Supplementary Information

for *In-Situ* Generation of Ion-Paired Chiral Ligands: Rapid Identification of Optimal Ligand for Palladium-Catalyzed Asymmetric Allylation

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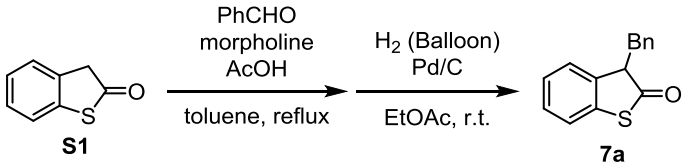
General Information: Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.16 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were measured on a Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Flash column chromatography was performed on PSQ60AB (spherical, 40-50 μm; FUJI SILYSIA CHEMICAL Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns (φ 4.6 mm x 250 mm, DAICEL CHIRALCEL OD-3 (OD3), CHIRALCEL OZ-3 (OZ3), CHIRALPAC IC-3 (IC3) and CHIRALPAC AD-3 (AD3)) with hexane (H) and isopropyl alcohol (IPA) as eluent.

All air- and moisture-sensitive reactions were performed under an atmosphere of argon (Ar) in dried glassware. The manipulations for Pd-catalyzed reactions were carried out with standard Schlenk techniques under Ar. Toluene was supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by both A2 alumina and Q5 reactant using a GlassContour solvent dispensing system. Allylic carbonates **5** were synthesized from the corresponding allylic alcohols.[1] Other simple chemicals were purchased and used as such.

Representative Procedures for Synthesis of Benzothiophenones 7:

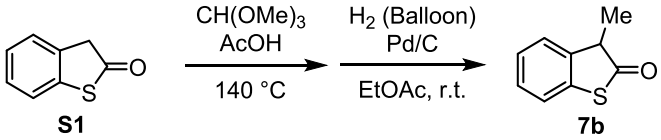


S1 **7a**

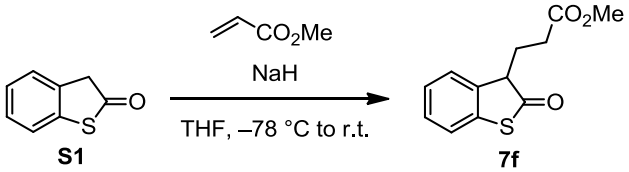
To a solution of **S1**[2] (891 mg, 3.74 mmol) in toluene (10 mL) were added benzaldehyde (0.76 mL, 7.48 mmol), morpholine (0.032 mL, 0.37 mmol), and acetic acid (0.021 mL, 0.37 mmol), and whole reaction

[1] R. Matsubara, T. F. Jamison, *J. Am. Chem. Soc.* **2010**, *132*, 6880.
[2] W. Chen, Y. Shi, H. Feng, M. Du, J. Z. Zhang, J. Hu, D. Yang, *J. Phys. Chem. B.* **2012**, *116*, 9231.

mixture was refluxed with stirring for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with the aid of EtOAc, and then concentrated. The resulting residue was dissolved in EtOAc (10 mL), and the flask was degassed by alternating vacuum evacuation/Ar backfill. After successive addition of 10% Pd/C (400 mg) at 0 °C, the reaction flask was evacuated again and refilled with H_2 three times. The resulting suspension was stirred for 12 h at room temperature. After flushing the remaining H_2 out with Ar, the mixture was filtered to remove Pd/C and the filtercake was rinsed with EtOAc. The filtrate was evaporated and the residue was purified by silica gel column chromatography (H/EtOAc = 30:1 as eluent) to give **7a** (737 mg, 3.07 mmol, 82% yield) as an off-yellow oil. Benzothiophenones (**7c**, **7d**, **7e**, **7g**, **7h** and **7i**) were synthesized by following the same procedure. **7a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.18 (5H, m), 7.12 (1H, ddd, J = 7.8, 6.8, 1.9 Hz), 7.08-7.05 (2H, m), 6.90 (1H, d, J = 7.8 Hz), 4.07 (1H, dd, J = 7.8, 4.8 Hz), 3.42 (1H, dd, J = 14.0, 4.8 Hz), 3.16 (1H, dd, J = 14.0, 7.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ206.1, 136.7, 136.2, 136.1, 129.7, 128.5, 128.5, 127.0, 125.9, 125.5, 123.1, 58.3, 38.9; IR (film) 3063, 3028, 2922, 1703, 1466, 1449, 1022, 748, 737, 696 cm^{-1}; HRMS (ESI, negative ion mode) Calcd for $C_{15}H_{11}O_1S_1^-$ ([M–H]$^-$) 239.0525. Found 239.0531.



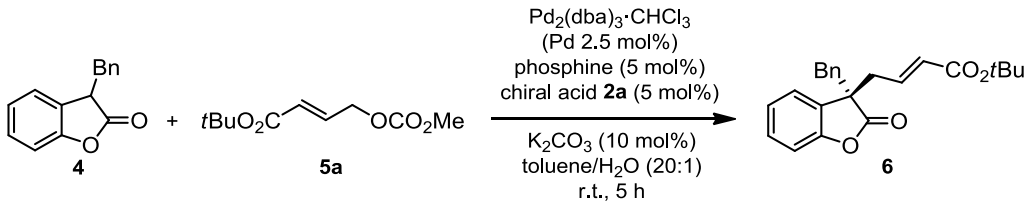
A round-bottomed flask was charged with **S1** (751mg, 5.0 mmol) and trimethyl orthoformate (2.5 mL, 15 mmol) in acetic acid (1.9 mL, 20 mmol). The solution was stirred at 140 °C in an oil bath for 12 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Extractive work-up was conducted with EtOAc three times, and the combined organic phases were washed with brine, dried over Na_2SO_4, and evaporated. To a solution of the resulting residue in EtOAc (3 mL) was added 10% Pd/C (87 mg) at 0 °C under Ar, the reaction flask was evacuated again and refilled with H_2 three times. The resulting suspension was stirred for 12 h at room temperature. After flushing the remaining H_2 out with Ar, the mixture was filtered to remove Pd/C and the filtercake was rinsed with EtOAc. The filtrate was evaporated and the residue was purified by silica gel column chromatography (H/EtOAc = 10:1 as eluent) to give **7b** (95 mg, 0.58 mmol, 71% yield) as a colorless oil. **7b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (1H, d, J = 7.8 Hz), 7.32-7.22 (3H, m), 3.83 (1H, q, J = 7.8 Hz), 1.55 (3H, d, J = 7.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ207.0, 138.3, 135.5, 128.5, 126.4, 124.6, 123.1, 52.2, 17.4; IR (film) 2978, 2932, 1711, 1468, 1445, 1101, 1005, 924, 750, 696 cm^{-1}; HRMS (ESI, negative ion mode) Calcd for $C_9H_7O_1S_1^-$ ([M–H]$^-$) 163.0223. Found 163.0211.



A dried two neck flask was charged with NaH (67 mg, 1.68 mmol) in THF (2 mL) under Ar. To this suspention was dropwised a solution of **S1** (253 mg, 1.68mmol) in THF (2 mL) at 0 ^{O}C, and the resulting mixture was stirred for 30 min at the same temperature. The reaction solution was then slowly transferred via cannula into a cooled solution of methyl acrylate (0.076 mL, 0.84 mmol) in THF (2 mL) at –78 °C. After stirring for 15 min, the reaction mixture was allowed to warm gradually to room temperature and quenched

with saturated aqueous NH_4Cl (10 mL). Extractive work-up was conducted with EtOAc three times. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (10:1 H/EtOAc) to afford **7f** (79 mg, 0.33 mmol, 40% yield) as a red liquid. **7f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (1H, d, J = 7.3 Hz), 7.33-7.26 (2H, m), 7.24 (1H, dd, J = 8.2, 1.2 Hz), 3.90 (1H, dd, J = 6.0, 4.1 Hz), 3.63 (3H, s), 2.51-2.2.40 (2H, m), 2.34-2.23 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 173.2, 136.1, 135.9, 128.7, 126.5, 124.9, 123.2, 55.7, 51.8, 29.5, 27.6; IR (film) 2951, 1732, 1703, 1593, 1447, 1437, 1211, 1175, 1009, 748 cm^{-1}; HRMS (ESI, negative ion mode) Calcd for $C_{12}H_{11}O_3S_1^-$ ([M–H]$^-$) 235.0423. Found 235.0427.

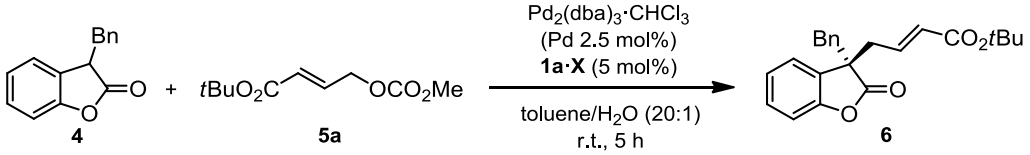
General Procedure for *In-Situ* Generation of Ion-Paired Chiral Ligand



To a Schlenk flask were added 3-benzylbenzofuranone **4** (22.4 mg, 0.1 mmol), $Pd_2(dba)_3$·$CHCl_3$ (1.29 mg, 0.0013 mmol), ammonium phosphine **1a·HSO$_4$** (2.5 mg, 0.005 mmol), chiral phosphoric acid **2a** (3.12 mg, 0.005 mmol) and K_2CO_3 (1.38 mg, 0.01 mmol) and the flask was degassed by alternating vacuum evacuation/Ar backfill. Then, toluene (1 mL) was added, and the resulting catalyst mixture was evacuated and refilled with Ar three times. After addition of H_2O (0.05 mL), allylic carbonate **5a** (21.6 mg, 0.1 mmol) was successively introduced at room temperature. After stirring for 5 h at the same temperature, the reaction mixture was directly subjected to the purification by column chromatography on silica gel (H/EtOAc = 10:1 as eluent) to afford **6** (34.6 mg, 0.095 mmol, 95% yield) as a colorless liquid.

Additional Control Experiments: To verify the activity of the catalyst prepared from $Pd_2(dba)_3$·$CHCl_3$ and precursors **1a·X**, the reactions of **4** with **5a** were conducted under the similar conditions described in Table 1 without chiral acid **2a** and K_2CO_3. The results were summarized in Table S1. The reason why the reaction using **1a·I** solely as a ligand showed higher conversion than that of the reaction with **1a·I**, **2a**, and K_2CO_3 (Table S1, entry 2 vs Table 1, entry 3) is unclear at present. While bond formation did not take place at all when **1a·HSO$_4$** was used as a ligand (entry 4), an attempted reaction with the same ligand in the absence of H_2O furnished allylated benzofuranone **6** in moderate yield (entry 5). These results suggested that **1a·HSO$_4$** would dissolve in water and thus could not form the corresponding Pd complex without ion-exchange event.

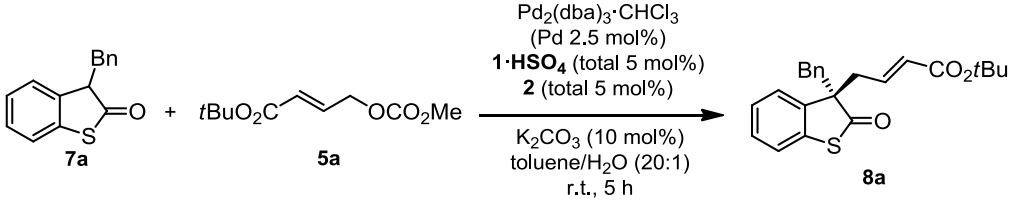
Table S1. Palladium-catalyzed allylation of **4** with **5a** using achiral **1a·X** as a ligand.[a]



entry	phosphine	yield [%][b]
1	**1a·Br**	62
2	**1a·I**	88
3	**1a·OAc**	90
4	**1a·HSO$_4$**	0
5[c]	**1a·HSO$_4$**	47

[a] Reactions were carried out with 0.10 mmol of **4** and 0.10 mmol of **5a** in the presence of $Pd_2(dba)_3$·$CHCl_3$ (Pd 2.5 mol%) and **1a·X** (5 mol%) in toluene (1.0 mL)/H_2O (0.05 mL) at room temperature. [b] Isolated yield of **6**. [c] The reaction was conducted without H_2O.

General Procedure for Asymmetric Allylation – Combinatorial Catalyst Screening



To a Schlenk flask were added 3-benzylbenzothiophenone **7a** (the amount is shown below), $Pd_2(dba)_3$·$CHCl_3$, ammonium phosphines **1·HSO$_4$**, chiral phosphoric acids **2** and K_2CO_3, and the flask was degassed by alternating vacuum evacuation/Ar backfill. Then, toluene was added, and the resulting catalyst mixture was evacuated and refilled with Ar three times. After addition of H_2O, allylic carbonate **5a** was successively introduced at room temperature. After stirring for 5 h at the same temperature, the reaction mixture was directly subjected to the purification by column chromatography on silica gel (H/EtOAc = 10:1 as eluent) to afford **8a** as a colorless liquid.

