Supporting Information

for

A Modular construction of *N*-arylated Amino Acid Esters enabled by a Photoredox-catalyzed Multicomponent Reaction

Qing Li, Hanhan sun, Fengying Yan, Yuanyuan Zhao, Yicheng Zhang, Chao Zhou, Man-yi Han, Hongji Li, Xianwei Sui*

Key Laboratory of Green and Precise Synthetic Chemistry and Applications, Ministry of Education, School of Chemistry and Materials Science, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China.

*Corresponding authors' emails: suixw@chnu.edu.cn

Table of Contents

Materials and Methods

Nuclear magnetic resonance spectra were recorded on Bruker 400 and 600 MHz instruments internally referenced to tetramethylsilane (0.0 ppm) or residue of $CDCl_3$ (7.26 ppm for 1H, and 77.00 ppm for 13C) signal. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, c = complex. High-resolution mass spectra (HRMS) were conducted at Micromass Q-Tof instrument (ESI). All reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated. All reactions were performed under an inert atmosphere of dry argon in dried glassware, unless otherwise stated. Solvents were distilled using standard techniques. Acetonitrile and dichloromethane were distilled over calcium hydride under an atmosphere of argon. Room temperature reactions were performed between 25-30 ^{o}C. The reactions that require heating were put in an oil bath with a temperature monitor. Kessil lamp (440 nm) was used as the light source.

Experimental Data

Preparation of substrates

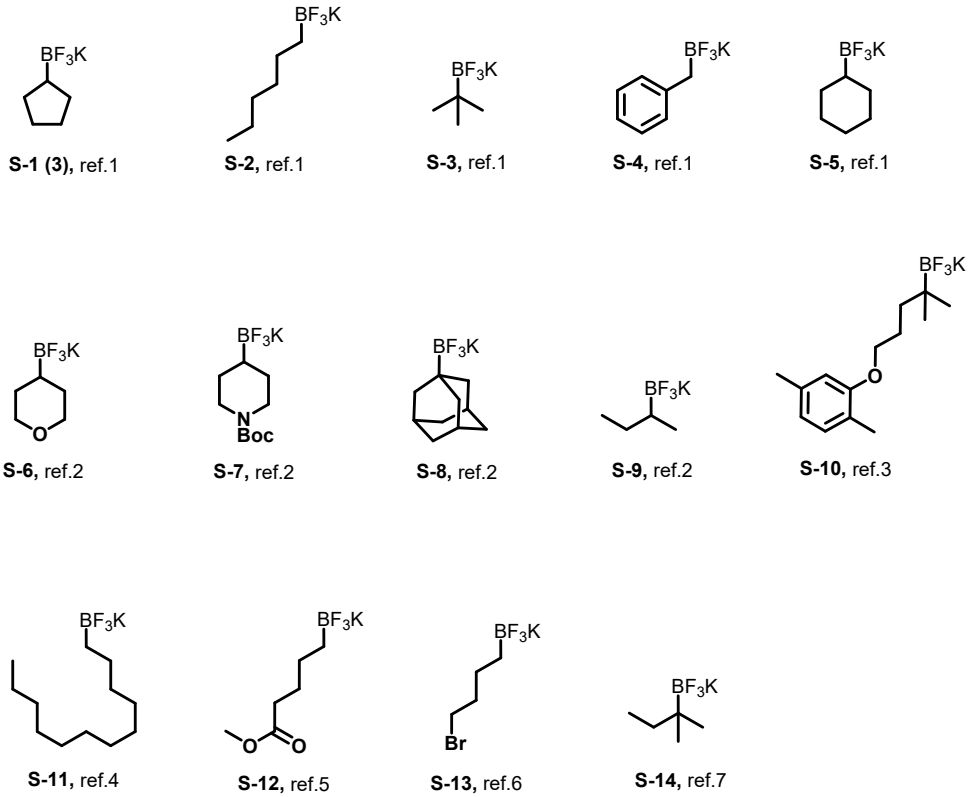
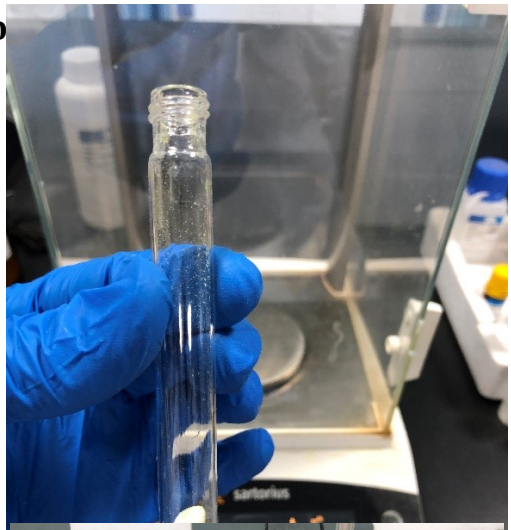
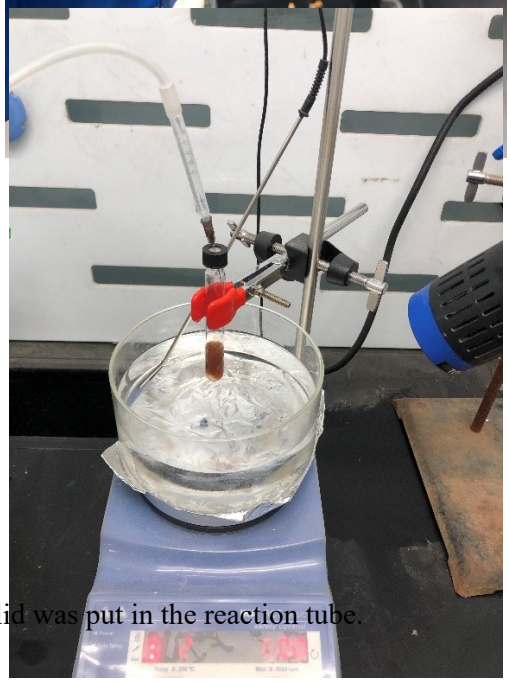


Figure S1. Syntheses of known substrates used in this study

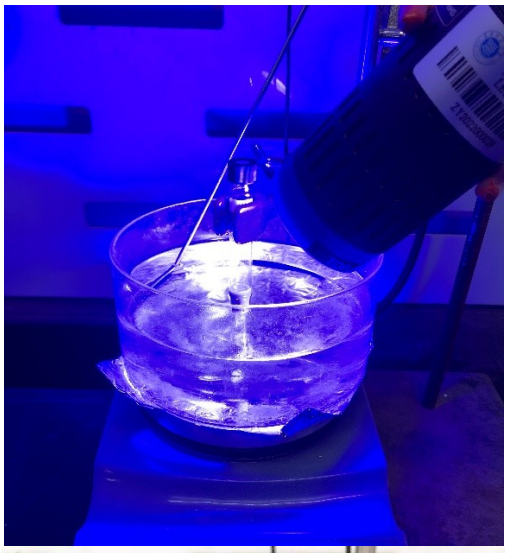
Grap



(**a**) Solid was put in the reaction tube.



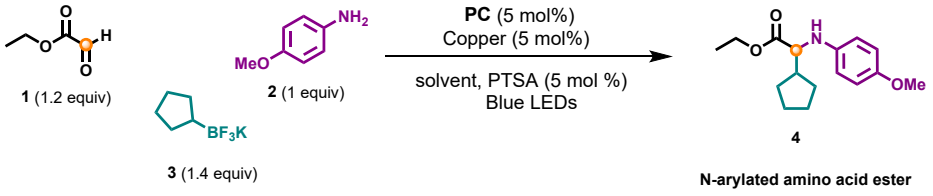
(**b**) Liquid was put in the tube under Ar.



(**c**) The reaction occurs under the LED.

(**d**) The reaction completes after 18 h.

Table S1 Optimization of the reaction condition[a]



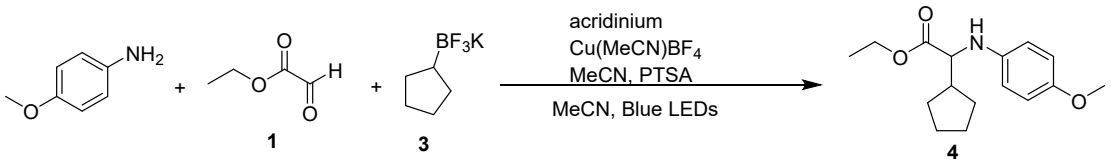
Entry	glyoxalate	Solvent	PC	Copper (5 mol%)	PTSA	Temp.	Time	yield
1	ethyl glyoxalate	DCM	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	18h	5%
2	ethyl glyoxalate	Dioxane	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	18h	25%
3	ethyl glyoxalate	DMF	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	18h	29%
4	ethyl glyoxalate	DMSO	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	18h	0%
5	**ethyl glyoxalate**	**CH_3CN**	**PC-I**	**$Cu(MeCN)BF_4$**	**5 mol%**	**rt**	**18h**	**87%**
6	ethyl glyoxalate	toluene	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	18h	14%
7	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	12h	61%
8	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	24h	82%
9	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)BF_4$	5 mol%	20 °C	18h	30%
10	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)BF_4$	5 mol%	35 °C	18h	68%
11	ethyl glyoxalate	CH_3CN	PC-I	$Cu(OTf)_2$	5 mol%	rt	18h	12%
12	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)PF_6$	5 mol%	rt	18h	43%
13	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)BF_4$	10 mol%	rt	18h	88%
14	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)BF_4$	20 mol%	rt	18h	79%
15	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)BF_4$	-	rt	18h	55%
16	ethyl glyoxalate	CH_3CN	PC-I	$Cu(MeCN)BF_4$ (10 mol%)	-	rt	18h	64%
17	ethyl glyoxalate	CH_3CN	PC-I	-	5 mol%	rt	18h	39%
18	ethyl glyoxalate	CH_3CN	PC-I	-	10 mol%	rt	18h	51%
19	ethyl glyoxalate	CH_3CN	PC-I	$NaBF_4$ (10 mol%)	5 mol%	rt	18h	40%
20	ethyl glyoxalate	CH_3CN	PC-I	$NaBF_4$ (20 mol%)	5 mol%	rt	18h	37%
21	benzaldehyde	CH_3CN	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	18h	13%[b]
22	cyclohexylformaldehyde	CH_3CN	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	18h	0%
23	hexyl aldehyde	CH_3CN	PC-I	$Cu(MeCN)BF_4$	5 mol%	rt	18h	0%

[a]Reaction condition: 2 (0.2 mmol), 1 (1.2 equiv), 3 (1.4 equiv), 9-Mesityl-10-methylacridinium perchlorate (PC-I) (5 mol%), $Cu(MeCN)BF_4$ (5 mol%) and PTSA in MeCN (2.0 mL) at room temperature under Ar and Blue LEDs irradiation. isolated yields. PTSA = *p*-tolylsulfonicacid. [b]corresponding product.

General Procedure for the Three-Components Coupling

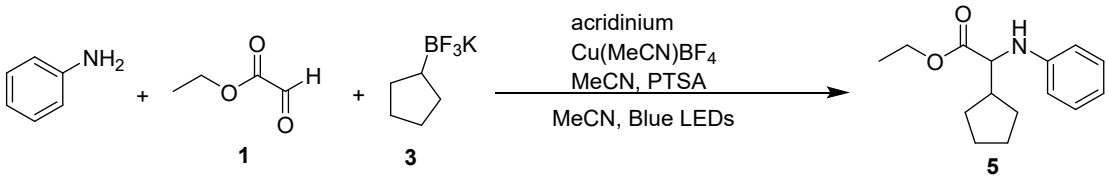
9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %), $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %), aniline (0.200 mmol, 1.0 equiv.) and alkyltrifluoroborate (0.28 mmol, 1.4 equiv.) were added to a Schlenk tube, and the mixture was degassed under vacuum and purged with argon for three times at room temperature. MeCN (2.0 ml) and aldehyde (0.240 mmol, 1.2 equiv.) were added and the mixture was stirred for 5 mins at room temperature before being stirred for 18 h above the LEDs at room temperature. The mixture was poured into water (20 mL) and extracted with ethyl acetate (3×15 ml). The organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered and concentrated. The reside was then purified by column chromatography on silica gel to give the three-components coupling product (see compound 4 for gram-scale synthesis).

Aniline Scopes of the Three-Components Coupling



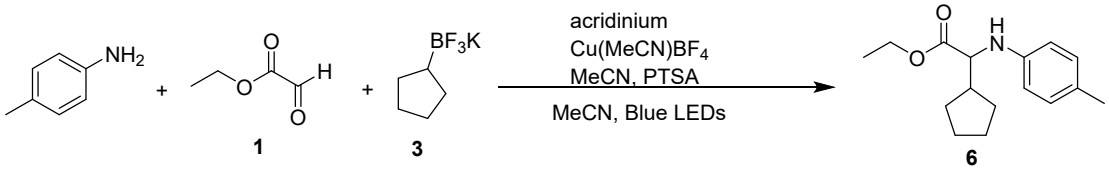
Compound **4** was synthesized following the **General Procedure for the three-components coupling.** The reaction of *p*-anisidine (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **4** (48.2 mg, 87%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.75 (d, *J* = 9.0 Hz, 2 H), 6.60 (d, *J* = 9.0 Hz, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 3.84 (s, 1 H), 3.77 (d, *J* = 8.4

Hz, 1 H), 3.73 (s, 3 H), 2.25-2.16 (m, 1 H), 1.88-1.79 (m, 1 H), 1.75-1.62 (m, 3 H), 1.61-1.54 (m, 2 H), 1.51-1.41 (m, 2 H), 1.22 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.4, 152.6, 141.5, 115.1, 114.8, 62.1, 60.7, 55.7, 43.2, 29.4, 29.0, 25.3, 25.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{16}H_{24}NO_3$ $[M+H]^+$ 278.1751, found 278.1750.



1 3 5

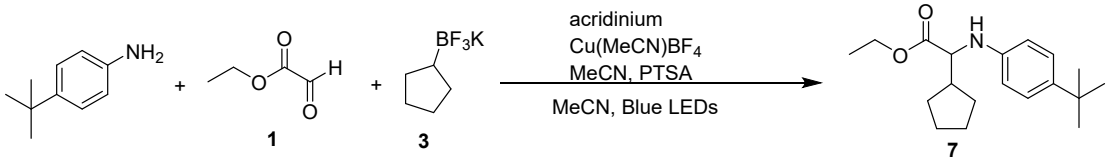
Compound **5** was synthesized following the **General Procedure for the three-components coupling.** The reaction of aniline (18.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and Cu(MeCN)BF_4 (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **5** (40.5 mg, 82%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.45, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.97 (t, *J* = 7.2 Hz, 2 H), 6.72 (t, *J* = 7.8 Hz, 1 H), 6.63 (d, *J* = 8.4 Hz, 2 H), 4.29-3.93 (c, 3 H), 3.86 (d, *J* = 7.8 Hz, 1 H), 2.32-2.18 (m, 1 H), 1.90-1.77 (m, 1 H), 1.76-1.61 (m, 3 H), 1.61-1.52 (m, 2 H), 1.51-1.41 (m, 2 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.2, 147.3, 129.2, 118.2, 113.5, 60.9, 60.8, 43.2, 29.3, 29.0, 25.3, 25.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{15}H_{22}NO_2$ $[M+H]^+$ 248.1645, found 248.1648.



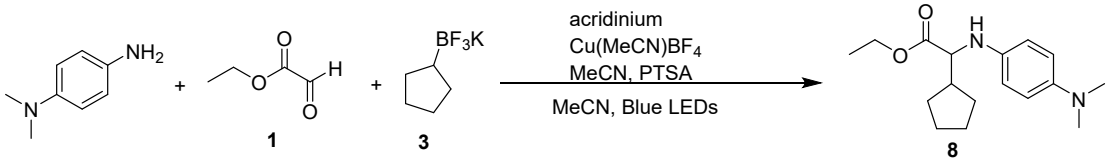
1 3 6

Compound **6** was synthesized following the **General Procedure for the three-components coupling.** The reaction of *p*-toluidine (21.4 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and Cu(MeCN)BF_4 (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **6** (46.1 mg, 88%) as a white gum after

purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.45, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.97 (d, *J* = 7.8 Hz, 2 H), 6.56 (d, *J* = 8.4 Hz, 2 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 4.09-3.86 (br, 1 H), 3.83 (d, *J* = 7.8 Hz, 1 H), 2.27-2.19 (c, 4 H), 1.87-1.79 (m, 1 H), 1.76-1.61 (m, 3 H), 1.61-1.52 (m, 2 H), 1.51-1.41 (m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.3, 145.0, 129.7, 127.4, 113.7, 61.2, 60.7, 43.2, 29.4, 29.0, 25.3, 25.1, 20.3, 14.2; **HRMS (ESI$^+$)** Calcd for $C_{16}H_{24}NO_2$ $[M+H]^+$ 262.1802, found 262.1795.

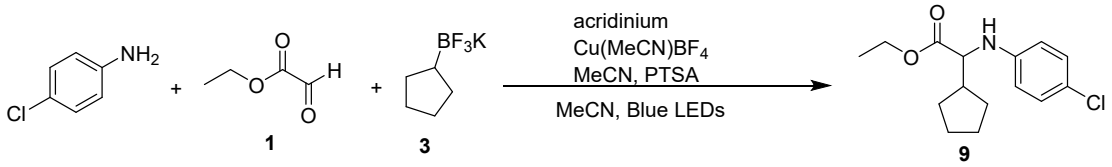


Compound **7** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 4-*tert*-Butylaniline (29.8 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **7** (52.3 mg, 86%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.45, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.19 (d, *J* = 8.4 Hz, 2 H), 6.59 (d, *J* = 9.0 Hz, 2 H), 4.16 (q, *J* = 6.6 Hz, 2 H), 4.12-3.91 (br, 1 H), 3.84 (d, *J* = 7.8 Hz, 1 H), 2.29-2.19 (m, 1 H), 1.87-1.77 (m, 1 H), 1.76-1.61 (m, 3 H), 1.61-1.52 (m, 2 H), 1.51-1.40 (m, 2 H), 1.27 (s, 9 H), 1.24 (t, *J* = 6.6 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.4, 144.9, 140.9, 126.0, 113.1, 61.0, 60.7, 43.2, 33.8, 31.4, 29.3, 29.0, 25.3, 25.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{19}H_{30}NO_2$ $[M+H]^+$ 304.2271, found 304.2258.

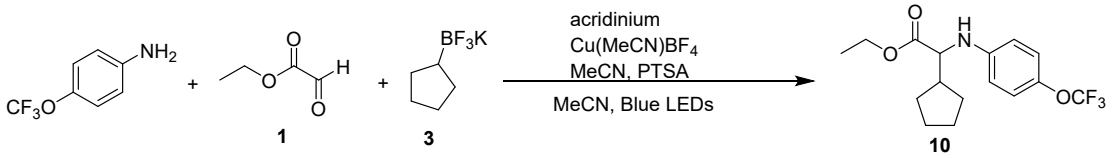


Compound **8** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 4-(dimethylamino)benzenamine (27.2 mg,

0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **8** (39.6 mg, 68%) as a white gum after purification via silica gel column chromatography with 3% ethyl acetate/hexanes (R_f = 0.5, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.70 (d, *J* = 8.4 Hz, 2 H), 6.62 (d, *J* = 7.8 Hz, 2 H), 4.14 (q, *J* = 6.6 Hz, 2 H), 3.76 (s, 2 H), 2.81 (s, 6 H), 2.25-2.16 (m, 1 H), 1.88-1.78 (m, 1 H), 1.75-1.60 (m, 3 H), 1.60-1.52 (m, 2 H), 1.51-1.40 (m, 2 H), 1.22 (t, *J* = 6.6 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.6, 144.6, 139.6, 115.6, 115.3, 62.2, 60.6, 43.2, 42.1, 29.4, 29.0, 25.4, 25.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{17}H_{27}N_2O_2$ $[M+H]^+$ 291.2067, found 291.2071.

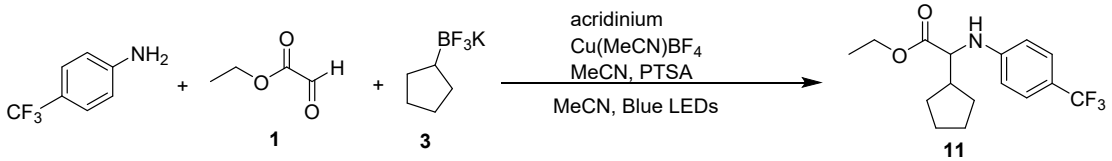


Compound **9** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 4-chloroaniline (25.5 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **9** (53.0 mg, 94%) as a white gum after purification via silica gel column chromatography with 3% ethyl acetate/hexanes (R_f = 0.5, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.10 (d, *J* = 9.0 Hz, 2 H), 6.55 (d, *J* = 9.0 Hz, 2 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 4.10 (s, 1 H), 3.80 (d, *J* = 7.8 Hz, 1 H), 2.28-2.18 (m, 1 H), 1.86-1.78 (m, 1 H), 1.76-1.62 (m, 3 H), 1.61-1.54 (m, 2 H), 1.49-1.39 (m, 2 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.8, 145.9, 129.1, 122.8, 114.6, 61.0, 60.9, 43.1, 29.3, 29.0, 25.3, 25.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{15}H_{21}ClNO_2$ $[M+H]^+$ 282.1255, found 282.1234.



1 3 10

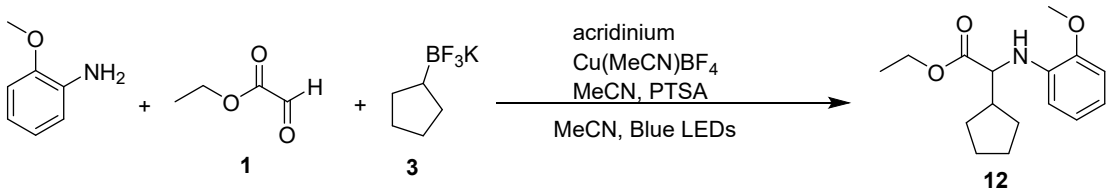
Compound **10** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 4-(trifluoromethoxy)aniline (35.4 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **10** (53.8 mg, 81%) as a white gum after purification via silica gel column chromatography with 6% ethyl acetate/hexanes (R_f = 0.3, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.01 (d, *J* = 8.4 Hz, 2 H), 6.58 (d, *J* = 9.0 Hz, 2 H), 4.43-3.97 (c, 3 H), 3.81 (d, *J* = 7.8 Hz, 1 H), 2.32-2.17 (m, 1 H), 1.90-1.78 (m, 1 H), 1.76-1.62 (m, 3 H), 1.62-1.53 (m, 2 H), 1.50-1.39 (m, 2 H), 1.24 (t, *J* = 6.6 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.8, 146.1, 141.0, 122.4, 113.8, 61.0, 60.9, 43.1, 29.3, 29.0, 25.3, 25.1, 14.2; **19F NMR** (565 MHz, CDCl3) δ -58.5; **HRMS (ESI$^+$)** Calcd for $C_{16}H_{21}F_3NO_3$ $[M+H]^+$ 332.1468, found 332.1474.



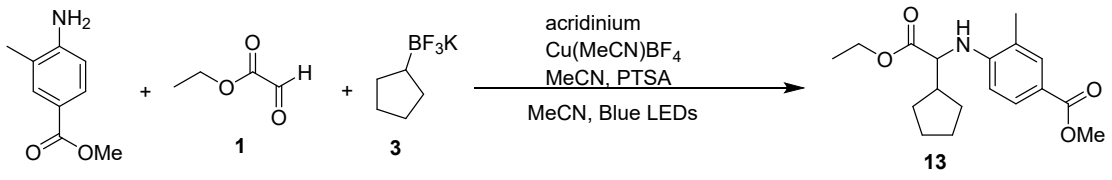
1 3 11

Compound **11** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 4-(trifluoromethyl)aniline (32.2 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **11** (49.8 mg, 75%) as a white gum after purification via silica gel column chromatography with 6% ethyl acetate/hexanes (R_f = 0.3, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.39 (d, *J* = 8.4 Hz, 2 H), 6.63 (d, *J* = 9.0 Hz, 2 H), 4.42 (d, *J* = 9.0 Hz, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 3.90 (t, *J* = 7.8 Hz, 1 H), 2.33-2.21 (m, 1 H), 1.88-1.78 (m, 1

H), 1.78-1.70 (m, 1 H), 1.70-1.62 (m, 2 H), 1.62-1.55 (m, 2 H), 1.49-1.39 (m, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.4, 149.8, 126.6 (q, *J* = 3.0 Hz), 124.8 (q, *J* = 270.3 Hz), 119.7 (q, *J* = 31.7 Hz), 112.5, 61.1, 60.2, 43.1, 29.2, 29.0, 25.3, 25.0, 14.2; **19F NMR** (565 MHz, CDCl3) δ -61.2; **HRMS (ESI$^+$)** Calcd for $C_{16}H_{21}F_3NO_3$ $[M+H]^+$ 332.1468, found 332.1465.

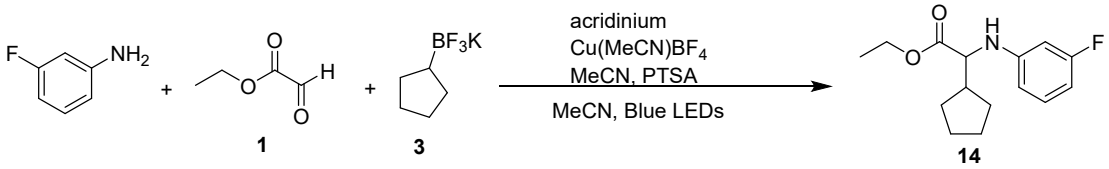


Compound **12** was synthesized following the **General Procedure for the three-components coupling.** The reaction of *o*-anisidine (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **12** (38.3 mg, 69%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.82 (t, *J* = 7.8 Hz, 1 H), 6.77 (d, *J* = 7.2 Hz, 1 H), 6.67 (t, *J* = 7.8 Hz, 1 H), 6.57 (d, *J* = 7.8 Hz, 1 H), 4.88-4.54 (br, 1 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.90-3.81 (c, 4 H), 2.35-2.25 (m, 1 H), 1.92-1.83 (m, 1 H), 1.78-1.70 (m, 1 H), 1.70-1.62 (m, 2 H), 1.62-1.53 (m, 2 H), 1.52-1.43 (m, 2 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.2, 147.0, 137.3, 121.1, 117.2, 110.3, 109.7, 60.7, 60.6, 55.5, 43.1, 29.5, 29.1, 25.3, 25.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{16}H_{24}NO_3$ $[M+H]^+$ 278.1751, found 278.1752.



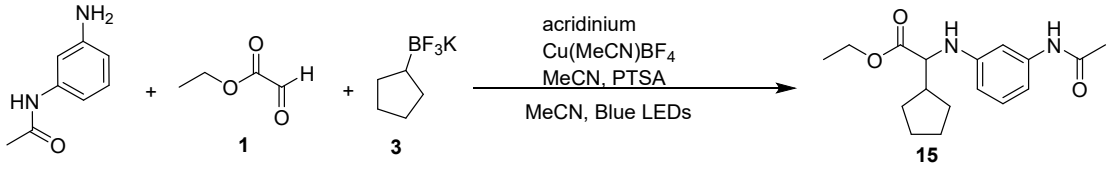
Compound **13** was synthesized following the **General Procedure for the three-components coupling.** The reaction of methyl 4-amino-3-methylbenzoate (33.0 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg,

0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and Cu(MeCN)BF_4 (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **13** (45.4 mg, 71%) as a white gum after purification via silica gel column chromatography with 6% ethyl acetate/hexanes (R_f = 0.3, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.36 (dd, *J* = 1.8, 7.8 Hz, 1 H), 7.25 (d, *J* = 1.8 Hz, 1 H), 7.10 (d, *J* = 7.8 Hz, 1 H), 4.25-4.13 (m, 2 H), 4.12-4.03 (br, 1 H), 4.01 (d, *J* = 7.8 Hz, 1 H), 3.87 (s, 3 H), 2.38-2.27 (m, 1 H), 2.24 (s, 3 H), 1.90-1.81 (m, 1 H), 1.80-1.73 (m, 1 H), 1.71-1.64 (m, 2 H), 1.62-1.58 (m, 2 H), 1.52-1.44 (m, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.1, 167.5, 145.4, 130.2, 129.0, 128.1, 119.3, 111.1, 61.0, 60.4, 51.9, 43.2, 29.3, 29.0, 25.3, 25.1, 17.7, 14.2; **HRMS (ESI$^+$)** Calcd for $C_{18}H_{26}NO_4$ $[M+H]^+$ 320.1856, found 320.1859.

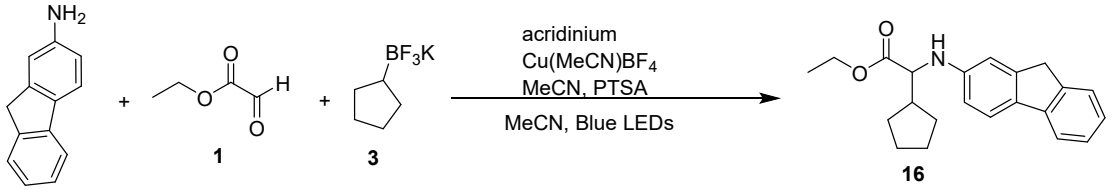


1 3 14

Compound **14** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 3-fluoroaniline (22.2 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and Cu(MeCN)BF_4 (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **14** (44.7 mg, 84%) as a white gum after purification via silica gel column chromatography with 6% ethyl acetate/hexanes (R_f = 0.3, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.08 (q, *J* = 8.4 Hz, 1 H), 6.44-6.36 (m, 2 H), 6.32 (d, *J* = 12.0 Hz, 1 H), 4.27-4.14 (c, 3 H), 3.82 (t, *J* = 8.4 Hz, 1 H), 2.30-2.18 (m, 1 H), 1.86-1.78 (m, 1 H), 1.77-1.63 (m, 3 H), 1.61-1.56 (m, 2 H), 1.49-1.39 (m, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.8, 164.0 (d, *J* = 243.1 Hz), 149.1 (d, *J* = 10.6 Hz), 130.3 (d, *J* = 10.6 Hz), 109.2, 104.6 (d, *J* = 21.1 Hz), 100.2 (d, *J* = 25.7 Hz); **19F NMR** (565 MHz, CDCl3) δ -112.7; **HRMS (ESI$^+$)** Calcd for $C_{15}H_{21}FNO_2$ $[M+H]^+$ 266.1551, found 266.1556.

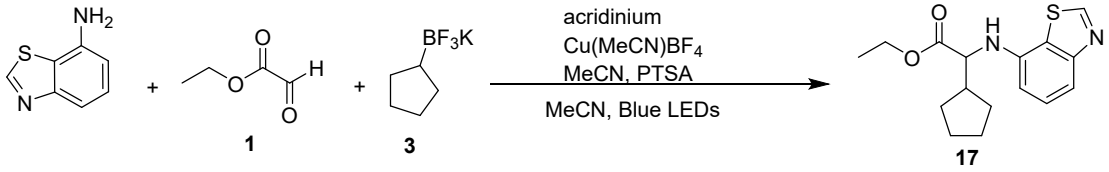


Compound **15** was synthesized following the **General Procedure for the three-components coupling.** The reaction of *N*-(3-aminophenyl)acetamide (30.0 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **15** (42.7 mg, 70%) as a white gum after purification via silica gel column chromatography with 15% ethyl acetate/hexanes (R_f = 0.3, 20% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.14-7.00 (c, 3 H), 6.67 (d, *J* = 7.8 Hz, 1 H), 6.37 (d, *J* = 8.4 Hz, 1 H), 4.22-4.14 (c, 3 H), 3.80 (t, *J* = 7.8 Hz, 1 H), 2.17-2.10 (m, 1 H), 2.14 (s, 3 H), 1.86-1.77 (m, 1 H), 1.76-1.69 (m, 1 H), 1.69-1.63 (m, 2 H), 1.59-1.53 (m, 2 H), 1.48-1.41 (m, 2 H), 1.24 (t, *J* = 9.0 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.0, 168.1, 148.1, 138.9, 129.7, 109.3, 109.2, 104.9, 60.9, 60.7, 43.1, 29.3, 29.0, 25.3, 25.1, 24.8, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{17}H_{25}N_2O_3$ $[M+H]^+$ 305.1860, found 305.1861.



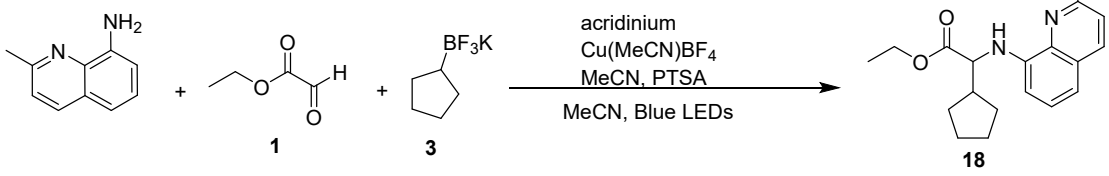
Compound **16** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 9*H*-fluoren-2-amine (36.2 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **16** (58.5 mg, 87%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.45, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.61 (d, *J* = 7.8 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 1 H), 7.45 (d, *J* = 7.2 Hz, 1 H), 7.30 (t, *J* = 7.8 Hz, 1 H),

7.17 (t, *J* = 7.2 Hz, 1 H), 6.84 (s, 1 H), 6.67 (d, *J* = 8.4 Hz, 1 H), 4.34-4.03 (c, 3 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 3.80 (s, 2 H), 2.34-2.22 (m, 1 H), 1.92-1.82 (m, 1 H), 1.80-1.72 (m, 1 H), 1.72-1.64 (m, 2 H), 1.64-1.55 (m, 2 H), 1.54-1.45 (m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.2, 146.8, 145.1, 142.2, 142.1, 132.7, 126.6, 124.9, 124.7, 120.6, 118.5, 112.6, 110.1, 61.3, 60.8, 43.2, 36.9, 29.4, 29.1, 25.3, 25.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{22}H_{26}NO_2$ $[M+H]^+$ 336.1958, found 336.1959.



1 3 17

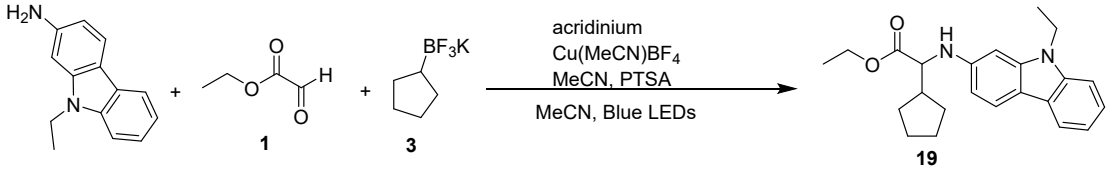
Compound **17** was synthesized following the **General Procedure for the three-components coupling.** The reaction of benzo[*d*]thiazol-7-amine (30.0 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **17** (47.0 mg, 77%) as a white gum after purification via silica gel column chromatography with 5.5% ethyl acetate/hexanes (R_f = 0.5, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 8.90 (s, 1 H), 7.68 (d, *J* = 8.4 Hz, 1 H), 7.31 (d, *J* = 2.4 Hz, 1 H), 6.84 (dd, *J* = 2.4, 9.0 Hz, 1 H), 4.44-4.22 (br, 1 H), 4.22-4.13 (m, 2 H), 3.96 (d, *J* = 7.8 Hz, 1 H), 2.34-2.25 (m, 1 H), 1.91-1.82 (m, 1 H), 1.80-1.73 (m, 1 H), 1.73-1.64 (m, 2 H), 1.64-1.59 (m, 2 H), 1.53-1.45 (m, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.0, 154.4, 146.7, 122.0, 115.3, 105.5, 61.0, 43.2, 29.4, 29.1, 25.3, 25.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{16}H_{21}N_2O_2S$ $[M+H]^+$ 305.1318, found 305.1314.



1 3 18

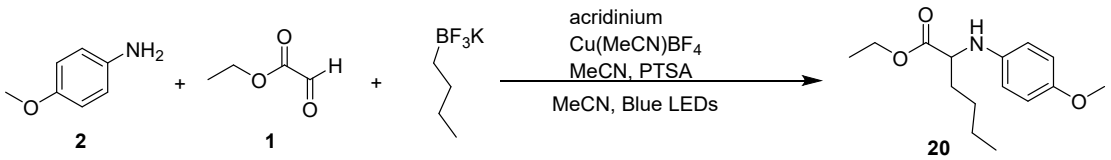
Compound **18** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 2-methylquinolin-8-amine (31.6 mg, 0.200

mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **18** (42.0 mg, 67%) as a white gum after purification via silica gel column chromatography with 5.5% ethyl acetate/hexanes (R_f = 0.5, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.92 (d, *J* = 7.8 Hz, 1 H), 7.30-7.19 (c, 1 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 6.68 (d, *J* = 8.4 Hz, 1 H), 6.63 (d, *J* = 7.2 Hz, 1 H), 2.71 (s, 3 H), 2.56-2.44 (m, 1 H), 2.04-1.93 (m, 1 H), 1.86-1.78 (m, 1 H), 1.77-1.67 (m, 2 H), 1.65-1.53 (m, 4 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.0, 155.8, 143.5, 137.6, 135.9, 126.6, 126.4, 122.2, 114.6, 105.3, 60.9, 60.7, 43.0, 29.6, 29.3, 25.4, 25.2, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{19}H_{25}N_2O_2$ $[M+H]^+$ 313.1911, found 313.1909.



