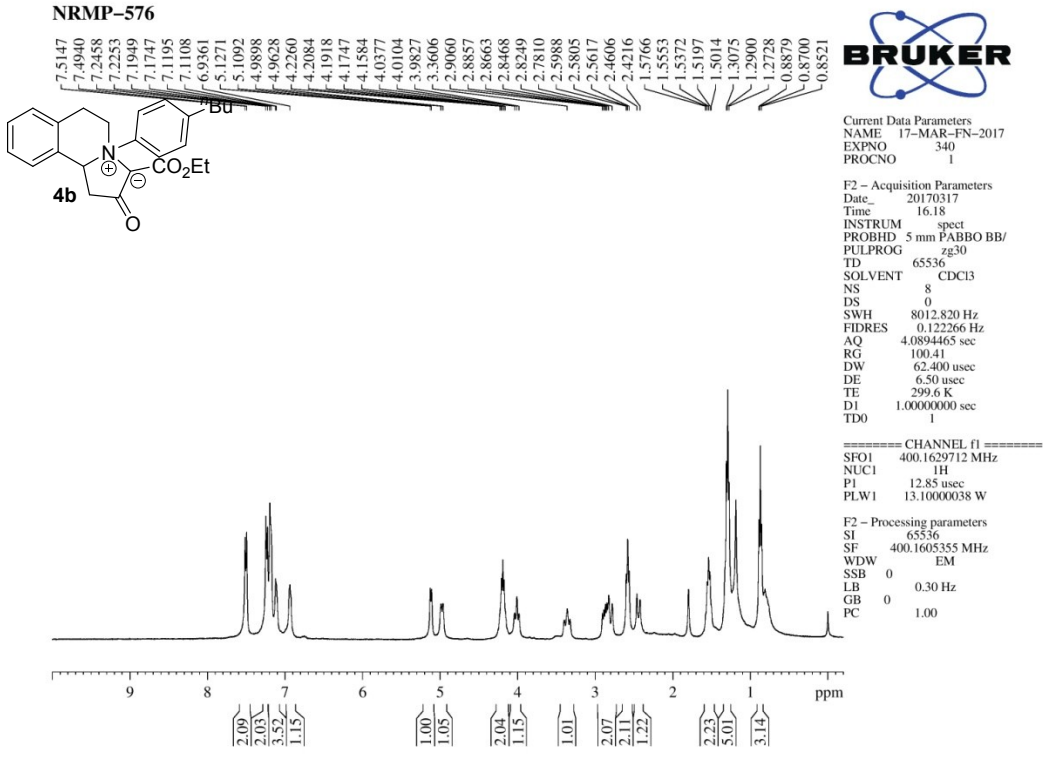

Figure 52. ^{1}H NMR spectra of 4b

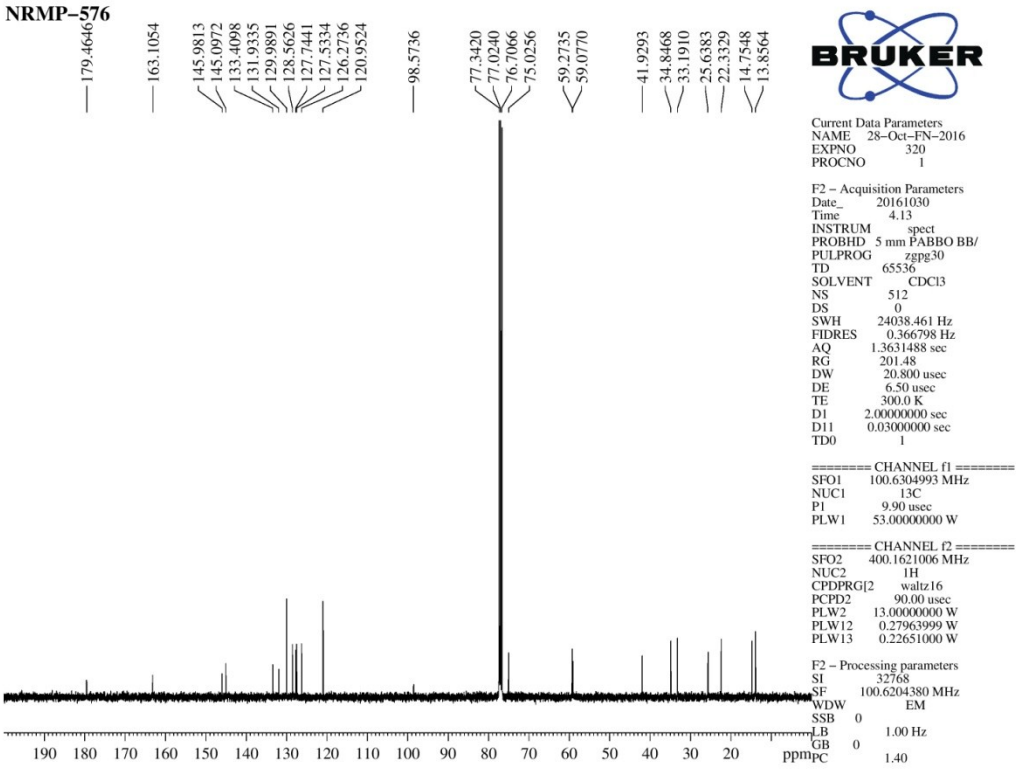

