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1. General Information

All reactions were carried out under an atmosphere of dry nitrogen. Anhydrous THF, toluene and 2-MeTHF were purchased from Sigma-Aldrich and used as solvent without further purification. Unless otherwise stated, reagents were commercially available and used as purchased. Chemicals were obtained from Sigma-Aldrich, Acros, or Matrix Scientific and solvents were purchased from Fisher Scientific. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wave ultraviolet light as well as by treatment with iodine. Flash chromatography was performed with silica gel (230–400 mesh). The NMR spectra were obtained using a Brüker 500 MHz Fourier-transform NMR spectrometer. The infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 1600 Series spectrometer. Optical rotations were recorded in HPLC-grade $CHCl_3$ using a JASCO DIP-370 digital polarimeter. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using electrospray ionization (ESI) in positive or negative mode. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and are uncorrected.

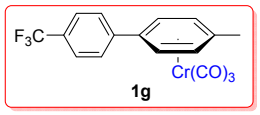
2. Preparation of Allylic Electrophiles

Allylic electrophiles were prepared according to literature procedures.[1]

3. Preparation of (η^6-toluene)$Cr(CO)_3$ Derivatives

Compounds **1a**,[2] **1b**,[3] **1c**,[4] **1d**,[4] **1e**,[4] **1f**,[4] **1h**,[5] **1i**,[5] **1j**,[3] **1k**,[6] and **1l**,[4] were prepared according to general literature procedures for the synthesis of arene tricarbonylchromium complexes. The complexes were crystallized from diethyl ether and hexanes to afford yellow crystalline solids.

Synthesis of (η^6-toluene)$Cr(CO)_3$ derivatives (**1g**):



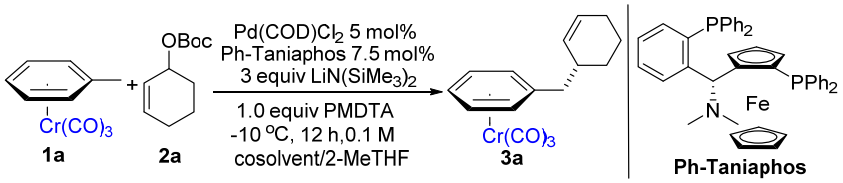
A solution of $Cr(CO)_6$ (1.10 g, 5.0 mmol), 4-trifloromethyl-4'-methylbiphenyl (1.18 g, 5.0 mmol) and THF (3 mL) in DME (8 mL) was heated under reflux (oil bath temp = 120 °C) under a nitrogen atmosphere for 4 days. During this time, the solution turned from colorless to yellow-orange. The yellow–orange solution was cooled to room temperature. The solution was filtered through Celite, and then evaporated under reduced pressure. The crude product was purified by silica gel chromatography (hexanes/ethyl acetate 9:1) to afford **1g** (0.87 g, 47% yield) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 5.78 (d, J = 7.0 Hz, 2H), 5.31 (d, J = 6.5 Hz, 2H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 232.8, 140.6, 130.9 (q, J = 32.5 Hz), 127.6, 126.0 (q, J = 3.8 Hz), 121.9 (q, J = 271.3 Hz), 109.3, 105.3, 94.0, 92.4, 20.6; IR (neat): λmax *1961, 1872* (strong CO stretch), 1618, 1326, 1169, 1126, 1071, 837, 663, 625 cm^{-1}; HRMS : calcd for $C_{17}H_{11}O_3ClCrF_3$ $[M+Cl]^-$ 406.9754, found 406.9757.

4. Procedure and Characterization for the Pd-catalyzed Asymmetric Allylic Alkylation of cyclic electrophiles

***General Procedure A**:* To an oven-dried microwave vial equipped with a stir bar was added $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and Ph-Taniaphos (5.16 mg, 0.0075 mmol) under nitrogen atmosphere inside a glove box at room temperature. Next, 1.4 mL of dry 2-MeTHF and 0.6 mL of dry toluene were added sequentially via syringe to give a reddish brown solution. After the catalyst/ligand solution was stirred

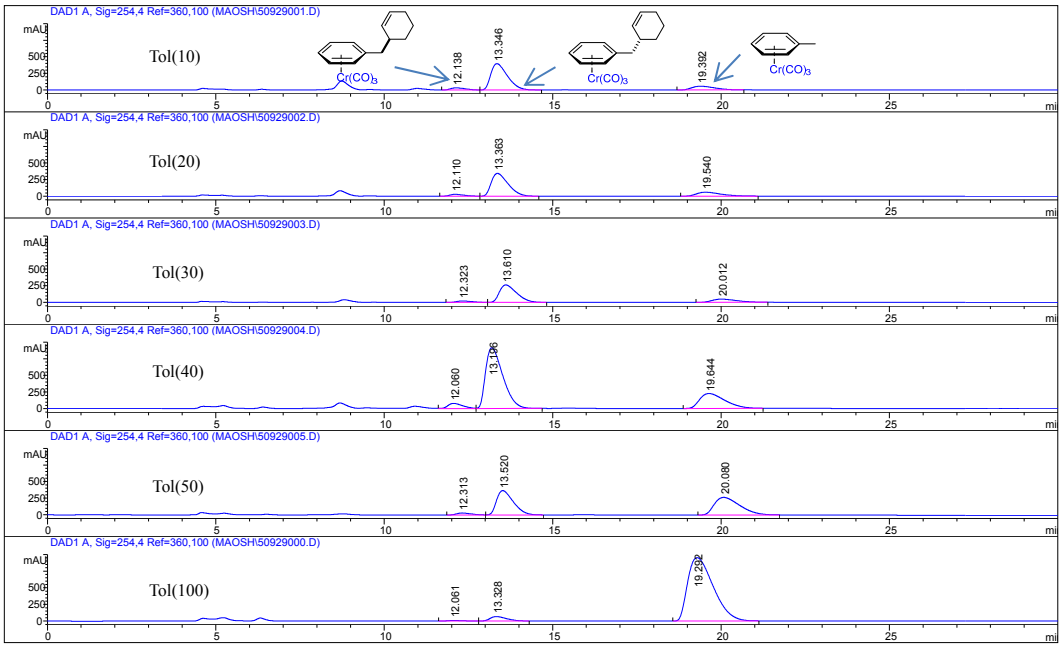
for 30 min at 24 °C inside the glove box, (η^6-arene-CH_2Z)$Cr(CO)_3$ (0.1 mmol, 1.0 equiv) was added to the reaction vial followed by $LiN(SiMe_3)_2$ (50.2 mg, 0.3 mmol, 3 equiv) to give a brown solution. The microwave vial was sealed, removed from the glove box. The microwave vial was cooled to -30 °C, and PMDTA (33 μL, 0.15 mmol, 1.5 equiv) was added via microsyringe and the resulting solution stirred for an additional 5 min. The allylic electrophile (0.2 mmol, 2.0 equiv) was then added via microsyringe under nitrogen atmosphere and the reaction mixture was stirred under nitrogen atmosphere for 12 h. The resulting reddish brown solution was then quenched by addition of 5 drops water via syringe, and then the vial opened to air. The reaction mixture was passed through a short pad of silica gel and rinsed with 10 mL 10:1 ethyl acetate: methanol to afford a reddish solution. The solvent was removed by rotary evaporator. The reddish brown residue was purified by flash chromatography.

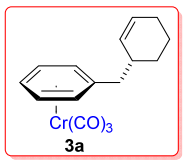
Optimization of the solvent composition



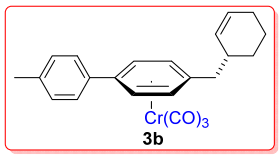
entry	cosolvent (%)[a]	yield (%)[b]	ee (%)[c]
1	Tol (10)	69	86.4
2	Tol (20)	72	86.4
3	Tol (30)	79	86.4
4	Tol (40)	66	86.9
5	Tol (50)	54	86.9
6	Tol (100)	trace	--

a: Cosolvent indicates toluene by volume in 2-MeTHF. b: Yields determined by ^{1}H NMR analysis of crude mixtures with CH_2Br_2 as internal standard. c: The ee was determined by chiral HPLC.

