

Supporting Information

Regioselective and stereospecific synthesis of functionalized 3,4-dihydro-2*H*-1,4-thiazines by catalyst-free [3+3] annulation of pyridinium 1,4-zwitterionic thiolates and aziridines

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1. General Information

All reactions were performed in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. NMR spectra were recorded on a Bruker AM400 (400 MHz) spectrometer or Agilent DD2 (600 MHz) spectrometer. Chemical shifts are reported in δ ppm referenced to an internal SiMe₄ standard for ¹H NMR and chloroform-*d* (δ 77.16) for ¹³C NMR. Data for ¹H NMR are recorded as follows: chemical shift (δ ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz) and integration. Data for ¹³C NMR and ¹⁹F NMR are reported in terms of chemical shift (δ , ppm). High-resolution mass spectra (HRMS) were recorded on a Thermo Q-Exactive Spectrometer (ESI source). Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Flash column chromatography was performed using silica gel (300-400 mesh). CCDC 2131863 (**3aa**) and CCDC 2131862 (**4au**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Pyridinium 1,4-zwitterionic thiolates **1**^[1] and aziridines **2**^[2] were prepared according to the representative methods.

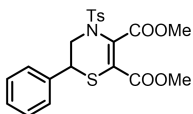
2. General Procedures and Analytical Data of the Products

2.1 General Procedure for [3+3] Cycloaddition



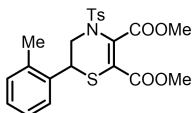
Pyridinium 1,4-zwitterionic thiolates **1** (0.20 mmol, 1.0 equiv.), aziridines **2** (0.30 mmol, 1.5 equiv.) and MeCN (2.0 mL) were sequentially added into a reaction tube under air atmosphere. Then the reaction mixture were stirred at 80 °C for 1 h. After the complete consumption of pyridinium 1,4-zwitterionic thiolates **1**, the reaction mixture was concentrated under reduced pressure and the resulting residue was purified by flash column chromatography (*n*-hexane/ethyl acetate = 6/1) on silica gel to afford the pure products **3** or **4**.

Dimethyl 2-phenyl-4-tosyl-3,4-dihydro-2*H*-1,4-thiazine-5,6-dicarboxylate (**3aa**)



Following the general procedure, the pure title compound was obtained in 84% yield as a white solid. m. p. 125-126 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.42-7.30 (m, 5H), 7.22-7.13 (m, 2H), 4.15 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.9 (s, 3H), 3.88-3.79 (m, 4H), 2.95 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.46 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 164.3, 145.4, 135.7, 134.8, 130.2, 129.5, 129.3, 129.1, 128.2, 128.1, 123.6, 53.3, 53.2, 49.4, 43.9, 21.8 ppm. HRMS (ESI) calcd for C₂₁H₂₂NO₆S₂ [M+H]⁺ 448.0883, found 448.0871.

Dimethyl 2-(*o*-tolyl)-4-tosyl-3,4-dihydro-2*H*-1,4-thiazine-5,6-dicarboxylate (**3ab**)

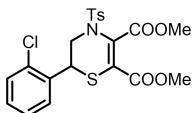


Following the general procedure, the pure title compound was obtained in 99% yield as a white solid. m. p. 94-95 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.24-7.14 (m, 4H), 4.34 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.10 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.98 (dd, *J* = 14.4, 10.4 Hz, 1H),

2.44 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 164.4, 145.2, 136.7, 135.1, 134.1, 131.0, 130.2, 129.2, 128.7, 128.3, 127.4, 127.1, 124.1, 53.4, 53.2, 48.5, 40.1, 21.8, 19.4 ppm. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 462.1040, found 462.1028.

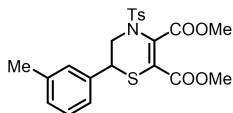
Dimethyl

2-(2-chlorophenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ac)



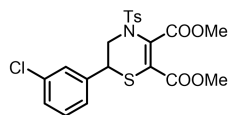
Following the general procedure, the pure title compound was obtained in 80% yield as a white solid. m. p. 92-93 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 2H), 7.40-7.33 (m, 3H), 7.33-7.22 (m, 3H), 4.48 (dd, $J = 10.4, 3.2$ Hz, 1H), 4.25 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.91 (s, 3H), 3.83 (s, 3H), 3.02 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.3 (2C), 145.3, 135.0, 134.0, 133.6, 130.4, 130.22, 130.18, 130.1, 129.3, 128.2, 127.8, 122.8, 53.38, 53.35, 48.0, 40.0, 21.8 ppm. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{ClNO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 482.0493, found 482.0486.

Dimethyl 2-(*m*-tolyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ad)



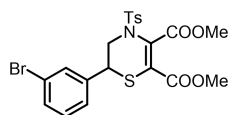
Following the general procedure, the pure title compound was obtained in 88% yield as a white solid. m. p. 146-147 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.25-7.21 (m, 1H), 7.17-7.11 (m, 1H), 7.02-6.94 (m, 2H), 4.14 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.90 (s, 3H), 3.87-3.80 (m, 4H), 2.94 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.46 (s, 3H), 2.33 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 164.4, 145.3, 139.1, 135.7, 134.9, 130.2, 129.9, 129.4, 129.1, 128.7, 128.3, 125.1, 123.8, 53.3, 53.2, 49.5, 44.0, 21.8, 21.5 ppm. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{23}\text{NNaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$ 484.0859, found 484.0865.

Dimethyl 2-(3-chlorophenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ae)



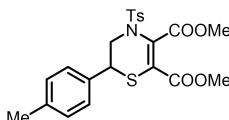
Following the general procedure, the pure title compound was obtained in 66% yield as a white solid. m. p. 174-175 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33-7.25 (m, 2H), 7.17 (s, 1H), 7.12-7.06 (m, 1H), 4.12 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.90 (s, 3H), 3.88-3.81 (m, 4H), 2.91 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.47 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 164.2, 145.5, 137.8, 135.1, 134.7, 130.5, 130.3, 129.8, 129.3, 128.3, 128.2, 126.3, 123.0, 53.4, 53.3, 49.3, 43.6, 21.8 ppm. HRMS (ESI) calcd for C₂₁H₂₁ClNO₆S₂ [M+H]⁺ 482.0493, found 482.0480.

Dimethyl 2-(3-bromophenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3af)



Following the general procedure, the pure title compound was obtained in 59% yield as a white solid. m. p. 172-173 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.51-7.43 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 1H), 7.25-7.21 (m, 1H), 7.16-7.10 (m, 1H), 4.11 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.90 (s, 3H), 3.88-3.80 (m, 4H), 2.91 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.47 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 164.2, 145.5, 138.1, 134.7, 132.3, 131.3, 130.8, 130.3, 129.8, 128.3, 126.8, 123.2, 123.1, 53.4, 53.3, 49.3, 43.6, 21.8 ppm. HRMS (ESI) calcd for C₂₁H₂₁⁷⁹BrNO₆S₂ [M+H]⁺ 525.9988, found 525.9972.

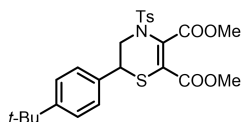
Dimethyl 2-(*p*-tolyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ag)



Following the general procedure, the pure title compound was obtained in 95% yield as a white solid. m. p. 110-111 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.13 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.90 (s, 3H), 3.82-3.79 (m, 4H), 2.93 (dd, *J* = 14.4, 10.4 Hz,

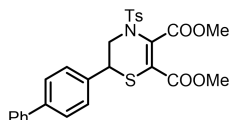
1H), 2.46 (s, 3H), 2.33 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 164.4, 145.3, 139.1, 134.8, 132.7, 130.2, 129.9, 129.3, 128.2, 127.9, 123.8, 53.3, 53.2, 49.4, 43.6, 21.8, 21.2 ppm. HRMS (ESI) calcd for C₂₂H₂₄NO₆S₂ [M+H]⁺ 462.1040, found 462.1053.

Dimethyl 2-(4-(tert-butyl)phenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ah)



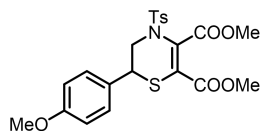
Following the general procedure, the pure title compound was obtained in 95% yield as a white solid. m. p. 89-90 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.33-7.25 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.07 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.82 (s, 3H), 3.78-3.70 (m, 4H), 2.87 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.38 (s, 3H), 1.22 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 164.4, 152.3, 145.3, 134.8, 132.7, 130.2, 129.4, 128.3, 127.8, 126.2, 123.9, 53.3, 53.2, 49.4, 43.6, 34.8, 31.3, 21.8 ppm. HRMS (ESI) calcd for C₂₅H₃₀NO₆S₂ [M+H]⁺ 504.1509, found 504.1497.

Dimethyl 2-([1,1'-biphenyl]-4-yl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ai)



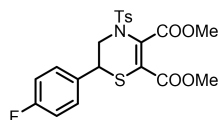
Following the general procedure, the pure title compound was obtained in 82% yield as a white solid. m. p. 80-81 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.52-7.45 (m, 4H), 7.39-7.34 (m, 2H), 7.33-7.26 (m, 3H), 7.20-7.15 (m, 2H), 4.11 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.87-3.81 (m, 4H), 3.76 (s, 3H), 2.92 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.39 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 164.4, 145.4, 142.1, 140.3, 134.8, 134.7, 130.3, 129.5, 129.0, 128.5, 128.3, 128.0, 127.9, 127.2, 123.7, 53.4, 53.3, 49.4, 43.8, 21.8 ppm. HRMS (ESI) calcd for C₂₇H₂₆NO₆S₂ [M+H]⁺ 524.1196, found 524.1188.

Dimethyl 2-(4-methoxyphenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3aj)



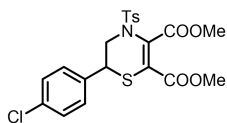
Following the general procedure, the pure title compound was obtained in 85% yield as a white solid. m. p. 118-119 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 4.12 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.89 (s, 3H), 3.84-3.80 (m, 4H), 3.79 (s, 3H), 2.92 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.46 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 164.4, 160.1, 145.3, 134.9, 130.2, 129.33, 129.26, 128.3, 127.6, 124.0, 114.6, 55.5, 53.3, 53.2, 49.6, 43.4, 21.8 ppm. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_7\text{S}_2$ $[\text{M}+\text{H}]^+$ 478.0989, found 478.0998.

Dimethyl 2-(4-fluorophenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ak)



Following the general procedure, the pure title compound was obtained in 81% yield as a white solid. m. p. 162-163 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.21-7.12 (m, 2H), 7.08-6.98 (m, 2H), 4.11 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.92-3.85 (m, 4H), 3.83 (s, 3H), 2.91 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.46 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 164.3, 163.0 (d, $J = 248.0$ Hz), 145.4, 134.8, 131.7 (d, $J = 3.0$ Hz), 130.3, 129.9 (d, $J = 9.0$ Hz), 129.7, 128.3, 123.4, 116.3 (d, $J = 22.0$ Hz), 53.4, 53.3, 49.5, 43.4, 21.8 ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -112.0 ppm. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{FNO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 466.0789, found 466.0778.

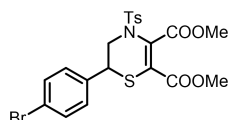
Dimethyl 2-(4-chlorophenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3al)



Following the general procedure, the pure title compound was obtained in 81% yield as a white solid. m. p. 130-131 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz,

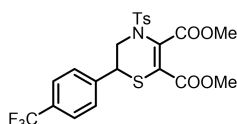
2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 4.10 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.93-3.85 (m, 4H), 3.83 (s, 3H), 2.91 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.46 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 164.3, 145.5, 135.1, 134.8, 134.4, 130.3, 129.7, 129.5, 129.5, 128.3, 123.2, 53.4, 53.3, 49.4, 43.5, 21.8 ppm. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{ClNO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 482.0493, found 482.0477.

Dimethyl 2-(4-bromophenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3am)



Following the general procedure, the pure title compound was obtained in 84% yield as a white solid. m. p. 112-114 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 4.10 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.90 (s, 3H), 3.86 (dd, $J = 10.4, 3.2$ Hz, 1H), 3.83 (s, 3H), 2.90 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.46 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.3, 164.2, 145.5, 134.8, 134.7, 132.5, 130.3, 129.72, 129.70, 128.2, 123.2, 123.1, 53.4, 53.3, 49.3, 43.5, 21.8 ppm. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}^{79}\text{BrNO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 525.9988, found 525.9977.

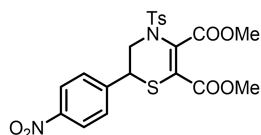
Dimethyl 4-tosyl-2-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3an)



Following the general procedure, the pure title compound was obtained in 66% yield as a white solid. m. p. 115-116 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.12 (dd, $J = 14.4, 3.4$ Hz, 1H), 3.98 (dd, $J = 10.4, 3.2$ Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.95 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.46 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.3, 164.2, 145.6, 139.9, 134.7, 131.4 (q, $J = 33.0$ Hz), 130.3, 130.0, 128.6, 128.3, 126.3 (q, $J = 3.0$ Hz), 126.2, 124.0 (q, $J = 236.0$ Hz), 53.4, 53.3, 49.3, 43.7, 21.8 ppm.

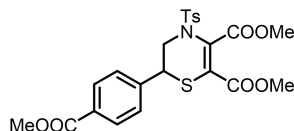
^{19}F NMR (376 MHz, CDCl_3) δ -62.8 ppm. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 516.0757, found 516.0773.

Dimethyl 2-(4-nitrophenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ao)



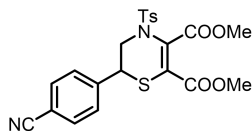
Following the general procedure, the pure title compound was obtained in 53% yield as a yellow solid. m. p. 160-161 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.21 (d, J = 9.0 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 4.12 (dd, J = 13.8, 3.0 Hz, 1H), 4.08 (dd, J = 10.2, 3.0 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.97 (dd, J = 13.8, 10.2 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3) δ 164.15, 164.06, 148.3, 145.6, 143.0, 134.7, 130.33, 130.29, 129.3, 128.3, 124.5, 122.3, 53.5, 53.4, 49.2, 43.7, 21.8 ppm. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_8\text{S}_2$ $[\text{M}+\text{H}]^+$ 493.0734, found 493.0722.

Dimethyl 2-(4-(methoxycarbonyl)phenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ap)



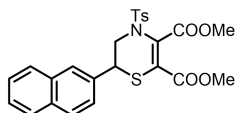
Following the general procedure, the pure title compound was obtained in 62% yield as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.17-4.11 (m, 1H), 3.97-3.93 (m, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.83 (s, 3H), 2.97 (dd, J = 14.4, 10.4 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 164.3, 164.2, 145.5, 140.7, 134.7, 130.9, 130.5, 130.3, 129.8, 128.22, 128.17, 122.9, 53.4, 53.3, 52.4, 49.2, 43.8, 21.8 ppm. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_8\text{S}_2$ $[\text{M}+\text{H}]^+$ 506.0938, found 506.0947.

Dimethyl 2-(4-cyanophenyl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3aq)



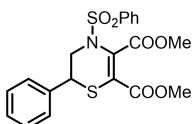
Following the general procedure, the pure title compound was obtained in 59% yield as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 4.13 (dd, $J = 14.4, 3.2$ Hz, 1H), 4.00 (dd, $J = 10.4, 3.2$ Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.94 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.15, 164.06, 145.6, 141.1, 134.6, 133.0, 130.3, 130.1, 129.0, 128.2, 122.4, 118.1, 113.1, 53.4, 53.3, 49.1, 43.9, 21.8 ppm. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 473.0836, found 473.0851.

Dimethyl 2-(naphthalen-2-yl)-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ar)



Following the general procedure, the pure title compound was obtained in 92% yield as a white solid. m. p. 79-80 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.91-7.89 (m, 2H), 7.86-7.76 (m, 3H), 7.68 (s, 1H), 7.54-7.47 (m, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.28-7.26 (m, 1H), 4.21 (dd, $J = 14.4, 3.2$ Hz, 1H), 4.09 (dd, $J = 10.4, 3.2$ Hz, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 3.06 (dd, $J = 14.0, 10.4$ Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 164.4, 145.4, 134.9, 133.5, 133.3, 133.0, 130.3, 129.6, 129.3, 128.3, 128.0, 127.9, 127.6, 126.9, 125.2, 123.8, 53.4, 53.3, 49.5, 44.4, 21.8 ppm. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 498.1040, found 498.1055.

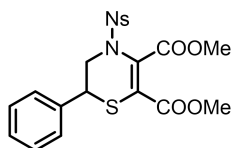
Dimethyl 2-phenyl-4-(phenylsulfonyl)-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3as)



Following the general procedure, the pure title compound was obtained in 91% yield as a white solid. m. p. 64-65 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.05-7.97 (m, 2H),

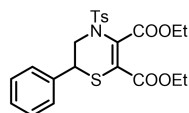
7.72-7.65 (m, 1H), 7.63-7.56 (m, 2H), 7.38-7.30 (m, 3H), 7.21-7.14 (m, 2H), 4.16 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.90 (s, 3H), 3.86 (dd, $J = 10.4, 2.8$ Hz, 1H), 3.83 (s, 3H), 2.97 (dd, $J = 14.4, 10.4$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.5, 164.3, 137.8, 135.7, 134.2, 129.7, 129.3 (3C), 129.2, 128.2, 128.1, 124.1, 53.4, 53.3, 49.4, 44.1 ppm. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 434.0727, found 434.0719.

Dimethyl 4-((4-nitrophenyl)-sulfonyl)-2-phenyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3at)



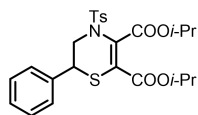
Following the general procedure, the pure title compound was obtained in 88% yield as a yellow solid. m. p. 83-84 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.39 (d, $J = 9.0$ Hz, 2H), 8.25 (d, $J = 8.4$ Hz, 2H), 7.40-7.34 (m, 3H), 7.30-7.25 (m, 2H), 4.27 (dd, $J = 10.2, 3.0$ Hz, 1H), 4.13 (dd, $J = 14.4, 3.0$ Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.02 (dd, $J = 14.4, 10.2$ Hz, 1H) ppm. ^{13}C NMR (151 MHz, CDCl_3) δ 164.3, 163.9, 150.9, 143.9, 135.3, 129.6, 129.43, 129.41, 128.1, 127.7, 126.5, 124.6, 53.5, 53.4, 49.6, 45.4 ppm. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_8\text{S}_2$ $[\text{M}+\text{H}]^+$ 479.0577, found 479.0563.

Diethyl 2-phenyl-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ea)



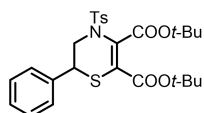
Following the general procedure, the pure title compound was obtained in 84% yield as a white solid. m. p. 89-90 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.40-7.30 (m, 5H), 7.23-7.15 (m, 2H), 4.49-4.38 (m, 1H), 4.36-4.20 (m, 3H), 4.14 (dd, $J = 14.4, 3.2$ Hz, 1H), 3.91 (dd, $J = 10.4, 2.8$ Hz, 1H), 2.96 (dd, $J = 14.4, 10.4$ Hz, 1H), 2.46 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H), 1.33 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 163.8, 145.2, 135.9, 135.0, 130.2, 129.4, 129.3, 129.1, 128.3, 128.1, 124.0, 62.6, 62.4, 49.4, 44.1, 21.8, 14.1, 13.9 ppm. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 476.1196, found 476.1192.

Diisopropyl 2-phenyl-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3fa)



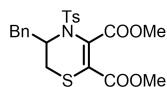
Following the general procedure, the pure title compound was obtained in 83% yield as a white solid. m. p. 79-80 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.32-7.21 (m, 5H), 7.17-7.08 (m, 2H), 5.18-5.08 (m, 1H), 5.07-4.97 (m, 1H), 4.02 (dd, *J* = 14.0, 3.2 Hz, 1H), 3.86 (dd, *J* = 10.4, 2.8 Hz, 1H), 2.88 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.38 (s, 3H), 1.35-1.19 (m, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 163.3, 145.1, 136.1, 135.1, 130.2, 129.5, 129.2, 129.0, 128.3, 128.2, 124.3, 70.5, 70.3, 49.3, 44.1, 21.9, 21.8, 21.8, 21.6, 21.3 ppm. HRMS (ESI) calcd for C₂₅H₃₀NO₆S₂ [M+H]⁺ 504.1509, found 504.1522.

Di-tert-butyl 2-phenyl-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ga)



Following the general procedure, the pure title compound was obtained in 70% yield as a white solid. m. p. 151-152 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.38-7.30 (m, 5H), 7.26-7.19 (m, 2H), 4.11-3.97 (m, 2H), 2.91 (dd, *J* = 14.0, 10.4 Hz, 1H), 2.44 (s, 3H), 1.59 (s, 9H), 1.53 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 163.0, 162.6, 144.9, 136.4, 135.4, 130.0 (3C), 129.2, 128.9, 128.4, 128.2, 125.0, 83.3, 83.0, 49.2, 44.6, 28.1, 27.7, 21.8 ppm. HRMS (ESI) calcd for C₂₇H₃₄NO₆S₂ [M+H]⁺ 532.1822, found 532.1811.

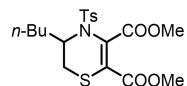
Dimethyl 3-benzyl-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (4au)



Following the general procedure, the pure title compound was obtained in 75% yield as a white solid. m. p. 130-131 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.21-7.14 (m, 3H), 7.09-7.00 (m, 2H), 4.31-4.17 (m, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.74-2.53 (m, 4H), 2.43 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.9, 164.7, 144.9, 136.5, 134.2, 130.0, 129.5, 128.7, 128.2, 127.7,

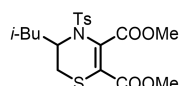
126.9, 121.9, 53.4, 53.1, 51.2, 37.0, 28.3, 21.8 ppm. HRMS (ESI) calcd for $C_{22}H_{24}NO_6S_2$ $[M+H]^+$ 462.1040, found 462.1031.

Dimethyl 3-butyl-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (4av)



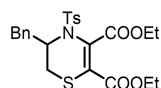
Following the general procedure, the pure title compound was obtained in 49% yield as a white solid. m. p. 132-134 °C 1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 4.10-4.02 (m, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 2.70-2.58 (m, 2H), 2.45 (s, 3H), 1.45-1.08 (m, 6H), 0.78 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8 (2C), 145.1, 134.6, 130.1, 128.3, 127.4, 122.4, 53.3, 53.1, 49.5, 30.4, 29.5, 27.4, 22.2, 21.8, 13.9 ppm. HRMS (ESI) calcd for $C_{19}H_{26}NO_6S_2$ $[M+H]^+$ 428.1196, found 428.1192.

Dimethyl 3-isobutyl-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (4aw)



Following the general procedure, the pure title compound was obtained in 41% yield as a white solid. m. p. 114-115 °C 1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.19-4.09 (m, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 2.65-2.59 (m, 2H), 2.45 (s, 3H), 1.72-1.58 (m, 2H), 1.12-1.03 (m, 1H), 0.81 (d, $J = 7.2$ Hz, 3H), 0.75 (d, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.8, 145.1, 134.6, 130.2, 128.3, 127.5, 122.7, 53.3, 53.1, 47.6, 39.9, 29.6, 24.1, 22.9, 22.2, 21.8 ppm. HRMS (ESI) calcd for $C_{19}H_{26}NO_6S_2$ $[M+H]^+$ 428.1196, found 428.1190.

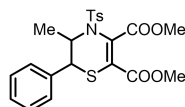
Diethyl 3-benzyl-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (4eu)



Following the general procedure, the pure title compound was obtained in 82% yield as a white solid. m. p. 99-100 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.2$ Hz, 2H), 7.19-7.14 (m, 3H), 7.09-6.98 (m, 2H), 4.46-4.36 (m, 1H), 4.35-4.18 (m, 4H), 2.80-2.72 (m, 1H), 2.70-2.62 (m, 2H), 2.61-2.54 (m, 1H),

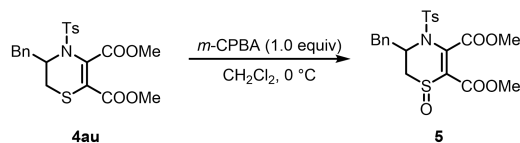
2.42 (s, 3H), 1.44-1.28 (m, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.5, 164.2, 144.8, 136.6, 134.3, 130.0, 129.5, 128.6, 128.2, 127.5, 126.9, 122.4, 62.6, 62.3, 51.2, 37.0, 28.5, 21.8, 14.1, 13.9 ppm. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{28}\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 490.1353, found 490.1371.

Dimethyl 3-methyl-2-phenyl-4-tosyl-3,4-dihydro-2H-1,4-thiazine-5,6-dicarboxylate (3ax)



Following the general procedure, the pure title compound was obtained in 50% yield as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.35-7.29 (m, 3H), 7.25-7.21 (m, 2H), 4.17-4.11 (m, 1H), 4.05 (d, $J = 3.2$ Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 2.45 (s, 3H), 0.87 (d, $J = 6.4$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 164.8, 164.5, 145.2, 135.5, 134.8, 130.2, 129.0, 128.7, 128.34, 128.30, 127.4, 121.8, 53.3, 53.2, 51.6, 47.8, 21.8, 12.0 ppm. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 462.1040, found 462.1043.

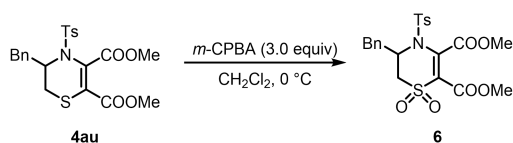
2.2 General Procedure for the Synthesis of Sulfoxides



m-CPBA (0.20 mmol, 1.0 equiv.) was added to the solution of 3,4-dihydro-1,4-thiazine **4au** (0.20 mmol) in DCM (2.0 mL) at 0 °C. Then the mixture was stirred at room temperature until the complete consumption of **4au** as monitored by TLC. The reaction mixture was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2:1), affording the corresponding sulfoxide **5** (99% yield, dr = 2:1). The major isomer: white solid, m. p. 173-174 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.35-7.27 (m, 3H), 7.22-7.17 (m, 2H), 4.44-4.34 (m, 1H), 3.40 (s, 3H), 3.88 (s, 3H), 3.21-3.08 (m, 2H), 3.01-2.89 (m, 1H), 2.63 (dd, $J = 3.6, 13.2$ Hz, 1H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 162.9, 146.3, 142.7, 135.1, 134.1, 130.6, 129.4, 129.3, 128.1, 127.8, 116.8, 55.7, 54.0, 53.3, 48.0, 37.0, 21.9 ppm. HRMS (ESI) calcd for

$C_{22}H_{24}NO_7S_2$ $[M+H]^+$ 478.0989, found: 478.0978. The minor isomer: colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.19-7.12 (m, 3H), 7.08-7.02 (m, 2H), 4.66-4.56 (m, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.40 (dd, $J = 2.8, 14.8$ Hz, 1H), 3.33 (dd, $J = 8.8, 13.6$ Hz, 1H), 2.80-2.66 (m, 2H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 163.7, 146.2, 138.3, 136.3, 133.5, 130.4, 129.9, 128.7, 128.4, 126.9, 121.7, 53.9, 53.5, 52.7, 50.2, 34.0, 21.9 ppm. HRMS (ESI) calcd for $C_{22}H_{24}NO_7S_2$ $[M+H]^+$ 478.0989, found: 478.0978.

