Supporting Information

Catalytic Enantioselective Construction of *trans*-Fused 2,3,3a,4,5,9b-Hexahydro-1*H*-Pyrrolo[3,2-*c*]quinoline Derivatives by Intramolecular [3+2] Cycloaddition

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1. General methods and materials

General. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZ500R (500 MHz for ^{1}H and 126 MHz for ^{13}C) spectrometer. Chemical shifts (δ) are reported in ppm referenced to tetramethylsilane as internal standard ($CDCl_3$: $\delta = 0$ ppm for ^{1}H) and residual solvent signal ($CDCl_3$: $\delta = 77.0$ ppm for $^{13}C\{^{1}H\}$). *J*-values are given in Hz. The high-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF mass spectrometer. Optical rotations were measured on a HORIBA polarimeter SEPA-300. HPLC analyses were performed on JASCO HPLC system (JASCO PU-2086Plus preparative HPLC pump and UV-2075Plus UV/Vis detector). All melting points were determined on a BÜCHI melting apparatus B-540 and are uncorrected. All manipulations were carried out with standard Schlenk technique under an argon atmosphere. Reactions were monitored by TLC (silica gel 60 F_{254}, 0.25 mm) analysis. Flash column chromatography was performed on flash silica gel 60N (spherical neutral, particle size 40–50 μm).

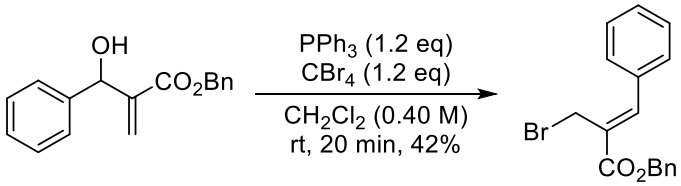
Materials. Anhydrous CH_2Cl_2, THF, Et_2O, 1,4-dioxane, toluene, MeOH, and MeCN were purchased and used without any purification. Aldehydes (*E*)-**1a–1f** and **1i** were prepared according to the procedure described in the literature.[1,2] The following known compounds were prepared according to the procedure described in the literature.

Benzyl 2-[hydroxy(phenyl)methyl]prop-2-enoate[3]
N-(2-Formylphenyl)-4-methylbenzenesulfonamide[4]
N-(5-Chloro-2-formylphenyl)-4-methylbenzenesulfonamide[5]
Methyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate[6]
N-(4-Chloro-2-formylphenyl)-4-methylbenzenesulfonamide[5]
N-(6-Formyl-1,3-benzodioxol-5-yl)-4-methylbenzenesulfonamide[7]
N-(2-Formyl-5-methoxyphenyl)-4-methylbenzenesulfonamide[8]
N-(2-Formylphenyl)-2-nitrobenzenesulfonamide[9]
N-(2-Formylphenyl)-2,4,6-trimethylbenzenesulfonamide[10]
N-(2-Formylphenyl)-1-naphthalenesulfonamide [11]

Racemic cycloadducts **3** were prepared according to the **general procedure B** in the presence of Cu complex prepared from $Cu(MeCN)_4OTf$ and 1,3-bis(diphenylphosphino)propane (dppp) instead of $Cu(MeCN)_4OTf$ and (*S*)-H8-binap **L4**. All other chemicals were purchased from commercial suppliers and used as received.

2. Experimental procedures

Preparation of benzyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate.



Using the modified procedure in the literature,[6] benzyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate was prepared. To a solution of benzyl 2-[hydroxy(phenyl)methyl]prop-2-enoate[3] (1.59 g, 5.93 mmol) and PPh_3 (1.94 g, 7.17 mmol) in CH_2Cl_2 (15.0 mL) was added CBr_4 (2.33 g, 6.96 mmol) at 0 °C. The mixture was stirred at rt for 20 min. The reaction mixture was filtered through a short plug of silica gel, which was rinsed with *n*-hexane and EtOAc (4:1) to give benzyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate (835.5 mg, 2.52 mmol, 42%) as pale yellow amorphous solid.

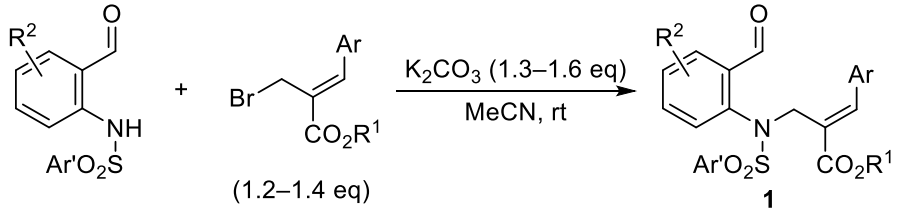
IR (KBr): 1707, 1621, 1258, 1217, 1161, 771, 758, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 4.42 (s, 2 H), 5.32 (s, 2 H), 7.33–7.36 (m, 1 H), 7.38–7.42 (m, 3 H), 7.44–7.47 (m, 4 H), 7.56–7.58 (m, 2 H), 7.86 (s, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 26.8, 67.2, 128.2, 128.3, 128.60, 128.64, 128.9, 129.6, 134.2, 135.7, 143.3, 166.0. (One carbon overlapped to others).

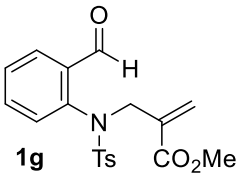
HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{15}{}^{79}BrNaO_2$, 353.0148; found, 353.0153.

General procedure A for the preparation of aldehyde 1.



Using the modified procedure in the literature,[1] aldehydes **1** were prepared. To a mixture of sulfonamide (1.0 eq) and K_2CO_3 (1.3–1.6 eq) in MeCN was added a solution of 2-(bromomethyl)acrylate derivative (1.2–1.4 eq) in MeCN. The reaction mixture was stirred at rt. The reaction was quenched by the addition of water. The mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : EtOAc = 2 : 1) to give **1**.

Methyl 2-{[*N*-(2-formylphenyl)-*N*-(4-methylbenzene-1-sulfonyl)amino]methyl}prop-2-enoate (1g).



1g

According to the **general procedure A**, *N*-(2-formylphenyl)-4-methylbenzenesulfonamide[4] (275.3 mg, 1.00 mmol), methyl 2-(bromomethyl)acrylate (258.4 mg, 1.40 mmol), K_2CO_3 (223.4 mg, 1.60 mmol), and MeCN (2.0 mL) were used. After a reaction time of 12 h, **1g** was obtained in 95% yield (352.8 mg, 0.945 mmol) as white solid.

Mp: 92.6–93.3 °C.

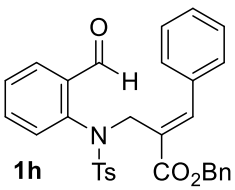
IR (KBr): 1721, 1685, 1637, 1597, 1353, 1216, 1164, 822 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 2.45 (s, 3 H), 3.66 (s, 3 H), 4.21 (br s, 1 H), 4.75 (br s, 1 H), 5.81 (d, J = 0.9 Hz, 1 H), 6.28 (d, J = 0.9 Hz, 1 H), 6.74–6.76 (m, 1 H), 7.28–7.30 (m, 2 H), 7.42–7.48 (m, 4 H), 7.97–7.99 (m, 1 H), 10.29 (d, J = 0.6 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 51.8, 52.1, 127.8, 128.1, 128.5, 128.6, 129.7, 130.2, 133.8, 134.0, 134.9, 135.7, 141.6, 144.4, 165.9, 189.9.

HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{19}H_{19}NNaO_5S$, 396.0876; found, 396.0891.

Benzyl (2*E*)-{[*N*-(2-formylphenyl)-*N*-(4-methylbenzene-1-sulfonyl)amino]methyl}-3-phenylprop-2-enoate (1h)



1h

According to the **general procedure A**, *N*-(2-formylphenyl)-4-methylbenzenesulfonamide[4] (126.5 mg, 0.46 mmol), benzyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate (182.4 mg, 0.55 mmol), K_2CO_3 (84.9 mg, 0.61 mmol), and MeCN (1.0 mL) were used. After a reaction time of 14 h, **1h** was obtained in 97% yield (235.0 mg, 0.447 mmol) as white amorphous solid.

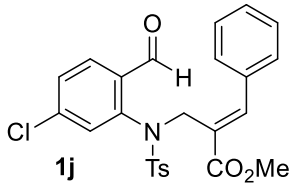
IR (KBr): 1694, 1632,1596, 1354, 1245, 1165, 818, 768, 718, 697 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 2.42 (s, 3 H), 4.57 (d, J = 13.5 Hz, 1 H), 5.08–5.14 (m, 3 H), 6.42 (d, J = 8.0 Hz, 1 H), 7.13–7.17 (m, 1 H), 7.18 (br d, J = 8.3 Hz, 2 H), 7.25–7.36 (m, 10 H), 7.40–7.42 (m, 3 H), 7.75 (s, 1 H), 7.84 (dd, J = 7.7, 1.6 Hz, 1 H), 9.79 (s, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.5, 46.2, 66.9, 126.0, 127.3, 127.8, 128.13, 128.14, 128.19, 128.20, 128.4, 128.6, 129.4, 129.5, 129.7, 132.6, 133.2, 133.8, 135.5, 136.0, 141.1, 144.2, 144.4, 166.7, 189.7.

HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{31}H_{27}NNaO_5S$, 548.1502; found; 548.1517.

Methyl (2*E*)-{[*N*-(5-chloro-2-formylphenyl)-*N*-(4-methylbenzene-1-sulfonyl)amino]methyl}-3-phenylprop-2-enoate (1j)



1j

According to the **general procedure A**, *N*-(5-chloro-2-formylphenyl)-4-methylbenzenesulfonamide[5] (142.5 mg, 0.46 mmol), methyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate[6] (140.8 mg, 0.55 mmol), K_2CO_3 (84.5 mg, 0.61 mmol), and MeCN (1.0 mL) were used. After a reaction time of 24 h, **1j** was obtained in 64% yield (142.7 mg, 0.295 mmol) as white solid.

Mp: 145.1–145.4 °C.

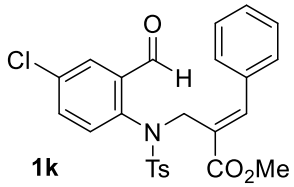
IR (KBr): 1709, 1692, 1641, 1587, 1358, 1259, 1167, 821, 755, 727, 702 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 2.44 (s, 3 H), 3.71 (s, 3 H), 4.44 (d, J = 13.6 Hz, 1 H), 5.01 (d, J = 13.6 Hz, 1 H), 6.36 (d, J = 1.9 Hz, 1 H), 7.23–7.34 (m, 7 H), 7.42–7.43 (m, 3 H), 7.76 (s, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 9.81 (d, J = 0.8 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 46.3, 52.4, 126.0, 127.9, 128.2, 128.7, 128.8, 129.1, 129.4, 129.59, 129.65, 132.4, 133.8, 134.6, 139.3, 142.5, 144.70, 144.72, 167.3, 188.7.

HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{25}H_{22}{}^{35}ClNNaO_5S$, 506.0799; found, 506.0818.

Methyl (2*E*)-2-{[*N*-(4-chloro-2-formylphenyl)-*N*-(4-methylbenzene-1-sulfonyl)amino]methyl}-3-phenylprop-2-enoate (1k)



1k

According to the **general procedure A**, *N*-(4-chloro-2-formylphenyl)-4-methylbenzenesulfonamide[5] (142.7 mg, 0.46 mmol), methyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate[6] (140.2 mg, 0.55 mmol), K_2CO_3 (83.5 mg, 0.60 mmol), and MeCN (1.0 mL) were used. After a reaction time of 32 h, **1k** was obtained in 97% yield (215.4 mg, 0.445 mmol) as white amorphous solid.

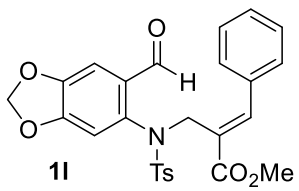
IR (KBr): 1703, 1692, 1638, 1487, 1354, 1254, 1166, 845, 819, 755, 725, 703 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3 H) , 3.70 (s, 3 H) , 4.50 (d, J = 13.7 Hz, 1 H) , 5.06 (d, J = 13.7 Hz, 1 H) , 6.38 (d, J = 8.6 Hz, 1 H), 7.18 (dd, J = 8.6, 2.6 Hz, 1 H) , 7.23 (br d, J = 8.2 Hz, 2 H) , 7.27–7.29 (m, 2 H) , 7.31–7.33 (m, 2 H), 7.41–7.43 (m, 3 H) , 7.74 (s, 1 H) , 7.84 (d, J = 2.6 Hz, 1 H), 9.69 (d, J = 0.8 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 46.2, 52.4, 125.8, 127.9, 128.3, 128.7, 128.9, 129.6, 129.66, 129.68, 132.6, 133.1, 133.8, 134.7, 137.2, 139.6, 144.55, 144.61, 167.4, 188.4.

HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{25}H_{22}{}^{35}ClNNaO_5S$, 506.0799; found, 506.0801.

Methyl (2*E*)-2-{[*N*-(6-formyl-1,3-benzodioxol-5-yl)-*N*-(4-methylbenzene-1-sulfonyl)amino]methyl}prop-2-enoate (1l)



1l

According to the **general procedure A**, *N*-(6-formyl-1,3-benzodioxol-5-yl)-4-methylbenzenesulfonamide[7] (147.0 mg, 0.46 mmol), methyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate[6] (140.8 mg, 0.55 mmol), K_2CO_3 (83.7 mg, 0.60 mmol), and MeCN (1.0 mL) were used. After a reaction time of 18 h, **1l** was obtained quantitatively (226.4 mg, 0.459 mmol) as white solid.

Mp: 130.1–130.4 °C.

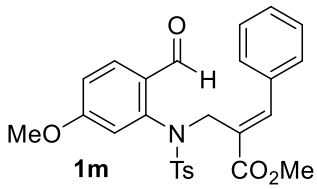
IR (KBr): 1720, 1685, 1612, 1480, 1353, 1249, 1167, 1039, 818, 752, 712 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3 H), 3.70 (s, 3 H), 4.47 (d, J = 13.4 Hz, 1 H), 5.00 (d, J = 13.4 Hz, 1 H), 5.88 (s, 1 H), 5.99 (dd, J = 7.7, 1.3 Hz, 2 H), 7.24–7.26 (m, 5 H), 7.38–7.40 (m, 5 H), 7.75 (s, 1 H), 9.65 (s, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 46.4, 52.3, 102.4, 106.2, 108.0, 126.1, 128.3, 128.6, 129.3, 129.4, 129.6, 131.6, 133.4, 134.0, 137.3, 144.4, 144.7, 147.9, 151.7, 167.3, 188.4.

HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{26}H_{23}NNaO_7S$, 516.1087; found, 516.1094.

Methyl (2*E*)-2-{[*N*-(2-formyl-4-methoxyphenyl)-*N*-(4-methylbenzene-1-sulfonyl)amino]methyl}-3-phenylprop-2-enoate (1m)



1m

According to the **general procedure A**, *N*-(2-formyl-5-methoxyphenyl)-4-methylbenzene-1-sulfonamide[8] (113.0 mg, 0.37 mmol), methyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate[6] (113.3 mg, 0.44 mmol), K_2CO_3 (67.1 mg, 0.48 mmol), and MeCN (0.80 mL) were used. After a reaction time of 23 h, **1m** was obtained quantitatively (176.5 mg, 0.368 mmol) as white solid.

Mp: 149.8–150.1 °C.

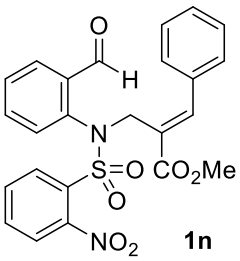
IR (KBr): 1718, 1681, 1622, 1599, 1352, 1250, 1165, 820, 768, 696 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3 H), 3.48 (s, 3 H), 3.68 (s, 3 H), 4.53 (d, J = 13.4 Hz, 1 H), 5.04 (dd, J = 13.4, 0.9 Hz, 1 H), 5.89 (d, J = 2.4 Hz, 1 H), 6.83 (ddd, J = 8.7, 2.4, 0.8 Hz, 1 H), 7.23–7.27 (m, 4 H), 7.37–7.39 (m, 5 H), 7.71 (s, 1 H), 7.83 (d, J = 8.7 Hz, 1 H), 9.71 (s, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 46.3, 52.3, 55.2, 112.3, 114.9, 126.0, 128.4, 128.6, 129.4, 129.48, 129.51, 129.59, 129.61, 133.2, 133.9, 143.0, 144.3, 144.5, 163.4, 167.5, 188.7.

HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{26}H_{25}NNaO_6S$, 502.1295; found, 502.1311.

Methyl (2*E*)-2-{[*N*-(2-formylphenyl)-*N*-(2-nitrobenzene-1-sulfonyl)amino]methyl}-3-phenylprop-2-enoate (1n)



1n

According to the **general procedure A**, *N*-(2-formylphenyl)-2-nitrobenzenesulfonamide[9] (140.5 mg, 0.46 mmol), methyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate[6] (136.7 mg, 0.54 mmol), K_2CO_3 (87.8 mg, 0.63 mmol), and MeCN–CH_2Cl_2 (2:1, 1.5 mL) were used. After a reaction time of 26 h, **1n** was obtained in 53% yield (118.3 mg, 0.246 mmol) as pale yellow solid.

Mp: 149.6–150.0 °C.

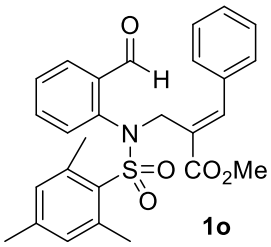
IR (KBr): 1717, 1689, 1621, 1594, 1545, 1373, 1361, 1272, 1170, 772, 747, 691 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 3.77 (s, 3 H), 5.05 (d, J = 13.9 Hz, 1 H), 5.18 (dd, J = 13.9, 0.6 Hz, 1 H), 6.71 (d, J = 7.9 Hz, 1 H), 7.03–7.05 (m, 2 H), 7.20–7.24 (m, 1 H), 7.26–7.31 (m, 4 H), 7.35–7.41 (m, 2 H), 7.60–7.66 (m, 2 H), 7.76 (s, 1 H), 7.83 (dd, J = 7.7, 1.6 Hz, 1 H), 9.83 (s, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 47.7, 52.3, 124.0, 126.1, 128.47, 128.53, 128.9, 129.1, 129.2, 130.5, 130.8, 131.1, 132.1, 133.7, 133.9, 134.1, 135.8, 138.8, 145.7, 148.2, 167.2, 189.2.

HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{24}H_{20}N_2NaO_7S$, 503.0883; found, 503.0899.

Methyl (2*E*)-2-{[*N*-(2-formylphenyl)-*N*-(2,4,6-trimethylbenzene-1-sulfonyl)amino]methyl}-3-phenylprop-2-enoate (1o)



1o

According to the **general procedure A**, *N*-(2-formylphenyl)-2,4,6-trimethylbenzenesulfonamide[10] (140.0 mg, 0.46 mmol), methyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate[6] (146.2 mg, 0.57 mmol), K_2CO_3 (103.2 mg, 0.74 mmol), and MeCN–CH_2Cl_2 (1:1, 2.0 mL) were used. After a reaction time of 24 h, **1o** was obtained in 95% yield (207.9 mg, 0.435 mmol) as white amorphous solid.

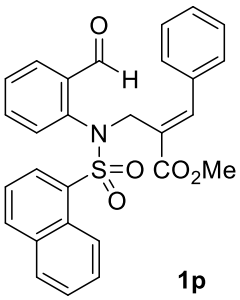
IR (KBr): 1697, 1628, 1597, 1342, 1256, 1209, 772, 724, 702 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 2.20 (s, 6 H), 2.25 (s, 3 H), 3.68 (s, 3 H), 4.88 (d, J = 12.9 Hz, 1 H), 5.24 (d, J = 12.9 Hz, 1 H), 6.83 (s, 2 H), 6.85 (dd, J = 8.0, 1.0 Hz, 1 H), 7.13–7.15 (m, 2 H), 7.24 (dt, J = 7.7, 1.8 Hz, 1 H), 7.30–7.35 (m, 4 H), 7.67 (s, 1 H), 7.72 (dd, J = 7.7, 1.6 Hz, 1 H), 9.59 (s, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 20.9, 23.1, 45.7, 52.2, 126.4, 127.6, 128.6, 128.7, 129.2, 129.3, 130.8, 130.9, 132.1, 133.7, 133.9, 136.0, 140.3, 140.4, 143.2, 145.0, 167.4, 189.4.

HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd for $C_{27}H_{27}NNaO_5S$, 500.1502; found, 500.1506.

Methyl (2*E*)-2-(*N*-(2-formylphenyl)-*N*-(naphthalene-1-sulfonyl)amino)methyl-3-phenylprop-2-enoate (1p)



1p

According to the **general procedure A**, *N*-(2-formylphenyl)-1-naphthalenesulfonamide[11] (138.7 mg, 0.45 mmol), methyl (2*Z*)-2-(bromomethyl)-3-phenylprop-2-enoate[6] (135.5 mg, 0.53 mmol), K_2CO_3 (88.4 mg, 0.63 mmol), and MeCN–CH_2Cl_2 (3.3:1, 1.3 mL) were used. After a reaction time of 24 h, **1p** was obtained in 91% yield (199.1 mg, 0.410 mmol) as white solid.

Mp: 116.7–117.2 °C.

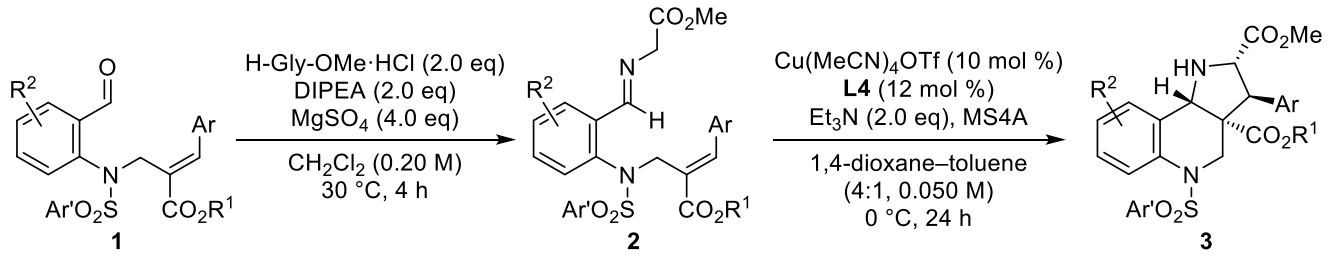
IR (KBr): 1695, 1622, 1595, 1352, 1254, 1162, 768, 729, 709 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 3.59 (s, 3 H), 4.62 (d, J = 13.5 Hz, 1 H), 5.14 (dd, J = 13.5, 0.9 Hz, 1 H), 6.36 (dd, J = 8.1, 0.9 Hz, 1 H), 7.02 (ddd, J = 8.0, 7.3, 1.7 Hz, 1 H), 7.18–7.20 (m, 2 H), 7.27–7.41 (m, 6 H), 7.49–7.52 (m, 1 H), 7.71 (s, 1 H), 7.84–7.89 (m, 3 H), 8.05 (br d, J = 8.2 Hz, 1 H), 8.16–8.17 (m, 1 H), 9.87 (d, J = 0.6 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 46.6, 52.2, 124.0, 125.1, 126.4, 126.9, 127.88 ,127.92, 128.4, 128.61, 128.65, 129.0, 129.1, 129.3, 129.4, 131.4, 132.0, 133.3, 133.9, 134.1, 134.9, 136.0, 140.8, 144.5, 167.3, 189.8.

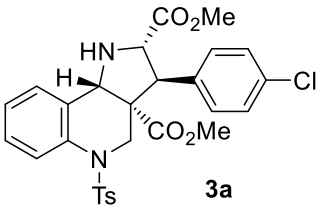
HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{28}H_{23}NNaO_5S$, 508.1189; found, 508.1179.

General procedure B for Cu-catalyzed asymmetric intramolecular [3+2] cycloaddition of 2.



To a round bottom flask charged with aldehyde **1** (0.10 mmol), glycine methyl ester hydrochloride (25.6 mg, 0.20 mmol), and anhydrous $MgSO_4$ (50.7 mg, 0.40 mmol) under the Ar atmosphere, dry CH_2Cl_2 (0.50 mL, 0.20 M) and DIPEA (35.1 μL, 0.20 mmol) were added. The reaction mixture was stirred at 30 °C for 4 h. The reaction mixture was filtered and washed with water. The aqueous layer was extracted with diethyl ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo* to give crude imine **2**. To a Schlenk flask charged with $Cu(MeCN)_4OTf$ (3.8 mg, 0.010 mmol), (*S*)-H8-BINAP **L4** (7.6 mg, 0.012 mol), and activated MS4A (80.0 mg) under the Ar atmosphere, dry 1,4-dioxane–toluene (4:1, 0.50 mL) were added. The reaction mixture was stirred at 30 °C for 30 min and cooled to 0 °C. To this mixture, the solution of crude imine **2a** in dry 1,4-dioxane–toluene (4:1, 1.5 mL) was added. After addition of triethylamine (28.0 μL, 0.20 mmol), the entire mixture was stirred at 0 °C for 24 h. The reaction mixture was filtered through a short plug of silica gel, which was rinsed with *n*-hexane and EtOAc (1:1). The filtrate was evaporated in *vacuo* and the residue was purified by column chromatography on silica gel (*n*-hexane : EtOAc = 3:1 to 1:1) to afford **3**.

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-3-(4-chlorophenyl)-5-(4-methylbenzene-1-sulfonyl)-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3a)



3a

83% yield (46.3 mg, 0.083 mmol). Pale yellow amorphous solid.

$[\alpha]_D^{22}$ +75.5 (*c* 1.00, $CHCl_3$, 88% ee).

IR (KBr): 3310, 2953, 1740, 1599, 1492, 1354, 1218, 1167, 829, 814, 759 cm^{-1}.

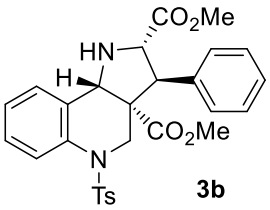
^1H NMR (500 MHz, $CDCl_3$): δ 2.44 (s, 3 H), 2.83 (d, J = 11.9 Hz, 1 H), 3.25–3.27 (m, 4 H), 3.36–3.41 (m, 1 H), 3.73 (s, 3 H), 3.83 (d, J = 4.8 Hz, 1 H), 3.91 (d, J = 11.9 Hz, 1 H), 4.20 (dd, J = 8.9 Hz, 4.8 Hz, 1 H), 6.91 (br d, J = 8.3 Hz, 2 H), 7.12 (br d, J = 8.3 Hz, 2 H), 7.18 (br d, J = 8.3 Hz, 2 H), 7.216–7.225 (m, 2 H), 7.31–7.35 (m, 3 H), 7.74 (br d, J = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 50.2, 52.2, 52.6, 56.4, 60.1, 64.6, 69.7, 122.3, 125.8, 126.2, 126.8, 128.1, 129.5, 129.6, 129.9, 130.3, 134.0, 134.90, 134.92, 136.7, 143.9, 171.9, 173.1.

HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{28}H_{27}{}^{35}ClN_2NaO_6S$, 577.1171; found, 577.1172.

The enantiomeric excess was determined by HPLC analysis to be 88% ee, t_R = 26.6 min (minor), t_R = 42.9 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 2/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-5-(4-methylbenzene-1-sulfonyl)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3b)



3b

87% yield (45.2 mg, 0.087 mmol). White amorphous solid.

$[\alpha]_D^{22}$ +67.9 (*c* 1.00, $CHCl_3$, 89% ee).

IR (KBr): 3310, 2952, 1744, 1716, 1599, 1488, 1354, 1235, 1218, 1169, 812, 760, 724, 704 cm^{-1}.

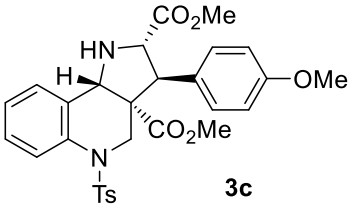
^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3 H), 2.88 (d, *J* = 12.0 Hz, 1 H), 3.21–3.31 (m, 4 H), 3.41 (br s, 1 H), 3.73 (s, 3 H), 3.85 (d, *J* = 4.9 Hz, 1 H), 3.90 (d, *J* = 12.0 Hz, 1 H), 4.28 (br s, 1 H), 6.97–6.98 (m, 2 H), 7.08 (br d, *J* = 8.3 Hz, 2 H), 7.16 (br d, *J* = 8.3 Hz, 2 H), 7.19–7.22 (m, 2 H), 7.29–7.33 (m, 1 H), 7.40–7.41 (m, 3 H), 7.74 (br d, *J* = 8.1 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 50.4, 52.1, 52.5, 57.1, 60.3, 64.6, 69.5, 122.3, 125.7, 126.3, 126.8, 128.0, 128.2, 128.6, 129.3, 129.6, 130.7, 134.86, 134.89, 138.2, 143.8, 172.2, 173.3.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{28}N_2NaO_6S$, 543.1560; found, 543.1572.

The enantiomeric excess was determined by HPLC analysis to be 89% ee, t_R = 19.9 min (minor), t_R = 30.1 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 2/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-3-(4-methoxyphenyl)-5-(4-methylbenzene-1-sulfonyl)-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3c)



3c

25% yield (13.5 mg, 0.025 mmol). White amorphous solid.

$[\alpha]_D^{22}$ +89.8 (*c* 0.250, $CHCl_3$, 88% ee).

IR (KBr): 3316, 2953, 1741, 1514, 1354, 1252, 1218, 1168, 832, 812, 761 cm^{-1}.

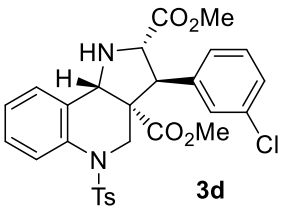
^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3 H), 2.93 (d, *J* = 12.0 Hz, 1 H), 3.24 (br s, 1 H), 3.26 (s, 3 H), 3.38 (br s, 1 H), 3.72 (s, 3 H), 3.80 (d, *J* = 5.0 Hz, 1 H), 3.89 (s, 3 H), 3.90 (d, *J* = 12.0 Hz, 1 H), 4.21 (br s, 1 H), 6.88–6.92 (m, 4 H), 7.13 (br d, *J* = 8.3 Hz, 2 H), 7.17 (br d, *J* = 8.3 Hz, 2 H), 7.20–7.22 (m, 2 H), 7.29–7.32 (m, 1 H), 7.74 (br d, *J* = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 50.5, 52.1, 52.5, 55.3, 56.5, 60.4, 64.6, 69.7, 114.6, 122.3, 125.7, 126.2, 126.8, 127.9, 129.5, 129.6, 130.0, 130.8, 134.9, 143.8, 159.2, 172.2, 173.4. (One carbon overlapped to others)

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{30}N_2NaO_7S$, 573.1666; found, 573.1668.

The enantiomeric excess was determined by HPLC analysis to be 88% ee, t_R = 22.2 min (minor), t_R = 41.3 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 1/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-3-(3-chlorophenyl)-5-(4-methylbenzene-1-sulfonyl)-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3d)



3d

90% yield (50.1 mg, 0.090 mmol). Pale yellow amorphous solid.

$[\alpha]_D^{22}$ +59.9 (*c* 1.00, $CHCl_3$, 88% ee).

IR (KBr): 3312, 2953, 1741, 1597, 1484, 1355, 1249, 1218, 1168, 811, 761 cm^{-1}.

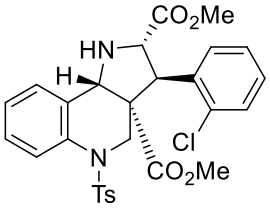
^1H NMR (500 MHz, $CDCl_3$): δ 2.42 (s, 3 H), 2.91 (d, *J* = 12.0 Hz, 1 H), 3.18 (br s, 1 H), 3.27 (s, 3 H), 3.39 (br s, 1 H), 3.73 (s, 3 H), 3.83 (d, *J* = 4.9 Hz, 1 H), 3.93 (d, *J* = 12.0 Hz, 1 H), 4.23 (d, *J* = 3.7 Hz, 1 H), 6.92 (br d, *J* = 7.4 Hz, 1 H), 7.03 (br s, 1 H), 7.10 (br d, *J* = 8.3 Hz, 2 H), 7.19–7.23 (m, 4 H), 7.30–7.41 (m, 3 H), 7.76 (br d, *J* = 8.1 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 50.4, 52.2, 52.6, 56.7, 60.1, 64.7, 69.3, 122.3, 125.8, 126.3, 126.6, 127.4, 128.1, 128.2, 128.5, 129.7, 130.58, 130.62, 134.6, 134.8, 135.2, 140.2, 143.9, 171.8, 173.0.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{27}{}^{35}ClN_2NaO_6S$, 577.1171; found, 577.1186.

The enantiomeric excess was determined by HPLC analysis to be 88% ee, t_R = 21.0 min (minor), t_R = 33.4 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 2/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-3-(2-chlorophenyl)-5-(4-methylbenzene-1-sulfonyl)-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3e)



3e

93% yield (51.6 mg, 0.093 mmol). White amorphous solid.

$[\alpha]_D^{22}$ +73.2 (*c* 1.00, $CHCl_3$, 87% ee).

IR (KBr): 3313, 2593, 1745, 1730, 1598, 1484, 1355, 1241, 1217, 1167, 812, 752 cm^{-1}.

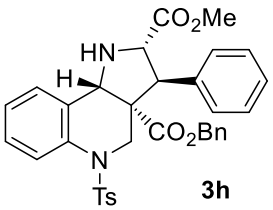
^1H NMR (500 MHz, $CDCl_3$): δ 2.41 (s, 3 H), 2.79 (d, *J* = 12.0 Hz, 1 H), 3.11–3.13 (m, 1 H), 3.27 (s, 3 H), 3.42 (br s, 1 H), 3.74 (s, 3 H), 4.08 (d, *J* = 12.0 Hz, 1 H), 4.30 (br s, 1 H), 4.46 (d, *J* = 5.2 Hz, 1 H), 6.96 (br d, *J* = 7.6 Hz, 1 H), 7.03 (br d, *J* = 8.2 Hz, 2 H), 7.12 (br d, *J* = 8.2 Hz, 2 H), 7.20–7.23 (m, 2 H), 7.30–7.33 (m, 2 H), 7.35–7.38 (m, 1 H), 7.53 (br d, *J* = 7.9 Hz, 1 H), 7.72 (br d, *J* = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 49.5, 52.2, 52.6, 52.9, 60.0, 64.5, 67.9, 122.1, 125.8, 126.3, 126.7, 127.4, 128.0, 128.2, 129.1, 129.6, 130.3, 130.6, 134.91, 134.95, 135.3, 135.7, 143.7, 171.9, 173.1.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{27}{}^{35}ClN_2NaO_6S$, 577.1171; found, 577.1187.

The enantiomeric excess was determined by HPLC analysis to be 87% ee, t_R = 16.9 min (minor), t_R = 21.6 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 2/1, flow rate = 0.5 mL/min, λ = 254 nm).

Benzyl methyl (2*S*,3*S*,3a*R*,9b*S*)-5-(4-methylbenzene-1-sulfonyl)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3h)



3h

67% yield (39.8 mg, 0.067 mmol). White amorphous solid.

$[\alpha]_D^{22}$ +32.5 (*c* 1.00, $CHCl_3$, 90% ee).

IR (KBr): 3313, 2953, 1742, 1600, 1491, 1355, 1246, 1210, 1167, 756, 701 cm^{-1}.

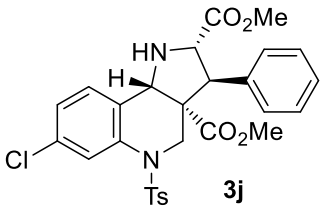
^1H NMR (500 MHz, $CDCl_3$): δ 2.41 (s, 3 H), 2.88 (d, *J* = 12.0 Hz, 1 H), 3.24–3.26 (m, 1 H), 3.40 (br s, 1 H), 3.65 (s, 3 H), 3.84 (d, *J* = 5.0 Hz, 1 H), 3.94 (d, *J* = 12.0 Hz, 1 H), 4.28 (br s, 1 H), 4.63 (d, *J* = 12.0 Hz, 1 H), 4.81 (d, *J* = 12.0 Hz, 1 H), 6.96–6.97 (m, 2 H), 7.02–7.07 (m, 4 H), 7.09–7.14 (m, 4 H), 7.18–7.21 (m, 1 H), 7.27–7.30 (m, 3 H), 7.38–7.40 (m, 3 H), 7.62 (br d, *J* = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 50.5, 52.4, 57.2, 60.3, 64.5, 67.1, 69.4, 122.2, 125.7, 126.3, 126.8, 127.9, 128.2, 128.4, 128.47, 128.55, 128.6, 129.3, 129.5, 130.6, 134.6, 134.7, 134.8, 138.1, 143.7, 172.0, 172.6.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{34}H_{32}N_2NaO_6S$, 619.1873; found, 619.1876.

The enantiomeric excess was determined by HPLC analysis to be 90% ee, t_R = 23.4 min (minor), t_R = 36.4 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 2/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-7-chloro-5-(4-methylbenzenesulfonyl)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3j)



3j

75% yield (41.6 mg, 0.075 mmol). White amorphous solid.

$[\alpha]_D^{22}$ –14.7 (*c* 1.00, $CHCl_3$, 85% ee).

IR (KBr): 3303, 2953, 1740, 1601, 1488, 1357, 1217, 1168, 818, 760, 706 cm^{-1}.