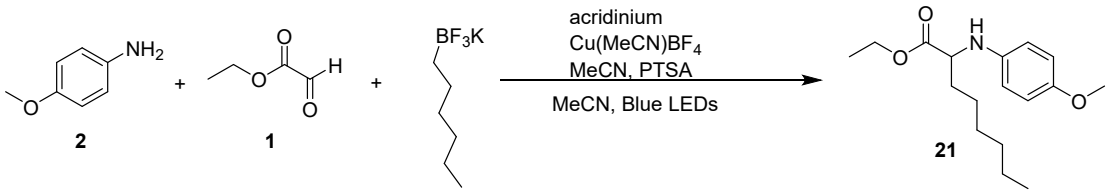
Compound **19** was synthesized following the **General Procedure for the three-components coupling.** The reaction of 9-ethyl-9*H*-carbazol-2-amine (42.0 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **19** (65.0 mg, 89%) as a white gum after purification via silica gel column chromatography with 6% ethyl acetate/hexanes (R_f = 0.35, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 8.10 (d, *J* = 7.8 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.38 (s, 1 H), 7.34 (d, *J* = 8.4 Hz, 1 H), 7.24 (d, *J* = 8.4 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 6.92 (d, *J* = 7.8 Hz, 1 H), 4.30 (q, *J* = 7.2 Hz, 2 H), 4.21-4.11 (m, 2 H), 4.11-3.99 (br, 1 H), 3.97 (d, *J* = 7.8 Hz, 1 H), 2.35-2.25 (m, 1 H), 1.97-1.88 (m, 1 H), 1.84-1.75 (m, 1 H), 1.75-1.66 (m, 2 H), 1.66-1.52 (m, 4 H), 1.39 (t, *J* = 7.8 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.8, 140.7, 140.3, 134.4, 125.3, 123.5, 122.6, 120.3, 117.9,

115.3, 109.1, 108.3, 104.6, 62.8, 60.6, 43.3, 37.5, 29.6, 29.1, 25.4, 25.2, 14.3, 13.8; **HRMS (ESI$^+$)** Calcd for $C_{23}H_{29}N_2O_2$ $[M+H]^+$ 365.2224, found 365.2219.



2 **1** **20**

Compound **20** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], butyltrifluoroborate (32.8 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **20** (52.7 mg, 99%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.76 (d, *J* = 9.0 Hz, 2 H), 6.60 (d, *J* = 9.0 Hz, 2 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.95 (t, *J* = 6.6 Hz, 1 H), 3.73 (s, 3 H), 1.85-1.69 (m, 2 H), 1.46-1.31 (m, 4 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 0.91 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.6, 152.6, 141.1, 115.1, 114.8, 60.8, 57.8, 55.7, 32.9, 27.8, 22.4, 14.2, 13.9; **HRMS (ESI$^+$)** Calcd for $C_{15}H_{24}NO_3$ $[M+H]^+$ 266.1751, found 266.1750.

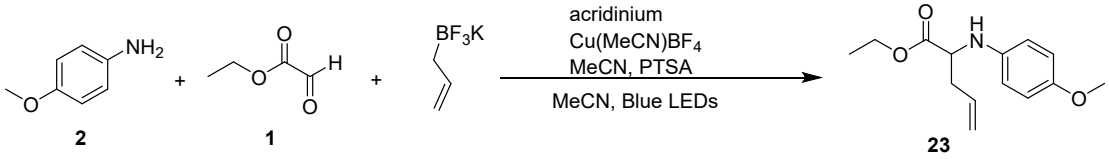


2 **1** **21**

Compound **21** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], hexyltrifluoroborate (53.8 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **21** (50.0 mg, 85%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.76 (d, *J* = 8.4 Hz, 2 H), 6.60 (d, *J* = 8.4 Hz, 2 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.95 (t, *J* = 6.6 Hz, 1 H),

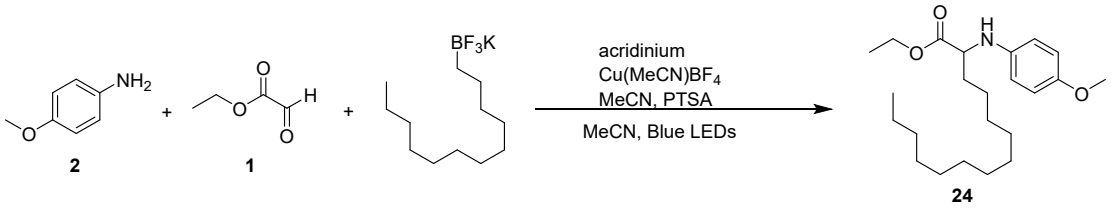
3.84 (s, 1 H), 3.73 (s, 3 H), 1.86-1.68 (m, 2 H), 1.49-1.37 (m, 2 H), 1.37-1.25 (m, 6 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 0.88 (t, *J* = 6.6 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.6, 152.6, 141.1, 115.0, 114.8, 60.8, 57.8, 55.7, 33.2, 31.6, 29.0, 25.6, 22.5, 14.2, 14.0; **HRMS (ESI$^+$)** Calcd for $C_{17}H_{28}NO_3$ $[M+H]^+$ 294.2064, found 294.2065.

Compound **22** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], (4-bromobutyl)trifluoroborate (67.8 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **22** (49.5 mg, 72%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.90 (d, *J* = 9.0 Hz, 2 H), 6.81 (d, *J* = 9.0 Hz, 2 H), 4.24 (t, *J* = 5.4 Hz, 1 H), 4.13-3.99 (m, 2 H), 3.75 (s, 3 H), 3.43-3.34 (m, 1 H), 3.20-3.11 (m, 1 H), 2.14-2.04 (m, 1 H), 2.01-1.91 (m, 1 H), 1.86-1.77 (m, 1 H), 1.70-1.55 (m, 2 H), 1.55-1.45 (m, 1 H), 1.13 (t, *J* = 6.6 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.2, 153.6, 145.5, 118.8, 114.3, 60.6, 60.3, 55.5, 48.1, 28.8, 25.6, 21.1, 14.2; **HRMS (ESI$^+$)** Calcd for $C_{15}H_{23}BrNO_3$ $[M+H]^+$ 344.0856, found 344.0855.



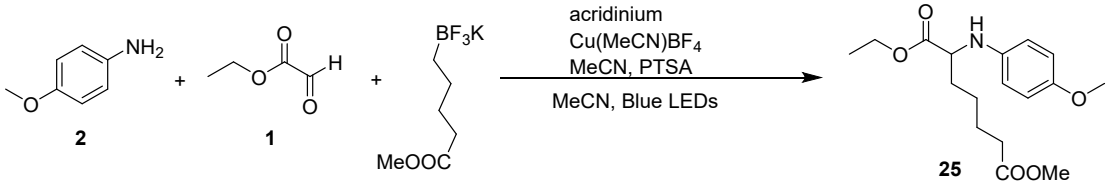
Compound **23** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], allyltrifluoroborate (41.4 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **23** (43.0 mg, 86%) as a white gum

after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.76 (d, *J* = 9.0 Hz, 2 H), 6.60 (d, *J* = 9.0 Hz, 2 H), 5.86-5.74 (m, 1 H), 5.24-5.11 (c, 2 H), 4.28-4.12 (m, 2 H), 4.05 (t, *J* = 6.6 Hz, 1 H), 4.00-3.82 (br, 1 H), 3.74 (s, 3 H), 2.67-2.49 (m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.6, 152.7, 140.7, 132.9, 118.8, 115.2, 114.8, 61.0, 57.2, 55.7, 37.2, 14.2; **HRMS (ESI$^+$)** Calcd for $C_{14}H_{20}NO_3$ $[M+H]^+$ 250.1438, found 250.1436.



2 1 24

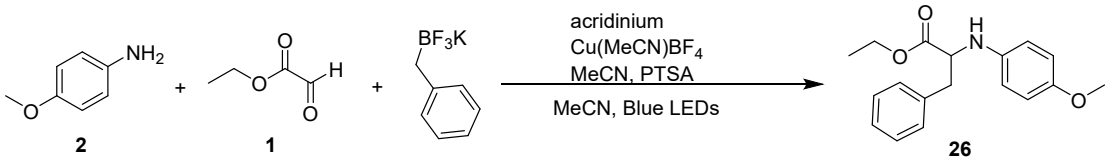
Compound **24** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], dodecyltrifluoroborate (77.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **24** (47.7 mg, 63%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.76 (d, *J* = 9.0 Hz, 2 H), 6.60 (d, *J* = 9.0 Hz, 2 H), 4.22-4.12 (m, 2 H), 3.95 (t, *J* = 6.6 Hz, 1 H), 3.91-3.77 (br, 1 H), 3.73 (s, 3 H), 1.86-1.68 (m, 2 H), 1.45-1.37 (m, 2 H), 1.33-1.21 (m, 21 H), 0.88 (t, *J* = 6.6 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.6, 152.7, 141.1, 115.1, 114.8, 60.8, 57.9, 55.7, 33.2, 31.9, 30.0, 29.6, 29.5, 29.4, 29.3, 25.6, 22.7, 14.2, 14.1; **HRMS (ESI$^+$)** Calcd for $C_{23}H_{40}NO_3$ $[M+H]^+$ 378.3003, found 378.3009.



2 1 25

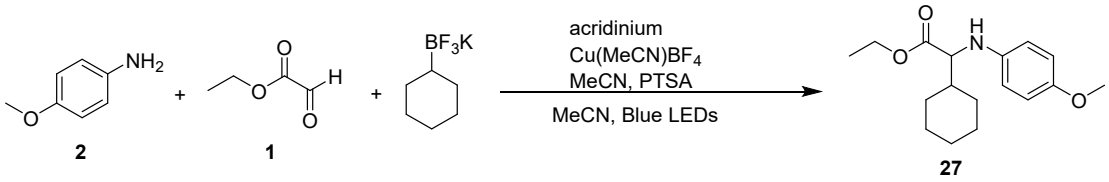
Compound **25** was synthesized following the **General Procedure for the three-**

components coupling. The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], methyl 5-(trifluoroborate)pentanoate (62.2 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **25** (40.2 mg, 67%) as a white gum after purification via silica gel column chromatography with 7% ethyl acetate/hexanes (R_f = 0.3, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.76 (d, *J* = 9.0 Hz, 2 H), 6.59 (d, *J* = 9.0 Hz, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 3.95 (t, *J* = 6.0 Hz, 1 H), 3.91-3.76 (br, 1 H), 3.73 (s, 3 H), 3.66 (s, 3 H), 2.32 (t, *J* = 7.2 Hz, 2 H), 1.87-1.78 (m, 1 H), 1.77-1.70 (m, 1 H), 1.70-1.63 (m, 2 H), 1.53-1.41 (m, 2 H), 1.22 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 174.3, 173.8, 152.7, 141.0, 115.1, 114.8, 60.9, 57.7, 55.7, 51.5, 33.8, 32.8, 25.2, 24.6, 14.2; **HRMS (ESI$^+$)** Calcd for $C_{17}H_{26}NO_5$ $[M+H]^+$ 324.1805, found 324.1809.



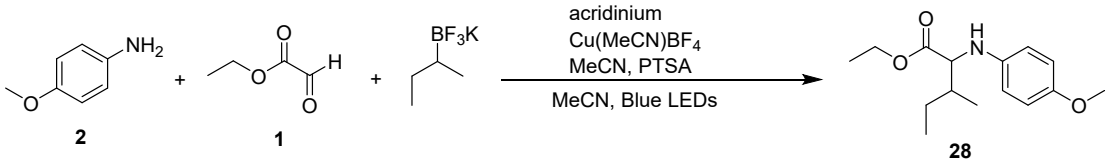
Compound **26** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], benzyltrifluoroborate (55.4 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **26** (46.2 mg, 77%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.30 (t, *J* = 7.2 Hz, 2 H), 7.24 (t, *J* = 7.2 Hz, 1 H), 7.19 (d, *J* = 6.6 Hz, 2 H), 6.76 (d, *J* = 9.0 Hz, 2 H), 6.58 (d, *J* = 9.0 Hz, 2 H), 4.26 (t, *J* = 6.6 Hz, 1 H), 4.17-4.06 (m, 2 H), 4.03-3.81 (br, 1 H), 3.74 (s, 3 H), 3.11 (t, *J* = 6.6 Hz, 2 H), 1.15 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.4, 152.8, 140.5, 136.5, 129.3, 128.4, 126.9, 115.2, 114.8, 61.0, 59.0, 55.7, 38.9, 14.1; **HRMS (ESI$^+$)** Calcd for $C_{18}H_{22}NO_3$ $[M+H]^+$

300.1594, found 300.1594.



2 1 27

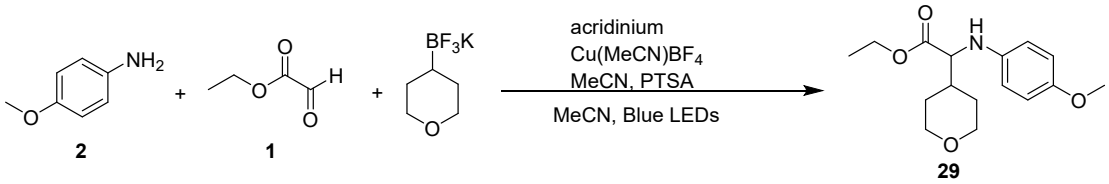
Compound **27** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], cyclohexyltrifluoroborate (53.2 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **27** (50.8 mg, 87%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.75 (d, *J* = 9.0 Hz, 2 H), 6.60 (d, *J* = 8.4 Hz, 2 H), 4.18-4.12 (m, 2 H), 4.03-3.81 (br, 1 H), 3.76 (d, *J* = 6.0 Hz, 1 H), 3.73 (s, 3 H), 1.90-1.83 (m, 1 H), 1.81-1.75 (m, 2 H), 1.75-1.70 (m, 1 H), 1.70-1.64 (m, 2 H), 1.27-1.14 (m, 8 H); **13C NMR** (150 MHz, CDCl3) δ 174.0, 152.6, 141.6, 115.2, 114.8, 63.4, 60.7, 55.7, 41.3, 29.7, 29.2, 26.2, 26.1, 26.1, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{17}H_{26}NO_3$ $[M+H]^+$ 292.1907, found 292.1904.



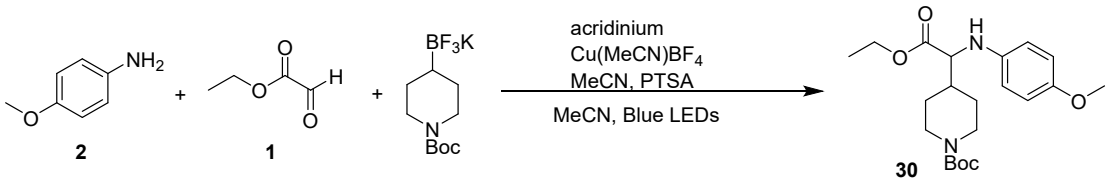
2 1 28

Compound **28** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], *sec*-butyltrifluoroborate (45.9 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **28** (45.2 mg, 85%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ

6.76 (d, *J* = 9.0 Hz, 2 H), 6.61 (dd, *J* = 1.8, 9.0 Hz, 2 H), 4.21-4.10 (m, 2 H), 3.96-3.80 (c, 2 H), 3.73 (s, 3 H), 1.93-1.78 (m, 1 H), 1.69-1.51 (m, 1 H), 1.35-1.26 (m, 1 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.03-0.92 (m, 6 H); **13C NMR** (150 MHz, CDCl3) δ 174.2, 173.8, 152.6, 152.5, 141.7, 141.4, 115.3, 115.2, 114.8, 62.4, 62.1, 60.7, 60.6, 55.7, 38.0, 37.9, 26.2, 25.6, 15.5, 14.9, 14.3, 11.7, 11.5; **HRMS (ESI$^+$)** Calcd for $C_{15}H_{24}NO_3$ $[M+H]^+$ 266.1751, found 266.1755.

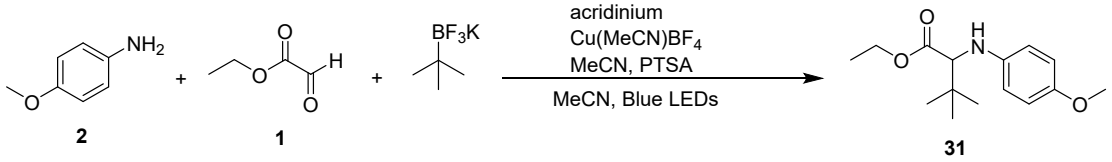


Compound **29** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], tetrahydro-2*H*-pyran-4-trifluoroborate (53.8 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **29** (53.5 mg, 91%) as a white gum after purification via silica gel column chromatography with 8% ethyl acetate/hexanes (R_f = 0.35, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.76 (d, *J* = 8.4 Hz, 2 H), 6.61 (d, *J* = 9.0 Hz, 2 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 4.06-3.96 (m, 2 H), 3.94-3.81 (br, 1 H), 7.58 (d, *J* = 6.6 Hz, 1 H), 3.74 (s, 3 H), 3.44-3.34 (m, 2 H), 2.01-1.90 (m, 1 H), 1.78 (d, *J* = 13.2 Hz, 1 H), 1.65-1.48 (m, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.4, 152.8, 141.2, 115.4, 114.8, 67.8, 67.6, 62.8, 61.0, 55.7, 33.8, 29.4, 29.4, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{16}H_{24}NO_4$ $[M+H]^+$ 294.1700, found 294.1689.



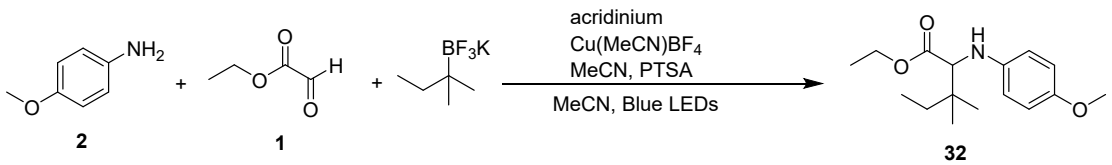
Compound **30** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], trifluoroborate (81.5 mg, 0.280

mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **30** (62.9 mg, 80%) as a white gum after purification via silica gel column chromatography with 10% ethyl acetate/hexanes (R_f = 0.2, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.76 (d, *J* = 9.0 Hz, 2 H), 6.60 (d, *J* = 9.0 Hz, 2 H), 4.31-4.00 (c, 4 H), 3.92-3.81 (br, 1 H), 3.78 (d, *J* = 6.0 Hz, 1 H), 3.73 (s, 3 H), 2.79-2.59 (br, 2 H), 1.91-1.78 (m, 2 H), 1.61 (d, *J* = 13.2 Hz, 1 H), 1.45 (s, 9 H), 1.43-1.29 (m, 2 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.4, 154.7, 152.9, 141.2, 115.4, 114.8, 79.5, 62.6, 61.0, 55.7, 39.8, 28.4, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{21}H_{33}N_2O_5$ $[M+H]^+$ 393.2384, found 393.2388.



2 **1** **31**

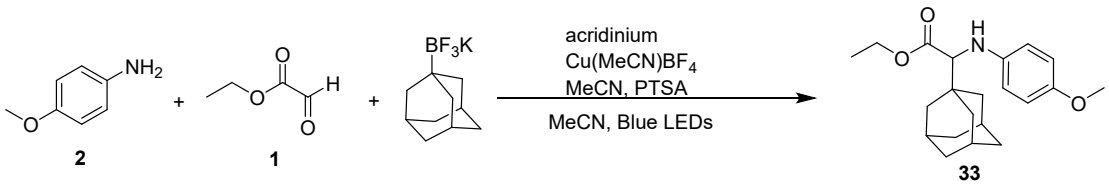
Compound **31** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], *tert*-butyltrifluoroborate (45.9 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **31** (44.1 mg, 83%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.76 (d, *J* = 9.0 Hz, 2 H), 6.64 (d, *J* = 8.4 Hz, 2 H), 4.19-4.07 (m, 2 H), 4.01-3.80 (br, 1 H), 3.73 (s, 3 H), 3.67 (s, 1 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.06 (s, 9 H); **13C NMR** (150 MHz, CDCl3) δ 173.6, 152.7, 141.8, 115.6, 114.8, 67.0, 60.4, 55.7, 34.3, 26.8, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{15}H_{24}NO_3$ $[M+H]^+$ 266.1751, found 266.1754.



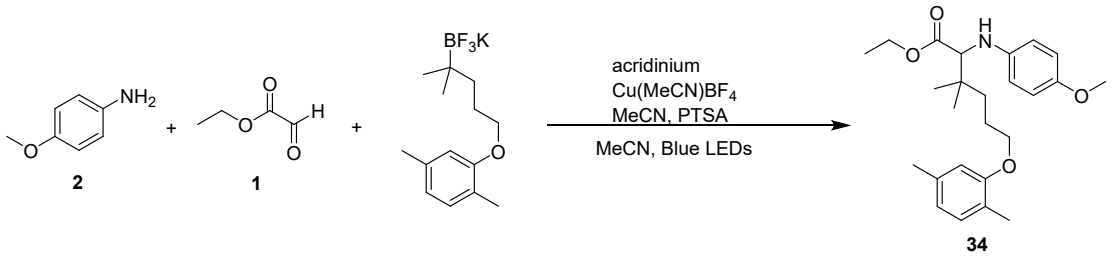
2 **1** **32**

Compound **32** was synthesized following the **General Procedure for the three-**

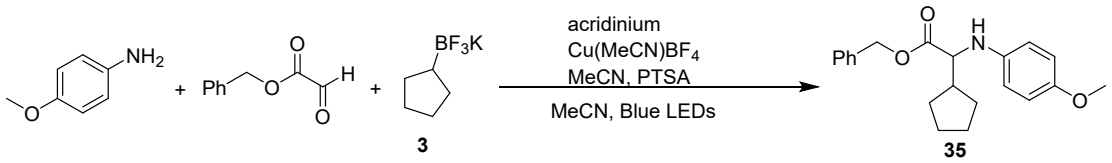
components coupling. The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], *tert*-pentyltrifluoroborate (49.8 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **32** (45.4 mg, 81%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.75 (d, *J* = 9.0 Hz, 2 H), 6.63 (d, *J* = 9.0 Hz, 2 H), 4.20-4.07 (m, 2 H), 4.06-3.79 (br, 1 H), 3.75 (s, 1 H), 3.73 (s, 3 H), 1.52-1.38 (m, 2 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.01 (s, 3 H), 0.98 (s, 3 H), 0.90 (t, *J* = 7.8 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.8, 152.7, 141.8, 115.6, 114.8, 65.3, 60.4, 55.7, 32.1, 23.4, 23.1, 14.3, 8.2; **HRMS (ESI$^+$)** Calcd for $C_{16}H_{26}NO_3$ $[M+H]^+$ 280.1907, found 280.1901.



Compound **33** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], 1-adamantyl trifluoroborate (49.8 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **33** (61.2 mg, 89%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f = 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.75 (d, *J* = 9.0 Hz, 2 H), 6.63 (d, *J* = 8.4 Hz, 2 H), 4.13 (q, *J* = 7.8 Hz, 2 H), 4.06-3.80 (br, 1 H), 3.73 (s, 3 H), 3.54 (s, 1 H), 2.02 (s, 3 H), 1.82 (d, *J* = 12.0 Hz, 3 H), 1.73 (d, *J* = 12.6 Hz, 3 H), 1.66 (d, *J* = 12.0 Hz, 3 H), 1.58 (d, *J* = 12.0 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.1, 152.6, 142.0, 115.5, 114.8, 68.0, 60.4, 55.7, 39.0, 36.9, 36.1, 28.4, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{21}H_{30}NO_3$ $[M+H]^+$ 344.2220, found 344.2220.

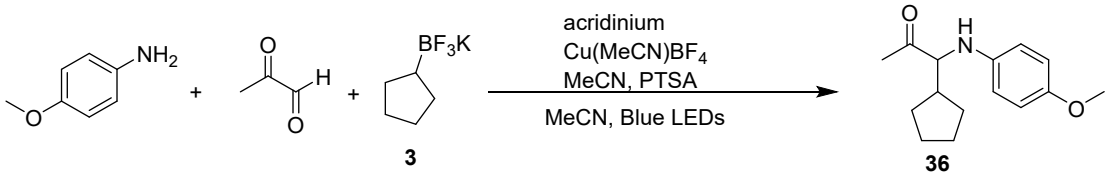


Compound **34** was synthesized following the **General Procedure for the three-components coupling.** The reaction of **2** (24.6 mg, 0.200 mmol, 1.0 equiv.), **1** [50.0 mg (50 wt.% in toluene), 0.240 mmol, 1.2 equiv.], (5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)trifluoroborate (87.4 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **34** (71.2 mg, 86%) as a white gum after purification via silica gel column chromatography with 8% ethyl acetate/hexanes (R_f = 0.35, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.00 (d, *J* = 7.2 Hz, 1 H), 6.76 (d, *J* = 9.0 Hz, 2 H), 6.69-6.63 (c, 3 H), 6.61 (s, 1 H), 4.19-4.09 (m, 2 H), 4.00-3.83 (c, 3 H), 3.78 (s, 1 H), 3.74 (s, 3 H), 2.30 (s, 3 H), 2.17 (s, 3 H), 1.94-1.77 (m, 2 H), 1.67-1.52 (m, 2 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.08 (s, 3 H), 1.07 (s, 3 H); **13C NMR** (150 MHz, CDCl3) δ 173.6, 157.0, 152.8, 141.7, 136.4, 130.3, 123.5, 120.6, 115.7, 114.8, 112.0, 68.3, 65.6, 60.5, 55.7, 36.6, 36.1, 24.1, 24.0, 23.5, 21.4, 15.8, 14.3; **HRMS (ESI$^+$)** Calcd for $C_{25}H_{36}NO_4$ $[M+H]^+$ 414.2639, found 414.2644.

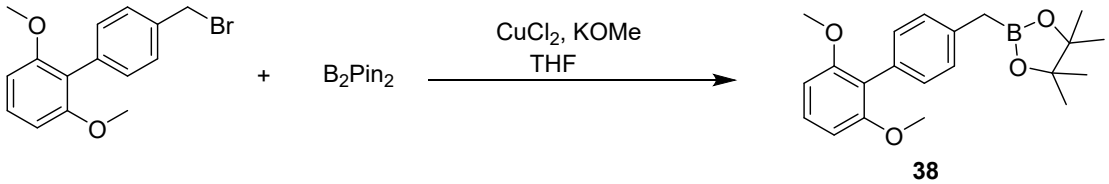


Compound **35** was synthesized following the **General Procedure for the three-components coupling.** The reaction of *p*-anisidine (24.6 mg, 0.200 mmol, 1.0 equiv.), benzyl 2-oxoacetate (39.4 mg, 0.240 mmol, 1.2 equiv.), **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **35** (59.8 mg, 88%) as a white gum after purification via silica gel column chromatography with 5% ethyl acetate/hexanes (R_f

= 0.4, 5% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 7.33-7.23 (m, 3 H), 7.19 (d, *J* = 7.2 Hz, 2 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 6.54 (d, *J* = 8.4 Hz, 2 H), 5.05 (s, 2 H), 3.88-3.75 (c, 2 H), 3.68 (s, 3 H), 2.23-2.11 (m, 1 H), 1.81-1.72 (m, 1 H), 1.67-1.54 (m, 3 H), 1.54-1.45 (m, 2 H), 1.44-1.35 (m, 2 H); **13C NMR** (150 MHz, CDCl3) δ 174.3, 152.7, 141.3, 135.6, 128.5, 128.2, 128.2, 115.2, 114.8, 66.5, 62.2, 55.7, 43.1, 29.4, 29.0, 25.3, 25.1; **HRMS (ESI$^+$)** Calcd for $C_{21}H_{26}NO_3$ $[M+H]^+$ 340.1907, found 340.1911.

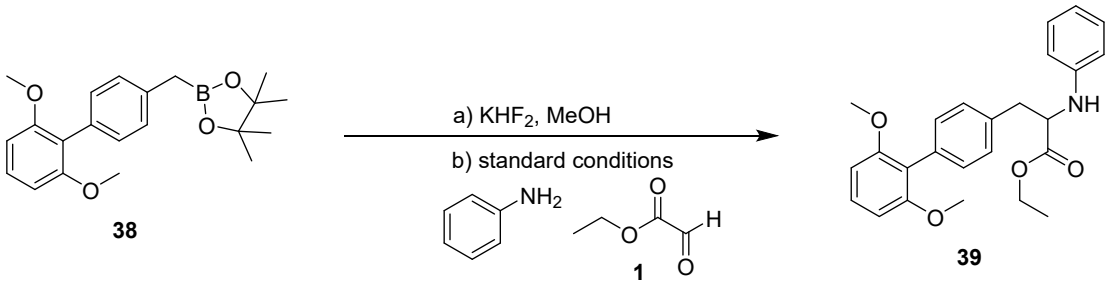


Compound **36** was synthesized following the **General Procedure for the three-components coupling.** The reaction of *p*-anisidine (24.6 mg, 0.200 mmol, 1.0 equiv.), 2-oxopropanal (17.3 mg, 0.240 mmol, 1.2 equiv.), **3** (49.3 mg, 0.280 mmol, 1.4 equiv.), 9-mesityl-10-methylacridinium perchlorate (4.1 mg, 0.0100 mmol, 5 %), *p*-tolylsulfonicacid (1.7 mg, 0.0100 mmol, 5 %) and $Cu(MeCN)BF_4$ (3.1 mg, 0.0100 mmol, 5 %) in MeCN (2.0 mL) delivered **36** (36.7 mg, 74%) as a white gum after purification via silica gel column chromatography with 10% ethyl acetate/hexanes (R_f = 0.3, 10% ethyl acetate/hexanes). **1H NMR** (600 MHz, CDCl3) δ 6.75 (d, *J* = 9.0 Hz, 2 H), 6.53 (d, *J* = 9.0 Hz, 2 H), 4.06-3.89 (br, 1 H), 3.73 (s, 3 H), 3.65 (d, *J* = 7.8 Hz, 1 H), 2.22-2.14 (m, 1 H), 2.13 (s, 3 H), 1.82-1.74 (m, 1 H), 1.74-1.62 (m, 3 H), 1.60-1.55 (m, 2 H), 1.48-1.33 (m, 2 H); **13C NMR** (150 MHz, CDCl3) δ 211.7, 152.4, 141.7, 115.0, 114.4, 69.0, 55.8, 42.1, 29.4, 29.0, 26.2, 25.3, 25.0; **HRMS (ESI$^+$)** Calcd for $C_{15}H_{22}NO_3$ $[M+H]^+$ 248.1645, found 248.1646.



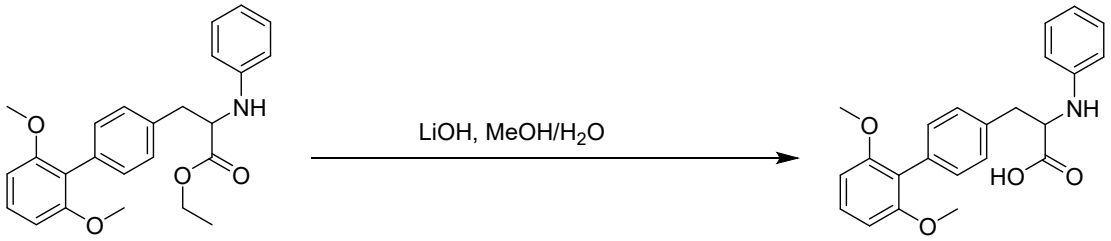
In a 50 mL thick-walled reaction tube equipped with a magnetic stirring bar, $CuCl_2$ (4.4 mg, 0.0326 mmol, 1 %), IMes (9.9 mg, 0.0326 mmol, 1 %) and THF (25 mL) was added. After stirring for 10 min, bis(pinacolato)diboron (0.993 g, 3.91 mmol, 1.2

equiv.) and KOMe (0.274 g, 3.91 mmol, 1.2 equiv.) was added and the reaction was stirred for an additional 10 min. To the mixture, alkyl bromide (1.00 g, 3.26 mmol, 1.2 equiv.) was added. The resulting reaction mixture was stirred vigorously at room temperature overnight. The reaction mixture was then diluted with Et_2O (80 mL) and filtered through a plug of celite. The organic layer was washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated. The reside was then purified by column chromatography on silica gel with 5% ethyl acetate/hexanes (R_f = 0.3, 5% ethyl acetate/hexanes) to give target product as a white gum (0.762 g, 66%). **1H NMR** (500 MHz, CDCl3) δ 7.29-7.25 (c, 5 H), 6.68 (d, *J* = 8.0 Hz, 2 H), 3.76 (s, 6 H), 2.37 (s, 2 H), 1.30 (s, 12 H); **13C NMR** (125 MHz, CDCl3) δ 157.7, 136.8, 130.7, 128.5, 128.3, 104.2, 104.2, 83.4, 55.9, 25.0, 24.8, 24.6; **HRMS (ESI$^+$)** Calcd for $C_{21}H_{28}BO_4$ $[M+H]^+$ 355.2075, found 355.2076.



To a solution of 38 (0.500 g, 1.41 mmol, 1 equiv.) in THF (1.5 mL) was added KHF_2 (aq. sat. solution, 5.0 mL), and the mixture was stirred vigorously for 2 h before being concentrated under reduced pressure. The residue was used for the three-component coupling without further purification. Compound **39** was synthesized following the **General Procedure for the three-components coupling.** The reaction of the above residue, aniline (93.0 mg, 1.00 mmol, 0.71 equiv.), **1** [0.244 g (50 wt.% in toluene), 1.17 mmol, 0.83 equiv.], 9-mesityl-10-methylacridinium perchlorate (28.9 mg, 0.0705 mmol, 5 %), *p*-tolylsulfonicacid (12.0 mg, 0.0705 mmol, 5 %) and $Cu(MeCN)BF_4$ (21.8 mg, 0.0705 mmol, 5 %) in MeCN (15 mL) delivered **39** (0.406 g, 71%) as a white gum after purification via silica gel column chromatography with 15% ethyl acetate/hexanes (R_f = 0.3, 15% ethyl acetate/hexanes). **1H NMR** (500 MHz, CDCl3) δ 7.26 (t, *J* = 8.5 Hz, 3 H), 7.24-7.20 (m, 2 H), 7.17 (dt, *J* = 7.0, 1.5 Hz, 2 H), 6.78-6.71 (m, 1 H), 6.64 (d, *J* = 8.5 Hz, 4 H), 4.38 (t, *J* = 7.0 Hz, 1 H), 4.30-4.16 (br, 1 H), 4.12 (q, *J* = 7.0 Hz,

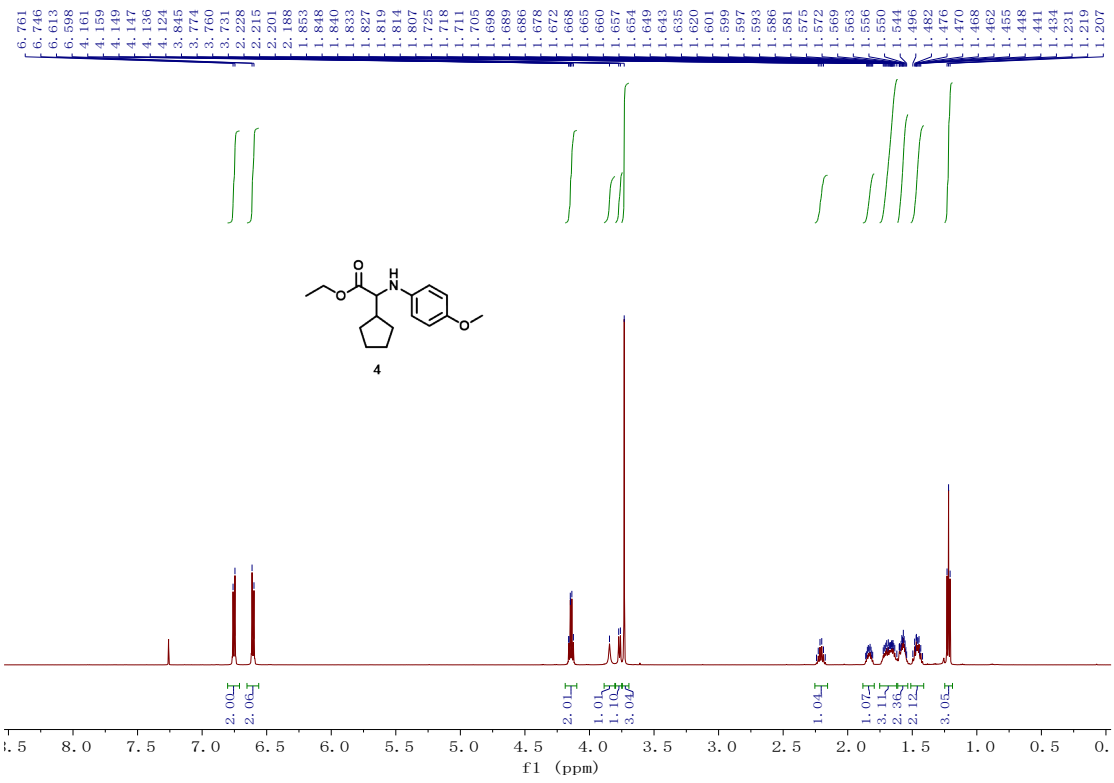
2 H), 3.71 (s, 6 H), 3.22-3.08 (m, 2 H), 1.16 (t, *J* = 7.0 Hz, 3 H); **13C NMR** (125 MHz, CDCl3) δ 173.5, 157.6, 146.5, 134.6, 132.8, 131.0, 129.3, 128.6, 128.5, 128.5, 119.2, 118.3, 113.6, 104.2, 104.1, 61.0, 57.8, 55.8, 38.8, 14.0; **HRMS (ESI$^+$)** Calcd for $C_{25}H_{28}NO_4$ $[M+H]^+$ 406.2103, found 406.2105.

