

Supporting Information

Controllable Methylenation with Ethylene Glycol as Methylene

Source: Bridging Enaminones and Synthesis of Tetrahydropyrimidines

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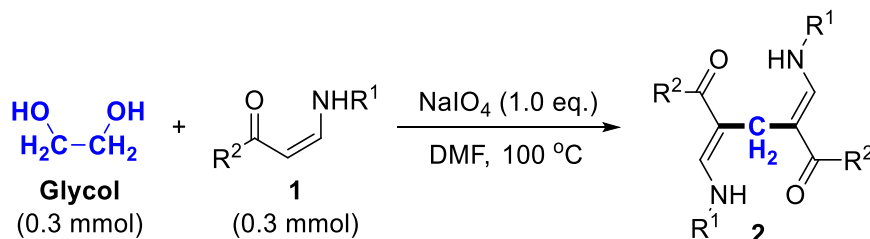
[‡] These authors contributed equally to this work.

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General Information

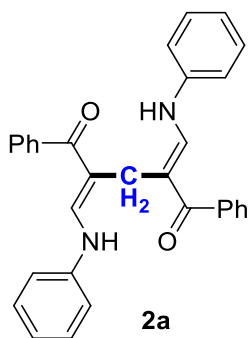
All glassware was oven dried at 100 °C for hours and cooled down under vacuum. Anhydrous DMF was prepared by distillation from CaH₂. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Purification of reaction products was carried out by flash chromatography on silica gel (200~300 mesh). ¹H NMR spectra were recorded at 500 or 400 MHz, ¹³C NMR spectra were recorded at 125 or 100 MHz, and in CDCl₃ (containing 0.03% TMS) solutions with Bruker Advance III spectrometers. ¹H NMR spectra were recorded with Me₄Si (δ = 0.00) or CDCl₃ (δ = 7.26) as the internal reference and ¹³C NMR spectra were recorded with CDCl₃ (δ = 77.16) as the internal reference. High-resolution mass spectra were obtained using a Bruker Maxis Impact mass spectrometer with a TOF (for ESI) analyzer. The enaminones **1** were prepared according to the literature methods.¹⁻⁹

Synthesis and characterization of 2



In an oven-dried Schlenk tube (25 mL) containing a magnetic stirring bar was added **1** (0.3 mmol), NaIO₄ (64.8 mg, 0.3 mmol). Then, the vessel was evacuated and refilled with Ar for three times. Under a stream of Ar, to this vessel were added DMF (1.5 mL) and ethylene glycol (16.8 μ L, 0.3 mmol). Then the vessel was stirred in a 100 °C oil bath for the corresponding time (see Table 2). The reaction could be monitored by TLC analysis. Finally, H₂O (7 mL) was added to reaction system, and the resulting mixture was directly filtered and washed with H₂O (5 mL \times 6) to give pure products **2**.

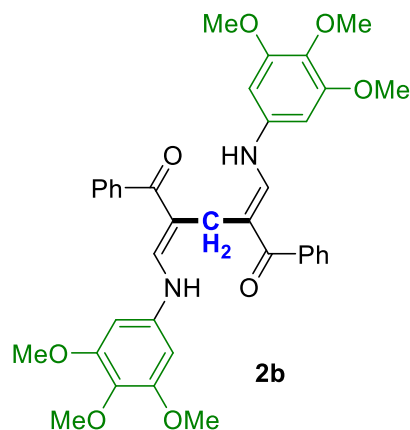
NOTE: Products **2b**, **2f**, **2i**, **2m**, **2q**, are new compounds. Other products **2** are known compounds,¹⁰ and the spectroscopic data are in agreement with that previously reported.



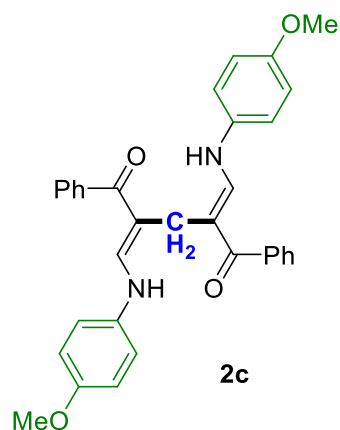
(2E,4E)-1,5-Diphenyl-2,4-bis((phenylamino)methylene)pentane-1,5-dione (**2a**).¹⁰

Compound **2a** was prepared in 92% yield (63 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 194-196 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.89 (d, J = 13.3 Hz, 2H), 7.78 (d, J = 13.3 Hz, 2H), 7.60-7.58 (m, 4H), 7.52-7.45 (m, 6H), 7.30-7.27 (m, 4H), 7.07-7.01 (m, 6H), 3.84 (s,

2H); ^{13}C NMR (125 MHz, CDCl_3): δ 197.5, 149.3, 140.8, 140.5, 130.3, 129.8, 128.9, 128.3, 123.3, 116.2, 113.8, 20.4; Analytical data for **2a** were consistent with our previous reports.¹⁰

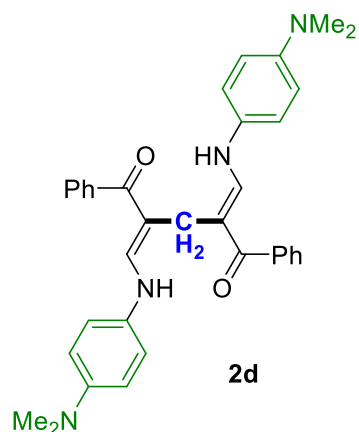


(*2E,4E*)-1,5-Diphenyl-2,4-bis(((3,4,5-trimethoxyphenyl)amino)methylene)pentane-1,5-dione (**2b**). Compound **2b** was prepared in 97% yield (93 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 4/1); Yellow solid; mp 213-215 °C; ^1H NMR (500 MHz, CDCl_3): δ 10.79 (d, $J = 13.2$ Hz, 2H), 7.65 (d, $J = 13.2$ Hz, 2H), 7.58 (d, $J = 7.1$ Hz, 4H), 7.49-7.42 (m, 8H), 6.25 (s, 2H), 3.81 (s, 12H), 3.79 (s, 8H); ^{13}C NMR (125 MHz, CDCl_3): δ 197.3, 154.2, 149.7, 140.4, 137.3, 134.5, 130.5, 129.0, 128.2, 113.7, 94.0, 61.2, 56.3, 20.4; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{37}\text{H}_{39}\text{N}_2\text{O}_8$ 639.2701, Found 639.2698.

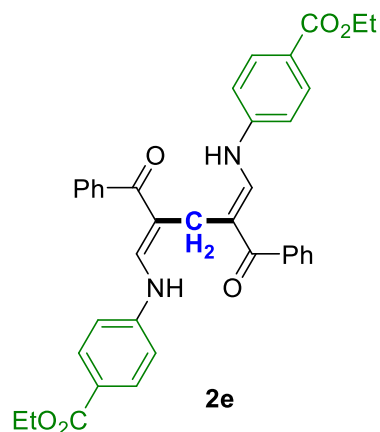


(*2E,4E*)-2,4-Bis(((4-methoxyphenyl)amino)methylene)-1,5-diphenylpentane-1,5-dione (**2c**).¹⁰ Compound **2c** was prepared in 92% yield (72 mg) according to the general

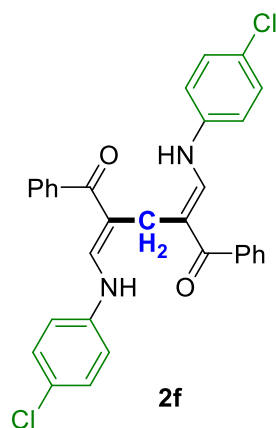
procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 10/1); Yellow solid; mp 180-182 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 10.89 (d, $J = 13.4$ Hz, 2H), 7.68 (d, $J = 13.4$ Hz, 2H), 7.56 (d, $J = 7.0$ Hz, 4H), 7.48-7.43 (m, 6H), 7.00 (d, $J = 8.7$ Hz, 4H), 6.83 (d, $J = 8.7$ Hz, 4H), 3.81 (s, 2H), 3.76 (s, 6H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 196.8, 156.1, 150.1, 140.7, 134.5, 130.1, 128.8, 128.3, 117.5, 115.0, 113.1, 55.7, 20.4; Analytical data for **2c** were consistent with our previous reports.¹⁰



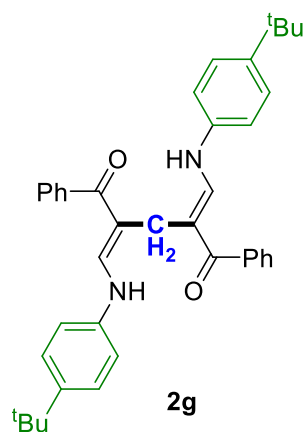
(2*E*,4*E*)-2,4-Bis(((4-(dimethylamino)phenyl)amino)methylene)-1,5-diphenylpentane-1,5-dione (**2d**).¹⁰ Compound **2d** was prepared in 90% yield (74 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 12/1); Yellow solid; mp 220-222 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 10.85 (d, $J = 13.5$ Hz, 2H), 7.67 (d, $J = 13.6$ Hz, 2H), 7.55 (d, $J = 6.4$ Hz, 4H), 7.45-7.42 (m, 6H), 6.97 (d, $J = 9.0$ Hz, 4H), 6.67 (d, $J = 9.0$ Hz, 4H), 3.81 (s, 2H), 2.89 (s, 12H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 196.2, 150.1, 147.6, 141.0, 131.5, 129.8, 128.8, 128.2, 117.6, 114.0, 112.7, 41.1, 20.3; Analytical data for **2d** were consistent with our previous reports.¹⁰



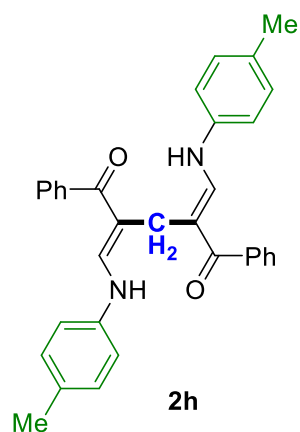
Diethyl 4,4'-(((1E,4E)-2,4-dibenzoylpenta-1,4-diene-1,5-diyl)bis(azanediyl))dibenzoate (**2e**).¹⁰ Compound **2e** was prepared in 99% yield (89 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 10/1); White solid; mp 218-220 °C; ¹H NMR (500 MHz, CDCl₃): δ 11.03 (d, $J = 13.0$ Hz, 2H), 7.97 (d, $J = 8.6$ Hz, 4H), 7.78 (d, $J = 13.0$ Hz, 2H), 7.60 (d, $J = 7.1$ Hz, 4H), 7.56-7.53 (m, 2H), 7.50-7.47 (m, 4H), 7.06 (d, $J = 8.6$ Hz, 4H), 4.34 (q, $J = 7.1$ Hz, 4H), 3.82 (s, 2H), 1.37 (t, $J = 7.1$ Hz, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 198.3, 166.2, 148.1, 144.5, 139.9, 131.6, 130.9, 128.9, 128.5, 125.0, 115.3, 115.1, 60.9, 20.7, 14.5; Analytical data for **2e** were consistent with our previous reports.¹⁰



(2E,4E)-2,4-Bis(((4-chlorophenyl)amino)methylene)-1,5-diphenylpentane-1,5-dione (**2f**). Compound **2f** was prepared in 96% yield (76 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 12/1); Yellow solid; mp 247-249 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.94 (d, $J = 13.0$ Hz, 2H), 7.68 (d, $J = 13.1$ Hz, 2H), 7.56 (d, $J = 7.0$ Hz, 4H), 7.53-7.51(m, 2H), 7.48-7.45(m, 4H), 7.23 (d, $J = 8.3$ Hz, 4H), 6.97 (d, $J = 8.3$ Hz, 4H), 3.79 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 197.8, 149.0, 140.2, 139.5, 130.6, 129.8, 128.9, 128.4, 128.3, 117.3, 114.2, 20.6; HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₁H₂₅Cl₂N₂O₂ 527.1288, Found 527.1283.

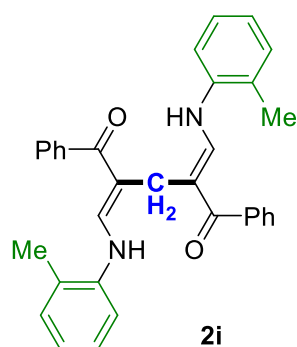


(2E,4E)-2,4-Bis(((4-(tert-butyl)phenyl)amino)methylene)-1,5-diphenylpentane-1,5-dione (**2g**).¹⁰ Compound **2g** was prepared in 94% yield (80 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 205-207 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.84 (d, $J = 13.4$ Hz, 2H), 7.75 (d, $J = 13.4$ Hz, 2H), 7.57 (d, $J = 6.9$ Hz, 4H), 7.51-7.43 (m, 6H), 7.31 (d, $J = 8.6$ Hz, 4H), 7.00 (d, $J = 8.6$ Hz, 4H), 3.83 (s, 2H), 1.29 (s, 18H); ¹³C NMR (125 MHz, CDCl₃): δ 197.2, 149.6, 146.4, 140.6, 138.4, 130.2, 128.9, 128.3, 126.6, 115.9, 113.5, 34.4, 31.5, 20.3; Analytical data for **2g** were consistent with our previous reports.¹⁰



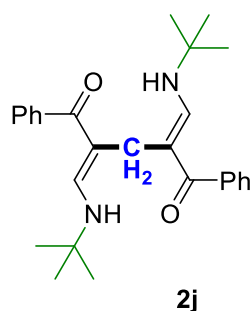
(2E,4E)-1,5-Diphenyl-2,4-bis((p-tolylamino)methylene)pentane-1,5-dione (**2h**).¹⁰ Compound **2h** was prepared in 98% yield (72 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 188-190 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.86 (d, $J = 13.3$ Hz, 2H), 7.74 (d, $J = 13.4$ Hz, 2H), 7.57 (d, $J = 6.9$ Hz, 4H), 7.51-7.44 (m, 6H), 7.08 (d, $J = 8.1$ Hz, 4H), 6.96 (d, $J = 8.2$ Hz, 4H), 3.83 (s, 2H), 2.29 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 197.1, 149.6,

140.6, 138.5, 133.0, 130.2, 130.2, 128.8, 128.3, 116.2, 113.4, 20.9, 20.4; Analytical data for **2h** were consistent with our previous reports.¹⁰



(2E,4E)-1,5-Diphenyl-2,4-bis((o-tolylamino)methylene)pentane-1,5-dione (**2i**).

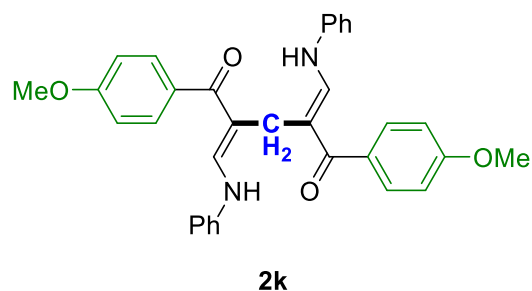
Compound **2i** was prepared in 92% yield (67 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 15/1); White solid; mp 156-158 °C; ^1H NMR (500 MHz, CDCl_3): δ 10.13 (d, $J = 12.9$ Hz, 2H), 7.68 (d, $J = 13.0$ Hz, 2H), 7.55 (d, $J = 6.7$ Hz, 4H), 7.47-7.40 (m, 6H), 7.19 (d, $J = 7.3$ Hz, 2H), 7.12-7.10 (m, 2H), 7.01-6.98 (m, 2H), 6.81 (d, $J = 8.0$ Hz, 2H), 3.89 (s, 2H), 2.58 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 197.4, 151.8, 140.7, 140.2, 131.4, 130.1, 129.1, 128.8, 128.2, 127.0, 124.1, 117.4, 113.9, 20.2, 18.5; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{33}\text{H}_{31}\text{N}_2\text{O}_2$ 487.2380, Found 487.2377.



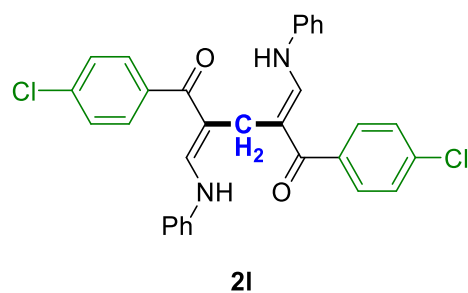
(2E,4E)-2,4-Bis((tert-butylamino)methylene)-1,5-diphenylpentane-1,5-dione (**2j**).¹⁰

Compound **2j** was prepared in 93% yield (58 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 12/1); Yellow solid; mp 122-124 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.94 (d, $J = 14.2$ Hz, 2H), 7.41-7.35 (m, 10H), 7.27 (d, $J = 14.4$, 2H), 3.54 (s, 2H), 1.23 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3): δ 194.3, 154.1,

141.7, 129.1, 128.3, 128.0, 110.1, 52.7, 29.9, 19.1; Analytical data for **2j** were consistent with our previous reports.¹⁰

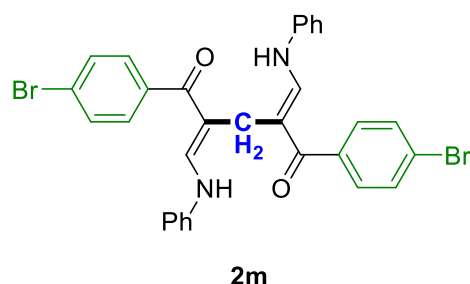


(2E,4E)-1,5-Bis(4-methoxyphenyl)-2,4-bis((phenylamino)methylene)pentane-1,5-dione (2k).¹⁰ Compound **2k** was prepared in 94% yield (73 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 9/1); Yellow solid; mp 189-191 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.91 (d, $J = 13.2$ Hz, 2H), 7.78 (d, $J = 13.3$ Hz, 2H), 7.60 (d, $J = 8.7$ Hz, 4H), 7.31-7.27 (m, 4H), 7.07 (d, $J = 7.8$ Hz, 4H), 7.02-6.99 (m, 2H), 6.97 (d, $J = 8.7$ Hz, 4H), 3.89 (s, 6H), 3.80 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 196.8, 161.6, 148.3, 141.1, 132.9, 131.1, 129.7, 123.0, 116.0, 113.6, 55.5, 21.2; Analytical data for **2k** were consistent with our previous reports.¹⁰

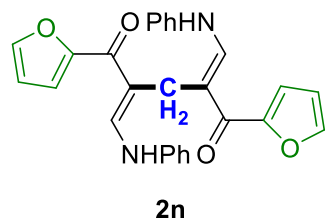


(2E,4E)-1,5-Bis(4-chlorophenyl)-2,4-bis((phenylamino)methylene)pentane-1,5-dione (2l).¹⁰ Compound **2l** was prepared in 95% yield (75 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 10/1); Yellow solid; mp 236-238 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.86 (d, $J = 13.3$ Hz, 2H), 7.71 (d, $J = 13.3$ Hz, 2H), 7.52 (d, $J = 8.3$ Hz, 4H), 7.44 (d, $J = 8.3$ Hz, 4H), 7.32-7.29 (m, 4H), 7.05-7.04 (m, 6H), 3.79 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 196.1, 149.2, 140.6, 138.8,

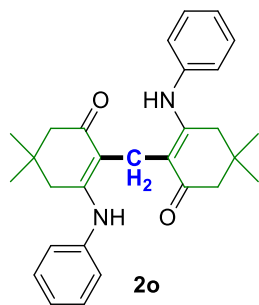
136.6, 130.3, 129.9, 128.7, 123.7, 116.2, 113.6, 20.6; Analytical data for **2l** were consistent with our previous reports.¹⁰



(2E,4E)-1,5-Bis(4-bromophenyl)-2,4-bis((phenylamino)methylene)pentane-1,5-dione (2m). Compound **2m** was prepared in 94% yield (87 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); Yellow solid; mp 262-263 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.87 (d, $J = 13.3$ Hz, 2H), 7.72 (d, $J = 13.4$ Hz, 2H), 7.60 (d, $J = 8.3$ Hz, 4H), 7.46 (d, $J = 8.3$ Hz, 4H), 7.33-7.29 (m, 4H), 7.06-7.04 (m, 6H), 3.79 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 196.1, 149.2, 140.6, 139.2, 131.6, 130.5, 129.9, 124.9, 123.7, 116.2, 113.5, 20.5; HRMS (ESI) m/z : [M+H]⁺ Calcd for C₃₁H₂₅Br₂N₂O₂ 615.0277, Found 615.0273.

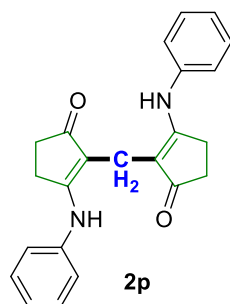


(2E,4E)-1,5-Di(furan-2-yl)-2,4-bis((phenylamino)methylene)pentane-1,5-dione (2n).¹⁰ Compound **2n** was prepared in 90% yield (59 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 10/1); Yellow solid; mp 168-170 °C; ¹H NMR (400 MHz, CDCl₃): δ 10.93 (d, $J = 13.2$ Hz, 2H), 8.55 (d, $J = 13.3$ Hz, 2H), 7.63 (s, 2H), 7.36-7.32 (m, 4H), 7.21 (d, $J = 7.8$ Hz, 4H), 7.10 (d, $J = 3.3$ Hz, 2H), 7.07-7.04 (m, 2H), 6.56-6.54 (m, 2H), 3.77 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 181.8, 153.5, 147.3, 145.1, 141.0, 129.8, 123.4, 116.9, 116.4, 112.9, 111.7, 20.8; Analytical data for **2n** were consistent with our previous reports.¹⁰

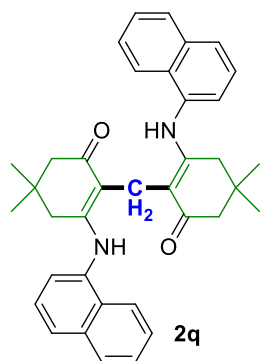


2,2'-Methylenebis(5,5-dimethyl-3-(phenylamino)cyclohex-2-en-1-one) (**2o**).¹⁰

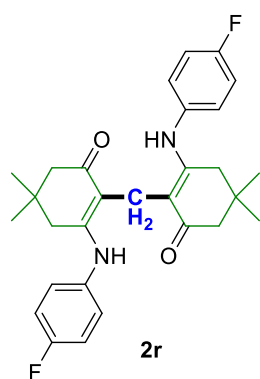
Compound **2o** was prepared in 93% yield (62 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); White solid; mp 190-192 °C; ^1H NMR (500 MHz, CDCl_3): δ 10.81 (s, 2H), 7.37-7.33 (m, 4H), 7.18-7.14 (m, 6H), 3.55 (s, 2H), 2.50-2.30 (m, 8H), 1.00 (s, 12H); ^{13}C NMR (125 MHz, CDCl_3): δ 196.3, 162.0, 139.6, 129.2, 125.0, 124.5, 110.3, 50.1, 41.0, 32.8, 28.8, 18.1; Analytical data for **2o** were consistent with our previous reports.¹⁰



2,2'-Methylenebis(3-(phenylamino)cyclopent-2-en-1-one) (**2p**).¹⁰ Compound **2p** was prepared in 93% yield (50 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 4/1); Yellow solid; mp 196-198 °C; ^1H NMR (500 MHz, CDCl_3): δ 9.51 (s, 2H), 7.35-7.32 (m, 4H), 7.24-7.22 (m, 4H), 7.12-7.10 (m, 2H), 3.15 (s, 2H), 2.84 (s, br, 4H), 2.49 (t, $J = 4.8$ Hz, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ 203.4, 172.1, 139.8, 129.4, 124.3, 121.0, 116.2, 33.4, 26.6, 14.6; Analytical data for **2p** were consistent with our previous reports.¹⁰

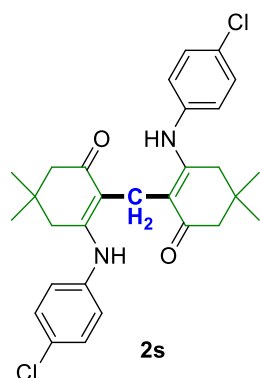


2,2'-Methylenebis(5,5-dimethyl-3-(naphthalen-1-ylamino)cyclohex-2-en-1-one) (**2q**). Compound **2q** was prepared in 93% yield (76 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 10/1); White solid; mp 275-277 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 10.80 (s, 2H), 7.94-7.89 (m, 4H), 7.82 (d, $J = 8.2$ Hz, 2H), 7.54-7.53 (m, 4H), 7.50-7.47 (m, 2H), 7.29 (d, $J = 7.2$ Hz, 2H), 3.86 (s, 2H), 2.26-2.17 (m, 8H), 0.96 (s, 12H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 196.0, 164.4, 135.7, 134.6, 131.3, 128.4, 127.5, 126.8, 126.6, 125.6, 125.0, 123.2, 109.4, 50.0, 40.5, 32.5, 28.2, 18.1; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{37}\text{H}_{39}\text{N}_2\text{O}_2$ 543.3006, Found 543.3004.

