Supporting Information

Silver-Mediated Formal [4π + 2σ] Cycloaddition Reactions of Bicyclobutanes with Nitrile Imines: Access to 2,3-Diazobicyclo[3.1.1]heptenes

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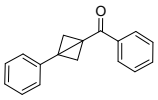
1. General information

Commercially available reagents were used without further purification unless otherwise stated. All reactions were carried out under argon atmosphere with dry solvents under anhydrous conditions. All solvents were purchased from Energy Chemical and stored over molecular sieves. Analytical thin-layer chromatography (TLC) was conducted with TLC plates (Silica gel 60 F254, Qingdao Haiyang) and visualization on TLC was achieved by UV light or Phosphomolybdic acid. Flash column chromatography was performed on silica gel 200-300 mesh with freshly distilled solvents. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 600, 400 and JEOL 400 MHz in $CDCl_3$ solvent. All chemical shifts in ^1H NMR spectra were given in parts per million (ppm) relative to the residual or $CDCl_3$ (7.26 ppm) as internal standards and coupling constants (*J*) were given in Hertz (Hz). ^{13}C NMR chemical shifts were reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) as internal standards. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constant (Hz), and integration. HRMS data were obtained by APCI-TOF method with Bruker mass spectrometer (MAXIS).

2. Preparation of substrates

2.1 Synthesis of BCB



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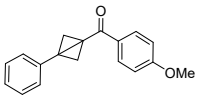

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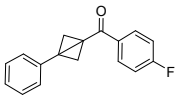

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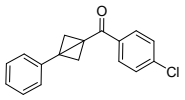

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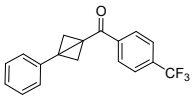

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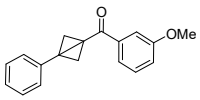

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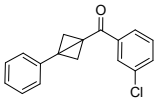

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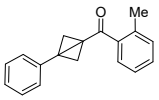

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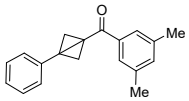

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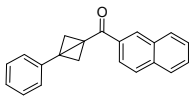

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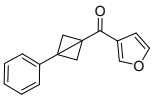

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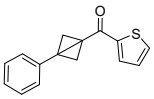

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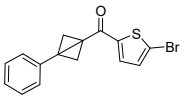

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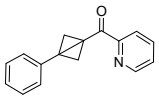

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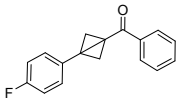

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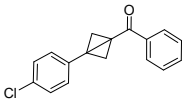

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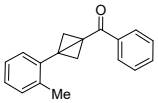

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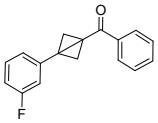

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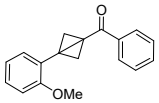
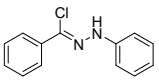


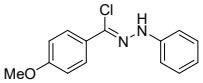
1s

1a-1s were prepared according to the literature procedure.[1]

2.2 Synthesis of hyrazonoyl chlorides



2a



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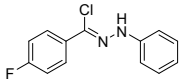

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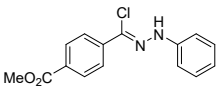

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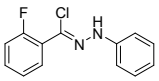

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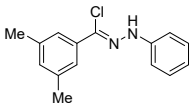

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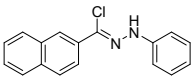

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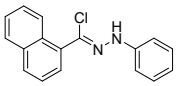

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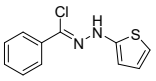

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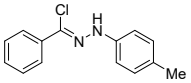

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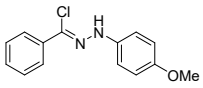

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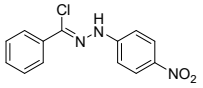

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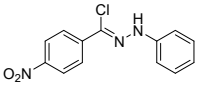
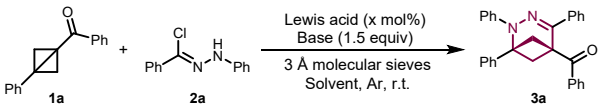


2m

2a-2m were prepared according to the literature procedure.[2,3]

3. Optimization of reaction conditions[a]

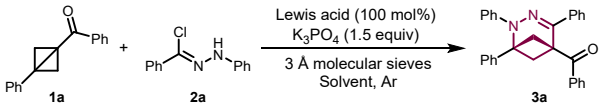
Table S1. Optimization of reaction conditions[a]



Entry	Lewis acid	Base	Solven	Yield
1	$Sc(OTf)_3$ (20)	K_3PO_4	DCM	trace
2	AgOTf (20)	K_3PO_4	DCM	12
3	$Eu(OTf)_3$ (20)	K_3PO_4	DCM	NR
4	$AgBF_4$ (20)	K_3PO_4	DCM	15
5	$AgBF_4$ (50)	K_3PO_4	DCM	20
6	$AgBF_4$ (100)	K_3PO_4	DCM	34
7	$AgBF_4$ (100)	Na_2CO	DCM	9
8	$AgBF_4$ (100)	K_2CO_3	DCM	7
9	$AgBF_4$ (100)	Et_3N	DCM	NR
10	$AgBF_4$ (100)	K_3PO_4	CH_3C	NR
11	$AgBF_4$ (100)	K_3PO_4	THF	NR
12	$AgBF_4$ (100)	K_3PO_4	DCE	33
13[b]	$AgBF_4$ (100)	K_3PO_4	DCM	40
14[b,c]	$AgBF_4$ (100)	K_3PO_4	DCM	65
15[b–d]	$AgBF_4$ (100)	K_3PO_4	DCM	64
16[b–d]	—	K_3PO_4	DCM	NR
17[b–d]	$AgBF_4$ (100)	—	DCM	21
18[b–e]	$AgBF_4$ (100)	K_3PO_4	DCM	23

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), Lewis acid (20–100 mol%), base (0.15 mmol), solvent (1 mL), 3 Å molecular sieves (50 mg), Ar atmosphere, room temperature (r.t.), 16 h. Yields were determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. DCM, dichloromethane; NR, no reaction. [b] Reaction temperature, −10 °C. [c] 3 equiv of **1a**. [d] Reaction time, 1 h. [e] Without 3 Å molecular sieves.

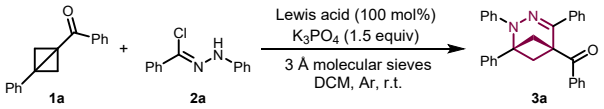
Table S2. The screening of the temperature[a]



Entry	Temperature	Yield
1	−30 °C	67
2	−50 °C	65

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), $AgBF_4$ (100 mol%), K_3PO_4 (0.15 mmol), DCM (1 mL), 3 Å molecular sieves (50 mg), Ar atmosphere, 1 h. Yields were determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

Table S3. The screening of the amount of **2a**[a]



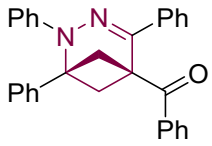
Entry	**1a**:**2a**	Yield
1	1:2	18
2	1:3	18

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 or 0.3 mmol), $AgBF_4$ (100 mol%), K_3PO_4 (0.15 mmol), DCM (1 mL), 3 Å molecular sieves (50 mg), Ar atmosphere, −10 °C, 1 h. Yields were determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

4. General procedure for reactions

To a 10 mL reaction vial equipped with a magnetic stir bar was added compounds **1** (0.3 mmol, 3.0 equiv), **2** (0.1 mmol, 1.0 equiv), $AgBF_4$ (100 mol%), K_3PO_4 (1.5 equiv), 3 Å molecular sieves (50 mg), and the tube was evacuated and backfilled with argon three times, dry DCM (1 mL) was added under argon atmosphere. The mixture was stirred at -10 °C for 1 h. Upon completion of reaction, the reaction mixture was filtered through celite pad and concentrated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel to afford **3**.

Phenyl((1r,5r)-1,2,4-triphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)methanone (3a)



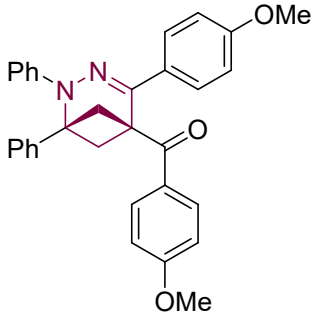
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:1). yellow solid, 18 mg, 42% yield. M. P. 150–151 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.76 (d, *J*=7.0, 2H), 7.47 (d, *J*=6.8, 2H), 7.38 (t, *J*=7.4, 1H), 7.31 – 7.18 (m, 5H), 7.18 – 7.01 (m, 7H), 6.98 (t, *J*=7.3, 1H), 6.81 (d, *J*=7.2, 2H), 2.73 – 2.66 (m, 2H), 2.66 – 2.59 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.6, 152.6, 146.0, 141.1, 137.2, 134.9, 133.2, 129.1, 128.4, 128.4, 128.2, 128.0, 127.9, 127.1, 126.7, 126.3, 125.0, 67.3, 52.7, 33.6.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}N_2O$ $[M + H]^+$ 429.1961, found 429.1964.

(4-Methoxyphenyl)((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)methanone (3b)



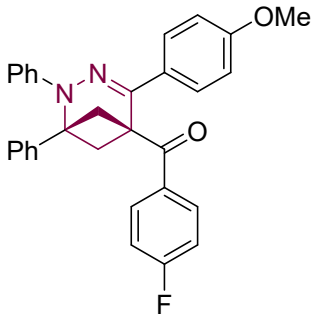
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:4). yellow solid, 26 mg, 53% yield. M. P. 178–179 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.75 (d, *J*=7.3, 2H), 7.43 (d, *J*=7.7, 2H), 7.25 – 7.18 (m, 3H), 7.11 – 6.94 (m, 5H), 6.87 – 6.63 (m, 6H), δ = 3.79 (s, 3H), 3.70 (s, 3H)., 2.75 – 2.53 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.5, 163.4, 159.5, 153.2, 146.2, 141.3, 131.5, 130.0, 128.4, 128.2, 128.1, 127.9, 127.1, 126.3, 124.9, 113.8, 113.7, 67.1, 55.5, 55.3, 52.5., 33.8.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}N_2O_3$ $[M + H]^+$ 489.2173, found 489.2169.

(4-Fluorophenyl)((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)methanone (3c)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:4). yellow solid, 18 mg, 38% yield. M. P. 145–146 °C

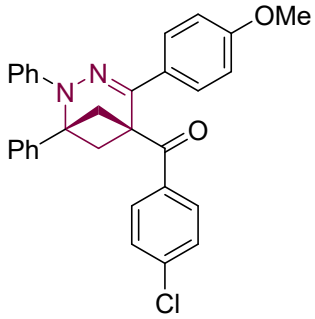
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.80 (dd, *J*=8.8, 5.4, 2H), 7.40 (d, *J*=8.9, 2H), 7.22 (d, *J*=2.2, 3H), 7.09 – 7.02 (m, 4H), 6.97 (q, *J*=8.6, 7.9, 3H), 6.80 (d, *J*=7.1, 2H), 6.69 (d, *J*=8.8, 2H), 3.70 (s, 3H), 2.71 – 2.56 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.3, 165.5 (d, *J*=255.6), 159.6, 152.3, 146.1, 141.2, 131.8 (d, *J*=9.3), 131.4 (d, *J*=2.9), 129.9, 128.4, 128.1, 128.0, 127.9, 127.1, 126.29, 125.0, 115.6 (d, *J*=22.0), 113.9, 67.1, 55.3, 52.7, 33.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -104.29.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{26}FN_2O_2$ $[M + H]^+$ 477.1973, found 477.1971.

(4-Chlorophenyl)((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)methanone (3d)



The crude product was purified by column chromatography on silica gel (PE/DCM =

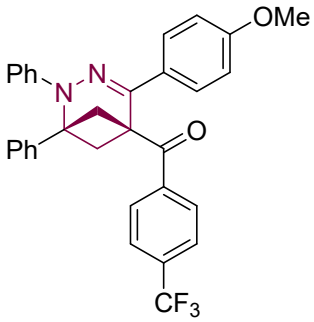
1:3). yellow solid, 21.5 mg, 43% yield. M. P. 182–183 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.70 (d, *J*=8.6, 2H), 7.38 (d, *J*=8.8, 2H), 7.25 – 7.18 (m, 5H), 7.07 – 7.00 (m, 4H), 6.97 (t, *J*=7.1, 1H), 6.78 (d, *J*=7.3, 2H), 6.68 (d, *J*=8.8, 2H), 3.69 (s, 3H), 2.61 (dt, *J*=13.1, 7.6, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.6, 159.7, 152.1, 146.1, 141.1, 139.5, 133.2, 130.5, 129.8, 128.8, 128.4, 128.0, 128.0, 127.9, 127.0, 126.3, 125.0, 113.90, 67.1, 55.3, 52.7, 33.6.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{26}ClN_2O_2$ $[M + H]^+$ 493.1677, found 493.1679.

((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(4-(trifluoromethyl)phenyl)methanone (3e)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 15 mg, 29% yield. M. P. 147–148 °C

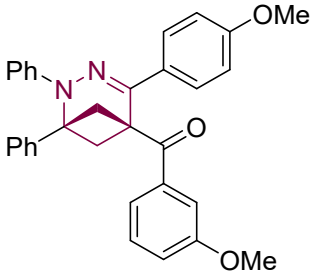
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.87 (d, *J*=8.0, 2H), 7.56 (d, *J*=8.1, 2H), 7.40 (d, *J*=7.0, 2H), 7.22 (s, 3H), 7.05 (t, *J*=6.8, 4H), 7.02 – 6.95 (m, 1H), 6.80 (d, *J*=7.7, 2H), 6.70 (d, *J*=7.6, 2H), 3.70 (s, 3H), 2.64 (p, *J*=7.1, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.9, 159.7, 151.7, 146.0, 141.0, 138.6, 134.3 (q, *J*=32.7), 129.8, 129.4, 128.4, 128.1, 128.0, 127.9, 127.1, 126.3, 125.5 (q, *J*=3.8), 125.1, 123.6 (q, *J*=270.4), 114.0, 67.1, 55.3, 52.9, 33.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -63.09.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{26}F_3N_2O_2$ $[M + H]^+$ 527.1941, found 527.1942.

(3-Methoxyphenyl)((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)methanone (3f)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 17 mg, 35% yield. M. P. 123–124 °C

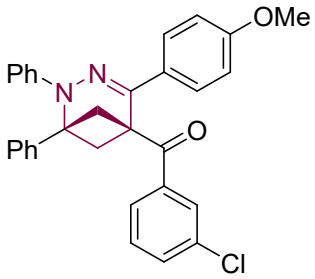
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.35 (d, *J*=8.5, 2H), 7.25 (d, *J*=6.2, 2H), 7.20

– 7.06 (m, 4H), 6.93 (dt, *J*=28.3, 8.1, 6H), 6.71 (d, *J*=7.7, 2H), 6.62 (d, *J*=8.5, 2H), 3.68 (s, 3H), 3.62 (s, 3H), 2.61 – 2.50 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.8, 159.6, 159.6, 152.8, 146.2, 141.3, 136.3, 130.1, 129.4, 128.4, 128.1, 127.9, 127.9, 127.1, 126.3, 124.9, 121.9, 120.0, 113.9, 113.1, 67.10, 55.5, 55.3, 52.9, 33.8.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}N_2O_3$ $[M + H]^+$ 489.2173, found 489.2169.

(3-Chlorophenyl)((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)methanone (3g)



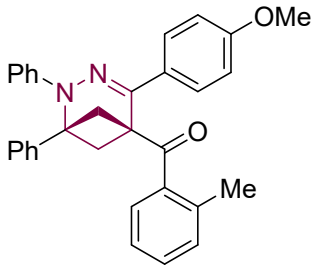
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:4). yellow solid, 13 mg, 26% yield. M. P. 135–136 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.78 (t, *J*=1.9, 1H), 7.61 (d, *J*=7.8, 1H), 7.41 – 7.35 (m, 3H), 7.22 (dd, *J*=5.1, 2.8, 4H), 7.09 – 7.02 (m, 4H), 6.98 (t, *J*=7.2, 1H), 6.82 – 6.78 (m, 2H), 6.71 (d, *J*=8.8, 2H), 3.70 (s, 3H), 2.64 (dt, *J*=13.2, 7.4, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.5, 159.7, 152.1, 146.1, 141.1, 136.4, 134.7, 133.1, 129.9, 129.7, 129.1, 128.4, 128.1, 128.0, 127.9, 127.2, 127.1, 126.3, 125.0, 113.9, 67.1, 55.3, 52.8, 33.6.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{26}ClN_2O_2$ $[M + H]^+$ 493.1677, found 493.1679.

((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(o-tolyl)methanone (3h)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:4). yellow solid, 17 mg, 36% yield. M. P. 169–170 °C

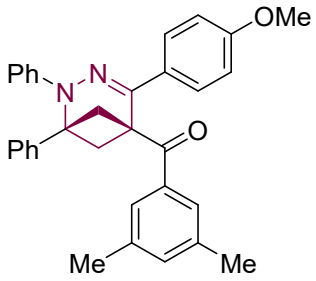
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.45 (d, *J*=9.0, 3H), 7.30 – 7.14 (m, 5H), 7.11 – 7.01 (m, 5H), 6.97 (t, *J*=7.2, 1H), 6.78 (d, *J*=7.3, 2H), 6.73 (d, *J*=8.8, 2H), 3.72 (s, 3H), 2.58 (s, 4H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 202.6, 159.6, 153.3, 146.2, 141.4, 140.2, 134.6, 132.4, 131.9, 130.2, 129.9, 128.4, 128.4, 127.9, 127.9, 127.2, 126.4, 125.4,

124.9, 113.8, 66.7, 55.3, 53.7, 34.1, 22.1.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}N_2O_2$ $[M + H]^+$ 473.2224, found 473.2223.

(3,5-Dimethylphenyl)((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)methanone (3i)



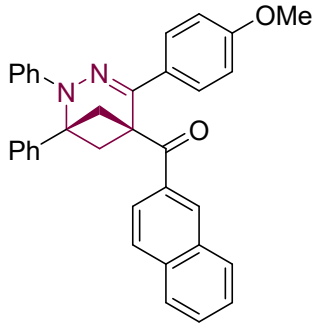
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 26 mg, 53% yield. M. P. 172–173 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.41 (d, *J*=8.8, 2H), 7.37 (s, 2H), 7.24 – 7.19 (m, 3H), 7.10 – 7.01 (m, 5H), 6.97 (t, *J*=7.2, 1H), 6.79 (d, *J*=7.7, 2H), 6.69 (d, *J*=8.8, 2H), 3.70 (s, 3H), 2.66 – 2.58 (m, 4H), 2.24 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 200.3, 159.6, 153.4, 146.3, 141.4, 137.9, 134.9, 130.3, 128.4, 128.1, 127.9, 127.1, 127.1, 126.3, 124.9, 113.8, 67.1, 55.3, 52.9, 33.9, 21.3.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{31}N_2O_2$ $[M + H]^+$ 487.2380, found 487.2380.

((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(naphthalen-2-yl)methanone (3j)



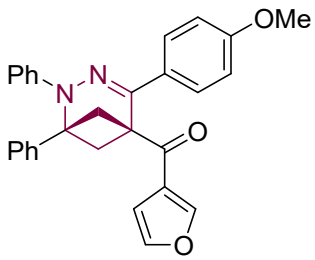
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 30 mg, 59% yield. M. P. 149–150 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.30 (s, 1H), 7.91 – 7.82 (m, 2H), 7.76 (dd, *J*=14.9, 8.3, 2H), 7.58 – 7.47 (m, 4H), 7.25 – 7.21 (m, 3H), 7.12 – 7.04 (m, 4H), 7.00 (t, *J*=7.3, 1H), 6.85 (d, *J*=7.6, 2H), 6.66 (d, *J*=8.8, 2H), 3.61 (s, 3H), 2.72 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.9, 159.5, 153.0, 146.2, 141.2, 135.5, 132.4, 132.2, 131.2, 130.1, 129.8, 128.7, 128.4, 128.3, 128.1, 127.9, 127.9, 127.8, 127.1, 126.8, 126.3, 124.9, 124.5, 113.9, 67.2, 55.2, 52.9, 33.9.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{29}N_2O_2$ $[M + H]^+$ 509.2224, found 509.2228.

Furan-3-yl((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)methanone (3k)



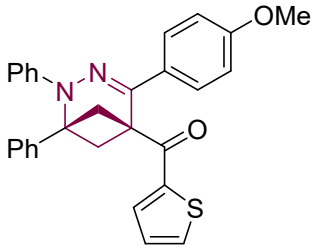
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 13 mg, 16% yield. M. P. 159–160 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.75 (s, 1H), 7.40 (d, *J*=8.8, 2H), 7.28 – 7.20 (m, 4H), 7.10 – 6.94 (m, 5H), 6.76 (dd, *J*=7.8, 5.6, 4H), 6.59 (d, *J*=1.9, 1H), 3.74 (s, 3H), 2.64 (dt, *J*=7.6, 4.0, 2H), 2.55 (dd, *J*=6.5, 2.4, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 194.6, 159.6, 152.4, 147.8, 146.0, 143.6, 141.0, 129.3, 128.3, 128.1, 127.9, 127.8, 127.0, 126.2, 125.4, 124.9, 113.8, 108.8, 67.0, 55.2, 53.1, 32.8.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{25}N_2O_3$ $[M + H]^+$ 449.1860, found 449.1861.

((1r,5r)-4-(4-Methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(thiophen-2-yl)methanone (3l)



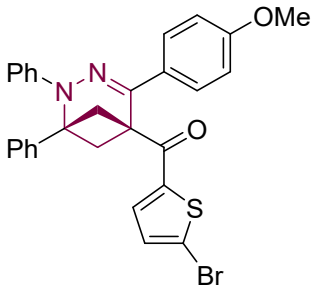
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:4). yellow solid, 23 mg, 49% yield. M. P. 137–138 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.50 (d, *J*=4.9, 1H), 7.45 – 7.39 (m, 3H), 7.25 – 7.21 (m, 3H), 7.09 – 7.00 (m, 4H), 6.98 (d, *J*=7.2, 1H), 6.94 – 6.91 (m, 1H), 6.78 (d, *J*=7.9, 2H), 6.71 (d, *J*=8.7, 2H), 3.71 (s, 3H), 2.76 – 2.68 (m, 2H), 2.67 – 2.60 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 192.8, 159.6, 152.8, 146.1, 142.2, 141.2, 133.8, 133.1, 129.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.1, 126.3, 125.0, 113.8, 67.2, 55.3, 52.9, 33.5.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{25}N_2O_2S$ $[M + H]^+$ 465.1631, found 465.1634.

(5-Bromothiophen-2-yl)((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo [3.1.1]
hept-3-en-5-yl)methanone (3m)



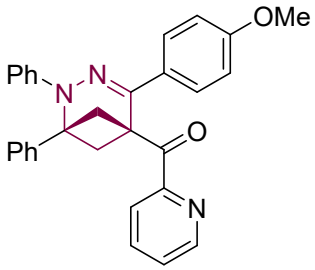
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:4). yellow solid, 25 mg, 46% yield. M. P. 85–86 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.40 (d, *J*=8.8, 2H), 7.23 (d, *J*=2.4, 3H), 7.12 (d, *J*=4.1, 1H), 7.08 – 6.94 (m, 5H), 6.89 (d, *J*=4.1, 1H), 6.76 (t, *J*=8.5, 4H), 3.74 (s, 3H), 2.74 – 2.64 (m, 2H), 2.65 – 2.55 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 191.7, 159.7, 152.1, 146.0, 143.7, 141.0, 133.2, 131.3, 129.4, 128.4, 128.1, 128.0, 127.9, 127.0, 126.3, 125.0, 123.0, 113.9, 67.3, 55.3, 52.6, 33.4.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}BrN_2O_2S$ $[M + H]^+$ 543.0736, found 543.0737.

((1r,5r)-4-(4-Methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(pyridin-2-yl)methanone (3n)



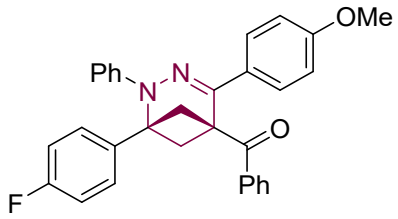
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:1). yellow solid, 16 mg, 35% yield. M. P. 178–179 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.70 (d, *J*=8.7, 2H), 7.39 (d, *J*=8.8, 2H), 7.24 (dt, *J*=14.8, 3.7, 5H), 7.09 – 7.01 (m, 4H), 6.98 (t, *J*=7.1, 1H), 6.79 (d, *J*=7.6, 2H), 6.69 (d, *J*=8.7, 2H), 3.71 (s, 3H), 2.68 – 2.57 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.5, 159.6, 152.0, 146.0, 141.0, 139.4, 133.1, 130.4, 129.7, 128.7, 128.3, 127.9, 127.9, 127.8, 126.9, 126.2, 124.9, 113.8, 67.0, 55.2, 52.6, 33.5.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{26}N_3O_2$ $[M + H]^+$ 460.2020, found 460.2024.

((1r,5r)-1-(4-Fluorophenyl)-4-(4-methoxyphenyl)-2-phenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3o)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 25 mg, 52% yield. M. P. 195–196 °C

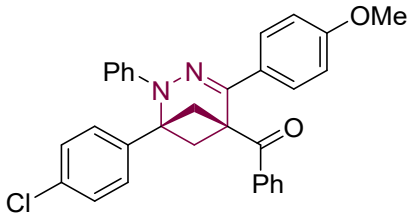
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.77 (d, *J*=7.0, 2H), 7.44 – 7.40 (m, 3H), 7.29 (t, *J*=7.7, 2H), 7.08 (t, *J*=7.5, 2H), 7.04 – 6.99 (m, 3H), 6.91 (t, *J*=8.6, 2H), 6.80 (d, *J*=7.7, 2H), 6.68 (d, *J*=8.8, 2H), 3.68 (s, 3H), 2.62 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.8, 162.3 (d, *J*=247.1), 159.6, 152.9, 146.0, 137.2 (d, *J*=3.3), 134.8, 133.3, 129.9, 129.1, 128.9, 128.8, 128.4, 128.1, 128.0, 126.5, 115.4 (d, *J*=21.6), 113.8, 66.6, 55.3, 52.7, 33.7.

^{19}F NMR (**376 MHz**, **Chloroform-*d***) δ = -113.55.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{26}FN_2O_2$ $[M + H]^+$ 477.1973, found 477.1971.

((1r,5r)-1-(4-Chlorophenyl)-4-(4-methoxyphenyl)-2-phenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3p)



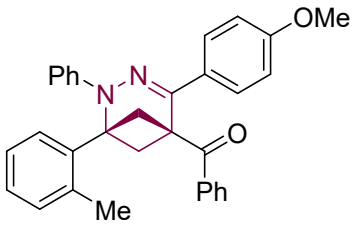
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 15 mg, 30% yield. M. P. 195–196 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.76 (d, *J*=7.6, 2H), 7.41 (d, *J*=8.6, 3H), 7.29 (t, *J*=7.7, 2H), 7.20 (d, *J*=8.1, 2H), 7.09 (t, *J*=7.6, 2H), 7.01 (dd, *J*=11.8, 7.7, 3H), 6.81 (d, *J*=7.7, 2H), 6.68 (d, *J*=8.6, 2H), 3.68 (s, 3H), 2.61 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.7, 159.7, 152.9, 146.0, 139.9, 134.8, 133.8, 133.3, 129.8, 129.2, 128.7, 128.5, 128.5, 128.2, 128.1, 126.4, 125.2, 113.6, 66.6, 55.3, 52.6, 33.7.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{26}ClN_2O_2$ $[M + H]^+$ 493.1677, found 493.1679.

((1r,5r)-4-(4-Methoxyphenyl)-2-phenyl-1-(o-tolyl)-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3q)



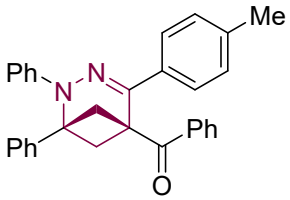
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 25.5 mg, 54% yield. M. P. 170–171 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.77 (d, *J*=7.0, 2H), 7.43 (d, *J*=8.8, 3H), 7.30 (t, *J*=7.7, 2H), 7.15 (t, *J*=7.3, 1H), 7.08 – 6.95 (m, 6H), 6.79 (d, *J*=7.1, 2H), 6.69 (d, *J*=8.8, 2H), 3.69 (s, 3H), 2.81 – 2.58 (m, 4H), 2.20 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 200.1, 159.5, 152.4, 146.2, 138.9, 137.6, 135.0, 133.2, 131.1, 130.1, 129.2, 128.5, 128.4, 128.3, 128.1, 127.8, 126.0, 125.8, 124.8, 113.8, 68.0, 55.3, 52.6, 36.2, 19.8.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}N_2O_2$ $[M + H]^+$ 473.2224, found 473.2223.

((1r,5r)-1,2-Diphenyl-4-(p-tolyl)-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3r)



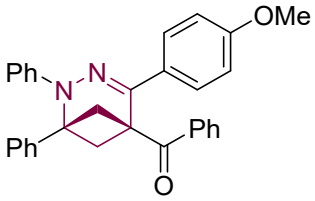
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:1). yellow solid, 13 mg, 30% yield. M. P. 201–202 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.77 (d, *J*=7.7, 2H), 7.38 (t, *J*=8.2, 3H), 7.29 (t, *J*=7.7, 2H), 7.22 (dd, *J*=4.9, 1.8, 3H), 7.10 – 7.02 (m, 4H), 6.97 (dd, *J*=12.1, 7.5, 3H), 6.80 (dd, *J*=7.9, 1.8, 2H), 2.64 (dt, *J*=13.8, 6.9, 4H), 2.19 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.8, 152.9, 146.1, 141.2, 138.1, 134.9, 134.4, 133.2, 129.1, 129.1, 128.4, 128.4, 127.9, 127.9, 127.1, 126.6, 126.3, 124.9, 67.2, 52.7, 33.7, 21.3.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{27}N_2O$ $[M + H]^+$ 443.2118, found 443.2122.

((1r,5r)-4-(4-Methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3s)

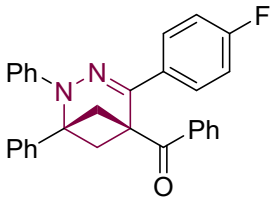


The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 28 mg, 61% yield. M. P. 199–200 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.77 (d, *J*=7.0, 2H), 7.42 (d, *J*=8.8, 3H), 7.29 (t, *J*=7.7, 2H), 7.22 (dd, *J*=5.0, 1.9, 3H), 7.09 – 7.02 (m, 4H), 6.98 (t, *J*=7.3, 1H), 6.83 – 6.77 (m, 2H), 6.68 (d, *J*=8.8, 2H), 3.69 (s, 3H), 2.69 – 2.58 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 200.0, 159.6, 152.8, 146.2, 141.3, 134.9, 133.2, 130.0, 129.2, 128.4, 128.4, 128.1, 127.9, 127.9, 127.1, 126.3, 124.9, 113.8, 67.1, 55.3, 52.8, 33.8.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{27}N_2O_2$ $[M + H]^+$ 459.2067, found 459.2068.

