Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Reductive Coupling of Imines with Redox-Active Esters by Visible Light Photoorganocatalysis

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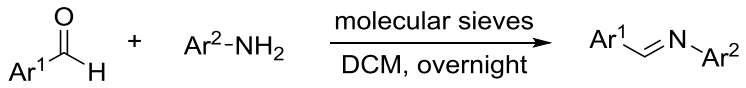
1. General methods

Unless otherwise noted, all reactions of substrates preparation were conducted in flame-dried glassware under argon atmosphere using anhydrous degassed solvent. Commercially available reagents were used without further purification. Solvents for chromatography were technical grade and distilled prior to use. Dry dichloromethane and chloroform used in reactions were obtained by distilling over calcium hydride and were stored over activated molecular sieves (4 Å). Diethyl ether, tetrahydrofuran, dimethylformamide and toluene used in reactions were obtained by distilling over sodium-benzophenone ketyl. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel 60 aluminium plates with F-254 indicator, visualized by UV irradiation. Column chromatography was performed using MN silica gel (particle size 0.040-0.063 mm). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a vnmrs-400 or vnmrs-600 spectrometer in $CDCl_3$ with residual proton signal of the deuterated solvents as the internal reference (δH = 7.26 ppm and δC = 77 ppm for $CDCl_3$). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), tt (triplet of triplet), dt (doublet of triplet), td (triplet of doublet); coupling constants (*J*) are in Hertz (Hz). IR spectra were recorded on a Jasco FT/IR-420 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were acquired on a Finnigan SSQ7000 (EI/CI) spectrometer and high resolution mass spectra on a Finnigan MAT 95 (EI/CI) or on a ThermoFisher Scientific LTQOrbitrap XL (ESI) spectrometer. Melting points were recorded on a Büchi 560 Melting Point Apparatus.

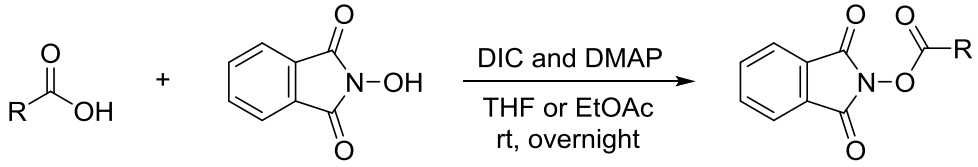
2. Substrate preparation

2.1 General procedure for the synthesis of imines[1]



In an oven-dried flask equipped with a magnetic stir bar and molecular sieves (4 Å, 2 g) was added a solution of the aldehyde (20 mmol) in dry DCM (50 mL). Then the amine (20 mmol) was added slowly and the stirring continued overnight. After filtration over Celite, the solvent was evaporated under reduced pressure and the product was purified by crystallization from a mixture of Et_2O/Pentane, or by distilling off the excess of aniline via Kugelrohr distillation.

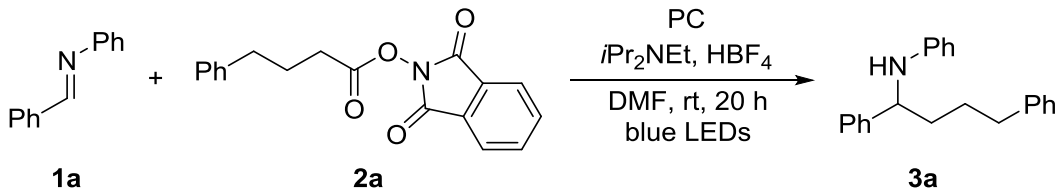
2.2 General procedure for the synthesis of *N*-hydroxyphthalimide esters (NHP esters)[2]



A round bottom flask containing a teflon-coated magnetic stir bar was charged with the corresponding acid (5.00 mmol, 1.00 equiv.) and dry EtOAc (25 mL). After sequential addition of *N*,*N*′-dicyclohexylcarbodiimide (7.50 mmol, 1.5 equiv.), DMAP (30.54 mg, 0.25 mmol, 0.05 equiv.), and *N*-hydroxyphthalimide (1.35 g, 8.30 mmol, 1.66 equiv.), the reaction mixture was allowed to stir overnight at room temperature. After this time, the heterogeneous mixture was filtered and the filtrate was concentrated under reduced pressure. Purification on silica gel (hexane: EA=6:1) afforded the *N*-hydroxyphthalimide esters as colorless solids.

3. Full optimization studies

3.1 Photoredox catalysts and light source screening



1a **2a** **3a**

Table S1 Catalyst screening[a]

Entry	Photocatalyst	NMR Yield (%)[b]
1[c]	$[Ir(ppy)_2(dtbbpy)]PF_6$	69
2	Fluorescein	48
3	Rose Bengal (RB)	53
4	Eosin Y	50
5	Methylen Blue	NR
6	Alizarin Red S	NR
7	Rhodamine B	trace
8[d]	Rose Bengal	42
9[e]	Rose Bengal	57

[a]The reactions of **1a** (0.2 mmol) with **2a** (0.1 mmol) were carried out in the presence of photocatalyst (5 mol%), *i*Pr_2NEt (5 equiv.) and HBF (5 equiv., 50% in water) in DMF (degased, 1 ml) under irradiation with blue LEDs (11 W, 450 nm) for 20 h at rt; [b]Yields were determined by ^{1}H-NMR analysis of the crude mixture relative to CH_2Br_2 as internal standard; [c]Photocatalyst (1 mol%); [d]High power blue LEDs irradiation; [e]Green LED irradiation.

3.2 Reducing agent screening

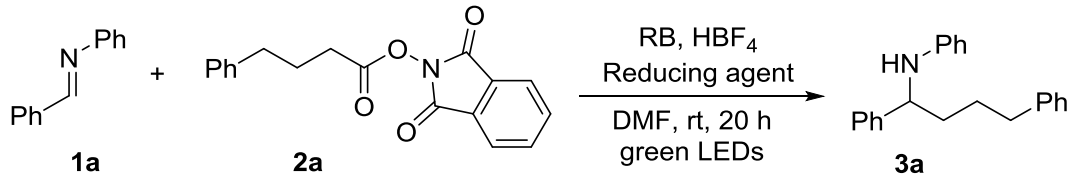


Table S2 Reducing agent screening[a]

Entry	Reducing agent	NMR Yield (%)[b]
1	*i*Pr_2NEt	57
2	*n*Bu_3N	52
3	Et_3N	43
4	HE	32
5	*i*Pr_2NEt (2.5 equiv) + HE (2.5 equiv)	40

[a]The reactions of **1a** (0.2 mmol) with **2a** (0.1 mmol) were carried out in the presence of photocatalyst (5 mol%), Reducing agent (5 equiv.) and HBF_4 (5 equiv., 50% in water) in DMF (degassed, 1 ml) under irradiation with Green LED irradiation for 20 h at rt; [b]Yields were determined by ^{1}H-NMR analysis of the crude mixture relative to CH_2Br_2 as internal standard.

3.3 Hydrogen source and additive screening

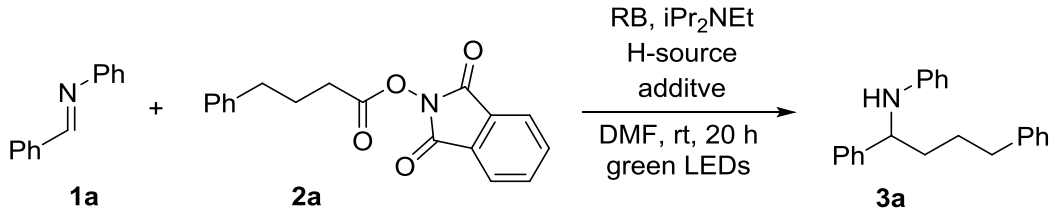


Table S2 Hydrogen source and additive screening[a]

Entry	H-source	Additive	NMR Yield (%)[b]
1	HBF_4 (5equiv., 50 % in ether)	-	trace
2	HCOOH (5 equiv.)	-	trace
3	CH_3COOH (5 equiv.)	-	trace
4	H_2O (10 equiv.)	-	40
5	H_2O (10 equiv.)	LiF (20 mol%)	48
6	H_2O (10 equiv.)	LiOAc (20 mol%)	54
7	H_2O (10 equiv.)	Li_2CO_3 (20 mol%)	58

[a]The reactions of **1a** (0.2 mmol) with **2a** (0.1 mmol) were carried out in the presence of rose bengal (RB, 5 mol%), *i*Pr_2NEt (5 equiv.), H-source (5 or 10 equiv.) and additive (20 mol%) in DMF (degassed, 1 ml) by green LED irradiation (11 W, 450 nm) for 20 h at rt; [b]Yields were determined by ^{1}H-NMR analysis of the crude mixture relative to CH_2Br_2 as internal standard.

3.4 Solvent screening

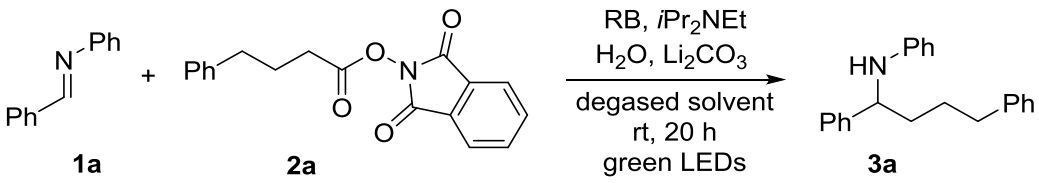
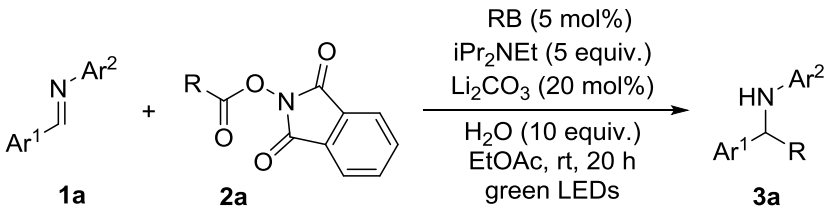


Table S3 Solvent screening[a]

Entry	Solvent	NMR Yield (%)[b]
1	DMF	57
2	THF	41
3	MeOH	trace
4	DMSO	24
5	MeCN	68
6	Tol	62
7	DCM	50
8	EA	72
9	$CHCl_3$	53
10	Aceton	70
11	Et_2O	47

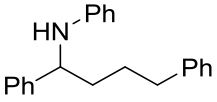
[a]The reactions of **1a** (0.2 mmol) with **2a** (0.1 mmol) were carried out in the presence of rose bengal (5 mol%), *i*Pr_2NEt (5 equiv.), H_2O (10 equiv.) and Li_2CO_3 (20 mol%) in different solvents (degassed, 1 ml) under irradiation with green LEDs (11 W, 450 nm) for 20 h at rt; [b]Yields were determined by ^{1}H-NMR analysis of the crude mixture relative to CH_2Br_2 as internal standard.

4. Preparation and characterization of amines



A Schlenk-tube was charged with substrates **1a** (0.4 mmol, 2 equiv.), **2a** (0.2 mmol 1 equiv.), rose bengal (5 mol%), and Li_2CO_3 (20 mol%). It was capped with a rubber septum, evacuated and backfilled with argon. Then, degassed EtOAc (2 mL) was added via syringe, at the same time the *i*Pr_2NEt (5 equiv.) and H_2O (10 equiv.) were also added. The vial was placed in a 100 mL beaker wrapped with green LEDs inside and the reaction mixture was stirred at rt for 20 h. After checking the course of the reaction by TLC, the solvent was evaporated under reduced pressure and the product was purified by column chromatography using Pentane/EA (100:1-6:1) as eluent.

***N*-(1,4-diphenylbutyl)aniline (3a)**[3]



Yellow oil was obtained after column chromatography (100% pentane to 100:1 pentane/EtOAc). Yield = 62% (37.2 mg, 0.12 mmol).

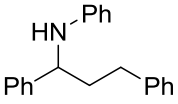
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 6H), 7.25 – 7.18 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.09 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 4.33 (t, *J* = 6.7 Hz, 1H), 4.05 (bs, 1H), 2.71 – 2.58 (m, 2H), 1.91 – 1.74 (m, 3H), 1.72 – 1.64 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 143.9, 141.9, 129.0, 128.5, 128.3, 128.3, 126.8, 126.3, 125.8, 117.1, 113.1, 58.0, 38.2, 35.6, 27.9.

MS (EI): *m/z* (%) = 302.2 ($[M+H]^+$, 16), 301.2 ($[M]^+$, 38), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3383, 2938, 2285, 1704, 1477, 1464, 1350, 1240, 1139, 727.

***N*-(1,3-diphenylpropyl)aniline (3b)[4]**



Yellow oil was obtained after column chromatography (100% pentane to 100:1 pentane/EtOAc). Yield = 69% (39.6 mg, 0.14 mmol).

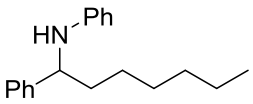
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 6H), 7.27 – 7.16 (m, 4H), 7.08 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.6 Hz, 2H), 4.36 (t, *J* = 6.7 Hz, 1H), 4.08 (bs, 1H), 2.83 – 2.64 (m, 2H), 2.23 – 2.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 143.7, 141.4, 129.0, 128.5, 128.4, 128.4, 127.0, 126.4, 125.9, 117.2, 113.2, 57.6, 40.1, 32.6.

MS (EI): *m/z* (%) = 288.2 ($[M+H]^+$, 15), 287.2 ($[M]^+$, 32), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3410, 3030, 2915, 2328, 1737, 1599, 1490, 1304, 718.

***N*-(1-phenylheptyl)aniline (3c)**



Yellow oil was obtained after column chromatography (100% pentane to 100:1 pentane/EtOAc). Yield = 61% (32.5 mg, 0.12 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 4H), 7.26 – 7.19 (m, 1H), 7.07 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 2H), 4.30 (t, *J* = 6.8 Hz, 1H), 4.07 (bs, 1H), 1.88 – 1.72 (m, 2H), 1.48 – 1.39 (m, 1H), 1.34 – 1.24 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H).

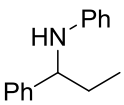
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 144.3, 129.0, 128.4, 126.7, 126.3, 117.0, 113.2, 58.25, 39.0, 31.7, 29.1, 26.3, 22.5, 14.0.

MS (EI): *m/z* (%) = 268.2 ($[M+H]^+$, 13), 267.2 ($[M]^+$, 33), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3411, 2925, 2339, 2095, 1733, 1599, 1494, 1308, 723.

HRMS (EI+, m/z): calculated for $C_{19}H_{26}N$ [M+H]+: 268.20598; found: 268.20590.

N-(1-phenylpropyl)aniline (3d)[5]



Yellow oil was obtained after column chromatography (100% pentane to 100:1 pentane/EtOAc). Yield = 73% (30.8 mg, 0.15 mmol).

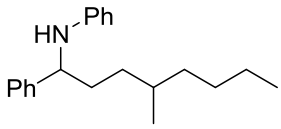
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.09 (dd, *J* = 8.6, 7.4 Hz, 2H), 6.65 (t, *J* = 7.4, 1H), 6.54 (d, *J* = 8.1, 2H), 4.25 (t, *J* = 6.7 Hz, 1H), 4.09 (bs, 1H), 1.92 – 1.80 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 143.8, 129.0, 128.4, 126.8, 126.4, 117.0, 113.1, 59.68, 31.6, 10.8.

MS (EI): *m/z* (%) = 212.2 ($[M+H]^+$, 16), 211.2 ($[M]^+$, 37), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3416, 2947, 2327, 2108, 1733, 1598, 1490, 1305, 707.

_N_-(4-methyl-1-phenyloctyl)aniline (3e)



Yellow oil was obtained after column chromatography (100% pentane to 100:1 pentane/EtOAc). Yield = 66% (38.9 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 7.08 (dd, *J* = 8.5, 7.2 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.5 Hz, 2H), 4.31 – 4.22 (m, 1H), 4.06 (bs, 1H), 1.87 – 1.70 (m, 2H), 1.46 – 1.08 (m, 9H), 0.97 – 0.73 (m, 6H).

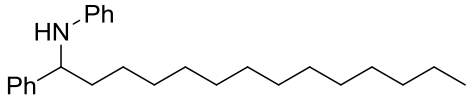
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 144.4, 144.3, 129.0, 128.4, 126.8, 126.3, 126.3, 117.0, 113.1, 58.6, 58.5, 36.5, 36.5, 36.4, 33.6, 33.5, 32.7, 32.6, 29.2, 22.9, 19.6, 19.5.

MS (EI): *m/z* (%) = 296.2 ($[M+H]^+$, 15), 295.2 ($[M]^+$, 28), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3413, 2926, 2340, 2093, 1740, 1600, 1493, 1308, 727.

HRMS (EI+, m/z): calculated for $C_{21}H_{30}N$ [M+H]+: 296.23728; found: 296.23734.

_N_-(1-phenyltetradecyl)aniline (3f)



Yellow oil was obtained after column chromatography (100% pentane to 100:1 pentane/EtOAc). Yield = 52% (37.9 mg, 0.10 mmol.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.25 – 7.19 (m, 1H), 7.09 (dd, *J* = 8.4, 7.2 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.1, 2H), 4.30 (t, *J* = 6.8 Hz, 1H), 4.06 (bs, 1H), 1.86 – 1.72 (m, 2H), 1.48 – 1.37 (m, 1H), 1.34 – 1.22 (m, 21H), 0.90 (t, *J* = 6.8 Hz, 3H).

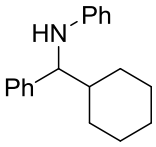
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 144.3, 129.0, 128.4, 126.7, 126.3, 117.0, 113.1, 58.2, 39.0, 31.9, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 26.3, 22.6, 14.1.

MS (EI): *m/z* (%) = 366.3 ($[M+H]^+$, 31), 365.3 ($[M]^+$, 46), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3415, 2916, 2323, 1738, 1599, 1483, 1299, 719.

HRMS (EI+, m/z): calculated for $C_{26}H_{40}N$ [M+H]+: 366.31553; found: 366.31577.

_N_-(cyclohexyl(phenyl)methyl)aniline (3g)[6]



Yellow oil was obtained after column chromatography (100% pentane to 100:1 pentane/EtOAc). Yield = 57% (30.2 mg, 0.11 mmol).

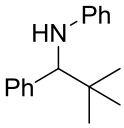
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 7.07 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 2H), 4.15 (bs, 1H), 4.13 (d, *J* = 6.3 Hz, 1H), 1.94 – 1.86 (m, 1H), 1.81 – 1.62 (m, 5H), 1.58 – 1.51 (m, 1H), 1.24 – 1.03 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 142.6, 129.1, 128.1, 127.1, 126.6, 116.8, 113.1, 63.3, 44.8, 30.2, 29.4, 26.4, 26.3, 26.3.

MS (EI): *m/z* (%) = 266.2 ($[M+H]^+$, 21), 265.2 ($[M]^+$, 20), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3415, 2902, 2344, 2090, 1748, 1589, 1486, 1295, 719.

_N_-(2,2-dimethyl-1-phenylpropyl)aniline (3h)[7]



Yellow oil was obtained after column chromatography (100% pentane to 100:1 pentane/EtOAc). Yield = 61% (29.1 mg, 0.12 mmol).

