

Supplementary Information for
AlCl₃-Catalyzed [3+3] Cycloaddition of Chalcones and β-Enamine
Ketones (Esters): A Highly Efficient Access to Multisubstituted
Cyclohexa-1,3-Dienamines

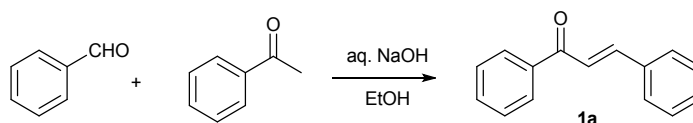
List of contents

1. General experimental information.	S2
2. General Procedure for the Synthesis of 1.	S2
3. General Procedure for the Synthesis of 2. ²	S3
4. General procedure and spectroscopic data of compounds 3 and 5.	S3
5 Copies of Product NMR Spectra.....	S17
Reference.....	S40

1. General experimental information.

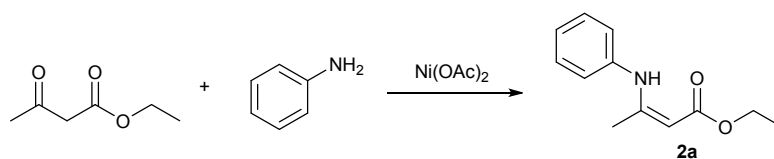
All reagents and solvents were of commercial quality and were used as received. Reactions were monitored by TLC analysis. Melting points were measured on an X-4 hot stage microscope, and are uncorrected. ^1H NMR spectra were recorded on an NMR instrument operated at 500 MHz. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl_3 : δ 7.26 ppm). ^{13}C NMR spectra were recorded on an NMR instrument operated at 126 MHz with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl_3 : δ 77.1 ppm). Topspin (Bruker) or Mestrenova (Mestrelab) software packages were used throughout for data processing;

2. General Procedure for the Synthesis of **1a**



To a solution of benzaldehyde (1.06 g, 10 mmol) and acetophenone (1.20 g, 10 mmol) in ethanol (30 mL) was added 30 mL aqueous sodium hydroxide (0.8 g, 20 mmol) dropwise via addition funnel at 0 °C. Stirred the reaction mixture for 3 h at 20-25 °C. After completion of the reaction (detected by TLC), the reaction mixture was filtered, wash with ethanol-water solution (1/1) and dried. The desired chalcone **1a** was obtained. **1a**: (1.77 g, 85%) ^1H NMR (500 MHz, CDCl_3) δ 8.02(d, J = 7.0 Hz, 2H), 7.82 (d, J =15.5 Hz, 1H), 7.65(d, J =5.5 Hz, 2H), 7.58(d, J =15.5 Hz, 1H), 7.51(d, J =8.0 Hz, 3H), 7.43(d, J =7.5 Hz, 3H); GC-MS[m/z]: 208.9 ($[\text{M}+1]^+$, 100%), 105.1(25%).

3. General Procedure for the Synthesis of **2**.²

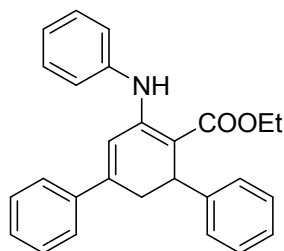


A mixture of ethyl acetoacetate (1.30 g, 10 mmol), aniline (1.12 g, 12 mmol), and $\text{Ni}(\text{OAc})_2$ (0.352 g, 2 mmol) was stirred at room temperature. After completion of the reaction (detected by TLC), ethyl acetate (10 mL) was added and the heterogeneous mixture was filtered. The filter cake was washed with diethyl ether and the catalyst was recovered. The organic phase was washed with water, dried over magnesium sulfate, and concentrated in vacuo. Further purification was carried out by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1/4) provided desired product **2a** (1.81 g, 88%). **2a**: ^1H NMR (500 MHz, CDCl_3) δ 10.38 (br s, 1H), 7.32 (t, 2H, $J=7.8$ Hz), 7.15 (t, 1H, $J=7.0$ Hz), 8.00 (d, 2H, $J=8.0$ Hz), 4.69 (s, 1H), 4.15 (q, 2H, $J=7.0$ Hz), 2.00 (s, 3H), 1.28 (t, 3H, $J=7.1$ Hz).

4. General procedure and spectroscopic data of compounds **3** and **5**.

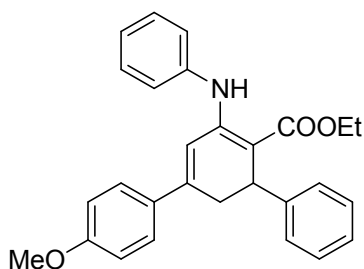
Chalcone **1a** (0.104 g, 0.5 mmol), β -enamine ester **2a** (0.123 g, 0.6 mmol), AlCl_3 (0.066 g, 0.5 mmol) were added to dry toluene (5 mL) under N_2 and stirring was continued for 8h at 80 °C. After completion of the reaction, as indicated by TLC, the mixture was dissolved in CH_2Cl_2 (30 mL) and then washed with aqueous ammonia (10 %) (15 mL $\times$ 2). The separated organic layer was concentrated under vacuum and the solvent was evaporated under reduced pressure. Pure products **3a** were obtained by silica gel column chromatography as a yellow solid (0.184 g, 93%), eluting with a petroleum ether-ethyl acetate mixture (20:1, v/v).

ethyl 5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**3a**):



yellow solid, **3a** (0.184 g, 93%); mp 113-115 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.80 (s, 1H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.34-7.28 (m, 7H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.20-7.13 (m, 4H), 6.70 (d, *J* = 2.9 Hz, 1H), 4.39 (d, *J* = 7.7 Hz, 1H), 4.24-4.05 (m, 2H), 3.27 (ddd, *J* = 16.6, 8.7, 2.9 Hz, 1H), 3.04 (dd, *J* = 16.7, 1.5 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.1, 151.2, 145.1, 144.0, 139.9, 139.9, 129.1 (2C), 128.5 (2C), 128.4; 128.0 (2C), 127.2 (2C), 126.0, 125.8 (2C), 123.8, 123.2 (2C), 118.0, 95.3, 59.3, 36.9, 34.6, 14.3; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₂₅NO₂ [M + H]⁺ 396.1964, found 396.1963.

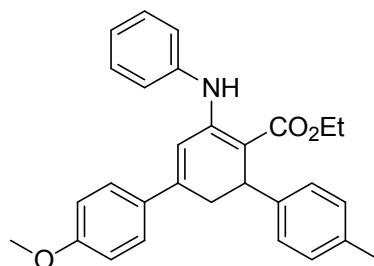
ethyl 4-methoxy-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**3b**):



yellow oil, **3b** (0.202 g, 95%); ¹H NMR (500 MHz, CDCl₃) δ 10.76 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 5H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.13 (dd, *J* = 11.6, 7.5 Hz, 4H), 6.84 - 6.79 (m, 2H), 6.60 (d, *J* = 2.8 Hz, 1H), 4.34 (d, *J* = 7.5 Hz, 1H), 4.20 - 4.04 (m, 2H), 3.79 (s, 3H), 3.19 (ddd, *J* = 16.6, 8.6, 2.8 Hz, 1H), 3.00 (dd, *J* = 16.6, 1.6 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.2, 160.1,

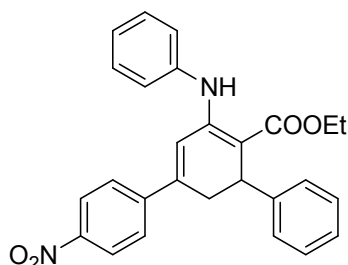
151.6, 145.3, 143.7, 140.1, 132.4, 129.2 (2C), 128.1 (2C), 127.3 (2C), 127.2 (2C), 126.0, 123.8, 123.3 (2C), 116.3, 114.1 (2C), 94.8, 59.3, 55.4, 36.9, 34.5, 14.4; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{27}NO_3$ $[M + H]^+$ 426.2069, found 426.2071.

Ethyl 4-methoxy-4''-methyl-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**3c**):



yellow solid, **3c** (0.204 g, 93%), mp 110-112 °C; 1H NMR (500 MHz, $CDCl_3$) δ 10.87 (s, 1H), 7.41 (t, $J = 7.9$ Hz, 2H), 7.35 (d, $J = 8.8$ Hz, 2H), 7.27 (d, $J = 7.2$ Hz, 2H), 7.22 (d, $J = 7.7$ Hz, 2H), 7.17 (t, $J = 7.4$ Hz, 1H), 7.09 (d, $J = 7.9$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 6.70 (d, $J = 2.7$ Hz, 1H), 4.41 (d, $J = 7.9$ Hz, 1H), 4.28 - 4.14 (m, 2H), 3.80 (s, 3H), 3.25 (ddd, $J = 16.5, 8.5, 2.8$ Hz, 1H), 3.07 (dd, $J = 16.6, 1.4$ Hz, 1H), 2.34 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 160.0, 151.3, 143.6, 142.1, 140.0, 135.2, 132.2, 129.0 (2C), 128.7 (2C), 127.1 (2C), 128.1 (2C), 123.6, 123.1 (2C), 116.1, 113.9 (2C), 95.0, 59.2, 55.1, 36.3, 34.4, 20.9, 14.4; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{29}NO_3$ $[M + H]^+$ 440.2226, found 440.2227.

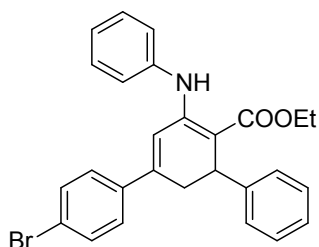
ethyl 4-nitro-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**3d**):



orange solid, **3d** (0.110 g, 50%), mp 109-111 °C; 1H NMR (500 MHz, $CDCl_3$) δ 10.71 (s, 1H), 8.14 - 8.10 (m, 2H), 7.41 - 7.34 (m, 4H), 7.27 - 7.21 (m, 4H), 7.18 - 7.13 (m,

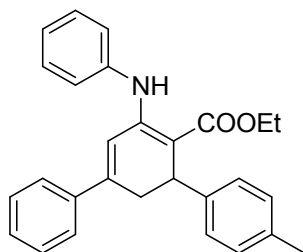
2H), 7.11 (d, $J = 7.6$ Hz, 2H), 6.75 (d, $J = 3.0$ Hz, 1H), 4.39 (dd, $J = 8.5, 1.2$ Hz, 1H), 4.20 - 4.06 (m, 2H), 3.28 (ddd, $J = 16.5, 8.6, 3.0$ Hz, 1H), 2.96 (dd, $J = 16.5, 1.6$ Hz, 1H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.9, 150.1, 147.3, 146.2, 144.2, 141.2, 139.6, 129.3 (2C), 128.2 (2C), 127.2 (2C), 126.5 (2C), 126.4, 124.1, 123.9 (2C), 123.1 (2C), 121.4, 96.5, 59.6, 36.7, 34.6, 14.3; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ 441.1814, found 441.1814.

ethyl 4-bromo-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate
(**3e**):



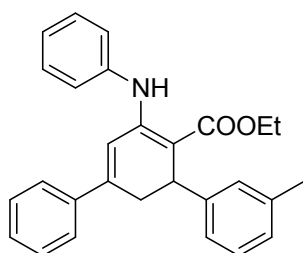
yellow solid, **3e** (0.142 g, 60%), mp 120-122 °C; ^1H NMR (500 MHz, CDCl_3) δ 10.75 (s, 1H), 7.42 – 7.34 (m, 4H), 7.28 – 7.21 (m, 4H), 7.17 – 7.12 (m, 6H), 6.65 (d, $J = 2.9$ Hz, 1H), 4.36 (d, $J = 7.4$ Hz, 1H), 4.20 - 4.08 (m, 2H), 3.23 (ddd, $J = 16.6, 8.6, 2.9$ Hz, 1H), 2.94 (dd, $J = 16.6, 1.6$ Hz, 1H), 1.19 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.1, 150.8, 144.7, 142.6, 139.8, 138.7, 131.7 (2C), 129.2 (2C), 128.1 (2C), 127.3 (2C), 127.2 (2C), 126.1, 123.9, 123.1 (2C), 122.5, 118.5, 95.5, 59.4, 36.7, 34.4, 14.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{27}\text{H}_{24}\text{BrNO}_2$ $[\text{M} + \text{H}]^+$ 474.1069, found 474.1040.

ethyl 4''-methyl-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate
(**3f**):



yellow solid, **3f** (0.159 g, 78%), mp 116-118 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.76 (s, 1H), 7.38 - 7.27 (m, 7H), 7.20 - 7.13 (m, 5H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 2.9 Hz, 1H), 4.35 (t, *J* = 7.0 Hz, 1H), 4.23 - 4.07 (m, 2H), 3.23 (ddd, *J* = 16.6, 8.6, 2.9 Hz, 1H), 3.01 (dd, *J* = 16.7, 1.6 Hz, 1H), 2.29 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.2, 151.0, 144.0, 141.9, 139.9, 139.9, 135.4, 129.1 (2C), 128.8 (2C), 128.5 (2C), 128.4, 127.1 (2C), 125.8 (2C), 123.7, 123.1 (2C), 118.0, 95.5, 59.4, 36.3, 34.5, 21.0, 14.4; HRMS (ESI-TOF) *m/z* calcd for C₂₈H₂₇NO₂ [M + H]⁺ 410.2120, found 410.2119.

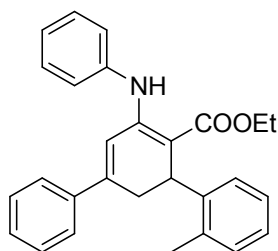
ethyl 3''-methyl-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**3g**):



yellow solid, **3g** (0.176 g, 86%), mp 108-110 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.77 (s, 1H), 7.39 - 7.27 (m, 7H), 7.17 - 7.09 (m, 6H), 6.98 - 6.96 (m, 1H), 6.68 (d, *J* = 2.9 Hz, 1H), 4.34 (dd, *J* = 8.6, 1.4 Hz, 1H), 4.23 - 4.07 (m, 2H), 3.25 (ddd, *J* = 16.7, 8.7, 2.9 Hz, 1H), 3.02 (dd, *J* = 16.7, 1.6 Hz, 1H), 2.30 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.2, 151.1, 145.0, 144.0, 139.9, 139.9, 137.4, 129.1 (2C), 128.5 (2C), 128.4, 128.1, 127.9, 126.8, 125.8 (2C), 124.3, 123.7, 123.1 (2C),

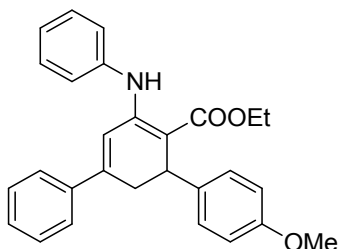
118.0, 95.3, 59.3, 36.7, 34.5, 21.6, 14.4; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{27}NO_2$ $[M + H]^+$ 410.2120, found 410.2122.

ethyl 2''-methyl-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate
(**3h**):



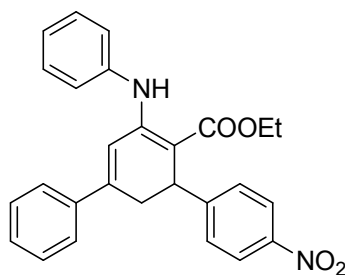
yellow solid, **3h** (0.166 g, 81%), mp 115-117 °C; 1H NMR (500 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.37 (t, $J = 7.9$ Hz, 2H), 7.28 - 7.25 (m, 5H), 7.19 - 7.13 (m, 5H), 7.06 - 7.01 (m, 2H), 6.71 (d, $J = 2.9$ Hz, 1H), 4.61 (dd, $J = 9.4, 1.2$ Hz, 1H), 4.16 - 3.96 (m, 2H), 3.25 (ddd, $J = 16.5, 9.5, 2.9$ Hz, 1H), 2.78 (dd, $J = 16.6, 1.4$ Hz, 1H), 2.53 (s, 3H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 151.3, 143.6, 142.6, 140.1, 139.9, 134.6, 130.1, 129.1 (2C), 128.5 (2C), 128.4, 127.0, 125.9, 125.8 (2C), 128.7, 123.6, 123.0 (2C), 118.2, 95.6, 59.3, 33.0, 32.4, 19.5, 14.2; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{27}NO_2$ $[M + H]^+$ 410.2120, found 410.2123.

ethyl 4''-methoxy-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate
(**3i**):



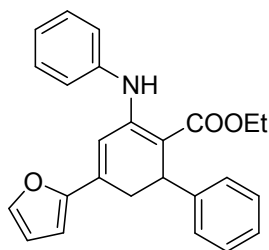
yellow solid, **3i** (0.155 g, 73%), mp 104-106 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.75 (s, 1H), 7.38 – 7.35 (m, 2H), 7.32 - 7.27 (m, 5H), 7.23 – 7.21 (m, 2H), 7.16 – 7.14 (m 3H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 2.9 Hz, 1H), 4.33 (d, *J* = 7.4 Hz, 1H), 4.22 - 4.08 (m, 2H), 3.76 (s, 3H), 3.22 (ddd, *J* = 16.6, 8.5, 2.9 Hz, 1H), 2.99 (dd, *J* = 16.6, 1.6 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.2, 157.9, 150.9, 144.0, 139.9, 137.1, 129.1 (2C), 128.7 (2C), 128.5, 128.4, 128.2 (2C), 125.8 (2C), 123.7, 123.1 (2C), 118.0, 113.4 (2C), 95.6, 59.3, 55.1, 35.9, 34.7, 14.4; HRMS (ESI-TOF) *m/z* calcd for C₂₈H₂₇NO₃ [M + H]⁺ 426.2069, found 426.2070.

ethyl 4''-nitro-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**3j**):



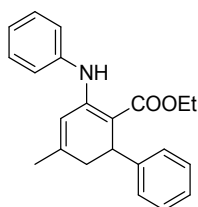
yellow oil, **3j** (0.158 g, 72%); ¹H NMR (500 MHz, CDCl₃) δ 10.79 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.44 - 7.40 (m, 2H), 7.38 - 7.33 (m, 2H), 7.28 - 7.23 (m, 5H), 7.16 - 7.12 (m, 3H), 6.66 (d, *J* = 2.9 Hz, 1H), 4.46 - 4.39 (m, 1H), 4.17 - 4.02 (m, 2H), 3.28 (ddd, *J* = 16.7, 8.8, 2.9 Hz, 1H), 2.95 (dd, *J* = 16.8, 1.6 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.7, 153.2, 151.7, 146.6, 143.8, 139.4, 139.3, 129.2 (2C), 128.9, 128.7 (2C), 128.1 (2C), 125.7 (2C), 124.3, 123.5 (2C), 123.5 (2C), 117.9, 93.3, 59.5, 37.1, 34.1, 14.4; HRMS (ESI-TOF) *m/z* calcd for C₂₇H₂₄N₂O₄ [M + H]⁺ 441.1814, found 441.1819.