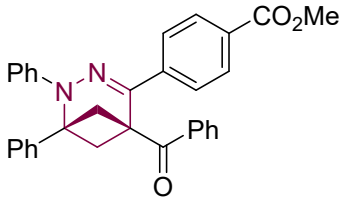
((1r,5r)-4-(4-Fluorophenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)
methanone (3t)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 14 mg, 30% yield. M. P. 156–157 °C
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.75 (d, *J*=7.3, 2H), 7.48 – 7.39 (m, 3H), 7.30 (t, *J*=7.7, 2H), 7.23 (dd, *J*=5.0, 1.8, 3H), 7.06 (td, *J*=7.8, 4.7, 4H), 6.99 (t, *J*=7.2, 1H), 6.90 – 6.75 (m, 4H), 2.69 (dt, *J*=8.0, 4.0, 2H), 2.66 – 2.57 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.6, 162.6 (d, *J*=247.9), 151.5, 145.9, 141.0, 134.8, 133.4, 129.1, 128.6, 128.6, 128.5, 128.5, 128.0, 128.0, 127.1, 126.3, 125.1, 115.4 (d, *J*=21.7), 67.3, 52.7, 33.6.
^{19}F NMR (376 MHz, Chloroform-*d*) δ = -113.15.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{24}FN_2O$ $[M + H]^+$ 447.1867, found 447.1865.

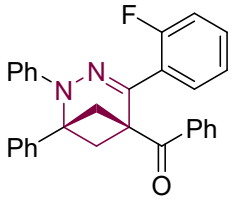
Methyl 4-((1r,5r)-5-benzoyl-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-4-yl)benzoate (3u)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 19.5 mg, 40% yield. M. P. 205–206 °C
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.81 (d, *J*=8.2, 2H), 7.75 (d, *J*=7.2, 2H), 7.53 (d, *J*=8.3, 2H), 7.40 (t, *J*=7.4, 1H), 7.32 – 7.20 (m, 5H), 7.11 – 6.97 (m, 5H), 6.81 (d, *J*=7.8, 2H), 3.83 (s, 3H), 2.72 (dt, *J*=8.3, 4.1, 2H), 2.62 – 2.55 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.3, 166.9, 150.6, 145.7, 141.4, 140.7, 134.7, 133.5, 129.7, 129.3, 129.0, 128.6, 128.5, 128.1, 128.0, 127.1, 126.5, 126.3, 125.3, 67.5, 52.5, 52.2, 33.4.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{27}N_2O_3$ $[M + H]^+$ 487.2016, found 487.2021.

((1r,5r)-4-(2-Fluorophenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3v)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 18.5 mg, 41% yield. M. P. 206–207 °C

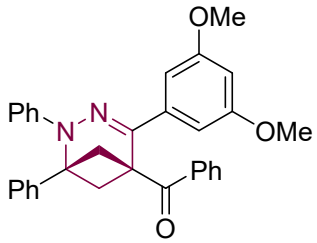
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.71 (d, *J*=7.8, 2H), 7.36 (q, *J*=7.0, 2H), 7.25 – 7.18 (m, 5H), 7.10 – 7.00 (m, 5H), 6.94 (dt, *J*=15.0, 7.3, 2H), 6.77 (dd, *J*=13.8, 8.2, 3H), 2.75 (t, *J*=6.6, 2H), 2.67 – 2.58 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.0, 159.6 (d, *J*=246.9), 149.1, 145.8, 141.1, 135.0, 133.0, 130.1, 130.0, 128.9, 128.5, 128.2, 128.1, 128.0, 127.2, 126.5, 125.5 (d, *J*=15.3), 125.2, 124.2 (d, *J*=3.5), 115.6 (d, *J*=21.6), 67.7, 53.1, 33.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = -112.43.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{24}FN_2O$ $[M + H]^+$ 447.1867, found 447.1865.

((1r,5r)-4-(3,5-Dimethoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3w)



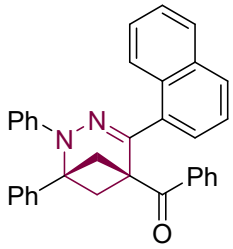
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 20 mg, 41% yield. M. P. 253–254 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79 (d, *J*=7.3, 2H), 7.42 (t, *J*=7.4, 1H), 7.31 (t, *J*=7.7, 2H), 7.22 (dd, *J*=5.0, 1.8, 3H), 7.10 – 7.02 (m, 4H), 6.99 (t, *J*=7.2, 1H), 6.81 (d, *J*=7.3, 2H), 6.64 (d, *J*=2.2, 2H), 6.22 (t, *J*=2.3, 1H), 3.65 (s, 6H), 2.65 (ddt, *J*=30.4, 7.9, 5.7, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.7, 160.7, 152.4, 146.0, 141.1, 139.0, 135.0, 133.3, 128.9, 128.5, 128.4, 128.0, 127.9, 127.1, 126.3, 125.0, 104.8, 101.3, 67.3, 55.4, 52.8, 33.6.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}N_2O_3$ $[M + H]^+$ 489.2173, found 489.2176.

((1r,5r)-4-(Naphthalen-1-yl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3x)



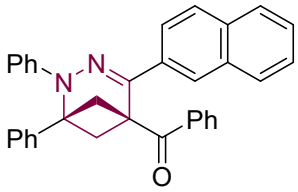
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 20 mg, 42% yield. M. P. 189–190 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.28 (d, *J*=8.4, 1H), 7.66 (d, *J*=8.1, 1H), 7.59 – 7.47 (m, 4H), 7.42 (dd, *J*=11.5, 7.2, 2H), 7.31 – 7.13 (m, 7H), 7.06 (t, *J*=7.6, 2H), 6.98 (t, *J*=7.7, 3H), 6.87 (d, *J*=7.9, 2H), 2.92 – 2.80 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.1, 152.3, 146.0, 141.2, 135.1, 135.0, 133.8, 132.7, 131.1, 128.7, 128.5, 128.3, 128.3, 128.0, 128.0, 127.8, 127.1, 126.5, 126.4, 126.4, 126.1, 126.0, 125.0, 124.9, 67.4, 54.2, 33.4.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{27}N_2O$ $[M + H]^+$ 479.2118, found 479.2115.

((1r,5r)-4-(Naphthalen-2-yl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3y)



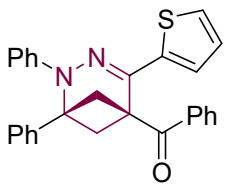
The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 26 mg, 54% yield. M. P. 190–191 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79 (s, 1H), 7.72 (d, *J*=7.2, 2H), 7.66 – 7.54 (m, 4H), 7.27 (dd, *J*=6.3, 3.3, 2H), 7.21 (t, *J*=7.3, 1H), 7.18 – 7.09 (m, 5H), 7.04 – 6.95 (m, 4H), 6.91 (t, *J*=7.2, 1H), 6.76 (d, *J*=7.7, 2H), 2.70 – 2.55 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.8, 152.2, 146.0, 141.1, 134.9, 134.6, 133.2, 133.1, 133.0, 129.0, 128.4, 128.2, 128.0, 128.0, 127.6, 127.1, 126.4, 126.2, 126.2, 125.8, 125.1, 124.6, 67.4, 52.8, 33.7.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{27}N_2O$ $[M + H]^+$ 479.2118, found 479.2115.

((1r,5r)-1,2-Diphenyl-4-(thiophen-2-yl)-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3z)

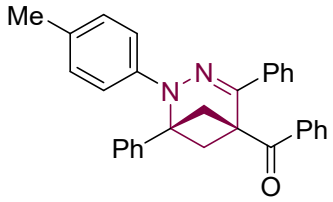


The crude product was purified by column chromatography on silica gel (PE/DCM = 1:1). white solid, 19.5 mg, 45% yield. M. P. 187–188 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.89 (d, *J*=7.3, 2H), 7.52 (t, *J*=7.3, 1H), 7.41 (t, *J*=7.6, 2H), 7.22 (p, *J*=4.0, 3H), 7.12 (d, *J*=4.4, 1H), 7.09 – 6.96 (m, 5H), 6.80 – 6.70 (m, 4H), 2.62 (s, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 200.1, 146.9, 145.7 140.8, 140.1, 135.5, 133.5, 129.2, 128.7, 128.4, 128.1, 127.9, 127.4, 127.2, 126.3, 126.0, 125.8, 125.0, 67.1, 52.4, 34.0.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}N_2OS$ $[M + H]^+$ 435.1526, found 435.1532.

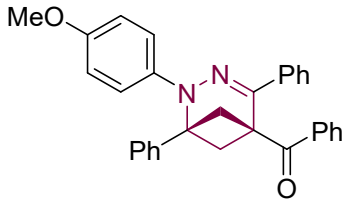
((1r,5r)-1,4-Diphenyl-2-(p-tolyl)-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3aa)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:1). yellow solid, 18 mg, 40% yield. M. P. 189–190 °C
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79 – 7.74 (m, 2H), 7.47 (d, *J*=6.9, 2H), 7.39 (t, *J*=7.4, 1H), 7.30 – 7.25 (m, 2H), 7.23 (dd, *J*=5.2, 1.9, 3H), 7.15 (t, *J*=7.3, 2H), 7.12 – 7.06 (m, 3H), 6.86 (d, *J*=8.1, 2H), 6.70 (d, *J*=8.4, 2H), 2.71 – 2.65 (m, 2H), 2.65 – 2.60 (m, 2H), 2.21 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.7, 152.4, 143.6, 141.2, 137.3, 134.9, 134.7, 133.2, 129.1, 128.6, 128.4, 128.4, 128.1, 127.9, 127.1, 126.7, 126.2, 67.2, 52.7, 33.5, 21.0.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{27}N_2O$ $[M + H]^+$ 443.2118, found 443.2122.

((1r,5r)-2-(4-Methoxyphenyl)-1,4-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3ab)

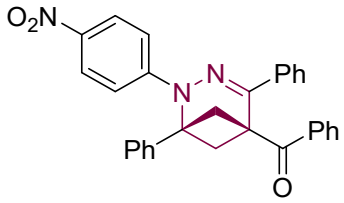


The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 22 mg, 48% yield. M. P. 200–201 °C
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.76 (d, *J*=7.0, 2H), 7.45 (d, *J*=6.8, 2H), 7.39 (t, *J*=7.4, 1H), 7.30 – 7.24 (m, 2H), 7.22 (dd, *J*=5.2, 1.9, 3H), 7.18 – 7.02 (m, 5H), 6.73 (d, *J*=8.9, 2H), 6.58 (d, *J*=8.9, 2H), 3.70 (s, 3H), 2.64 (dt, *J*=13.2, 6.9, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.7, 157.3, 152.5, 141.2, 139.4, 137.3, 134.9, 133.2, 129.1, 128.4, 128.4, 128.1, 127.9, 127.9, 127.2, 126.7, 113.2, 67.4, 55.5, 52.8, 33.4.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{27}N_2O_2$ $[M + H]^+$ 459.2067, found

459.2068.

((1r,5r)-2-(4-Nitrophenyl)-1,4-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(phenyl)methanone (3ac)



The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3). yellow solid, 16 mg, 34% yield. M. P. 187–188 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.89 (d, *J*=9.2, 2H), 7.76 – 7.70 (m, 2H), 7.47 (d, *J*=6.5, 2H), 7.40 (t, *J*=7.4, 1H), 7.36 – 7.32 (m, 3H), 7.30 – 7.24 (m, 2H), 7.23 – 7.14 (m, 5H), 6.89 (d, *J*=9.2, 2H), 2.81 (dt, *J*=7.9, 3.9, 2H), 2.63 – 2.54 (m, 2H).

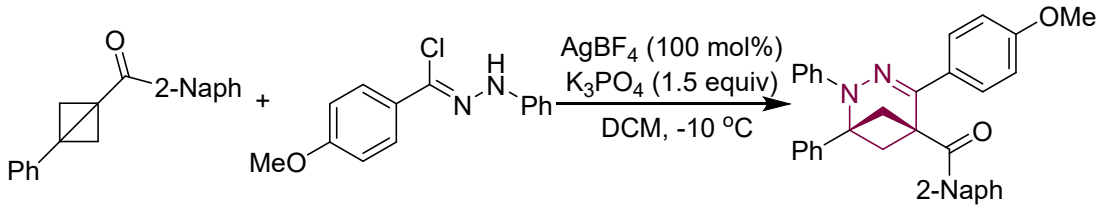
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.86, 154.01, 151.25, 142.76, 140.16, 136.51, 134.58, 133.47, 129.19, 129.04, 128.82, 128.58, 128.52, 126.76, 126.64, 123.75, 123.06, 67.26, 52.43, 34.67.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{24}N_3O_3$ $[M + H]^+$ 474.1812, found 474.1817.

5. Post-functionalizations

Gram-scale synthesis of 3j and synthetic transformations of 3ab and 3j

Gram-scale reaction

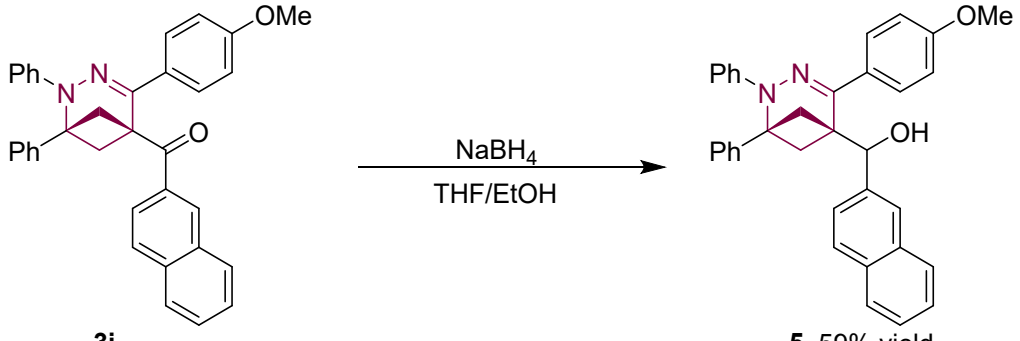


15 mmol 5 mmol **3j**, 48% yield (1.15 g)

To a 100 mL reaction vial equipped with a magnetic stir bar was added compounds naphthalen-2-yl(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (4.26 g, 15 mmol), (Z)-4-methoxy-*N*-phenylbenzohydrazonoyl chloride (1.3 g, 5 mmol), $AgBF_4$ (1 g, 5 mmol), K_3PO_4 (1.59 g, 7.5 mmol), 3 Å molecular sieves (500 mg), and the tube was evacuated and backfilled with argon three times, dry DCM (50 mL) was added under argon atmosphere. The mixture was stirred at -10 ℃ for 6 h. Upon completion of reaction, the reaction mixture was filtered through celite pad and concentrated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel (PE/DCM = 1:3) to afford **3j** (1.15 g, 48% yield) as a yellow solid.

Further transformations

Reduction of ketone:



3j **5**, 59% yield

To a reaction bottle with magneton, **3j** (50.8 mg, 0.1 mmol, 1.0 equiv) was dissolved in THF and EtOH (1 mL, v/v = 1/2). Subsequently, $NaBH_4$ (18.9 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture and stirred for two hours at room temperature.

The solvent was removed under reduced pressure and the mixture was treated with saturated aqueous $NaHCO_3$ (5 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo to give the crude product. The product was purified by column chromatography on silica gel (PE/EtOAc = 5:1) to afford **5** (30 mg, 59%) as a white solid. M. P. 226–227 °C

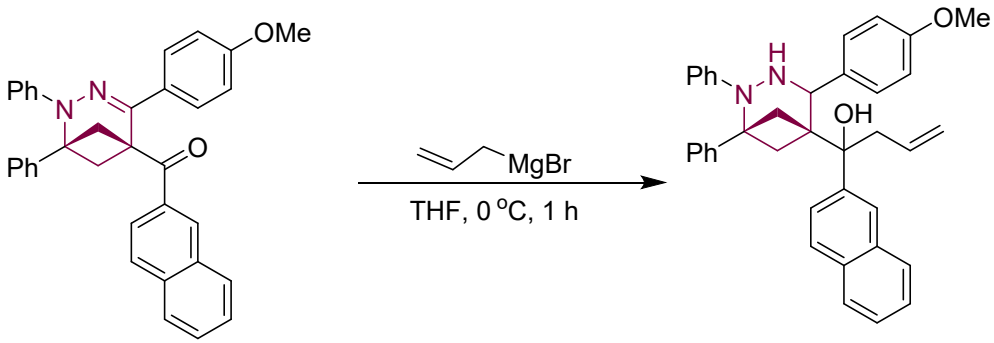
((1r,5r)-4-(4-Methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)(naphthalen-2-yl)methanol (5)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.78 (dd, J=22.5, 7.2, 3H), 7.58 – 7.49 (m, 3H), 7.49 – 7.38 (m, 2H), 7.33 (d, J=8.5, 1H), 7.15 (d, J=6.8, 3H), 7.02 – 6.84 (m, 7H), 6.62 (d, J=7.8, 2H), 5.53 (d, J=4.1, 1H), 5.21 (d, J=4.1, 1H), 3.78 (s, 3H), 2.26 (d, J=8.9, 1H), 2.18 (t, J=8.5, 1H), 2.06 (t, J=8.5, 1H), 1.65 (d, J=8.8, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 160.2, 158.9, 146.4, 142.6, 139.9, 132.5, 132.2, 130.4, 129.9, 128.2, 127.8, 127.5, 127.4, 127.0, 126.7, 126.0, 125.7, 125.7, 124.0, 113.2, 71.1, 66.8, 55.2, 47.2, 30.9.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{31}N_2O_2$ $[M + H]^+$ 511.2380, found 511.2387.

Allylation of ketone:



3j **6**, 83% yield

In a flame dried Schlenk flask, ketone **3j** (50.8 mg, 0.1 mmol) was stirred in anhydrous THF (1.0 mL). The solution was cooled to 0 °C and allyl-magnesium bromide (1.0 M in THF, 0.22 mL, 0.22 mmol) was added slowly. The reaction was stirred for 1 h at 0 °C before the addition of aqueous saturated NH_4Cl (3 mL). The mixture was extracted with EtOAc (3×5 mL). The organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated to give a crude product, which was purified by flash column chromatography on silica gel (PE/EtOAc = 7:1) to afford the corresponding allyl-alcohol **6** (46 mg, 83% yield,) as a yellow solid. M. P.

156–157 °C

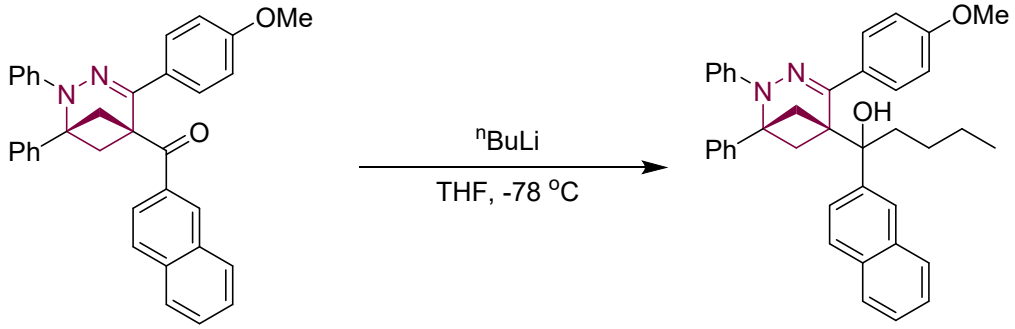
1-((1r,5r)-4-(4-Methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]heptan-5-yl)-1-(naphthalen-2-yl)but-3-en-1-ol (6)

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.74 (d, J=6.8, 1H), 7.63 (d, J=8.6, 1H), 7.52 (d, J=8.6, 1H), 7.44 – 7.35 (m, 2H), 7.28 – 7.14 (m, 6H), 7.10 (d, J=7.7, 2H), 6.91 (dt, J=23.0, 7.0, 3H), 6.74 (d, J=7.9, 2H), 6.64 (d, J=7.5, 2H), 6.30 (d, J=8.2, 2H), 5.28 (dtd, J=18.5, 9.6, 5.1, 1H), 5.05 – 4.93 (m, 2H), 3.53 (s, 3H), 2.90 (dd, J=13.5, 5.1, 1H), 2.74 (dd, J=14.0, 8.7, 2H), 2.64 (dd, J=13.4, 9.1, 1H), 2.55 (t, J=8.3, 1H), 2.45 (t, J=8.4, 1H), 2.40 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 160.5, 158.6, 146.1, 142.6, 141.2, 133.0, 132.9, 132.1, 131.7, 130.5, 128.3, 128.3, 127.7, 127.6, 127.3, 127.3, 126.4, 125.8, 125.7, 125.4, 124.7, 123.6, 120.5, 112.5, 75.5, 66.8, 55.1, 52.1, 42.4, 32.0.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{35}N_2O_2$ $[M + H]^+$ 551.2693, found 551.2693.

***N*-butylation of ketone:**



3j **7**, 53%

An oven-dried Schlenk tube equipped with a stir bar and charged with **3j** (50.8 mg, 0.1 mmol, 1.0 equiv.), after backfilled with N_2 and capped with a septum, then THF (2 mL) were added. The solution was cooled to -78 °C and ^{n}-BuLi (2.5 M in Hex, 0.13 mmol, 1.3 equiv.) was added. The reaction was stirred at -78 °C for 3 h before quenched with saturated NH_4Cl solution. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by flash column chromatography on silica gel (PE/EtOAc = 7:1) to afford product **7** (30 mg, 53% yield) as yellow solid. M. P. 185–186 °C

1-((1r,5r)-4-(4-methoxyphenyl)-1,2-diphenyl-2,3-diazabicyclo[3.1.1]hept-3-en-5-yl)-1-(naphthalen-2-yl)pentan-1-ol (7)

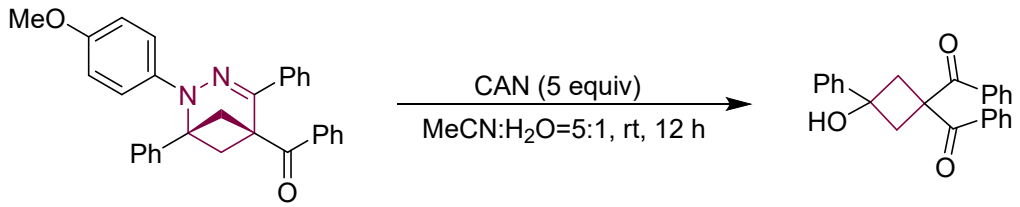
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.91 – 7.84 (m, 1H), 7.75 (d, *J*=8.6, 1H), 7.68

– 7.61 (m, 1H), 7.57 – 7.47 (m, 2H), 7.41 – 7.32 (m, 4H), 7.26 – 7.19 (m, 3H), 7.03 (dt, *J*=14.5, 7.0, 3H), 6.74 (d, *J*=7.4, 4H), 6.37 (d, *J*=8.1, 2H), 3.63 (s, 3H), 2.88 (dd, *J*=8.8, 5.3, 2H), 2.69 (t, *J*=8.3, 1H), 2.56 (t, *J*=8.5, 1H), 2.32 (s, 1H), 2.02 (p, *J*=6.5, 5.5, 2H), 1.34 – 1.10 (m, 4H), 0.79 (t, *J*=7.1, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 160.6, 158.7, 146.0, 142.7, 141.9, 133.2, 132.0, 131.6, 130.2, 128.4, 128.3, 127.8, 127.7, 127.4, 127.4, 127.4, 126.5, 125.9, 125.6, 124.8, 123.3, 112.9, 66.7, 55.2, 52.8, 37.2, 32.5, 30.5, 25.0, 23.1, 14.1.

HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{39}N_2O_2$ $[M + H]^+$ 567.3006, found 567.3008.

Synthetic transformation of 3ab:



3ab **8**, 56% yield

To a reaction bottle with magneton, **3ab** (50.8 mg, 0.1 mmol, 1.0 equiv) was dissolved in CH_3CN and H_2O (1 mL, v/v = 5/1). Subsequently, CAN (26.5 mg, 0.5 mmol, 5.0 equiv) was added to the reaction mixture and stirred for 12 h at room temperature. The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried over $NaSO_4$ and concentrated in vacuo to give the crude product. The product was purified by column chromatography on silica gel (PE/EtOAc = 5:1) to afford **8** (20 mg, 56%) as a white solid. M. P. 89–90 °C

(3-Hydroxy-3-phenylcyclobutane-1,1-diyl)bis(phenylmethanone) (8)

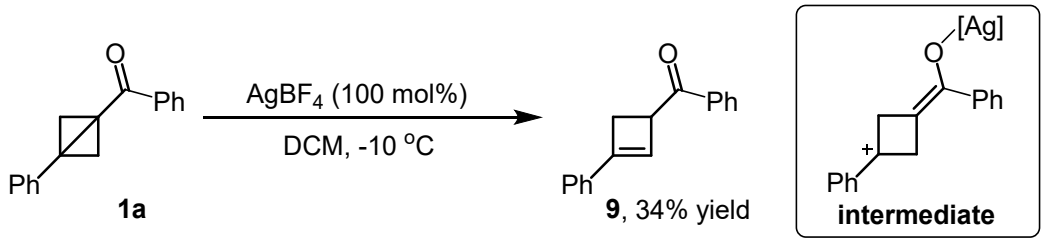
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.88 (d, *J*=7.8, 2H), 7.82 (d, *J*=7.9, 2H), 7.50 – 7.42 (m, 4H), 7.36 (t, *J*=7.6, 5H), 7.27 (d, *J*=9.6, 2H), 3.61 (d, *J*=13.6, 2H), 3.37 (d, *J*=14.2, 2H), 2.61 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 197.9, 196.5, 145.3, 134.7, 133.7, 133.7, 129.6, 129.5, 128.8, 128.8, 128.6, 127.7, 125.0, 73.4, 57.6, 45.0.

HRMS (+ESI) m/z: $[M+Na]^+$ calcd. for $C_{24}H_{20}NaO_3$: 379.1305; found: 379.1307.

6. Mechanistic studies

Control experiment: reaction without **2a**



To a 10 mL reaction vial equipped with a magnetic stir bar was added compound **1a** (0.1 mmol, 1.0 equiv), $AgBF_4$ (100 mol%), and the tube was evacuated and backfilled with argon three times. DCM (1 mL) were added under argon atmosphere. The mixture was then stirred rapidly for 1 hour. Upon completion of reaction, the reaction mixture was concentrated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel to afford **9** (8 mg, 34% yield) a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.03 (d, *J*=7.7, 2H), 7.59 (t, *J*=7.4, 1H), 7.50 (t, *J*=7.6, 2H), 7.43 – 7.32 (m, 4H), 7.29 (d, *J*=7.0, 1H), 6.49 (s, 1H), 4.49 (s, 1H), 3.19 (t, *J*=3.7, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 199.4, 147.8, 136.2, 134.0, 133.2, 128.8, 128.5, 128.4, 128.4, 125.8, 124.8, 46.0, 32.7.

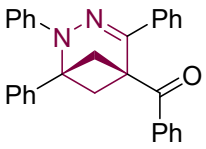
HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}O$ $[M + H]^+$ 235.1117, found 235.1122.

7. X-ray crystallographic data

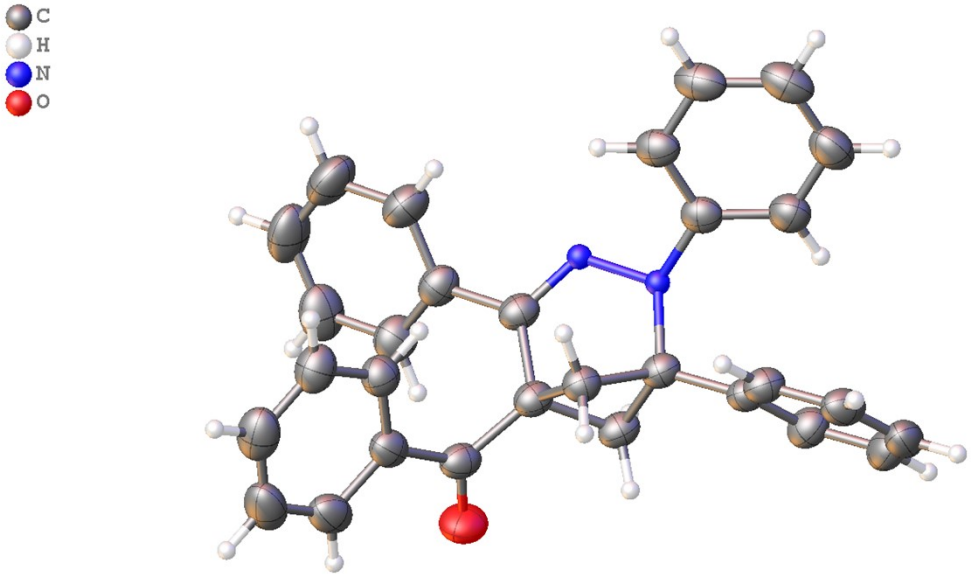
The structure of **3a** were determined by the X-ray diffraction analysis of single crystal, which recrystallized from a mixed solution of CH_2Cl_2 and *n*-pentane

Crystal data and structure refinement for **3a**.

Identification code	**3a**
CCDC Deposit number	2394900
Empirical formula	$C_{30}H_{24}N_2O$
Formula weight	428.51
Temperature/K	237.00
Crystal system	monoclinic
Space group	C2/c
a/Å	39.3453(15)
b/Å	6.1691(2)
c/Å	22.6081(9)
α/°	90
β/°	116.888(2)
γ/°	90
Volume/Å^3	4894.3(3)
Z	8
ρ_{calc}g/cm^3	1.163
μ/mm^{-1}	0.550
F(000)	1808.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.894 to 136.664
Index ranges	-46 ≤ h ≤ 46, -7 ≤ k ≤ 7, -27 ≤ l ≤ 27
Reflections collected	36235
Independent reflections	4481 [Rint = 0.0520, Rsigma = 0.0326]
Data/restraints/parameters	4481/0/298
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R1 = 0.0345, wR2 = 0.0899
Final R indexes [all data]	R1 = 0.0415, wR2 = 0.0951
Largest diff. peak/hole / e Å^{-3}	0.16/-0.15



3a



(CCDC: 2394900)

8. References

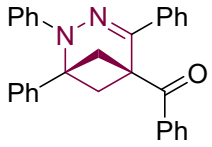
(1) H. S. Ren, T. X. Li, J. P. Xing, Z. Y. Li, Y. X. Zhang, J. Zheng, *Org. Lett.* 2024, **26**, 8, 1745–1750.

