

Supporting Information for

N-Heterocyclic carbene-catalyzed diastereoselective synthesis of sulfenylated indanes via sulfa-Michael-Michael (aldol) cascade reaction

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1.General methods and typical experimental procedures

1.1General methods

Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F₂₅₄. ¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) were recorded on a Bruker-DMX 400 spectrometer in CDCl₃, with tetramethylsilane as an internal standard and reported in ppm (δ). Benzenedi(enones)^[1] and *o*-formyl chalcone^[2] were synthesized according to the literature procedure. All other chemicals were obtained from commercial supplies and used as received without any further purification. Anhydrous THF, 1,4-dioxane and toluene were dried with the sodium/benzophenone system and distilled under nitrogen. Anhydrous DMSO, DMF, CH₂Cl₂ and CH₃CN were distilled from calcium hydride. CHCl₃ was distilled from phosphorus pentoxide. Petroleum ether, where used, has a boiling point range of 60–90 °C.

1.2 Representative procedure for NHC-catalyzed sulfa- Michael-Michael addition between mercaptans and benzenedi(enones)

To a solution of benzenedi(enone) **1a** (67.6 mg, 0.2 mmol) and ethanethiol **2a** (15 mg, 0.24 mmol) in toluene (2.0 mL) was added NHC **A** (0.78 mg, 1 mol%). The mixture was stirred at room temperature until full consumption of **1a** that was indicated by TLC (2 h). The solvent was

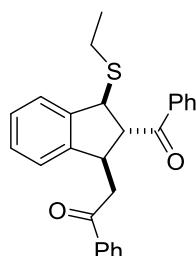
then removed under reduced pressure and the crude material was purified by flash column chromatography (silica gel, PE/EtOAc (v : v) = 20:1) to give the desired product **3a**.

1.3 Representative procedure for NHC-catalyzed sulfa-Michael-aldol cascade reaction of *o*-formyl chalcone and thiols.

To a solution of *o*-formyl chalcone **4a** (47.29 mg, 0.2 mmol) and ethanethiol **2a** (mg, 0.24 mmol) in THF (2.0 mL) was added NHC **A** (7.8 mg, 10 mol%). The mixture was stirred at room temperature until full consumption of **4a** that was indicated by TLC (48h). The solvent was then removed under reduced pressure and the crude material was purified by column chromatography (silica gel, PE/EtOAc (v : v) = 20:1).

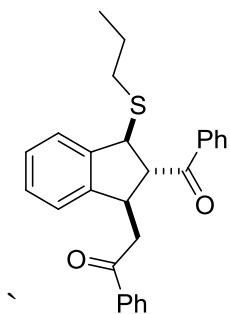
2. Spectroscopic data for all products

2-2-benzoyl-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethan-1-one (3a)



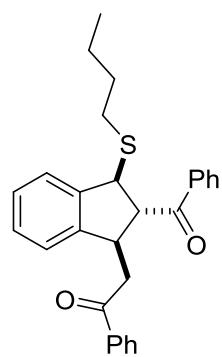
Yield: 92%, 73.6 mg; yellow liquid; ^1H NMR (400 MHz, CD_3Cl) δ 8.05 (dt, $J = 8.5, 1.7$ Hz, 2H), 7.87 (dt, $J = 8.5, 1.6$ Hz, 2H), 7.59–7.51 (m, 2H), 7.48–7.36 (m, 5H), 7.28–7.24 (m, 2H), 7.23–7.18 (m, 1H), 4.61 (d, $J = 5.4$ Hz, 1H), 4.24(dt, $J = J = 8.5, 1$ H), 4.16 (dd, $J = 14.8, 7.3$ Hz, 1H), 3.60 (dd, $J = 17.5, 5.5$ Hz, 1H), 3.45 (dd, $J = 17.5, 8.2$ Hz, 1H), 2.62–2.46 (m, 2H), 1.22 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CD_3Cl) δ 200.7, 198.3, 144.3, 142.1, 136.9, 136.8, 133.2, 128.8, 128.7, 128.2, 128.1, 127.6, 124.9, 124.0, 60.8, 52.2, 44.6, 43.8, 25.9, 14.6; IR (KBr thin film) 3448, 3064, 2969, 2926, 1874, 1596, 1579, 1477, 1448, 1359, 1224, 1181, 1001, 981, 770, 749, 728, 691 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{25}\text{O}_2\text{S}^+(\text{M}+\text{H})^+$ 401.15698, found 401.15710.

2-2-benzoyl-3-(propylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethan-1-one (3b)



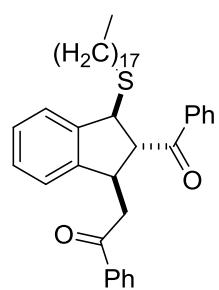
Yield: 83%, 68.8 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.09 – 8.01 (m, 2H), 7.89 – 7.82 (m, 2H), 7.57 – 7.50 (m, 3.3 Hz, 2H), 7.48 – 7.33 (m, 5H), 7.23 – 7.19 (m, 3H), 4.58 (d, J = 5.4 Hz, 1H), 4.25 (dt, J = 8.1, 5.5 Hz, 1H), 4.16 (dd, J = 10.9, 5.5 Hz, 1H), 3.60 (dd, J = 17.5, 5.4 Hz, 1H), 3.44 (dd, J = 17.5, 8.3 Hz, 1H), 2.59 – 2.43 (m, 2H), 1.61 – 1.52 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 200.8, 198.3, 144.3, 142.1, 142.1, 137.0, 136.8, 133.3, 133.2, 128.8, 128.7, 128.6, 128.2, 128.1, 127.6, 124.9, 124.0, 60.9, 52.5, 44.6, 43.7, 33.9, 22.8, 13.5; IR (KBr thin film) 3443, 2961, 1680, 1631, 1596, 1447, 1384, 1357, 1222, 1180, 1071, 1001, 767, 748, 728, 689 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{27}\text{O}_2\text{S}^+$ ($\text{M}+\text{H})^+$ 415.17263, found 415.17239.

2-2-benzoyl-3-(butylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethanone (3c)



Yield: 79%, 67.6 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.08 – 8.04 (m, 2H), 7.90 – 7.84 (m, 2H), 7.58 – 7.50 (m, 2H), 7.49 – 7.33 (m, 5H), 7.29 – 7.19 (m, 3H), 4.58 (d, J = 5.4 Hz, 1H), 4.25 (dt, J = 8.1, 5.5 Hz, 1H), 4.16 (dd, J = 10.9, 5.5 Hz, 1H), 3.60 (dd, J = 17.5, 5.4 Hz, 1H), 3.45 (dd, J = 17.5, 8.3 Hz, 1H), 2.58 – 2.45 (m, 2H), 1.57 – 1.47 (m, 2H), 1.46 – 1.29 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 200.8, 198.3, 144.3, 142.1, 137.0, 136.8, 133.3, 133.2, 128.8, 128.7, 128.6, 128.2, 127.6, 124.9, 124.0, 60.9, 52.5, 44.7, 43.7, 31.5, 22.0, 13.63; IR (KBr thin film) 3446, 3064, 2957, 2929, 2871, 1965, 1916, 1815, 1682, 1596, 1579, 1557, 1447, 1359, 1223, 1001, 982, 928, 901, 846, 749, 728, 691 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{29}\text{O}_2\text{S}^+$ [M+H] $^+$ 429.18828, found 429.18832.

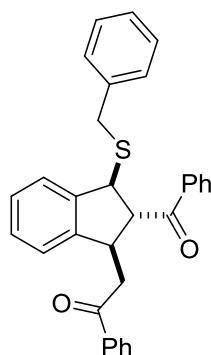
2-(2-benzoyl-3-(octadecylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethanol (3d)



Yield: 60%, 74.9 mg; yellow solid; mp 61.0–62.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 8.01 (m, 2H), 7.87 (dd, J = 8.3, 1.2 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.48 – 7.40 (m, 4H), 7.38 – 7.33 (m, 1H), 7.28 – 7.18 (m, 3H), 4.57 (d, J = 5.3 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.15 (t, J = 5.4 Hz, 1H),

3.60 (dd, $J = 17.5, 5.4$ Hz, 1H), 3.45 (dd, $J = 17.5, 8.3$ Hz, 1H), 2.59 – 2.40 (m, 2H), 1.52 (d, $J = 7.5$ Hz, 2H), 1.23 (d, $J = 20.2$ Hz, 30H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.8, 193, 144.3, 142.1, 137.0, 136.8, 133.2, 128.8, 128.6, 128.6, 128.2, 128.1, 127.6, 124.9, 124.0, 60.9, 52.5, 44.7, 43.7, 31.98, 31.95, 29.72, 29.68, 29.67, 29.6, 29.5, 29.4, 29.38, 29.2, 28.9, 22.7, 14.2; IR (KBr thin film) 3445, 3064, 2923, 2852, 1683, 1597, 1580, 1457, 1447, 1358, 1222, 1180, 1072, 1001, 982, 767, 748, 726, 690 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{42}\text{H}_{57}\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 625.40738, found 625.40759.

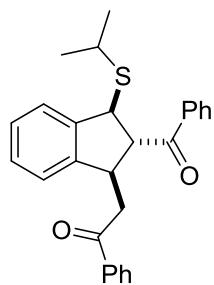
2-(2-benzoyl-3-(benzylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethanone (3e)



Yield: 86%, 79.4 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.88 (m, 2H), 7.88 – 7.82 (m, 2H), 7.58 – 7.51 (m, 2H), 7.44 – 7.39 (m, 4H), 7.33 – 7.14 (m, 9H), 4.57 (d, $J = 5.3$ Hz, 1H), 4.22 – 4.13 (m, 1H), 4.12 – 4.03 (m, 1H), 3.71 (s, 2H), 3.53 (dd, $J = 17.5, 5.6$ Hz, 1H), 3.35 (dd, $J = 17.5, 8.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.8, 198.3, 144.4, 141.5, 138.1, 136.9, 133.5, 133.2, 129.0, 128.8, 128.6, 128.6,

128.3, 128.1, 127.7, 127.1, 125.1, 60.5, 52.3, 44.6, 43.8, 36.4; IR (KBr thin film) 3435, 3061, 2360, 2341, 1682, 1596, 1579, 1493, 1476, 1447, 1384, 1357, 1223, 1180, 1070, 1025, 1001, 981, 748, 727, 690, 668 cm⁻¹; HRMS (ESI) m/z calcd for C₃₁H₂₇O₂S⁺ (M+H)⁺ 463.17263, found 463.17249.

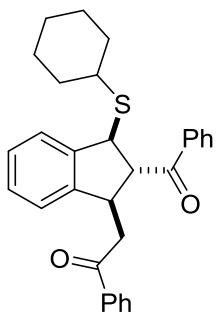
2-(2-benzoyl-3-(isopropylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethan-1-one (3f)



Yield: 82%, 67.9 mg; yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 8.02 (m, 2H), 7.89 – 7.83 (m, 2H), 7.58 – 7.51 (m, 2H), 7.49 – 7.35 (m, 5H), 7.29 – 7.17 (m, 3H), 4.63 (d, J = 5.3 Hz, 1H), 4.26 – 4.20 (m, 1H), 4.14 (t, J = 5.4 Hz, 1H), 3.59 (dd, J = 17.5, 5.6 Hz, 1H), 3.45 (dd, J = 17.5, 8.1 Hz, 1H), 2.99 – 2.92 (m, 1H), 1.26 (d, J = 6.7 Hz, 4H), 1.20 (d, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.8, 198.4, 144.1, 124.0, 61.6, 51.2, 44.8, 43.9, 36.0, 23.8, 23.5; IR (KBr thin film) 3458, 3064, 2960, 2925, 2865, 1682, 1596, 1579, 1476, 1447, 1360, 1223, 1181, 1156, 1001, 982, 769, 729, 691 cm⁻¹; HRMS (ESI) m/z calcd for C₂₇H₂₇O₂S⁺ (M+H)⁺ 415.17263, found 415.17218.

