Supporting Information

Nickel-Catalysed C-N Cross-coupling of Organoboronic Acids and Isoxazoles

Yupeng Zhao,[a‡] Changshu Wu,[a‡] Jiaming Zhang,[a] Yang Gao,*[a, b] Zhuoxuan Yuan,[a] Xianwei Li[a], Qian Chen,[a] and Yanping Huo[a, b]

Table of Contents

1. General Methods

1.1 General analytical information:

All reactions were performed in oven-dried glassware containing a Teflon-coated stirring bar and dry septum under argon atmosphere. All optimization reactions were monitored by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. NMR spectra were recorded at ambient temperature using $CDCl_3$ as solvent, with proton, carbon, and fluorine resonances at 400, 100 and 375 MHz, respectively. All NMR data are reported in ppm relative to the solvent signal. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Column chromatography was performed with 200-300 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}). Mass spectral data were acquired on a Varian GC-MS Saturn 2100 T. The ionization was achieved by EI AGC. HRMS analyses were carried out on a Waters GCT Premier CAB163 with a TOF mass analyzer. The MS ionization was achieved by EI^{+}. Melting points were measured on a Mettler FP 61 and are uncorrected. Parallel heating mantle were used in our experiments.

1.2 General reagent information:

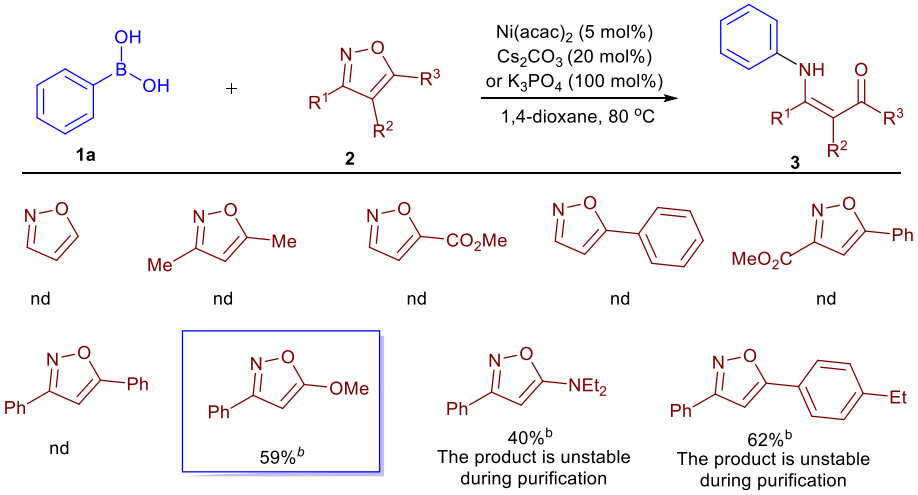
All solvents were purified and dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system. Commercial reagents were purchased from Aldrich Chemical and Bide Pharmatech, and were used as received.

1.3 General procedure A for the synthesis of compound 3.

An oven-dried 20 mL vial equipped with a Teflon-coated stirring bar was charged with $Ni(acac)_2$ (10 mol%), K_3PO_4 (0.2 mmol) and organoboronic acid (0.3 mmol), and closed with a septum cap. Then, 1,4-dioxane (1 mL) and isoxzale (0.2 mmol) were successively added via syringe. The mixture was stirred under air at 80 °C for 10 h. After completion of the reaction, the resulting mixture was diluted with 10 mL diethyl ether and filtered through a Celite pipette. The filtrate was washed with brine (3 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient).

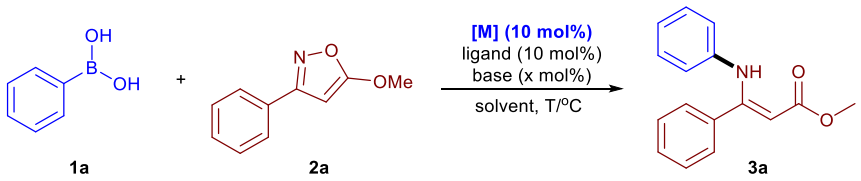
2. Supplementary information for the optimization of reaction conditions.

Table S1. Screening of isoxazole derivatives[a]



[a] Reaction conditions: phenylboronic acid **1a** (0.10 mmol), isoxazole derivatives **2** (0.10 mmol), $Ni(acac)_2$ (10 mol%), Cs_2CO_3 (20 mol%), 1,4-dioxane (1.0 mL) under 100 °C for overnight. [b] Yield was determined by ^1H NMR analysis with 1,3,5-trimetho1xybenzene as an internal standard.

Table S2. Optimisation of transition metal-catalysts[a]

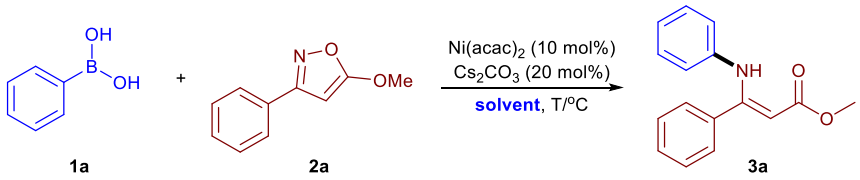


Entry	Catalyst	Yield (%) [b]
1	**$Ni(acac)_2$**	**66**
2	$NiCl_2$	nd
3	$Ni(ClO_4)_2{\cdot}6H_2O$	nd
4	$Ni(BF_4)_2{\cdot}6H_2O$	nd
5	$Ni(OAc)_2{\cdot}4H_2O$	nd
6[c]	$Ni(OAc)_2{\cdot}4H_2O$	trace
7	-	nd
8[d]	$Ni(acac)_2$	49
9[e]	$Ni(acac)_2$	19
10[f]	$Ni(acac)_2$	16
11	$Cu(OAc)_2$	nd
12	$CoCl_2$	nd
13	$Co(acac)_2$	nd

14	$Ni(^tBuacac)_2$	60
15[c]	$NiCl_2$	20
16[c]	NiI_2	59

[a] Reaction conditions: phenylboronic acid **1a** (0.15 mmol), 5-methoxy-3-phenylisoxazole **2a** (0.10 mmol), $Ni(acac)_2$ (10 mol%), Cs_2CO_3 (20 mol%), 1,4-dioxane (1.0 mL) under 80 °C for 10 h. [b] Yield was determined by ^1H NMR analysis with 1,3,5-trimetho1xybenzene as an internal standard. [c] acac (20 mol%) was added. [d] PPh_3 (10 mol%) was added. [e] PPh_3 (10 mol%) was added and no Cs_2CO_3. [f] No Cs_2CO_3.

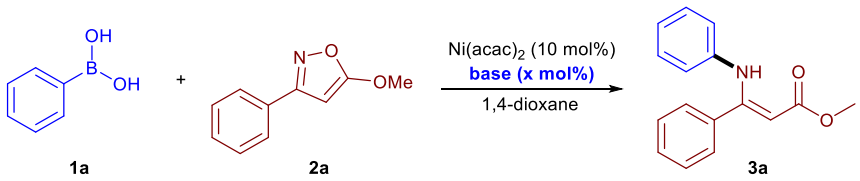
Table S3. Optimisation of solvents[a]



Entry	Solvent	Yield (%) [b]
1	**1,4-dioxane**	**66**
2	DMSO	trace
3	NMP	nd
4	DMA	trace
5	Tol	58
6	MeCN	25
7	DCE	59

[a] Reaction conditions: phenylboronic acid **1a** (0.15 mmol), 5-methoxy-3-phenylisoxazole **2a** (0.10 mmol), $Ni(acac)_2$ (10 mol%), Cs_2CO_3 (20 mol%), solvent (1.0 mL) at 80 °C for 10 h. [b] Yield was determined by ^1H NMR analysis with 1,3,5-trimetho1xybenzene as an internal standard.

Table S4. Optimisation of bases[a]

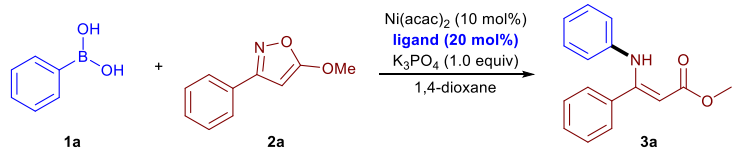


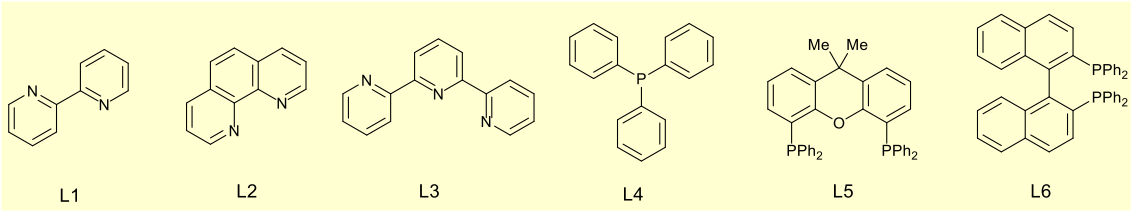
Entry	Base	Yield (%) [b]
1	none	66
2	K_2CO_3	nd
3	Na_2CO_3	trace

4	t-BuOK	trace
5	KOAc	26
6	K_3PO_4	70
7[c]	**K_3PO_4**	**90，93**[d]
10[e]	Cs_2CO_3	82

[a] Reaction conditions: phenylboronic acid **1a** (0.15 mmol), 5-methoxy-3-phenylisoxazole **2a** (0.10 mmol), $Ni(acac)_2$ (10 mol%), base (20 mol%), 1,4-dioxane (1.0 mL) at 80 °C for 10 h. [b] Yield was determined by ^1H NMR analysis with 1,3,5-trimetho1xybenzene as an internal standard. [c] K_3PO_4 (1.0 equiv) was used. [d] Isolated yield. [e] Cs_2CO_3 (1.0 equiv) was used.

Table S5. Optimisation of ligands[a]





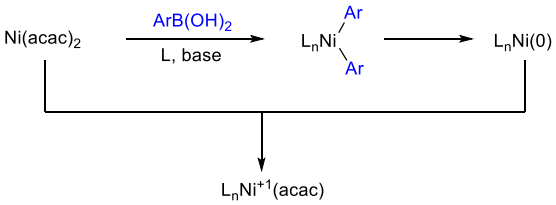
Entry	Ligand	Yield (%) [b]
1	**-**	**90**
2	L_1	nd
3	L_2	trace
4	L_3	nd
5	L_4	69
6	L_5	72
7	L_6	65

[a] Reaction conditions: phenylboronic acid **1a** (0.15 mmol), 5-methoxy-3-phenylisoxazole **2a** (0.10 mmol), $Ni(acac)_2$ (10 mol%), K_3PO_4 (1.0 equiv), Ligand (10 mol%), 1,4-dioxane (1.0 mL) at 80 °C for 10 h. [b] Yield was determined by ^1H NMR analysis with 1,3,5-trimetho1xybenzene as an internal standard.

3. Supplementary information on the reaction mechanism.

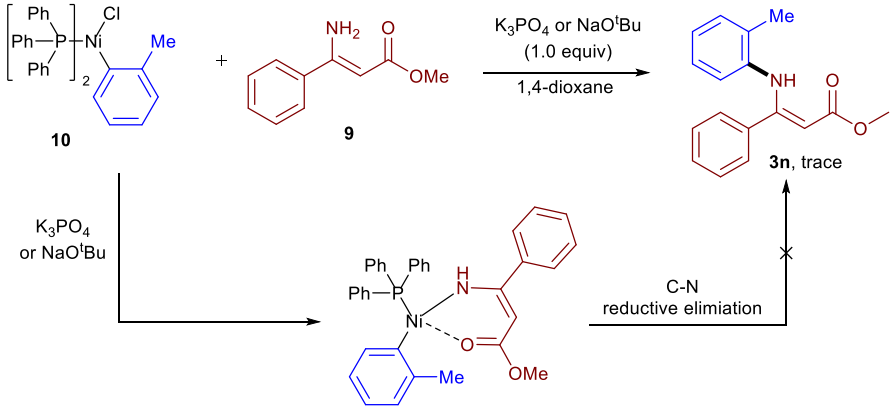
3.1 For the generation of Ni(I) species.

According to Liu's work, $L_nNi^{+1}(acac)$ can be formed via the reaction of $Ni(acac)_2$ and phenylboronic acid. First, transmetallation of phenylboronic acid with $Ni(acac)_2$ gives diphenylnickel^{+2} species, which undergoes reductive elimination to form a Ni(0) species. Then, $L_nNi^{+1}(acac)$ can be formed via the comproportion of Ni(0) and $Ni(acac)_2$.



3.2 Simulating the C-N bond reductive elimination process.

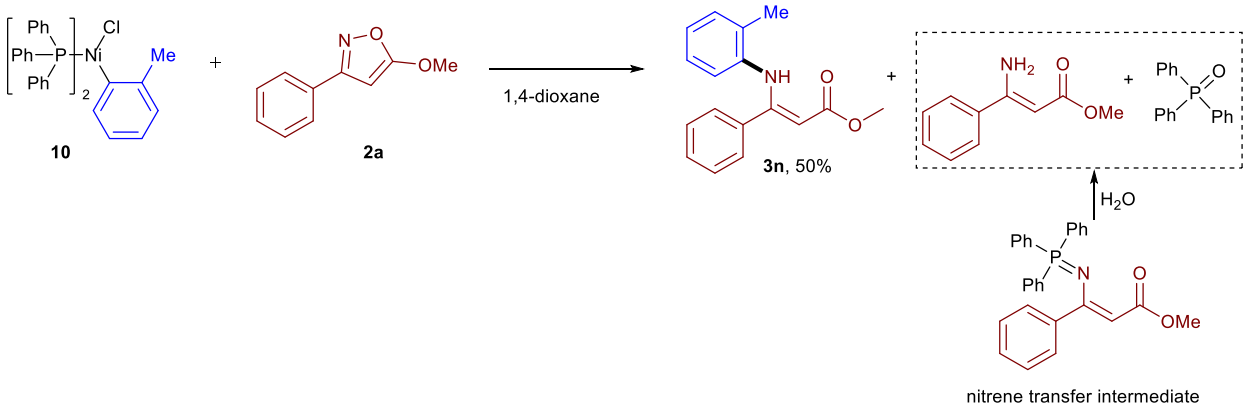
The reaction of arylnickel complex **10** and methyl (Z)-3-amino-3-phenylacrylate (**9**) was carried out to simulate C-N bond reductive elimination from a Ni(II) intermediate. However, the desired C-N coupling product **3n** was not facilely formed with either K_3PO_4 or NaO^{t}Bu as base, which indicated that C-N reductive elimination from the corresponding Ni(II) intermediate is difficult under the current conditions. The result is in consistent with the literature report, which documents that C-N bond reductive elimination from Ni(II) intermediate usually has high energy barrier, and sterically hindered ligand is needed to promote this chemical process.



3.3 The reaction of arylnickel complex 10 and isoxazole.

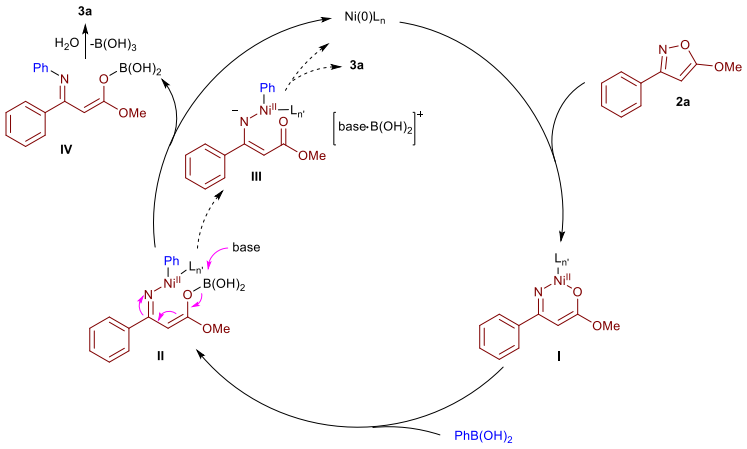
The reaction of arylnickel complex **10** and isoxazole was carried out in 1,4-dioxane without any additives, and the desired C-N coupling product **3n** was detected in 50% yield. In addition, a certain amount of triphenylphosphine oxide and methyl (Z)-3-amino-3-phenylacrylate (**9**) was detected in this reaction, which may be formed via the hydrolysis of corresponding iminophosphorane, a known adduct derived from nitrene

transfer to phosphine. This result indicates that a polarity reversed amine source is crucial for the C-N bond formation and an arylnickel(I or II) species may be a reactive intermediate in this reaction.



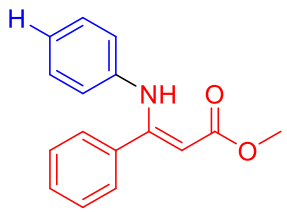
3.4 Proposed Ni(0)/Ni(II) catalytic cylcle.

The in-situ generated Ni(0) first undergoes oxidative addition with isoxazole through N-O bond cleavage to give cyclonickel(II) **I**. The transmetallation of intermediate **I** with $PhB(OH)_2$ affords phenylnickel(II) **II**, which will undergo reductive elimination to give imine intermediate **IV**. Finally, the desired product **3a** is formed after hydrolysis of **IV**. Alternatively, intermediate **II** may undergo deborization and isomerization to give intermediate **III**, which goes through reductive elimination to afford the final product **3a**. In addition, Ni(0) is regenerated in the reductive elimination process.



4. Synthesis and Characterization of the Corresponding Products

Methyl (Z)-3-phenyl-3-(phenylamino)acrylate (3a)[1]



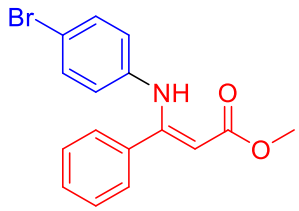
The title compound **3a** was prepared following the **general procedure A** from phenylboronic acid **1a** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (47.1 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.34 (q, *J* = 2.9, 2.4 Hz, 3H), 7.32 – 7.27 (m, 2H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.69 – 6.65 (m, 2H), 5.00 (s, 1H), 3.75 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.2, 140.3, 135.9, 129.5, 128.6, 128.4, 128.2, 123.0, 122.3, 90.6, 50.7 ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{15}NO_2$ $[M+H]^+$ 254.1176, found 254.1170.

Methyl (Z)-3-((4-bromophenyl)amino)-3-phenylacrylate (3b)[1]

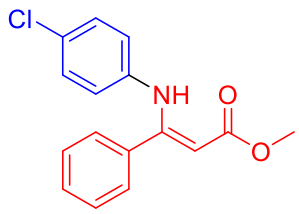


The title compound **3b** was prepared following the **general procedure A** from (4-bromophenyl)boronic acid **1b** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (55.6 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.34 (dd, *J* = 5.7, 1.9 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 5.03 (s, 1H), 3.74 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 158.6, 139.5, 135.4, 131.6, 129.7, 128.6, 128.1, 123.5, 115.8, 91.6, 50.8 ppm. **HRMS** (ESI) m/z calcd. for $C_{16}H_{14}BrNO_2$ $[M+H]^+$ 332.0281, found 332.0284.

Methyl (Z)-3-((4-chlorophenyl)amino)-3-phenylacrylate (3c)



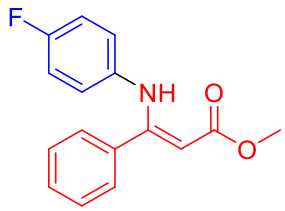
The title compound **3c** was prepared following the **general procedure A** from (4-chlorophenyl)boronic acid **1c** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (48.9 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.34 (dq, *J* = 4.4, 2.0 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.06 – 7.02 (m, 2H), 6.60 – 6.56 (m, 2H), 5.03 (s, 1H), 3.75 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 158.8, 139.0, 135.5, 129.7, 128.7, 128.6, 128.2, 128.1, 123.3, 91.4, 50.1 ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{14}ClNO_2$ $[M+H]^+$ 288.0786, found 288.0779.

Methyl (Z)-3-((4-fluorophenyl)amino)-3-phenylacrylate (3d)



The title compound **3d** was prepared following the **general procedure A** from (4-fluorophenyl)boronic acid **1d** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (46.1 mg, 85%).

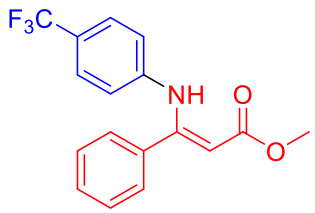
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.34 – 7.30 (m, 2H), 7.30 – 7.27 (m, 3H), 6.78 (t, *J* = 8.6 Hz, 2H), 6.67 – 6.62 (m, 2H), 5.00 (s, 1H), 3.74 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 159.4, 159.0 (d, *J* = 243.0 Hz), 136.4 (d, *J* = 7.2 Hz), 135.6, 129.5, 128.4, 128.3, 124.1 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 9.2 Hz), 90.4, 50.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.7 ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{14}FNO_2$ $[M+H]^+$ 272.1081, found 272.1088.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzenaminium (3e)



The title compound **3e** was prepared following the **general procedure A** from (4-(trifluoromethyl)phenyl)boronic acid **1e** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (56.5 mg, 88%).

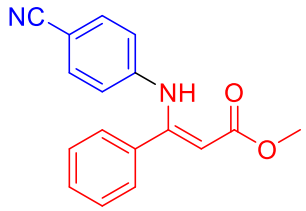
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.41 – 7.34 (m, 4H), 7.32 (dd, J = 8.3, 1.5 Hz, 3H), 6.68 (d, J = 8.4 Hz, 2H), 5.12 (s, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 157.9, 143.6, 135.3, 129.9, 128.7, 128.0, 125.8 (q, *J* = 3.8 Hz), 124.24 (q, *J* = 32.7 Hz), 124.16 (q, *J* = 271.3 Hz), 120.9, 93.2, 50.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.9 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{14}F_3NO_2$ $[M+H]^+$ 322.1050, found 322.1047.

(Z)-4-Cyano-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (3f)



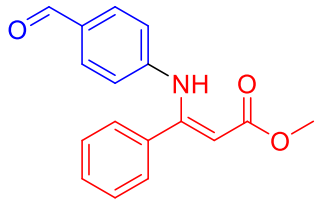
The title compound **3f** was prepared following the **general procedure A** from (4-cyanophenyl)boronic acid **1f** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (45.6 mg, 82%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.45 – 7.40 (m, 1H), 7.36 (s, 2H), 7.35 (d, *J* = 3.0 Hz, 3H), 7.33 (s, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 5.16 (s, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 157.1, 144.6, 135.0, 132.8, 130.2, 128.9, 127.9, 120.7, 119.0, 105.0, 94.7, 51.1 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{14}N_2O_2$ $[M+H]^+$ 279.1128, found 279.1121.

(Z)-4-Formyl-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (3g)



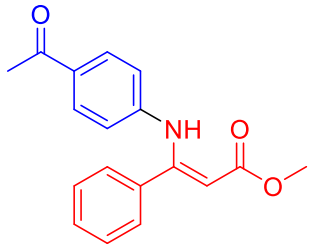
The title compound **3g** was prepared following the **general procedure A** from (4-formylphenyl)boronic acid **1g** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (40.5 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 9.79 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 (d, *J* = 6.5 Hz, 3H), 6.69 (d, *J* = 8.6 Hz, 2H), 5.16 (s, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 170.0, 157.2, 146.1, 135.3, 130.7, 130.6, 130.1, 128.9, 127.9, 120.5, 94.5, 51.0 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{15}NO_3$ $[M+H]^+$ 282.1125, found 282.1136.

(Z)-4-Acetyl-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (3h)



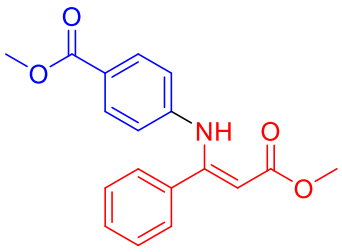
The title compound **3h** was prepared following the **general procedure A** from (4-acetylphenyl)boronic acid **1h** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (49.0 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 1.4 Hz, 3H), 7.35 – 7.32 (m, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 5.12 (s, 1H), 3.76 (s, 3H), 2.47 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 170.1, 157.6, 144.8, 135.4, 131.2, 129.9, 129.3, 128.8, 127.9, 120.3, 93.7, 50.9, 26.2 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{17}NO_3$ $[M+H]^+$ 296.1281, found 296.1275.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-4-(methoxycarbonyl) benzenaminium (3i)



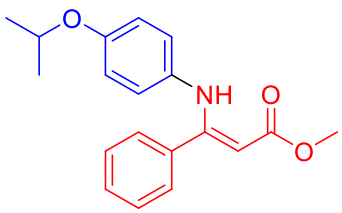
The title compound **3i** was prepared following the **general procedure A** from (4-(methoxycarbonyl)phenyl)boronic acid **1i** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (50.4 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.33 – 7.28 (m, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 5.10 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 166.6, 157.7, 144.6, 135.4, 130.4, 129.8, 128.7, 127.9, 123.8, 120.4, 93.3, 51.8, 50.8 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{17}NO_4$ $[M+H]^+$ 312.1230, found 312.1228.

(Z)-4-Isopropoxy-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (3j)



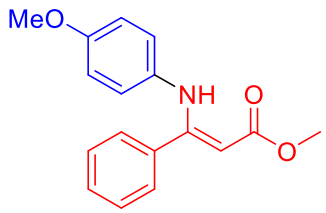
The title compound **3j** was prepared following the **general procedure A** from (4-isopropoxyphenyl)boronic acid **1j** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (54.8 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.33 – 7.28 (m, 3H), 7.26 (dd, *J* = 6.4, 1.1 Hz, 2H), 6.61 (s, 4H), 4.93 (s, 1H), 4.37 (h, *J* = 6.1 Hz, 1H), 3.73 (s, 3H), 1.25 (d, *J* = 6.1 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 160.0, 154.1, 136.0, 133.2, 129.2, 128.3, 128.3, 124.3, 116.0, 88.9, 70.1, 50.6, 22.0 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{21}NO_3$ $[M+H]^+$ 312.1594, found 312.1599.

(Z)-4-Methoxy-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (3k)



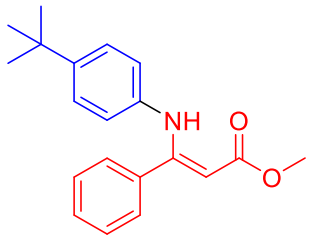
The title compound **3k** was prepared following the **general procedure A** from (4-methoxyphenyl)boronic acid **1k** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (49.3 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.32 – 7.27 (m, 3H), 7.27 – 7.23 (m, 2H), 6.62 (d, *J* = 1.3 Hz, 4H), 4.93 (s, 1H), 3.72 (s, 3H), 3.67 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 160.0, 155.8, 135.9, 133.3, 129.2, 128.3, 128.2, 124.3, 113.8, 89.0, 55.2, 50.5 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{17}NO_3$ $[M+H]^+$ 284.1281, found 284.1276.

(Z)-4-(*tert*-Butyl)-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (3l)



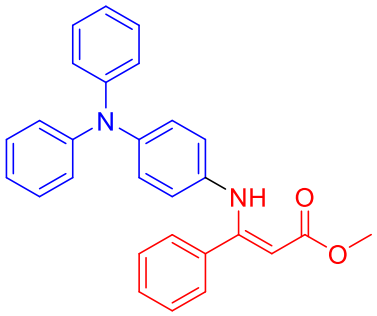
The title compound **3l** was prepared following the **general procedure A** from (4-(tert-butyl)phenyl)boronic acid **1l** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (55.7 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.35 (td, *J* = 7.0, 6.5, 1.5 Hz, 3H), 7.32 – 7.27 (m, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 4.97 (s, 1H), 3.74 (s, 3H), 1.23 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.4, 145.9, 137.6, 136.1, 129.4, 128.4, 128.2, 125.5, 121.7, 90.0, 50.6, 34.1, 31.3 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}NO_2$ $[M+H]^+$ 310.1802, found 310.1808.

(Z)-4-(Diphenylamino)-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (3m)



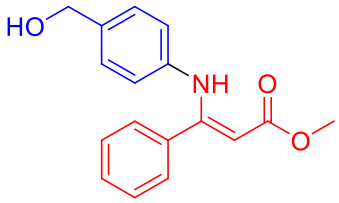
The title compound **3m** was prepared following the **general procedure A** from (4-(diphenylamino)phenyl)boronic acid **1m** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (71.4 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.40 – 7.36 (m, 2H), 7.36 – 7.29 (m, 3H), 7.21 (t, *J* = 7.8 Hz, 4H), 7.02 – 6.95 (m, 6H), 6.85 – 6.80 (m, 2H), 6.60 – 6.54 (m, 2H), 4.99 (d, *J* = 1.8 Hz, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 159.4, 147.7, 143.2, 136.0, 135.4, 129.4, 129.1, 128.3, 128.2, 124.6, 123.7, 123.2, 122.4, 89.9, 50.6 ppm.

HRMS (ESI) m/z calcd. for $C_{28}H_{24}N_2O_2$ $[M+H]^+$ 421.1902, found 421.1907.

(Z)-4-(Hydroxymethyl)-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (3n)



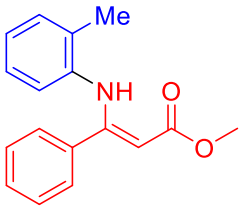
The title compound **3n** was prepared following the **general procedure A** from (4-(hydroxymethyl)phenyl)boronic acid **1n** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (47.0 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.32 (dt, *J* = 8.8, 1.6 Hz, 3H), 7.29 – 7.25 (m, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 8.5 Hz, 2H), 4.98 (s, 1H), 4.51 (s, 2H), 3.72 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.1, 139.7, 135.8, 135.5, 129.5, 128.5, 128.2, 127.5, 122.2, 90.7, 64.8, 50.7 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{17}NO_3$ $[M+H]^+$ 284.1281, found 284.1273.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-2-methylbenzenaminium (3o)



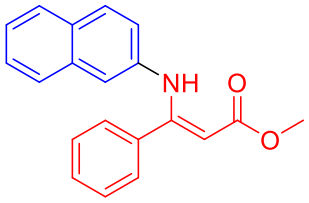
The title compound **3o** was prepared following the **general procedure A** from o-tolylboronic acid **1o** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (26.3 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.29 (dt, *J* = 8.8, 2.2 Hz, 3H), 7.26 – 7.23 (m, 2H), 7.14 – 7.10 (m, 1H), 6.88 – 6.82 (m, 1H), 6.78 (td, *J* = 7.7, 1.6 Hz, 1H), 6.33 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.03 (s, 1H), 3.74 (s, 3H), 2.41 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 160.0, 138.9, 136.1, 130.4, 130.2, 129.4, 128.3, 128.0, 125.8, 123.9, 123.5, 90.2, 50.7, 18.2 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{17}NO_2$ $[M+H]^+$ 268.1332, found 268.1326.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)naphthalen-2-aminium (3p)



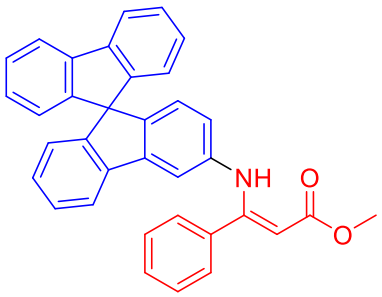
The title compound **3p** was prepared following the **general procedure A** from naphthalen-2-ylboronic acid **1p** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (55.2 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.36 – 7.29 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.06 (s, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.0, 137.9, 135.8, 133.6, 129.8, 129.5, 128.5, 128.3, 128.2, 127.5, 127.0, 126.3, 124.6, 122.4, 118.4, 91.0, 50.7 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{17}NO_2$ $[M+H]^+$ 304.1332, found 304.138.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-9,9'-spirobi[fluoren]-3-aminium (3q)



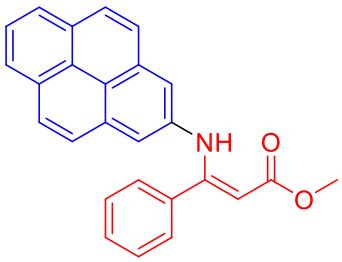
The title compound **3q** was prepared following the **general procedure A** from 9,9'-spirobi[fluoren]-2-ylboronic acid **1q** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (79.6 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.12 – 7.01 (m, 8H), 6.75 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 2H), 5.82 (d, *J* = 2.1 Hz, 1H), 4.85 (s, 1H), 3.67 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.0, 149.5, 148.5, 148.3, 141.5, 141.4, 139.9, 136.7, 135.3, 129.3, 128.0, 127.9, 127.7, 127.7, 127.6, 127.1, 123.9, 123.8, 121.5, 120.0, 119.8, 119.4, 118.1, 90.0, 50.6 ppm.

