

Supporting Information for

Iridium-catalyzed intramolecular asymmetric allylic amination of anthranilic acid derivatives: enantioselective construction of chiral benzodiazepinones

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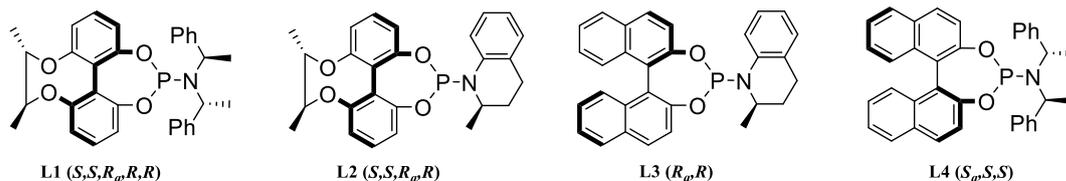
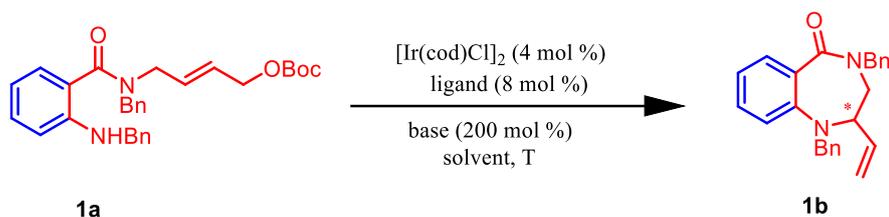
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1. General Considerations

Unless otherwise stated, all syntheses and manipulations of air- and moisture-sensitive materials were carried out in a nitrogen-filled glovebox or under nitrogen atmosphere using standard Schlenk techniques. All glassware was oven-dried prior to use. The heat source for all reactions is oil bath. All solvents were freshly distilled and degassed according to standard methods. Reactions were magnetically stirred and monitored by analytical thin-layer chromatography (TLC). TLC was performed using Merck silica gel 60 F254 TLC aluminum plates and visualized under ultraviolet light. Organic solutions were concentrated by rotary evaporation at 20 – 45 °C.

All chemicals and reagents available from commercial sources were directly used without further purification. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (200 – 300 mesh). ¹H, ¹⁹F, and ¹³C NMR spectra were recorded on a Bruker Ascend 400 MHz or 600 MHz spectrometer at ambient temperature. High-resolution mass spectra (HRMS) were obtained with Shimadzu LC-20AT mass spectrometer. The mass analyzer type is ion trap. Optical rotations were measured on SGW® 5 automatic polarimeter. Enantiomeric excesses (ee values) of the products were determined by chiral HPLC analysis using an Agilent HP 1200 instrument (*n*-hexane/2-propanol as eluent) with a Chiralpak IC-3, IA-3 or OD-H Column. The phosphoramidite ligands **L1** – **L4** are known compounds and were prepared according to the reported procedures.^[1]

2. Table S1 Optimization of Reaction Conditions^a



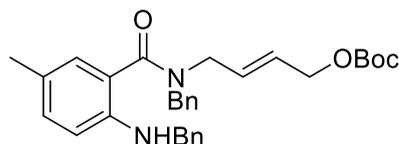
Entry	Ligand	T [°C]	Base	Solvent	t [h]	Yield ^b [%]	ee ^c [%]
1	L1	70	DBU	THF	2	85	92
2	L2	70	DBU	THF	2	68	35
3	L3	70	DBU	THF	2	72	19
4	L4	70	DBU	THF	2	60	-91
5	L1	30	DBU	THF	6	85	94
6	L1	40	DBU	THF	4	99	97
7	L1	50	DBU	THF	2	82	95
8	L1	40	DABCO	THF	4	92	95
9	L1	40	K ₃ PO ₄	THF	4	93	92
10	L1	40	DIPA	THF	4	93	88
11	L1	40	DBU	C ₂ H ₅ OH	4	47	60
12	L1	40	DBU	PhMe	4	95	95
13	L1	40	DBU	MeCN	4	90	85
14	L1	40	DBU	DCM	4	89	85
15 ^d	L1	40	DBU	THF	4	94	95
16 ^e	L1	40	DBU	THF	4	85	86

^a Conditions: [Ir(cod)Cl]₂ (4 mol%), **L** (8 mol%), DBU (0.2 mmol), and **1a** (0.1 mmol) in THF (2.0 mL). ^b Isolated yields. ^c Determined by chiral HPLC analysis. ^d [Ir(cod)Cl]₂ (2 mol%), **L1**

127.33, 127.17, 119.96, 116.27, 112.04, 82.32, 66.48, 47.72, 27.79. HRMS(ESI) calcd for $C_{30}H_{35}N_2O_4$ $[M+H]^+$: 487.2592, Found: 487.2588.

(E)-4-(N-benzyl-2-(benzylamino)-5-methylbenzamido)but-2-en-1-yl tert-butyl carbonate

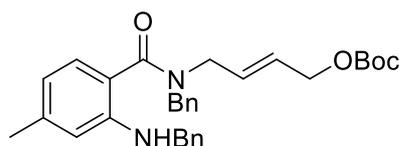
(2a)



Yellow oil, 470 mg, 94 % yield; 1H NMR (600 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.34 (d, $J = 2.7$ Hz, 2H), 7.33 – 7.28 (m, 5H), 7.28 – 7.27 (m, 1H), 7.24 (d, $J = 5.0$ Hz, 1H), 6.99 (d, $J = 8.3$ Hz, 1H), 6.94 (d, $J = 2.1$ Hz, 1H), 6.58 (d, $J = 8.3$ Hz, 1H), 5.75 – 5.70 (m, 1H), 5.69 – 5.65 (m, 1H), 4.64 (s, 2H), 4.53 (d, $J = 5.6$ Hz, 2H), 4.32 (s, 2H), 3.98 – 3.85 (m, 2H), 2.18 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.81, 153.27, 139.31, 136.87, 131.35, 129.79, 128.73, 128.71, 128.63, 128.60, 128.49, 127.52, 127.33, 127.09, 125.58, 124.46, 119.13, 112.20, 82.29, 66.49, 47.96, 27.78, 20.21. HRMS(ESI) calcd for $C_{31}H_{37}N_2O_4$ $[M+H]^+$: 501.2748, Found: 501.2744.

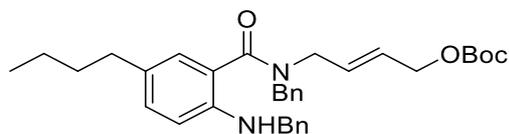
(E)-4-(N-benzyl-2-(benzylamino)-4-methylbenzamido)but-2-en-1-yl tert-butyl carbonate

(3a)



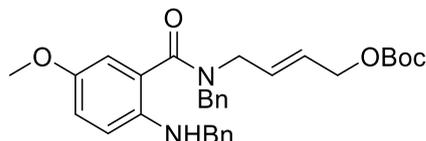
Yellow oil, 457 mg, 91% yield; 1H NMR (600 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.36 – 7.34 (m, 2H), 7.33 (d, $J = 7.4$ Hz, 2H), 7.31 – 7.26 (m, 4H), 7.21 (d, $J = 6.9$ Hz, 2H), 7.04 (d, $J = 7.7$ Hz, 1H), 6.51 – 6.47 (m, 1H), 5.77 – 5.71 (m, 1H), 5.69 – 5.65 (m, 1H), 4.64 (s, 2H), 4.53 (d, $J = 5.6$ Hz, 2H), 4.34 (s, 2H), 3.97 – 3.88 (m, 2H), 2.24 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.06, 153.27, 146.72, 141.21, 139.21, 136.90, 129.87, 128.70, 128.63, 127.71, 127.47, 127.38, 127.36, 127.29, 127.13, 117.03, 112.57, 82.28, 66.52, 47.70, 27.79, 21.86. HRMS(ESI) calcd for $C_{31}H_{37}N_2O_4$ $[M+H]^+$: 501.2748, Found: 501.2742.

**(E)-4-(N-benzyl-4-(benzylamino)-4'-butyl-[1,1'-biphenyl]-3-carboxamido)but-2-en-1-yl
tert-butyl carbonate (4a)**



Yellow oil, 415 mg, 83% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.36 (s, 1H), 7.34 (d, $J = 3.8$ Hz, 2H), 7.33 – 7.27 (m, 5H), 7.26 – 7.22 (m, 2H), 7.00 (dd, $J = 8.4, 2.1$ Hz, 1H), 6.95 (d, $J = 2.1$ Hz, 1H), 6.60 (d, $J = 8.3$ Hz, 1H), 5.80 – 5.72 (m, 1H), 5.71 – 5.66 (m, 1H), 4.64 (s, 2H), 4.53 (d, $J = 4.7$ Hz, 2H), 4.33 (s, 2H), 4.08 – 3.82 (m, 2H), 2.48 – 2.38 (m, 2H), 1.66 – 1.52 (m, 2H), 1.50 (s, 9H), 1.29 – 1.24 (m, 2H), 0.86 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.06, 153.27, 146.72, 141.21, 139.21, 136.90, 129.87, 128.70, 128.67, 128.63, 127.71, 127.47, 127.38, 127.35, 127.29, 127.13, 117.03, 112.57, 82.28, 66.52, 47.70, 27.79, 21.86. HRMS(ESI) calcd for $\text{C}_{34}\text{H}_{43}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 543.3217, Found: 543.3208.

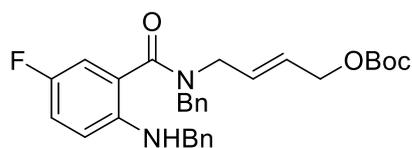
(E)-4-(N-benzyl-2-(benzylamino)-5-methoxybenzamido)but-2-en-1-yl tert-butyl carbonate (5a)



Yellow oil, 470 mg, 94% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.36 (s, 1H), 7.33 (d, $J = 7.0$ Hz, 3H), 7.31 – 7.26 (m, 4H), 7.24 (d, $J = 9.3$ Hz, 2H), 6.79 (d, $J = 9.0$ Hz, 1H), 6.74 (d, $J = 2.9$ Hz, 1H), 6.63 (d, $J = 8.9$ Hz, 1H), 5.81 – 5.71 (m, 1H), 5.71 – 5.67 (m, 1H), 4.63 (s, 2H), 4.52 (d, $J = 5.4$ Hz, 2H), 4.30 (s, 2H), 3.71 – 3.52 (m, 2H), 3.63 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.28, 153.26, 151.04, 139.30, 136.74, 134.44, 129.74, 129.63, 129.00, 128.75, 128.60, 128.26, 127.54, 127.50, 127.39, 127.12, 113.60, 112.70, 82.30, 66.44, 55.79, 48.47, 27.81, 27.78. HRMS(ESI) calcd for $\text{C}_{31}\text{H}_{37}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 517.2697, Found: 517.2698.

(E)-4-(N-benzyl-2-(benzylamino)-5-fluorobenzamido)but-2-en-1-yl tert-butyl carbonate

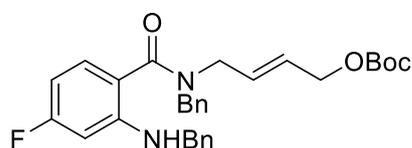
(6a)



Yellow oil, 426 mg, 85% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.34 (s, 1H), 7.34 – 7.32 (m, 3H), 7.32 – 7.26 (m, 4H), 7.26 – 7.20 (m, 2H), 6.92 (dt, $J = 8.6, 4.2$ Hz, 1H), 6.89 (dd, $J = 8.4, 3.1$ Hz, 1H), 6.60 (dd, $J = 9.0, 4.3$ Hz, 1H), 5.78 – 5.71 (m, 1H), 5.71 – 5.65 (m, 1H), 4.64 (s, 2H), 4.54 (d, $J = 5.2$ Hz, 2H), 4.31 (d, $J = 4.4$ Hz, 2H), 3.95 (d, $J = 20.2$ Hz, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.32, 154.52 (d, $J = 236.9$ Hz), 153.25, 142.63, 138.83, 129.52, 129.25, 128.82, 128.69, 128.23, 128.12, 127.81, 127.70, 127.30 (d, $J = 5.8$ Hz), 121.03, 117.33 (d, $J = 21.8$ Hz), 113.80 (d, $J = 24.0$ Hz), 113.11 (d, $J = 7.2$ Hz), 82.35, 66.36, 48.21, 27.78. ^{19}F NMR (565 MHz, CDCl_3) δ -128.05. HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{FN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 505.2497, Found: 505.2487.

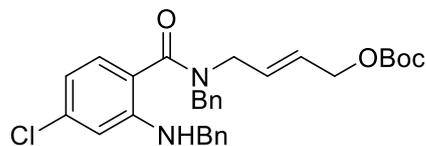
(E)-4-(N-benzyl-2-(benzylamino)-4-fluorobenzamido)but-2-en-1-yl tert-butyl carbonate

(7a)



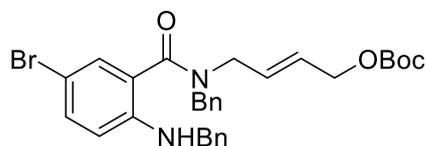
Yellow oil, 510 mg, 88% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.35 (d, $J = 2.6$ Hz, 2H), 7.34 (s, 1H), 7.34 – 7.27 (m, 5H), 7.24 – 7.18 (m, 2H), 7.11 (dd, $J = 8.4, 6.4$ Hz, 1H), 6.35 (dd, $J = 11.8, 2.4$ Hz, 1H), 6.31 (td, $J = 8.3, 2.4$ Hz, 1H), 5.76 – 5.71 (m, 1H), 5.70 – 5.65 (m, 1H), 4.64 (s, 2H), 4.54 (d, $J = 4.5$ Hz, 2H), 4.32 (d, $J = 5.1$ Hz, 2H), 3.95 (s, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.33, 164.90 (d, $J = 246.9$ Hz), 153.26, 149.12 (d, $J = 11.8$ Hz), 138.30, 136.65, 129.51, 129.01 (d, $J = 10.8$ Hz), 128.80, 128.78, 128.76, 128.74, 127.61, 127.56, 127.38, 127.27, 115.34, 102.67 (d, $J = 22.5$ Hz), 99.19 (d, $J = 26.3$ Hz), 82.36, 66.43, 47.61, 27.78. ^{19}F NMR (565 MHz, CDCl_3) δ -108.56. HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{FN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 505.2497, Found: 505.2492.

(E)-4-(N-benzyl-2-(benzylamino)-4-chlorobenzamido)but-2-en-1-yl tert-butyl carbonate
(8a)



Yellow oil, 450 mg, 90% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.35 (s, 1H), 7.34 (d, $J = 1.8$ Hz, 2H), 7.34 – 7.26 (m, 5H), 7.25 – 7.17 (m, 2H), 7.06 (d, $J = 8.1$ Hz, 1H), 6.66 (d, $J = 1.9$ Hz, 1H), 6.61 (d, $J = 7.5$ Hz, 1H), 5.78 – 5.70 (m, 1H), 5.70 – 5.66 (m, 1H), 4.63 (s, 2H), 4.54 (d, $J = 5.3$ Hz, 2H), 4.32 (d, $J = 5.4$ Hz, 2H), 3.94 (s, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.03, 153.25, 147.79, 138.26, 136.99, 136.55, 129.38, 128.81, 128.78, 128.29, 127.65, 127.44, 127.39, 127.36, 127.33, 117.94, 116.08, 111.94, 82.37, 66.40, 47.61, 27.79. HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 521.2202, Found: 521.2190.

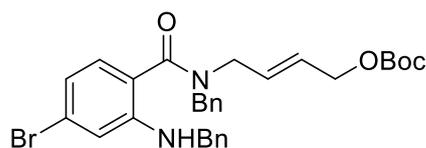
(E)-4-(N-benzyl-2-(benzylamino)-5-bromobenzamido)but-2-en-1-yl tert-butyl carbonate
(9a)



Yellow oil, 463 mg, 92% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.34 (s, 1H), 7.33 – 7.32 (m, 3H), 7.32 – 7.26 (m, 5H), 7.26 – 7.23 (m, 2H), 7.23 – 7.20 (m, 1H), 6.54 (d, $J = 8.8$ Hz, 1H), 5.77 – 5.70 (m, 1H), 5.70 – 5.65 (m, 1H), 4.64 (s, 2H), 4.54 (d, $J = 5.4$ Hz, 2H), 4.32 (d, $J = 5.4$ Hz, 2H), 3.93 (s, 2H), 1.51 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.17, 153.25, 145.36, 138.48, 136.45, 133.51, 129.65, 129.16, 128.82, 128.73, 128.71, 127.95, 127.72, 127.35, 127.23, 121.64, 113.75, 107.94, 82.35, 66.36, 47.70, 27.80. HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{BrN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 565.1696, Found: 565.1691.

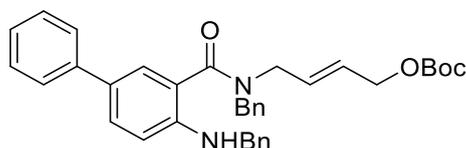
(E)-4-(N-benzyl-2-(benzylamino)-4-bromobenzamido)but-2-en-1-yl tert-butyl carbonate

(10a)



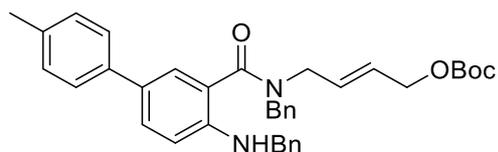
Yellow oil, 450 mg, 90% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.35 (s, 1H), 7.34 – 7.31 (m, 3H), 7.31 – 7.27 (m, 3H), 7.25 (d, $J = 2.2$ Hz, 1H), 7.23 – 7.14 (m, 2H), 6.98 (t, $J = 7.3$ Hz, 1H), 6.81 (d, $J = 4.3$ Hz, 1H), 6.77 – 6.74 (m, 1H), 5.78 – 5.69 (m, 1H), 5.69 – 5.63 (m, 1H), 4.62 (s, 2H), 4.53 (d, $J = 6.5$ Hz, 2H), 4.30 (d, $J = 5.9$ Hz, 2H), 3.92 (s, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.19, 153.27, 138.21, 134.51, 129.78, 129.21, 129.03, 128.85, 128.79, 128.39, 127.76, 127.72, 127.47, 127.40, 127.14, 125.42, 119.10, 114.86, 82.41, 66.40, 47.60, 27.81. HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{BrN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 565.1696, Found: 565.1691.

(E)-4-(N-benzyl-4-(benzylamino)-[1,1'-biphenyl]-3-carboxamido)but-2-en-1-yl tert-butyl carbonate (11a)



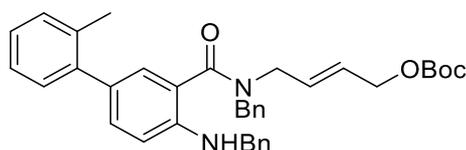
Yellow oil, 405 mg, 81% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.54 – 7.42 (m, 2H), 7.41 (d, $J = 2.3$ Hz, 1H), 7.37 (t, $J = 6.4$ Hz, 4H), 7.35 (s, 1H), 7.35 – 7.31 (m, 4H), 7.31 – 7.26 (m, 3H), 7.26 – 7.21 (m, 2H), 6.74 (d, $J = 8.5$ Hz, 1H), 5.85 – 5.75 (m, 1H), 5.74 – 5.68 (m, 1H), 4.69 (s, 2H), 4.54 (d, $J = 5.5$ Hz, 2H), 4.41 (d, $J = 5.1$ Hz, 2H), 4.03 (s, 2H), 1.49 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.74, 153.27, 140.35, 138.98, 136.82, 129.52, 128.83, 128.72, 128.70, 127.60, 127.55, 127.31, 127.24, 126.35, 126.14, 125.76, 112.52, 112.44, 82.30, 66.47, 47.77, 27.79. HRMS(ESI) calcd for $\text{C}_{36}\text{H}_{39}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 563.2905, Found: 563.2889.

(E)-4-(N-benzyl-4-(benzylamino)-4'-methyl-[1,1'-biphenyl]-3-carboxamido)but-2-en-1-yl tert-butyl carbonate (12a)



Yellow oil, 472 mg, 94% yield; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.47 – 7.39 (m, 2H), 7.38 (d, J = 3.1 Hz, 1H), 7.36 (d, J = 5.3 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.28 (dd, J = 14.1, 7.0 Hz, 3H), 7.24 (d, J = 3.7 Hz, 2H), 7.15 (s, 2H), 6.73 (d, J = 8.6 Hz, 1H), 5.84 – 5.74 (m, 1H), 5.73 – 5.68 (m, 1H), 4.69 (s, 2H), 4.53 (d, J = 4.4 Hz, 2H), 4.40 (s, 2H), 4.12 – 3.91 (m, 2H), 2.35 (s, 3H), 1.49 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.78, 153.27, 139.03, 137.49, 136.03, 129.65, 129.43, 129.32, 128.81, 128.68, 127.55, 127.53, 127.30, 127.21, 127.18, 126.00, 125.53, 112.42, 82.30, 66.49, 47.78, 27.78, 20.99. HRMS(ESI) calcd for $\text{C}_{37}\text{H}_{41}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 577.3061, Found: 577.3052.

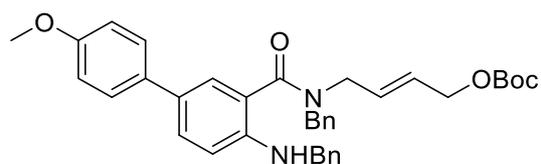
(E)-4-(N-benzyl-4-(benzylamino)-2'-methyl-[1,1'-biphenyl]-3-carboxamido)but-2-en-1-yl tert-butyl carbonate (13a)



Yellow oil, 400 mg, 80 % yield; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.40 (d, J = 7.5 Hz, 2H), 7.38 (s, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.0 Hz, 3H), 7.28 (d, J = 6.6 Hz, 2H), 7.25 – 7.24 (m, 1H), 7.22 – 7.16 (m, 4H), 7.13 (d, J = 2.1 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 5.77 – 5.72 (m, 1H), 5.70 – 5.66 (m, 1H), 4.68 (s, 2H), 4.51 (d, J = 5.6 Hz, 2H), 4.40 (d, J = 5.1 Hz, 2H), 4.00 (s, 2H), 2.22 (s, 3H), 1.49 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.70, 153.27, 153.25, 141.14, 139.07, 135.43, 131.77, 130.32, 130.00, 129.87, 128.79, 128.71, 127.59, 127.38, 127.25, 126.87, 125.81, 111.74, 82.28, 66.44, 47.88, 27.78, 20.55. HRMS(ESI) calcd for $\text{C}_{37}\text{H}_{41}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 577.3061, Found: 577.3058.

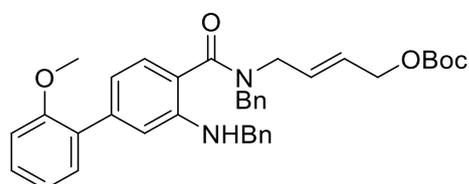
(E)-4-(N-benzyl-4-(benzylamino)-4'-methoxy-[1,1'-biphenyl]-3-carboxamido)but-2-en-1-

yl *tert*-butyl carbonate (14a)



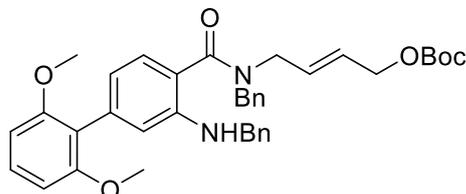
Yellow oil, 470 mg, 94% yield; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.41 – 7.37 (m, 2H), 7.37 (s, 1H), 7.35 (d, $J = 1.9$ Hz, 3H), 7.34 – 7.30 (m, 3H), 7.30 – 7.26 (m, 3H), 7.24 (d, $J = 10.2$ Hz, 2H), 6.93 – 6.82 (m, 2H), 6.72 (d, $J = 8.6$ Hz, 1H), 5.85 – 5.74 (m, 1H), 5.73 – 5.68 (m, 1H), 4.68 (s, 2H), 4.53 (d, $J = 5.5$ Hz, 2H), 4.42 – 4.36 (m, 2H), 4.11 – 3.91 (m, 2H), 3.82 (s, 3H), 1.49 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.78, 158.51, 153.27, 139.06, 136.83, 133.07, 129.65, 129.11, 128.82, 128.68, 127.57, 127.53, 127.30, 127.20, 127.18, 125.32, 114.20, 112.46, 82.30, 66.48, 55.33, 47.80, 27.78. HRMS(ESI) calcd for $\text{C}_{37}\text{H}_{41}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 593.3010, Found: 593.3005.

(*E*)-4-(*N*-benzyl-3-(benzylamino)-2'-methoxy-[1,1'-biphenyl]-4-carboxamido)but-2-en-1-yl *tert*-butyl carbonate (15a)



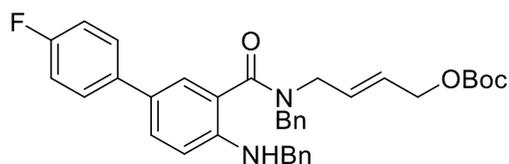
Yellow oil, 460 mg, 92% yield; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.40 (d, $J = 1.6$ Hz, 1H), 7.38 (s, 1H), 7.35 (dd, $J = 7.2, 1.9$ Hz, 2H), 7.34 – 7.30 (m, 3H), 7.30 – 7.27 (m, 4H), 7.25 (s, 1H), 7.20 (d, $J = 7.8$ Hz, 1H), 6.99 (t, $J = 6.9$ Hz, 1H), 6.94 (d, $J = 8.3$ Hz, 1H), 6.90 (d, $J = 1.6$ Hz, 1H), 6.83 (d, $J = 7.9$ Hz, 1H), 5.85 – 5.76 (m, 1H), 5.75 – 5.69 (m, 1H), 4.72 (s, 2H), 4.56 (d, $J = 5.9$ Hz, 2H), 4.39 (s, 2H), 4.10 – 3.93 (m, 2H), 3.69 (s, 3H), 1.52 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.93, 156.50, 153.30, 141.27, 139.32, 130.70, 130.57, 128.78, 128.75, 128.62, 127.52, 127.40, 127.09, 126.90, 120.79, 117.64, 113.58, 111.36, 82.30, 66.54, 55.47, 47.75, 27.81. HRMS(ESI) calcd for $\text{C}_{37}\text{H}_{41}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 593.3010, Found: 593.3009.

(E)-4-(N-benzyl-3-(benzylamino)-2',6'-dimethoxy-[1,1'-biphenyl]-4-carboxamido)but-2-en-1-yl *tert*-butyl carbonate (16a)



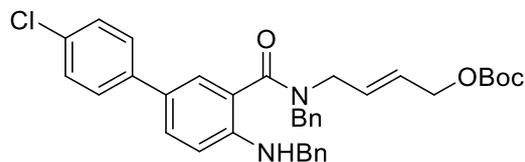
Yellow oil, 472 mg, 94% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.38 (d, $J = 1.8$ Hz, 1H), 7.36 (s, 1H), 7.34 – 7.31 (m, 4H), 7.29 – 7.26 (m, 3H), 7.26 – 7.22 (m, 2H), 7.19 (d, $J = 7.8$ Hz, 1H), 6.71 (d, $J = 1.6$ Hz, 1H), 6.66 (dd, $J = 7.8, 1.4$ Hz, 1H), 6.61 (d, $J = 8.3$ Hz, 2H), 5.82 – 5.76 (m, 1H), 5.72 – 5.68 (m, 1H), 4.73 (s, 2H), 4.55 (d, $J = 4.7$ Hz, 2H), 4.34 (s, 2H), 4.06 – 3.98 (m, 2H), 3.63 (s, 6H), 1.51 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.13, 157.69, 153.30, 146.34, 139.50, 137.11, 129.98, 128.71, 128.52, 127.81, 127.44, 126.95, 126.51, 119.60, 119.11, 118.01, 115.14, 104.32, 82.28, 66.56, 55.85, 47.70, 27.81. HRMS(ESI) calcd for $\text{C}_{38}\text{H}_{43}\text{N}_2\text{O}_6$ $[\text{M}+\text{H}]^+$: 623.3116, Found: 623.3109.

(E)-4-(N-benzyl-4-(benzylamino)-4'-fluoro-[1,1'-biphenyl]-3-carboxamido)but-2-en-1-yl *tert*-butyl carbonate (17a)



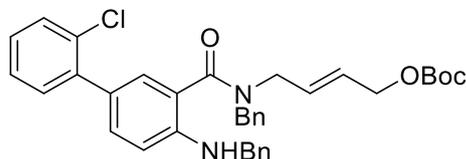
Yellow oil, 432 mg, 86% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.38 (d, $J = 7.8$ Hz, 2H), 7.37 (d, $J = 2.9$ Hz, 2H), 7.36 – 7.32 (m, 4H), 7.29 (dd, $J = 8.5, 6.7$ Hz, 3H), 7.27 (s, 1H), 7.26 – 7.19 (m, 2H), 7.09 – 6.95 (m, 2H), 6.73 (d, $J = 8.5$ Hz, 1H), 5.84 – 5.74 (m, 1H), 5.74 – 5.69 (m, 1H), 4.69 (s, 2H), 4.54 (d, $J = 5.4$ Hz, 2H), 4.40 (d, $J = 5.0$ Hz, 2H), 4.03 (s, 2H), 1.49 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.66, 161.89 (d, $J = 245.3$ Hz), 153.27, 138.91, 136.80, 136.49 (d, $J = 3.3$ Hz), 129.58, 129.37, 128.85, 128.71, 128.16, 127.63, 127.57, 127.28, 127.26, 125.61, 115.52 (d, $J = 21.5$ Hz), 112.46, 82.35, 66.46, 47.74, 27.77. ^{19}F NMR (565 MHz, CDCl_3) δ -117.03. HRMS(ESI) calcd for $\text{C}_{36}\text{H}_{38}\text{FN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 581.2810, Found: 581.2802.

**(E)-4-(N-benzyl-4-(benzylamino)-4'-chloro-[1,1'-biphenyl]-3-carboxamido)but-2-en-1-yl
tert-butyl carbonate (18a)**



Yellow oil, 471 mg, 94% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.40 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.39 – 7.36 (m, 4H), 7.35 (d, $J = 2.1$ Hz, 2H), 7.34 (s, 1H), 7.33 – 7.29 (m, 3H), 7.29 – 7.26 (m, 3H), 7.23 (d, $J = 8.7$ Hz, 2H), 6.73 (d, $J = 8.6$ Hz, 1H), 5.86 – 5.76 (m, 1H), 5.75 – 5.71 (m, 1H), 4.69 (s, 2H), 4.55 (d, $J = 4.6$ Hz, 2H), 4.40 (d, $J = 5.0$ Hz, 2H), 4.04 (s, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.60, 153.28, 138.84, 138.77, 136.80, 132.27, 129.56, 129.35, 128.87, 128.83, 128.74, 128.72, 127.68, 127.57, 127.28, 127.27, 125.55, 112.47, 82.36, 66.46, 47.70, 27.79. HRMS(ESI) calcd for $\text{C}_{36}\text{H}_{38}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 597.2515, Found: 597.2512.

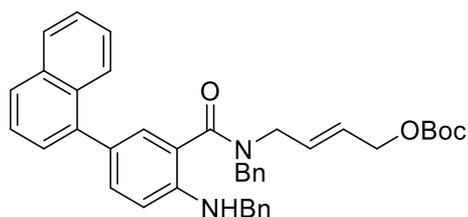
**(E)-4-(N-benzyl-4-(benzylamino)-2'-chloro-[1,1'-biphenyl]-3-carboxamido)but-2-en-1-yl
tert-butyl carbonate (19a)**



Yellow oil, 466 mg, 92% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.44 – 7.37 (m, 4H), 7.36 (s, 1H), 7.36 – 7.33 (m, 1H), 7.31 – 7.27 (m, 6H), 7.23 (d, $J = 7.1$ Hz, 2H), 7.20 (t, $J = 7.5$ Hz, 2H), 6.74 (d, $J = 8.3$ Hz, 1H), 5.81 – 5.72 (m, 1H), 5.71 – 5.66 (m, 1H), 4.71 (s, 2H), 4.52 (d, $J = 5.8$ Hz, 2H), 4.40 (d, $J = 3.5$ Hz, 2H), 4.02 (s, 2H), 1.49 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.53, 153.26, 146.01, 139.77, 138.93, 132.50, 132.05, 131.28, 129.93, 128.77, 128.72, 128.01, 127.57, 127.36, 127.27, 126.88, 119.30, 111.62, 82.28, 66.48, 47.76, 27.78. HRMS(ESI) calcd for $\text{C}_{36}\text{H}_{38}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 597.2515, Found: 597.2508.

(E)-4-(N-benzyl-2-(benzylamino)-5-(naphthalen-1-yl)benzamido)but-2-en-1-yl tert-butyl

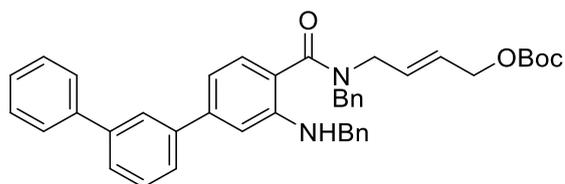
carbonate (20a)



Yellow oil, 455 mg, 91% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.91 – 7.86 (m, 2H), 7.80 (d, J = 8.2 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.42 (s, 1H), 7.39 (d, J = 7.5 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.34 – 7.29 (m, 4H), 7.28 (d, J = 5.9 Hz, 2H), 7.26 – 7.21 (m, 2H), 6.81 (d, J = 8.4 Hz, 1H), 5.79 – 5.71 (m, 1H), 5.70 – 5.65 (m, 1H), 4.70 (s, 2H), 4.47 (d, J = 5.7 Hz, 2H), 4.45 (s, 2H), 4.08 – 3.95 (m, 2H), 1.47 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.65, 153.23, 145.69, 139.53, 139.02, 133.88, 132.59, 131.74, 128.79, 128.76, 128.74, 128.26, 127.74, 127.59, 127.38, 127.29, 127.22, 126.83, 125.96, 125.93, 125.70, 125.44, 111.93, 82.27, 66.42, 47.89, 27.76. HRMS(ESI) calcd for $\text{C}_{40}\text{H}_{41}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 613.3061, Found: 613.3052.

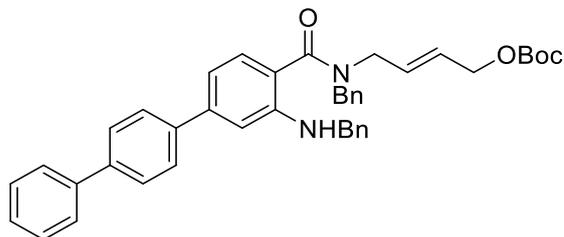
(E)-4-(N-benzyl-3-(benzylamino)-[1,1':3',1''-terphenyl]-4-carboxamido)but-2-en-1-yl

tert-butyl carbonate (21a)



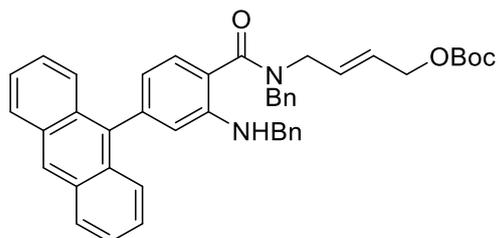
Yellow oil, 44.5 mg, 45% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.39 (m, 2H), 7.38 (d, J = 2.5 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.31 (s, 1H), 7.30 – 7.26 (m, 4H), 7.26 – 7.18 (m, 6H), 7.14 – 7.11 (m, 2H), 7.01 (d, J = 7.8 Hz, 1H), 6.48 (d, J = 1.6 Hz, 1H), 6.46 (d, J = 7.8 Hz, 1H), 5.79 – 5.70 (m, 1H), 5.69 – 5.63 (m, 1H), 4.63 (s, 2H), 4.53 (d, J = 6.2 Hz, 2H), 4.05 (s, 2H), 3.93 (d, J = 7.4 Hz, 2H), 1.51 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.82, 153.28, 144.13, 141.60, 140.64, 140.46, 139.02, 130.51, 130.14, 129.74, 129.70, 128.73, 128.59, 127.93, 127.62, 127.54, 127.42, 127.40, 127.14, 126.89, 126.49, 118.06, 117.92, 114.08, 82.31, 66.50, 47.69, 27.81. HRMS(ESI) calcd for $\text{C}_{42}\text{H}_{43}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 639.3218, Found: 639.3208.

**(E)-4-(N-benzyl-3-(benzylamino)-[1,1':4',1''-terphenyl]-4-carboxamido)but-2-en-1-yl
tert-butyl carbonate (22a)**



Yellow oil, 473 mg, 94% yield. ^1H NMR (600 MHz, CDCl_3) δ 7.64 – 7.61 (m, 3H), 7.56 (d, J = 8.1 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.40 (s, 1H), 7.36 (td, J = 7.4, 4.1 Hz, 3H), 7.34 – 7.26 (m, 5H), 7.25 (d, J = 3.1 Hz, 2H), 7.23 (d, J = 7.8 Hz, 1H), 6.99 – 6.85 (m, 2H), 5.83 – 5.75 (m, 1H), 5.73 – 5.68 (m, 1H), 4.70 (s, 2H), 4.55 (d, J = 5.6 Hz, 2H), 4.44 (s, 2H), 4.08 – 3.91 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.74, 153.28, 143.39, 140.66, 140.46, 140.02, 138.99, 129.71, 128.81, 128.79, 128.77, 128.71, 128.70, 127.74, 127.56, 127.47, 127.45, 127.43, 127.41, 127.37, 127.27, 127.04, 115.13, 110.66, 82.33, 66.51, 47.83, 27.80. HRMS(ESI) calcd for $\text{C}_{42}\text{H}_{43}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 639.3218, Found: 639.3213.

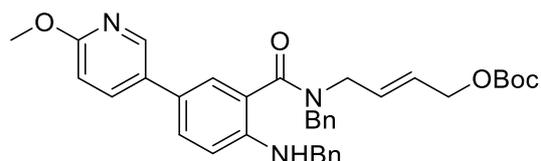
**(E)-4-(4-(anthracen-9-yl)-N-benzyl-2-(benzylamino)benzamido)but-2-en-1-yl tert-butyl
carbonate (23a)**



Yellow oil, 467 mg, 92% yield; ^1H NMR (600 MHz, CDCl_3) δ 8.46 (s, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.44 (ddd, J = 8.2, 6.4, 1.2 Hz, 2H), 7.36 (d, J = 7.6 Hz, 2H), 7.34 – 7.31 (m, 6H), 7.30 (d, J = 2.9 Hz, 4H), 7.25 (t, J = 3.3 Hz, 1H), 6.81 (d, J = 1.5 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 5.88 – 5.82 (m, 1H), 5.79 – 5.75 (m, 1H), 4.80 (s, 2H), 4.58 (d, J = 5.7 Hz, 2H), 4.28 (s, 2H), 4.13 – 4.08 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.83, 153.28, 146.55, 141.72, 138.66, 136.82, 131.30, 129.90, 129.85, 128.82, 128.64, 128.59, 128.23, 127.67, 127.63, 127.51, 127.22, 126.81, 126.56, 125.36, 125.10, 119.37, 118.93, 115.23,

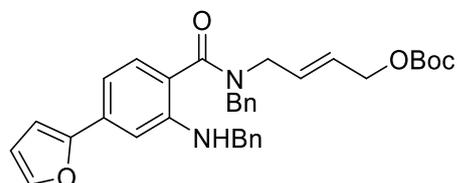
82.36, 66.50, 47.72, 27.79. HRMS(ESI) calcd for $C_{44}H_{43}N_2O_4$ $[M+H]^+$: 663.3217, Found: 663.3207.

**(E)-4-(N-benzyl-2-(benzylamino)-5-(6-methoxypyridin-3-yl)benzamido)but-2-en-1-yl
tert-butyl carbonate (24a)**



Yellow oil, 458 mg, 92% yield; 1H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.36 (d, $J = 2.2$ Hz, 3H), 7.36 – 7.34 (m, 2H), 7.34 – 7.31 (m, 2H), 7.31 – 7.26 (m, 4H), 7.26 – 7.21 (m, 2H), 6.74 (d, $J = 8.5$ Hz, 2H), 5.84 – 5.73 (m, 1H), 5.72 – 5.67 (m, 1H), 4.68 (s, 2H), 4.53 (d, $J = 5.4$ Hz, 2H), 4.40 (s, 2H), 4.10 – 3.95 (m, 2H), 3.94 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.50, 163.03, 153.25, 145.81, 143.99, 138.86, 136.72, 129.53, 129.45, 129.07, 128.85, 128.80, 128.73, 128.72, 127.70, 127.62, 127.48, 127.26, 127.05, 125.87, 125.31, 112.63, 110.71, 82.33, 66.43, 53.47, 47.73, 27.77. HRMS(ESI) calcd for $C_{36}H_{40}N_3O_5$ $[M+H]^+$: 594.2962, Found: 594.2949.

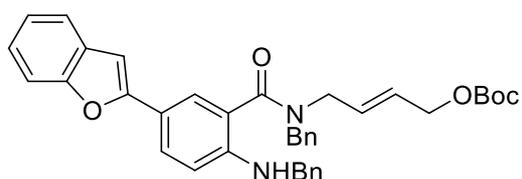
(E)-4-(N-benzyl-2-(benzylamino)-4-(furan-2-yl)benzamido)but-2-en-1-yl tert-butyl carbonate (25a)



Yellow oil, 480 mg, 96% yield; 1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, $J = 1.8$ Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 2H), 7.36 – 7.30 (m, 3H), 7.30 – 7.27 (m, 3H), 7.25 – 7.19 (m, 2H), 7.16 (d, $J = 7.9$ Hz, 1H), 7.02 (d, $J = 1.6$ Hz, 1H), 6.96 (d, $J = 7.9$ Hz, 1H), 6.58 (d, $J = 3.4$ Hz, 1H), 6.43 (dd, $J = 3.4, 1.8$ Hz, 1H), 5.81 – 5.71 (m, 1H), 5.71 – 5.66 (m, 1H), 4.66 (s, 2H), 4.53 (d, $J = 6.0$ Hz, 2H), 4.41 (s, 2H), 4.07 – 3.84 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.62,

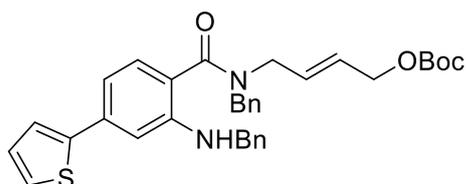
162.60, 153.73, 153.27, 146.96, 142.31, 138.94, 136.72, 133.15, 129.63, 128.76, 128.70, 127.76, 127.55, 127.51, 127.49, 127.28, 118.59, 111.95, 111.67, 106.98, 105.90, 82.32, 66.48, 47.78, 36.47, 31.45, 27.78. HRMS(ESI) calcd for $C_{34}H_{37}N_2O_5$ $[M+H]^+$: 553.2697, Found: 553.2688.

(E)-4-(5-(benzofuran-2-yl)-N-benzyl-2-(benzylamino)benzamido)but-2-en-1-yl tert-butyl carbonate (26a)



Yellow oil, 457 mg, 91% yield; 1H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, $J = 8.4$ Hz, 2H), 7.52 – 7.37 (m, 3H), 7.37 – 7.34 (m, 5H), 7.33 – 7.26 (m, 4H), 7.26 – 7.15 (m, 3H), 6.74 (d, $J = 8.4$ Hz, 1H), 5.86 – 5.80 (m, 1H), 5.76 – 5.73 (m, 1H), 4.71 (s, 2H), 4.58 (d, $J = 5.5$ Hz, 2H), 4.42 (d, $J = 5.5$ Hz, 2H), 4.03 (s, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.30, 155.93, 154.54, 153.29, 138.63, 136.74, 129.58, 129.42, 128.85, 128.78, 128.75, 127.87, 127.79, 127.73, 127.61, 127.34, 127.27, 124.21, 123.46, 122.76, 120.34, 118.72, 112.18, 110.86, 98.75, 82.34, 66.48, 47.61, 27.79. HRMS(ESI) calcd for $C_{38}H_{39}N_2O_5$ $[M+H]^+$: 603.2854, Found: 603.2845.

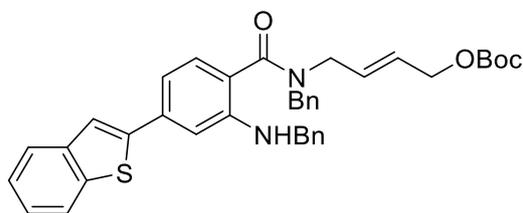
(E)-4-(N-benzyl-2-(benzylamino)-4-(thiophen-2-yl)benzamido)but-2-en-1-yl tert-butyl carbonate (27a)



Yellow oil, 467 mg, 93% yield; 1H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, $J = 7.1$ Hz, 2H), 7.37 (s, 1H), 7.36 – 7.32 (m, 2H), 7.32 – 7.26 (m, 4H), 7.25 (dd, $J = 5.0, 1.2$ Hz, 2H), 7.22 (dd, $J = 3.6,$

1.2 Hz, 1H), 7.16 (d, $J = 7.8$ Hz, 1H), 7.04 (dd, $J = 5.1, 3.6$ Hz, 1H), 6.93 – 6.88 (m, 2H), 5.82 – 5.73 (m, 1H), 5.72 – 5.67 (m, 1H), 4.67 (s, 2H), 4.55 (d, $J = 5.8$ Hz, 2H), 4.41 (d, $J = 4.5$ Hz, 2H), 3.97 (s, 2H), 1.51 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.55, 153.27, 147.09, 144.28, 138.87, 136.84, 129.66, 128.82, 128.77, 128.73, 128.70, 127.93, 127.88, 127.57, 127.52, 127.46, 127.30, 125.15, 123.53, 118.68, 113.98, 109.35, 82.34, 66.49, 47.80, 27.80, 27.75. HRMS(ESI) calcd for $\text{C}_{34}\text{H}_{37}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 569.2469, Found: 569.2464.

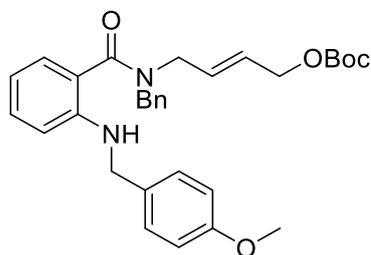
(*E*)-4-(4-(benzo[*b*]thiophen-2-yl)-*N*-benzyl-2-(benzylamino)benzamido)but-2-en-1-yl *tert*-butyl carbonate (28a)



Yellow oil, 425 mg, 85% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.6$ Hz, 1H), 7.75 (d, $J = 6.8$ Hz, 1H), 7.46 (s, 1H), 7.42 (d, $J = 7.6$ Hz, 2H), 7.37 (q, $J = 6.6$ Hz, 3H), 7.34 – 7.30 (m, 4H), 7.28 (d, $J = 5.6$ Hz, 2H), 7.24 – 7.18 (m, 2H), 7.06 – 6.94 (m, 2H), 5.85 – 5.74 (m, 1H), 5.73 – 5.67 (m, 1H), 4.68 (s, 2H), 4.56 (d, $J = 5.2$ Hz, 2H), 4.44 (s, 2H), 4.11 – 3.85 (m, 2H), 1.51 (s, 9H). ^{13}C NMR (151 MHz, CF_3COOD) δ 175.66, 157.56, 151.32, 148.38, 144.81, 143.83, 143.05, 141.03, 133.85, 133.08, 133.05, 132.14, 131.89, 131.78, 131.75, 131.65, 128.81, 128.75, 127.94, 126.53, 124.28, 123.78, 118.83, 114.17, 86.61, 70.75, 52.10, 32.08. HRMS(ESI) calcd for $\text{C}_{38}\text{H}_{39}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 619.2626, Found: 619.2624.

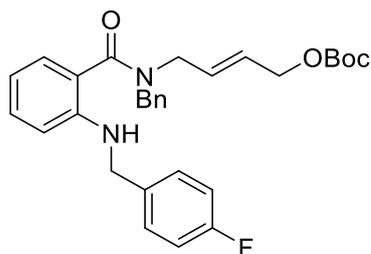
(*E*)-4-(*N*-benzyl-2-(benzylamino)-4-(5a,9a-dihydrodibenzo[*b,d*]thiophen-3-yl)benzamido)but-2-en-1-yl *tert*-butyl carbonate (29a)

(E)-4-(N-benzyl-2-((4-methoxybenzyl)amino)benzamido)but-2-en-1-yl tert-butyl carbonate (31a)



Yellow oil, 430 mg, 86% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.30 (t, $J = 7.2$ Hz, 2H), 7.29 – 7.26 (m, 3H), 7.25 – 7.17 (m, 3H), 7.14 (dd, $J = 7.6, 1.6$ Hz, 1H), 6.88 (d, $J = 8.7$ Hz, 2H), 6.69 (d, $J = 8.3$ Hz, 1H), 6.64 (t, $J = 7.5$ Hz, 1H), 5.85 – 5.70 (m, 1H), 5.71 – 5.63 (m, 1H), 4.65 (s, 2H), 4.53 (d, $J = 5.8$ Hz, 2H), 4.27 (s, 2H), 4.04 – 3.83 (m, 2H), 3.80 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.76, 158.85, 153.27, 146.40, 136.79, 131.04, 130.91, 129.71, 128.73, 128.60, 128.53, 127.53, 127.47, 127.14, 119.97, 116.21, 114.09, 112.00, 82.31, 66.49, 55.30, 47.21, 27.79. HRMS(ESI) calcd for $\text{C}_{31}\text{H}_{37}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 517.2697, Found: 517.2689.

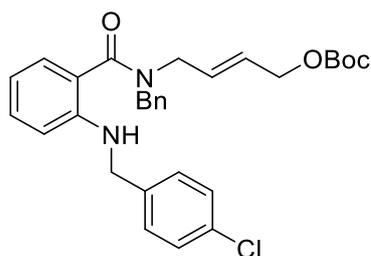
(E)-4-(N-benzyl-2-((4-fluorobenzyl)amino)benzamido)but-2-en-1-yl tert-butyl carbonate (32a)



Yellow oil, 445 mg, 90% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.32 (d, $J = 6.1$ Hz, 3H), 7.30 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 7.20 – 7.16 (m, 1H), 7.15 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.02 (t, $J = 8.7$ Hz, 2H), 6.64 (d, $J = 8.1$ Hz, 2H), 5.84 – 5.71 (m, 1H), 5.72 – 5.64 (m, 1H), 4.66 (s, 2H), 4.54 (d, $J = 4.5$ Hz, 2H), 4.32 (s, 2H), 4.08 – 3.77 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.76, 162.04 (d, $J = 244.8$ Hz), 153.26, 146.32, 136.75, 134.73 (d, $J = 3.1$ Hz), 130.96, 129.62, 128.83 (d, $J = 8.1$ Hz), 128.75, 127.72, 127.58, 127.52, 127.22, 119.93,

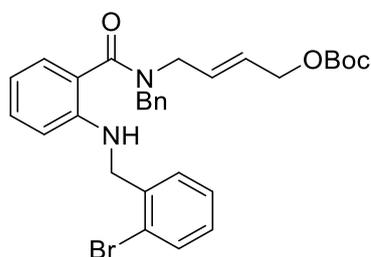
116.41, 115.47 (d, $J = 21.3$ Hz), 112.03, 82.35, 66.45, 47.00, 27.78. ^{19}F NMR (565 MHz, CDCl_3) δ -115.72. HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{FN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 505.2498, Found: 505.2488.

(E)-4-(N-benzyl-2-((4-chlorobenzyl)amino)benzamido)but-2-en-1-yl *tert*-butyl carbonate
(33a)



Yellow oil, 450 mg, 90% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.37 – 7.30 (m, 3H), 7.28 (d, $J = 4.1$ Hz, 5H), 7.23 (d, $J = 6.9$ Hz, 1H), 7.17 (t, $J = 7.5$ Hz, 1H), 7.15 (d, $J = 7.8$ Hz, 1H), 6.65 (t, $J = 7.6$ Hz, 1H), 6.60 (d, $J = 8.2$ Hz, 1H), 5.82 – 5.72 (m, 1H), 5.71 – 5.65 (m, 1H), 4.66 (s, 1H), 4.55 (d, $J = 5.5$ Hz, 2H), 4.32 (s, 2H), 4.06 – 3.82 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.76, 153.26, 137.63, 136.77, 132.83, 130.98, 129.62, 128.79, 128.77, 128.55, 128.50, 127.79, 127.60, 127.54, 127.26, 119.84, 116.46, 112.07, 82.38, 66.47, 47.01, 27.79. HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 521.2202, Found: 521.2194.

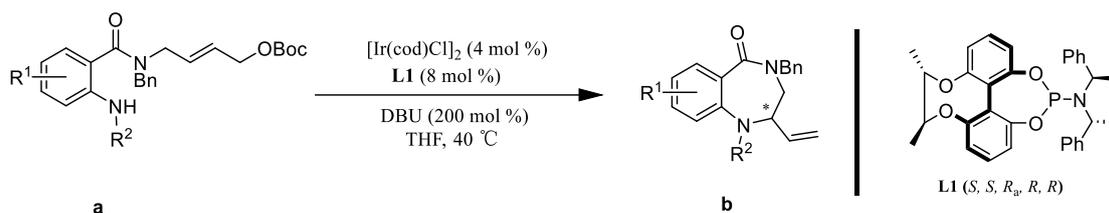
(E)-4-(N-benzyl-2-((2-bromobenzyl)amino)benzamido)but-2-en-1-yl *tert*-butyl carbonate
(34a)



Yellow oil, 480 mg, 96% yield; ^1H NMR (600 MHz, CDCl_3) δ 7.57 (d, $J = 7.9$ Hz, 1H), 7.37 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.34 – 7.27 (m, 4H), 7.24 (t, $J = 6.8$ Hz, 2H), 7.17 (t, $J = 8.6$ Hz, 2H),

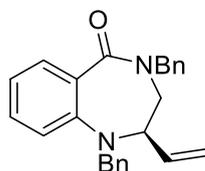
7.13 (td, $J = 7.6, 1.8$ Hz, 1H), 6.65 (t, $J = 7.4$ Hz, 1H), 6.58 (d, $J = 8.2$ Hz, 1H), 5.86 – 5.73 (m, 1H), 5.71 – 5.67 (m, 1H), 4.67 (s, 2H), 4.55 (d, $J = 4.6$ Hz, 2H), 4.43 (s, 2H), 4.11 – 3.85 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.78, 153.27, 146.14, 137.81, 136.76, 132.81, 131.39, 131.02, 129.67, 128.88, 128.78, 128.66, 127.62, 127.57, 127.32, 123.29, 119.78, 116.40, 112.09, 112.05, 82.32, 66.48, 47.74, 27.80. HRMS(ESI) calcd for $\text{C}_{30}\text{H}_{34}\text{BrN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 565.1696, Found: 565.1696.

3.2 General Procedure for the Allylic Amination of a



In a dry Schlenk tube filled with argon, $[\text{Ir}(\text{cod})\text{Cl}]_2$ (2.7 mg, 0.004 mmol, 4 mol %), phosphoramidite ligand **L1** (4.2 mg, 0.008 mmol, 8 mol %), and *n*-propylamine (0.5 mL) were dissolved in THF (1.0 mL). The reaction mixture was heated at 50 °C for 30 min, followed by removal of the volatile solvent under vacuum to give a yellow solid. In this tube, allylic anthranilic acid derivatives **a** (0.1 mmol), DBU (30.5 mg, 0.2 mmol, 200 mol %) and THF (2.0 mL) were added and stirred at 40°C until the reaction was complete. Then the solvent was evaporated and the residue was purified by silica gel column chromatography using petroleum/EtOAc as the eluent to give the desired products **b**.

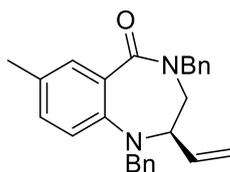
(*R*)-1,4-dibenzyl-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (**1b**)



R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 36.4 mg, 99% yield; 97% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ } ^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 9.928 min, t_R (major) = 13.703 min]; $[\alpha]_{\text{D}}^{25} = -24.20^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (dd, $J = 7.6, 1.7 \text{ Hz}$, 1H), 7.34 (td, $J = 7.8, 1.8 \text{ Hz}$, 2H), 7.31 – 7.29 (m, 3H), 7.28 (d, $J = 5.7 \text{ Hz}$, 3H), 7.25 (d, $J = 5.8 \text{ Hz}$, 3H), 7.07 (t, $J = 7.5 \text{ Hz}$, 1H), 6.94 (d, $J = 8.1 \text{ Hz}$, 1H), 5.52 – 5.46 (m, 1H), 5.23 – 5.18 (m, 1H), 5.02 – 4.96 (m, 1H), 4.86 (d, $J = 14.8 \text{ Hz}$, 1H), 4.74 (d, $J = 14.8 \text{ Hz}$, 1H), 4.37 (d, $J = 14.1 \text{ Hz}$, 1H), 4.13 (d, $J = 14.1 \text{ Hz}$, 1H), 3.67 – 3.62 (m, 1H), 3.30 (dd, $J = 15.2, 11.1 \text{ Hz}$, 1H), 3.12 (dd, $J = 15.3, 5.2 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.72, 145.45, 137.81, 137.29, 133.74, 131.61, 131.47, 129.89,

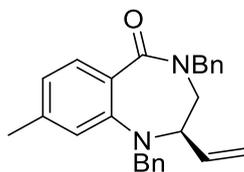
128.60, 128.46, 128.39, 128.18, 127.47, 127.10, 122.64, 121.21, 119.34, 66.61, 53.71, 50.78, 50.39. HRMS(ESI) calcd for C₂₅H₂₅N₂O [M+H]⁺: 369.1962, Found: 369.1957.

(R)-1,4-dibenzyl-7-methyl-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (2b)



R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 36.3 mg, 95% yield; 93% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 14.876 min, t_R (major) = 23.373 min]; [α]_D²⁵ = -51.00° (c = 0.75, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.52 (d, *J* = 2.2 Hz, 1H), 7.30 (td, *J* = 5.9, 3.1 Hz, 3H), 7.27 (d, *J* = 2.9 Hz, 3H), 7.25 (s, 1H), 7.25 – 7.20 (m, 3H), 7.14 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 5.52 – 5.45 (m, 1H), 5.21 – 5.17 (m, 1H), 5.00 – 4.96 (m, 1H), 4.84 – 4.76 (m, 2H), 4.34 (d, *J* = 14.1 Hz, 1H), 4.10 (d, *J* = 14.1 Hz, 1H), 3.64 – 3.59 (m, 1H), 3.28 (dd, *J* = 15.2, 11.1 Hz, 1H), 3.10 (dd, *J* = 15.2, 5.2 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.89, 142.85, 138.02, 137.39, 133.82, 132.23, 131.37, 130.17, 128.58, 128.57, 128.42, 128.39, 128.16, 127.43, 127.03, 121.13, 119.21, 66.56, 53.73, 50.85, 50.32, 20.56. HRMS(ESI) calcd for C₂₆H₂₇N₂O [M+H]⁺: 383.2118, Found: 383.2108.

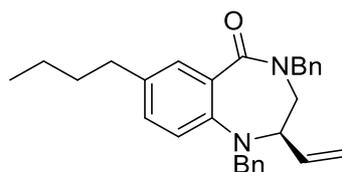
(R)-1,4-dibenzyl-8-methyl-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (3b)



R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 35.9 mg, 94% yield; 91% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 23.790 min, t_R (major) = 30.569 min]; [α]_D²⁵ = -13.92° (c = 0.75,

CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.30 – 7.27 (m, 4H), 7.26 (s, 1H), 7.26 – 7.21 (m, 4H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.75 (s, 1H), 5.52 – 5.45 (m, 1H), 5.22 – 5.18 (m, 1H), 4.99 – 4.94 (m, 1H), 4.82 (d, *J* = 14.8 Hz, 1H), 4.74 (d, *J* = 14.8 Hz, 1H), 4.37 (d, *J* = 14.0 Hz, 1H), 4.12 (d, *J* = 14.0 Hz, 1H), 3.65 – 3.58 (m, 1H), 3.29 (dd, *J* = 15.2, 11.2 Hz, 1H), 3.08 (dd, *J* = 15.2, 5.2 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.84, 145.66, 141.98, 137.96, 137.38, 133.81, 129.88, 128.58, 128.57, 128.44, 128.20, 128.19, 127.40, 127.08, 123.42, 121.84, 119.24, 66.28, 53.75, 50.79, 50.35, 21.66. HRMS(ESI) calcd for C₂₆H₂₇N₂O [M+H]⁺: 383.2118, Found: 383.2109.

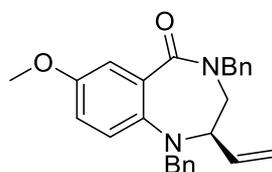
(*R*)-1,4-dibenzyl-7-(4-butylphenyl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4b)



R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 38.7 mg, 91% yield; 86% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, *v* = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, *t_R* (minor) = 11.172 min, *t_R* (major) = 12.965 min]; [α]_D²⁵ = -72.45° (*c* = 0.75, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.53 (d, *J* = 2.3 Hz, 1H), 7.32 – 7.29 (m, 3H), 7.28 (s, 1H), 7.27 (d, *J* = 1.9 Hz, 2H), 7.25 (dd, *J* = 3.1, 1.7 Hz, 2H), 7.24 – 7.20 (m, 2H), 7.15 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 5.53 – 5.45 (m, 1H), 5.22 – 5.17 (m, 1H), 5.00 – 4.94 (m, 1H), 4.84 – 4.74 (m, 2H), 4.34 (d, *J* = 14.0 Hz, 1H), 4.11 (d, *J* = 14.0 Hz, 1H), 3.65 – 3.58 (m, 1H), 3.28 (dd, *J* = 15.2, 11.2 Hz, 1H), 3.09 (dd, *J* = 15.2, 5.2 Hz, 1H), 2.58 (t, *J* = 7.8 Hz, 2H), 1.64 – 1.60 (m, 2H), 1.39 – 1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.95, 143.19, 138.05, 137.43, 137.29, 133.84, 131.57, 131.30, 129.53, 128.57, 128.43, 128.41, 128.20, 127.41, 127.02, 121.05, 119.18, 66.36, 53.74, 50.86, 50.36, 34.79, 33.41, 22.43, 13.95. HRMS(ESI) calcd for C₂₅H₃₃N₂O [M+H]⁺: 425.2587, Found: 425.2577.

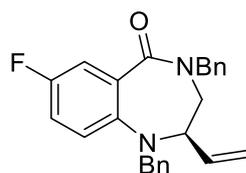
(R)-1,4-dibenzyl-7-methoxy-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one

(5b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Orange oil, 37.0 mg, 93% yield; 88% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 27.140 min, t_R (major) = 35.538 min]; $[\alpha]_D^{25} = -26.90^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.31 (dd, $J = 7.5, 2.0 \text{ Hz}$, 3H), 7.29 (s, 1H), 7.27 (d, $J = 3.0 \text{ Hz}$, 3H), 7.26 – 7.24 (m, 3H), 7.24 – 7.21 (m, 1H), 6.90 (dd, $J = 8.7, 3.0 \text{ Hz}$, 1H), 6.87 (d, $J = 8.7 \text{ Hz}$, 1H), 5.50 – 5.44 (m, 1H), 5.22 – 5.17 (m, 1H), 5.01 – 4.96 (m, 1H), 4.80 (d, $J = 2.7 \text{ Hz}$, 2H), 4.30 (d, $J = 13.9 \text{ Hz}$, 1H), 4.07 (d, $J = 13.9 \text{ Hz}$, 1H), 3.81 (s, 3H), 3.61 – 3.56 (m, 1H), 3.25 (dd, $J = 15.2, 11.3 \text{ Hz}$, 1H), 3.08 (dd, $J = 15.2, 5.4 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.56, 155.35, 138.56, 138.06, 137.32, 133.61, 132.70, 128.60, 128.43, 128.41, 128.17, 127.47, 127.04, 122.51, 119.28, 118.08, 113.73, 66.50, 55.65, 53.88, 50.98, 50.38. HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 399.2068, Found: 399.2058.

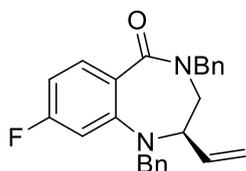
(R)-1,4-dibenzyl-7-fluoro-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (6b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 36.7 mg, 95% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 16.602 min, t_R (major) = 27.280 min]; $[\alpha]_D^{25} = -117.30^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.42 (dd, $J = 8.6, 3.1 \text{ Hz}$, 1H), 7.30 (dd, $J = 7.7, 1.8 \text{ Hz}$, 3H), 7.28 (s, 1H), 7.27 (d, $J = 1.6 \text{ Hz}$, 2H), 7.25 (d, $J = 2.0 \text{ Hz}$, 2H), 7.25 – 7.20 (m, 2H), 7.03 (td, $J = 8.3, 3.1 \text{ Hz}$, 1H), 6.88 (dd, $J = 8.8, 4.6 \text{ Hz}$, 1H), 5.51 – 5.41 (m, 1H), 5.25 – 5.18

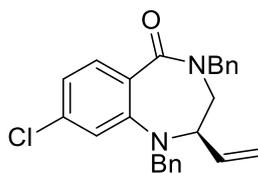
(m, 1H), 5.03 – 4.96 (m, 1H), 4.84 (d, $J = 14.8$ Hz, 1H), 4.74 (d, $J = 14.8$ Hz, 1H), 4.31 (d, $J = 14.0$ Hz, 1H), 4.09 (d, $J = 14.0$ Hz, 1H), 3.65 – 3.57 (m, 1H), 3.26 (dd, $J = 15.3, 11.2$ Hz, 1H), 3.12 (dd, $J = 15.3, 5.3$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 169.43, 158.47 (d, $J = 242.9$ Hz), 141.31 (d, $J = 2.7$ Hz), 137.57, 137.06, 133.29, 133.26, 133.21, 128.66, 128.44 (d, $J = 17.6$ Hz), 128.21, 127.60, 127.21, 122.61 (d, $J = 7.7$ Hz), 119.63, 118.17 (d, $J = 22.3$ Hz), 116.46 (d, $J = 23.9$ Hz), 66.60, 53.95, 50.80, 50.42. ^{19}F NMR (565 MHz, CDCl_3) δ -120.16. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 387.1868, Found: 387.1858.

(*R*)-1,4-dibenzyl-8-fluoro-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (7b)



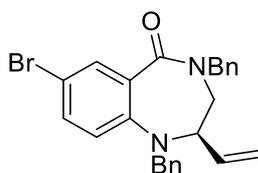
$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Orange oil, 35.5 mg, 92% yield; 87% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, $v = 1.0$ mL \cdot min $^{-1}$, $T = 25$ °C, $\lambda = 254$ nm, t_R (minor) = 17.834 min, t_R (major) = 25.655 min]; $[\alpha]_D^{25} = -22.75^\circ$ ($c = 0.75$, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3) δ 7.73 (dd, $J = 8.6, 6.8$ Hz, 1H), 7.33 – 7.29 (m, 2H), 7.29 (s, 1H), 7.29 – 7.26 (m, 2H), 7.25 (dd, $J = 5.3, 2.0$ Hz, 3H), 7.23 (q, $J = 2.6$ Hz, 2H), 6.75 (td, $J = 8.2, 2.4$ Hz, 1H), 6.62 (dd, $J = 10.9, 2.4$ Hz, 1H), 5.53 – 5.47 (m, 1H), 5.25 – 5.22 (m, 1H), 5.02 – 4.98 (m, 1H), 4.92 (d, $J = 14.8$ Hz, 1H), 4.65 (d, $J = 14.8$ Hz, 1H), 4.33 (d, $J = 14.2$ Hz, 1H), 4.11 (d, $J = 14.2$ Hz, 1H), 3.69 – 3.64 (m, 1H), 3.33 (dd, $J = 15.3, 10.8$ Hz, 1H), 3.16 (dd, $J = 15.3, 5.0$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 169.84, 165.06 (d, $J = 250.3$ Hz), 147.74 (d, $J = 9.7$ Hz), 137.12, 133.55, 132.11 (d, $J = 10.3$ Hz), 128.65, 128.58, 128.23 (d, $J = 7.8$ Hz), 127.56, 127.37, 127.29, 126.92 (d, $J = 2.9$ Hz), 119.69, 119.52, 109.38 (d, $J = 21.7$ Hz), 108.15 (d, $J = 23.3$ Hz), 66.84, 53.84, 50.62, 50.56. ^{19}F NMR (565 MHz, CDCl_3) δ -108.10. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 387.1868, Found: 387.1859.

(R)-1,4-dibenzyl-8-chloro-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (8b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); colorless oil, 38.6 mg, 96% yield; 94% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 70/30, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 12.257 min, t_R (major) = 16.315 min]; $[\alpha]_D^{25} = -25.80^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.66 (d, $J = 8.3 \text{ Hz}$, 1H), 7.31 (d, $J = 6.8 \text{ Hz}$, 1H), 7.30 (s, 1H), 7.29 – 7.26 (m, 3H), 7.25 (d, $J = 1.3 \text{ Hz}$, 3H), 7.24 (dd, $J = 3.9, 1.9 \text{ Hz}$, 2H), 7.04 (dd, $J = 8.2, 2.0 \text{ Hz}$, 1H), 6.92 (d, $J = 2.0 \text{ Hz}$, 1H), 5.52 – 5.44 (m, 1H), 5.26 – 5.21 (m, 1H), 5.01 – 4.95 (m, 1H), 4.87 (d, $J = 14.8 \text{ Hz}$, 1H), 4.67 (d, $J = 14.8 \text{ Hz}$, 1H), 4.34 (d, $J = 14.0 \text{ Hz}$, 1H), 4.11 (d, $J = 14.0 \text{ Hz}$, 1H), 3.67 – 3.60 (m, 1H), 3.30 (dd, $J = 15.3, 11.0 \text{ Hz}$, 1H), 3.13 (dd, $J = 15.3, 5.1 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 169.73, 146.84, 137.53, 137.13, 137.01, 133.36, 131.30, 129.51, 128.66, 128.58, 128.37, 128.22, 127.59, 127.33, 122.67, 121.32, 119.80, 66.53, 53.78, 50.58, 50.49. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 403.1572, Found: 403.1562.

(R)-1,4-dibenzyl-7-bromo-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (9b)

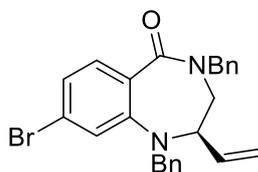


$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 41.0 mg, 92% yield; 94% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 15.426 min, t_R (major) = 20.121 min]; $[\alpha]_D^{25} = -26.25^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.83 (d, $J = 2.5 \text{ Hz}$, 1H), 7.41 (dd, $J = 8.6, 2.5 \text{ Hz}$, 1H), 7.30 (d, $J = 6.9 \text{ Hz}$, 3H), 7.28 (s, 1H), 7.27 (d, $J = 5.0 \text{ Hz}$, 2H), 7.26 – 7.21 (m, 4H), 6.79 (d, $J = 8.6 \text{ Hz}$, 1H), 5.51 – 5.43 (m, 1H), 5.25 – 5.20 (m, 1H), 5.04 – 4.98 (m, 1H), 4.87 (d, $J = 14.8$

Hz, 1H), 4.70 (d, $J = 14.8$ Hz, 1H), 4.33 (d, $J = 14.2$ Hz, 1H), 4.11 (d, $J = 14.2$ Hz, 1H), 3.69 – 3.61 (m, 1H), 3.29 (dd, $J = 15.3, 10.9$ Hz, 1H), 3.15 (dd, $J = 15.3, 5.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 169.14, 144.33, 137.29, 136.99, 134.35, 133.45, 132.94, 132.74, 128.68, 128.56, 128.25, 128.20, 127.62, 127.27, 122.81, 119.68, 115.23, 66.77, 53.74, 50.59, 50.51. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 447.1067, Found: 447.1057.

(R)-1,4-dibenzyl-8-bromo-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one

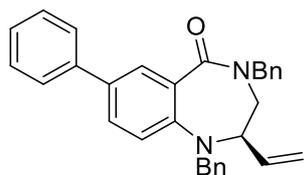
(10b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 40.1 mg, 90% yield; 95% ee [Daicel Chiralcel IA-3 (4.6 mm x 250 mmL), *n*-hexane/2-propanol = 60/40, $v = 1.0$ mL \cdot min $^{-1}$, $T = 25$ °C, $\lambda = 254$ nm, t_R (minor) = 40.730 min, t_R (major) = 15.617 min]; $[\alpha]_D^{25} = -95.73^\circ$ ($c = 0.75$, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3) δ 7.60 (d, $J = 8.2$ Hz, 1H), 7.39 – 7.31 (m, 3H), 7.31 (s, 1H), 7.30 – 7.26 (m, 4H), 7.25 (d, $J = 2.8$ Hz, 2H), 7.22 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.09 (d, $J = 1.9$ Hz, 1H), 5.52 – 5.45 (m, 1H), 5.26 – 5.22 (m, 1H), 5.02 – 4.97 (m, 1H), 4.87 (d, $J = 14.8$ Hz, 1H), 4.69 (d, $J = 14.7$ Hz, 1H), 4.35 (d, $J = 14.0$ Hz, 1H), 4.12 (d, $J = 14.0$ Hz, 1H), 3.67 – 3.61 (m, 1H), 3.31 (dd, $J = 15.3, 11.1$ Hz, 1H), 3.13 (dd, $J = 15.3, 5.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 169.78, 146.93, 137.12, 136.99, 133.31, 131.43, 130.04, 128.67, 128.59, 128.41, 128.23, 127.60, 127.36, 125.90, 125.65, 124.30, 119.87, 66.50, 53.78, 50.57, 50.48. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 447.1067, Found: 447.1057.

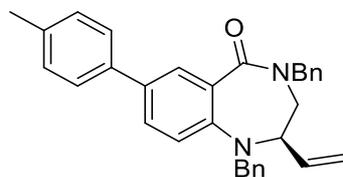
(R)-1,4-dibenzyl-7-phenyl-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one

(11b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); colorless oil, 41.3 mg, 93% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 70/30, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 23.255 min, t_R (major) = 15.547 min]; $[\alpha]_D^{25} = -15.65^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.00 (d, $J = 2.4 \text{ Hz}$, 1H), 7.61 (dd, $J = 8.3, 1.3 \text{ Hz}$, 2H), 7.60 – 7.56 (m, 1H), 7.42 (t, $J = 7.7 \text{ Hz}$, 2H), 7.34 – 7.32 (m, 2H), 7.31 (d, $J = 1.3 \text{ Hz}$, 2H), 7.30 (d, $J = 4.1 \text{ Hz}$, 3H), 7.29 – 7.27 (m, 1H), 7.27 (s, 1H), 7.25 (d, $J = 6.7 \text{ Hz}$, 2H), 7.01 (d, $J = 8.3 \text{ Hz}$, 1H), 5.57 – 5.51 (m, 1H), 5.26 – 5.21 (m, 1H), 5.04 – 4.99 (m, 1H), 4.89 (d, $J = 14.8 \text{ Hz}$, 1H), 4.77 (d, $J = 14.8 \text{ Hz}$, 1H), 4.43 (d, $J = 14.1 \text{ Hz}$, 1H), 4.18 (d, $J = 14.1 \text{ Hz}$, 1H), 3.72 – 3.66 (m, 1H), 3.38 (dd, $J = 15.3, 11.0 \text{ Hz}$, 1H), 3.17 (dd, $J = 15.3, 5.1 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.63, 144.76, 139.97, 137.74, 137.26, 135.31, 133.84, 131.46, 130.03, 128.76, 128.69, 128.64, 128.54, 128.52, 128.36, 128.20, 127.51, 127.23, 127.16, 127.07, 126.69, 121.50, 119.42, 66.66, 53.77, 50.76, 50.49. HRMS(ESI) calcd for $\text{C}_{31}\text{H}_{29}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 445.2275, Found: 445.2265.

(R)-1,4-dibenzyl-7-(p-tolyl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one
(12b)

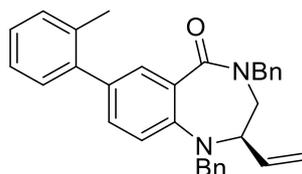


$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 42.6 mg, 93% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 25.595 min, t_R (major) = 13.119 min]; $[\alpha]_D^{25} = -40.73^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.98 (d, $J = 2.3 \text{ Hz}$, 1H), 7.57 (dd, $J = 8.3, 2.4 \text{ Hz}$, 1H), 7.51 (d, $J = 8.1 \text{ Hz}$, 2H), 7.33 – 7.32 (m, 1H), 7.31 (d, $J = 2.0 \text{ Hz}$, 2H), 7.30 (s, 1H), 7.30 – 7.26

(m, 4H), 7.26 – 7.24 (m, 2H), 7.23 (d, $J = 7.9$ Hz, 2H), 7.00 (d, $J = 8.3$ Hz, 1H), 5.57 – 5.50 (m, 1H), 5.24 – 5.21 (m, 1H), 5.04 – 4.98 (m, 1H), 4.88 (d, $J = 14.8$ Hz, 1H), 4.77 (d, $J = 14.8$ Hz, 1H), 4.42 (d, $J = 14.1$ Hz, 1H), 4.17 (d, $J = 14.1$ Hz, 1H), 3.72 – 3.65 (m, 1H), 3.37 (dd, $J = 15.3, 11.0$ Hz, 1H), 3.16 (dd, $J = 15.3, 5.1$ Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.70, 144.50, 137.79, 137.29, 137.08, 136.81, 135.31, 133.85, 131.47, 129.82, 129.49, 128.63, 128.50, 128.38, 128.26, 128.20, 127.49, 127.14, 126.52, 121.49, 119.39, 66.61, 53.77, 50.77, 50.47, 21.09. HRMS(ESI) calcd for $\text{C}_{32}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 459.2431, Found: 459.2423.

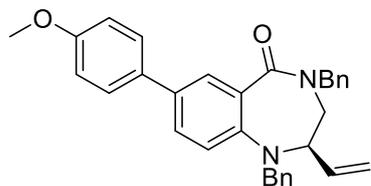
(*R*)-1,4-dibenzyl-7-(*o*-tolyl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one

(13b)



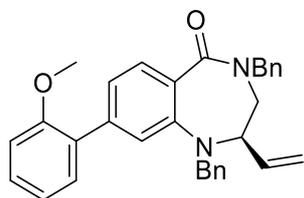
$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 42.6 mg, 93% yield; 93% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 70/30, $v = 1.0$ mL \cdot min $^{-1}$, $T = 25$ °C, $\lambda = 254$ nm, t_R (minor) = 10.920 min, t_R (major) = 14.338 min]; $[\alpha]_D^{25} = -175.6^\circ$ ($c = 0.75$, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3) δ 7.72 (d, $J = 2.3$ Hz, 1H), 7.34 – 7.31 (m, 3H), 7.31 (s, 1H), 7.31 – 7.26 (m, 5H), 7.25 (dd, $J = 3.6, 2.0$ Hz, 3H), 7.24 (d, $J = 1.9$ Hz, 2H), 7.23 – 7.21 (m, 1H), 6.99 (d, $J = 8.2$ Hz, 1H), 5.58 – 5.52 (m, 1H), 5.25 – 5.21 (m, 1H), 5.03 – 4.97 (m, 1H), 4.88 (d, $J = 14.8$ Hz, 1H), 4.73 (d, $J = 14.8$ Hz, 1H), 4.43 (d, $J = 14.0$ Hz, 1H), 4.18 (d, $J = 14.0$ Hz, 1H), 3.71 – 3.64 (m, 1H), 3.39 (dd, $J = 15.3, 11.1$ Hz, 1H), 3.17 (dd, $J = 15.3, 5.1$ Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.60, 144.40, 140.78, 137.80, 137.30, 136.14, 135.38, 133.83, 132.44, 130.89, 130.68, 130.40, 129.87, 128.61, 128.49, 128.46, 128.24, 127.47, 127.20, 127.13, 125.81, 120.75, 119.39, 66.39, 53.78, 50.84, 50.49, 20.60. HRMS(ESI) calcd for $\text{C}_{32}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 459.2431, Found: 459.2422.