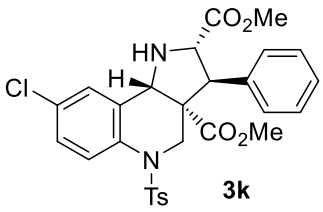
^1H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3 H), 2.85 (d, *J* = 12.0 Hz, 1 H), 3.24 (br s, 1 H), 3.30–3.43 (m, 4 H), 3.73 (s, 3 H), 3.86 (d, *J* = 4.8 Hz, 1 H), 3.90 (d, *J* = 12.0 Hz, 1 H), 4.28 (br s, 1 H), 6.97–6.99 (m, 2 H), 7.12 (br d, *J* = 8.4 Hz, 2 H), 7.15–7.20 (m, 4 H), 7.39–7.41 (m, 3 H), 7.79 (d, *J* = 1.9 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 50.6, 52.3, 52.6, 57.1, 59.9, 64.1, 69.3, 123.3, 125.7, 125.9, 126.8, 128.2, 128.5, 129.0, 129.4, 129.7, 133.4, 134.7, 136.0, 137.9, 144.1, 172.0, 173.0.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{27}{}^{35}ClN_2NaO_6S$, 577.1171; found, 577.1172.

The enantiomeric excess was determined by HPLC analysis to be 85% ee, t_R = 17.9 min (minor), t_R = 25.2 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 2/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-8-chloro-5-(4-methylbenzene-1-sulfonyl)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3k)



3k

77% yield (42.6 mg, 0.077 mmol). White amorphous solid.

$[\alpha]_D^{22}$ +0.49 (*c* 1.00, $CHCl_3$, 92% ee).

IR (KBr): 3308, 2953, 1741, 1479, 1356, 1218, 1168, 813, 755, 724, 706 cm^{-1}.

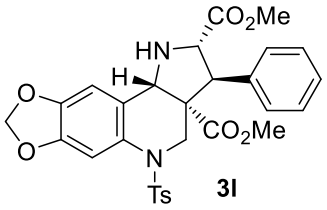
^1H NMR (500 MHz, $CDCl_3$): δ 2.44 (s, 3 H), 2.83 (d, *J* = 12.0 Hz, 1 H), 3.21 (br s, 1 H), 3.30–3.39 (m, 4 H), 3.73 (s, 3 H), 3.86 (d, *J* = 4.8 Hz, 1 H), 3.89 (d, *J* = 12.0 Hz, 1 H), 4.27 (d, *J* = 4.1 Hz, 1 H), 6.96–6.98 (m, 2 H), 7.08 (br d, *J* = 8.1 Hz, 2 H), 7.18 (br d, *J* = 8.1 Hz, 2 H), 7.21 (d, *J* = 2.5 Hz, 1 H), 7.28 (dd, *J* = 8.7, 2.5 Hz, 1 H), 7.39–7.41 (m, 3 H), 7.69 (d, *J* = 8.7 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.6, 50.4, 52.3, 52.6, 57.0, 60.0, 64.1, 69.2, 122.7, 126.8, 127.3, 128.0, 128.2, 128.5, 129.4, 129.7, 131.4, 132.4, 133.4, 134.6, 137.9, 144.0, 172.0, 173.0.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{27}{}^{35}ClN_2NaO_6S$, 577.1171; found, 577.1180.

The enantiomeric excess was determined by HPLC analysis to be 92% ee, t_R = 19.9 min (minor), t_R = 34.2 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 2/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,10b*S*)-5-(4-methylbenzene-1-sulfonyl)-3-phenyl-2,3,3a,4,5,10b-hexahydro-1*H*-[1,3]dioxolo[4,5-g]pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3l)



3l

19% yield (10.9 mg, 0.019 mmol). Pale yellow amorphous solid.

$[\alpha]_D^{22}$ –48.9 (*c* 0.100, $CHCl_3$, 93% ee).

IR (KBr): 3317, 2953, 1742, 1721, 1598, 1503, 1354, 1283, 1230, 1167, 1038, 930, 818, 706 cm^{-1}.

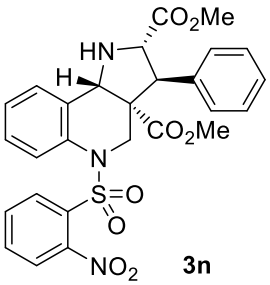
^1H NMR (500 MHz, $CDCl_3$): δ 2.44 (s, 3 H), 2.83 (d, *J* = 12.1 Hz, 1 H), 3.04–3.06 (m, 1 H), 3.33 (br s, 1 H), 3.38 (s, 3 H), 3.72 (s, 3 H), 3.80 (d, *J* = 5.0 Hz, 1 H), 3.85 (d, *J* = 12.1 Hz, 1 H), 4.22 (br s, 1 H), 6.00 (d, *J* = 17.1 Hz, 1 H), 6.00 (d, *J* = 17.1 Hz, 1 H), 6.71 (d, *J* = 0.9 Hz, 1 H), 6.93–6.95 (m, 2 H), 7.11 (br d, *J* = 8.1 Hz, 2 H), 7.19 (br d, *J* = 8.1 Hz, 2 H), 7.28 (s, 1 H), 7.39–7.40 (m, 3 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.7, 50.2, 52.3, 52.5, 57.1, 60.7, 64.5, 69.3, 101.5, 102.6, 108.7, 124.9, 127.0, 128.2, 128.5, 128.6, 129.3, 129.6, 134.5, 138.1, 143.8, 145.7, 146.9, 172.0, 173.3.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{28}N_2NaO_8S$, 587.1459; found, 587.1468.

The enantiomeric excess was determined by HPLC analysis to be 93% ee, t_R = 24.9 min (minor), t_R = 46.4 min (major) (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 1/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-5-(2-nitorobenzene-1-sulfonyl)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3n)



3n

53% yield (29.3 mg, 0.053 mmol). Yellow amorphous solid.

$[\alpha]_D^{22}$ +48.0 (*c* 0.500, $CHCl_3$, 80% ee).

IR (KBr): 3313, 2953, 1739, 1589, 1545, 1367, 1216, 1171, 750, 704 cm^{-1}.

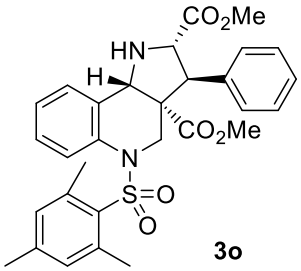
^1H NMR (500 MHz, $CDCl_3$): δ 3.12 (d, *J* = 11.4 Hz, 1 H), 3.31 (s, 3 H), 3.53 (br s, 1 H), 3.75 (s, 3 H), 3.93 (d, *J* = 5.1 Hz, 1 H), 3.96 (d, *J* = 11.4 Hz, 1 H), 4.04 (br s, 1 H), 4.46 (d, *J* = 4.9 Hz, 1 H), 7.12–7.14 (m, 2 H), 7.19–7.25 (m, 2 H), 7.31–7.35 (m, 4 H), 7.48–7.49 (m, 1 H), 7.53–7.60 (m, 2 H), 7.65–7.70 (m, 2 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 50.8, 52.2, 52.5, 57.3, 60.0, 65.0, 69.5, 122.5, 123.9, 124.5, 125.5, 127.9, 128.1, 128.5, 129.4, 129.8, 130.9, 131.7, 132.0, 133.7, 134.6, 137.9, 148.0, 172.2, 173.3.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{27}H_{25}N_3NaO_8S$, 574.1255; found, 574.1260.

The enantiomeric excess was determined by HPLC analysis to be 80% ee, t_R = 25.0 min (minor), t_R = 40.4 min (major) (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 1/2, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-5-(2,4,6-trimethylbenzene-1-sulfonyl)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3o)



3o

75% yield (41.1 mg, 0.075 mmol). White amorphous solid.

$[\alpha]_D^{22}$ +132.3 (*c* 1.00, $CHCl_3$, 81% ee).

IR (KBr): 3308, 2952, 1742, 1604, 1487, 1347, 1246, 1217, 1162, 758, 727, 704 cm^{-1}.

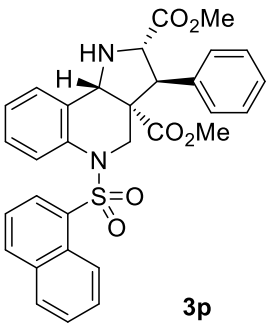
^1H NMR (500 MHz, $CDCl_3$): δ 2.09 (s, 6 H), 2.33 (s, 3 H), 2.67 (d, *J* = 11.1 Hz, 1 H), 3.27 (s, 3 H), 3.50 (br s, 1 H), 3.73 (s, 3 H), 3.80 (d, *J* = 11.1 Hz, 1 H), 3.82 (br s, 1 H), 3.88 (d, *J* = 5.1 Hz, 1 H), 4.37 (br s, 1 H), 6.82 (s, 2 H), 6.94 (br d, *J* = 7.2 Hz, 2 H), 7.16 (dt, *J* = 7.5, 1.0 Hz, 1 H), 7.22–7.32 (m, 5 H), 7.51 (dd, *J* = 8.0, 0.9 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 20.9, 22.8, 48.5, 52.1, 52.5, 57.2, 60.2, 65.2, 69.5, 122.2, 124.8, 124.9, 127.70, 127.71, 128.1, 129.2, 129.7, 132.2, 133.0, 136.3, 138.2, 139.9, 142.2, 172.2, 173.4.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{30}H_{32}N_2NaO_6S$, 571.1873; found, 571.1881.

The enantiomeric excess was determined by HPLC analysis to be 81% ee, t_R = 14.6 min (minor), t_R = 35.0 min (major) (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 1/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (2*S*,3*S*,3a*R*,9b*S*)-5-(naphthalene-1-sulfonyl)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (3p)



3p

77% yield (42.7 mg, 0.077 mmol). White amorphous solid.

$[\alpha]_D^{22}$ +70.3 (*c* 1.00, $CHCl_3$, 89% ee).

IR (KBr): 3318, 2953, 1739, 1604, 1488, 1352, 1246, 1214, 1164, 806, 759, 724, 705 cm^{-1}.

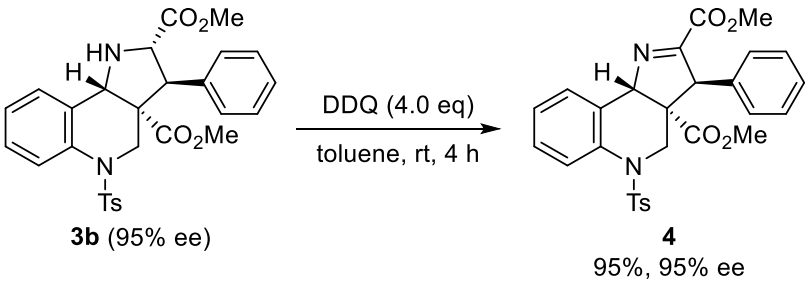
^1H NMR (500 MHz, $CDCl_3$): δ 2.81 (d, *J* =11.6 Hz, 1 H), 3.20 (br s, 1 H), 3.28 (s, 3 H), 3.32 (br s, 1 H), 3.68 (s, 3 H), 3.78 (d, *J* = 5.2 Hz, 1 H), 3.90 (d, *J* =11.6 Hz, 1 H), 4.12 (d, *J* = 3.7 Hz, 1 H), 6.72 (br d, *J* = 7.2 Hz, 2 H), 7.11 (br d, *J* = 7.5 Hz, 1 H), 7.15–7.25 (m, 4 H), 7.28–7.31 (m, 1 H), 7.34–7.37 (m, 1 H), 7.42–7.47 (m, 2 H), 7.71 (br d, *J* = 8.7 Hz, 1 H), 7.77 (br d, *J* = 8.1 Hz, 1 H), 7.86 (br d, *J* = 8.2 Hz, 1 H), 7.88 (dd, *J* = 7.3, 1.1 Hz, 1 H), 8.05 (br d, *J* = 8.2 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 49.9, 52.1, 52.4, 57.0, 60.5, 64.9, 69.5, 122.2, 124.0, 124.5, 125.5, 125.8, 127.0, 127.7, 127.8, 127.9, 128.1, 128.2, 128.6, 129.2, 130.2, 130.6, 133.6, 134.15, 134.17, 135.3, 138.0, 172.0, 173.3.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{31}H_{28}N_2NaO_6S$, 579.1560; found, 579.1567.

The enantiomeric excess was determined by HPLC analysis to be 89% ee, t_R = 26.9 min (minor), t_R = 40.4 min (major) (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 2/1, flow rate = 0.5 mL/min, λ = 254 nm).

Dimethyl (3*S*,3a*R*,9b*S*)-5-(4-methylbenzene-1-sulfonyl)-3-phenyl-3a,4,5,9b-tetrahydro-3*H*-pyrrolo[3,2-*c*]quinoline-2,3a-dicarboxylate (4).



3b (95% ee) **4** 95%, 95% ee

Using the procedure in the literature,[12] **4** was prepared. To a solution of **3b** (26.0 mg, 0.050 mmol) in toluene (0.50 mL) was added DDQ (46.8 mg, 0.20 mmol). The reaction mixture was stirred for 3 h at rt. The reaction was quenched by the addition of sat. $NaHCO_3$ aq. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : EtOAc : CH_2Cl_2 = 3 : 1 : 1) to give **4** (24.7 mg, 0.0476 mmol, 95%) as white amorphous solid.

$[\alpha]_D^{22}$ +101.3 (*c* 0.500, $CHCl_3$, 95% ee).

IR (KBr): 2954, 1736, 1621, 1602, 1363, 1273, 1234, 1168, 814, 734, 705 cm^{-1}.

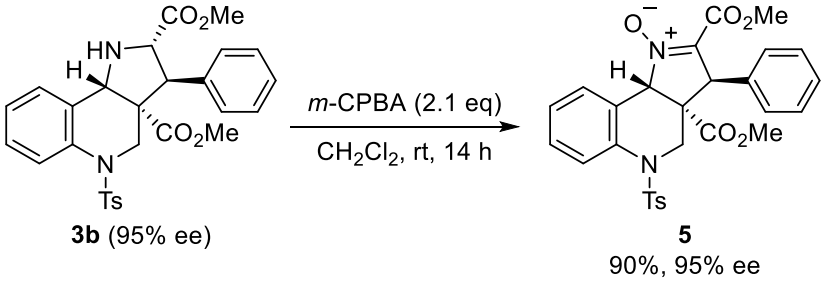
^1H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 3 H), 2.66 (d, J = 12.8 Hz, 1 H), 3.71 (s, 3 H), 3.77 (s, 3 H), 4.46 (s, 1 H), 4.61 (d, J = 12.8 Hz, 1 H), 5.27 (d, J = 1.1 Hz, 1 H), 7.11–7.15 (m, 3 H), 7.24 (br d, J = 8.1 Hz, 2 H), 7.28–7.34 (m, 4 H), 7.46 (br d, J = 8.5 Hz, 1 H), 7.60 (br d, J = 8.4 Hz, 2 H), 8.31 (dd, J = 7.9, 1.6 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.5, 51.1, 52.7, 53.1, 54.2, 62.0, 79.3, 119.1, 120.6, 123.5, 126.8, 127.75, 127.82, 128.1, 129.2, 129.9, 132.4, 137.1, 137.2, 139.1, 144.2, 168.5, 170.7, 171.3.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{26}N_2NaO_6S$, 541.1404; found, 541.1408.

The enantiomeric excess was determined by HPLC analysis to be 95% ee, t_R = 13.4 min (minor), t_R = 17.7 min (major) (Chiralpak AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 1/1, flow rate = 0.5 mL/min).

(3*S*,3a*R*,9b*S*)-2,3a-Dimethoxycarbonyl-5-(4-methylbenzene-1-sulfonyl)-3-phenyl-3a,4,5,9b-tetrahydro-3*H*-pyrrolo[3,2-*c*]quinoline 1-oxide (**5**).



3b (95% ee) → **5** 90%, 95% ee

Using the procedure in the literature,[13] **5** was prepared. To a solution of **3b** (26.0 mg, 0.050 mmol) in CH_2Cl_2 (1.3 mL) was added *m*-CPBA (65%, 27.9 mg, 0.105 mmol). The reaction mixture was stirred for 14 h at rt. The reaction was quenched by the addition of sat. $NaHCO_3$ aq. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : EtOAc : CH_2Cl_2 = 6 : 1 : 5) to give **5** (24.0 mg, 0.0449 mmol, 90%) as white amorphous solid.

$[\alpha]_D^{22}$ +107.0 (*c* 0.500, $CHCl_3$, 95% ee).

IR (KBr): 2953, 1742, 1597, 1563, 1353, 1245, 1228, 1166, 803, 761, 732, 703 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3 H), 2.59 (d, J = 12.9 Hz, 1 H), 3.74 (s, 3 H), 3.85 (s, 3 H), 4.49–4.52 (m, 2 H), 4.93 (d, J = 1.0 Hz, 1 H), 7.20–7.23 (m, 3 H), 7.25–7.27 (m, 2 H), 7.29–7.39 (m, 5 H), 7.61 (br d, J = 8.4 Hz, 2 H), 9.46 (dd, J = 8.1, 1.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 21.5, 48.6, 50.7, 53.5, 53.6, 57.2, 81.9, 117.9, 119.4, 124.0, 126.6, 127.3, 127.5, 128.8, 129.6, 130.0, 131.3, 135.2, 135.8, 136.1, 137.9, 144.2, 167.5, 171.1.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{27}N_2O_7S$, 535.1533; found, 535.1535.

The enantiomeric excess was determined by HPLC analysis to be 95% ee, t_R = 17.1 min (minor), t_R = 30.4 min (major) (Chiralpak AS-H, λ = 254 nm, *n*-hexane/*i*-PrOH = 1/1, flow rate = 0.5 mL/min).

3. X-ray crystallographic data for 3a

The single crystals of compound **3a** (>99% ee) suitable for X-ray diffraction study were obtained by recrystallization from hexane, Et_2O and CH_2Cl_2 at rt. The X-ray diffraction experiment of **3a** was conducted with CuKα radiation at 103.15 K. Using Olex2[14], the structure was solved with the SHELXT[15] structure solution program using Intrinsic Phasing and refined with the SHELXL[16] refinement package using Least Squares minimization.

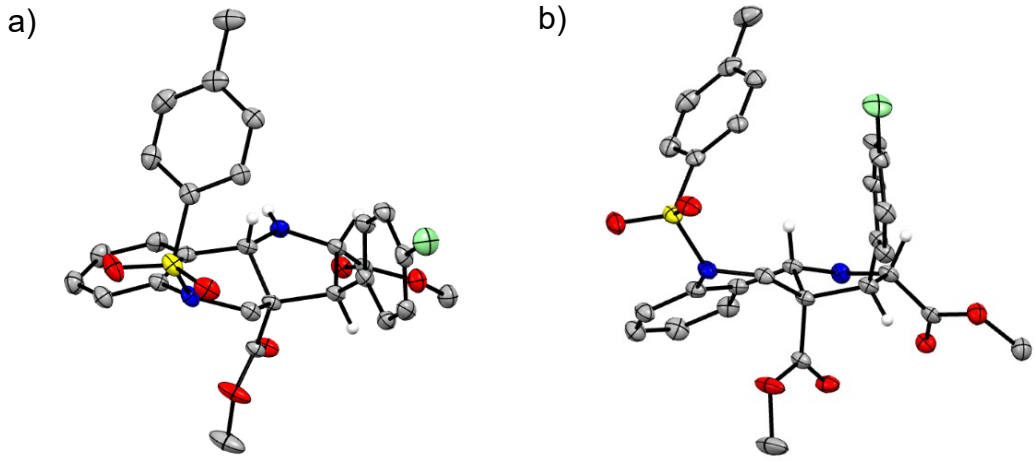


Figure S1. POV-Ray drawing of **3a** with 50% ellipsoid probability.
Hydrogen atoms except for important ones are omitted for clarity.
(a) Top view and (b) front view.

Table S1. Crystallographic Parameters for Compound **3a**

Formula	$C_{28}H_{27}ClN_2O_6S$	d_{calc}, g/cm^3	1.405
Formula Wight	555.02	μ, mm^{-1}	2.426
Crystal System	orthorhombic	F_{000}	1160.0
a, Å	9.28230(10)	Reflection collected	52731
b, Å	10.48500(10)	Data/restraints/parameters	5453/0/346
c, Å	26.9650(2)	Goodness-of-fit on F^2	1.049
α, degree	90	Final R indexes [I>=2σ (I)] R_1	0.0299
β, degree	90	Final R indexes [I>=2σ (I)] wR_2	0.0807
γ, degree	90	Final R indexes [all data] R_1	0.0301
V, Å^3	2624.37(4)	Final R indexes [all data] wR_2	0.0809
Space Group	$P2_12_12_1$	Largest diff. peak/hole / e Å^{-3}	0.54/ –0.47
Z	4	Flack parameter	0.000(2)

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 2214513. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

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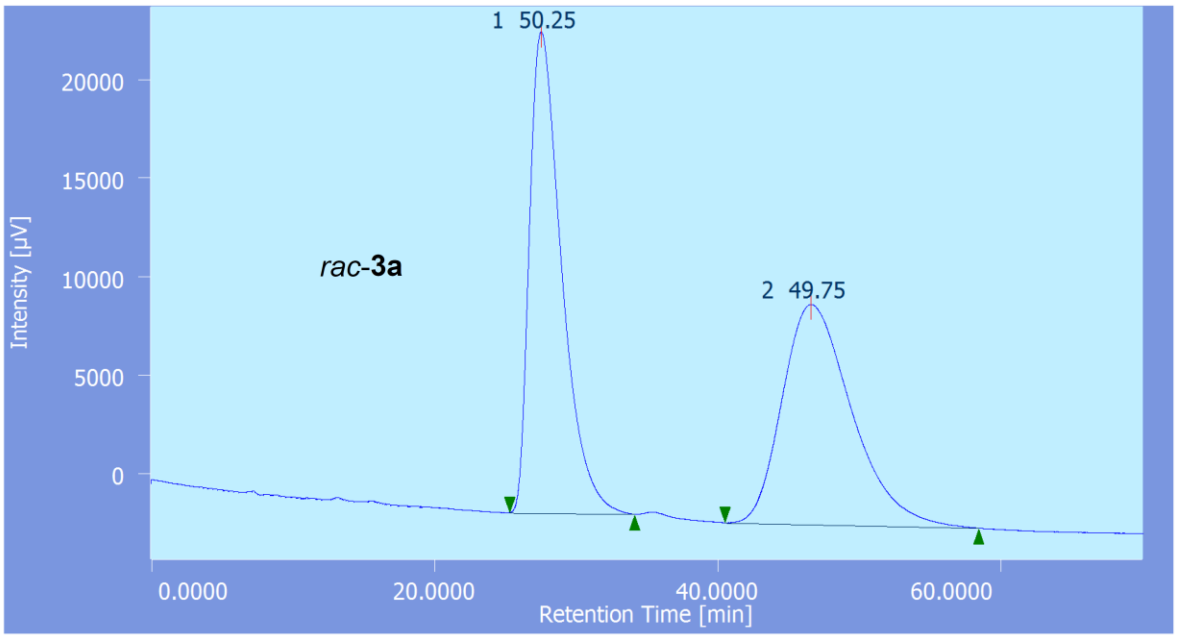
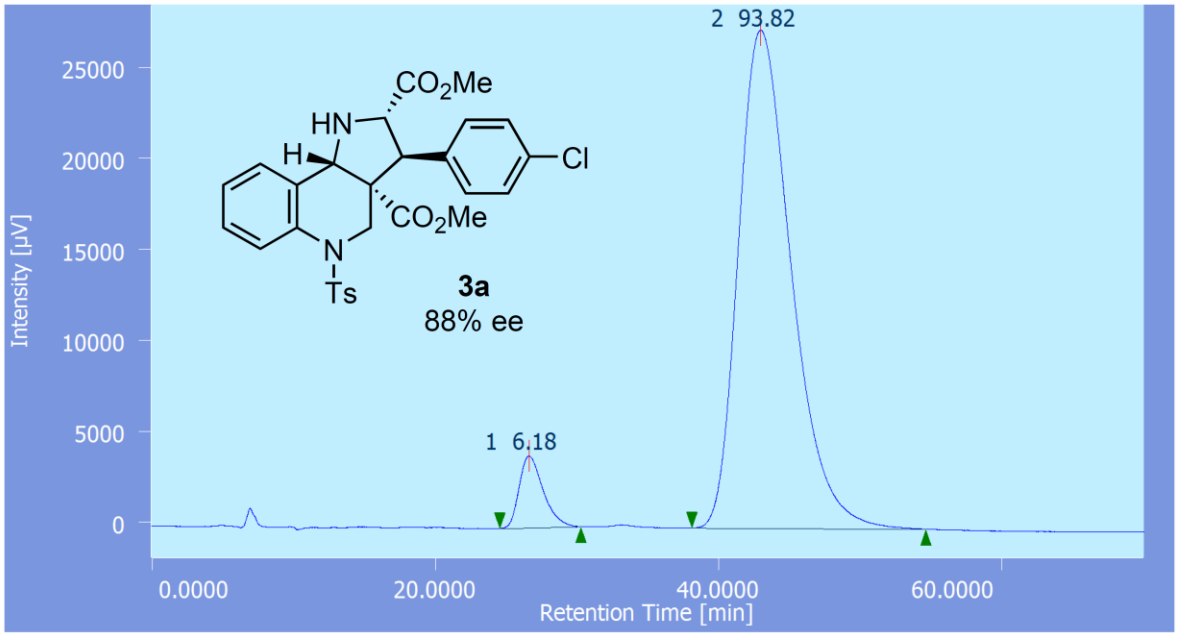
5. Copy of HPLC charts

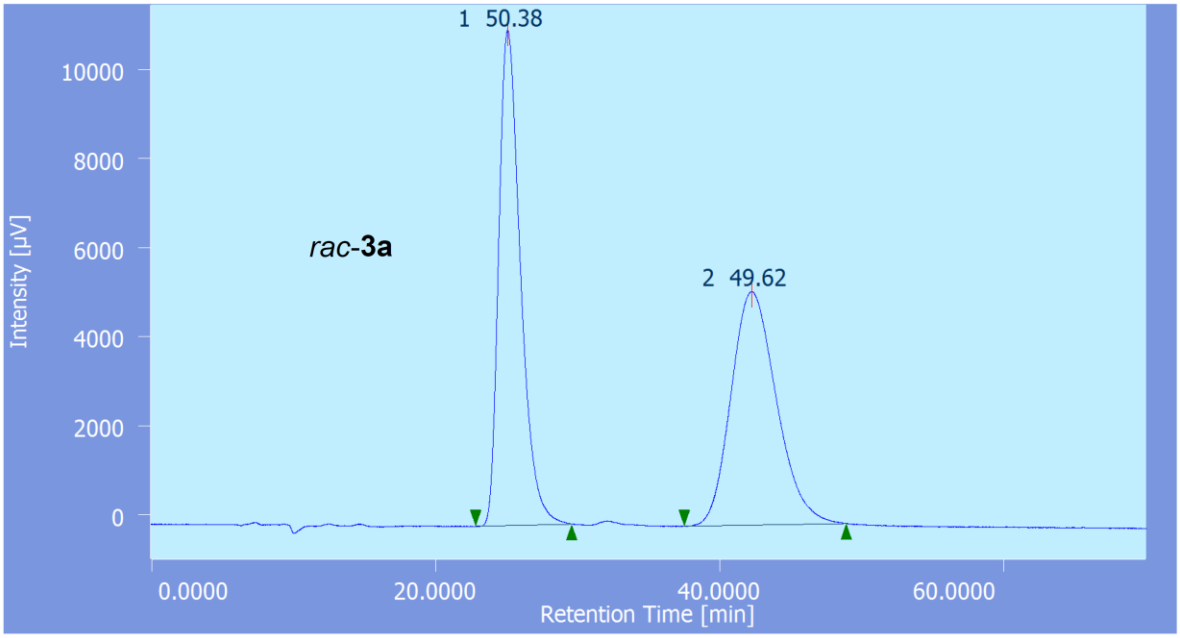
Cycloadduct **3a**

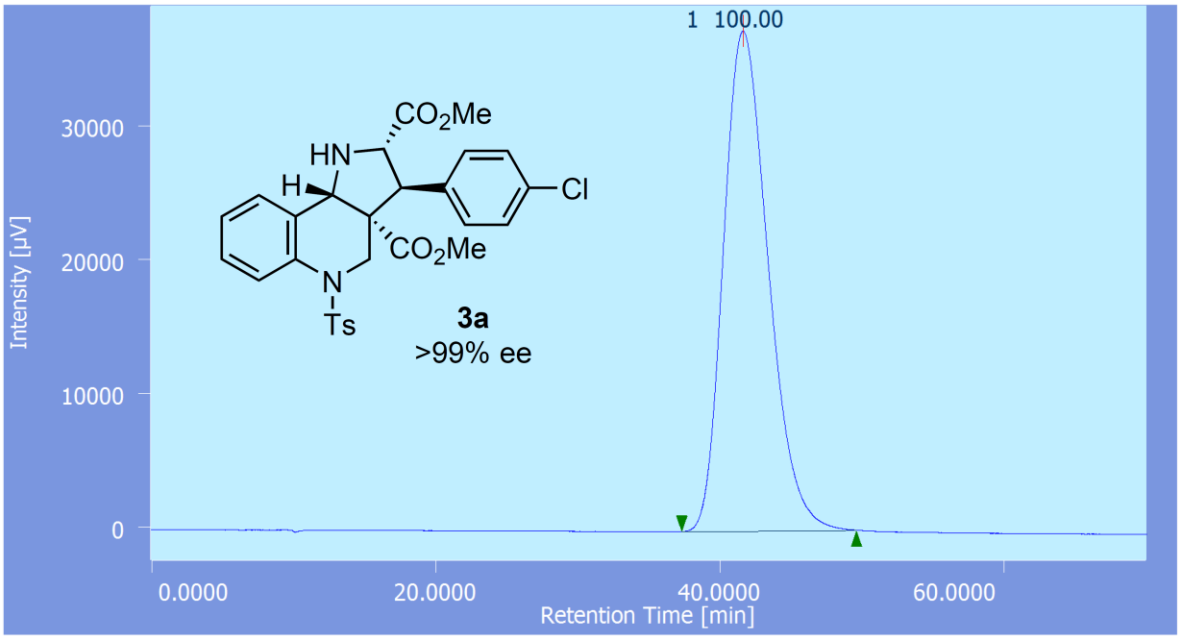




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 26.6 min, 42.9 min

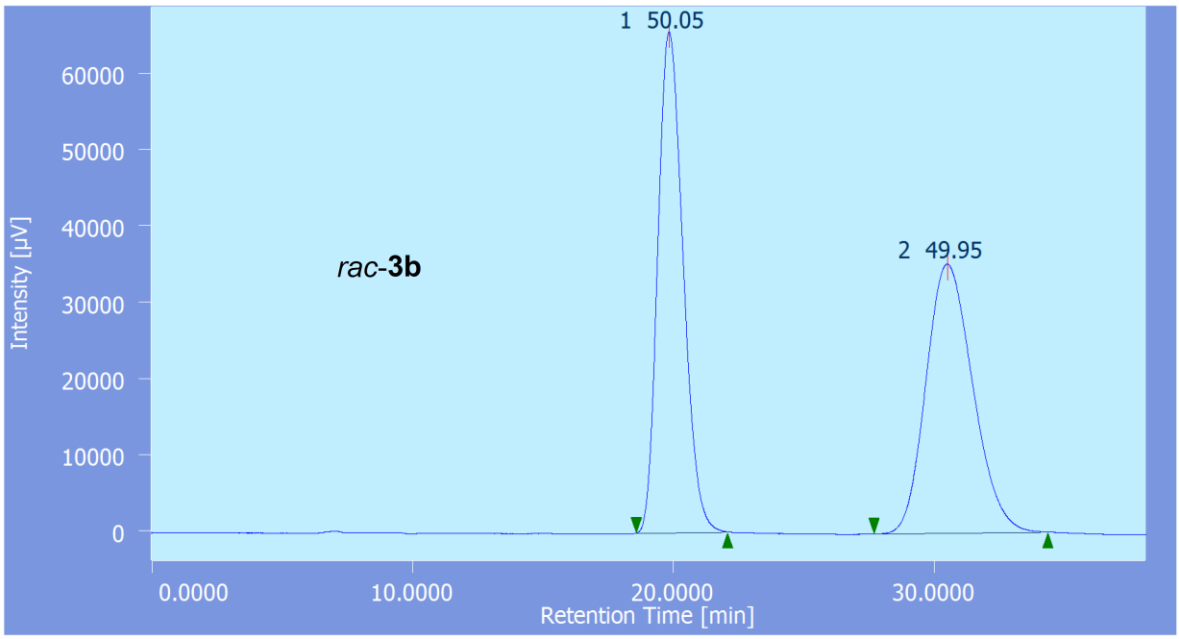
Cycloadduct **3a** (after recrystallization)

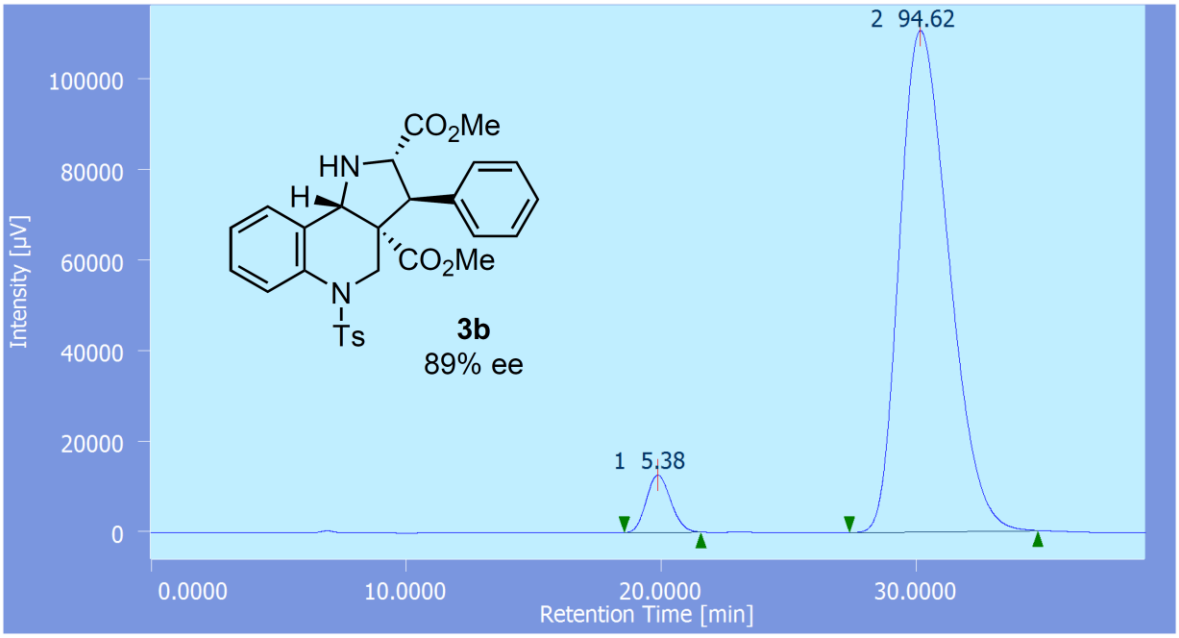




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 41.6 min

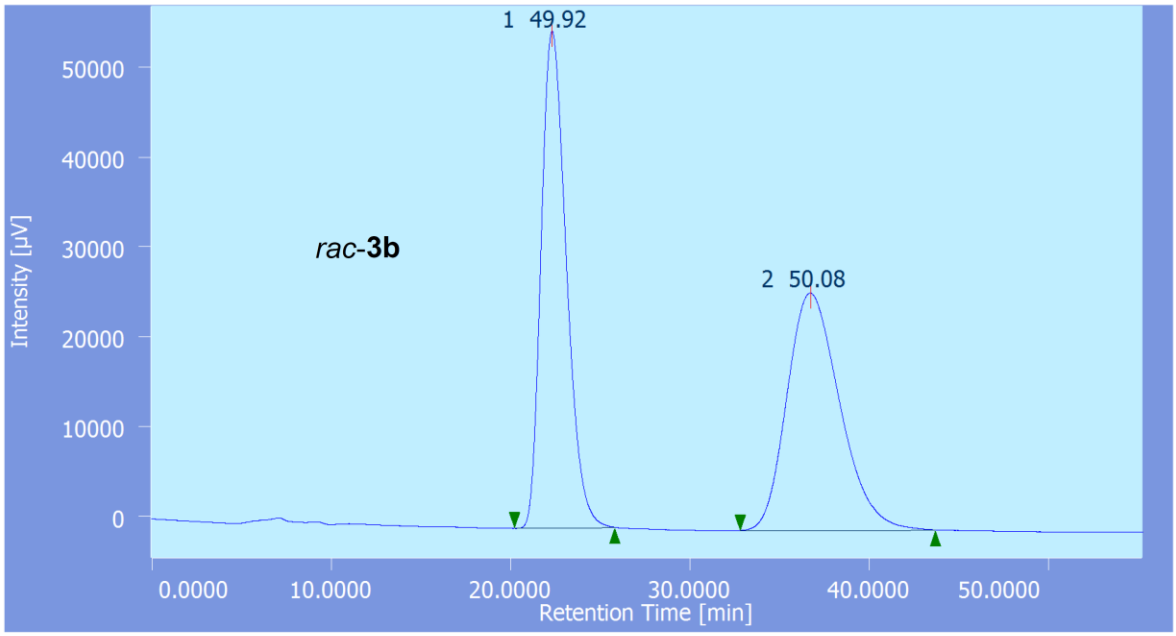
Cycloadduct **3b**

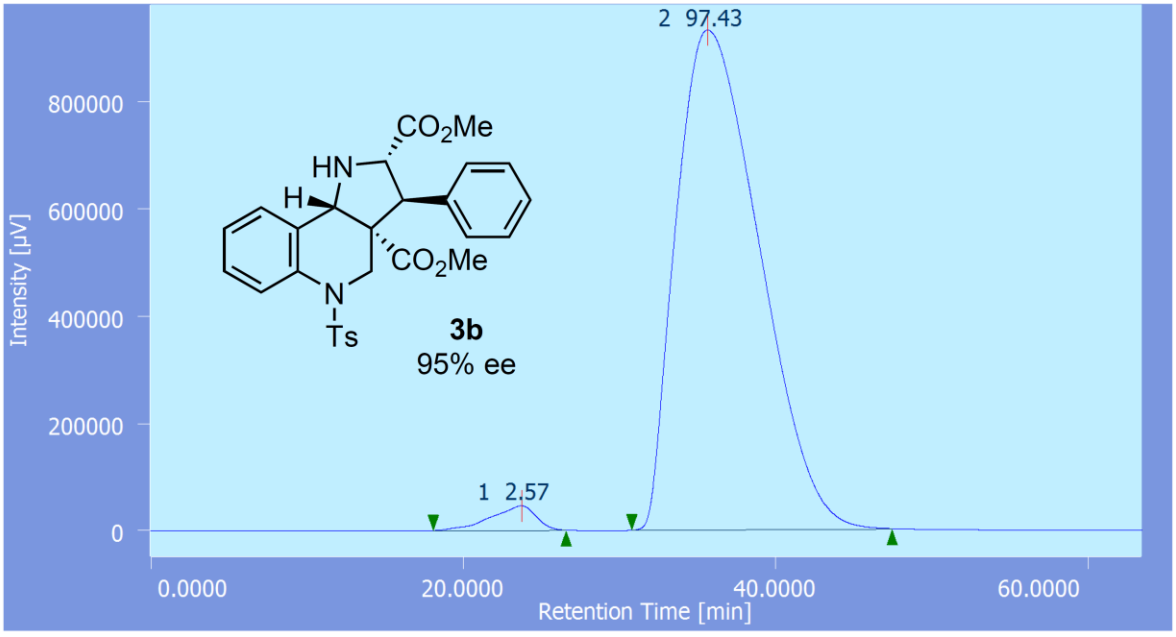




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 19.9 min, 30.1 min

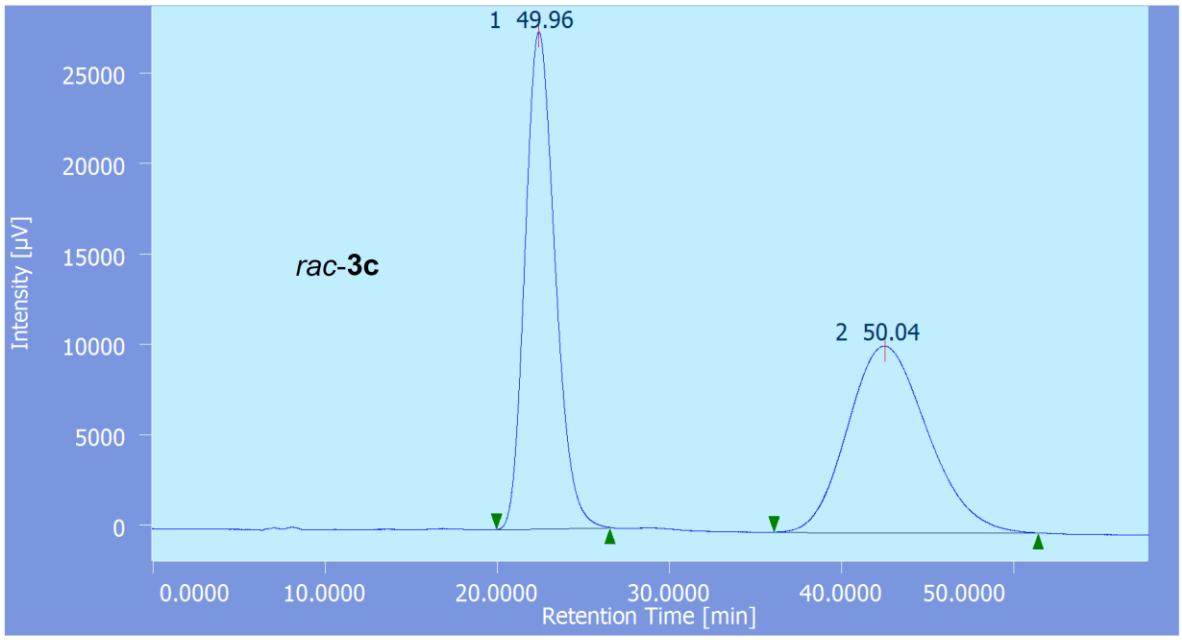
Cycloadduct **3b** (after recrystallization)