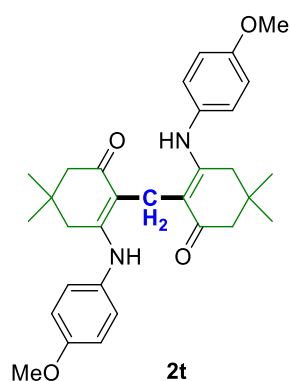


2,2'-Methylenebis(3-((4-fluorophenyl)amino)-5,5-dimethylcyclohex-2-en-1-one) (**2r**).¹⁰ Compound **2r** was prepared in 93% yield (67 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); White solid; mp 235-237 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 10.75 (s, 2H), 7.11-7.08 (m, 4H), 7.07-7.03 (m, 4H), 3.51 (s, 2H), 2.42-2.28 (m, 8H), 0.99 (s, 12H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 196.4, 162.2, 160.4 (d, $J_{\text{C-F}} = 243.4$ Hz), 135.6 (d, $J_{\text{C-F}} = 2.9$ Hz), 126.5 (d, $J_{\text{C-F}} = 8.2$ Hz),

116.1 (d, $J_{C-F} = 22.5$ Hz), 110.0, 50.0, 40.9, 32.8, 28.4, 18.1; Analytical data for **2r** were consistent with our previous reports.¹⁰



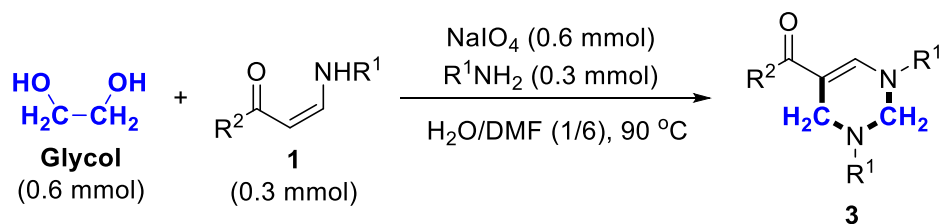
2,2'-Methylenebis(3-((4-chlorophenyl)amino)-5,5-dimethylcyclohex-2-en-1-one) (**2s**).¹⁰ Compound **2s** was prepared in 95% yield (73 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); Yellow solid; mp 237-239 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.86 (s, 2H), 7.31 (d, $J = 8.6$ Hz, 4H), 7.08 (d, $J = 8.6$ Hz, 4H), 3.49 (s, 2H), 2.51-2.29 (m, 8H), 1.00-0.97 (m, 12H); ¹³C NMR (125 MHz, CDCl₃): δ 196.8, 161.6, 138.3, 130.3, 129.3, 125.5, 110.8, 50.1, 41.0, 32.9, 29.1, 27.4, 18.3; Analytical data for **2s** were consistent with our previous reports.¹⁰



2,2'-Methylenebis(3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-en-1-one) (**2t**).¹⁰ Compound **2t** was prepared in 93% yield (70 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 4/1); White solid; mp 178-180 °C; ¹H NMR (500 MHz, CDCl₃): δ 10.58 (s, 2H), 7.04 (d, $J = 8.1$ Hz, 4H), 6.87 (d, $J = 7.9$ Hz, 4H), 3.81 (s, 6H), 3.53 (s, 2H), 2.26 (s, br, 8H), 0.98 (s, 12H); ¹³C NMR (125

MHz, CDCl₃): δ 195.7, 162.7, 157.5, 132.5, 126.5, 114.4, 109.2, 55.6, 50.0, 40.8, 32.6, 28.4, 17.8; Analytical data for **2t** were consistent with our previous reports.¹⁰

Synthesis and characterization of 3

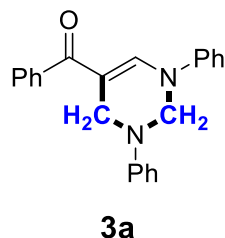


In an oven-dried Schlenk tube (25 mL) containing a magnetic stirring bar was added **1** (0.3 mmol), NaIO₄ (129.5 mg, 0.6 mmol), H₂O/DMF (3.5 mL, v/v = 1/6) and ethylene glycol (33.5 μL, 0.6 mmol), R¹NH₂ (0.3 mmol). Then the vessel was stirred in a 90 °C oil bath for the corresponding time (see Table 3). The reaction could be monitored by TLC analysis.

For **3a**, **3c-3e**, H₂O (7 mL) was added to reaction system, and the resulting mixture was directly filtered and washed with H₂O (5 mL × 6) to give pure products.

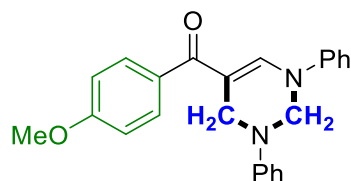
For **3b**, **3f-3k**, the resulting mixture was brine (20 mL), and extracted with ethyl acetate (30 mL). The organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated under reduced pressure and subjected to column chromatography for purification directly, using petroleum ether/ethyl acetate (3:1–7:1) as the eluent.

NOTE: Products **3d-3f**, **3i**, are new compounds. Other products **3** are known compounds,¹¹ and the spectroscopic data are in agreement with that previously reported.



(1,3-Diphenyl-1,2,3,4-tetrahydropyrimidin-5-yl)(phenyl)methanone (**3a**).¹¹ Compound **3a** was prepared in 95% yield (97 mg) according to the general procedure. *R_f* = 0.2

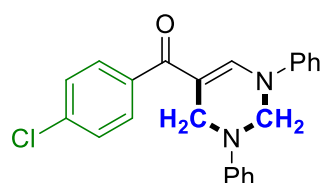
(petroleum ether/ethyl acetate = 4/1); Yellow solid; mp 134-137 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.56-7.52 (m, 3H), 7.46-7.43 (m, 1H), 7.42-7.38 (m, 2H), 7.36-7.33 (m, 2H), 7.25-7.23 (m, 2H), 7.15-7.12 (m, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.95-6.90 (m, 3H), 5.16 (s, 2H), 4.51 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 193.5, 148.6, 146.1, 144.0, 139.7, 130.4, 129.9, 129.4, 128.5, 128.3, 124.6, 121.3, 118.7, 117.9, 110.9, 65.6, 47.2; Analytical data for **3a** were consistent with our previous reports.¹¹



3b

(1,3-Diphenyl-1,2,3,4-tetrahydropyrimidin-5-yl)(4-methoxyphenyl)methanone (3b).¹¹

Compound **3b** was prepared in 86% yield (96 mg) according to the general procedure. *R_f* = 0.2 (petroleum ether/ethyl acetate = 5/1); Yellow solid; mp 119-121 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.58-7.54 (m, 3H), 7.36-7.32 (m, 2H), 7.25-7.21 (m, 2H), 7.15-7.11 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.92-6.88 (m, 3H), 5.16 (s, 2H), 4.50 (s, 2H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 192.6, 161.6, 148.6, 145.2, 144.2, 132.2, 130.6, 129.9, 129.4, 124.4, 121.2, 118.5, 118.0, 113.6, 111.1, 65.5, 55.5, 47.4; Analytical data for **3b** were consistent with our previous reports.¹¹

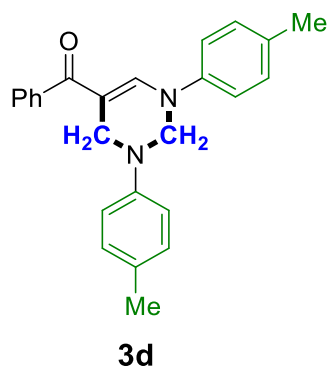


3c

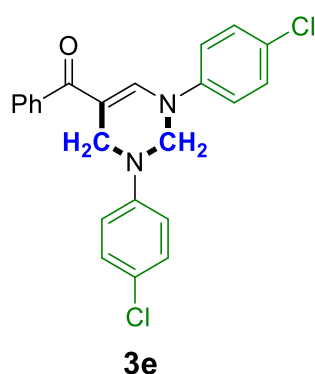
(4-Chlorophenyl)(1,3-diphenyl-1,2,3,4-tetrahydropyrimidin-5-yl)methanone (3c).¹¹

Compound **3c** was prepared in 83% yield (93mg) according to the general procedure. *R_f* = 0.2 (petroleum ether/ethyl acetate = 10/1); Yellow solid; mp 138-141 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.50-7.47 (m, 3H), 7.38-7.34 (m, 4H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.17-7.14 (m, 1H), 6.99-6.90 (m, 5H), 5.16 (s, 2H), 4.49 (s, 2H); ¹³C NMR (125

MHz, CDCl₃): δ 192.0, 148.5, 146.0, 144.0, 138.0, 136.5, 130.0, 130.0, 129.5, 128.6, 124.9, 121.4, 118.8, 117.9, 110.8, 65.7, 47.1; Analytical data for **3c** were consistent with our previous reports.¹¹

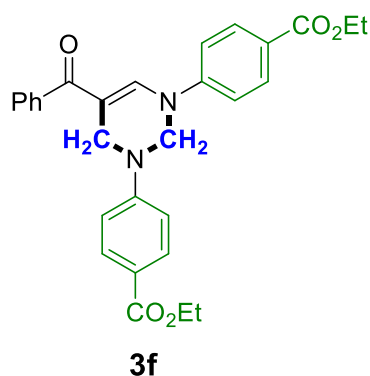


(1,3-Di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)(phenyl)methanone (**3d**). Compound **3d** was prepared in 92% yield (102 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); Yellow solid; mp 139-141 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.54-7.53 (m, 2H), 7.47-7.37 (m, 4H), 7.13 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 5.09 (s, 2H), 4.46 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 193.3, 146.4, 146.3, 141.8, 139.9, 134.5, 130.7, 130.4, 130.3, 129.9, 128.5, 128.2, 118.9, 118.1, 110.3, 66.2, 47.3, 20.8, 20.6; HRMS (ESI) m/z : [M+H]⁺ Calcd for C₂₅H₂₅N₂O 369.1961; found, 369.1958.

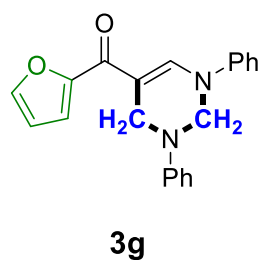


(1,3-Bis(4-chlorophenyl)-1,2,3,4-tetrahydropyrimidin-5-yl)(phenyl)methanone (**3e**). Compound **3e** was prepared in 77% yield (95mg) according to the general procedure.

$R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); Yellow solid; mp 127-129 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.54 (d, $J = 7.2$ Hz, 2H), 7.48-7.45 (m, 1H), 7.42-7.39 (m, 3H), 7.29 (d, $J = 8.6$ Hz, 2H), 7.18 (d, $J = 8.7$ Hz, 2H), 6.88-6.83 (m, 4H), 5.08 (s, 2H), 4.45 (s, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 193.5, 147.0, 145.3, 142.6, 139.3, 130.7, 130.1, 130.1, 129.4, 128.5, 128.4, 126.4, 119.8, 119.2, 111.3, 65.8, 47.2; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{19}\text{Cl}_2\text{N}_2\text{O}$ 409.0869; found, 409.0865.

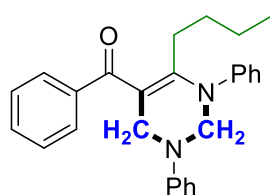


Diethyl 4,4'-(5-benzoylpyrimidine-1,3(2H,4H)-diyl)dibenzoate (3f). Compound **3f** was prepared in 55% yield (80 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 15/1); White solid; mp 120-122 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.03 (d, $J = 8.7$ Hz, 2H), 7.90 (d, $J = 8.8$ Hz, 2H), 7.57-7.55 (m, 3H), 7.50-7.47 (m, 1H), 7.44-7.40 (m, 2H), 6.96-6.90 (m, 4H), 5.25 (s, 2H), 4.57 (s, 2H), 4.38-4.28 (m, 4H), 1.39-1.32 (m, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 193.6, 166.4, 165.8, 151.8, 147.0, 144.2, 139.0, 131.7, 131.4, 131.0, 128.6, 128.5, 126.1, 122.7, 116.8, 116.1, 113.0, 63.8, 61.2, 60.7, 47.0, 14.5, 14.5; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_5$ 485.2071; found, 485.2070.



(1,3-Diphenyl-1,2,3,4-tetrahydropyrimidin-5-yl)(furan-2-yl)methanone (3g).¹¹

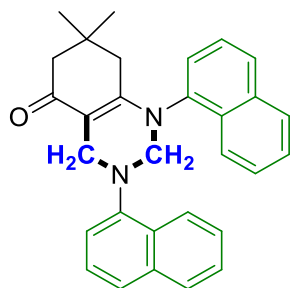
Compound **3g** was prepared in 83% yield (82mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 12/1); White solid; mp 104-107 °C; ^1H NMR (500 MHz, CDCl_3): δ 8.38 (s, 1H), 7.51 (s, 1H), 7.42-7.39 (m, 2H), 7.23-7.17 (m, 3H), 7.09-7.06 (m, 3H), 6.98 (d, $J = 8.1$ Hz, 2H), 6.91-6.88 (m, 1H), 6.49-6.48 (m, 1H), 5.16 (s, 2H), 4.48 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 177.9, 153.8, 148.6, 144.7, 144.5, 144.3, 130.0, 129.4, 124.7, 121.3, 118.8, 118.0, 116.0, 111.6, 110.1, 65.7, 47.0; Analytical data for **3g** were consistent with our previous reports.¹¹



3h

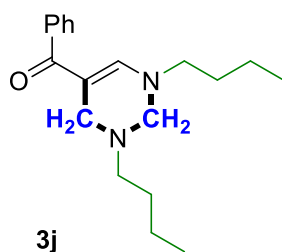
(6-Butyl-1,3-diphenyl-1,2,3,4-tetrahydropyrimidin-5-yl)(phenyl)methanone (3h).¹¹

Compound **3h** was prepared in 81% yield (96 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 7.68-7.66 (m, 2H), 7.46-7.40 (m, 3H), 7.34-7.31 (m, 2H), 7.25-7.21 (m, 3H), 7.03 (d, $J = 7.2$ Hz, 2H), 6.92 (d, $J = 7.9$ Hz, 2H), 6.89-6.87 (m, 1H), 4.89 (s, 2H), 4.32 (s, 2H), 2.11 (t, $J = 8.0$ Hz, 2H), 1.15-1.09 (m, 2H), 0.76-0.68 (m, 2H), 0.46 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 196.3, 157.0, 148.4, 144.6, 142.5, 130.8, 129.5, 129.3, 128.4, 128.0, 127.4, 126.8, 120.6, 117.3, 109.4, 70.6, 49.9, 30.8, 30.7, 22.3, 13.3; Analytical data for **3h** were consistent with our previous reports.¹¹



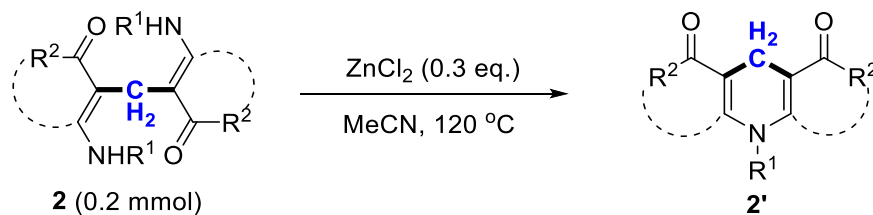
3i

7,7-Dimethyl-1,3-di(naphthalen-1-yl)-2,3,4,6,7,8-hexahydroquinazolin-5(1H)-one (**3i**). Compound **3i** was prepared in 80% yield (104 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 4/1); Yellow solid; mp 171-173 °C; ^1H NMR (500 MHz, CDCl_3): δ 8.09 (d, $J = 8.2$ Hz, 1H), 7.82-7.76 (m, 3H), 7.62 (d, $J = 8.1$ Hz, 1H), 7.46-7.30 (m, 9H), 4.92 (s, 2H), 4.53 (d, $J = 16.3$ Hz, 1H), 4.45 (d, $J = 16.3$ Hz, 1H), 2.36-2.29 (m, 2H), 2.15 (d, $J = 16.8$ Hz, 1H) 1.79 (d, $J = 12.5$ Hz, 1H), 0.99 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 193.8, 158.3, 146.3, 138.8, 135.0, 134.6, 131.0, 128.7, 128.6, 128.6, 128.5, 127.4, 126.9, 126.0, 125.9, 125.8, 125.7, 125.7, 124.4, 123.4, 122.4, 116.7, 105.0, 71.9, 50.3, 47.9, 40.7, 32.6, 29.1, 27.9; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}$ 433.2274; found, 433.2269.

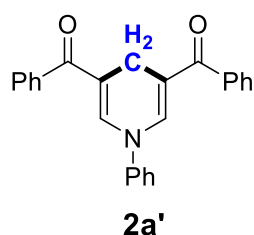


(1,3-Dibutyl-1,2,3,4-tetrahydropyrimidin-5-yl)(phenyl)methanone (**3j**). Compound **3j** was prepared in 75% yield (67 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.38 (m, 5H), 7.06 (s, 1H), 3.99 (s, 2H), 3.68 (s, 2H), 3.09 (t, $J = 6.8$ Hz, 2H), 2.53 (t, $J = 7.1$ Hz, 2H), 1.56-1.48 (m, 4H), 1.40-1.27 (m, 4H), 0.96-0.90 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.3, 150.5, 140.7, 129.6, 128.4, 128.1, 105.0, 67.3, 54.3, 53.1, 47.7, 31.1, 30.1, 20.7, 19.8, 14.1, 13.7; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{29}\text{N}_2\text{O}$ 301.2274; found, 301.2272.

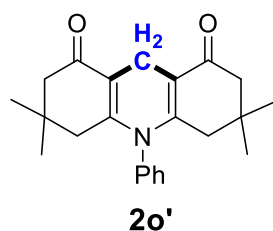
Synthesis and characterization of 1,4-dihydropyridines



In an oven-dried seal tube (25 mL) containing a magnetic stirring bar was added **2** (0.2 mmol) and ZnCl₂ (8.2 mg, 0.06 mmol). Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under a stream of Ar, to this vessel was added MeCN (3 mL). Then the vessel was sealed and stirred in a 120 °C oil bath for the corresponding time (see Scheme 2). The reaction could be monitored by TLC analysis. The resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly, using petroleum ether/ethyl acetate/dichloromethane/Et₃N as the eluent.

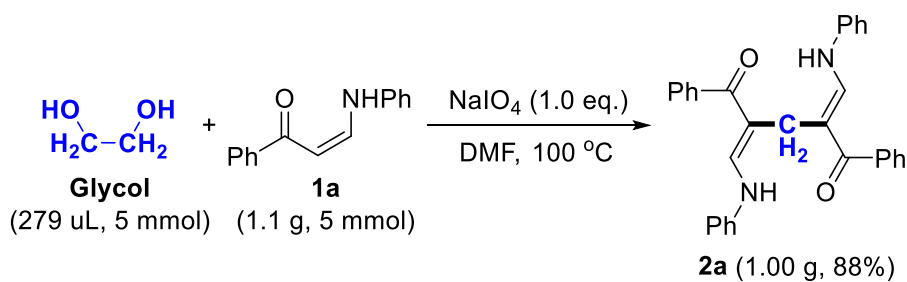


(1-Phenyl-1,4-dihydropyridine-3,5-diyl)bis(phenylmethanone) (**2a'**). Compound **2a'** was prepared in 70% yield (56 mg) according to the general procedure. $R_f = 0.2$ ((petroleum ether/ethyl acetate/dichloromethane/Et₃N = 100/10/10/1); Yellow solid; mp 142-144 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.63-7.62 (m, 4H), 7.51-7.48 (m, 2H), 7.45-7.42 (m, 4H), 7.37-7.34 (m, 2H), 7.24-7.21 (m, 1H), 7.17 (s, 2H), 7.06 (d, $J = 7.7$ Hz, 2H), 3.65 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 194.9, 143.2, 141.6, 139.1, 131.2, 130.2, 128.6, 128.5, 126.8, 120.9, 117.4, 21.9; Analytical data for **2a'** were consistent with our previous reports.¹⁰



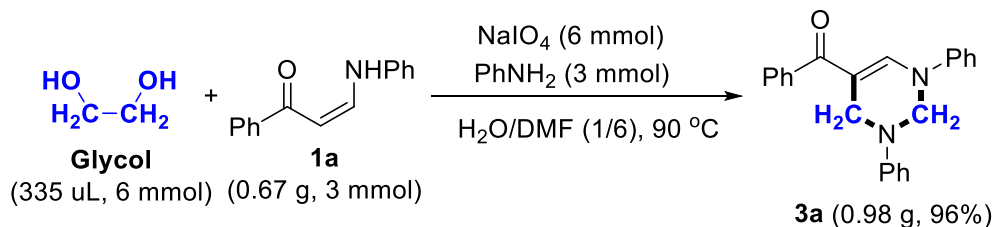
3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (**2o'**). Compound **2o'** was prepared in 64% yield (45 mg) according to the general procedure. $R_f = 0.2$ (petroleum ether/ethyl acetate/dichloromethane/Et₃N = 100/10/10/1); Yellow solid; mp 248-250 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.51-7.49 (m, 3H), 7.16 (d, $J = 7.7$ Hz, 2H), 3.22 (s, 2H), 2.20 (s, 4H), 1.78 (s, 4H), 0.91 (s, 12H); ¹³C NMR (125 MHz, CDCl₃): δ 196.8, 151.0, 139.4, 130.1, 130.2, 130.0, 129.3, 110.96, 50.1, 42.0, 32.4, 28.4, 18.6; Analytical data for **2o'** were consistent with our previous reports.¹⁰

Gram-Scale Preparation of 2a



In an oven-dried Schlenk tube (100 mL) containing a magnetic stirring bar was added **1a** (1.1 g, 5 mmol), NaIO₄ (1.1 g, 5 mmol). Then, the vessel was evacuated and refilled with Ar for three times. Under a stream of Ar, to this vessel were added DMF (25 mL) and ethylene glycol (279 μL , 5 mmol). Then the vessel was stirred in a 100 $^\circ\text{C}$ oil bath for about 5 hours. The reaction could be monitored by TLC analysis. Finally, H₂O (60 mL) was added to reaction system, and the resulting mixture was directly filtered and washed with H₂O (50 mL \times 6) to give pure products **2a** (1.00 g, 88%).