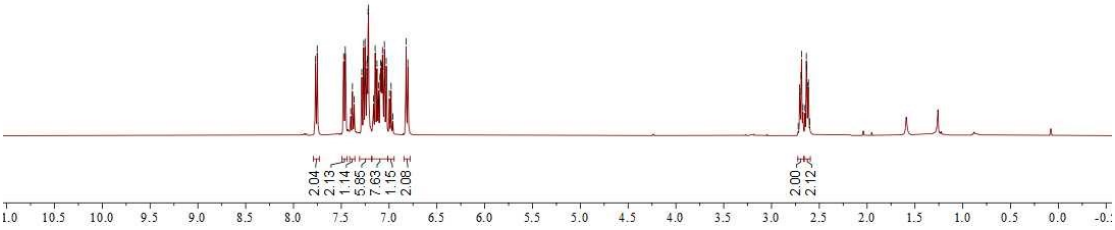
(2) L. K. B. Garve, M. Petzold, P. G. Jones, D. B. Werz, *Org. Lett*. 2016, **18**, 564−567.

(3) S. Y. Du, Z. G. Yang, J. H. Tang, Z. K. Chen, X. F. Wu, *Org. Lett.* 2021, **23**, 6, 2359–2363

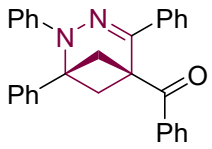
9. NMR spectra of the products

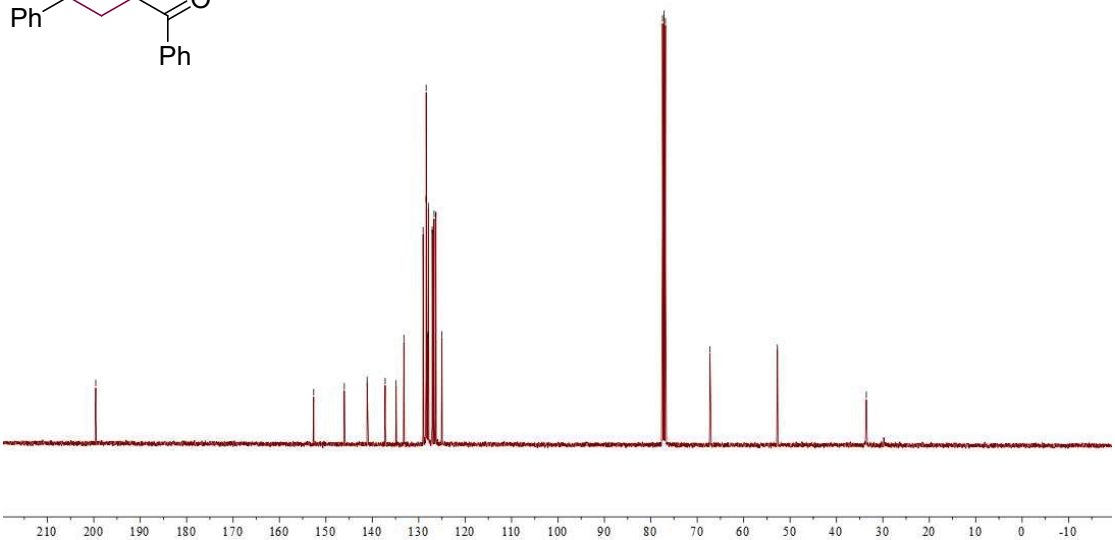
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



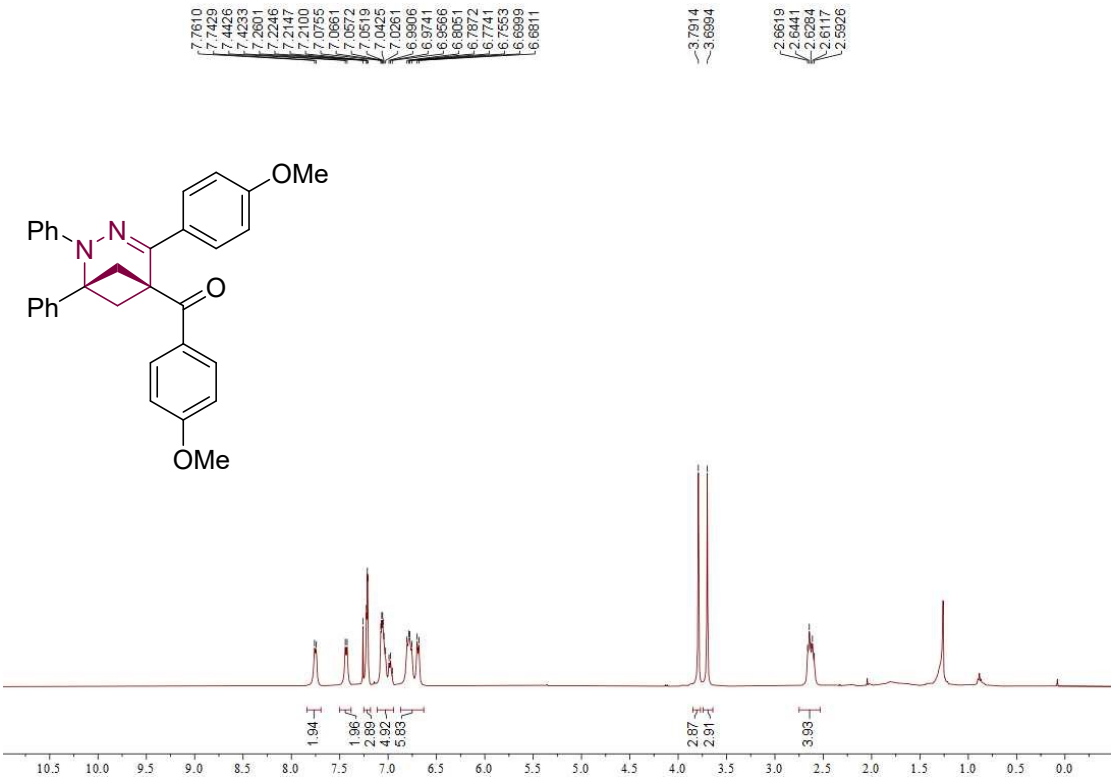


^{13}C NMR (101 MHz, $CDCl_3$) of **3a**

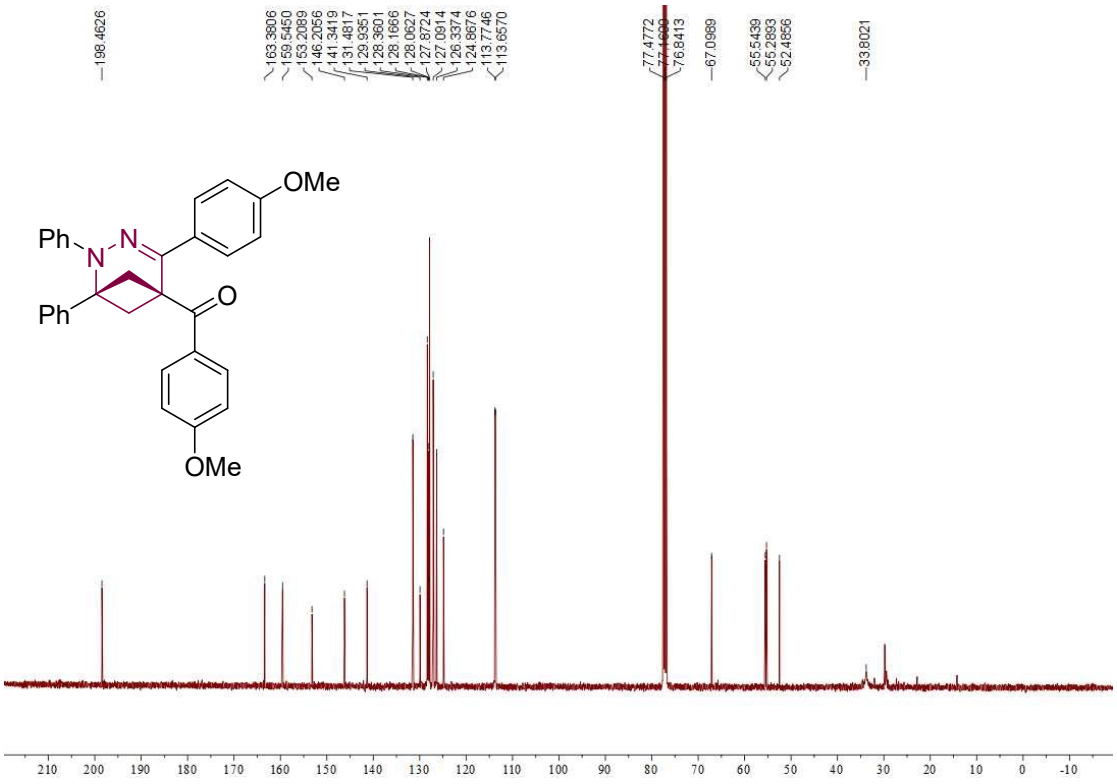




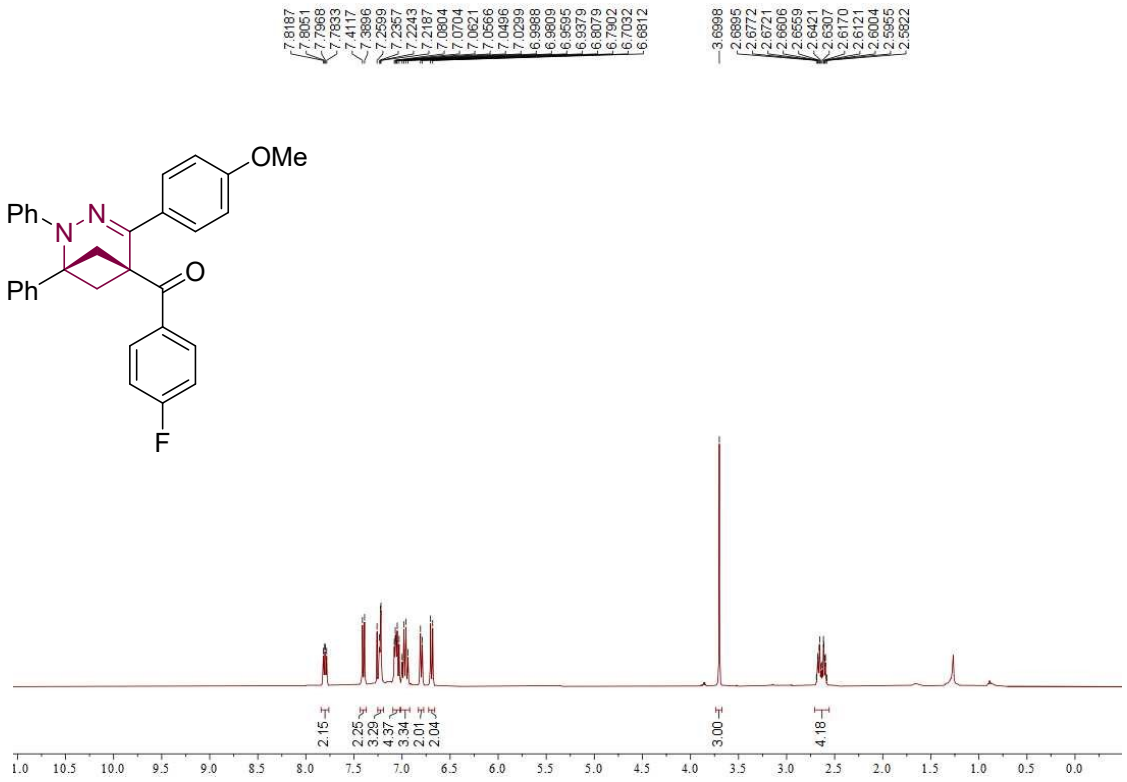
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



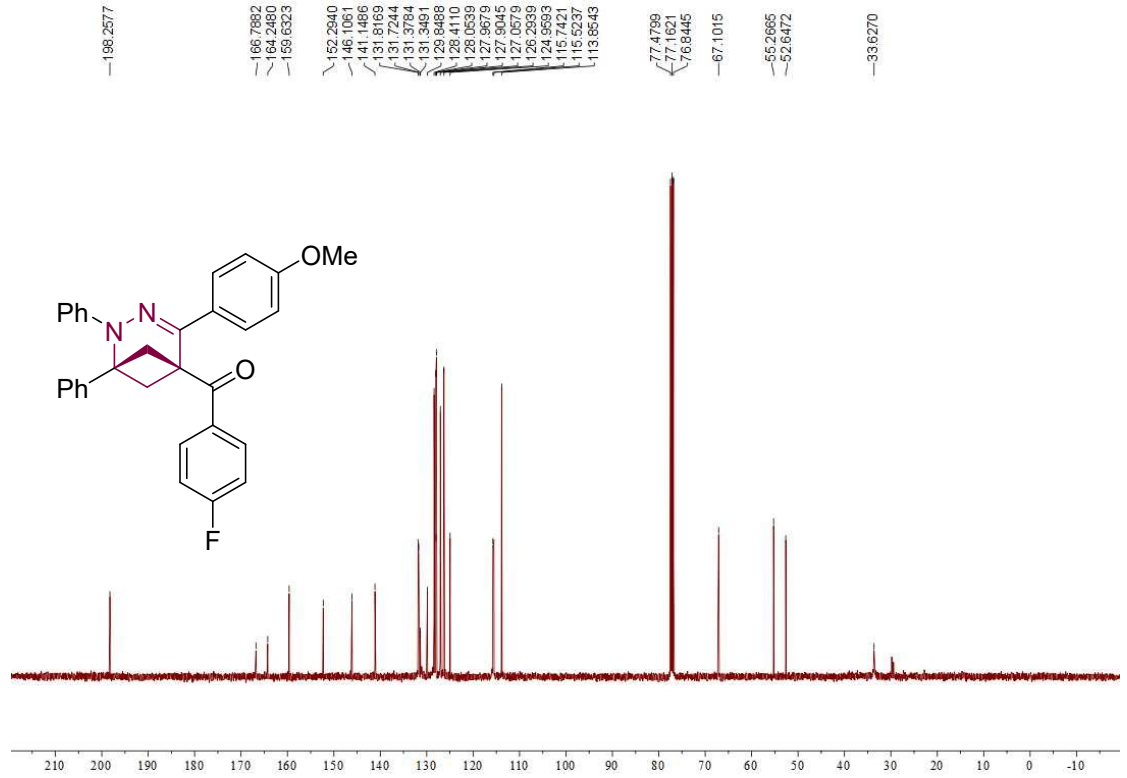
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



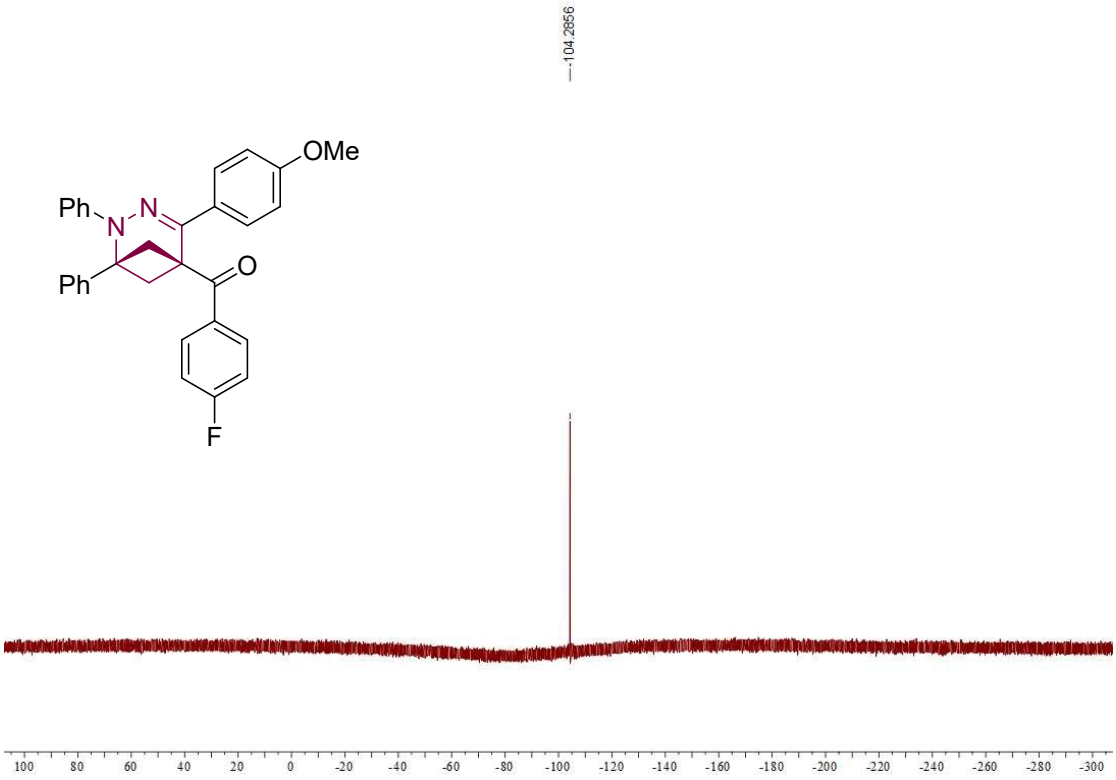
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



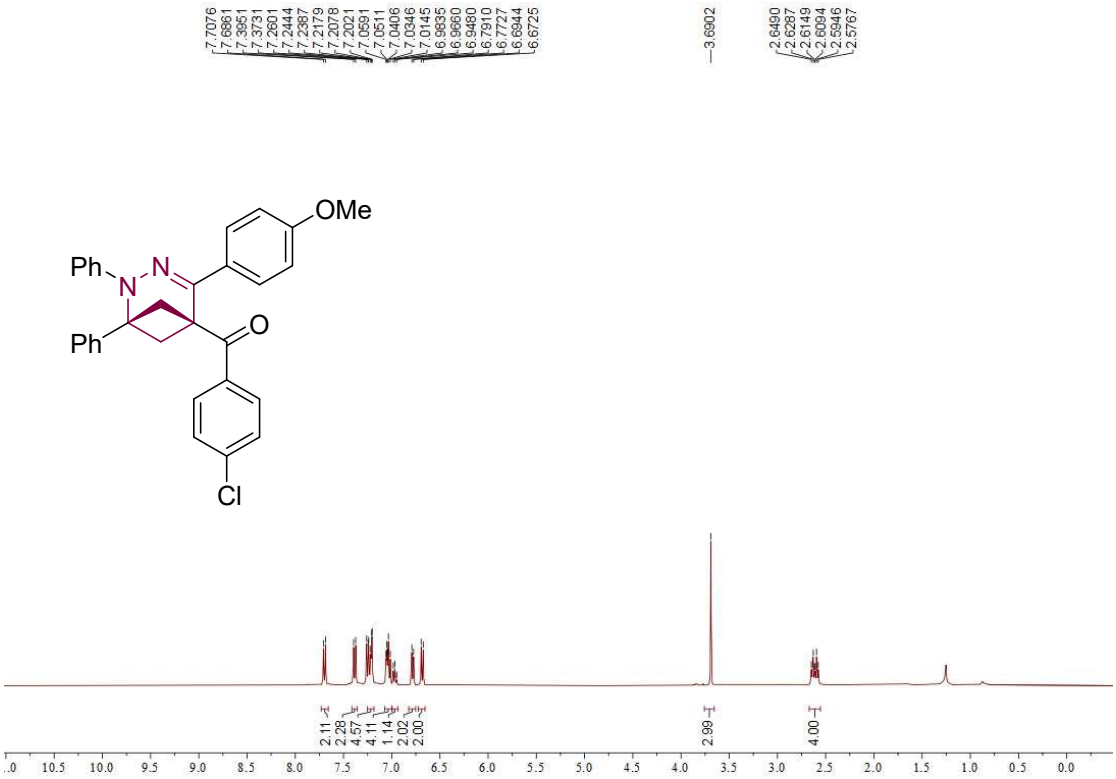
^{13}C NMR (101 MHz, $CDCl_3$) of 3c



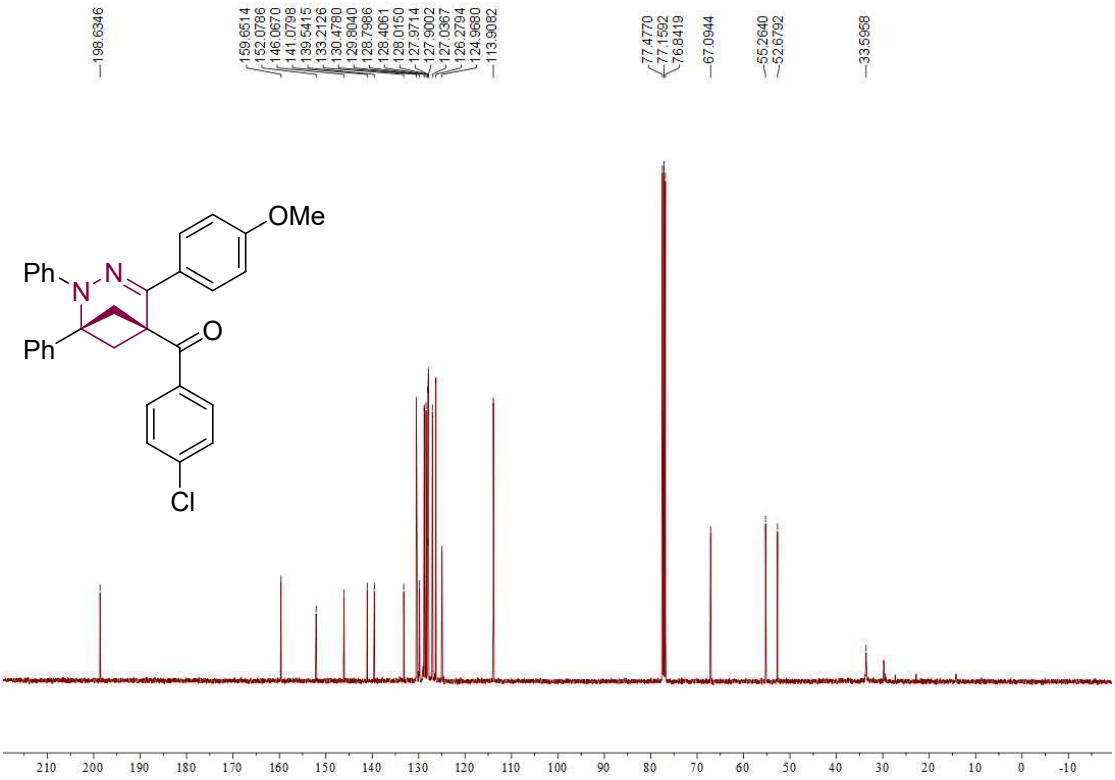
^{19}F NMR (376 MHz, $CDCl_3$) of **3c**



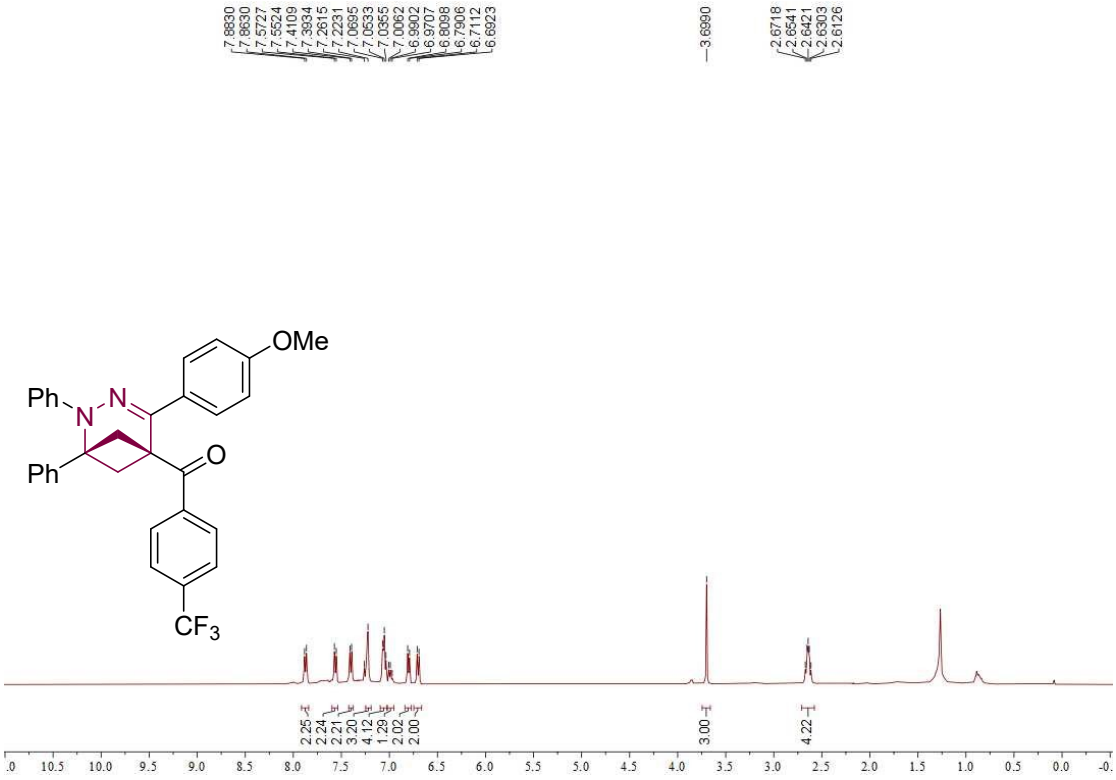
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



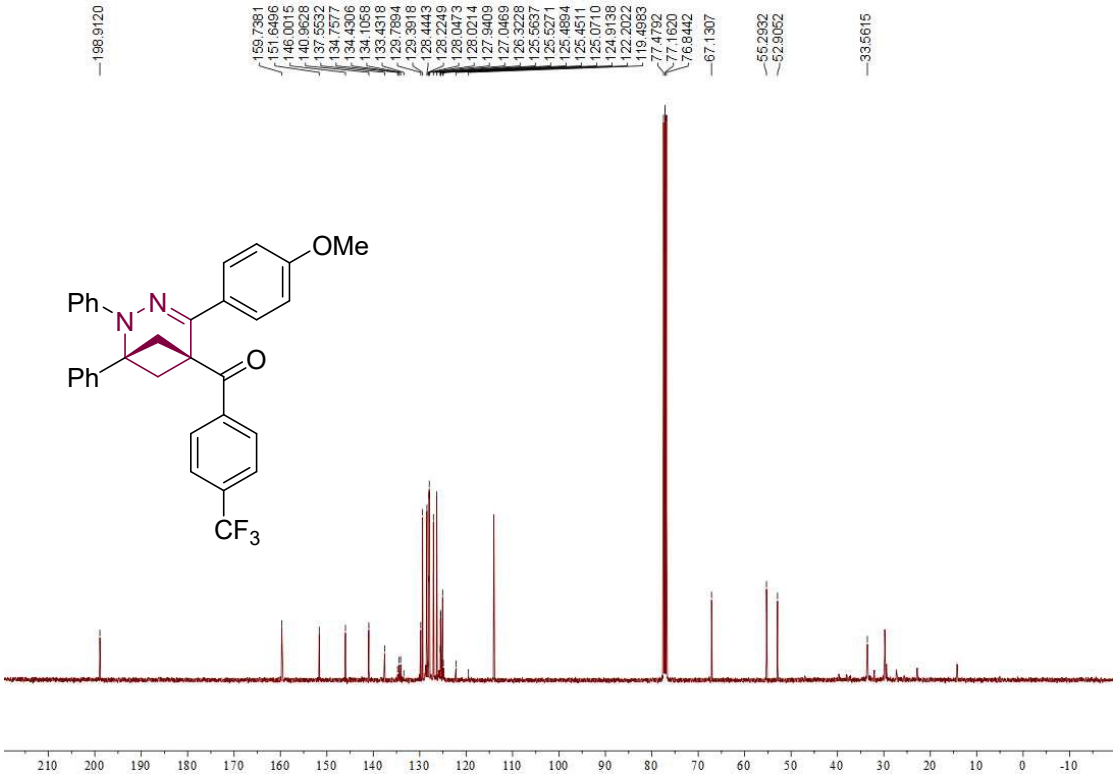
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



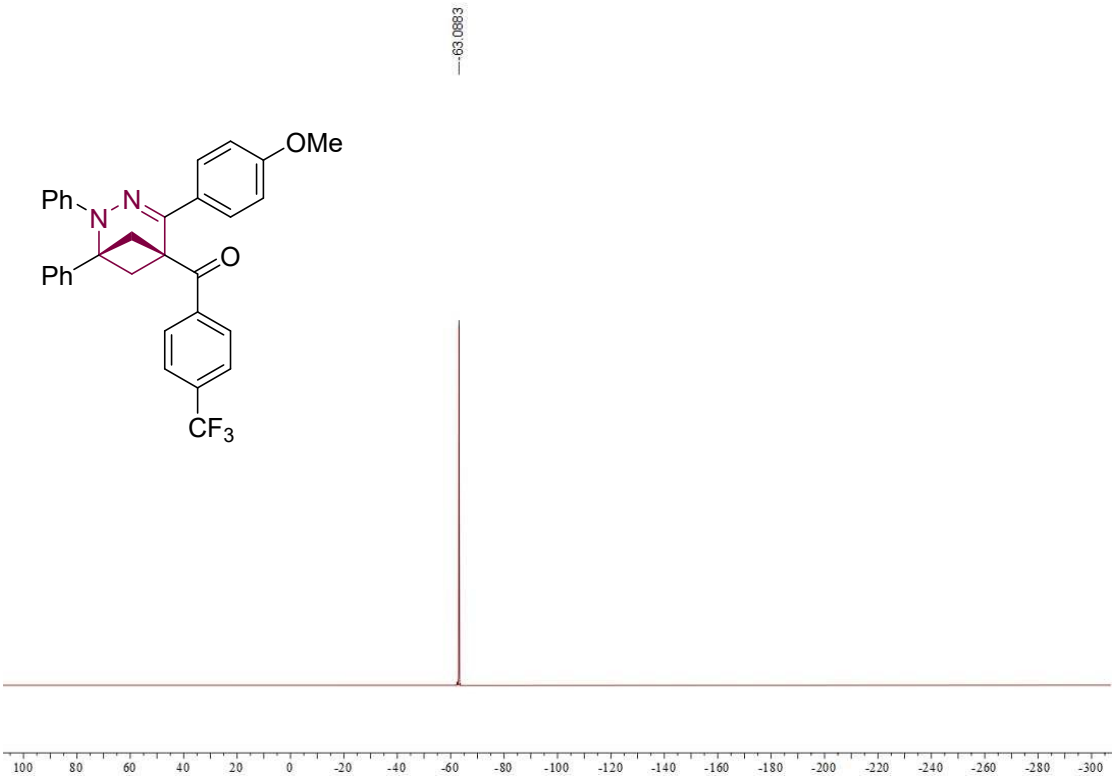
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