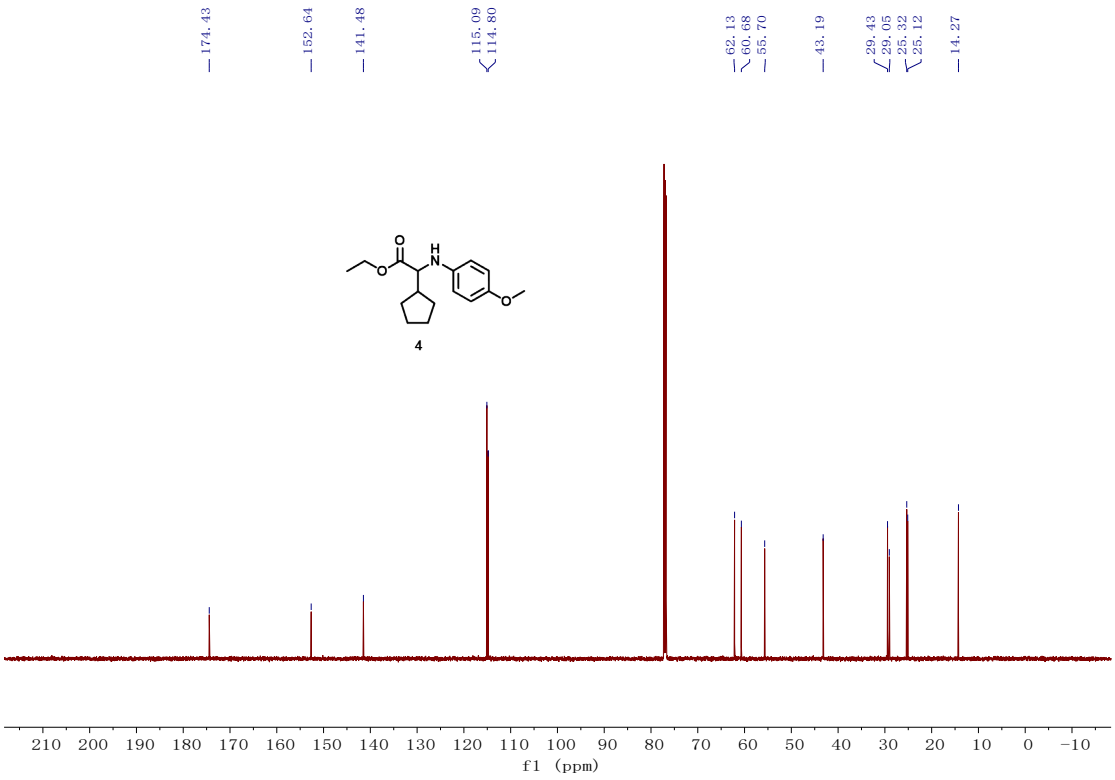


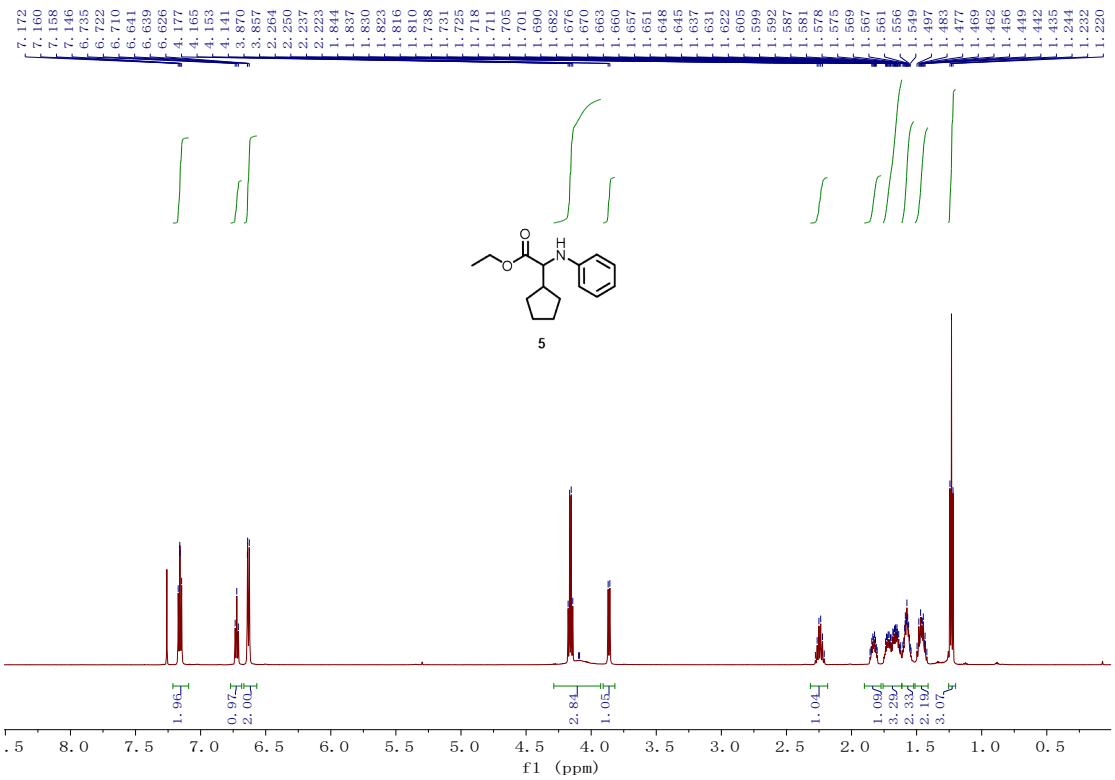
39 **40**

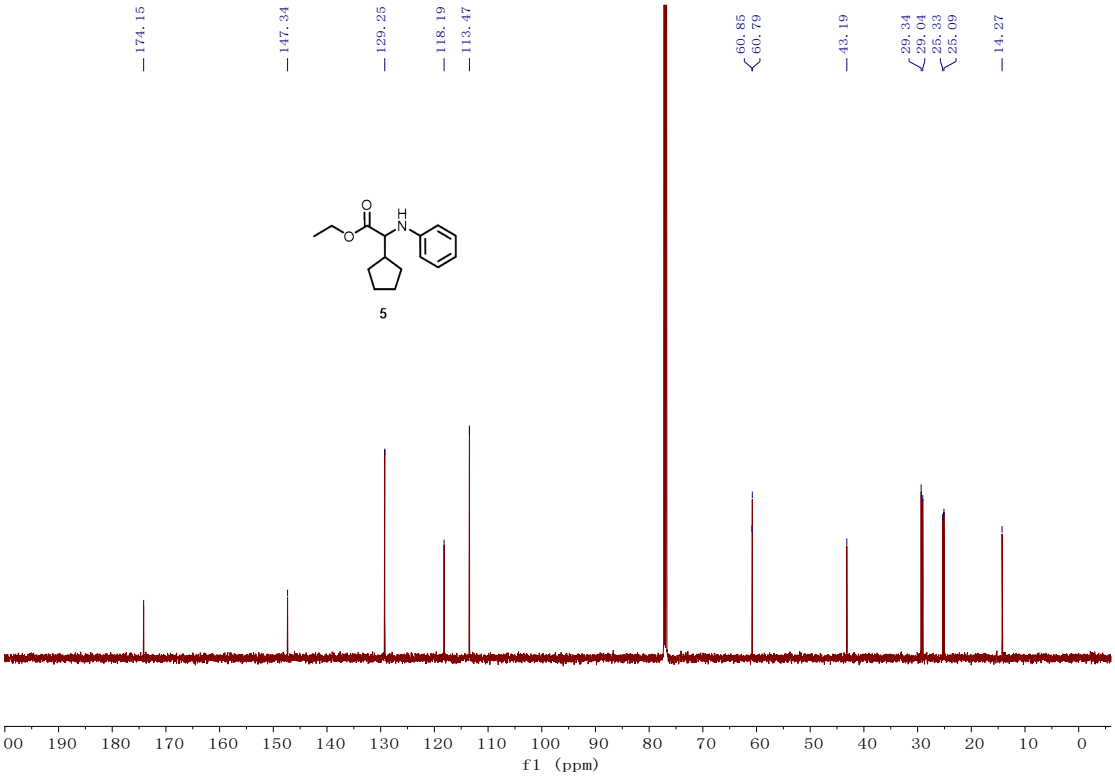
To a solution of 39 (0.300 g, 0.795 mmol, 1 equiv.) in MeOH/H2O (6 mL/2 mL) was added LiOH (22.9 g, 0.954 mmol, 1.2 equiv.), and the mixture was stirred at room temperature for 2 h. The reaction was poured into water (50 mL) and extracted with ethyl acetate (3×25 ml). The organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. The reside was then purified by column chromatography on silica gel to give 40 as a white gum after purification via silica gel column chromatography with 40% ethyl acetate/hexanes (R_f = 0.3, 30% ethyl acetate/hexanes). **1H NMR** (500 MHz, CDCl3) δ 7.32-7.23 (m, 5 H), 7.19 (t, *J* = 8.0 Hz, 2 H), 6.80 (t, *J* = 7.5 Hz, 1 H), 6.64 (d, *J* = 8.5 Hz, 4 H), 4.35 (t, *J* = 6.0 Hz, 1 H), 3.71 (s, 6 H), 3.31 (dd, *J* = 14.0, 5.0 Hz, 1 H), 3.15 (dd, *J* = 14.0, 7.5 Hz, 1 H), 2.98 (d, *J* = 8.5 Hz, 4 H); **13C NMR** (125 MHz, CDCl3) δ 176.1, 157.6, 146.2, 134.0, 133.1, 131.4, 129.4, 128.7, 128.5, 119.4, 118.9, 114.1, 104.2, 58.1, 55.9, 38.1; **HRMS (ESI$^+$)** Calcd for $C_{23}H_{24}NO_4$ $[M+H]^+$ 378.1700, found 378.1705.

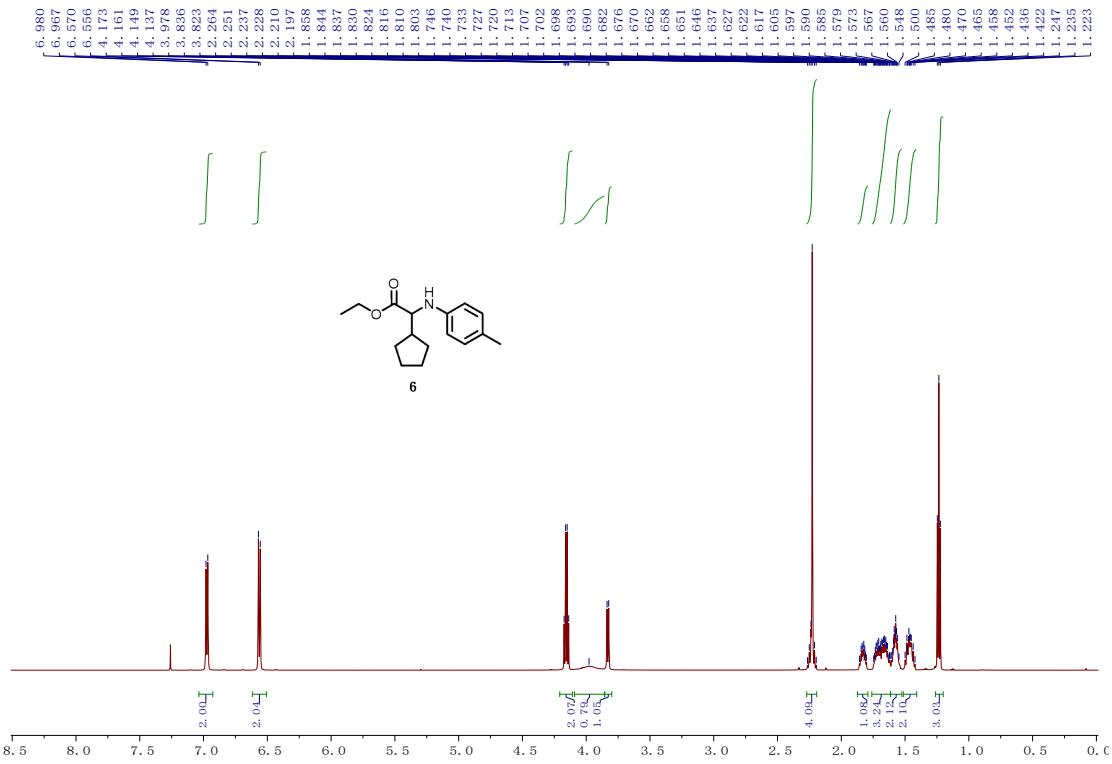
NMR DATA

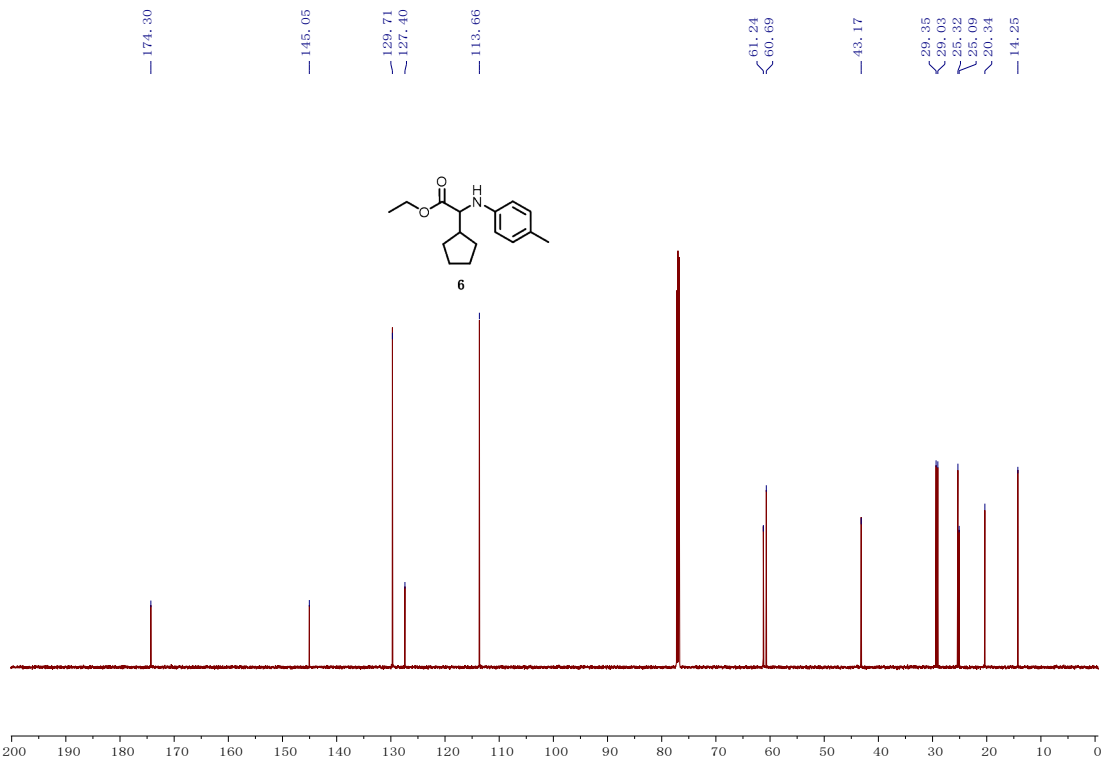

6.761
6.746
6.613
6.598
4.161
4.159
4.149
4.147
4.136
4.124
3.845
3.774
3.760
3.731
2.228
2.215
2.201
2.188
1.853
1.848
1.840
1.833
1.827
1.819
1.814
1.807
1.725
1.718
1.711
1.705
1.698
1.689
1.686
1.678
1.672
1.668
1.665
1.660
1.657
1.654
1.649
1.643
1.635
1.620
1.601
1.599
1.597
1.593
1.586
1.581
1.575
1.572
1.569
1.563
1.556
1.550
1.544
1.496
1.482
1.476
1.470
1.468
1.462
1.455
1.448
1.441
1.434
1.231
1.219
1.207
4
2.00
2.06
2.01
1.01
1.10
3.04
1.04
1.07
3.11
2.36
2.12
3.05
f1 (ppm)

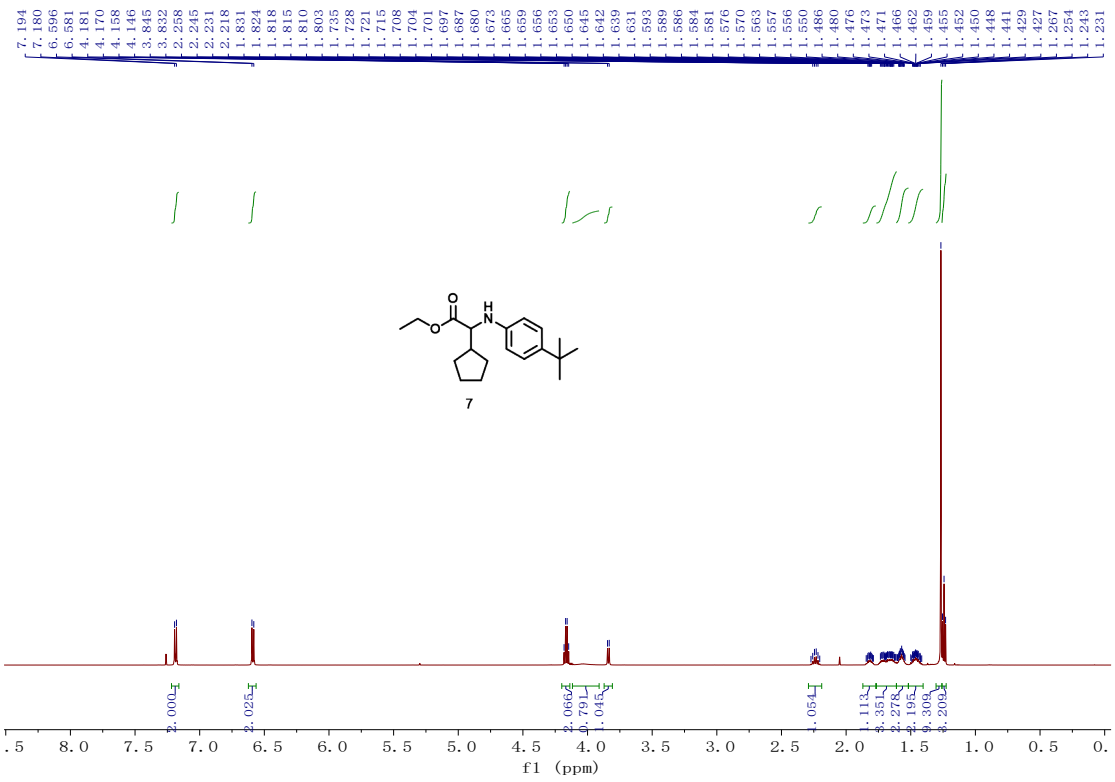

174.43
152.64
141.48
115.09
114.80
62.13
60.68
55.70
43.19
29.43
29.05
25.32
25.12
14.27
4
f1 (ppm)

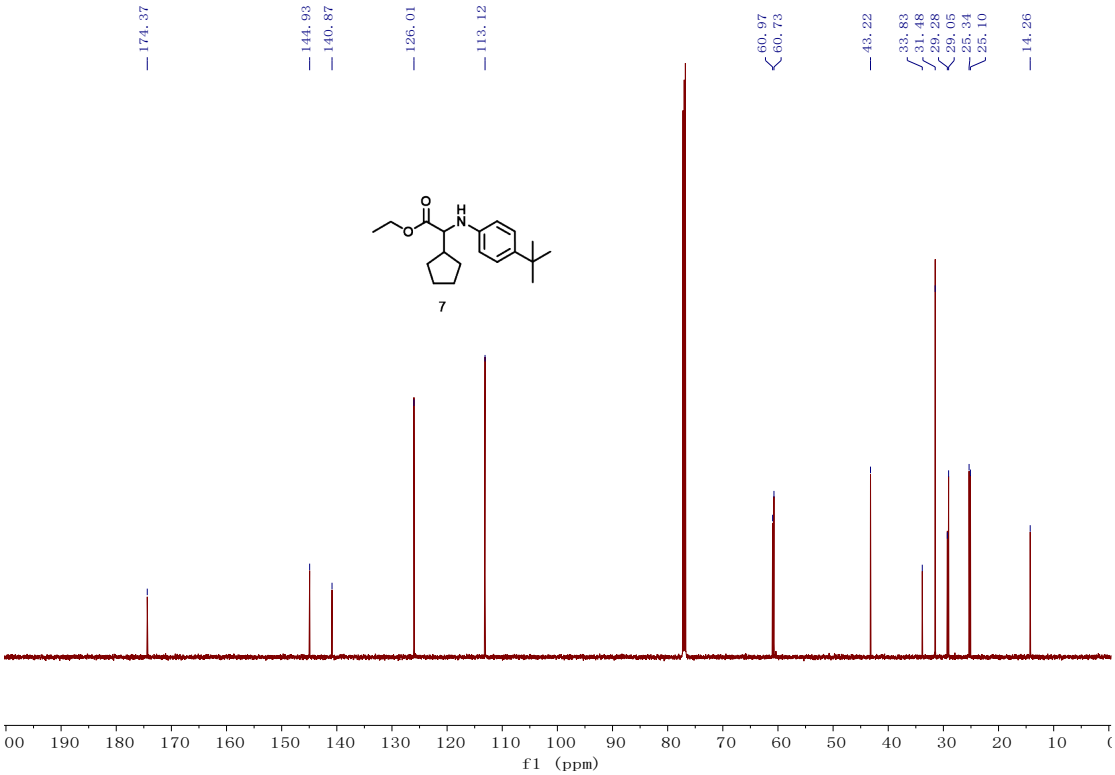

7.172
7.160
7.158
7.146
6.735
6.722
6.710
6.641
6.639
6.626
4.177
4.165
4.153
4.141
3.870
3.857
2.264
2.250
2.237
2.223
1.844
1.837
1.830
1.823
1.816
1.810
1.738
1.731
1.725
1.718
1.711
1.705
1.701
1.690
1.682
1.676
1.670
1.663
1.660
1.657
1.651
1.648
1.645
1.637
1.631
1.622
1.605
1.599
1.592
1.587
1.581
1.578
1.575
1.569
1.567
1.561
1.556
1.549
1.497
1.483
1.477
1.469
1.462
1.456
1.449
1.442
1.435
1.244
1.232
1.220
O
O
H
N
5
1.96
0.97
2.00
2.84
1.05
1.04
1.09
3.29
2.33
2.19
3.07
f1 (ppm)

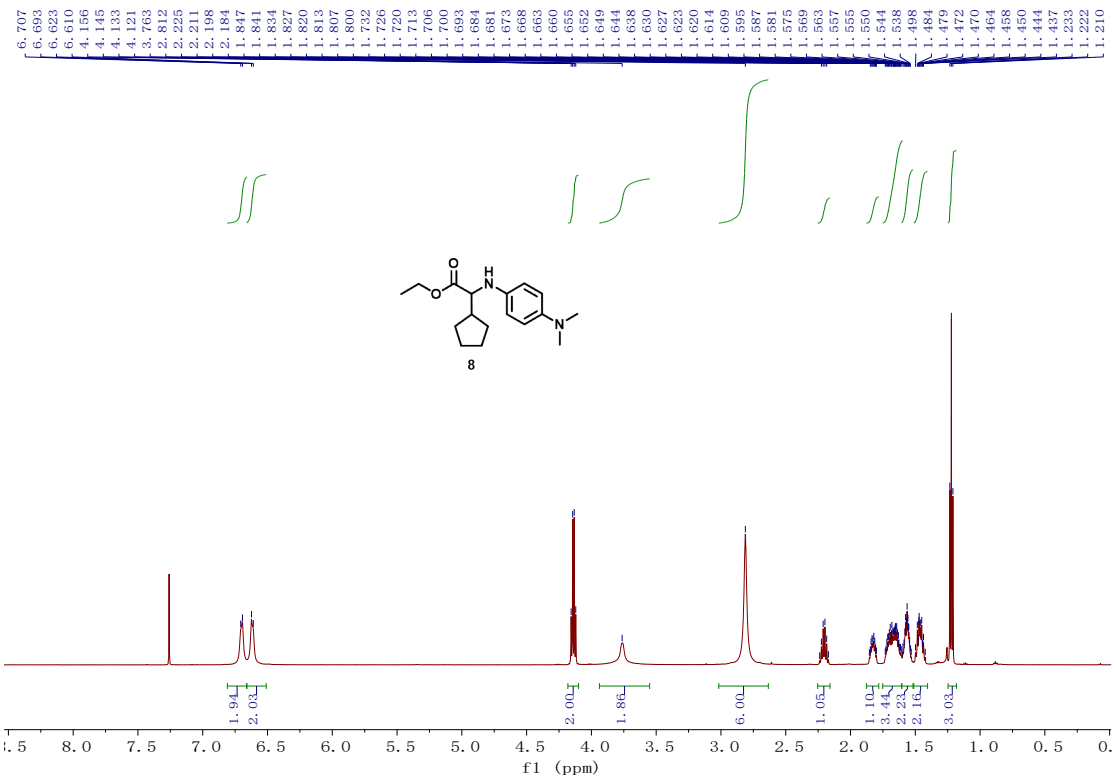

174.15
147.34
129.25
118.19
113.47
60.85
60.79
43.19
29.34
29.04
25.33
25.09
14.27
O
O
H
N
5
f1 (ppm)

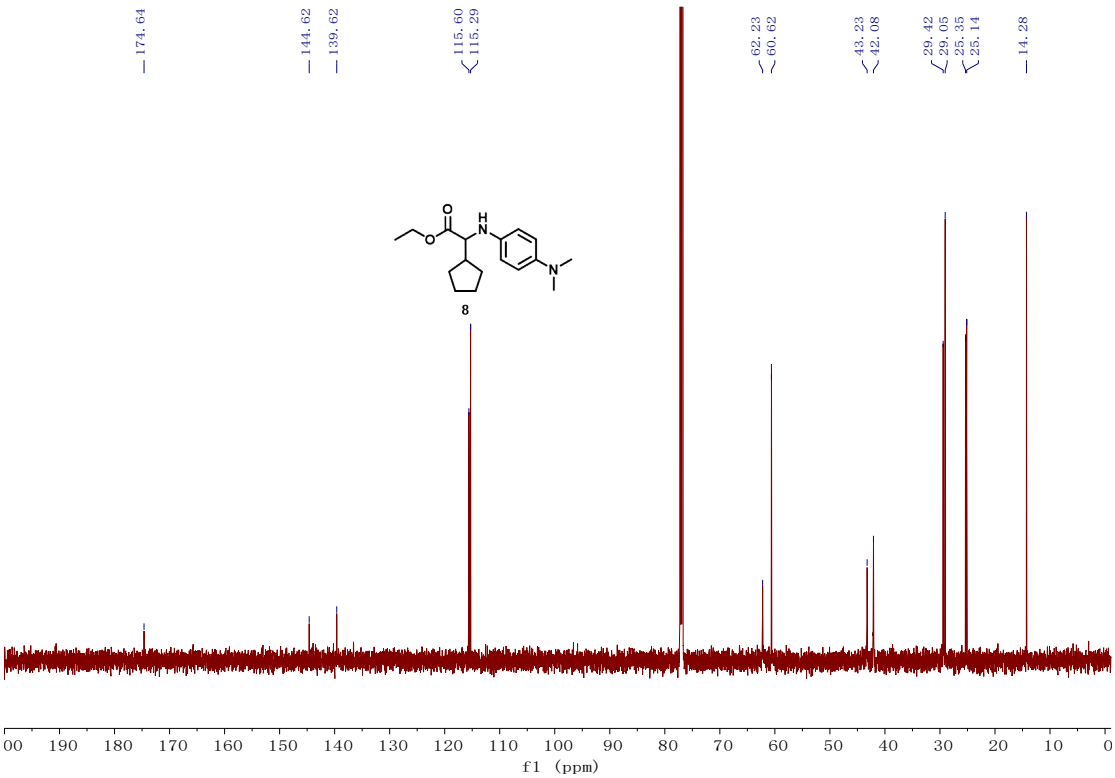

6.980
6.967
6.570
6.556
4.173
4.161
4.149
4.137
3.978
3.836
3.823
2.264
2.251
2.237
2.228
2.210
2.197
1.858
1.844
1.837
1.830
1.824
1.816
1.810
1.803
1.746
1.740
1.733
1.727
1.720
1.713
1.707
1.702
1.698
1.693
1.690
1.682
1.676
1.670
1.662
1.658
1.651
1.646
1.637
1.627
1.622
1.617
1.605
1.597
1.590
1.585
1.579
1.573
1.567
1.560
1.548
1.500
1.485
1.480
1.470
1.465
1.458
1.452
1.436
1.422
1.247
1.235
1.223
6
2.00
2.04
2.07
0.79
1.05
4.09
1.08
3.24
2.12
2.10
3.04
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

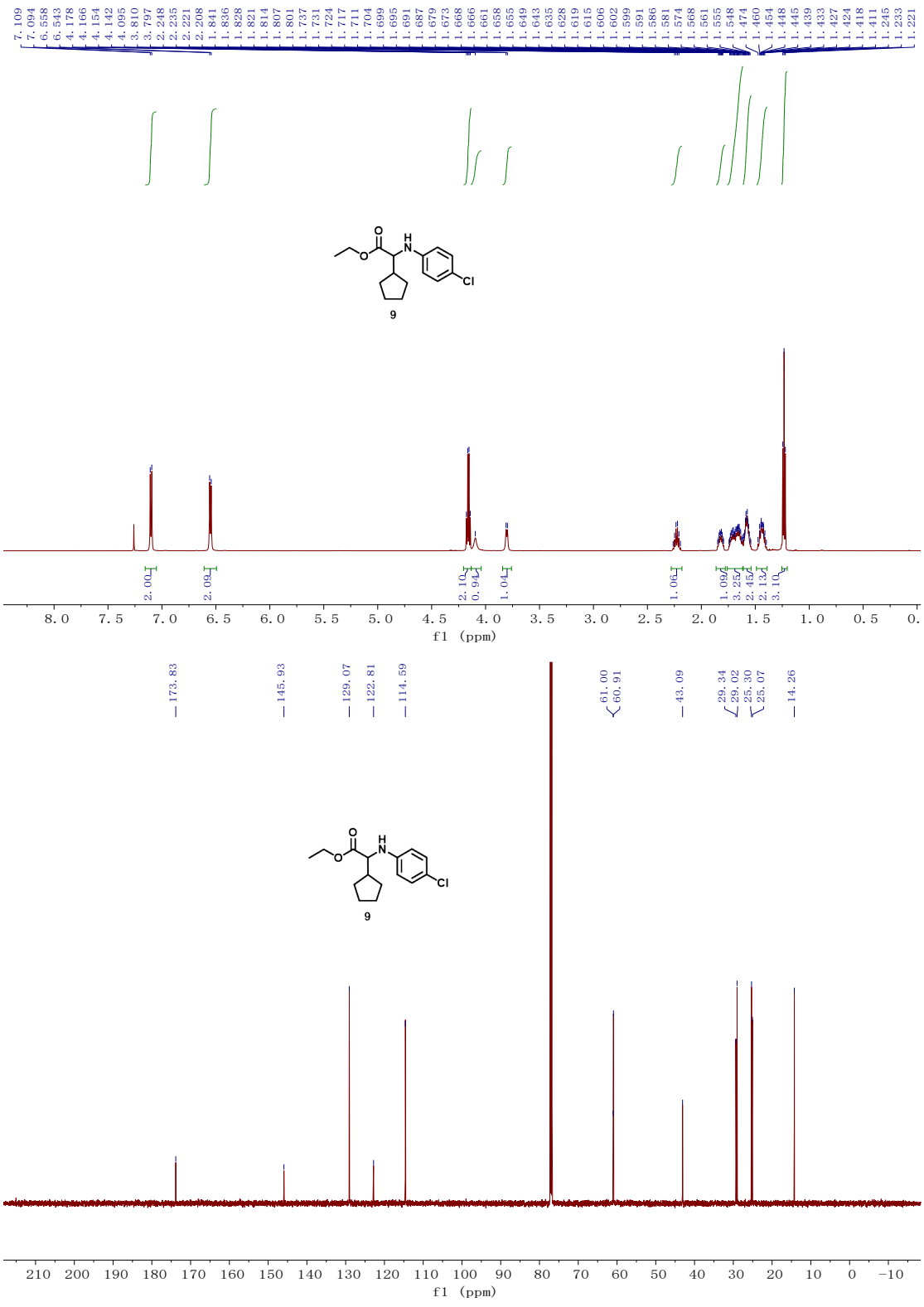

174.30
145.05
129.71
127.40
113.66
61.24
60.69
43.17
29.35
29.03
25.32
25.09
20.34
14.25
6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

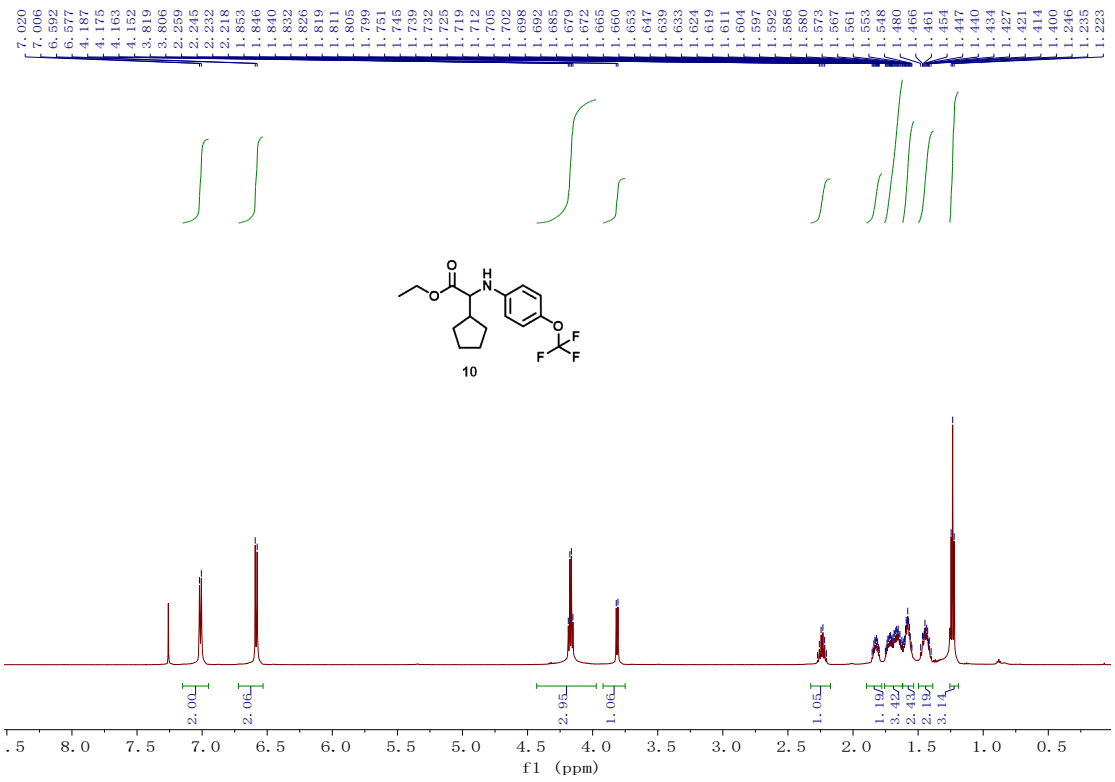

7.194
7.180
6.596
6.581
4.181
4.170
4.158
4.146
3.845
3.832
2.258
2.245
2.231
2.218
1.831
1.824
1.818
1.815
1.810
1.803
1.735
1.728
1.721
1.715
1.708
1.704
1.701
1.697
1.687
1.680
1.673
1.665
1.659
1.656
1.653
1.650
1.645
1.642
1.639
1.631
1.593
1.589
1.586
1.584
1.581
1.576
1.570
1.563
1.557
1.556
1.550
1.486
1.480
1.476
1.473
1.471
1.466
1.462
1.459
1.455
1.452
1.450
1.448
1.441
1.429
1.427
1.267
1.254
1.243
1.231
O
O
H
N
7
2.000
2.025
2.066
0.791
1.045
1.054
1.113
3.351
2.278
2.195
9.309
8.209
f1 (ppm)

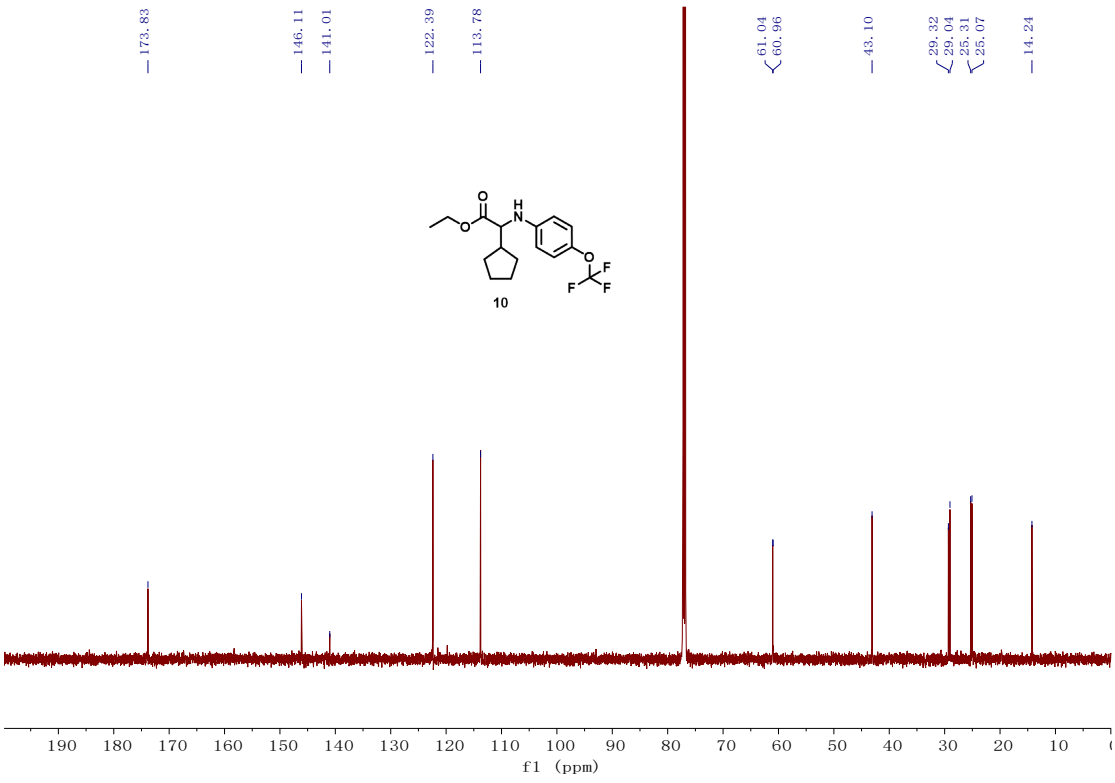

174.37
144.93
140.87
126.01
113.12
60.97
60.73
43.22
33.83
31.48
29.28
29.05
25.34
25.10
14.26
O
O
H
N
7
f1 (ppm)