Figure 53. ^{13}C NMR spectra of 4b

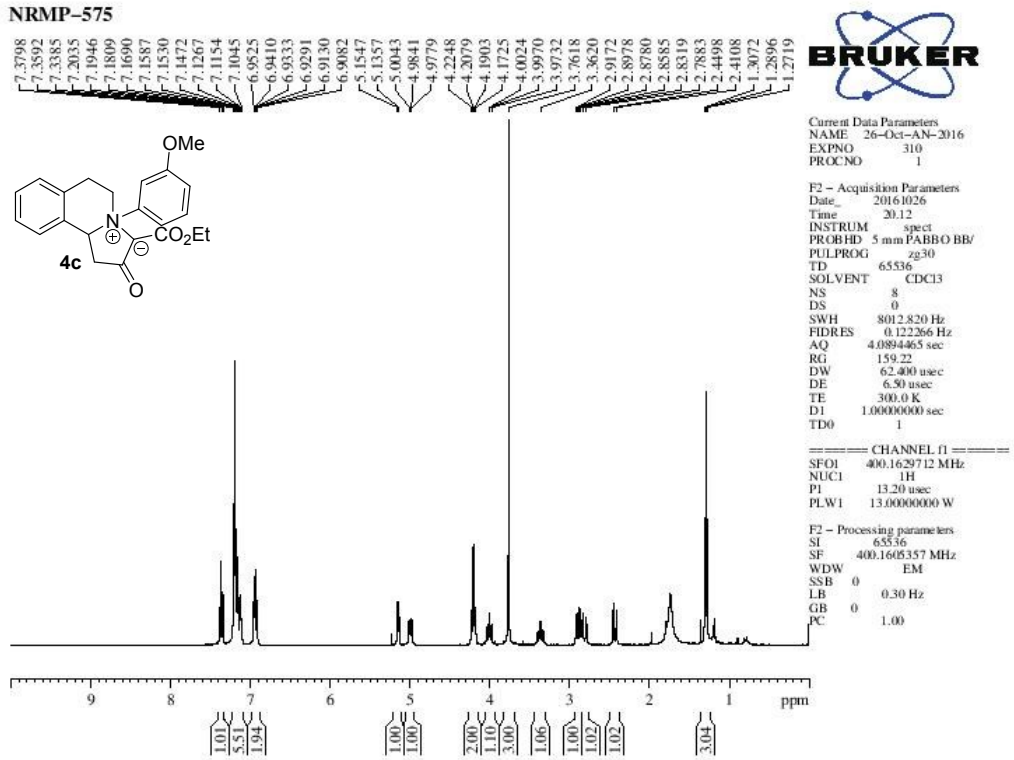

Figure 54. ^{1}H NMR spectra of 4c