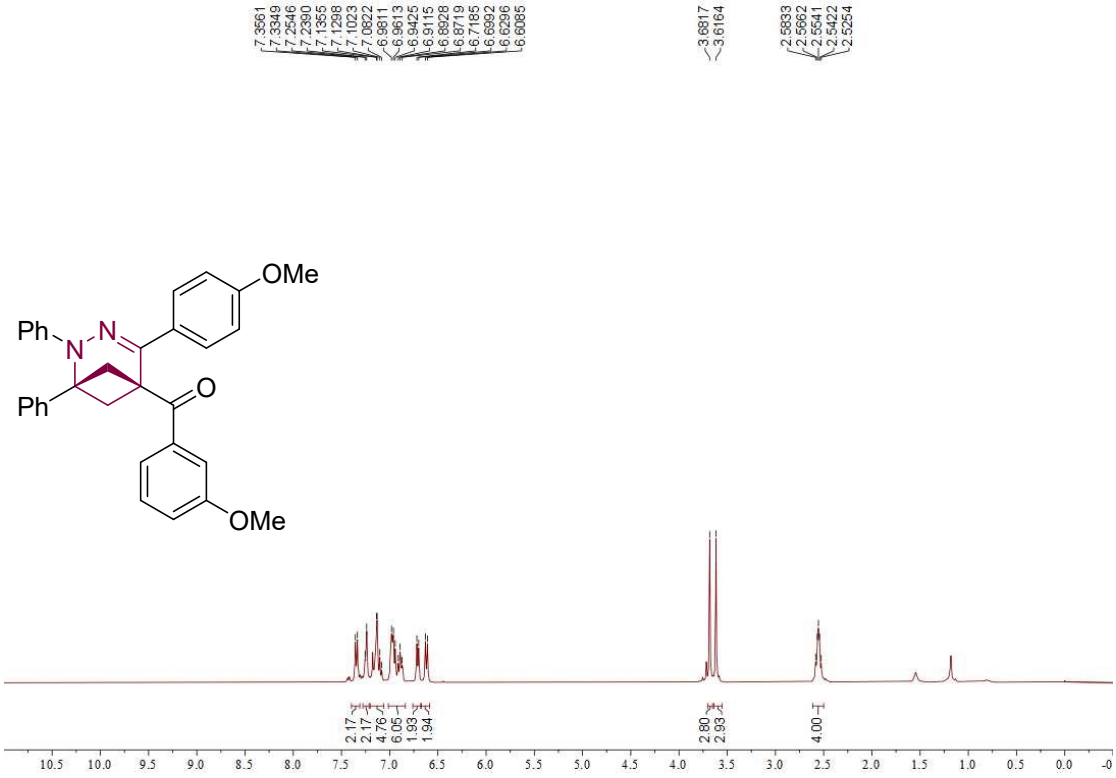
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



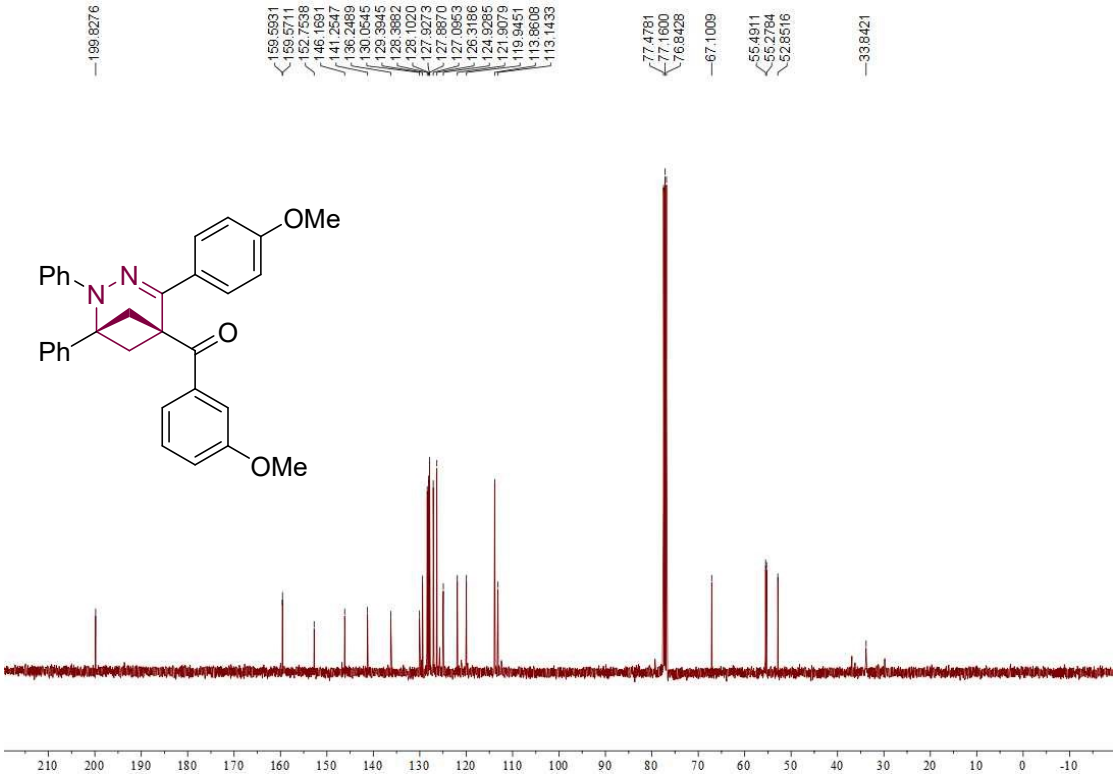
^{19}F NMR (376 MHz, $CDCl_3$) of **3e**



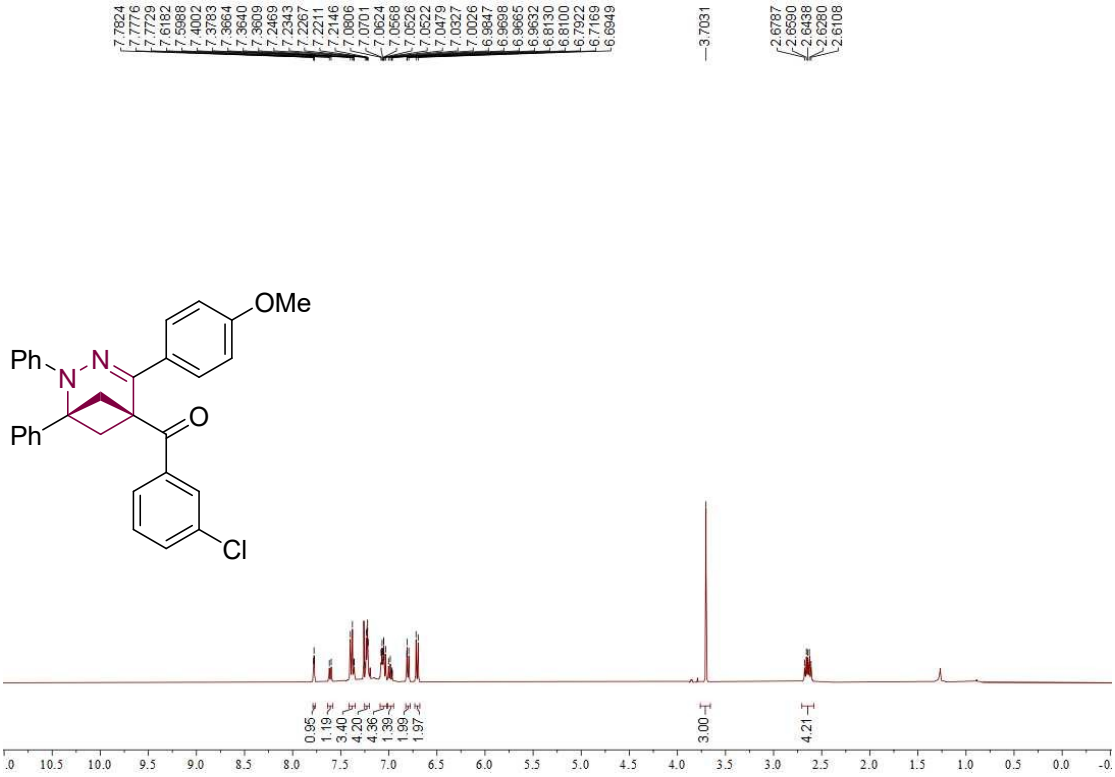
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



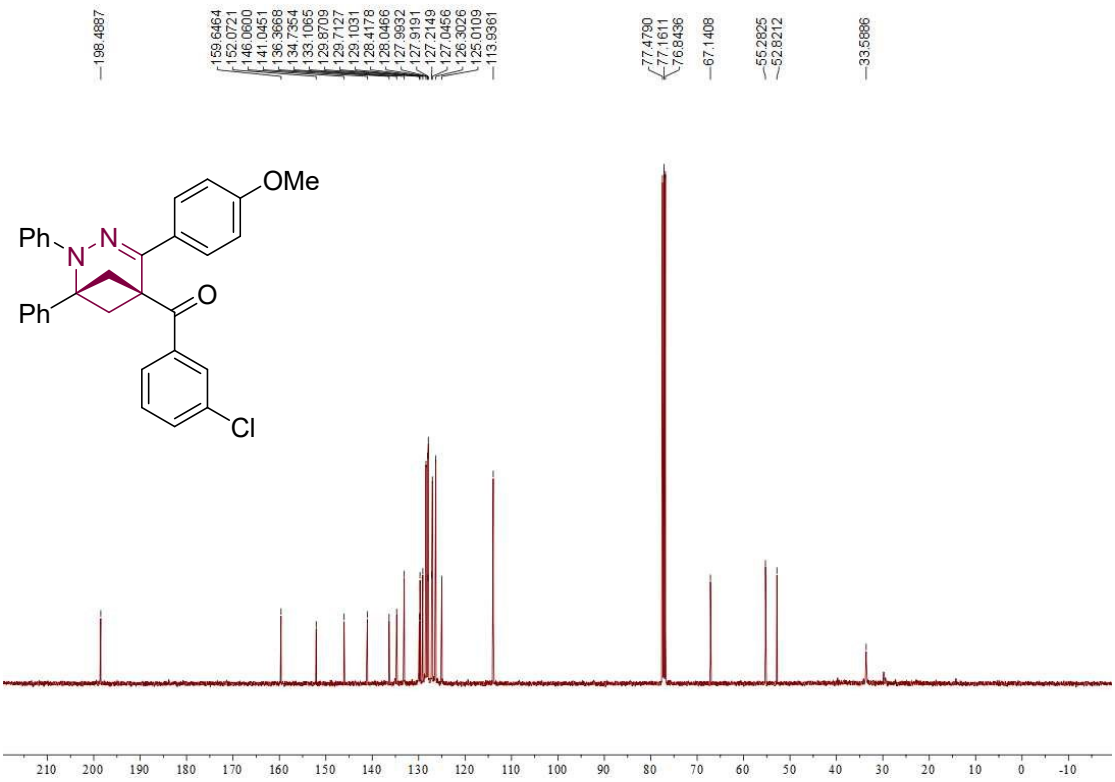
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



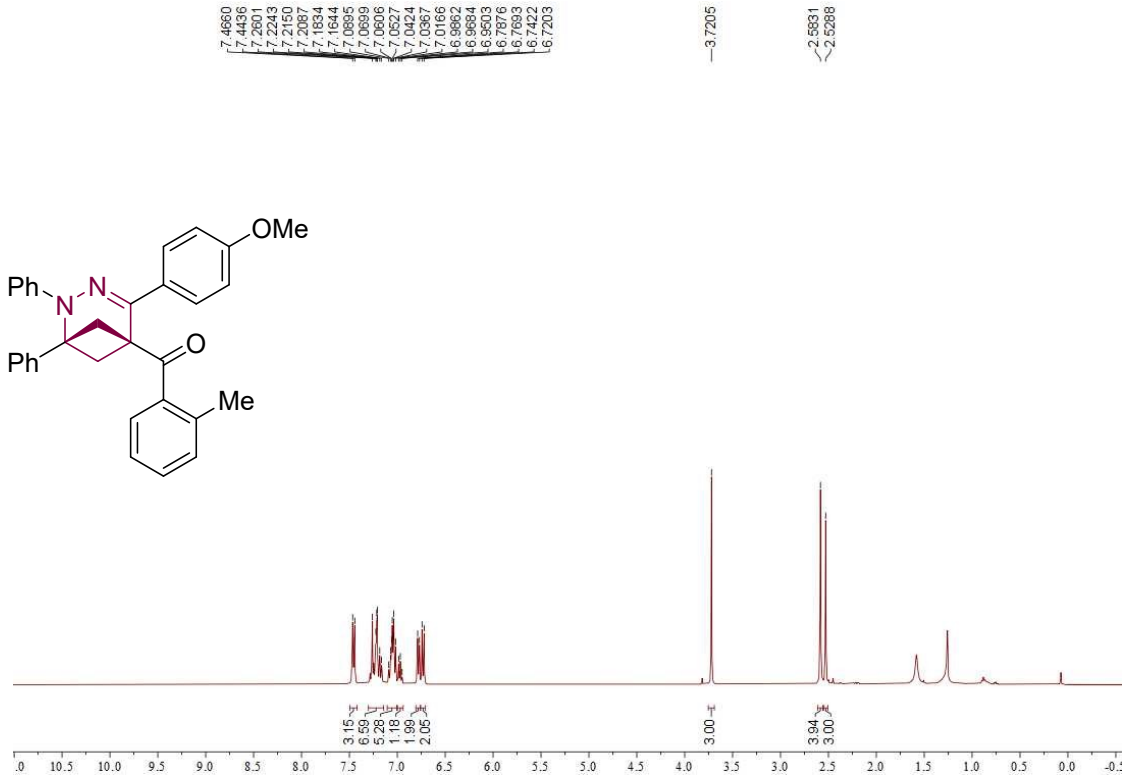
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



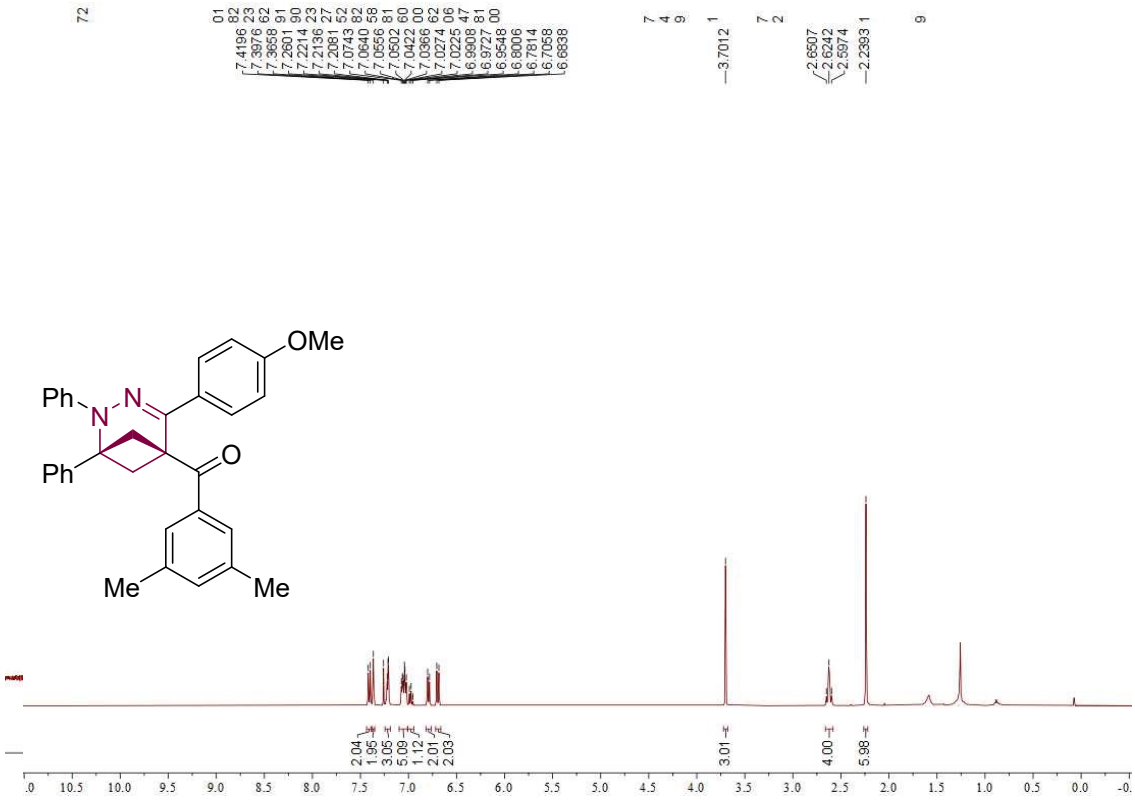
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



^{1}H NMR (400 MHz, $CDCl_3$) of **3h**

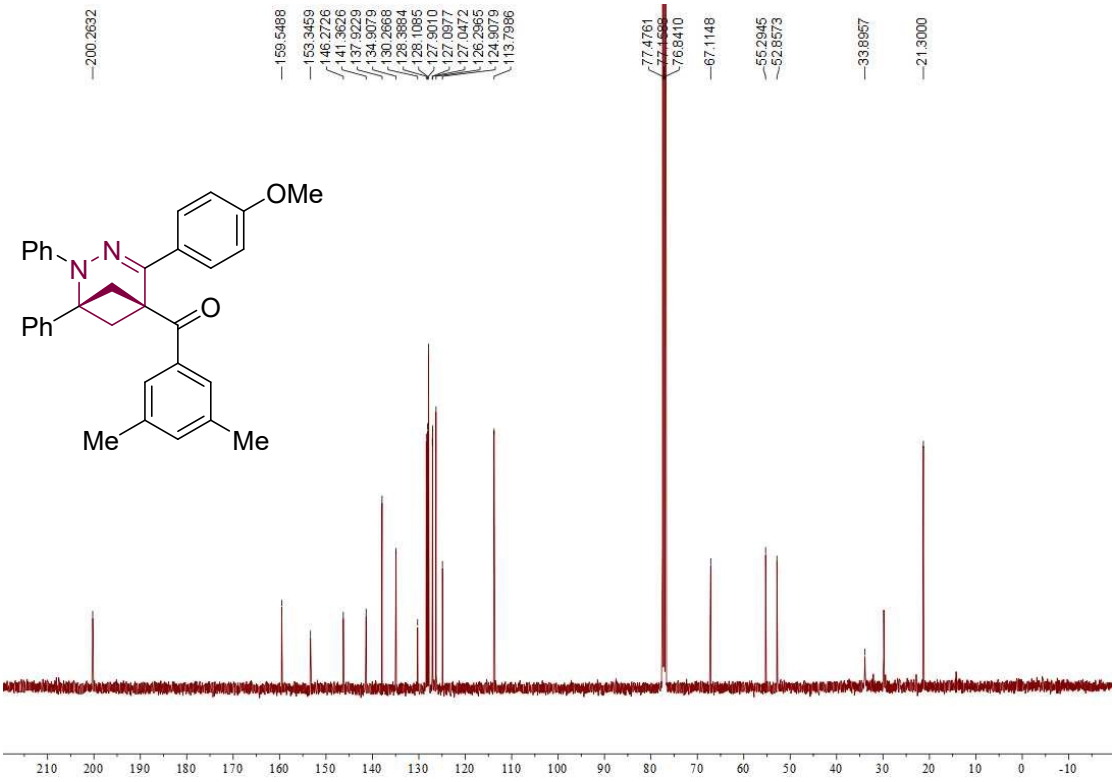


^{13}C NMR (101 MHz, $CDCl_3$) of **3h**

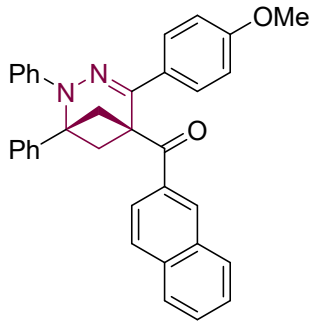


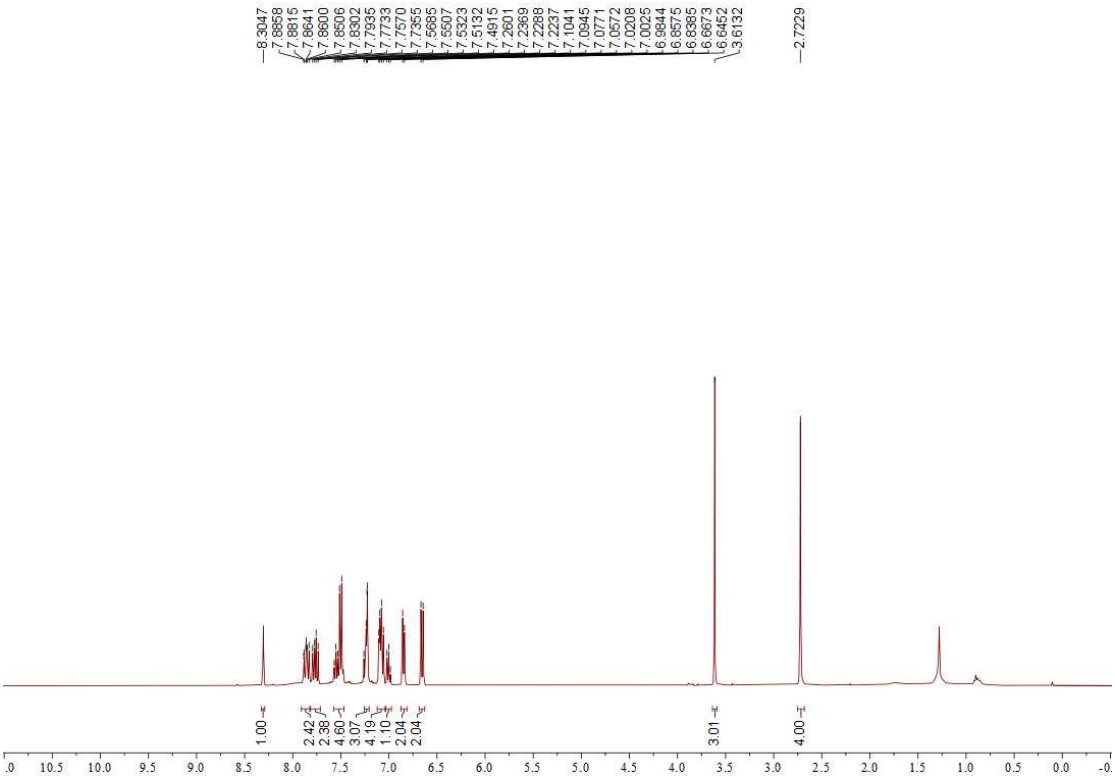
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**

^{13}C NMR (101 MHz, $CDCl_3$) of **3i**

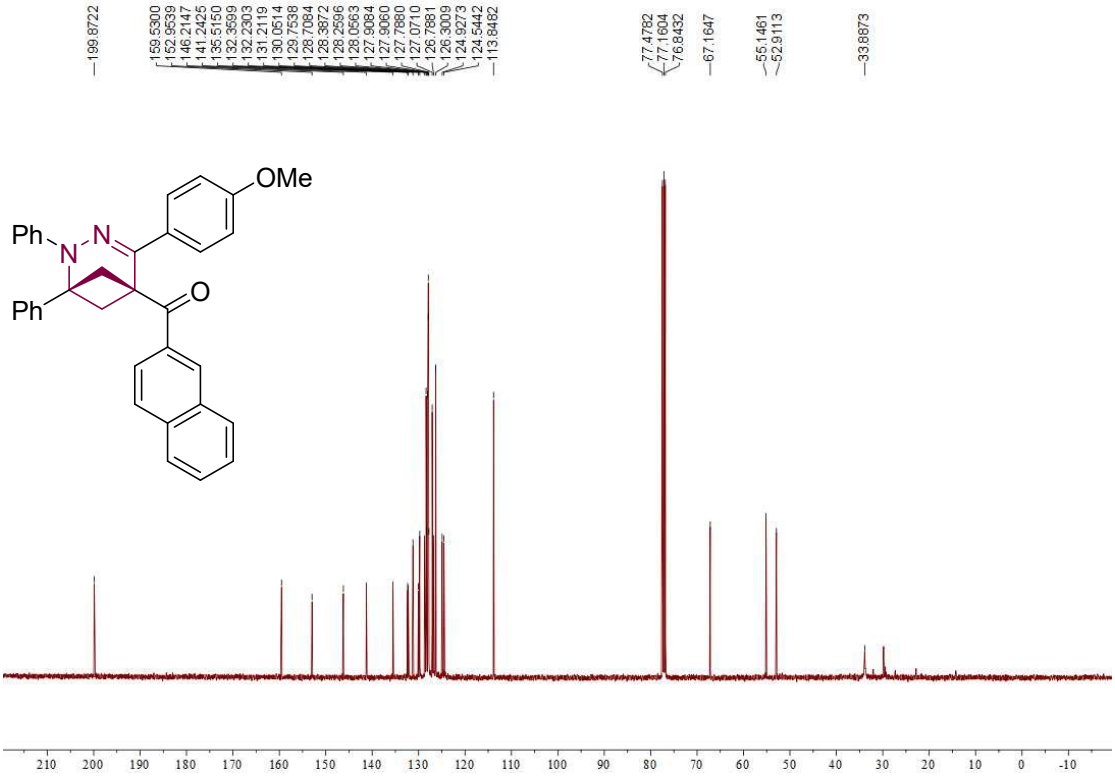


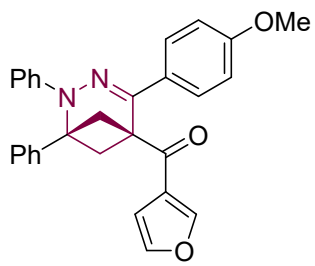
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



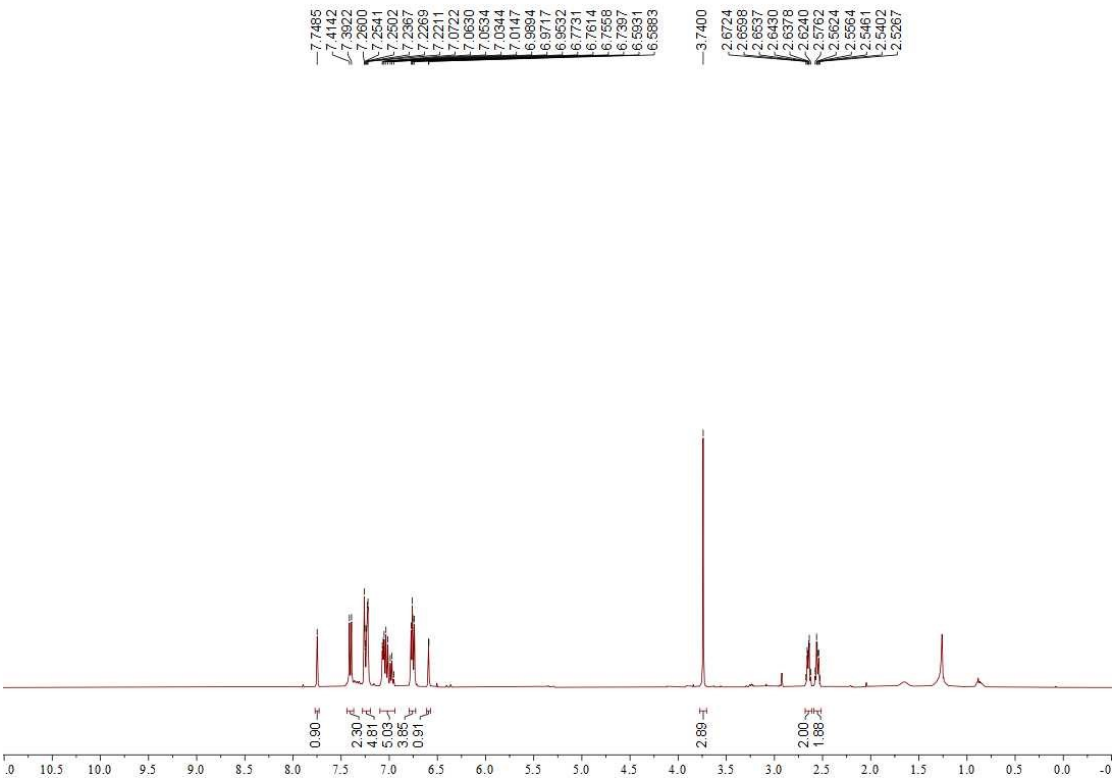


^{13}C NMR (101 MHz, $CDCl_3$) of **3j**

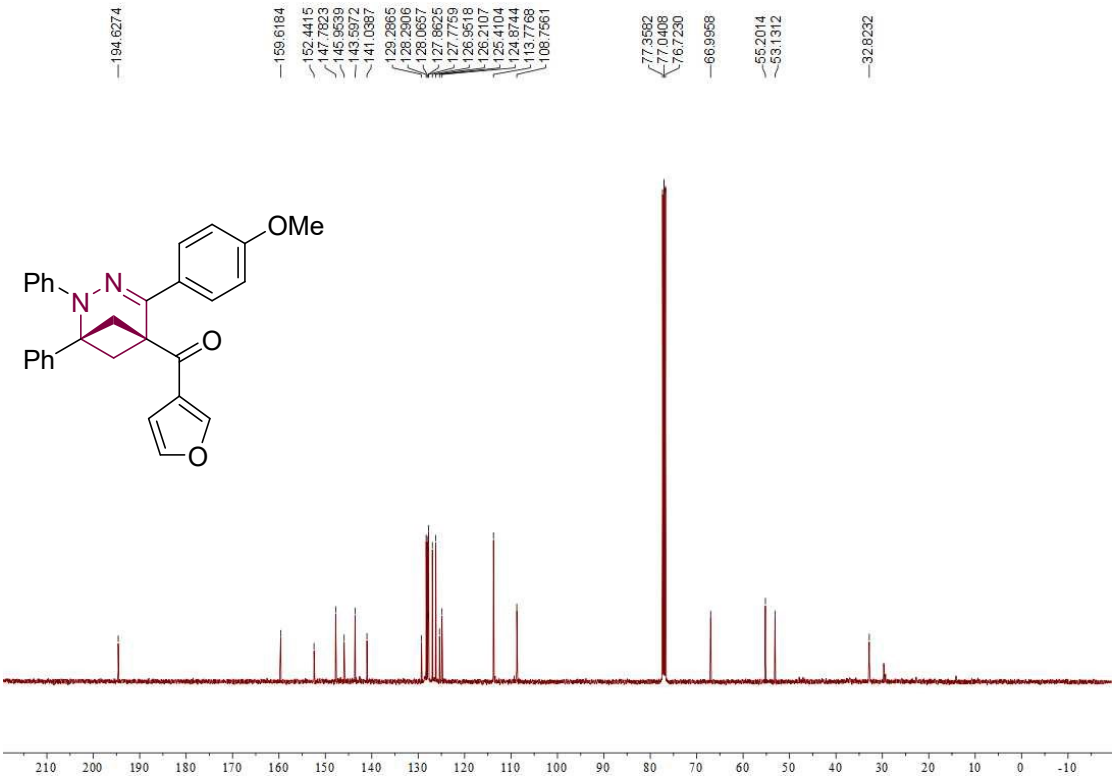




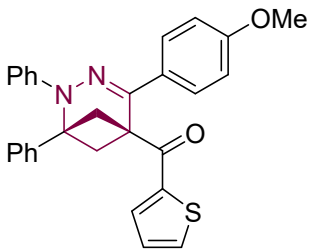
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**