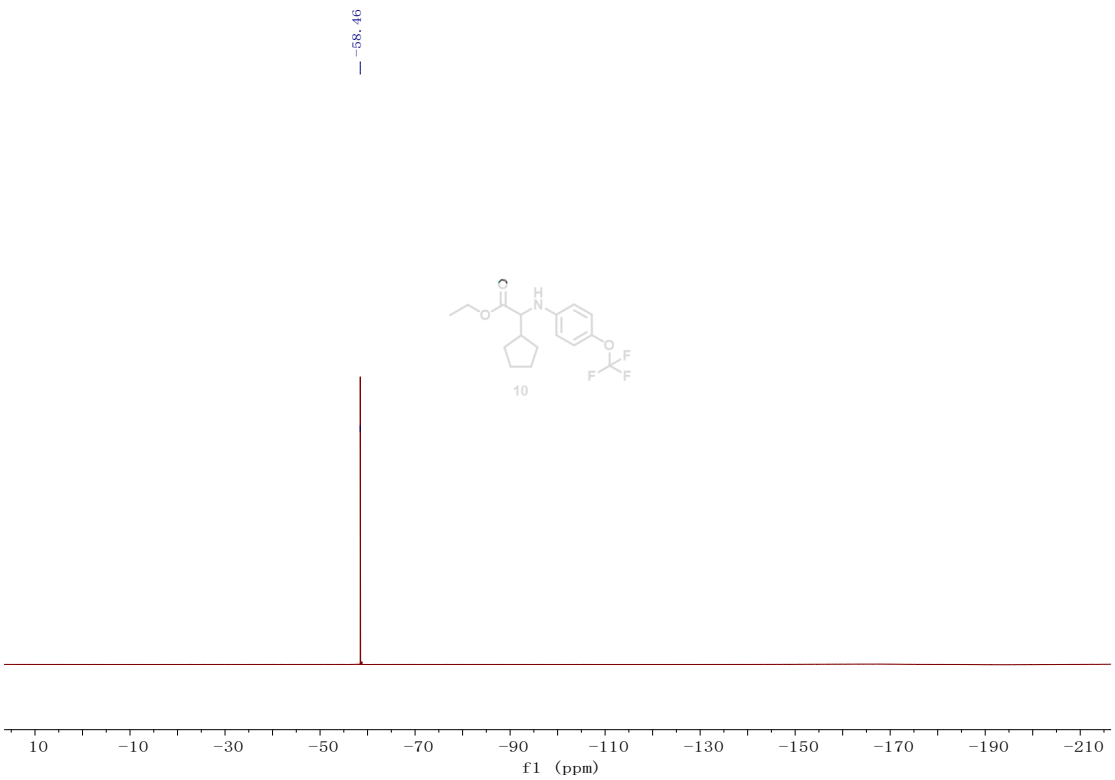

6.707 6.693 6.623 6.610 4.156 4.145 4.133 4.121 3.763 2.812 2.225 2.211 2.198 2.184 1.847 1.841 1.834 1.827 1.820 1.813 1.807 1.800 1.732 1.726 1.720 1.713 1.706 1.700 1.693 1.684 1.681 1.673 1.668 1.663 1.660 1.655 1.652 1.649 1.644 1.638 1.630 1.627 1.623 1.620 1.614 1.609 1.595 1.587 1.581 1.575 1.569 1.563 1.557 1.555 1.550 1.544 1.538 1.498 1.484 1.479 1.472 1.470 1.464 1.458 1.450 1.444 1.437 1.233 1.222 1.210
8
1.94 2.03 2.00 1.86 6.00 1.05 1.10 3.44 2.23 2.16 3.03
f1 (ppm)

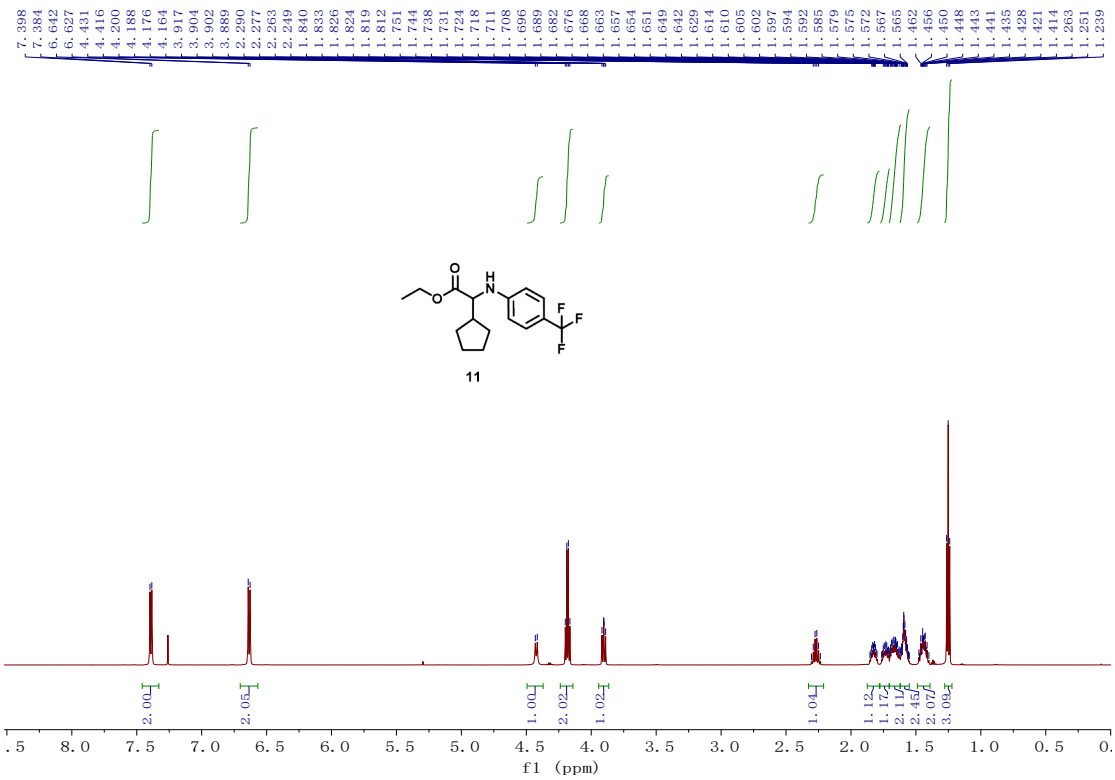

174.64 144.62 139.62 115.60 115.29 62.23 60.62 43.23 42.08 29.42 29.05 25.35 25.14 14.28
8
f1 (ppm)

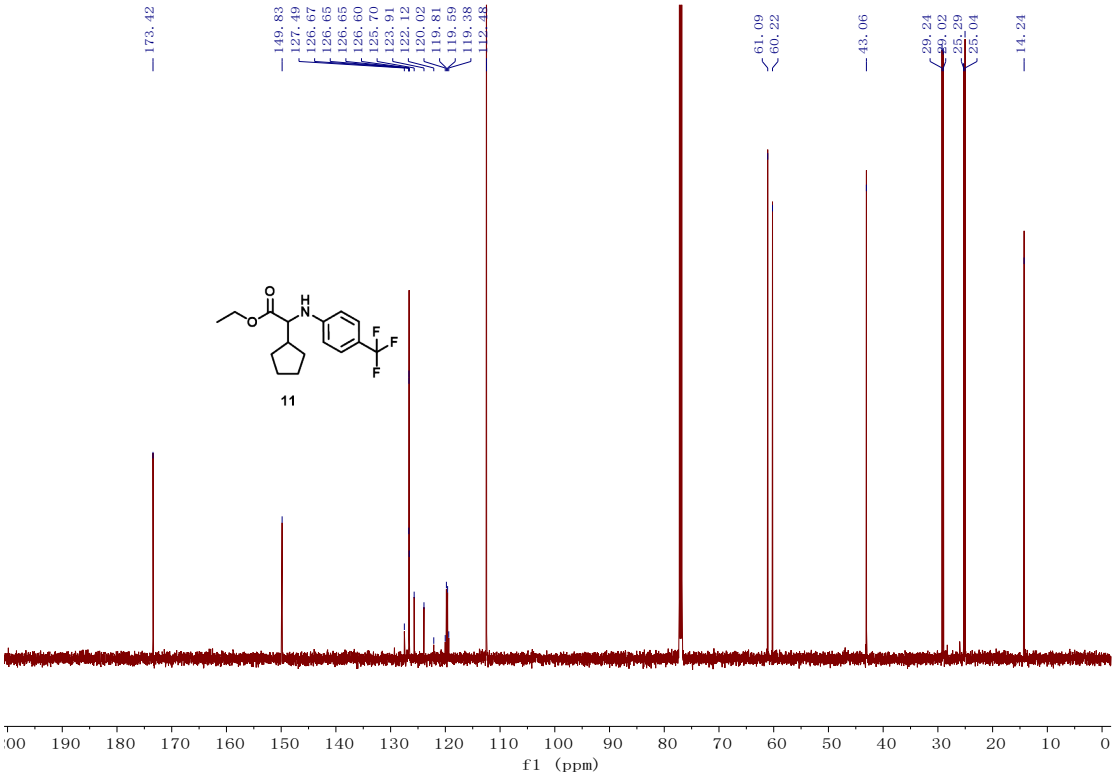

7.109
7.094
6.558
6.543
4.178
4.166
4.154
4.142
4.095
3.810
3.797
2.248
2.235
2.221
2.208
1.841
1.836
1.828
1.821
1.814
1.807
1.801
1.737
1.731
1.724
1.717
1.711
1.704
1.699
1.695
1.691
1.687
1.679
1.673
1.668
1.666
1.661
1.658
1.655
1.649
1.643
1.635
1.628
1.619
1.615
1.606
1.602
1.599
1.591
1.586
1.581
1.574
1.568
1.561
1.555
1.548
1.474
1.460
1.454
1.448
1.445
1.439
1.433
1.427
1.424
1.418
1.411
1.245
1.233
1.221
O
O
H
N
Cl
9
2.00
2.09
2.10
0.94
1.04
1.06
1.09
3.25
2.45
2.13
3.10
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.
f1 (ppm)
173.83
145.93
129.07
122.81
114.59
61.00
60.91
43.09
29.34
29.02
25.30
25.07
14.26
O
O
H
N
Cl
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

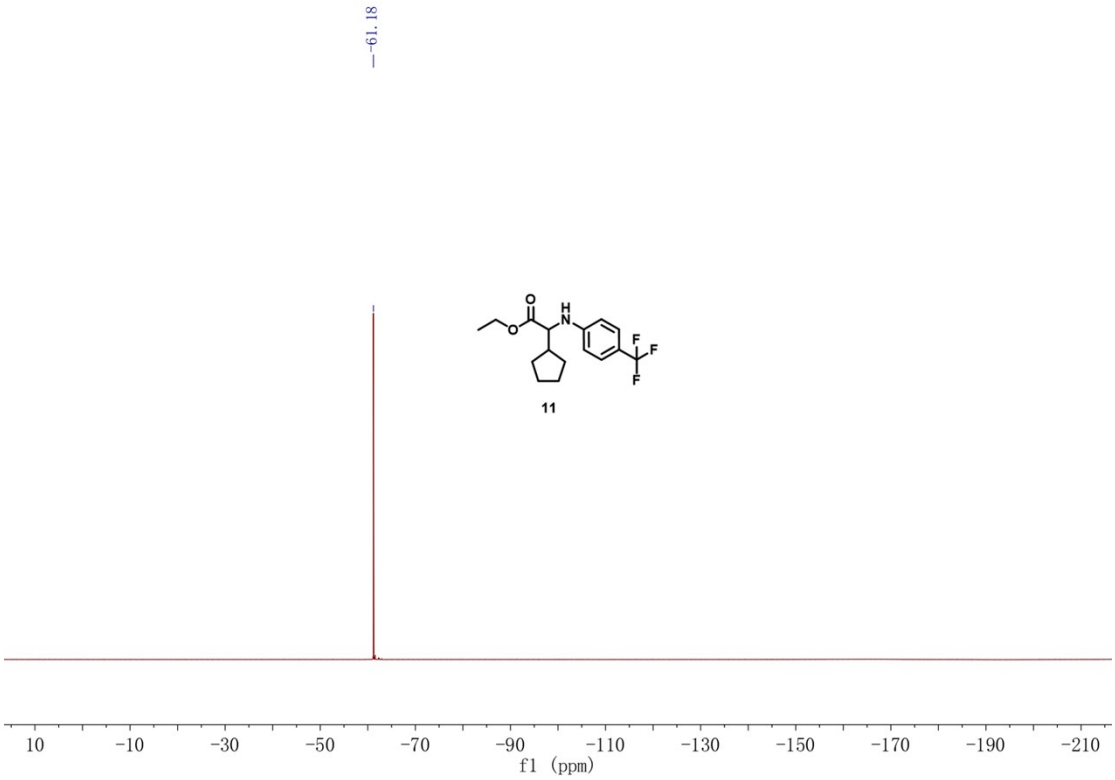

7.020
7.006
6.592
6.577
4.187
4.175
4.163
4.152
3.819
3.806
2.259
2.245
2.232
2.218
1.853
1.846
1.840
1.832
1.826
1.819
1.811
1.805
1.799
1.751
1.745
1.739
1.732
1.725
1.719
1.712
1.705
1.702
1.698
1.692
1.685
1.679
1.672
1.665
1.660
1.653
1.647
1.639
1.633
1.624
1.619
1.611
1.604
1.597
1.592
1.586
1.580
1.573
1.567
1.561
1.553
1.548
1.480
1.466
1.461
1.454
1.447
1.440
1.434
1.427
1.421
1.414
1.400
1.246
1.235
1.223
10
2.00
2.06
2.95
1.06
1.05
1.19
3.42
2.43
2.19
3.14
f1 (ppm)

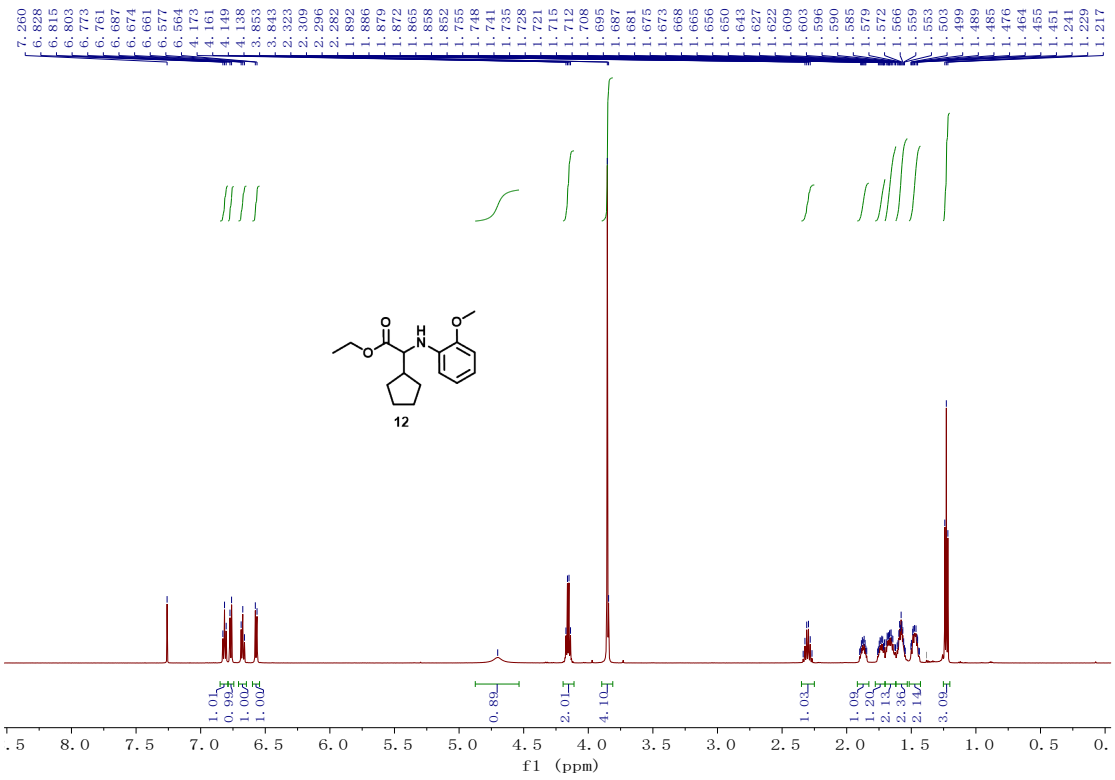

173.83
146.11
141.01
122.39
113.78
61.04
60.96
43.10
29.32
29.04
25.31
25.07
14.24
10
f1 (ppm)

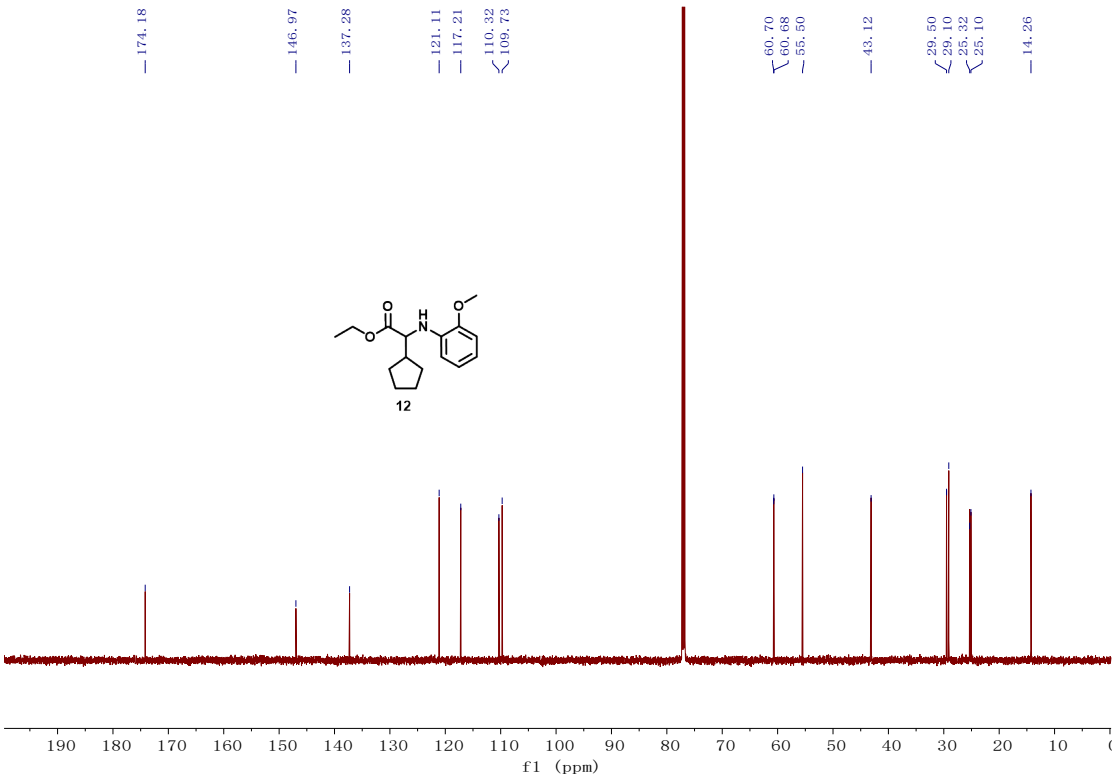

-58.46
10
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

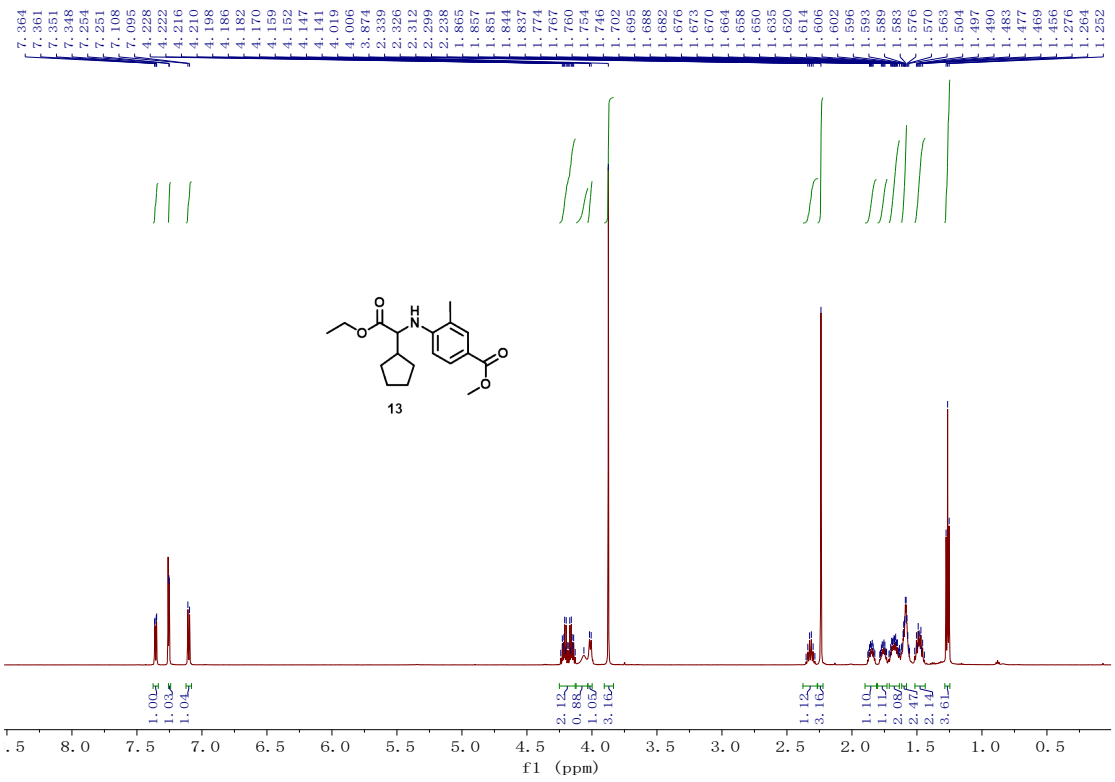

7.398
7.384
6.642
6.627
4.431
4.416
4.200
4.188
4.176
4.164
3.917
3.904
3.902
3.889
2.290
2.277
2.263
2.249
1.840
1.833
1.826
1.824
1.819
1.812
1.751
1.744
1.738
1.731
1.724
1.718
1.711
1.708
1.696
1.689
1.682
1.676
1.668
1.663
1.657
1.654
1.651
1.649
1.642
1.629
1.614
1.610
1.605
1.602
1.597
1.594
1.592
1.585
1.579
1.575
1.572
1.567
1.565
1.462
1.456
1.450
1.448
1.443
1.441
1.435
1.428
1.421
1.414
1.263
1.251
1.239
O
O
H
N
F
F
F
11
2.00
2.05
1.00
2.02
1.02
1.04
1.12
1.17
2.11
2.45
2.07
3.09
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
f1 (ppm)

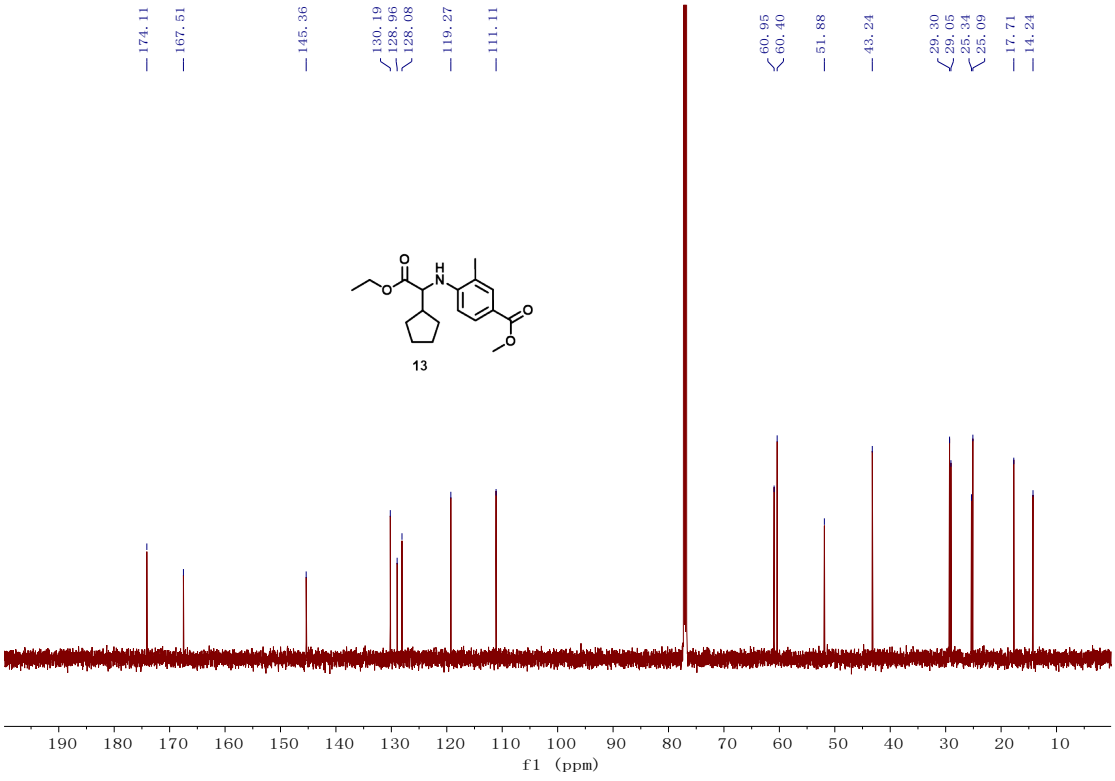

173.42
149.83
127.49
126.67
126.65
126.65
126.60
125.70
123.91
122.12
120.02
119.81
119.59
119.38
112.48
61.09
60.22
43.06
29.24
29.02
25.29
25.04
14.24
O
O
H
N
F
F
F
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

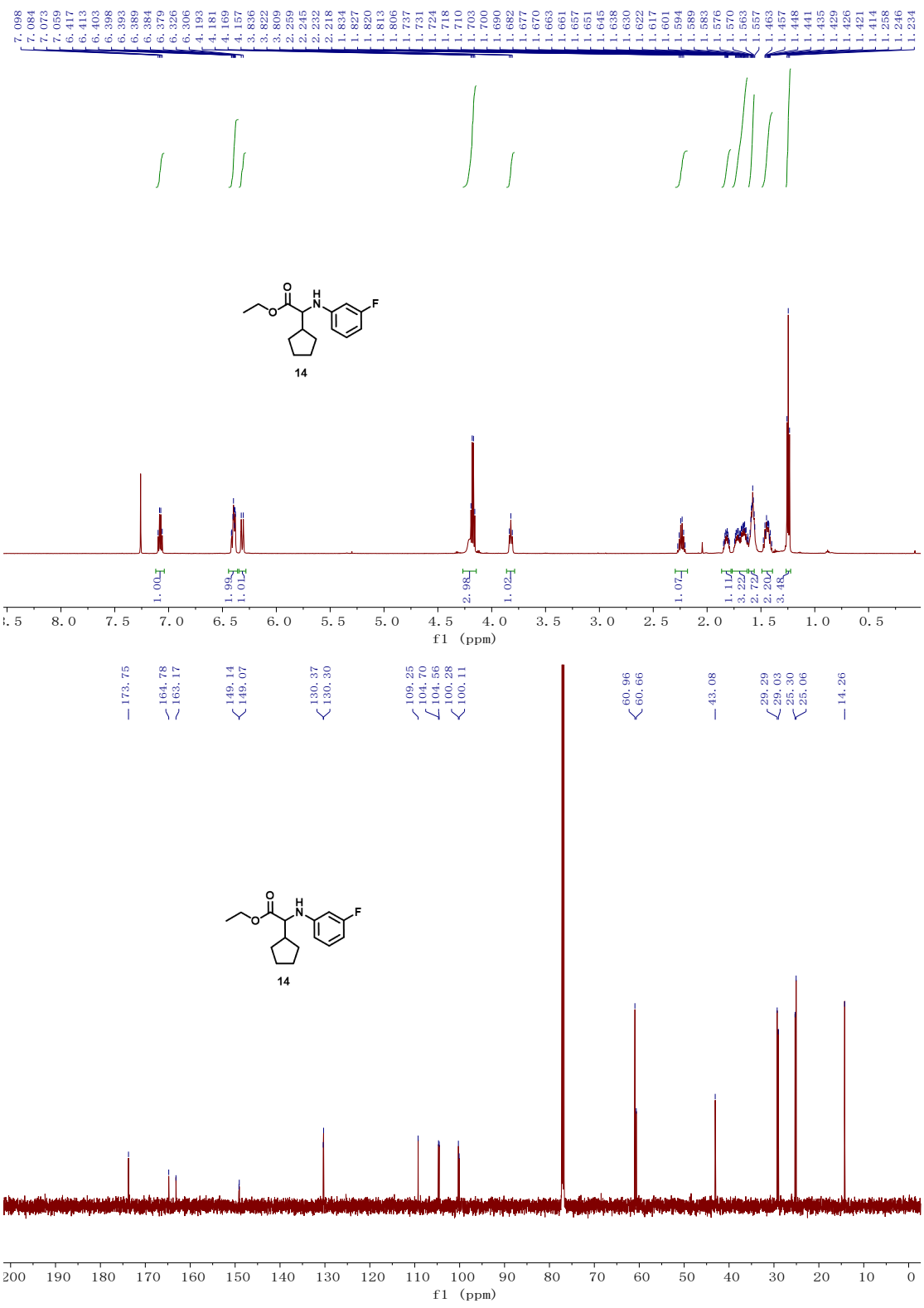

-61.18
O
O
H
N
F
F
F
11
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

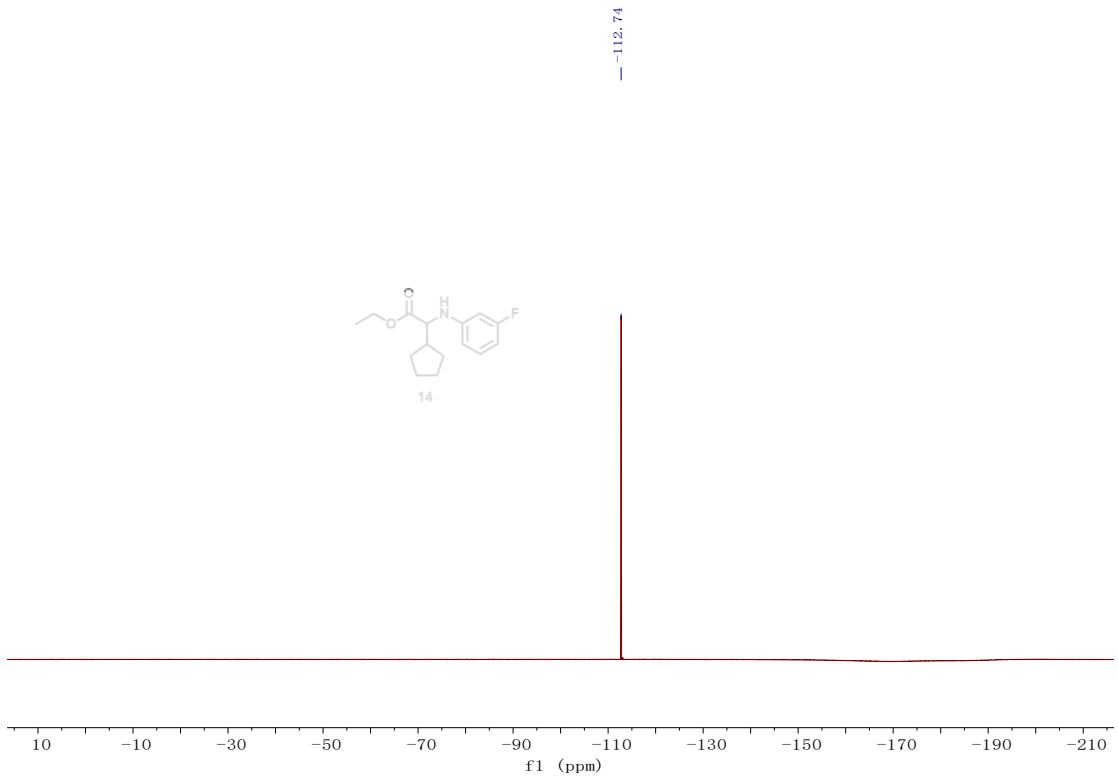

7.260
6.828
6.815
6.803
6.773
6.761
6.687
6.674
6.661
6.577
6.564
4.173
4.161
4.149
4.138
3.853
3.843
2.323
2.309
2.296
2.282
1.892
1.886
1.879
1.872
1.865
1.858
1.852
1.755
1.748
1.741
1.735
1.728
1.721
1.715
1.712
1.708
1.695
1.687
1.681
1.675
1.673
1.668
1.665
1.656
1.650
1.643
1.627
1.622
1.609
1.603
1.596
1.590
1.585
1.579
1.572
1.566
1.559
1.553
1.503
1.499
1.489
1.485
1.476
1.464
1.455
1.451
1.241
1.229
1.217
12
1.01
0.99
1.00
1.00
0.89
2.01
4.10
1.03
1.09
1.20
2.13
2.36
2.14
3.09
f1 (ppm)

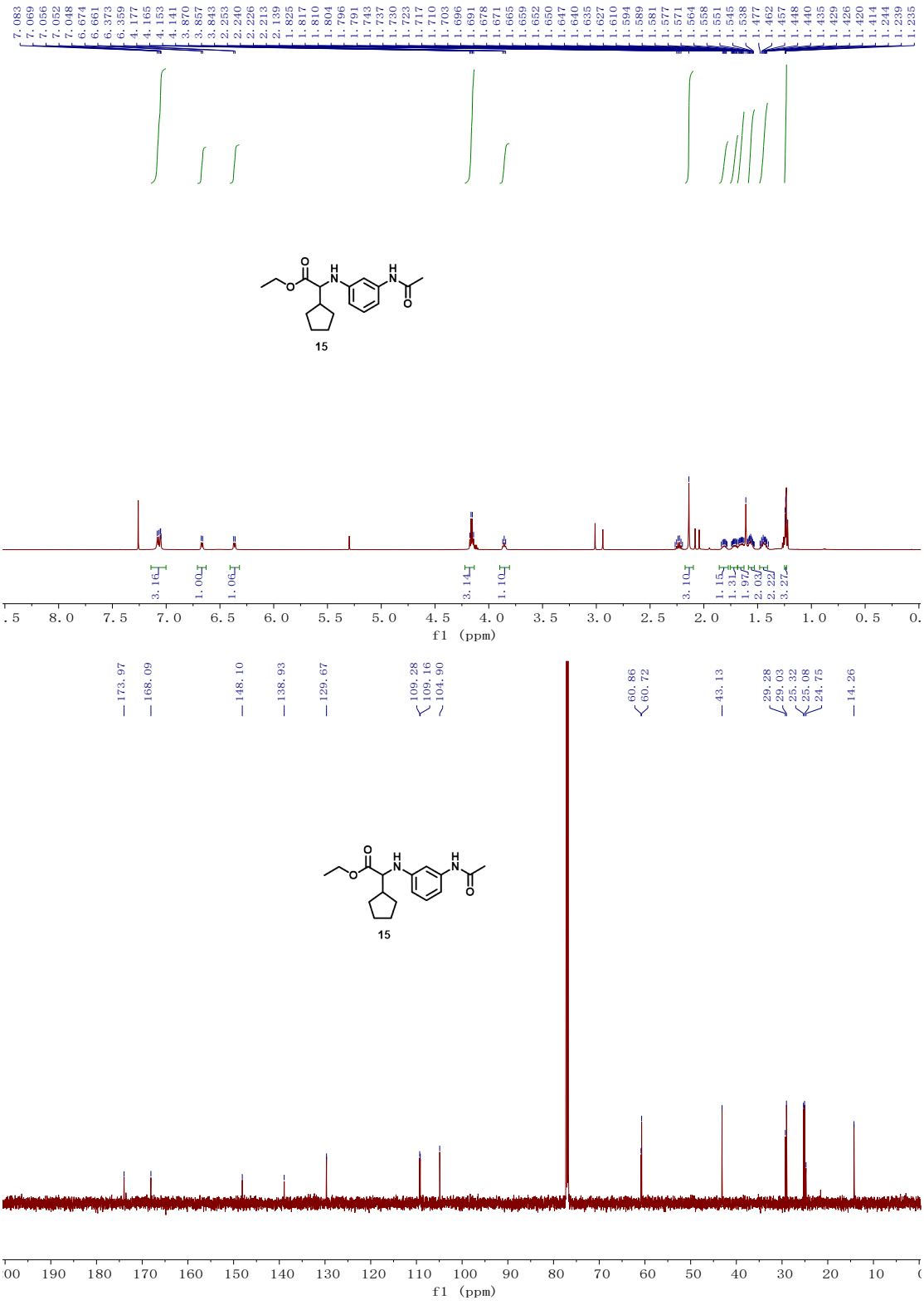

174.18
146.97
137.28
121.11
117.21
110.32
109.73
60.70
60.68
55.50
43.12
29.50
29.10
25.32
25.10
14.26
12
f1 (ppm)