Step 1:

benzothiophenone **7a**	0.4 mmol	1.0 equiv
allylic carbonate **5a**	0.4 mmol	1.0 equiv
$Pd_2(dba)_3$·$CHCl_3$	0.0052 mmol	2.5 mol%
4 × ammonium phosphine **1·HSO$_4$**	each 0.005 mmol	5 mol%
6 × phosphoric acid **2**	each 0.0033 mmol	5 mol%
K_2CO_3	0.04 mmol	10 mol%
toluene 4.0 mL, H_2O 0.2 mL		

Step 2:

benzothiophenone **7a**	0.2 mmol	1.0 equiv
allylic carbonate **5a**	0.2 mmol	1.0 equiv
$Pd_2(dba)_3$·$CHCl_3$	0.0026 mmol	2.5 mol%
2 × ammonium phosphine **1·HSO$_4$**	each 0.005 mmol	5 mol%

3 × phosphoric acid **2**	each 0.0033 mmol	5 mol%
K_2CO_3	0.02 mmol	10 mol%
toluene 2.0 mL, H_2O 0.1 mL		

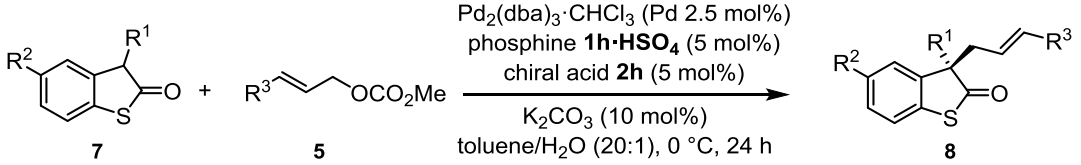
Step 3:

benzothiophenone **7a**	0.1 mmol	1.0 equiv
allylic carbonate **5a**	0.1 mmol	1.0 equiv
$Pd_2(dba)_3{\cdot}CHCl_3$	0.0013 mmol	2.5 mol%
ammonium phosphine **1·HSO$_4$**	0.005 mmol	5 mol%
phosphoric acid **2**	0.005 mmol	5 mol%
K_2CO_3	0.01 mmol	10 mol%
toluene 1.0 mL, H_2O 0.05 mL		

Table S2. The results of all possible 144 combinations of **1·HSO$_4$** and **2**

XX% ee (yield)	1a	1b	1c	1d	1e	1f	1g	1h	1i	1j	1k	1l
2a	79% ee (99%)	73% ee (99%)	83% ee (92%)	90% ee (91%)	88% ee (94%)	85% ee (96%)	90% ee (96%)	88% ee (99%)	80% ee (88%)	55% ee (86%)	81% ee (92%)	78% ee (99%)
2b	84% ee (94%)	74% ee (99%)	85% ee (93%)	92% ee (94%)	89% ee (96%)	88% ee (92%)	94% ee (99%)	94% ee (97%)	80% ee (88%)	57% ee (94%)	82% ee (90%)	70% ee (93%)
2c	70% ee (94%)	60% ee (90%)	76% ee (90%)	58% ee (89%)	67% ee (92%)	43% ee (86%)	86% ee (95%)	84% ee (83%)	64% ee (85%)	22% ee (88%)	55% ee (85%)	77% ee (84%)
2d	65% ee (94%)	52% ee (90%)	50% ee (90%)	68% ee (89%)	74% ee (99%)	66% ee (88%)	52% ee (98%)	78% ee (82%)	65% ee (85%)	13% ee (99%)	58% ee (85%)	35% ee (89%)
2e	56% ee (91%)	54% ee (93%)	62% ee (99%)	64% ee (90%)	71% ee (96%)	60% ee (88%)	65% ee (96%)	67% ee (86%)	60% ee (87%)	49% ee (96%)	52% ee (84%)	62% ee (92%)
2f	56% ee (86%)	77% ee (84%)	61% ee (92%)	68% ee (83%)	69% ee (90%)	62% ee (90%)	66% ee (96%)	67% ee (81%)	42% ee (83%)	56% ee (91%)	60% ee (80%)	65% ee (81%)
2g	70% ee (95%)	77% ee (90%)	79%ee (99%)	84% ee (93%)	88% ee (90%)	90% ee (88%)	89% ee (95%)	92% ee (89%)	83% ee (89%)	62% ee (96%)	83% ee (95%)	66% ee (90%)
2h	72% ee (99%)	83% ee (96%)	73% ee (92%)	87% ee (95%)	88% ee (99%)	92% ee (91%)	78% ee (89%)	94% ee (99%)	80% ee (93%)	64% ee (89%)	76% ee 95%)	86% ee (99%)
2i	74% ee (83%)	57% ee (93%)	67% ee (99%)	85% ee (99%)	65% ee (97%)	67% ee (88%)	70% ee (90%)	79% ee (86%)	69% ee (93%)	57% ee (83%)	67% ee (80%)	70% ee (90%)
2j	59% ee (88%)	61% ee (92%)	57% ee (89%)	71% ee (94%)	69% ee (97%)	71% ee (82%)	71% ee (90%)	78% ee (87%)	60% ee (88%)	39% ee (96%)	66% ee (87%)	40% ee (89%)
2k	50% ee (99%)	54% ee (92%)	31% ee (91%)	47% ee (91%)	52% ee (99%)	54% ee (90%)	59% ee (95%)	47% ee (93%)	35% ee (94%)	47% ee (90%)	42% ee (94%)	53% ee (90%)
2l	62% ee (74%)	65% ee (82%)	58% ee (83%)	62% ee (80%)	58% ee (85%)	64% ee (88%)	50% ee (80%)	61% ee (84%)	57% ee (86%)	61% ee (80%)	58% ee (82%)	40% ee (93%)

General Procedure for Asymmetric Allylation of Benzothiophenones 7:

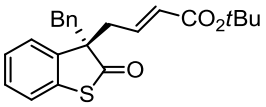


7 5 8

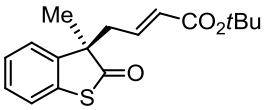
To a Schlenk flask were added benzothiophenone **7a** (22.4 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (1.29 mg, 0.0013 mmol), ammonium phosphine **1h·HSO$_4$** (2.5 mg, 0.005 mmol), chiral phosphoric acid **2h** (3.12 mg, 0.005 mmol) and K_2CO_3 (1.38 mg, 0.01 mmol), and the flask was degassed by alternating vacuum

evacuation/Ar backfill. Then, toluene (1 mL) was added, and the resulting catalyst mixture was evacuated and refilled with Ar three times. After addition of H_2O (0.05 mL), allylic carbonate **5a** (21.6 mg, 0.1 mmol) was successively introduced at 0 ºC. After stirring for 24 h at the same temperature, the reaction mixture was directly subjected to the purification by column chromatography on silica gel (H/EtOAc = 10:1 as eluent) to afford **8a** (36.1 mg, 0.095 mmol, 95% yield) as a colorless liquid.

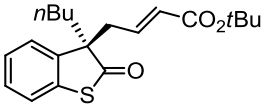
Characterization Data for the Alkylated Product 8:



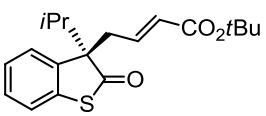
8a: $[\alpha]_D^{21}$ = –27.8 (*c* = 0.94, $CHCl_3$) for 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.16 (4H, m), 7.13-7.04 (3H, m), 6.79 (1H, dd, *J* = 8.2, 1.8 Hz), 6.43 (1H, ddd, *J* = 15.6, 8.4, 6.8 Hz), 5.73 (1H, d, *J* = 15.6 Hz), 3.24 (1H, d, *J* = 13.3 Hz), 3.07 (1H, d, *J* = 13.3 Hz), 2.92 (1H, dd, *J* = 14.2, 8.4 Hz), 2.76 (1H, dd, *J* = 14.2, 6.8 Hz), 1.40 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ208.6, 165.2, 140.1, 137.9, 135.7, 134.6, 130.1, 128.8, 128.0, 127.2, 127.0, 126.2, 125.0, 123.2, 80.5, 64.6, 46.0, 41.7, 28.2; IR (film) 2978, 2930, 1705, 1653, 1368, 1152, 980, 922, 735, 700 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{23}H_{24}O_3S_1Na^+$ ($[M+Na]^+$) 403.1338. Found 403.1340.; HPLC OZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 10.3 min (minor), 11.7 min (major).



8b: $[\alpha]_D^{21}$ = –50.5 (*c* = 1.0, $CHCl_3$) for 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (1H, dd, *J* = 7.3, 1.8 Hz), 7.29 (1H, dt, *J* = 7.3, 1.8 Hz), 7.26 (1H, dt, *J* = 7.3, 1.8 Hz), 7.18 (1H, dd, *J* = 7.3, 1.8 Hz), 6.47 (1H, ddd, *J* = 15.6, 8.6, 7.0 Hz), 5.70 (1H, dd, *J* = 15.6, 1.4 Hz), 2.74 (1H, ddd, *J* = 14.2, 8.6, 1.4 Hz), 2.63 (1H, ddd, *J* = 14.2, 7.0, 1.4 Hz), 1.46 (3H, s), 1.42 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ208.7, 165.3, 140.5, 140.4, 134.4, 128.7, 127.1, 126.7, 124.2, 123.3, 80.5, 59.2, 42.4, 28.2, 25.3; IR (film) 2976, 2930, 1707, 1653, 1368, 1337, 1155, 984, 955, 758 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{17}H_{20}O_3S_1Na^+$ ($[M+Na]^+$) 327.1025. Found 327.1024.; HPLC IC3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 18.0 min (major), 29.0 min (minor).

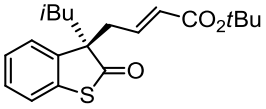


8c: $[\alpha]_D^{21}$ = +41.4 (*c* = 1.0, $CHCl_3$) for 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (1H, dd, *J* = 7.4, 1.8 Hz), 7.30 (1H, dt, *J* = 7.4, 1.8 Hz), 7.27 (1H, dt, *J* = 7.4, 1.8 Hz), 7.15 (1H, dd, 7.4, 1.8 Hz), 6.44 (1H, ddd, *J* = 15.8, 8.6, 6.9 Hz), 5.68 (1H, brd, *J* = 15.8 Hz), 2.71 (1H, ddd, *J* = 14.1, 8.6, 0.9 Hz), 2.60 (1H, ddd, *J* = 14.1, 6.9, 1.4 Hz), 2.01 (1H, dt, *J* = 12.9, 4.4 Hz), 1.79 (1H, dt, *J* = 12.9, 4.4 Hz), 1.41 (9H, s), 1.28-1.05 (3H, m), 0.92-0.78 (1H, m), 0.77 (3H, t, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ209.1, 165.3, 140.2, 139.2, 135.6, 128.6, 127.0, 126.6, 124.2, 123.3, 80.4, 63.6, 42.8, 39.7, 28.2, 26.1, 22.9, 13.8; IR (film) 2959, 2932, 1703, 1653, 1368, 1254, 1153, 980, 920, 743 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{20}H_{26}O_3S_1Na^+$ ($[M+Na]^+$) 369.1495. Found 369.1494.; HPLC IC3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 210 nm, 15.8 min (major), 16.5 min (minor).

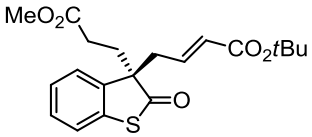


8d: $[\alpha]_D^{21}$ = +97.1 (*c* = 1.0, $CHCl_3$) for 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (1H, dd, *J* = 7.6, 1.4 Hz), 7.30 (1H, dt, *J* = 7.6, 1.4 Hz), 7.25 (1H, dt, *J* = 7.6, 1.4 Hz), 7.17 (1H, dd, *J* = 7.6, 1.4 Hz), 6.35 (1H, ddd, *J* = 15.6, 8.7, 6.7 Hz), 5.68 (1H, dt, *J* = 15.6, 1.4 Hz), 2.83 (1H, ddd, *J* = 14.1, 8.7, 1.4 Hz), 2.71 (1H, ddd, *J* = 14.1, 6.7, 1.4 Hz), 2.19 (1H, sep, *J* = 7.1 Hz), 1.39 (9H, s), 0.95 (3H, d, *J* = 7.1 Hz), 0.94 (3H, d, *J* = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ208.8, 165.3, 140.9, 138.6, 136.1, 128.5, 126.9, 126.3, 124.7, 123.1, 80.4, 66.2, 39.6, 38.2, 28.2, 17.4, 16.9; IR (film) 2974, 2934, 1703, 1653, 1368, 1327, 1152, 982, 910, 750 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for

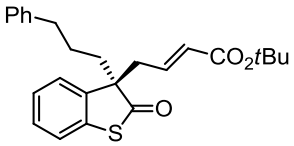
$C_{19}H_{24}O_3S_1Na^+$ ([M+Na]$^+$) 355.1338. Found 355.1337.; HPLC OZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 10.0 min (minor), 10.9 min (major).