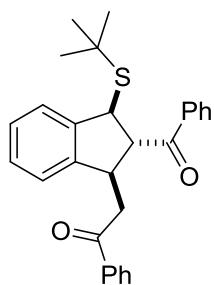
2-(2-benzoyl-3-(cyclohexylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethan-1-one (3g)

than-1-one (3g)



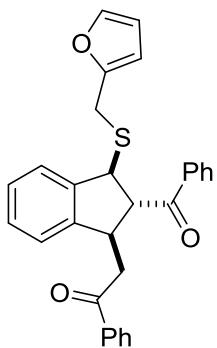
Yield: 79%, 71.76 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 8.01 (m, 2H), 7.88 (dd, J = 8.3, 1.1 Hz, 2H), 7.61 – 7.50 (m, 2H), 7.50 – 7.37 (m, 4H), 7.35 (d, J = 7.3 Hz, 1H), 7.27 – 7.18 (m, 3H), 4.63 (d, J = 5.3 Hz, 1H), 4.29 – 4.21 (m, 1H), 4.19 – 4.11 (m, 1H), 3.60 (dd, J = 17.5, 5.5 Hz, 1H), 3.45 (dd, J = 17.5, 8.3 Hz, 1H), 2.70 – 2.62 (m, 1H), 1.97 – 1.81 (m, 2H), 1.72 – 1.62 (m, 2H), 1.60 – 1.51 (m, 1H), 1.40 – 1.11 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.9, 198.4, 144.1, 142.8, 137.0, 136.8, 133.22, 133.18, 128.8, 128.6, 128.1, 128.08, 127.6, 125.0, 124.0, 61.7, 50.8, 44.9, 44.5, 43.8, 34.0, 33.6, 25.98, 25.96, 25.7; IR (KBr thin film) 3439, 3063, 3025, 2928, 2851, 1682, 1596, 1579, 1477, 1447, 1359, 1223, 1180, 1001, 982, 770, 748, 691 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{31}\text{O}_2\text{S}^+$ ($\text{M}+\text{H})^+$ 455.20393, found 455.20328.

2-(2-benzoyl-3-(tert-butylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethan-1-one (3h)



Yield: 81%, 69.4 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.05 – 7.98 (m, 2H), 7.86 – 7.80 (m, 2H), 7.58 – 7.49 (m, 2H), 7.47 – 7.37 (m, 5H), 7.28 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 4.64 (d, J = 6.4 Hz, 1H), 4.20 (dd, J = 12.8, 6.4 Hz, 1H), 4.14 (dd, J = 12.9, 6.5 Hz, 1H), 3.55 (dd, J = 17.3, 6.0 Hz, 1H), 3.36 (dd, J = 17.3, 7.3 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.7, 198.2, 143.7, 143.4, 137.7, 136.7, 133.2, 133.16, 128.8, 128.58, 128.56, 128.1, 127.81, 127.79, 125.5, 123.53, 62.61, 49.74, 44.87, 44.80, 44.09, 31.55; IR (KBr thin film) 3350, 3064, 2960, 2898, 2863, 1964, 1914, 1815, 1682, 1596, 1580, 1471, 1447, 1365, 1226, 1180, 1158, 1074, 1025, 1001, 981, 864, 791, 767, 748, 697 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{29}\text{O}_2\text{S}^+$ ($\text{M}+\text{H})^+$ 429.18828, found 429.18805.

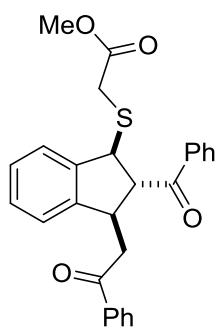
2-(2-benzoyl-3-((furan-2-ylmethyl)thio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethan-1-one (3i)



Yield: 88%, 79.5 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.01 – 7.94 (m, 2H), 7.89 – 7.80 (m, 2H), 7.57 – 7.49 (m, 2H), 7.42 (q, J = 7.9 Hz, 5H), 7.33 – 7.29 (m, 1H), 7.26 – 7.17 (m, 4H), 6.18 (dd, J = 3.2, 1.9 Hz, 1H), 6.02 – 5.99 (m, 1H), 4.64 (d, J = 5.1 Hz, 1H), 4.20 (dt, J = 8.0, 5.4 Hz, 1H), 4.10 (dd, J = 10.2, 5.1 Hz, 1H), 3.79 – 3.68 (m, 2H), 3.57 (dd, J = 17.5, 5.6 Hz, 1H), 3.43 (dd, J = 17.5, 8.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.6, 198.3, 151.2, 144.5, 142.2, 141.4, 136.8, 133.3, 133.2, 128.8, 128.63, 128.62, 128.3, 128.1, 127.8, 125.1, 124.1, 60.4, 52.3, 44.8, 43.8, 28.5; IR (KBr thin film) 3435, 2360, 1681, 1596, 1579, 1447, 1384, 1356, 1222, 1149, 1069, 1010, 933, 747, 689 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{25}\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 453.15189, found 453.15155.

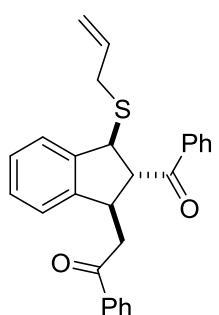
Methyl

2-((2-benzoyl-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-inden-1-yl)thio)acetate (3j)



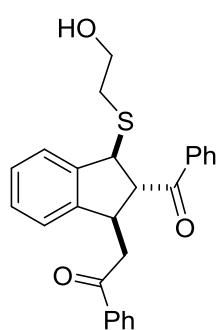
Yield: 79%, 70.1 mg; yellow liquid ; ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 8.02 (m, 2H), 7.91 – 7.85 (m, 2H), 7.60 – 7.52 (m, 2H), 7.49 – 7.38 (m, 5H), 7.30 – 7.20 (m, 3H), 4.76 (d, *J* = 4.8 Hz, 1H), 4.29 – 4.18 (m, 2H), 3.59 (s, 3H), 3.49 (dd, *J* = 17.6, 7.8 Hz, 1H), 3.27(q, *J* = 33.0, 18.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 200.3, 198.2, 170.7, 144.7, 140.7, 136.8, 133.3, 128.8, 128.7, 128.6, 128.6, 128.1, 127.8, 125.2, 124.3, 59.8, 52.8, 52.5, 44.6, 43.6, 33.1; IR(KBr thin film) 3445, 3064, 2950, 2342, 1972, 1737, 1682, 1633, 1596, 1579, 1556, 1478, 1447, 1435, 1405, 1357, 1282, 1223, 1182, 1157, 1129, 1001, 901, 846, 749, 728, 690 cm⁻¹; HRMS (ESI) m/z calcd for C₂₇H₂₅O₄S⁺(M+H)⁺ 445.14681, found 445.14700.

2-(3-(allylthio)-2-benzoyl-2,3-dihydro-1H-inden-1-yl)-1-phenylethan-1-one (3k)



Yield: 80%, 65.9 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.09 – 7.99 (m, 2H), 7.91 – 7.86 (m, 2H), 7.61 – 7.50 (m, 2H), 7.50 – 7.34 (m, 5H), 7.31 – 7.17 (m, 3H), 5.82 – 5.72 (m, 1H), 5.04 – 4.88 (m, 2H), 4.56 (d, J = 4.9 Hz, 1H), 4.25 – 4.18 (m, 2H), 3.60 (dd, J = 17.5, 5.2 Hz, 1H), 3.45 (dd, J = 17.5, 8.0 Hz, 1H), 3.19 – 3.09 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.6, 198.3, 144.4, 142.0, 136.9, 136.8, 133.9, 133.27, 133.26, 128.8, 128.7, 128.6, 128.3, 128.2, 127.7, 125.1, 124.1, 117.9, 60.9, 51.4, 44.8, 43.9, 35.3; IR (KBr thin film) 3459, 3064, 3025, 2977, 2914, 1964, 1914, 1871, 1682, 1634, 1596, 1979, 1487, 1426, 1404, 1359, 1284, 1224, 1181, 1075, 1044, 1025, 1001, 987, 922, 890, 846, 796, 768, 749, 727, 690 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 413.15698, found 413.15662.

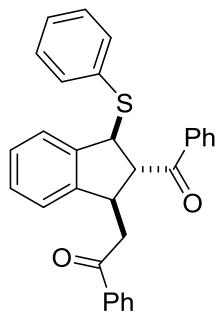
**2-(2-benzoyl-3-((2-hydroxyethyl)thio)-2,3-dihydro-1*H*-inden-1-yl)-1-p
henylethan-1-one (3l)**



Yield: 65%, 53.8 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.06 – 8.01 (m, 2H), 7.90 – 7.82 (m, 2H), 7.60 – 7.51 (m, 2H), 7.42 (dq, J = 15.2, 7.8 Hz, 5H), 7.30 – 7.23 (m, 3H), 7.22 – 7.17 (m, 1H), 4.66 (d, J = 5.5 Hz,

1H), 4.26 – 4.17 (m, 2H), 3.74 – 3.65 (m, 2H), 3.60 (dd, J = 17.5, 5.1 Hz, 1H), 3.45 (dd, J = 17.5, 7.6 Hz, 1H), 2.74 (td, J = 6.1, 1.1 Hz, 2H), 1.97 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.8, 198.3, 144.1, 141.6, 137.0, 136.7, 133.4, 133.3, 128.743, 128.736, 128.7, 128.4, 128.1, 127.9, 124.9, 124.0, 61.0, 60.9, 52.2, 44.3, 43.9, 34.9; IR (KBr thin film) 3437, 3064, 2923, 2359, 2341, 1682, 1596, 1579, 1476, 1447, 1403, 1384, 1359, 1224, 1181, 1046, 1001, 902, 749, 728, 690 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{25}\text{O}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 417.15189, found 417.15152.

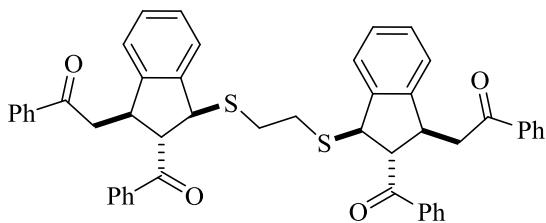
2-(2-benzoyl-3-(phenylthio)-2,3-dihydro-1H-inden-1-yl)-1-phenylethanol-1-one (3m)



Yield: 82%, 73.4 mg; yellow solid; mp 102-104 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (dd, J = 8.3, 1.1 Hz, 2H), 7.82 (dd, J = 8.2, 1.1 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.39 (dt, J = 13.1, 7.7 Hz, 4H), 7.32 – 7.15 (m, 9H), 4.91 (d, J = 3.9 Hz, 1H), 4.25 (dt, J = 9.0, 4.7 Hz, 1H), 4.12 (t, J = 3.9 Hz, 1H), 3.42 (dd, J = 17.7, 5.3 Hz, 1H), 3.10 (dd, J = 17.7, 8.9 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.0, 198.4, 145.1, 141.4, 136.3, 133.4, 133.2, 133.1, 129.1, 128.8, 128.6, 128.5, 128.11, 128.06, 127.7, 125.3, 124.3, 58.7, 55.9, 44.9, 43.1; IR (KBr thin film) 3435, 3060, 1718, 1682,

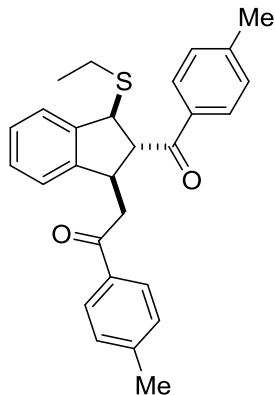
1596, 1579, 1478, 1447, 1438, 1384, 1358, 1285, 1224, 1180, 1158, 1068, 1001, 986, 927, 901, 879, 846, 768, 747, 724, 689 cm⁻¹; HRMS (ESI) m/z calcd for C₃₀H₂₅O₂S⁺ (M+H)₊ 449.15698, found 449.15662.