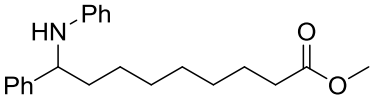
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dt, *J* = 15.2, 4.6 Hz, 4H), 7.24 – 7.19 (m, 1H), 7.05 (dd, *J* = 8.5, 7.2 Hz, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.7 Hz, 2H), 4.27 (bs, 1H), 4.05 (s, 1H), 1.00 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 141.1, 128.9, 128.4, 127.6, 126.7, 116.8, 113.1, 67.1, 34.8, 27.0.

MS (EI): *m/z* (%) = 240.2 ($[M+H]^+$, 5), 239.2 ($[M]^+$, 11), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3425, 2942, 2323, 2098, 1731, 1599, 1491, 1302, 709.

Methyl 9-phenyl-9-(phenylamino)nonanoate (3i)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 63% (42.7 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 4H), 7.25 – 7.19 (m, 1H), 7.08 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 1H), 4.07 (bs, 1H), 3.67 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.85 – 1.73 (m, 2H), 1.72 – 1.49 (m, 2H), 1.46 – 1.38 (m, 1H), 1.34 – 1.28 (m, 7H).

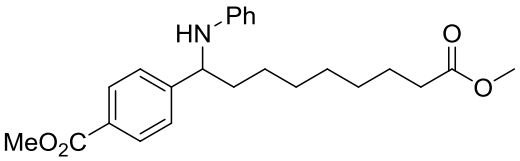
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 147.4, 144.2, 129.0, 128.4, 126.8, 126.3, 117.0, 113.17, 58.1, 51.4, 38.9, 34.0, 29.2, 29.0, 28.9, 26.2, 24.8.

MS (EI): *m/z* (%) = 340.2 ($[M+H]^+$, 38), 339.2 ($[M]^+$, 31), 182.1 (100).

IR (ATR): $\tilde{\nu}$ =3413, 2922, 2320, 2019, 1733, 1600, 1491, 1305, 1162, 705.

HRMS (EI+, m/z): calculated for $C_{22}H_{30}NO_2$ [M+H]+: 340.22711; found: 340.22723.

Methyl 4-(9-methoxy-9-oxo-1-(phenylamino)nonyl)benzoate (3j)



Yellow oil was obtained after column chromatography (20:1 to 9:1 pentane/EtOAc). Yield = 58% (46.1 mg, 0.12 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.07 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 1H), 4.05 (bs, 1H), 3.87 (s, 3H), 3.64 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.63 – 1.52 (m, 3H), 1.26 (s, 7H).

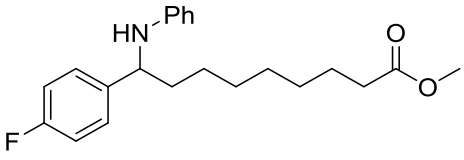
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.20 166.94 149.8, 146.9, 129.9, 129.0, 128.8, 126.3, 117.4, 113.2, 58.1, 51.9, 51.3, 38.7, 33.9, 29.2, 29.0, 28.9, 26.1, 24.8.

MS (EI): *m/z* (%) = 398.3 ($[M+H]^+$, 3), 397.2 ($[M]^+$, 7), 240.2 (100).

IR (ATR): $\tilde{\nu}$ =3406, 2929, 2328, 2086, 1705, 1604, 1488, 1350, 1089, 710.

HRMS (EI+, m/z): calculated for $C_{24}H_{31}NO_4K$ [M+K]+: 436.18847; found: 436.18842.

Methyl 9-(4-fluorophenyl)-9-(phenylamino)nonanoate (3k)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 66% (47.1 mg, 0.13 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 14.4, 7.2 Hz, 2H), 7.09 (t, *J* = 7.9 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.27 (t, *J* = 6.8 Hz, 1H), 4.05 (bs, 1H), 3.67 (s, 3H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.65 – 1.58 (m, 2H), 1.43 – 1.36 (m, 1H), 1.29 (s, 7H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 161.7 (d, *J* = 244.3 Hz), 147.2, 139.9 (d, *J* = 3.0 Hz), 129.0, 127.7 (d, *J* = 7.9 Hz), 117.2, 115.3 (d, *J* = 21.2 Hz), 113.2, 57.5, 51.47, 39.0, 34.0, 29.2, 29.0, 29.0, 26.1, 24.8.

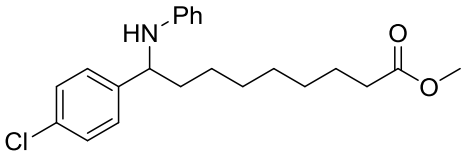
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.32.

MS (EI): *m/z* (%) = 358.2 ($[M+H]^+$, 15), 357.2 ($[M]^+$, 16), 200.1 (100).

IR (ATR): $\tilde{\nu}$ =3401, 2928, 2335, 2092, 1731, 1601, 1499, 1214, 744.

HRMS (EI+, m/z): calculated for $C_{22}H_{28}NO_2FNa$ [M+Na]+: 380.19963; found: 380.20059.

Methyl 9-(4-chlorophenyl)-9-(phenylamino)nonanoate (3l)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 63% (46.9 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 4H), 7.08 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.2 Hz, 2H), 4.25 (t, *J* = 6.8 Hz, 1H), 4.02 (bs, 1H), 3.65 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.65 – 1.56 (m, 2H), 1.41 – 1.34 (m, 1H), 1.28 (s, 7H).

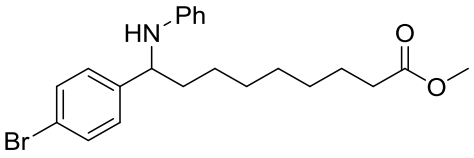
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 147.1, 142.8, 132.3, 129.0, 128.6, 127.7, 117.3, 113.2, 57.6, 51.4, 38.8, 34.0, 29.2, 29.0, 28.9, 26.1, 24.8.

MS (EI): *m/z* (%) = 374.2 ($[M+H]^+$, 40), 373.2 ($[M]^+$, 24), 216.1 (100).

IR (ATR): $\tilde{\nu}$ =3403, 2928, 2322, 2080, 1730, 1600, 1491, 1183, 1012, 734.

HRMS (EI+, m/z): calculated for $C_{22}H_{29}NO_2Cl$ [M+H]+: 374.18813; found: 374.18817.

Methyl 9-(4-bromophenyl)-9-(phenylamino)nonanoate (3m)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 60% (50.0 mg, 0.12 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.08 (dd, *J* = 8.7, 7.3 Hz 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.4 Hz, 2H), 4.23 (t, *J* = 6.8 Hz, 1H), 4.03 (bs, 1H), 3.65 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.66 (m, 2H), 1.65 – 1.54 (m, 2H), 1.44 – 1.35 (m, 1H), 1.28 (s, 7H).

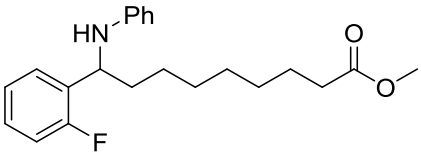
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 147.1, 143.4, 131.6, 129.0, 128.1, 120.4, 117.3, 113.2, 57.7, 51.4, 38.8, 34.0, 29.2, 29.0, 28.9, 26.1, 24.8.

MS (EI): *m/z* (%) = 418.3 ($[M+H]^+$, 16), 417.2 ($[M]^+$, 24), 260.0 (100).

IR (ATR): $\tilde{\nu}$ =3401, 2926, 2338, 2091, 1731, 1600, 1490, 1195, 745.

HRMS (EI+, m/z): calculated for $C_{22}H_{29}NO_2Br$ [M+H]+: 418.13762; found: 418.13763.

Methyl 9-(2-fluorophenyl)-9-(phenylamino)nonanoate (3n)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 65% (46.4 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.17 – 7.02 (m, 4H), 6.90 (t, *J* = 8.3 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.7 Hz, 2H), 4.28 (t, *J* = 6.7 Hz, 1H), 4.04 (bs, 1H), 3.66 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.64 – 1.56 (m, 2H), 1.45 – 1.38 (m, 1H), 1.29 (s, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 163.14 (d, *J* = 245.8 Hz) , 147.26 (d, *J* = 5.9 Hz), 147.1, 130.0, 129.96 (d, *J* = 8.1 Hz), 121.99 (d, *J* = 2.5 Hz), 117.3, 113.74 (d, *J* = 21.3 Hz)., 113.2, 113.10 (d, *J* = 21.7 Hz), 57.8, 51.4, 38.8, 34.01, 29.2, 29.0, 28.9, 26.1, 24.8.

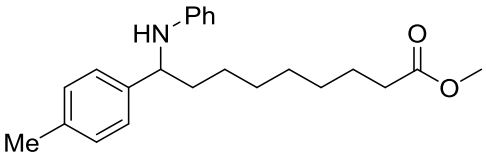
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.12.

MS (EI): *m/z* (%) = 358.2 ($[M+H]^+$, 13), 357.2 ($[M]^+$, 12), 200.1 (100).

IR (ATR): $\tilde{\nu}$ =3396, 2915, 2348, 2091, 1736, 1597, 1475, 1215, 736.

HRMS (EI+, m/z): calculated for $C_{22}H_{28}NO_2FNa$ [M+Na]+: 380.19963; found: 380.20053.

Methyl 9-(phenylamino)-9-(p-tolyl)nonanoate (3o)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 58% (40.9 mg, 0.12 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.10 (m, 4H), 7.10 – 7.05 (m, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.6 Hz, 2H), 4.26 (t, *J* = 6.8 Hz, 1H), 4.03 (bs, 1H), 3.67 (s, 3H), 2.33 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.71 (m, 2H), 1.64 – 1.56 (m, 2H), 1.45 – 1.38 (m, 1H), 1.31 (s, 7H).

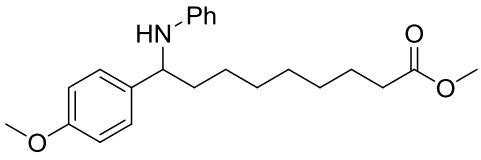
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 147.5, 141.1, 136.3, 129.1, 129.0, 126.2, 116.9, 113.1, 57.8, 51.4, 38.9, 34.0, 29.2, 29.0, 29.0, 26.2, 24.8, 21.0.

MS (EI): *m/z* (%) = 354.3 ($[M+H]^+$, 9), 353.3 ($[M]^+$, 12), 196.1 (100).

IR (ATR): $\tilde{\nu}$ =3402, 2925, 2337, 2094, 1732, 1600, 1497, 1201, 739.

HRMS (EI+, m/z): calculated for $C_{23}H_{31}NO_2Na$ [M+Na]+: 376.22470; found: 376.22495.

Methyl 9-(4-methoxyphenyl)-9-(phenylamino)nonanoate (3p)



Yellow oil was obtained after column chromatography (20:1 to 9:1 pentane/EtOAc). Yield = 45% (33.2 mg, 0.09 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 5.7 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.54 – 6.48 (d, 2H), 4.24 (t, *J* = 6.8 Hz, 1H), 4.02 (bs, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.69 (m, 2H), 1.68 – 1.48 (m, 2H), 1.44 – 1.35 (m, 1H), 1.28 (s, 7H).

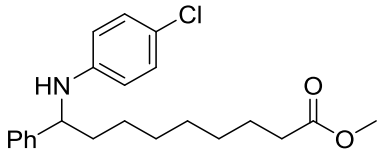
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 158.4, 147.4, 136.2, 129.0, 127.3, 117.0, 113.8, 113.2, 57.5, 55.1, 51.4, 38.9, 34.0, 29.2, 29.0, 29.0, 26.2, 24.8.

MS (EI): *m/z* (%) = 370.3 ($[M+H]^+$, 5), 369.3 ($[M]^+$, 12), 212.1 (100).

IR (ATR): $\tilde{\nu}$ =3403, 2928, 2327, 2081, 1713, 1603, 1490, 1241, 1806, 713.

HRMS (EI+, m/z): calculated for $C_{23}H_{31}NO_3Na$ [M+Na]+: 392.21962; found: 392.21994.

4-chloro-N-(9-methoxy-1-phenyldec-9-en-1-yl)aniline (3q)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 64% (47.7 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 8.8 Hz, 2H), 4.22 (t, *J* = 6.8 Hz, 1H), 4.07 (bs, 1H), 3.64 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.63 – 1.54 (m, 2H), 1.43 – 1.34 (m, 1H), 1.27 (s, 7H).

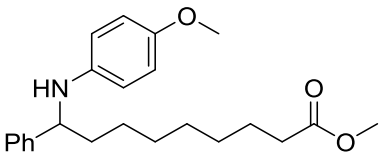
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 145.9, 143.6, 128.8, 128.5, 126.9, 126.2, 121.6, 114.2, 58.3, 51.4, 38.8, 34.0, 29.2, 29.0, 28.9, 26.1, 24.8.

MS (EI): *m/z* (%) = 374.2 ($[M+H]^+$, 10), 373.2 ($[M]^+$, 16), 216.1 (100).

IR (ATR): $\tilde{\nu}$ =3401, 2927, 2330, 2083, 1729, 1600, 1492, 1187, 812, 701.

HRMS (EI+, m/z): calculated for $C_{22}H_{29}NO_2Cl$ [M+H]+: 374.18813; found: 374.18851.

Methyl 9-((4-methoxyphenyl)amino)-9-phenylnonanoate (3r)



Yellow oil was obtained after column chromatography (20:1 to 9:1 pentane/EtOAc). Yield = 41% (30.2 mg, 0.08 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.24 – 7.17 (m, 1H), 6.67 (d, *J* = 8.9 Hz, 2H), 6.46 (d, *J* = 8.9 Hz, 2H), 4.21 (t, *J* = 6.8 Hz, 1H), 3.84 (bs, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.68 – 1.50 (m, 2H), 1.42 – 1.36 (m, 1H), 1.28 (s, 7H).

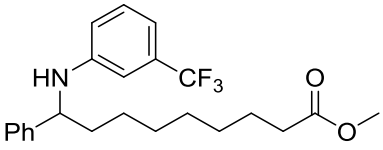
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 151.8, 144.4, 141.7, 128.4, 126.7, 126.4, 114.7, 114.4, 59.0, 55.7, 51.4, 38.9, 34.0, 29.3, 29.0, 29.0, 26.2, 24.8.

MS (EI): *m/z* (%) = 370.3 ($[M+H]^+$, 16), 369.2 ($[M]^+$, 28), 212.1 (100).

IR (ATR): $\tilde{\nu}$ =3398, 2927, 2331, 2079, 1731, 1505, 1228, 1035, 813, 723.

HRMS (EI+, m/z): calculated for $C_{23}H_{31}NO_3Na$ [M+Na]+: 392.21962; found: 392.22009.

Methyl 9-phenyl-9-((4-(trifluoromethyl)phenyl)amino)nonanoate (3s)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 51% (41.5 mg, 0.10 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 4H), 7.25 – 7.21 (m, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.76 (s, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 4.30 (t, *J* = 6.7 Hz, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.62 – 1.58 (m 2H), 1.45 – 1.38 (m, 1H), 1.29 (s, 7H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 147.4, 143.3, 131.2 (q, *J* = 31.7 Hz), 128.6, 127.1, 126.2, 124.2 (q, *J* = 270.2 Hz), 115.7, 113.4, 109.7, 58.1, 51.4, 38.7, 33.9, 29.1, 29.0, 28.9, 26.1, 24.8.

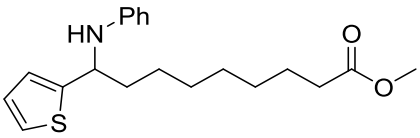
^{19}F NMR (282 MHz, $CDCl_3$) δ -62.96.

MS (EI): *m/z* (%) = 408.3 ($[M+H]^+$, 25), 407.3 ($[M]^+$, 17), 250.2 (100).

IR (ATR): $\tilde{\nu}$ =3395, 2930, 2331, 2103, 1727, 1613, 1492, 1440, 1342, 1161, 782, 698.

HRMS (EI+, m/z): calculated for $C_{23}H_{28}NO_2F_3Na$ [M+Na]+: 430.19643; found: 430.19659.

Methyl 9-(phenylamino)-9-(thiophen-2-yl)nonanoate (3t)



Yellow oil was obtained after column chromatography (100:1 to 20:1 pentane/EtOAc). Yield = 55% (37.9 mg, 0.11 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.09 (m, 3H), 6.97 – 6.91 (m, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* =7.6 Hz, 2H), 4.61 (t, *J* = 6.8 Hz, 1H), 3.99 (bs, 1H), 3.67 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.64 – 1.57 (m, 2H), 1.47 – 1.39 (m, 1H), 1.35 – 1.27 (m, 7H).

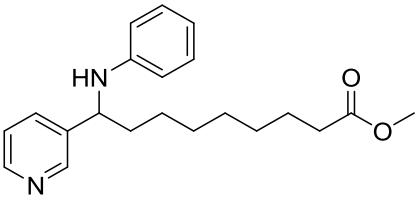
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 149.3, 147.1, 129.1, 126.6, 123.5, 123.4, 117.6, 113.3, 54.1, 51.4, 38.8, 34.0, 29.1, 29.0, 29.0, 26.0, 24.8.

MS (EI): *m/z* (%) = 346.3 ($[M+H]^+$, 16), 345.3 ($[M]^+$, 31), 188.1 (100).

IR (ATR): $\tilde{\nu}$ =3394, 3053, 2928, 2855, 2329, 2113, 1732, 1600, 1432, 1171, 749.

HRMS (EI+, m/z): calculated for $C_{20}H_{27}NO_2SNa$ [M+Na]+: 368.16547; found: 368.16519.

Methyl 9-(phenylamino)-9-(pyridin-3-yl)nonanoate (3u)



Yellow oil was obtained after column chromatography (9:1 to 6:1 pentane/EtOAc). Yield = 49% (33.3 mg, 0.10 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.48 (d, *J* = 3.9 Hz, 1H), 7.65 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.23 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.50 – 6.45 (m, 2H), 4.34 (t, *J* = 6.8 Hz, 1H), 3.66 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.86 – 1.72 (m, 2H), 1.67 – 1.55 (m, 3H), 1.40 – 1.38 (m, 1H), 1.31 (s, 7H).

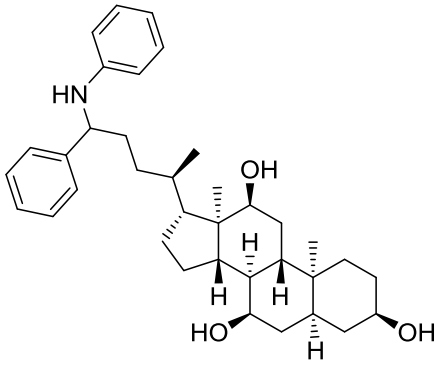
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 148.5, 148.3, 146.8, 139.6, 133.9, 129.1, 123.6, 117.6, 113.2, 55.9, 51.4, 38.7, 33.9, 29.1, 29.0, 28.9, 26.0, 24.8.

MS (EI): *m/z* (%) = 341.3 ($[M+H]^+$, 27), 340.3 ($[M]^+$, 25), 183.1 (100).

IR (ATR): $\tilde{\nu}$ =3368, 3253, 2928, 2856, 2315, 2100, 1738, 1599, 1496, 1429, 1318, 1166, 708.

HRMS (EI+, m/z): calculated for $C_{21}H_{29}N_2O_2$ [M+H]+: 341.22235; found: 341.22244.