2.3 General Procedure for the Synthesis of Sulfones



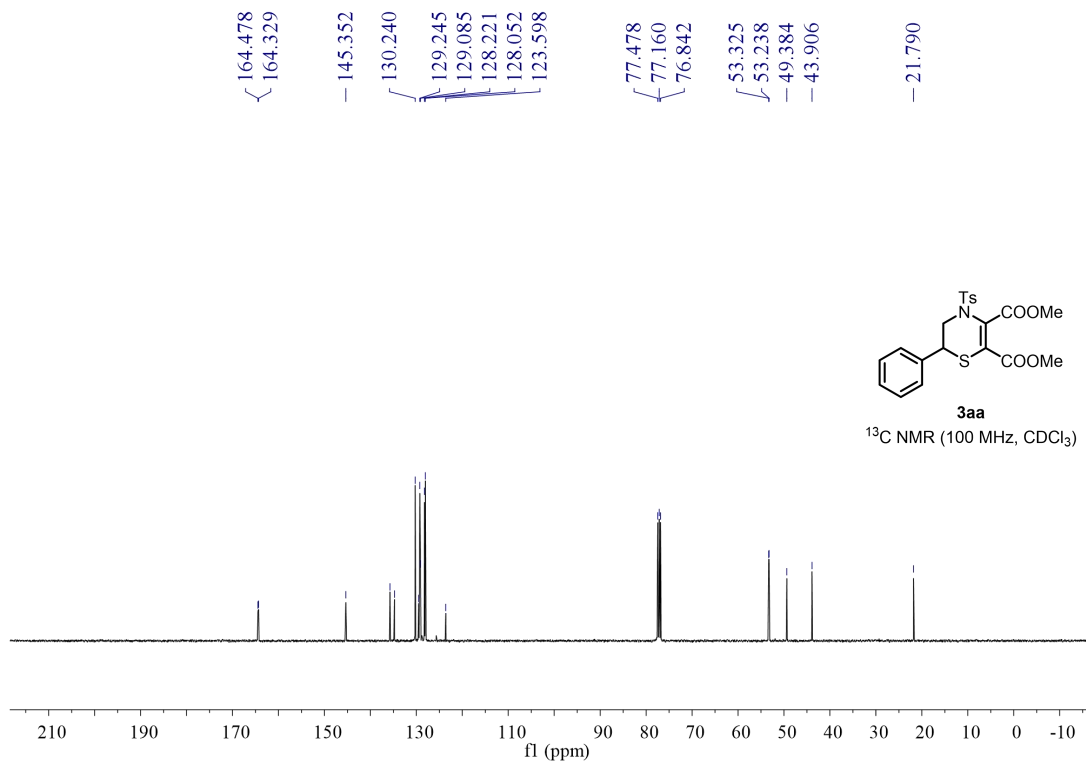
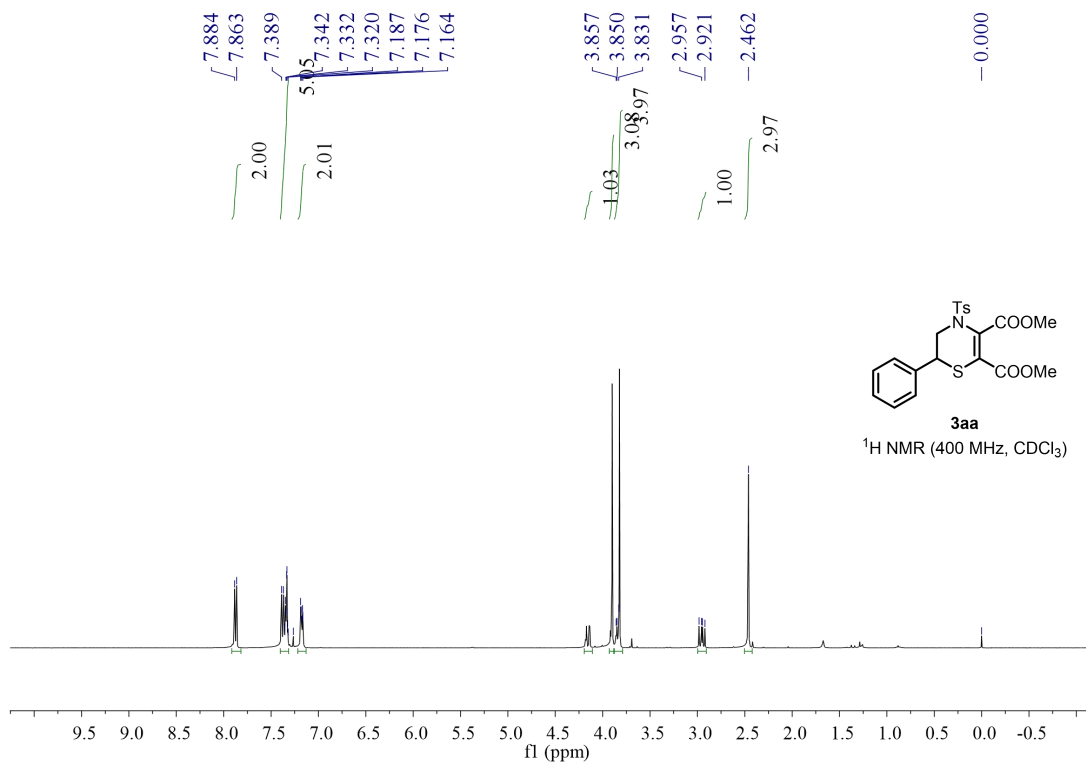
m-CPBA (0.60 mmol, 3.0 equiv.) was added to the solution of 3,4-dihydro-1,4-thiazine **4au** (0.20 mmol) in DCM (2.0 mL) at 0 °C. Then the mixture was stirred at room temperature. After the complete consumption of **4au** as monitored by TLC, the mixture was diluted with DCM and washed with saturated aqueous solution of $NaHSO_3$. Then the aqueous layer was extracted with DCM three times. The combined organic layers were washed with saturated brine solution and dried over anhydrous Na_2SO_4 . After the evaporation of solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1), affording the corresponding sulfone **6** as a white solid (97% yield). m. p. 81-82 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.28-7.20 (m, 3H), 7.14-7.09 (m, 2H), 4.56-4.48 (m, 1H), 3.97 (s, 3H), 3.93 (s, 3H), 2.40 (dd, $J = 10.0, 13.6$ Hz, 1H), 3.24-3.19 (m, 2H), 2.86 (dd, $J = 5.6, 13.6$ Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.9, 146.8, 142.7, 135.2, 133.4, 130.7, 129.7, 129.0, 128.3, 127.5, 118.0, 58.4, 54.2, 53.6, 52.7, 35.1, 21.9 ppm. HRMS (ESI) calcd for $C_{22}H_{24}NO_8S_2$ $[M+H]^+$ 494.0938, found: 494.0931.

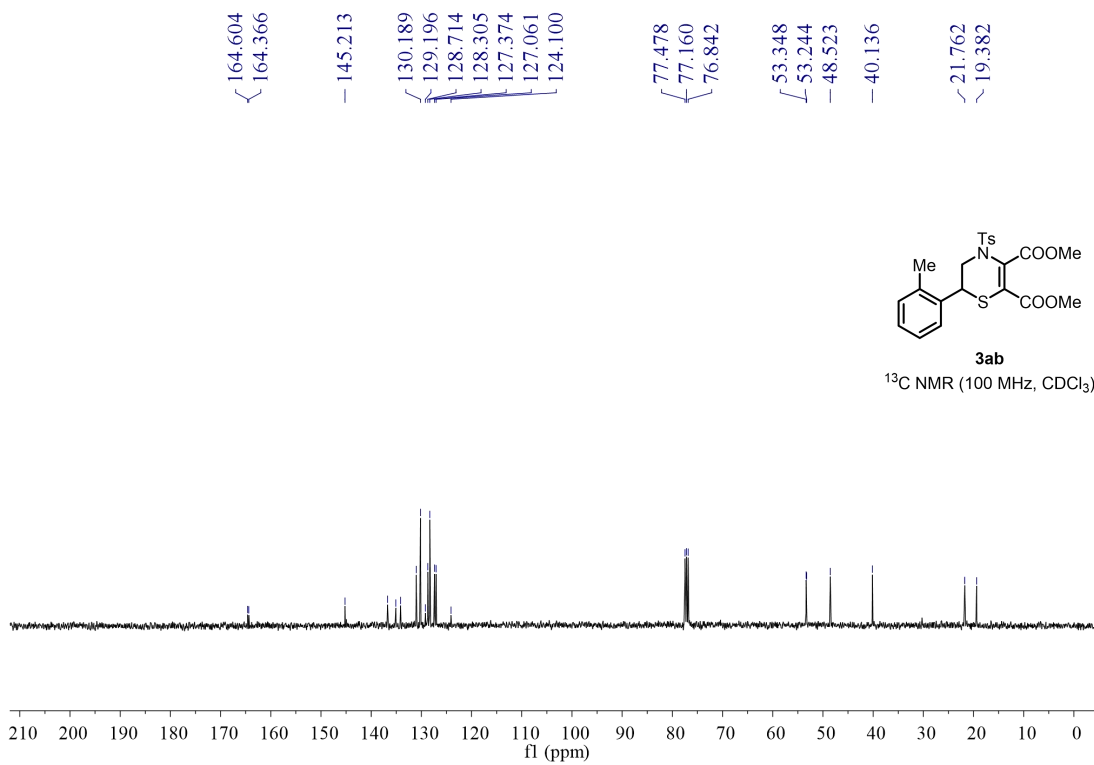
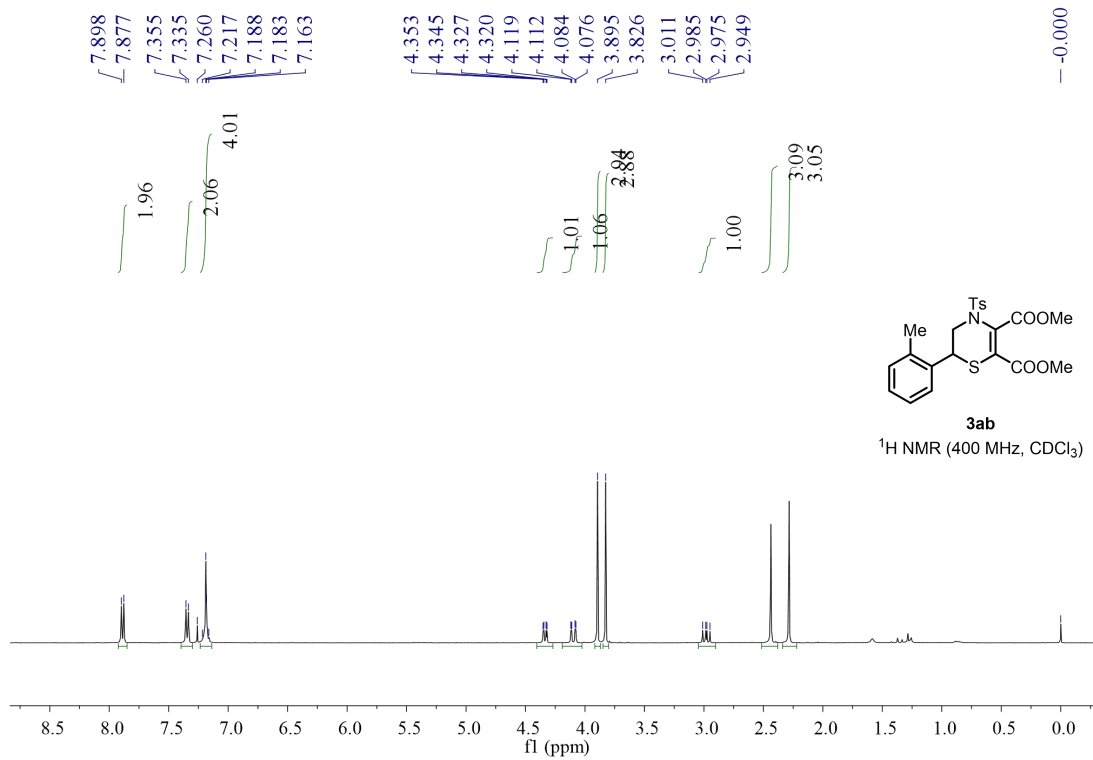
3. References

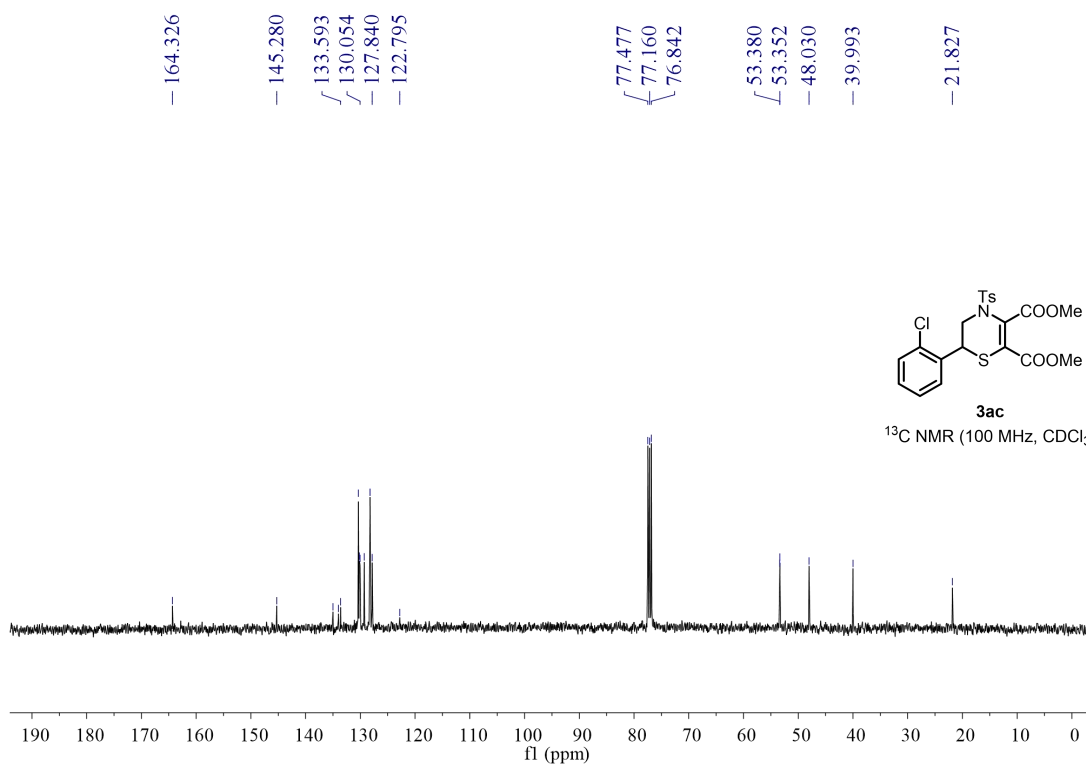
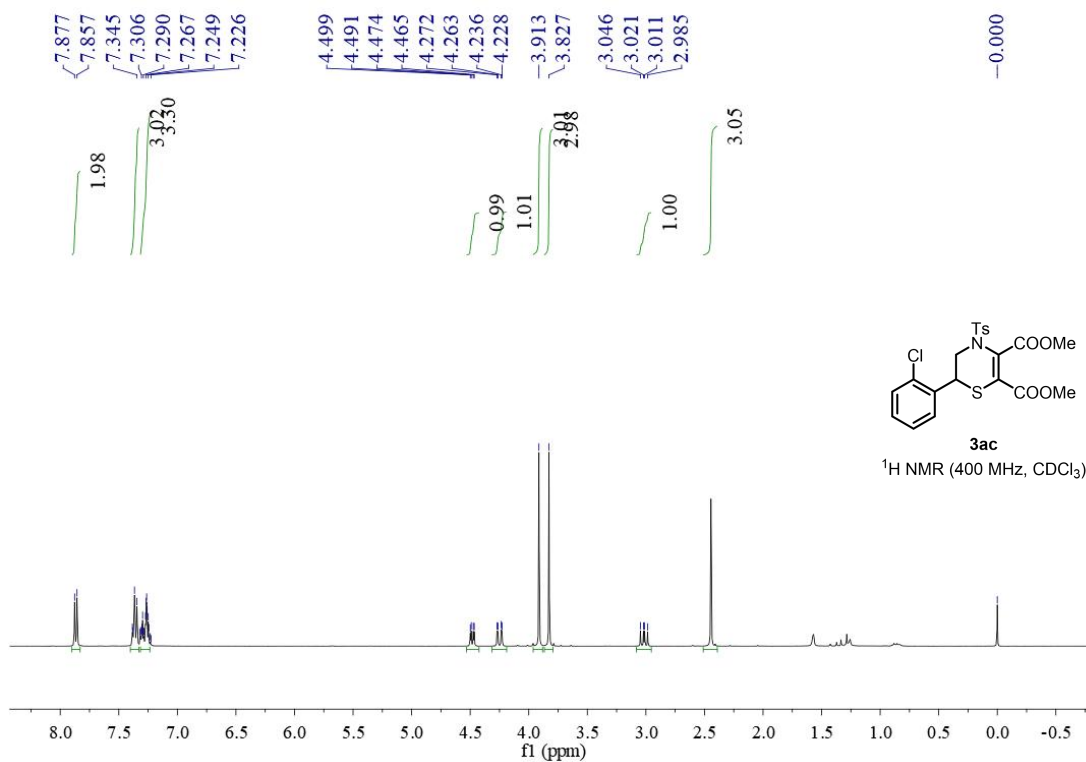
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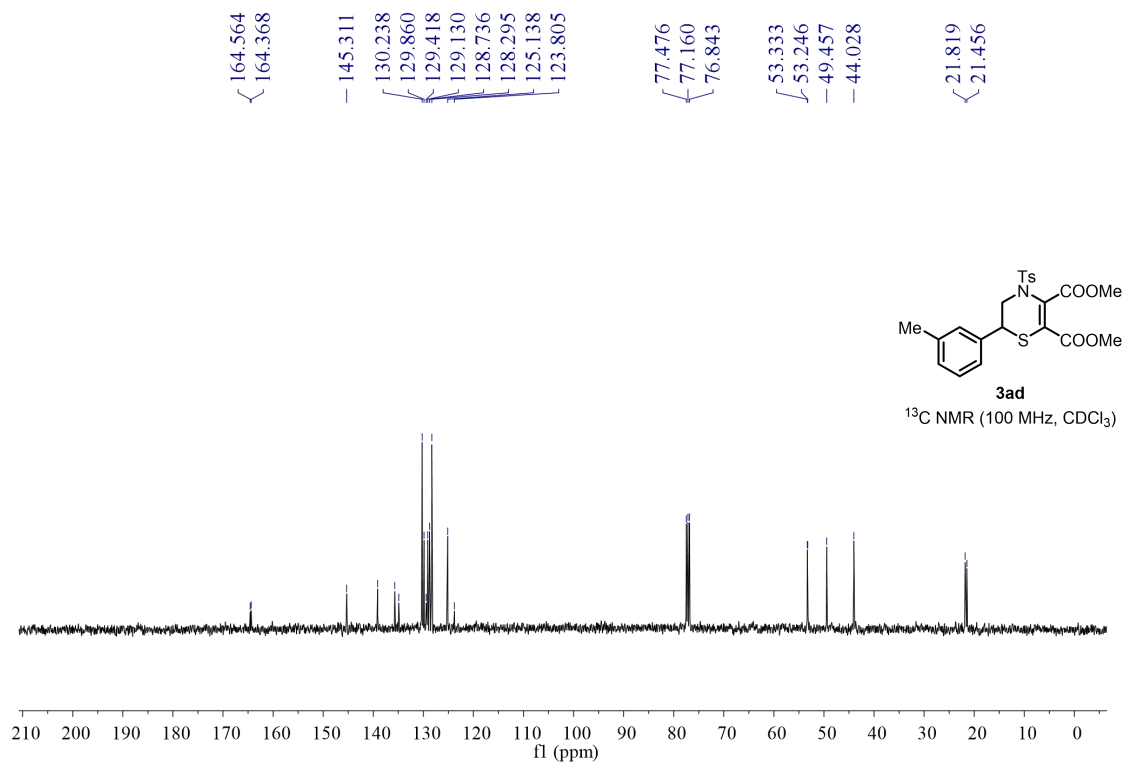
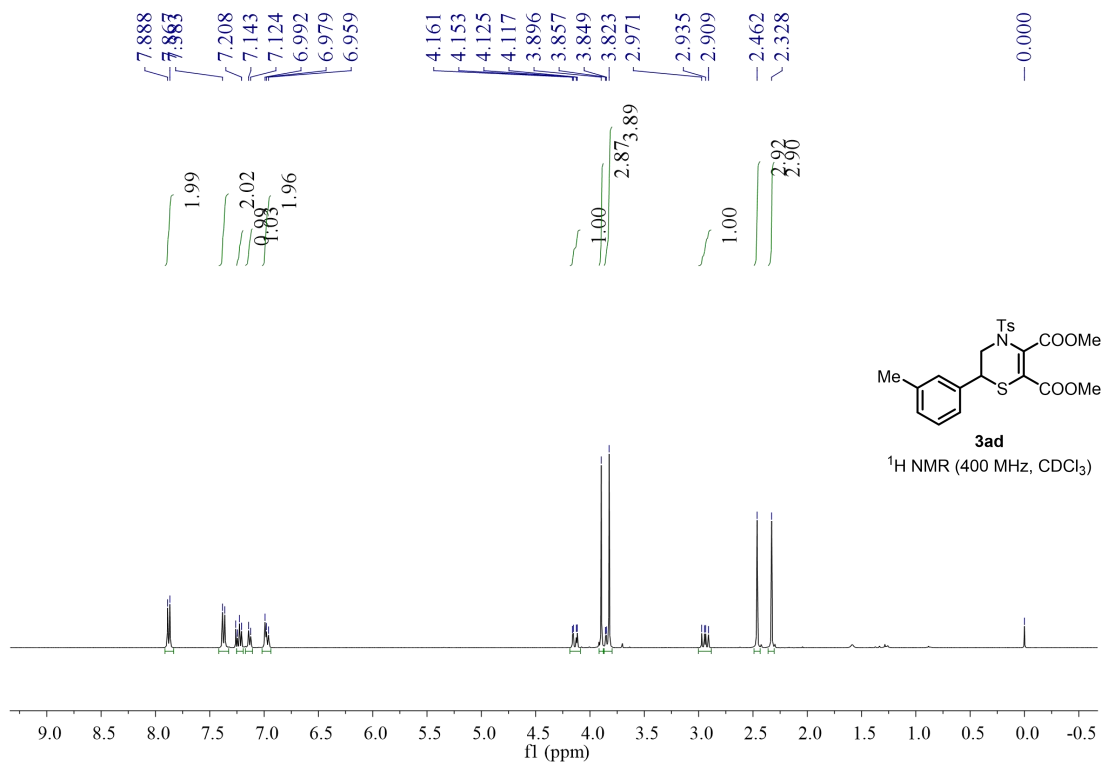
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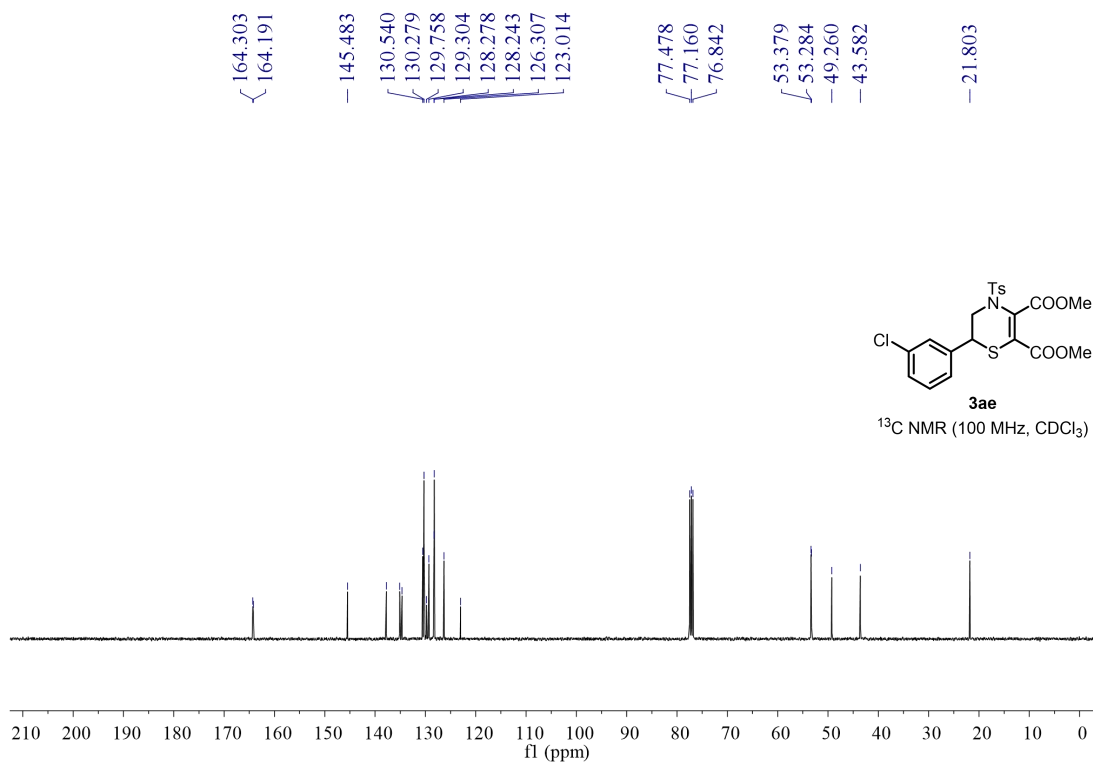
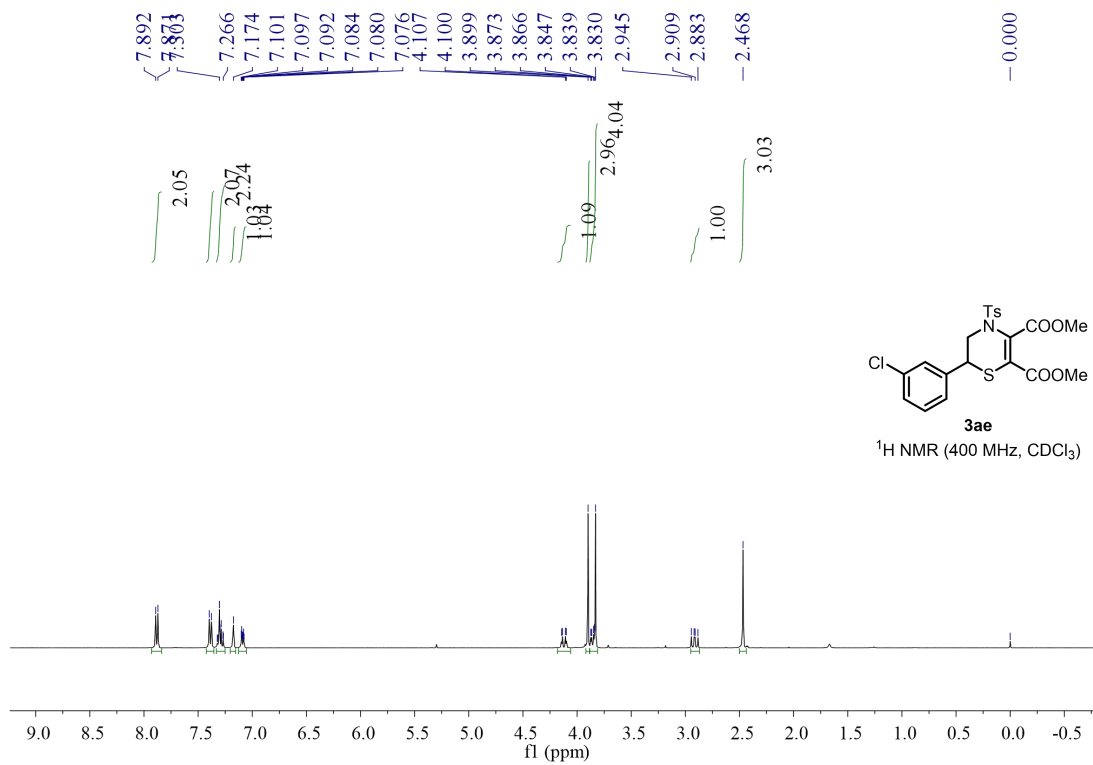
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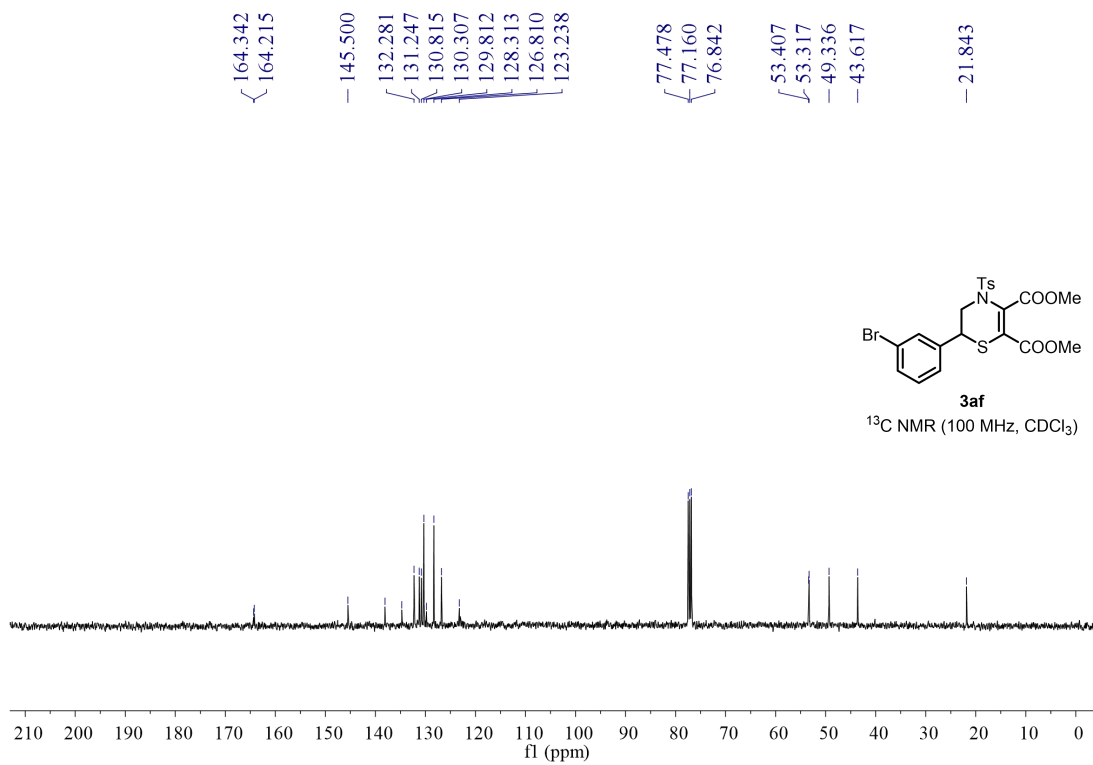
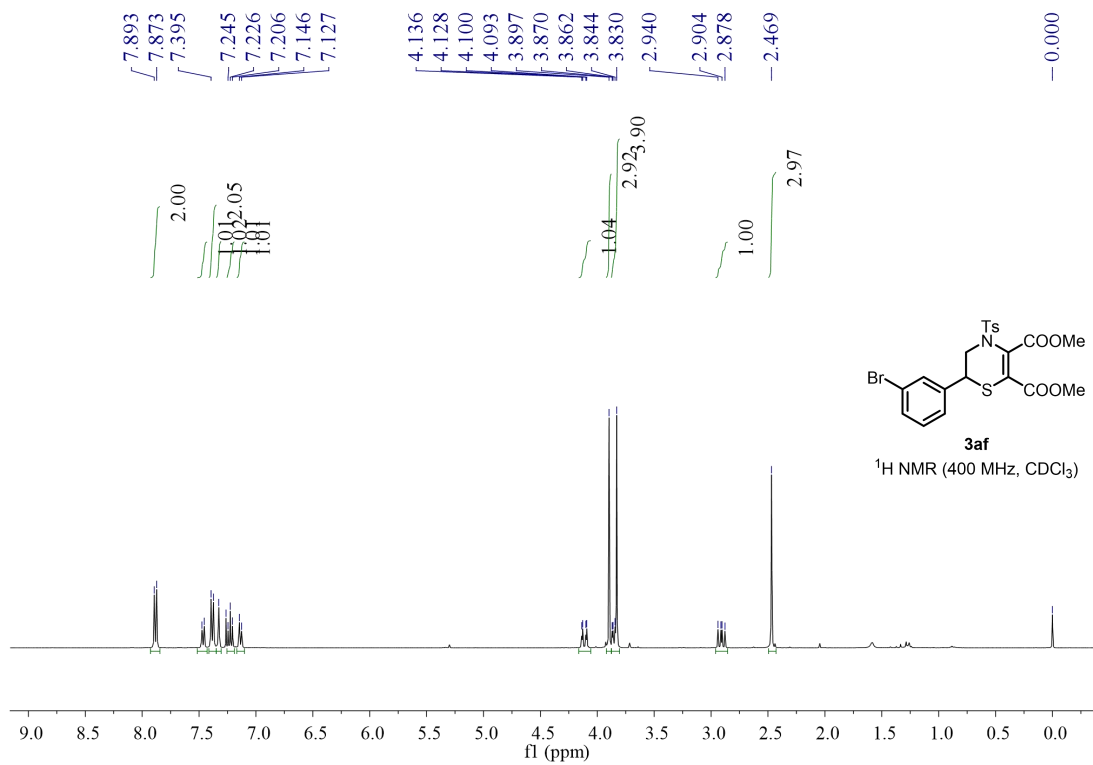