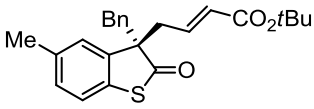
8e: $[\alpha]_D^{21}$ = +28.9 (*c* = 0.75, $CHCl_3$) for 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, dd, *J* = 7.6, 1.6 Hz), 7.30 (1H, dt, *J* = 7.6, 1.6 Hz), 7.27 (1H, dt, *J* = 7.6, 1.6 Hz), 7.15 (1H, dd, *J* = 7.6, 1.6 Hz), 6.44 (1H, ddd, *J* = 15.6, 8.6, 7.0 Hz), 5.66 (1H, dt, *J* = 15.6, 1.4 Hz), 2.64 (1H, ddd, *J* = 13.9, 8.6, 1.4 Hz), 2.52 (1H, ddd, *J* = 13.9, 7.0, 1.4 Hz), 2.01 (1H, dd, *J* = 14.1, 8.0 Hz), 1.84 (1H, dd, *J* = 14.1, 5.5 Hz), 1.49-1.35 (1H, m), 1.42 (9H, s), 0.75 (3H, d, *J* = 6.7 Hz), 0.64 (3H, d, *J* = 6.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.0, 165.3, 139.9, 139.1, 135.4, 128.6, 127.2, 126.4, 124.7, 123.3, 80.5, 63.2, 47.6, 44.7, 28.2, 25.5, 24.1, 23.6; IR (film) 2959, 2932, 1705, 1653, 1468, 1368, 1333, 1153, 982, 743 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{20}H_{26}O_3S_1Na^+$ ([M+Na]$^+$) 369.1495. Found 369.1495.; HPLC OZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 8.0 min (minor), 8.7 min (major).



8f: $[\alpha]_D^{21}$ = +59.6 (*c* = 0.97, $CHCl_3$) for 92% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (1H, dd, *J* = 7.3, 1.6 Hz), 7.32 (1H, dt, *J* = 7.3, 1.6 Hz), 7.29 (1H, dt, *J* = 7.3, 1.6 Hz), 7.18 (1H, dd, *J* = 7.3, 1.6 Hz), 6.42 (1H, ddd, *J* = 15.6, 8.7, 7.1 Hz), 5.70 (1H, dt, *J* = 15.6, 1.5 Hz), 3.56 (3H, s), 2.75 (1H, ddd, *J* = 14.1, 8.7, 1.5 Hz), 2.63 (1H, ddd, *J* = 13.9, 7.1, 1.5 Hz), 2.36-2.15 (3H, m), 1.96-1.84 (1H, m), 1.41 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 172.8, 165.1, 139.5, 137.7, 135.5, 129.1, 127.5, 126.9, 124.4, 123.5, 80.6, 62.7, 51.8, 42.5, 34.2, 28.8, 28.2; IR (film) 2978, 2953, 1738, 1703, 1655, 1447, 1368, 1152, 984, 745 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{20}H_{24}O_5S_1Na^+$ ([M+Na]$^+$) 399.1237. Found 399.1226.; HPLC OZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 19.7 min (minor), 23.2 min (major).

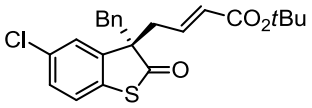


8g: $[\alpha]_D^{21}$ = +24.9 (*c* = 0.82, $CHCl_3$) for 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (1H, dd, *J* = 7.6, 1.6 Hz), 7.28 (1H, dt, *J* = 7.6, 1.6 Hz), 7.26-7.20 (3H, m), 7.17-7.12 (1H, m), 7.07 (1H, dd, *J* = 7.6, 1.6 Hz), 7.02 (1H, d, *J* = 8.2 Hz), 7.02 (1H, d, *J* = 8.2 Hz), 6.41 (1H, ddd, *J* = 15.7, 8.6, 7.0 Hz), 5.67 (1H, dt, *J* = 15.7, 1.4 Hz), 2.70 (1H, ddd, *J* = 14.1, 8.6, 1.4 Hz), 2.57 (1H, ddd, *J* = 14.1, 7.0, 1.4 Hz), 2.54 (1H, ddd, *J* = 14.4, 8.7, 6.4 Hz), 2.43 (1H, ddd, *J* = 14.4, 8.7, 6.4 Hz), 2.06 (1H, ddd, *J* = 13.3, 12.8, 4.5 Hz), 1.82 (1H, ddd, *J* = 13.3, 12.8, 4.5 Hz), 1.54-1.42 (1H, m), 1.41 (9H, s), 1.25-1.14 (1H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 165.3, 141.4, 140.1, 138.8, 135.5, 128.7, 128.4, 128.4, 127.1, 126.7, 126.0, 124.1, 123.4, 80.5, 63.5, 42.8, 39.3, 35.8, 28.2, 25.6; IR (film) 2976, 2934, 2361, 1703, 1601, 1368, 1150, 982, 746, 698 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{25}H_{28}O_3S_1Na^+$ ([M+Na]$^+$) 431.1651. Found 431.1650.; HPLC OZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 9.5 min (minor), 10.6 min (major).

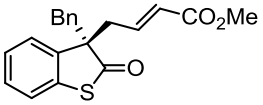


8h: $[\alpha]_D^{21}$ = –39.1 (*c* = 1.0, $CHCl_3$) for 96% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.05 (5H, m), 6.99 (1H, s), 6.79-6.77 (2H, m), 6.42 (1H, ddd, *J* = 15.6, 8.7, 6.7 Hz), 5.74 (1H, d, *J* = 15.6 Hz), 3.21 (1H, d, *J* = 13.3 Hz), 3.06 (1H, d, *J* = 13.3 Hz), 2.89 (1H, dd, *J* = 14.2, 8.7 Hz), 2.74 (1H, dd, *J* = 14.2, 6.7 Hz), 2.38 (3H, s), 1.41 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.0, 165.3, 140.3, 137.8, 136.1, 134.7, 132.2, 130.2, 129.6, 127.9, 127.1, 127.0, 125.7, 122.9, 80.5, 64.5, 46.1, 41.6, 28.2, 21.5; IR (film) 2976, 2920, 1697, 1653, 1325, 1150, 978, 922, 731, 700

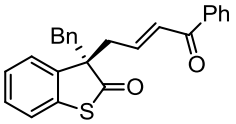
cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{24}H_{26}O_3S_1Na^+$ ([M+Na]$^+$) 417.1495. Found 417.1491.; HPLC AD3, H/IPA = 19:1, flow rate = 0.5 mL/min, λ = 210 nm, 12.4 min (minor), 14.1 min (major).



8i: $[\alpha]_D^{19}$ = –42.6 (*c* = 1.0, $CHCl_3$) for 95% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, dd, *J* = 8.0, 1.8 Hz), 7.17 (1H, d, *J* = 1.8 Hz), 7.15-7.08 (3H, m), 7.12 (1H, dd, *J* = 8.0, 1.8 Hz), 6.81 (2H, m), 6.42 (1H, ddd, *J* = 15.6, 8.7, 6.6 Hz), 5.75 (1H, brd, *J* = 15.6 Hz), 3.25 (1H, d, *J* = 13.3 Hz), 3.05 (1H, d, *J* = 13.3 Hz), 2.93 (1H, ddd, *J* = 14.2, 8.7, 0.9 Hz), 2.74 (1H, ddd, *J* = 14.2, 6.6, 1.4 Hz), 1.41 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 165.1, 139.7, 139.4, 134.1, 132.3, 130.1, 129.1, 128.1, 127.5, 127.3, 125.3, 124.2, 80.7, 64.9, 46.1, 41.5, 28.2, one peak for aromatic carbon was not found probably due to overlapping; IR (film) 2978, 2927, 1709, 1655, 1456, 1368, 1152, 980, 922, 700 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{23}H_{23}O_3Cl_1S_1Na^+$ ([M+Na]$^+$) 437.0949. Found 437.0948.; HPLC OD3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 12.2 min (major), 13.5 min (minor).

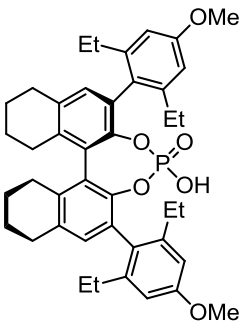


8j: $[\alpha]_D^{21}$ = –27.0 (*c* = 0.96, $CHCl_3$) for 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (2H, m), 7.21-7.17 (2H, m), 7.14-7.05 (3H, m), 6.79 (2H, d, *J* = 7.3 Hz), 6.53 (1H, ddd, *J* = 15.8, 8.3, 7.3 Hz), 5.79 (1H, d, *J* = 15.8 Hz), 3.64 (3H, s), 3.25 (1H, d, *J* = 13.3 Hz), 3.08 (1H, d, *J* = 13.3 Hz), 2.96 (1H, dd, *J* = 14.2, 8.3 Hz), 2.79 (1H, dd, *J* = 14.2, 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 166.3, 141.7, 137.7, 135.7, 134.5, 130.2, 128.9, 128.0, 127.1, 126.3, 125.1, 125.0, 123.3, 64.6, 51.6, 46.2, 41.7; IR (film) 3030, 2949, 1703, 1659, 1437, 1325, 1275, 1167, 737, 700 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{20}H_{18}O_3S_1Na^+$ ([M+Na]$^+$) 361.0869. Found 361.0862.; HPLC OZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 17.7 min (minor), 22.2 min (major).

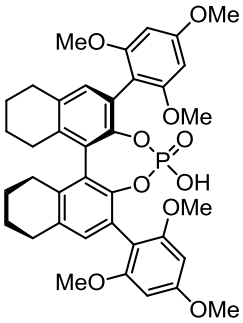


8k: $[\alpha]_D^{21}$ = +17.1 (*c* = 1.0, $CHCl_3$) for 89% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (2H, m), 7.51 (1H, t, *J* = 7.8 Hz), 7.39 (2H, t, *J* = 7.8 Hz), 7.33-7.24 (3H, m), 7.21 (1H, dd, *J* = 7.8, 1.7 Hz), 7.16-7.07 (3H, m), 6.83-6.81 (2H, m), 6.76 (1H, d, *J* = 15.6 Hz), 6.53 (1H, ddd, *J* = 15.6, 8.2, 7.1 Hz), 3.30 (1H, d, *J* = 13.3 Hz), 3.14 (1H, d, *J* = 13.3 Hz), 3.08 (1H, dd, *J* = 14.2, 8.2 Hz), 2.90 (1H, dd, *J* = 14.2, 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 190.7, 141.4, 137.9, 137.5, 135.7, 134.5, 132.9, 130.3, 130.2, 128.9, 128.7, 128.6, 128.0, 127.1, 126.4, 125.2, 123.3, 65.0, 46.2, 42.4; IR (film) 3061, 3030, 2920, 1703, 1670, 1622, 1447, 1281, 922, 698 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{25}H_{20}O_2S_1Na^+$ ([M+Na]$^+$) 407.1076. Found 407.1063.; HPLC OZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 27.9 min (minor), 44.2 min (major).

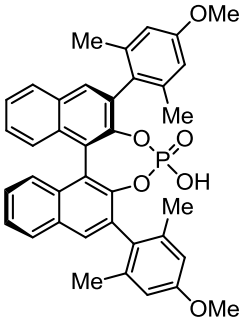
Characterization Data for Chiral Phosphoric Acids 2



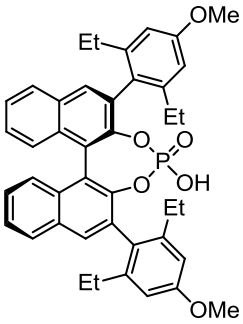
2b: $[\alpha]_D^{21}$ = –35.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (2H, s), 6.58 (2H, s), 6.57 (2H, s), 3.69 (6H, s), 2.87-2.69 (6H, m), 2.43-2.19 (10H, m), 1.90-1.80 (6H, m), 1.71-1.64 (2H, m), 1.11 (6H, t, *J* = 7.6 Hz), 0.97 (6H, t, *J* = 7.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 144.5, 144.0, 143.9 (d, $J_{P\text{-}C}$ = 8.6 Hz), 136.5, 134.4, 132.5, 129.6 (d, $J_{P\text{-}C}$ = 3.9 Hz), 128.0, 126.9, 110.9, 110.6, 55.0, 29.4, 27.9, 27.1, 26.9, 23.0, 22.9, 15.6, 14.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 2.1; IR (film) 2959, 2930, 1601, 1578, 1190, 1157, 1016, 953, 901, 748 cm^{-1}; HRMS (ESI, negative ion mode) Calcd for $C_{42}H_{48}O_6P_1^-$ ([M−H]$^-$) 679.3179. Found 679.3179.