(R)-1,4-dibenzyl-7-(4-methoxyphenyl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (14b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Dark green oil, 43.6 mg, 92% yield; 91% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 65/35, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 35.008 min, t_R (major) = 23.326 min]; $[\alpha]_D^{25} = -62.47^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.94 (d, $J = 2.3 \text{ Hz}$, 1H), 7.54 (dd, $J = 8.6, 2.5 \text{ Hz}$, 3H), 7.35 – 7.30 (m, 3H), 7.30 (s, 1H), 7.29 – 7.26 (m, 3H), 7.26 – 7.23 (m, 3H), 6.99 (d, $J = 8.4 \text{ Hz}$, 1H), 6.96 (d, $J = 8.7 \text{ Hz}$, 2H), 5.58 – 5.49 (m, 1H), 5.25 – 5.20 (m, 1H), 5.04 – 4.98 (m, 1H), 4.88 (d, $J = 14.8 \text{ Hz}$, 1H), 4.77 (d, $J = 14.8 \text{ Hz}$, 1H), 4.41 (d, $J = 14.1 \text{ Hz}$, 1H), 4.16 (d, $J = 14.1 \text{ Hz}$, 1H), 3.85 (s, 3H), 3.71 – 3.65 (m, 1H), 3.37 (dd, $J = 15.3, 11.0 \text{ Hz}$, 1H), 3.16 (dd, $J = 15.3, 5.1 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.70, 159.02, 144.17, 137.82, 137.31, 135.06, 133.86, 132.59, 131.54, 129.57, 128.62, 128.49, 128.37, 128.19, 128.00, 127.72, 127.48, 127.12, 121.51, 119.36, 114.22, 66.62, 55.34, 53.76, 50.79, 50.46. HRMS(ESI) calcd for $\text{C}_{32}\text{H}_{31}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 475.2381, Found: 475.2377.

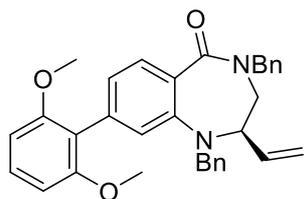
(R)-1,4-dibenzyl-8-(2-methoxyphenyl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (15b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 44.1 mg, 93% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 70/30, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 17.323 min, t_R (major) = 23.123 min]; $[\alpha]_D^{25} = -80.45^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.77 (d, $J = 7.9 \text{ Hz}$, 1H), 7.35 – 7.31 (m, 4H), 7.31 (s,

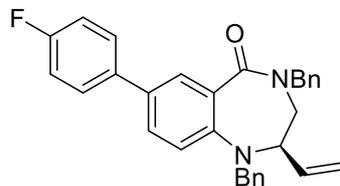
1H), 7.31 – 7.26 (m, 3H), 7.26 – 7.24 (m, 4H), 7.23 (dd, $J = 7.5, 1.8$ Hz, 1H), 7.12 (d, $J = 1.6$ Hz, 1H), 7.02 (td, $J = 7.5, 1.1$ Hz, 1H), 6.98 (d, $J = 8.3$ Hz, 1H), 5.58 – 5.51 (m, 1H), 5.22 – 5.18 (m, 1H), 5.03 – 4.97 (m, 1H), 4.89 (d, $J = 14.8$ Hz, 1H), 4.77 (d, $J = 14.8$ Hz, 1H), 4.44 (d, $J = 14.1$ Hz, 1H), 4.16 (d, $J = 14.1$ Hz, 1H), 3.76 (s, 3H), 3.69 – 3.64 (m, 1H), 3.39 (dd, $J = 15.2, 11.1$ Hz, 1H), 3.15 (dd, $J = 15.2, 5.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.78, 156.53, 145.16, 142.04, 138.03, 137.38, 133.93, 130.67, 130.09, 129.68, 129.56, 129.05, 128.60, 128.48, 128.46, 128.19, 127.44, 127.09, 123.87, 122.61, 120.92, 119.21, 111.54, 66.51, 55.65, 53.81, 50.80, 50.41. HRMS(ESI) calcd for $\text{C}_{32}\text{H}_{31}\text{N}_2\text{O}_2[\text{M}+\text{H}]^+$: 475.2381, Found: 475.2383.

(*R*)-1,4-dibenzyl-8-(2,6-dimethoxyphenyl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (16b)



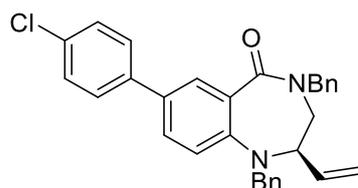
$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); White oil, 47.3 mg, 94% yield; 91% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0$ mL \cdot min $^{-1}$, $T = 25$ °C, $\lambda = 254$ nm, t_R (minor) = 13.686 min, t_R (major) = 20.212 min]; $[\alpha]_D^{25} = -175.6^\circ$ ($c = 0.75$, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, $J = 7.8$ Hz, 1H), 7.32 (t, $J = 1.4$ Hz, 1H), 7.31 (s, 1H), 7.30 (d, $J = 2.5$ Hz, 4H), 7.29 – 7.26 (m, 2H), 7.26 – 7.22 (m, 3H), 7.10 (dd, $J = 7.8, 1.5$ Hz, 1H), 6.98 (d, $J = 1.5$ Hz, 1H), 6.64 (d, $J = 8.4$ Hz, 2H), 5.59 – 5.52 (m, 1H), 5.22 – 5.17 (m, 1H), 5.02 – 4.96 (m, 1H), 4.86 – 4.79 (m, 2H), 4.40 (d, $J = 14.1$ Hz, 1H), 4.13 (d, $J = 14.0$ Hz, 1H), 3.67 (s, 6H), 3.67 – 3.64 (m, 1H), 3.41 (dd, $J = 15.2, 11.1$ Hz, 1H), 3.14 (dd, $J = 15.2, 5.2$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.99, 157.64, 144.99, 138.22, 137.88, 137.47, 134.04, 129.38, 129.07, 128.97, 128.57, 128.51, 128.40, 128.14, 127.37, 126.96, 125.44, 124.12, 119.09, 119.04, 104.46, 66.13, 55.93, 53.69, 50.79, 50.36. HRMS(ESI) calcd for $\text{C}_{33}\text{H}_{33}\text{N}_2\text{O}_3[\text{M}+\text{H}]^+$: 505.2486, Found: 505.2474.

(R)-1,4-dibenzyl-7-(4-fluorophenyl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (17b)



R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); Dark green oil, 43.0 mg, 93% yield; 91% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 23.603 min, t_R (major) = 17.089 min]; $[\alpha]_D^{25}$ = -28.50° (c = 0.75, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.93 (d, J = 2.4 Hz, 1H), 7.56 (d, J = 5.3 Hz, 1H), 7.55 (d, J = 5.3 Hz, 1H), 7.52 (dd, J = 8.3, 2.4 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.30 (s, 1H), 7.29 – 7.27 (m, 3H), 7.27 – 7.26 (m, 1H), 7.25 (d, J = 5.3 Hz, 2H), 7.10 (t, J = 8.7 Hz, 2H), 7.00 (d, J = 8.3 Hz, 1H), 5.58 – 5.50 (m, 1H), 5.26 – 5.21 (m, 1H), 5.05 – 5.00 (m, 1H), 4.90 (d, J = 14.8 Hz, 1H), 4.76 (d, J = 14.8 Hz, 1H), 4.42 (d, J = 14.2 Hz, 1H), 4.17 (d, J = 14.2 Hz, 1H), 3.72 – 3.66 (m, 1H), 3.37 (dd, J = 15.3, 10.9 Hz, 1H), 3.18 (dd, J = 15.3, 5.1 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 170.52, 162.34 (d, J = 246.0 Hz), 144.70, 137.45 (d, J = 68.7 Hz), 136.14 (d, J = 3.3 Hz), 134.32, 133.81, 131.49, 129.87, 128.59 (d, J = 17.7 Hz), 128.43, 128.35, 128.32, 128.25, 128.20, 128.17, 127.54, 127.17, 121.54, 119.45, 115.61 (d, J = 21.3 Hz), 66.73, 53.77, 50.76, 50.52. ¹⁹F NMR (565 MHz, CDCl₃) δ -116.04. HRMS(ESI) calcd for C₃₁H₂₈FN₂O [M+H]⁺: 463.2181, Found: 463.2169.

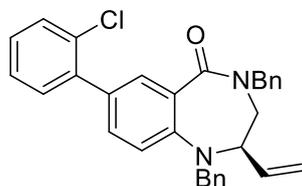
(R)-1,4-dibenzyl-7-(4-chlorophenyl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (18b)



R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); Dark green oil, 45.4 mg, 95% yield; 88% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL•min⁻¹, T = 25 °C,

$\lambda = 254 \text{ nm}$, t_R (minor) = 21.607 min, t_R (major) = 17.476 min]; $[\alpha]_D^{25} = -35.25^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.95 (d, $J = 2.4 \text{ Hz}$, 1H), 7.56 – 7.53 (m, 1H), 7.53 – 7.50 (m, 2H), 7.40 – 7.36 (m, 2H), 7.32 (t, $J = 2.0 \text{ Hz}$, 1H), 7.32 – 7.30 (m, 2H), 7.30 (s, 1H), 7.29 – 7.26 (m, 4H), 7.26 – 7.22 (m, 2H), 7.00 (d, $J = 8.4 \text{ Hz}$, 1H), 5.58 – 5.49 (m, 1H), 5.26 – 5.22 (m, 1H), 5.05 – 5.00 (m, 1H), 4.90 (d, $J = 14.8 \text{ Hz}$, 1H), 4.75 (d, $J = 14.8 \text{ Hz}$, 1H), 4.42 (d, $J = 14.2 \text{ Hz}$, 1H), 4.18 (d, $J = 14.2 \text{ Hz}$, 1H), 3.73 – 3.67 (m, 1H), 3.37 (dd, $J = 15.3, 10.9 \text{ Hz}$, 1H), 3.19 (dd, $J = 15.3, 5.0 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.44, 145.01, 138.44, 137.61, 137.19, 133.92, 133.80, 133.11, 131.46, 129.84, 128.91, 128.65, 128.54, 128.46, 128.30, 128.21, 127.89, 127.55, 127.19, 121.55, 119.48, 66.76, 53.77, 50.73, 50.54. HRMS(ESI) calcd for $\text{C}_{31}\text{H}_{28}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 479.1885, Found: 479.1877.

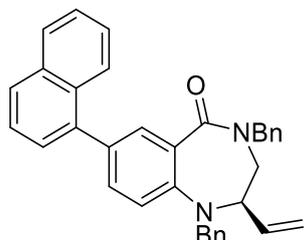
(*R*)-1,4-dibenzyl-7-(2-chlorophenyl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (19b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 44.9 mg, 94% yield; 95% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 36.773 min, t_R (major) = 41.401 min]; $[\alpha]_D^{25} = -62.10^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.84 (d, $J = 2.3 \text{ Hz}$, 1H), 7.49 (dd, $J = 8.3, 2.3 \text{ Hz}$, 1H), 7.46 (dd, $J = 7.8, 1.4 \text{ Hz}$, 1H), 7.39 (dd, $J = 7.5, 1.8 \text{ Hz}$, 1H), 7.33 (s, 1H), 7.31 (dd, $J = 6.5, 3.9 \text{ Hz}$, 3H), 7.29 (d, $J = 2.1 \text{ Hz}$, 2H), 7.29 – 7.26 (m, 3H), 7.25 – 7.23 (m, 3H), 6.99 (d, $J = 8.3 \text{ Hz}$, 1H), 5.60 – 5.52 (m, 1H), 5.26 – 5.21 (m, 1H), 5.04 – 4.98 (m, 1H), 4.90 (d, $J = 14.8 \text{ Hz}$, 1H), 4.72 (d, $J = 14.8 \text{ Hz}$, 1H), 4.44 (d, $J = 14.1 \text{ Hz}$, 1H), 4.19 (d, $J = 14.1 \text{ Hz}$, 1H), 3.73 – 3.66 (m, 1H), 3.41 (dd, $J = 15.3, 10.9 \text{ Hz}$, 1H), 3.18 (dd, $J = 15.3, 5.0 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.43, 145.09, 139.40, 137.68, 137.24, 133.86, 132.77, 132.44, 131.41, 131.14, 130.01, 128.62, 128.51, 128.42, 128.39, 128.24, 127.49, 127.16, 126.88, 120.50, 119.42, 66.51,

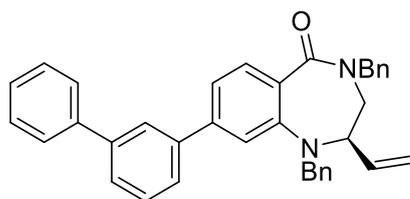
53.76, 50.75, 50.54. HRMS(ESI) calcd for C₃₁H₂₈ClN₂O [M+H]⁺: 479.1885, Found: 479.1879.

(R)-1,4-dibenzyl-7-(naphthalen-1-yl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (20b)



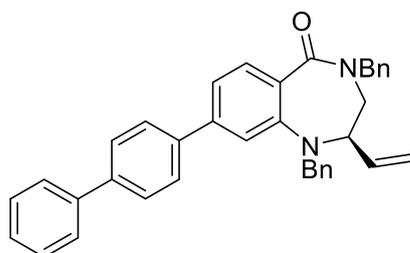
R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); colorless oil, 45.0 mg, 91% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 13.016 min, t_R (major) = 22.227 min]; [α]_D²⁵ = -14.95° (c = 0.75, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.47 – 7.43 (m, 2H), 7.34 (d, *J* = 3.1 Hz, 2H), 7.33 (s, 2H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 2.1 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.25 (s, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 5.64 – 5.55 (m, 1H), 5.29 – 5.24 (m, 1H), 5.06 – 5.00 (m, 1H), 4.89 (d, *J* = 14.8 Hz, 1H), 4.75 (d, *J* = 14.8 Hz, 1H), 4.47 (d, *J* = 14.1 Hz, 1H), 4.22 (d, *J* = 14.1 Hz, 1H), 3.74 – 3.69 (m, 1H), 3.46 (dd, *J* = 15.3, 11.0 Hz, 1H), 3.21 (dd, *J* = 15.3, 5.1 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 170.55, 144.84, 139.17, 137.77, 137.29, 134.93, 133.89, 133.83, 133.29, 131.53, 131.47, 131.16, 128.62, 128.54, 128.46, 128.31, 128.26, 127.64, 127.50, 127.18, 127.06, 126.07, 125.96, 125.75, 125.40, 120.93, 119.47, 66.49, 53.83, 50.86, 50.53. HRMS(ESI) calcd for C₃₅H₃₁N₂O [M+H]⁺: 495.2431, Found: 495.2422.

(R)-8-([1,1'-biphenyl]-3-yl)-1,4-dibenzyl-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (21b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); colorless oil, 48.4 mg, 93% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 10.821 min, t_R (major) = 14.387 min]; $[\alpha]_D^{25} = -30.40^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.70 (d, $J = 7.8 \text{ Hz}$, 1H), 7.46 – 7.40 (m, 4H), 7.28 (dd, $J = 8.0, 6.2 \text{ Hz}$, 2H), 7.26 – 7.23 (m, 3H), 7.23 – 7.20 (m, 4H), 7.19 (s, 1H), 7.16 – 7.14 (m, 2H), 7.14 – 7.12 (m, 2H), 7.12 – 7.09 (m, 2H), 6.54 (d, $J = 1.6 \text{ Hz}$, 1H), 5.12 – 5.05 (m, 2H), 4.85 – 4.79 (m, 1H), 4.75 (s, 2H), 3.75 – 3.68 (m, 2H), 3.52 – 3.46 (m, 1H), 3.20 (dd, $J = 15.2, 11.4 \text{ Hz}$, 1H), 3.01 (dd, $J = 15.2, 5.3 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.64, 145.21, 144.87, 141.57, 140.72, 139.88, 137.77, 137.24, 133.46, 130.65, 130.11, 129.89, 129.77, 129.52, 128.57, 128.51, 128.35, 128.15, 128.05, 127.87, 127.60, 127.41, 127.00, 126.49, 124.13, 123.78, 119.10, 65.54, 53.24, 50.75, 50.32. HRMS(ESI) calcd for $\text{C}_{37}\text{H}_{33}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 521.2588, Found: 521.2580.

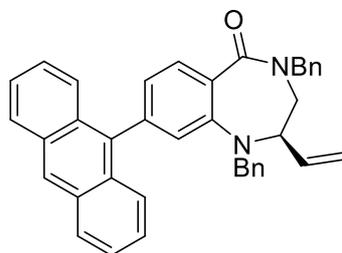
(*R*)-8-([1,1'-biphenyl]-4-yl)-1,4-dibenzyl-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (22b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); White oil, 47.8 mg, 92% yield; 91% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 17.024 min, t_R (major) = 19.583 min]; $[\alpha]_D^{25} = -22.60^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.81 (d, $J = 7.9 \text{ Hz}$, 1H), 7.67 (d, $J = 8.3 \text{ Hz}$, 2H), 7.64 (d, $J = 7.0 \text{ Hz}$, 2H), 7.59 (d, $J = 8.3 \text{ Hz}$, 2H), 7.46 (t, $J = 7.8 \text{ Hz}$, 2H), 7.39 – 7.34 (m, 2H), 7.32 (d, $J = 4.4 \text{ Hz}$, 6H), 7.28 (dd, $J = 8.4, 2.5 \text{ Hz}$, 2H), 7.24 (d, $J = 8.2 \text{ Hz}$, 2H), 7.17 (s, 1H), 5.58 – 5.51 (m, 1H), 5.24 – 5.21 (m, 1H), 5.04 – 5.00 (m, 1H), 4.91 (d, $J = 14.7 \text{ Hz}$, 1H), 4.75 (d, $J = 14.7 \text{ Hz}$, 1H), 4.49 (d, $J = 14.0 \text{ Hz}$, 1H), 4.21 (d, $J = 14.0 \text{ Hz}$, 1H), 3.72 – 3.67 (m, 1H), 3.39 (dd, $J = 15.2, 11.4 \text{ Hz}$, 1H), 3.01 (dd, $J = 15.2, 5.3 \text{ Hz}$, 1H).

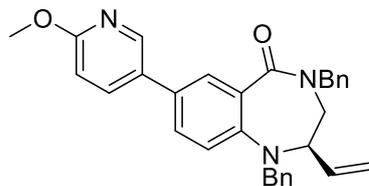
= 15.3, 11.1 Hz, 1H), 3.17 (dd, $J = 15.3, 5.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.59, 145.87, 144.10, 140.73, 140.58, 139.49, 137.78, 137.31, 133.80, 130.56, 130.19, 128.85, 128.63, 128.53, 128.45, 128.22, 127.54, 127.50, 127.48, 127.20, 127.07, 127.05, 121.29, 120.03, 119.44, 66.71, 53.94, 50.80, 50.46. HRMS(ESI) calcd for $\text{C}_{37}\text{H}_{33}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 521.2588, Found: 521.2586.

(*R*)-8-(anthracen-9-yl)-1,4-dibenzyl-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (23b)



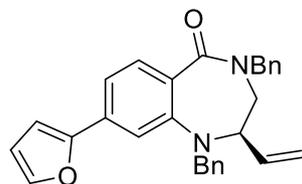
$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 49.5 mg, 91% yield; 90% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 70/30, $v = 1.0$ mL \cdot min $^{-1}$, $T = 25$ °C, $\lambda = 254$ nm, t_R (minor) = 18.187 min, t_R (major) = 26.311 min]; $[\alpha]_D^{25} = -60.27^\circ$ ($c = 0.75$, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3) δ 8.52 – 8.42 (m, 1H), 8.04 (d, $J = 8.5$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.93 (d, $J = 7.7$ Hz, 1H), 7.60 (d, $J = 8.9$ Hz, 1H), 7.48 – 7.41 (m, 3H), 7.40 (s, 1H), 7.33 (dt, $J = 10.5, 7.7$ Hz, 4H), 7.31 – 7.27 (m, 3H), 7.27 – 7.27 (m, 1H), 7.23 (dd, $J = 6.8, 1.9$ Hz, 2H), 7.22 – 7.19 (m, 1H), 7.13 (dd, $J = 7.6, 1.5$ Hz, 1H), 6.99 (d, $J = 1.6$ Hz, 1H), 5.62 – 5.56 (m, 1H), 5.21 – 5.17 (m, 1H), 5.08 – 5.03 (m, 1H), 5.03 (d, $J = 8.2$ Hz, 1H), 4.82 (d, $J = 14.7$ Hz, 1H), 4.35 (d, $J = 14.5$ Hz, 1H), 4.05 (d, $J = 14.5$ Hz, 1H), 3.80 – 3.74 (m, 1H), 3.56 (dd, $J = 15.3, 10.8$ Hz, 1H), 3.31 (dd, $J = 15.3, 5.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.70, 144.93, 142.37, 137.66, 137.42, 136.08, 133.92, 131.29, 131.24, 130.63, 130.00, 129.91, 129.83, 128.69, 128.59, 128.44, 128.27, 128.23, 128.15, 127.58, 127.03, 126.79, 126.58, 126.40, 125.71, 125.68, 125.47, 125.19, 125.02, 124.31, 119.37, 67.63, 53.83, 51.07, 50.58. HRMS(ESI) calcd for $\text{C}_{39}\text{H}_{33}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 545.2588, Found: 545.2578.

(R)-1,4-dibenzyl-7-(6-methoxypyridin-3-yl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (24b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Drak green oil, 43.2 mg, 91% yield; 91% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 75/25, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 40.432 min, t_R (major) = 36.747 min]; $[\alpha]_D^{25} = -23.25^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.38 (d, $J = 2.5 \text{ Hz}$, 1H), 7.90 (d, $J = 2.4 \text{ Hz}$, 1H), 7.80 (dd, $J = 8.6, 2.6 \text{ Hz}$, 1H), 7.50 (dd, $J = 8.3, 2.4 \text{ Hz}$, 1H), 7.32 (d, $J = 2.4 \text{ Hz}$, 1H), 7.31 (d, $J = 1.8 \text{ Hz}$, 2H), 7.30 (s, 1H), 7.29 – 7.26 (m, 3H), 7.26 – 7.23 (m, 3H), 7.01 (d, $J = 8.4 \text{ Hz}$, 1H), 6.80 (d, $J = 8.6 \text{ Hz}$, 1H), 5.57 – 5.49 (m, 1H), 5.25 – 5.20 (m, 1H), 5.05 – 4.99 (m, 1H), 4.91 (d, $J = 14.8 \text{ Hz}$, 1H), 4.74 (d, $J = 14.8 \text{ Hz}$, 1H), 4.42 (d, $J = 14.2 \text{ Hz}$, 1H), 4.17 (d, $J = 14.2 \text{ Hz}$, 1H), 3.98 (s, 3H), 3.72 – 3.66 (m, 1H), 3.38 (dd, $J = 15.3, 10.9 \text{ Hz}$, 1H), 3.18 (dd, $J = 15.3, 5.0 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.44, 163.48, 144.74, 144.61, 137.64, 137.19, 137.11, 133.78, 132.06, 131.67, 129.55, 129.06, 128.65, 128.53, 128.32, 128.21, 128.11, 127.55, 127.18, 121.70, 119.47, 110.76, 66.76, 53.76, 53.54, 50.76, 50.54. HRMS(ESI) calcd for $\text{C}_{31}\text{H}_{30}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 476.2333, Found: 476.2323.

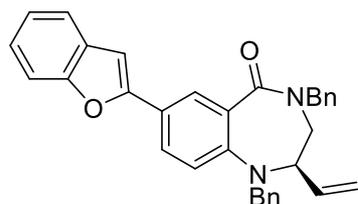
(R)-1,4-dibenzyl-8-(furan-2-yl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (25b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Orange oil, 40.4 mg, 93% yield; 89% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 13.514 min, t_R (major) = 15.032 min]; $[\alpha]_D^{25} = -90.50^\circ$ ($c = 0.75$,

CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.37 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.31 (s, 1H), 7.30 (q, *J* = 2.5 Hz, 4H), 7.27 (d, *J* = 1.6 Hz, 2H), 7.25 (d, *J* = 2.4 Hz, 2H), 7.25 – 7.22 (m, 2H), 6.68 (d, *J* = 3.4 Hz, 1H), 6.48 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.56 – 5.48 (m, 1H), 5.24 – 5.20 (m, 1H), 5.02 – 4.96 (m, 1H), 4.85 (d, *J* = 14.8 Hz, 1H), 4.74 (d, *J* = 14.8 Hz, 1H), 4.45 (d, *J* = 13.9 Hz, 1H), 4.19 (d, *J* = 13.9 Hz, 1H), 3.68 – 3.63 (m, 1H), 3.34 (dd, *J* = 15.3, 11.2 Hz, 1H), 3.12 (dd, *J* = 15.2, 5.2 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 170.41, 153.30, 146.17, 142.60, 137.73, 137.24, 133.90, 133.69, 130.50, 130.07, 128.62, 128.50, 128.22, 127.49, 127.18, 119.49, 118.07, 116.36, 111.87, 106.35, 66.36, 53.84, 50.76, 50.42. HRMS(ESI) calcd for C₂₉H₂₇N₂O₂ [M+H]⁺: 435.2067, Found: 435.2058.

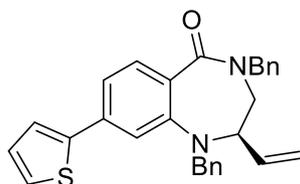
(*R*)-7-(benzofuran-2-yl)-1,4-dibenzyl-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (26b)



R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 45.5 mg, 94% yield; 93% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 70/30, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 21.620 min, t_R (major) = 15.458 min]; [α]_D²⁵ = -12.60° (c = 0.75, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 8.23 (d, *J* = 2.2 Hz, 1H), 7.83 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.49 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.33 (t, *J* = 2.0 Hz, 1H), 7.32 (s, 1H), 7.32 – 7.28 (m, 3H), 7.28 – 7.26 (m, 4H), 7.26 – 7.23 (m, 2H), 7.22 (td, *J* = 7.4, 1.1 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 1.0 Hz, 1H), 5.57 – 5.51 (m, 1H), 5.26 – 5.23 (m, 1H), 5.07 – 5.01 (m, 1H), 4.92 (d, *J* = 14.7 Hz, 1H), 4.76 (d, *J* = 14.7 Hz, 1H), 4.44 (d, *J* = 14.3 Hz, 1H), 4.19 (d, *J* = 14.3 Hz, 1H), 3.74 – 3.71 (m, 1H), 3.38 (dd, *J* = 15.4, 10.7 Hz, 1H), 3.21 (dd, *J* = 15.4, 4.9 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 170.17, 155.33, 154.82, 145.63, 137.47, 137.13, 133.82, 131.24, 129.38, 128.68, 128.56, 128.26, 128.21, 127.95, 127.57, 127.24, 126.99, 124.82, 124.02, 122.89, 121.37, 120.79, 119.55, 111.06, 100.65, 66.86, 53.78, 50.61,

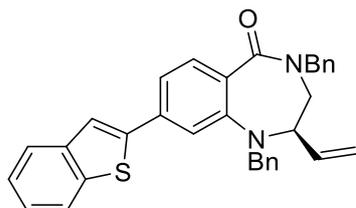
50.57. HRMS(ESI) calcd for C₃₃H₂₉N₂O₂ [M+H]⁺: 485.2224, Found: 485.2213.

(R)-1,4-dibenzyl-8-(thiophen-2-yl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (27b)



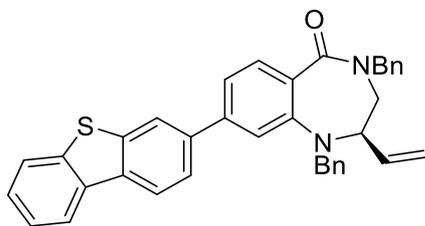
R_f = 0.40 (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 42.7 mg, 95% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 29.452 min, t_R (major) = 35.638 min]; [α]_D²⁵ = -12.50° (c = 0.75, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.33 (s, 1H), 7.32 – 7.32 (m, 1H), 7.32 – 7.31 (m, 3H), 7.30 (d, *J* = 4.7 Hz, 3H), 7.30 – 7.27 (m, 2H), 7.27 – 7.26 (m, 2H), 7.25 (dd, *J* = 5.8, 2.4 Hz, 1H), 7.15 (d, *J* = 1.7 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.58 – 5.51 (m, 1H), 5.26 – 5.21 (m, 1H), 5.05 – 4.99 (m, 1H), 4.91 (d, *J* = 14.8 Hz, 1H), 4.72 (d, *J* = 14.8 Hz, 1H), 4.45 (d, *J* = 14.0 Hz, 1H), 4.19 (d, *J* = 14.0 Hz, 1H), 3.71 – 3.65 (m, 1H), 3.37 (dd, *J* = 15.3, 11.0 Hz, 1H), 3.16 (dd, *J* = 15.3, 5.1 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 170.32, 146.00, 143.69, 137.63, 137.59, 137.26, 133.79, 130.73, 130.15, 128.63, 128.53, 128.44, 128.22, 128.11, 127.51, 127.21, 125.58, 123.87, 120.07, 119.51, 118.66, 66.72, 53.89, 50.75, 50.47. HRMS(ESI) calcd for C₂₉H₂₇N₂OS [M+H]⁺: 451.1839, Found: 451.1829.

(R)-8-(benzo[b]thiophen-2-yl)-1,4-dibenzyl-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (28b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); White oil, 46.5 mg, 93% yield; 95% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 15.980 min, t_R (major) = 17.733 min]; $[\alpha]_D^{25} = -20.70^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.83 (dd, $J = 7.9, 1.2 \text{ Hz}$, 1H), 7.81 – 7.76 (m, 2H), 7.54 (s, 1H), 7.42 (dd, $J = 8.0, 1.7 \text{ Hz}$, 1H), 7.37 (dd, $J = 7.2, 1.3 \text{ Hz}$, 1H), 7.34 (dd, $J = 5.7, 1.4 \text{ Hz}$, 1H), 7.32 (s, 3H), 7.32 (s, 3H), 7.30 – 7.26 (m, 3H), 7.26 – 7.24 (m, 2H), 5.59 – 5.52 (m, 1H), 5.27 – 5.22 (m, 1H), 5.06 – 5.00 (m, 1H), 4.92 (d, $J = 14.7 \text{ Hz}$, 1H), 4.72 (d, $J = 14.7 \text{ Hz}$, 1H), 4.48 (d, $J = 13.9 \text{ Hz}$, 1H), 4.22 (d, $J = 13.9 \text{ Hz}$, 1H), 3.72 – 3.67 (m, 1H), 3.38 (dd, $J = 15.4, 11.0 \text{ Hz}$, 1H), 3.17 (dd, $J = 15.3, 5.1 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.17, 146.02, 143.45, 140.52, 139.67, 137.55, 137.52, 137.21, 133.74, 130.89, 130.77, 128.65, 128.57, 128.45, 128.24, 127.55, 127.26, 124.66, 123.76, 122.30, 120.60, 120.35, 119.59, 119.23, 66.76, 53.91, 50.74, 50.50. HRMS(ESI) calcd for $\text{C}_{33}\text{H}_{29}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$: 501.1995, Found: 501.1983.

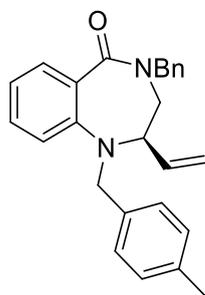
(*R*)-1,4-dibenzyl-8-(5a,9a-dihydrodibenzo[*b,d*]thiophen-3-yl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (29b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Brown oil, 50.8 mg, 92% yield; 90% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 18.498 min, t_R (major) = 25.193 min]; $[\alpha]_D^{25} = -80.30^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.20 – 8.14 (m, 2H), 7.89 (d, $J = 7.8 \text{ Hz}$, 1H), 7.83 – 7.80 (m, 1H), 7.55 (t, $J = 7.6 \text{ Hz}$, 1H), 7.48 – 7.46 (m, 2H), 7.44 (dd, $J = 7.5, 1.1 \text{ Hz}$, 1H), 7.41 – 7.40 (m, 1H), 7.38 (d, $J = 1.7 \text{ Hz}$, 1H), 7.35 (d, $J = 2.7 \text{ Hz}$, 2H), 7.34 (d, $J = 2.1 \text{ Hz}$, 3H), 7.32 (t, $J = 1.8 \text{ Hz}$, 1H), 7.30 – 7.29 (m, 1H), 7.28 (s, 1H), 7.27 – 7.26 (m, 2H), 5.60 – 5.54 (m, 1H), 5.24 – 5.20 (m, 1H), 5.05 – 4.99 (m, 1H), 4.93 (d, $J = 14.7 \text{ Hz}$, 1H), 4.78 (d, $J = 14.7 \text{ Hz}$, 1H), 4.53 (d, $J = 14.1 \text{ Hz}$, 1H), 4.21 (d, $J = 14.1 \text{ Hz}$, 1H), 3.74 – 3.68 (m, 1H), 3.44 (dd, $J = 15.3,$

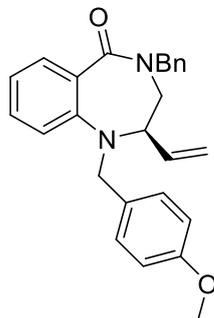
11.1 Hz, 1H), 3.20 (dd, $J = 15.3, 5.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.50, 145.93, 143.96, 139.55, 138.52, 137.73, 137.23, 136.36, 136.33, 135.69, 133.75, 130.67, 130.65, 128.66, 128.56, 128.54, 128.22, 127.53, 127.20, 126.90, 126.70, 125.09, 124.45, 122.63, 122.58, 121.74, 121.09, 120.85, 119.52, 66.66, 53.89, 50.81, 50.49. HRMS(ESI) calcd for $\text{C}_{37}\text{H}_{33}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$: 553.2308, Found: 553.2305.

(*R*)-4-benzyl-1-(4-methylbenzyl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (30b)



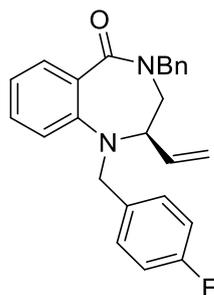
$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 35.1 mg, 92% yield; 93% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL}\cdot\text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 10.088 min, t_R (major) = 13.627 min]; $[\alpha]_{\text{D}}^{25} = -112.99^\circ$ ($c = 0.75$, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3) δ 7.71 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.35 – 7.32 (m, 1H), 7.30 (dd, $J = 7.4, 2.3$ Hz, 2H), 7.27 – 7.22 (m, 3H), 7.16 (d, $J = 7.9$ Hz, 2H), 7.10 (d, $J = 7.8$ Hz, 2H), 7.08 – 7.05 (m, 1H), 6.94 (d, $J = 8.1$ Hz, 1H), 5.51 – 5.45 (m, 1H), 5.24 – 5.18 (m, 1H), 5.02 – 4.96 (m, 1H), 4.83 (d, $J = 14.8$ Hz, 1H), 4.77 (d, $J = 14.8$ Hz, 1H), 4.33 (d, $J = 13.9$ Hz, 1H), 4.09 (d, $J = 13.9$ Hz, 1H), 3.68 – 3.63 (m, 1H), 3.29 (dd, $J = 15.2, 11.1$ Hz, 1H), 3.11 (dd, $J = 15.2, 5.2$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.75, 145.57, 137.33, 136.64, 134.72, 133.77, 131.60, 131.44, 129.87, 129.14, 128.59, 128.34, 128.18, 127.44, 122.55, 121.23, 119.28, 66.40, 53.42, 50.78, 50.36, 21.12. HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 383.2118, Found: 383.2109.

(R)-4-benzyl-1-(4-methoxybenzyl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (31b)



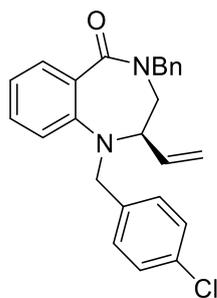
$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 36.6 mg, 92% yield; 93% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 13.674 min, t_R (major) = 19.474 min]; $[\alpha]_D^{25} = -71.55^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.71 (dd, $J = 7.6, 1.7 \text{ Hz}$, 1H), 7.35 – 7.33 (m, 1H), 7.30 (dd, $J = 7.5, 2.0 \text{ Hz}$, 2H), 7.29 – 7.26 (m, 1H), 7.25 (d, $J = 2.1 \text{ Hz}$, 2H), 7.18 (d, $J = 8.6 \text{ Hz}$, 2H), 7.07 (t, $J = 7.5 \text{ Hz}$, 1H), 6.93 (d, $J = 8.0 \text{ Hz}$, 1H), 6.83 (d, $J = 8.6 \text{ Hz}$, 2H), 5.50 – 5.44 (m, 1H), 5.21 – 5.18 (m, 1H), 5.00 – 4.96 (m, 1H), 4.83 (d, $J = 14.8 \text{ Hz}$, 1H), 4.75 (d, $J = 14.8 \text{ Hz}$, 1H), 4.29 (d, $J = 13.8 \text{ Hz}$, 1H), 4.07 (d, $J = 13.7 \text{ Hz}$, 1H), 3.80 (s, 3H), 3.66 – 3.61 (m, 1H), 3.29 (dd, $J = 15.2, 11.2 \text{ Hz}$, 1H), 3.10 (dd, $J = 15.2, 5.2 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.74, 158.69, 145.53, 137.34, 133.76, 131.57, 131.55, 129.82, 129.77, 129.53, 128.59, 128.19, 127.46, 122.60, 121.29, 119.25, 113.85, 66.30, 55.26, 53.08, 50.83, 50.35. HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 399.2068, Found: 399.2059.

(R)-4-benzyl-1-(4-fluorobenzyl)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (32b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 36.7 mg, 95% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 10.915 min, t_R (major) = 16.970 min]; $[\alpha]_D^{25} = -21.93^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (dd, $J = 7.6, 1.7 \text{ Hz}$, 1H), 7.37 – 7.33 (m, 1H), 7.33 – 7.30 (m, 2H), 7.30 – 7.26 (m, 3H), 7.23 – 7.19 (m, 2H), 7.09 (t, $J = 7.5 \text{ Hz}$, 1H), 7.00 – 6.94 (m, 2H), 6.92 (d, $J = 8.1 \text{ Hz}$, 1H), 5.52 – 5.45 (m, 1H), 5.23 – 5.19 (m, 1H), 5.01 – 4.96 (m, 1H), 4.89 (d, $J = 14.7 \text{ Hz}$, 1H), 4.71 (d, $J = 14.7 \text{ Hz}$, 1H), 4.32 (d, $J = 14.0 \text{ Hz}$, 1H), 4.09 (d, $J = 14.0 \text{ Hz}$, 1H), 3.61 – 3.56 (m, 1H), 3.31 (dd, $J = 15.2, 11.2 \text{ Hz}$, 1H), 3.12 (dd, $J = 15.2, 5.2 \text{ Hz}$, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 170.59, 161.93 (d, $J = 244.9 \text{ Hz}$), 145.16, 137.31, 133.63, 133.42 (d, $J = 2.9 \text{ Hz}$), 131.67, 131.60, 129.87 (d, $J = 2.4 \text{ Hz}$), 129.83, 128.61, 128.23, 127.55, 122.87, 121.22, 119.41, 115.28 (d, $J = 21.3 \text{ Hz}$), 66.68, 52.97, 50.86, 50.40. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -115.61. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 387.1867, Found: 387.1859.

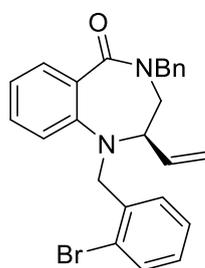
(*R*)-4-benzyl-1-(4-chlorobenzyl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (33b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 37.9 mg, 94% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 11.258 min, t_R (major) = 20.833 min]; $[\alpha]_D^{25} = -73.82^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 7.6 \text{ Hz}$, 1H), 7.38 – 7.35 (m, 1H), 7.34 – 7.31 (m, 2H), 7.30 – 7.27 (m, 4H), 7.26 (d, $J = 2.0 \text{ Hz}$, 1H), 7.20 (d, $J = 8.2 \text{ Hz}$, 2H), 7.11 (t, $J = 7.7 \text{ Hz}$, 1H), 6.92 (d, $J = 8.0 \text{ Hz}$, 1H), 5.52 – 5.46 (m, 1H), 5.25 – 5.20 (m, 1H), 5.02 – 4.97

(m, 1H), 4.91 (d, $J = 14.7$ Hz, 1H), 4.72 (d, $J = 14.7$ Hz, 1H), 4.33 (d, $J = 14.1$ Hz, 1H), 4.10 (d, $J = 14.1$ Hz, 1H), 3.61 – 3.55 (m, 1H), 3.32 (dd, $J = 15.2, 11.2$ Hz, 1H), 3.14 (dd, $J = 15.2, 5.2$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.53, 145.08, 137.29, 136.32, 133.55, 132.76, 131.66, 131.64, 129.89, 129.70, 128.63, 128.25, 127.58, 122.94, 121.16, 119.52, 66.78, 53.04, 50.83, 50.39. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 403.1572, Found: 403.1562.

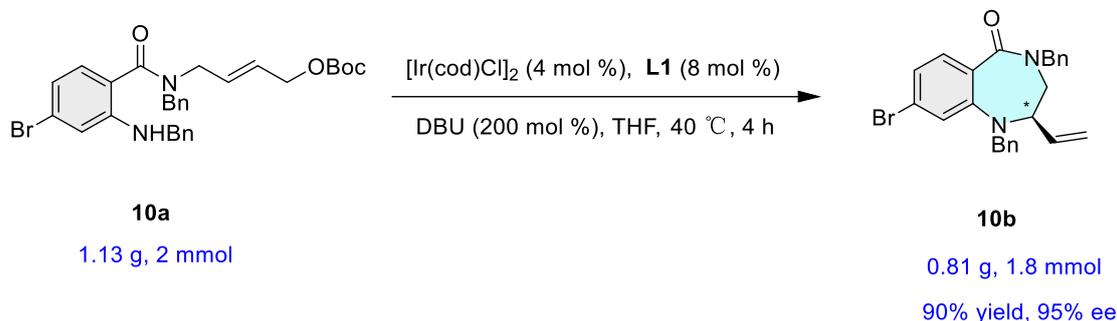
(*R*)-4-benzyl-1-(2-bromobenzyl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (34b)



$R_f = 0.40$ (petroleum/EtOAc = 4 : 1, v/v); Yellow oil, 41.9 mg, 94% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0$ mL \cdot min $^{-1}$, $T = 25$ $^\circ\text{C}$, $\lambda = 254$ nm, t_R (minor) = 11.367 min, t_R (major) = 13.856 min]; $[\alpha]_D^{25} = +175.6^\circ$ ($c = 0.75$, CH_2Cl_2). ^1H NMR (600 MHz, CDCl_3) δ 7.72 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.34 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.32 – 7.29 (m, 3H), 7.25 – 7.24 (m, 2H), 7.23 (d, $J = 2.2$ Hz, 2H), 7.20 (d, $J = 7.4$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 5.60 – 5.54 (m, 1H), 5.26 – 5.23 (m, 1H), 5.11 – 5.07 (m, 1H), 4.97 (d, $J = 14.8$ Hz, 1H), 4.66 (d, $J = 14.7$ Hz, 1H), 4.46 (d, $J = 15.2$ Hz, 1H), 4.23 (d, $J = 15.2$ Hz, 1H), 3.65 – 3.61 (m, 1H), 3.32 (dd, $J = 15.3, 10.7$ Hz, 1H), 3.18 (dd, $J = 15.2, 5.0$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 170.59, 144.76, 137.27, 136.62, 134.15, 132.97, 131.65, 130.22, 130.13, 128.61, 128.27, 127.49, 127.35, 124.05, 122.72, 121.11, 119.46, 67.63, 53.41, 50.72, 50.48. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 447.1067, Found: 447.1057.

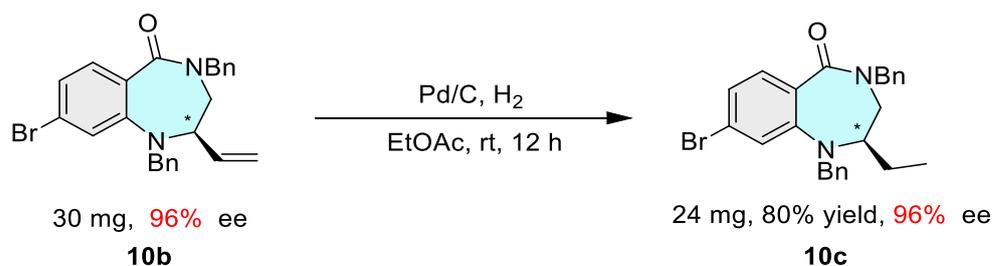
3.3 General Procedure for the Synthetic Applications

3.3.1 Gram-scale Reaction



Representative Procedure: in a dry Schlenk tube (50.0 mL) filled with argon, $[\text{Ir}(\text{cod})\text{Cl}]_2$ (53.76 mg, 0.080 mmol, 4 mol %), ligand **L1** (84 mg, 0.16 mmol, 8 mol %), and *n*-propylamine (5.0 mL) were dissolved in THF (5.0 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed in vacuum to give a yellow solid. In glove box, substrate (1.13 g, 2 mmol), DBU (0.61 g, 4 mmol, 200 mol %) and solvent (20.0 mL) were added into the above tube and stirred at 40 °C until the reaction was complete. Then the solvent was evaporated and the residue was purified by silica gel column chromatography using petroleum/EtOAc as the eluent to give the desired product **10b** (90% yield, 95% ee).

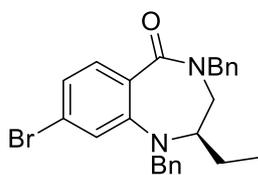
3.3.2 Procedure for the Synthesis of 10c



10b (0.05 mmol), palladium on activated carbon (10% Pd) (5.3 mg) and EtOAc (2.0 mL) were added to a round bottom flask fitted with a hydrogen balloon. The tube was degassed and back-filled with hydrogen for three cycles. The mixture was stirred until TLC showed that the reaction completed. The reaction mixture was filtered through a celite pad, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 5/1) to give product **10c** (80% yield, 96% ee).

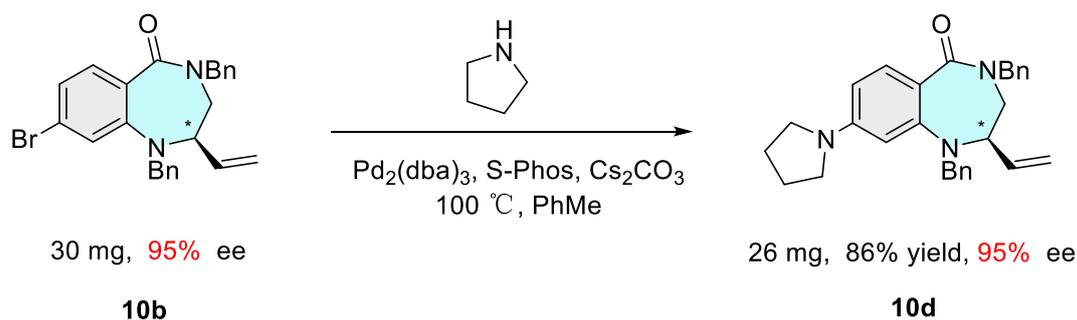
(R)-1,4-dibenzyl-8-bromo-2-ethyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one

(10c)



$R_f = 0.40$ (petroleum/EtOAc = 5 : 1, v/v); Yellow oil, 24 mg, 80% yield; 96% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 60/40, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 37.165 min, t_R (major) = 14.703 min]; $[\alpha]_D^{25} = -18.00^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.59 (d, $J = 8.2 \text{ Hz}$, 1H), 7.33 (d, $J = 8.2 \text{ Hz}$, 2H), 7.31 (d, $J = 3.9 \text{ Hz}$, 3H), 7.28 (d, $J = 10.5 \text{ Hz}$, 5H), 7.18 (dd, $J = 8.2, 1.8 \text{ Hz}$, 1H), 7.09 (d, $J = 1.8 \text{ Hz}$, 1H), 4.81 (d, $J = 14.6 \text{ Hz}$, 1H), 4.76 (d, $J = 14.7 \text{ Hz}$, 1H), 4.44 (d, $J = 14.1 \text{ Hz}$, 1H), 4.25 (d, $J = 14.1 \text{ Hz}$, 1H), 3.28 – 3.24 (m, 1H), 3.24 – 3.20 (m, 1H), 3.17 (d, $J = 8.3 \text{ Hz}$, 1H), 1.72 – 1.64 (m, 2H), 0.69 (t, $J = 7.5 \text{ Hz}$, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 169.93, 147.29, 137.30, 137.09, 131.36, 130.39, 128.67, 128.60, 128.32, 128.24, 127.60, 127.36, 125.80, 125.43, 124.84, 63.85, 53.87, 50.49, 50.06, 21.24, 9.71. HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 449.1223, Found: 449.1212.

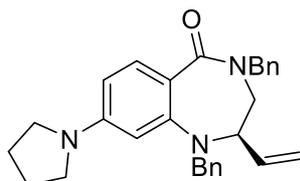
3.3.3 Procedure for the Synthesis of 10d



In a dry Schlenk tube filled with argon, **10b** (30.0 mg, 0.07 mmol, 1.0 equiv), $\text{Pd}_2(\text{dba})_3$ (2.0 mg, 0.002 mmol, 0.03 equiv), S-Phos (2.3 mg, 0.006 mmol, 0.08 equiv) and Cs_2CO_3 (44.0 mg, 0.14 mmol, 2.0 equiv) were dissolved in PhMe (3.0 mL). The mixture reacted at 40°C until color change occurred, followed by the addition of pyrrolidine (9.0 mg, 0.13 mmol, 1.8 equiv).

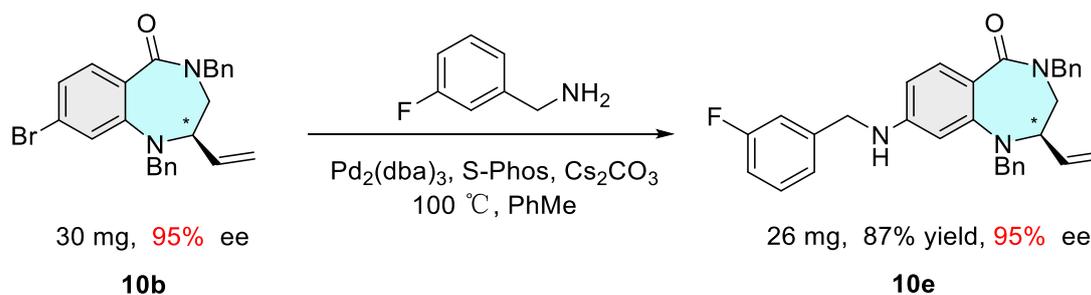
The reaction mixture was heated at 100 °C for 24 h. Then the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using petroleum/EtOAc (5 : 1) as the eluent to give the desired product **10d** (86% yield, 95% ee).

(*R*)-1,4-dibenzyl-8-(pyrrolidin-1-yl)-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (10d)



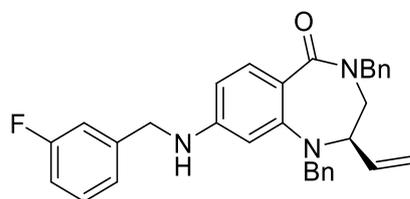
$R_f = 0.40$ (petroleum/EtOAc = 5 : 1, v/v); Yellow oil, 26 mg, 86% yield; 95% ee [Daicel Chiralcel OD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 16.443 min, t_R (major) = 8.277 min]; $[\alpha]_D^{25} = -40.85^\circ$ ($c = 0.75$, CH_2Cl_2). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.63 (d, $J = 8.6 \text{ Hz}$, 1H), 7.31 (s, 1H), 7.29 (d, $J = 4.9 \text{ Hz}$, 4H), 7.25 – 7.23 (m, 2H), 7.23 – 7.22 (m, 2H), 7.22 – 7.20 (m, 1H), 6.25 (d, $J = 10.8 \text{ Hz}$, 1H), 6.01 (d, $J = 2.3 \text{ Hz}$, 1H), 5.58 – 5.52 (m, 1H), 5.20 – 5.17 (m, 1H), 4.98 – 4.95 (m, 1H), 4.86 (d, $J = 14.9 \text{ Hz}$, 1H), 4.68 (d, $J = 14.9 \text{ Hz}$, 1H), 4.41 (d, $J = 14.0 \text{ Hz}$, 1H), 4.12 (d, $J = 14.0 \text{ Hz}$, 1H), 3.62 (d, $J = 5.2 \text{ Hz}$, 1H), 3.36 (dd, $J = 15.0, 11.1 \text{ Hz}$, 1H), 3.30 – 3.24 (m, 4H), 3.09 (dd, $J = 15.0, 5.2 \text{ Hz}$, 1H), 2.02 – 1.96 (m, 4H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.48, 150.48, 147.31, 138.36, 137.87, 134.44, 131.55, 128.49, 128.40, 128.23, 128.18, 127.21, 126.97, 118.85, 118.07, 105.92, 103.76, 66.59, 54.12, 50.95, 50.44, 47.53, 25.43. HRMS(ESI) calcd for $\text{C}_{29}\text{H}_{32}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 438.2540, Found: 438.2536.

3.3.4 Procedure for the Synthesis of 10e



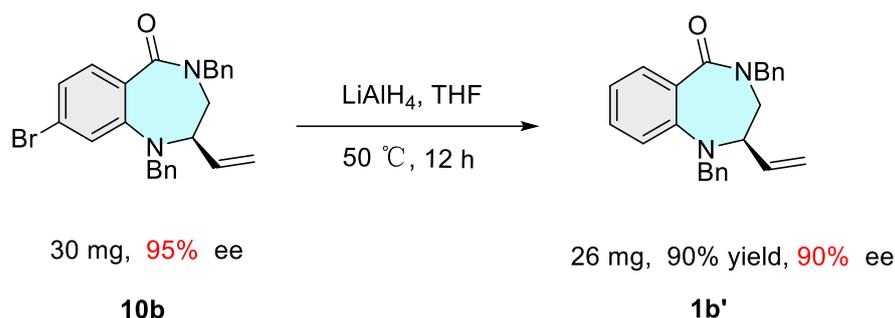
In a dry Schlenk tube filled with argon, **10b** (30.0 mg, 0.07 mmol, 1.0 equiv), Pd₂(dba)₃ (2.0 mg, 0.002 mmol, 0.03 equiv), S-Phos (2.3 mg, 0.006 mmol, 0.08 equiv) and Cs₂CO₃ (44.0 mg, 0.14 mmol, 2.0 equiv) were dissolved in PhMe (3.0 mL). The mixture reacted at 40 °C until color change occurred, followed by the addition of 3-fluorobenzylamine (15.7 mg, 0.13 mmol, 1.8 equiv). The reaction mixture was heated at 100 °C for 24 h. Then the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using petroleum/EtOAc (5 : 1) as the eluent to give the desired product **10e** (87% yield, 95% ee).

(R)-1,4-dibenzyl-8-((3-fluorophenyl)amino)-2-vinyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (10e)



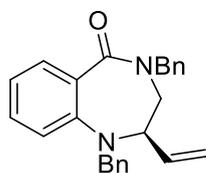
R_f = 0.40 (petroleum/EtOAc = 5 : 1, v/v); Yellow oil, 26 mg, 87% yield; 95% ee [Daicel Chiralcel OD-H (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 20.863 min, t_R (major) = 15.758 min]; [α]_D²⁵ = -40.75° (c = 0.75, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 3.2 Hz, 2H), 7.28 (s, 1H), 7.27 – 7.26 (m, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.21 (m, 3H), 7.21 – 7.19 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 9.6 Hz, 1H), 6.98 – 6.92 (m, 1H), 6.29 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.08 (d, *J* = 2.2 Hz, 1H), 5.52 – 5.46 (m, 1H), 5.19 – 5.14 (m, 1H), 4.98 – 4.92 (m, 1H), 4.88 (d, *J* = 14.9 Hz, 1H), 4.64 (d, *J* = 14.9 Hz, 1H), 4.30 (s, 2H), 4.26 (d, *J* = 14.3 Hz, 1H), 4.03 (d, *J* = 14.0 Hz, 1H), 3.64 – 3.59 (m, 1H), 3.35 (dd, *J* = 15.1, 10.8 Hz, 1H), 3.12 (dd, *J* = 15.1, 5.0 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 171.16, 163.23 (d, *J* = 246.9 Hz), 150.93, 147.49, 141.82, 137.90 (d, *J* = 46.9 Hz), 134.29, 131.91, 130.30 (d, *J* = 8.2 Hz), 128.62, 128.54, 128.37, 128.35, 128.25, 128.24, 127.26 (d, *J* = 41.7 Hz), 122.85, 120.29, 119.11, 114.33 (d, *J* = 13.0 Hz), 114.19 (d, *J* = 12.7 Hz), 106.94, 104.92, 66.63, 54.00, 50.91, 50.60, 47.50. ¹⁹F NMR (565 MHz, CDCl₃) δ -112.75. HRMS(ESI) calcd for C₃₂H₃₁FN₃O [M+H]⁺: 492.2446, Found: 492.2443.

3.3.5 Procedure for the Synthesis of **1b'**



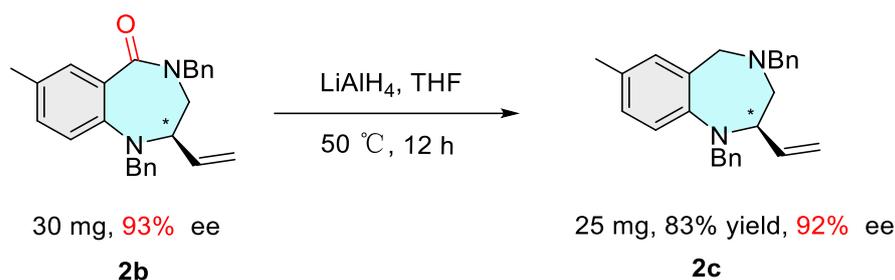
To a solution of 10b **10b** (30.0 mg, 0.07 mmol, 1.0 equiv) in THF (10 mL) at 0 °C, LiAlH₄ (7.66 mg, 0.21 mmol, 3.0 equiv) was added in three portions. The reaction mixture was stirred for 12 h at 50 °C. It was cooled back down to 0 °C and MeOH was added. Then the mixture was filtered through celite and the obtained solution was concentrated in vacuo. The crude residue was purified using column chromatography (eluent: petroleum ether/EtOAc = 5 : 1) to provide the desired product **1b'** (90% yield, 90% ee).

(*R*)-1,4-dibenzyl-2-vinyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (**1b'**)



R_f = 0.40 (petroleum/EtOAc = 5 : 1, v/v); Yellow oil, 26 mg, 90% yield; 90% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, v = 1.0 mL•min⁻¹, T = 25 °C, λ = 254 nm, t_R (minor) = 13.081 min, t_R (major) = 7.952 min]; [α]_D²⁵ = -21.50° (c = 0.75, CH₂Cl₂).
¹H NMR (600 MHz, CDCl₃) δ 7.72 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.34 (td, *J* = 7.7, 1.8 Hz, 2H), 7.30 (dd, *J* = 7.2, 2.1 Hz, 3H), 7.28 – 7.27 (m, 2H), 7.26 – 7.21 (m, 4H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 5.52 – 5.45 (m, 1H), 5.23 – 5.18 (m, 1H), 5.02 – 4.96 (m, 1H), 4.86 (d, *J* = 14.8 Hz, 1H), 4.74 (d, *J* = 14.8 Hz, 1H), 4.37 (d, *J* = 14.1 Hz, 1H), 4.13 (d, *J* = 14.0 Hz, 1H), 3.68 – 3.61 (m, 1H), 3.30 (dd, *J* = 15.2, 11.1 Hz, 1H), 3.12 (dd, *J* = 15.2, 5.2 Hz, 1H).
¹³C NMR (151 MHz, CDCl₃) δ 170.73, 145.46, 137.81, 137.28, 133.71, 131.63, 131.46, 129.89, 128.61, 128.47, 128.40, 128.19, 127.48, 127.11, 122.65, 121.21, 119.38, 66.61, 53.71, 50.76, 50.37. HRMS(ESI) calcd for C₂₅H₂₅N₂O [M+H]⁺: 369.1961, Found: 369.1954.

3.3.6 Procedure for the Synthesis of 2c



To a solution of **2b** (30 mg, 0.08 mmol, 1.0 equiv) in THF (10 mL) at 0 °C, LiAlH₄ (18 mg, 0.48 mmol, 6.0 equiv) was added in three portions. The reaction mixture was stirred for 12 h at 50 °C. It was cooled back down to 0 °C and MeOH was added. Then the mixture was filtered through celite and the obtained solution was concentrated in vacuo. The crude residue was purified using column chromatography (eluent: petroleum ether/EtOAc = 5 : 1) to provide the desired product **2c** (83% yield, 92% ee).

(*R*)-1,4-dibenzyl-7-methyl-2-vinyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepine (**2c**)



R_f = 0.40 (petroleum/EtOAc = 5 : 1, v/v); Yellow oil, 25 mg, 83% yield; 92% ee [Daicel Chiralcel IC-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $\lambda = 254 \text{ nm}$, t_R (minor) = 4.749 min, t_R (major) = 5.018 min]; $[\alpha]_D^{25} = -17.65^\circ$ ($c = 0.75$, CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃) δ 7.41 (d, $J = 7.5 \text{ Hz}$, 2H), 7.36 – 7.33 (m, 4H), 7.33 – 7.31 (m, 2H), 7.30 (s, 1H), 7.25 – 7.23 (m, 1H), 7.02 (d, $J = 8.1 \text{ Hz}$, 1H), 6.89 – 6.88 (m, 1H), 6.83 (d, $J = 8.0 \text{ Hz}$, 1H), 5.77 – 5.61 (m, 1H), 5.09 – 5.06 (m, 1H), 5.03 – 4.99 (m, 1H), 4.42 (d, $J = 13.9 \text{ Hz}$, 1H), 4.16 (d, $J = 13.9 \text{ Hz}$, 1H), 3.82 (d, $J = 12.9 \text{ Hz}$, 1H), 3.76 (d, $J = 12.9 \text{ Hz}$, 1H), 3.70 (d, $J = 13.4 \text{ Hz}$, 1H), 3.64 (d, $J = 13.4 \text{ Hz}$, 1H), 3.60 – 3.55 (m, 1H), 2.78 (dd, $J = 12.8, 5.1 \text{ Hz}$, 1H), 2.69 (d, $J = 12.9 \text{ Hz}$, 1H), 2.28 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 146.50, 139.40, 136.54, 131.43, 130.80, 130.58, 128.84, 128.51, 128.39, 128.31, 128.22, 127.01, 126.92, 124.00, 119.24, 116.46, 61.68, 60.28, 58.67, 55.76, 29.73, 20.58. HRMS(ESI) calcd for C₂₆H₂₉N₂ [M+H]⁺: 369.2325, Found: 369.2315.

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- [1] (a) Arnold, L. A.; Naasz, R.; Minnaard, A. J.; Feringa, B. L. Catalytic Enantioselective Synthesis of Prostaglandin E1 Methyl Ester Using a Tandem 1,4-Addition-Aldol Reaction to a Cyclopenten-3,5-dione Monoacetal. *J. Am. Chem. Soc.* 2001, 123, 5841–5842. (b) Defieber, C.; Ariger, M. A.; Moriel, P.; Carreira, E. M. Iridium-Catalyzed Synthesis of Primary Allylic Amines from Allylic Alcohols: Sulfamic Acid as Ammonia Equivalent. *Angew. Chem. Int. Ed.* 2007, 46, 3139–3143. (c) Zhuang, Y.; He, Y.; Zhou, Z.; Xia, W.; Cheng, C.; Wang, M.; Chen, B.; Zhou, Z.; Pang, J.; Qiu, L. Synthesis of a Class of Chiral-Bridged Phosphoramidite Ligands and Their Applications in the First Iridium-Catalyzed Asymmetric Addition of Arylboronic Acids to Isatins. *J. Org. Chem.* 2015, 80, 6968–6975. (d) Jiang, X.; Chen, X.; Li, Y.; Liang, H.; Zhang, Y.; He, X.; Chen, B.; Chan, W. T. K.; Chan, A. S. C.; Qiu, L. Enantioselective Syntheses of Tricyclic Benzimidazoles via Intramolecular Allylic Aminations with Chiral Bridged Biphenyl Phosphoramidite Ligands, *Org. Lett.* 2019, 21, 608–613.