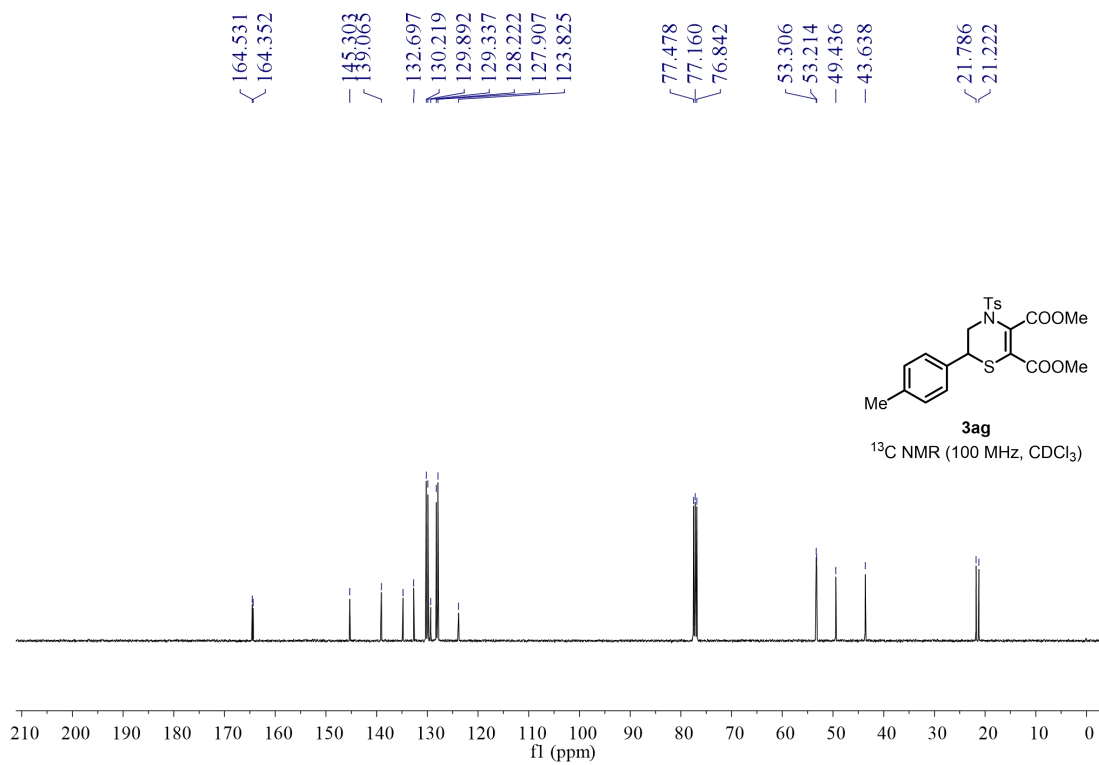
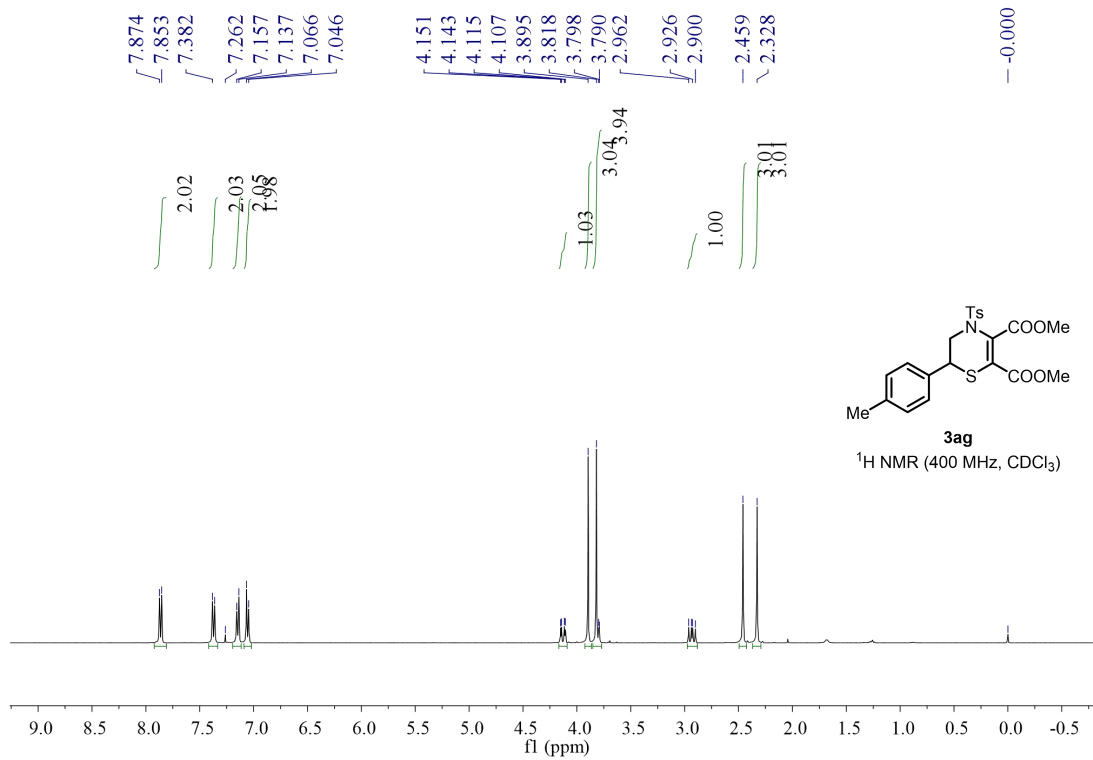


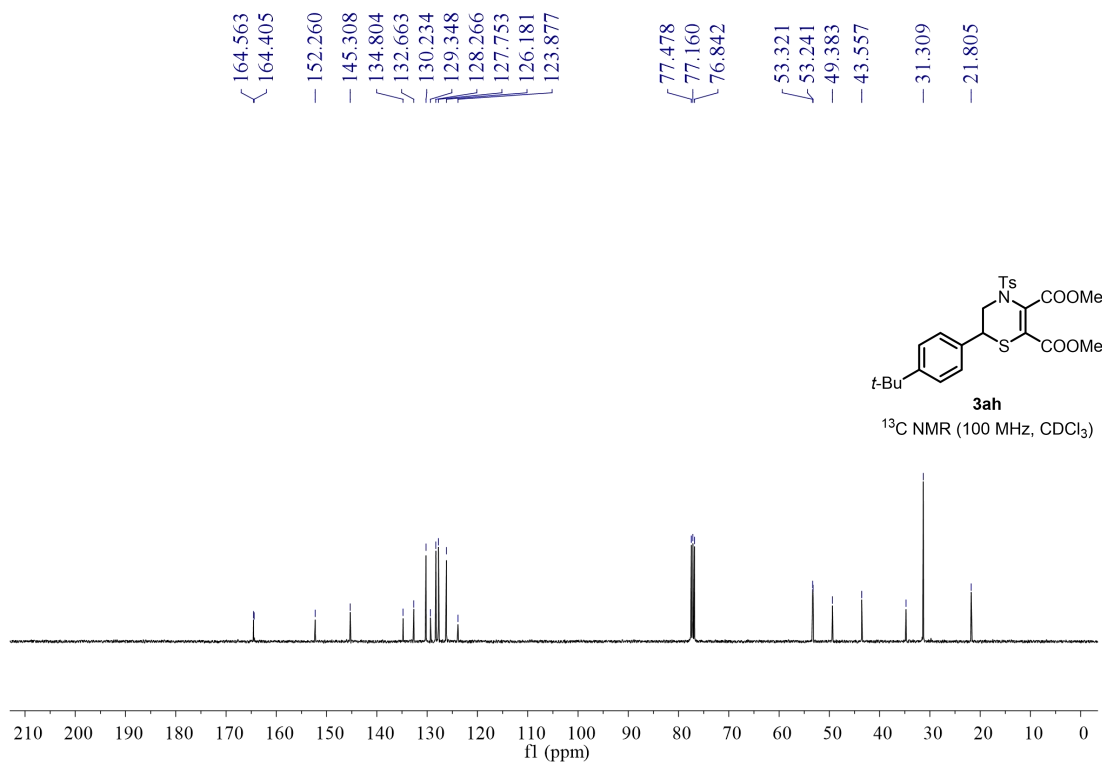
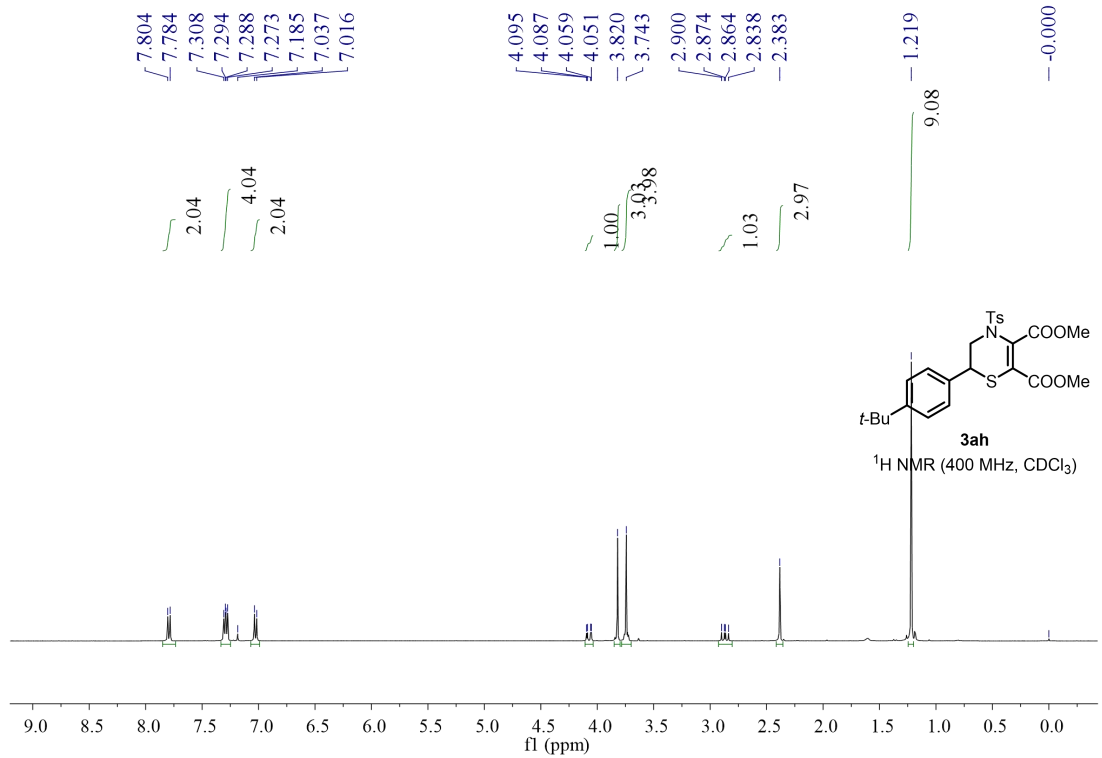


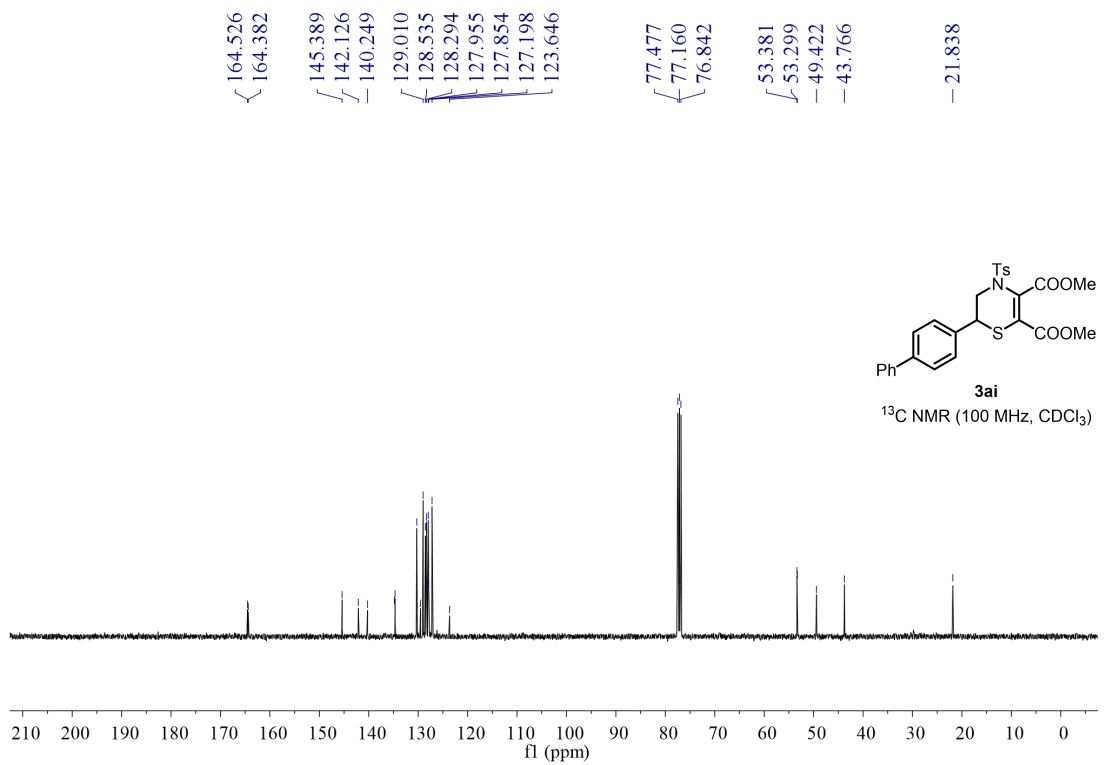
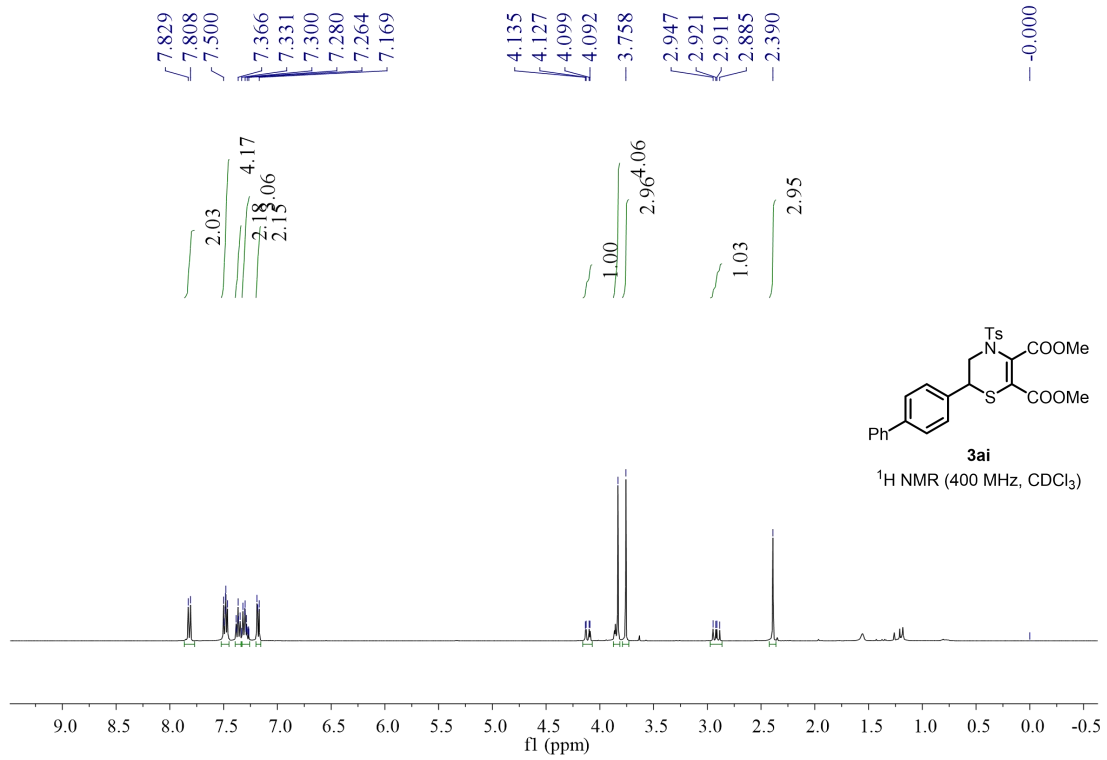