2,2'-(ethane-1,2-diylbis(sulfanediyl))bis(2-benzoyl-2,3-dihydro-1H-indene-3,1-diyl)bis(1-phenylethan-1-one) (3n)



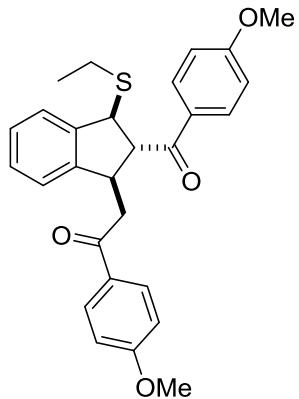
Yield: 68%, 52.3 mg; yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.95 (m, 4H), 7.87 – 7.82 (m, 4H), 7.52 – 7.47 (m, 4H), 7.41 – 7.36 (m, 8H), 7.30 – 7.25 (m, 2H), 7.24 – 7.21 (m, 4H), 7.18 (d, *J* = 2.4 Hz, 2H), 4.54 (dd, *J* = 11.9, 5.9 Hz, 2H), 4.14 – 4.10 (m, 2H), 4.15 – 4.07 (m, 2H), 3.61 – 3.51 (m, 2H), 3.45 – 3.37 (m, 2H), 2.68 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 200.48, 200.45, 198.20, 144.21, 141.54, 141.48, 136.82, 136.72, 136.91, 133.33, 133.30, 133.29, 133.27, 128.73, 128.70, 128.63, 128.36, 128.08, 127.71, 124.91, 124.89, 124.04, 124.02, 60.77, 52.47, 44.40, 43.65, 31.66; IR (KBr thin film) 3438, 3063, 2358, 1682, 1596, 1579, 1477, 1447, 1404, 1384, 1359, 1223, 1181, 1001, 982, 902, 748, 689 cm⁻¹; HRMS (ESI) m/z calcd for C₅₀H₄₃O₄S₂⁺ (M+H)₊ 771.25973, found 771.26007.

2-(3-(ethylthio)-2-(4-methylbenzoyl)-2,3-dihydro-1H-inden-1-yl)-1-(p-tolyl)ethan-1-one (3o)



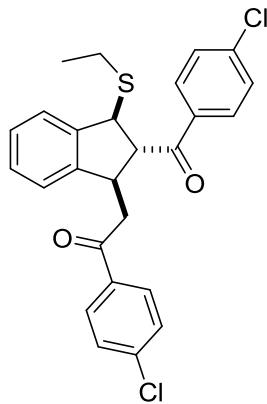
Yield: 86%, 73.6 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.97 – 7.90 (m, 2H), 7.77 (d, J = 6.6 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.28 – 7.17 (m, 7H), 4.60 (d, J = 5.5 Hz, 1H), 4.25 – 4.18 (m, 1H), 4.14 (dd, J = 11.3, 5.6 Hz, 1H), 3.54 (dd, J = 17.3, 5.6 Hz, 1H), 3.40 (dd, J = 17.3, 7.9 Hz, 1H), 2.61 – 2.47 (m, 2H), 2.39 (s, 6H), 2.38 (s, 3H), 1.21(t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.4, 197.9, 144.4, 144.1, 144.0, 134.5, 129.4, 129.3, 128.9, 128.3, 128.1, 127.6, 124.9, 124.0, 60.7, 52.3, 44.4, 44.0, 25.9, 21.7, 14.6; IR (KBr thin film) 3444, 3029, 2968, 2924, 2870, 2590, 1921, 1806, 1679, 1606, 1571, 1477, 1455, 1407, 1358, 1286, 1254, 1228, 1205, 1181, 1119, 1039, 1017, 978, 903, 809, 753, 715, 637 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{29}\text{O}_2\text{S}^+(\text{M}+\text{H})^+$ 429.18828, found 429.18835.

2-(3-(ethylthio)-2-(4-methoxybenzoyl)-2,3-dihydro-1H-inden-1-yl)-1-(4-methoxyphenyl)ethan-1-one (3p)



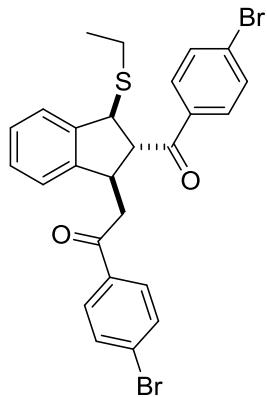
Yield: 89%, 81.7mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.05 – 7.99 (m, 2H), 7.88 – 7.81 (m, 2H), 7.36 (d, J = 6.9 Hz, 1H), 7.27 – 7.16 (m, 3H), 6.95 – 6.84 (m, 4H), 4.59 (d, J = 5.6 Hz, 1H), 4.21 (dd, J = 13.5, 5.8 Hz, 1H), 4.13 (dd, J = 11.5, 5.8 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.50 (dd, J = 17.0, 5.6 Hz, 1H), 3.37 (dd, J = 17.0, 8.0 Hz, 1H), 2.63 – 2.45 (m, 2H), 1.22 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 196.9, 144.5, 142.2, 131.1, 130.4, 130.03, 129.99, 128.1, 127.5, 124.8, 113.8, 113.7, 60.6, 55.5, 52.4, 44.2, 44.0, 25.9, 14.65; IR (KBr thin film) 3459, 3068, 3006, 2965, 2931, 2839, 2574, 2427, 2308, 2054, 1913, 1673, 1600, 1574, 1510, 1456, 1420, 1359, 1309, 1258, 1171, 1114, 1028, 984, 903, 880, 839, 807, 756, 737, 702 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{29}\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$)⁺ 461.17811, found 461.17838.

2-(2-(4-chlorobenzoyl)-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-(4-chlorophenyl)ethan-1-one (3q)



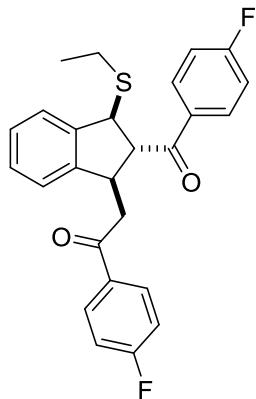
Yield: 68%, 63.6 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (t, $J = 1.8$ Hz, 1H), 7.93 (dt, $J = 7.8, 1.2$ Hz, 1H), 7.82 (t, $J = 1.7$ Hz, 1H), 7.74 (dt, $J = 7.8, 1.3$ Hz, 1H), 7.55 – 7.50 (m, 2H), 7.44 – 7.33 (m, 3H), 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 1H), 4.54 (d, $J = 5.5$ Hz, 1H), 4.22 (dt, $J = 9.6, 5.1$ Hz, 1H), 4.04 (t, $J = 5.5$ Hz, 1H), 3.58 (dd, $J = 17.7, 4.8$ Hz, 1H), 3.40 (dd, $J = 17.7, 9.1$ Hz, 1H), 2.62 – 2.47 (m, 2H), 1.23 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.4, 197.1, 143.7, 141.8, 138.5, 138.1, 135.0, 133.3, 133.2, 130.0, 129.96, 128.9, 128.3, 128.2, 127.9, 126.8, 126.2, 125.0, 123.9, 61.0, 52.4, 44.6, 43.5, 25.9, 14.6; IR (KBr thin film) 3435, 3067, 2969, 2927, 1954, 1682, 1634, 1590, 1570, 1474, 1456, 1423, 1357, 1285, 1223, 1075, 1052, 997, 944, 902, 787, 749, 711 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{O}_2\text{S}^+(\text{M}+\text{H})^+$ 469.07903, found 469.07910.

2-(2-(4-bromobenzoyl)-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-(4-bromophenyl)ethan-1-one (3r)



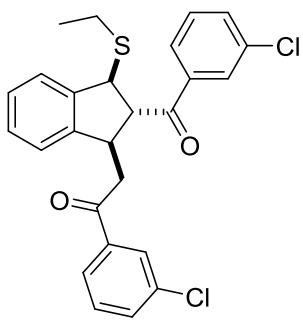
Yield: 67%, 74.4 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.88 (m, 2H), 7.74 – 7.69 (m, 2H), 7.62 – 7.53 (m, 4H), 7.39 – 7.34 (m, 1H), 7.30 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 4.52 (d, $J = 5.5$ Hz, 1H), 4.21 (dt, $J = 9.6, 5.1$ Hz, 1H), 4.04 (t, $J = 5.5$ Hz, 1H), 3.56 (dd, $J = 17.6, 4.9$ Hz, 1H), 3.37 (dd, $J = 17.6, 9.1$ Hz, 1H), 2.63 – 2.42 (m, 2H), 1.21 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.7, 197.4, 143.8, 141.9, 135.7, 135.3, 132.0, 130.3, 129.6, 128.6, 128.6, 128.3, 127.8, 125.0, 123.9, 60.8, 52.5, 44.5, 43.6, 26.0, 14.6; IR (KBr thin film) 3453, 3067, 2967, 2926, 1919, 1682, 1631, 1584, 1567, 1535, 1482, 1455, 1396, 1358, 1249, 1221, 1177, 1107, 1071, 1025, 1009, 985, 903, 814, 770, 749 cm^{-1} .

2-(3-(ethylthio)-2-(3-fluorobenzoyl)-2,3-dihydro-1H-inden-1-yl)-1-(4-fluorophenyl)ethan-1-one (3s)



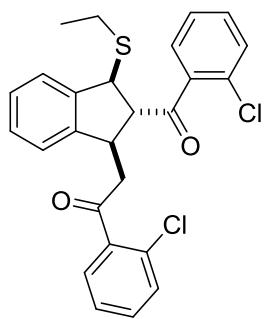
Yield: 67%, 58.4mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.05 (m, 2H), 7.92 – 7.87 (m, 2H), 7.38 – 7.34 (m, 1H), 7.27 (dd, J = 6.2, 2.8 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.16 – 7.06 (m, 4H), 4.54 (d, J = 5.4 Hz, 1H), 4.23 (dt, J = 9.6, 5.1 Hz, 1H), 4.07 (t, J = 5.4 Hz, 1H), 3.58 (dd, J = 17.5, 5.0 Hz, 1H), 3.40 (dd, J = 17.5, 8.9 Hz, 1H), 2.62 – 2.47 (m, 2H), 1.22 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 196.7, 167.2, 167.1, 164.6, 144.0, 141.9, 131.5, 131.4, 133.34, 133.31, 133.16, 133.13, 130.77, 130.68, 128.3, 127.8, 125.0, 123.9, 115.9, 115.9, 115.7, 115.6, 60.7, 52.4, 44.5, 43.7, 25.9, 14.6; ^{19}F NMR (376 MHz, CDCl_3) δ -104.65, -105.04; IR (KBr thin film) 3434, 2926, 2359, 2342, 1682, 1597, 1506, 1457, 1384, 1358, 1228, 1156, 1099, 987, 845, 747, 668 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{F}_2\text{O}_2\text{S}^+$ ($\text{M}+\text{H})^+$ 437.13813, found 437.13788.

2-(2-(3-chlorobenzoyl)-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-(3-chlorophenyl)ethan-1-one (3t)



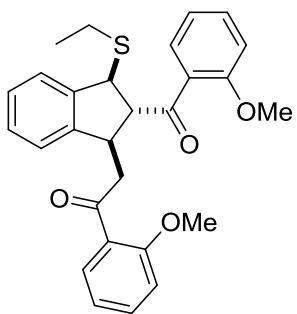
Yield: 76%, 71.1 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.03 – 7.94 (m, 2H), 7.84 – 7.73 (m, 2H), 7.46 – 7.33 (m, 5H), 7.30 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 4.53 (d, $J = 5.5$ Hz, 1H), 4.22 (dt, $J = 9.7, 5.1$ Hz, 1H), 4.05 (t, $J = 5.5$ Hz, 1H), 3.57 (dd, $J = 17.6, 4.9$ Hz, 1H), 3.38 (dd, $J = 17.6, 9.0$ Hz, 1H), 2.61 – 2.45 (m, 2H), 1.22 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.5, 197.1, 143.9, 141.9, 139.9, 139.8, 135.2, 135.0, 130.2, 129.5, 128.98, 128.96, 128.3, 127.8, 125.0, 123.9, 60.8, 52.5, 44.5, 43.6, 26.0, 14.6; IR (KBr thin film) 3443, 2969, 2926, 1682, 1632, 1598, 1570, 1487, 1456, 1400, 1384, 1359, 1283, 1205, 1221, 1207, 1176, 1091, 1012, 986, 902, 818, 773, 748 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{O}_2\text{S}^+(\text{M}+\text{H})^+$ 469.07903, found 469.07913.