4. Copies of NMR Spectra

Figure S1. ^1H NMR (600 MHz, CDCl_3) spectrum of 1a

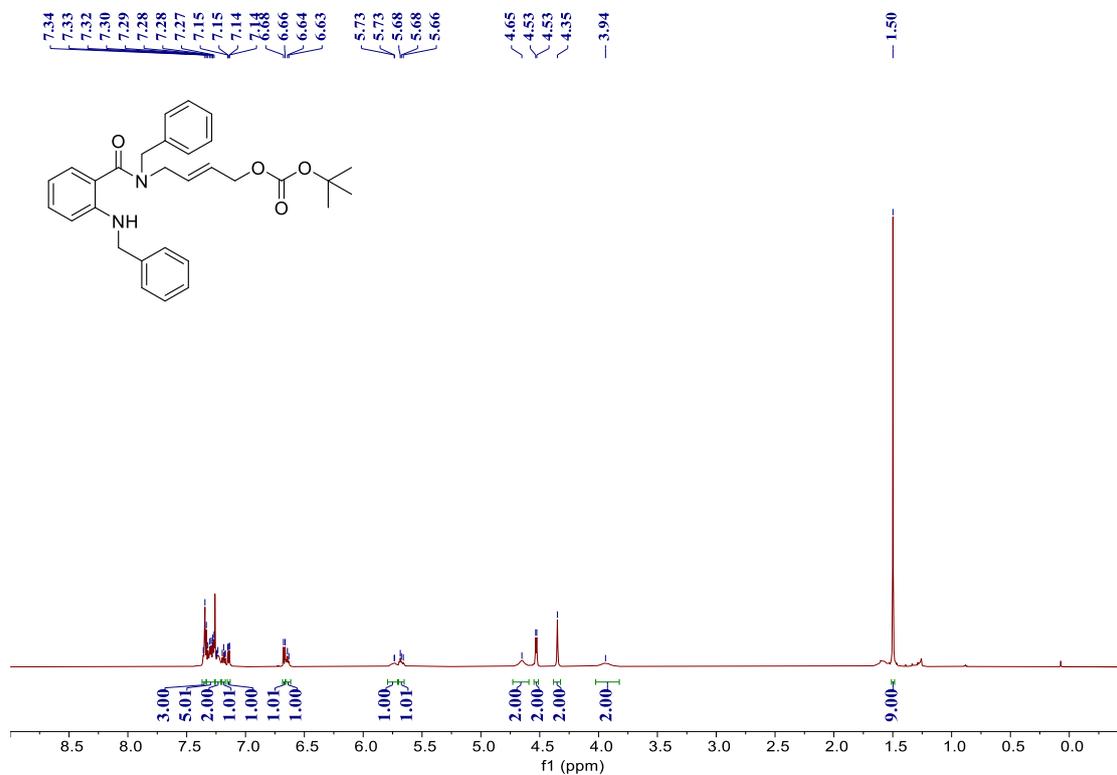


Figure S2. ^{13}C NMR (151 MHz, CDCl_3) spectrum of 1a

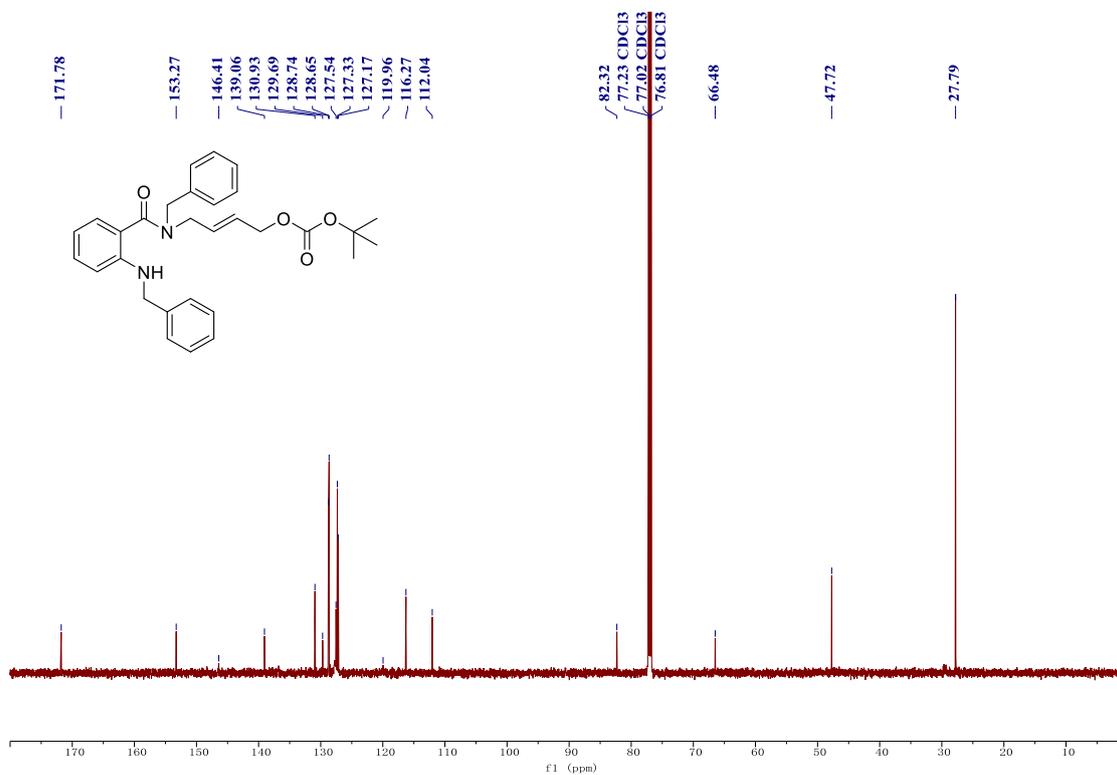


Figure S3. ¹H NMR (600 MHz, CDCl₃) spectrum of 2a

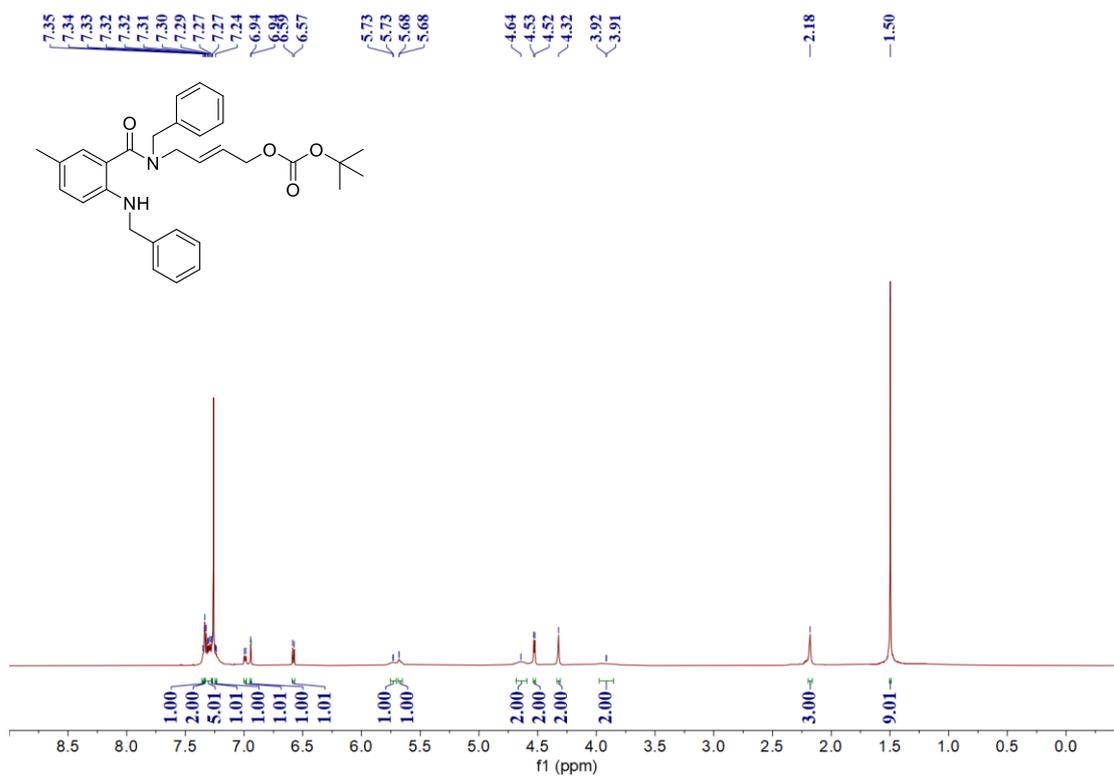


Figure S4. ¹³C NMR (151 MHz, CDCl₃) spectrum of 2a

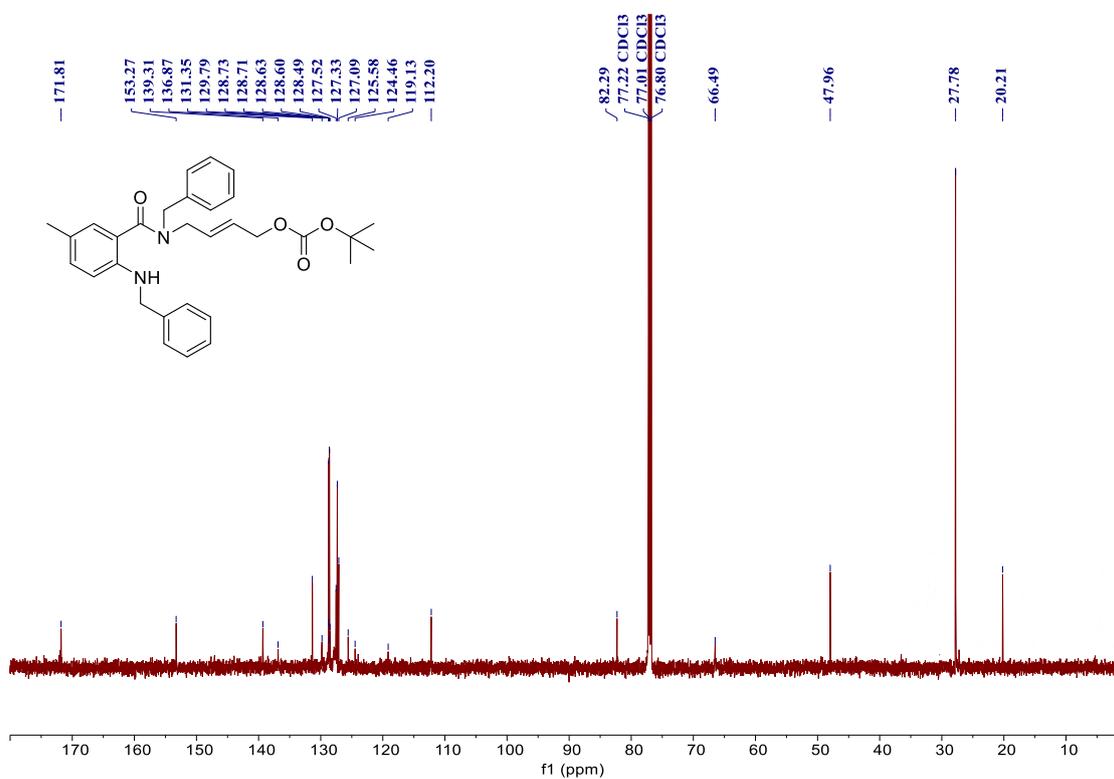


Figure S5. ¹H NMR (600 MHz, CDCl₃) spectrum of 3a

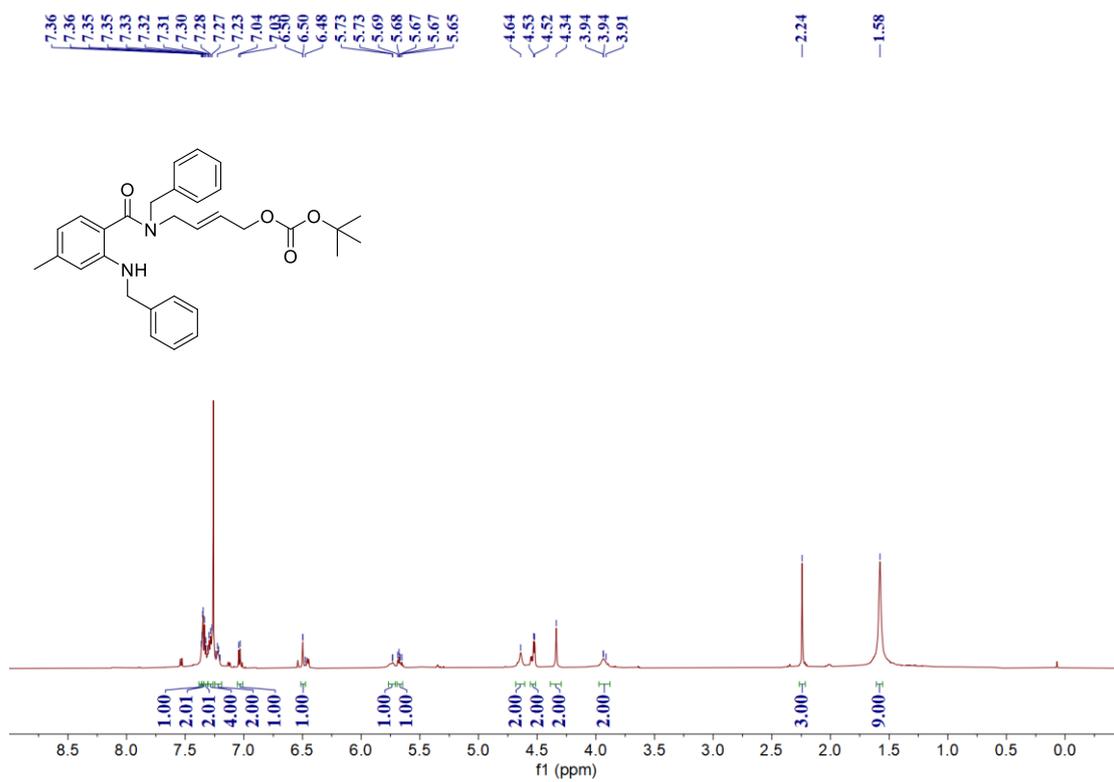


Figure S6. ¹³C NMR (151 MHz, CDCl₃) spectrum of 3a

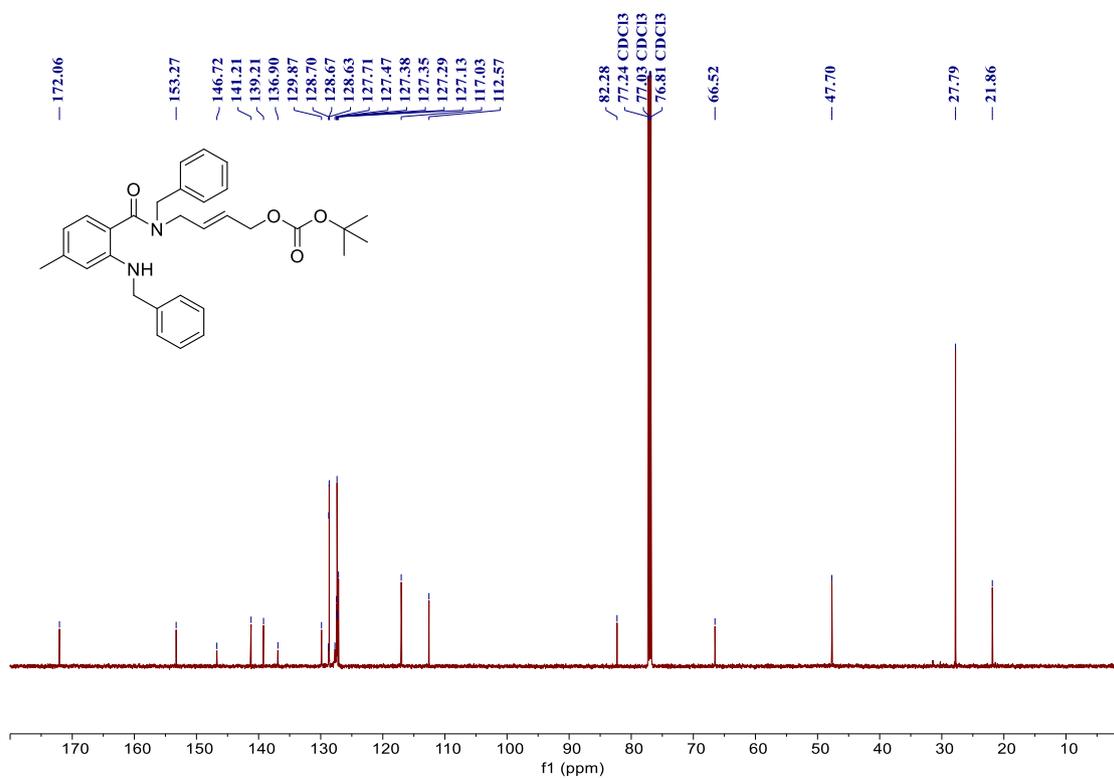


Figure S7. ¹H NMR (600 MHz, CDCl₃) spectrum of 4a

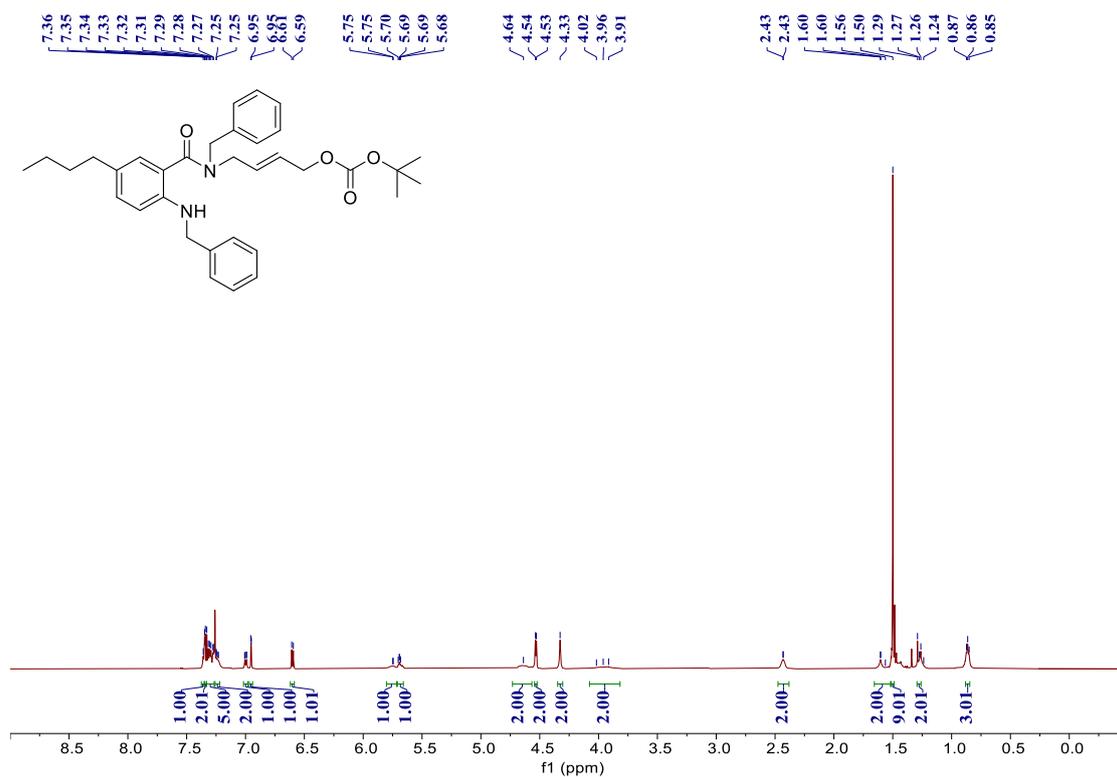


Figure S8. ¹³C NMR (151 MHz, CDCl₃) spectrum of 4a

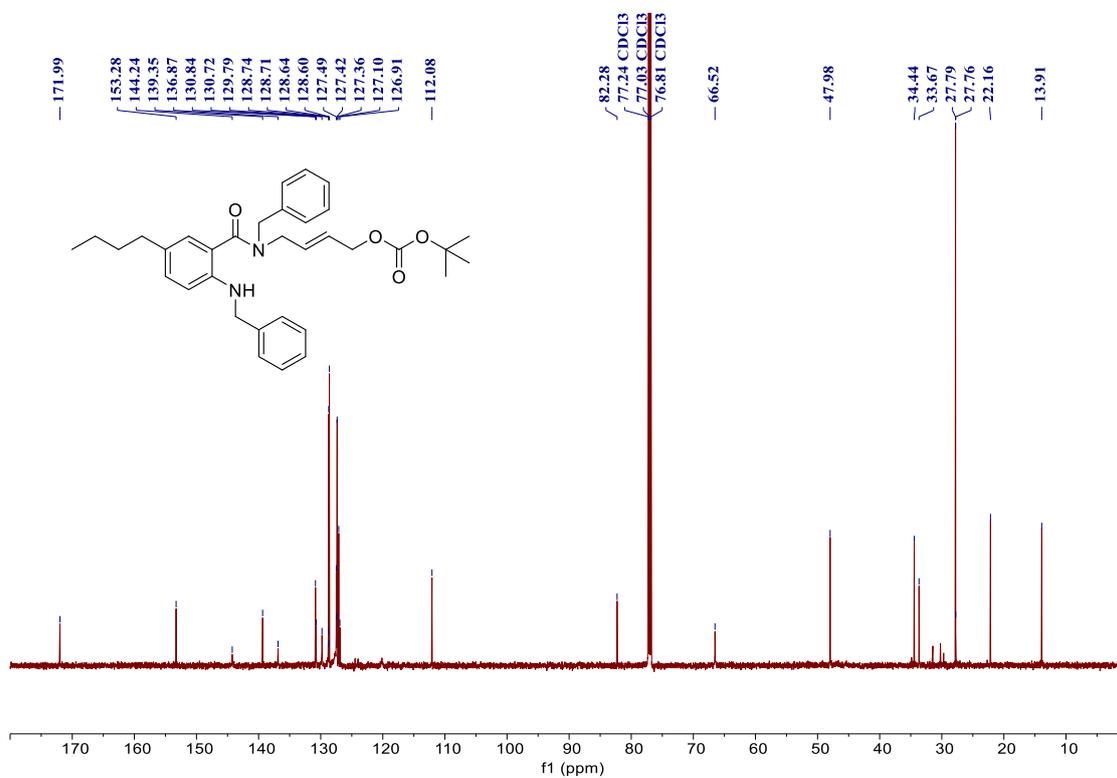


Figure S11. ¹H NMR (600 MHz, CDCl₃) spectrum of 6a

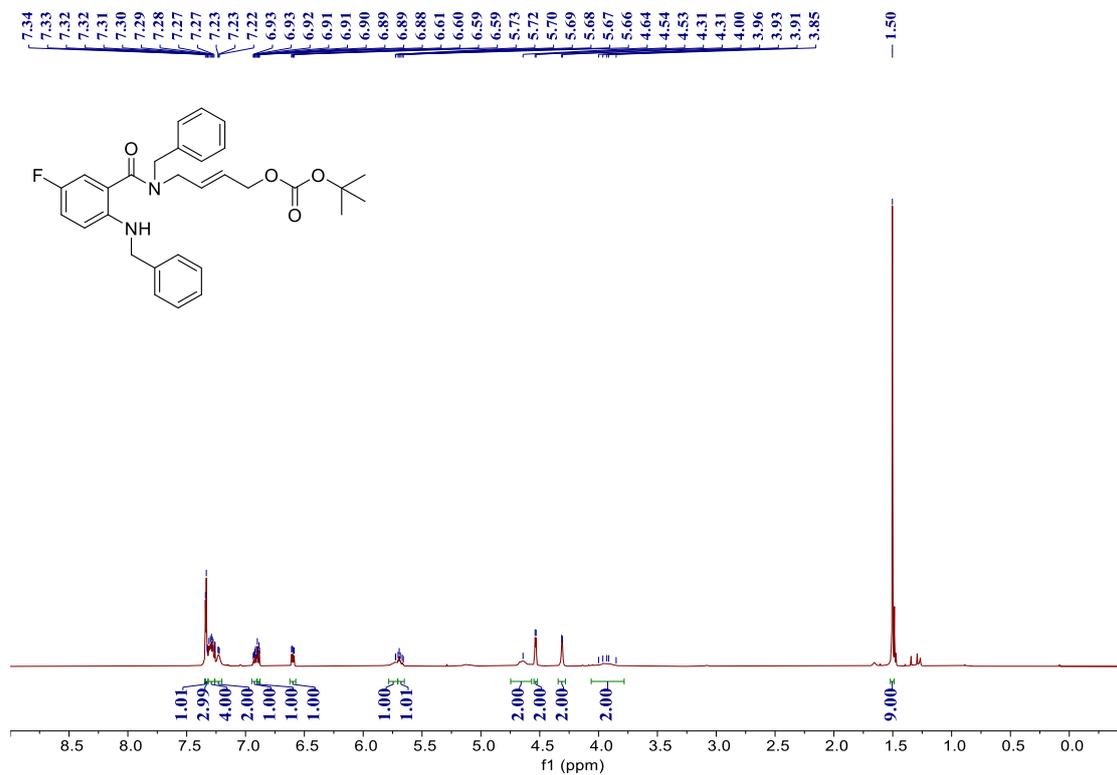


Figure S12. ¹³C NMR (151 MHz, CDCl₃) spectrum of 6a

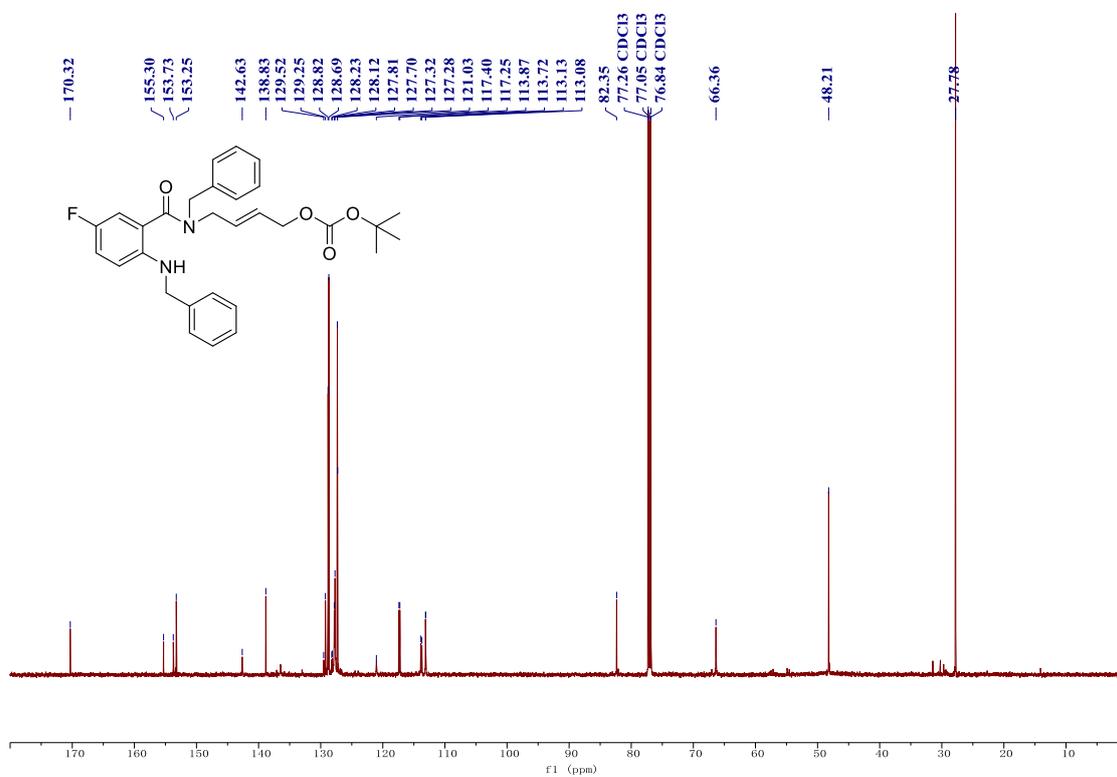


Figure S13. ^{19}F NMR (565 MHz, CDCl_3) spectrum of 6a

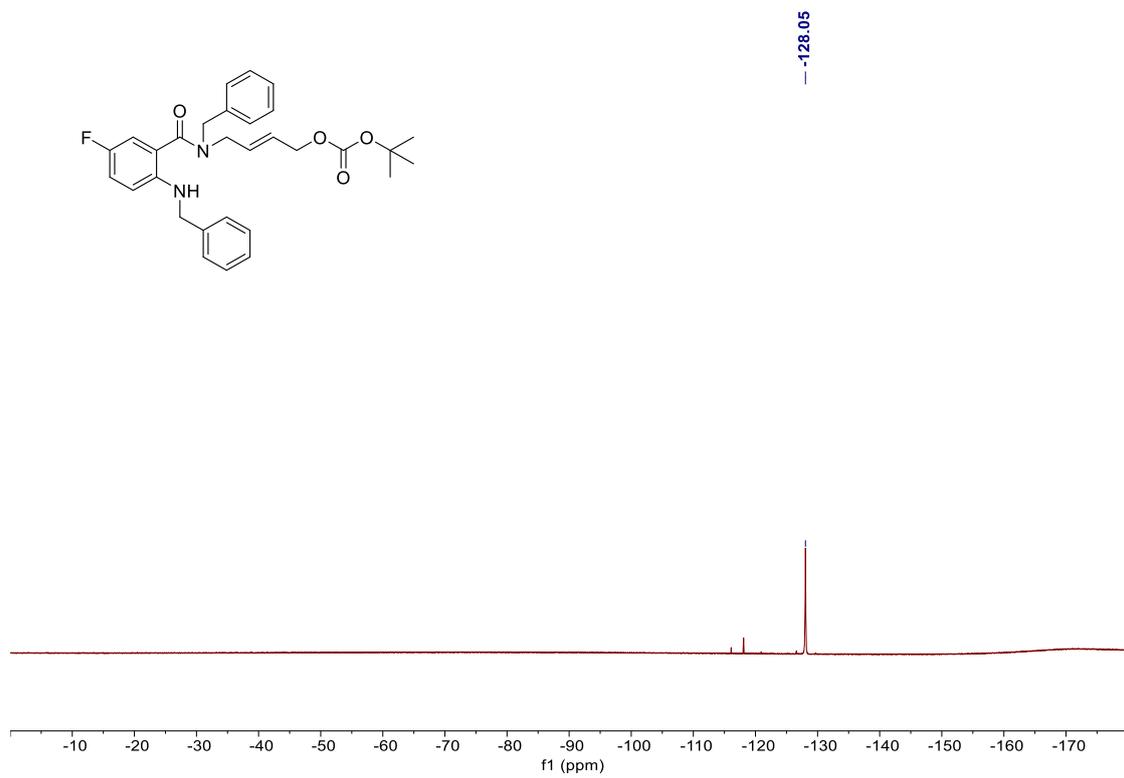


Figure S14. ¹H NMR (600 MHz, CDCl₃) spectrum of 7a

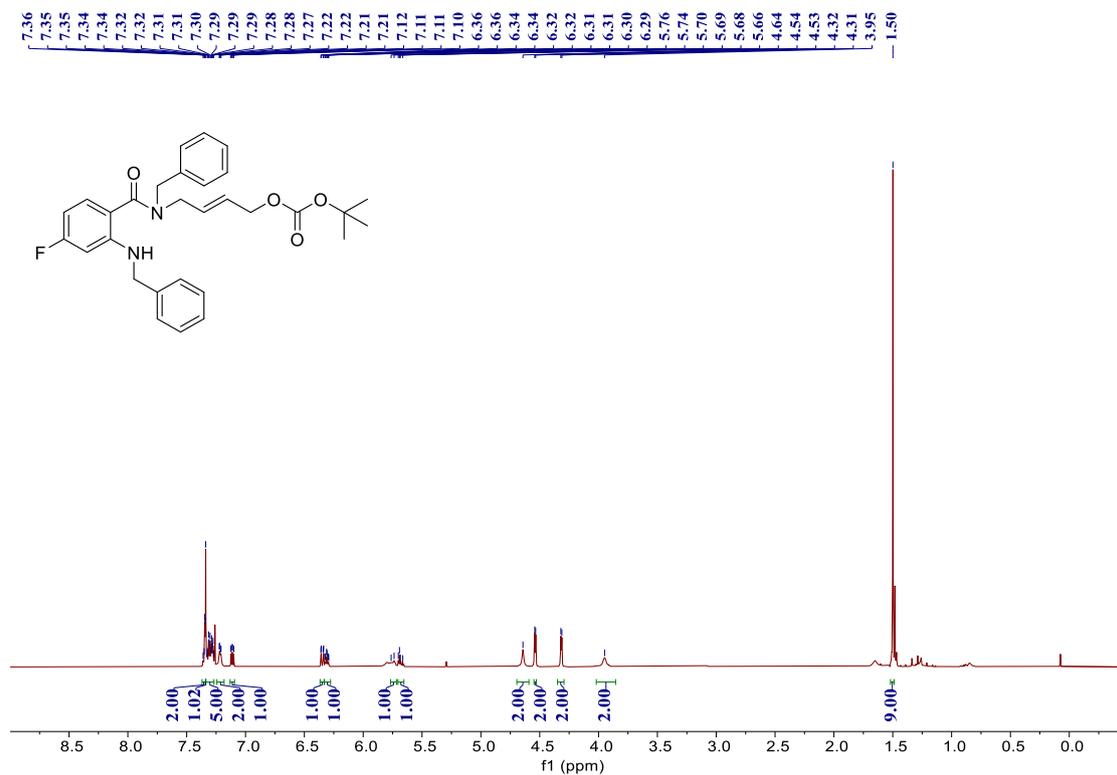


Figure S15. ¹³C NMR (151 MHz, CDCl₃) spectrum of 7a

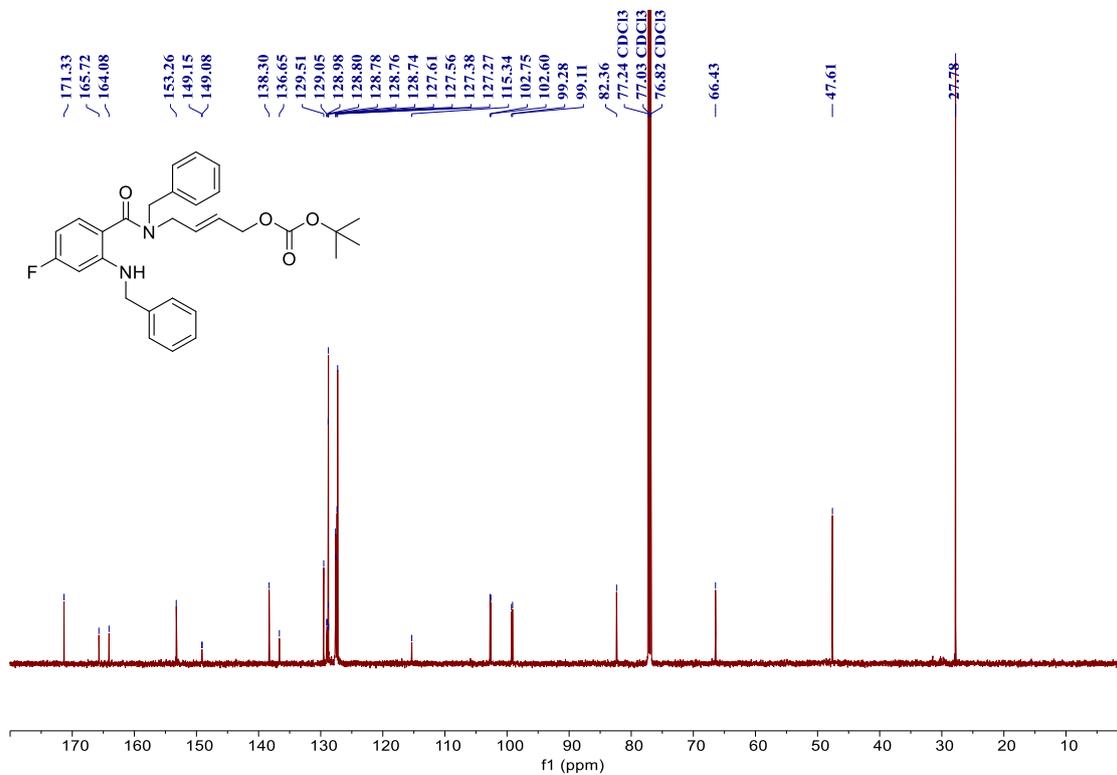


Figure S16. ^{19}F NMR (565 MHz, CDCl_3) spectrum of 7a

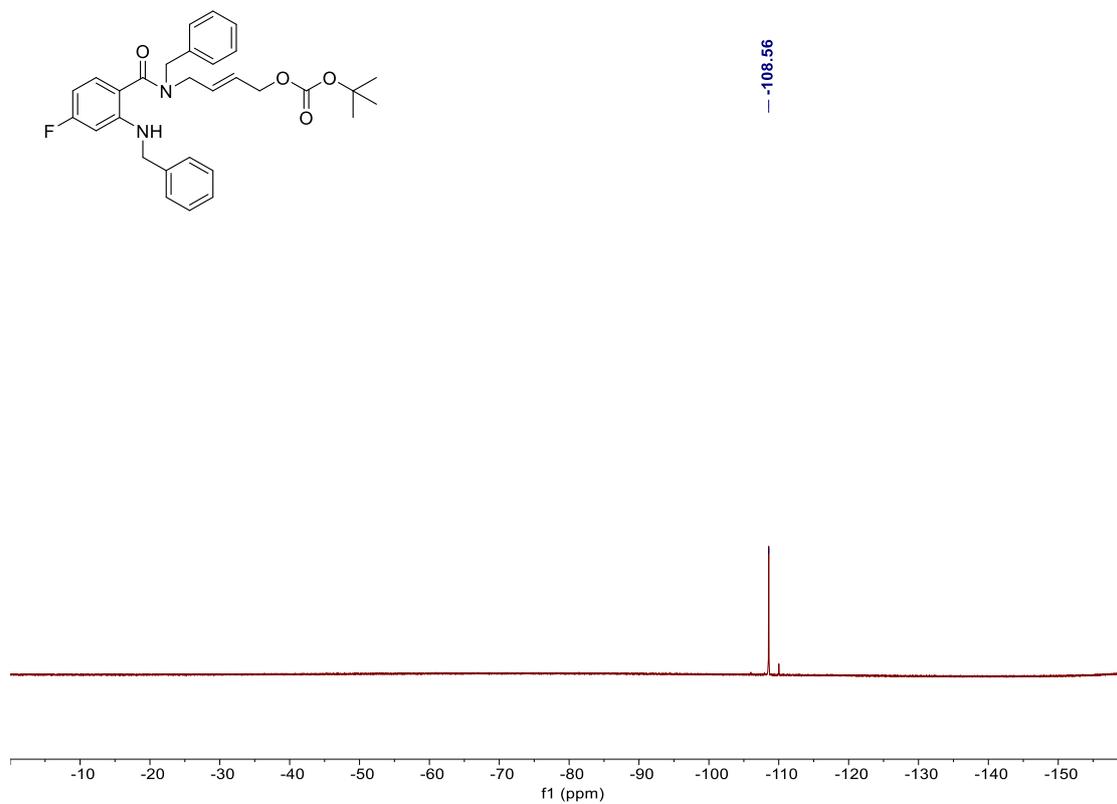


Figure S17. ¹H NMR (600 MHz, CDCl₃) spectrum of 8a

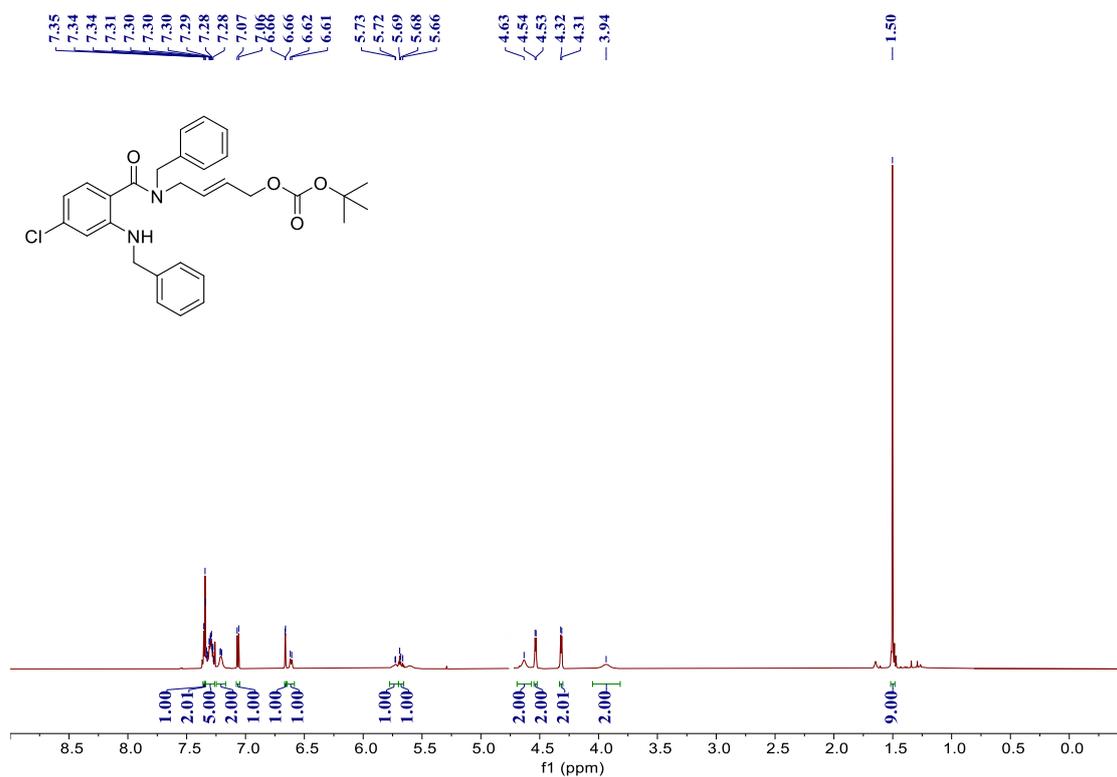


Figure S18. ¹³C NMR (151 MHz, CDCl₃) spectrum of 8a

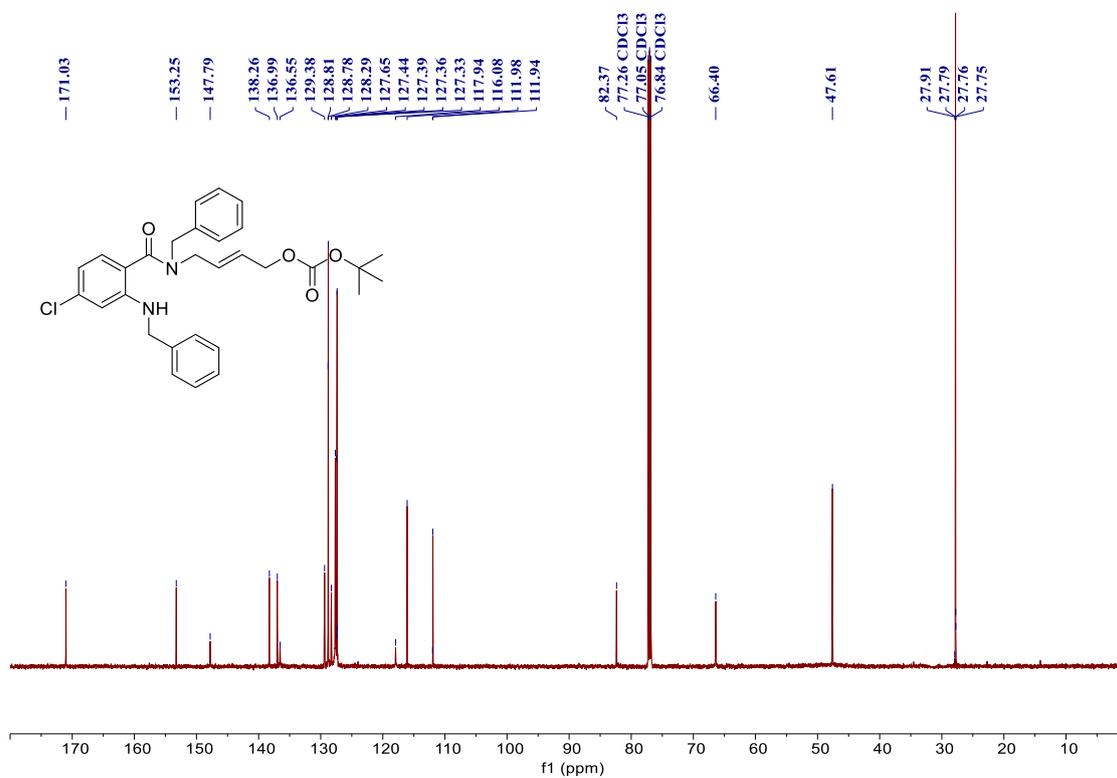


Figure S19. ¹H NMR (600 MHz, CDCl₃) spectrum of 9a

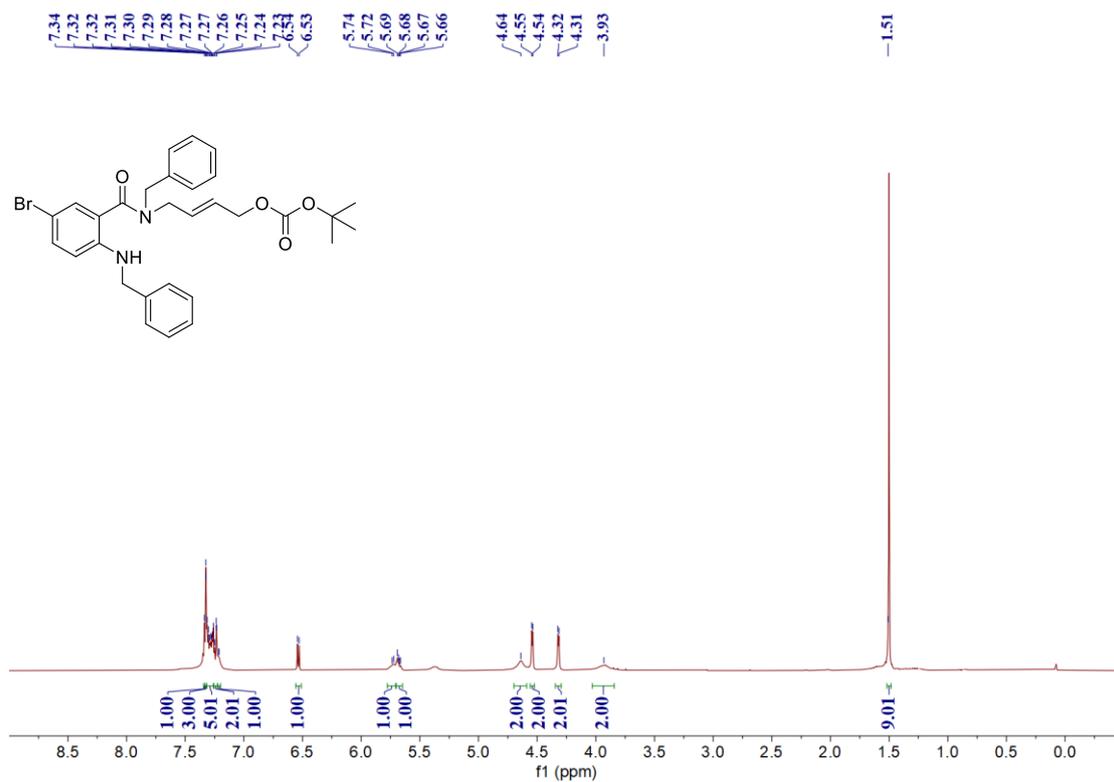


Figure S20. ¹³C NMR (151 MHz, CDCl₃) spectrum of 9a

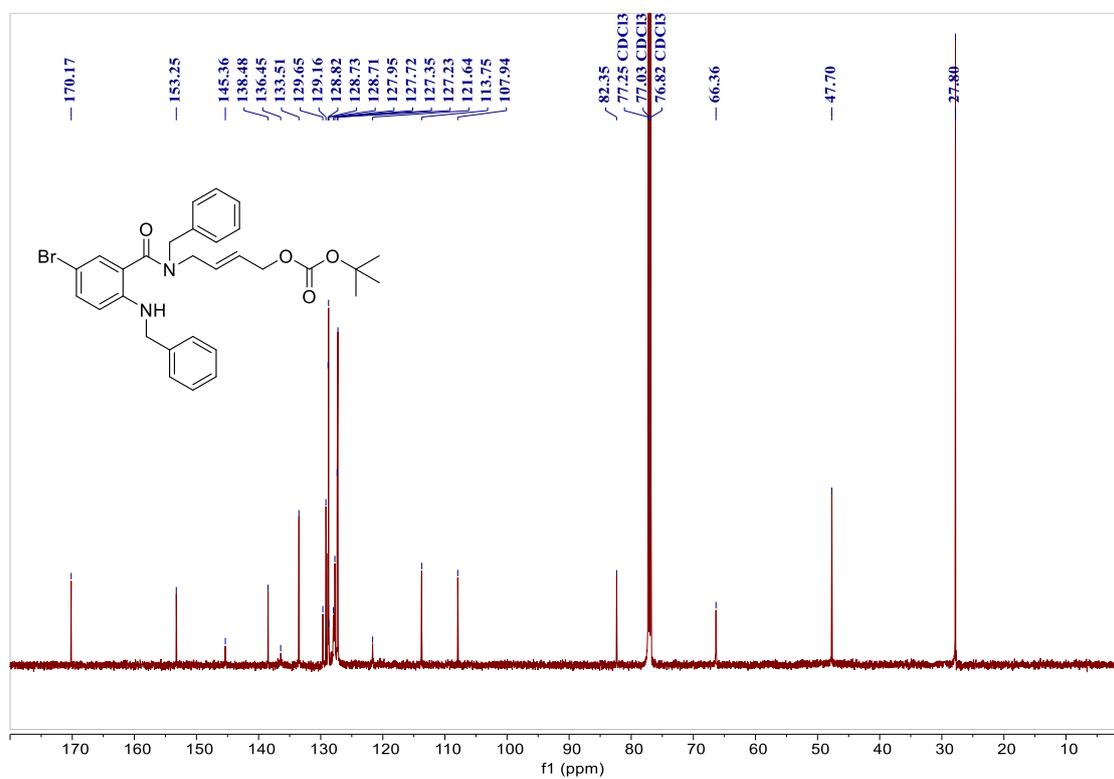


Figure S21. ¹H NMR (600 MHz, CDCl₃) spectrum of 10a

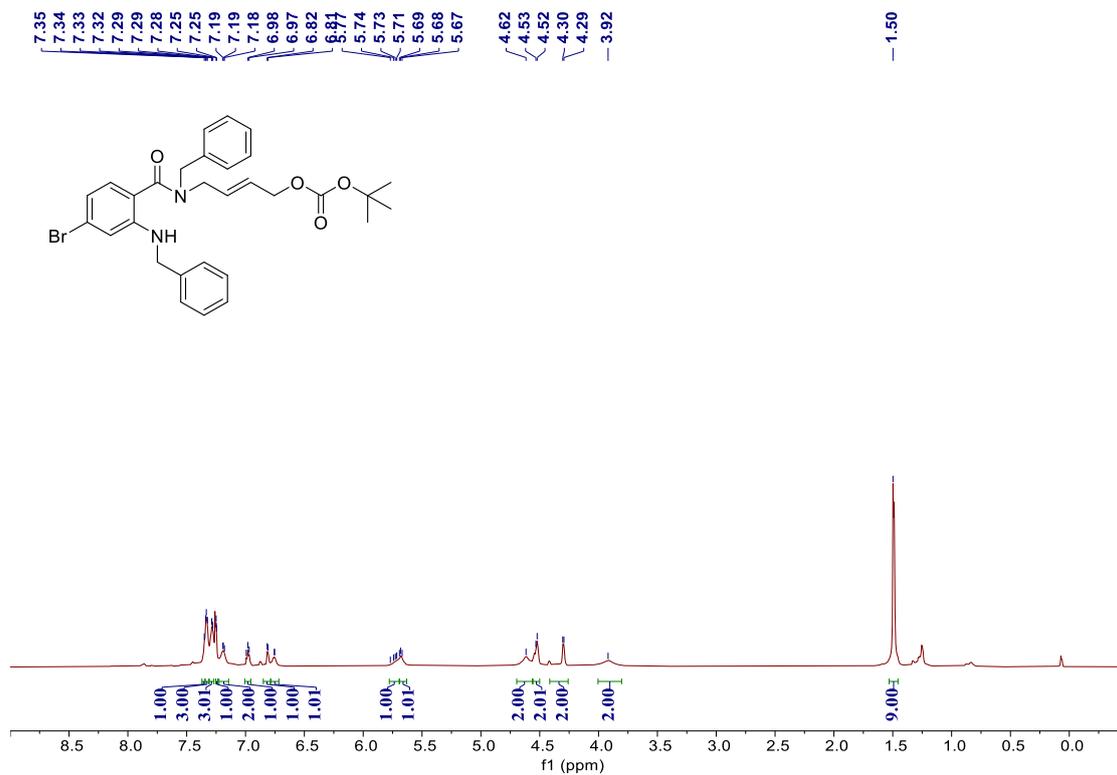


Figure S22. ¹³C NMR (151 MHz, CDCl₃) spectrum of 10a

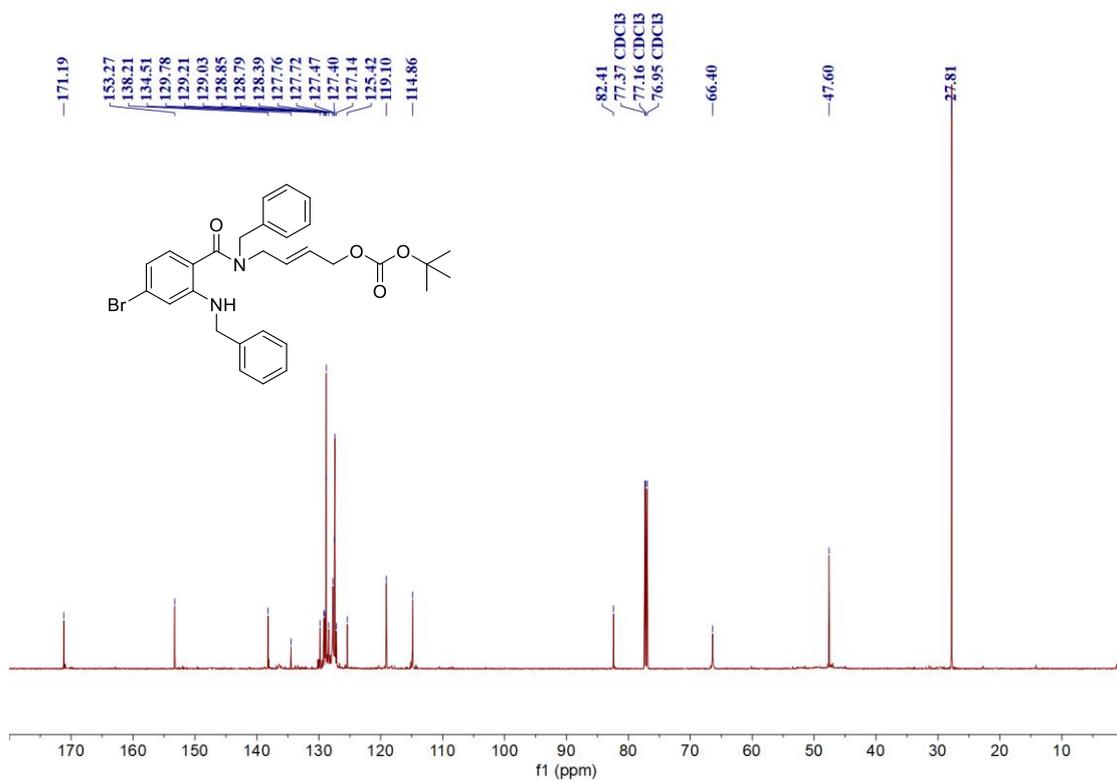


Figure S23. ¹H NMR (600 MHz, CDCl₃) spectrum of 11a

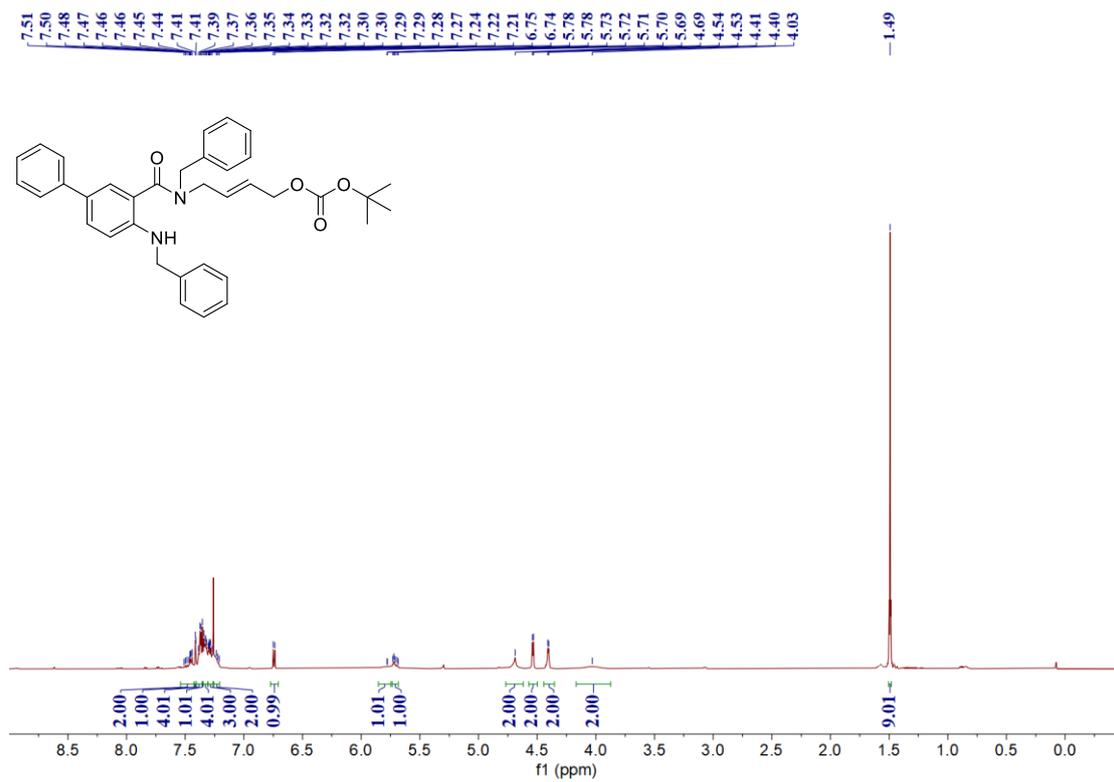


Figure S24. ¹³C NMR (151 MHz, CDCl₃) spectrum of 11a

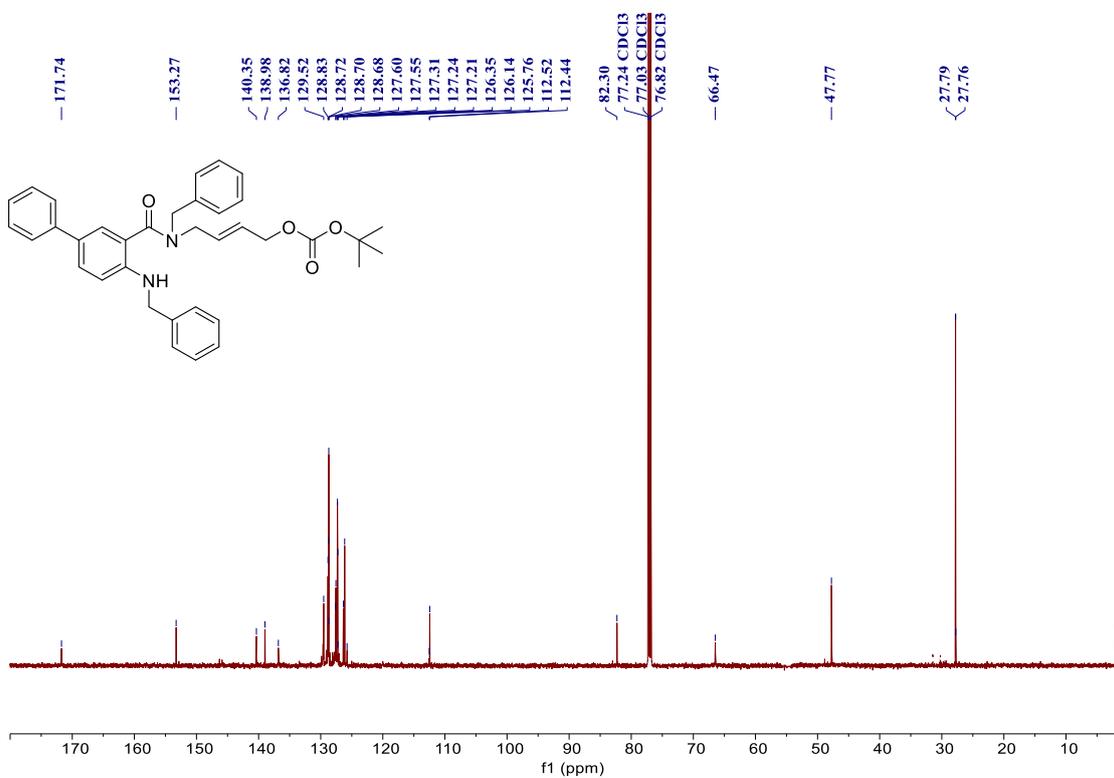


Figure S25. ¹H NMR (600 MHz, CDCl₃) spectrum of 12a

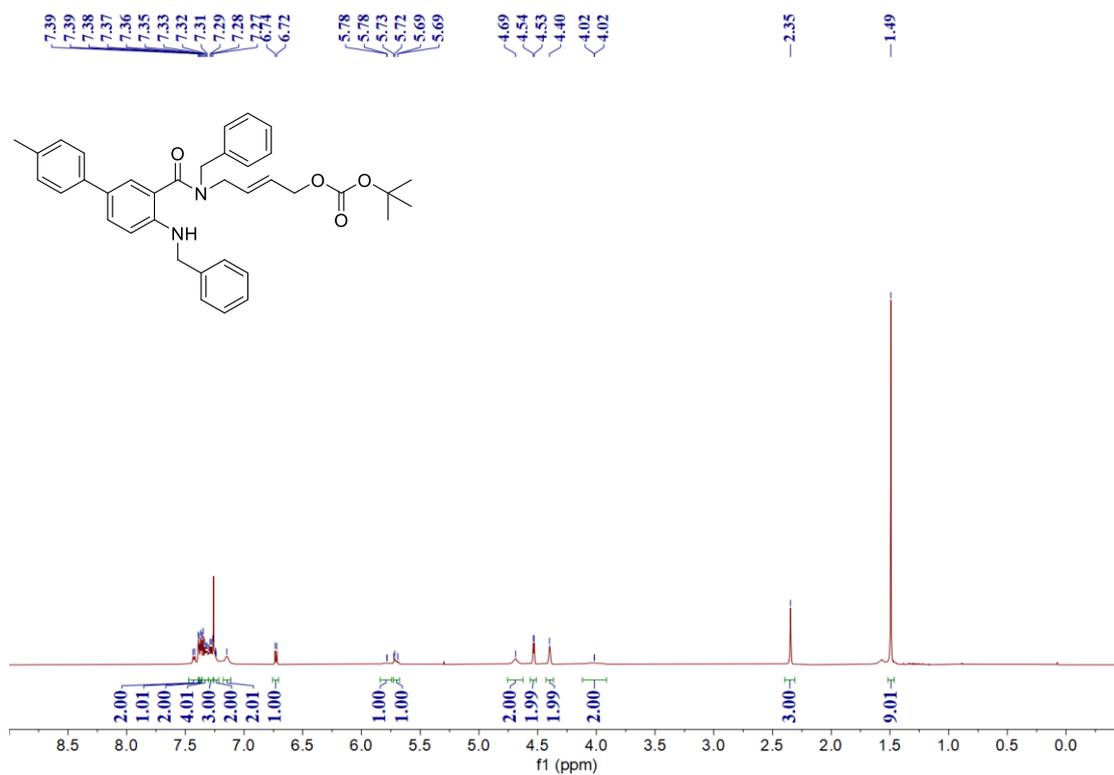


Figure S26. ¹³C NMR (151 MHz, CDCl₃) spectrum of 12a

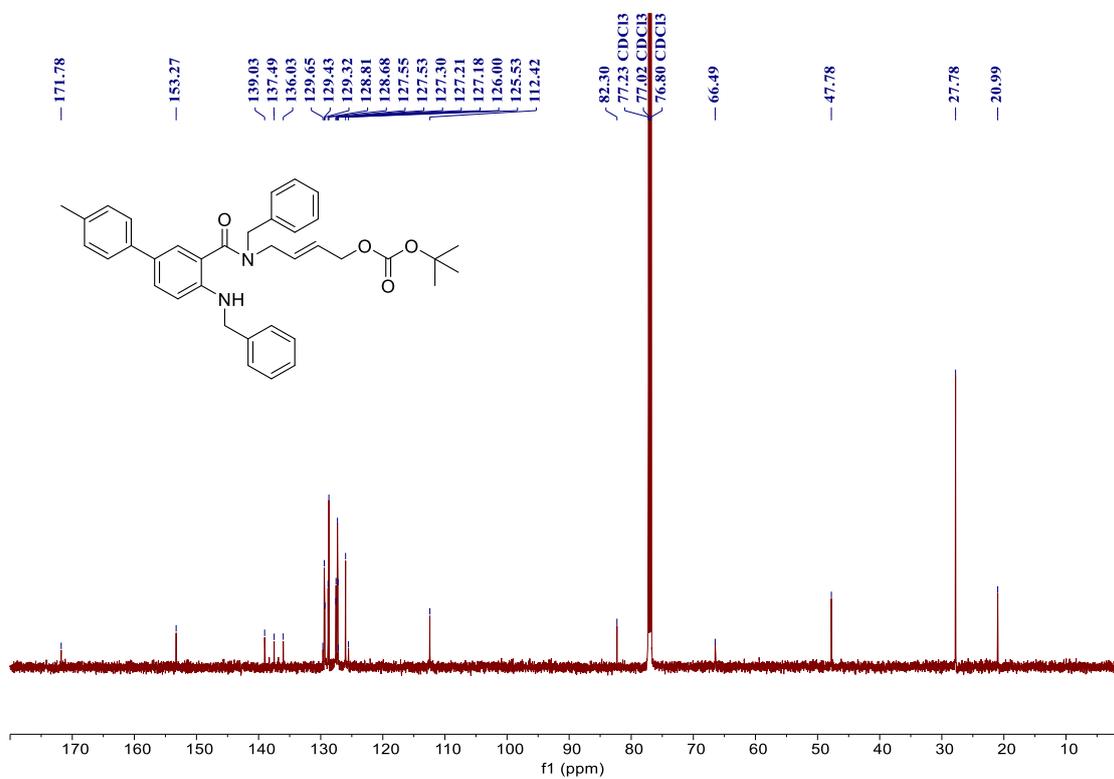


Figure S29. ¹H NMR (600 MHz, CDCl₃) spectrum of 14a

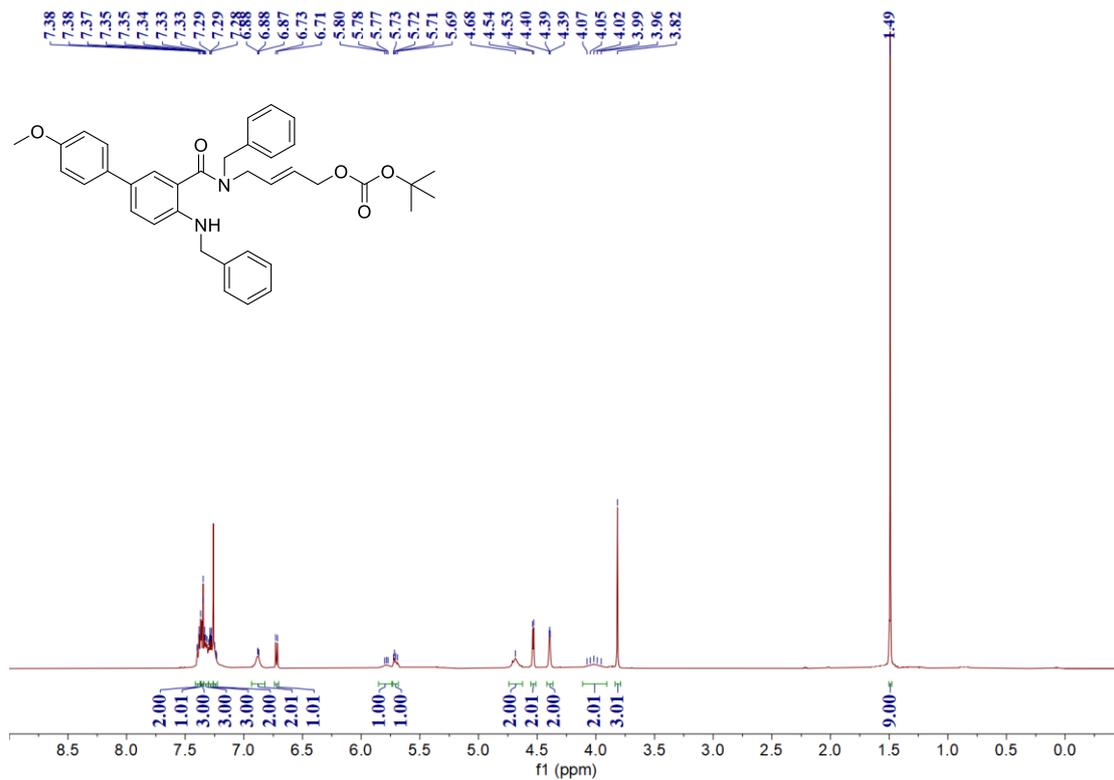


Figure S30. ¹³C NMR (151 MHz, CDCl₃) spectrum of 14a

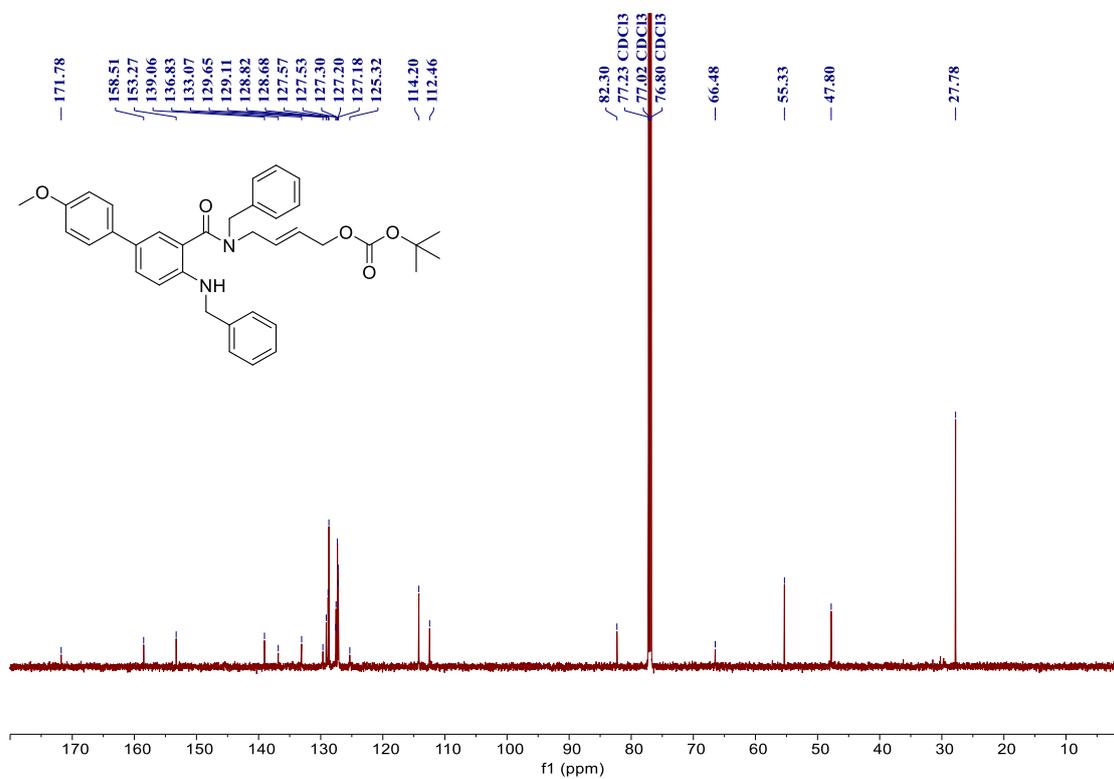


Figure S35. ¹H NMR (600 MHz, CDCl₃) spectrum of 17a

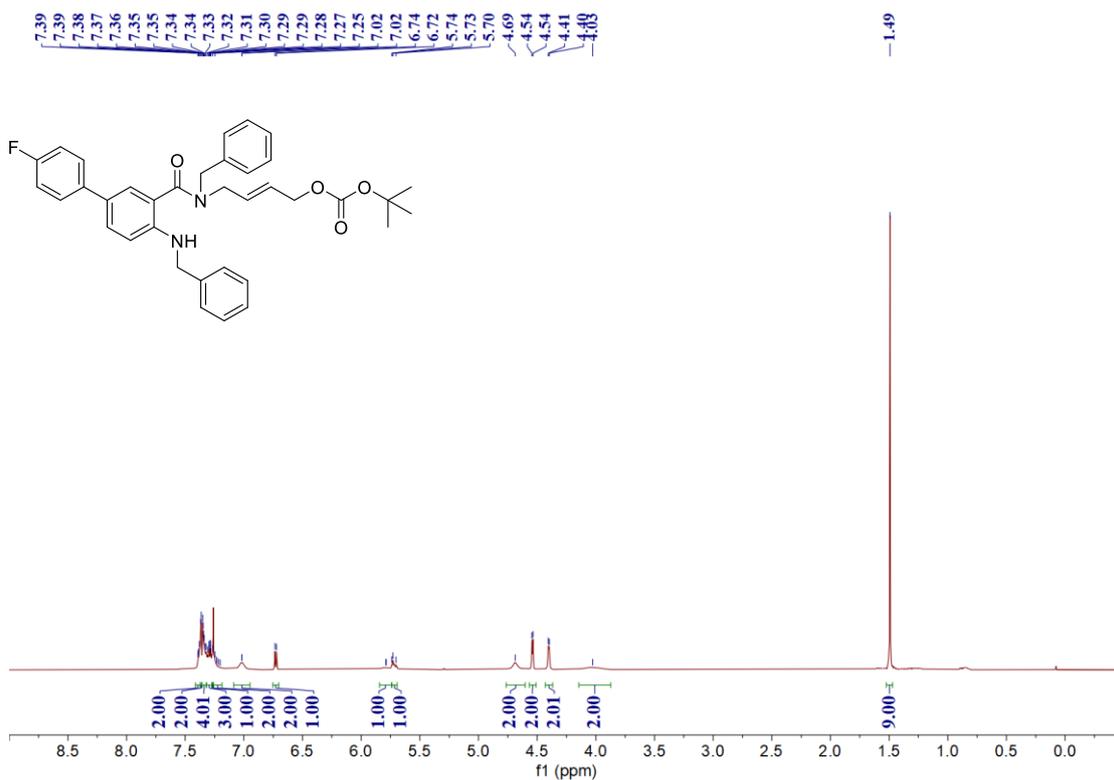


Figure S36. ¹³C NMR (151 MHz, CDCl₃) spectrum of 17a

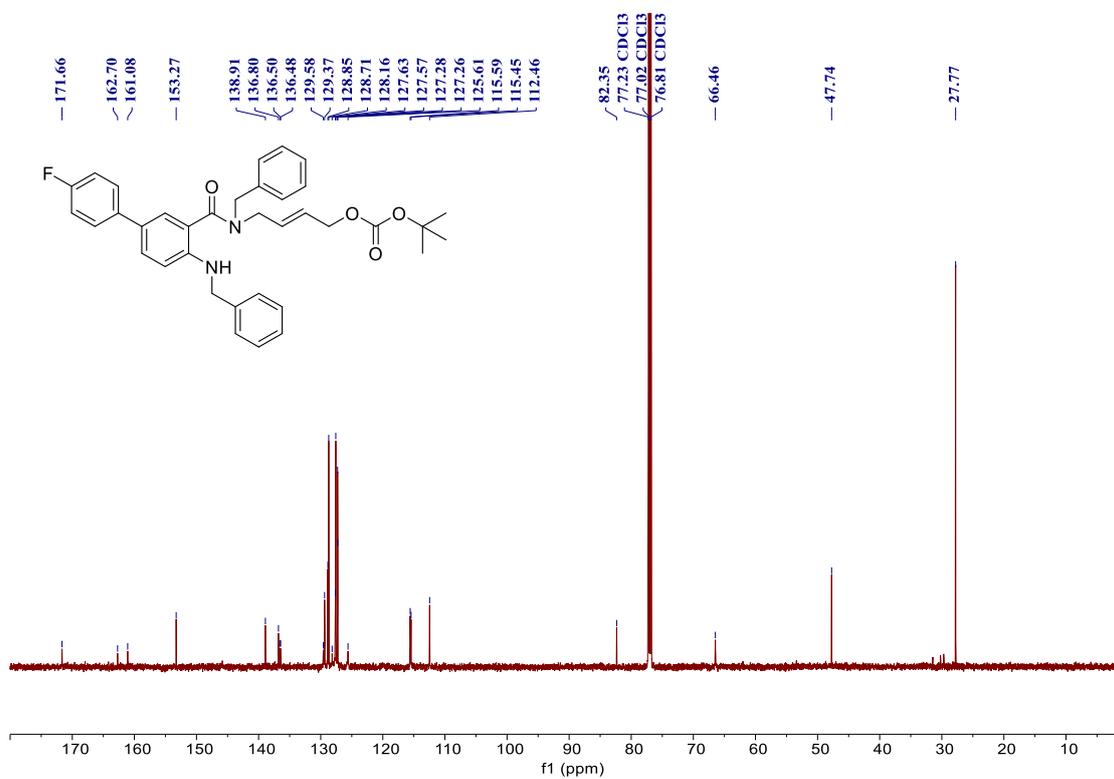


Figure S37. ^{19}F NMR (565 MHz, CDCl_3) spectrum of 17a

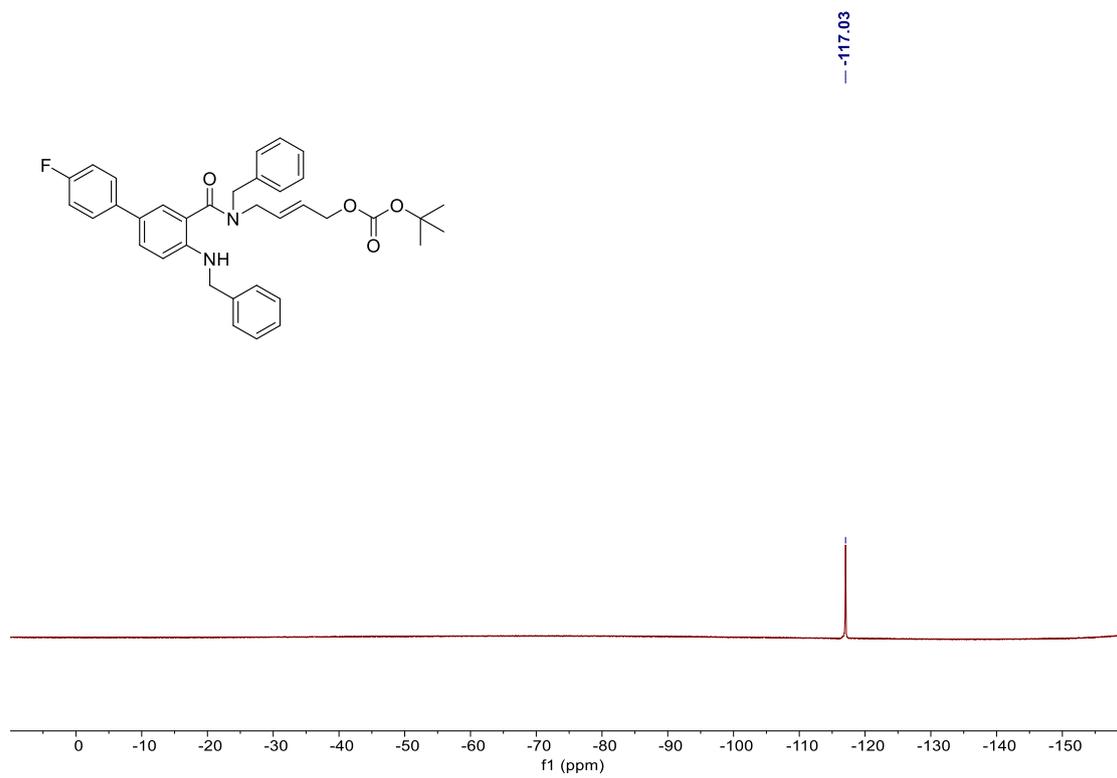


Figure S38. ¹H NMR (600 MHz, CDCl₃) spectrum of 18a

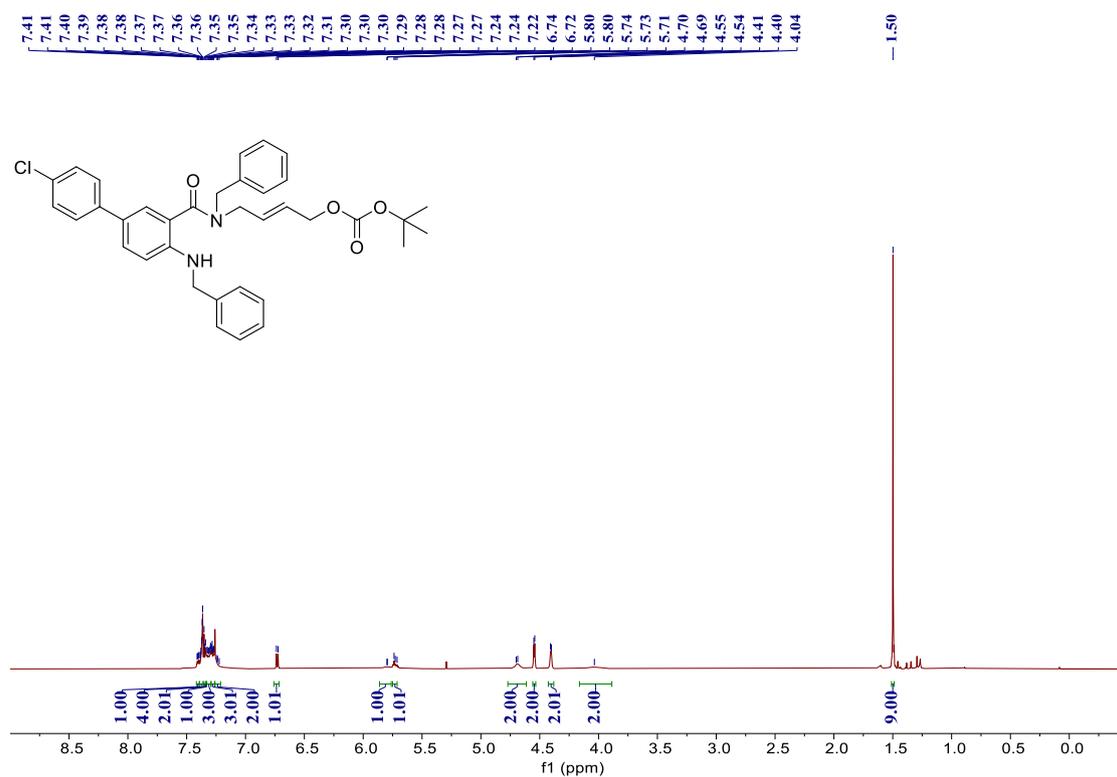


Figure S39. ¹³C NMR (151 MHz, CDCl₃) spectrum of 18a

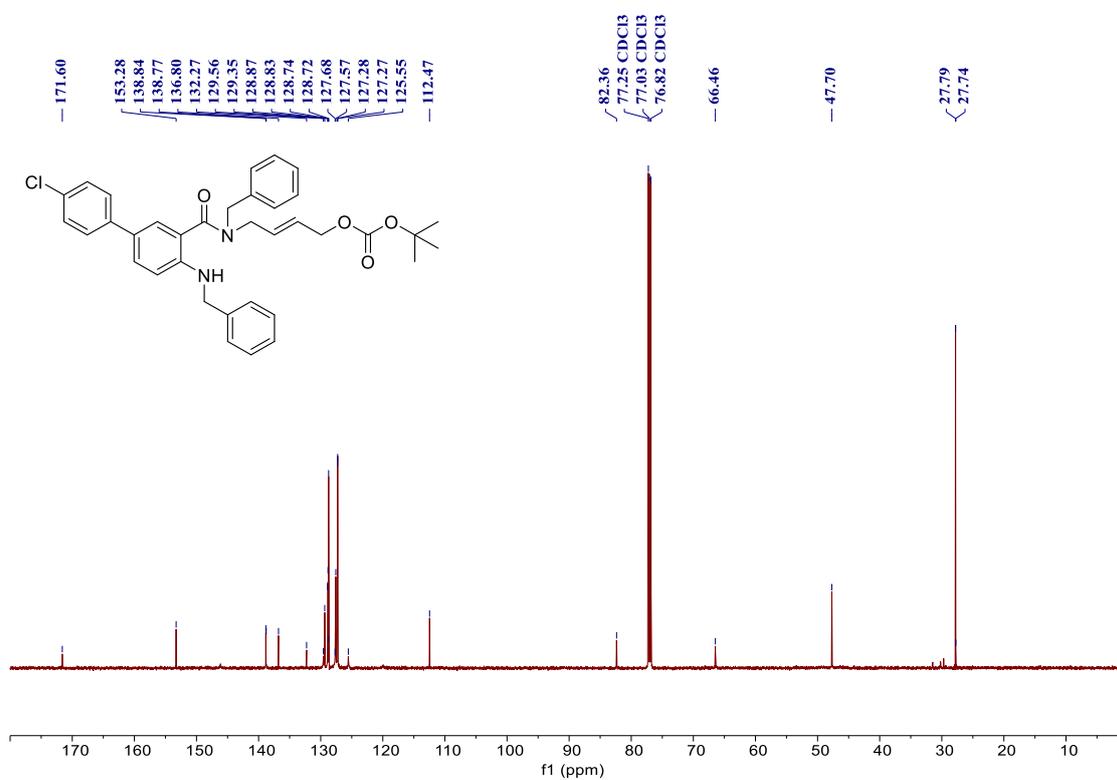


Figure S40. ¹H NMR (600 MHz, CDCl₃) spectrum of 19a

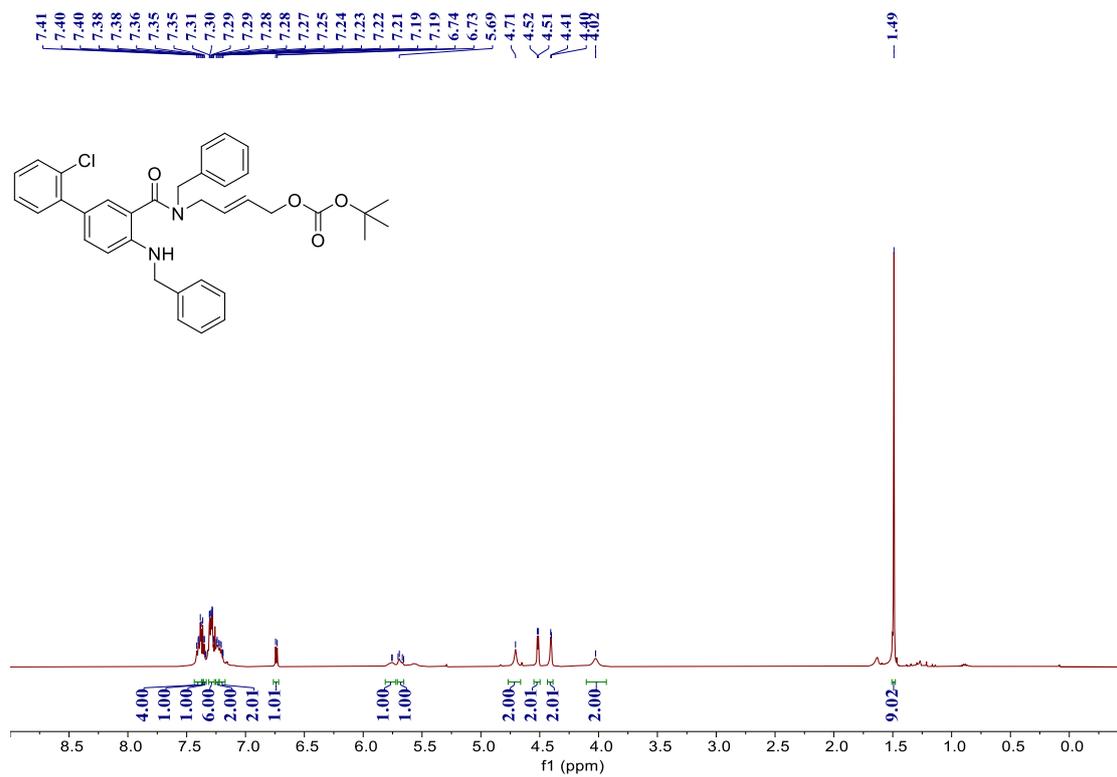


Figure S41. ¹³C NMR (151 MHz, CDCl₃) spectrum of 19a

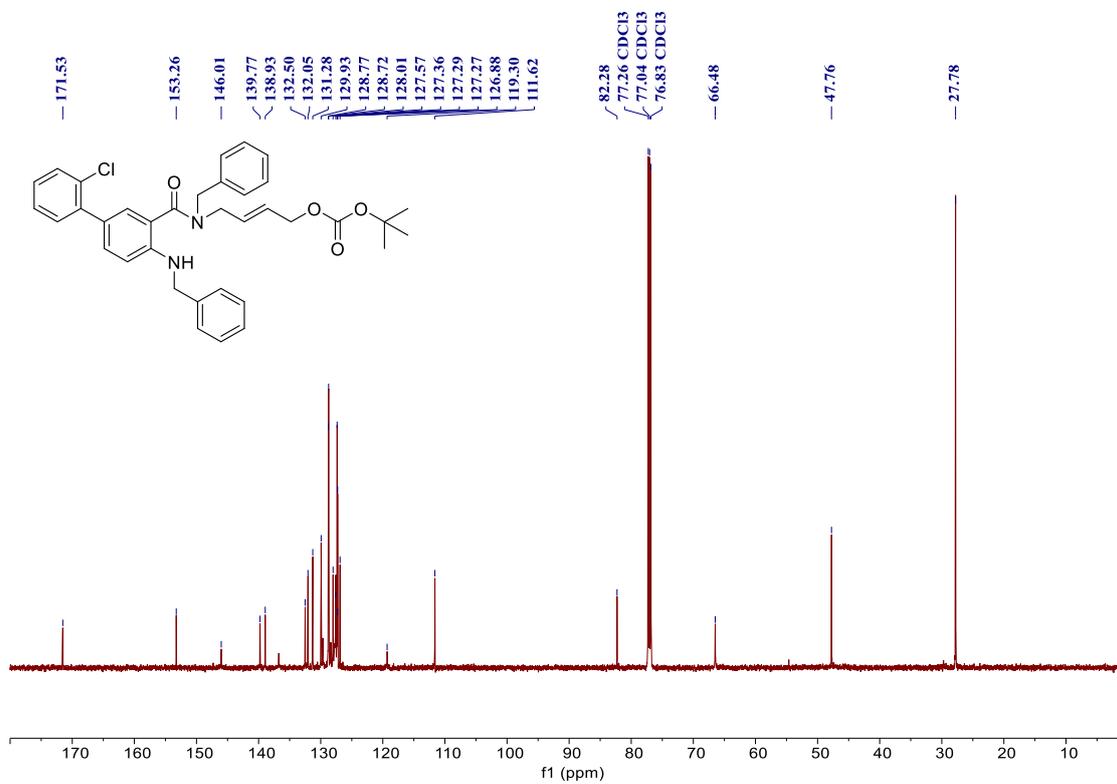


Figure S42. ¹H NMR (600 MHz, CDCl₃) spectrum of 20a

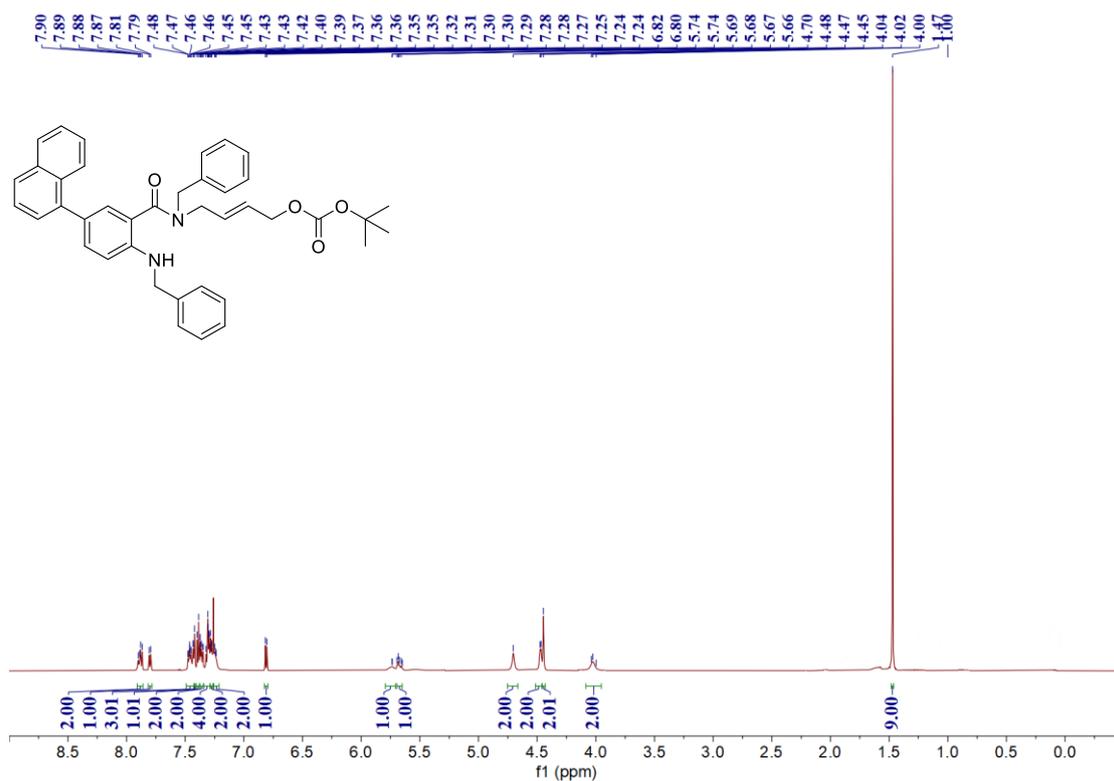


Figure S43. ¹³C NMR (151 MHz, CDCl₃) spectrum of 20a

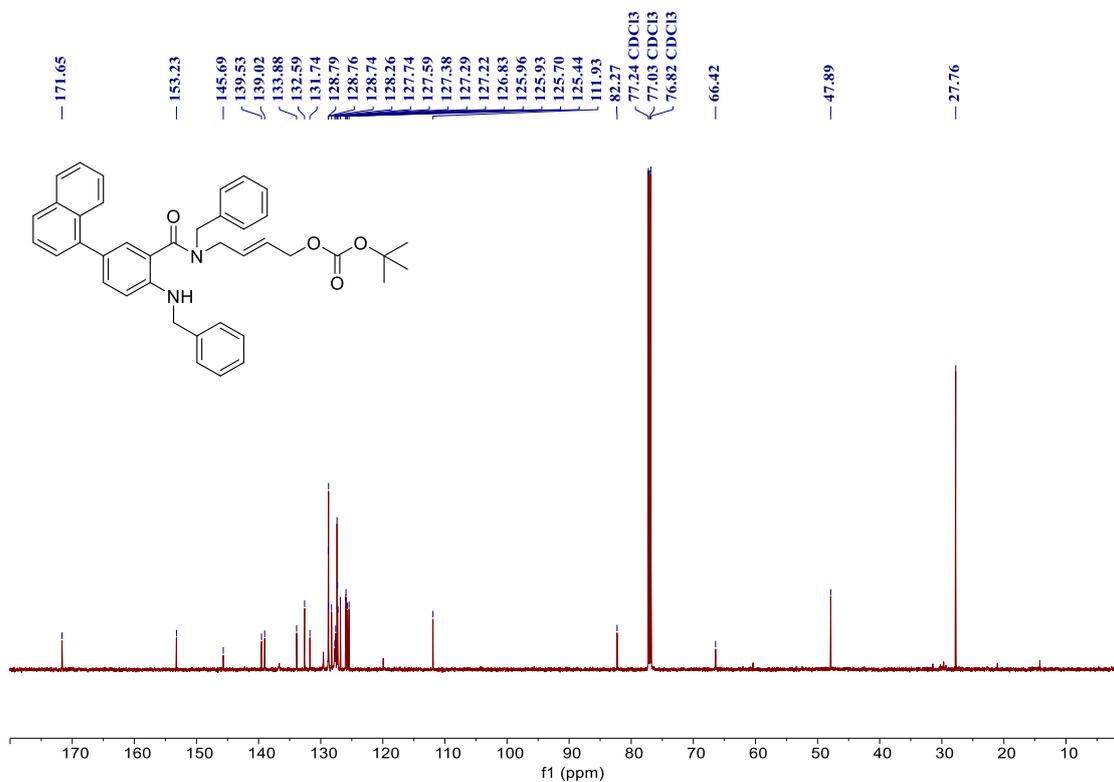


Figure S44. ¹H NMR (600 MHz, CDCl₃) spectrum of 21a

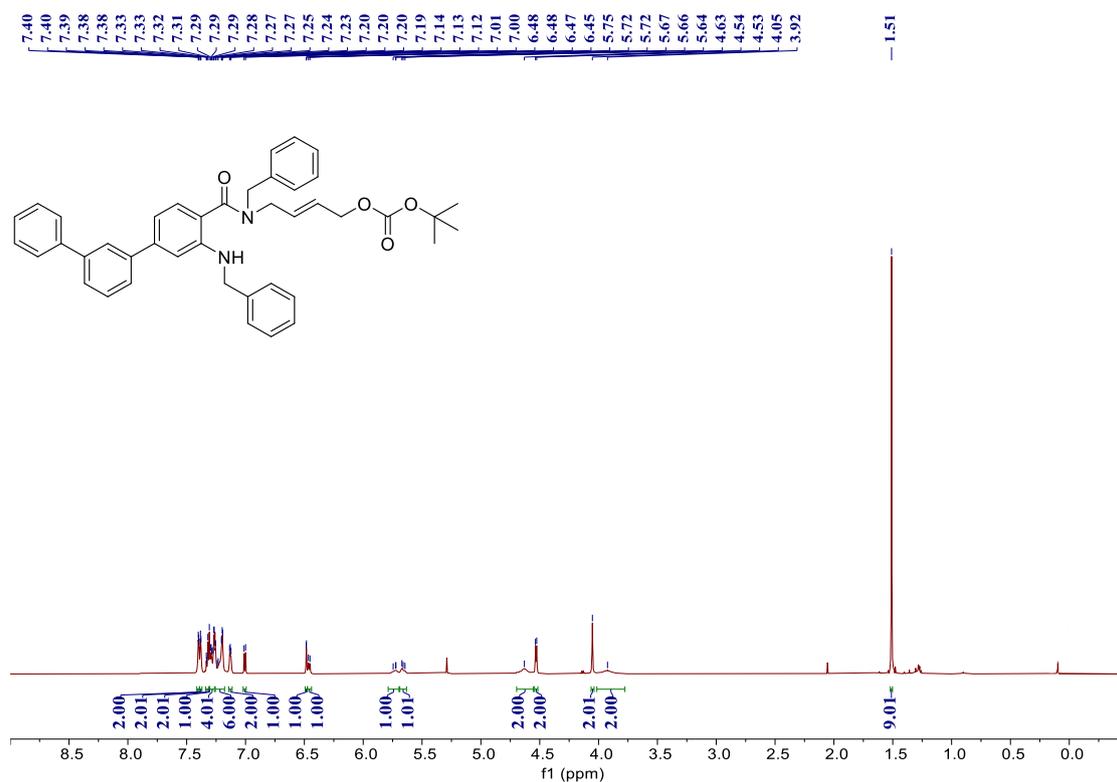


Figure S45. ¹³C NMR (151 MHz, CDCl₃) spectrum of 21a

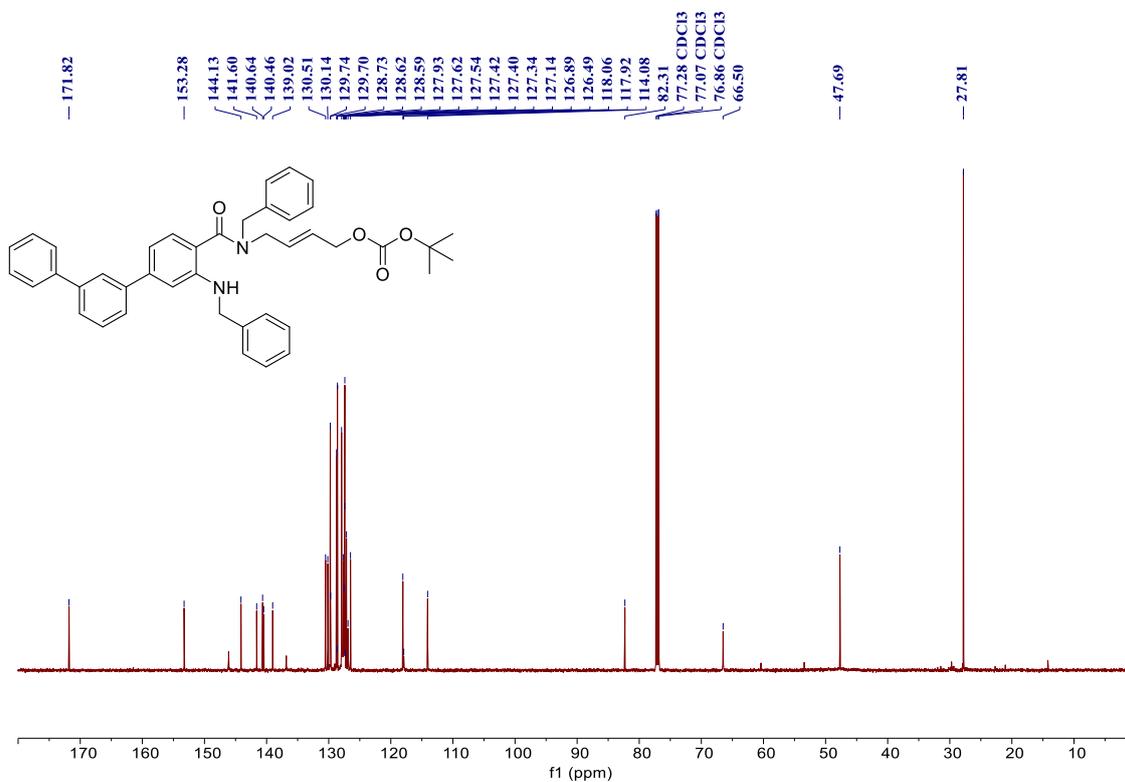


Figure S46. ¹H NMR (600 MHz, CDCl₃) spectrum of 22a