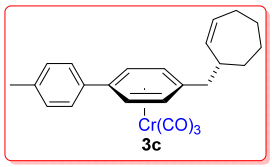




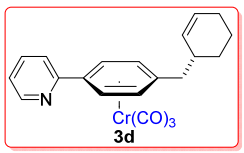
(-)-(η^6-(2-Cyclohexen-1-ylmethyl)-benzene)Cr(CO)$_3$ (3a): The reaction was performed following General Procedure A with **1a** (22.8 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.3 mmol) and **2a** (40.0 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (28.1 mg, 91% yield, 92% ee) as a yellow solid. $[\alpha]_D^{25}$ = -74.0 (*c* 1.4, CHCl$_3$). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (1% isopropanol in hexanes, 1 mL/min, 254 nm, minor t_r = 12.80 min, major t_r = 14.35 min). The NMR spectral data match the previously published data.[4]



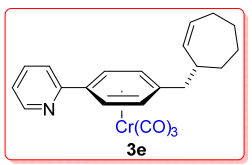
(-)-(η^6-(2-Cyclohexen-1-ylmethyl)-4-(*p*-tolyl)-benzene)Cr(CO)$_3$ (3b): The reaction was performed following General Procedure A with **1b** (31.8 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.3 mmol) and **2a** (40.0 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:15) to give the product (34.2 mg, 86% yield, 94% ee) as a yellow solid. $[\alpha]_D^{25}$ = -59.7 (*c* 0.6, CHCl$_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (5% isopropanol in hexanes, 0.8 mL/min, 254 nm, major t_r = 8.96 min, minor t_r = 11.63 min). The NMR spectral data match the previously published data.[4]



(-)-(η^6-(2-Cycloheptene-1-ylmethyl)-4-(*p*-tolyl)-benzene)Cr(CO)$_3$ (3c): The reaction was performed following General Procedure A with **1b** (31.8 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (67.0 mg, 0.4 mmol) and **2b** (63.6 mg, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:15) to give the product (35.1 mg, 85% yield, 82% ee) as a yellow solid. $[\alpha]_D^{25}$ = -15.1 (*c* 1.0, CHCl$_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (5% isopropanol in hexanes, 1 mL/min, 254 nm, major t_r = 7.00 min, minor t_r = 8.22 min). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.38 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 5.85-5.80 (m, 1H), 5.74 (d, *J* = 6.5 Hz, 2H), 5.59 (d, *J* = 12.0 Hz, 1H), 5.35 (d, *J* = 6.5 Hz, 2H), 2.48-2.40 (m, 3H), 2.37 (s, 3H), 2.19-2.10 (m, 2H), 1.98-1.94 (m, 1H), 1.74-1.66 (m, 2H), 1.59-1.56 (m, 1H), 1.39-1.35 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 233.4, 139.1, 135.5, 133.6, 132.8, 129.7, 127.1, 111.2, 109.0, 93.7, 93.2, 42.0, 41.9, 33.2, 30.3, 28.9, 26.9, 21.4. IR (neat): 2922, 2852, *1962, 1881* (strong CO stretch), 1472, 1445, 817, 668, 625, 533. HRMS: calcd for $C_{24}H_{24}O_3Cr$ $[M]^+$ 412.1131, found 412.1132.

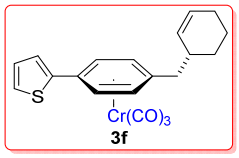


(-)-(η^6-(2-Cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene)Cr(CO)$_3$ (3d): The reaction was performed following General Procedure A with **1c** (30.5 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.3 mmol) and **2a** (40.0 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:20) to give the product (30.8 mg, 80% yield, 96% ee) as a yellow solid. $[\alpha]_D^{25}$ = -73.9 (*c* 0.5, CHCl$_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (5% isopropanol in hexanes, 1 mL/min, 254 nm, major t_r = 12.29 min, minor t_r = 15.21 min). The NMR spectral data match the previously published data.[4]

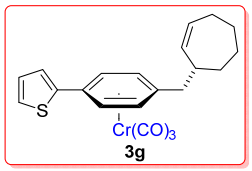


(-)-(η^6-(2-Cycloheptene-1-ylmethyl)-4-(2-pyridyl)-benzene)Cr(CO)$_3$ (3e): The reaction was performed following General Procedure A with **1c** (30.5 mg,

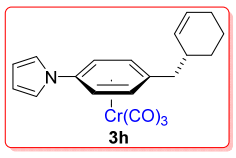
0.1 mmol), $LiN(SiMe_3)_2$ (67.0 mg, 0.4 mmol) and **2b** (63.6 mg, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:15) to give the product (27.9 mg, 70% yield, 87% ee) as a yellow solid. $[\alpha]_D^{25}$ = -19.3 (*c* 0.7, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (10% isopropanol in hexanes, 1 mL/min, 230 nm, major t_r = 9.03 min, minor t_r = 10.85 min). ^1H NMR (500 MHz, $CDCl_3$) δ: 8.59 (d, *J* = 4.5 Hz, 1H), 7.75-7.71 (m, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 1H), 6.24 (d, *J* = 6.5 Hz, 2H), 5.83-5.81 (m, 1H), 5.58 (d, *J* = 11.5 Hz, 1H), 5.36 (d, *J* = 7.0 Hz, 2H), 2.52-2.49 (m, 2H), 2.46-2.43 (m, 1H), 2.17-2.10 (m, 2H), 1.97-1.93 (m, 1H), 1.75-1.65 (m, 2H), 1.59-1.55 (m, 1H), 1.38-1.33 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 233.0, 153.9, 149.7, 137.1, 135.4, 132.8, 123.5, 120.1, 112.5, 103.9, 93.1, 93.00, 92.95, 42.1, 42.0, 33.1, 30.2, 28.9, 26.9. IR (neat): 2922, 2851, *1963, 1885* (strong CO stretch), 1586, 1571, 1461, 1432, 786, 666, 623, 532. HRMS: calcd for $C_{22}H_{22}NO_3Cr$ $[M+H]^+$ 400.1005, found 400.1001.



(-)-(η⁶-(2-Cyclohexen-1-ylmethyl)-4-(2-thiophenyl)-benzene)Cr(CO)₃ (3f): The reaction was performed following General Procedure A with **1d** (31.0 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2a** (40 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:15) to give the product (32.8 mg, 84% yield, 96% ee) as a yellow solid. $[\alpha]_D^{25}$ = -69.2 (*c* 0.5, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (5% isopropanol in hexanes, 1 mL/min, 254 nm, major t_r = 8.92 min, minor t_r = 12.28 min). The NMR spectral data match the previously published data.[4]

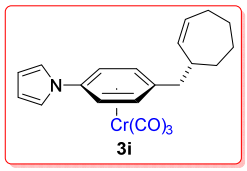


(-)-(η⁶-(2-Cycloheptene-1-ylmethyl)-4-(2-thiophenyl)-benzene)Cr(CO)₃ (3g): The reaction was performed following General Procedure A with **1d** (31.0 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (67.0 mg, 0.4 mmol) and **2b** (63.6 mg, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:20) to give the product (22.2 mg, 55% yield, 83% ee) as a yellow solid. $[\alpha]_D^{25}$ = -20.0 (*c* 0.7, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (10% isopropanol in hexanes, 1 mL/min, 254 nm, major t_r = 11.94 min, minor t_r = 15.02 min). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.28 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 7.23 (dd, *J* = 3.5 Hz, 1.0 Hz, 1H), 7.02 (dd, *J* = 4.5 Hz, 3.5 Hz, 1H), 5.83-5.81 (m, 1H), 5.76 (d, *J* = 6.5 Hz 2H), 5.58-5.56 (m, 1H), 5.33 (d, *J* = 6.5 Hz 2H), 2.47-2.36 (m, 3H), 2.19-2.09 (m, 2H), 1.98-1.93 (m, 1H), 1.73-1.65 (m, 2H), 1.59-1.54 (m, 1H), 1.38-1.32 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 233.1, 139.9, 135.4, 132.8, 128.1, 126.3, 125.0, 110.9, 102.0, 93.3, 91.8, 91.7, 41.99, 41.97, 33.2, 30.3, 28.9, 26.9. IR (neat): 2921, 2851, *1960, 1875* (strong CO stretch), 1471, 1444, 1347, 1216, 852, 702, 666, 624, 531. HRMS: calcd for $C_{21}H_{20}O_3SCr$ $[M]^+$ 404.0538, found 404.0548.

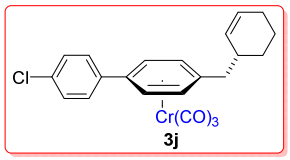


(-)-(η⁶-(2-Cyclohexen-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)Cr(CO)₃ (3h): The reaction was performed following General Procedure A with **1e** (29.3, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2a** (40 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (30.6, 82% yield, 94% ee) as a yellow solid. $[\alpha]_D^{25}$ = -68.5 (*c* 1.0, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (5% isopropanol in hexanes, 1 mL/min, 254 nm, major t_r = 9.37 min, minor t_r = 14.20 min). The NMR

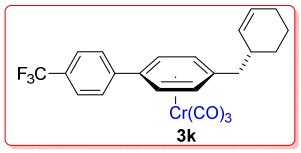
spectral data match the previously published data.[4]



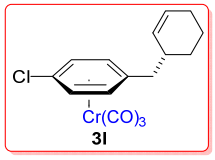
(-)-(η^6-(2-Cycloheptene-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)Cr(CO)$_3$ (3i): The reaction was performed following General Procedure A with **1e** (39.3 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (67.0 mg, 0.40 mmol) and **2b** (63.6 mg, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:15) to give the product (24.4 mg, 63% yield, 80% ee) as a yellow solid. $[\alpha]_D^{25}$ = -17.1 (*c* 0.9, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (10% isopropanol in hexanes, 1 mL/min, 254 nm, major t_r = 9.41 min, minor t_r = 12.03 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: .6.96 (t, *J* = 2.0 Hz, 2H), 6.29 (t, *J* = 2.5 Hz, 2H), 5.84-5.81 (m, 1H), 5.60 (d, *J* = 6.5 Hz 2H), 5.56-5.54 (m, 1H), 5.44 (d, *J* = 6.5 Hz 2H), 2.46-2.32 (m, 3H), 2.17-2.10 (m, 2H), 1.97-1.93 (m, 1H), 1.72-1.65 (m, 2H), 1.59-1.54 (m, 1H), 1.37-1.31 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 232.7, 135.2, 132.9, 119.9, 116.5, 111.8, 108.4, 94.0, 84.8, 84.7, 42.0, 41.6, 33.2, 30.3, 28.9, 26.9. IR (neat): 2922, 2851, *1965, 1883* (strong CO stretch), 1543, 1491, 1326, 1117, 1065, 918, 726, 668, 624, 533. HRMS: calcd for $C_{21}H_{21}NO_3Cr$ $[M]^+$ 387.0927, found 387.0924.