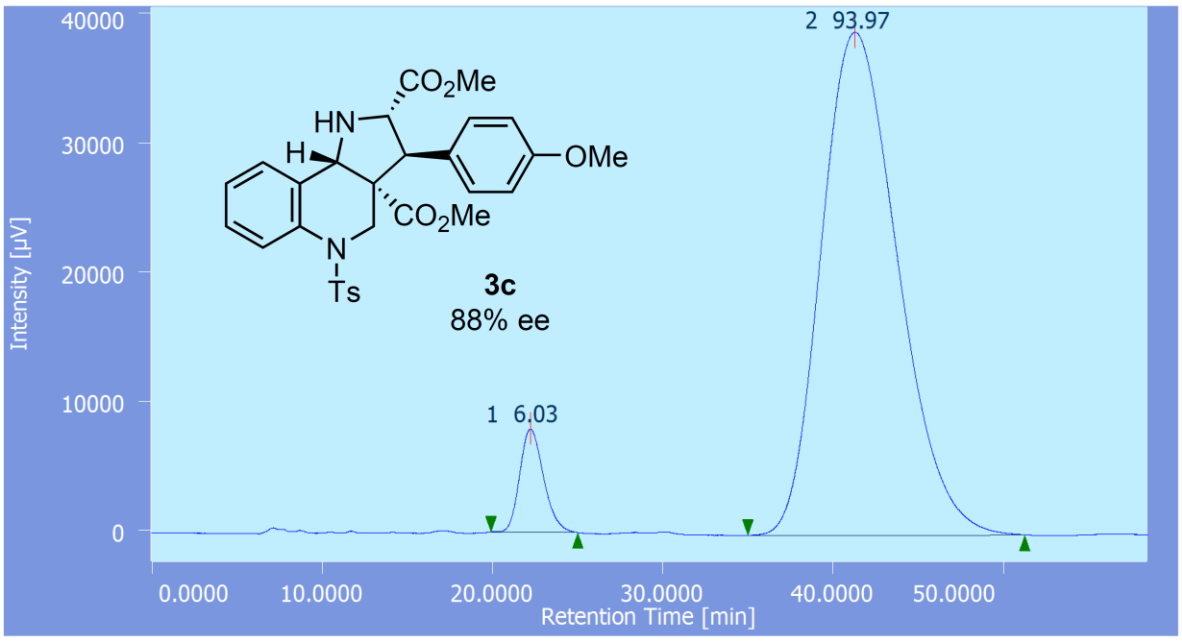




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 23.7 min, 35.6 min

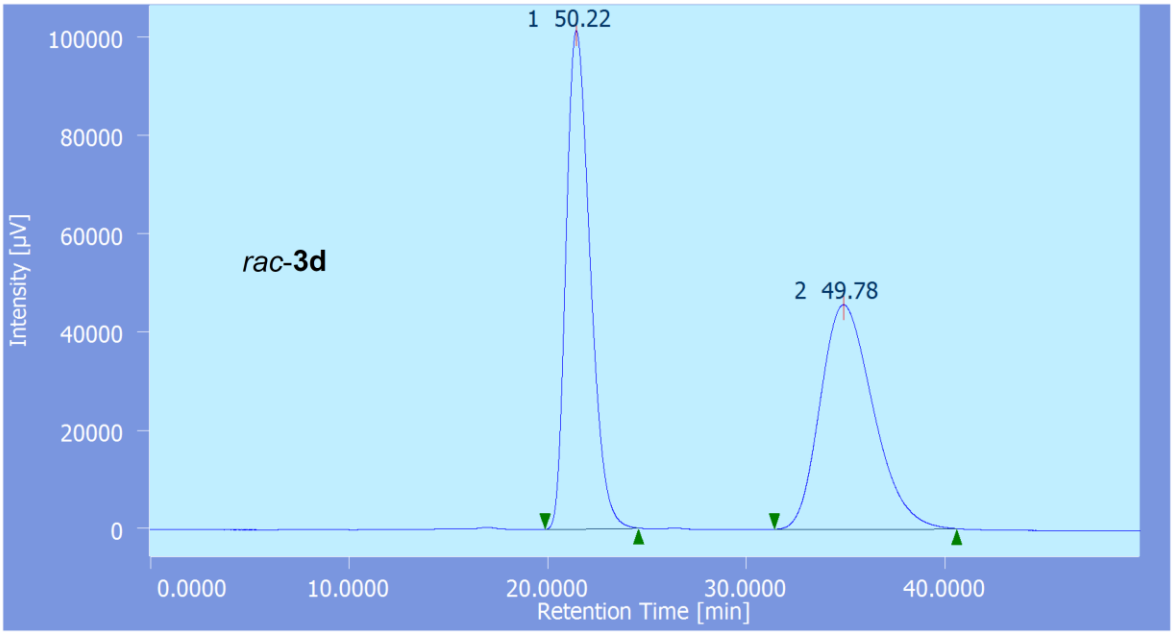
Cycloadduct **3c**

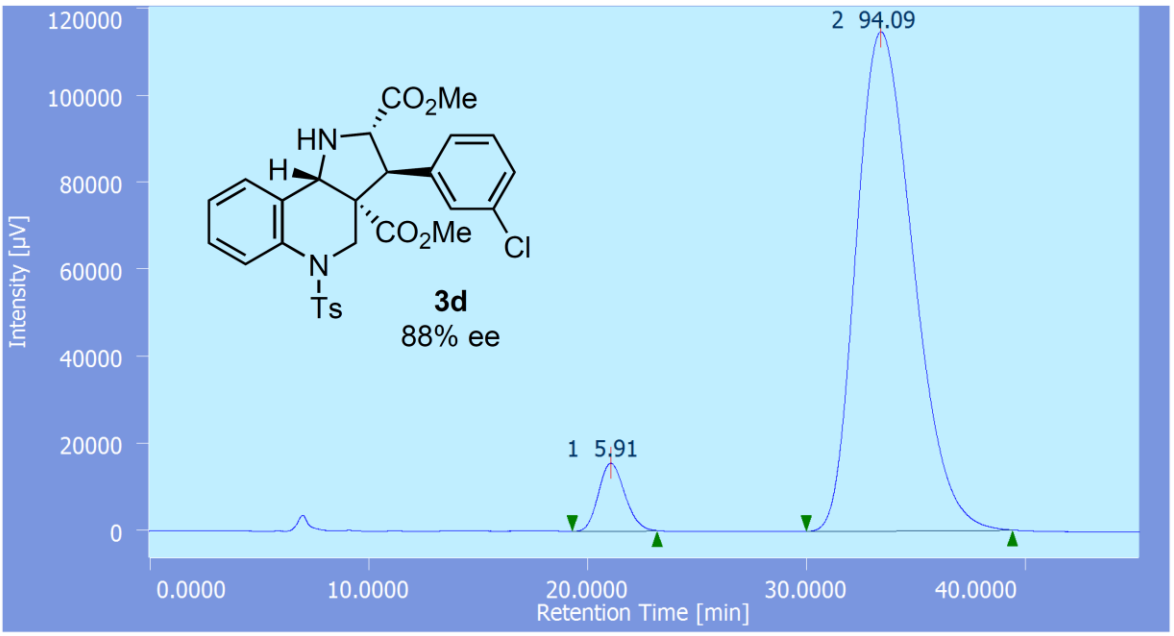




Chiralpak AS-H, Hexane/*i*-PrOH = 1/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 22.2 min, 41.3 min

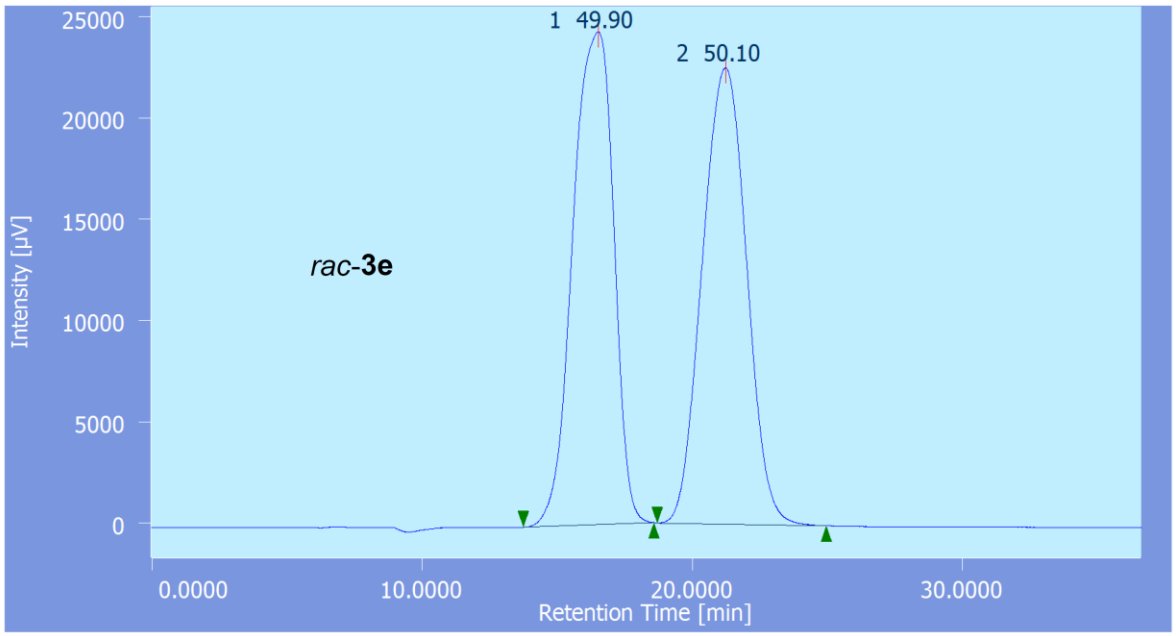
Cycloadduct **3d**

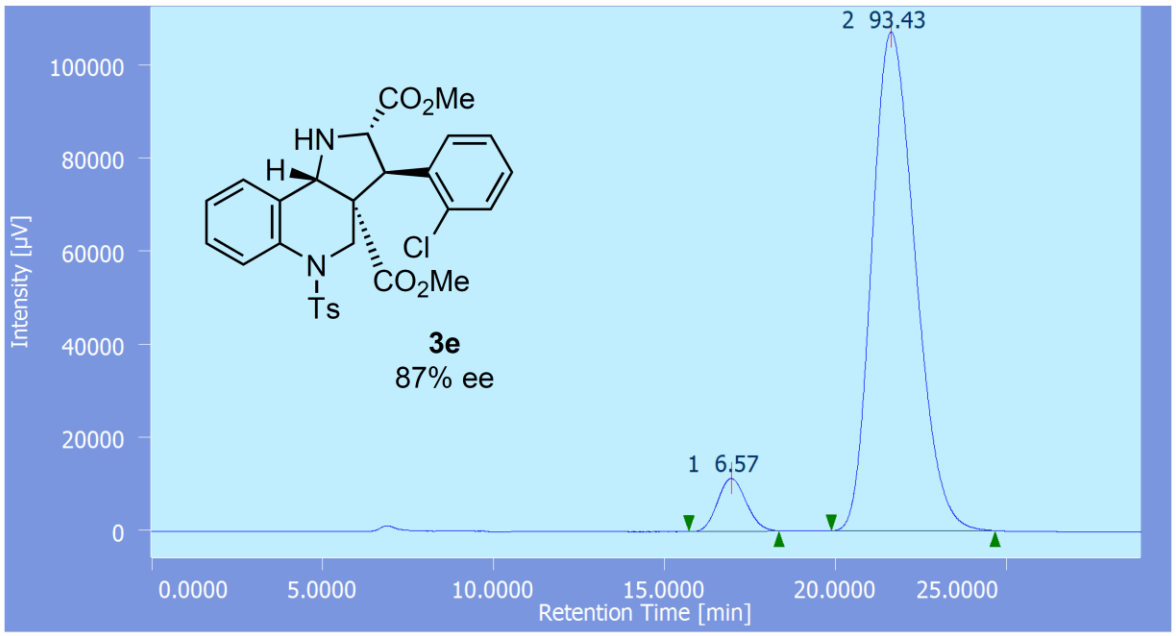




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 21.0 min, 33.4 min

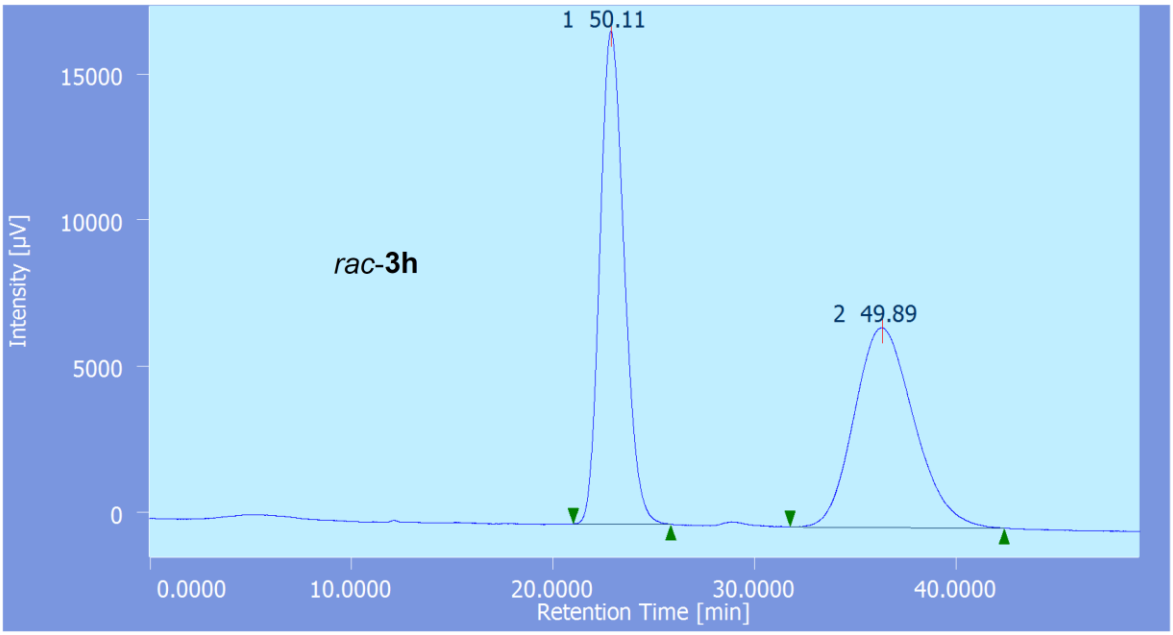
Cycloadduct **3e**

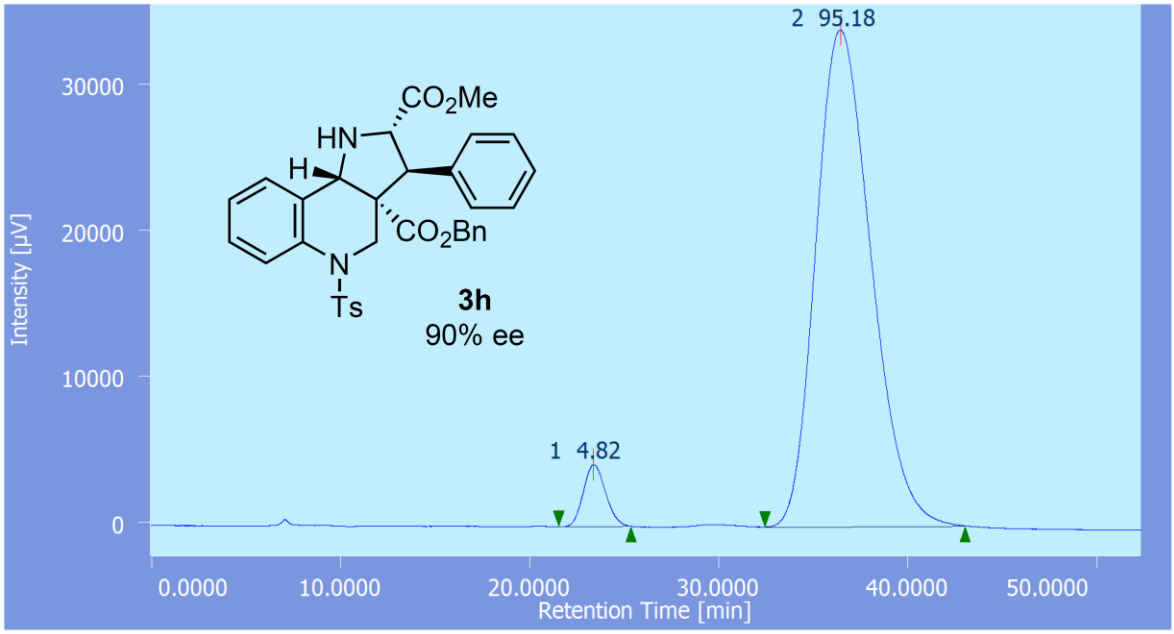




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 16.9 min, 21.6 min

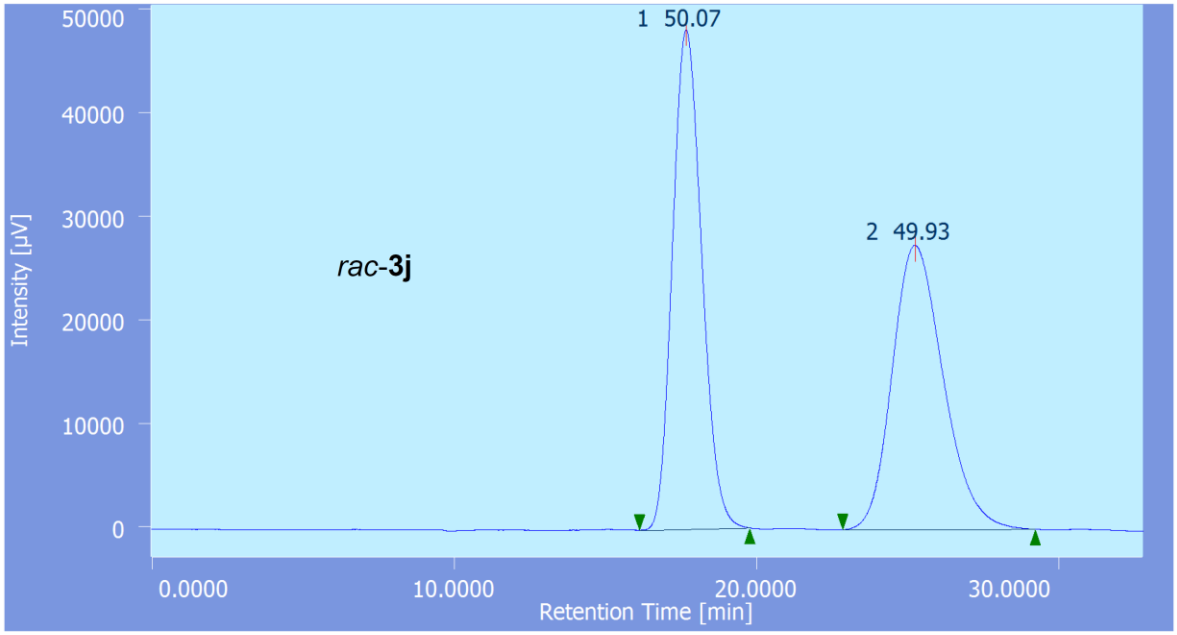
Cycloadduct **3h**

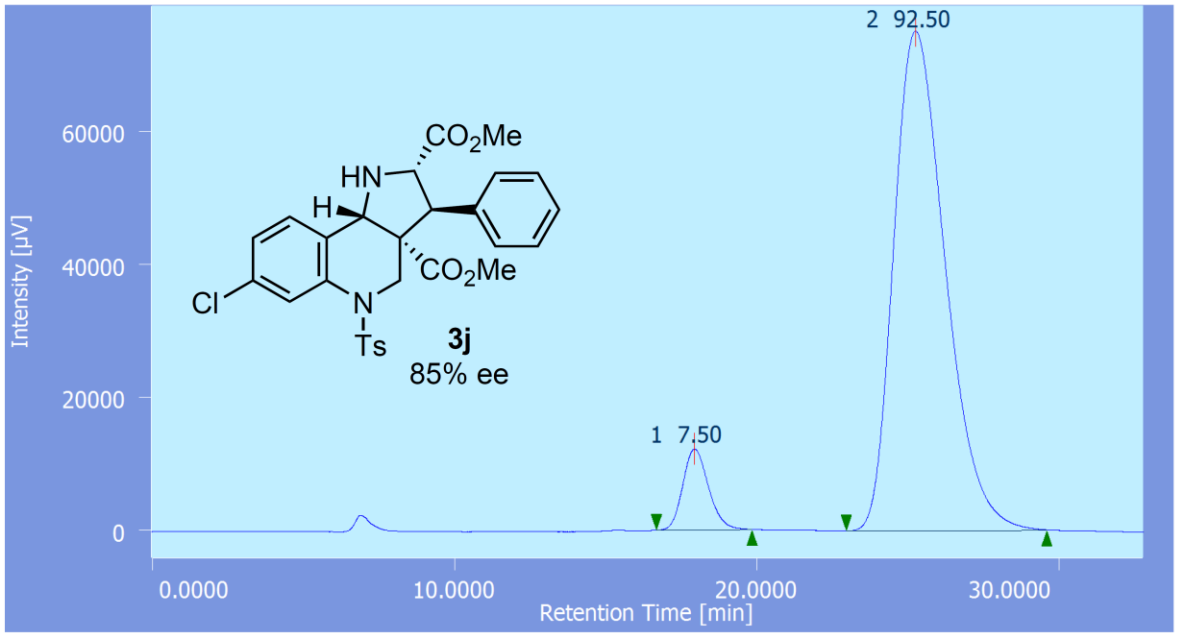




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 23.4 min, 36.4 min

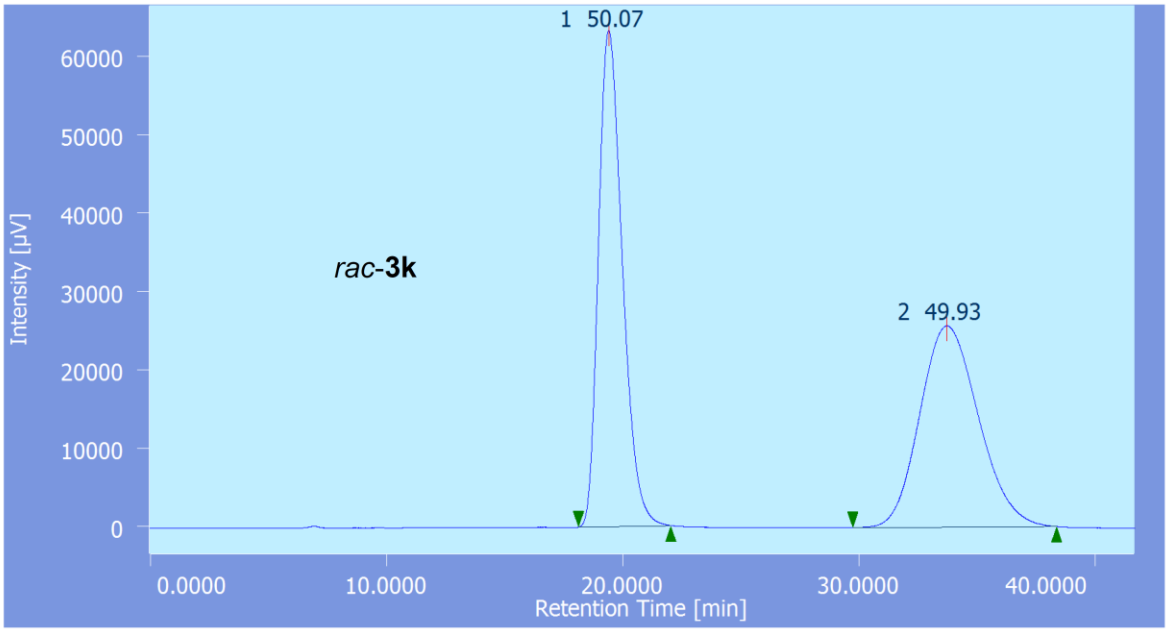
Cycloadduct **3j**

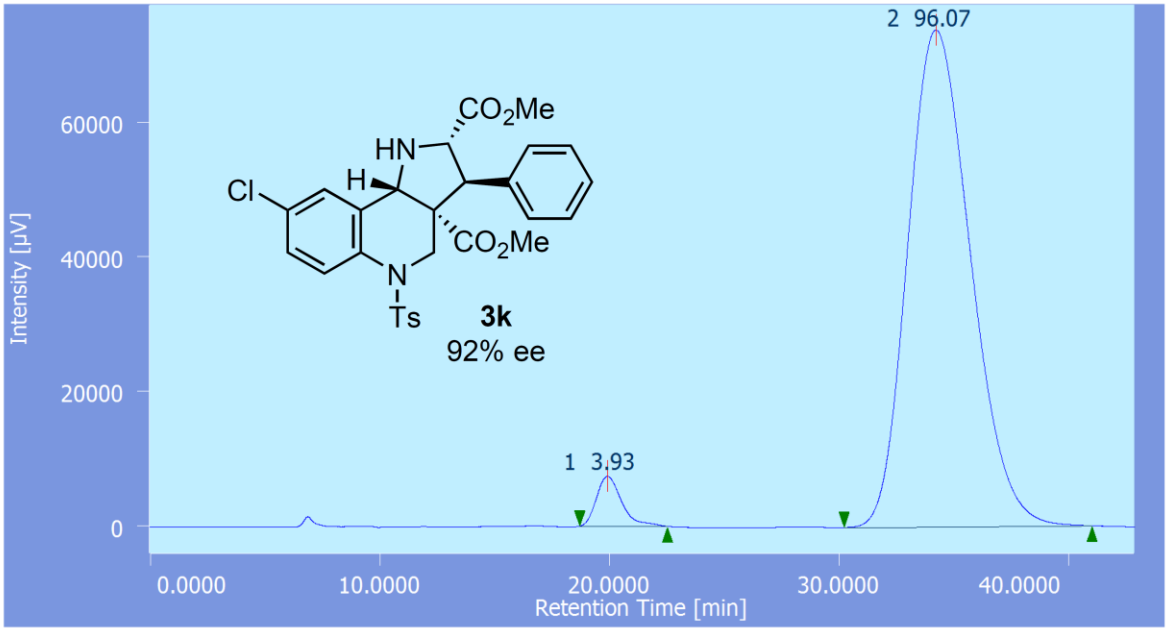




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 17.9 min, 25.2 min

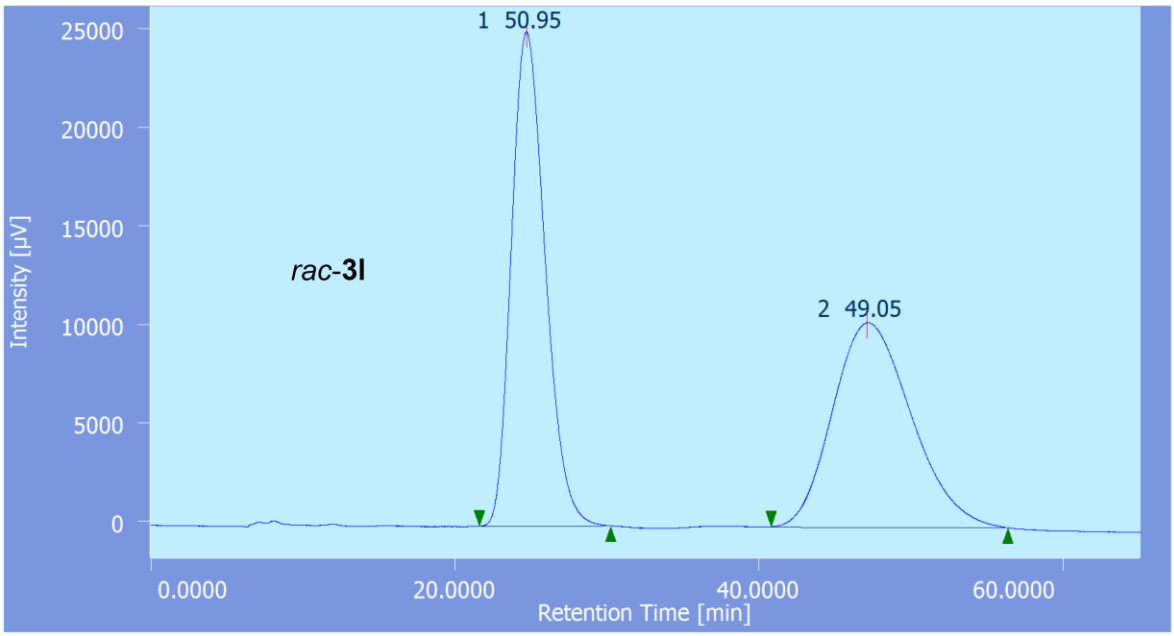
Cycloadduct **3k**

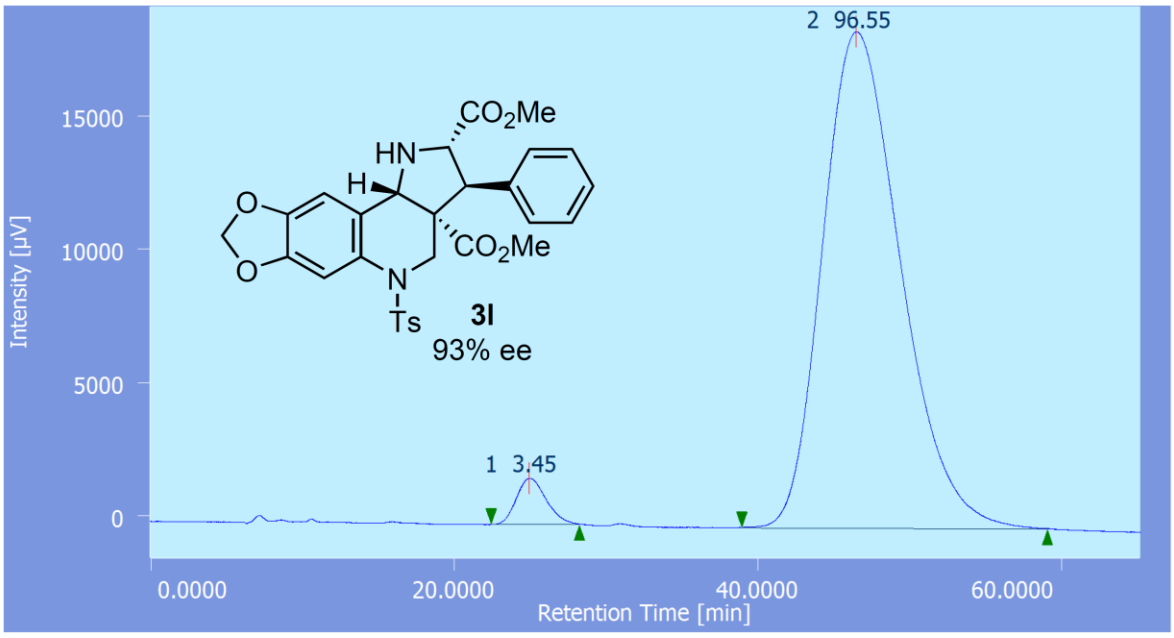




Chiralpak AS-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 19.9 min, 34.2 min

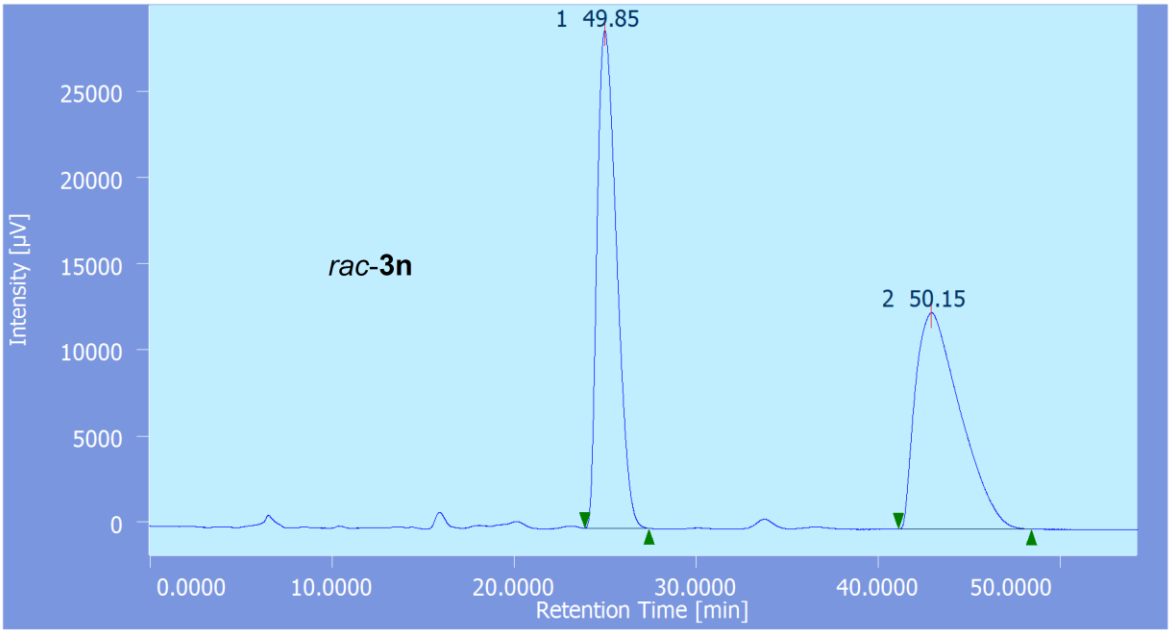
Cycloadduct **3l**

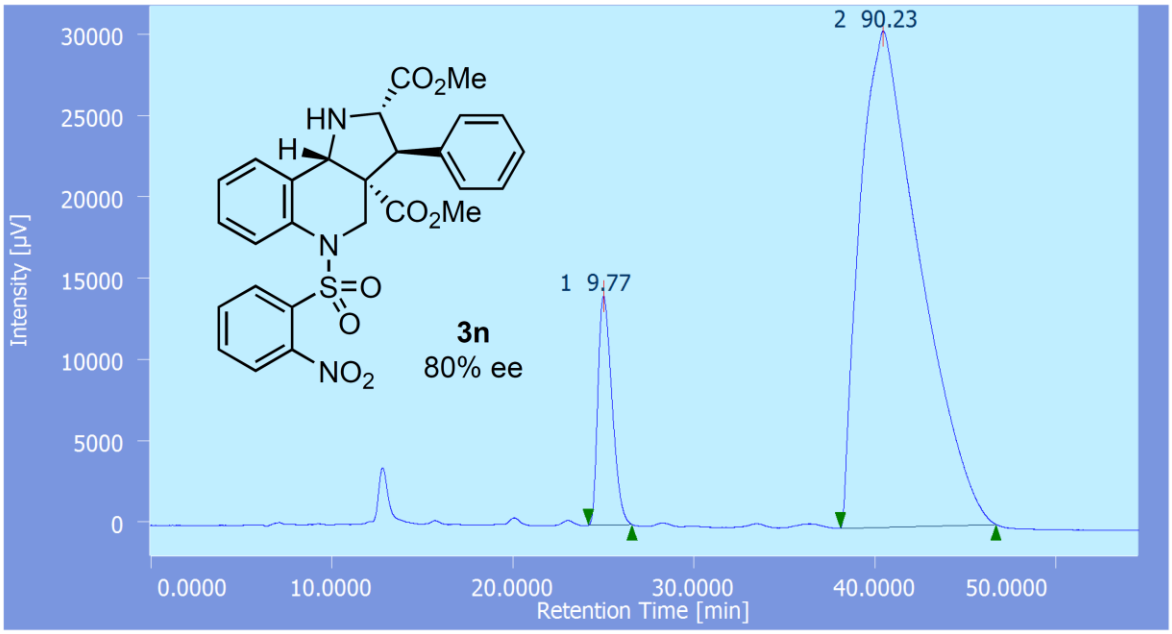




Chiralpak AS-H, Hexane/*i*-PrOH = 1/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 24.9 min, 46.4 min

