Support information

Metal-free Photosensitized Intermolecular Carboimination of Alkenes: A Green and Direct Access to both β-Amino Acids and β-Amino Ketones

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General information

Reagents, solvents and experimental conditions

All alkenes were purchased from commercial suppliers. Compound oxime[1] was prepared according to literature reports. Both chemicals and solvents were purchased from commercial suppliers and used without further purification, except otherwise stated. Toluene was purified by distillation over sodium-ketyl benzophenone under argon atmosphere. All other over-dried solvents were purchased from Adamas and were directly stored under 3 or 4 Å molecular sieves, replacing the collected volume with nitrogen. All reactions were carried out in over-dried standard schlenk tubes under an atmosphere of argon unless otherwise noted. Solvents for chromatographic purification (petroleum ether, CH_2Cl_2 and EtOAc) were analytical reagent purchased from Greagent.

Analytical techniques

NMR-spectra were recorded on Bruker advance III 400 MHz and 600MHz spectrometers at ambient temperature. Deuterated solvents were purchased from Cambridge chemical ($CDCl_3$, deuteration > 99.8%).^{1}H and ^{13}C chemicals shifts (δ) are quoted in parts per million (ppm) against tetramethylsilane (TMS, δ = 0.00 ppm) and were internally referenced to residual $CHCl_3$ (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C). Coupling constants (J) are reported in Hertz (Hz) to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quintet, p = pentet, m = multiplet.
Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminum sheets and were visualized using UV light (254 nm) and stained with basic aqueous potassium permanganate or ethanolic phosphomolybdic acid solution.

Compound purification

Flash chromatography was carried out using silica gel (300-400 mesh) under a light positive pressure of argon, eluting with the specified solvent system as mentioned.

Photochemical set-up

The following set-up was used for the reaction optimization (0.1 mmol scale) and substrate scope (0.5 mmol scale): the black light shield device (Figure 1) was equipped with Kessil Blue LEDs (40 W, A160WE), JOANLAB magnetic stirrer, and SUNON DP200A fans. Stirring was ensured by magnetic stirring plates (1,000 rpm). A vial equipped with a crimp-top hollow aluminum cap (containing a PTFE-coated silicone gasket) and a PTFE-coated rare-earth “extra power” oval stirring bar was used for small scale reactions.

For the large-scale reactions (> 10 mmol), the set-up shown in Figure 2 was used: two Kessil Blue LEDs (40 W, A160WE) were placed at ~5cm from the reaction vessel, while stirring was ensured by a magnetic stirring plate (1,000 rpm). A PTFE-coated rare-earth “extra power” oval stirring bar was used.

Figure 1

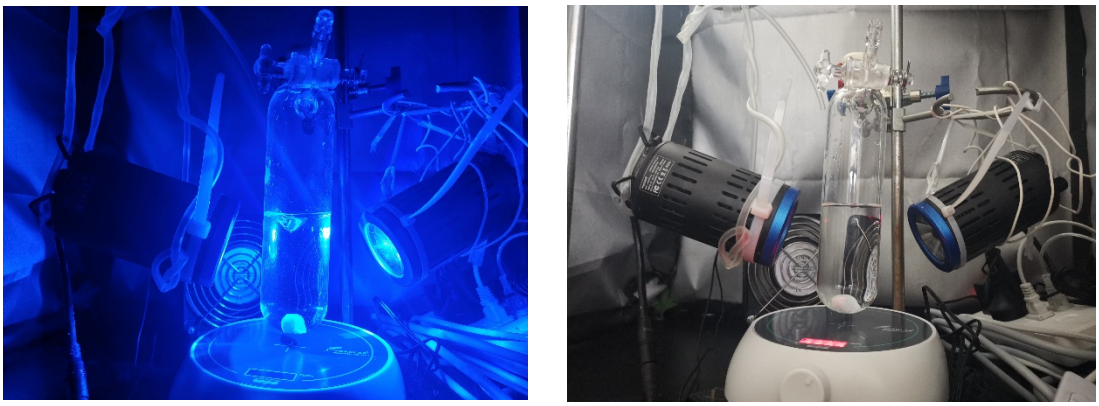
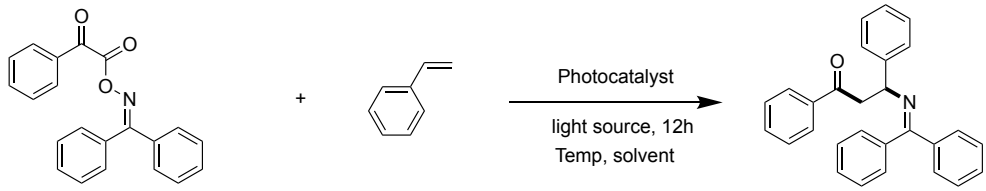


Figure 2

Experimental Details

Optimization of intermolecular 1,2-iminoacylation

Table 1. Optimization of photosensitized intermolecular 1,2-iminoacylation of styrene **2a**

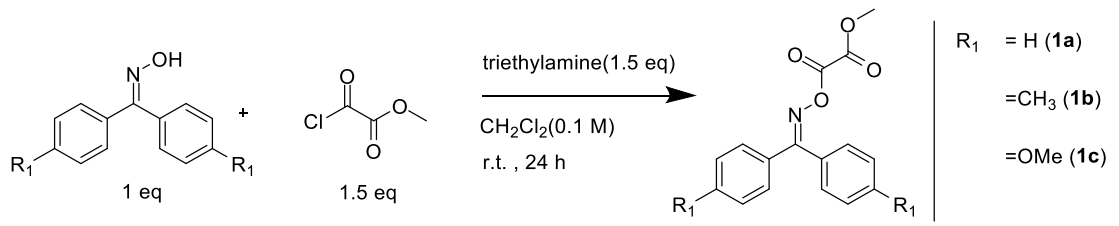


4a **2a** **5aa**

Entry	Solvent	concentration(M)	light source	PC(x %)	Temp	Yield (%)[a]
1	CH_2Cl_2	0.1	40w Blue LEDs	Thioxanthone (5%)	r.t	45(**5aa**)
2	CH_2Cl_2	0.1	40w Blue LEDs	none	r.t	45(44)[b]
3	EtOAc	0.1	40w Blue LEDs	none	r.t	45
4	$ClCH_2CH_2Cl$	0.1	40w Blue LEDs	none	r.t	36
5	$PHCF_3$	0.1	40w Blue LEDs	none	r.t	34
6	THF	0.1	40w Blue LEDs	none	r.t	18
7	DMF	0.1	40w Blue LEDs	none	r.t	24
8	MeOH	0.1	40w Blue LEDs	none	r.t	20
9	CH_2Cl_2	0.2	40w Blue LEDs	none	r.t	37
10	CH_2Cl_2	0.05	40w Blue LEDs	none	r.t	41
11	CH_2Cl_2	0.02	40w Blue LEDs	none	r.t	36
12	CH_2Cl_2	0.1	20w Blue LEDs	none	r.t	43
13	CH_2Cl_2	0.1	10w Blue LEDs	none	r.t	26
14	CH_2Cl_2	0.1	90w Blue LEDs	none	r.t	36
15	CH_2Cl_2	0.1	40w White LEDs	none	r.t	36
16	CH_2Cl_2	0.1	40w 395nm	none	r.t	36
17	CH_2Cl_2	0.1	40w 420nm	none	r.t	34
18	CH_2Cl_2	0.1	40w 445nm	none	r.t	36
19	CH_2Cl_2	0.1	40w 460nm	none	r.t	26
20	CH_2Cl_2	0.1	dark	none	r.t	0
21	CH_2Cl_2	0.1	40w Blue LEDs	none	40	40
22	CH_2Cl_2	0.1	40w Blue LEDs	none	10	44
23	CH_2Cl_2	0.1	40w Blue LEDs	none	0	44

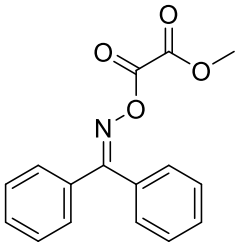
Reaction conditions: oxime phenylglyoxylate **4a** (1 equiv), alkene **2a** (1.1 equiv) and photocatalys in solvent (0.1 M), irradiation with 40 W blue LEDs (Kessil A160WE Tuna Blue controllable LED aquarium light, λ_{max} = 462 nm flanked by a second peak at λ = 382 nm) under an argon atmosphere at room temperature for 12 h. [a]Yields were determined by ^{1}H NMR spectroscopic analysis with dibromomethane as the internal standard. [b]Yield of the isolated product. N.D.= not determined.

General procedure A for the preparation of oxime ester（1a-1b）



After stirring a solution of oxime from previous step (10 mmol, 1 equiv) in 200 ml CH_2Cl_2 at 0℃ for 10 min under argon, the methyl 2-chloro-2-oxoacetate (15 mmol, 1.5 equiv) was slowly added dropwise. Then, triethylamine (15 mmol, 1.5 equiv) was added dropwise. After 10 minutes, the reaction flask was placed at room temperature and shield from light to react for 24 h until the reaction was complete as observed from TLC monitoring. The mixture was diluted with water (100 mL) and the CH_2Cl_2 layer was separated, dried over anhydrous Na_2SO_4. Removal of the solvent, followed by column chromatography, and obtained the product (Storage conditions: -20 ℃, keep away from light).

Methyl 2-(((diphenylmethylene)amino)oxy)-2-oxoacetate (1a)



According to the **General procedure A** using diphenylmethanone oxime (1.97 g, 10 mmol) and methyl 2-chloro-2-oxoacetate (1.85 g, 15 mmol), the reaction afforded white solid (2.33 g, 8.23 mmol, yield 82%), purifying by column chromatography silica gel (eluent: petroleum ether: ethyl acetate = 10:1, v:v).

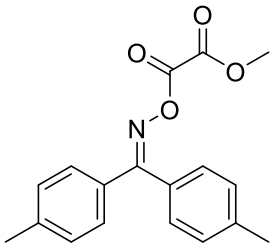
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 - 7.59 (m, 2 H), 7.54 - 7.47 (m, 4 H), 7.44 - 7.38 (m, 4 H), 3.89 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.43, 158.24, 155.76, 134.05, 131.59, 131.49, 130.29, 129.37, 129.17, 128.55, 128.29, 53.50.

HRMS (ESI): *m/z* calculated for [$C_{16}H_{13}NNaO_4$] [M+Na^+]: 306.0737, measured: 306.0738

IR (neat): *v* = 2956, 2924, 2852, 1783, 1748, 1445, 1276, 1261,764, 750, 693 cm^{-1}.

Methyl 2-(((di-p-tolylmethylene)amino)oxy)-2-oxoacetate (1b)



According to the **General procedure A** using di-p-tolylmethanone oxime (2.25g, 10 mmol) and methyl 2-chloro-2-oxoacetate (1.85g, 15 mmol), the reaction afforded white solid (2.56 g, 8.23 mmol, yield 82%), purifying by column chromatography silica gel (eluent: petroleum ether: ethyl acetate = 10:1, v:v).

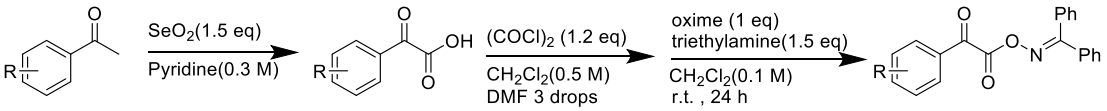
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.2 Hz, 2 H), 7.30 (s, 4 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 3.90 (s, 3 H), 2.45 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.43, 158.41, 156.30, 141.88, 140.53, 131.45, 129.43, 129.41, 129.21, 128.87, 128.75, 53.46, 21.51, 21.48.

HRMS (ESI): *m/z* calculated for [$C_{18}H_{17}NNaO_4$] [M+Na^+]: 334.1050, measured: 334.1049.

IR (neat): *v* = 3031, 2956, 2923, 1784, 1752, 1613, 1597, 1326,1302, 1275, 1194, 1141, 825, 781, 765, 730 cm^{-1}.

General procedure B for the preparation of phenyl oxalyl oxime ester(4a-4f)

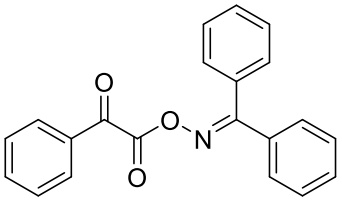


Following a previous literature report[2], in a dry reaction flask equipped with a condenser, SeO_2 (22.5 mmol, 1.5 equiv), pyridine (50 ml) and acetophenone(15 mmol, 1 equiv) were added in sequence, refluxed at 110 ℃ for 2h under argon, and then cooled down to 90 ℃ overnight. After that, the reaction was cooled to room temperature and diluted with ethyl ester and passed through a short column of diatomaceous earth to remove solids. Then concentrated under reduced pressure and dissolved with 1N NaOH (30 ml). After the solution was extracted with ethyl ester, the aqueous phase was retained and acidified with 1N HCl to pH = 2, extracted with ethyl ester, and dried over anhydrous Na_2SO_4. This product was sufficiently pure as determined from NMR and was used without further purification for the preparation of oxime ester.

To a solution of phenylformylformic acid from previous step (15 mmol 1 equiv) in 30 ml CH_2Cl_2, oxalyl dichloride (18 mmol, 1.2 equiv) was added under argon. Then with vigorous stirring at room temperature, 3 drops of DMF were added dropwise. After stirring at room temperature overnight, the crude product was obtained by concentration under reduced pressure without further purification.

After stirring a solution of diphenylmethanone oxime from previous step (10 mmol, 1 equiv) in 50 ml CH_2Cl_2 at 0 ℃ for 10min under argon, the crude solution prepared earlier (dissolved in 50 ml DCM) and triethylamine were added sequentially. The reaction mixture was stirred at room temperature for 24 hours and the consumption of the starting material was observed by TLC. The mixture was diluted with water (100 mL) and the CH_2Cl_2 layer was separated, dried over anhydrous Na_2SO_4. Removal of the solvent, followed by column chromatography, and obtained the product (Storage conditions: -20 ℃, keep away from light).

1-(((diphenylmethylene)amino)oxy)-2-phenylethane-1,2-dione (4a)



According to the **General procedure B** using acetophenone (1.8g, 15 mmol) and diphenylmethanone oxime (1.97g, 10 mmol), the reaction afforded white solid (1.9 g, 5.78 mmol, yield 58%), purifying by column chromatography silica gel (eluent: petroleum ether: ethyl acetate = 10:1, v:v).

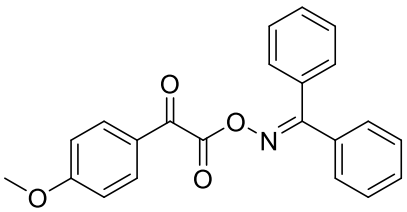
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.3 Hz, 2 H), 7.67 (t, *J* = 6.8 Hz, 1 H), 7.58 - 7.44 (m, 8 H), 7.48 - 7.33 (m, 4 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 186.01, 166.70, 163.46, 134.93, 134.02, 132.55, 131.58, 131.40, 130.18, 129.77, 129.20, 129.01, 128.98, 128.52, 128.38.

HRMS (ESI): *m/z* calculated for $[C_{21}H_{15}NO_4H]$ $[M+H^+]$: 330.1125, measured: 330.1123.

IR (neat): *v* = 3063, 1761, 1688, 1596, 1581, 1564, 1494, 1449, 1320, 1278, 1194, 1156, 1076, 1027, 1002, 951, 870, 766, 741, 697, 639, 575 cm^{-1}.

1-(((diphenylmethylene)amino)oxy)-2-(4-methoxyphenyl)ethane-1,2-dione (4b)



According to the **General procedure B** using 1-(4-methoxyphenyl)ethan-1-one (2.25g, 15 mmol) and diphenylmethanone oxime (1.97g, 10 mmol), the reaction afforded white solid (2.7 g, 7.5 mmol, yield 75%), purifying by column chromatography silica gel (eluent: petroleum ether: ethyl acetate = 8:1, v:v).

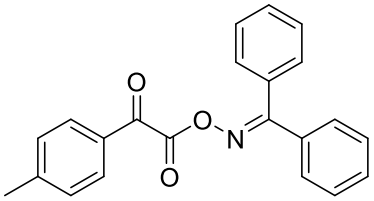
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.9 Hz, 2 H), 7.51 (d, *J* = 8.4 Hz, 2 H), 7.49 - 7.42 (m, 4 H), 7.40 - 7.33 (m, 4 H), 6.95 (d, *J* = 8.9 Hz, 2 H), 3.88 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.28, 166.71, 165.07, 163.43, 134.13, 132.38, 131.67, 131.38, 130.16, 129.24, 129.06, 128.52, 128.37, 125.56, 114.35, 55.69.

HRMS (ESI): *m/z* calculated for [$C_{22}H_{17}NNaO_4$] [M+Na^+]: 382.1050, measured: 382.1051.

IR (neat): *v* = 3061, 2937, 2842, 1761, 1674, 1599, 1574, 1512, 1446, 1326, 1308, 1267, 1187, 1149, 1027, 949, 766, 696,647, 618, 572 cm^{-1}.

1-(((diphenylmethylene)amino)oxy)-2-(p-tolyl)ethane-1,2-dione (4c)



According to the **General procedure B** using 1-(p-tolyl)ethan-1-one (2.0g, 15 mmol) and diphenylmethanone oxime (1.97g, 10 mmol), the reaction afforded white solid (1.7 g, 5 mmol, yield 50%), purifying by column chromatography silica gel (eluent: petroleum ether: ethyl acetate = 10:1, v:v).

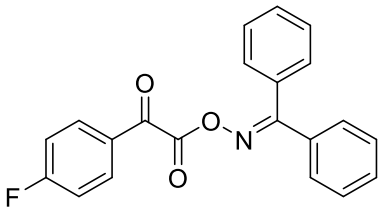
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.3 Hz, 2 H), 7.53 - 7.44 (m, 6 H), 7.44 - 7.34 (m, 4 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 2.46 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.60, 166.63, 163.54, 146.31, 134.09, 131.61, 131.37, 130.16, 130.11, 129.94, 129.73, 129.22, 129.04, 128.51, 128.37, 21.96.

HRMS (ESI): *m/z* calculated for [$C_{22}H_{17}NNaO_3$] [M+Na^+]: 366.1101, measured: 366.1100.

IR (neat): *v* = 3061, 2923, 1763, 1682, 1605, 1446, 1329, 1304, 1279, 1193, 1153, 947, 767, 756, 695, 573 cm^{-1}.

1-(((diphenylmethylene)amino)oxy)-2-(4-fluorophenyl)ethane-1,2-dione (4d)



According to the **General procedure B** using 1-(4-fluorophenyl)ethan-1-one (2.1g, 15 mmol) and diphenylmethanone oxime (1.97g, 10 mmol), the reaction afforded white solid (1.57 g, 4.52 mmol, yield 45%), purifying by column chromatography silica gel (eluent: petroleum ether: ethyl acetate = 10:1, v:v).

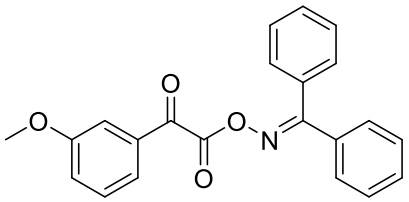
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (dd, *J* = 8.7, 5.4 Hz, 2 H), 7.55 - 7.47 (m, 6 H), 7.42 - 7.34 (m,4 H), 7.18 (t, *J* = 8.6 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.18, 168.08, 166.98 (d, *J* = 110.0 Hz), 165.51, 162.89, 133.94, 132.71, 132.61 (d, *J* = 9.9 Hz), 131.58, 131.49, 130.23, 129.20, 129.10, 129.07(d, *J* = 2.5 Hz), 128.99, 128.56, 128.41, 116.49, 116.27 (d, *J* = 22.3 Hz).

HRMS (ESI): *m/z* calculated for [$C_{21}H_{14}FNNaO_3$] [M+Na^+]: 370.0850, measured: 370.0849

IR (neat): *v* = 3063, 1764, 1689, 1599, 1507, 1446, 1415, 1329, 1303, 1276, 1240, 1171, 1151, 950, 765, 696 cm^{-1}.

1-(((diphenylmethylene)amino)oxy)-2-(3-methoxyphenyl)ethane-1,2-dione (4e)



According to the **General procedure B** using 1-(3-methoxyphenyl)ethan-1-one (2.25g, 15 mmol) and diphenylmethanone oxime (1.97g, 10 mmol), the reaction afforded white solid (2.87 g, 8 mmol, yield 80%), purifying by column chromatography silica gel (eluent: petroleum ether: ethyl acetate = 8:1, v:v).

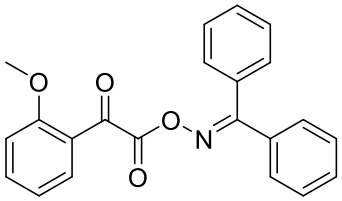
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 - 7.45 (m, 8 H), 7.39 (q, *J* = 8.4 Hz, 5 H), 7.22 (dd, *J* = 8.5, 2.3 Hz, 1 H), 3.88 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.88, 166.60, 163.44, 160.04, 134.04, 133.79, 131.55, 131.38, 130.18, 130.01, 129.21, 129.03, 128.51, 128.36, 122.97, 122.04, 112.81, 55.55.

HRMS (ESI): *m/z* calculated for [$C_{22}H_{17}NNaO_4$] [M+Na^+]: 382.1050, measured: 382.1047.

IR (neat): *v* = 3062, 2941, 2838, 1765, 1688, 1598, 1583, 1487, 1446, 1329, 1291, 1242, 1187, 1143, 1043, 1012, 962, 908, 856, 757, 697, 678 cm^{-1}.

1-(((diphenylmethylene)amino)oxy)-2-(2-methoxyphenyl)ethane-1,2-dione (4f)



According to the **General procedure B** using 1-(2-methoxyphenyl)ethan-1-one (2.25g, 15 mmol) and diphenylmethanone oxime (1.97g, 10 mmol), the reaction afforded white solid (2.76 g, 7.7 mmol, yield 77%), purifying by column chromatography silica gel (eluent: petroleum ether: ethyl acetate = 8:1, v:v).

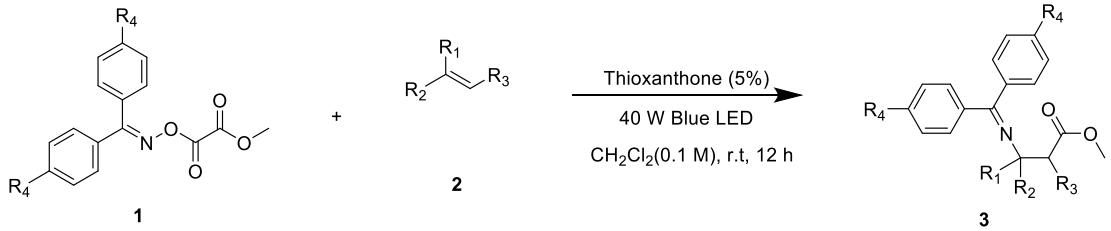
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.62 (t, *J* = 7.9 Hz, 1 H), 7.47 - 7.34 (m, 8 H), 7.31 (t, *J* = 7.6 Hz, 2 H), 7.11 (t, *J* = 7.5 Hz, 1 H), 7.01 (d, *J* = 8.4 Hz, 1 H), 3.88 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.55, 164.74, 160.44, 136.58, 134.32, 131.56, 131.08, 130.29, 130.05, 129.13, 129.05, 128.43, 128.29, 122.76, 121.39, 112.30, 56.20.

HRMS (ESI): *m/z* calculated for [$C_{22}H_{17}NNaO_4$] [M+Na^+]: 382.1050, measured: 382.1048.

IR (neat): *v* = 3062**,** 2976, 2945, 2842, 1771, 1669, 1599, 1582, 1486, 1446, 1439, 1333, 1310, 1266, 1180, 1159, 1112, 1020, 950, 908, 874, 759, 697, 663, 575 cm^{-1}.

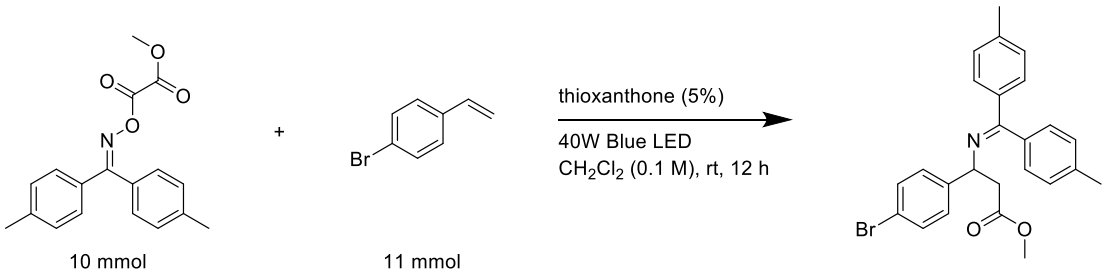
General procedure C for the 1,2-iminocarboxylation of alkenes.



In an over-dried vial equipped with a crimp-top hollow aluminum cap (containing a PTFE-coated silicone gasket), methyl 2-(((di-p-tolylmethylene)amino)oxy)-2-oxoacetate (**1b**) (0.5 mmol, 1 equiv) and thioxanthone (5% mmol) were added. After adding the magnetic stirrer, the special crimping

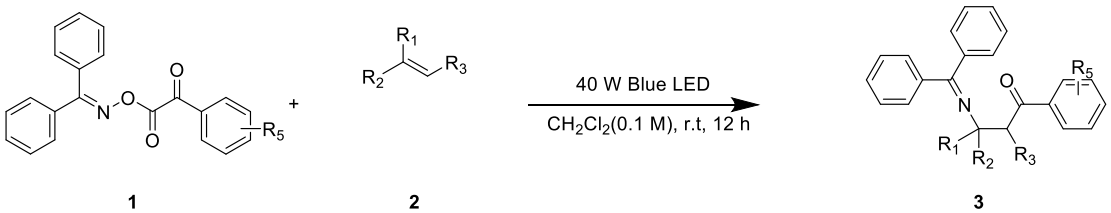
forceps was used to seal the vial. The air in the bottle was replaced with argon in the dark with the aid of a needle. Then, sequentially injected 5 ml CH_2Cl_2(0.1 M) (dry and degas for more than 20 min) and alkenes (0.55 mmol, 1.1 equiv)(if the alkenes is a solid, it is dissolved in the solvent) with a syringe. After stirring for 10 minutes in the dark, then stirred at 1000 rpm and irradiated using the described set-up for 12 hours, unless otherwise stated. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of Ethyl acetate (3 x 3 mL) and concentrated under reduced pressure. The crude products were purified by column chromatography to yield the desired compound.

Scale up reaction for the 1,2-iminocarboxylation of alkenes



In an oven-dried 200 mL Schlenk tube equipped with a PTFE-coated stirring bar, oxime ester **1a** (3.11 g, 10 mmol, 1 equiv) and thioxanthone (11 mg, 0.5 mmol, 5 mol%) were charged, then the vessel was purged and filled-back with argon four times. Dry CH_2Cl_2(100 ml) was added under argon counterflow, followed by styrene (2 g, 11 mmol, 1.1 equiv). The vessel was sealed with the rubber stopper and irradiated under vigorous stirring (1000 rpm) with two 40 W blue LED lights for 14 hours. The solvent was evaporated under reduced pressure and the crude was purified by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1) . The oil **3bk** (3.03 g, 6.74 mmol, 67% yield) was afforded.

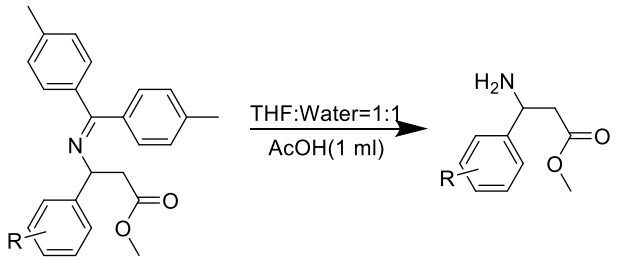
General procedure D for the 1,2-iminoacylation of alkenes.



In an over-dried vial equipped with a crimp-top hollow aluminum cap (containing a PTFE-coated silicone gasket), 1-(((diphenylmethylene)amino) oxy)-2-phenylethane-1,2-dione (**4a**) (0.5 mmol, 1 equiv) were added. After adding the magnetic stirrer, the special crimping forceps was used to seal the vial. The air in the bottle was replaced with argon in the dark with the aid of a needle. Then, sequentially injected 5 ml CH_2Cl_2(0.1 M) (dry and degas for more than 20min) and alkenes (0.55 mmol, 1.1 equiv) (if the alkenes is solid, it is dissolved in the solvent) with a syringe. After stirring

for 10 minutes in the dark, then stirred at 1000 rpm and irradiated using the described set-up for 12 hours, unless otherwise stated. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of Ethyl acetate (3 x 3 mL) and concentrated under reduced pressure. The crude products were purified by column chromatography silica gel to yield the desired compound.

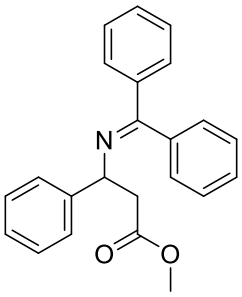
General procedure E for the hydrolysis of the products of 1,2-iminocarboxylation.



To a flask was added methyl 3-((di-p-tolylmethylene) amino)-3-phenylpropanoate(**3ba**) (1 mmol, 1 equiv), and THF (2 mL). A solution of AcOH (1 ml.) in water (2 mL) was added. The solution was stirred at room temperature. After the reaction was finished, the THF was removed under reduced pressure. 1N HCl (2 ml) was added and the solution was extracted with ether (5 ml×2), the aqueous phase was retained and added K_2CO_3 to Ph > 8, extracted with CH_2Cl_2 (5 ml) over three times, and dried over anhydrous Na_2SO_4. The solution was removed under reduced pressure to get crude products.

Characterization data for oxime carbonates and products

Methyl 3-((diphenylmethylene)amino)-3-phenylpropanoate (3aa)



According to the **General Procedure C,** using oxime ester **1a** (0.5 mmol, 1 equiv) and styrene(**2a**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3aa** (85 mg, 0.248 mmol, 50%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 6.8 Hz, 2 H), 7.51 - 7.44 (m, 3 H), 7.43 - 7.27 (m, 8 H), 7.14 - 7.07 (m, 2 H), 4.93 (dd, *J* = 9.2, 4.4 Hz, 1 H), 3.64 (s, 3 H), 3.14 (dd, *J* = 15.2, 9.2 Hz, 1 H), 2.84 (dd, *J* = 15.2, 4.5 Hz, 1 H).

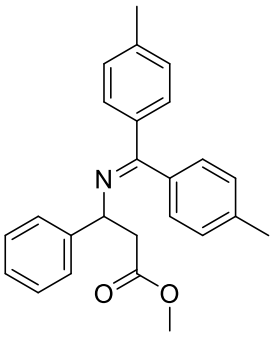
^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.80, 168.27, 143.67, 139.94, 136.81, 130.06, 128.71, 128.50, 128.24, 128.02, 127.88, 127.11, 127.01, 62.97, 51.47, 44.28.

HRMS (ESI): m/z calculated for [$C_{23}H_{21}NO_2H$] [M+H$^+$]: 344.1646, measured: 344.1645.

IR (neat): *v* = 3026, 2952, 2919, 1739, 1621, 1444, 1265,1172, 773, 771cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-phenylpropanoate (3ba)

According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and styrene(**2a**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3ba** (110 mg, 0.296 mmol, 60%), purifying by



column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

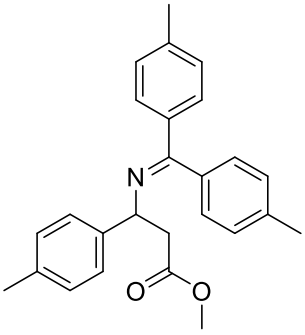
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 3.6 Hz, 4 H), 7.25 (d, *J* = 8.4 Hz, 3 H), 7.16 (d, *J* = 7.9 Hz, 2 H), 6.97 (d, *J* = 6.0 Hz, 2 H), 4.92 (dd, J = 9.2 Hz, 4.6, 1 H), 3.63 (s, 3 H), 3.10 (dd, *J* = 15.1, 9.2 Hz, 1 H), 2.82 (dd, *J* = 15.1, 4.5 Hz, 1 H), 2.46 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.89, 168.36, 143.89, 140.18, 138.21, 137.57, 133.92, 129.05, 128.84, 128.73, 128.70, 128.47, 127.86, 127.02, 62.88, 51.50, 44.36, 21.45, 21.38.

HRMS (ESI): *m/z* calculated for [$C_{25}H_{25}NO_2H$] [M+H$^+$]: 372.1959, measured: 372.1954.

IR (neat): *v* = 3028, 2950, 2922, 1739, 1733, 1622, 1605, 1605, 1452, 1436, 1312, 1295, 1181, 1164, 824, 734, 701 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(p-tolyl)propanoate (3bb)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-methyl-4-vinylbenzene (**2b**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bb** (97 mg, 0.252 mmol, 50%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

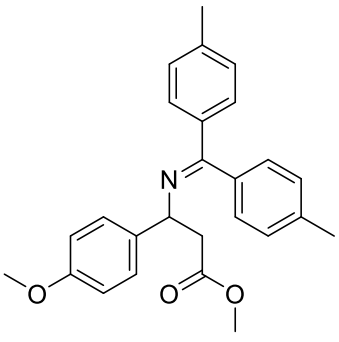
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.2 Hz, 2H), 7.30 - 7.23 (m, 4 H), 7.17 (t, *J* = 8.0 Hz, 4 H), 7.02 (d, *J* = 7.7 Hz, 2 H), 4.93 (dd, *J* = 9.2, 4.5 Hz, 1 H), 3.65 (s, 3 H), 3.12 (dd, *J* = 15.0, 9.2 Hz, 1 H), 2.83 (dd, *J* = 15.0, 4.5 Hz, 1 H), 2.48 (s, 3 H), 2.41 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.94, 168.08, 140.97, 140.09, 138.17, 137.69, 136.55, 134.01, 129.17, 128.85, 128.75, 128.70, 127.93, 126.90, 62.66, 51.45, 44.43, 21.46, 21.38, 21.17.

HRMS (ESI): *m/z* calculated for [$C_{26}H_{27}NO_2H$] [M+H$^+$]: 386.2115, measured: 386.2113.

IR (neat): *v* = 3024, 2950, 2922, 1740, 1622, 1605, 1511, 1436, 1311, 1276, 1261, 1163, 822, 764, 750 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(4-methoxyphenyl)propanoate (3bc)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-methoxy-4-vinylbenzene (**2c**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bc** (85 mg, 0.212 mmol, 42%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.1 Hz, 2 H), 7.28 - 7.22 (m, 4 H), 7.16 (d, *J* = 7.9 Hz, 2 H), 6.98 (d, *J* = 7.8 Hz, 2 H), 6.87 (d, *J* = 6.9 Hz, 2 H), 4.88 (dd, *J* = 8.9, 4.6 Hz, 1 H), 3.82 (s, 3 H), 3.62 (s, 3 H), 3.06 (dd, *J* = 15.1, 9.1 Hz, 1 H), 2.80 (dd, *J* = 15.0, 4.8 Hz, 1 H), 2.46 (s, 3 H), 2.39 (s, 3 H).

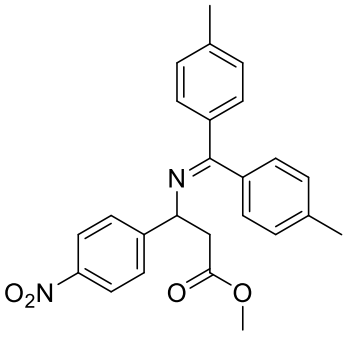
^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.93, 167.99, 158.53, 140.09, 138.15, 137.63, 136.09, 133.98, 128.83, 128.70, 128.68, 128.03, 127.86, 113.81, 62.27, 55.23, 51.44, 44.41, 21.43, 21.36.

HRMS (ESI): *m/z* calculated for [$C_{26}H_{27}NO_3H$] [M+H$^+$]: 402.2064, measured: 402.2062.

IR (neat): *v* = 3025, 2995, 2951, 2923, 2836, 1737, 1605, 1510, 1437, 1358, 1295, 1247, 1163,

1110, 1035, 828, 764, 750, 736 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(4-nitrophenyl)propanoate (3bd)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-nitro-4-vinylbenzene (**2d**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bd** (130 mg, 0.313 mmol, 63%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

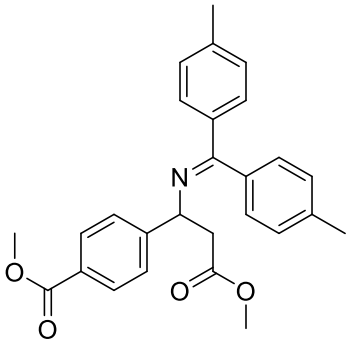
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.8 Hz, 2 H), 7.58 (d, *J* = 8.3 Hz, 2 H), 7.50 (d, *J* = 8.7 Hz, 2 H), 7.26 (d, *J* = 7.7 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 6.92 (d, *J* = 7.6 Hz, 2 H), 5.01 (dd, *J* = 8.5, 5.1 Hz, 1 H), 3.63 (s, 3 H), 3.06 (dd, *J* = 15.3, 8.5 Hz, 1 H), 2.83 (dd, *J* = 15.3, 5.2 Hz, 1 H), 2.46 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.15, 169.75, 151.27, 147.02, 140.75, 138.62, 136.99, 133.52, 129.09, 128.82, 128.78, 127.98, 127.53, 123.77, 62.25, 51.66, 43.85, 21.43, 21.39.

HRMS (ESI): *m/z* calculated for [$C_{25}H_{24}N_2O_4H$] [M+H^+]: 417.1809, measured: 417.1808.

IR (neat): *v* = 3026, 2950, 2921, 2851, 1740, 1604, 1522, 1436, 1346, 1312, 1296, 1267, 1166, 856, 827, 750, 701 cm^{-1}.

Methyl 4-(1-((di-p-tolylmethylene)amino)-3-methoxy-3-oxopropyl)benzoate (3be)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 4-vinylbenzoate (**2e**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3be** (137 mg, 0.319 mmol, 64%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.3 Hz, 2 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.1 Hz, 2 H), 7.24 (d, *J* = 7.7 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 4.98 (dd, *J* = 9.0, 4.6 Hz, 1 H), 3.93 (s, 3H), 3.62 (s, 3H), 3.09 (dd, *J* = 15.1, 9.0 Hz, 1H), 2.82 (dd, *J* = 15.3, 4.7 Hz, 1H), 2.45 (s, 3H), 2.39 (s, 3H).

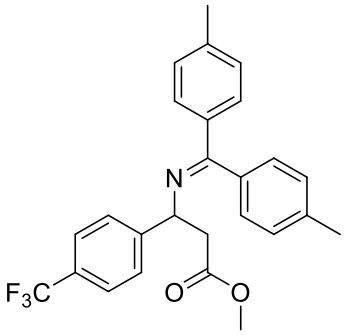
^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.51, 169.13, 167.02, 149.12, 140.44, 138.38, 137.30, 133.74, 129.85, 128.95, 128.92, 128.76, 128.76, 127.70, 127.07, 62.64, 52.07, 51.55, 44.06, 21.43, 21.38.

HRMS (ESI): *m/z* calculated for [$C_{27}H_{27}NO_4H$] [M+H^+]: 430.2013, measured: [$C_{27}H_{27}NO_4H$] [M+H^+]:430.2010.

IR (neat): *v* = 3026, 2995, 2951, 2923, 1724, 1607, 1436, 1311, 1279, 1181, 1113, 1019, 824, 773, 734, 708 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(4-(trifluoromethyl)phenyl)propanoate (3bf)

According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-(trifluoromethyl)-4-vinylbenzene (**2f**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bf** (137 mg, 0.312 mmol, 62%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl



acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.0 Hz, 4 H), 7.41 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 6.90 (d, *J* = 7.6 Hz, 2 H), 4.94 (dd, *J* = 8.9, 4.8 Hz, 1 H), 3.58 (s, 3 H), 3.03 (dd, *J* = 15.2, 8.8 Hz, 1 H), 2.77 (dd, *J* = 15.2, 4.8 Hz, 1 H), 2.41 (s, 3 H), 2.34 (s, 3 H).

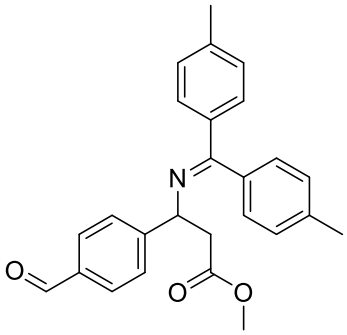
^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.46, 169.19, 147.87, 140.53, 138.46, 137.23, 133.69, 129.73, 129.41, 129.09(q, *J* = 32.4 Hz), 129.00, 128.78, 128.76, 127.68, 127.43, 125.49, 125.45, 125.42, 125.38 (q, *J* = 3.8 Hz), 128.30, 125.60, 122.90, 120.19(q, *J* = 271.8 Hz),62.46, 51.59, 44.07, 21.43, 21.38.

^{19}F NMR (377 MHz, $CDCl_3$): δ = -62.35.

HRMS (ESI): *m/z* calculated for [$C_{26}H_{24}F_3NO_2H$] [M+H$^+$]: 440.1832, measured: 440.1828.

IR (neat): *v* = 2921, 2850, 1740, 1619, 1605, 1437, 1417, 1325, 1275, 1266, 1165, 1125, 1068, 829, 764, 750 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(4-formylphenyl)propanoate (3bg)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 4-vinylbenzaldehyde (**2g**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bg** (145 mg, 0.363 mmol, 73%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

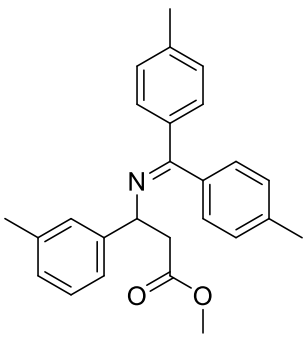
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.59 (d, *J* = 8.1 Hz, 2 H), 7.50 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 7.7 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.93 (d, *J* = 7.6 Hz, 2 H), 4.99 (dd, *J* = 8.8, 4.8 Hz, 1 H), 3.62 (s, 3 H), 3.08 (dd, *J* = 15.2, 8.8 Hz, 1 H), 2.83 (dd, *J* = 15.2, 4.9 Hz, 1 H), 2.45 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.03, 171.38, 169.33, 150.88, 140.56, 138.47, 137.20, 135.40, 133.66, 130.04, 129.00, 128.79, 128.77, 127.75, 127.64, 62.69, 51.61, 43.97, 21.44, 21.39.

HRMS (ESI): *m/z* calculated for [$C_{26}H_{25}NO_3H$] [M+H$^+$]: 400.1098, measured: 400.1096.

IR (neat): *v* = 3027, 2952, 2923, 2735, 1739, 1704, 1622, 1606, 1436, 1295, 1209, 1166, 828, 735 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(m-tolyl)propanoate (3bh)



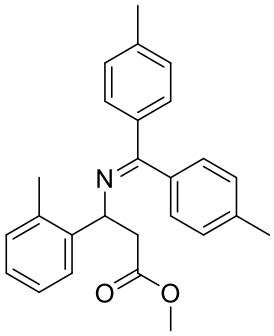
According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-methyl-3-vinylbenzene (**2h**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bh** (100 mg, 0.2597 mmol, 52%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (dd, *J* = 8.2, 1.5 Hz, 2 H), 7.20 (d, *J* = 7.7 Hz, 2 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 7.11 (d, *J* = 7.5 Hz, 3 H), 7.03 (dd, *J* = 15.2 Hz, 6.9, 2 H), 6.93 (d, *J* = 6.4 Hz, 2 H), 4.85 (dd, *J* = 9.3, 4.4 Hz, 1 H), 3.57 (s, 3 H), 3.05 (dd, *J* = 13.6, 9.4 Hz, 1 H), 2.76 (dd, *J* = 15.0, 4.4 Hz, 1 H), 2.40 (s, 3 H), 2.33 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.95, 168.28, 143.87, 140.14, 138.20, 138.04, 137.68, 133.97,

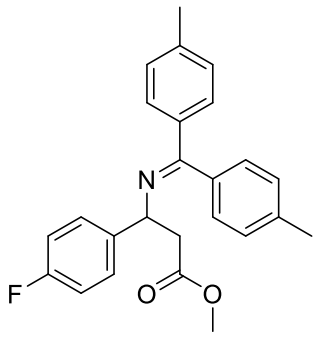
128.83, 128.78, 128.72, 128.35, 127.96, 127.80, 127.69, 124.05, 62.91, 51.49, 44.46, 21.58, 21.48, 21.40.
HRMS (ESI): *m/z* calculated for [$C_{26}H_{27}NO_2H$] [M+H$^+$]: 386.2115, measured: 386.2110.
IR (neat): *v* = 3025, 2950, 2922, 2867, 1740, 1623, 1606, 1435, 1311, 1294, 1266, 1233, 1181, 1163, 824, 786, 734, 706 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(o-tolyl)propanoate (3bi)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-methyl-2-vinylbenzene (**2i**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bi** (100 mg, 0.26 mmol, 52%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50: 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.6 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 3 H), 7.15 - 7.07 (m, 3 H), 7.03 (d, *J* = 7.4 Hz, 1 H), 6.84 (d, *J* = 7.5 Hz, 2 H), 5.05 (dd, *J* = 9.7, 3.7 Hz, 1 H), 3.60 (s, 3 H), 3.04 (dd, *J* = 15.2, 9.7 Hz, 1 H), 2.66 (dd, *J* = 15.2, 3.7 Hz, 1 H), 2.40 (s, 3 H), 2.35 (s, 3 H), 1.91 (s, 3 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.06, 168.31, 142.75, 140.09, 137.98, 137.53, 134.39, 134.13, 130.14, 128.87, 128.66, 127.60, 126.53, 126.27, 59.03, 51.47, 43.44, 21.39, 21.35, 18.89.
HRMS (ESI): *m/z* calculated for [$C_{26}H_{27}NO_2H$] [M+H$^+$]: 386.2115, measured: 386.2114.
IR (neat): *v* = 3023, 2990, 2950, 1739, 1604, 1436, 1275, 1261, 1165, 823, 764, 750 cm^{-1}.

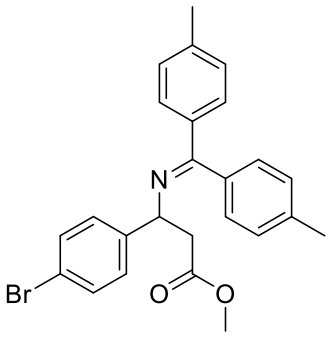
Methyl 3-((di-p-tolylmethylene)amino)-3-(4-fluorophenyl)propanoate (3bj)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-fluoro-4-vinylbenzene(**2j**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bj** (135 mg, 0.347 mmol, 69%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.1 Hz, 2 H), 7.32 - 7.25 (m, 4 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.06 - 6.95 (m, 4 H), 4.93 (dd, *J* = 8.9, 4.8 Hz, 1 H), 3.64 (s, 3 H), 3.07 (dd, *J* = 15.1, 8.9 Hz, 1 H), 2.81 (dd, *J* = 15.1, 4.8 Hz, 1 H), 2.47 (s, 3 H), 2.40 (s, 3 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.70, 168.49, 163.04, 160.61 (d, *J* = 244.9 Hz), 140.34, 139.66, 139.63 (d, *J* = 3.1 Hz), 138.31, 137.42, 133.85, 128.94, 128.76, 128.74 (d, *J* = 2.2 Hz), 128.59, 128.51, 127.76, 115.38, 115.17 (d, *J* = 21.1 Hz), 62.15, 51.52, 44.38, 21.45, 21.39.
^{19}F NMR (377 MHz, $CDCl_3$): δ = -115.59.
HRMS (ESI): *m/z* calculated for [$C_{25}H_{24}FNO_2H$] [M+H$^+$]: 390.1864, measured: [$C_{25}H_{24}FNO_2H$] [M+H$^+$]: 390.1860.
IR (neat): *v* = 3026, 2995, 2951, 2923, 1739, 1622, 1604, 1568, 1506, 1435, 1407, 1359, 1311, 1295, 1156, 1182, 1121, 1050, 1016, 829, 734 cm^{-1}.

Methyl 3-(4-bromophenyl)-3-((di-p-tolylmethylene)amino)propanoate (3bk)

According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-bromo-4-vinylbenzene(**2k**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bk** (142 mg, 0.316 mmol, 63%),



purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

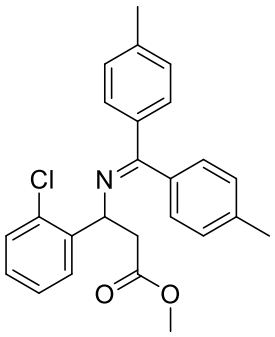
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.2 Hz, 2 H), 7.46 (d, *J* = 6.8 Hz, 2 H), 7.27 (d, *J* = 7.7 Hz, 2 H), 7.23 (d, *J* = 7.0 Hz, 2 H), 7.18 (d, *J* = 7.9 Hz, 2 H), 6.98 (d, *J* = 7.5 Hz, 2 H), 4.91 (dd, *J* = 9.0, 4.8 Hz, 1 H), 3.64 (s, 3 H), 3.07 (dd, *J* = 15.2, 8.9 Hz, 1 H), 2.81 (dd, *J* = 15.2, 4.9 Hz, 1 H), 2.47 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.57, 168.81, 142.96, 140.40, 138.37, 137.36, 133.79, 131.59, 128.97, 128.82, 128.77, 128.74, 127.74, 120.84, 62.26, 51.56, 44.18, 21.48, 21.42.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{24}{}^{79}BrNO_2H]$ $[M+H^+]$: 450.1064, $[C_{25}H_{24}{}^{81}BrNO_2H]$ $[M+H^+]$: 452.1043, measured: $[C_{25}H_{24}{}^{81}BrNO_2H]$ $[M+H^+]$: 452.1040.

IR (neat): *v* = 3026, 2994, 2950, 2922, 1740, 1622, 1605, 1486, 1435, 1294, 1164, 1011, 825, 734 cm^{-1}.

Methyl 3-(2-chlorophenyl)-3-((di-p-tolylmethylene)amino)propanoate (3bl)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-chloro-2-vinylbenzene (**2l**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bl** (114 mg, 0.281 mmol, 56%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

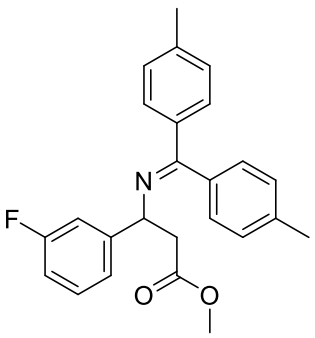
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 7.7, 1.8 Hz, 1 H), 7.67 - 7.60 (m, 2 H), 7.39 - 7.15 (m, 8 H), 6.92 (d, *J* = 7.7 Hz, 2 H), 5.36 (dd, *J* = 9.5, 3.6 Hz, 1 H), 3.66 (s, 3 H), 3.01 (dd, *J* = 15.1, 9.5 Hz, 1 H), 2.89 (dd, *J* = 15.1, 3.7 Hz, 1 H), 2.45 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.62, 169.47, 141.80, 140.34, 138.25, 137.53, 133.84, 131.79, 129.30, 129.28, 128.94, 128.87, 128.74, 127.97, 127.66, 127.14, 59.11, 51.53, 42.75, 21.46, 21.40.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{24}{}^{35}ClNO_2H]$ $[M+H^+]$: 406.1569, $[C_{25}H_{24}{}^{37}ClNO_2H]$ $[M+H^+]$: 408.1539, measured: 406.1572.

IR (neat): *v* = 3026, 2950, 2922, 1741, 1621, 1604, 1569, 1508, 1470, 1437, 1359, 1295, 1261, 1181, 1165, 1046, 1033, 1021, 821, 758, 736 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(3-fluorophenyl)propanoate (3bm)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1-fluoro-3-vinylbenzene (**2m**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bm** (101 mg, 0.259 mmol, 52%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.9 Hz, 2 H), 7.28 (dd, *J* = 6.9, 3.4 Hz, 3 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.14 - 7.06 (m, 2 H), 7.03 - 6.90 (m, 3 H), 4.94 (dd, *J* = 9.0, 4.7 Hz, 1 H), 3.64 (s, 3 H), 3.08 (dd, *J* = 15.2, 9.0 Hz, 1 H), 2.82 (dd, *J* = 15.2, 4.7 Hz, 1 H), 2.47 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.57, 168.88, 164.13, 161.69 (d, *J* = 245.5 Hz), 146.51, 146.44 (d,

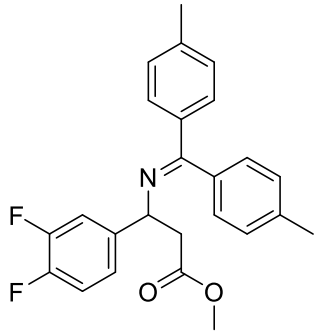
J = 7.0 Hz), 140.41, 138.37, 137.36, 133.75, 129.94, 129.86 (d, *J* = 8.1 Hz), 128.95, 128.78, 128.76, 127.76, 122.57, 122.55 (d, *J* = 2.7 Hz), 114.12, 114.03 (d, *J* = 8.6 Hz), 113.90, 113.82 (d, *J* = 7.9 Hz), 62.34, 51.54, 44.22, 21.44, 21.38.

^{19}F NMR (376 MHz, $CDCl_3$) :δ = -112.82.

HRMS (ESI): *m/z* calculated for [$C_{25}H_{24}FNO_2H$] [M+H$^+$]: 390.1864, measured: 390.1867.

IR (neat): *v* = 3026, 2951, 2922, 1740, 1605, 1590, 1486, 1437, 1311, 1294, 1276, 1262, 1181, 1166, 824, 785, 764, 750 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(3,4-difluorophenyl)propanoate (3bn)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1,2-difluoro-4-vinylbenzene (**2n**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bn** (135 mg, 0.332 mmol, 66%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 8.2, 2.7 Hz, 2 H), 7.32 - 7.25 (m, 3 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 7.11 (d, *J* = 8.5 Hz, 1 H), 7.06 - 6.96 (m, 3 H), 4.91 (dt, *J* = 8.4, 4.0 Hz, 1 H), 3.65 (s, 3 H), 3.05 (dd, *J* = 15.2, 8.7 Hz, 1 H), 2.81 (dd, *J* = 15.2, 5.0 Hz, 1 H), 2.48 (s, 3 H), 2.41 (s, 3 H).

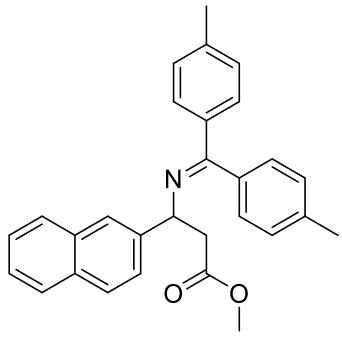
^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.41, 169.03, 151.60, 151.48, 150.66, 150.53 (dd, *J* = 95.0, 12.7 Hz), 149.14, 149.02, 148.20, 148.08 (dd, *J* = 94.2, 12.6 Hz), 140.96, 140.91, 140.87 (t, *J* = 4.5 Hz), 140.56, 138.49, 137.21, 133.66, 129.03, 128.81, 128.78, 127.67, 122.88, 122.85, 122.82, 122.79 (dd, *J* = 6.1, 3.6 Hz), 117.19, 117.02 (d, *J* = 17.0 Hz), 116.12, 115.94 (d, *J* = 17.7 Hz), 61.82, 51.57, 44.21, 21.43, 21.38.

^{19}F NMR (377 MHz, $CDCl_3$): δ = -137.47, -140.07.

HRMS (ESI): *m/z* calculated for [$C_{25}H_{23}F_2NO_2H$] [M+H$^+$]: 408.1770, measured: 408.1766.

IR (neat): *v* = 3026, 2951, 2923, 1740, 1621, 1606, 1515, 1435, 1312, 1276, 1165, 1114, 824, 765, 750 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(naphthalen-2-yl)propanoate (3bo)



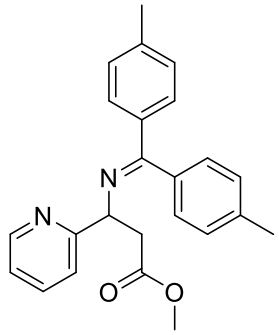
According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 2-vinylnaphthalene (**2o**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bo** (90 mg, 0.213 mmol, 43%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 9.0, 4.7 Hz, 3 H), 7.76 (d, *J* = 1.7 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 7.56 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.55 - 7.45 (m, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 7.6 Hz, 2 H), 5.14 (dd, *J* = 9.1, 4.5 Hz, 1 H), 3.66 (s, 3 H), 3.21 (dd, *J* = 15.1, 9.2 Hz, 1 H), 2.95 (dd, *J* = 15.1, 4.6 Hz, 1 H), 2.49 (s, 3 H), 2.43 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.87, 168.75, 141.49, 140.28, 138.30, 137.64, 133.97, 133.54, 132.75, 128.90, 128.83, 128.77, 128.20, 128.00, 127.92, 127.69, 125.96, 125.66, 125.55, 125.39, 63.07, 51.54, 44.42, 21.48, 21.42.

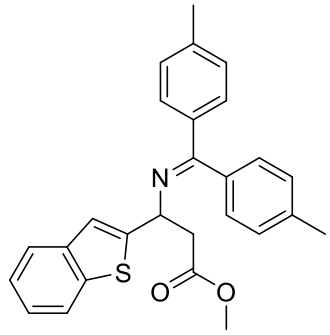
HRMS (ESI): *m/z* calculated for [$C_{29}H_{27}NO_2H$] [M+H$^+$]: 422.2115, measured: 422.2113.
IR (neat): ν = 3023, 2921, 1739, 1622, 1604, 1276, 1261, 1665, 822, 764, 750 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-(pyridin-2-yl)propanoate (3bp)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 2-vinylpyridine (**2p**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bp** (115 mg, 0.309 mmol, 62%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 8:1).
^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.55 (d, *J* = 3.1 Hz, 1 H), 7.64 (t, *J* = 8.8 Hz, 3 H), 7.38 (d, *J* = 7.9 Hz, 1 H), 7.23 (d, *J* = 8.1 Hz, 2 H), 7.15 (dd, *J* = 11.2, 6.4 Hz,3 H), 7.01 (d, *J* = 7.9 Hz, 2 H), 5.11 (dd, *J* = 8.6, 4.6 Hz, 1 H), 3.62 (s, 3 H), 3.16 (dd, *J* = 15.2, 4.6 Hz, 1 H), 3.05 (dd, *J* = 15.2, 8.6 Hz, 1 H), 2.41 (s, 3 H), 2.39 (s, 3 H).
^{13}C NMR (101 MHz, CDCl$_3$): δ = 171.98, 169.81, 162.23, 149.08, 140.43, 138.36, 137.42, 136.56, 133.62, 129.00, 128.89, 128.75, 127.69, 122.02, 121.74, 64.23, 51.45, 42.23, 21.40, 21.39.
HRMS (ESI): *m/z* calculated for [$C_{24}H_{24}N_2O_2H$] [M+H$^+$]: 373.1911, measured: 373.1907.
IR (neat): ν = 3647, 3025, 2951, 2923, 1739, 1622, 1605, 1588, 1434, 1295, 1164, 822, 734 cm^{-1}.

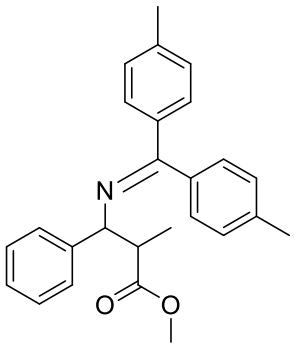
Methyl 3-(benzo[b]thiophen-2-yl)-3-((di-p-tolylmethylene)amino)propanoate (3bq)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 2-vinylbenzo[b]thiophene (**2q**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bq** (80 mg, 0.187 mmol, 38%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.82 (d, *J* = 7.7 Hz, 1 H), 7.71 (d, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 8.1 Hz, 2 H), 7.40 - 7.25 (m, 4 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.12 - 7.05 (m, 3 H), 5.31 (dd, *J* = 8.7, 5.0 Hz, 1 H), 3.66 (s, 3 H), 3.17 (dd, *J* = 15.4, 8.6 Hz, 1 H), 2.99 (dd, *J* = 15.4, 5.0 Hz, 1 H), 2.46 (s, 3 H), 2.41 (s, 3 H).
^{13}C NMR (101 MHz, CDCl$_3$): δ = 171.25, 169.65, 148.13, 140.58, 139.54, 139.45, 138.51, 137.18, 133.32, 129.00, 128.93, 128.79, 127.81, 124.09, 123.79, 123.31, 122.37, 119.47, 59.26, 51.60, 44.35, 21.44, 21.40.
HRMS (ESI): *m/z* calculated for [$C_{27}H_{25}NO_2SH$] [M+H$^+$]: 428.1679, measured: 428.1680.
IR (neat): ν = 3027, 2951, 2922, 1739, 1624, 1606, 1436, 1313, 1295, 1233, 1153, 828, 747, 728 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-2-methyl-3-phenylpropanoate (3br)

According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and prop-1-en-1-ylbenzene(**2r**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3br** (101 mg, 0.262 mmol, 53%)(D.R:1.5:1), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl



acetate = 50:1) .