Gram-Scale Preparation of 3a

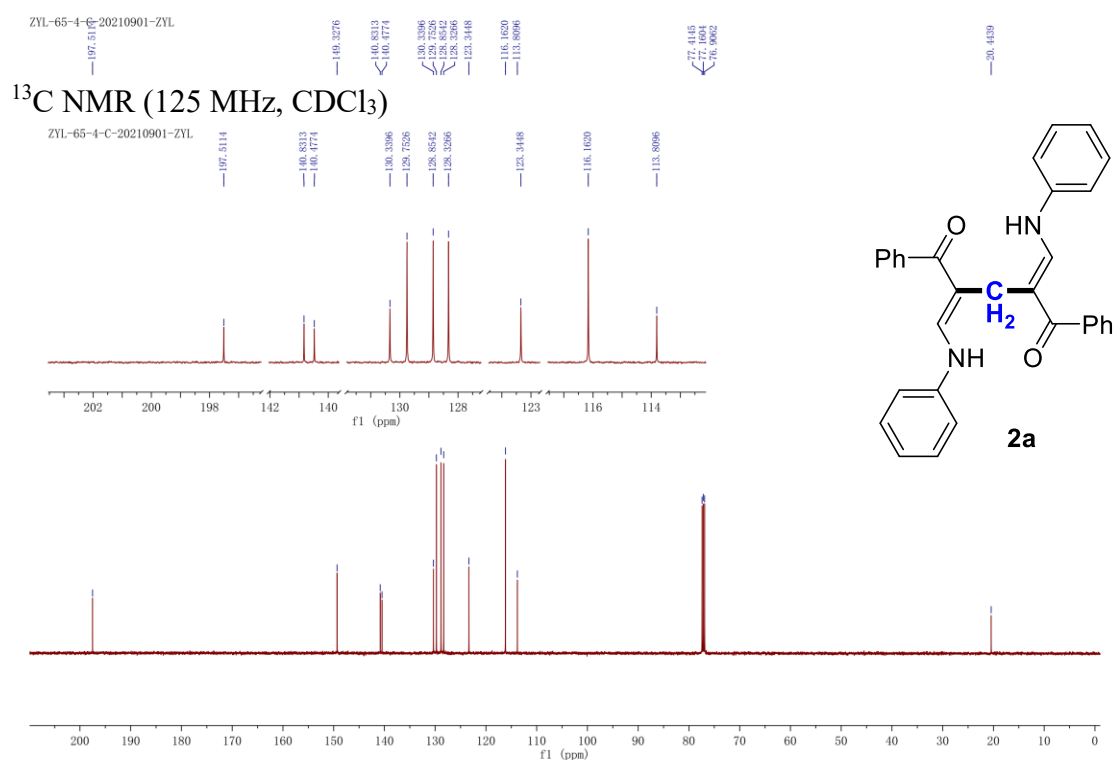
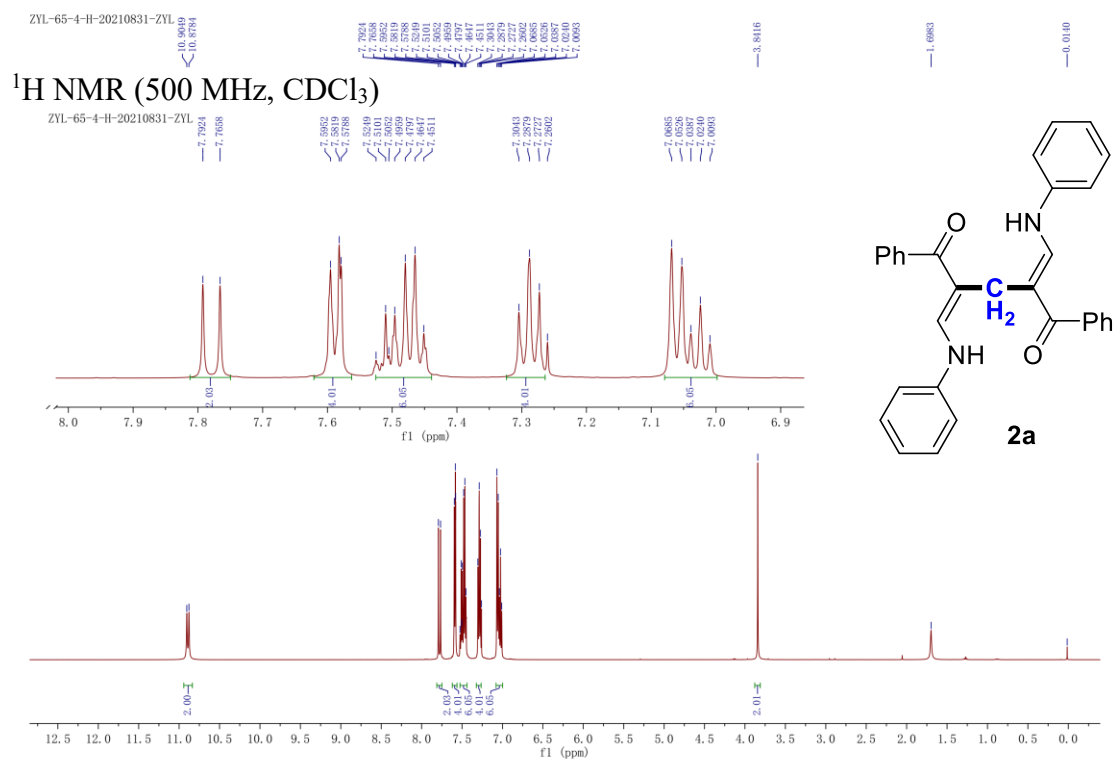


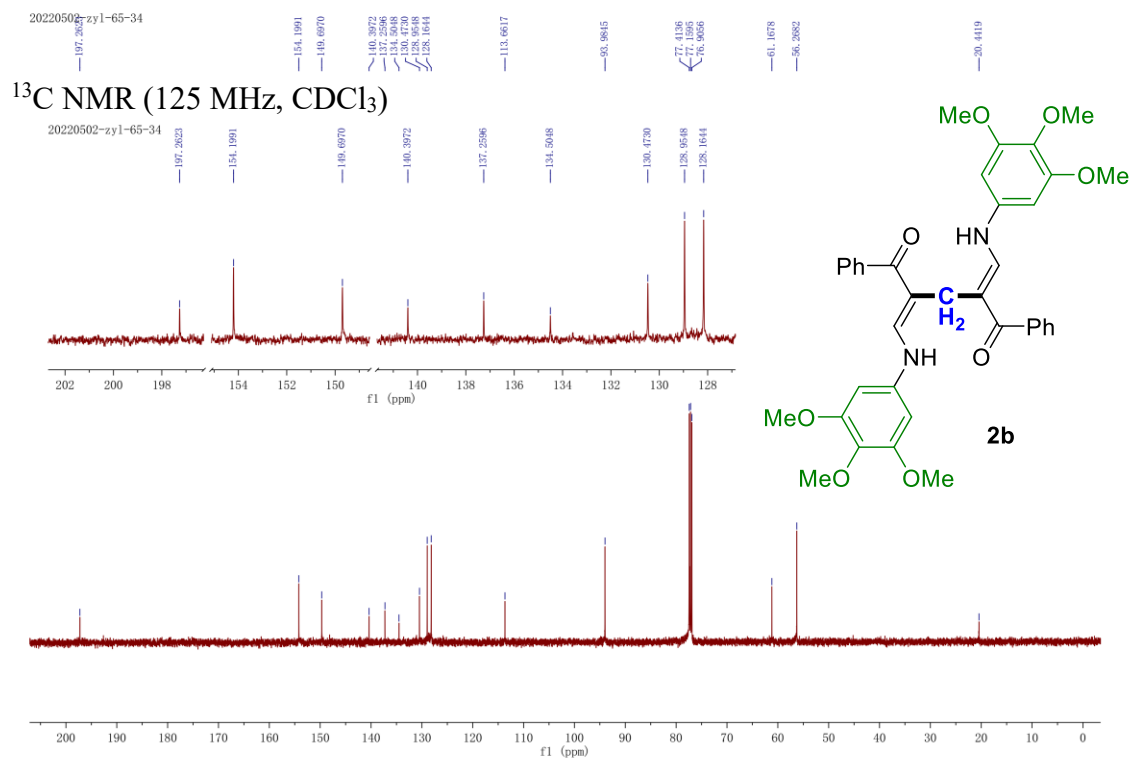
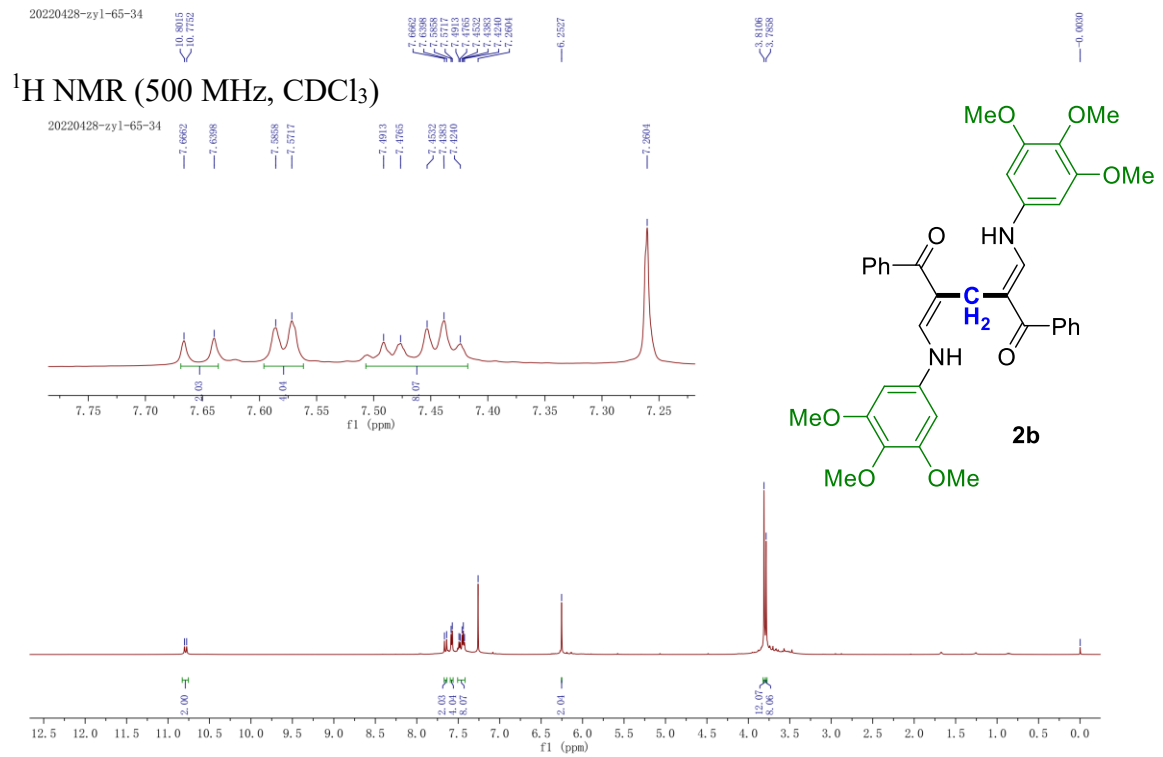
In an oven-dried Schlenk tube (100 mL) containing a magnetic stirring bar was added **1a** (0.67 g, 3 mmol), NaIO₄ (1.3 g, 6 mmol), H₂O/DMF (35 mL, v/v = 1/6) and ethylene glycol (335 μL , 6 mmol), PhNH₂ (273 μL , 3 mmol). Then the vessel was stirred in a 90 $^\circ\text{C}$ oil bath for about 4 hours. The reaction could be monitored by TLC analysis. Then, H₂O (50 mL) was added to reaction system, and the resulting mixture was directly filtered and washed with H₂O (50 mL \times 6) to give pure **3a** (0.98 g, 96%).

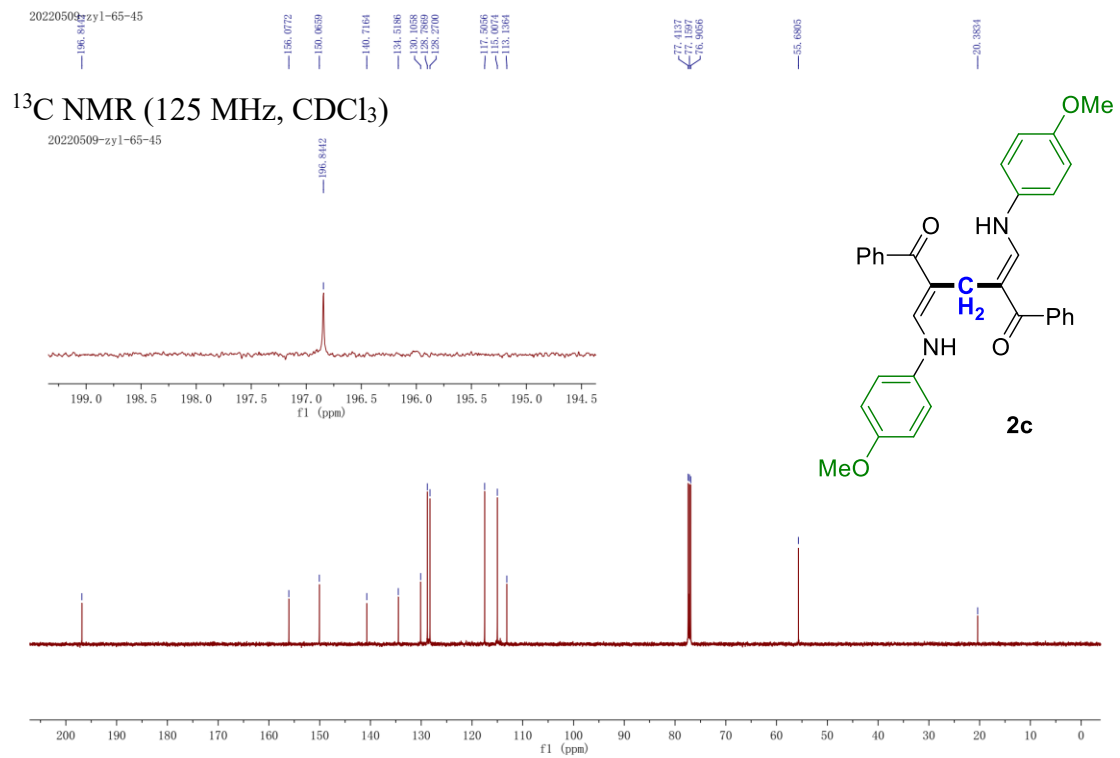
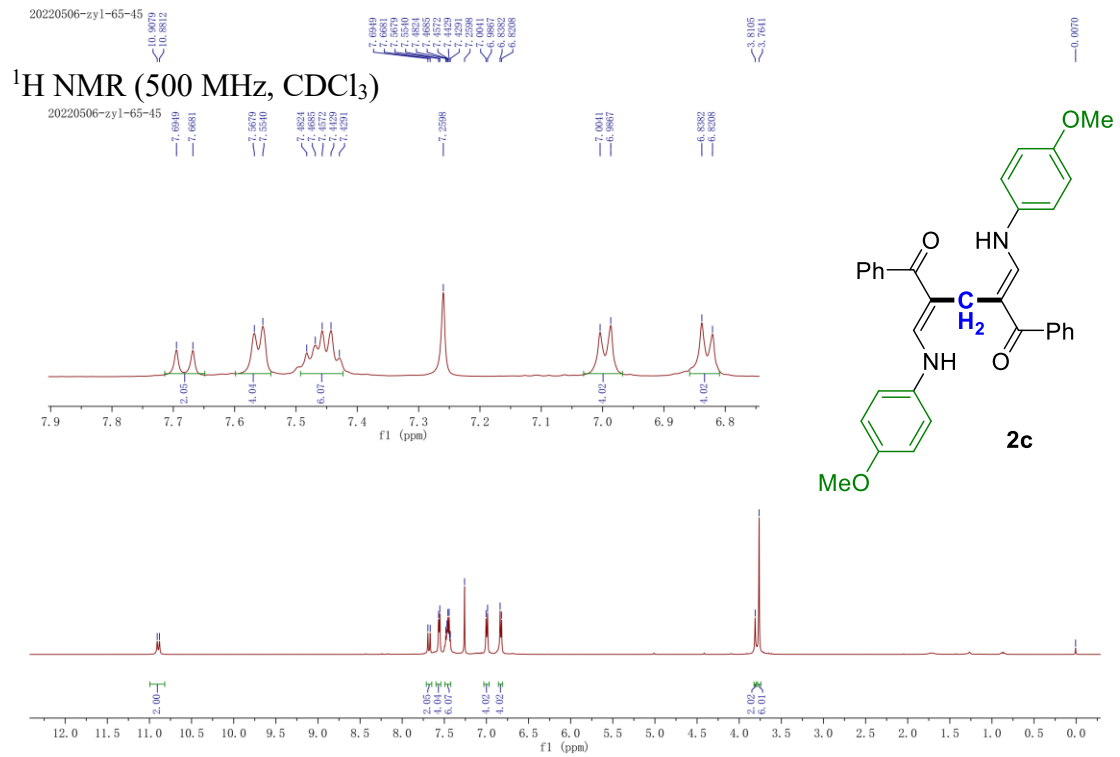
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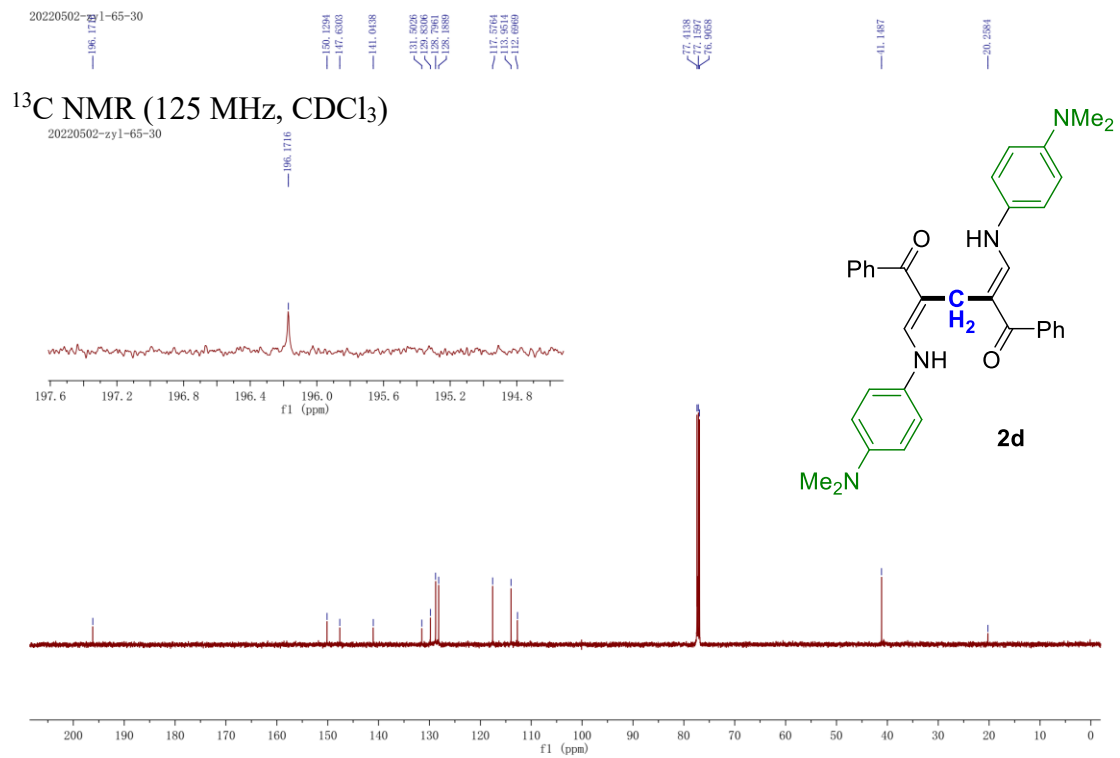
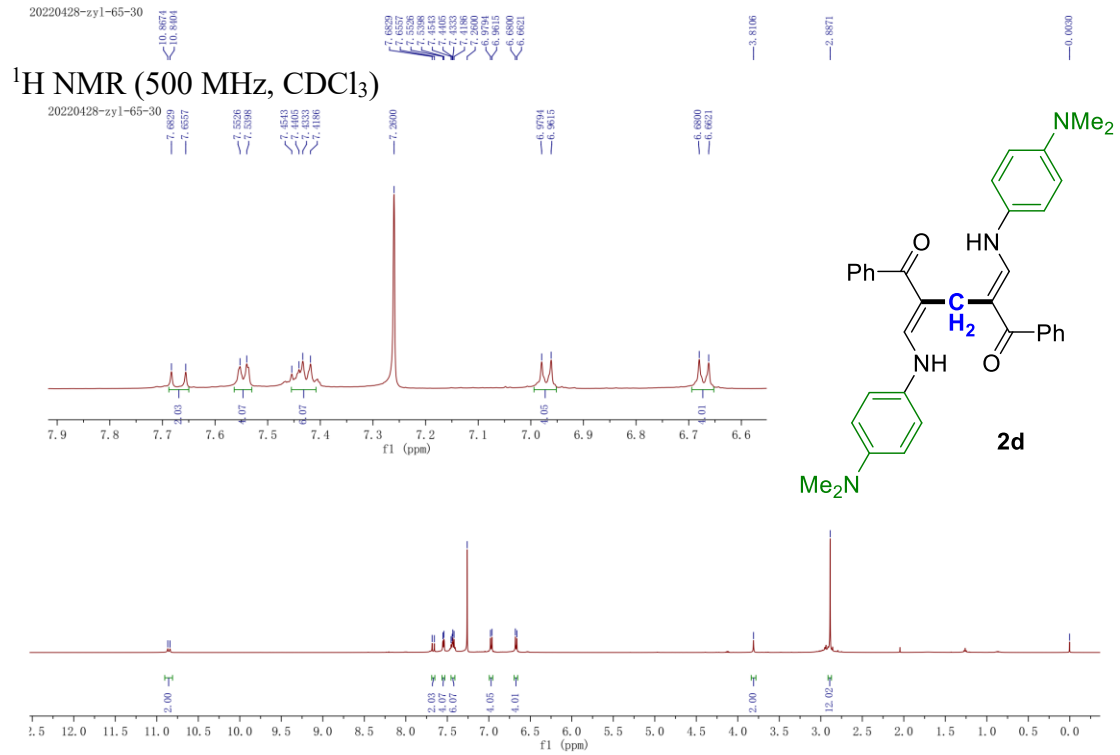
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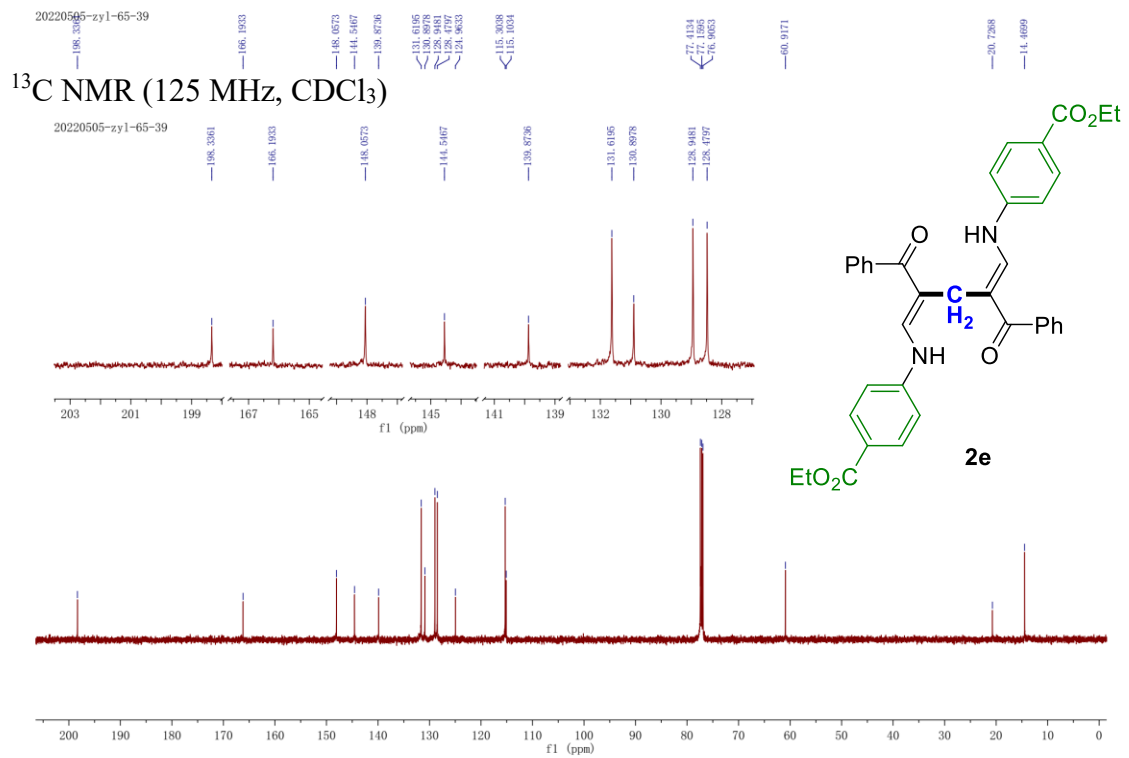
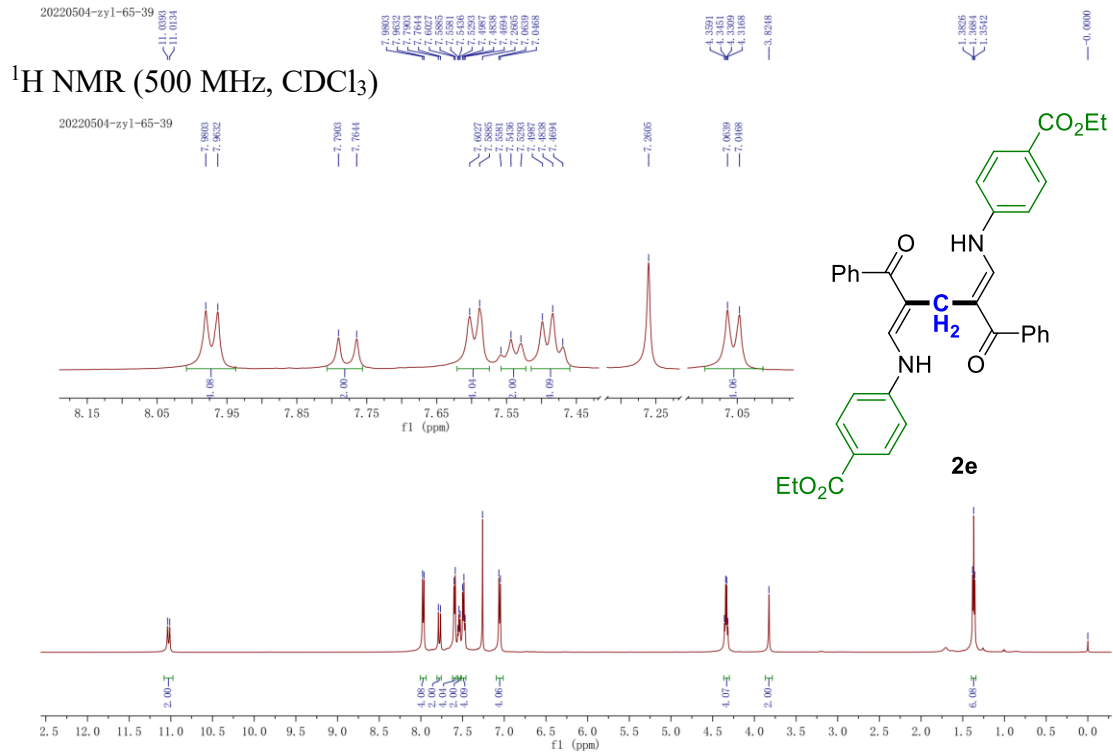
NMR spectra of compounds **2**