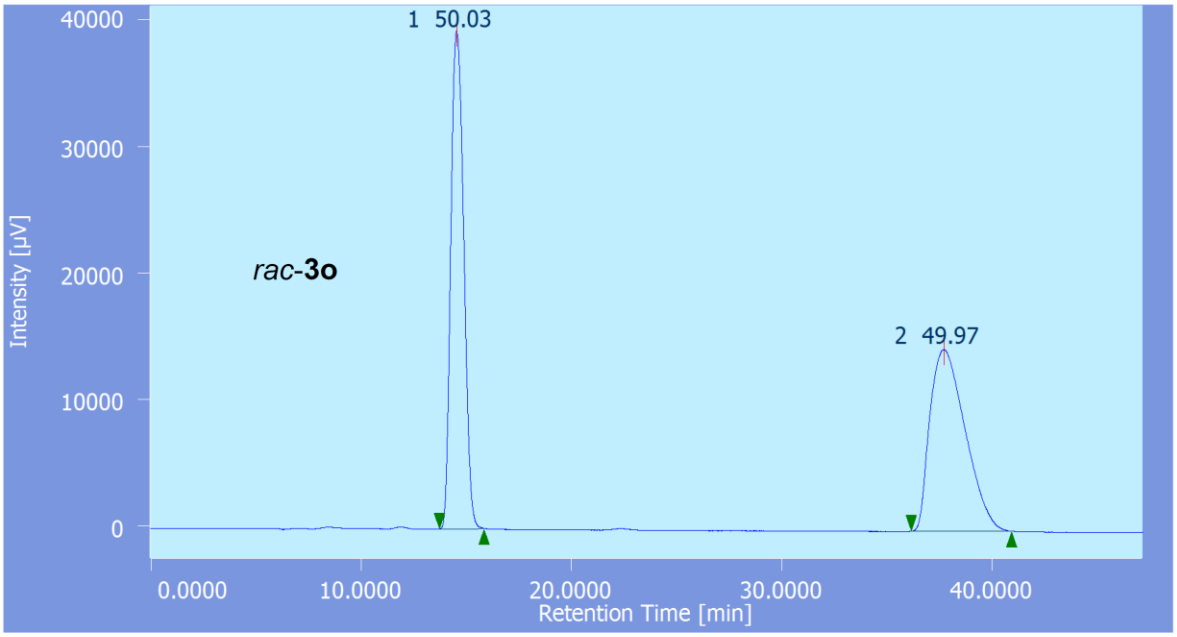
Cycloadduct **3n**

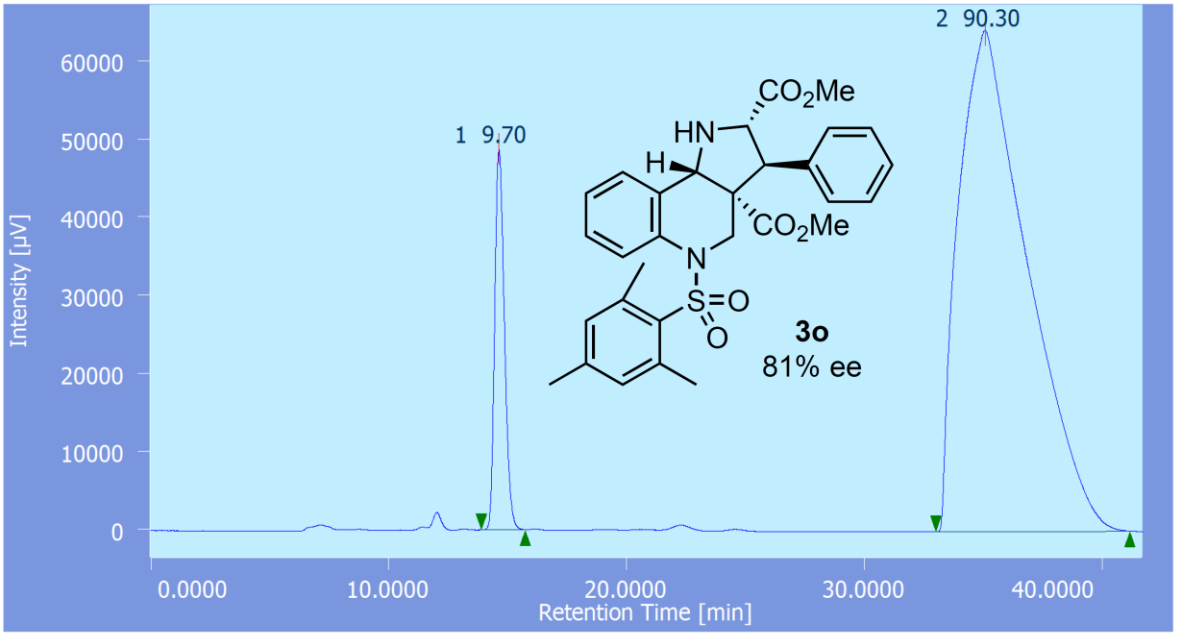




Chiralpak AD-H, Hexane/*i*-PrOH = 1/2, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 25.0 min, 40.4 min

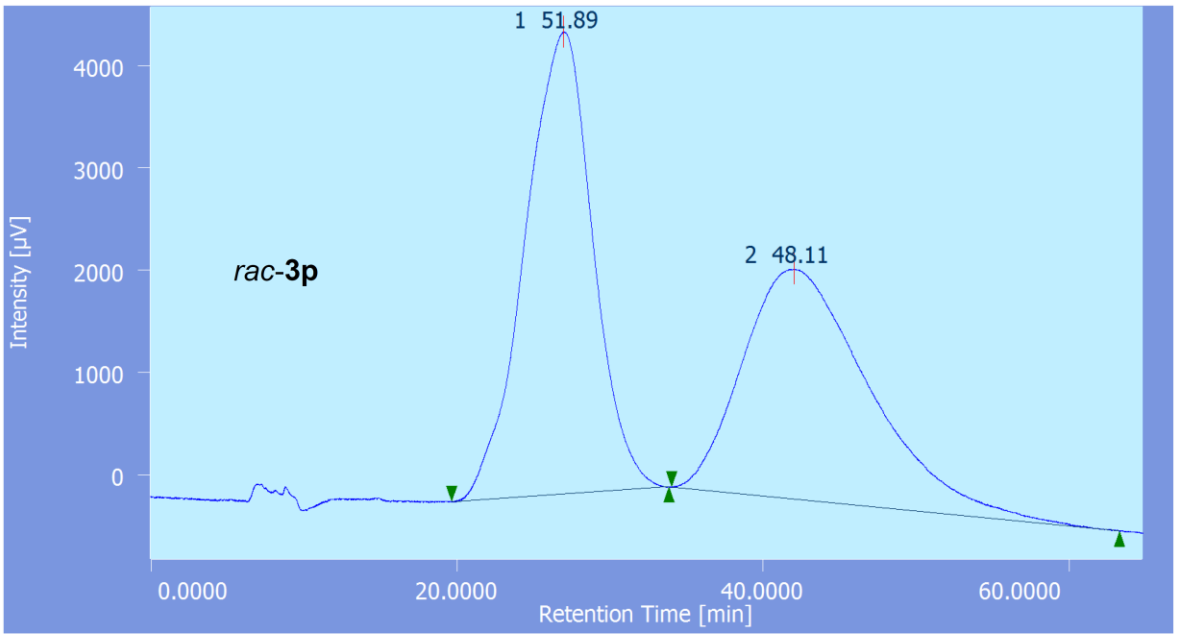
Cycloadduct **3o**

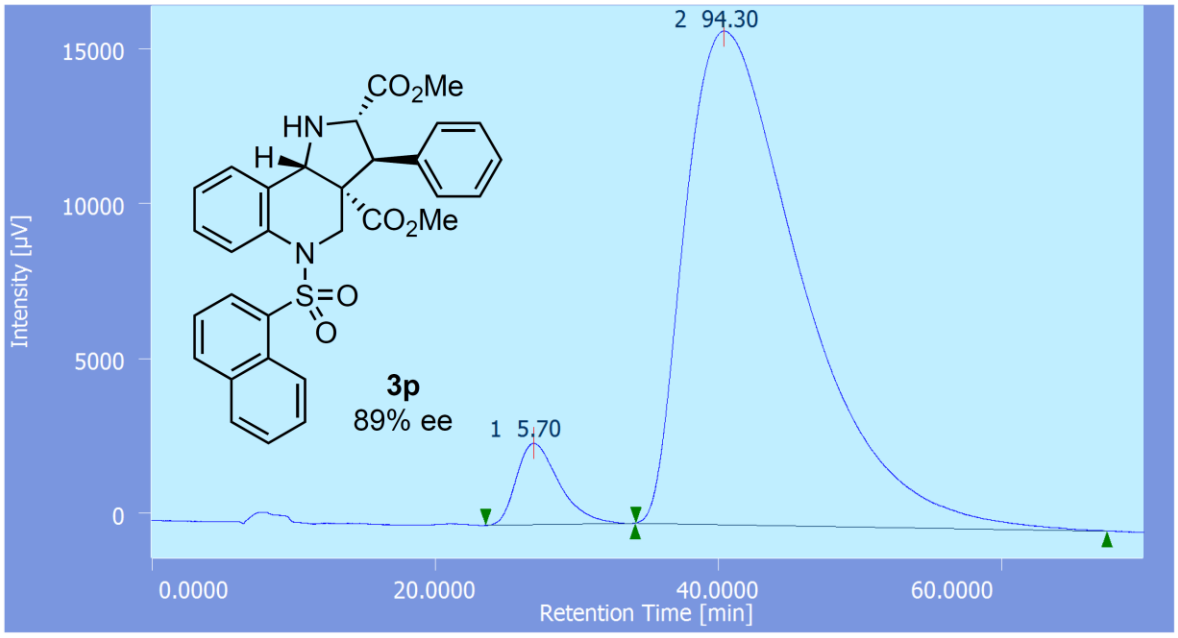




Chiralpak AD-H, Hexane/*i*-PrOH = 1/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 14.6 min, 35.0 min

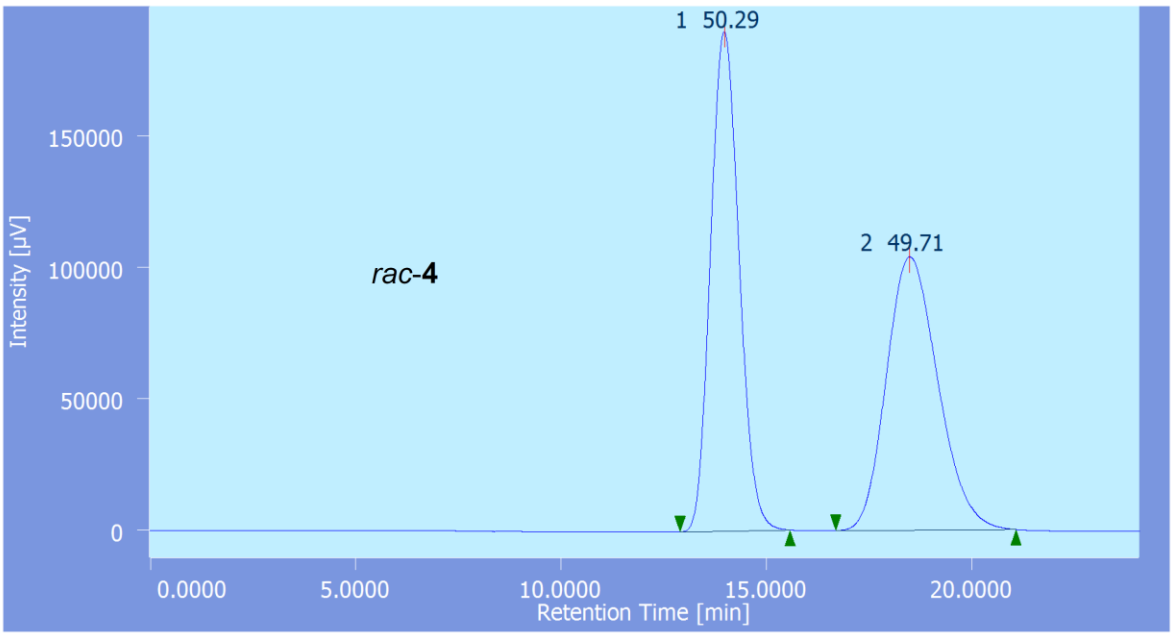
Cycloadduct **3p**

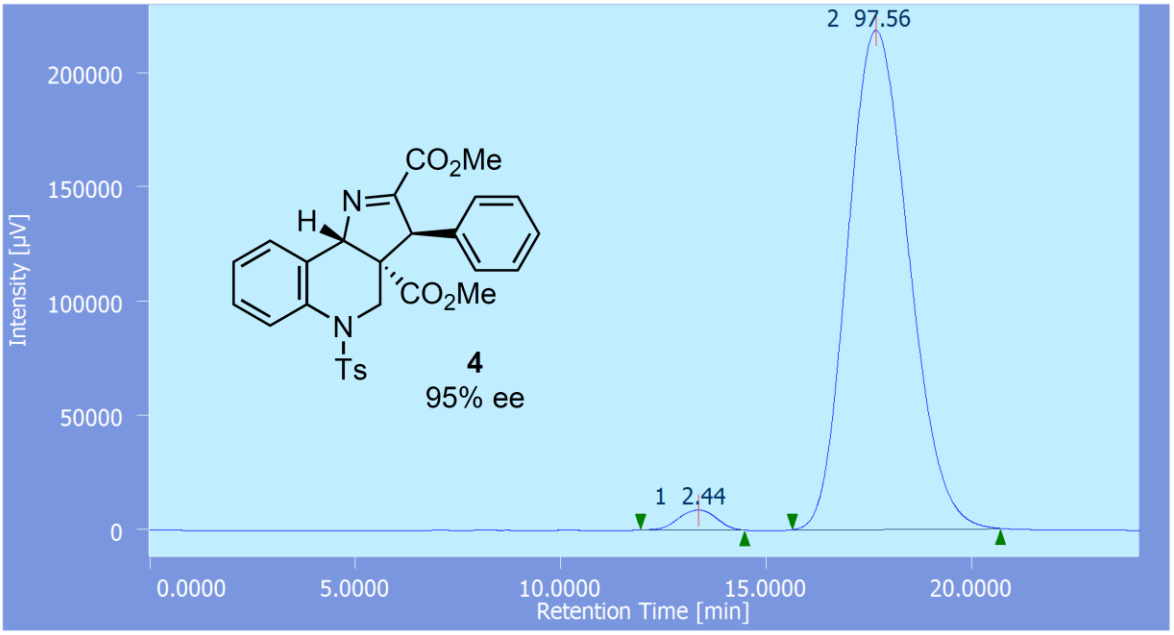




Chiralcel OJ-H, Hexane/*i*-PrOH = 2/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 26.9 min, 40.4 min

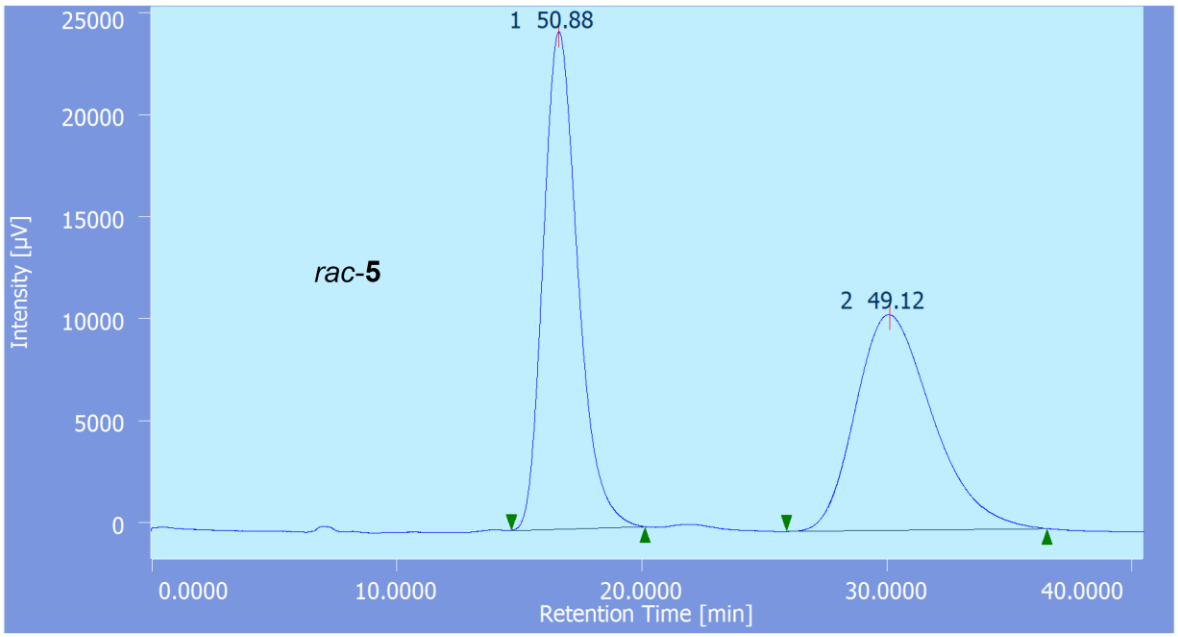
Cyclic iminoester **4** from dehydrogenation of **3b** (95% ee)

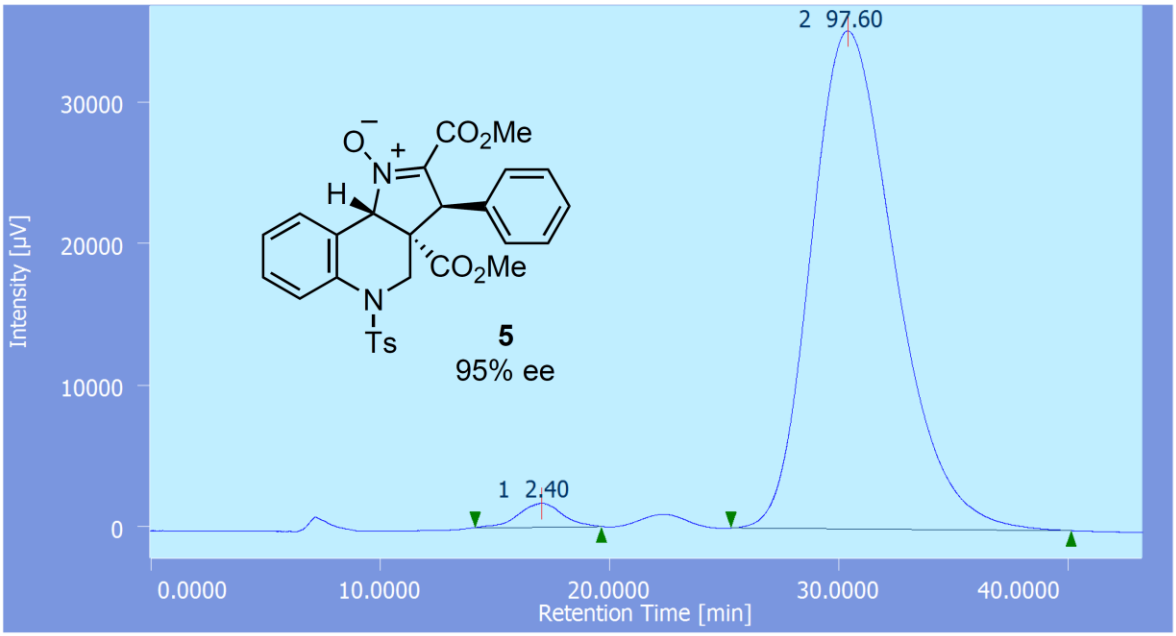




Chiralpak AS-H, Hexane/*i*-PrOH = 1/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 13.4 min, 17.7 min

Nitrone **5** from cycloadduct **3b** (95% ee)

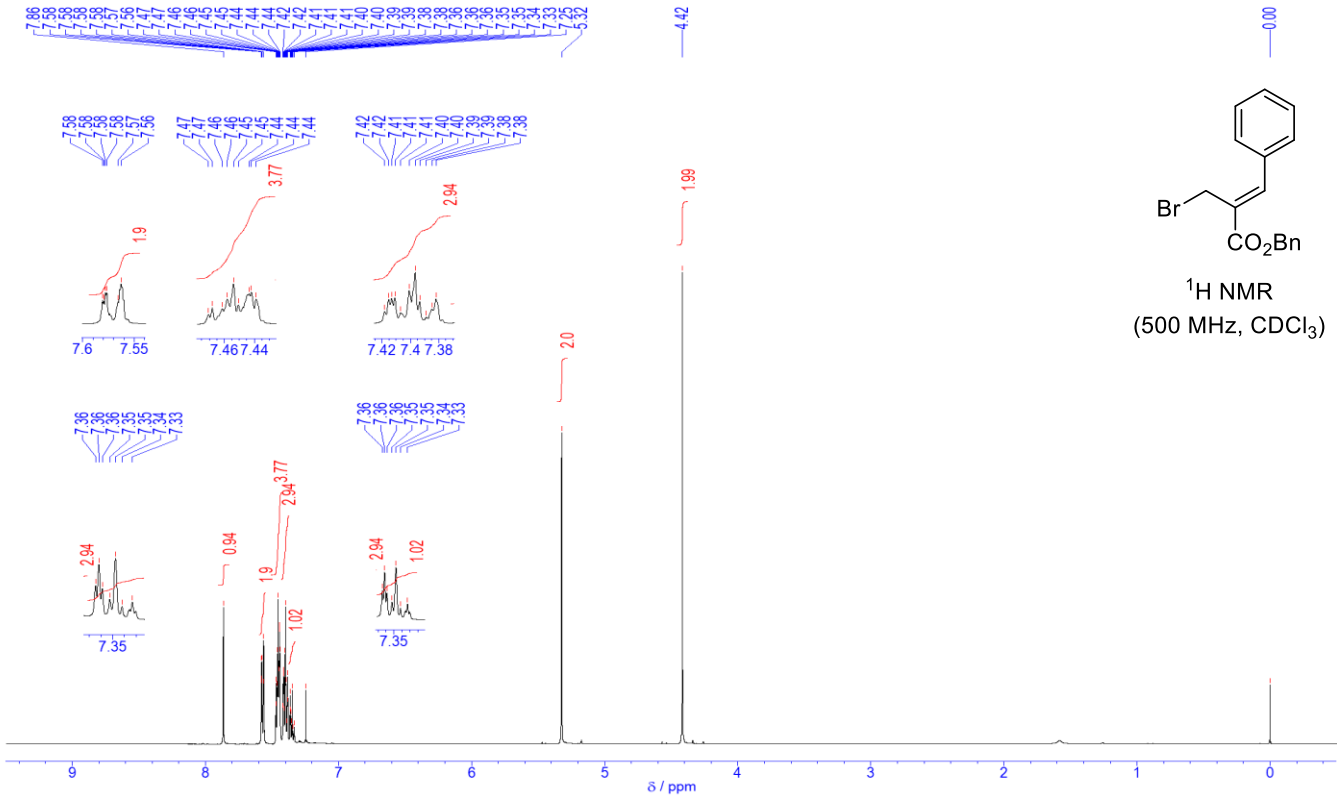


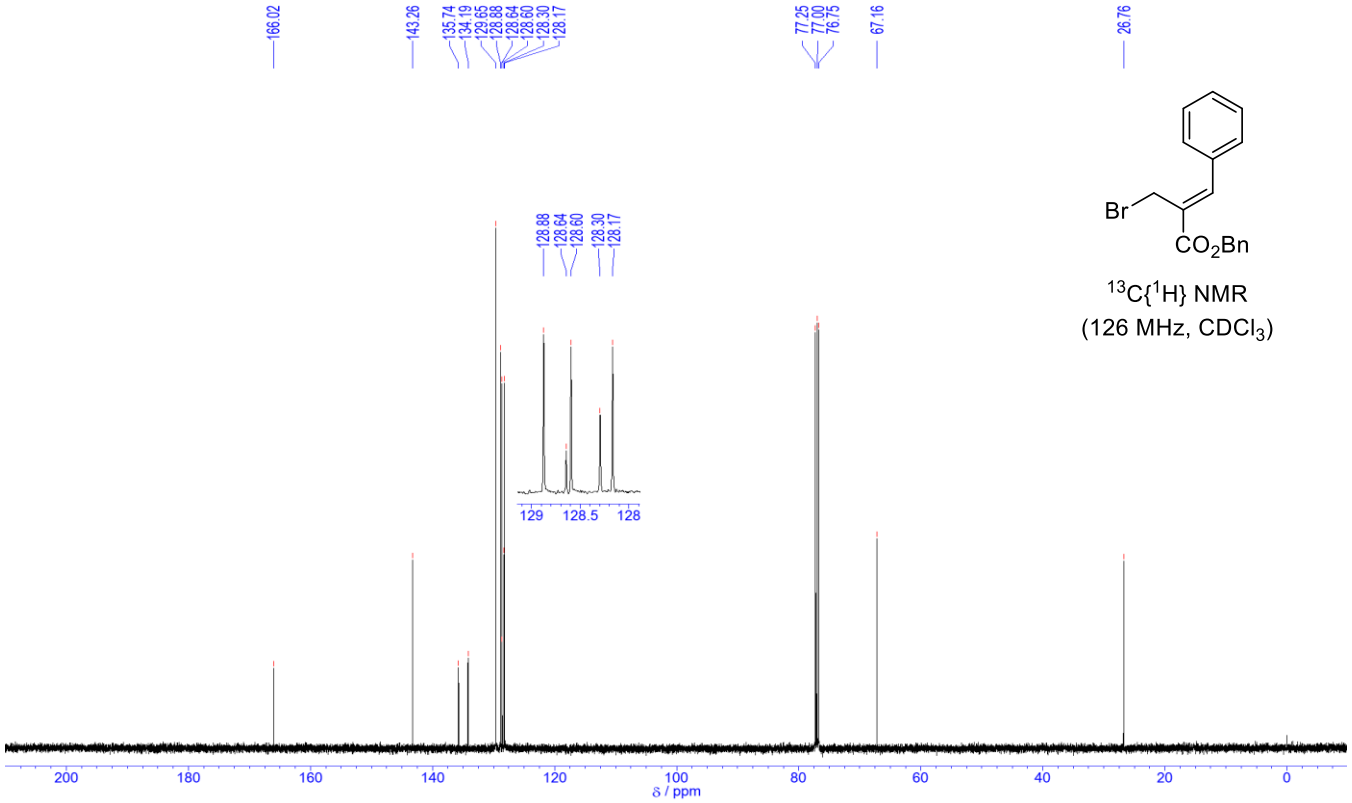


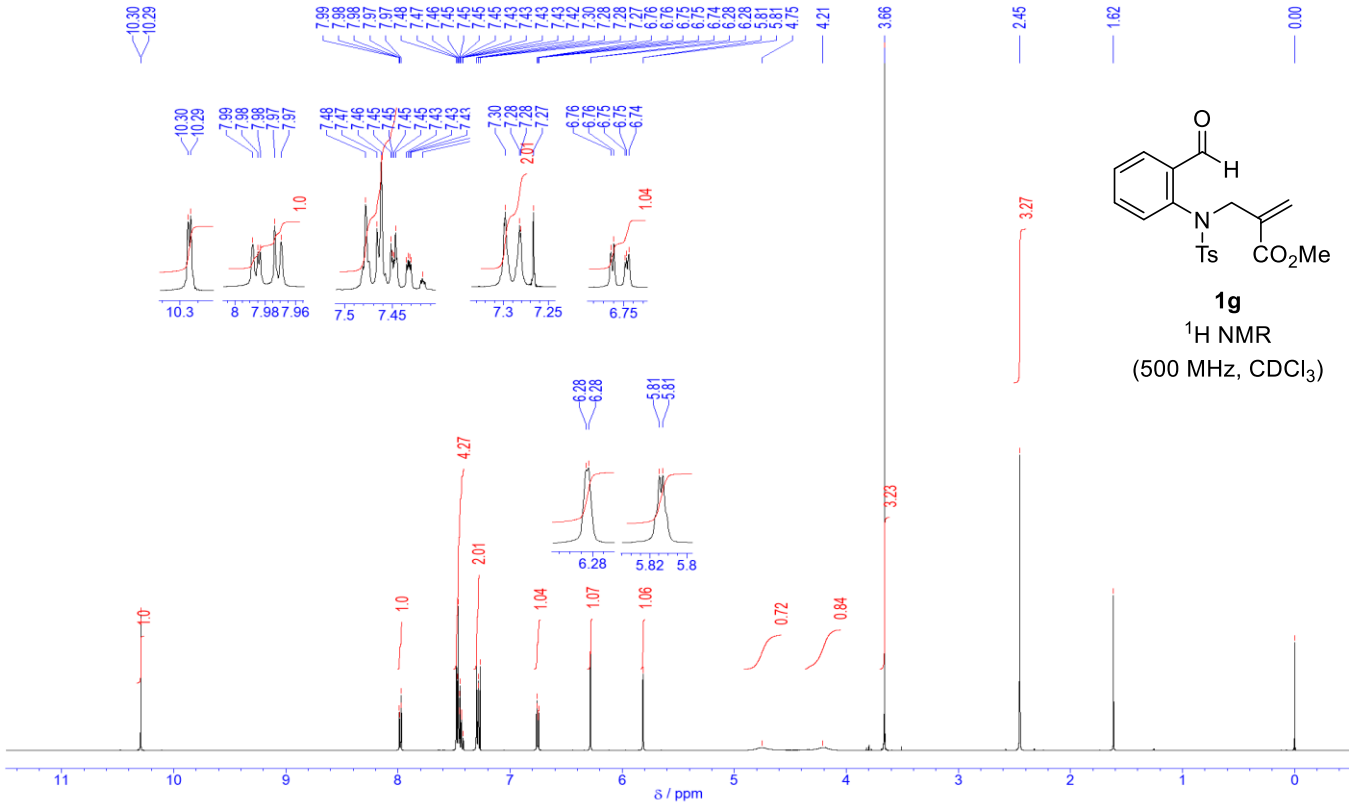
Chiralpak AS-H, Hexane/*i*-PrOH = 1/1, Flow rate = 0.5 mL/min, Wave length = 254 nm
t_R: 17.1 min, 30.4 min

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

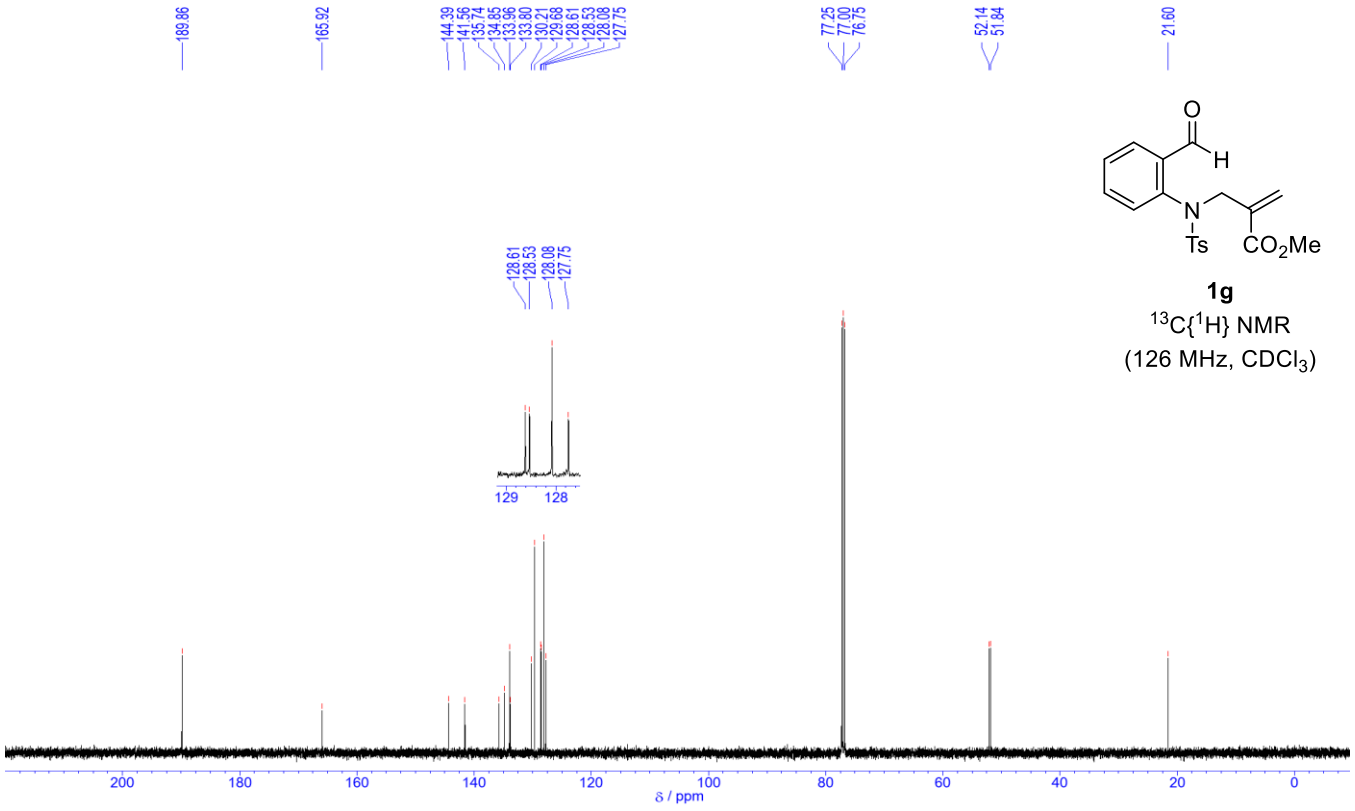
6.1 bromide and aldehydes **1**



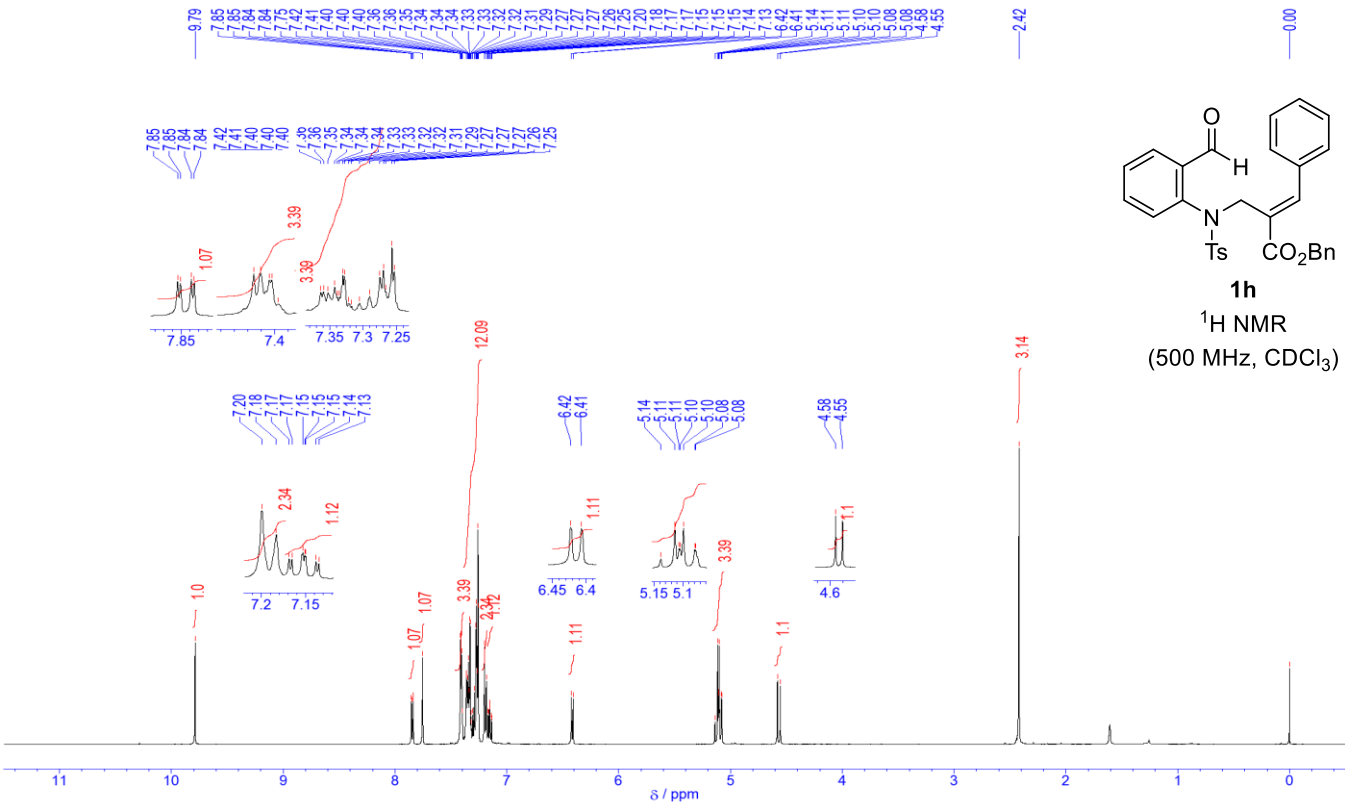




1g
^{1}H NMR
(500 MHz, $CDCl_3$)