HRMS (ESI) m/z calcd. for $C_{35}H_{25}NO_2$ $[M+H]^+$ 492.1958, found 492.1953.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)pyren-1-aminium (3r)



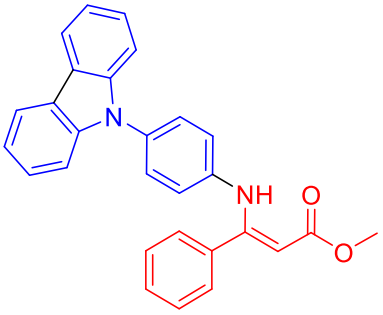
The title compound **3r** was prepared following the **general procedure A** from pyren-1-ylboronic acid **1r** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (51.3 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.01 (s, 1H), 8.52 (d, J = 9.2 Hz, 1H), 8.20 – 8.13 (m, 3H), 7.99 (t, *J* = 7.7 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 7.18 – 7.10 (m, 3H), 5.24 (s, 1H), 3.83 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 160.5, 136.0, 134.2, 131.4, 131.2, 129.4, 128.4, 128.2, 127.9, 127.8, 127.2, 126.4, 126.2, 125.3, 125.1, 124.9, 124.8, 124.4, 123.1, 121.4, 91.0, 50.9 ppm.

HRMS (ESI) m/z calcd. for $C_{26}H_{19}NO_2$ $[M+H]^+$ 378.1489, found 378.1486.

(Z)-4-(9H-Carbazol-9-yl)-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl) benzenaminium (3s)



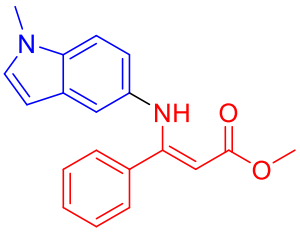
The title compound **3s** was prepared following the **general procedure A** from (4-(9H-carbazol-9-yl)phenyl)boronic acid **1s** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (51.9 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 8.08 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.44 – 7.41 (m, 2H), 7.37 (dd, *J* = 2.2, 1.0 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.25 – 7.20 (m, 6H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.07 (s, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 158.8, 140.9, 139.7, 135.7, 132.3, 129.8, 128.7, 128.3, 127.4, 125.9, 123.2, 123.0, 120.3, 119.8, 109.6, 91.7, 50.9 ppm.

HRMS (ESI) m/z calcd. for $C_{28}H_{22}N_2O_2$ $[M+H]^+$ 419.1754, found 419.1748.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-1-methyl-1H-indol-5-aminium (3t)



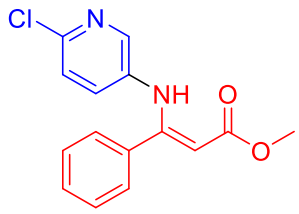
The title compound **3t** was prepared following the **general procedure A** from (1-methyl-1H-indol-5-yl)boronic acid **1t** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (53.3 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.36 – 7.32 (m, 2H), 7.26 – 7.17 (m, 3H), 7.02 – 6.99 (m, 2H), 6.95 (d, *J* = 3.1 Hz, 1H), 6.64 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.27 (dd, *J* = 3.1, 0.8 Hz, 1H), 4.94 (s, 1H), 3.74 (s, 3H), 3.67 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 160.7, 136.3, 133.8, 132.6, 129.5, 129.0, 128.4, 128.3, 128.1, 118.9, 115.4, 109.0, 100.7, 88.1, 50.5, 32.8 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{18}N_2O_2$ $[M+H]^+$ 307.1441, found 370.1436.

(Z)-6-Chloro-N-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)pyridin-3-aminium (3u)



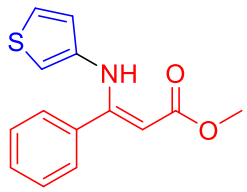
The title compound **3u** was prepared following the **general procedure A** from (6-chloropyridin-3-yl)boronic acid **1u** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (49.0 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.81 (d, *J* = 2.9 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 – 7.29 (m, 4H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.9 Hz, 1H), 5.12 (s, 1H), 3.75 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 157.9, 144.7, 142.6, 136.3, 134.6, 131.3, 130.1, 128.9, 128.0, 123.6, 93.2, 51.0 ppm.

HRMS (ESI) m/z calcd. for $C_{15}H_{13}ClN_2O_2$ $[M+H]^+$ 289.0738, found 289.0732.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)thiophen-3-aminium (3v)



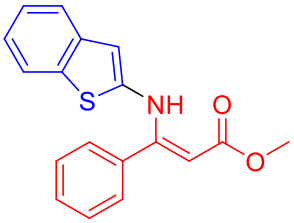
The title compound **3v** was prepared following the **general procedure A** from thiophen-3-ylboronic acid **1v** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (45.6 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 7.40 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 7.02 (dd, *J* = 5.2, 3.2 Hz, 1H), 6.48 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.05 (dd, *J* = 3.4, 1.4 Hz, 1H), 4.93 (s, 1H), 3.74 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 159.8, 139.0, 135.8, 129.6, 128.4, 128.2, 124.3, 123.5, 110.2, 89.3, 50.7 ppm.

HRMS (ESI) m/z calcd. for $C_{14}H_{13}NO_2S$ $[M+H]^+$ 260.0738, found 260.0733.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzo[b]thiophen-2-aminium (3w)



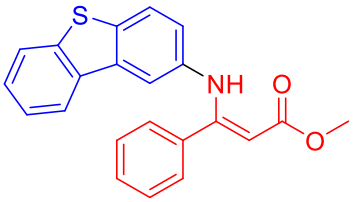
The title compound **3w** was prepared following the **general procedure A** from benzo[*b*]thiophen-2-ylboronic acid **1w** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (30.3 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.51 (ddt, *J* = 8.0, 1.3, 0.7 Hz, 1H), 7.46 – 7.43 (m, 3H), 7.42 – 7.38 (m, 1H), 7.36 – 7.32 (m, 2H), 7.23 – 7.19 (m, 1H), 7.14 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 6.39 (t, *J* = 0.8 Hz, 1H), 5.06 (s, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 159.0, 143.8, 138.4, 135.7, 134.7, 130.0, 128.5, 124.4, 123.1, 122.3, 121.7, 112.3, 91.6, 50.9 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{15}NO_2S$ $[M+H]^+$ 310.0896, found 310.0891.

(Z)-N-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)dibenzo[b,d]thiophen-2-aminium (3x)



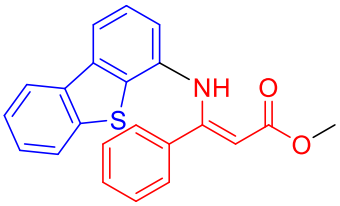
The title compound **3x** was prepared following the **general procedure A** from dibenzo[*b,d*]thiophen-2-ylboronic acid **1x** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (59.6 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.79 (d, *J* = 7.1 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.40 – 7.38 (m, 2H), 7.31 (ddd, *J* = 14.3, 7.8, 6.1 Hz, 3H), 6.82 (dd, *J* = 8.5, 2.2 Hz, 1H), 5.09 (s, 1H), 3.79 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 159.3, 140.1, 137.4, 135.9, 135.8, 135.1, 133.9, 129.5, 128.5, 128.3, 126.8, 124.3, 122.8, 122.6, 122.2, 121.3, 114.9, 90.5, 50.7 ppm.

HRMS (ESI) m/z calcd. for $C_{22}H_{17}NO_2S$ $[M+H]^+$ 360.1053, found 360.1044.

Methyl (Z)-3-(dibenzo[b,d]thiophen-4-ylamino)-3-phenylacrylate (3y)



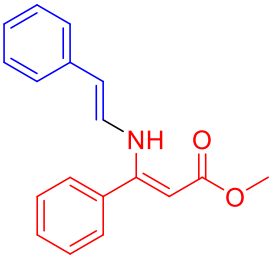
The title compound **3y** was prepared following the **general procedure A** from dibenzo[*b,d*]thiophen-4-ylboronic acid **1y** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (61.0 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 8.11 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.38 – 7.35 (m, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.19 (s, 1H), 3.80 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 159.6, 139.1, 136.7, 136.1, 135.8, 135.6, 133.8, 129.7, 128.4, 127.9, 126.9, 124.7, 124.6, 123.0, 121.9, 121.5, 117.0, 91.9, 50.9 ppm.

HRMS (ESI) m/z calcd. for $C_{22}H_{17}NO_2S$ $[M+H]^+$ 360.1053, found 360.1048.

(Z)-3-Methoxy-3-oxo-1-phenyl-N-((E)-styryl)prop-1-en-1-aminium (3z)



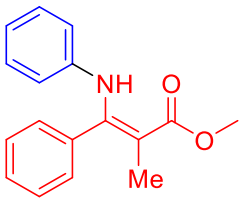
The title compound **3z** was prepared following the **general procedure A** from (E)-styrylboronic acid **1z** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (35.2 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (d, *J* = 11.5 Hz, 1H), 7.48 – 7.42 (m, 6H), 7.22 – 7.17 (m, 2H), 7.10 – 7.06 (m, 2H), 6.80 (dd, *J* = 14.0, 11.4 Hz, 1H), 6.08 (d, *J* = 14.0 Hz, 1H), 4.83 (s, 1H), 3.74 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 158.5, 136.7, 134.8, 129.9, 128.7, 128.5, 128.4, 126.8, 125.8, 125.0, 110.5, 88.3, 50.7 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{17}NO_2$ $[M+H]^+$ 280.1332, found 280.1127.

Methyl (Z)-2-methyl-3-phenyl-3-(phenylamino)acrylate (3aa)



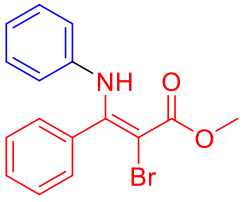
The title compound **3aa** was prepared following the **general procedure A** from phenylboronic acid **1a** (0.30 mmol) and 5-methoxy-4-methyl-3-phenylisoxazole **2b** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (45.9 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.90 (s, 1H), 7.33 (dd, *J* = 4.9, 2.0 Hz, 3H), 7.24 (dd, *J* = 6.7, 3.0 Hz, 2H), 6.99 (dd, *J* = 8.5, 7.3 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.55 – 6.51 (m, 2H), 3.79 (s, 3H), 1.68 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 156.3, 140.9, 135.4, 129.4, 128.6, 128.4, 128.4, 122.2, 121.7, 94.1, 51.1, 14.1 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{17}NO_2$ $[M+H]^+$ 268.1332, found 268.1336.

Methyl (E)-2-bromo-3-phenyl-3-(phenylamino)acrylate (3ab)



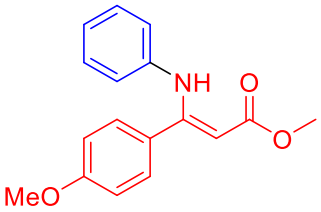
The title compound **3ab** was prepared following the **general procedure A** from phenylboronic acid **1a** (0.30 mmol) and 4-bromo-5-methoxy-3-phenylisoxazole **2c** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (54.3 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (s, 1H), 7.35 – 7.32 (m, 3H), 7.32 – 7.23 (m, 2H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.84 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 159.1, 139.6, 135.3, 129.4, 129.2, 128.6, 128.3, 123.9, 122.8, 81.7, 52.3 ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{14}BrNO_2$ $[M+H]^+$ 332.0281, found 332.0275.

Methyl (Z)-3-(4-methoxyphenyl)-3-(phenylamino)acrylate (3ac)



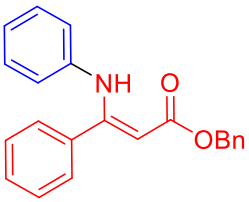
The title compound **3ac** was prepared following the **general procedure A** from phenylboronic acid **1a** (0.30 mmol) and 5-methoxy-3-(4-methoxyphenyl)isoxazole **2d** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (44.7mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.12 – 7.07 (m, 2H), 6.94 – 6.90 (m, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.70 – 6.67 (m, 2H), 4.97 (s, 1H), 3.80 (s, 3H), 3.74 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 160.6, 159.0, 140.6, 129.7, 128.6, 128.0, 122.9, 122.3, 113.8, 90.0, 55.3, 50.6 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{17}NO_3$ $[M+H]^+$ 284.1281, found 284.1276.

Benzyl (Z)-3-phenyl-3-(phenylamino)acrylate (3ad)



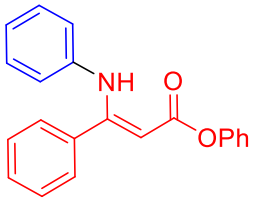
The title compound **3ad** was prepared following the **general procedure A** from phenylboronic acid **1a** (0.30 mmol) and 5-(benzyloxy)-3-phenylisoxazole **2f** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (48.1 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.43 – 7.40 (m, 2H), 7.40 – 7.36 (m, 2H), 7.36 – 7.32 (m, 4H), 7.30 – 7.27 (m, 2H), 7.08 (dd, *J* = 8.5, 7.3 Hz, 2H), 6.94 – 6.89 (m, 1H), 6.67 (d, *J* = 7.3 Hz, 2H), 5.21 (s, 2H), 5.07 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 159.6, 140.3, 136.9, 135.9, 129.5, 128.6, 128.6, 128.4, 128.3, 128.0, 128.0, 123.1, 122.4, 90.7, 65.2 ppm.

HRMS (ESI) m/z calcd. for $C_{22}H_{19}NO_2$ $[M+H]^+$ 330.1489, found 330.1484.

Phenyl (Z)-3-phenyl-3-(phenylamino)acrylate (3ae)



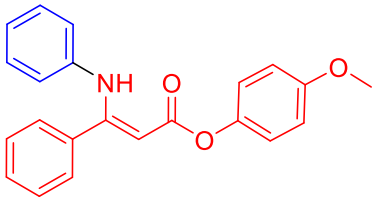
The title compound **3ae** was prepared following the **general procedure A** from phenylboronic acid **1a** (0.30 mmol) and 5-phenoxy-3-phenylisoxazole **2g** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (43.5 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.39 – 7.36 (m, 4H), 7.33 – 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 7.18 – 7.15 (m, 2H), 7.09 – 7.04 (m, 2H), 6.95 – 6.90 (m, 1H), 6.68 – 6.65 (m, 2H), 5.20 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 161.0, 150.9, 139.8, 135.6, 129.3, 128.6, 128.5, 128.2, 123.5, 122.4, 122.0, 119.1, 89.4, 79.5 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{17}NO$ $[M+H]^+$ 316.1332, found 316.1334.

4-Methoxyphenyl (Z)-3-phenyl-3-(phenylamino)acrylate (3af)



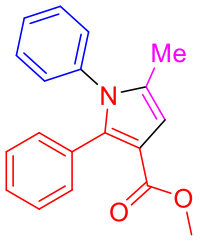
The title compound **3af** was prepared following the **general procedure A** from phenylboronic acid **1a** (0.30 mmol) and 5-(4-methoxyphenoxy)-3-phenylisoxazole **2h** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (48.4 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.38 (td, *J* = 6.1, 1.6 Hz, 3H), 7.34 – 7.30 (m, 2H), 7.09 (d, *J* = 4.6 Hz, 2H), 7.07 (t, *J* = 3.3 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 3H), 6.68 – 6.65 (m, 2H), 5.19 (s, 1H), 3.81 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 160.9, 157.0, 144.4, 139.9, 135.6, 129.7, 128.7, 128.5, 128.3, 123.4, 122.7, 122.4, 114.4, 89.4, 55.6 ppm.

HRMS (ESI) m/z calcd. for $C_{22}H_{19}NO_3$ $[M+H]^+$ 346.1438, found 346.1433.

Methyl 5-methyl-1,2-diphenyl-1H-pyrrole-3-carboxylate (4)[2]



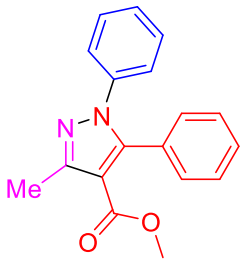
Methyl (Z)-3-phenyl-3-(phenylamino)acrylate **3a** (0.2 mmol) was stirred in MeCN (2.0 mL) together with Ag_2CO_3 (0.6 mmol) at 110 °C under an atmosphere of argon. After completion of the reaction (as indicated by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (6 mL), and filtered through a short pad of silica, which was then washed with EtOAc (6 mL). Removal of the solvent in vacuo and purification of the residue by column chromatography using a mixture of PE and EtOAc as eluent provided methyl 5-methyl-1,2-diphenyl-1H-pyrrole-3-carboxylate **4** as a yellow oil (39.2 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 3H), 7.18 – 7.14 (m, 5H), 7.05 – 7.02 (m, 2H), 6.53 (d, *J* = 1.2 Hz, 1H), 3.69 (s, 3H), 2.08 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 138.7, 137.9, 131.8, 131.1, 130.3, 128.8, 128.5, 127.9, 127.5, 127.3, 112.6, 108.7, 50.9, 13.0 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{17}NO_2$ $[M+H]^+$ 291.1260, found 291.1253.

Methyl 3-methyl-1,5-diphenyl-1H-pyrazole-4-carboxylate (5)[3]



To an oven-dried screw-capped vial (20 mL) with a magnetic stirring bar were weighed in air methyl (Z)-3-phenyl-3-(phenylamino)acrylate **3a** (0.2 mmol) and $Cu(OAc)_2$ (0.3 mmol) before adding the liquid acetonitrile (6.0 mmol) as a reaction partner. The srew-capped vial was closed and the reaction mixture was

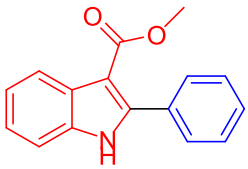
stirred vigorously at room temperature to suspend the solids well. The reaction vial was placed into a preheated metal block (110 °C) and the reaction mixture was stirred at this temperature for 24 h. After cooling to room temperature, the reaction mixture was analyzed by TLC. EtOAc (3 mL) was added and the mixture was shortly stirred at room temperature to suspend the metallic precipitates and filtered through a short pad of silica. The solid was washed thoroughly with EtOAc (4 x 3 mL) and the combined filtrates were concentrated in vacuo. The crude product was dissolved in CH_2Cl_2 (ca. 5 mL), adsorbed on silica (ca. 2 g) and purified by flash column chromatography (silica, gradient of PE/EtOAc-mixtures = 10:1) to give compound **5** as a yellow oil (42.2 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 3H), 7.26 – 7.22 (m, 5H), 7.19 – 7.14 (m, 2H), 3.69 (s, 3H), 2.59 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 151.7, 146.4, 139.1, 130.3, 128.9, 128.7, 127.9, 127.6, 125.3, 111.6, 51.0, 14.3 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{16}N_2O_2$ $[M+H]^+$ 293.1285, found 293.1289.

Methyl 2-phenyl-1H-indole-3-carboxylate (6)[4]



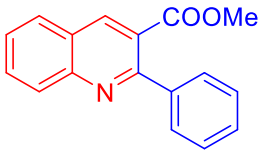
Methyl (Z)-3-phenyl-3-(phenylamino)acrylate **3a** (0.2 mmol) was stirred in DMF (1.0 mL) together with $Pd(OAC)_2$ (10 mol%), $Cu(OAc)_2$ (0.6 mmol), and K_2CO_3 (0.6 mmol) at 80 °C under an atmosphere of argon. After completion of the reaction (as indicated by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (3 mL), and filtered through a short pad of silica, which was then washed with EtOAc (6 mL). Removal of the solvent in vacuo and purification of the residue by column chromatography using a mixture of PE and EtOAc as eluent provided 3-(Methoxycarbonyl)-2-phenyl-1H-indol-1-ium **8** as a yellow oil (22.5 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.16 – 8.11 (m, 1H), 7.58 (dd, *J* = 7.4, 2.4 Hz, 2H), 7.38 (dd, *J* = 5.1, 2.1 Hz, 3H), 7.30 (d, *J* = 0.8 Hz, 1H), 7.23 – 7.18 (m, 2H), 3.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 144.5, 135.1, 132.0, 129.5, 129.2, 128.2, 127.5, 123.3, 122.2, 122.1, 111.0, 104.5, 50.ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{13}NO_2$ $[M+H]^+$ 252.1019, found 252.1017.

3-(Methoxycarbonyl)-2-phenylquinolin-1-ium (7)



The title compound **7** was prepared following the **general procedure A** from (2-formylphenyl)boronic acid **4** (0.30 mmol) and 5-methoxy-3-phenylisoxazole **2a** (0.20 mmol) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a yellow oil (25.8 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 0.9 Hz, 1H), 8.19 (dq, *J* = 8.5, 0.9 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.82 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.52 – 7.41 (m, 4H), 3.76 – 3.73 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 158.0, 148.4, 140.5, 139.2, 131.6, 129.5, 128.6, 128.5, 128.2, 127.2, 126.1, 125.8, 125.0, 52.4 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{13}NO_2$ $[M+H]^+$ 264.1019, found 264.1024.

5. References

1 (a) X. Xu, X. Zhang, Z. Wang and M. Kong, *RSC Adv.*, 2015, **5**, 40950–40952. (b) X. Zhang, B. Yang, G. Li, X. Shu, D. Mungra and J. Zhu, *Synlett*, 2012, **23**, 622–626.

2 M. Zhao, F. Wang and X. Li, *Org. Lett.*, 2012, **14**, 1412–1415.

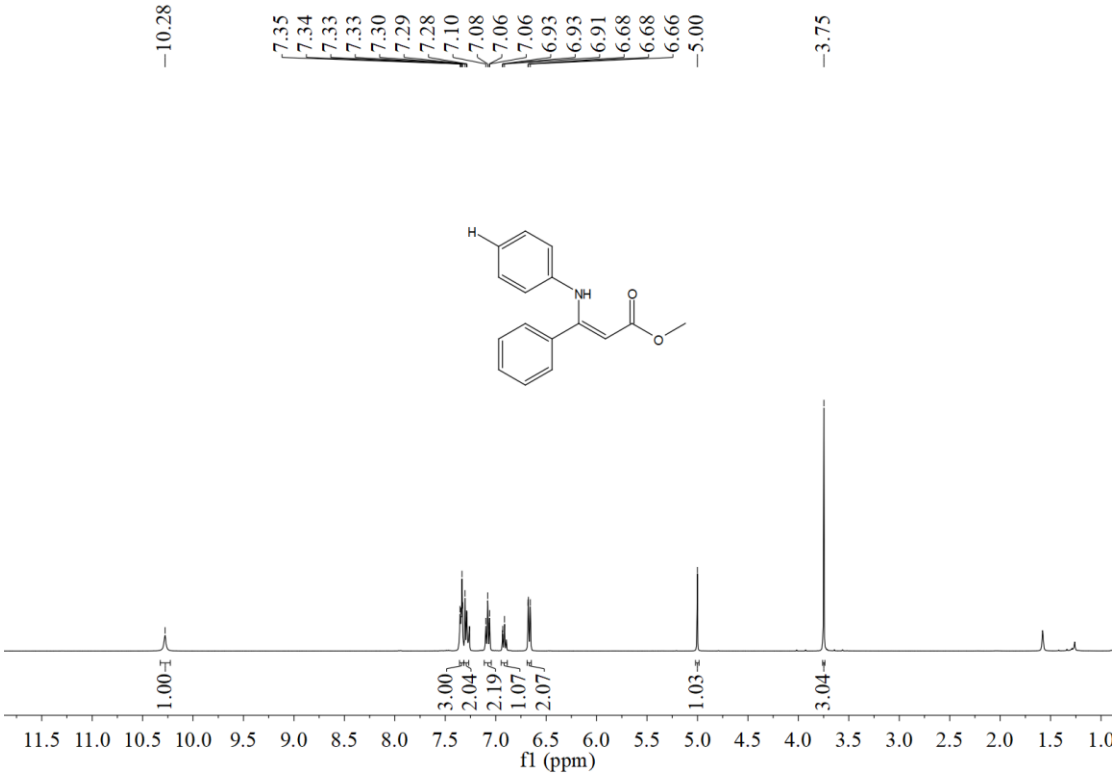
3 J. J. Neumann, M. Suri and F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 7790–7794.

4 X. Ji, H. Huang, W. Wu, X. Li and H. Jiang, *J. Org. Chem.*, 2013, **78**, 11155–11162.

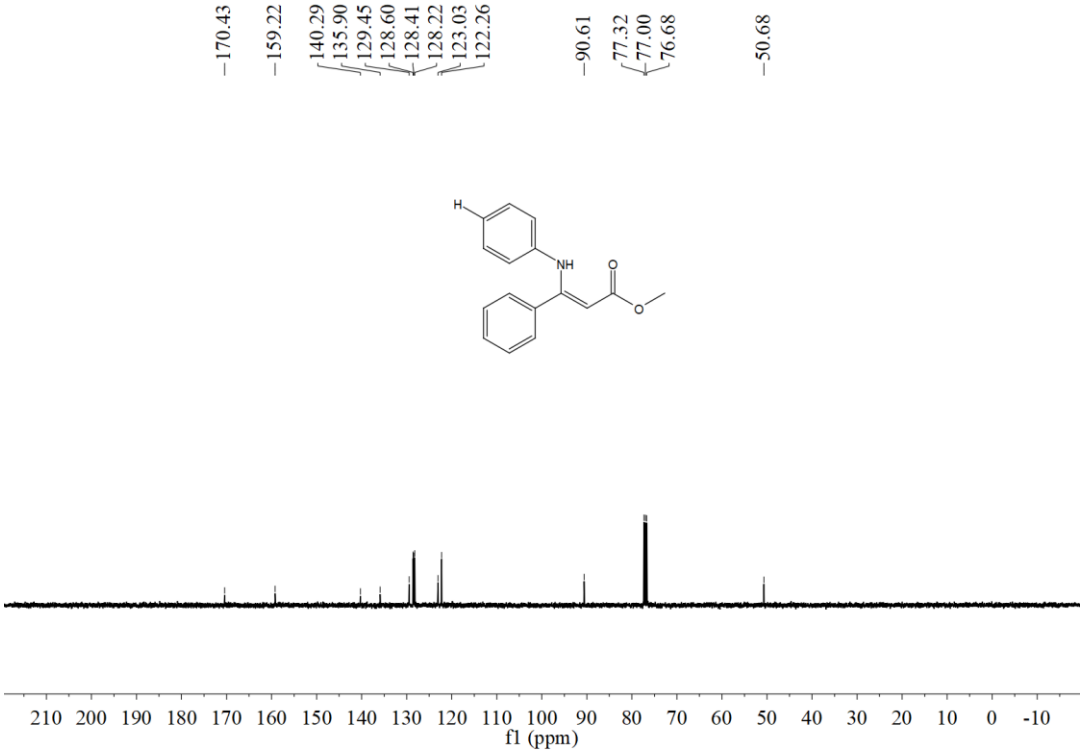
6. NMR Spectra

Methyl (Z)-3-phenyl-3-(phenylamino)acrylate **(3a)**

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

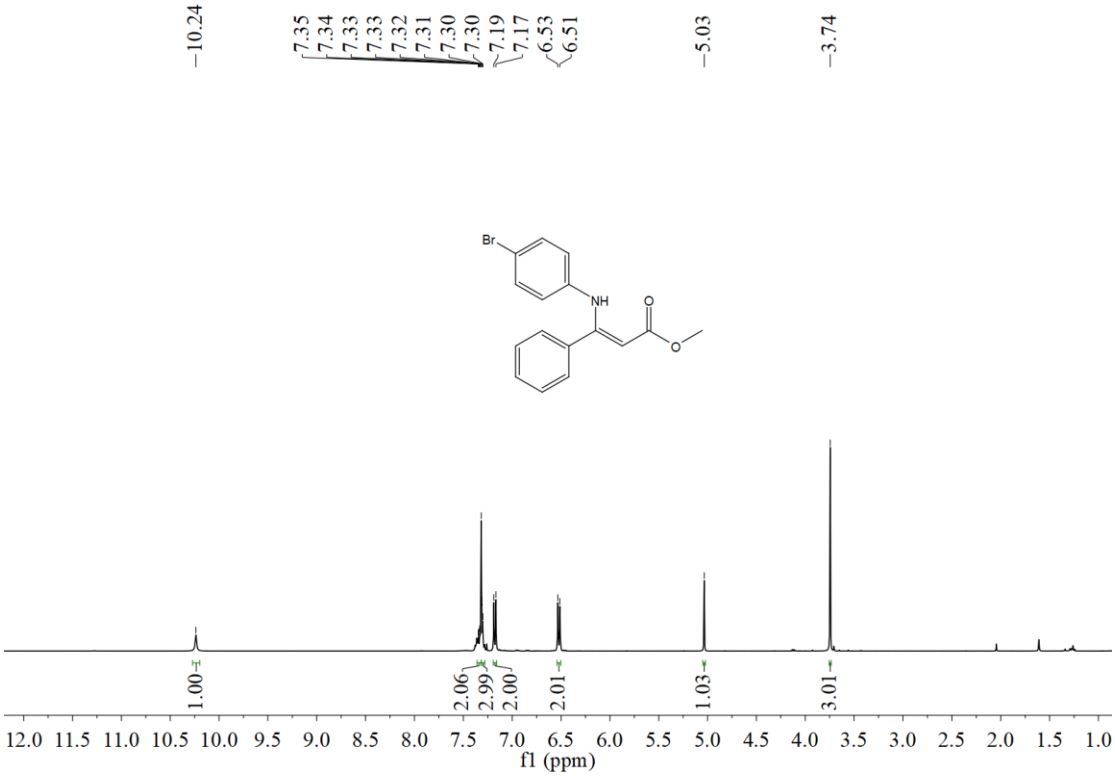


^{13}C NMR (100 MHz, $CDCl_3$)

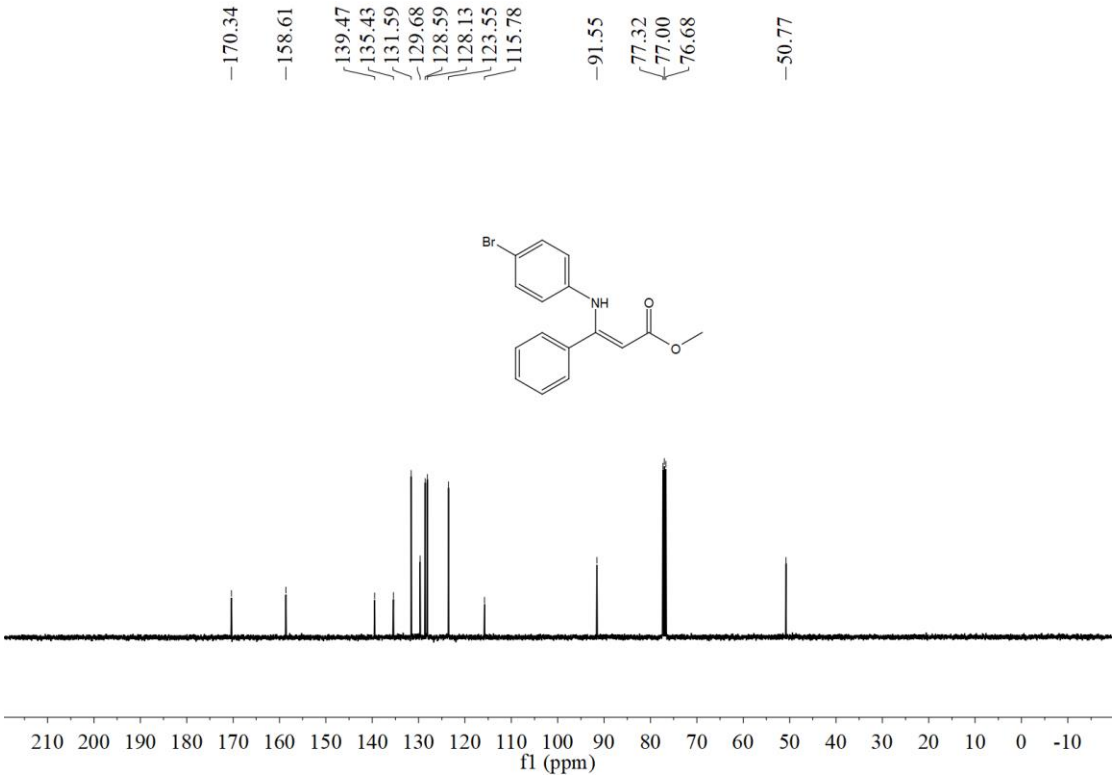


Methyl (Z)-3-((4-bromophenyl)amino)-3-phenylacrylate (**3b**)