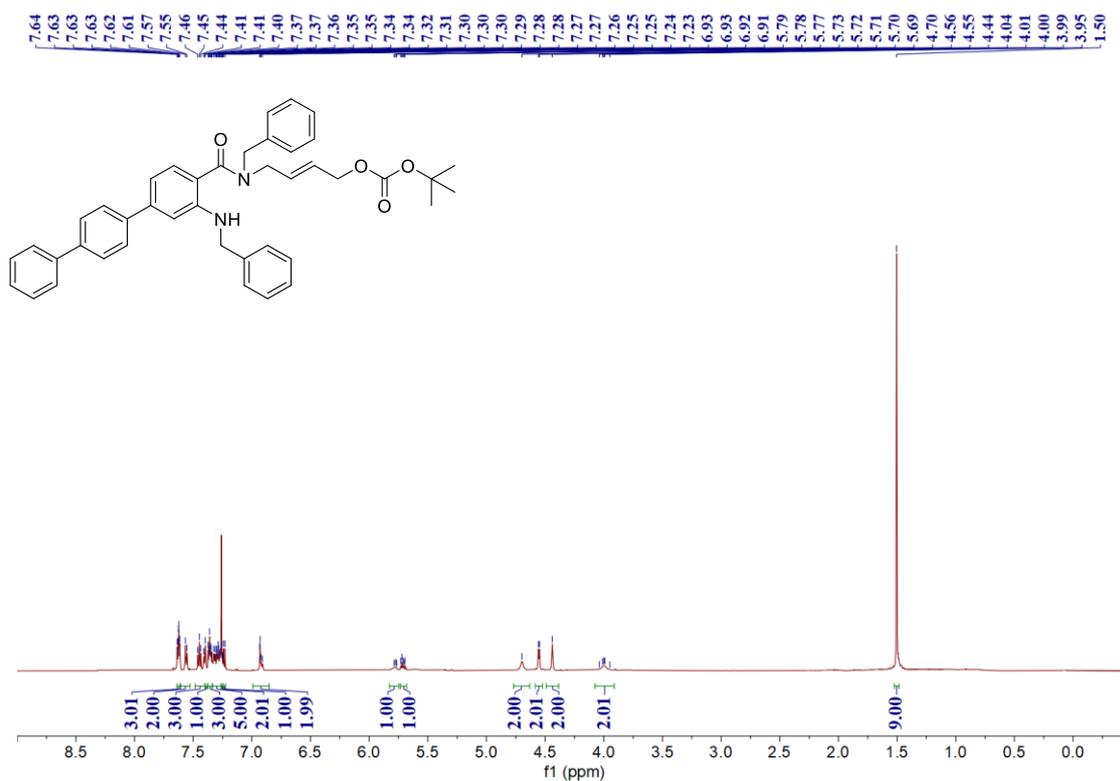


Figure S47. ¹³C NMR (151 MHz, CDCl₃) spectrum of 22a

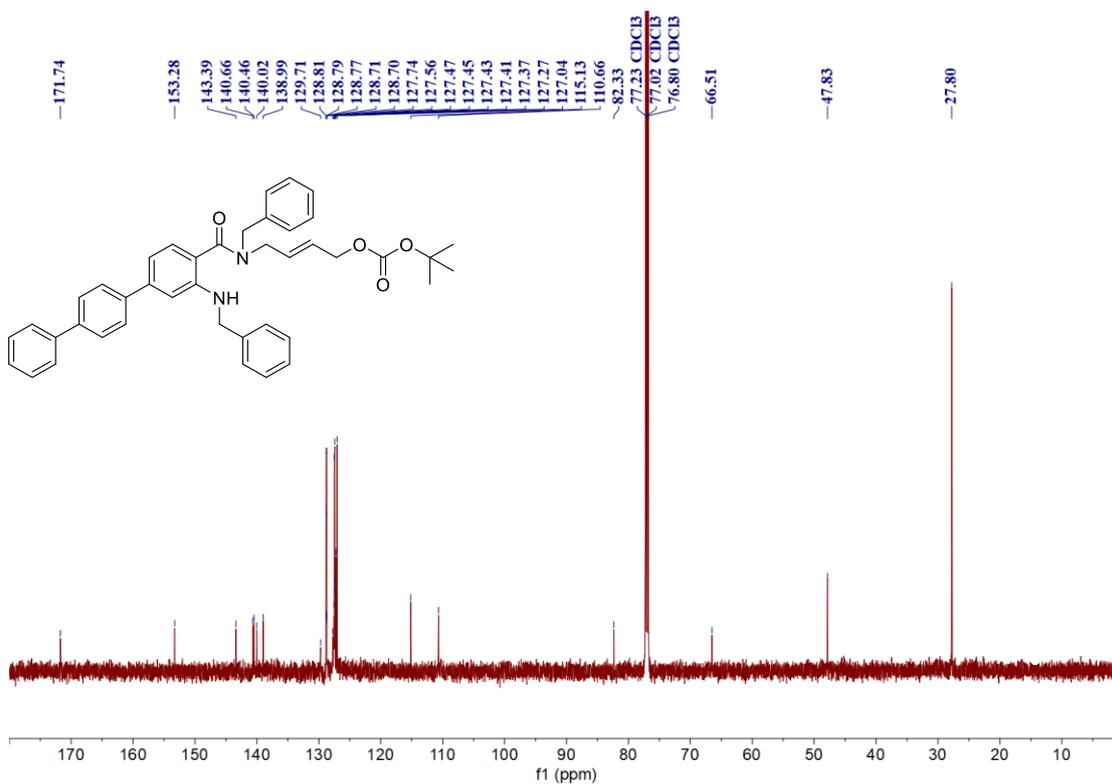


Figure S48. ¹H NMR (600 MHz, CDCl₃) spectrum of 23a

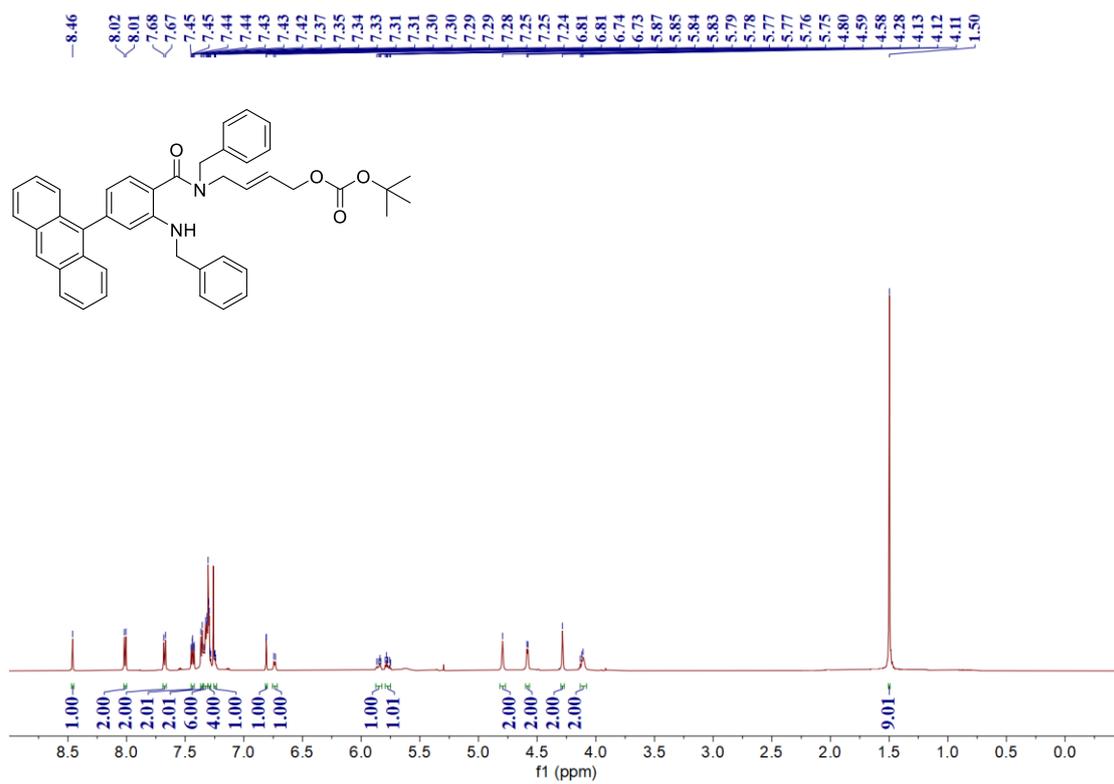


Figure S49. ¹³C NMR (151 MHz, CDCl₃) spectrum of 23a

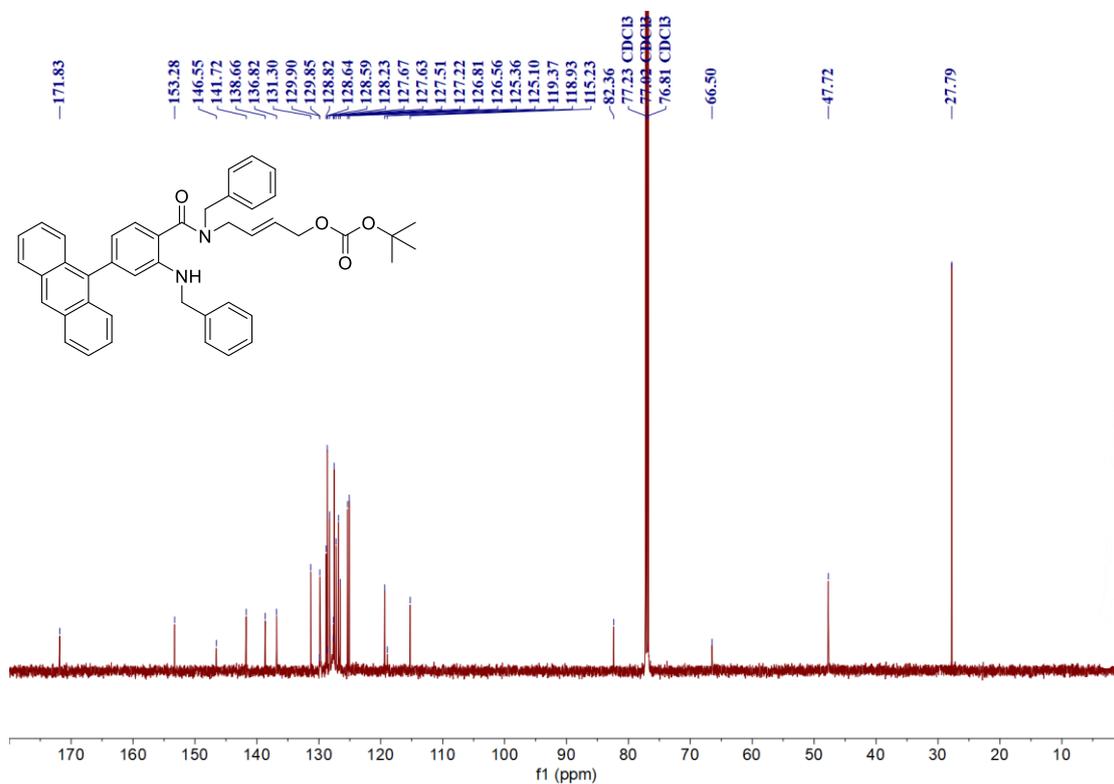


Figure S50. ¹H NMR (600 MHz, CDCl₃) spectrum of 24a

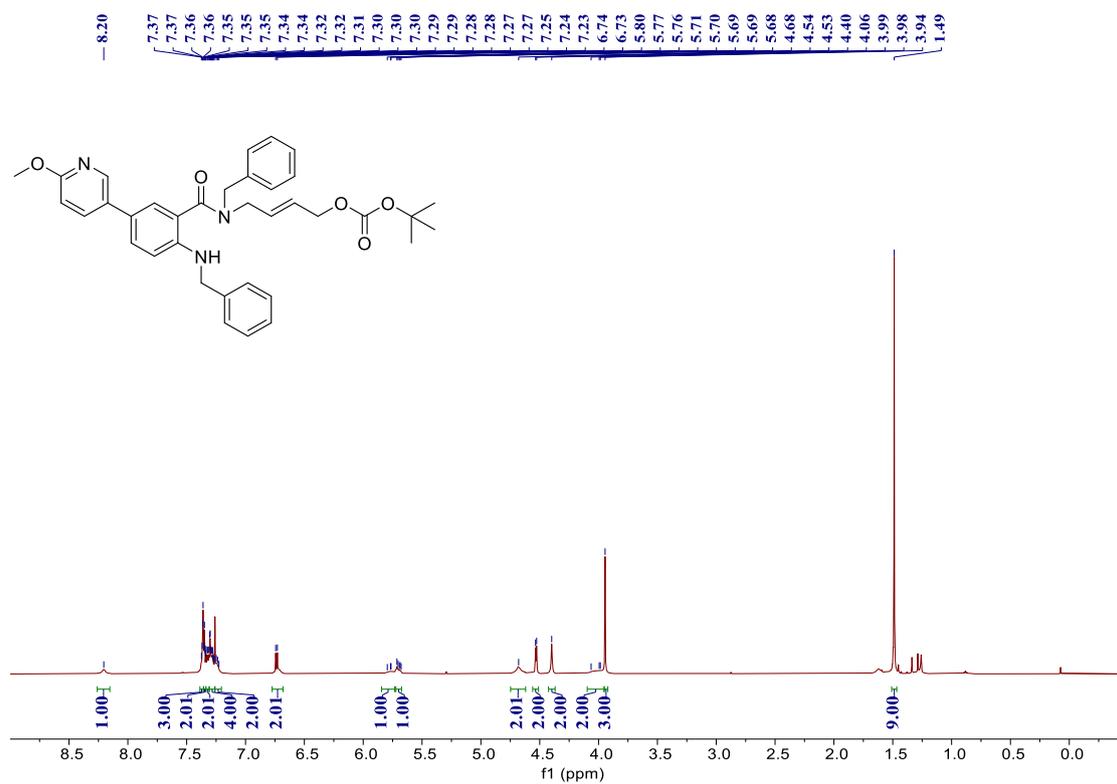


Figure S51. ¹³C NMR (151 MHz, CDCl₃) spectrum of 24a

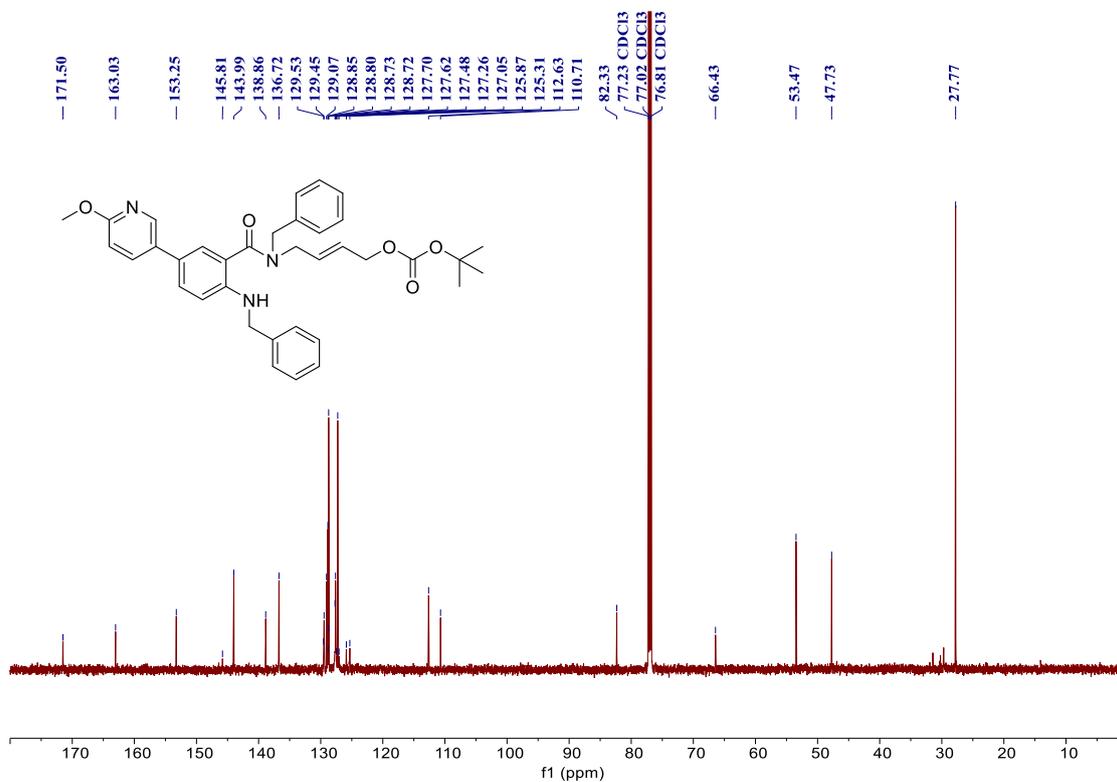


Figure S52. ¹H NMR (600 MHz, CDCl₃) spectrum of 25a

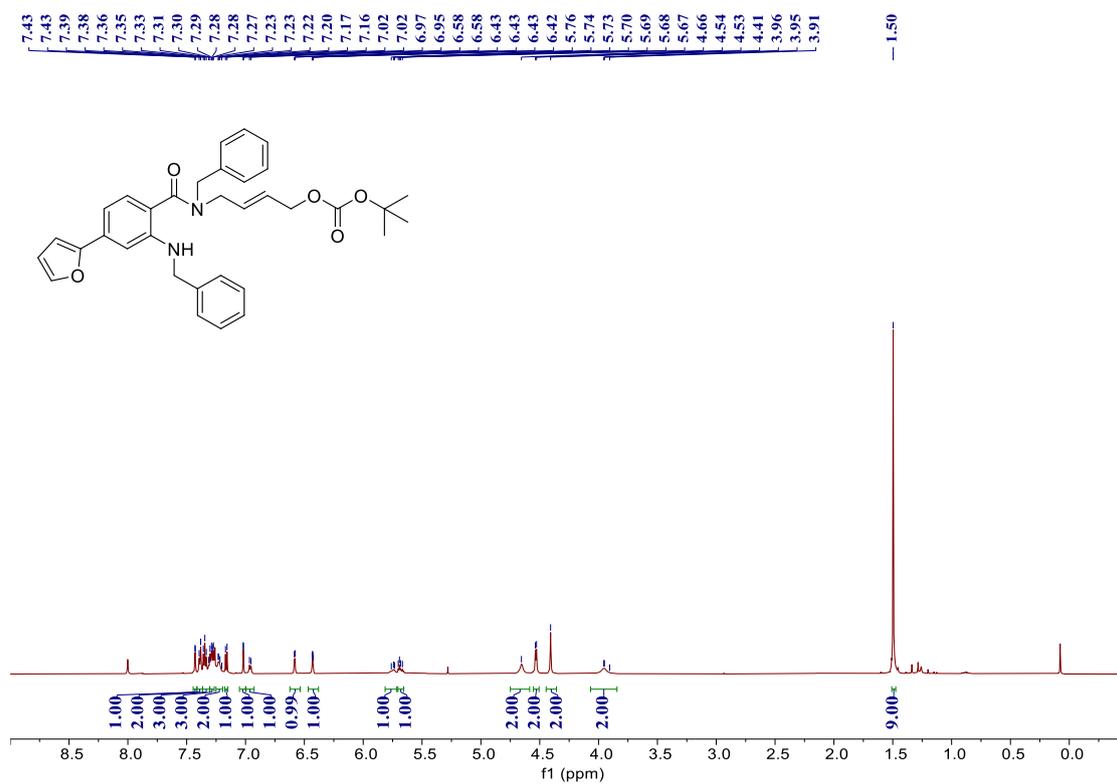


Figure S53. ¹³C NMR (151 MHz, CDCl₃) spectrum of 25a

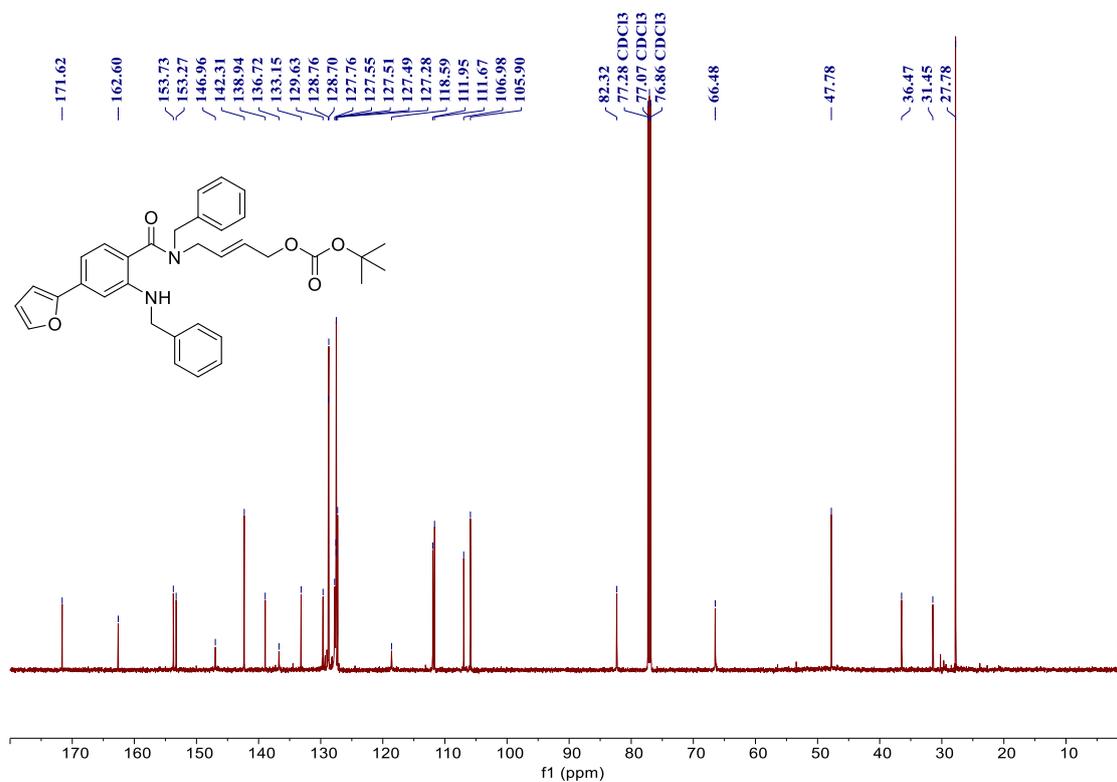


Figure S54. ¹H NMR (600 MHz, CDCl₃) spectrum of 26a

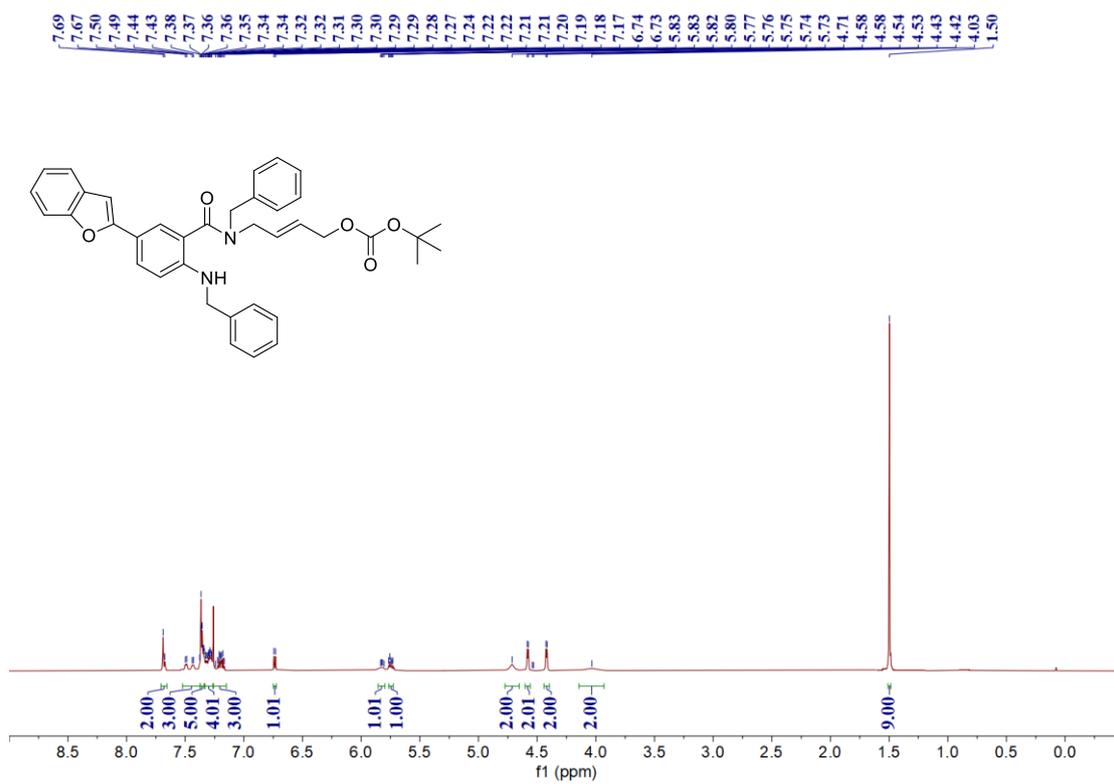


Figure S55. ¹³C NMR (151 MHz, CDCl₃) spectrum of 26a

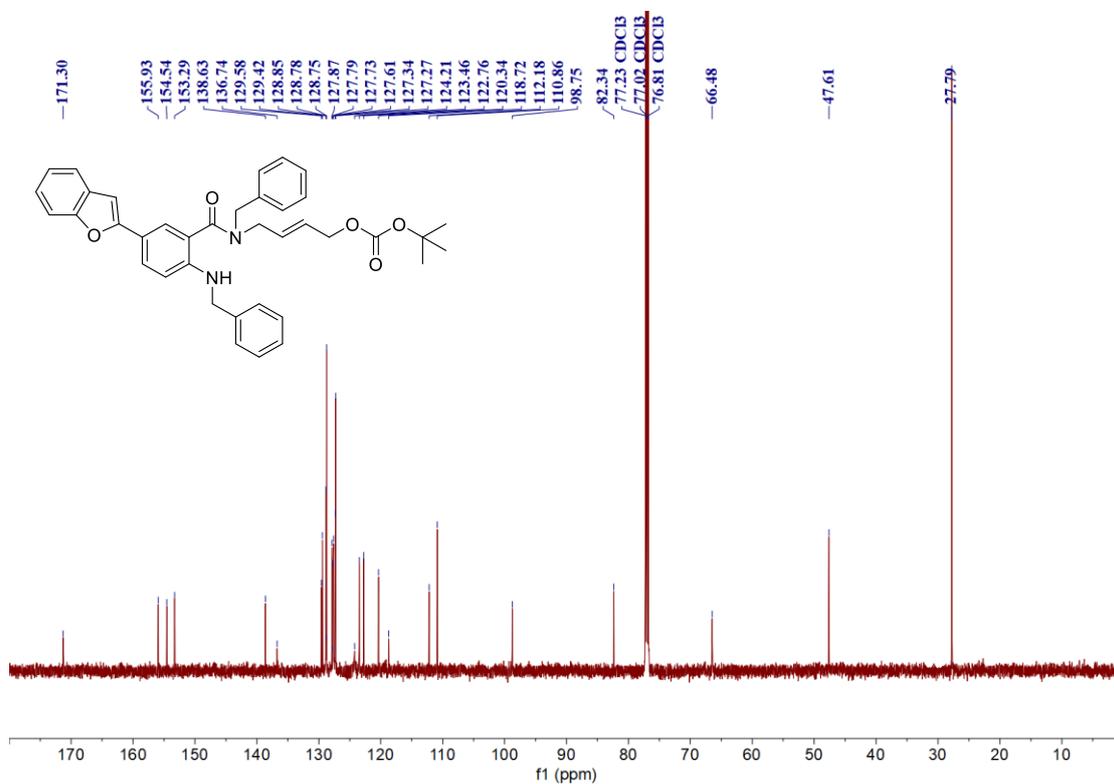


Figure S56. ¹H NMR (600 MHz, CDCl₃) spectrum of 27a

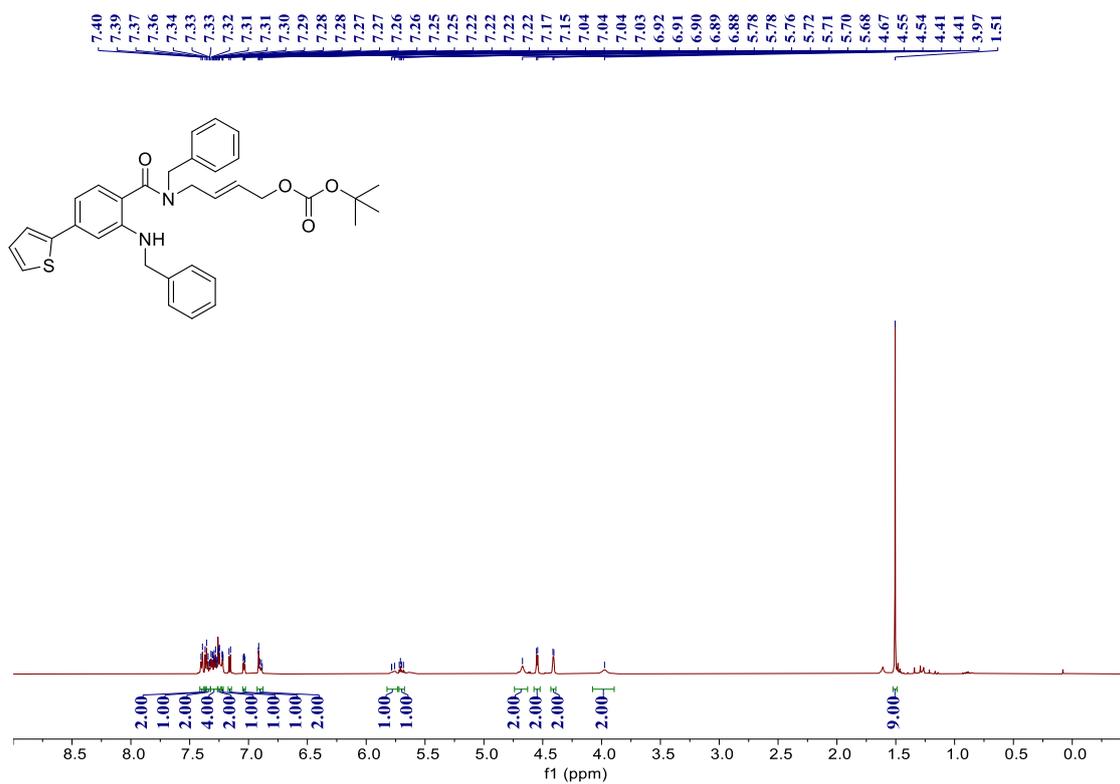


Figure S57. ¹³C NMR (151 MHz, CDCl₃) spectrum of 27a

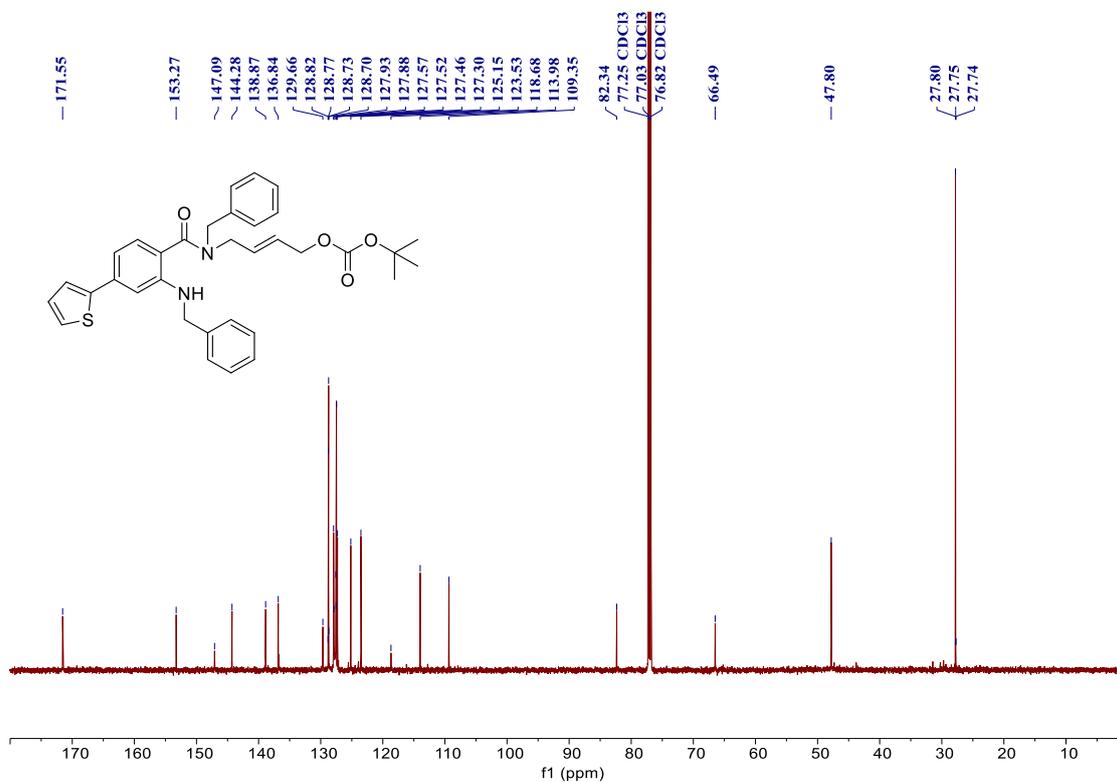


Figure S58. ¹H NMR (600 MHz, CDCl₃) spectrum of 28a

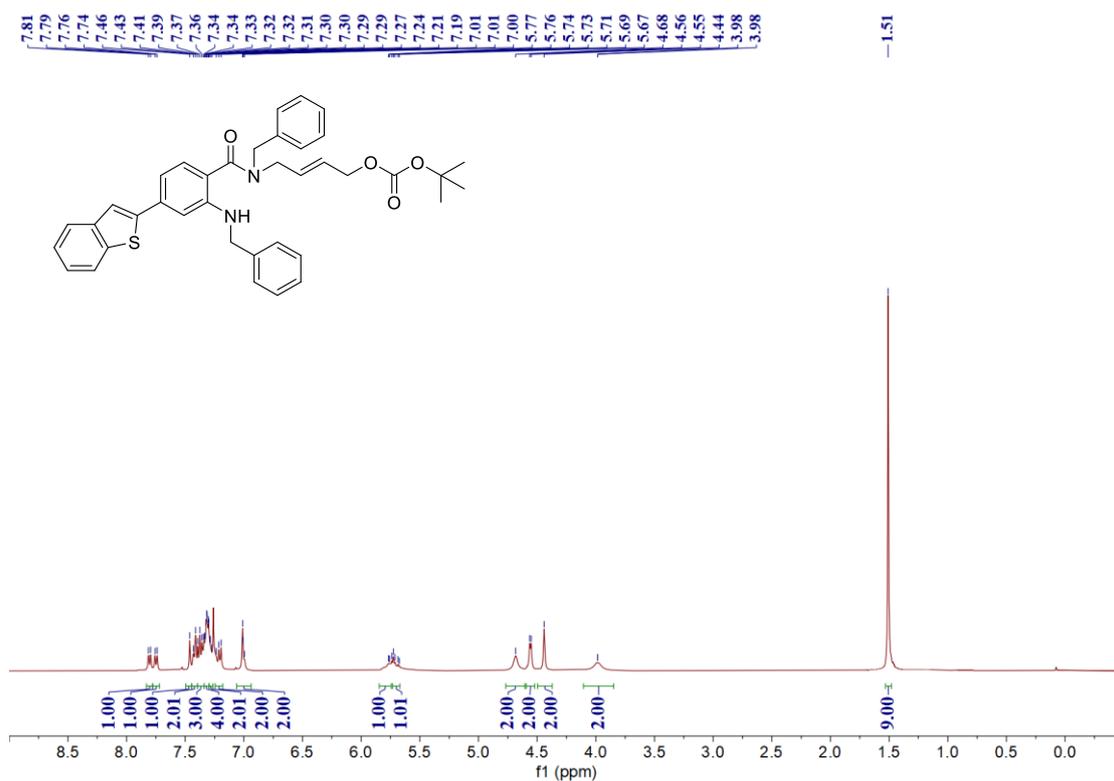


Figure S59. ¹³C NMR (151 MHz, CDCl₃) spectrum of 28a

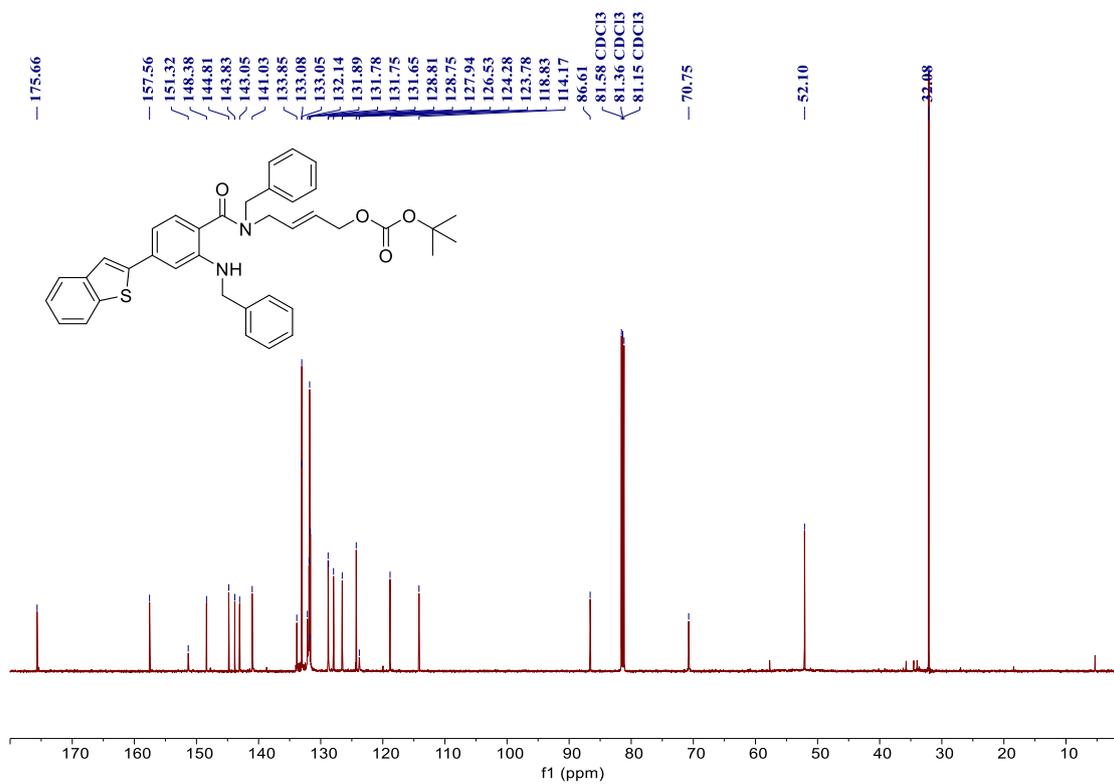


Figure S60. ¹H NMR (600 MHz, CDCl₃) spectrum of 29a

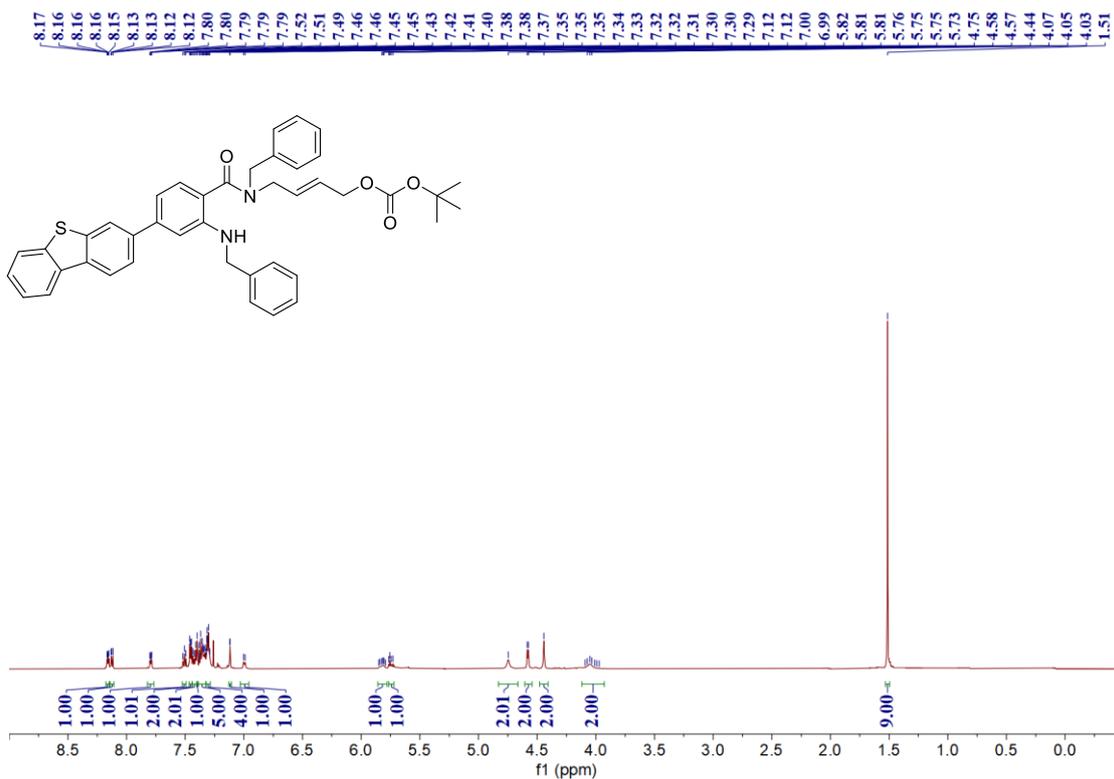


Figure S61. ¹³C NMR (151 MHz, CDCl₃) spectrum of 29a

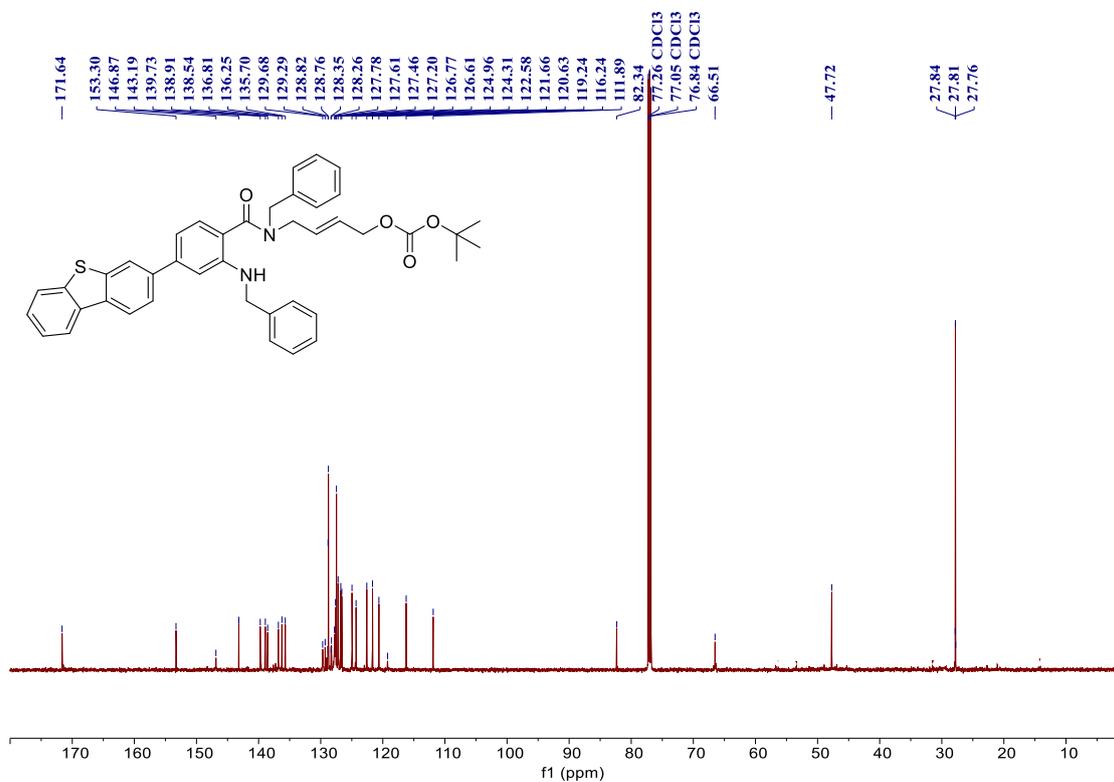


Figure S62. ¹H NMR (600 MHz, CDCl₃) spectrum of 30a

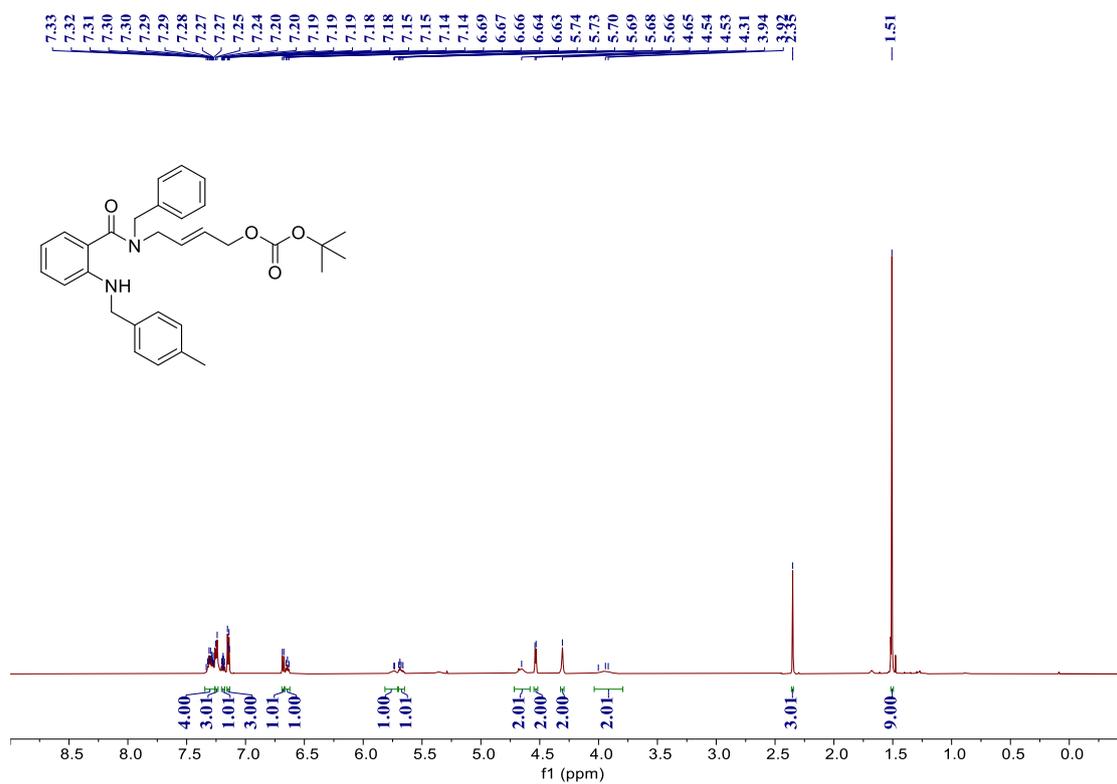


Figure S63. ¹³C NMR (151 MHz, CDCl₃) spectrum of 30a

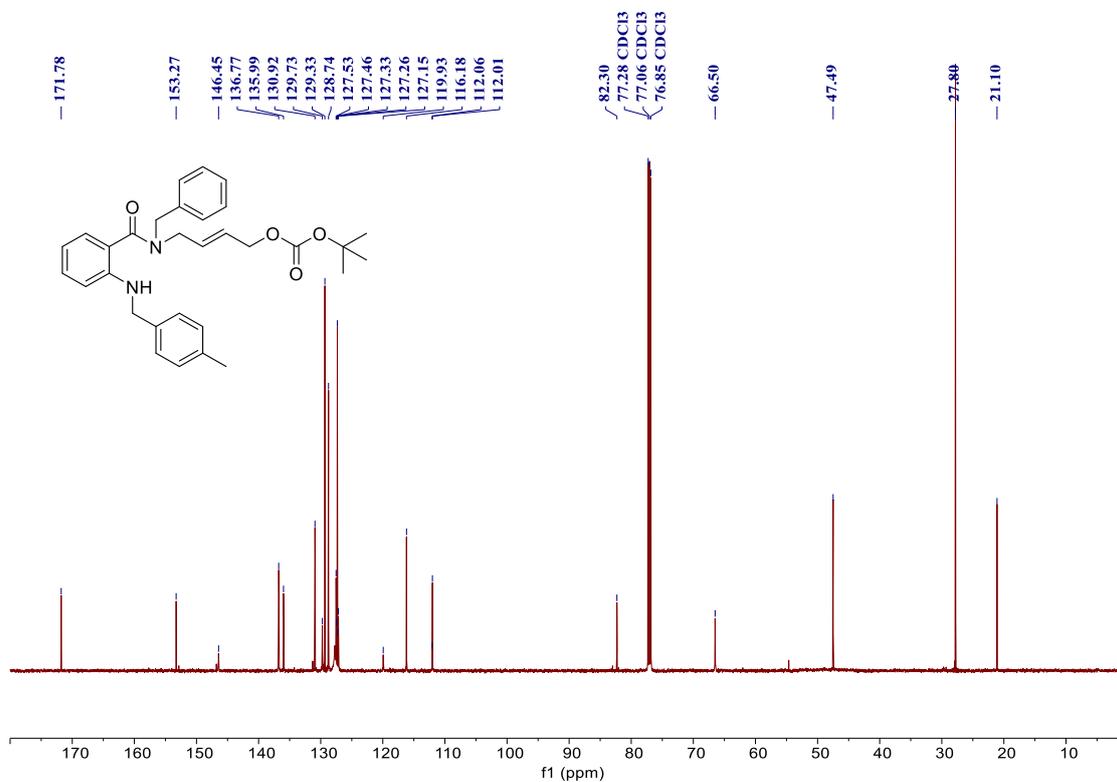


Figure S64. ¹H NMR (600 MHz, CDCl₃) spectrum of 31a

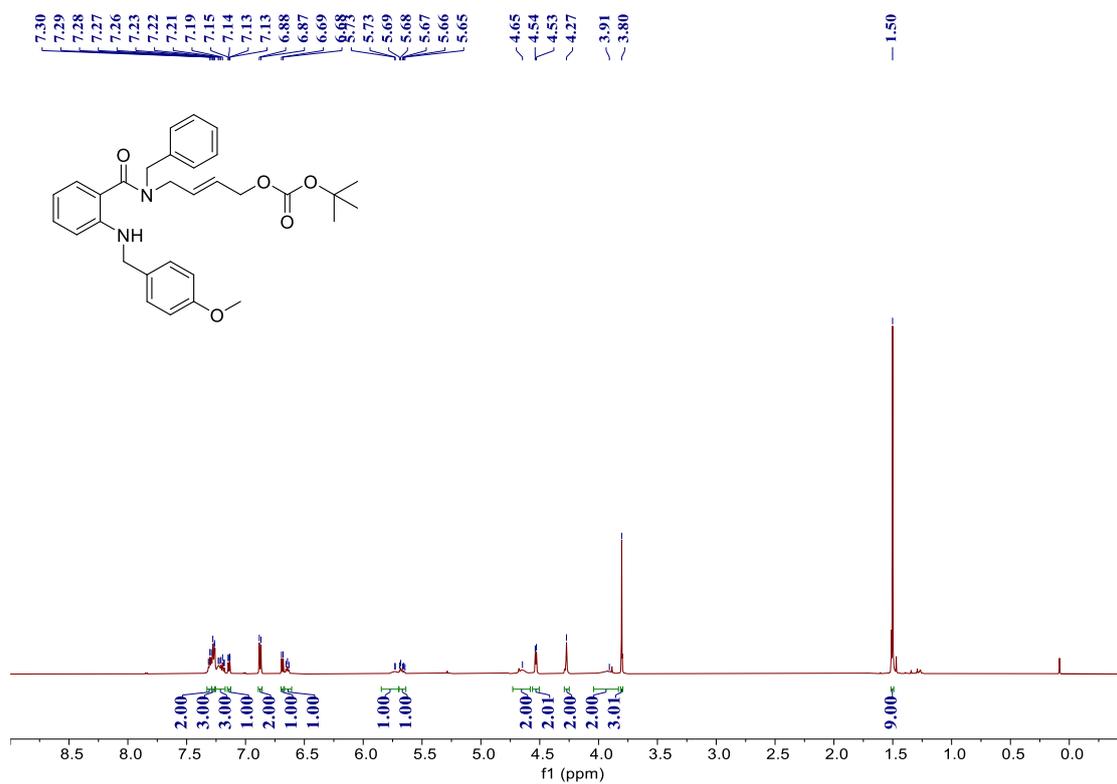


Figure S65. ¹³C NMR (151 MHz, CDCl₃) spectrum of 31a

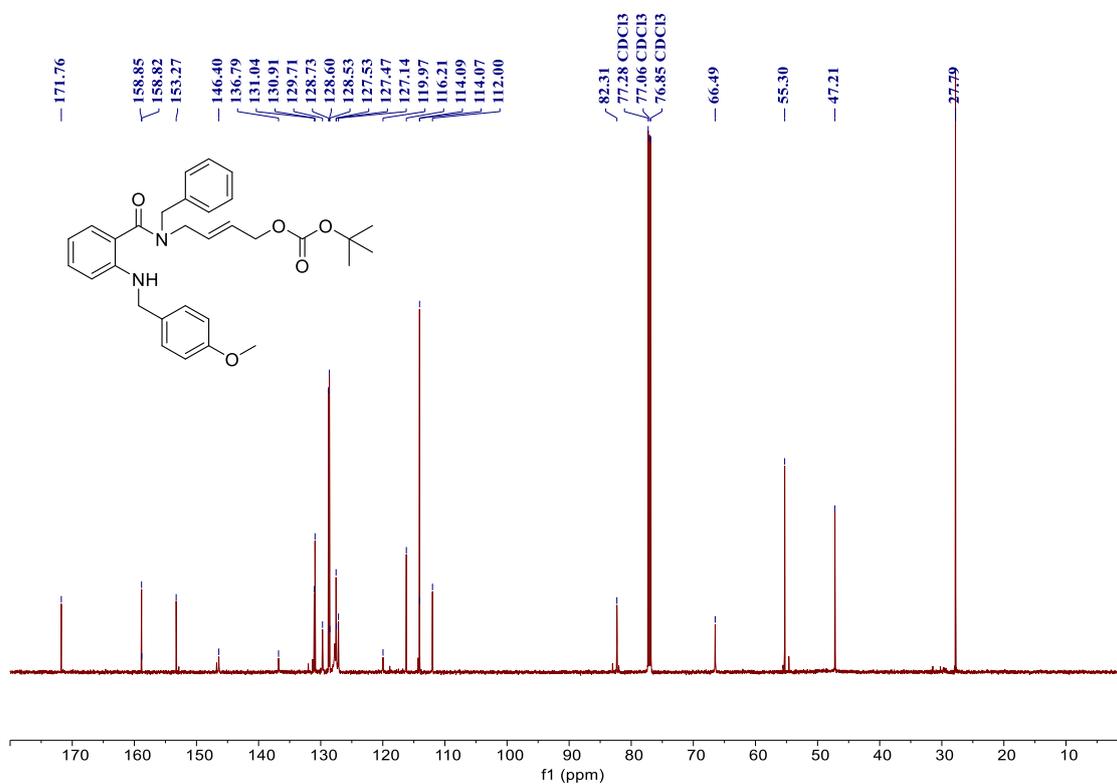


Figure S66. ¹H NMR (600 MHz, CDCl₃) spectrum of 32a

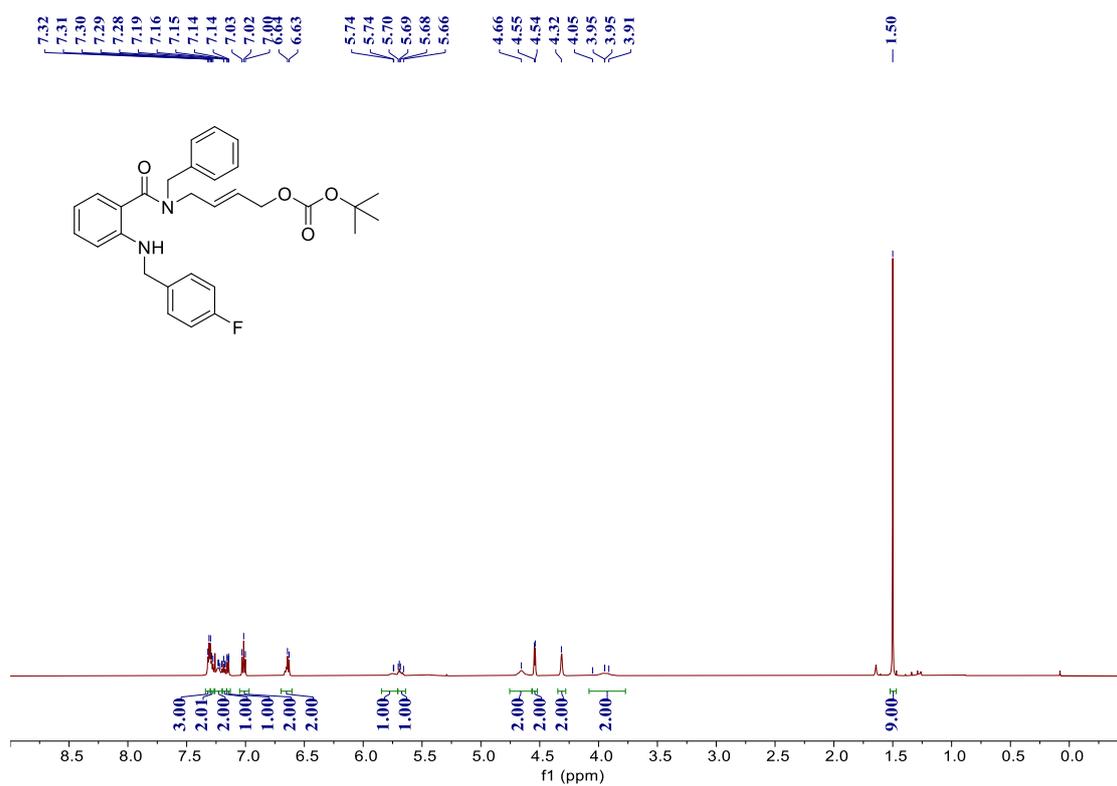


Figure S67. ¹³C NMR (151 MHz, CDCl₃) spectrum of 32a

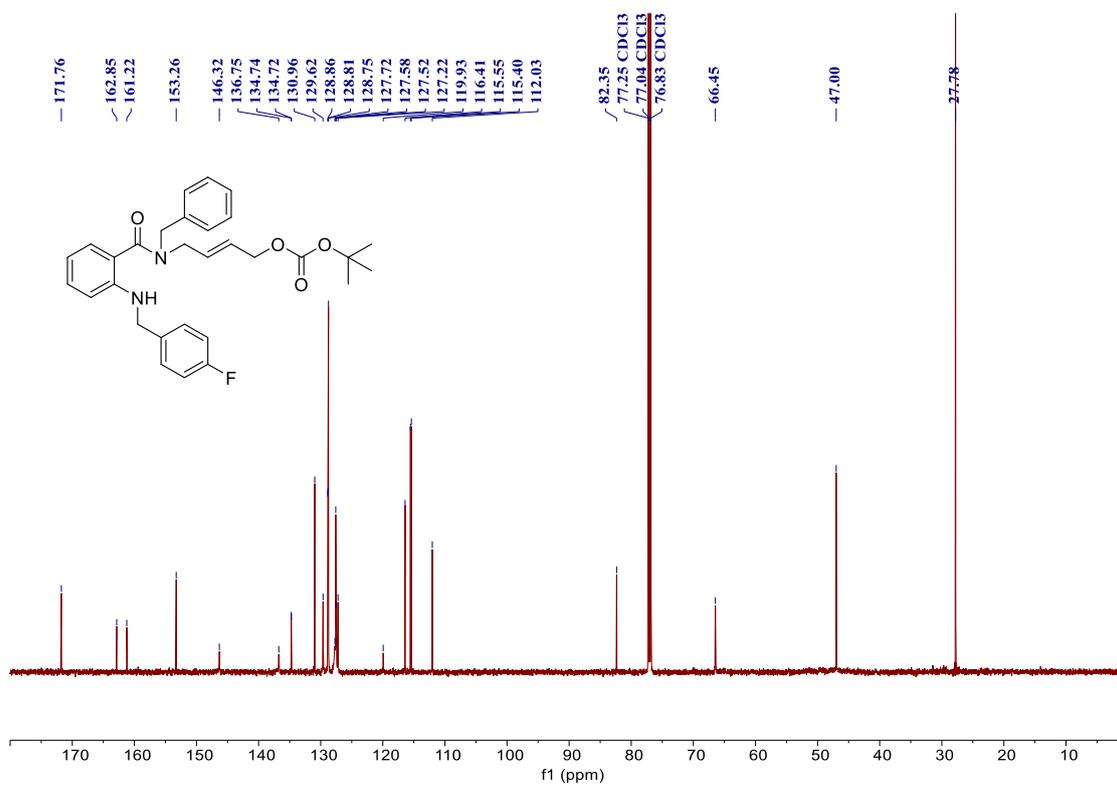


Figure S69. ¹H NMR (600 MHz, CDCl₃) spectrum of 33a

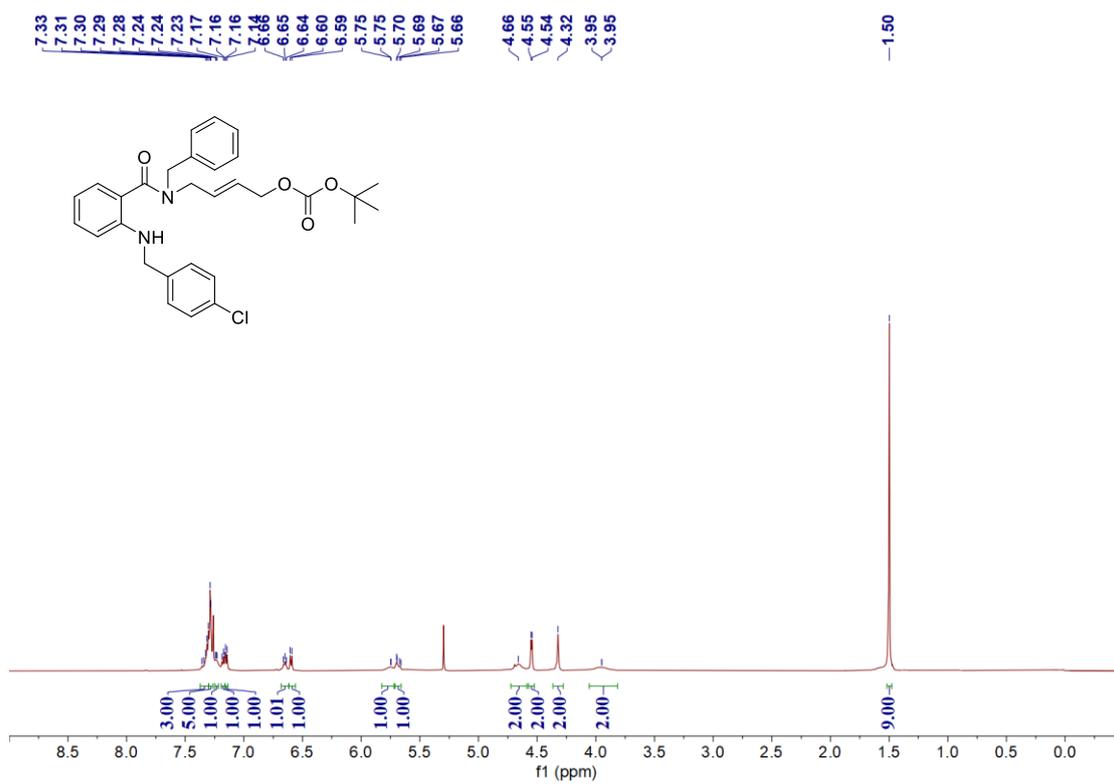


Figure S70. ¹³C NMR (151 MHz, CDCl₃) spectrum of 33a

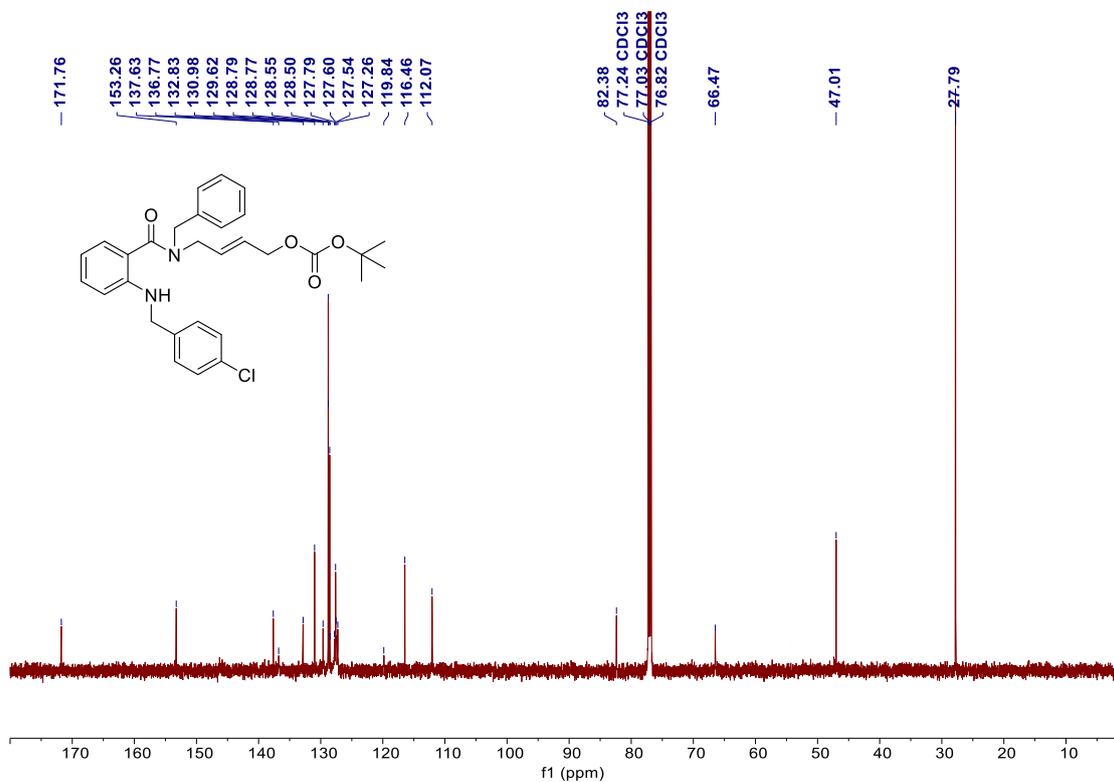


Figure S71. ¹H NMR (600 MHz, CDCl₃) spectrum of 34a

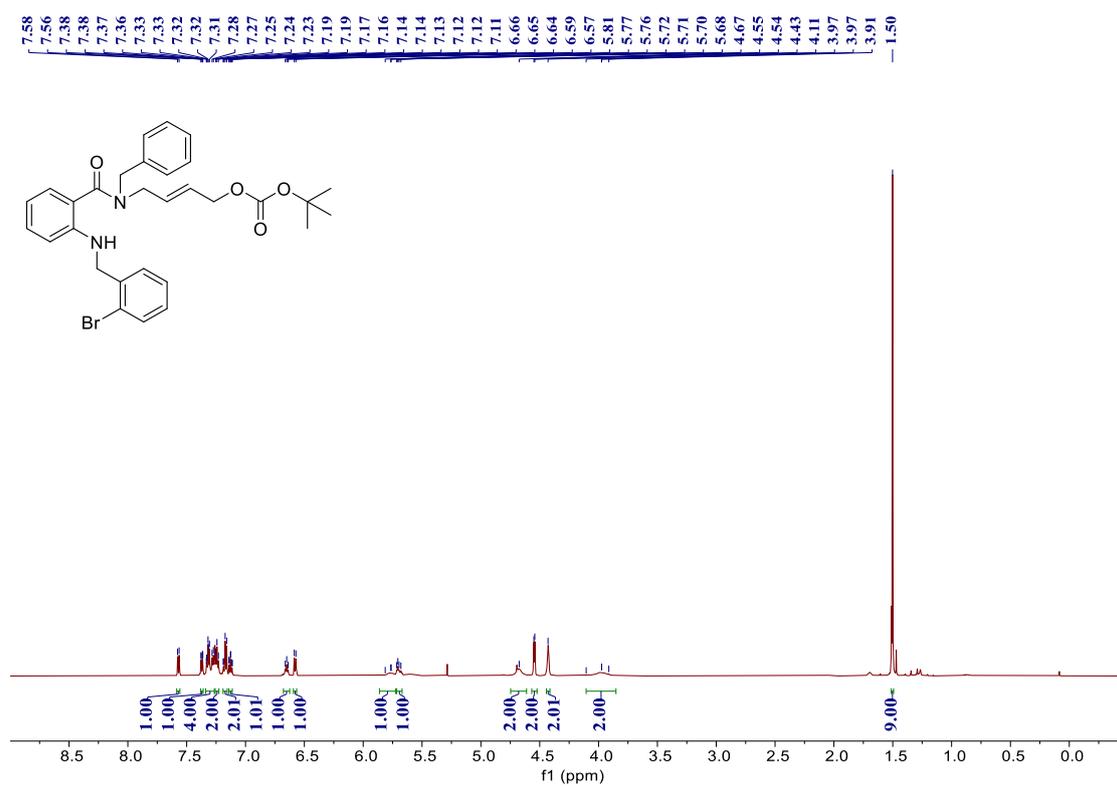


Figure S72. ¹³C NMR (151 MHz, CDCl₃) spectrum of 34a

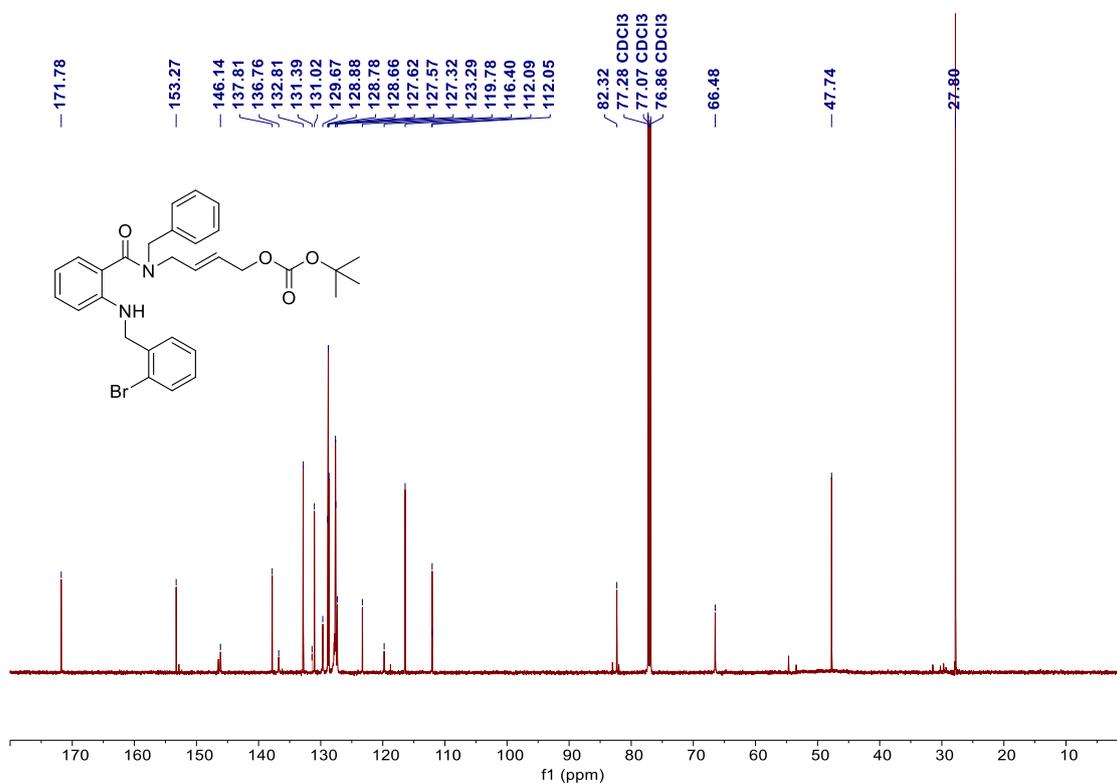


Figure S73. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-1b

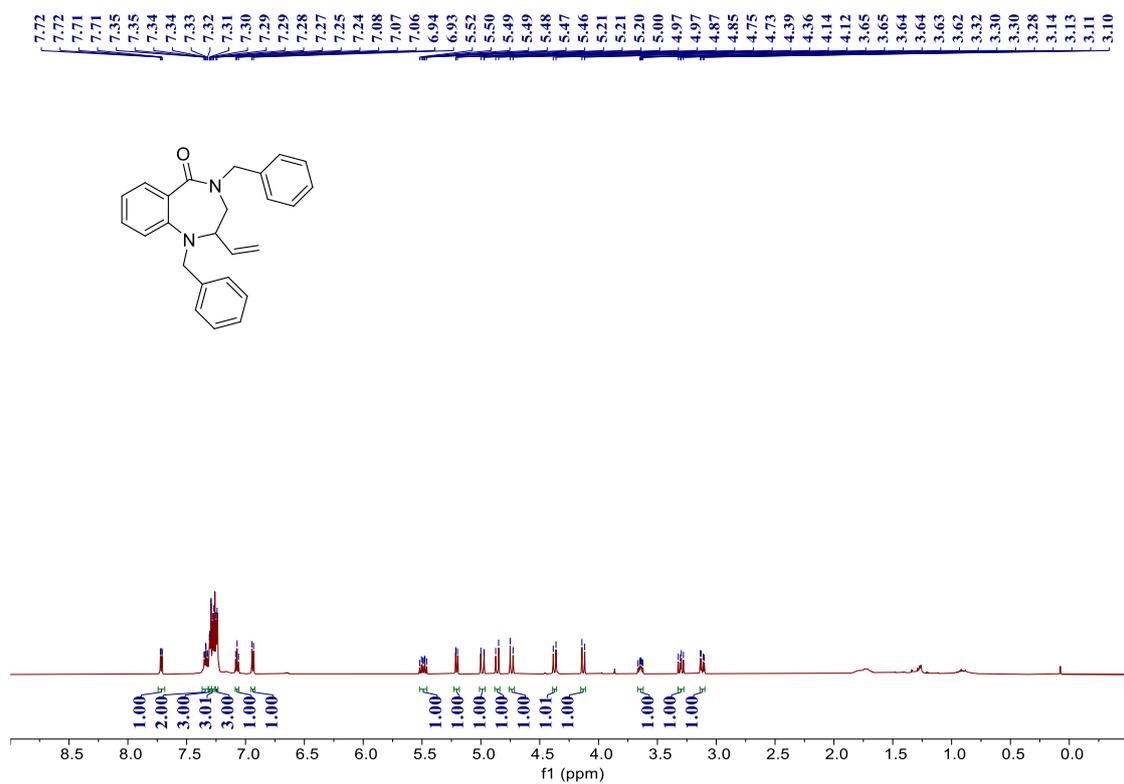


Figure S74. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-1b

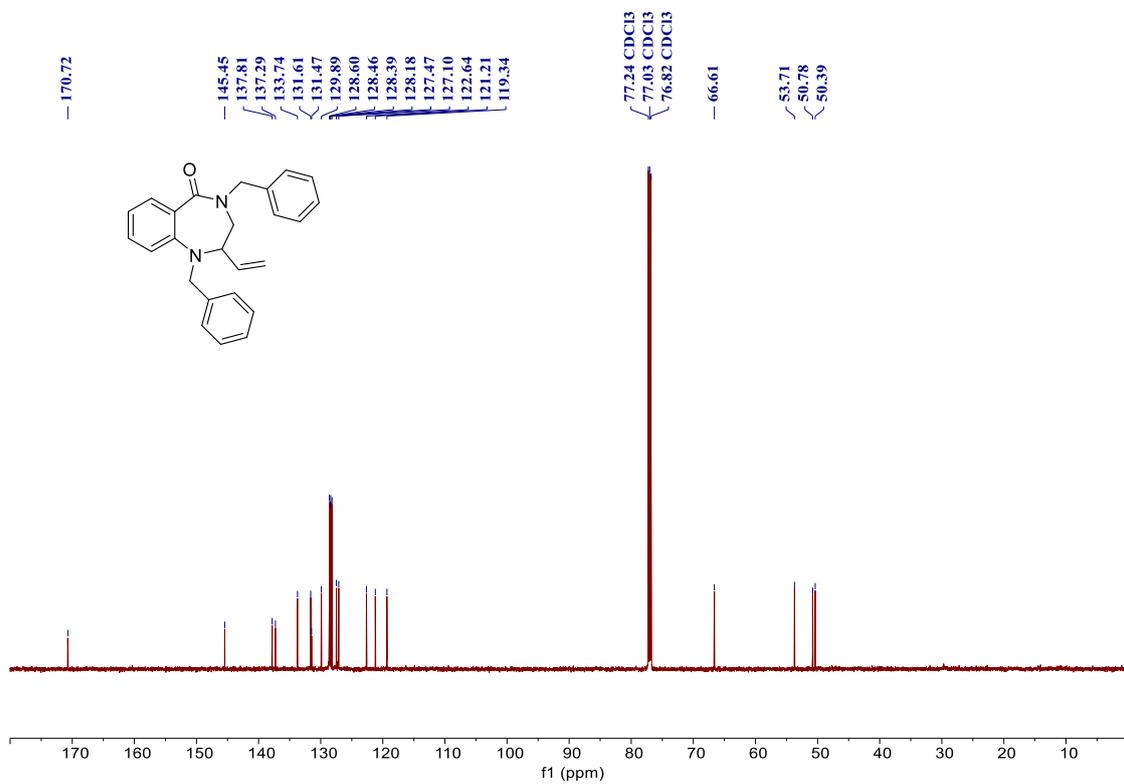


Figure S75. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-2b

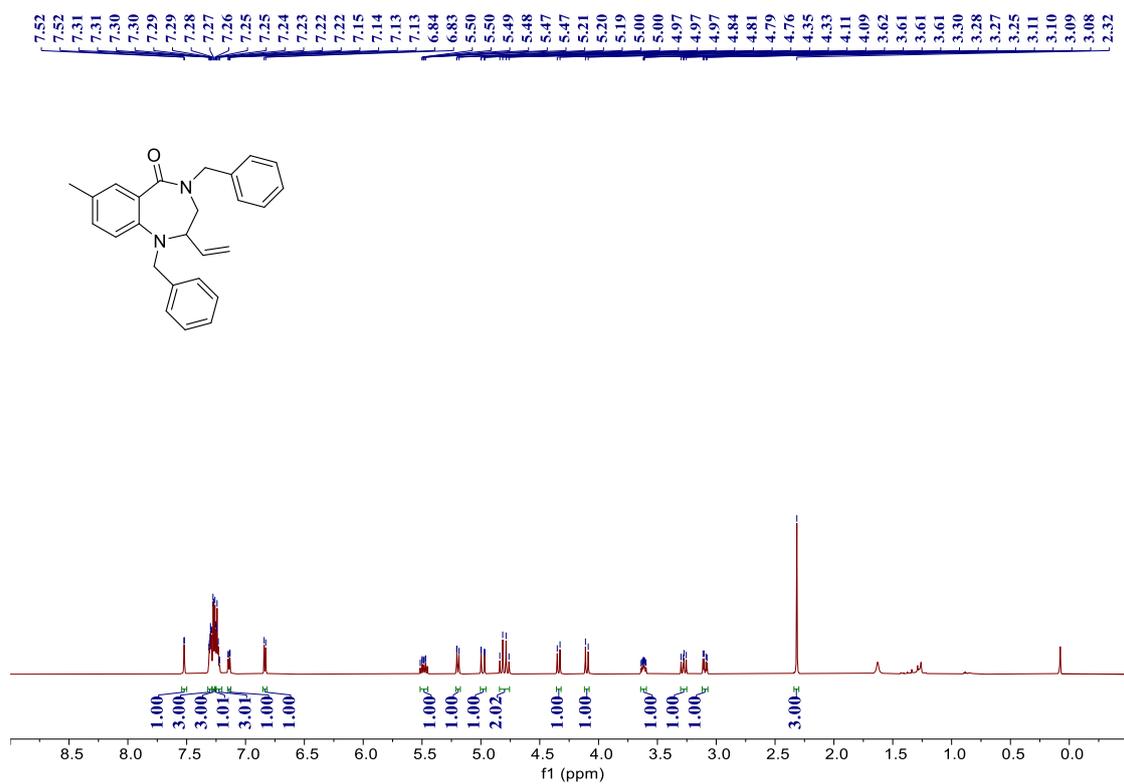


Figure S76. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-2b

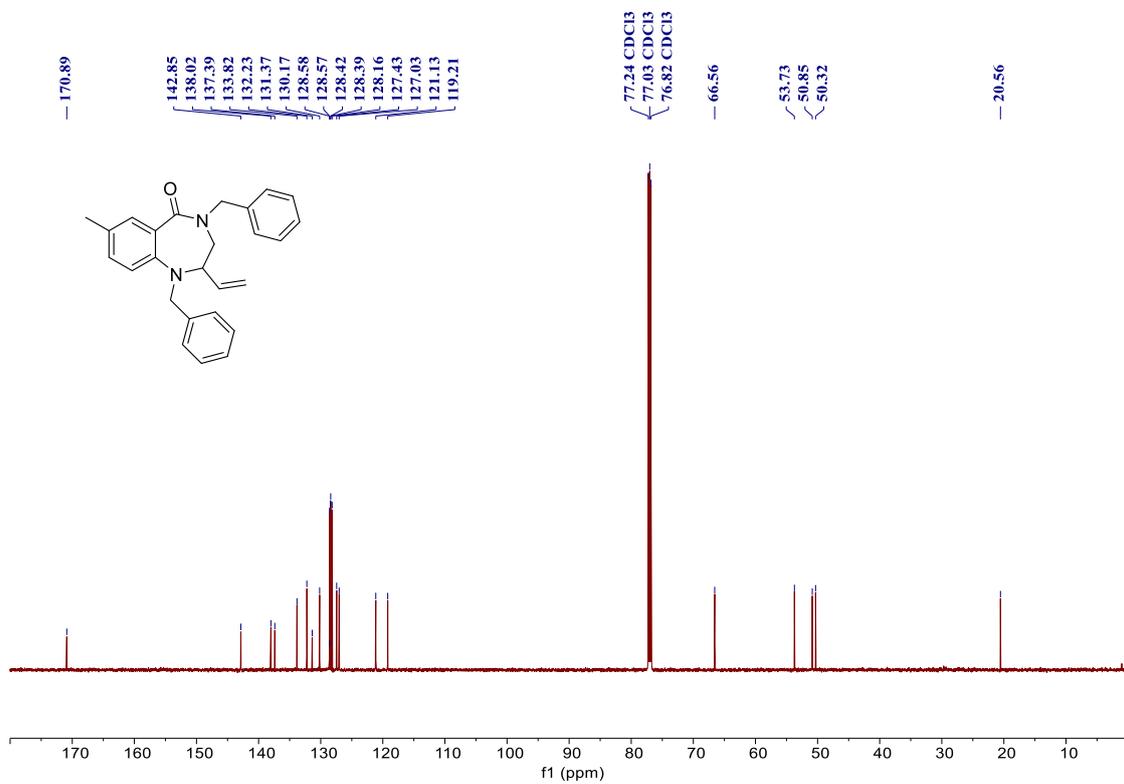


Figure S77. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-3b

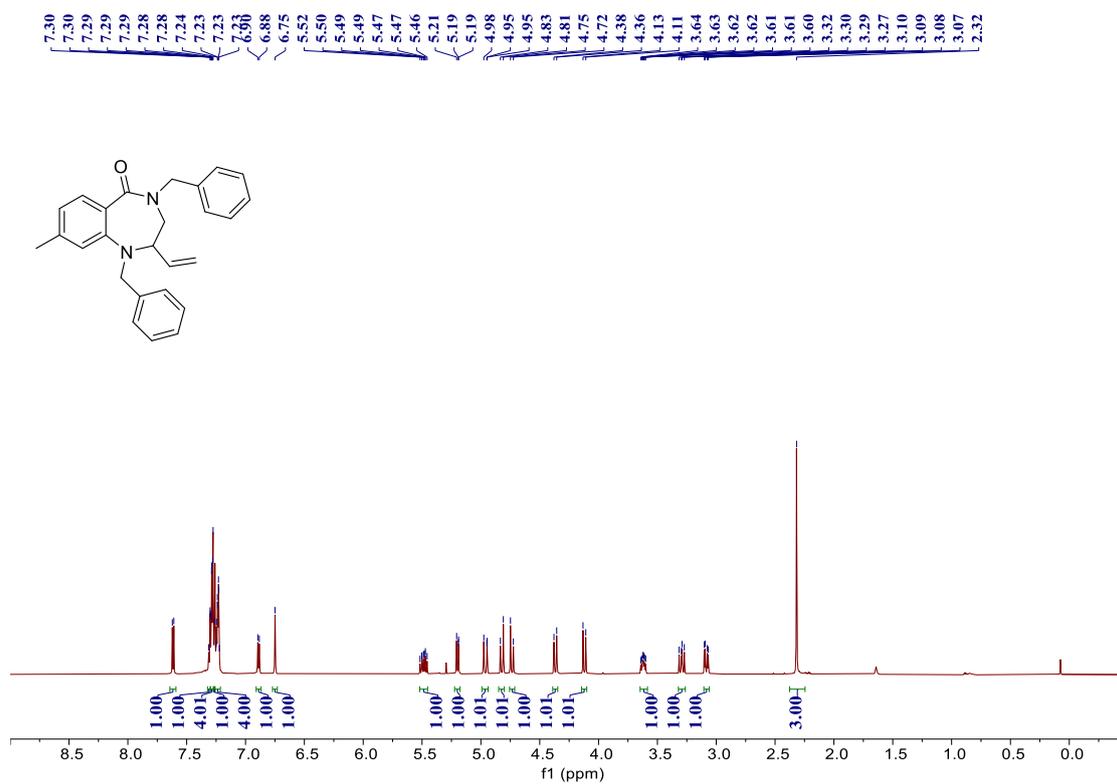


Figure S78. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-3b

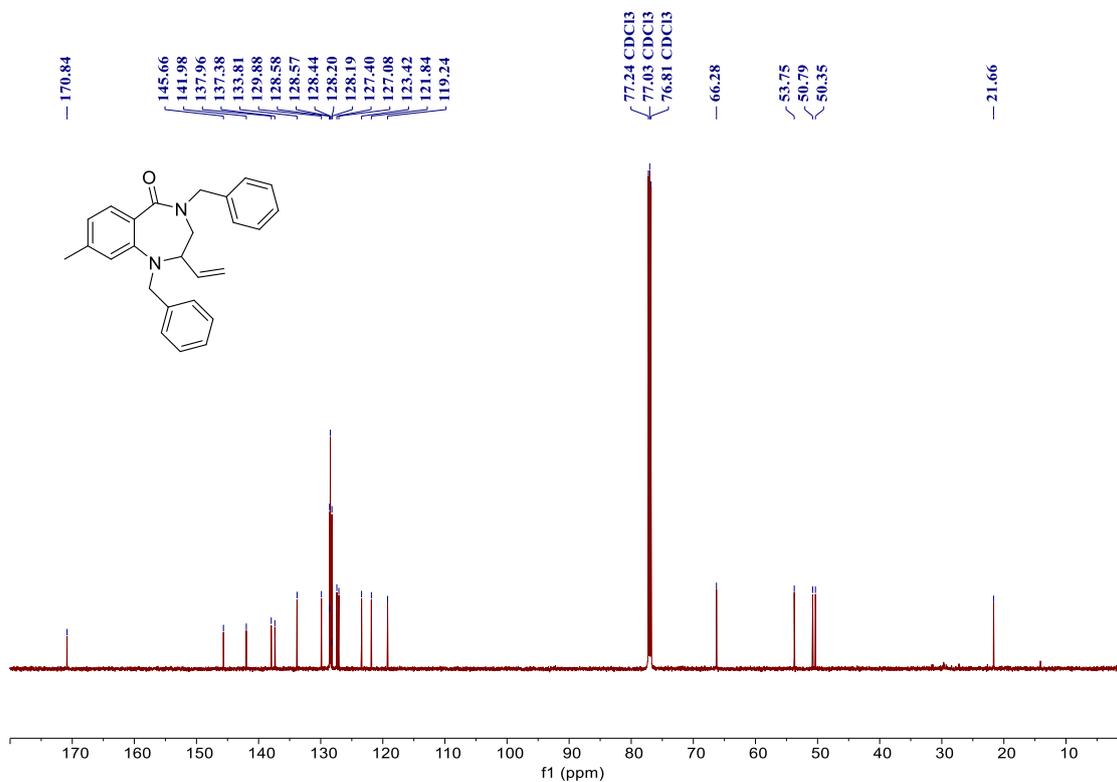


Figure S79. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-4b

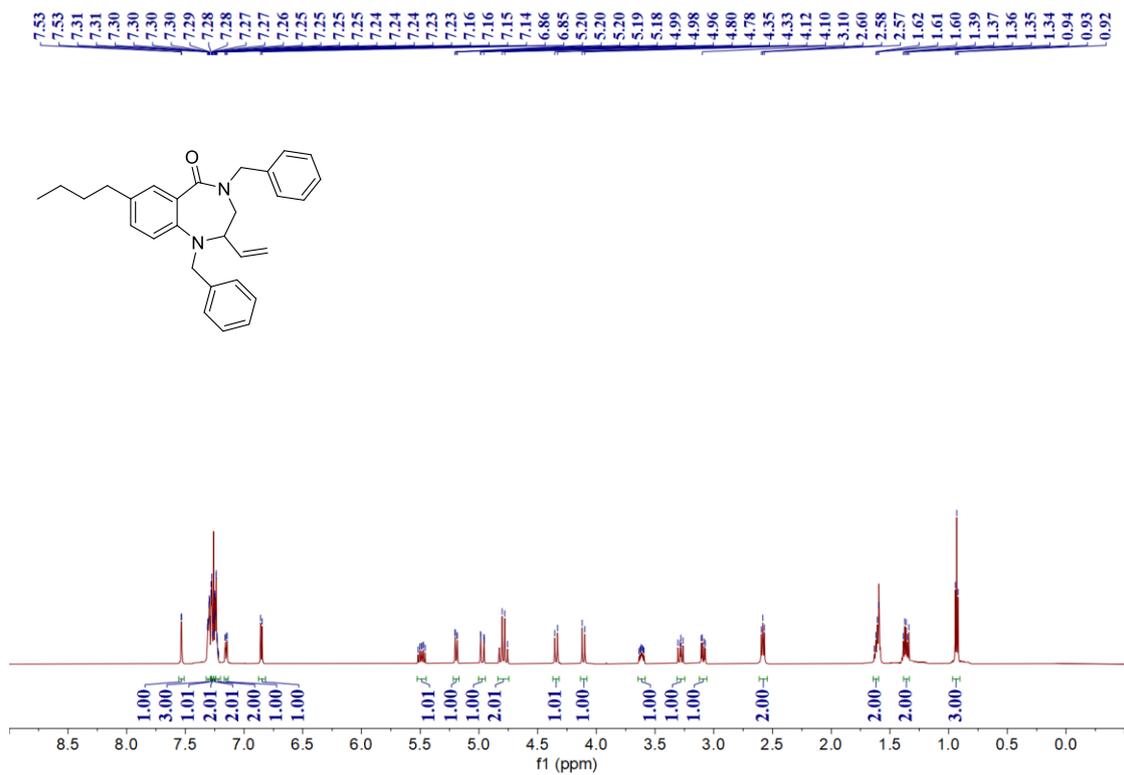


Figure 80. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-4b

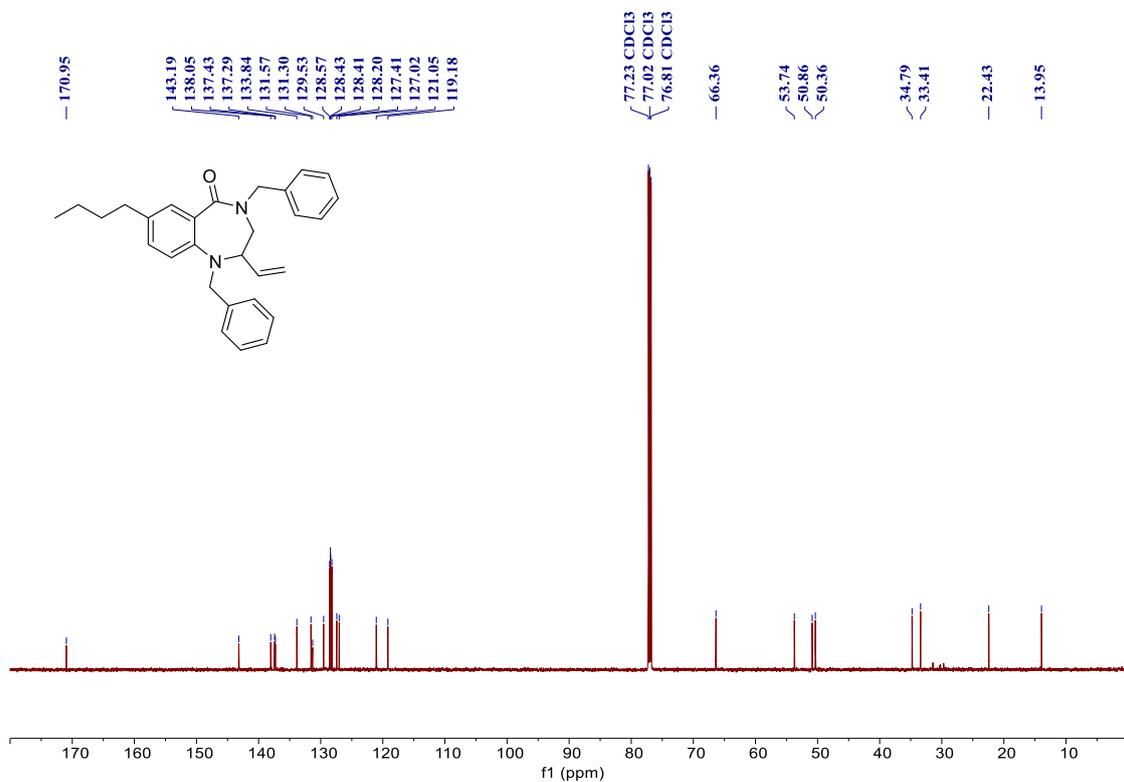


Figure S81. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-5b

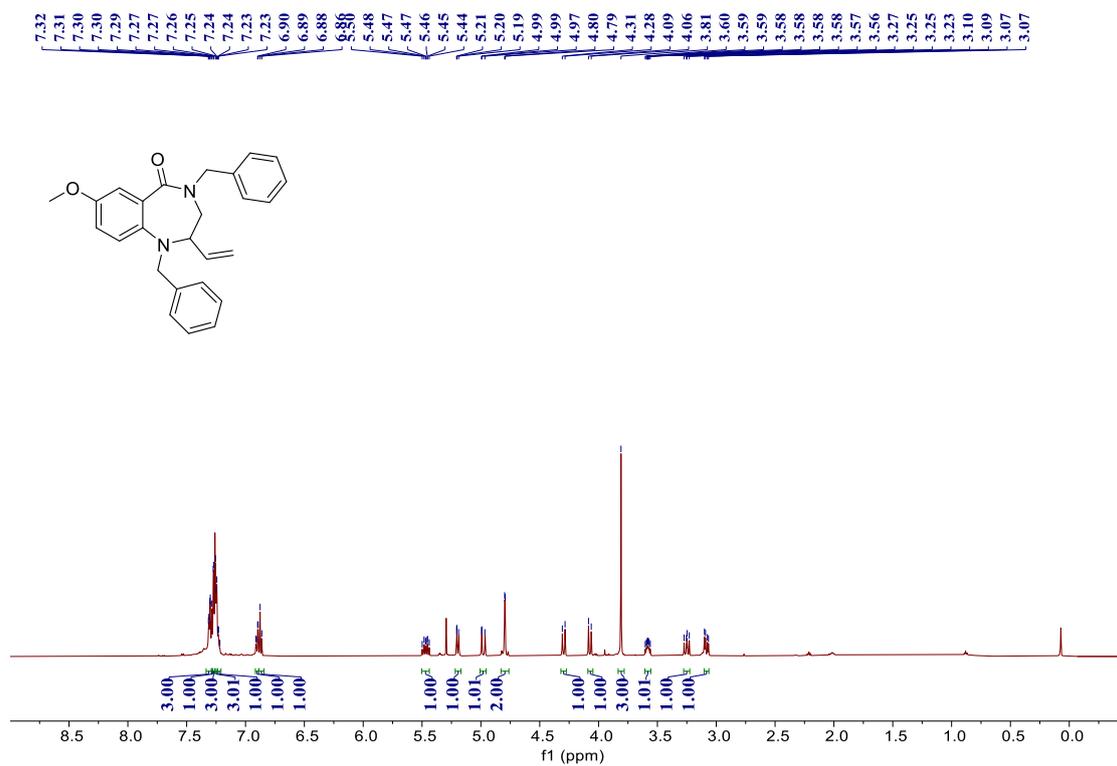


Figure S82. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-5b

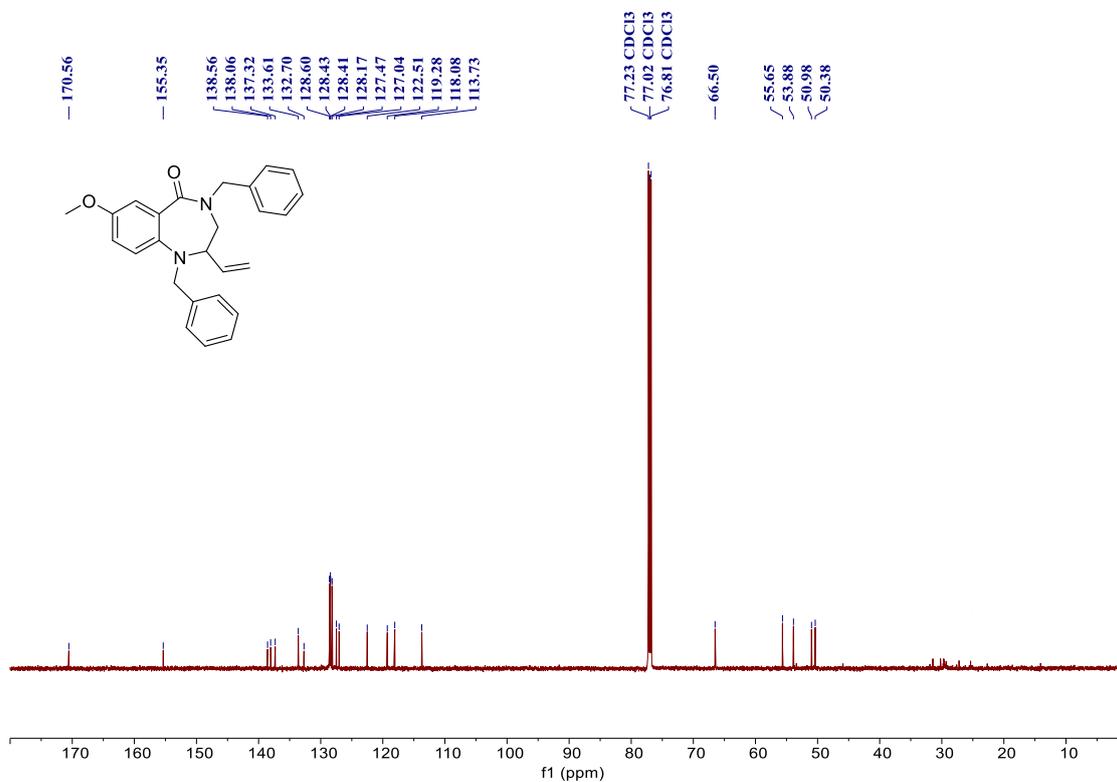


Figure S85. ^{19}F NMR (565 MHz, CDCl_3) spectrum of (*R*)-6b

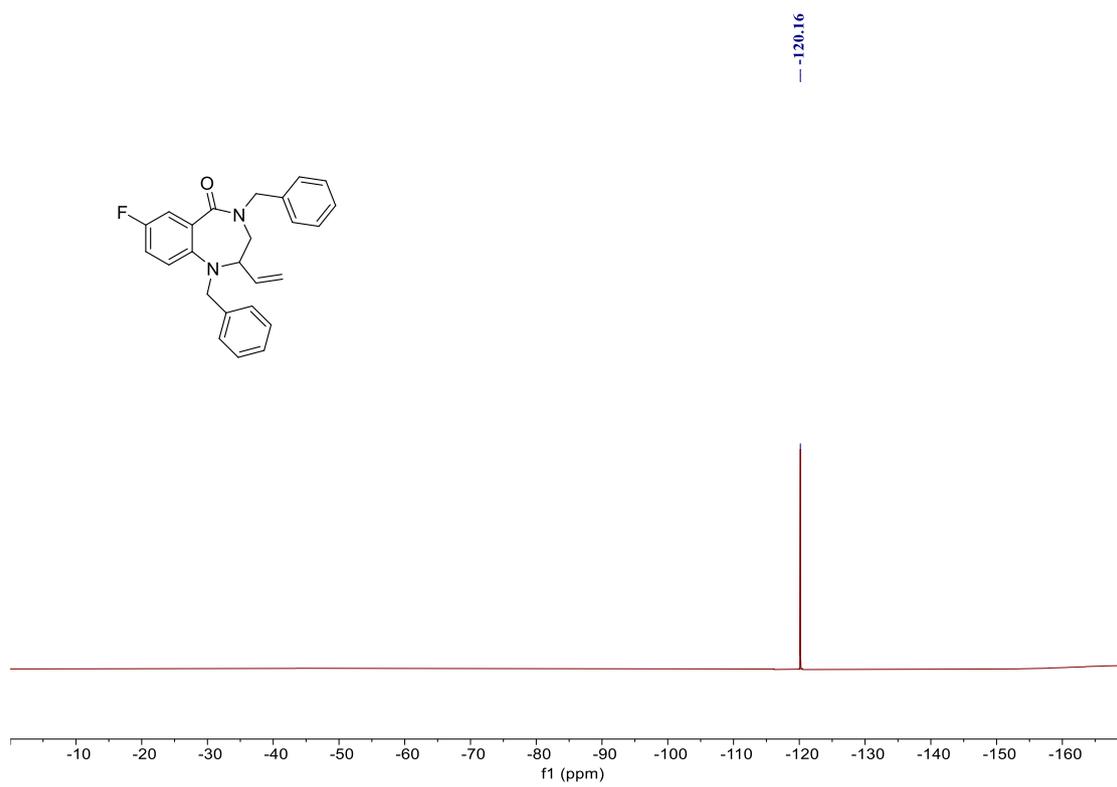


