

Supplementary Information

**Visible-light-mediated Green Synthesis of Tertiary Alcohols from
Dicarbonyl Compounds and Arylamines in Water**

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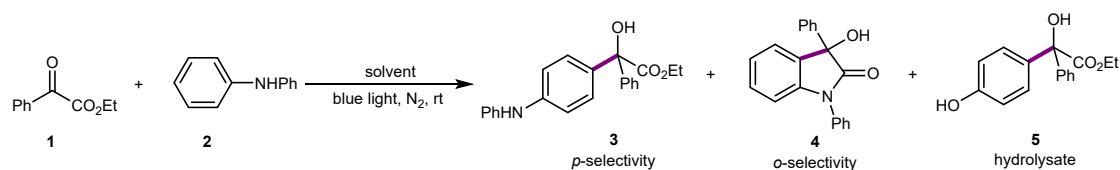
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1. General Information

All solvents were purified according to the reported method (W. L. F. Armarego and C. L. L. Chai, Purification of Laboratory Chemicals, Bulterworth-Heinemann, Oxford, UK, 7th edition, 2013). If no special indicated, commercial reagents were used without further purification. Column chromatographic purification of all products was conducted using 200-300 dry mesh silica gel. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-ECZ400S/L1 spectrometers, NMR (400 MHz for ^1H NMR, 101 MHz for ^{13}C NMR). Multiplicity (s = singlet, D = doublet, t = triplet, m = multiplet, Q = quartet, Coupling Constant (J) in Hz). Tetramethylsilane (TMS) served as the internal standard for ^1H NMR, and CDCl_3 served as the internal standard for ^{13}C NMR. Infrared spectra were collected on a Bruker VERTEX70 as a thin film, and selected maximum absorbance were reported in wavenumbers. High-resolution mass spectra (HRSM) were obtained on a Waters I-Class VION IMS QTof and are reported as m/z (relative intensity). UV-vis spectra experiments were measured on an Ultraviolet-visible Spectrophotometer (YOKE L6).

2. Experimental Procedure

2.1 Optimization Studies^a



entry	solvent	total yield	yield of 3	yield of 4	yield of 5
1	CH ₃ OH	43%	30%	9%	4%
2	CH ₃ CN	24%	21%	3%	trace
3	THF	48%	40%	2%	6%
4	DCM	37%	30%	5%	2%
5	PhCH ₃	44%	34%	3%	7%
6	PhH	38%	31%	7%	trace
7	H ₂ O	80%	56%	11%	13%
8 ^b	H ₂ O	0%	0%	0%	0%

^aExperiments were run with 0.2 mmol ethyl benzylformate **1**, 0.4 mmol diphenylamine **2** in solvent (1.0 mL) under N₂ using 40 W blue LEDs for 48 h. Isolated yields were indicated. ^bWithout light irradiation.

2.2 General Procedure

A 10 mL of Schlenk tube equipped with magnetic bar was added subsequently the carbonyl compounds (0.2 mmol, 1 equiv.), the arylamines (0.4 mmol, 2 equiv.), water as a solvent (1 mL). The Schlenk tube was degassed by three freeze-pump-thaw cycles. Then, under the irradiation of blue light (5 cm away from the light source) for 48 h or 72 h at room temperature, the reaction mixture was extracted three times with EtOAc. The combined organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified rapidly by flash column chromatography (about 10% EtOAc in petroleum ether) on silica gel to furnish the desired products.

3. Mechanistic Investigations

3.1 Free Radical Capture Experiment

A 10 mL of Schlenk tube equipped with magnetic bar was added subsequently the ethyl benzylformate **1** (0.2 mmol, 1 equiv.), diphenylamine **2** (0.4 mmol, 2 equiv.), the radical trapping agent TEMPO (10 equiv.), water as a solvent (1 mL). The Schlenk tube was degassed by three freeze-pump-thaw cycles. Then, under the irradiation of blue light for 48 h at room temperature, the reaction mixture was extracted three times with EtOAc. The combined organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified rapidly by flash column chromatography (10% EtOAc in petroleum ether) on silica gel to furnish the desired products.

3.2 Uv-vis Absorption Spectrum

The absorption spectrum of ethyl benzylformate **1** (0.2 mmol) was measured at room temperature at a concentration of 0.2 M in THF (1 mL).

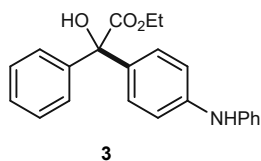
The absorption spectrum of diphenylamine **2** (0.2 mmol) was measured at room temperature at a concentration of 0.2 M in THF (1 mL).

The absorption spectrum of the EDA complex (0.2 mmol ethyl benzylformate and 0.2 mmol diphenylamine **2**) was measured in THF (1 mL) at room temperature.

The absorption spectrum of the EDA complex (0.2 mmol ethyl benzylformate, 0.2 mmol diphenylamine **2** and 72 μ L water) was measured in THF (1 mL) at room temperature.

The absorption spectrum of the EDA complex (0.2 mmol ethyl benzylformate, 0.2 mmol diphenylamine **2** and 108 μ L water) was measured in THF (1 mL) at room temperature.

4. Characterization of Products



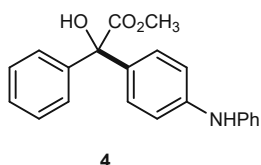
The title compound was prepared according to the general procedure using ethyl benzoylformate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1), providing the product as a light yellow oil (60% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.45 (m, 2H), 7.37 – 7.20 (m, 7H), 7.08 – 7.03 (m, 2H), 7.00 – 6.95 (m, 2H), 6.95 – 6.90 (m, 1H), 5.78 (s, 1H), 4.29 (q, J = 7.1 Hz, 2H), 4.22 (s, 1H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.7, 143.1, 142.6, 142.2, 134.2, 129.4, 128.6, 128.1, 128.0, 127.5, 121.4, 118.4, 116.6, 80.8, 63.0, 14.1.

HRMS (LCMS-ESI) m/z Calcd. for C₂₂H₂₁NO₃ [M+H]⁺ 348.1594, found: 348.1595.

IR (film) ν_{max} (cm⁻¹) 3466, 3351, 2981, 1707, 1593, 1523, 1495, 1447, 1323, 1301, 1255, 1189, 1167, 1090, 1053, 1008, 916, 847, 746, 734, 695, 597, 496.



The title compound was prepared according to the general procedure using methyl benzoylformate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.), in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a white solid (67% yield).

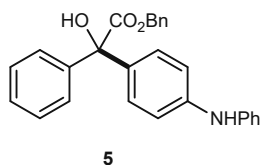
¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.44 (m, 2H), 7.37 – 7.32 (m, 3H), 7.28 – 7.24 (m, 4H), 7.10 – 7.07 (m, 2H), 7.02 – 6.99 (m, 2H), 6.97 – 6.92 (m, 1H), 5.76 (s, 1H), 4.14 (s, 1H), 3.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.3, 143.2, 142.6, 142.1, 134.0, 129.5, 128.6, 128.2,

128.1, 127.5, 127.2, 121.5, 118.5, 116.6, 81.0, 53.7.

HRMS (LCMS-ESI) m/z Calcd. for $C_{21}H_{19}NO_3$ $[M+H]^+$ 334.1438, found: 334.1439.

IR (film) ν_{\max} (cm^{-1}) 3452, 3340, 2921, 1715, 1594, 1516, 1449, 1430, 1307, 1256, 1170, 1089, 745, 733, 697, 591, 479.



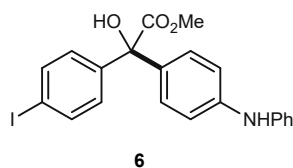
The title compound was prepared according to the general procedure using benzyl 2-oxo-2-phenylacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H_2O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1), providing the product as a light yellow oil (58% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.33 – 7.26 (m, 9H), 7.24 – 7.20 (m, 3H), 7.09 – 7.06 (m, 2H), 6.99 – 6.92 (m, 3H), 5.75 (s, 1H), 5.28 (s, 2H), 4.15 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 143.1, 142.7, 142.1, 135.0, 134.1, 129.5, 128.7, 128.7, 128.6, 128.2, 128.2, 128.1, 127.6, 121.5, 118.3, 116.7, 81.0, 68.4.

HRMS (LCMS-ESI) m/z Calcd. for $C_{27}H_{23}NO_3$ $[M+H]^+$ 410.1751, found: 410.1750.

IR (film) ν_{\max} (cm^{-1}) 3492, 3392, 3030, 1720, 1595, 1514, 1495, 1447, 1314, 1224, 1163, 1058, 906, 826, 783, 746, 496.



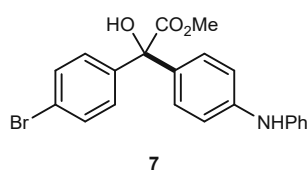
The title compound was prepared according to the general procedure using methyl 2-(4-iodophenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H_2O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a light yellow oil (68% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.63 (m, 2H), 7.28 – 7.23 (m, 2H), 7.23 – 7.18 (m, 4H), 7.08 – 7.05 (m, 2H), 6.99 – 6.92 (m, 3H), 5.78 (s, 1H), 4.15 (s, 1H), 3.83 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.8, 143.5, 142.4, 141.8, 137.2, 133.6, 129.6, 129.5, 128.4, 121.7, 118.6, 116.6, 94.2, 80.7, 53.8.

HRMS (LCMS-ESI) m/z Calcd. for C₂₁H₁₈INO₃ [M+H]⁺ 460.0404, found: 460.0405.

IR (film) ν_{max} (cm⁻¹) 3485, 3390, 3028, 2951, 1723, 1594, 1513, 1495, 1314, 1244, 1163, 1064, 1005, 987, 906, 821, 784, 730, 695, 491.



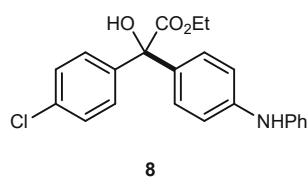
The title compound was prepared according to the general procedure using methyl 2-(4-bromophenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 48 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a light yellow oil (67% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.44 (m, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 7.23 – 7.19 (m, 2H), 7.09 – 7.06 (m, 2H), 7.02 – 6.98 (m, 2H), 6.97 – 6.93 (m, 1H), 5.78 (s, 1H), 4.15 (s, 1H), 3.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 143.5, 142.4, 141.1, 133.6, 131.3, 129.5, 129.4, 128.4, 122.3, 121.7, 118.6, 116.6, 80.6, 53.8.

HRMS (LCMS-ESI) m/z Calcd. for C₂₁H₁₈BrNO₃ [M+H]⁺ 412.0543, found: 412.0542.

IR (film) ν_{max} (cm⁻¹) 3484, 3392, 3029, 2952, 1724, 1595, 1514, 1495, 1314, 1245, 1163, 1071, 1009, 987, 907, 824, 785, 730, 695, 492.



The title compound was prepared according to the general procedure using ethyl 2-(4-

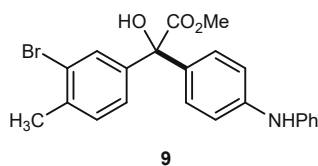
chlorophenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a white solid (57% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.40 (m, 2H), 7.31 – 7.22 (m, 6H), 7.10–7.05 (m, 2H), 7.01 – 6.97 (m, 2H), 6.97 – 6.92 (m, 1H), 5.79 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.22 (s, 1H), 1.27 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.4, 143.4, 142.5, 140.7, 134.0, 133.9, 129.5, 129.1, 128.4, 128.2, 121.7, 118.6, 116.6, 80.3, 63.2, 14.2.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₂H₂₀ClNO₃ [M+H]⁺ 382.1205, found: 382.1207.

IR (film) ν_{max} (cm⁻¹) 3452, 3396, 2919, 2849, 1712, 1594, 1517, 1490, 1317, 1300, 1252, 1205, 1171, 1091, 1066, 1009, 922, 813, 771, 752, 743, 732, 691, 573, 505, 491.



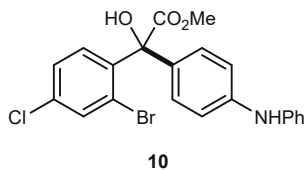
The title compound was prepared according to the general procedure using methyl 2-(3-bromo-4-methylphenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (67.6 mg, 0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the title compound as a white solid (84% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 1.9 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.25 – 7.23 (m, 2H), 7.22 – 7.18 (m, 2H), 7.10 – 7.08 (m, 2H), 7.01 – 6.99 (m, 2H), 6.95 (dd, *J* = 6.7, 5.8 Hz, 1H), 5.78 (s, 1H), 4.14 (s, 1H), 3.85 (s, 3H), 2.39 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 143.4, 142.4, 141.4, 137.8, 133.7, 131.3, 130.5, 129.5, 128.4, 126.6, 124.8, 121.7, 118.6, 116.6, 80.3, 53.8, 22.7.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₂H₂₀BrNO₃ [M+H]⁺ 426.0699, found: 426.0689.

IR (film) ν_{\max} (cm⁻¹) 3481, 3371, 1717, 1596, 1519, 1492, 1336, 1313, 1172, 830, 778, 749, 733, 695, 682, 461.



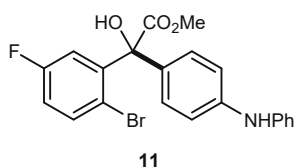
The title compound was prepared according to the general procedure using methyl 2-(2-bromo-4-chlorophenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a white solid (74% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 2.2 Hz, 1H), 7.50 – 7.48 (m, 2H), 7.33 – 7.29 (m, 2H), 7.15 – 7.12 (m, 3H), 7.10 – 7.07 (m, 2H), 7.01 – 6.97 (m, 1H), 6.85 (d, J = 8.5 Hz, 1H), 5.84 (s, 1H), 4.18 (s, 1H), 3.87 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.7, 143.9, 142.3, 140.3, 134.9, 133.9, 132.2, 130.7, 129.5, 128.1, 127.1, 124.4, 121.9, 118.9, 116.6, 80.9, 53.9.

HRMS (LCMS-ESI) m/z Calcd. for C₂₁H₁₇BrClNO₃ [M+H]⁺ 446.0153, found: 446.0157.

IR (film) ν_{\max} (cm⁻¹) 3489, 3389, 2951, 2925, 1731, 1595, 1554, 1514, 1496, 1318, 1246, 1167, 1142, 1107, 1082, 1041, 826, 795, 751, 736, 695, 491.



The title compound was prepared according to the general procedure using methyl 2-(2-bromo-5-fluorophenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (67.6 mg, 0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a light yellow oil (75% yield).

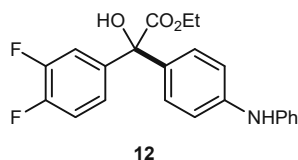
¹H NMR (400 MHz, CDCl₃) δ 7.56 (dd, J = 8.7, 5.4 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.33 – 7.28 (m, 2H), 7.16 – 7.12 (m, 2H), 7.11 – 7.07 (m, 2H), 6.99 (t, J = 7.4 Hz, 1H),

6.89 (ddd, $J = 8.7, 7.4, 3.1$ Hz, 1H), 6.66 (dd, $J = 10.2, 3.1$ Hz, 1H), 5.90 (s, 1H), 4.23 (s, 1H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 174.44, 162.65, 160.20, 144.04, 143.87, 143.80, 142.25, 135.54, 135.47, 130.33, 129.55, 128.09, 121.96, 119.17, 118.97, 118.92, 118.02, 116.94, 116.72, 116.61, 81.03, 53.89.

HRMS (LCMS-ESI) m/z Calcd. for $\text{C}_{21}\text{H}_{17}\text{BrFNO}_3$ $[\text{M}+\text{H}]^+$ 430.0449, found: 430.0451.

IR (film) ν_{max} (cm^{-1}) 3474, 3386, 2950, 2922, 1729, 1595, 1514, 1496, 1459, 1317, 1246, 1128, 1174, 1148, 1081, 1034, 815, 777, 750, 731, 694, 602, 585, 492.



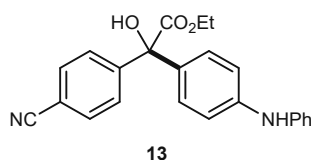
The title compound was prepared according to the general procedure using ethyl 2-(3,4-difluorophenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H_2O under blue light for 48 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a white solid (57% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.34 (dd, $J = 4.1, 2.3$ Hz, 1H), 7.28 – 7.23 (m, 5H), 7.14 – 7.06 (dd, $J = 7.0, 1.5$ Hz, 3H), 7.01 – 6.96 (m, 3H), 5.81 (s, 1H), 4.33 (dd, $J = 7.1, 1.0$ Hz, 2H), 4.24 (s, 1H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 174.08, 151.34, 151.21, 151.18, 151.06, 148.86, 148.73, 148.59, 143.57, 142.36, 139.13, 139.09, 139.05, 133.56, 129.52, 128.31, 123.82, 123.78, 123.75, 123.72, 121.81, 118.72, 117.18, 116.99, 116.80, 116.62, 116.57, 79.98, 63.34, 14.16.

HRMS (LCMS-ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{19}\text{F}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$ 384.1406, found: 384.1403.

IR (film) ν_{max} (cm^{-1}) 3458, 3361, 1714, 1594, 1511, 1495, 1446, 1319, 1300, 1106, 1065, 823, 772, 752, 727, 693, 605, 579, 462.



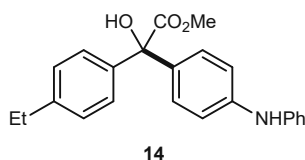
The title compound was prepared according to the general procedure using ethyl 2-(4-cyanophenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow oil (62% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.60 (m, 4H), 7.30 – 7.25 (m, 2H), 7.22 – 7.18 (m, 2H), 7.12 – 7.07 (m, 2H), 7.03 – 6.99 (m, 2H), 6.99 – 6.94 (m, 1H), 5.85 (s, 1H), 4.33 (dd, J = 7.1, 3.7 Hz, 2H), 4.29 (s, 1H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.7, 147.2, 143.7, 142.3, 133.2, 131.9, 129.5, 128.5, 128.3, 121.9, 118.8, 116.5, 111.8, 80.5, 63.46, 14.15.

HRMS (LCMS-ESI) m/z Calcd. for C₂₃H₂₀N₂O₃ [M+H]⁺ 373.1547, found: 373.1548.

IR (film) ν_{\max} (cm⁻¹) 3475, 3382, 3053, 2983, 2229, 1724, 1595, 1515, 1496, 1317, 1241, 1181, 1160, 1072, 1018, 820, 750, 735, 695, 656, 556, 532, 493.



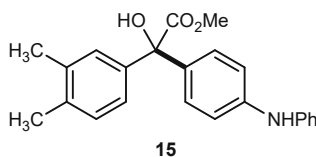
The title compound was prepared according to the general procedure using methyl 2-(4-ethylphenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a colourless oil (74% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.33 (m), 7.30 – 7.23 (m), 7.20 – 7.15 (m), 7.11 – 7.06 (m), 7.03 – 6.98 (m), 6.97 – 6.91 (m), 5.76 (s), 4.11 (s), 3.84 (s), 2.65 (q, J = 7.6 Hz), 1.24 (t, J = 7.6 Hz).

¹³C NMR (101 MHz, CDCl₃) δ 175.5, 144.2, 143.1, 142.7, 139.5, 134.2, 129.5, 128.6, 127.7, 127.4, 121.5, 118.4, 116.6, 80.9, 53.6, 28.6, 15.5.

HRMS (LCMS-ESI) m/z Calcd. for C₂₃H₂₃NO₃ [M+H]⁺ 362.1751, found: 362.1748.

IR (film) ν_{\max} (cm⁻¹) 3493, 3390, 2963, 1722, 1595, 1512, 1496, 1314, 1244, 1163, 1070, 831, 795, 749, 694, 613, 585, 495.



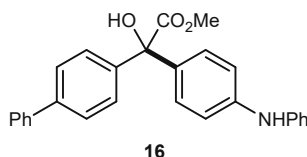
The title compound was prepared according to the general procedure using methyl 2-(3,4-dimethylphenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a light yellow oil (76% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.24 (m, 3H), 7.24 – 7.20 (m, 2H), 7.15 – 7.10 (m, 2H), 7.07 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.02 – 6.97 (m, 2H), 6.92 (dd, *J* = 10.5, 4.1 Hz, 1H), 5.79 (s, 1H), 4.10 (s, 1H), 3.83 (s, 3H), 2.24 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 175.5, 143.1, 142.6, 139.6, 136.6, 134.1, 129.4, 128.6, 124.9, 121.5, 118.4, 116.6, 80.9, 53.6, 20.1, 19.6.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₃H₂₃NO₃ [M+H]⁺ 362.1751, found: 362.1746.

IR (film) ν_{\max} (cm⁻¹) 3395, 3388, 3026, 2950, 1722, 1595, 1513, 1496, 1446, 1315, 1244, 1177, 1154, 1120, 1071, 908, 821, 781, 749, 728, 694, 495.



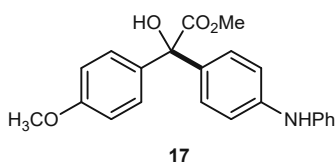
The title compound was prepared according to the general procedure using methyl 4-phenylbenzoylformate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a white solid (70% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.55 (m, 4H), 7.54 – 7.50 (m, 2H), 7.46 – 7.41 (m, 2H), 7.37 – 7.29 (m, 3H), 7.28 – 7.25 (m, 2H), 7.12 – 7.07 (m, 2H), 7.05 – 7.01 (m, 2H), 6.98 – 6.92 (m, 1H), 5.77 (s, 1H), 4.17 (s, 1H), 3.88 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.3, 143.2, 142.5, 141.1, 140.9, 140.6, 134.0, 129.5, 128.9, 128.6, 127.9, 127.5, 127.2, 126.9, 121.6, 118.5, 116.6, 80.8, 53.7.

HRMS (LCMS-ESI) m/z Calcd. for C₂₇H₂₃NO₃ [M+H]⁺ 410.1751, found: 410.1752.

IR (film) ν_{max} (cm⁻¹) 3489, 3391, 3029, 2952, 1723, 1595, 1514, 1495, 1314, 1244, 1164, 1069, 1007, 987, 907, 838, 792, 750, 731, 694, 590, 493.



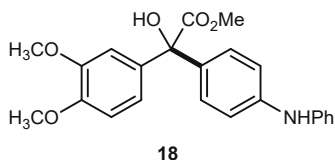
The title compound was prepared according to the general procedure using methyl 4-methoxybenzoate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 48 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a white solid (50% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.33 (m, 2H), 7.29 – 7.23 (m, 4H), 7.10 – 7.05 (m, 2H), 7.03 – 6.98 (m, 2H), 6.97 – 6.91 (m, 1H), 6.90 – 6.84 (m, 2H), 5.77 (s, 1H), 4.10 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.5, 159.3, 143.1, 142.6, 134.3, 134.2, 129.4, 128.7, 128.5, 121.4, 118.4, 116.6, 113.5, 80.6, 55.4, 53.6.

HRMS (LCMS-ESI) m/z Calcd. for C₂₂H₂₁NO₄ [M+H]⁺ 364.1543, found: 364.1540.