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

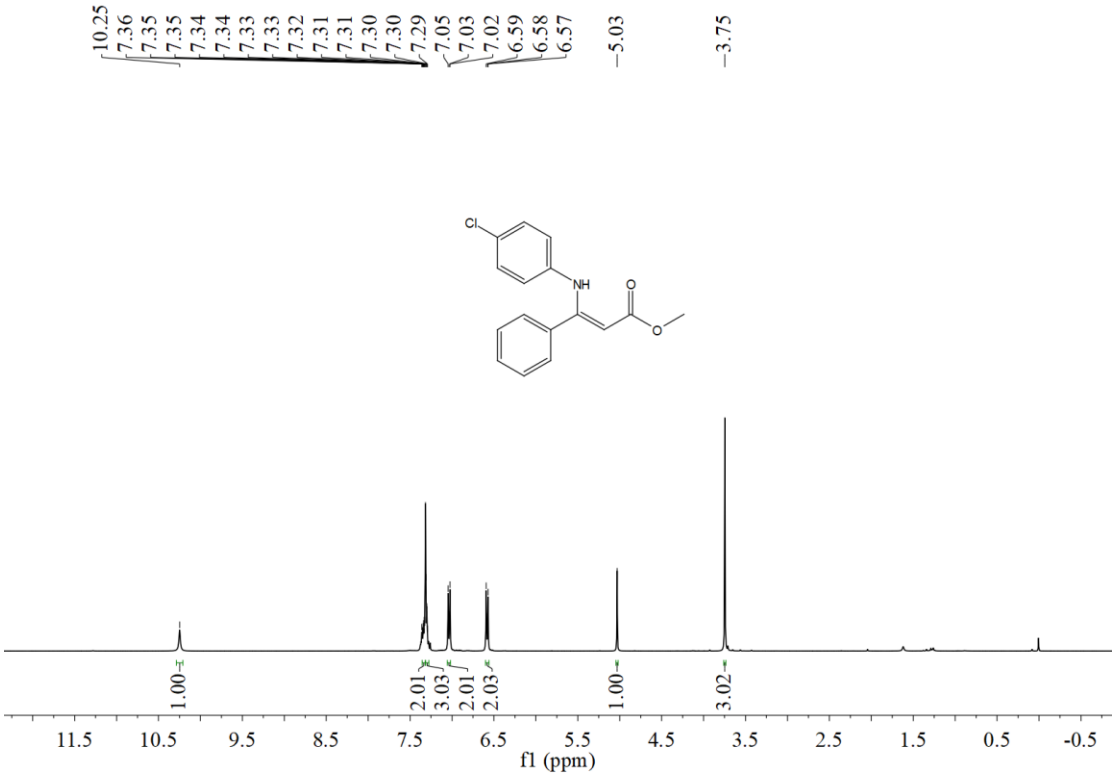


^{13}C NMR (100 MHz, $CDCl_3$)

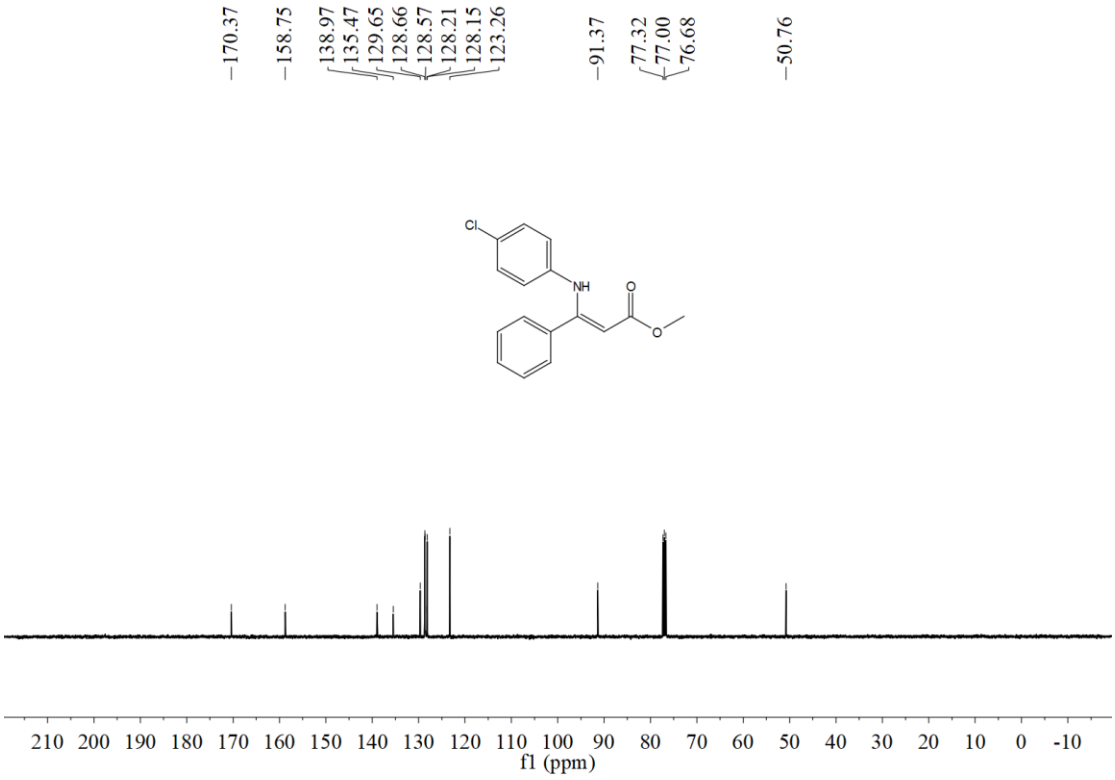


Methyl (Z)-3-((4-chlorophenyl)amino)-3-phenylacrylate (**3c**)

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

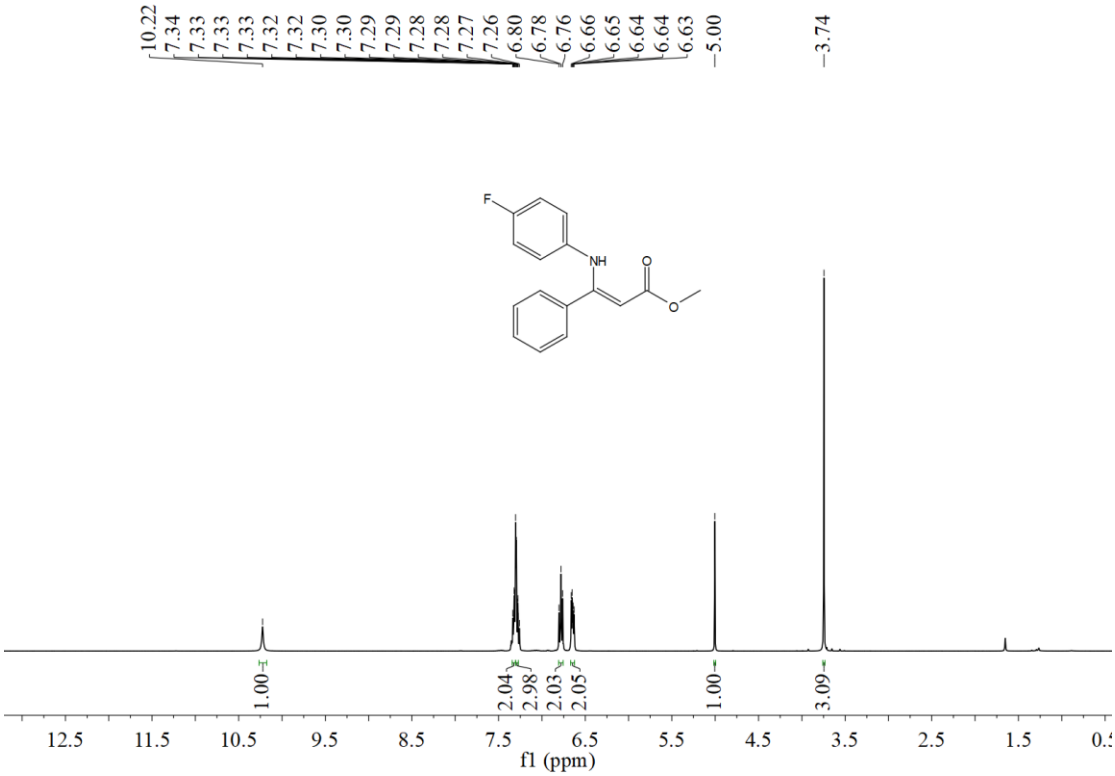


^{13}C NMR (100 MHz, $CDCl_3$)

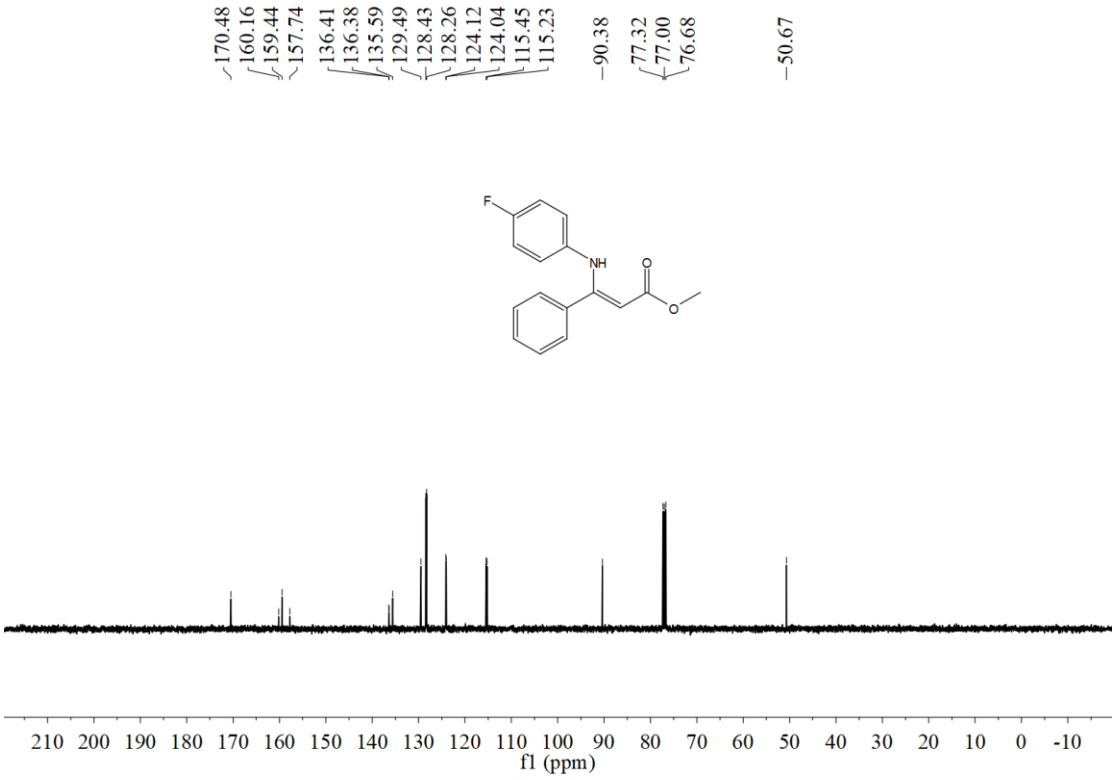


Methyl (Z)-3-((4-fluorophenyl)amino)-3-phenylacrylate (**3d**)

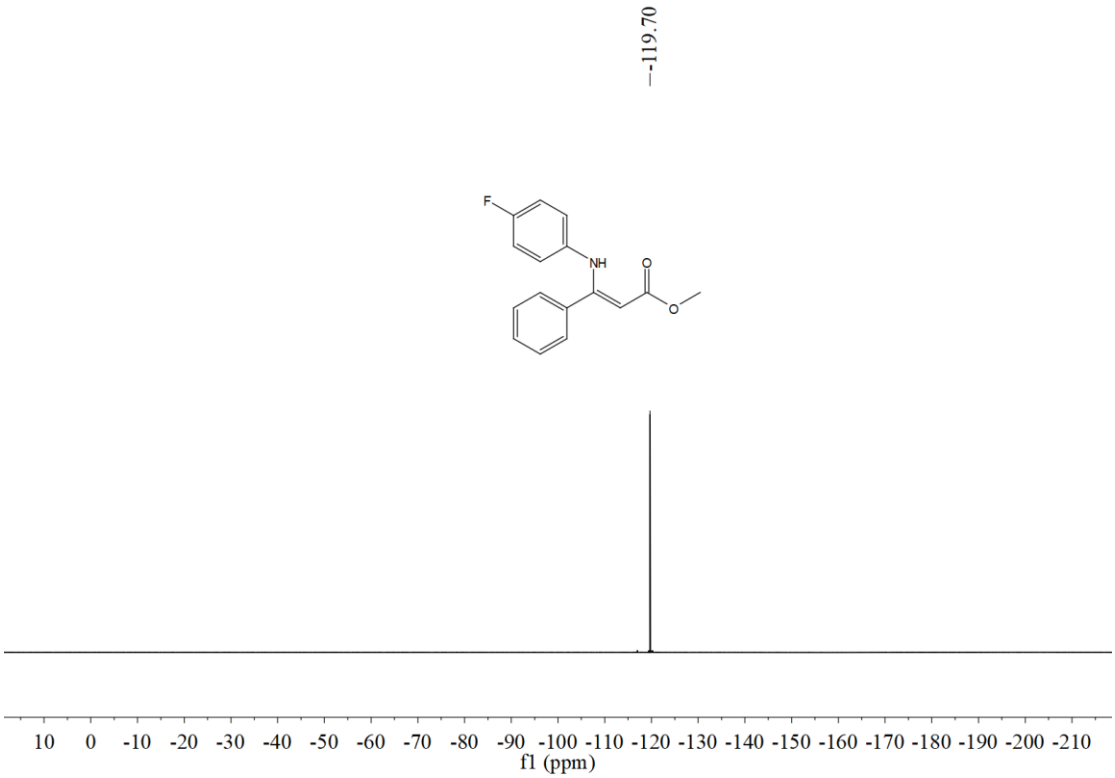
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

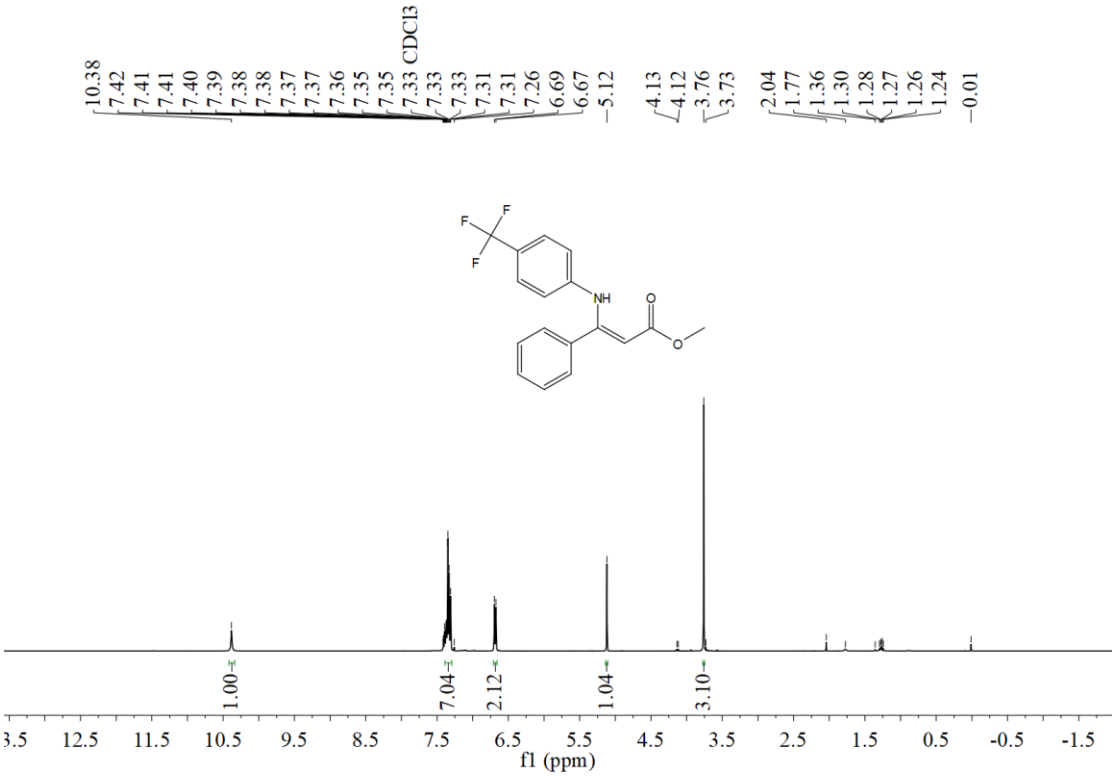


^{19}F NMR (376 MHz, $CDCl_3$)

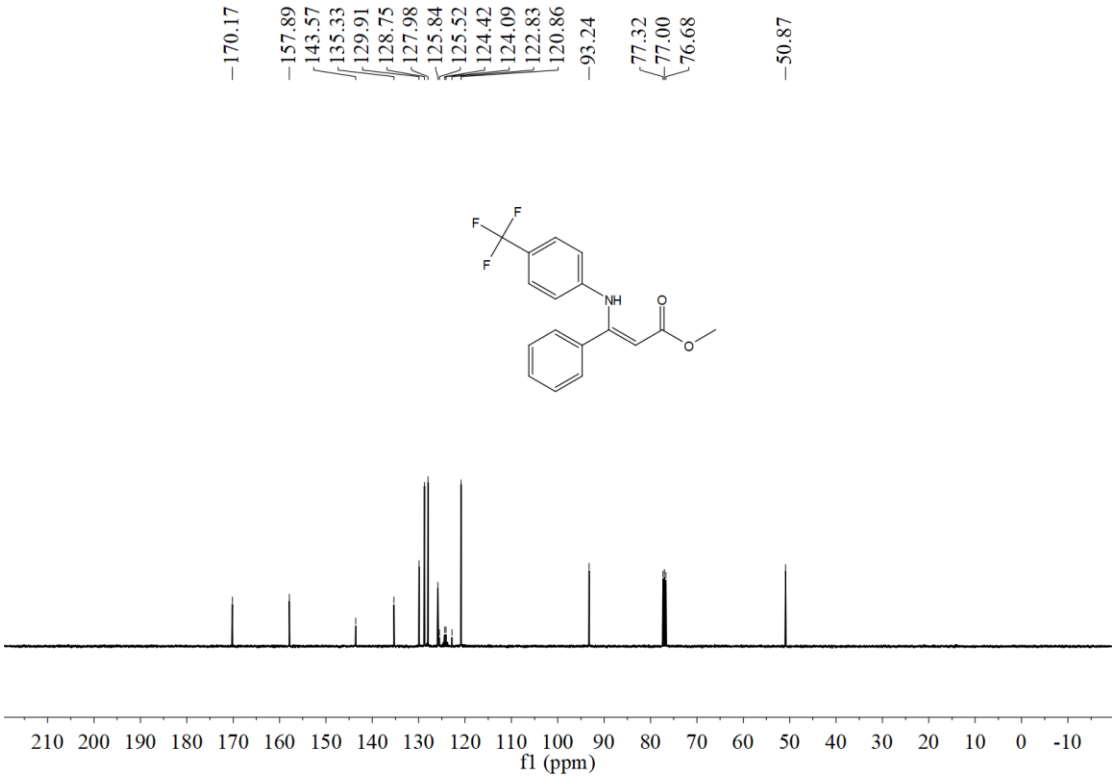


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-4-(trifluoromethyl)benzenaminium (**3e**)

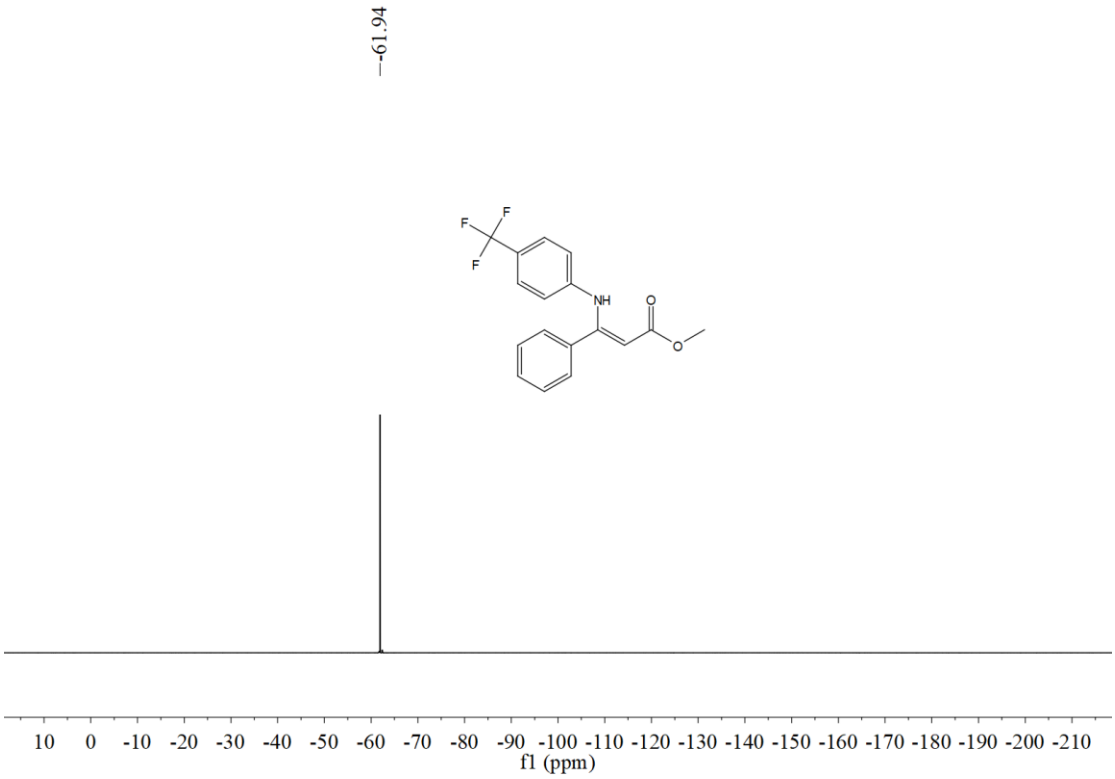
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

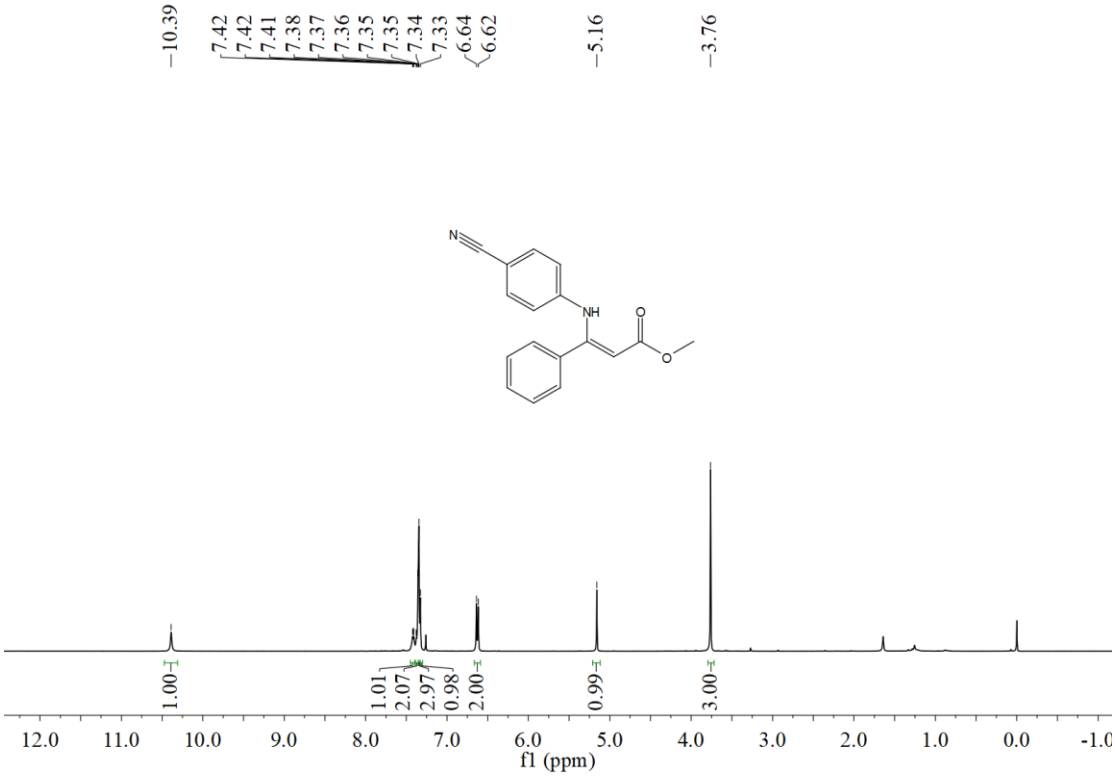


^{19}F NMR (376 MHz, $CDCl_3$)

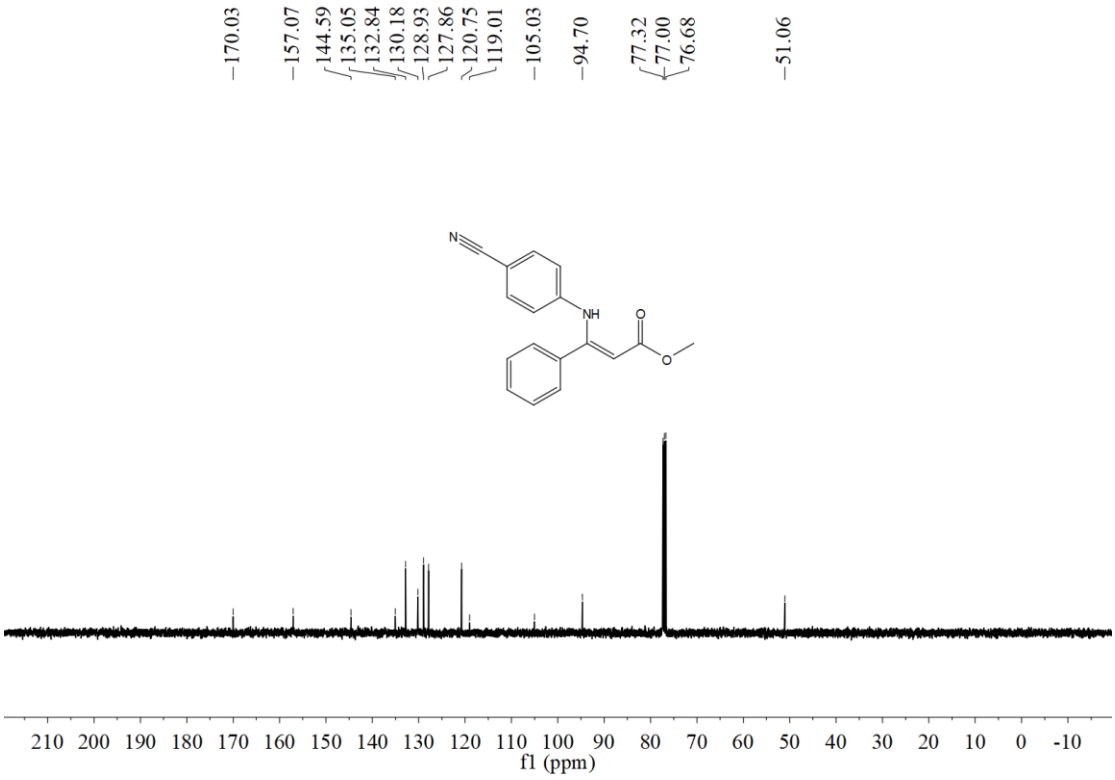


(*Z*)-4-Cyano-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3f**)

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

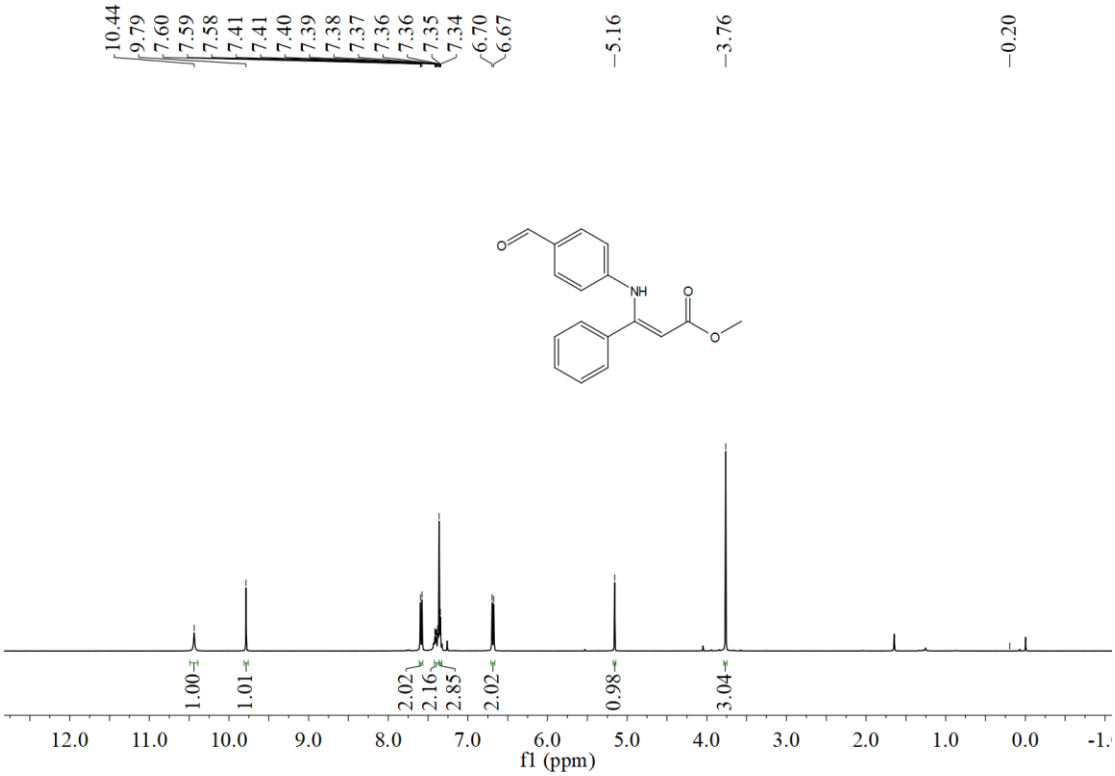


^{13}C NMR (100 MHz, $CDCl_3$)