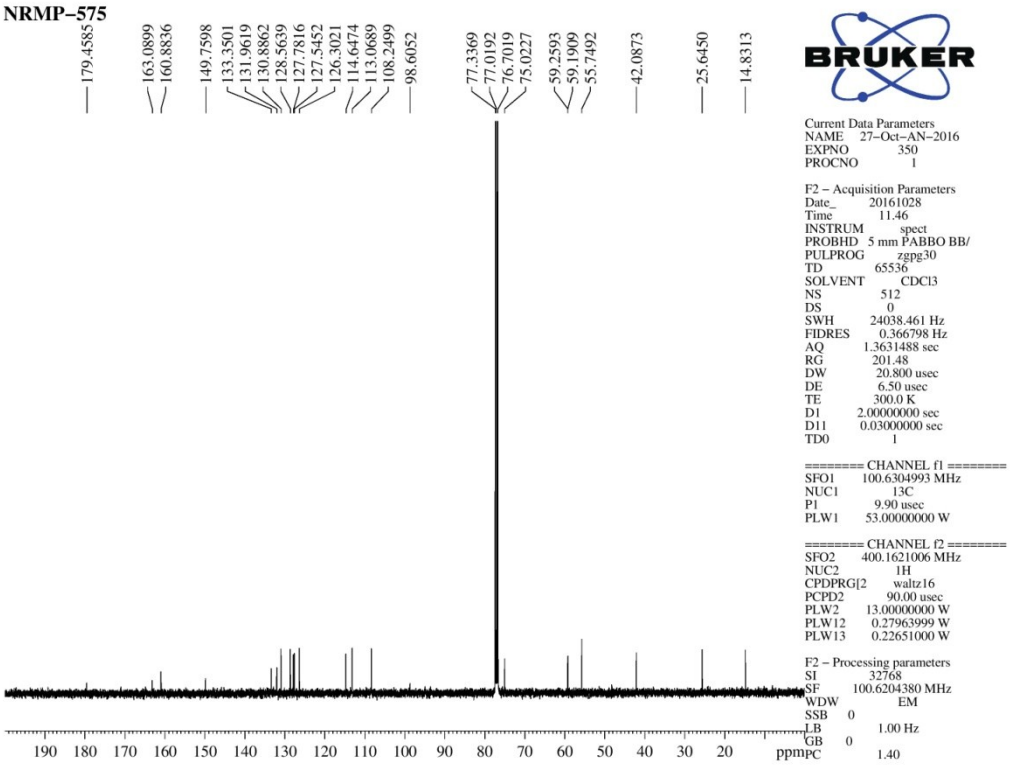

Figure 55. ^{13}C NMR spectra of 4c

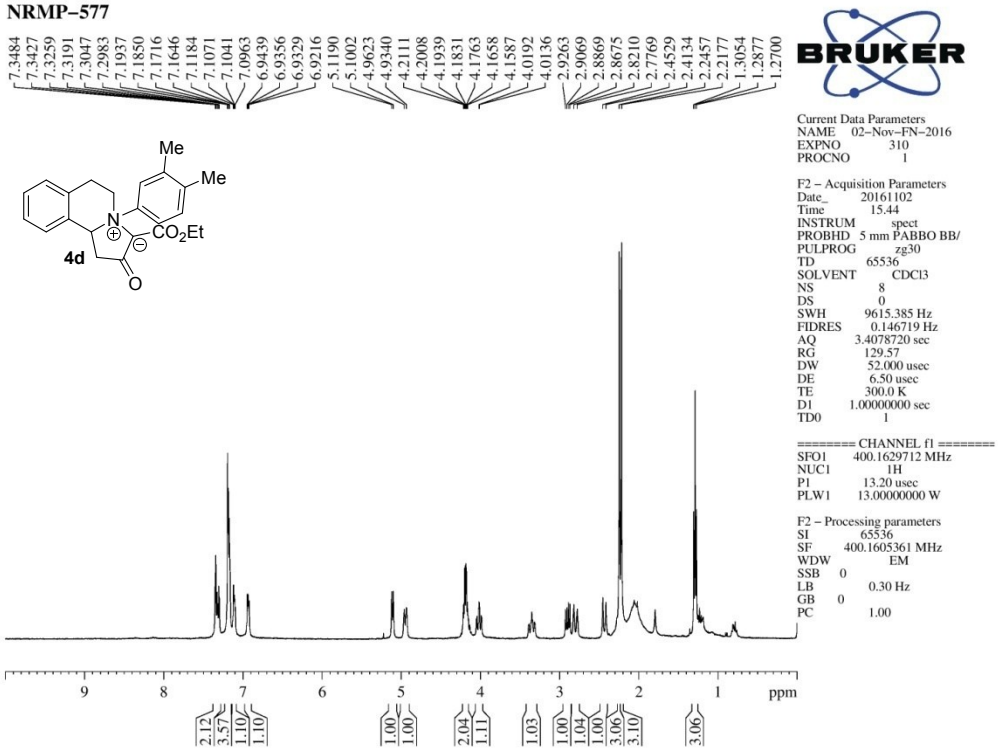