IR (film) ν_{max} (cm⁻¹) 3486, 3387, 3028, 2952, 2837, 1722, 1595, 1509, 1496, 1311, 1244, 1176, 1067, 1030, 987, 908, 830, 802, 780, 750, 730, 695, 568, 495.



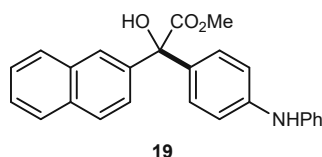
The title compound was prepared according to the general procedure using methyl 2-(3,4-dimethoxyphenyl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a colourless oil (50% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.23 (m, 4H), 7.09 (dt, *J* = 8.8, 1.7 Hz, 2H), 7.05 – 7.00 (m, 3H), 6.98 – 6.93 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.78 (s, 1H), 4.12 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.4, 148.8, 148.6, 143.2, 142.5, 134.4, 134.0, 129.4, 128.5, 121.5, 119.8, 118.4, 116.5, 110.7, 110.3, 80.7, 77.4, 55.9, 53.6.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₃H₂₃NO₅ [M+H]⁺ 394.1649, found: 394.1642.

IR (film) ν_{max} (cm⁻¹) 3490, 3364, 2923, 2851, 1726, 1595, 1511, 1496, 1463, 1412, 1318, 1254, 1176, 1139, 1072, 1024, 751, 734, 696, 496.



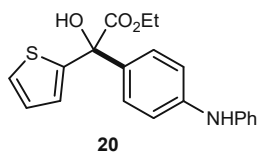
The title compound was prepared according to the general procedure using methyl 2-(naphthalen-2-yl)-2-oxoacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 48 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a light yellow oil (52% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 1.8 Hz, 1H), 7.85 – 7.78 (m, 3H), 7.54 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.31 – 7.26 (m, 3H), 7.25 – 7.23 (m, 1H), 7.11 – 7.06 (m, 2H), 7.04 – 6.99 (m, 2H), 6.97 – 6.91 (m, 1H), 5.77 (s, 1H), 4.24 (s, 1H), 3.87 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.3, 143.3, 142.5, 139.4, 133.9, 133.0, 132.8, 129.5, 128.7, 128.6, 127.9, 127.6, 126.5, 126.3, 126.2, 125.8, 121.6, 118.5, 116.6, 81.2, 53.7.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₅H₂₁NO₃ [M+H]⁺ 384.1594, found: 384.1594.

IR (film) ν_{max} (cm⁻¹) 3500, 3360, 2919, 2850, 1713, 1594, 1518, 1313, 1263, 1244, 1158, 1120, 1061, 817, 782, 754, 722, 696, 479.



The title compound was prepared according to the general procedure using ethyl 2-oxo-2-(thiophen-2-yl)acetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.)

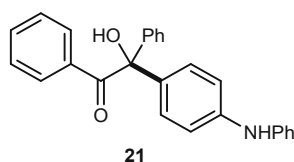
in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a white solid (53% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.35 (m, 2H), 7.31 – 7.24 (m, 3H), 7.16 – 7.13 (m, 1H), 7.11 – 7.06 (m, 2H), 7.03 – 6.98 (m, 3H), 6.98 – 6.93 (m, 1H), 5.79 (s, 1H), 4.49 (s, 1H), 4.43 – 4.25 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.7, 146.4, 143.5, 142.5, 133.8, 129.4, 127.8, 126.8, 126.3, 125.8, 121.6, 118.5, 116.6, 78.5, 63.4, 14.1.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₀H₁₉NO₃S [M+H]⁺ 354.1158, found: 354.1155.

IR (film) ν_{max} (cm⁻¹) 3469, 3351, 2983, 1712, 1593, 1520, 1496, 1322, 1248, 1228, 1185, 1142, 1067, 1041, 1005, 962, 906, 877, 748, 733, 700, 596, 504.



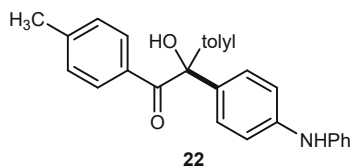
The title compound was prepared according to the general procedure using dibenzoyl (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1.5 mL of H₂O/CH₃OH (v:v = 1:1) under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a light yellow solid (57% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.73 (m, 2H), 7.47 – 7.43 (m, 3H), 7.37 – 7.30 (m, 4H), 7.30–7.24 (m, 5H), 7.11 – 7.08 (m, 2H), 7.02 – 6.99 (m, 2H), 6.98 – 6.93 (m, 1H), 5.77 (s, 1H), 5.02 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 201.06, 143.27, 142.40, 142.15, 135.25, 133.75, 133.01, 130.98, 129.61, 129.47, 128.47, 128.41, 128.22, 128.17, 121.68, 118.61, 116.66, 84.86.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₆H₂₁NO₂ [M+H]⁺ 380.1645, found: 380.1639.

IR (film) ν_{max} (cm⁻¹) 3382, 2922, 2852, 1668, 1595, 1515, 1495, 1446, 1316, 1233, 1178, 1053, 982, 881, 820, 749, 698, 495.



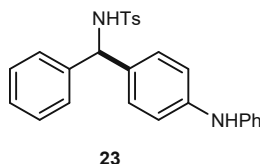
The title compound was prepared according to the general procedure using 1,2-di-*p*-tolylethane-1,2-dione (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1.5 mL of H₂O:CH₃OH (v:v = 1:1) under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1), providing the product as a yellow oil (65% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.66 (m, 2H), 7.33 – 7.31 (m, 2H), 7.28 – 7.23 (m, 4H), 7.15 – 7.11 (m, 2H), 7.10 – 7.06 (m, 4H), 7.00 – 6.98 (m, 2H), 6.96 – 6.92 (m, 1H), 5.76 (s, 1H), 5.14 (s, 1H), 2.33 (s, 3H), 2.33 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 200.5, 144.0, 143.1, 142.5, 139.4, 137.9, 134.3, 132.4, 131.3, 129.7, 129.5, 129.1, 129.0, 128.4, 121.6, 118.5, 116.7, 84.4, 21.8, 21.3.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₈H₂₅NO₂ [M+H]⁺ 408.1958, found: 408.1954.

IR (film) ν_{max} (cm⁻¹) 3381, 3028, 2921, 1661, 1595, 1513, 1495, 1446, 1312, 1240, 1180, 1159, 1019, 979, 908, 815, 770, 749, 729, 696, 616, 601, 494.



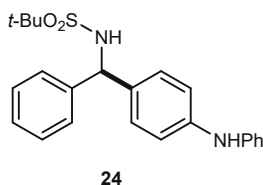
The title compound was prepared according to the general procedure using *N*-benzylidene-4-methylbenzenesulfonamide (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1), providing the product as a light yellow oil (45% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.54 (m, 2H), 7.27 – 7.22 (m, 2H), 7.21 – 7.17 (m, 3H), 7.15 – 7.11 (m, 4H), 7.04 – 6.99 (m, 2H), 6.97 – 6.90 (m, 3H), 6.89 – 6.85 (m, 2H), 5.70 (s, 1H), 5.51 (d, *J* = 7.1 Hz, 1H), 5.23 (d, *J* = 7.0 Hz, 1H), 2.36 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.21, 142.73, 140.81, 137.53, 132.85, 129.44, 128.59, 128.58, 127.53, 127.39, 127.33, 121.38, 118.13, 117.34, 61.05, 21.61.

HRMS (LCMS-ESI) m/z Calcd. for $C_{26}H_{24}N_2O_2S$ $[M+H]^+$ 429.1631, found: 429.1630.

IR (film) ν_{\max} (cm^{-1}) 3378, 3272, 3028, 1596, 1516, 1495, 1449, 1313, 1153, 1092, 1045, 1027, 810, 743, 695, 667, 565, 543, 495.



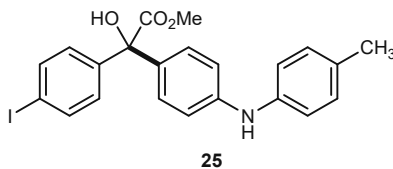
The title compound was prepared according to the general procedure using *N*-benzylidene-2-methylpropane-2-sulfonamide (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H_2O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1), providing the product as a white solid (33% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.28 – 7.23 (m, 3H), 7.14 (d, J = 8.5 Hz, 2H), 7.07 – 7.04 (m, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.93 (dd, J = 10.8, 3.9 Hz, 1H), 5.76 (s, 1H), 5.72 (d, J = 9.1 Hz, 1H), 4.92 (d, J = 9.2 Hz, 1H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.75, 142.69, 142.22, 134.36, 129.46, 128.79, 128.69, 127.56, 127.49, 121.38, 118.19, 117.46, 61.36, 60.08, 24.25.

HRMS (LCMS-ESI) m/z Calcd. for $C_{23}H_{26}N_2O_2S$ $[M+H]^+$ 395.1788, found: 395.1783.

IR (film) ν_{\max} (cm^{-1}) 3393, 3259, 1597, 1524, 1495, 1446, 1306, 1288, 1275, 1119, 1085, 1057, 951, 929, 753, 739, 698, 667, 636, 562, 502.



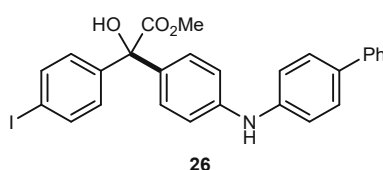
The title compound was prepared according to the general procedure using methyl 4-iodobenzoylformate (0.2 mmol, 1 equiv.), 4-methyldiphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H_2O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow oil (41% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.60 (m, 2H), 7.23 – 7.15 (m, 4H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.04 – 6.98 (m, 2H), 6.96 – 6.91 (m, 2H), 5.68 (s, 1H), 4.10 (s, 1H), 3.84 (s, 3H), 2.30 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 144.2, 141.8, 139.5, 137.2, 132.9, 131.6, 130.0, 129.6, 128.4, 119.6, 115.7, 94.2, 80.7, 53.8, 20.8.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₂H₂₀INO₃ [M+H]⁺ 474.0561, found: 474.0558.

IR (film) ν_{max} (cm⁻¹) 3491, 3391, 3027, 2922, 2853, 1727, 1606, 1514, 1484, 1435, 1315, 1250, 1164, 1068, 1006, 819, 786, 742, 498.



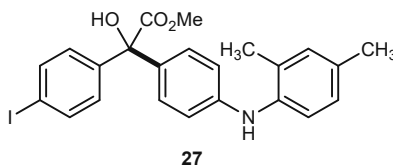
The title compound was prepared according to the general procedure using methyl 4-iodobenzoylformate (0.2 mmol, 1 equiv.), *N*-phenyl-[1,1'-biphenyl]-4-amine (0.4 mmol, 2 equiv.) in 1.5 mL of H₂O:CH₃OH (v:v = 1:1) under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow oil (48% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.65 (m, 2H), 7.56 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.21 (m, 4H), 7.15 – 7.12 (m, 2H), 7.05 – 7.01 (m, 2H), 5.84 (s, 1H), 4.15 (s, 1H), 3.84 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.8, 141.8, 137.3, 129.6, 128.9, 128.5, 128.1, 126.9, 126.7, 118.7, 117.0, 94.3, 80.7, 53.8.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₇H₂₂INO₃ [M+H]⁺ 536.0717, found: 536.0722.

IR (film) ν_{max} (cm⁻¹) 3491, 3389, 3028, 2951, 1723, 1600, 1511, 1483, 1310, 1241, 1162, 1064, 1005, 986, 821, 784, 761, 736, 696, 491.



The title compound was prepared according to the general procedure using methyl 4-iodobenzoylformate (0.2 mmol, 1 equiv.), 2,4-dimethyl-*N*-phenylaniline (0.4 mmol, 2

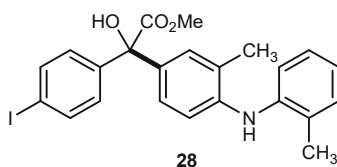
equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow oil (60% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.63 (m, 2H), 7.23 – 7.20 (m, 2H), 7.16 – 7.11 (m, 3H), 7.03 (s, 1H), 6.95 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.78 – 6.74 (m, 2H), 5.35 (s, 1H), 4.10 (s, 1H), 3.83 (s, 3H), 2.29 (s, 3H), 2.19 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 145.2, 141.9, 137.5, 137.2, 133.2, 132.4, 131.9, 130.6, 129.6, 128.3, 127.4, 121.8, 115.3, 94.1, 80.7, 53.7, 20.9, 18.0.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₃H₂₂INO₃ [M+H]⁺ 488.0717, found: 488.0724.

IR (film) ν_{max} (cm⁻¹) 3392, 3389, 2951, 1725, 1607, 1510, 1483, 1307, 1248, 1183, 1163, 1065, 1005, 987, 907, 818, 783, 729, 485, 443.



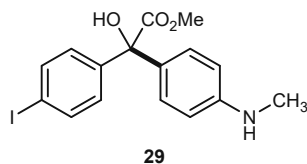
The title compound was prepared according to the general procedure using methyl 4-methoxybenzoylformate (0.2 mmol, 1 equiv.), di-*o*-tolylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow oil (70% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.65 (m, 2H), 7.28 – 7.20 (m, 3H), 7.17 – 7.08 (m, 3H), 7.03 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.96 (td, *J* = 7.3, 1.4 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 5.20 (s, 1H), 4.14 (s, 1H), 3.86 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.9, 142.5, 141.8, 141.0, 137.2, 133.5, 131.1, 129.6, 128.9, 126.9, 125.9, 125.8, 122.5, 119.9, 115.9, 94.2, 80.7, 53.8, 18.0.

HRMS (LCMS-ESI) *m/z* Calcd. for C₂₃H₂₂INO₃ [M+H]⁺ 488.0717, found: 488.0724.

IR (film) ν_{max} (cm⁻¹) 3491, 3027, 2951, 1725, 1586, 1506, 1482, 1435, 1248, 1156, 1120, 1070, 1006, 907, 820, 782, 729, 647, 498, 439.



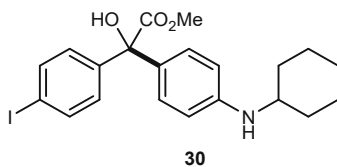
The title compound was prepared according to the general procedure using methyl 4-iodobenzoylformate (0.2 mmol, 1 equiv.), *N*-methylaniline (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow oil (59% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.62 (m, 2H), 7.24 – 7.18 (m, 2H), 7.17 – 7.10 (m, 2H), 6.58 – 6.52 (m, 2H), 4.06 (s, 1H), 3.82 (s, 3H), 2.82 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 149.2, 142.1, 137.1, 130.3, 129.7, 128.3, 112.0, 94.0, 80.8, 53.7, 30.7.

HRMS (LCMS-ESI) *m/z* Calcd. for C₁₆H₁₆INO₃ [M+H]⁺ 398.0248, found: 398.0248.

IR (film) ν_{max} (cm⁻¹) 3486, 3417, 2950, 1723, 1612, 1520, 1482, 1434, 1391, 1324, 1245, 1183, 1163, 1063, 1005, 987, 908, 820, 781, 731, 592, 530.



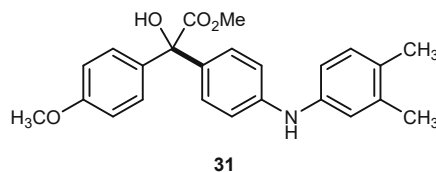
The title compound was prepared according to the general procedure using methyl 4-iodobenzoylformate (0.2 mmol, 1 equiv.), *N*-cyclohexylaniline (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1), providing the product as a colourless oil (76% yield).

¹H-NMR (400 MHz, CDCl₃) δ 7.66 – 7.61 (m, 2H), 7.23 – 7.18 (m, 2H), 7.10 – 7.05 (m, 2H), 6.54 – 6.48 (m, 2H), 4.02 (s, 1H), 3.82 (s, 3H), 3.67 (s, 1H), 3.23 (tt, *J* = 10.1, 3.7 Hz, 1H), 2.03 (dd, *J* = 12.8, 3.1 Hz, 2H), 1.78 – 1.69 (m, 2H), 1.69 – 1.57 (m, 1H), 1.41 – 1.29 (m, 2H), 1.27 – 1.21 (m, 1H), 1.20 – 1.09 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 175.1, 147.4, 142.1, 137.1, 129.7, 128.4, 112.5, 94.0, 80.7, 53.6, 51.7, 33.5, 26.0, 25.1.

HRMS (LCMS-ESI) m/z Calcd. for $C_{21}H_{24}INO_3$ $[M+H]^+$ 466.0874, found: 466.0881.

IR (film) ν_{\max} (cm^{-1}) 3492, 3400, 2926, 2851, 1724, 1611, 1515, 1483, 1449, 1391, 1325, 1248, 1183, 1163, 1064, 1005, 987, 908, 819, 784, 730, 646, 605, 495.



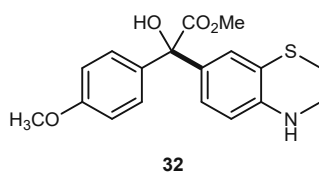
The title compound was prepared according to the general procedure using methyl 4-iodobenzoylformate (0.2 mmol, 1 equiv.), 2,4-dimethyl-*N*-phenylaniline (0.4 mmol, 2 equiv.) in 1 mL of H_2O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1), providing the product as a light yellow oil (63% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.25 – 7.21 (m, 2H), 7.02 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.7 Hz, 2H), 6.89 (s, 1H), 6.88 – 6.82 (m, 3H), 5.66 (s, 1H), 4.09 (s, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.21 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 159.3, 144.0, 140.1, 137.7, 134.4, 133.5, 130.4, 130.2, 128.8, 128.5, 120.9, 116.8, 115.8, 113.5, 80.7, 55.4, 53.5, 20.0, 19.1.

HRMS (LCMS-ESI) m/z Calcd. for $C_{24}H_{25}NO_4$ $[M+H]^+$ 392.1856, found: 392.1854.

IR (film) ν_{\max} (cm^{-1}) 3492, 3387, 2952, 2837, 1723, 1605, 1506, 1442, 1321, 1244, 1177, 1067, 1031, 987, 908, 828, 802, 781, 729, 567.



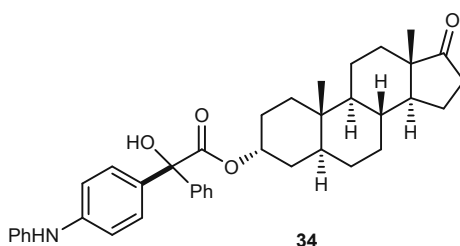
The title compound was prepared according to the general procedure using methyl 4-methoxybenzoylformate (0.2 mmol, 1 equiv.), 3,4-dihydro-2*H*-1,4-benzothiazine (0.4 mmol, 2 equiv.) in 1 mL of H_2O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 3/1), providing the product as a light yellow oil (67% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.30 (m, 2H), 7.02 (d, *J* = 2.2 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.86 – 6.82 (m, 2H), 6.40 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 4H), 3.62 – 3.57 (m, 2H), 3.04 – 2.99 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 175.5, 159.3, 141.4, 134.2, 131.8, 129.4, 128.8, 126.7, 124.9, 115.0, 113.4, 80.5, 55.4, 53.6, 42.4, 25.9.

HRMS (LCMS-ESI) *m/z* Calcd. for C₁₈H₁₉NO₄S [M+H]⁺ 346.1108, found: 346.1113.

IR (film) ν_{max} (cm⁻¹) 3047, 2955, 2927, 1728, 1605, 1509, 1460, 1312, 1249, 1178, 1071, 1031, 833, 781.



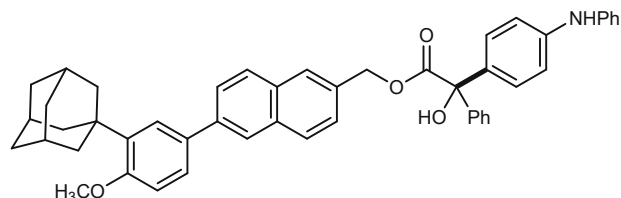
The title compound was prepared according to the general procedure using (3*R*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 2-oxo-2-phenylacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1), providing the product as a white solid (61% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.49 (m, 1H), 7.49 – 7.44 (m, 1H), 7.38 – 7.29 (m, 4H), 7.29 – 7.25 (m, 2H), 7.24 – 7.21 (m, 1H), 7.09 – 7.05 (m, 2H), 7.04 – 6.99 (m, 2H), 6.92 (dt, *J* = 13.0, 6.6 Hz, 1H), 5.84 (s, 1H), 5.18 – 5.13 (m, 1H), 4.32 (d, *J* = 8.4 Hz, 1H), 2.38 (ddd, *J* = 21.8, 19.4, 8.5 Hz, 1H), 2.07 – 1.85 (m, 1H), 1.81 – 1.59 (m, 5H), 1.56 – 1.49 (m, 1H), 1.48 – 1.35 (m, 5H), 1.19 – 1.03 (m, 5H), 0.96 – 0.83 (m, 3H), 0.80 (d, *J* = 7.1 Hz, 3H), 0.73 (d, *J* = 1.4 Hz, 3H), 0.53 – 0.41 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 221.48, 174.13, 143.00, 142.76, 142.56, 142.49, 142.33, 134.65, 134.23, 129.43, 128.72, 128.68, 128.16, 128.05, 127.97, 127.63, 127.58, 121.45, 121.34, 118.25, 117.87, 116.52, 116.33, 80.78, 73.51, 73.47, 54.22, 54.16, 51.50, 51.40, 47.84, 47.80, 39.54, 35.91, 35.85, 35.78, 34.89, 32.73, 32.59, 32.53, 31.64, 30.70, 30.64, 27.92, 26.04, 21.76, 20.03, 13.87, 11.37.

HRMS (LCMS-ESI) m/z Calcd. for $C_{39}H_{45}NO_4$ $[M+Na]^+$ 614.3241, found: 614.3244.

IR (film) ν_{\max} (cm^{-1}) 3492, 3363, 2922, 2853, 1724, 1597, 1517, 1497, 1448, 1322, 1247, 1161, 1059, 974, 879, 832, 748, 584, 497.



35

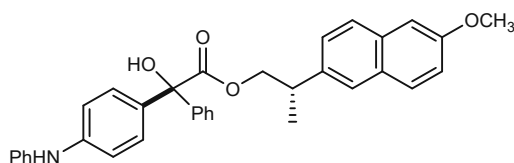
The title compound was prepared according to the general procedure using (6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)methyl 2-oxo-2-phenylacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H_2O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a white solid (44% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.87–7.73 (m, 3H), 7.66–7.60 (m, 2H), 7.56–7.49 (m, 3H), 7.38–7.24 (m, 8H), 7.09 (dd, J = 8.5, 1.0 Hz, 2H), 7.04–6.94 (m, 4H), 5.81 (s, 1H), 5.56–5.41 (m, 2H), 4.25 (s, 1H), 3.91 (s, 3H), 2.22 (d, J = 2.2 Hz, 6H), 2.14 (s, 3H), 1.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.68, 158.76, 143.13, 142.61, 142.07, 139.63, 139.00, 134.04, 133.59, 132.96, 132.03, 131.92, 129.48, 128.74, 128.58, 128.47, 128.20, 128.15, 127.63, 127.11, 126.32, 125.99, 125.91, 125.72, 124.87, 121.50, 118.37, 116.68, 112.17, 81.03, 68.48, 55.28, 40.70, 37.24, 29.22.