Figure S86. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-7b

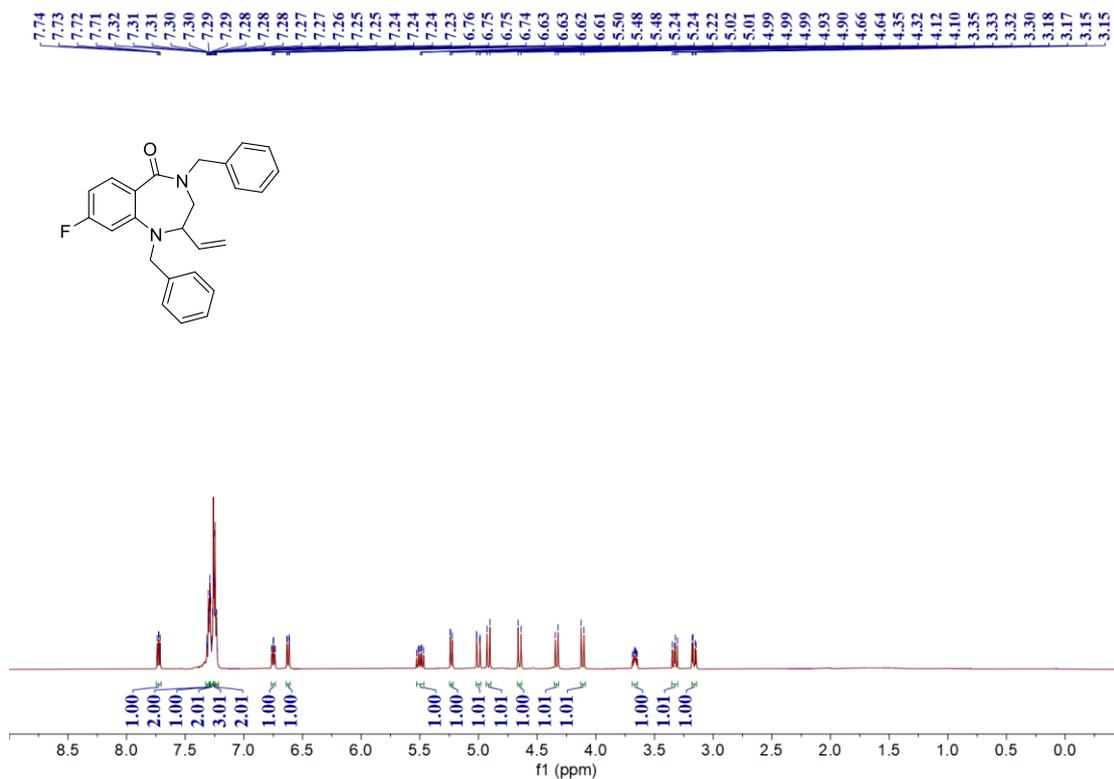


Figure S87. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-7b

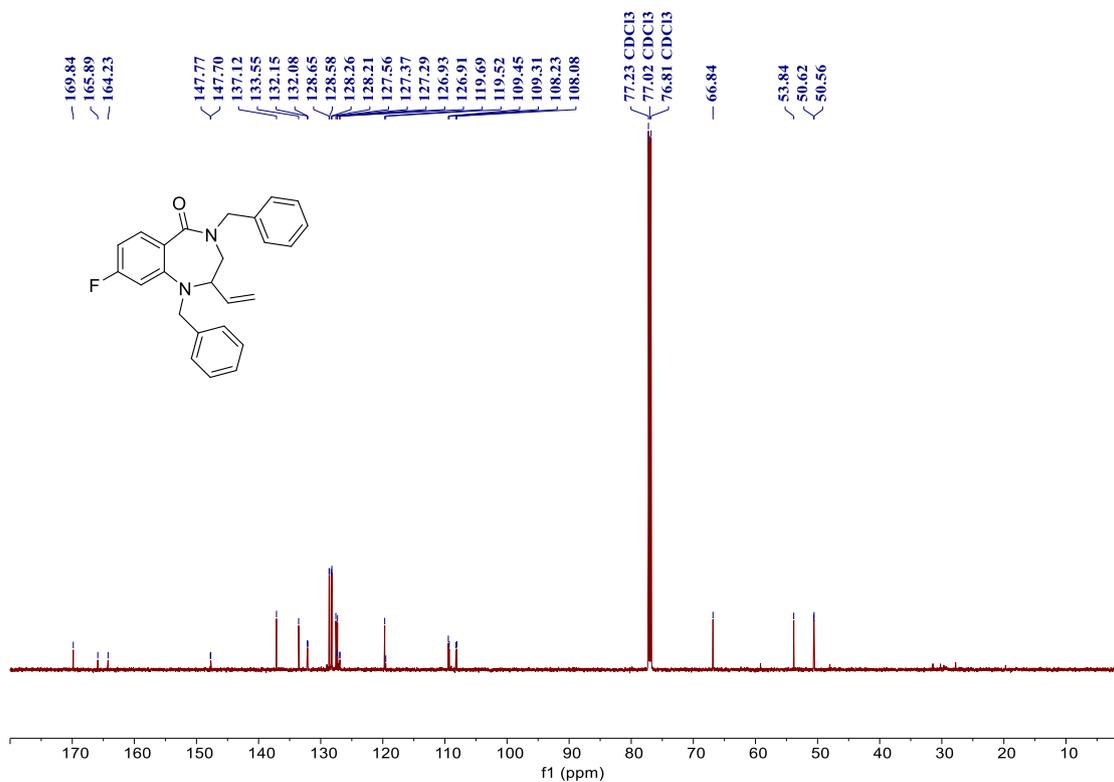


Figure S88. ^{19}F NMR (565 MHz, CDCl_3) spectrum of (*R*)-7b

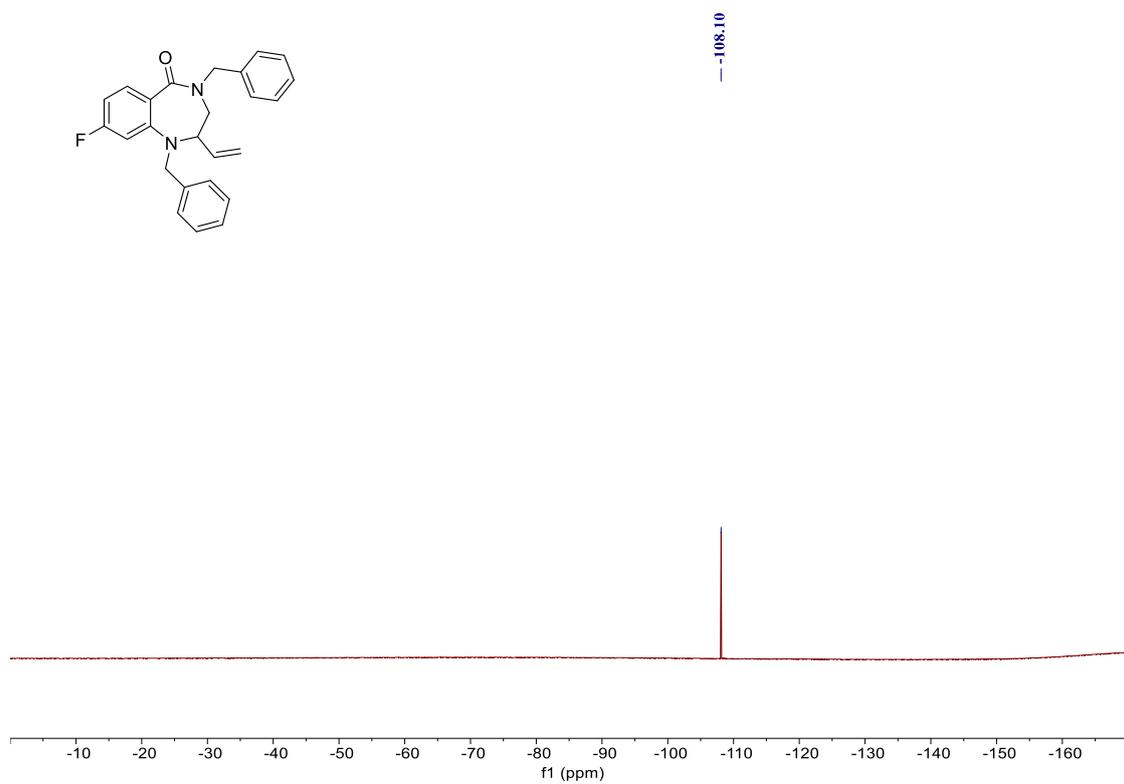


Figure S89. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-8b

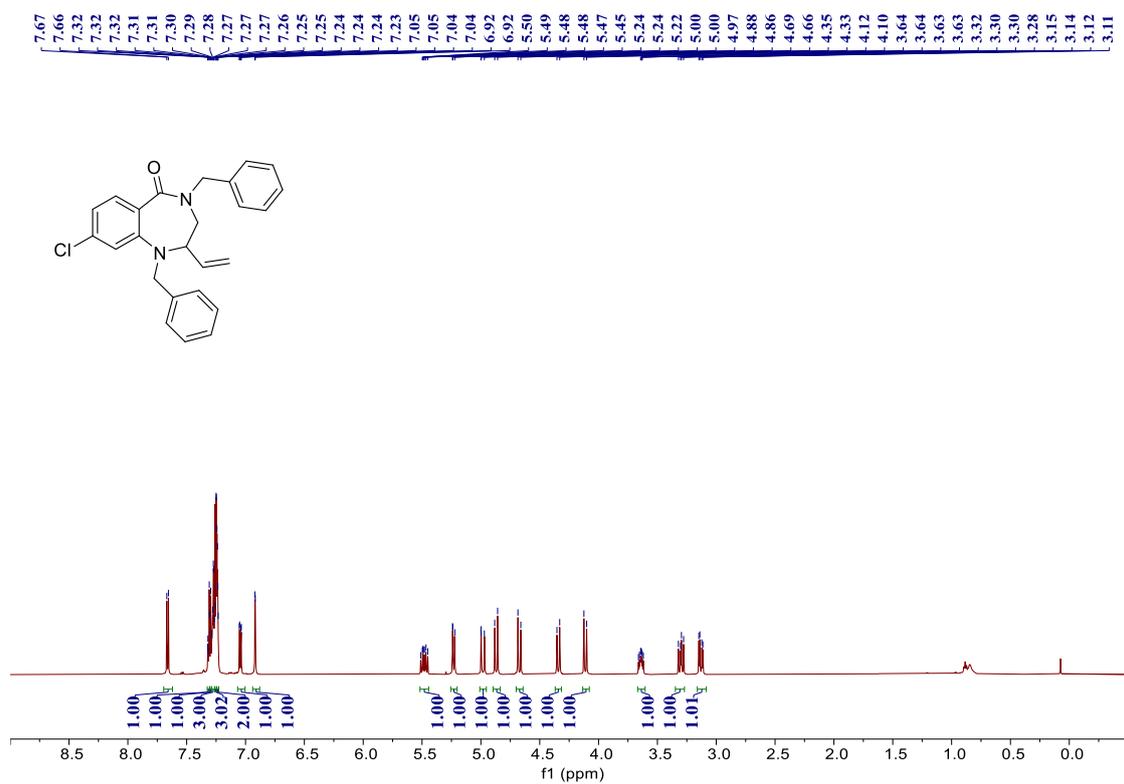


Figure S90. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-8b

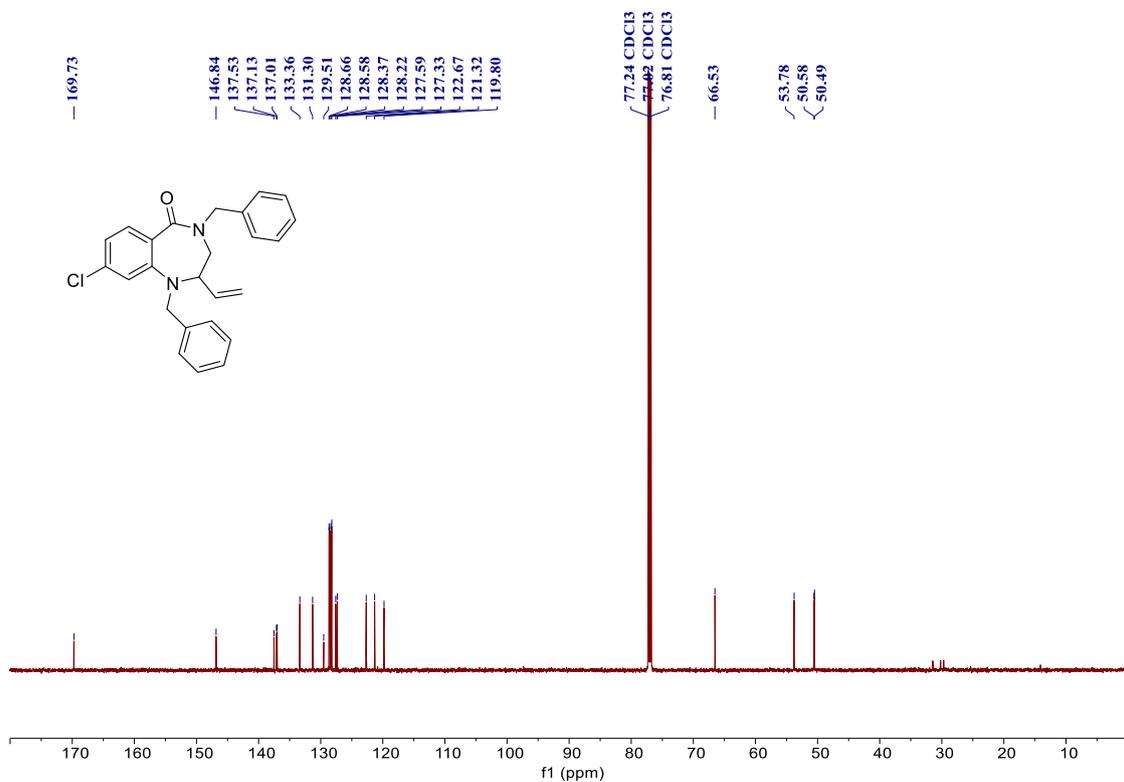


Figure S91. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-9b

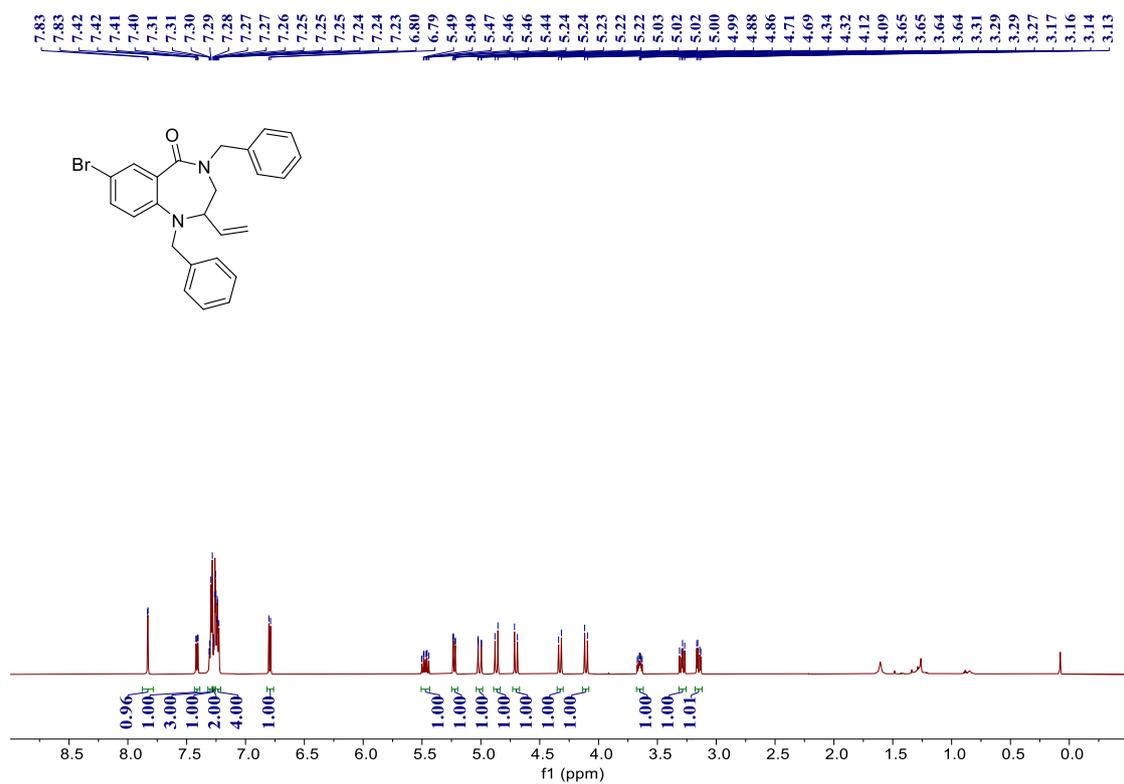


Figure S92. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-9b

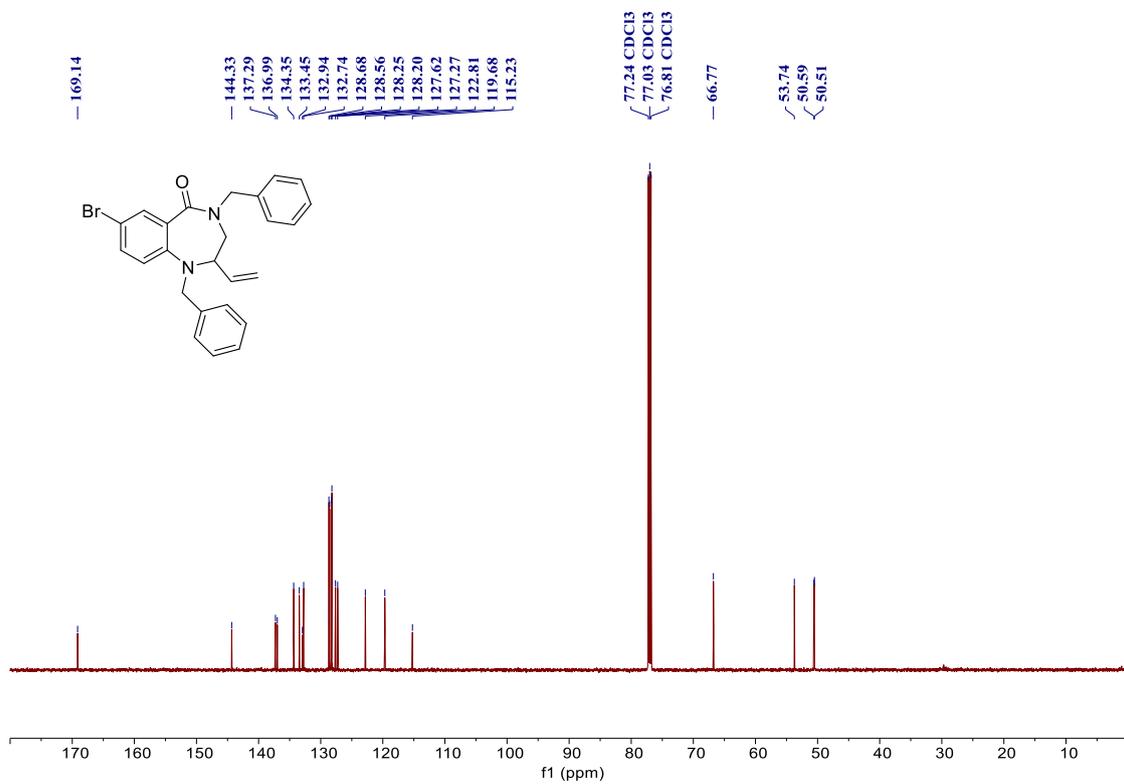


Figure S93. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-10b

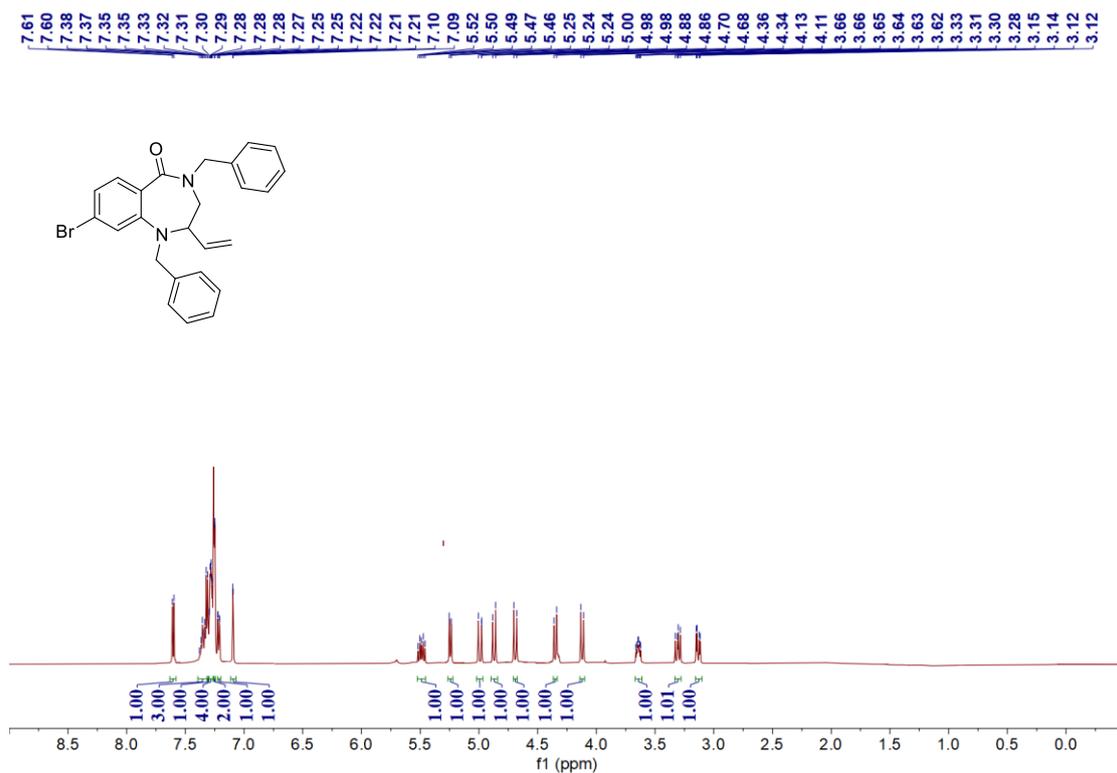


Figure S94. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-10b

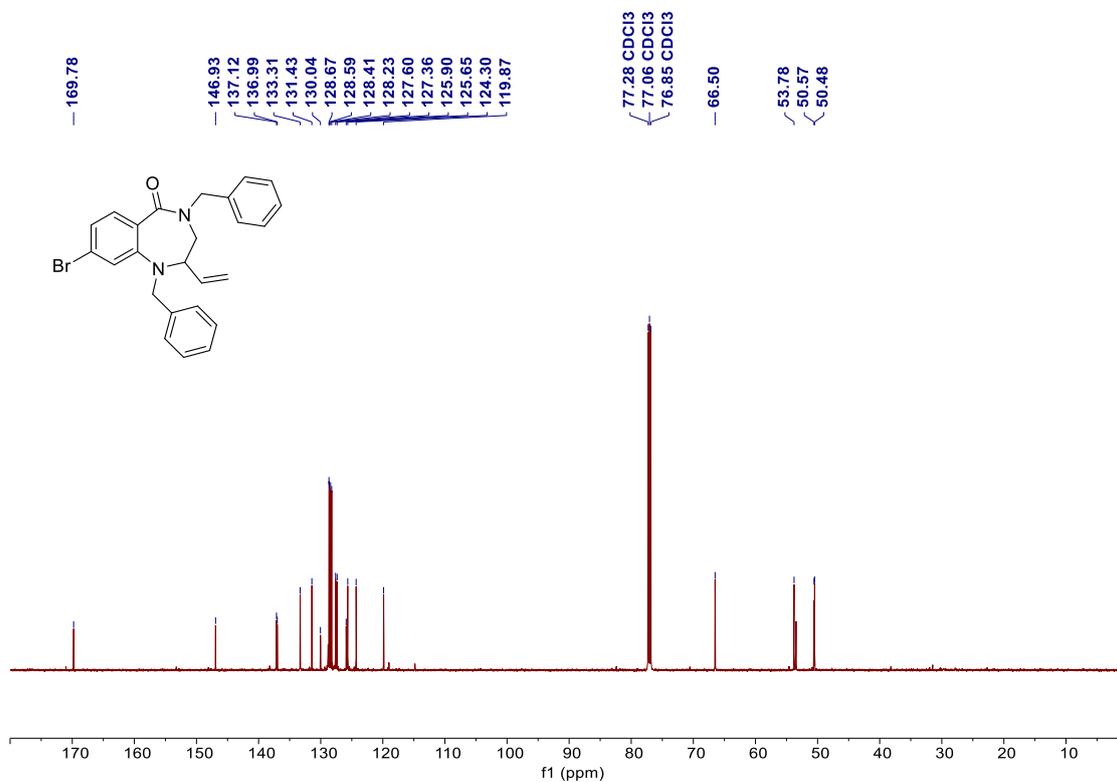


Figure S95. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-11b

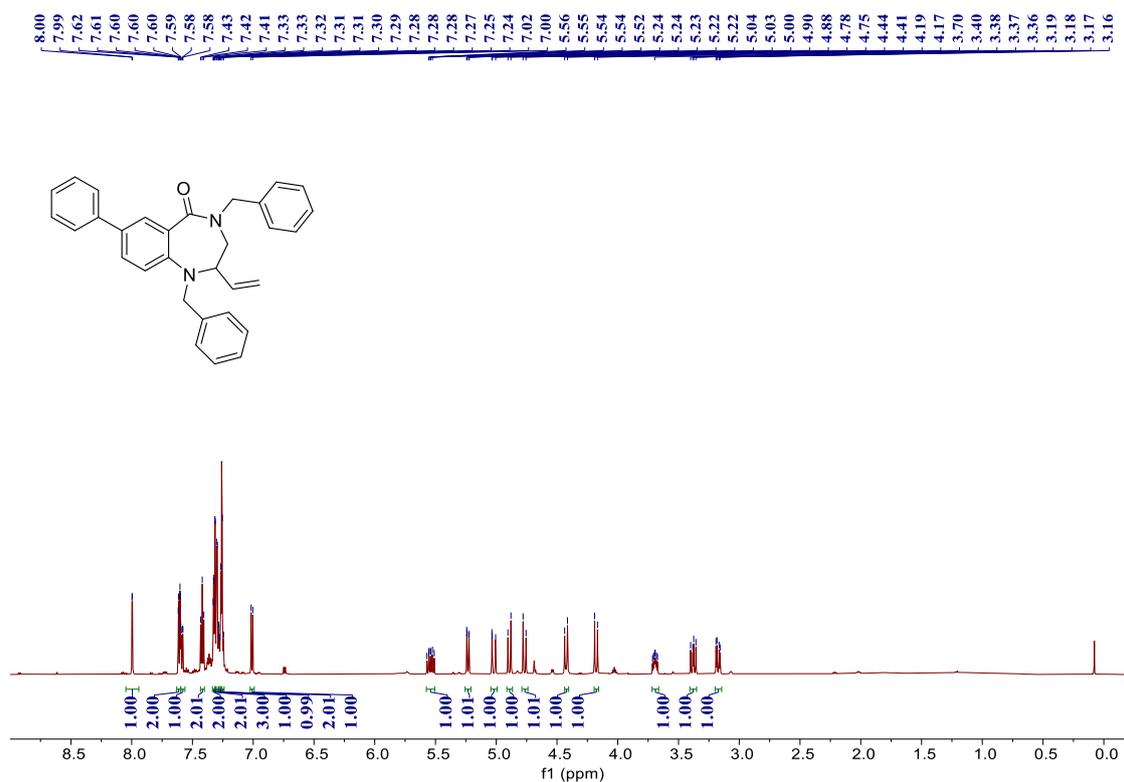


Figure S96. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-11b

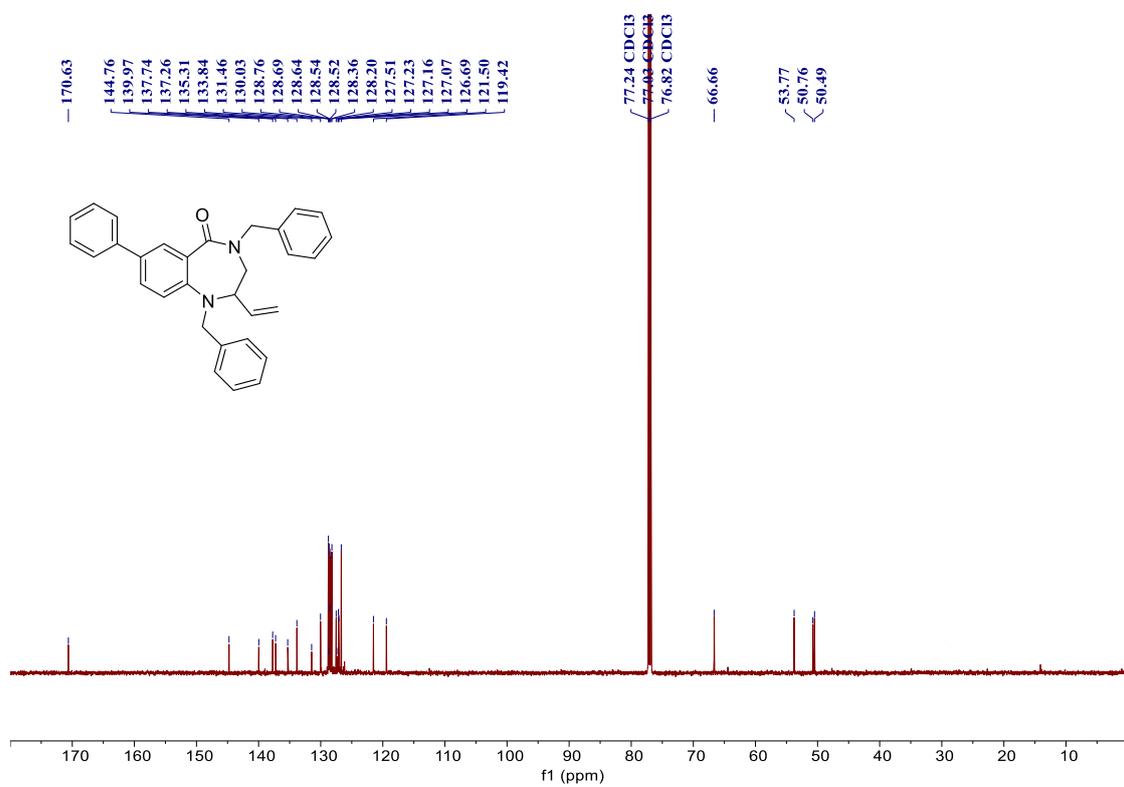


Figure S97. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-12b

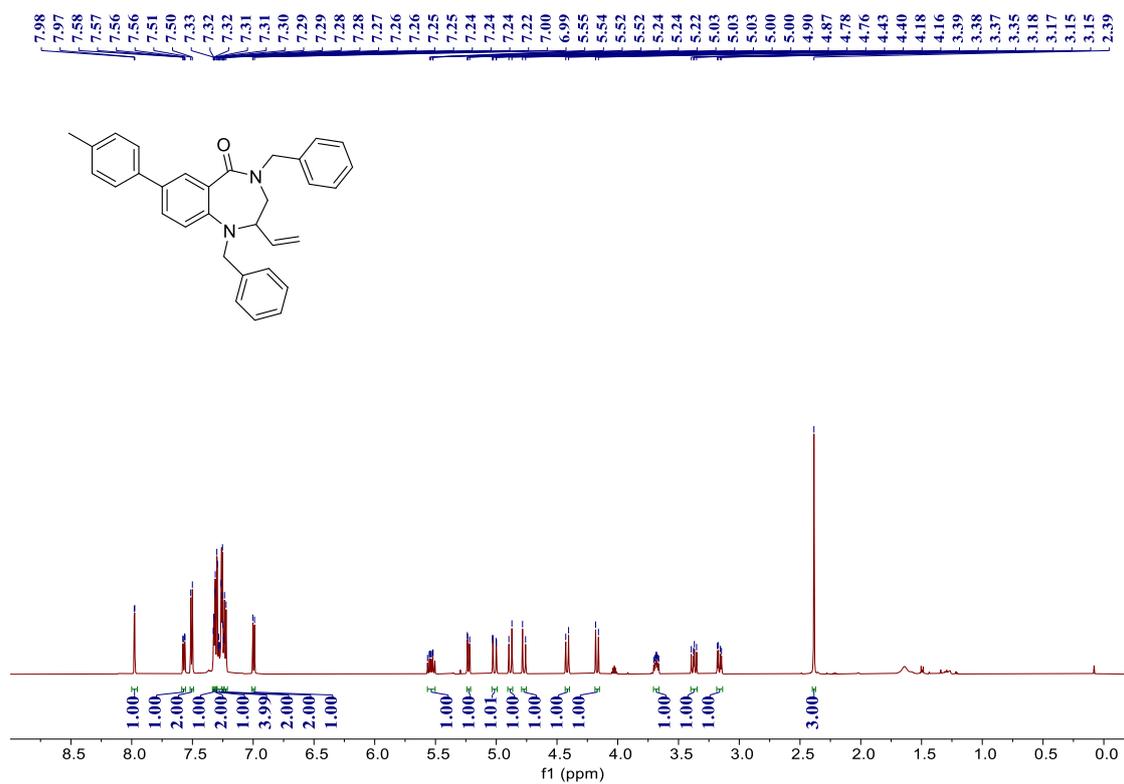


Figure S98. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-12b

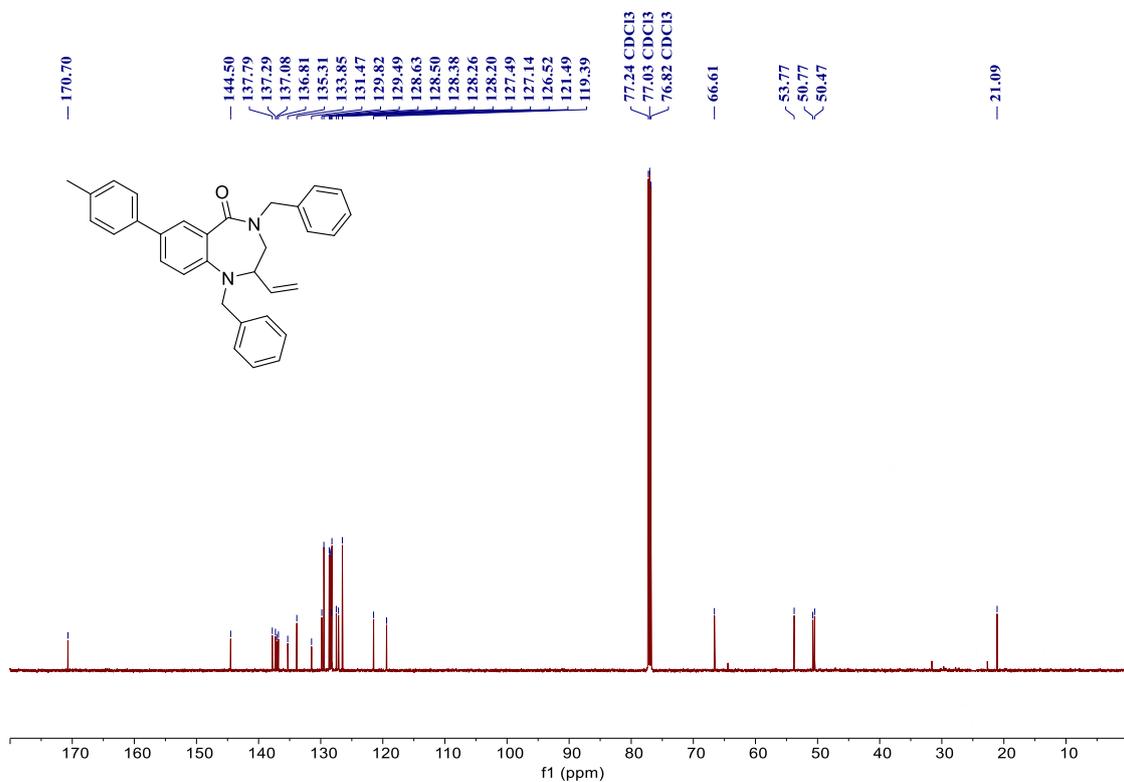


Figure S99. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-13b

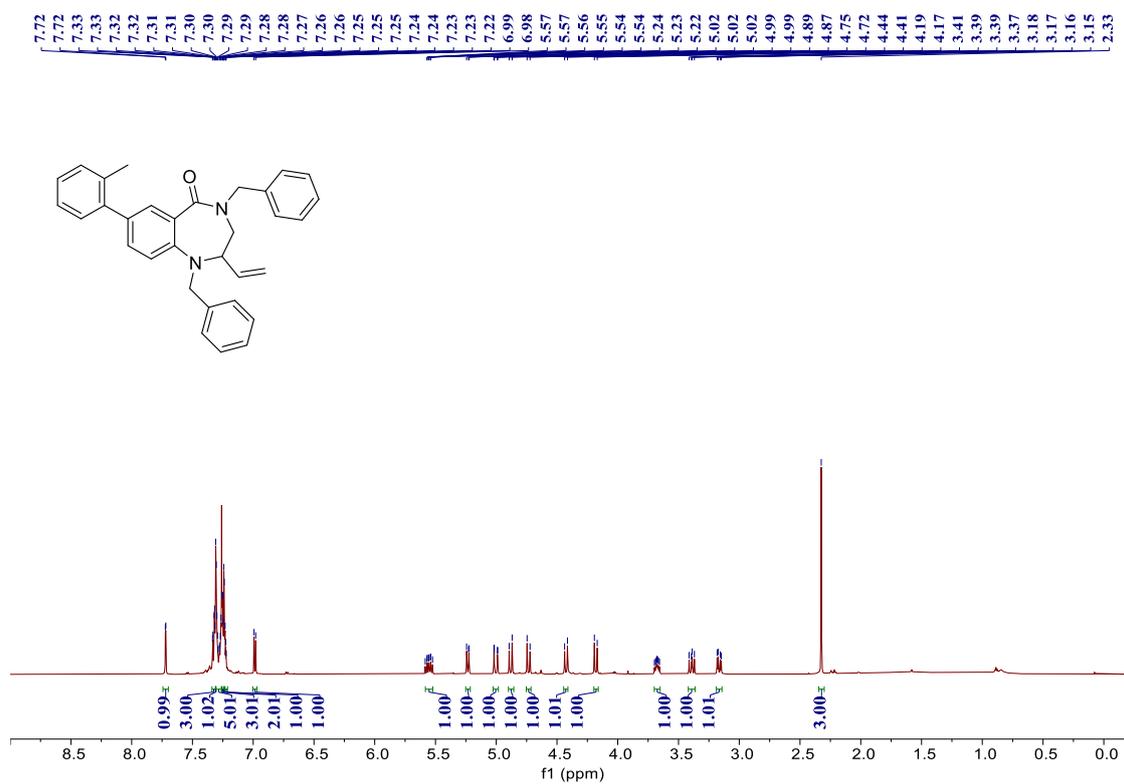


Figure S100. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-13b

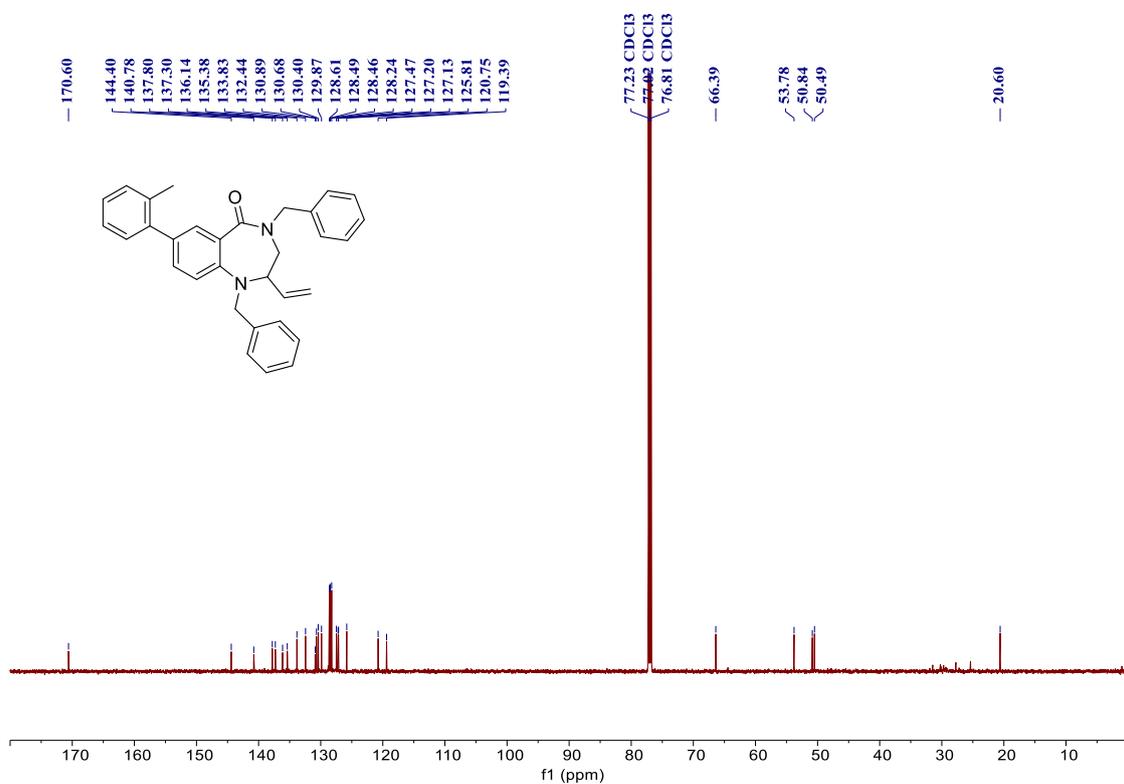


Figure S101. ¹H NMR (600 MHz, CDCl₃) spectrum of (R)-14b

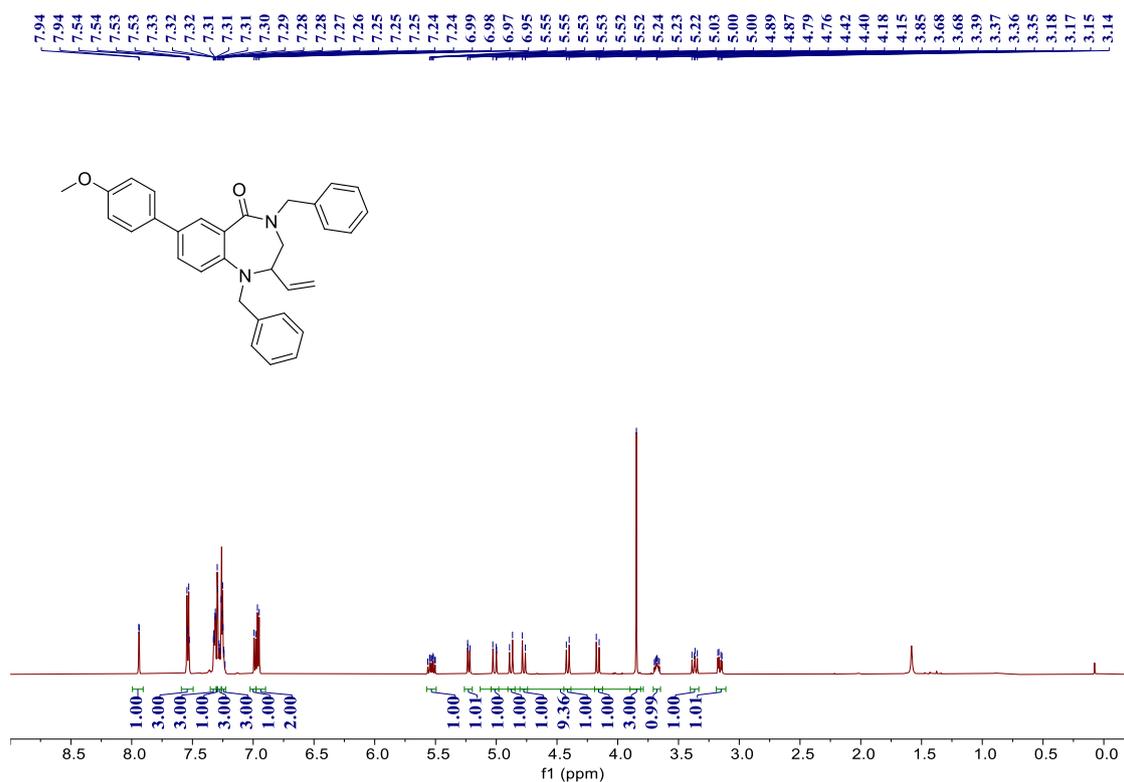


Figure S102. ¹³C NMR (151 MHz, CDCl₃) spectrum of (R)-14b

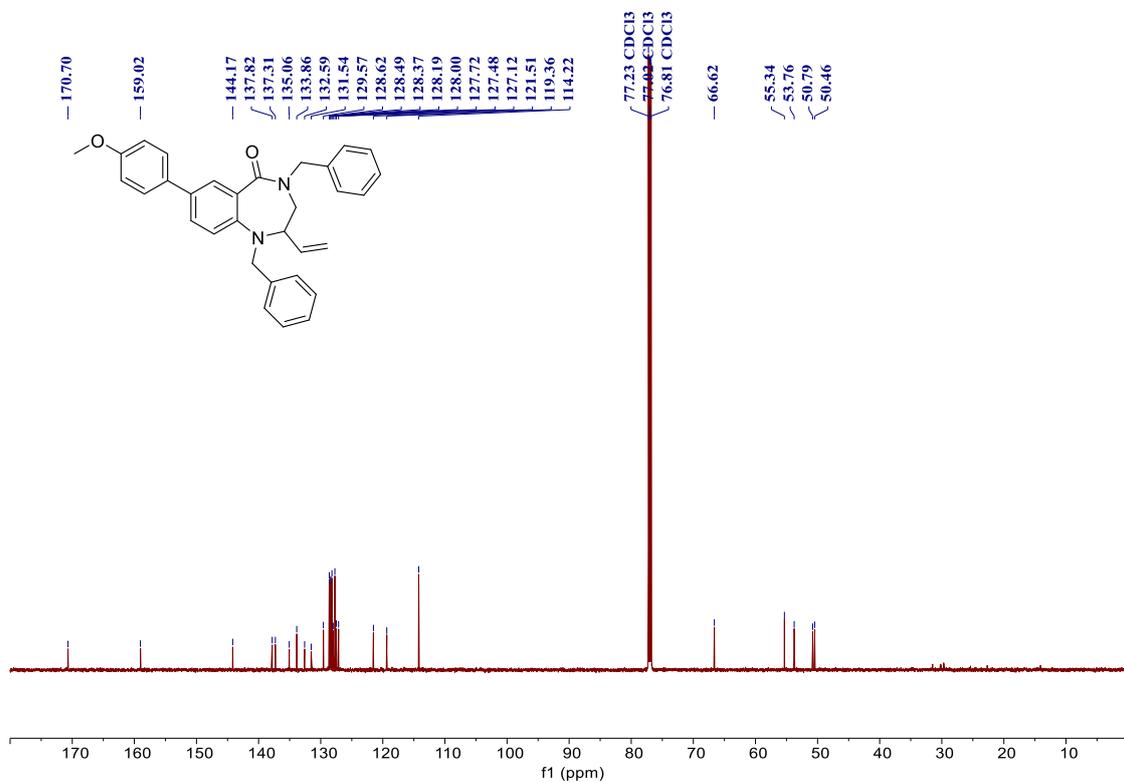


Figure S103. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-15b

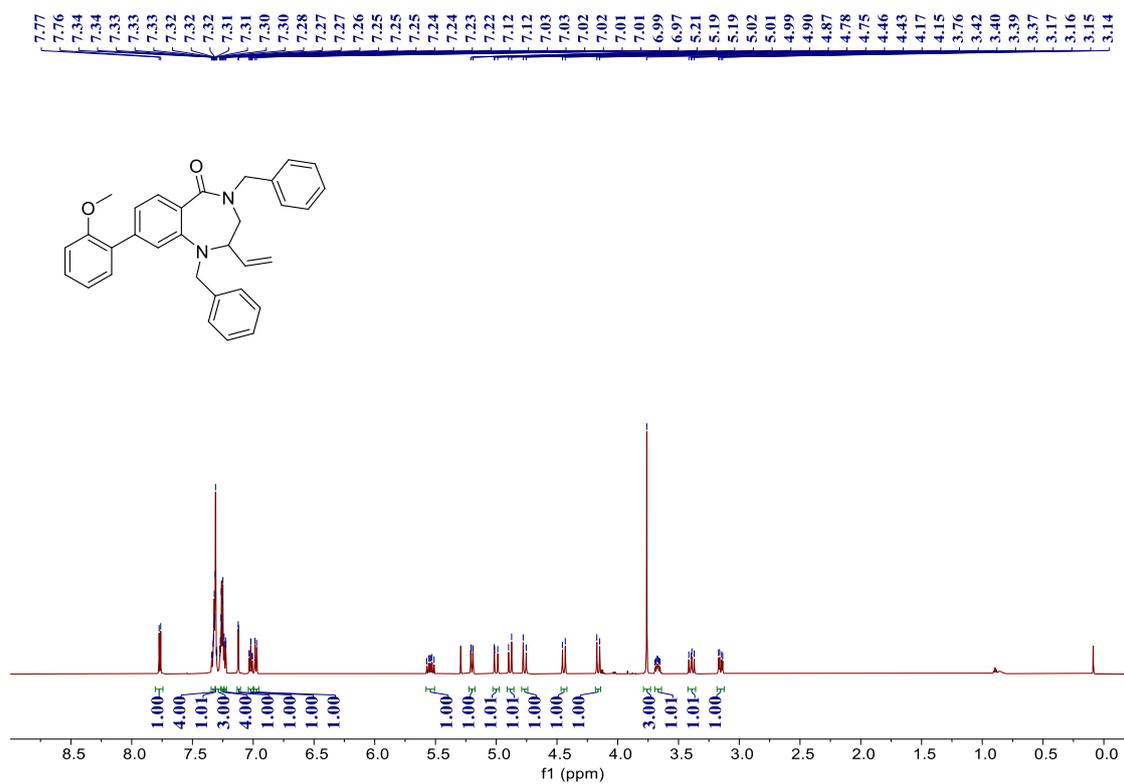


Figure S104. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-15b

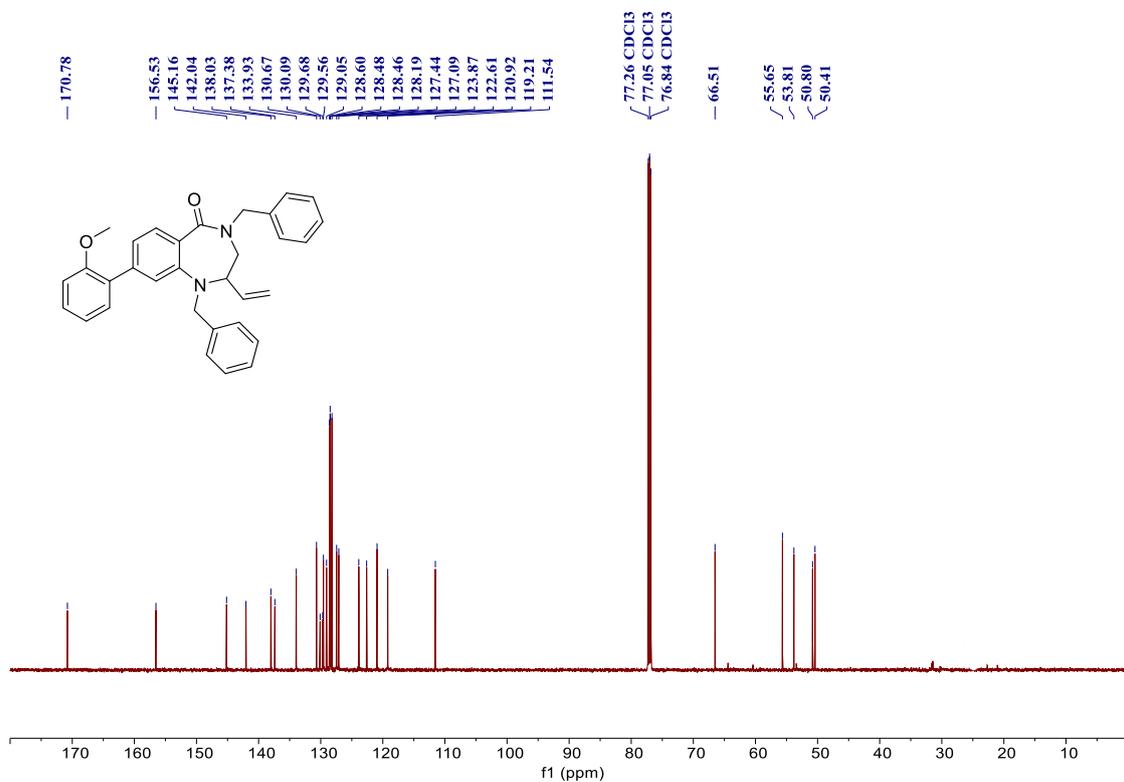


Figure S105. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-16b

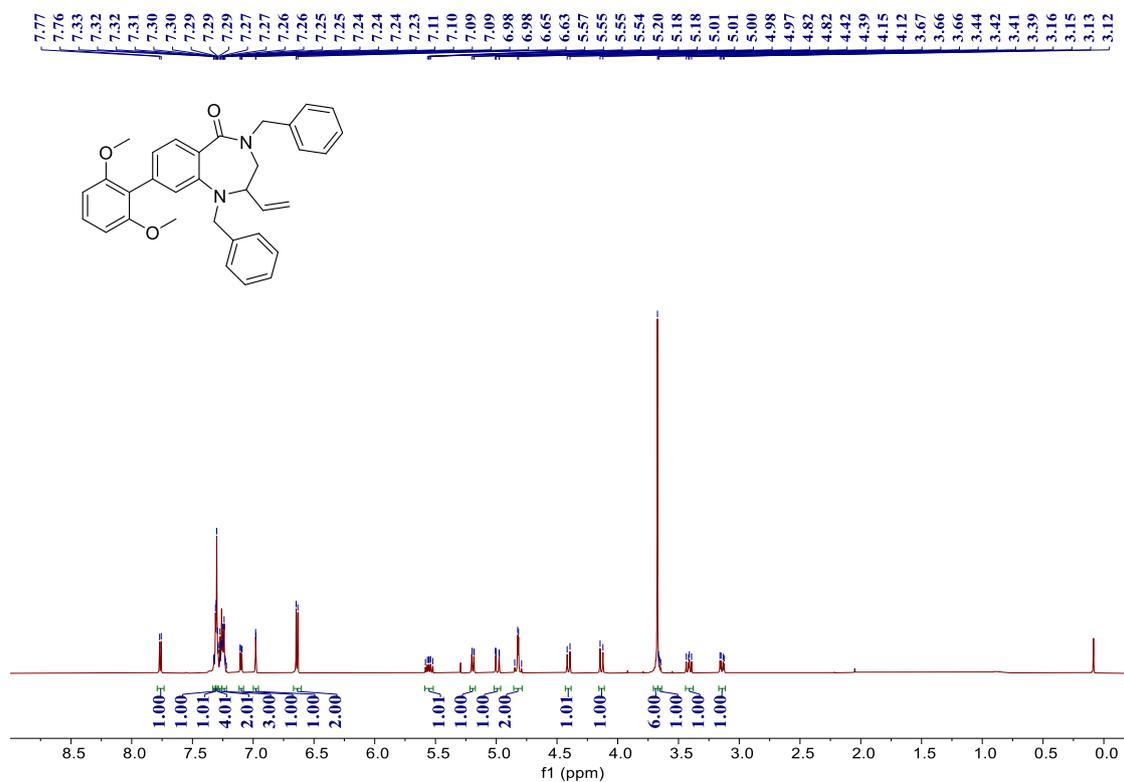


Figure S106. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-16b

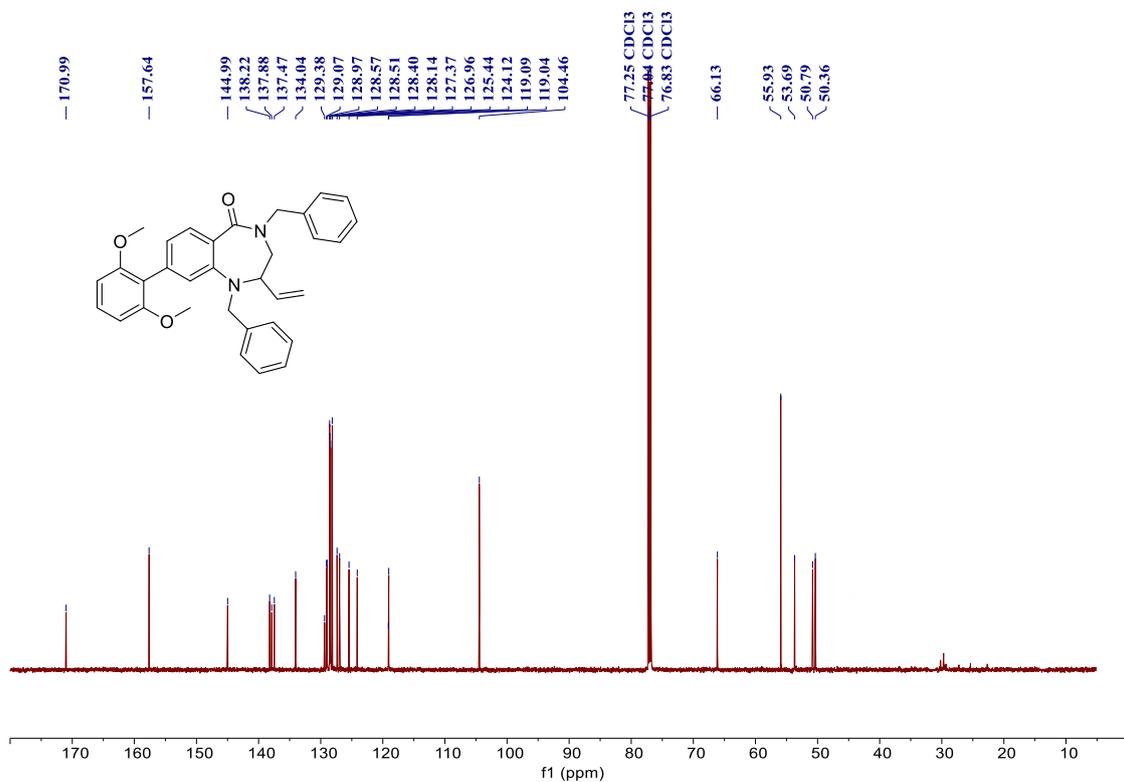


Figure S107. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-17b

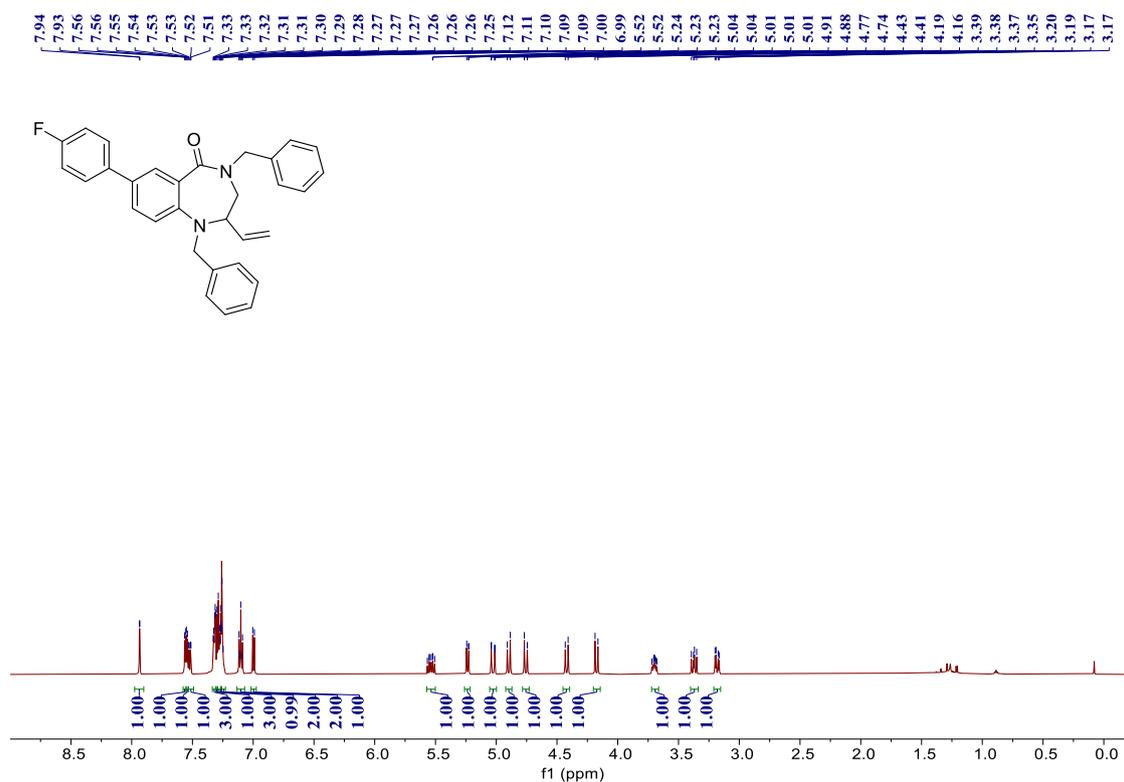


Figure S108. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-17b

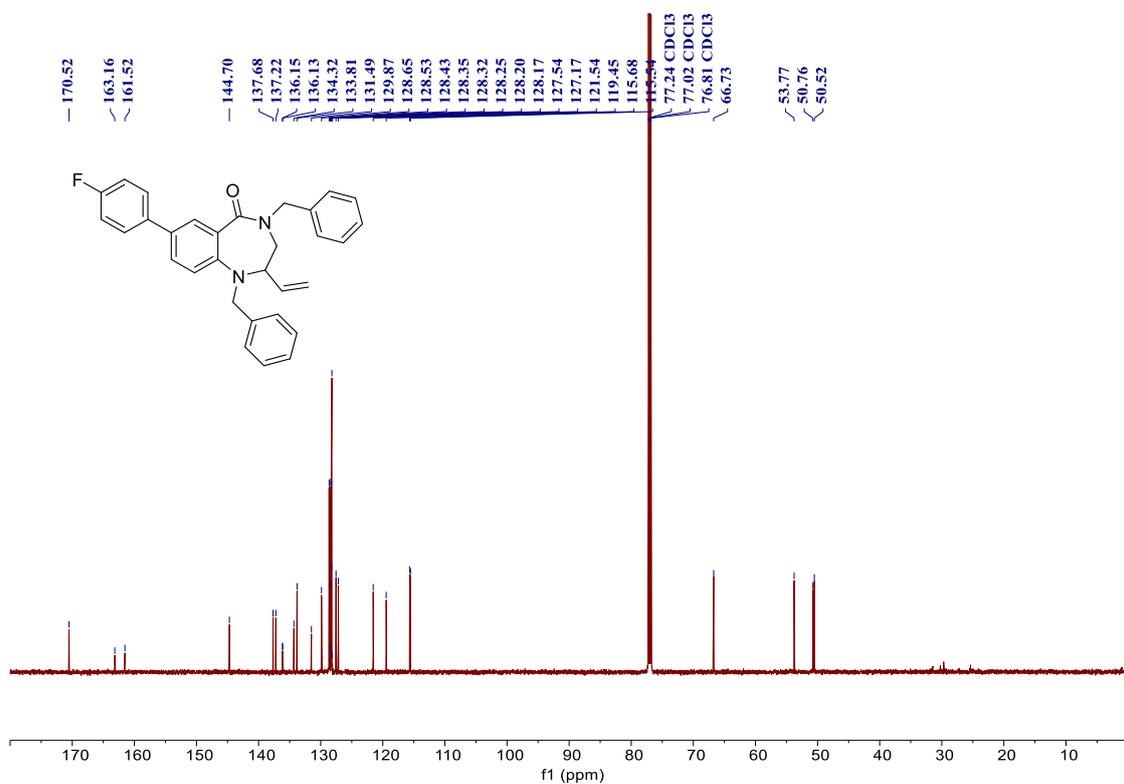


Figure S109. ^{19}F NMR (565 MHz, CDCl_3) spectrum of (*R*)-17b

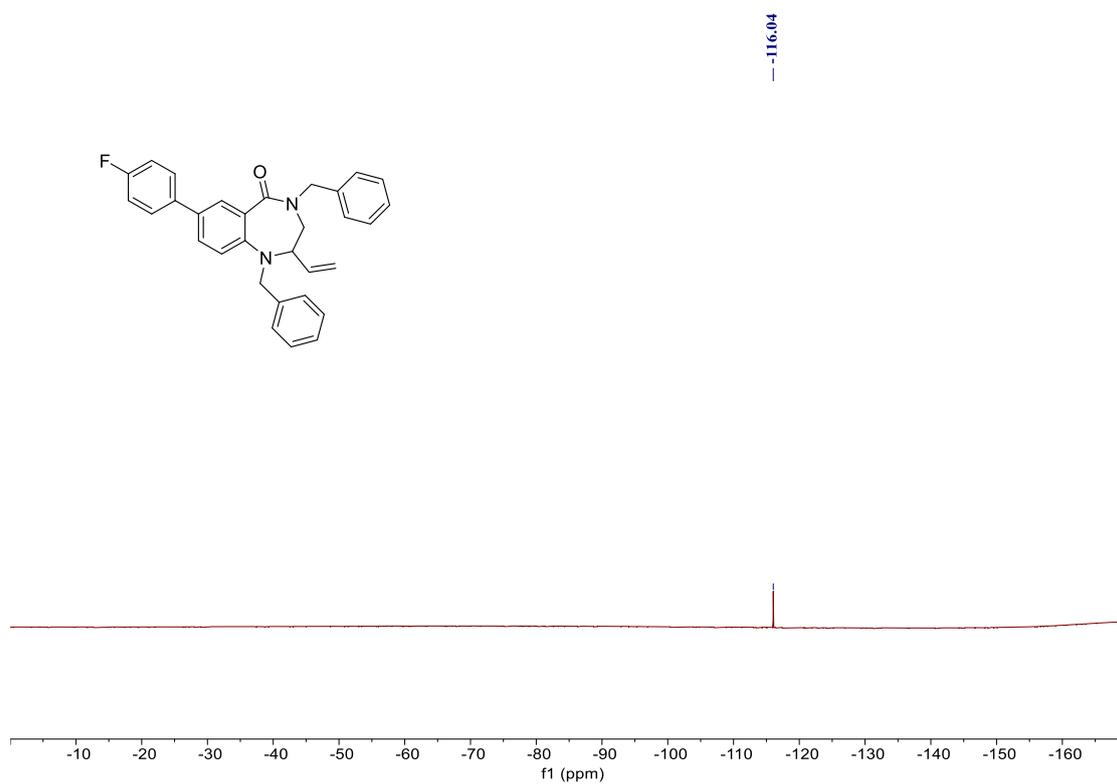


Figure S112. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-19b

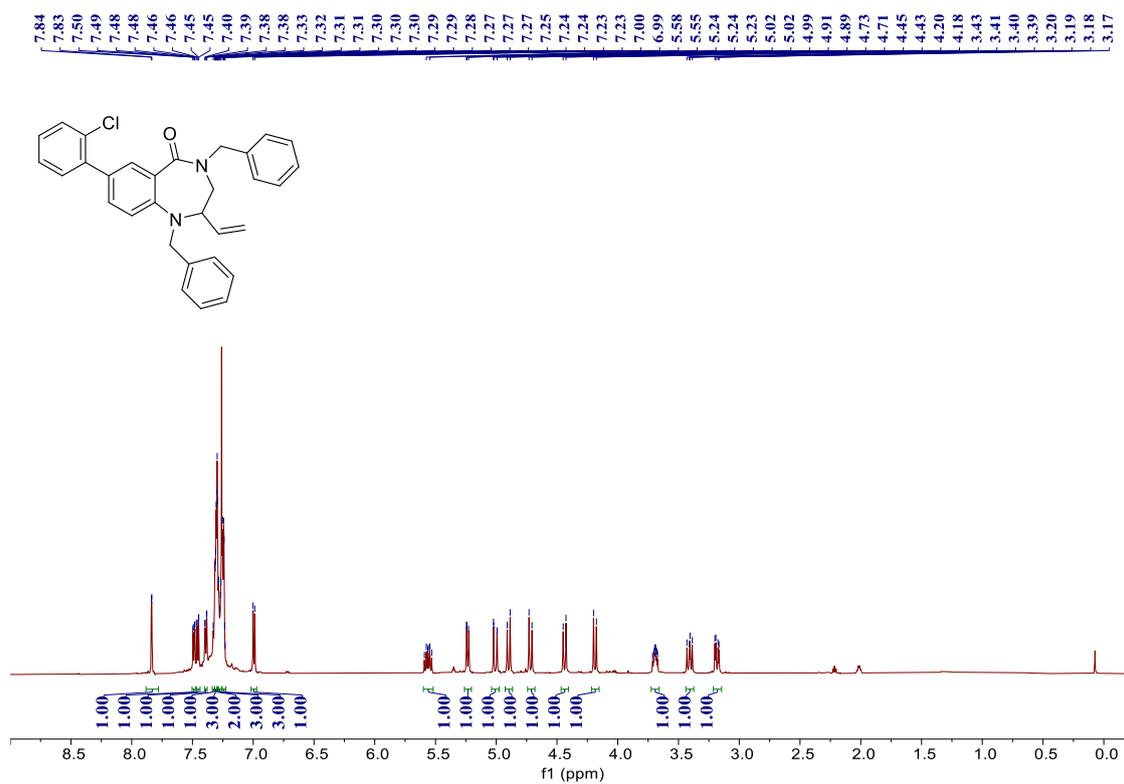


Figure S113. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-19b

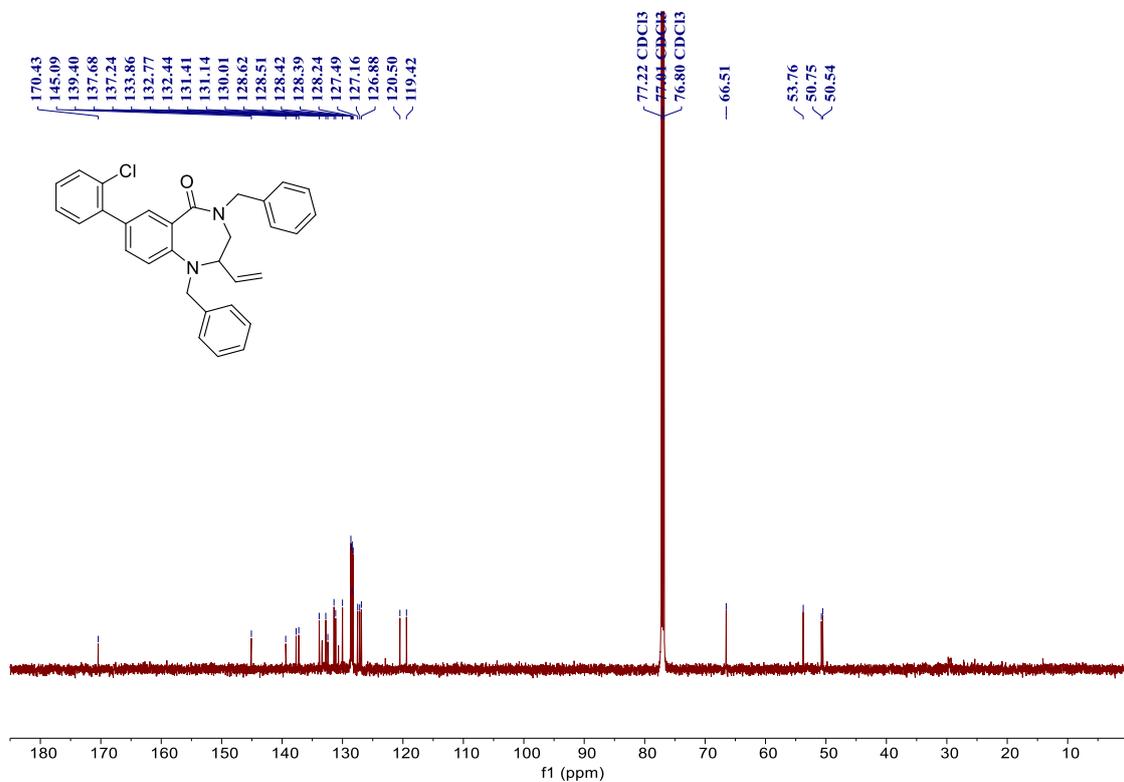


Figure S114. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-20b

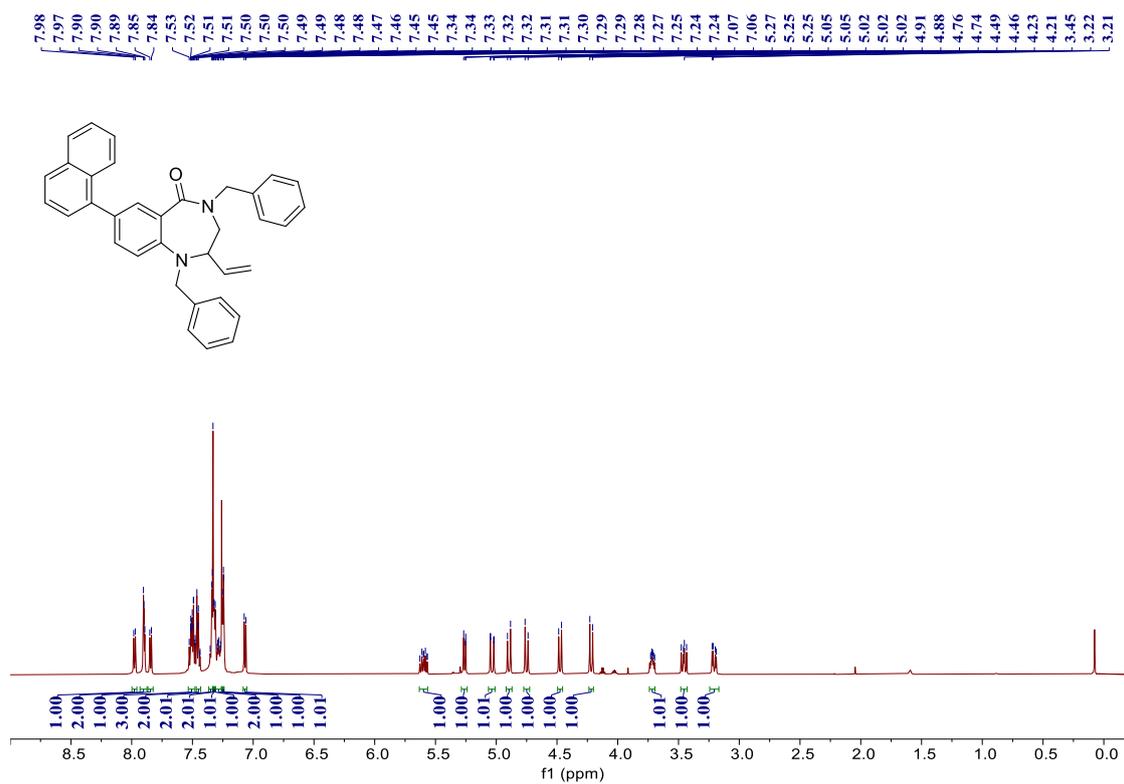


Figure S115. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-20b

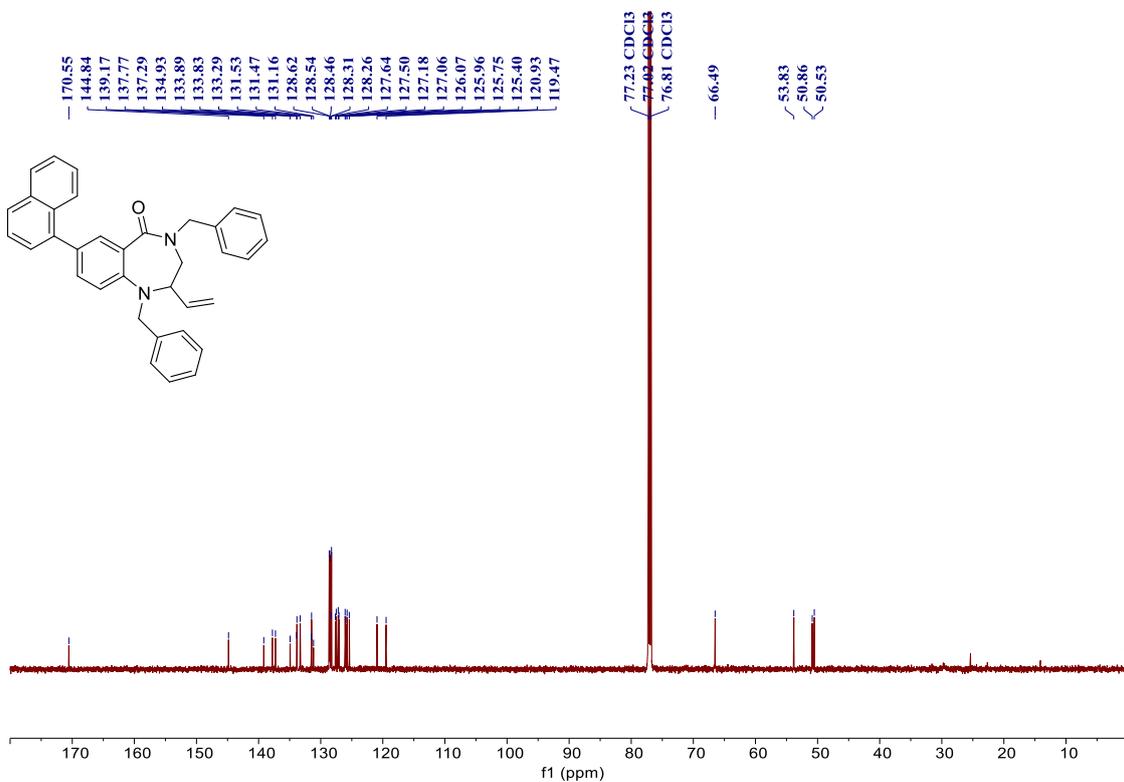


Figure S118. ¹H NMR (600 MHz, CDCl₃) spectrum of (R)-22b

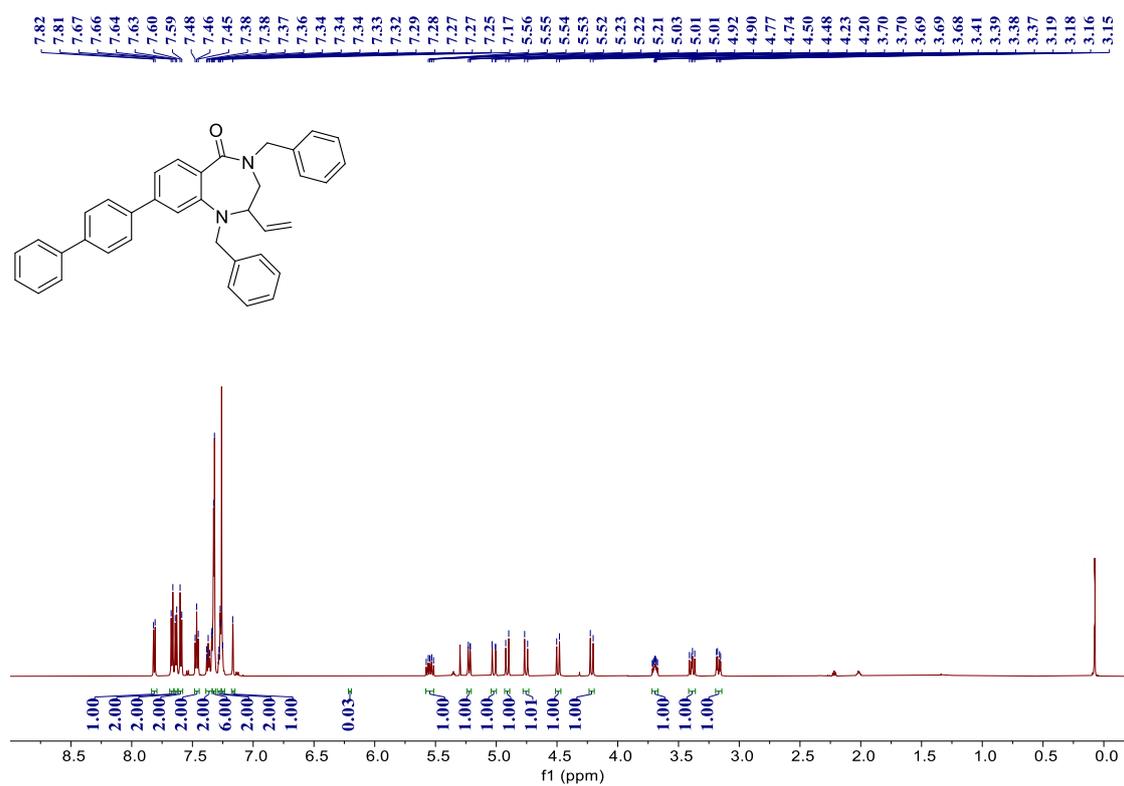


Figure S119. ¹³C NMR (151 MHz, CDCl₃) spectrum of (R)-22b

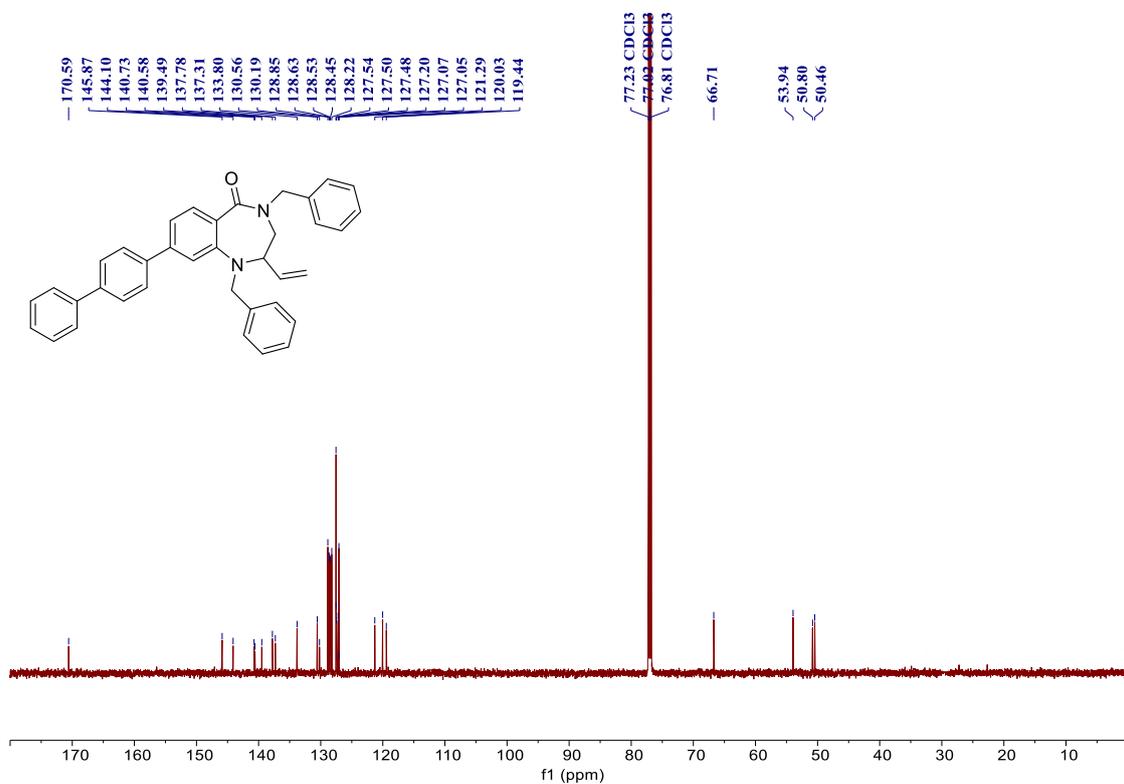


Figure S122. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-24b

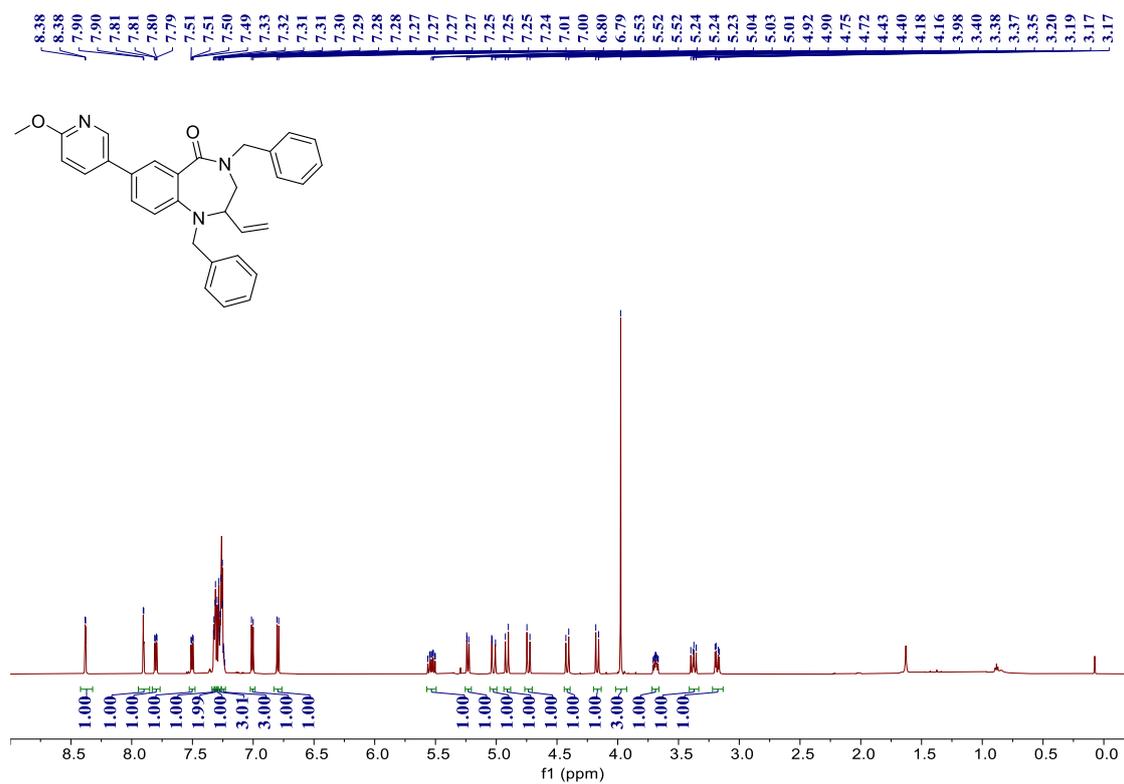


Figure S123. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-24b

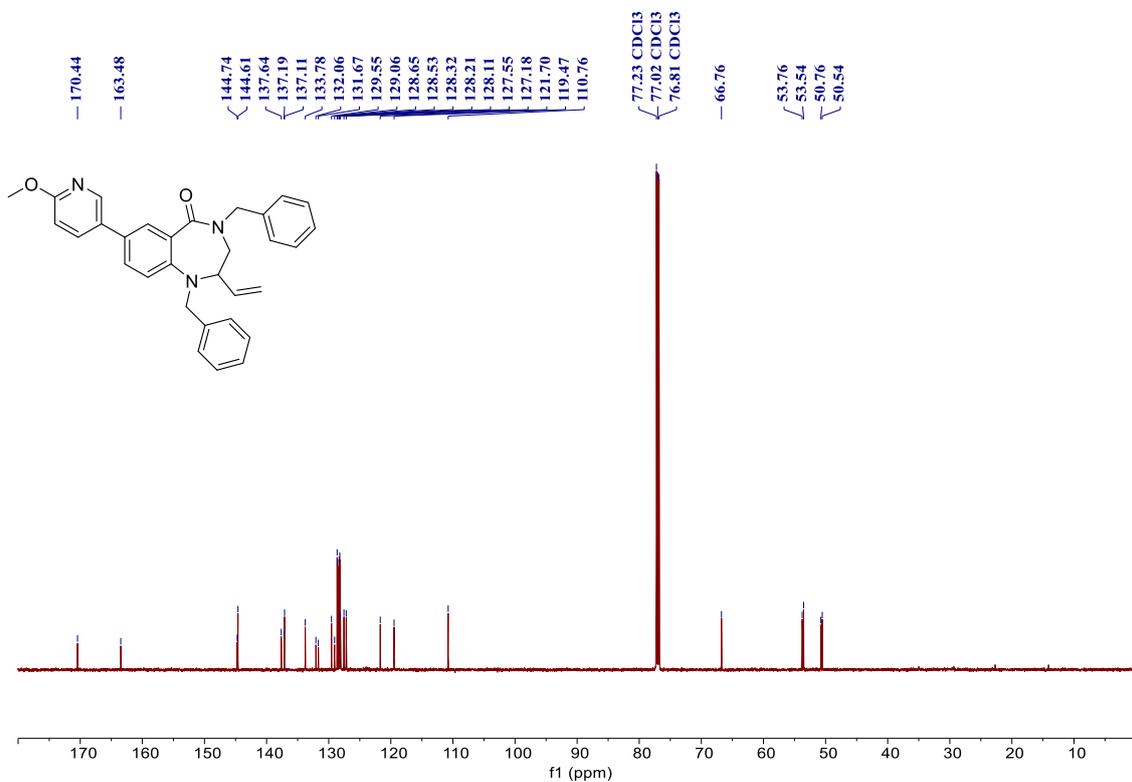


Figure S124. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-25b