Figure 56. ^{1}H NMR spectra of 4d

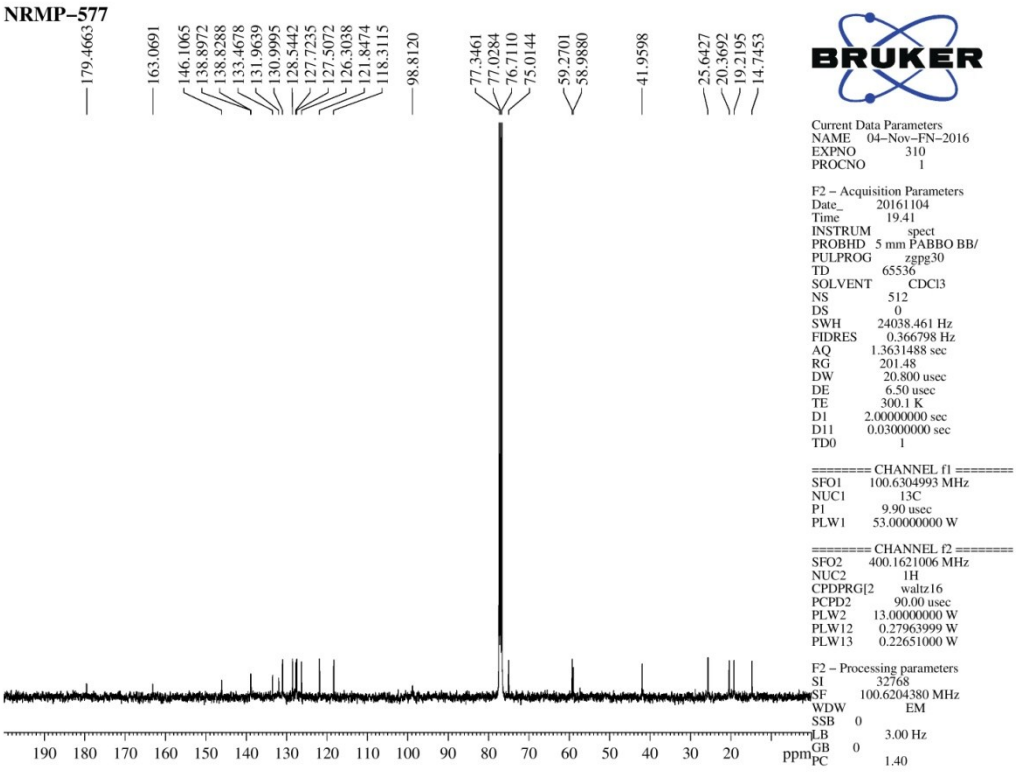

Figure 57. ^{13}C NMR spectra of 4d