HRMS (LCMS-ESI) m/z Calcd. for $C_{48}H_{45}NO_4$ $[M+H]^+$ 700.3421, found: 700.3425.

IR (film) ν_{\max} (cm^{-1}) 3394, 2901, 2847, 1596, 1513, 1495, 1445, 1314, 1235, 1182, 1138, 1102, 1060, 1027, 904, 881, 808, 747, 730, 696, 648, 477.



36

The title compound was prepared according to the general procedure using (*S*)-2-(6-

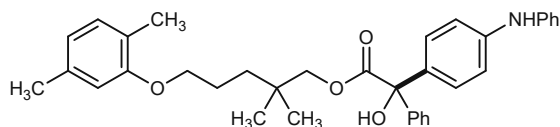
methoxynaphthalen-2-yl)propyl 2-oxo-2-phenylacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow oil (42% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.61 (t, J = 9.0 Hz, 2H), 7.44 (s, 1H), 7.36 – 7.31 (m, 1H), 7.28 – 7.18 (m, 6H), 7.15 – 7.00 (m, 7H), 6.93 (tdd, J = 7.4, 1.7, 0.9 Hz, 1H), 6.87 – 6.81 (m, 1H), 6.76 – 6.71 (m, 1H), 5.66 (s, 1H), 4.46 (ddd, J = 10.7, 7.5, 5.7 Hz, 1H), 4.35 (td, J = 10.6, 6.3 Hz, 1H), 4.14 (s, 1H), 3.87 (d, J = 7.2 Hz, 3H), 3.20 (dd, J = 6.8, 3.6 Hz, 1H), 1.26 (d, J = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.81, 157.55, 142.85, 142.75, 142.70, 142.09, 142.05, 137.81, 137.77, 134.11, 134.06, 133.67, 129.44, 129.30, 129.06, 128.53, 128.40, 128.02, 127.94, 127.90, 127.46, 127.33, 127.17, 126.17, 126.11, 125.84, 121.37, 121.32, 118.94, 118.20, 118.11, 116.64, 105.64, 80.81, 71.63, 55.40, 38.82, 38.78, 18.00.

HRMS (LCMS-ESI) m/z Calcd. for C₃₄H₃₁NO₄ [M+H]⁺ 518.2326, found: 518.2329.

IR (film) ν_{\max} (cm⁻¹) 3492, 3393, 3056, 2962, 1720, 1596, 1514, 1496, 1317, 1263, 1232, 1215, 1162, 1060, 1030, 852, 810, 734, 696, 674, 623, 584, 475.



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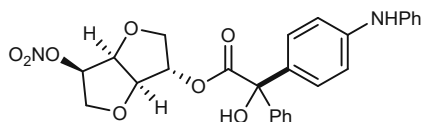
The title compound was prepared according to the general procedure using 5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl 2-oxo-2-phenylacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a yellow oil (45% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.44 (m, 2H), 7.34 – 7.22 (m, 7H), 7.04 – 6.90 (m, 6H), 6.66 (d, J = 7.4 Hz, 1H), 6.56 (s, 1H), 5.65 (s, 1H), 4.24 (s, 1H), 3.98 (s, 2H), 3.76 (t, J = 6.4 Hz, 2H), 2.29 (s, 3H), 2.13 (s, 3H), 1.63 – 1.55 (m, 2H), 1.27 – 1.22 (m, 2H), 0.83 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 175.04, 157.07, 143.04, 142.69, 142.27, 136.59, 134.30, 130.43, 129.44, 128.68, 128.09, 127.61, 123.64, 121.39, 120.81, 118.21, 116.76, 112.03, 81.03, 74.45, 68.25, 35.21, 33.80, 24.33, 24.26, 24.07, 21.55, 15.93.

HRMS (LCMS-ESI) m/z Calcd. for C₃₅H₃₉NO₄ [M+H]⁺ 538.2952, found: 538.2953.

IR (film) ν_{max} (cm⁻¹) 3492, 3391, 3027, 2954, 1721, 1596, 1511, 1496, 1313, 1249, 1157, 1129, 1089, 1057, 994, 908, 805, 746, 732, 696, 586, 495, 447.



38

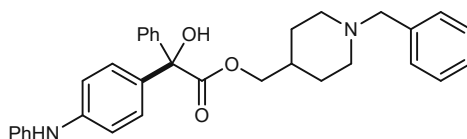
The title compound was prepared according to the general procedure using (3*S*,3*aR*,6*R*,6*aS*)-6-(nitrooxy)hexahydrofuro[3,2-*b*]furan-3-yl 2-oxo-2-phenylacetate (0.2 mmol, 1 equiv.), diphenylamine (0.4 mmol, 2 equiv.) in 1 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow solid (32% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.41 (m, 2H), 7.37 – 7.32 (m, 3H), 7.32 – 7.26 (m, 3H), 7.25 – 7.23 (m, 1H), 7.11 – 7.08 (m, 2H), 7.03 – 6.99 (m, 2H), 6.99 – 6.94 (m, 1H), 5.78 (s, 1H), 5.36 (s, 1H), 5.31 (td, *J* = 5.5, 2.7 Hz, 1H), 4.85 – 4.79 (m, 1H), 4.33 (dd, *J* = 19.4, 4.9 Hz, 1H), 4.05 – 3.98 (m, 4H), 3.85 (ddd, *J* = 11.3, 5.5, 4.2 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 173.9, 142.4, 133.4, 129.5, 128.6, 128.5, 128.4, 128.3, 127.4, 127.3, 121.8, 118.7, 118.6, 116.6, 116.5, 86.2, 81.7, 81.2, 80.9, 79.3, 73.1, 69.5.

HRMS (LCMS-ESI) m/z Calcd. for C₂₆H₂₄N₂O₈ [M+H]⁺ 493.1605, found: 493.1601.

IR (film) ν_{max} (cm⁻¹) 3392, 2923, 1732, 1639, 1595, 1515, 1496, 1317, 1280, 1234, 1166, 1094, 1061, 1002, 966, 848, 749, 697, 494.



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The title compound was prepared according to the general procedure using (1-benzylpiperidin-4-yl)methyl 2-oxo-2-phenylacetate (1 g, 1 equiv.), diphenylamine (2 equiv.) in 10 mL of H₂O under blue light for 72 hours. The resulting crude residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1), providing the product as a light yellow oil (73% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.43 (m, 2H), 7.36 – 7.23 (m, 12H), 7.09 – 7.05 (m, 2H), 7.02 – 6.98 (m, 2H), 6.94 (t, J = 7.3 Hz, 1H), 5.77 (s, 1H), 4.09 (d, J = 6.7 Hz, 2H), 3.47 (s, 2H), 2.83 (d, J = 11.6 Hz, 2H), 1.90 (td, J = 11.8, 2.0 Hz, 2H), 1.71 – 1.57 (m, 1H), 1.51 (d, J = 12.2 Hz, 2H), 1.30 – 1.17 (m, 2H).

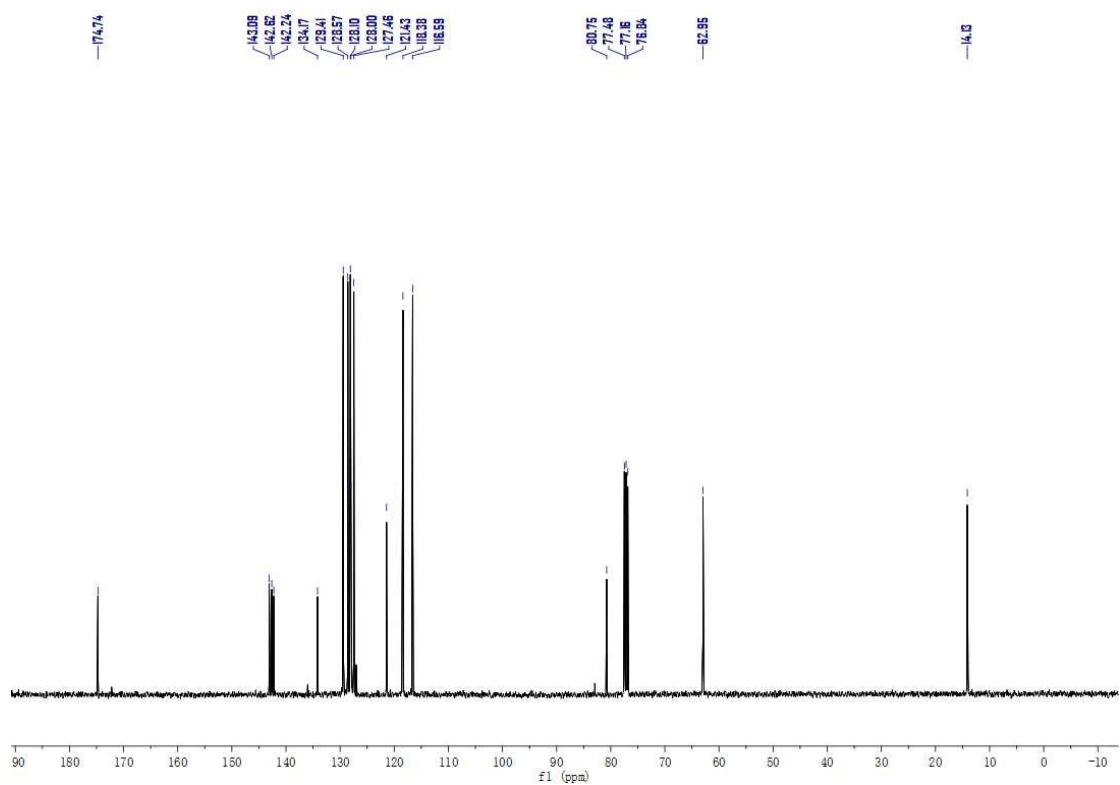
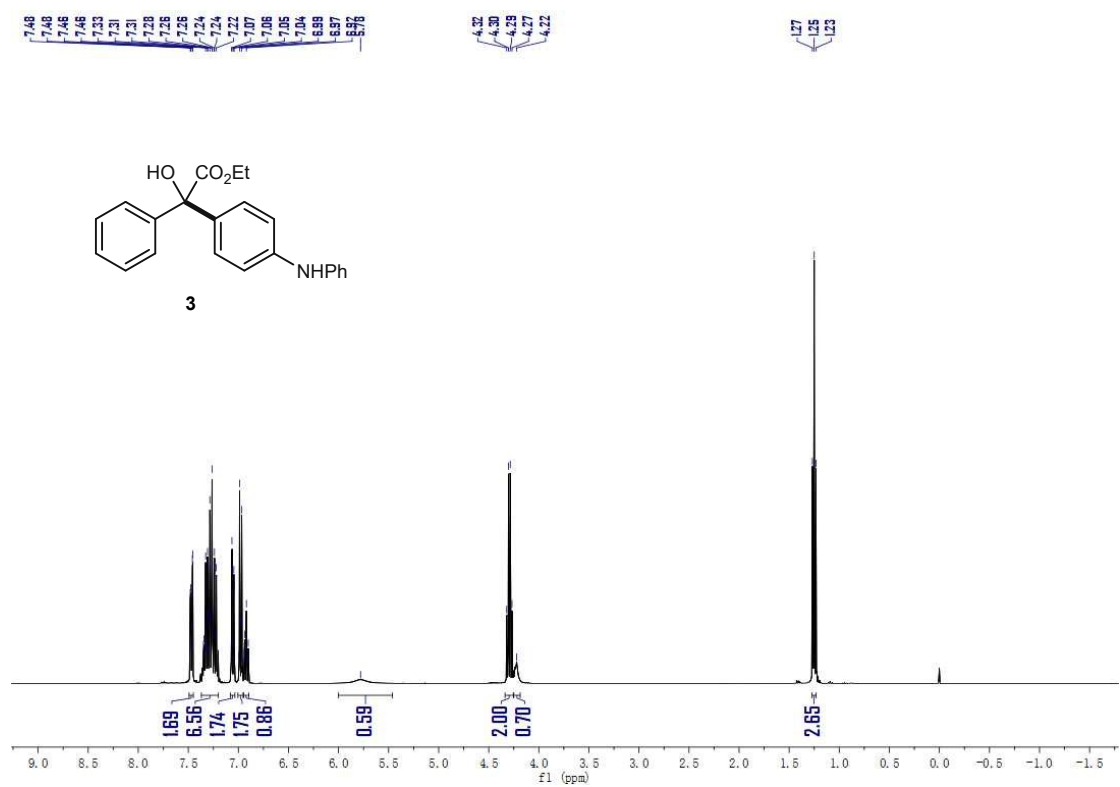
¹³C NMR (101 MHz, CDCl₃) δ 174.89, 143.08, 142.69, 142.22, 138.25, 134.24, 129.46, 129.28, 128.64, 128.29, 128.12, 128.06, 127.52, 127.13, 121.46, 118.31, 116.73, 80.94, 71.15, 63.32, 53.05, 35.23, 28.69.

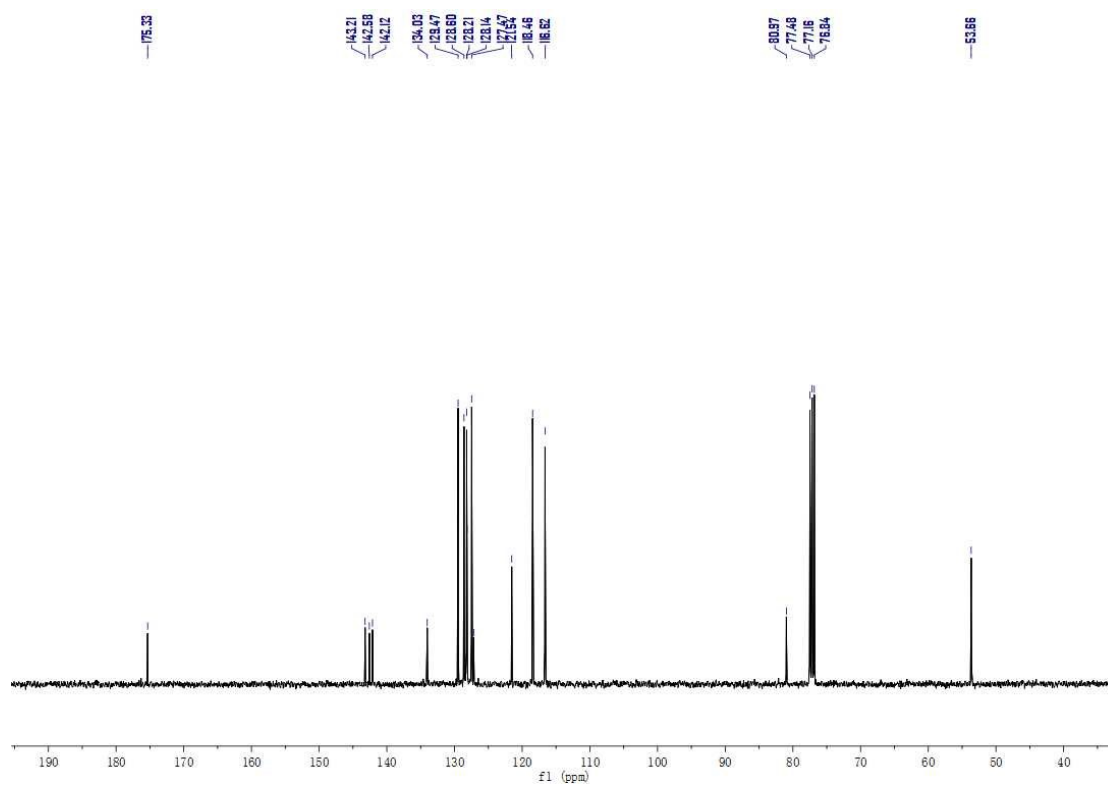
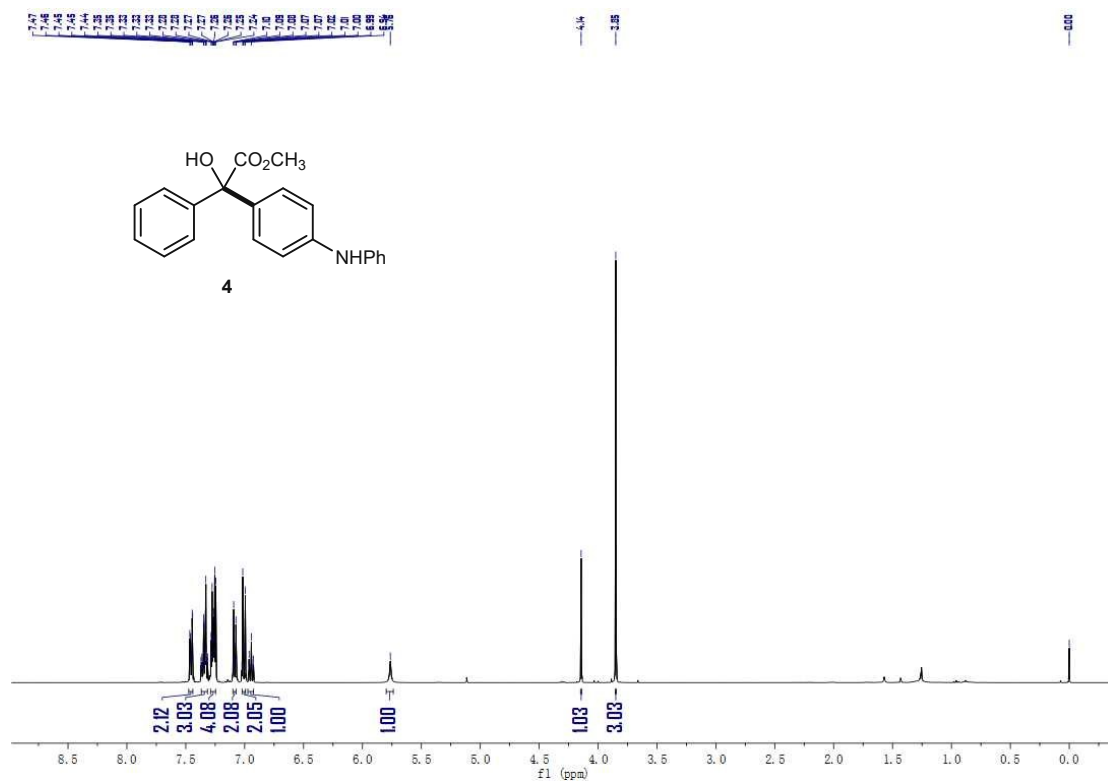
HRMS (LCMS-ESI) m/z Calcd. for C₃₃H₃₄N₂O₃ [M+H]⁺ 507.2642, found: 507.2649.

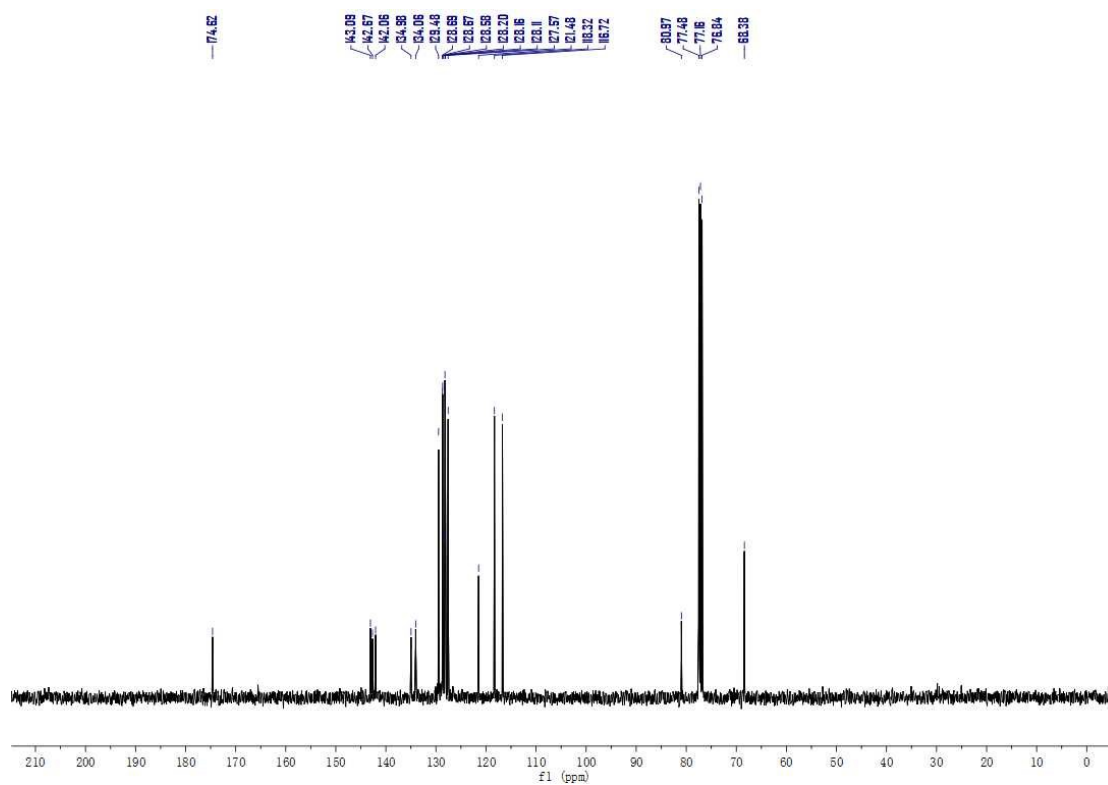
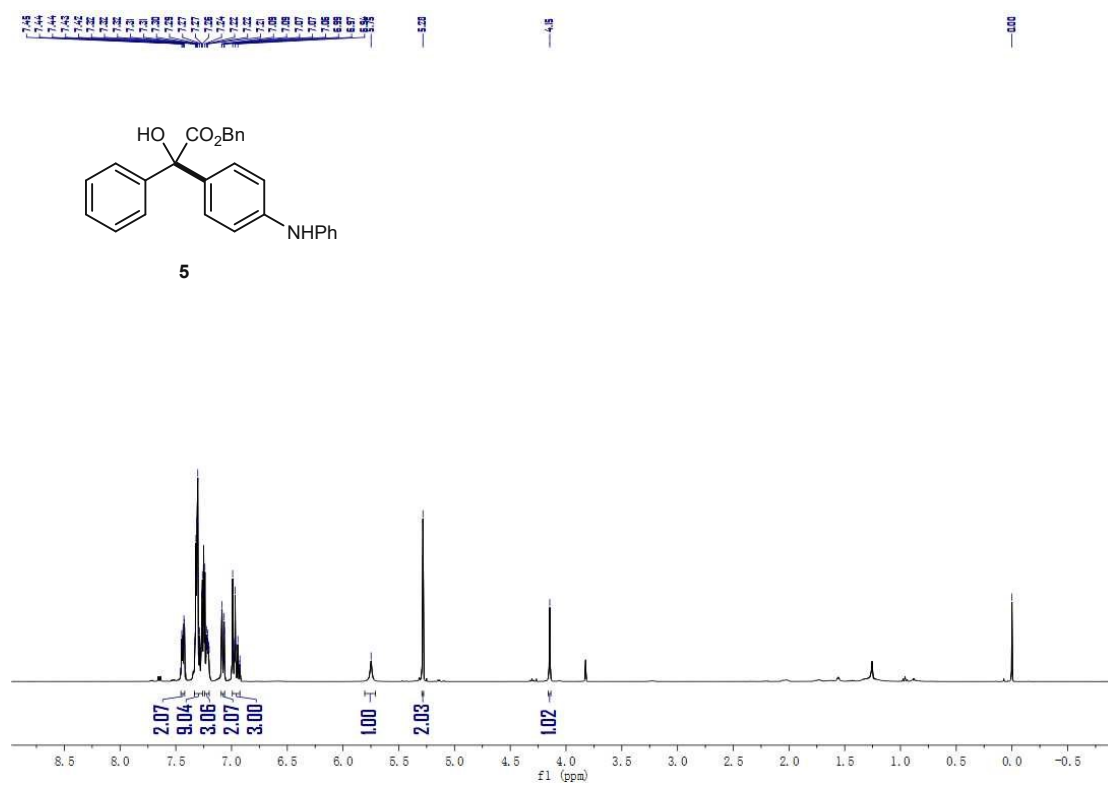
IR (film) ν_{max} (cm⁻¹) 3495, 3392, 3028, 2924, 1721, 1595, 1514, 1495, 1448, 1316, 1248, 1165, 1062, 1029, 976, 833, 739, 607, 497.