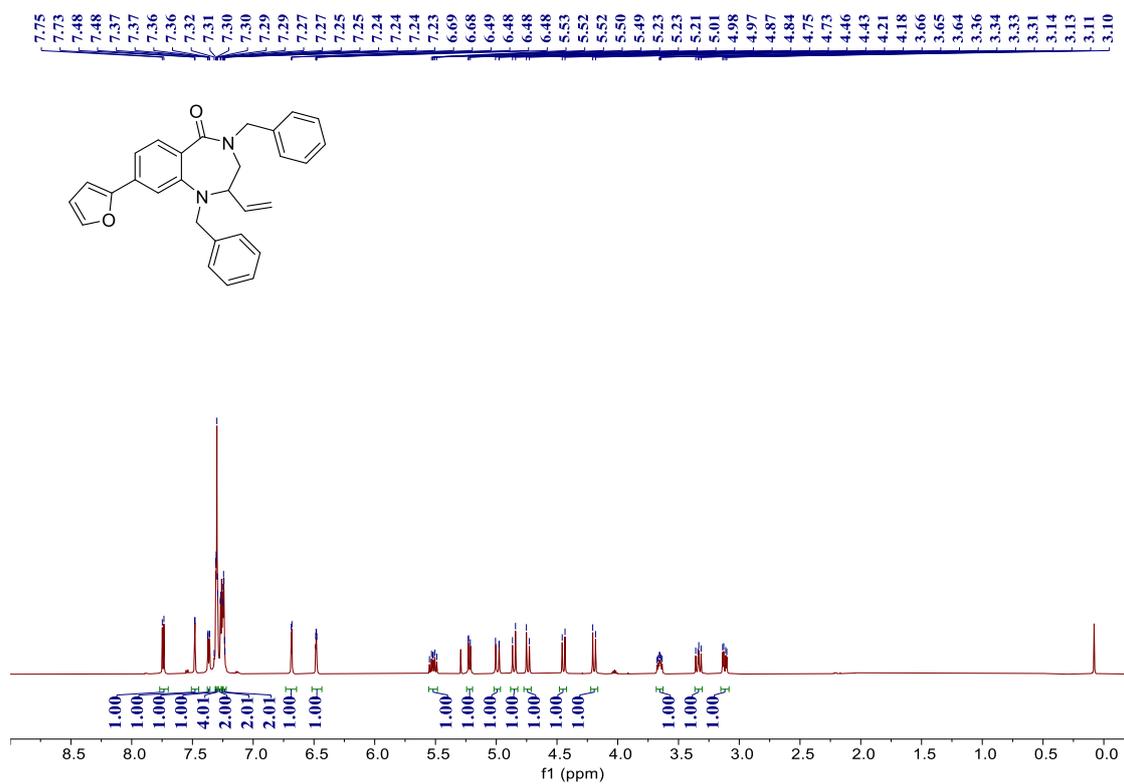


Figure S125. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-25b

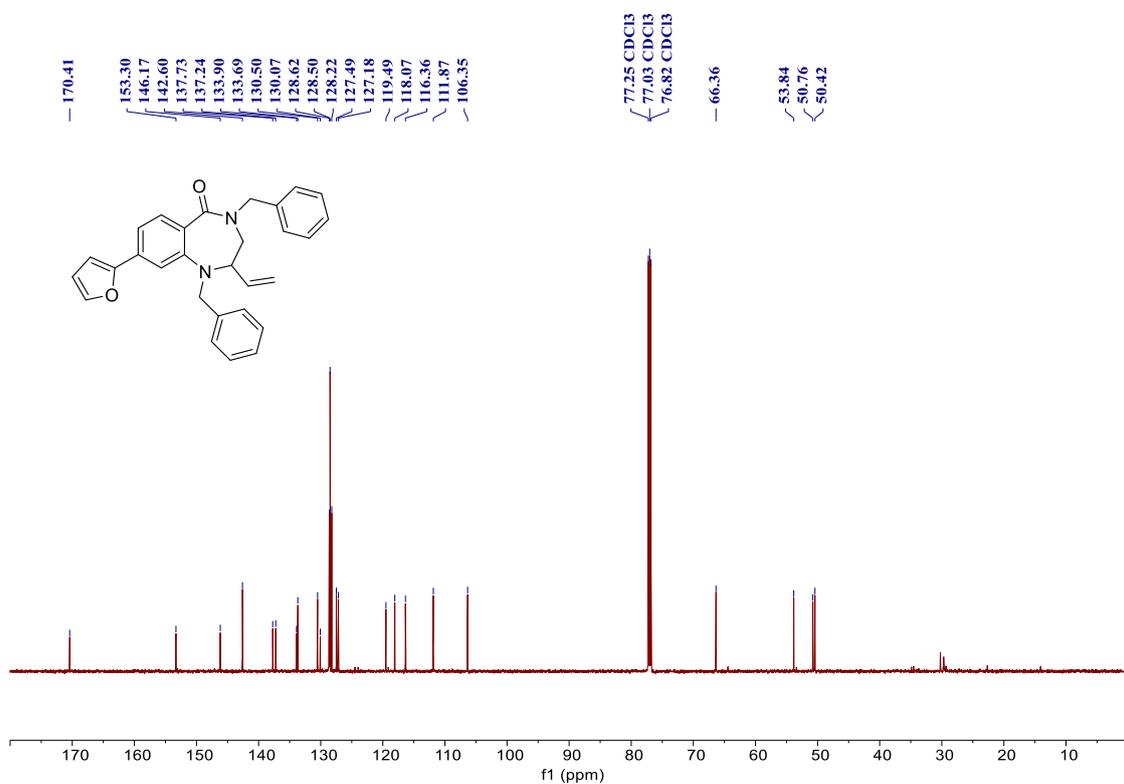


Figure S126. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-26b

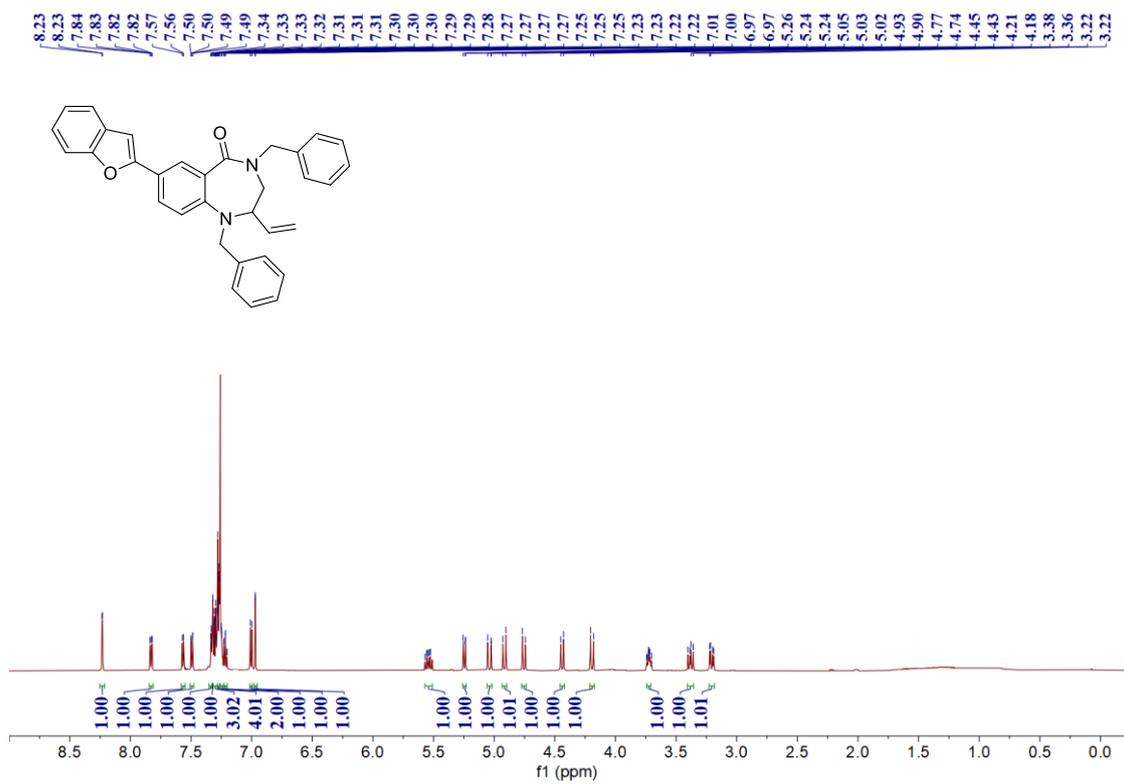


Figure S127. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-26b

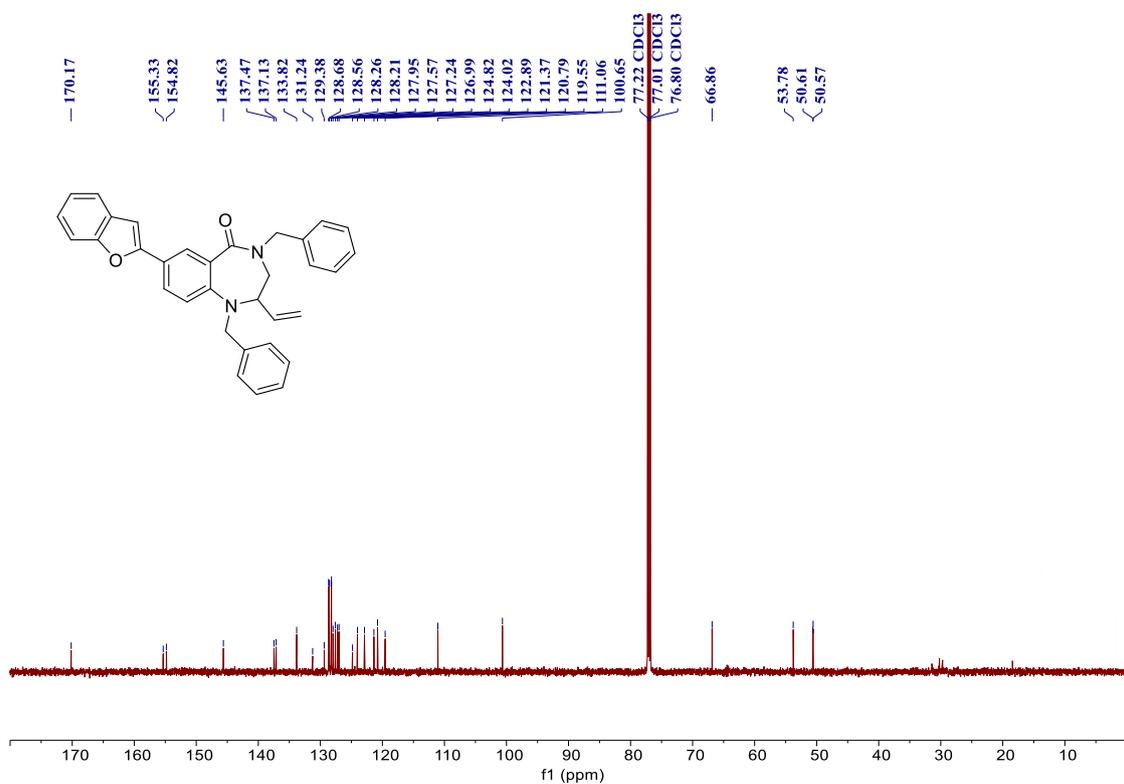


Figure S128. ¹H NMR (600 MHz, CDCl₃) spectrum of (R)-27b

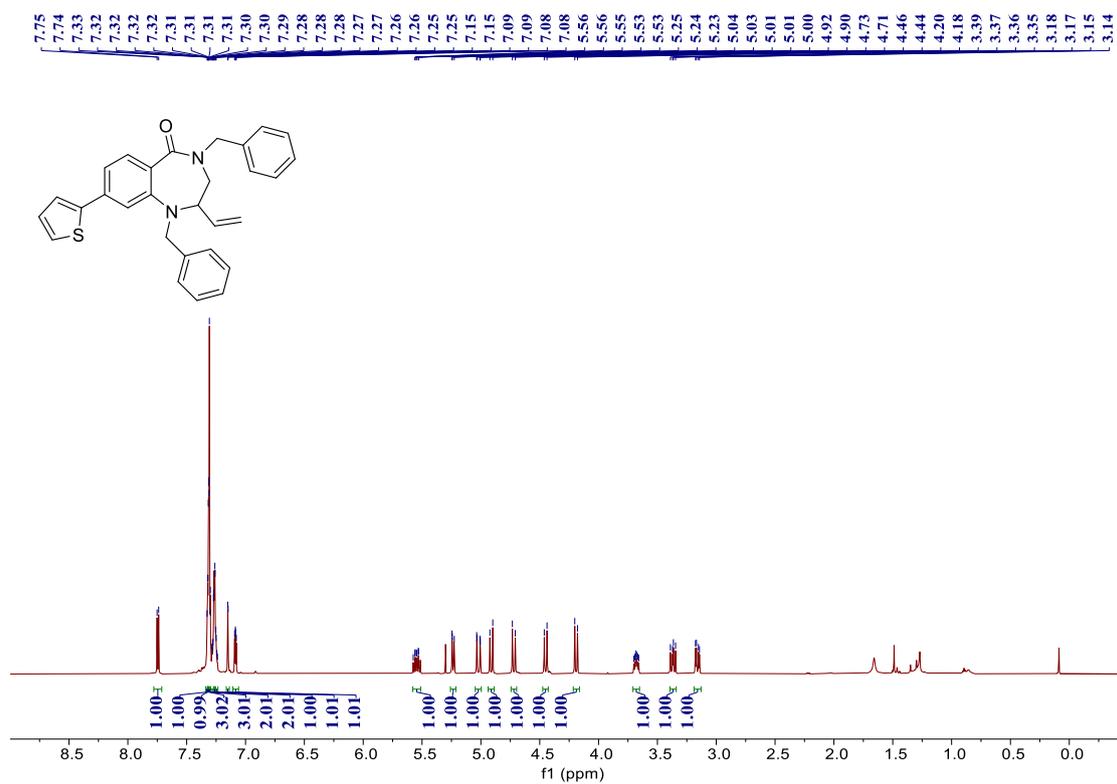


Figure S129. ¹³C NMR (151 MHz, CDCl₃) spectrum of (R)-27b

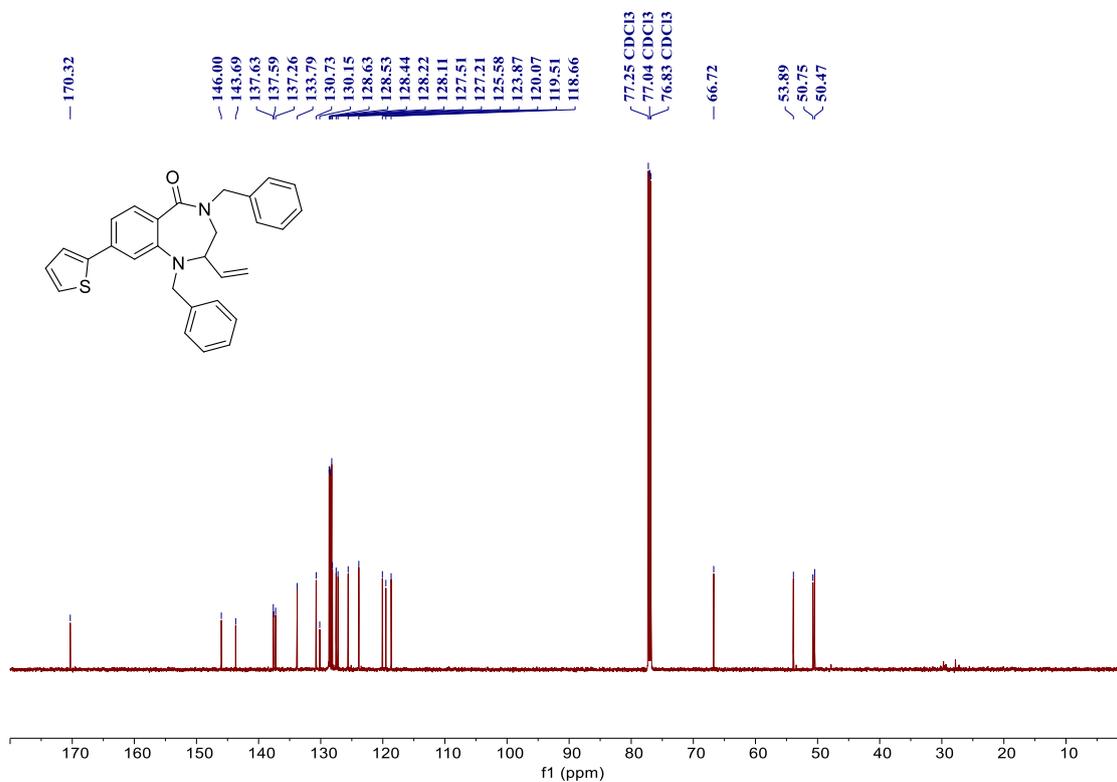


Figure S130. ¹H NMR (600 MHz, CDCl₃) spectrum of (R)-28b

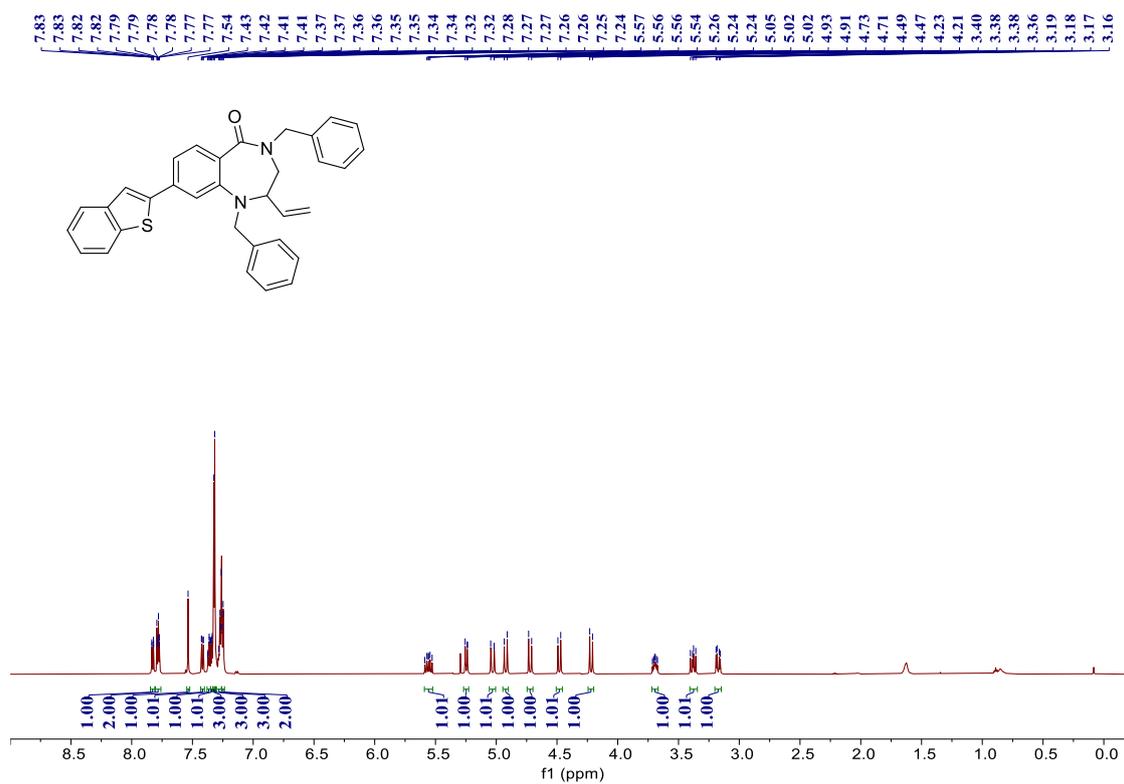


Figure S131. ¹³C NMR (151 MHz, CDCl₃) spectrum of (R)-28b

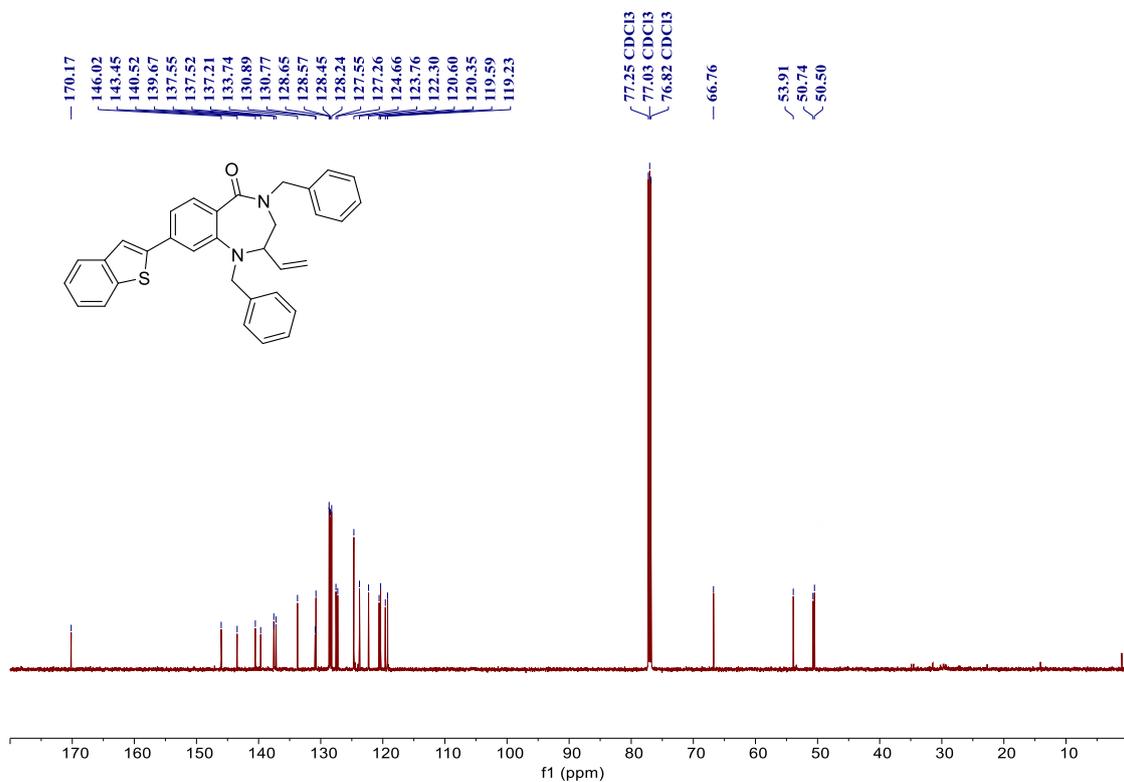


Figure S132 ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-29b

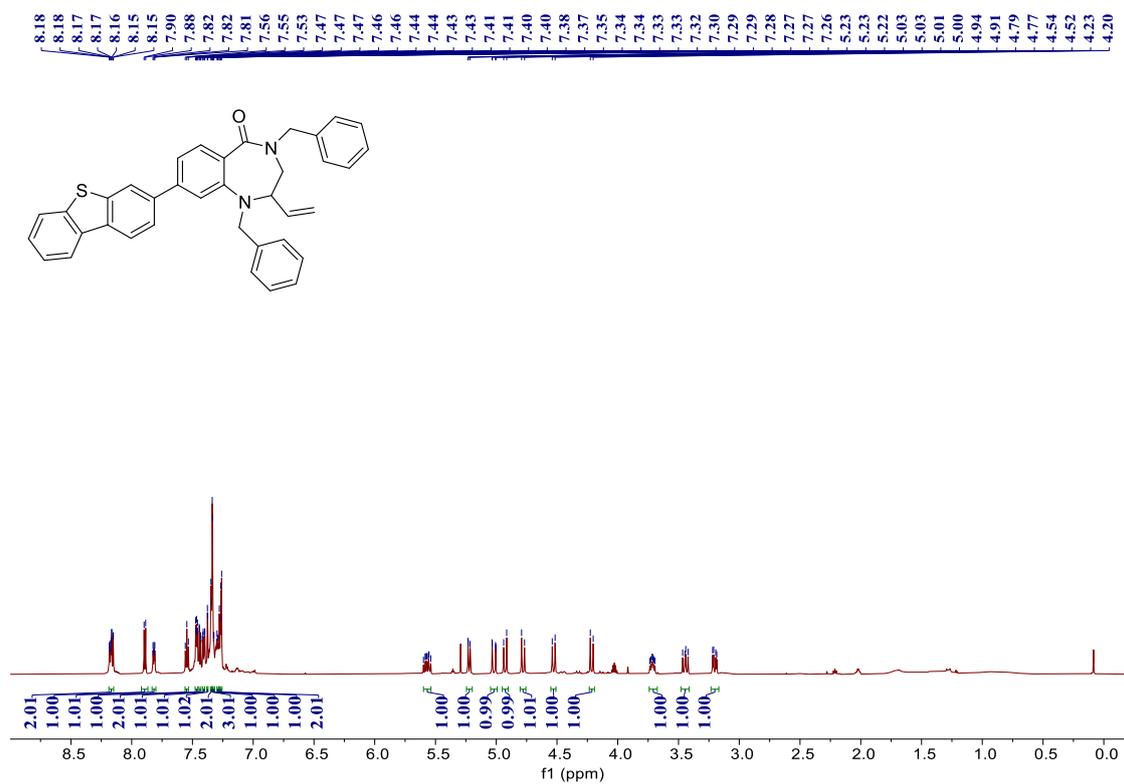


Figure S133. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-29b

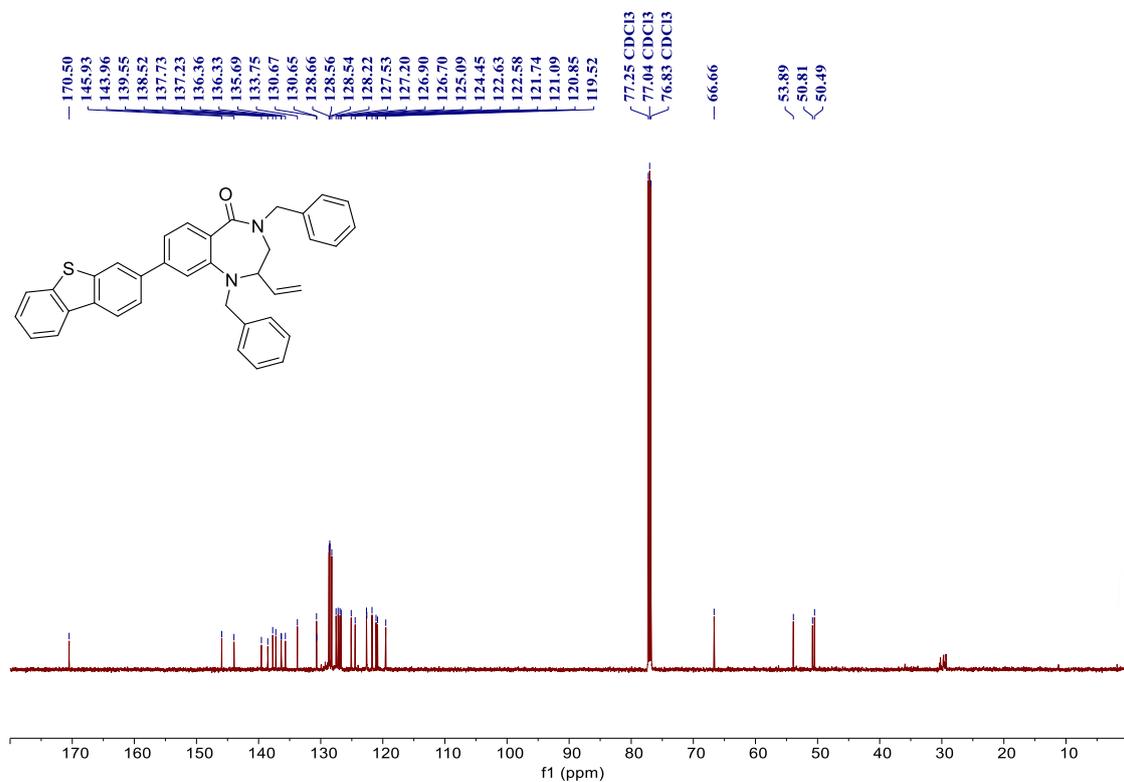


Figure S134. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-30b

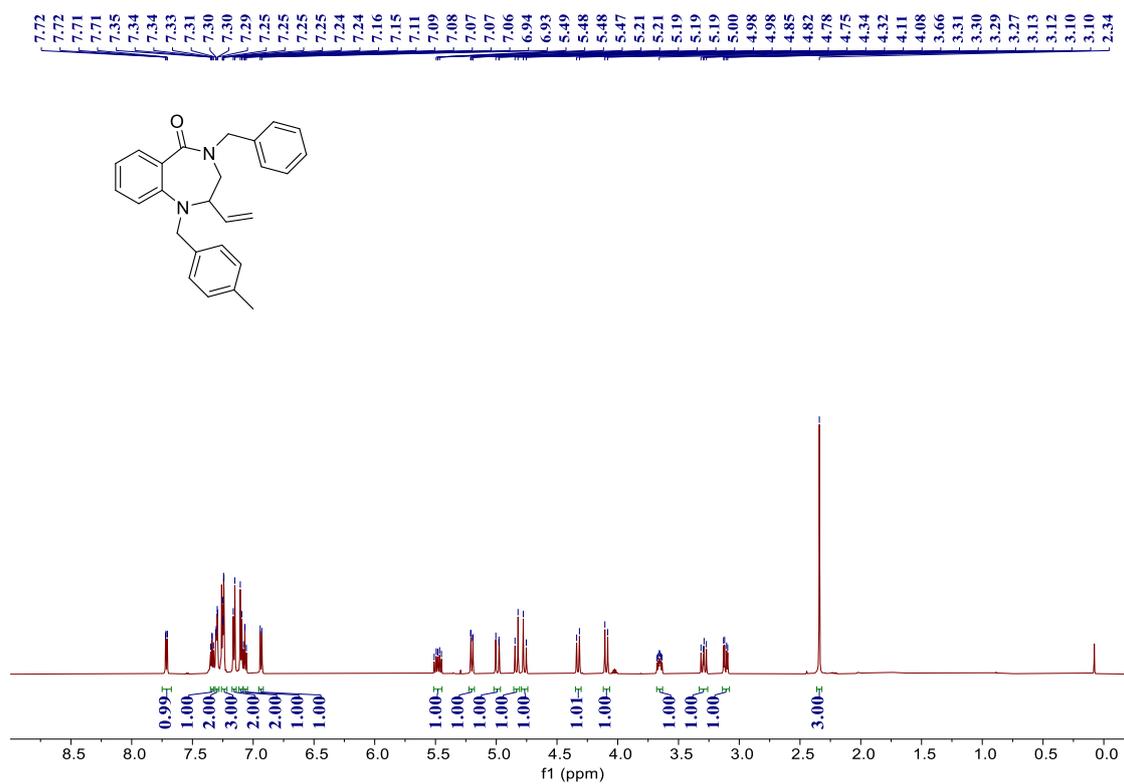


Figure S135. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-30b

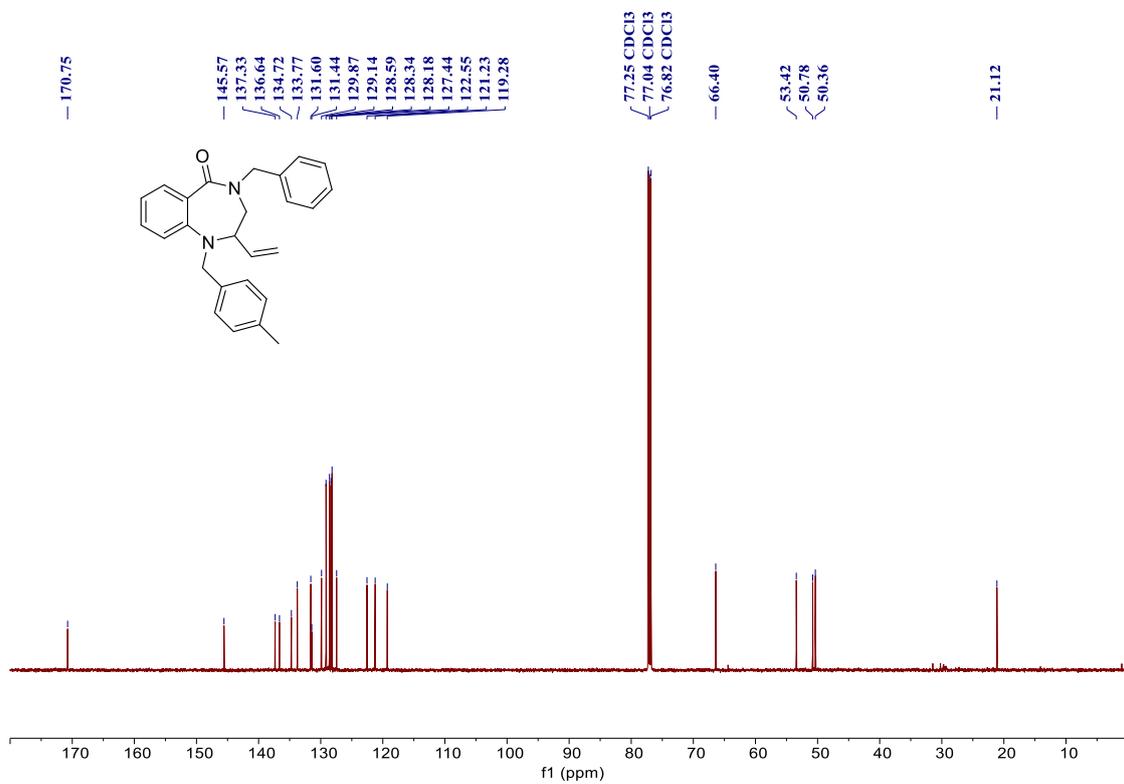


Figure S136. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-31b

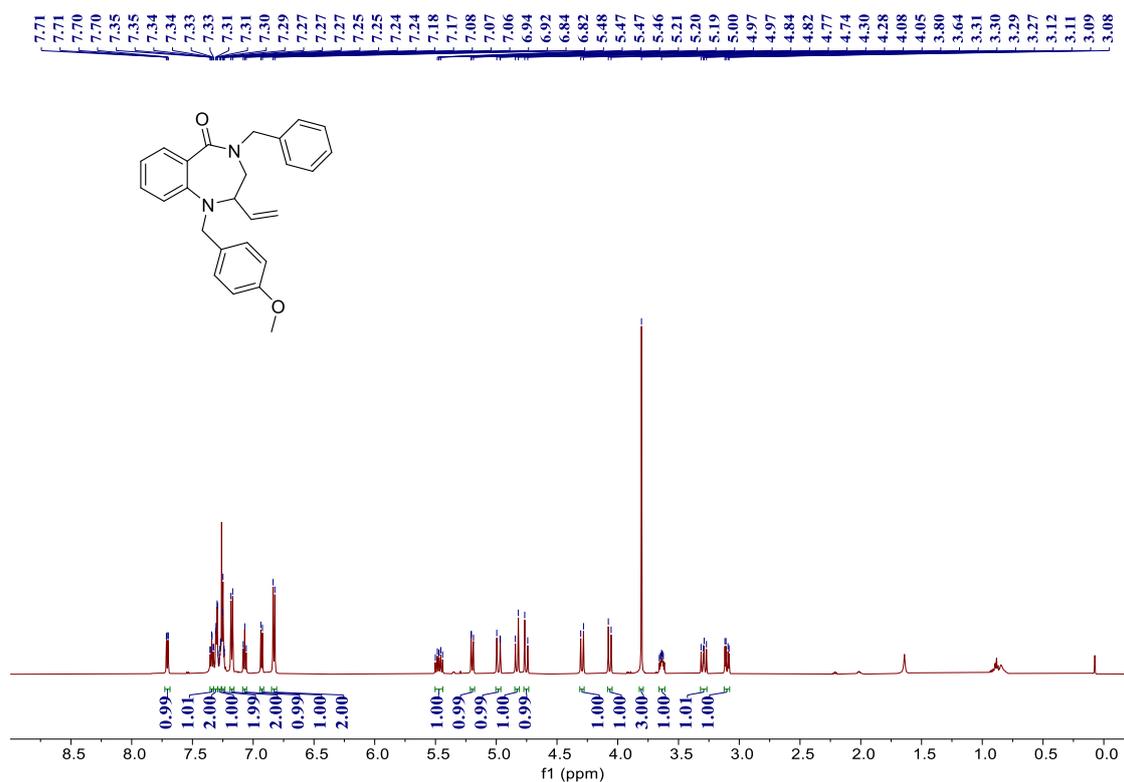


Figure S137. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-31b

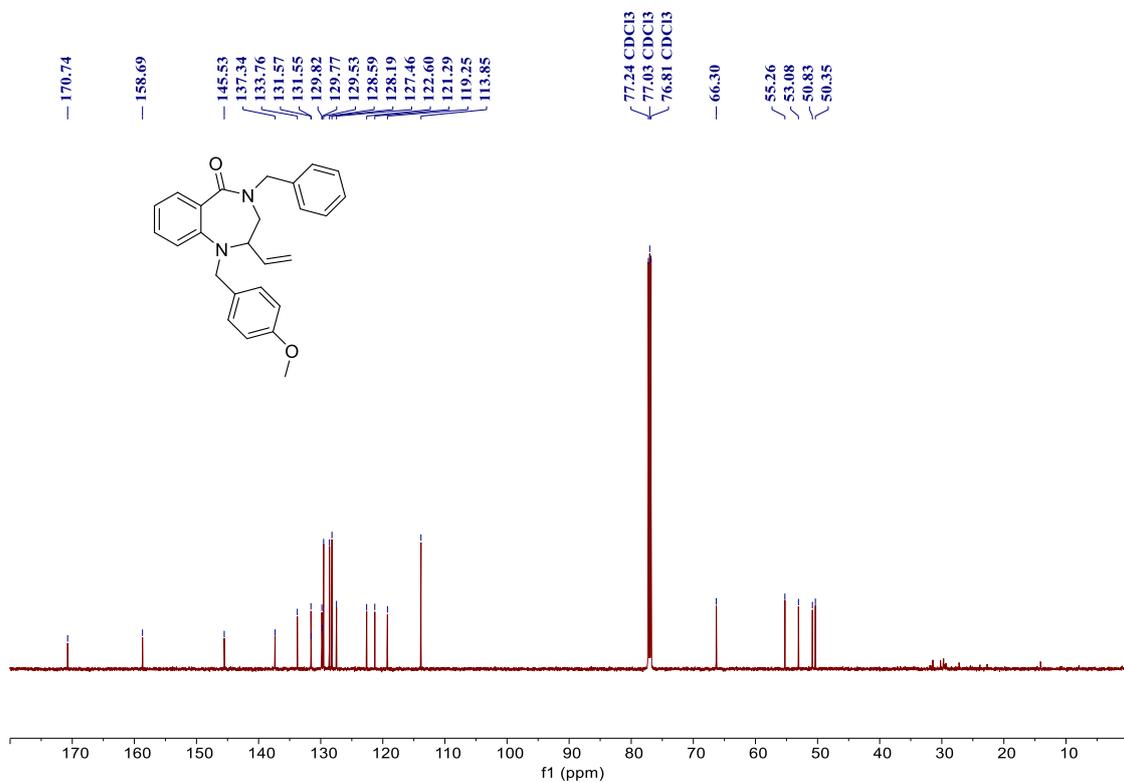


Figure S138. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-32b

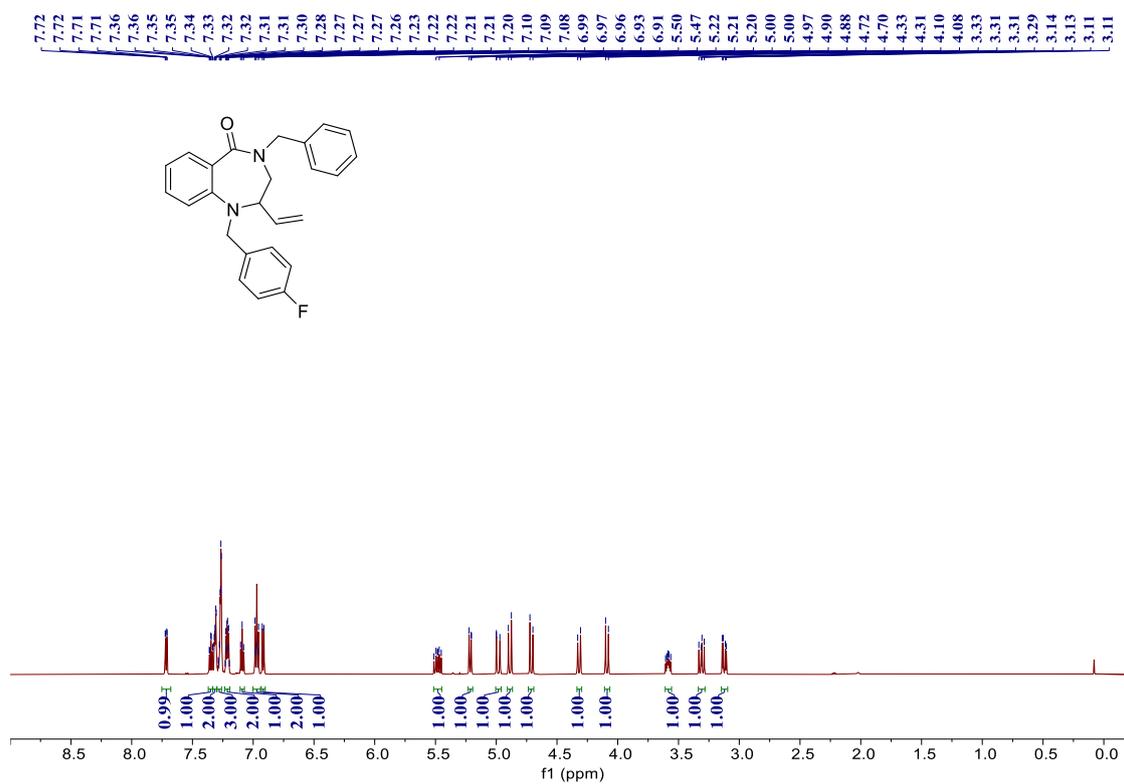


Figure S139. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-32b

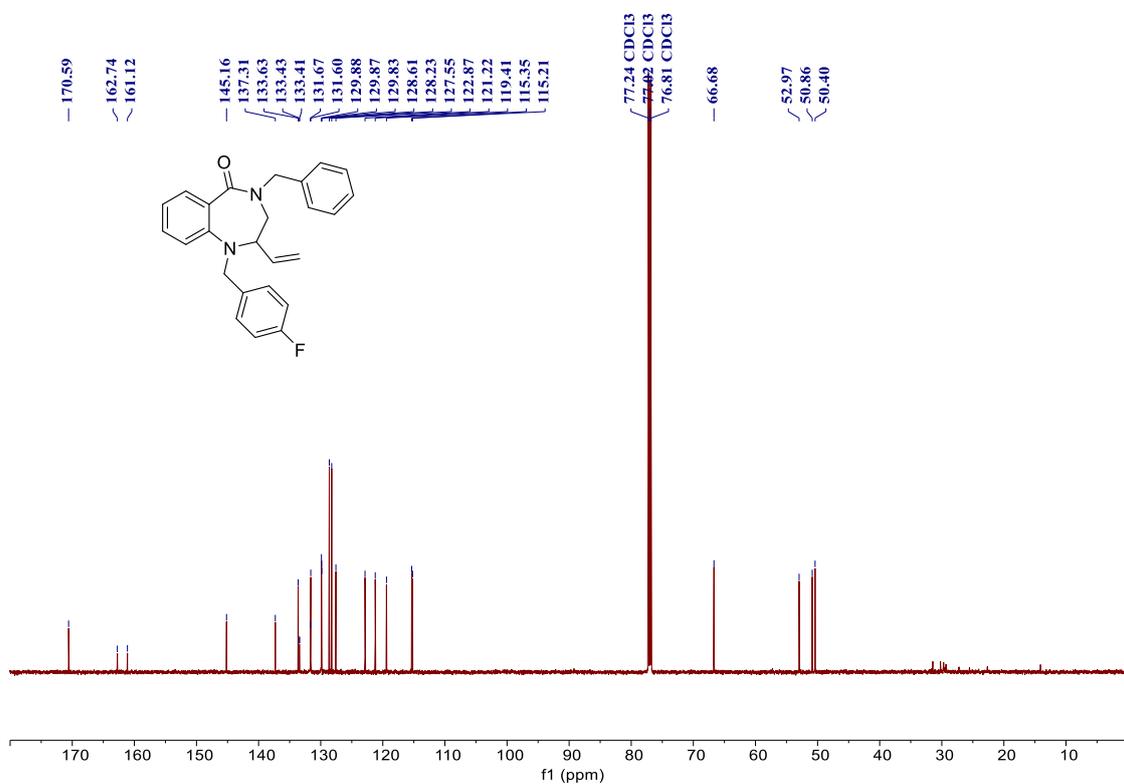


Figure S140. ^{19}F NMR (565 MHz, CDCl_3) spectrum of (*R*)-32b

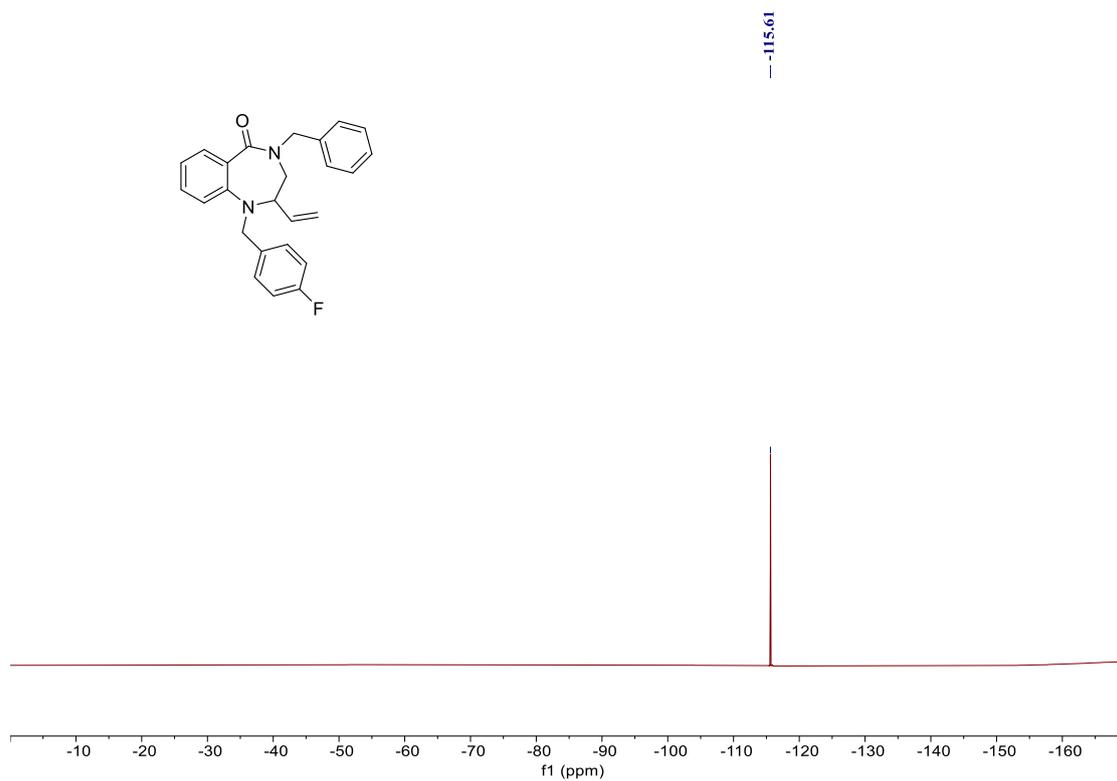


Figure S141. ¹H NMR (600 MHz, CDCl₃) spectrum of (R)-33b

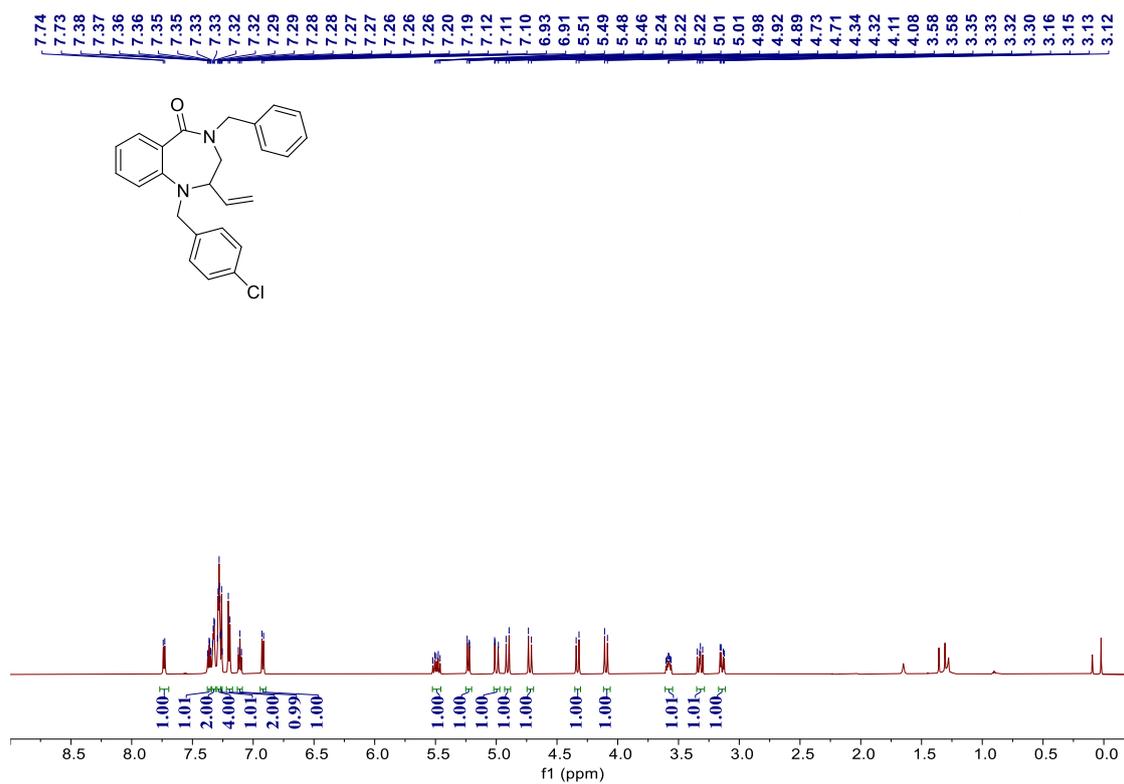


Figure S142. ¹³C NMR (151 MHz, CDCl₃) spectrum of (R)-33b

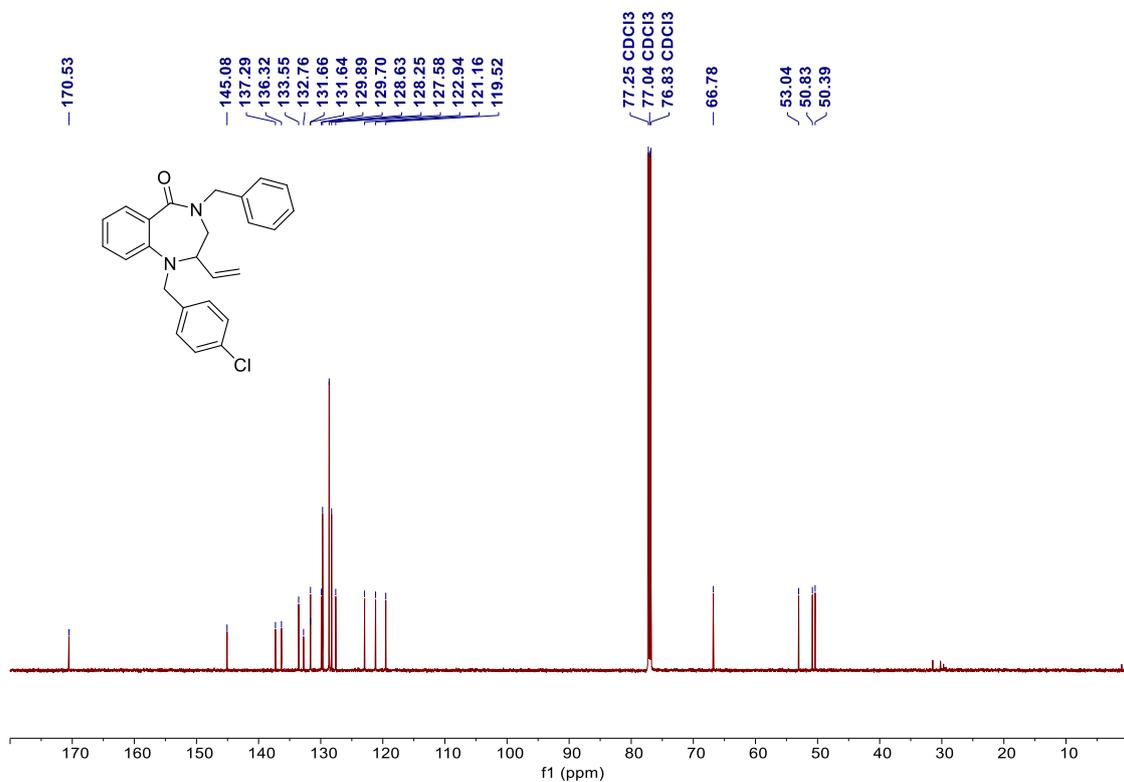


Figure S143. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-34b

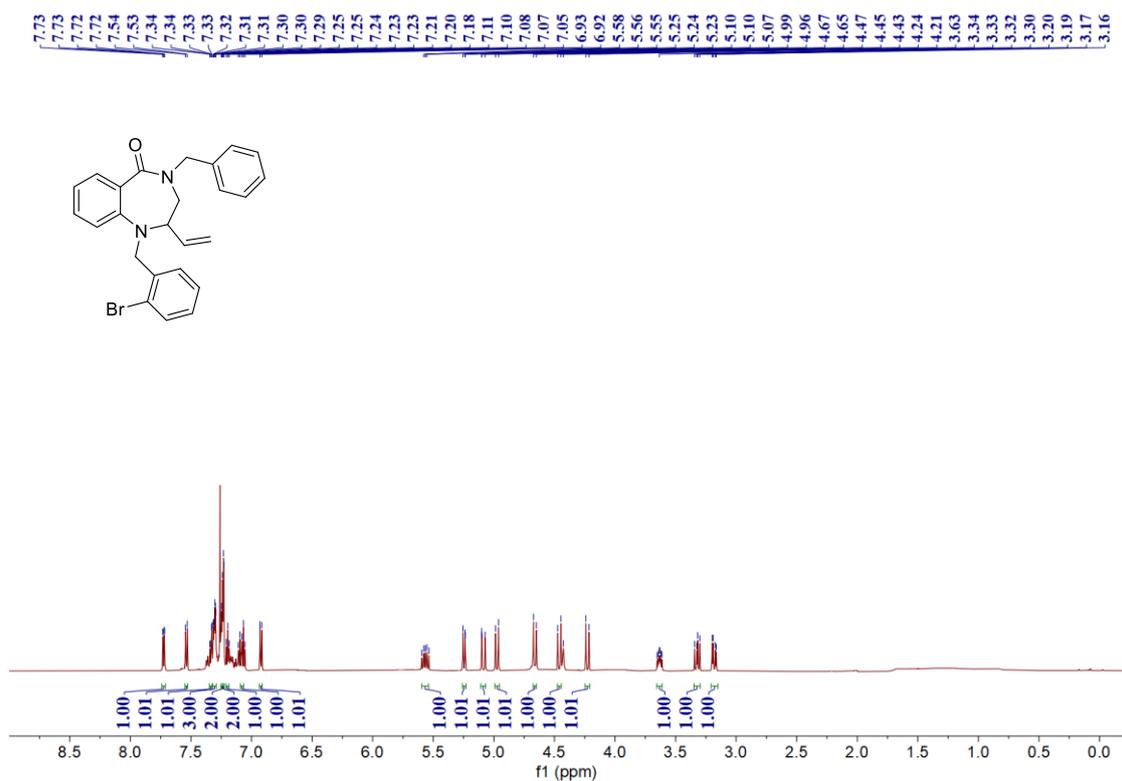


Figure S144. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-34b

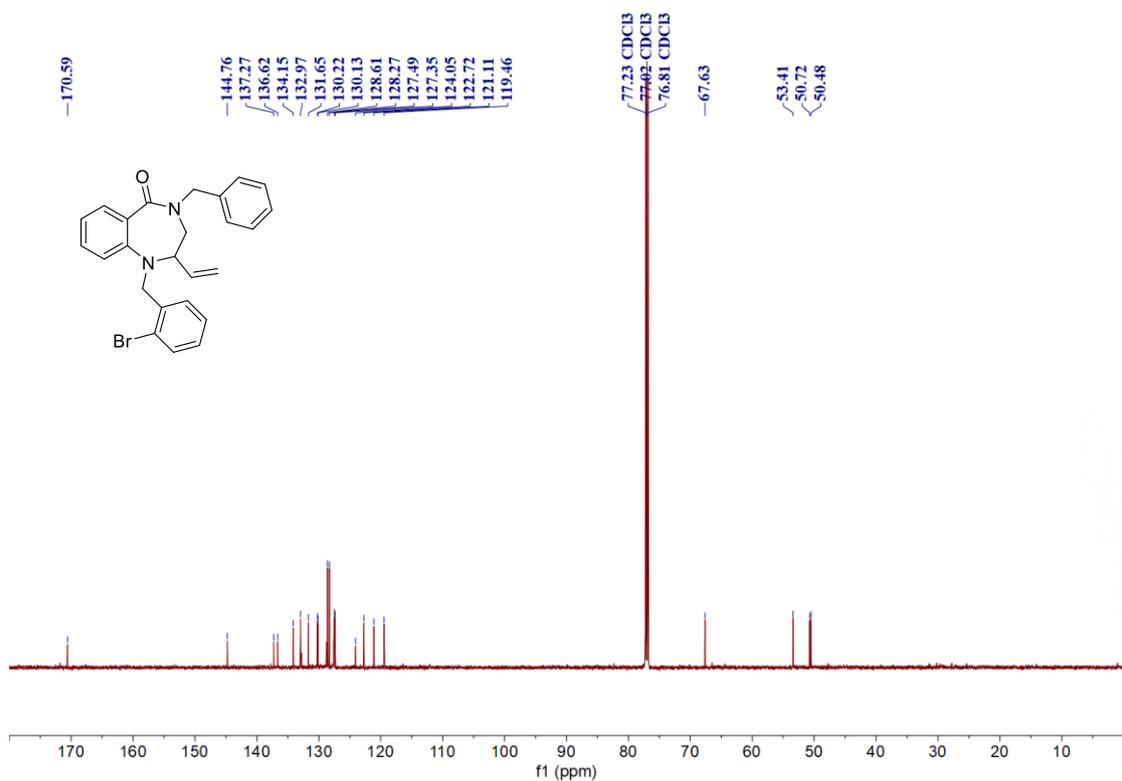


Figure S145. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-10c

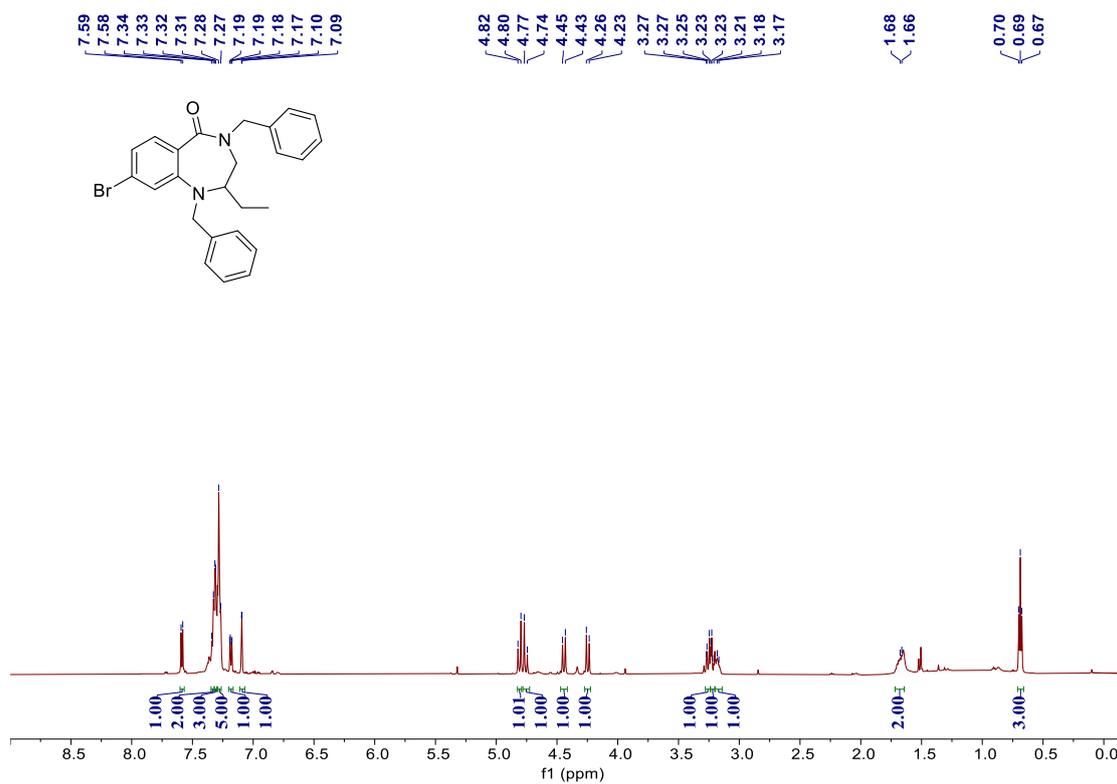


Figure S146. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-10c

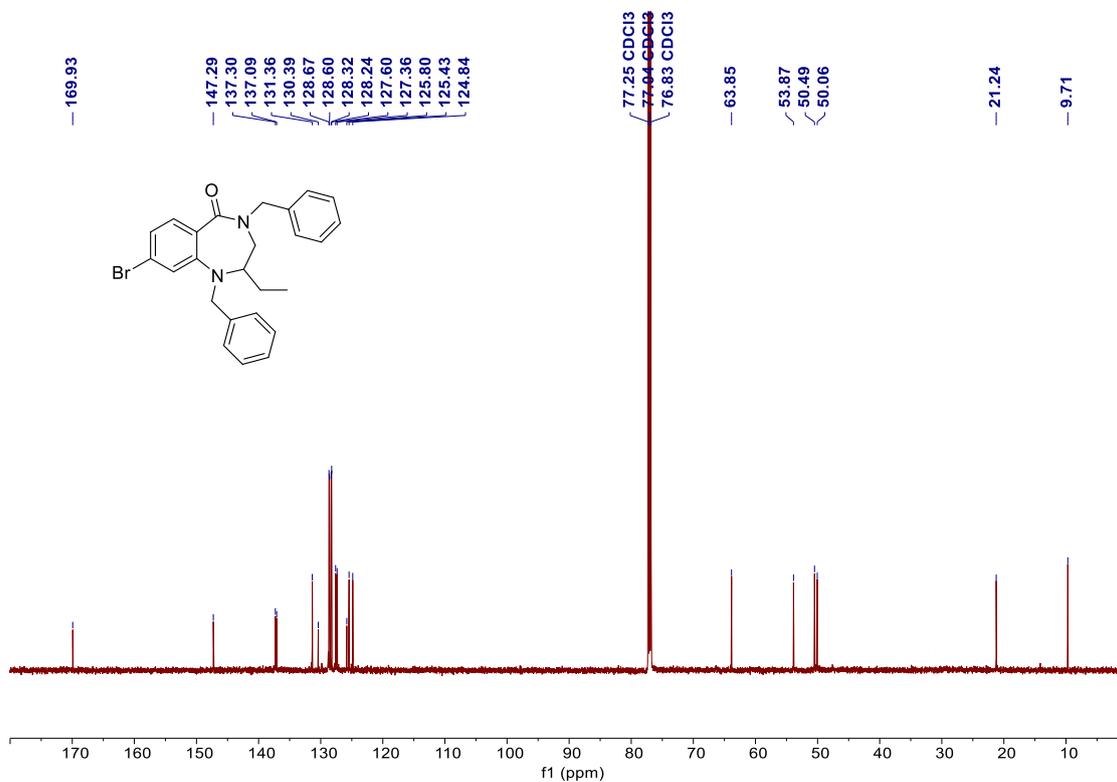


Figure S147. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-10d

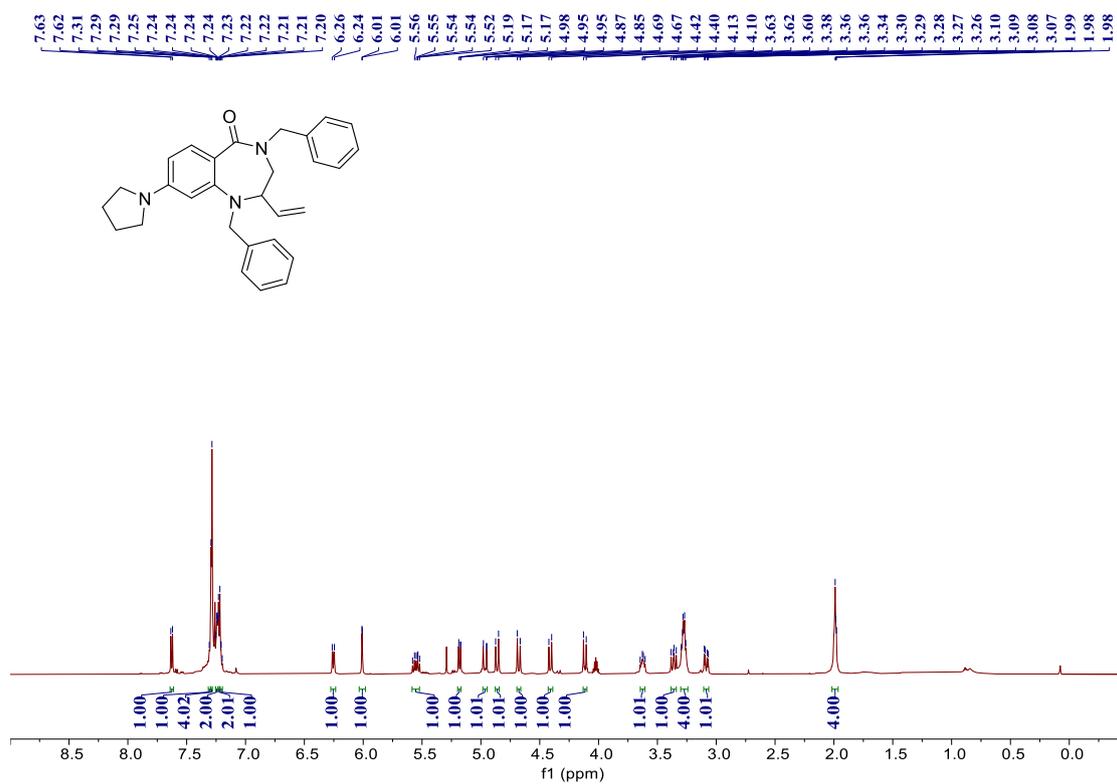


Figure S148. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-10d

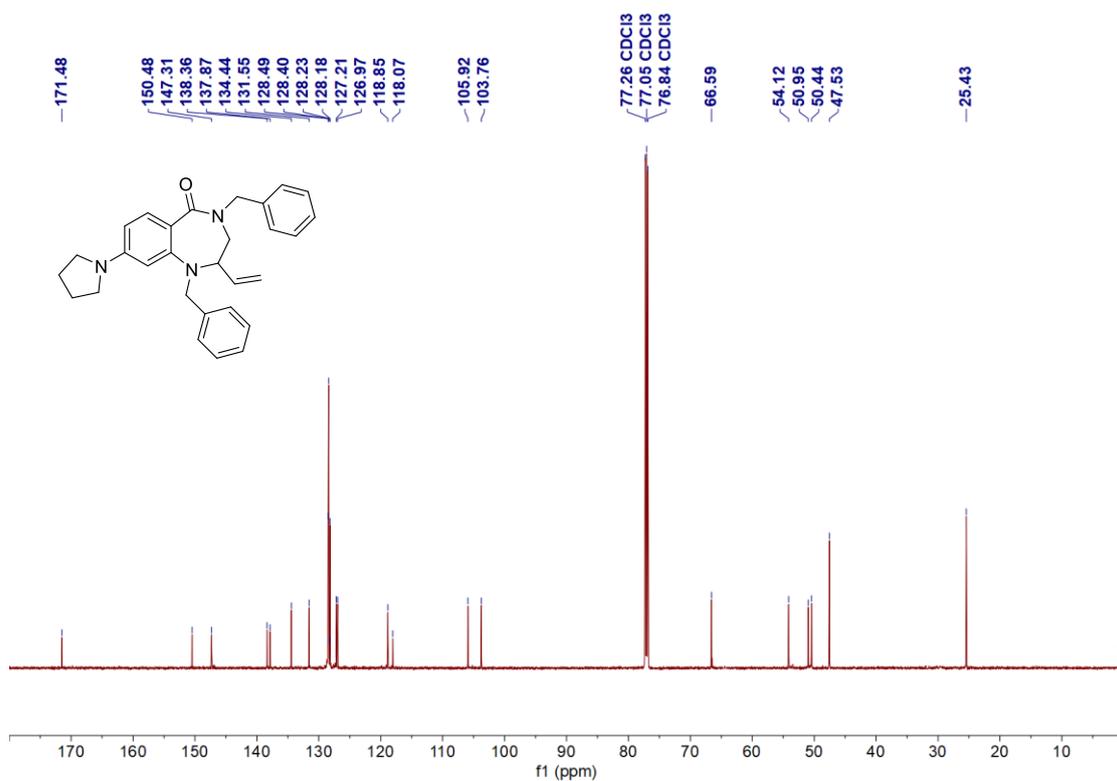


Figure S149. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-10e

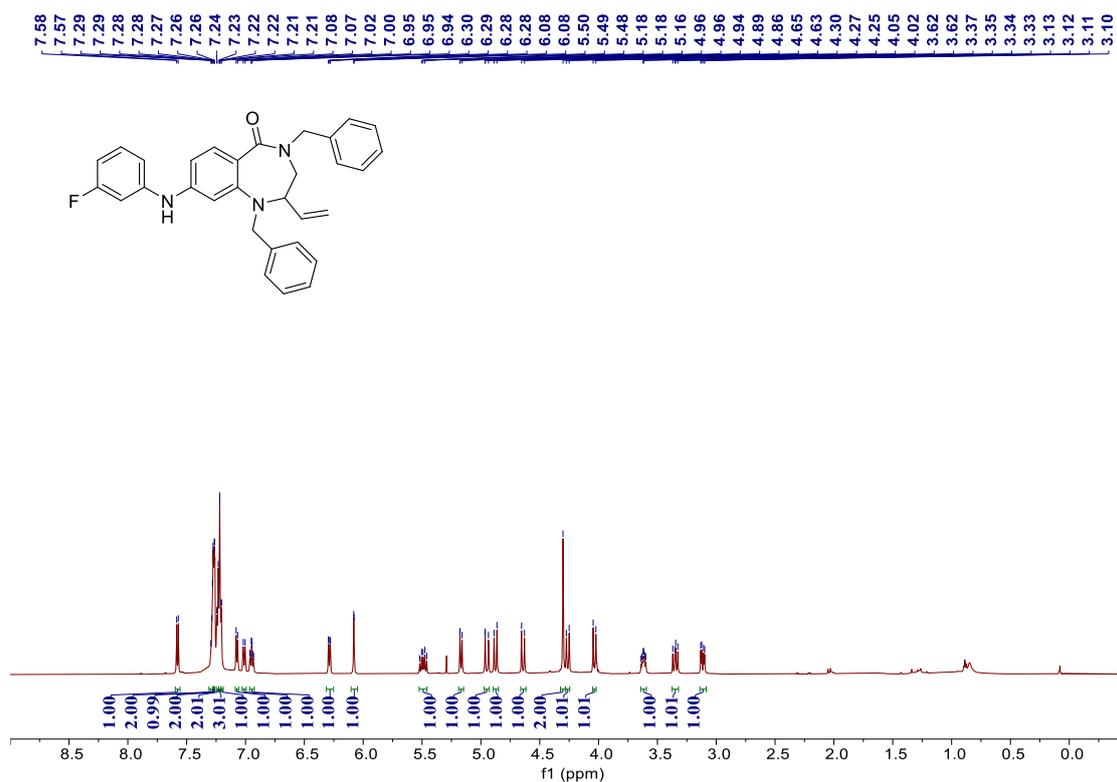


Figure S150. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-10e

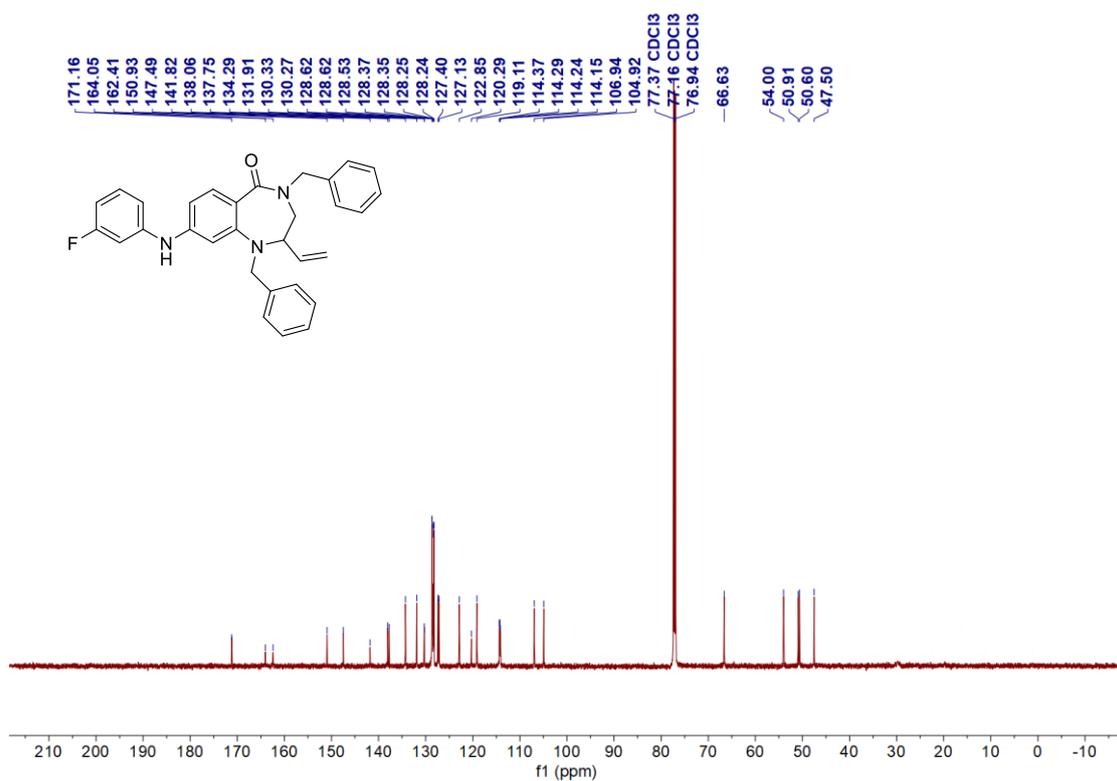


Figure S151. ^{19}F NMR (565 MHz, CDCl_3) spectrum of (*R*)-10e

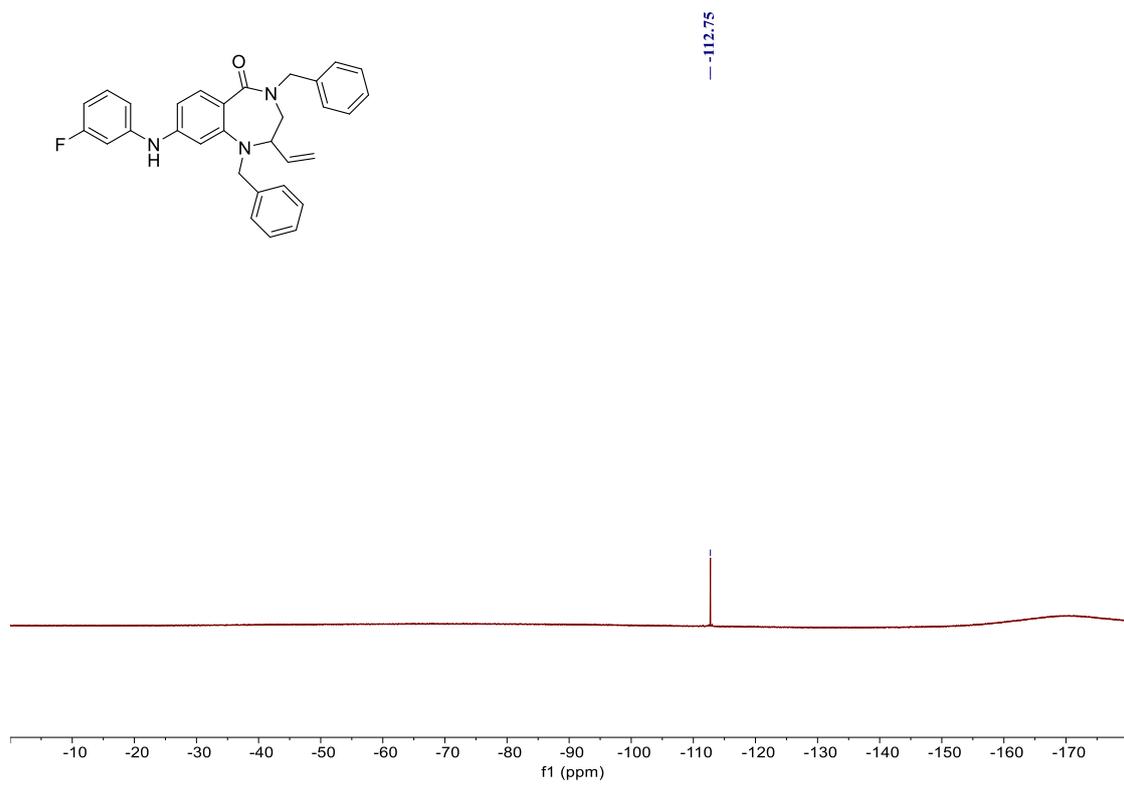


Figure S152. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-1b'

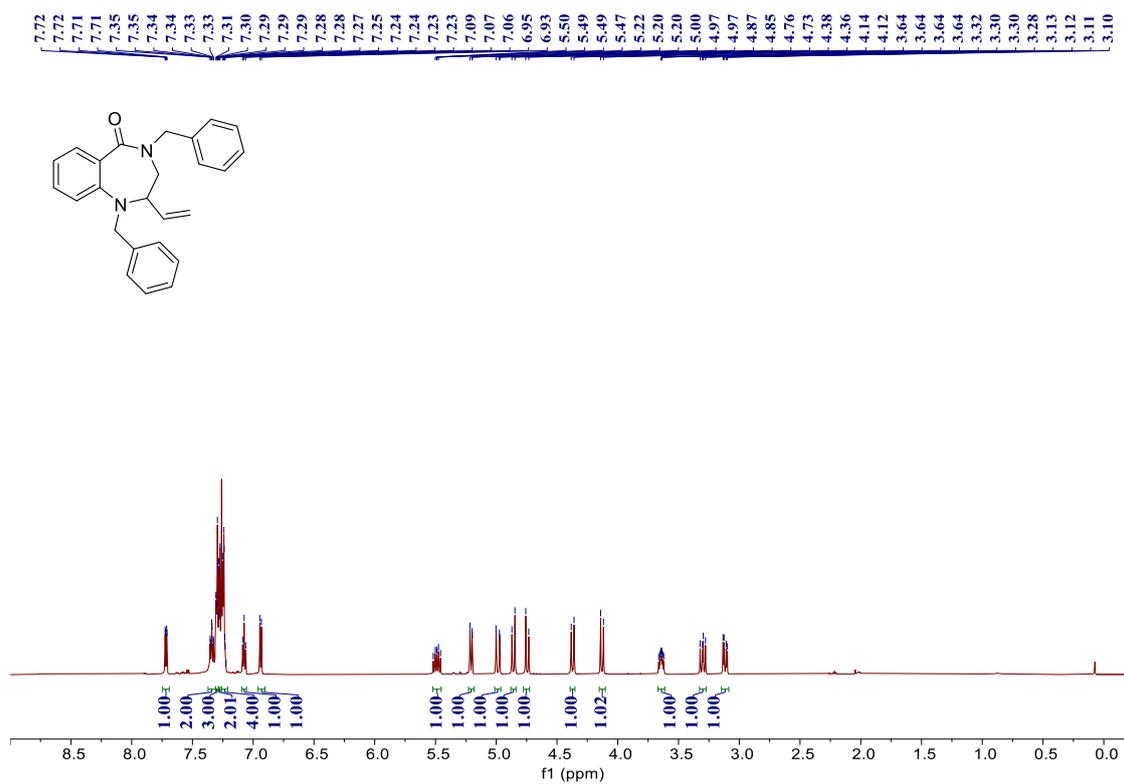


Figure S153. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-1b'

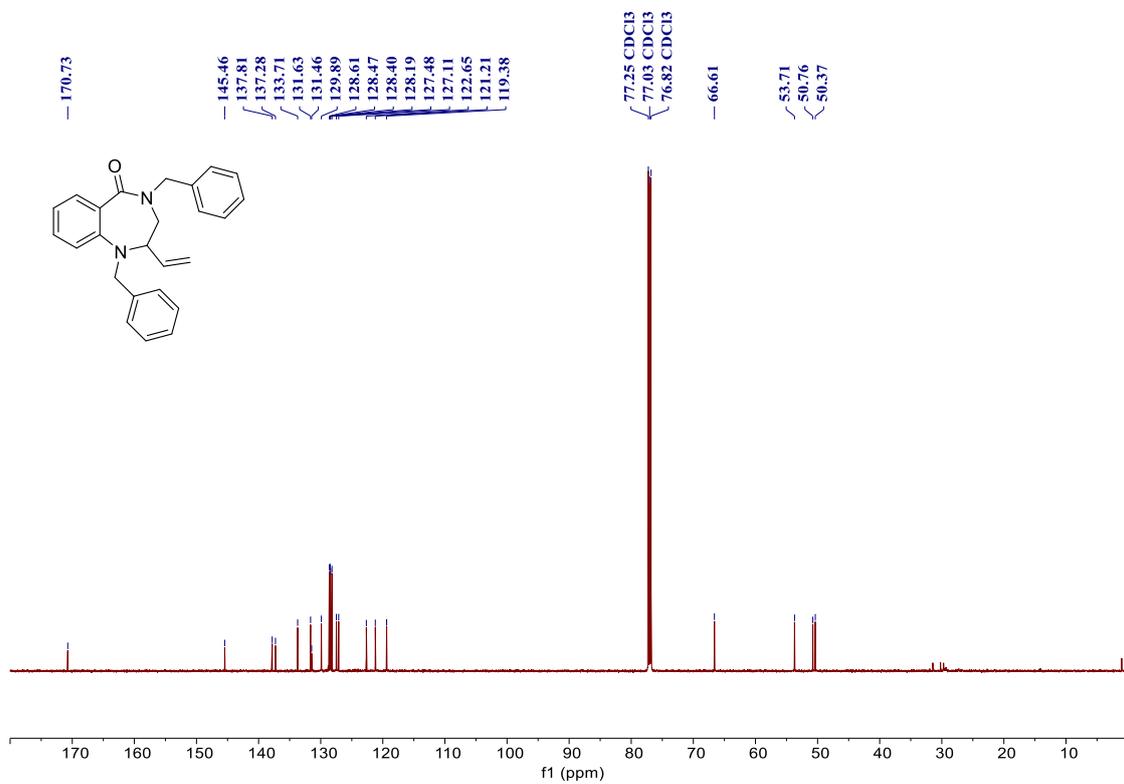


Figure S154. ¹H NMR (600 MHz, CDCl₃) spectrum of (*R*)-2c

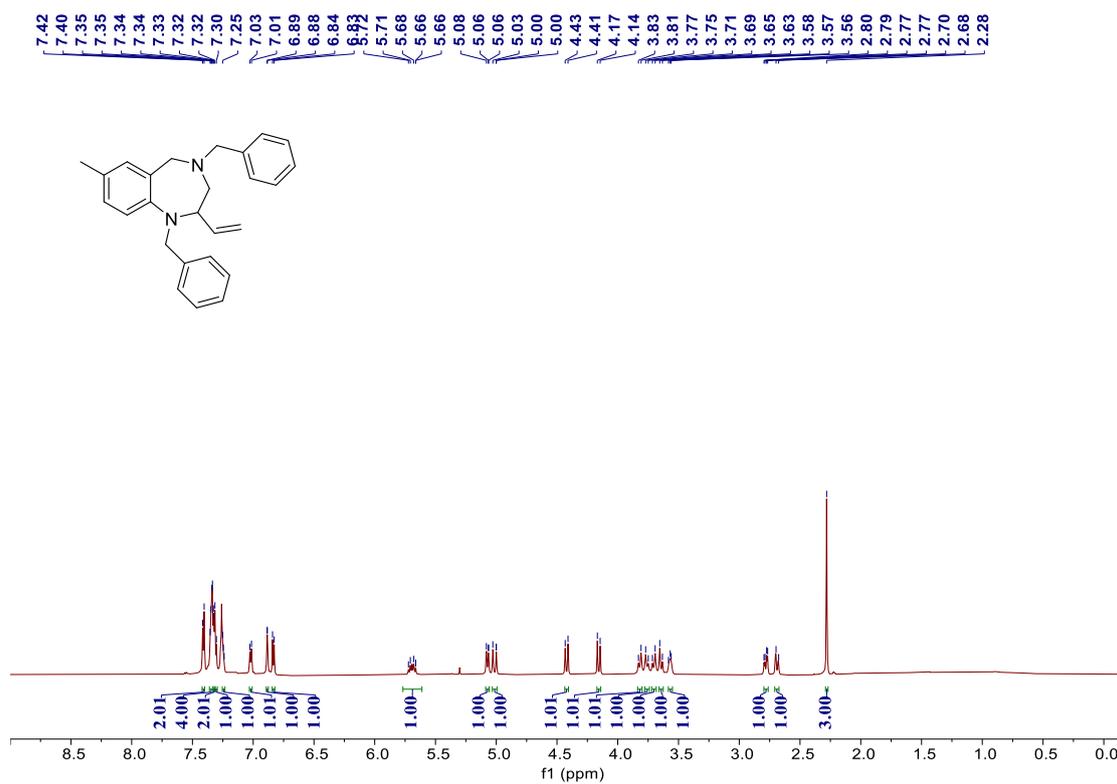
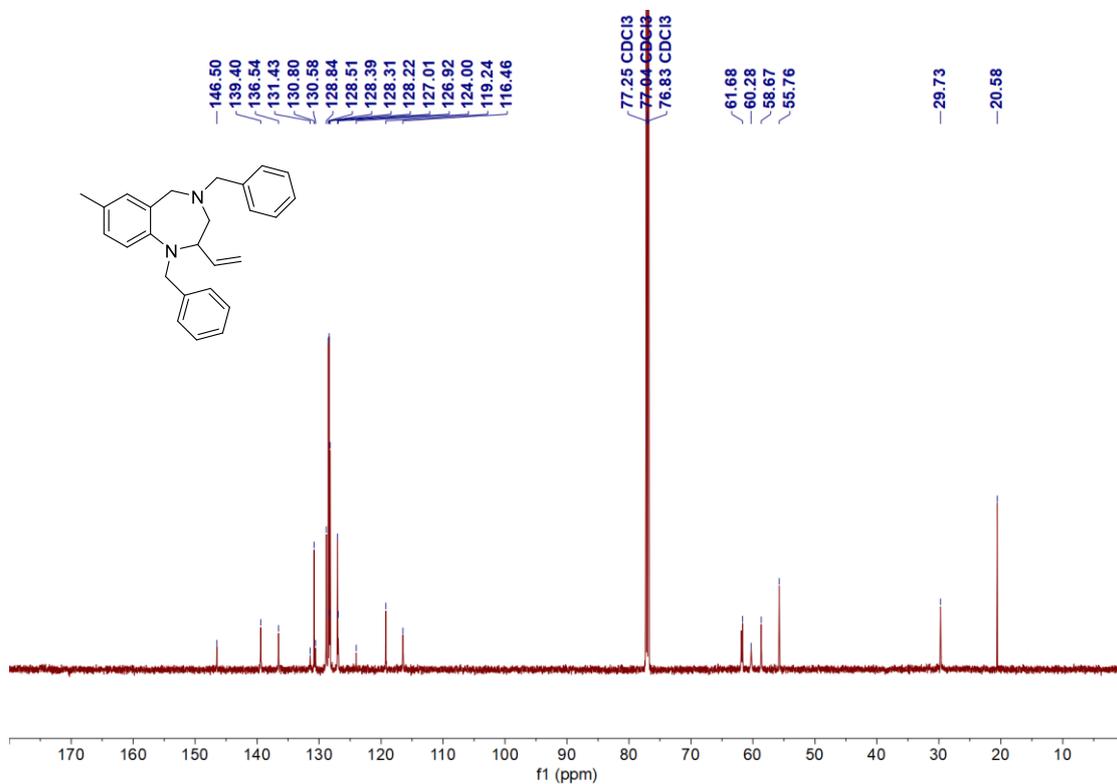


Figure S155. ¹³C NMR (151 MHz, CDCl₃) spectrum of (*R*)-2c

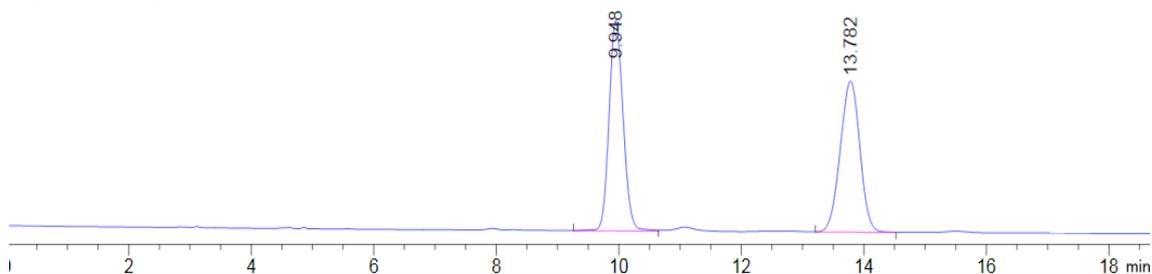


5. Copies of HPLC Chromatograms

Figure S156. HPLC spectra of (*R*)-1b

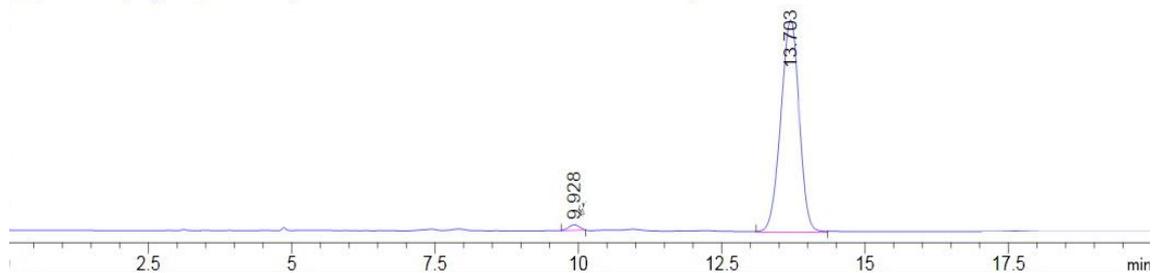