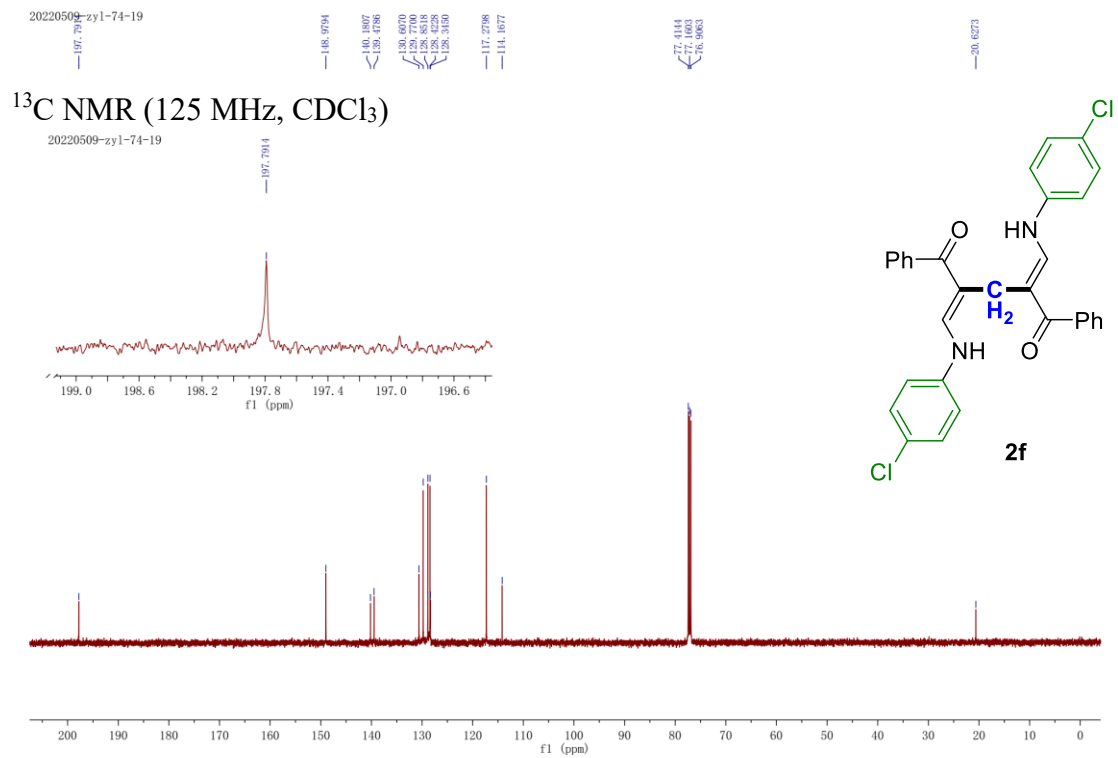
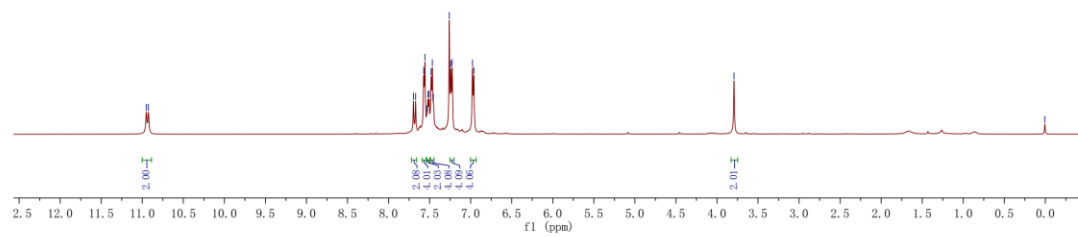
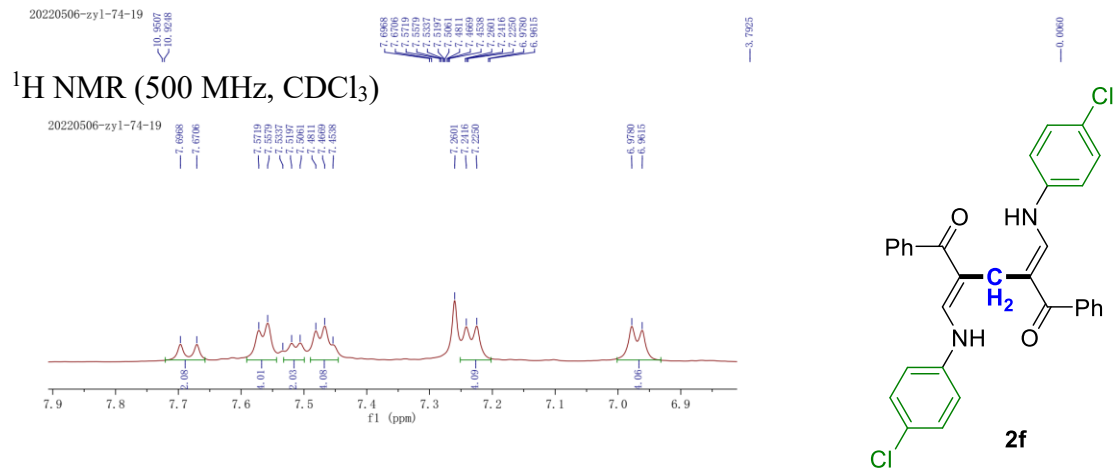


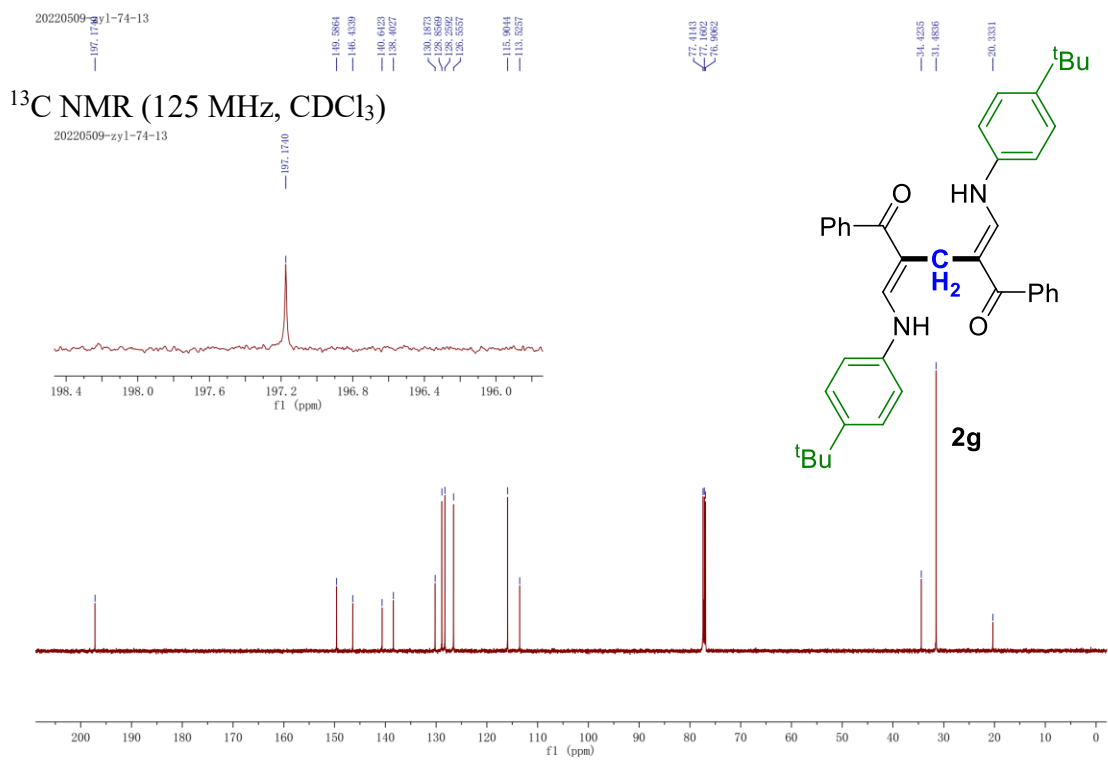
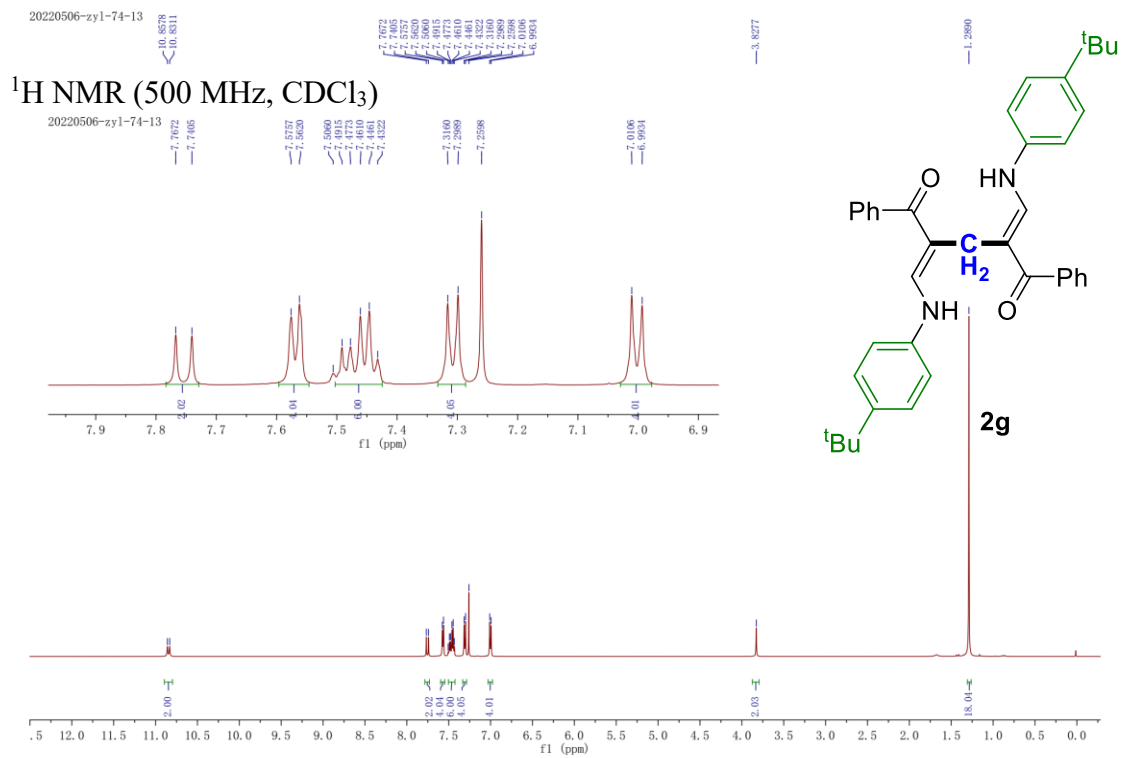


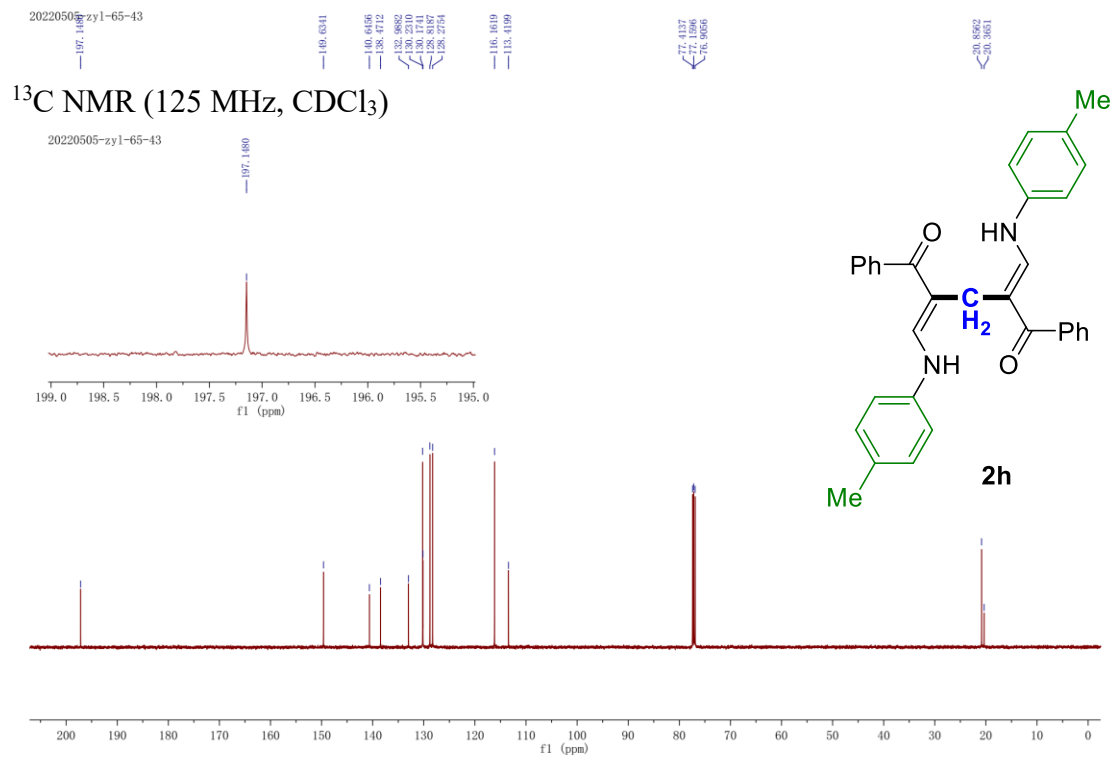
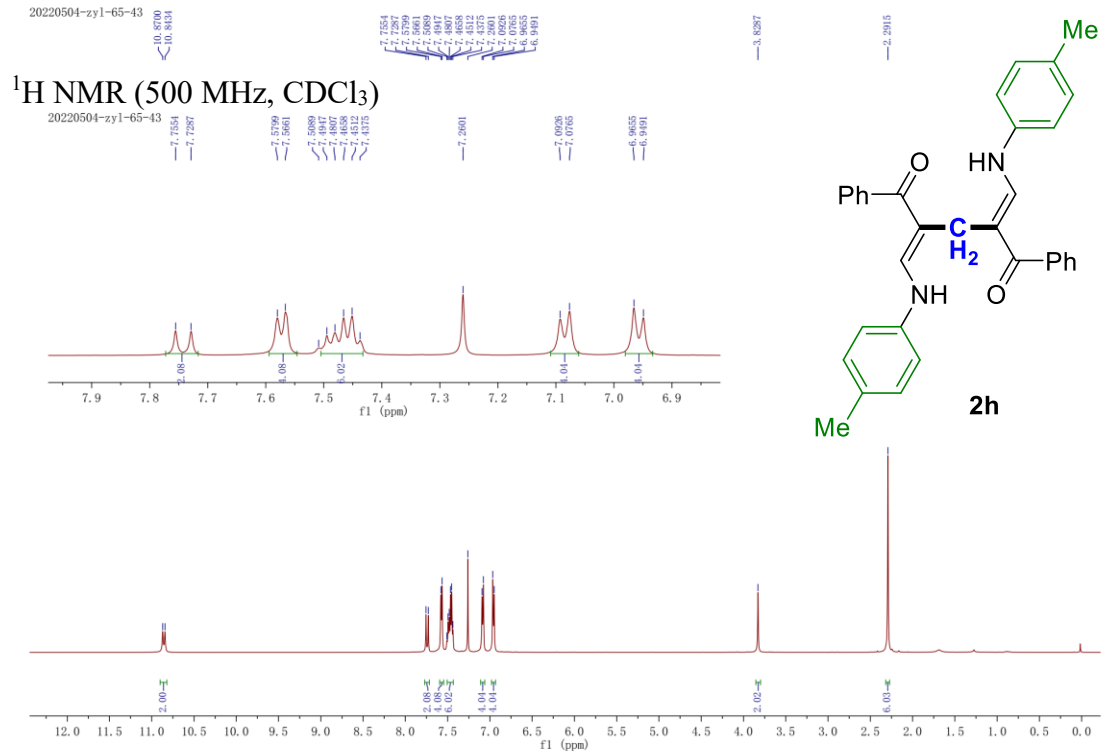


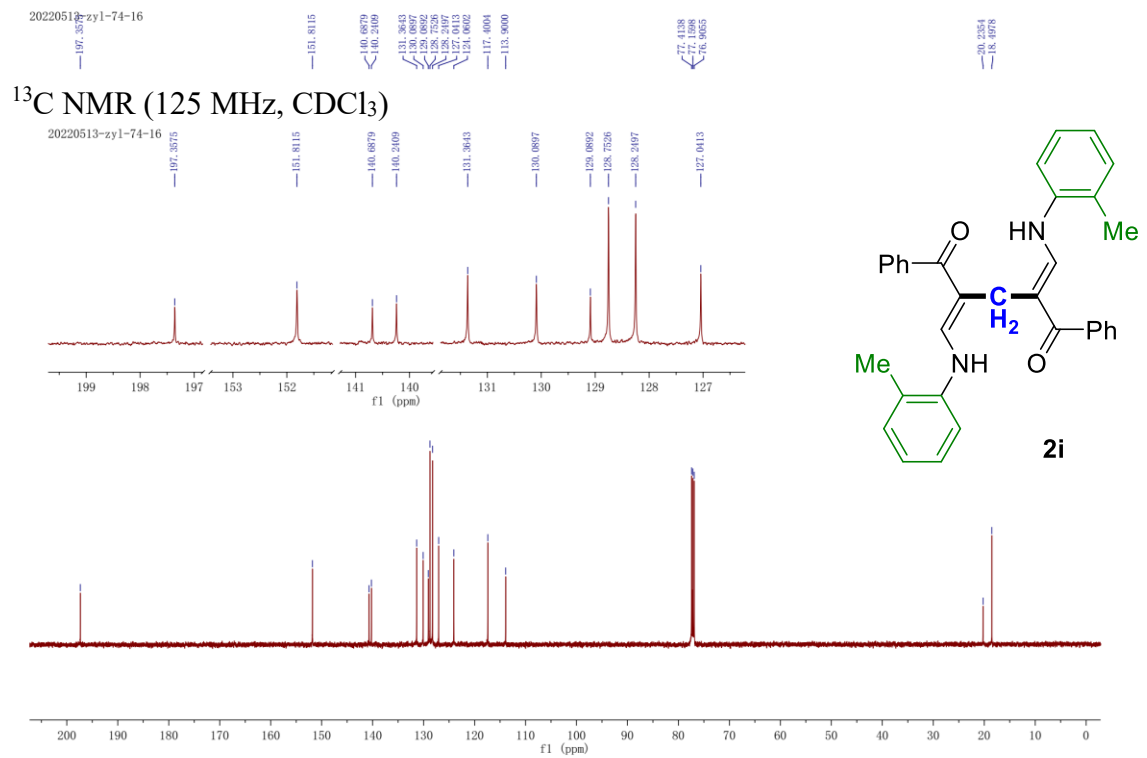
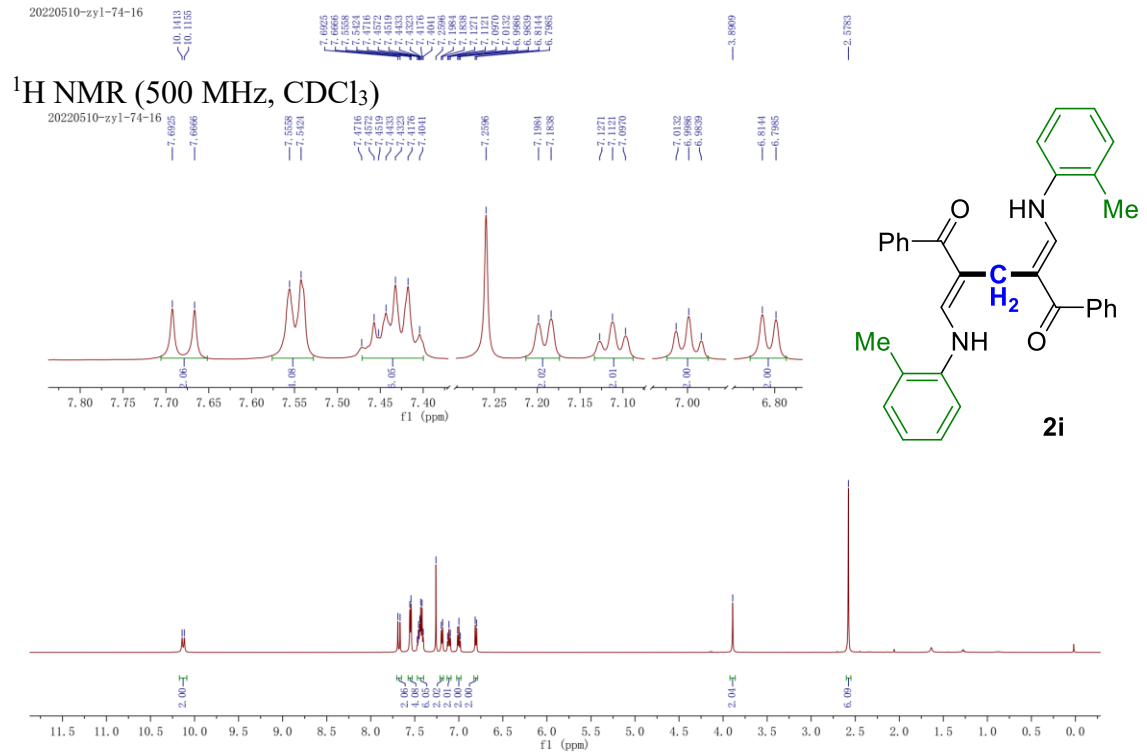


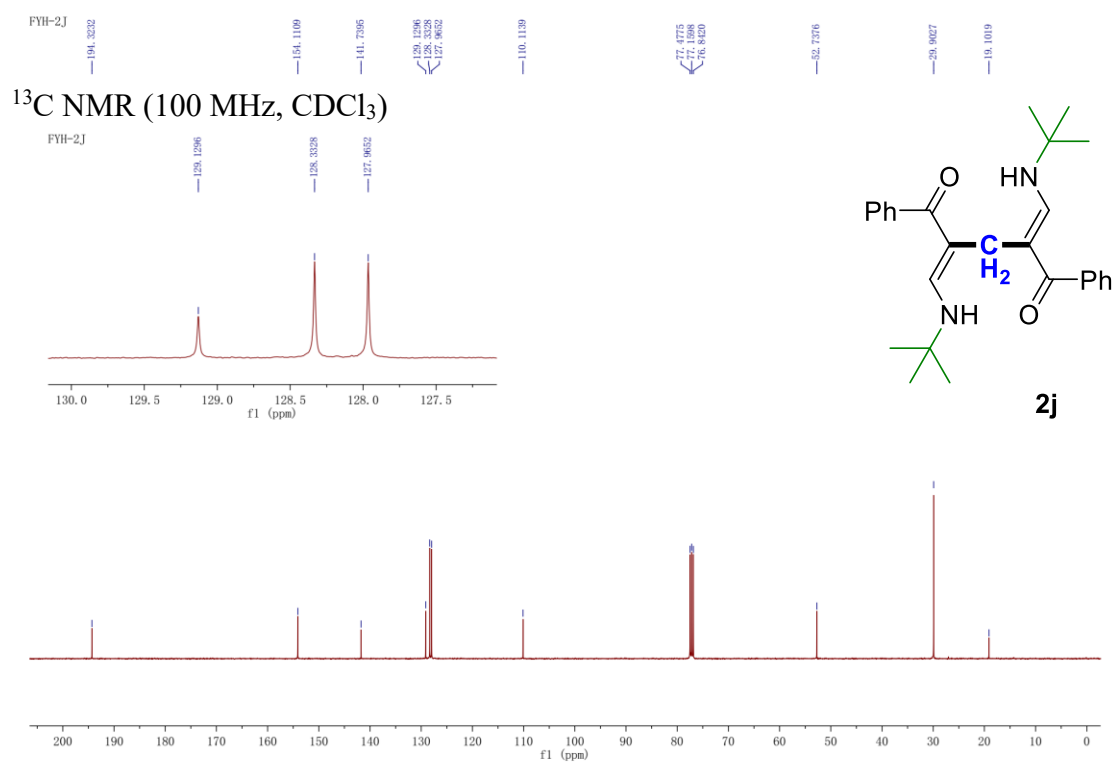
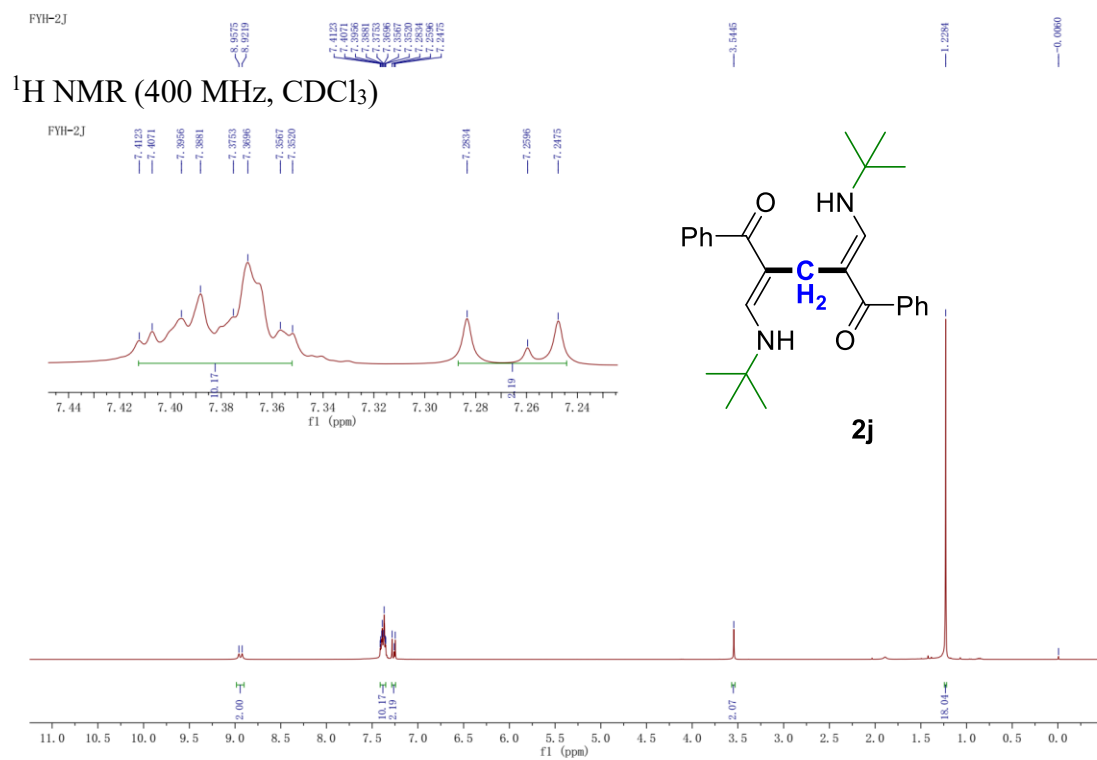