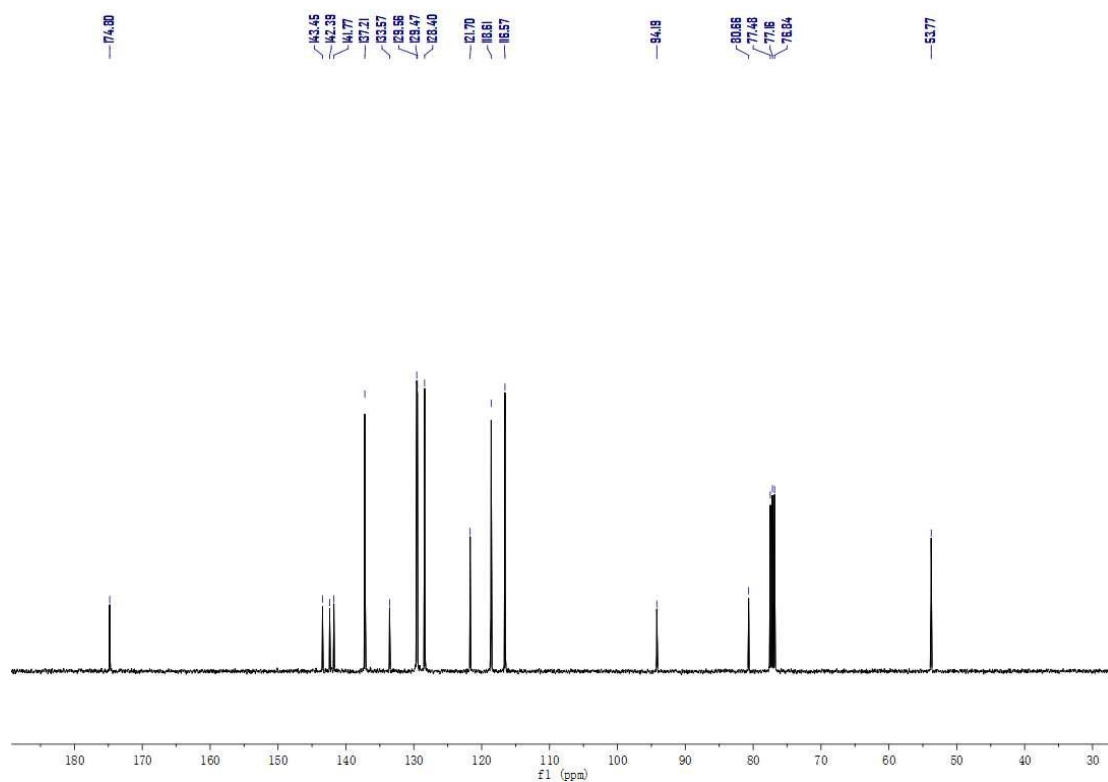
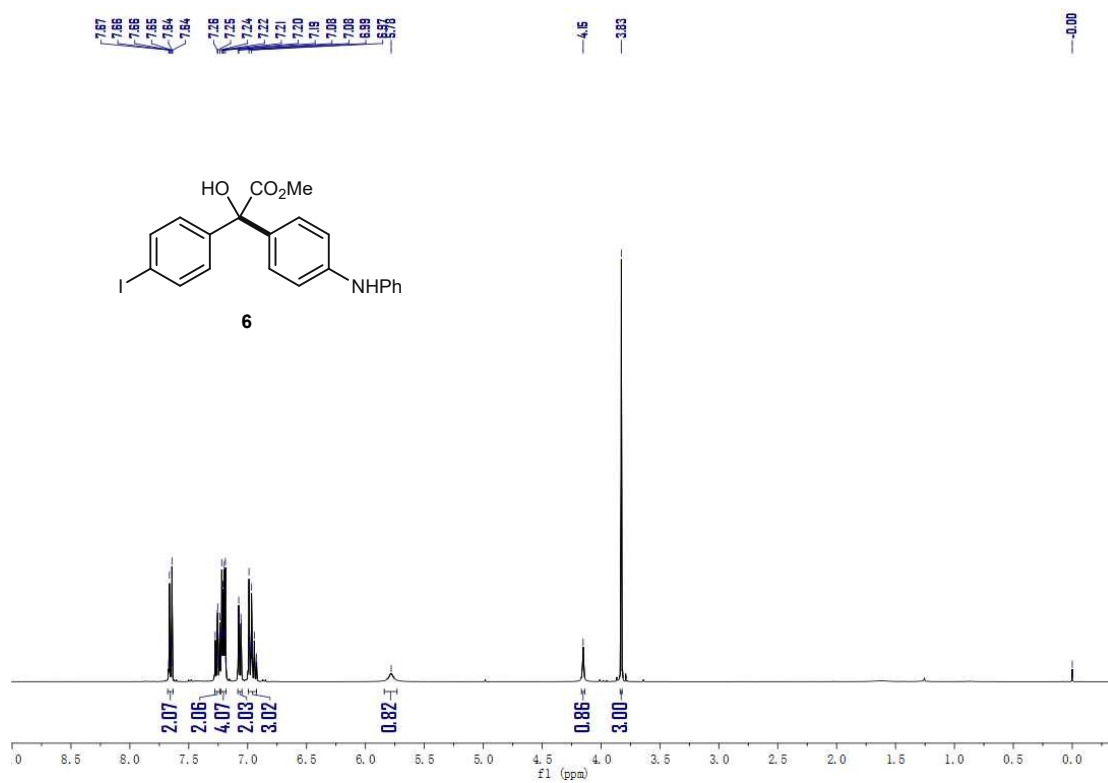
HRMS (LCMS-ESI) m/z Calcd. for C₃₃H₃₄N₂O₃ [M+H]⁺ 507.2642, found: 507.2649.

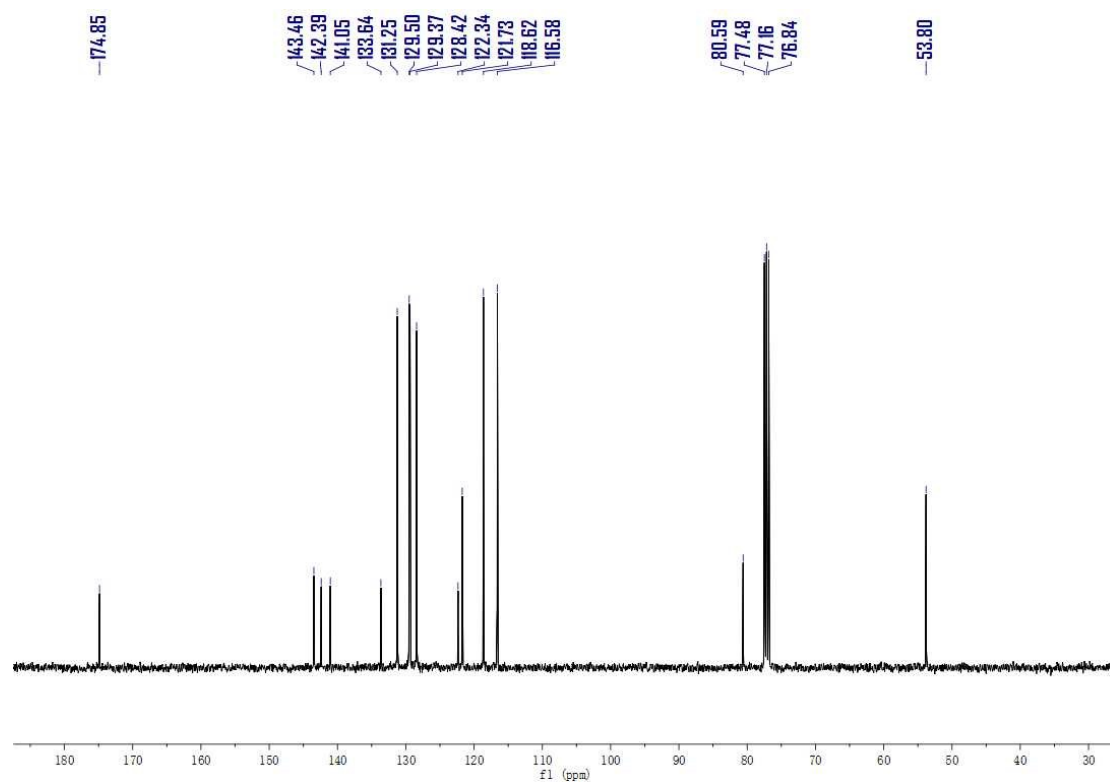
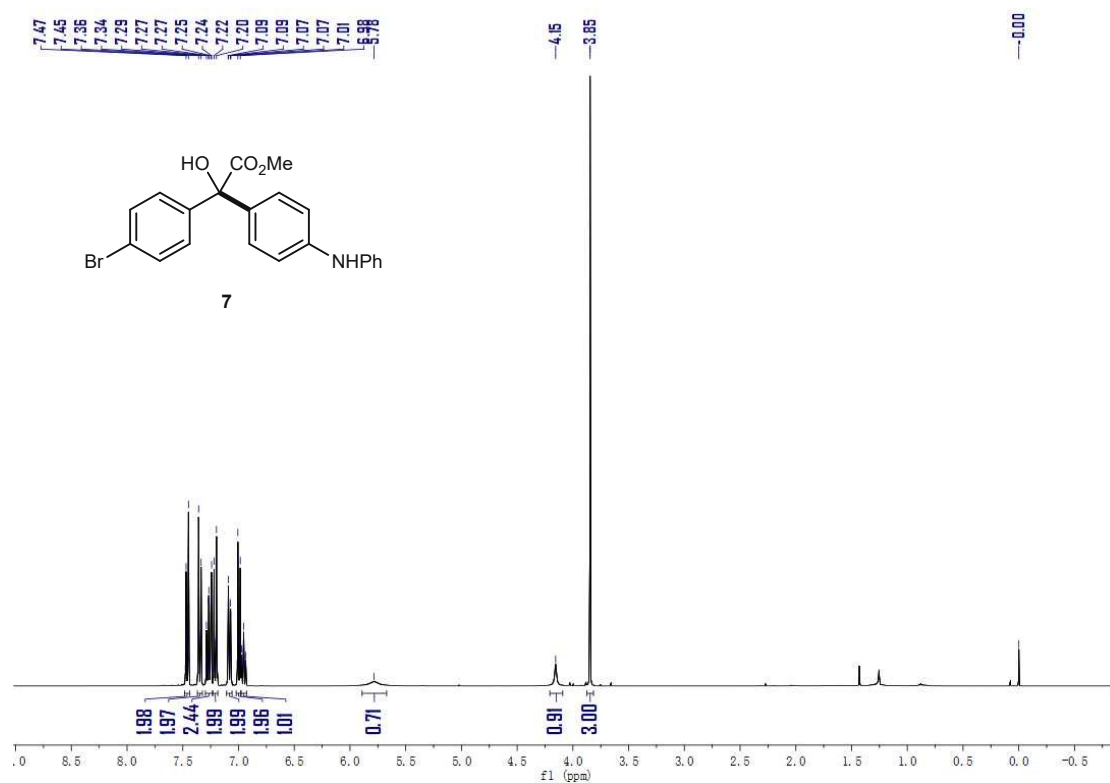
5. NMR Spectra

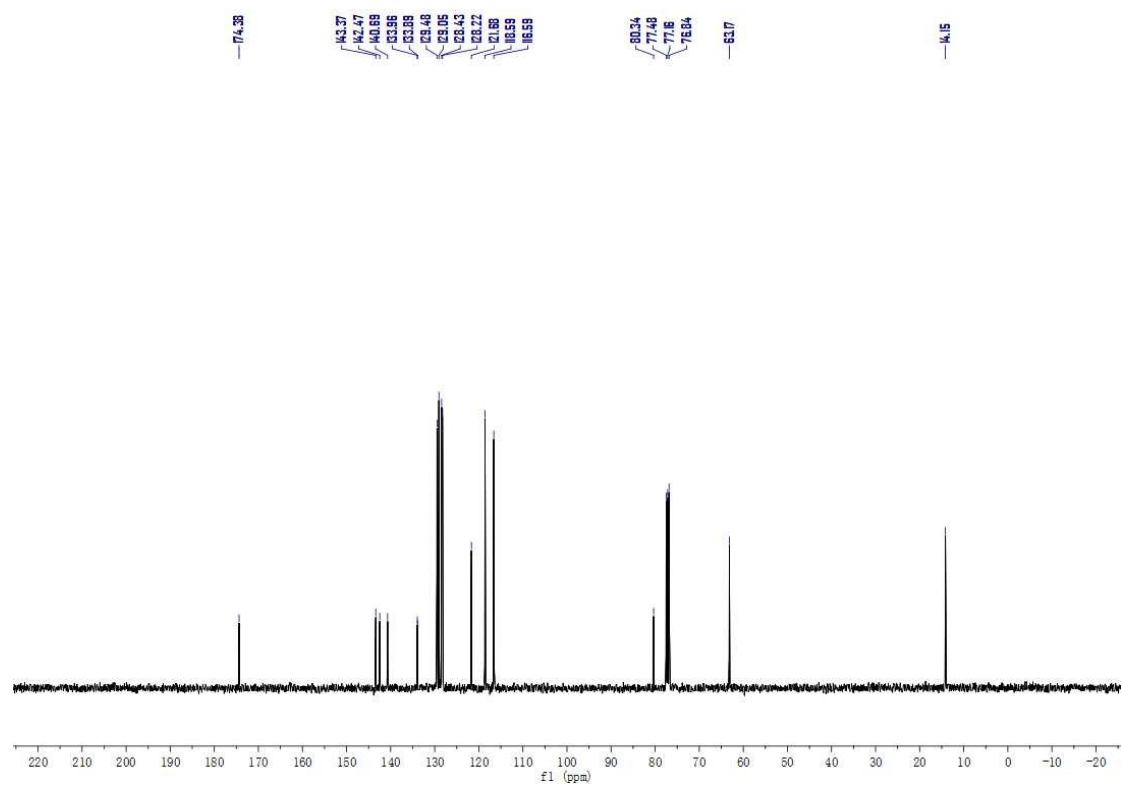
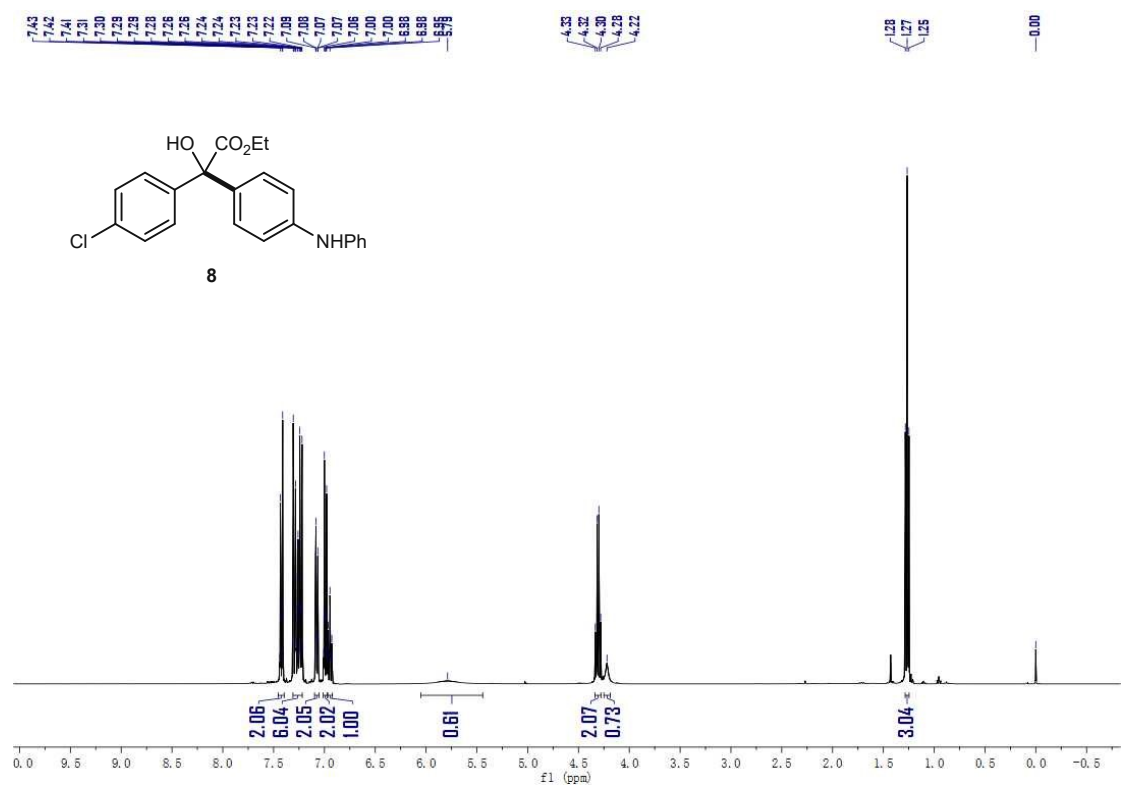


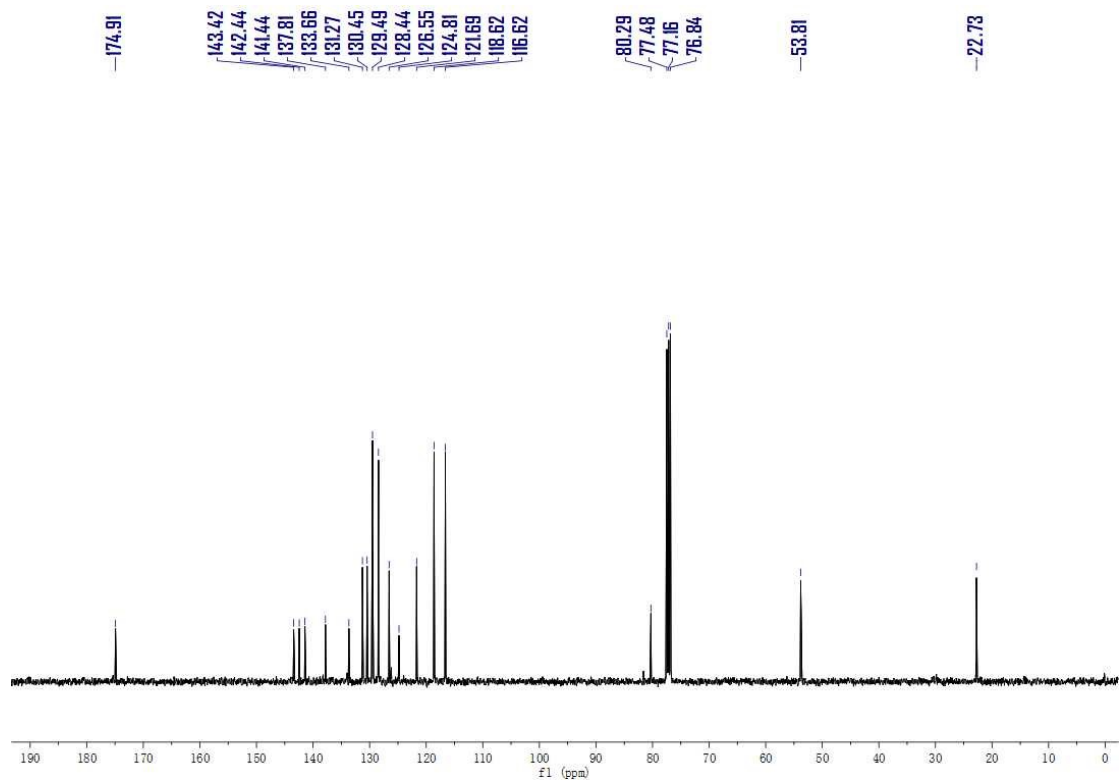
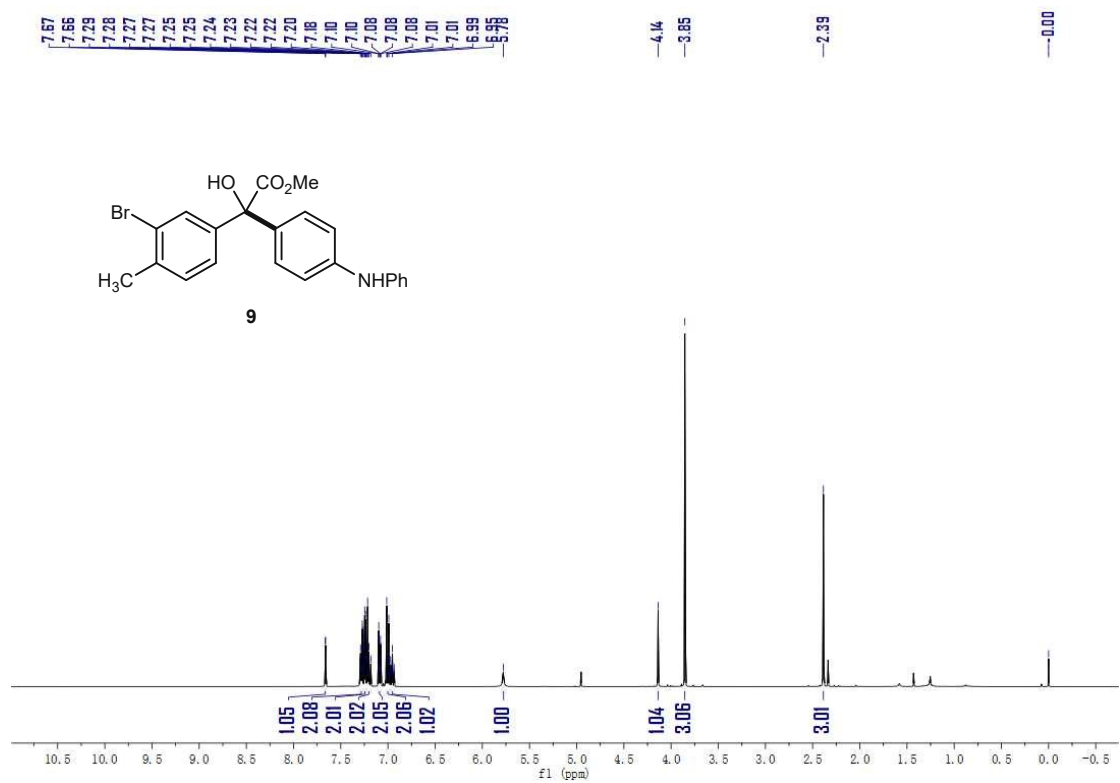