ethyl 5-(furan-2-yl)-3-(phenylamino)-1,6-dihydro-[1,1'-biphenyl]-2-carboxylate (**3k**):



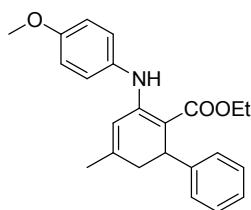
yellow solid, **3k** (0.146 g, 76%), mp 147-149 °C; ^1H NMR (500 MHz, CDCl_3) δ 10.77 (s, 1H), 7.38 - 7.34 (m, 3H), 7.26 - 7.20 (m, 4H), 7.15 - 7.122 (m, 4H), 6.80 (d, J = 2.8 Hz, 1H), 6.42 (d, J = 3.4 Hz, 1H), 6.37 (dd, J = 3.4, 1.8 Hz, 1H), 4.32 (d, J = 7.4 Hz, 1H), 4.18 - 4.04 (m, 2H), 3.10 (ddd, J = 16.5, 8.6, 2.8 Hz, 1H), 2.85 (dd, J = 16.5, 1.6 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 153.3, 151.2, 145.0, 143.6, 139.9, 132.4, 129.1 (2C), 128.1 (2C), 127.3 (2C), 126.0, 123.8, 123.3 (2C), 114.2, 111.8, 109.8, 94.9, 59.3, 36.3, 31.9, 14.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 386.1756, found 386.1757.

ethyl 5-methyl-3-(phenylamino)-1,6-dihydro-[1,1'-biphenyl]-2-carboxylate (**3l**):



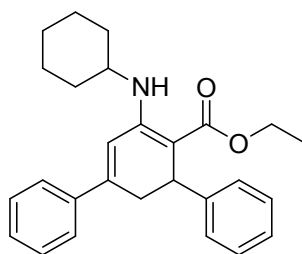
yellow solid, **3l** (0.080 g, 48%), mp 102-104 °C; ^1H NMR (500 MHz, CDCl_3) δ 10.75 (s, 1H), 7.46 - 7.30 (m, 3H), 7.27 - 7.23 (m, 3H), 7.22 - 7.05 (m, 4H), 6.11 (dd, J = 2.6, 1.4 Hz, 1H), 4.18 (d, J = 7.8 Hz, 1H), 4.15 - 4.03 (m, 2H), 3.08 - 2.77 (m, 1H), 2.33 (dd, J = 17.0, 1.3 Hz, 1H), 1.77 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.3, 151.8, 145.9, 145.4, 139.8, 129.0 (2C), 128.0 (2C), 127.2 (2C), 125.9, 123.8, 123.6 (2C), 117.0, 93.2, 59.1, 37.2, 36.7, 24.4, 14.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 334.1807, found 334.1813.

ethyl 3-((4-methoxyphenyl)amino)-5-methyl-1,6-dihydro-[1,1'-biphenyl]-2-carboxylate (**3m**):



yellow oil, **3m** (0.080 g, 44%); ^1H NMR (500 MHz, CDCl_3) δ 10.61 (s, 1H), 7.27 - 7.20 (m, 4H), 7.19 - 7.13 (m, 1H), 7.09 - 7.00 (m, 2H), 6.93 - 6.85 (m, 2H), 5.98 (dd, $J = 2.6, 1.4$ Hz, 1H), 4.16 (d, $J = 7.9$ Hz, 1H), 4.12 - 4.02 (m, 2H), 3.83 (s, 3H), 2.93 - 2.82 (m, 1H), 2.31 (dd, $J = 17.0, 1.3$ Hz, 1H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.4, 156.8, 152.8, 146.3, 145.7, 132.6, 127.9 (2C), 127.2 (2C), 126.0 (2C), 125.8, 116.8, 114.2 (2C), 91.5, 59.0, 55.5, 37.4, 36.8, 24.4, 14.4; HRMS (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 364.1913, found 364.1913.

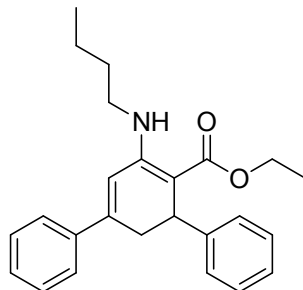
ethyl 5'-(cyclohexylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**3n**):



yellow oil, **3n** (0.146 g, 73%); ^1H NMR (500 MHz, CDCl_3) δ 9.17 (d, $J = 8.0$ Hz, 1H), 7.39 - 7.28 (m, 7H), 7.24 - 7.13 (m, 3H), 6.66 (d, $J = 2.8$ Hz, 1H), 4.31 (d, $J = 7.4$ Hz, 1H), 4.18 - 4.01 (m, 2H), 3.67 - 3.57 (m, 1H), 3.19 (ddd, $J = 16.8, 8.5, 2.9$ Hz, 1H), 2.95 (dd, $J = 16.8, 1.6$ Hz, 1H), 2.11 - 1.63 (m, 5H), 1.53 - 1.30 (m, 5H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.3, 154.2, 146.0, 145.9, 140.5, 128.5 (2C), 128.4, 127.8 (2C), 127.2 (2C), 125.8 (2C), 125.7, 116.5, 89.4, 58.6, 51.0, 36.7,

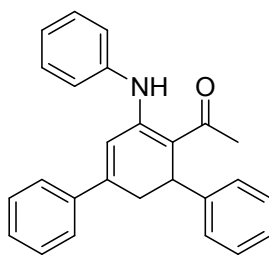
35.2, 34.6, 34.2, 25.5, 24.7, 24.6, 14.5; HRMS (ESI-TOF) m/z calcd for $C_{27}H_{31}NO_2$ $[M + H]^+$ 402.2433, found 402.2433.

ethyl 5'-(butylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**3o**):



yellow oil, **3o** (0.090 g, 48%); 1H NMR (500 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.45 – 7.30 (m, 6H), 7.27 – 7.10 (m, 4H), 6.64 (d, J = 2.9 Hz, 1H), 4.28 (d, J = 7.8 Hz, 1H), 4.14 – 4.03 (m, 2H), 3.48 - 3.33 (m, 2H), 3.17 (ddd, J = 16.8, 8.4, 2.9 Hz, 1H), 2.95 (dd, J = 16.8, 1.5 Hz, 1H), 1.71 – 1.63 (m, 2H), 1.54 - 1.45 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 155.1, 146.3, 145.9, 140.4, 128.5 (2C), 128.5, 127.9 (2C), 127.2 (2C), 125.8 (2C), 125.7, 116.3, 89.4, 58.7, 42.7, 36.8, 35.2, 32.8, 20.2, 14.5, 13.9; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{29}NO_2$ $[M + H]^+$ 376.2277, found 376.2278.

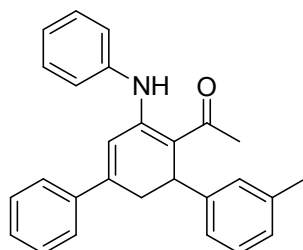
1-(5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-yl)ethanone (**3p**):



yellow solid, **3p** (0.102 g, 56%), mp 94-96 °C; 1H NMR (500 MHz, $CDCl_3$) δ 13.20 (s, 1H), 7.42 - 7.38 (m, 2H), 7.29 - 7.17 (m, 13H), 6.71 (d, J = 2.9 Hz, 1H), 4.26 (dd, J = 7.9, 1.3 Hz, 1H), 3.31 (ddd, J = 16.4, 8.1, 2.9 Hz, 1H), 3.07 (dd, J = 16.4, 1.7 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 153.0, 145.4, 143.8, 139.6,

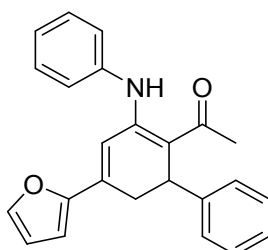
139.0, 129.1 (2C), 128.7, 128.5 (2C), 128.3 (2C), 127.5 (2C), 126.4, 125.8 (2C), 124.8, 124.2 (2C), 117.6, 103.0, 39.1, 35.7, 27.7; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{23}NO$ $[M + H]^+$ 366.1858, found 366.1862.

1-(3''-methyl-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-yl)ethanone (**3q**):



yellow oil, **3q** (0.114 g, 60%); 1H NMR (500 MHz, $CDCl_3$) δ 13.19 (s, 1H), 7.42 - 7.38 (m, 2H), 7.28 - 7.07 (m, 12H), 6.71 (d, $J = 2.8$ Hz, 1H), 4.22 (d, $J = 7.2$ Hz, 1H), 3.29 (ddd, $J = 16.4, 8.2, 2.8$ Hz, 1H), 3.06 (dd, $J = 16.4, 1.6$ Hz, 1H), 2.31 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 153.0, 145.4, 143.8, 139.6, 139.06, 137.8, 129.1 (2C), 128.6, 128.5 (2C), 128.2 (2C), 127.2, 125.8 (2C), 124.7, 124.6, 124.2 (2C), 117.6, 103.0, 39.0, 35.7, 27.7, 21.5; HRMS (ESI-TOF) m/z calcd for $C_{27}H_{25}NO$ $[M + H]^+$ 380.2014, found 380.2012.

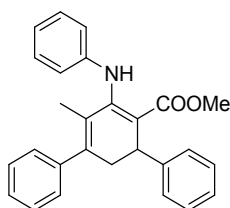
1-(5-(furan-2-yl)-3-(phenylamino)-1,6-dihydro-[1,1'-biphenyl]-2-yl)ethanone (**3r**):



yellow oil, **3r** (0.115 g, 65%); 1H NMR (500 MHz, $CDCl_3$) δ 13.25 (s, 1H), 7.42 - 7.38 (m, 2H), 7.33 (d, $J = 1.6$ Hz, 1H), 7.27 - 7.15 (m, 8H), 6.84 (d, $J = 2.7$ Hz, 1H), 6.42 (d, $J = 3.4$ Hz, 1H), 6.35 (dd, $J = 3.4, 1.8$ Hz, 1H), 4.22 (dd, $J = 8.0, 1.4$ Hz, 1H), 3.16 (ddd, $J = 16.3, 8.0, 2.7$ Hz, 1H), 2.90 (dd, $J = 16.3, 1.6$ Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 153.2, 153.0, 143.9, 143.8, 139.0, 133.5, 129.1

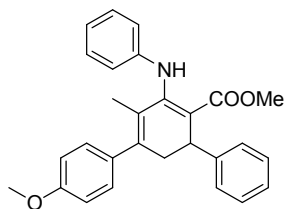
(2C), 128.4 (2C), 127.5 (2C), 126.4, 124.8, 124.3 (2C), 113.6, 111.9, 110.5, 102.8, 38.6, 33.1, 27.6; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{21}NO_2$ $[M + H]^+$ 356.1651, found 356.1651.

ethyl 6'-methyl-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**5a**):



yellow oil, **5a** (0.160 g, 81%); 1H NMR (500 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.39-7.30 (m, 7H), 7.24-7.20 (m, 3H), 7.15 - 7.09 (m, 3H), 6.75 (dd, $J = 8.1, 1.4$ Hz, 2H), 4.33 (dd, $J = 7.1, 1.4$ Hz, 1H), 3.70 (s, 3H), 3.20 (ddd, $J = 16.3, 7.2, 2.7$ Hz, 1H), 2.80 (dd, $J = 16.3, 1.6$ Hz, 1H), 1.62 (d, $J = 2.4$ Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 155.8, 143.0, 142.7, 141.6, 141.6, 129.1 (2C), 128.1 (2C), 127.9 (3C), 127.5 (2C), 127.1, 127.0, 126.2, 122.8, 120.9 (2C), 118.7, 102.4, 51.2, 39.4, 36.8, 16.8; HRMS (ESI-TOF) m/z calcd for $C_{27}H_{25}NO_2$ $[M + H]^+$ 396.1964, found 396.1964.

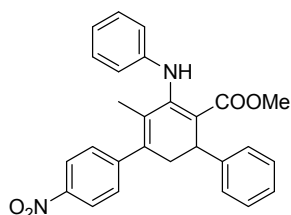
ethyl 4-methoxy-6'-methyl-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl] -4'-carboxylate (**5b**):



yellow oil, **5b** (0.181 g, 85%); 1H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.37 - 7.29 (m, 6H), 7.27 - 7.24 (m, 1H), 7.13 - 7.06 (m, 3H), 6.78 - 6.69 (m, 4H), 4.30 (d, $J = 5.8$ Hz, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.19 - 3.11 (m, 1H), 2.78 (dd, $J = 16.3, 1.5$

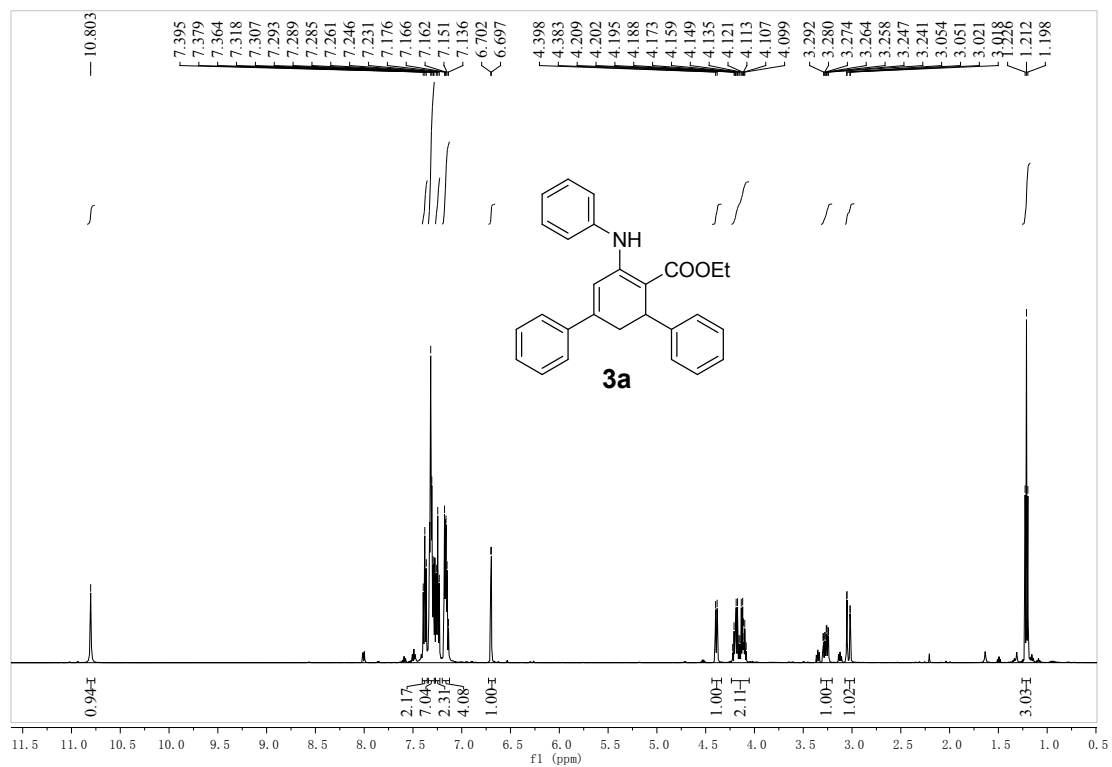
Hz, 1H), 1.62 (d, $J = 2.4$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.3, 158.7, 156.1, 143.1, 142.9, 141.4, 133.8, 129.4 (2C), 129.1 (2C), 128.1 (2C), 127.5 (2C), 126.4, 126.2, 122.8, 121.0 (2C), 113.4 (2C), 102.1, 55.2, 51.2, 39.5, 36.8, 17.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 426.2069, found 426.2095.

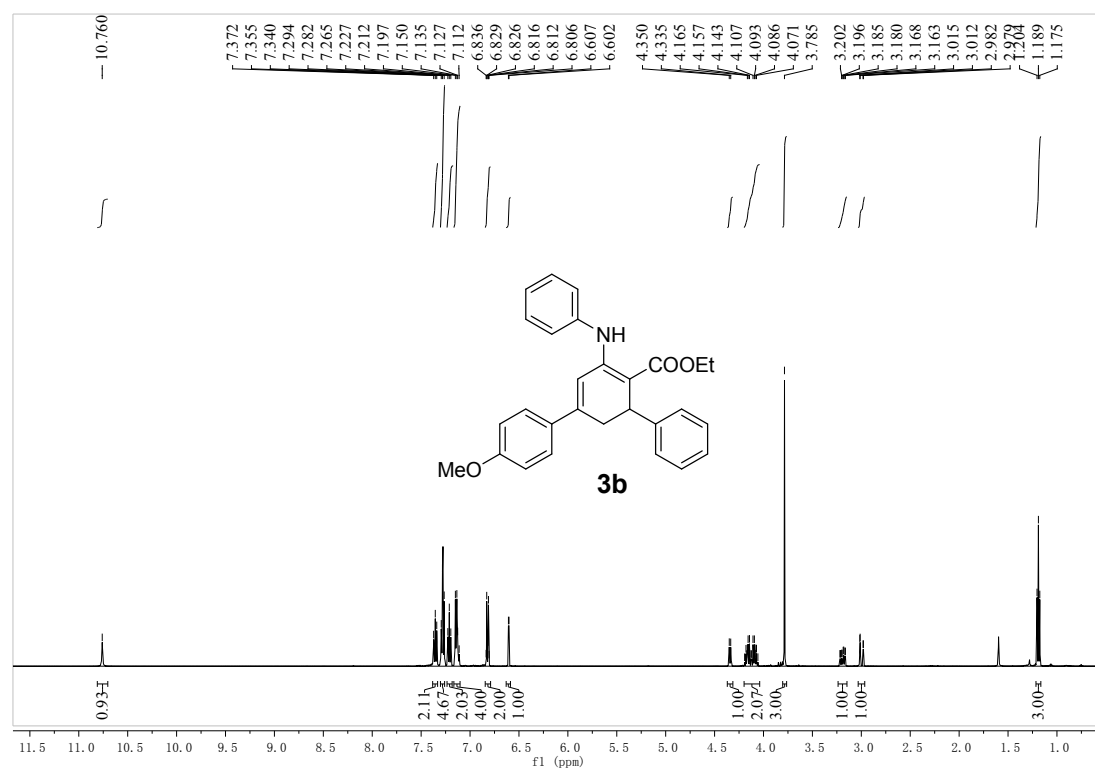
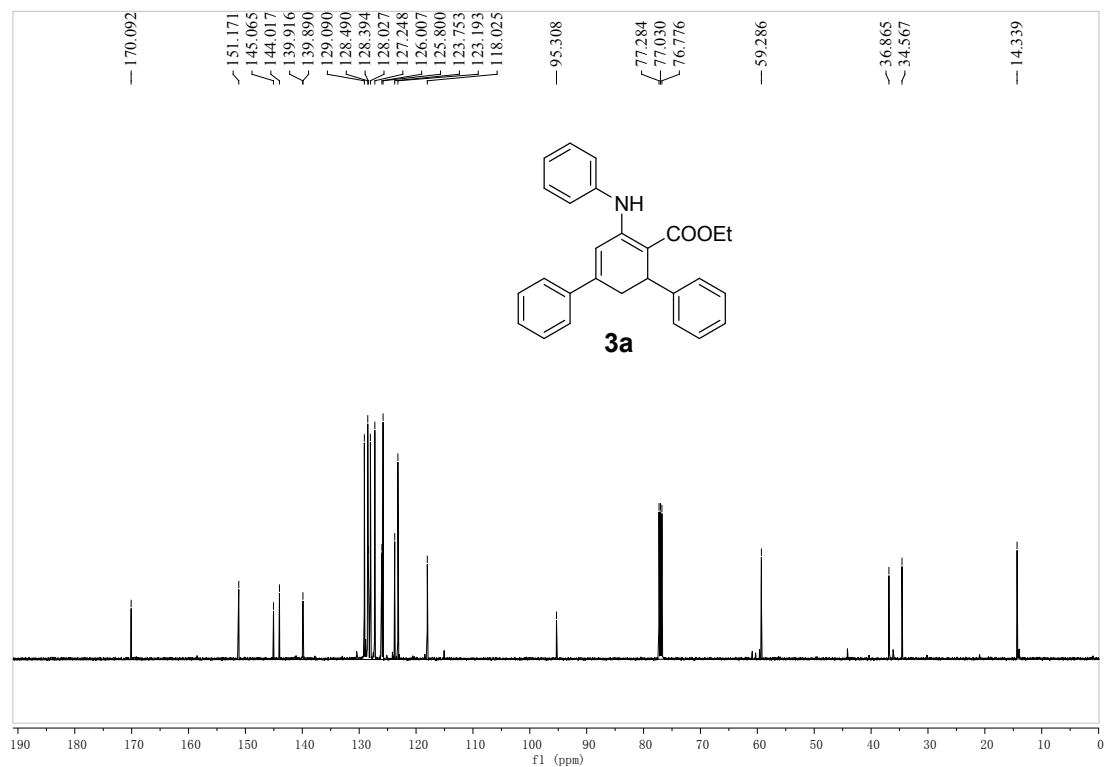
ethyl 6'-methyl-4-nitro-5'-(phenylamino)-2',3'-dihydro-[1,1':3',1''-terphenyl]-4'-carboxylate (**5c**):