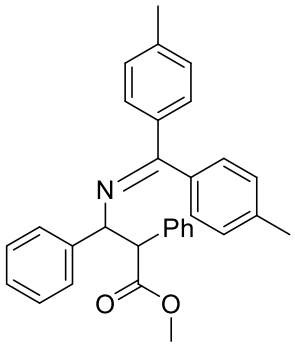
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 6.2 Hz, 1.81 H), 7.51 (d, *J* = 7.6 Hz, 0.70 H), 7.40 - 7.25 (m, 6.69 H), 7.19 (d, *J* = 8.5 Hz, 3.45 H), 7.15 - 7.06 (m, 8.03 H), 7.05 - 6.96 (m, 3.27 H), 4.99 (dd, *J* = 16.2, 10.9 Hz, 1.25 H), 4.41 (d, *J* = 12.2 Hz, 1.25 H), 3.71 (s, 3 H), 3.41 (s, 0.97 H), 2.49 (s, 4 H), 2.42 (s, 2 H), 2.35 (s, 1.37 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.33, 172.50, 168.61, 167.82, 142.62, 141.81, 140.17, 139.89, 138.11, 137.79, 137.62, 136.85, 135.76, 134.03, 133.85, 129.30, 128.93, 128.75, 128.72, 128.65, 128.57, 128.52, 128.34, 128.21, 128.16, 128.04, 127.96, 127.89, 127.79, 127.71, 127.64, 127.58, 127.33, 127.27, 127.21, 126.82, 70.55, 69.54, 61.05, 60.48, 51.94, 51.62, 21.52, 21.47, 21.41, 21.35.

HRMS (ESI): *m/z* calculated for [$C_{26}H_{27}NO_2H$] [$M+H^+$]: 386.2115, measured: 386.2114.

IR (neat): *v* = 3084, 3060, 3027, 2978, 2949, 2923, 1738, 1622, 1605, 1453, 1434, 1312, 1295, 1255, 1181, 1165, 1113, 1056, 1028, 1019, 824, 733, 702 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-2,3-diphenylpropanoate (3bs)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and (E)-1,2-diphenylethene (**2s**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bs** (77 mg, 0.172 mmol, 35%) (D.R:3.1:1), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

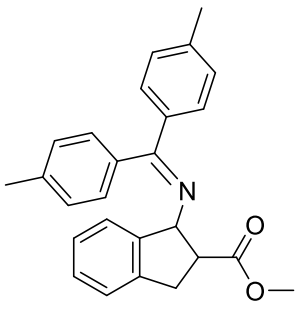
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.2 Hz, 2 H), 7.56 (d, *J* = 8.2 Hz, 1.41 H), 7.32 - 7.22 (m, 12.29 H), 7.16 (dd, *J* = 11.7, 8.0 Hz, 3.41 H), 6.91 (t, *J* = 6.5 Hz, 3.41 H), 4.66 (d, *J* = 7.6 Hz, 1 H), 4.50 (d, *J* = 9.4 Hz, 0.7 H), 3.68 (s, 2 H), 3.44 (s, 3 H), 3.29 - 3.20 (m, 0.71 H), 3.12 (p, *J* = 7.0 Hz, 1 H), 2.47 (d, *J* = 5.6 Hz, 5.12 H), 2.39 (d, *J* = 7.0 Hz, 5.12 H), 1.24 (d, *J* = 7.0 Hz, 3.03 H), 0.95 (d, *J* = 7.1 Hz, 2.10 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.02, 175.22, 168.34, 167.87, 143.17, 142.35, 140.18, 140.03, 138.16, 138.09, 137.76, 137.60, 133.98, 133.92, 128.92, 128.72, 128.65, 128.31, 128.18, 128.13, 128.03, 127.83, 127.58, 127.13, 126.93, 69.83, 68.29, 51.53, 51.26, 48.53, 48.32, 21.47, 21.42, 21.38, 21.36, 14.42, 13.95.

HRMS (ESI): *m/z* calculated for [$C_{31}H_{29}NO_2H$] [$M+H^+$]: 448.2272, measured: 448.2272.

IR (neat): *v* = 3028, 2921, 1736, 1676, 1603, 1509, 1454, 1276, 1261, 1162, 823, 764, 750, 699 cm^{-1}.

***Trans*-Methyl 1-((di-p-tolylmethylene)amino)-2,3-dihydro-1H-indene-2-carboxylate (3bt)**



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and 1H-indene (**2t**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bt** (106 mg, 0.277 mmol, 55%) (D.R>20:1), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 7.9 Hz, 2 H), 7.29 - 7.24 (m, 5 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.14 - 7.07 (m, 1 H), 5.35 (d, *J* = 8.2 Hz, 1 H), 3.73 (s, 4 H), 3.39 (dd, *J* = 15.8, 8.9

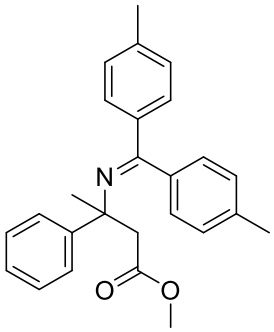
Hz, 1 H), 3.24 (dd, *J* = 15.8, 10.3 Hz, 1 H), 2.45 (s, 3 H), 2.42 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.53, 169.90, 143.28, 140.86, 140.44, 138.34, 137.38, 133.82, 129.10, 128.95, 128.81, 128.00, 127.70, 126.88, 124.57, 123.99, 69.73, 52.70, 51.75, 34.74, 21.42.

HRMS (ESI): *m/z* calculated for [$C_{26}H_{25}NO_2H$] [M+H$^+$]: 384.1959, measured: 384.1960.

IR (neat): *v* = 3025, 2951, 2923, 2857, 1738, 1619, 1603, 1566, 1507, 1459, 1435, 1366, 1329, 1311, 1293, 1244, 1181, 1168, 1113, 1056, 1022, 1000, 824, 747, 738 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3-phenylbutanoate (3bu)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and prop-1-en-2-ylbenzene (**2u**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bu** (120 mg, 0.312 mmol, 62%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

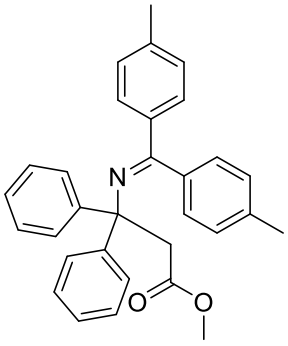
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.0 Hz, 2 H), 7.21 (tt, *J* = 4.9, 2.3 Hz, 5 H), 7.13 (d, *J* = 7.9 Hz, 2 H), 6.92 (d, *J* = 7.7 Hz, 2 H), 6.52 (d, *J* = 7.5 Hz, 2 H), 3.62 (s, 3 H), 3.21 (d, *J* = 13.7 Hz, 1 H), 2.94 (d, *J* = 13.7 Hz, 1 H), 2.38 (s, 3 H), 2.33 (s, 3 H), 1.58 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.81, 166.93, 148.62, 139.89, 139.25, 137.15, 135.85, 128.63, 128.60, 128.36, 127.95, 127.86, 127.83, 126.32, 62.75, 52.07, 51.23, 25.40, 21.31, 21.28.

HRMS (ESI): *m/z* calculated for [$C_{26}H_{27}NO_2H$] [M+H$^+$]: 386.2115, measured: 386.2115.

IR (neat): *v* = 3057, 3024, 2949, 2924, 1738, 1624, 1604, 1507, 1494, 1446, 1436, 1311, 1280, 1182, 1161, 1114, 1072, 1014, 826, 785, 766, 732, 699 cm^{-1}.

Methyl 3-((di-p-tolylmethylene)amino)-3,3-diphenylpropanoate (3bv)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and ethene-1,1-diyldibenzene (**2v**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bv** (185 mg, 0.414 mmol, 83%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

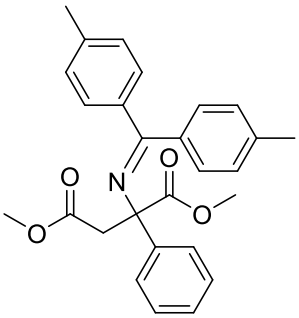
^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.64 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 8.3 Hz, 4 H), 7.31 - 7.14 (m, 8 H), 6.92 (d, *J* = 7.5 Hz, 2 H), 6.51 (d, *J* = 8.0 Hz, 2 H), 3.44 (s, 3 H), 3.23 (s, 2 H), 2.40 (s, 3 H), 2.36 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.76, 167.94, 149.12, 140.08, 139.72, 136.98, 135.80, 128.71, 128.52, 128.02, 127.79, 127.76, 127.55, 126.22, 67.16, 51.33, 44.77, 21.41, 21.38.

HRMS (ESI): *m/z* calculated for [$C_{31}H_{29}NO_2H$] [M+H$^+$]: 448.2272, measured: 448.2271.

IR (neat): v = 3084, 3057, 3024, 2949, 2923, 2868, 1738, 1626, 1604, 1506, 1491, 1446, 1322, 1279, 1209, 1180, 1150, 1020, 826, 753, 732, 699 cm^{-1}.

Dimethyl 2-((di-p-tolylmethylene)amino)-2-phenylsuccinate (3bw)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and methyl 2-phenylacrylate (**2w**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bw** (138 mg, 0.322 mmol, 64%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 15:1) .

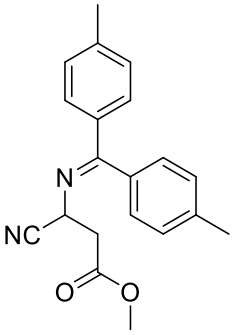
^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.67 - 7.57 (dd, *J* = 8.0, 10.7 Hz, 4 H), 7.39 - 7.29 (m, 3 H), 7.21 - 7.12 (dd, *J* = 7.9, 12.3 Hz, 4 H), 7.01 - 6.94 (d, *J* = 7.8 Hz, 2 H), 3.59 - 3.55 (s, 3 H), 3.54 - 3.51 (s, 3 H), 3.44 - 3.36 (d, *J* = 14.3 Hz, 1 H), 3.26 - 3.18 (d, *J* = 14.3 Hz, 1 H), 2.45 - 2.39 (d, *J* = 5.9 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.33, 170.30, 169.25, 143.13, 140.58, 138.69, 138.16, 134.42, 128.81, 128.72, 128.39, 128.24, 128.01, 127.35, 126.51, 69.76, 52.33, 51.51, 44.86, 21.42, 21.39.

HRMS (ESI): *m/z* calculated for [$C_{27}H_{27}NO_4H$] [$M+H^+$]: 430.2013, measured: 430.2011.

IR (neat): *v* = 3025, 2950, 1732, 1627, 1604, 1507, 1494, 1447, 1434, 1311, 1280, 1233, 1216, 1181, 1149, 1114, 1065, 1038, 1022, 995, 910, 823, 731, 699, 666, 648, 630, 556, 487 cm^{-1}.

Methyl 3-cyano-3-((di-p-tolylmethylene)amino)propanoate (3bx)



According to the **General Procedure C,** using oxime ester **1b** (0.5 mmol, 1 equiv) and acrylonitrile (**2x**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **3bx** (84 mg, 0.263 mmol, 53%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

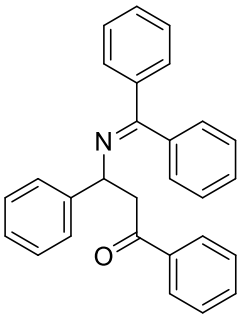
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.0, 2 H), 7.36 (d, *J* = 7.8 Hz, 2 H), 7.18 (t, *J* = 7.8 Hz, 4 H), 4.71 (dd, *J* = 8.2, 5.5 Hz, 1 H), 3.71 (s, 3 H), 3.09 (dd, *J* = 16.3, 8.2 Hz, 1 H), 3.00 (dd, *J* = 16.3, 5.6 Hz, 1 H), 2.48 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.86, 169.42, 141.76, 139.49, 135.97, 132.35, 129.61, 129.16, 128.93, 127.45, 118.72, 52.11, 48.98, 39.23, 21.44.

HRMS (ESI): *m/z* calculated for [$C_{20}H_{20}N_2O_2H$] [$M+H^+$]: 321.1598, measured: 321.1593.

IR (neat): *v* = 3028, 2998, 2953, 1743, 1619, 1602, 1566, 1508, 1438, 1408, 1364, 1314, 1297, 1273, 1182, 1115, 1046, 1021, 991, 824, 783, 735 cm^{-1}.

3-((diphenylmethylene)amino)-1,3-diphenylpropan-1-one (5aa)



According to the **General Procedure D,** using oxime ester **4a** (0.5 mmol, 1 equiv) and styrene(**2a**) (0.55 mmol, 1.1 equiv), the reaction afforded solid **5aa** (87 mg, 0.223 mmol, 45%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

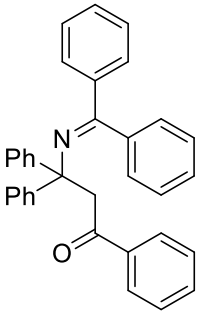
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 - 7.95 (m, 2 H), 7.67 - 7.62 (m, 2 H), 7.58 - 7.52 (m, 1 H), 7.48 - 7.42 (m, 5 H), 7.40 - 7.26 (m, 8 H), 7.15 - 7.06 (m, 2 H), 5.16 (dd, *J* = 8.7, 4.2 Hz, 1 H), 3.94 (dd, *J* = 15.9, 8.7 Hz, 1 H), 3.36 (dd, *J* = 15.9, 4.2 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.40, 168.11, 144.39, 139.92, 137.45, 136.94, 132.89, 129.95, 128.64, 128.52, 128.50, 128.39, 128.32, 128.22, 127.95, 127.84, 127.11, 127.00, 62.93, 48.52.

HRMS (ESI): *m/z* calculated for [$C_{28}H_{23}NOH$] [M+H$^+$]: 390.1853, measured: 390.1853.

IR (neat): *v* = 3082, 3060, 3027, 2925, 2854, 1687, 1623, 1598, 1578, 1492, 1447, 1393, 1360, 1315, 1286, 1200, 1179, 1027, 1001, 988, 781, 750, 698 cm^{-1}.

3-((diphenylmethylene)amino)-1,3,3-triphenylpropan-1-one (5av)



According to the **General Procedure D,** using oxime ester **4a** (0.5 mmol, 1 equiv) and ethene-1,1-diyldibenzene (**2v**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5da** (214mg, 0.460 mmol, 92.0%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

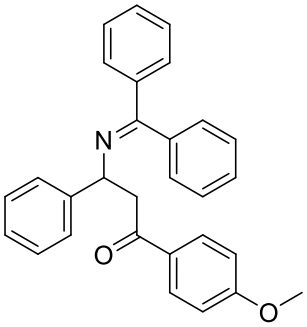
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.5 Hz, 2 H), 7.53 (d, *J* = 7.8 Hz, 2 H), 7.45 - 7.35 (m, 8 H), 7.29 - 7.13 (m, 9 H), 7.05 (t, *J* = 7.6 Hz, 2 H), 6.63 (d, *J* = 7.5 Hz, 2 H), 3.88 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.10, 166.41, 149.49, 141.97, 138.94, 138.16, 132.16, 129.80, 128.54, 128.01, 127.91, 127.86, 127.78, 127.60, 127.42, 127.36, 126.14, 67.43, 47.70.

HRMS (ESI): *m/z* calculated for [$C_{34}H_{27}NOH$] [M+H$^+$]: 466.2166, measured: 466.2162.

IR (neat): *v* = 3058, 3023, 2925, 1695, 1672, 1630, 1597, 1579, 1489, 1446, 1350, 1318, 1277, 1216, 1180, 1001, 753, 697, 599, 590 cm^{-1}.

3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (5ba)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and styrene(**2a**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5ba** (105 mg, 0.250 mmol, 50%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

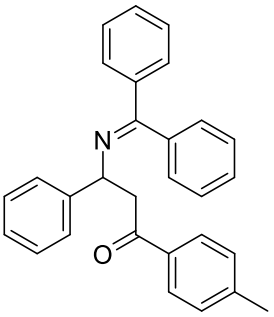
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.8 Hz, 2 H), 7.57 (dd, *J* = 8.0, 1.5 Hz, 2 H), 7.41 - 7.18 (m, 11 H), 7.04 (dd, *J* = 6.5, 2.8 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 5.07 (dd, *J* = 8.7, 4.2 Hz, 1 H), 3.89 - 3.77 (m, 4 H), 3.24 (dd, *J* = 15.7, 4.2 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.92, 167.96, 163.34, 144.48, 139.94, 136.92, 130.62, 130.54, 129.92, 128.63, 128.50, 128.37, 128.21, 127.94, 127.83, 127.11, 126.94, 113.61, 63.03, 55.48, 48.17.

HRMS (ESI): *m/z* calculated for [$C_{29}H_{25}NO_2H$] [M+H$^+$]: 420.1959, measured: 420.1959.

IR (neat): *v* = 3059, 3027, 2933, 2839, 1677, 1600, 1576, 1510, 1491, 1446, 1419, 1360, 1314, 1259, 1205, 1169,1028, 988, 932, 765, 750, 699, 569cm^{-1}.

3-((diphenylmethylene)amino)-3-phenyl-1-(p-tolyl)propan-1-one (5ca)



According to the **General Procedure D,** using oxime ester **4c** (0.5 mmol, 1 equiv) and styrene(**2a**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5ca** (86.7mg, 0.215 mmol, 43%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

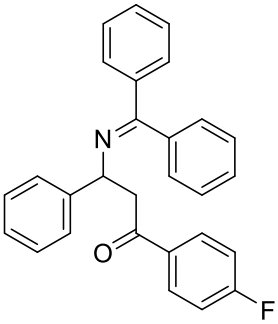
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.3 Hz, 2 H), 7.69 - 7.60 (m, 2 H), 7.45 (dd, *J* = 5.1, 1.9 Hz, 3 H), 7.40 - 7.23 (m, 10 H), 7.16 - 7.06 (m, 2 H), 5.15 (dd, *J* = 8.7, 4.2 Hz, 1 H), 3.92 (dd, *J* = 16.0, 8.7 Hz, 1 H), 3.34 (dd, *J* = 16.0, 4.2 Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.02, 168.02, 144.47, 143.64, 139.96, 136.97, 134.98, 129.93, 129.19, 128.65, 128.51, 128.45, 128.38, 128.21, 127.95, 127.86, 127.12, 126.96, 62.93, 48.41, 21.67.

HRMS (ESI): *m/z* calculated for [$C_{29}H_{25}NOH$] [M+H$^+$]: 404.2009, measured: 404.2006.

IR (neat): *v* = 3082, 3059, 3029, 2920, 1955, 1812, 1683, 1624, 1607, 1576, 1492, 1446, 1407, 1359, 1314, 1288, 1220, 1198, 1180, 1075, 1028, 1000, 982, 944, 912, 812, 772, 699, 649, 570 cm^{-1}.

3-((diphenylmethylene)amino)-1-(4-fluorophenyl)-3-phenylpropan-1-one (5da)



According to the **General Procedure D,** using oxime ester **4d** (0.5 mmol, 1 equiv) and styrene(**2a**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5da** (98 mg, 0.241 mmol, 48%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 8.9, 5.4 Hz, 2 H), 7.65 (d, *J* = 6.8 Hz, 2 H), 7.46 (d, *J* = 3.1 Hz, 3 H), 7.41 - 7.33 (m, 7 H), 7.31 (d, *J* = 6.5 Hz, 1 H), 7.12 (t, *J* = 8.7 Hz, 4 H), 5.14 (dd, *J* = 8.8, 4.3 Hz, 1 H), 3.91 (dd, *J* = 15.9, 8.8, 1 H), 3.32 (dd, *J* = 15.8, 4.2 Hz, 1 H).

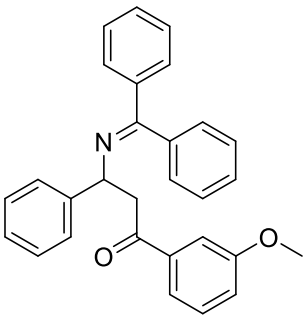
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.86, 168.20, 166.94, 164.42 (d, *J* = 254.3 Hz), 144.26, 139.83, 136.87, 133.90, 133.87 (d, *J* = 2.9 Hz), 131.03, 130.94 (d, *J* = 9.3 Hz), 130.05, 128.63, 128.58, 128.46, 128.25, 127.99, 127.82, 127.08, 115.67, 115.46(d, *J* = 21.9 Hz), 62.99, 48.44.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -105.53.

HRMS (ESI): *m/z* calculated for [$C_{28}H_{22}NOH$] [M+H$^+$]: 408.1759, measured: 408.1758.

IR (neat): *v* = 3060, 2924, 1687, 1624, 1598, 1506, 1492, 1446, 1409, 1360, 1315, 1277, 1234, 1156, 1028, 990, 913, 835, 748, 699, 572 cm^{-1}.

3-((diphenylmethylene)amino)-1-(3-methoxyphenyl)-3-phenylpropan-1-one (5ea)



According to the **General Procedure D,** using oxime ester **4e** (0.5 mmol, 1 equiv) and styrene(**2a**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5ea** (41.9mg, 0.10 mmol, 20%), purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

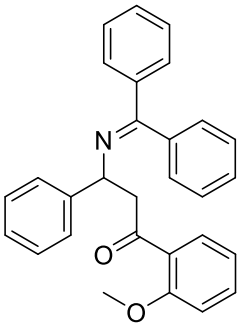
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.1 Hz, 2 H), 7.57 (d, *J* = 7.8 Hz, 1 H), 7.50 (s, 1H), 7.45 (d, *J* = 2.7 Hz, 3 H), 7.34 (p, *J* = 7.8 Hz, 8 H), 7.28 (d, *J* = 6.4 Hz, 1 H), 7.10 (s, 3 H), 5.14 (dd, *J* = 8.4, 4.0 Hz, 1 H), 3.92 (dd, *J* = 16.1, 8.7 Hz, 1 H), 3.86 (s, 3 H), 3.36 (dd, *J* = 15.3, 3.8 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.17, 168.10, 159.79, 144.38, 139.91, 138.79, 136.93, 129.95, 129.48, 128.64, 128.51, 128.39, 128.20, 127.94, 127.84, 127.10, 126.99, 121.06, 119.63, 112.29, 62.89, 55.45, 48.64.

HRMS (ESI): *m/z* calculated for [$C_{29}H_{25}NO_2H$] [$M+H^+$]: 420.1959, measured: 420.1956.

IR (neat): *v* = 3059, 3028, 2939, 2907, 2835, 1736, 1686, 1624, 1597, 1583, 1490, 1464, 1447, 1430, 1358, 1315, 1288, 1267, 1192, 1166, 1075, 1042, 1029, 945, 914, 848, 770, 744, 700, 552 cm^{-1}.

3-((diphenylmethylene)amino)-1-(2-methoxyphenyl)-3-phenylpropan-1-one (5fa)



According to the **General Procedure D,** using oxime ester **4f** (0.5 mmol, 1 equiv) and styrene(**2a**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5fa** (45.2mg, 0.1076 mmol, 22%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

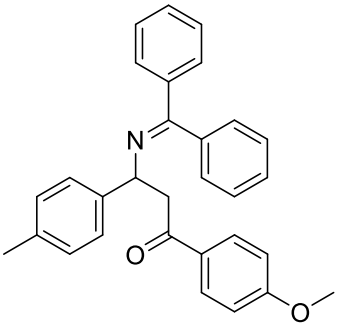
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 - 7.57 (m, 3 H), 7.48 - 7.29 (m, 11 H), 7.25 (q, *J* = 4.1 Hz, 1 H), 7.02 - 6.92 (m, 3 H), 6.90 (s, 1 H), 5.08 (dd, *J* = 9.1, 4.1 Hz, 1 H), 3.81 (s, 4 H), 3.49 (dd, *J* = 16.0, 4.1 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.72, 167.97, 158.27, 144.69, 140.08, 136.98, 133.15, 130.35, 129.83, 128.97, 128.66, 128.37, 128.21, 128.03, 127.90, 127.85, 127.11, 126.72, 120.64, 111.48, 63.07, 55.42, 53.65.

HRMS (ESI): *m/z* calculated for [$C_{29}H_{25}NO_2H$] [$M+H^+$]: 420.1959, measured: 420.1960.

IR (neat): *v* = 3058, 3026, 2941, 2838, 1674, 1597, 1578, 1485, 1465, 1437, 1290, 1244, 1180, 1163, 1026, 781, 699 cm^{-1}.

3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(p-tolyl)propan-1-one (5bb)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 1-methyl-4-vinylbenzene (**2b**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bb** (115mg, 0.266 mmol, 53%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.8 Hz, 2 H), 7.61 - 7.43 (m, 2 H), 7.43 - 7.33 (m, 3 H), 7.29 (d, *J* = 7.0 Hz, 1 H), 7.23 (dd, *J* = 15.4 Hz, 7.9, 4H), 7.14 - 6.99 (m, 4H), 6.84 (d, *J* = 8.9 Hz, 2H), 5.05 (dd, *J* = 8.7, 4.2 Hz, 1 H), 3.79 (s, 4 H), 3.22 (dd, *J* = 15.7, 4.3 Hz, 1 H), 2.30 (s, 3 H).

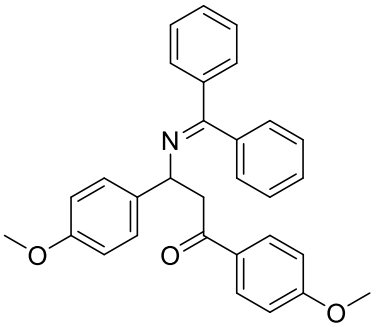
^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.03, 167.77, 163.36, 141.51, 140.03, 137.01, 136.49, 130.65, 130.61, 129.90, 129.22, 128.67, 128.38, 128.23, 127.95, 127.90, 127.01, 113.64, 62.86, 55.48, 48.24, 21.22.

HRMS (ESI): *m/z* calculated for [$C_{30}H_{27}NO_2H$] [$M+H^+$]: 434.2115, measured: 434.2115.

IR (neat): *v* = 3056, 3022, 2923, 2839, 1677, 1600, 1576, 1510, 1445, 1419, 1359, 1314, 1275, 1259, 1216, 1169, 1029, 988, 809, 765, 750, 698, 566 cm^{-1}.

3-((diphenylmethylene)amino)-1,3-bis(4-methoxyphenyl)propan-1-one (5bc)

According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 1-methyl-4-vinylbenzene (**2c**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5cc** (96.3mg, 0.214 mmol,



43%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 9:1).

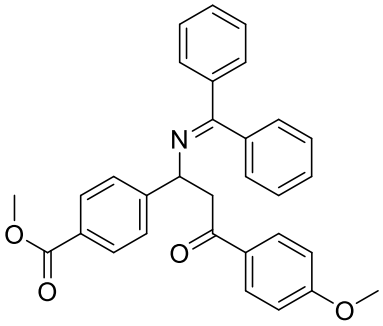
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 9.0 Hz, 2 H), 7.65 - 7.58 (m, 2 H), 7.43 (dd, *J* =4.9, 1.9 Hz, 3 H), 7.37 (t, *J* = 7.2 Hz, 1 H), 7.29 (dd, *J* = 15.0, 8.1 Hz, 4 H), 7.09 (d, *J* = 3.5 Hz, 2 H), 6.89 (dd, *J* = 16.9, 8.8 Hz, 4 H), 5.07 (q, *J* = 4.5 Hz, 1 H), 3.87 (s, 3 H), 3.82 (s, 4 H), 3.28 (dd, *J* = 15.7, 4.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.04, 167.58, 163.32, 158.47, 139.98, 136.96, 136.60, 130.61, 130.58, 129.85, 128.59, 128.33, 128.20, 128.10, 127.91, 127.83, 113.83, 113.60, 62.46, 55.47, 55.25, 48.20.

HRMS (ESI): *m/z* calculated for [$C_{30}H_{27}NO_3H$] [M+H$^+$]: 450.2064, measured: 450.2068.

IR (neat): *v* = 3057, 3004, 2956, 2921, 2850, 1676, 1600, 1576, 1510, 1463, 1444, 1360, 1314, 1303, 1275, 1259, 1169, 1030, 988, 830, 765, 750, 698, 568 cm^{-1}.

Methyl4-(1-((diphenylmethylene)amino)-3-(4-methoxyphenyl)-3-oxopropyl)benzoate (5be)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and methyl 4-vinylbenzoate (**2e**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5be** (126mg, 0.264 mmol, 53%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

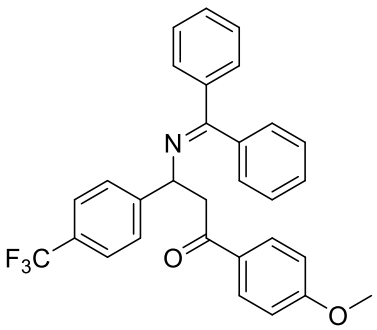
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 8.9 Hz, 2 H), 7.67 - 7.60 (m, 2 H), 7.44 (dd, *J* = 5.2, 3.2 Hz, 5 H), 7.37 - 7.27 (m, 3 H), 7.11 - 7.04 (m, 2 H), 6.91 (d, *J* = 8.9 Hz, 2 H), 5.19 (dd, *J* = 8.5, 4.4 Hz, 1 H), 3.92 (s, 3 H), 3.85 (s, 4 H), 3.31 (dd, *J* = 15.9, 4.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.38, 168.72, 167.03, 163.47, 149.76, 139.69, 136.77, 130.59, 130.35, 130.16, 129.88, 128.82, 128.66, 128.55, 128.34, 128.02, 127.69, 127.18, 113.69, 62.78, 55.48, 52.08, 47.84.

HRMS (ESI): *m/z* calculated for [$C_{31}H_{27}NO_4H$] [M+H$^+$]: 478.2013, measured: 478.2007.

IR (neat): *v* = 3058, 3022, 2952, 2906, 2841, 1722, 1678, 1600, 1575, 1510, 1491, 1436, 1419, 1359, 1313, 1280, 1259, 1219, 1205, 1170, 1112, 1029, 1020, 988, 832, 775, 702, 569 cm^{-1}.

3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)propan-1-one (5bf)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and methyl 1-(trifluoromethyl)-4-vinylbenzene (**2f**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bf** (134mg, 0.275 mmol, 55%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.9, 2H), 7.66 - 7.62 (m, 2H), 7.59 (d, *J* = 8.2, 2H), 7.52 - 7.44 (m, 5H), 7.38 (d, *J* = 7.2, 1H), 7.33 (t, *J* = 7.3, 2H), 7.08 (dt, *J* = 4.6, 2.6, 2H), 6.92 (d, *J* = 8.9, 2H), 5.19 (dd, *J* = 8.2, 4.7, 1H), 3.87 (s, 3H), 3.83 (dd, *J* = 16.0, 8.3, 1H), 3.32 (dd, *J* = 16.0, 4.7, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.28, 168.76, 163.51, 148.47, 139.62, 136.71, 130.57, 130.30,

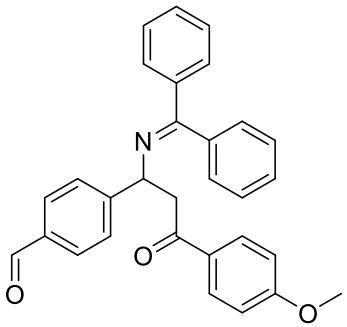
130.19, 128.65, 128.58, 128.37, 128.01, 127.66, 127.52,, 125.48, 125.44, 125.40, 125.36 (q, *J* = 3.9 Hz), 128.32, 125.62, 122.92, 120.22 (d, *J* = 271.9 Hz), 114.01, 113.99 (d, *J* = 2.4 Hz), 113.69, 62.56, 55.47, 47.85.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.35.

HRMS (ESI): *m/z* calculated for [$C_{30}H_{24}F_3NO_2H$] [M+H$^+$]: 488.1832, measured: 488.1825.

IR (neat): *v* = 3059, 2935, 2841, 1677, 1618, 1601, 1576, 1510, 1419, 1325, 1260, 1168, 1123, 1068, 1030, 1018, 968, 832, 765, 750, 698, 606 cm^{-1}.

4-(1-((diphenylmethylene)amino)-3-(4-methoxyphenyl)-3-oxopropyl)benzaldehyde (5bg)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and methyl 4-vinylbenzaldehyde (**2g**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bg** (125mg, 0.280 mmol, 56%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

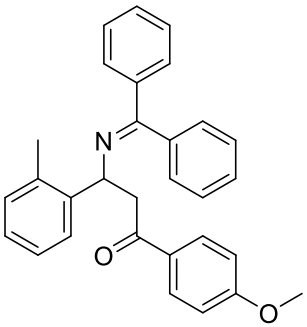
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 7.94 (d, *J* = 8.9 Hz, 2 H), 7.84 (d, *J* = 8.3 Hz, 2 H), 7.70 - 7.60 (m, 2 H), 7.54 (d, *J* = 8.2 Hz, 2 H), 7.47 - 7.36 (m, 4 H), 7.36 - 7.29 (m, 2 H), 7.11 - 7.04 (m, 2 H), 6.92 (d, *J* = 8.9 Hz, 2 H), 5.21 (dd, *J* = 8.3, 4.7 Hz, 1 H), 3.86 (s, 4 H), 3.33 (dd, *J* = 16.0, 4.7 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.19, 192.04, 169.01, 163.53, 151.47, 139.54, 136.66, 135.31, 130.58, 130.27, 130.26, 130.06, 128.68, 128.63, 128.40, 128.04, 127.86, 127.65, 113.72, 62.82, 55.49, 47.70.

HRMS (ESI): *m/z* calculated for [$C_{30}H_{25}NO_2H$] [M+H$^+$]: 448.1908, measured: 448.1912.

IR (neat): *v* = 3059, 3027, 2959, 2932, 2841, 1699, 1661, 1601, 1575, 1511, 1491, 1463, 1447, 1420, 1357, 1317, 1278, 1259, 1210, 1169, 1113, 1075, 1030, 990, 942, 920, 831, 765, 737, 703, 639, 571 cm^{-1}.

3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(o-tolyl)propan-1-one (5bi)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 1-methyl-2-vinylbenzene(**2i**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bi** (105mg, 0.242 mmol, 49%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

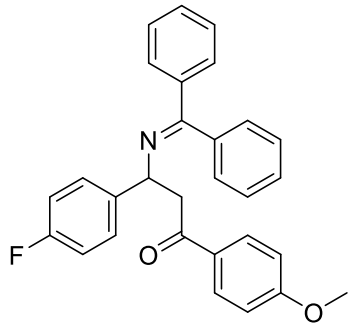
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.9 Hz, 2 H), 7.74 (d, *J* = 7.7 Hz, 1 H), 7.66 (d, *J* = 7.0 Hz, 2 H), 7.42 (dd, *J* = 5.3, 2.0 Hz, 3 H), 7.37 (d, *J* = 7.1 Hz, 1 H), 7.32 (t, *J* = 7.3 Hz, 2 H), 7.25 (d, *J* = 1.5 Hz, 1 H), 7.17 (d, *J* = 1.5 Hz, 1 H), 7.09 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.06 - 7.02 (m, 2 H), 6.99 - 6.92 (m, 2 H), 5.32 (dd, *J* = 9.2, 3.2 Hz, 1 H), 4.00 - 3.83 (m, 4 H), 3.15 (dd, *J* = 15.9, 3.3 Hz, 1 H), 1.94 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.13, 168.04, 163.37, 143.50, 139.93, 137.50, 134.21, 130.63, 130.23, 129.87, 128.59, 128.31, 128.19, 127.94, 127.62, 126.50, 126.32, 113.64, 59.02, 55.48, 47.40, 18.95.

HRMS (ESI): *m/z* calculated for [$C_{30}H_{27}NO_2H$] [M+H$^+$]: 434.2115, measured: 434.2113.

IR (neat): *v* = 3059, 3022, 2934, 2840, 1677, 1622, 1600, 1576, 1510, 1489, 1461, 1445, 1360, 1314, 1259, 1207, 1169, 1029, 988, 832, 764, 750, 698, 575 cm^{-1}.

3-((diphenylmethylene)amino)-3-(4-fluorophenyl)-1-(4-methoxyphenyl)propan-1-one (5bj)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 1-fluoro-4-vinylbenzene (**2j**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bj** (120mg, 0.275 mmol, 55%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.8 Hz, 2 H), 7.70 - 7.61 (m, 2 H), 7.46 (dd, *J* = 4.9 Hz, 1.9, 3 H), 7.41 - 7.29 (m, 5 H), 7.14 - 7.06 (m, 2 H), 7.02 (t, *J* = 8.7 Hz, 2 H), 6.93 (d, *J* = 8.9 Hz, 2 H), 5.13 (dd, *J* = 8.3, 4.7 Hz, 1 H), 3.87 (s, 3 H), 3.82 (dd, *J* = 15.8, 8.4 Hz, 1 H), 3.31 (dd, *J* = 15.7, 4.7 Hz, 1 H).

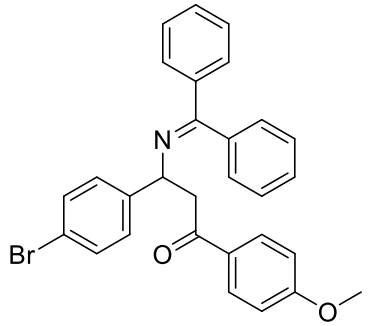
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.70, 168.13, 163.44, 162.99, 160.56 (d, *J* = 244.7), 140.19, 140.16(d, *J* = 3.0), 139.80, 136.86, 130.60, 130.46, 130.06, 128.68, 128.63, 128.61, 128.48, 128.31, 128.00, 127.74, 115.37, 115.16 (d, *J* = 21.2), 113.67, 62.32, 55.48, 48.13.

^{19}F NMR (377 MHz, $CDCl_3$): δ = -115.68.

HRMS (ESI): *m/z* calculated for [$C_{29}H_{24}FNO_2H$] [M+H$^+$]: 438.1864, measured: 438.1861.

IR (neat): *v* = 3059, 2960, 2934, 2841, 1679, 1600, 1576, 1507, 1463, 1446, 1419, 1360, 1314, 1288, 1259, 1220, 1170, 1157, 1030, 988, 834, 781, 767, 743, 698, 564, 546 cm^{-1}.

3-(4-bromophenyl)-3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)propan-1-one (5bk)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 1-bromo-4-vinylbenzene (**2k**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bk** (130mg, 0.262 mmol, 52%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.8 Hz, 2 H), 7.64 (d, *J* = 8.4 Hz, 2 H), 7.49 - 7.43 (m, 5 H), 7.42 - 7.36 (m, 1 H), 7.33 (t, *J* = 7.4, 2H), 7.26 (d, *J* = 8.4, 2H), 7.10 (d, *J* = 4.5, 2H), 6.93 (d, *J* = 8.6, 2 H), 5.11 (dd, *J* = 8.4, 4.3 Hz, 1 H), 3.87 (s, 3 H), 3.82 (dd, *J* = 15.8, 8.4 Hz, 1 H), 3.30 (dd, *J* = 15.8, 4.6 Hz, 1 H).

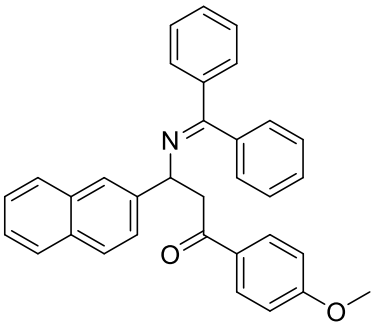
^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.48, 168.41, 163.47, 143.52, 139.74, 136.80, 131.59, 130.60, 130.13, 128.93, 128.93, 128.65, 128.53, 128.35, 128.02, 127.73, 120.72, 113.70, 62.40, 55.50, 47.96.

HRMS (ESI): *m/z* calculated for [$C_{29}H_{24}{}^{79}BrNO_2H$] [M+H$^+$]: 498.1064, [$C_{29}H_{24}{}^{81}BrNO_2H$] [M+H$^+$]: 500.1043, measured: 500.1047.

IR (neat): *v* = 3058, 3023, 2962, 2934, 2906, 2839, 1678, 1600, 1575, 1510, 1485, 1445, 1420, 1359, 1314, 1287, 1259, 1218, 1205, 1169, 1113, 1072, 1030, 1011, 829, 781, 771, 737, 698, 566 cm^{-1}.

3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(naphthalen-2-yl)propan-1-one (5bo)

According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 2-vinylnaphthalene (**2o**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bo** (105mg, 0.224 mmol,



45%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

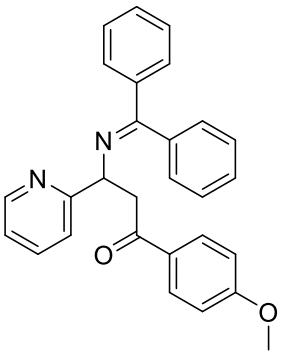
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.9 Hz, 2 H), 7.76 (t, *J* = 8.0 Hz, 3 H), 7.69 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 2 H), 7.52 (d, *J* = 8.4 Hz, 1 H), 7.44 - 7.23 (m, 8 H), 7.04 (d, *J* = 6.6 Hz, 2 H), 6.85 (d, *J* = 6.7 Hz, 2 H), 5.24 (dd, *J* = 8.8, 4.1 Hz, 1 H), 3.90 (dd, *J* = 15.8, 8.8 Hz, 1 H), 3.79 (s, 3 H), 3.32 (dd, *J* = 15.8, 4.2 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.87, 168.37, 163.41, 142.08, 140.01, 136.98, 133.57, 132.71, 130.65, 130.59, 130.00, 128.72, 128.45, 128.26, 128.21, 128.00, 127.89, 127.71, 125.98, 125.64, 125.57, 125.55, 113.67, 63.21, 55.48, 48.21.

HRMS (ESI): *m/z* calculated for [$C_{33}H_{27}NO_2H$] [$M+H^+$]: 470.2115, measured: 470.2118.

IR (neat): *v* = 3056, 2921, 2850, 1676, 1600, 1575, 1509, 1445, 1419, 1359, 1275, 1260, 1169, 1029, 988, 818, 765, 750, 699 cm^{-1}.

3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(pyridin-2-yl)propan-1-one (5bp)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 2-vinylpyridine (**2p**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bp** (140mg, 0.333 mmol, 67%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 3:1).

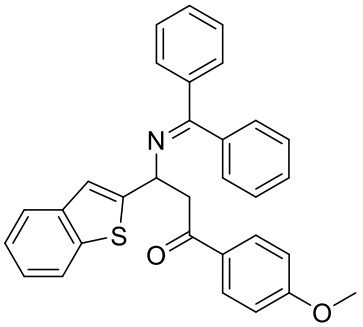
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 6.8 Hz, 1 H), 7.95 (d, *J* = 8.7 Hz, 2 H), 7.65 (d, *J* = 7.6 Hz, 3 H), 7.43 - 7.35 (m, 4 H), 7.31 (dd, *J* = 8.5, 6.9 Hz, 3 H), 7.16 (dd, *J* = 6.4, 4.8 Hz, 1 H), 7.12 - 7.05 (m, 2 H), 6.89 (d, *J* = 8.9 Hz, 2 H), 5.28 (dd, *J* = 8.1, 4.8 Hz, 1 H), 3.86 (s, 3 H), 3.82 - 3.65 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.84, 169.29, 163.29, 162.53, 149.20, 139.81, 136.65, 136.57, 130.61, 130.46, 130.12, 128.81, 128.47, 128.33, 127.97, 127.71, 122.03, 122.00, 113.59, 64.49, 55.45, 46.13.

HRMS (ESI): *m/z* calculated for [$C_{28}H_{24}N_2O_2H$] [$M+H^+$]: 421.1911, measured: 421.1911.

IR (neat): *v* = 3058, 3007, 2932, 2840, 1674, 1600, 1575, 1510, 1491, 1466, 1446, 1433, 1420, 1361, 1315, 1259, 1217, 1170, 1113, 1075, 1029, 991, 942, 920, 834, 782, 770, 700, 639, 571 cm^{-1}.

3-(benzo[b]thiophen-2-yl)-3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)propan-1-one (5bq)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 2-vinylbenzo[b]thiophene (**2q**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bq** (101mg, 0.213 mmol, 43%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 9.0 Hz, 2 H), 7.84 (d, *J* = 9.3 Hz, 1 H), 7.73 - 7.67 (m, 3 H), 7.48 (dd, *J* = 4.8, 1.8 Hz, 3 H), 7.41 (d, *J* = 7.2 Hz, 1 H), 7.37 - 7.30 (m, 4 H), 7.27 - 7.20 (m, 2 H), 7.08 (s, 1 H), 6.93 (d, *J* = 8.9 Hz, 2 H), 5.54 (dd, *J* = 7.6, 5.1 Hz, 1 H), 3.87 (s, 4 H), 3.51 (dd, *J* =

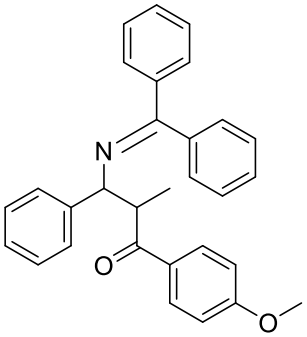
16.2, 4.7 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.03, 169.29, 163.52, 148.68, 139.61, 139.59, 139.39, 136.31, 130.89, 130.62, 130.30, 128.85, 128.69, 128.40, 128.07, 127.82, 124.13, 123.79, 123.34, 122.37, 119.55, 113.72, 59.33, 55.50, 48.16.

HRMS (ESI): *m/z* calculated for [$C_{31}H_{25}NO_2SH$] [M+H$^+$]: 476.1679, measured: 476.1675.

IR (neat): *v* = 3057, 2933, 2839, 1676, 1600, 1576, 1510, 1491, 1458, 1437, 1420, 1357, 1315, 1260, 1219, 1169, 1113, 1029, 986, 941, 829, 765, 749, 699, 598 cm^{-1}.

3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-2-methyl-3-phenylpropan-1-one (5br)



According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and prop-1-en-1-ylbenzene (**2r**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5cr** (78mg, 0.180 mmol, 36%) (D:R=1.33:1) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1).

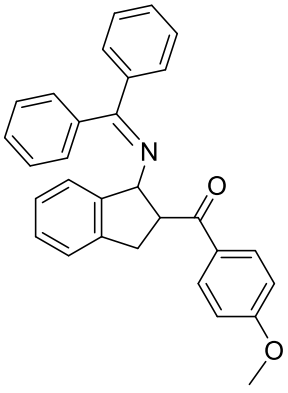
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 8.9 Hz, 0.97 H), 7.81 - 7.69 (m, 4.05 H), 7.51 - 7.23 (m, 14.07 H), 7.23 - 7.15 (m, 3.09 H), 7.11 (t, *J* = 7.3 Hz, 1.07 H), 7.07 - 6.93 (m, 3.18 H), 6.82 (d, *J* = 8.9 Hz, 2.03 H), 4.79 (d, *J* = 8.3 Hz, 1 H), 4.67 (d, *J* = 9.4 Hz, 0.47 H), 4.31 (dd, *J* = 9.3, 7.0 Hz, 0.48 H), 4.27 - 4.15 (m, 1.02 H), 3.90 (s, 1.42 H), 3.83 (s, 3.02 H), 1.27 (d, *J* = 6.8 Hz, 3.01 H), 0.92 (d, *J* = 7.0 Hz, 1.44 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.76, 201.59, 167.98, 167.32, 163.26, 163.13, 143.26, 142.78, 140.04, 139.89, 136.96, 136.83, 130.89, 130.41, 130.17, 129.99, 129.66, 128.64, 128.48, 128.35, 128.29, 128.17, 128.14, 128.09, 128.03, 127.89, 127.80, 127.71, 127.08, 126.78, 113.64, 113.49, 70.58, 68.74, 55.49, 55.40, 48.63, 48.45, 15.61, 14.99.

HRMS (ESI): *m/z* calculated for [$C_{30}H_{27}NO_2H$] [M+H$^+$]: 434.2115, measured: 434.2118.

IR (neat): *v* = 3060, 3028, 2965, 2931, 2841, 1673, 1600, 1575, 1510, 1491, 1454, 1419, 1355, 1314, 1255, 1212, 1171, 1074, 1030,971, 841, 781, 766, 699, 606, 585, 562 cm^{-1}.

***Tans*-(1-((diphenylmethylene)amino)-2,3-dihydro-1H-inden-2-yl)(4-methoxyphenyl) methanone (5bt)**



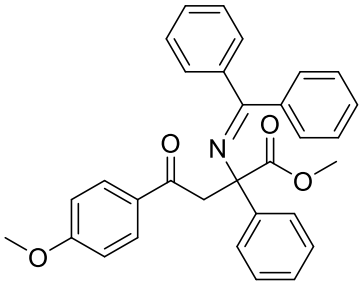
According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and 1H-indene (**2t**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5ct** (75.7mg, 0.180 mmol, 36%) (D:R > 20:1) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 9.0 Hz, 2 H), 7.65 (d, *J* = 7.1 Hz, 2 H), 7.38 - 7.29 (m, 6 H), 7.27 - 7.12 (m, 3 H), 7.04 (d, *J* = 4.6 Hz, 1 H), 6.94 - 6.82 (m, 4 H), 5.28 (d, *J* = 9.0 Hz, 1 H), 4.75 - 4.63 (m, 1 H), 3.79 (s, 3 H), 3.40 (dd, *J* = 15.8, 10.0 Hz, 1 H), 3.26 (dd, *J* = 15.8, 8.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.74, 169.78, 163.57, 143.13, 141.43, 139.57, 136.23, 131.40, 130.25, 130.20, 128.76, 128.51, 128.40, 128.04, 127.75, 127.67, 126.81, 124.62, 123.91, 113.64, 70.39, 55.49, 55.48, 35.07.

HRMS (ESI): *m/z* calculated for [$C_{30}H_{26}NO_2H$] [$M+H^+$]: 432.1959, measured: 432.1963.
IR (neat): ν = 3024, 2921, 2850, 1671, 1599, 1576, 1510, 1459, 1446, 1420, 1365, 1314, 1248, 1170, 1029, 838, 765, 749, 698 cm^{-1}.

Methyl 2-((diphenylmethylene)amino)-4-(4-methoxyphenyl)-4-oxo-2-phenylbutanoate (5bw)



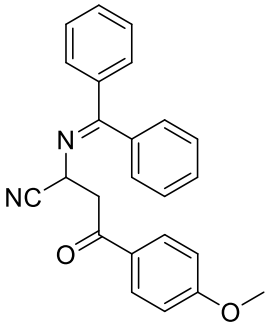
According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and methyl 2-phenylacrylate (**2w**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bw** (162 mg, 0.340 mmol, 68 %) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 8:1, v/v) .

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 - 7.65 (m, 4 H), 7.60 - 7.53 (d, *J* = 6.8 Hz, 2 H), 7.42 - 7.36 (d, *J* = 7.1 Hz, 1 H), 7.35 - 7.27 (m, 6H), 7.21 - 7.13 (t, *J* = 7.7 Hz, 2 H), 6.88 - 6.81 (m, 4 H), 4.02 - 3.93 (d, *J* = 16.5 Hz, 1 H), 3.92 - 3.80 (s, 4 H), 3.69 - 3.64 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.78, 174.05, 167.42, 163.30, 143.32, 141.24, 137.92, 130.39, 130.36, 130.17, 128.87, 128.31, 128.27, 127.94, 127.92, 127.73, 127.38, 126.87, 113.45, 70.11, 55.45, 52.62, 47.88.

HRMS (ESI): *m/z* calculated for [$C_{31}H_{27}NO_4H$] [$M+H^+$]: 478.2013, measured: 478.2014.
IR (neat): ν = 3059, 2950, 2840, 1728, 1680, 1630, 1599, 1575, 1510, 1491, 1446, 1420, 1349, 1313, 1259, 1224, 1170, 1051, 1029, 908, 831, 729, 698, 648 cm^{-1}.

2-((diphenylmethylene)amino)-4-(4-methoxyphenyl)-4-oxobutanenitrile (5bx)



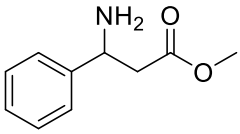
According to the **General Procedure D,** using oxime ester **4b** (0.5 mmol, 1 equiv) and acrylonitrile (**2x**) (0.55 mmol, 1.1 equiv), the reaction afforded oil **5bx** (113mg, 0.307 mmol, 61%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.9 Hz, 2 H), 7.66 - 7.48 (m, 5 H), 7.48 - 7.26 (m, 5 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 4.94 (dd, *J* = 8.2, 5.0 Hz, 1 H), 3.93 - 3.80 (m, 4 H), 3.54 (dd, *J* = 17.2, 5.0 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.28, 174.47, 164.04, 138.53, 135.45, 131.21, 130.52, 129.47, 129.21, 129.07, 129.00, 128.20, 127.51, 119.38, 113.99, 55.59, 48.75, 42.97.

HRMS (ESI): *m/z* calculated for [$C_{24}H_{20}N_2O_2H$] [$M+H^+$]: 369.1598, measured: 369.1600.
IR (neat): ν = 3056, 3023, 2916, 2841, 1678, 1601, 1575, 1511, 1491, 1446, 1421, 1360, 1317, 1293, 1262, 1219, 1171, 1114, 1076, 1029, 990, 934, 913, 833, 812, 783, 766, 750, 699, 587 cm^{-1}.

Methyl 3-amino-3-phenylpropanoate (6)[6]



According to the **General Procedure E,** using methyl 3-((di-p-tolylmethylene)amino)-3-phenylpropanoate **3ba** (1 mmol, 1 equiv), the crude products without further purification. (147mg, 0.821 mmol, 82.1%).

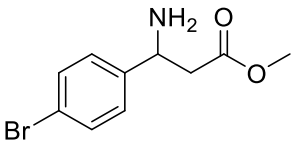
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.28 (m, 5 H), 4.65 (s, 2 H), 3.70 (s, 3 H), 2.28 (s, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.7, 140.6, 129.2, 128.5, 127.3, 59.1, 52.9.

HRMS (ESI): *m/z* calculated for $C_9H_{11}NO_2$ [M+H$^+$]:166.0863, measured: 166.0865.

IR (neat): *v* = 3378, 3309, 3085, 3063, 3029, 3003, 2953, 2848, 1733, 1605, 1494, 1453, 1437, 1350, 1319, 1255, 1198, 1173, 1073, 1021, 1002, 990, 913, 847, 803, 764, 701, 595, 540 cm^{-1}.

Methyl 3-amino-3-(4-bromophenyl)propanoate (7)



According to the **General Procedure E,** using methyl methyl 3-(4-bromophenyl)-3-((di-p-tolylmethylene)amino)propanoate **3bk** (1 mmol, 1 equiv), the crude products without further purification. (217mg, 0.844 mmol, 84.4%).

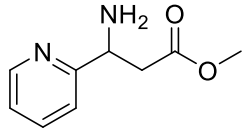
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 4.40 (t, *J* = 6.8 Hz, 1 H), 3.69 (s, 3 H), 2.64 (d, *J* = 6.8 Hz, 2 H), 1.77 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.16, 143.61, 131.72, 128.01, 121.15, 52.08, 51.73, 43.81.

HRMS (ESI): *m/z* calculated for $C_{10}H_{12}{}^{79}BrNO_2$ [M+H$^+$]:258.0125, $C_{10}H_{12}{}^{81}BrNO_2$ [M+H$^+$]:260.0104, measured: 260.0101.

IR (neat): *v* = 3370, 2952, 1732, 1591, 1488, 1437, 1408, 1359, 1315, 1257, 1200, 1174, 1073, 1010, 826, 727, 635, 534 cm^{-1}.

Methyl 3-amino-3-(pyridin-2-yl)propanoate (8)



According to the **General Procedure E,** using methyl 3-((di-p-tolylmethylene)amino)-3-phenylpropanoate **3bp** (1 mmol, 1 equiv), the reaction afforded oil **7** (143mg, 0.794 mmol, 79.4%) purifying by column chromatography silica gel (eluent: petroleum ether /ethyl acetate = 3:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 1 H), 7.68 - 7.57 (m, 1 H), 7.32 (d, *J* = 7.9 Hz, 1 H), 7.18 - 7.10 (m, 1 H), 4.41 (s, 1 H), 3.64 (s, 3 H), 2.84 (dd, *J* = 17.3, 5.1 Hz, 1 H), 2.72 (dd, *J* = 15.3, 7.8 Hz, 1 H), 2.25 (s, 2 H).

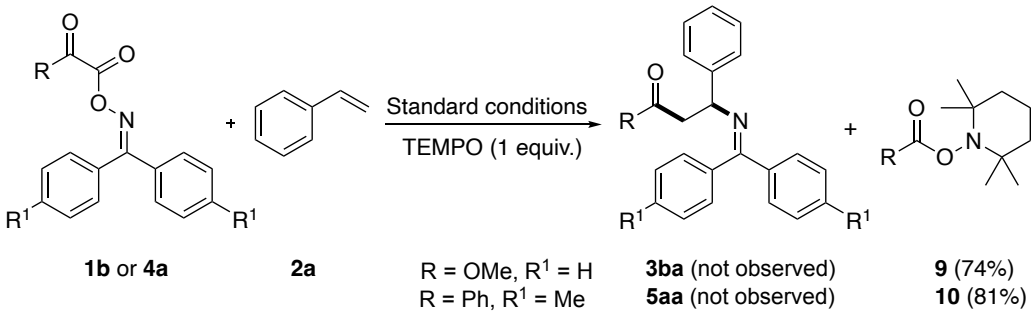
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.37, 162.67, 149.27, 136.72, 122.28, 121.00, 53.66, 51.61, 42.58.

HRMS (ESI): m/z calculated for [$C_9H_{13}N_2O_2H$] [M+H$^+$]: 181.0972, measured: 181.0974.

IR (neat): *v* = 3364, 3010, 2954, 1731, 1655, 1593, 1571, 1475, 1438, 1362, 1262, 1203, 1177, 1153, 998, 752, 631cm^{-1}.

Mechanistic studies

TEMPO as a radical scavenger in the 1,2-carboimination



In an over-dried vial equipped with a crimp-top hollow aluminum cap (containing a PTFE-coated silicone gasket), **1b** or **4a** (0.5 mmol, 1 equiv), TEMPO (0.5 mmol, 1 equiv) were added (thioxanthone was added in the reaction with **1b**, 5% mmol). After adding the magnetic stirrer, the special crimping forceps was used to seal the vial. The air in the bottle was replaced with argon in the dark with the aid of a needle. Then, sequentially injected 5 ml CH_2Cl_2 (0.1 M) (dry and degas for more than 20 min) and alkenes (0.55 mmol, 1.1 equiv) with a syringe. After stirring for 10 minutes in the dark, then stirred at 1000 rpm and irradiated using the described set-up for 12 hours. The formation of **3ba** or **5aa** was completely suppressed. Meanwhile, we found that the TEMPO-trapped product **9** and **10** was obtained in 74% yield (78.9 mg) and 81% yield (105.1 mg) respectively.

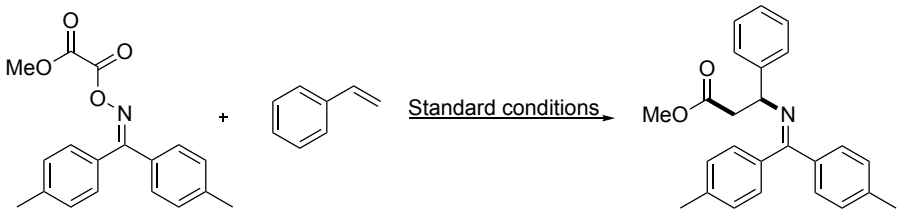
Methyl (2,2,6,6-Tetramethylpiperidin-1-yl) Carbonate (9)[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 1.75-1.49 (m, 5H), 1.43-1.35 (m, 1H), 1.17 (s, 6H), 1.13 (s, 6H)

2,2,6,6-Tetramethylpiperidin-1-yl benzoate (10) [8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.0 Hz, 2 H), 7.60-7.41 (m, 3H), 1.84-1.65 (m, 3H), 1.62-1.52 (m, 2 H), 1.50-1.41 (m, 1 H), 1.28 (s, 6 H), 1.12 (s, 6H);

On/Off experiment



In an over-dried vial equipped with a crimp-top hollow aluminum cap (containing a PTFE-coated silicone gasket), methyl 2-(((di-p-tolylmethylene)amino)oxy)-2-oxoacetate (**1b**) (0.5 mmol, 1 equiv) and thioxanthone (5% mmol) were added. After adding the magnetic stirrer, the special crimping forceps was used to seal the vial. The air in the bottle was replaced with argon in the dark with the aid of a needle. Then, sequentially injected 5 ml CH_2Cl_2 (0.1 M) (dry and degas for more than 20 min) and alkenes (0.55 mmol, 1.1 equiv) with a syringe. Then the crude was stirred at 1000 rpm and irradiated. During "On" period the lamp was turned on; during "Off" period the lamp was turned off and the tube was covered with a cap without the interruption of stirring. After each period, the

aliquot of reaction mixture was taken under the flow of Ar and analyzed with GC.