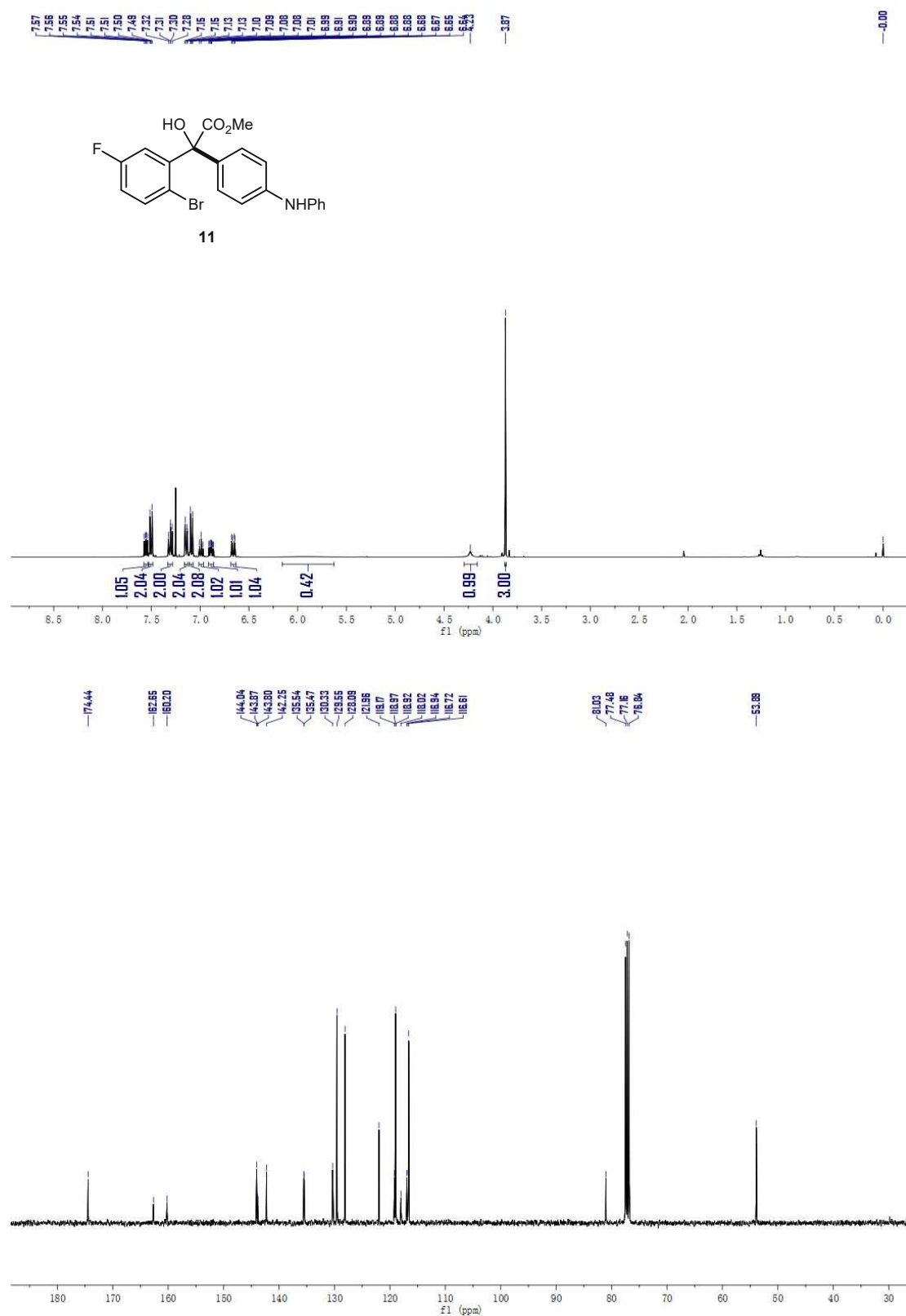


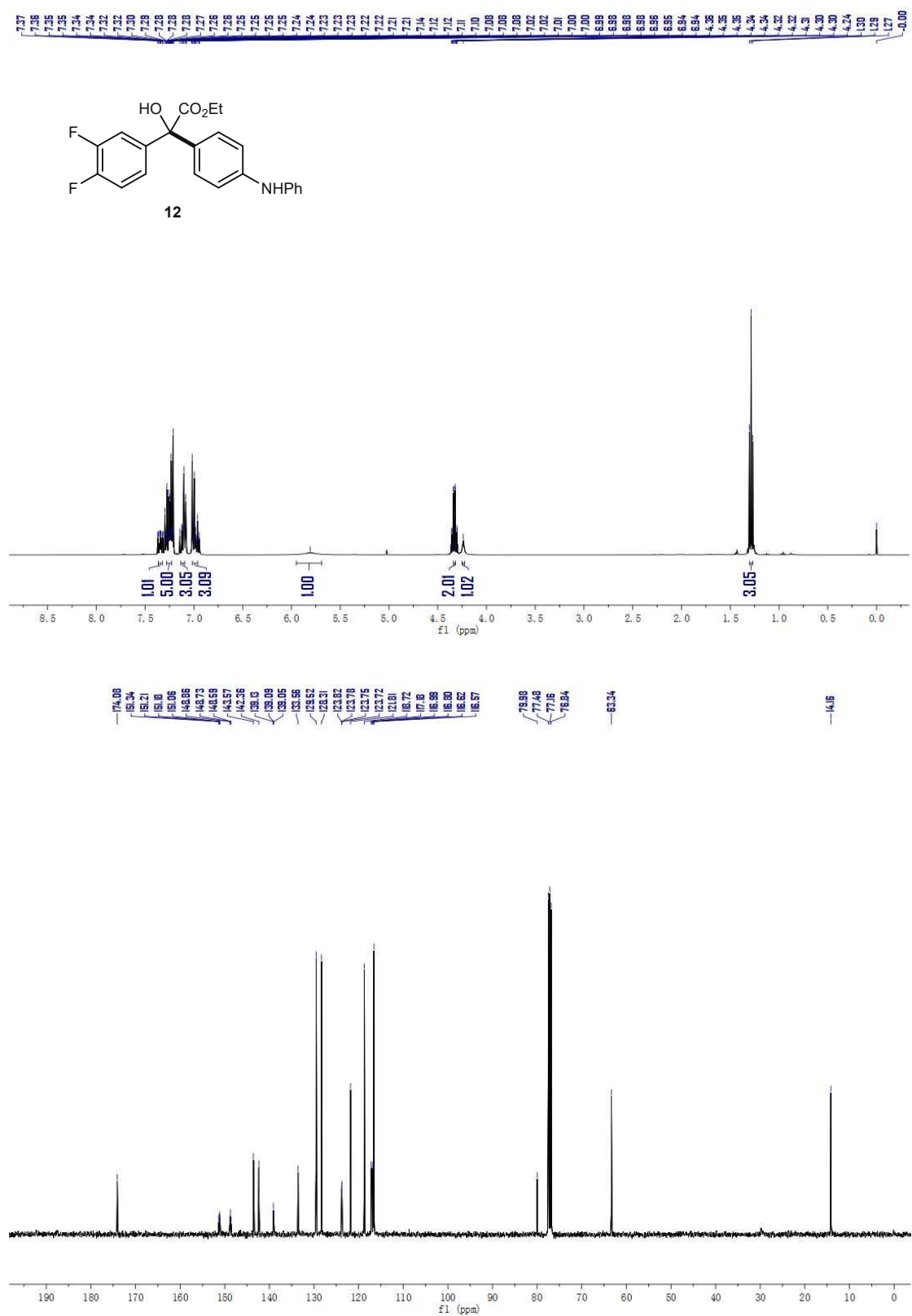


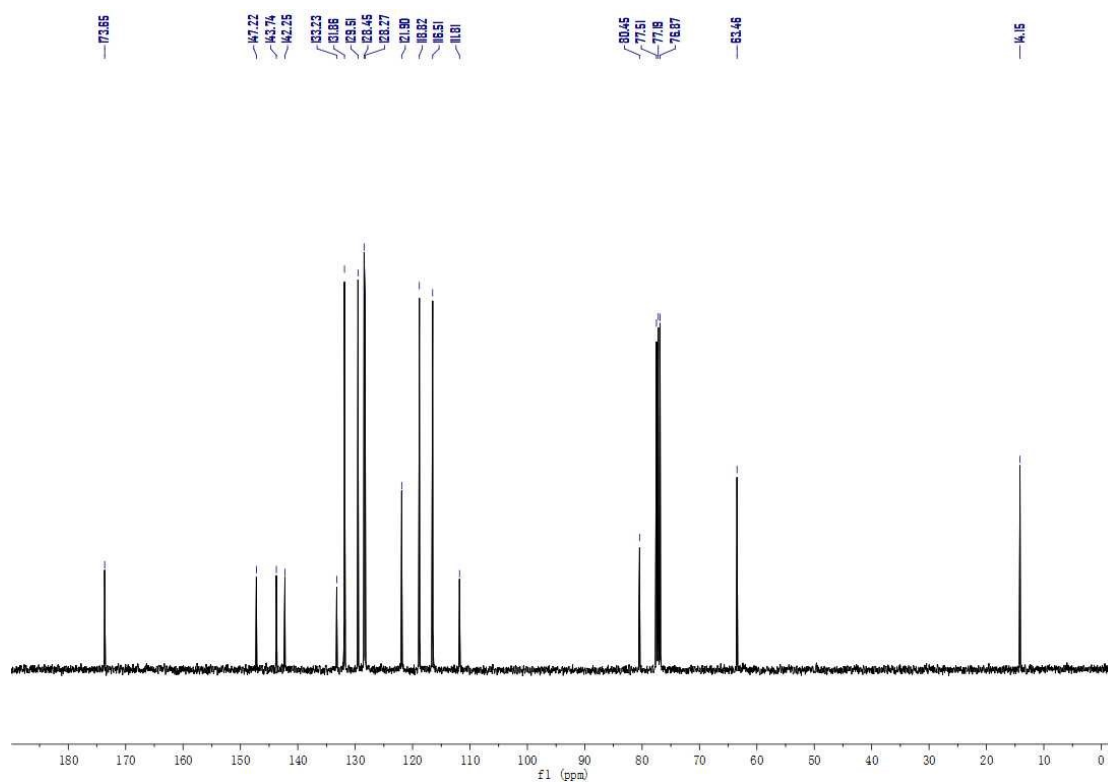
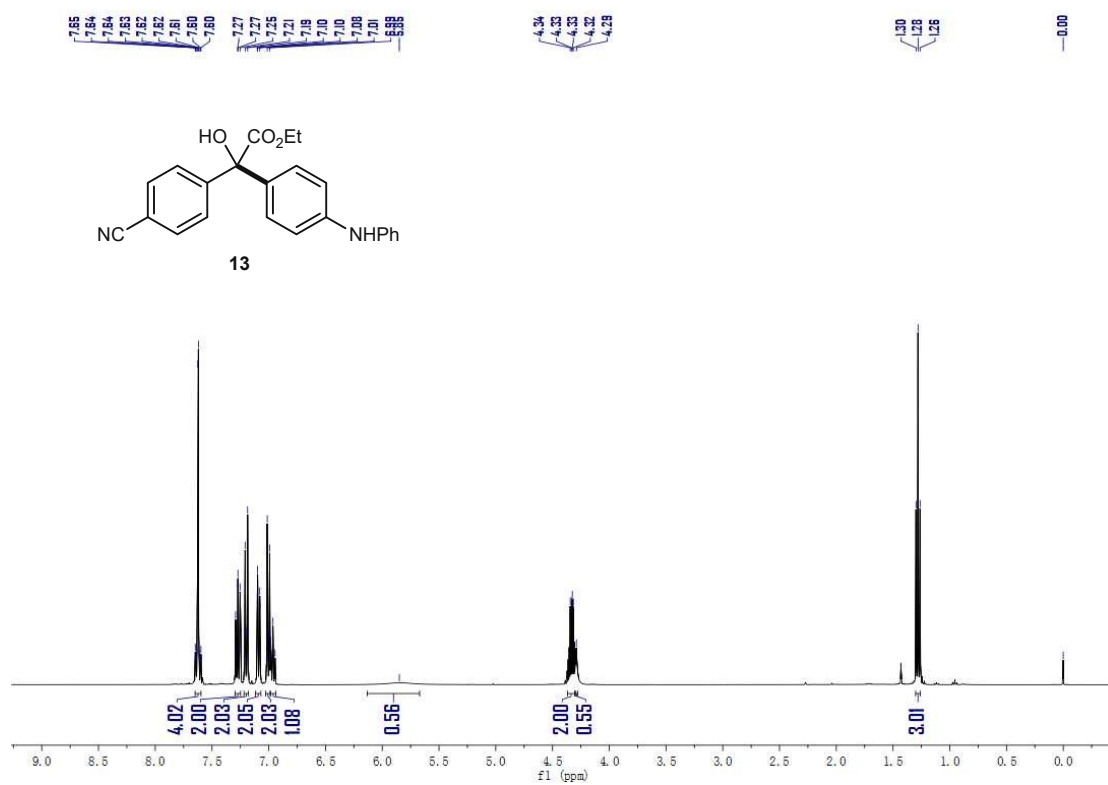