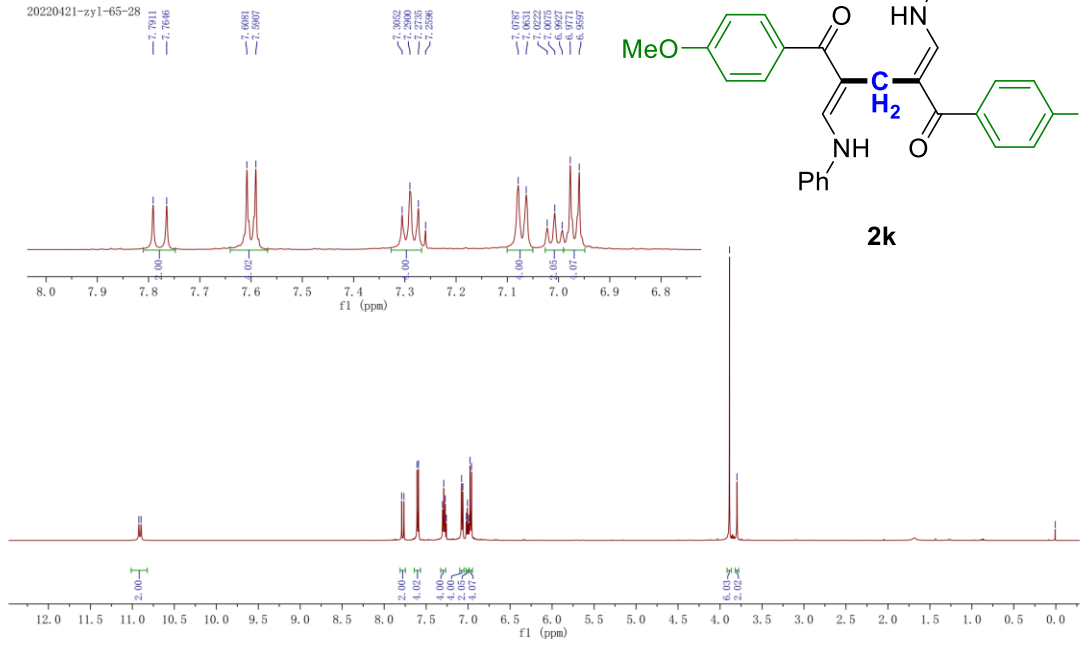




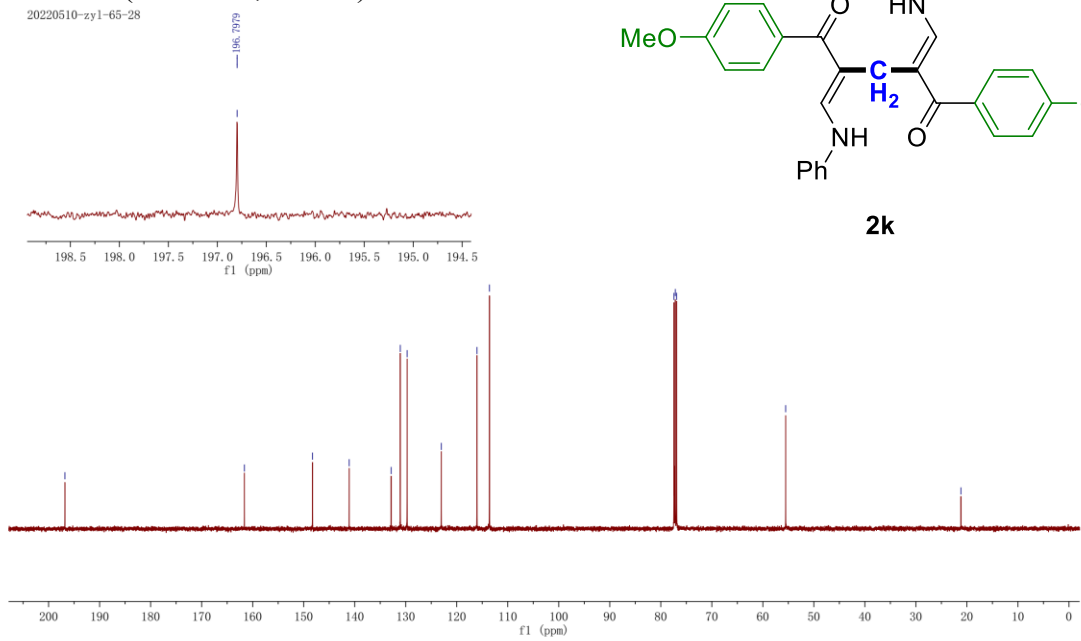


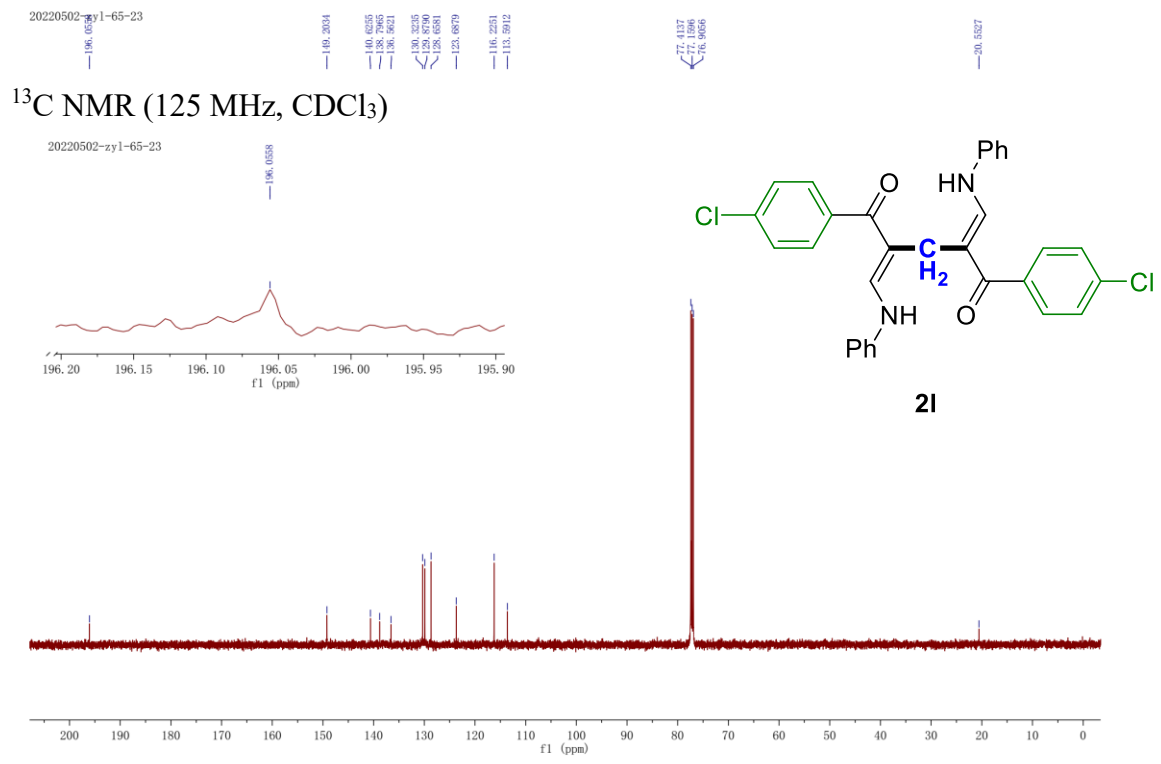
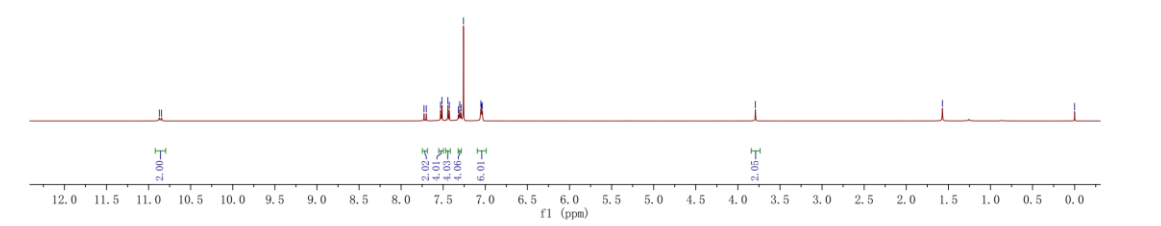
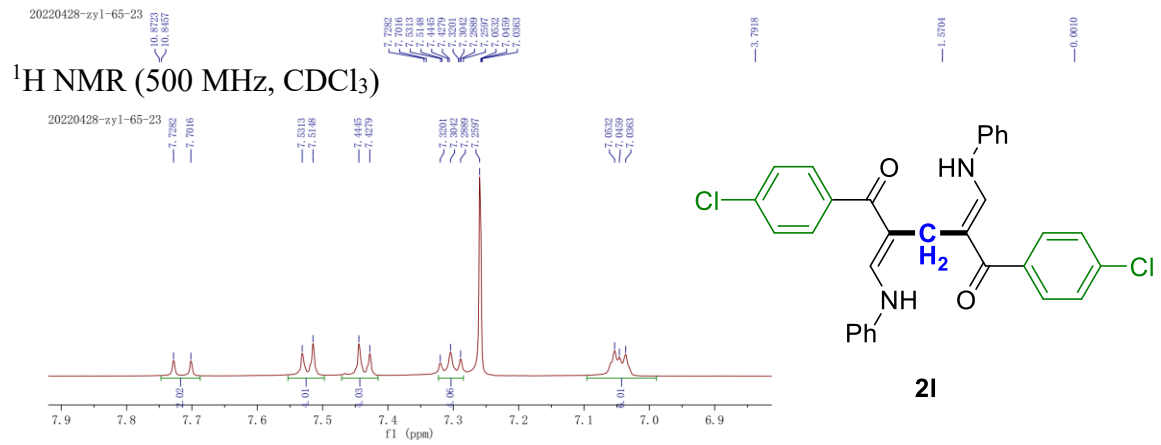


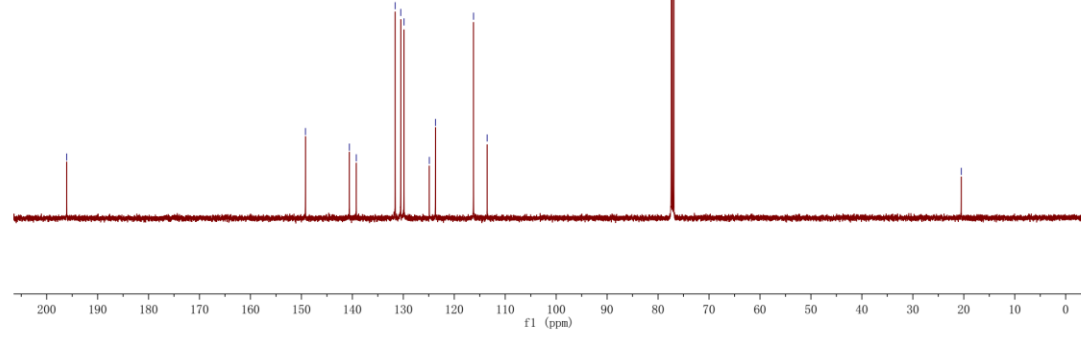
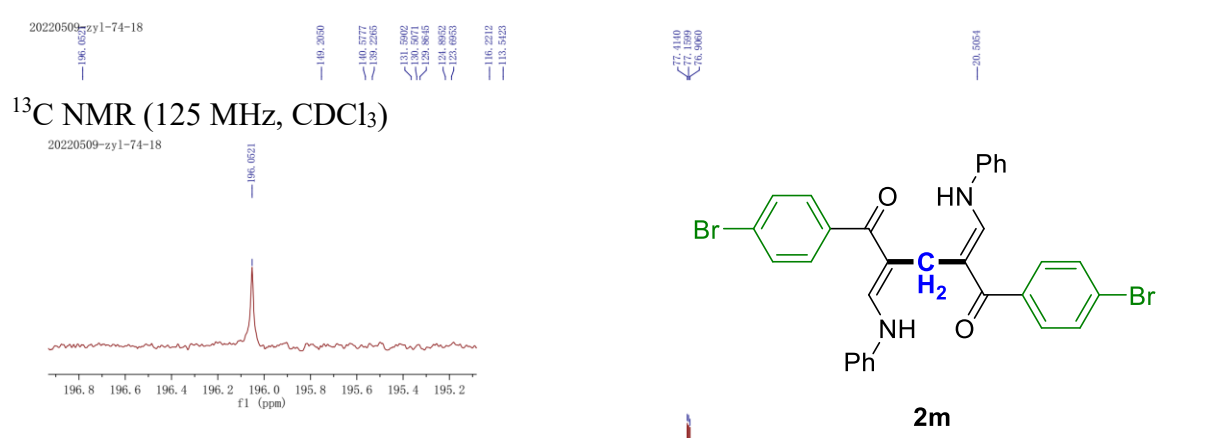
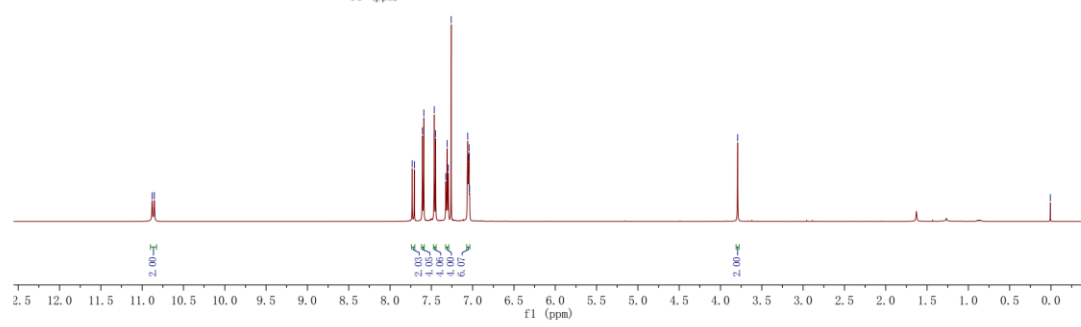
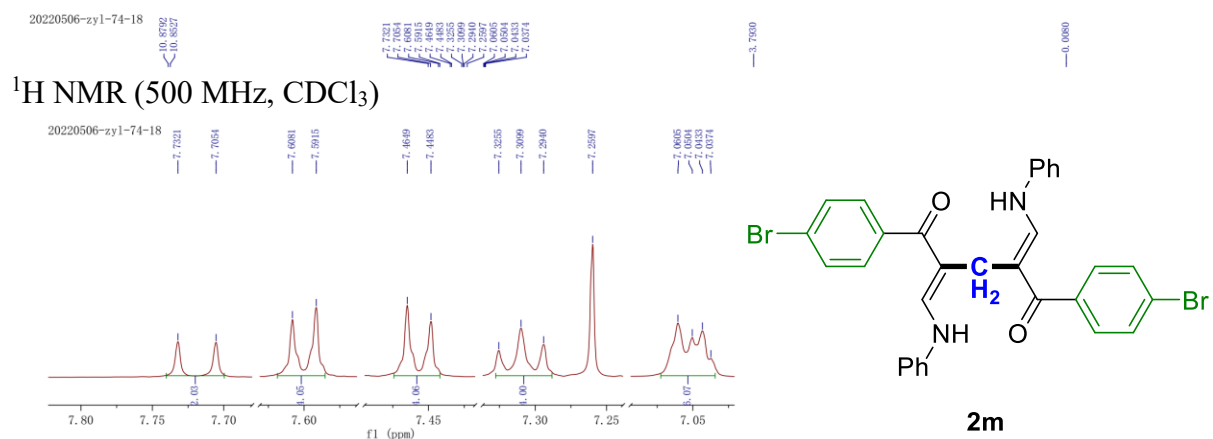
20220421-zyl-65-28
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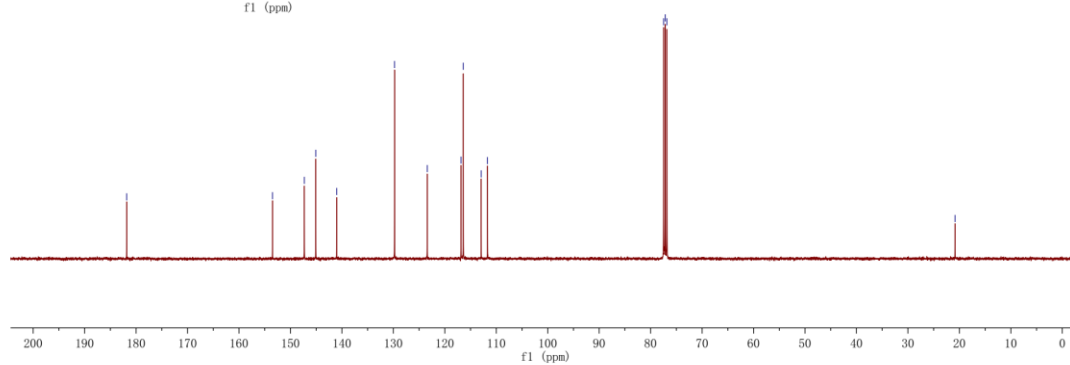
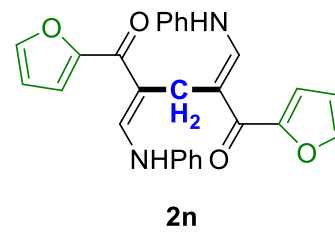
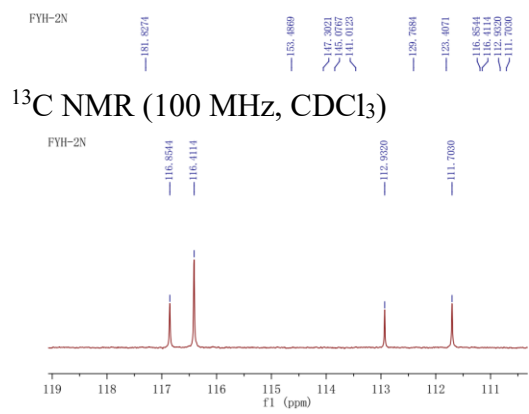
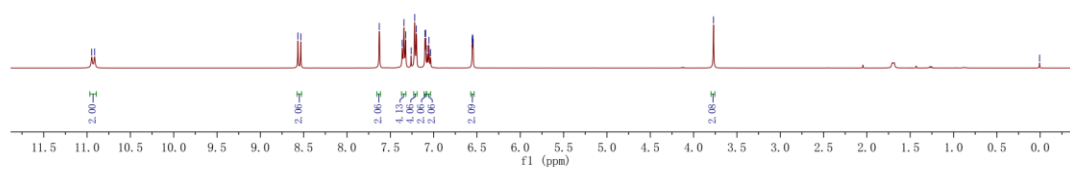
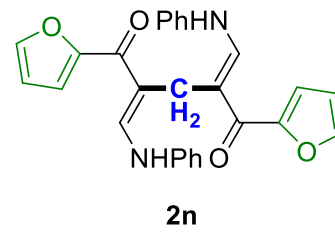
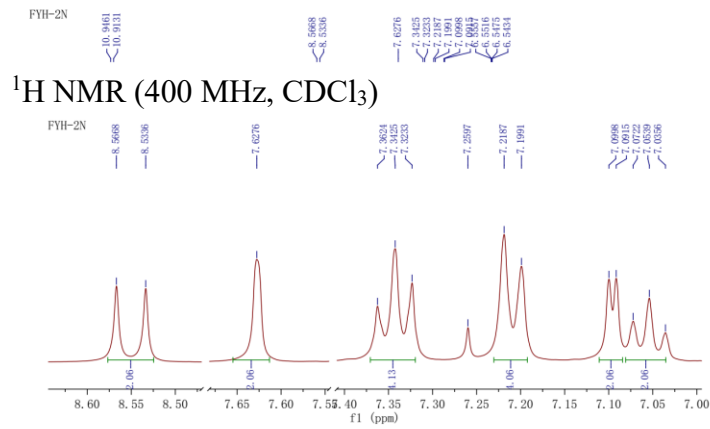