(-)-(η^6-(2-Cyclohexen-1-ylmethyl)-4-(*p*-chlorophenyl)-benzene)Cr(CO)$_3$ (3j): The reaction was performed following General Procedure A with **1f** (33.9 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.30 mmol) and **2a** (40 µL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (34.8 mg, 83% yield, 94% ee) as a yellow solid. $[\alpha]_D^{25}$ = -49.8 (*c* 0.6, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (10% isopropanol in hexanes, 1 mL/min, 254 nm, major t_r = 8.81 min, minor t_r = 11.86 min). The NMR spectral data match the previously published data.[4]



(-)-(η^6-(2-Cyclohexen-1-ylmethyl)-4-(*p*-trifloromethylphenyl)-benzene)Cr(CO)$_3$ (3k): The reaction was performed following General Procedure A with **1g** (37.2 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.3 mmol) and **2a** (40 µL, 0.2 mmol) for 4h. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (38.0 mg, 84% yield, 94% ee) as a yellow solid. $[\alpha]_D^{25}$ = -53.7 (*c* 1.2, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (5% isopropanol in hexanes, 1 mL/min, 254 nm, major t_r = 11.90 min, minor t_r = 14.18 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: .7.66 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 5.77-5.76 (m, 3H), 5.58 (d, *J* = 9.5 Hz 1H), 5.32 (d, *J* = 6.5 Hz 2H), 2.43-2.35 (m, 3H), 2.00 (m, 2H), 1.82-1.73 (m, 2H), 1.68-1.61 (m, 1H), 1.37-1.31 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 232.7, 140.6, 131.0 (q, *J* = 32.5 Hz), 129.7, 129.0, 127.6, 126.0 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 271.3 Hz), 111.6, 105.9, 93.62, 93.61, 92.80, 92.78, 41.9, 37.8, 28.9, 25.4, 21.2. IR (neat): 2931, 2861, *1966, 1889* (strong CO stretch), 1618, 1326, 1169, 1127, 1071, 1020, 1008, 840, 662, 622, 534. HRMS: calcd for $C_{23}H_{19}O_3ClF_3Cr$ $[M+Cl]^+$ 487.0380, found 487.0404.

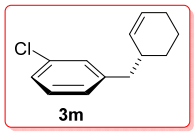


(-)-(η^6-(2-Cyclohexen-1-ylmethyl)-4-chloro-benzene)Cr(CO)$_3$ (3l): The reaction was performed following General Procedure A with **1h** (26.3 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.3 mmol) and **2a** (40 µL, 0.2 mmol) for 2.5h.

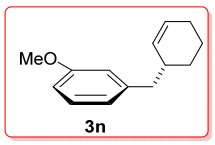
The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:20) to give the product (24.0 mg, 70% yield, 94% ee) as a yellow solid. $[\alpha]_D^{25}$ = -74.4 (*c* 1.4, $CHCl_3$). The ee was determined after conversion of **3l** to **3b** (using published method[7]) by HPLC using a Daicel Chiralpak AD-H column (5% isopropanol in hexanes, 0.8 mL/min, 254 nm, major t_r = 9.81 min, minor t_r = 12.91 min). The NMR spectral data of **3l** match the previously published data.[4]

5. Procedure and Characterization for the Two-step One-pot Allylic Substitution/Demetallation.

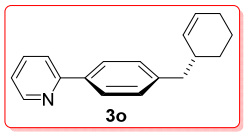
***General Procedure B**:* The reaction was conducted according to General Procedure A described above. After 12 h, the reaction was quenched with 3 drops of water, diluted with 20 mL of diethyl ether, and the solution was exposed to sunlight by placing it on the windowsill and stirring for 24 h at room temperature. The reaction mixture was then filtered through a pad of $MgSO_4$ and silica, concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel.



(-)-(2-Cyclohexen-1-ylmethyl)-3-chlorobenzene (3m): The reaction was performed following General Procedure B with **1i** (26.3 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2a** (40 µL, 0.2 mmol) for 2.5h. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:30) to give the product (15.7 mg, 76% yield, 91% ee) as a colorless oil. $[\alpha]_D^{25}$ = -28.9 (*c* 0.6, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (0.5% isopropanol in hexanes, 0.4 mL/min, 230 nm, minor t_r = 13.55 min, major t_r = 14.45 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22-7.17 (m, 3H), 7.05 (d, *J* = 7.0 Hz, 1H), 5.71-5.68 (m, 1H), 5.55-5.52 (m, 1H), 2.61 (dd, *J* = 15.0 Hz, 10.0 Hz, 1H), 2.52 (dd, *J* = 15.0 Hz, 10.0 Hz, 1H), 2.38-2.34 (m, 1H), 2.00-1.96 (m, 2H), 1.73-1.68 (m, 2H), 1.53-1.48 (m, 1H), 1.28-1.20 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 143.2, 134.2, 131.0, 129.6, 129.4, 127.96, 127.56, 126.2, 42.6, 37.2, 29.0, 25.5, 21.4. IR (neat): 2925, 2856, 1597, 1573, 1475, 1428, 1384, 1079, 871, 773, 723, 699. HRMS: calcd for $C_{13}H_{15}Cl$ $[M]^+$ 206.0862, found 206.0864.

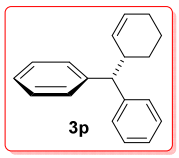


(-)-(2-Cyclohexen-1-ylmethyl)-3-methoxybenzene (3n): The reaction was performed following General Procedure B with **1j** (25.8 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2a** (40 µL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:30) to give the product (14.5 mg, 72% yield, 91% ee) as a colorless oil. $[\alpha]_D^{25}$ = -37.8 (*c* 0.9, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (1% isopropanol in hexanes, 0.5 mL/min, 230 nm, minor t_r = 16.73 min, major t_r = 19.50 min). The NMR spectral data match the previously published data.[4]

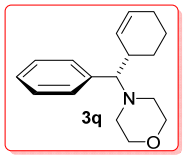


(-)-(2-Cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene (3o): The reaction was performed following General Procedure B with **1c** (30.5 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2a** (40 µL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (18.4 mg, 74% yield, 94% ee) as a white solid. Mp 59–60 ^{o}C $[\alpha]_D^{25}$ = -35.3 (*c* 0.8, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak OD-H column (5% isopropanol in hexanes, 1 mL/min, 230 nm, minor t_r = 11.75 min, major t_r = 14.70 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.68 (d, *J* = 5.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.73-7.71 (m, 2H), 7.29-7.26 (m, 2H), 7.21-7.18 (m, 1H), 5.72-5.69 (m, 1H), 5.60-5.58 (m, 1H), 2.69 (dd, *J* = 13.5 Hz, 7.5

Hz, 1H), 2.60 (dd, J = 13.5 Hz, 8.0 Hz, 1H), 2.42-2.40 (m, 1H), 1.99-1.98 (m, 2H), 1.75-1.72 (m, 2H), 1.53-1.51 (m, 1H), 1.31-1.27 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 157.7, 149.8, 142.2, 137.2, 136.9, 131.4, 129.8, 127.7, 126.9, 122.0, 120.5, 42.7, 37.4, 29.1, 25.6, 21.5. IR (neat): 3014, 2924, 2854, 1586, 1466, 1435, 1185, 1152, 1016, 859, 773, 741, 720, 670. HRMS: calcd for $C_{18}H_{20}N$ $[M+H]^+$ 250.1596, found 250.1596.



(-)-3-(Diphenylmethyl)-1-cyclohexene (3p): The reaction was performed following General Procedure B with **1k** (30.4 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2a** (40 µL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:30) to give the product (24.3 mg, 98% yield, 92% ee) as a colorless oil. $[\alpha]_D^{25}$ = -10.4 (*c* 1.9, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (3% isopropanol in hexanes, 0.8 mL/min, 230 nm, minor t_r = 21.14 min, major t_r = 24.66 min). The NMR spectral data match the previously published data.

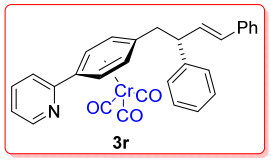


(-)-4-(Cyclohex-2-en-1-yl(phenyl)methyl)morpholine (3q): The reaction was performed following General Procedure B with **1l** (31.3 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol) and **2a** (40 µL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:30) to give the product (24.7 mg, 96% yield, 83% ee for major product, 93% ee for minor product) as a colorless oil. $[\alpha]_D^{25}$ = -28.6 (*c* 2.1, $CHCl_3$).The ee was determined by HPLC with a Daicel Chiralpak OD-H column (2% isopropanol in hexanes, 0.6 mL/min, 230 nm, for major product major t_r = 12.23 min, minor t_r = 15.49 min, for minor product minor t_r = 10.68 min, major t_r = 13.36 min). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.34-7.31 (m, 2H), 7.29-7.25 (m, 1H), 7.18 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 7.0 Hz, 1H), 6.15 (d, J = 10.0 Hz, major diastereomer), 5.79-5.77 (m, major diastereomer), 5.67-5.64 (m, minor diastereomer), 5.53 (d, J = 10.5 Hz, minor diastereomer), 3.71-3.65 (m, 4H), 3.20 (d, J = 10.0 Hz, major diastereomer), 3.15 (d, J = 8.5 Hz, minor diastereomer), 2.83-2.75 (m, 1H), 2.48-2.32 (m, 4H), 1.98-1.89 (m), 1.70-1.63 (m, 1H), 1.51-1.47 (m), 1.33-1.26 (m, minor diastereomer), 1.04-0.96 (m, major diastereomer). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 138.1, 136.6, 129.9, 129.5, 129.3, 128.8, 128.5, 127.96, 127.92, 127.23, 127.21, 74.9, 74.5, 67.6, 67.5, 50.8, 50.0, 35.7, 34.8, 27.2, 26.9, 25.8, 25.7, 22.0, 21.8. IR (neat): 3025, 2951, 2925, 2890, 2852, 1492, 1451, 1287, 1119, 1071, 1003, 901, 870, 754, 724, 705, 550. HRMS: calcd for $C_{17}H_{24}NO$ $[M+H]^+$ 258.1858, found 258.1860.