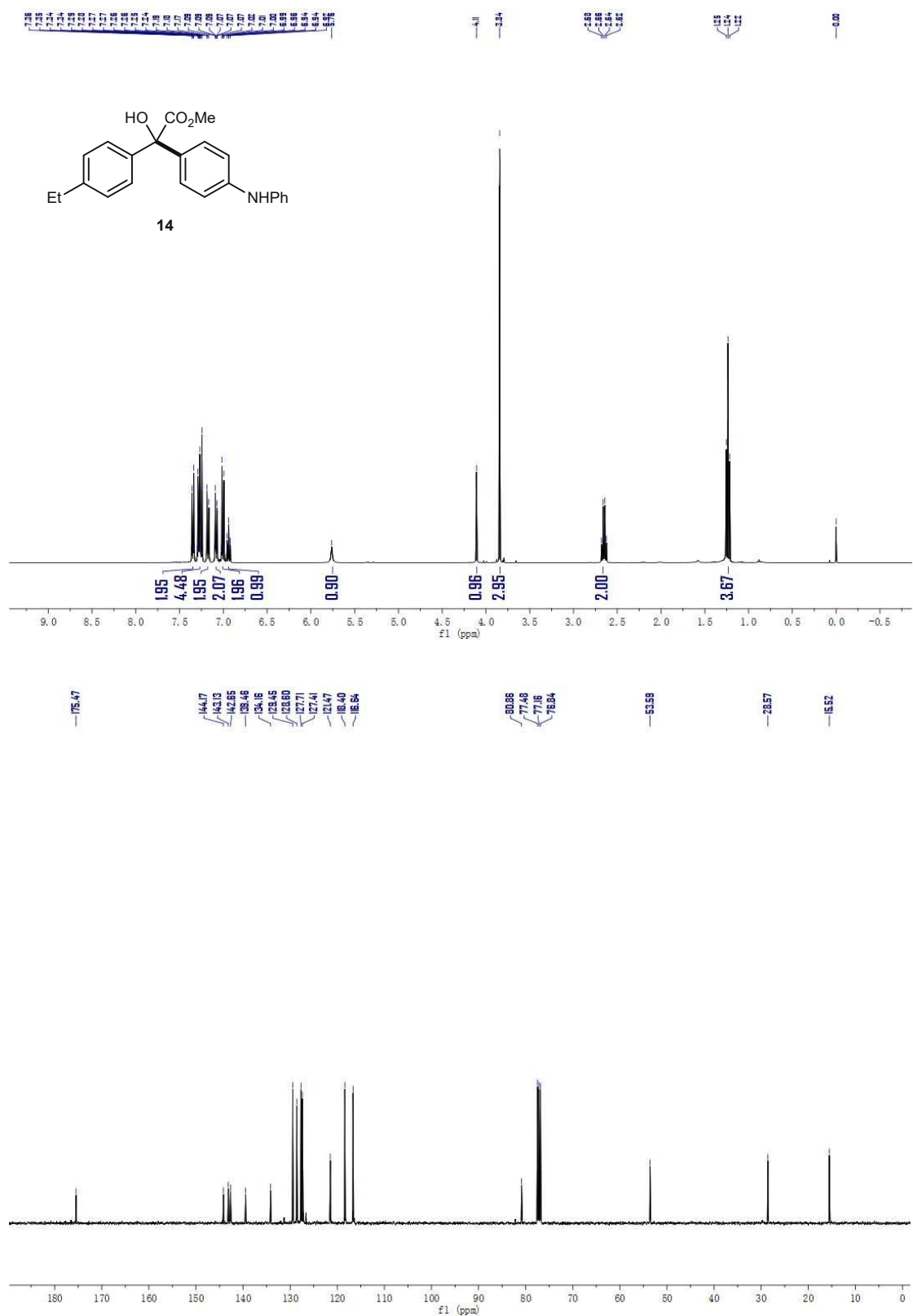


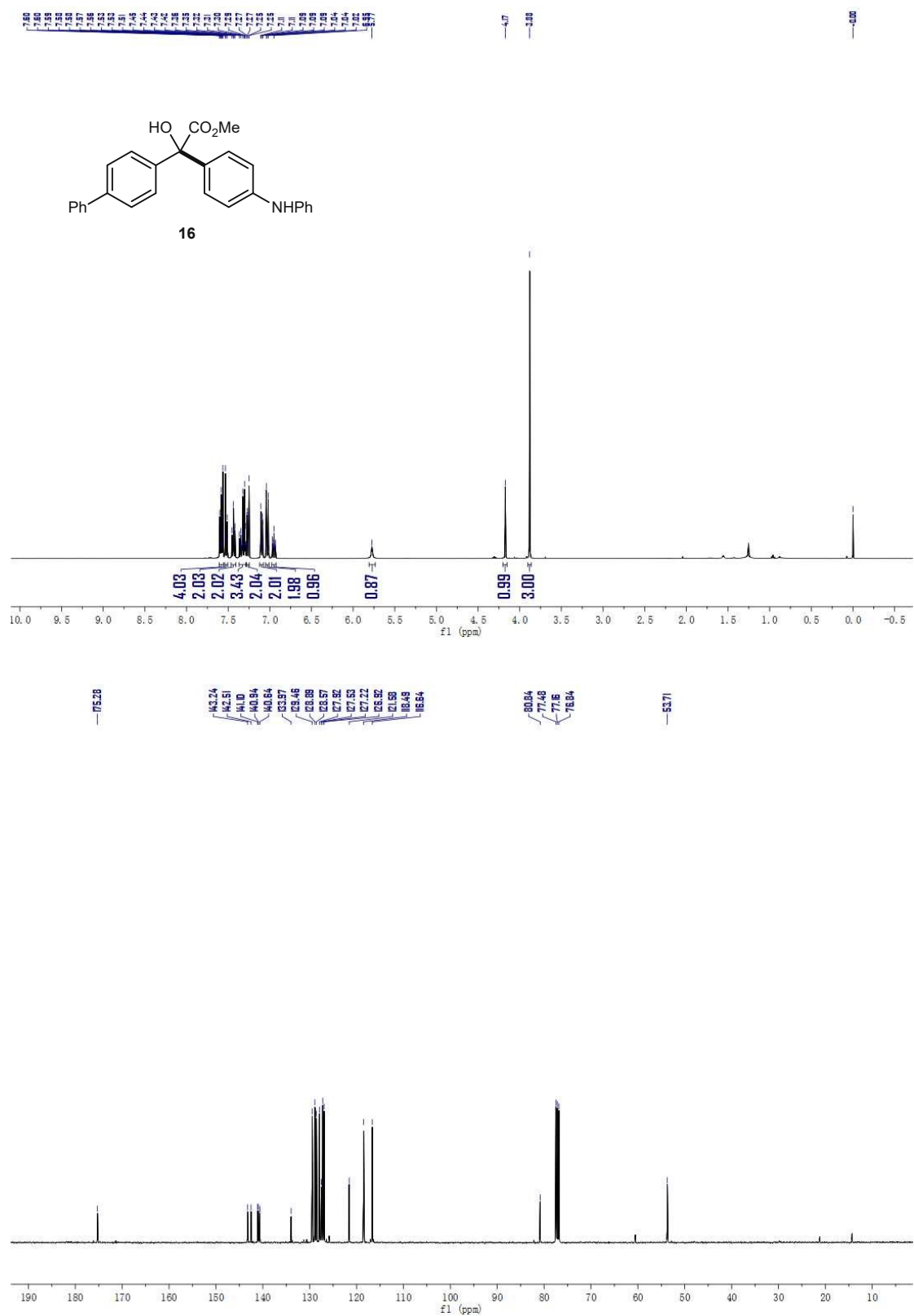




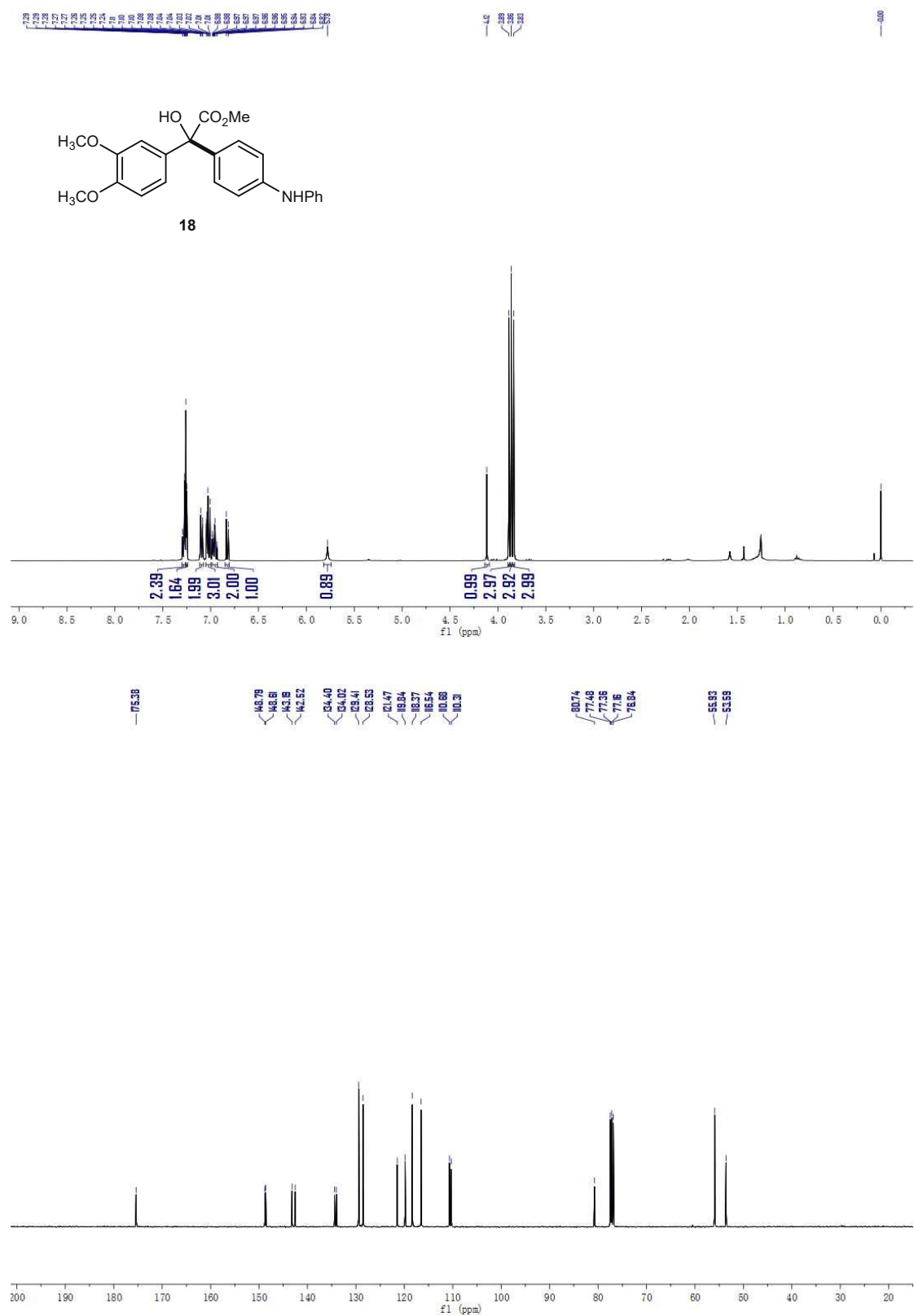


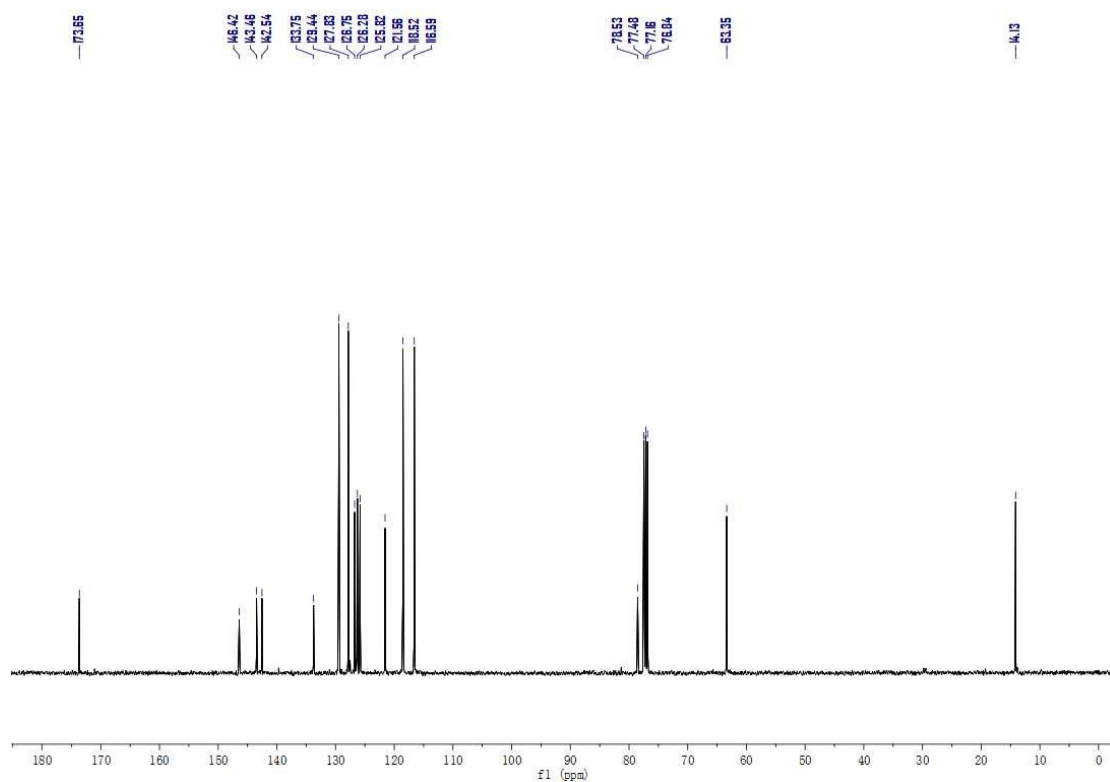
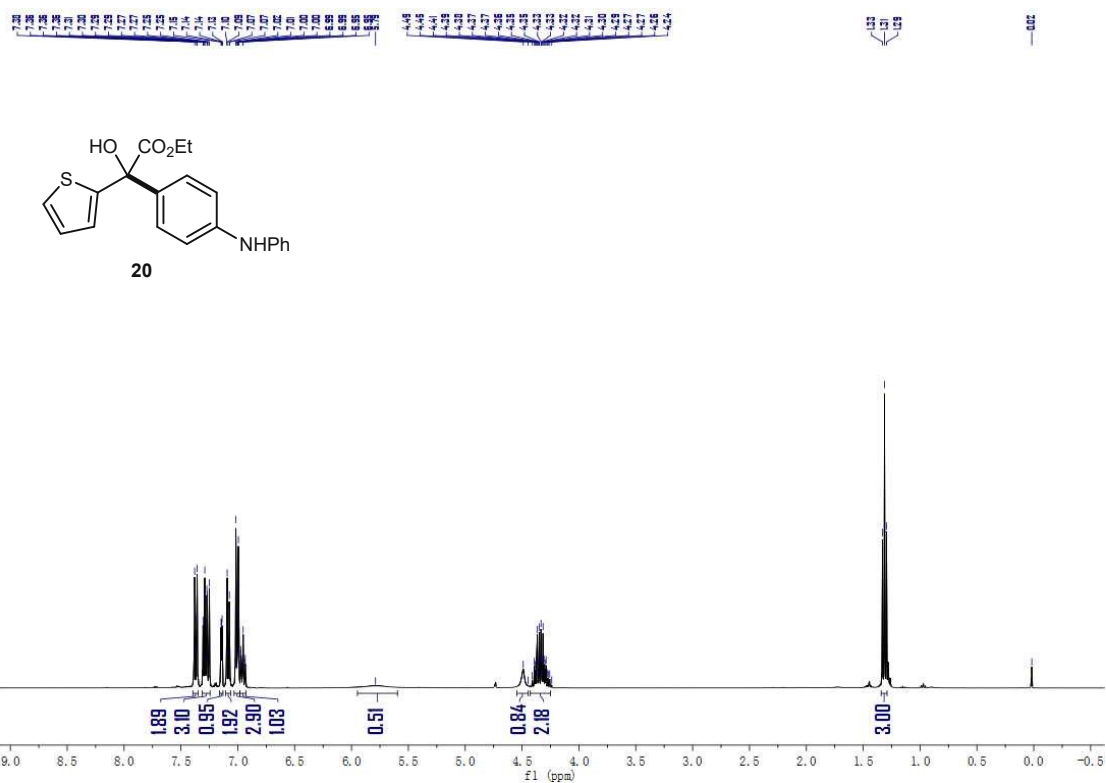


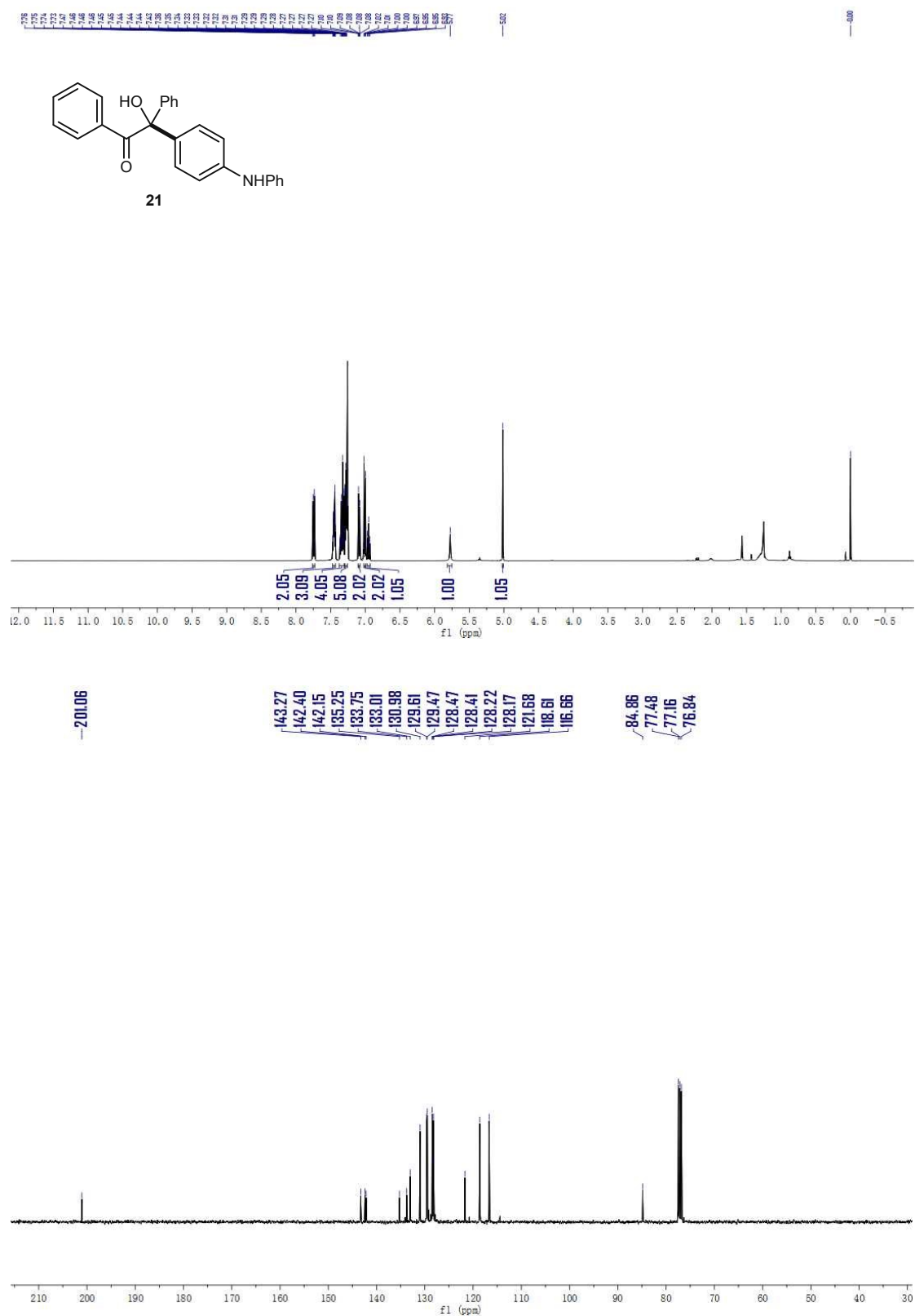


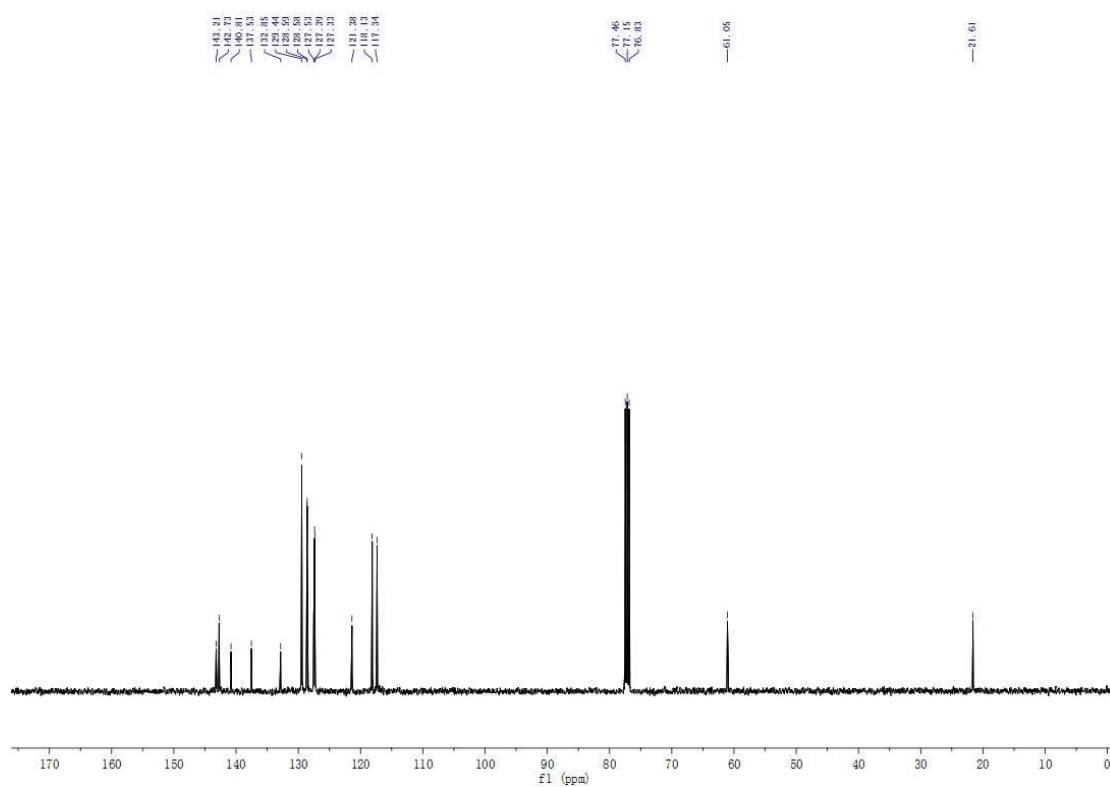


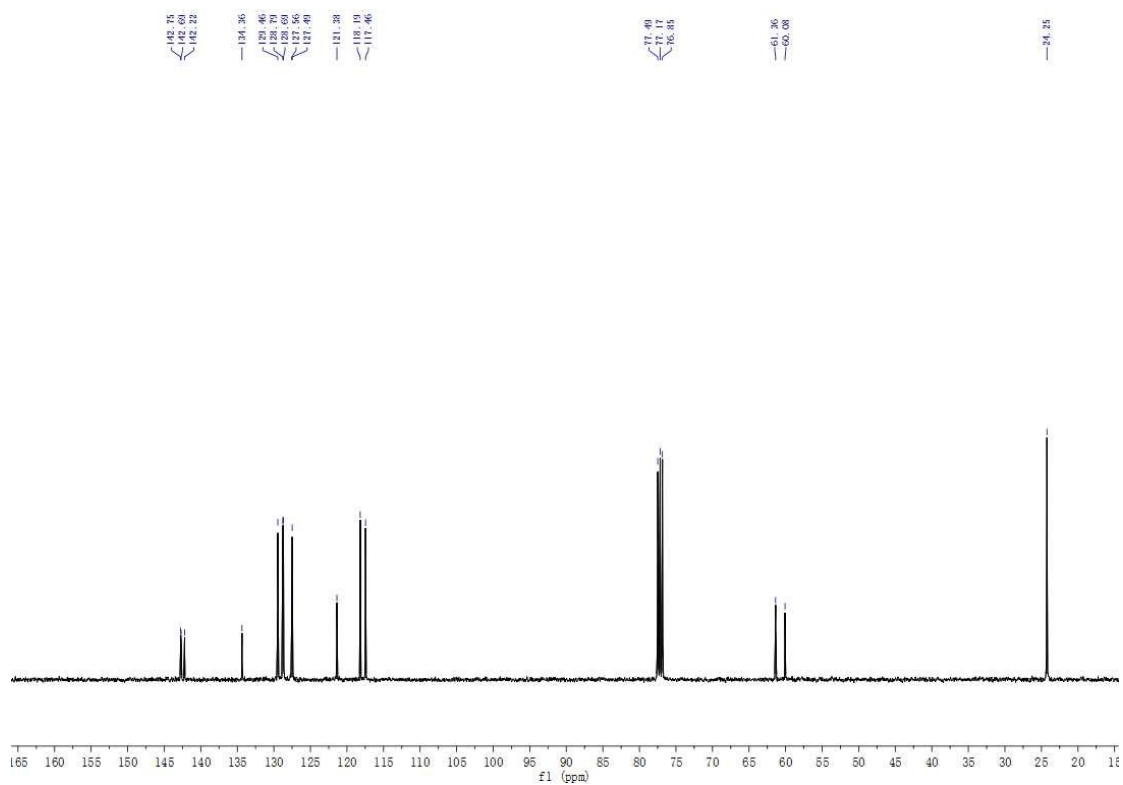
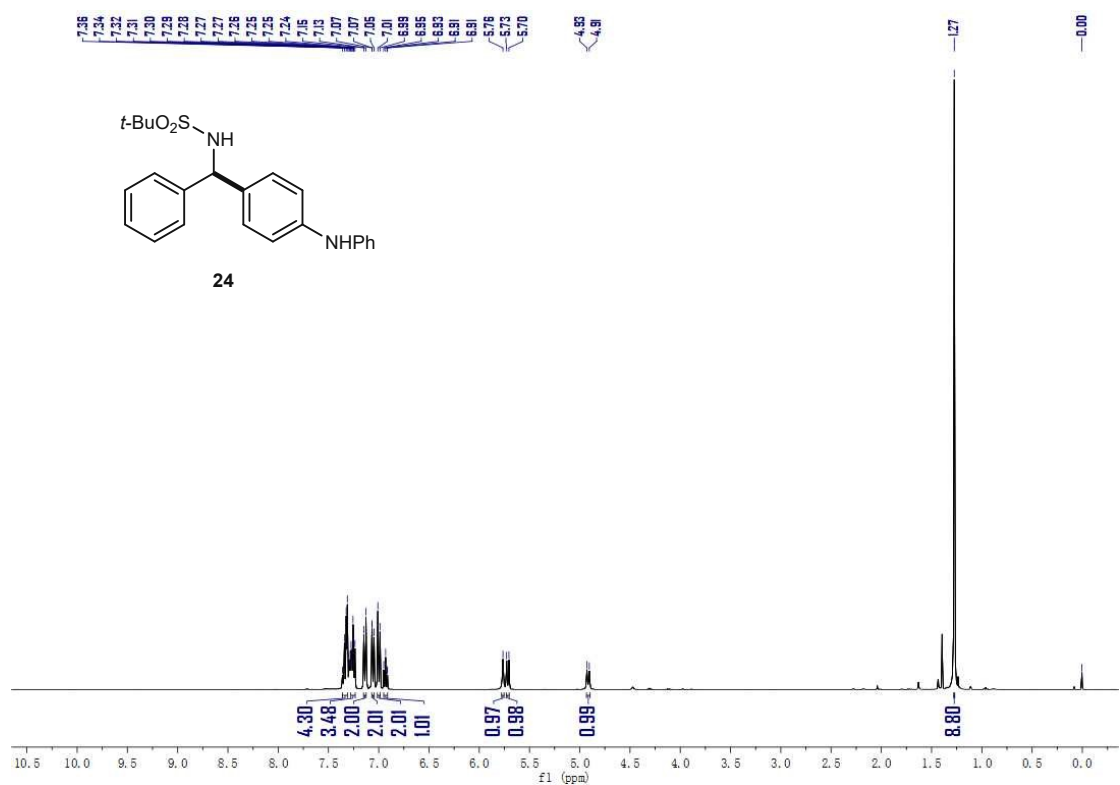