(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-10,13-dimethyl-17-((2R)-5-phenyl-5-(phenylamino)pentan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triol (5)



After 48h yellow solid was obtained after column chromatography (2:1 pentane/EtOAc to 100% EtOAc). Yield = 54% (58.8 mg, 0.11 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 4H), 7.21 – 7.17 (m, 1H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 5.6 Hz, 2H), 4.28 – 4.18 (m, 1H), 3.99 (bs, 1H), 3.96 – 3.92 (m, 1H), 3.83 (s, 1H), 3.46 – 3.39 (m, 1H), 2.40 (s, 3H), 2.24 – 2.16 (m, 2H), 1.96 – 1.86 (m, 3H), 1.78 – 1.71 (m, 4H), 1.69 – 1.60 (m, 3H), 1.50 – 1.35 (m, 7H), 1.27 – 1.20 (m, 2H), 1.12 – 1.03 (m, 2H), 0.99 – 0.95 (m, 3H), 0.89- 0.85 (m, 3H), 0.69 – 0.64 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 129.03, 128.47, 126.94, 126.89, 126.54, 126.38, 113.39, 73.03, 71.92, 68.44, 46.37, 41.66, 41.43, 39.59, 39.49, 36.84, 35.34, 35.23, 34.71, 32.33, 32.24, 30.47, 28.14, 27.45, 26.40, 23.19, 22.44, 17.73, 17.13, 12.46, 10.46.

LRMS (ESI): *m/z* = 546.39215 ($[M+H]^+$).

IR (ATR): $\tilde{\nu}$ =3386, 2929, 1901, 1738, 1601, 1366, 1217, 1052, 726.

m.p.: 117- 122 °C.

HRMS (ESI+, m/z): calculated for $C_{36}H_{52}NO_3$ [M+H]+: 546.39417; found: 546.39233.

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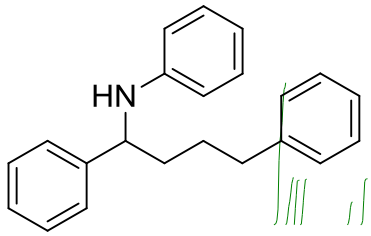
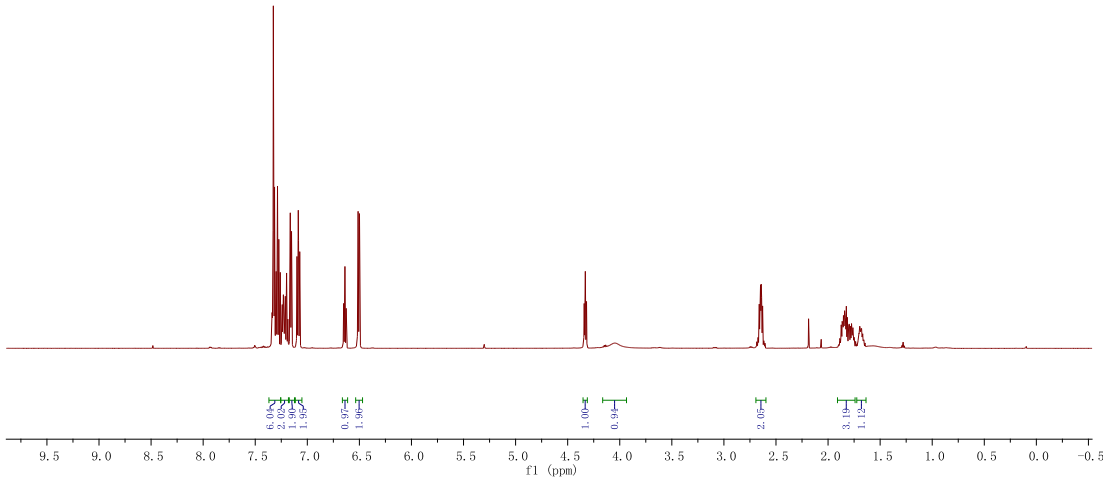
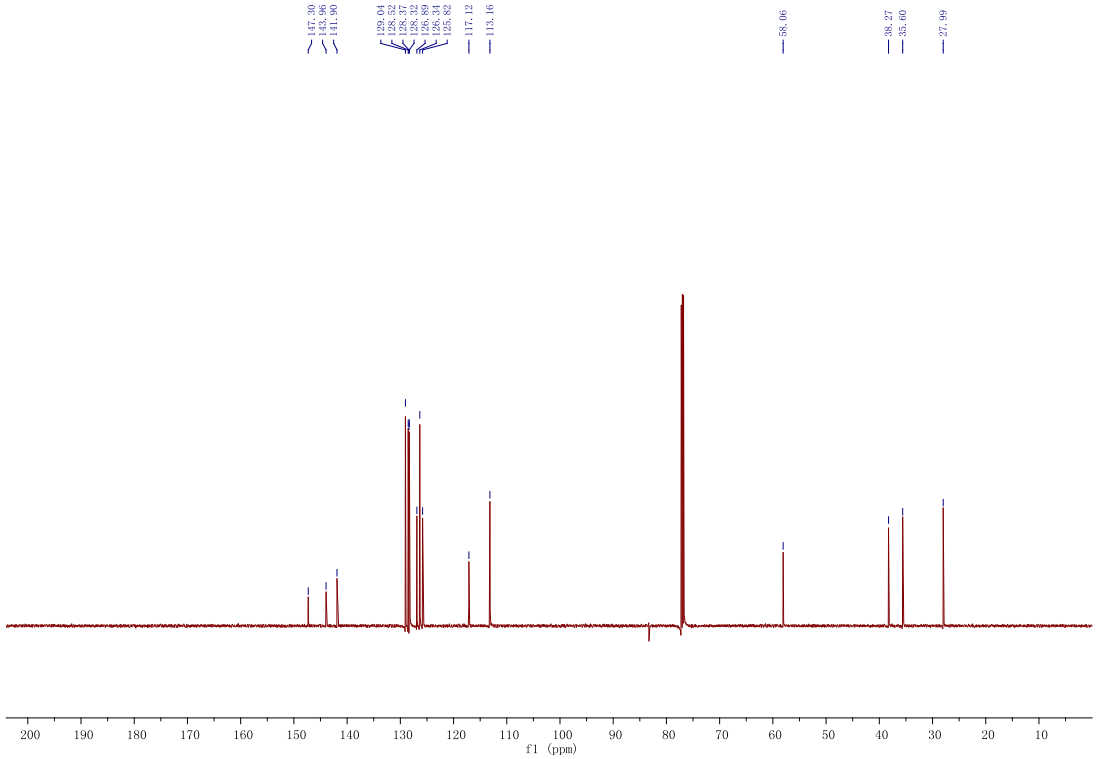
1. NMR spectra

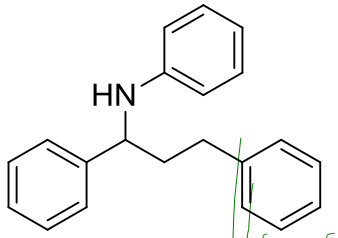
N-(1,4-diphenylbutyl)aniline (3a)

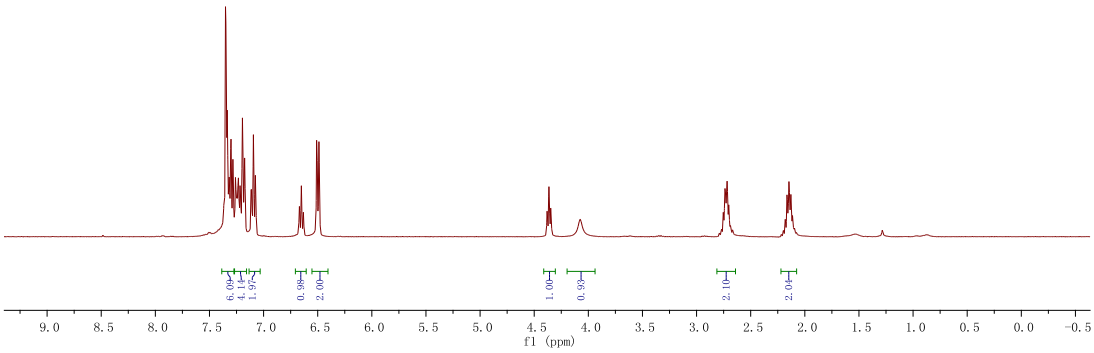


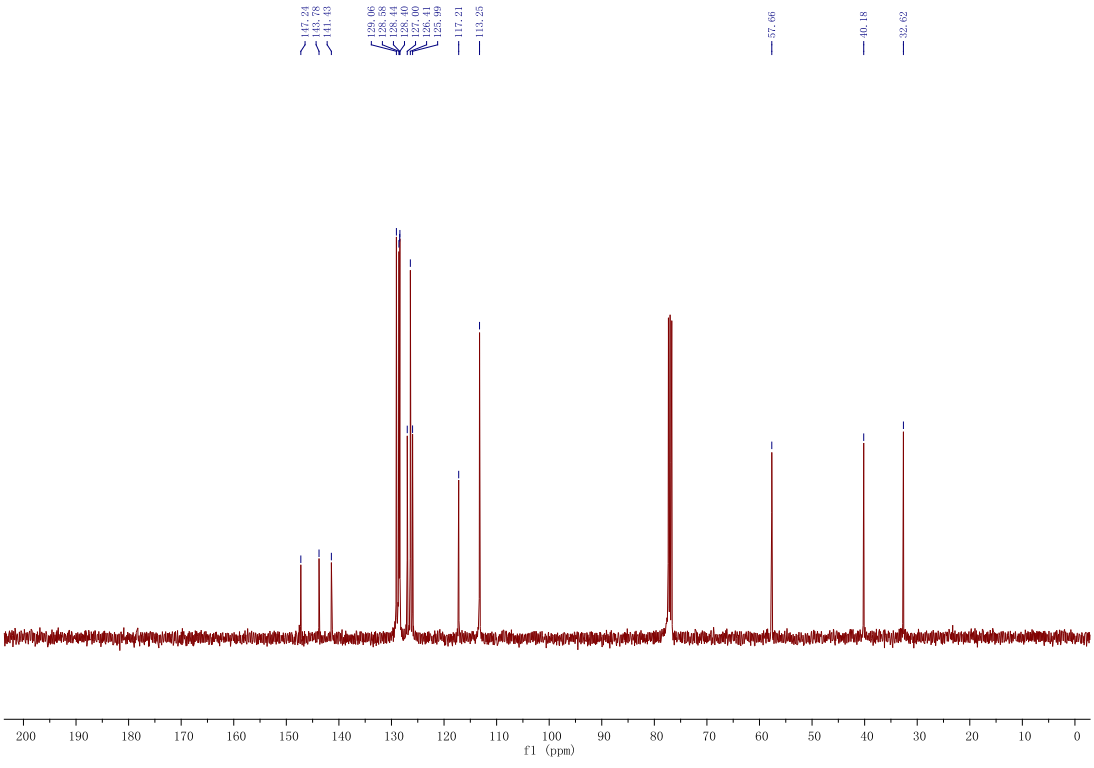




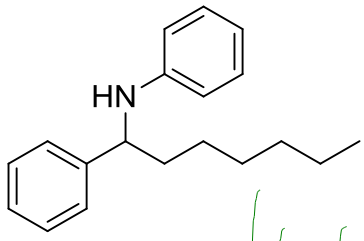
N-(1,3-diphenylpropyl)aniline (3b)

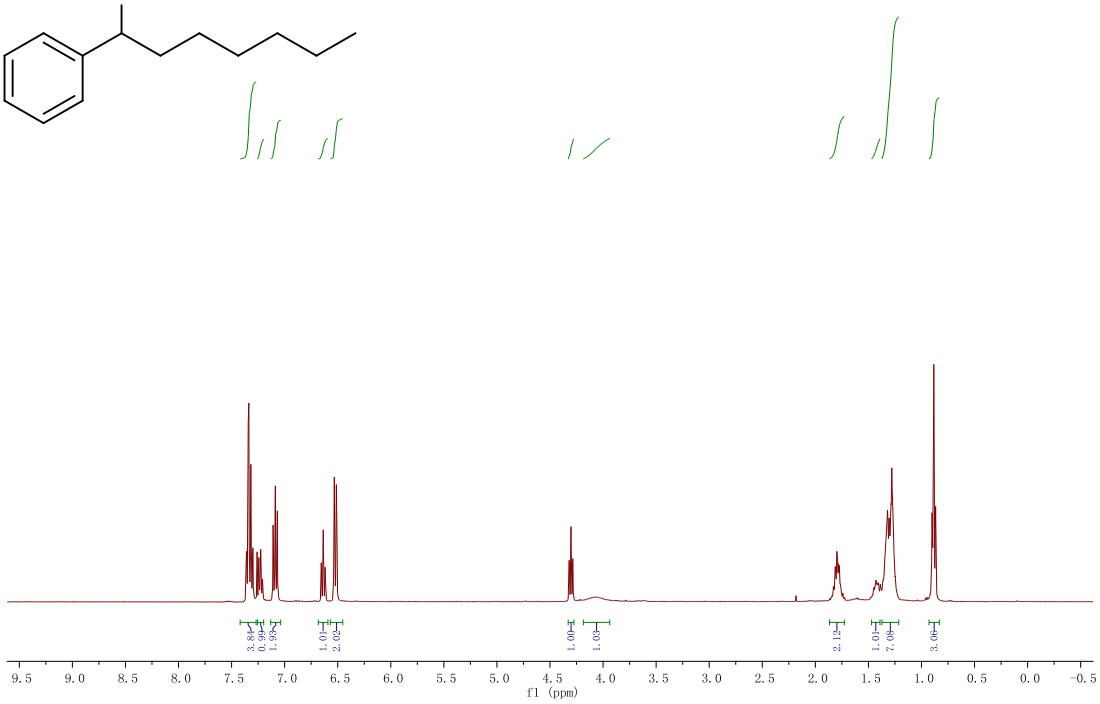


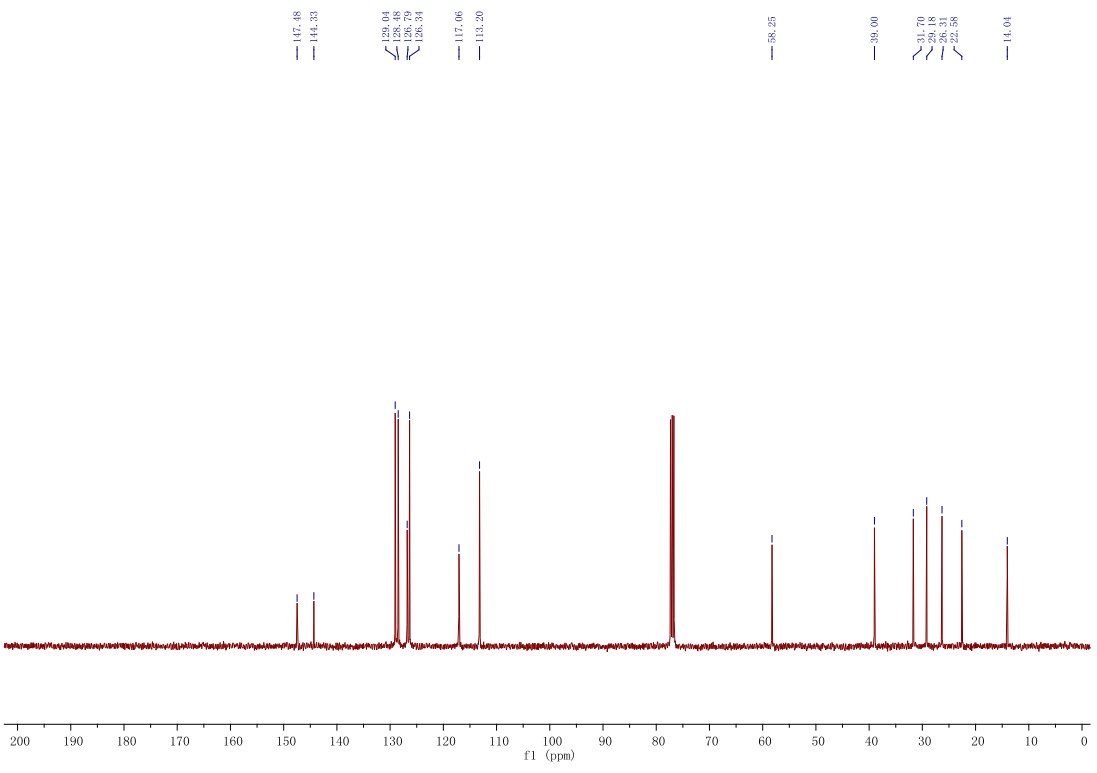




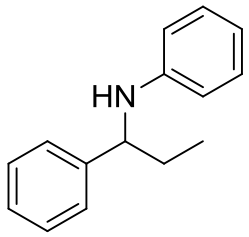
N-(1-phenylheptyl)aniline (3c)