2-(2-(2-chlorobenzoyl)-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-(2-chlorophenyl)ethan-1-one (3u)



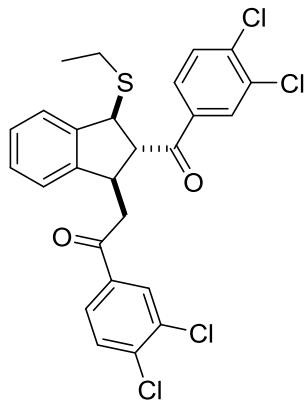
Yield: 63%, 58.9 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.02 – 7.97 (m, 2H), 7.82 – 7.77 (m, 2H), 7.46 – 7.38 (m, 4H), 7.36 (dd, J = 6.2, 2.5 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.22 – 7.17 (m, 1H), 4.53 (d, J = 5.5 Hz, 1H), 4.22 (dt, J = 9.7, 5.1 Hz, 1H), 4.05 (t, J = 5.5 Hz, 1H), 3.57 (dd, J = 17.6, 4.9 Hz, 1H), 3.38 (dd, J = 17.6, 9.0 Hz, 1H), 2.59 – 2.45 (m, 2H), 1.22 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.5, 197.1, 143.9, 141.9, 139.9, 139.8, 135.2, 135.0, 130.2, 129.5, 128.98, 128.96, 128.3, 127.8, 124.97, 123.88, 60.82, 52.45, 44.49, 43.63, 25.95, 14.56; IR (KBr thin film) 3440, 2990, 2924, 2360, 2343, 1677, 1630, 1588, 1571, 152, 1400, 1364, 1208, 1091, 1050, 1012, 988, 774, 749, 668 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{O}_2\text{S}^+$ (M^+H)⁺ 469.07903, found 469.07922.

2-(3-(ethylthio)-2-(2-methoxybenzoyl)-2,3-dihydro-1H-inden-1-yl)-1-(2-methoxyphenyl)ethan-1-one (3v)



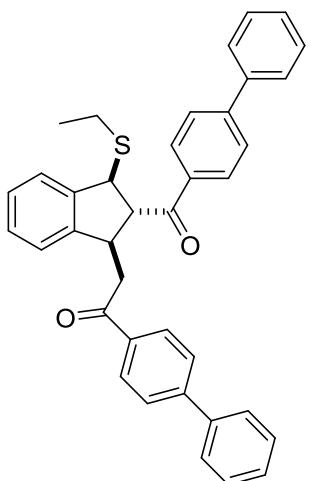
Yield: 65%, 59.8mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.66 – 7.60 (m, 1H), 7.58 – 7.52 (m, 1H), 7.45 – 7.39 (m, 2H), 7.37 (d, J = 6.8 Hz, 1H), 7.19 (dt, J = 19.8, 6.1 Hz, 3H), 7.00 (t, J = 7.3 Hz, 1H), 6.92 (dt, J = 15.3, 7.6 Hz, 3H), 4.72 (d, J = 5.7 Hz, 1H), 4.32 (t, J = 5.9 Hz, 1H), 4.14 (dd, J = 12.6, 6.3 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.56 (dd, J = 17.6, 6.2 Hz, 1H), 3.44 (dd, J = 17.7, 7.1 Hz, 1H), 2.59 – 2.45 (m, 2H), 1.20 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 203.39, 200.38, 158.5, 158.0, 144.8, 142.3, 133.5, 133.2, 130.7, 130.4, 128.7, 128.1, 127.9, 127.3, 124.8, 124.0, 120.8, 120.7, 111.50, 111.46, 64.7, 55.2, 51.2, 50.2, 43.9, 25.5, 14.7; IR (KBr thin film) 3447, 3069, 2966, 2926, 2837, 1671, 1596, 1578, 1484, 1435, 1396, 1353, 1285, 1244, 1179, 1162, 1112, 1051, 1021, 987, 885, 804, 755, 658 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{29}\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 461.17811, found 461.17819.

2-(2-(3,4-dichlorobenzoyl)-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-(3,4-dichlorophenyl)ethan-1-one (3W)



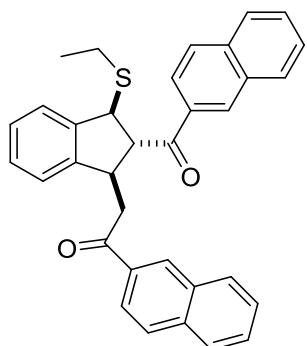
Yield: 67%, 71.8 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 2.0$ Hz, 1H), 7.93 (d, $J = 2.0$ Hz, 1H), 7.89 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.69 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.53 (dd, $J = 15.7, 8.4$ Hz, 2H), 7.38 – 7.33 (m, 1H), 7.31 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 4.49 (d, $J = 5.6$ Hz, 1H), 4.21 (dt, $J = 9.7, 4.9$ Hz, 1H), 3.97 (t, $J = 5.5$ Hz, 1H), 3.57 (dd, $J = 17.7, 4.5$ Hz, 1H), 3.37 (dd, $J = 17.7, 9.5$ Hz, 1H), 2.61 – 2.46 (m, 2H), 1.23 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.4, 196.2, 143.4, 141.7, 138.1, 13.9, 136.5, 136.0, 133.5, 133.4, 130.8, 130.79, 130.75, 130.1, 128.4, 128.0, 127.8, 127.1, 125.0, 123.8, 60.9, 52.5, 44.4, 43.5, 25.9, 14.5; IR (KBr thin film) 3435, 2359, 2341, 1684, 1636, 1583, 1559, 1457, 1384, 1201, 1030, 749, 668 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{21}\text{Cl}_4\text{O}_2\text{S}^+(\text{M}+\text{H})^+$ 537.00109, found 537.00018.

2-(2-((1,1'-biphenyl)-4-carbonyl)-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-((1,1'-biphenyl)-4-yl)ethan-1-one (3x)



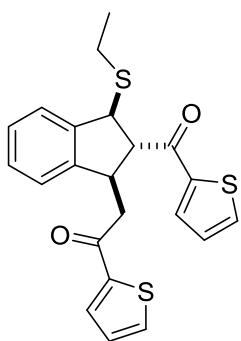
Yield: 75%, 82.9mg; yellow solid; mp 92.3-94.3; ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 8.4$ Hz, 2H), 7.95 – 7.88 (m, 2H), 7.68 – 7.63 (m, 2H), 7.63 – 7.51 (m, 6H), 7.46 – 7.34 (m, 7H), 7.30 – 7.18 (m, 3H), 4.66 (d, $J = 5.72$ Hz), 4.33 – 4.26 (m, 1H), 4.21 (t, $J = 5.8$ Hz, 1H), 3.61 (dd, $J = 17.3, 5.3$ Hz, 1H), 3.50 (dd, $J = 17.3, 8.4$ Hz, 1H), 2.65 – 2.48 (m, 2H), 1.23 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 200.4, 197.9, 144.1, 142.1, 135.7, 135.5, 129.4, 128.97, 128.96, 128.7, 128.3, 128.23, 128.20, 127.7, 127.27, 127.26, 127.2, 125.0, 123.9, 61.1, 52.4, 44.4, 44.1, 26.0, 14.7; IR (KBr thin film) 3446, 3058, 3031, 2965, 2926, 2870, 2359, 2341, 1951, 1807, 1682, 1673, 1603, 1581, 1558, 1514, 1486, 1404, 1360, 1264, 1228, 1191, 1157, 1116, 1076, 1050, 1025, 1006, 986, 904, 850, 811, 763, 747, 696 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{38}\text{H}_{33}\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 553.21958, found 553.21906.

2-(2-(2-naphthoyl)-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-(naphthalen-2-yl)ethan-1-one (3y)



Yield: 80%, 80.02 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.58 (s, 1H), 8.34 (s, 1H), 8.11 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.80 (ddd, $J = 29.8, 16.0, 8.6$ Hz, 8H), 7.58 – 7.38 (m, 6H), 7.33 – 7.25 (m, 3H), 4.70 (d, $J = 5.3$ Hz, 1H), 4.37 (dd, $J = 10.3, 5.7$ Hz, 2H), 3.75 – 3.59 (m, 2H), 2.66 – 2.49 (m, 2H), 1.22 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.7, 198.3, 144.3, 142.2, 135.7, 135.6, 134.3, 134.1, 132.5, 132.4, 130.6, 129.9, 129.7, 129.6, 128.6, 128.5, 128.5, 128.4, 128.2, 127.72, 127.71, 127.69, 126.8, 126.7, 125.0, 124.5, 124.0, 123.7, 61.2, 52.5, 44.5, 44.3, 26.2, 14.7; IR (KBr thin film) 3434, 3058, 2966, 2926, 2870, 2357, 2342, 1924, 1675, 1626, 1595, 1577, 1507, 1468, 1436, 1384, 1358, 1336, 1276, 1219, 1184, 1123, 1048, 1024, 986, 942, 897, 863, 821, 775, 755, 703 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{29}\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 501.18828, found 501.18845.

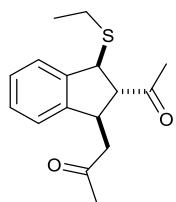
2-3-(ethylthio)-2-(thiophene-2-carbonyl)-2,3-dihydro-1H-inden-1-yl)-1-(thiophen-2-yl)ethan-1-one (3z)



Yield: 70%, 57.6 mg; yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.69 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.62 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.17 (m, 3H), 7.12 – 7.08 (m, 2H), 4.64 (d, *J* = 6.1 Hz, 1H), 4.22 (dd, *J* = 13.6, 6.8 Hz, 1H), 4.03 (dd, *J* = 12.4, 6.0 Hz, 1H), 3.54–3.35 (m, 2H), 2.65–2.44 (m, 2H), 1.23 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 193.3, 191.1, 143.7, 141.9, 134.7, 134.1, 132.9, 132.2, 128.4, 128.2, 127.8, 124.9, 123.8, 62.4, 52.4, 44.6, 44.3, 25.7, 14.7; IR (KBr thin film) 3445, 2966, 2925, 1656, 1558, 1517, 1476, 1415, 1383, 1356, 1238, 856, 751, 724, 666 cm⁻¹.

1-(2-acetyl-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)propan-2-one

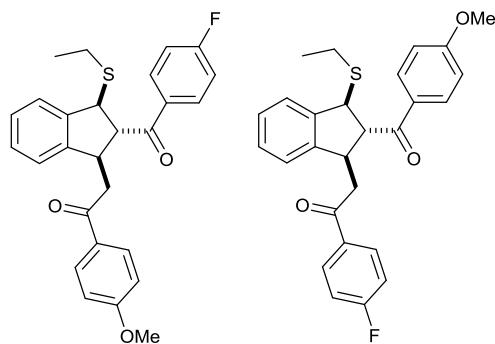
(3aa)



Yield: 67%, 37.0 mg; yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.34 (m, 1H), 7.26 – 7.19 (m, 2H), 7.13 – 7.08 (m, 1H), 4.43 (d, *J* = 5.8

Hz, 1H), 3.89 – 3.84 (m, 1H), 3.13 (dd, J = 11.5, 6.0 Hz, 1H), 3.05 (dd, J = 17.6, 4.9 Hz, 1H), 2.87 (dd, J = 17.6, 9.0 Hz, 1H), 2.65 – 2.48 (m, 2H), 2.39 (s, 3H), 2.20 (s, 3H), 1.28 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.5, 207.4, 143.5, 141.7, 128.1, 127.7, 125.0, 123.7, 65.6, 50.6, 49.8, 42.0, 30.9, 30.3, 29.8, 25.1, 14.6; IR (KBr thin film) 3435, 3069, 2968, 2927, 1713, 1654, 1477, 1456, 1404, 1359, 1255, 1228, 1159, 1067, 1023, 970, 747 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{21}\text{O}_2\text{S}^+$ ($\text{M}+\text{H})^+$ 277.12568, found 277.12585.