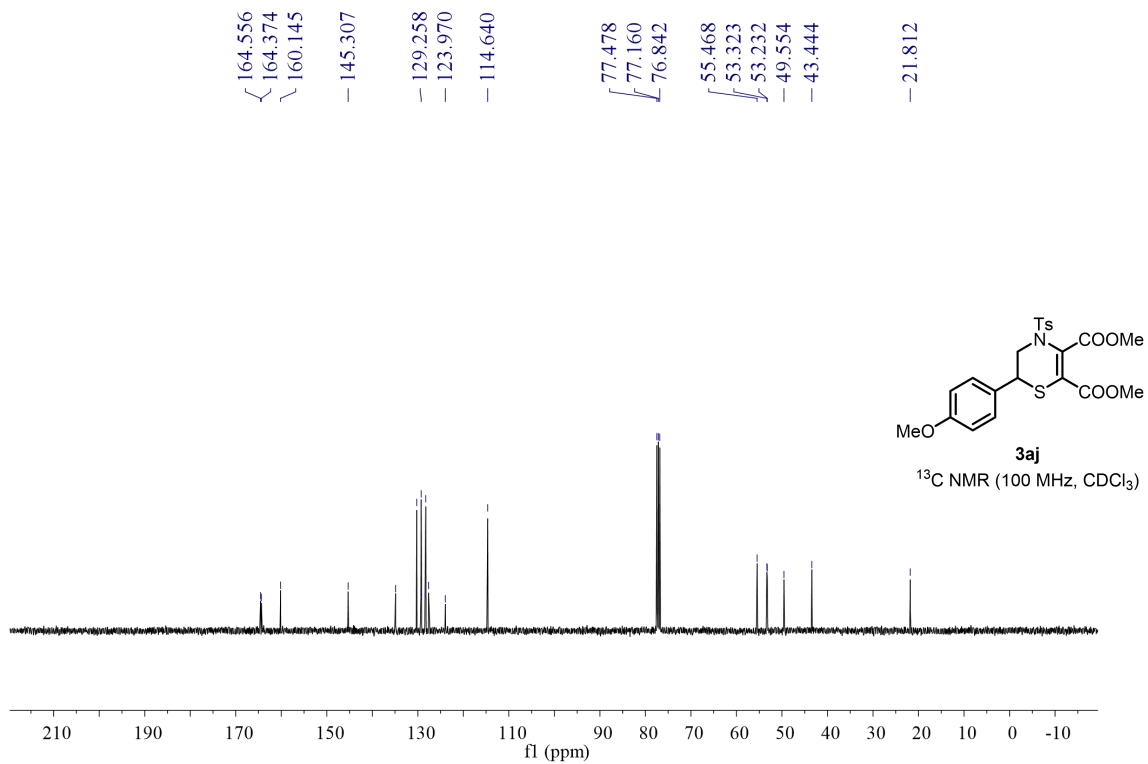
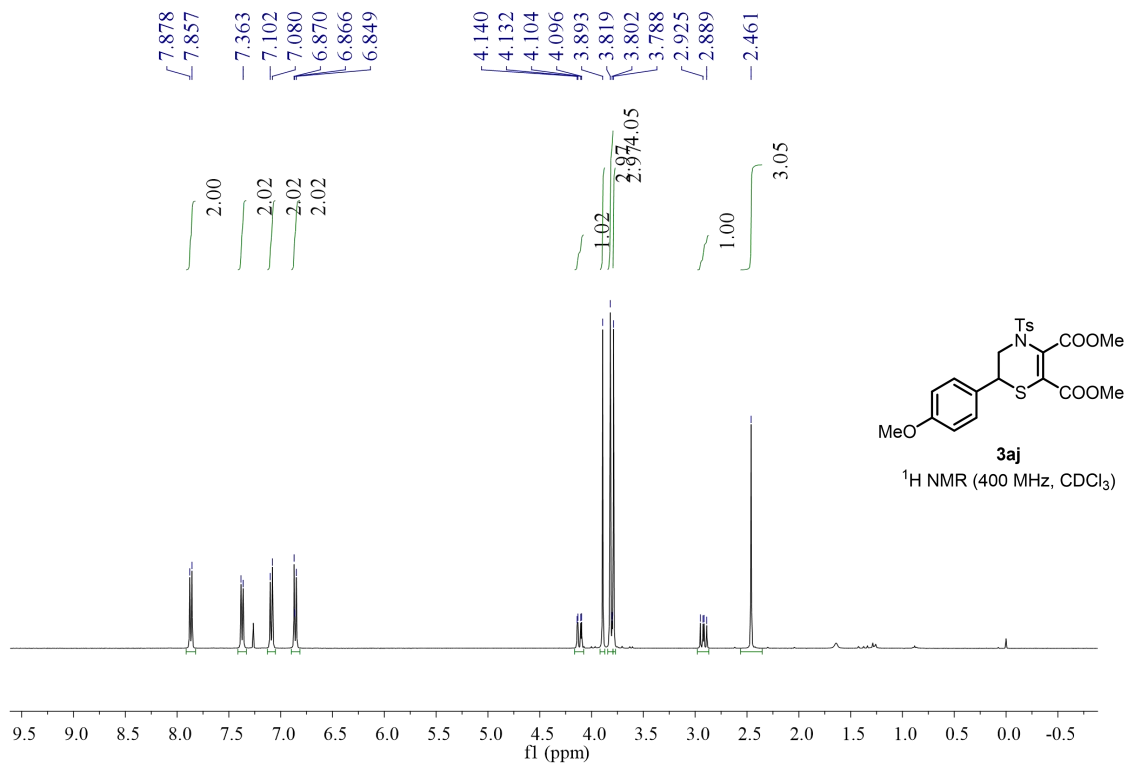


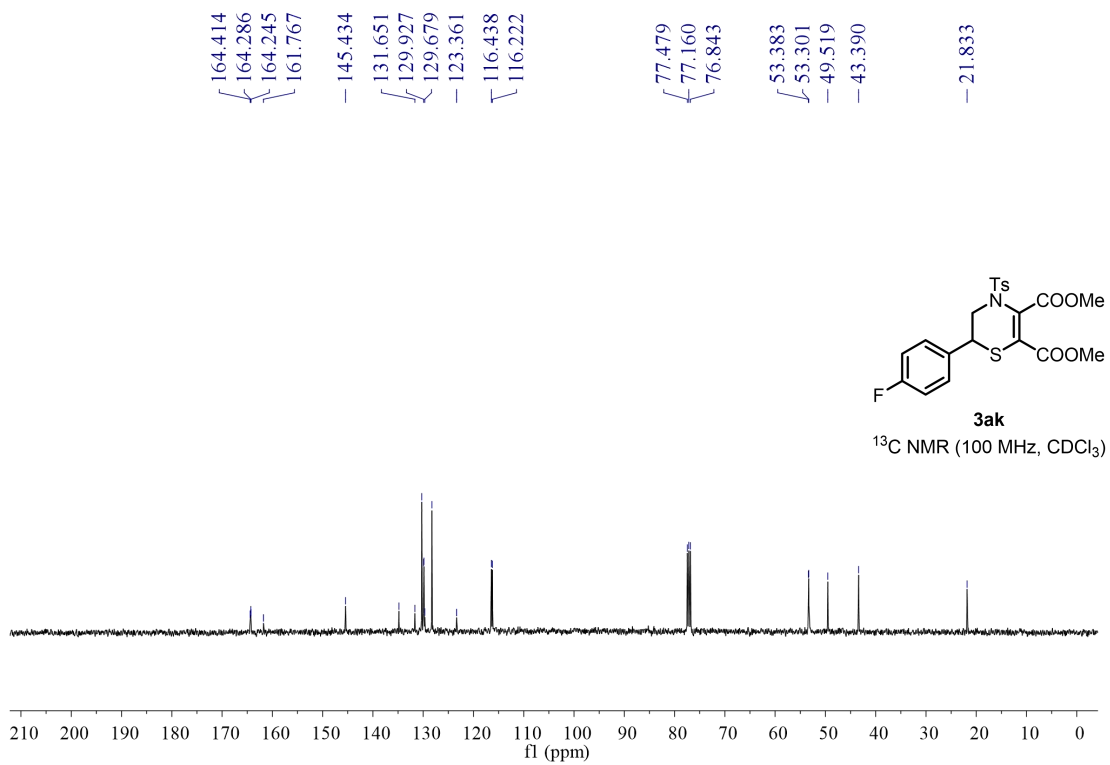
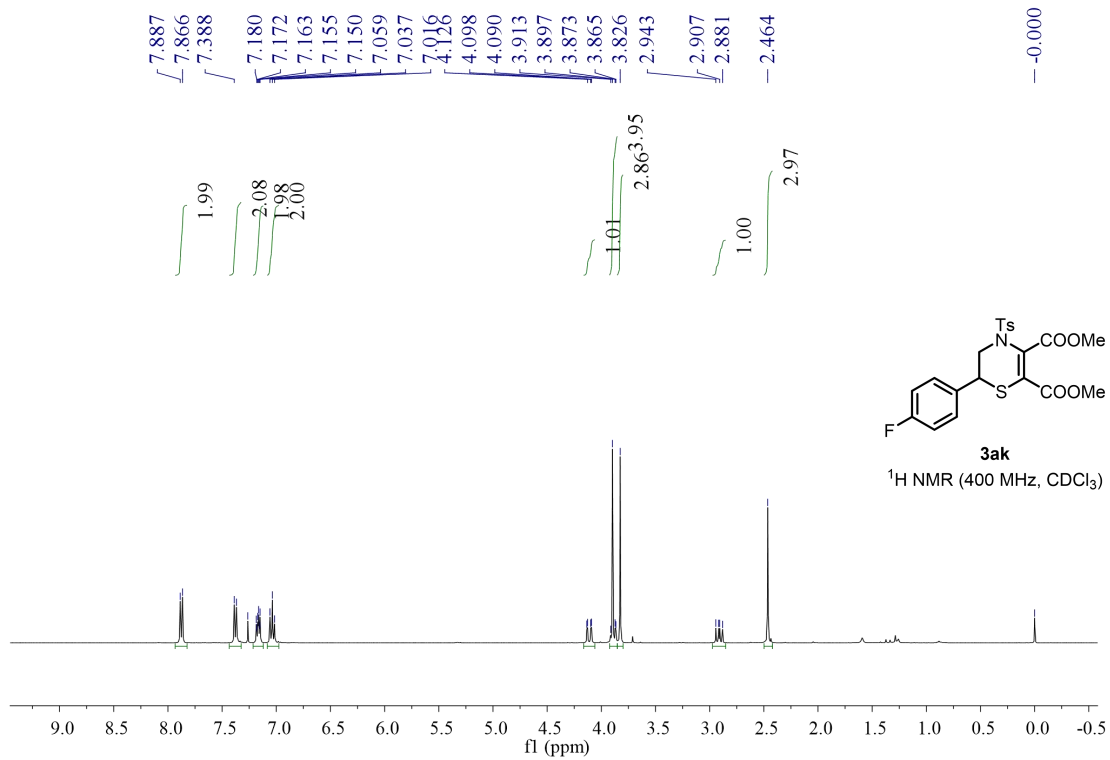




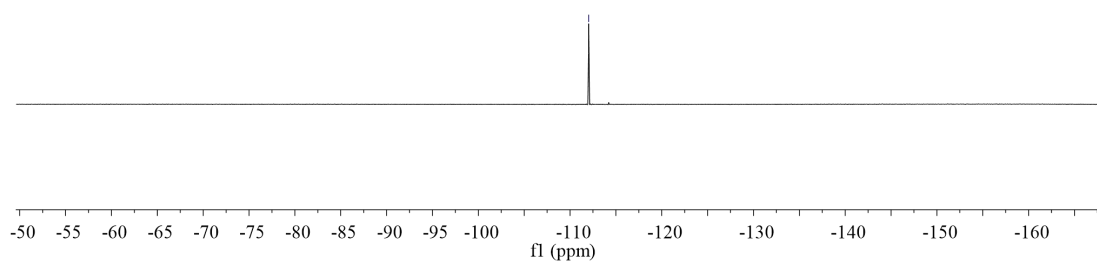
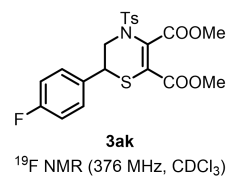


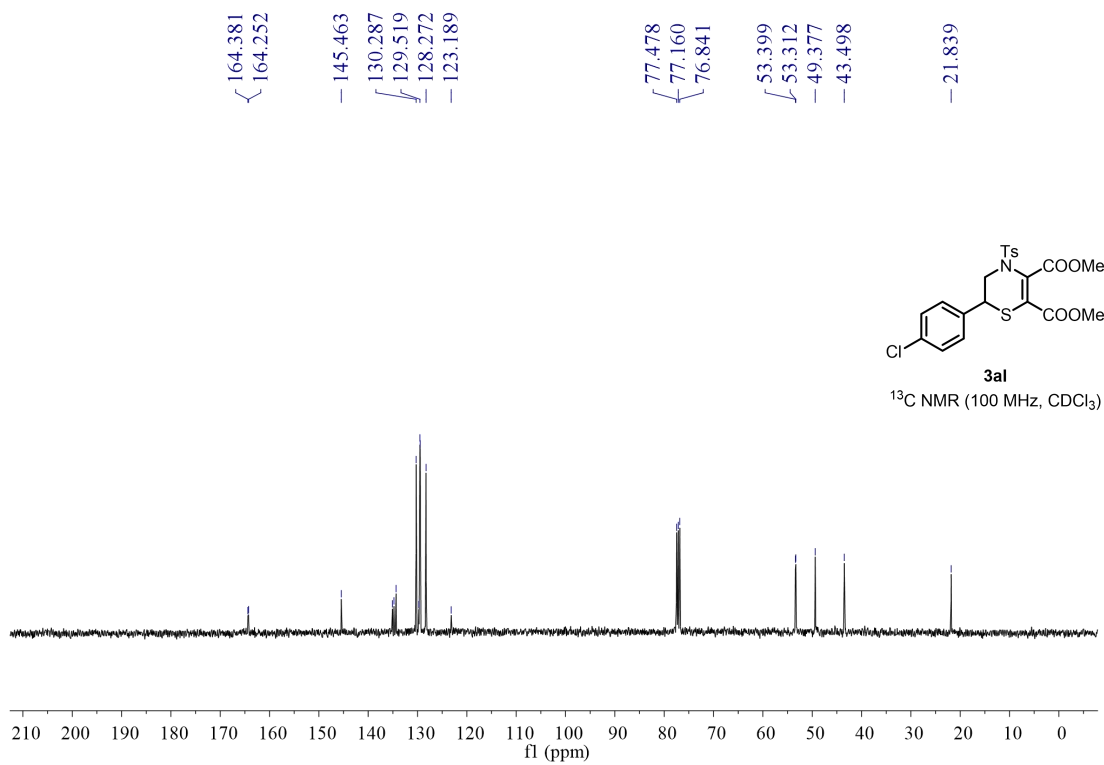
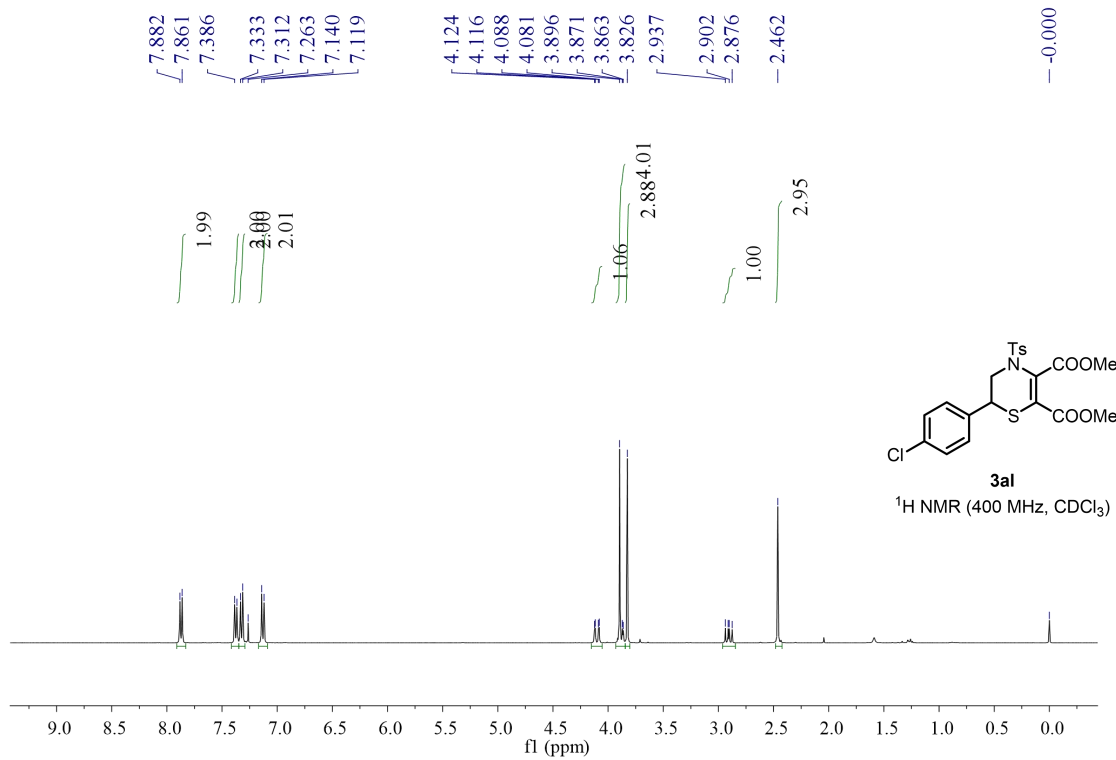


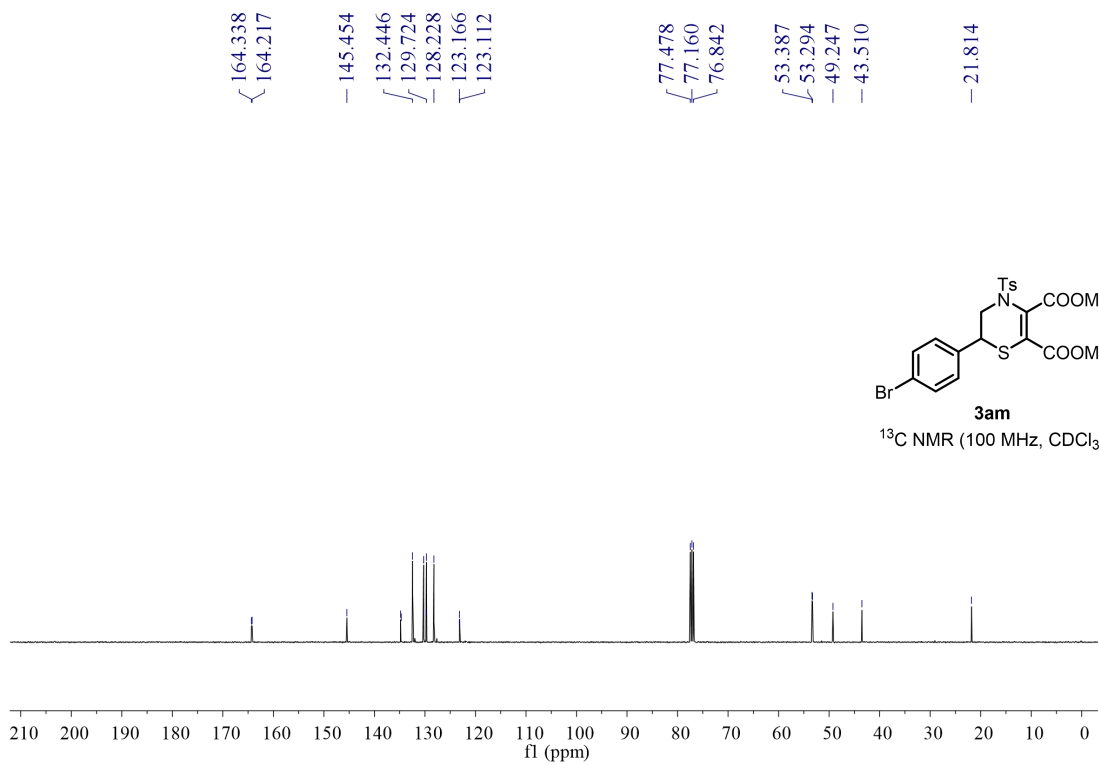
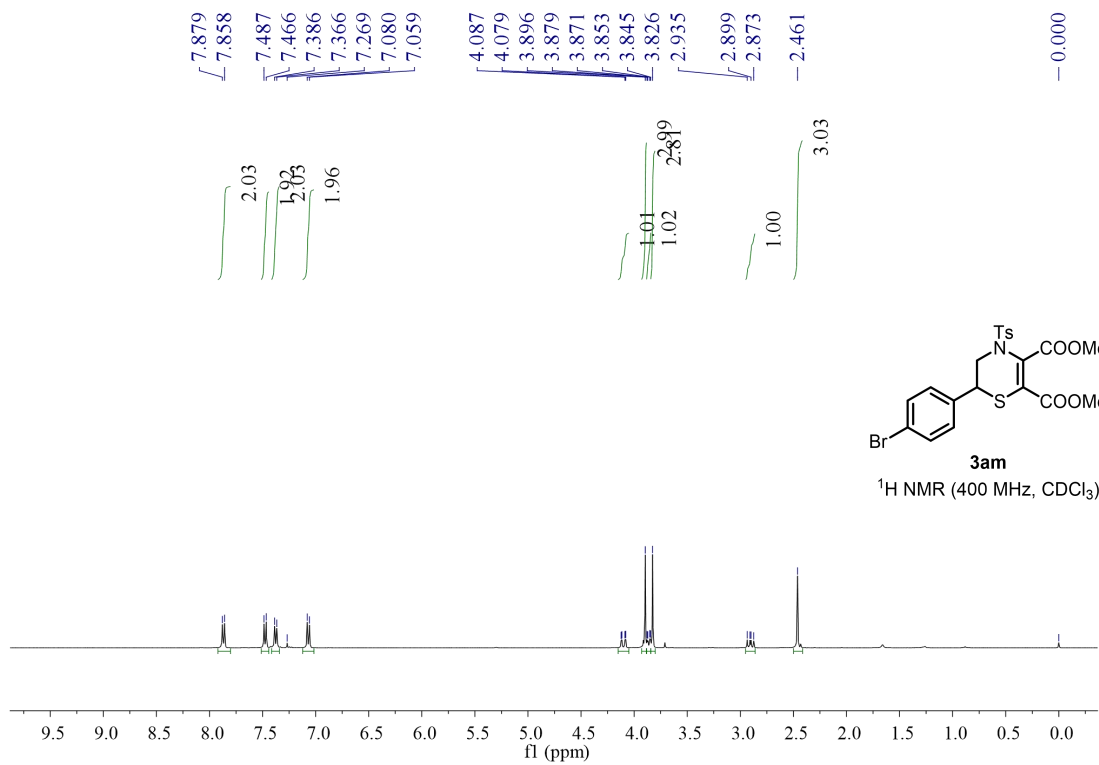


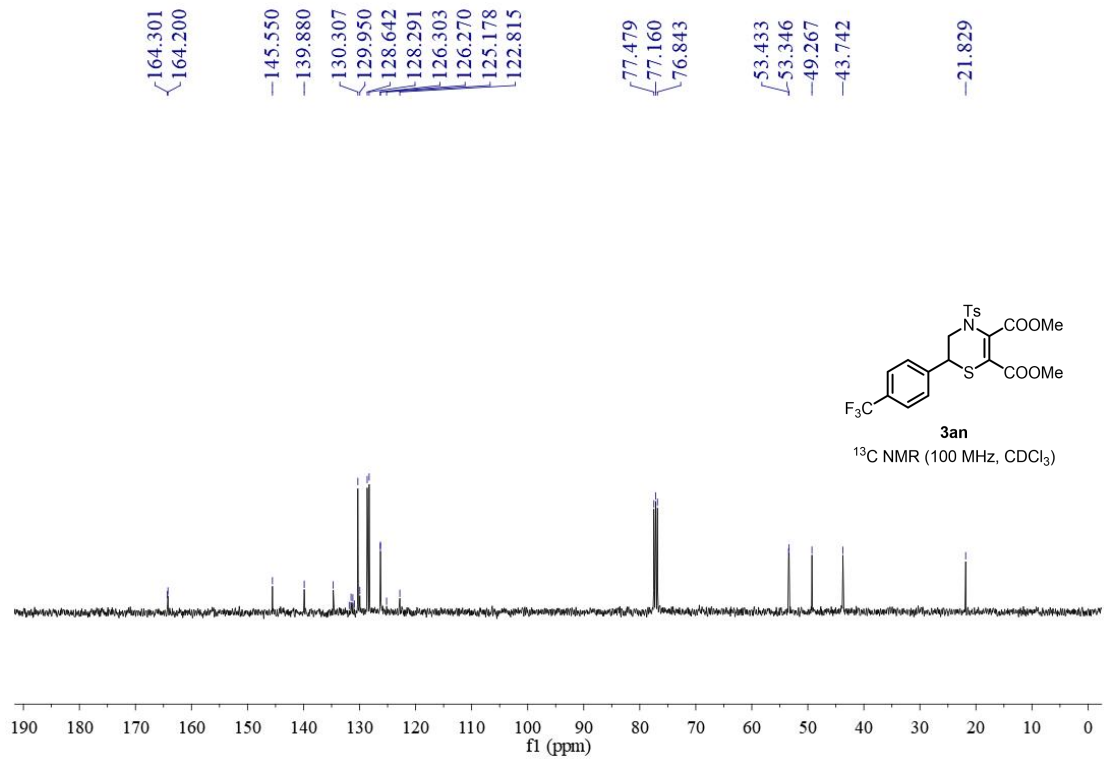
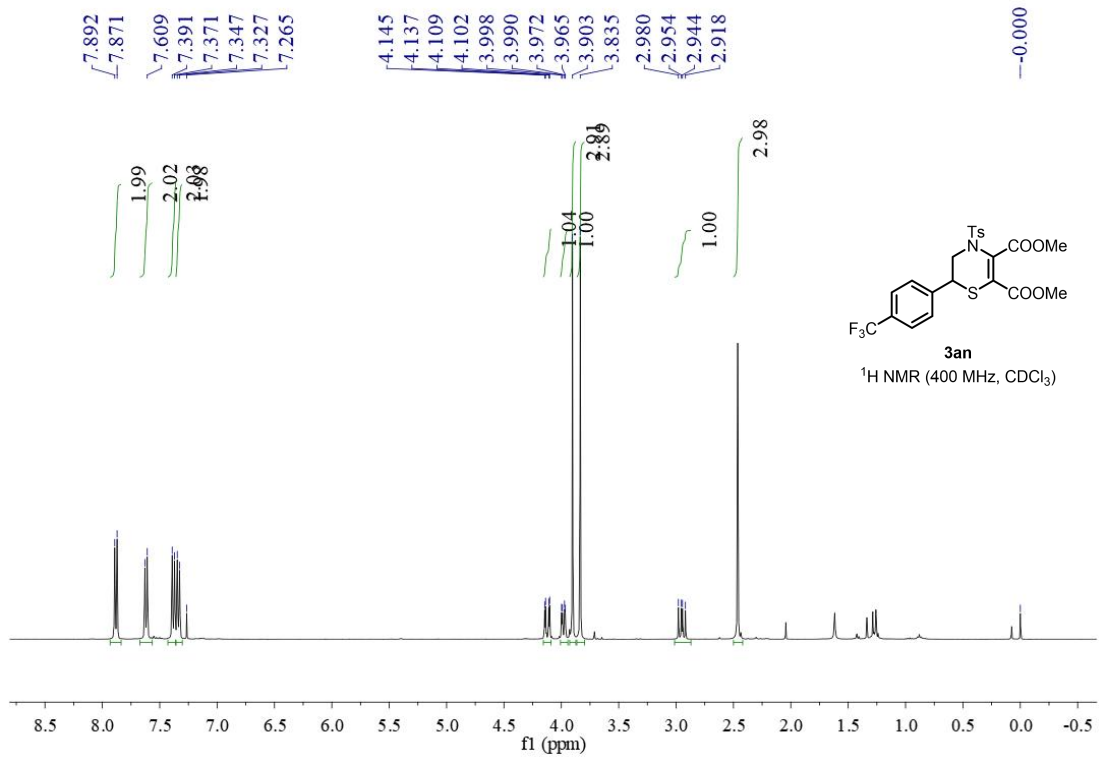


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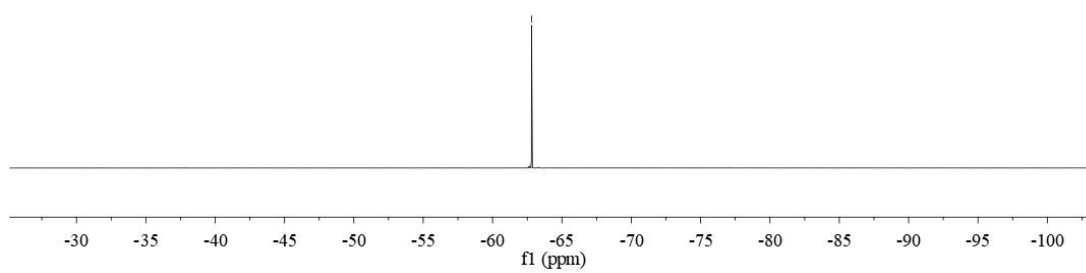
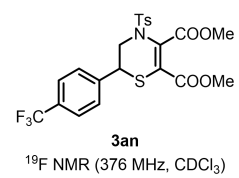