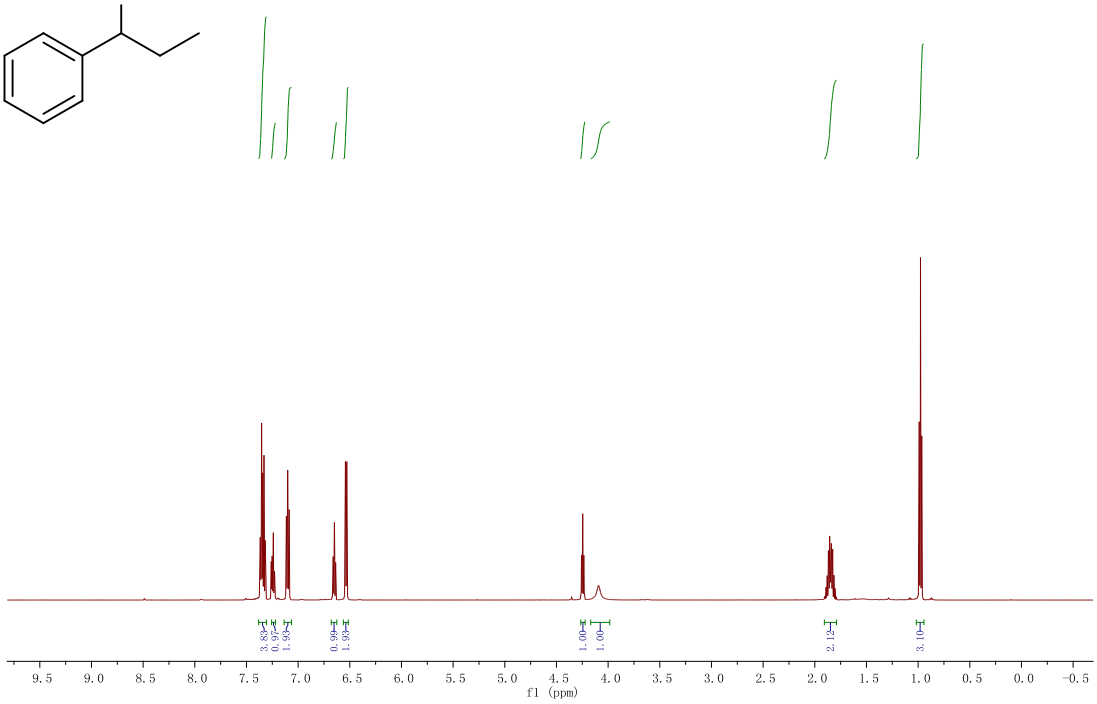


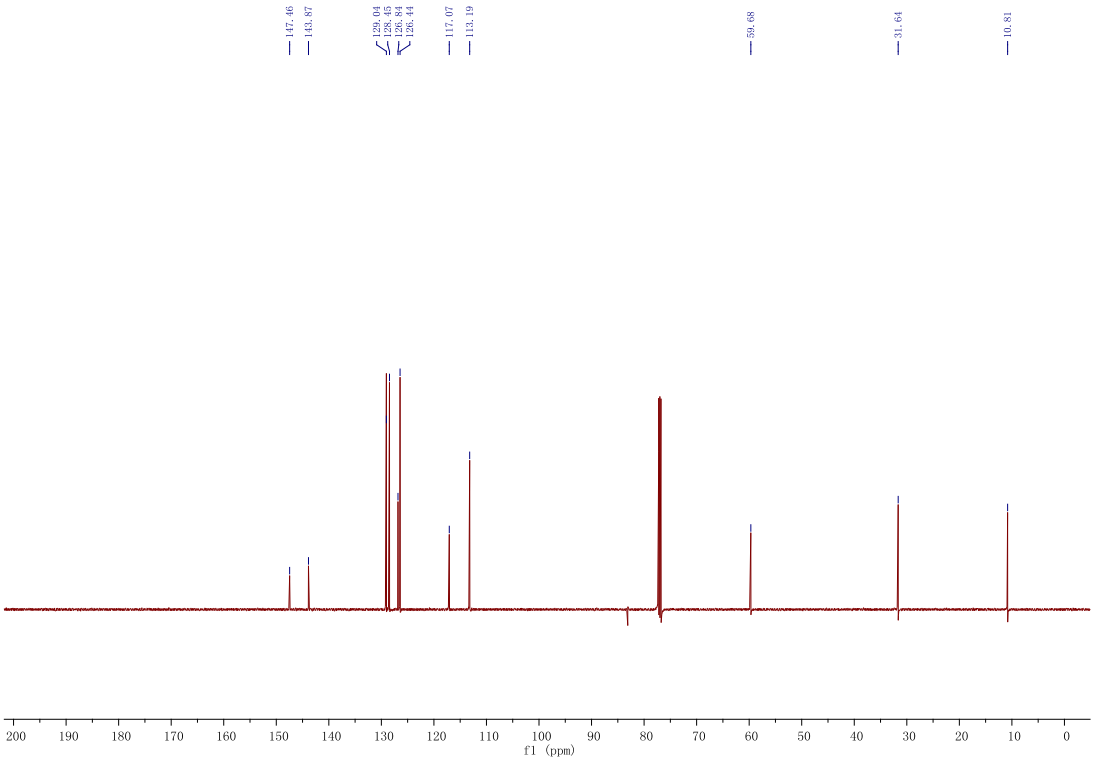




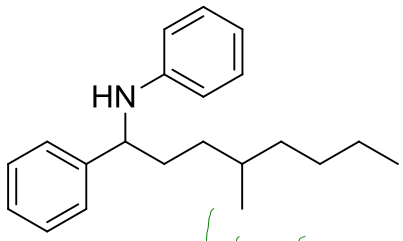
N-(1-phenylpropyl)aniline (3d)

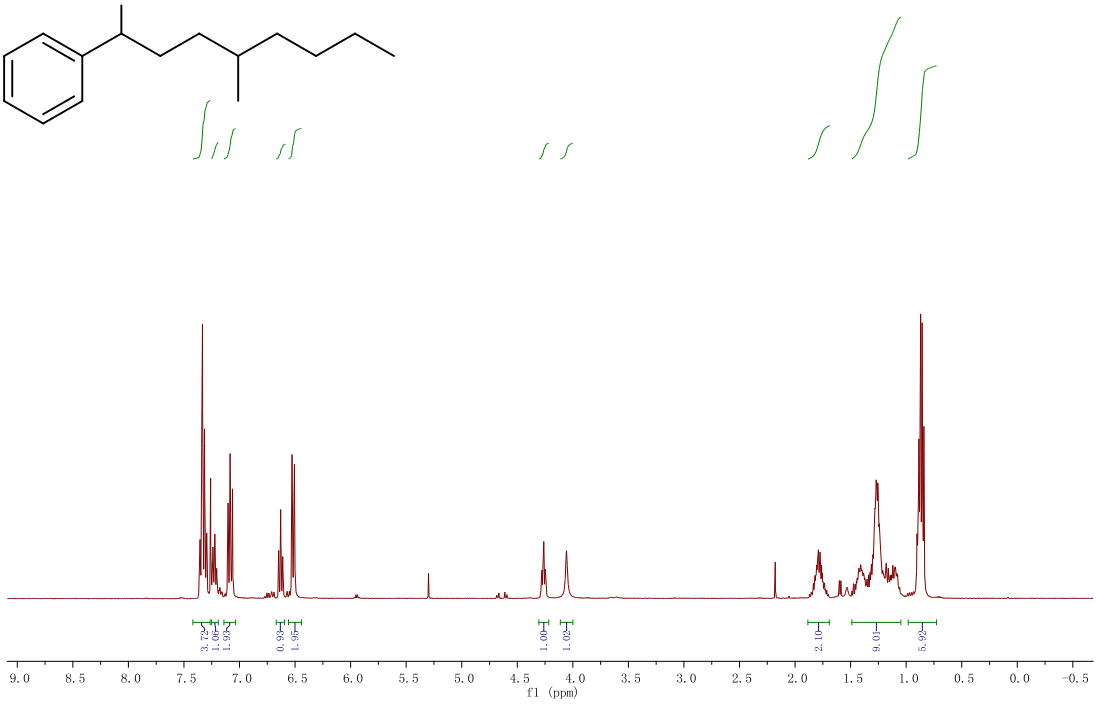


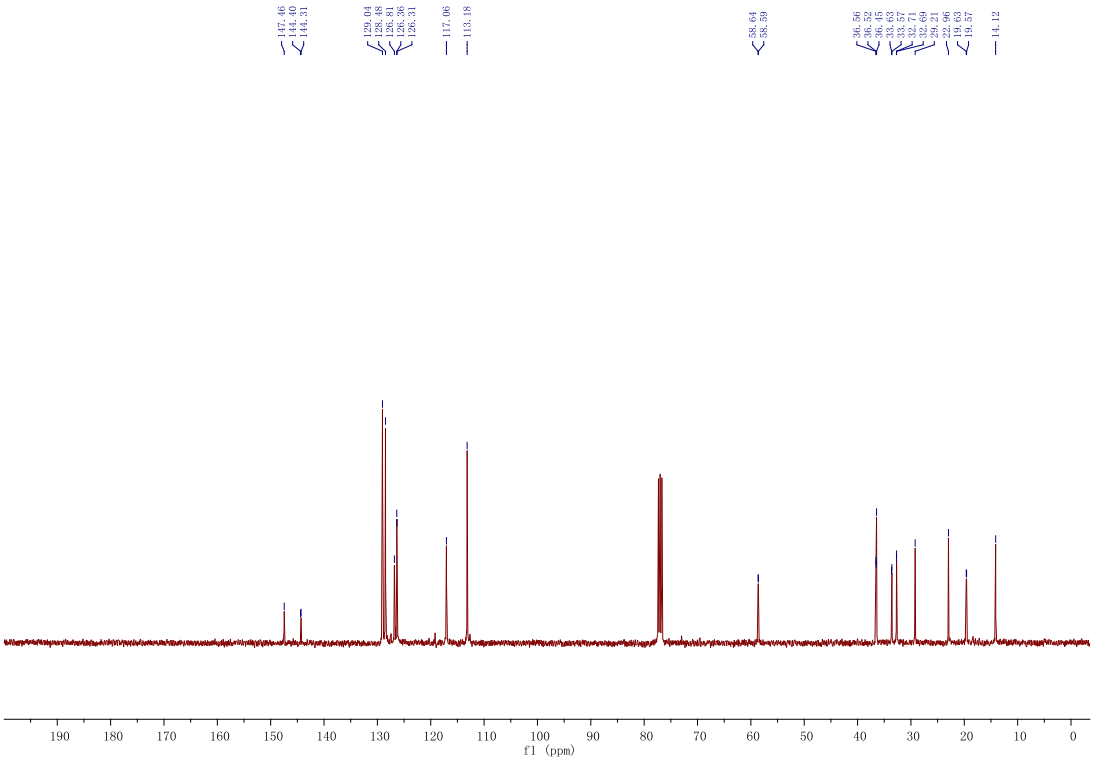




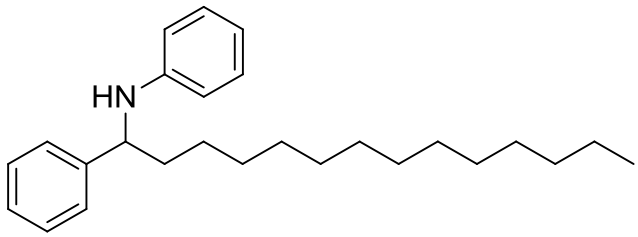
N-(4-methyl-1-phenyloctyl)aniline (3e)

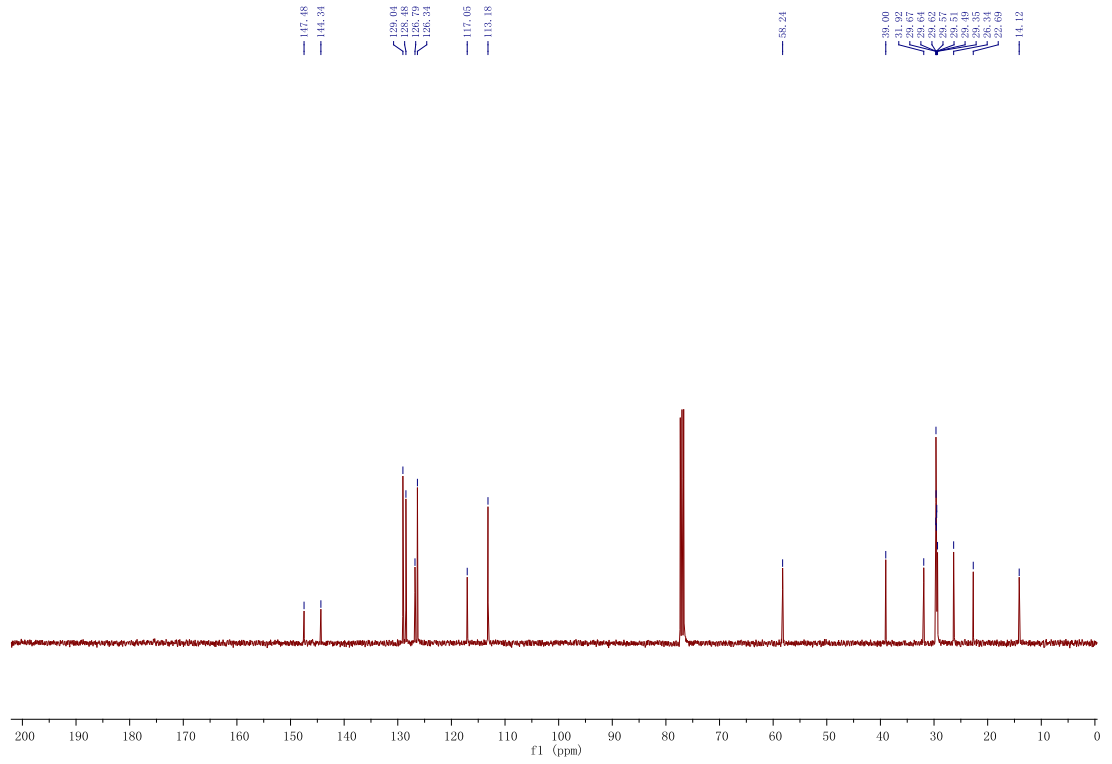




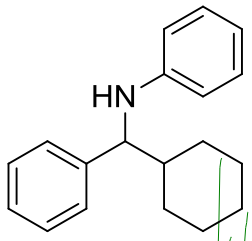


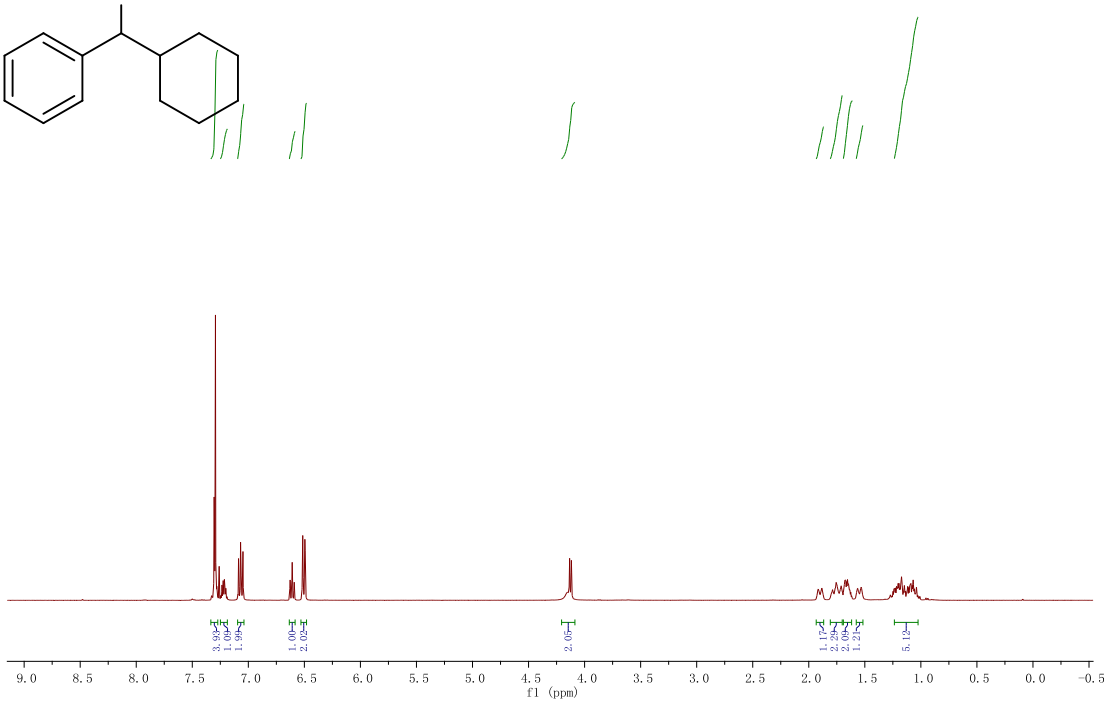
N-(1-phenyltetradecyl)aniline (3f)

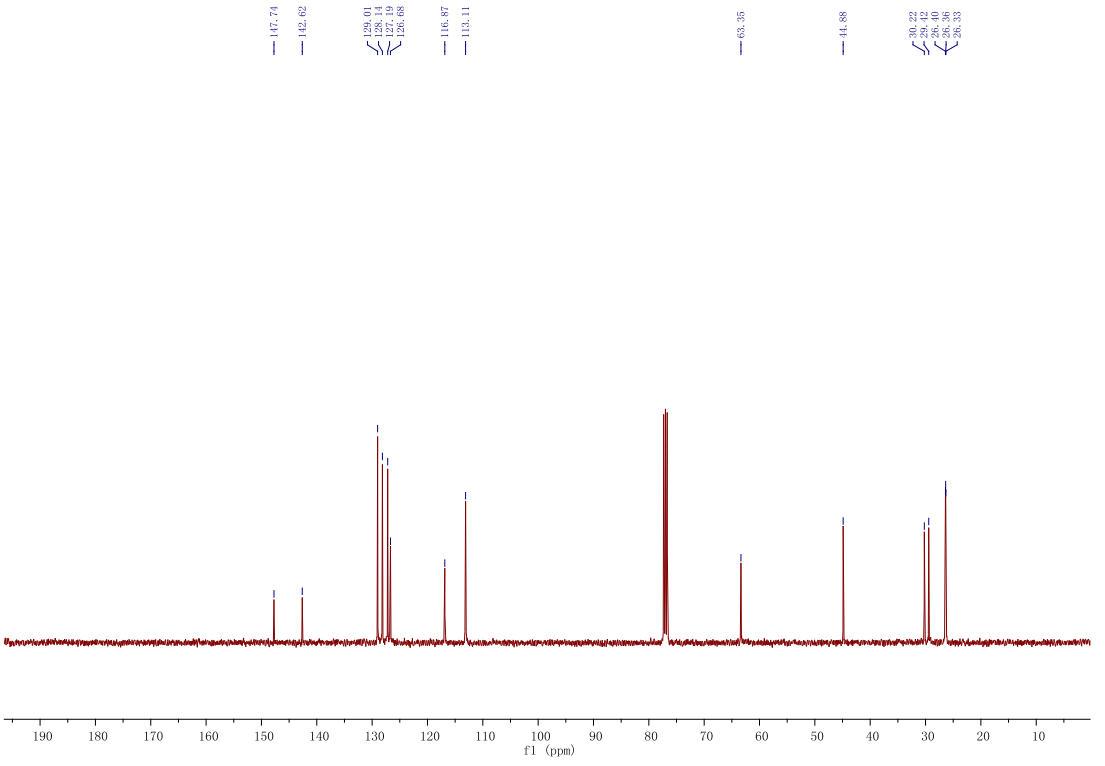




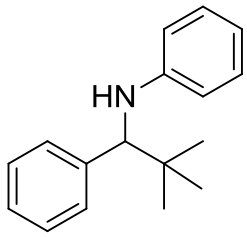
N-(cyclohexyl(phenyl)methyl)aniline (3g)