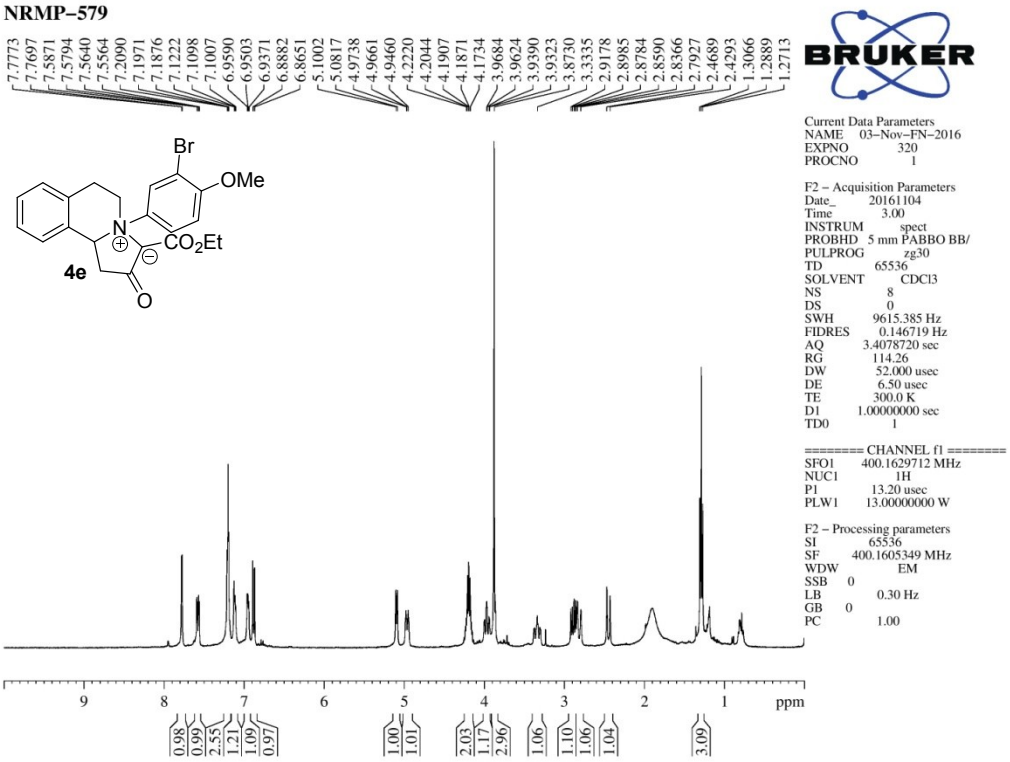

Figure 58. ^{1}H NMR spectra of 4e

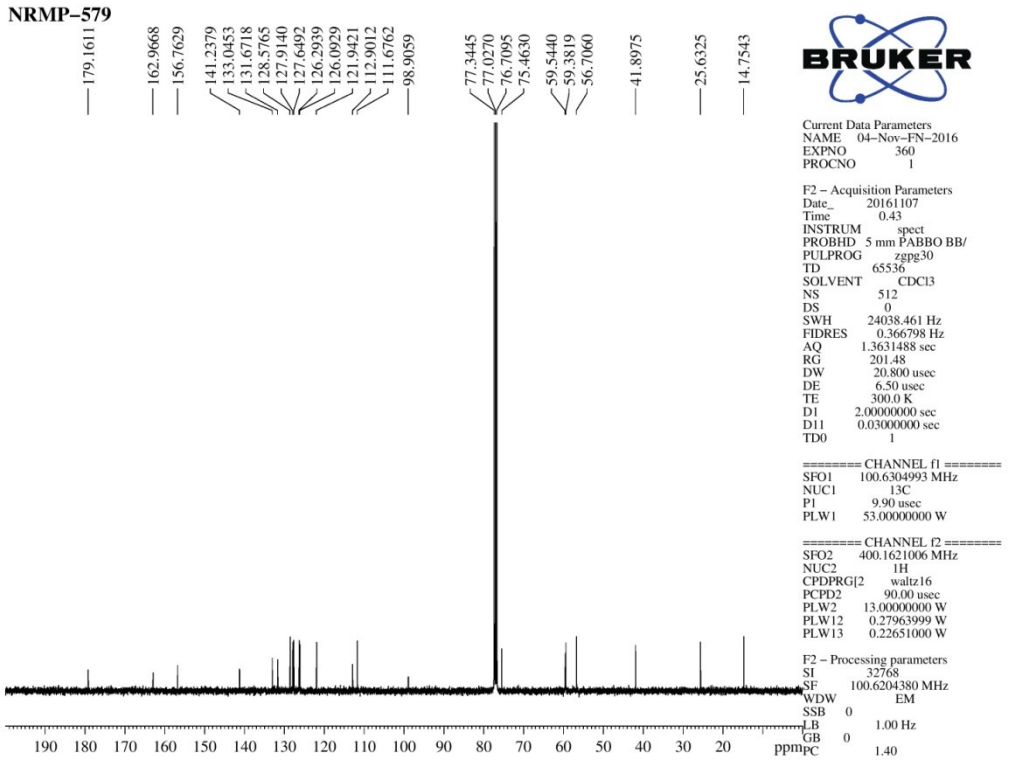