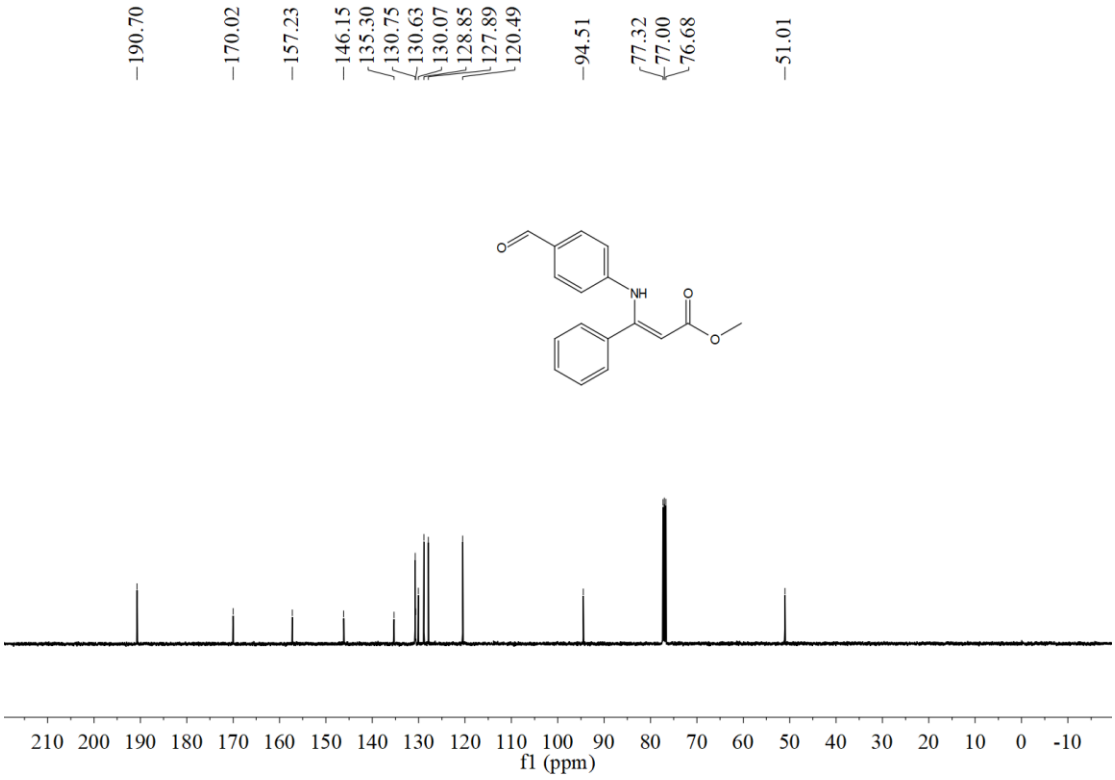


(*Z*)-4-Formyl-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3g**)

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

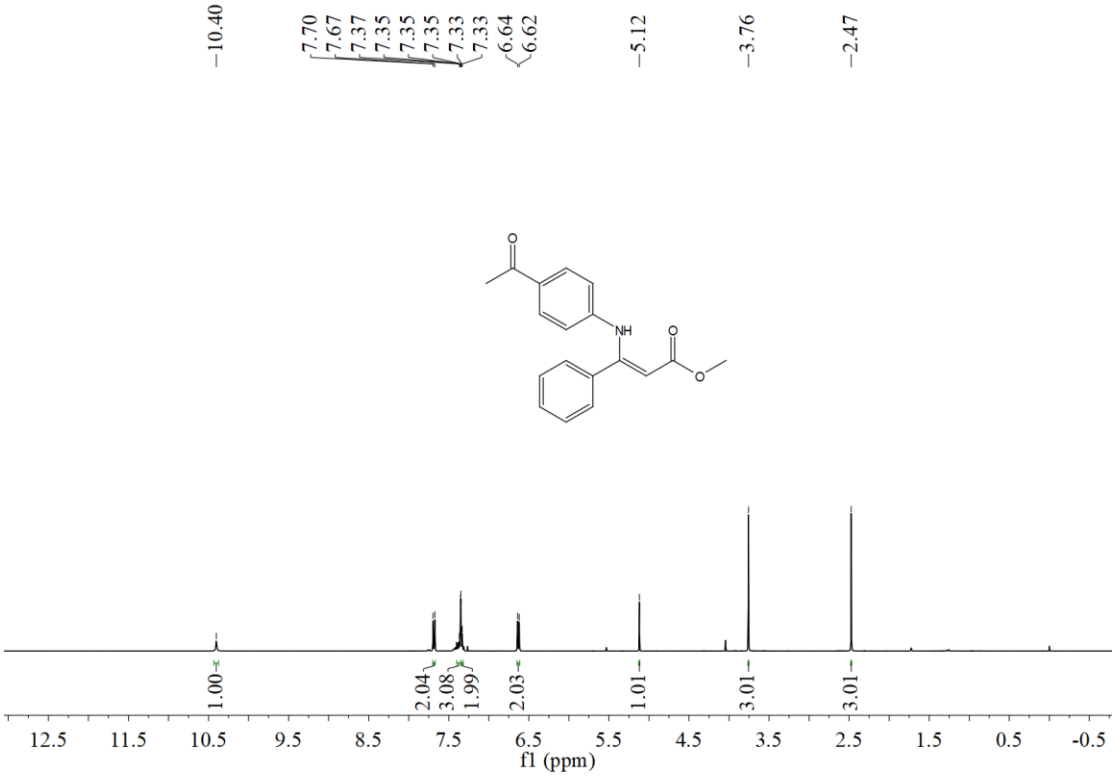


^{13}C NMR (100 MHz, $CDCl_3$)

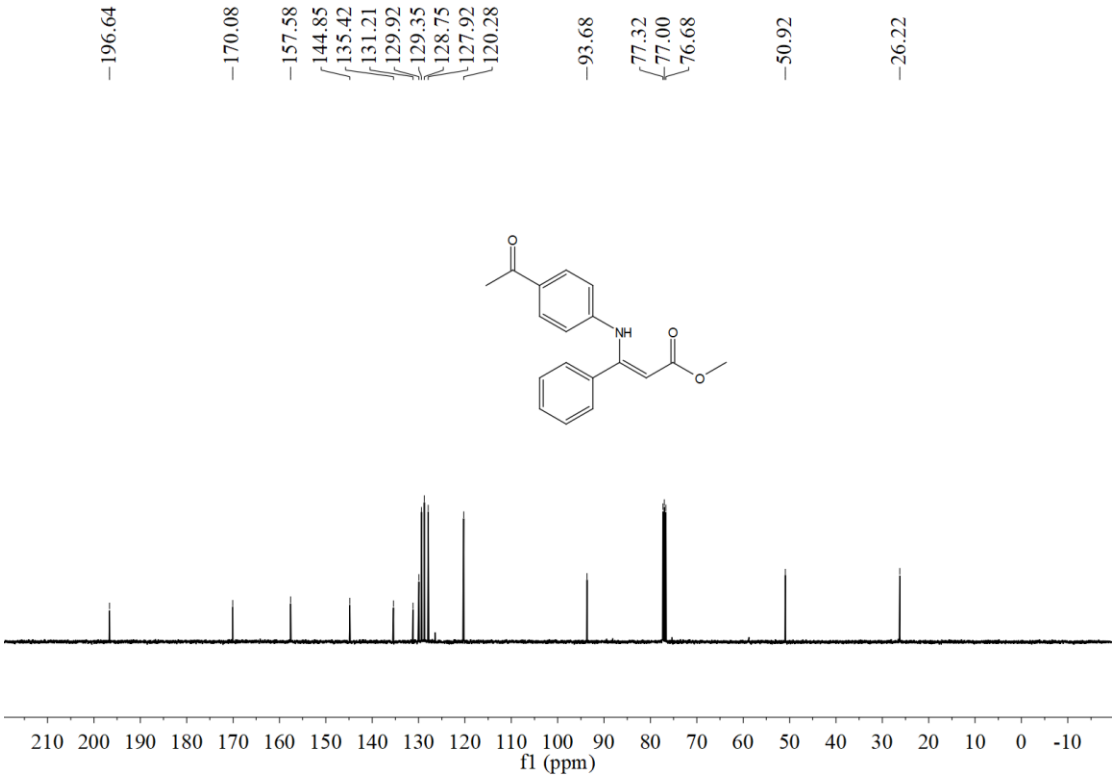


(*Z*)-4-Acetyl-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3h**)

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

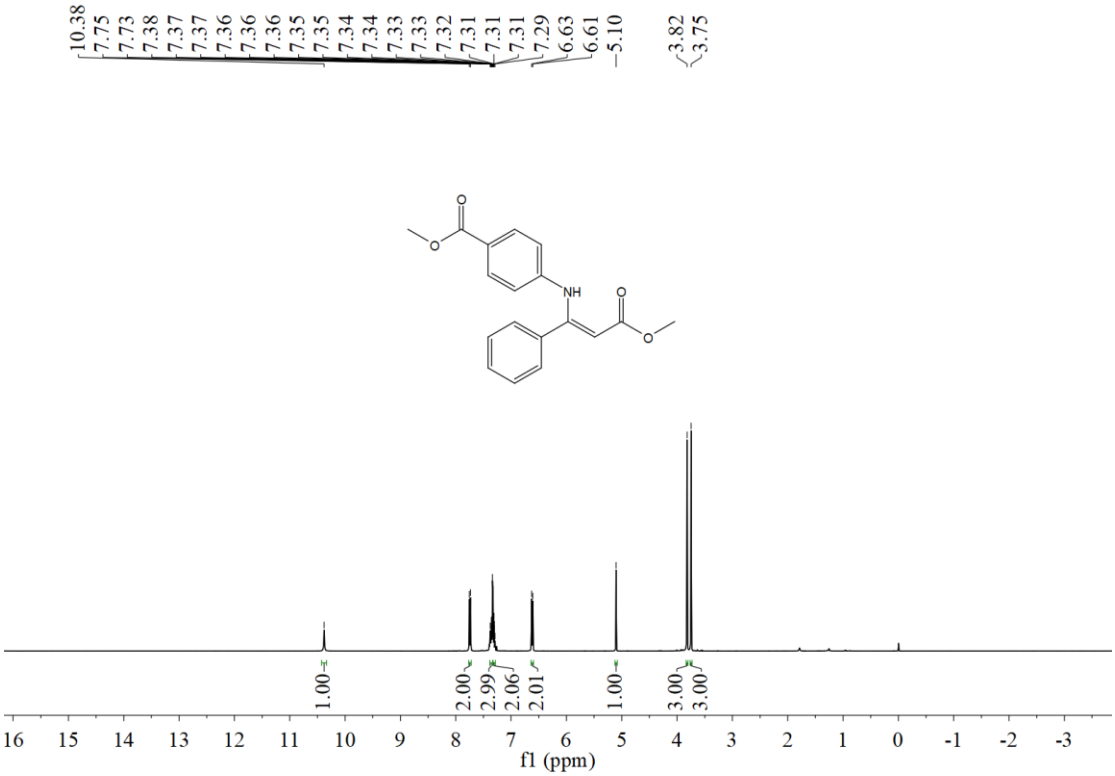


^{13}C NMR (100 MHz, $CDCl_3$)

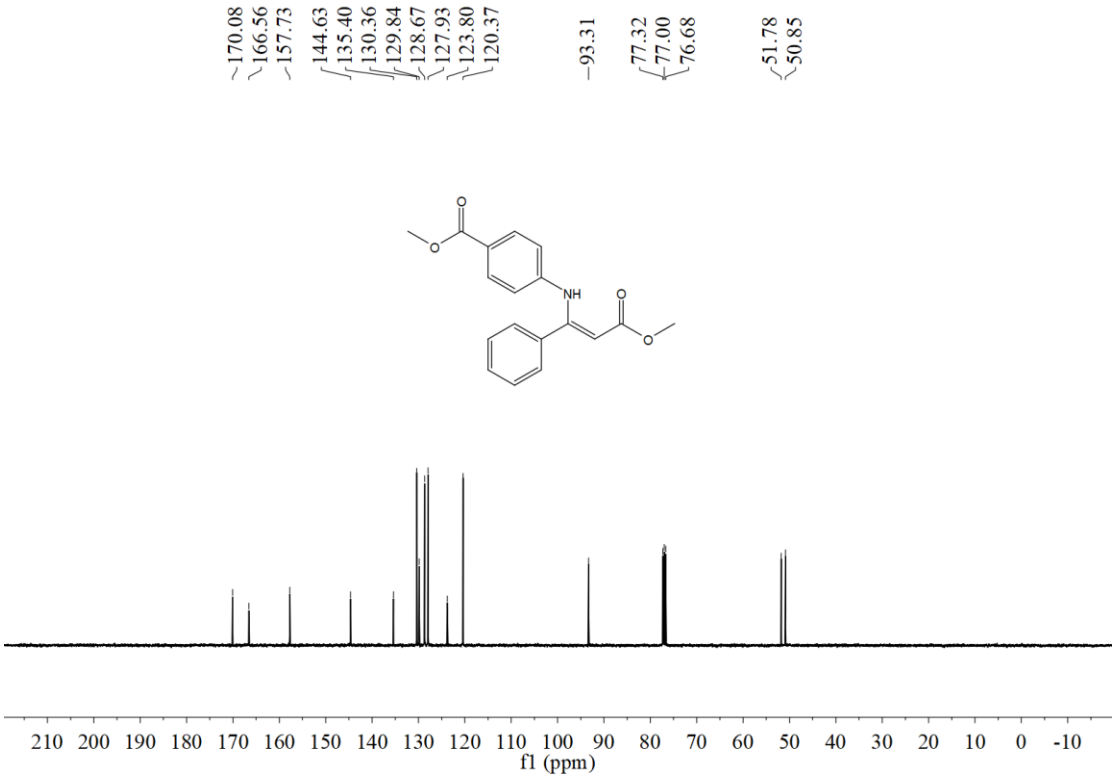


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-4-(methoxycarbonyl)benzenaminium (**3i**)

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

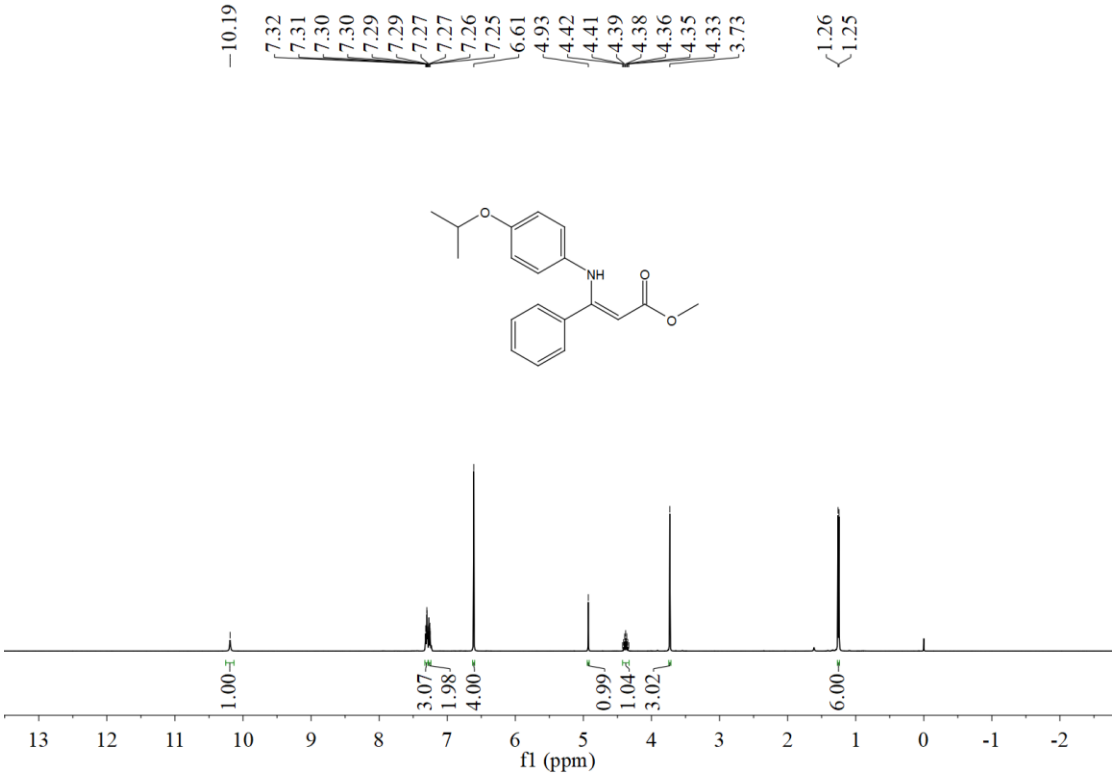


^{13}C NMR (100 MHz, $CDCl_3$)

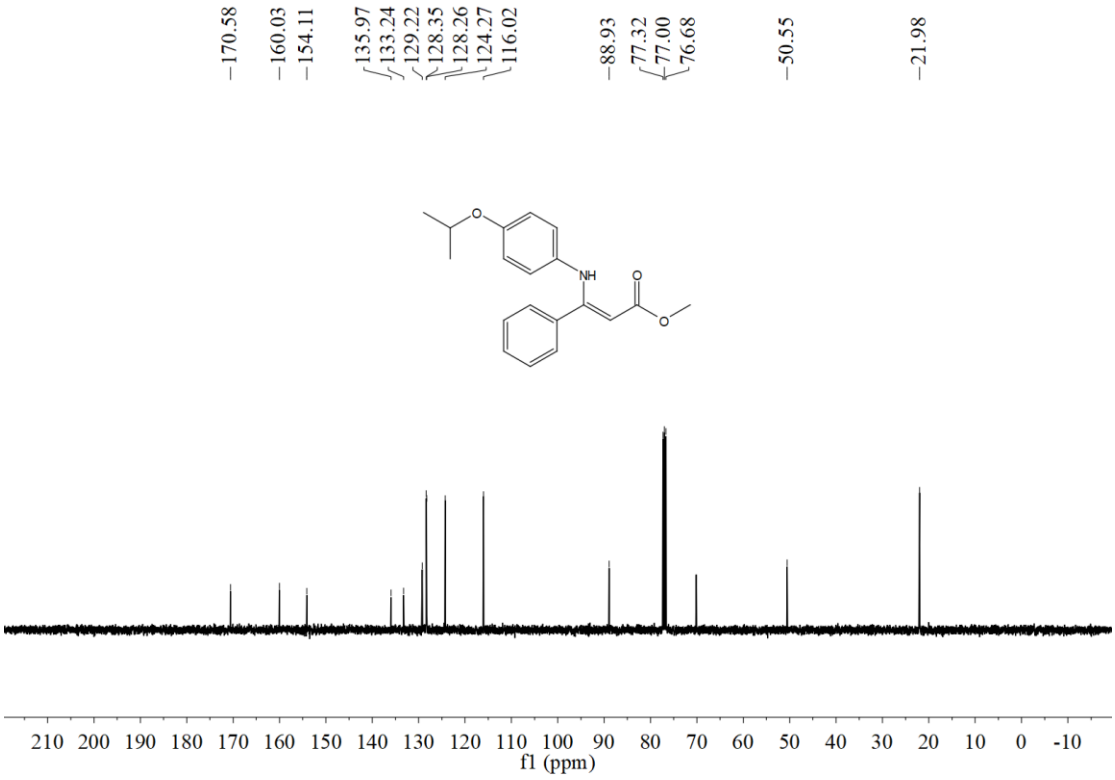


(*Z*)-4-Isopropoxy-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3j**)

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

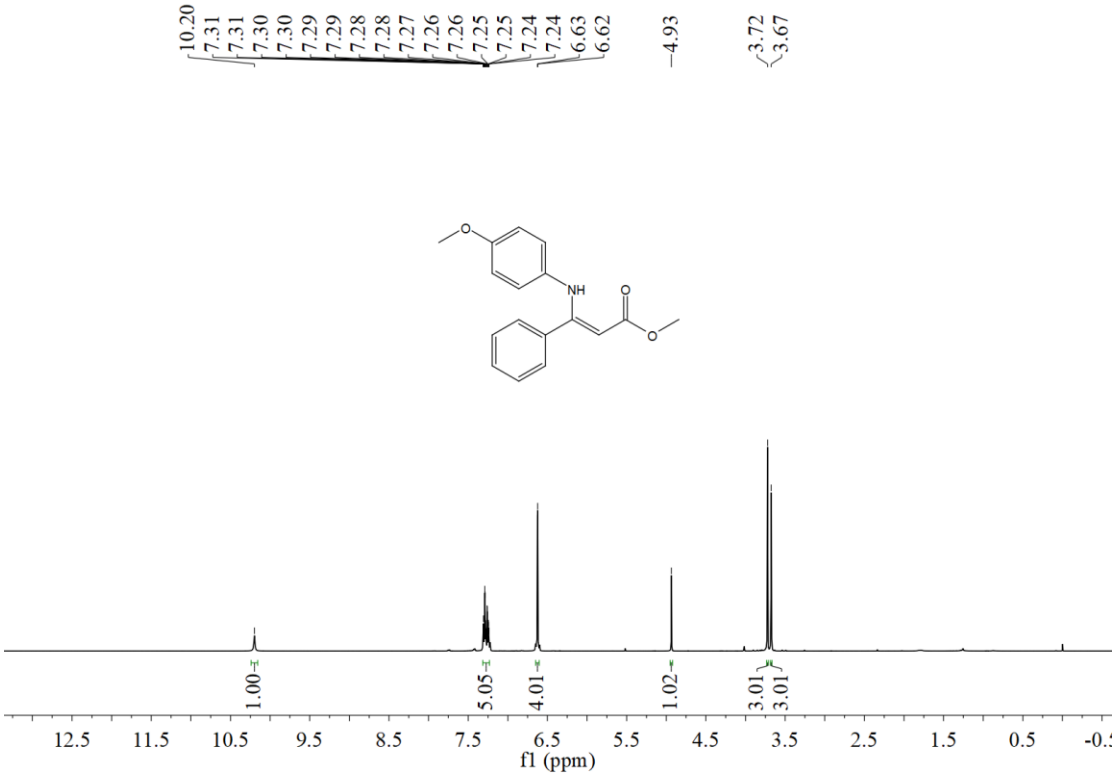


^{13}CNMR (100 MHz, $CDCl_3$)

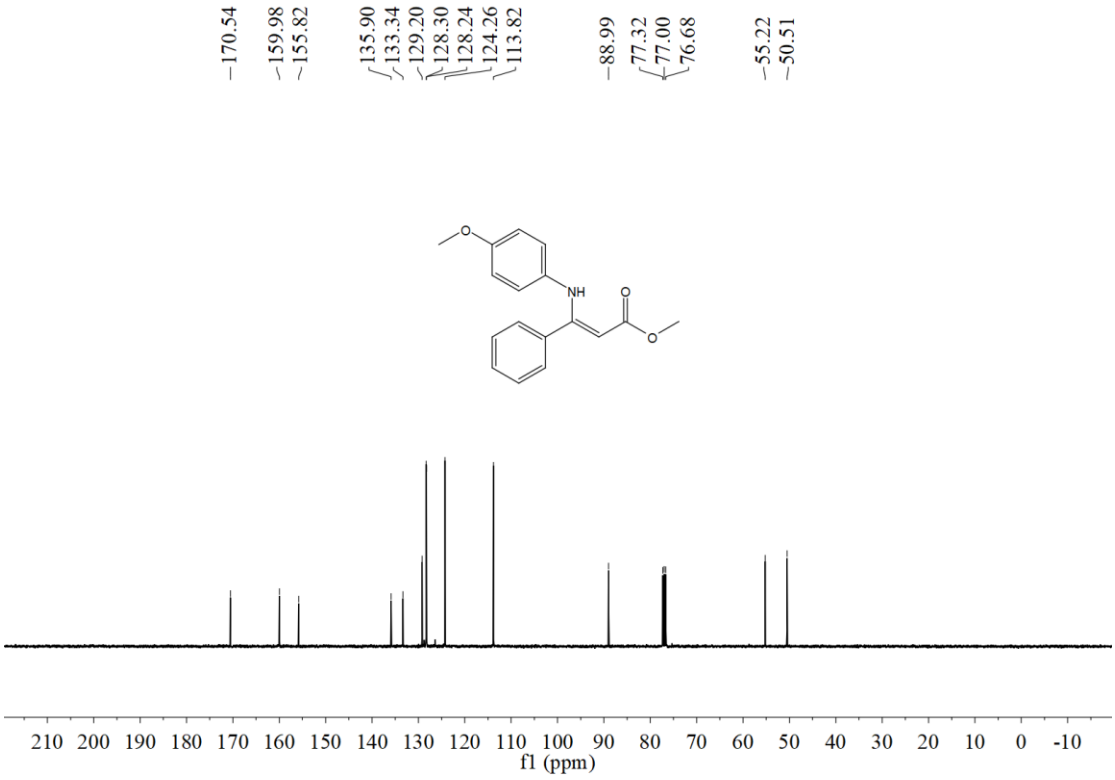


(*Z*)-4-Methoxy-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3k**)

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

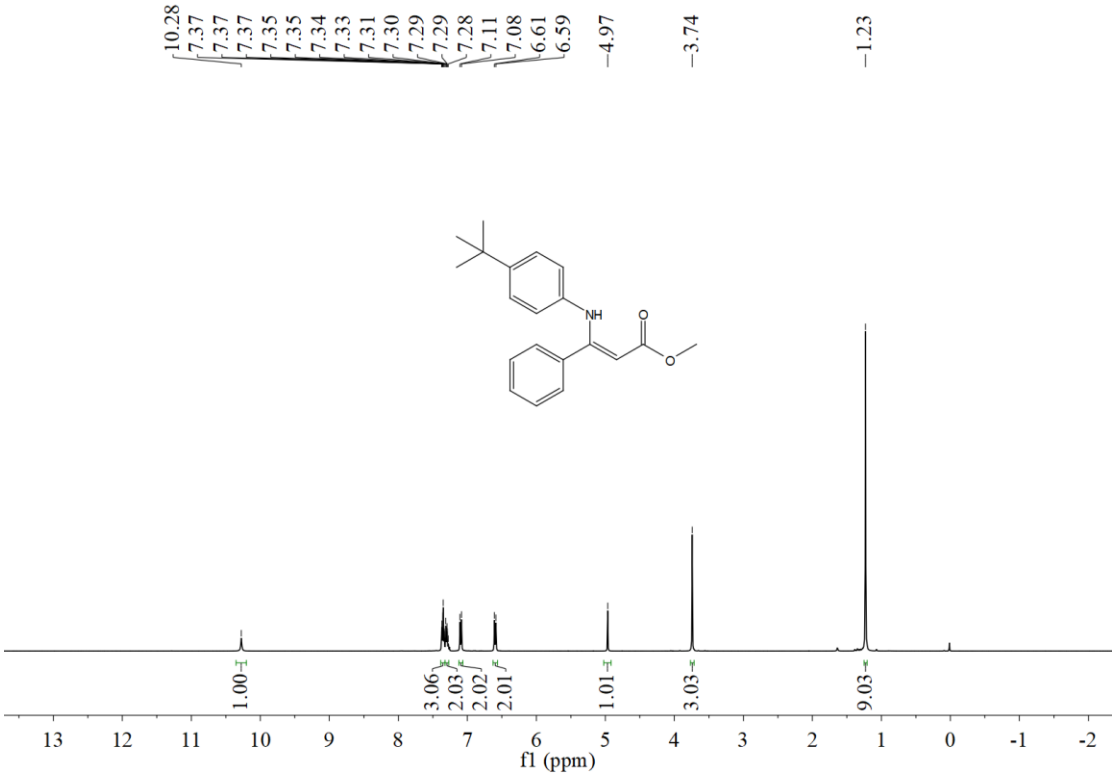


^{13}C NMR (100 MHz, $CDCl_3$)

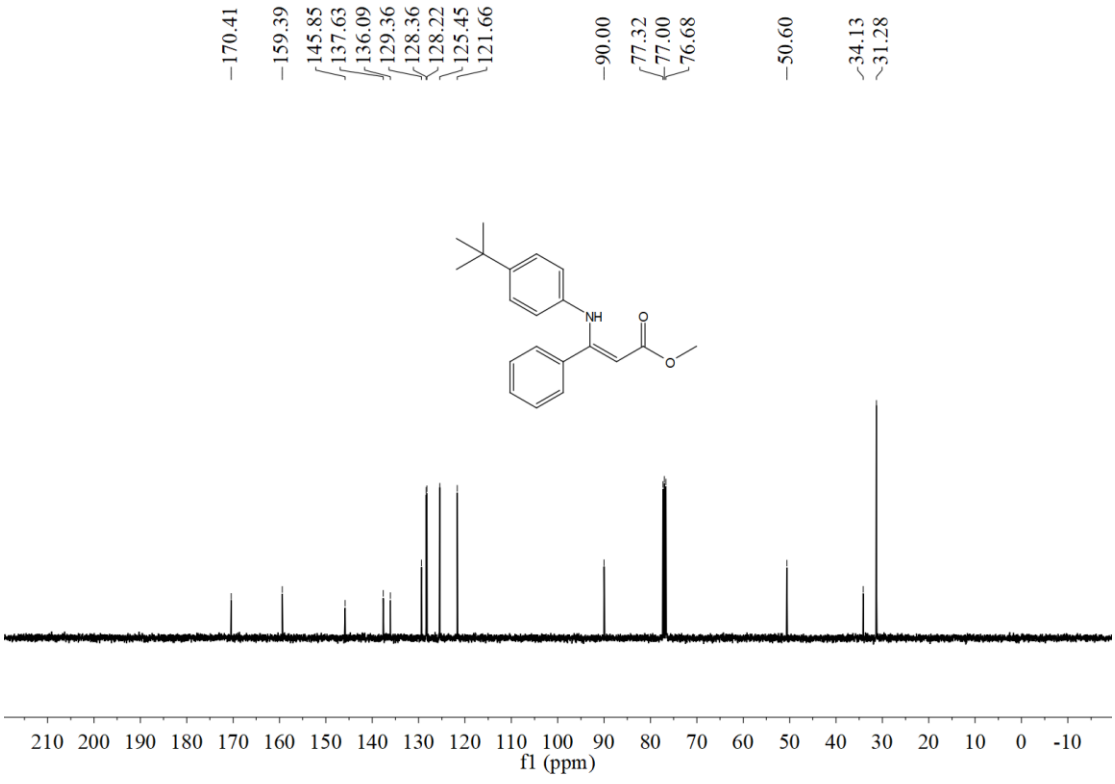


(*Z*)-4-(*tert*-Butyl)-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3l**)

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

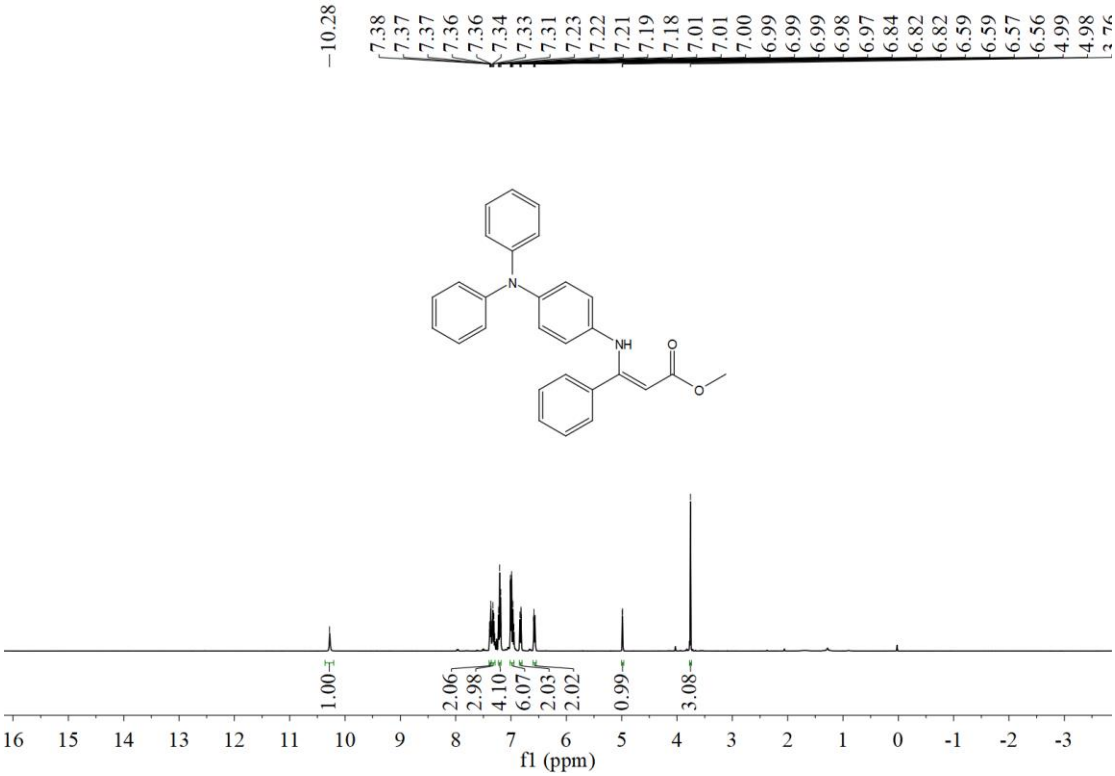


^{13}C NMR (100 MHz, $CDCl_3$)