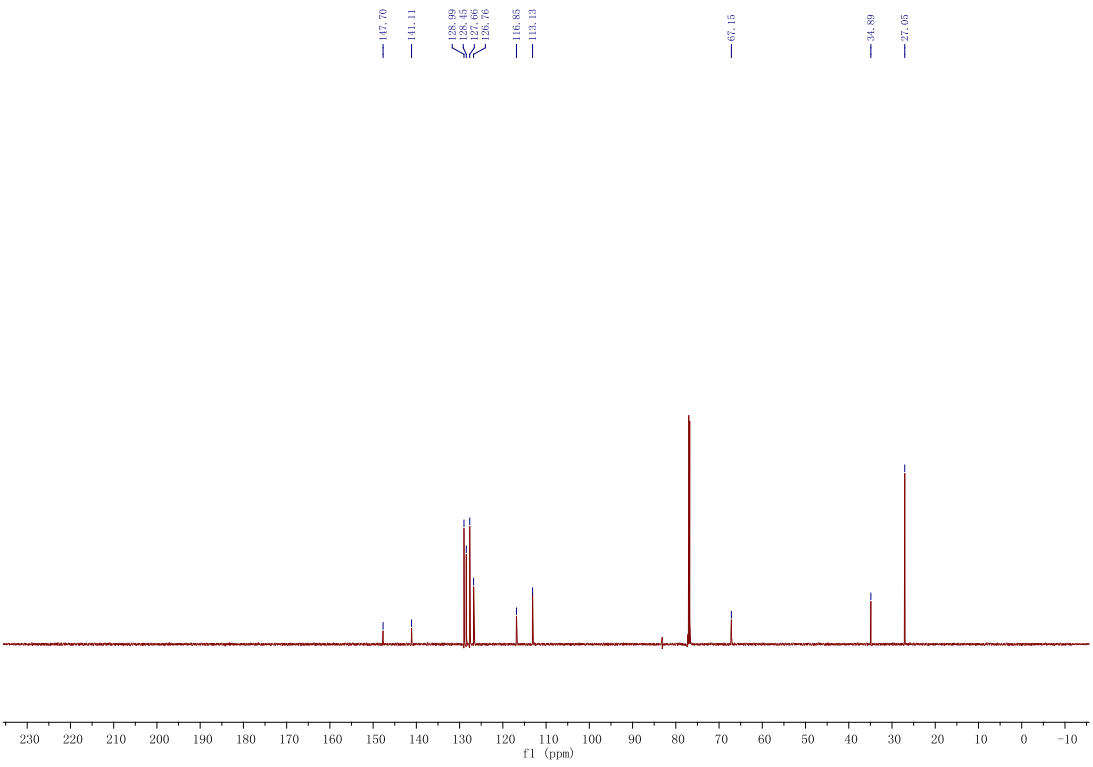




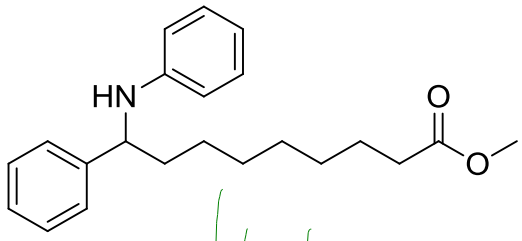


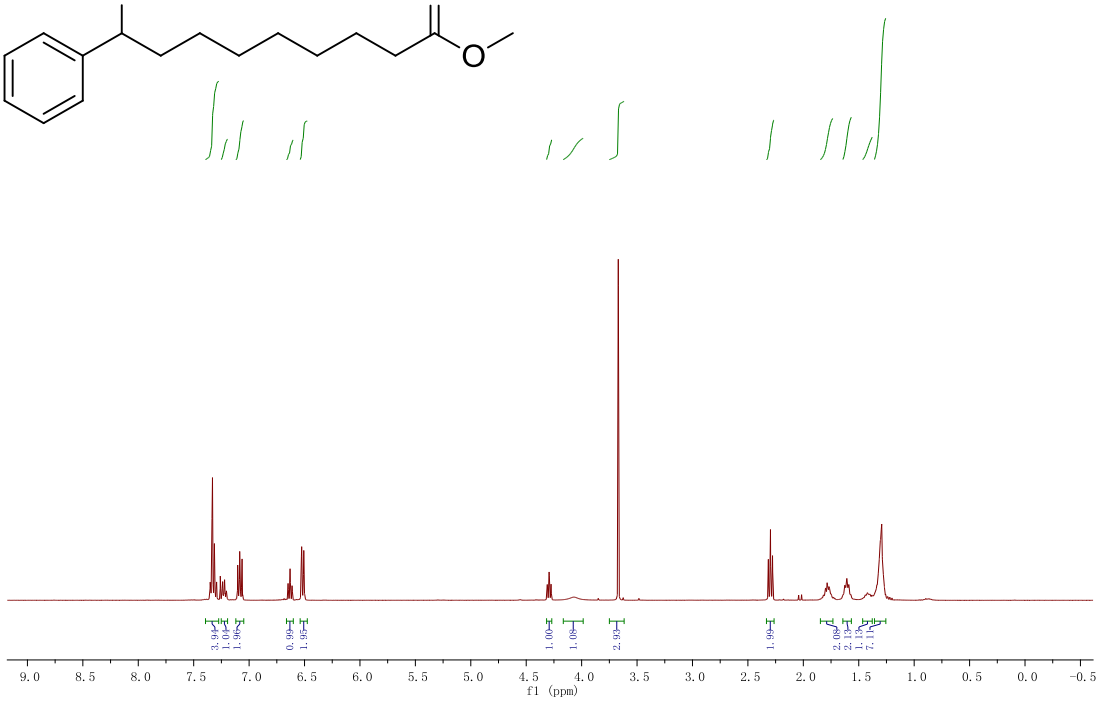
N-(2,2-dimethyl-1-phenylpropyl)aniline (3h)

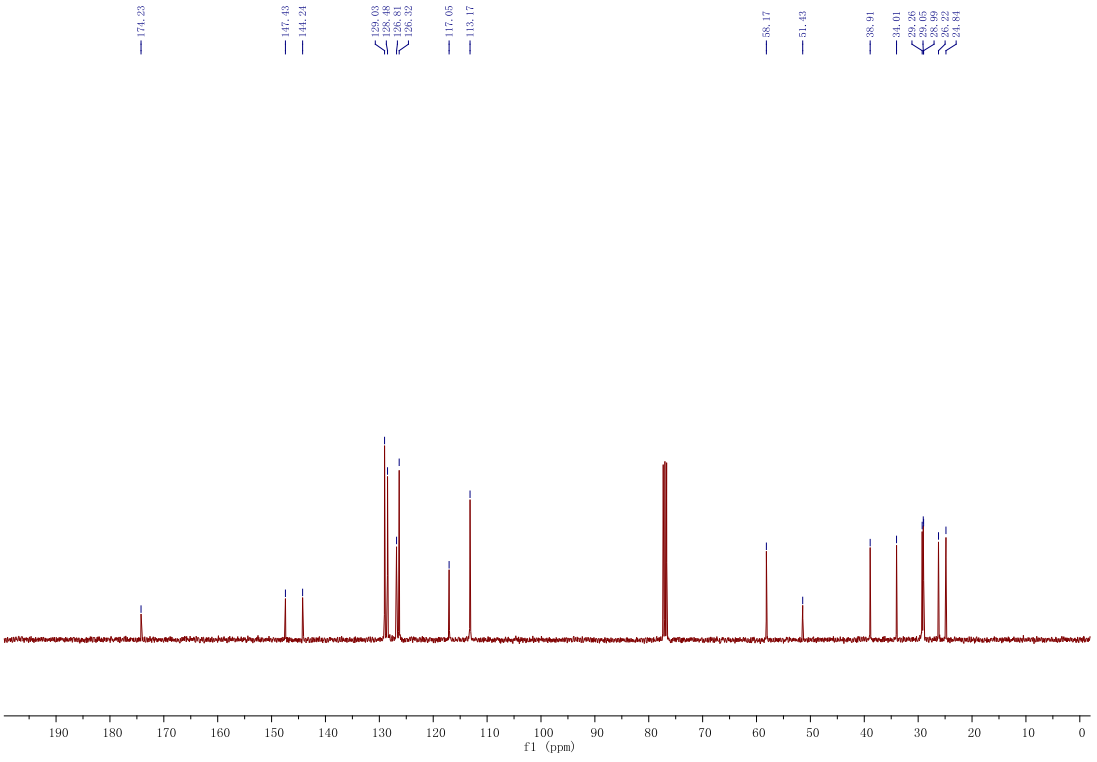




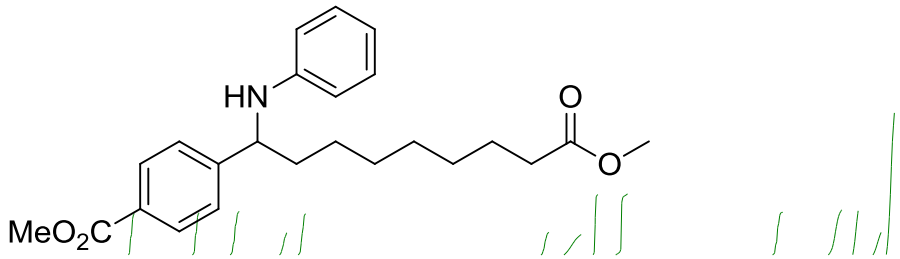
Methyl 9-phenyl-9-(phenylamino)nonanoate (3i)

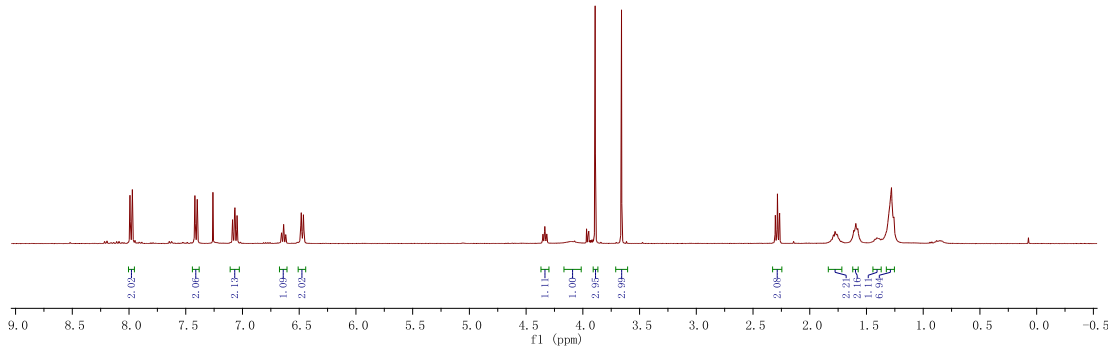


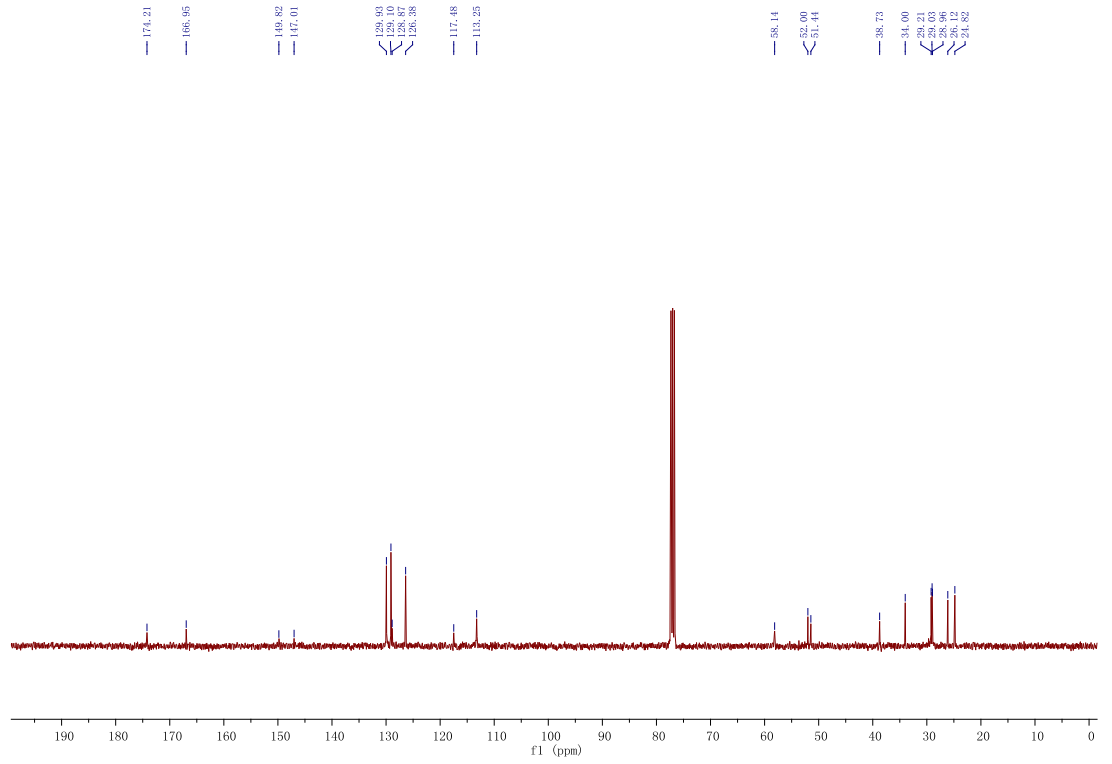




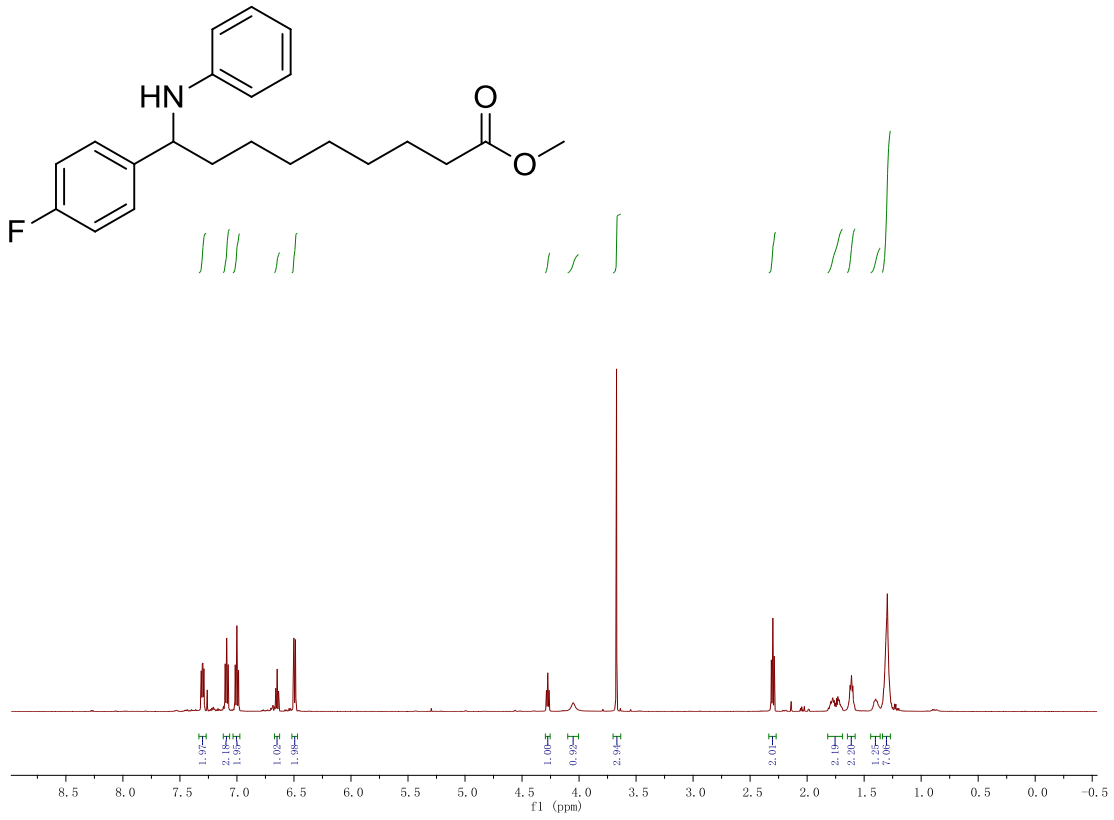
Methyl 4-(9-methoxy-9-oxo-1-(phenylamino)nonyl)benzoate (3j)

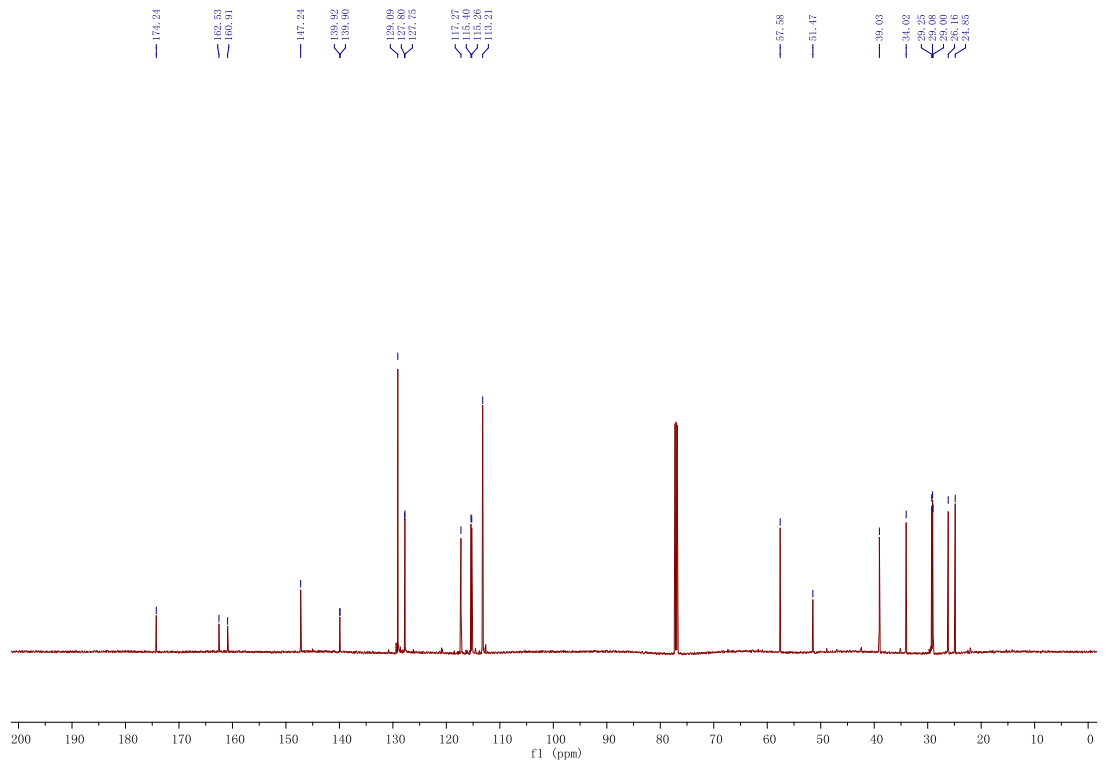






Methyl 9-(4-fluorophenyl)-9-(phenylamino)nonanoate (3k)