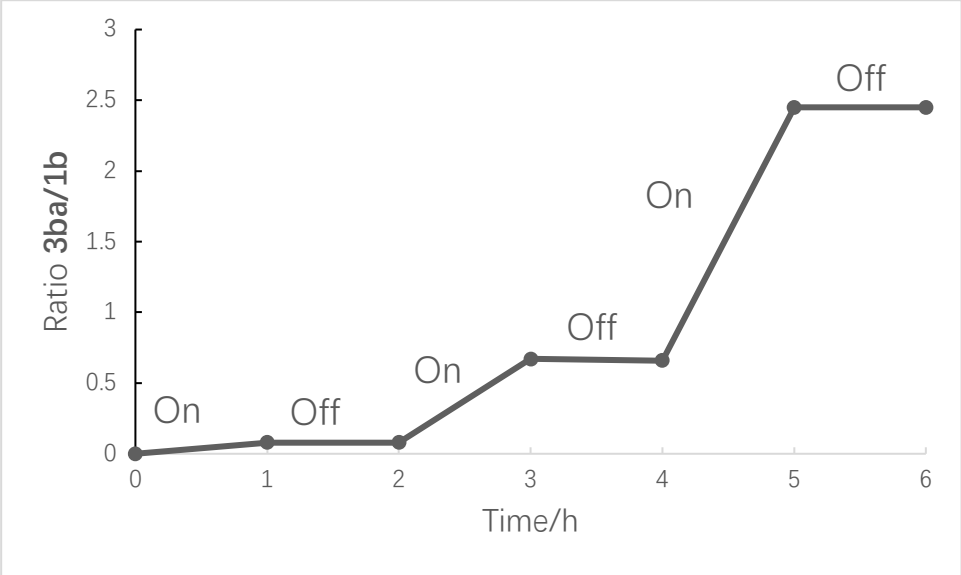


Figure 1. On/Off experiment

Reference：

[1] T. Patra, M. Das, C. G. Daniliuc, F. Glorius, *Nat Catal* **2021**, *4*, 54-61.

[2] J. Li, X. C. Lu, Y. Xu, J. X. Wen, G. Q. Hou, L. Liu, *Org Lett* **2020**, *22*, 9621-9626.

[3] Y. Ye, J. Liu, B. Xu, S. Jiang, R. Bai, S. Li, T. Xie, X. Y. Ye, *Chem Sci* **2021**, *12*, 13209-13215.

[4] D. Xu, Y. Chen, C. M. Liu, J. X. Xu, Z. H. Yang, *Green Chem* **2021**, *23*, 6050-6058.

[5] A. Falk, A. Cavalieri, G. S. Nichol, D. Vogt, H. G. Schmalz, *Adv Synth Catal* **2015**, *357*, 3317-3320.

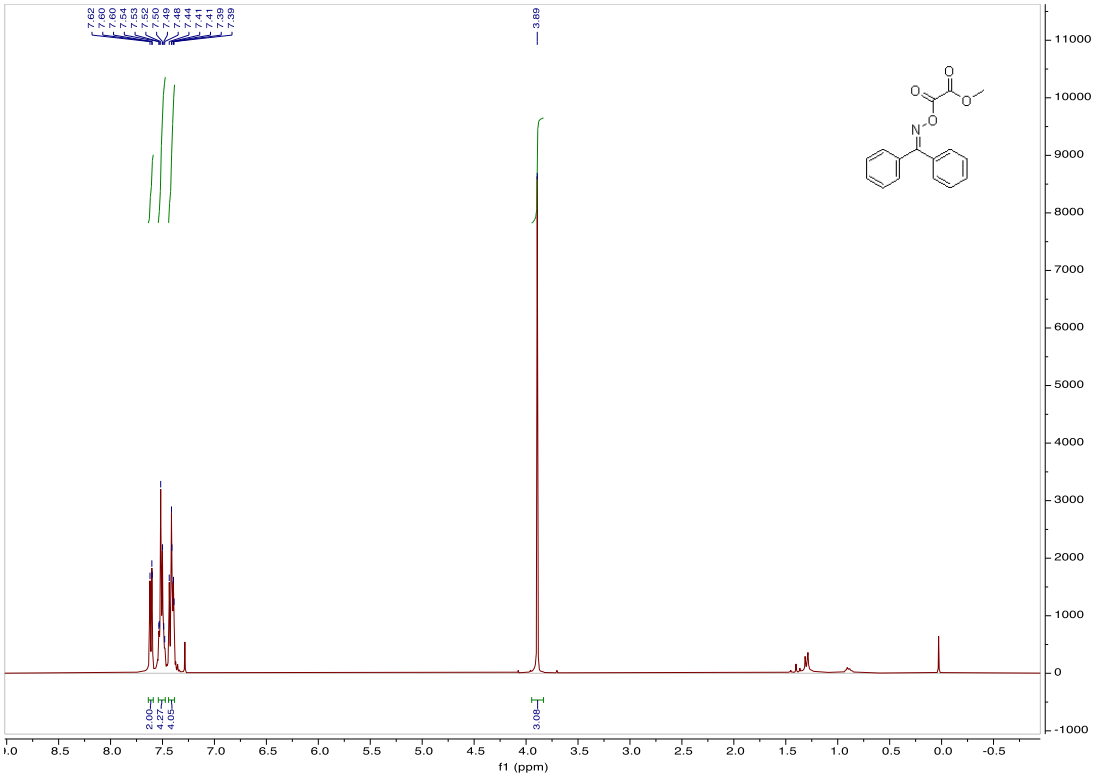
[6] C. Wang, A. Pettman, J. Basca, J. Xiao, *Angew Chem Int Ed* 2010, 49, 7548-7552.

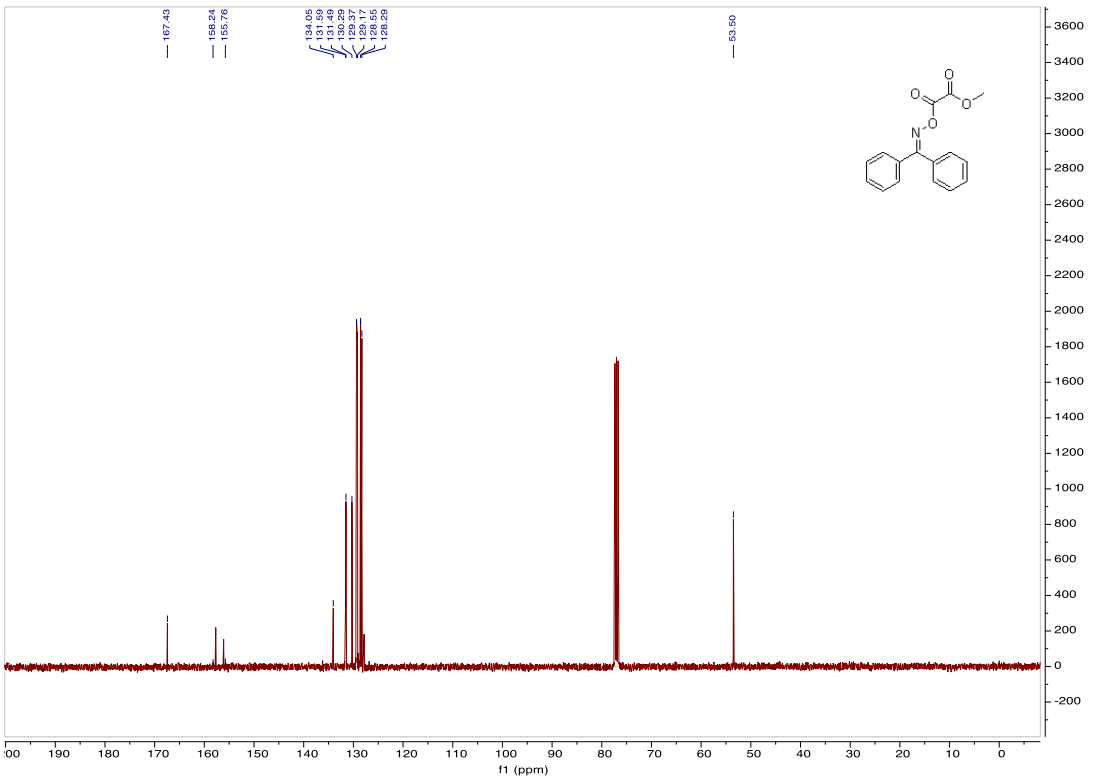
[7] T. Taniguchi, Y. Sugiura, H. Zaimoku, H. Ishibashi, *Angew. Chem., Int. Ed.* **2010**, *49*, 10154-10157.

[8] A. Hossian, M. K. Manna, K. Manna, R. Jana, *Org. Biomol. Chem.* **2017**, *15*, 6592-6603.

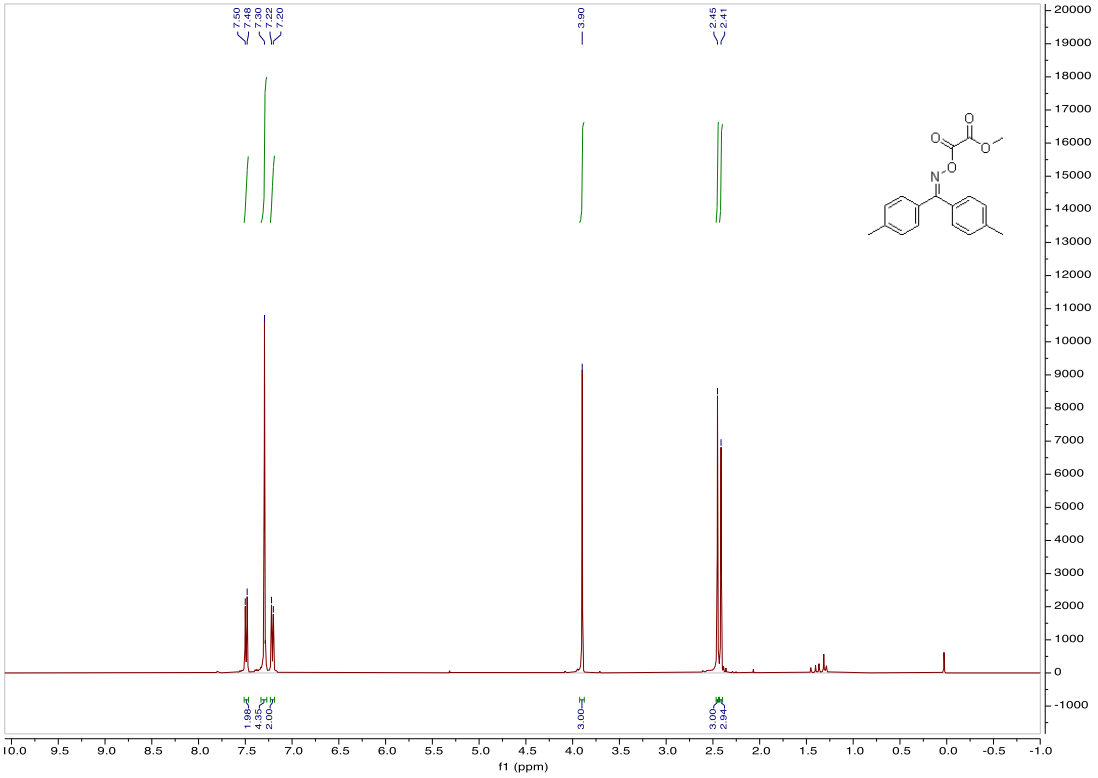
NMR Spectra

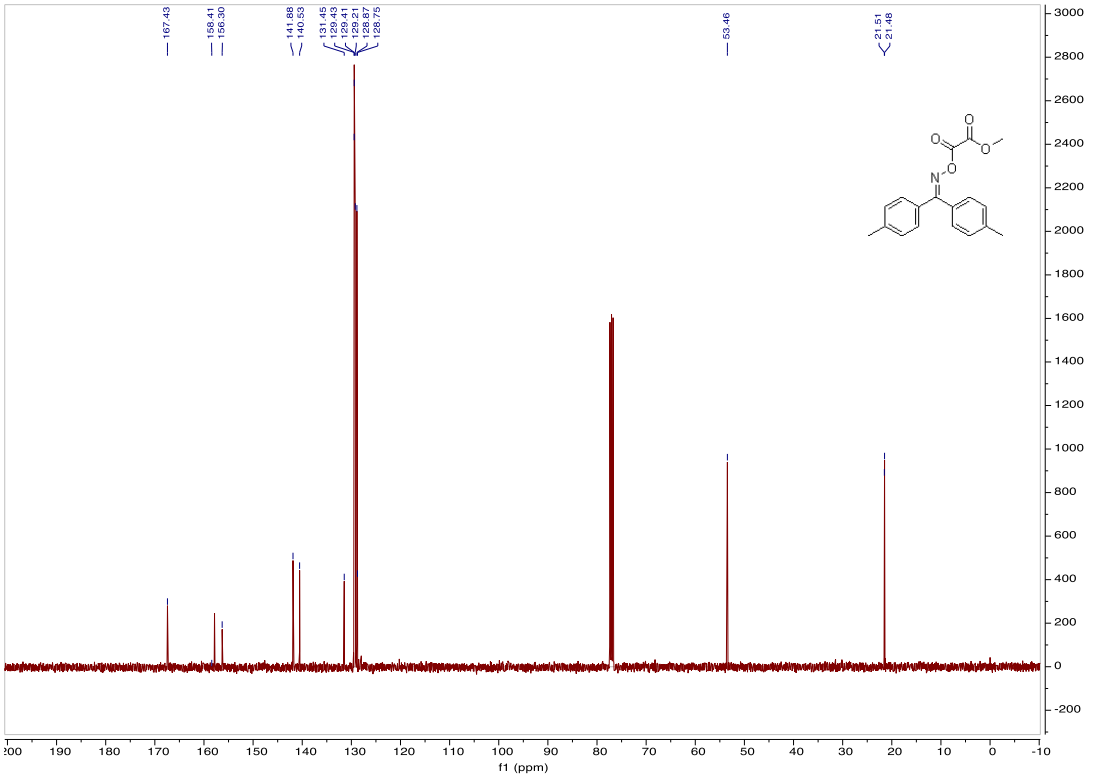
Methyl 2-((((diphenylmethylene)amino)oxy)-2-oxoacetate (1a)



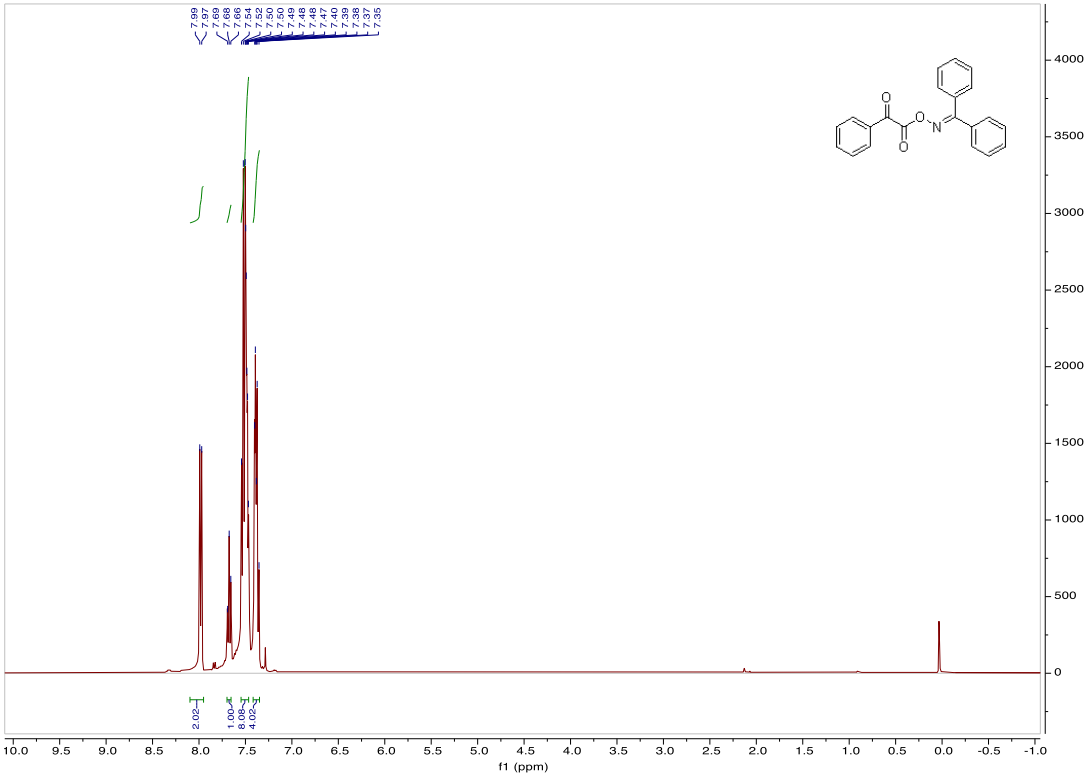


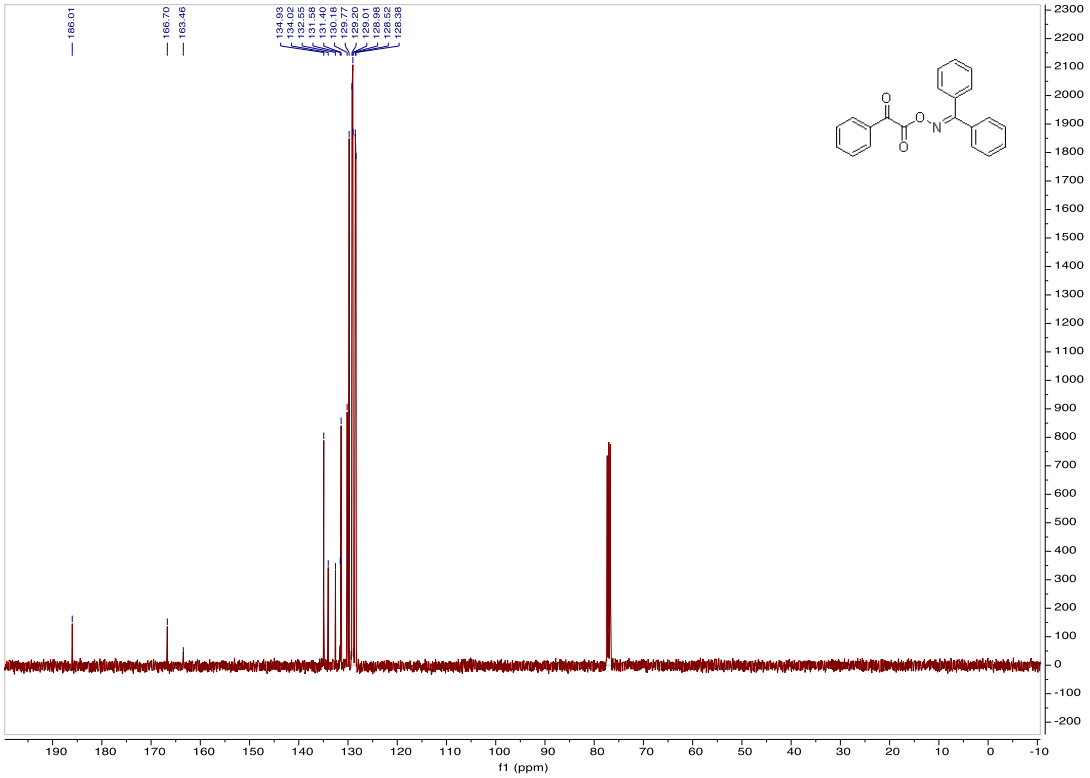
Methyl 2-(((di-p-tolylmethylene)amino)oxy)-2-oxoacetate (1b)



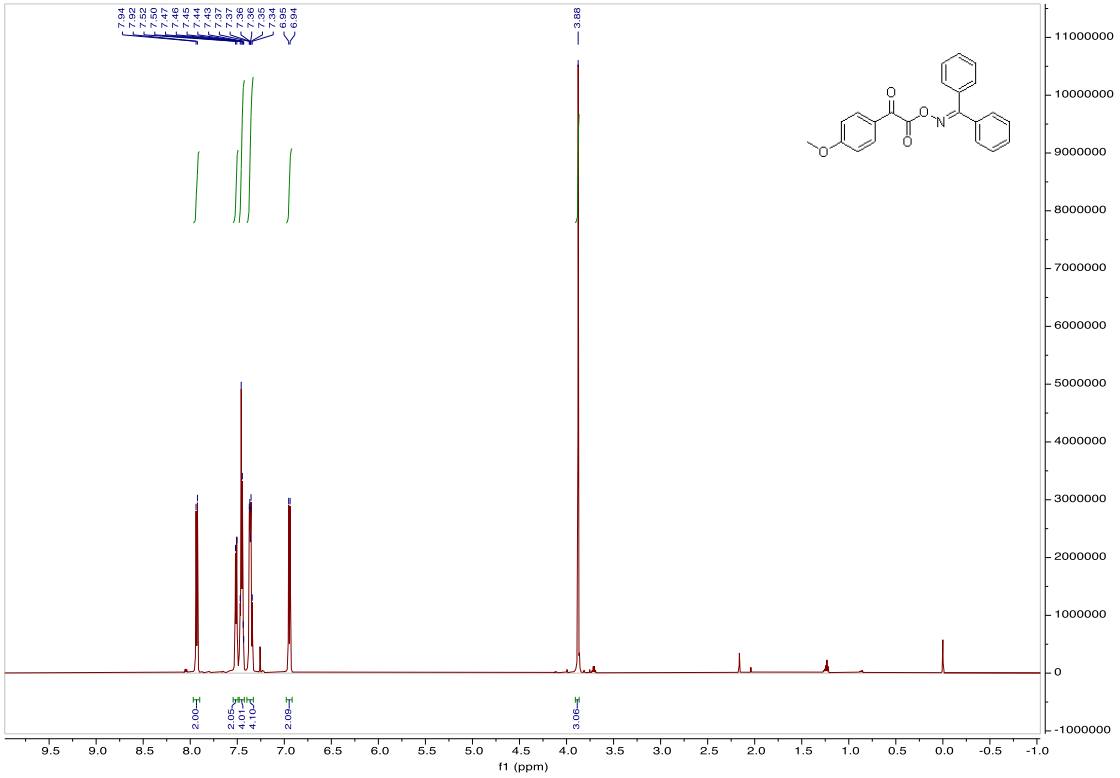


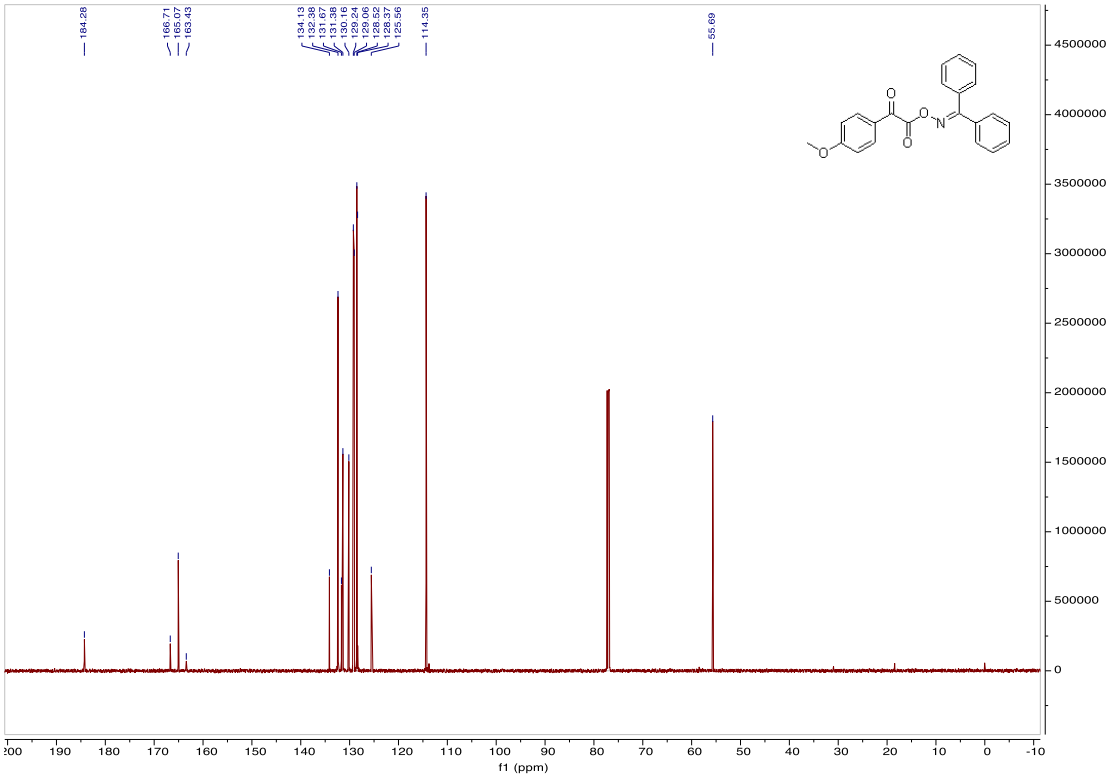
1-(((diphenylmethylene)amino)oxy)-2-phenylethane-1,2-dione (4a)



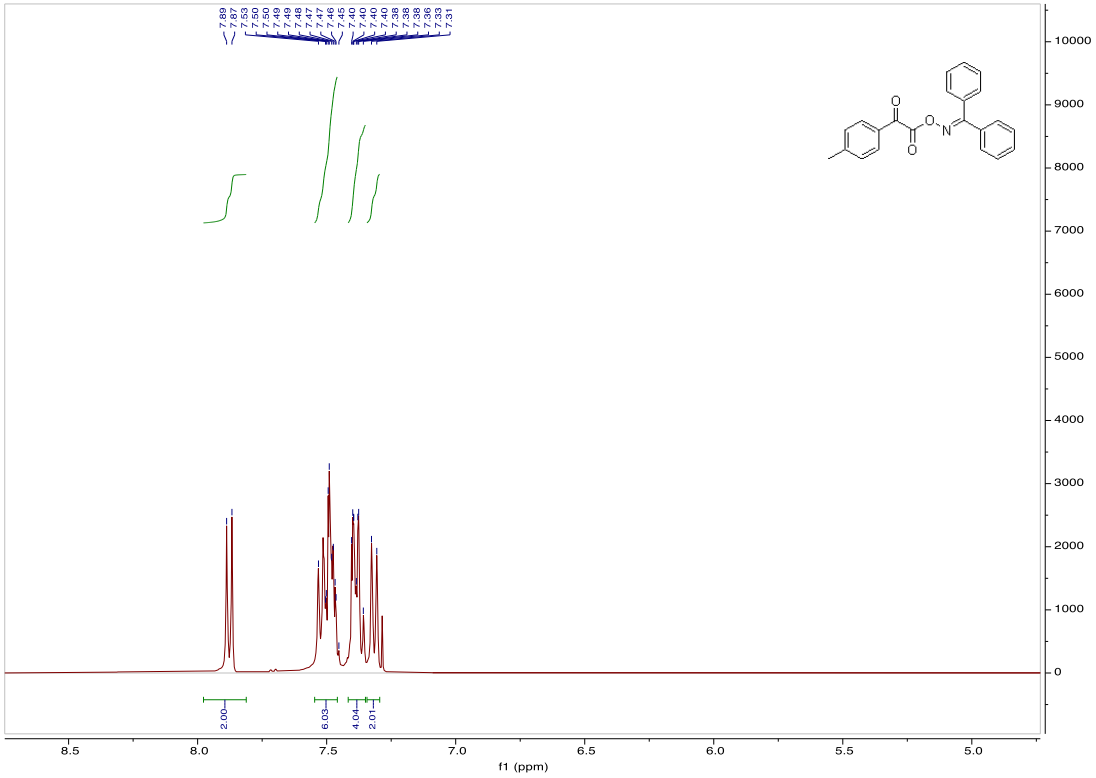


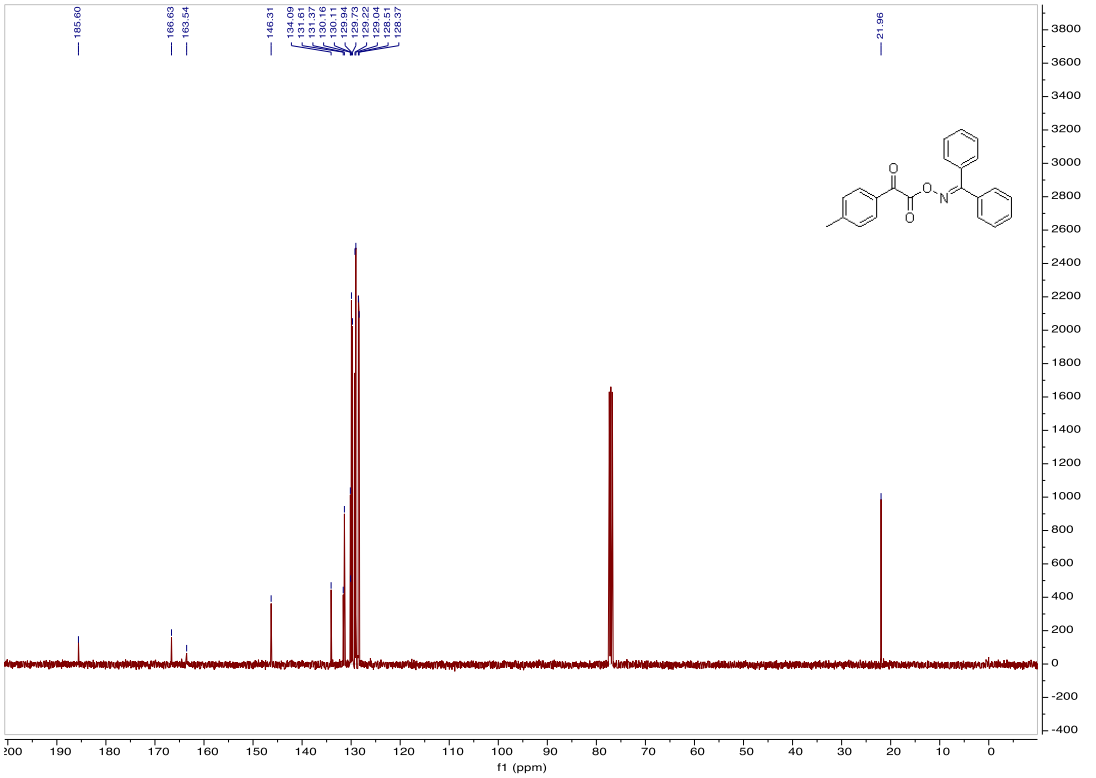
1-(((diphenylmethylene)amino)oxy)-2-(4-methoxyphenyl)ethane-1,2-dione (4b)



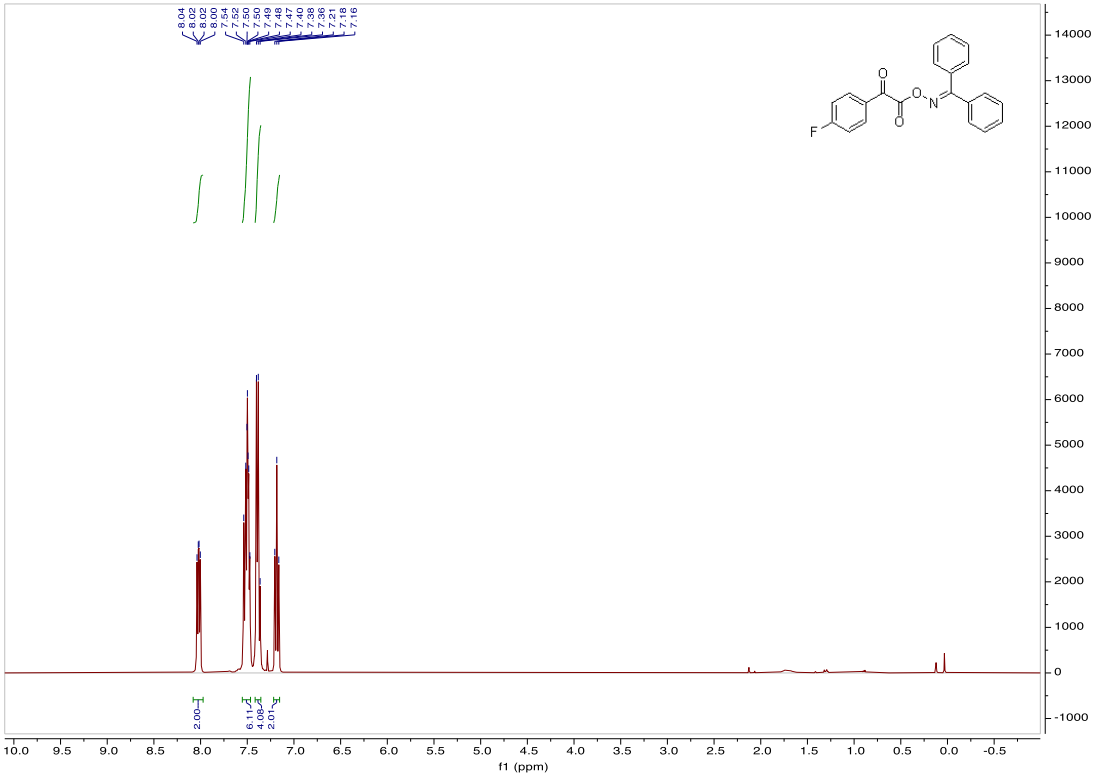


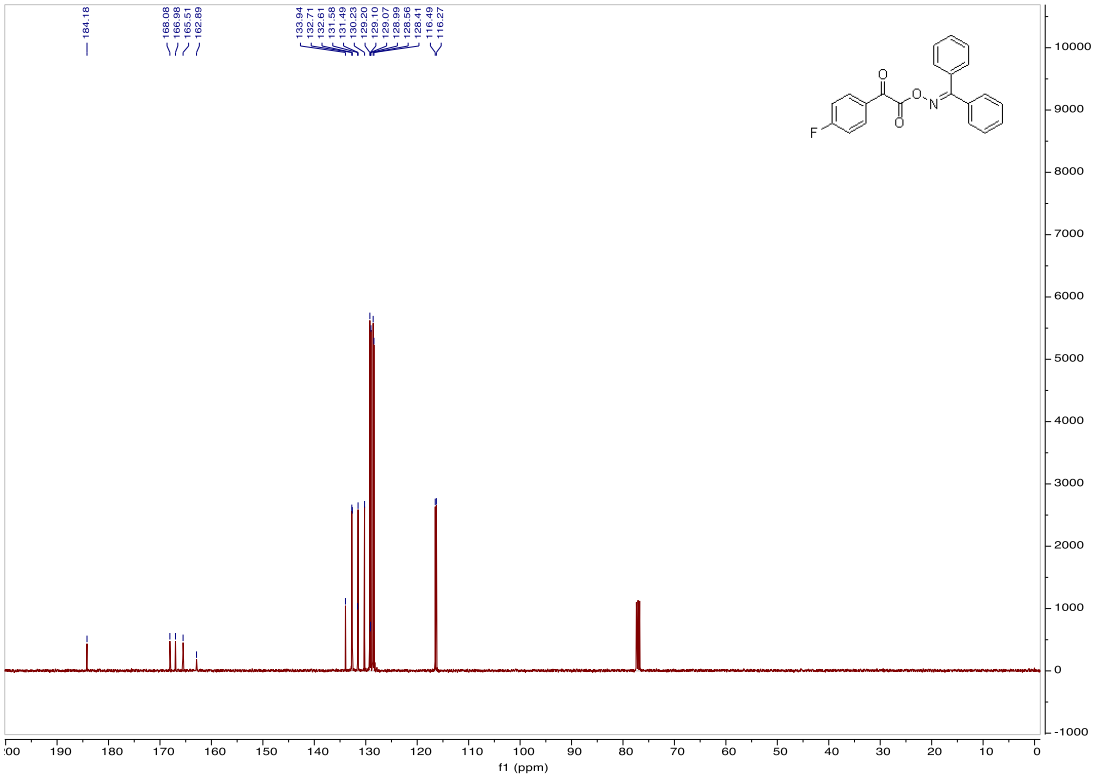
1-(((diphenylmethylene)amino)oxy)-2-(p-tolyl)ethane-1,2-dione (4c)

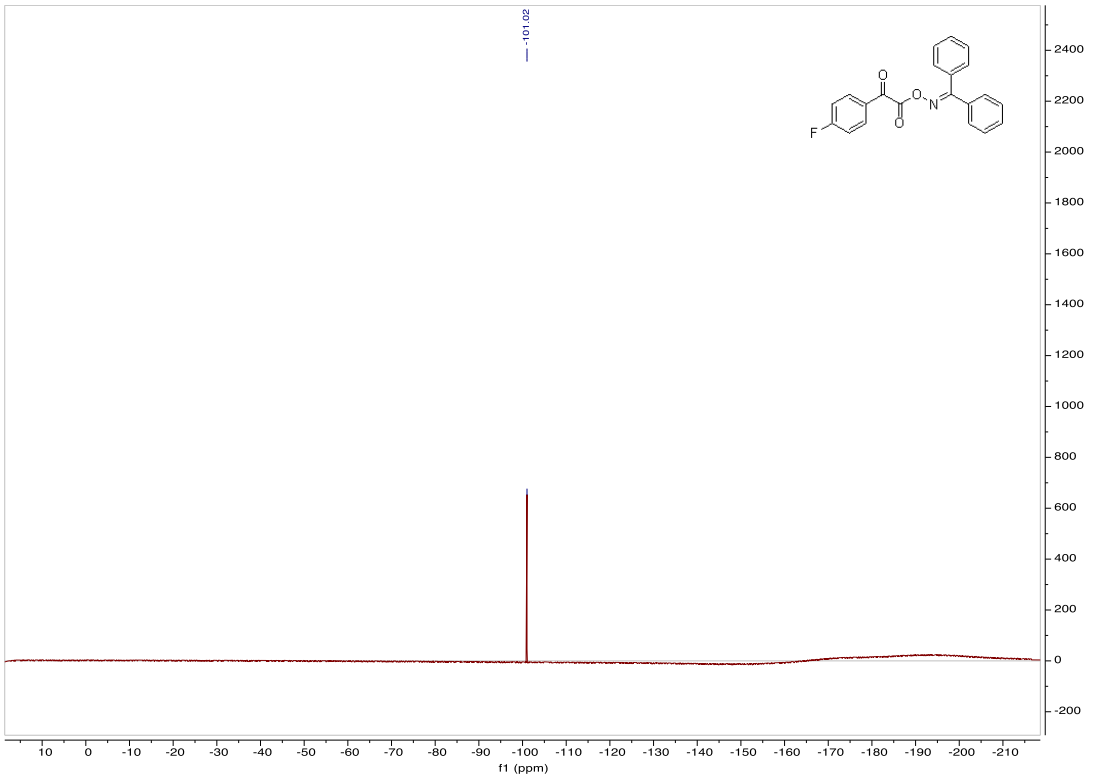




1-(((diphenylmethylene)amino)oxy)-2-(4-fluorophenyl)ethane-1,2-dione (4d)






-101.02
F
O
O
O
N
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10
0
-10
-20
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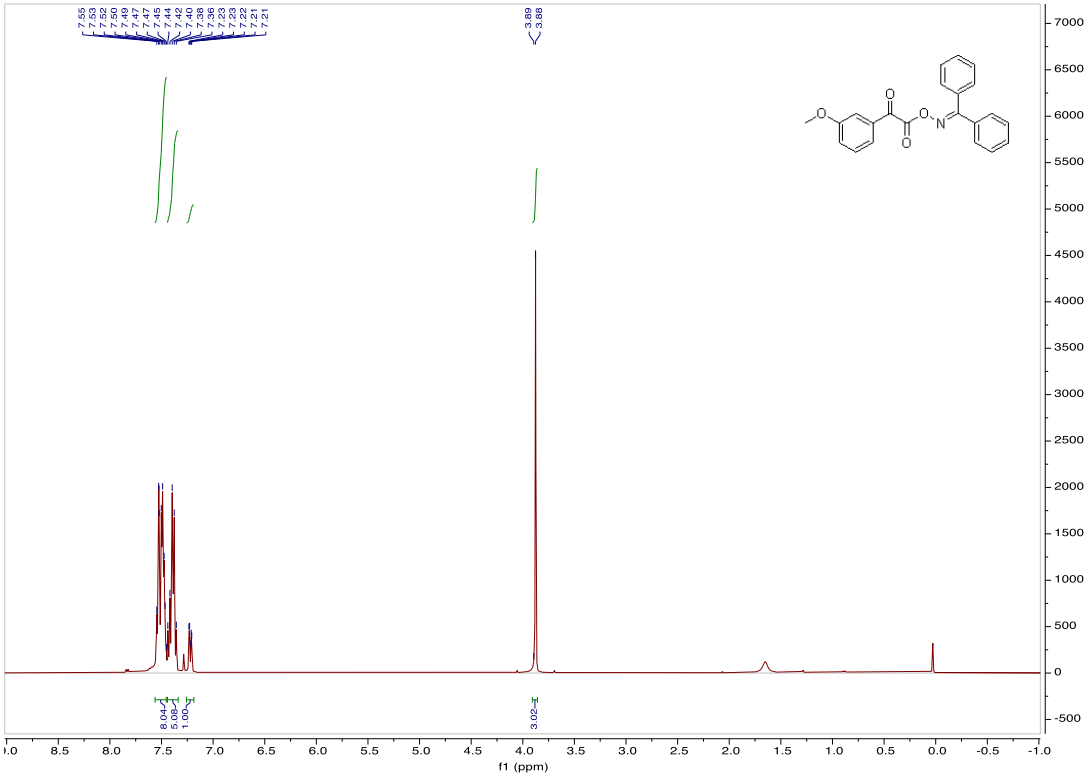
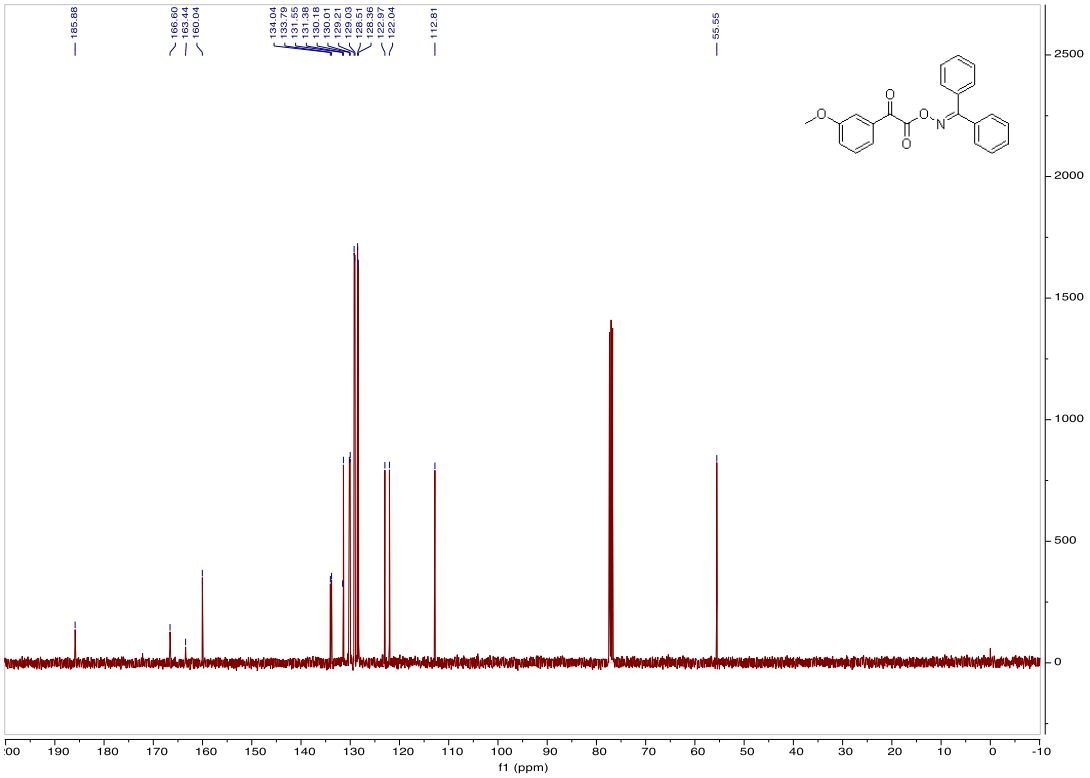
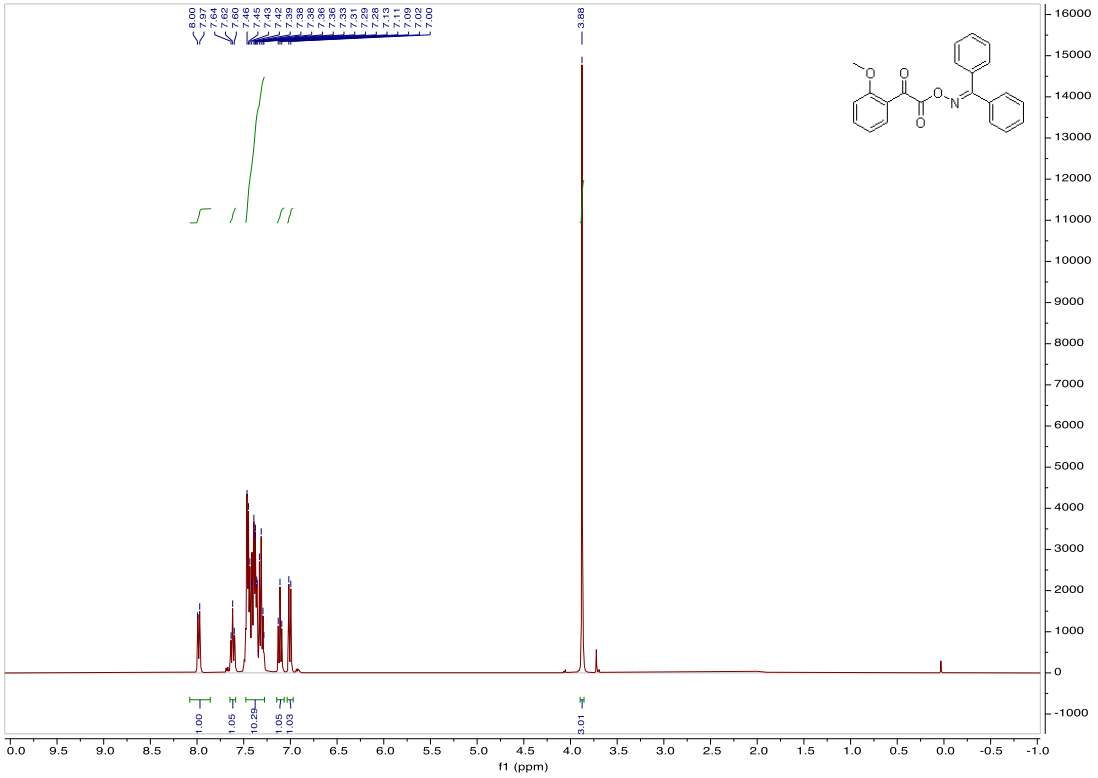
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

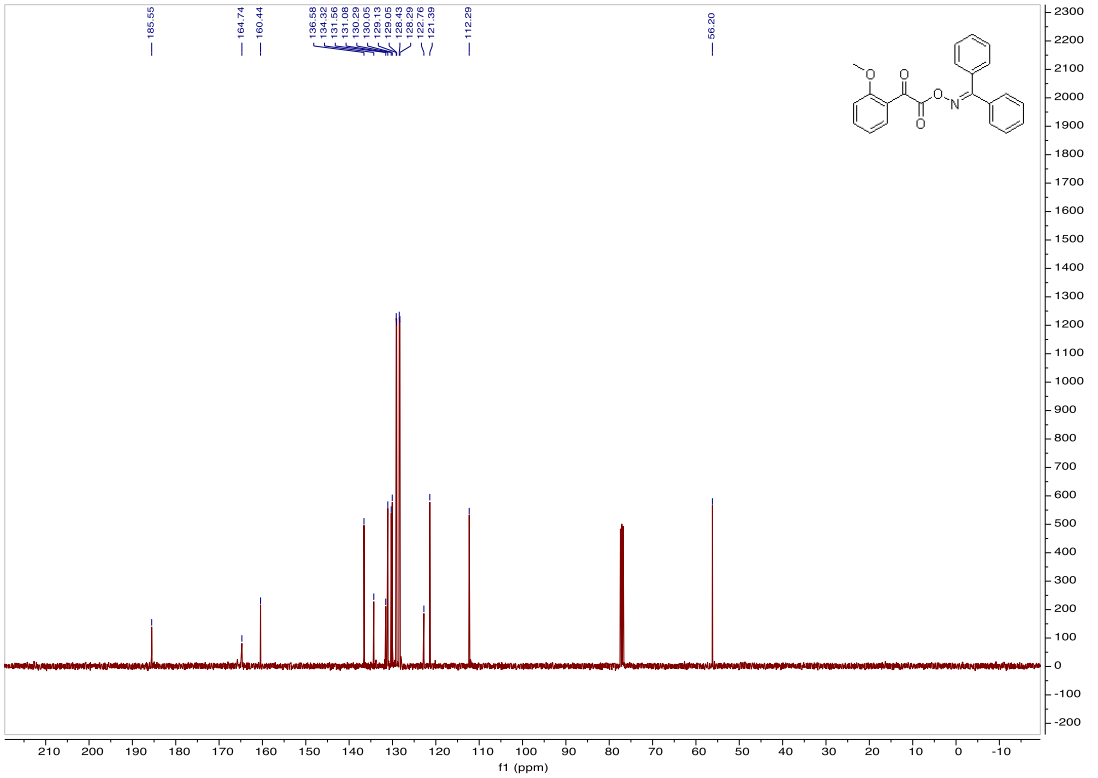
1-(((diphenylmethylene)amino)oxy)-2-(3-methoxyphenyl)ethane-1,2-dione (4e)



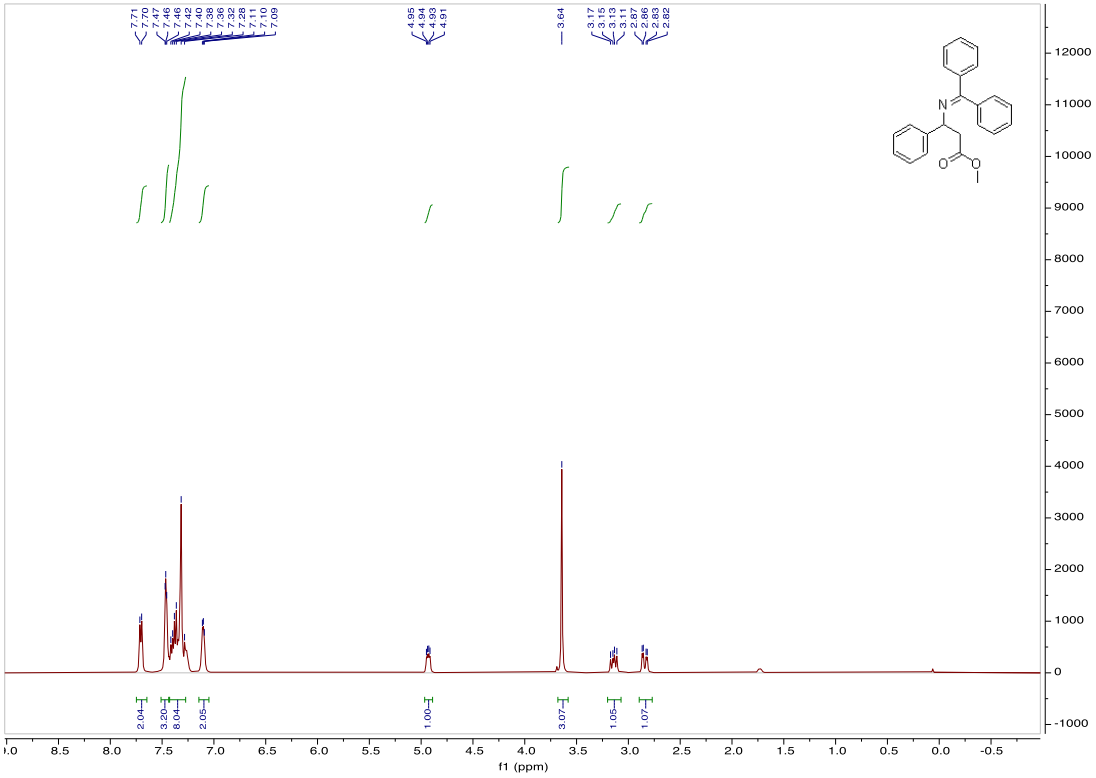


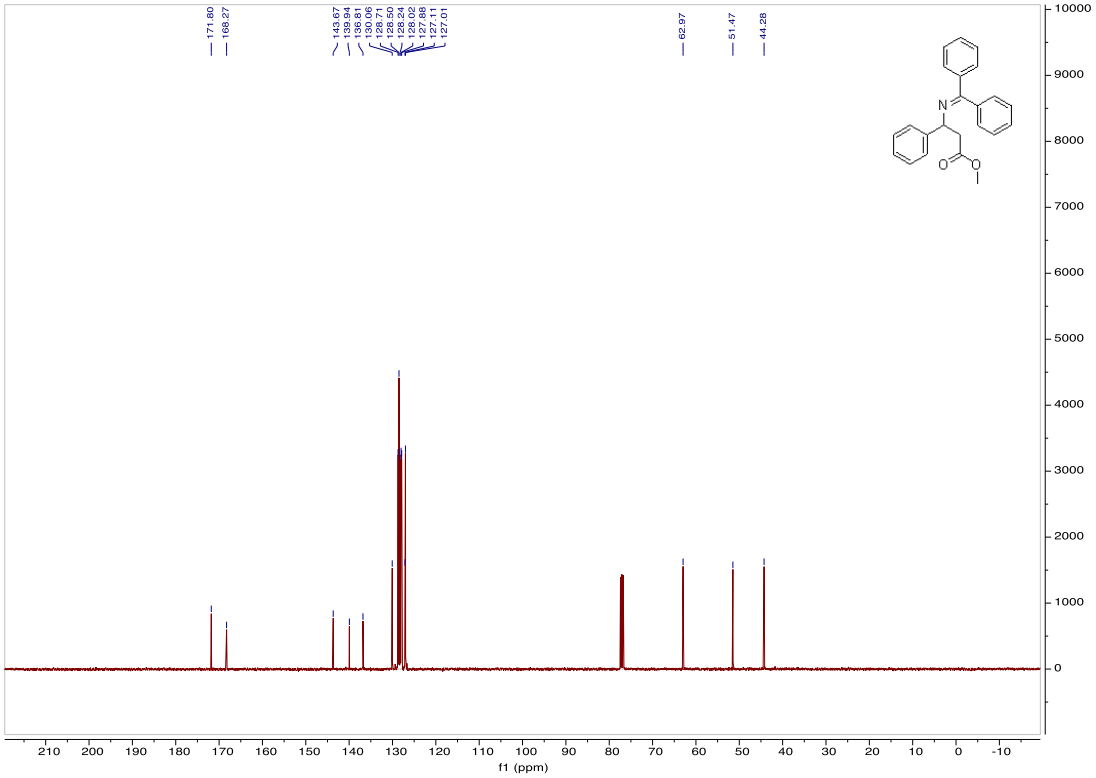
1-(((diphenylmethylene)amino)oxy)-2-(2-methoxyphenyl)ethane-1,2-dione (4f)



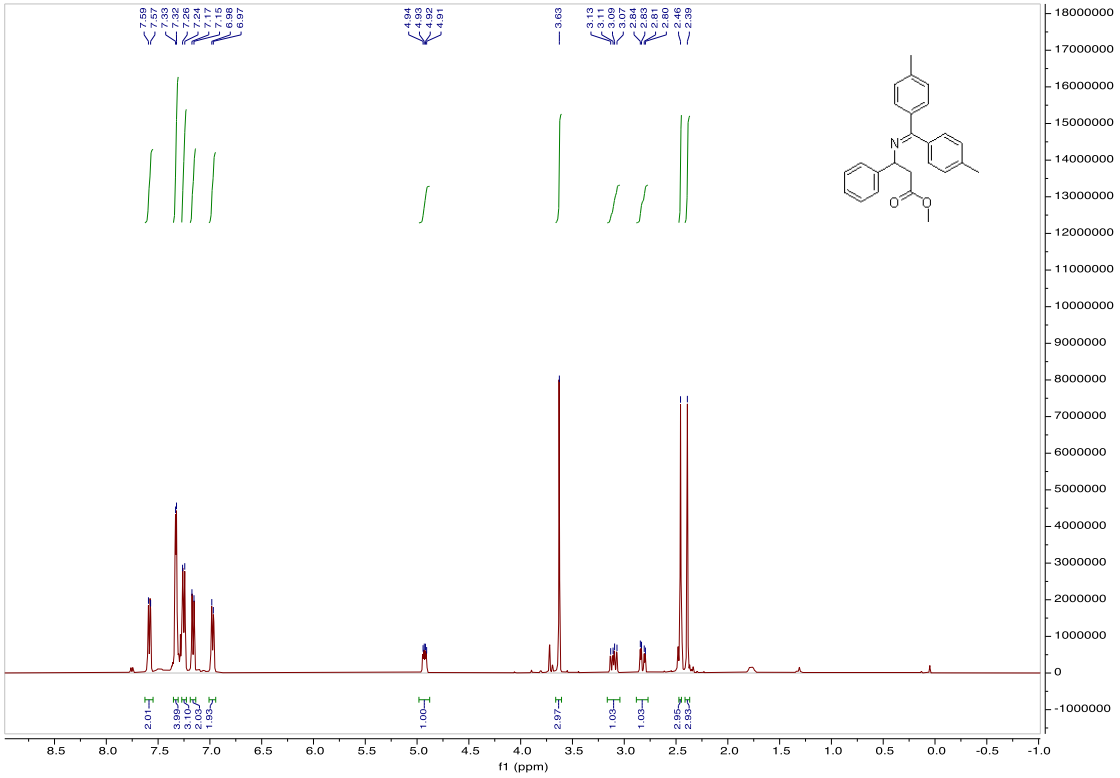


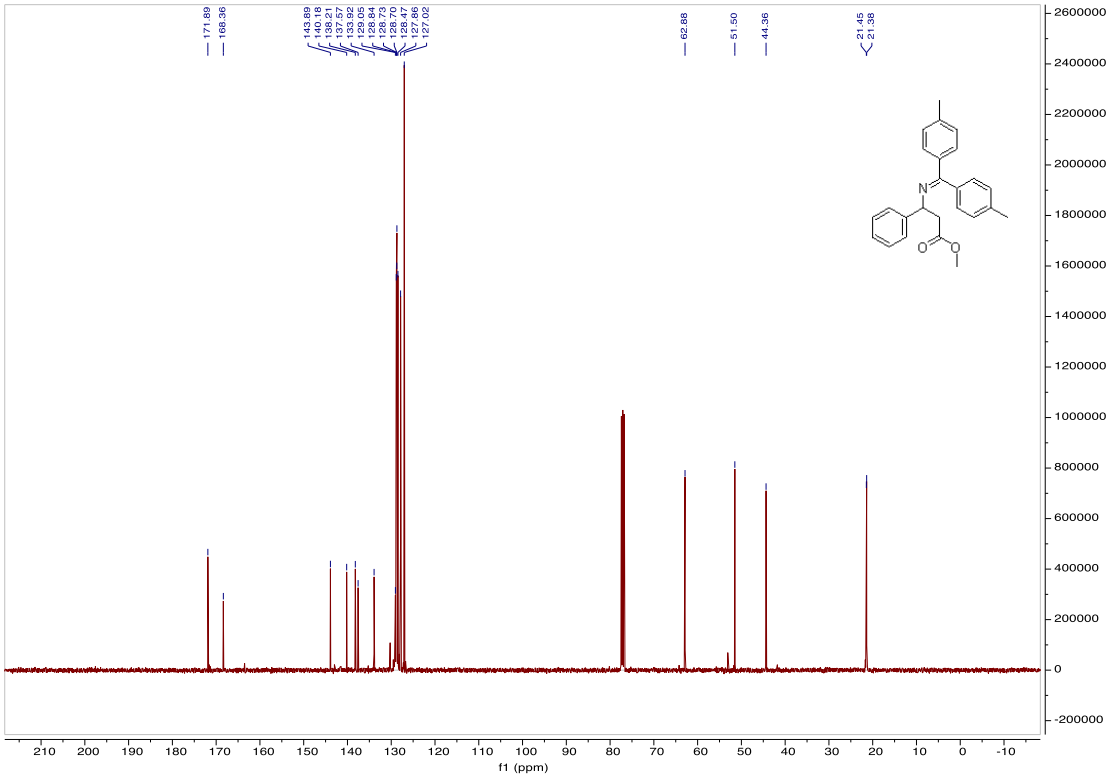
Methyl 3-((diphenylmethylene)amino)-3-phenylpropanoate (3aa)