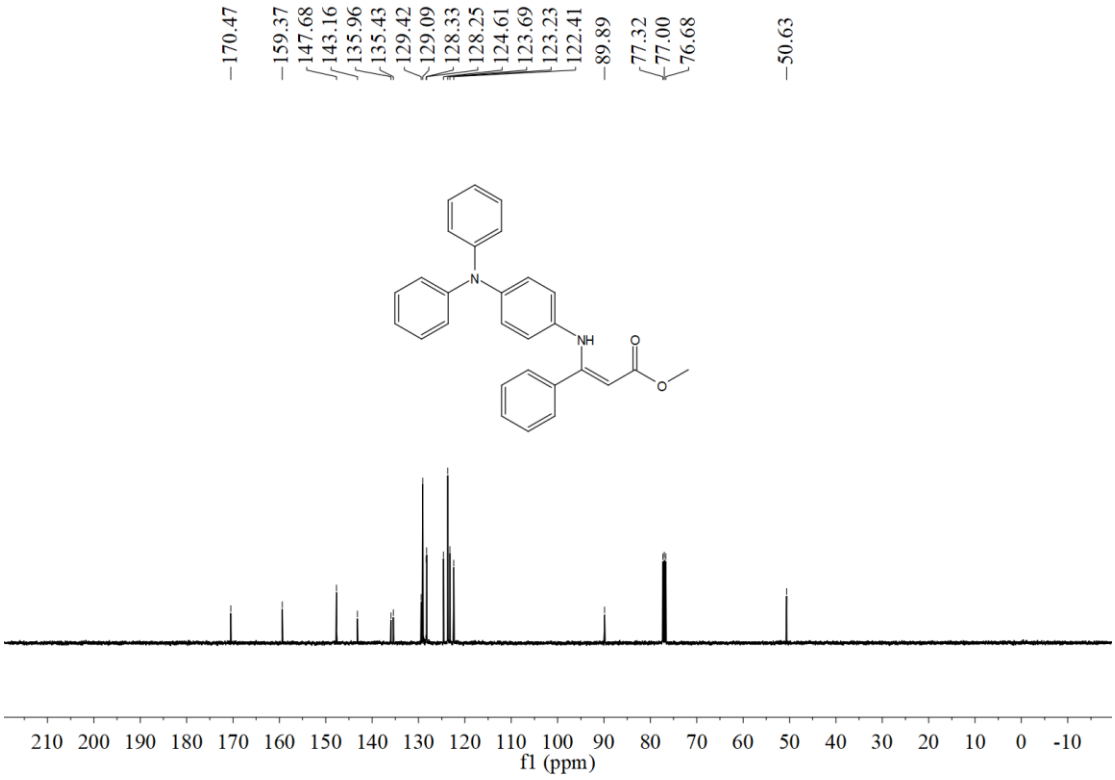


(*Z*)-4-(Diphenylamino)-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3m**)

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

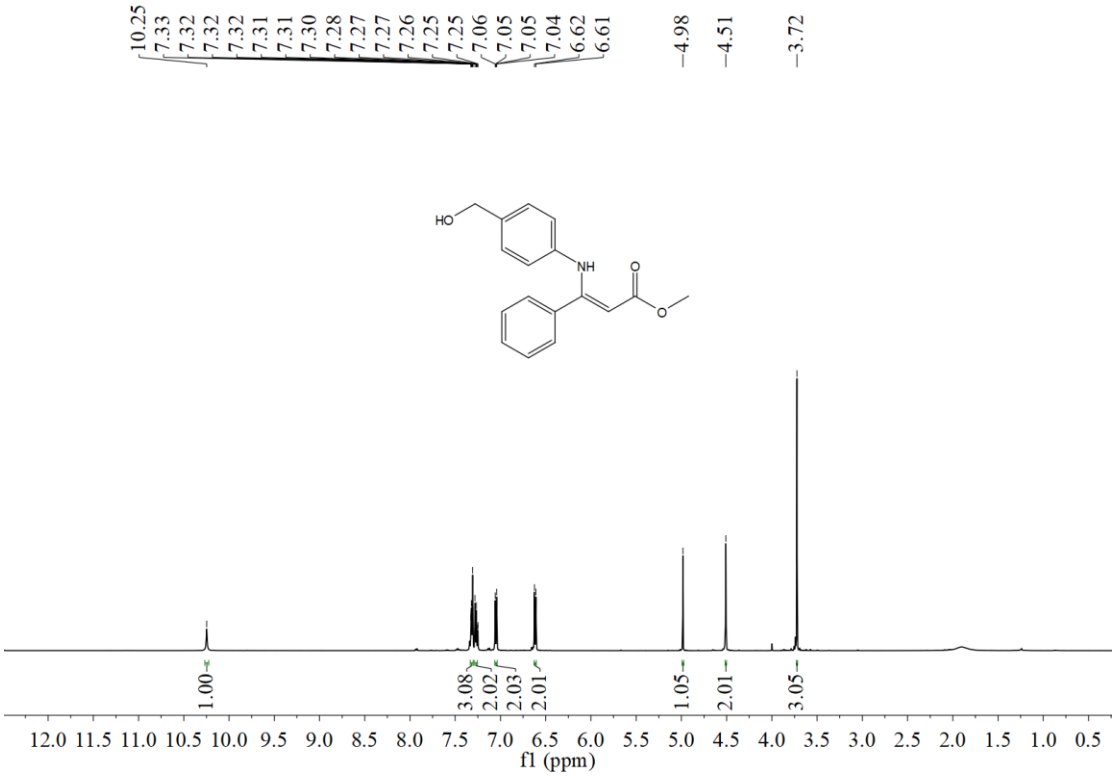


^{13}C NMR (100 MHz, $CDCl_3$)

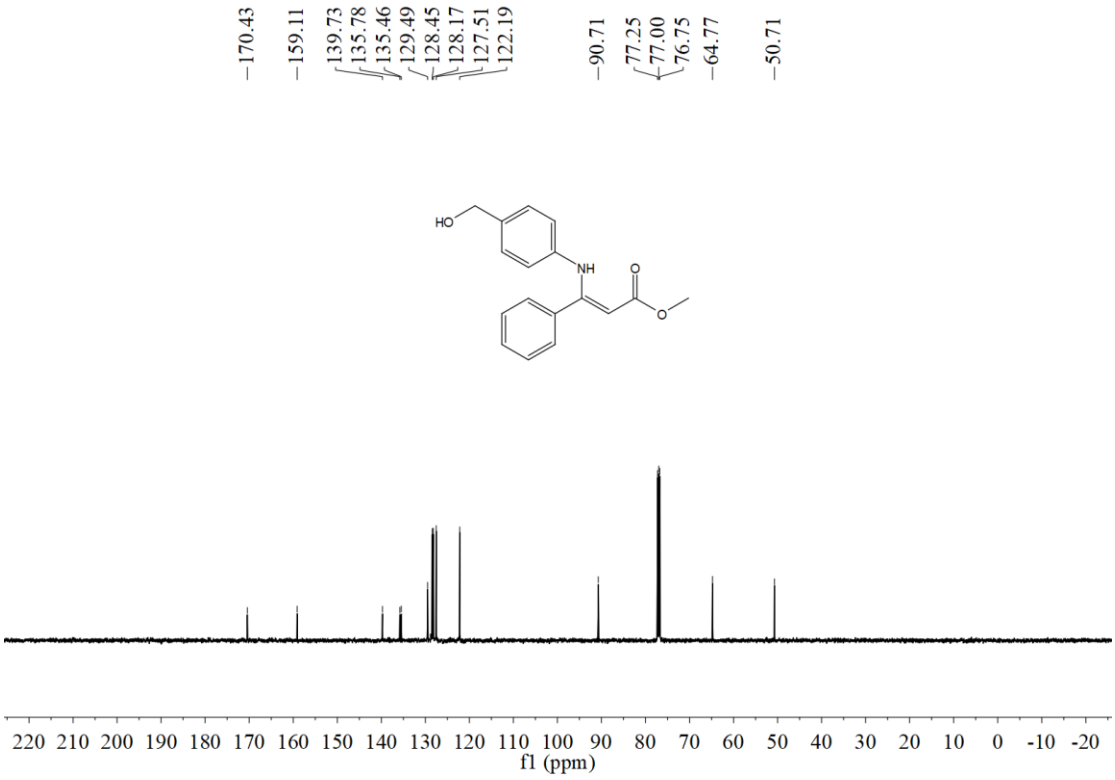


(*Z*)-4-(Hydroxymethyl)-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3n**)

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

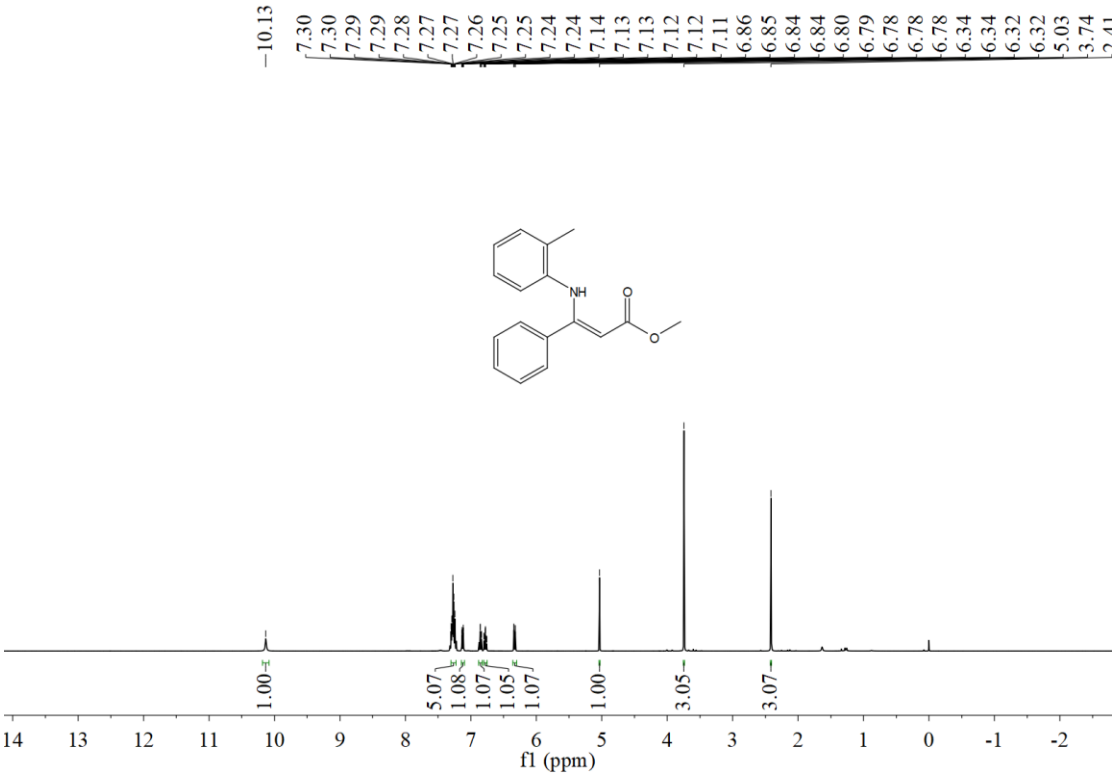


^{13}C NMR (100 MHz, $CDCl_3$)

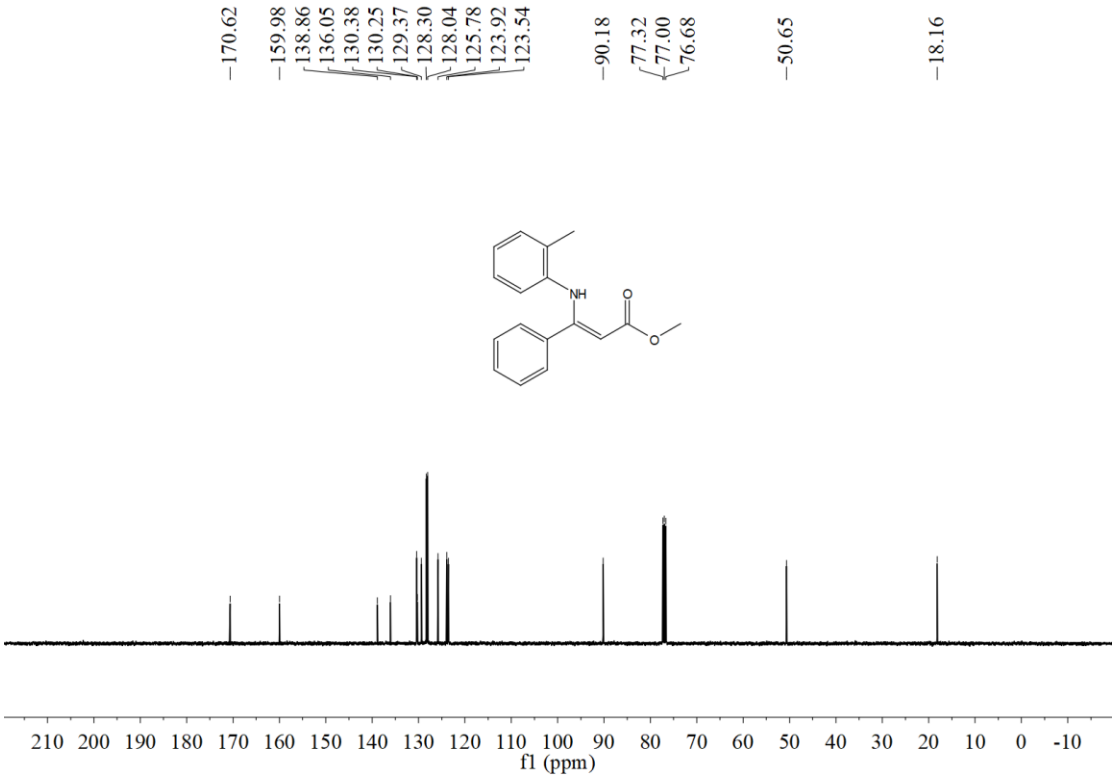


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-2-methylbenzenaminium (**3o**)

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

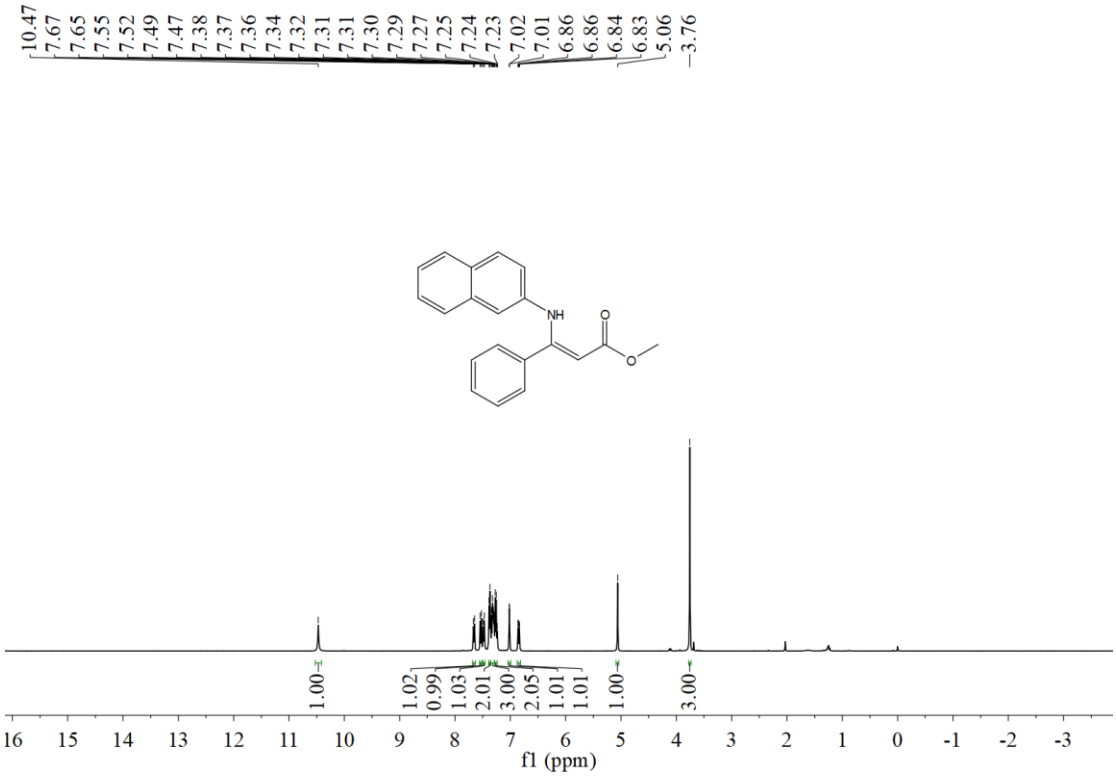


^{13}CNMR (100 MHz, $CDCl_3$)

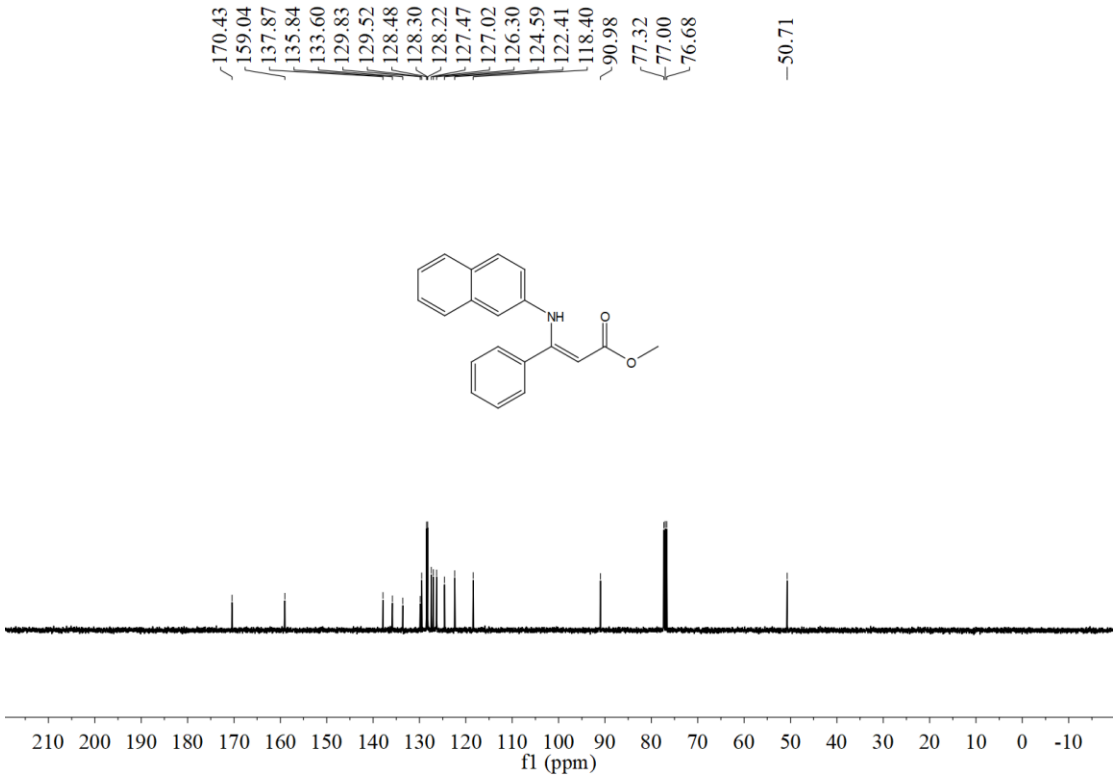


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)naphthalen-2-aminium (**3p**)

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

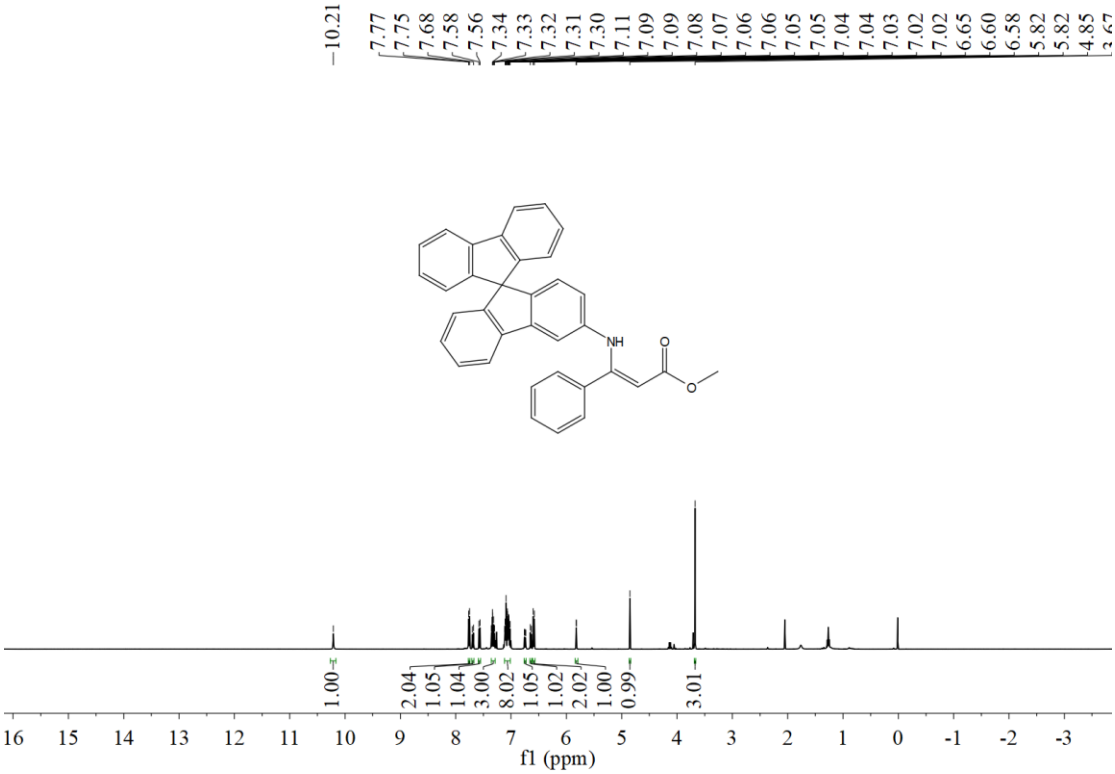


^{13}C NMR (100 MHz, $CDCl_3$)

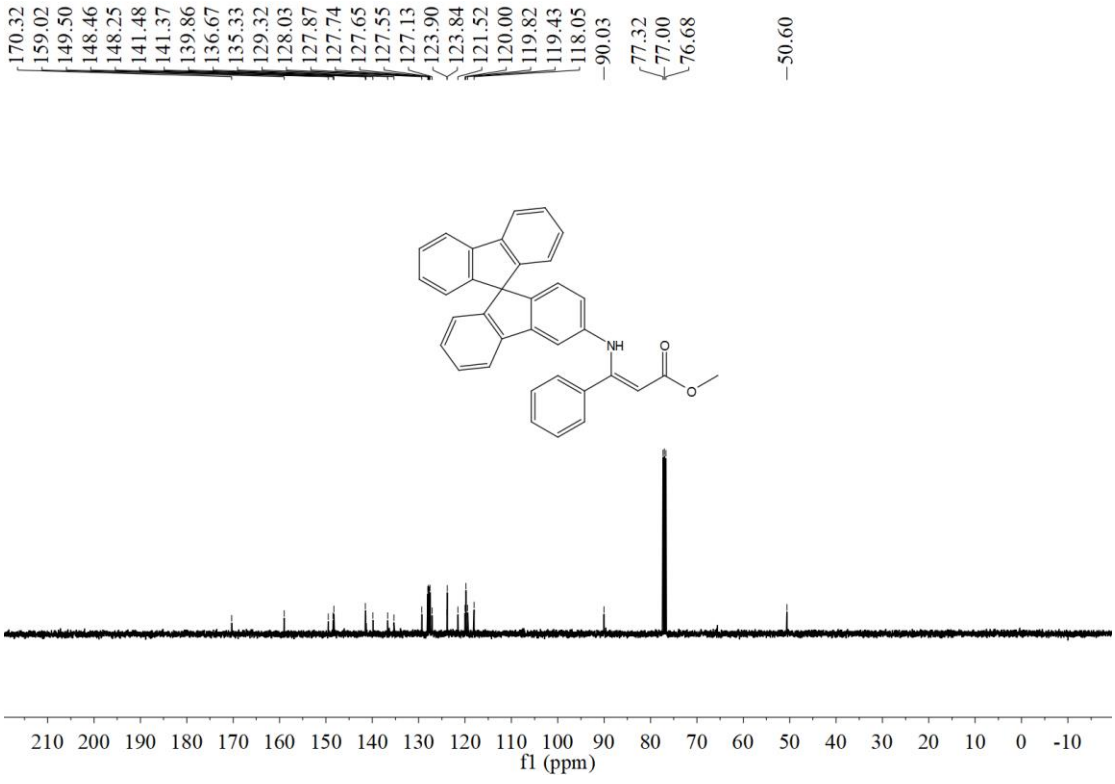


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-9,9'-spirobi[fluoren]-3-aminium (**3q**)

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

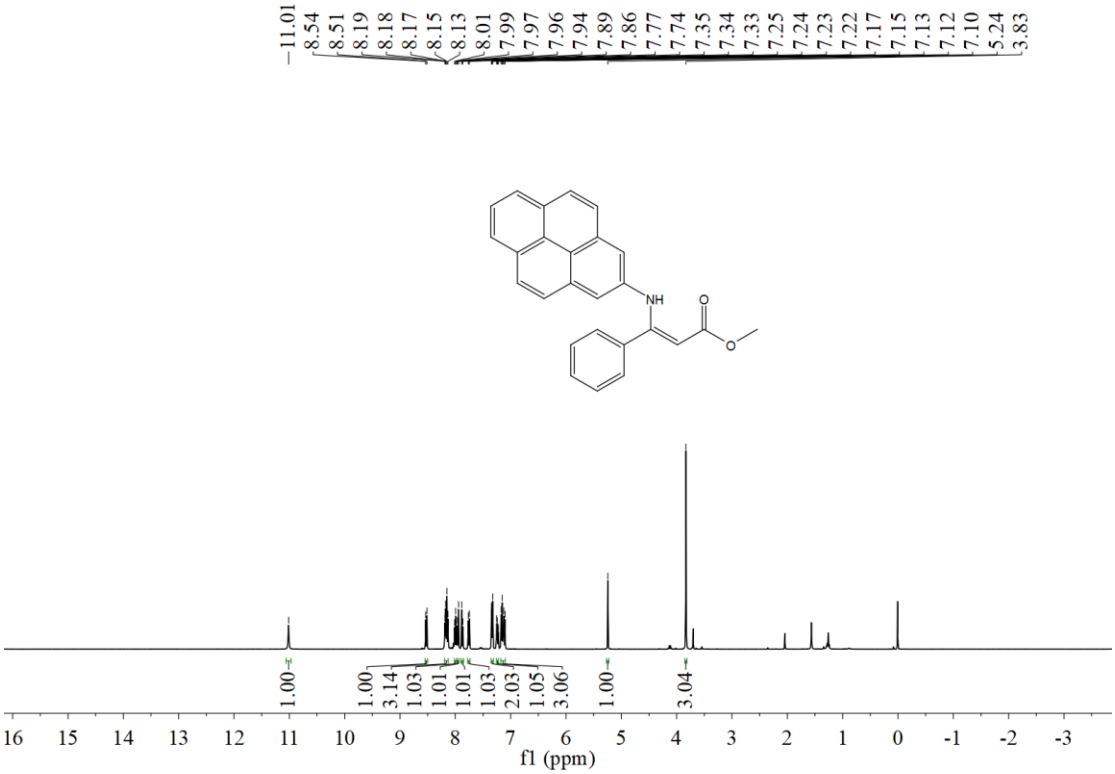


^{13}C NMR (100 MHz, $CDCl_3$)

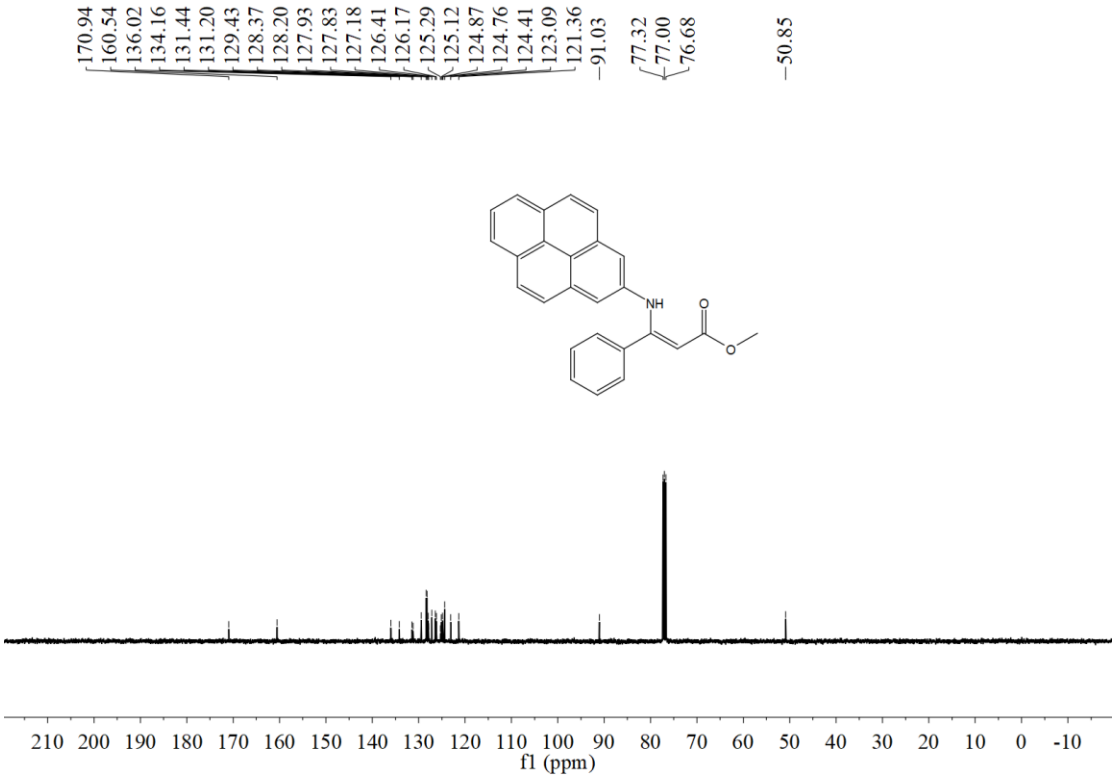


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)pyren-1-aminium (**3r**)

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

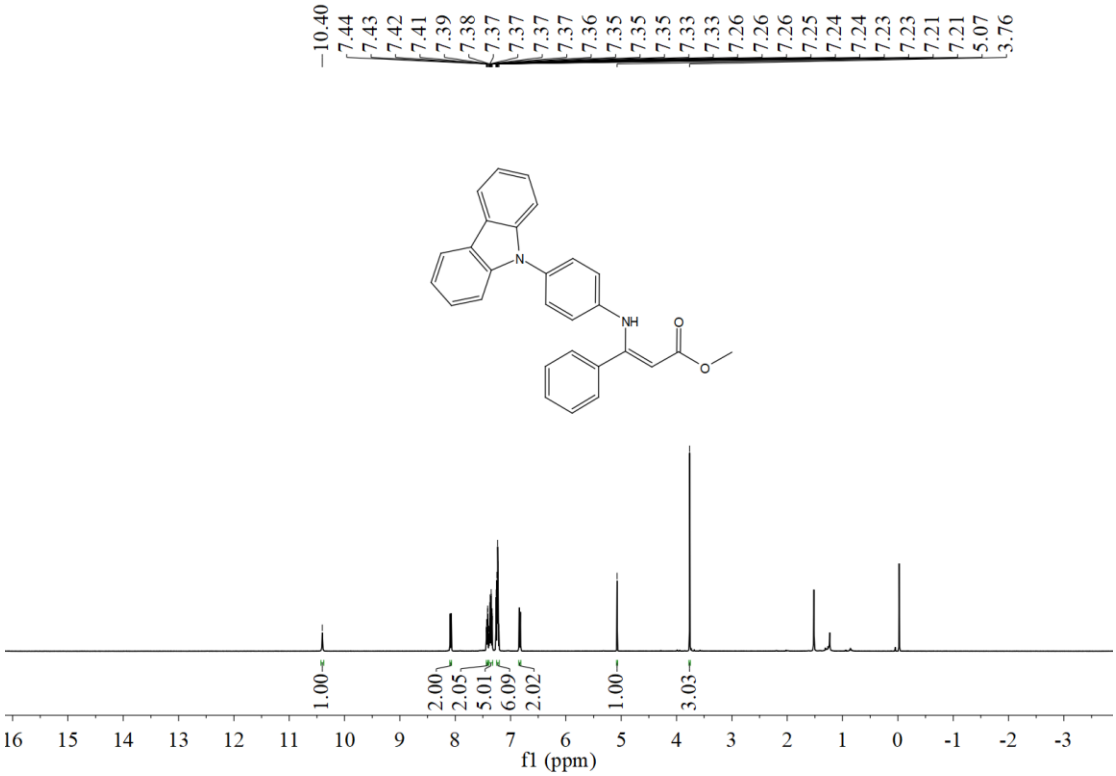


^{13}C NMR (100 MHz, $CDCl_3$)