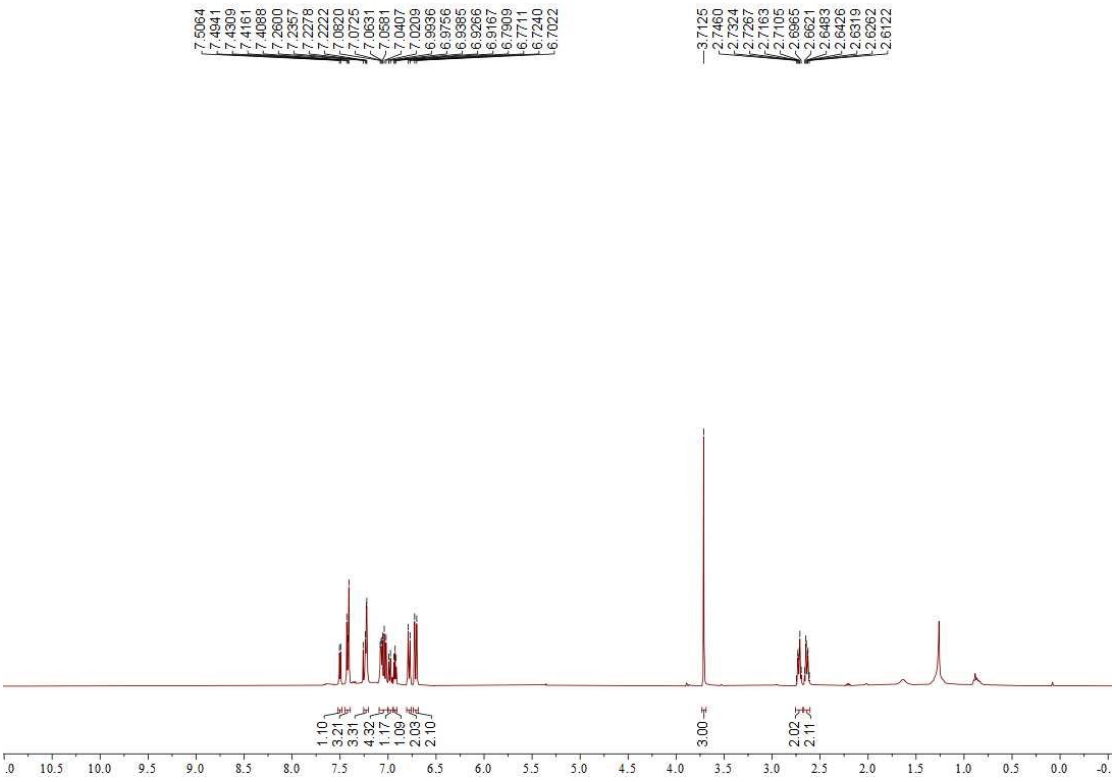


^{13}C NMR (101 MHz, $CDCl_3$) of **3k**

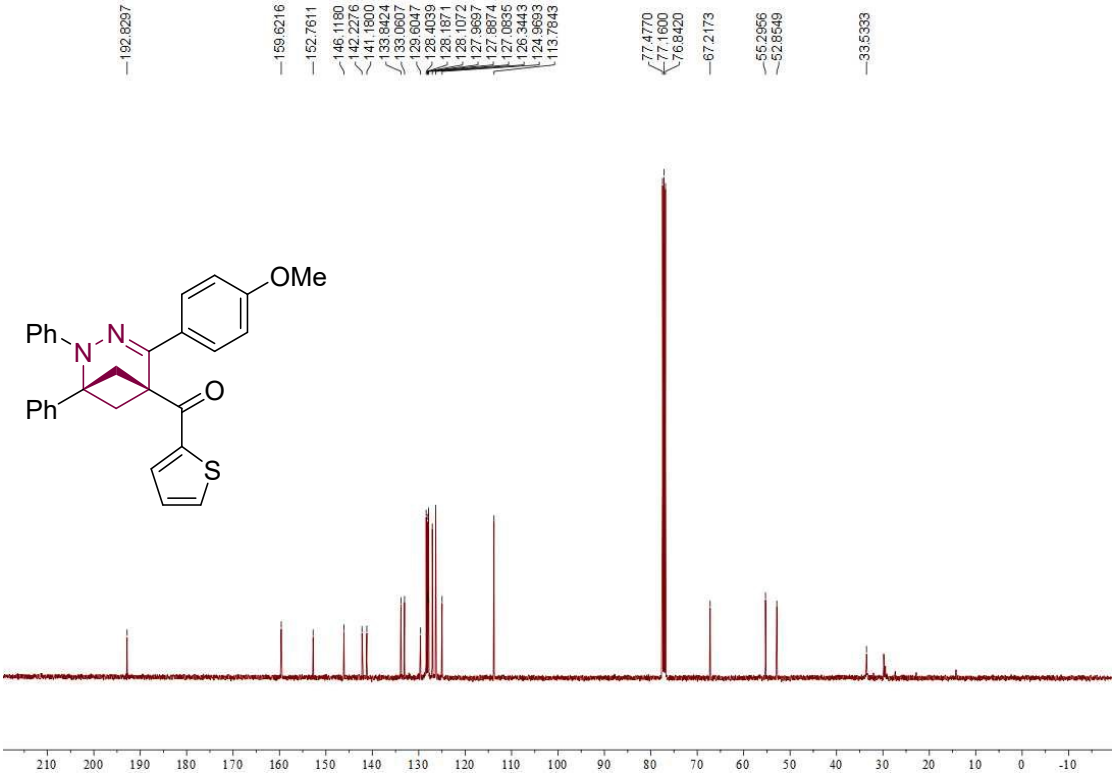


^{1}H NMR (400 MHz, $CDCl_3$) of **3l**

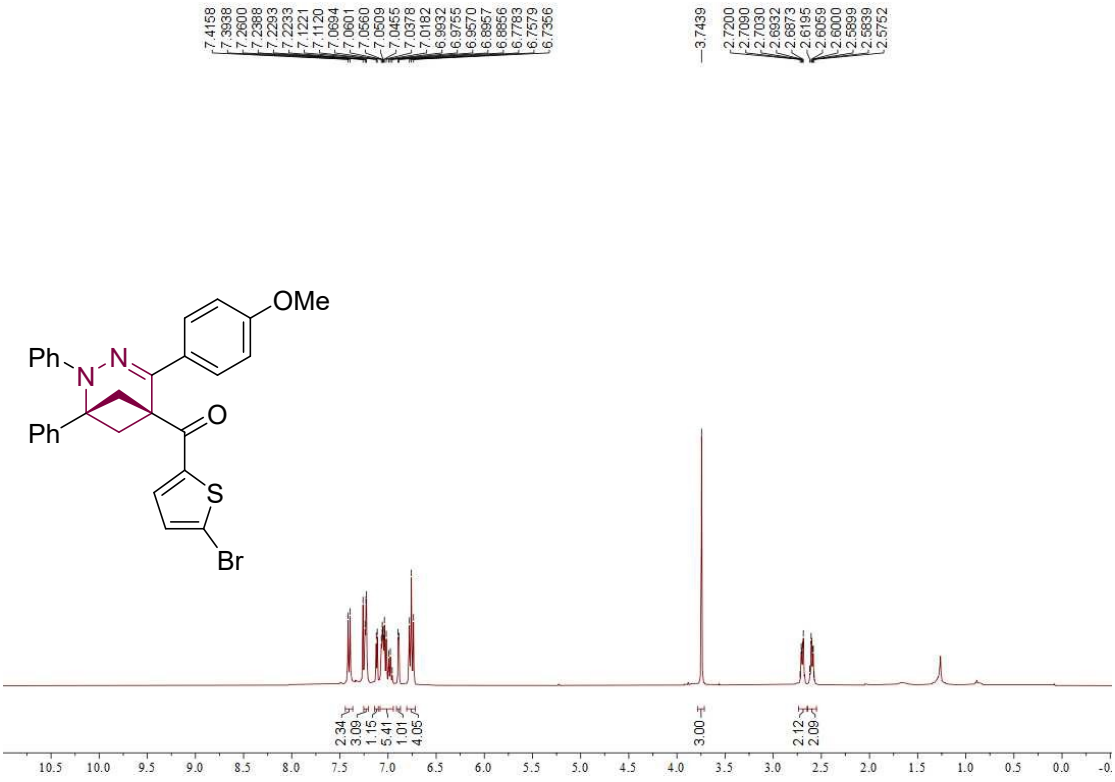




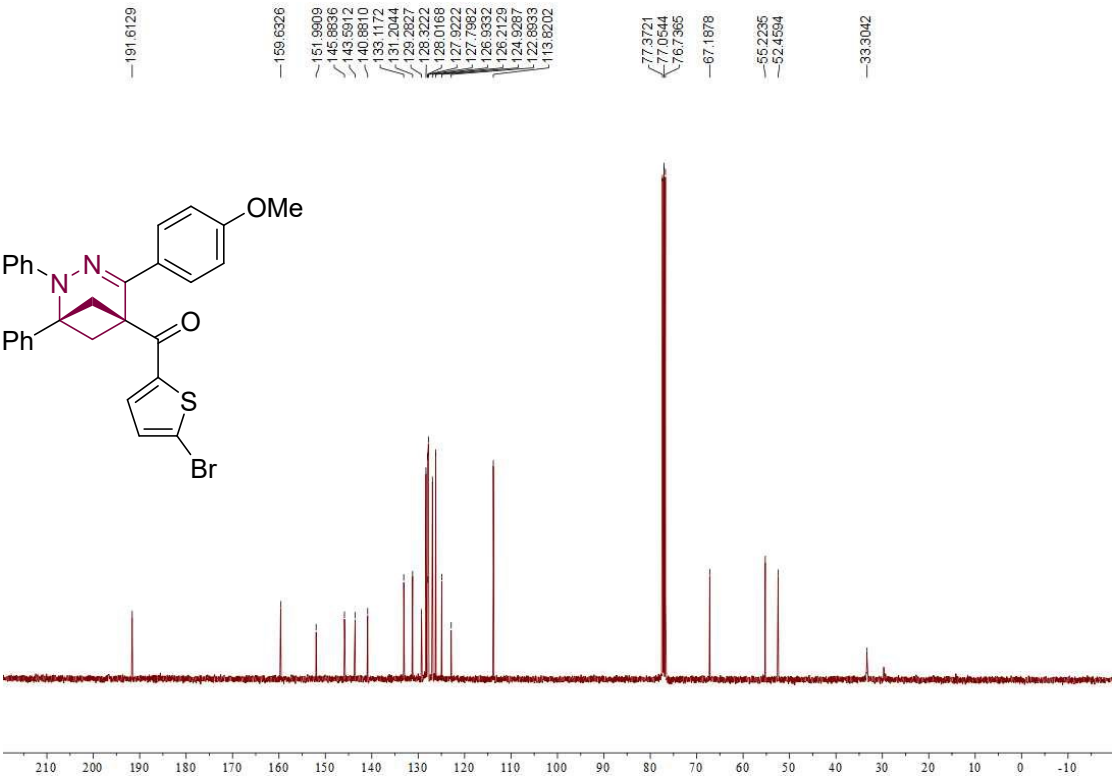
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



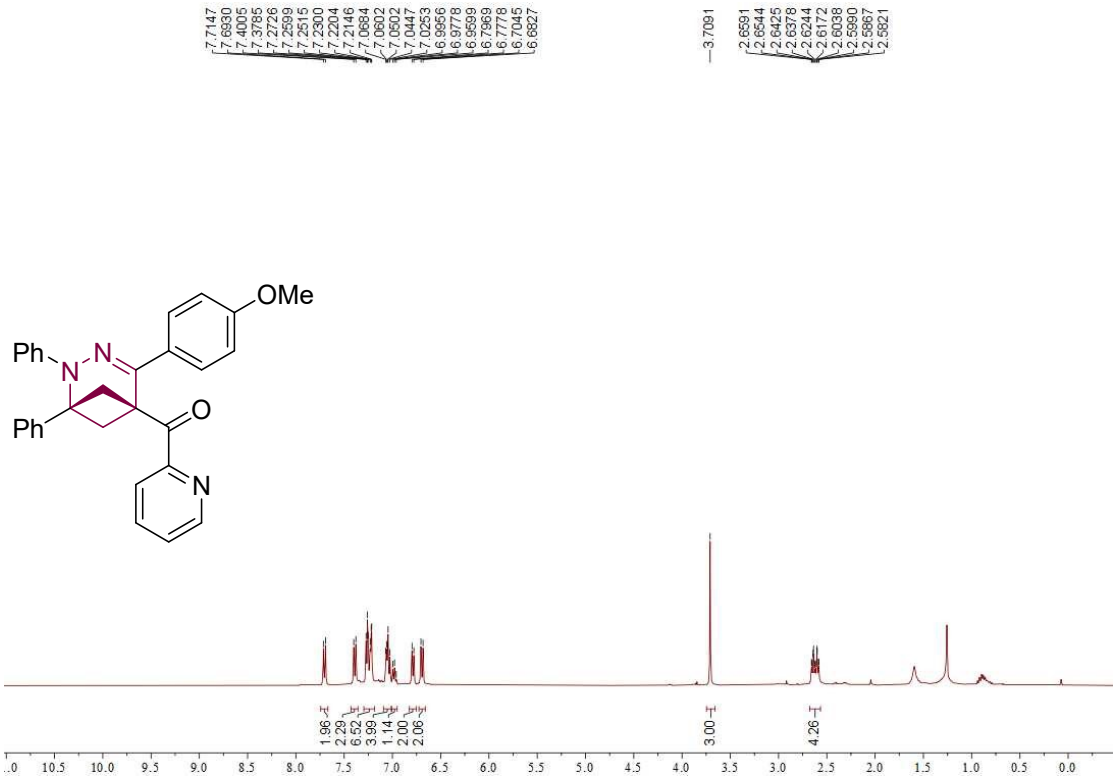
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



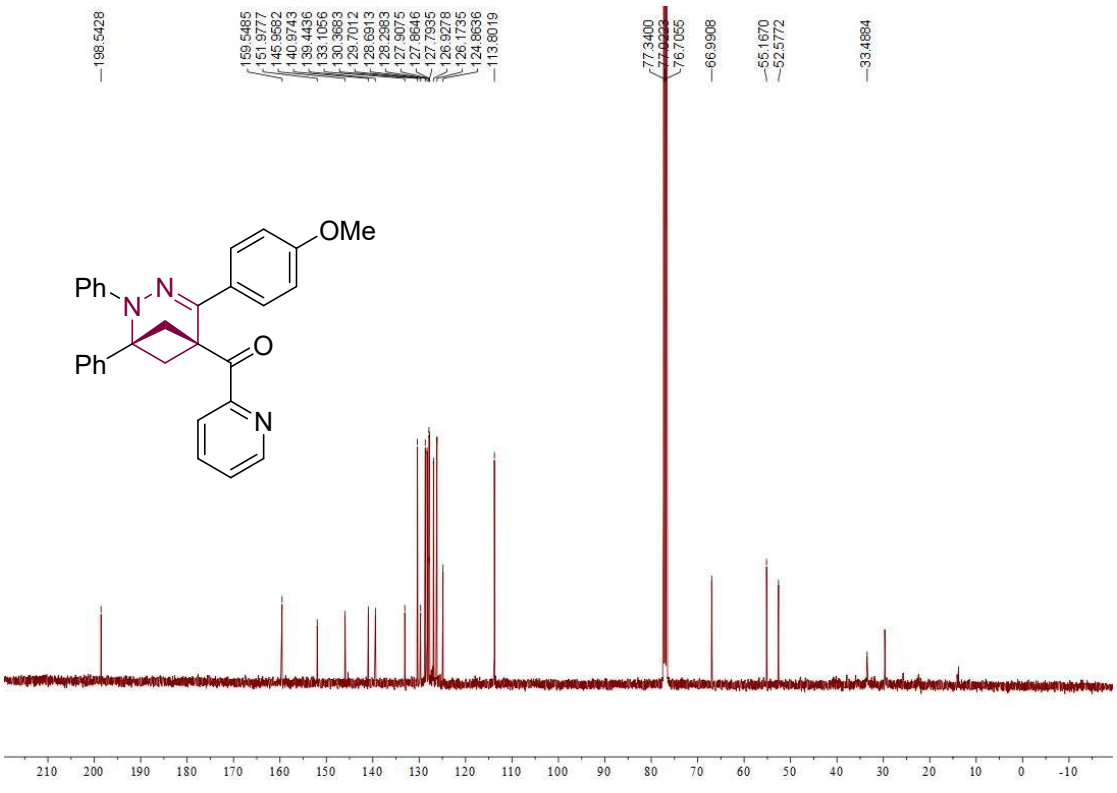
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



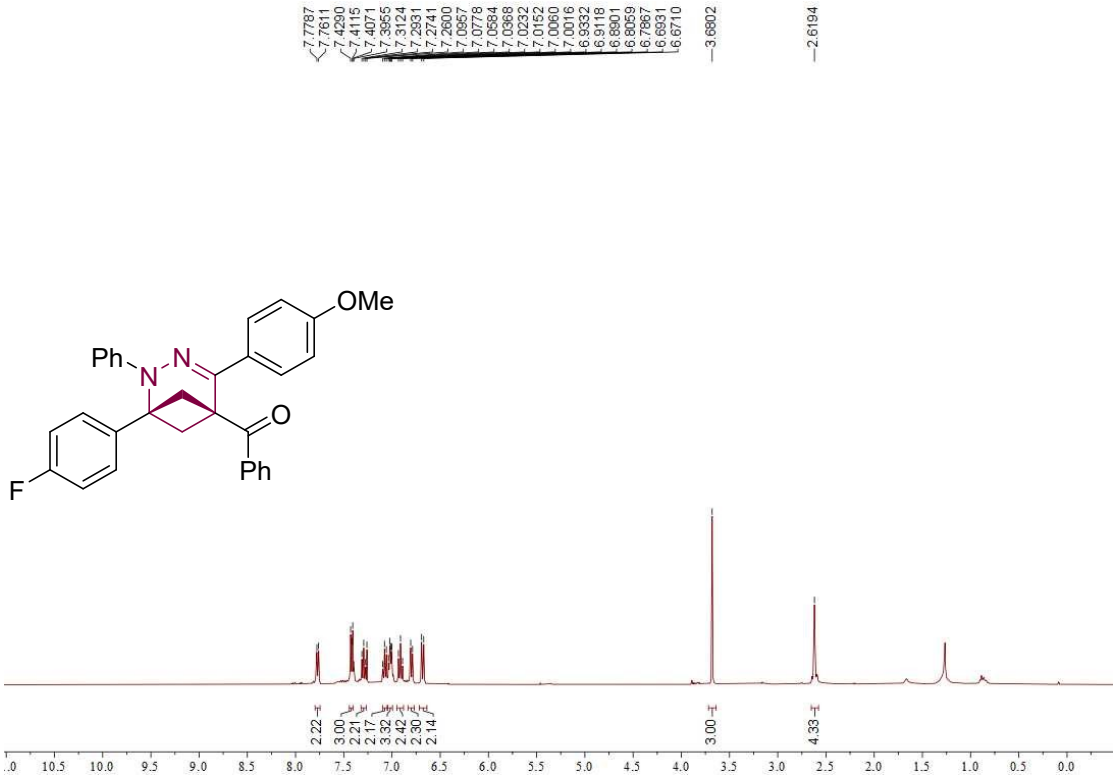
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



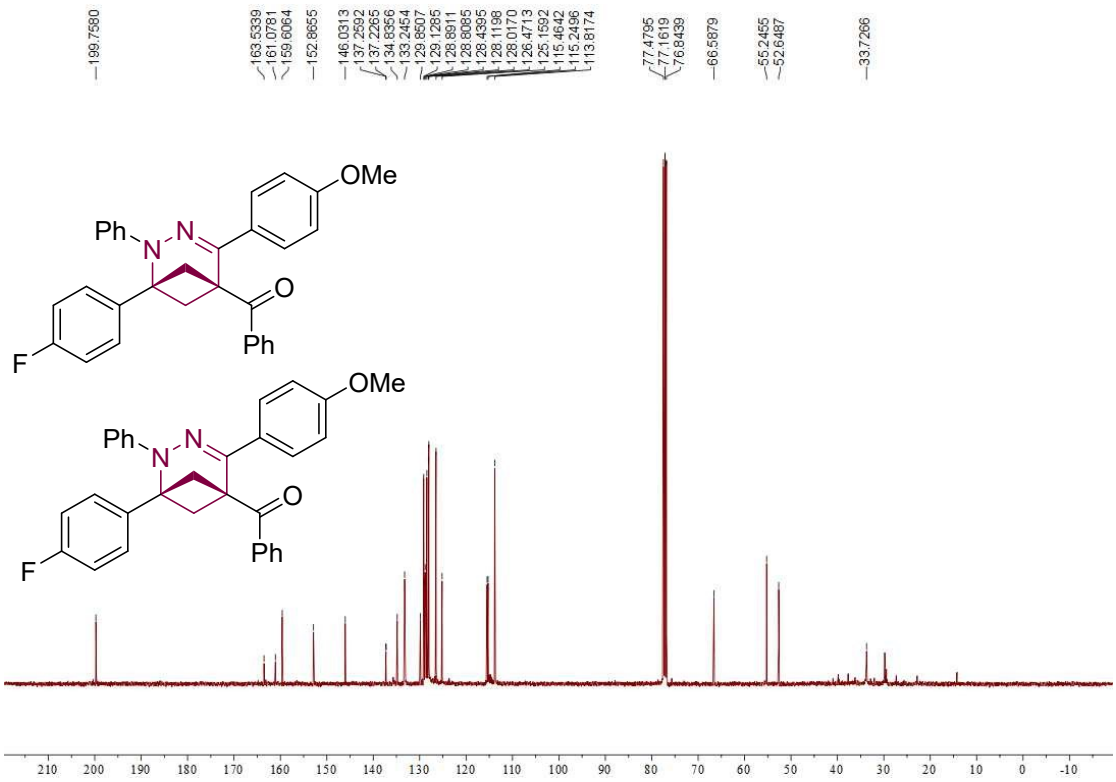
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



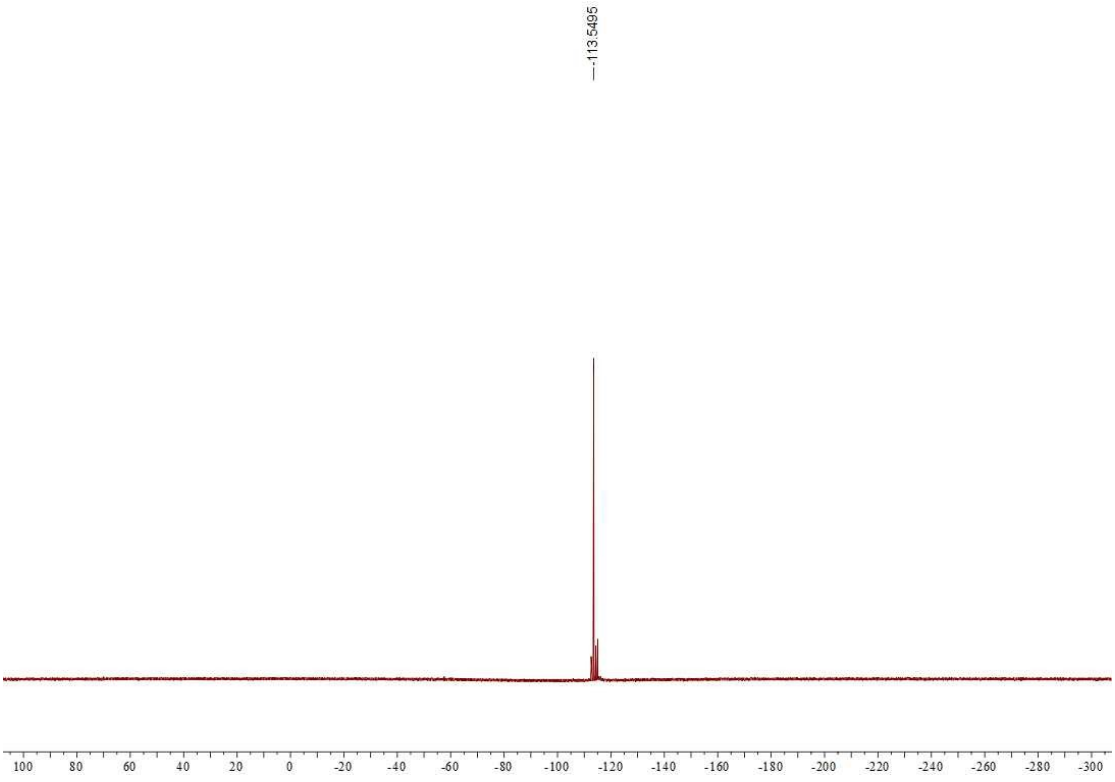
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



^{19}F NMR (376 MHz, $CDCl_3$) of **3o**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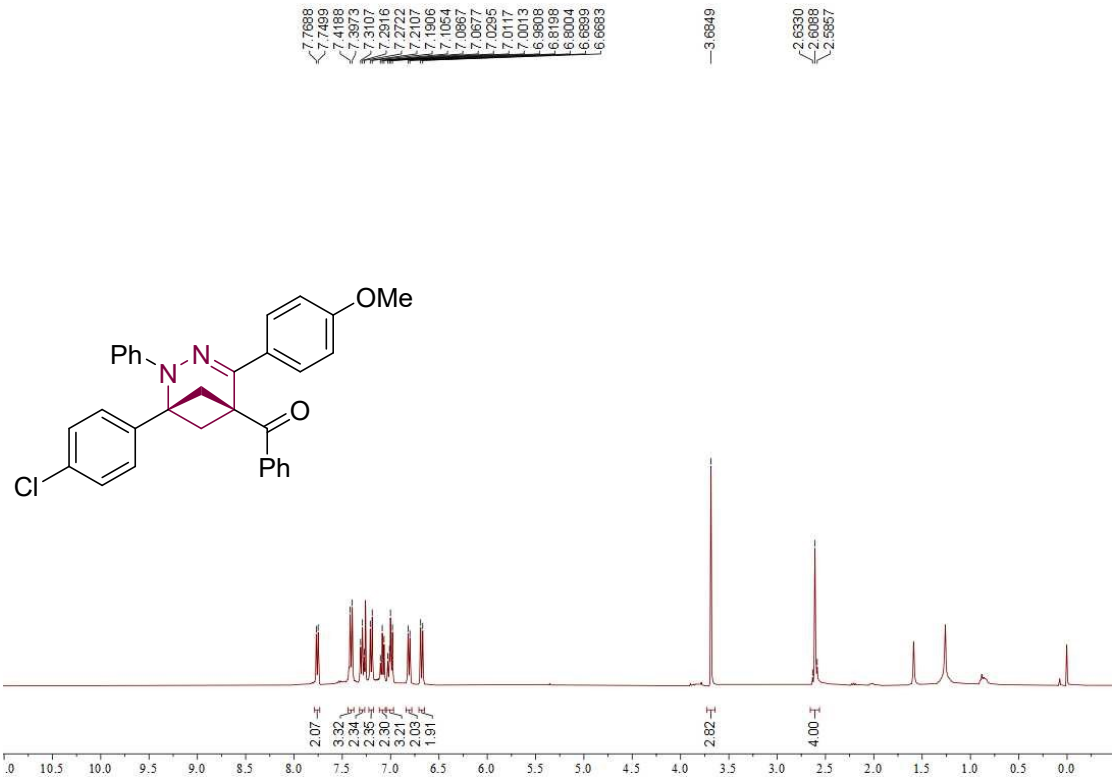
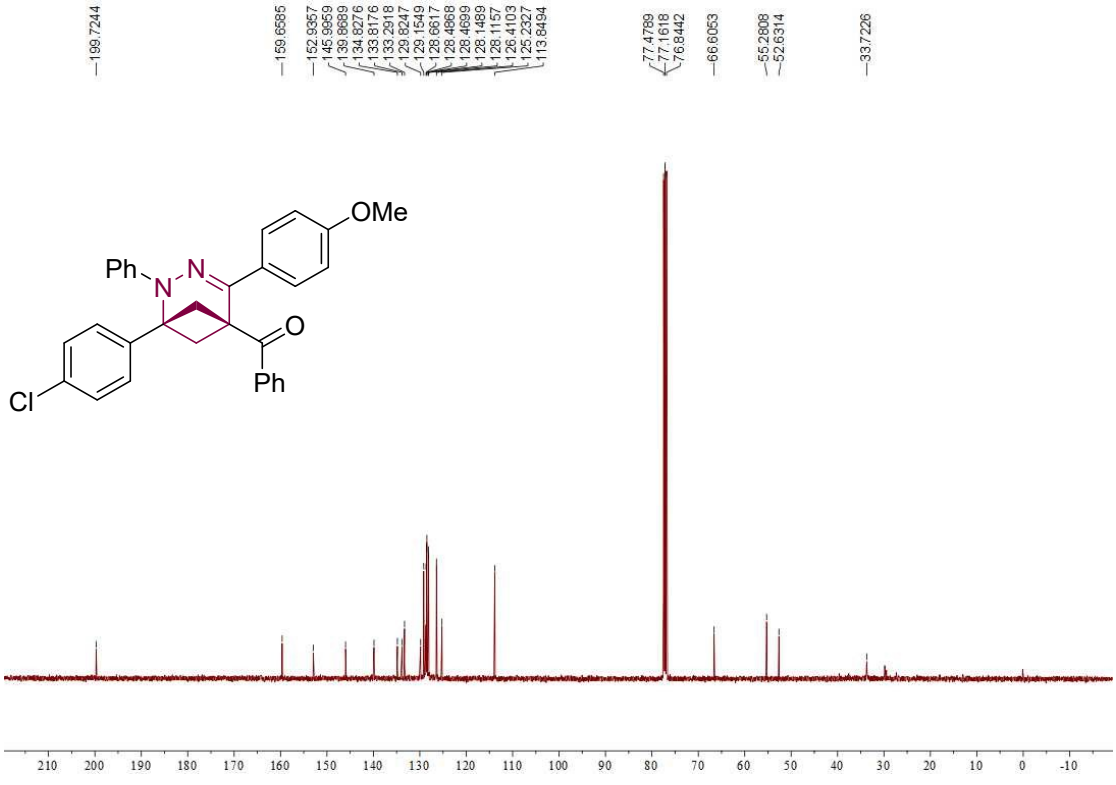
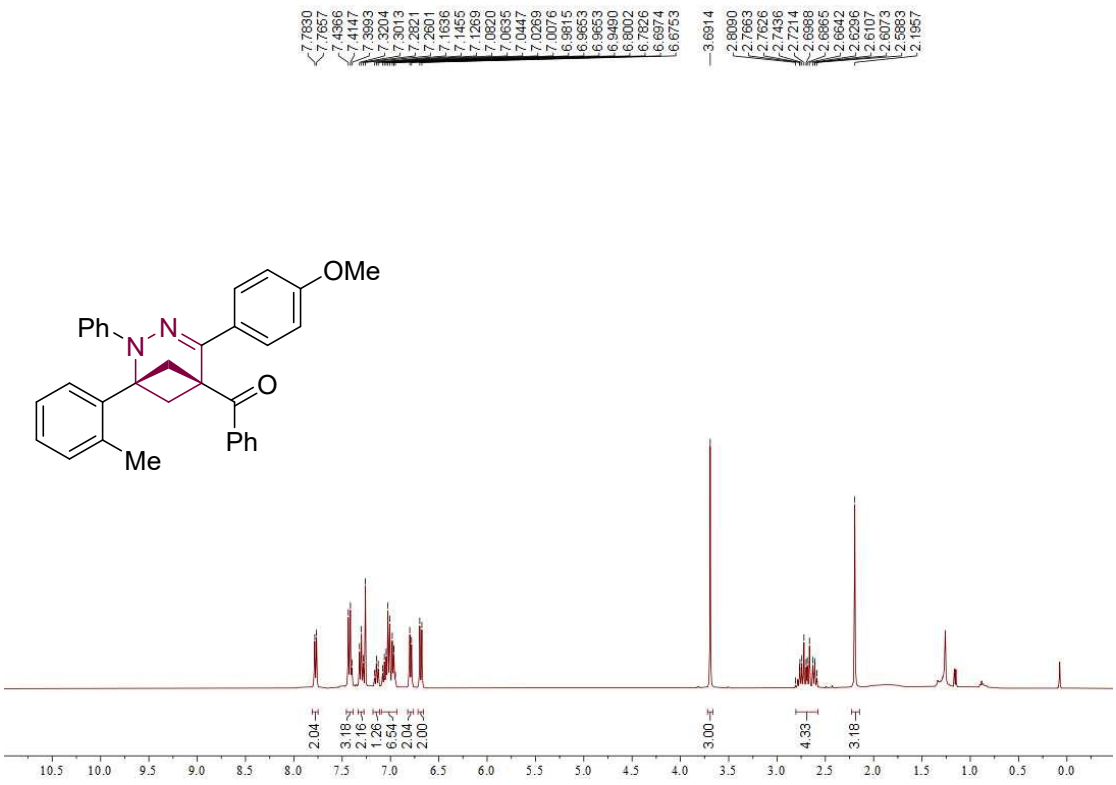
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