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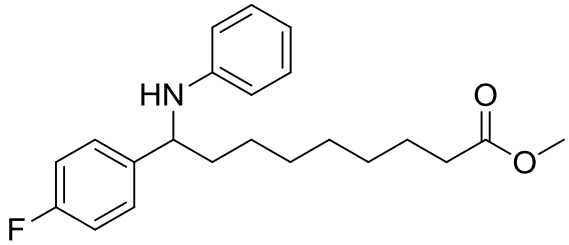
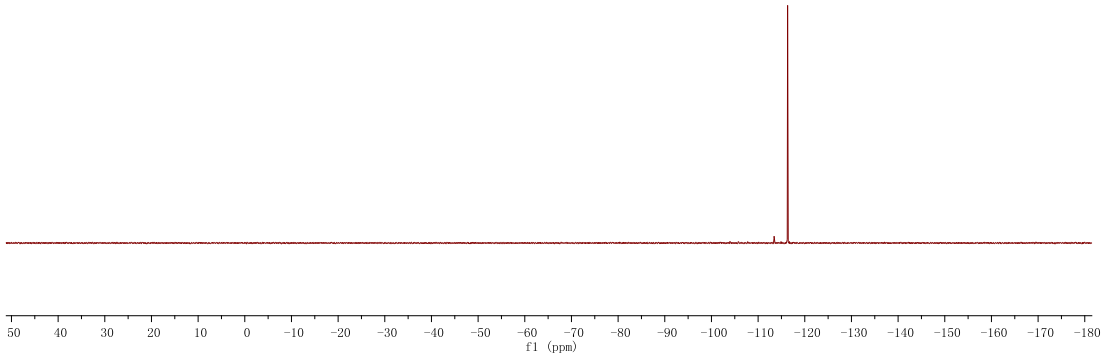
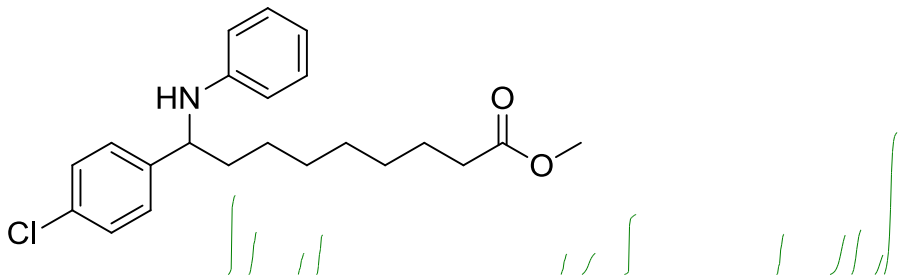
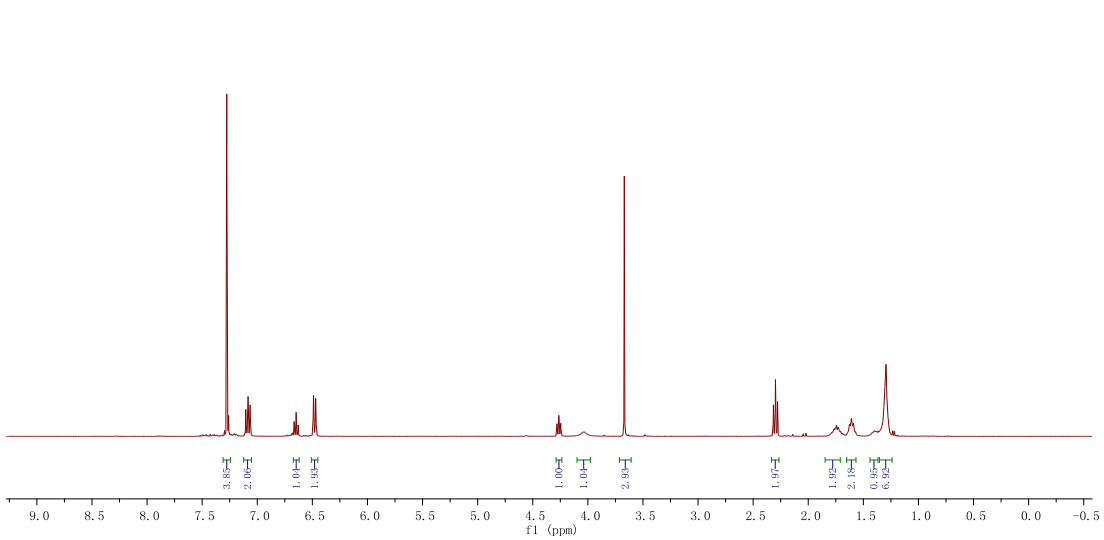
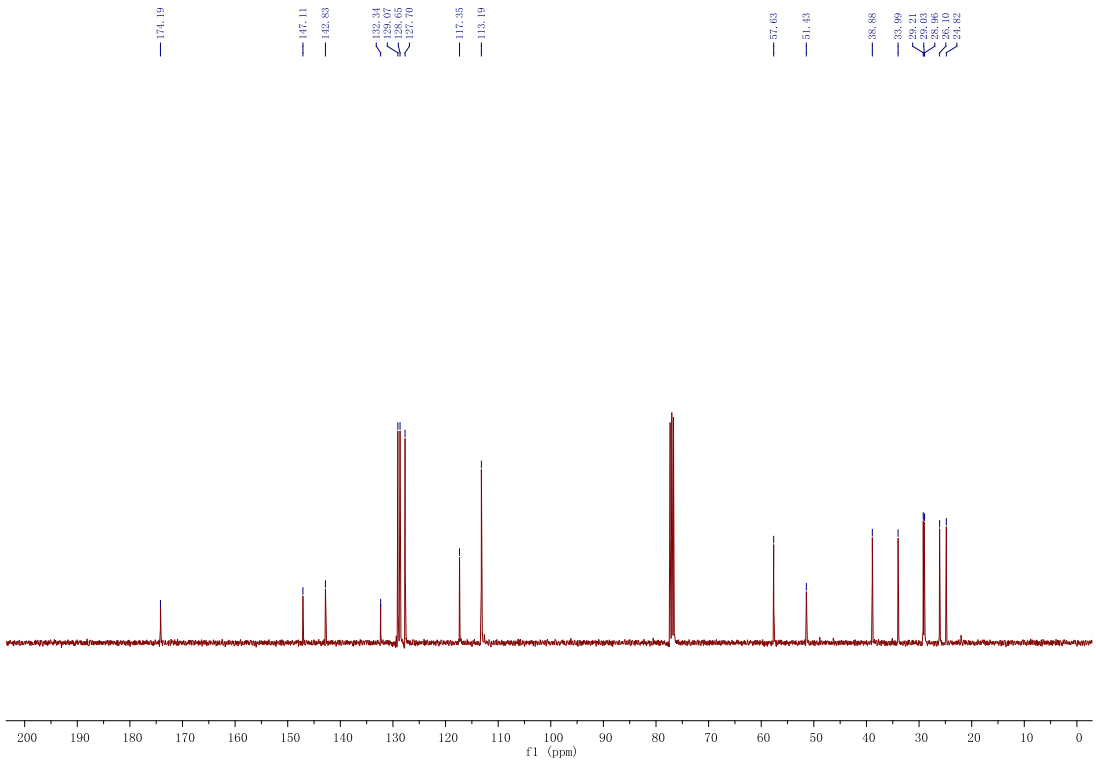




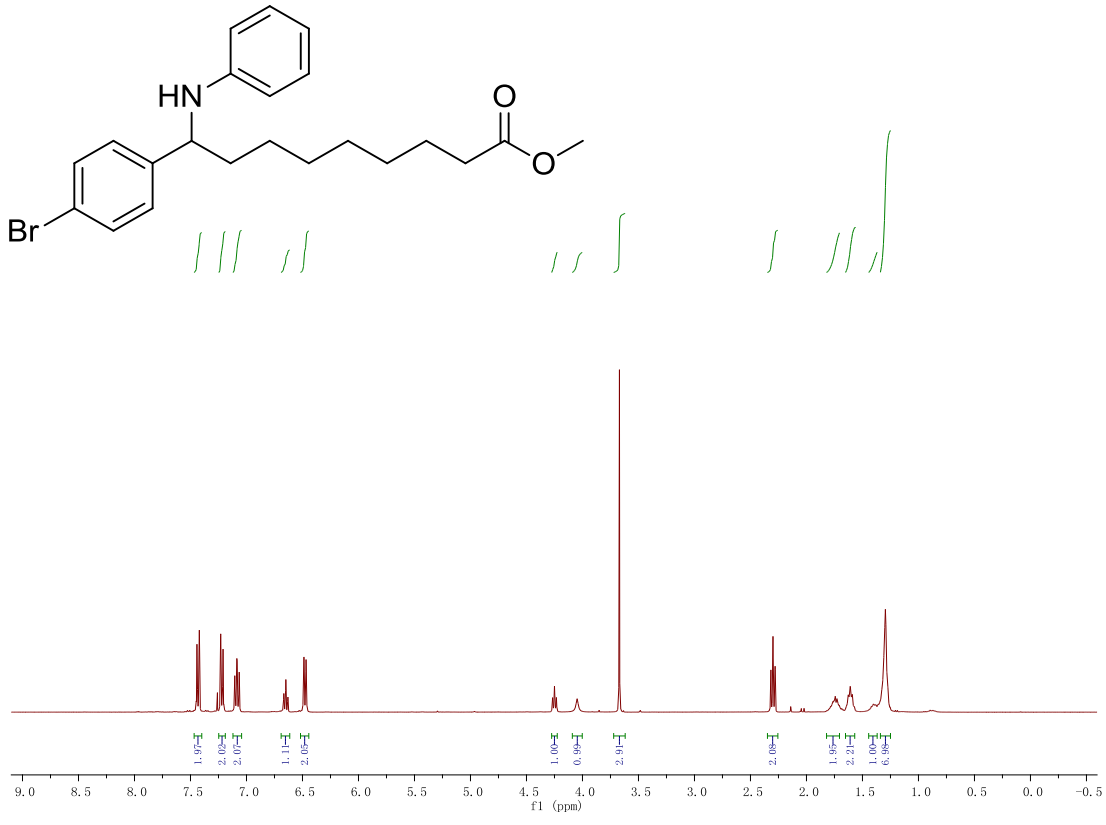
Methyl 9-(4-chlorophenyl)-9-(phenylamino)nonanoate (3l)

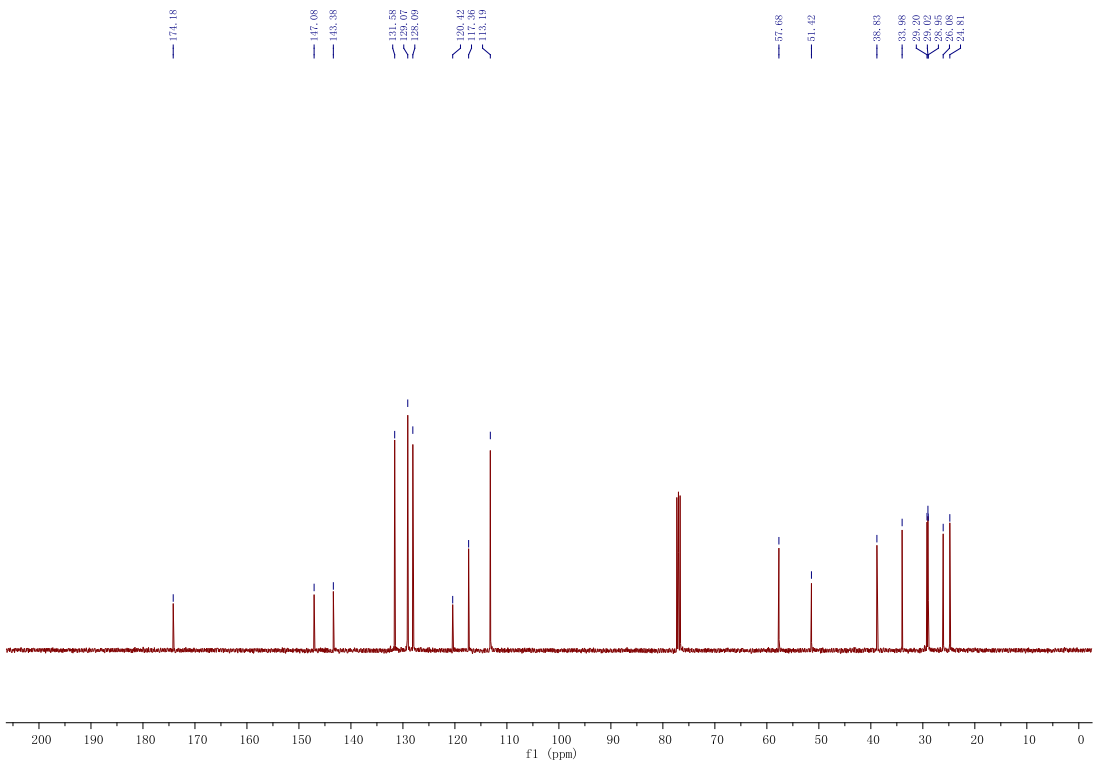




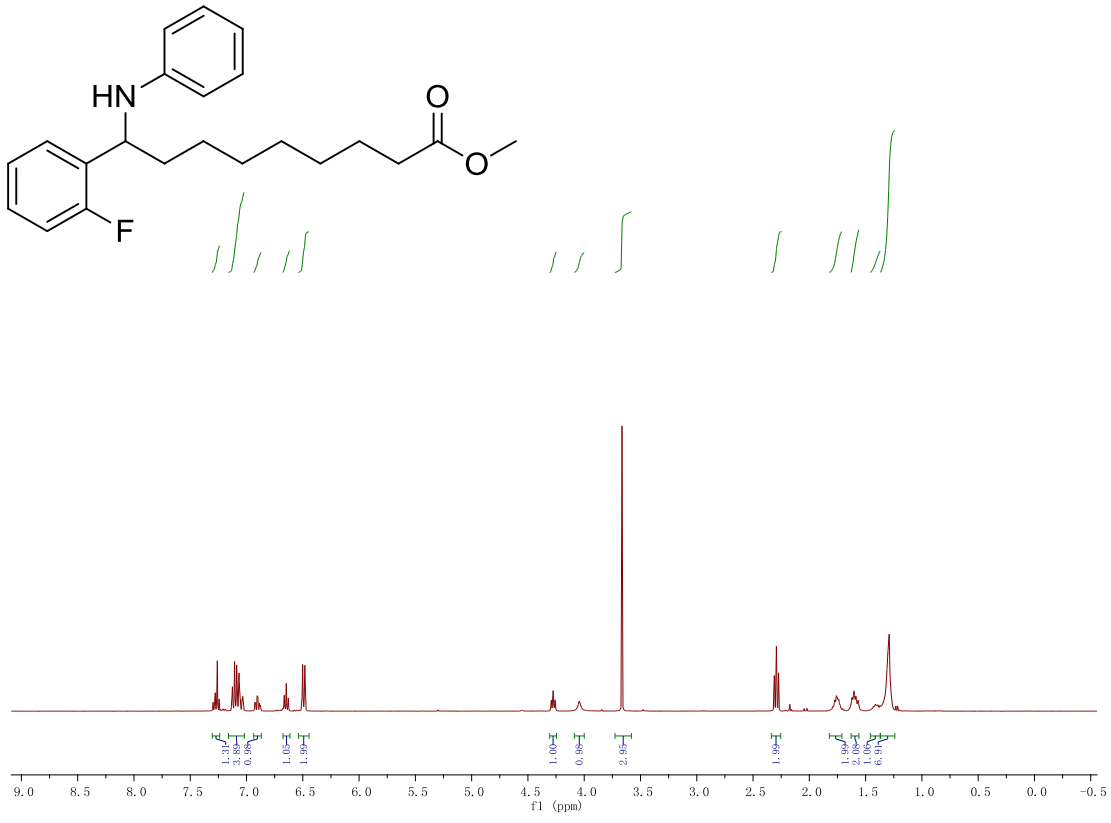


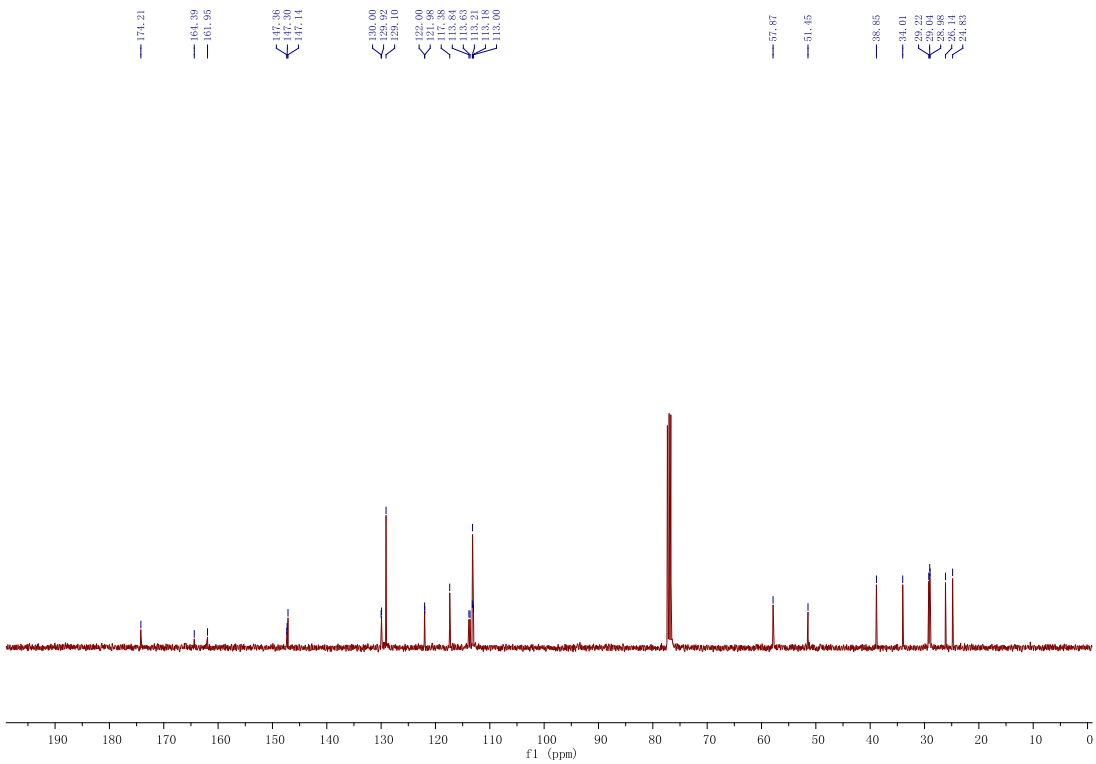
Methyl 9-(4-bromophenyl)-9-(phenylamino)nonanoate (3m)



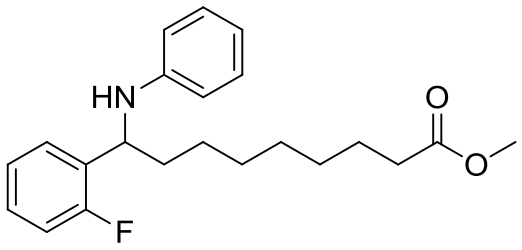


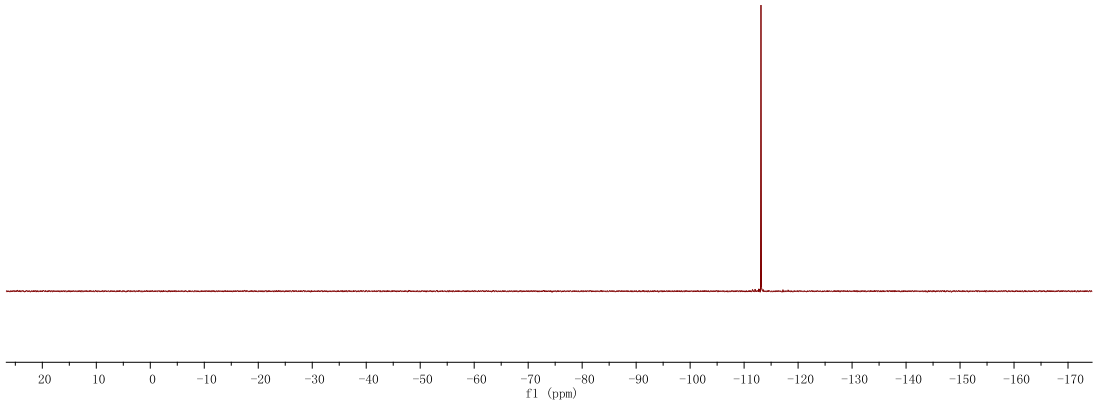
Methyl 9-(2-fluorophenyl)-9-(phenylamino)nonanoate (3n)