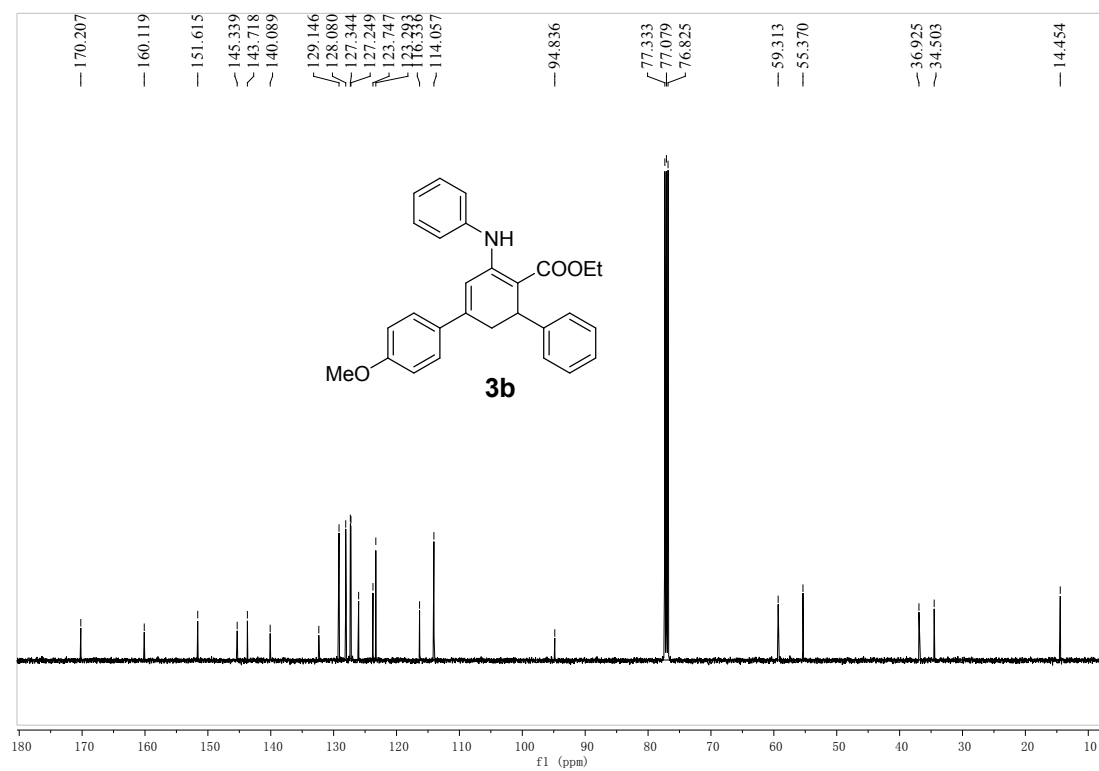


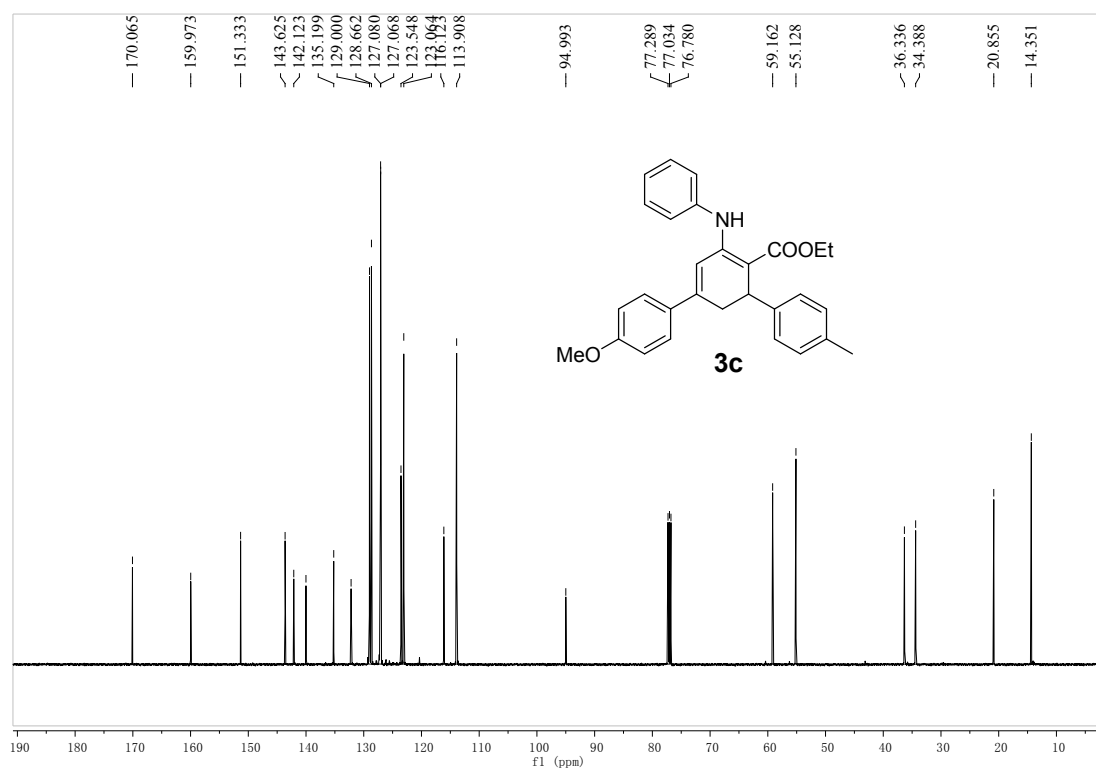
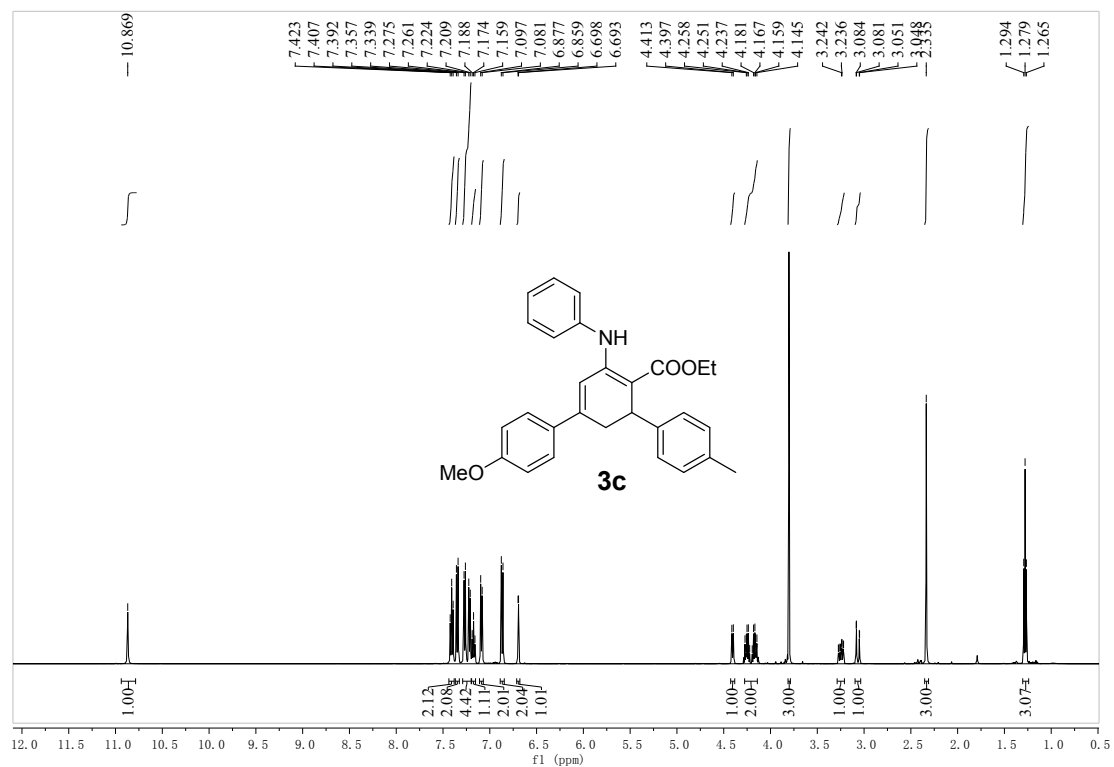
yellow solid, **5c** (0.161 g, 73%), mp 128-130 °C; ^1H NMR (500 MHz, CDCl_3) δ 10.35 (s, 1H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.27 - 7.21 (m, 4H), 7.18 - 7.13 (m, 3H), 7.02 - 6.94 (m, 3H), 6.67 (d, $J = 8.8$ Hz, 2H), 4.22 (d, $J = 5.6$ Hz, 1H), 3.58 (s, 3H), 3.17 - 3.02 (m, 1H), 2.59 (dd, $J = 16.1, 1.6$ Hz, 1H), 1.45 (d, $J = 2.4$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.1, 155.0, 148.5, 146.7, 142.8, 142.1, 139.0, 129.4, 129.3 (2C), 128.8 (2C), 128.4 (2C), 127.5 (2C), 126.6, 123.4 (2C), 123.2, 121.0 (2C), 103.1, 51.4, 39.2, 36.8, 16.9; HRMS (ESI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ 441.1814, found 441.1807.

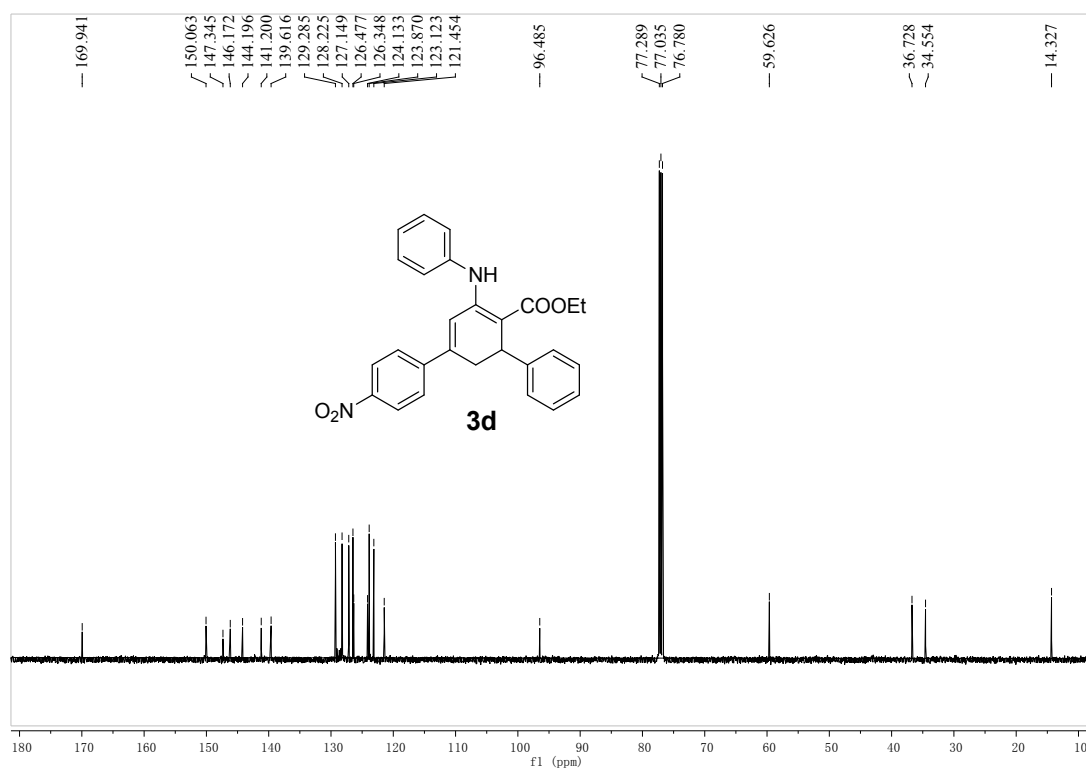
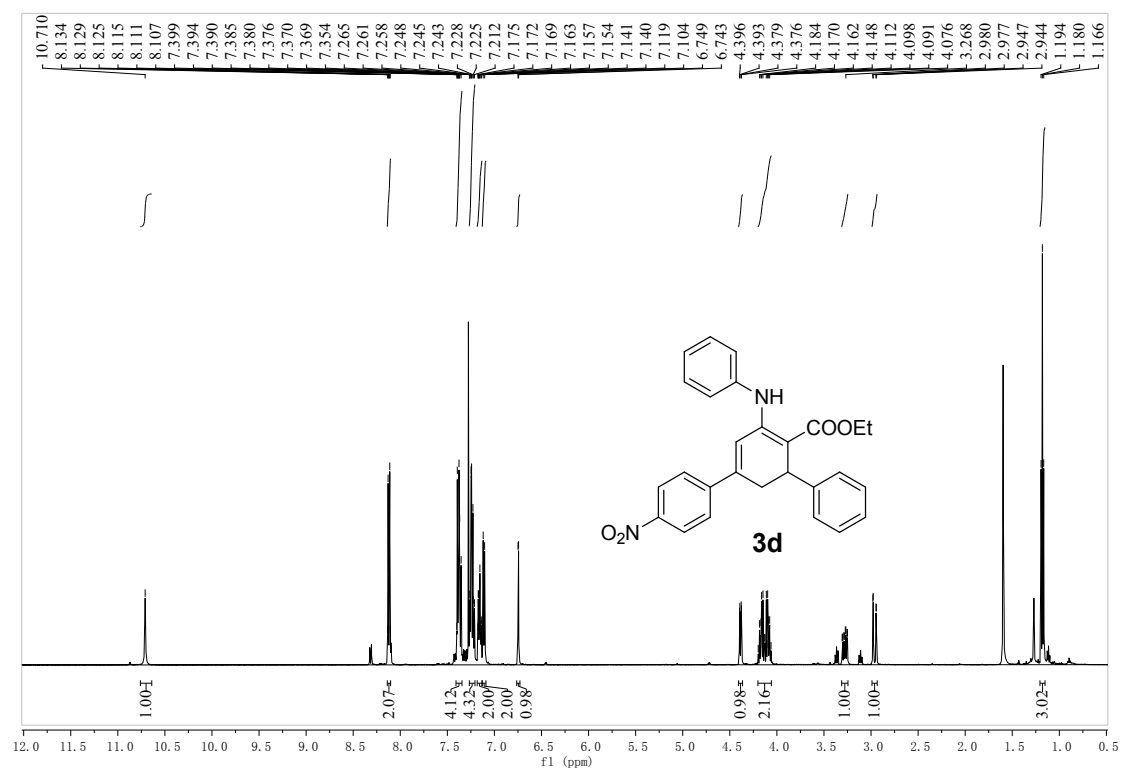
5 Copies of Product NMR Spectra