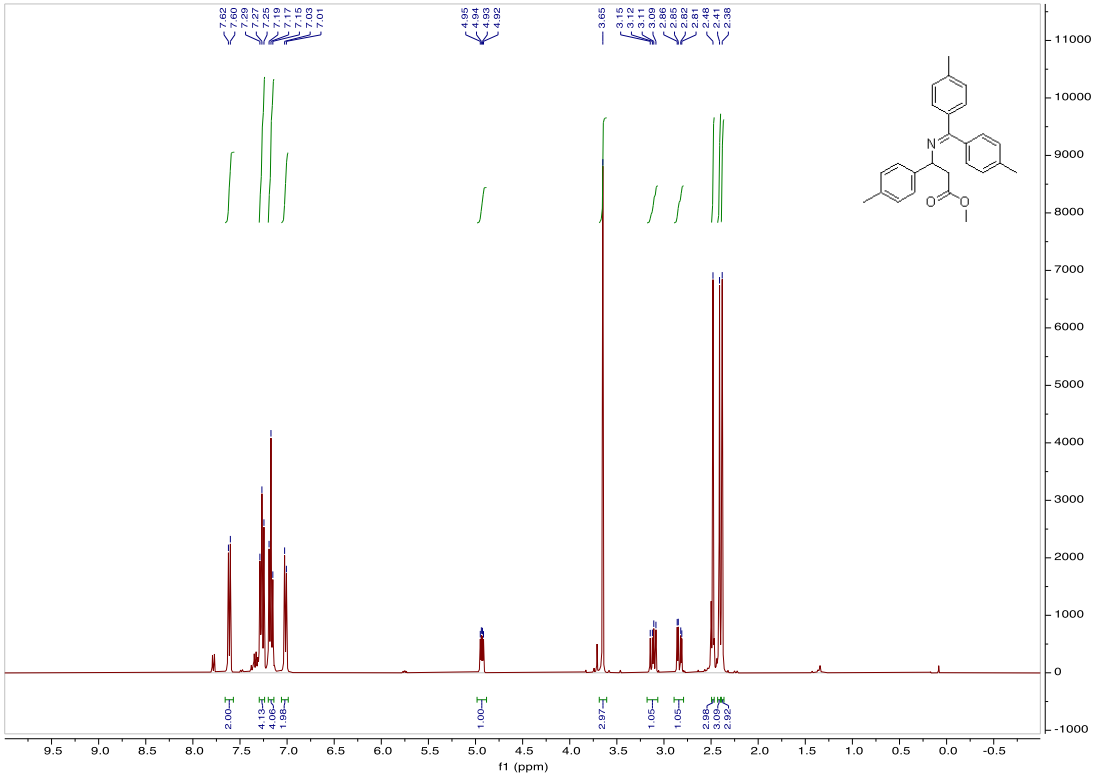


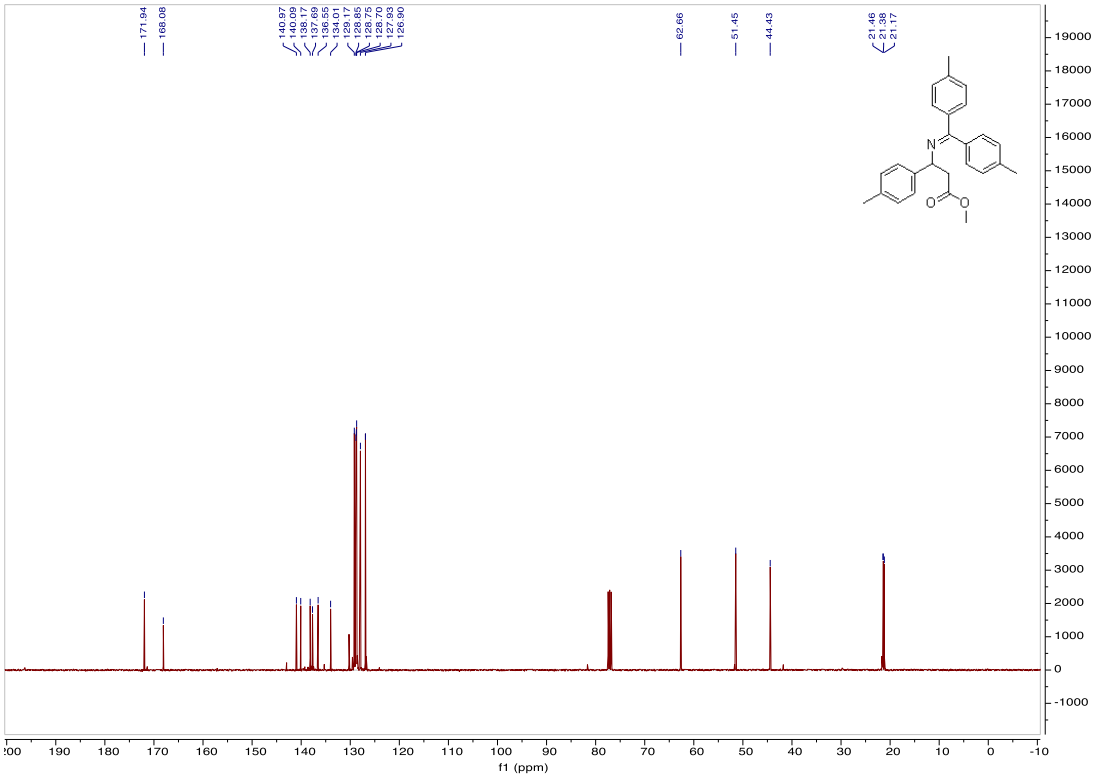
Methyl 3-((di-p-tolylmethylene)amino)-3-phenylpropanoate (3ba)



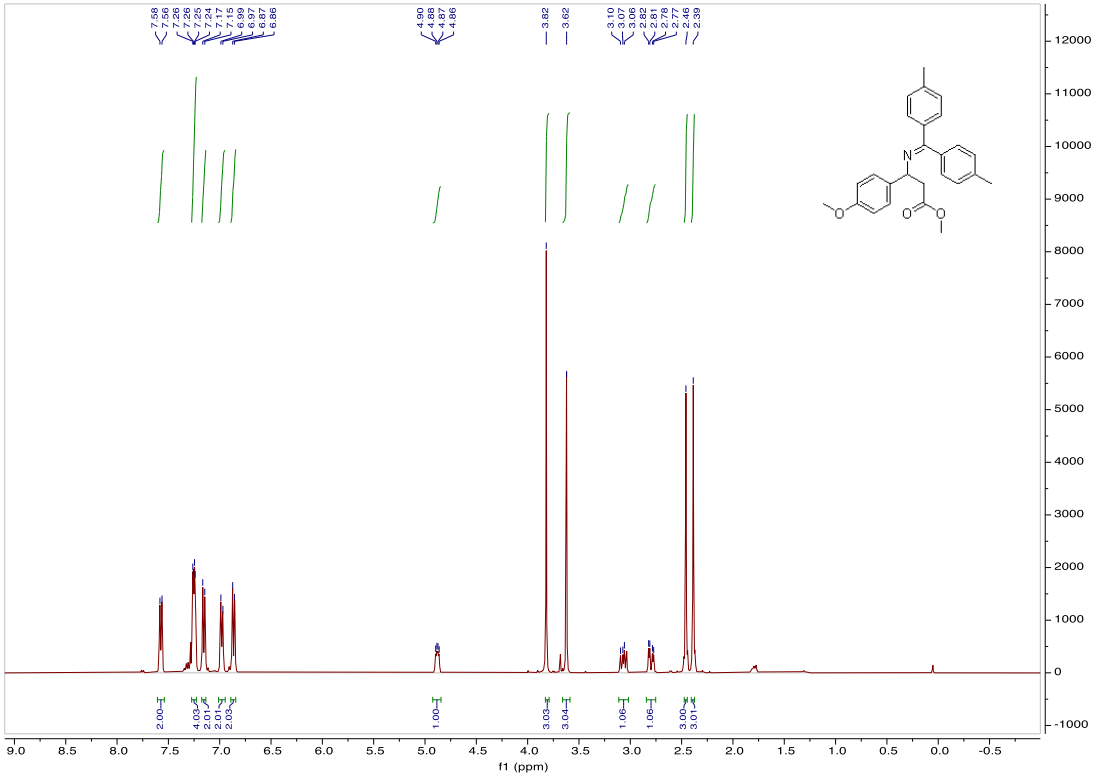


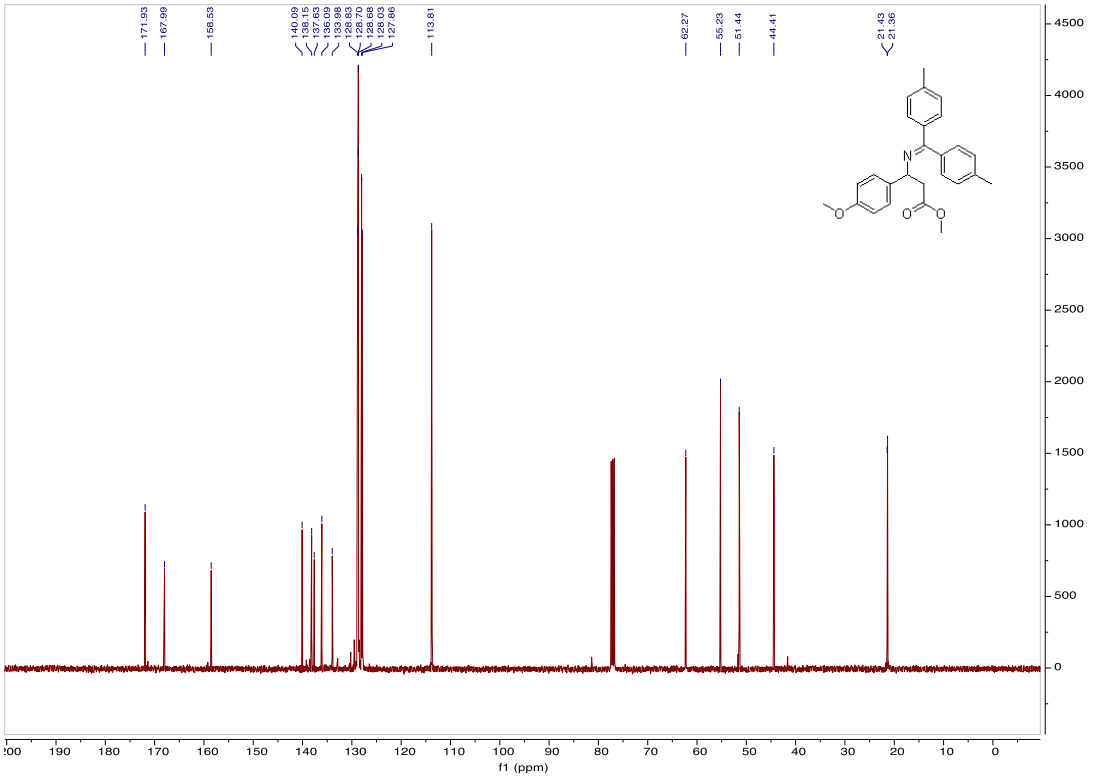
Methyl 3-((di-p-tolylmethylene)amino)-3-(p-tolyl)propanoate (3bb)



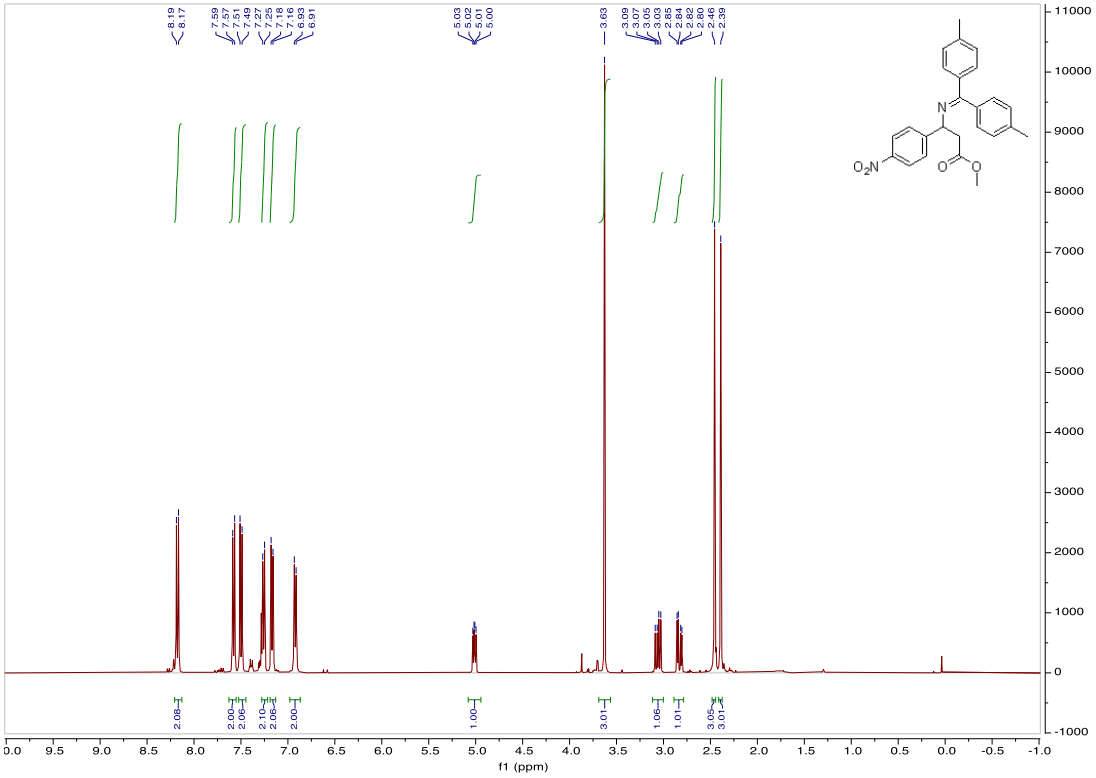


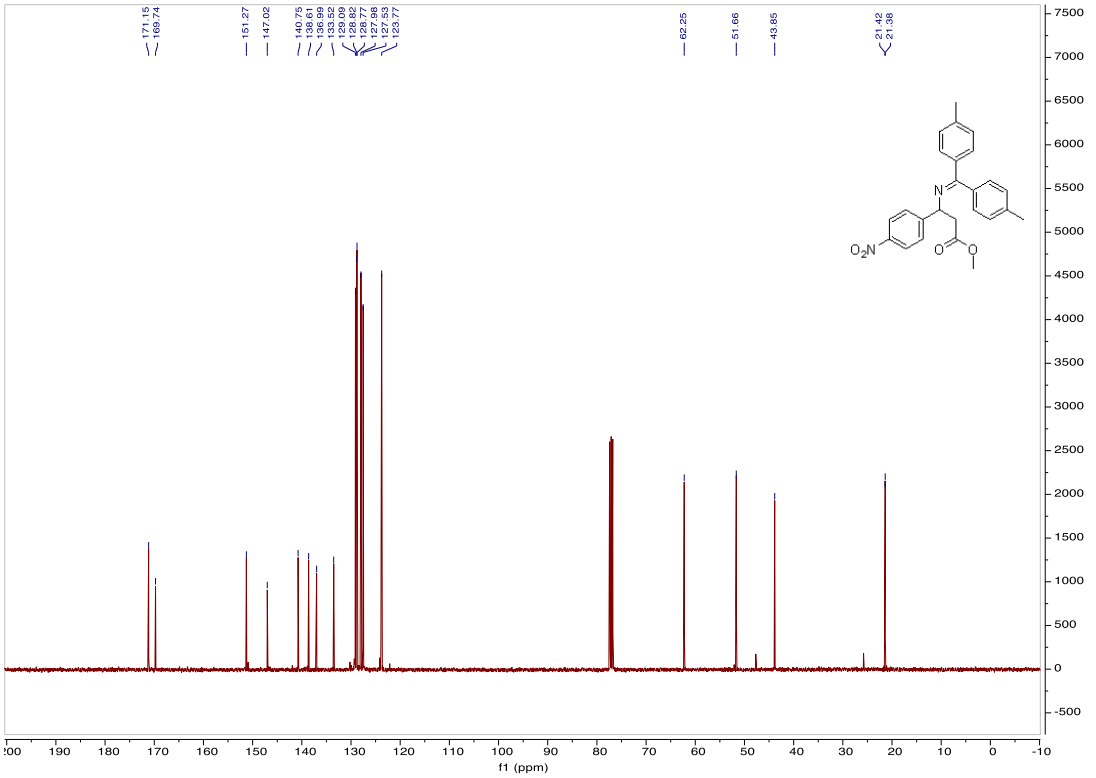
Methyl 3-((di-p-tolylmethylene)amino)-3-(4-methoxyphenyl)propanoate (3bc)



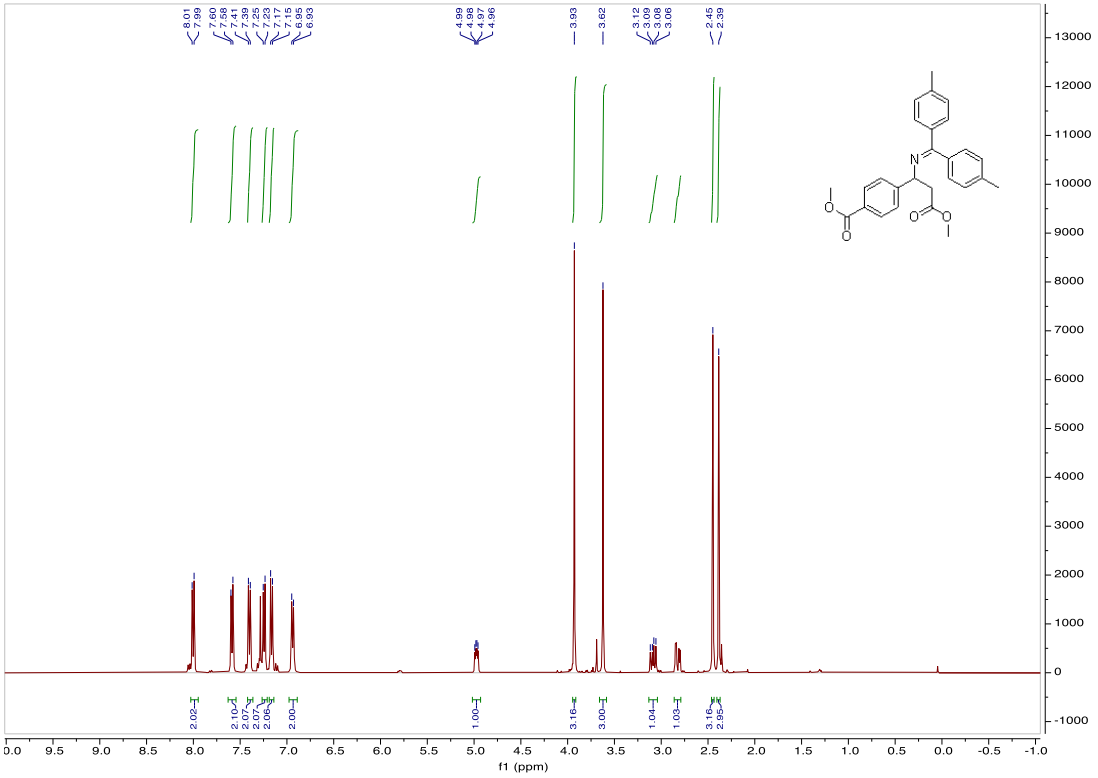


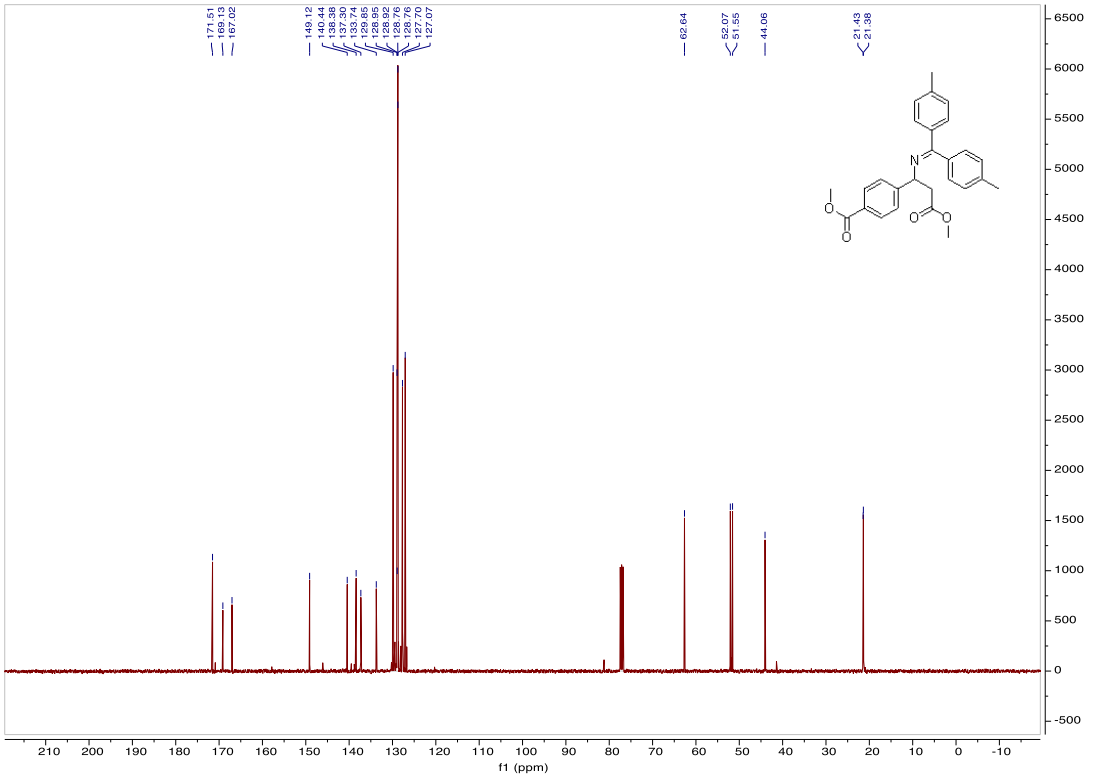
Methyl 3-((di-p-tolylmethylene)amino)-3-(4-nitrophenyl)propanoate (3bd)



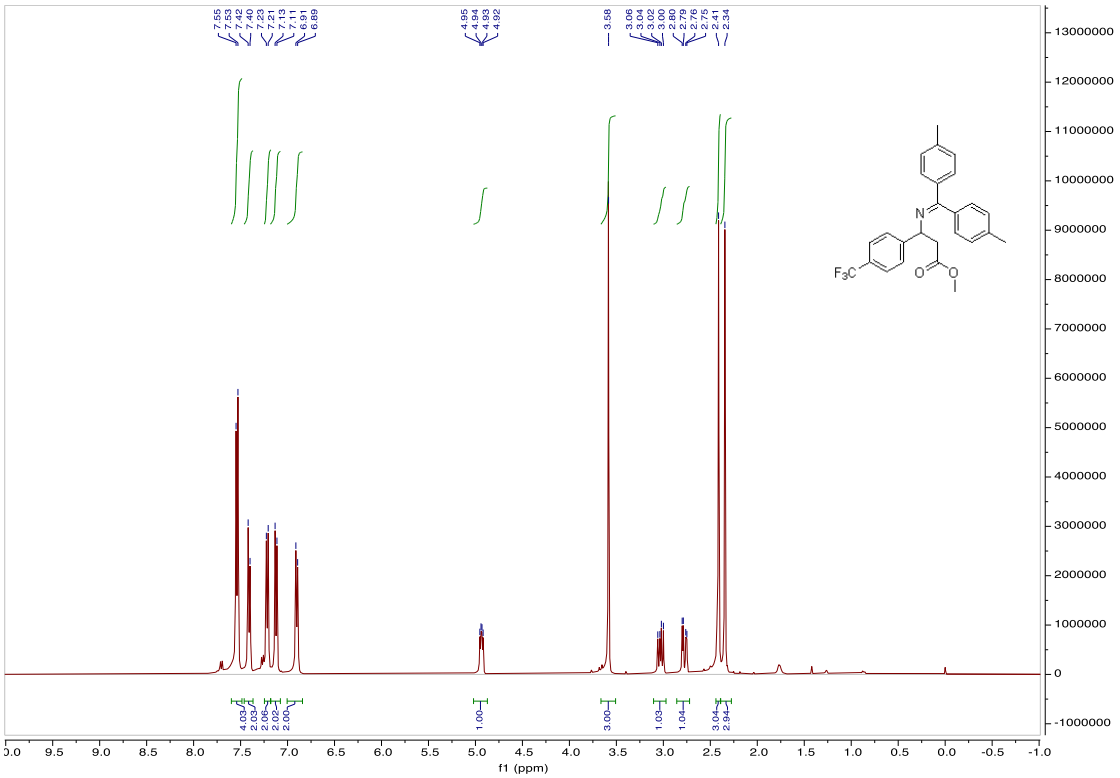


Methyl 4-(1-((di-p-tolylmethylene)amino)-3-methoxy-3-oxopropyl)benzoate (3be)





Methyl 3-((di-p-tolylmethylene)amino)-3-(4-(trifluoromethyl)phenyl)propanoate (3bf)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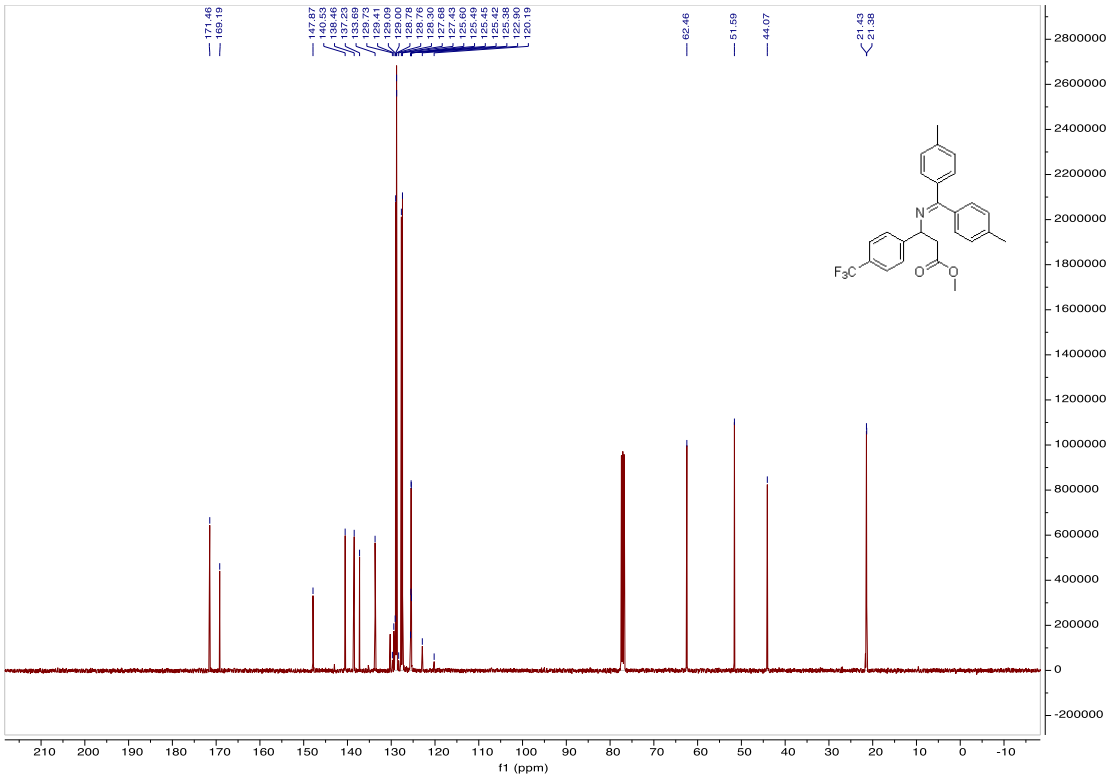
7.53
7.42
7.40
7.23
7.21
7.13
7.11
6.89
4.95
4.94
4.93
4.92
3.58
3.06
3.04
3.02
3.00
2.80
2.79
2.76
2.75
2.41
2.34
4.03
2.03
2.06
2.02
2.00
1.00
3.00
1.03
1.04
3.04
2.94
f1 (ppm)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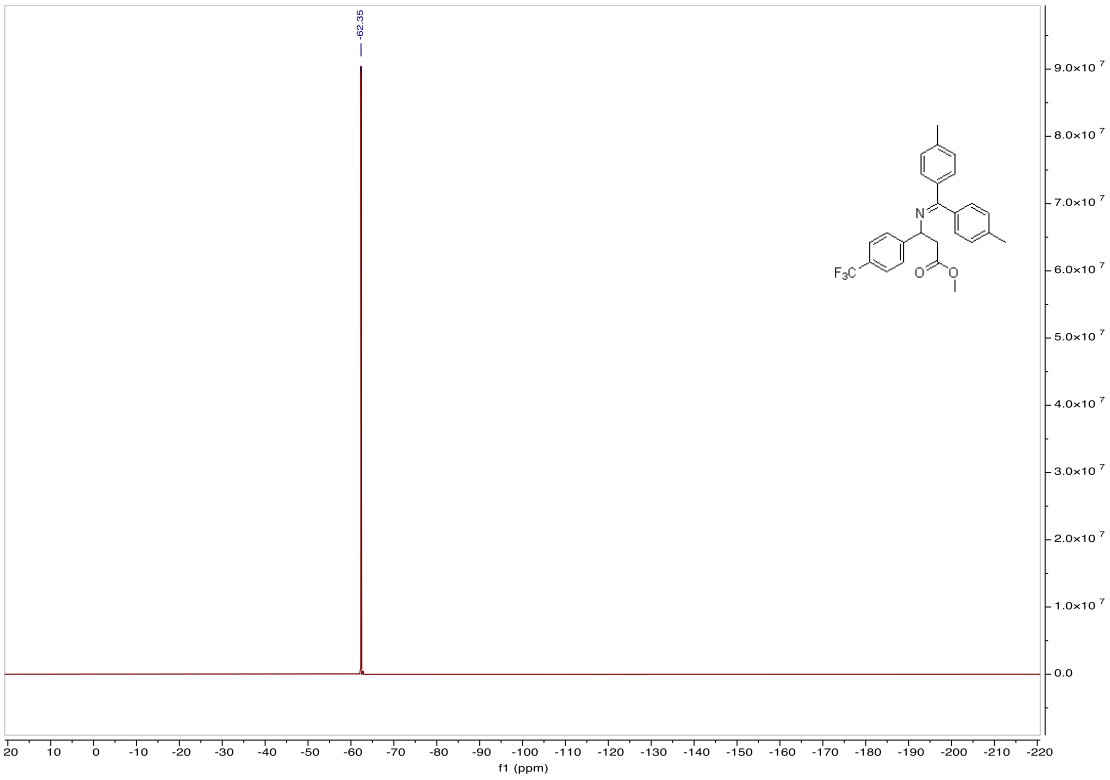
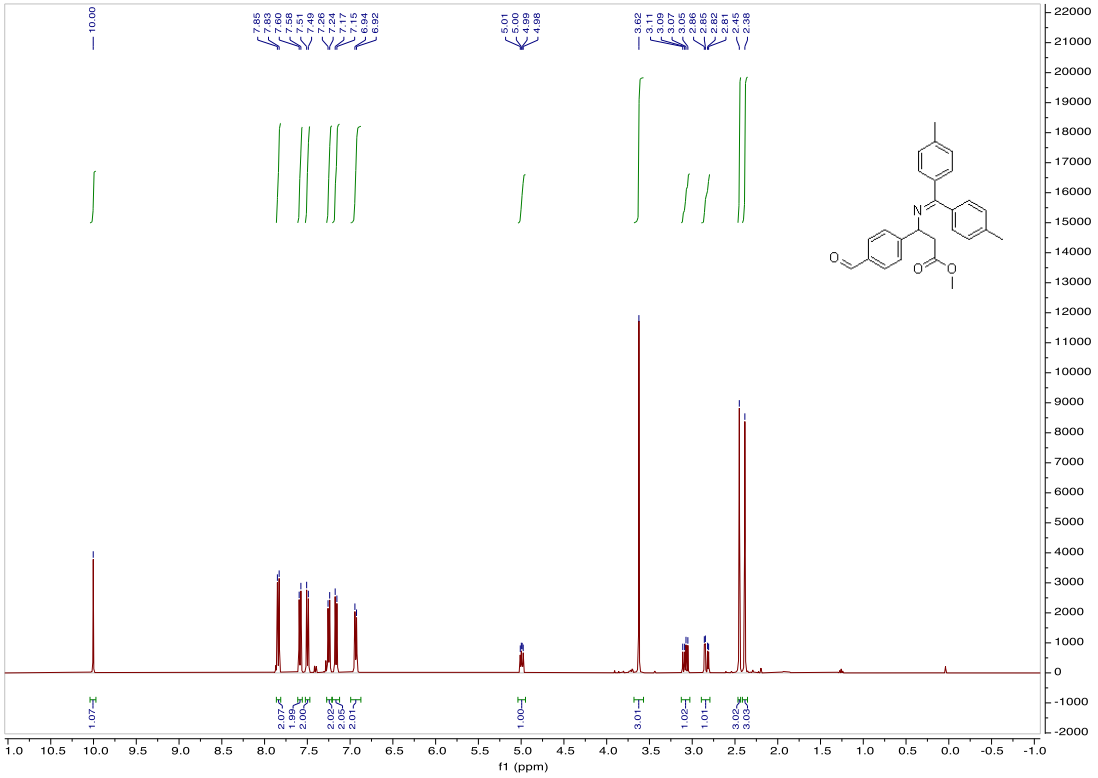
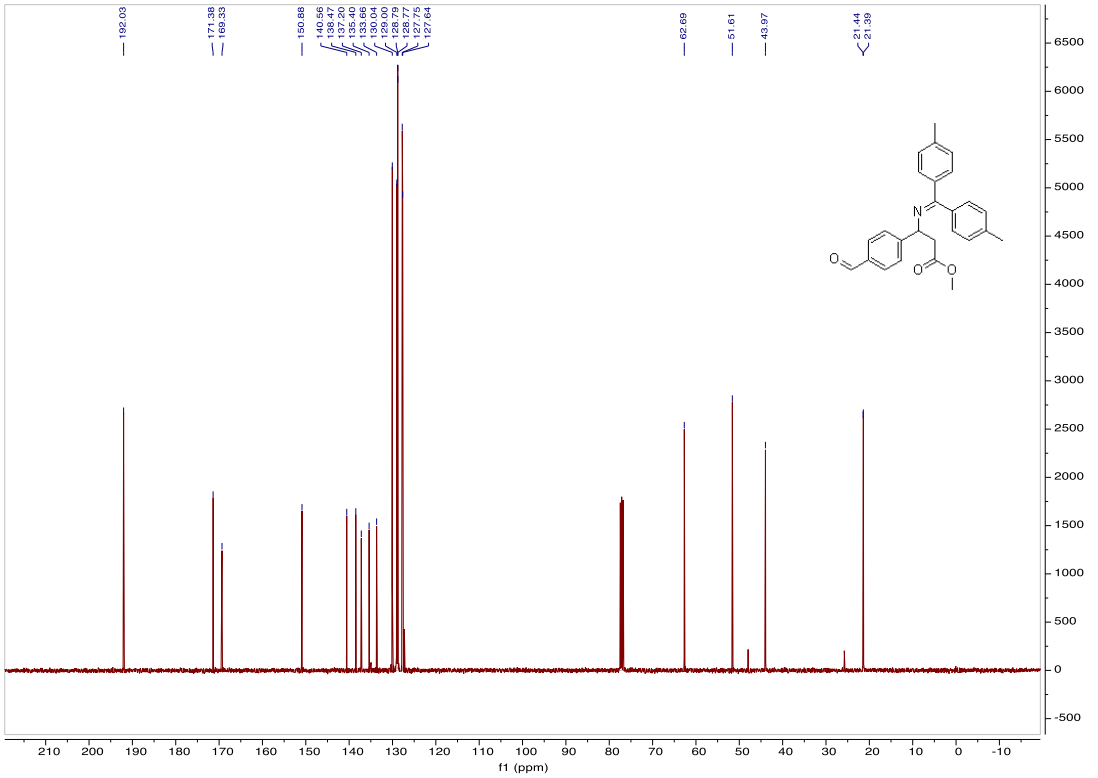
169.19
147.87
144.53
138.46
137.23
133.69
129.73
129.41
129.09
129.00
128.78
128.76
128.30
127.68
127.43
125.49
125.49
125.45
125.42
125.38
123.99
120.19
62.46
51.59
44.07
21.43
21.38
f1 (ppm)

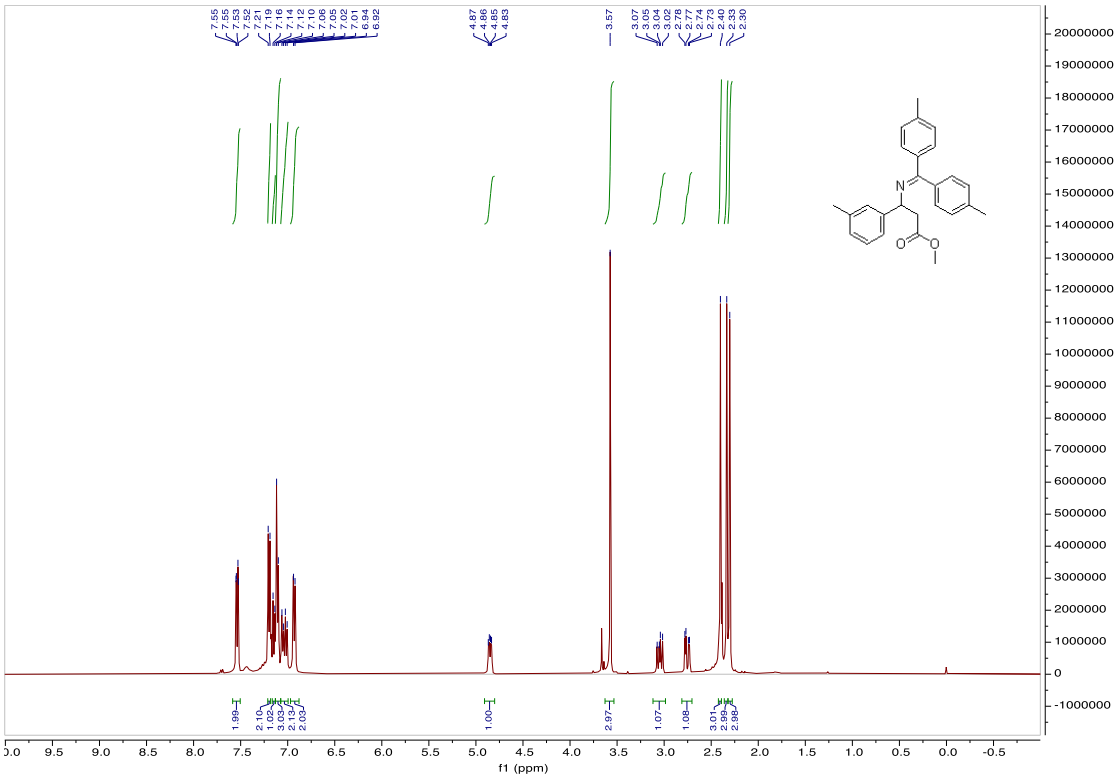

-62.35
9.0x10 7
8.0x10 7
7.0x10 7
6.0x10 7
5.0x10 7
4.0x10 7
3.0x10 7
2.0x10 7
1.0x10 7
0.0
N
F3C
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

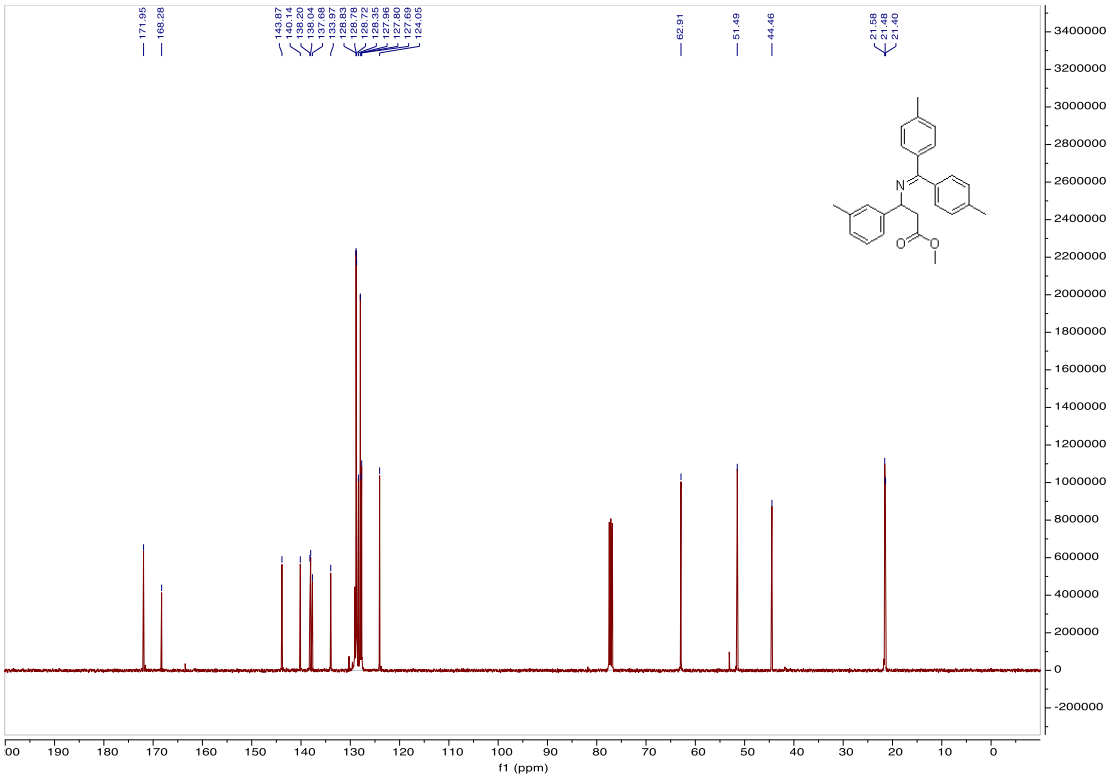
Methyl 3-((di-p-tolylmethylene)amino)-3-(4-formylphenyl)propanoate (3bg)



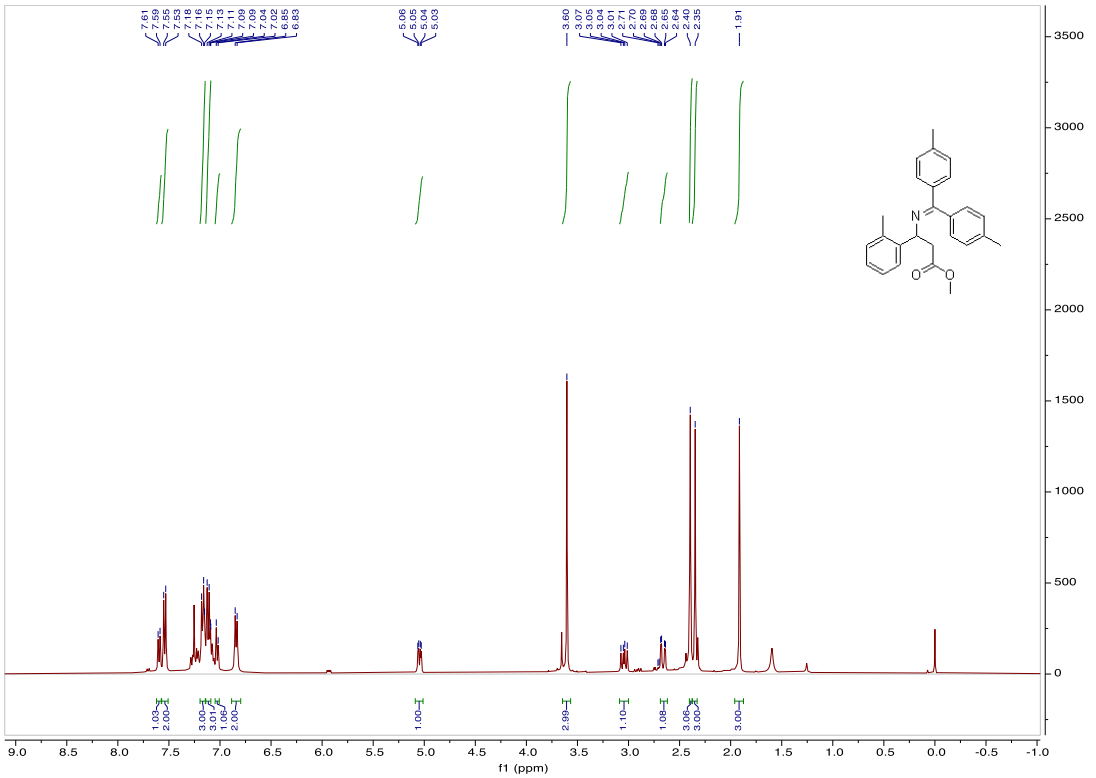


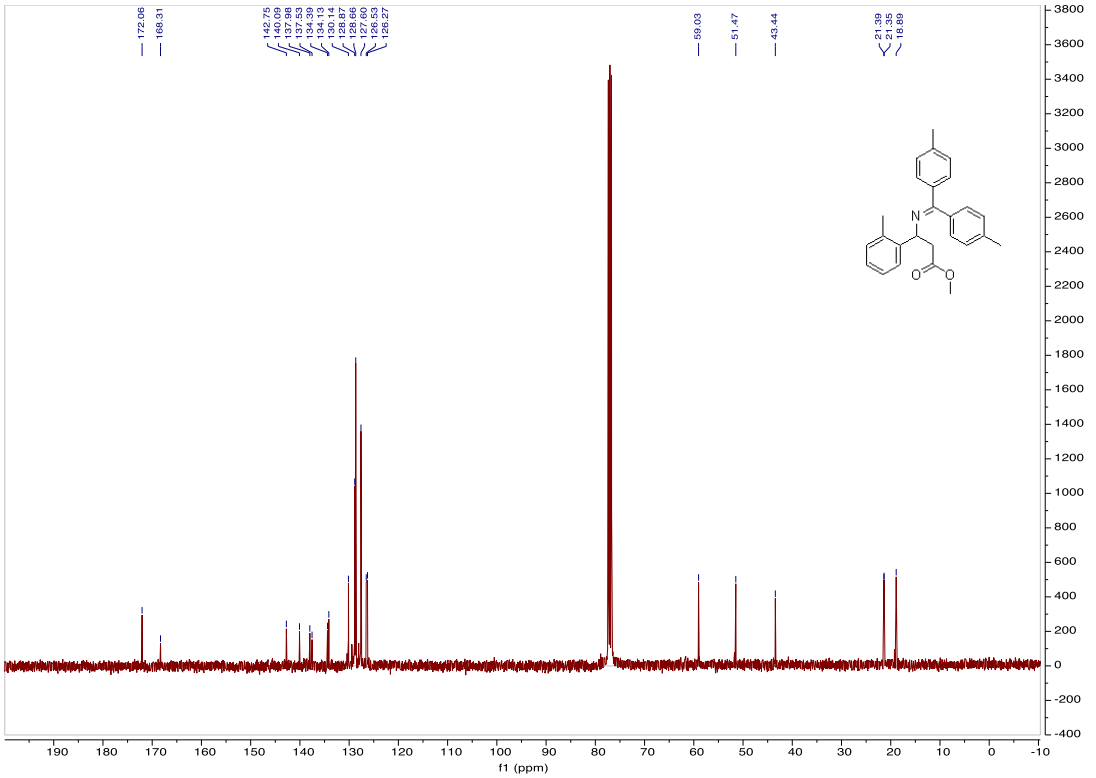
Methyl 3-((di-p-tolylmethylene)amino)-3-(m-tolyl)propanoate (3bh)



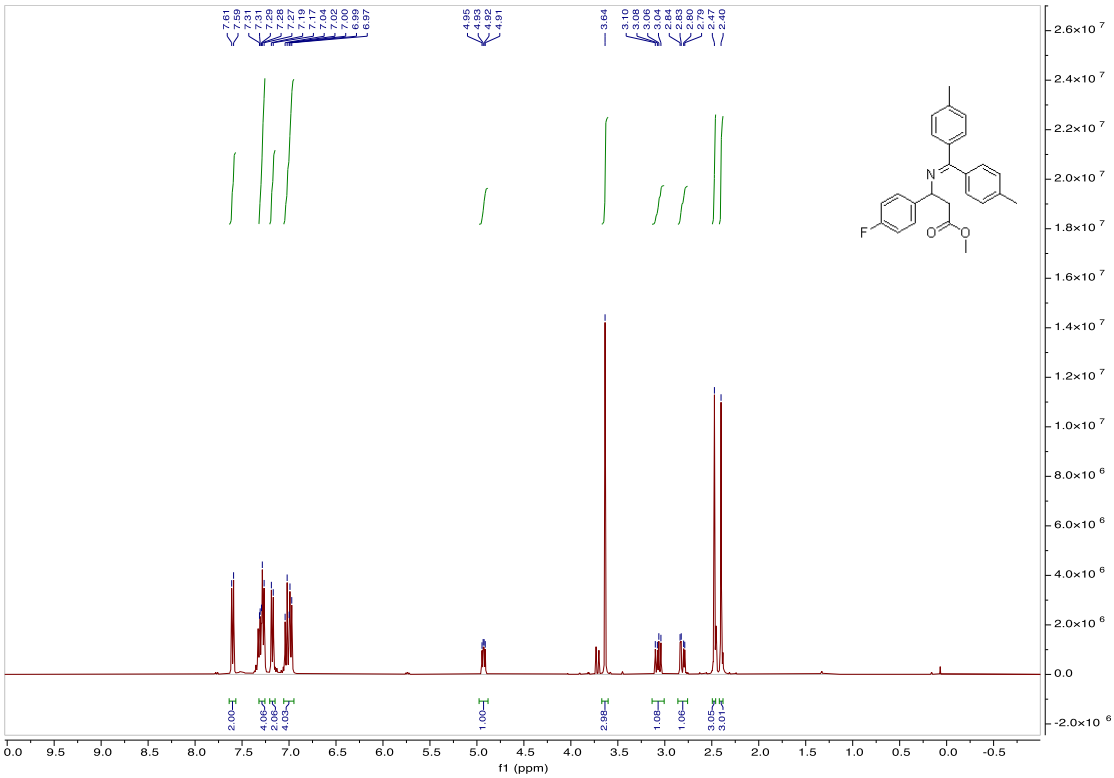


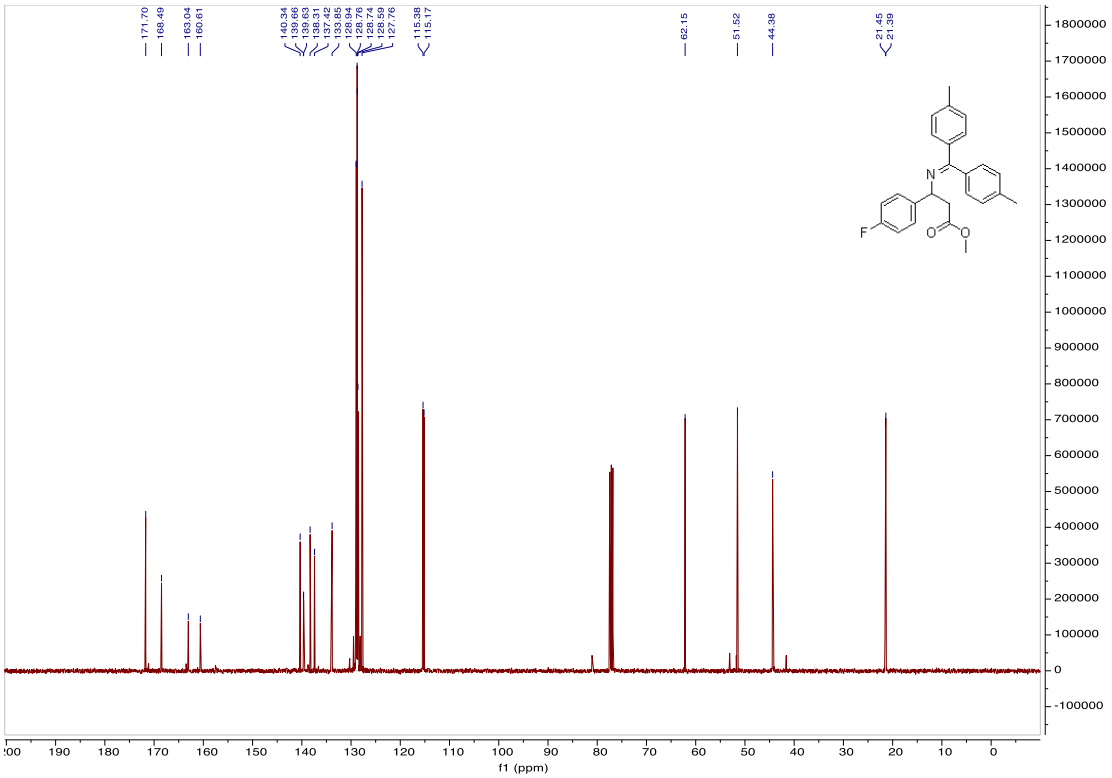
Methyl 3-((di-p-tolylmethylene)amino)-3-(o-tolyl)propanoate (3bi)

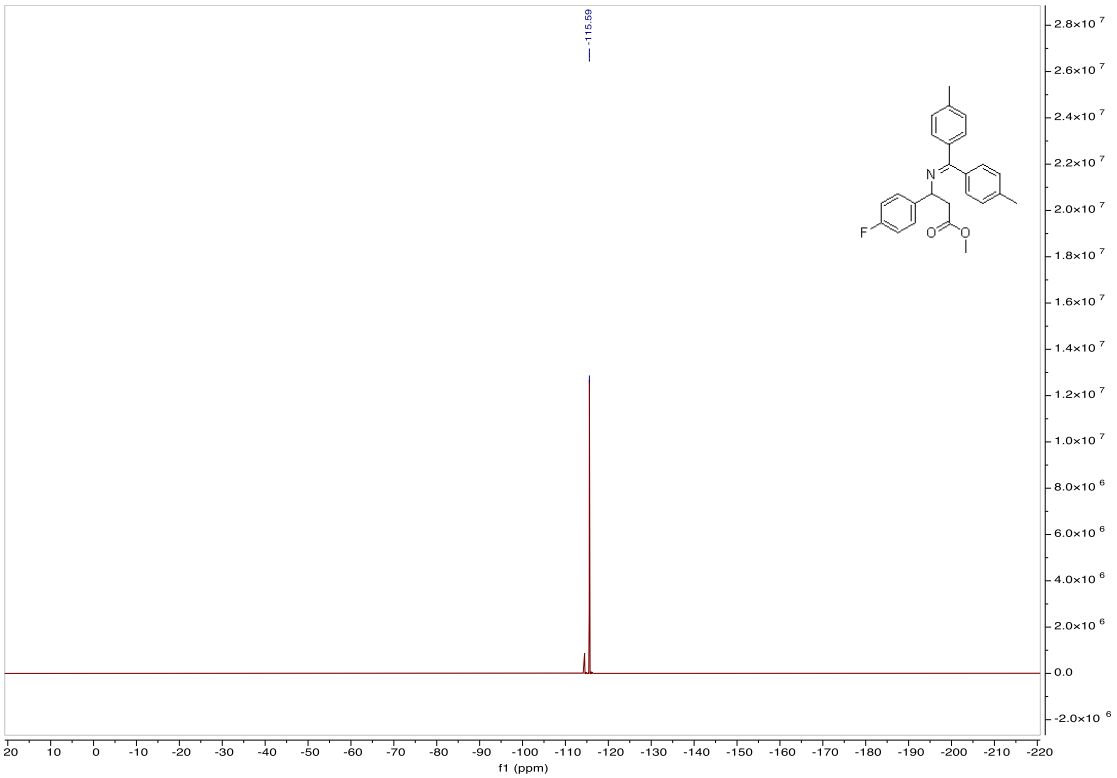




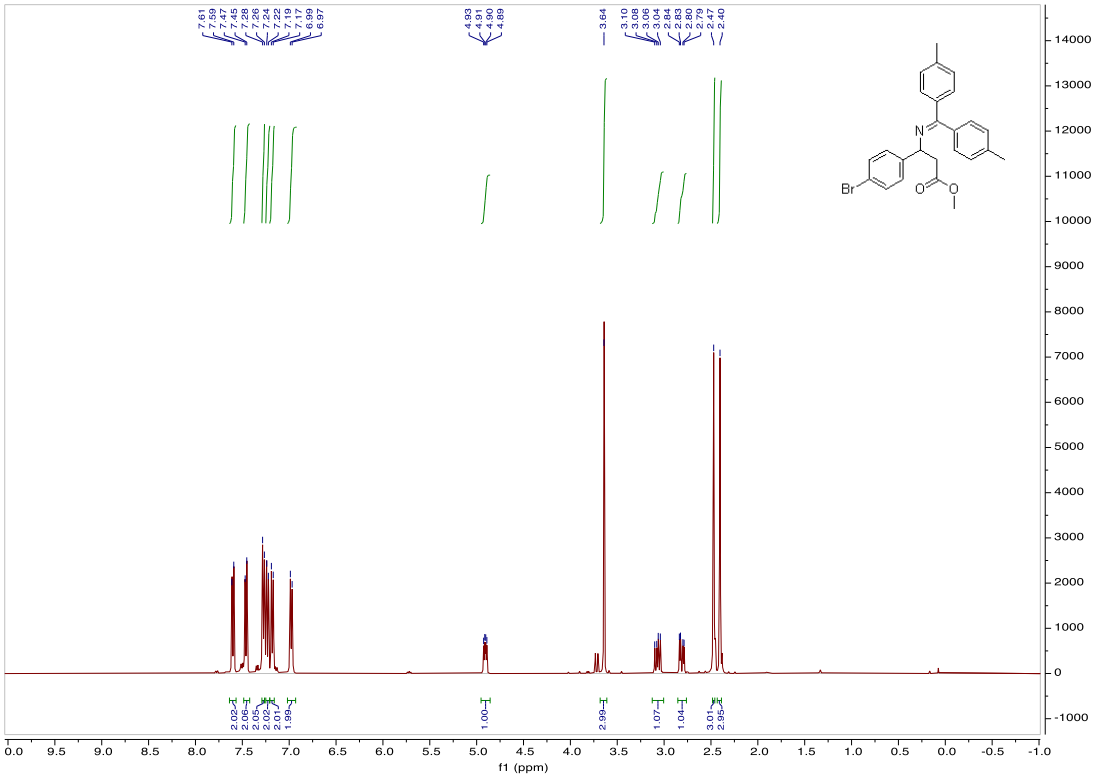
Methyl 3-((di-p-tolylmethylene)amino)-3-(4-fluorophenyl)propanoate (3bj)