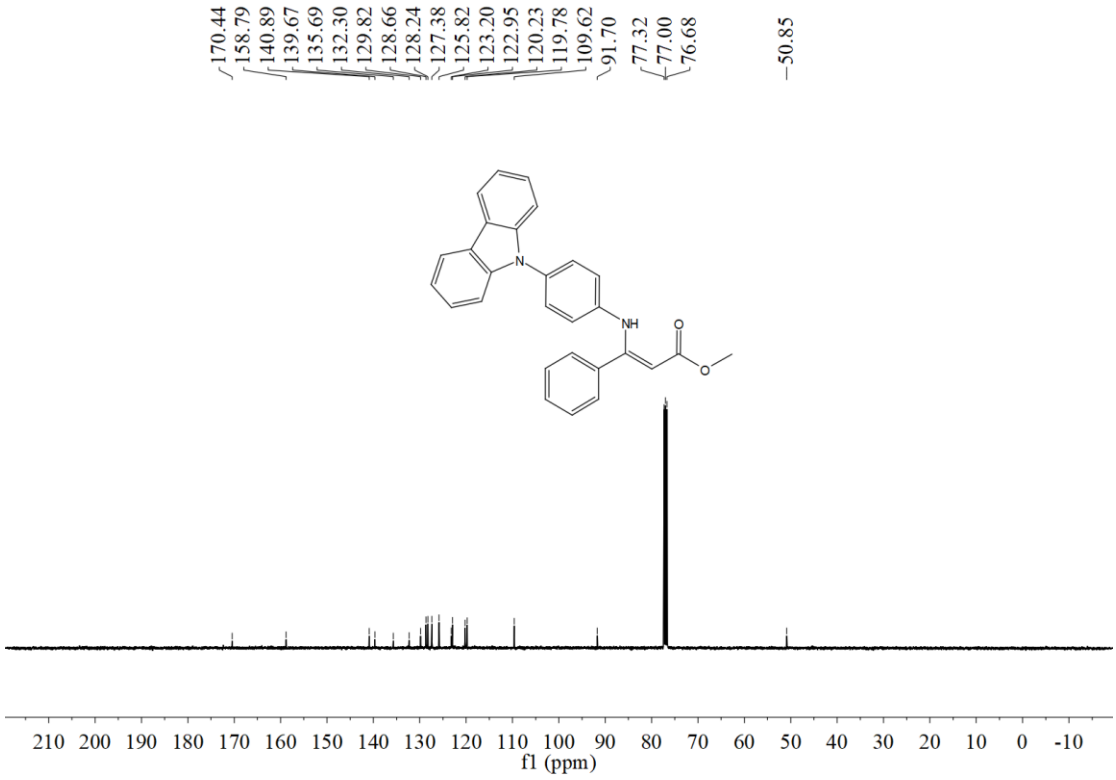


(*Z*)-4-(9H-Carbazol-9-yl)-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzenaminium (**3s**)

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

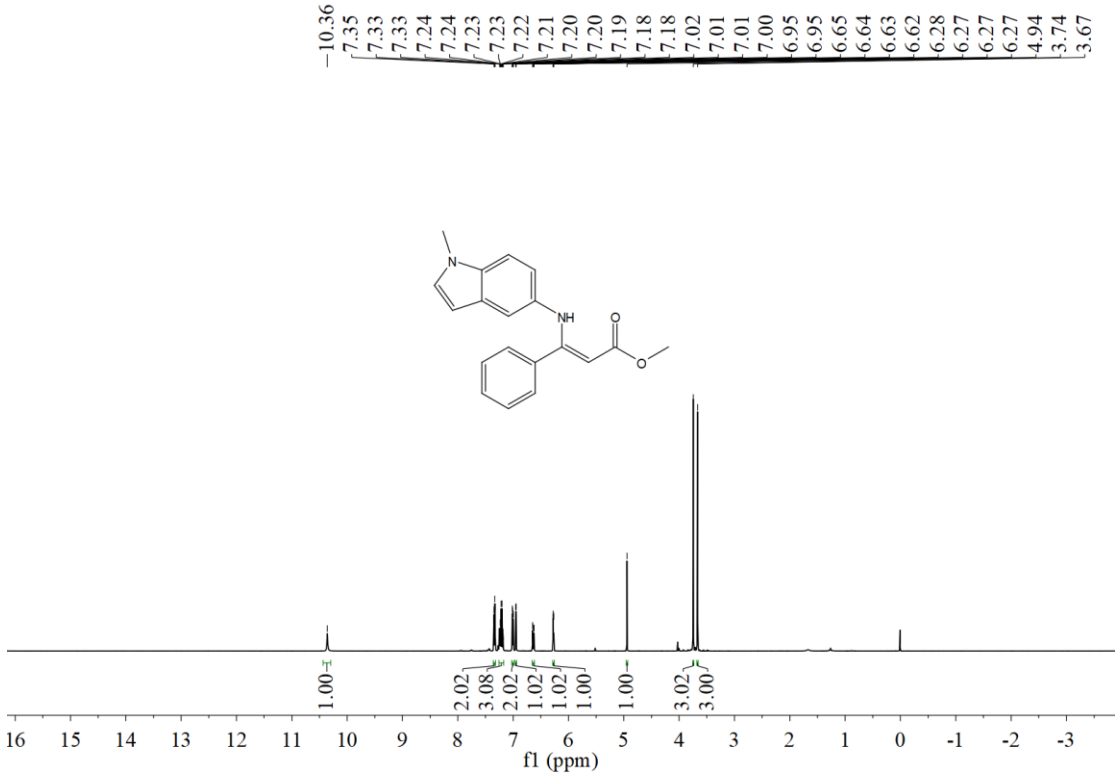


^{13}CNMR (100 MHz, $CDCl_3$)

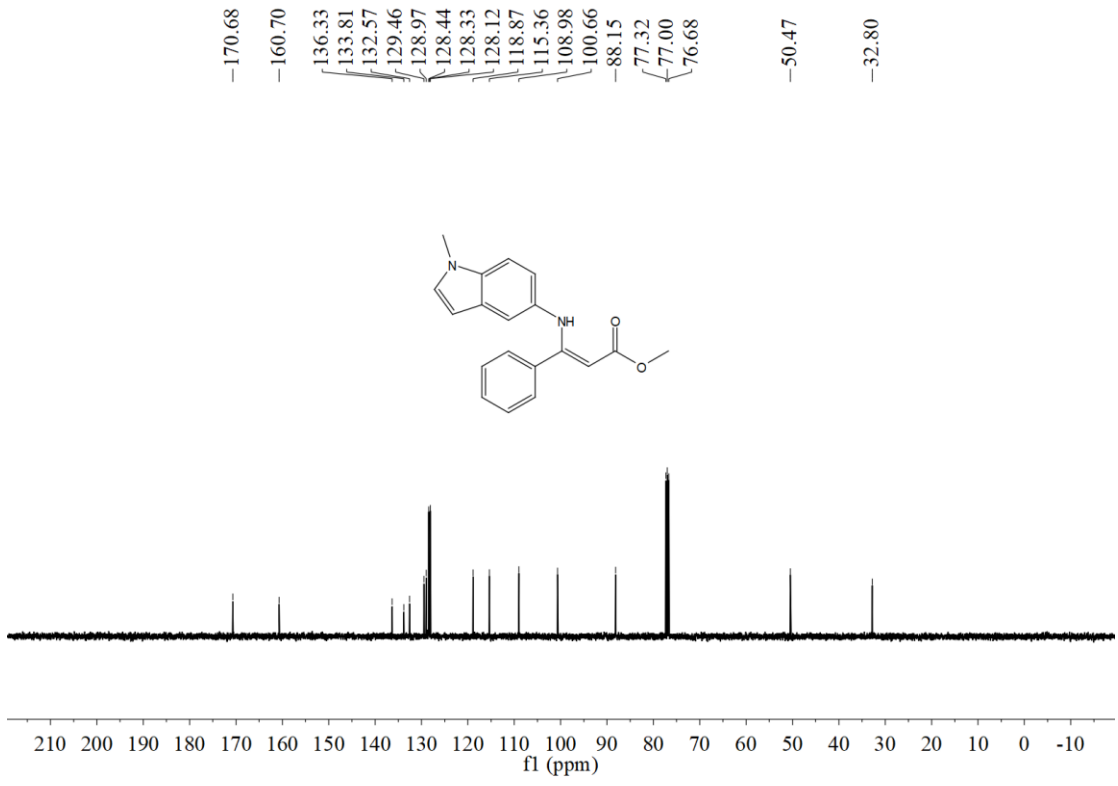


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)-1-methyl-1H-indol-5-aminium (**3t**)

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

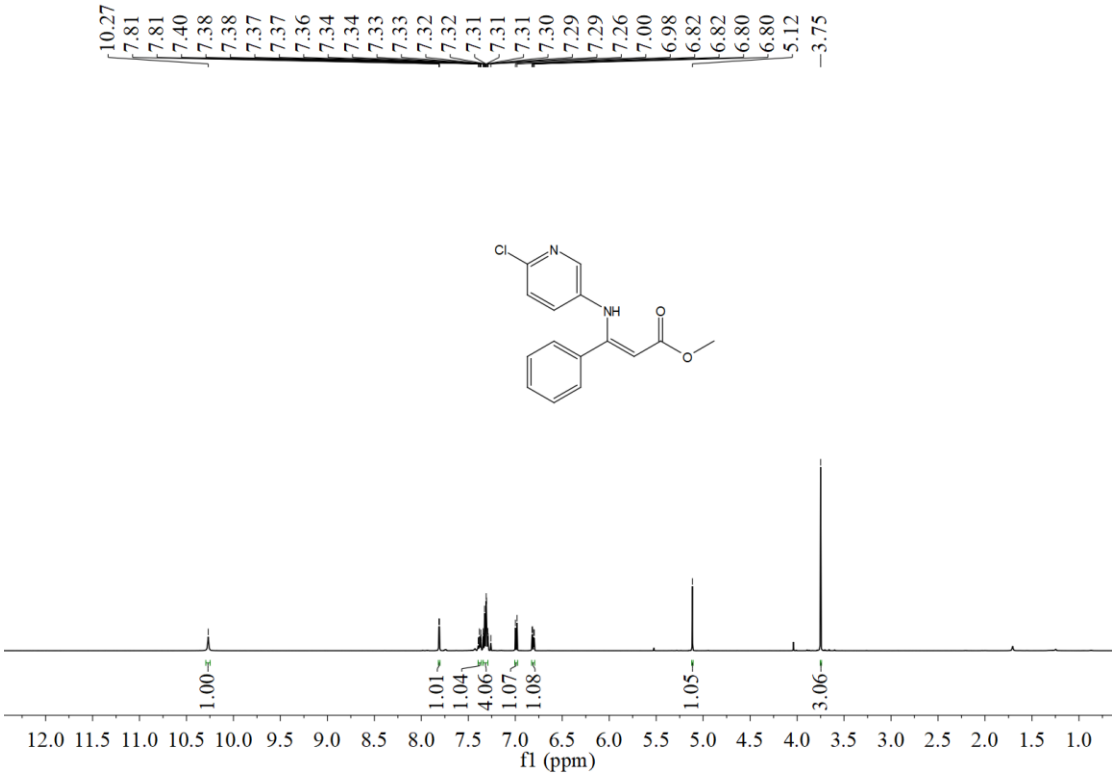


^{13}C NMR (100 MHz, $CDCl_3$)

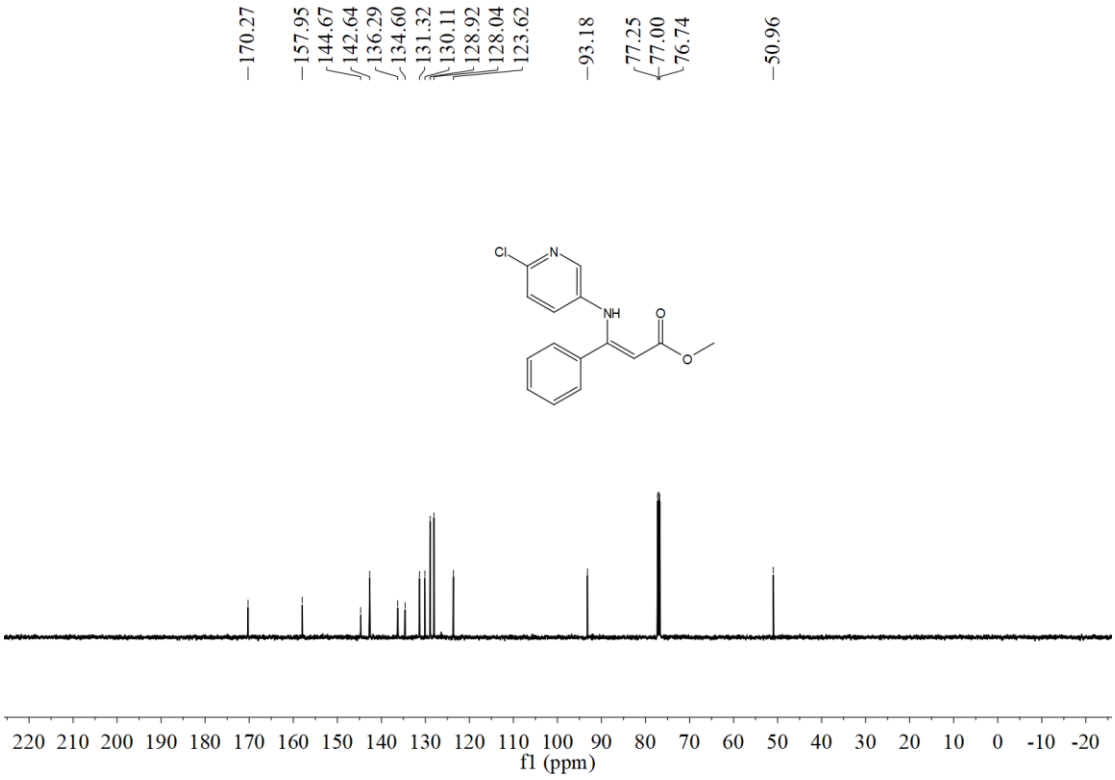


(*Z*)-6-Chloro-*N*-(3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)pyridin-3-aminium (**3u**)

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

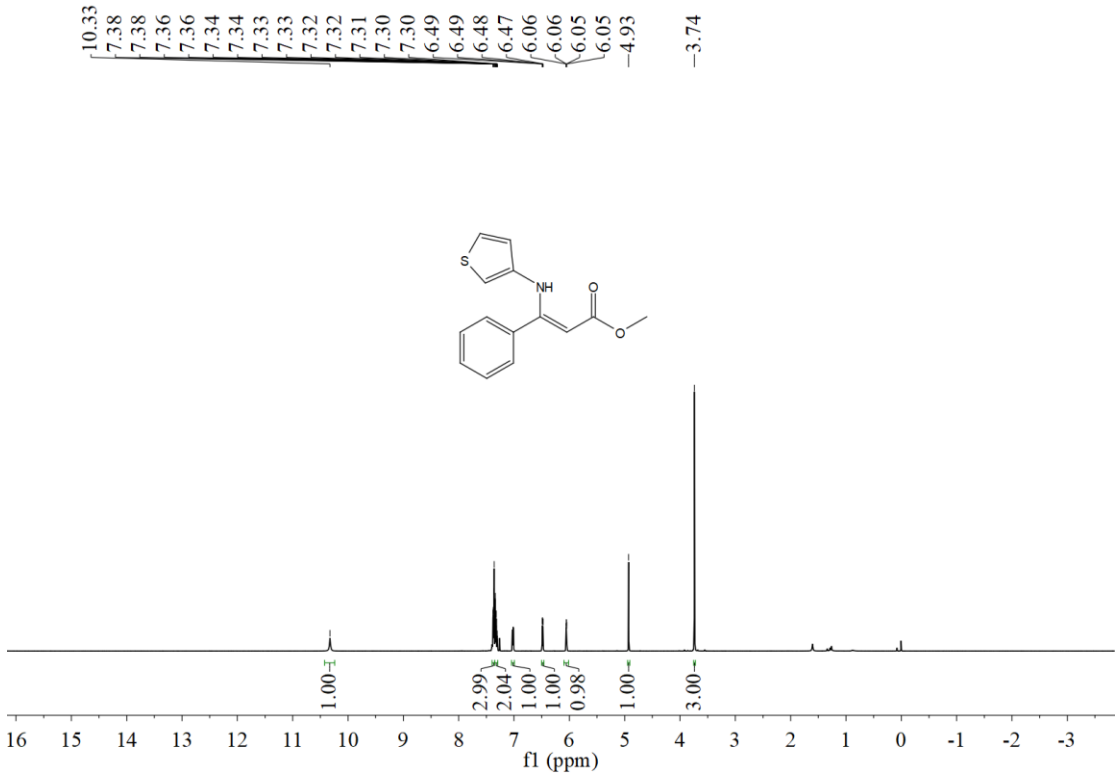


^{13}C NMR (100 MHz, $CDCl_3$)

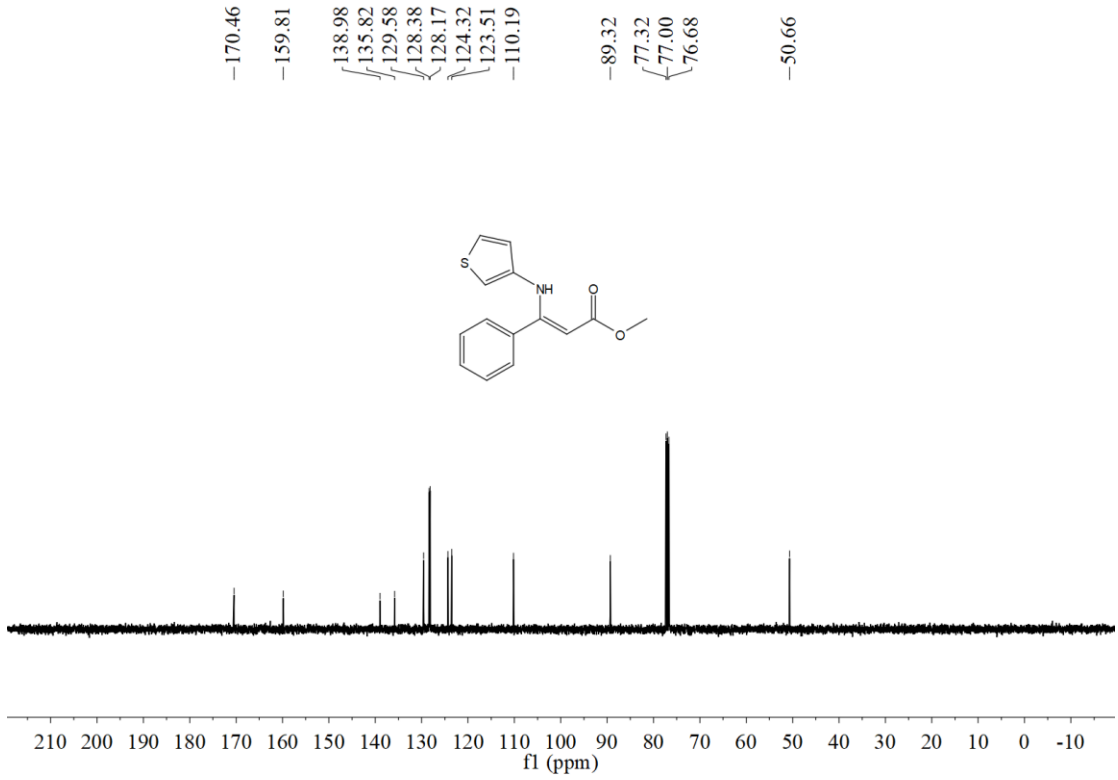


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)thiophen-3-aminium (**3v**)

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

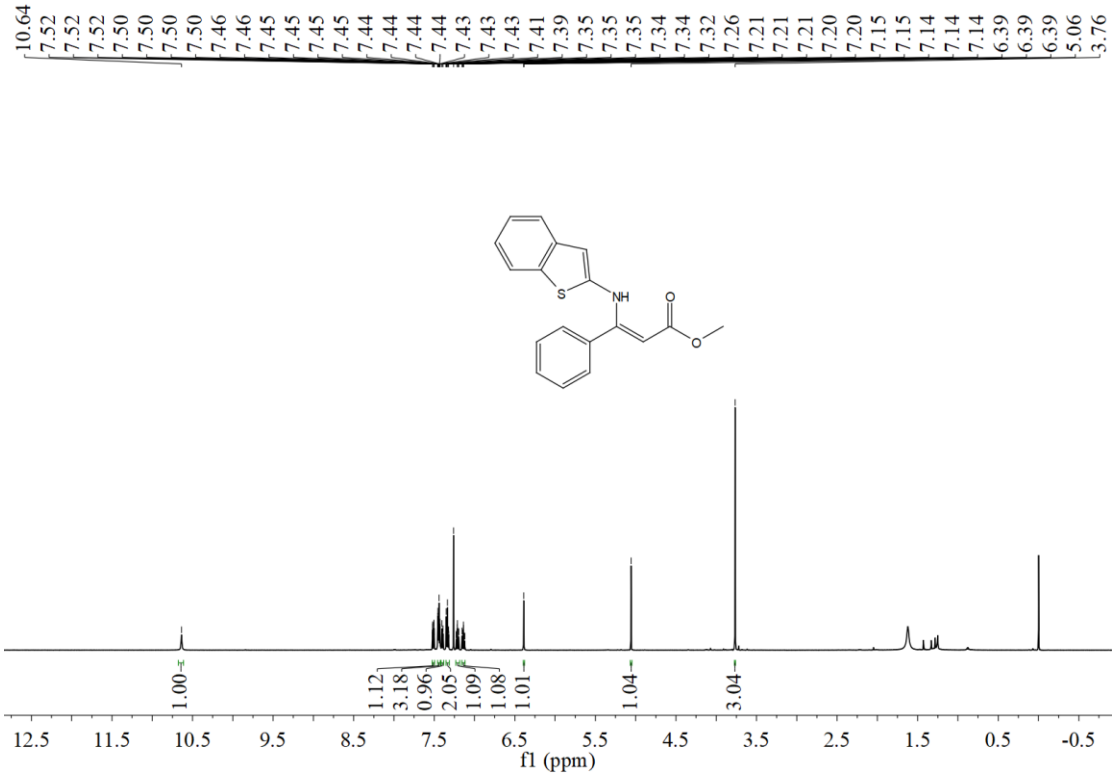


^{13}C NMR (100 MHz, $CDCl_3$)

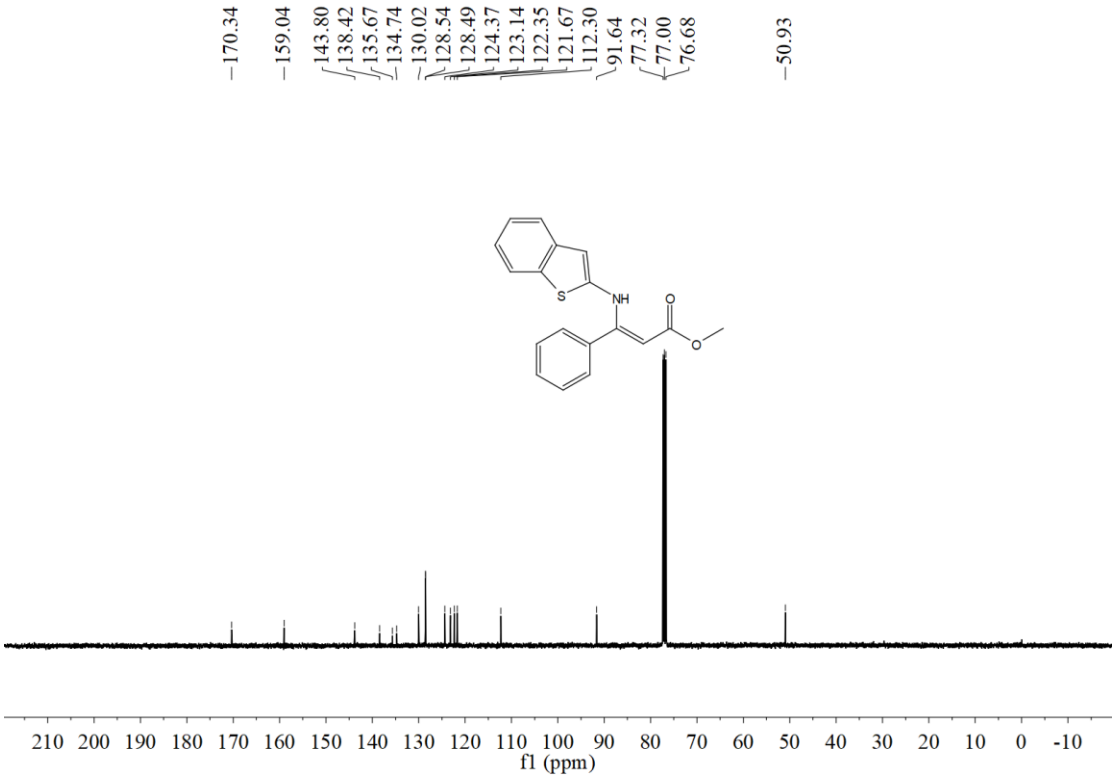


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)benzo[b]thiophen-2-aminium (**3w**)

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

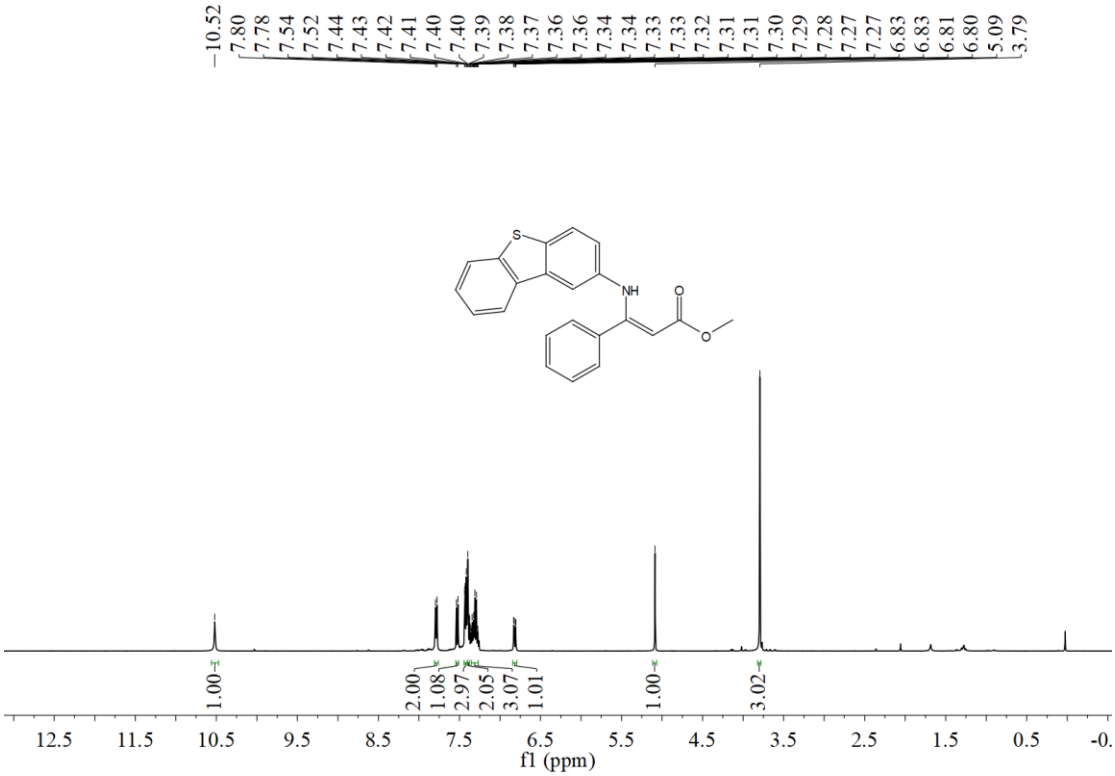


^{13}C NMR (100 MHz, $CDCl_3$)

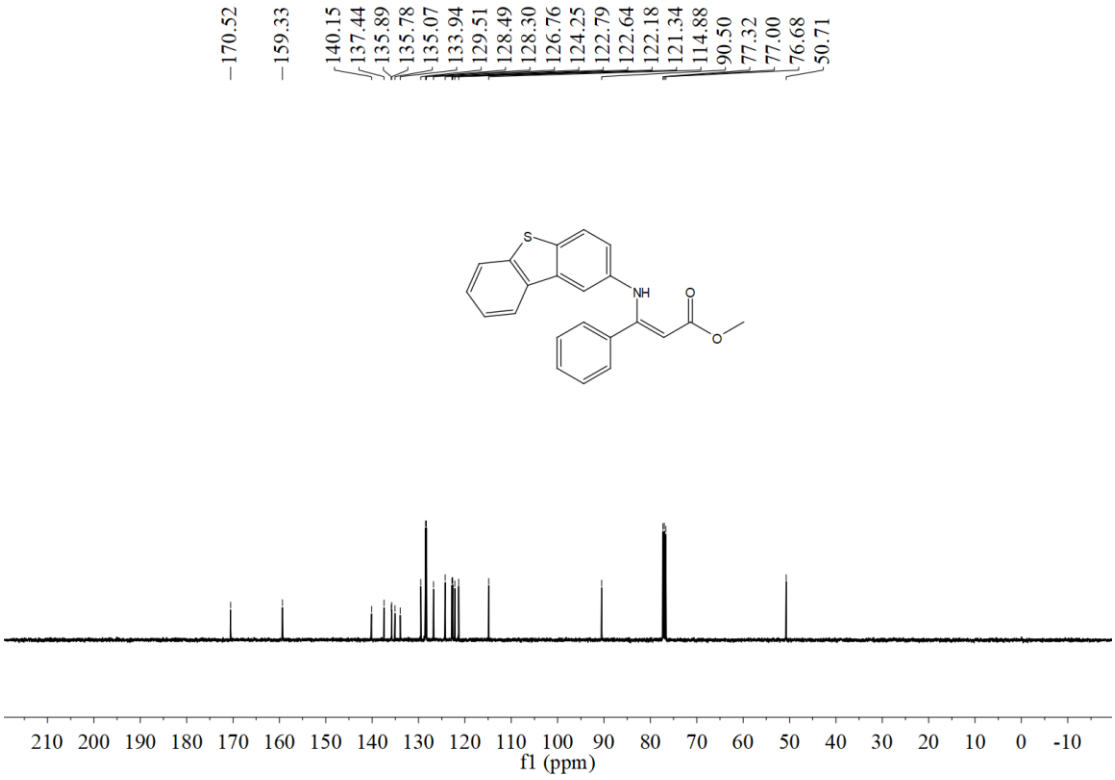


(*Z*)-*N*-(3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl)dibenzo[b,d]thiophen-2-aminium (**3x**)