6. Procedure and Characterization for the Pd-catalyzed Asymmetric Allylic Alkylation of acyclic electrophiles

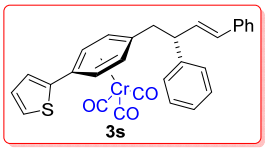
General Procedure C*:* To an oven-dried microwave vial equipped with a stir bar was added $Pd(COD)Cl_2$ (1.43 mg, 0.005 mmol) and (*R*)-CTH-JAFAPHOS (5.61 mg, 0.0075 mmol) under nitrogen atmosphere inside a glove box at room temperature. Next, 2.1 mL of dry 2-MeTHF and 0.9 mL of dry toluene were added sequentially via syringe. After the catalyst/ligand solution was stirred for 30 min at 24 °C inside the glove box, (η^6-arene-CH_2Z)$Cr(CO)_3$ (0.1 mmol, 1.0 equiv) was added to the reaction vial followed by $LiN(SiMe_3)_2$ (67.2 mg, 0.4 mmol, 4 equiv). The microwave vial was sealed and removed from the glove box. The microwave vial was cooled to -30 °C, PMDTA (33 µL, 0.15 mmol, 1.5 equiv) was added via microsyringe, and the resulting yellow solution stirred for additional 5 min. A

solution of the allylic electrophile in 2-MeTHF/toluene (v/v = 0.7 mL/ 0.3 mL, 0.3 mmol, 3 equiv) was added via syringe over 10 min under nitrogen atmosphere and the reaction mixture was stirred under nitrogen atmosphere for 12 h at –30 °C . Next, 5 drops water was added via syring, and then the vial opened to air. The reaction mixture was passed through a short pad of silica gel and rinsed with 5 mL 10:1 ethyl acetate: methanol. The solvent was removed by rotary evaporator. The residue was purified by flash chromatography.



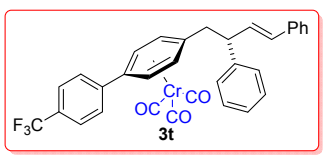
3r

(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-4-(2-pyridyl)-benzene)Cr(CO)$_3$ (3r): The reaction was performed following General Procedure C with **1c** (30.5 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (67.0 mg, 0.40 mmol) and **2c** (96.0 mg, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (35.8 mg, 72% yield, >99% ee) as a yellow solid. $[\alpha]_D^{25}$ = +5.0 (*c* 1.4, $CHCl_3$). The ee was determined by SFC with a Daicel Chiralpak AD-H column (30% methanol in CO_2, 4 mL/min, 270 nm, minor t_r = 3.00 min, major t_r = 3.71 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.58-8.57 (m, 1H), 7.71-7.69 (m, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.34-7.28 (m, 6H), 7.24-7.20 (m, 5H), 6.42 (s, 1H), 6.41 (s, 1H), 6.19 (dd, *J* = 7.0 Hz, 1.0 Hz, 1H), 6.09 (dd, *J* = 6.5 Hz, 1.0 Hz, 1H), 5.33 (dd, *J* = 6.5 Hz, 1.5 Hz, 1H), 5.00 (dd, *J* = 7.0 Hz, 1.5 Hz, 1H), 3.70-3.66 (m, 1H), 2.94 (dd, *J* = 13.5 Hz, 7.0 Hz, 1H), 2.86 (dd, *J* = 14.0 Hz, 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 232.9, 153.7, 149.7, 142.4, 137.1, 131.9, 131.1, 129.0, 128.8, 128.1, 127.8, 127.2, 126.5, 123.5, 120.1, 110.8, 103.7, 93.09, 93.07, 92.9, 92.8, 51.7, 42.2. IR (neat): 3059, 3027, *1961, 1881* (strong CO stretch), 1587, 1493, 1461, 1432, 960, 786, 738, 699, 666, 627, 532. HRMS: calcd for $C_{30}H_{24}NO_3Cr$ $[M+H]^+$ 498.1161, found 498.1165.



3s

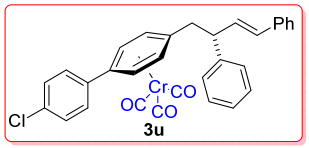
(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(2-thiophenyl)-benzene)Cr(CO)$_3$ (3s): The reaction was performed following General Procedure C with **1d** (31.0 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (67.0 mg, 0.40 mmol) and **2c** (96.0 mg, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (32.7 mg, 65% yield, 94% ee) as a yellow solid. $[\alpha]_D^{25}$ = +3.0 (*c* 0.7, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (10% isopropanol in hexanes, 1 mL/min, 254 nm, minor t_r = 11.03 min, major t_r = 11.91 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28-7.19 (m, 12H), 7.00 (dd, *J* = 5.0 Hz, 3.5 Hz, 1H), 6.41 (s, 1H), 6.40 (d, *J* = 2.0 Hz, 1H), 5.71 (dd, *J* = 6.5 Hz, 1.5 Hz, 1H), 5.60 (dd, *J* = 7.0 Hz, 1.0 Hz, 1H), 5.29 (dd, *J* = 7.0 Hz, 1.5 Hz, 1H), 4.98 (dd, *J* = 6.5 Hz, 1.5 Hz, 1H), 3.66-365 (m, 1H), 2.88 (dd, *J* = 14.0 Hz, 7.0 Hz, 1H), 2.81 (dd, *J* = 13.5 Hz, 7.5 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 232.8, 142.3, 139.6, 136.9, 131.7, 130.9, 128.9, 128.6, 127.8, 128.6, 127.0, 126.3, 126.2, 124.7, 109.0, 101.8, 93.17, 93.15, 91.2, 91.1, 51.5, 41.9. IR (neat): 3082, 3060, 2927, 3027, *1961, 1885* (strong CO stretch), 1599, 1494, 1452, 1259, 967, 909, 852, 745, 735, 700, 666, 624, 532. HRMS: calcd for $C_{29}H_{22}O_3SCr$ $[M]^+$ 502.0695, found 502.0693.



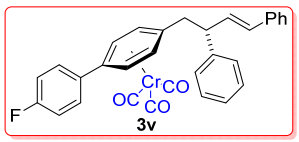
3t

(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(2-thiophenyl)-benzene)Cr(CO)$_3$ (3t): The reaction was performed following General Procedure C with **1g** (37.2 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (67.0 mg, 0.40 mmol) **2c** (96.0 mg, 0.3 mmol) and 10 mol% Pd for 4h. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product

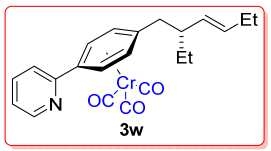
(33.9 mg, 60% yield, 92% ee) as a yellow solid. $[\alpha]_D^{25}$ = +3.9 (*c* 0.7, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (10% isopropanol in hexanes, 1 mL/min, 254 nm, minor t_r = 13.91 min, major t_r = 15.66 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.34-7.21 (m, 10H), 6.41 (s, 1H), 6.40 (d, *J* = 2.5 Hz, 1H), 5.70 (dd, *J* = 7.0 Hz, 2.0 Hz 1H), 5.60 (dd, *J* = 6.5 Hz, 1.5 Hz 1H), 5.30 (dd, *J* = 6.5 Hz, 1.5 Hz 1H), 5.00 (dd, *J* = 6.5 Hz, 1.5 Hz 1H), 3.68-367 (m, 1H), 2.92 (dd, *J* = 14.0 Hz, 7.0 Hz, 1H), 2.86 (dd, *J* = 13.5 Hz, 8.0 Hz, 1H). ^{13}C{^{1}H} 232.6, 142.4, 140.4, 137.1, 131.9, 131.2, 131.0 (q, *J* = 32.5 Hz), 129.1, 128.8, 128.0, 127.8, 127.5, 127.3, 126.5, 126.0 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 263.8 Hz), 110.4, 105.8, 93.21, 93.15, 93.04, 93.00, 51.7, 42.1. IR (neat): 3583, 2923, *1963, 1883*, (strong CO stretch) 1616.,1493, 1451, 1325, 1167, 1124, 1070, 1007, 966, 840, 746, 695. HRMS: calcd for $C_{32}H_{23}O_3F_3Cr$ $[M]^+$ 564.1004, found 564.1001.