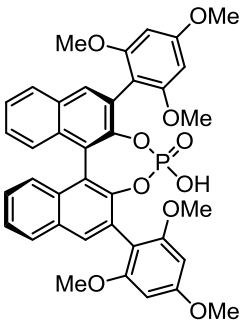
2c: $[\alpha]_D^{20}$ = –69.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (2H, s), 6.08 (4H, s), 3.72 (6H, s), 3.55 (6H, s), 3.53 (6H, s), 2.87-2.79 (4H, m), 2.78-2.71 (2H, m), 2.39-2.30 (2H, m), 1.86-1.74 (6H, m), 1.71-1.61 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 158.8, 158.7, 144.7 (d, $J_{P\text{-}C}$ = 8.7 Hz), 136.6, 134.2, 133.0, 126.7, 124.1 (d, $J_{P\text{-}C}$ = 2.9 Hz), 107.8, 91.2, 90.7, 56.0, 55.9, 55.3, 29.4, 28.1, 22.9, 22.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 1.1; IR (film) 2934, 2837, 1585, 1454, 1414, 1204, 1123, 1016, 903, 725 cm^{-1}; HRMS (ESI, negative ion mode) Calcd for $C_{38}H_{40}O_{10}P_1^-$ ($[M-H]^-$) 687.2354. Found 687.2363.



2g: $[\alpha]_D^{21}$ = –60.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2H, d, *J* = 8.2 Hz), 7.79 (2H, s), 7.50 (2H, t, *J* = 7.6 Hz), 7.39-7.30 (4H, m), 6.56 (2H, d, *J* = 2.3 Hz), 6.49 (2H, d, *J* = 2.3 Hz), 3.39 (6H, s), 2.12 (6H, s), 1.99 (6H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 145.7 (d, $J_{P\text{-}C}$ = 8.7 Hz), 138.5 (d, $J_{P\text{-}C}$ = 2.9 Hz), 132.8, 132.1, 132.0, 131.6, 128.6, 128.3, 127.2, 126.5, 125.8, 122.3, 113.0, 112.8, 54.9, 21.5, 20.8, one peak for aromatic carbon was not found probably due to overlapping; ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.1; IR (film) 2955, 2920, 1605, 1312, 1194, 1150, 1020, 905, 750, 729 cm^{-1}; HRMS (ESI, negative ion mode) Calcd for $C_{38}H_{32}O_6P_1^-$ ($[M-H]^-$) 615.1931. Found 615.1932.



2h: $[\alpha]_D^{21}$ = –23.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (2H, d, *J* = 8.5 Hz), 7.81 (2H, s), 7.50 (2H, ddd, *J* = 8.5, 6.4, 2.2 Hz), 7.36-7.30 (4H, m), 6.62 (2H, d, *J* = 2.5 Hz), 6.56 (2H, d, *J* = 2.5 Hz), 3.58 (6H, s), 2.39-2.20 (8H, m), 1.11 (6H, t, *J* = 7.7 Hz), 0.98 (6H, t, *J* = 7.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 146.1 (d, $J_{P\text{-}C}$ = 8.7 Hz), 144.9, 144.4, 132.4 (d, $J_{P\text{-}C}$ = 2.9 Hz), 132.4, 132.3, 131.2, 128.3, 127.9, 127.3, 126.3, 125.7, 122.3, 110.8, 110.7, 55.1, 27.2, 27.0, 15.6, 14.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.8; IR (film) 2963, 2932, 1601, 1578, 1192, 1148, 1018, 995, 962, 748 cm^{-1}; HRMS (ESI, negative ion mode) Calcd for $C_{42}H_{40}O_6P_1^-$ ($[M-H]^-$) 671.2557. Found 671.2558.



2i: $[\alpha]_D^{21}$ = –93.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (2H, d, *J* = 8.6 Hz), 7.89 (2H, s), 7.46-7.42 (4H, m), 7.29-7.24 (2H, m), 6.15 (2H, d, *J* = 1.8 Hz), 6.11 (2H, d, *J* = 1.8 Hz), 3.75 (6H, s), 3.59 (6H, s), 3.54 (6H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 159.2, 158.8, 146.4 (d, $J_{P\text{-}C}$ = 10.6 Hz), 133.4, 132.2, 131.5, 128.5, 127.6, 127.0 (d, $J_{P\text{-}C}$ = 2.9 Hz), 126.0, 125.3, 121.9 (d, $J_{P\text{-}C}$ = 1.9 Hz), 107.7, 91.3, 91.2, 56.2, 56.1, 55.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.3; IR (film) 2938, 2837, 1609, 1585, 1410, 1225, 1204, 1123, 1018, 750 cm^{-1}; HRMS (ESI, negative ion mode) Calcd for $C_{38}H_{32}O_{10}P_1^-$ ($[M-H]^-$) 679.1728. Found 679.1740.

Crystallographic Structure Determination:

Recrystallization of 8a (CCDC 995705): A single crystal of **8a** was obtained from a solution of hexane and diethyl ether at room temperature. The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 103 K on a Brucker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least

squares on *F2* by using SHELXTL.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. The crystallographic data are summarized in Table S3 and ORTEP diagram is shown in Fig. S1.

Table S3. Crystal data and structure refinement for **8a**.

Empirical formula	C23 H24 O3 S	
Formula weight	380.48	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.5465(17) Å	α = 90°.
	b = 7.844(2) Å	β = 90°.
	c = 38.945(10) Å	γ = 90°.
Volume	1999.9(9) $Å^3$	
Z	4	
Density (calculated)	1.264 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	808	
Crystal size	0.3 x 0.4 x 0.8 mm^3	
Theta range for data collection	2.09 to 29.14°.	
Index ranges	-8<=h<=8, -10<=k<=10, -44<=l<=53	
Reflections collected	12232	
Independent reflections	5092 [R(int) = 0.0215]	
Completeness to theta = 29.14°	94.8 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5092 / 0 / 247	
Goodness-of-fit on F^2	0.662	
Final R indices [I>2sigma(I)]	R1 = 0.0235, wR2 = 0.0420	
R indices (all data)	R1 = 0.0559, wR2 = 0.0426	
Absolute structure parameter	0.00(5)	
Largest diff. peak and hole	0.168 and -0.182 $e.Å^{-3}$	

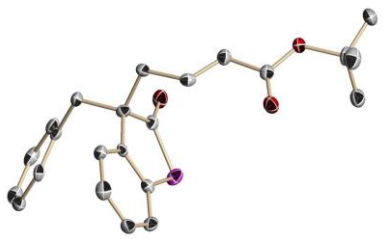
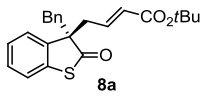


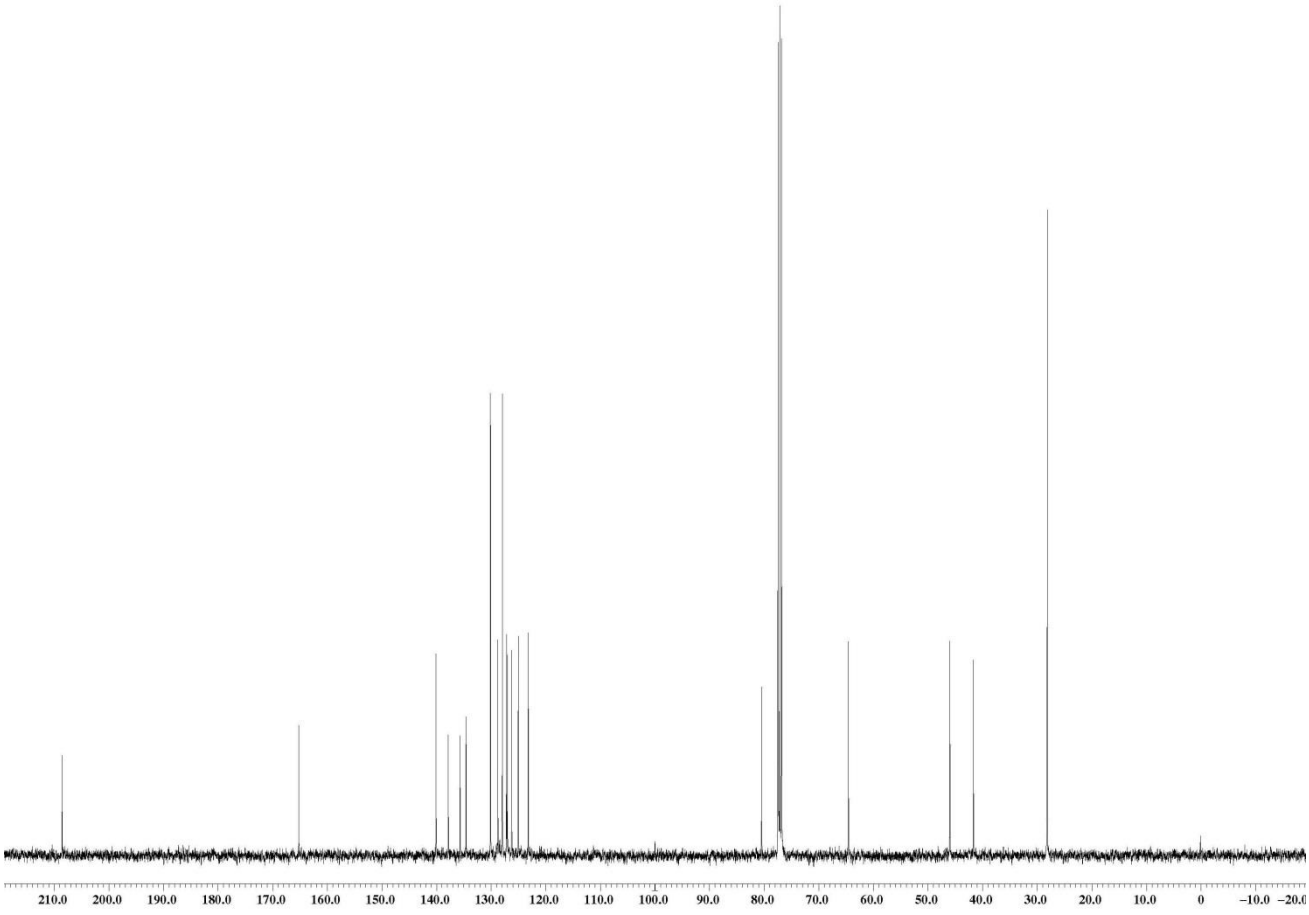
Figure S1. Molecular structure of **8a**. All calculated hydrogen atoms are omitted for clarity. purple = sulfur, red = oxygen, black = carbon.

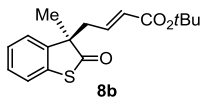
[3] Sheldrick, G. M. SHELXTL 5.1, Bruker AXS Inc., Madison, Wisconsin, 1997.

Copies of ^{1}H and ^{13}C NMR Spectra:



8a

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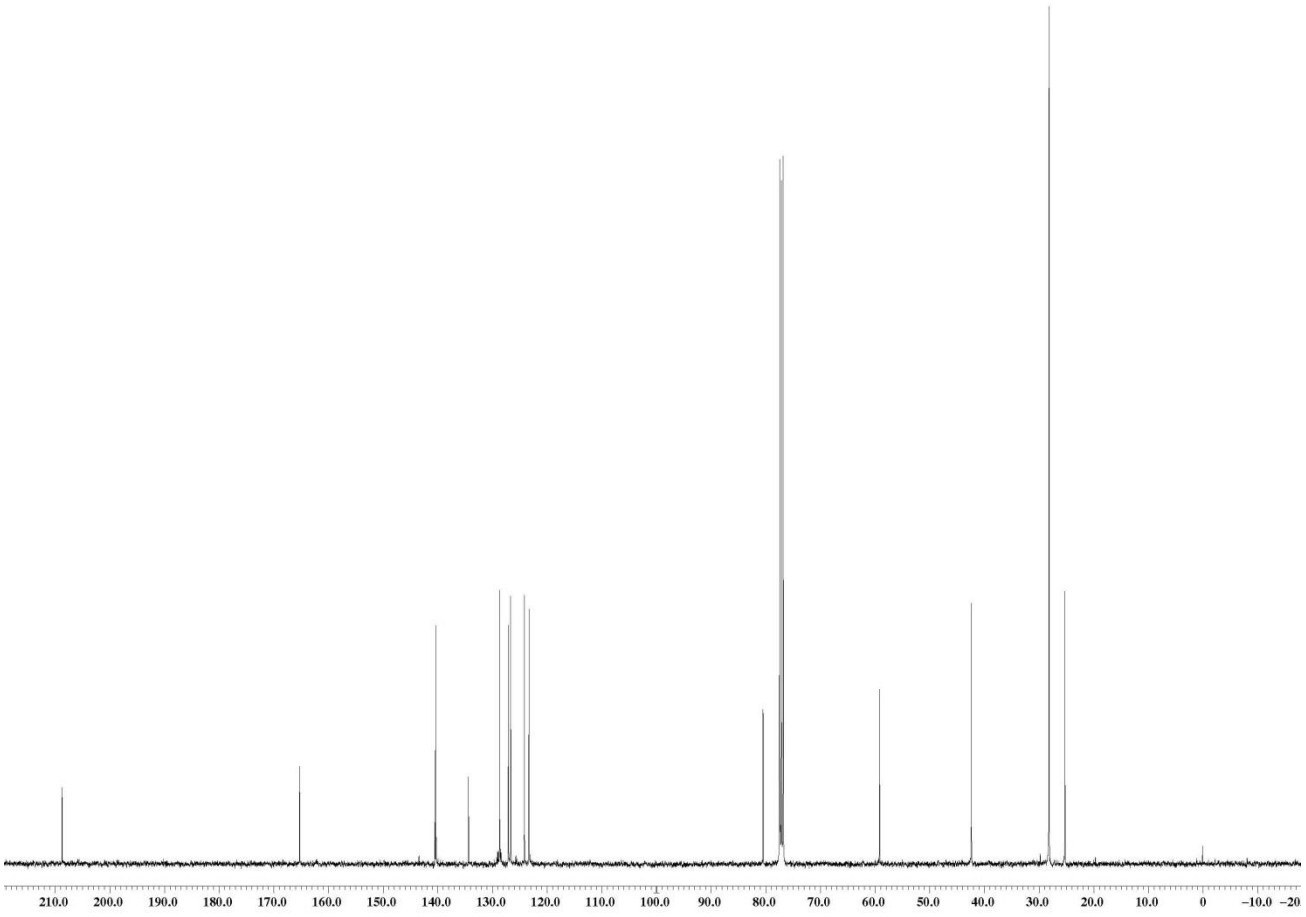
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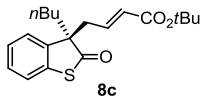
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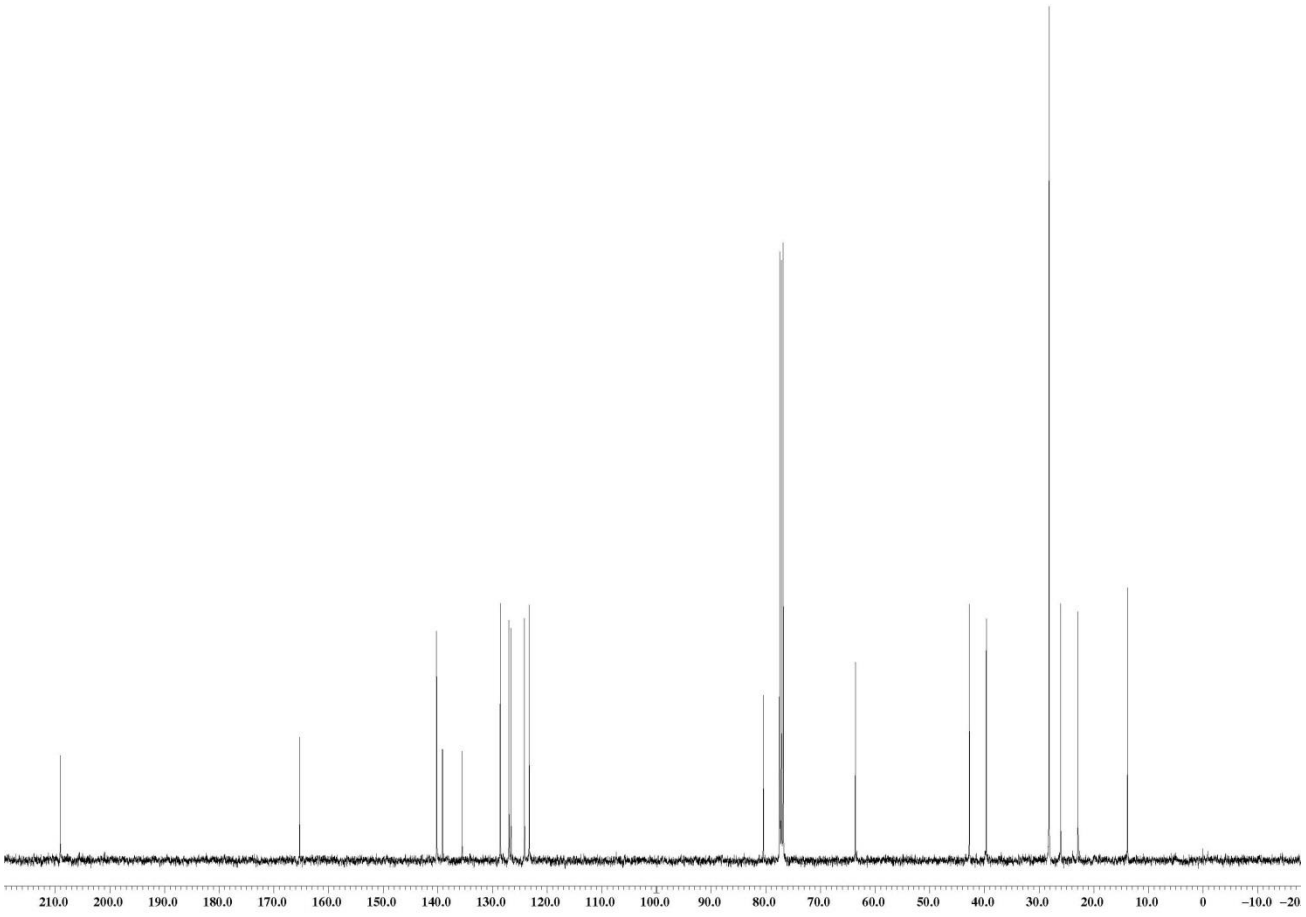
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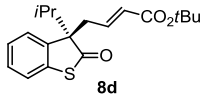
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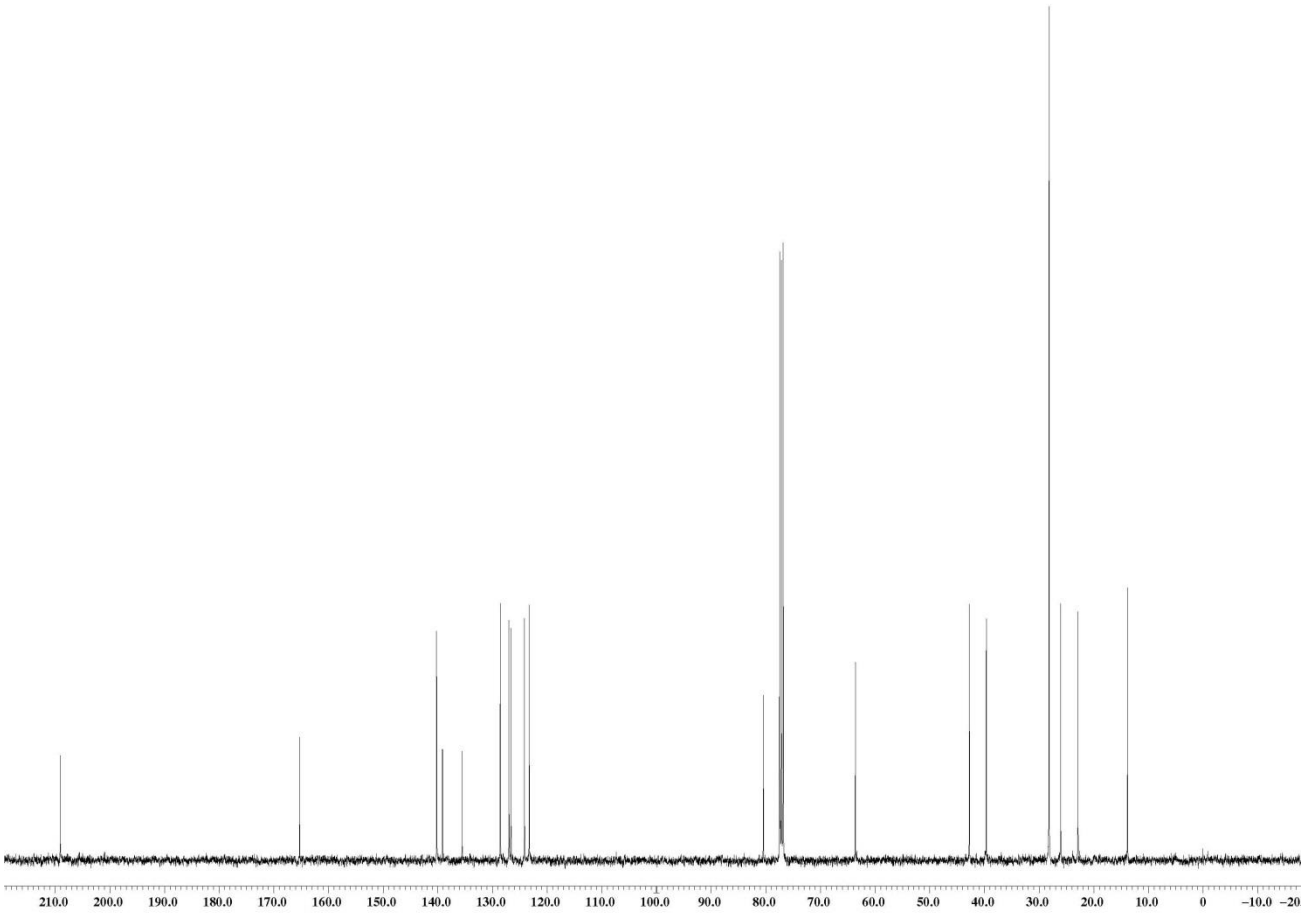
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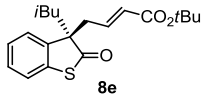
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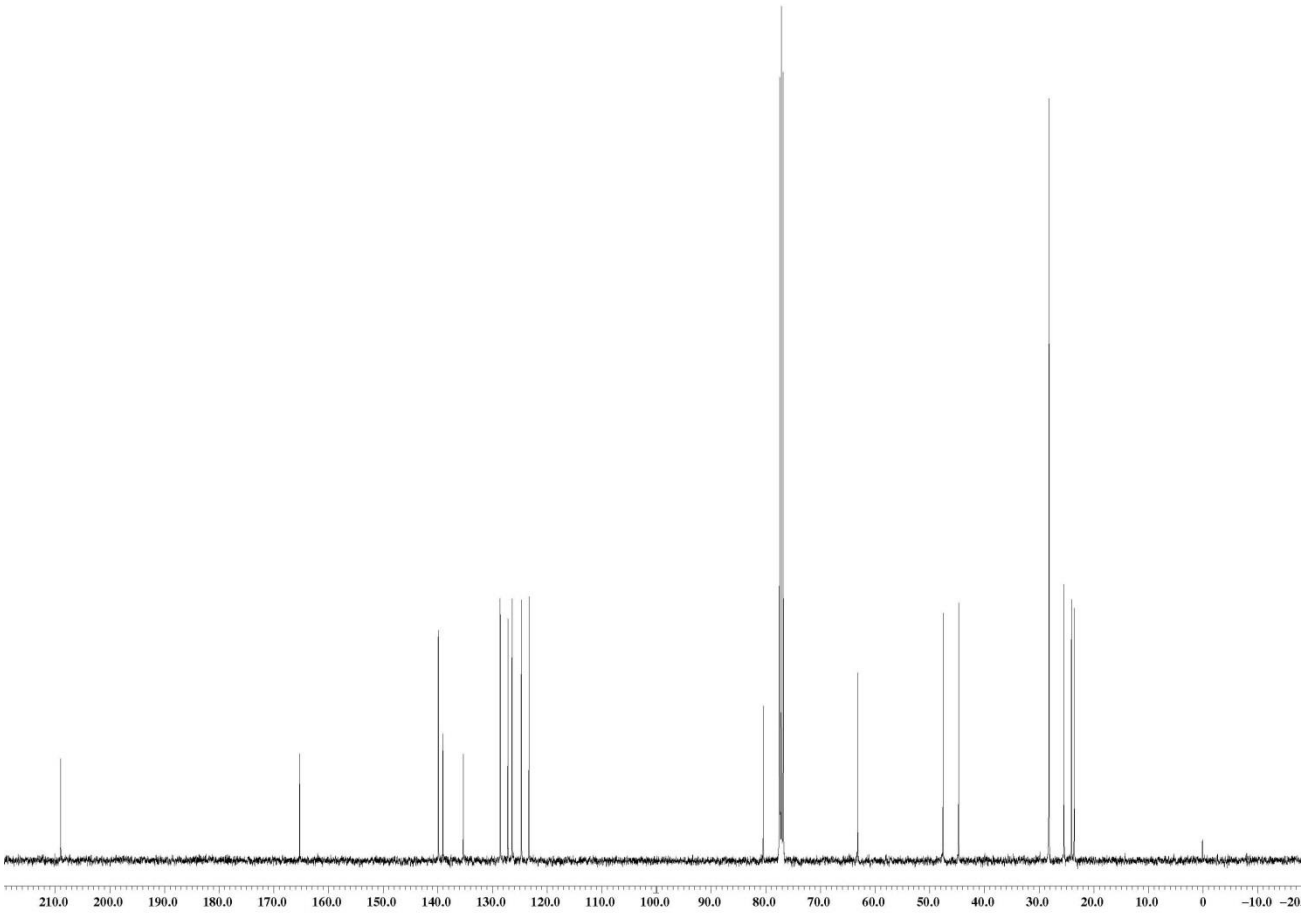
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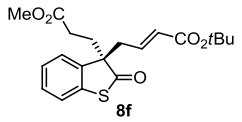
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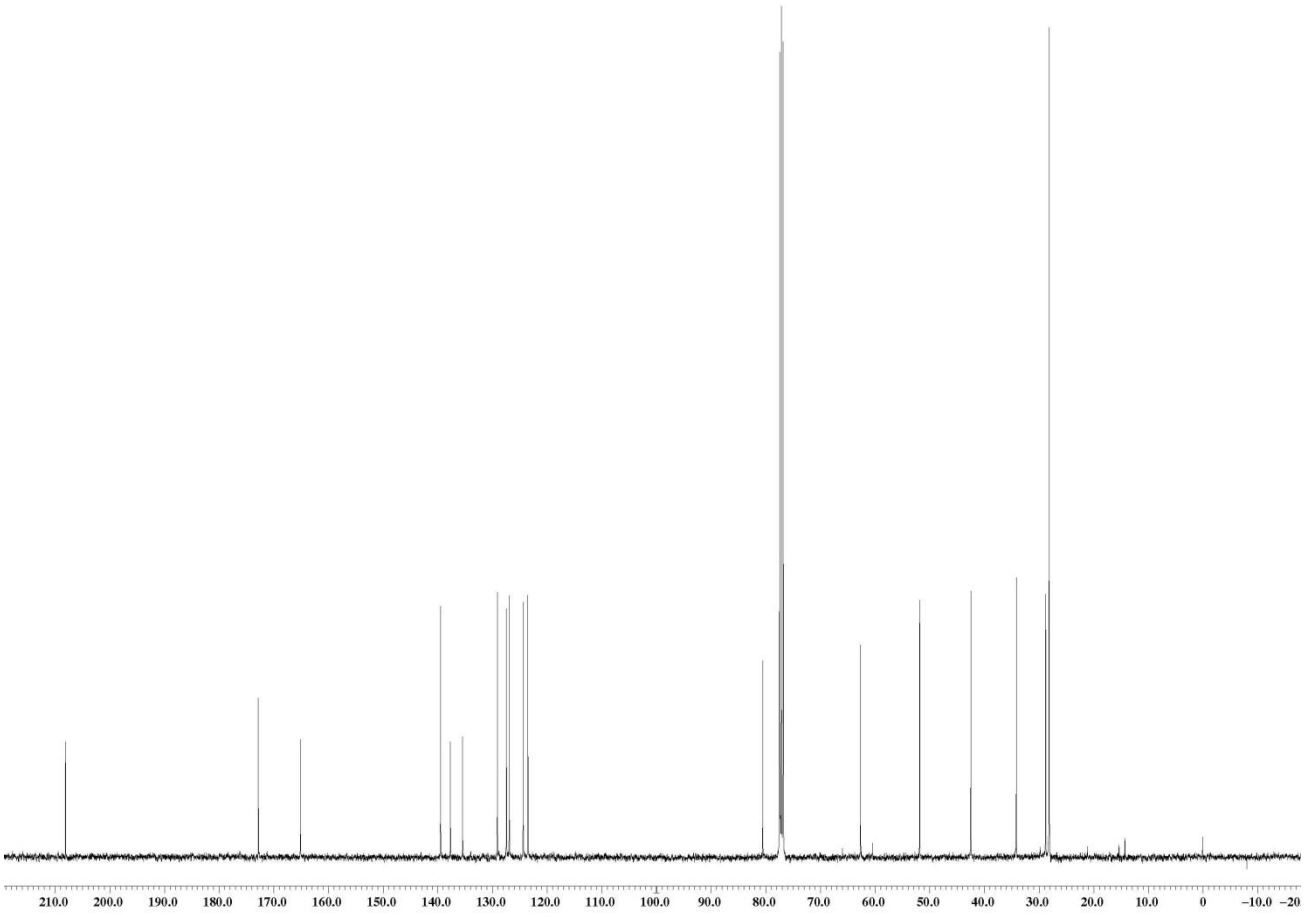
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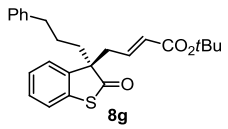