Figure 59. ^{13}C NMR spectra of 4e

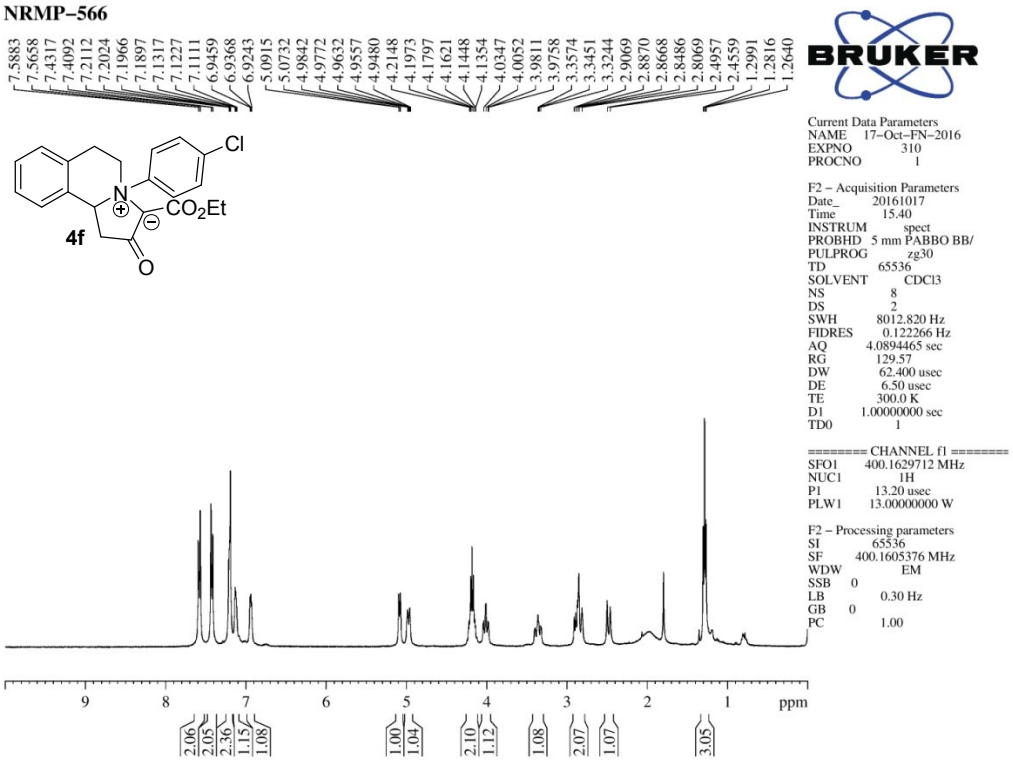

Figure 60. ^{1}H NMR spectra of 4f