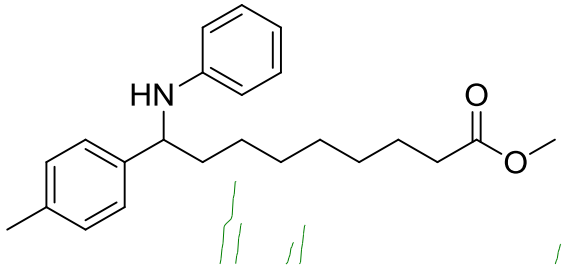


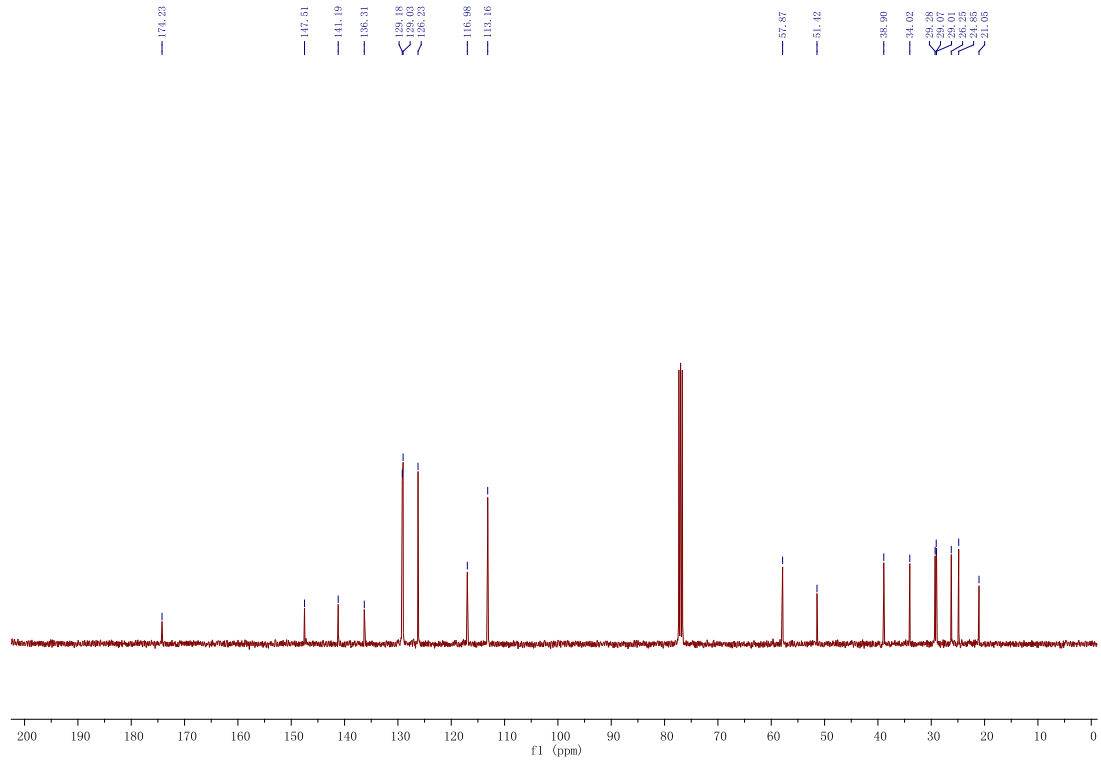
Methyl 9-(2-fluorophenyl)-9-(phenylamino)nonanoate (3n)



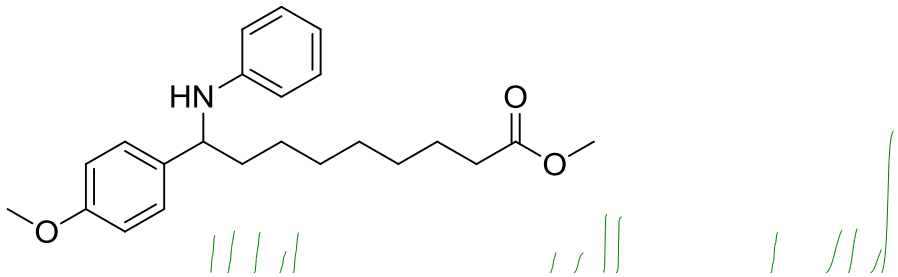


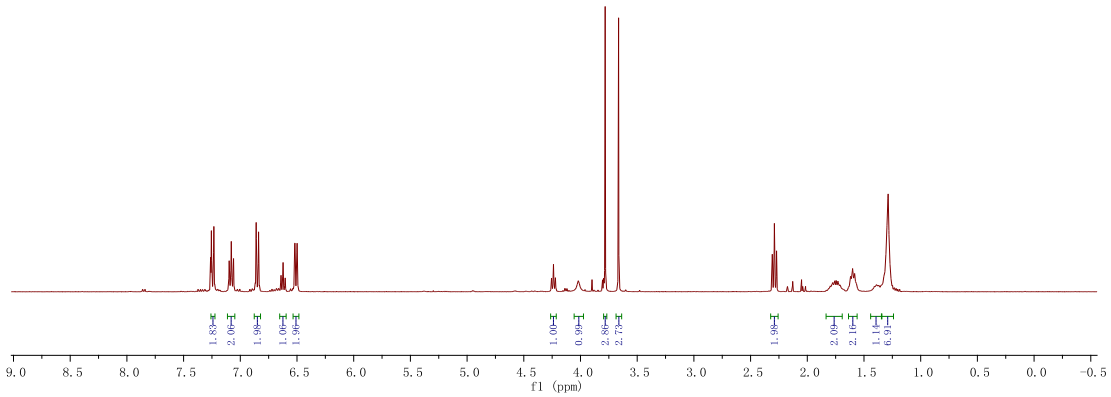
Methyl 9-(phenylamino)-9-(p-tolyl)nonanoate (3o)

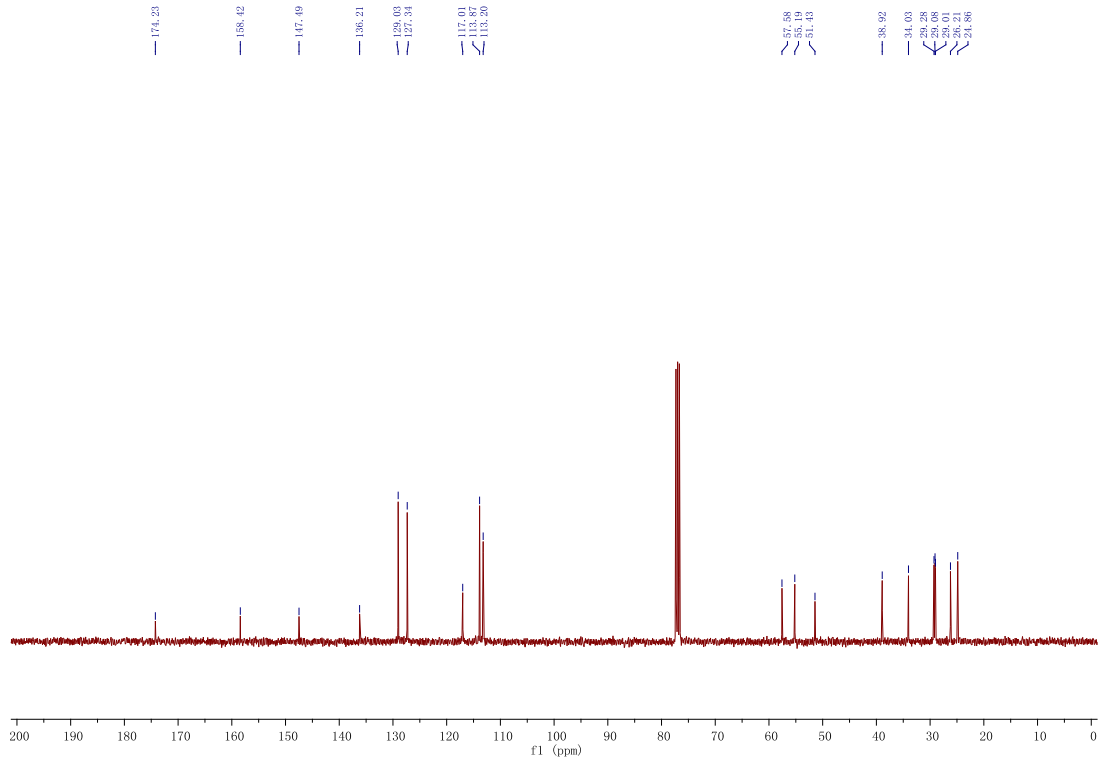




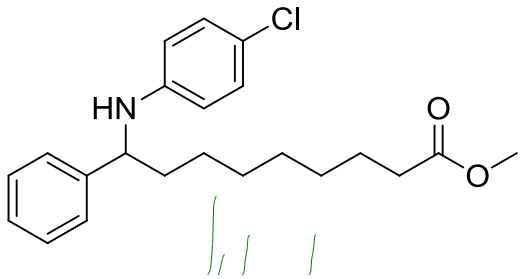
Methyl 9-(4-methoxyphenyl)-9-(phenylamino)nonanoate (3p)

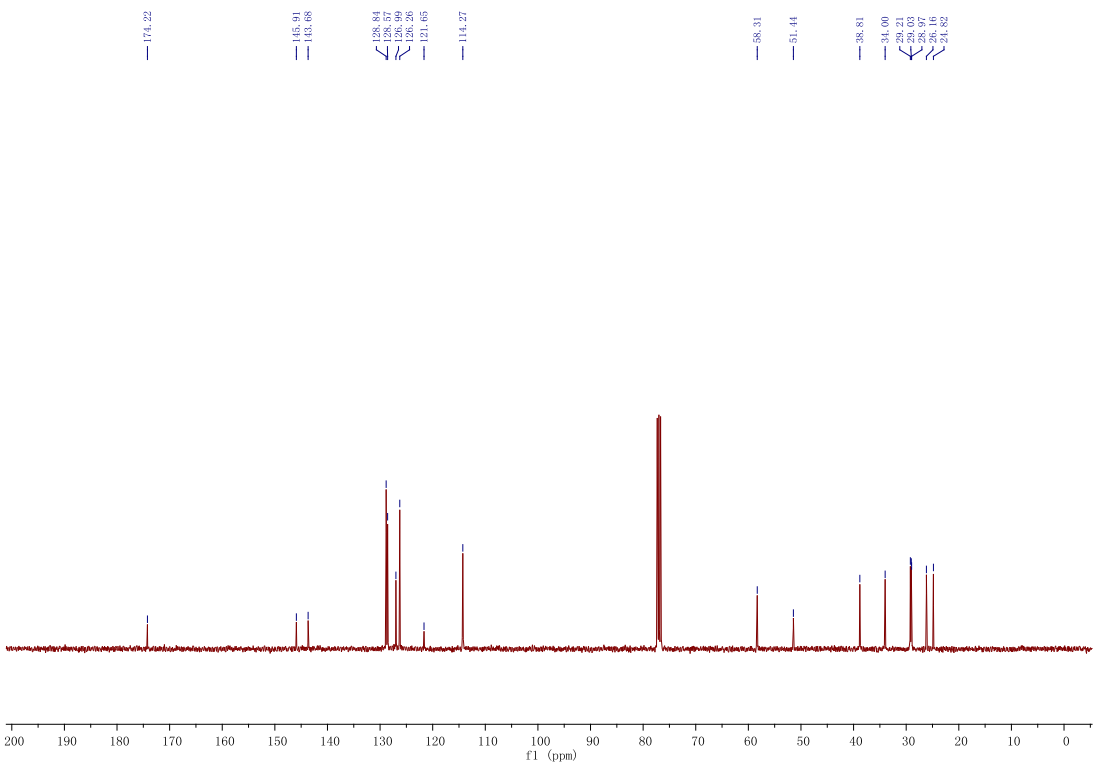




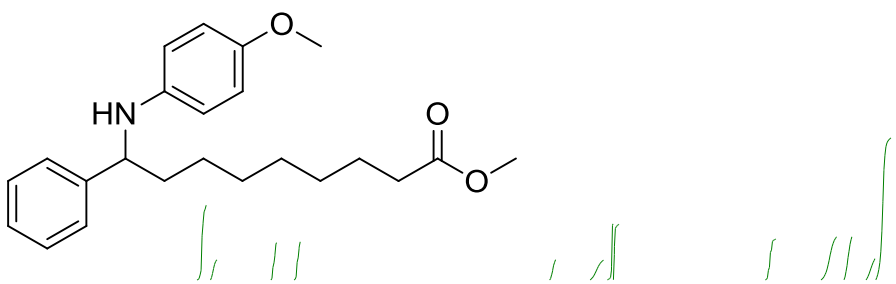


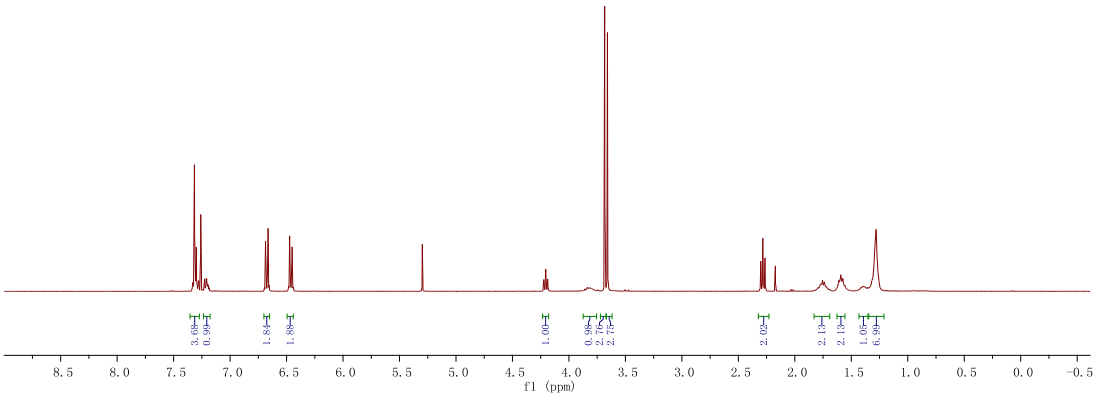
Methyl 9-((4-chlorophenyl)amino)-9-phenylnonanoate (3q)

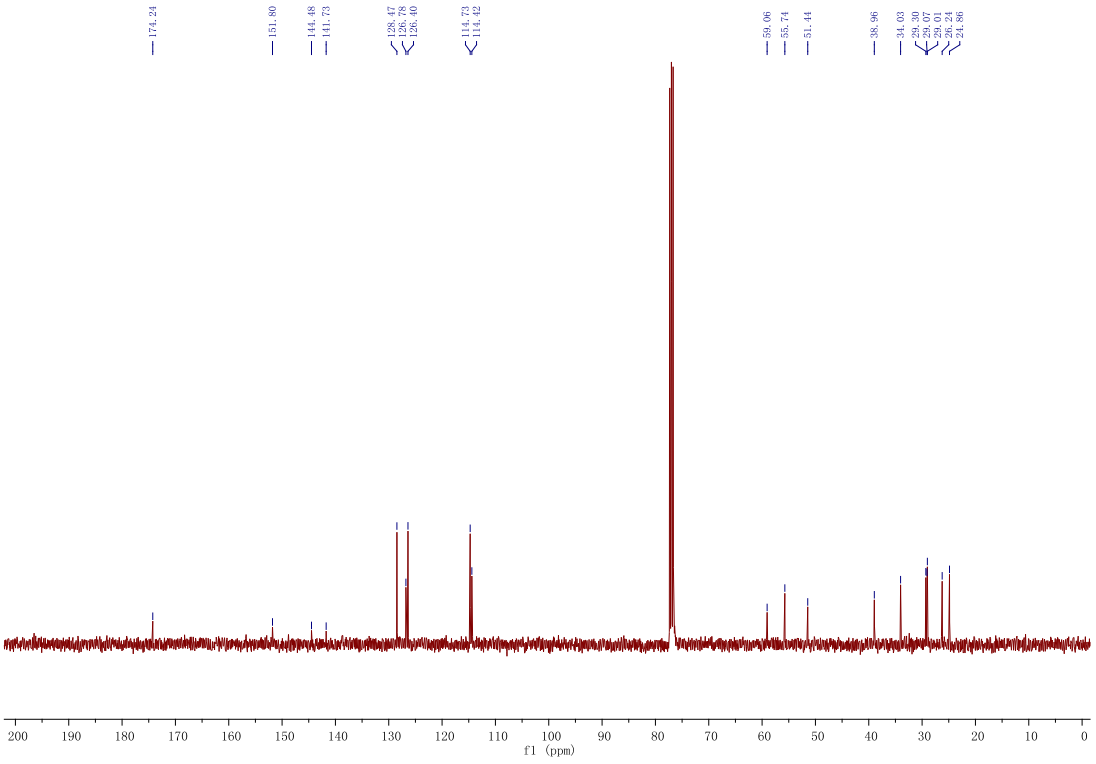




Methyl 9-((4-methoxyphenyl)amino)-9-phenylnonanoate (3r)







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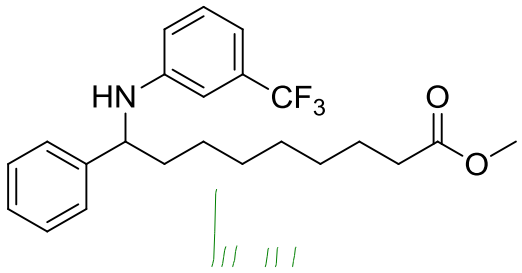