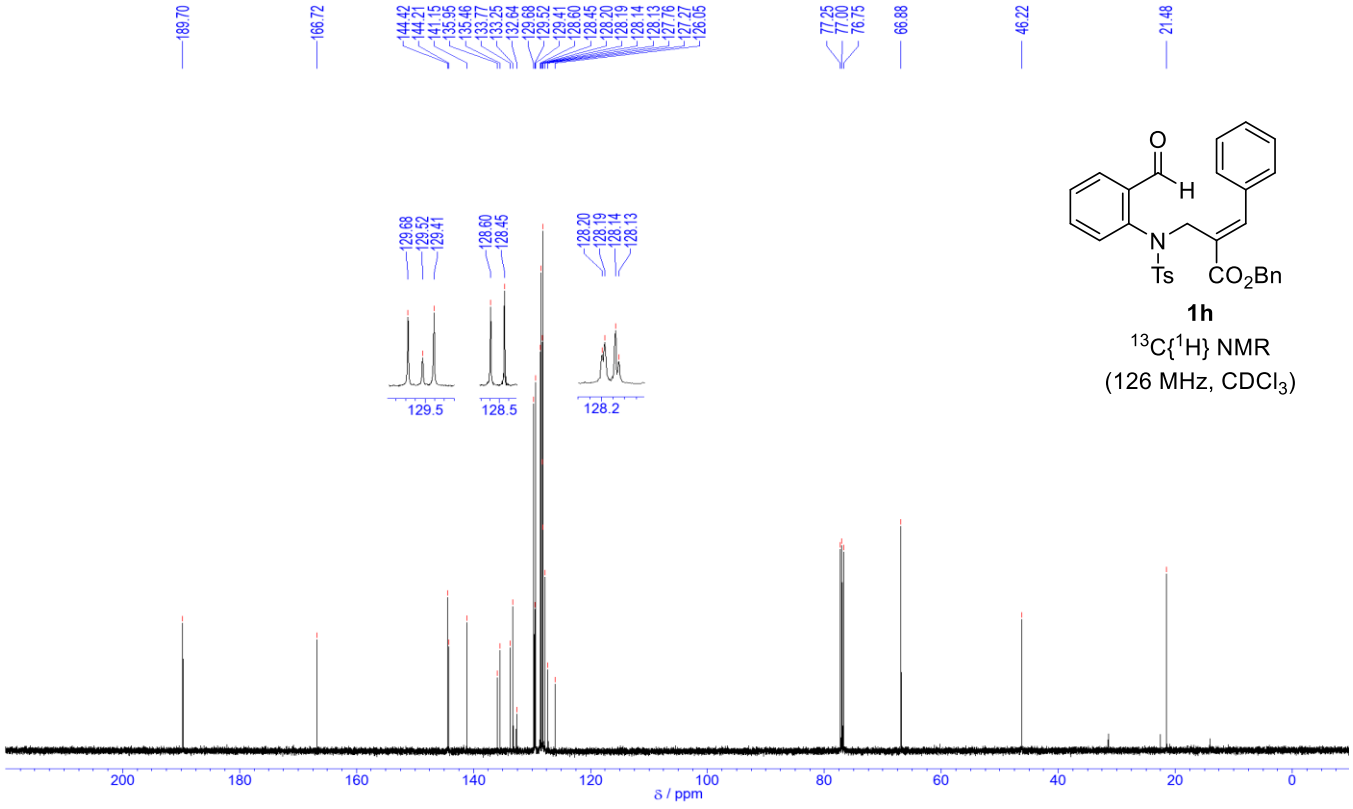
1g
$^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)



1h

^{1}H NMR

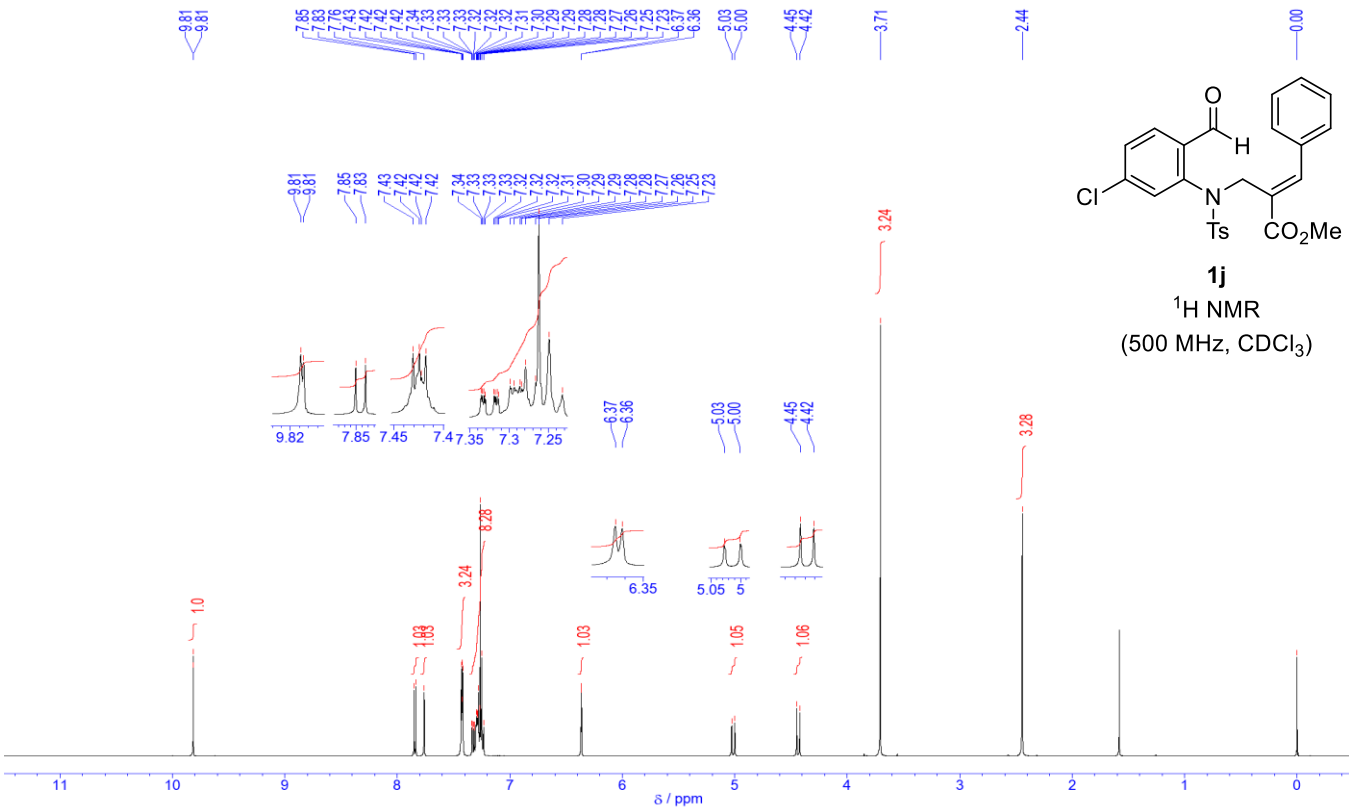
(500 MHz, $CDCl_3$)

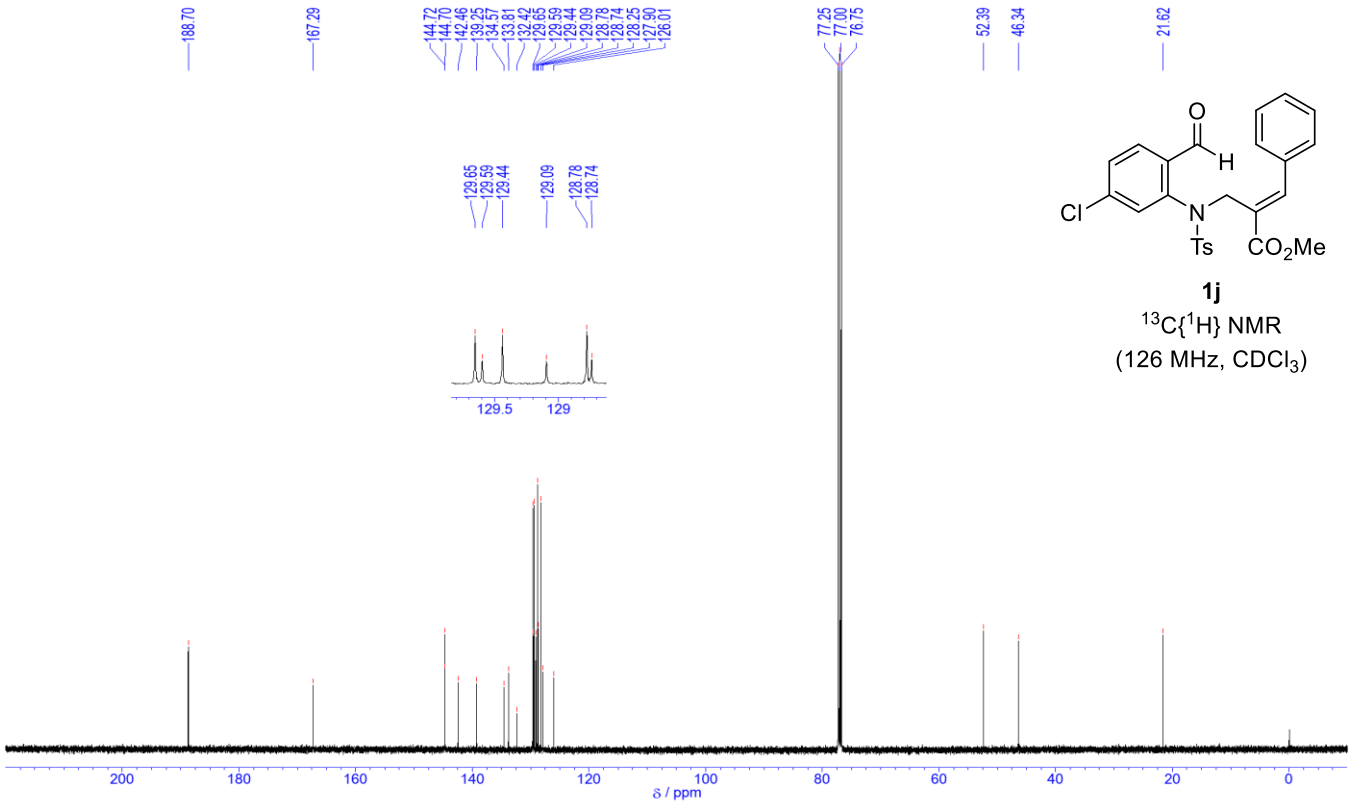


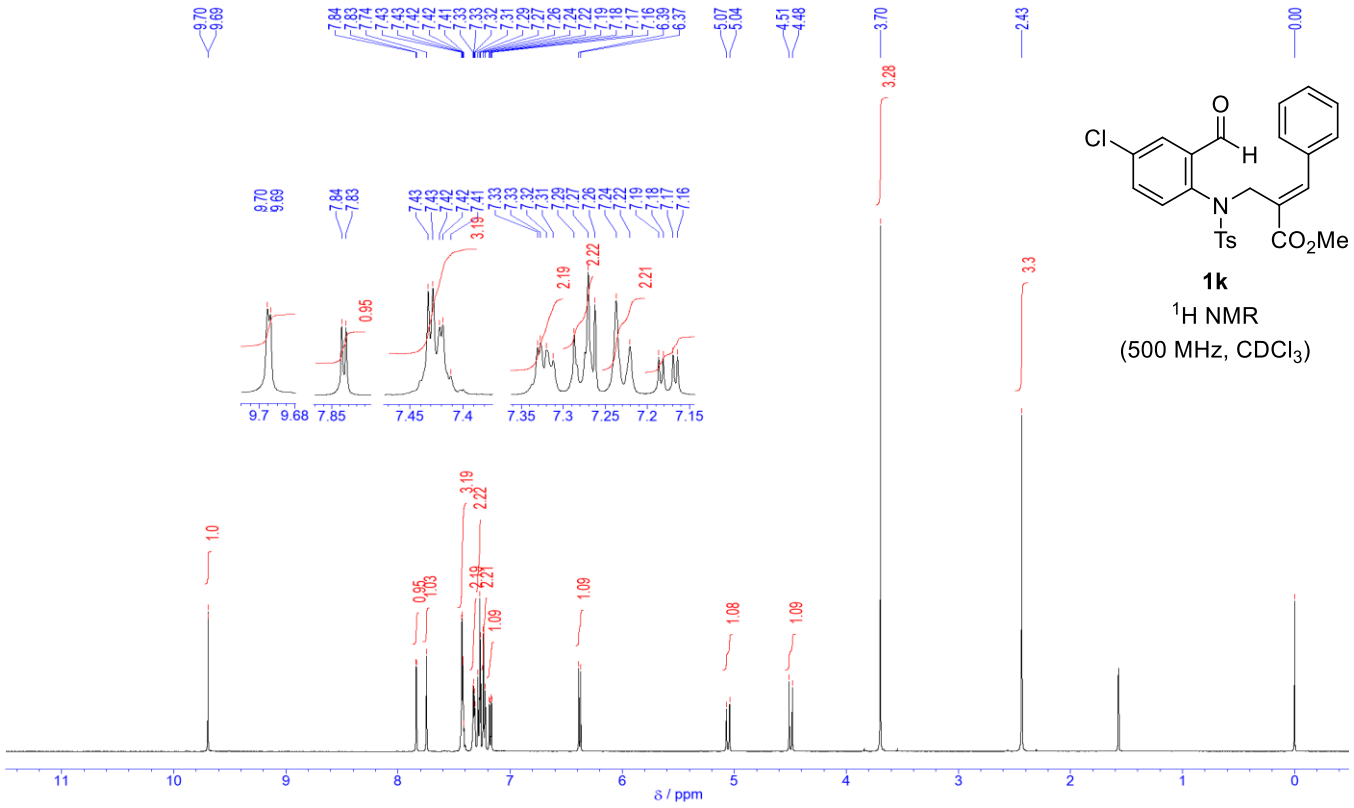
1h

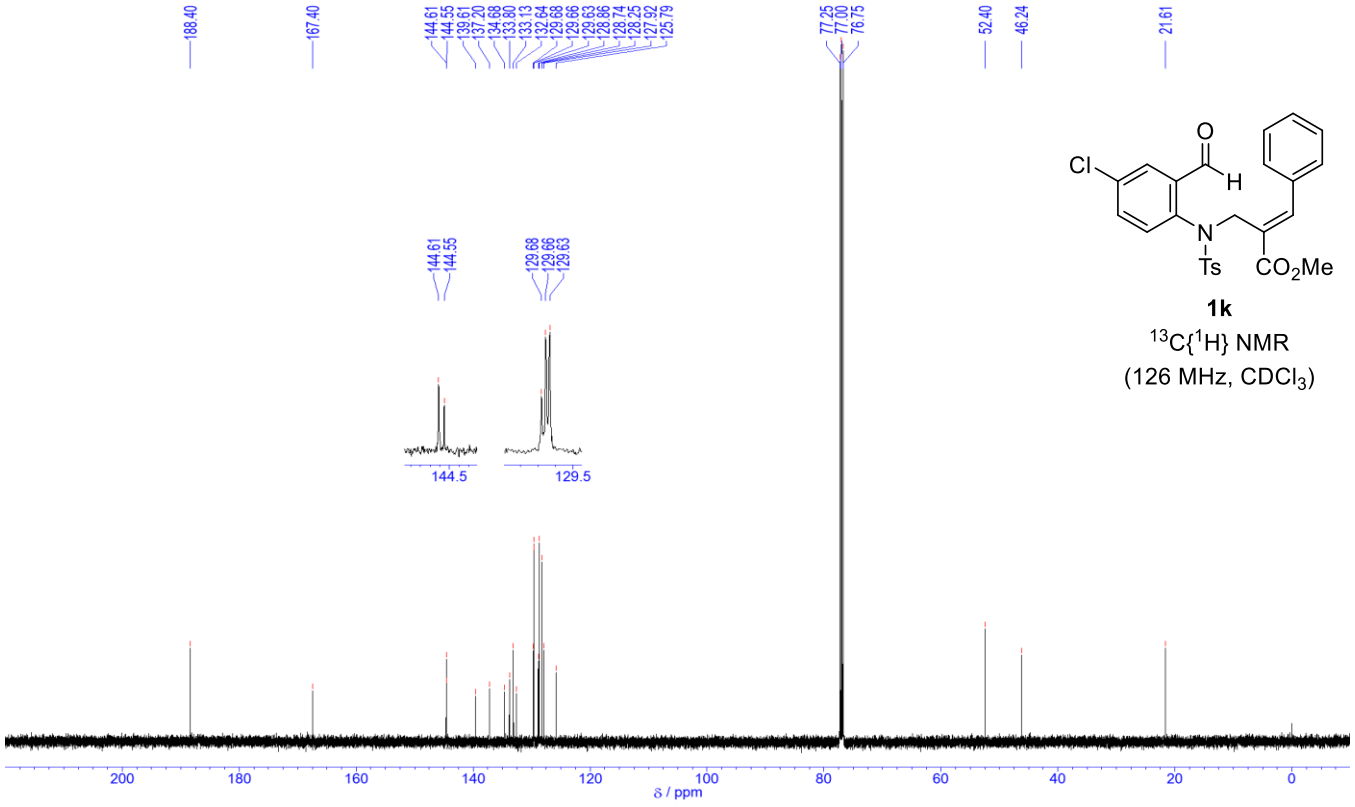
$^{13}C\{^{1}H\}$ NMR

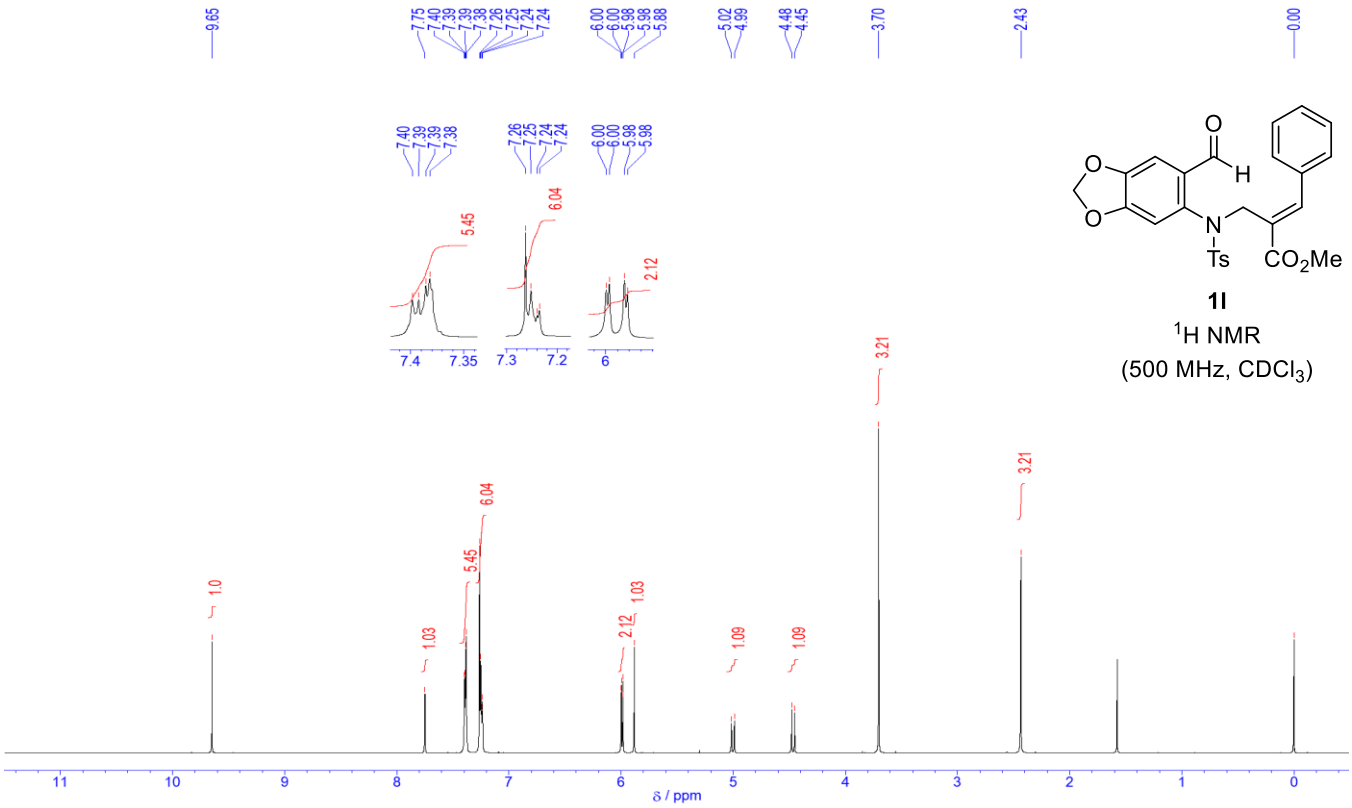
(126 MHz, $CDCl_3$)


1j
1H NMR
(500 MHz, CDCl3)
δ / ppm


1j
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm


1k
1H NMR
(500 MHz, CDCl3)
δ / ppm

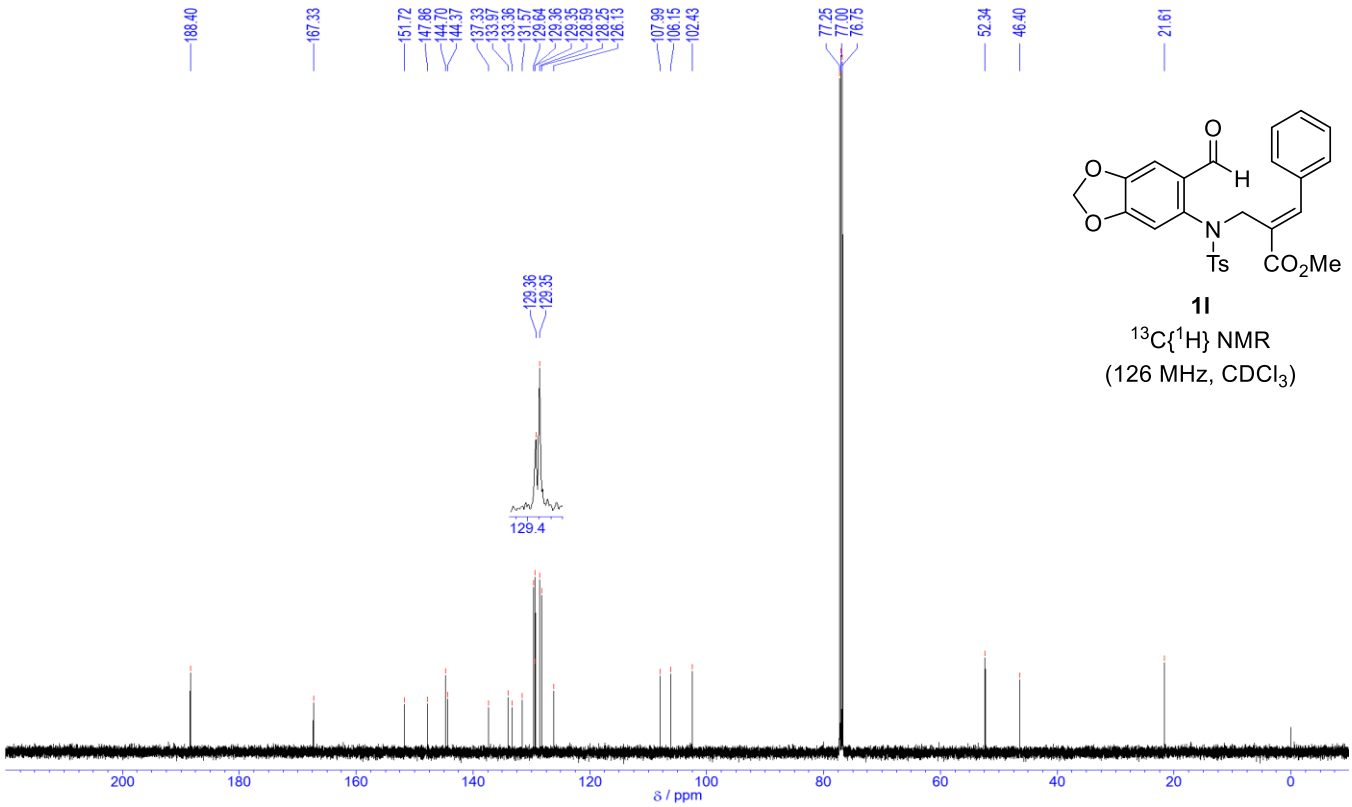

1k
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm



1l

^{1}H NMR

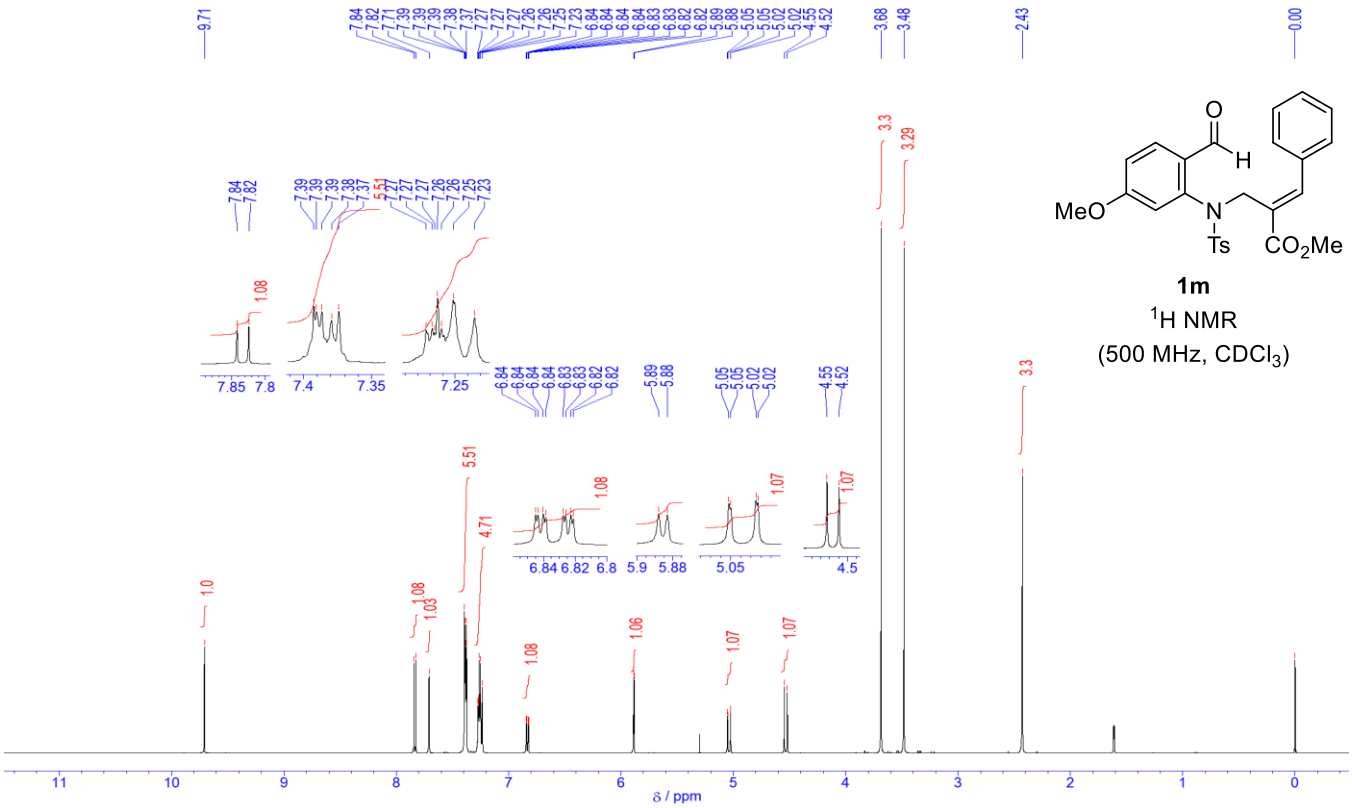
(500 MHz, $CDCl_3$)



1l

$^{13}C\{^{1}H\}$ NMR

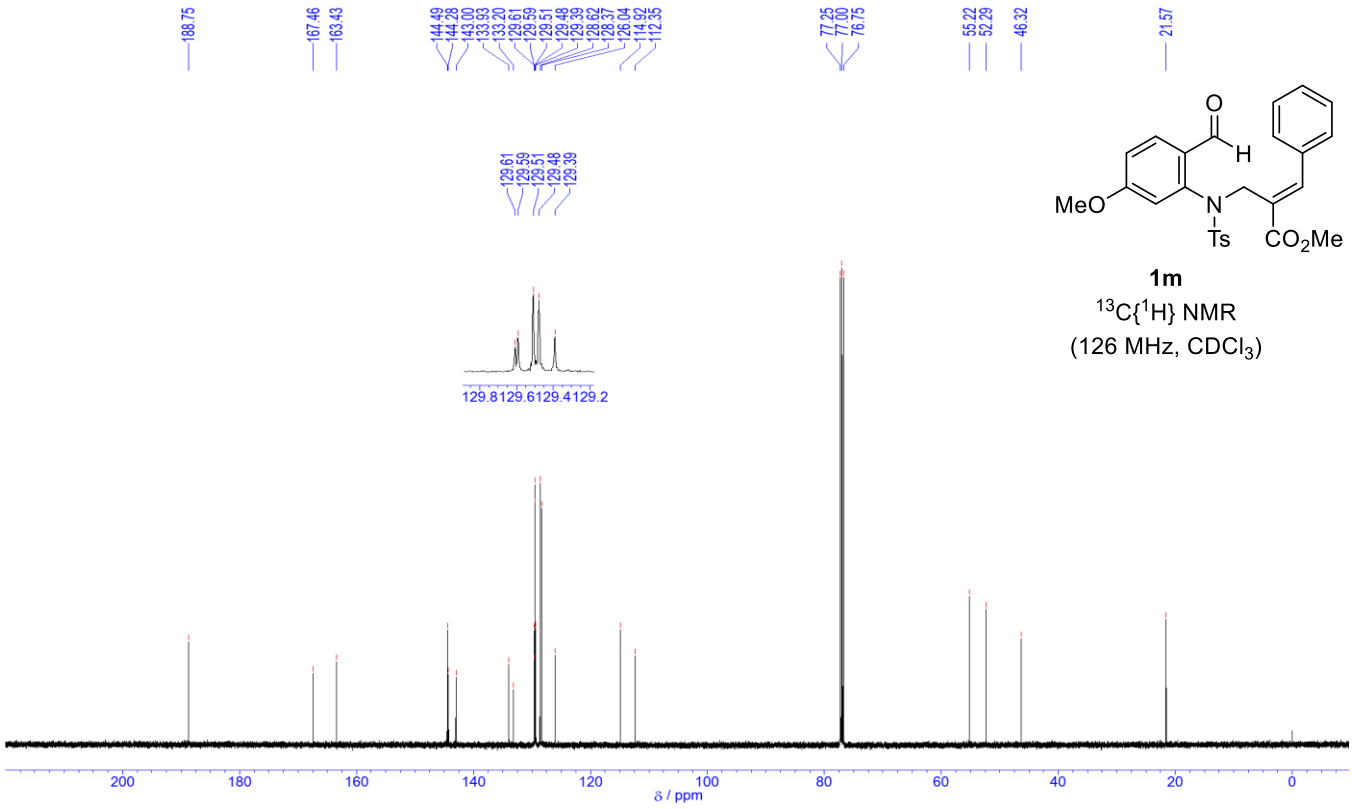
(126 MHz, $CDCl_3$)



1m

^{1}H NMR

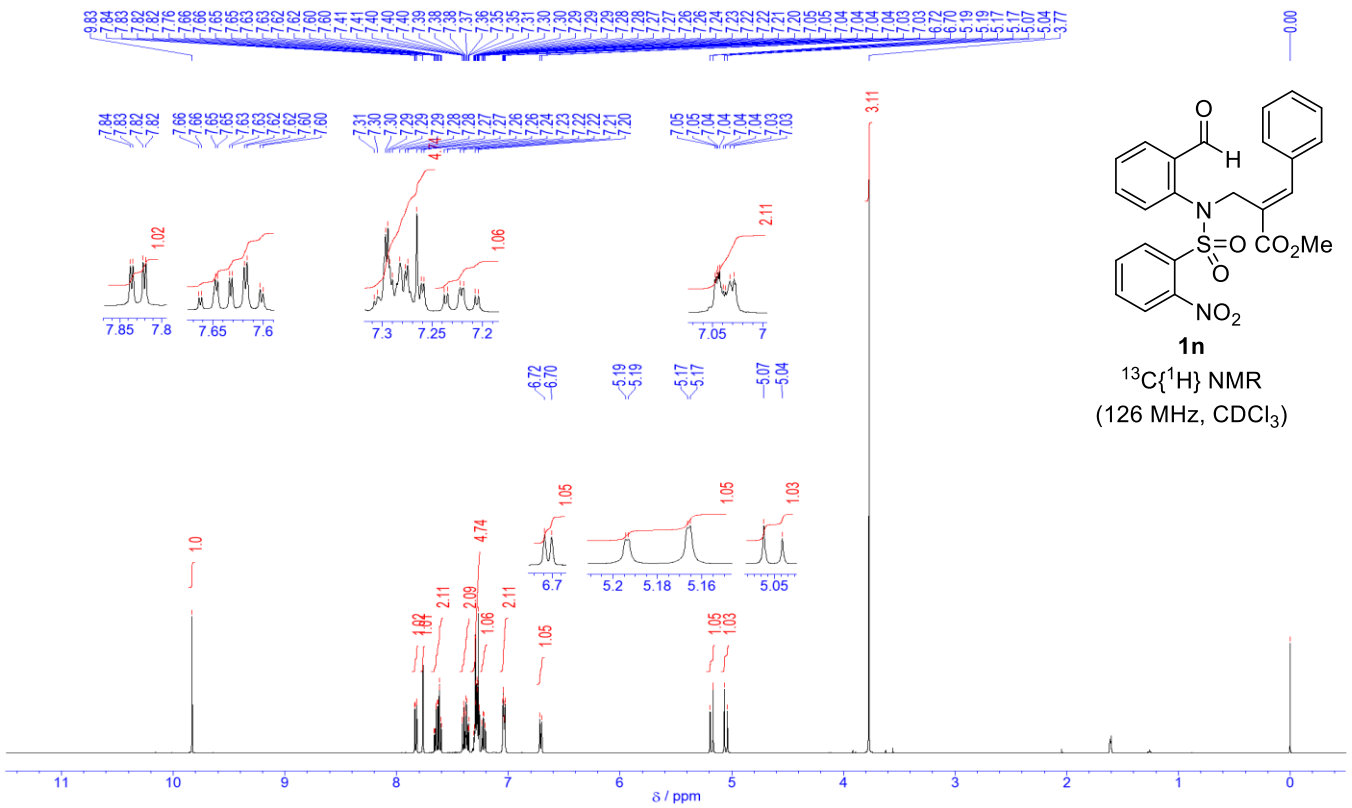
(500 MHz, $CDCl_3$)



1m

$^{13}C\{^{1}H\}$ NMR

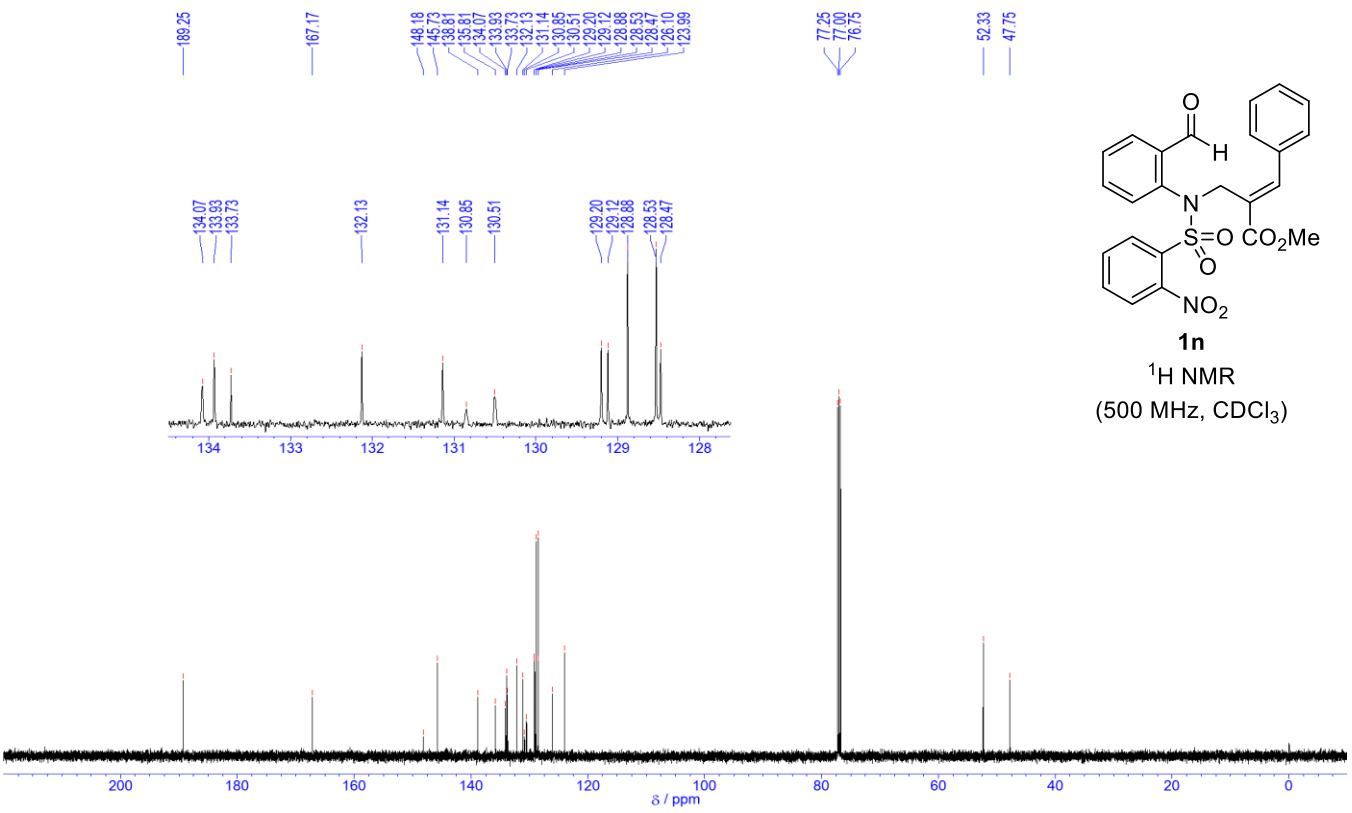
(126 MHz, $CDCl_3$)