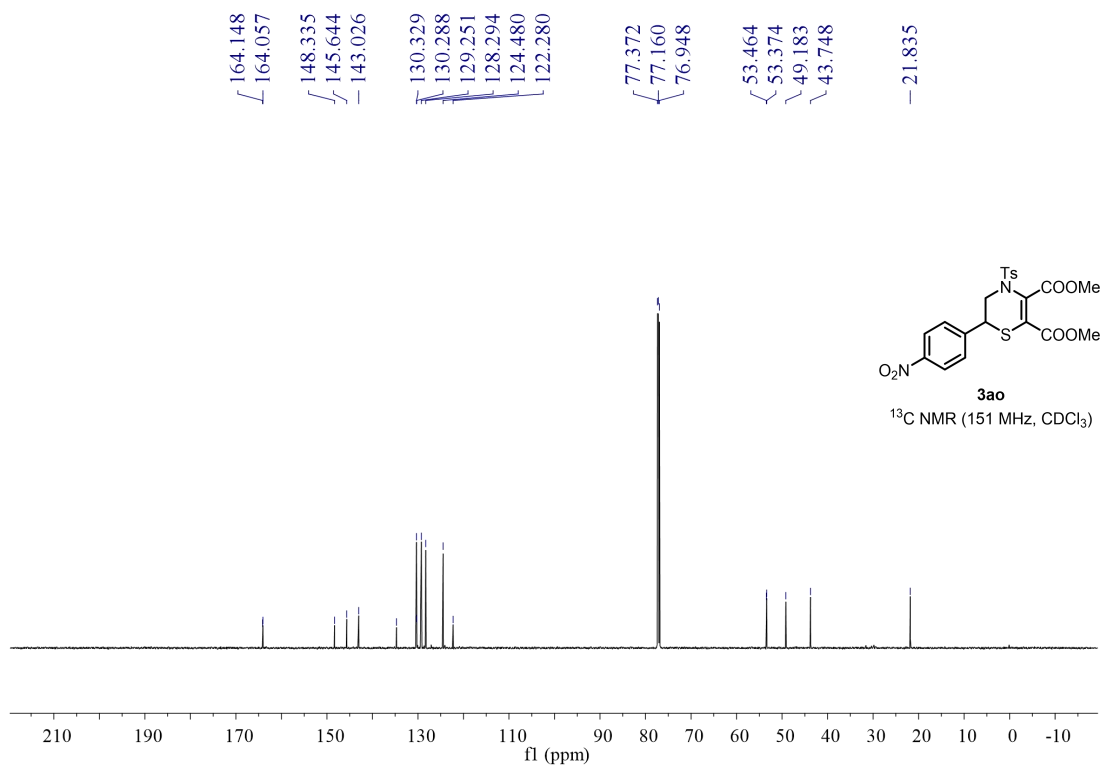
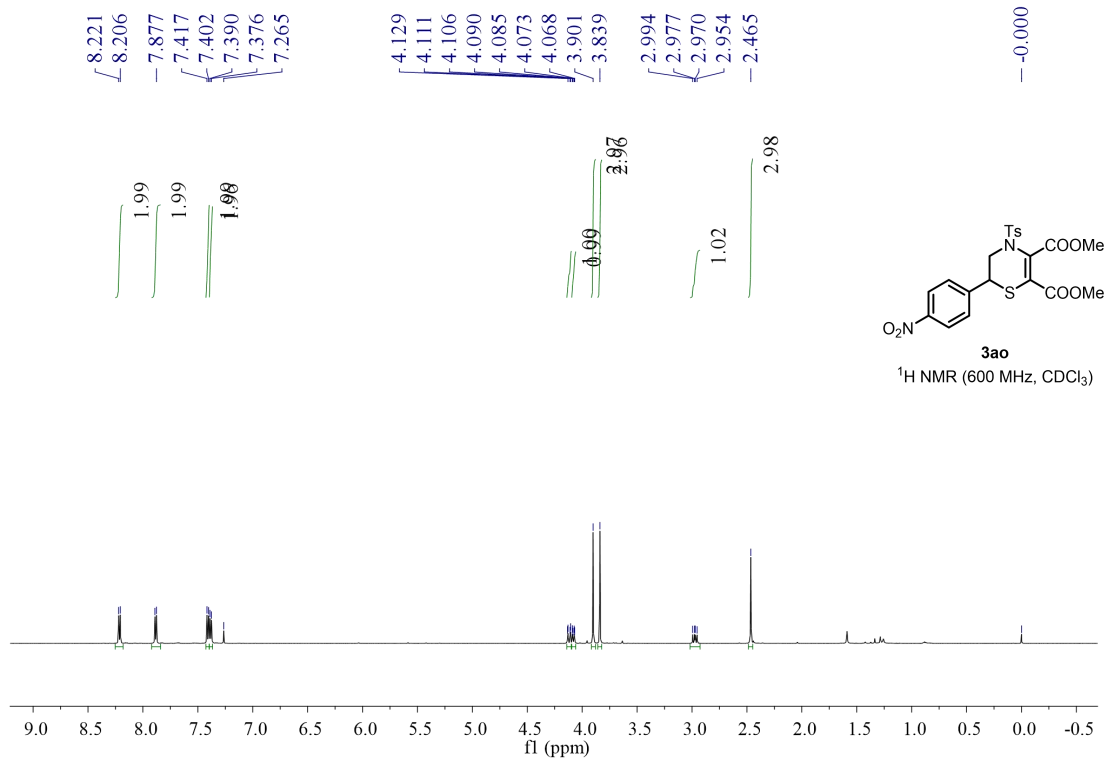


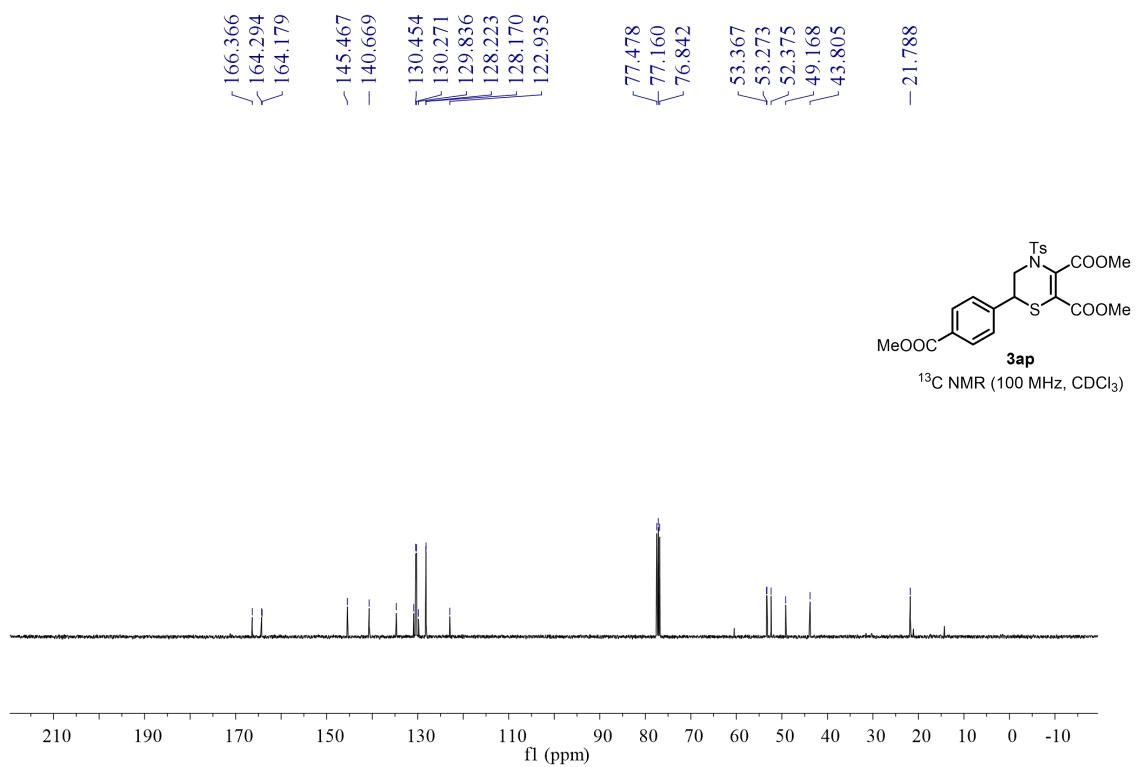
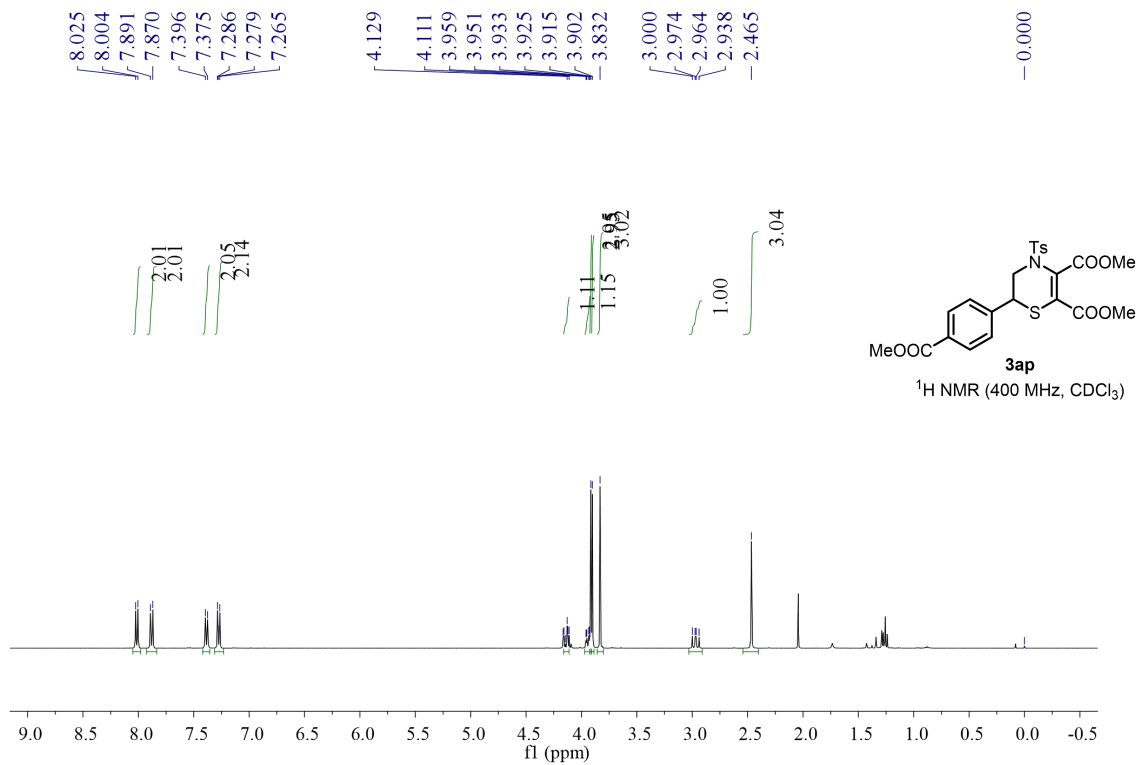


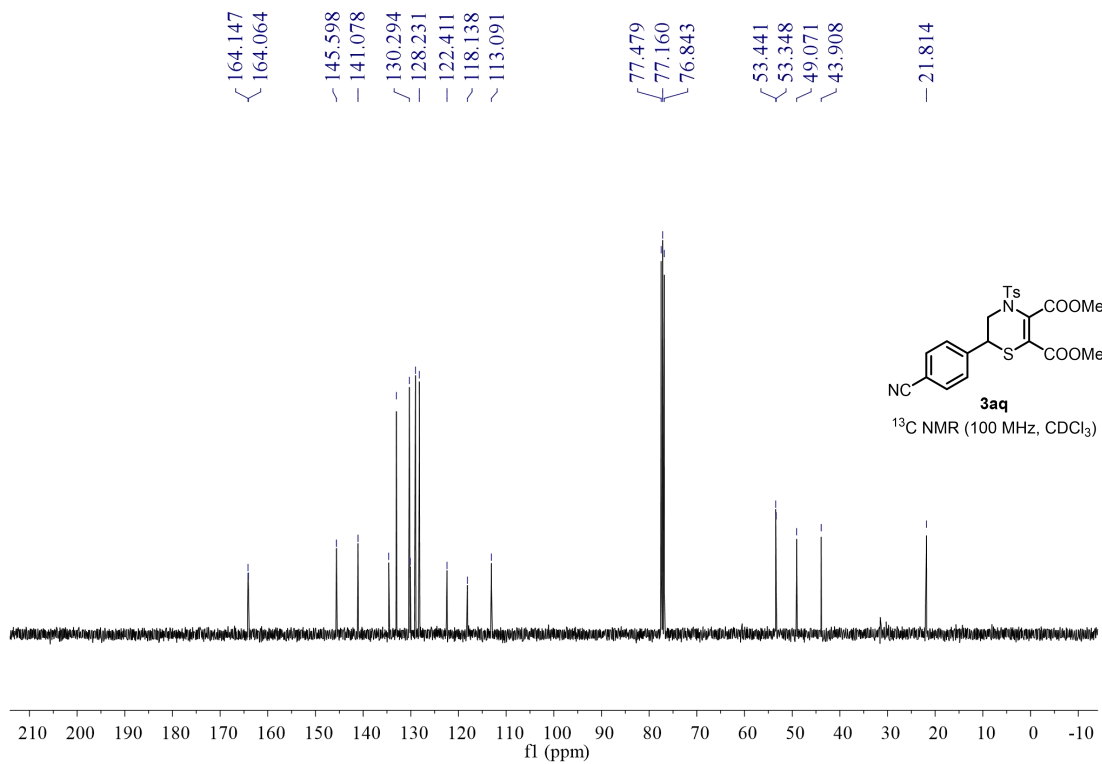
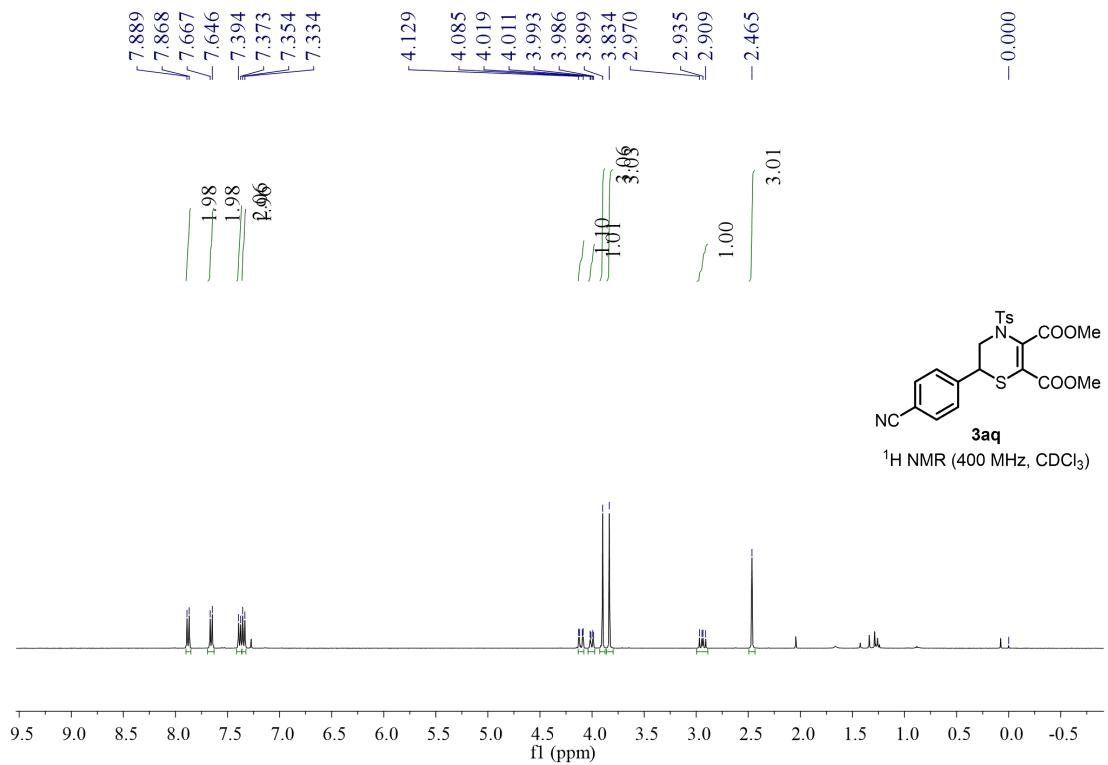


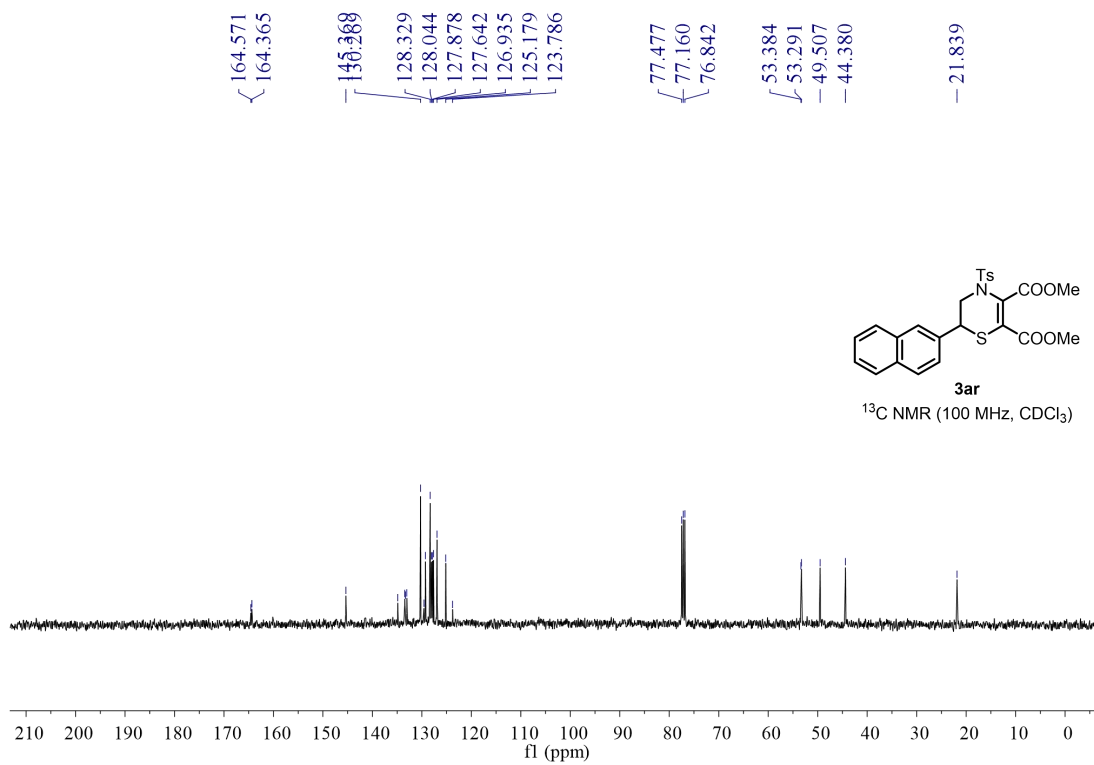
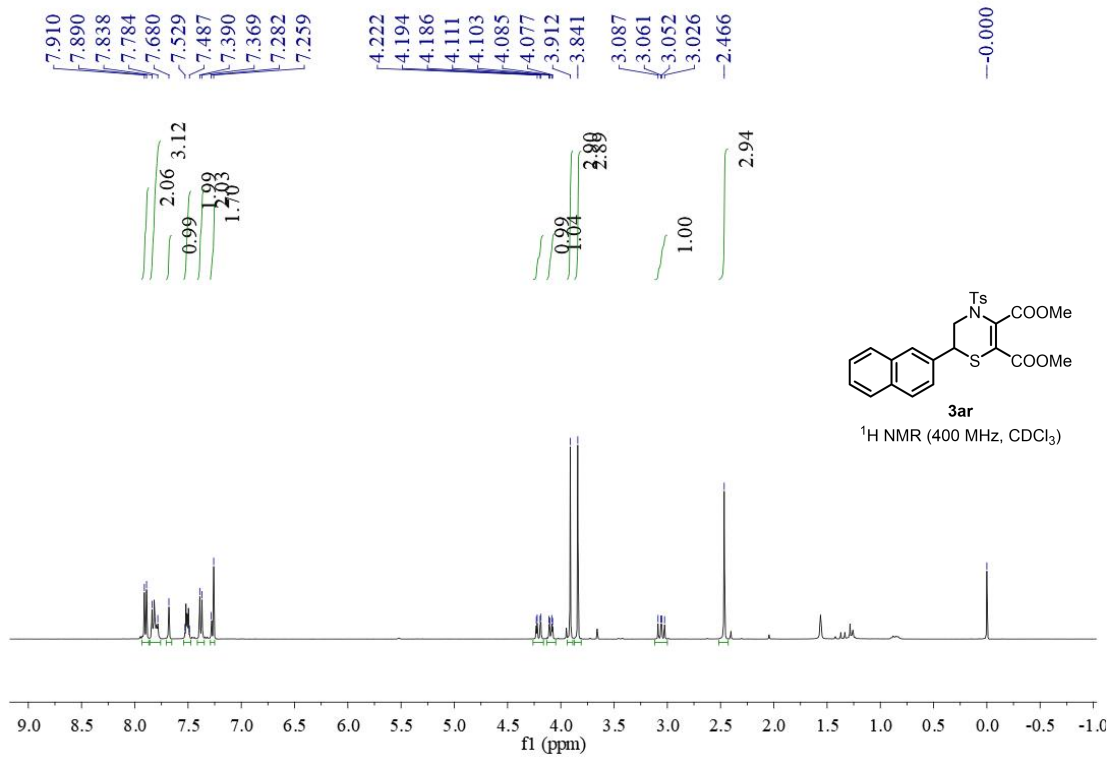
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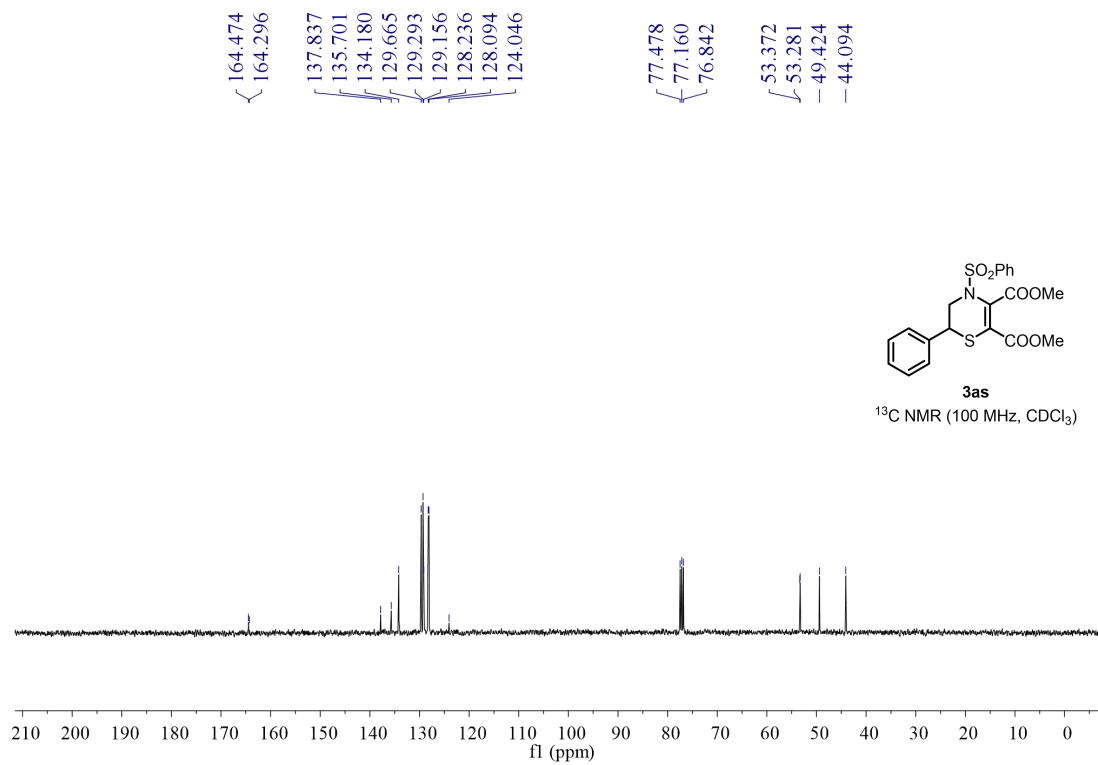
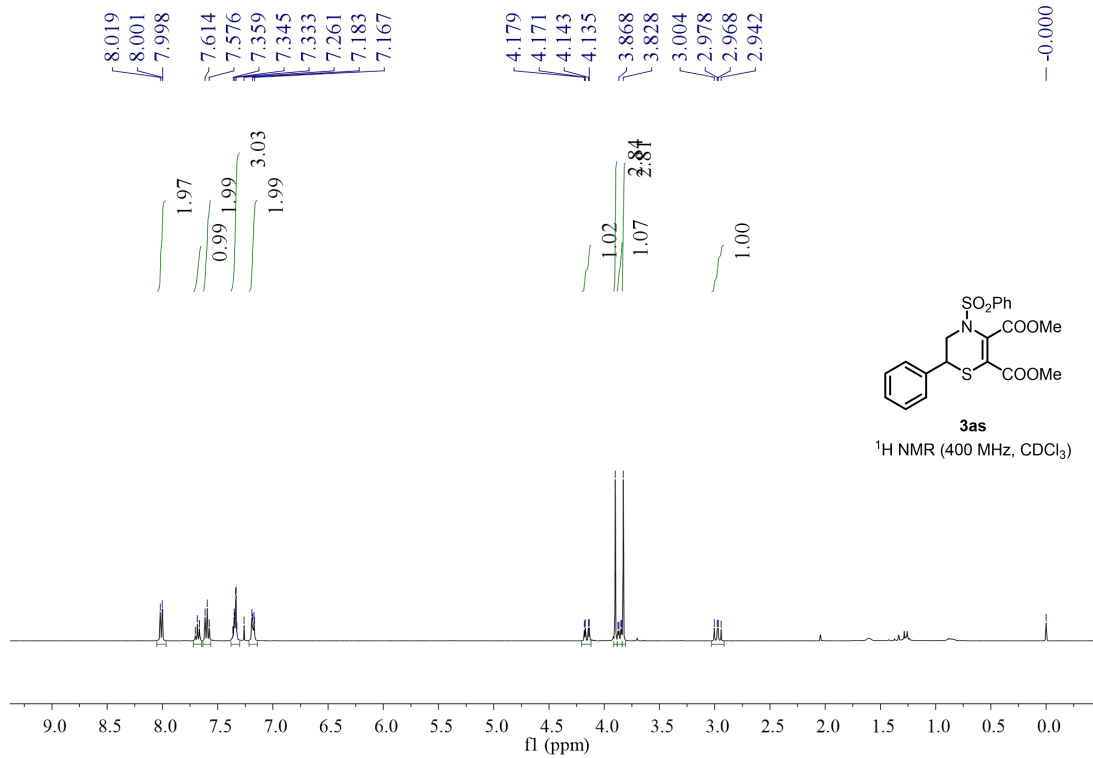