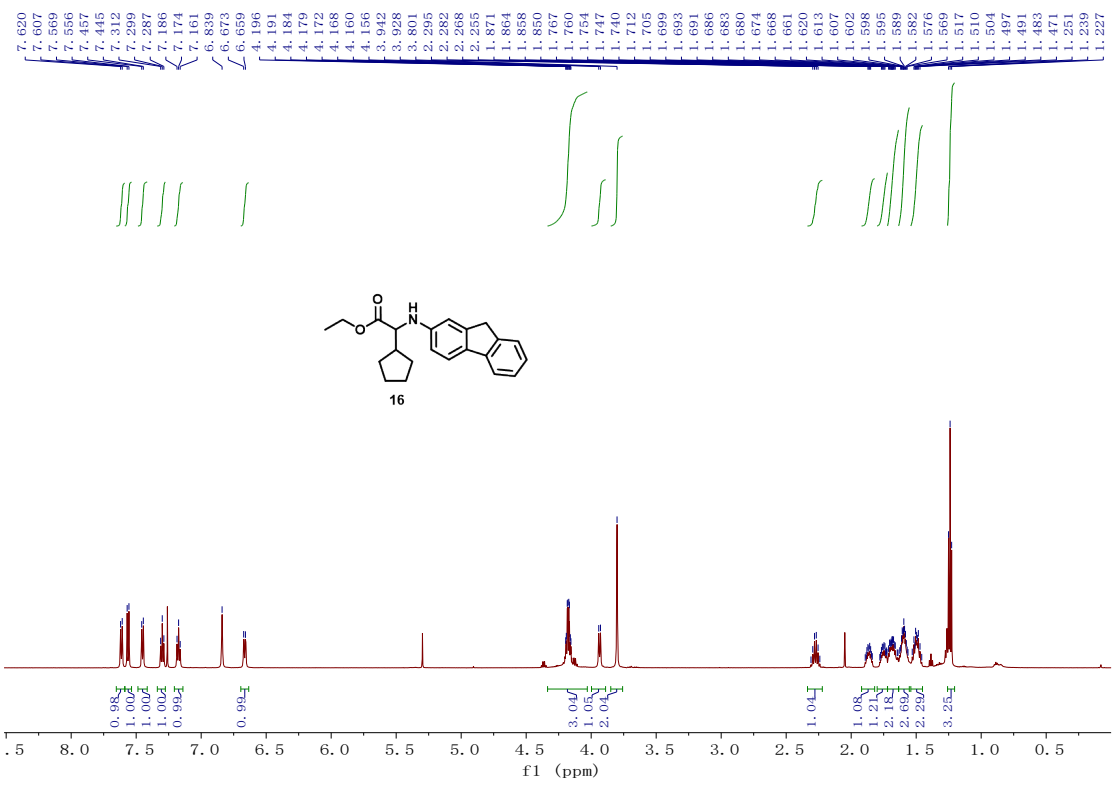

7.364
7.361
7.351
7.348
7.254
7.251
7.108
7.095
4.228
4.222
4.216
4.210
4.198
4.186
4.182
4.170
4.159
4.152
4.147
4.141
4.019
4.006
3.874
2.339
2.326
2.312
2.299
2.238
1.865
1.857
1.851
1.844
1.837
1.774
1.767
1.760
1.754
1.746
1.702
1.695
1.688
1.682
1.676
1.673
1.670
1.664
1.658
1.650
1.635
1.620
1.614
1.606
1.602
1.596
1.593
1.589
1.583
1.576
1.570
1.563
1.504
1.497
1.490
1.483
1.477
1.469
1.456
1.276
1.264
1.252
13
1.00
1.03
1.04
2.12
0.88
1.05
3.16
1.12
3.16
1.10
1.11
2.08
2.47
2.14
3.61
f1 (ppm)

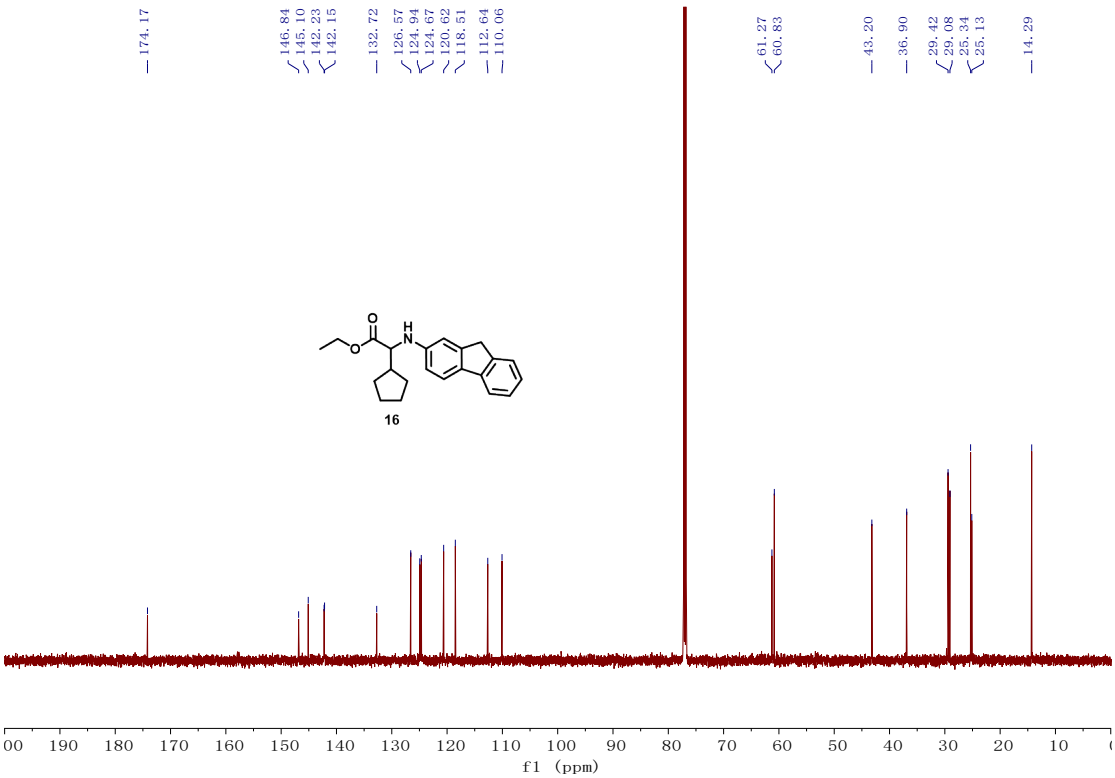

174.11
167.51
145.36
130.19
128.96
128.08
119.27
111.11
60.95
60.40
51.88
43.24
29.30
29.05
25.34
25.09
17.71
14.24
13
f1 (ppm)

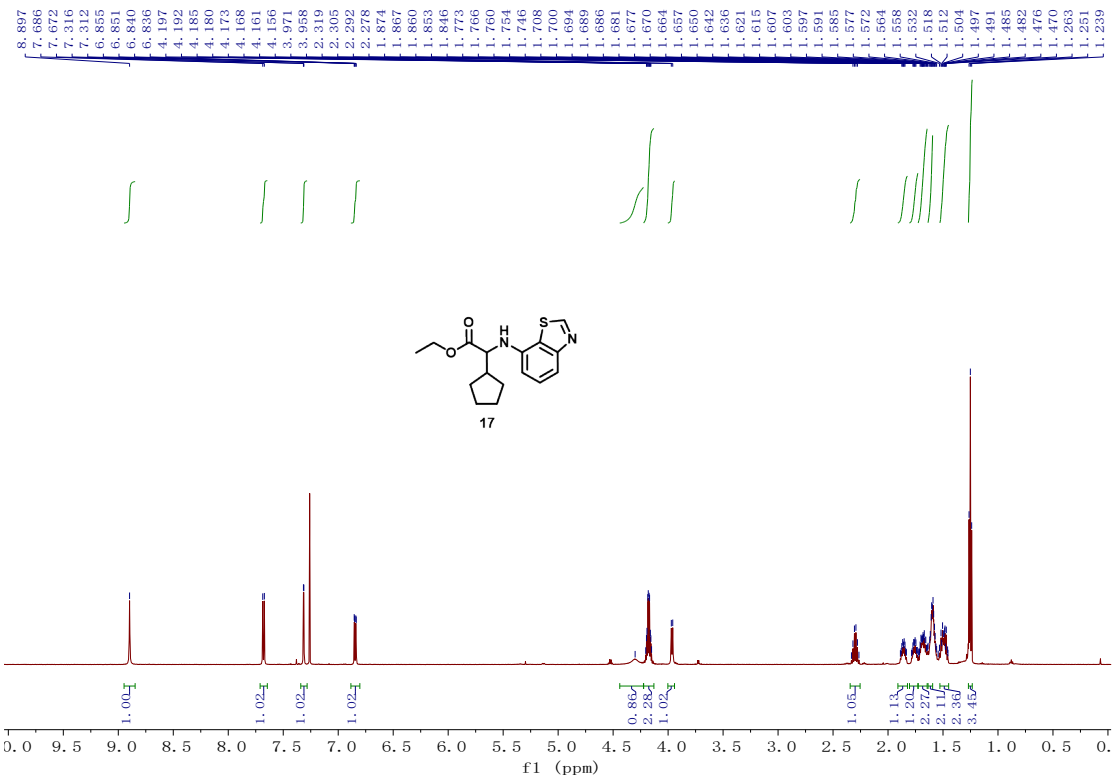

7.098
7.084
7.073
7.059
6.417
6.413
6.403
6.398
6.393
6.389
6.384
6.379
6.326
6.306
4.193
4.181
4.169
4.157
3.836
3.822
3.809
2.259
2.245
2.232
2.218
1.834
1.827
1.820
1.813
1.806
1.737
1.731
1.724
1.718
1.710
1.703
1.700
1.690
1.682
1.677
1.670
1.663
1.661
1.657
1.651
1.645
1.638
1.630
1.622
1.617
1.601
1.594
1.589
1.583
1.576
1.570
1.563
1.557
1.463
1.457
1.448
1.441
1.435
1.429
1.426
1.421
1.414
1.258
1.246
1.234
O
O
H
N
F
14
1.00
1.99
1.01
2.98
1.02
1.07
1.11
3.22
2.72
2.20
3.48
f1 (ppm)
173.75
164.78
163.17
149.14
149.07
130.37
130.30
109.25
104.70
104.56
100.28
100.11
60.96
60.66
43.08
29.29
29.03
25.30
25.06
14.26
O
O
H
N
F
14
f1 (ppm)

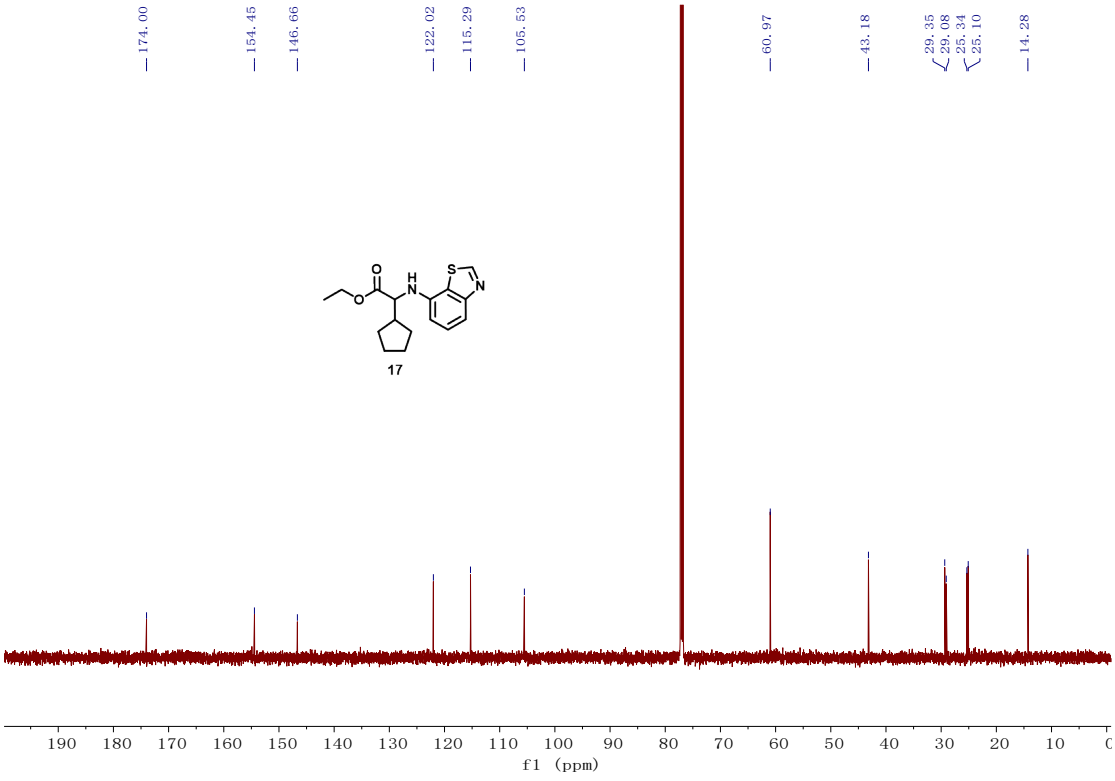

-112.74
O
O
H
N
F
14
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

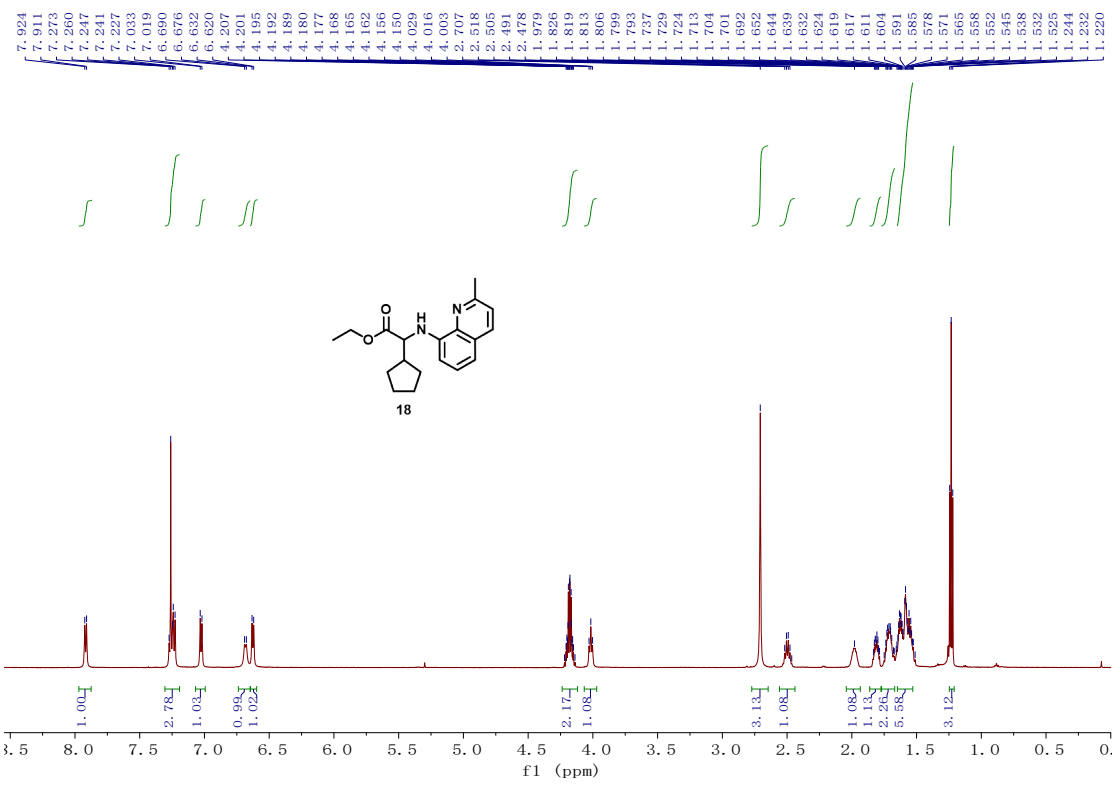

7.083
7.069
7.056
7.052
7.048
6.674
6.661
6.373
6.359
4.177
4.165
4.153
4.141
3.870
3.857
3.843
2.253
2.240
2.226
2.213
2.139
1.825
1.817
1.810
1.804
1.796
1.791
1.743
1.737
1.730
1.723
1.717
1.710
1.703
1.696
1.691
1.678
1.671
1.665
1.659
1.652
1.650
1.647
1.640
1.635
1.627
1.610
1.594
1.589
1.581
1.577
1.571
1.564
1.558
1.551
1.545
1.538
1.477
1.462
1.457
1.448
1.440
1.435
1.429
1.426
1.420
1.414
1.244
1.239
1.235
15
3.16
1.00
1.06
3.14
1.10
3.10
1.15
1.31
1.97
2.03
2.22
3.27
f1 (ppm)
173.97
168.09
148.10
138.93
129.67
109.28
109.16
104.90
60.86
60.72
43.13
29.28
29.03
25.32
25.08
24.75
14.26
15
f1 (ppm)

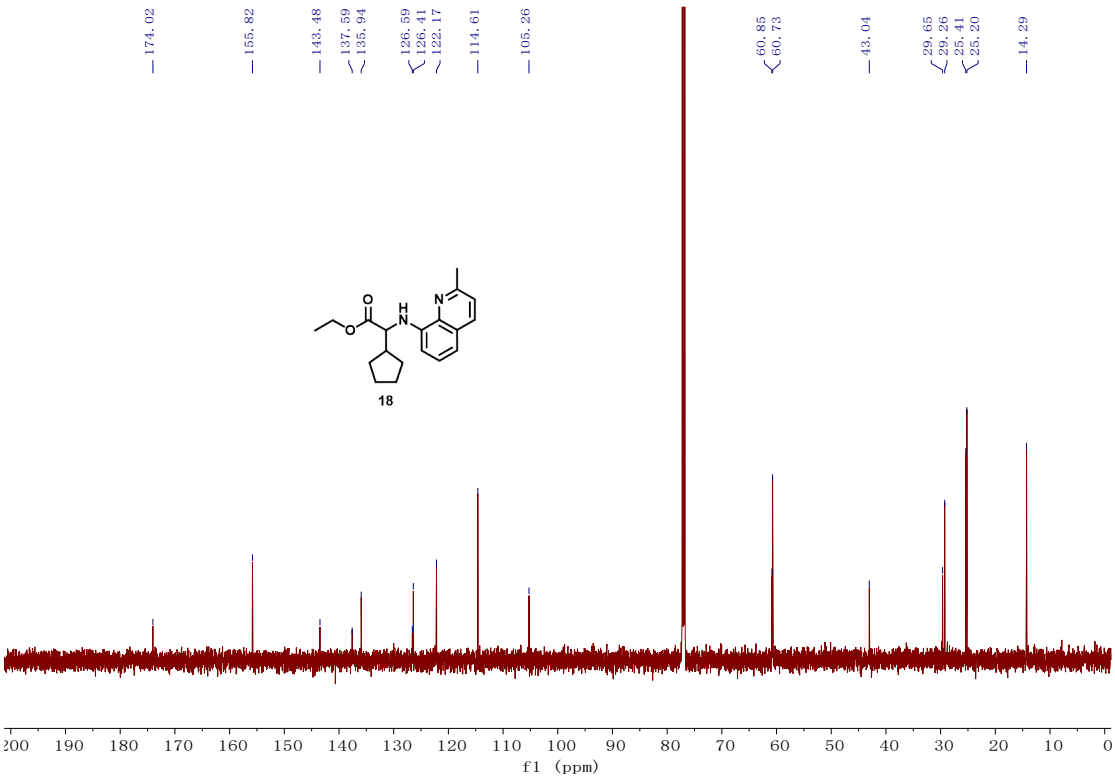

7.620
7.607
7.569
7.556
7.457
7.445
7.312
7.299
7.287
7.186
7.174
7.161
6.839
6.673
6.659
4.196
4.191
4.184
4.179
4.172
4.168
4.160
4.156
3.942
3.928
3.801
2.295
2.282
2.268
2.255
1.871
1.864
1.858
1.850
1.767
1.760
1.754
1.747
1.740
1.712
1.705
1.699
1.693
1.691
1.686
1.683
1.680
1.674
1.668
1.661
1.620
1.613
1.607
1.602
1.598
1.595
1.589
1.582
1.576
1.569
1.517
1.510
1.504
1.497
1.491
1.483
1.471
1.251
1.239
1.227
O
O
H
N
16
0.98
1.00
1.00
0.99
0.99
3.04
1.05
2.04
1.04
1.08
1.21
2.18
2.69
2.29
3.25
f1 (ppm)

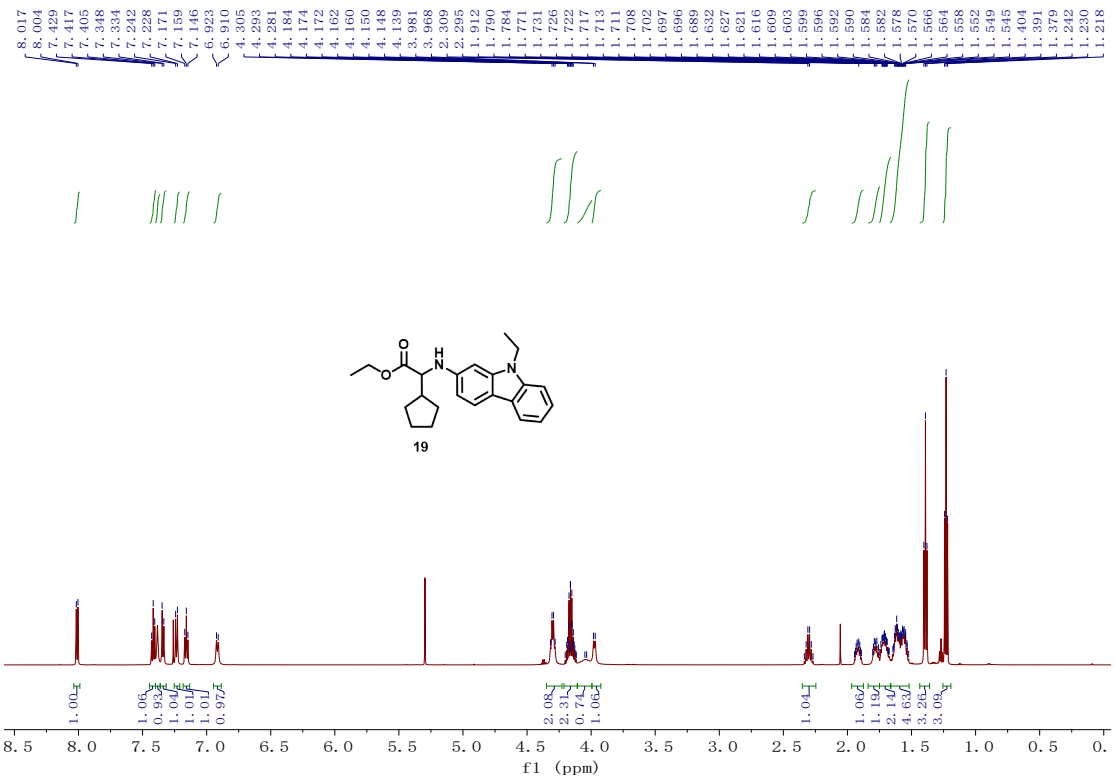

174.17
146.84
145.10
142.23
142.15
132.72
126.57
124.94
124.67
120.62
118.51
112.64
110.06
61.27
60.83
43.20
36.90
29.42
29.08
25.34
25.13
14.29
O
O
H
N
16
f1 (ppm)

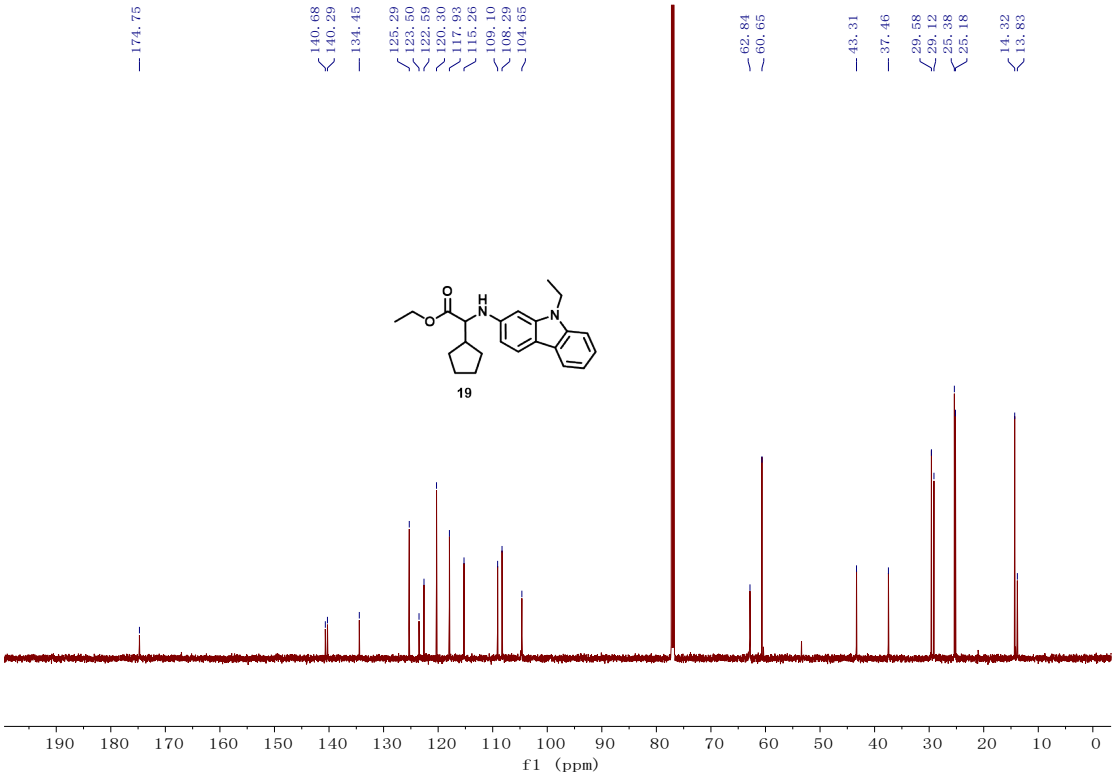

8.897
7.686
7.672
7.316
7.312
6.855
6.851
6.840
6.836
4.197
4.192
4.185
4.180
4.173
4.168
4.161
4.156
3.971
3.958
2.319
2.305
2.292
2.278
1.874
1.867
1.860
1.853
1.846
1.773
1.766
1.760
1.754
1.746
1.708
1.700
1.694
1.689
1.686
1.681
1.677
1.670
1.664
1.657
1.650
1.642
1.636
1.621
1.615
1.607
1.603
1.597
1.591
1.585
1.577
1.572
1.564
1.558
1.532
1.518
1.512
1.504
1.497
1.491
1.485
1.482
1.476
1.470
1.263
1.251
1.239
O
O
H
N
S
N
17
1.00
1.02
1.02
1.02
0.86
2.28
1.02
1.05
1.13
1.20
2.27
2.11
2.36
3.45
f1 (ppm)

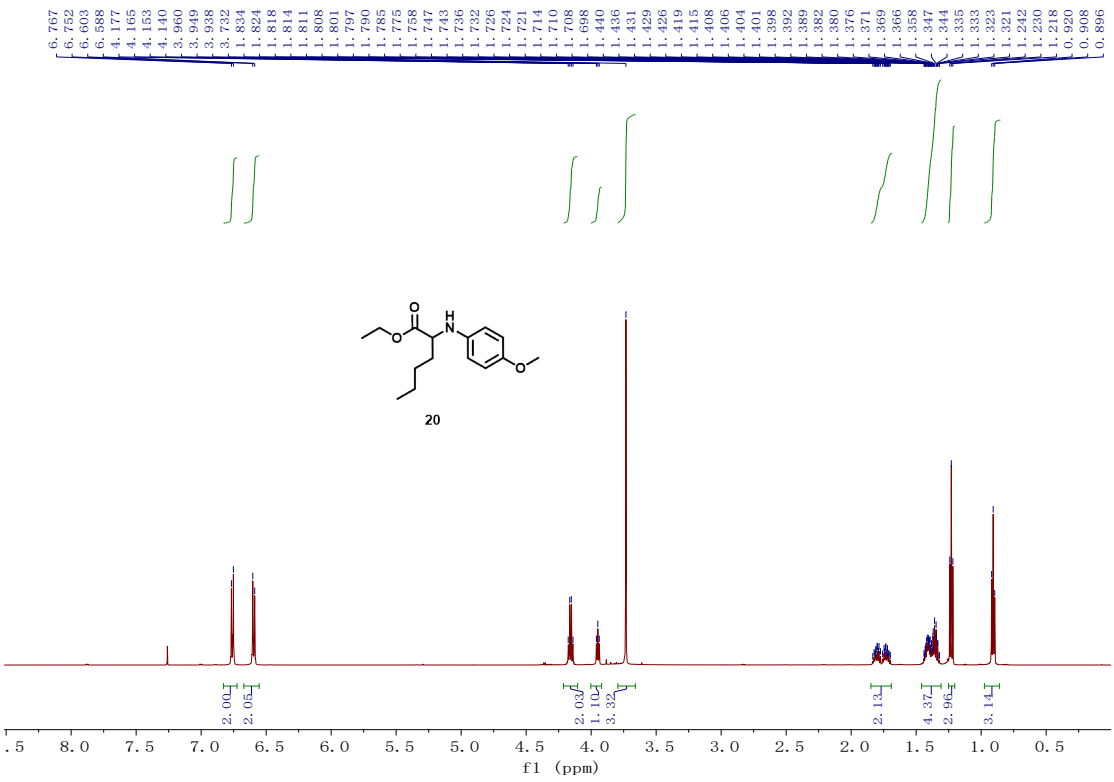

174.00
154.45
146.66
122.02
115.29
105.53
60.97
43.18
29.35
29.08
25.34
25.10
14.28
O
O
H
N
S
N
17
f1 (ppm)

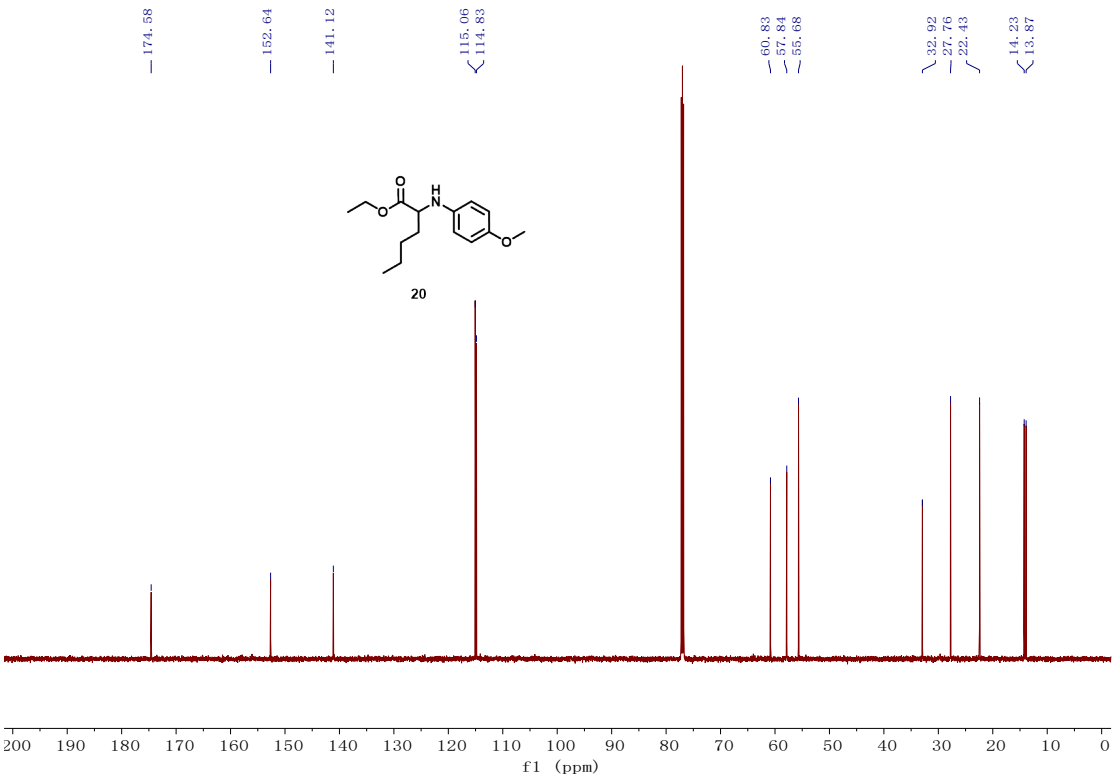

7.924
7.911
7.273
7.260
7.247
7.241
7.227
7.033
7.019
6.690
6.676
6.632
6.620
4.207
4.201
4.195
4.192
4.189
4.180
4.177
4.168
4.165
4.162
4.156
4.150
4.029
4.016
4.003
2.707
2.518
2.505
2.491
2.478
1.979
1.826
1.819
1.813
1.806
1.799
1.793
1.737
1.729
1.724
1.713
1.704
1.701
1.692
1.652
1.644
1.639
1.632
1.624
1.619
1.617
1.611
1.604
1.591
1.585
1.578
1.571
1.565
1.558
1.552
1.545
1.538
1.532
1.525
1.244
1.232
1.220
18
1.00
2.78
1.03
0.99
1.02
2.17
1.08
3.13
1.08
1.08
1.13
2.26
5.58
3.12
f1 (ppm)

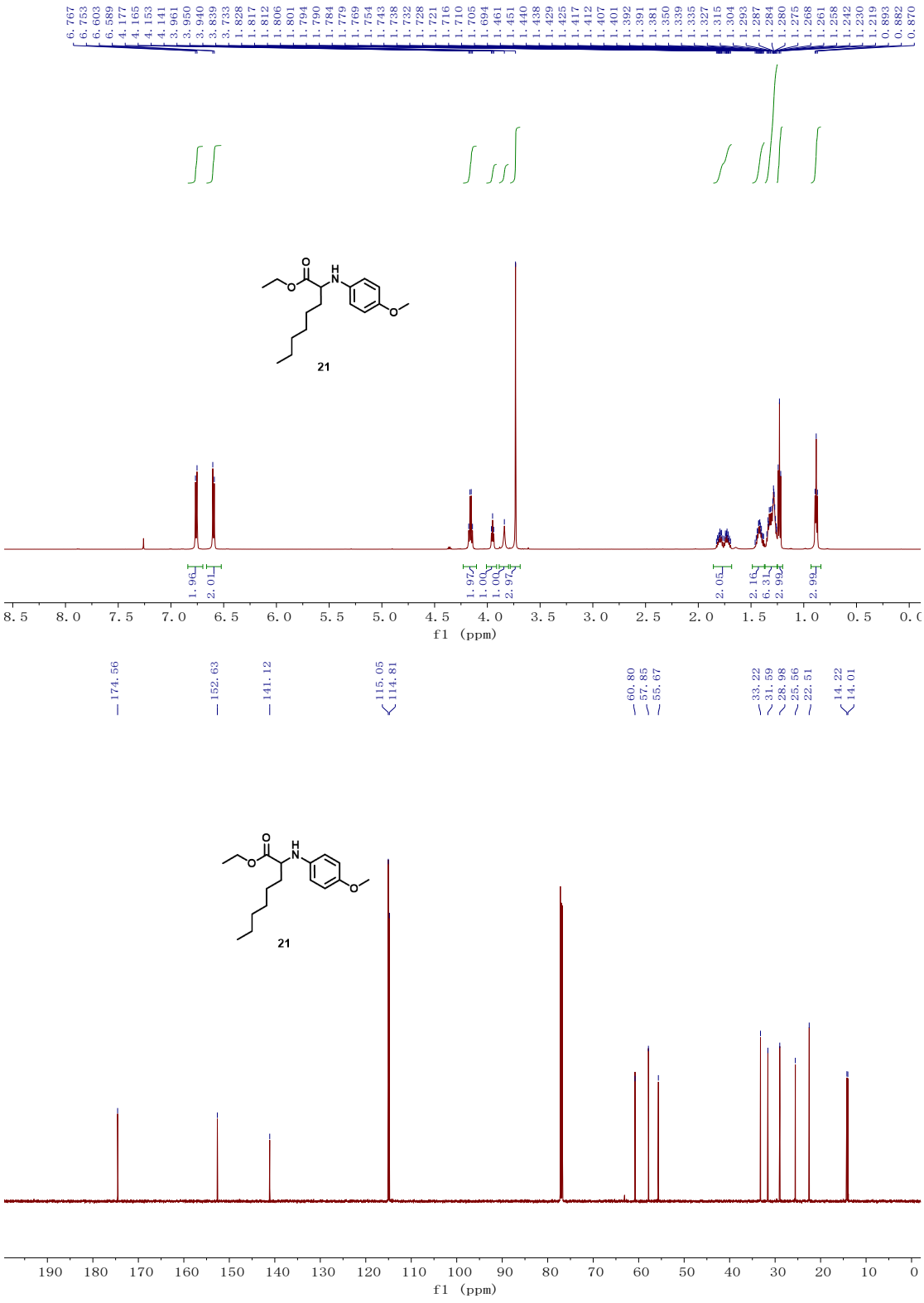

174.02
155.82
143.48
137.59
135.94
126.59
126.41
122.17
114.61
105.26
60.85
60.73
43.04
29.65
29.26
25.41
25.20
14.29
18
f1 (ppm)