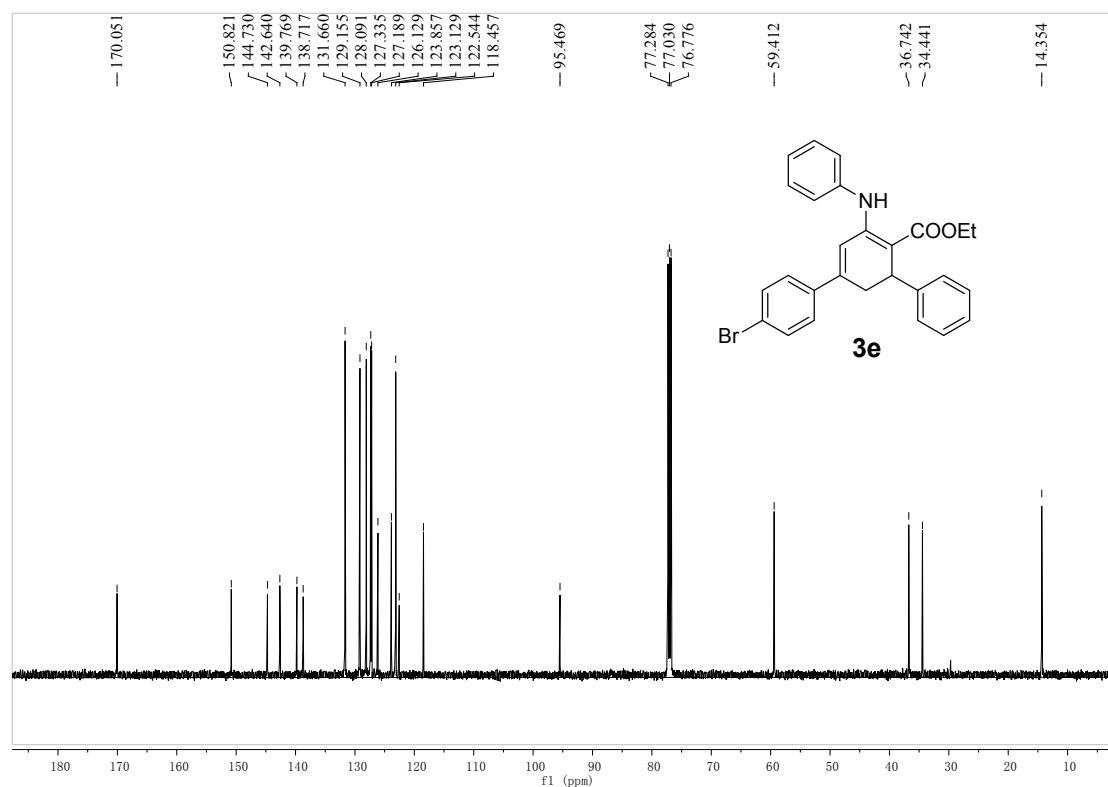
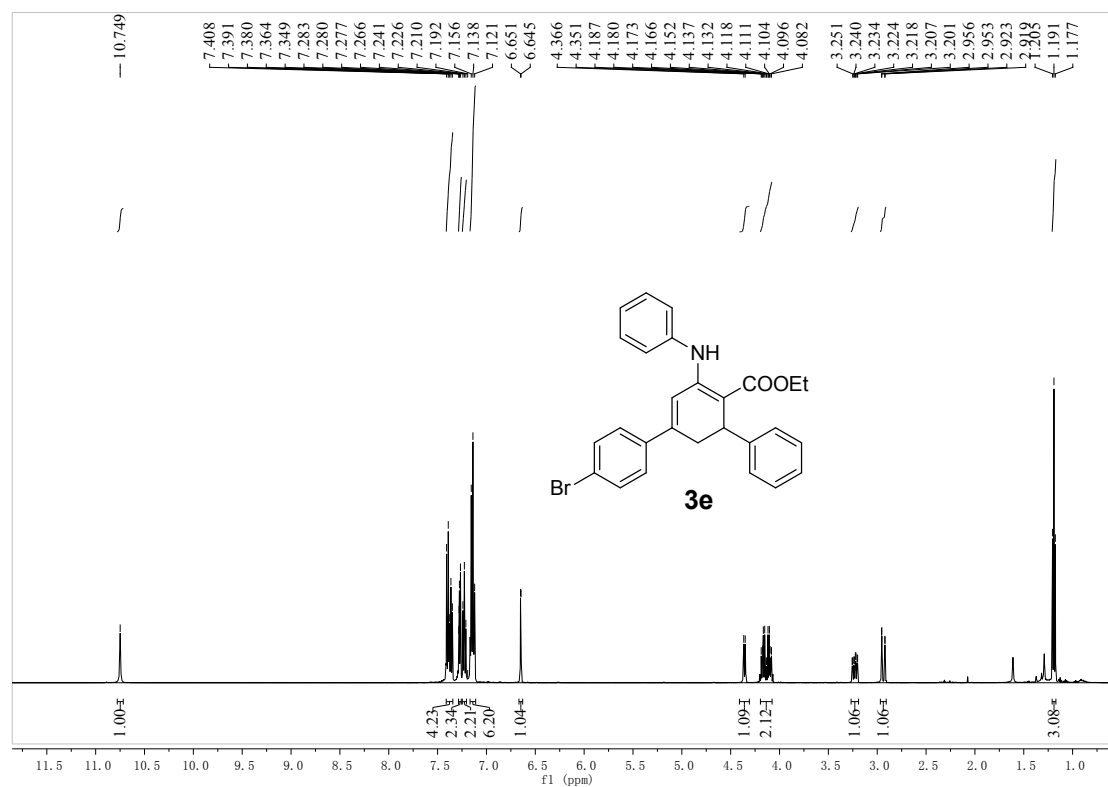


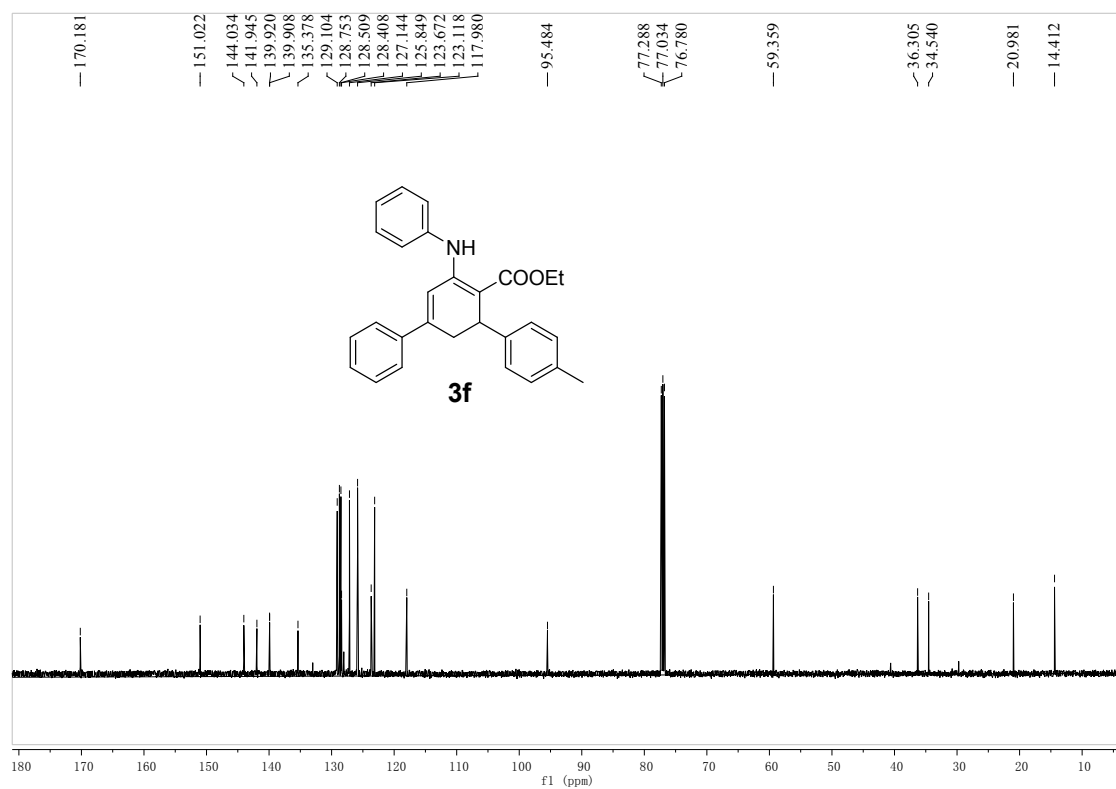
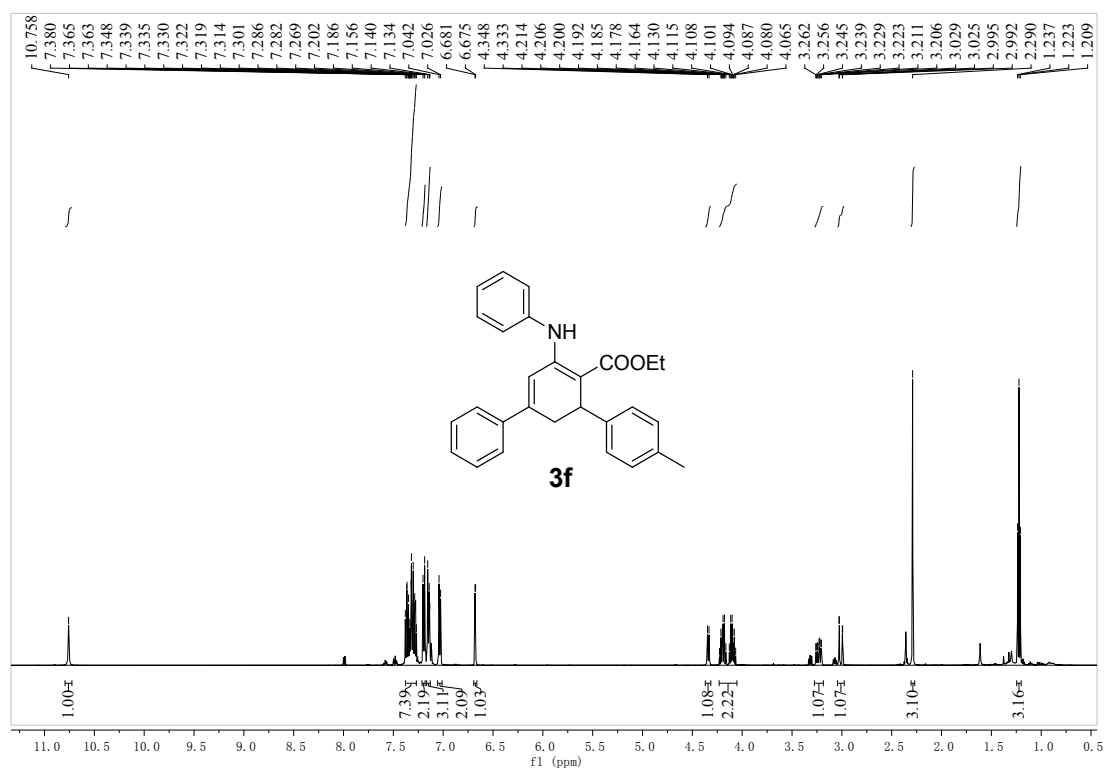


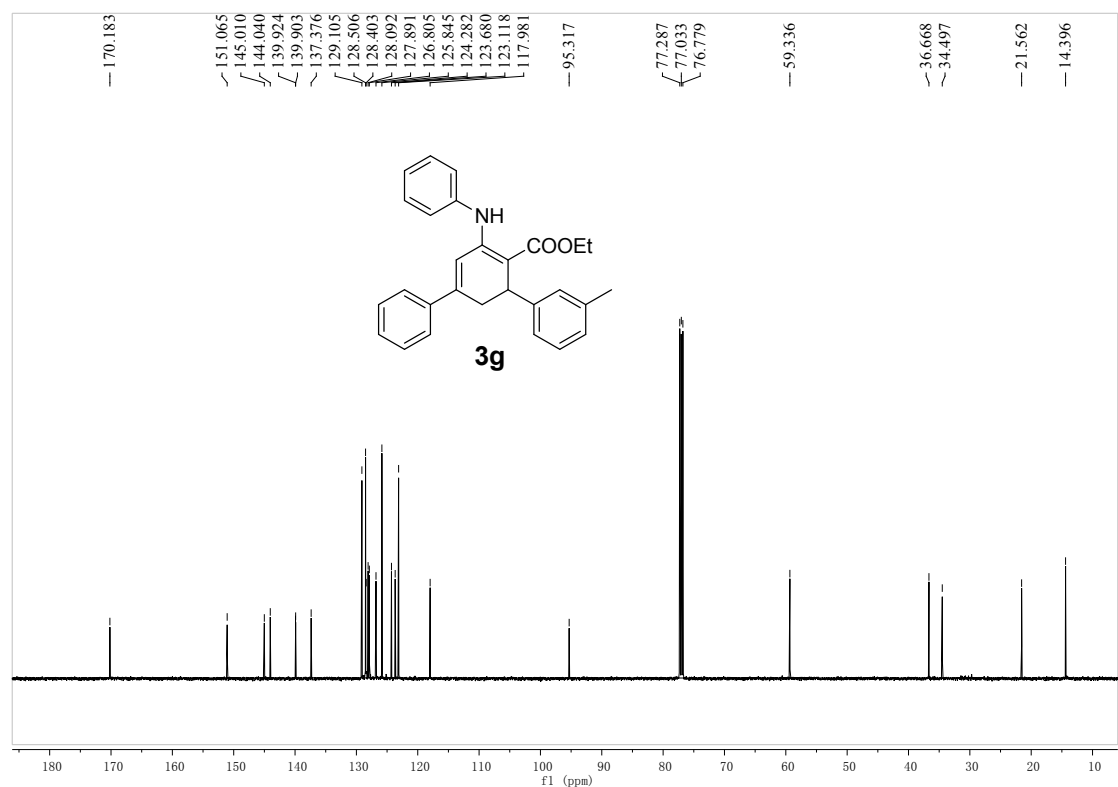
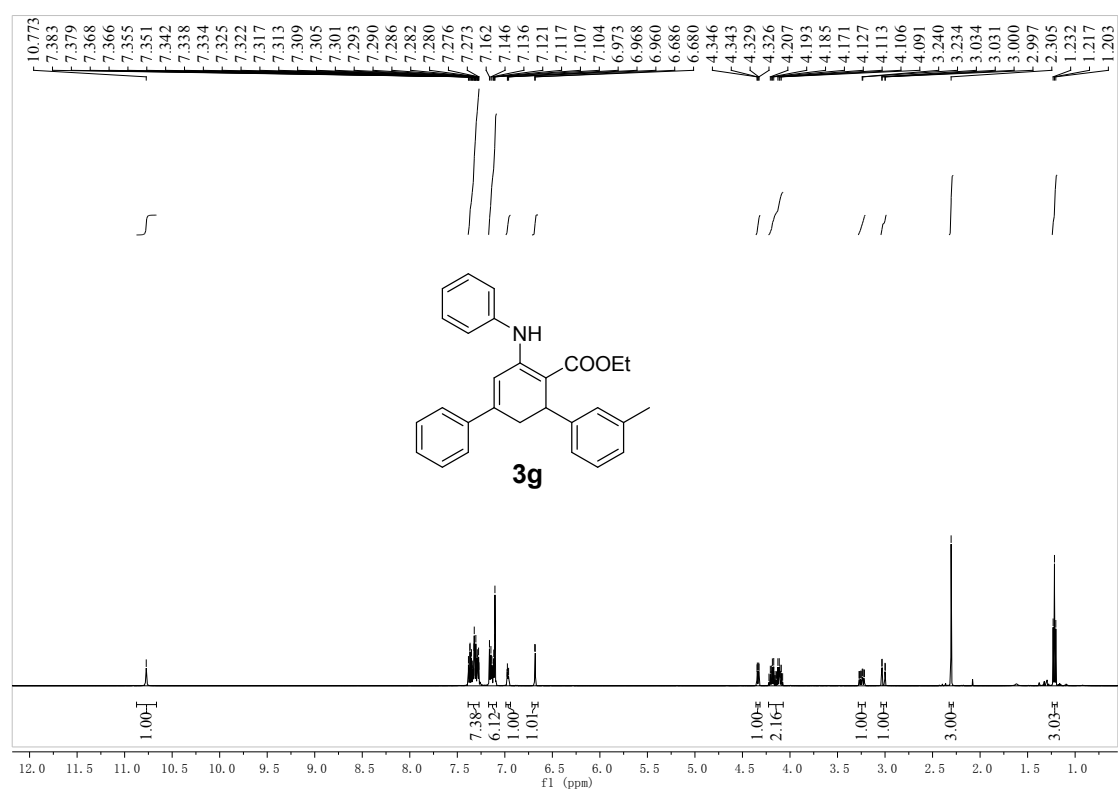


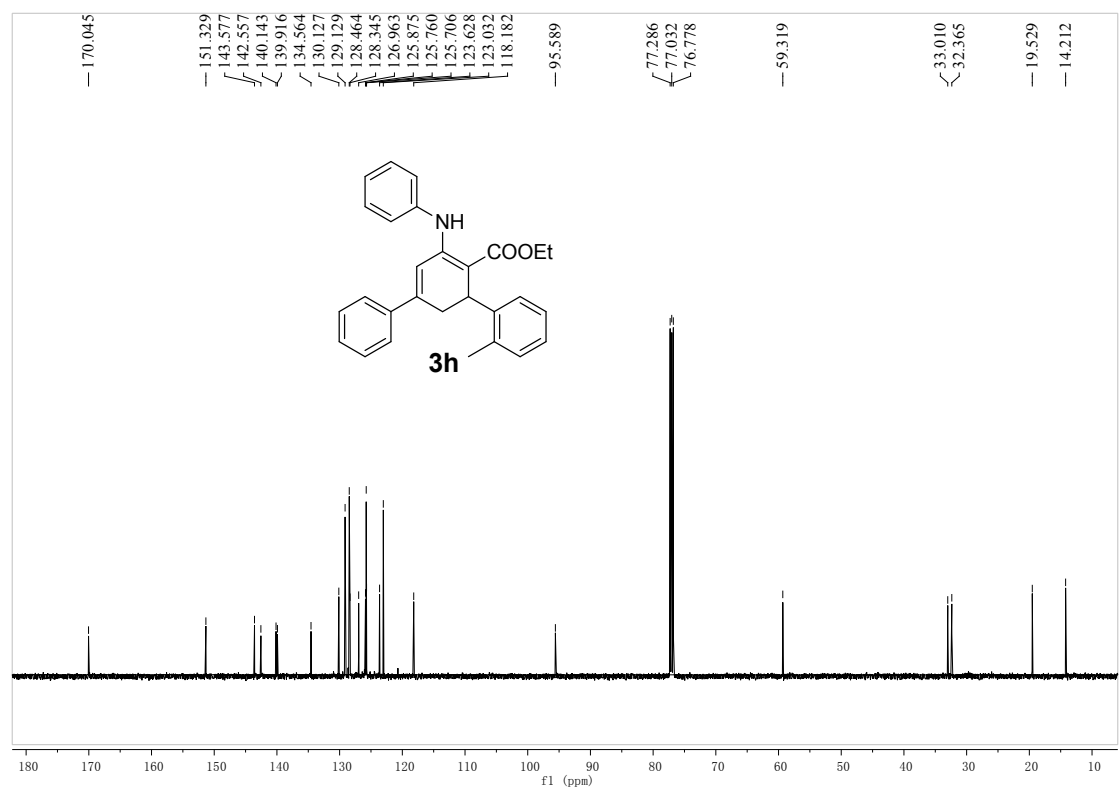
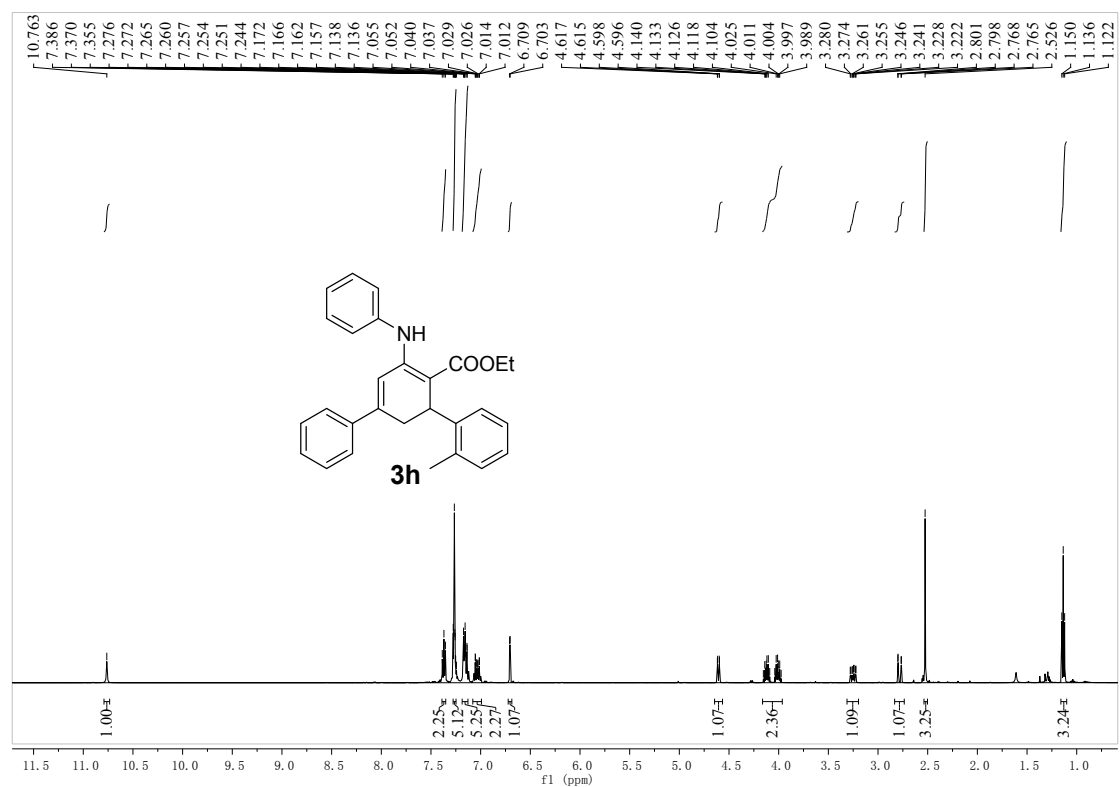