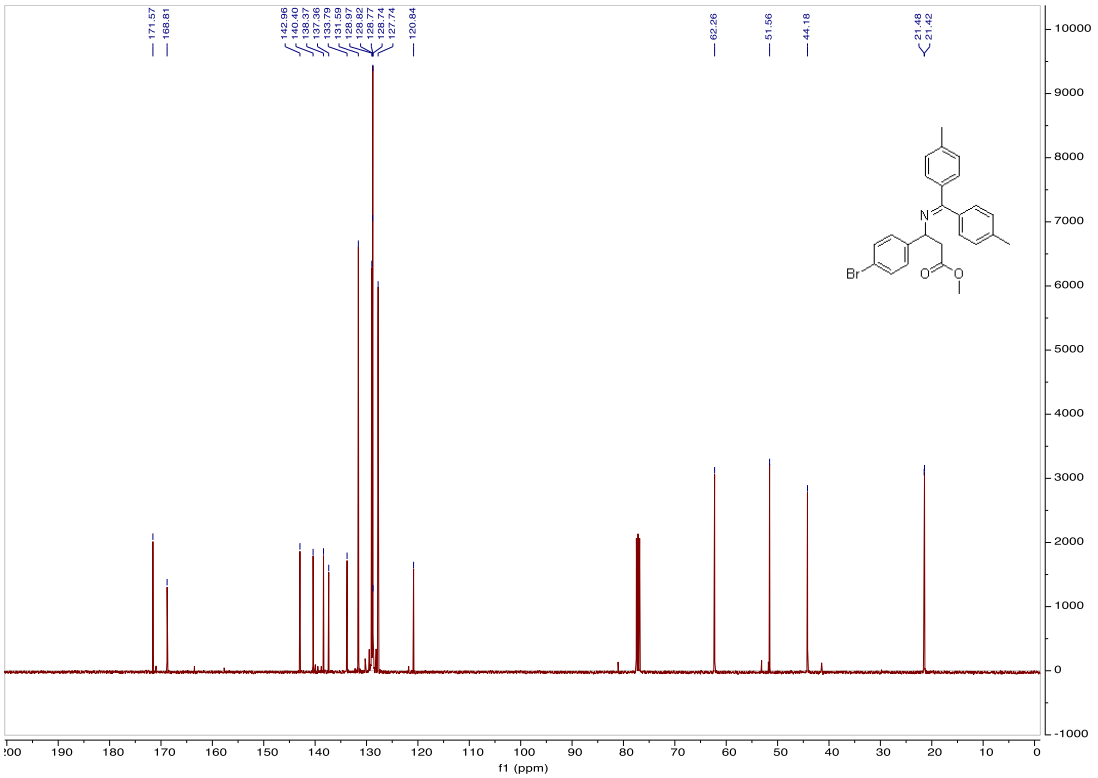

7.61
7.59
7.31
7.29
7.28
7.27
7.19
7.17
7.04
7.02
7.00
6.99
6.97
4.95
4.93
4.92
4.91
3.64
3.10
3.08
3.06
3.04
2.84
2.83
2.80
2.79
2.47
2.40
F
N
O
O
2.00
4.06
2.06
4.03
1.00
2.98
1.08
1.06
3.05
3.01
f1 (ppm)


171.70
168.49
163.04
160.61
140.34
139.66
139.60
138.31
137.42
133.85
133.84
128.76
128.74
128.59
127.76
115.38
115.17
62.15
51.52
44.38
21.45
21.39
F
N
O
O
f1 (ppm)

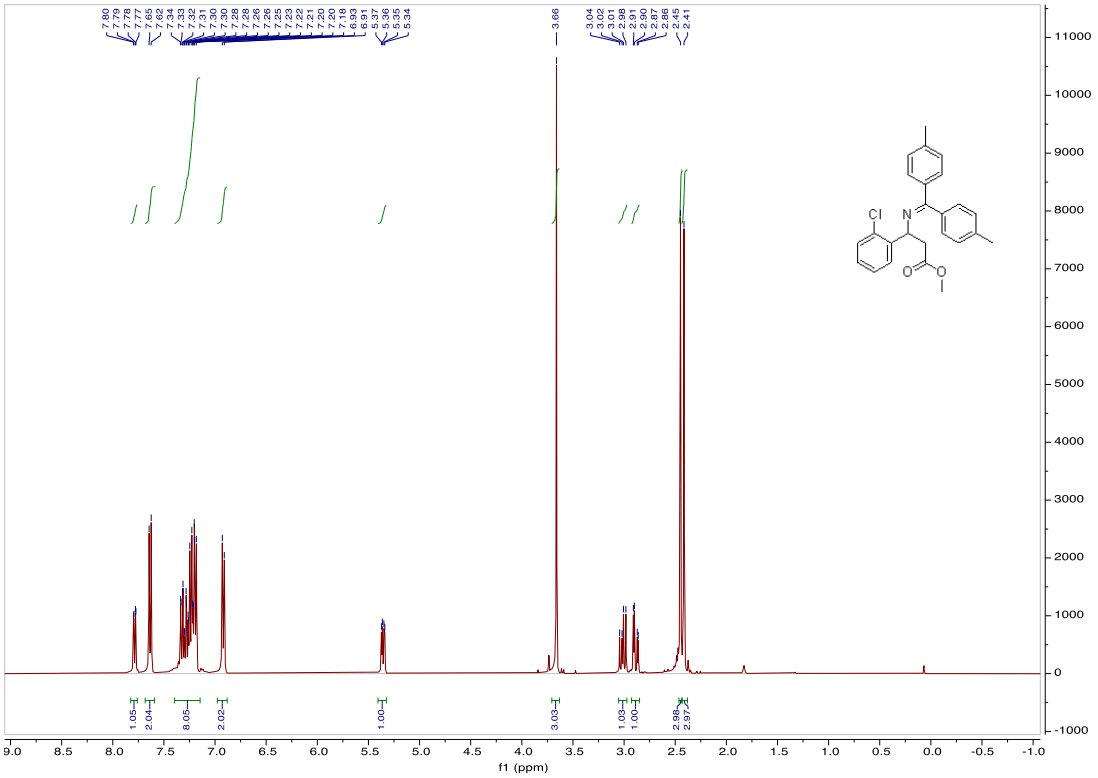


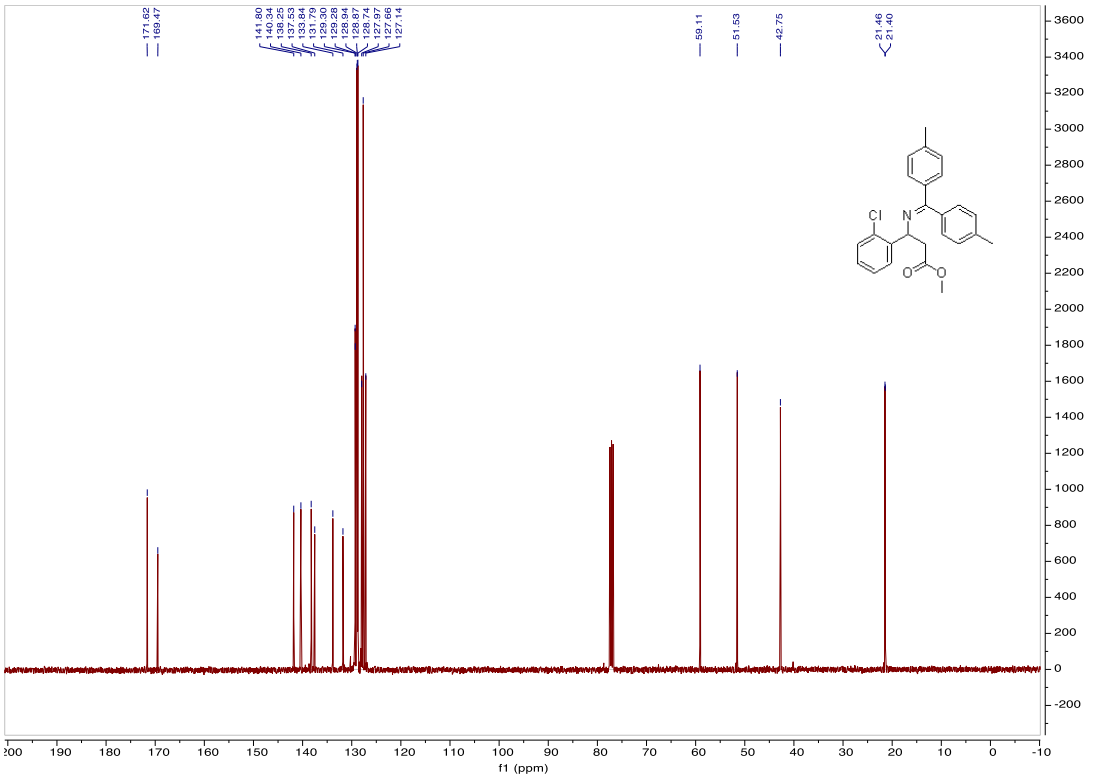
Methyl 3-(4-bromophenyl)-3-((di-p-tolylmethylene)amino)propanoate (3bk)



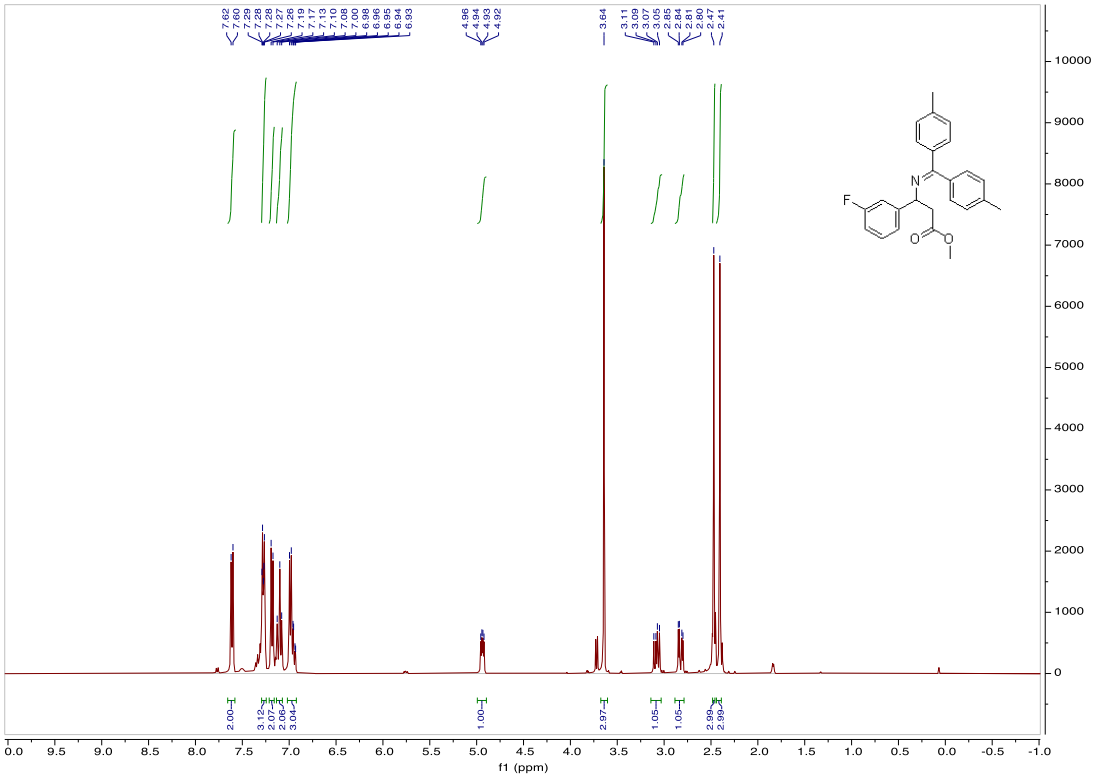


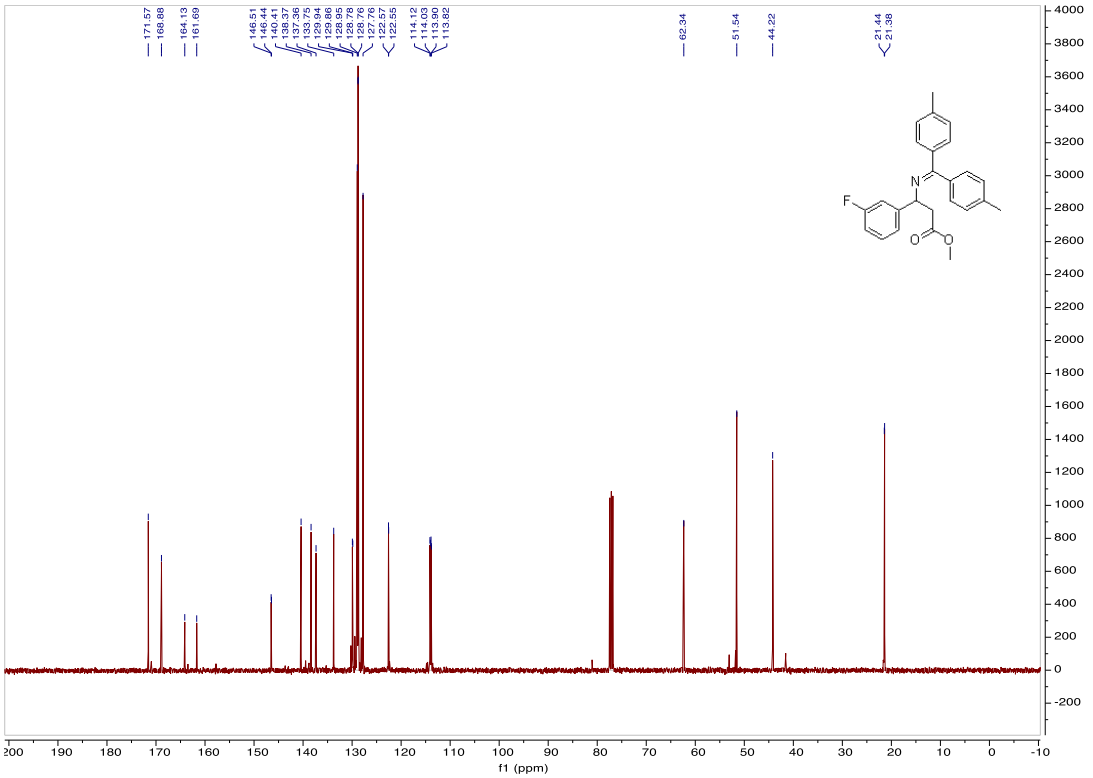
Methyl 3-(2-chlorophenyl)-3-((di-p-tolylmethylene)amino)propanoate (3bl)





Methyl 3-((di-p-tolylmethylene)amino)-3-(3-fluorophenyl)propanoate (3bm)

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164.13
161.69
146.51
146.44
140.41
138.37
137.36
133.75
129.94
129.86
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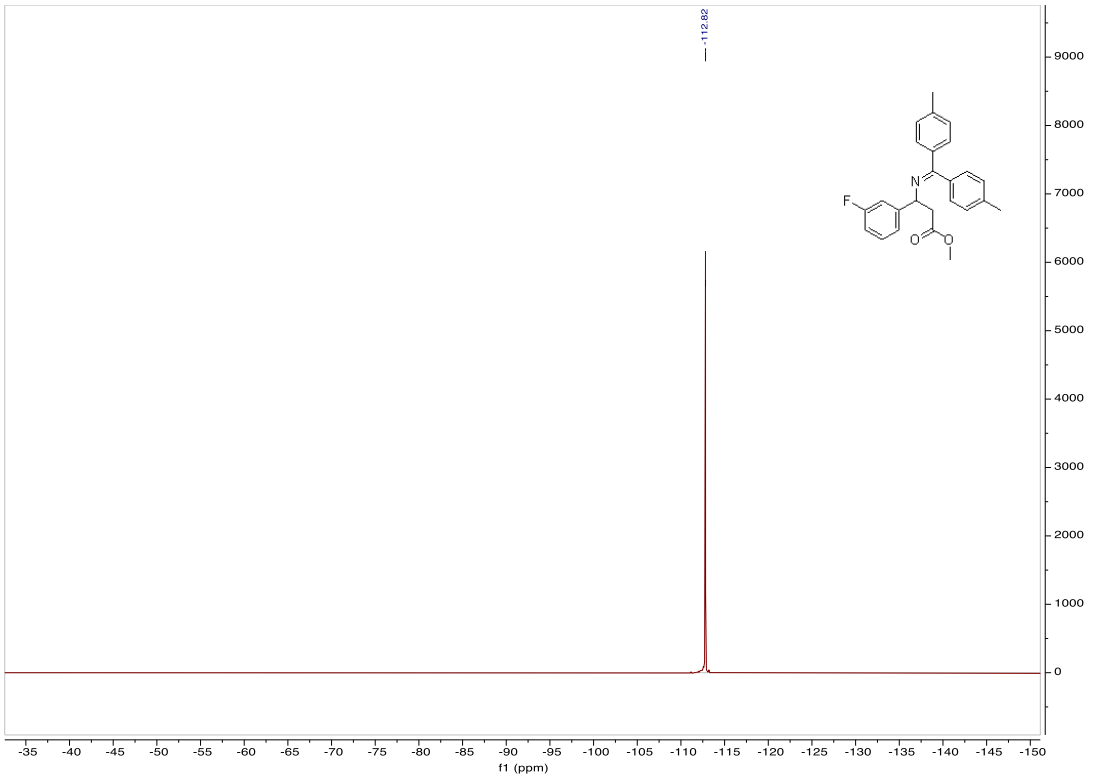
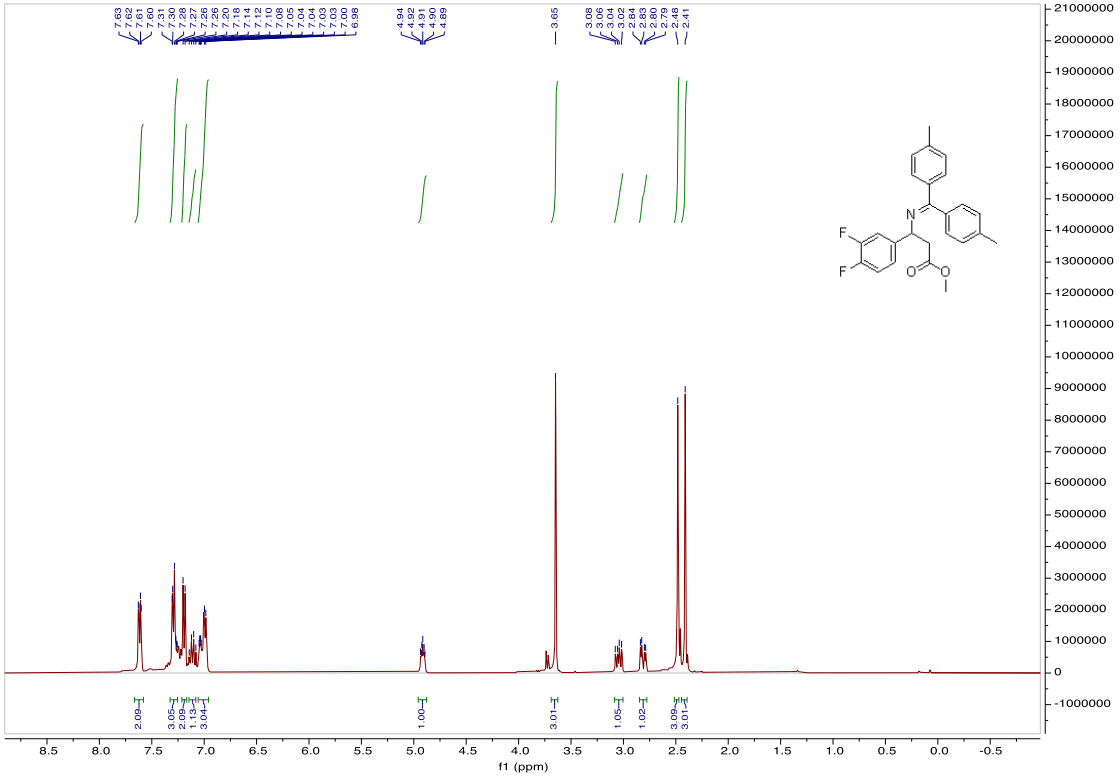
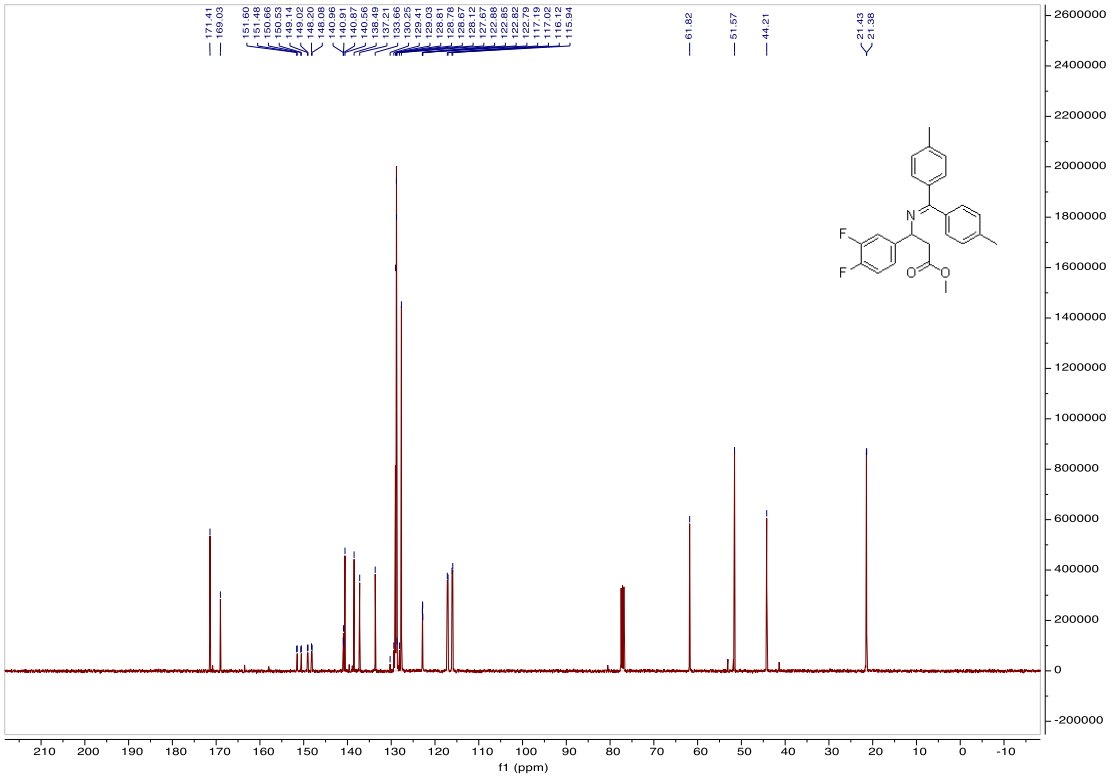
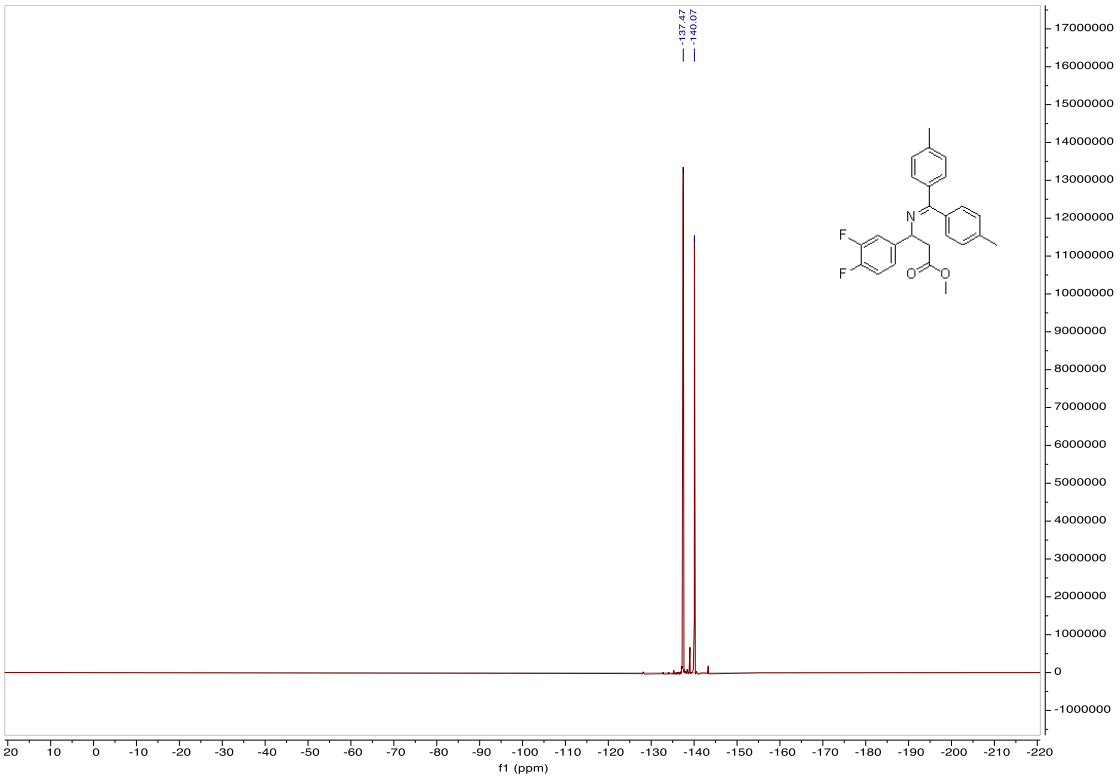
128.78
128.76
127.76
122.57
122.55
114.12
114.03
113.80
113.82
62.34
51.54
44.22
21.44
21.38
F
N
O
O
f1 (ppm)


-112.82
F
N
O
O
f1 (ppm)

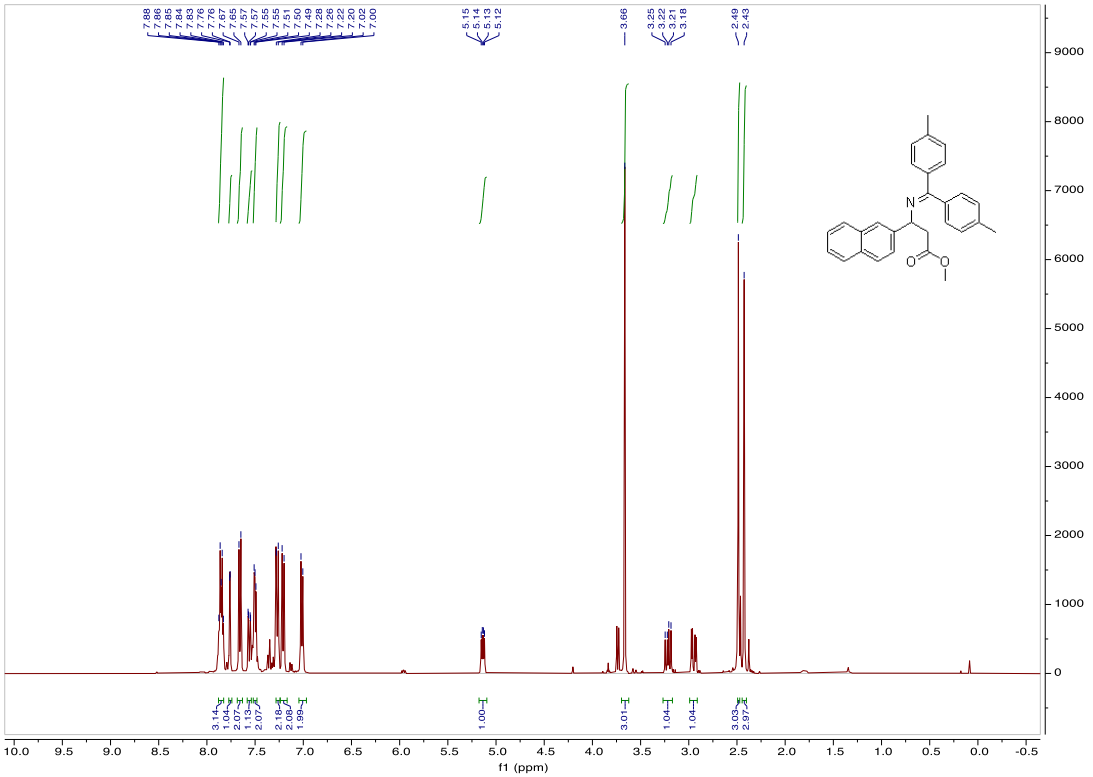
Methyl 3-((di-p-tolylmethylene)amino)-3-(3,4-difluorophenyl)propanoate (3bn)

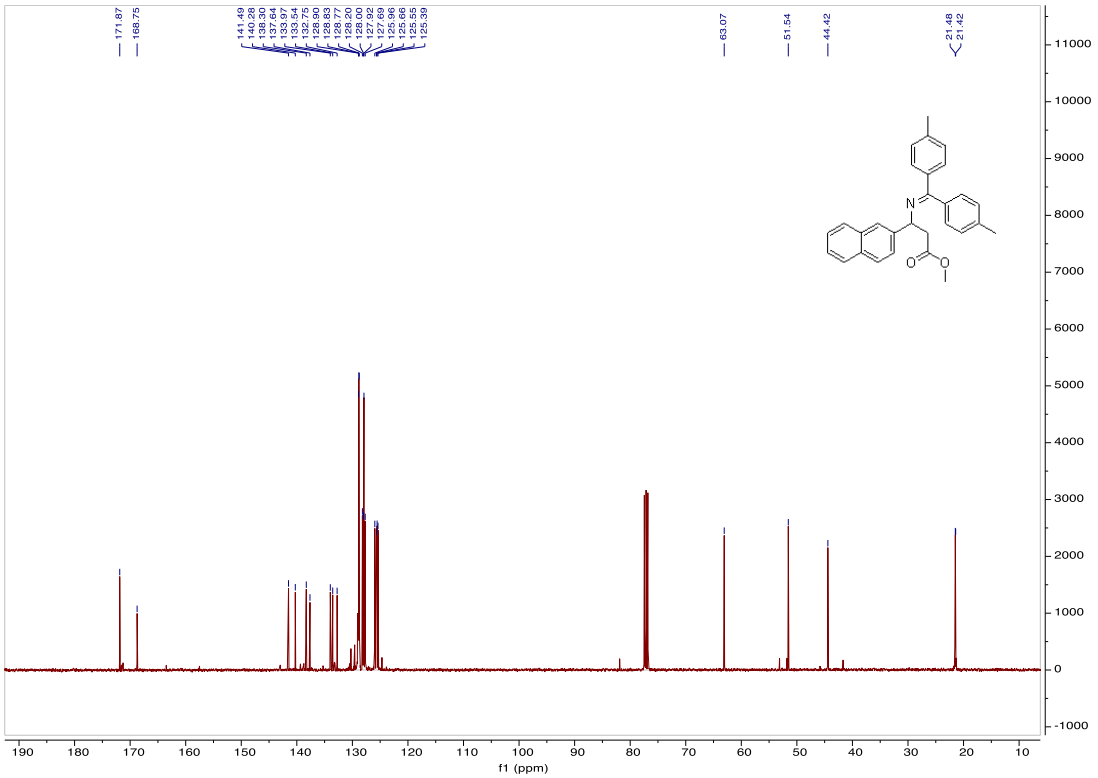




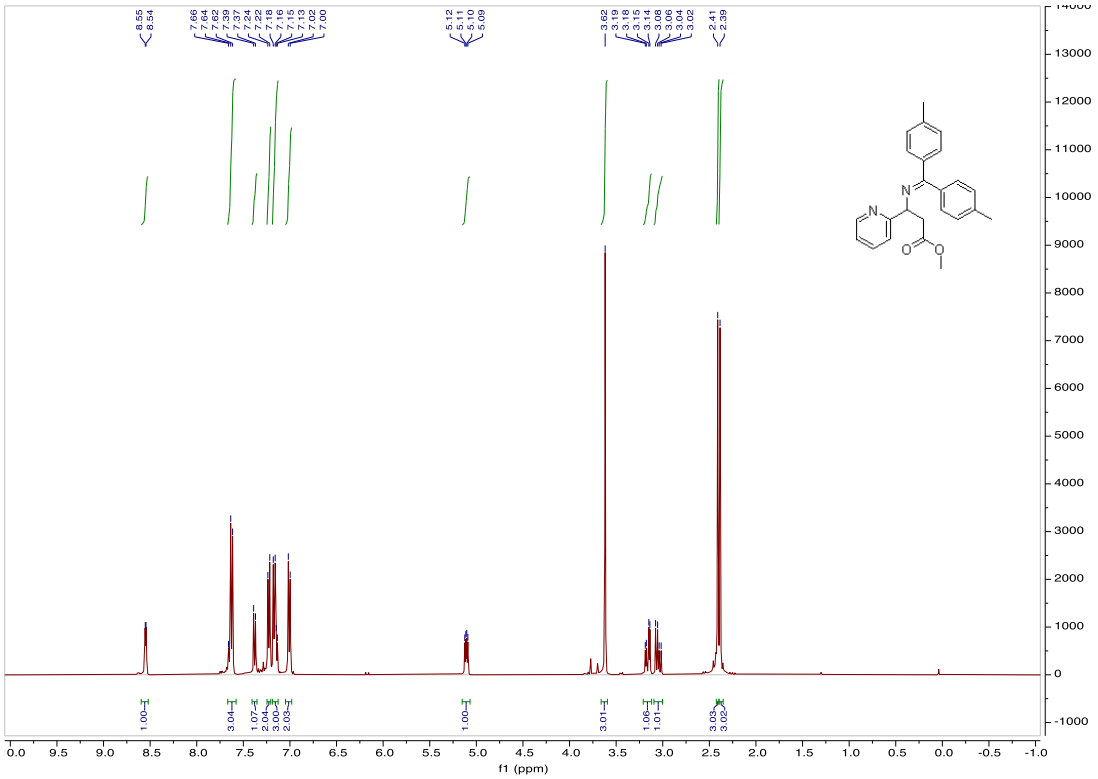


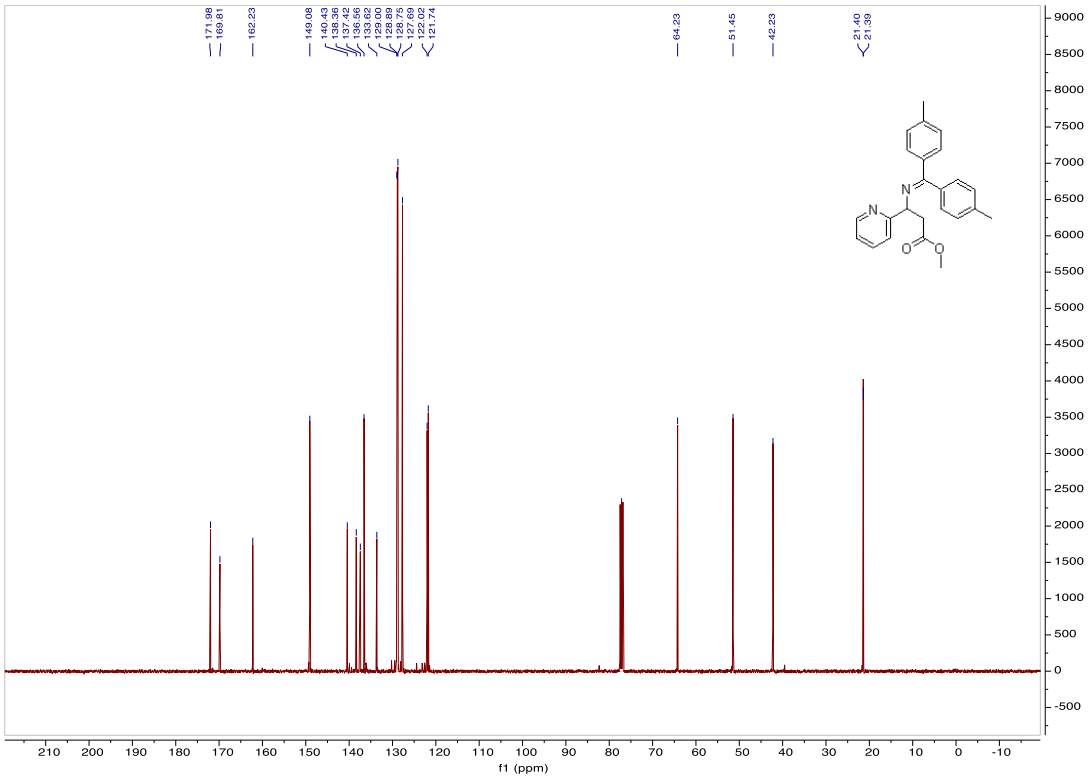
Methyl 3-((di-p-tolylmethylene)amino)-3-(naphthalen-2-yl)propanoate (3bo)





Methyl 3-((di-p-tolylmethylene)amino)-3-(pyridin-2-yl)propanoate (3bp)




171.98
169.81
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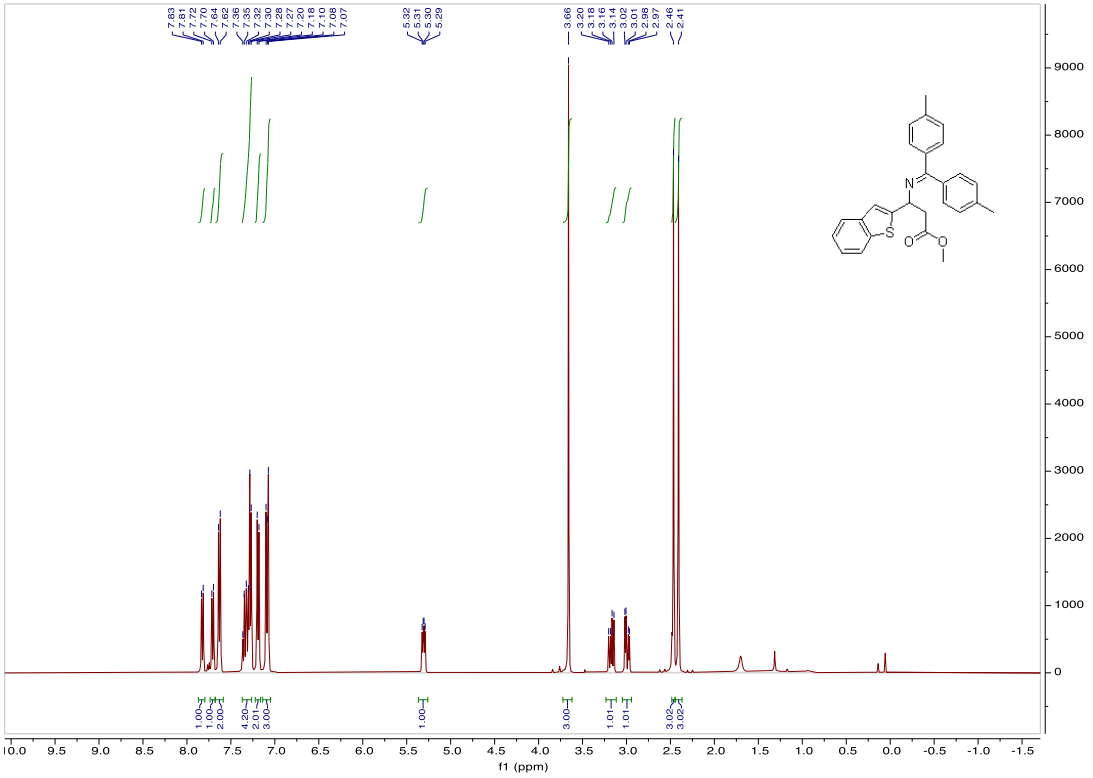
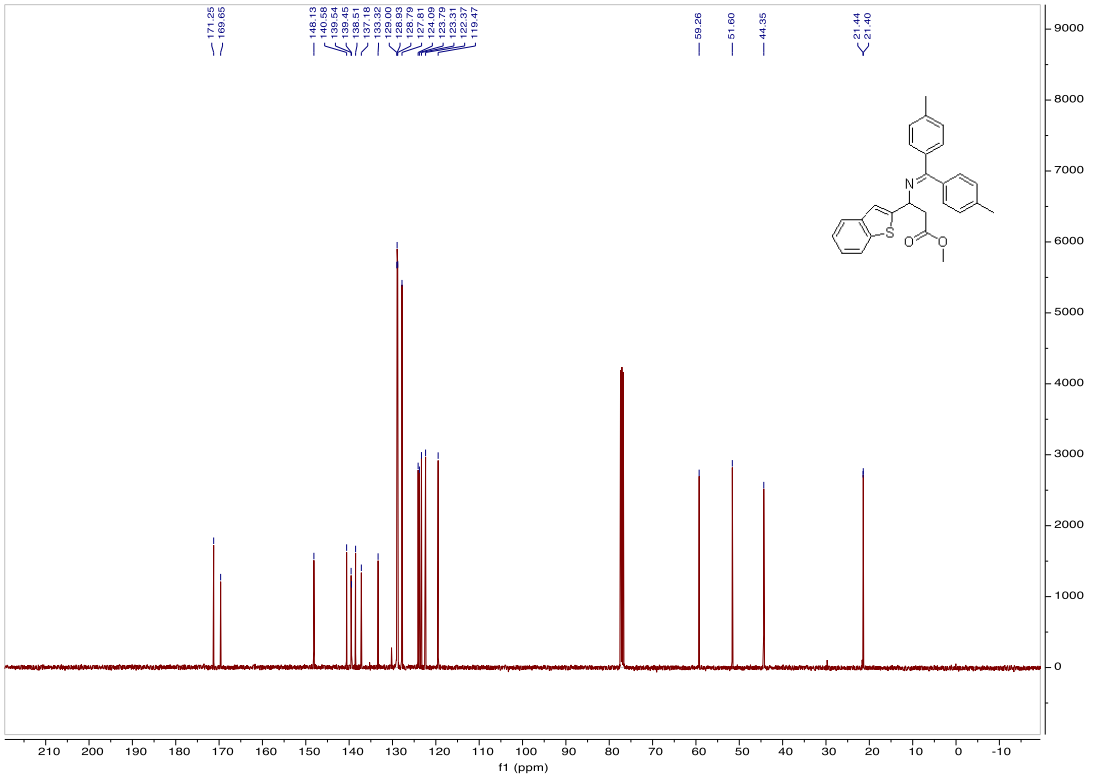
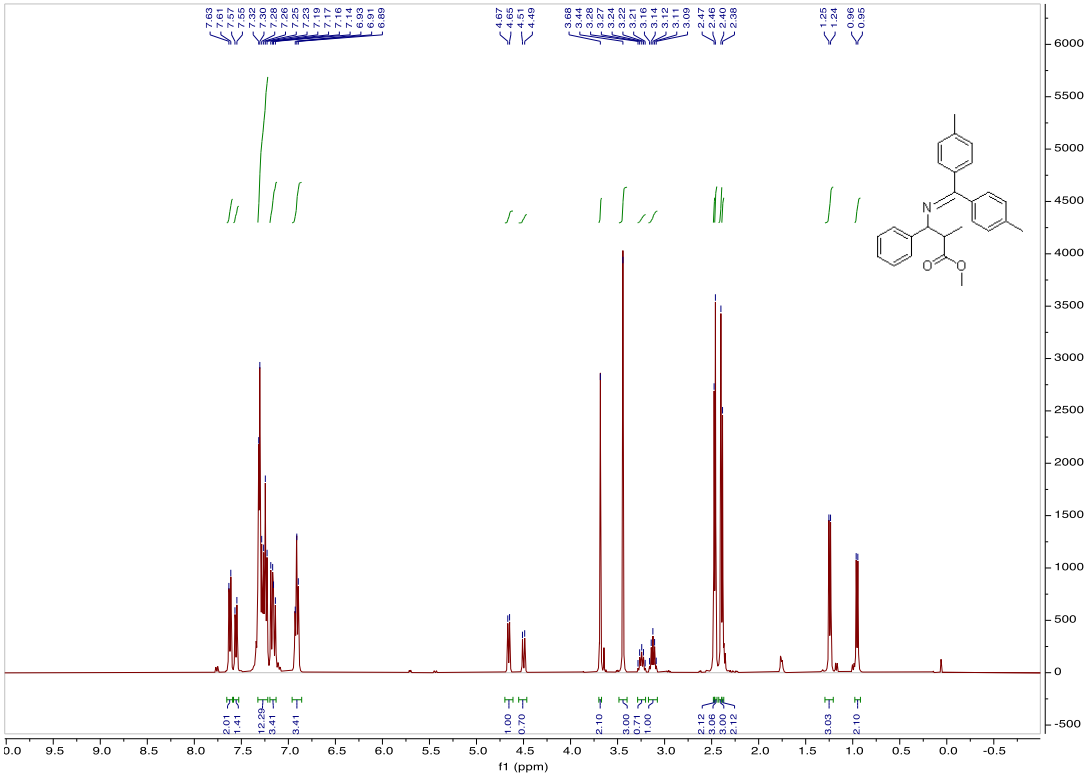
149.08
140.43
138.86
137.42
136.56
133.62
129.00
128.89
128.75
127.69
122.02
121.74
64.23
51.45
42.23
21.40
21.39
N
N
O
O
f1 (ppm)

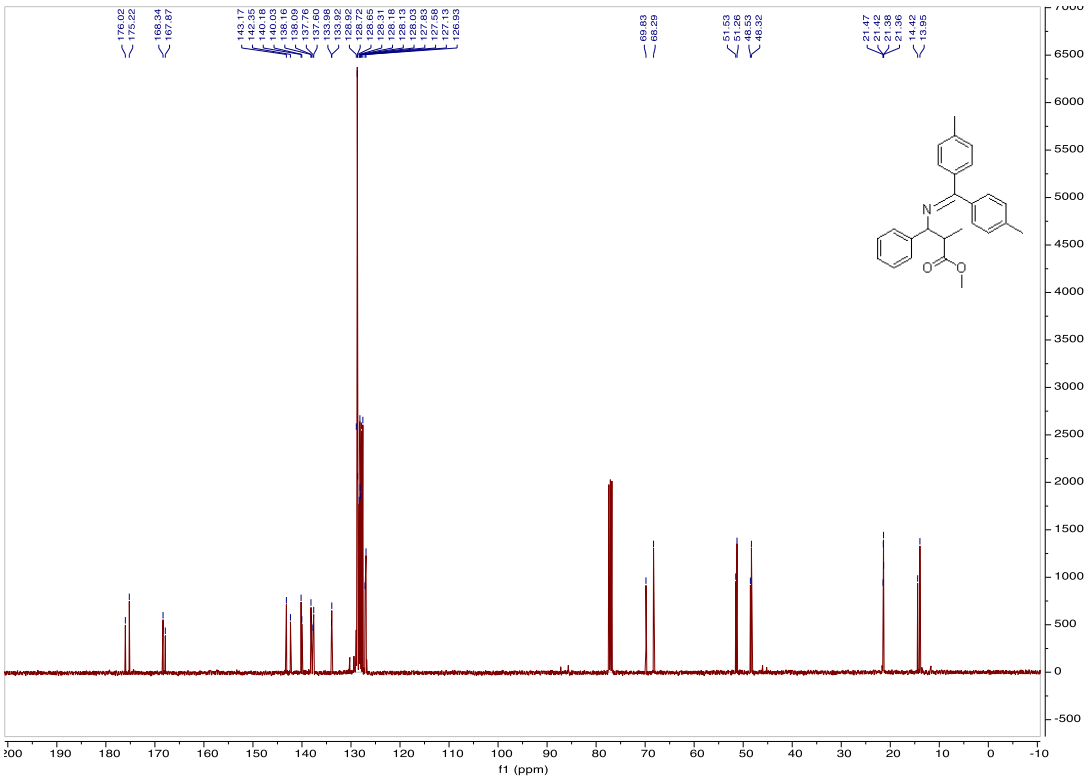
Methyl 3-(benzo[b]thiophen-2-yl)-3-((di-p-tolylmethylene)amino)propanoate (3bq)



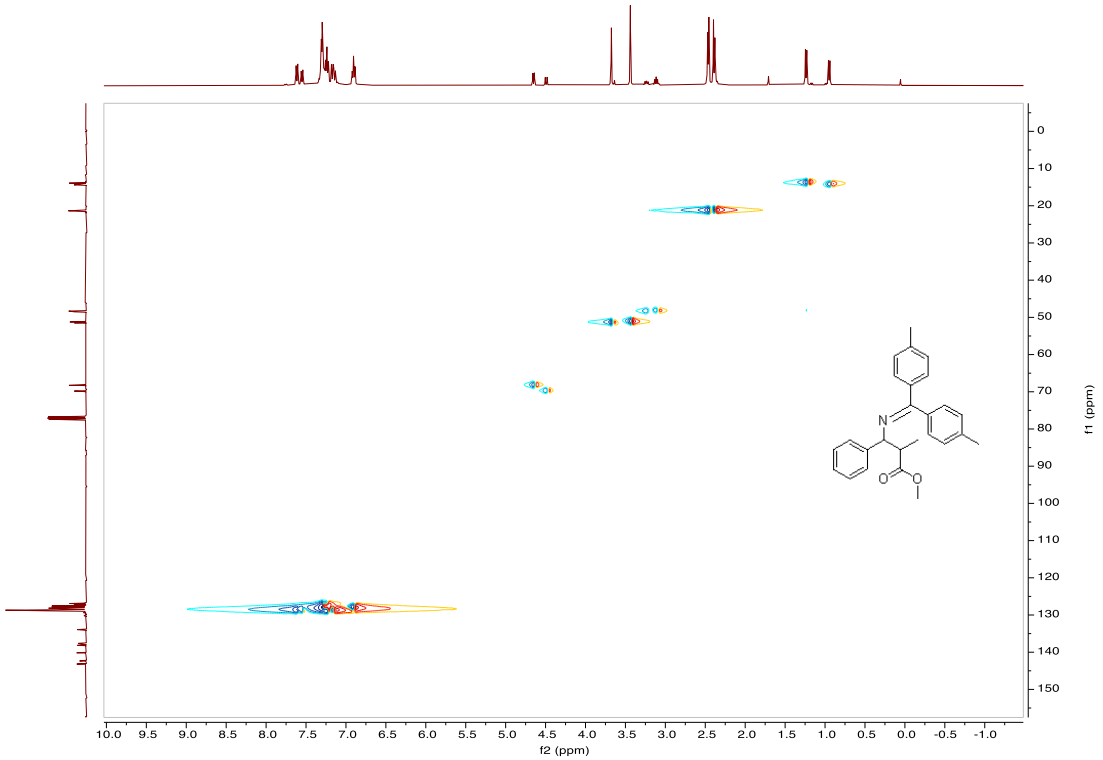


Methyl 3-((di-p-tolylmethylene)amino)-2-methyl-3-phenylpropanoate (3br)

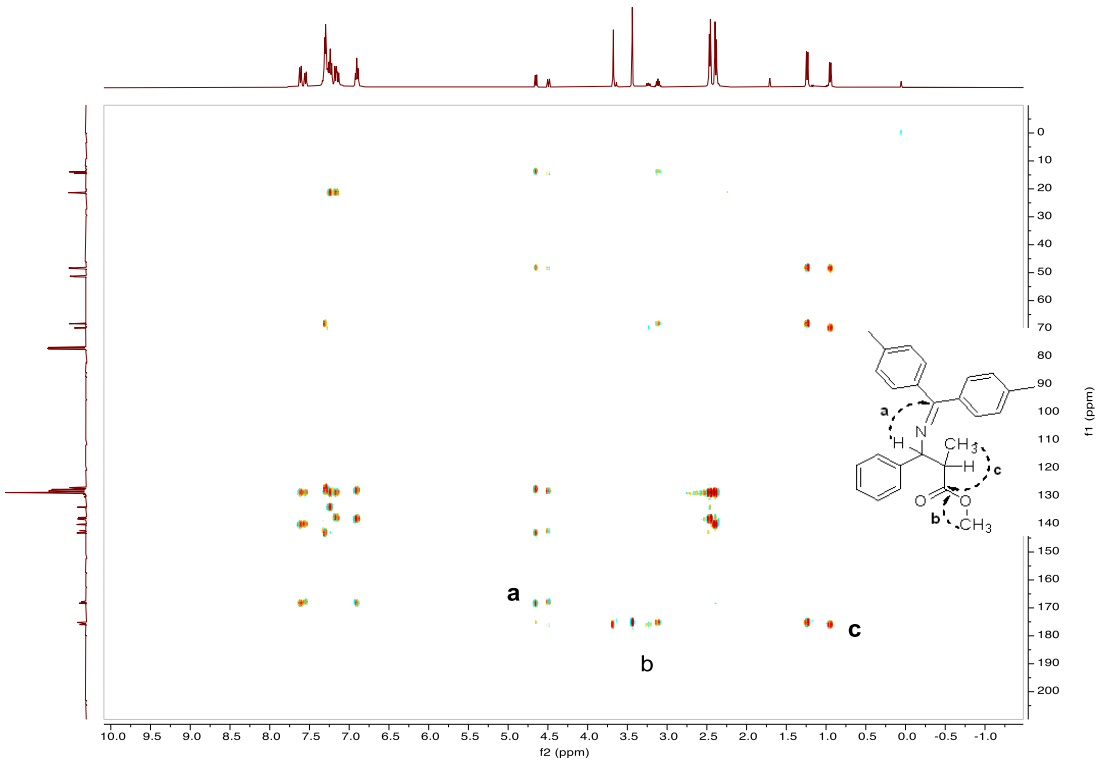




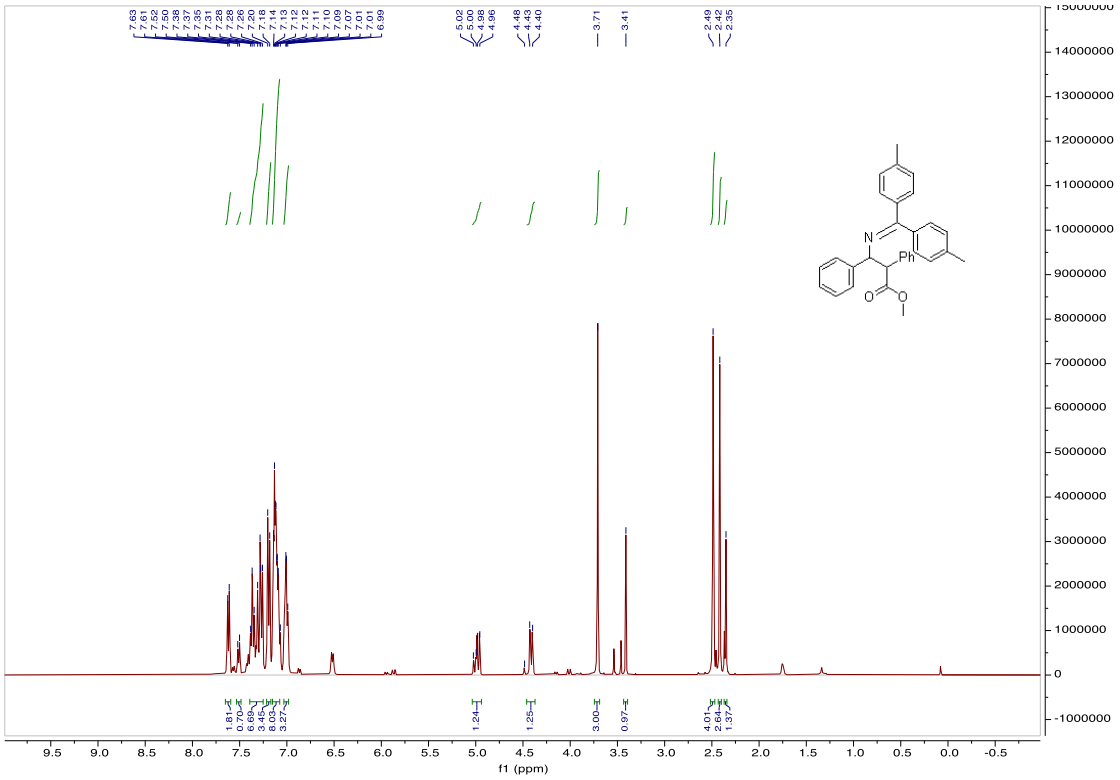
{1H-13C}-HSQC

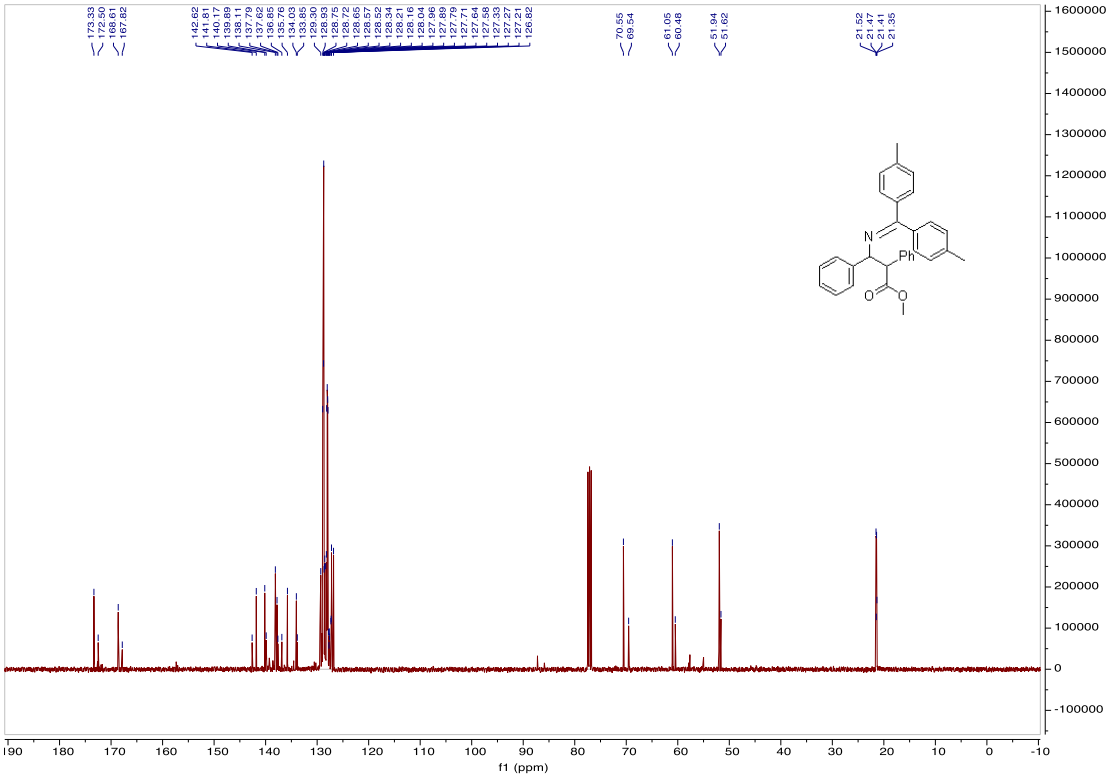


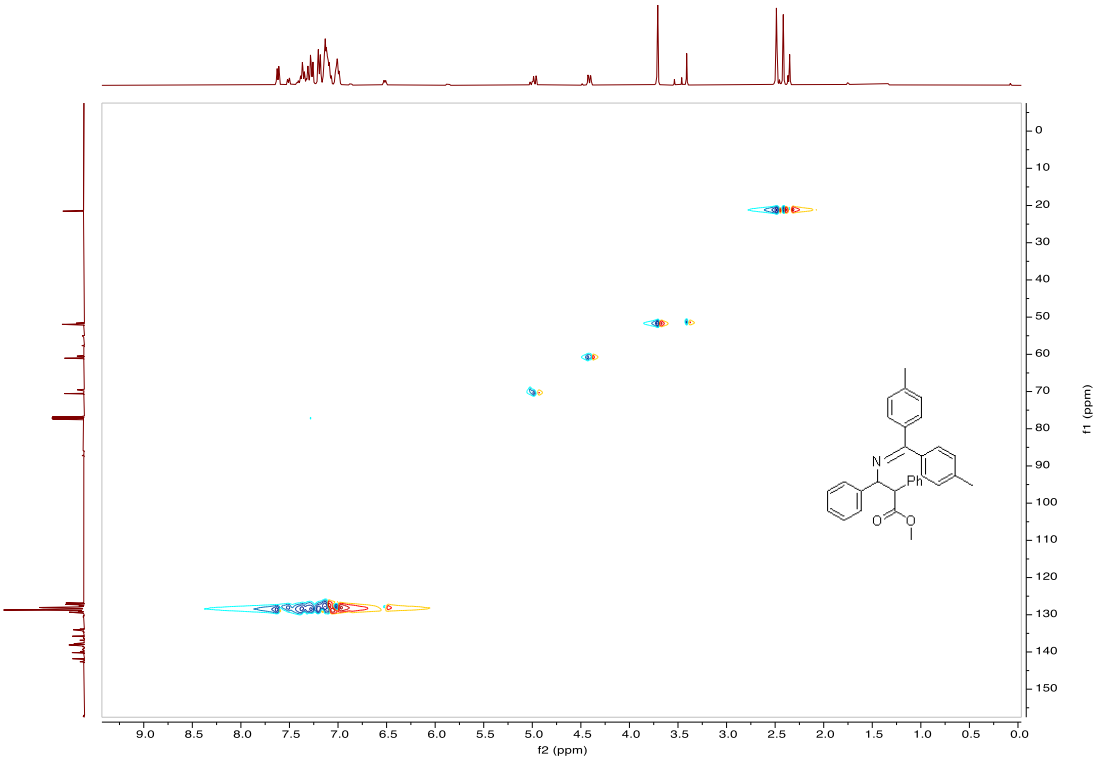
{1H-13C}-HMBC

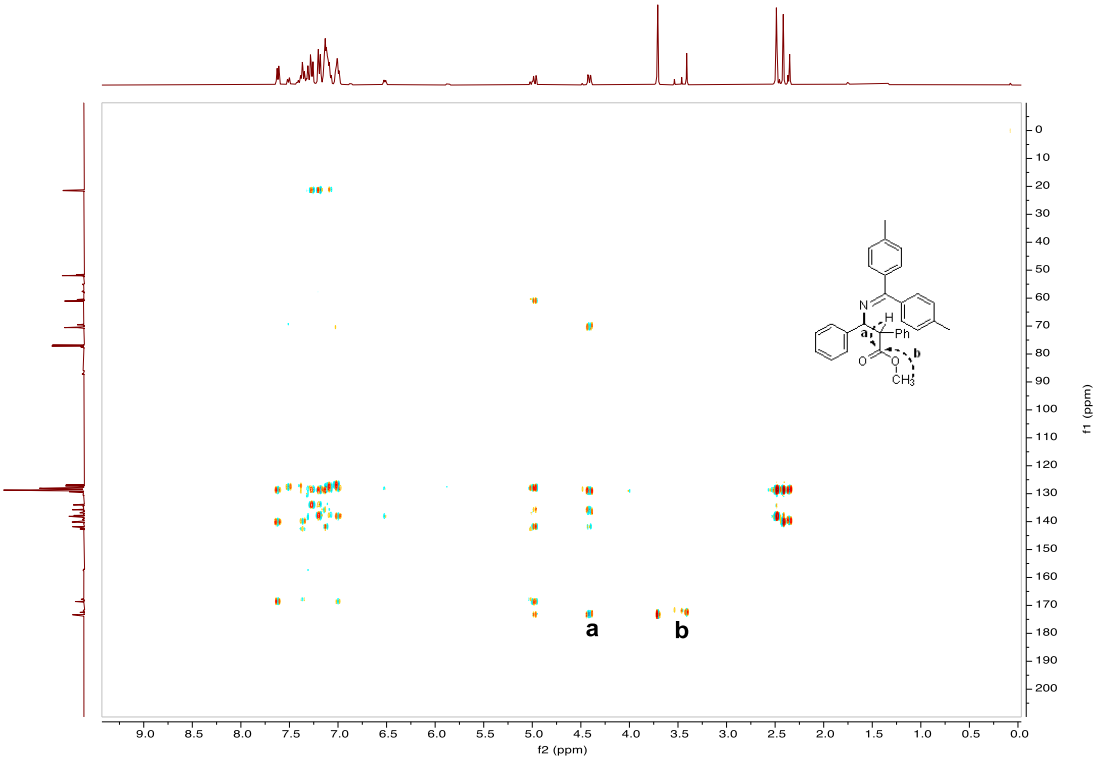


Methyl 3-((di-p-tolylmethylene)amino)-2,3-diphenylpropanoate (3bs)