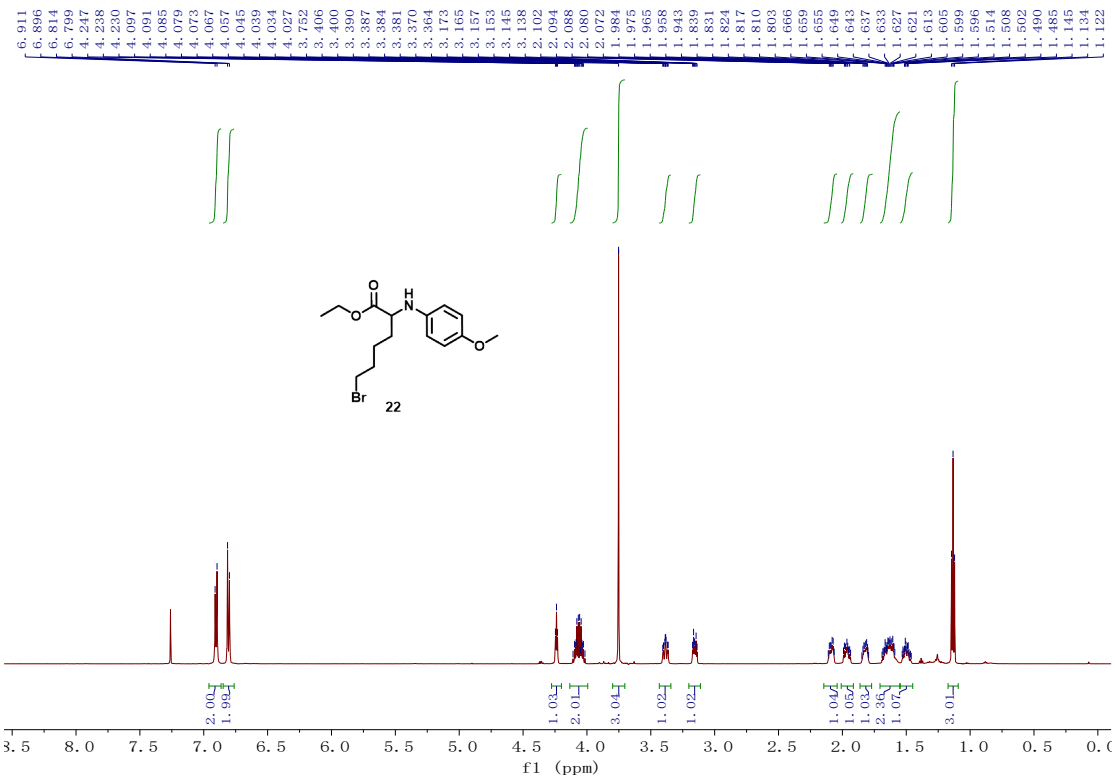

8.017
8.004
7.429
7.417
7.405
7.348
7.334
7.242
7.228
7.171
7.159
7.146
6.923
6.910
4.305
4.293
4.281
4.184
4.174
4.172
4.162
4.160
4.150
4.148
4.139
3.981
3.968
2.309
2.295
1.912
1.790
1.784
1.771
1.731
1.726
1.722
1.717
1.713
1.711
1.708
1.702
1.697
1.696
1.689
1.632
1.627
1.621
1.616
1.609
1.603
1.599
1.596
1.592
1.590
1.584
1.582
1.578
1.570
1.566
1.564
1.558
1.552
1.549
1.545
1.404
1.391
1.379
1.242
1.230
1.218
19
1.00
1.06
0.93
1.04
1.01
1.01
0.97
2.08
2.31
0.74
1.06
1.04
1.06
1.19
2.14
4.63
3.26
3.09
f1 (ppm)

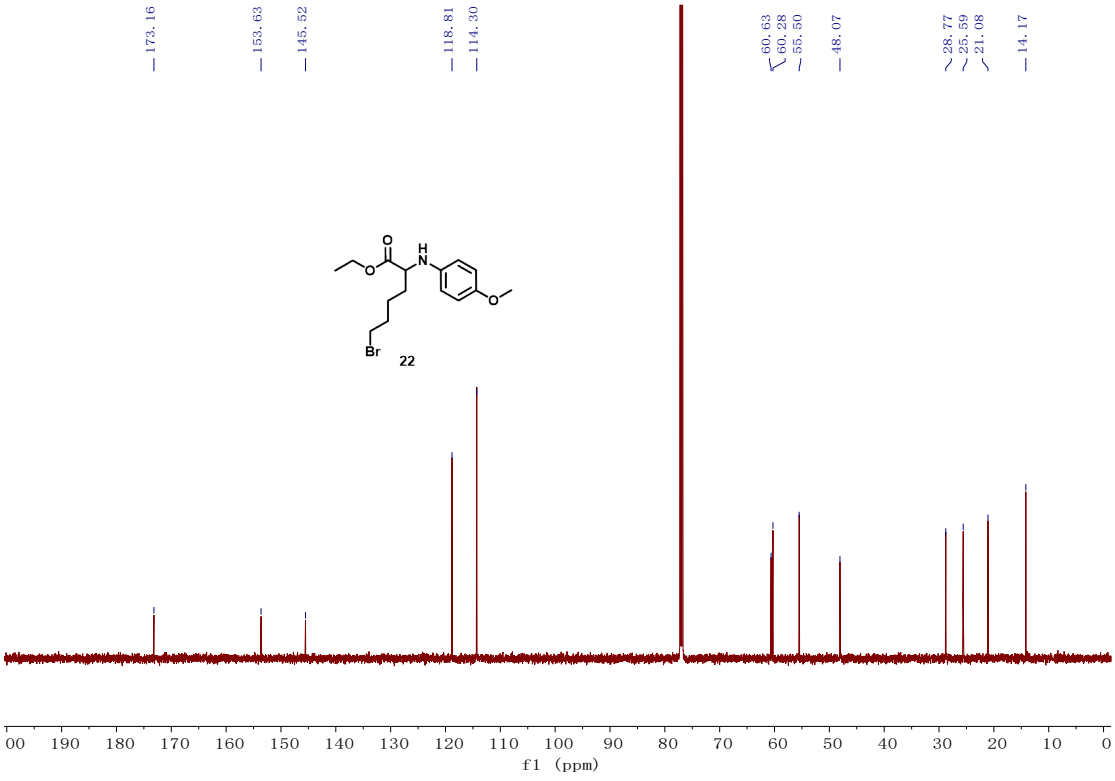

174.75
140.68
140.29
134.45
125.29
123.50
122.59
120.30
117.93
115.26
109.10
108.29
104.65
62.84
60.65
43.31
37.46
29.58
29.12
25.38
25.18
14.32
13.83
19
f1 (ppm)

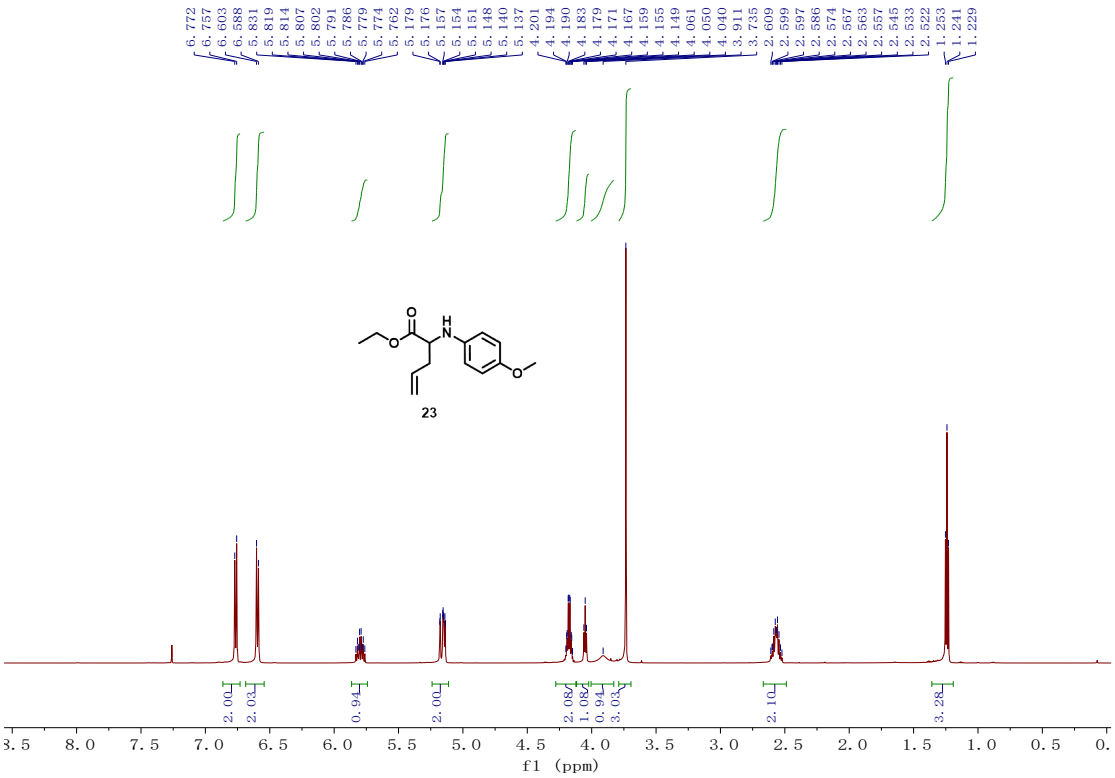

6.767
6.752
6.603
6.588
4.177
4.165
4.153
4.140
3.960
3.949
3.938
3.732
1.834
1.824
1.818
1.814
1.811
1.808
1.801
1.797
1.790
1.785
1.775
1.758
1.747
1.743
1.736
1.732
1.726
1.724
1.721
1.714
1.710
1.708
1.698
1.440
1.436
1.431
1.429
1.426
1.419
1.415
1.408
1.406
1.404
1.401
1.398
1.392
1.389
1.382
1.380
1.376
1.371
1.369
1.366
1.358
1.347
1.344
1.335
1.333
1.323
1.321
1.242
1.230
1.218
0.920
0.908
0.896
20
2.00
2.05
2.03
1.10
3.32
2.13
4.37
2.96
3.14
f1 (ppm)

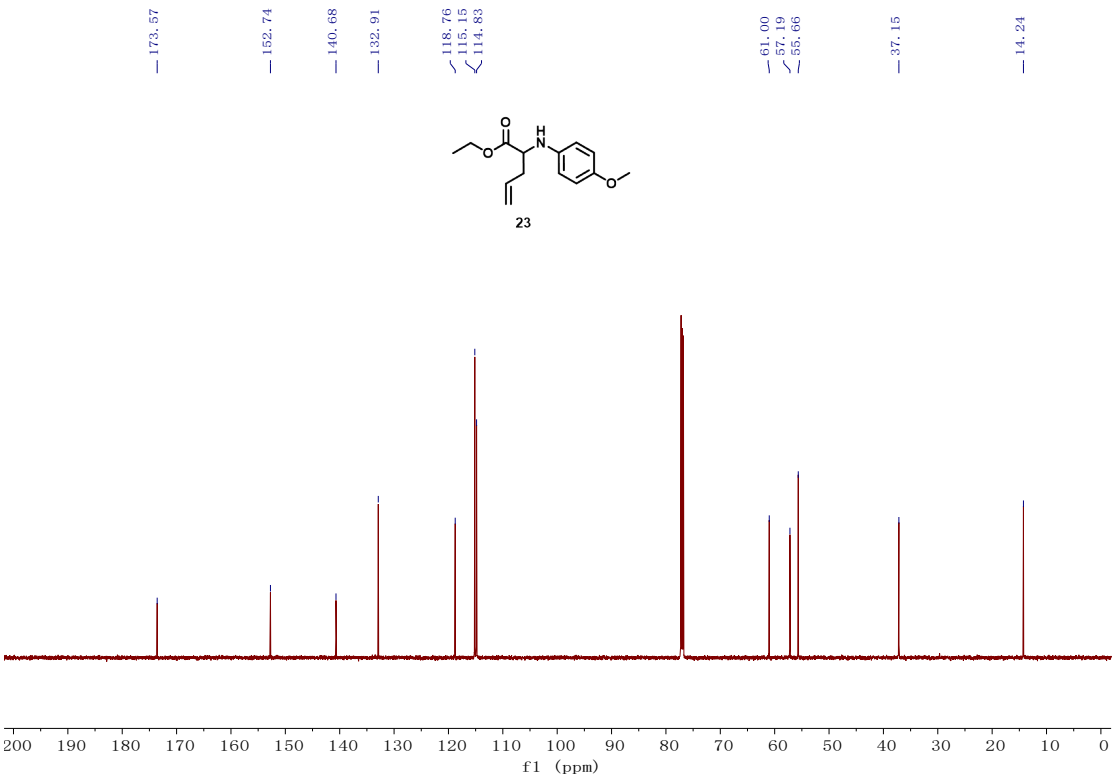

174.58
152.64
141.12
115.06
114.83
60.83
57.84
55.68
32.92
27.76
22.43
14.23
13.87
20
f1 (ppm)

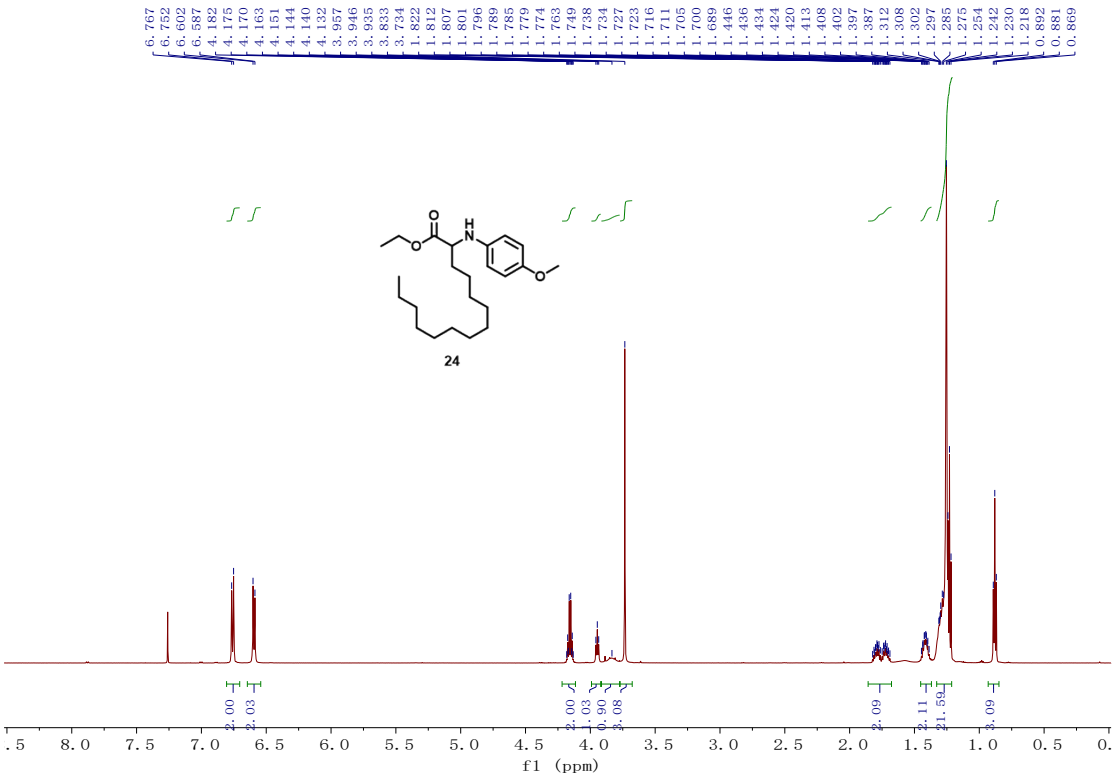

6.767
6.753
6.603
6.589
4.177
4.165
4.153
4.141
3.961
3.950
3.940
3.839
3.733
1.828
1.817
1.812
1.806
1.801
1.794
1.790
1.784
1.779
1.769
1.754
1.743
1.738
1.732
1.728
1.721
1.716
1.710
1.705
1.694
1.461
1.451
1.440
1.438
1.429
1.425
1.417
1.412
1.407
1.401
1.392
1.391
1.381
1.350
1.339
1.335
1.327
1.315
1.304
1.293
1.287
1.284
1.280
1.275
1.268
1.261
1.258
1.242
1.230
1.219
0.893
0.882
0.870
O
O
H
N
O
21
1.96
2.01
1.97
1.00
1.00
2.97
2.05
2.16
6.31
2.92
2.99
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
f1 (ppm)
174.56
152.63
141.12
115.05
114.81
60.80
57.85
55.67
33.22
31.59
28.98
25.56
22.51
14.22
14.01
O
O
H
N
O
21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

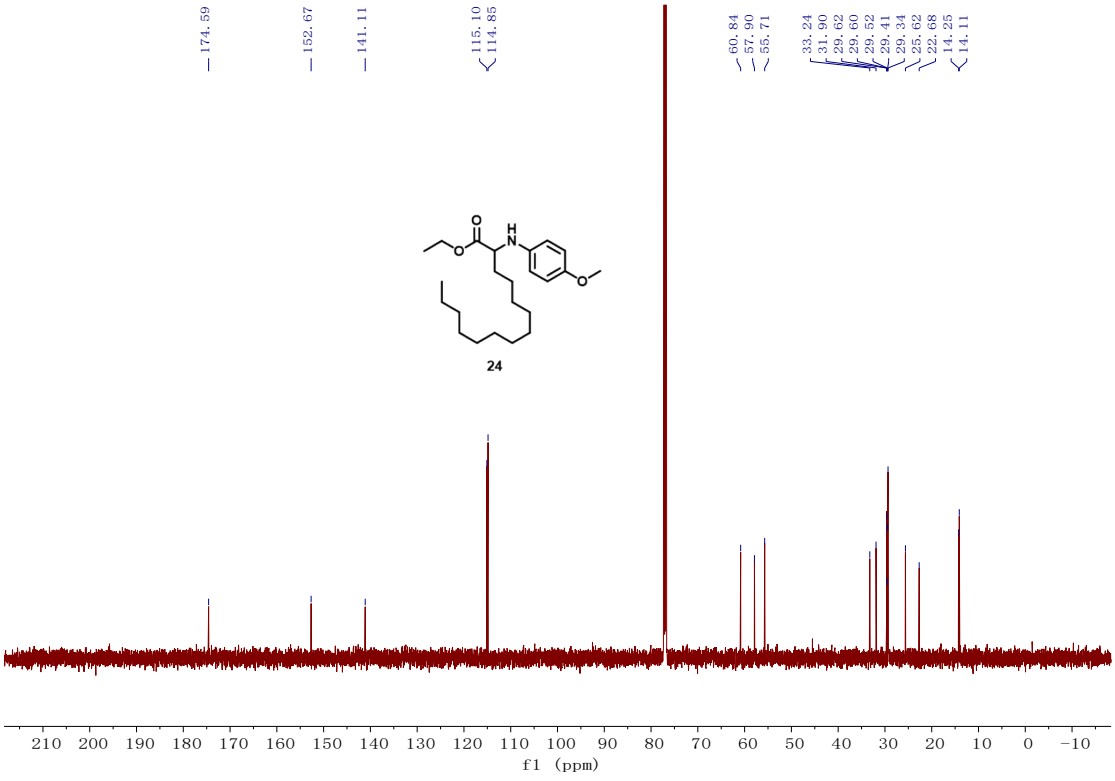

6.911
6.896
6.814
6.799
4.247
4.238
4.230
4.097
4.091
4.085
4.079
4.073
4.067
4.057
4.045
4.039
4.034
4.027
3.752
3.406
3.400
3.390
3.387
3.384
3.381
3.370
3.364
3.173
3.165
3.157
3.153
3.145
3.138
2.102
2.094
2.088
2.080
2.072
1.984
1.975
1.965
1.958
1.943
1.839
1.831
1.824
1.817
1.810
1.803
1.666
1.659
1.655
1.649
1.643
1.637
1.633
1.627
1.621
1.613
1.605
1.599
1.596
1.514
1.508
1.502
1.490
1.485
1.145
1.134
1.122
O
O
H
N
O
Br
22
2.00
1.99
1.03
2.01
3.04
1.02
1.02
1.04
1.05
1.03
2.36
1.07
3.01
f1 (ppm)

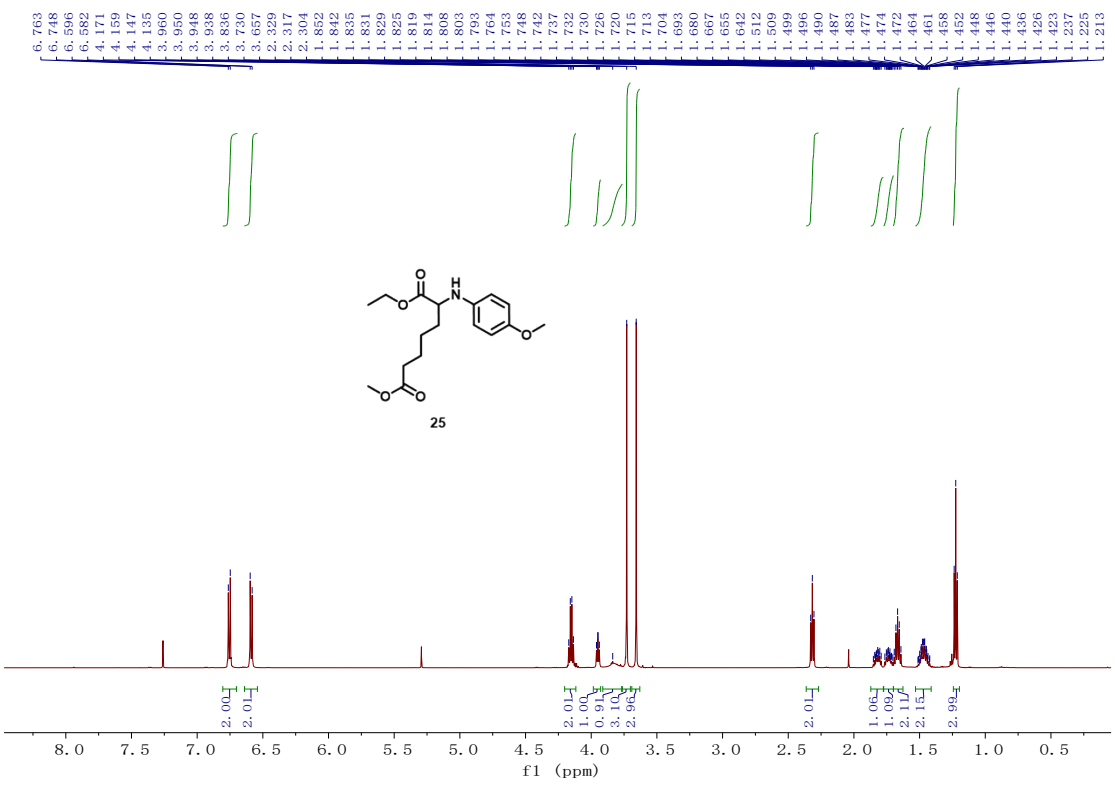

173.16
153.63
145.52
118.81
114.30
60.63
60.28
55.50
48.07
28.77
25.59
21.08
14.17
O
O
H
N
O
Br
22
f1 (ppm)

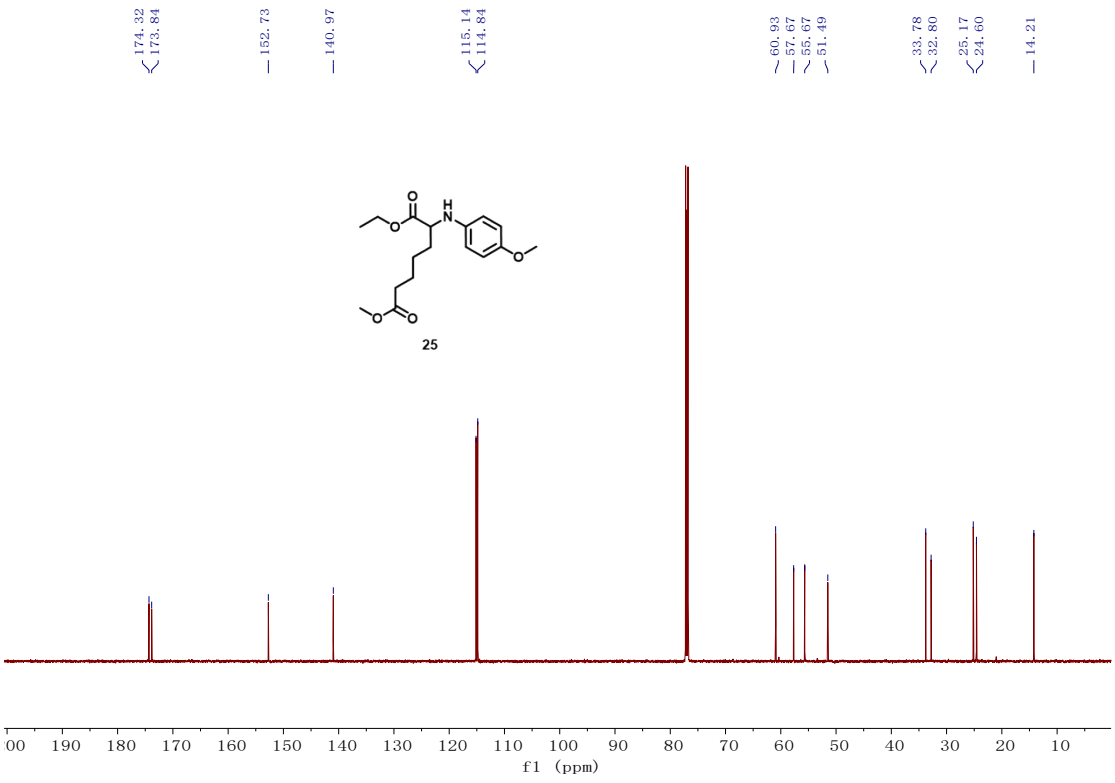

6.772
6.757
6.603
6.588
5.831
5.819
5.814
5.807
5.802
5.791
5.786
5.779
5.774
5.762
5.179
5.176
5.157
5.154
5.151
5.148
5.140
5.137
4.201
4.194
4.190
4.183
4.179
4.171
4.167
4.159
4.155
4.149
4.061
4.050
4.040
3.911
3.735
2.609
2.599
2.597
2.586
2.574
2.567
2.563
2.557
2.545
2.533
2.522
1.253
1.241
1.229
23
2.00
2.03
0.94
2.00
2.08
1.08
0.94
3.03
2.10
3.28
f1 (ppm)

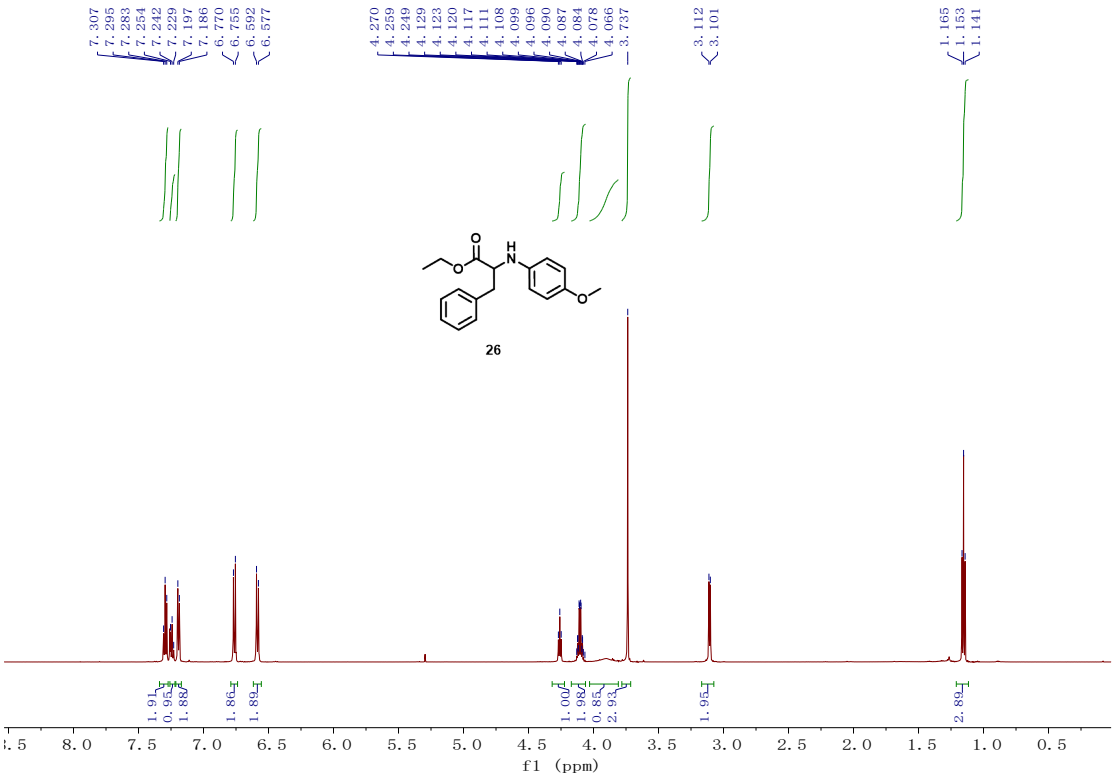

173.57
152.74
140.68
132.91
118.76
115.15
114.83
61.00
57.19
55.66
37.15
14.24
23
f1 (ppm)

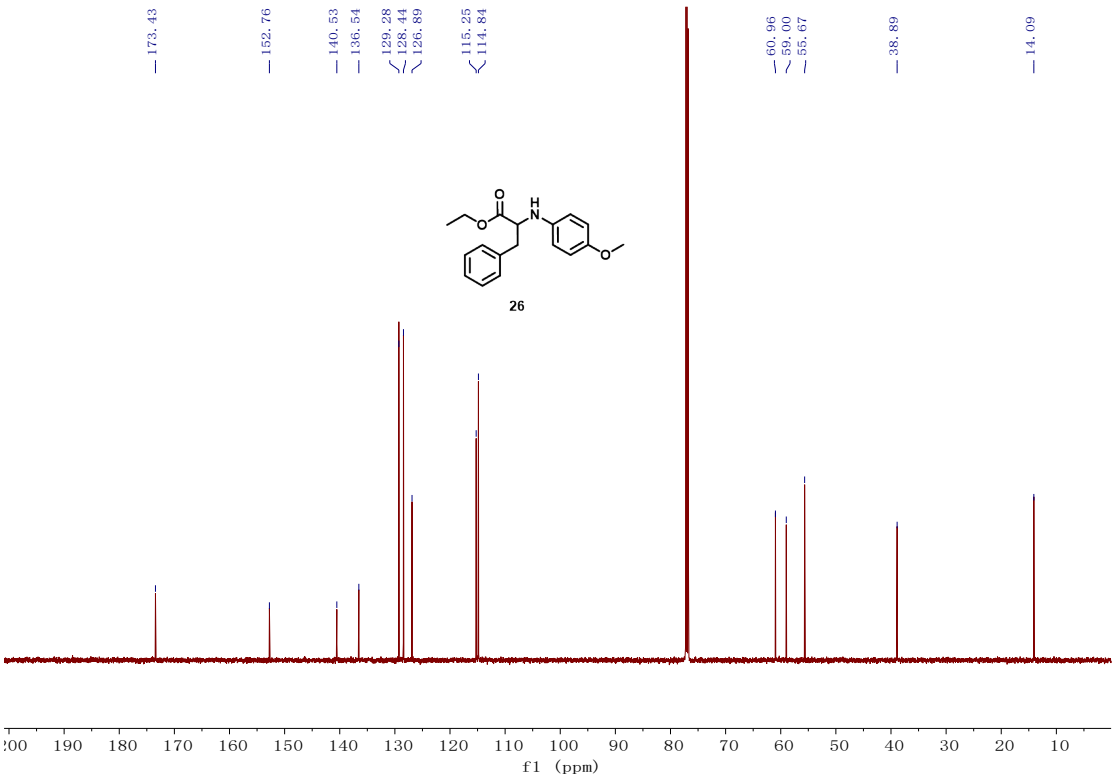

6.767
6.752
6.602
6.587
4.182
4.175
4.170
4.163
4.151
4.144
4.140
4.132
3.957
3.946
3.935
3.833
3.734
1.822
1.812
1.807
1.801
1.796
1.789
1.785
1.779
1.774
1.763
1.749
1.738
1.734
1.727
1.723
1.716
1.711
1.705
1.700
1.689
1.446
1.436
1.434
1.424
1.420
1.413
1.408
1.402
1.397
1.387
1.312
1.308
1.302
1.297
1.285
1.275
1.254
1.242
1.230
1.218
0.892
0.881
0.869
24
2.00
2.03
2.00
1.03
0.90
3.08
2.09
2.11
21.59
3.09
f1 (ppm)

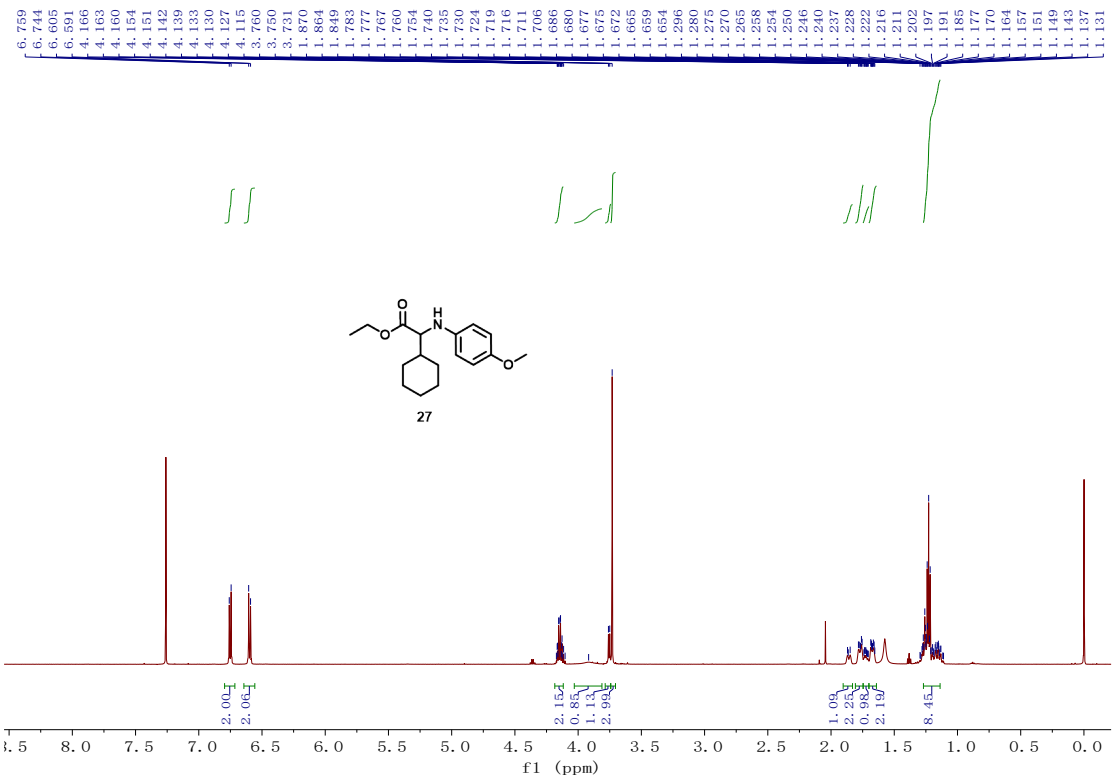

174.59
152.67
141.11
115.10
114.85
60.84
57.90
55.71
33.24
31.90
29.62
29.60
29.52
29.41
29.34
25.62
22.68
14.25
14.11
24
f1 (ppm)

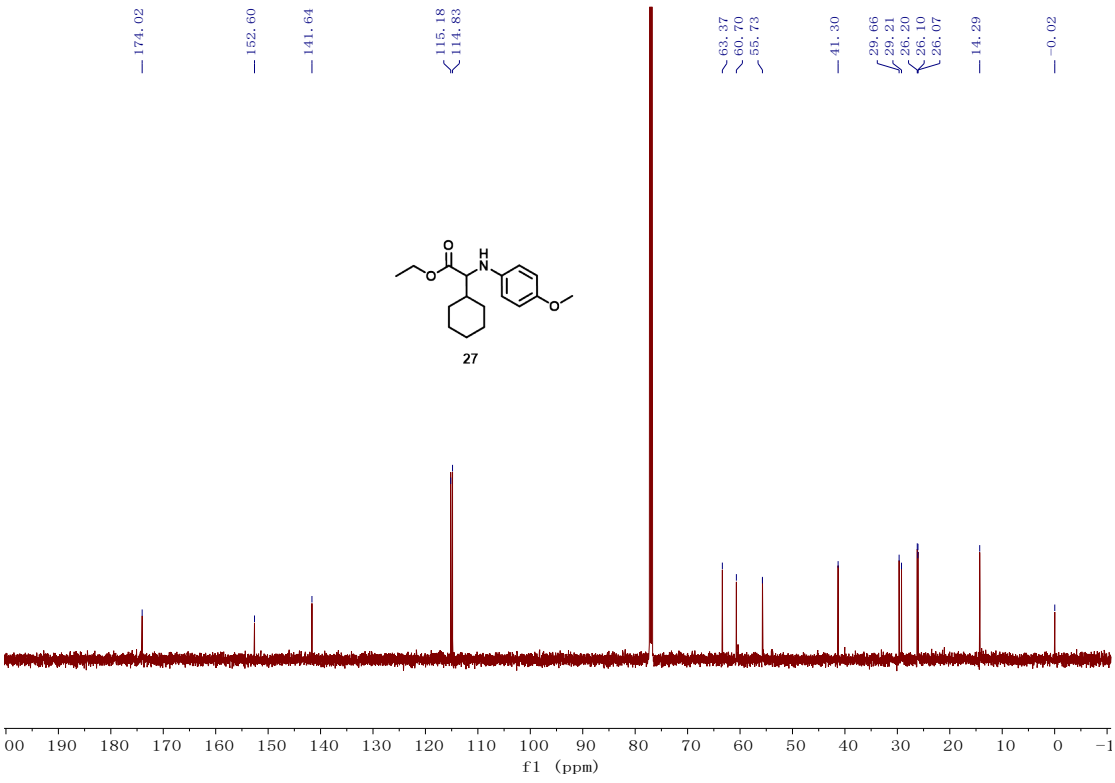

6.763
6.748
6.596
6.582
4.171
4.159
4.147
4.135
3.960
3.950
3.948
3.938
3.836
3.730
3.657
2.329
2.317
2.304
1.852
1.842
1.835
1.831
1.829
1.825
1.819
1.814
1.808
1.803
1.793
1.764
1.753
1.748
1.742
1.737
1.732
1.730
1.726
1.720
1.715
1.713
1.704
1.693
1.680
1.667
1.655
1.642
1.512
1.509
1.499
1.496
1.490
1.487
1.483
1.477
1.474
1.472
1.464
1.461
1.458
1.452
1.448
1.446
1.440
1.436
1.426
1.423
1.237
1.225
1.213
25
2.00
2.01
2.01
1.00
0.91
3.10
2.96
2.01
1.06
1.09
2.11
2.15
2.99
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
f1 (ppm)