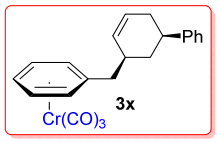
(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(*p*-chlorophenyl)-benzene)Cr(CO)$_3$ (3u): The reaction was performed following General Procedure C with **1f** (33.9 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (67.0 mg, 0.40 mmol) **2c** (96.0 mg, 0.3 mmol) and 10 mol% Pd. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (32.9 mg, 62% yield, 94% ee) as a yellow solid. $[\alpha]_D^{25}$ = +2.8 (*c* 0.7, $CHCl_3$). The ee was determined by SFC with a Daicel Chiralpak AD-H column (40% methanol in CO_2, 4 mL/min, 254 nm, minor t_r = 5.45 min, major t_r = 7.00 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37-7.29 (m, 10H), 7.24-7.21 (m, 4H), 6.41 (s, 1H), 6.40 (d, *J* = 2.0 Hz, 1H), 5.65 (dd, *J* = 6.5 Hz, 1.5 Hz, 1H), 5.55 (dd, *J* = 6.5 Hz, 1.5 Hz, 1H), 5.30 (dd, *J* = 5.0 Hz, 2.0 Hz, 1H), 5.00 (d, *J* = 7.0 Hz, 1.5 Hz, 1H), 3.68-364 (m, 1H), 2.91 (dd, *J* = 14.0 Hz, 7.5 Hz, 1H), 2.84 (dd, *J* = 14.0 Hz, 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 232.7, 142.3, 136.9, 134.9, 131.7, 130.9, 129.0, 128.8, 128.6, 128.2, 127.8, 127.6, 127.1, 126.3, 51.5, 41.8. IR (neat): 3585.2, 2923.6, *1964, 1885* (strong CO stretch), 1616 ,1598, 1451, 1325,1025, 1007, 966, 840, 746, 695. HRMS: calcd for $C_{31}H_{23}O_3ClCr$ $[M]^+$ 530.0741, found 530.0743.



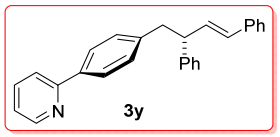
(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(*p*-fluorophenyl)-benzene)Cr(CO)$_3$ (3v): The reaction was performed following General Procedure C with **1m** (32.2 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (67.0 mg, 0.40 mmol) **2c** (96.0 mg, 0.3 mmol) and 10 mol% Pd. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (36.5 mg, 71% yield, >99% ee) as a yellow solid. $[\alpha]_D^{25}$ = +6.1 (*c* 0.7, $CHCl_3$). The ee was determined by HPLC with a Daicel Chiralpak IB column (5% isopropanol in hexanes, 0.4 mL/min, 254 nm, minor t_r = 31.84 min, major t_r = 34.22 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43-7.40 (m, 2H), 7.35-7.28 (m, 6H), 7.20-7.20 (m, 4H), 7.08-7.05 (m, 2H), 6.41 (s, 1H), 6.40 (d, *J* = 1.5 Hz, 1H), 5.64 (dd, *J* = 6.5 Hz, 1.5 Hz, 1H), 5.54 (dd, *J* = 6.5 Hz, 1.5 Hz, 1H), 5.31 (dd, *J* = 5.0 Hz, 2.0 Hz, 1H), 5.01 (d, *J* = 7.0 Hz, 1.5 Hz, 1H), 3.68-3.65 (m, 1H), 2.90 (dd, *J* = 13.5 Hz, 7.0 Hz, 1H), 2.84 (dd, *J* = 13.5 Hz, 7.5 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 233.1, 163.3 (*J* = 13.5 Hz), 142.5, 137.1, 132.7 (*J* = 3.8 Hz), 132.0, 131.2, 129.1, 129.0 (*J* = 8.8 Hz), 128.9, 128.1, 127.8, 127.3, 126.5, 116.1 (*J* = 21.3 Hz), 109.8, 107.7, 93.6, 93.5, 92.93, 92.87, 51.7, 42.0. IR (neat): 3082, 3027, *1960, 1878* (strong CO stretch), 1604 ,1515, 1493, 1471, 1451,1235, 1158, 1104, 967, 835, 746, 700, 665, 625, 534. HRMS: calcd for $C_{31}H_{23}O_3FCr$ $[M]^+$ 514.1016, found 514.1036.



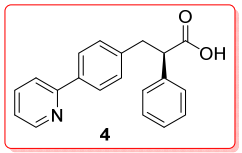
(*E*)-(η^6-(2-ethylhex-3-en-1-yl)-4-(2-pyridyl)-benzene)Cr(CO)$_3$ (3w): The reaction was performed following General Procedure C with **1c** (30.5 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (67.0 mg, 0.4 mmol) and **2d** (64.2 mg, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (25.3 mg, 63% yield, 64% ee) as a yellow solid. $[\alpha]_D^{25}$ = +5.2 (*c* 0.5, CHCl$_3$). The ee was determined by HPLC with a Daicel Chiralpak IB column (1% isopropanol in hexanes, 1.0 mL/min, 230 nm, minor t_r = 13.86 min, major t_r = 15.74 min). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 8.59 (d, *J* = 4.5 Hz, 1H), 7.74-7.71 (m, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 1H), 6.23 (d, *J* = 6.5 Hz, 1H), 6.20 (d, *J* = 6.5 Hz, 1H), 5.36-5.33 (m, 1H), 5.31 (d, *J* = 7.0 Hz, 1H), 5.26 (d, *J* = 6.5 Hz, 1H), 5.15-5.10 (m, 1H), 2.46 (dd, *J* = 13.5 Hz, 5.5 Hz, 1H), 2.32 (dd, *J* = 13.5 Hz, 8.5 Hz, 1H), 2.09-2.05 (m, 1H), 2.01-1.96 (m, 2H), 1.53-1.48 (m, 1H), 1.34-1.28 (m, 1H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 233.1, 153.9, 149.7, 137.1, 134.4, 131.3, 123.4, 120.1, 112.4, 103.7, 93.6, 93.2, 92.9, 47.3, 41.5, 28.1, 25.8, 14.2, 11.9. IR (neat): 2962, 2930, *1964, 1886* (strong CO stretch), 1587, 1571, 1462, 1432, 970, 785, 741, 666, 624, 532. HRMS: calcd for $C_{22}H_{24}NO_3Cr$ $[M]^+$ 402.1161, found 402.1178.



(-)-(η^6-(5-phenyl-2-cyclohexen-1-ylmethyl)-benzene)Cr(CO)$_3$ (3x): The reaction was performed following General Procedure A with **1a** (28.2 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (50.2 mg, 0.3 mmol) and **2d** (54.8 mg, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (23.1 mg, 60% yield, 67% ee) as a yellow solid. $[\alpha]_D^{25}$ = -75.7 (*c* 0.6, CHCl$_3$). The ee was determined by SFC with a Daicel Chiralpak IA column (10% methanol in CO$_2$, 4 mL/min, 270 nm, minor t_r = 5.54 min, major t_r = 6.18 min). The NMR spectral data match the previously published data.



(*E*)-2-(4-(2,4-diphenylbut-3-en-1-yl)phenyl)pyridine (3y): The AAA reaction was performed as in General Procedure C and exposure to sunlight was carried out as in General Procedure B with **1c** (30.5 mg, 0.1 mmol), LiN(SiMe$_3$)$_2$ (67.0 mg, 0.40 mmol) and **2c** (96.0 mg, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product (25.3 mg, 70% yield, >99% ee) as a white solid. Mp 98–100 °C; $[\alpha]_D^{25}$ = +19.8 (*c* 0.5, CHCl$_3$). The ee was determined by SFC with a Daicel Chiralpak AD-H column (30% methanol in CO$_2$, 4 mL/min, 270 nm, minor t_r = 4.23 min, major t_r = 5.26 min). ^{1}H NMR (500 MHz, CDCl$_3$) δ: 8.65 (d, *J* = 4.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.69-7.65 (m, 2H), 7.31-7.16 (m, 12H), 6.43 (dd, *J* = 15.5 Hz, 7.5 Hz, 1H), 6.32 (d, *J* = 15.5 Hz, 1H), 3.79-3.75 (m, 1H), 3.19 (dd, *J* = 13.5 Hz, 7.5 Hz, 1H), 3.14 (dd, *J* = 13.5 Hz, 7.5 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 157.6, 149.8, 143.8, 141.1, 137.6, 137.3, 136.8, 133.3, 130.3, 130.0, 128.69, 128.65, 128.1, 127.3, 126.8, 126.6, 126.4, 122.0, 120.5, 51.0, 42.7. IR (neat): 3058, 3026, 2924, 2855, 1587, 1577, 1561, 1494, 1467, 1451, 1435, 1153, 1016, 988, 965, 847, 777. 743, 699. HRMS: calcd for $C_{27}H_{24}N$ $[M+H]^+$ 362.1909, found 362.1910.