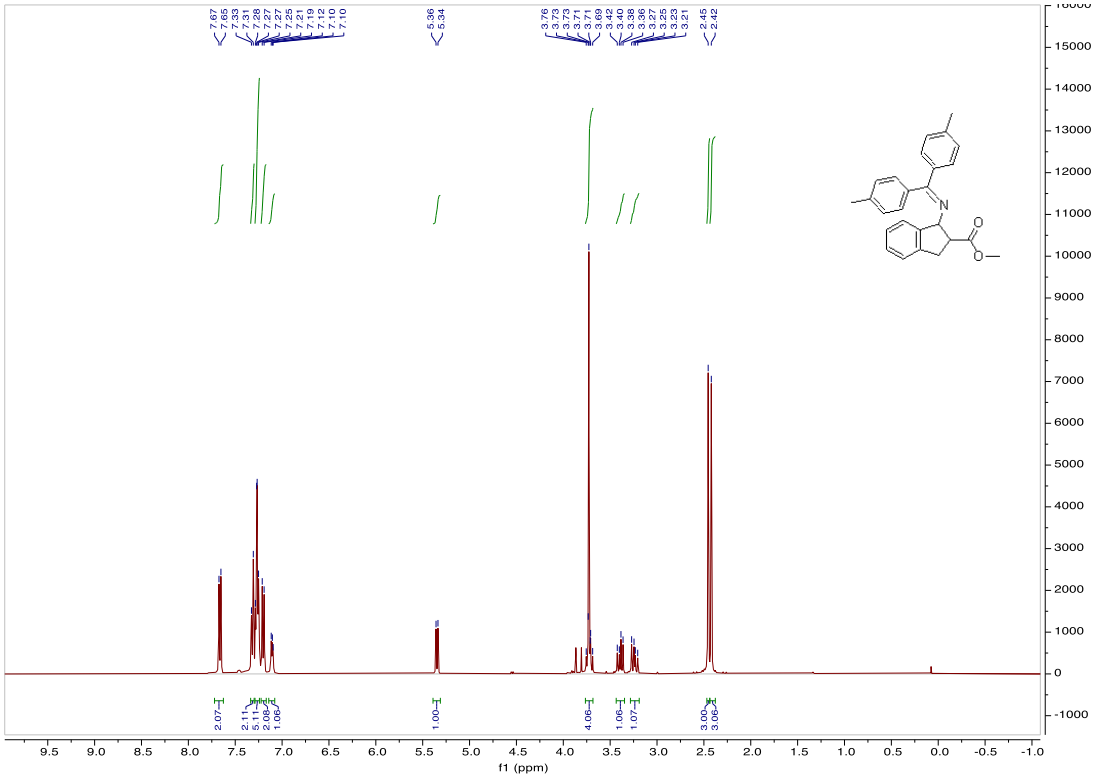


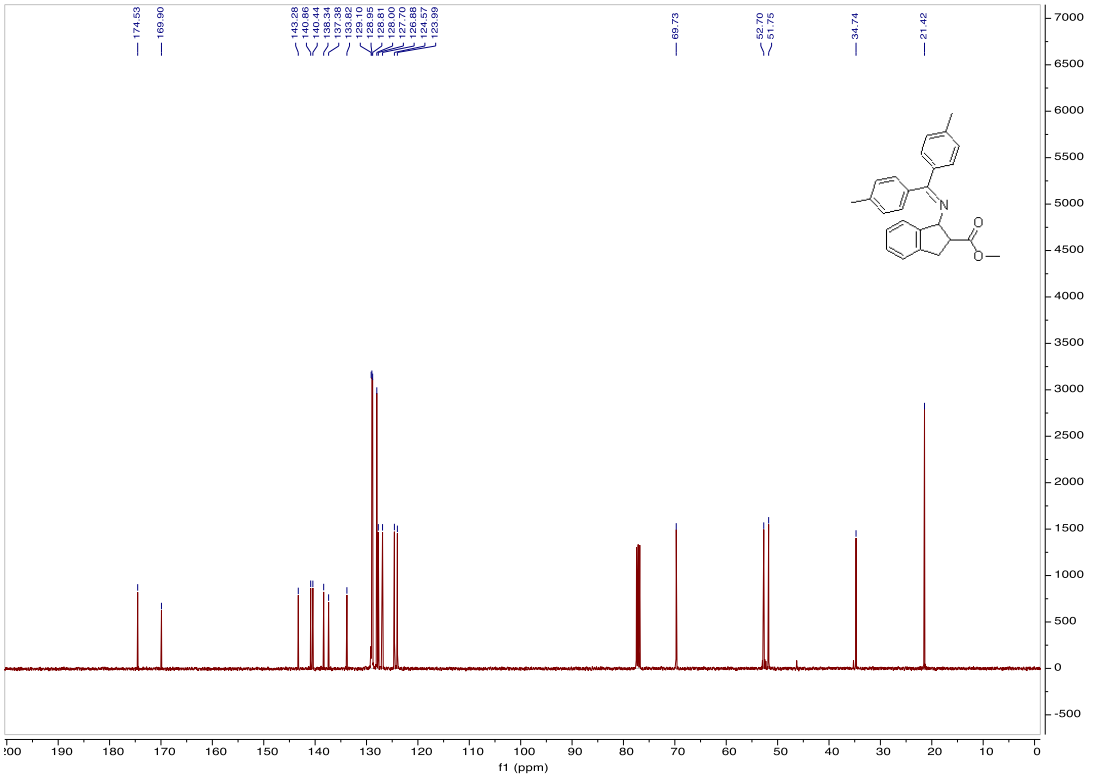


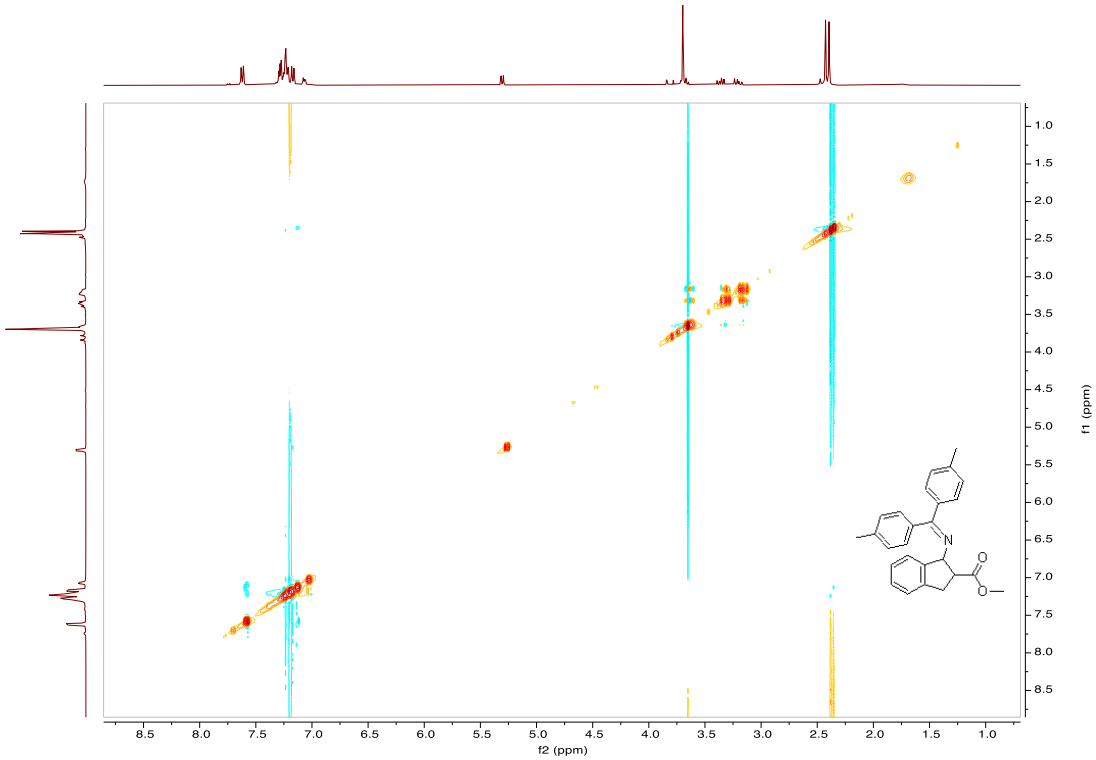

f2 (ppm)
f1 (ppm)
N
Ph
O
O


f2 (ppm)
f1 (ppm)
N
H
Ph
O
O
CH3
a
b

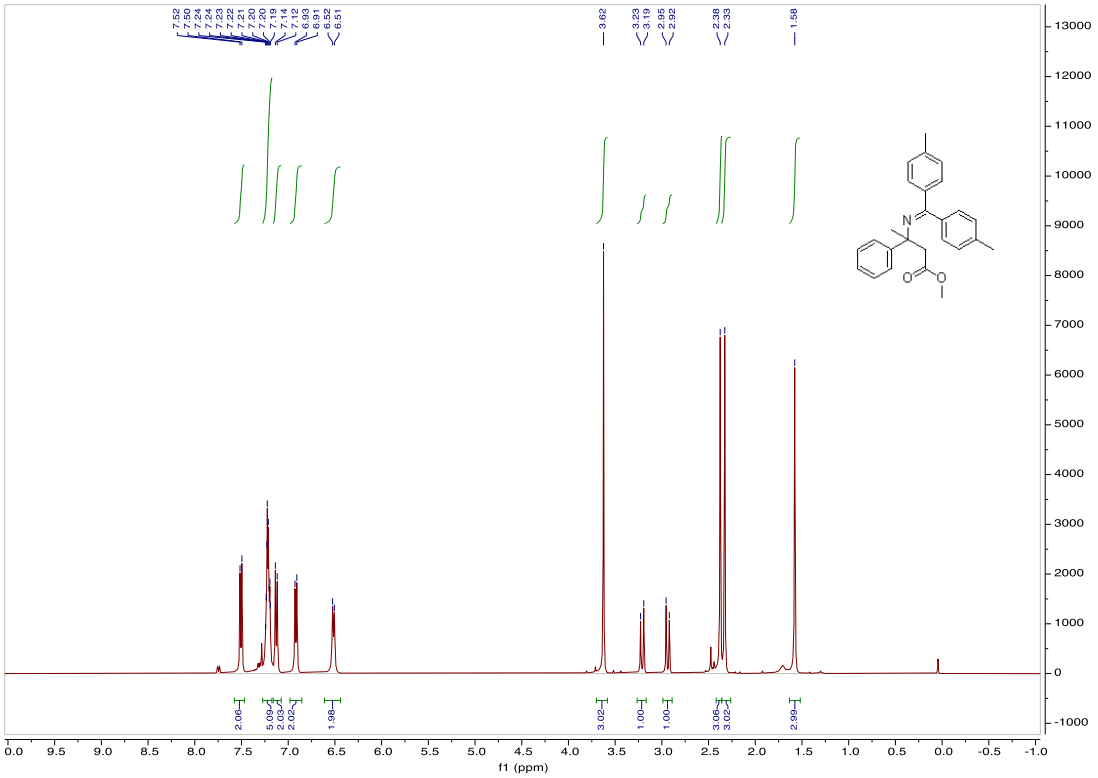
Methyl 1-((di-p-tolylmethylene)amino)-2,3-dihydro-1H-indene-2-carboxylate (3bt)

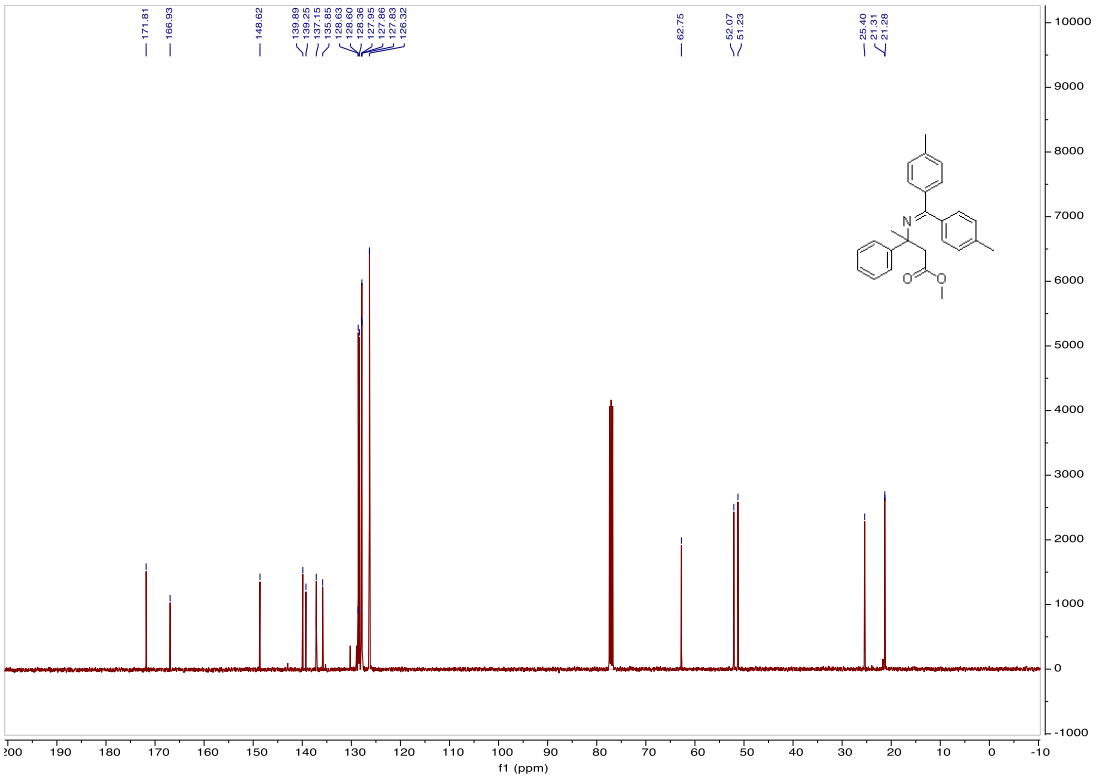






Methyl 3-((di-p-tolylmethylene)amino)-3-phenylbutanoate (3bu)




171.81
166.93
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139.25
137.15
135.85
128.63
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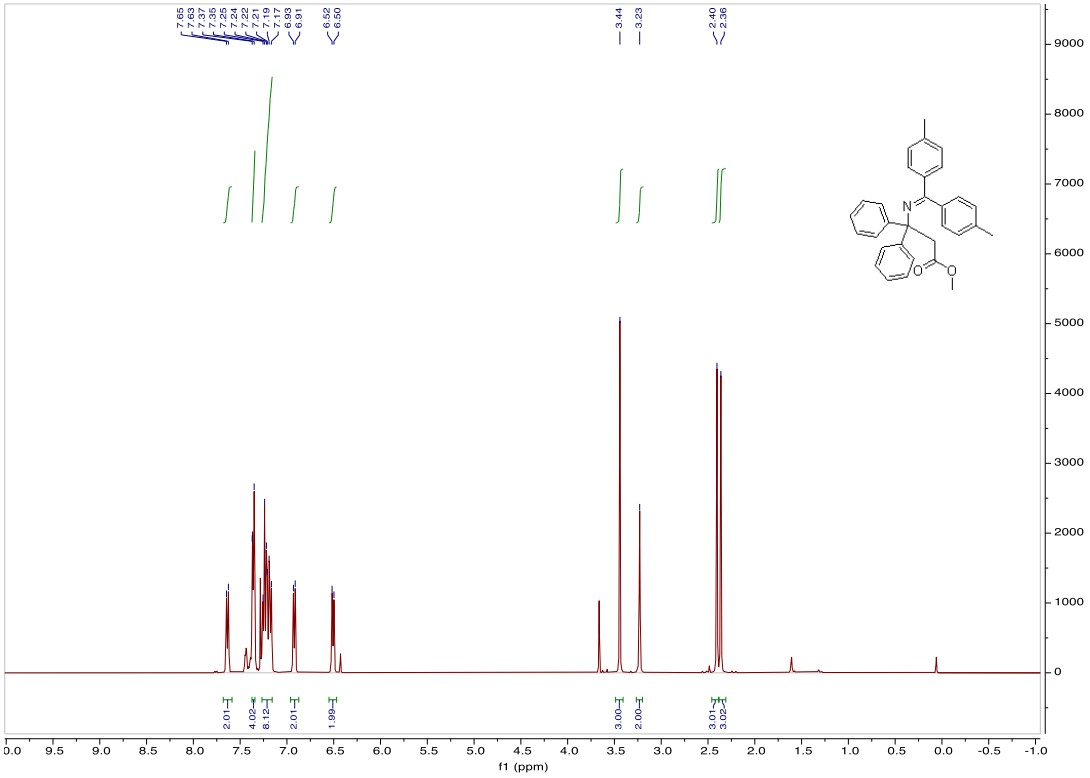
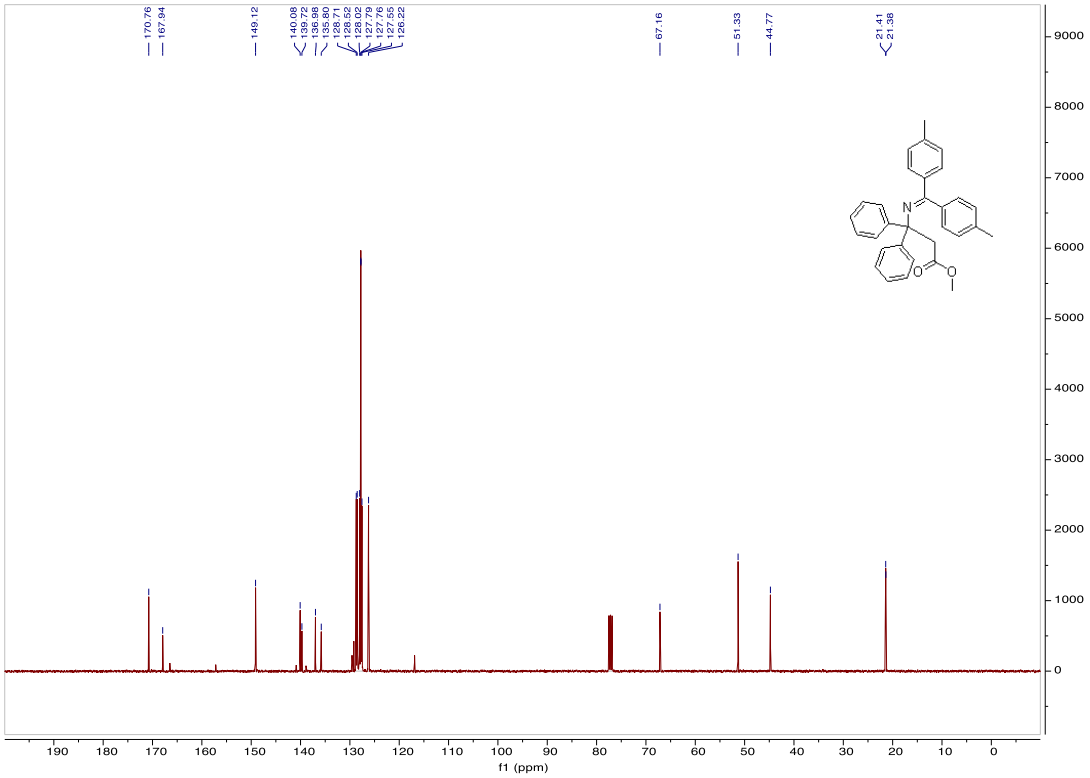
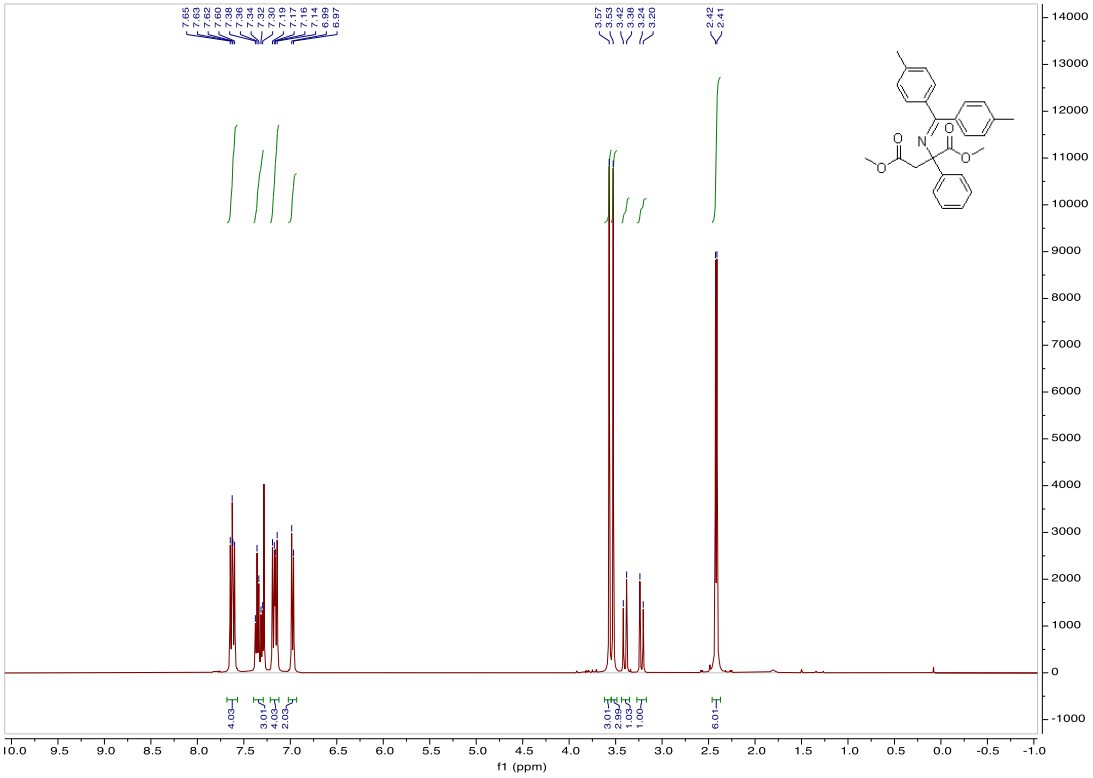
127.86
127.63
126.32
62.75
52.07
51.23
25.40
21.31
21.28
N
O
O
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

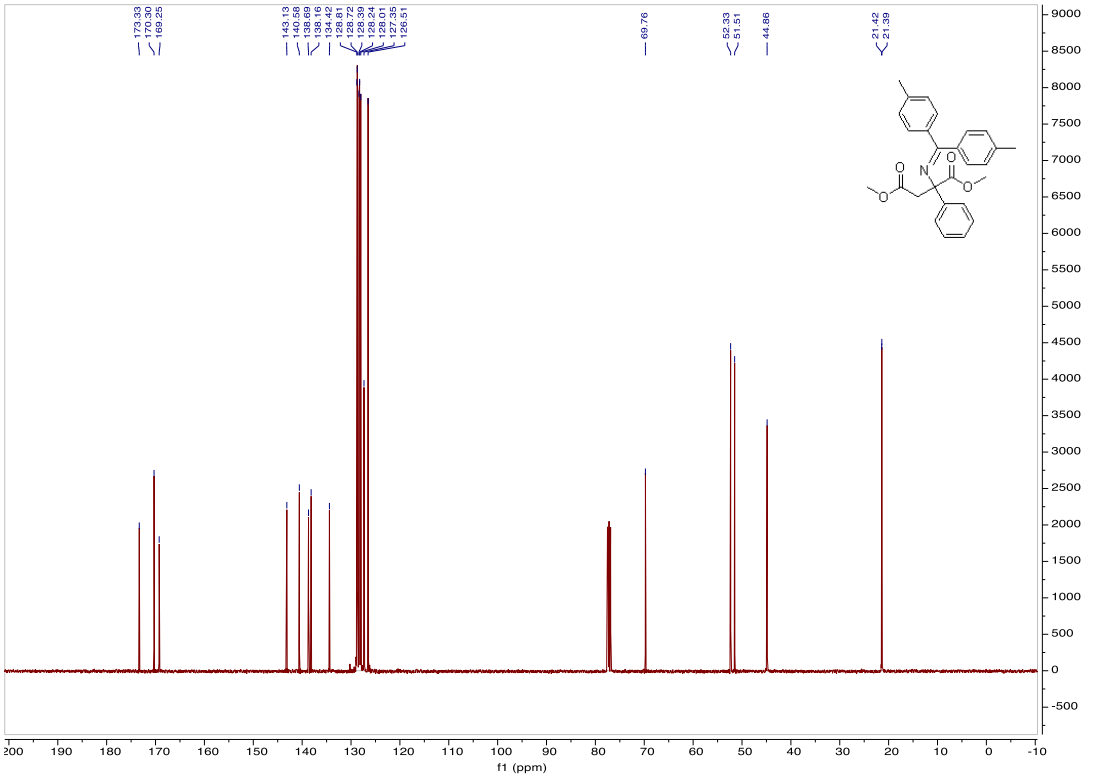
Methyl 3-((di-p-tolylmethylene)amino)-3,3-diphenylpropanoate (3bv)



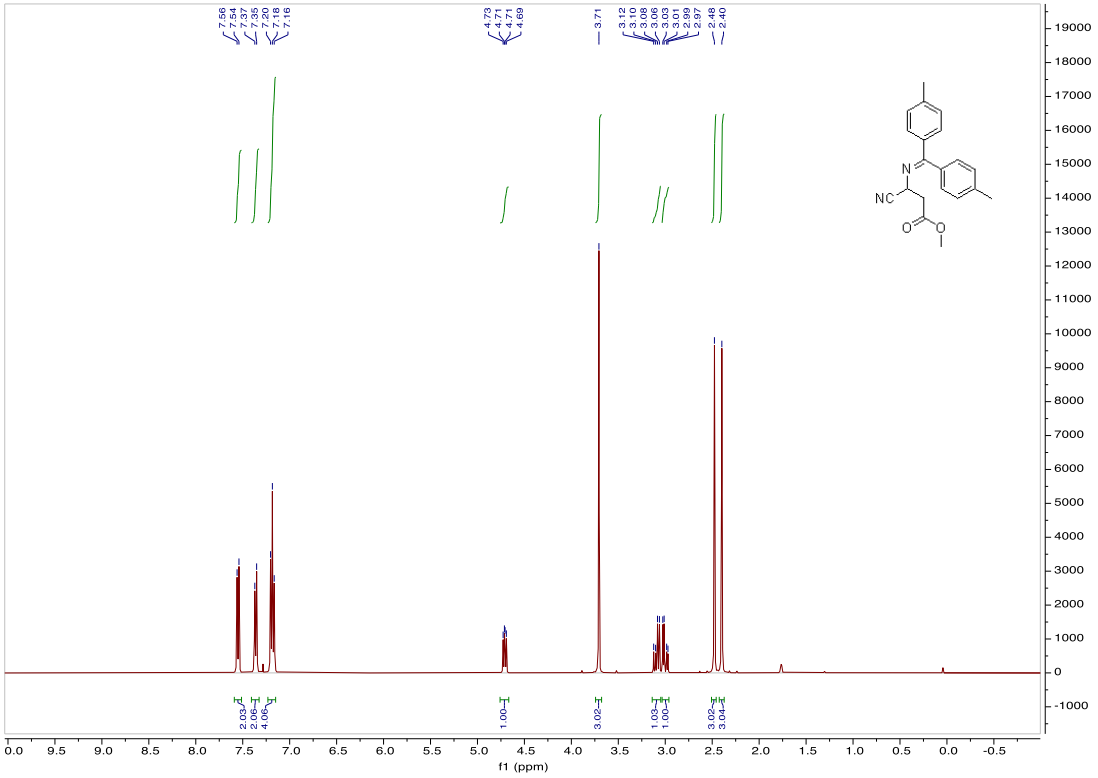


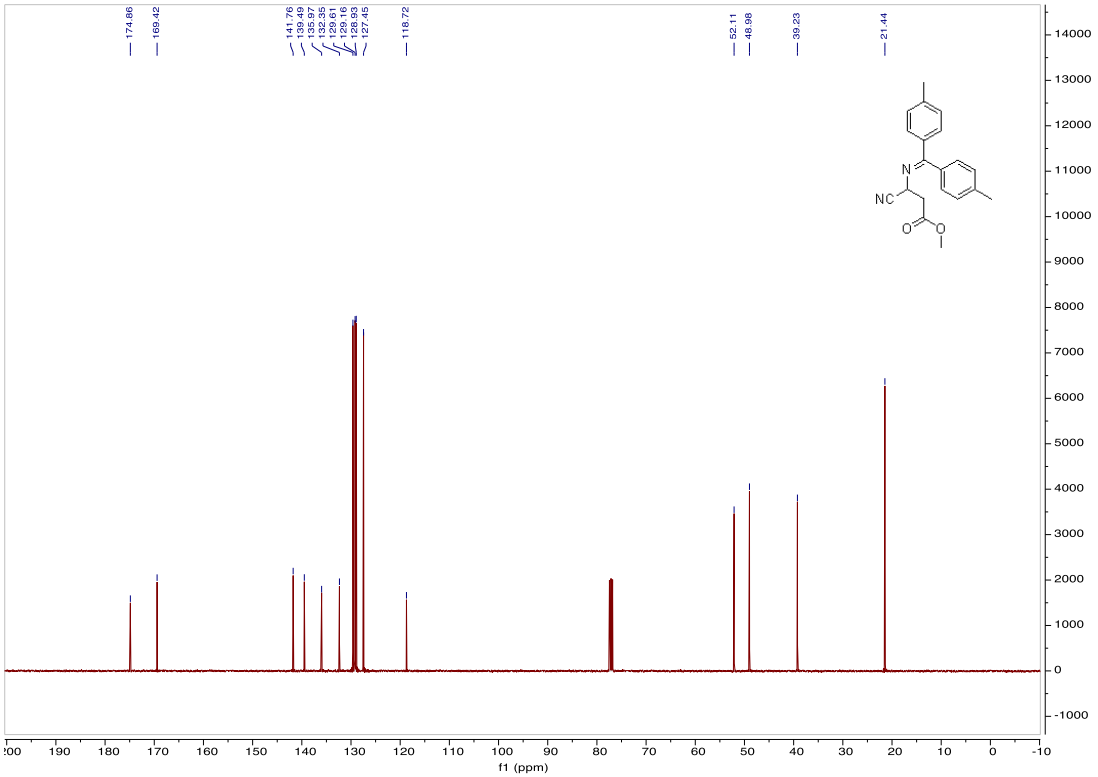
Dimethyl 2-((di-p-tolylmethylene)amino)-2-phenylsuccinate (3bw)



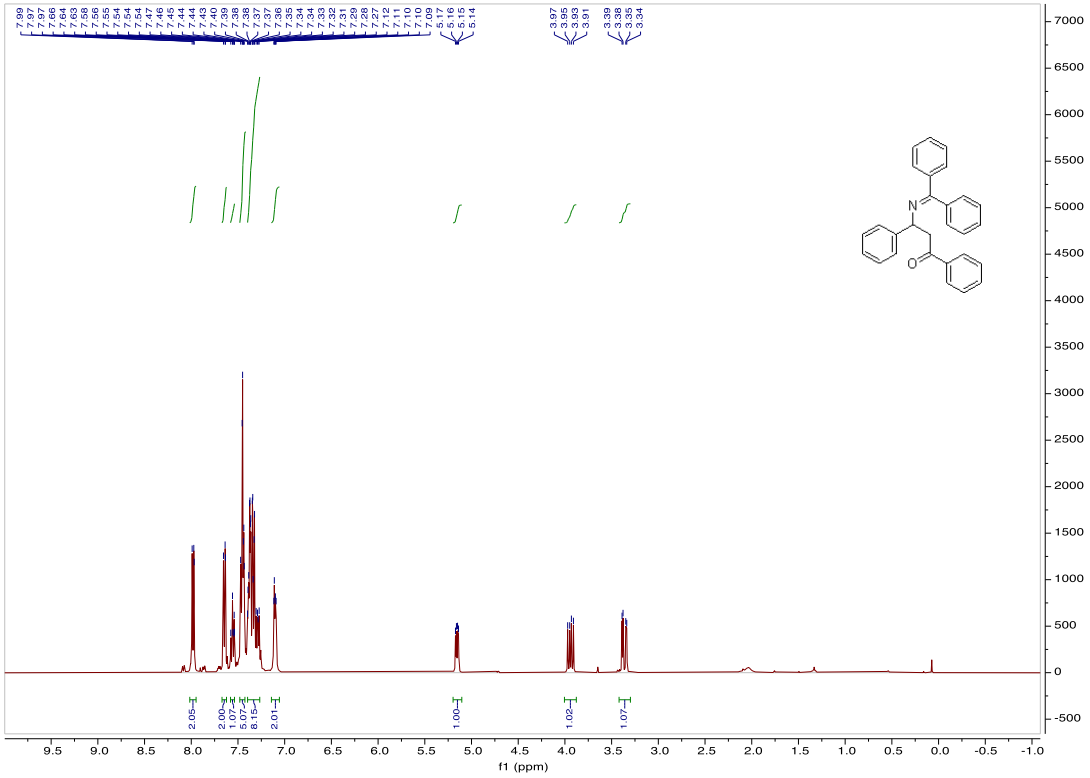


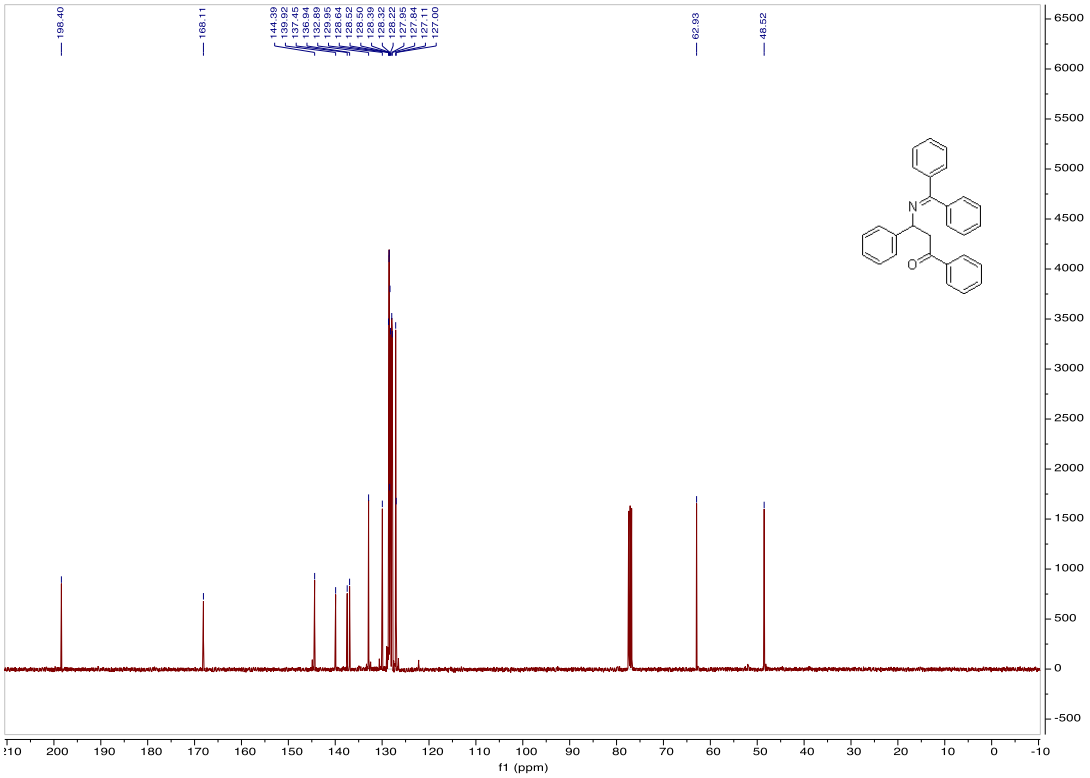
Methyl 3-cyano-3-((di-p-tolylmethylene)amino)propanoate (3bx)



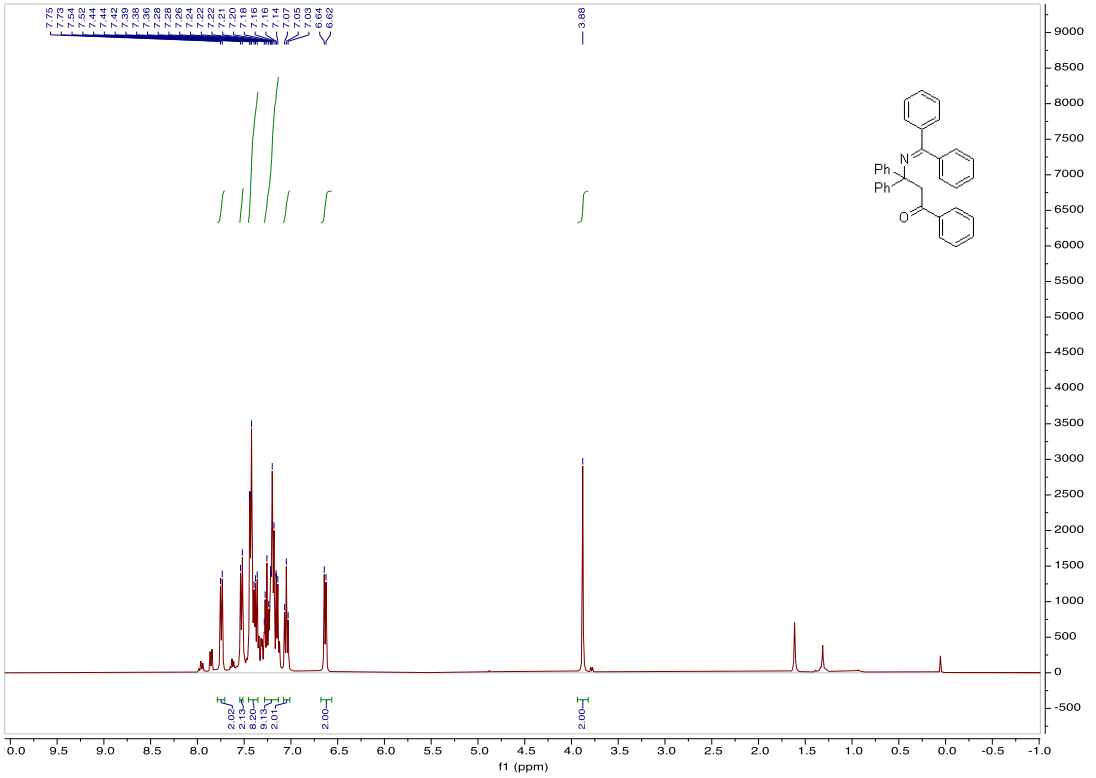


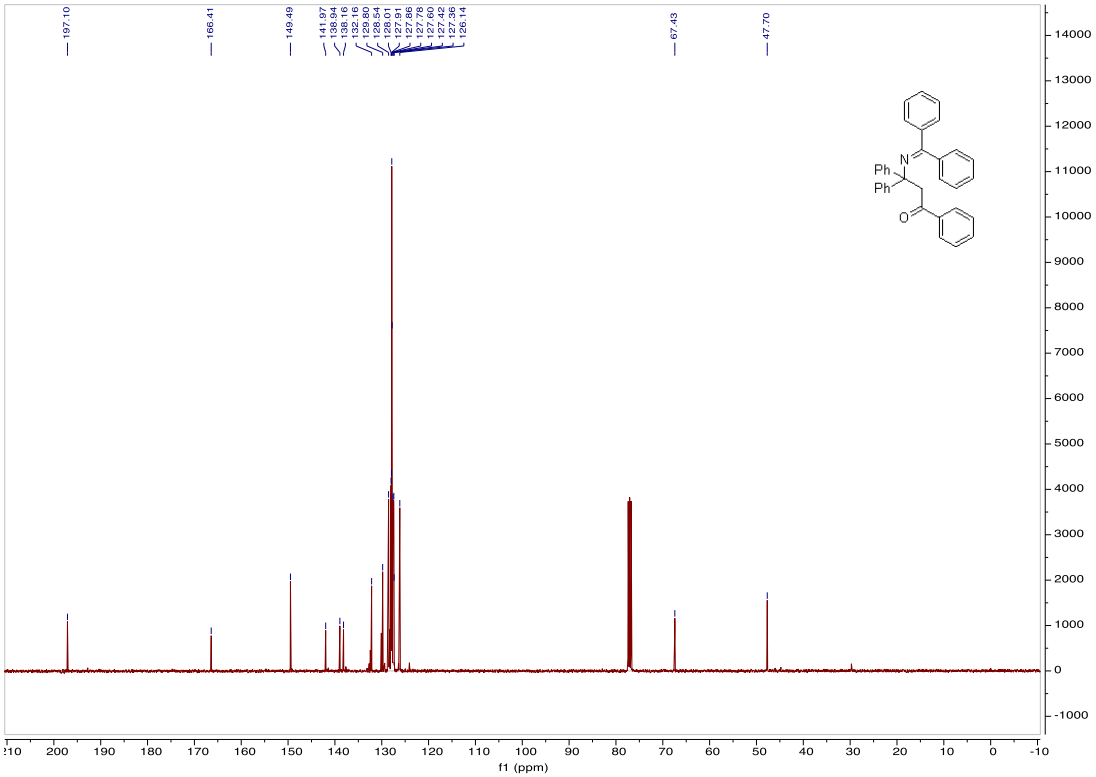
3-((diphenylmethylene)amino)-1,3-diphenylpropan-1-one (5aa)



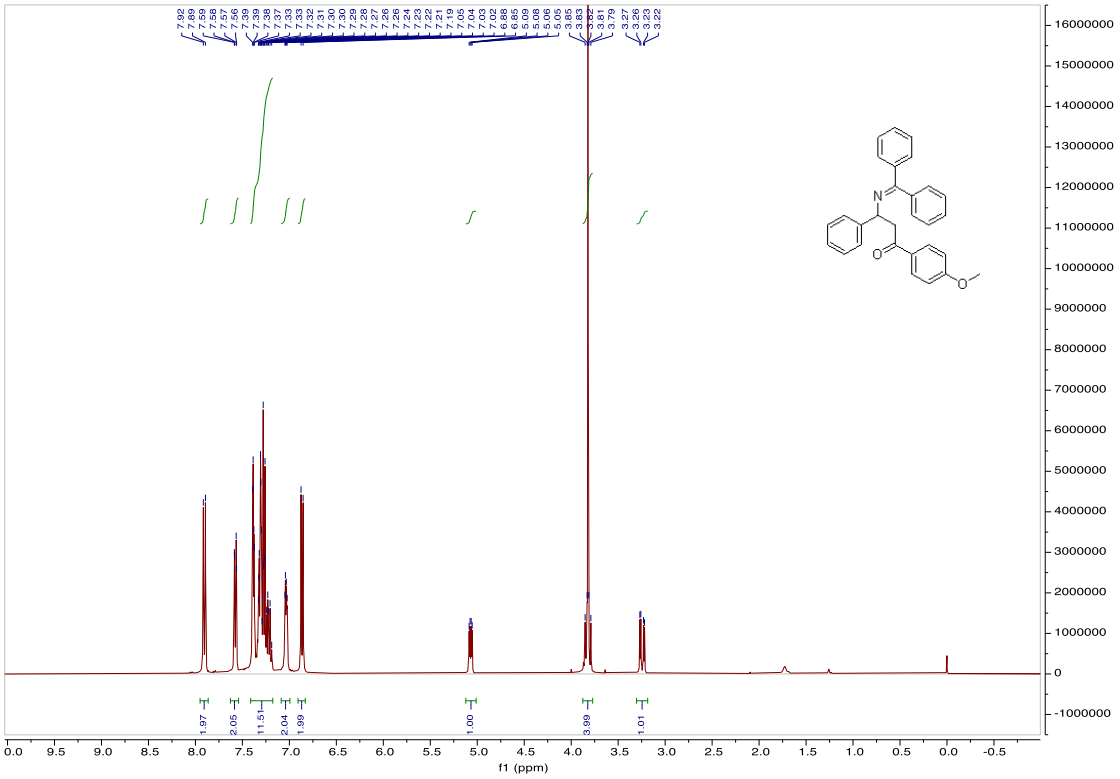


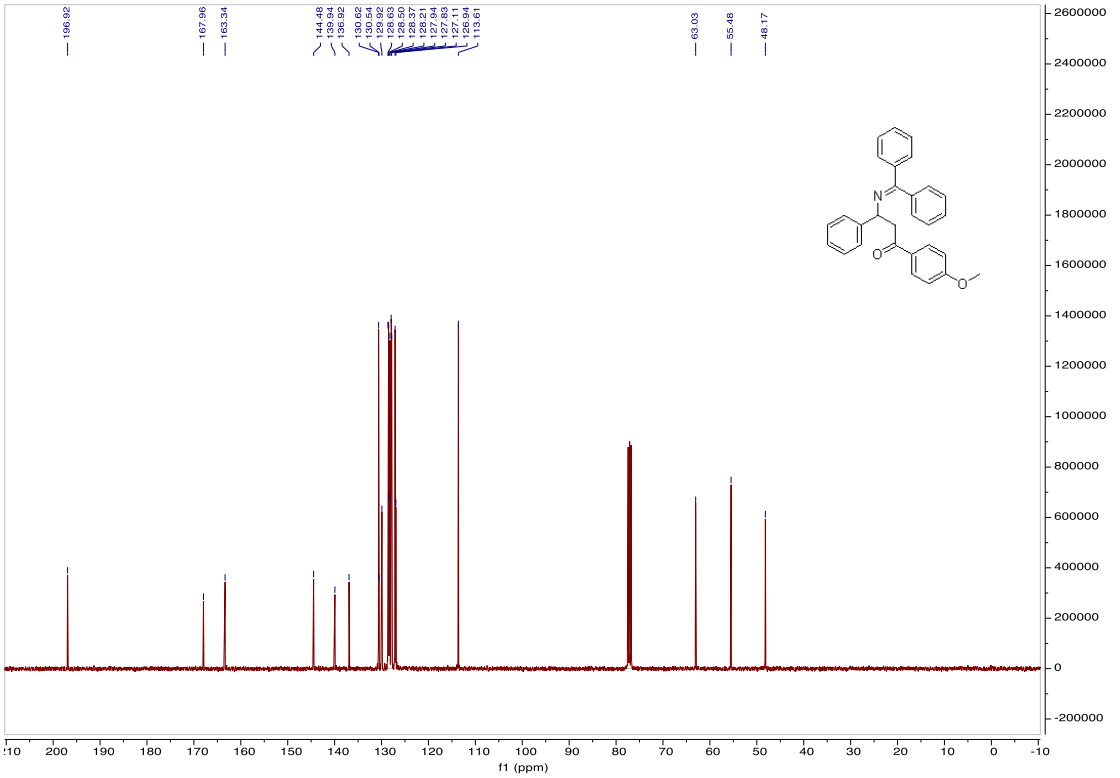
3-((diphenylmethylene)amino)-1,3,3-triphenylpropan-1-one (5av)



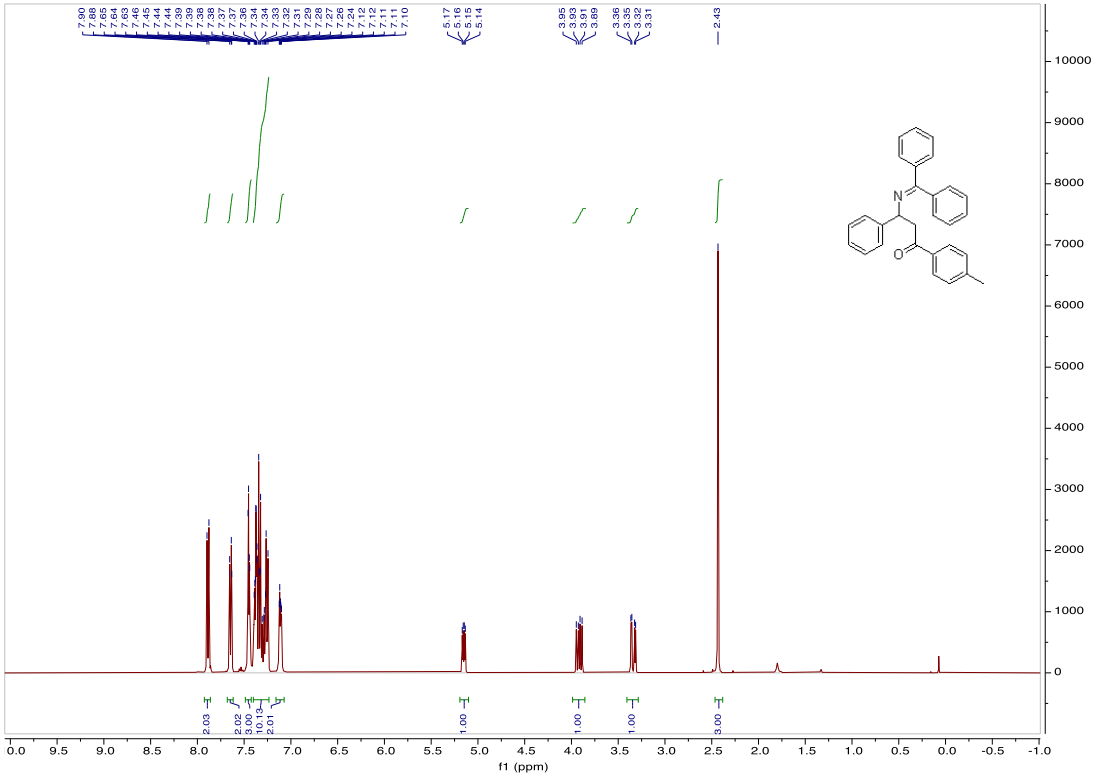


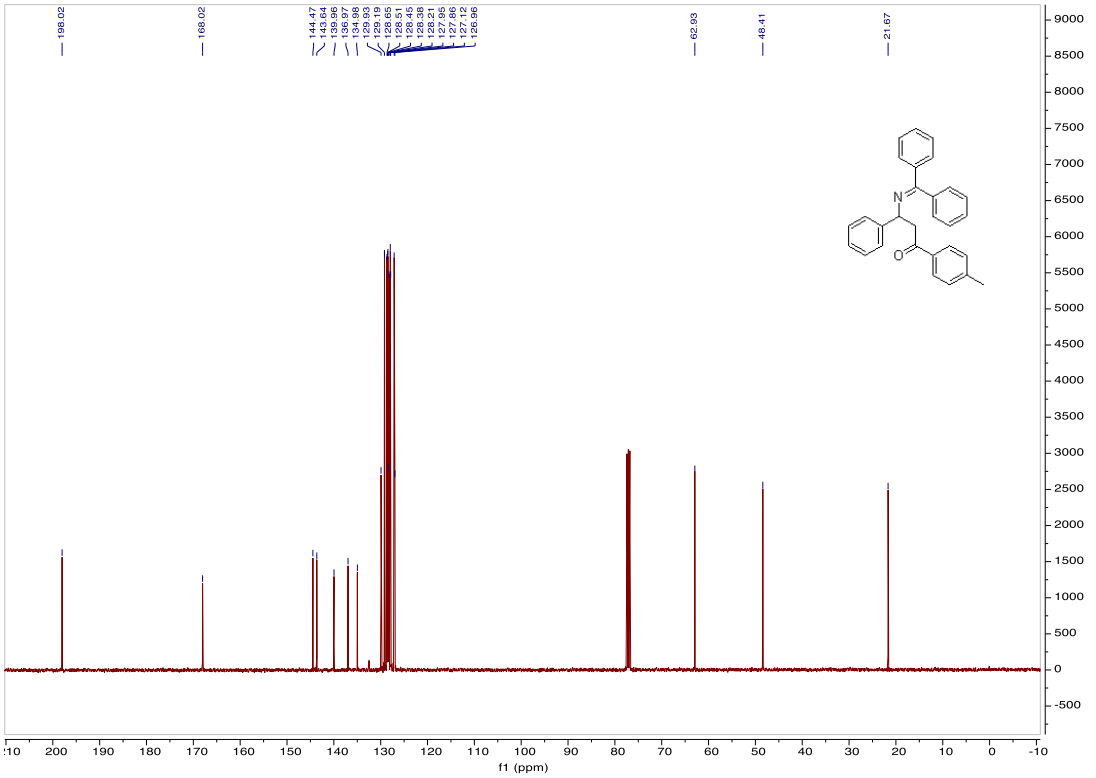
3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (5ba)



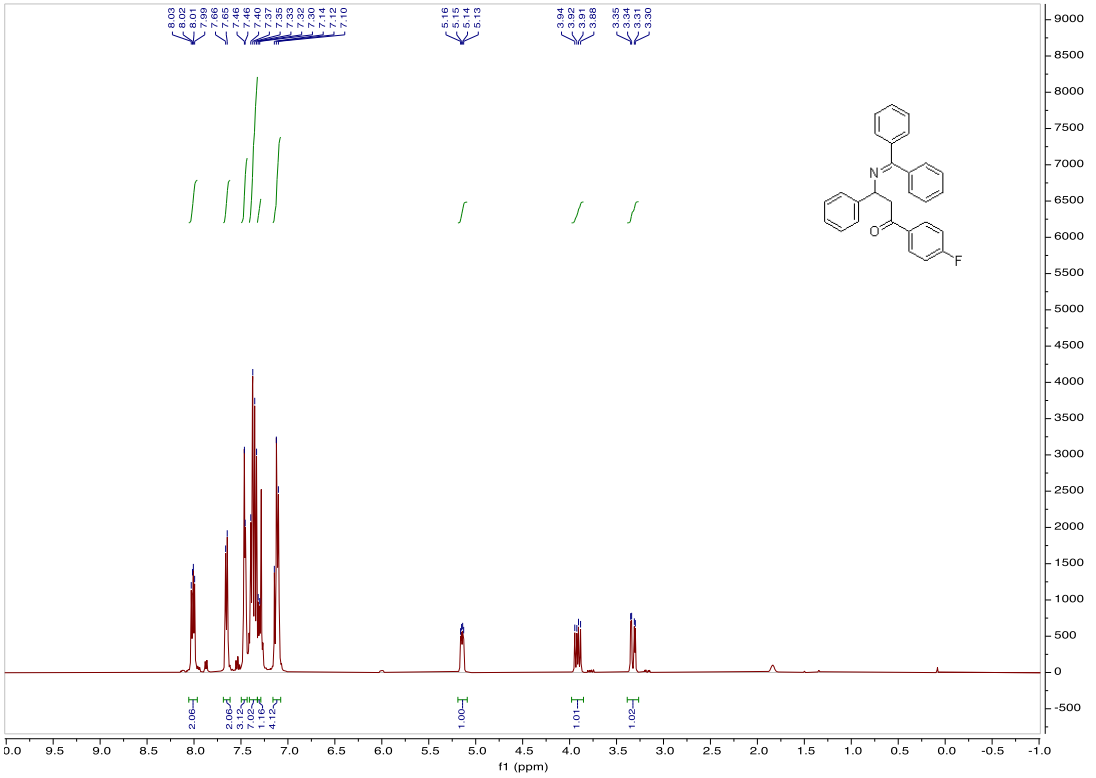


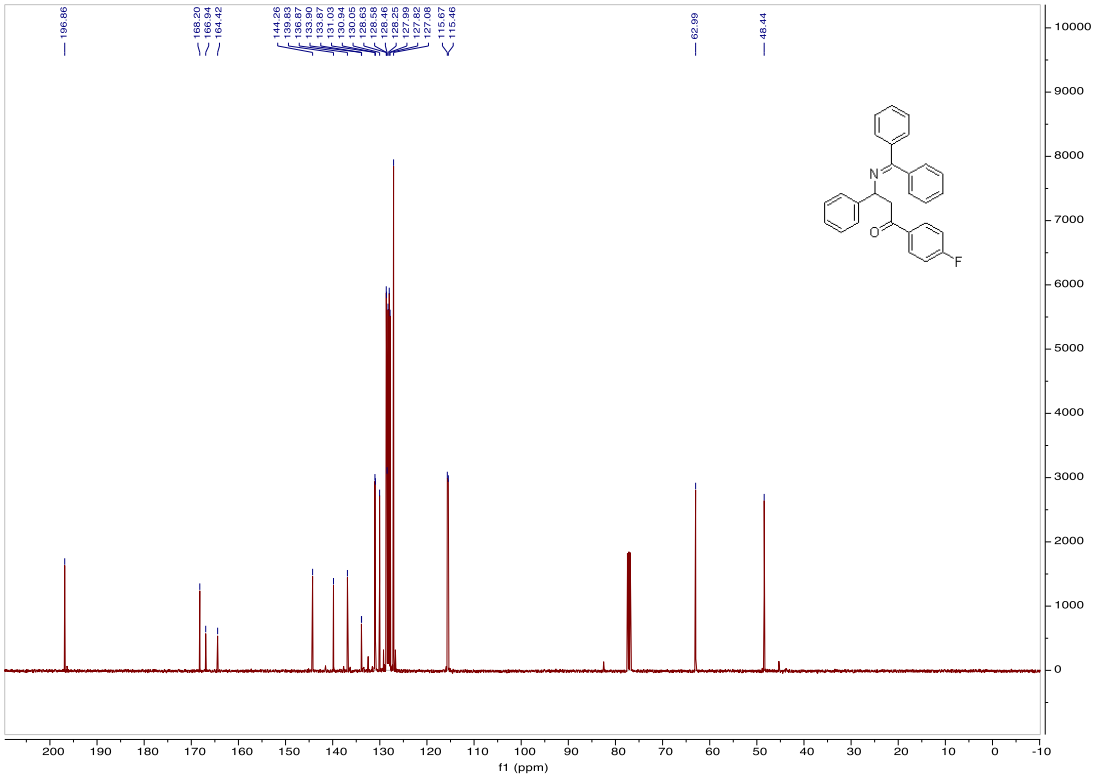
3-((diphenylmethylene)amino)-3-phenyl-1-(p-tolyl)propan-1-one (5ca)