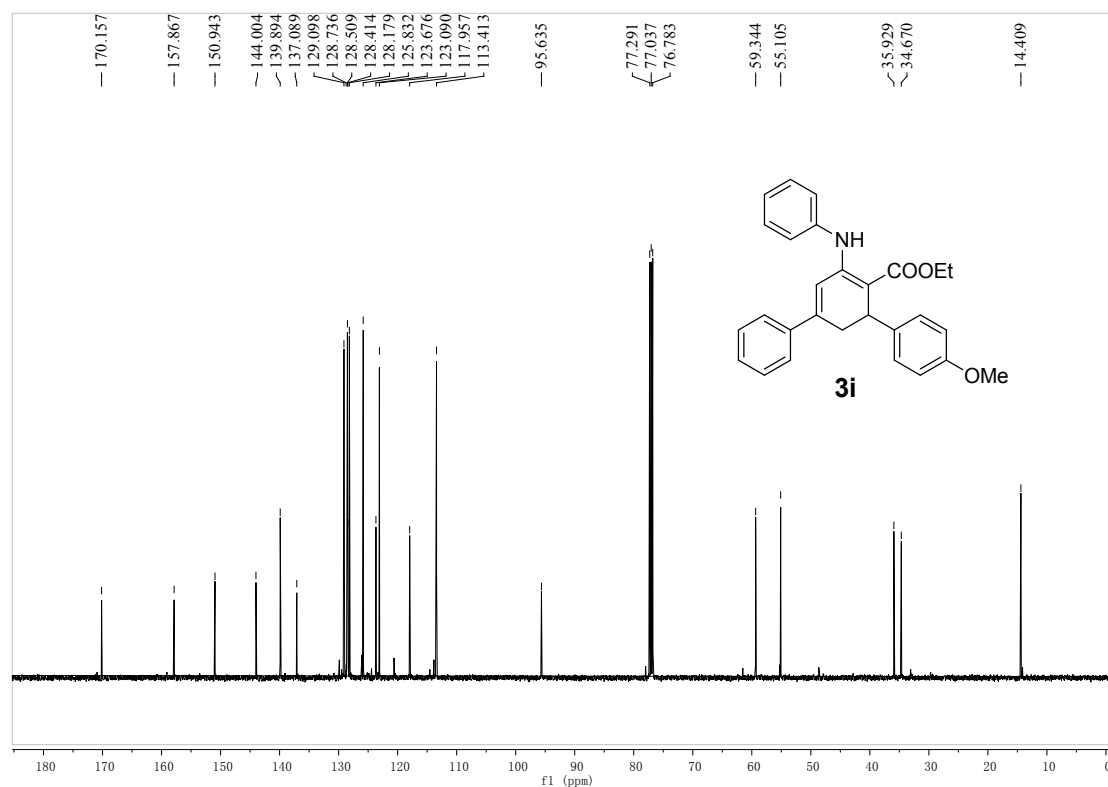
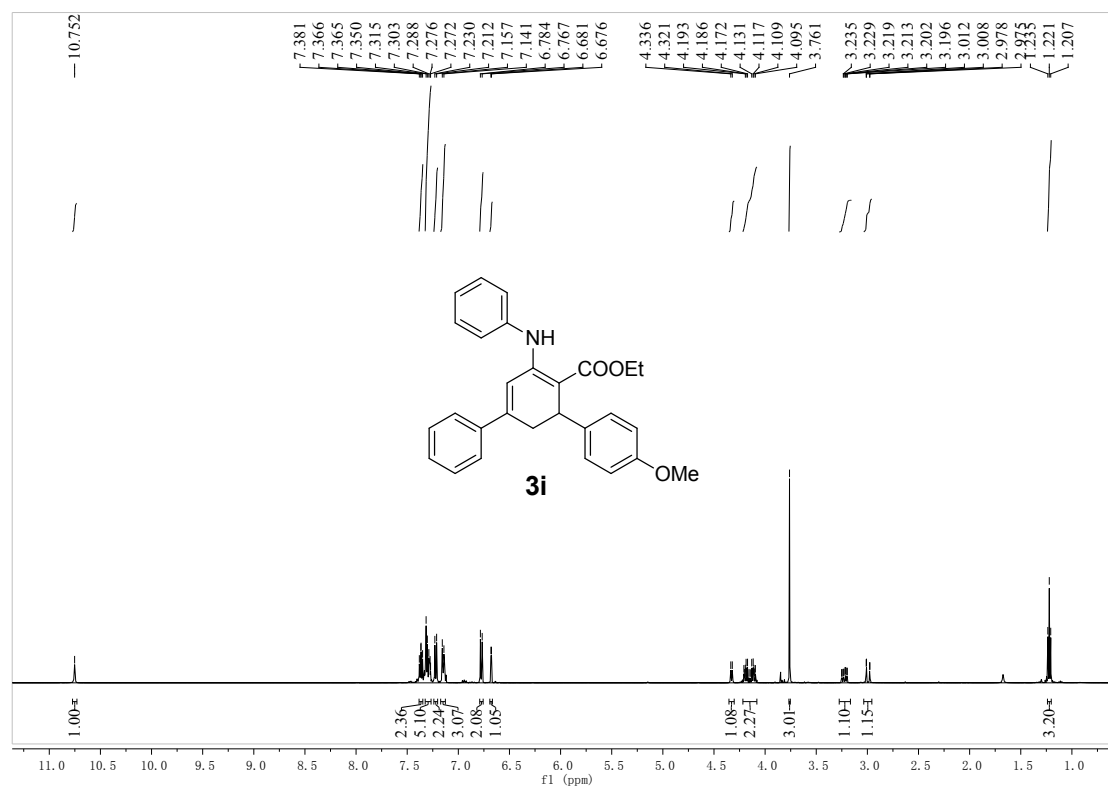


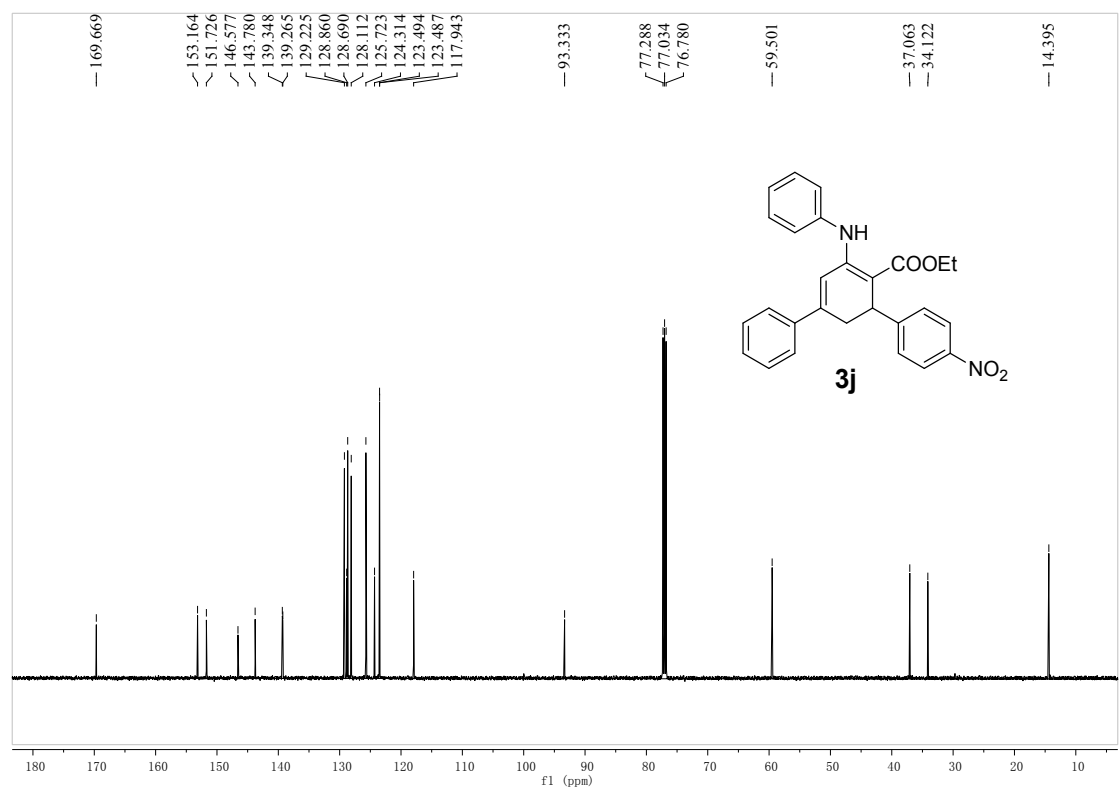
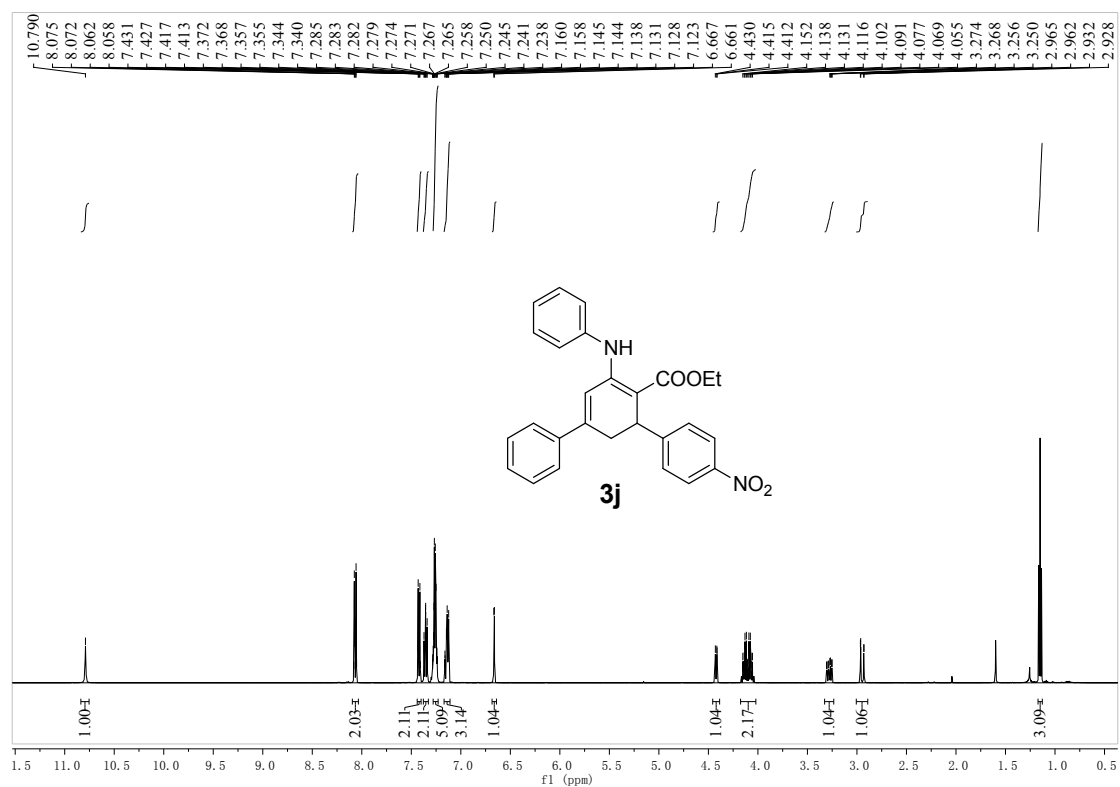


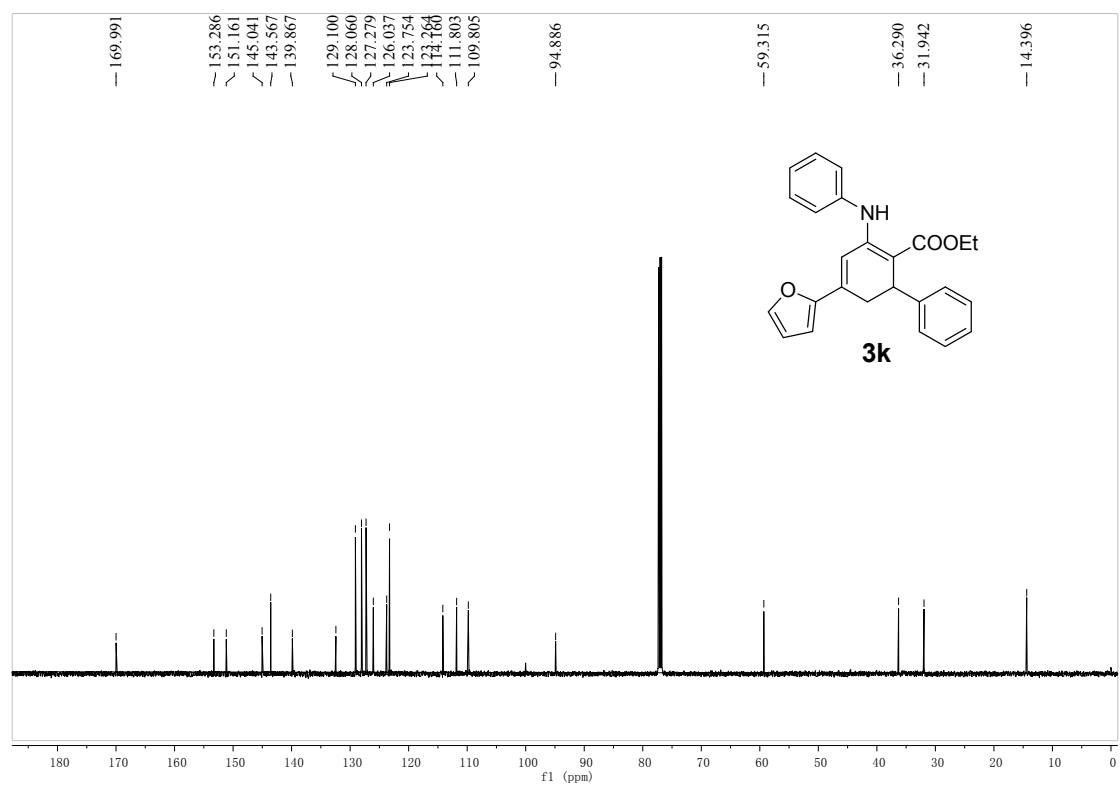
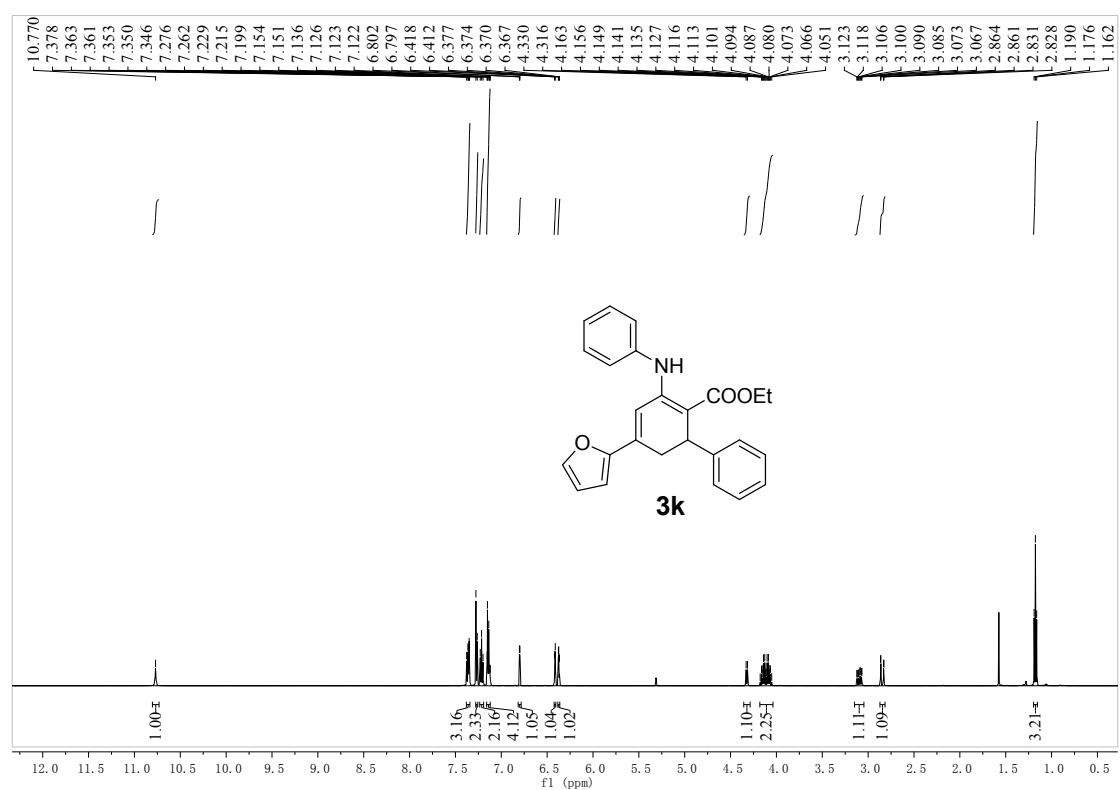