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

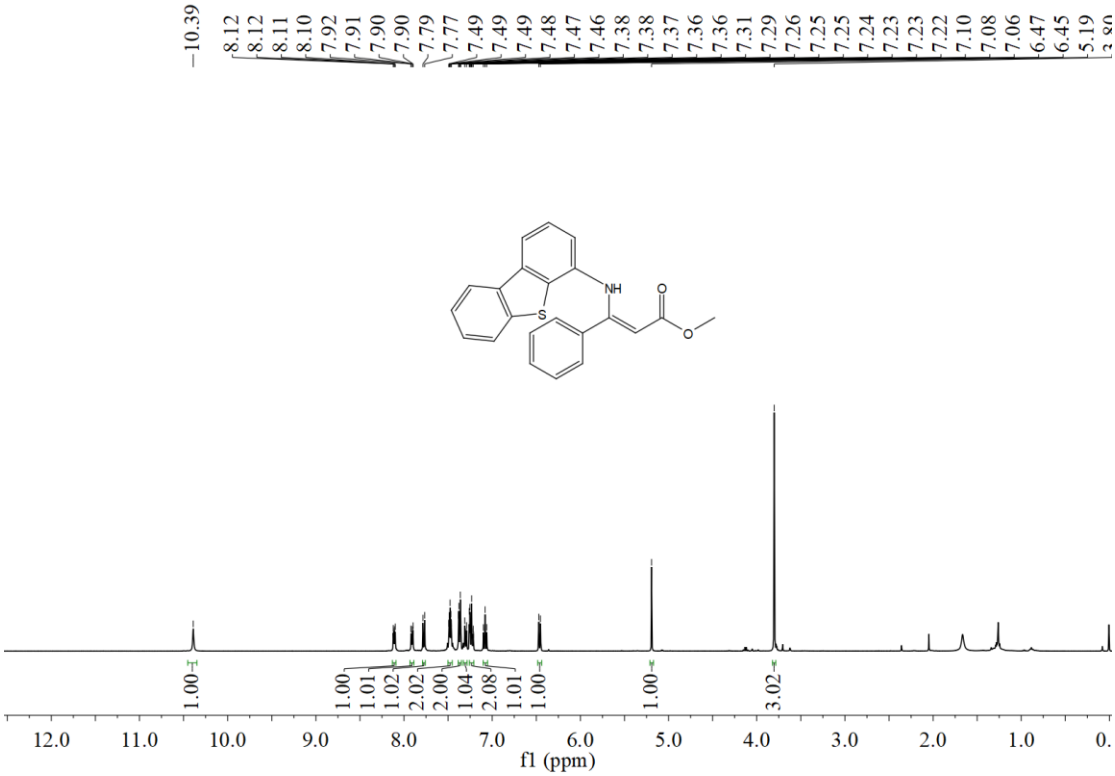


^{13}C NMR (100 MHz, $CDCl_3$)

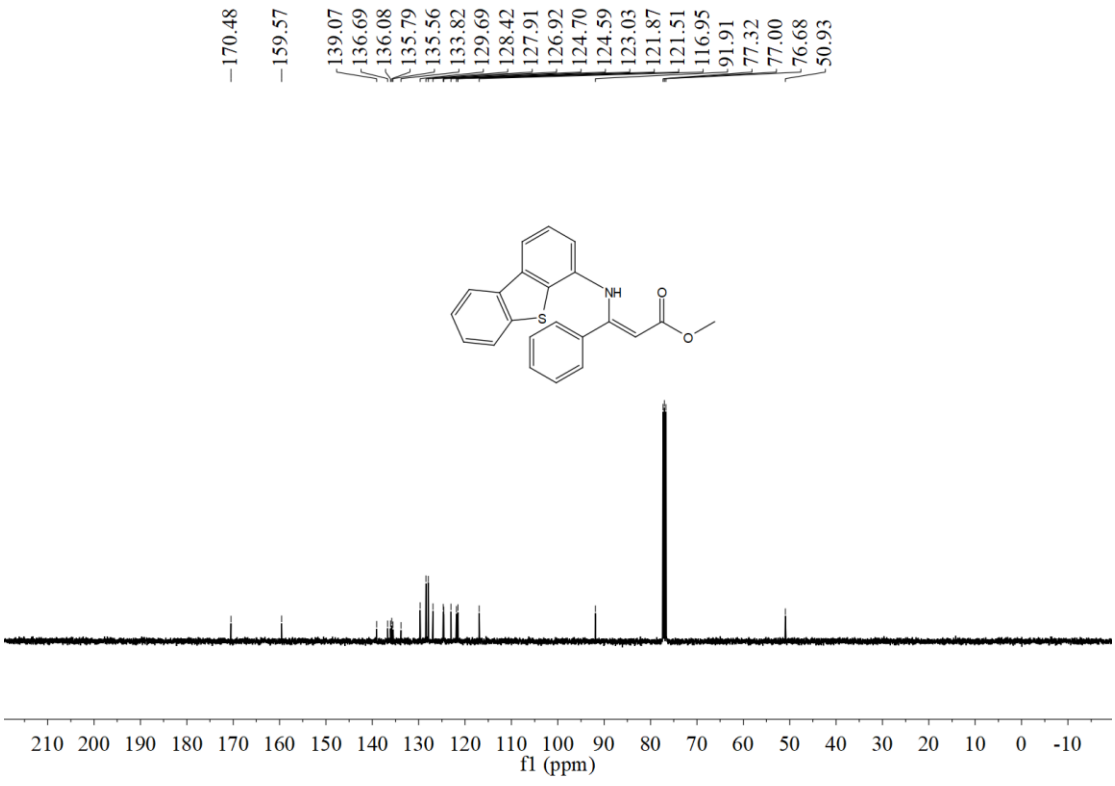


Methyl (*Z*)-3-(dibenzo[b,d]thiophen-4-ylamino)-3-phenylacrylate (**3y**)

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

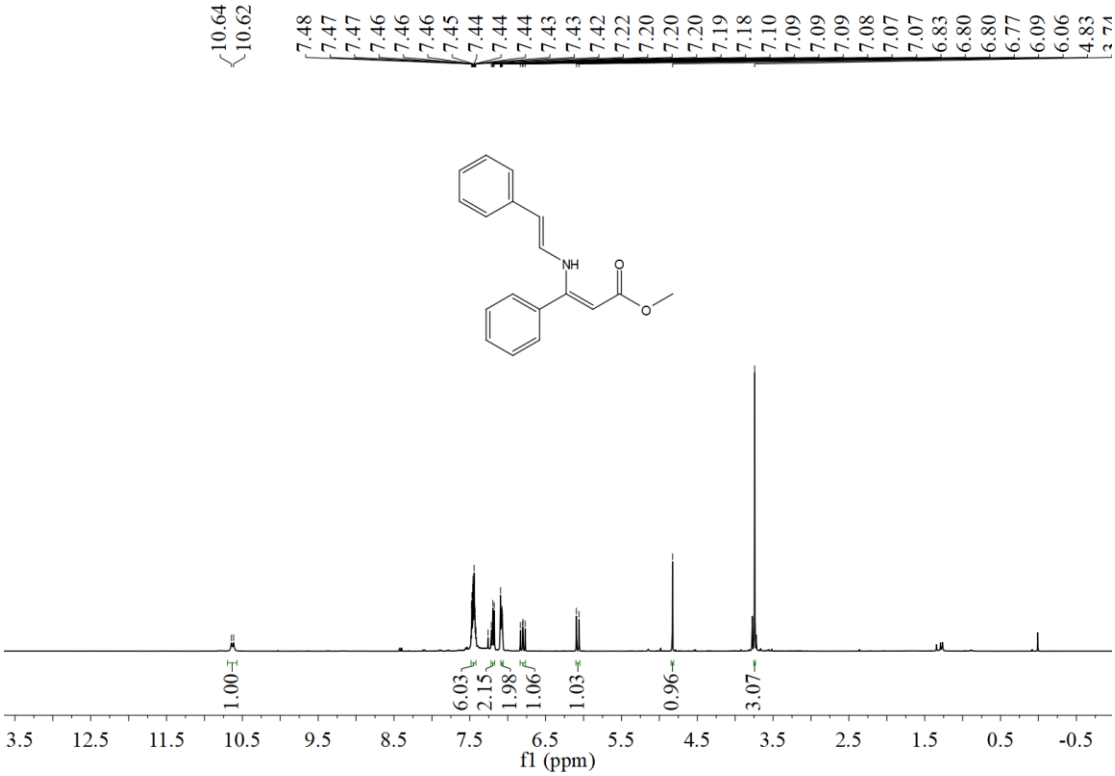


^{13}C NMR (100 MHz, $CDCl_3$)

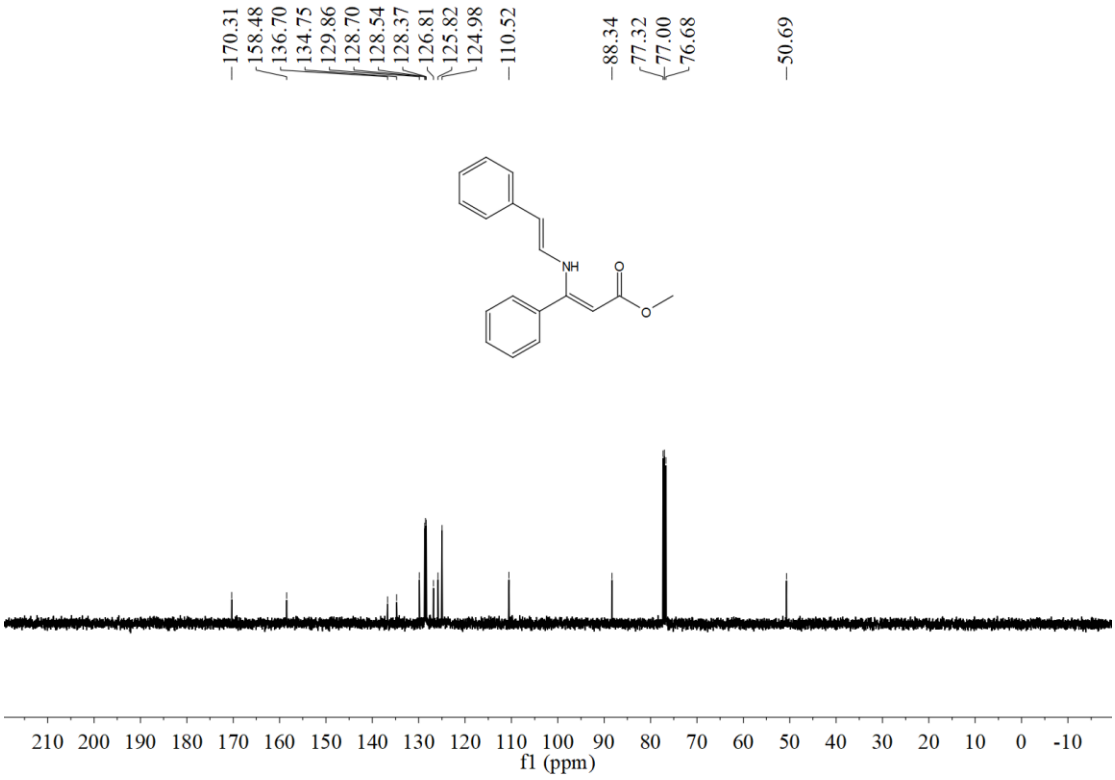


(*Z*)-3-Methoxy-3-oxo-1-phenyl-N-((E)-styryl)prop-1-en-1-aminium (**3z**)

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

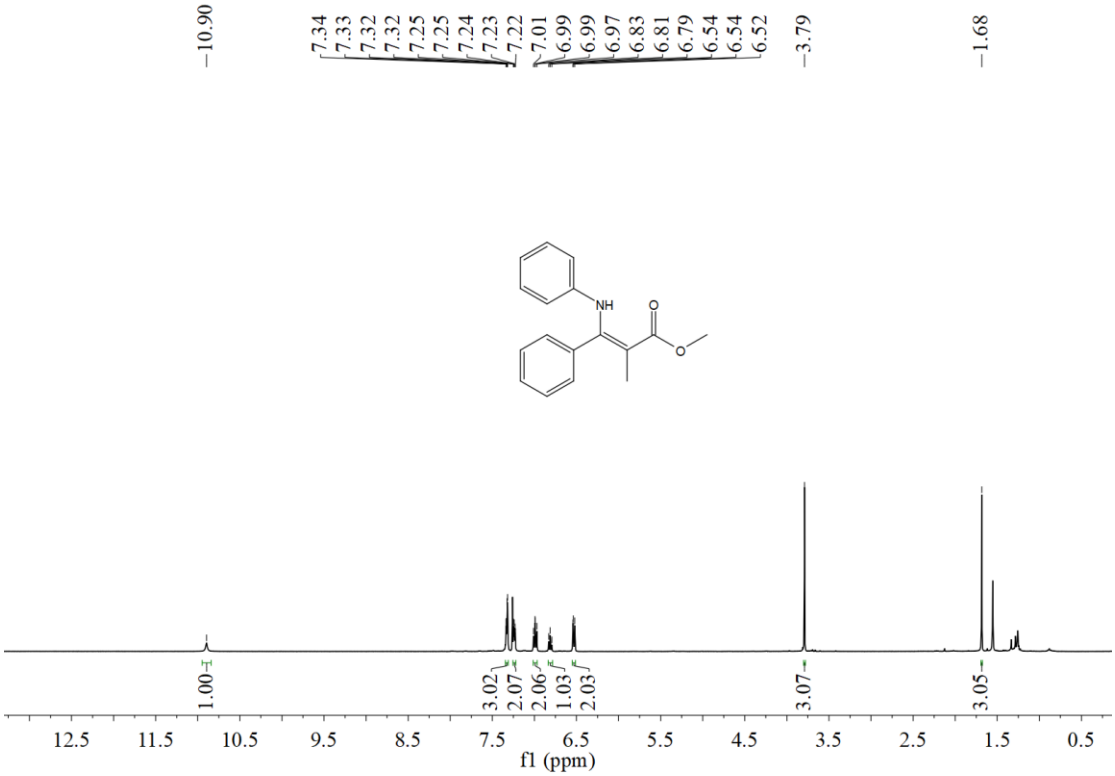


^{13}C NMR (100 MHz, $CDCl_3$)

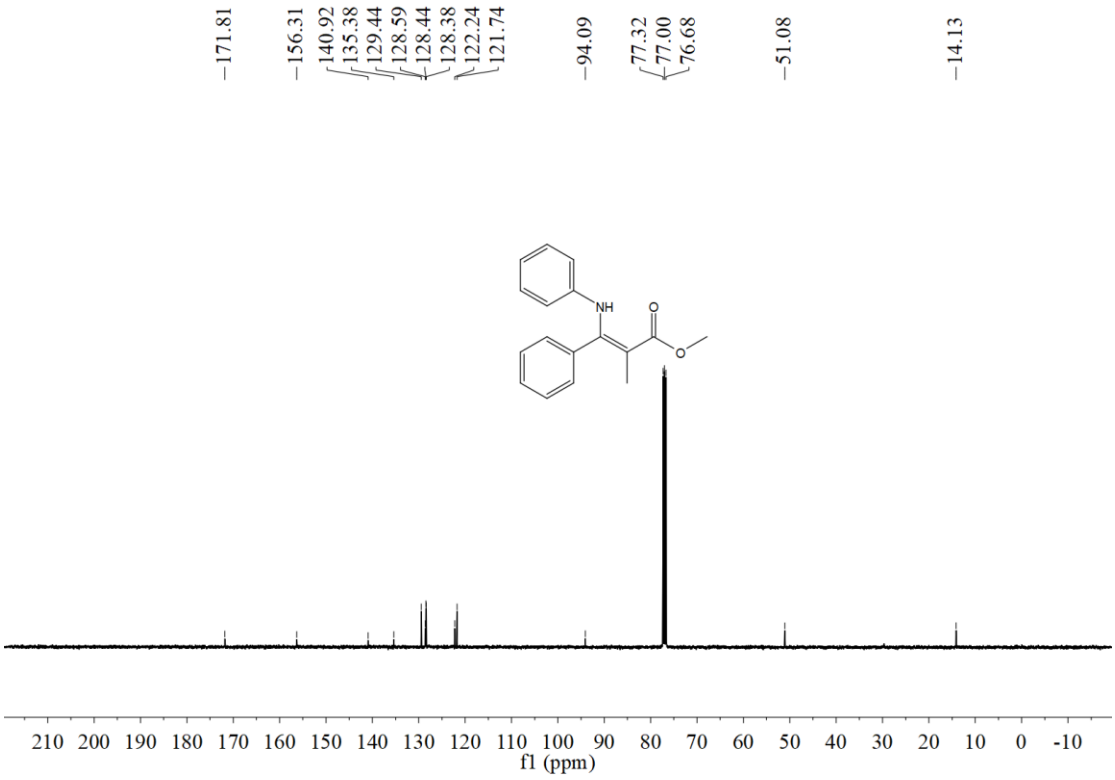


Methyl (*Z*)-2-methyl-3-phenyl-3-(phenylamino)acrylate (**3aa**)

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

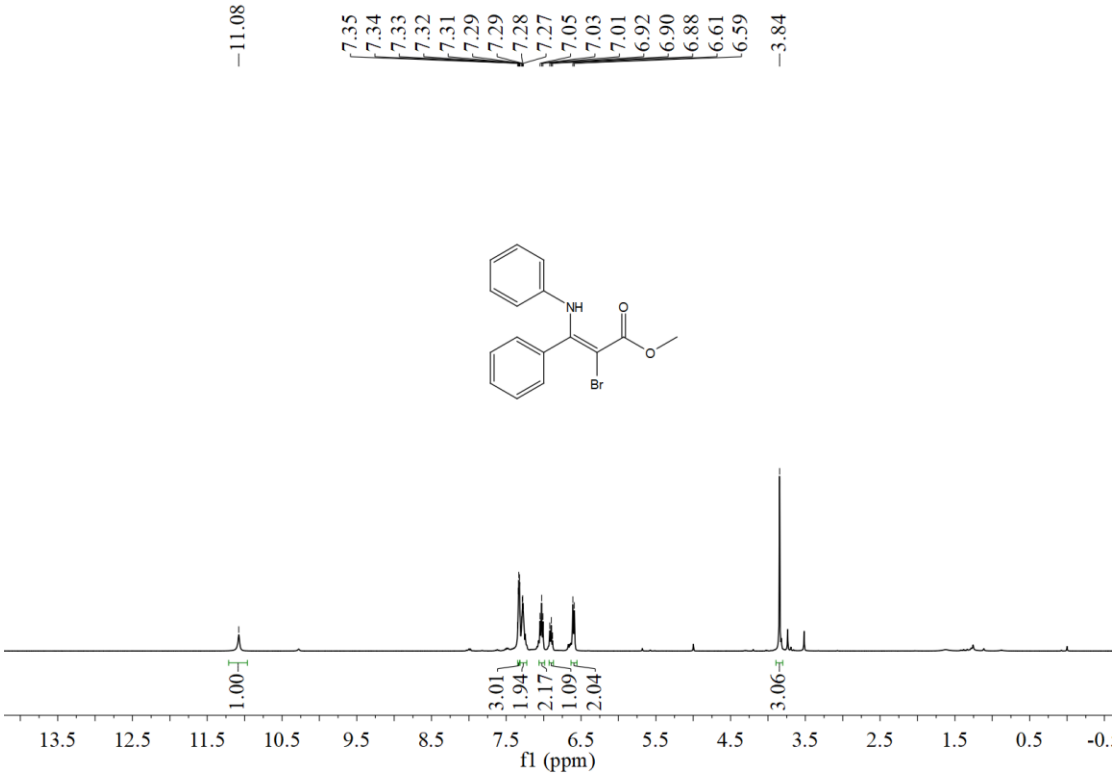


^{13}CNMR (100 MHz, $CDCl_3$)

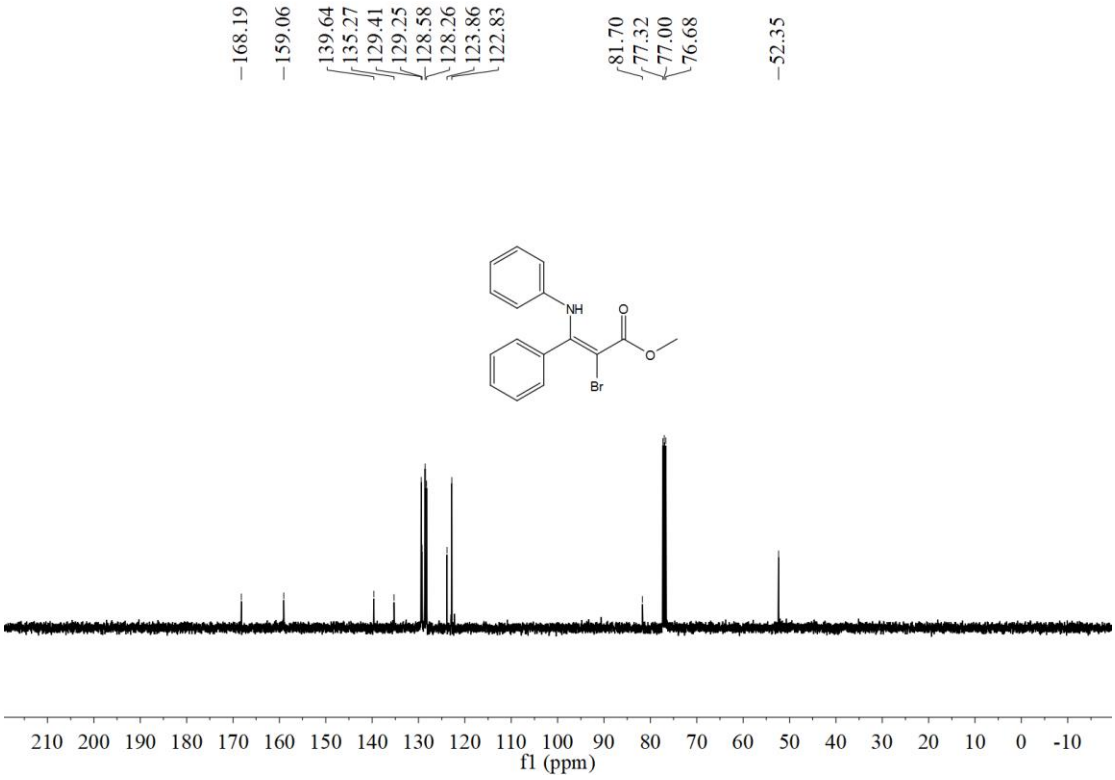


Methyl (*Z*)-2-bromo-3-phenyl-3-(phenylamino)acrylate (**3ab**)

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

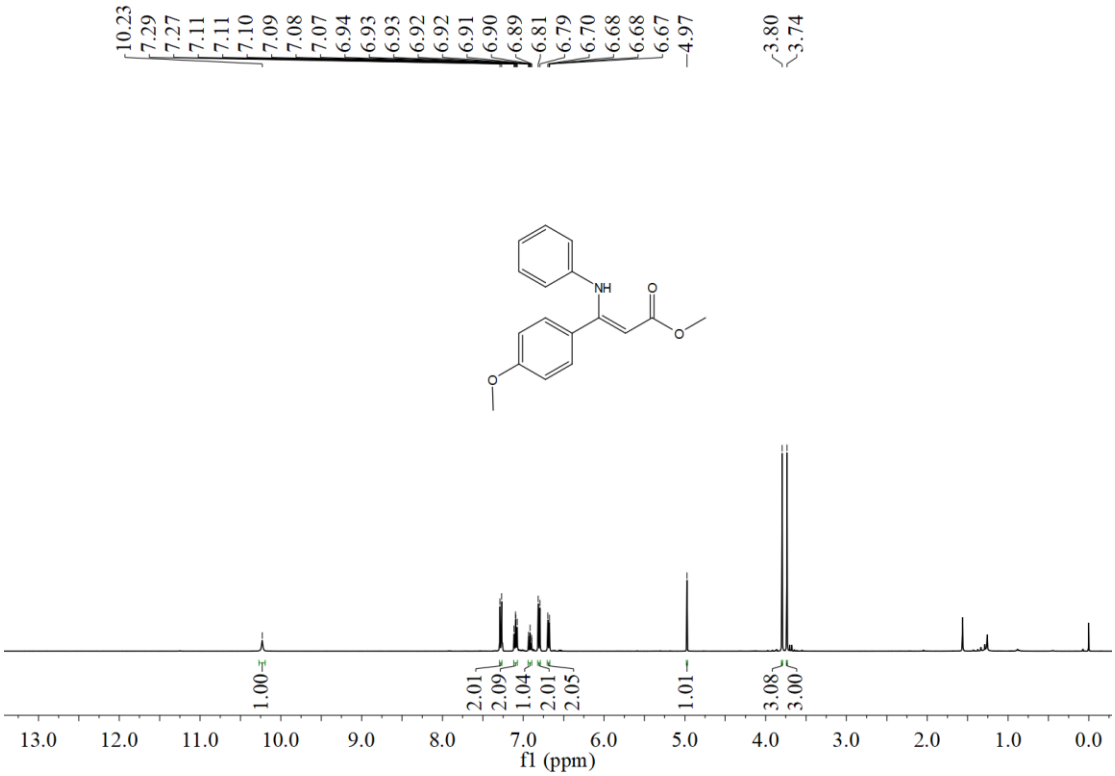


^{13}C NMR (100 MHz, $CDCl_3$)

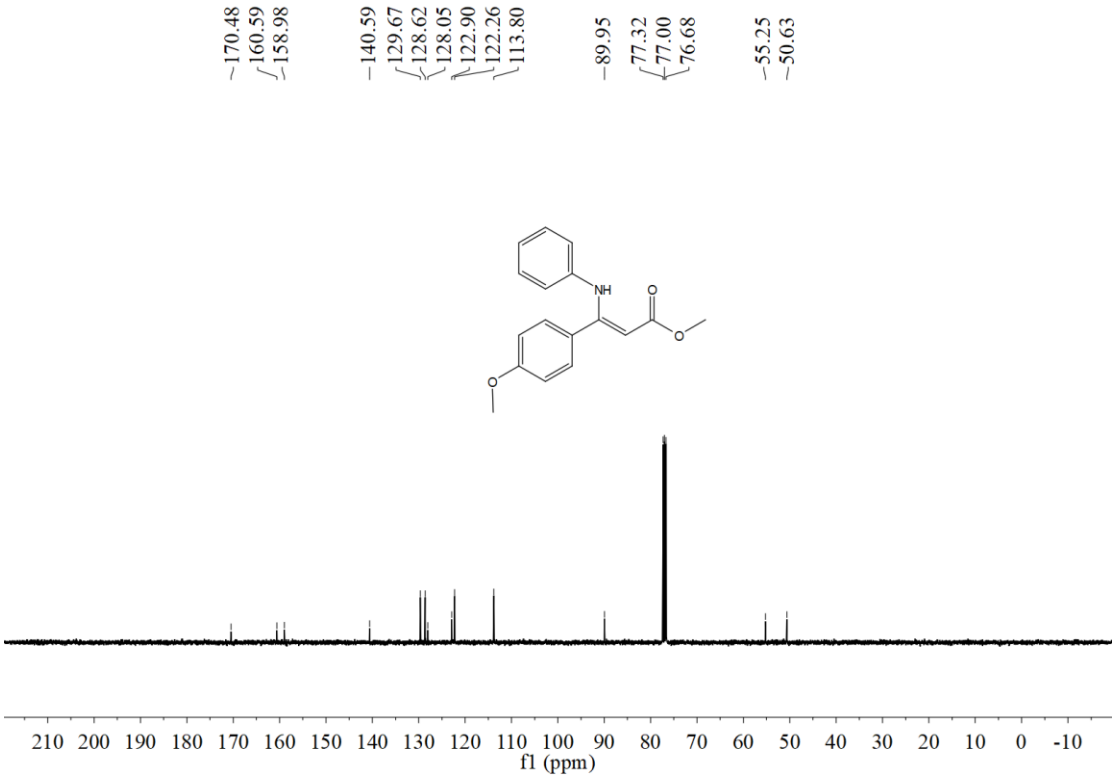


Methyl (*Z*)-3-(4-methoxyphenyl)-3-(phenylamino)acrylate (**3ac**)

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

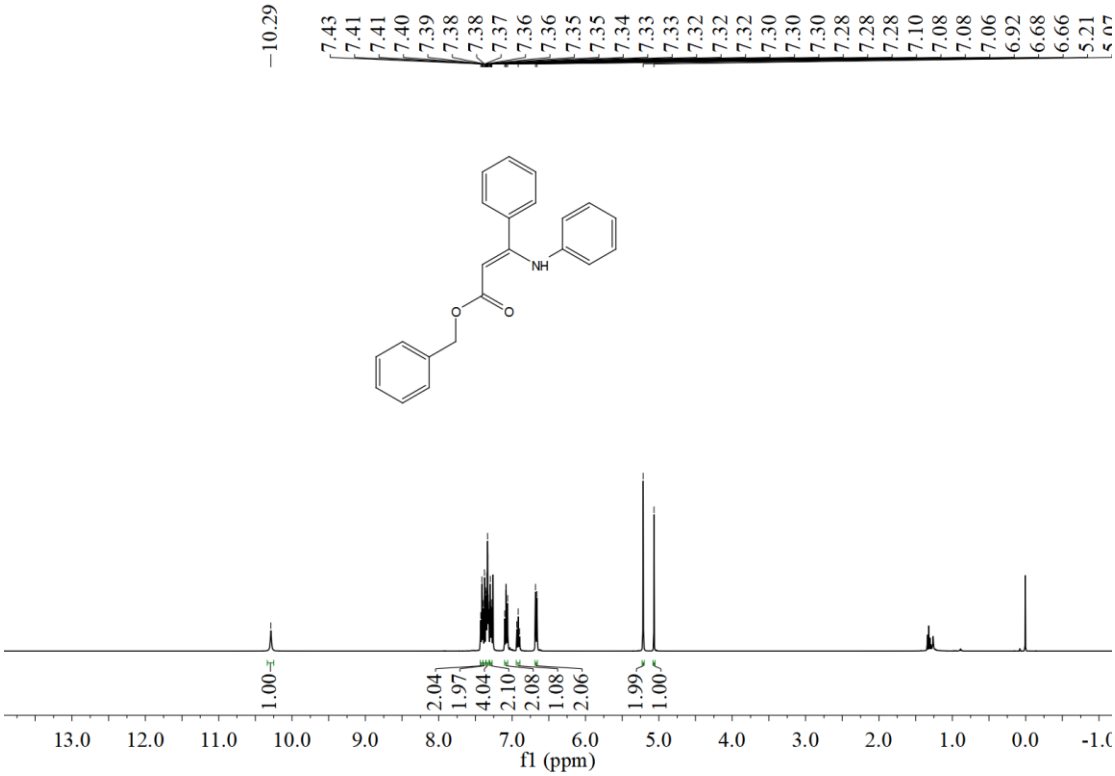


^{13}CNMR (100 MHz, $CDCl_3$)

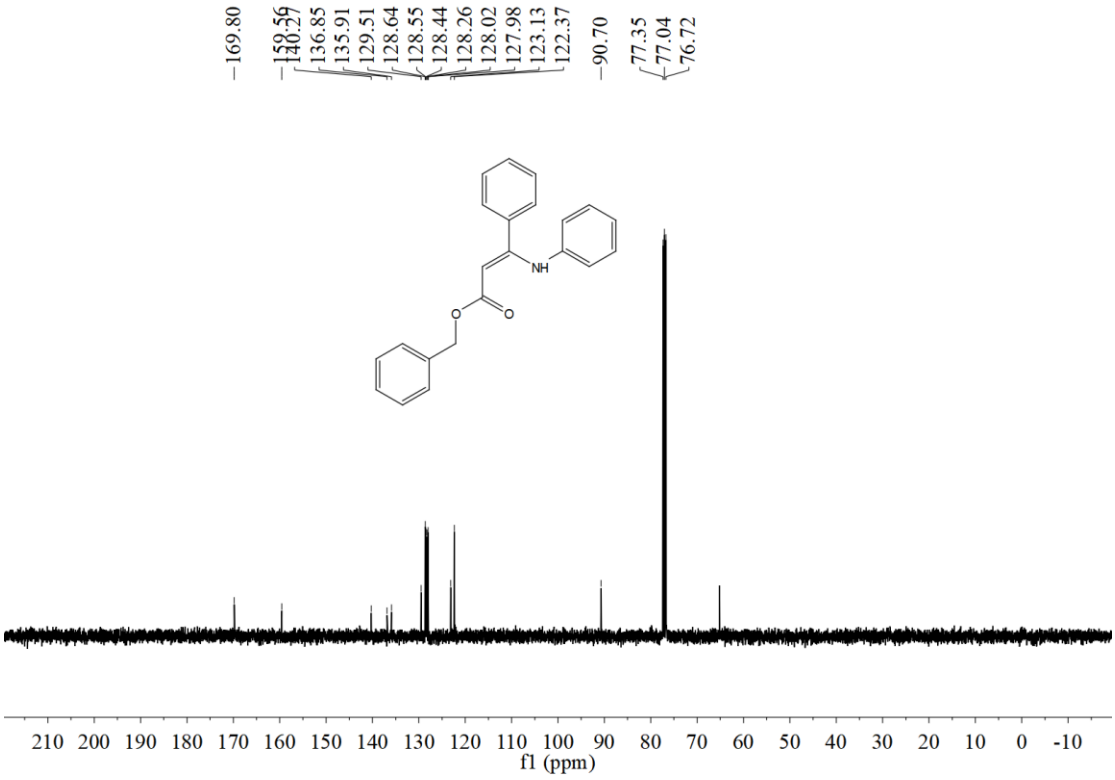


Benzyl (*Z*)-3-phenyl-3-(phenylamino)acrylate (**3ad**)