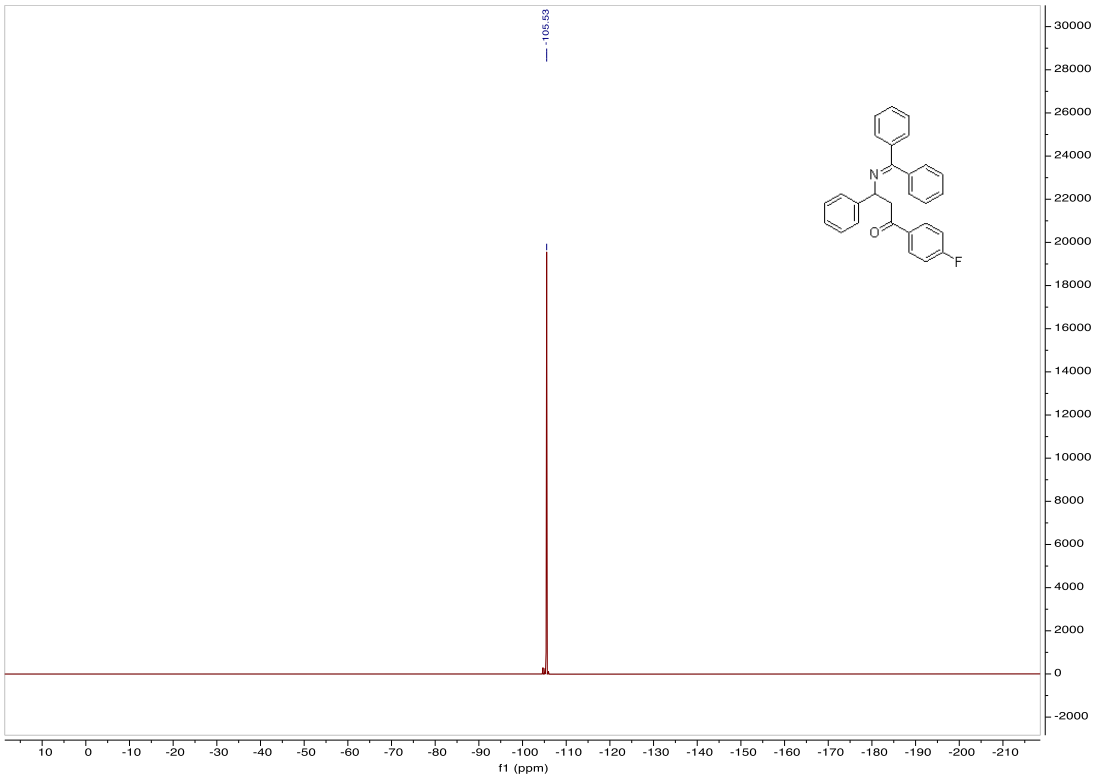




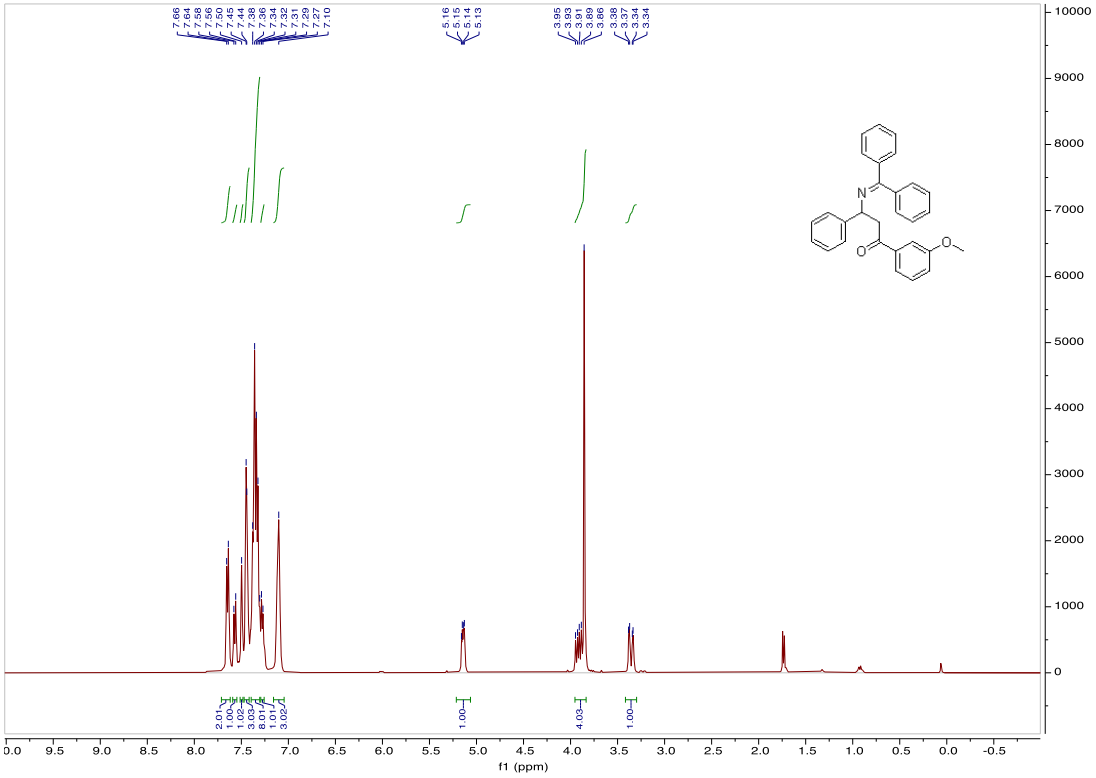
3-((diphenylmethylene)amino)-1-(4-fluorophenyl)-3-phenylpropan-1-one (5da)

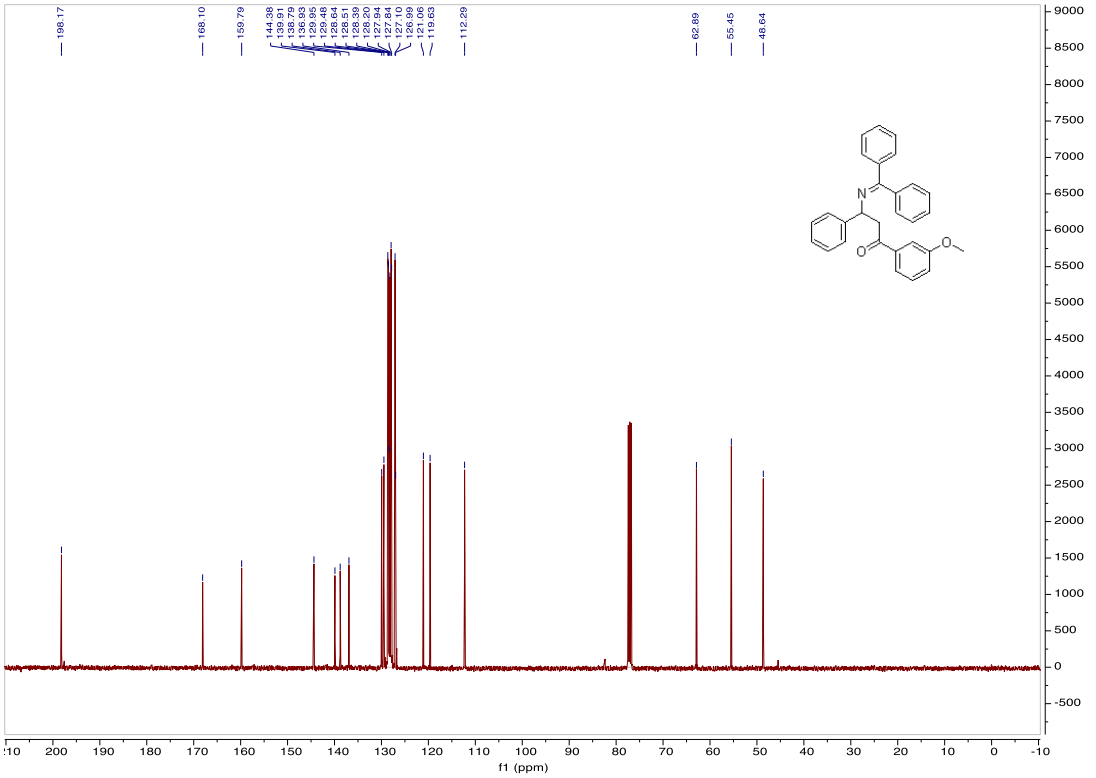




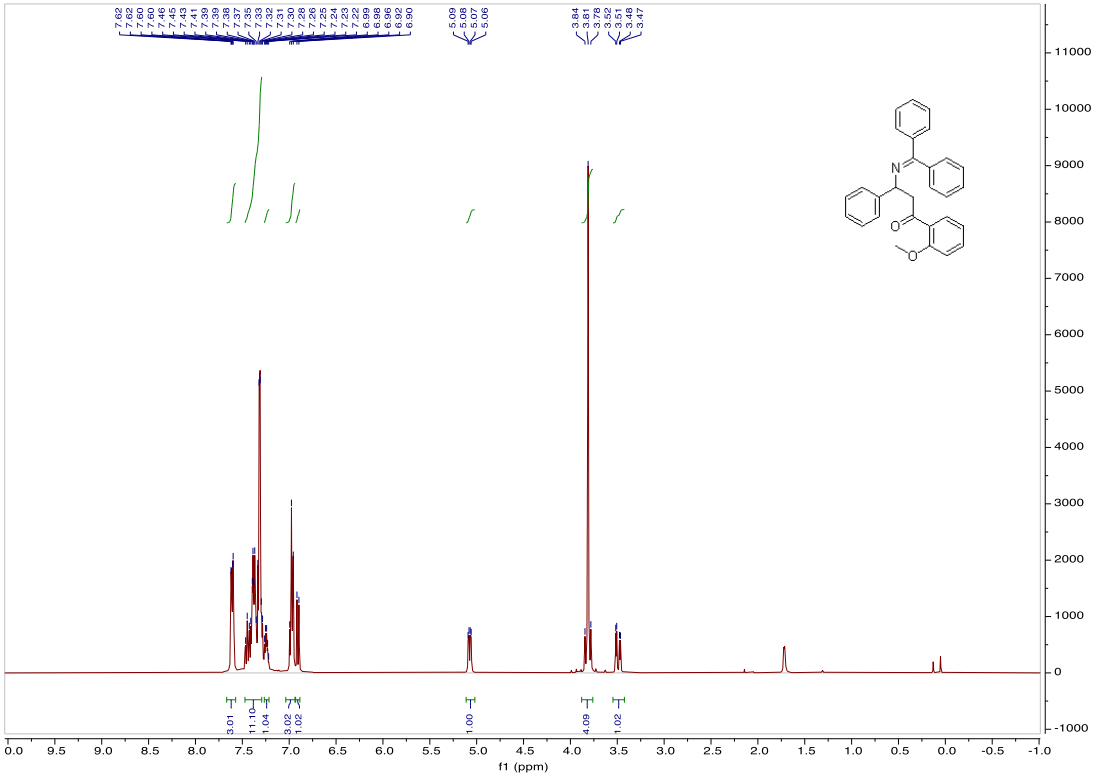

-105.53
N
O
F
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

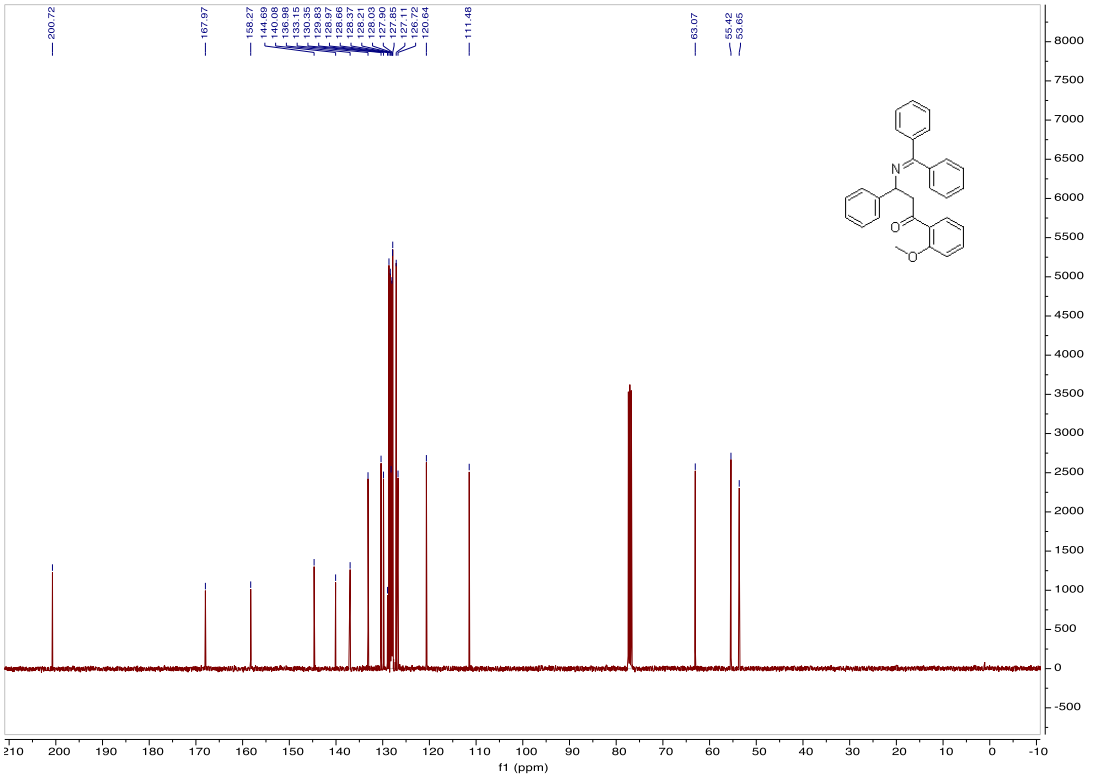
3-((diphenylmethylene)amino)-1-(3-methoxyphenyl)-3-phenylpropan-1-one (5ea)



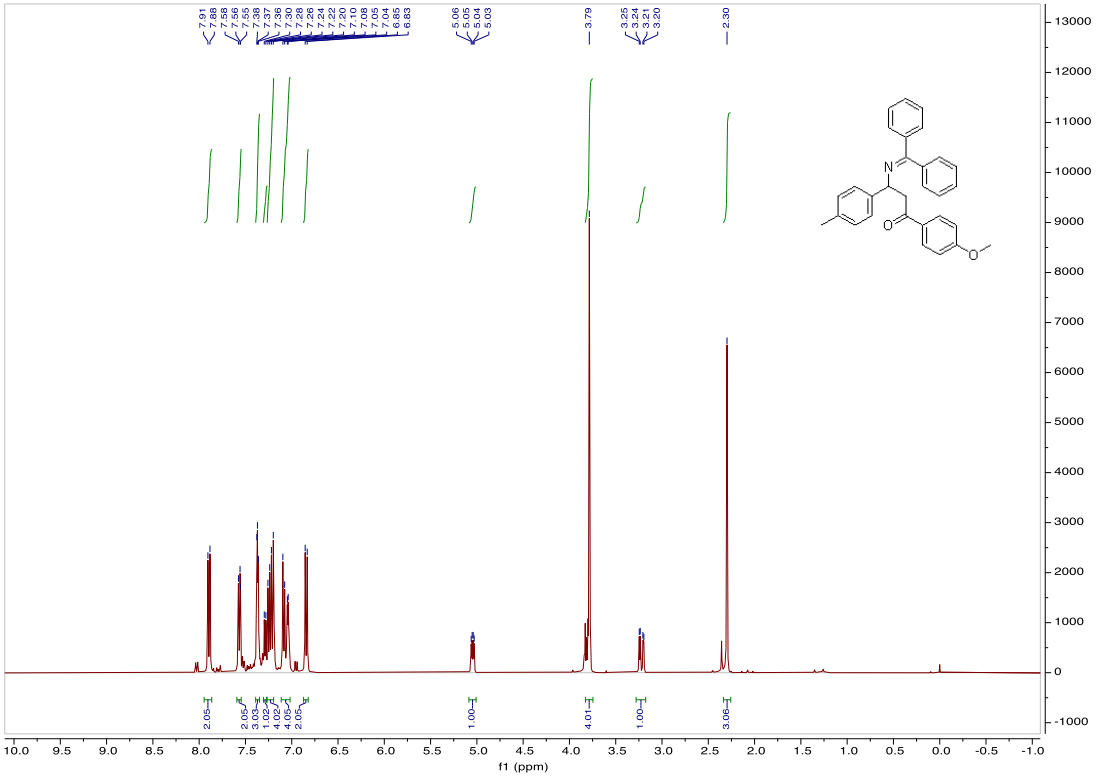


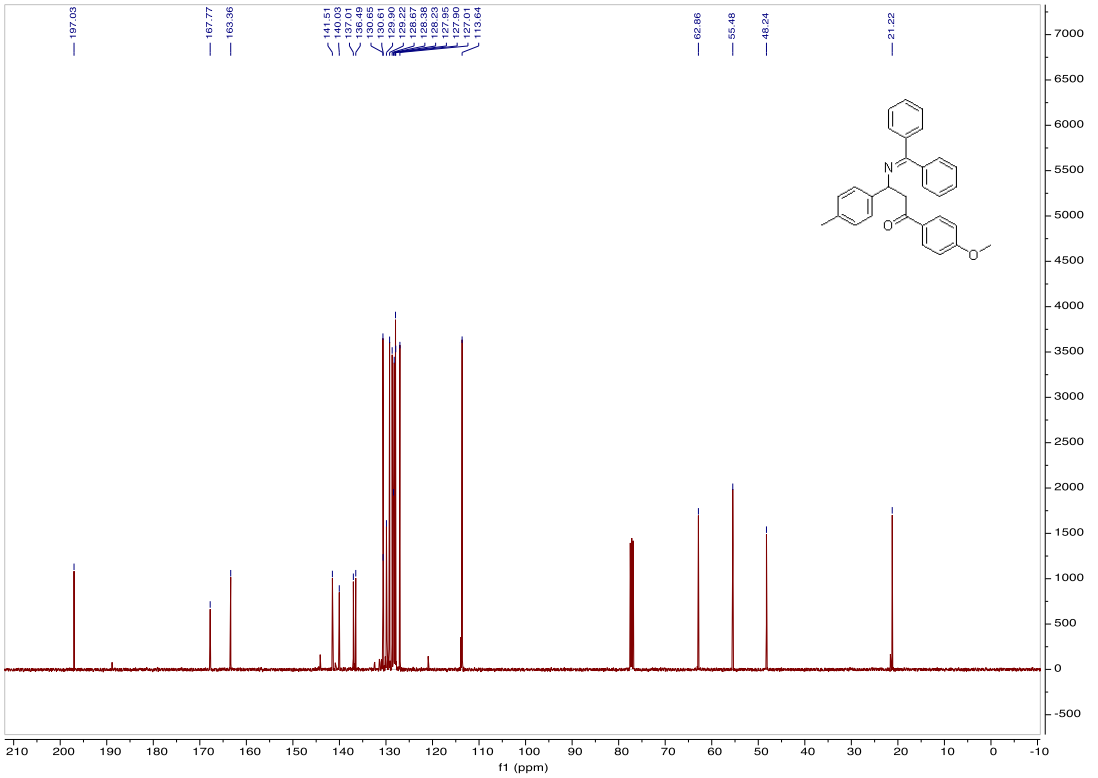
3-((diphenylmethylene)amino)-1-(2-methoxyphenyl)-3-phenylpropan-1-one (5fa)



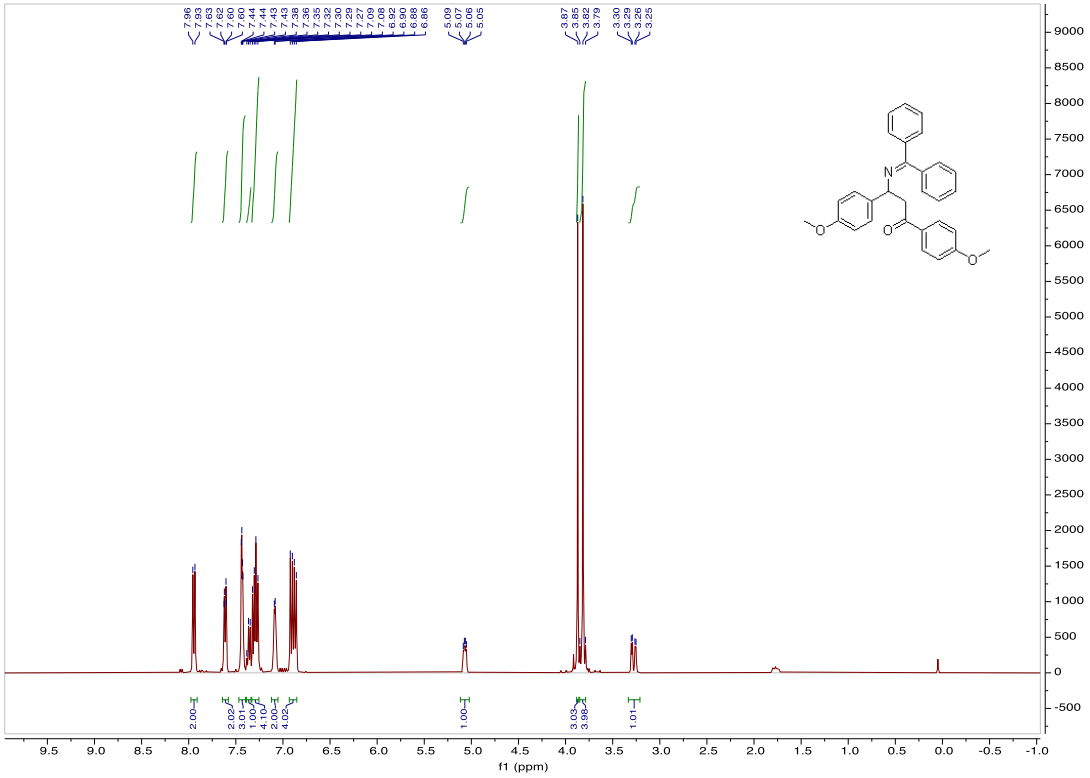


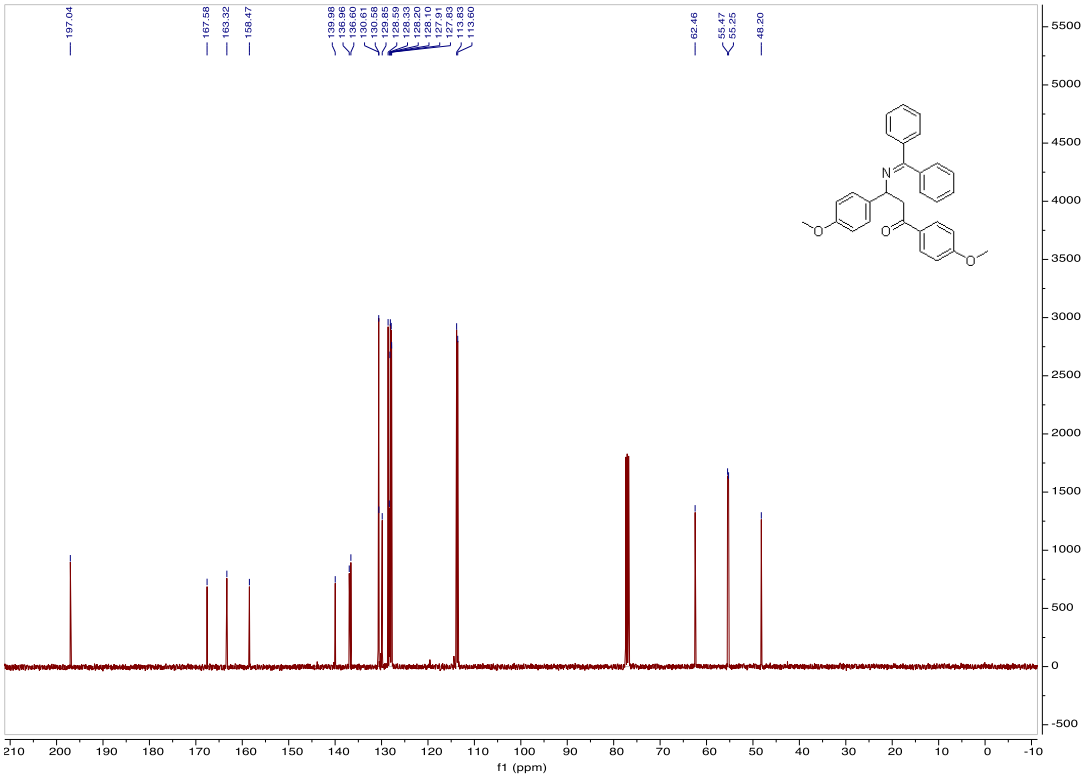
3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(p-tolyl)propan-1-one (5bb)



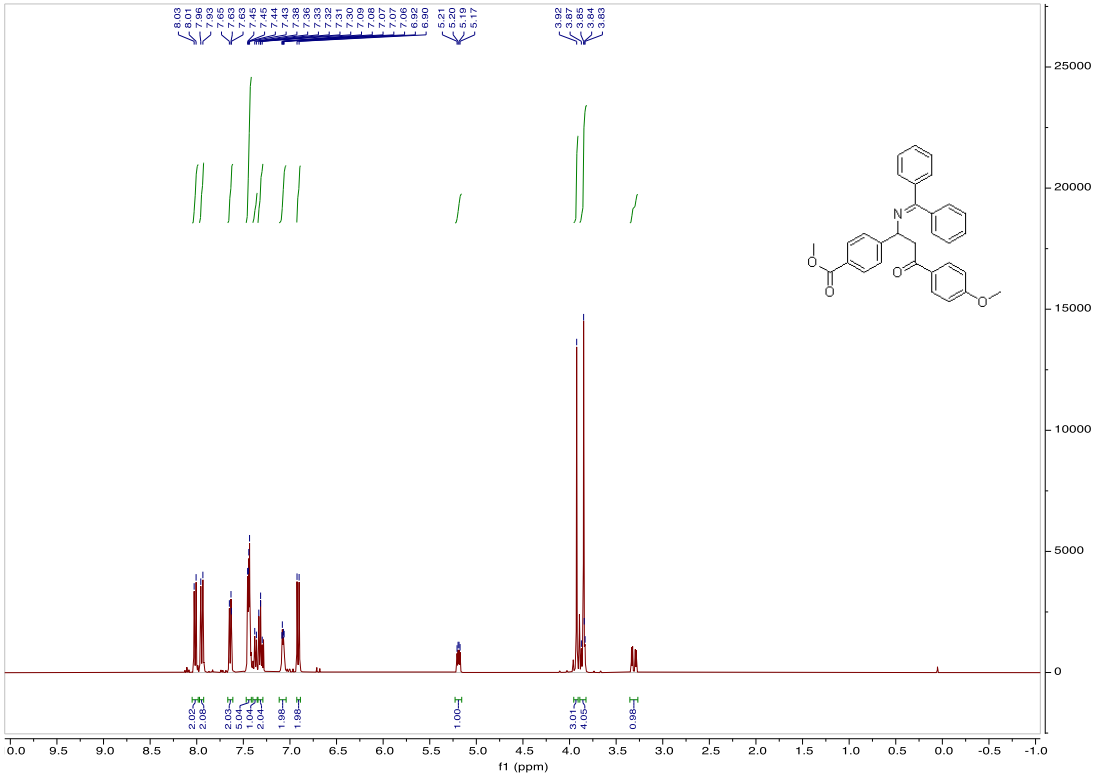


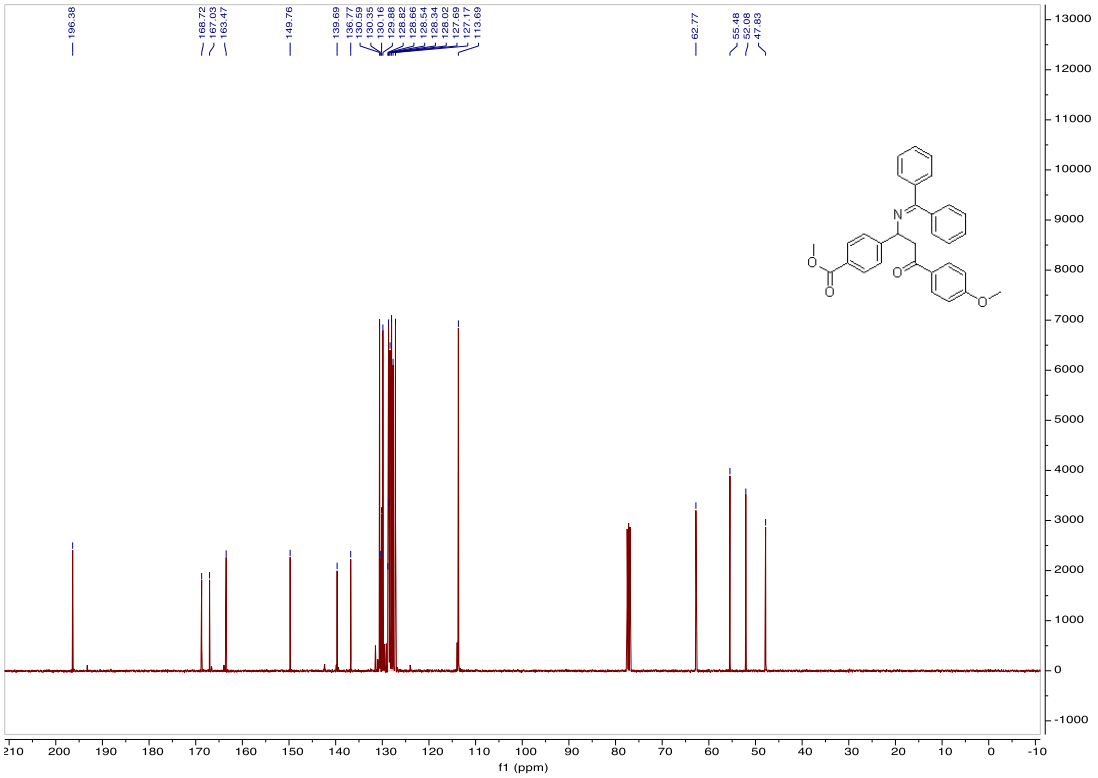
3-((diphenylmethylene)amino)-1,3-bis(4-methoxyphenyl)propan-1-one (5bc)



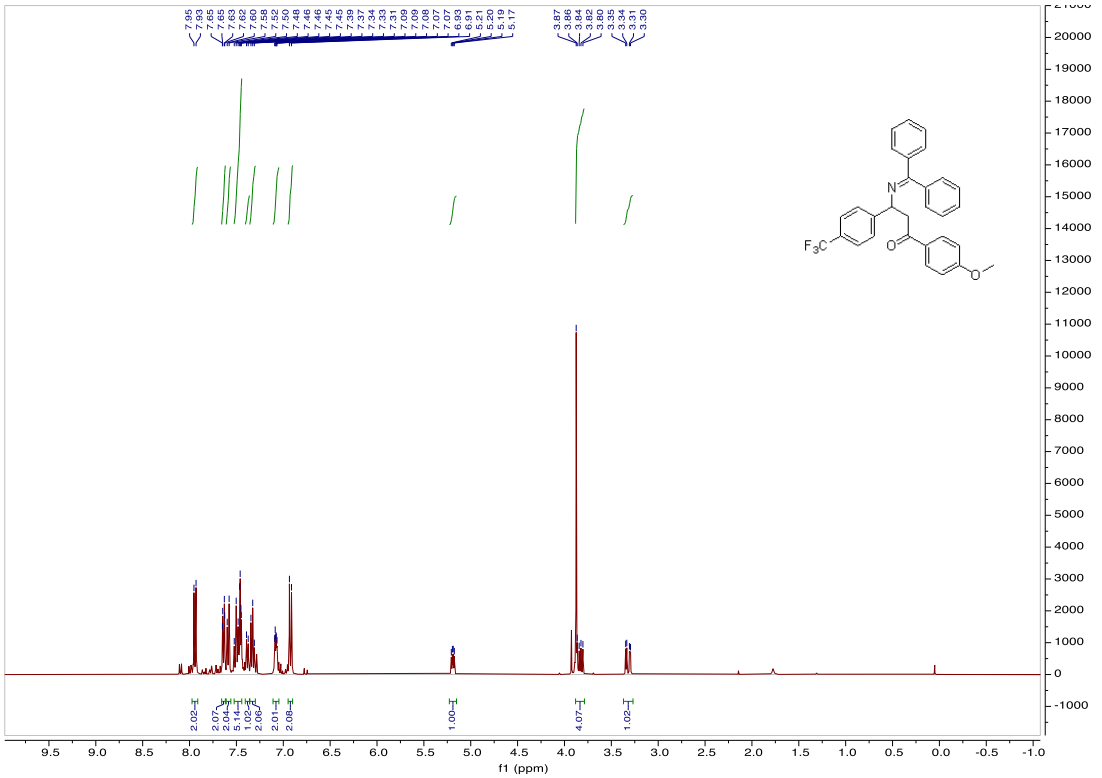


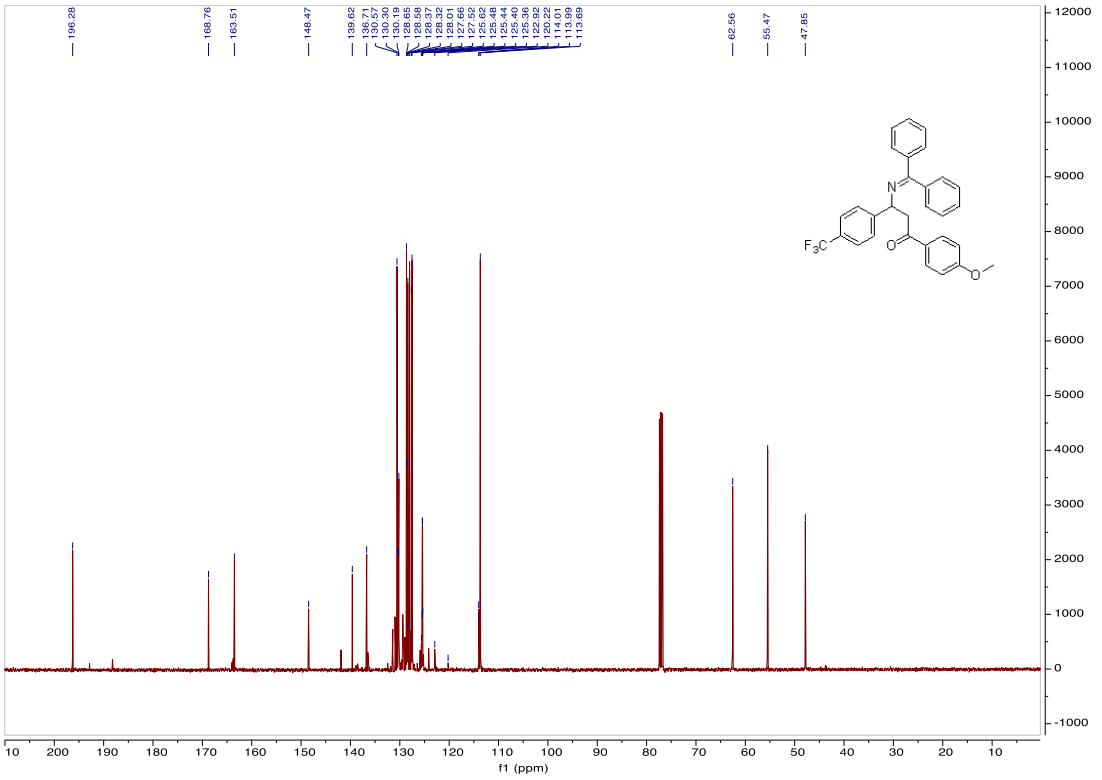
Methyl4-(1-((diphenylmethylene)amino)-3-(4-methoxyphenyl)-3-oxopropyl)benzoate (5be)

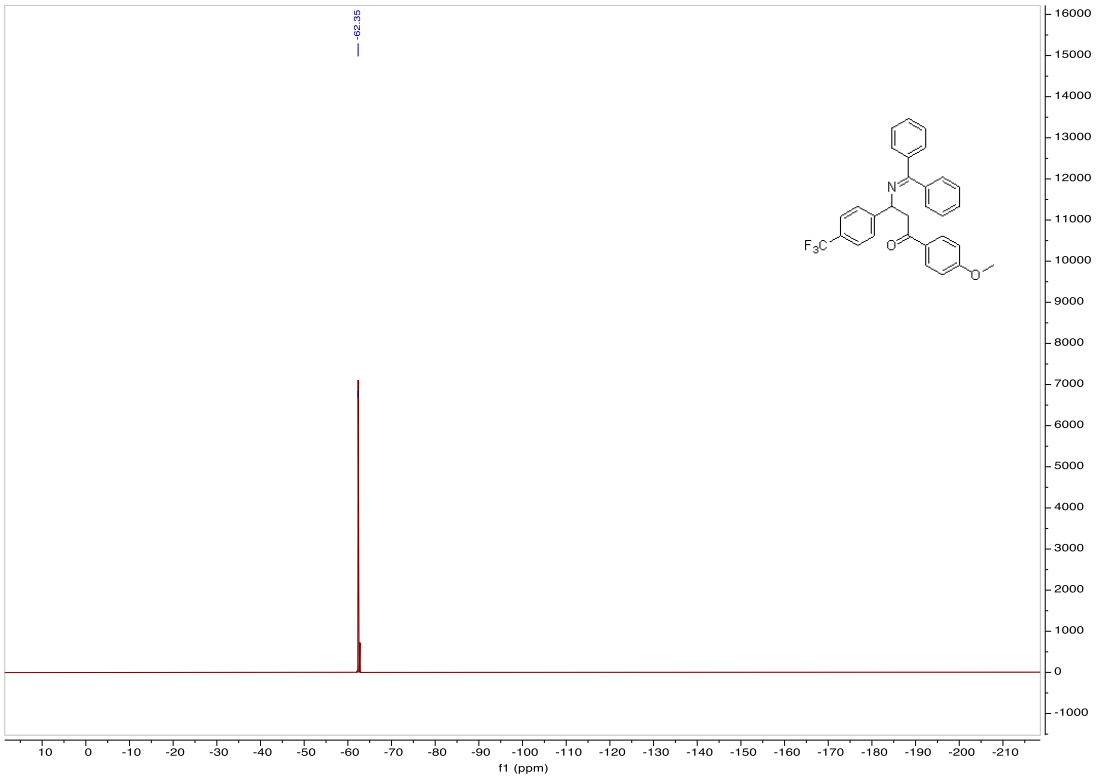




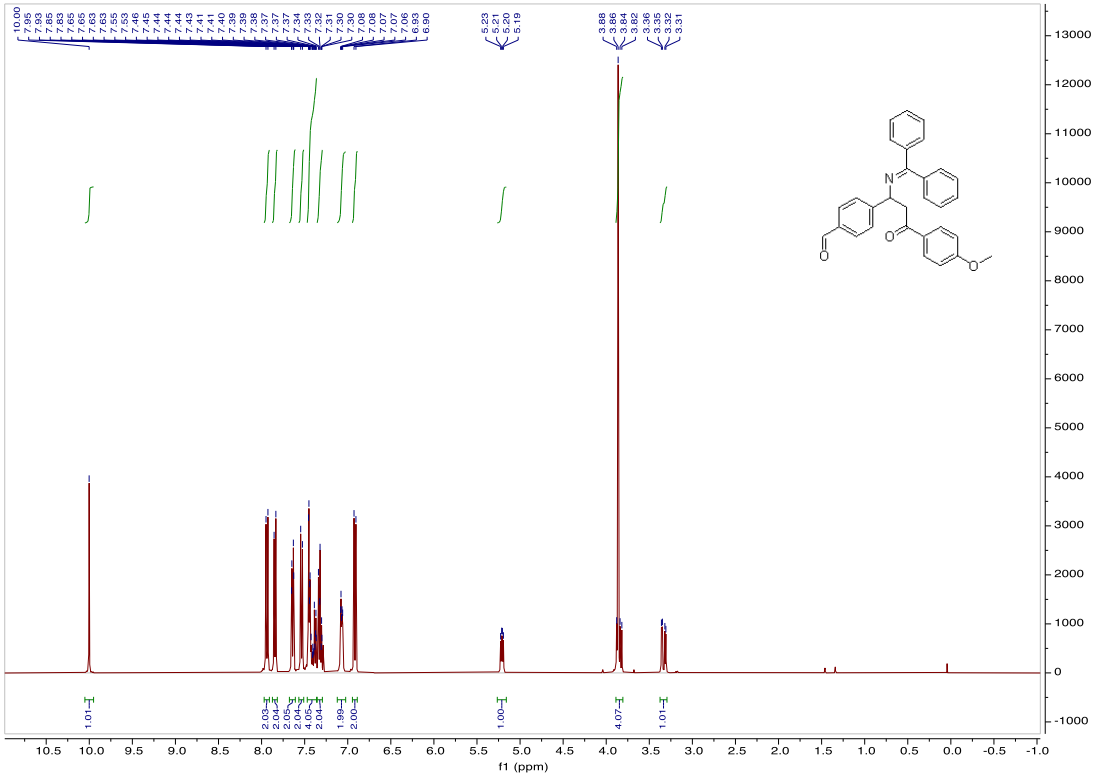
3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)propan-1-one (5bf)

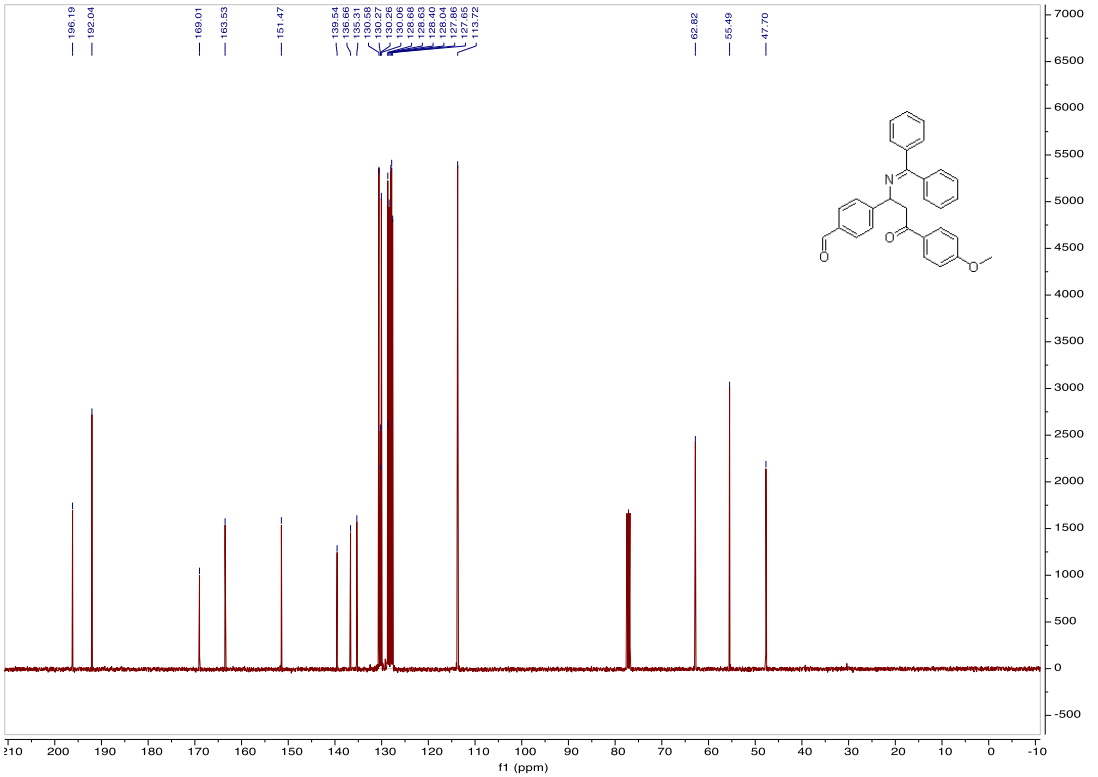




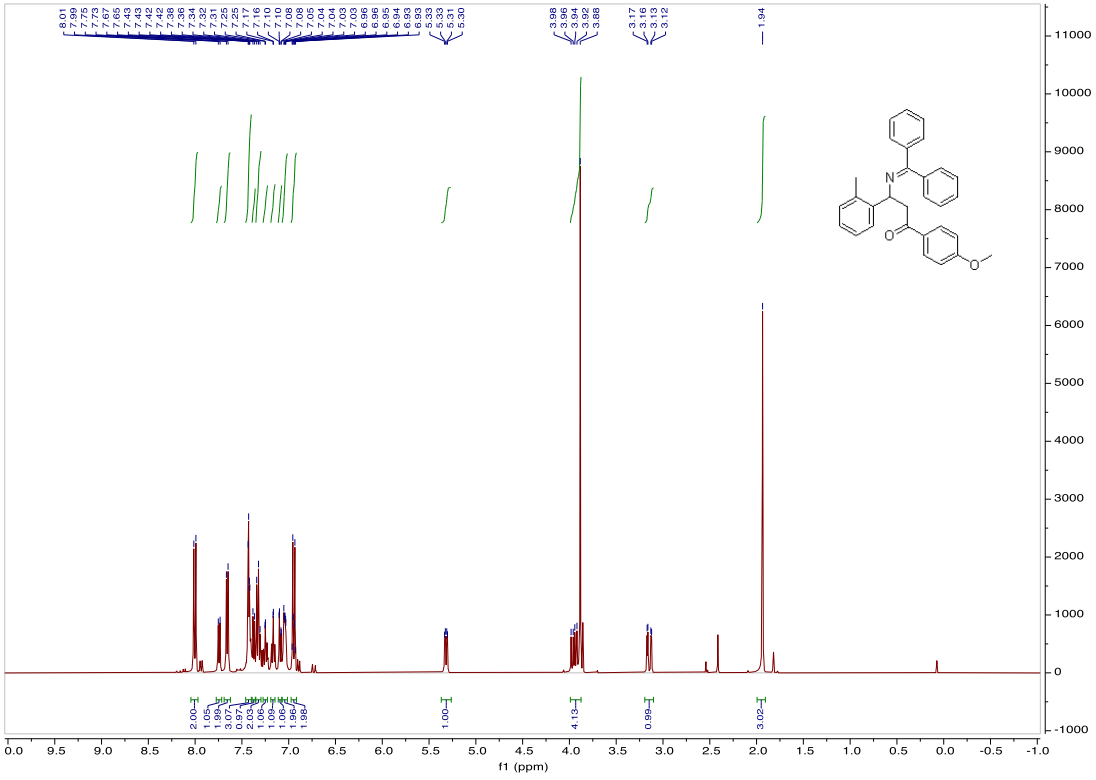

-62.35
N
O
O
F3C
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

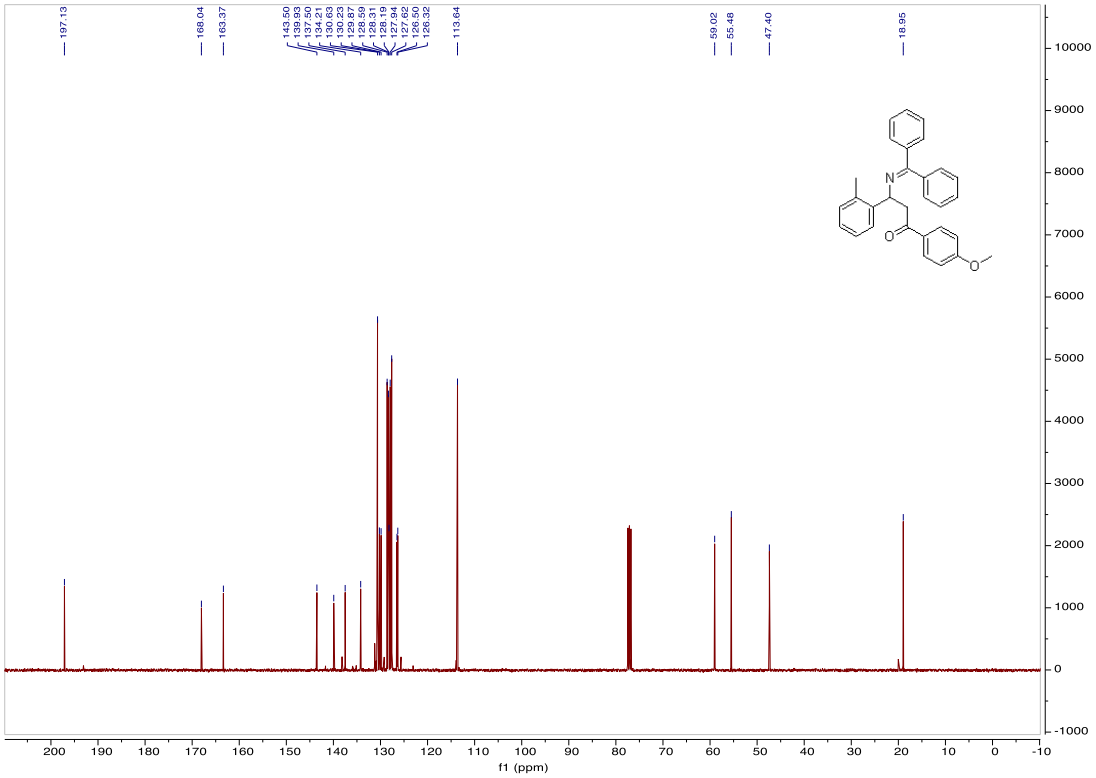
4-(1-((diphenylmethylene)amino)-3-(4-methoxyphenyl)-3-oxopropyl)benzaldehyde (5bg)



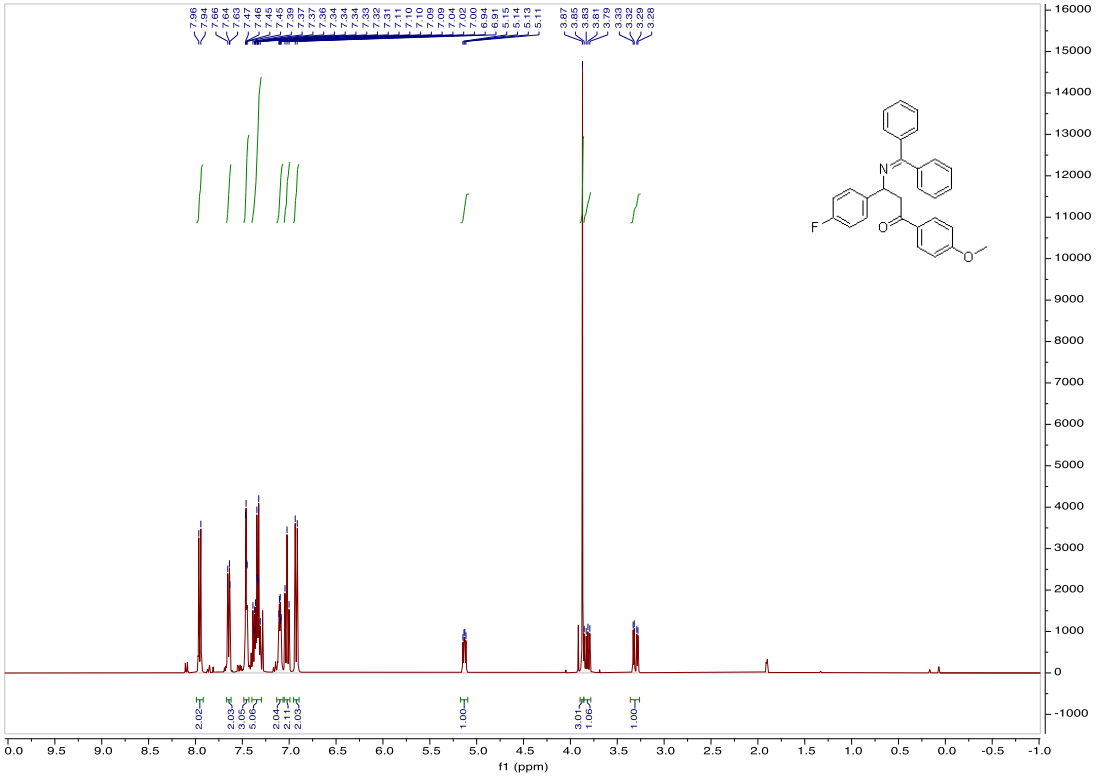


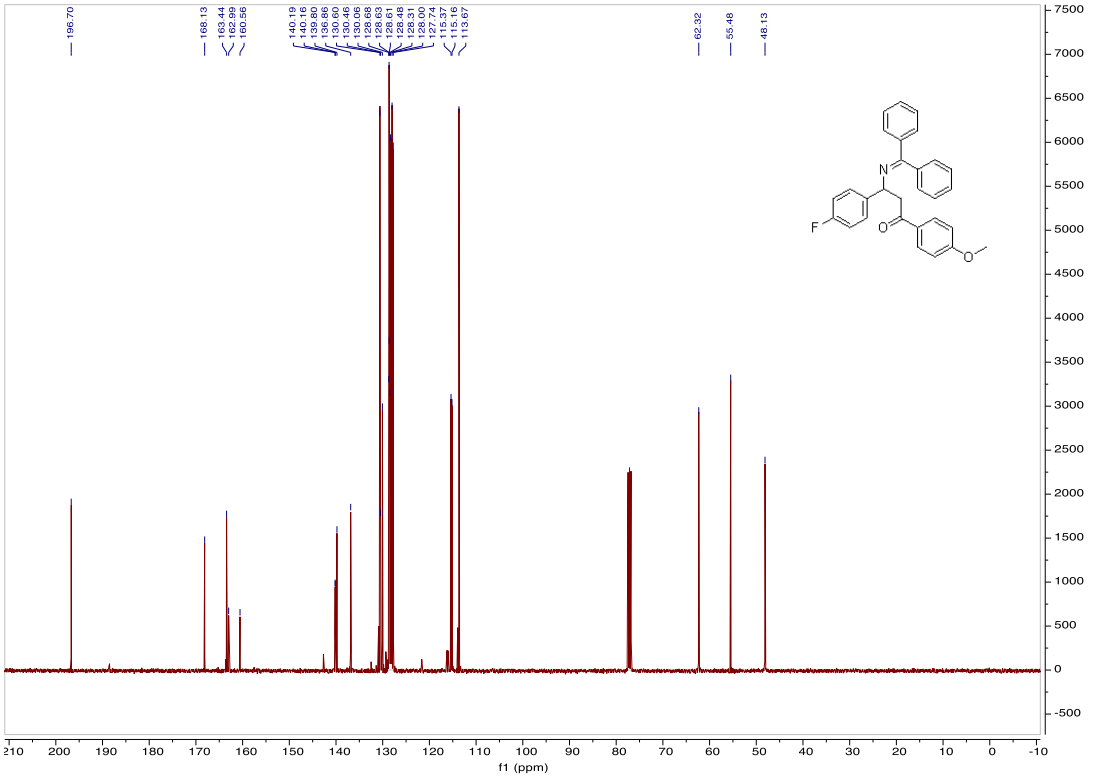
3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(o-tolyl)propan-1-one (5bi)

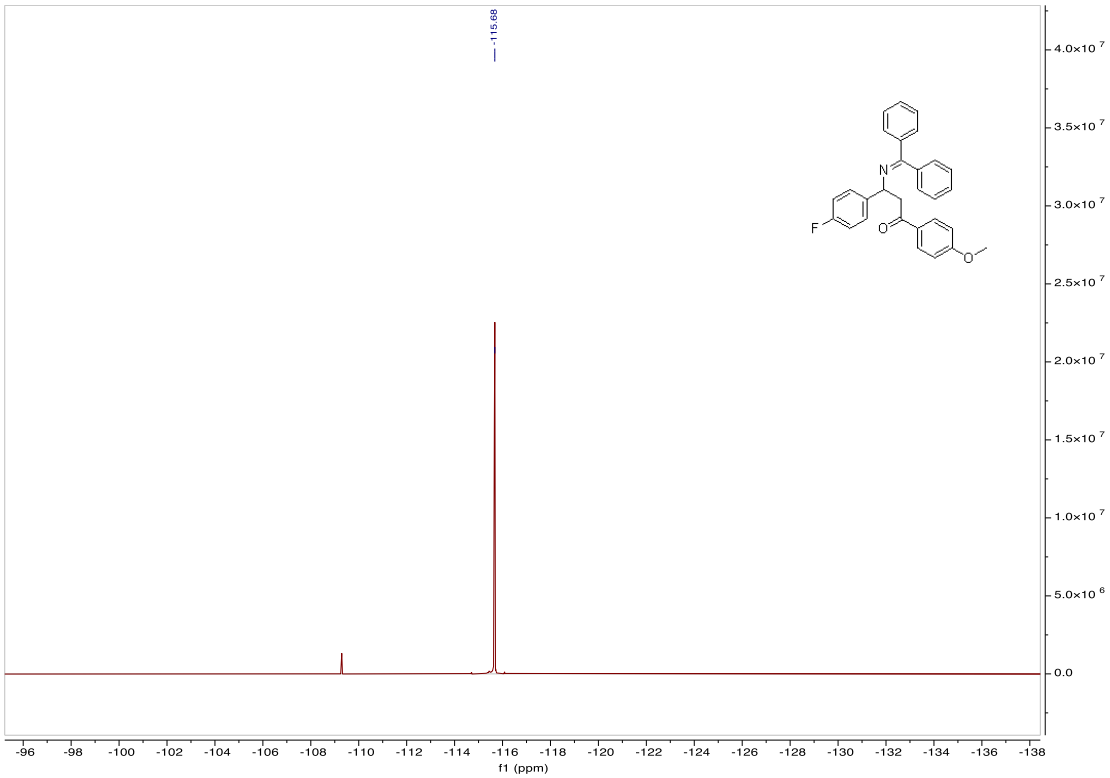




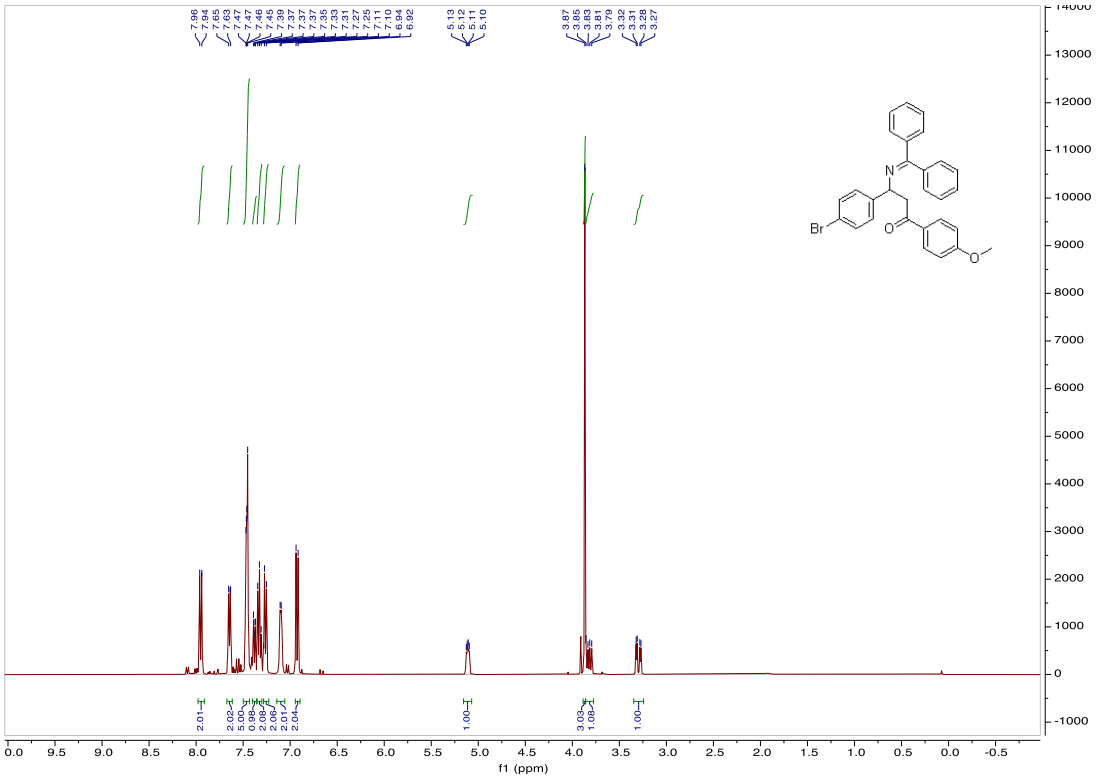
3-((diphenylmethylene)amino)-3-(4-fluorophenyl)-1-(4-methoxyphenyl)propan-1-one (5bj)