1b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-250718-002-00.D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	9.948	BB	0.2508	1.38708e4	866.47595	49.9628
2	13.782	BB	0.3478	1.38914e4	623.85541	50.0372

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-250718-002-EE.D)

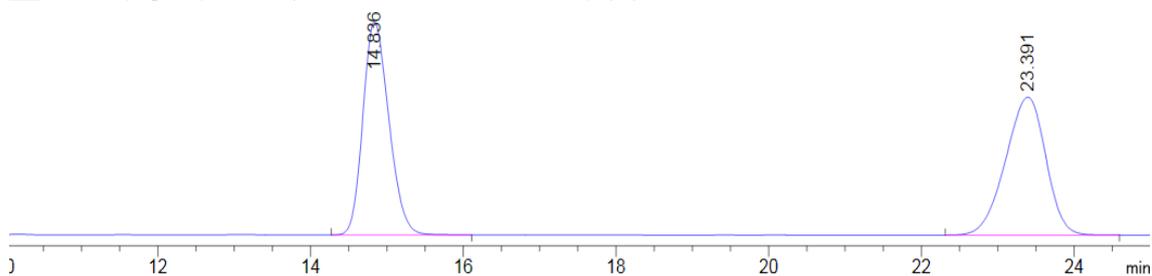


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	9.928	MM	0.2220	292.06796	21.92232	1.4897
2	13.703	MM	0.3746	1.93138e4	859.22412	98.5103

Figure S157. HPLC spectra of (R)-2b

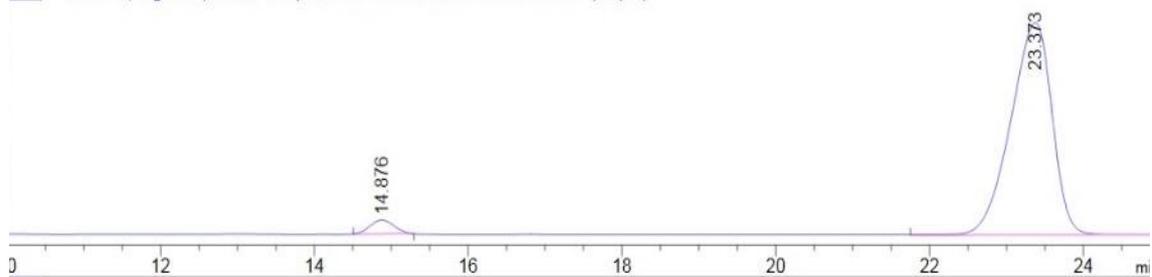
2b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-004-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	14.836	BB	0.3678	1.60535e4	679.01288	49.8757
2	23.391	BB	0.5721	1.61336e4	439.65802	50.1243

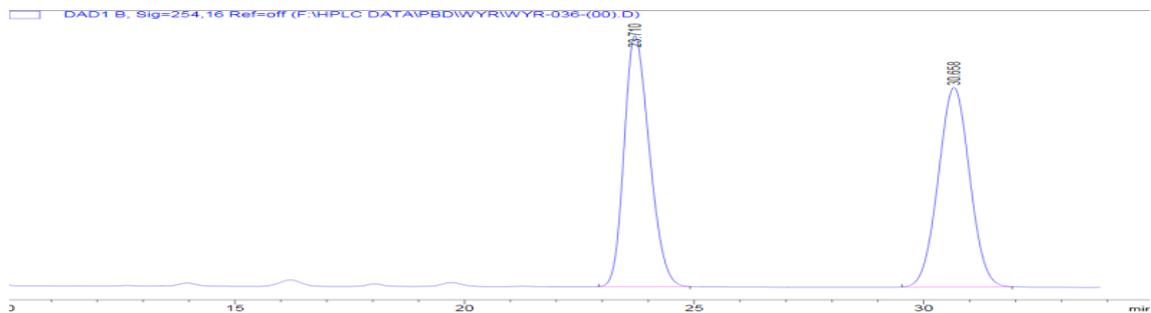
DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-004-(EE).D)



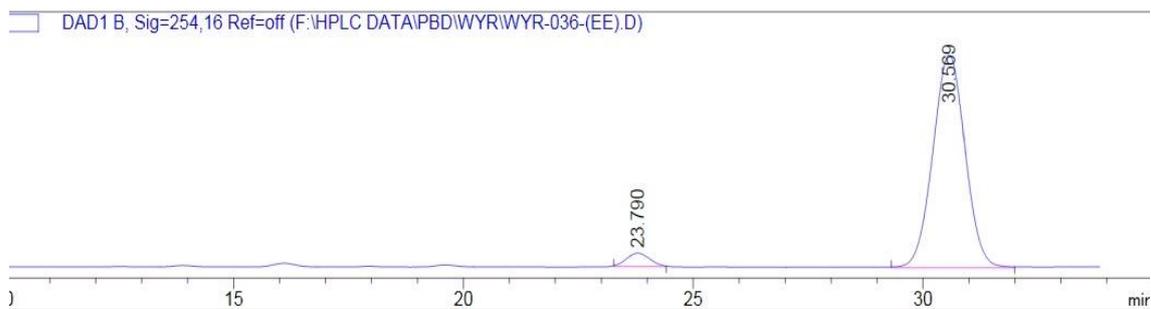
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	14.876	MM	0.3616	1177.16968	54.25694	3.6145
2	23.373	MM	0.6254	3.13907e4	836.57233	96.3855

Figure S158. HPLC spectra of (*R*)-3b

3b (The top one is racemic, and the bottom one is chiral)



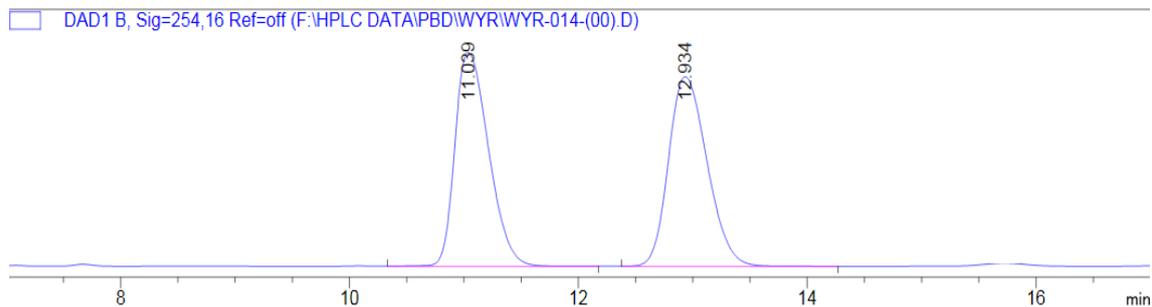
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	23.710	BB	0.5927	1.37524e4	359.18719	50.2192
2	30.658	BB	0.7425	1.36324e4	285.76950	49.7808



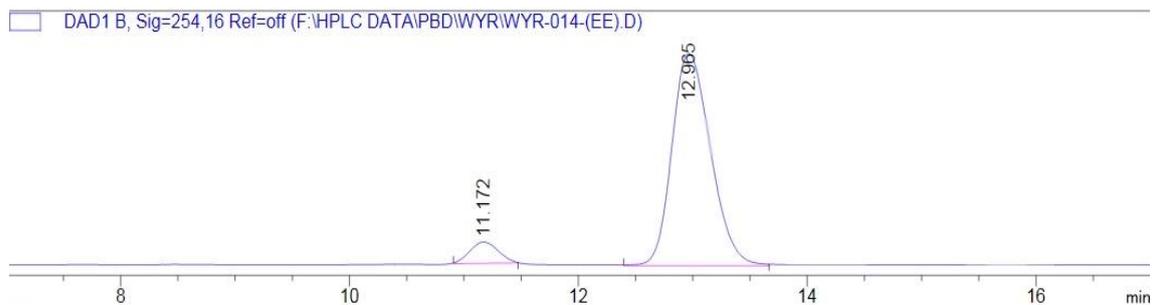
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	23.790	MM	0.5937	1187.70667	33.33949	4.4191
2	30.569	MM	0.8132	2.56887e4	526.51373	95.5809

Figure S159. HPLC spectra of (*R*)-4b

4b (The top one is racemic, and the bottom one is chiral)



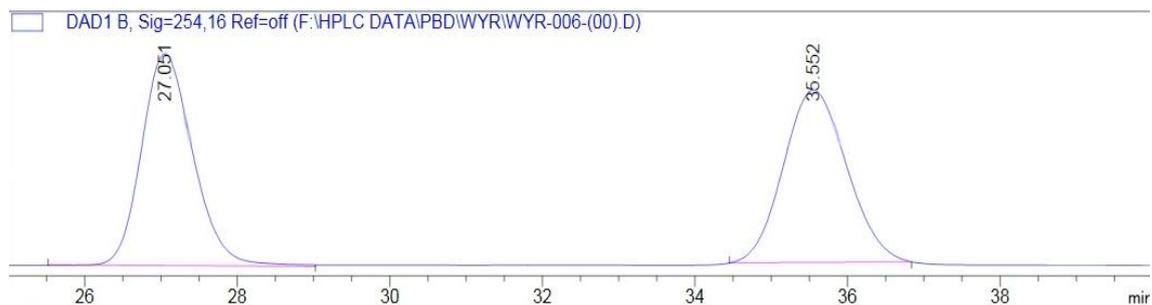
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	11.039	VB	0.3230	5.30497e4	2589.99023	49.6336
2	12.934	BB	0.3697	5.38329e4	2294.54346	50.3664



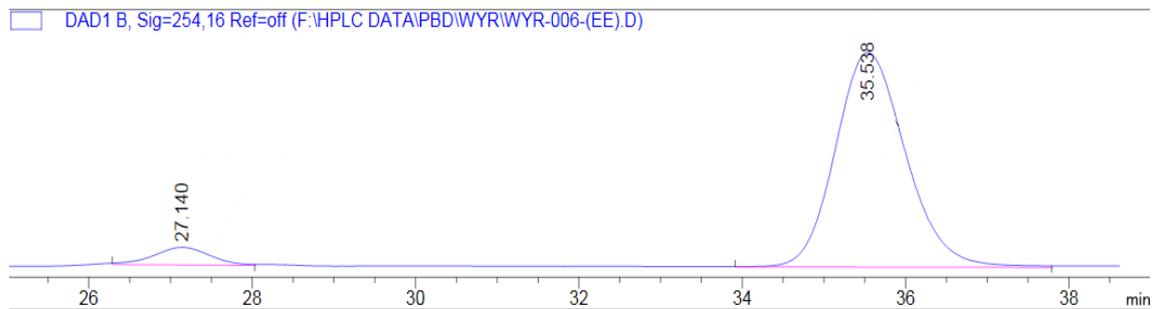
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	11.172	MM	0.2857	3850.05200	224.61230	6.8061
2	12.965	MM	0.3908	5.27178e4	2248.43530	93.1939

Figure S160. HPLC spectra of (*R*)-5b

5b (The top one is racemic, and the bottom one is chiral)



#	[min]	[min]	[mAU*s]	[mAU]	%
1	27.051 MM	0.7796	8306.96387	177.58951	49.9252
2	35.552 MM	0.9609	8331.87109	144.51689	50.0748



#	[min]	[min]	[mAU*s]	[mAU]	%
1	27.140 MM	0.7976	554.46692	11.58588	6.1075
2	35.538 MM	0.9976	8524.05176	142.40506	93.8925

Figure S161. HPLC spectra of (R)-6b

6b (The top one is racemic, and the bottom one is chiral)

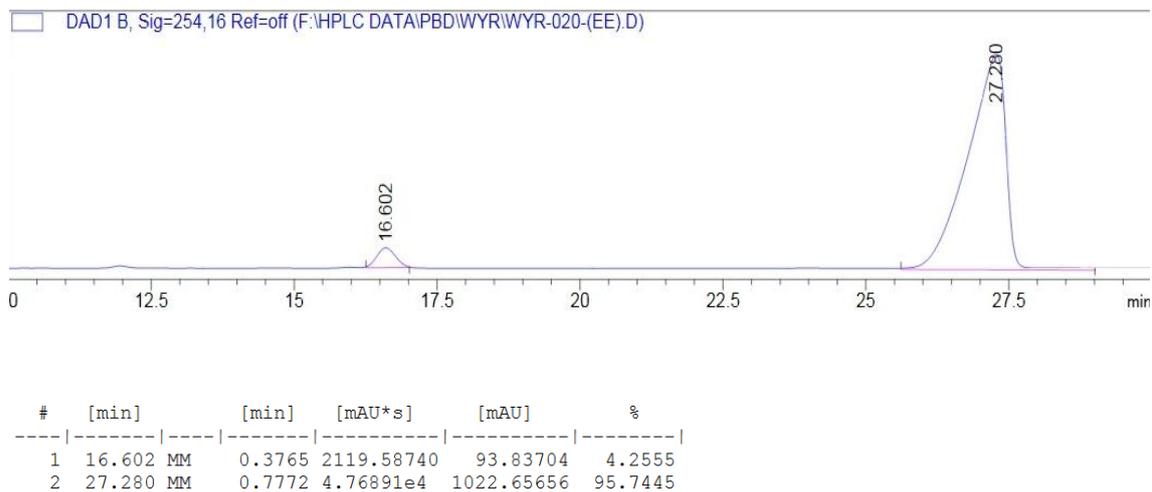
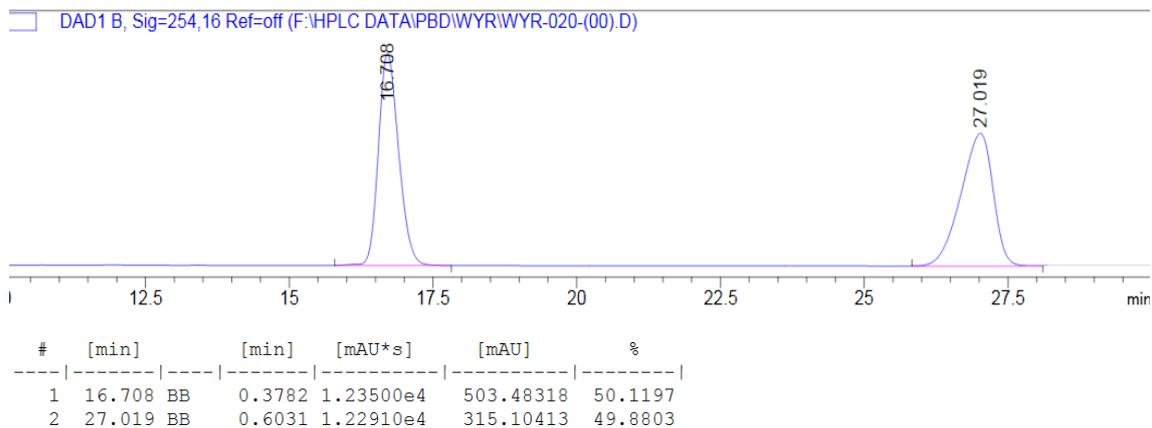
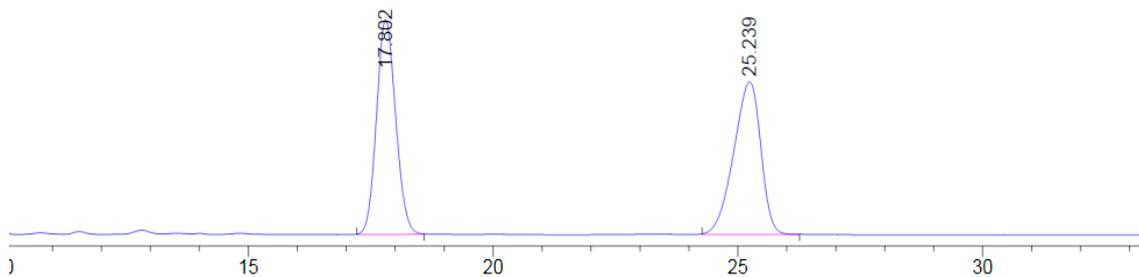


Figure S162. HPLC Analysis of (R)-7b

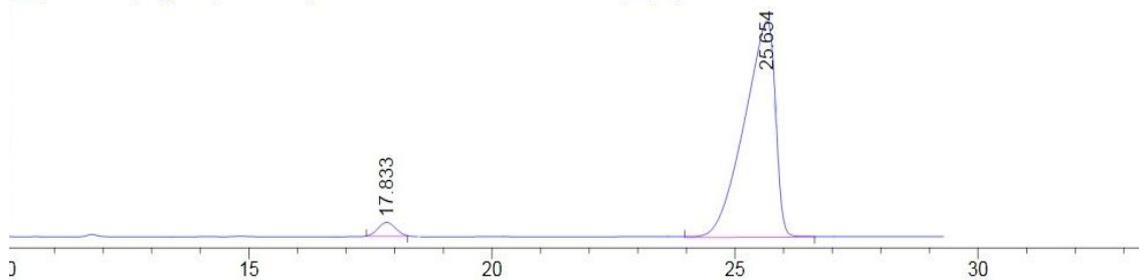
7b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-034-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	17.802	BB	0.4216	4045.22168	148.58424	49.8552
2	25.239	BB	0.5995	4068.72241	105.59445	50.1448

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-034-(EE).D)

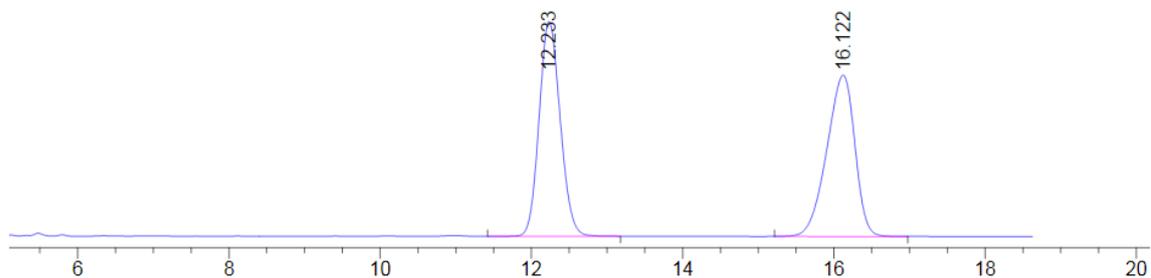


#	[min]	[min]	[mAU*s]	[mAU]	%	
18	17.834	BB	0.4100	919.29401	34.15770	3.7345
19	25.655	BB	0.6445	2.21653e4	494.96527	90.0429

Figure S163. HPLC Analysis of (R)-8b

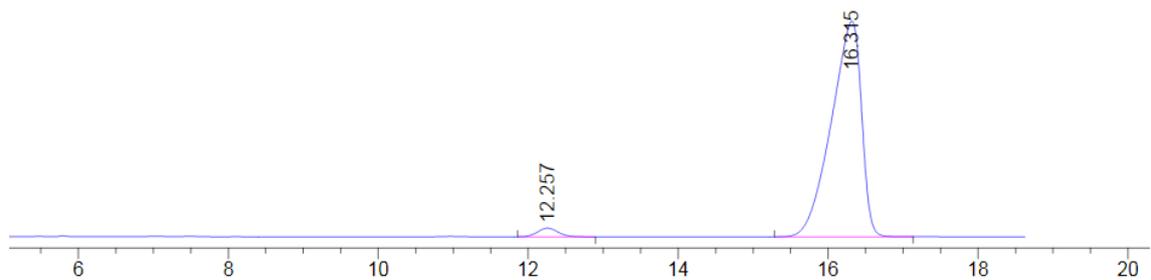
8b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-028-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%
1	12.233 VB	0.3024	7358.86279	379.22000	49.9725
2	16.122 BB	0.4018	7366.95508	284.76425	50.0275

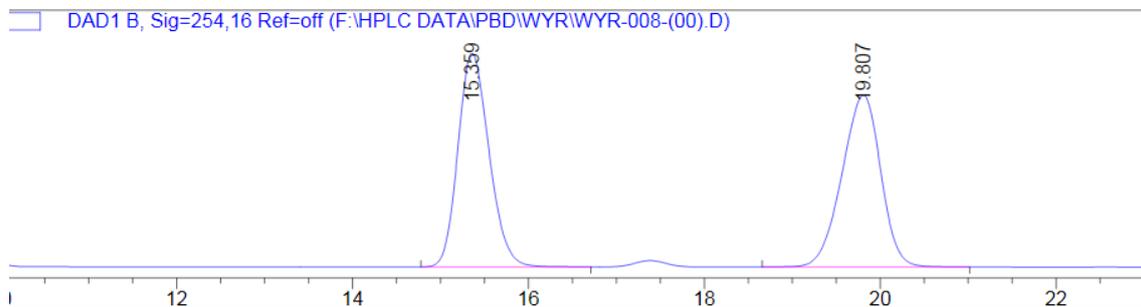
DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-028-(EE).D)



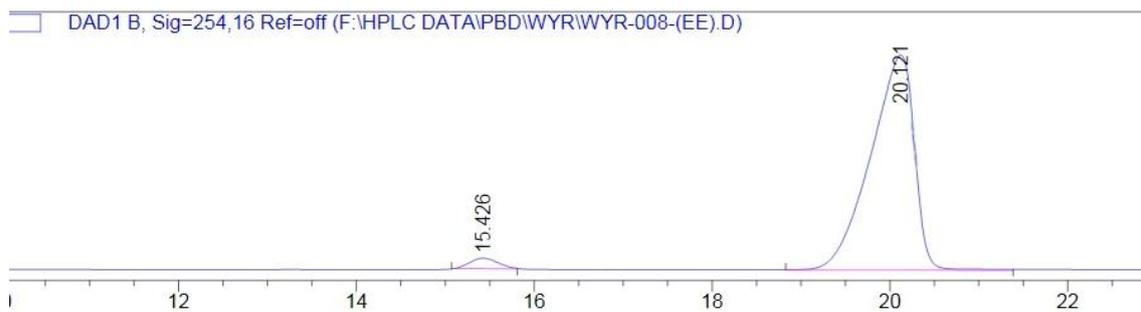
#	[min]	[min]	[mAU*s]	[mAU]	%
1	12.257 BB	0.3020	511.98923	26.43028	2.7126
2	16.315 BB	0.4264	1.83623e4	656.27197	97.2874