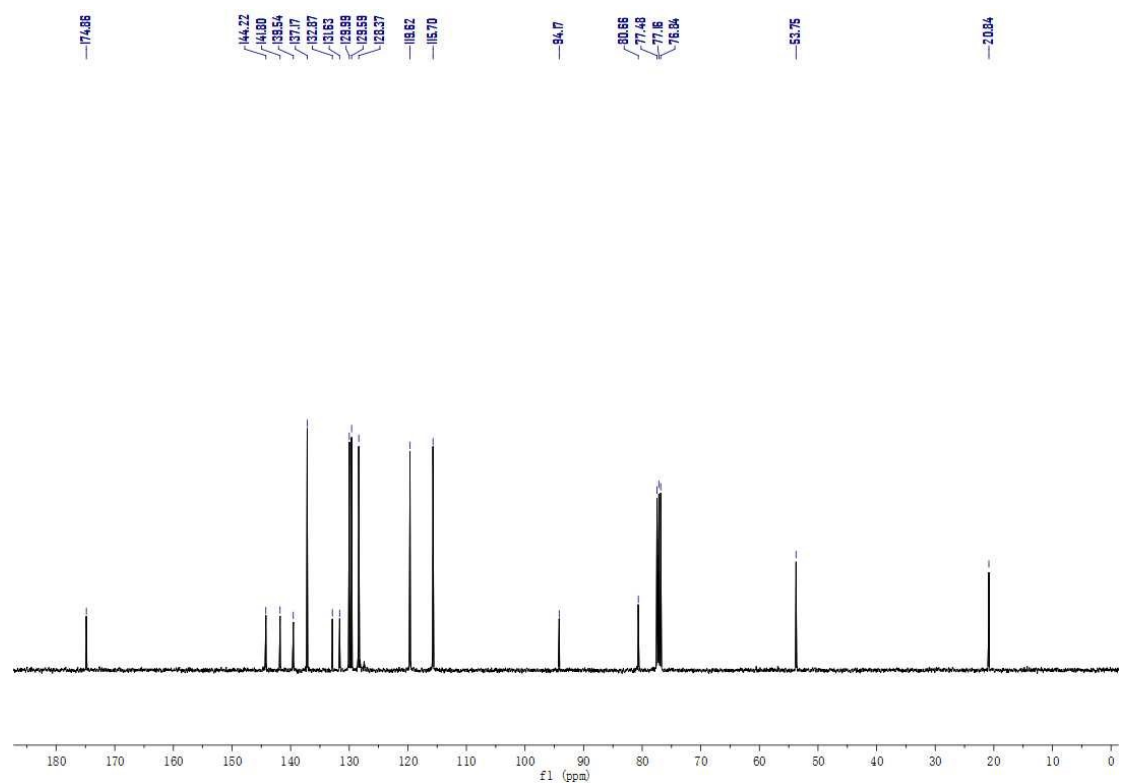
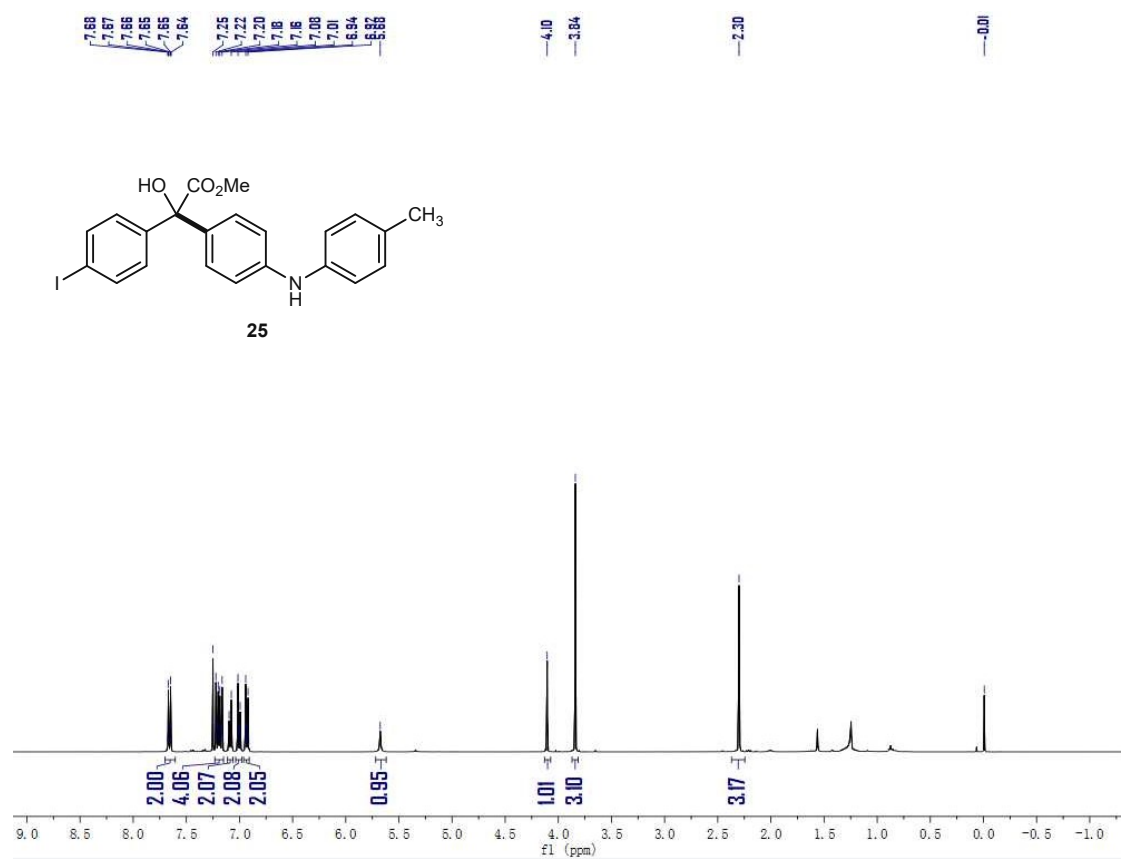


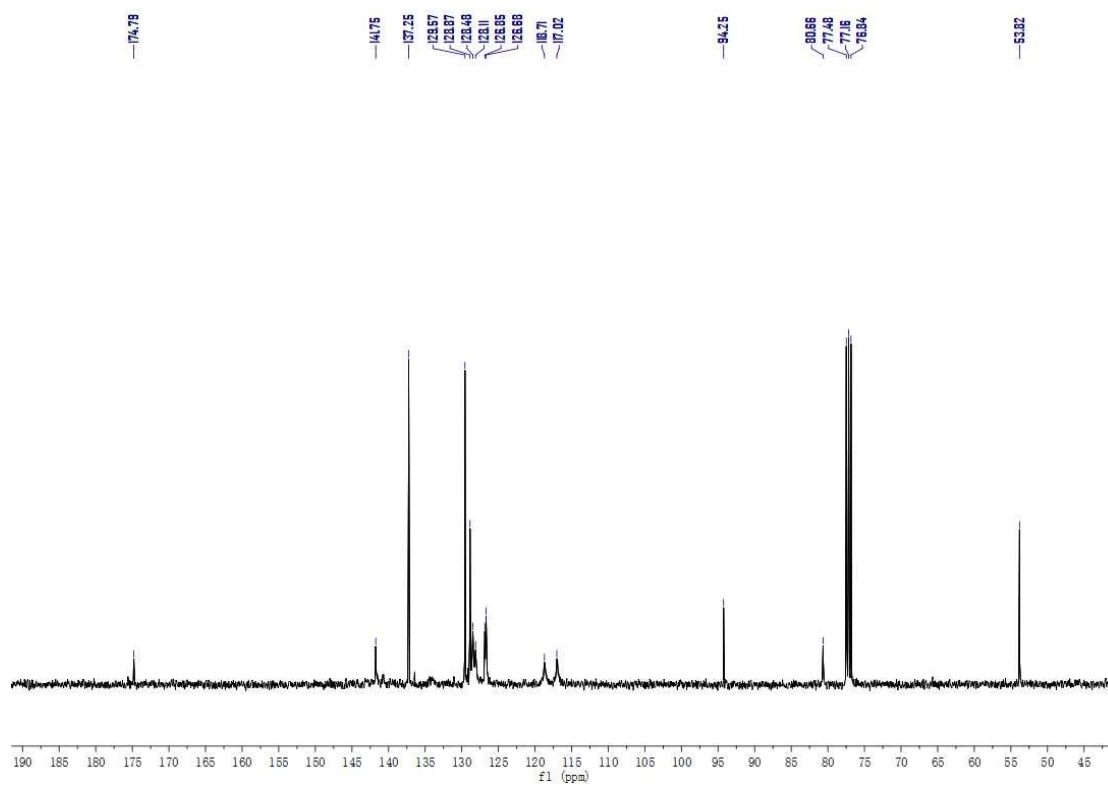
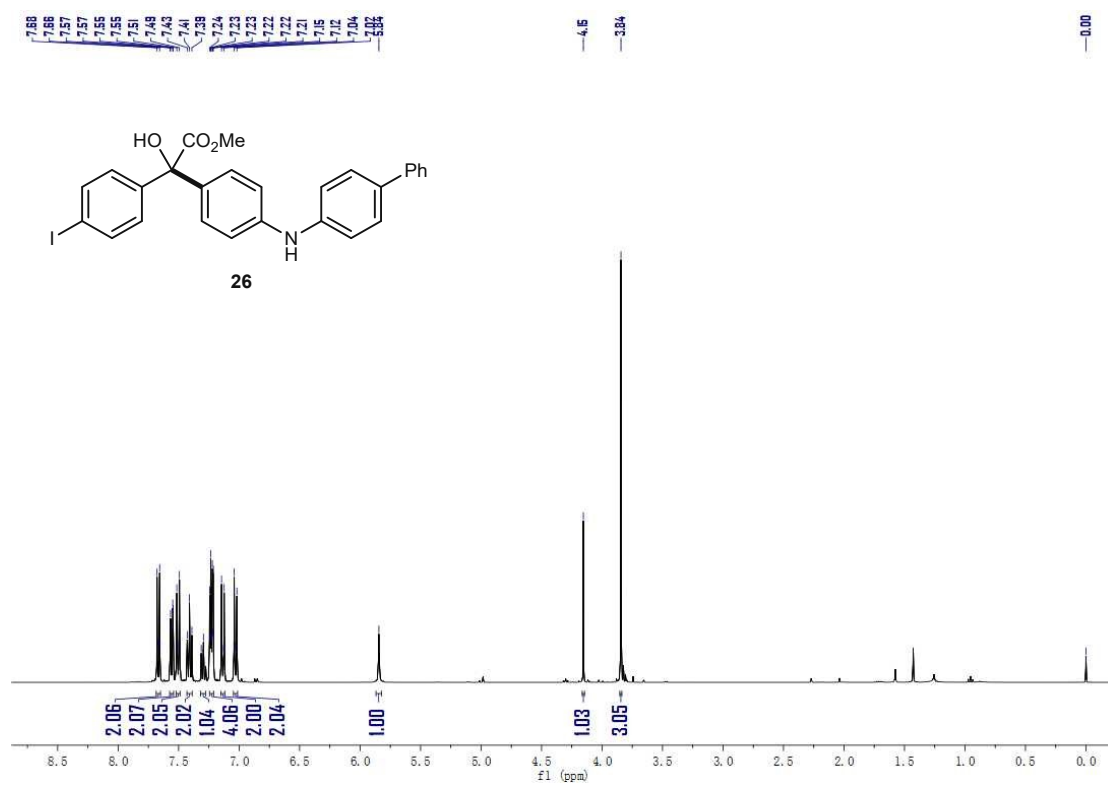


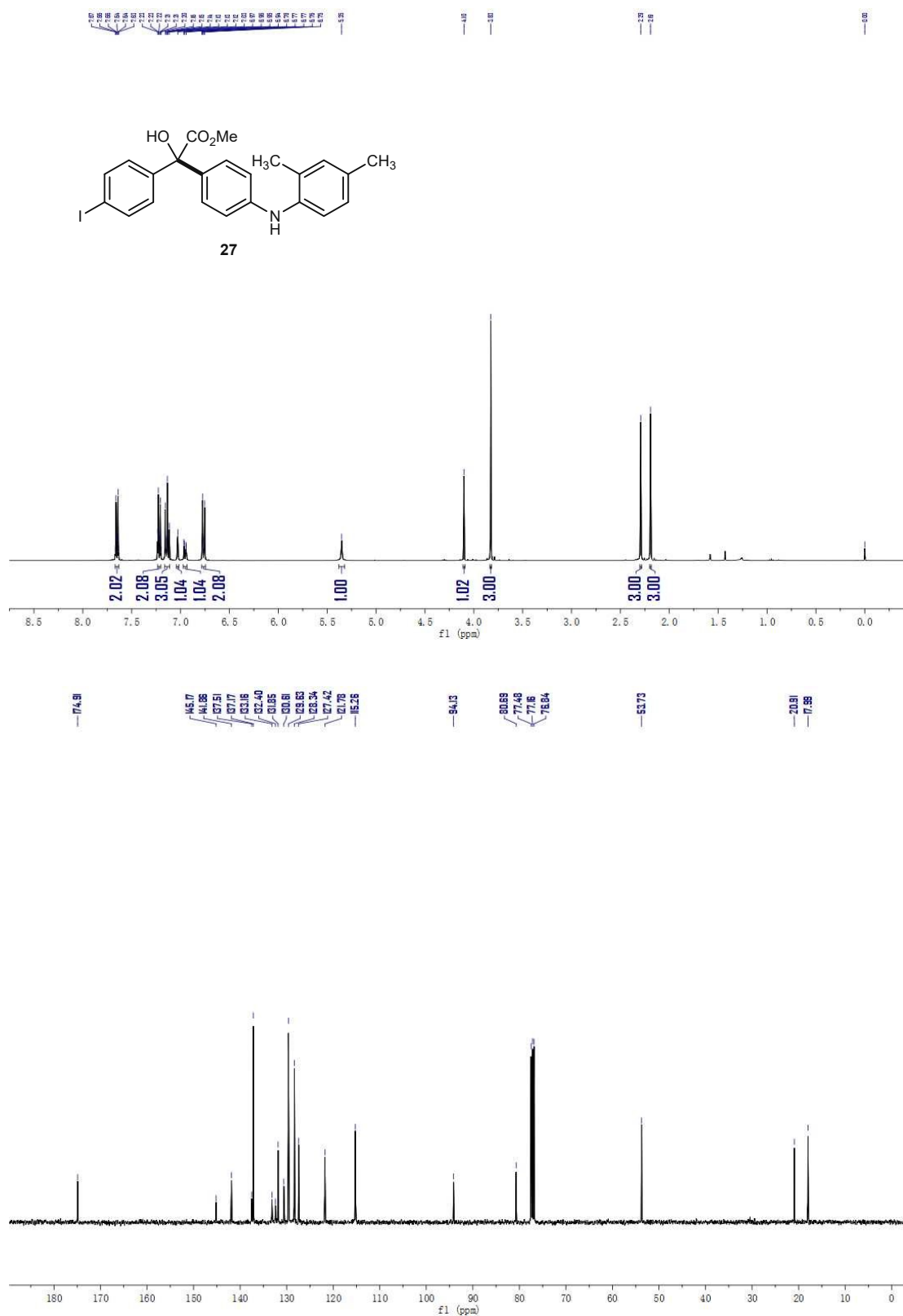


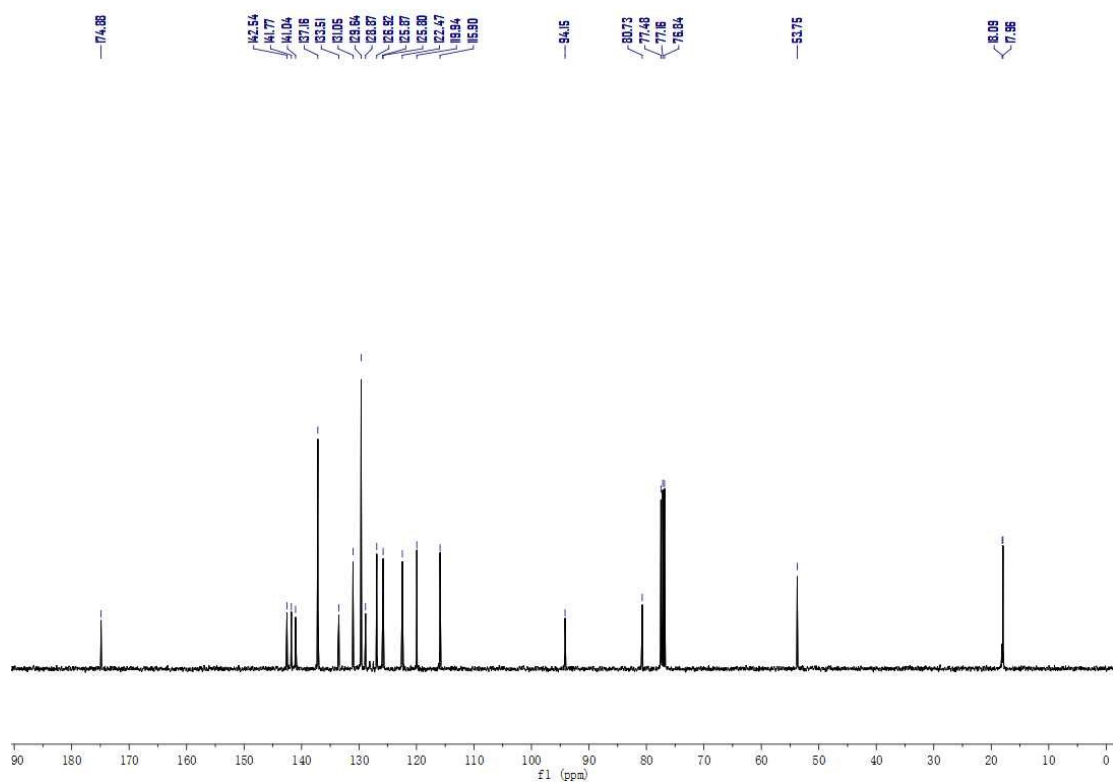
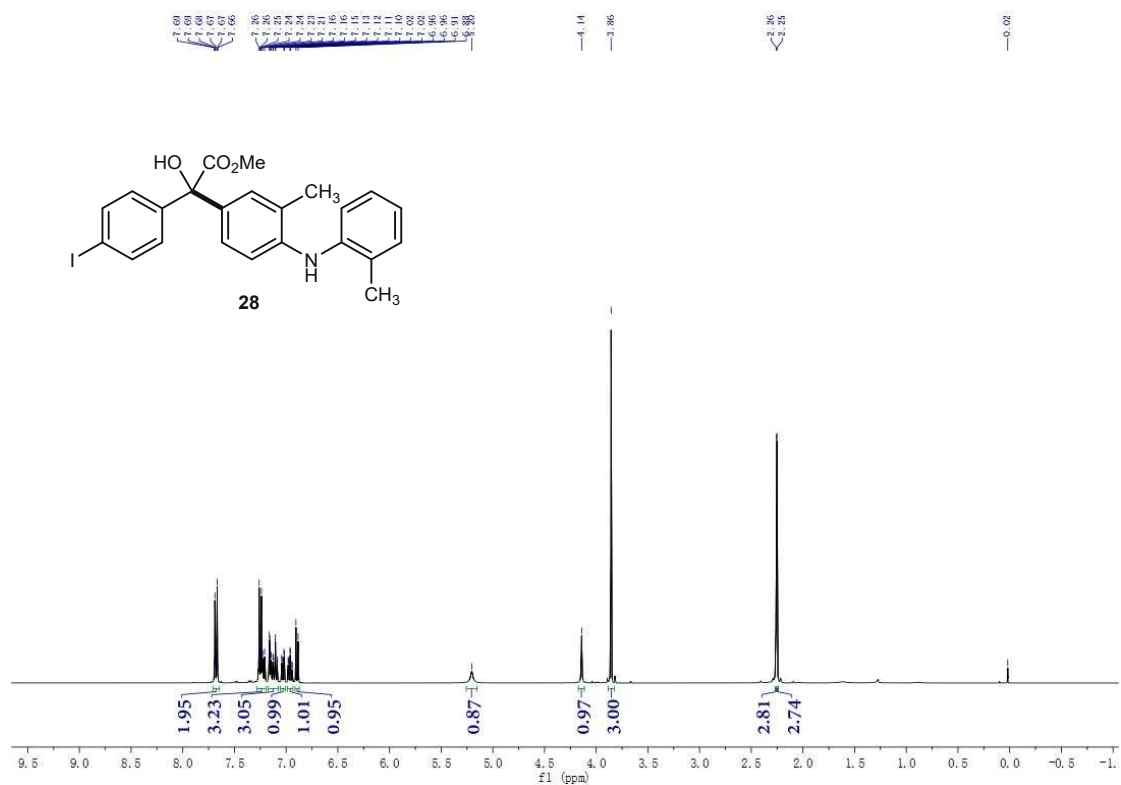


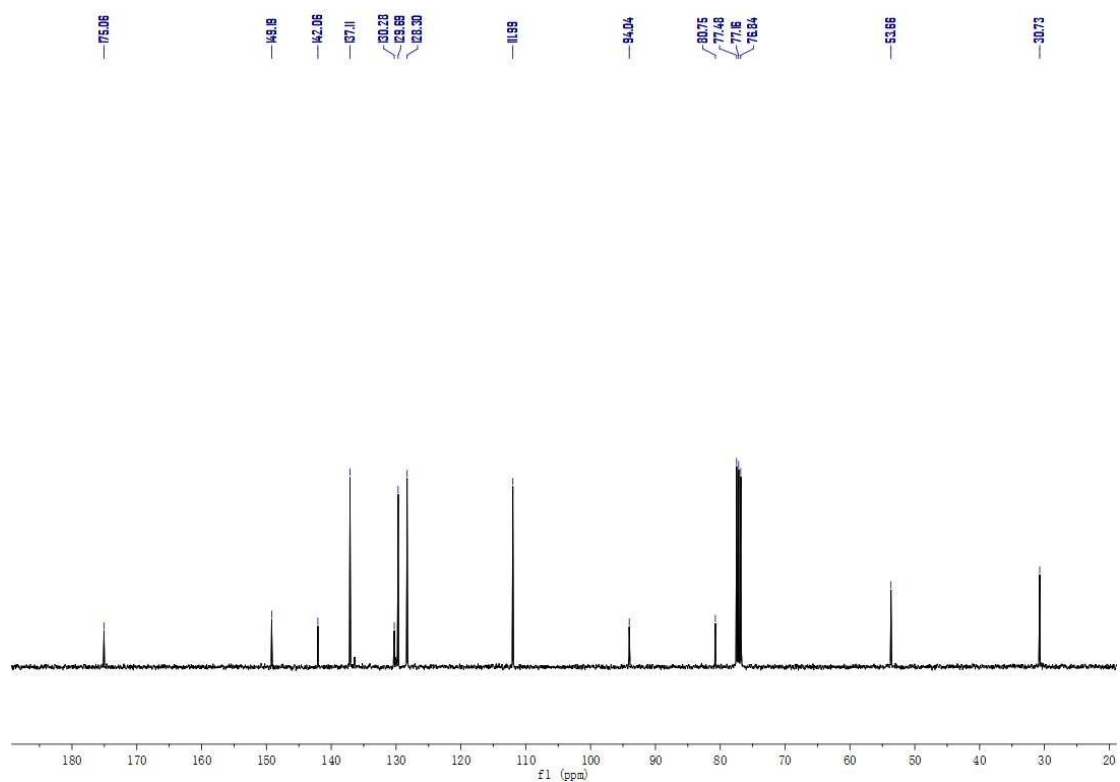
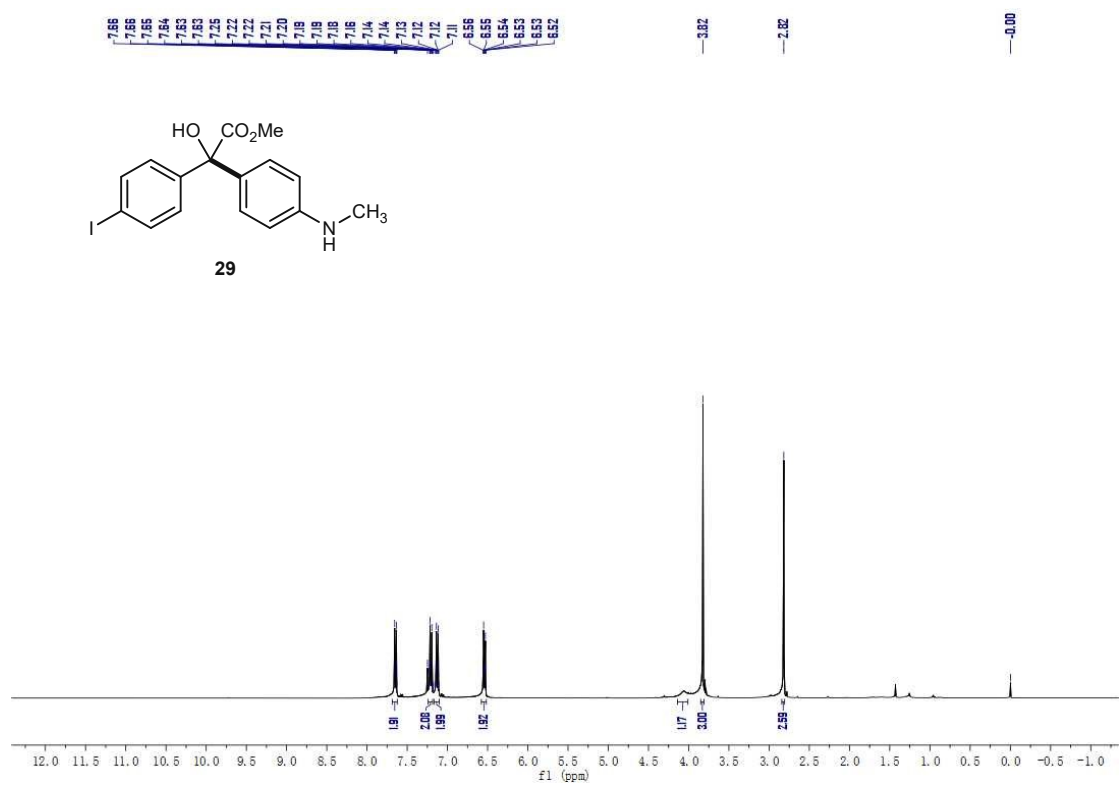