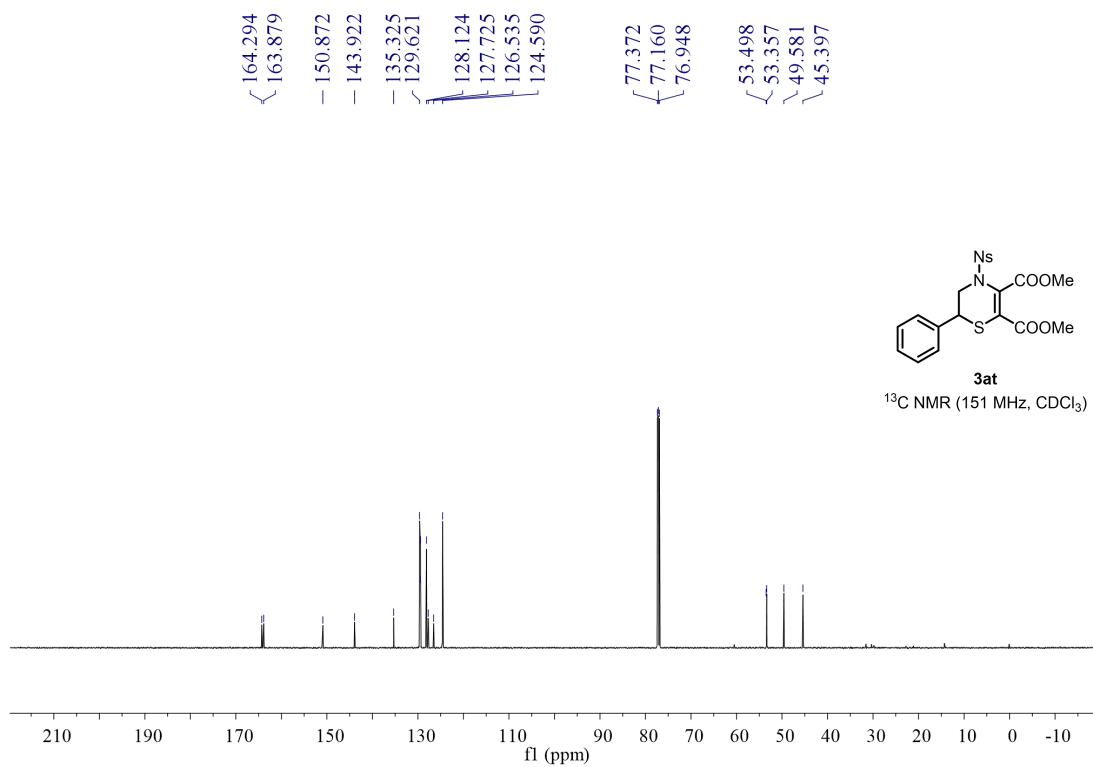
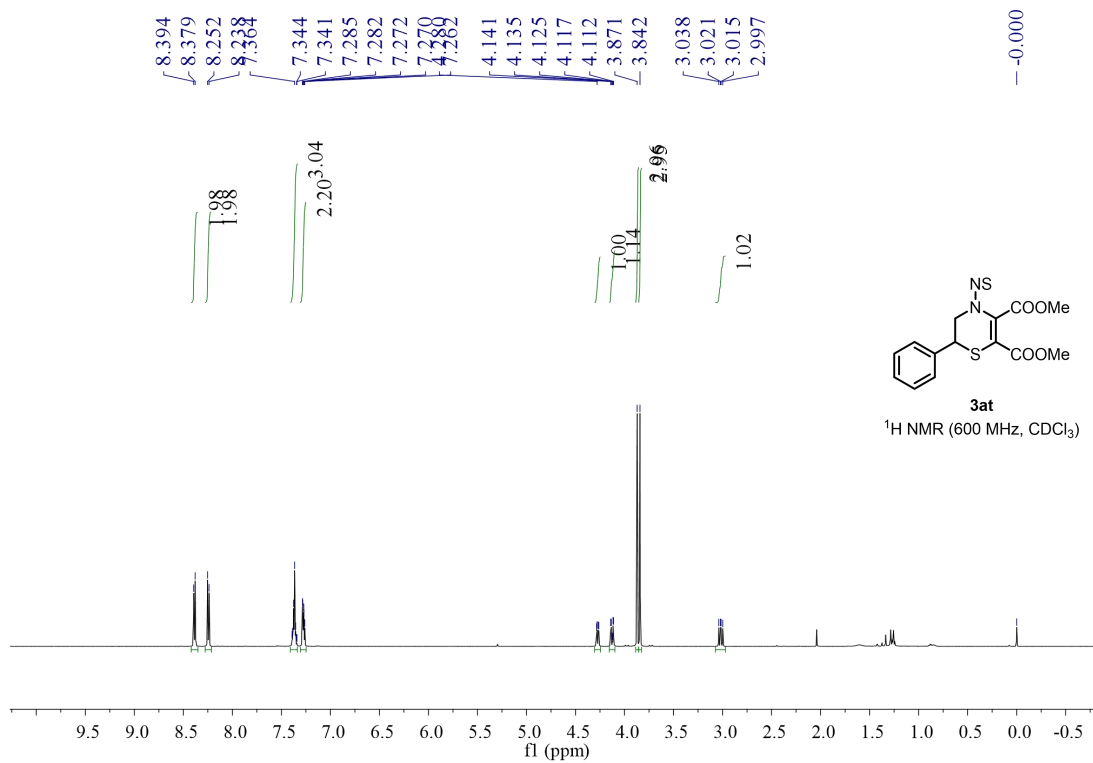


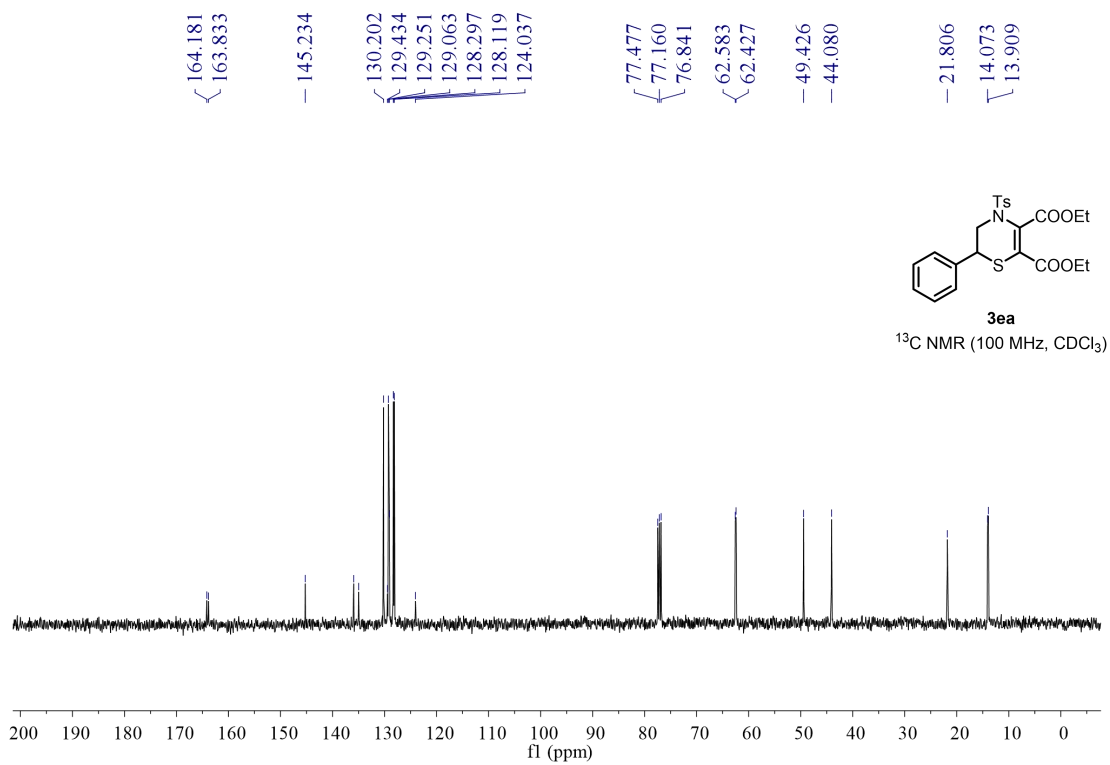
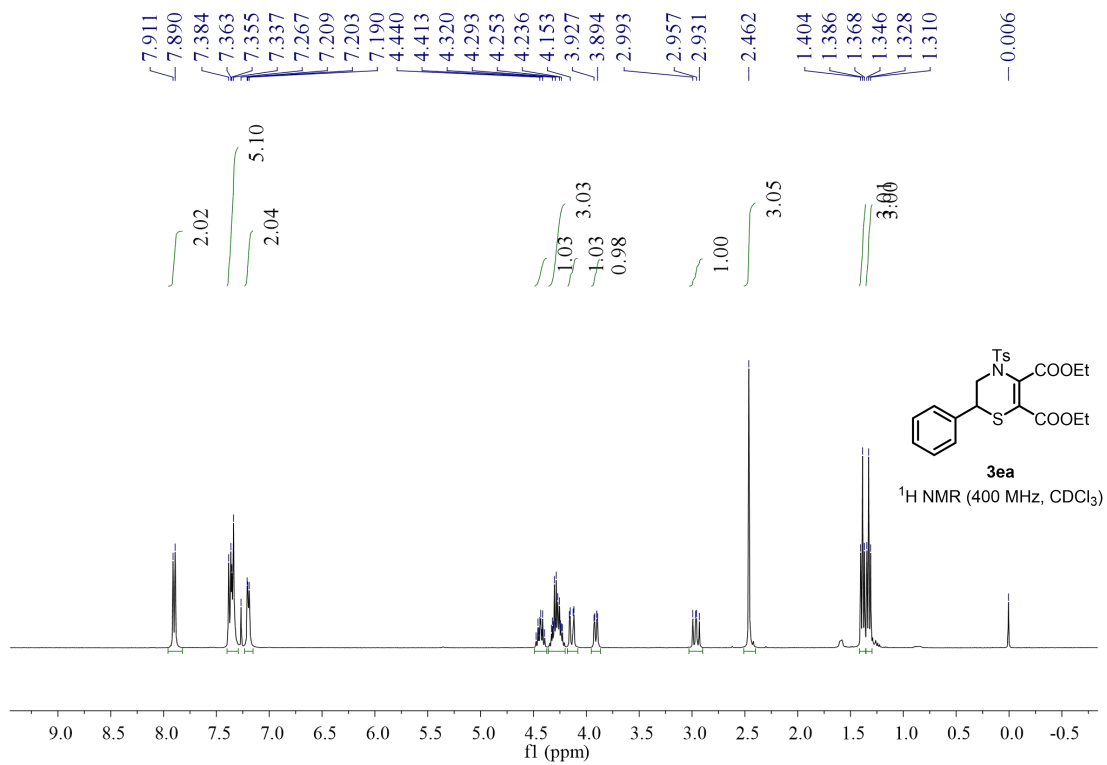


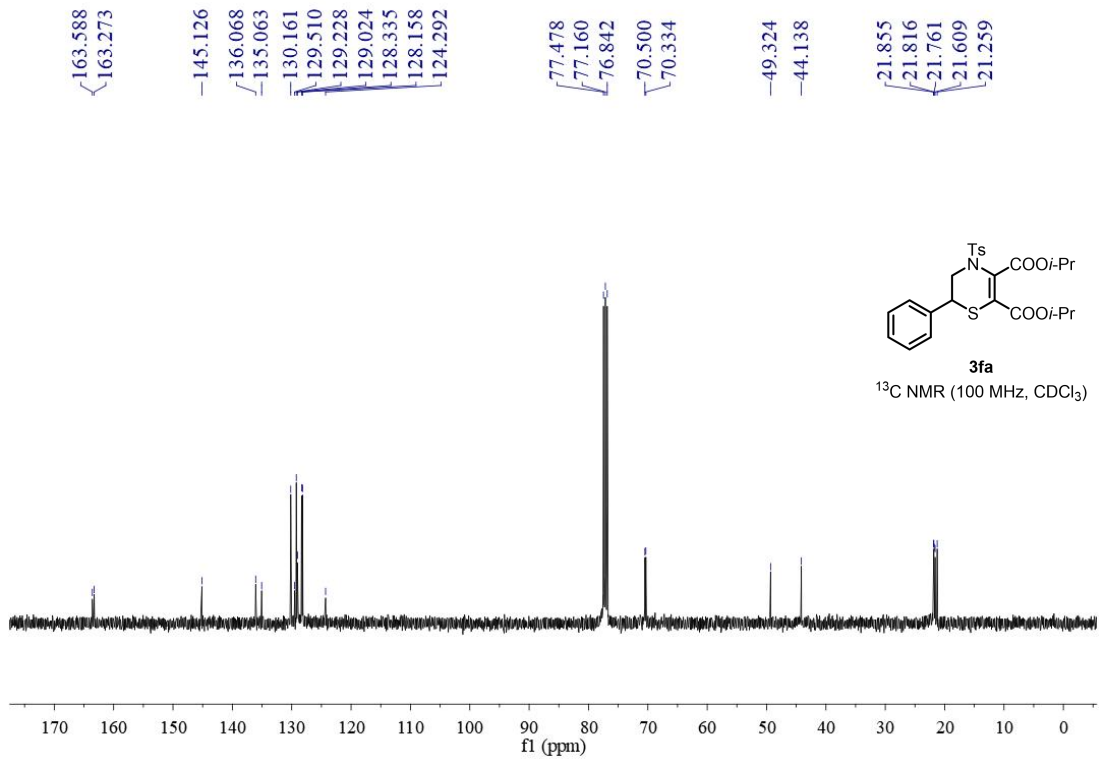
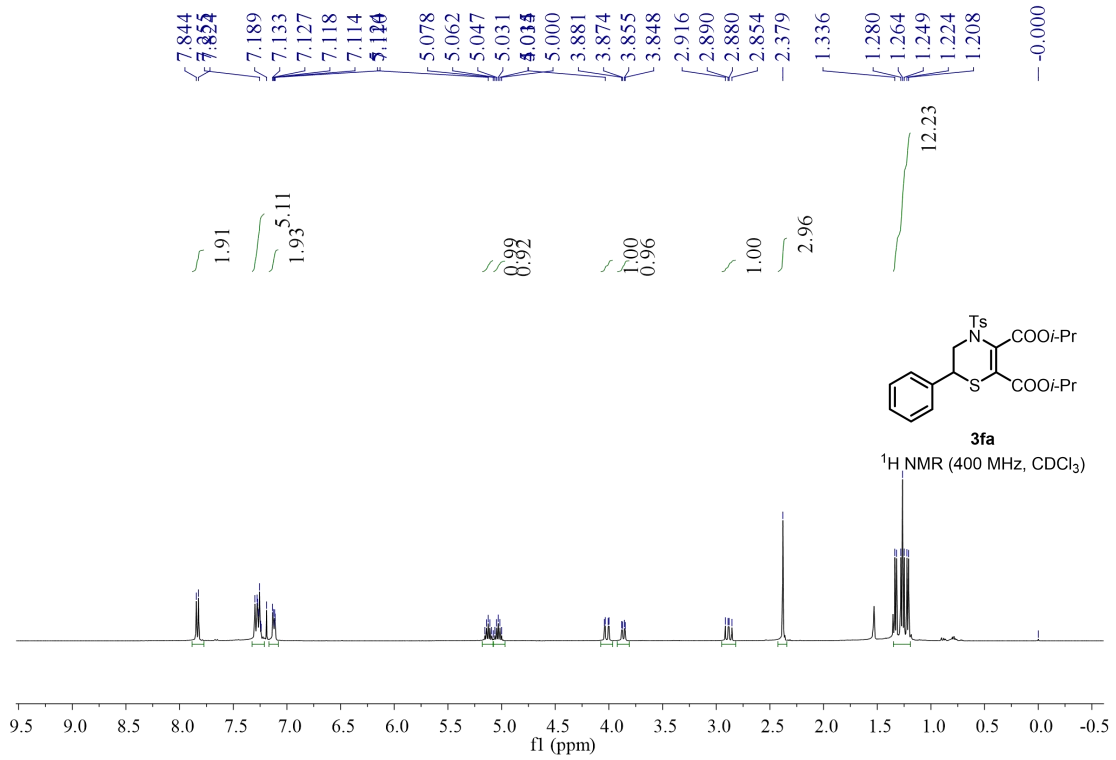


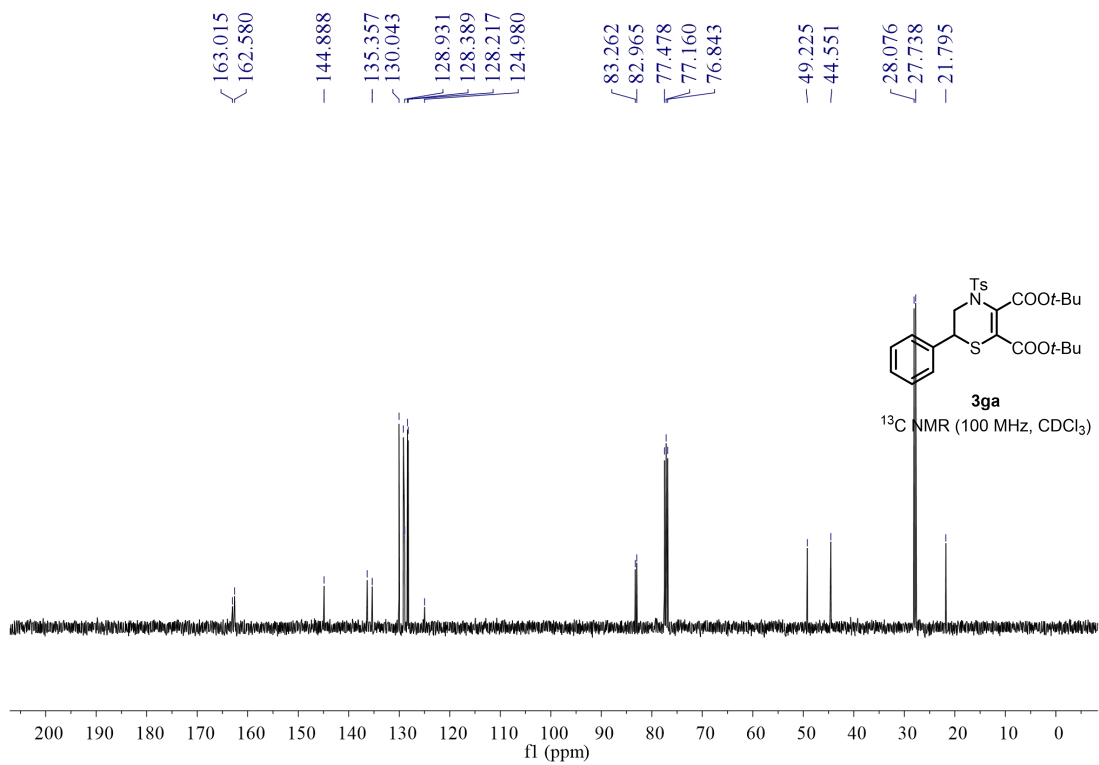
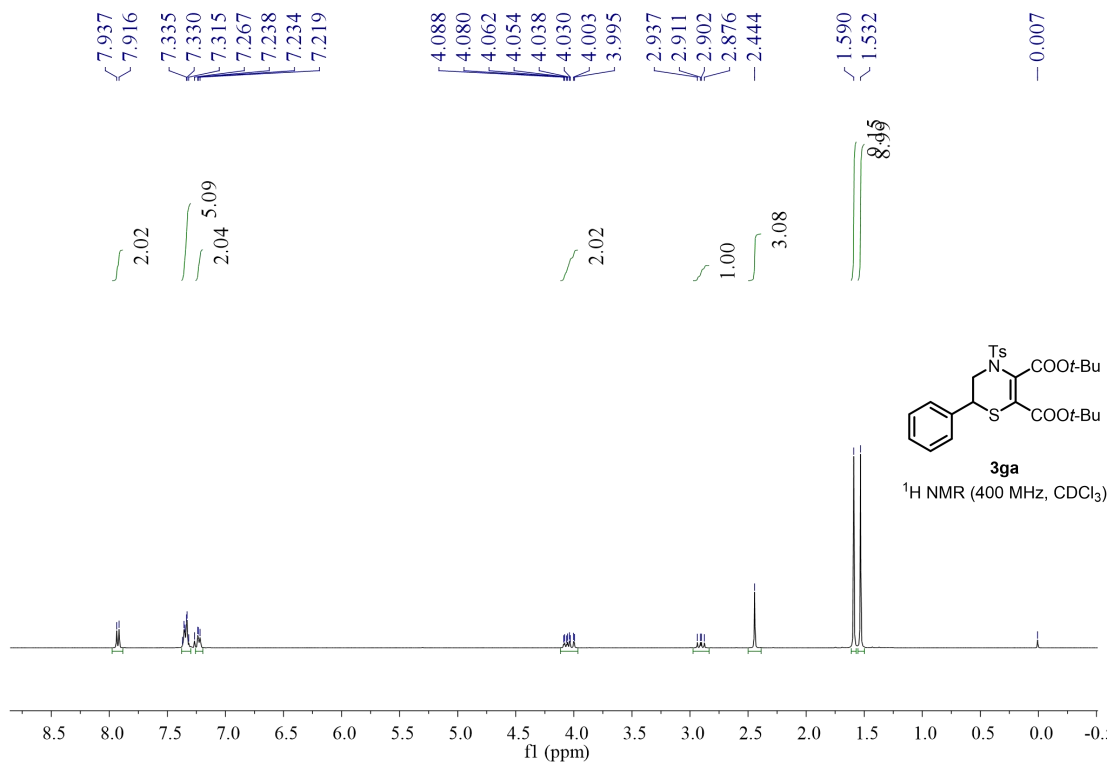


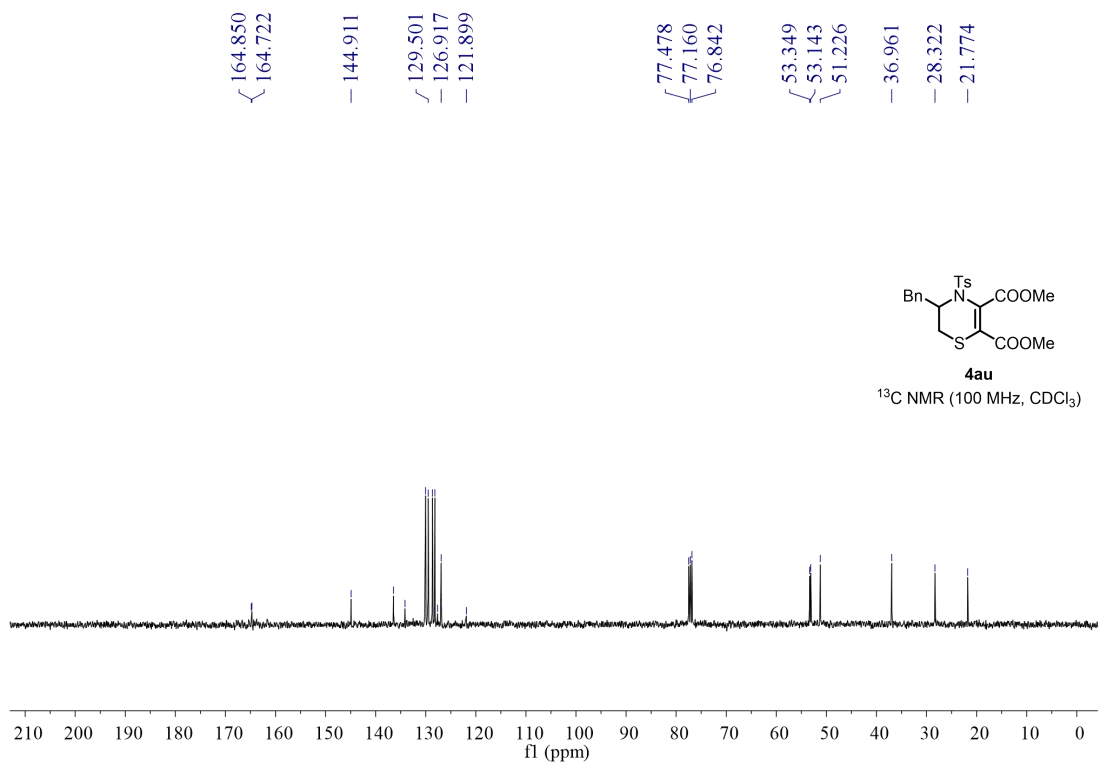
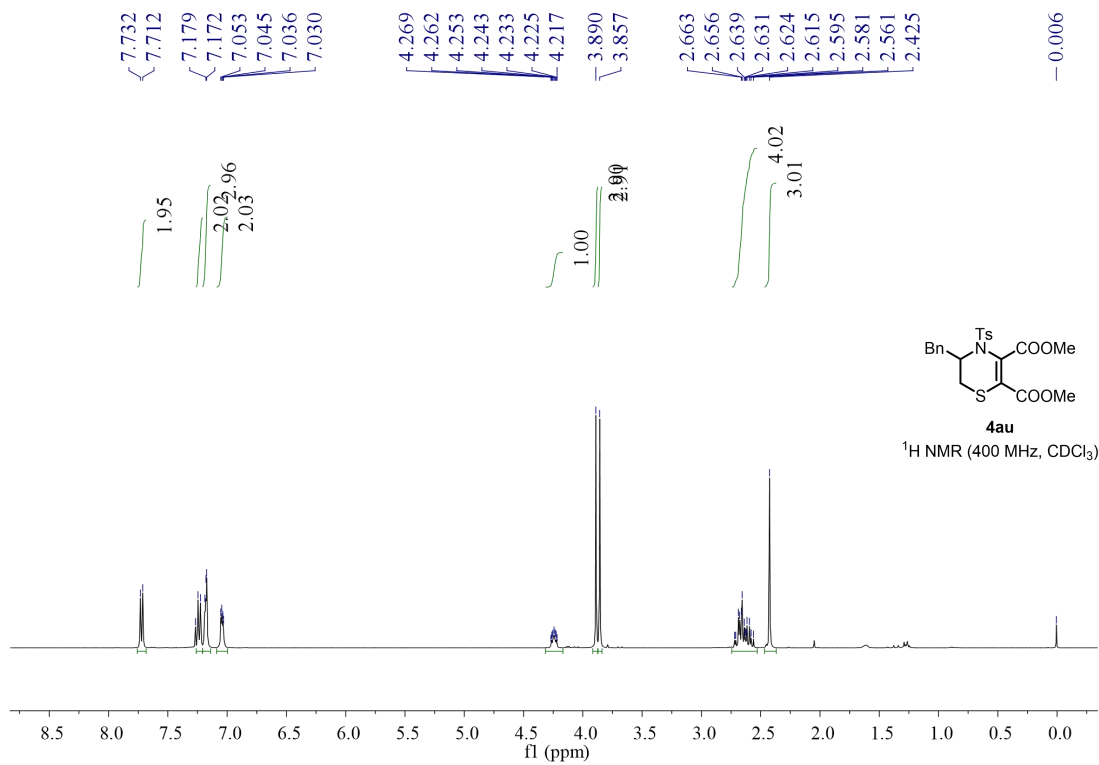