2-3-(ethylthio)-2-(4-fluorobenzoyl)-2,3-dihydro-1H-inden-1-yl)-1-(4-methoxyphenyl)ethan-1-one (3ac) and
2-3-(ethylthio)-2-(4-methoxybenzoyl)-2,3-dihydro-1H-inden-1-yl)-1-(4-fluorophenyl)ethan-1-one (3ac')

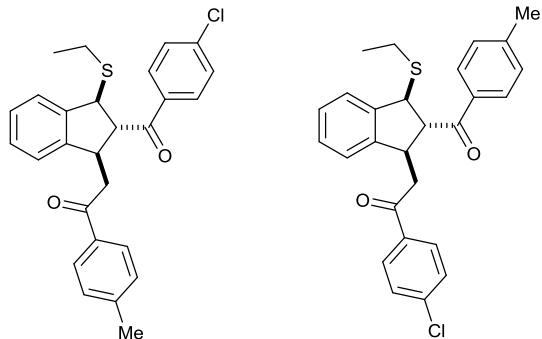


A mixture of inseparable regioisomers, **3ac/3ac'** = 3:1; Pale yellow liquid (61.0 mg, 68% yield); ^1H NMR (400 MHz, CDCl_3) of **3ac**: δ 8.10 – 8.00 (m, 2 H), 7.87 – 7.83 (m, 2H), 7.39 – 7.35 (m, 1H), 7.28 – 7.24 (m, 2H), 7.24 – 7.17 (m, 1H), 7.15 – 7.05 (m, 2H), 6.91 – 6.87(m, 2H), 4.55 (d, J = 5.5 Hz, 1H), 4.23 – 4.18(m, 1H), 4.15 – 4.06 (m, 1H), 3.86 (s, 3H), 3.54

(dd, $J = 17.2, 5.1$ Hz, 1H), 3.37 (dd, $J = 17.2, 9.0$ Hz, 1H), 2.61 – 2.46 (m, 2H), 1.22 (td, $J = 7.4, 2.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) of **3ac** and **3ac'**, δ 199.4, 199.1, 196.82, 196.77, 167.1, 164.6, 163.74, 163.65, 144.24, 144.18, 142.16, 141.94, 133.43, 133.41, 131.5, 131.4, 131.1, 130.8, 130.7, 130.4, 129.92, 129.85, 128.2, 128.1, 127.7, 127.62, 124.9, 123.93, 123.9, 115.8, 115.6, 113.85, 113.78, 60.8, 60.6, 55.5, 52.5, 52.4, 44.3, 44.2, 44.0, 43.9, 31.6, 26.0, 25.9, 22.7, 14.63, 14.58; IR (KBr thin film) **3ac** and **3ac'** 3435, 2358, 1673, 1599, 1505, 1384, 1228, 1169, 1047, 838 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{26}\text{FO}_2\text{S}^+$ ($\text{M}+\text{H}$)⁺ 433.16321, found 433.16260.

^1H NMR (400 MHz, CDCl_3) of **3ac'**: 8.10 – 8.00 (m, 0.7 H), 7.92 – 7.88 (m, 0.7H), 7.39 – 7.35 (m, 0.33H), 7.28 – 7.24 (m, 0.8H), 7.24 – 7.17 (m, 0.4H), 7.15 – 7.05 (m, 0.7H), 6.94 – 6.92(m, 0.7H), 4.58 (d, $J = 5.6$ Hz, 0.33H), 4.55 (d, $J = 5.5$ Hz, 1H), 4.23 – 4.18(m, 0.33H), 4.15 – 4.06 (m, 0.33H), 3.87 (s, 1H), 3.54 (dd, $J = 17.2, 5.1$ Hz, 0.33H), 3.37 (dd, $J = 17.2, 9.0$ Hz, 0.33 H), 2.61 – 2.46 (m, 0.7H), 1.22 (td, $J = 7.4, 2.7$ Hz, 1.0H).

1-(4-chlorophenyl)-2-3-(ethylthio)-2-(4-methylbenzoyl)-2,3-dihydro-1H-inden-1-yl)ethan-1-one (3ad) and
2-2-(4-chlorobenzoyl)-3-(ethylthio)-2,3-dihydro-1H-inden-1-yl)-1-(p-tolyl)ethan-1-one (3ad')



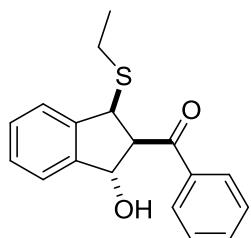
A mixture of inseparable regioisomers, **3ad/3ad'** = 2.5:1; Pale yellow liquid (78.1 mg, 87% yield); ^1H NMR (400 MHz, CD₃Cl) of **3ad**: δ 8.01–7.97 (m, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.45–7.34 (m, 3H), 7.31–7.15 (m, 5H), 4.54 (d, J = 5.6 Hz, 1H), 4.25–4.15 (m, 1H), 4.16–4.04 (m, 1H), 3.62–3.50 (m, 1H), 3.44–3.35 (m, 1H), 2.60–2.45 (m, 2H), 2.39 (s, 3H), 1.25–1.18 (m, 3H); ^{13}C NMR (100 MHz, CDCl₃) of **3ad** and **3ad'**: δ 200.1, 199.8, 197.9, 197.1, 144.22, 144.18, 144.12, 144.07, 142.1, 141.9, 139.68, 139.65, 135.4, 135.1, 134.4, 134.2, 130.2, 129.5, 129.4, 129.3, 128.9, 128.87, 128.23, 128.20, 128.17, 127.70, 127.67, 124.9, 123.9, 60.9, 60.8, 52.5, 52.21, 44.4, 44.36, 43.9, 43.8, 21.7, 14.62, 14.59; IR (KBr thin film) of **3ad** and **3ad'**: 3442, 2968, 2925, 1679, 1606, 1588, 1571, 1456, 1384, 1360, 1226, 1180, 1091, 1002, 991, 810, 749 cm⁻¹; HRMS (ESI) m/z calcd for C₂₇H₂₆ClO₂S⁺ (M+H)⁺ 449.13365, found 449.13330.

^1H NMR (400 MHz, CDCl₃) of **3ad'**: ^1H NMR (400 MHz, CD₃Cl) 87.95–7.92 (m, 0.82H), 7.81–7.78 (m, 0.86H), 7.45–7.34 (m, 1.2H), 7.31–7.15 (m, 2H), 4.62–4.58 (m, 0.42 H), 4.25–4.15 (m, 0.47 H),

4.16–4.04 (m, 0.58 H), 3.62–3.50 (m, 0.51 H), 3.44–3.35 (m, 0.46 H),
2.60–2.45 (m, 1.2H), 2.41 (s, 1.1H), 1.25–1.18 (m, 1H).

1-(ethylthio)-3-hydroxy-2,3-dihydro-1H-inden-2-yl)(phenyl)methano

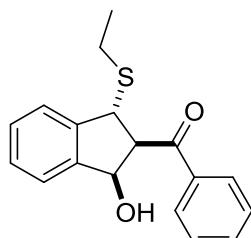
ne (5a)



Yield: 57%, 33.9 mg; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.19 – 8.14 (m, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 7.48 (m, 2H), 7.47 – 7.42 (m, 1H), 7.39 – 7.29 (m, 3H), 5.28 (d, $J = 4.2$ Hz, 1H), 4.75 (d, $J = 6.0$ Hz, 1H), 4.36 – 4.24 (m, 1H), 2.74 – 2.35 (m, 3H), 1.22 (t, $J = 7.4$ Hz, 3H).
 ^{13}C NMR (100 MHz, CDCl_3) δ 199.5, 142.2, 142.0, 136.6, 133.7, 129.4, 129.1, 128.8, 128.5, 125.2, 124.4, 65.8, 48.6, 25.5, 14.6; IR (KBr thin film) 3435, 1667, 1595, 1557, 1538, 1447, 1384, 1250, 1052, 781, 700 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{S}^+$ ($\text{M}+\text{H})^+$ 297.09438, found 297.09476.

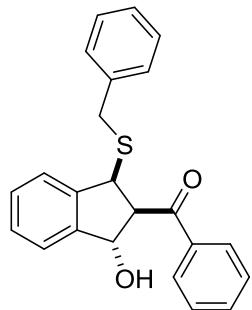
1-(ethylthio)-3-hydroxy-2,3-dihydro-1H-inden-2-yl)(phenyl)methano

ne (5a')



Yield: 10%, 5.96 mg; yellow liquid, ^1H NMR (400 MHz, CDCl_3) δ 8.09 (dd, $J = 8.4, 1.4$ Hz, 2H), 7.66 – 7.61 (m, 1H), 7.56 – 7.52 (m, 2H), 7.50 – 7.45 (m, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 1H), 5.57 (dd, $J = 8.6, 6.6$ Hz, 1H), 5.04 (d, $J = 6.5$ Hz, 1H), 4.49 (dd, $J = 13.2, 6.6$ Hz, 1H), 2.67 – 2.49 (m, 2H), 2.28 (d, $J = 8.9$ Hz, 1H), 1.27 (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.44, 142.59, 142.54, 136.73, 133.63, 129.59, 128.92, 128.49, 128.42, 125.39, 124.61, 61.61, 48.38, 25.66, 14.77.

1-(benzylthio)-3-hydroxy-2,3-dihydro-1H-inden-2-yl)(phenyl)methanone (5b)



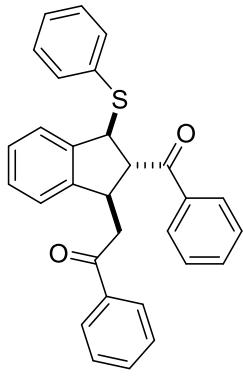
Yield: 64%, 46.1 mg; ^1H NMR (400 MHz, CDCl_3) δ 8.04 – 7.98 (m, 2H), 7.63 – 7.56 (m, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.40 – 7.28 (m, 4H), 7.25 – 7.13 (m, 5H), 5.17 (dd, $J = 7.6, 5.3$ Hz, 1H), 4.74 (d, $J = 6.0$ Hz, 1H), 4.21 – 4.11 (m, 1H), 3.77 – 3.61 (m, 2H), 2.41 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.6, 142.4, 141.2, 138.2, 136.6, 133.6, 129.4, 129.1, 129.0, 128.7, 128.6, 128.5, 127.2, 125.3, 124.5, 78.6, 65.6, 48.9, 35.8; IR (KBr thin film) 3445, 3062, 3028, 2916, 1673, 1596, 1579, 1497, 1474, 1358, 1250, 1158, 1105, 1027, 1001, 912, 889, 825, 782, 767,

747, 730, 699 cm⁻¹; HRMS (ESI) m/z calcd for C₁₈H₁₉O₂S⁺ (M+H)⁺ 299.11003, found 299.11020.

3. References

- (1) X. Q. Fang, K. Jiang, Ch. Xing, L. Hao, Y. R. Chi, *Angew. Chem. Int. Ed.*, 2011, **50**, 1910.
- (2) N. Li, G. G. Liu, J. Chen, F. F. Pan, B. Wu and X. W. Wang, *Eur. J. Org. Chem.*, 2014, **13**, 2677.

4. Single-crystal X-ray structure analysis

Compounds	X-ray structures
 3m	 3m

CCDC 1905585 (**3m**) , contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Table 1 Crystal data and structure refinement for **3m**

Identification code	3m
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Empirical formula	C ₃₀ H ₂₄ O ₂ S
Formula weight	448.55
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	7.6174(3)
b/Å	26.7210(13)
c/Å	34.0314(14)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å ³	6926.9(5)
Z	12
ρ _{calc} g/cm ³	1.290
μ/mm ⁻¹	0.166
F(000)	2832.0
Crystal size/mm ³	0.2 × 0.18 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.72 to 52.8
Index ranges	-9 ≤ h ≤ 9, -28 ≤ k ≤ 33, -42 ≤ l ≤ 39
Reflections collected	37759
Independent reflections	13802 [R _{int} = 0.1019, R _{sigma} = 0.1321]
Data/restraints/parameters	13802/0/894
Goodness-of-fit on F ²	1.031
Final R indexes [I>=2σ (I)]	R ₁ = 0.0637, wR ₂ = 0.1007
Final R indexes [all data]	R ₁ = 0.1403, wR ₂ = 0.1306
Largest diff. peak/hole / e Å ⁻³	0.28/-0.30
Flack parameter	0.39(8)