1n

$^{13}C\{^{1}H\}$ NMR

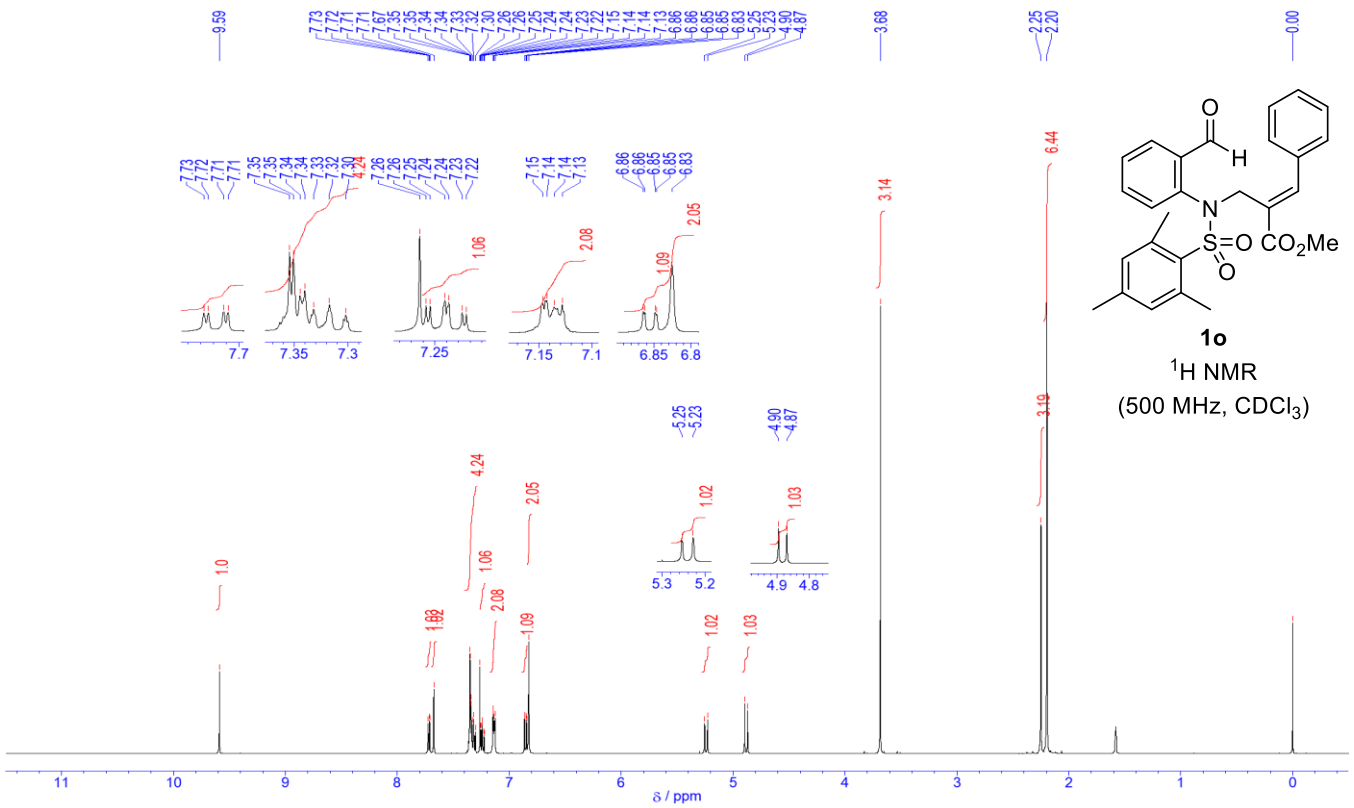
(126 MHz, $CDCl_3$)

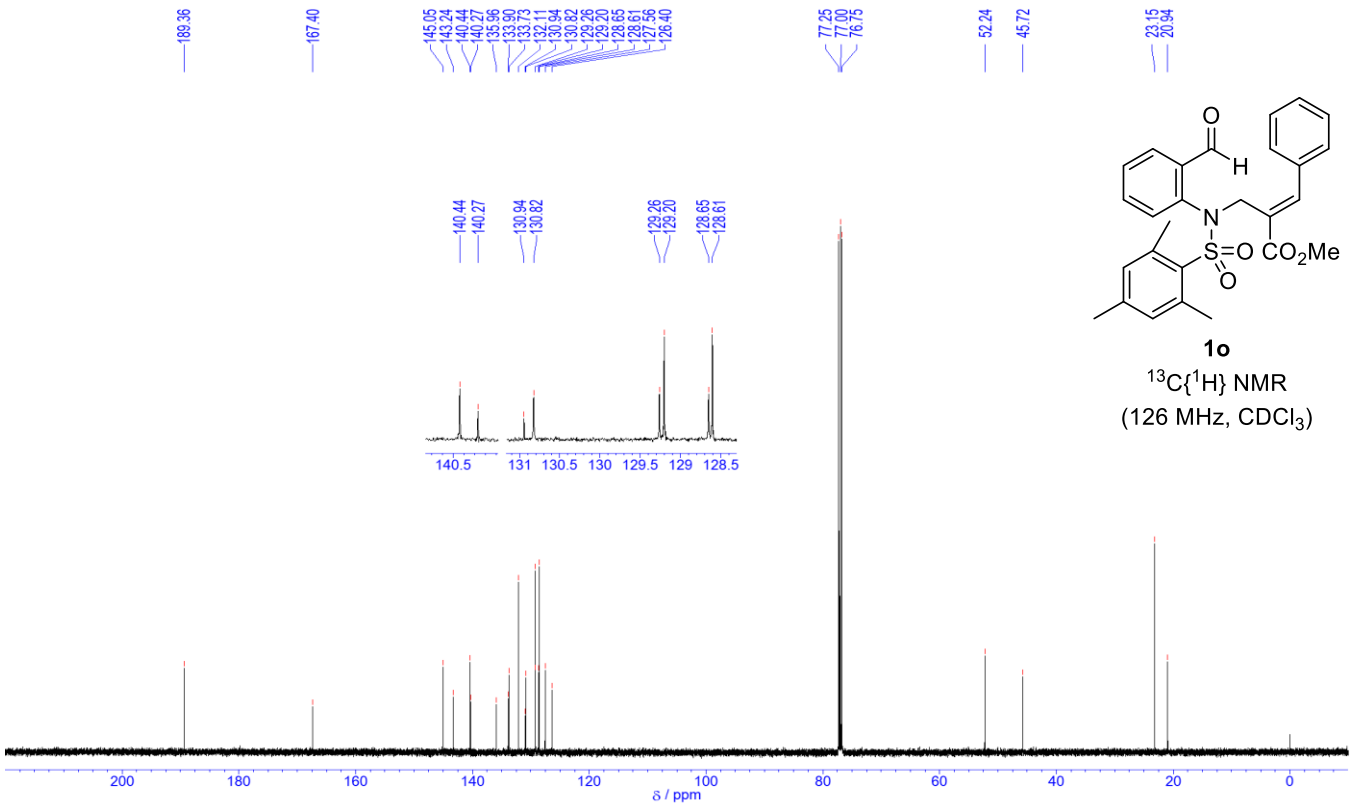


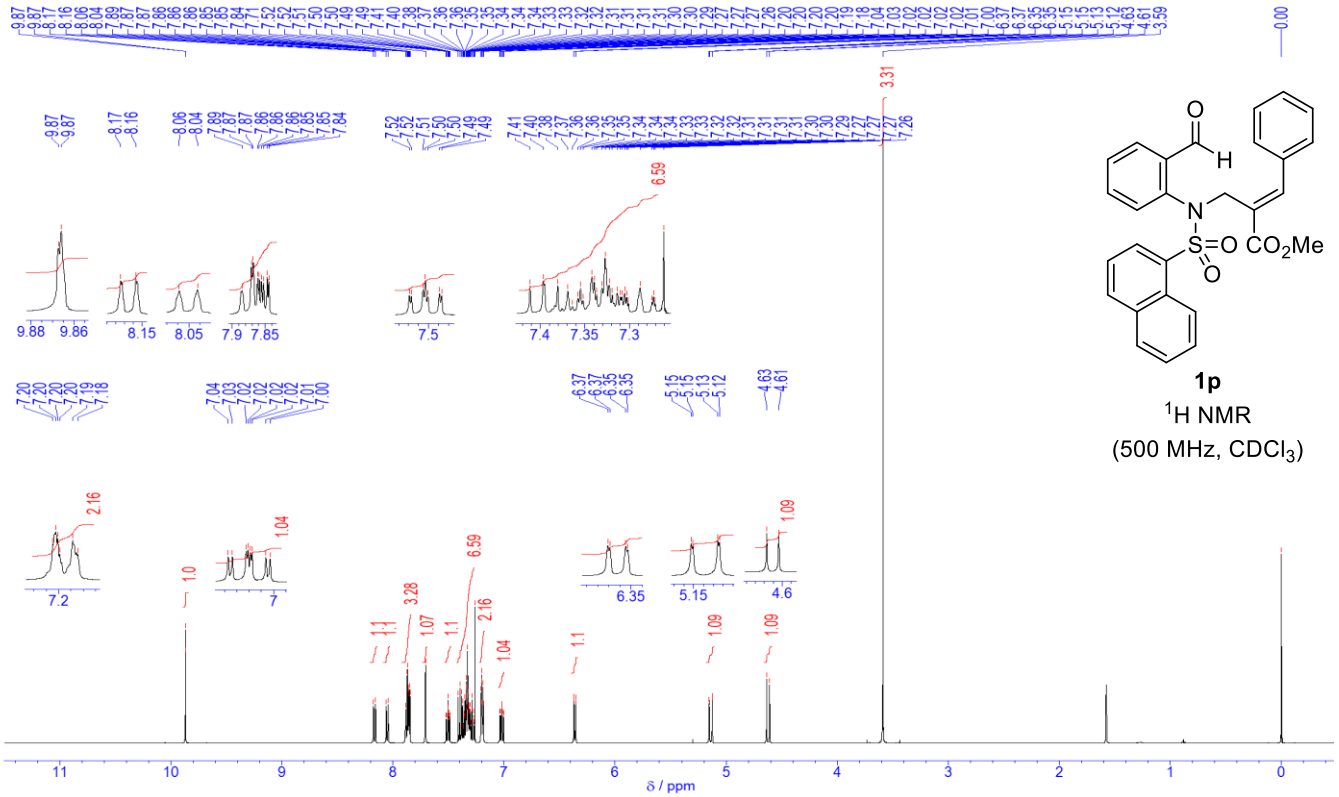
1n

^{1}H NMR

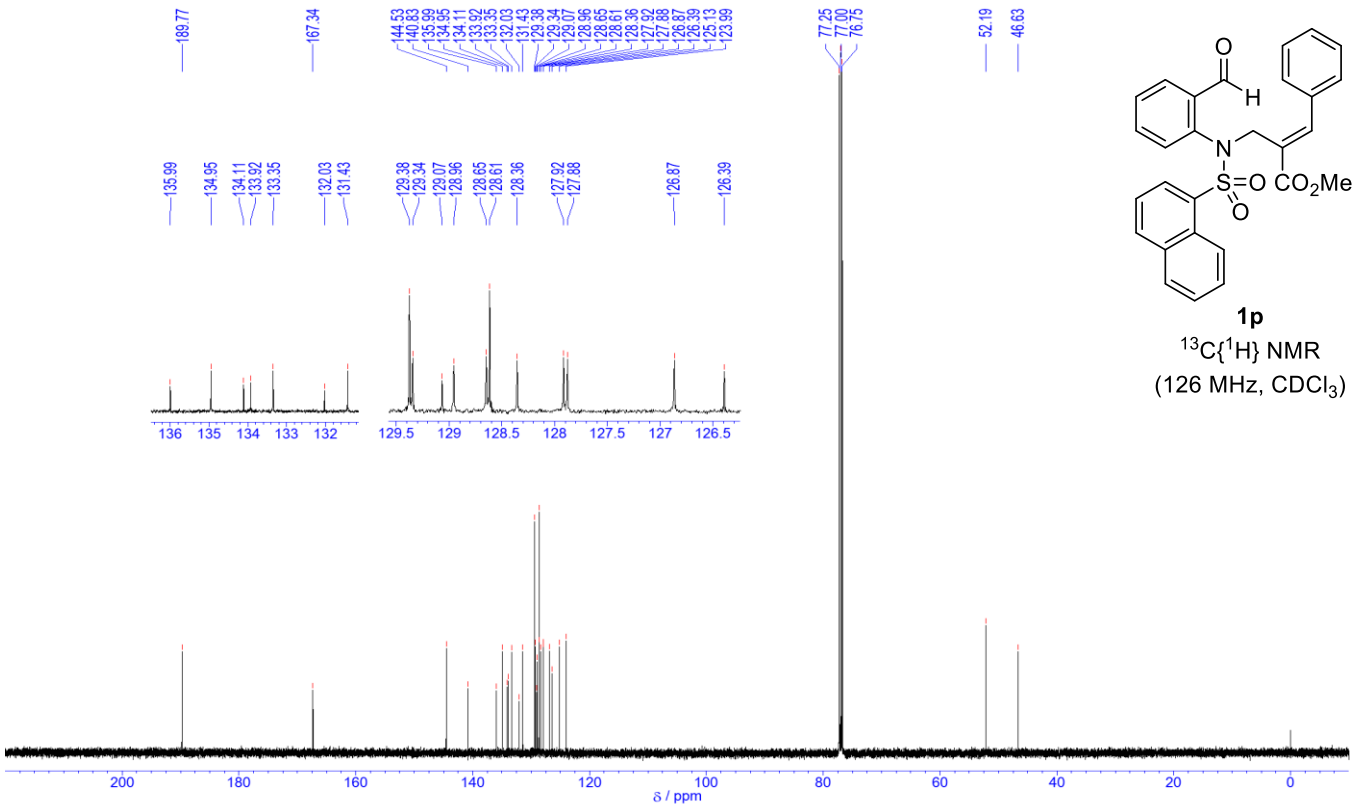
(500 MHz, $CDCl_3$)


1o
1H NMR
(500 MHz, CDCl3)
δ / ppm


1o
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm

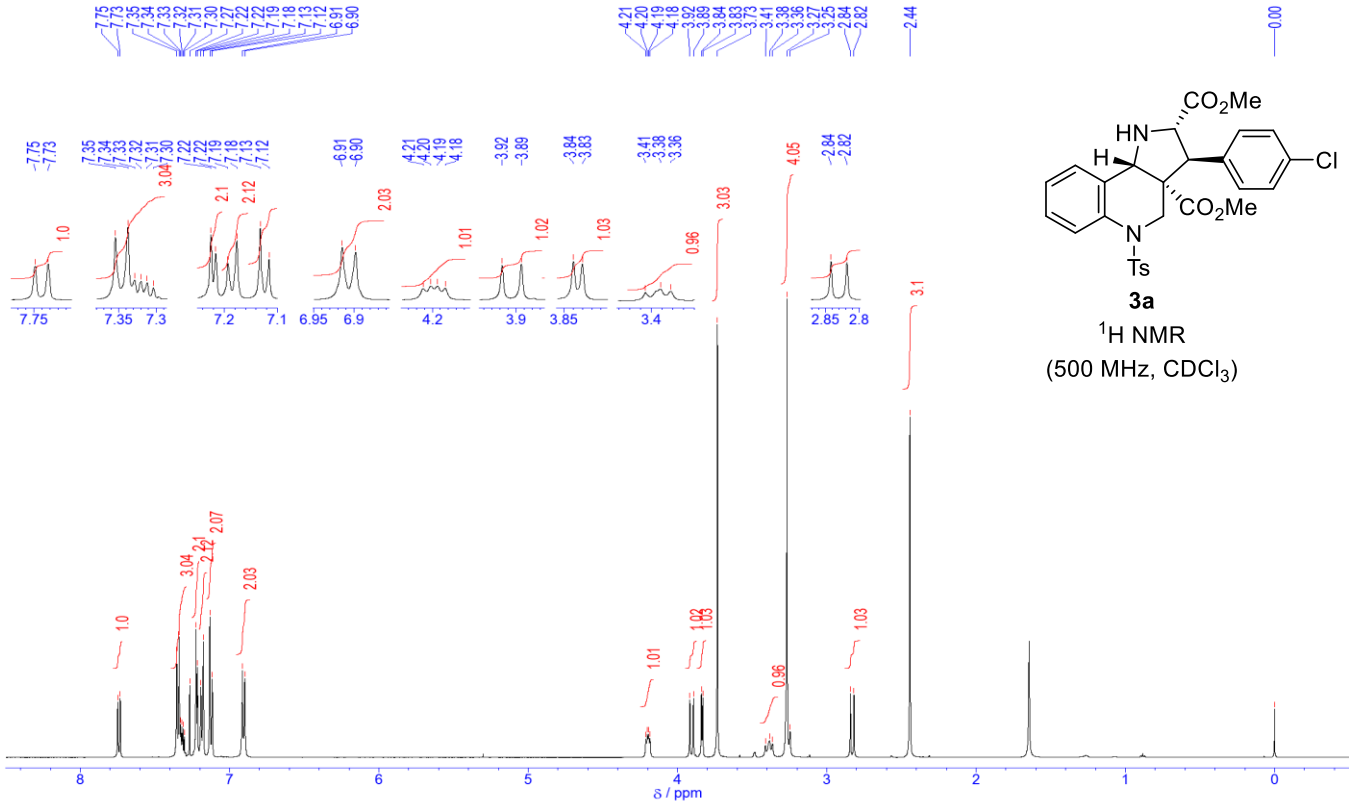


1p
^{1}H NMR
(500 MHz, $CDCl_3$)



1p
$^{13}C\{^{1}H\}$ NMR
(126 MHz, $CDCl_3$)

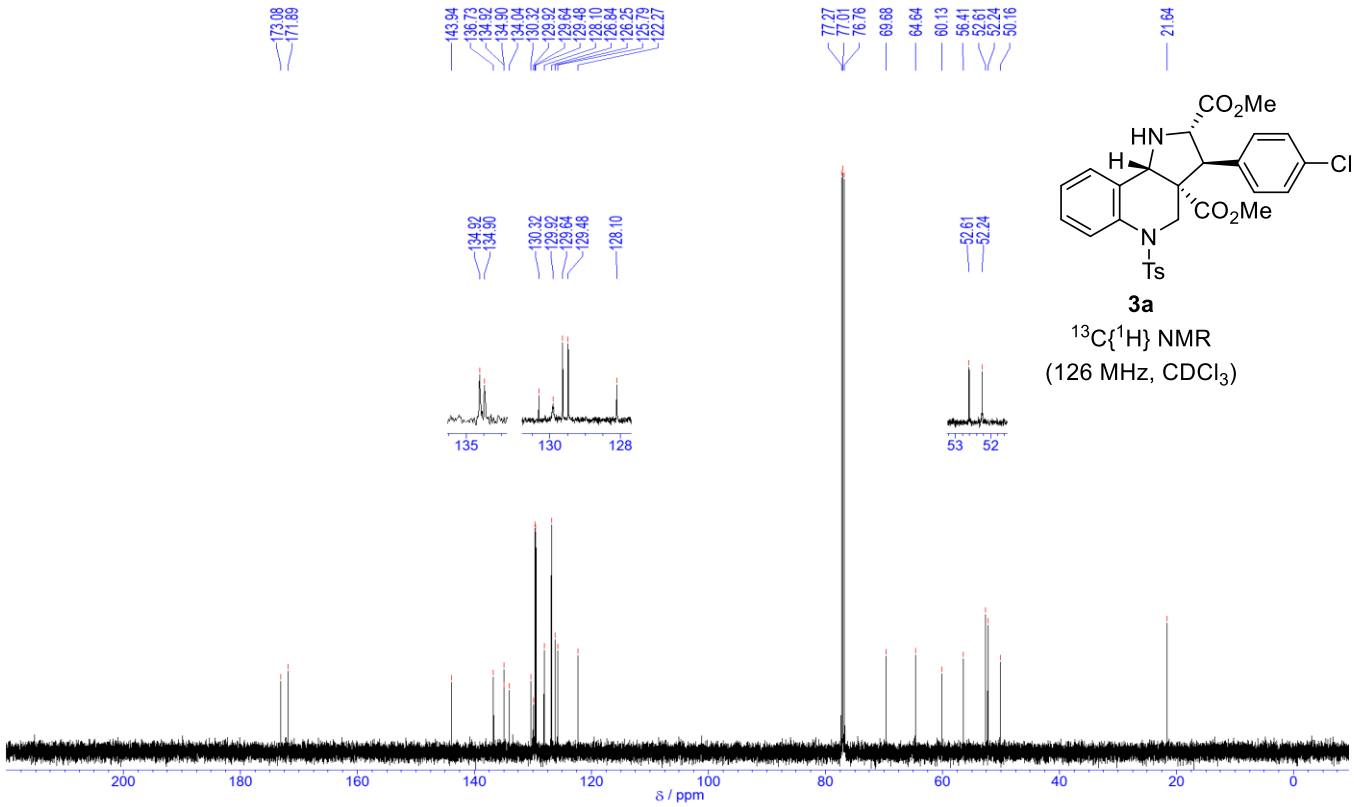
6.2 [3+2] cycloadducts **3**



3a

^{1}H NMR

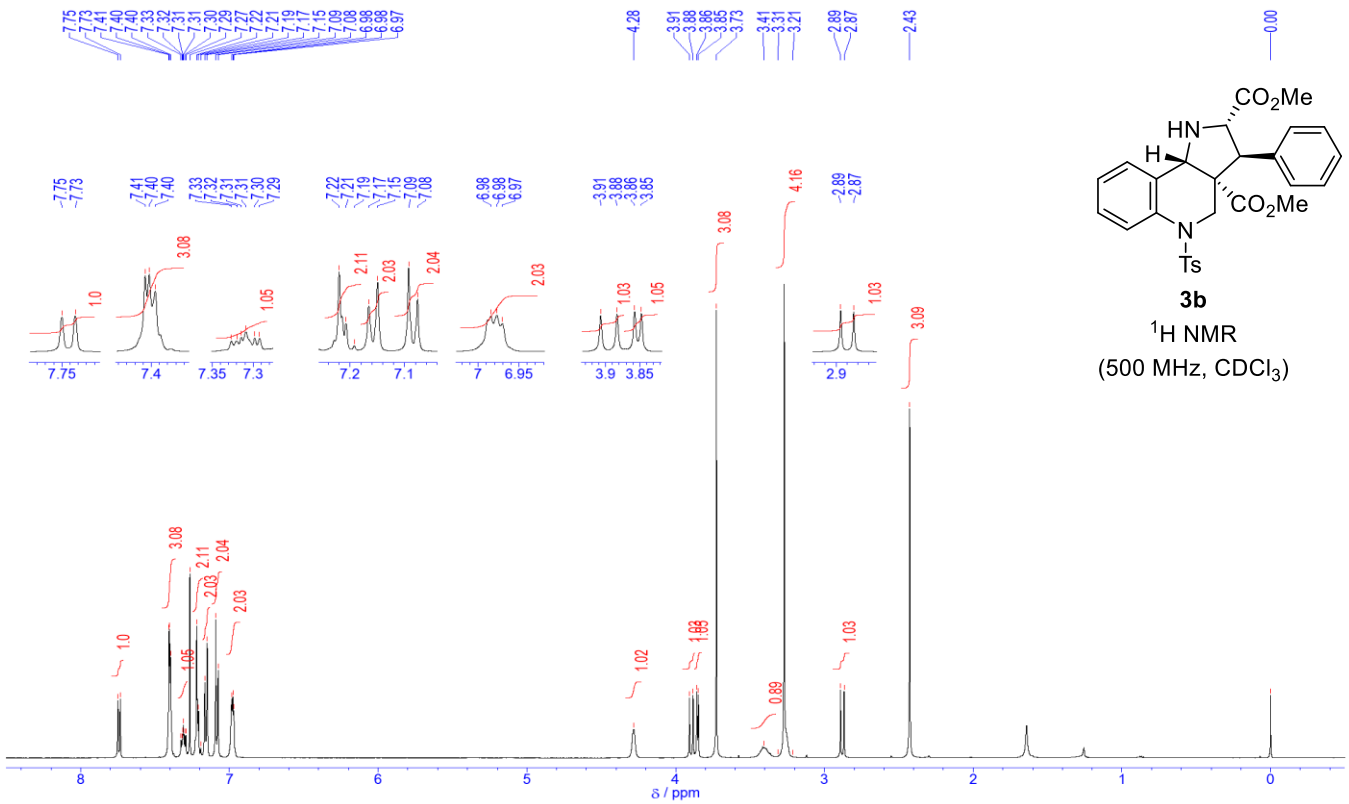
(500 MHz, $CDCl_3$)



3a

$^{13}C\{^{1}H\}$ NMR

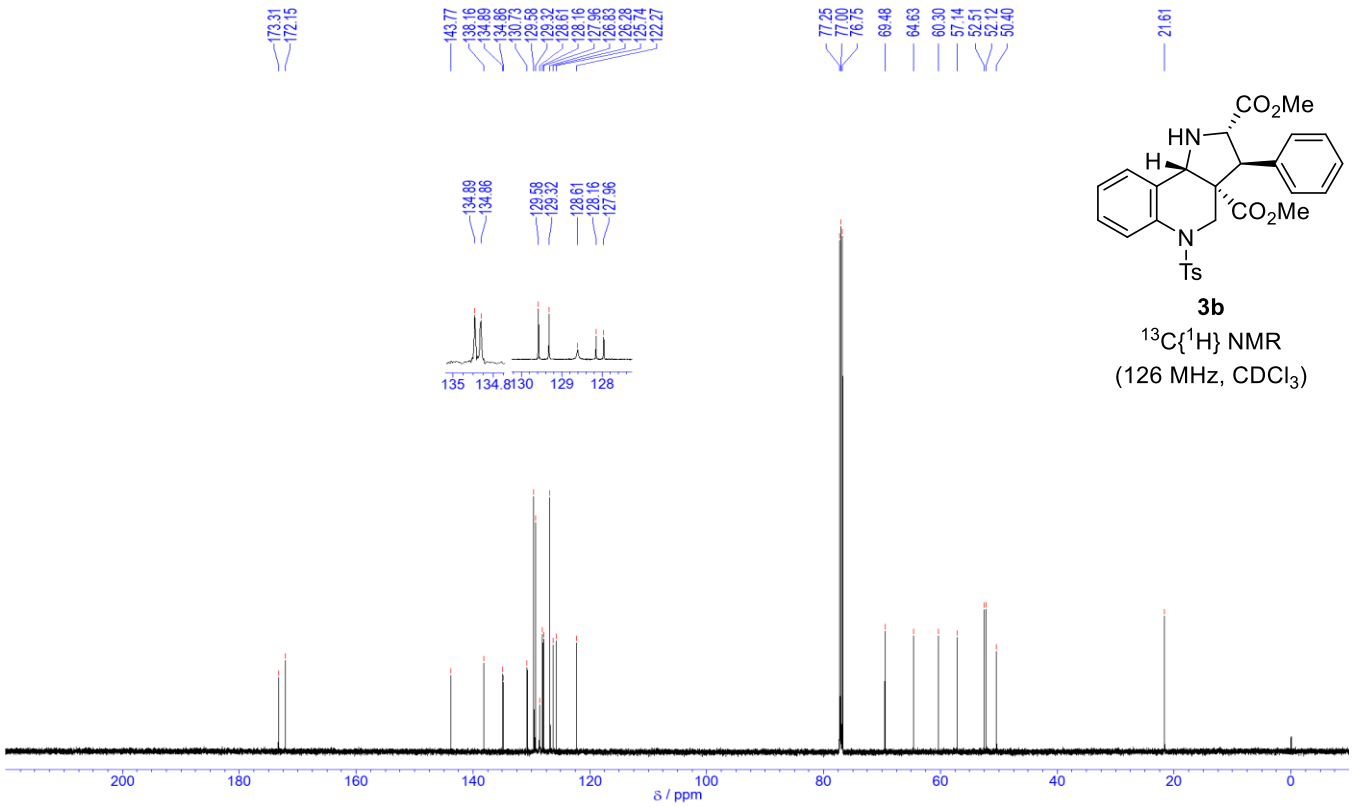
(126 MHz, $CDCl_3$)



3b

^{1}H NMR

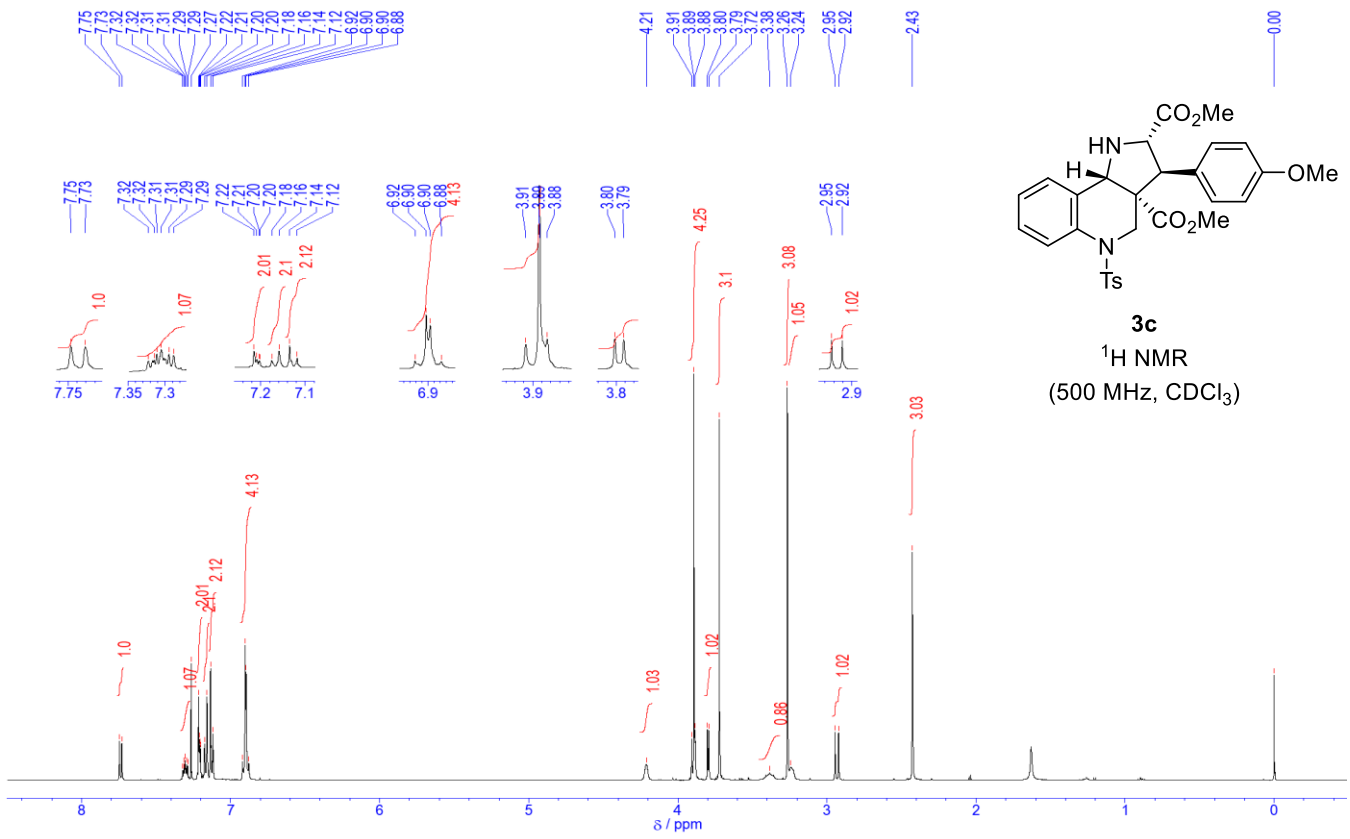
(500 MHz, $CDCl_3$)



3b

$^{13}C\{^{1}H\}$ NMR

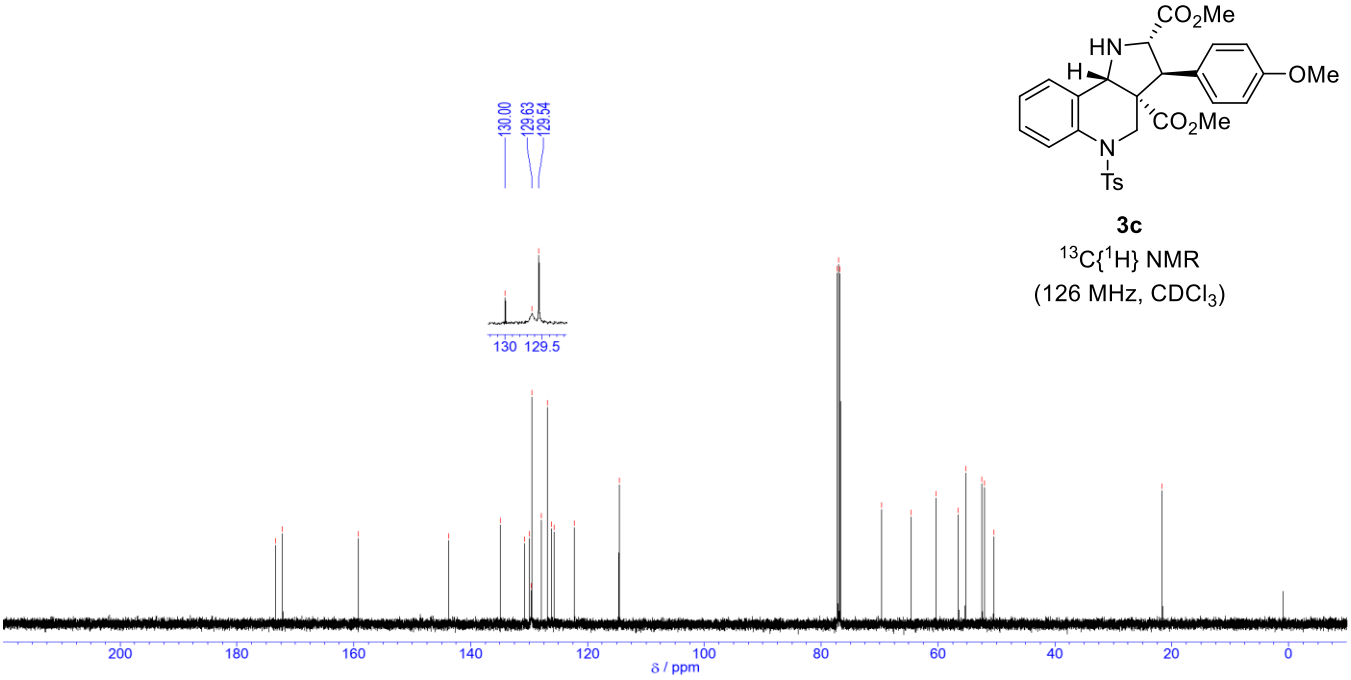
(126 MHz, $CDCl_3$)



3c

^{1}H NMR

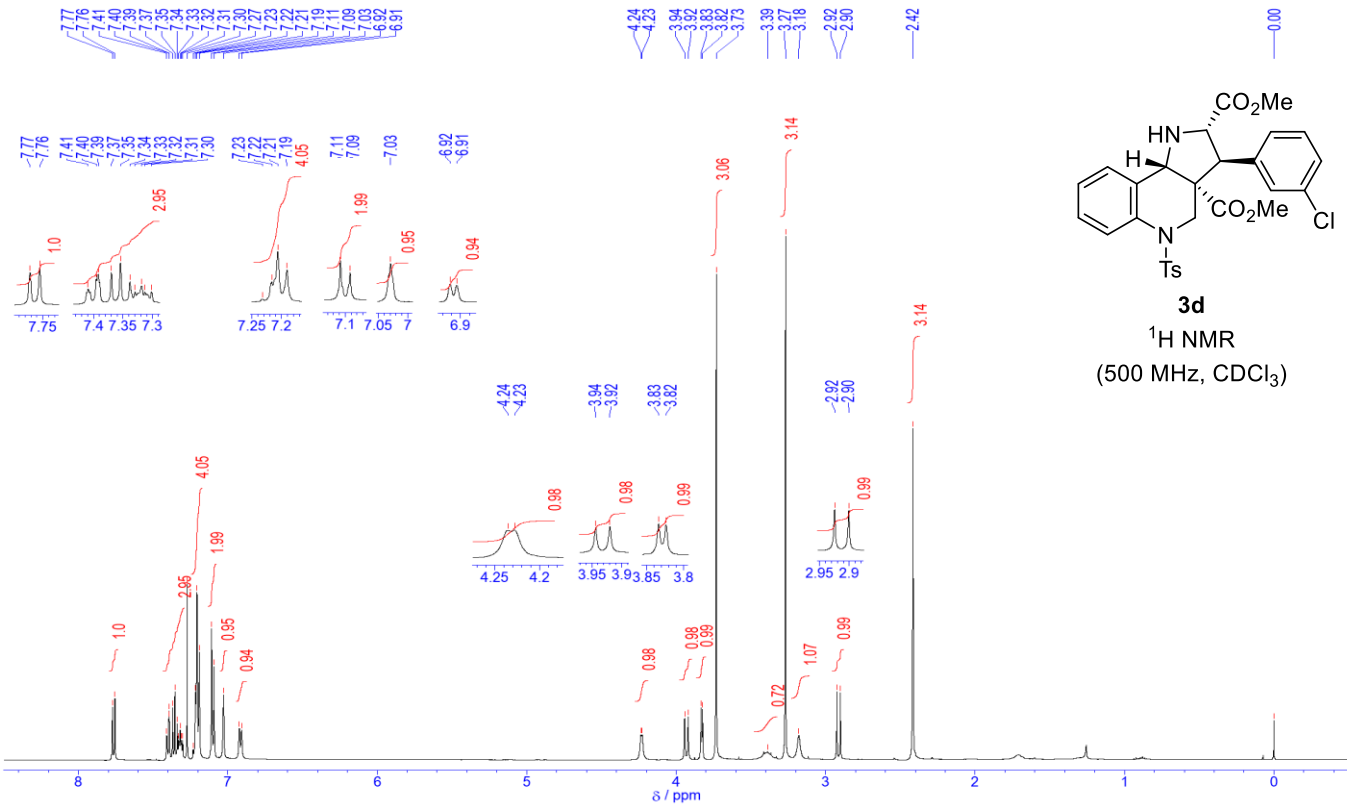
(500 MHz, $CDCl_3$)