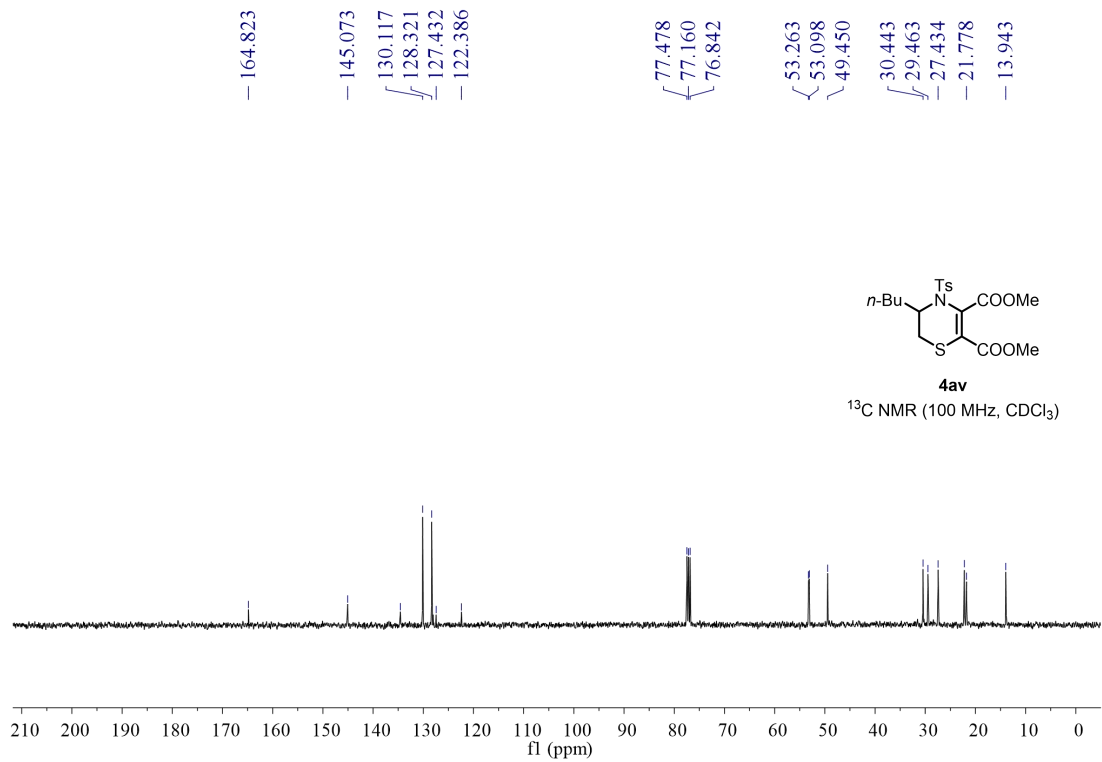
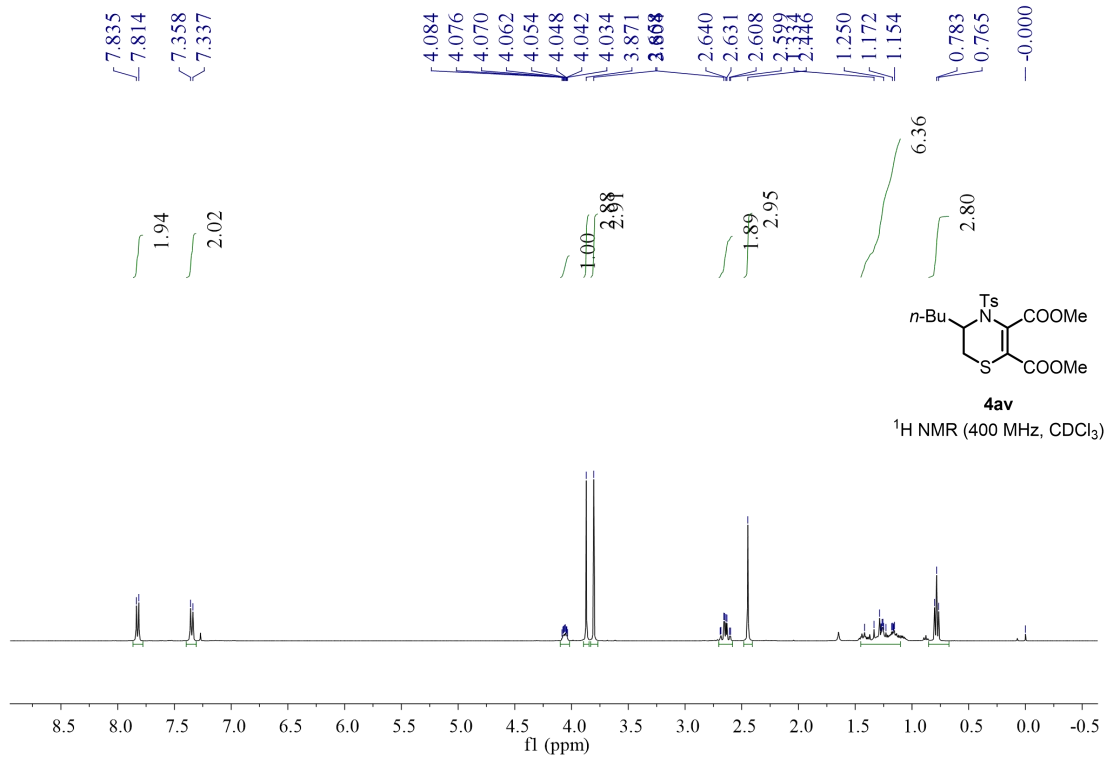


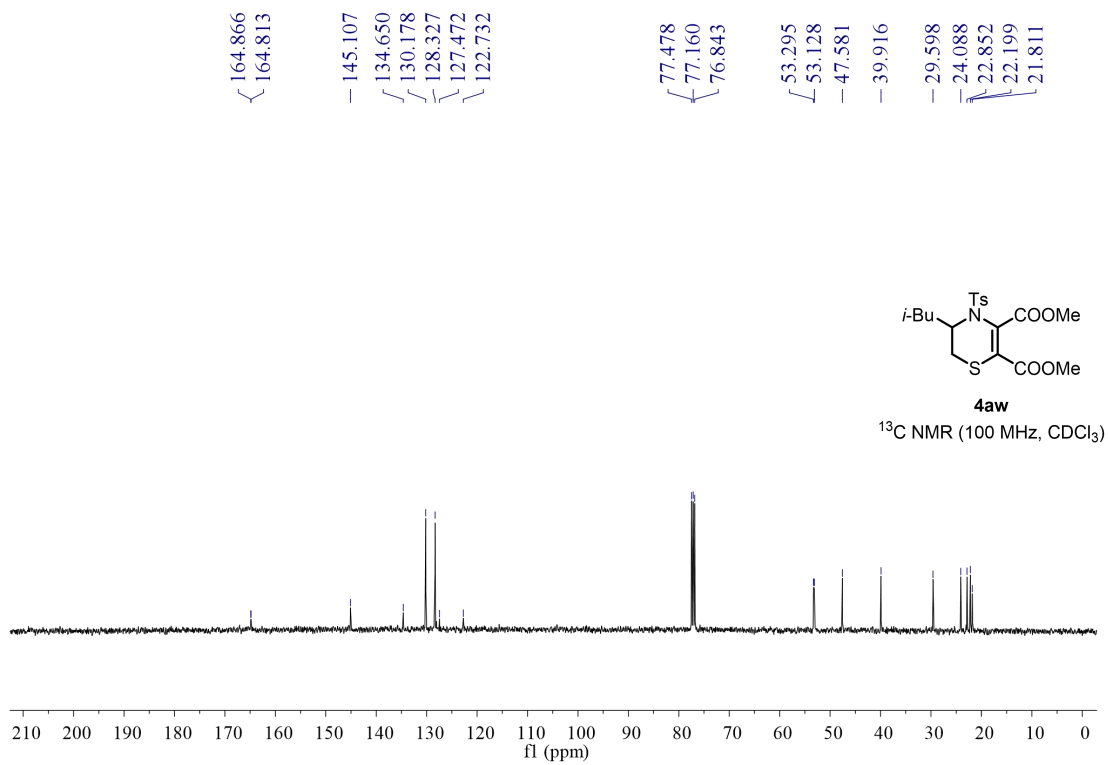
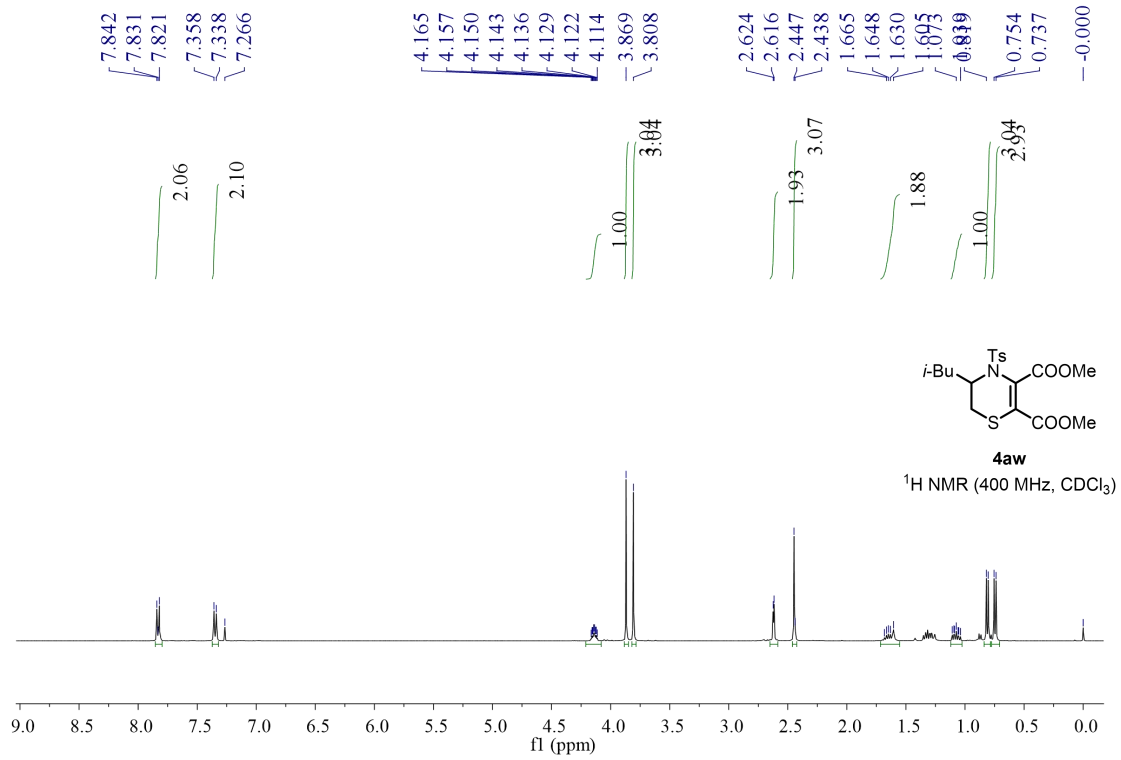


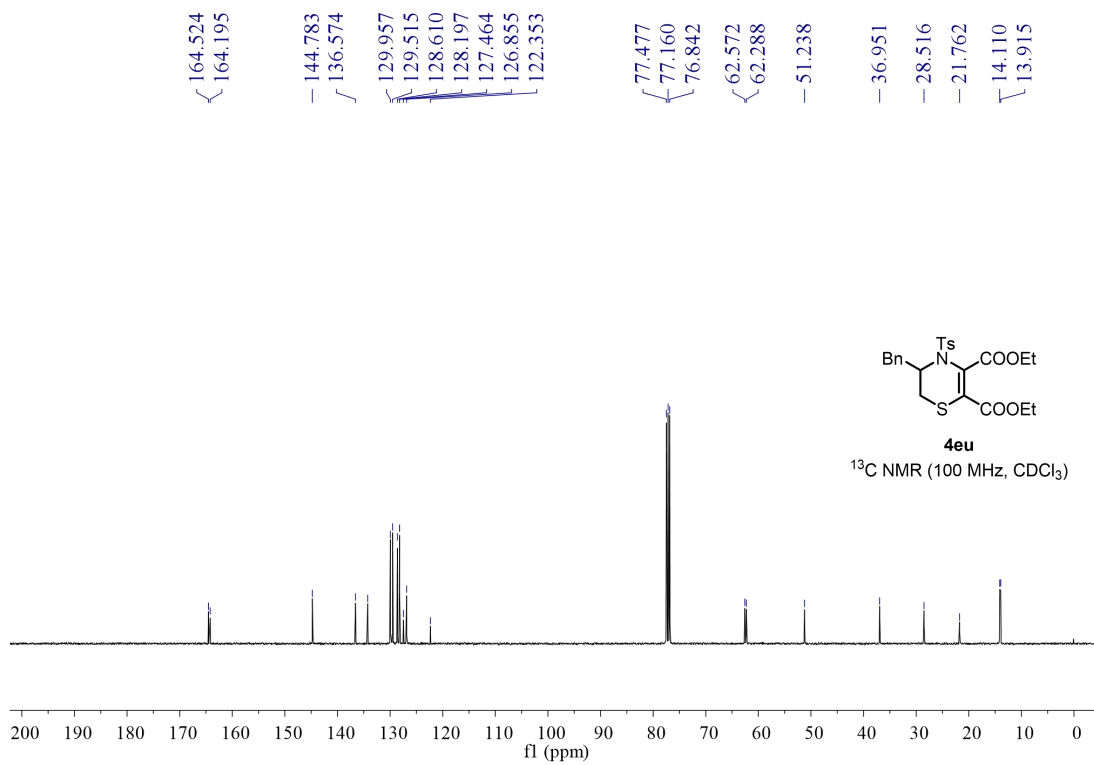
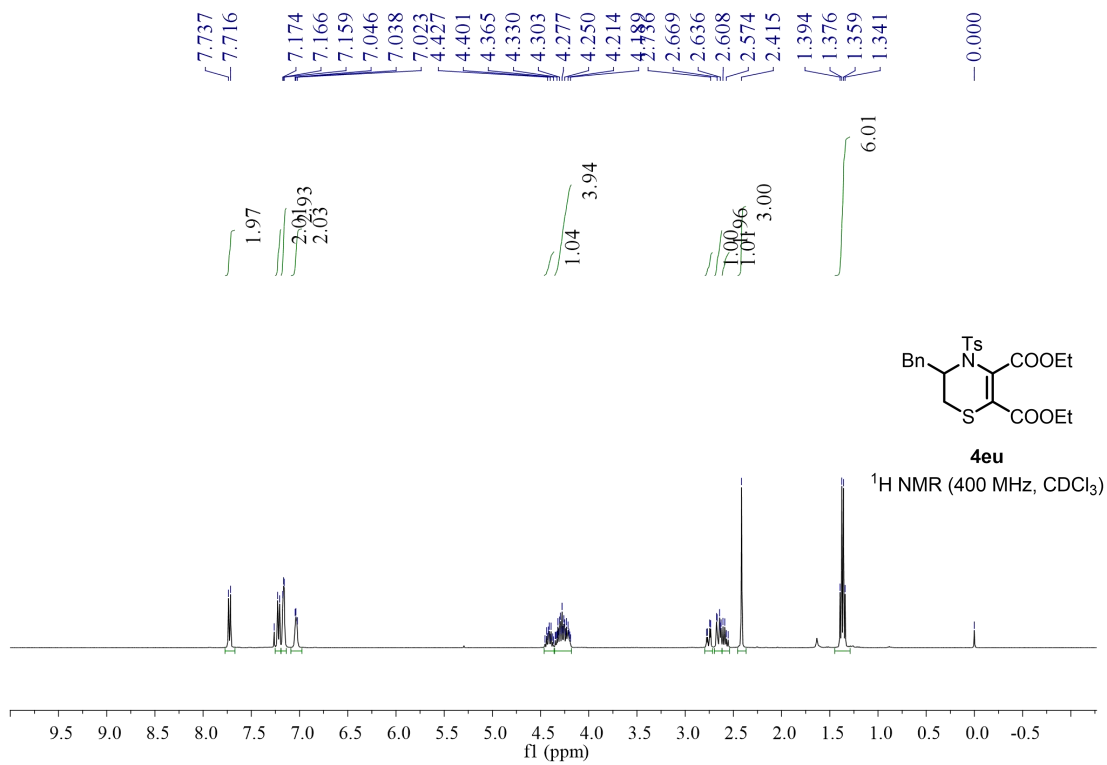


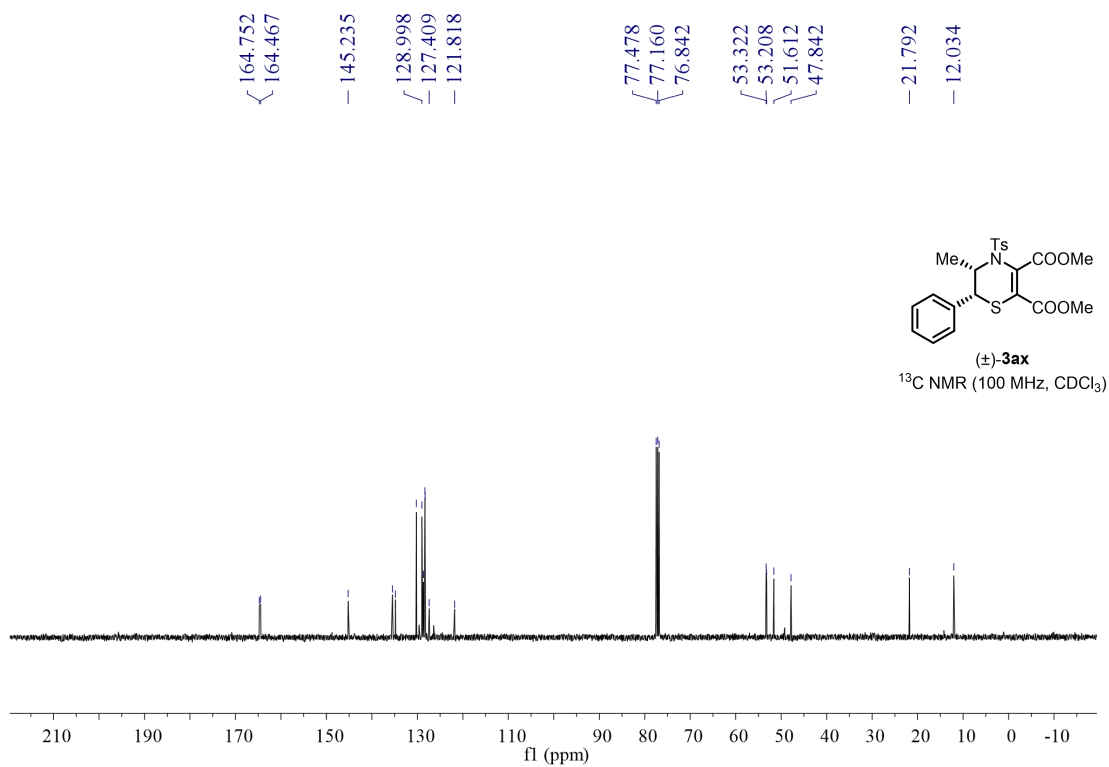
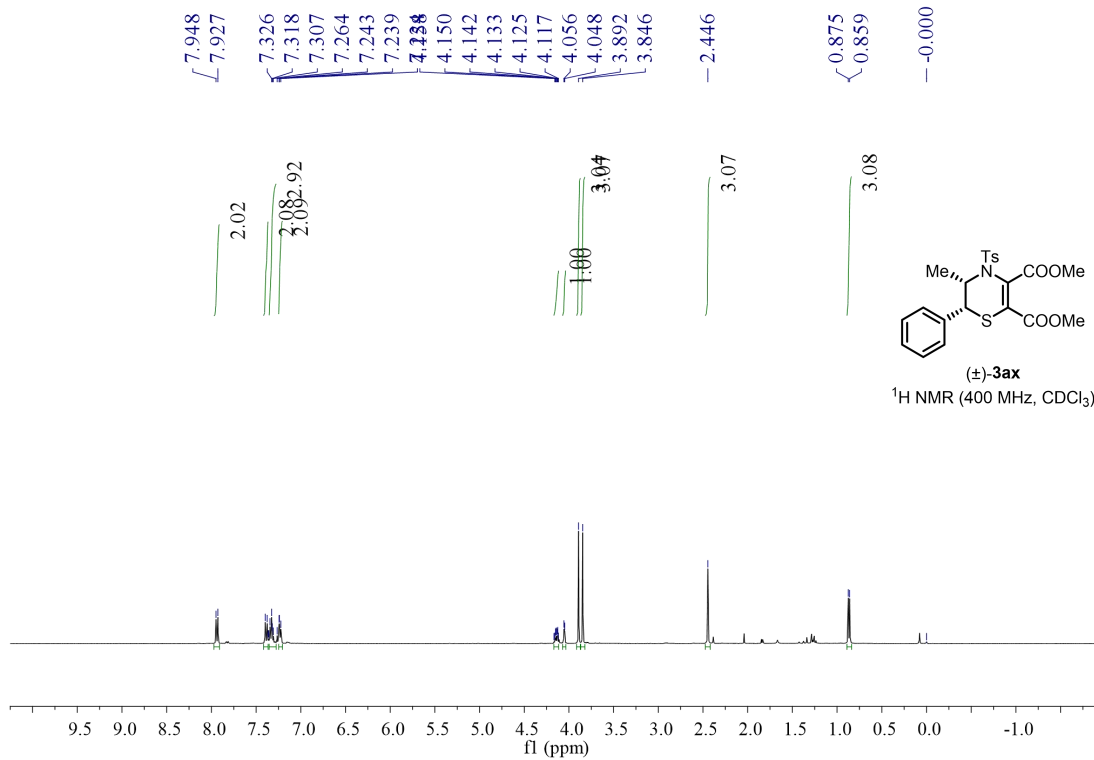