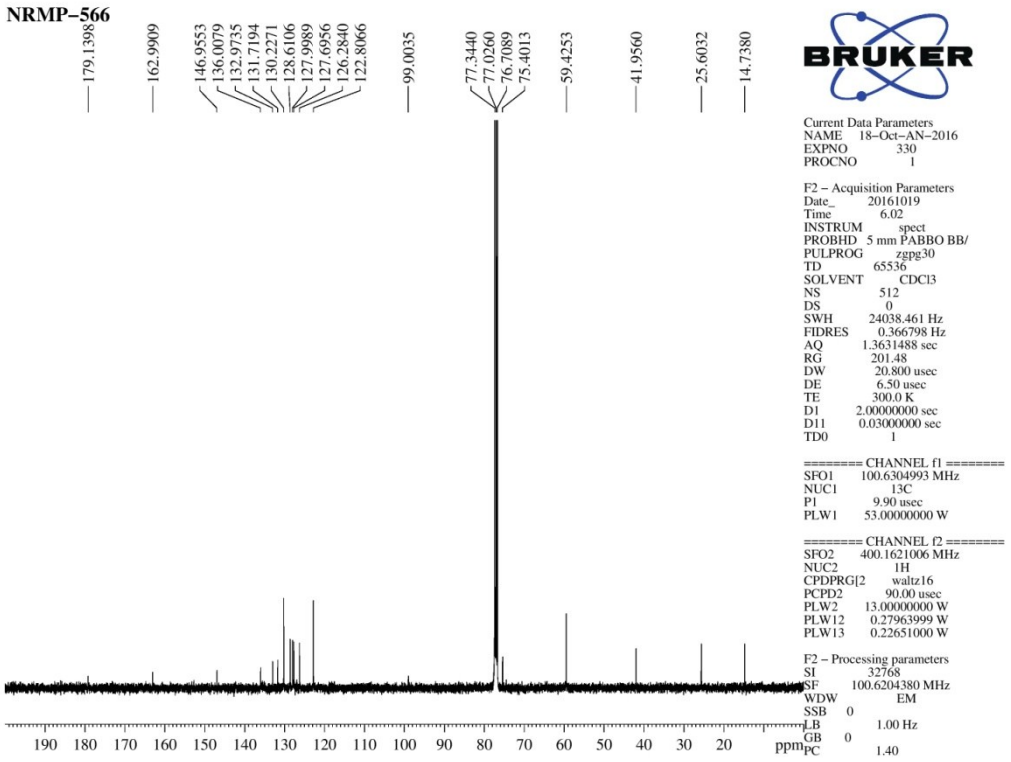

Figure 61. ^{13}C NMR spectra of 4f

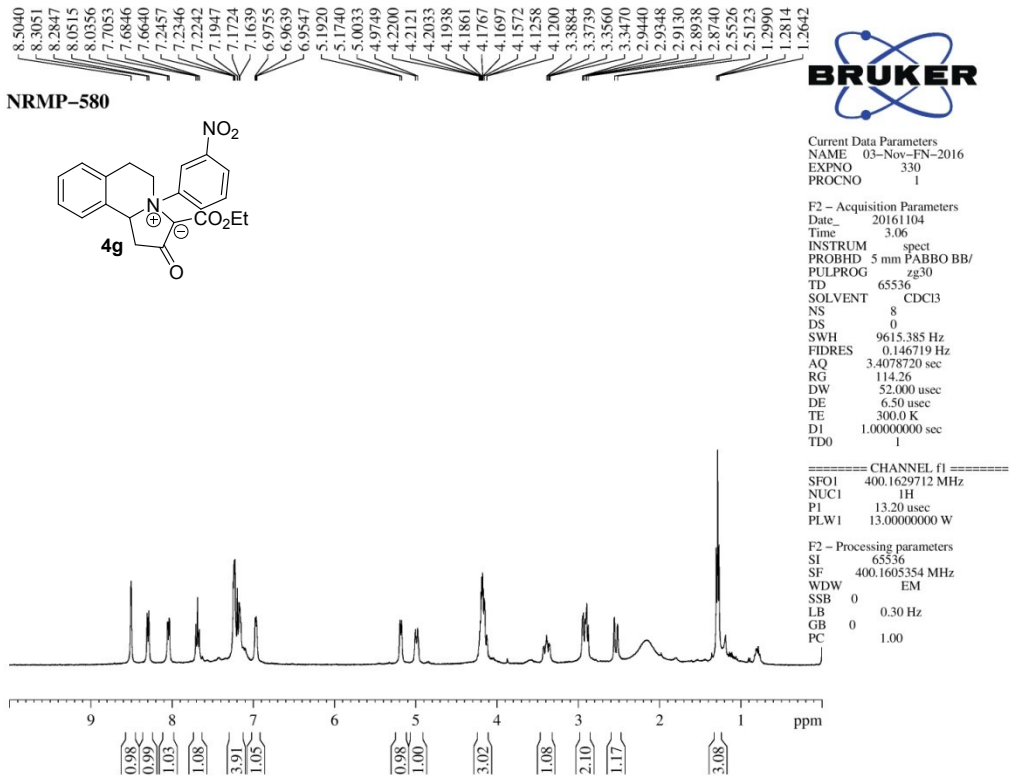