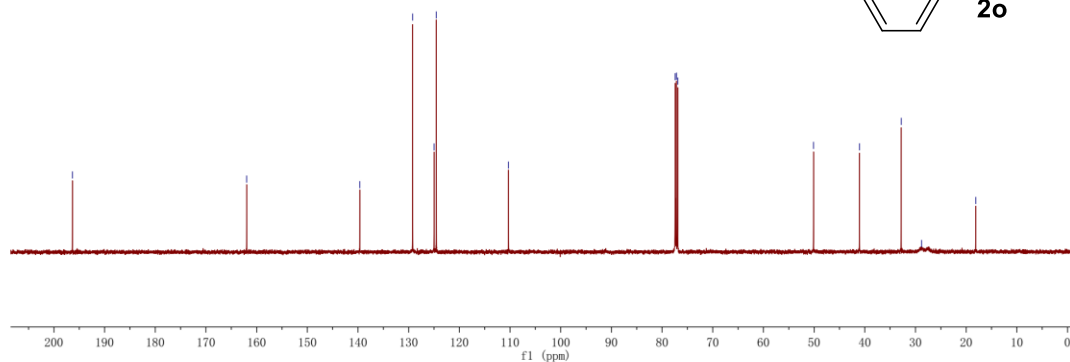
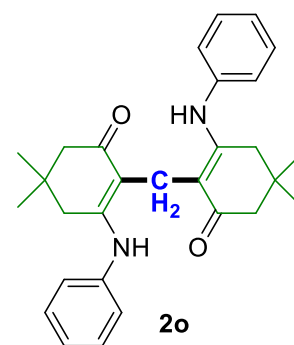
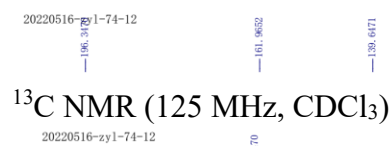
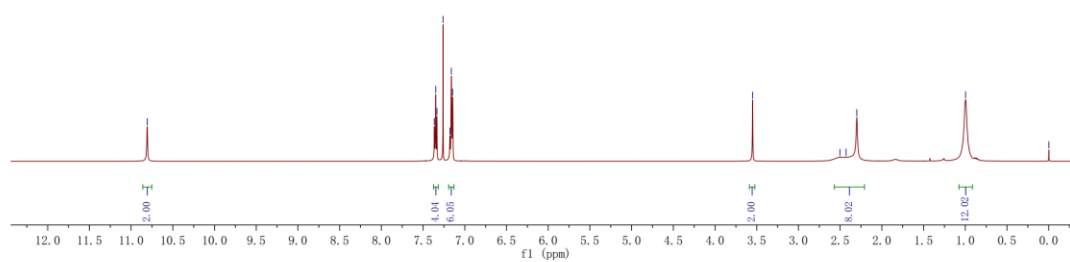
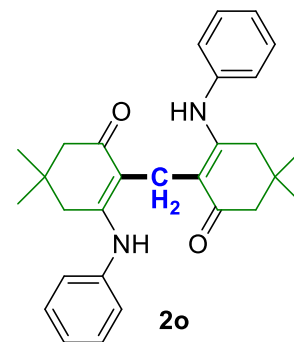
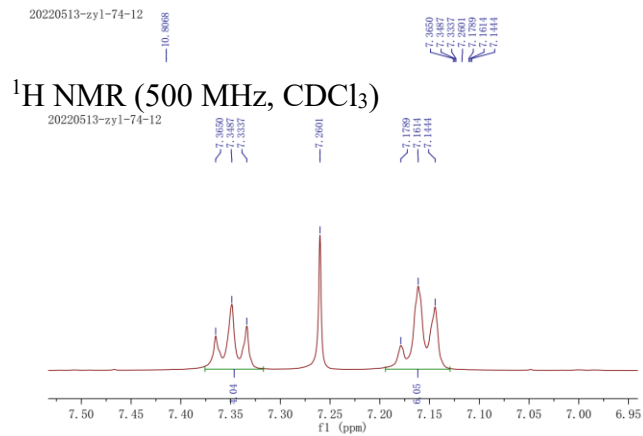
20220510-zyl-65-28
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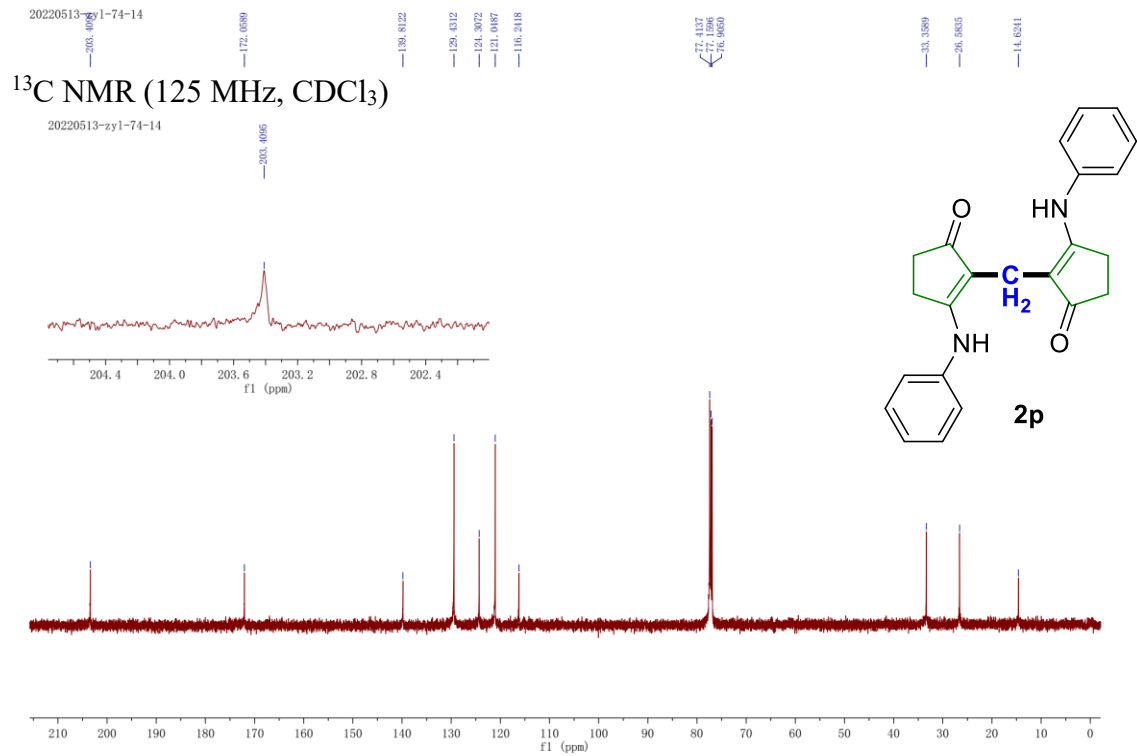
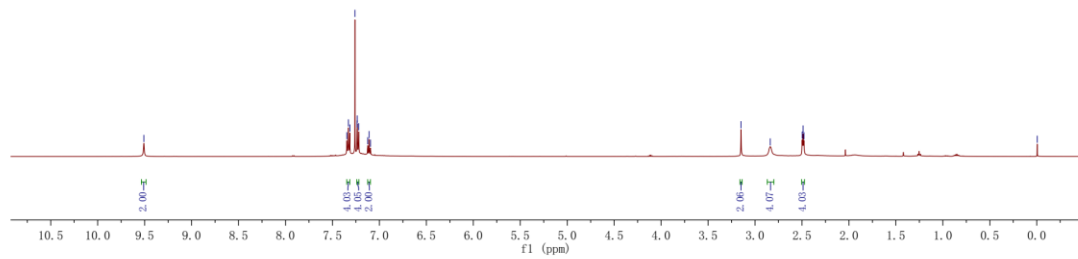
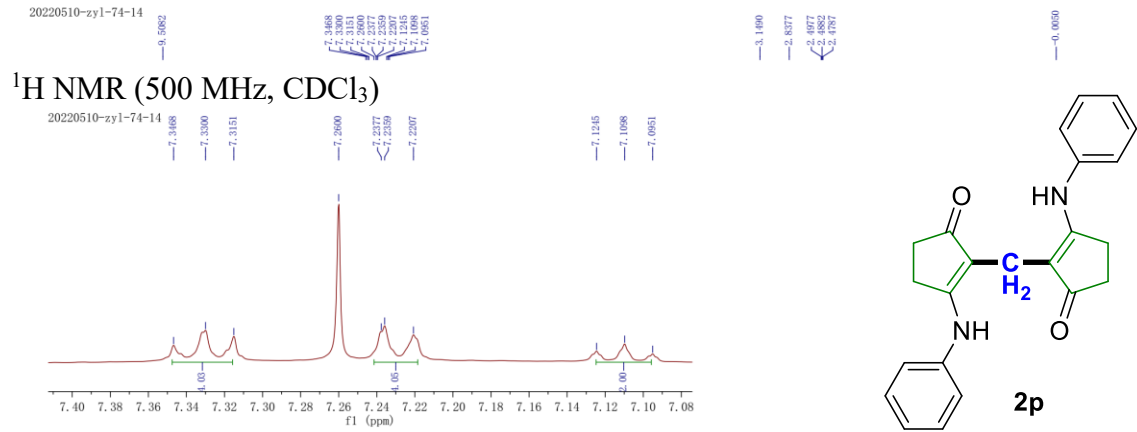


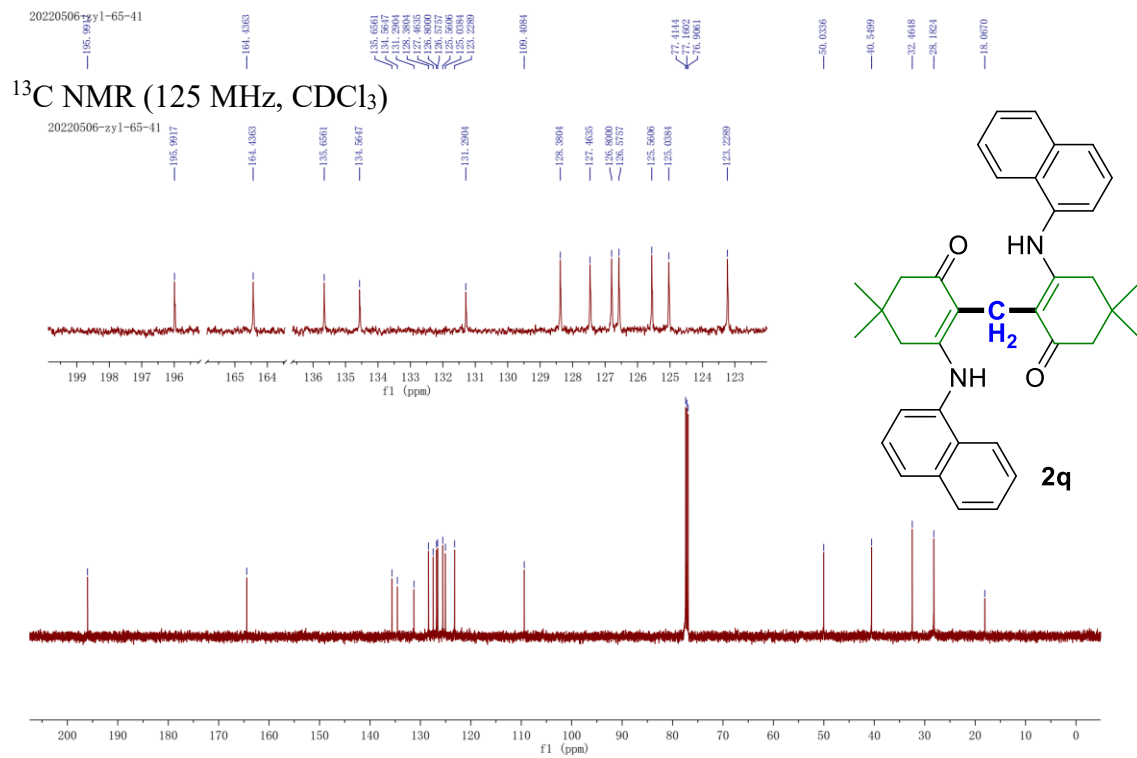
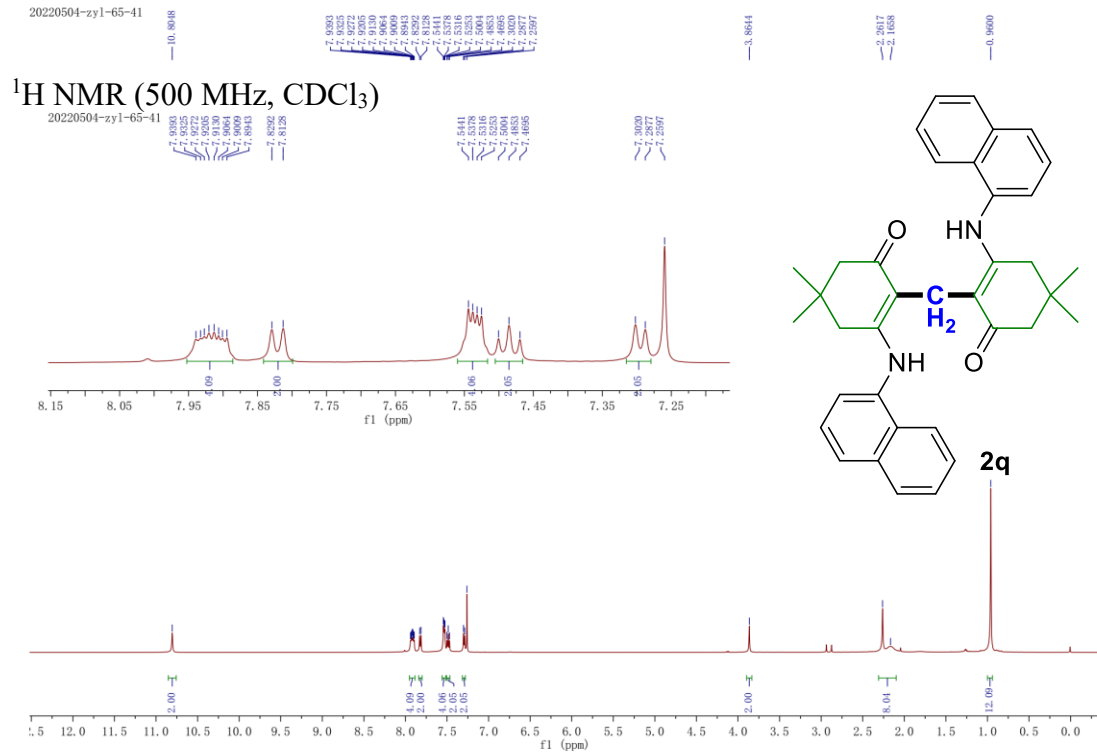


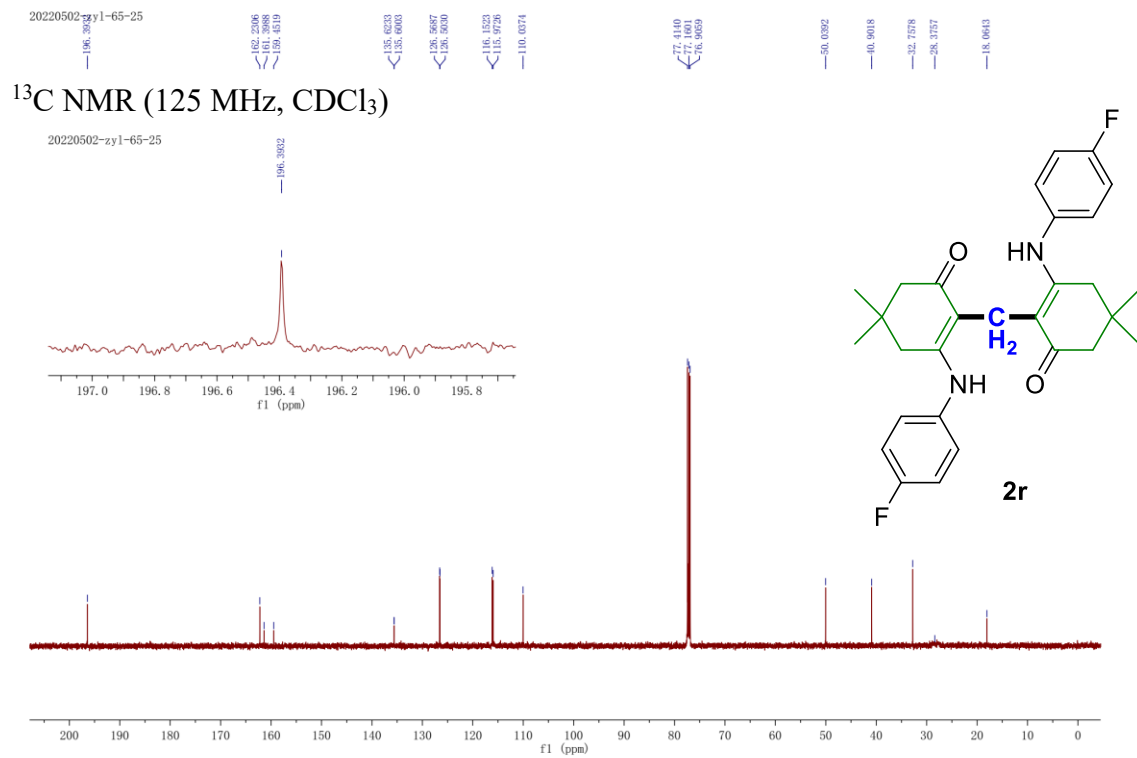
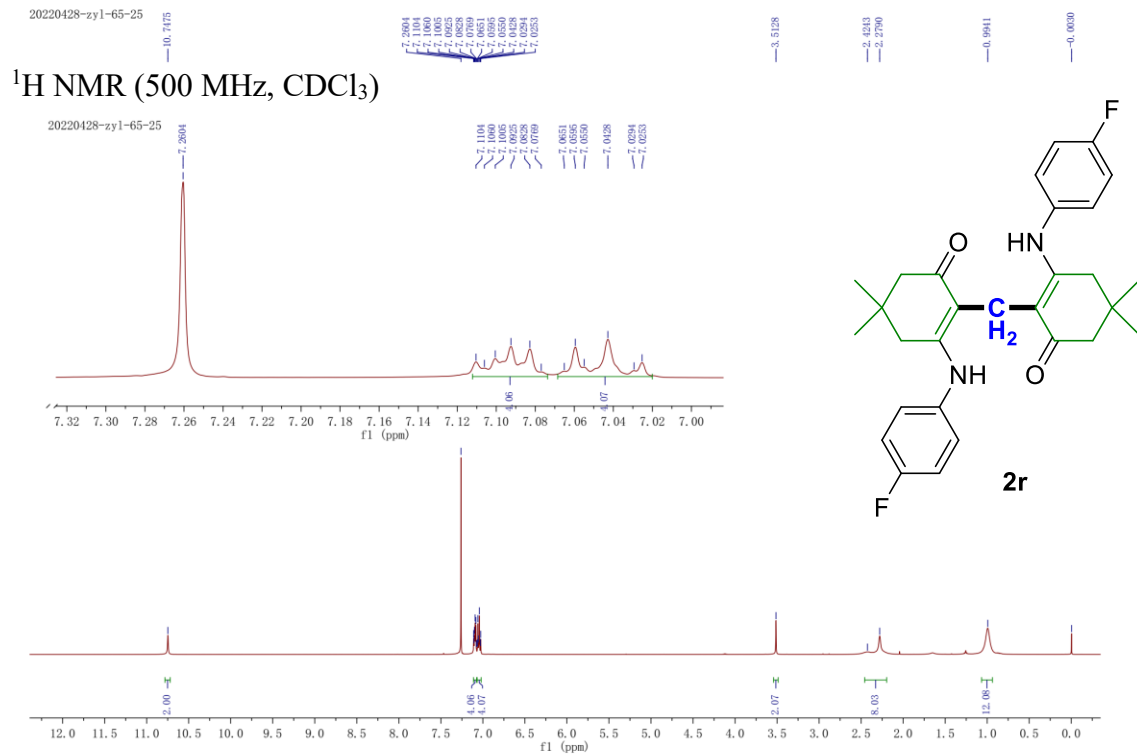


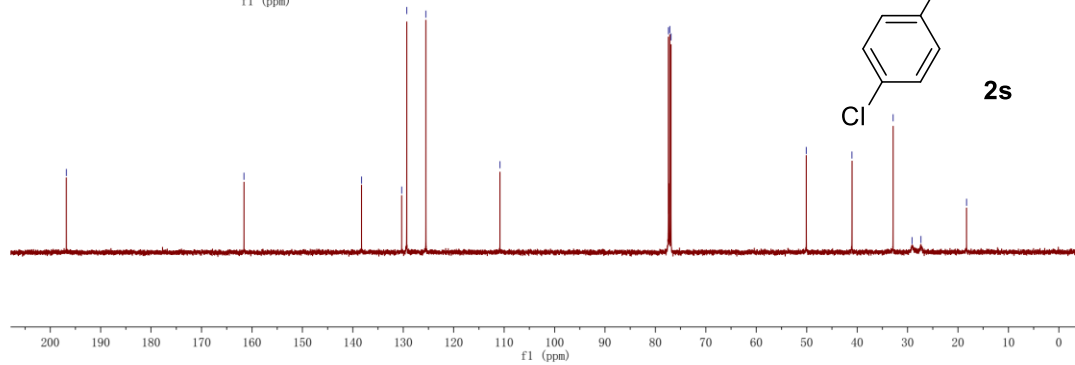
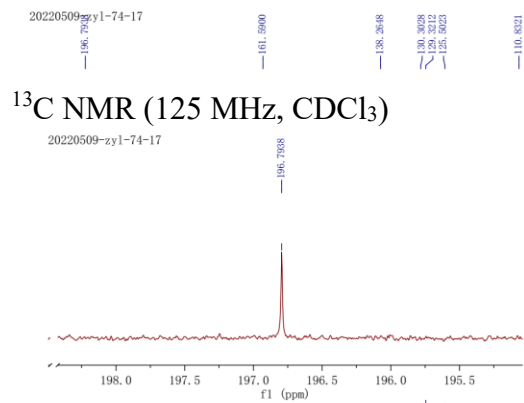
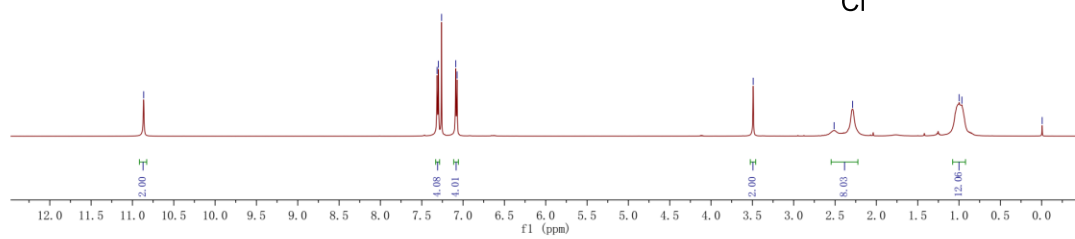
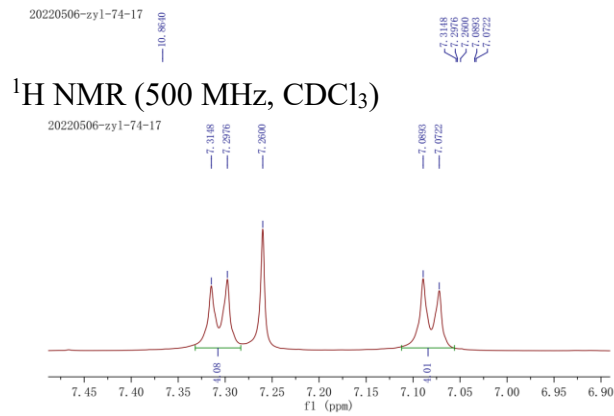








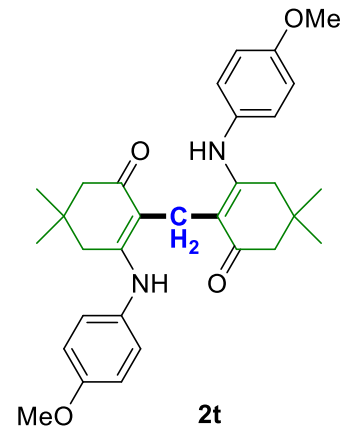
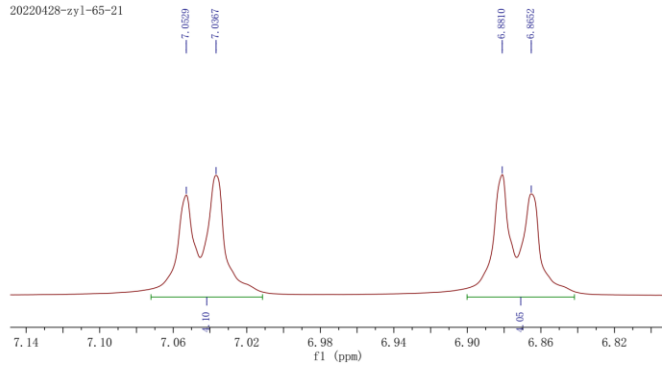




20220428-zy1-65-21

^1H NMR (500 MHz, CDCl_3)

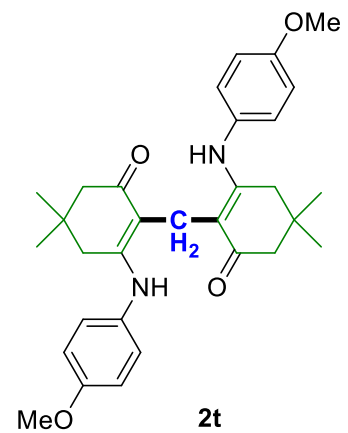
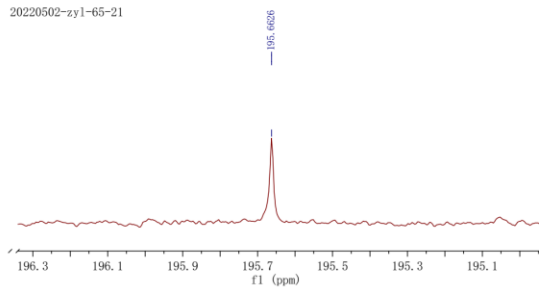
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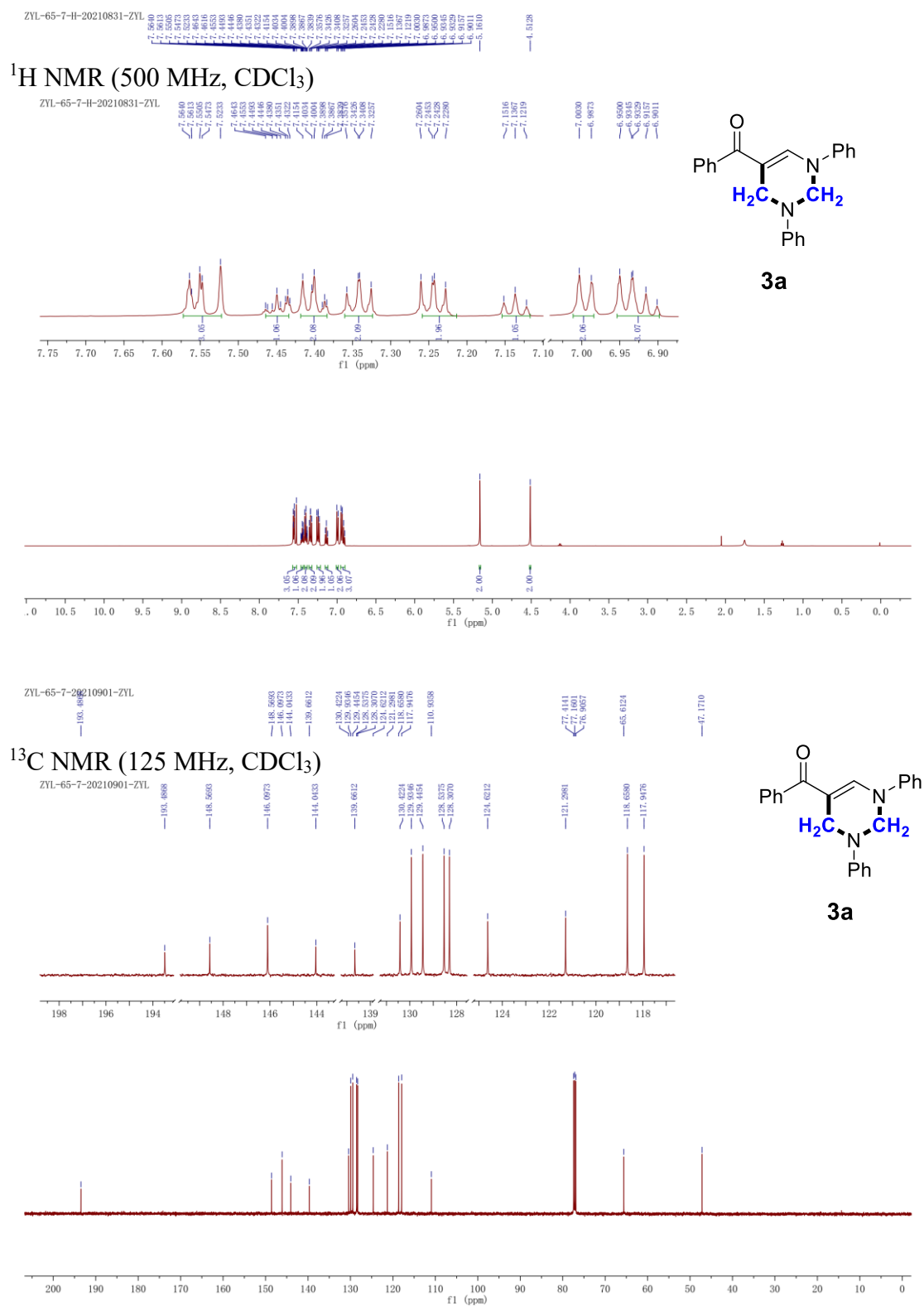
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^{13}C NMR (125 MHz, CDCl_3)