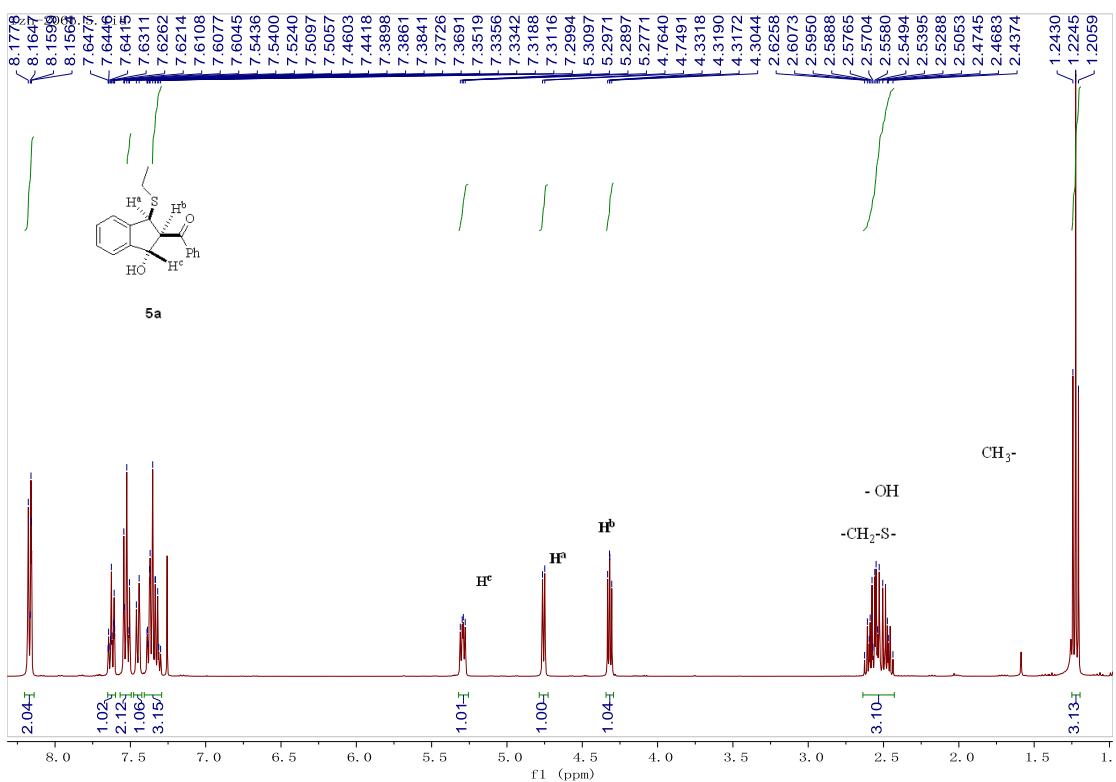
5. Determination of the relative configuration of the diastereomers **5a** and **5a'**

Through the analysis of ¹H ~ ¹H COSY, HSQC and HMBC of **5a**, three characteristic protons (H^a ~ H^c) at the high field are assigned as shown in ¹H NMR. Further analysis of the NOESY spectra of **5a** indicates that H^a has correlation with H^b, while H^c has no obvious

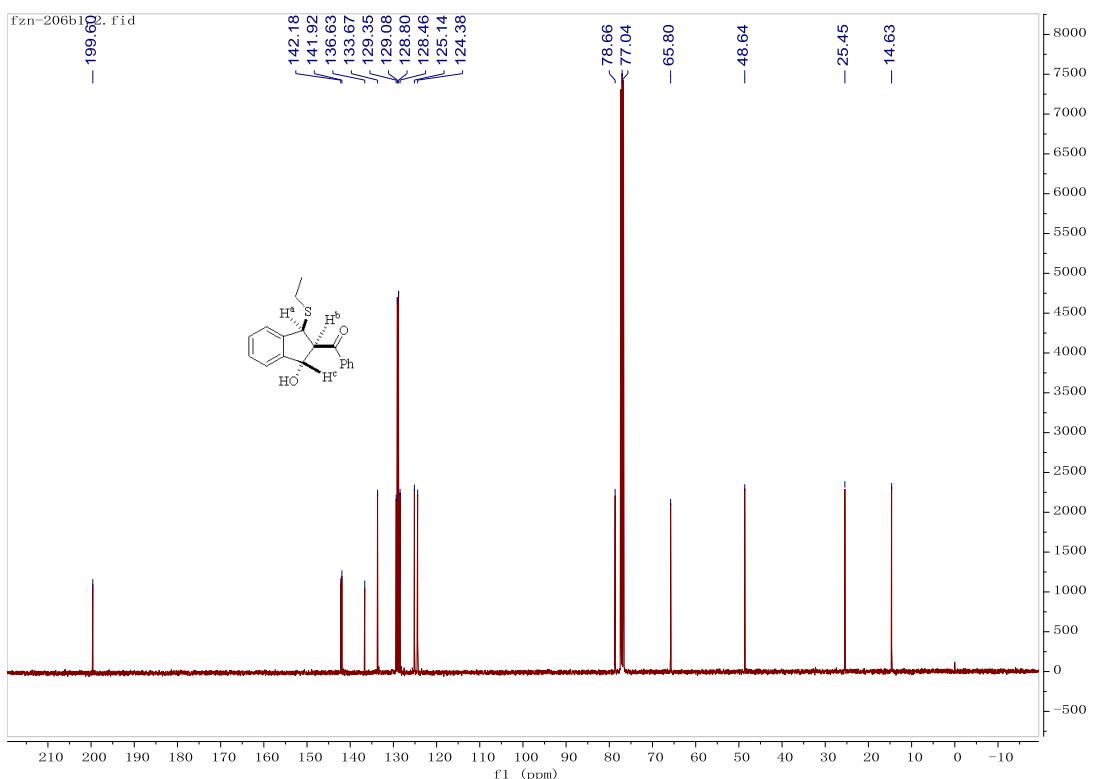
correlation with H^a and H^b. Therefore, H^a adapts cis-position with H^b, while H^c adapts the trans-position with H^a and H^b. Based on these results, we confirm that **5a** is the *cis, trans*-diastereomer.

Similarly, through the analysis of ¹H ~ ¹H COSY, ¹H NMR and ¹³C NMR of **5a'**, three characteristic protons of **5a'** (H^a ~ H^c) at the high field are assigned as shown in ¹H NMR. Further analysis of the NOESY spectra of **5a'** indicates that H^b has correlation with H^c, while H^a has no obvious correlation with H^b and H^c. Therefore, H^b adapts cis-position with H^c, while H^a adapts the trans-position with H^b and H^c. Based on these results, we confirm that **5a** is the *trans, cis*-diastereomer.