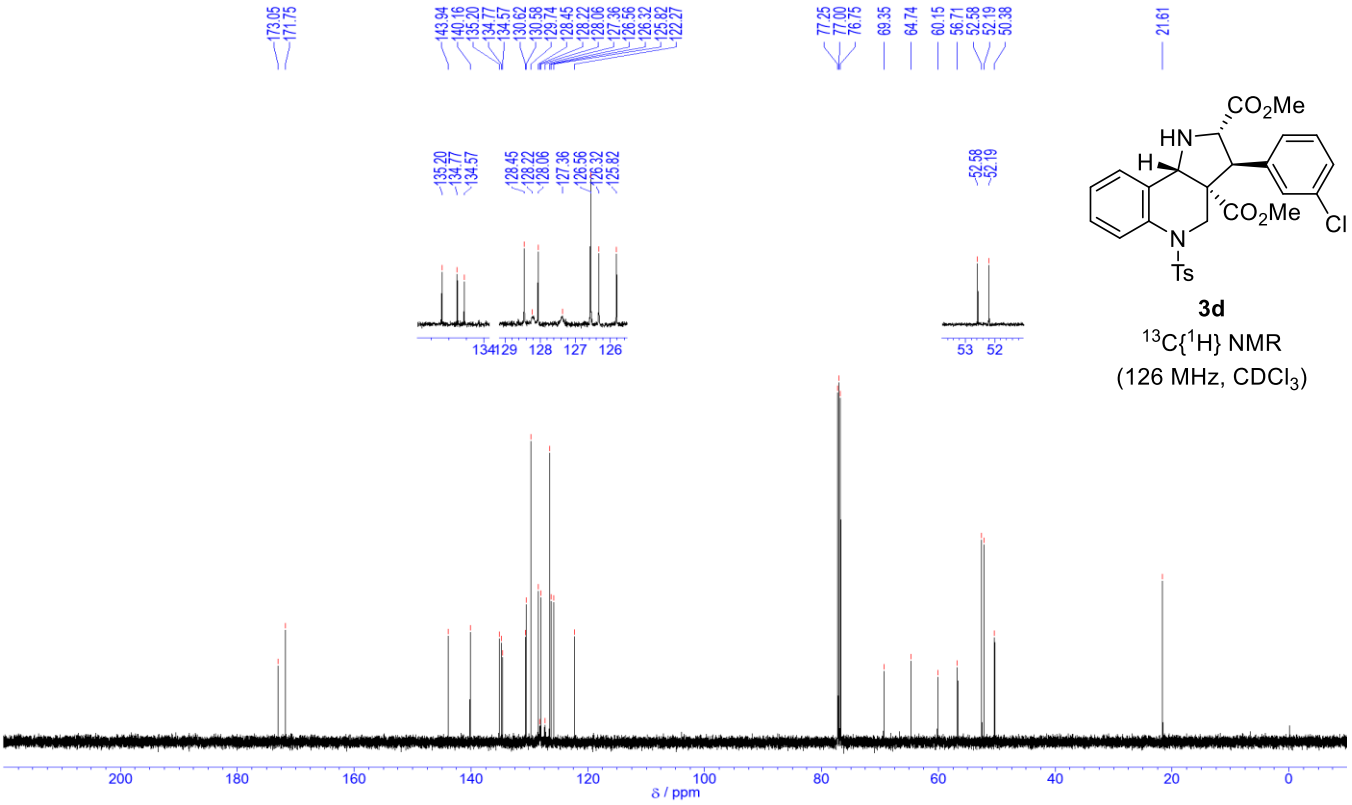


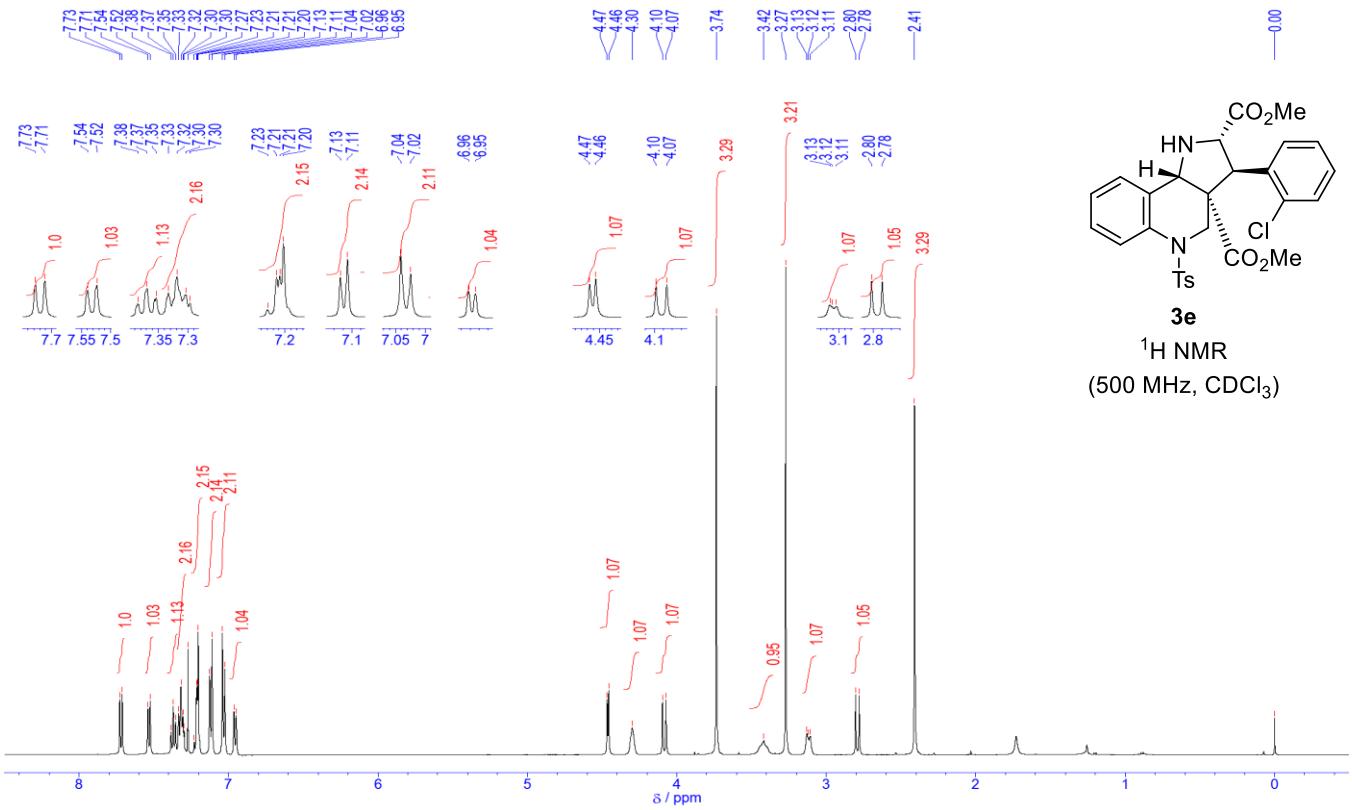
3c

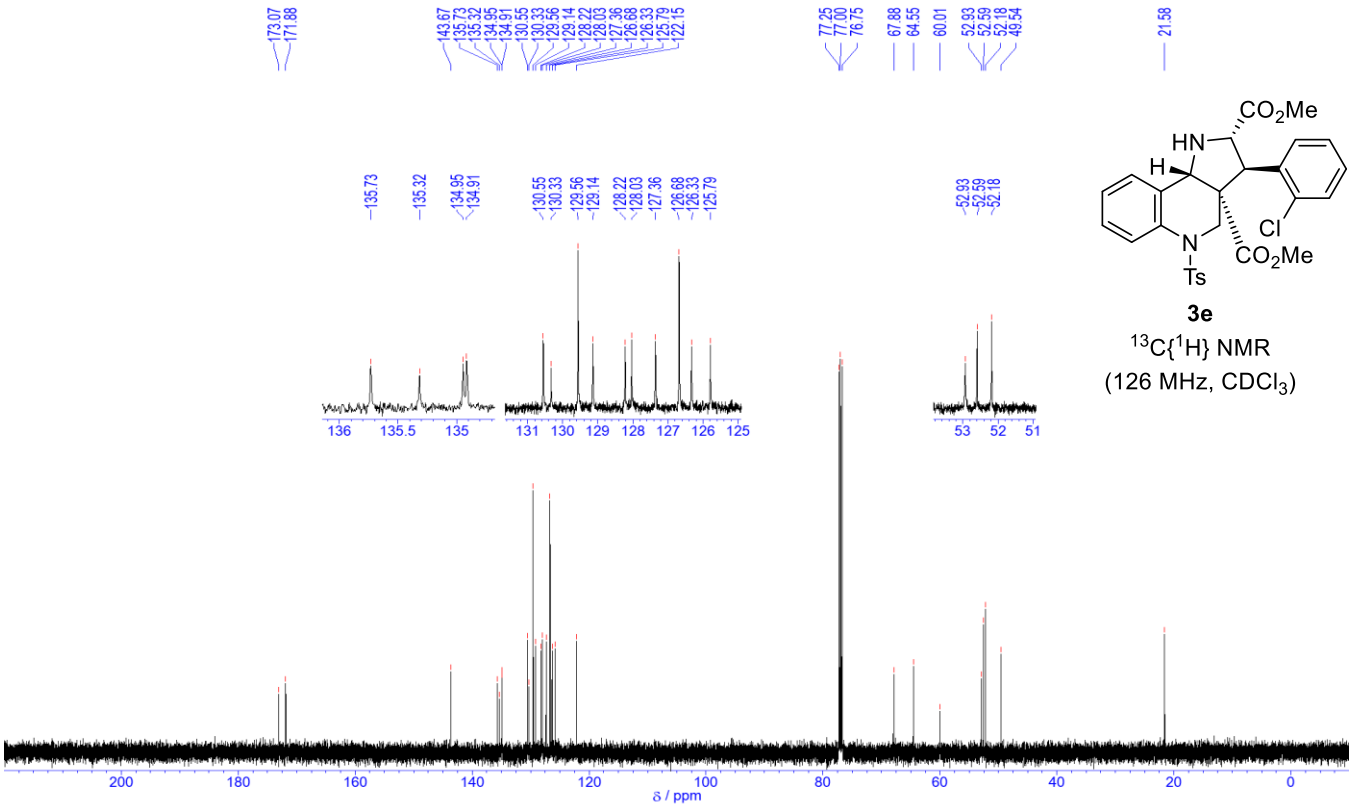
$^{13}C\{^{1}H\}$ NMR

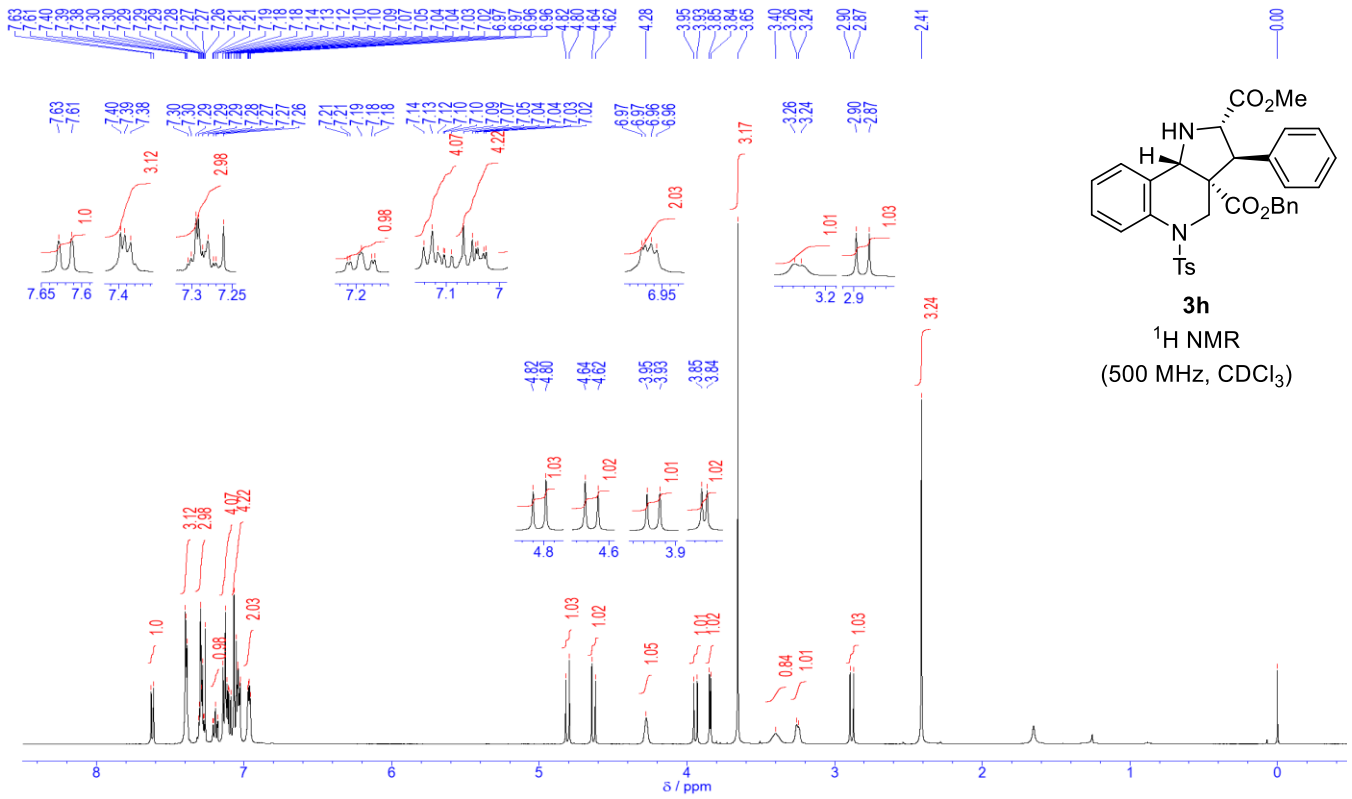
(126 MHz, $CDCl_3$)


CO2Me
HN
H
CO2Me
Cl
N
Ts
3d
1H NMR
(500 MHz, CDCl3)
δ / ppm


CO2Me
HN
H
CO2Me
Cl
N
Ts
3d
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm


CO2Me
HN
H
Cl
N
CO2Me
Ts
3e
1H NMR
(500 MHz, CDCl3)
δ / ppm

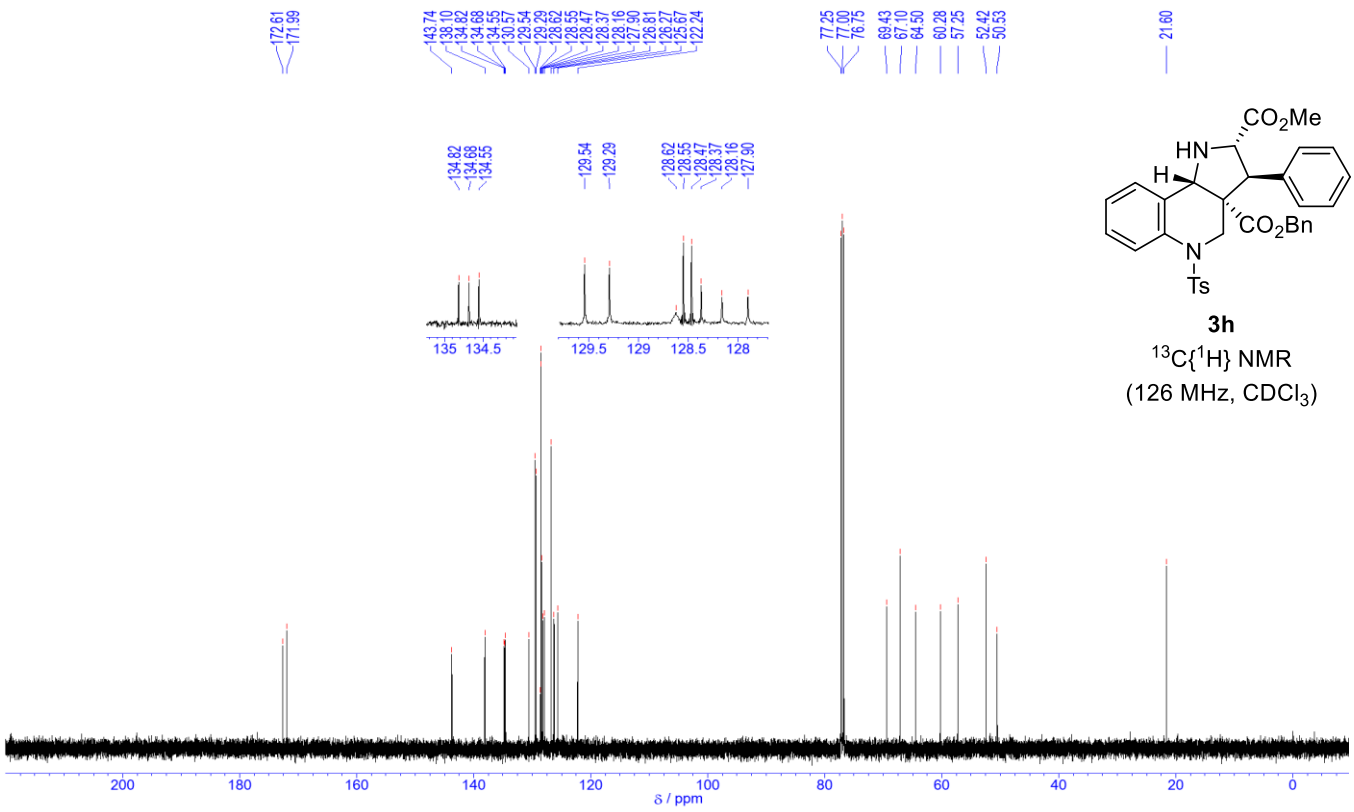

CO2Me
HN
H
Cl
N
CO2Me
Ts
3e
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm



3h

^{1}H NMR

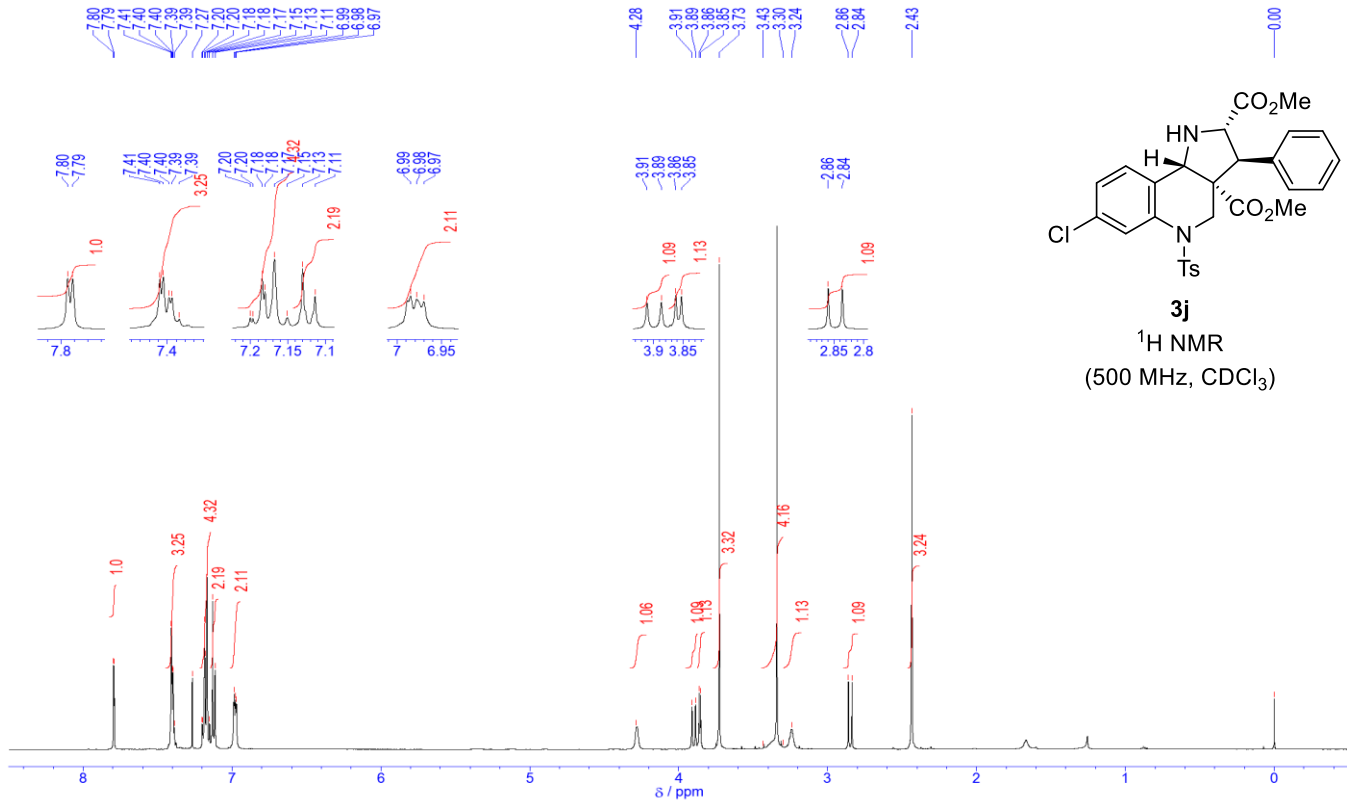
(500 MHz, $CDCl_3$)

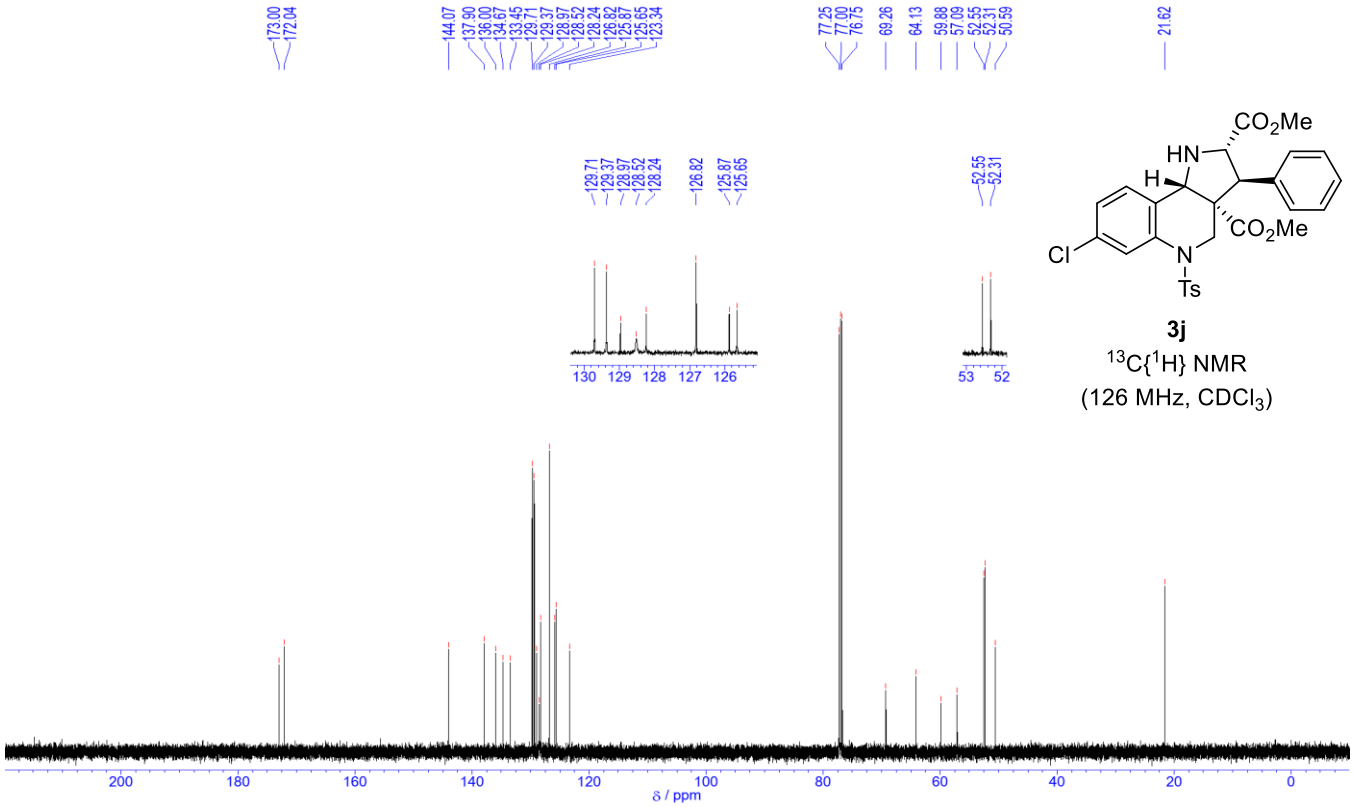


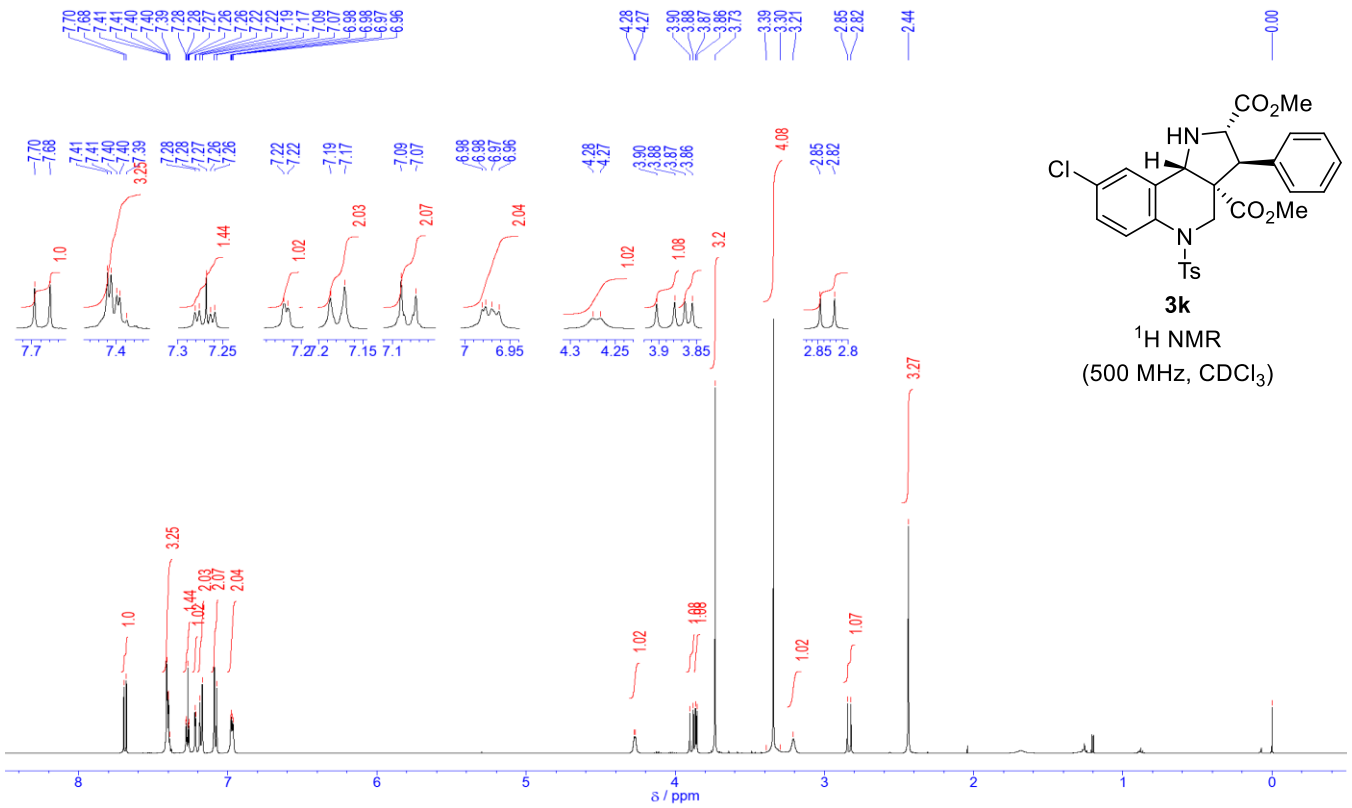
3h

$^{13}C\{^{1}H\}$ NMR

(126 MHz, $CDCl_3$)


CO2Me
HN
H
CO2Me
Cl
N
Ts
3j
1H NMR
(500 MHz, CDCl3)
δ / ppm

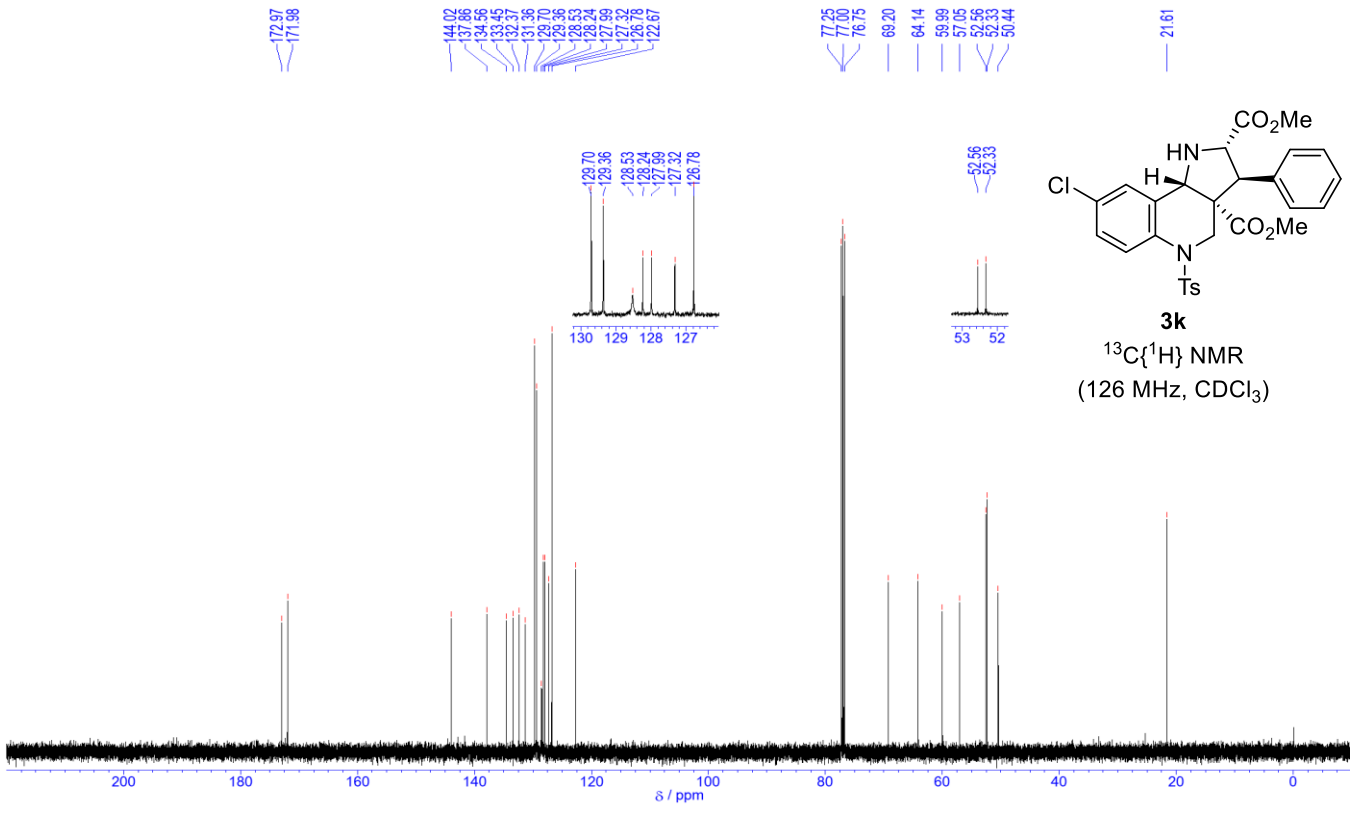

CO2Me
HN
H
CO2Me
Cl
N
Ts
3j
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm



3k

^{1}H NMR

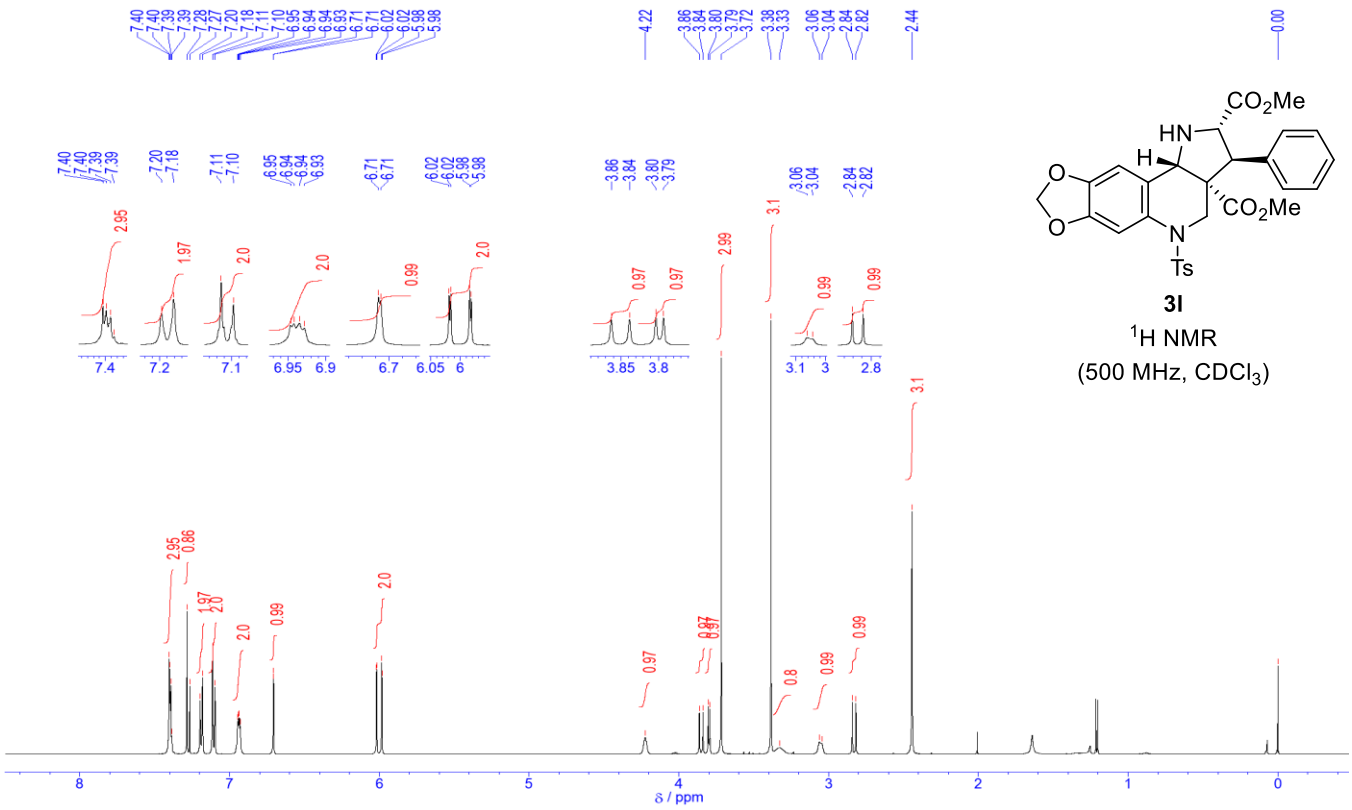
(500 MHz, $CDCl_3$)