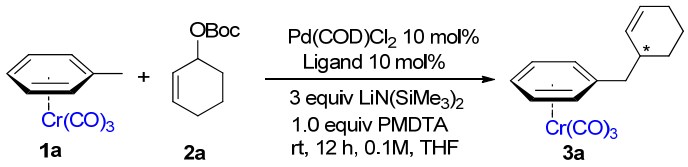


(-)-2-phenyl-3-(4-(pyridin-2-yl)phenyl)propanoic acid (4): To a stirred solution of **3y** (10.0 mg, 0.027 mmol) and potassium carbonate (1.9 mg, 0.014

mmol) in *t*-butyl alcohol (1.6 mL) and water (0.3 mL)was added dropwise an aqueous solution (1.4 mL) of sodium metaperiodate (30.0 mg, 0.14 mmol), potassium permanganate (1.2 mg, 0.007 mmol), and potassium carbonate (1.9 mg, 0.014 mmol) at 0 °C. The resulting mixture was stirred at the same temperature for 30 min, then warmed to room temperature and further stirred for 24 h. The mixture was evaporated to remove *t*-butyl alcohol. The resulting aqueous solution was extracted with dichloromethane (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated to give a residue, which was purified by preparative (SiO_2: ethyl acetate: DCM, 1:3) to furnish **4** (5.0 mg, 61% yield, >99% ee) as a colorless oil. $[\alpha]_D^{25}$ = -160.0 (*c* 0.3, $CHCl_3$). The ee was determined by SFC with a Daicel Chiralpak IA column (30% methanol in CO_2, 4 mL/min, 254 nm, major t_r = 2.56 min, minor t_r = 3.42 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.64 (d, *J* = 4.0 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.74 (td, *J* = 7.5 Hz, 2.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40-7.36 (m, 2H), 7.34-7.31 (m, 2H), 7.28-7.26 (m, 3H), 7.23-7.20 (m, 1H), 3.93 (dd, *J* = 9.5 Hz, 6.5 Hz, 1H), 3.52 (dd, *J* = 13.5 Hz, 9.0 Hz, 1H), 3.07 (dd, *J* = 14.0 Hz, 6.5 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 177.2, 157.4, 149.3, 140.6, 138.9, 137.6, 137.1, 129.6, 128.9, 128.3, 127.7, 127.4, 122.4, 121.3, 53.6, 39.6. IR (neat): 3061, 3029, 2926, 2531, 1449, 1716, 1598, 1561, 1495, 1469, 1436, 1221, 1179, 1157, 911, 848, 778, 730, 699. HRMS: calcd for $C_{20}H_{18}NO_2$ $[M+H]^+$ 304.1338, found 304.1334.

7. List of predosed chiral ligands screened for catalyst identification

7.1 143 chiral ligands screening with cyclic electrophile



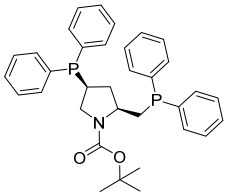
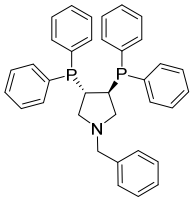
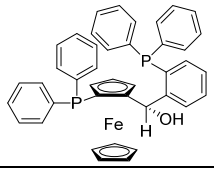
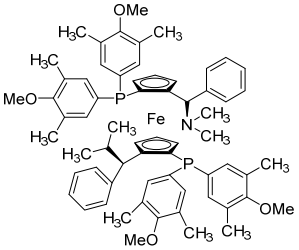
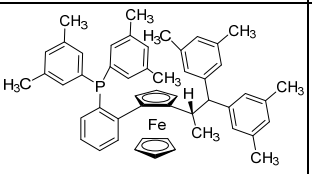
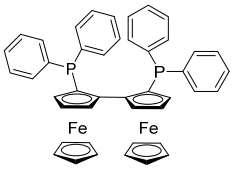
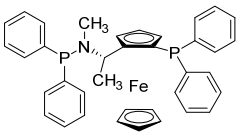
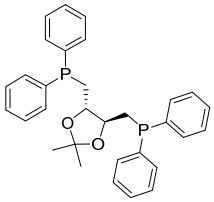
General Experimental for the ligand screening:

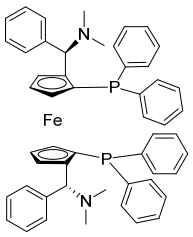
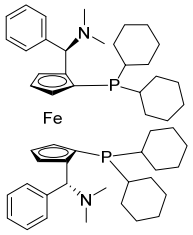
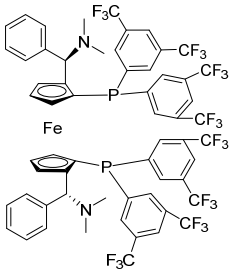
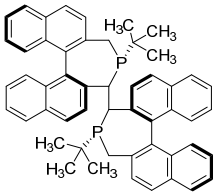
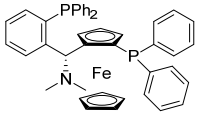
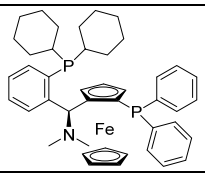
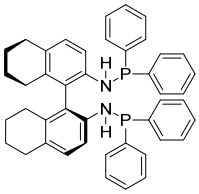
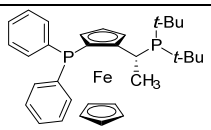
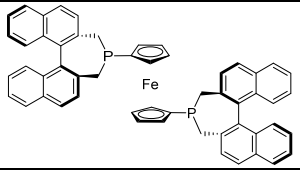
Set up:

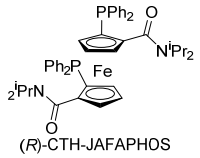
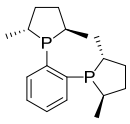
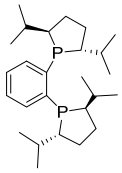
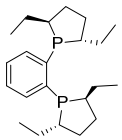
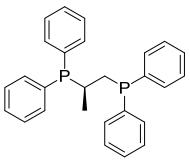
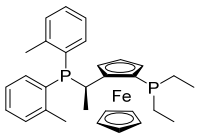
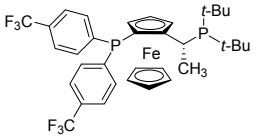
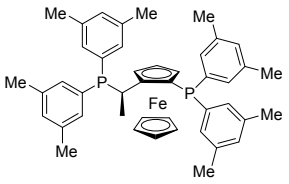
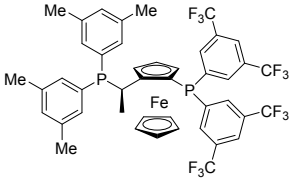
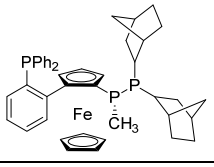
Experiments were set up inside a glovebox under a nitrogen atmosphere. Two 96-well aluminum blocks containing 1 mL glass vials were predosed with $Pd(COD)Cl_2$ (1 μmol) and the chiral phosphine ligands (2 μmol for monodentate ligands and 1 μmol for bidentate ligands) in THF. The solvent was removed to dryness using a GeneVac and 3 equiv. $LiN(SiMe_3)_2$ (30 μmol) in THF was added to the ligand/catalyst mixture. The solvent was removed on the GeneVac and a parylene stir bar was then added to each reaction vial. 1 Equiv (η^6-$C_6H_5CH_3$)$Cr(CO)_3$ (**1a**, 10 μmol), 2 equiv *tert*-butyl cyclohex-2-enyl carbonate (**2a**, 20 μmol), 1 equiv PMDTA (pentamethyldiethylenetriamine, 10 μmol) additive, and biphenyl (1 μmol/reaction) (used as an internal standard) were then dosed together into each reaction vial as a solution in THF (100 μL, 0.1 M). The 96-well plates were then sealed and stirred for 18 h at RT.

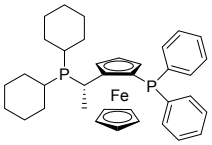
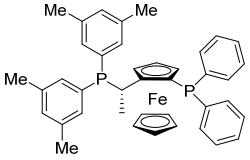
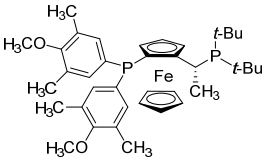
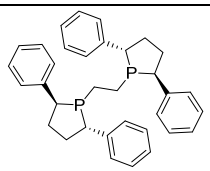
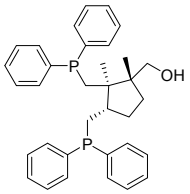
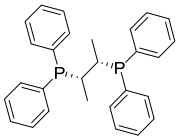
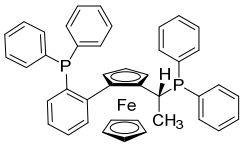
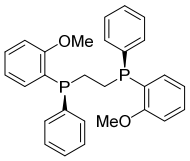
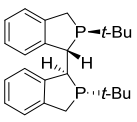
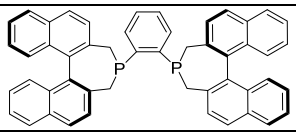
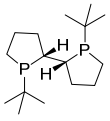
Work up:

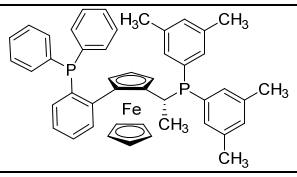
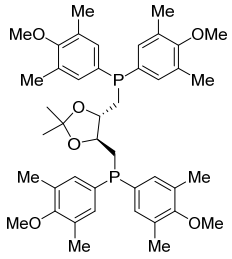
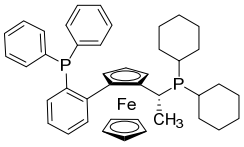
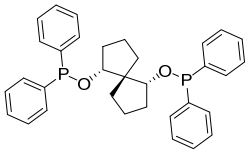
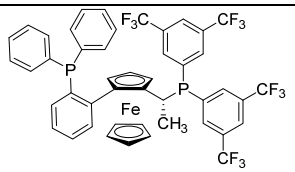
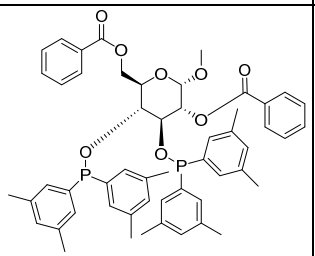
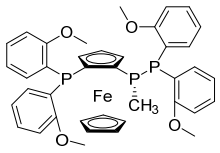
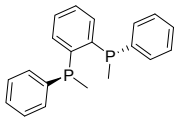
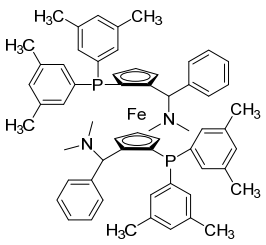
Upon opening the plate to air, 500 μL of acetonitrile/DMSO (3/1) was added into each vial. The plates were covered again and the vials stirred for 10 min. to ensure good homogenization. Into two separate 96-well LC blocks were added 700 μL of acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC blocks were then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