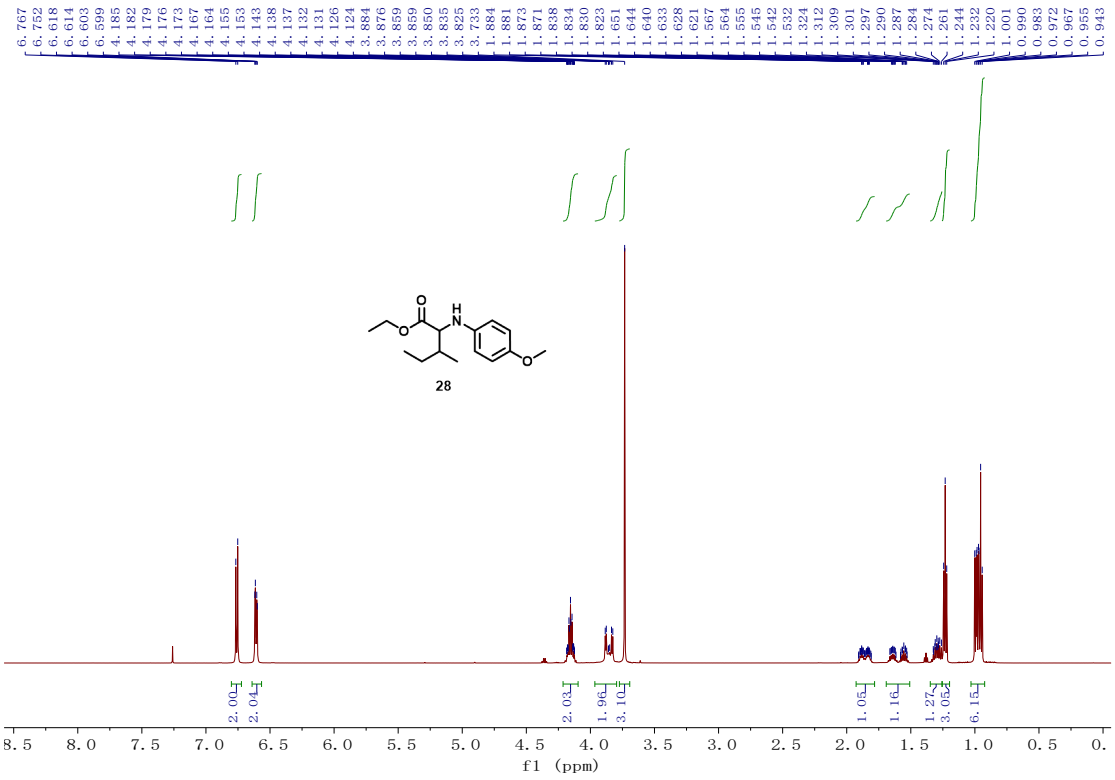

174.32
173.84
152.73
140.97
115.14
114.84
60.93
57.67
55.67
51.49
33.78
32.80
25.17
24.60
14.21
25
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

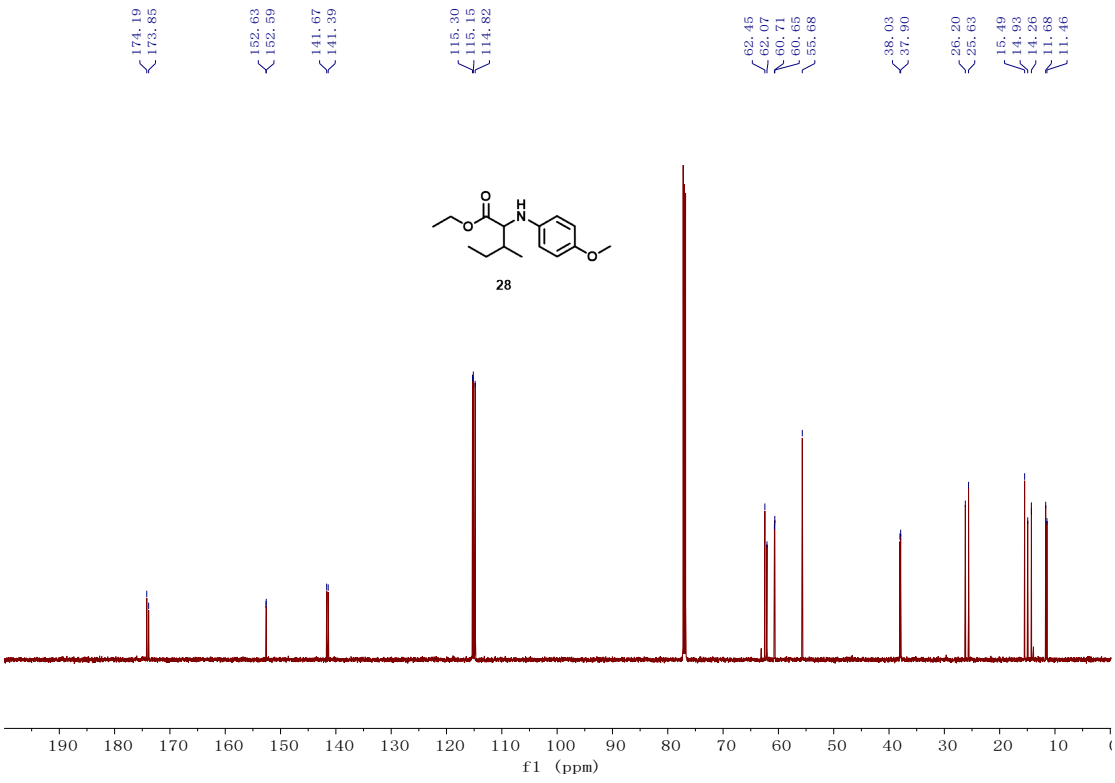

7.307
7.295
7.283
7.254
7.242
7.229
7.197
7.186
6.770
6.755
6.592
6.577
4.270
4.259
4.249
4.129
4.123
4.120
4.117
4.111
4.108
4.099
4.096
4.090
4.087
4.084
4.078
4.066
3.737
3.112
3.101
1.165
1.153
1.141
26
1.91
0.95
1.88
1.86
1.89
1.00
1.98
0.85
2.93
1.95
2.89
f1 (ppm)

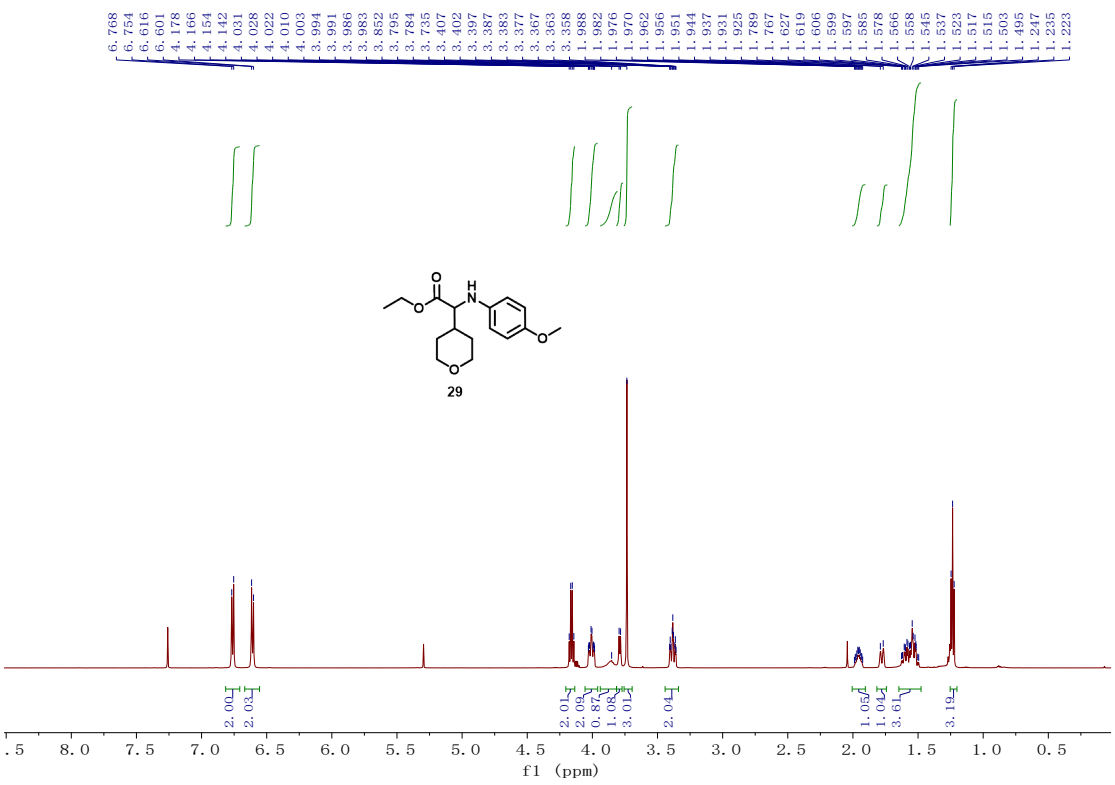

173.43
152.76
140.53
136.54
129.28
128.44
126.89
115.25
114.84
60.96
59.00
55.67
38.89
14.09
26
f1 (ppm)

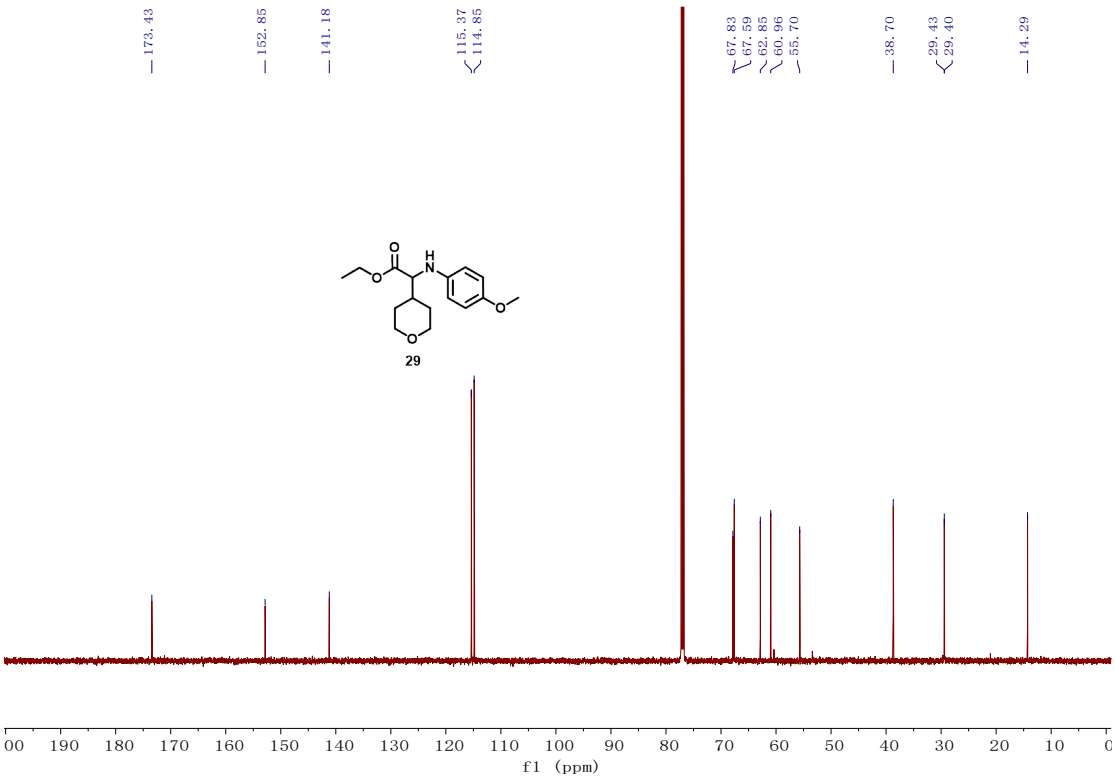

6.759
6.744
6.605
6.591
4.166
4.163
4.160
4.154
4.151
4.142
4.139
4.133
4.130
4.127
4.115
3.760
3.750
3.731
1.870
1.864
1.849
1.783
1.777
1.767
1.760
1.754
1.740
1.735
1.730
1.724
1.719
1.716
1.711
1.706
1.686
1.680
1.677
1.675
1.672
1.665
1.659
1.654
1.296
1.280
1.275
1.270
1.265
1.258
1.254
1.250
1.246
1.240
1.237
1.228
1.222
1.216
1.211
1.202
1.197
1.191
1.185
1.177
1.170
1.164
1.157
1.151
1.149
1.143
1.137
1.131
27
2.00
2.06
2.15
0.85
1.13
2.99
1.09
2.25
0.98
2.19
8.45
f1 (ppm)

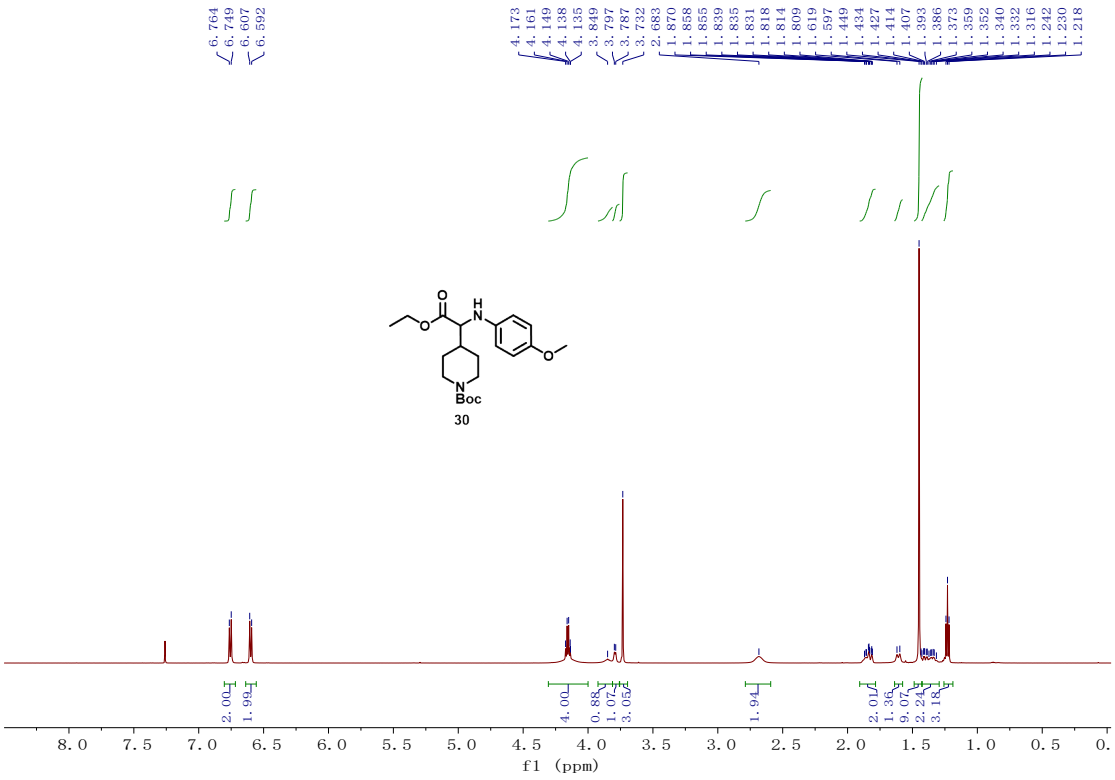

174.02
152.60
141.64
115.18
114.83
63.37
60.70
55.73
41.30
29.66
29.21
26.20
26.10
26.07
14.29
-0.02
27
f1 (ppm)

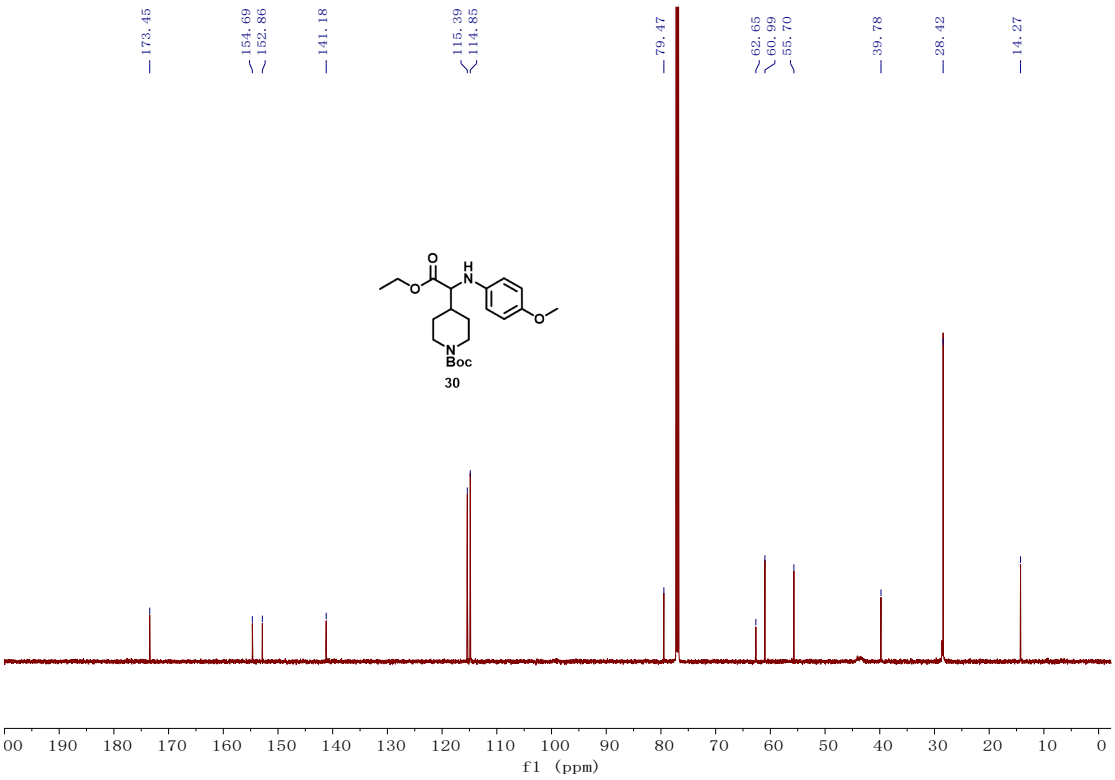

6.767 6.752 6.618 6.614 6.603 6.599 4.185 4.182 4.179 4.176 4.173 4.167 4.164 4.155 4.153 4.143 4.138 4.137 4.132 4.131 4.126 4.124 3.884 3.876 3.859 3.859 3.850 3.835 3.825 3.733 1.884 1.881 1.873 1.871 1.838 1.834 1.830 1.823 1.651 1.644 1.640 1.633 1.628 1.621 1.567 1.564 1.555 1.545 1.542 1.532 1.324 1.312 1.309 1.301 1.297 1.290 1.287 1.284 1.274 1.261 1.244 1.232 1.220 1.001 0.990 0.983 0.972 0.967 0.955 0.943
28
2.00 2.04 2.03 1.96 3.10 1.05 1.16 1.27 3.05 6.15
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.
f1 (ppm)

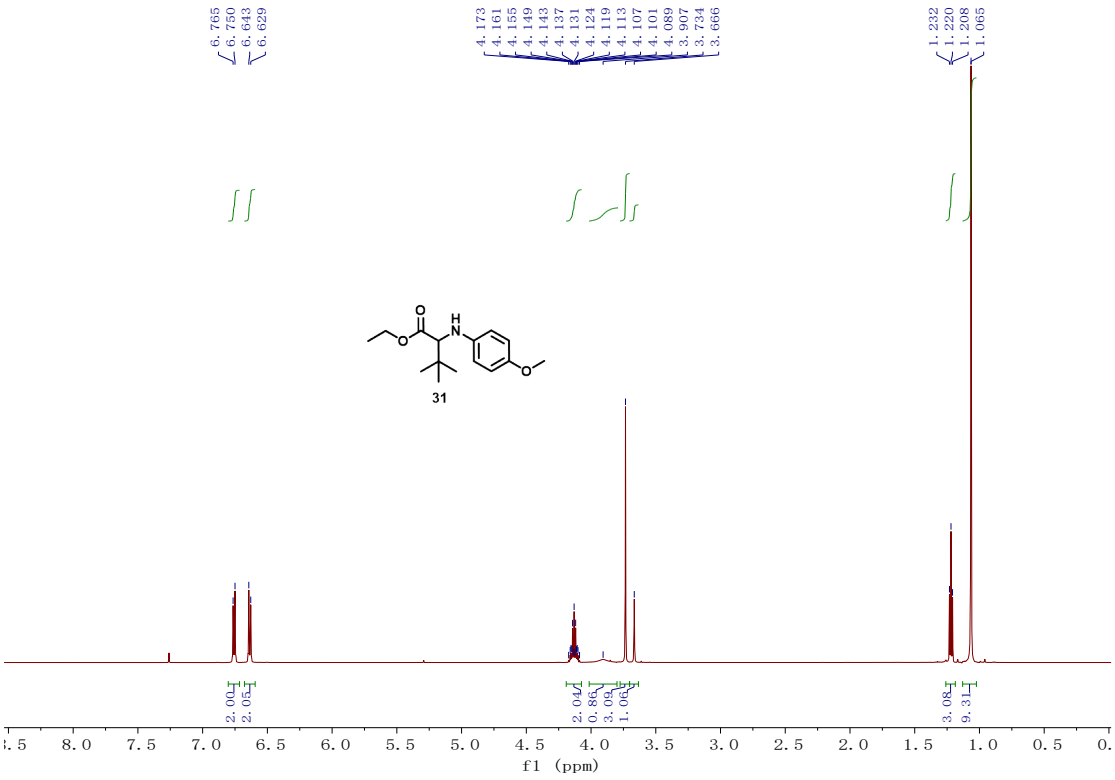

174.19 173.85 152.63 152.59 141.67 141.39 115.30 115.15 114.82 62.45 62.07 60.71 60.65 55.68 38.03 37.90 26.20 25.63 15.49 14.93 14.26 11.68 11.46
28
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

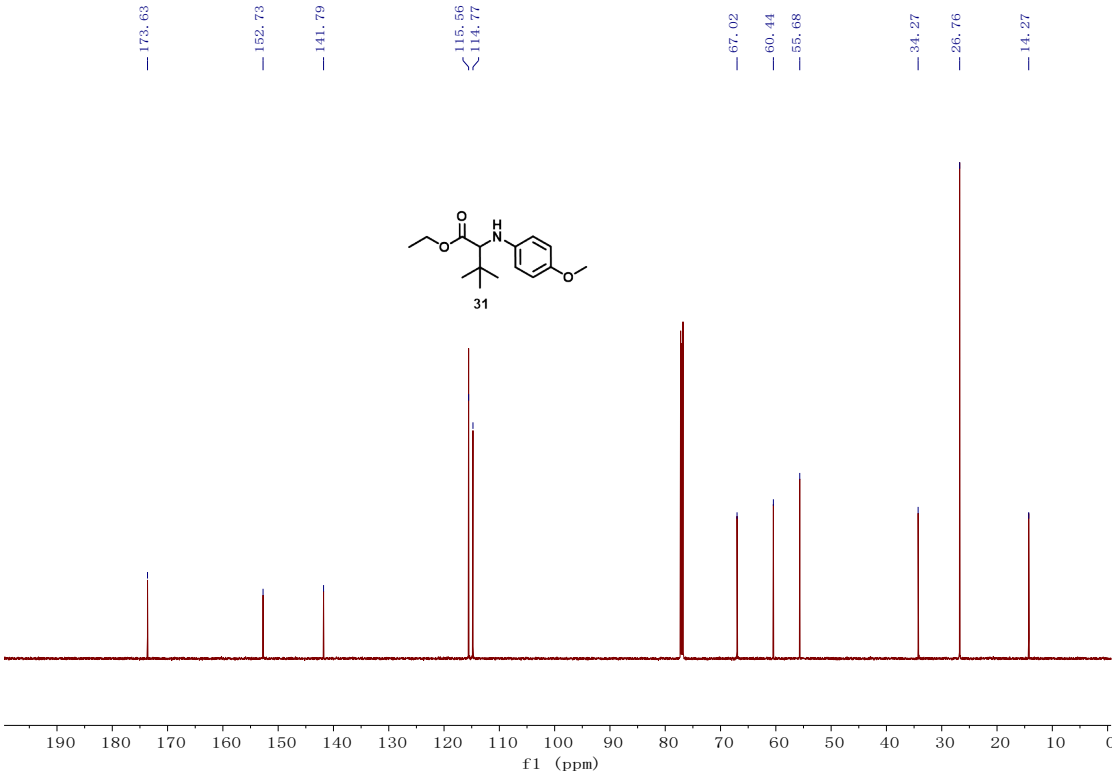

6.768
6.754
6.616
6.601
4.178
4.166
4.154
4.142
4.031
4.028
4.022
4.010
4.003
3.994
3.991
3.986
3.983
3.852
3.795
3.784
3.735
3.407
3.402
3.397
3.387
3.383
3.377
3.367
3.363
3.358
1.988
1.982
1.976
1.970
1.962
1.956
1.951
1.944
1.937
1.931
1.925
1.789
1.767
1.627
1.619
1.606
1.599
1.597
1.585
1.578
1.566
1.558
1.545
1.537
1.523
1.517
1.515
1.503
1.495
1.247
1.235
1.223
O
O
H
N
O
29
2.00
2.03
2.01
2.09
0.87
1.08
3.01
2.04
1.05
1.04
3.61
3.19
f1 (ppm)

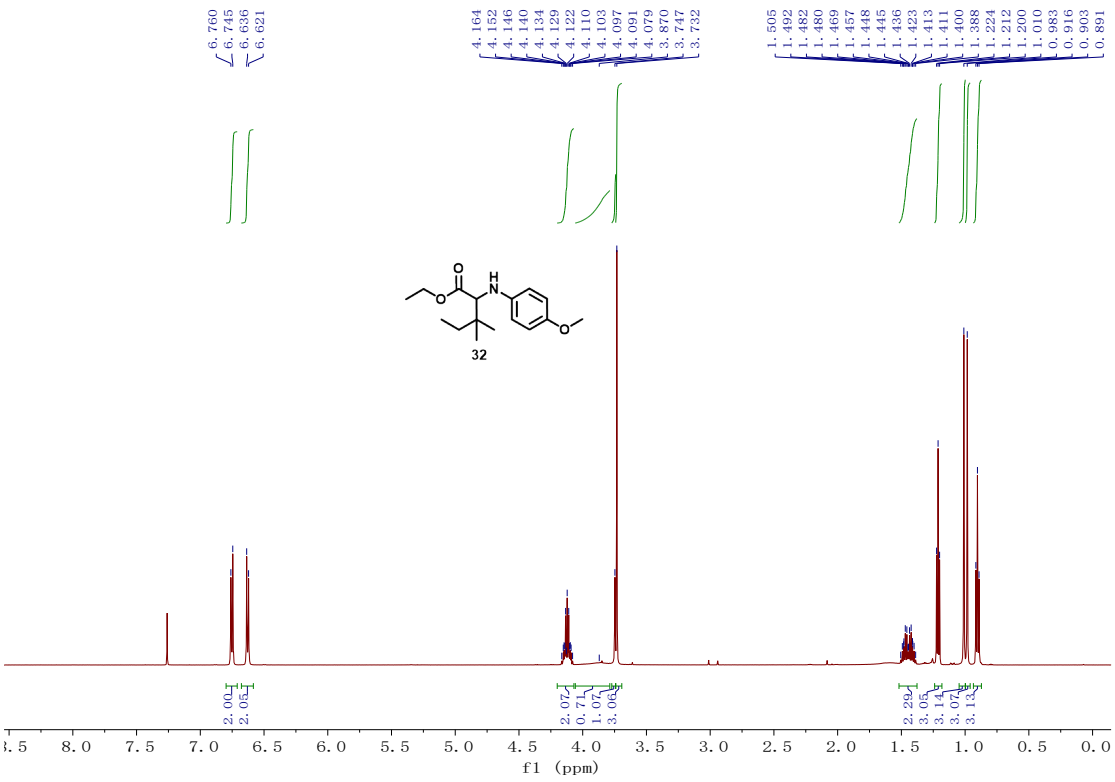

173.43
152.85
141.18
115.37
114.85
67.83
67.59
62.85
60.96
55.70
38.70
29.43
29.40
14.29
O
O
H
N
O
29
f1 (ppm)


6.764
6.749
6.607
6.592
4.173
4.161
4.149
4.138
4.135
3.849
3.797
3.787
3.732
2.683
1.870
1.858
1.855
1.839
1.835
1.831
1.818
1.814
1.809
1.619
1.597
1.449
1.434
1.427
1.414
1.407
1.393
1.386
1.373
1.359
1.352
1.340
1.332
1.316
1.242
1.230
1.218
2.00
1.99
4.00
0.88
1.07
3.05
1.94
2.01
1.36
9.07
2.24
3.18
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.
f1 (ppm)
O
O
H
N
O
N
Boc
30

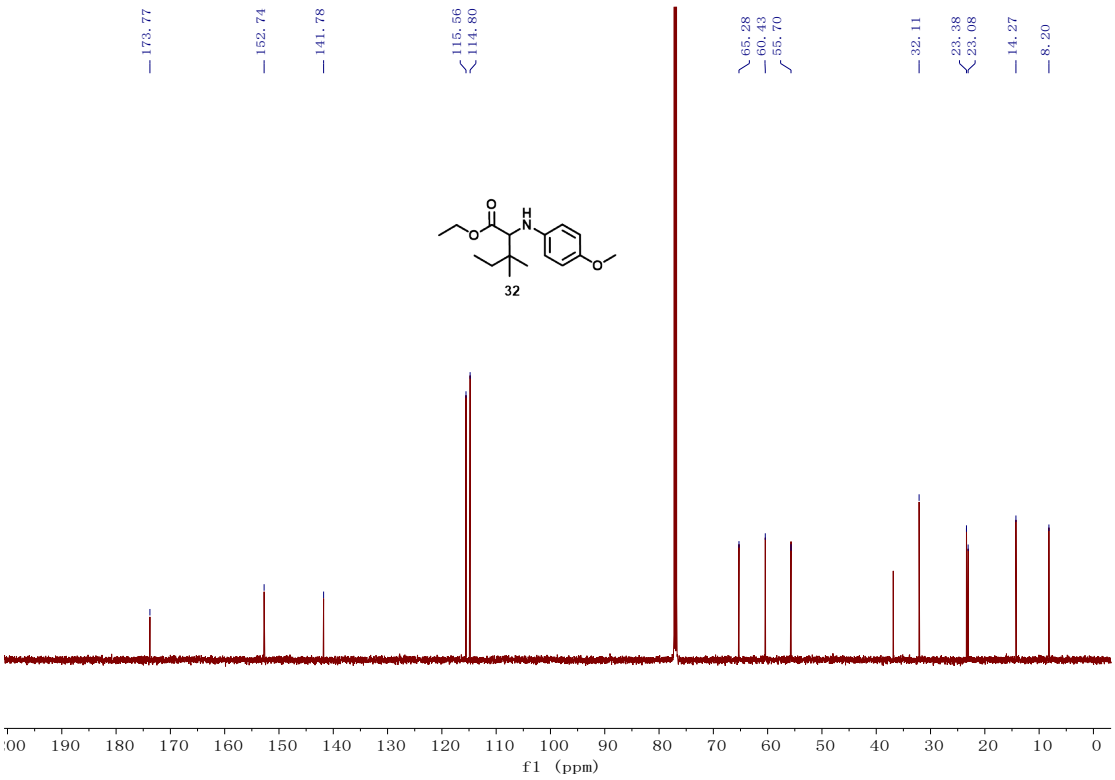

173.45
154.69
152.86
141.18
115.39
114.85
79.47
62.65
60.99
55.70
39.78
28.42
14.27
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
H
N
O
N
Boc
30


6.765
6.750
6.643
6.629
4.173
4.161
4.155
4.149
4.143
4.137
4.131
4.124
4.119
4.113
4.107
4.101
4.089
3.907
3.734
3.666
1.232
1.220
1.208
1.065
2.00
2.05
2.04
0.86
3.09
1.06
3.08
9.31
f1 (ppm)

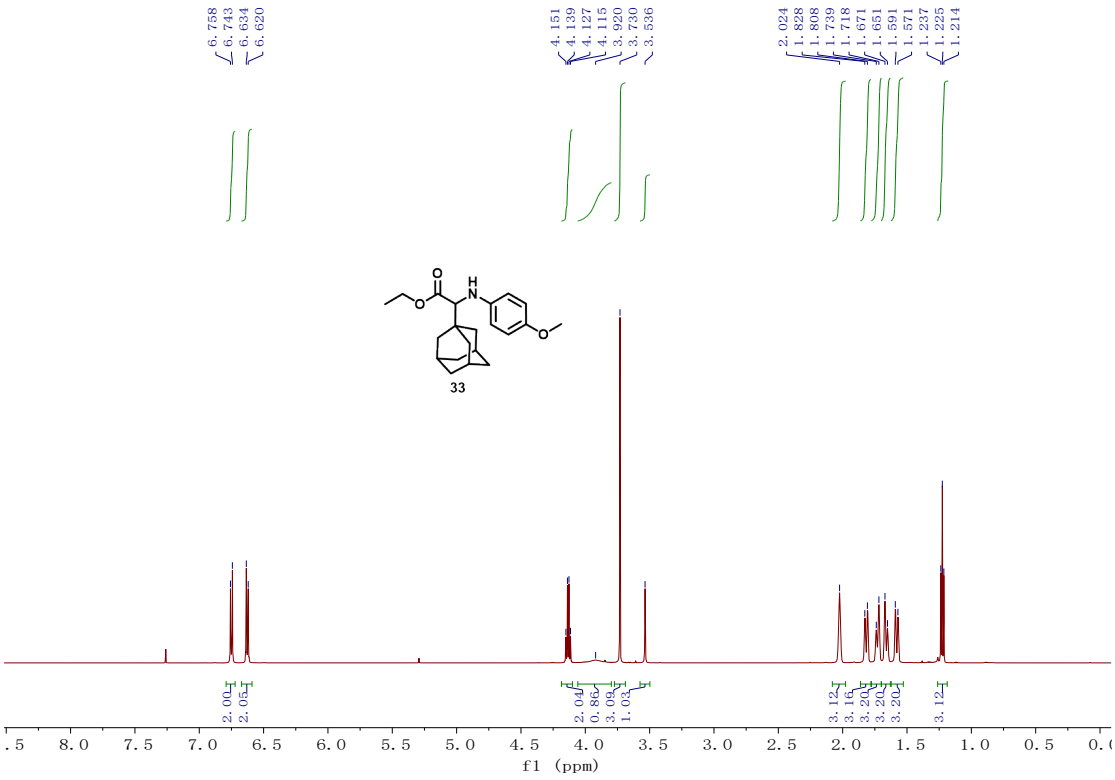

173.63
152.73
141.79
115.56
114.77
67.02
60.44
55.68
34.27
26.76
14.27
f1 (ppm)

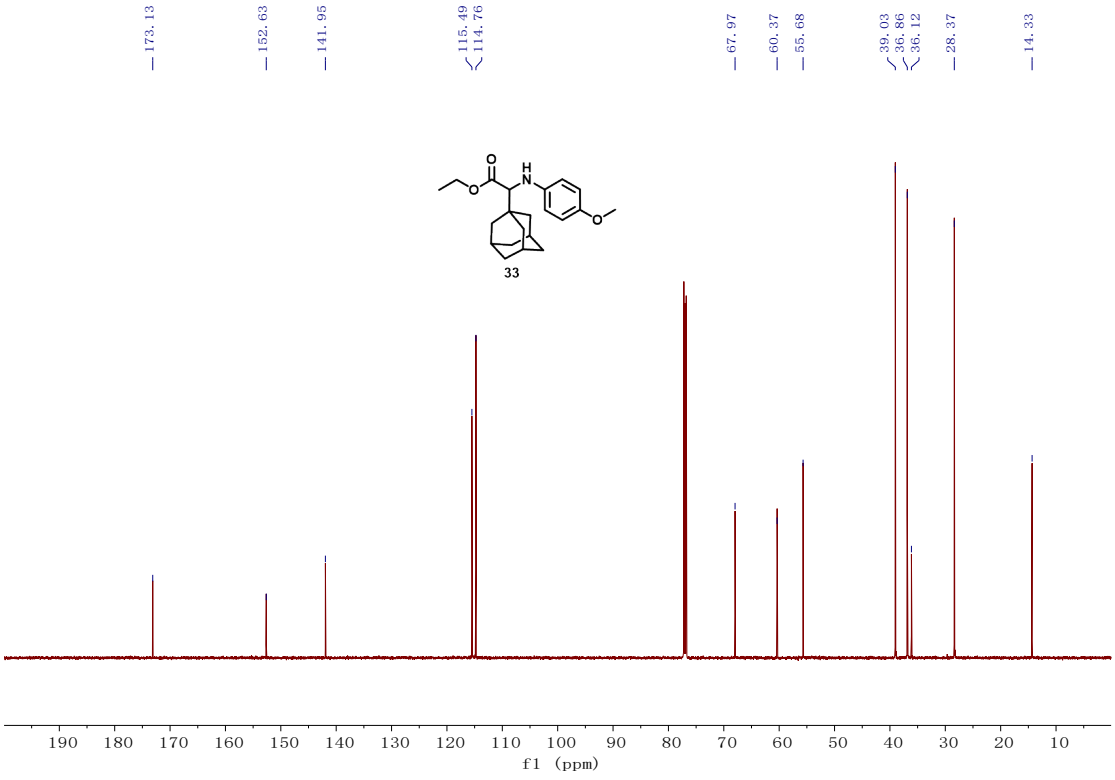

6.760
6.745
6.636
6.621
4.164
4.152
4.146
4.140
4.134
4.129
4.122
4.110
4.103
4.097
4.091
4.079
3.870
3.747
3.732
1.505
1.492
1.482
1.480
1.469
1.457
1.448
1.445
1.436
1.423
1.413
1.411
1.400
1.388
1.224
1.212
1.200
1.010
0.983
0.916
0.903
0.891
2.00
2.05
2.07
0.71
1.07
3.06
2.29
3.05
3.14
3.07
3.13
f1 (ppm)