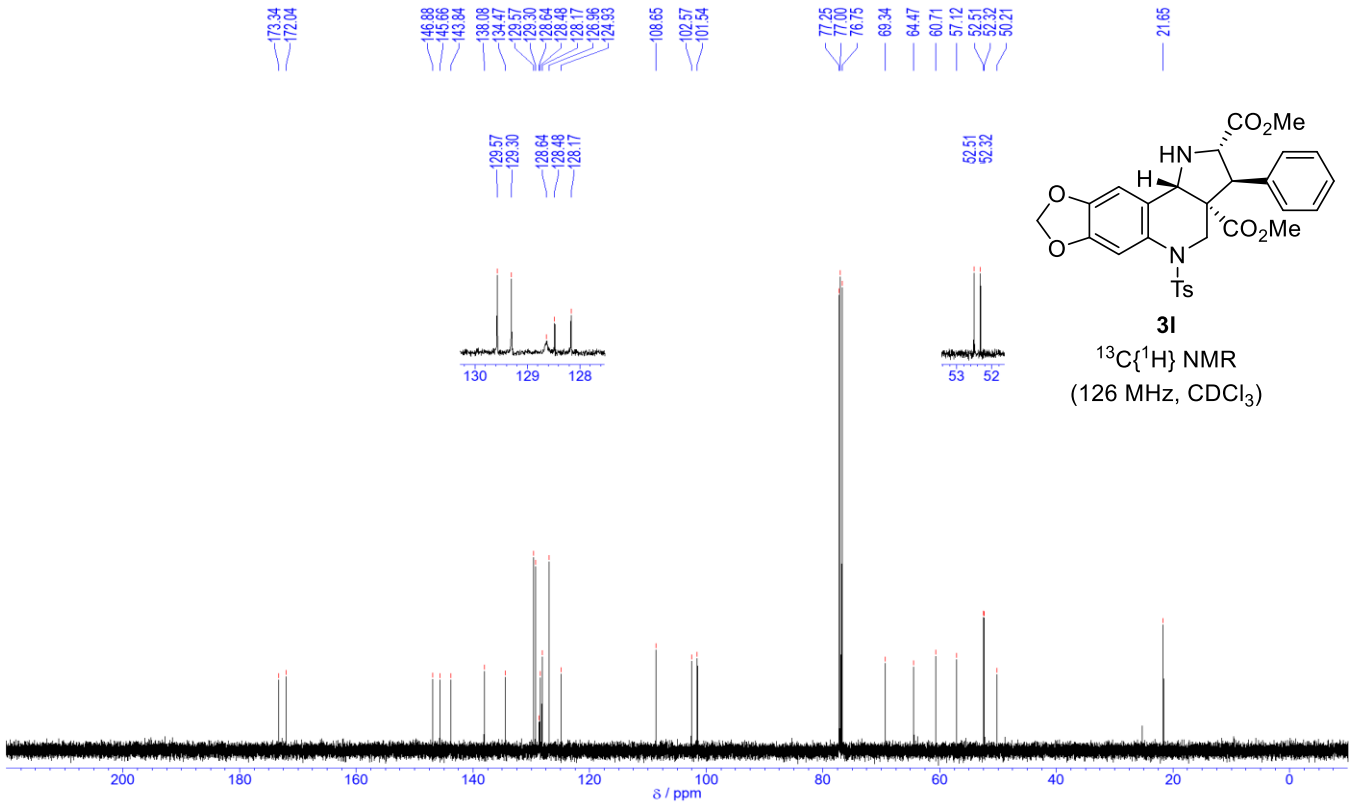


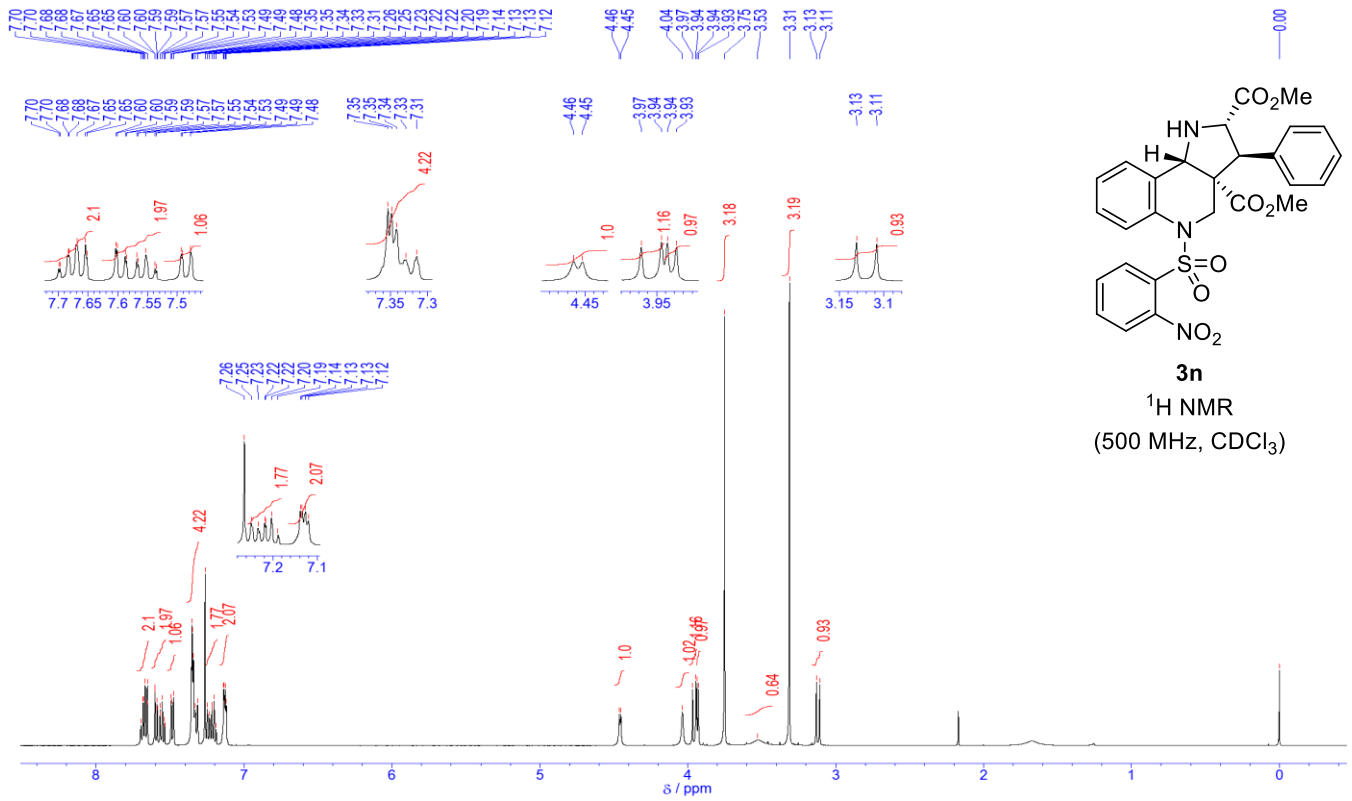
3k

$^{13}C\{^{1}H\}$ NMR

(126 MHz, $CDCl_3$)


CO2Me
HN
H
CO2Me
O
O
N
Ts
3l
1H NMR
(500 MHz, CDCl3)
δ / ppm

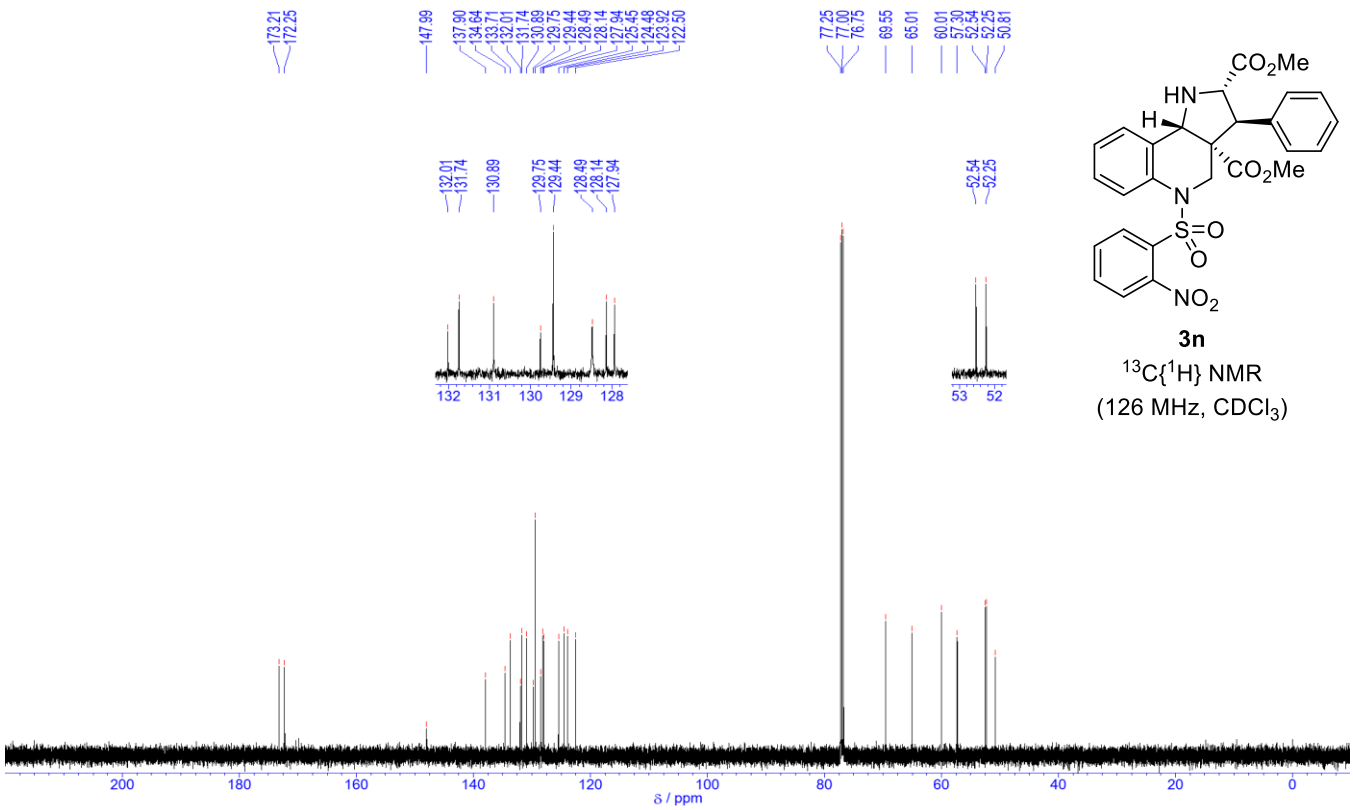

CO2Me
HN
H
CO2Me
O
O
N
Ts
3l
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm



3n

^{1}H NMR

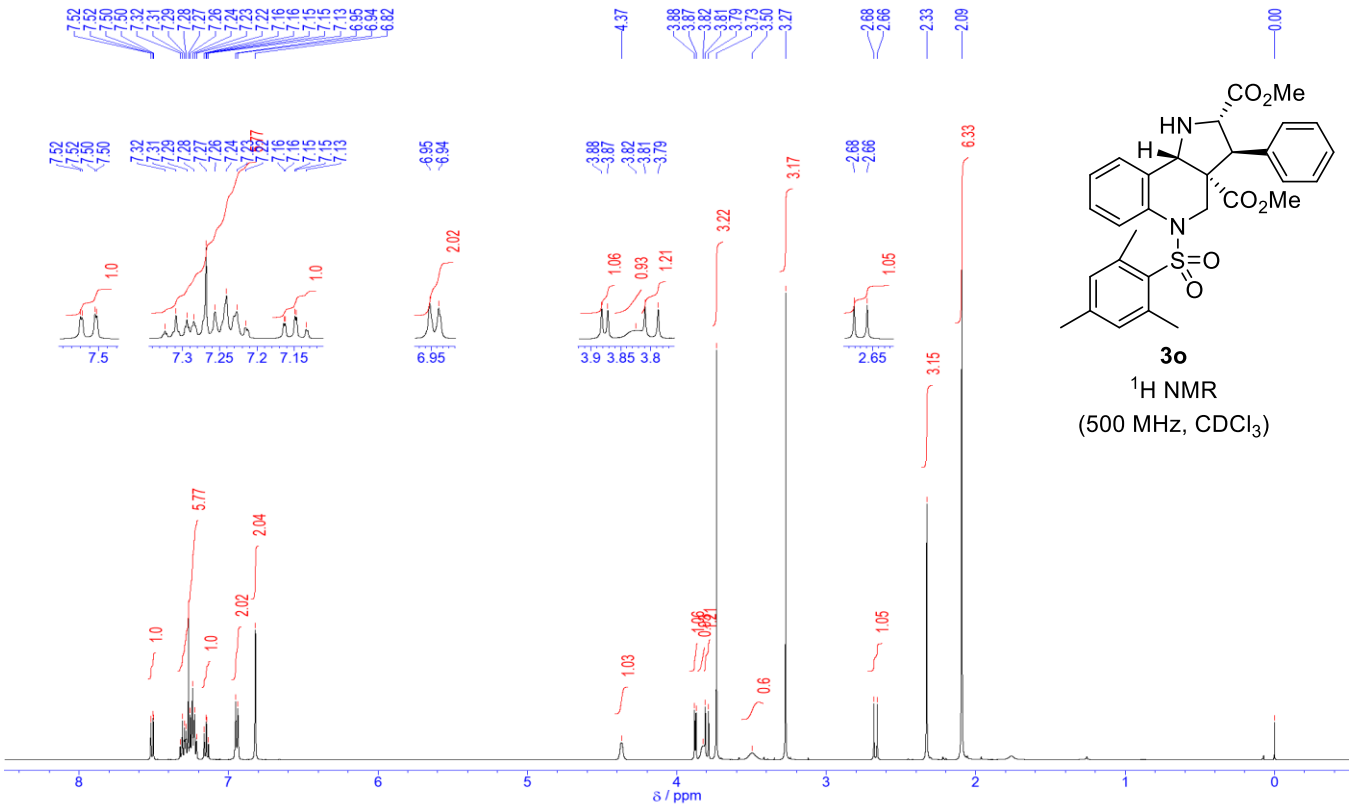
(500 MHz, $CDCl_3$)

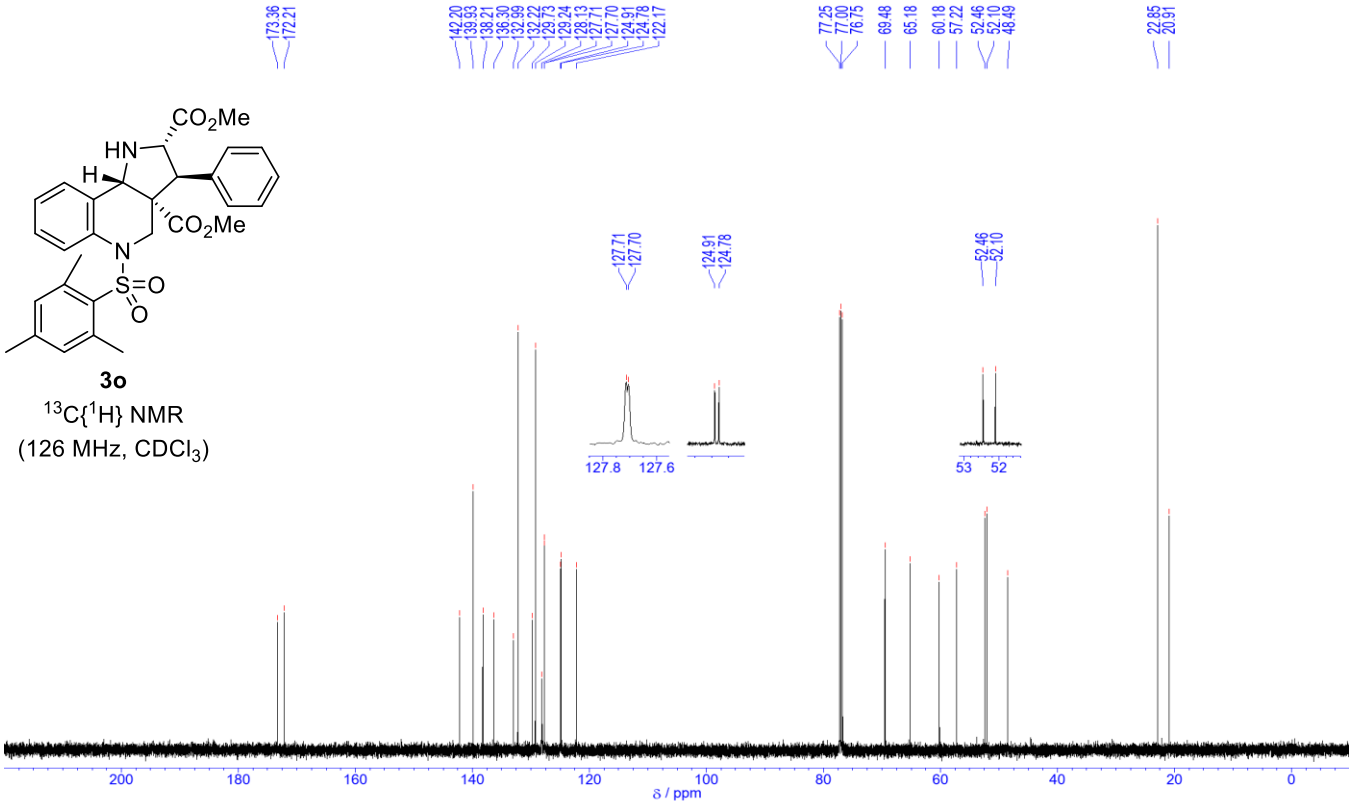


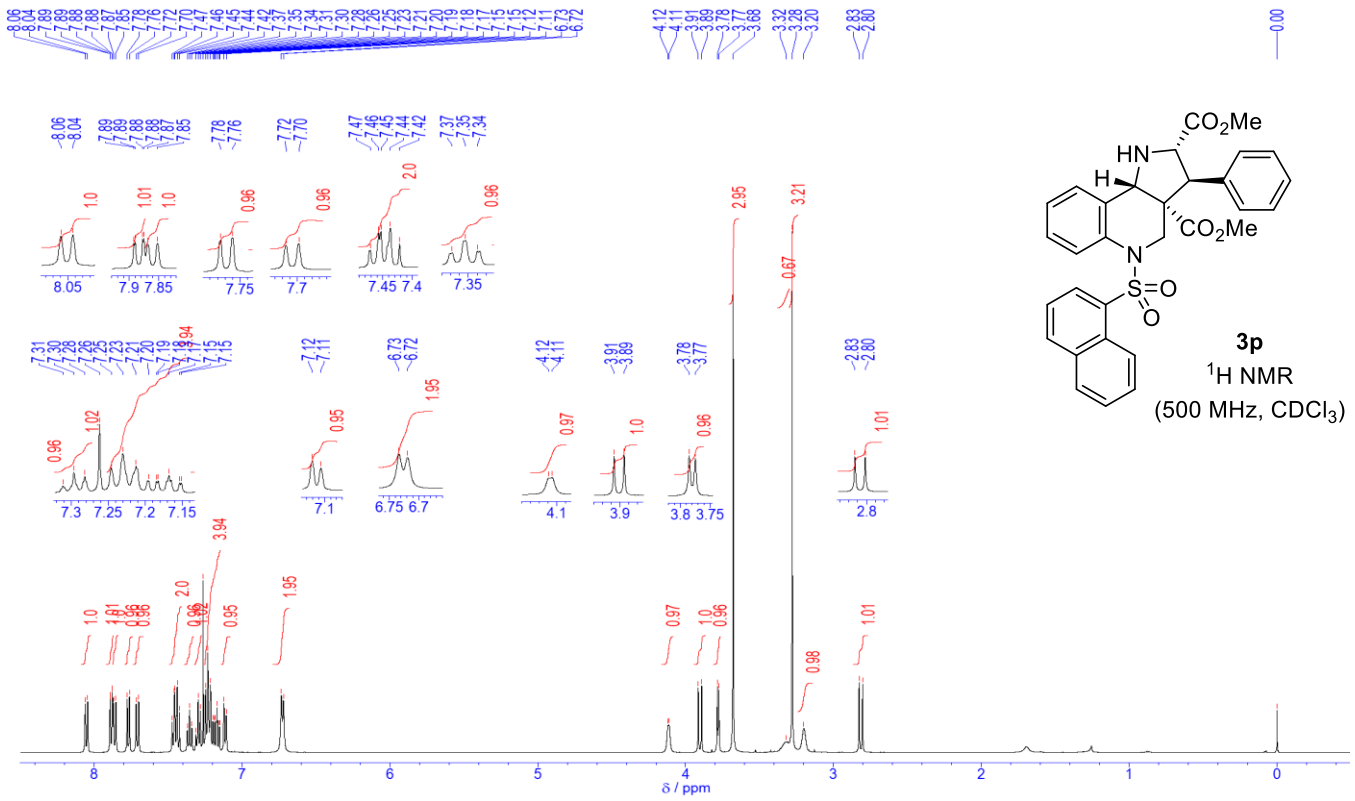
3n

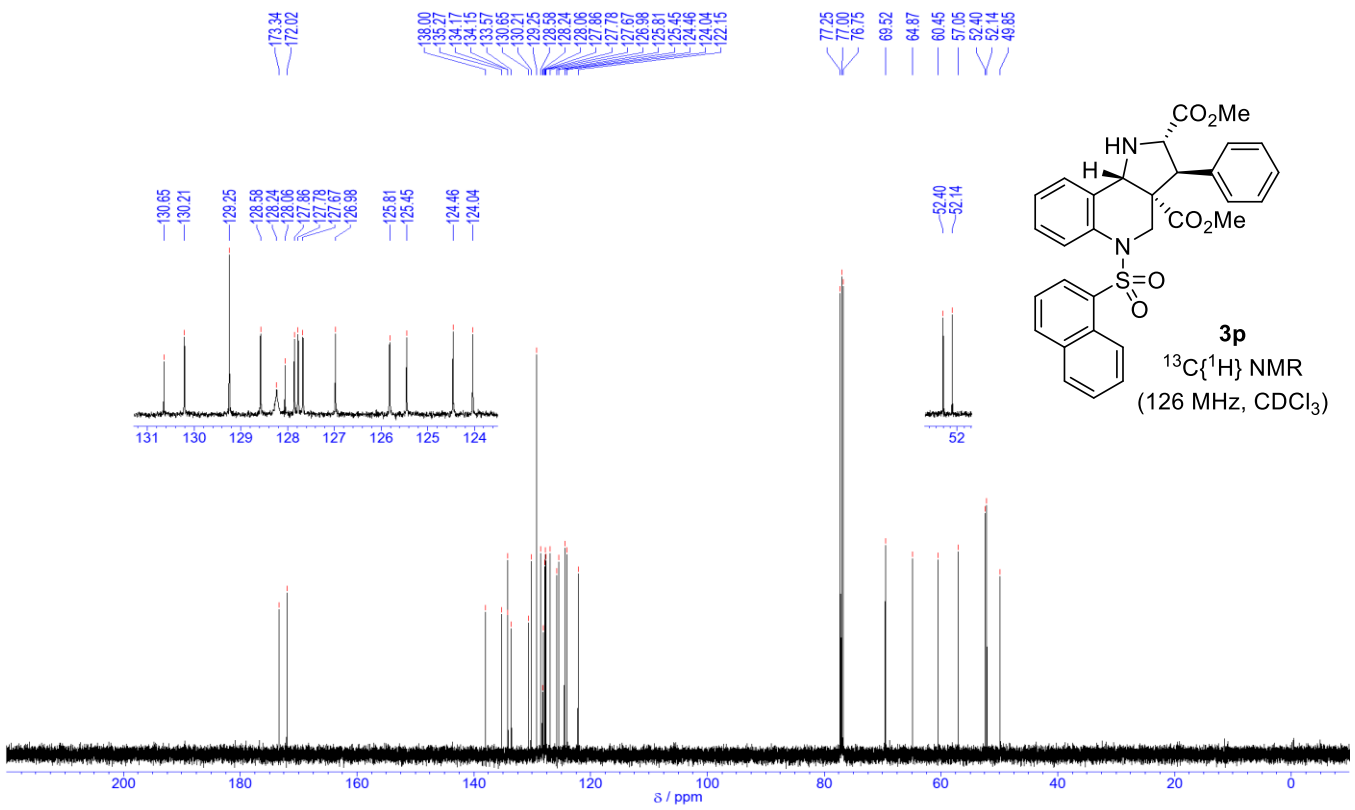
$^{13}C\{^{1}H\}$ NMR

(126 MHz, $CDCl_3$)

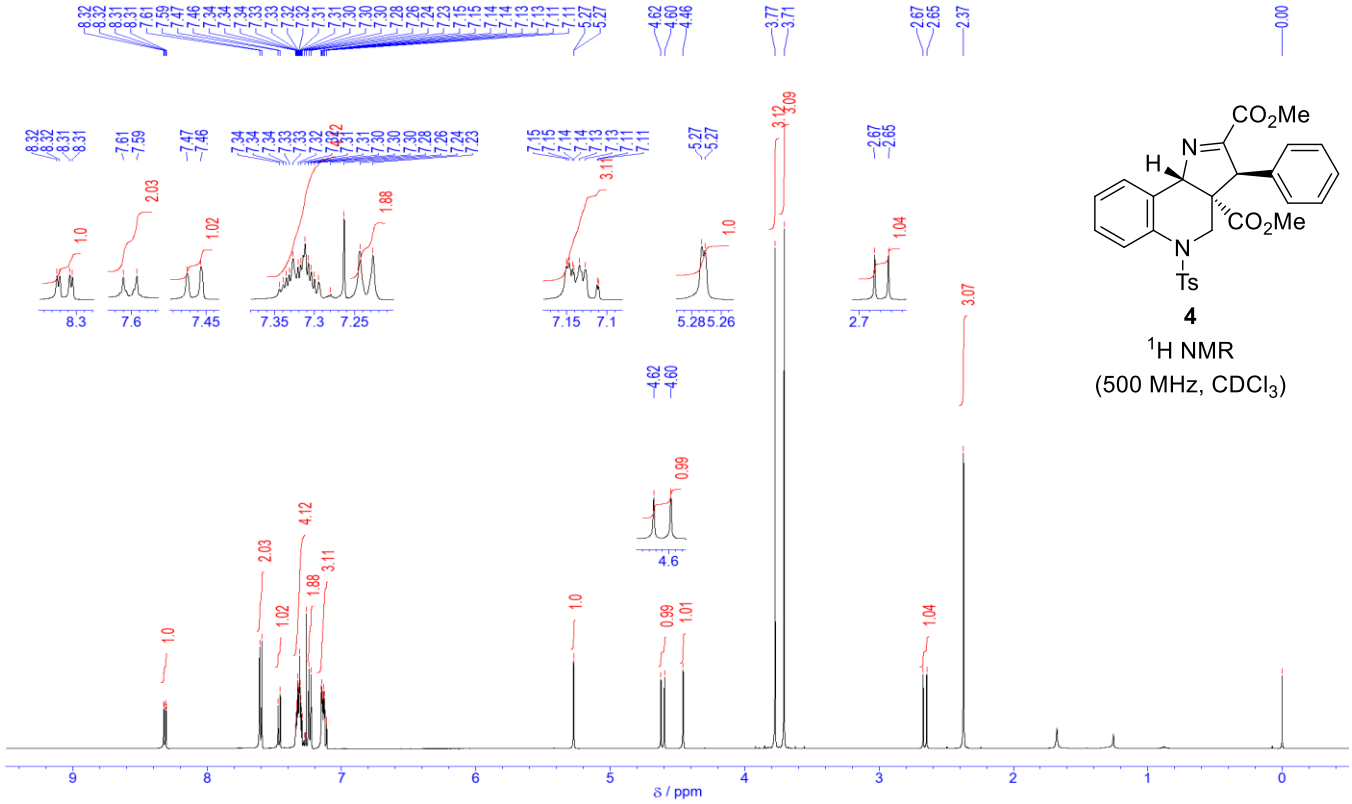

CO2Me
HN
H
CO2Me
N
S=O
O
3o
1H NMR
(500 MHz, CDCl3)
δ / ppm

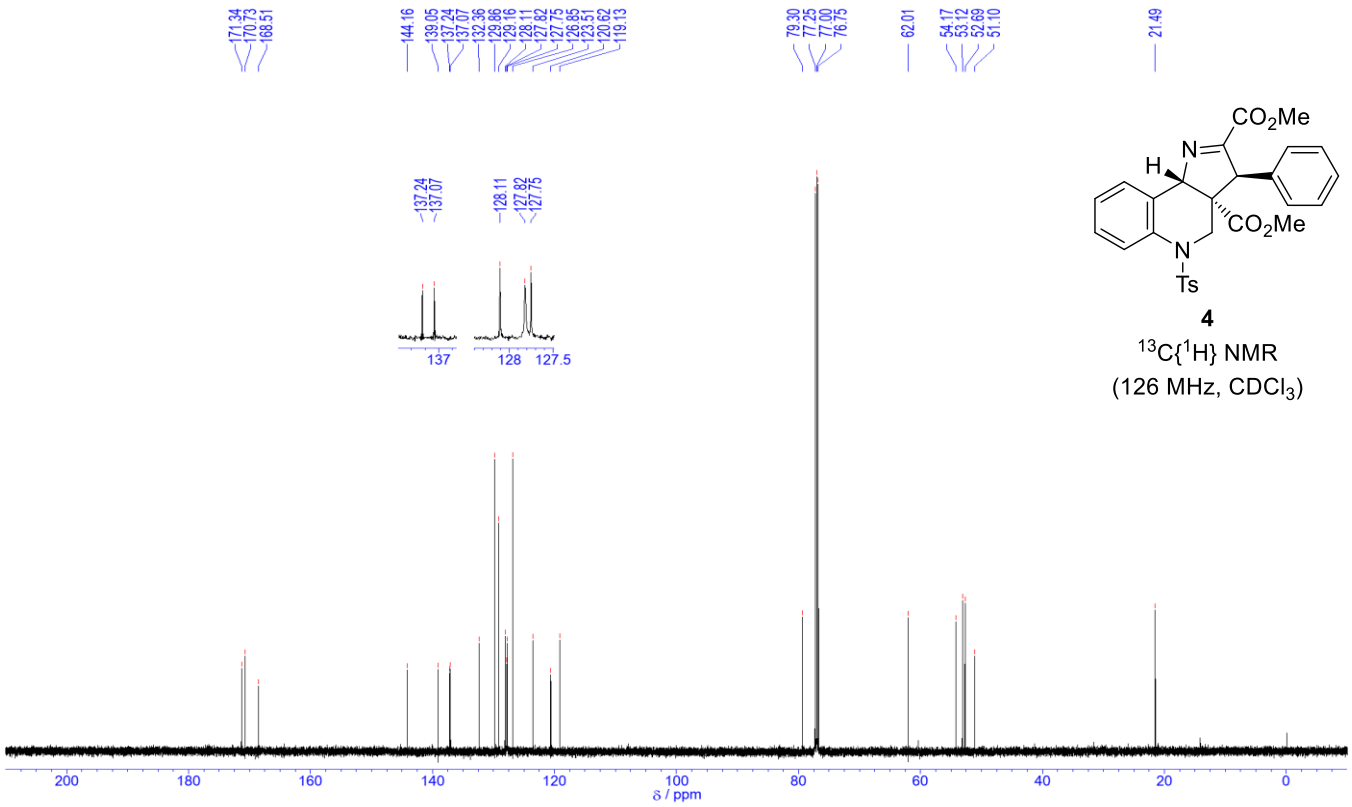

CO2Me
HN
H
CO2Me
N
S=O
O
3o
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm

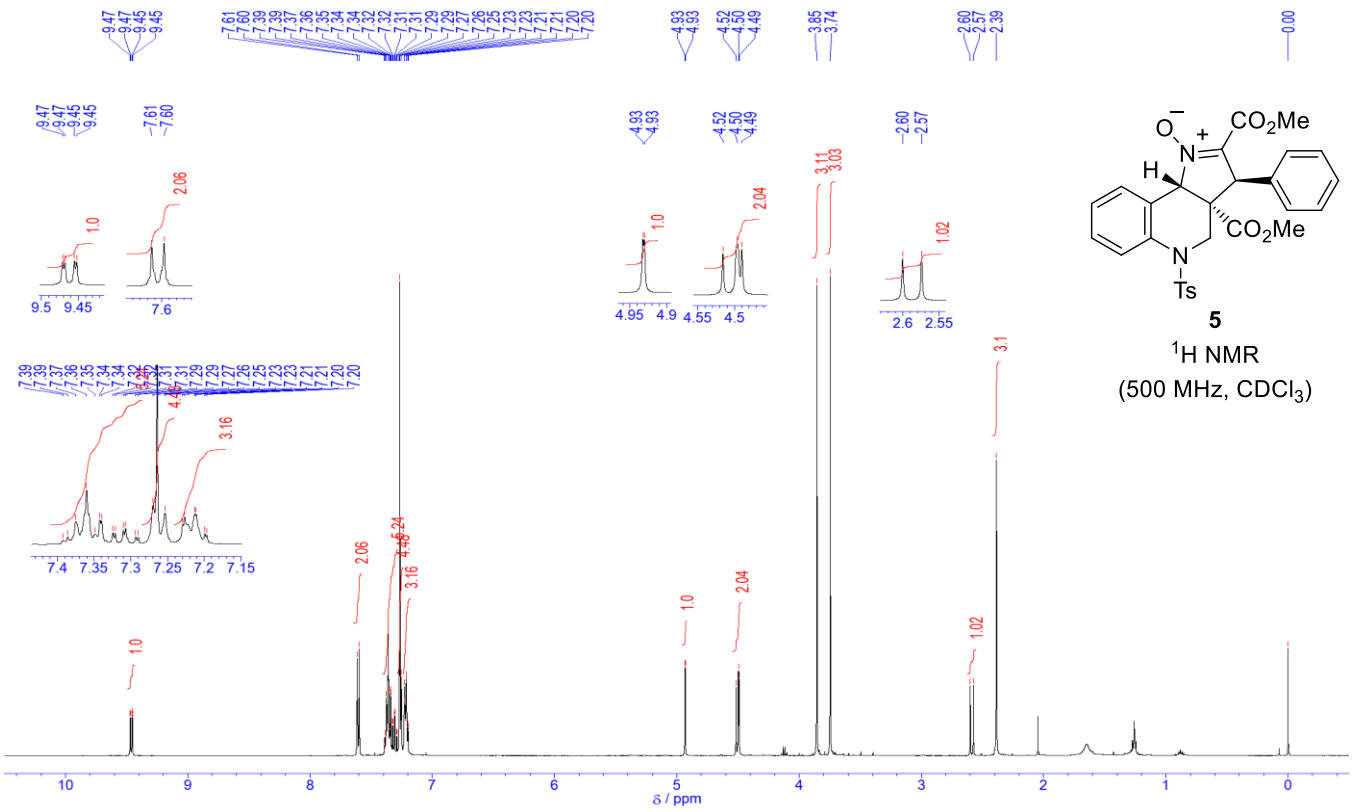

CO2Me
HN
H
CO2Me
N
S=O
O
3p
1H NMR
(500 MHz, CDCl3)
δ / ppm


CO2Me
HN
H
CO2Me
N
S=O
O
3p
13C{1H} NMR
(126 MHz, CDCl3)
δ / ppm

6.3 transformations of **3b**



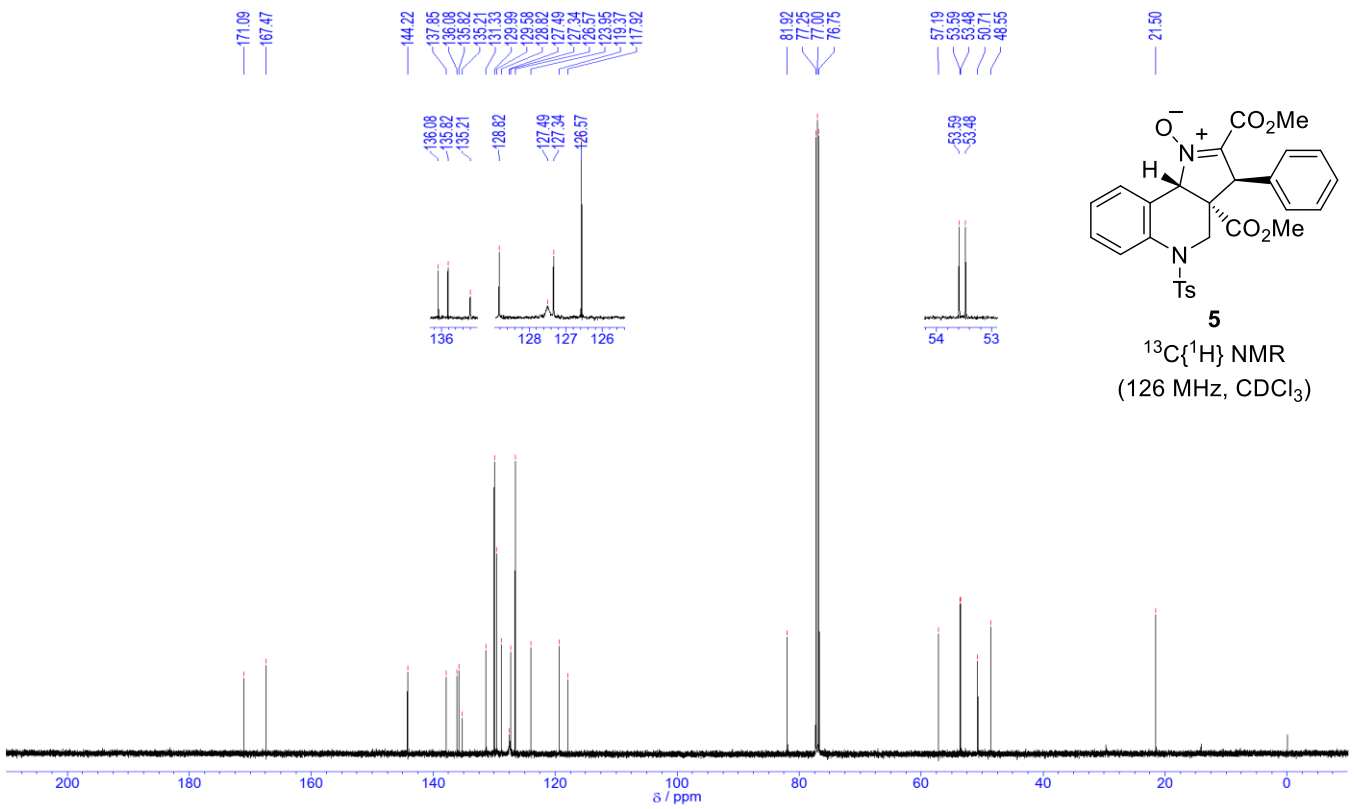




5

^{1}H NMR

(500 MHz, $CDCl_3$)



5

$^{13}C\{^{1}H\}$ NMR

(126 MHz, $CDCl_3$)