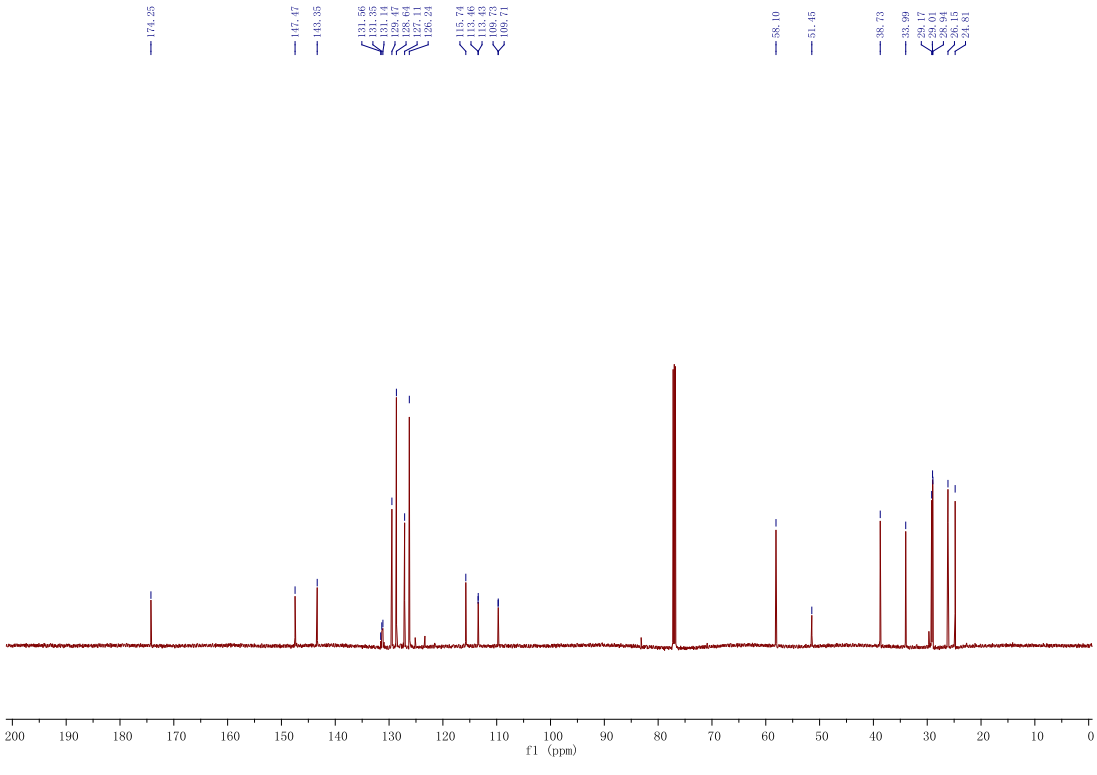

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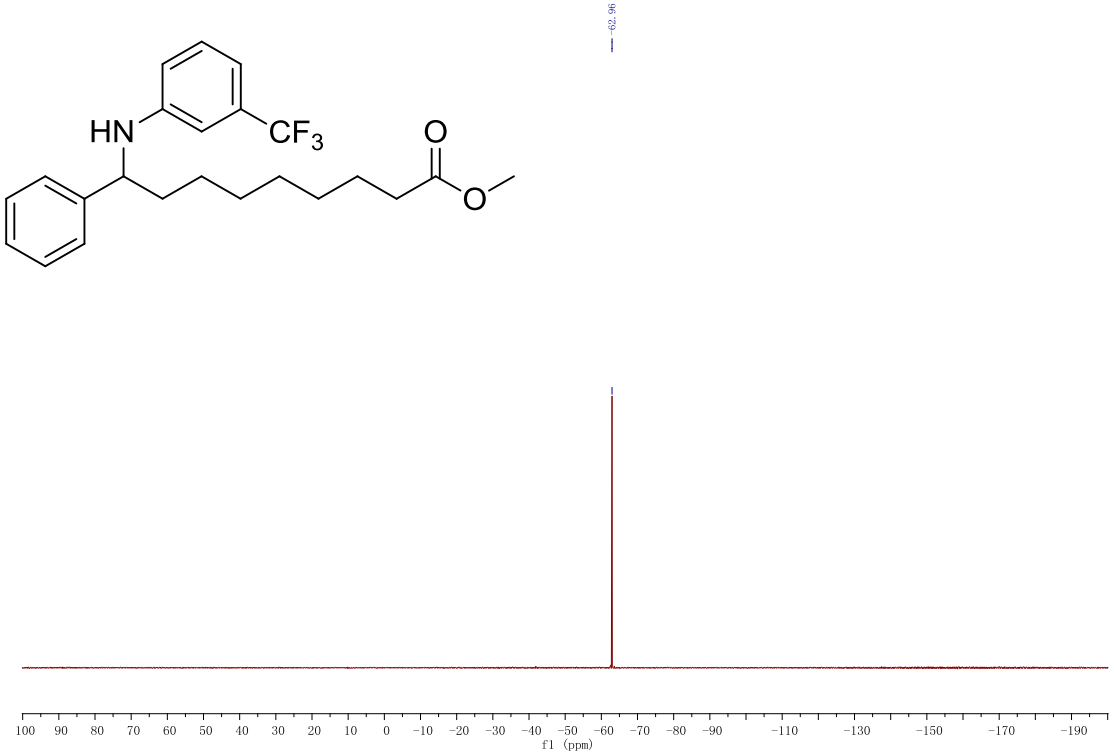
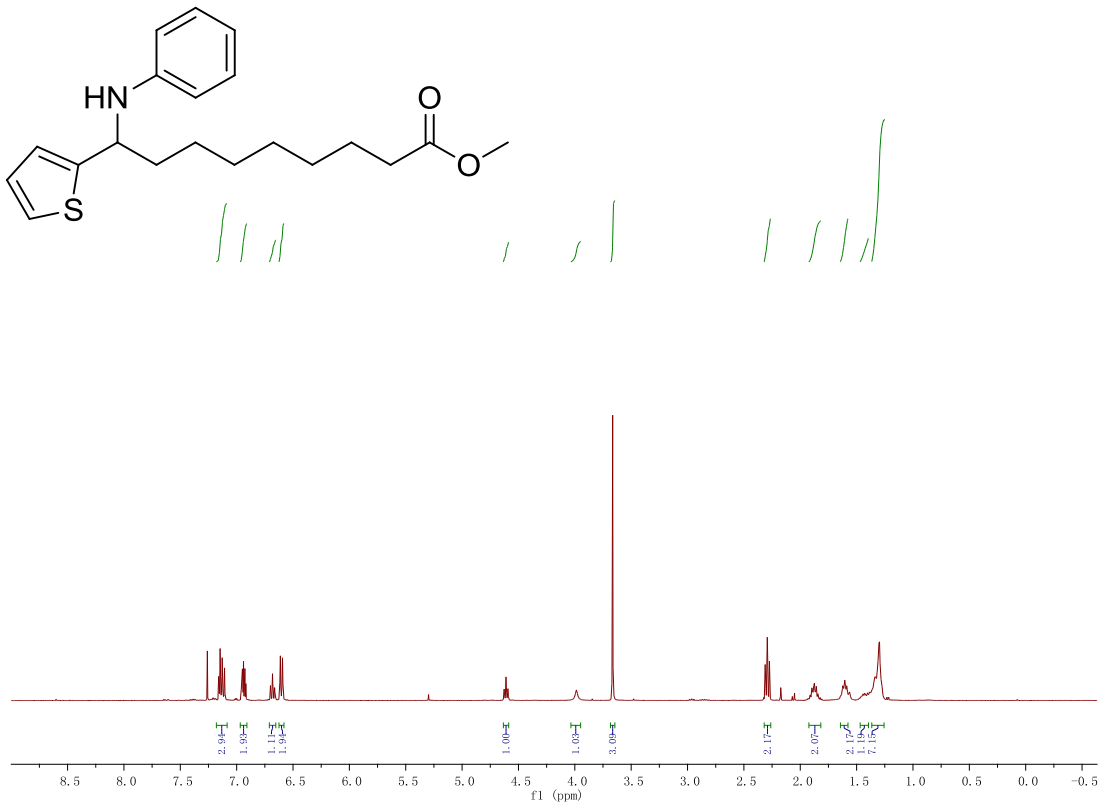
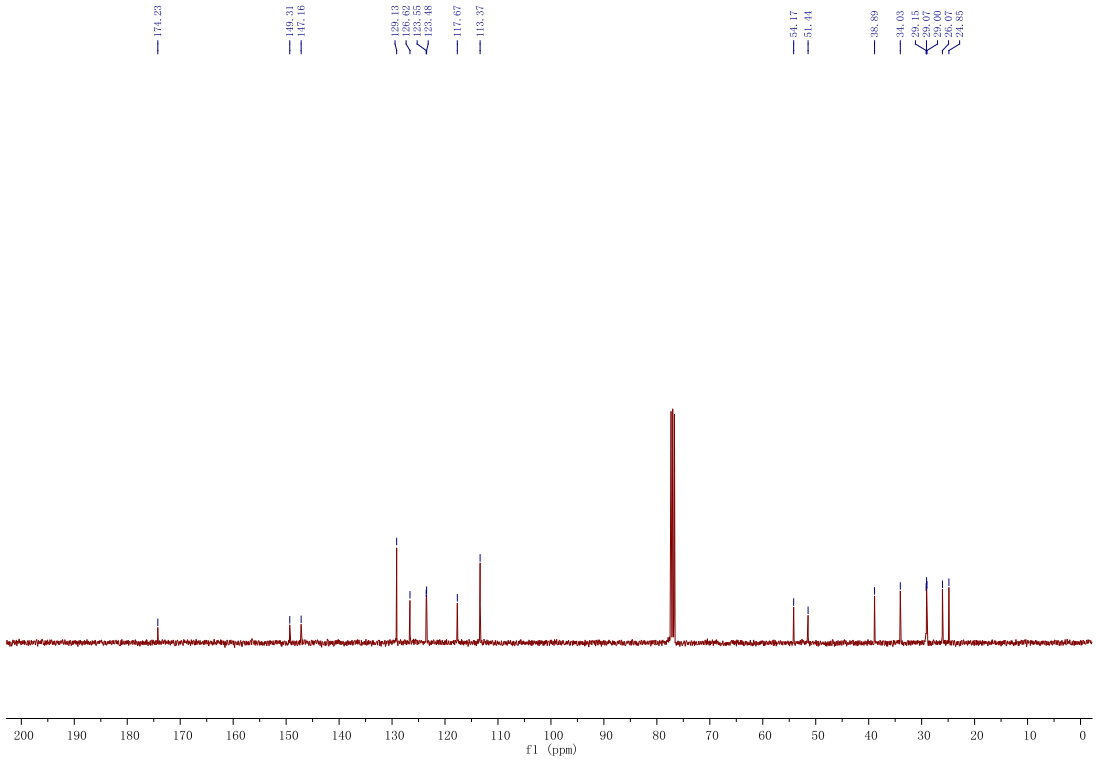
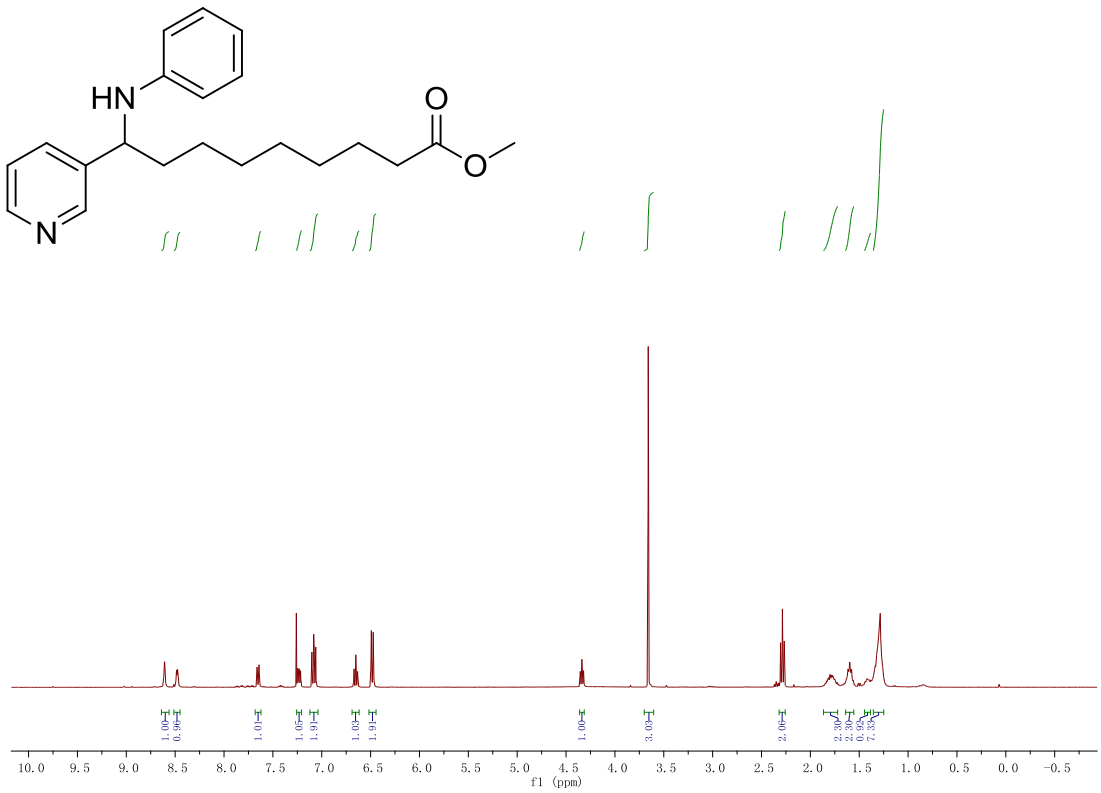


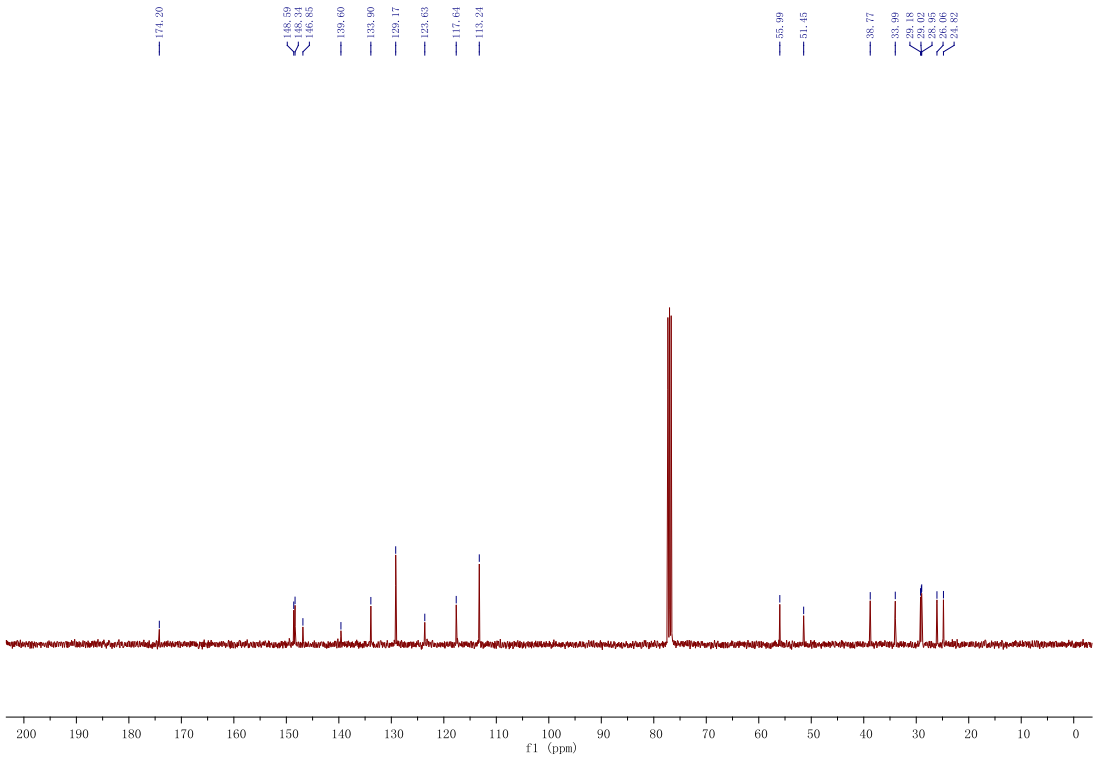
Methyl 9-(phenylamino)-9-(thiophen-2-yl)nonanoate (3t)



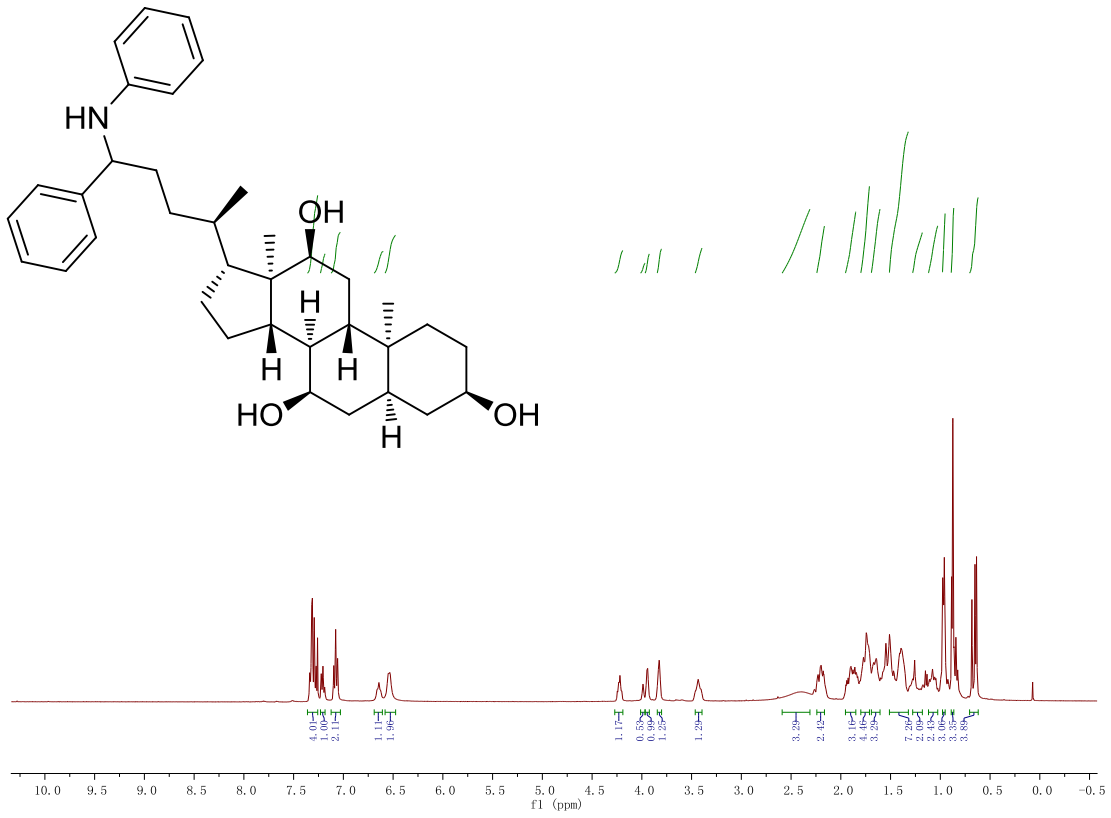


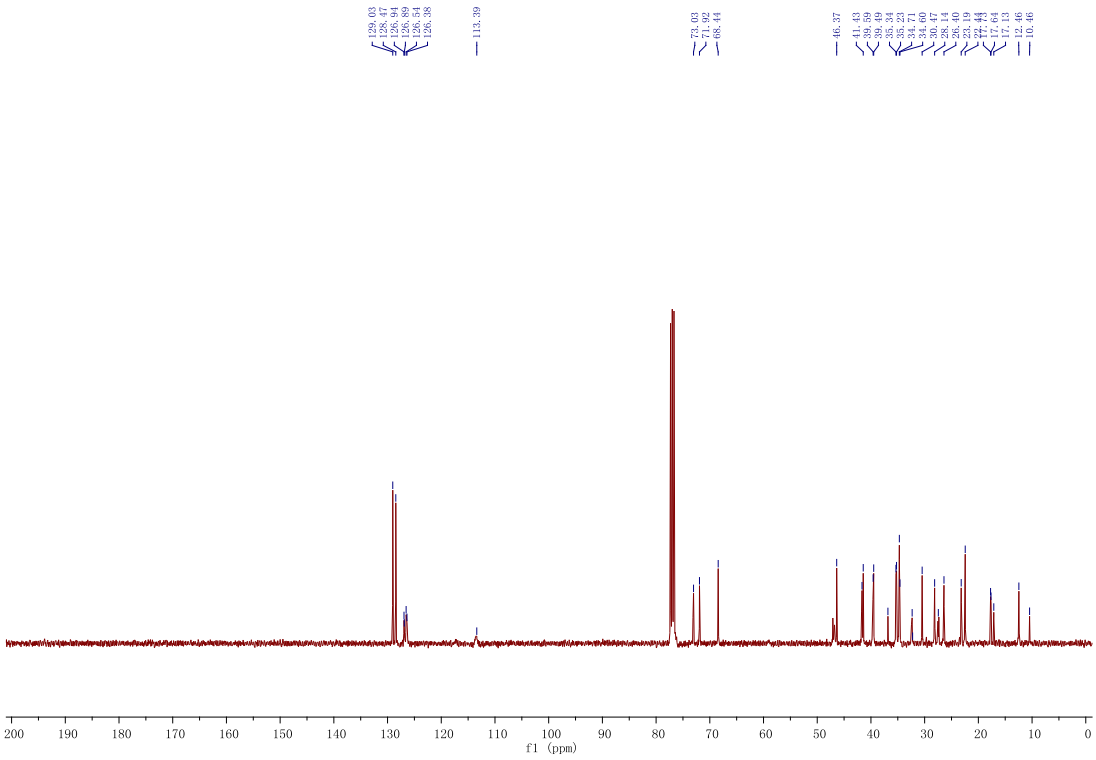
Methyl 9-(phenylamino)-9-(pyridin-3-yl)nonanoate (3u)





(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-10,13-dimethyl-17-((2R)-5-phenyl-5-(phenylamino)pentan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triol (5)

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f1 (ppm)