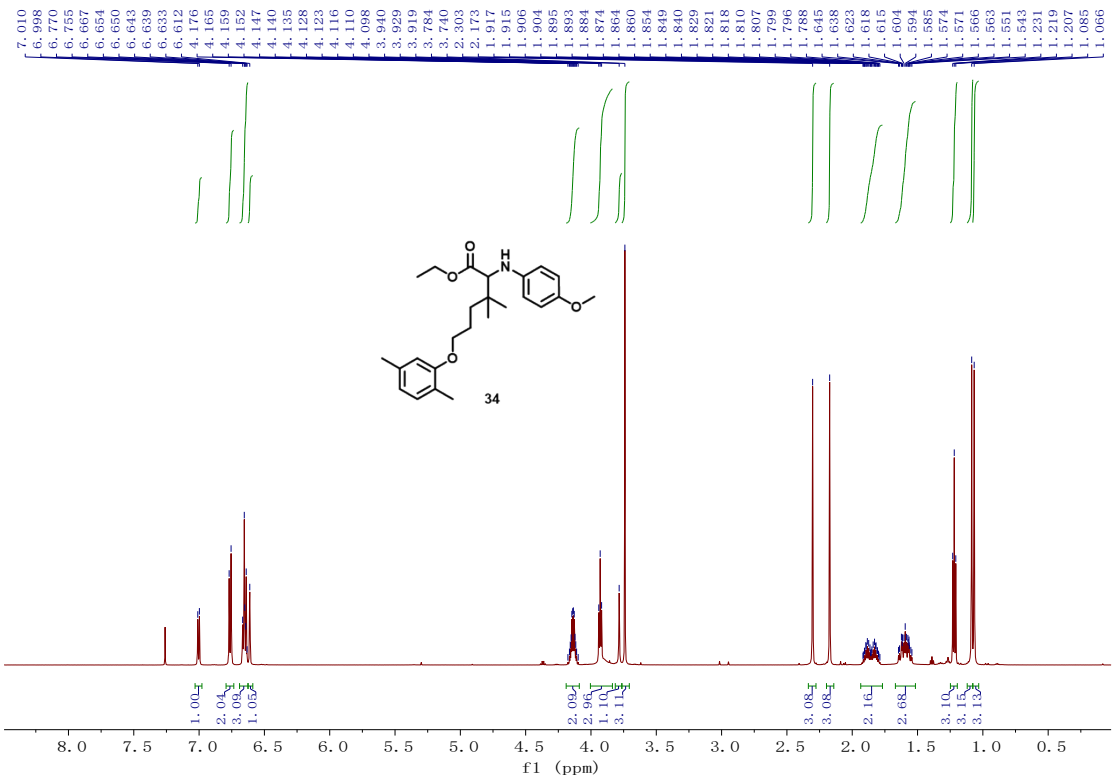
32

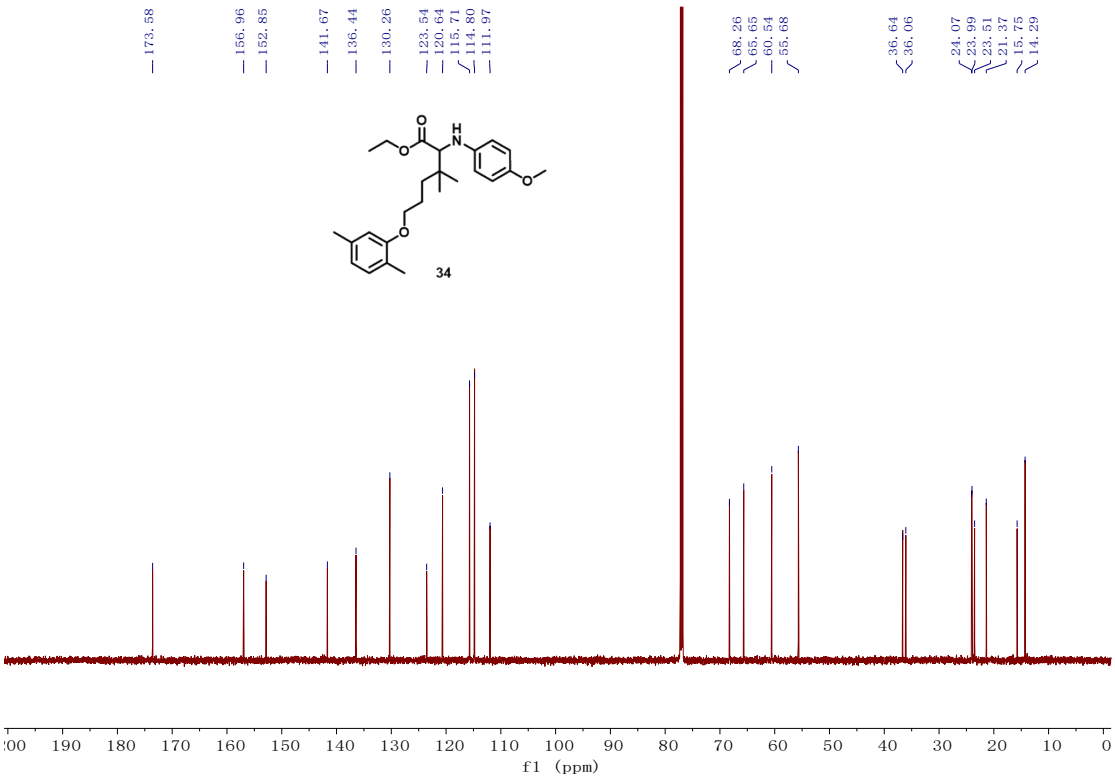

173.77
152.74
141.78
115.56
114.80
65.28
60.43
55.70
32.11
23.38
23.08
14.27
8.20
f1 (ppm)

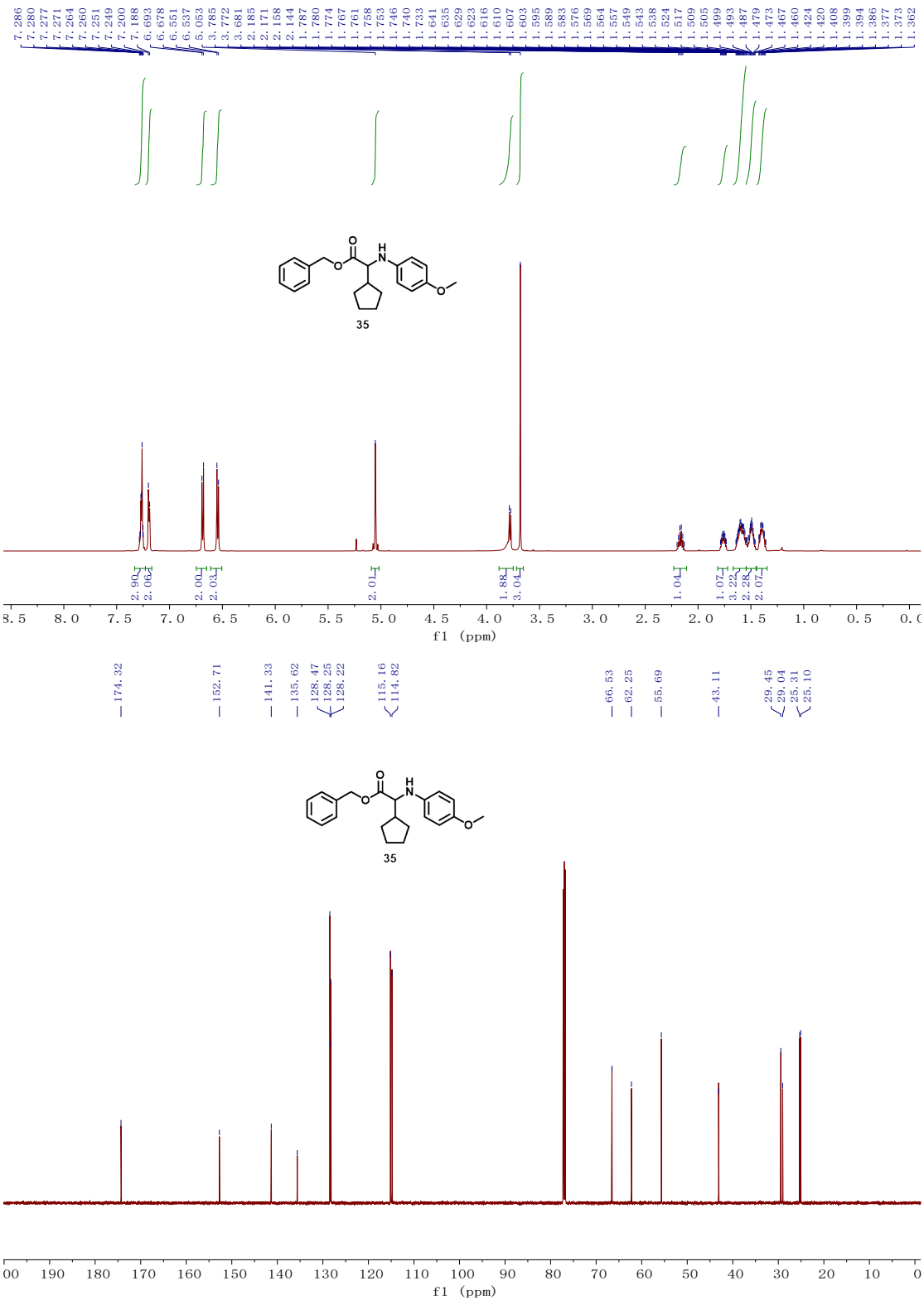
32

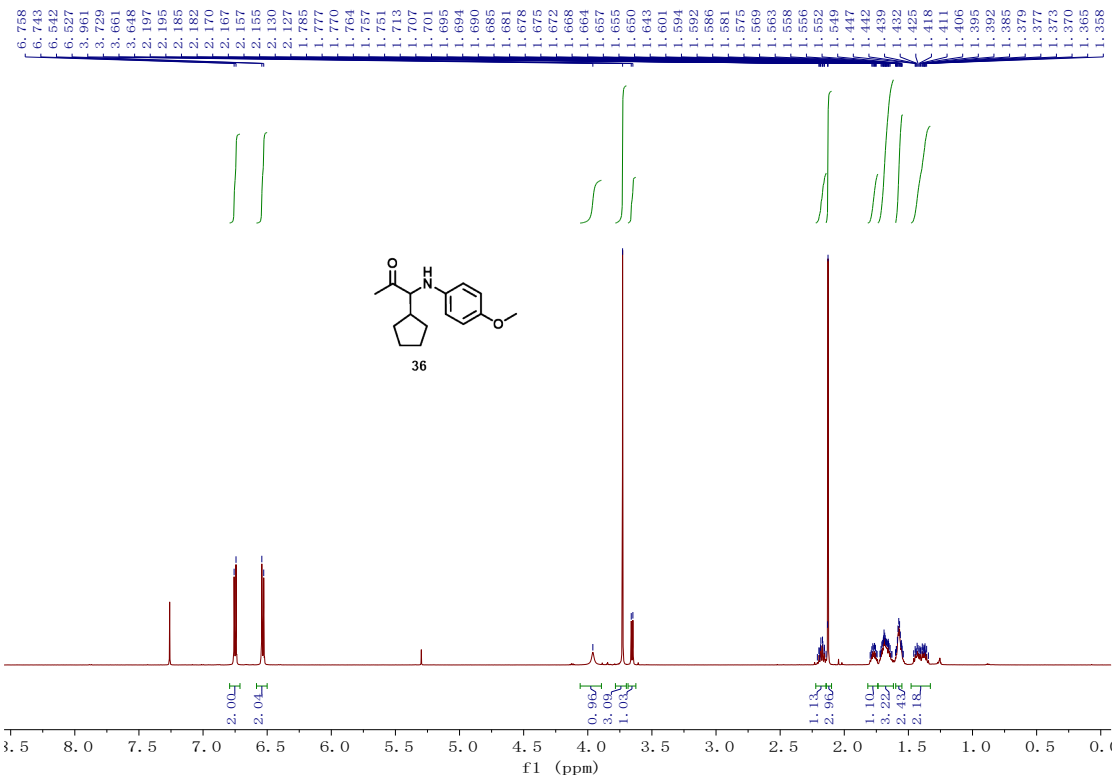

6.758
6.743
6.634
6.620
4.151
4.139
4.127
4.115
3.920
3.730
3.536
2.024
1.828
1.808
1.739
1.718
1.671
1.651
1.591
1.571
1.237
1.225
1.214
33
2.00
2.05
2.04
0.86
3.09
1.03
3.12
3.16
3.20
3.20
3.20
3.12
f1 (ppm)

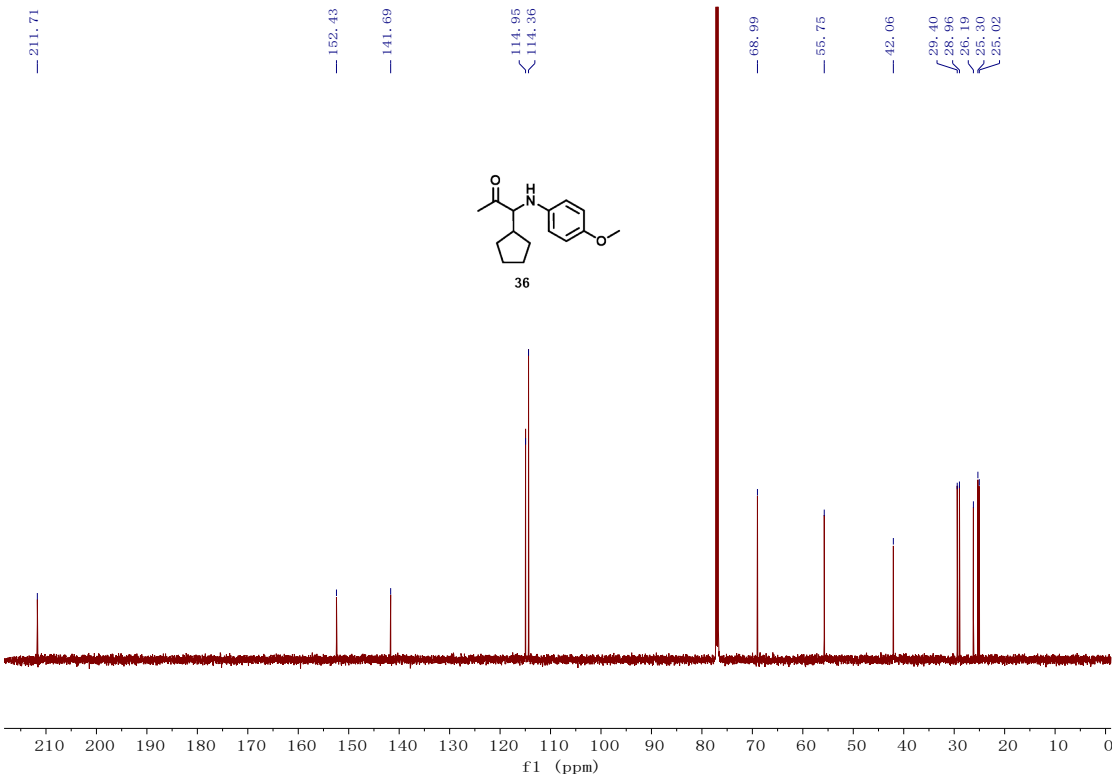

173.13
152.63
141.95
115.49
114.76
67.97
60.37
55.68
39.03
36.86
36.12
28.37
14.33
33
f1 (ppm)

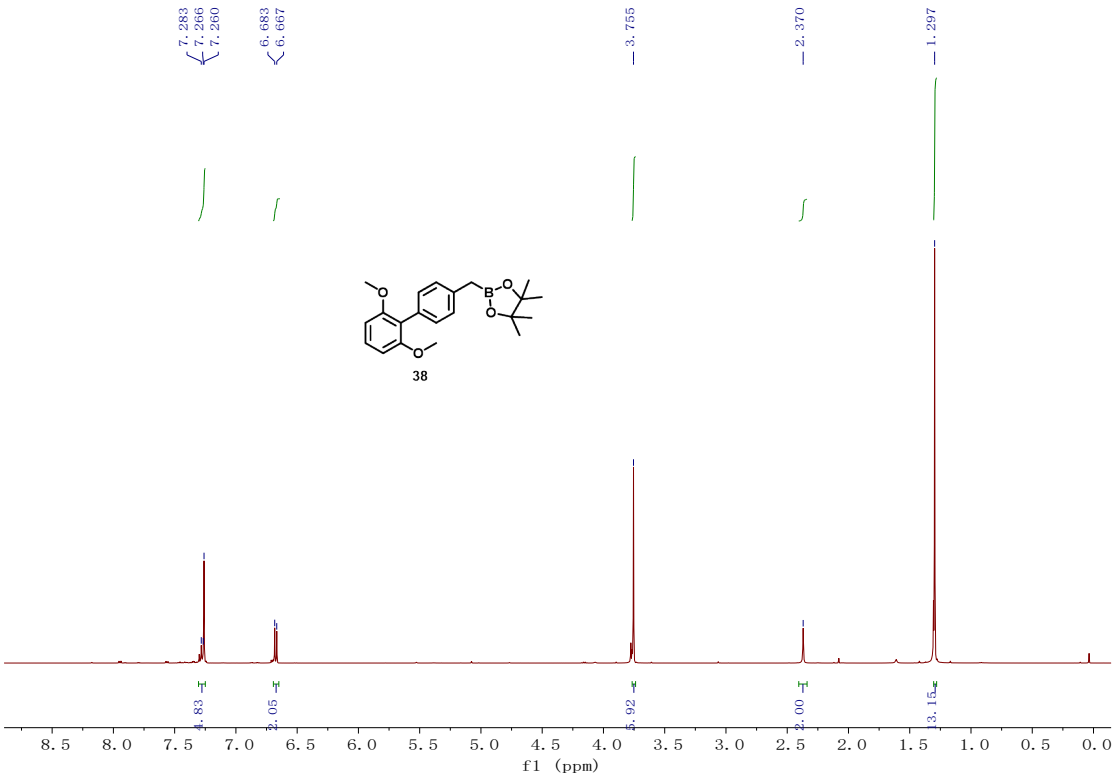

7.010
6.998
6.770
6.755
6.667
6.654
6.650
6.643
6.639
6.633
6.612
4.176
4.165
4.159
4.152
4.147
4.140
4.135
4.128
4.123
4.116
4.110
4.098
3.940
3.929
3.919
3.784
3.740
2.303
2.173
1.917
1.915
1.906
1.904
1.895
1.893
1.884
1.874
1.864
1.860
1.854
1.849
1.840
1.829
1.821
1.818
1.810
1.807
1.799
1.796
1.788
1.645
1.638
1.623
1.618
1.615
1.604
1.594
1.585
1.574
1.571
1.566
1.563
1.551
1.543
1.231
1.219
1.207
1.085
1.066
34
1.00
2.04
3.09
1.05
2.09
2.96
1.10
3.11
3.08
3.08
2.16
2.68
3.10
3.15
3.13
f1 (ppm)

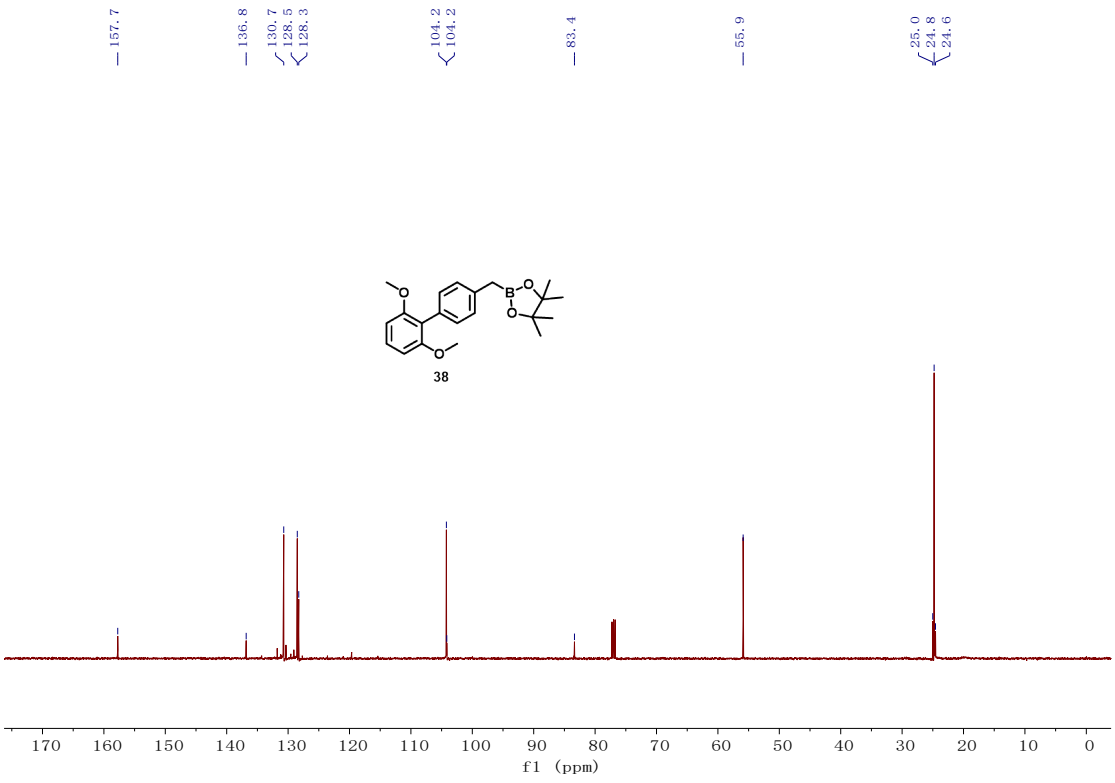

173.58
156.96
152.85
141.67
136.44
130.26
123.54
120.64
115.71
114.80
111.97
68.26
65.65
60.54
55.68
36.64
36.06
24.07
23.99
23.51
21.37
15.75
14.29
34
f1 (ppm)

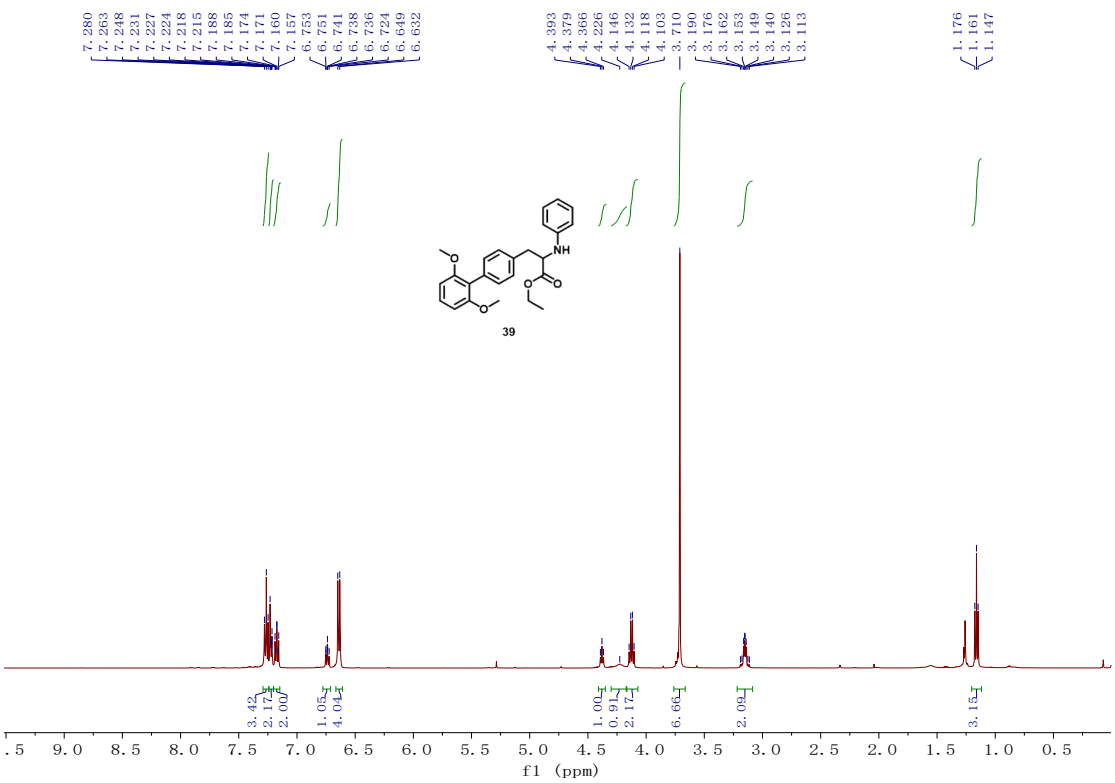

7.286
7.280
7.277
7.271
7.264
7.260
7.251
7.249
7.200
7.188
6.693
6.678
6.551
6.537
5.053
3.785
3.772
3.681
2.185
2.171
2.158
2.144
1.787
1.780
1.774
1.767
1.761
1.758
1.753
1.746
1.740
1.733
1.641
1.635
1.629
1.623
1.616
1.610
1.607
1.603
1.595
1.589
1.583
1.576
1.569
1.564
1.557
1.549
1.543
1.538
1.524
1.517
1.509
1.505
1.499
1.493
1.487
1.479
1.473
1.467
1.460
1.424
1.420
1.408
1.399
1.394
1.386
1.377
1.373
1.362
35
2.90
2.06
2.00
2.03
2.01
1.88
3.04
1.04
1.07
3.22
2.28
2.07
f1 (ppm)
174.32
152.71
141.33
135.62
128.47
128.25
128.22
115.16
114.82
66.53
62.25
55.69
43.11
29.45
29.04
25.31
25.10
35
f1 (ppm)

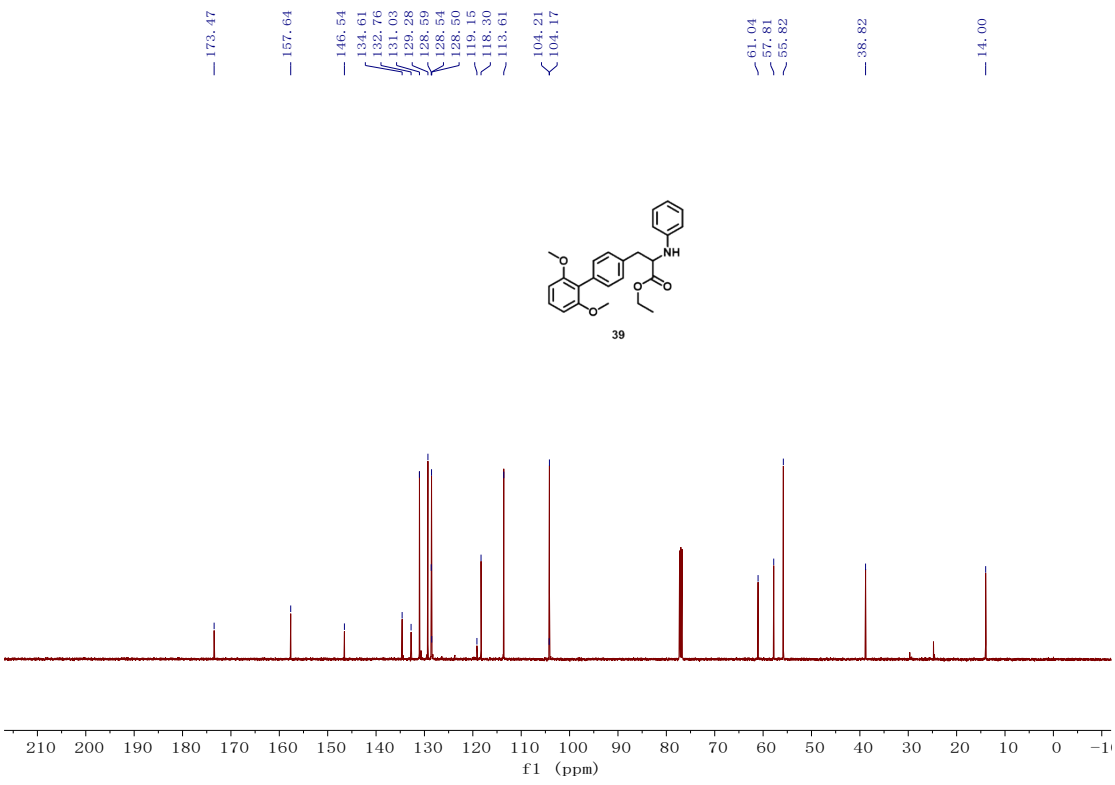

6.758
6.743
6.542
6.527
3.961
3.729
3.661
3.648
2.197
2.195
2.185
2.182
2.170
2.167
2.157
2.155
2.130
2.127
1.785
1.777
1.770
1.764
1.757
1.751
1.713
1.707
1.701
1.695
1.694
1.690
1.685
1.681
1.678
1.675
1.672
1.668
1.664
1.657
1.655
1.650
1.643
1.601
1.594
1.592
1.586
1.581
1.575
1.569
1.563
1.558
1.556
1.552
1.549
1.447
1.442
1.439
1.432
1.425
1.418
1.411
1.406
1.395
1.392
1.385
1.379
1.377
1.373
1.370
1.365
1.358
O
H
N
O
36
2.00
2.04
0.96
3.09
1.03
1.13
2.96
1.10
3.22
2.43
2.18
f1 (ppm)

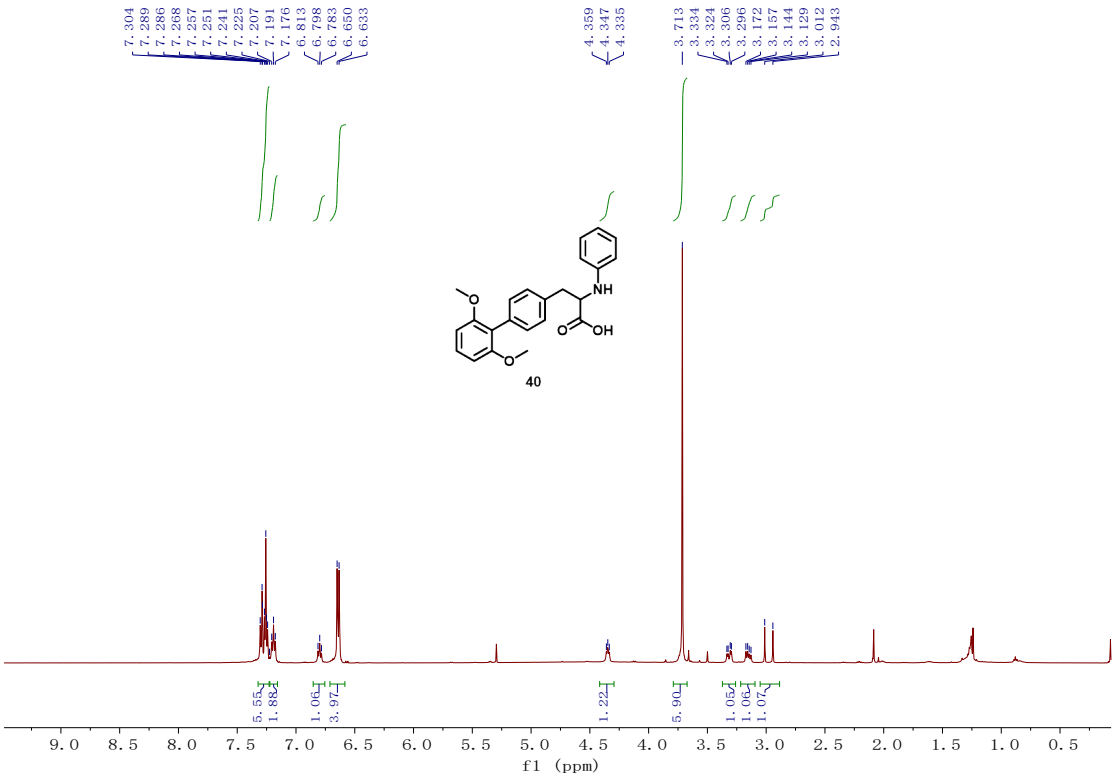

211.71
152.43
141.69
114.95
114.36
68.99
55.75
42.06
29.40
28.96
26.19
25.30
25.02
O
H
N
O
36
f1 (ppm)

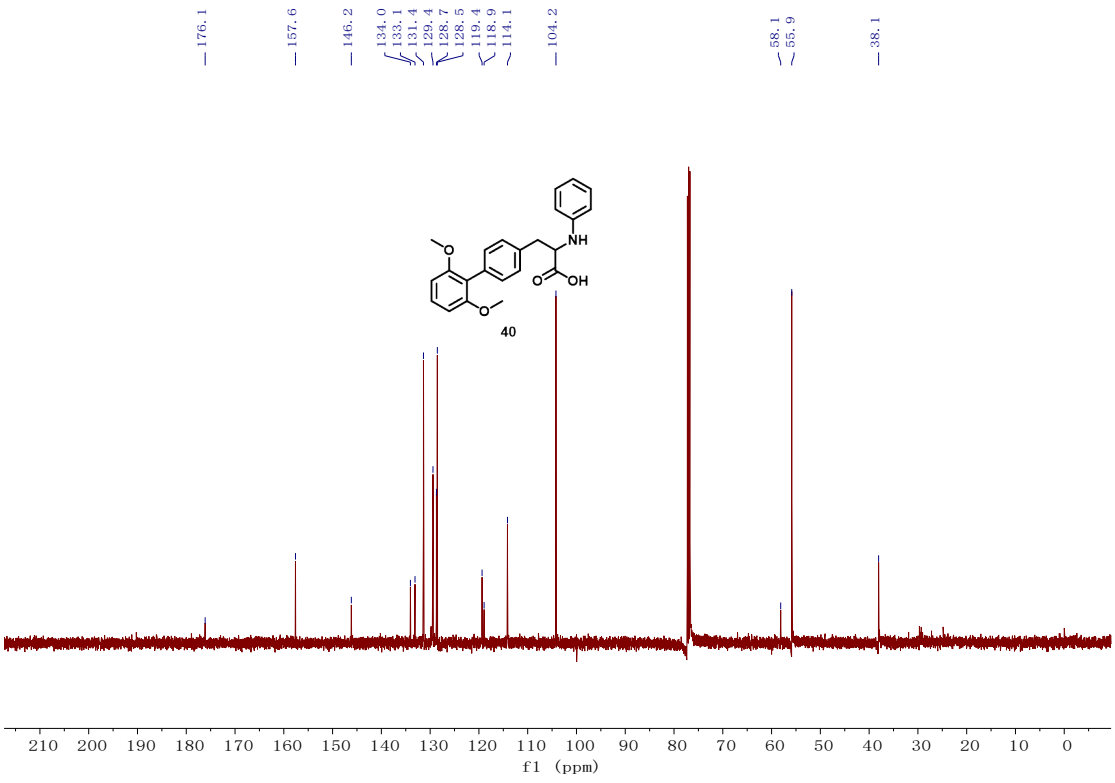

7.283
7.266
7.260
6.683
6.667
3.755
2.370
1.297
38
4.83
2.05
5.92
2.00
3.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.7
136.8
130.7
128.5
128.3
104.2
104.2
83.4
55.9
25.0
24.8
24.6
38
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.280
7.263
7.248
7.231
7.227
7.224
7.218
7.215
7.188
7.185
7.174
7.171
7.160
7.157
6.753
6.751
6.741
6.738
6.736
6.724
6.649
6.632
4.393
4.379
4.366
4.226
4.146
4.132
4.118
4.103
3.710
3.190
3.176
3.162
3.153
3.149
3.140
3.126
3.113
1.176
1.161
1.147
NH
O
O
O
O
39
3.42
2.17
2.00
1.05
4.04
1.00
0.91
2.17
6.66
2.09
3.15
f1 (ppm)


173.47
157.64
146.54
134.61
132.76
131.03
129.28
128.59
128.54
128.50
119.15
118.30
113.61
104.21
104.17
61.04
57.81
55.82
38.82
14.00
NH
O
O
O
O
39
f1 (ppm)


7.304
7.289
7.286
7.268
7.257
7.251
7.241
7.225
7.207
7.191
7.176
6.813
6.798
6.783
6.650
6.633
4.359
4.347
4.335
3.713
3.334
3.324
3.306
3.296
3.172
3.157
3.144
3.129
3.012
2.943
NH
OH
O
O
40
5.55
1.88
1.06
3.97
1.22
5.90
1.05
1.06
1.07
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
f1 (ppm)


176.1
157.6
146.2
134.0
133.1
131.4
129.4
128.7
128.5
119.4
118.9
114.1
104.2
58.1
55.9
38.1
NH
OH
O
O
40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

REFERENCES

1. Yi, J.; Badir, S. O.; Alam, R.; Molander, G. A. *Org. Lett*. **2019**, *21*, 4853-4858.
2. Campbell, M. W.; Compton, J. S.; Kelly, C. B.; Molander, G. A. *J. Am. Chem. Soc.* **2019**, *141*, 20069-20078.
3. Huang, W.; Keess, S.; Molander, G. A. *J. Am. Chem. Soc.* **2022**, *144*, 12961-12969.
4. Manthou, V. S.; Perganti, D.; Rotas, G.; Falaras, P.; Vougioukalakis, G. C. *Synlett* **2017**, *28*, 929-933.
5. Huang, H.; Zhang, G.; Gong, L.; Zhang, S.; Chen, Y. *J. Am. Chem. Soc.* **2014**, *136*, 2280-2283.
6. Zhou, S.; Lv, K.; Fu, R.; Zhu, C.; Bao, X. *ACS Catal.* **2021**, *11*, 5026-5034.
7. Yan, H.; Hou, Z. W.; Xu, H. C. *Angew. Chem. Int. Ed.* **2019**, *58*, 4592-4595.