Figure 62. ^{1}H NMR spectra of 4g

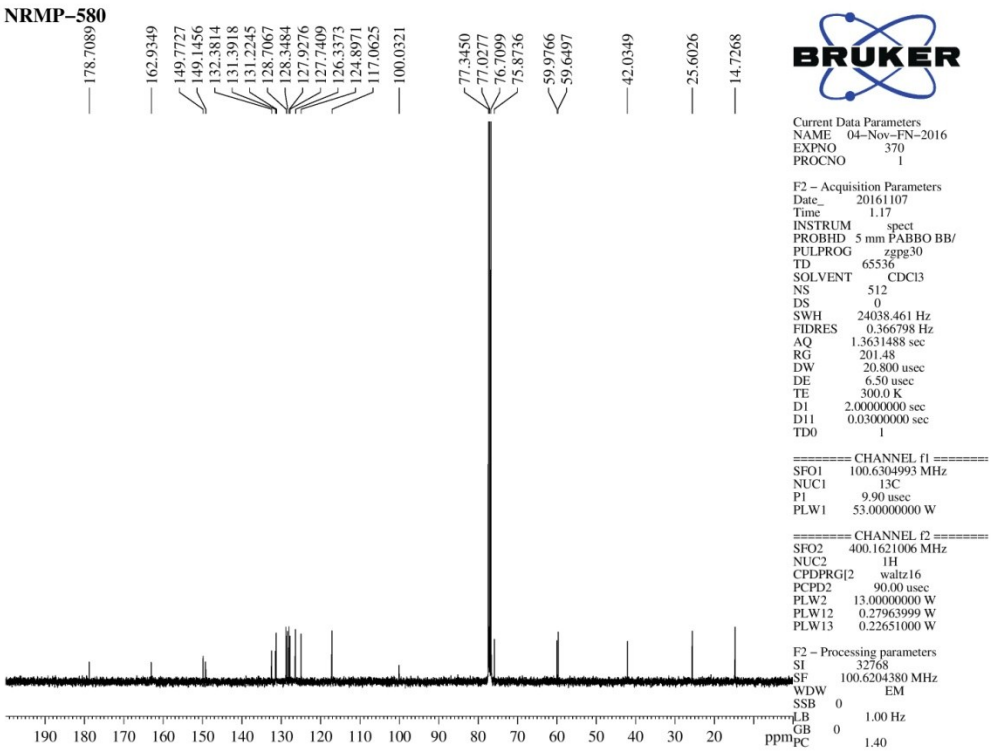

Figure 63. ^{13}C NMR spectra of 4g