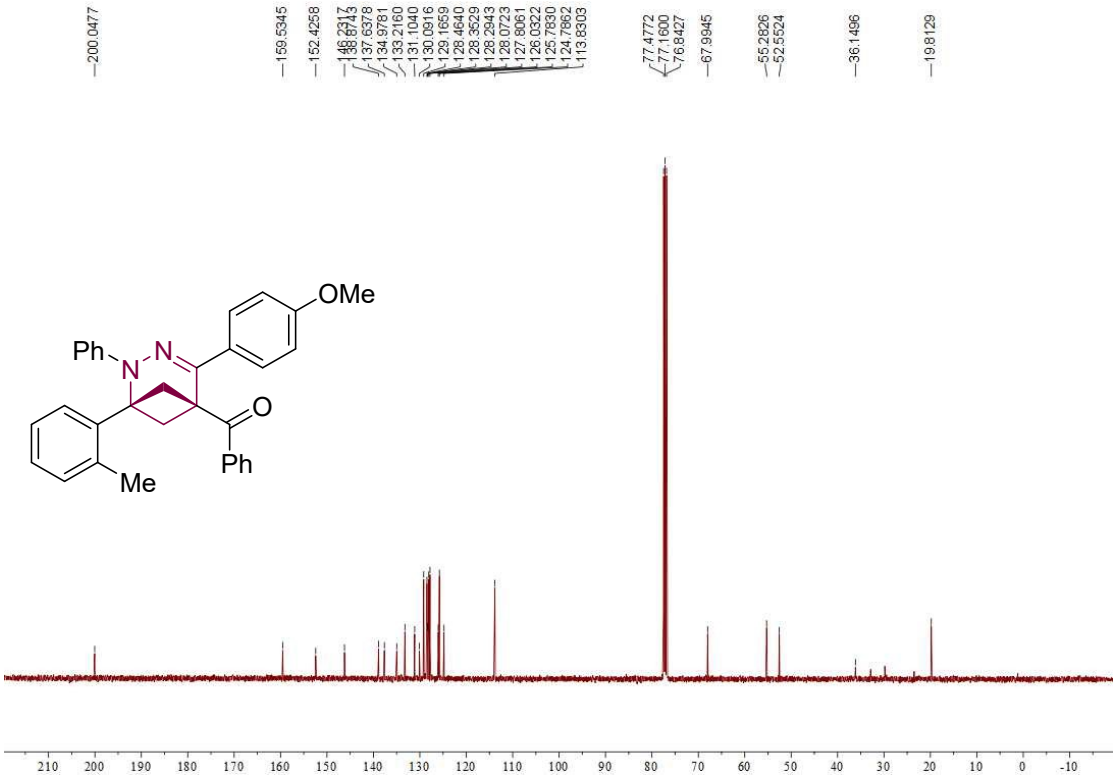
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



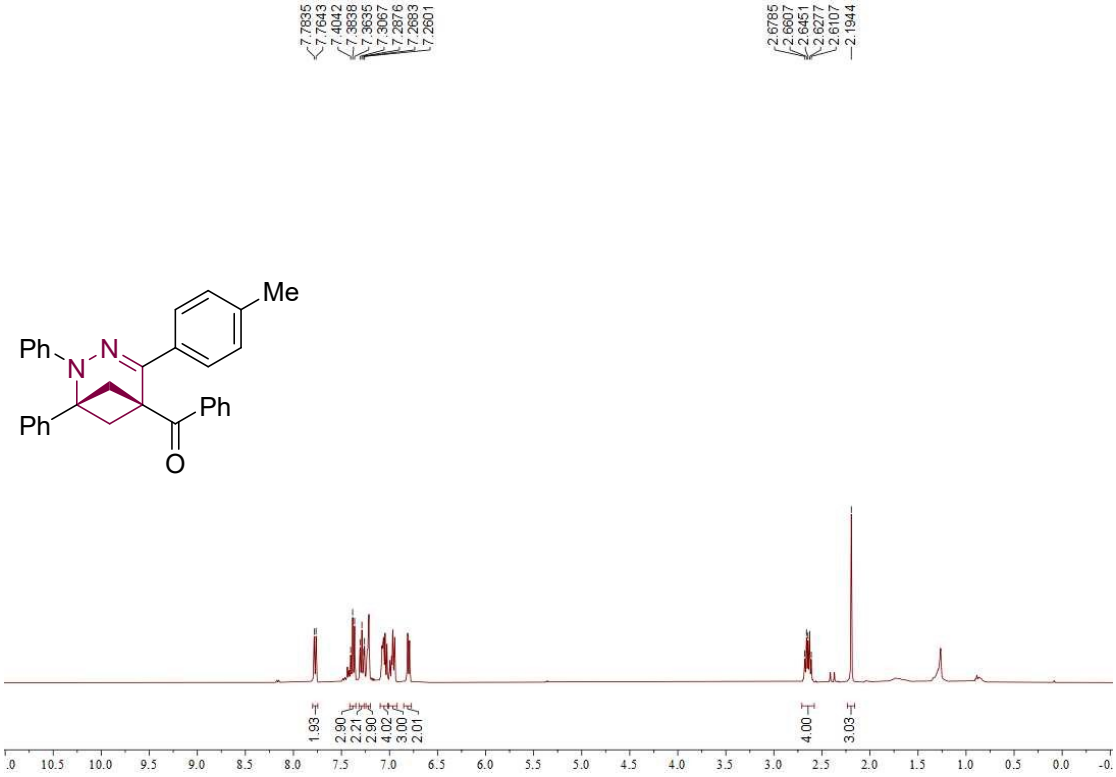
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



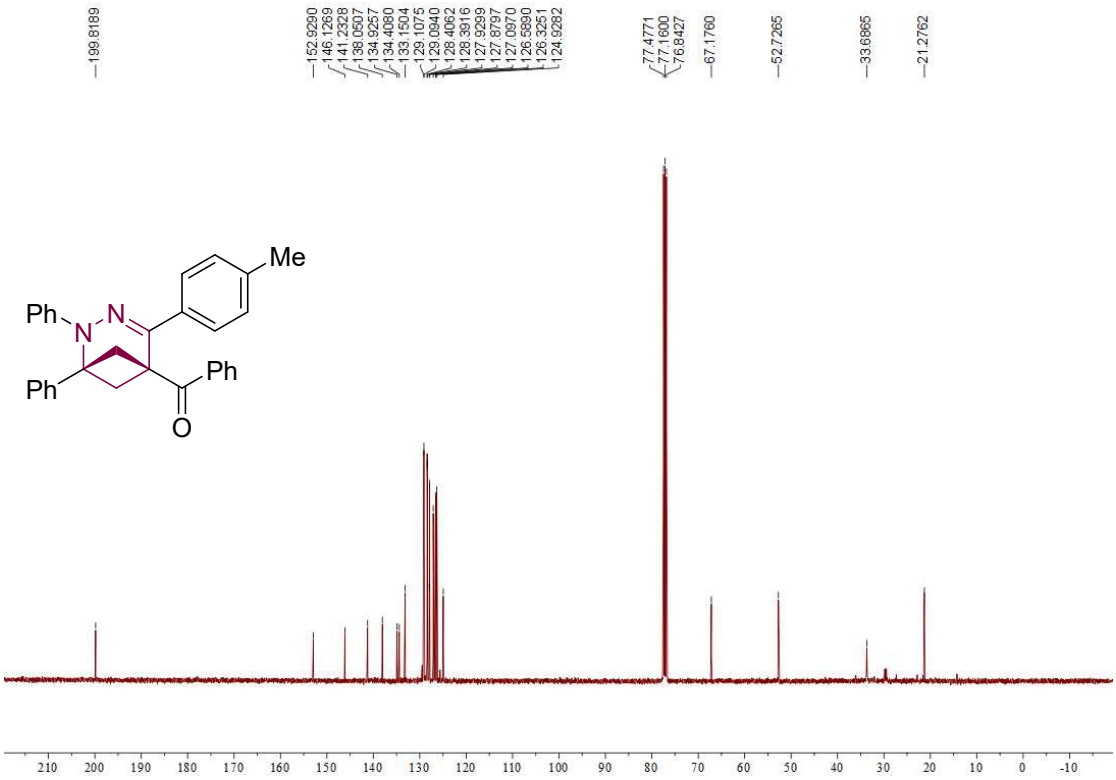
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



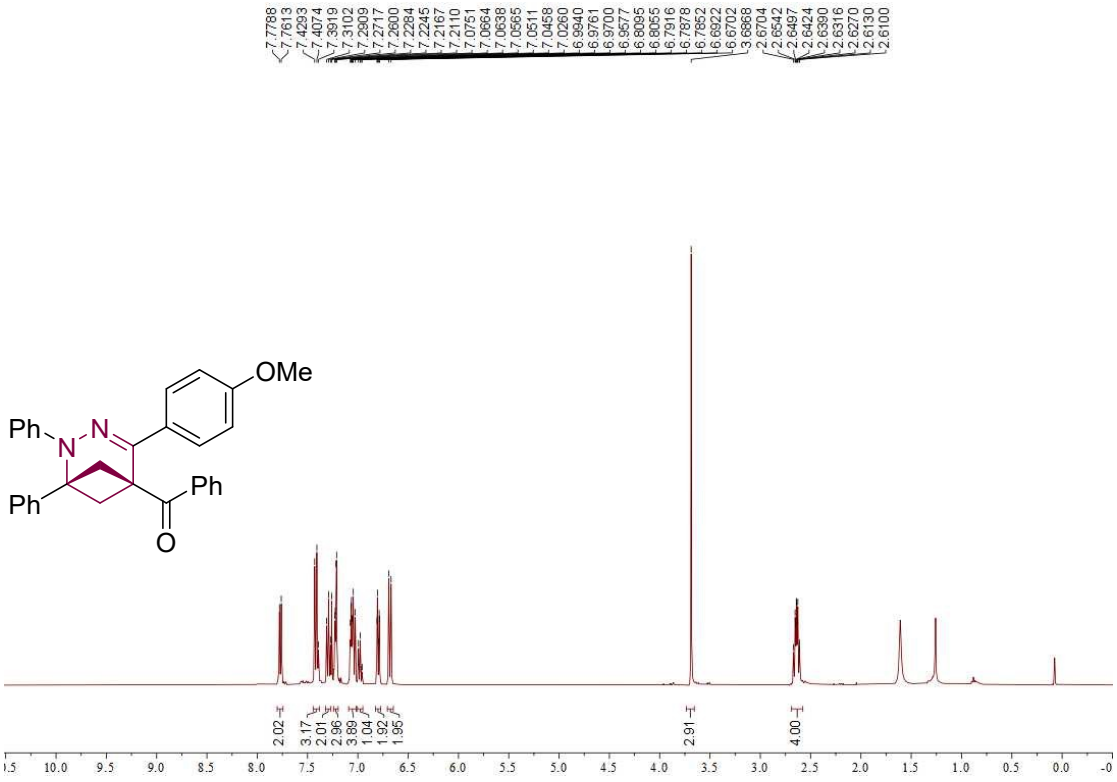
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



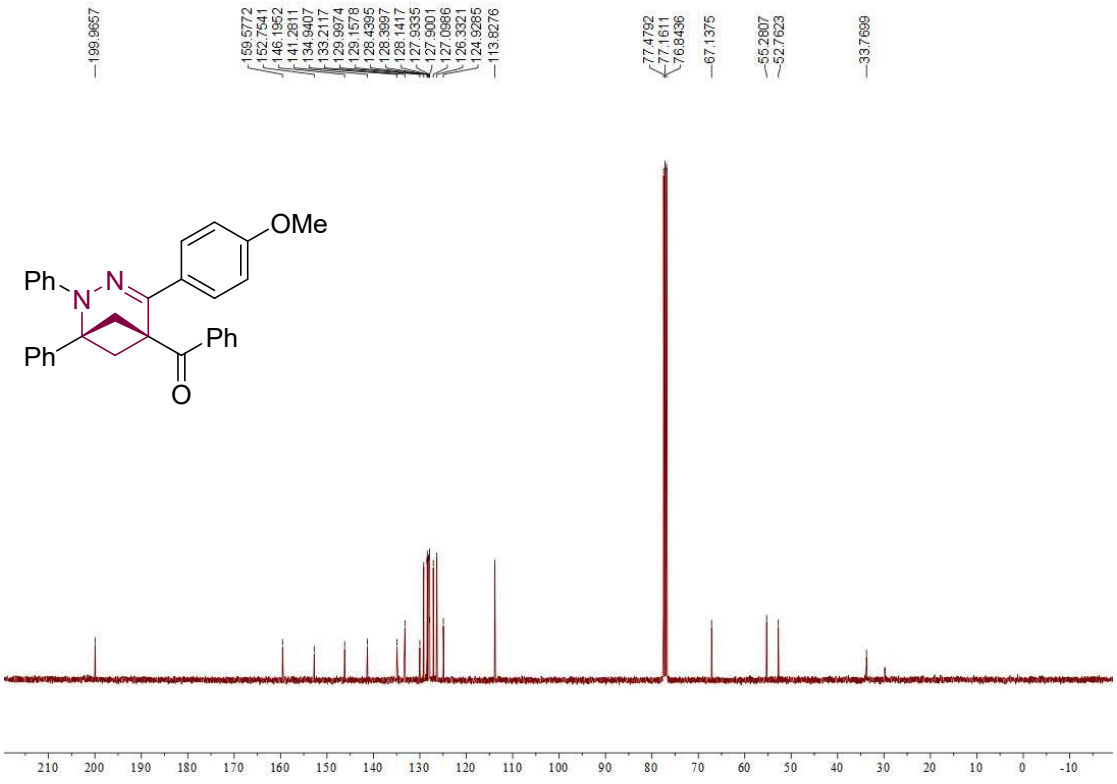
^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



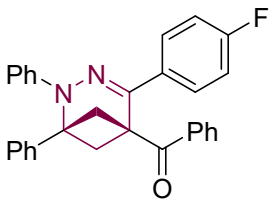
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**

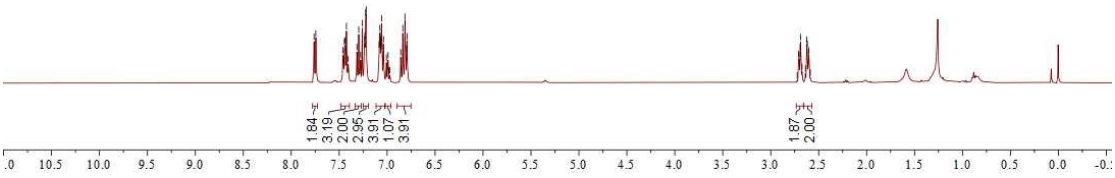


^{13}C NMR (101 MHz, $CDCl_3$) of **3s**

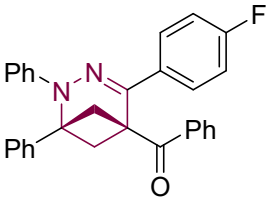


^{1}H NMR (400 MHz, $CDCl_3$) of **3t**

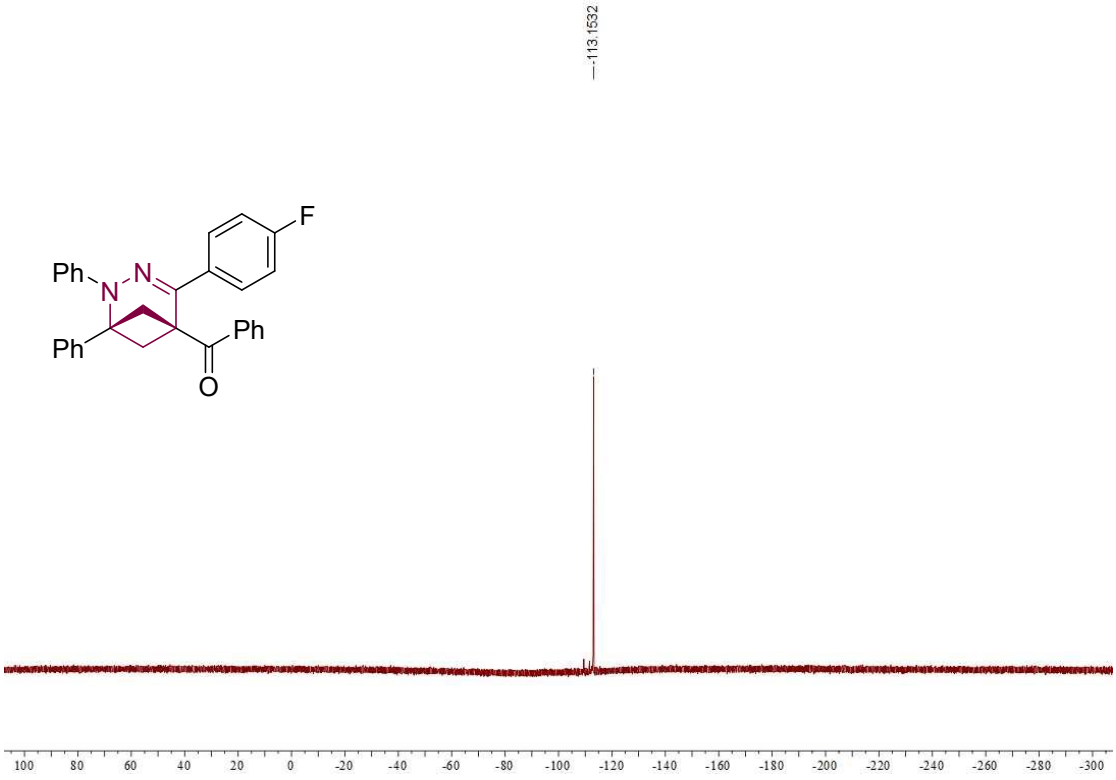




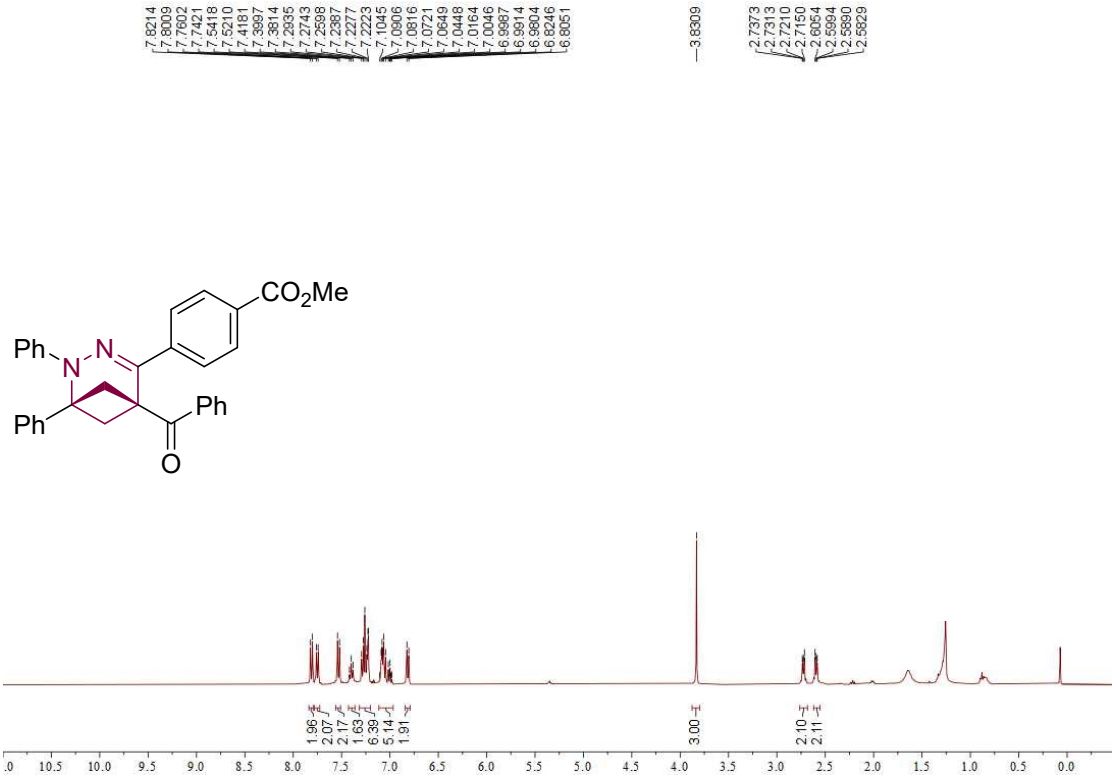
^{13}C NMR (101 MHz, $CDCl_3$) of **3t**



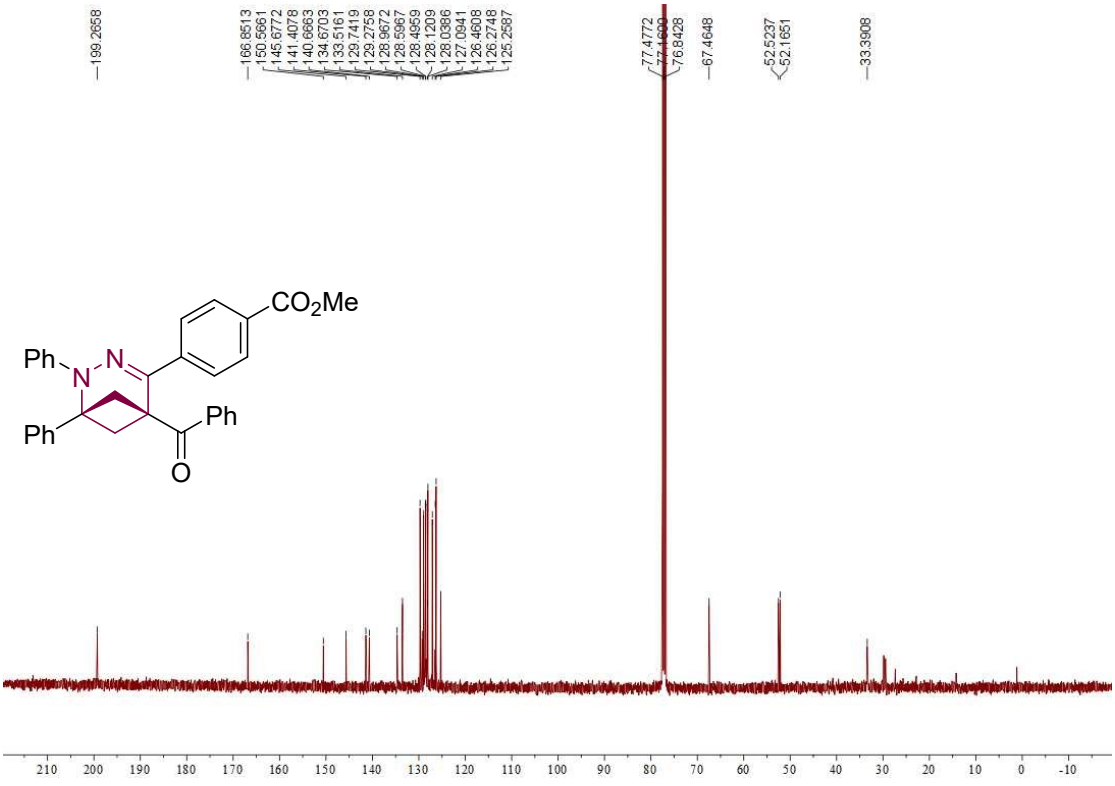
^{19}F NMR (376 MHz, $CDCl_3$) of **3t**



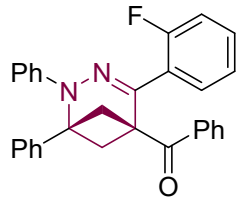
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**

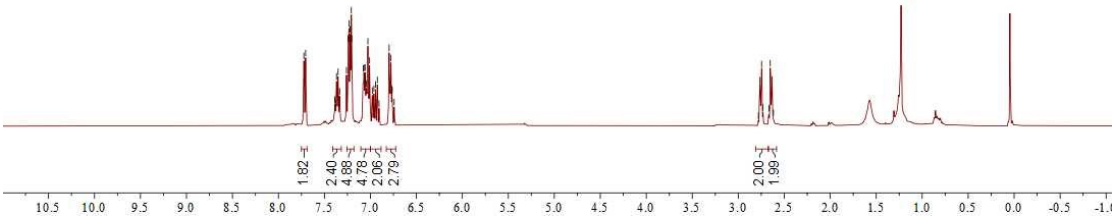


^{13}C NMR (101 MHz, $CDCl_3$) of **3u**

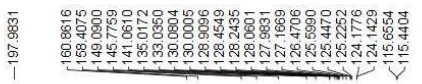


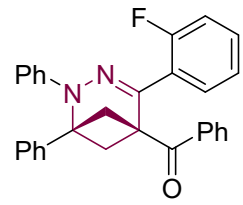
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**