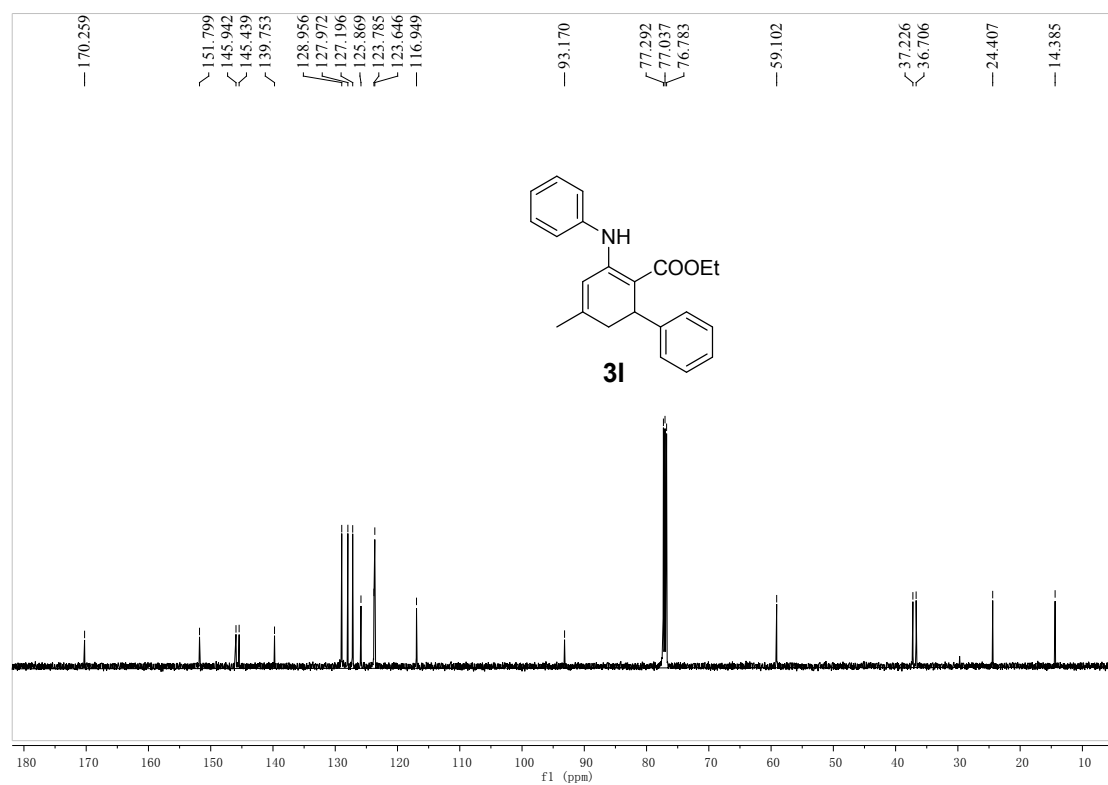
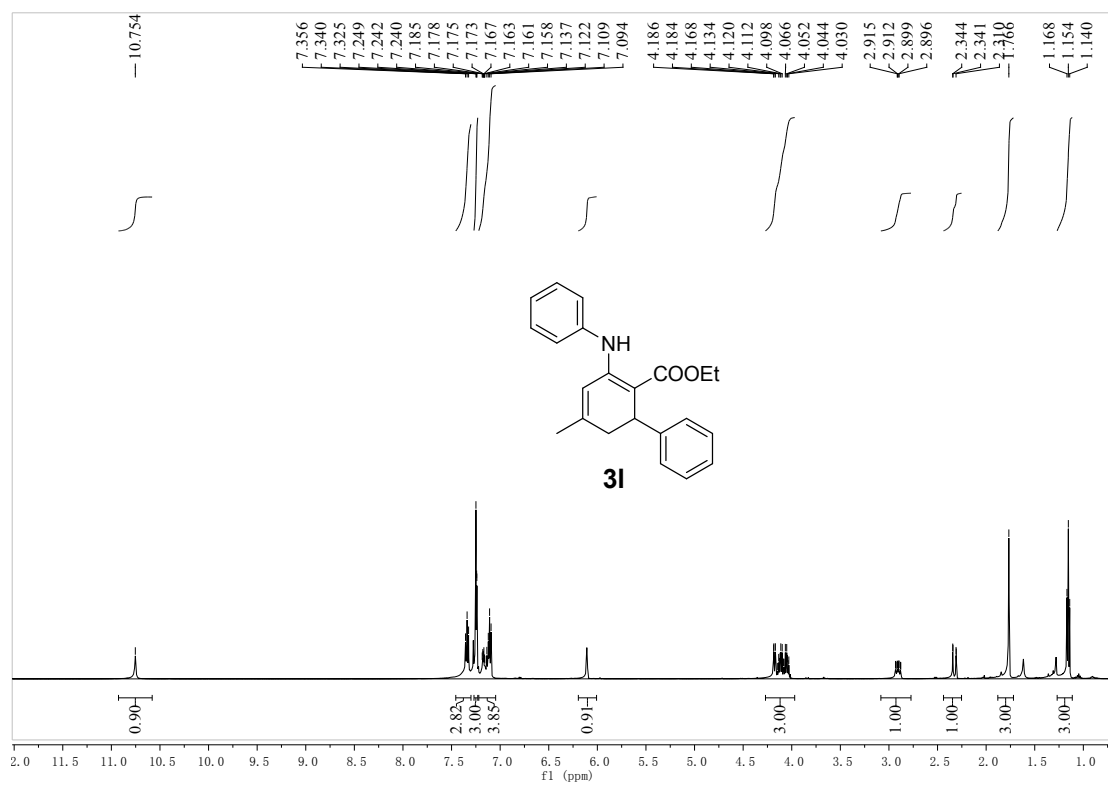


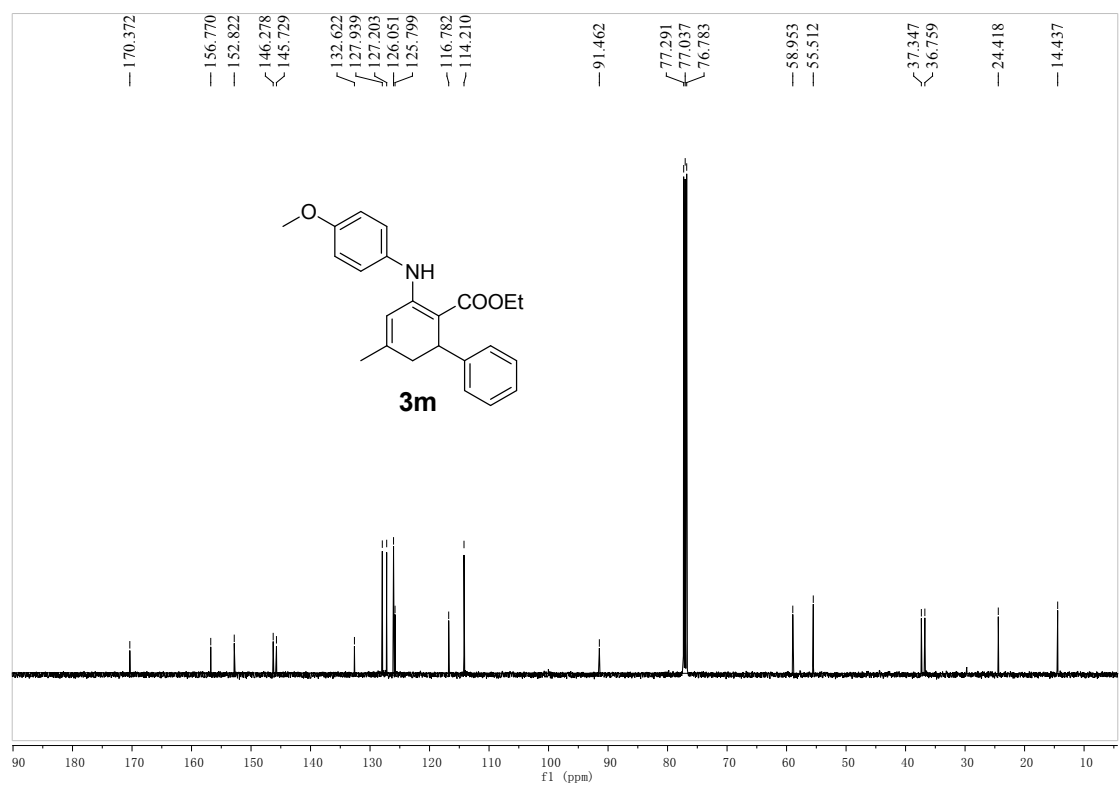
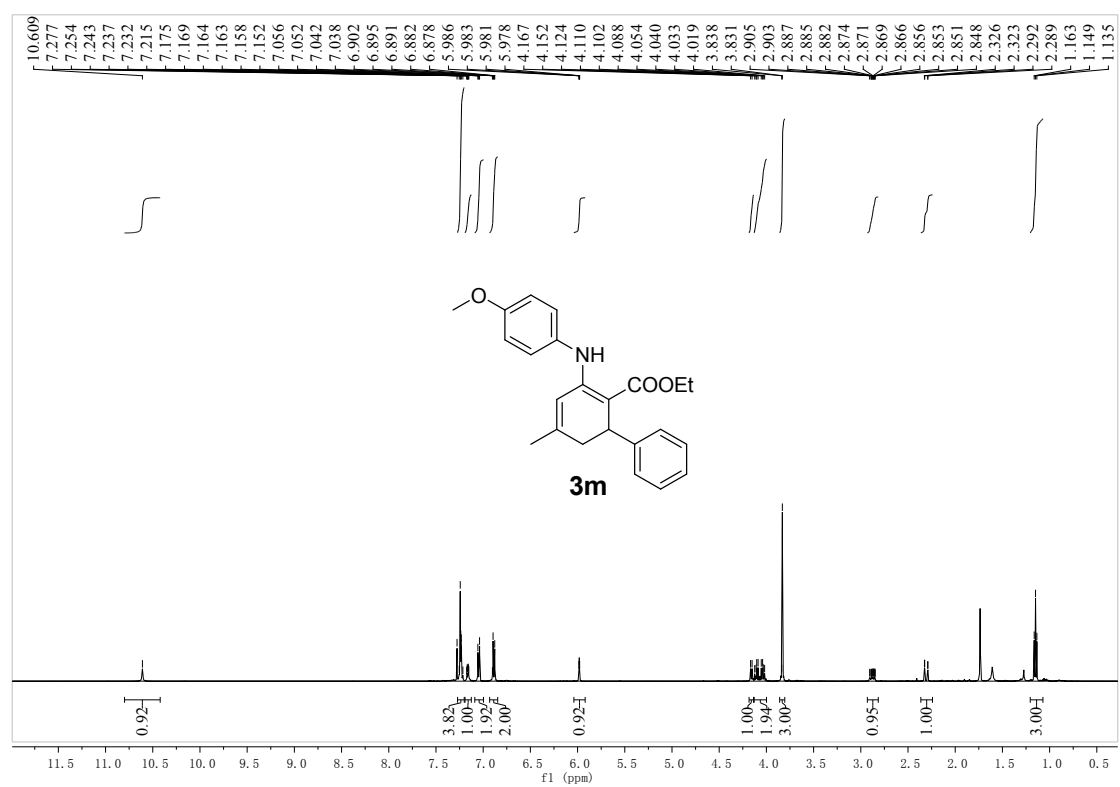


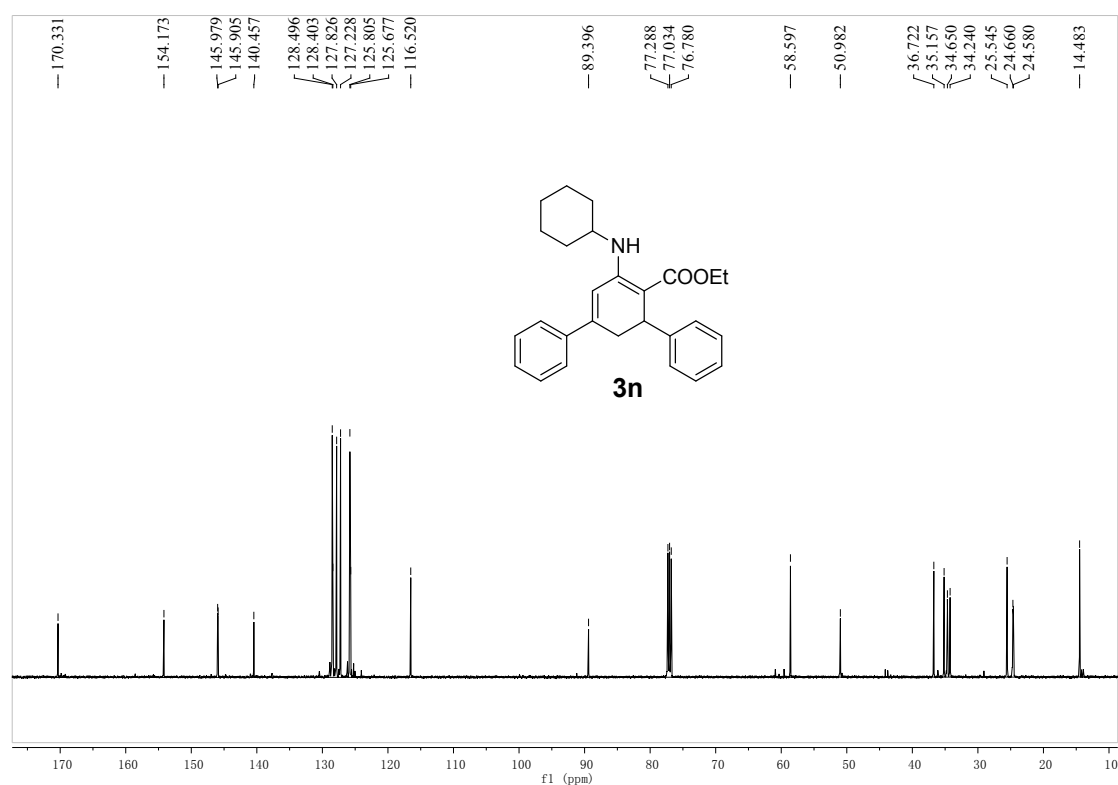
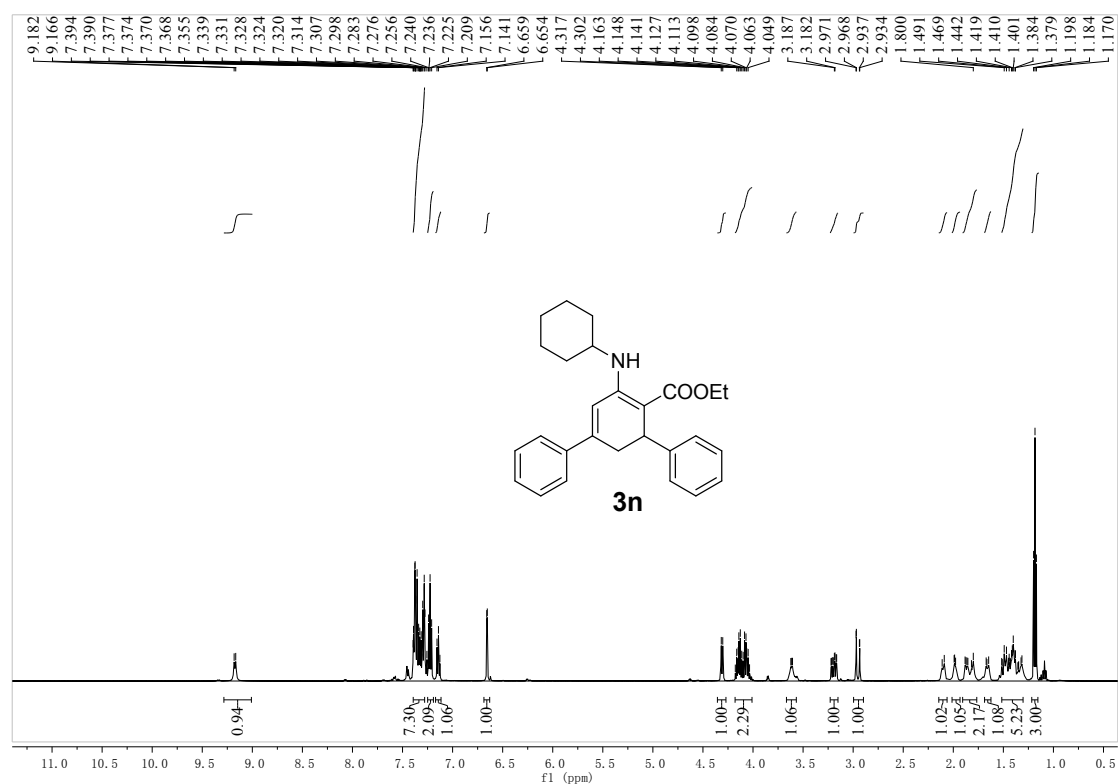