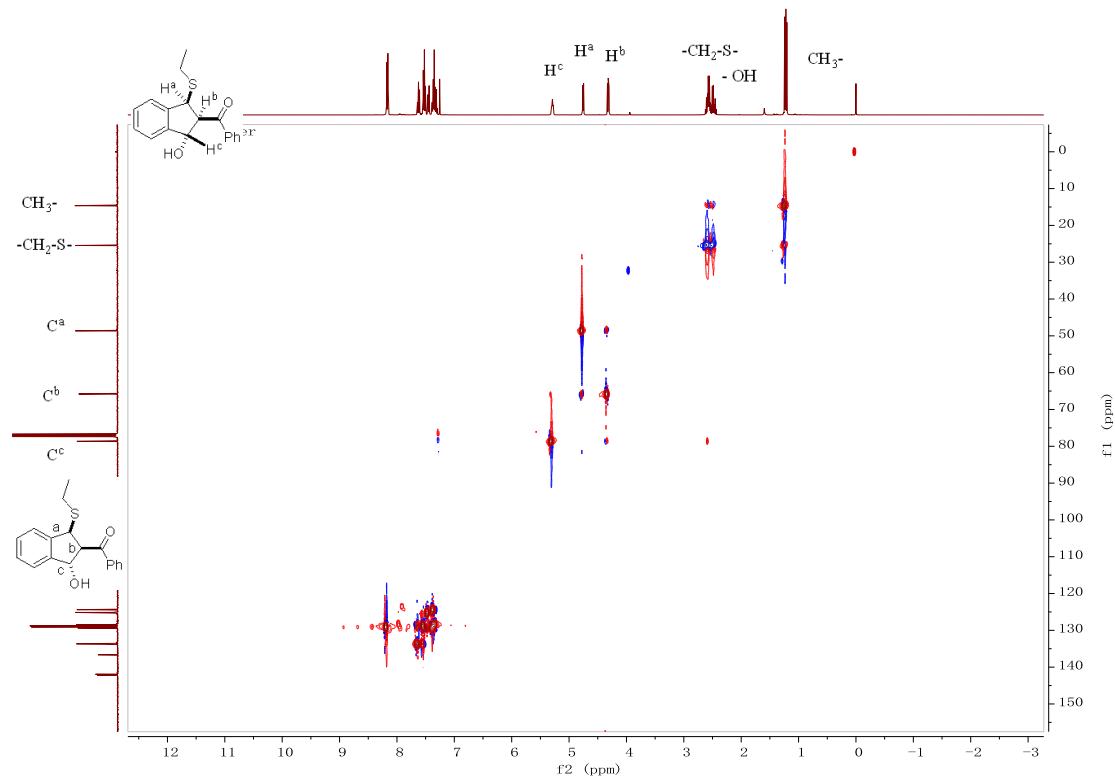
¹H NMR of 5a



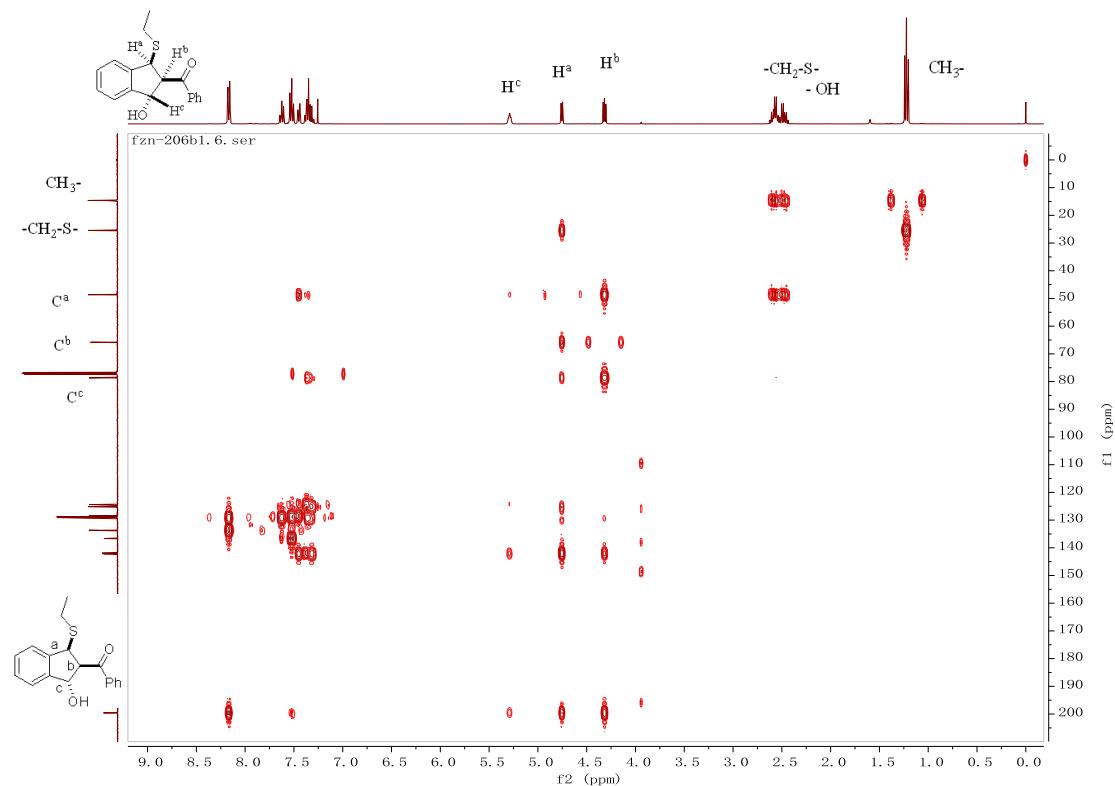
¹³C NMR of **5a**



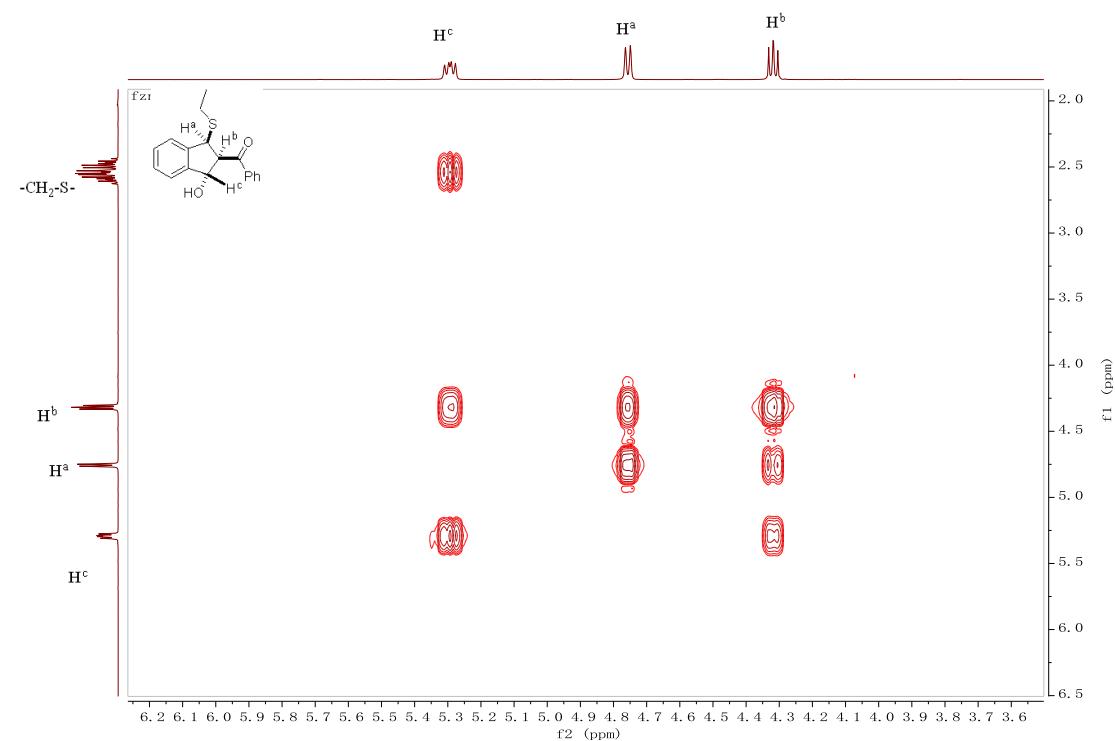
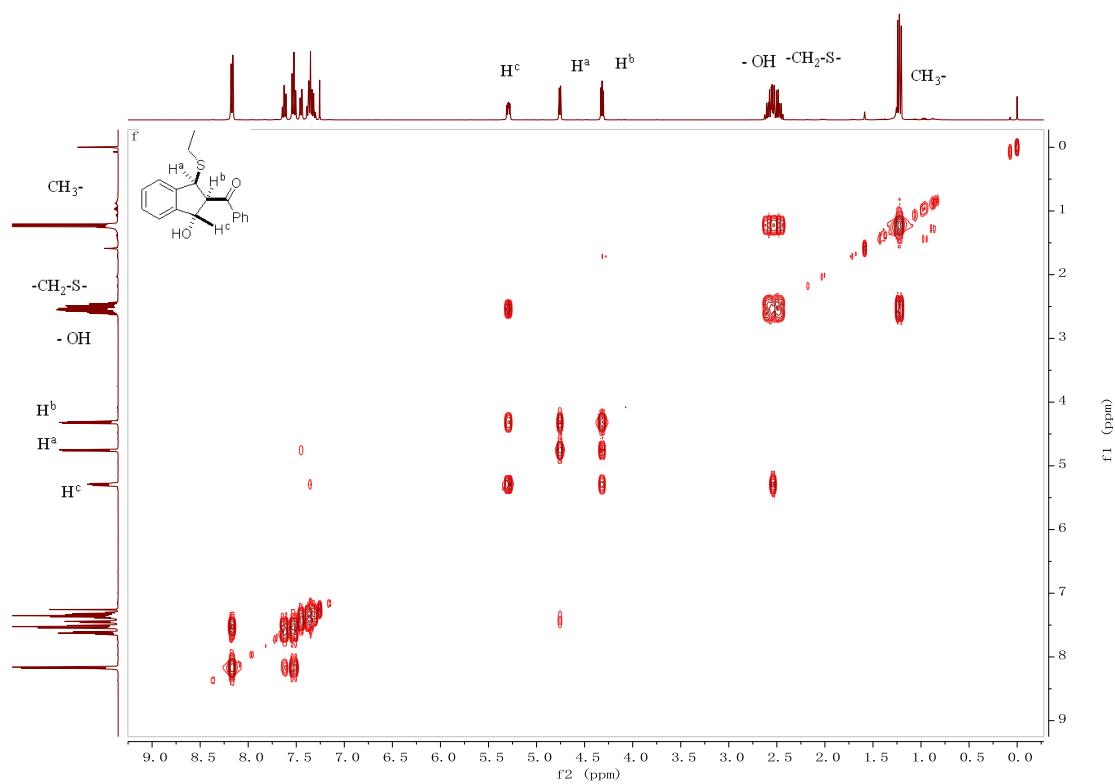
HSQC of **5a**



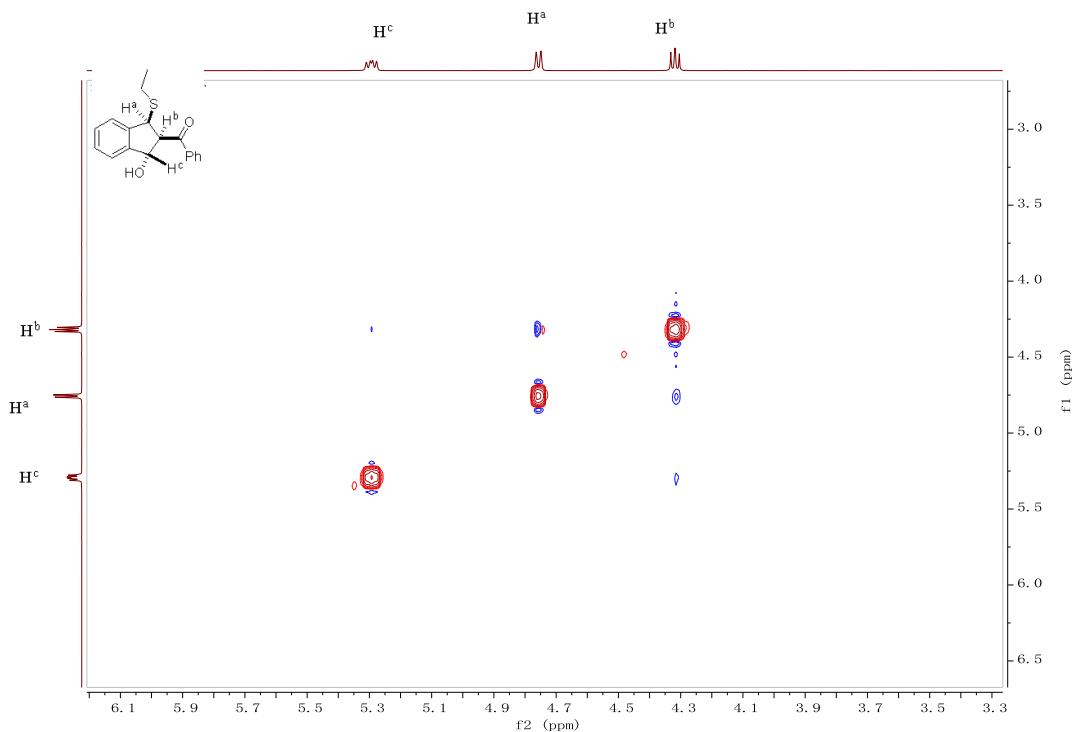
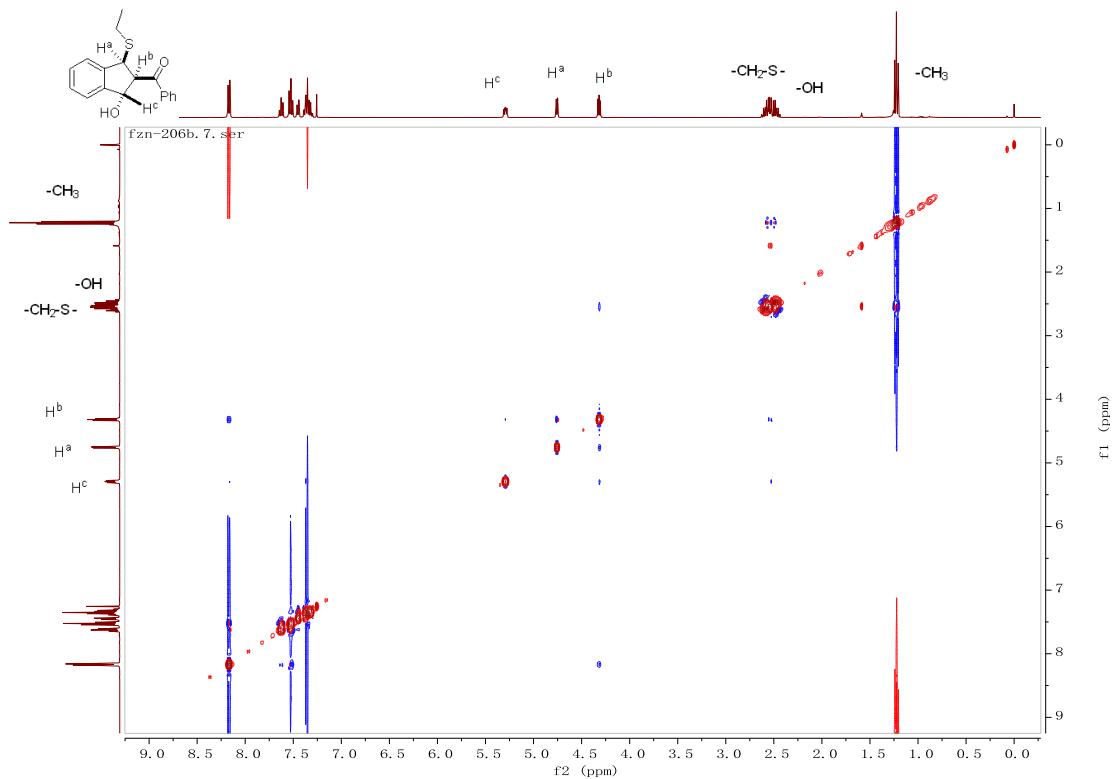
HMBC of **5a**