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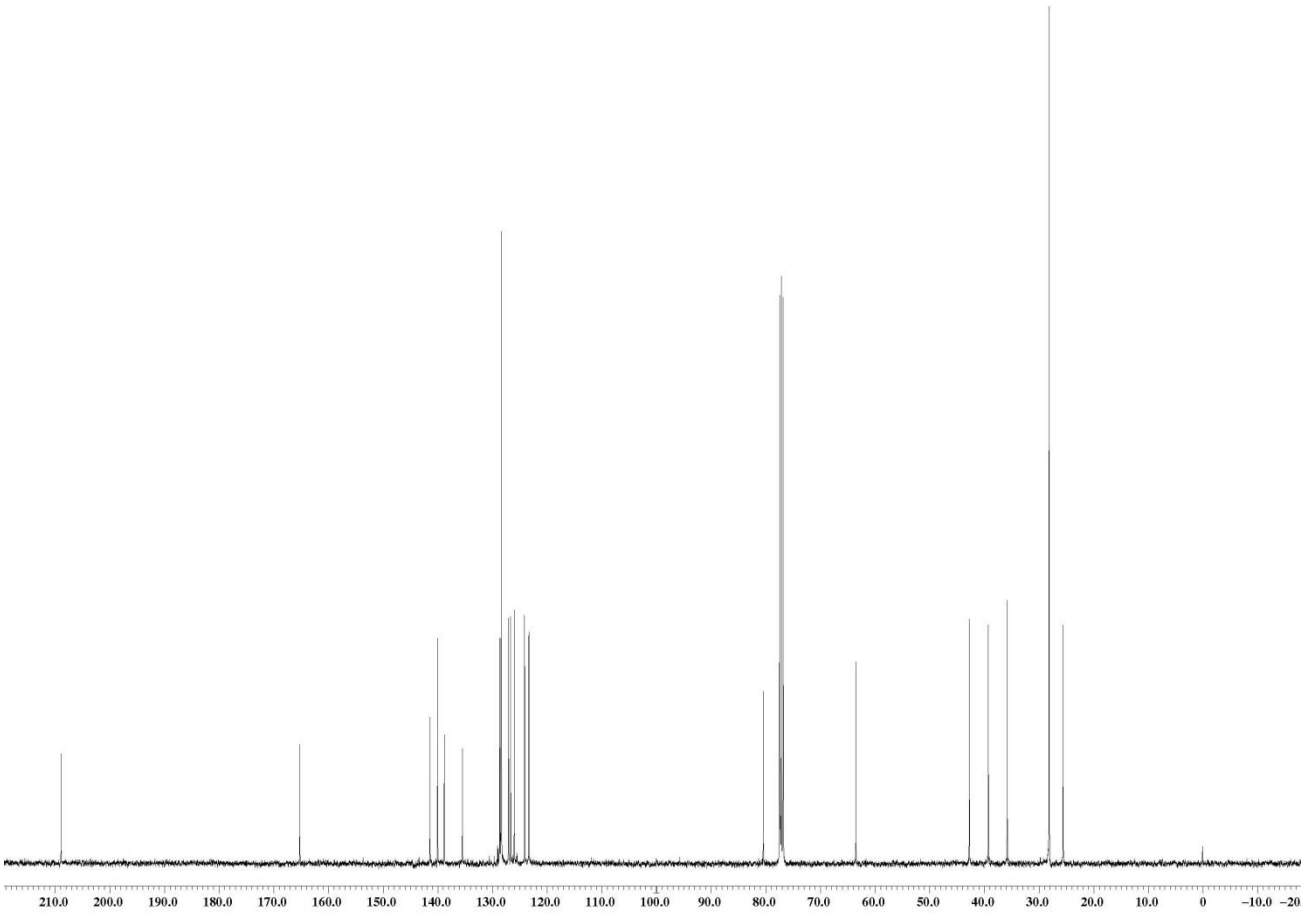
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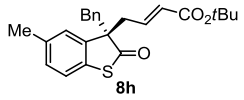
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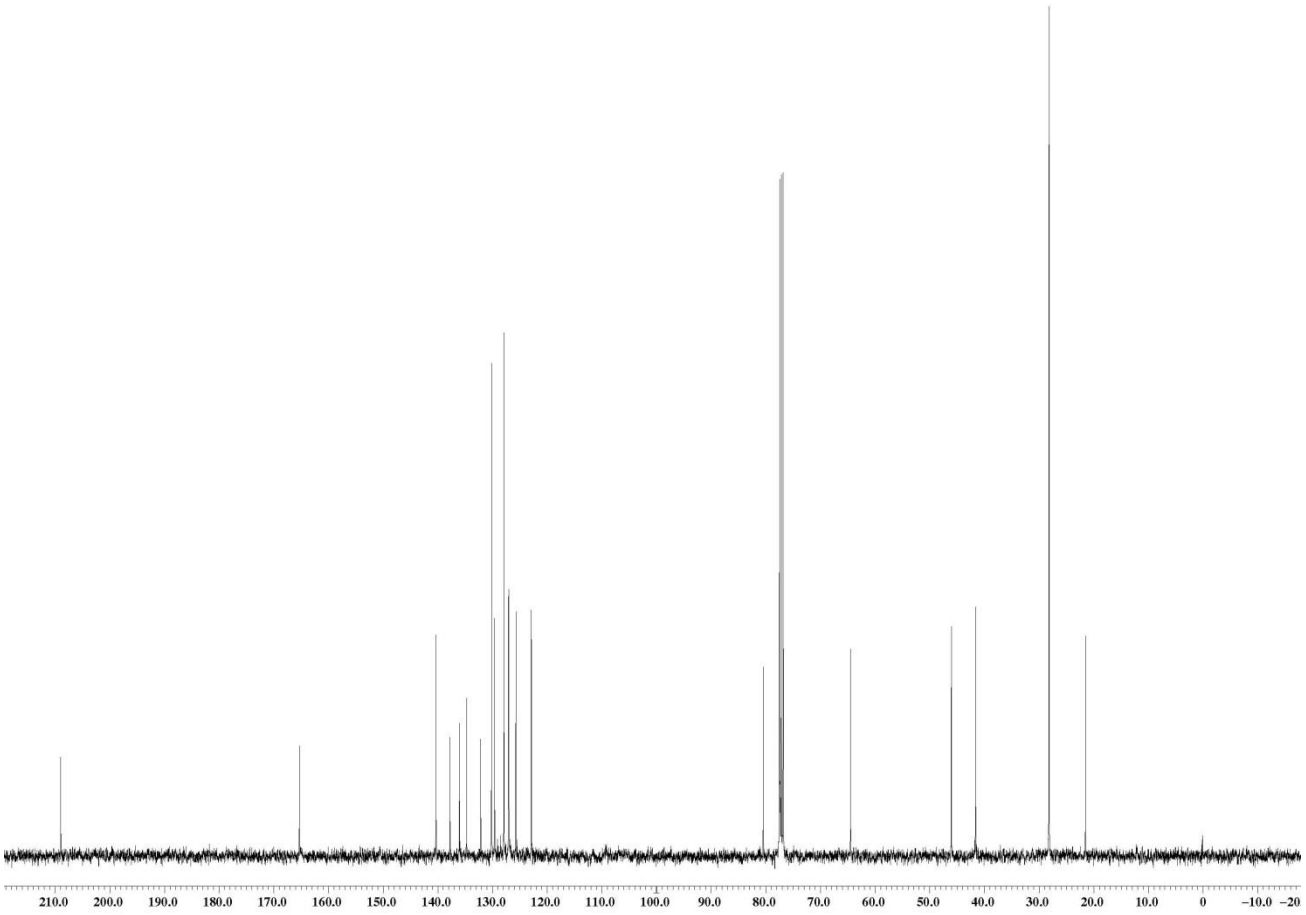
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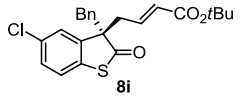
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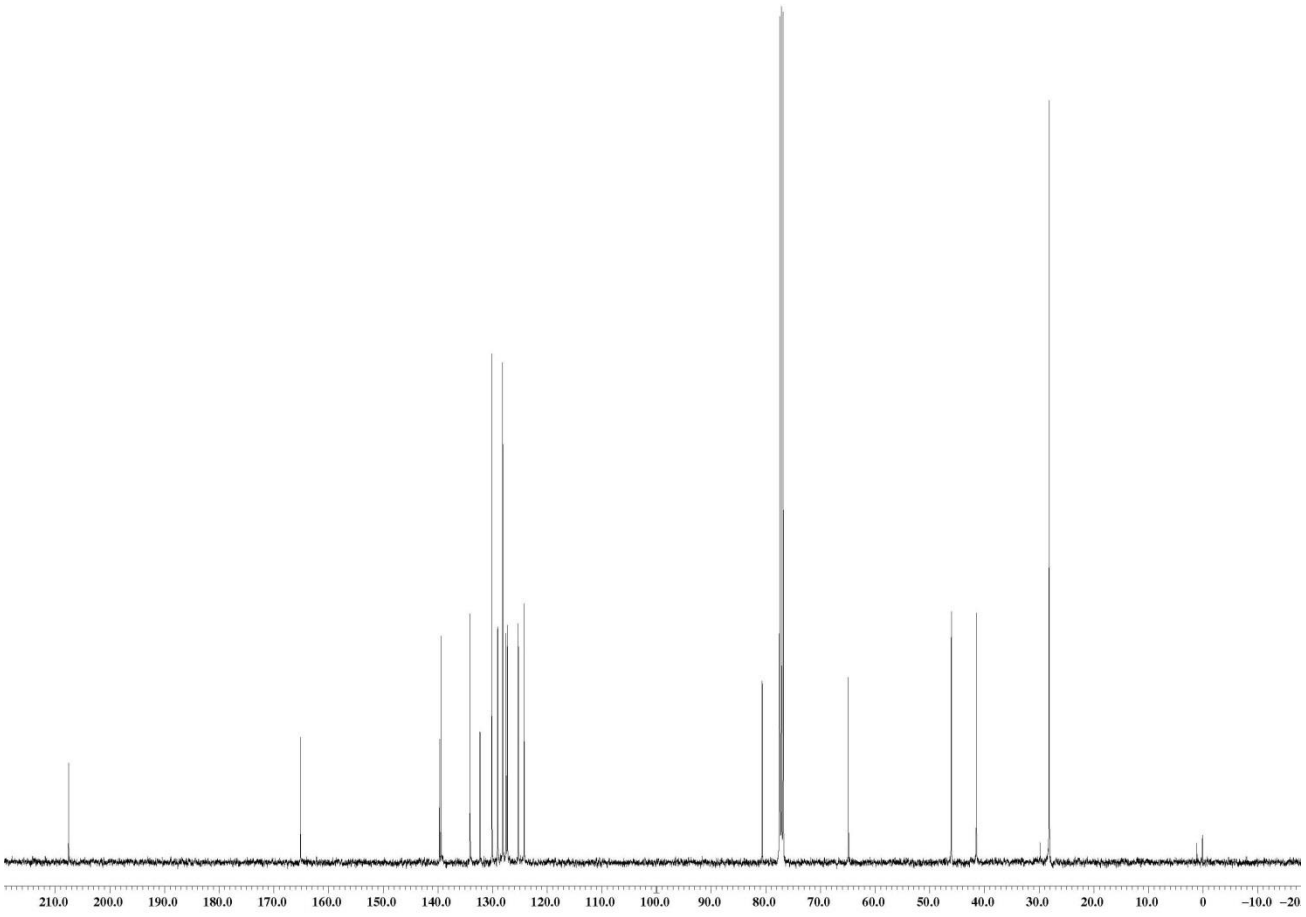
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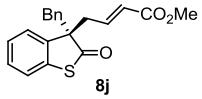
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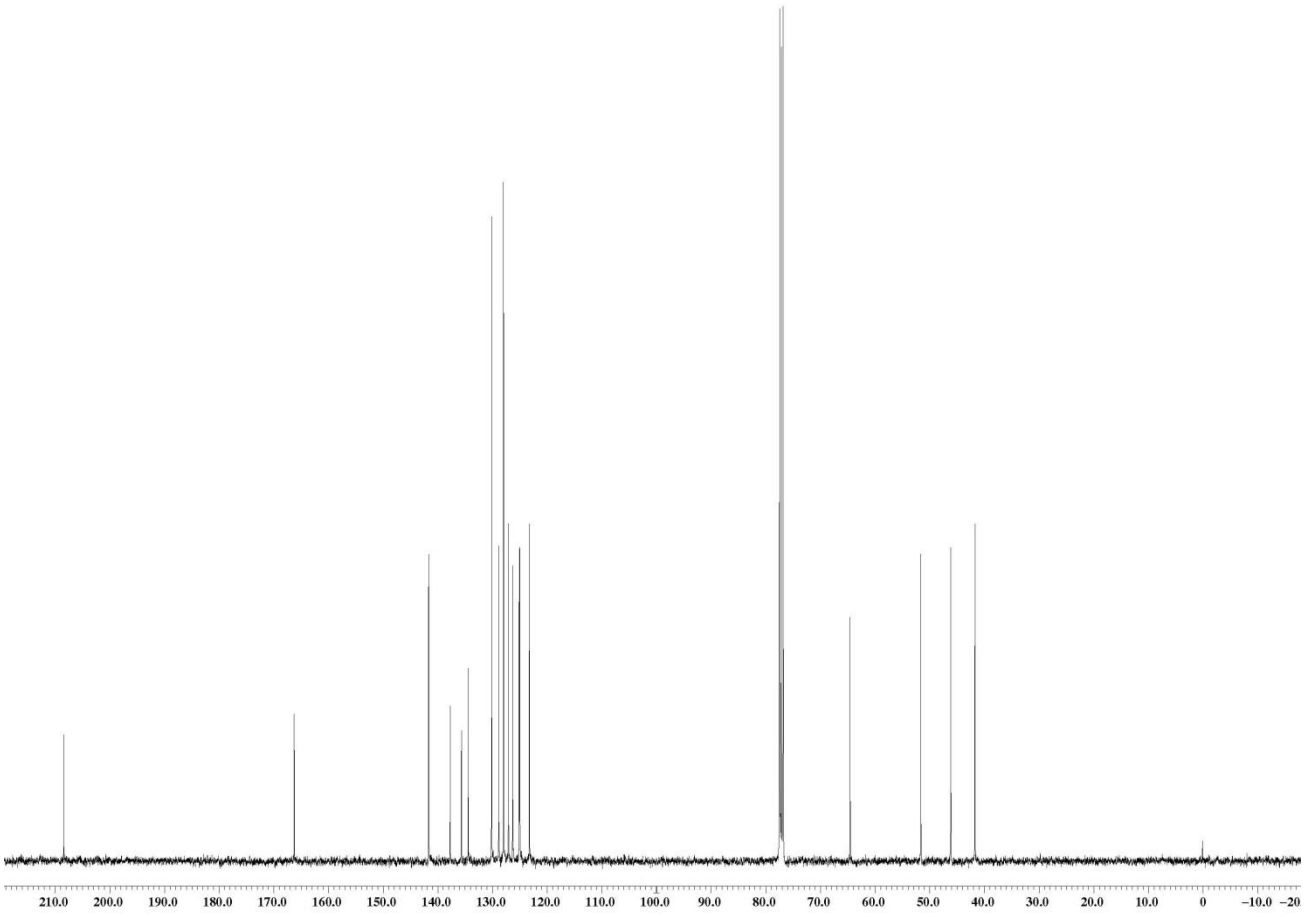
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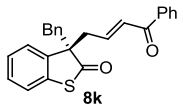
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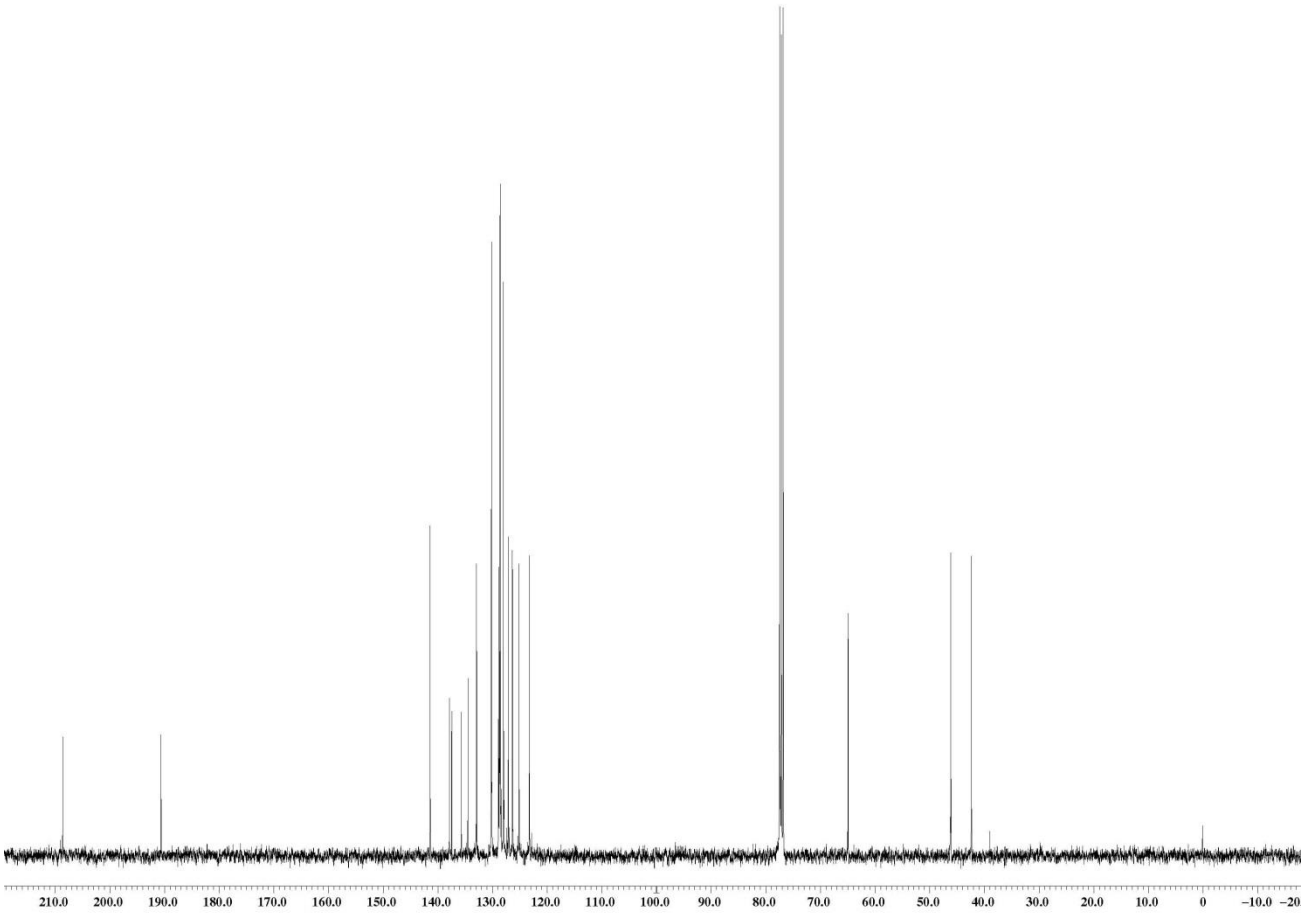
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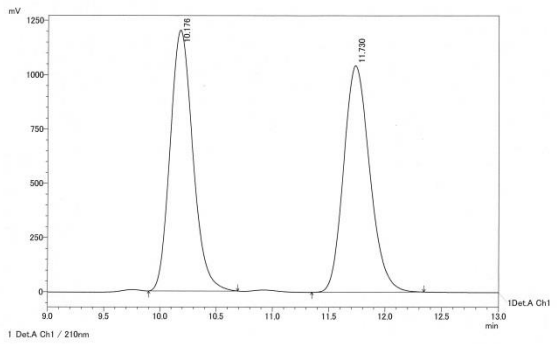
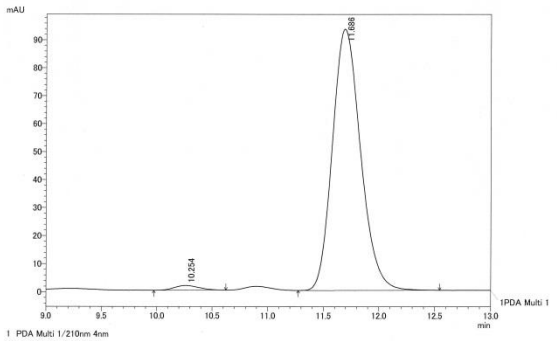
Copies of HPLC Chromatograms:

8a





PDA Ch1 210nm 4nm

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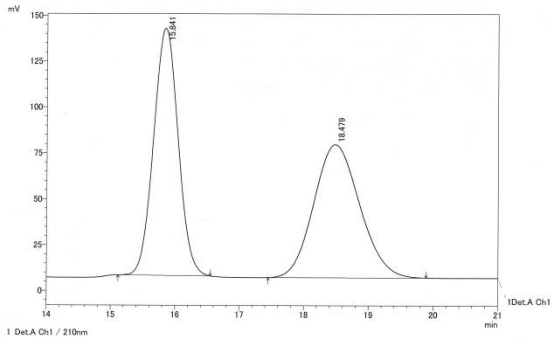
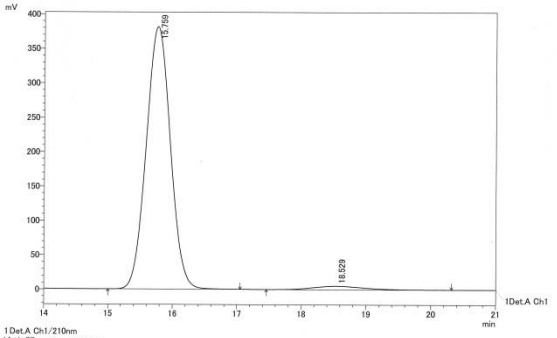
8c