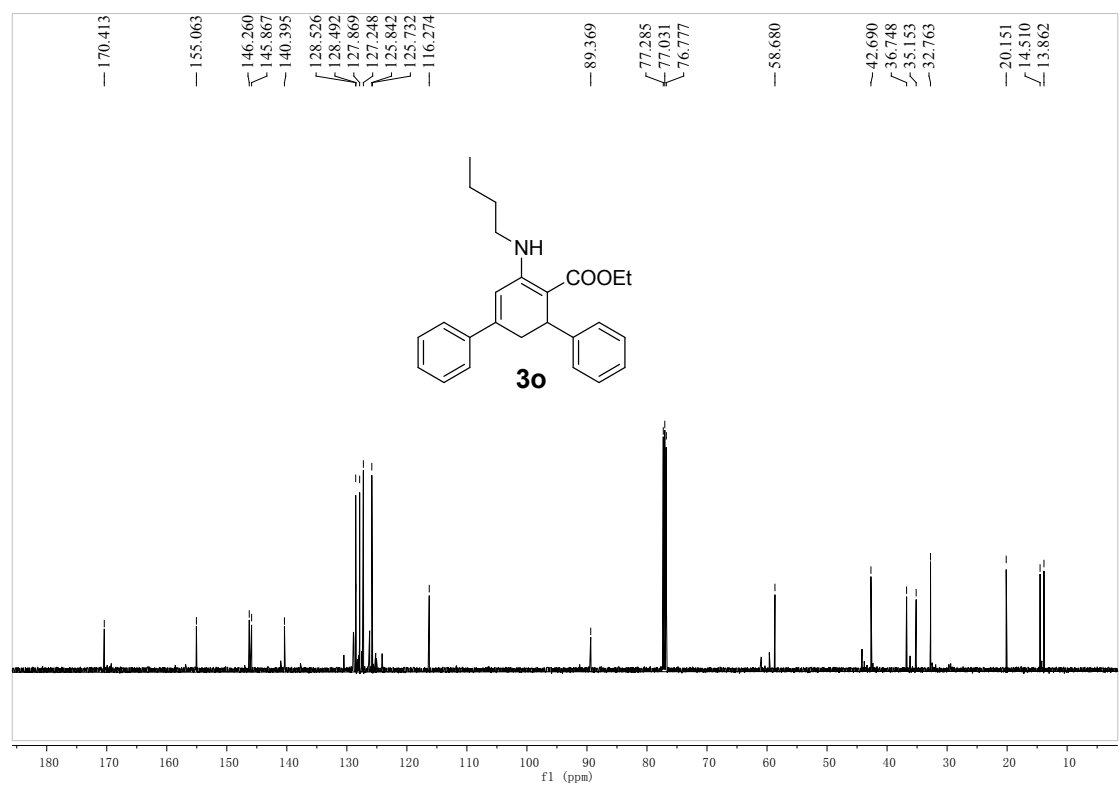
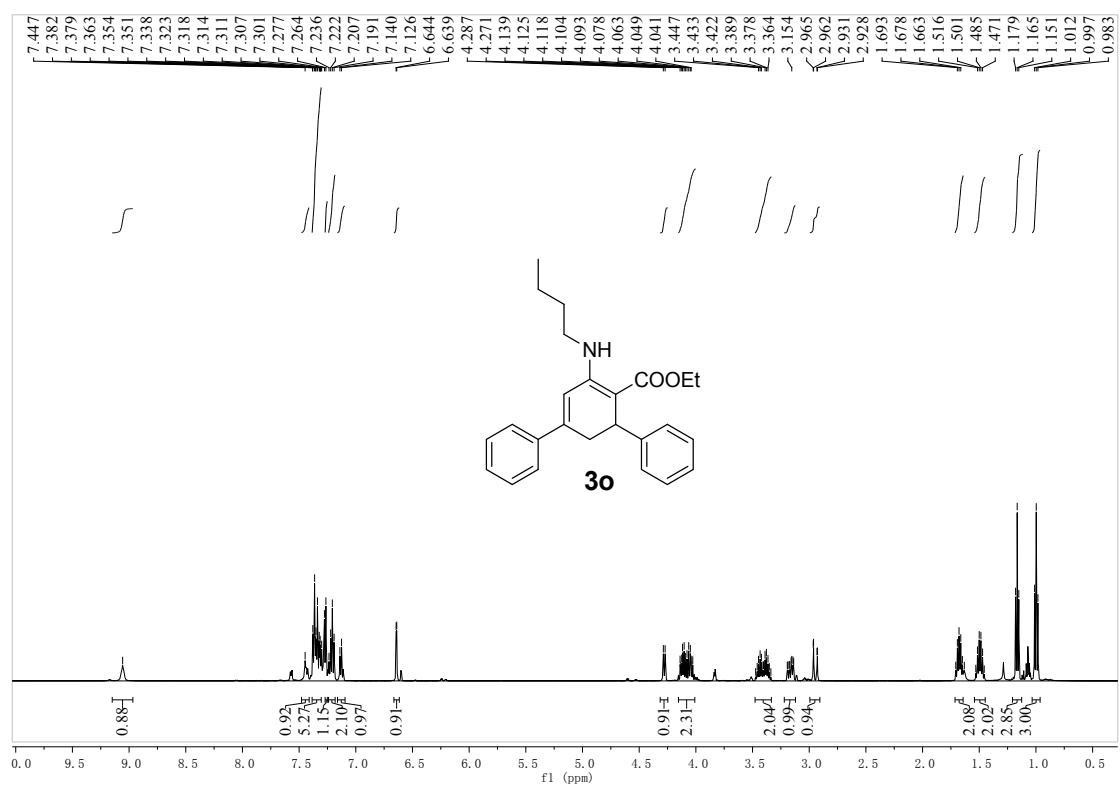


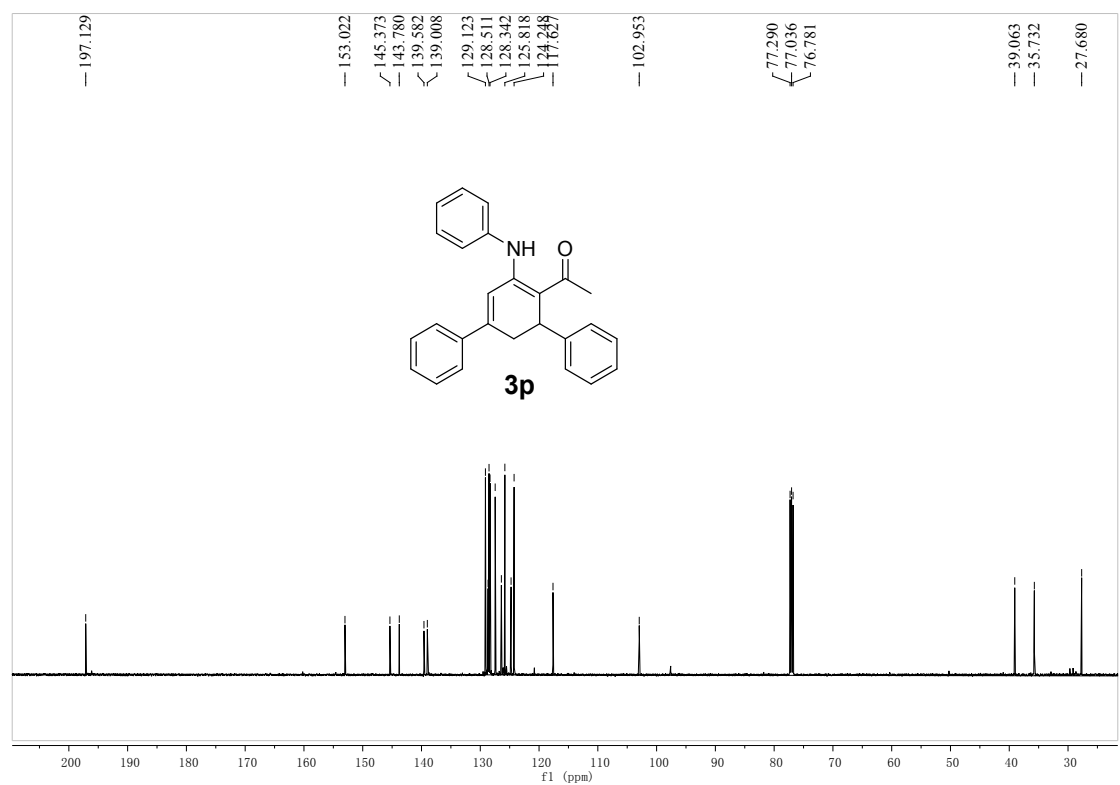
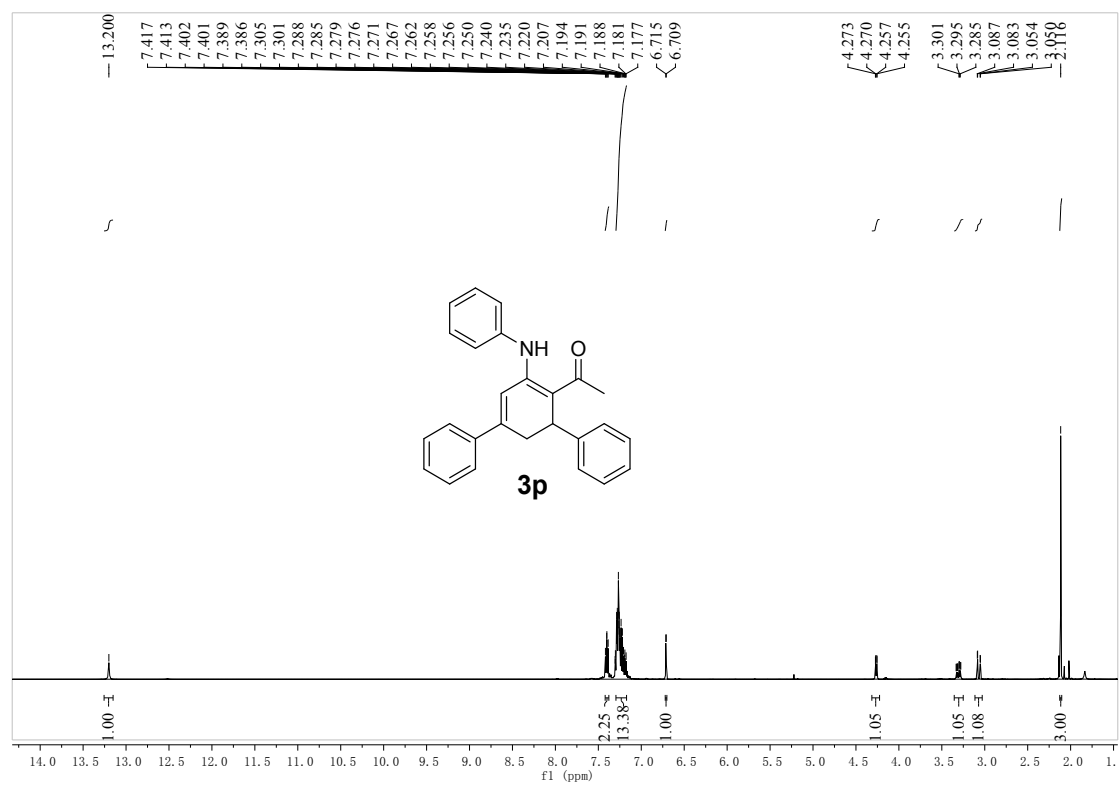


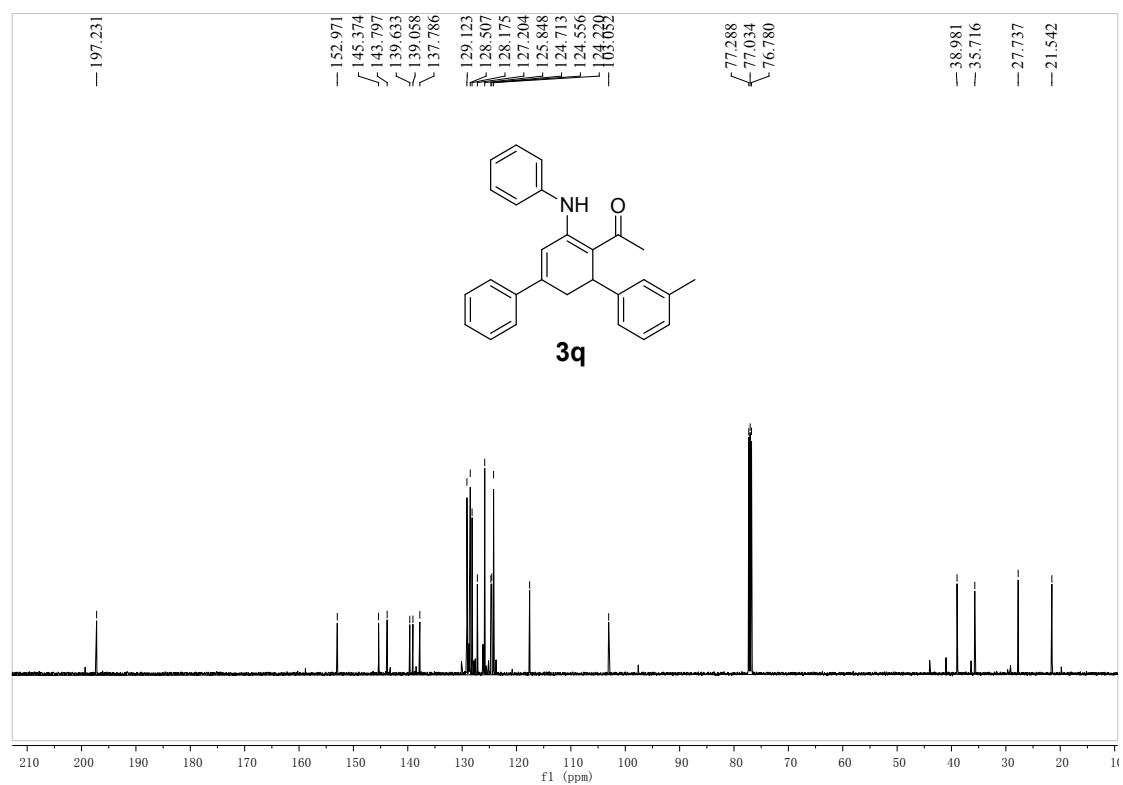
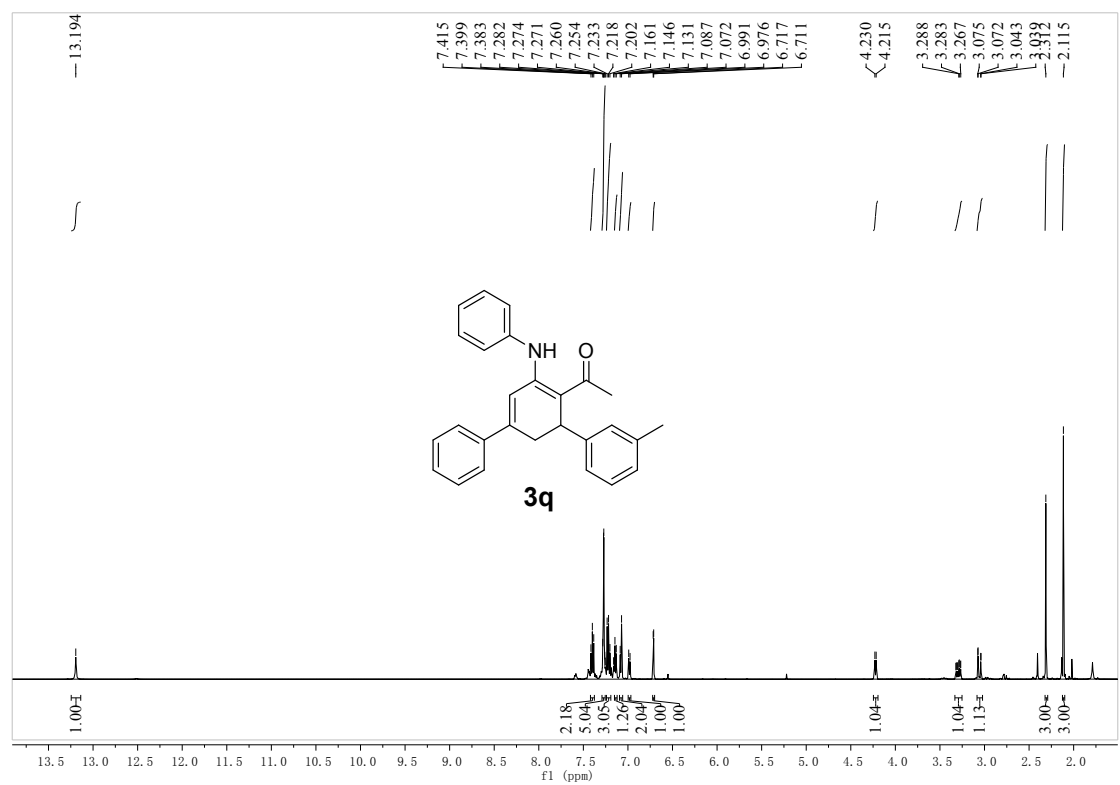


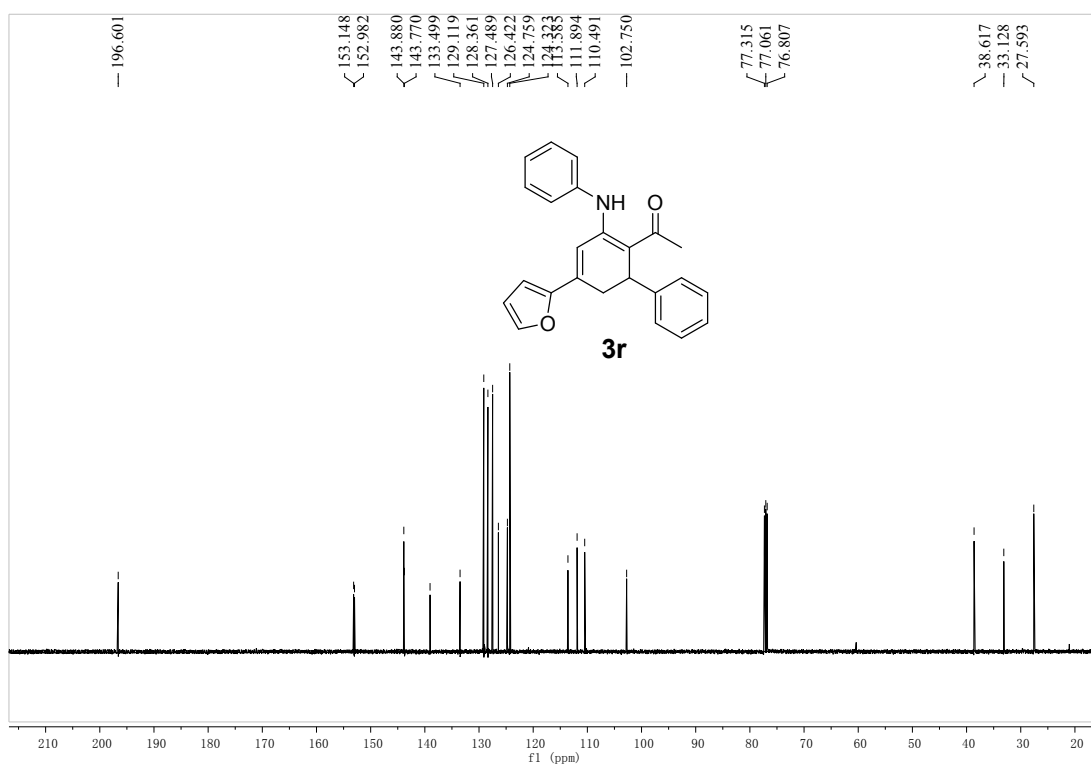
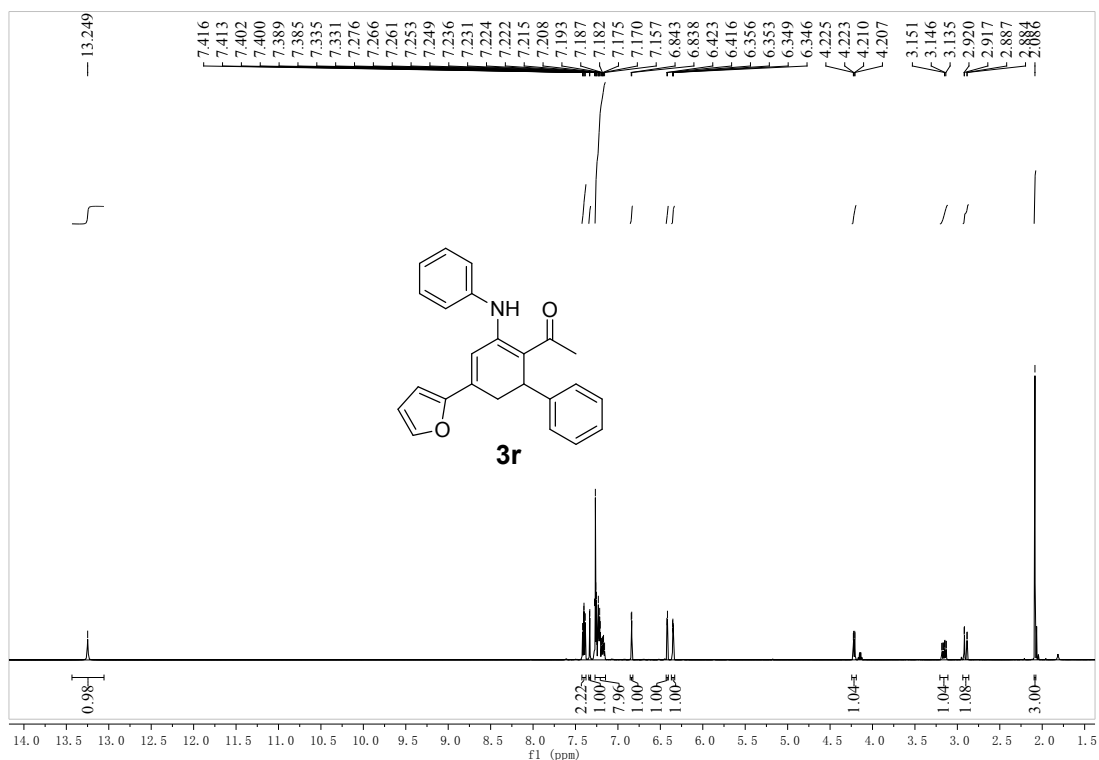