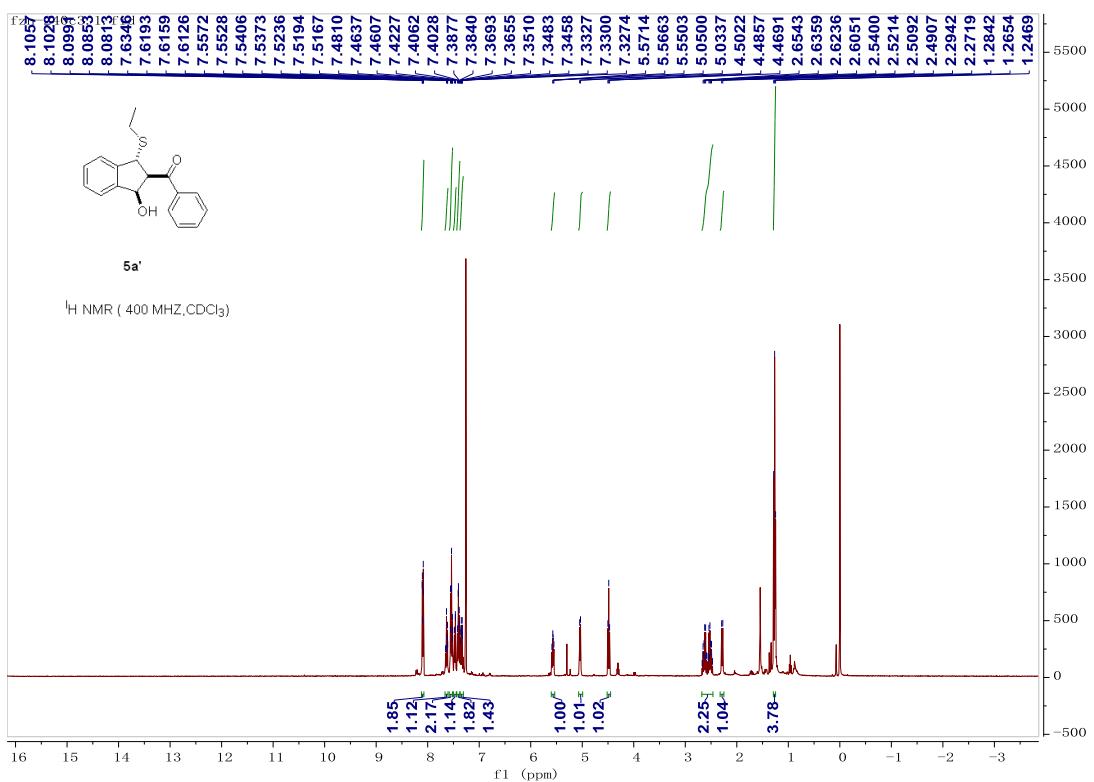
¹H-¹H COSY of **5a**



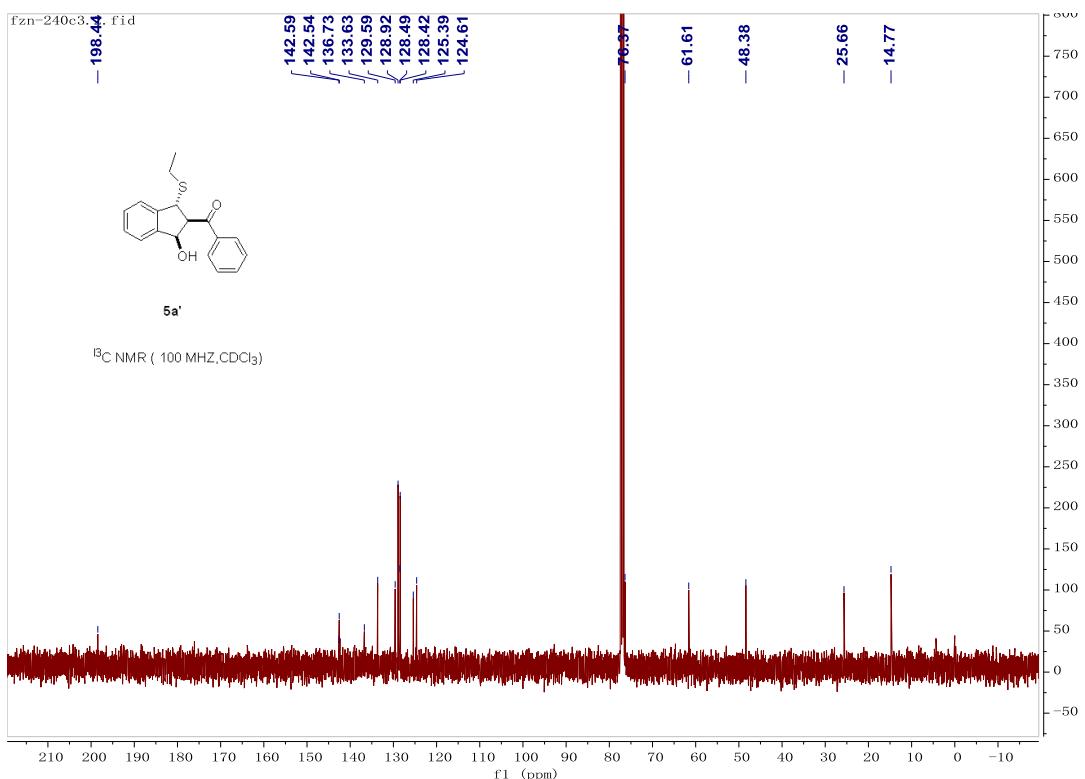
NOESY of **5a**



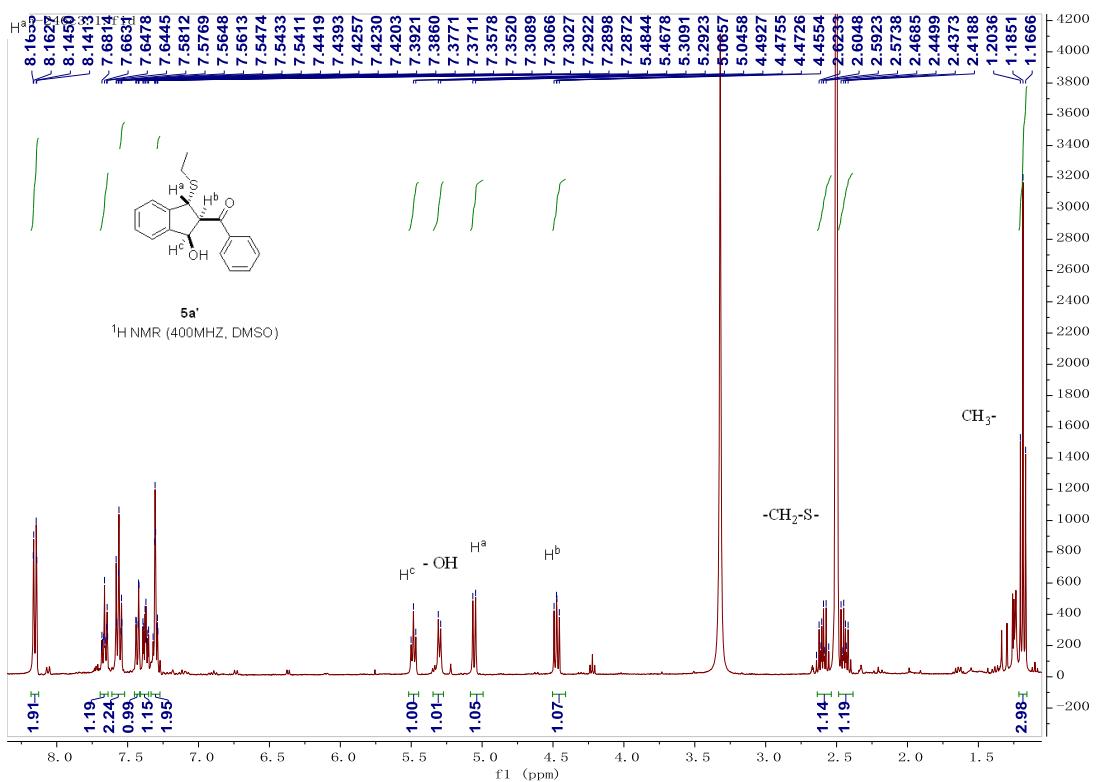
¹H NMR of 5a'



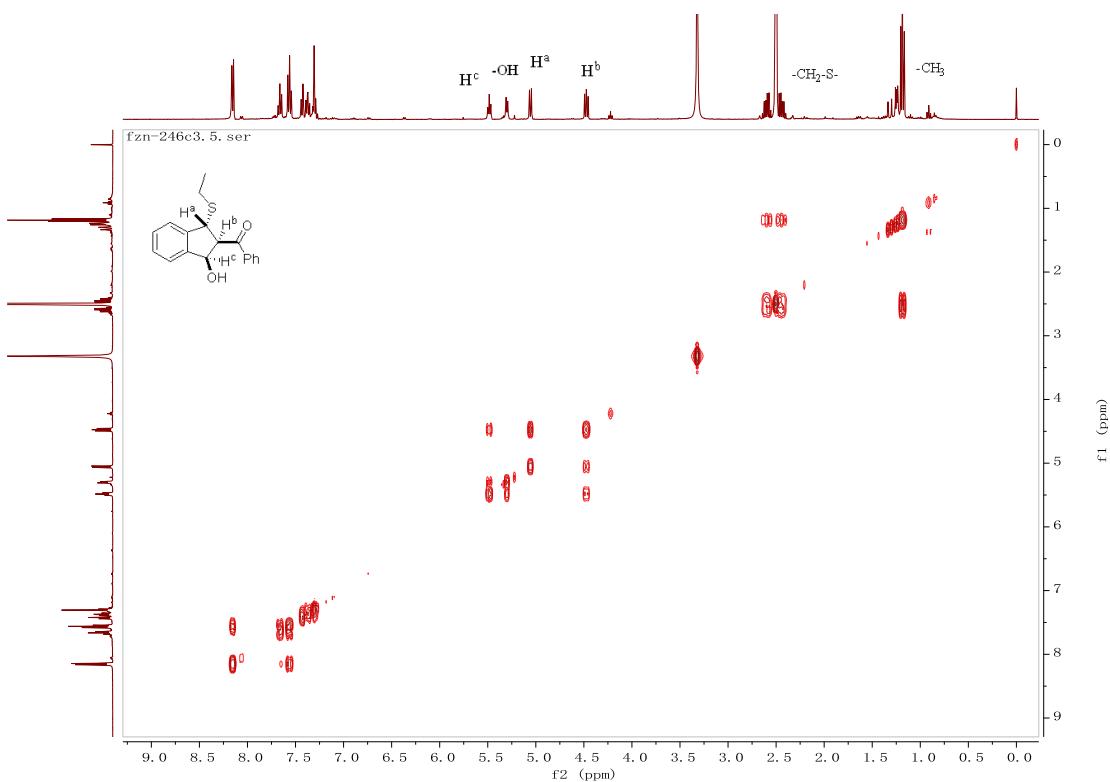
¹³C NMR of 5a'



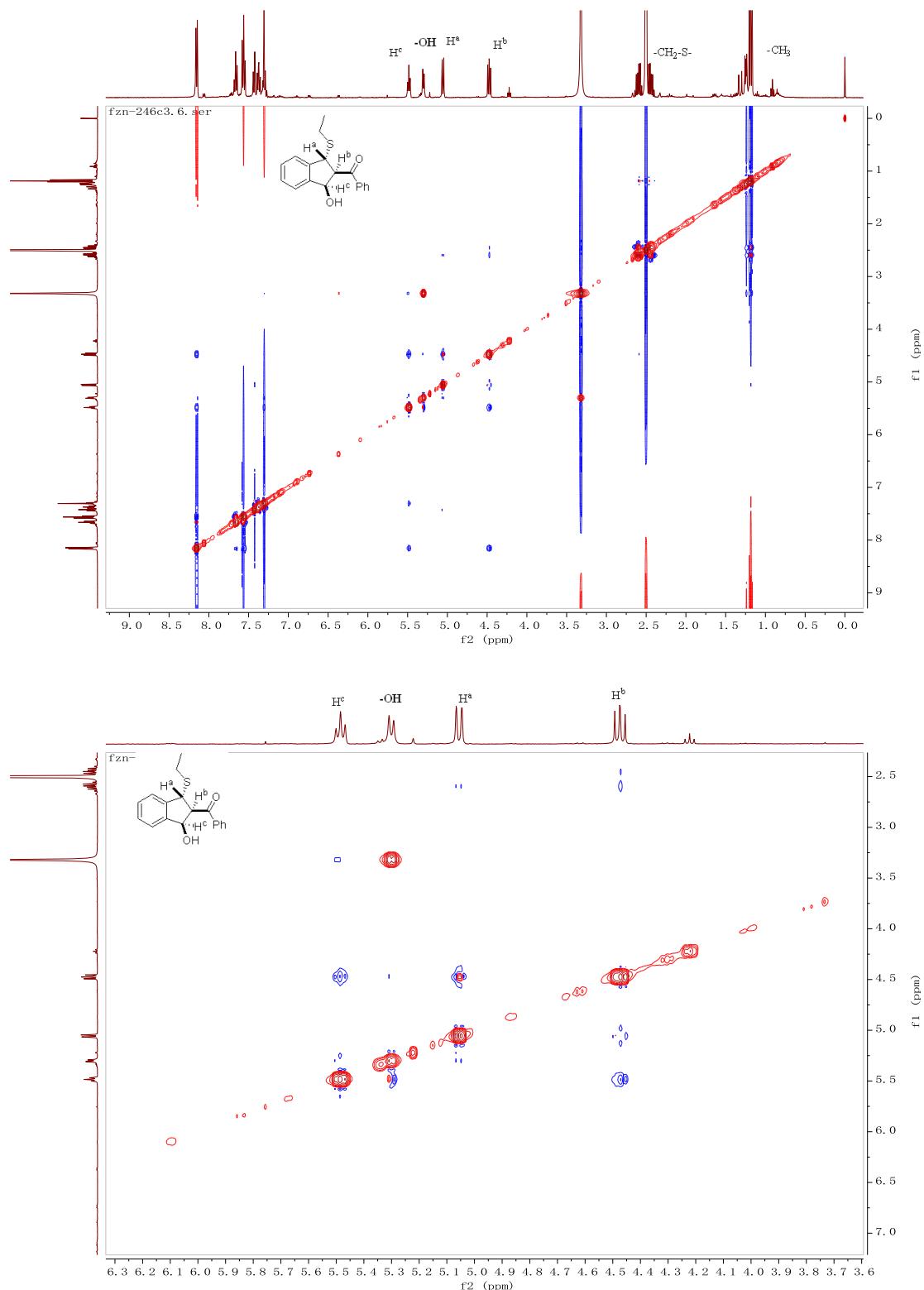
¹H NMR (400 MHz, DMSO-*d*₆) of **5a'**



¹H-¹H COSY (DMSO-*d*₆) of **5a'**



NOESY (400 MHz, DMSO-*d*₆) of **5a'**



6. Copies of ^1H NMR and ^{13}C NMR spectra