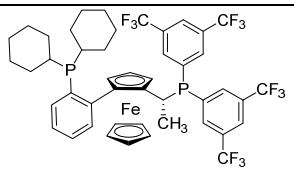
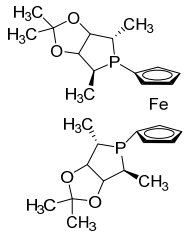
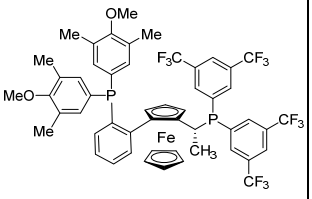
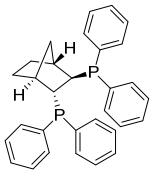
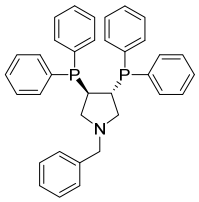
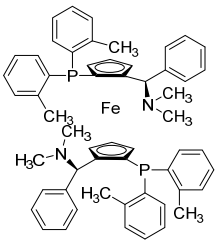
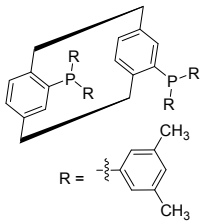
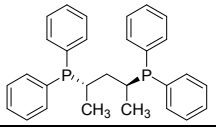
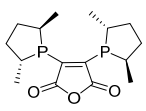
ligand	Structure	Ee(%)	Conv.
(2*S*,4*S*)-^{t}Bu-(-)-4-(Diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrolidine carboxylate		-30	61
(3*S*,4*S*)-(-)-1-Benzyl-3,4-bis(diphenylphosphino)pyrrolidine. ((*S*)-Depyphos also called Deguphos or Catasium D)		-6	19
(*S*)-1-Diphenylphosphino-2-[(*S*)-hydroxy-[2-(diphenylphosphino)phenyl]methyl]ferrocene. (SL-T021-2)		1	62
(1*R*,1'*R*)-1,1'-Bis[bis(4-methoxy-3,5-dimethylphenyl)phosphino]-2,2'-bis[(*R*)-(dimethylamino)phenylmethyl]ferrocene. ((*R*,*R*)-SL-M004-1)		-7	40
(*R*)-1-[(*R*)-2-(2'-Di-3,5-xylylphosphinophenyl)-ferrocenyl]-ethyl-di-3,5-xylylphosphine. (SL-W009-1)		-3	41
(*R*, *R*")-2,2"-Bis(Diphenylphosphino)-1,1"-biferrocene. (*R*, *R*)-BIFEP		22	60
(*S*)-N-Diphenylphosphino-N-methyl-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine. (*S*)-Methyl BOPHOZ(TM)		25	62
(4*S*,5*S*)-(+)-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane. ((*S*,*S*)-DIOP)		-15	35

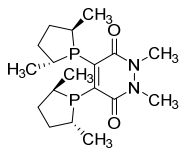
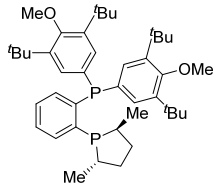
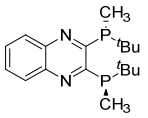
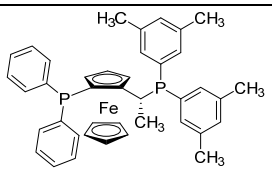
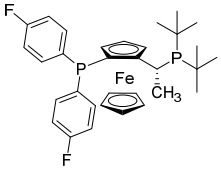
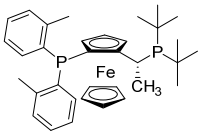
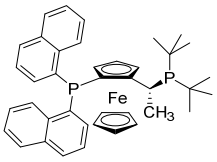
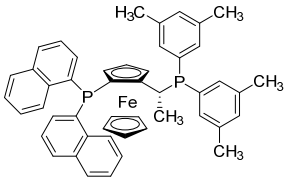
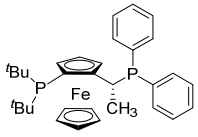
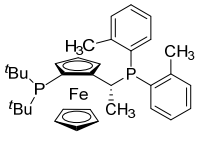
(S_P,S'_P)-1,1'-Bis[(*R*)-(dimethylamino)phenylmethyl]-2,2'-bis(diphenylphosphino)ferrocene. ((*S*, *S*)-SL-M001-1)		-21	53
(S_P,S'_P)-1,1'-Bis(dicyclohexylphosphino)-2,2'-bis[(*R*)-α-(dimethylamino)benzyl]ferrocene. ((*S*, *S*)-SL-M002-1)		6	31
(S_P,S'_P)-1,1'-Bis[bis[3,5-bis(trifluoromethyl)phenyl]phosphino]-2,2'-bis[(*R*)-(dimethylamino)phenylmethyl]ferrocene. ((*S*, *S*)-SL-M003-1)		-10	58
(3*S*,3'*S*,4*S*,4'*S*,11b*S*,11'b*S*)-(+)-4,4'-Di-*tert*-butyl-4,4',5,5'-tetrahydro-3,3'-bi-3H-dinaphtho[2,1-c:1',2'-e]phosphepin. (*S*)-BINAPINE		-	-
(*R*)-1-[(*R*)-α-(Dimethylamino)-2-(diphenylphosphino)benzyl]-2-diphenylphosphinoferrocene (SL-T001-1)		-82	65
(*R*)-1-Dicyclohexylphosphino-2-[(*S*)-alpha-(N,N-dimethylamino)-odicyclohexylphosphinophenyl)methyl]ferrocene ((*R*,*S*)-SL-T002-1)		-9	53
(*S*)-(-)-2,2'-Bis(N-diphenylphosphinoamino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl. CTH-(*S*)-BINAM		16	35
(R)-1-[(*S*)-2-Diethylphosphino)ferrocenyl]ethyl di(tert-butyl)-phosphine. (SL-J301-1)		-	-
(*S*)-1,1'-Bis-{4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]-phosphino}ferrocene. (*S, S*-f-Binaphane)		40	43

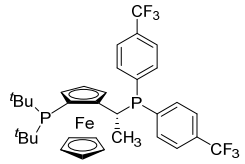
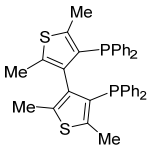
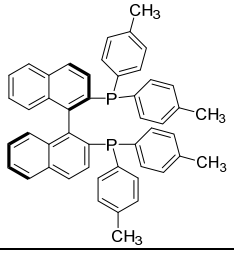
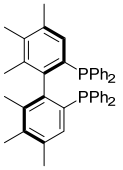
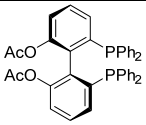
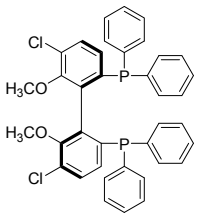
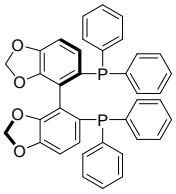
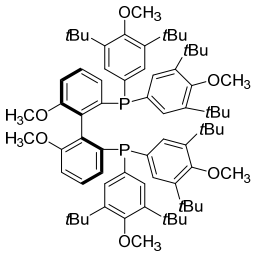
(*R*)-(+)-1,1'-Bis(diphenylphosphino)-2,2'-bis(N,N-diisopropylamido)ferrocene. (*R*)-CTH-JAFAPHOS		-16	43
1,2-Bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene. ((*R*,*R*)-Me-DuPhos)		-	-
1,2-Bis[(2*R*,5*R*)-2,5-diisopropylphospholano]benzene. ((*R*,*R*)-*i*-Pr-DuPhos)		-	-
1,2-Bis[(2*R*,5*R*)-2,5-diethylphospholano]benzene. ((*R*,*R*)-Et-DuPhos)		-	-
(*R*)-(+)-Bis-(1,2-Diphenylphosphino)propane		5	22
(*R*)-1-[(*S*)-2-Di-ethylphosphino)ferrocenyl]ethyldi-(2-methylphenyl)phosphine. (SL-J302-1)		-	-
(2*R*)-1-[(1*R*)-1-[Bis(1,1-dimethylethyl)phosphino]ethyl]-2-[bis[4-(trifluoromethyl)phenyl]phosphino]ferrocene. (SL-J011-1)		-	-
(*R*)-1-[(*S*)-2-Bis(3,5-dimethylphenyl)phosphino)ferrocenyl]ethyl bis(3,5-dimethylphenyl)- phosphine. (SL-J408-1)		-	-
(*R*)-1-[(*S*)-2-Bis(3,5-dimethylphenyI)phosphino)ferrocenyl]ethyl-bis[bis-(3,5-trifluoromethyl)phenyl]-phosphine. (SL-J412-1)		-13	37
(1*S*)-1-[(1*R*)-1-[Bis(bicyclo[2.2.1]hept-2-yl)phosphino]ethyl]-2-[2-(diphenylphosphino)phenyl]ferrocene. (SL-W022-1)		42	56