検出器A Ch1 210nm

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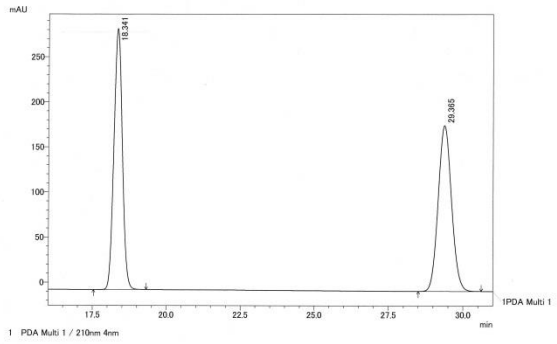
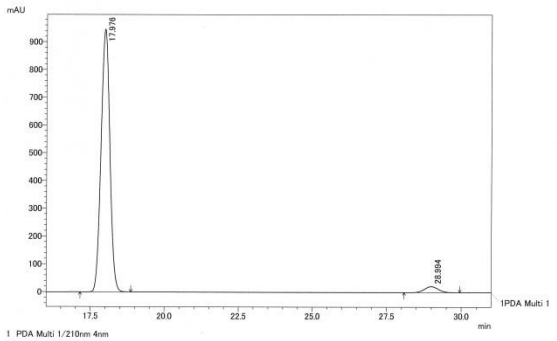
8b

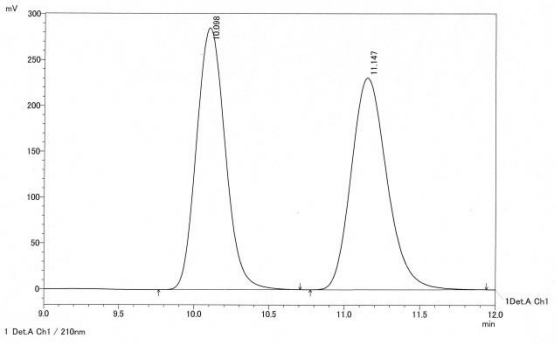


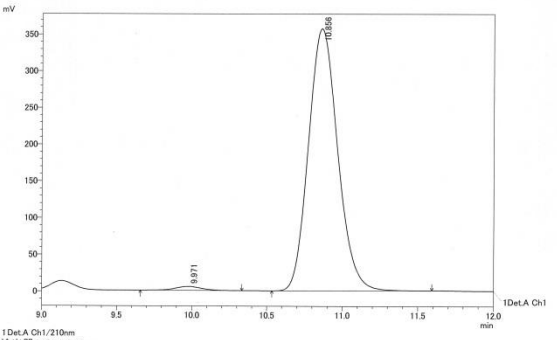


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	17.976	96.521
2	28.994	3.479
合計		100.000

8d

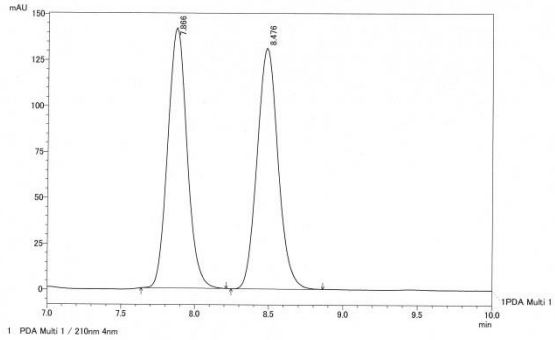


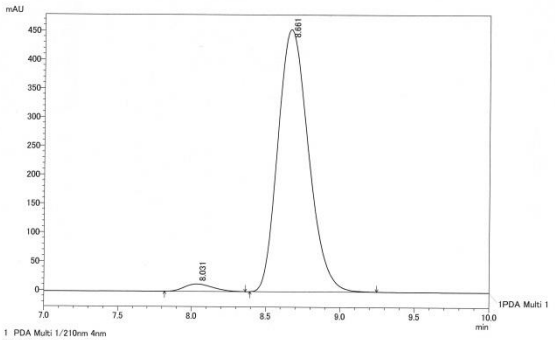


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	9.971	1.293
2	10.856	98.707
合計		100.000

8e

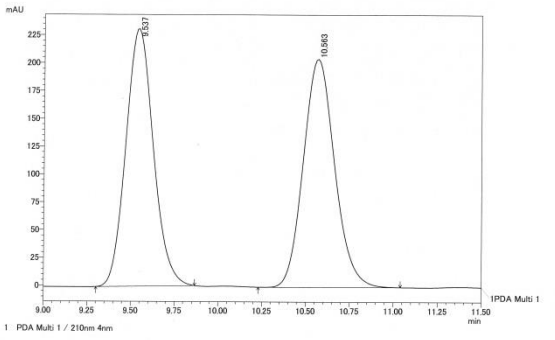


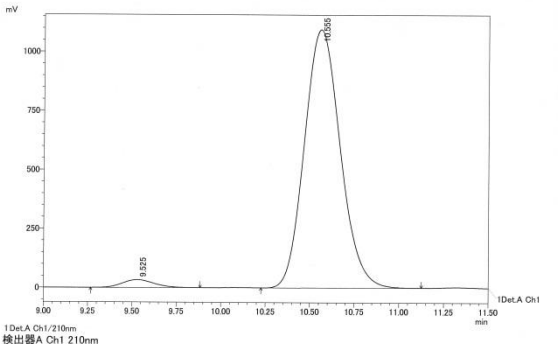


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	8.031	2.564
2	8.661	97.436
合計		100.000

8g

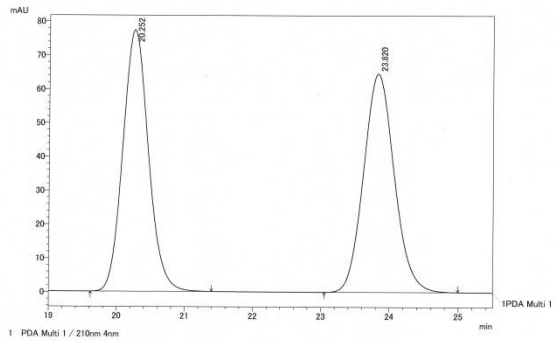


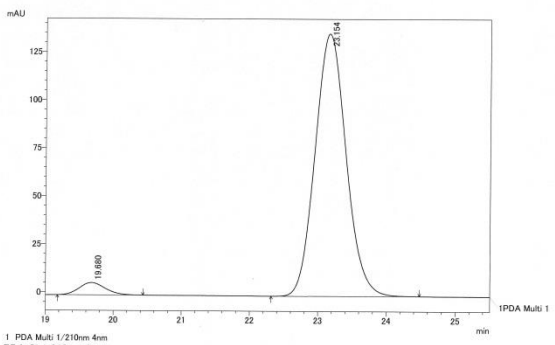


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	9.525	2.612
2	10.555	97.388
合計		100.000

8f

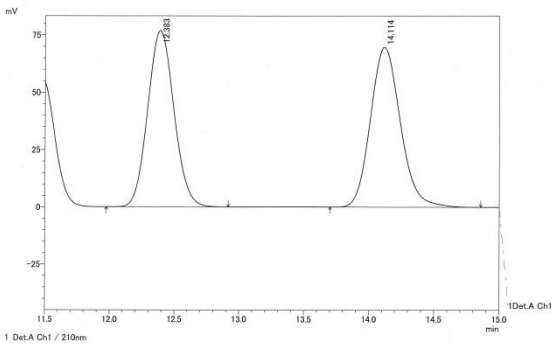


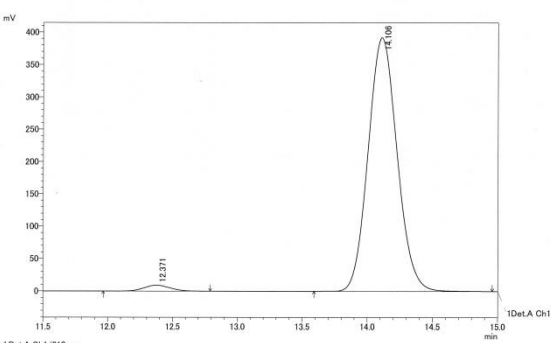


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	19.680	3.809
2	23.154	96.191
合計		100.000

8h

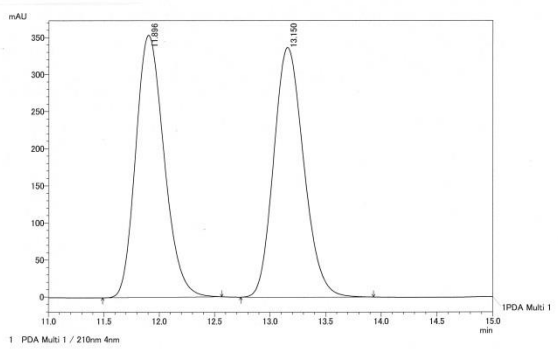


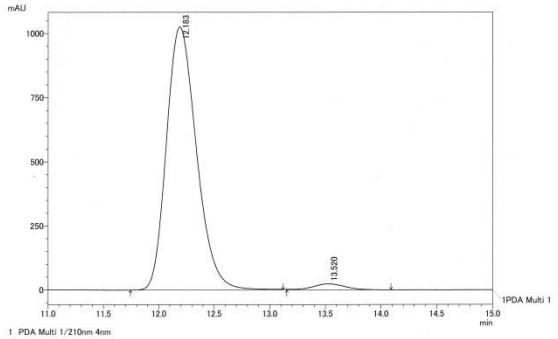


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	12.371	2.046
2	14.106	97.954
合計		100.000

8i

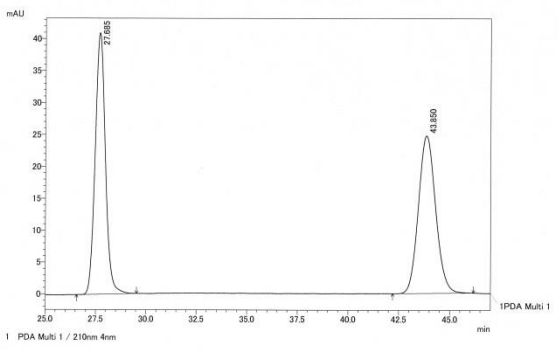


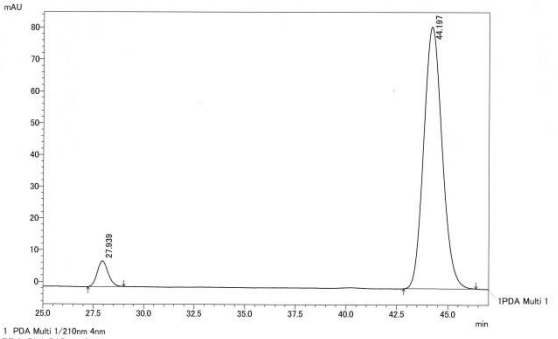


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	12.183	97.587
2	13.520	2.413
合計		100.000

8k

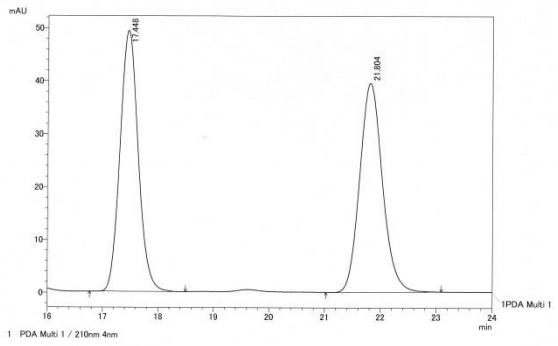


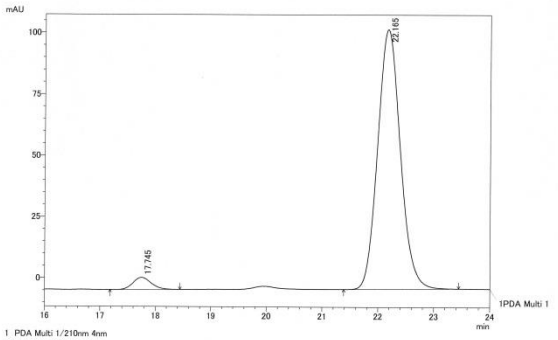


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	27.939	5.553
2	44.197	94.447
合計		100.000

8j





PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	17.745	3.640
2	22.165	96.360
合計		100.000