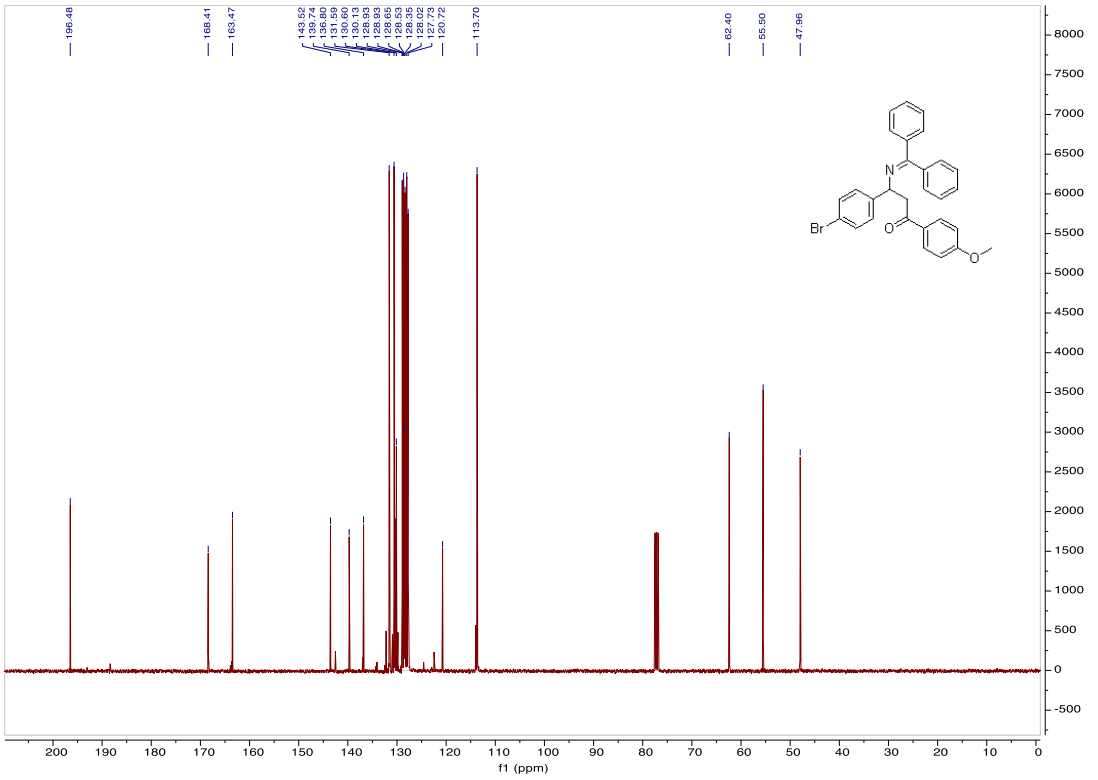




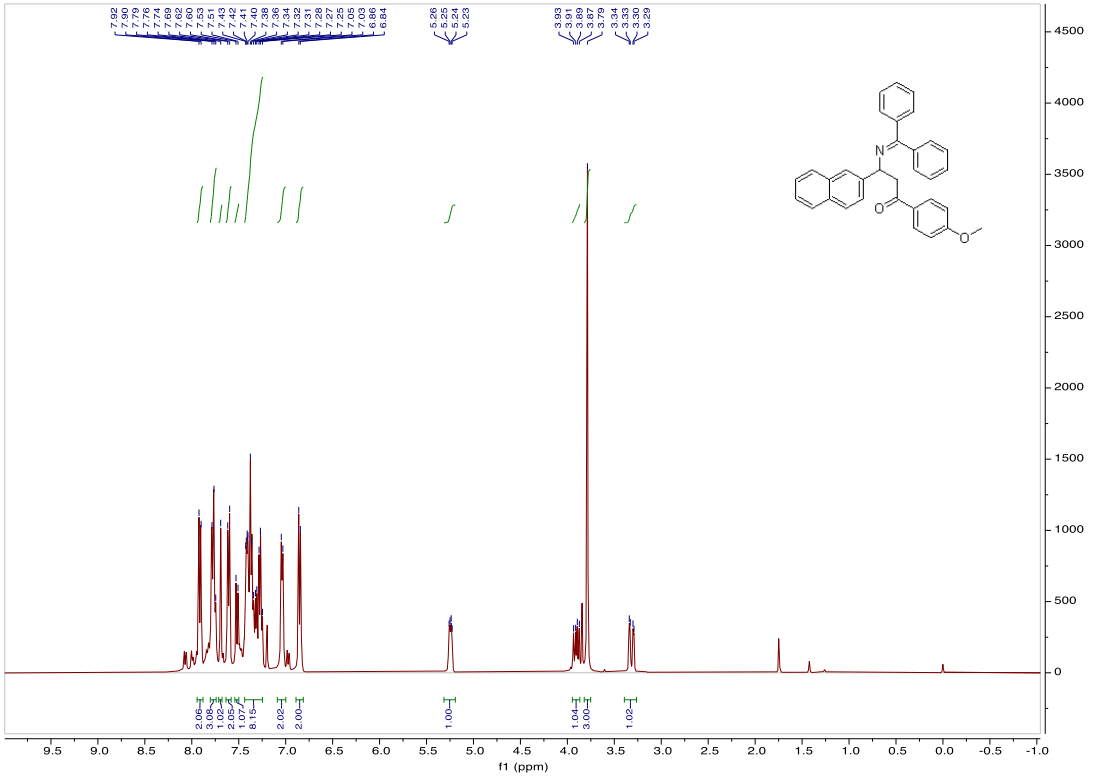

-115.68
4.0x10 7
3.5x10 7
3.0x10 7
2.5x10 7
2.0x10 7
1.5x10 7
1.0x10 7
5.0x10 6
0.0
N
F
O
O
-96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138
f1 (ppm)

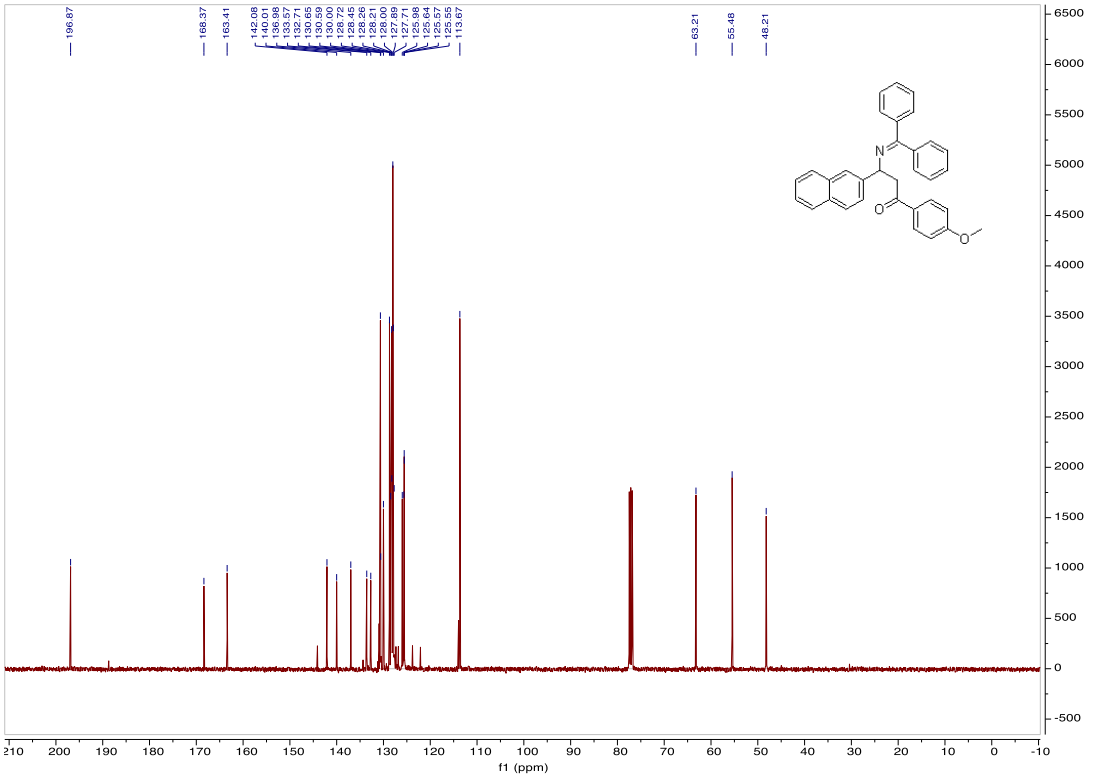
3-(4-bromophenyl)-3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)propan-1-one (5bk)



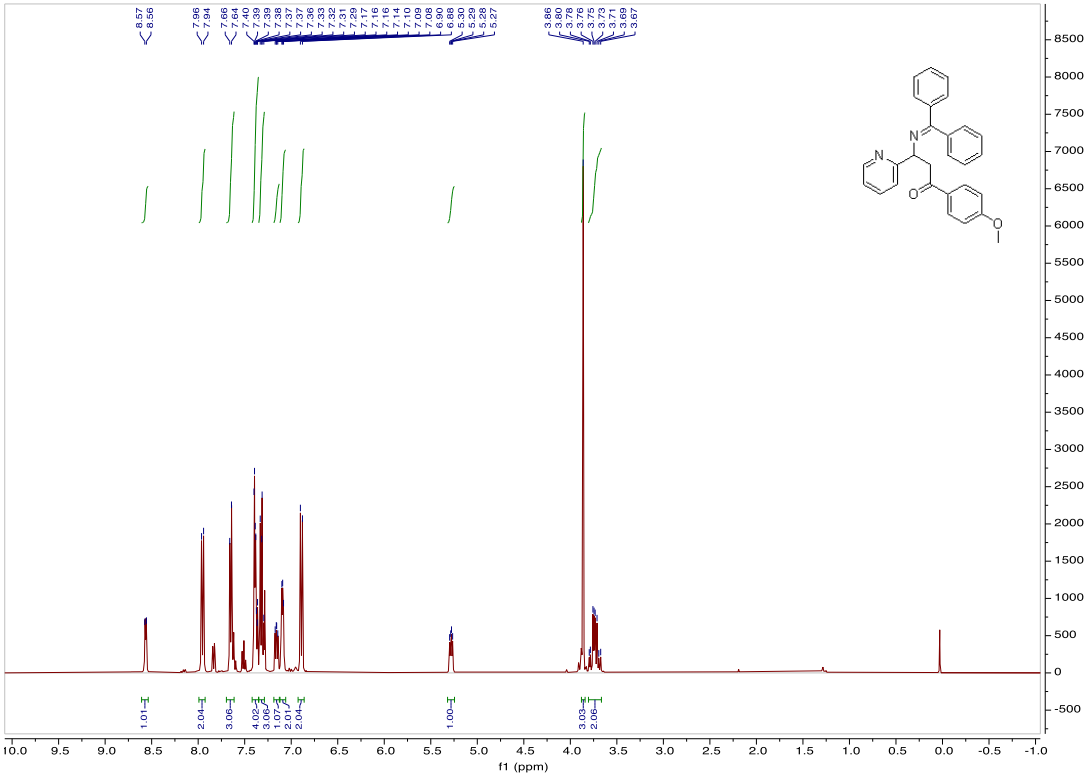


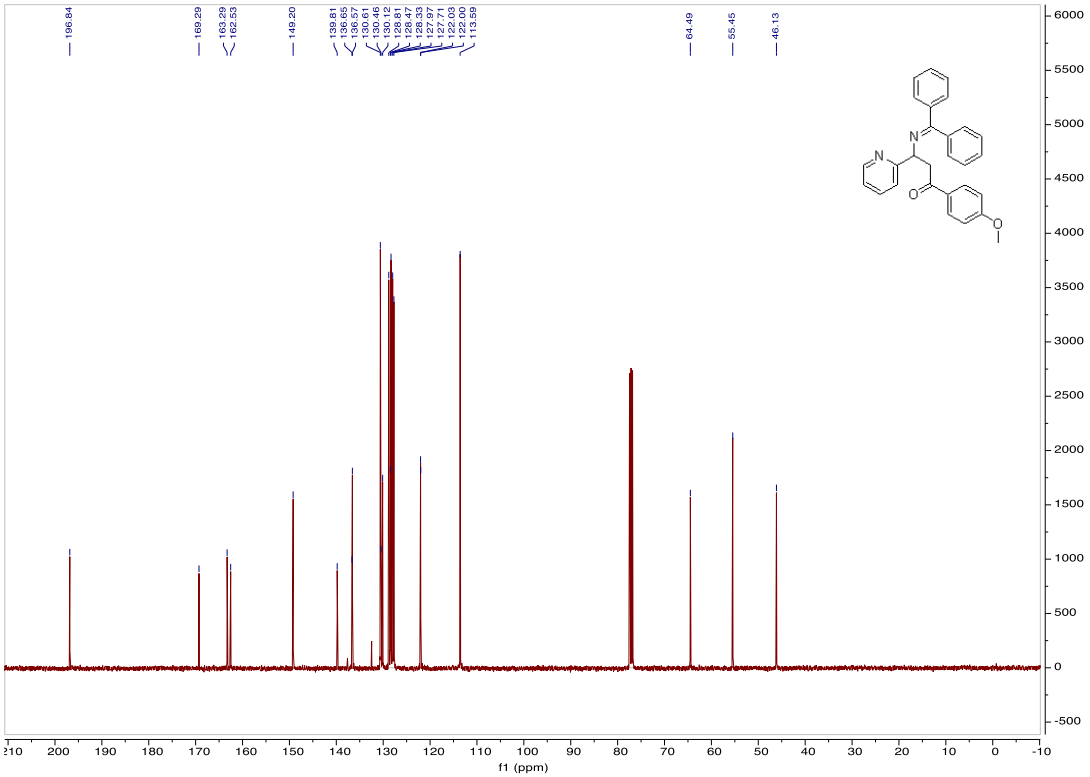
3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(naphthalen-2-yl)propan-1-one (5bo)



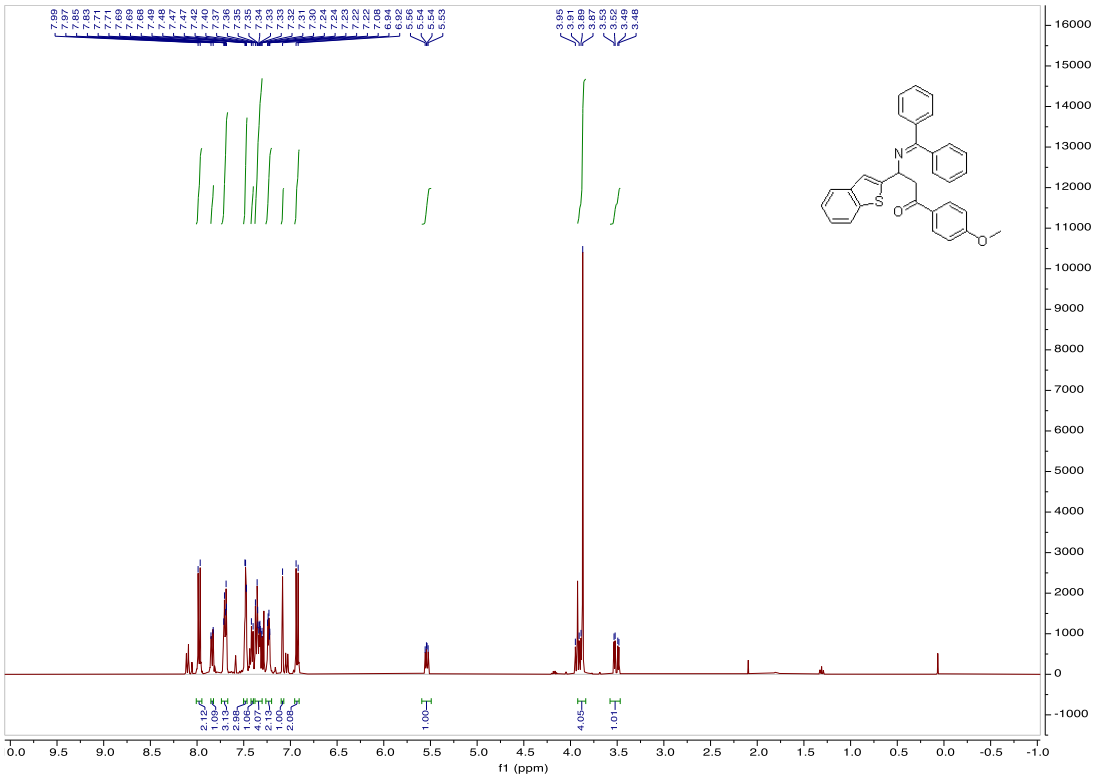


3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-3-(pyridin-2-yl)propan-1-one (5bp)





3-(benzo[b]thiophen-2-yl)-3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)propan-1-one (5bq)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7.71
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7.69
7.68
7.68
7.49
7.48
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5.54
5.54
5.53
3.95
3.91
3.89
3.87
3.53
3.52
3.49
3.48
2.12
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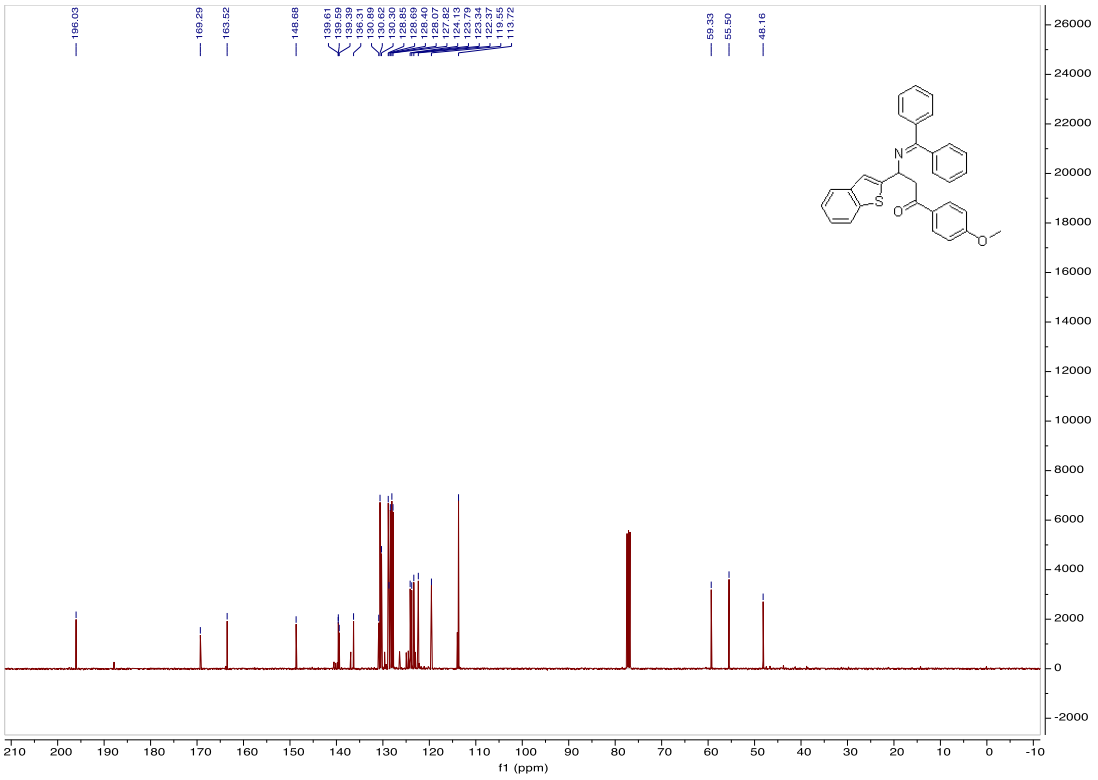
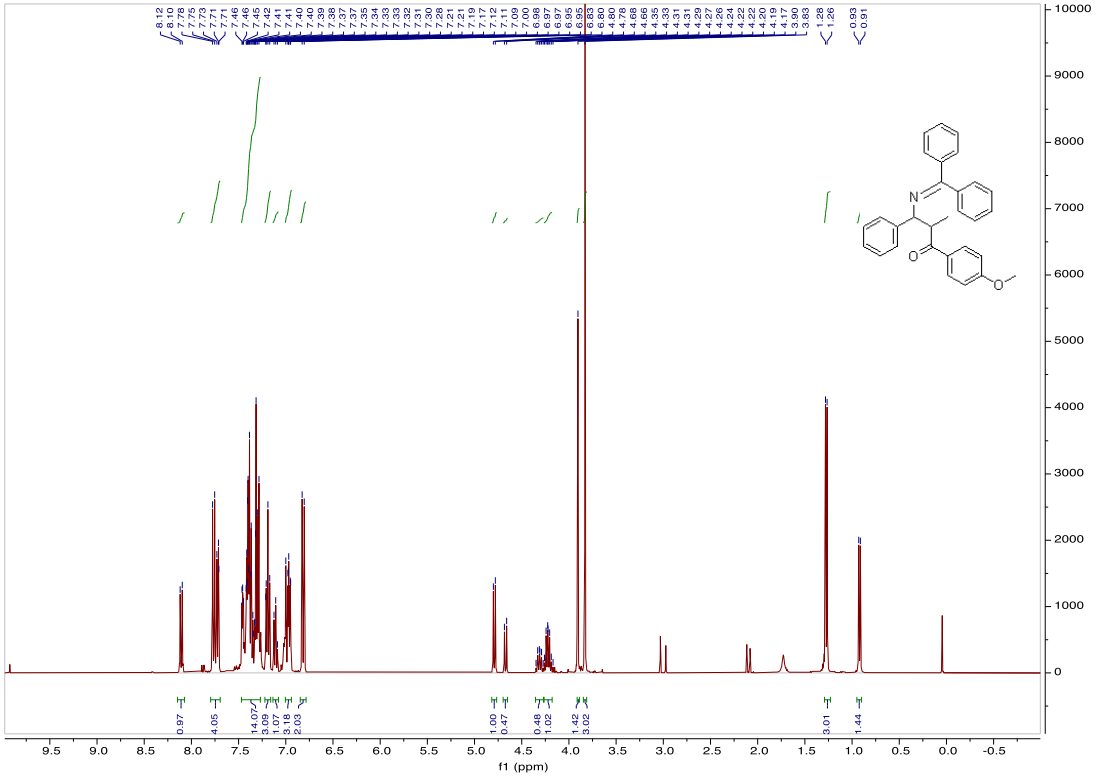
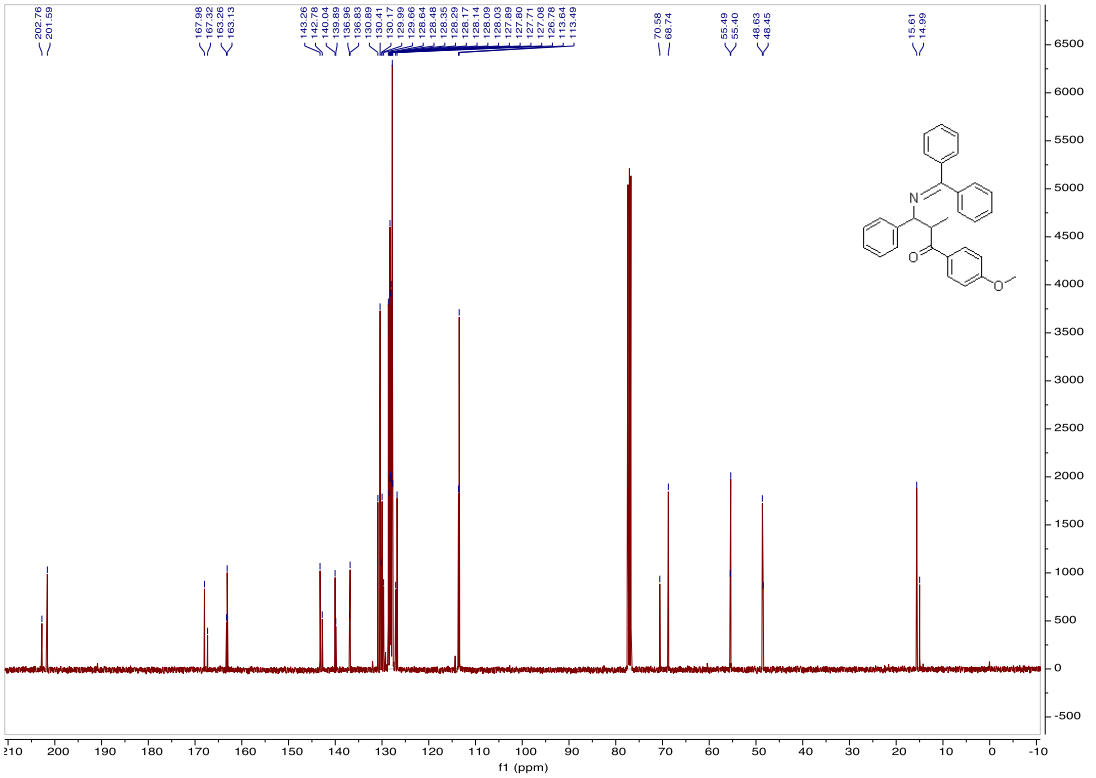
2.13
1.00
2.09
1.00
4.05
1.01
f1 (ppm)

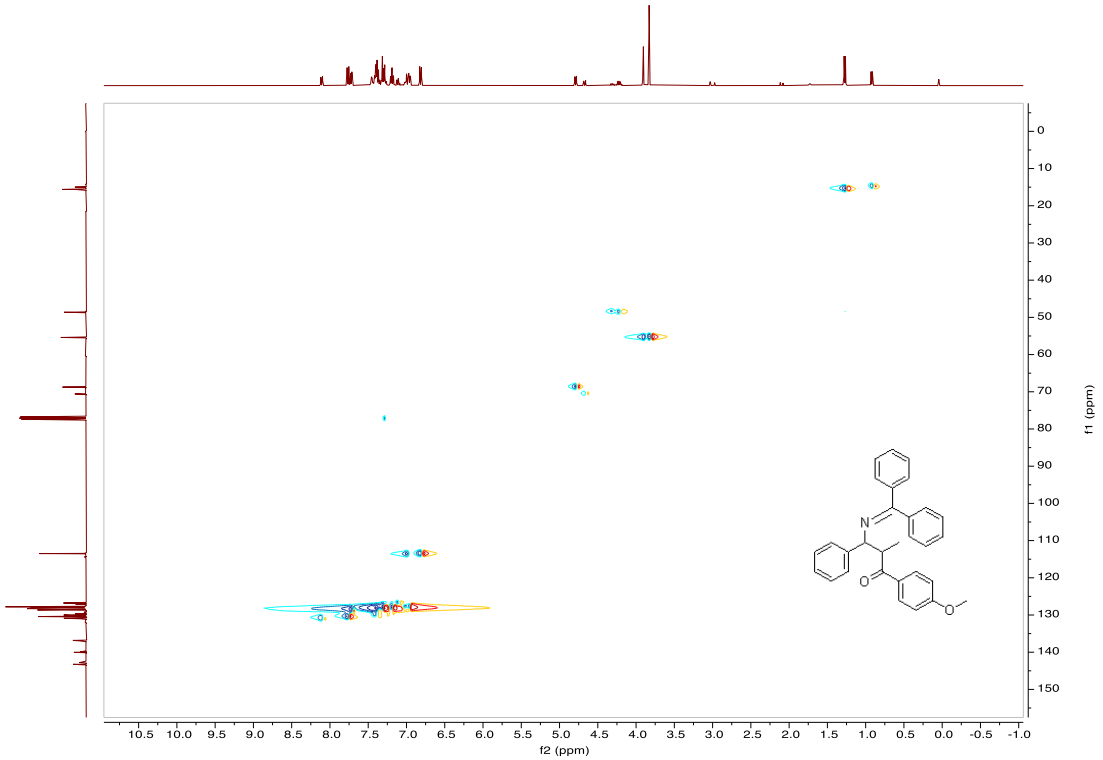

196.03
169.29
163.52
148.68
139.61
139.59
139.39
136.31
130.89
130.62
130.50
128.85
128.69
128.40
128.37
127.82
124.13
123.79
123.34
122.77
119.55
113.72
59.33
55.50
48.16
f1 (ppm)

3-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-2-methyl-3-phenylpropan-1-one (5br)

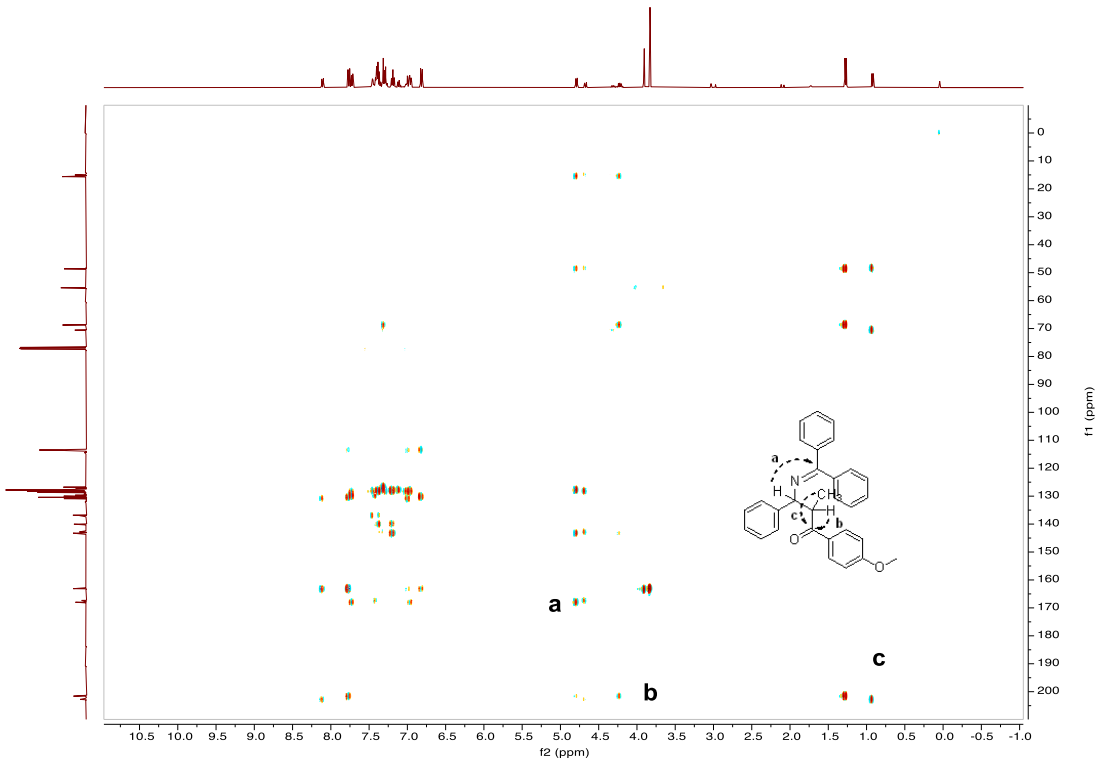




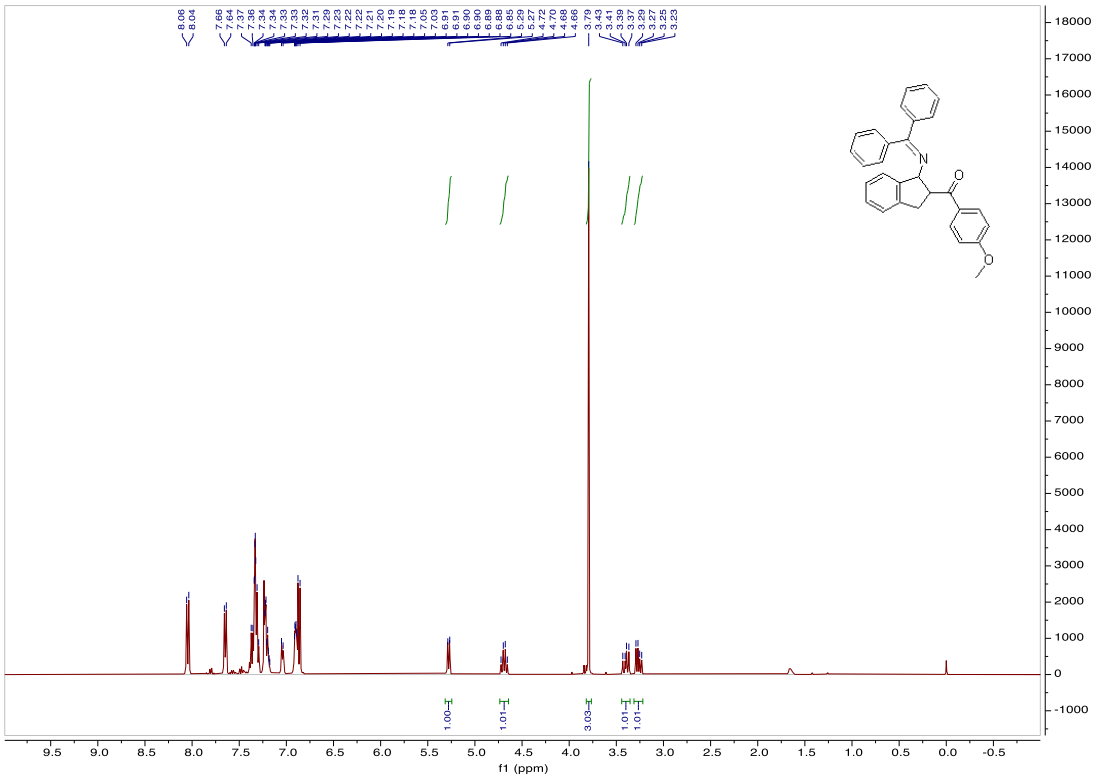
{1H-13C}-HSQC

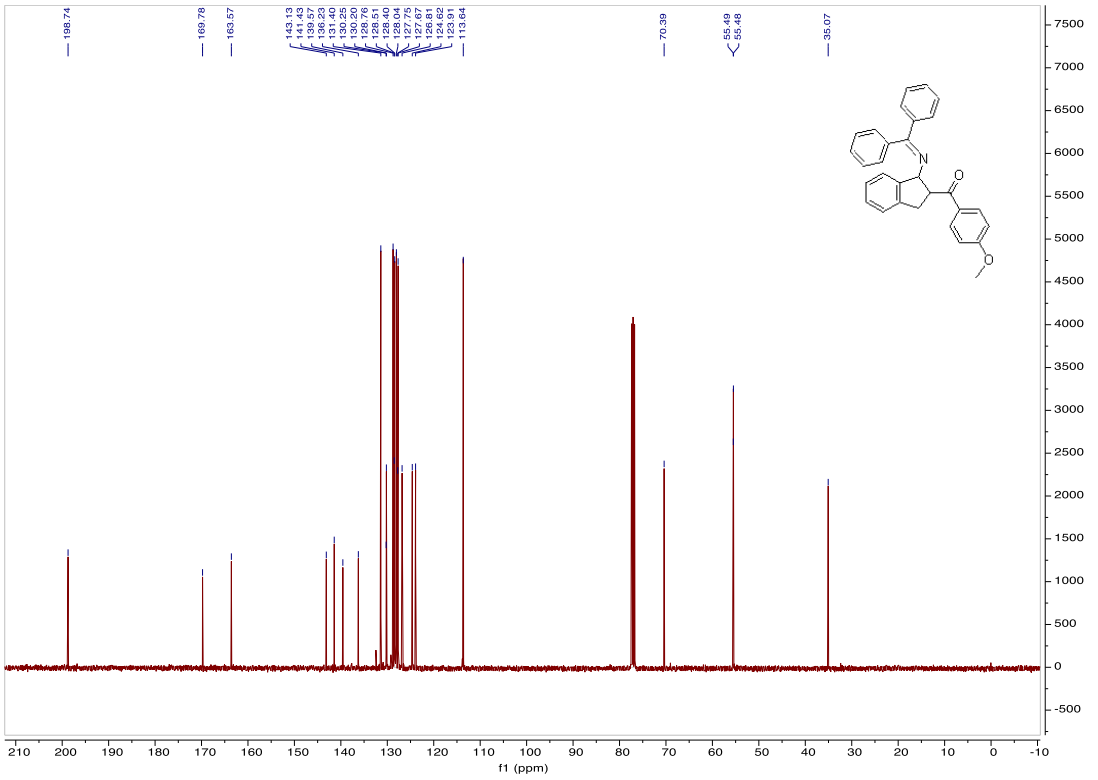


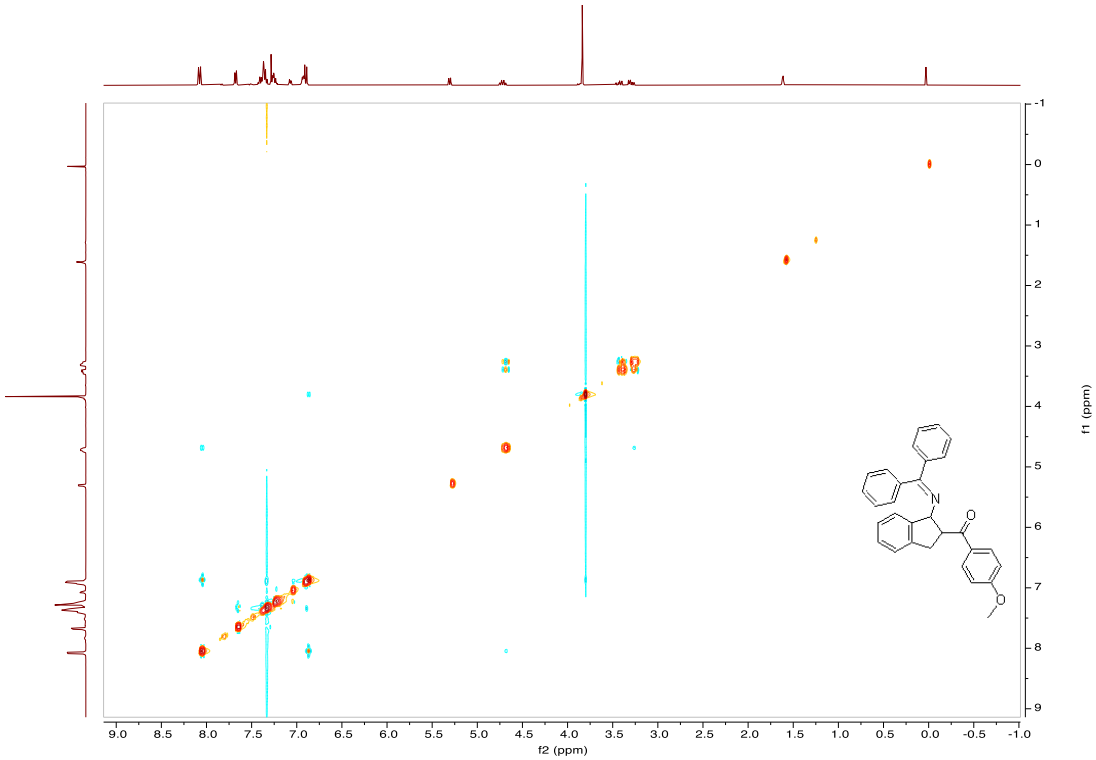
{1H-13C}-HMBC



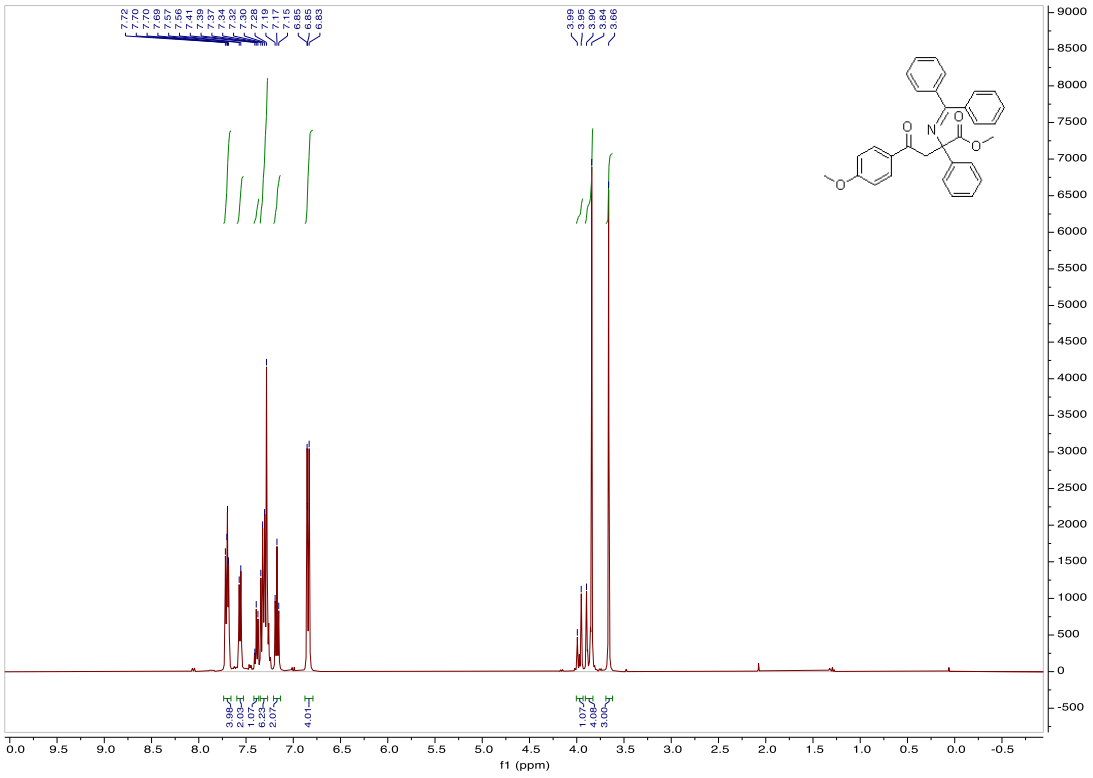
(1-((diphenylmethylene)amino)-2,3-dihydro-1H-inden-2-yl)(4-methoxyphenyl)methanone (5bt)

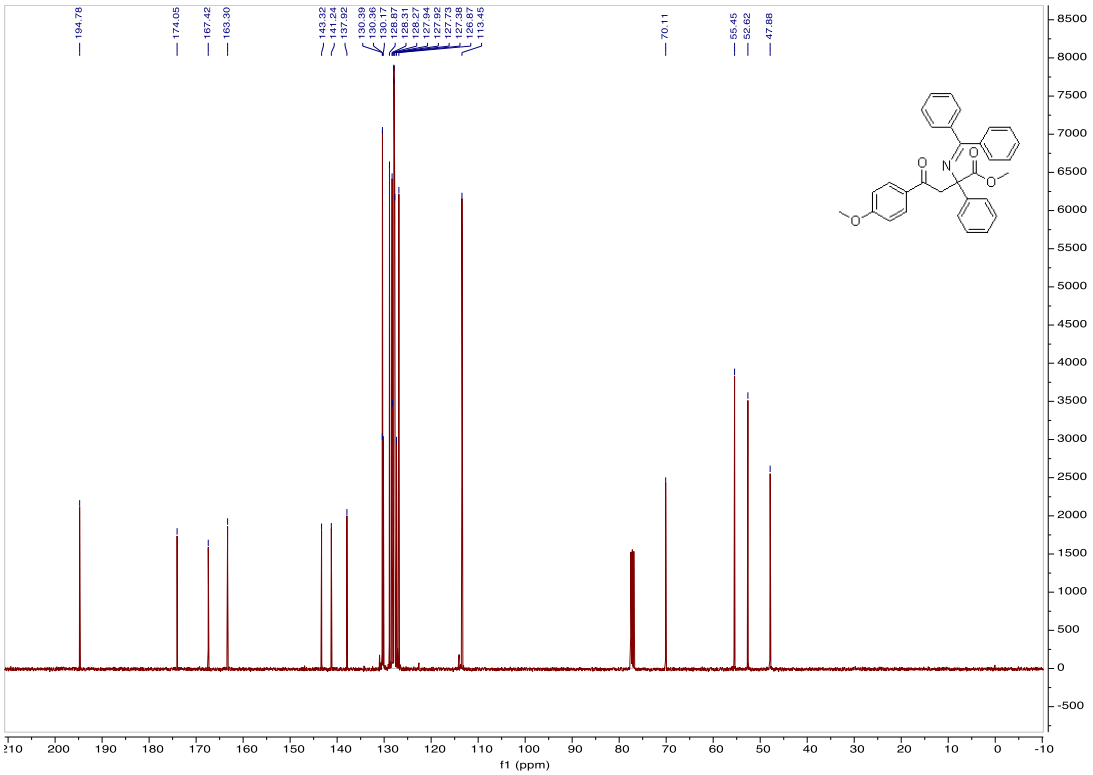




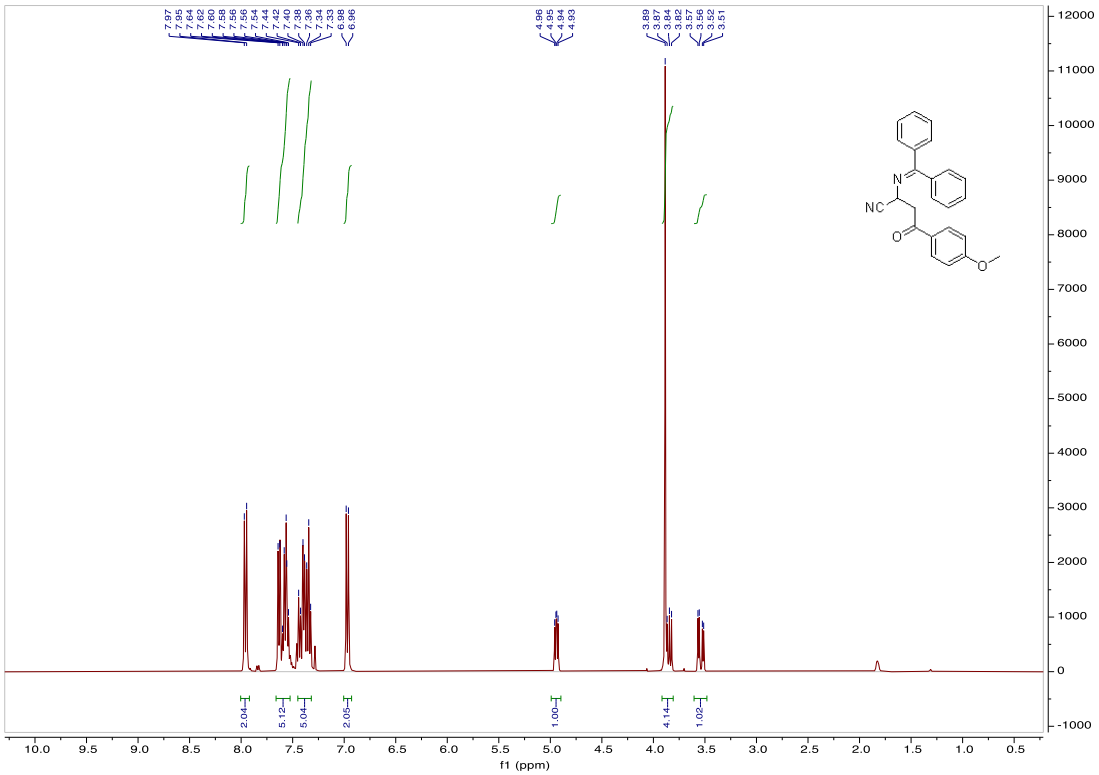

f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
0
1
2
3
4
5
6
7
8
9
N
O
O

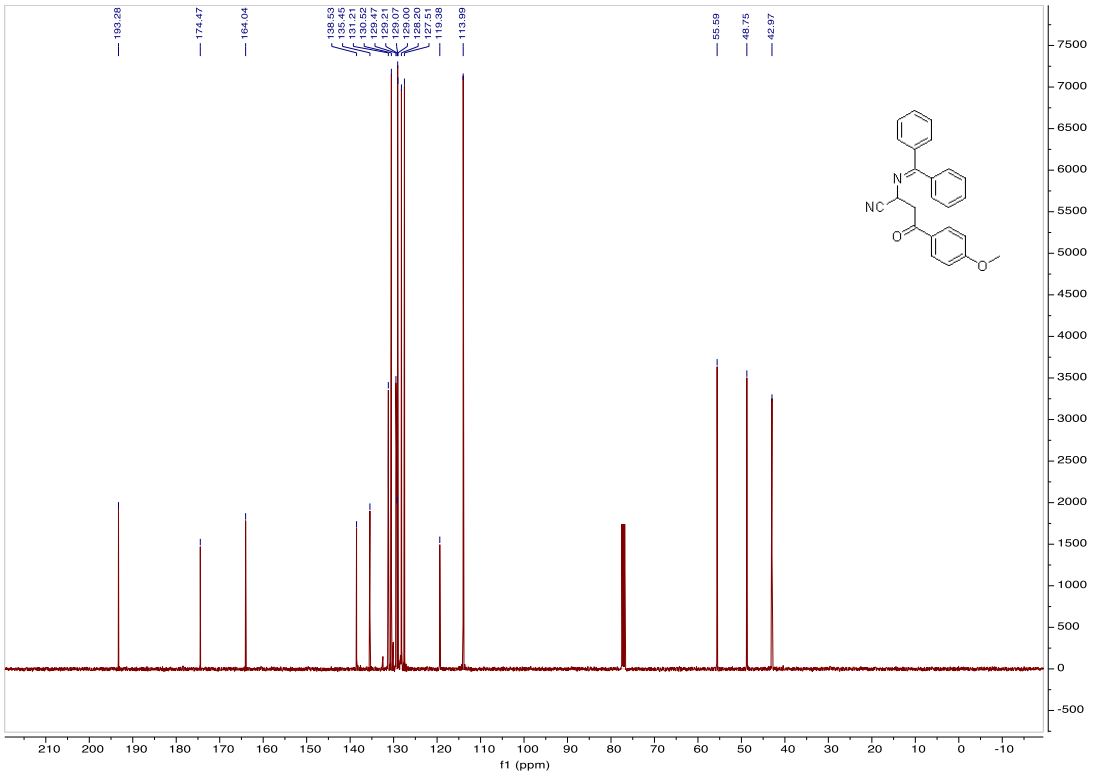
Methyl 2-((diphenylmethylene)amino)-4-(4-methoxyphenyl)-4-oxo-2-phenylbutanoate (5cw)



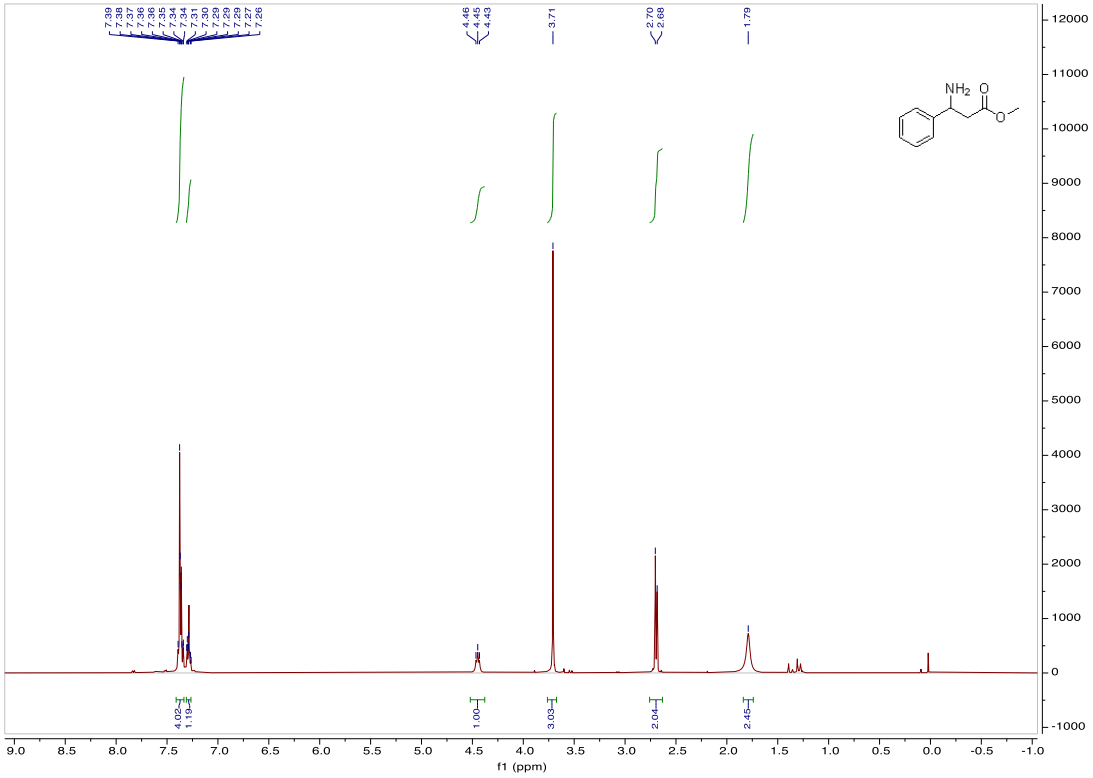


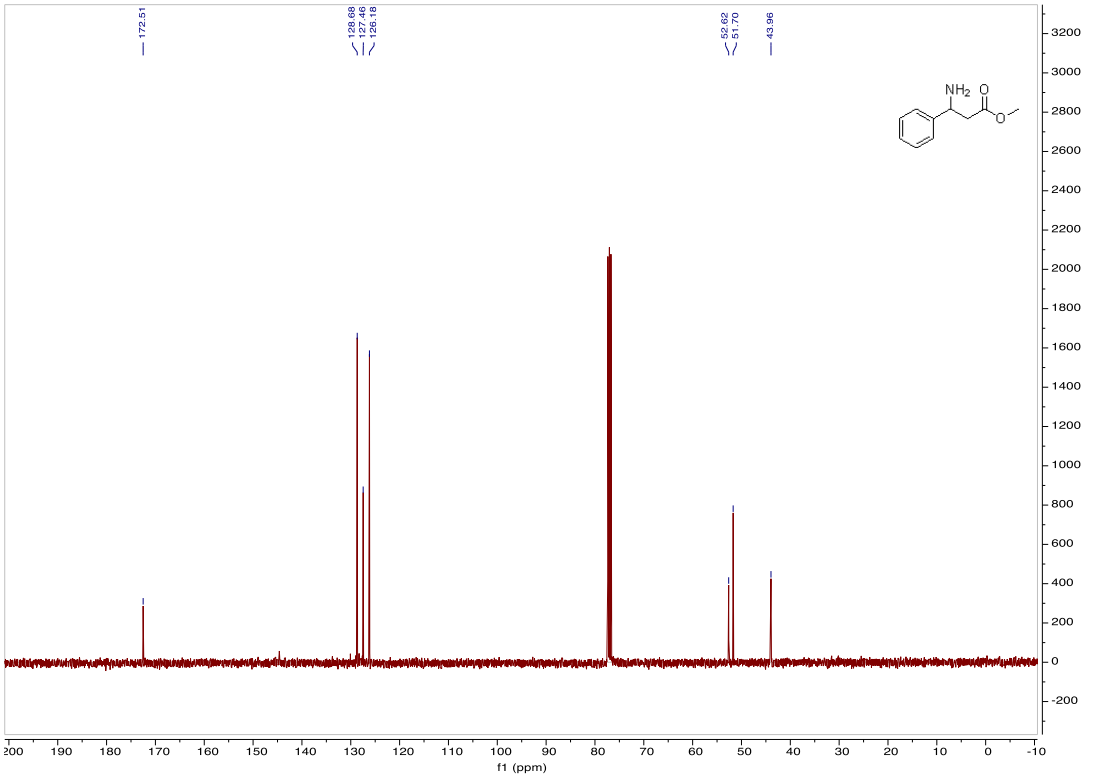
2-((diphenylmethylene)amino)-4-(4-methoxyphenyl)-4-oxobutanenitrile (5cx)



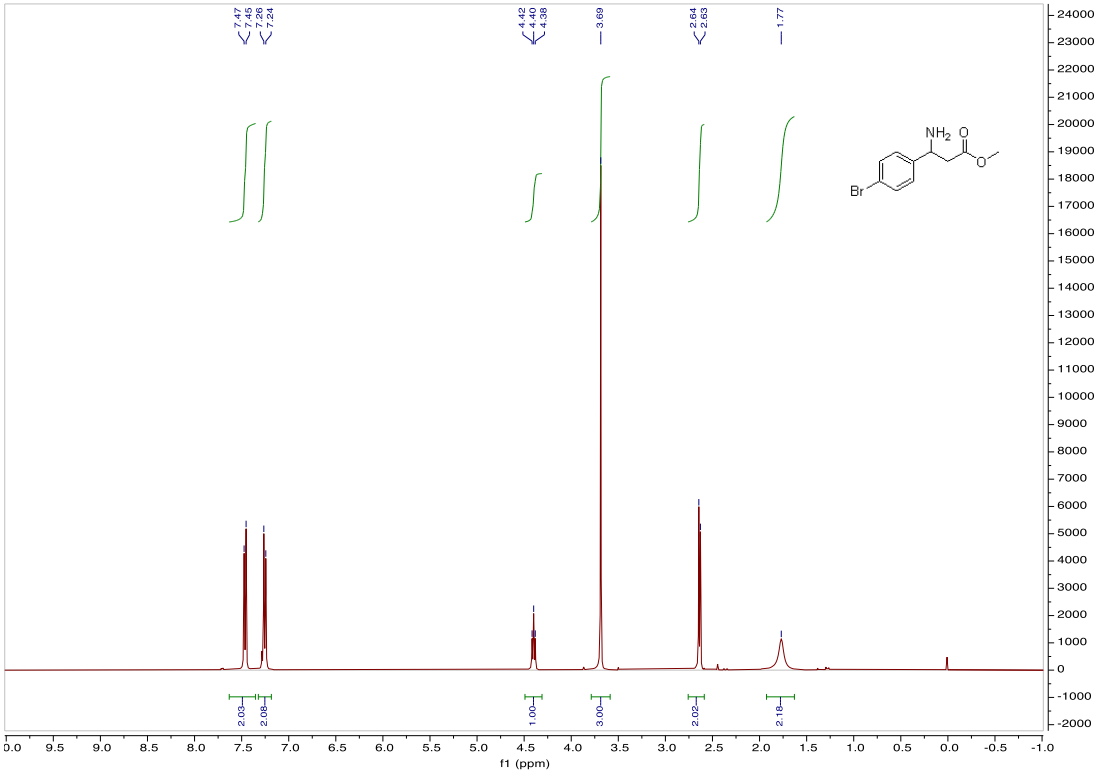


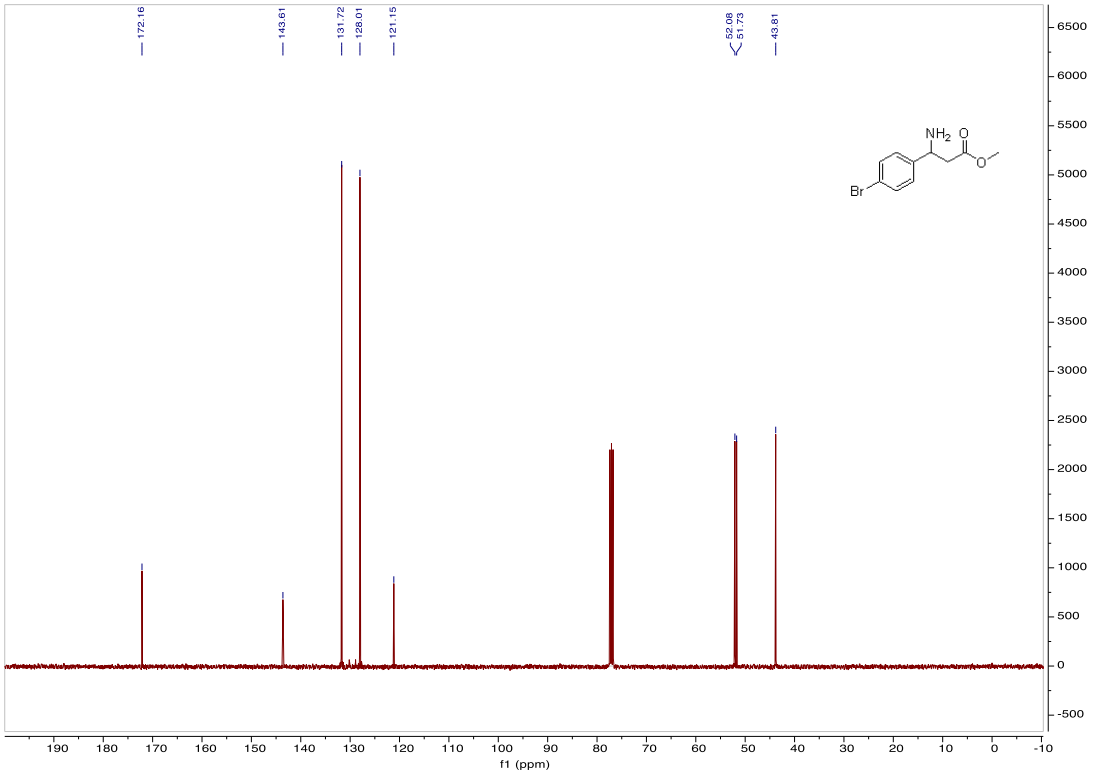
Methyl 3-amino-3-phenyl-propanoate (6)





Methyl 3-amino-3-(4-bromophenyl)propanoate (7)


7.47
7.45
7.26
7.24
4.42
4.40
4.38
3.69
2.64
2.63
1.77
NH2
O
O
Br
2.03
2.08
1.00
3.00
2.02
2.18
f1 (ppm)


172.16
143.61
131.72
128.01
121.15
52.08
51.73
43.81
NH2
O
O
Br
f1 (ppm)

Methyl 3-amino-3-(pyridin-2-yl)propanoate (8)