20220502-zy1-65-21

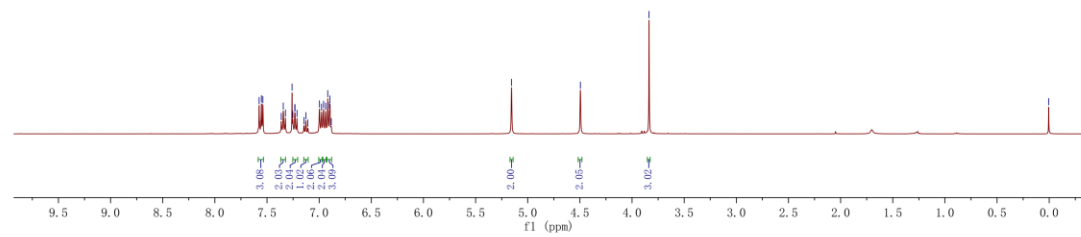
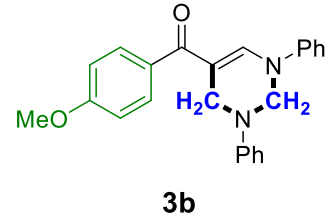
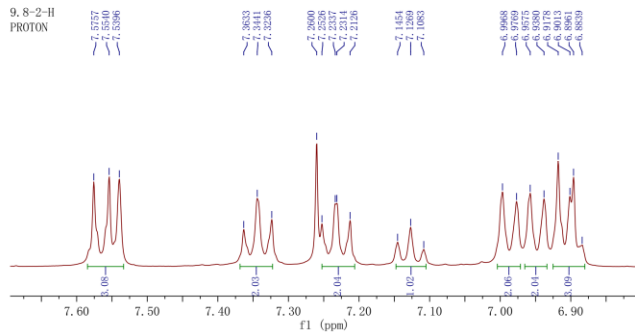


NMR spectra of compounds 3



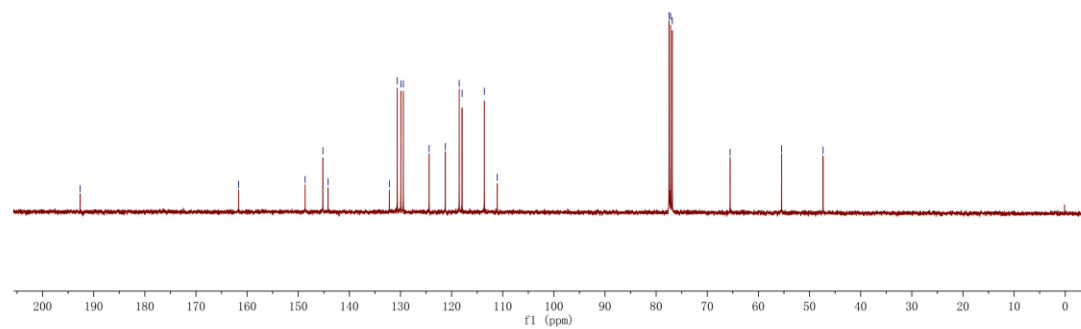
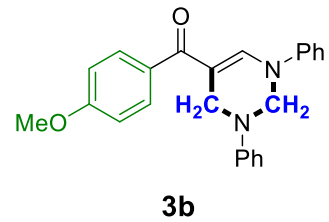
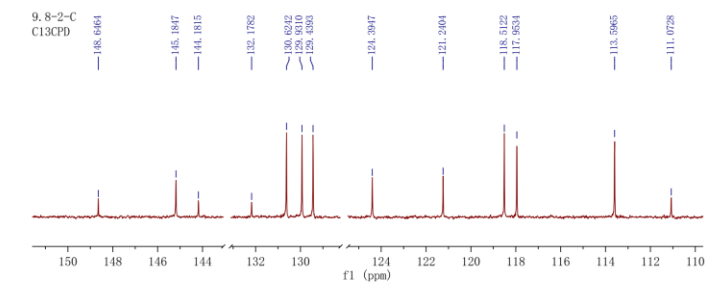
9.8-2-H
PROTON

¹H NMR (500 MHz, CDCl₃)



9.8-2-C
C13CPD

¹³C NMR (125 MHz, CDCl₃)



20220524-zyl-74-4

7.5047
7.4879
7.4823
7.3729
7.3578
7.3411
7.3290
7.2200
7.1579
7.1422
6.9793
6.9535
6.9379
6.9012

-5.1582

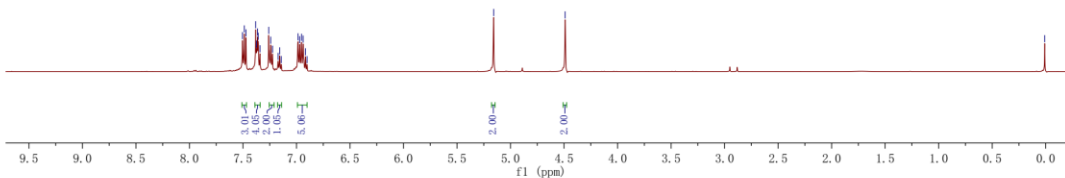
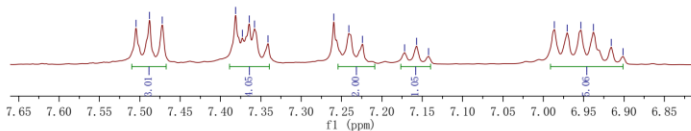
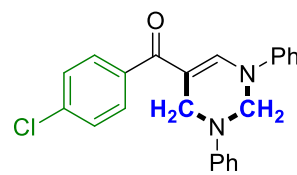
-1.4885

-0.0090

^1H NMR (500 MHz, CDCl_3)

20220524-zyl-74-4

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7.3729
7.3578
7.3411
7.3290
7.2200
7.1579
7.1422
6.9793
6.9535
6.9379
6.9012



20220525-zyl-74-45

148.5002
138.5181
133.9614
138.0195
136.6481
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129.9274
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117.9485
110.8124

77.4337
77.0054
76.9054

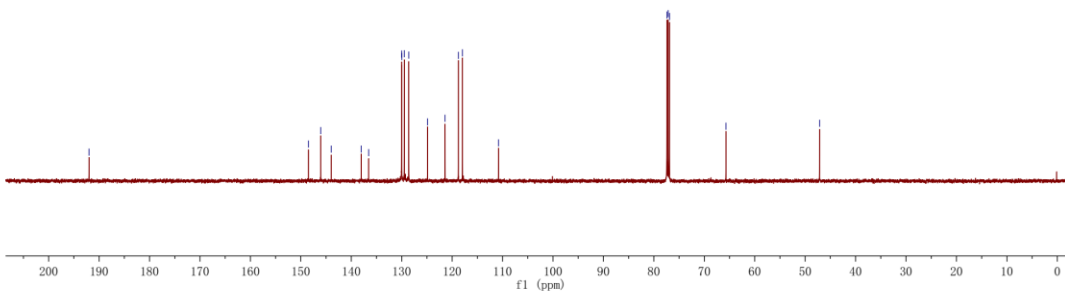
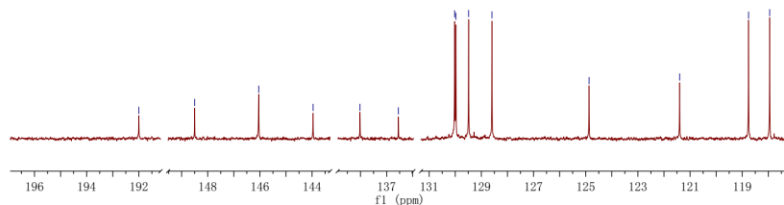
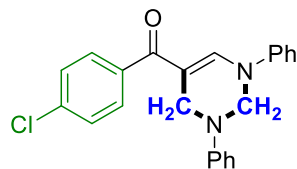
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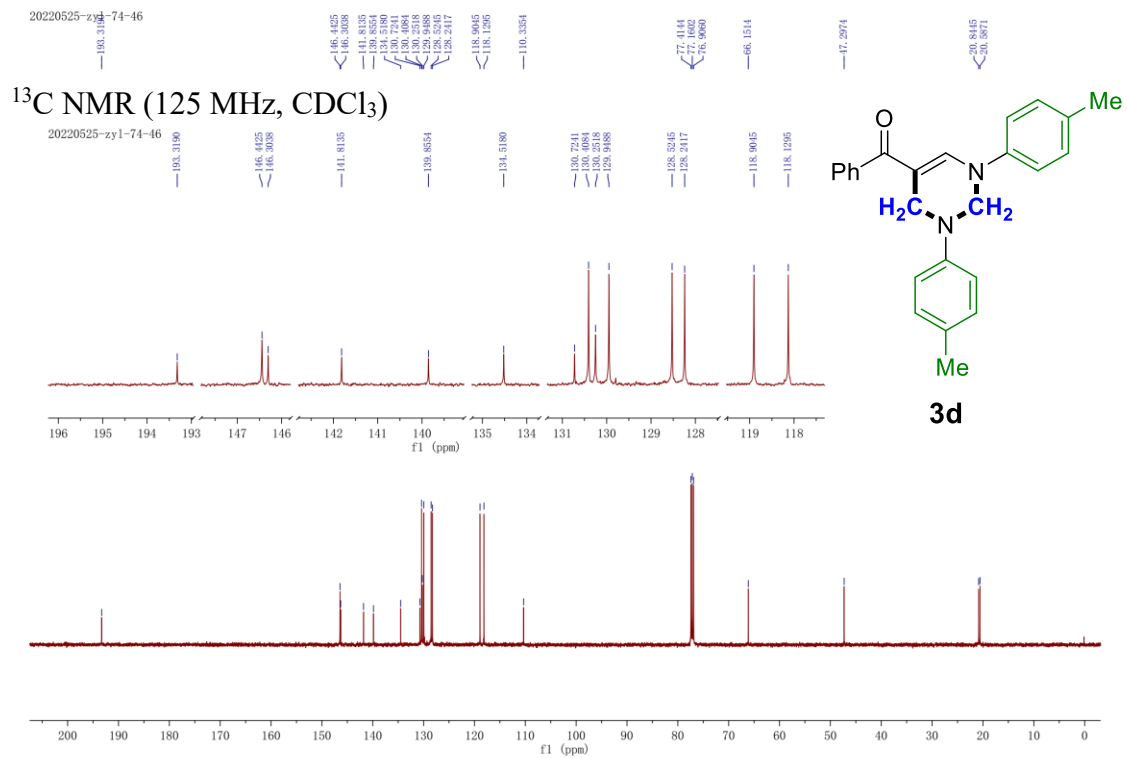
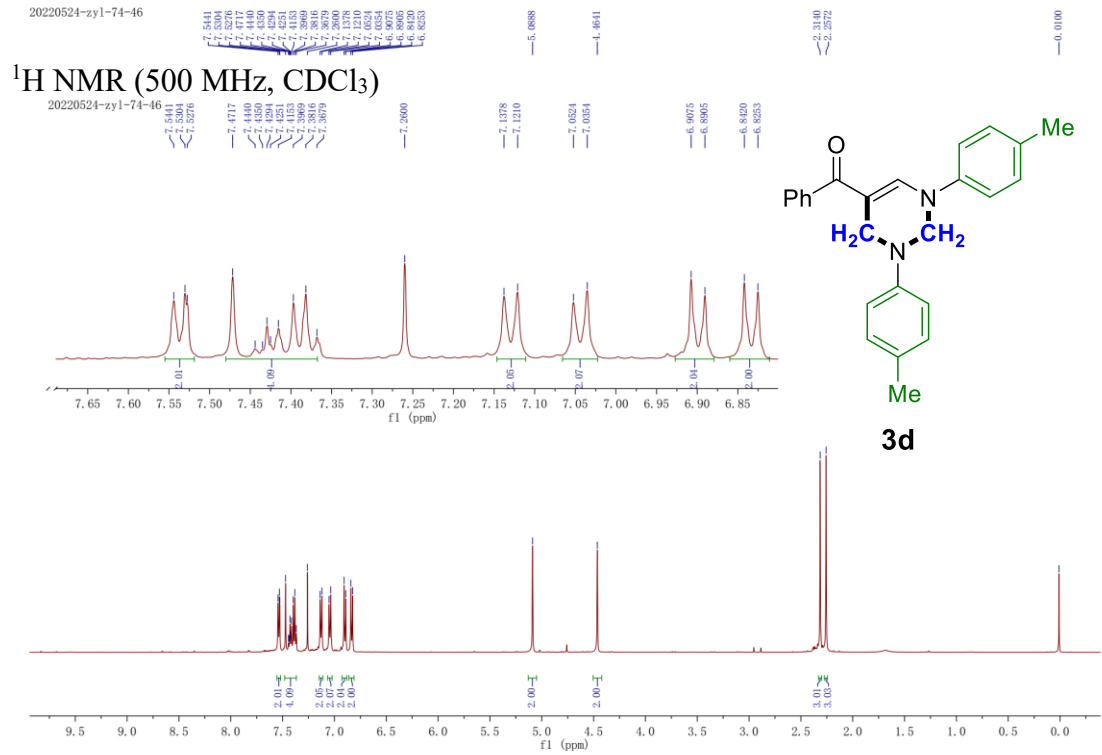
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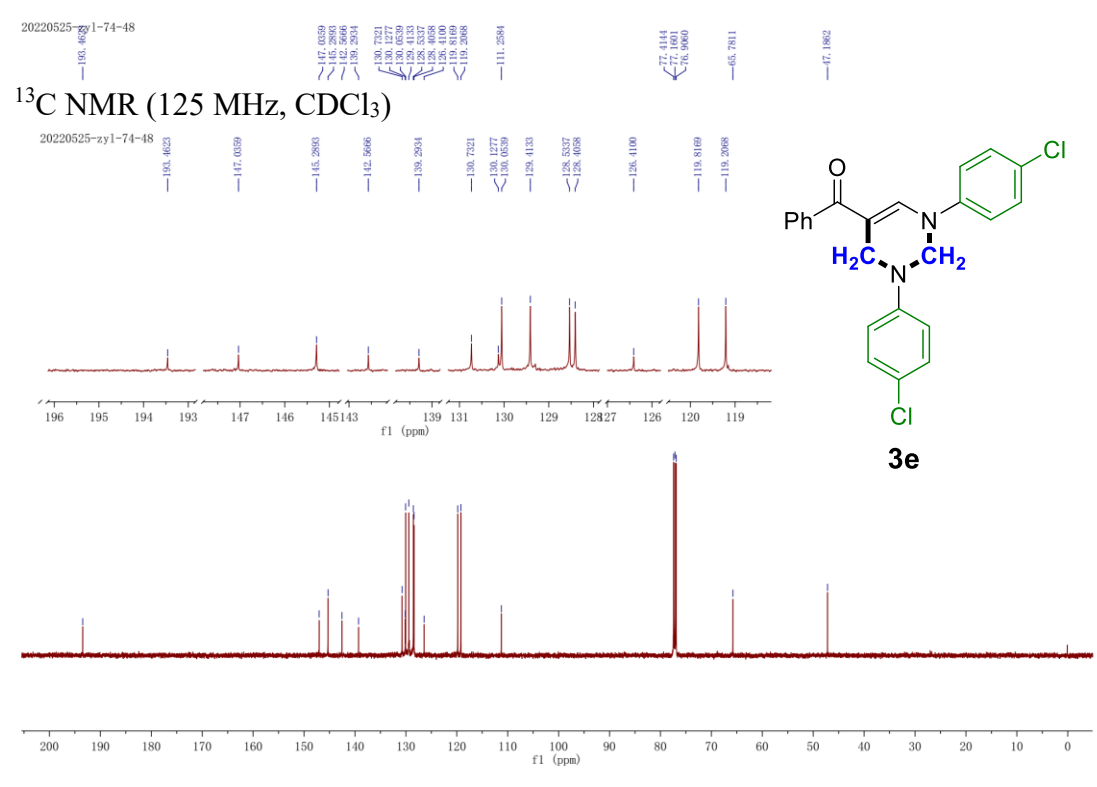
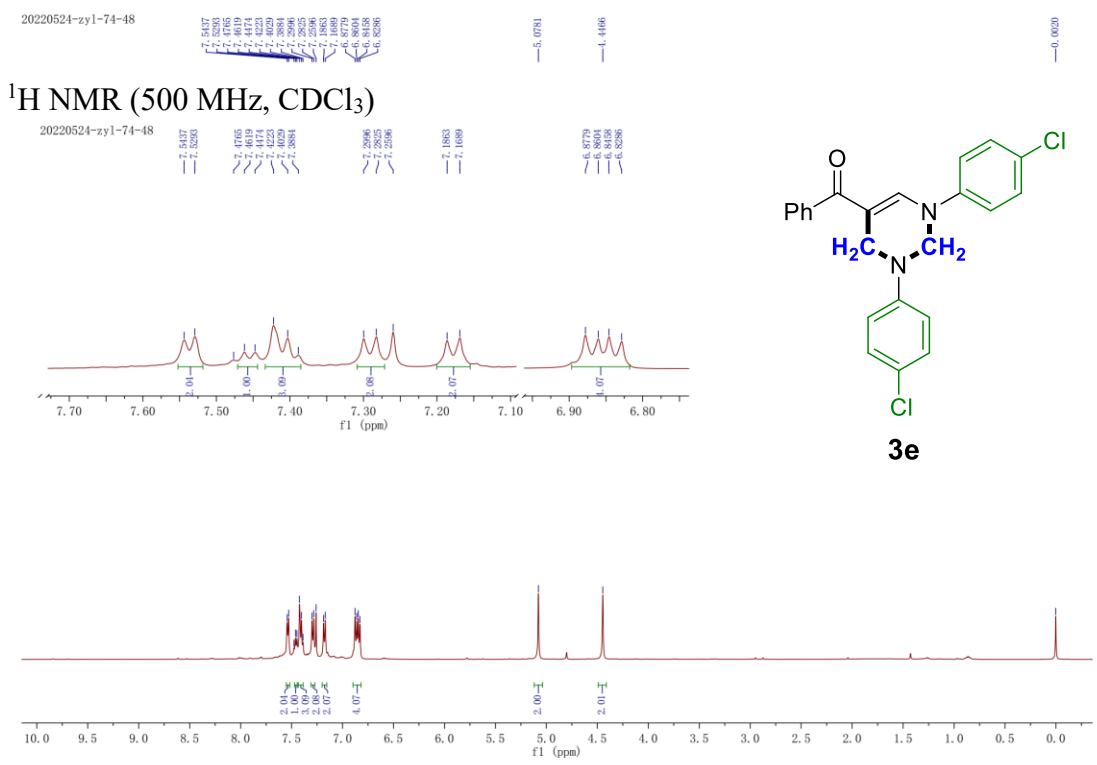
^{13}C NMR (125 MHz, CDCl_3)

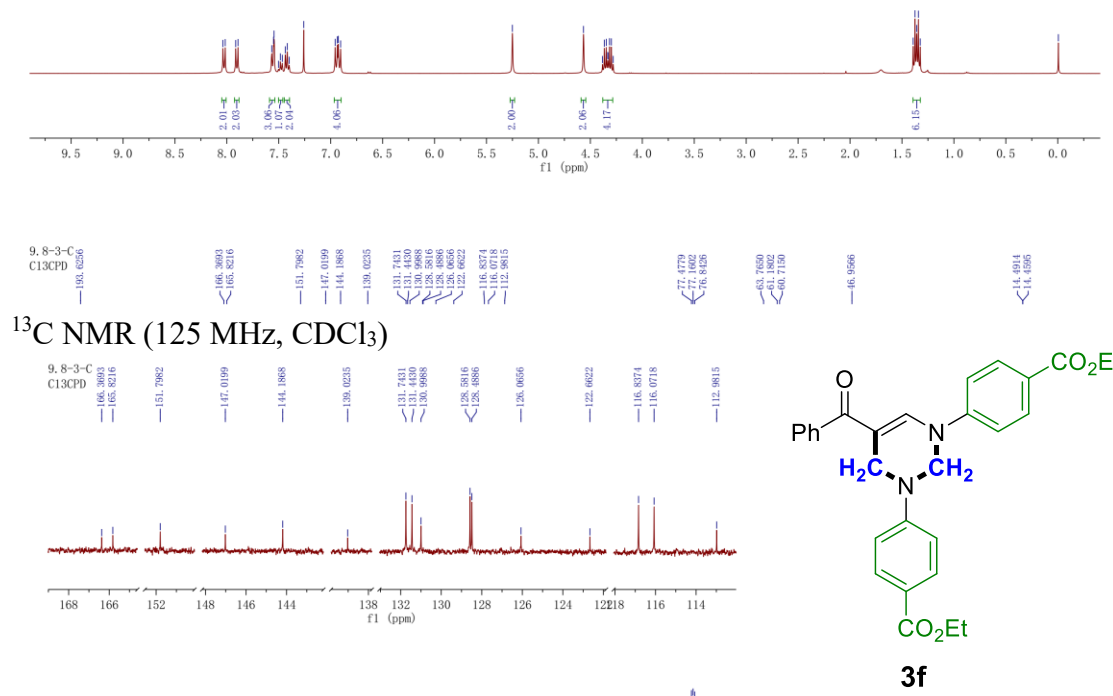
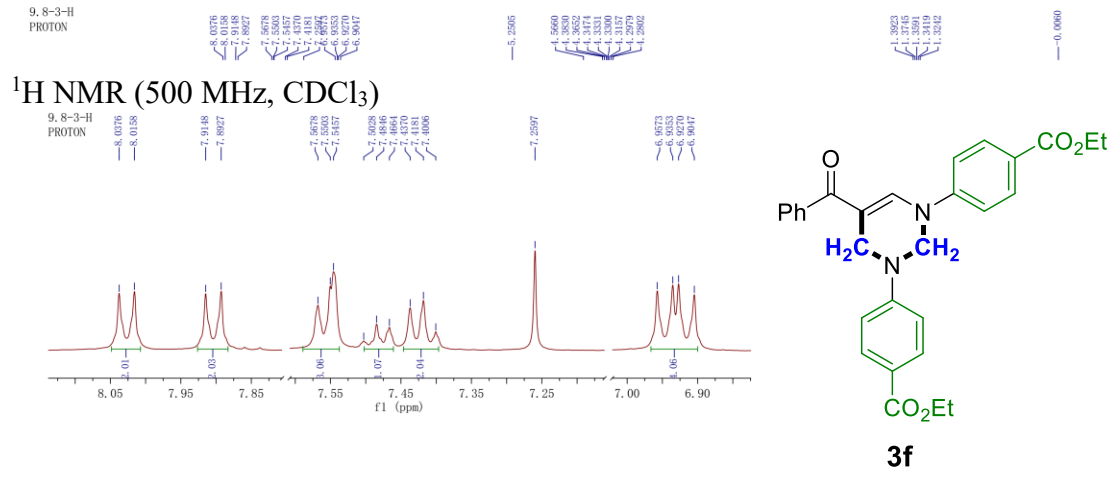
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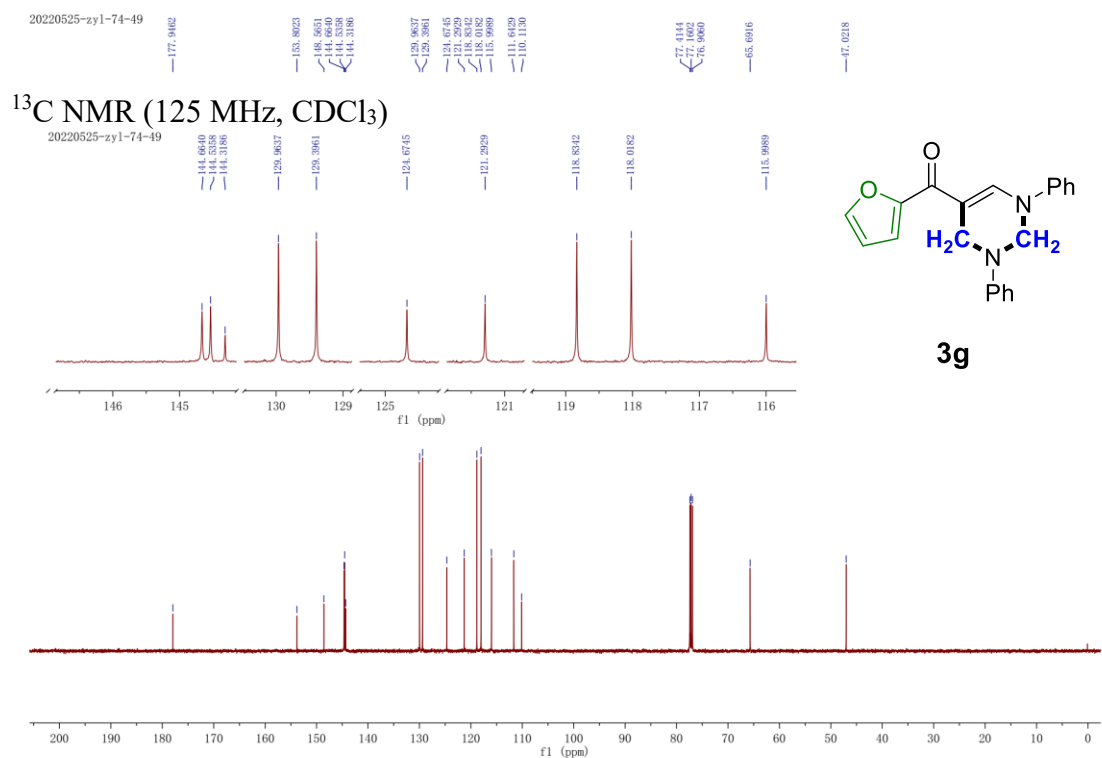
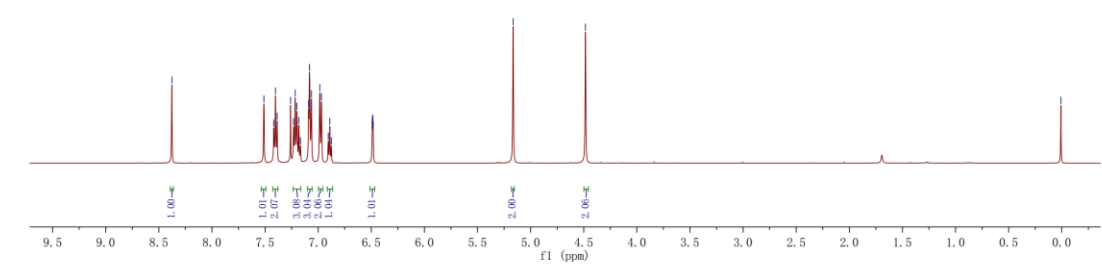
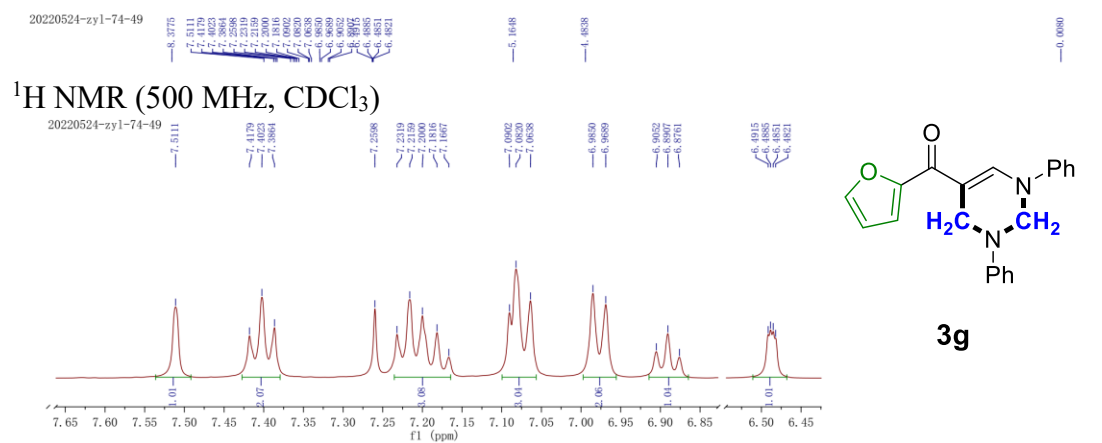
192.0001
148.5002
146.0441
143.9014
138.0195
136.6481
130.0232
129.9753
129.9274
124.8710
118.7579
117.9485
110.8124