Figure S164. HPLC Analysis of (R)-9b

9b (The top one is racemic, and the bottom one is chiral)



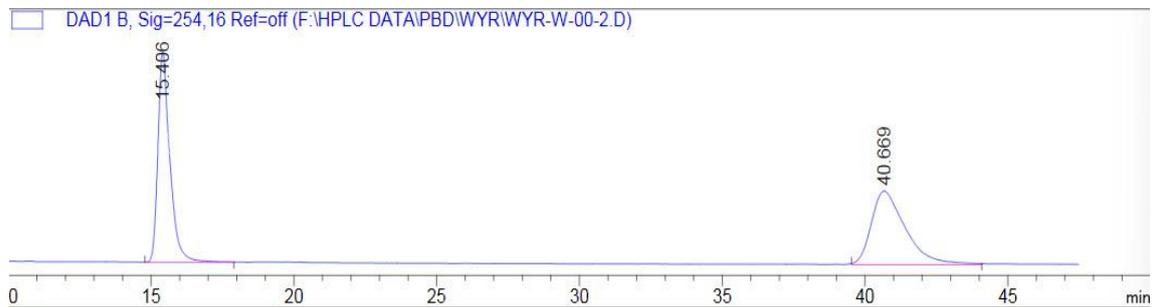
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.359	BB	0.3831	1.47226e4	598.30640	49.9386
2	19.807	BB	0.4781	1.47589e4	480.82721	50.0614



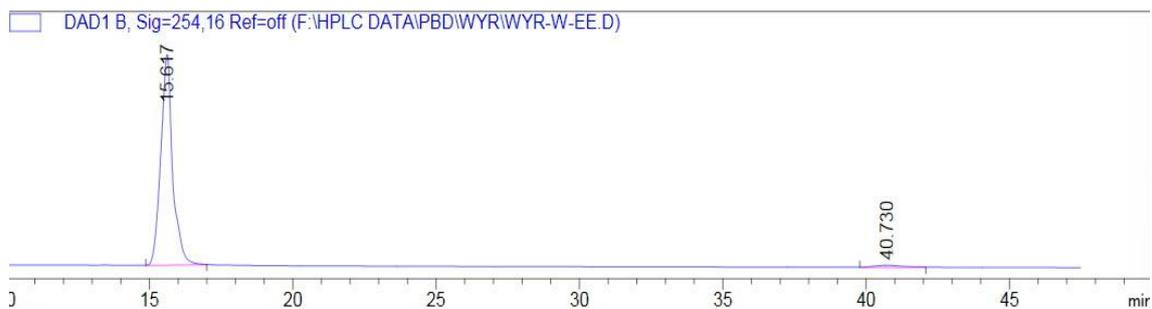
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.426	MM	0.3693	2018.21985	91.08578	3.0568
2	20.121	MM	0.5711	6.40066e4	1868.05615	96.9432

Figure S165. HPLC Analysis of (R)-10b

10b (The top one is racemic, and the bottom one is chiral)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.406	MM	0.4902	2198.04272	74.72559	50.1568
2	40.669	MM	1.3932	2184.29883	26.12969	49.8432

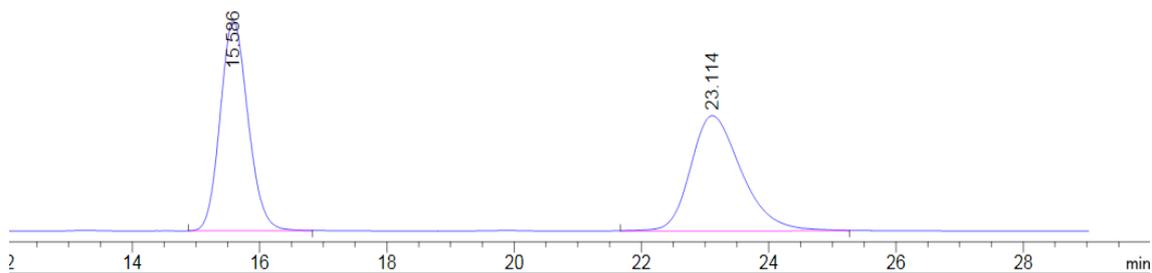


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.617	BB	0.4206	1.65974e4	575.24371	97.6699
2	40.730	MM	1.1867	395.96661	5.56118	2.3301

Figure S166. HPLC Analysis of (R)-11b

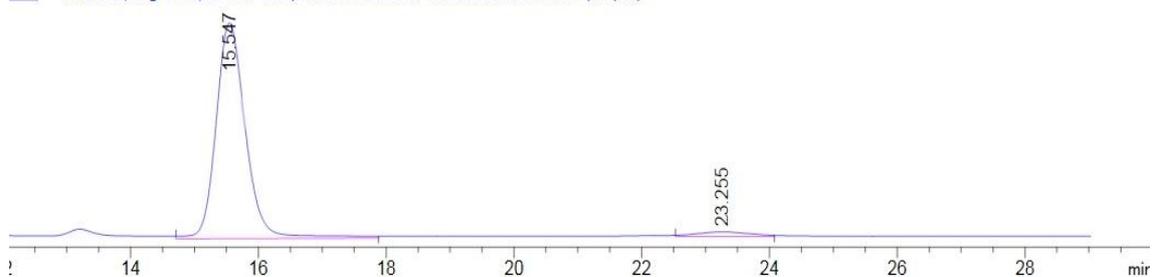
11b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-026-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.586	BB	0.4717	6724.29150	220.52118	50.0017
2	23.114	BB	0.8483	6723.84766	121.00643	49.9983

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-026-(EE).D)

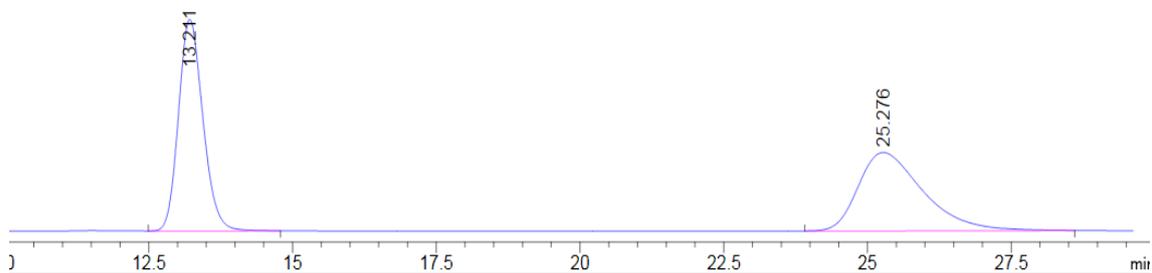


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.547	MM	0.5354	1.77752e4	553.33423	96.1825
2	23.255	MM	0.9578	705.50812	12.27664	3.8175

Figure S167. HPLC Analysis of (R)-12b

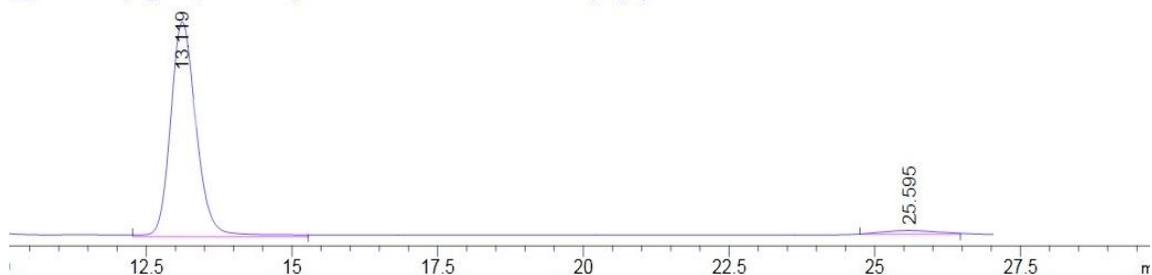
12b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-030-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	13.211	VB	0.4567	1.55281e4	525.60907	50.4049
2	25.276	BB	1.1948	1.52787e4	194.85397	49.5951

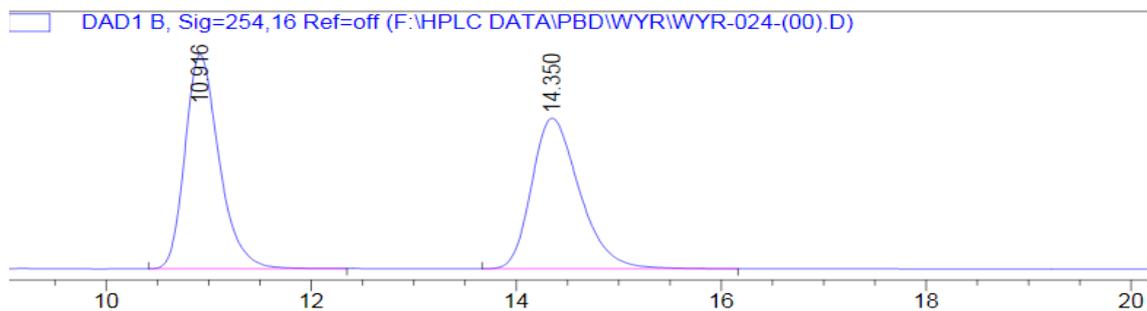
DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-030-(EE).D)



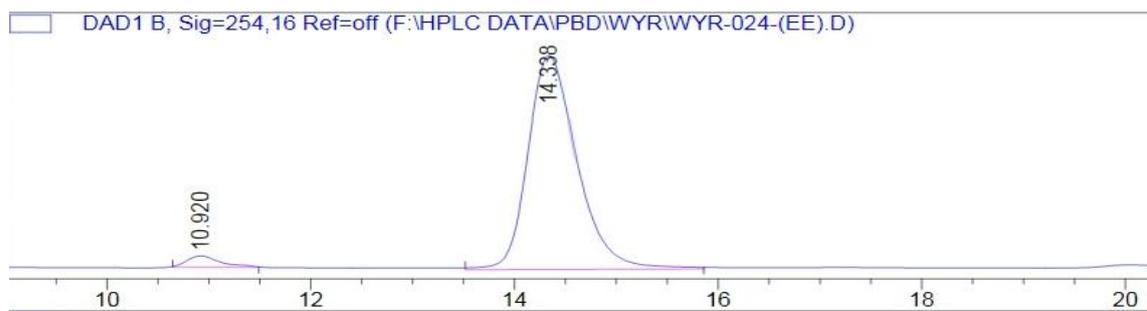
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	13.119	MM	0.5170	1.32088e4	425.79712	96.0197
2	25.595	MM	1.1295	547.54706	8.07982	3.9803

Figure S168. HPLC Analysis of (R)-13b

13b (The top one is racemic, and the bottom one is chiral)



#	[min]	[min]	[mAU*s]	[mAU]	%	
18	10.916	BB	0.3690	1.94783e4	820.40973	46.9162
19	14.350	BB	0.5100	1.96220e4	596.16168	47.2625

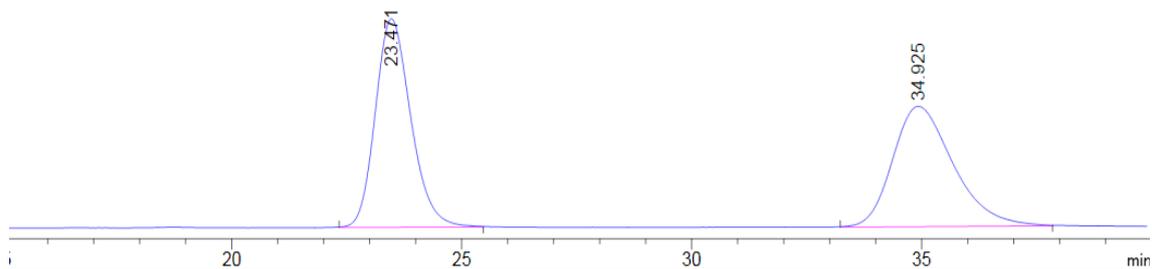


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	10.920	MM	0.3923	612.43927	26.01868	3.6797
2	14.338	MM	0.5584	1.60311e4	478.46783	96.3203

Figure S169. HPLC Analysis of (R)-14b

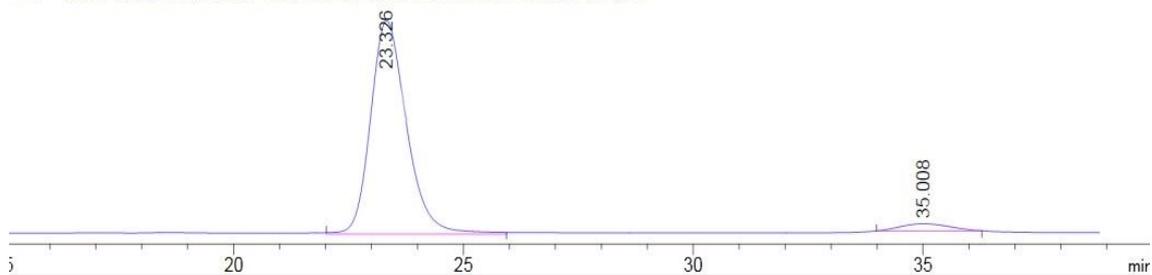
14b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-018-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	23.471	BB	0.8263	6332.79834	117.96165	50.4343
2	34.925	BB	1.3758	6223.74316	68.00082	49.5657

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-018-(EE).D)

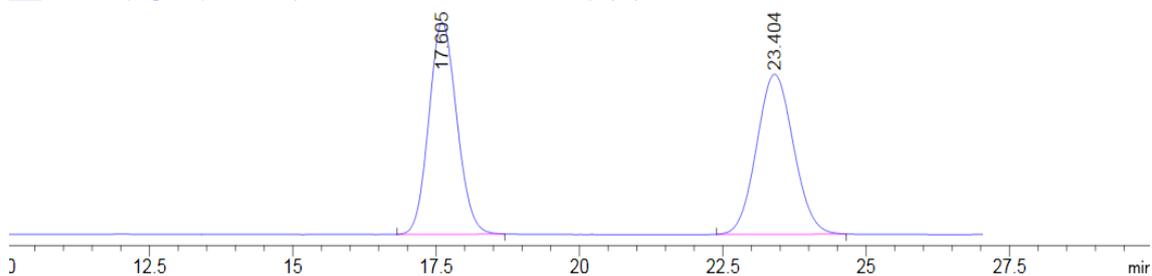


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	23.326	MM	0.9114	1.05397e4	192.73305	95.3428
2	35.008	MM	1.2946	514.83228	6.62788	4.6572

Figure S170. HPLC Analysis of (R)-15b

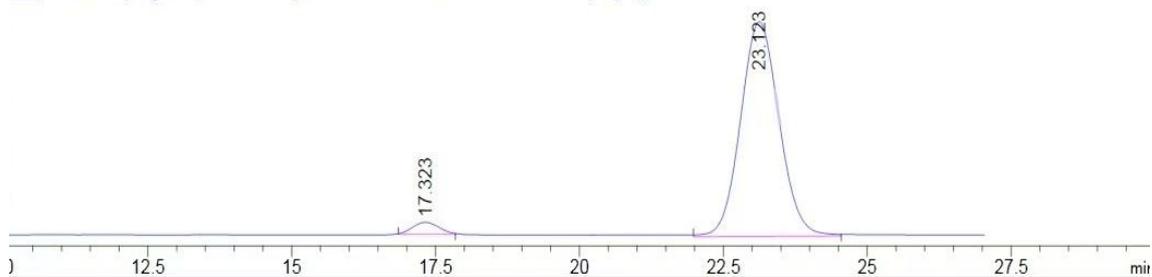
15b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-044-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	17.605	BB	0.5281	1.18616e4	349.38156	50.0228
2	23.404	BB	0.7024	1.18508e4	263.64627	49.9772

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-044-(EE).D)

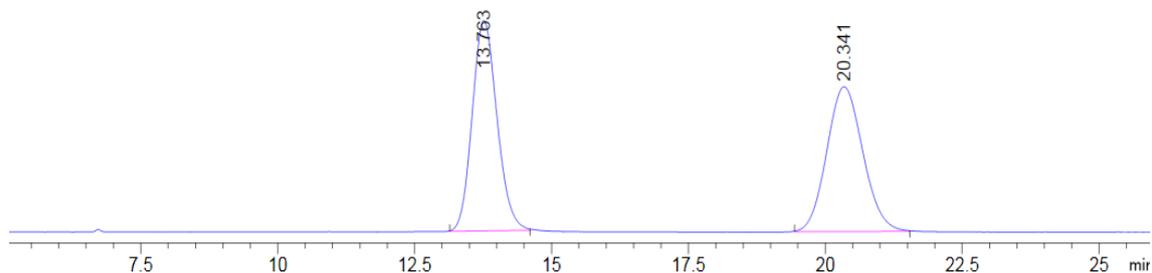


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	17.323	MM	0.5411	1108.34717	34.14174	3.8271
2	23.123	MM	0.7772	2.78524e4	597.28027	96.1729

Figure S171. HPLC Analysis of (R)-16b

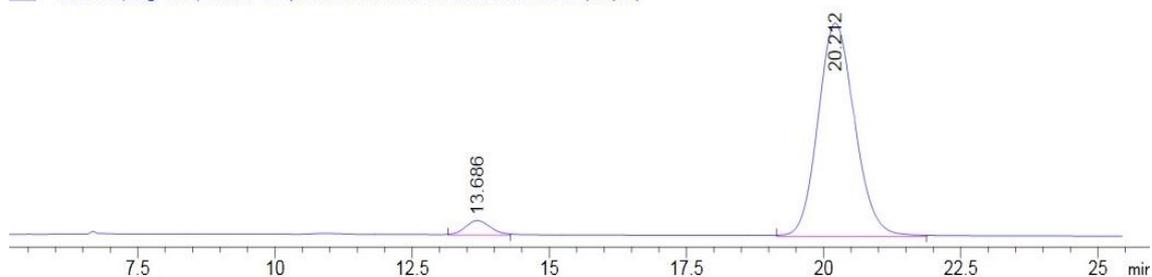
16b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\WYR\WYR-046-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	13.763	BB	0.4894	2135.15723	67.80888	49.9426
2	20.341	BB	0.7136	2140.06421	46.61850	50.0574

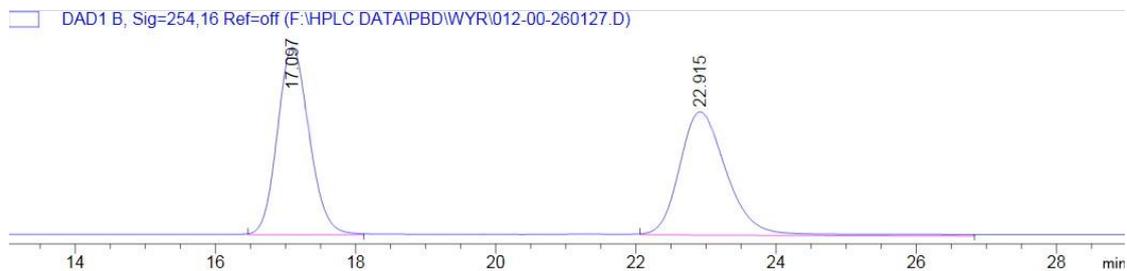
DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\WYR\WYR-046-(EE).D)



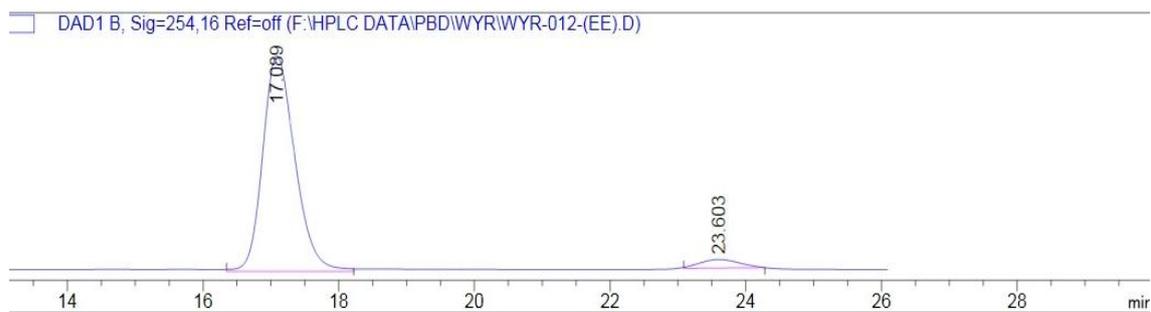
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	13.686	MM	0.5324	711.19824	22.26192	4.4462
2	20.212	MM	0.7764	1.52845e4	328.12326	95.5538

Figure S172. HPLC Analysis of (R)-17b

17b (The top one is racemic, and the bottom one is chiral)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	17.097	MM	0.5246	1.53623e4	488.01981	50.1816
2	22.915	MM	0.7934	1.52511e4	320.38617	49.8184

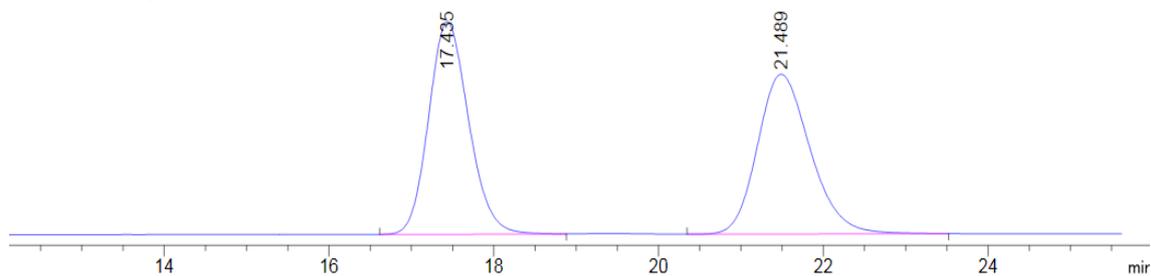


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	17.089	MM	0.5496	4.56298e4	1383.77612	95.4789
2	23.603	MM	0.6677	2160.67847	53.93091	4.5211

Figure S173. HPLC Analysis of (R)-18b

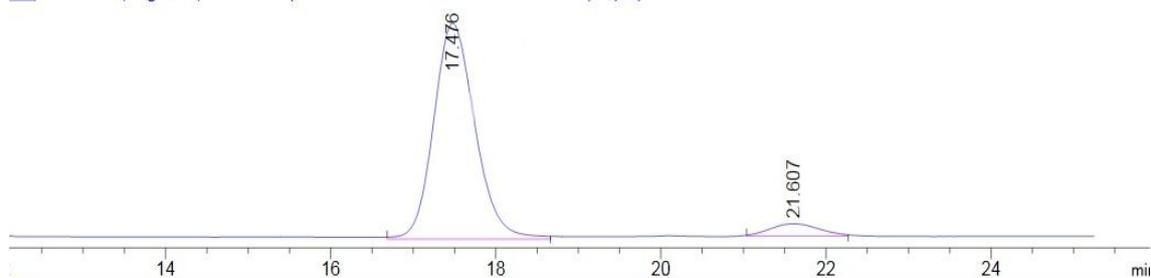
18b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-010-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	17.435	BB	0.5227	1.27201e4	376.00586	50.2434
2	21.489	VB	0.6886	1.25969e4	282.27728	49.7566

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-010-(EE).D)

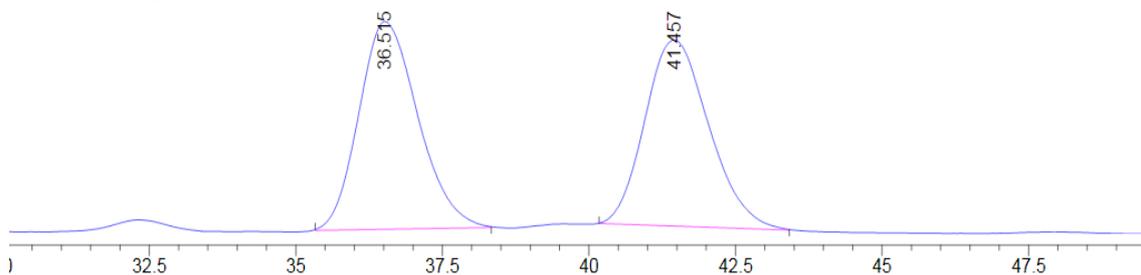


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	17.476	MM	0.5790	1.68786e4	485.86426	93.7801
2	21.607	MM	0.6763	1119.46033	27.58725	6.2199

Figure S174. HPLC Analysis of (R)-19b

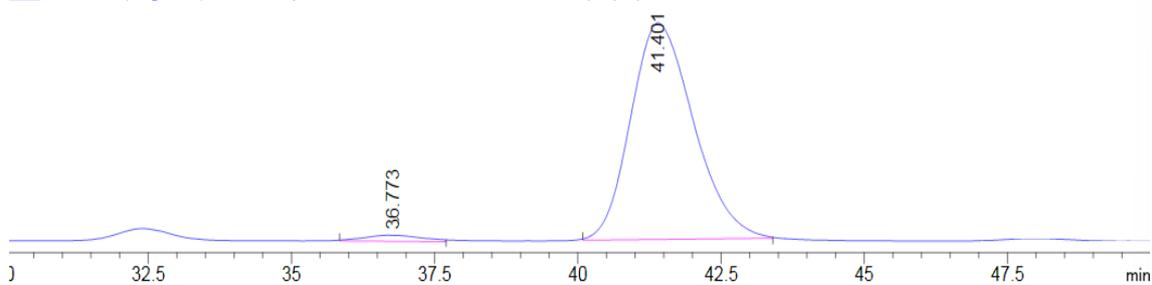
19b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-032-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	36.515	BB	1.0785	2607.06104	37.16066	50.7689
2	41.457	BB	1.1240	2528.08960	33.28786	49.2311

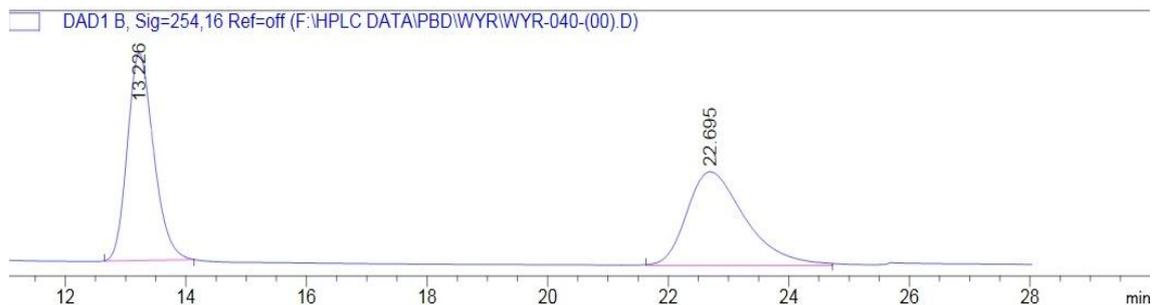
DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-032-(EE).D)



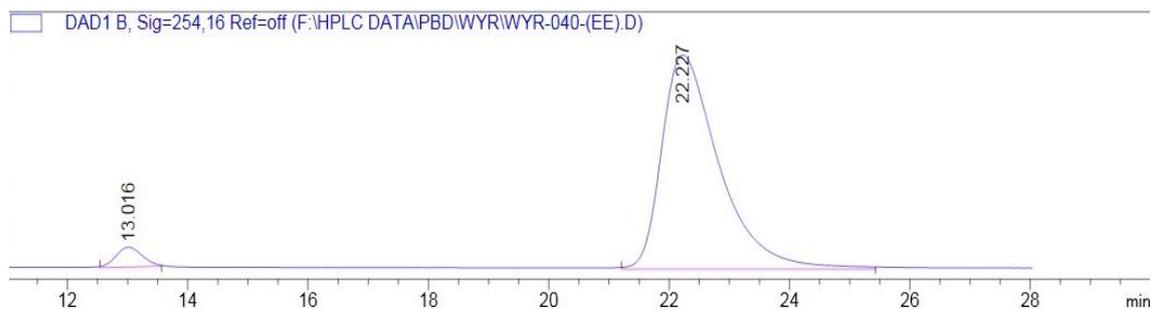
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	36.773	MM	1.1830	165.31377	2.32893	2.5261
2	41.401	BB	1.1750	6379.01904	83.52313	97.4739

Figure S175. HPLC Analysis of (R)-20b

20b (The top one is racemic, and the bottom one is chiral)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	13.226	MM	0.5040	4234.96973	140.05269	49.8573
2	22.695	MM	1.1211	4259.20508	63.31704	50.1427

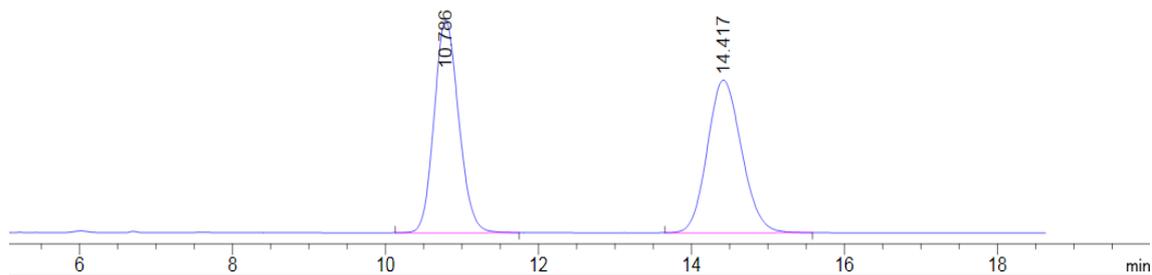


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	13.016	MM	0.5090	603.99597	19.77583	4.0978
2	22.227	MM	1.1114	1.41355e4	211.98453	95.9022

Figure S176. HPLC Analysis of (R)-21b

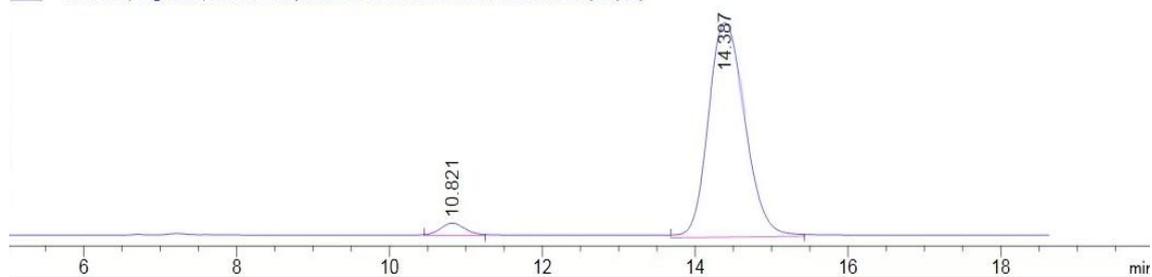
21b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-048-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	10.786	BB	0.3467	2.57482e4	1152.12366	49.9673
2	14.417	BB	0.4853	2.57819e4	827.88818	50.0327

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-048-(EE).D)

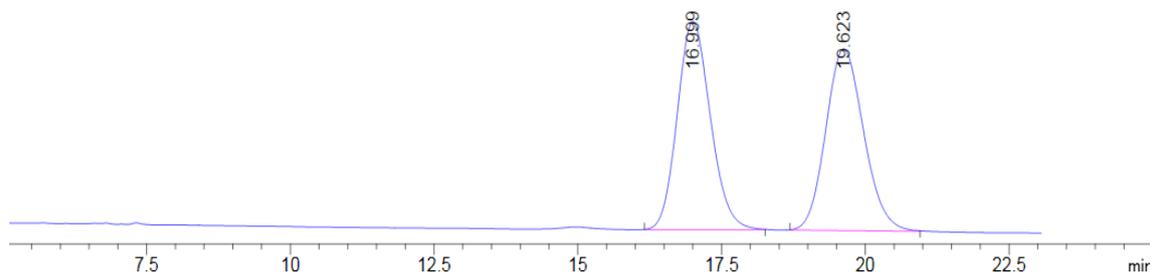


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	10.821	MM	0.3810	3175.40112	138.91943	3.8020
2	14.387	MM	0.5555	8.03440e4	2410.72510	96.1980

Figure S177. HPLC Analysis of (R)-22b

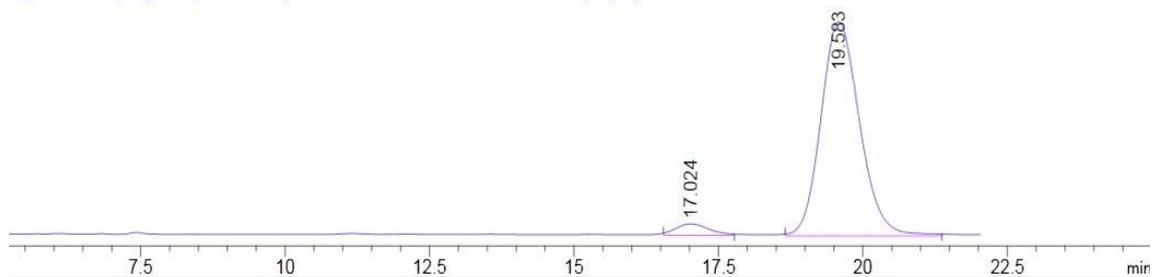
22b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-056-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%
1	16.999 BB	0.6217	7962.47168	198.60802	50.0322
2	19.623 BB	0.7130	7952.23828	173.40660	49.9678

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-056-(EE).D)

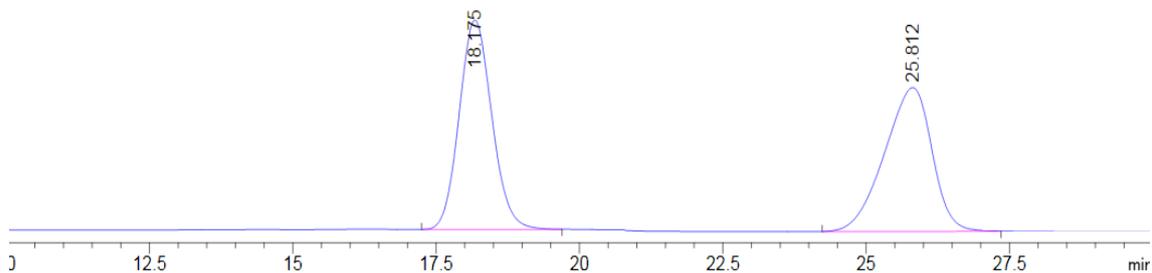


#	[min]	[min]	[mAU*s]	[mAU]	%
1	17.024 MM	0.6723	1101.32971	27.30394	4.4307
2	19.583 MM	0.7773	2.37554e4	509.37354	95.5693

Figure S178. HPLC Analysis of (R)-23b

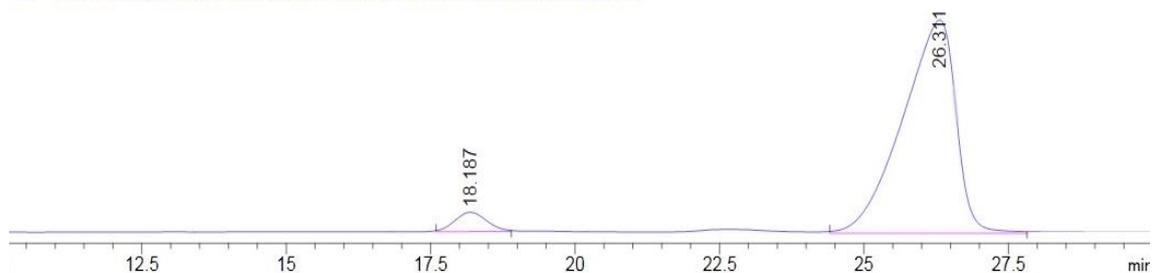
23b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-042-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	18.175	BB	0.6157	2.26833e4	570.76727	49.9621
2	25.812	BB	0.8975	2.27177e4	392.34137	50.0379

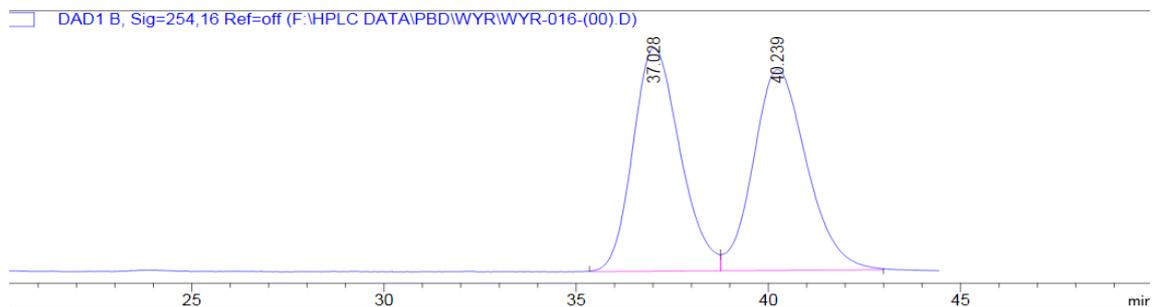
DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-042-(EE).D)



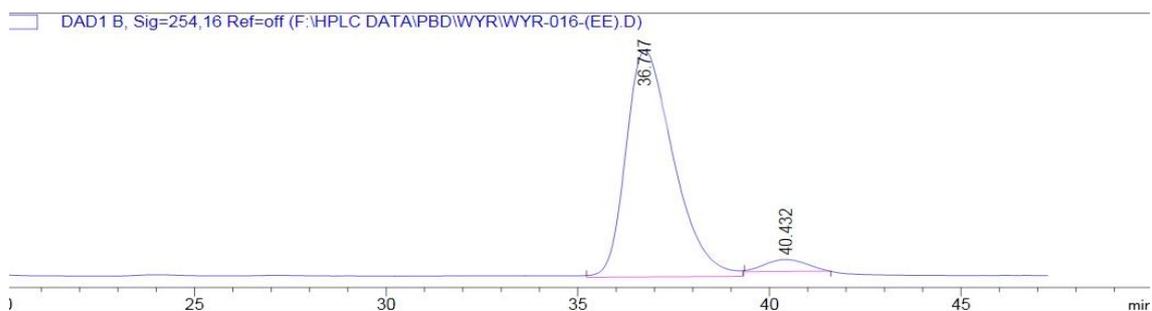
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	18.187	MM	0.6386	2778.71509	72.52562	5.1170
2	26.311	MM	1.0760	5.15253e4	798.06409	94.8830

Figure S179. HPLC Analysis of (R)-24b

24b (The top one is racemic, and the bottom one is chiral)



#	[min]	[min]	[mAU*s]	[mAU]	%
1	37.028 BV	1.3019	5948.52734	69.82379	49.5107
2	40.239 VB	1.4488	6066.09668	62.69772	50.4893

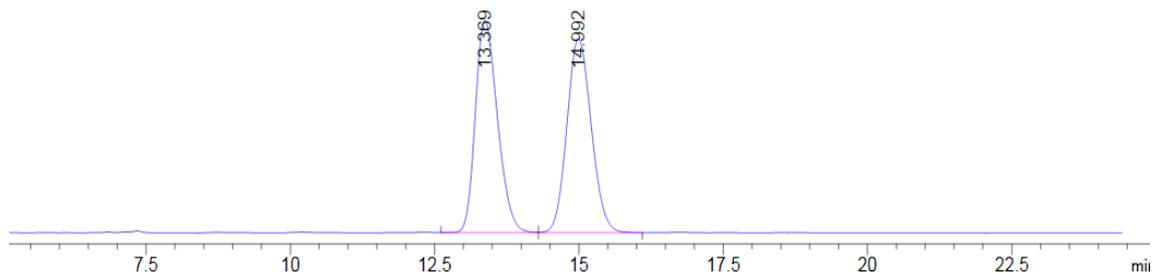


#	[min]	[min]	[mAU*s]	[mAU]	%
1	36.747 MM	1.4389	3.40259e4	394.11526	95.6628
2	40.432 MM	1.2515	1542.69275	20.54523	4.3372

Figure S180. HPLC Analysis of (R)-25b

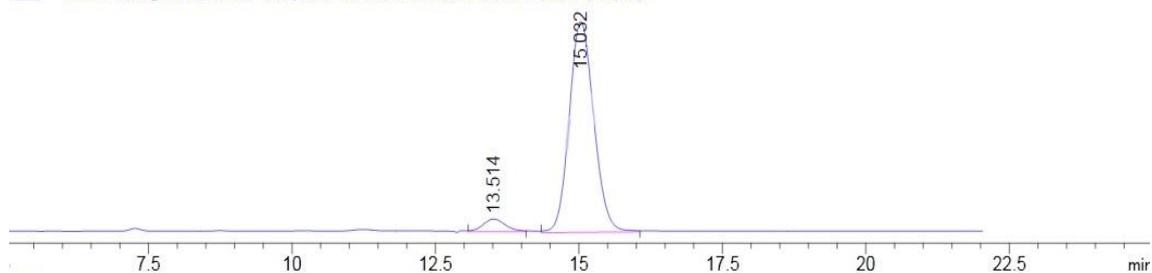
25b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-054-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	13.369	VV	0.4149	3.56558e4	1337.82837	49.7862
2	14.992	VB	0.4591	3.59620e4	1222.67859	50.2138

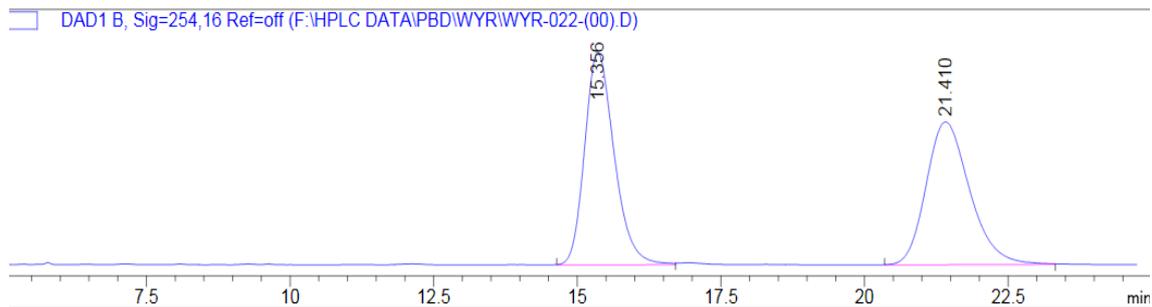
DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-054-(EE).D)



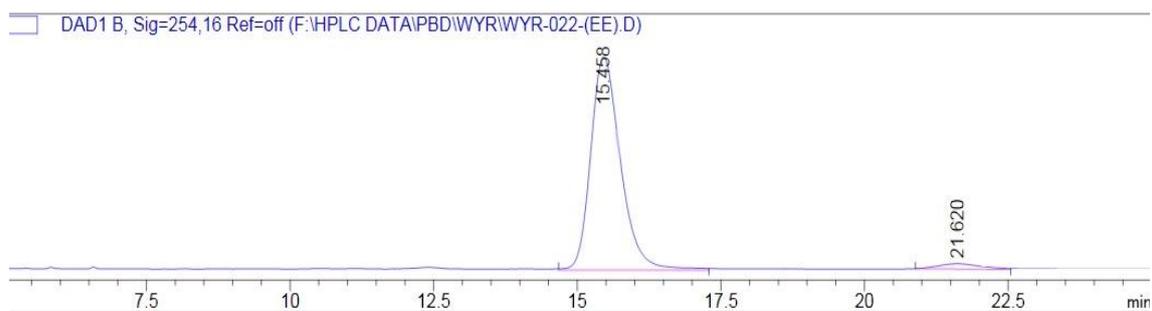
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	13.514	MM	0.4675	2769.58911	98.74653	5.4360
2	15.032	MM	0.4967	4.81795e4	1616.51624	94.5640

Figure S181. HPLC Analysis of (R)-26b

26b (The top one is racemic, and the bottom one is chiral)



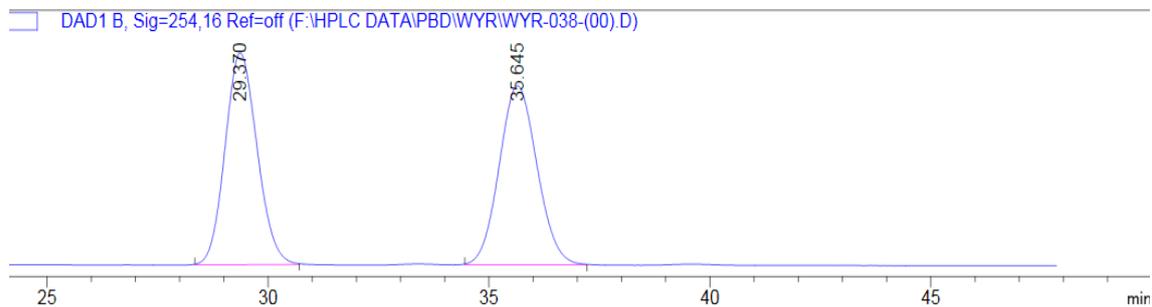
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.356	BB	0.5531	4490.87207	125.61510	50.1769
2	21.410	BB	0.8082	4459.21240	84.43122	49.8231



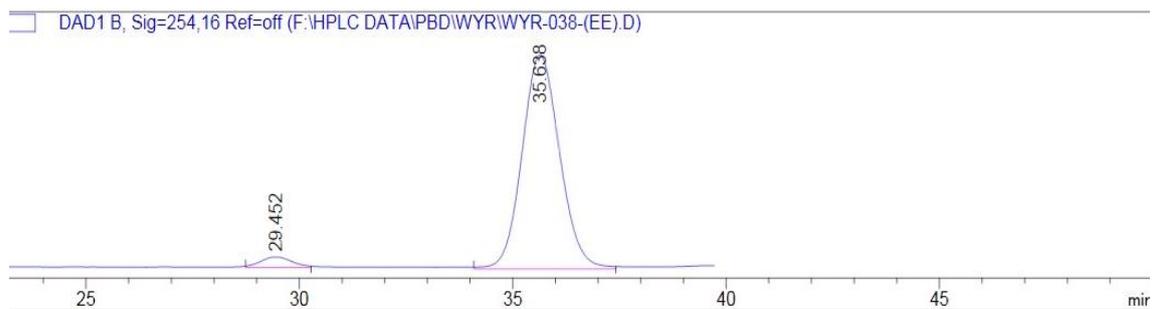
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.458	MM	0.6033	7970.59375	220.20822	96.4985
2	21.620	MM	0.8738	289.21707	5.51660	3.5015

Figure S182. HPLC Analysis of (R)-27b

27b (The top one is racemic, and the bottom one is chiral)



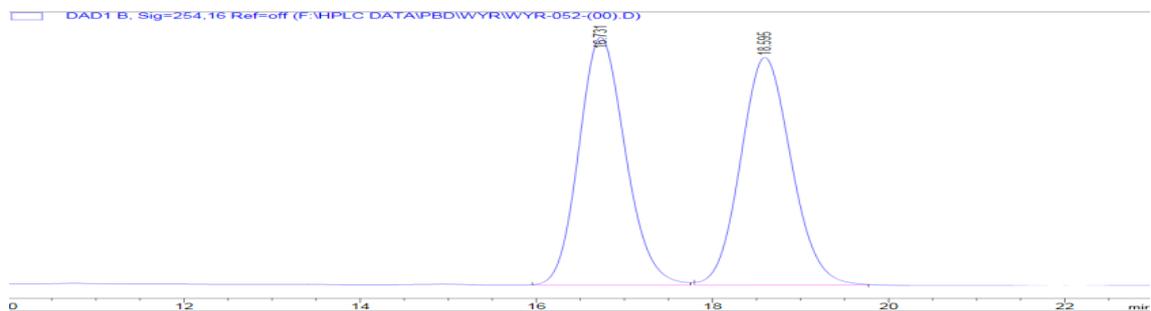
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	29.370	BB	0.7852	6079.64648	120.37775	50.0219
2	35.645	BB	0.9228	6074.31592	101.99316	49.9781



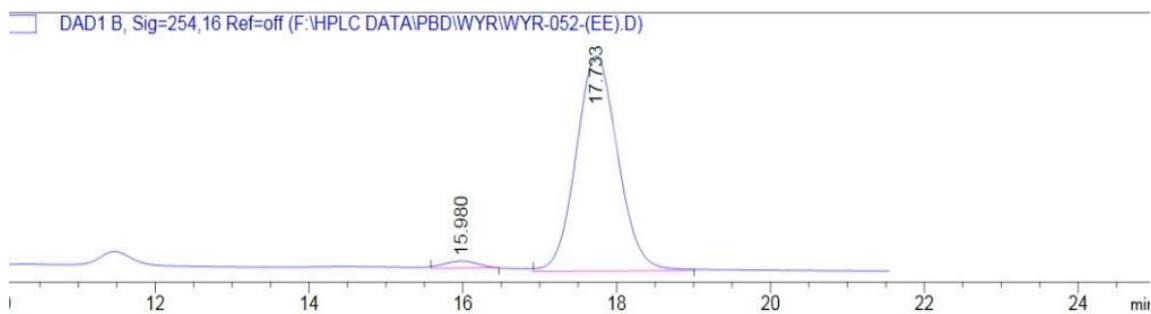
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	29.452	MM	0.8535	482.65375	9.42480	3.9487
2	35.638	MM	1.0224	1.17405e4	191.39067	96.0513

Figure S183. HPLC Analysis of (R)-28b

28b (The top one is racemic, and the bottom one is chiral)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	16.731	BB	0.5658	8191.82422	223.38947	49.9835
2	18.595	BB	0.6184	8197.24609	205.05785	50.0165

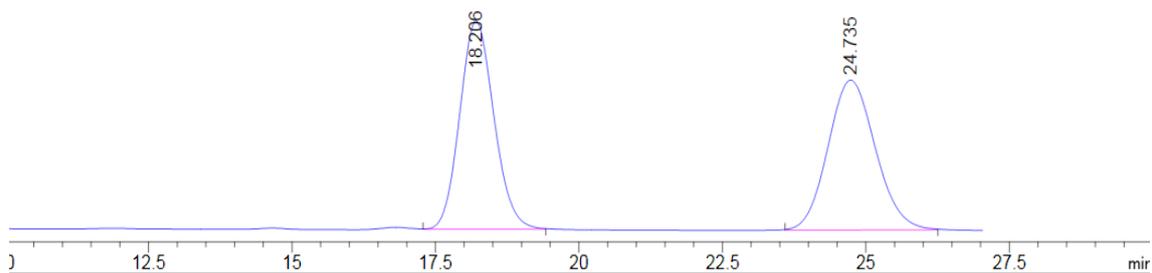


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.980	MM	0.5044	202.06464	6.67714	2.5119
2	17.733	MM	0.6269	7842.37549	208.49625	97.4881

Figure S184. HPLC Analysis of (R)-29b

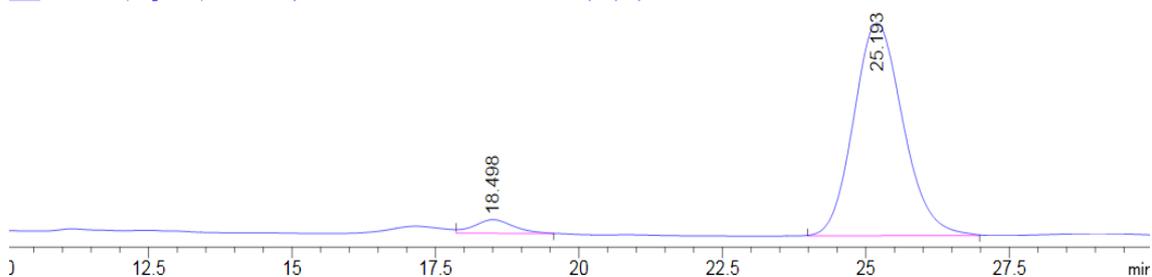
29b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-050-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	18.206	VB	0.6415	7180.90576	173.26491	50.0927
2	24.735	BB	0.8820	7154.33594	124.58268	49.9073

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-050-(EE).D)

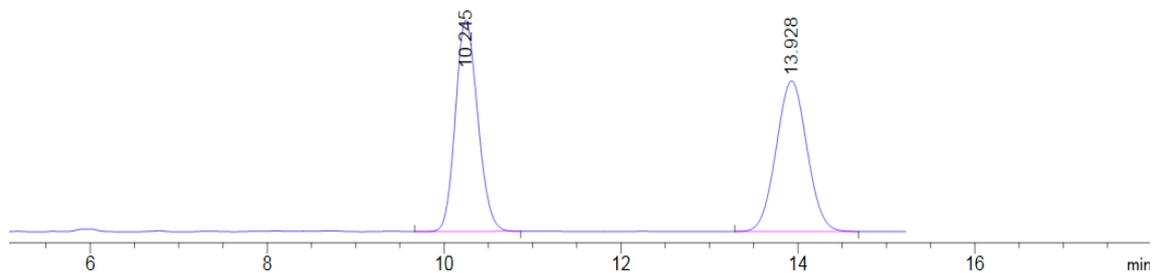


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	18.498	VB	0.7042	528.90186	10.89869	4.8997
2	25.193	BB	0.9234	1.02656e4	171.73819	95.1003

Figure S185. HPLC Analysis of (R)-30b

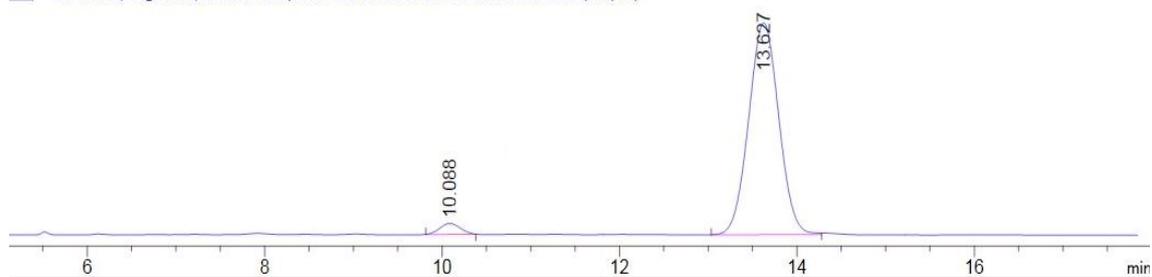
30b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-066-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	10.245	VB	0.2751	1.22178e4	695.10071	50.3282
2	13.928	BB	0.3801	1.20585e4	495.22195	49.6718

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-066-(EE).D)

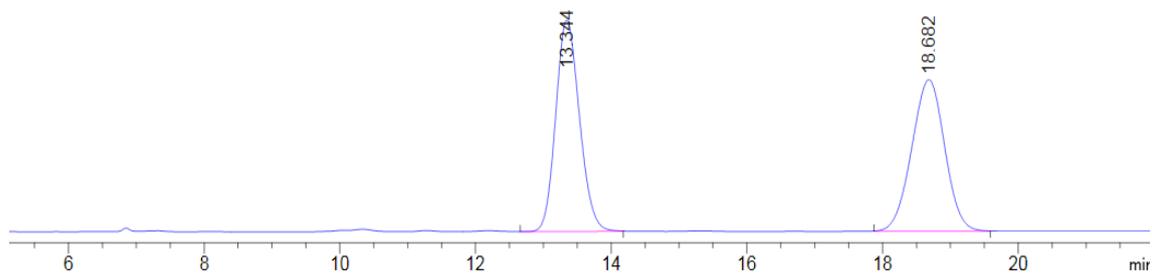


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	10.088	MM	0.2662	403.27432	25.25102	3.3948
2	13.627	BB	0.3688	1.14760e4	487.25967	96.6052

Figure S186. HPLC Analysis of (R)-31b

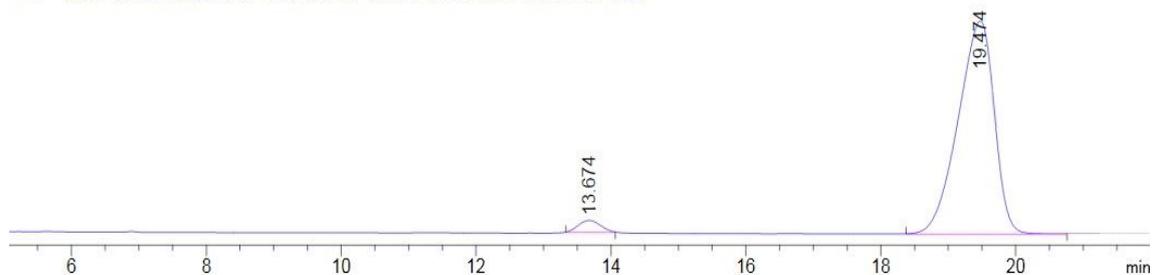
31b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-062-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%
1	13.344 VB	0.3776	7726.36816	317.79971	50.0401
2	18.682 BB	0.5268	7713.99805	227.97527	49.9599

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-062-(EE).D)

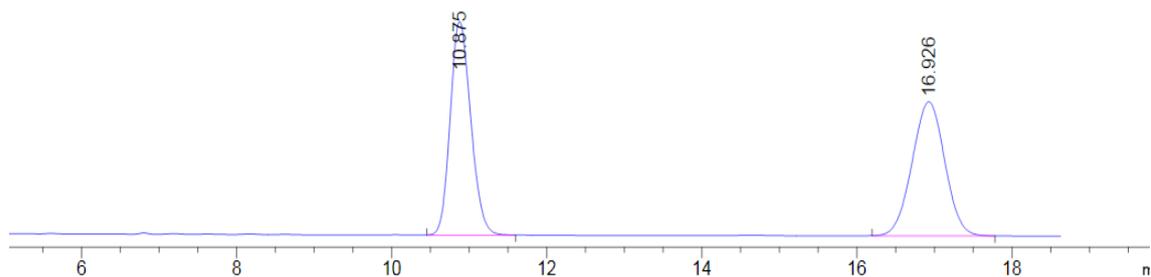


#	[min]	[min]	[mAU*s]	[mAU]	%
1	13.674 MM	0.3878	1086.93384	46.71397	3.4372
2	19.474 MM	0.6217	3.05354e4	818.53687	96.5628

Figure S187. HPLC Analysis of (R)-32b

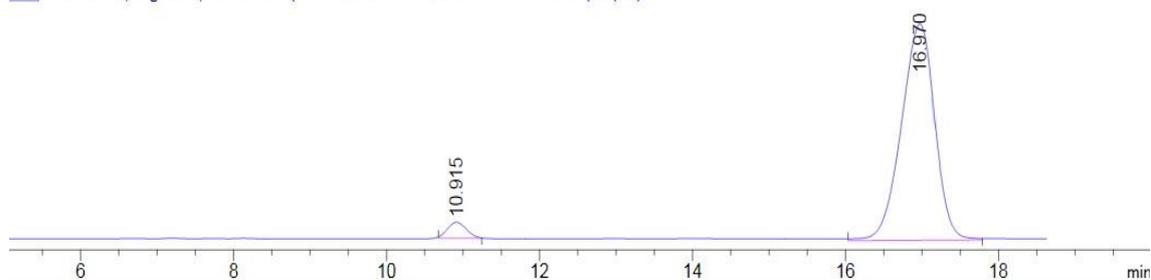
32b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-060-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	10.875	BB	0.2873	1.06380e4	576.45734	49.9946
2	16.926	BB	0.4570	1.06403e4	361.90051	50.0054

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-060-(EE).D)

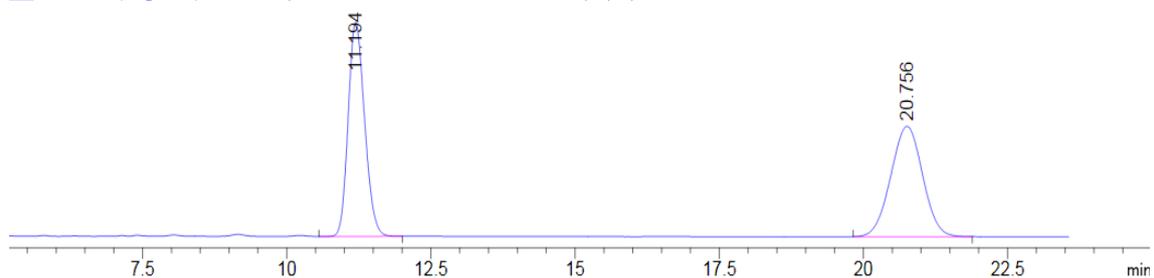


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	10.915	MM	0.2895	1460.61414	84.07654	4.0953
2	16.970	MM	0.5061	3.42047e4	1126.37329	95.9047

Figure S188. HPLC Analysis of (R)-33b

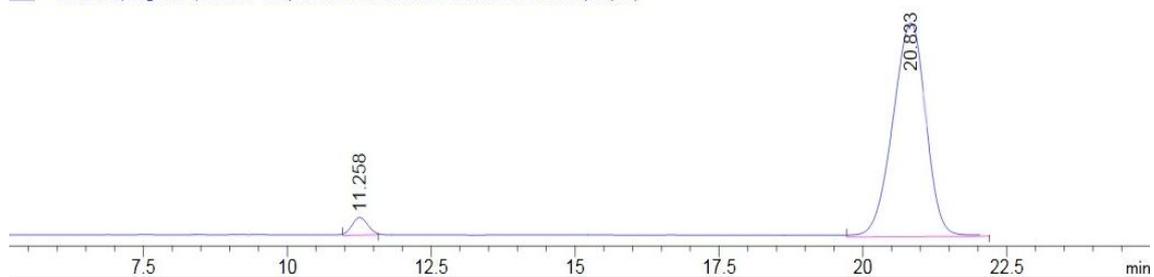
33b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-058-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%
1	11.194	VB	0.3098 1.79926e4	905.63239	49.9906
2	20.756	BB	0.6012 1.79993e4	467.43301	50.0094

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\IPBD\WYR\WYR-058-(EE).D)

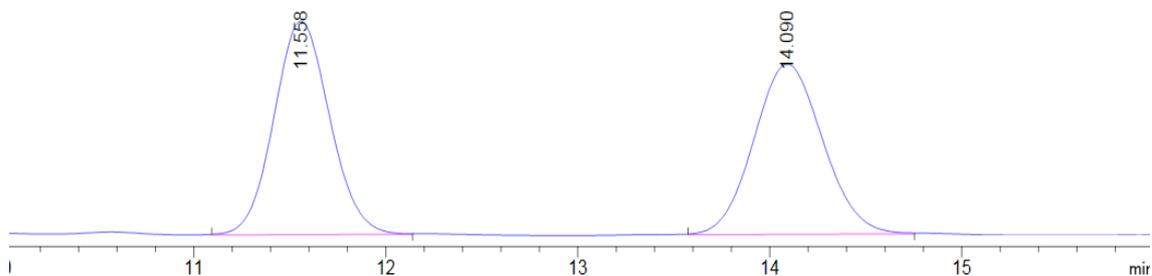


#	[min]	[min]	[mAU*s]	[mAU]	%
1	11.258	MM	0.3210 2397.99951	124.51681	3.8348
2	20.833	MM	0.6677 6.01343e4	1500.98779	96.1652

Figure S189. HPLC Analysis of (R)-34b

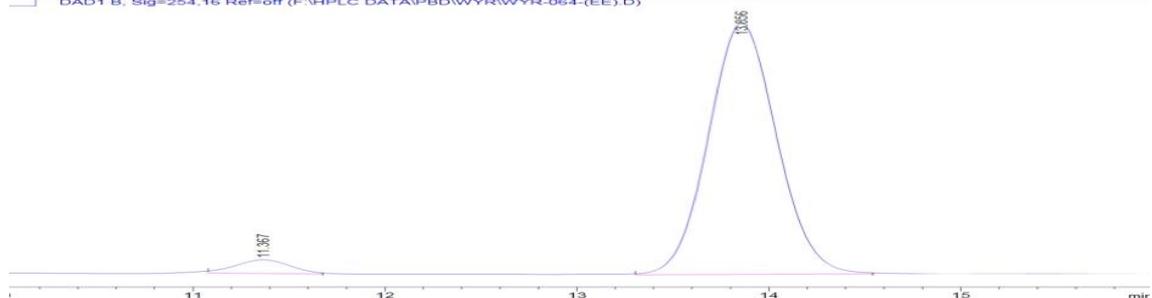
34b (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-064-(00).D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	11.558	BB	0.3138	2037.71204	100.81480	50.3312
2	14.090	BB	0.3895	2010.89099	80.47341	49.6688

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-064-(EE).D)

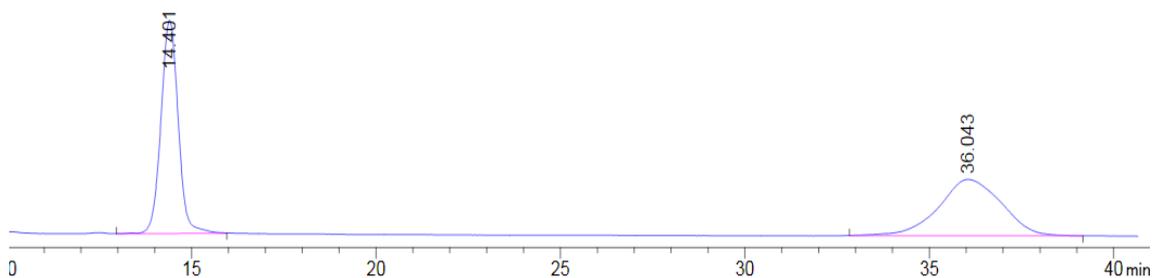


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	11.367	MM	0.3293	200.52440	10.14790	4.1365
2	13.856	MM	0.4117	4647.10645	188.14307	95.8635

Figure S190. HPLC Analysis of (R)-10c

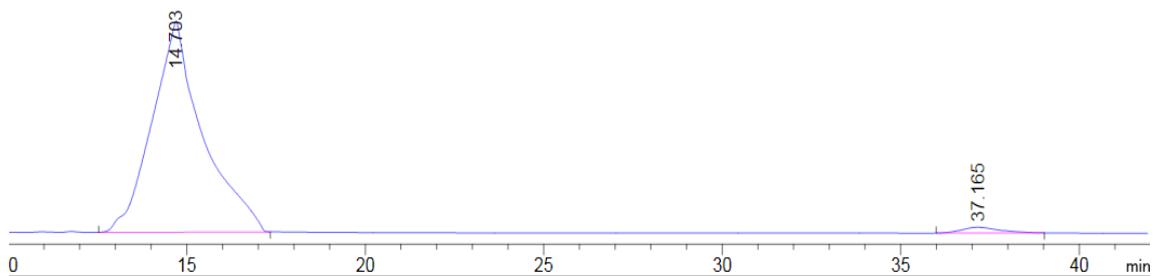
10c (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBDWYR\10C-00.D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	14.401	VB	0.5087	2526.39575	77.41867	50.9167
2	36.043	BB	1.5383	2435.42749	20.52583	49.0833

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBDWYR\WYR-C-EE.D)

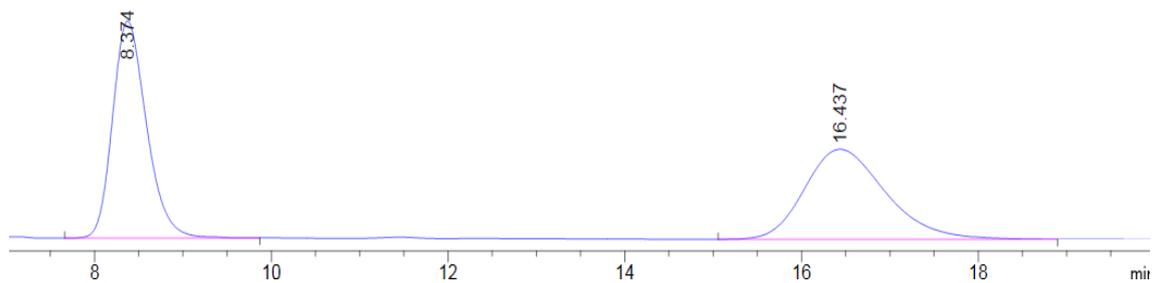


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	14.703	BB	1.1900	7.66150e4	781.35791	97.9369
2	37.165	BB	1.0545	1613.93152	21.53222	2.0631

Figure S191. HPLC Analysis of (R)-10d

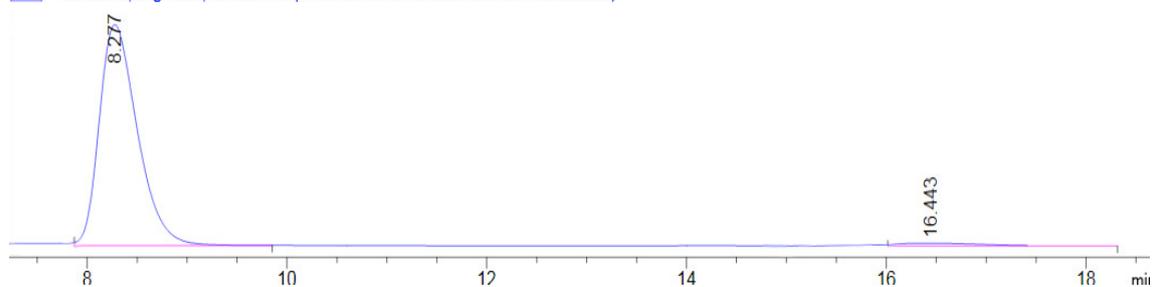
10d (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-E-00.D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	8.374	BB	0.4068	5407.58398	204.31845	50.5018
2	16.437	BB	0.9688	5300.11182	84.37703	49.4982

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-E-EE.D)

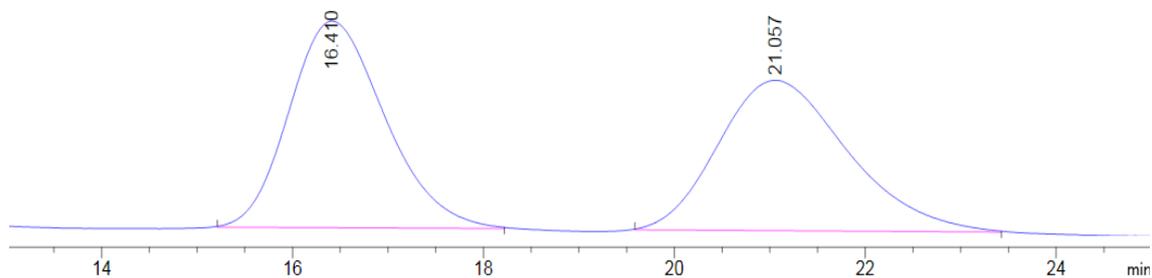


#	[min]	[min]	[mAU*s]	[mAU]	%	
1	8.277	VB	0.4085	3.47227e4	1312.92590	97.4055
2	16.443	VB	0.8729	924.86115	14.80250	2.5945

Figure S192. HPLC Analysis of (R)-10e

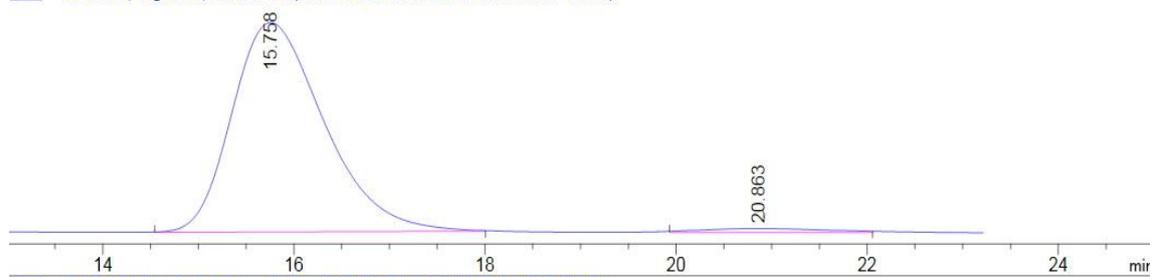
10e (The top one is racemic, and the bottom one is chiral)

DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-F-00.D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	16.410	BB	1.0333	2633.74170	37.78043	50.4166
2	21.057	BB	1.3163	2590.21680	27.46482	49.5834

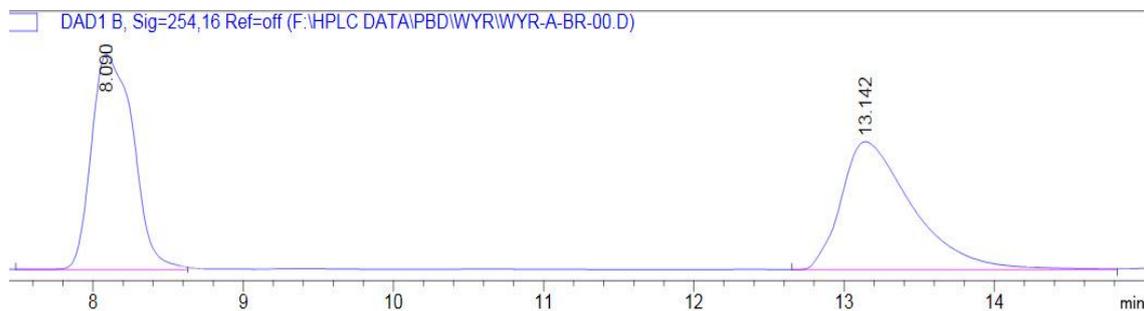
DAD1 B, Sig=254,16 Ref=off (F:\HPLC DATA\PBD\WYR\WYR-F-EE.D)



#	[min]	[min]	[mAU*s]	[mAU]	%	
1	15.758	BB	1.0269	1.79663e4	268.41965	97.3729
2	20.863	MM	1.5094	484.73395	5.35249	2.6271

Figure S193. HPLC Analysis of (R)-1b'

1b' (The top one is racemic, and the bottom one is chiral)



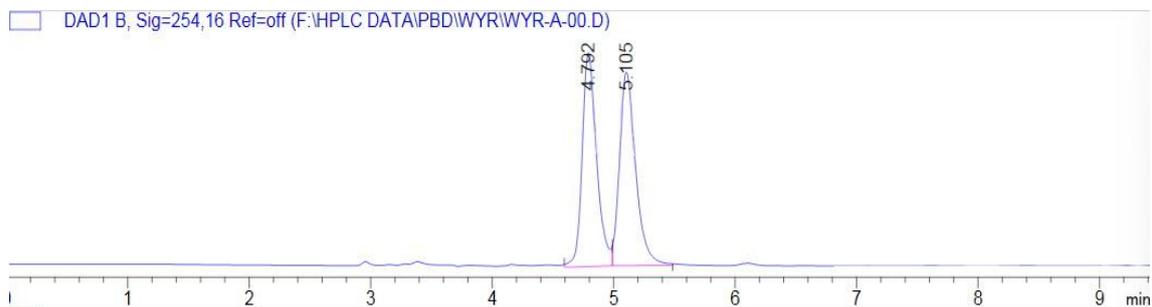
#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.090 VV	0.2737	3.02762e4	1564.67200	49.5474
2	13.142 VV	0.4981	3.08293e4	931.54236	50.4526



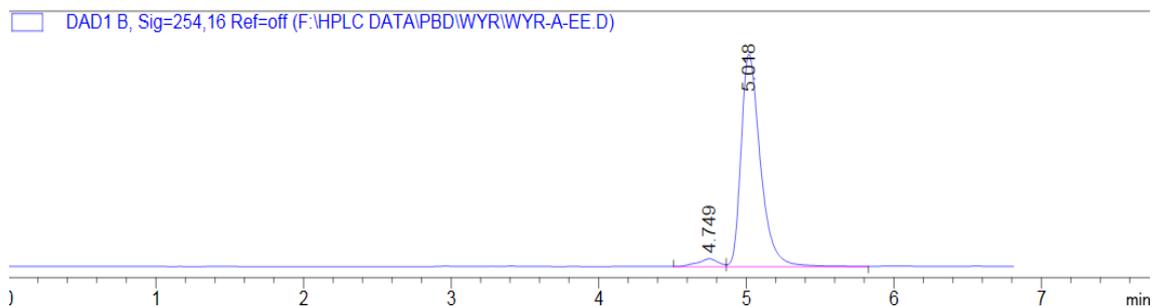
#	[min]	[min]	[mAU*s]	[mAU]	%
1	7.952 MM	0.2787	1.81198e4	1083.48218	94.8074
2	13.081 MM	0.4240	992.41565	39.01350	5.1926

Figure S194. HPLC Analysis of (R)-2c

2c (The top one is racemic, and the bottom one is chiral)



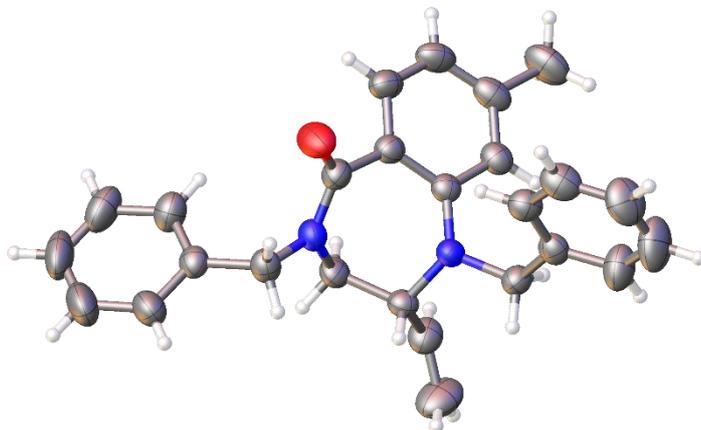
#	[min]	[min]	[mAU*s]	[mAU]	%
1	4.792 MM	0.1383	3654.85327	440.33969	49.9479
2	5.105 MM	0.1530	3662.48022	398.94604	50.0521



#	[min]	[min]	[mAU*s]	[mAU]	%
1	4.749 VV	0.1411	695.41956	70.51366	3.8437
2	5.018 VB	0.1380	1.73969e4	1915.22229	96.1563

6. X-ray Crystallographic Data

Figure S195. X-Ray Crystallographic Data for Compound (*R*)-3b



Structure factors have been supplied for datablock(s) (CCDC: 2495915)

Bond precision:	C-C = 0.0023 Å	Wavelength=1.54184	
Cell:	a=8.42816(5)	b=11.09278(9)	c=22.92566(15)
	alpha=90	beta=90	gamma=90
Temperature:	294 K		
	Calculated	Reported	
Volume	2143.36(3)	2143.36(3)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C ₂₆ H ₂₆ N ₂ O	C ₂₆ H ₂₆ N ₂ O	
Sum formula	C ₂₆ H ₂₆ N ₂ O	C ₂₆ H ₂₆ N ₂ O	
Mr	382.49	382.49	
D _x ,g cm ⁻³	1.185	1.185	
Z	4	4	
Mu (mm ⁻¹)	0.561	0.561	
F ₀₀₀	816.0	816.0	
F ₀₀₀ '	818.20		

h,k,lmax	10,13,28	10,13,28
Nref	4492[2567]	4394
Tmin,Tmax	0.979,0.984	0.624,1.000
Tmin'	0.975	

Correction method= # Reported T Limits: Tmin=0.624 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.71/0.98

Theta(max)= 76.210

R(reflections)= 0.0370(4250)

wR2(reflections)= 0.1028(4394)

S = 1.017

Npar= 264