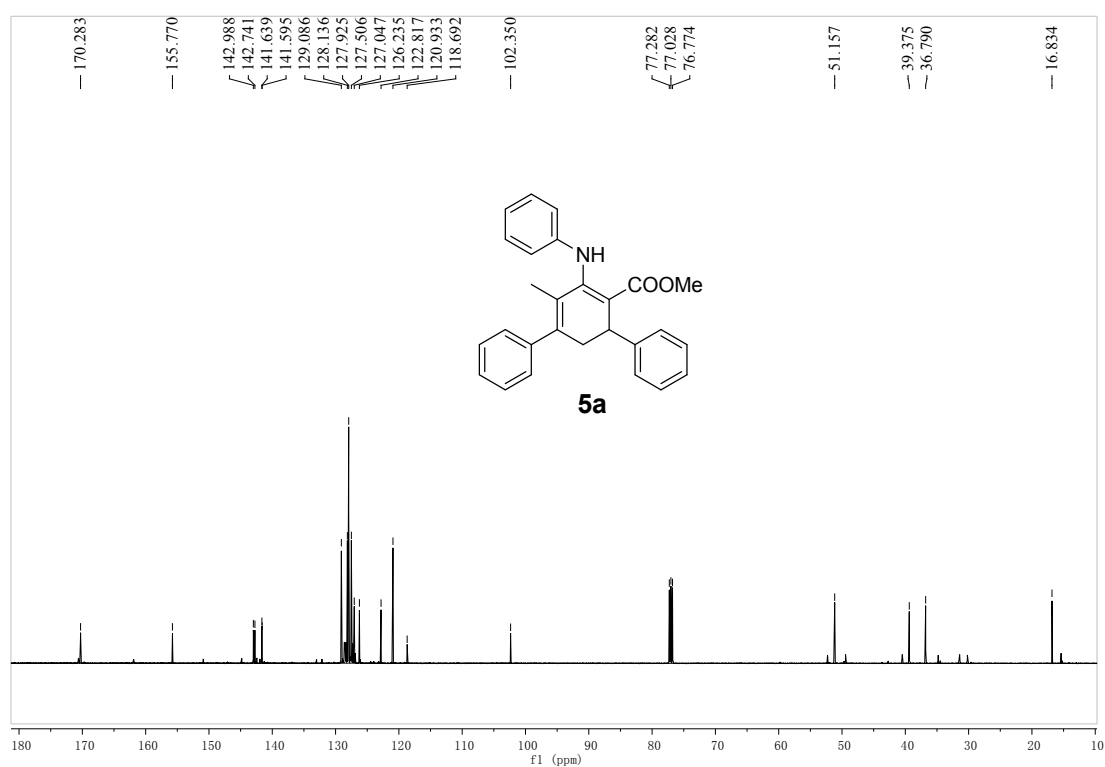
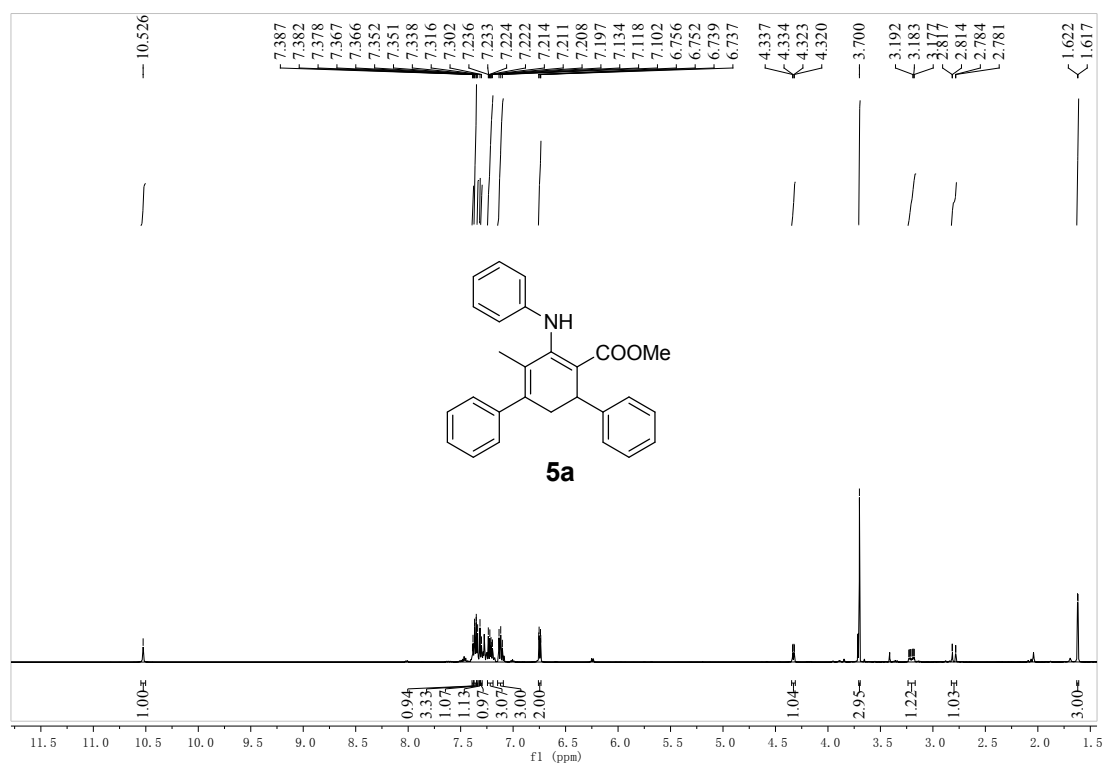


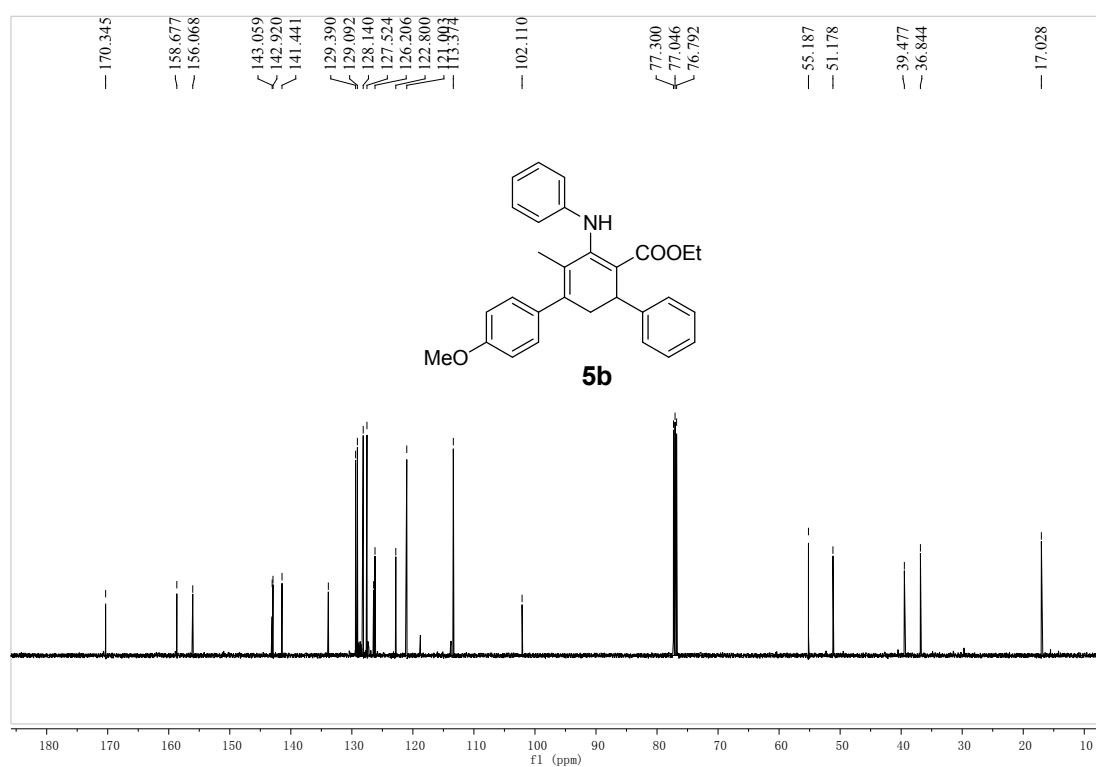
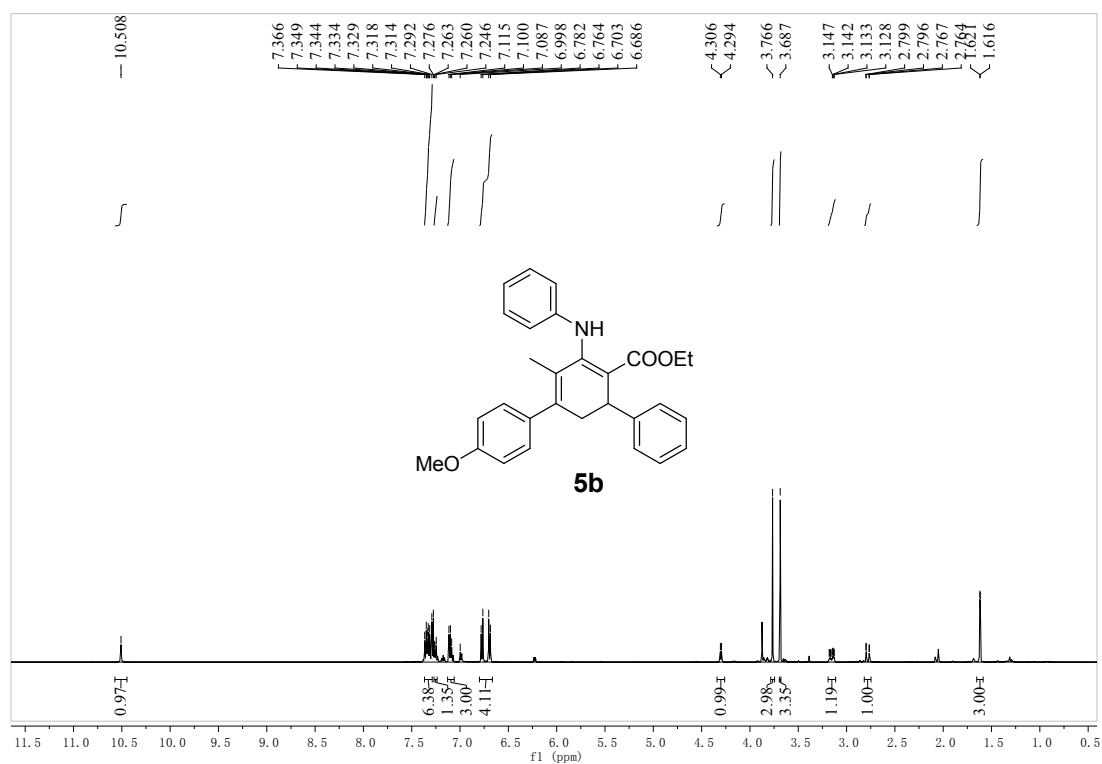


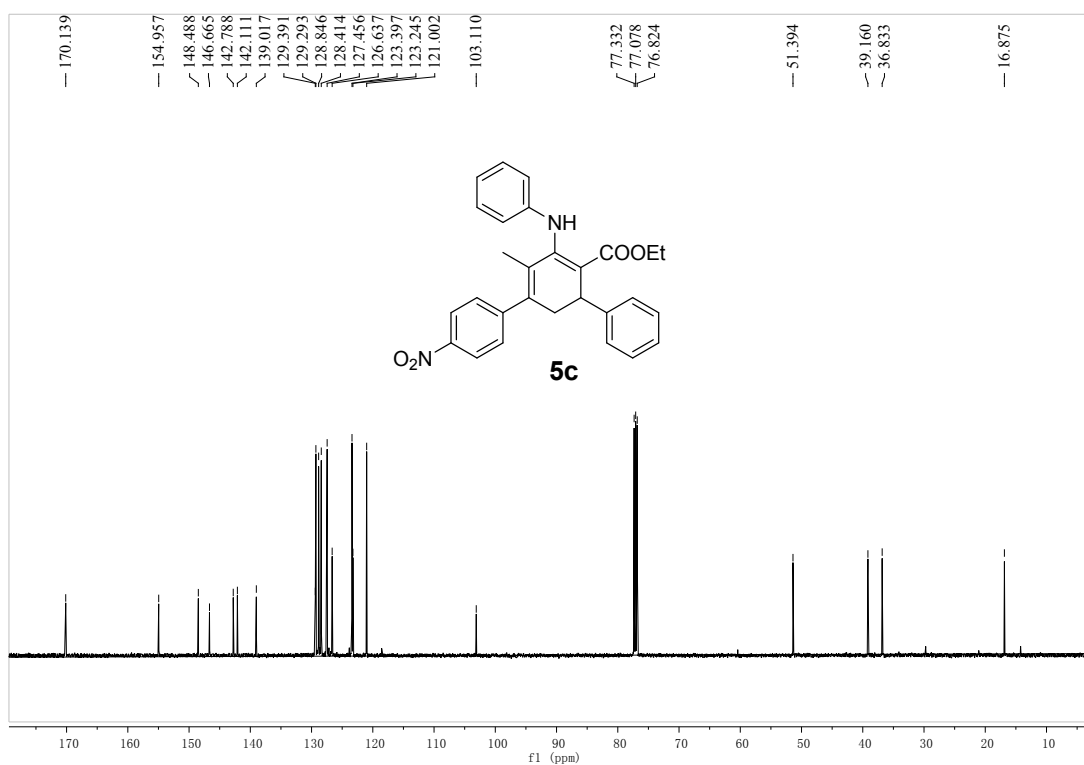
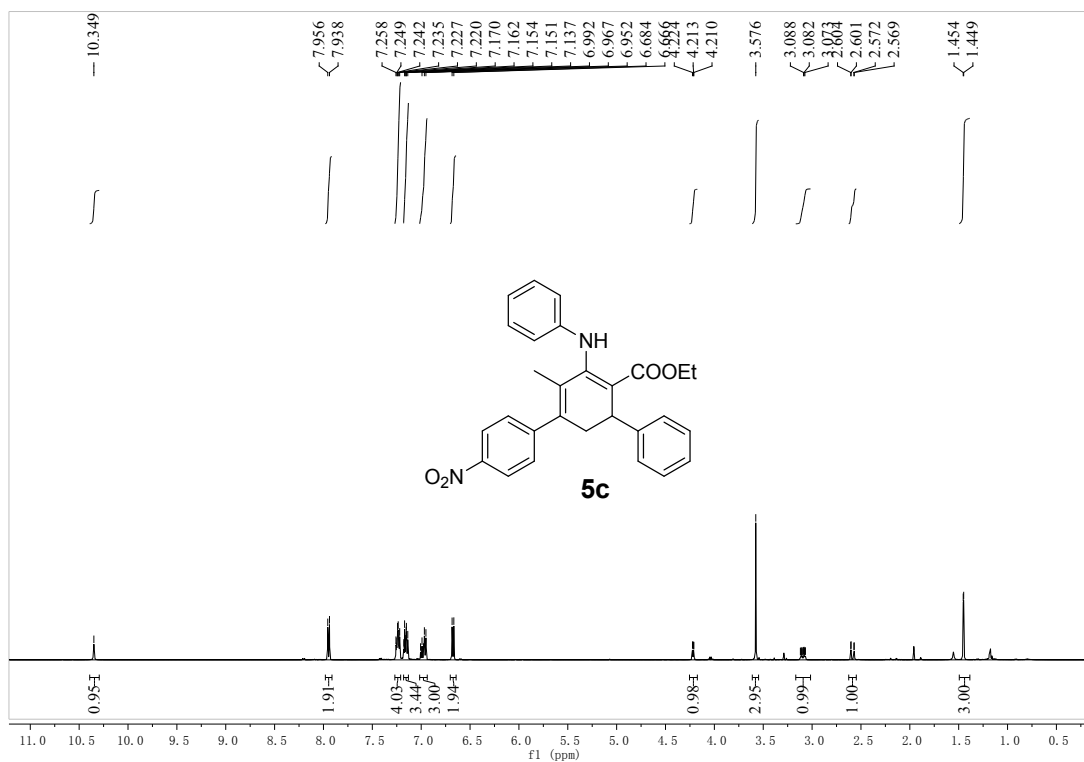












Reference

1. K. N. Sarma, M. C. S. Subha and K. C. Rao, *E-J.Chem.*, 2010, **7**, 745-750.
2. J. Y. Liu, G. E. Cao, W. Xu, J. Cao and W. L. Wang, *Applied Organometallic Chemistry*, 2010, **24**, 685-691.