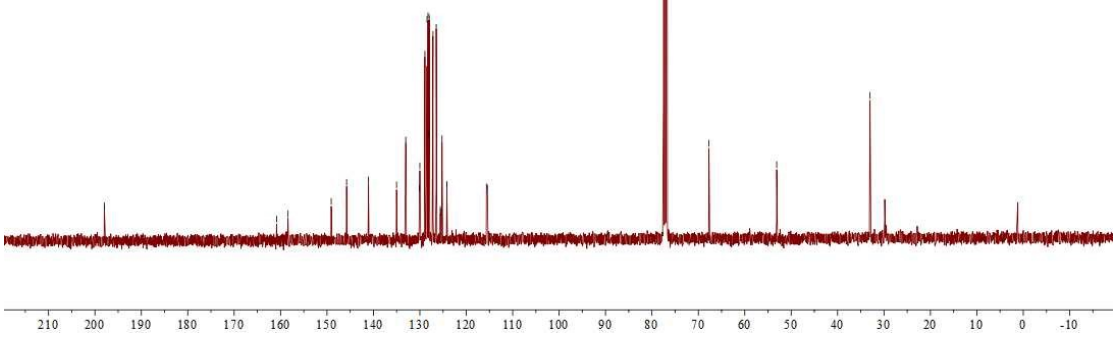


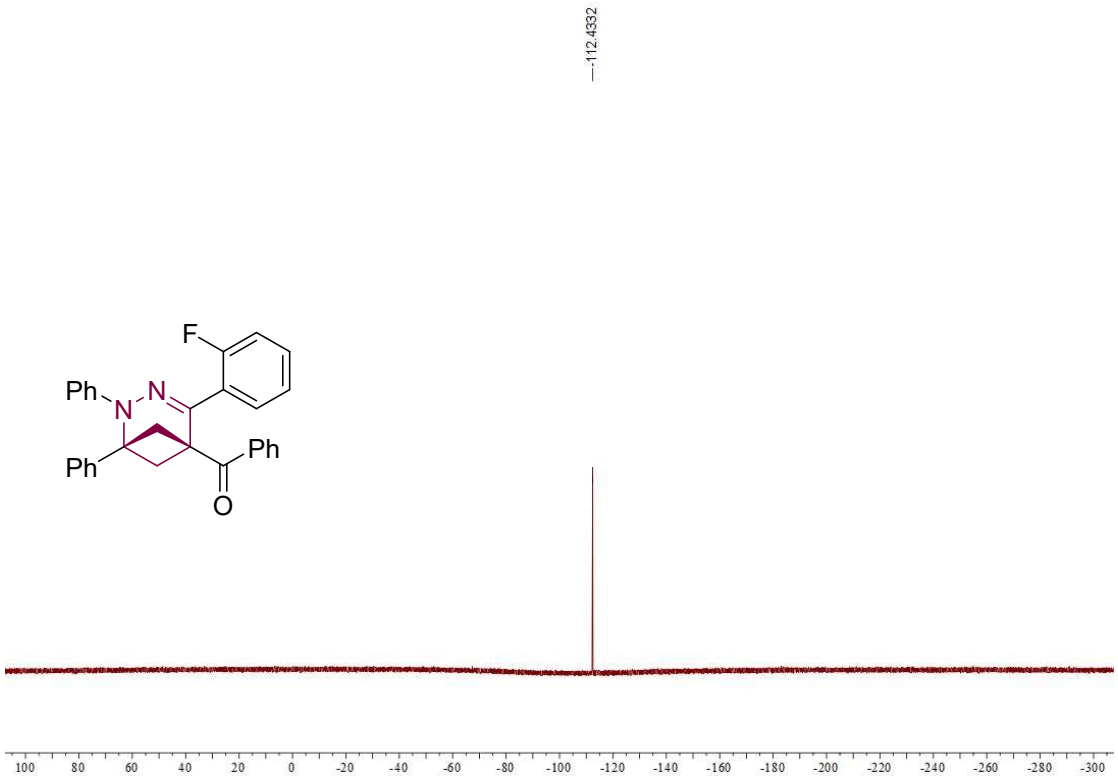


^{13}C NMR (101 MHz, $CDCl_3$) of **3v**



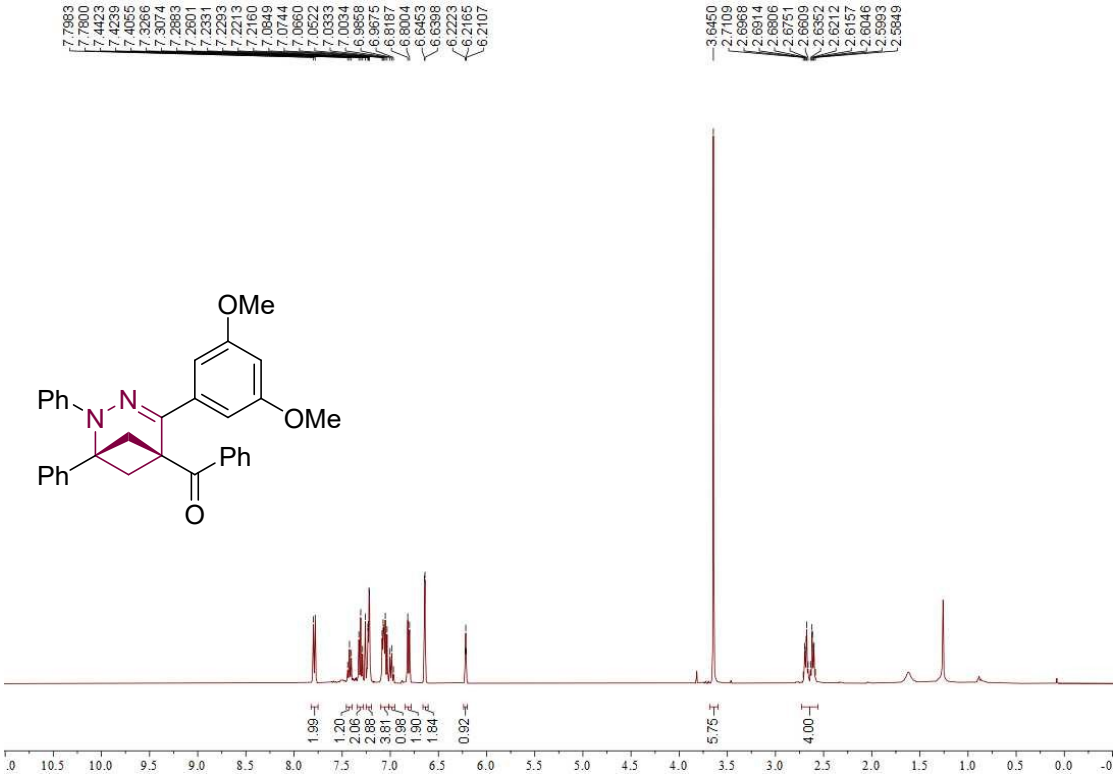




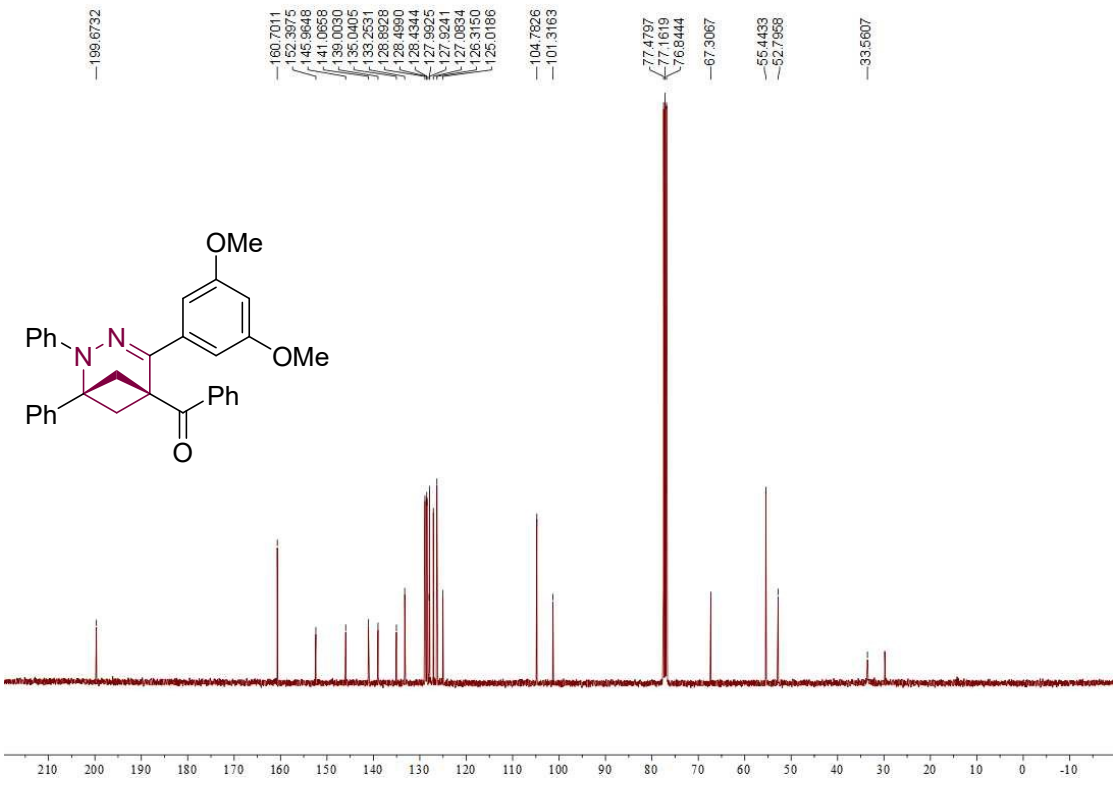


^{19}F NMR (376 MHz, $CDCl_3$) of **3v**

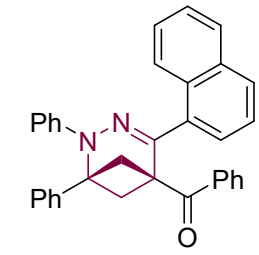
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**

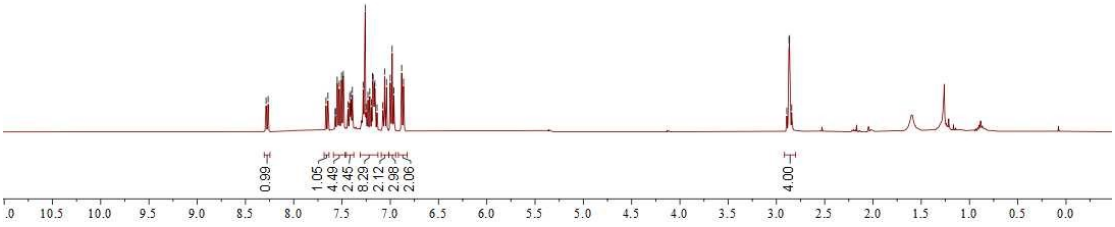


^{13}C NMR (101 MHz, $CDCl_3$) of **3w**

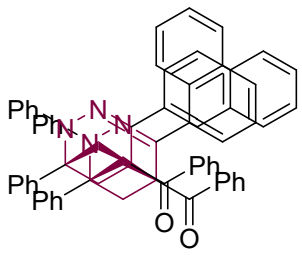


^{1}H NMR (400 MHz, $CDCl_3$) of **3x**

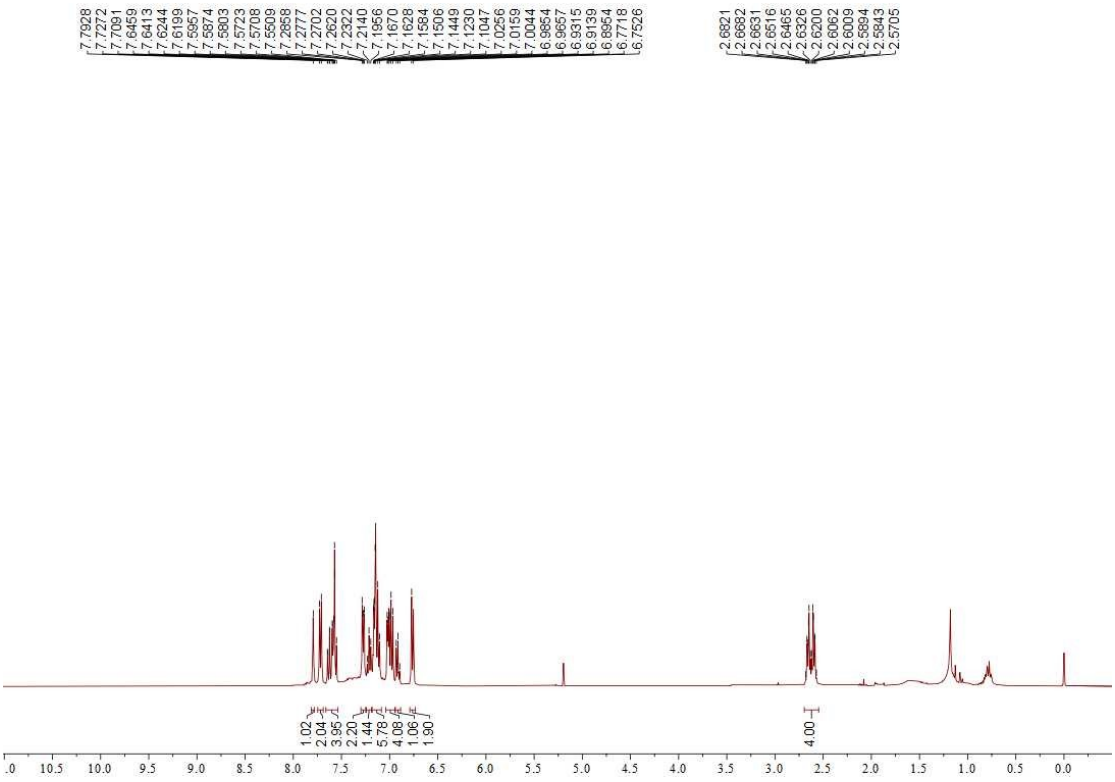




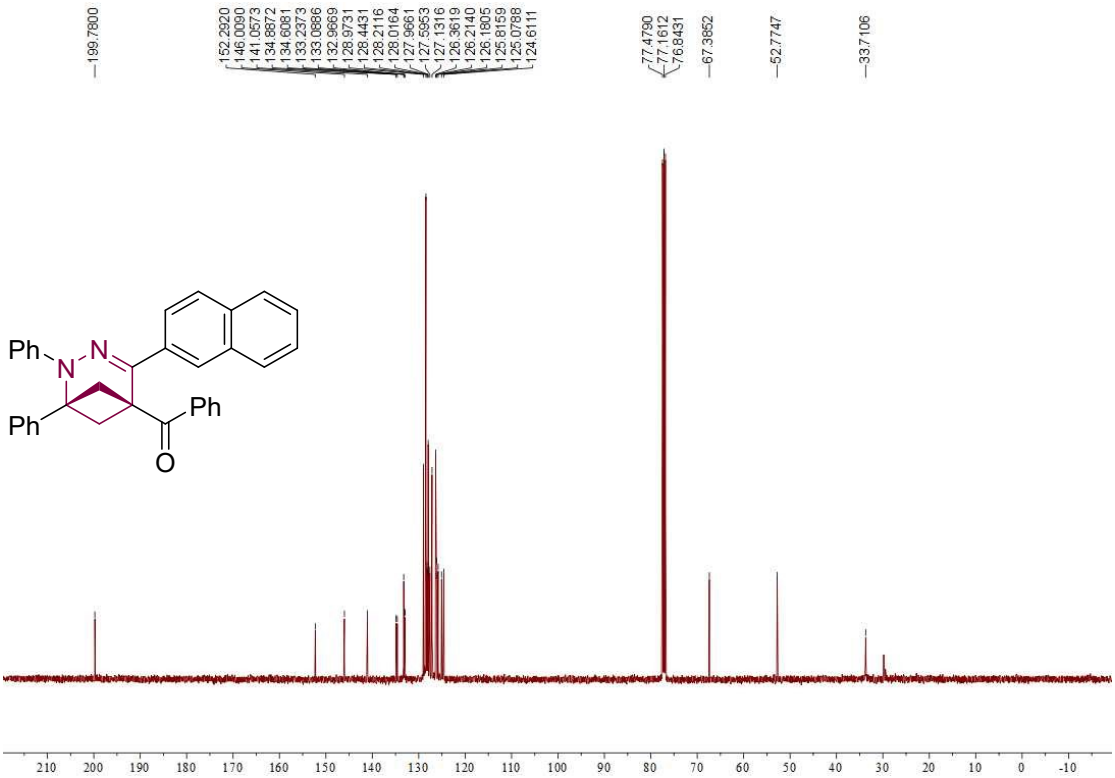
^{13}C NMR (101 MHz, $CDCl_3$) of **3x**



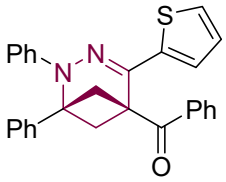
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**

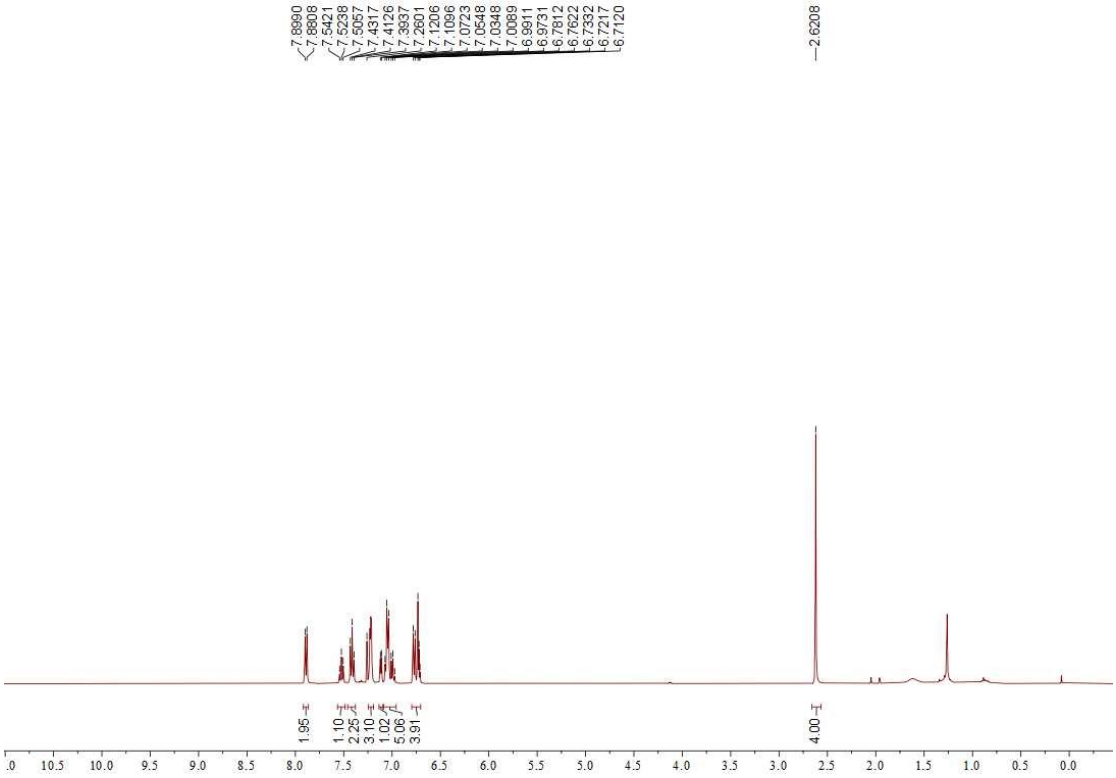


^{13}C NMR (101 MHz, $CDCl_3$) of **3y**

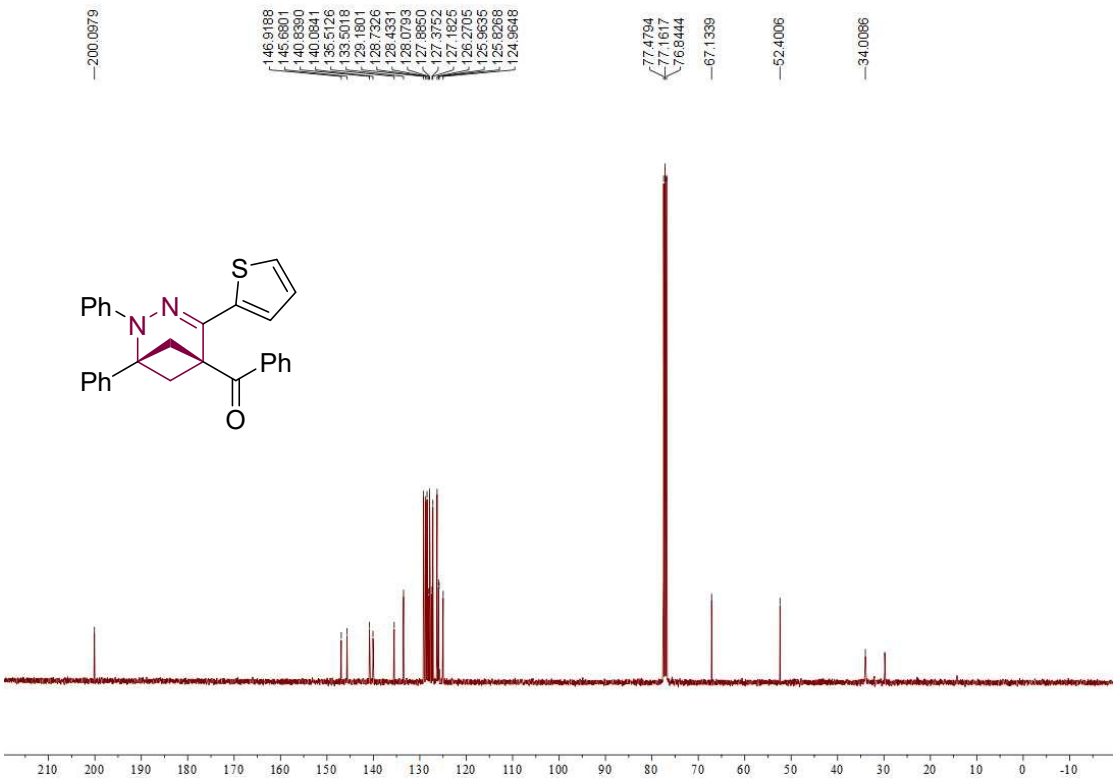


^{1}H NMR (400 MHz, $CDCl_3$) of **3z**

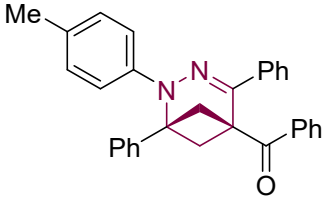


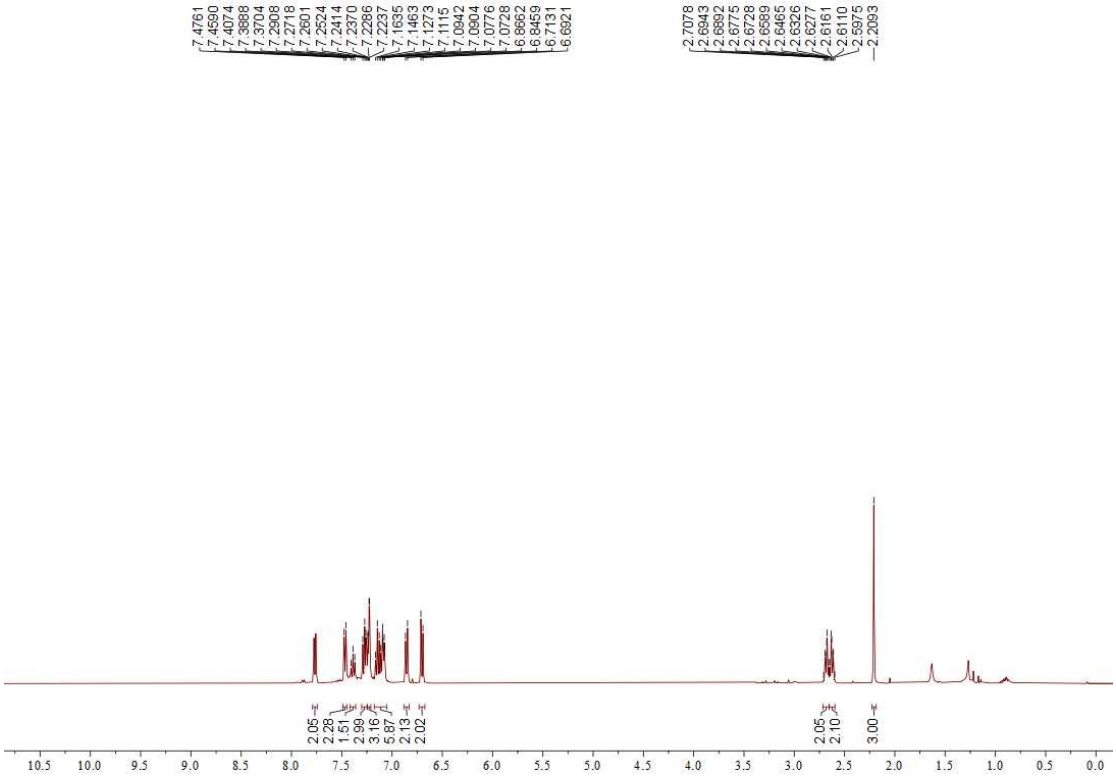


^{13}C NMR (101 MHz, $CDCl_3$) of **3z**

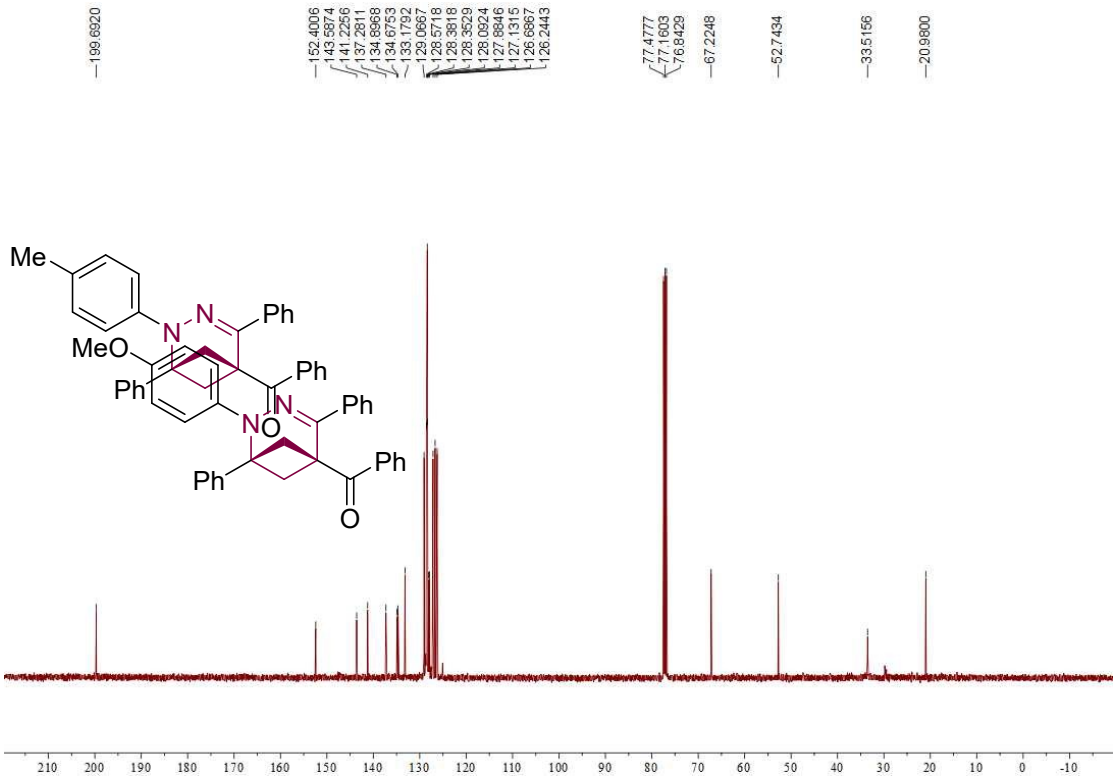


^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**

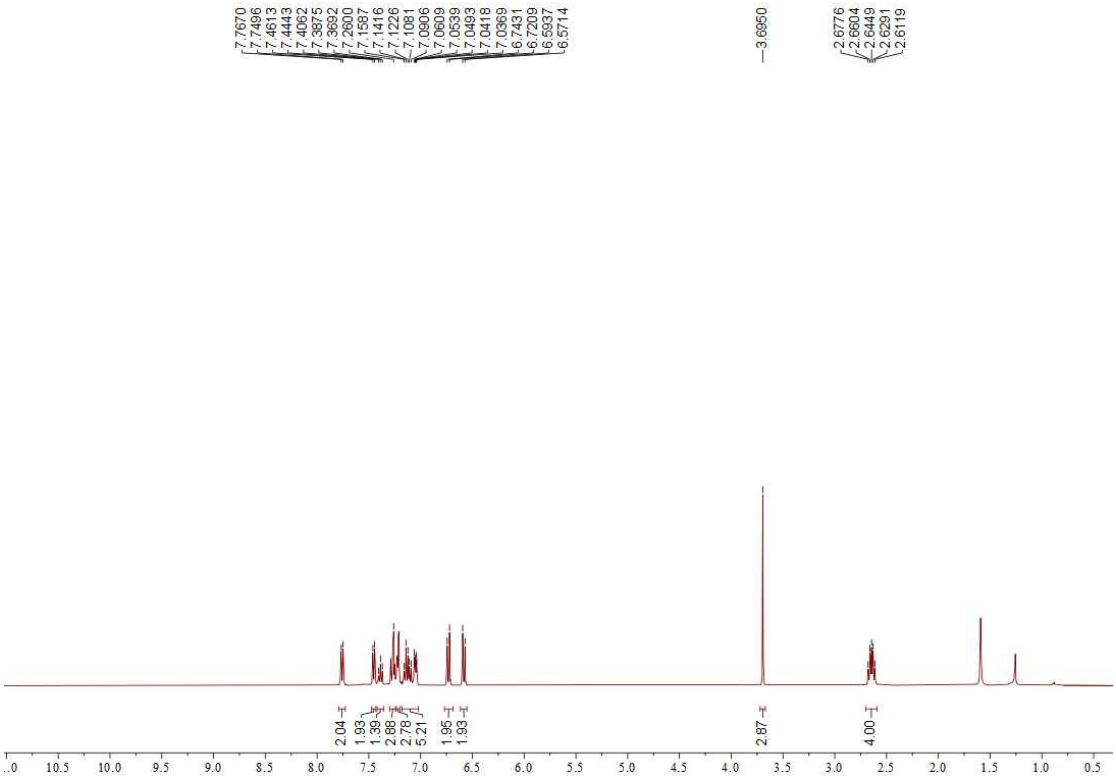




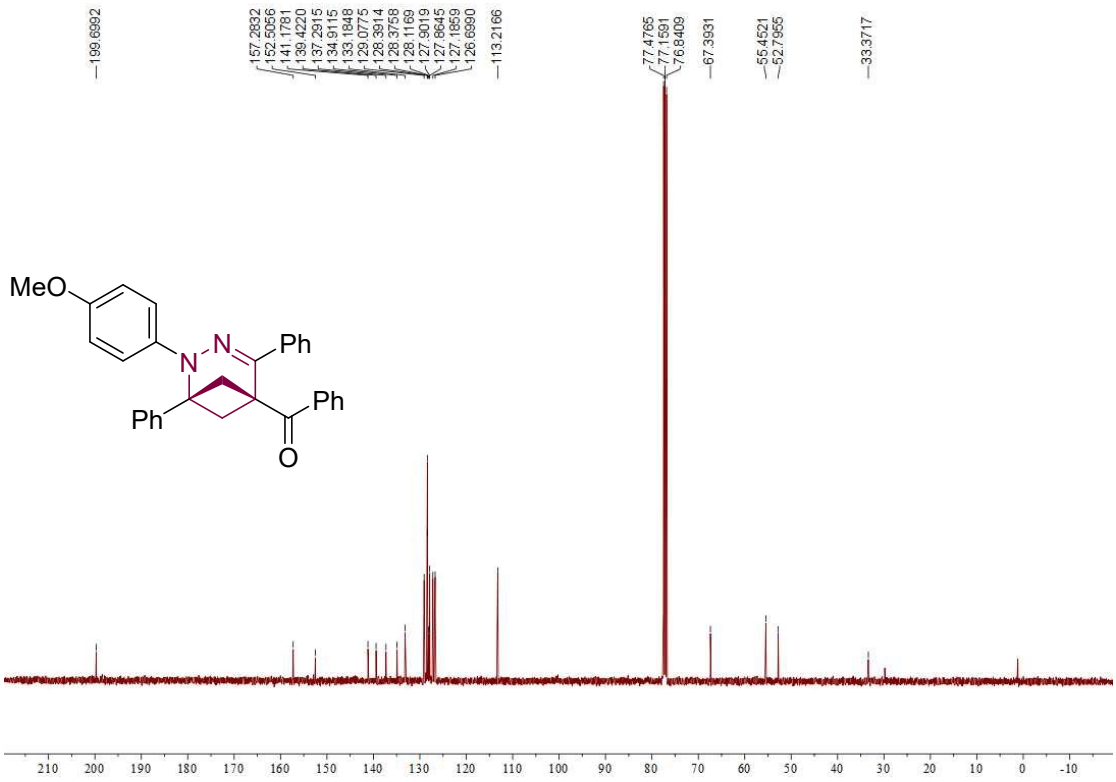
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



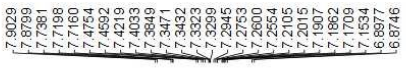
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**