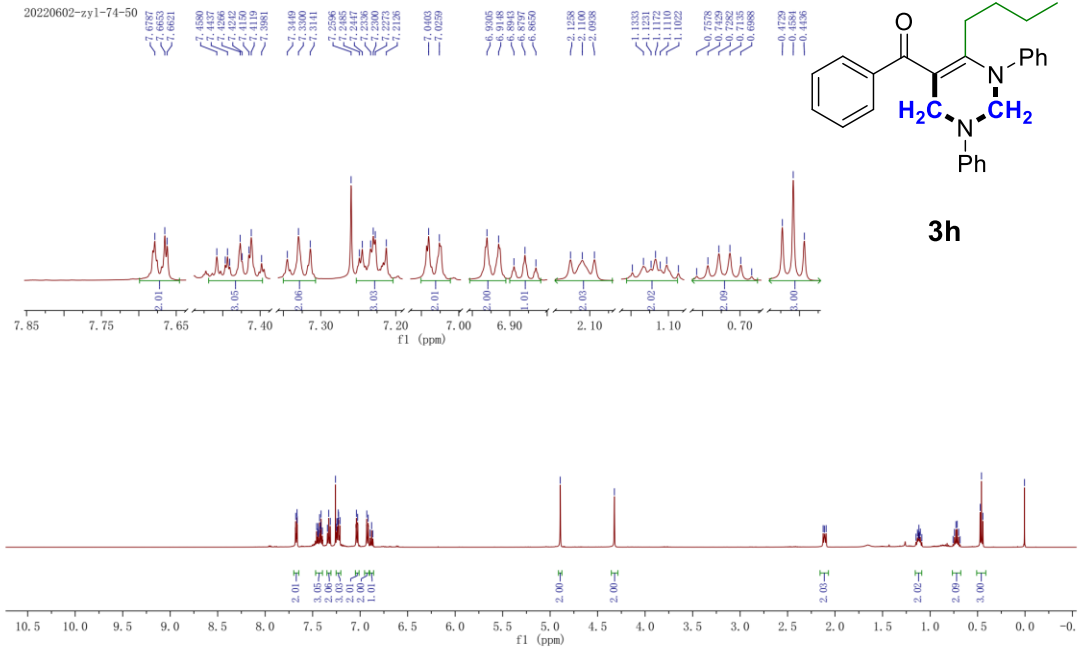






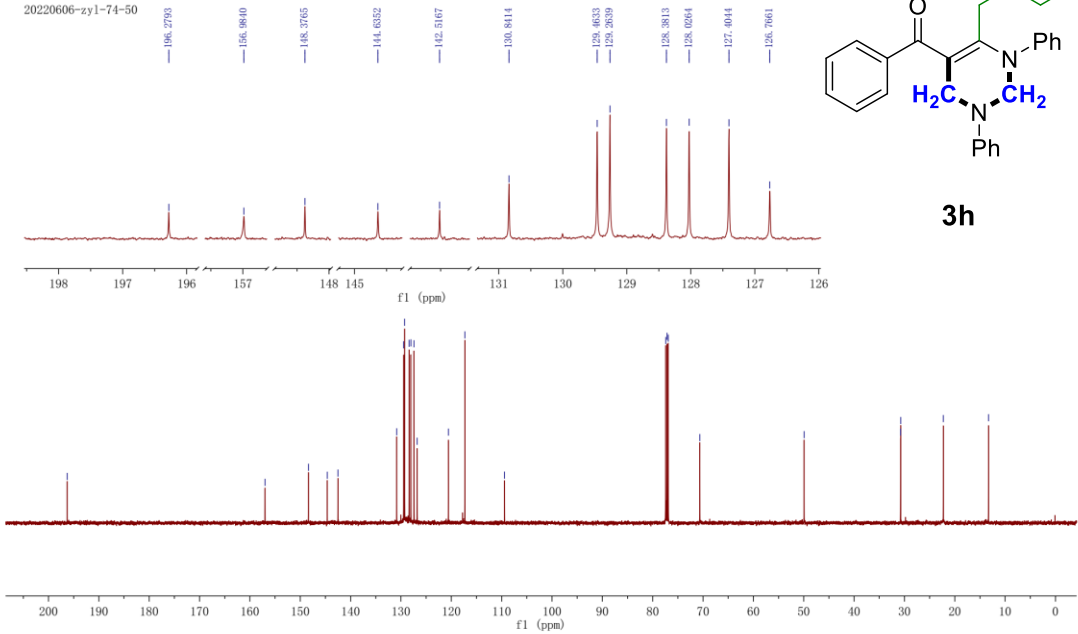
20220602-zy1-74-50

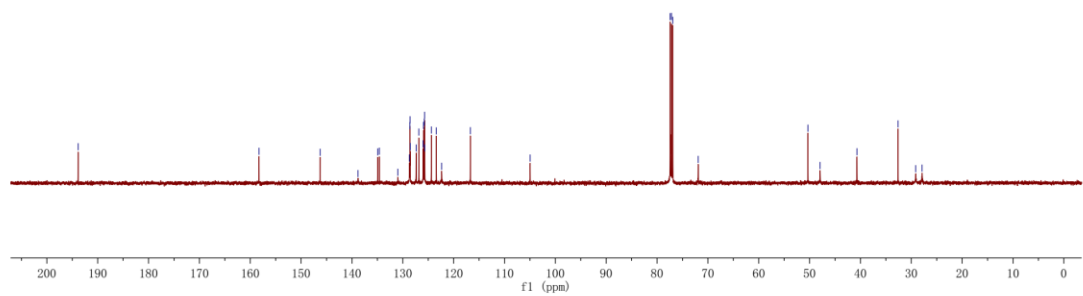
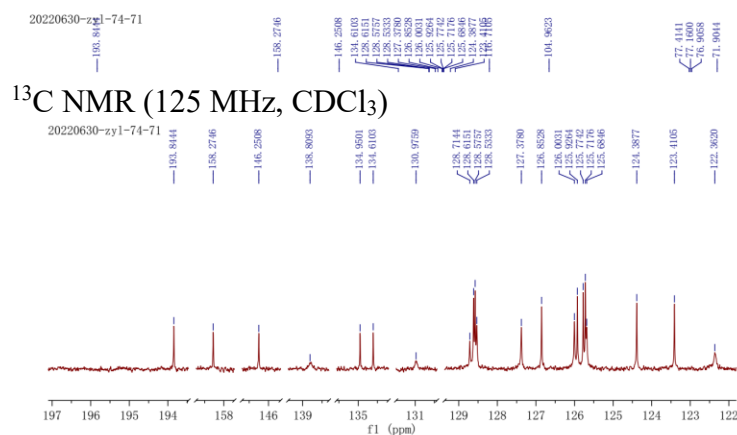
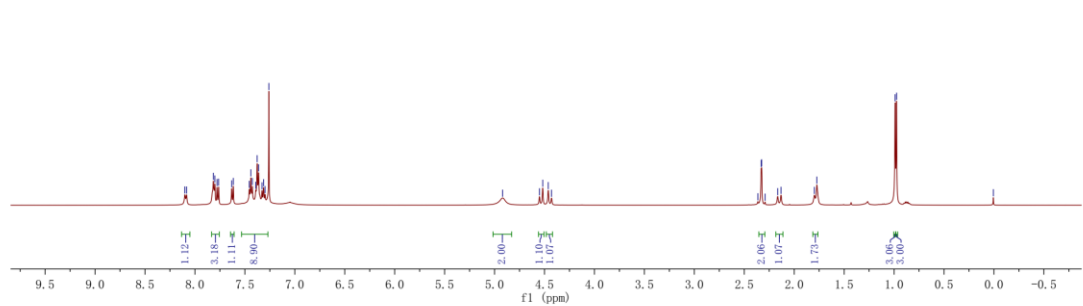
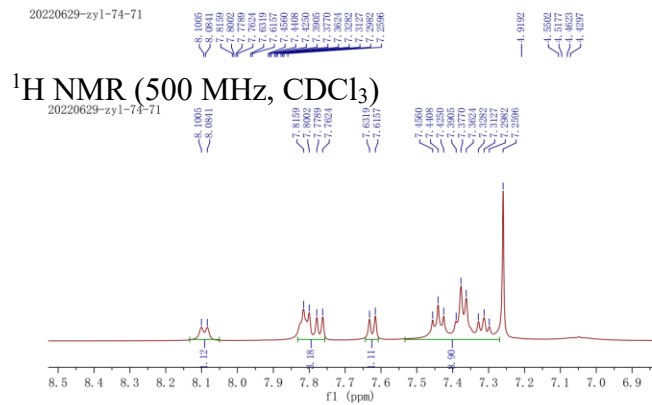
¹H NMR (500 MHz, CDCl₃)



20220606-zy1-74-50

¹³C NMR (125 MHz, CDCl₃)

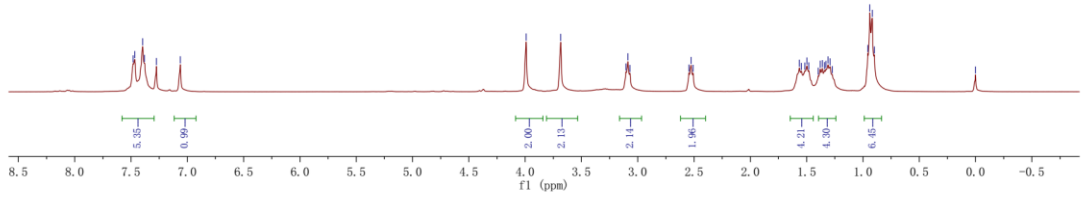
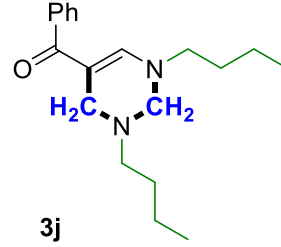
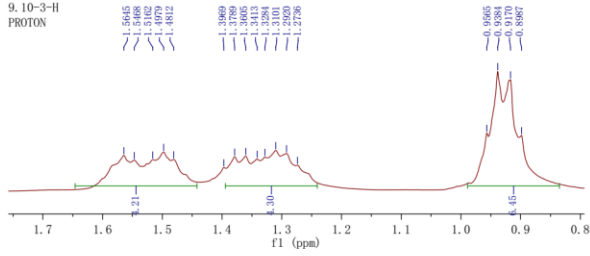




9.10-3-H
PROTON

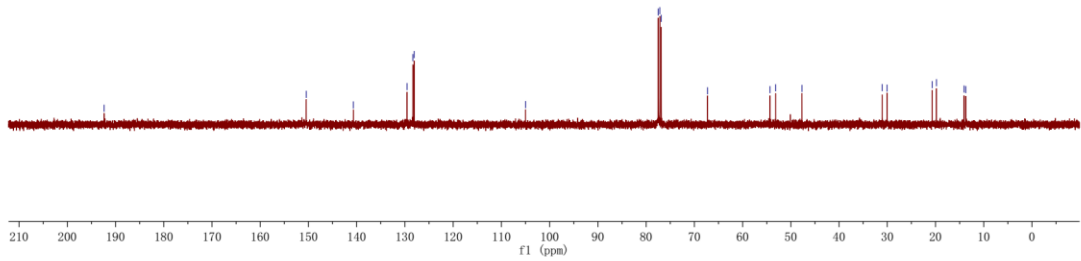
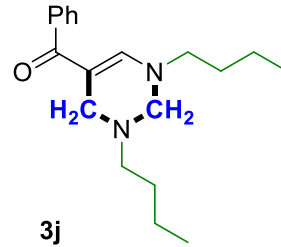
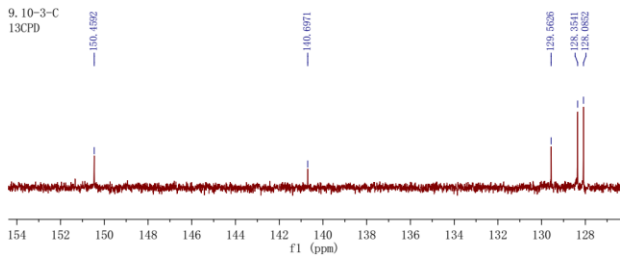


9.10-3-H
PROTON



9.10-3-C
13CPD

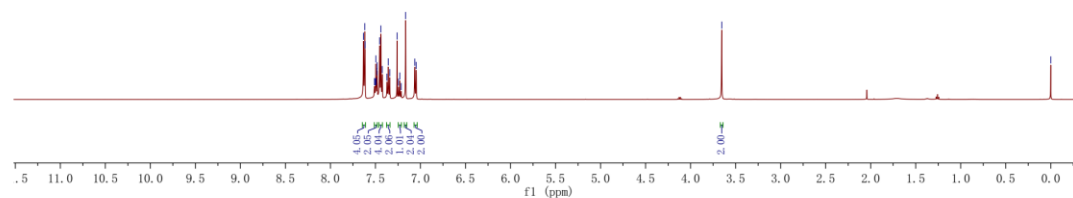
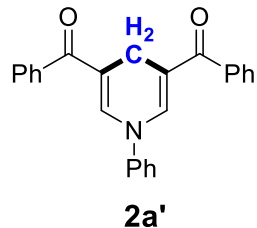
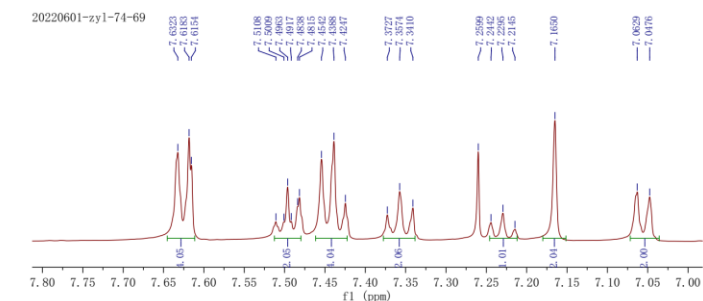
9.10-3-C
13CPD



NMR spectra of compounds 2'

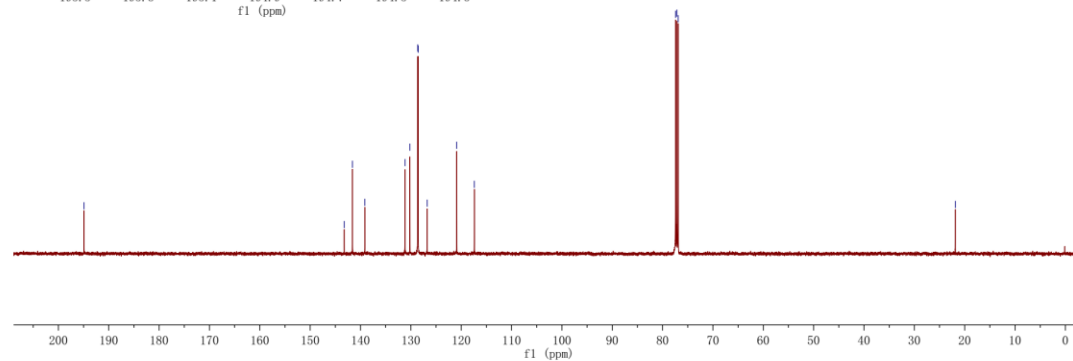
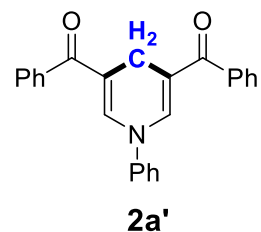
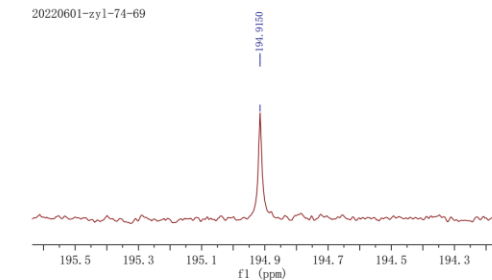
20220601-zy1-74-69

¹H NMR (500 MHz, CDCl₃)



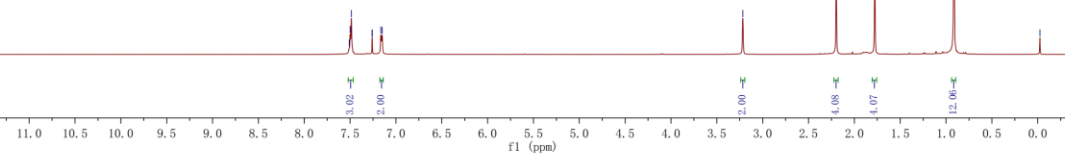
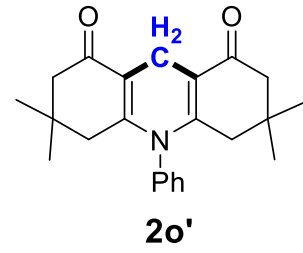
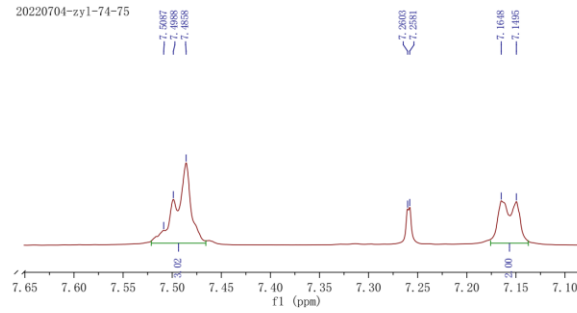
¹³C NMR (125 MHz, CDCl₃)

20220601-zy1-74-69



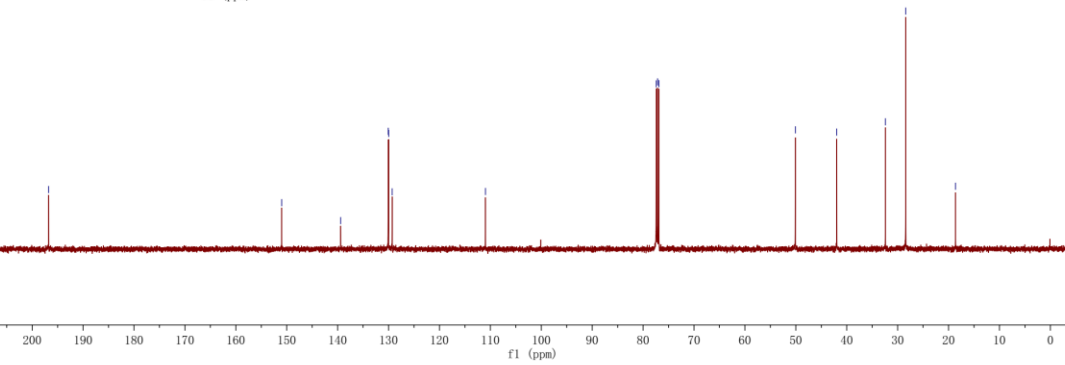
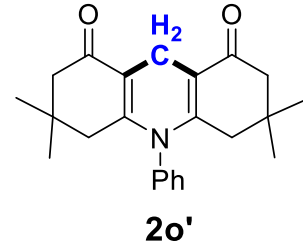
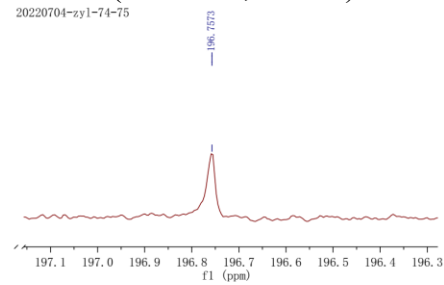
20220704-zy1-74-75

¹H NMR (500 MHz, CDCl₃)

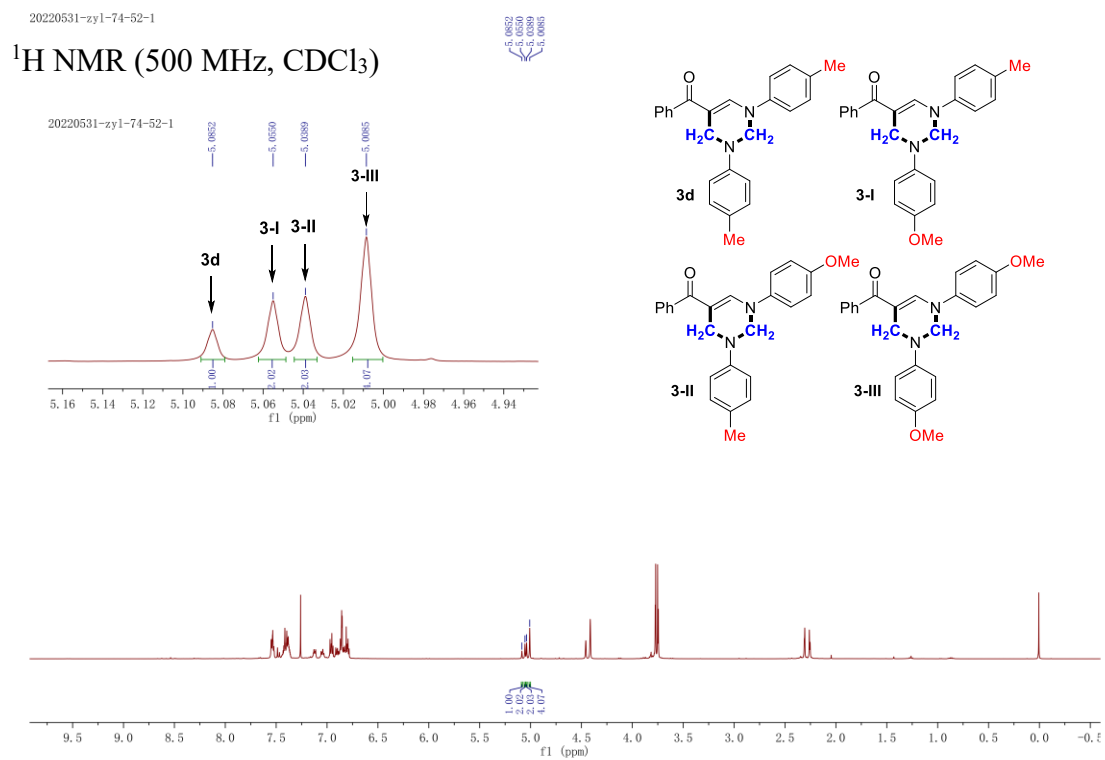


20220704-zy1-74-75

¹³C NMR (125 MHz, CDCl₃)



Cross reaction result



The above ratio is derived from a comparison of spectra of known compounds.¹¹