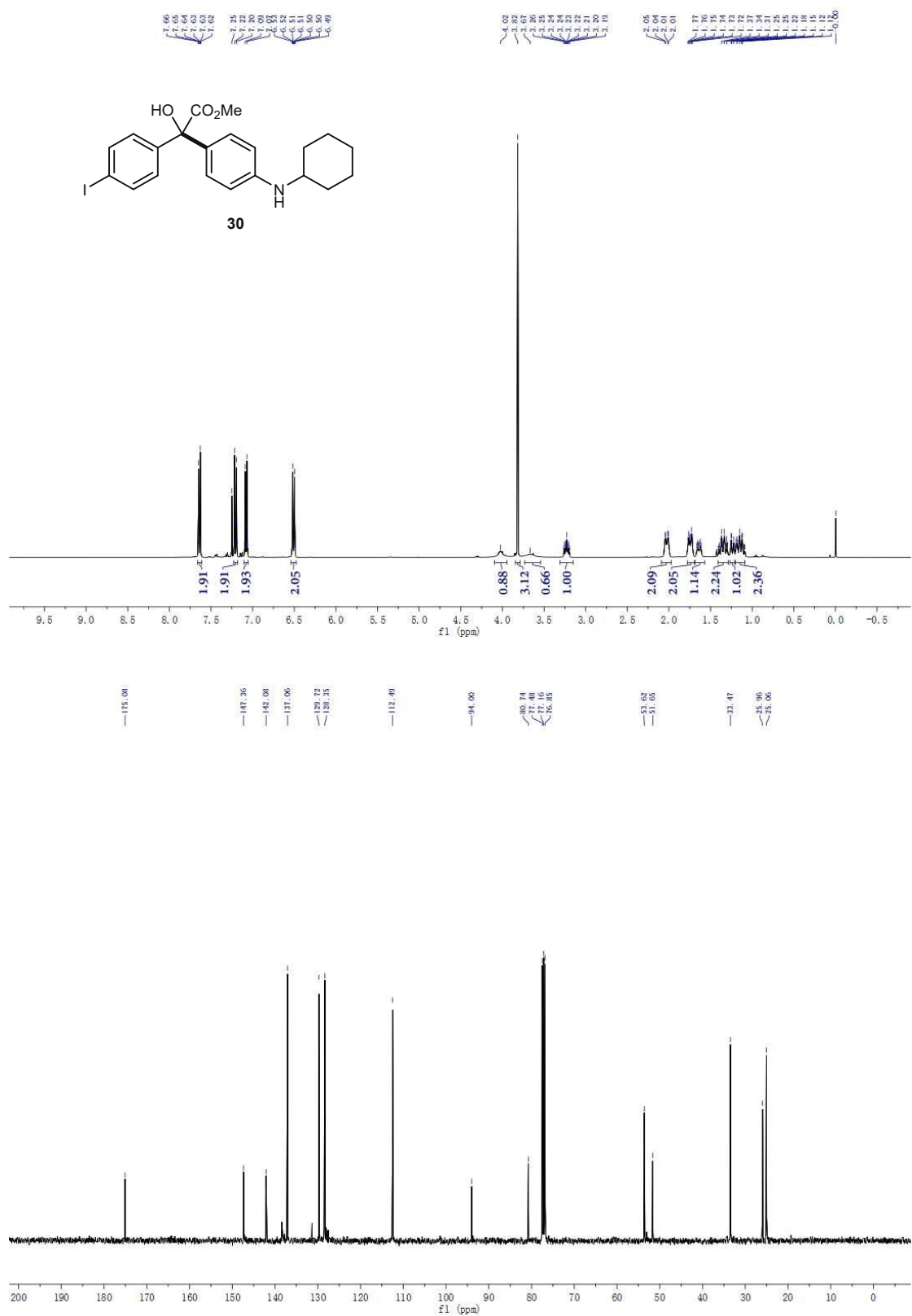


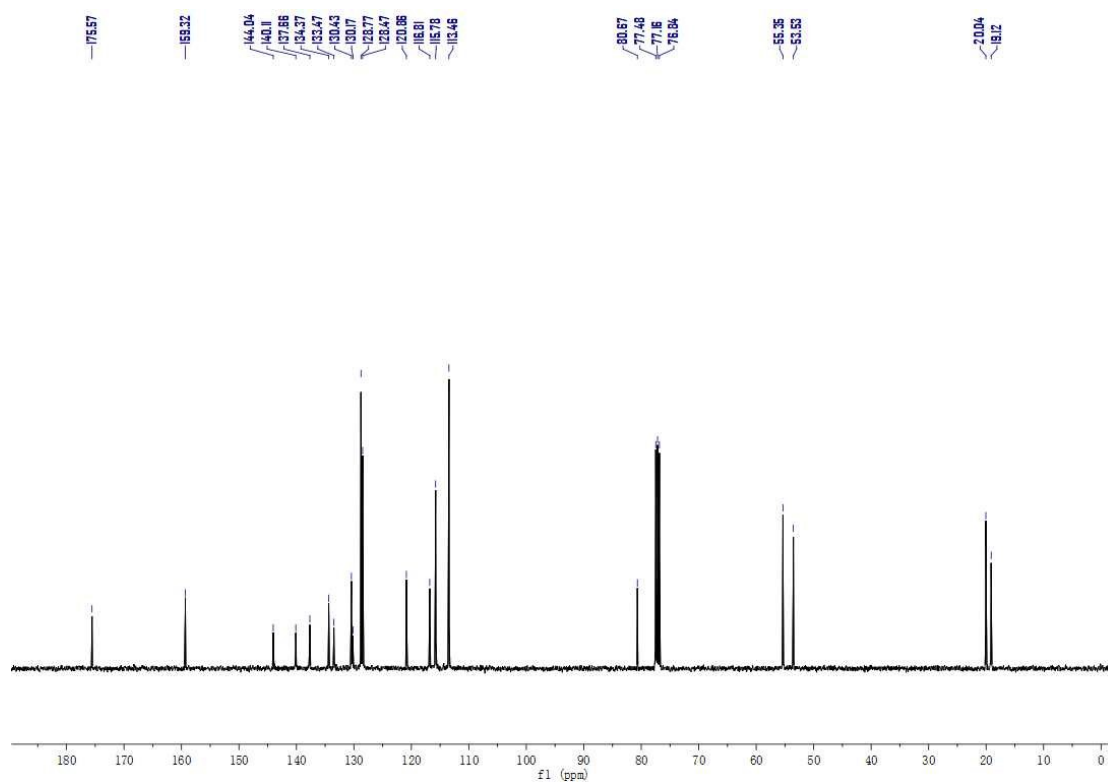
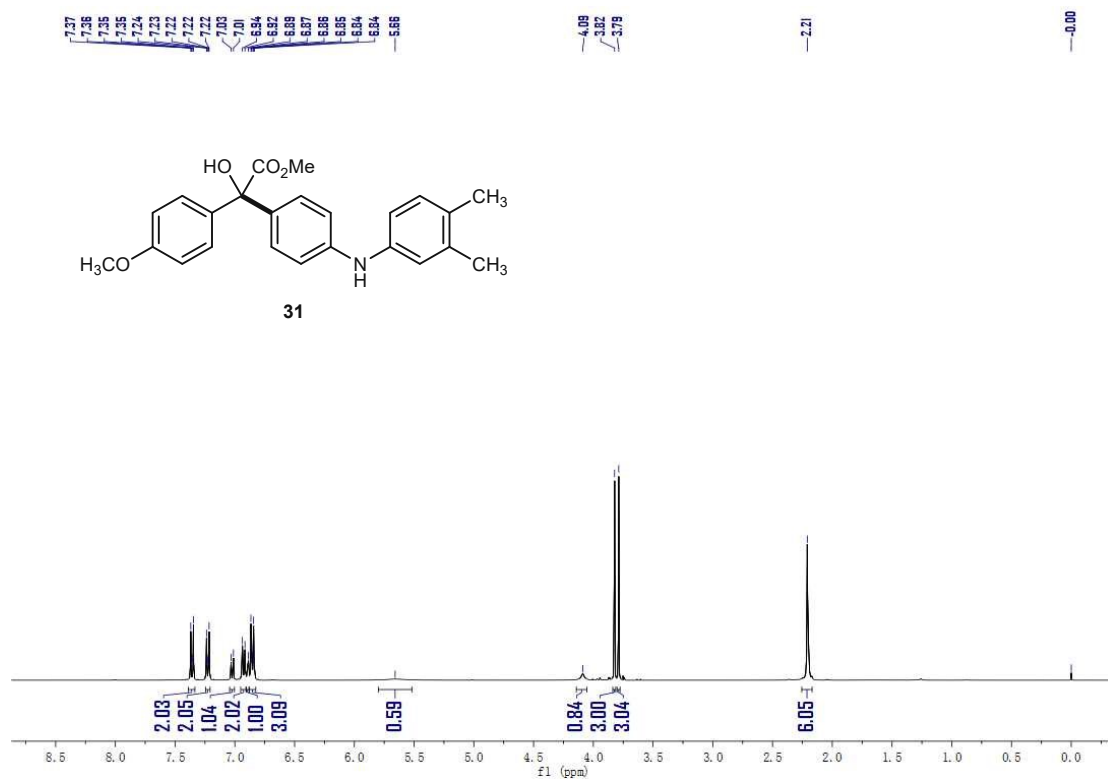


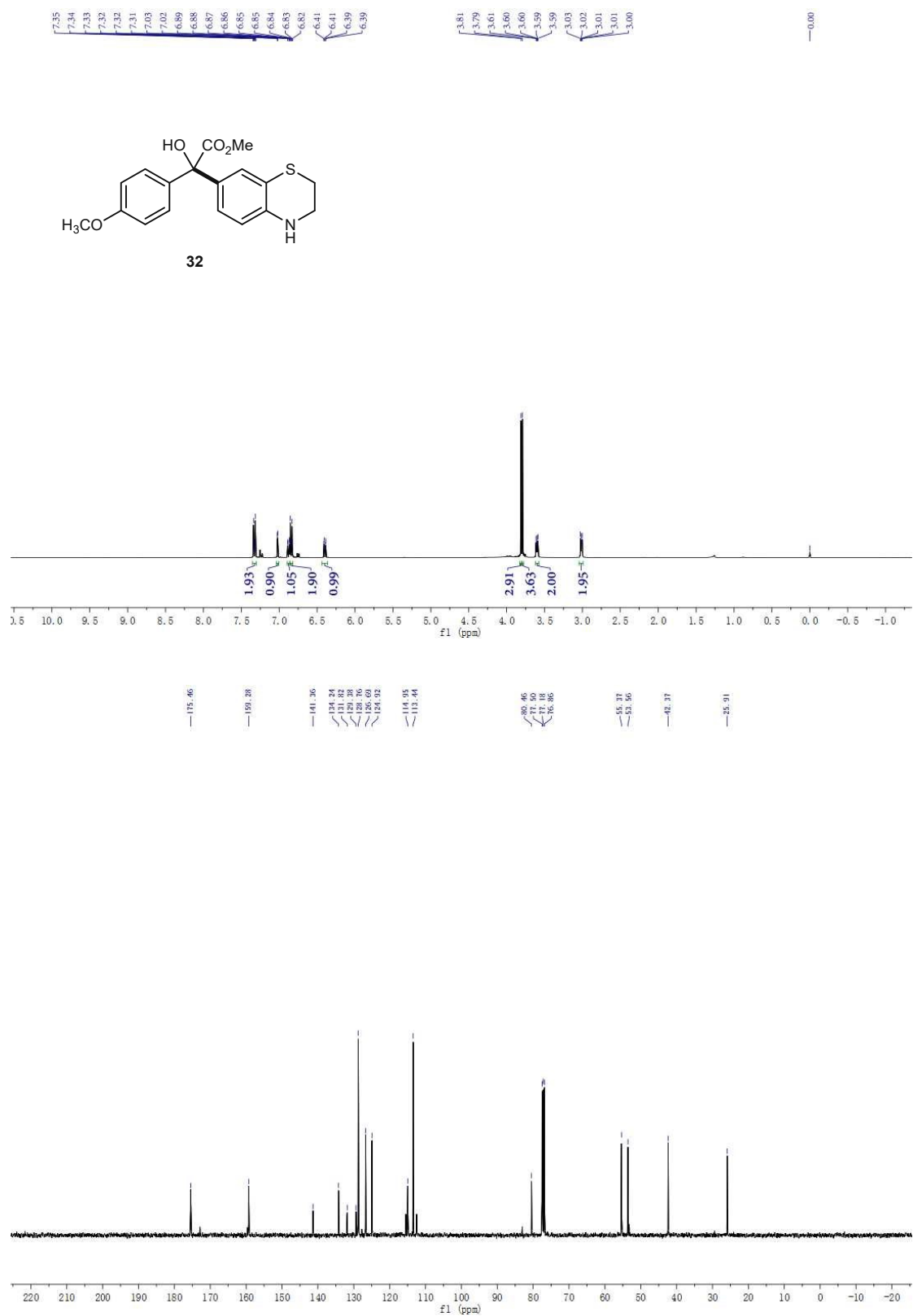




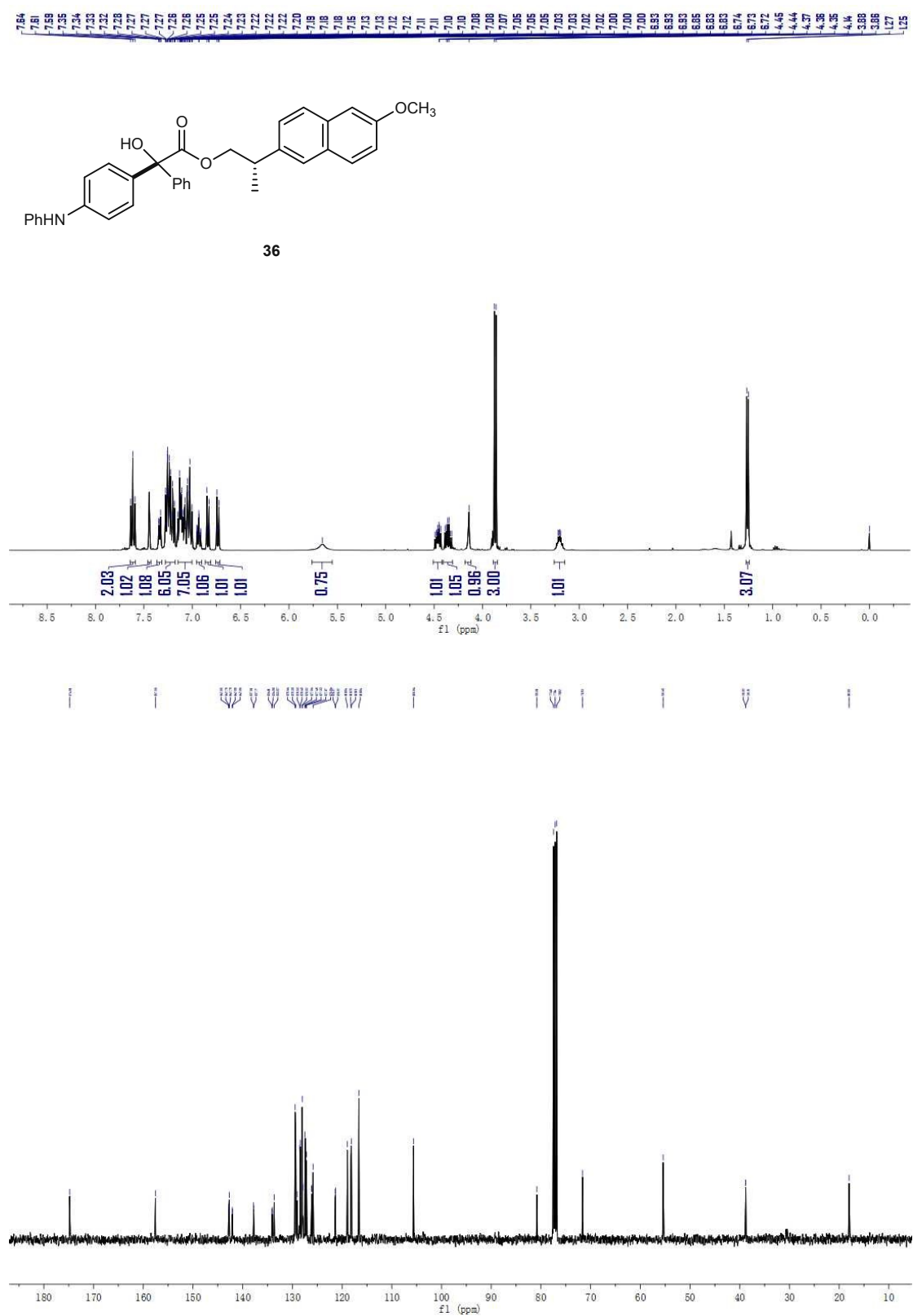


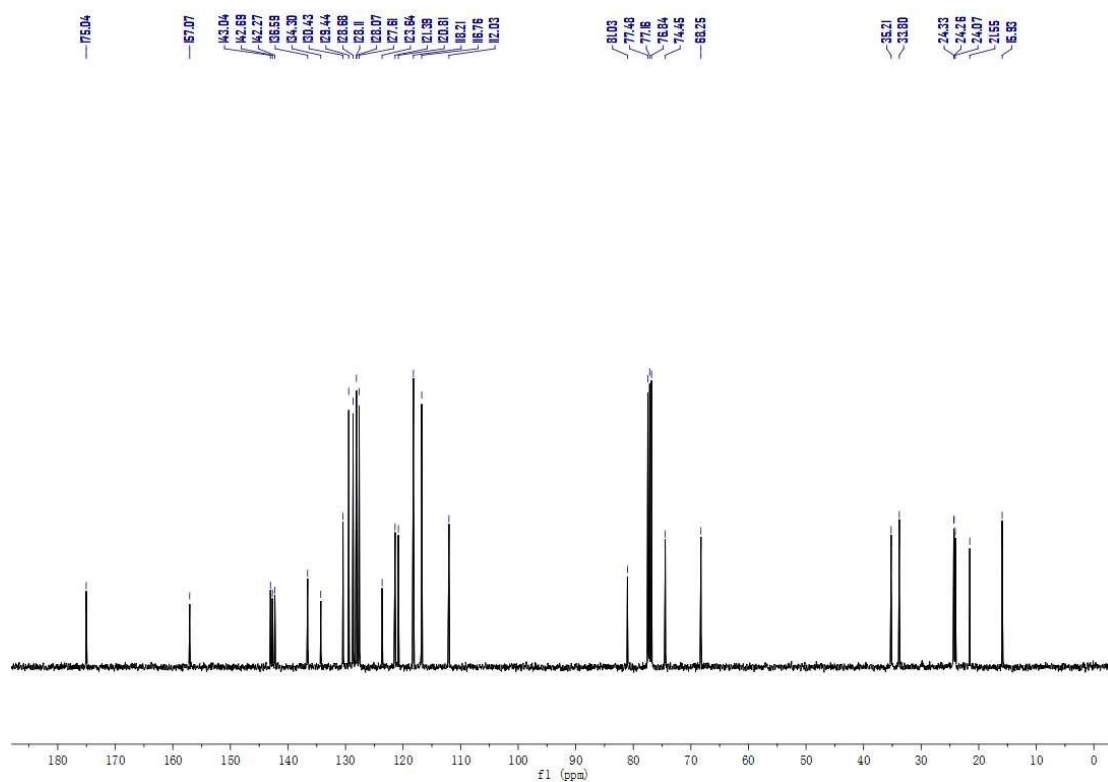


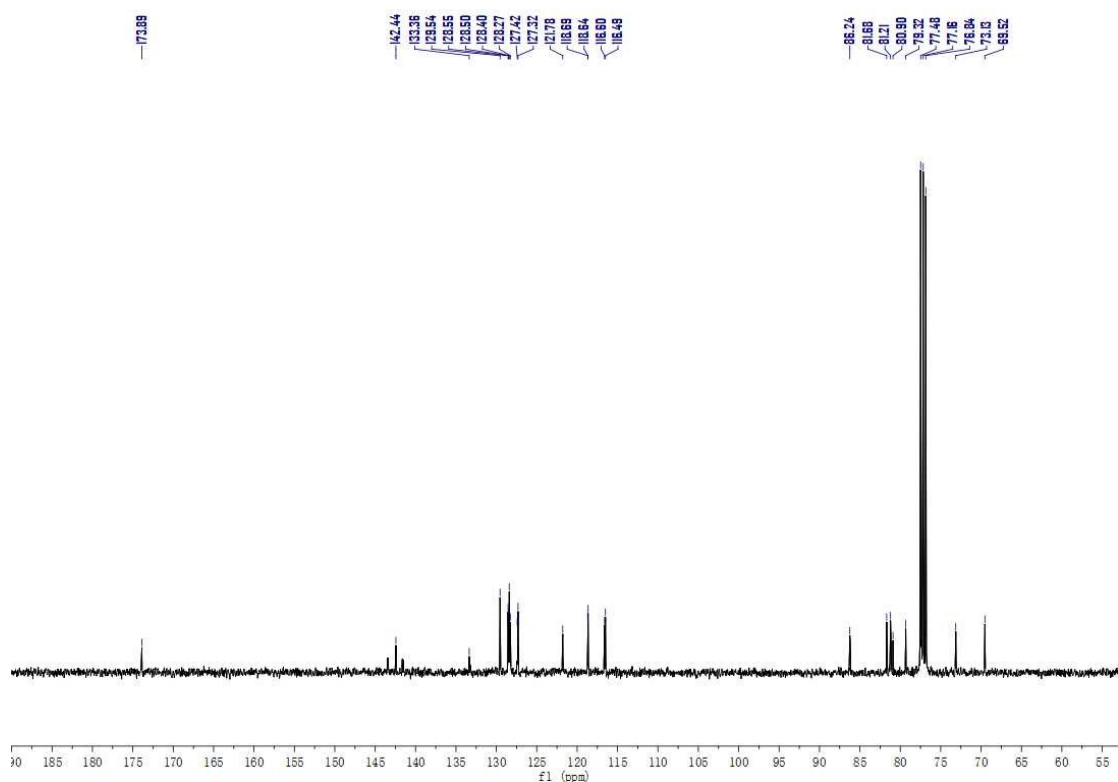


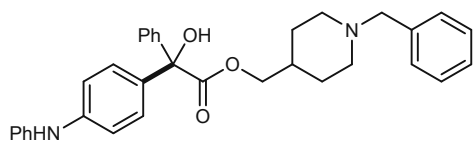












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