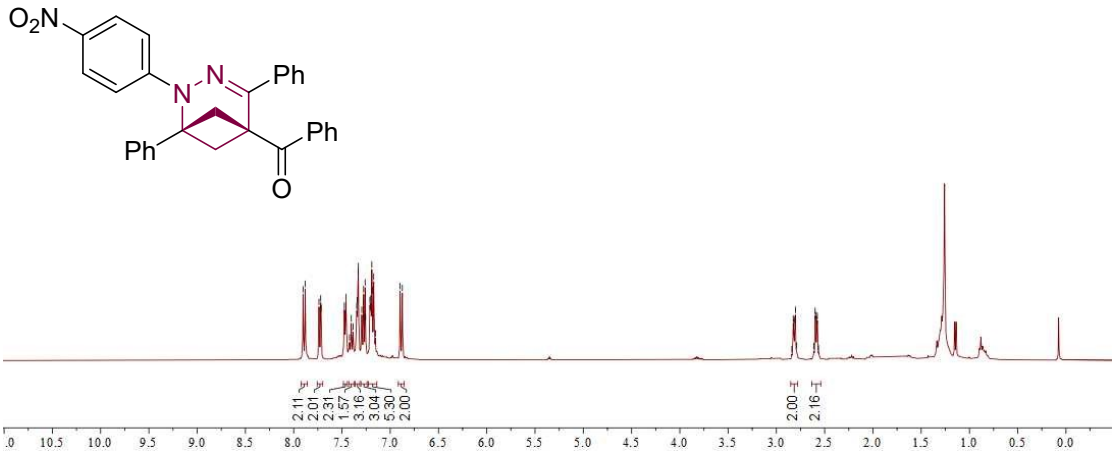


^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**

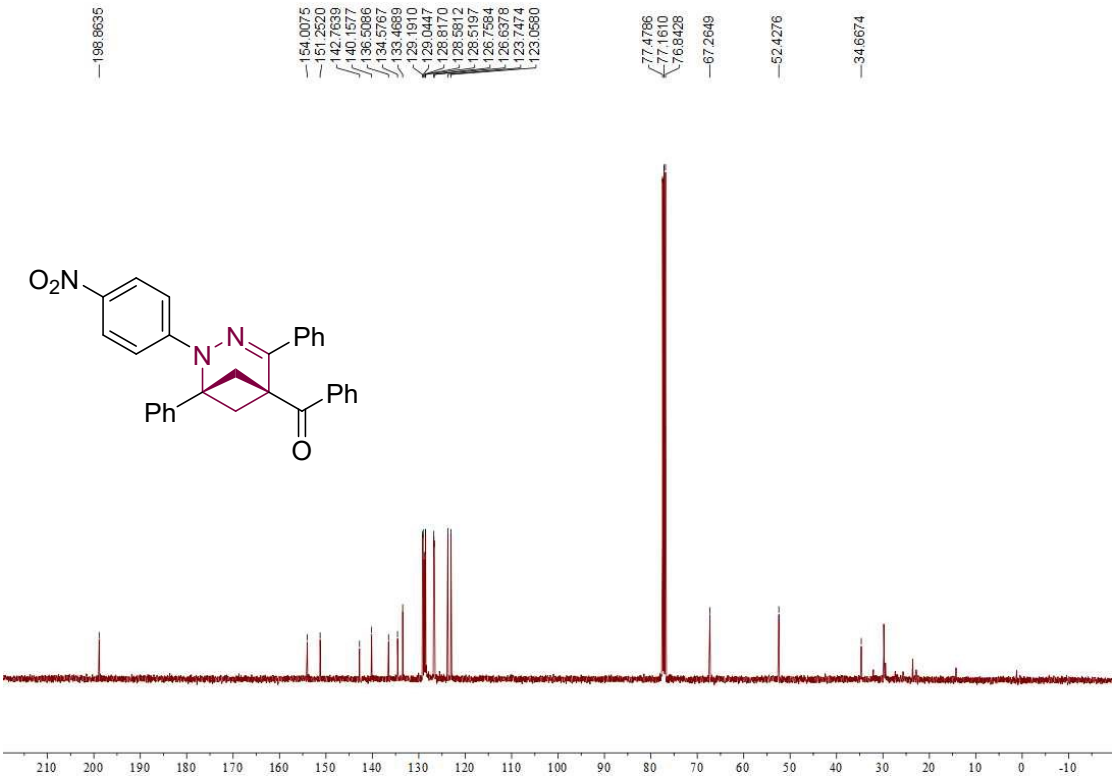


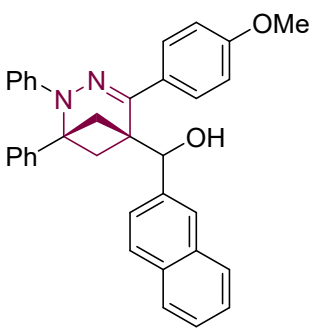
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



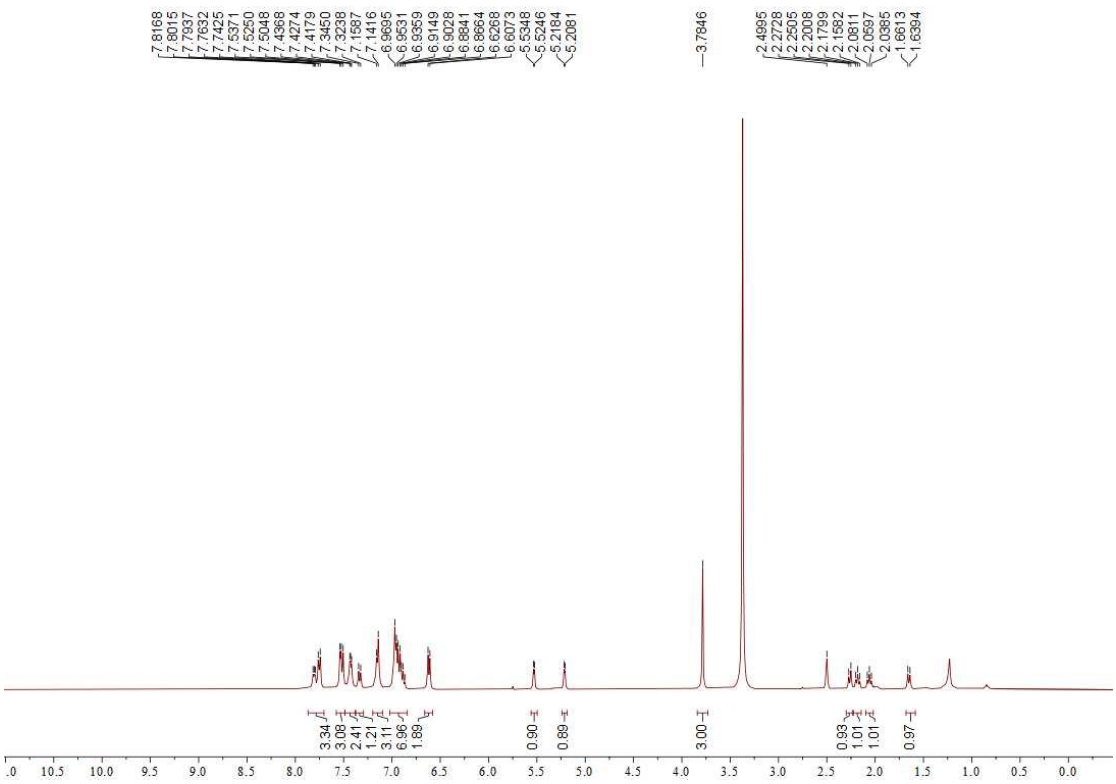


^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**

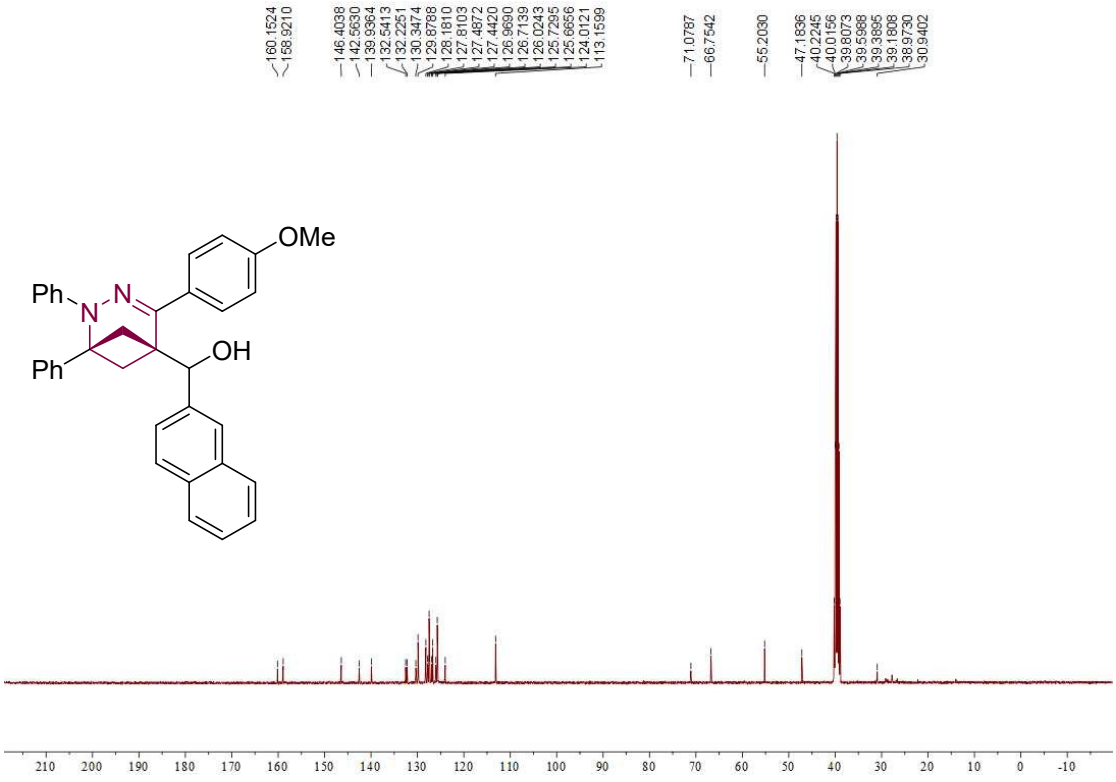


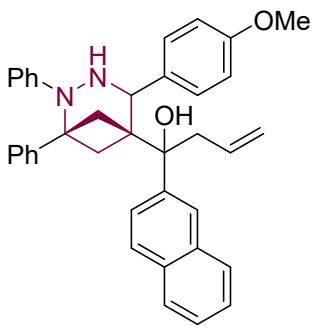


^{1}H NMR (400 MHz, DMSO) of **5**

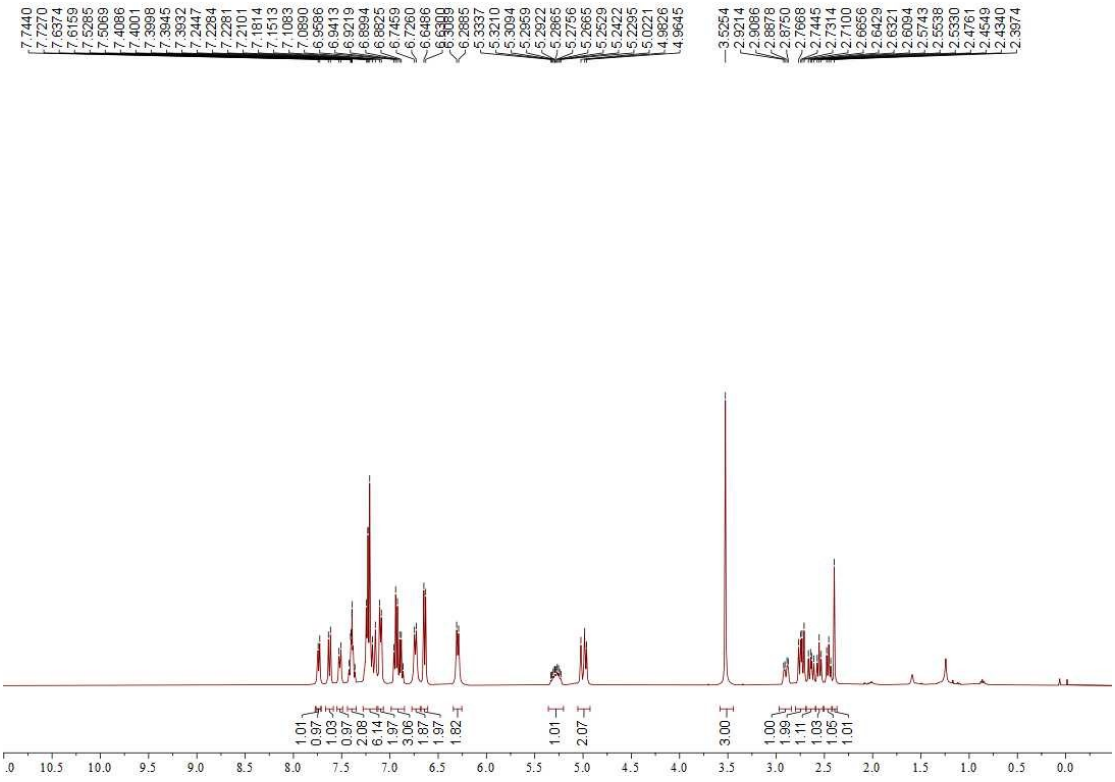


^{13}C NMR (101 MHz, DMSO) of **5**

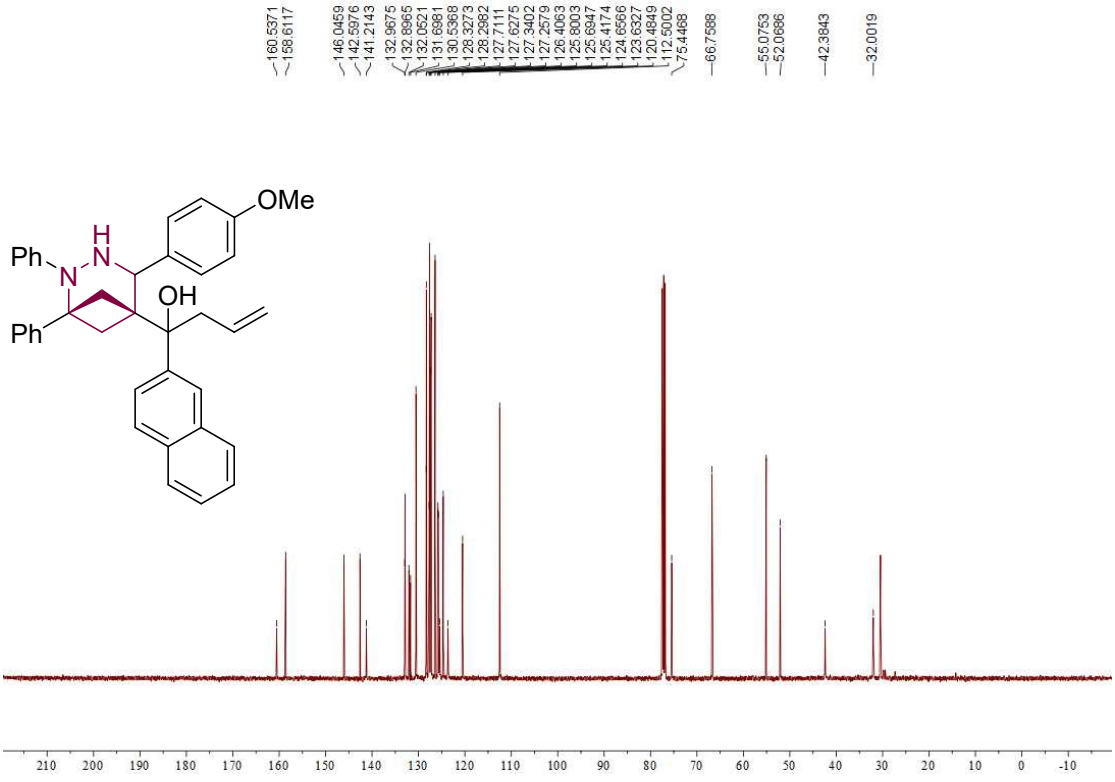


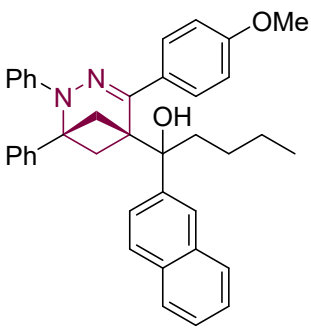


^{1}H NMR (400 MHz, $CDCl_3$) of **6**

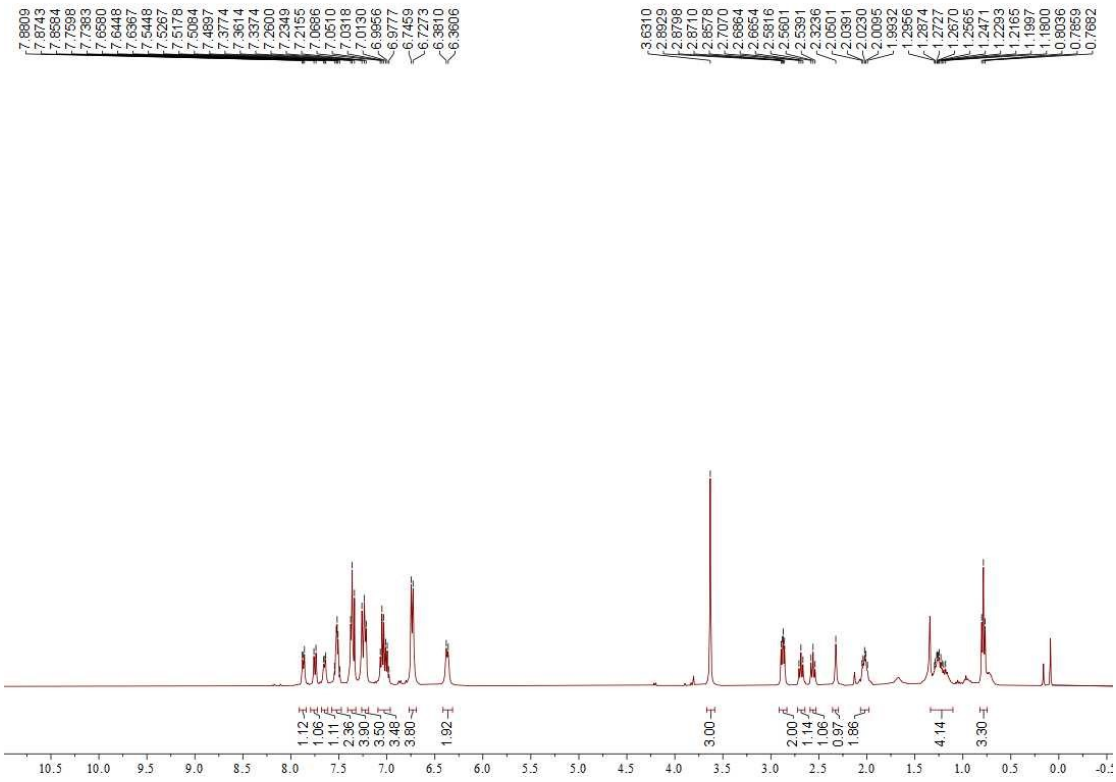


^{13}C NMR (101 MHz, $CDCl_3$) of **6**

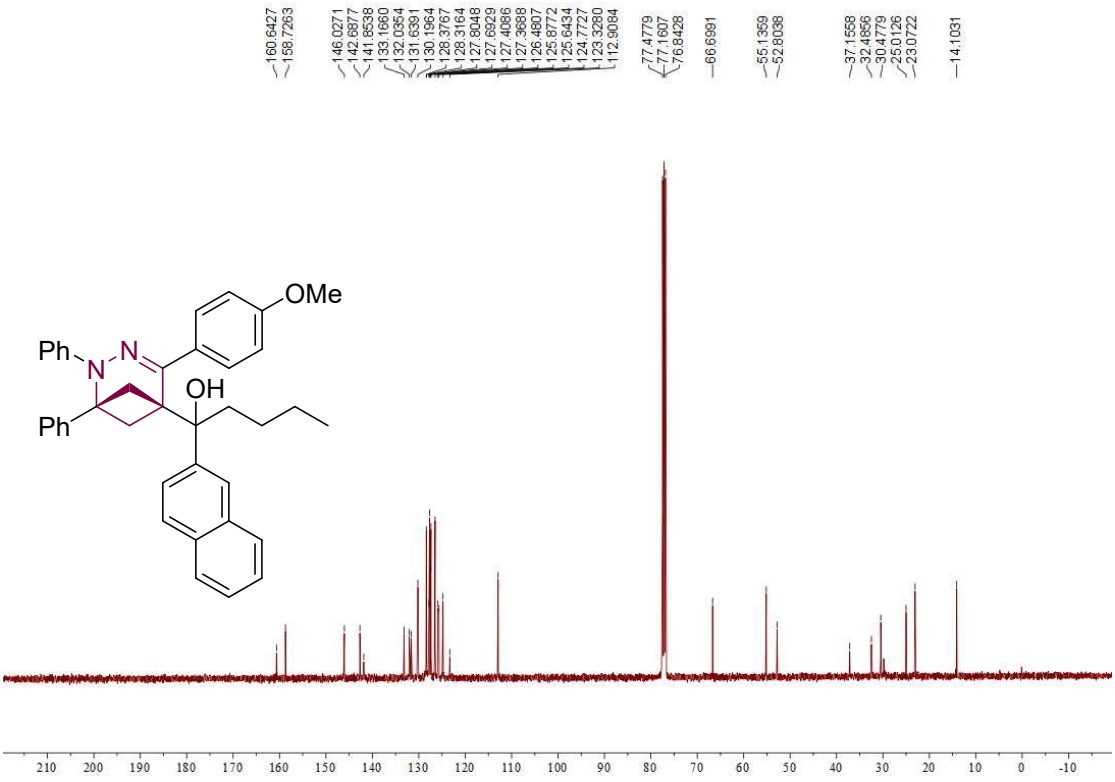




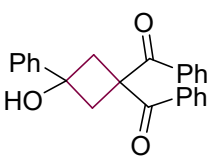
^{1}H NMR (400 MHz, $CDCl_3$) of **7**

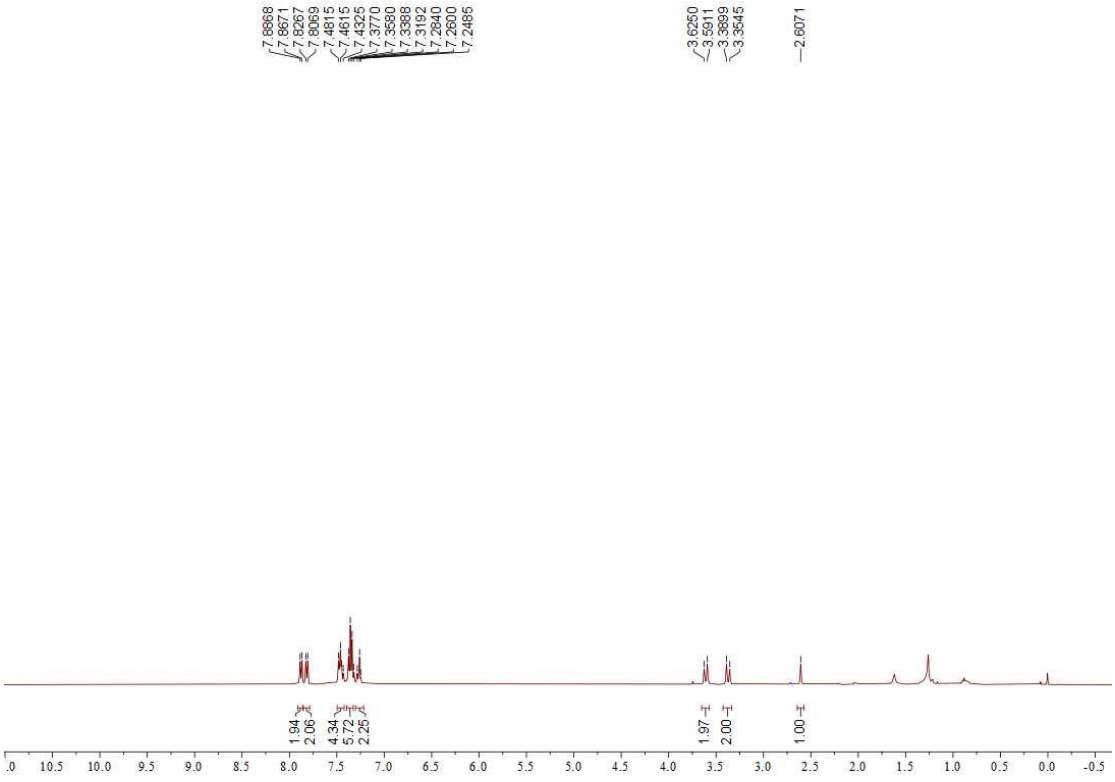


^{13}C NMR (101 MHz, $CDCl_3$) of **7**

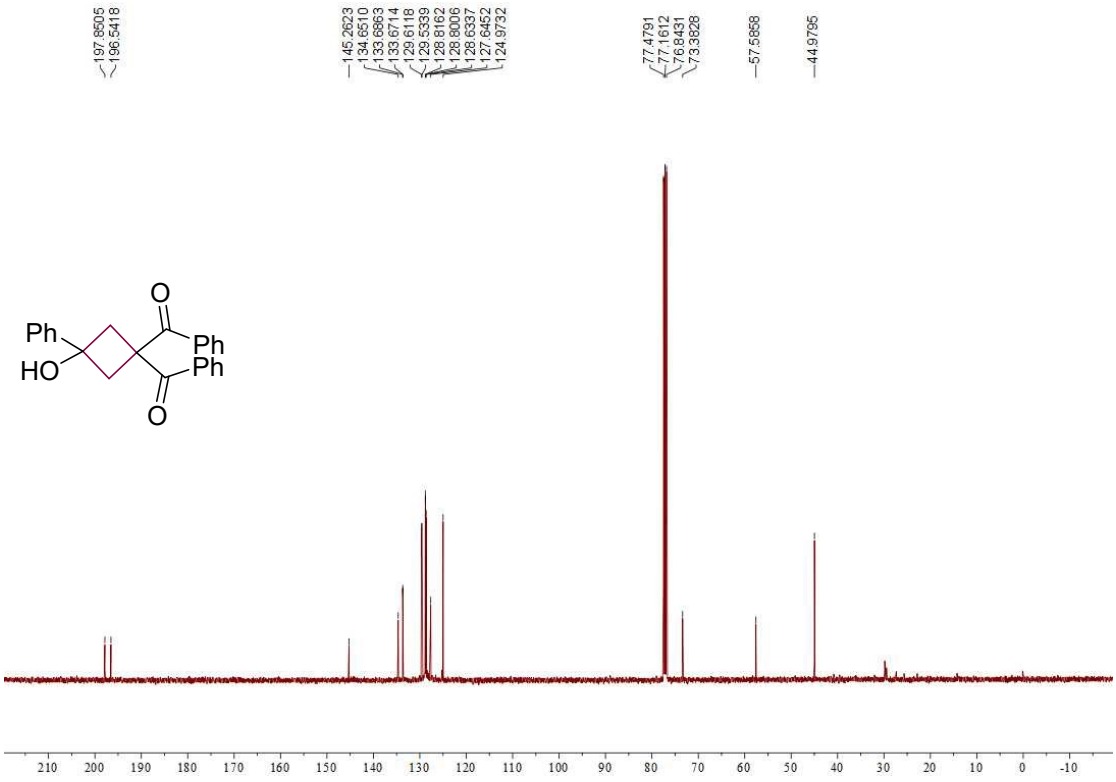


^{1}H NMR (400 MHz, $CDCl_3$) of **8**

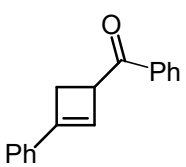


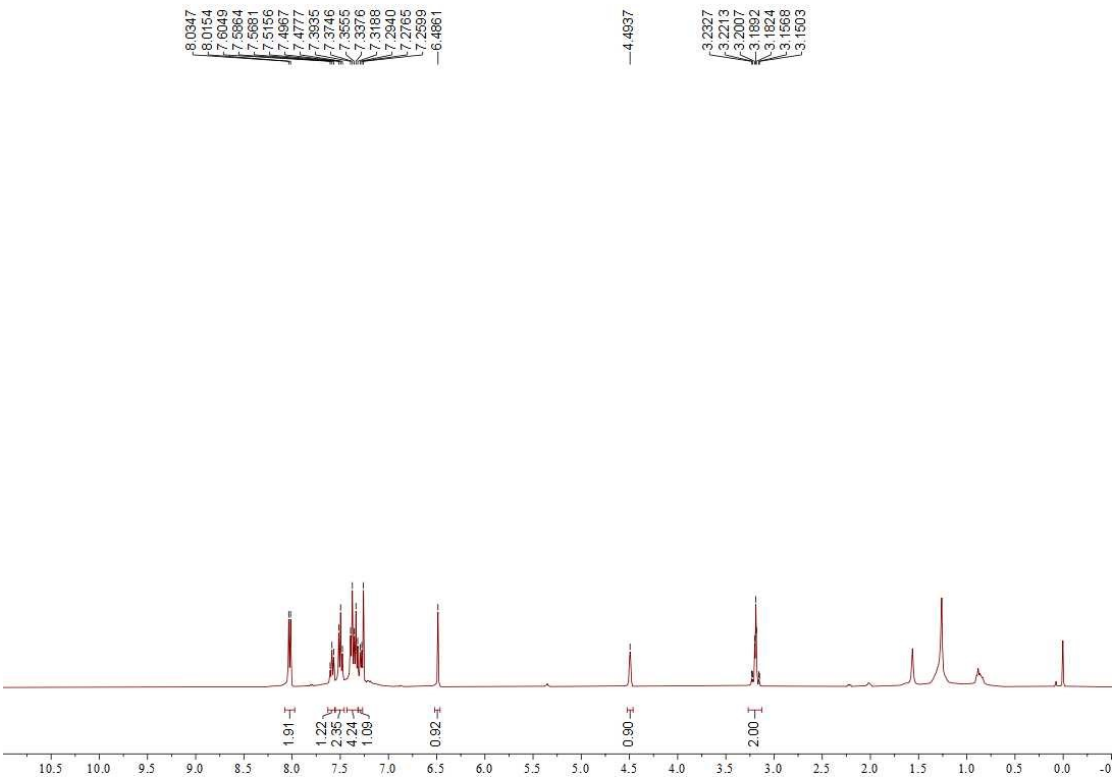


^{13}C NMR (101 MHz, $CDCl_3$) of **8**



^{1}H NMR (400 MHz, $CDCl_3$) of **9**





^{13}C NMR (101 MHz, $CDCl_3$) of **9**