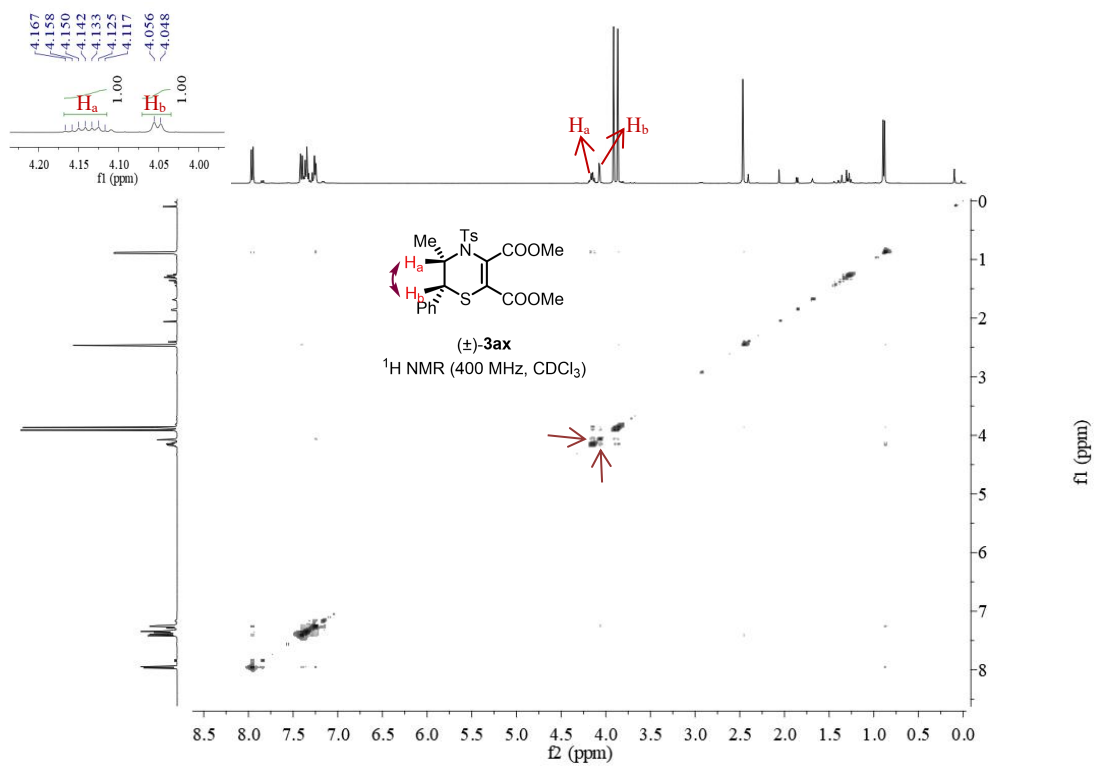


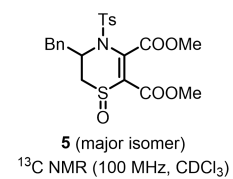
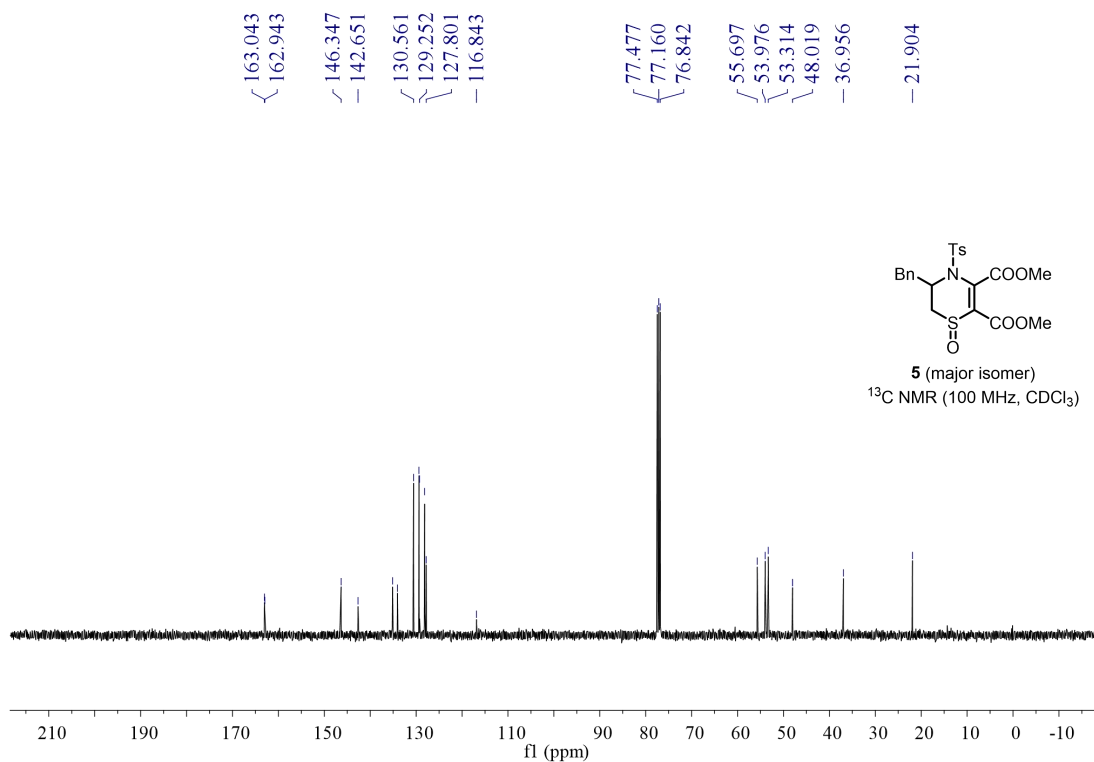
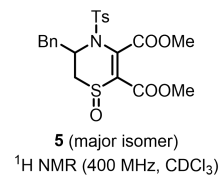
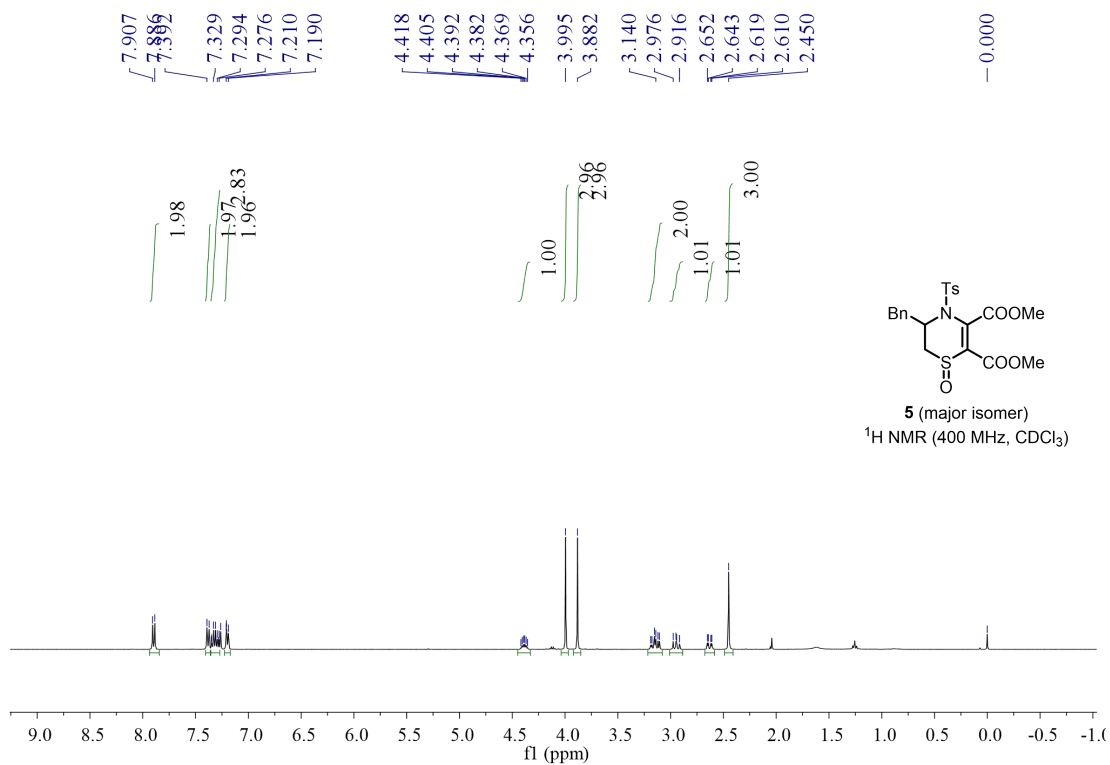


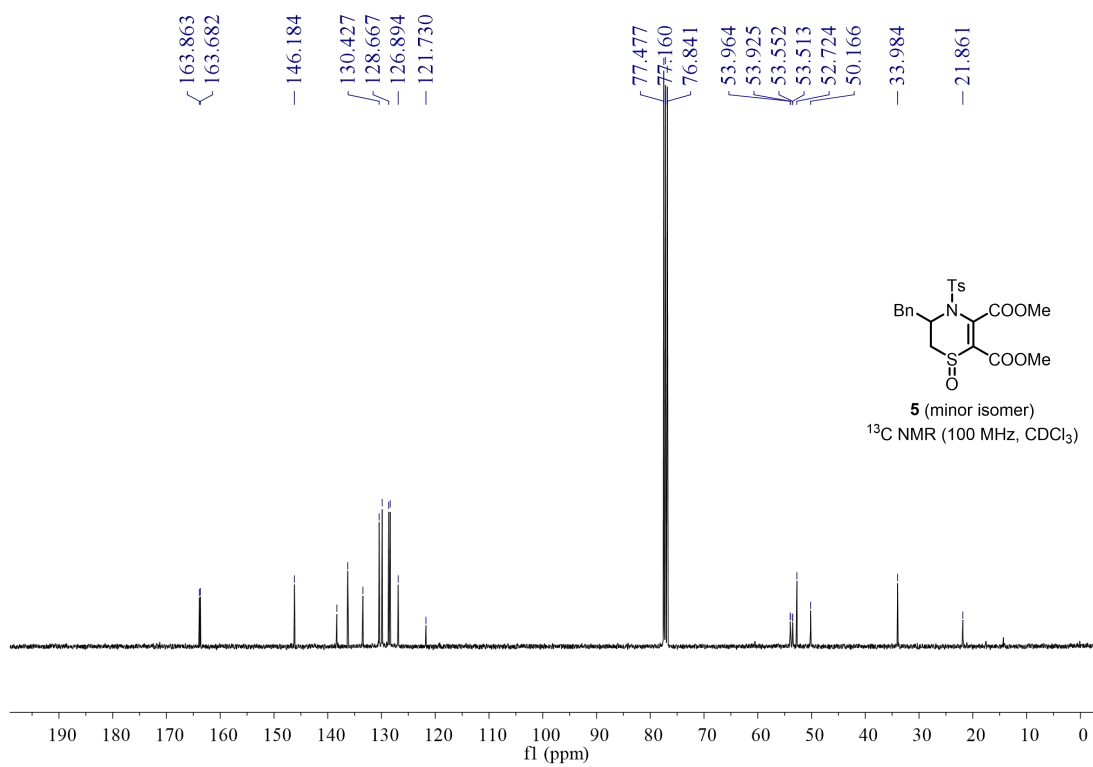
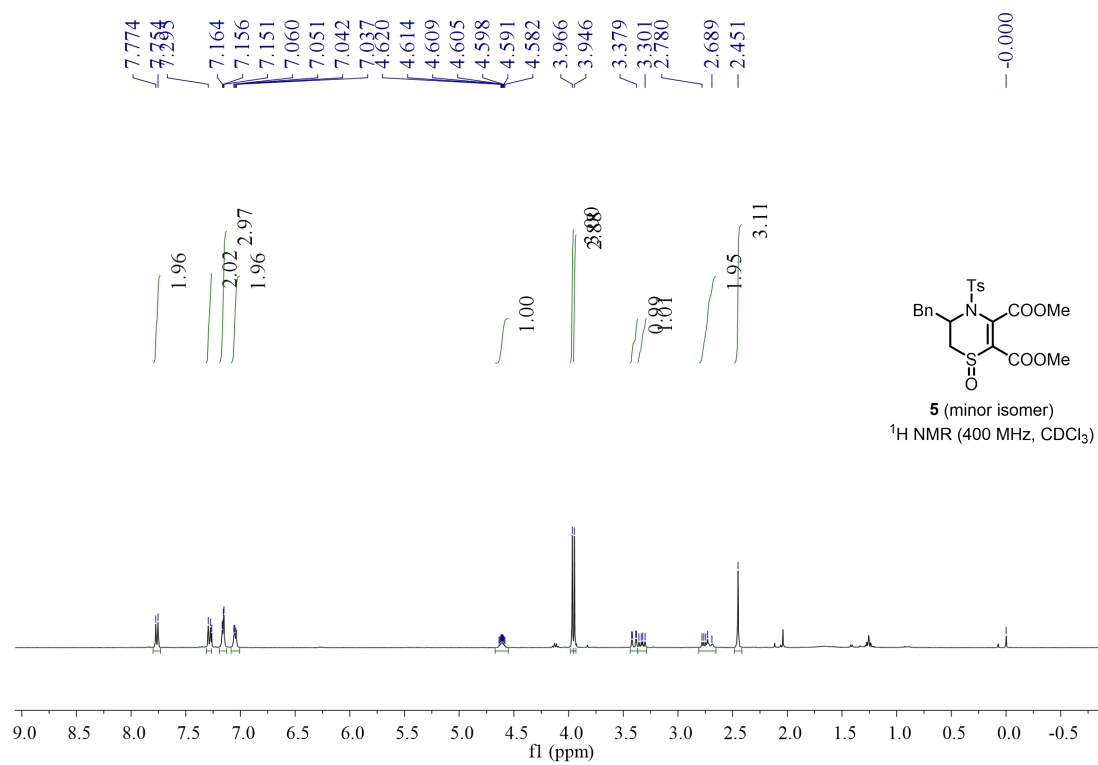


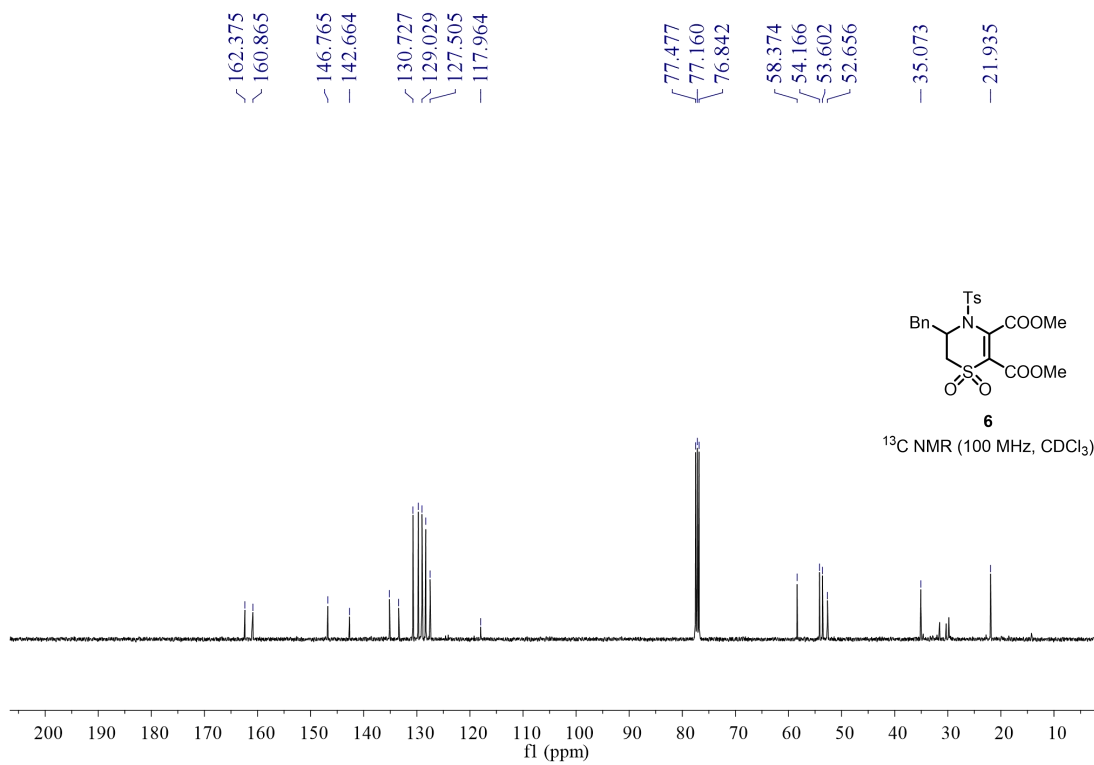
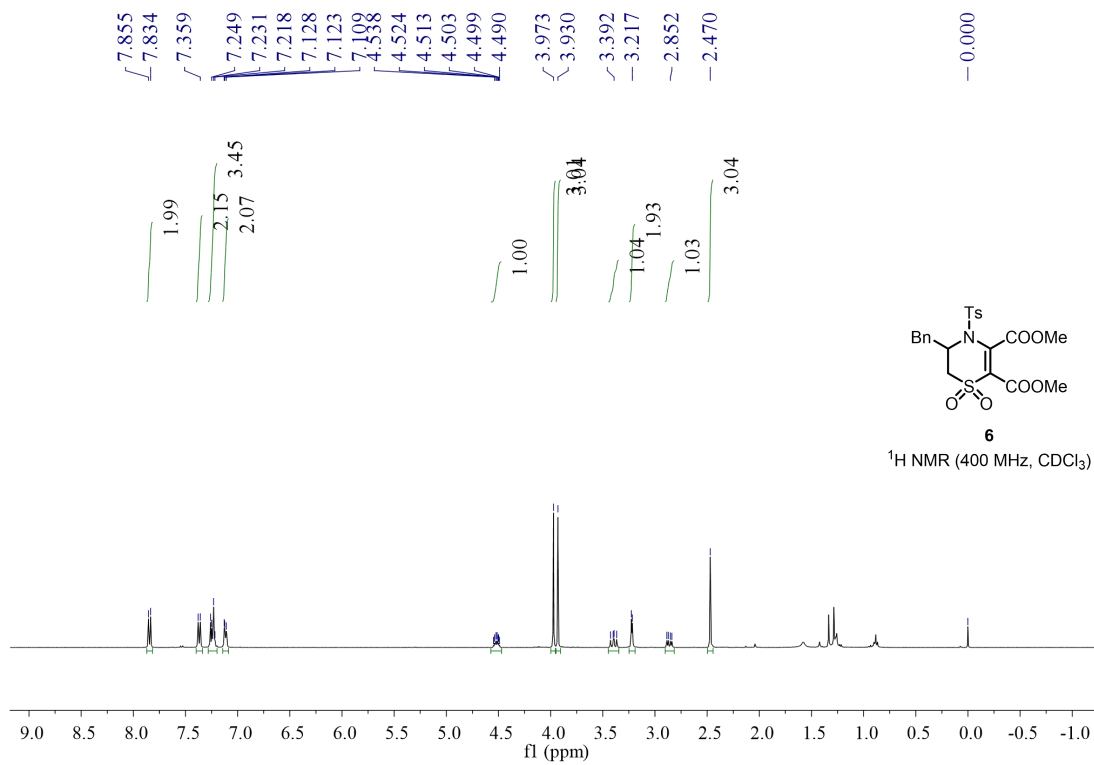










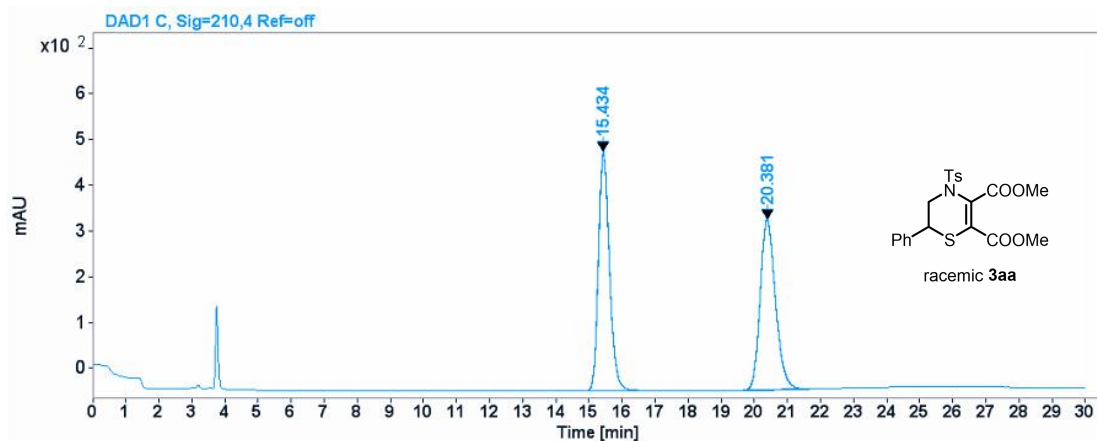


5. HPLC Chromatograms

(1) HPLC chromatogram of 3aa

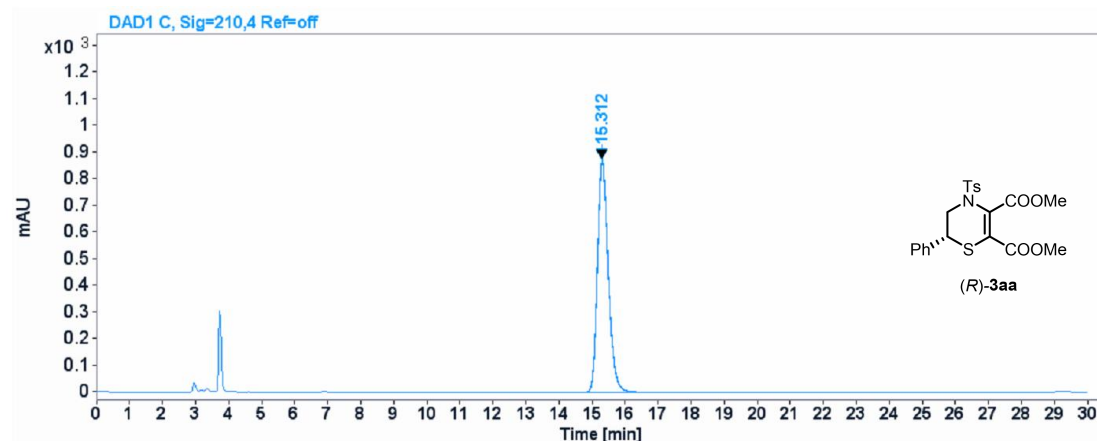
Enantiomeric excess was determined by HPLC with a Chiralpak[®] IA column (*n*-hexane/*i*-propanol = 85/15, 1.0 mL/min, 210 nm, 25 °C);

$t_r(R) = 15.434$ min, $t_r(S) = 20.381$ min; >99.9% ee.



Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
15.434	0.352	12023.389	522.671	50.1385
20.381	0.494	11956.984	372.792	49.8615
	Sum	23980.3730		



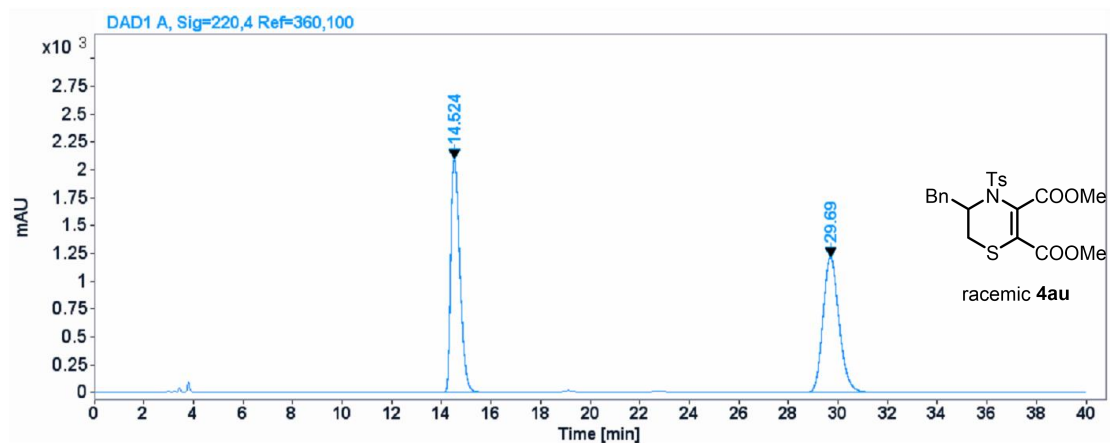
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
15.312	0.351	19991.742	874.622	100.0000
	Sum	19991.7422		

(2) HPLC chromatogram of 4au

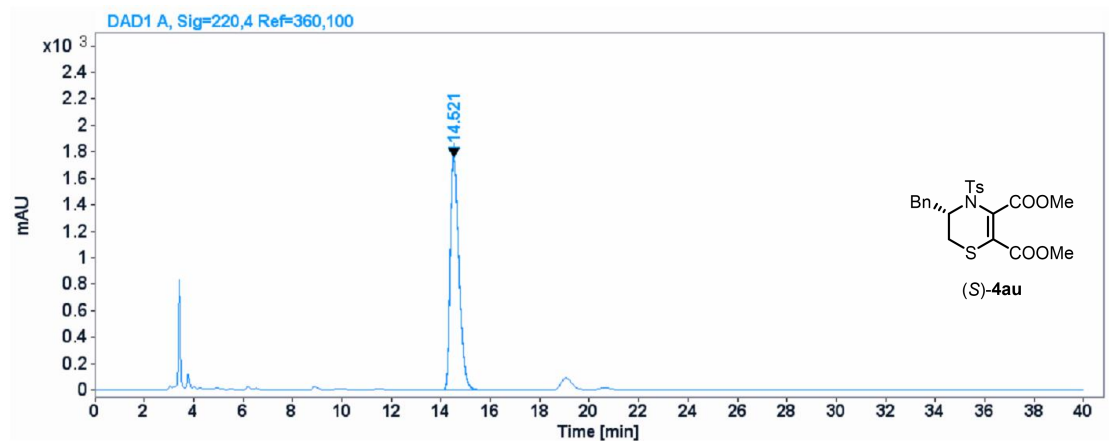
Enantiomeric excess was determined by HPLC with a Chiralpak® IA column (*n*-hexane/*i*-propanol = 85/15, 1.0 mL/min, 220 nm, 25 °C);

$t_r(S) = 14.524$ min, $t_r(R) = 29.690$ min; >99.9% ee.



Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
14.524	0.395	52882.863	2093.065	49.1925
29.690	0.696	54618.930	1215.952	50.8075
	Sum	107501.7930		



Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
14.521	0.379	42781.031	1753.463	100.0000
	Sum	42781.0313		

6. Single-Crystal X-Ray Diffraction Data

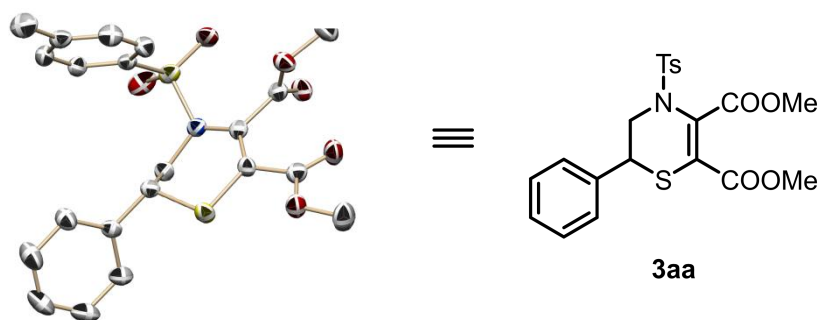


Fig S-1. ORTEP drawing of **3aa** (CCDC 2131863) with 50% ellipsoid probability

Identification code	3aa
Empirical formula	C ₂₁ H ₂₁ NO ₆ S ₂
Formula weight	447.51 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.7997(13) Å α = 89.275(4)°
	b = 14.3445(19) Å β = 78.412(4)°
	c = 15.2780(17) Å γ = 85.250(5)°
Volume	2096.6(5) Å ³
Z	4
Absorption coefficient	0.293 mm ⁻¹
F(000)	936
Theta range for data collection	2.13 to 28.37°
Limiting indices	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -20 ≤ l ≤ 19
Absorption correction	Multi-Scan
Data / parameters	10412 / 547
Goodness-of-fit on F²	1.026
Final R indices [I > 2σ(I)]	R1 = 0.0526, wR2 = 0.1114
R indices (all data)	R1 = 0.0938, wR2 = 0.1307
Largest diff. peak and hole	0.399 and -0.443 eÅ ⁻³

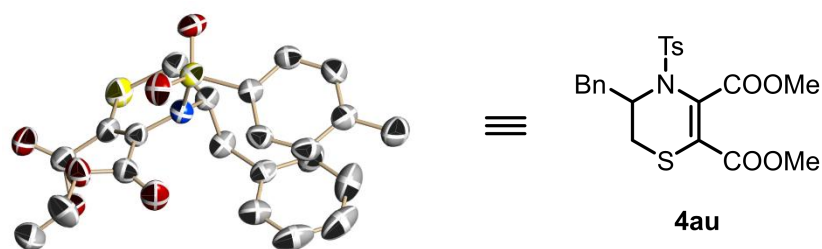


Fig S-2. ORTEP drawing of **4au** (CCDC 2131862) with 50% ellipsoid probability

Identification code	4au
Empirical formula	C ₂₂ H ₂₃ NO ₆ S ₂
Formula weight	461.53 g/mol
Temperature	303(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.5702(2) Å α = 105.3577(14)°
	b = 16.2305(6) Å β = 92.5527(13)°
	c = 19.0613(7) Å γ = 90.4286(14)°
Volume	2255.7(2) Å ³
Z	4
Absorption coefficient	0.274 mm ⁻¹
F(000)	968
Theta (max)	28.49°
Limiting indices	-10 ≤ h ≤ 10, -21 ≤ k ≤ 21, -25 ≤ l ≤ 25
Absorption correction	Multi-Scan
Data / parameters	11319 / 565
Goodness-of-fit on F²	1.016
Final R indices [I > 2σ(I)]	R1 = 0.0469
R indices (all data)	wR2 = 0.1254