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

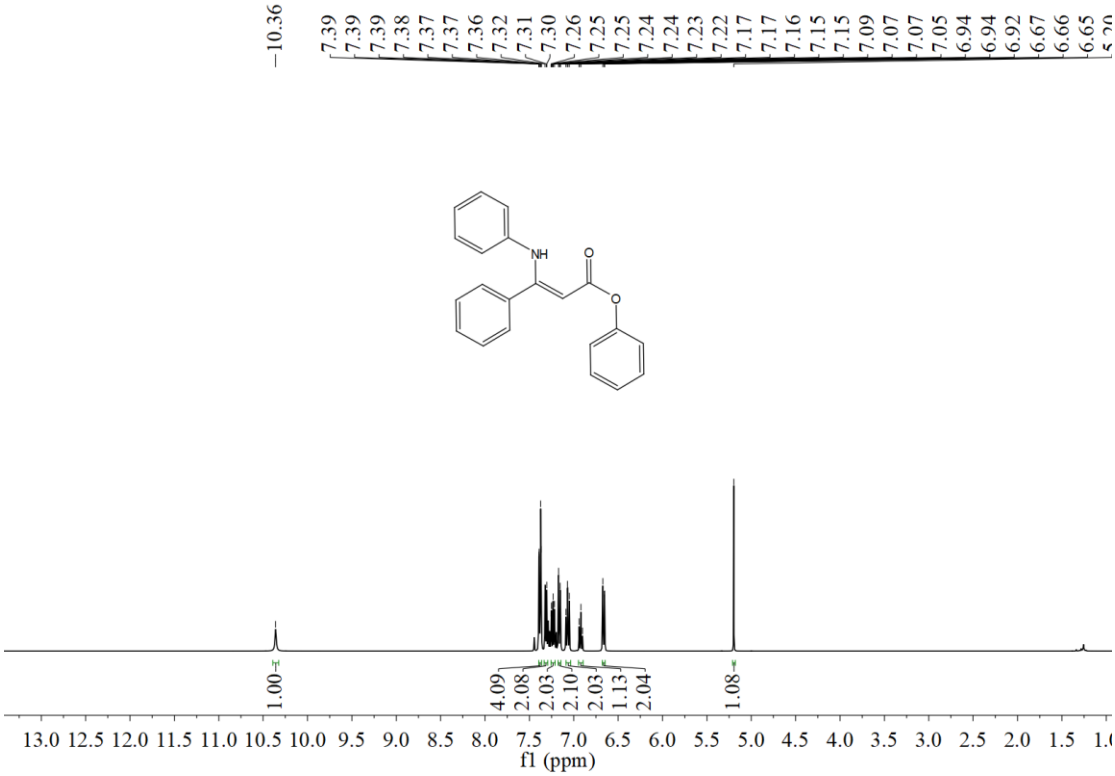


^{13}C NMR (100 MHz, $CDCl_3$)

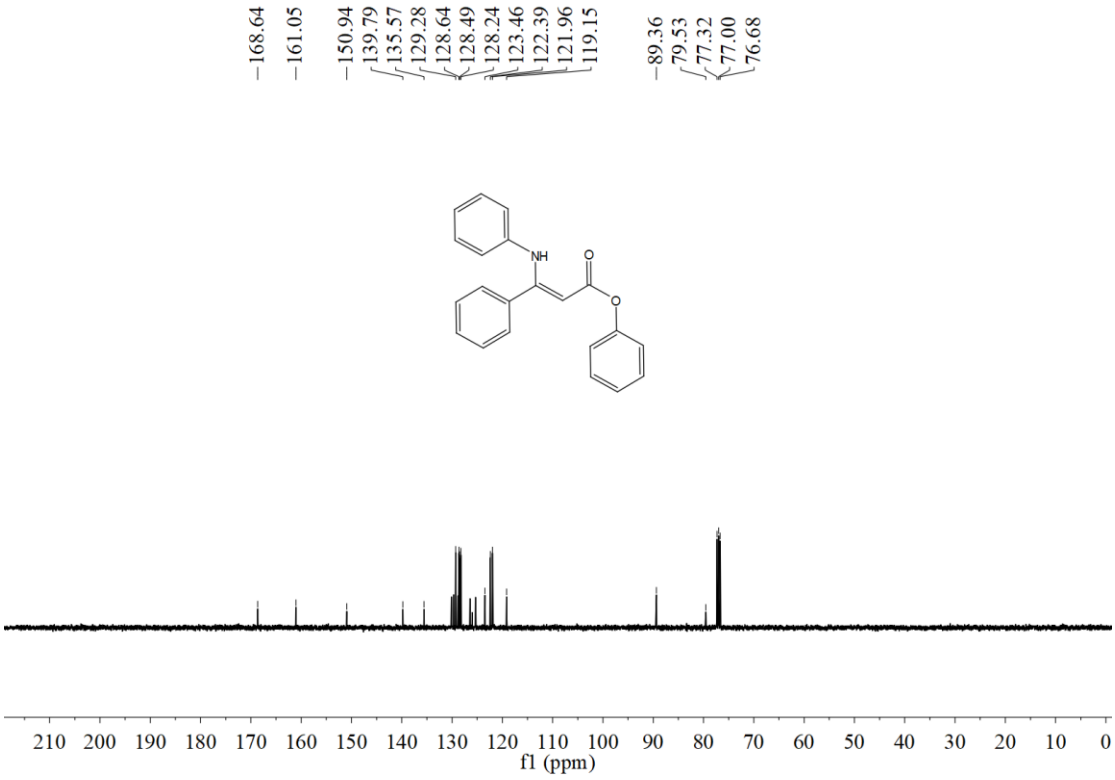


Phenyl (*Z*)-3-phenyl-3-(phenylamino)acrylate (**3ae**)

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

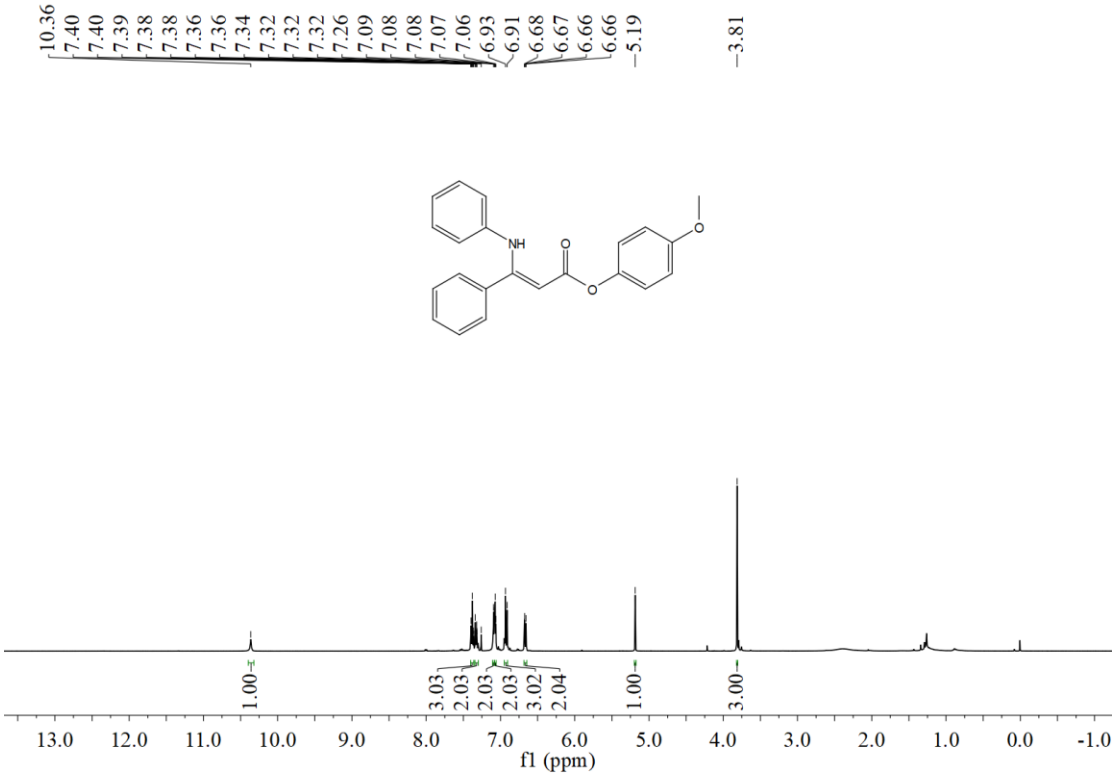


^{13}C NMR (100 MHz, $CDCl_3$)

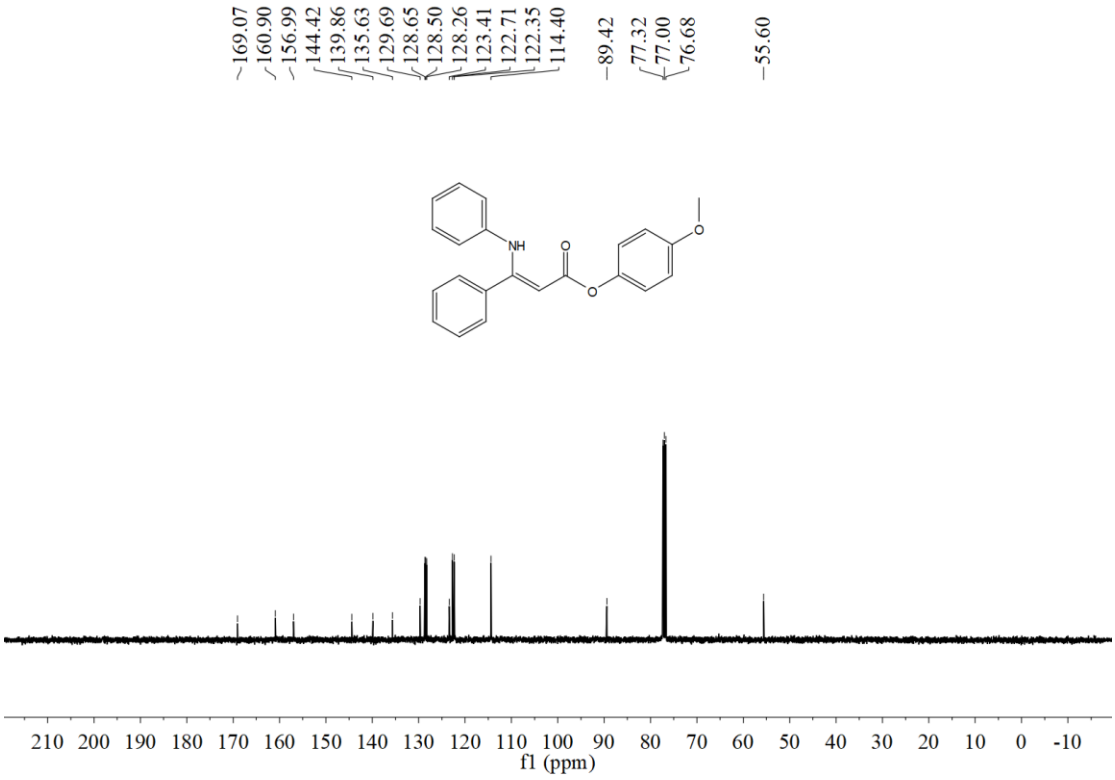


4-Methoxyphenyl (*Z*)-3-phenyl-3-(phenylamino)acrylate (**3af**)

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

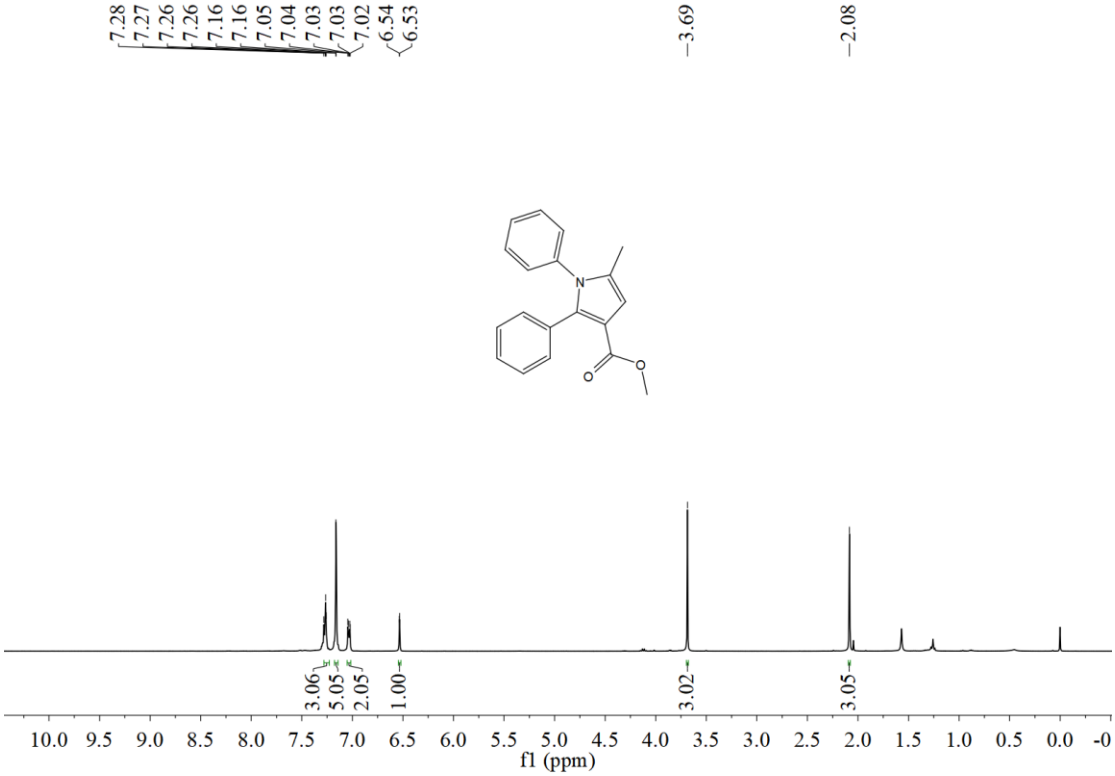


^{13}C NMR (100 MHz, $CDCl_3$)

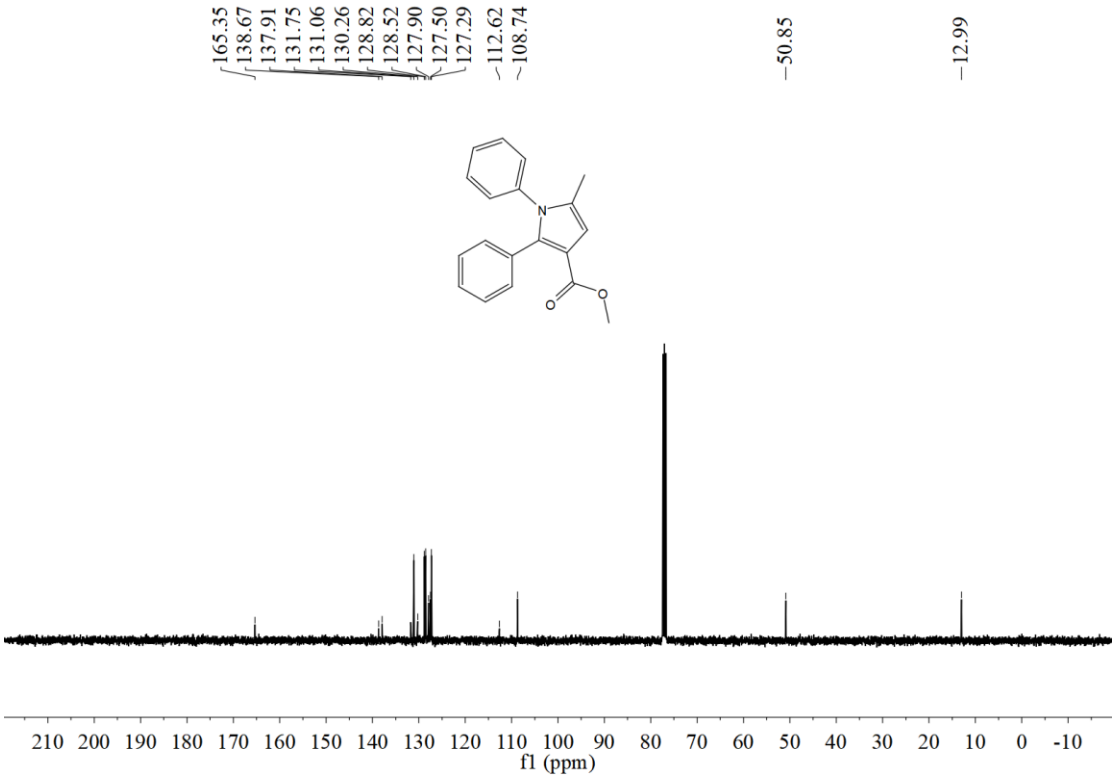


Methyl 5-methyl-1,2-diphenyl-1H-pyrrole-3-carboxylate (**4**)

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

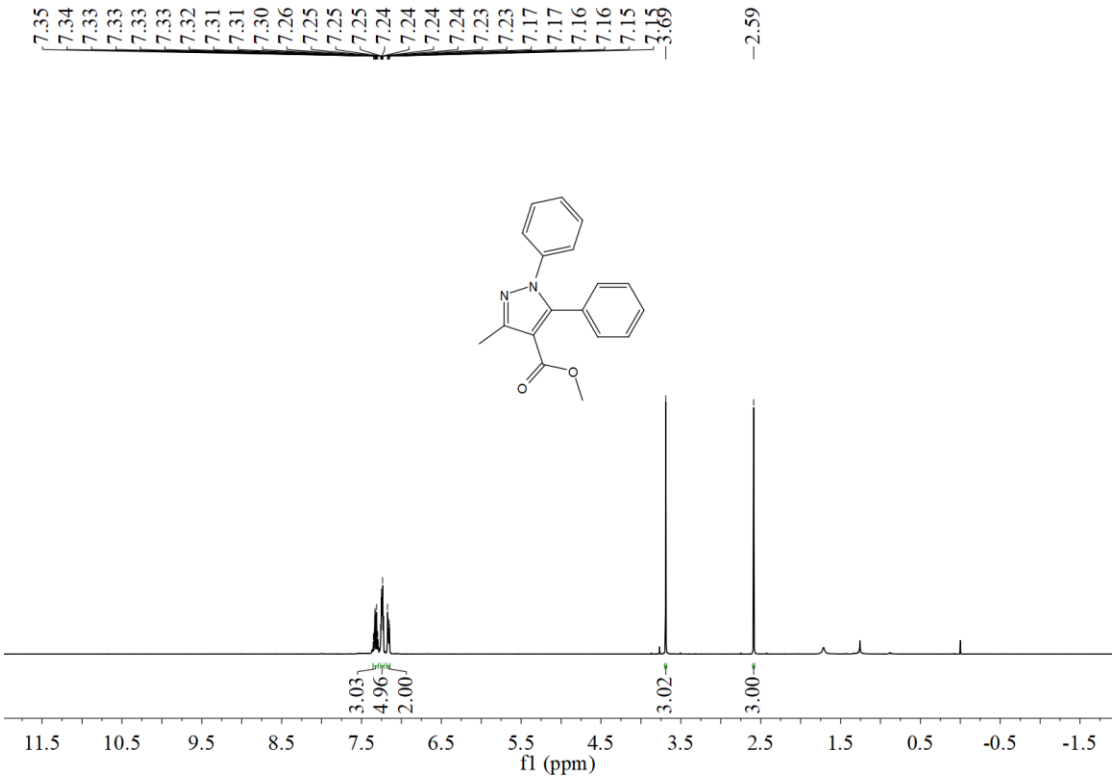


^{13}C NMR (100 MHz, $CDCl_3$)

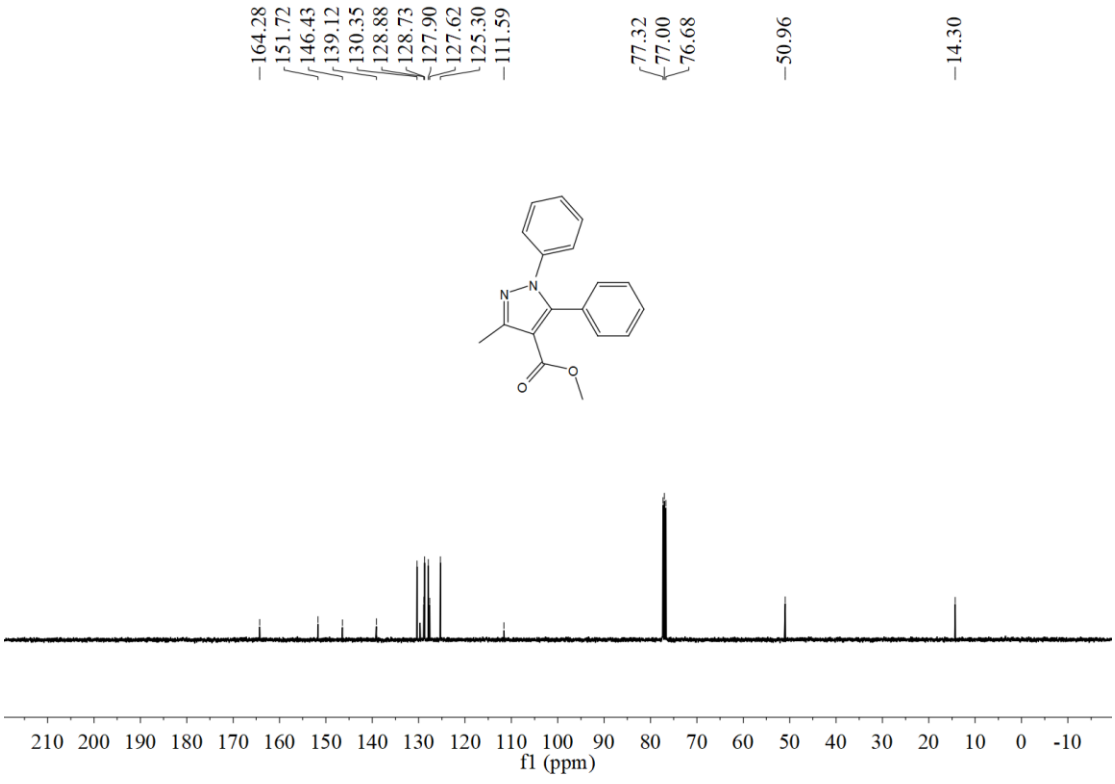


Methyl 3-methyl-1,5-diphenyl-1H-pyrazole-4-carboxylate (**5**)

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

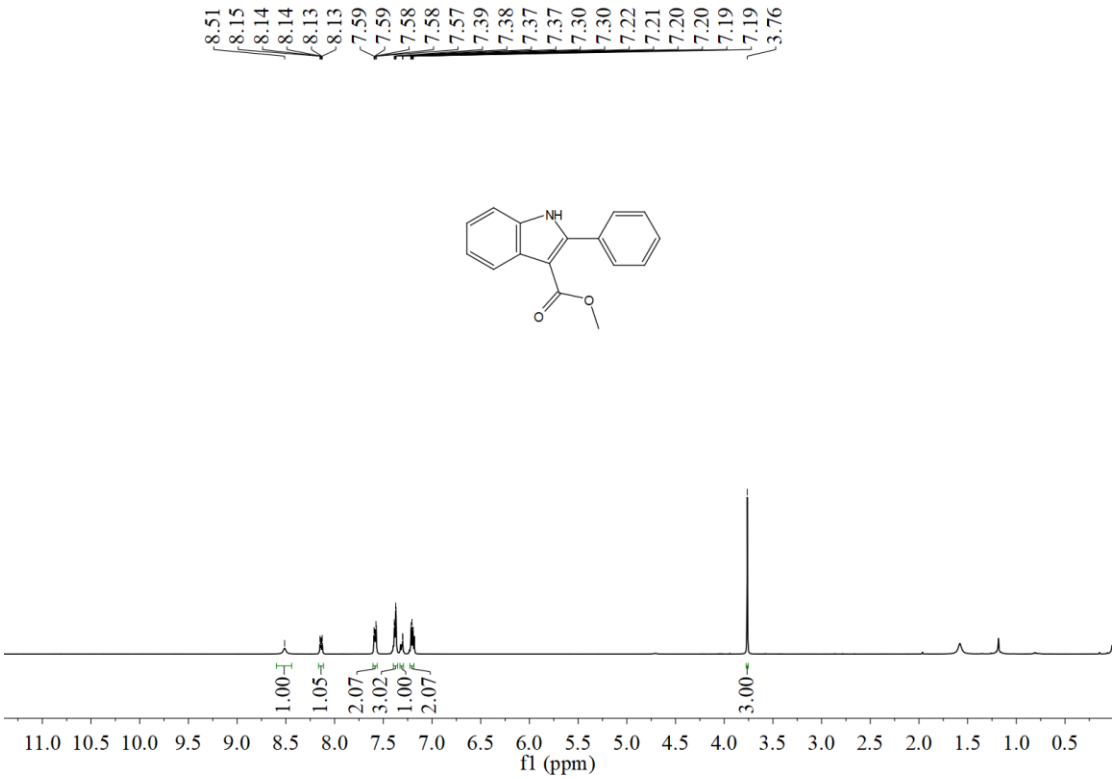


^{13}C NMR (100 MHz, $CDCl_3$)

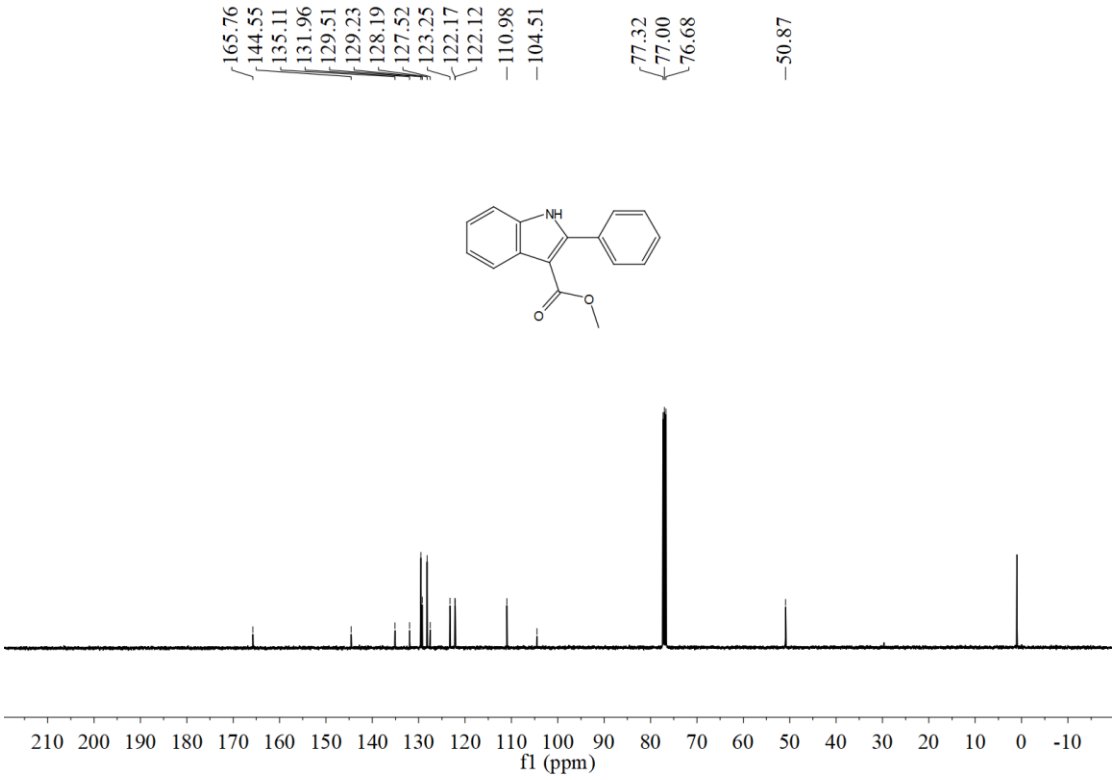


Methyl 2-phenyl-1H-indole-3-carboxylate (6)

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

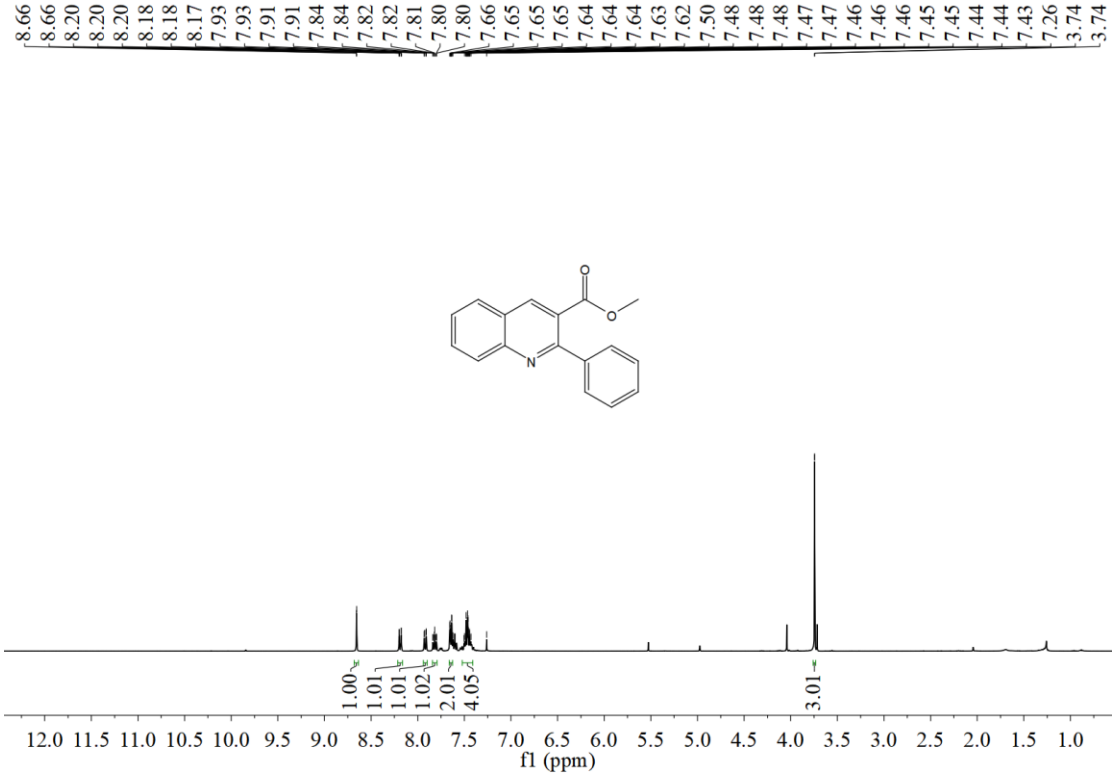


^{13}C NMR (100 MHz, $CDCl_3$)



3-(Methoxycarbonyl)-2-phenylquinolin-1-ium (**7**)

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



^{13}C NMR (100 MHz, $CDCl_3$)