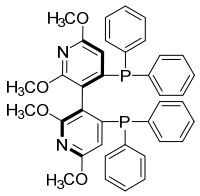
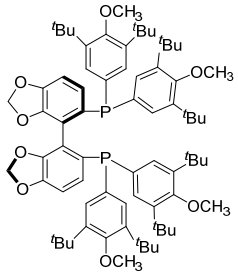
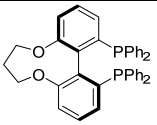
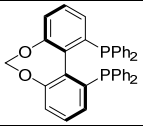
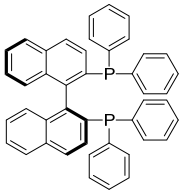
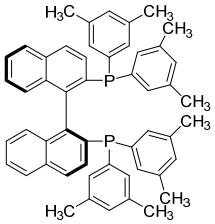
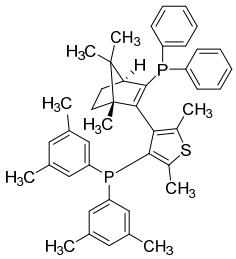
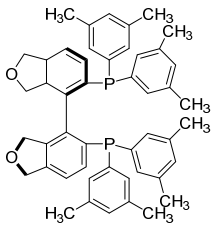
Bis(*S*)-1-[(*R*)-2-(Diphenylphosphino)ferrocenyl]ethyl-di cyclohexylphosphine. (SL-J851-2, bis SL-J001)		28	32
Bis(*S*)-1-[(*R*)-2-Diphenylphosphino)-ferrocenyl]ethyl-di -3,5-xylylphosphine. (SL-J852-2, bis SL-J005)		25	27
Bis(*S*)-1-[(*R*)-2-Di-(4-methoxy-3,5-dimethylphenyl)pho sphino)ferrocenyl]ethyldi-tert.-butylphosphine. (SL-J853-2, bis SL-J013)		-5	25
(+)-1,2-Bis((2*S*,5*S*)-2,5-diphenylphospholano)ethane. (*S*,*S*)-Ph-BPE		11	47
[(1*R*,2*R*,3*S*)-(+)-1,2-Dimethyl-2,3-bis(diphenylphosphin omethyl)cyclopentyl]methanol. ((+)-catASium I)		-1	43
(2*S*,3*S*)-(-)-Bis(diphenylphosphino)butane. ((*S*,*S*)-CHIRAPHOS)		4	26
(*R*)-1-[(*R*)-2-(2'-Diphenylphosphinophenyl)ferrocenyl]- ethyldiphenylphosphine. (SL-W002-1)		11	50
(*S*,*S*)-(+)-1,2-Bis[(2-methoxyphenyl)(phenyl)phosphino] ethane. ((*S*,*S*)-DIPAMP)		-	-
(1*S*,1'*S*,2*R*,2'*R*)-2,2'-Di-tert-butyl-2,3,2',3'-tetrahydro-1H, 1'H-(1,1')biisophosphindolyl. ((1*S*,1'*S*,2*R*,2'*R*)-DuanPhos)		16	26
(*R*,*R*)-(-)-1,2-Bis{(*R*)-4,5-dihydro-3H-binaphtho[1,2-c:2' ,1'-e]phosphepino}benzene. ((*R*)-BINAPHANE)		4	37
(1*S*, 1*S*',2*R*, 2*R*')-1,1'-Di-tert-butyl-(2, 2')-diphospholane. ((*S*,*S*,*R*,*R*)-TangPhos)		-	-

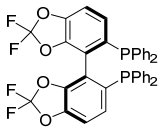
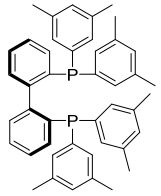
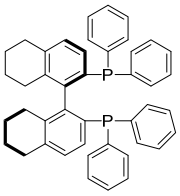
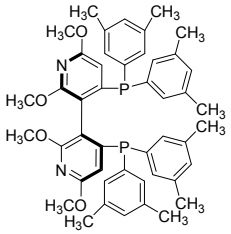
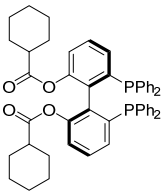
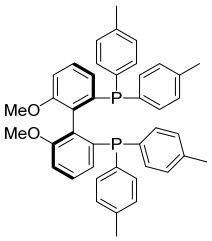
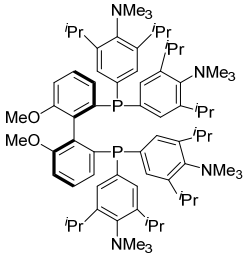
(*R*)-1-[(*R*)-2-(2'-Diphenylphosphinophenyl)ferrocenyl]ethyldi-(3,5-xylyl)phosphine. (SL-W006-1)		11	49
(4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(Methylene)bis(bis(3,5-diMethylphenyl)phosphine). ((-)-MOD DIOP)		-19	48
(*R*)-1-[(*R*)-2-(2'-Diphenylphosphinophenyl)ferrocenyl]ethyldicyclohexylphosphine. (SL-W003-1)		32	43
1*R*,5*R*,6*R*-(+)-1,6-Bis(diphenylphosphinoxy)spiro[4.4]nonane. (CTH-(R)-SpiroP)		23	37
(*R*)-1-[*(R)*-2-(2'-Diphenylphosphinophenyl)ferrocenyl]ethyldi(bis-3,5-trifluoromethylphenyl)phosphine. (SL-W001-1)		22	63
Methyl-*alpha*-D-glucopyranosie-2,6-dibenzoate-3,4-di(BIS(3,5-dimethyphenyl)phosphinite). (CarboPhos)		8	30
(*R*)-1-[(*S*)-2-Bis(2-methoxyphenyl)phosphino)ferrocenyl]ethylbis(2-methoxyphenyl)-phosphine. (SL-J430-1)		1	25
(1*S*, 2*S*)-(-)-Bis(methylphenylphosphino)benzene		-	-
(*S*,*S*)-(-)-2,2'-Bis[(*R*)-(N,N-dimethylamino)(phenyl)methyl]-1,1'-bis(di(3,5-dimethylphenyl)phosphino)ferrocene. (M009-1)		-10	47

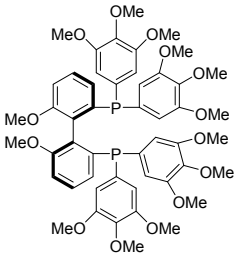
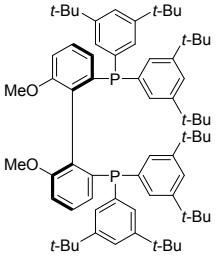
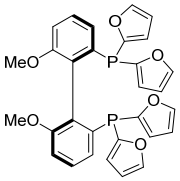
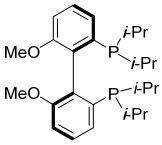
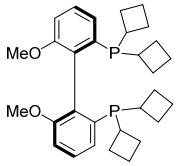
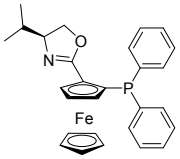
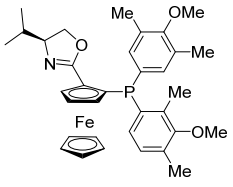
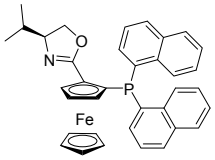
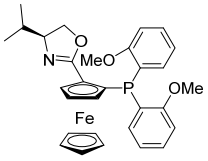
(*R*)-1-[(*R*)-2-(2'-Dicyclohexylphosphinophenyl)ferrocenyl]ethyl-di-(bis-(3,5-trifluoromethyl)phenyl)-phosphine. (SL-W008-1)		12	60
1,1-Bis[(2*S*,3*S*,4*S*,5*S*)-2,5-dimethyl-3,4-O-isopropylidene-3,4-dihydroxyphospholanyl]ferrocene. (*S*)-Me-f-KetalPhos		-15	34
(1*S*)-1-[(1*R*)-1-[Bis[3,5-bis(trifluoromethyl)phenyl]phosphino]ethyl]-2-[2-[bis(4-methoxy-3,5-dimethylphenyl)phosphino]phenyl]ferrocene. (SL-W005-1)		11	61
(2*R*,3*R*)-(-)-2,3-Bis(diphenylphosphino)bicylo[2.2.1]hept-5-ene. ((*R*,*R*)-NorPhos)		10	23
(3*R*,4*R*)-3,4-Bis(diphenylphosphino)-1-benzylpyrrolidine. (catASium D(R))		23	49
(*S*,*S*)-(-)-2,2'-Bis[(*R*)-(N,N-dimethylamino)(phenyl)methyl]-1,1'-bis(di(2-methylphenyl)phosphino)ferrocene. (M012-1)		10	19
(*R*)-(-)-4,12-Bis(di(3,5-xylyl)phosphino)-[2.2]-paracyclophane. (CTH-(*R*)-3,5-xylyl-PHANEPHOS)		-23	63
(2*S*, 4*S*)-(-)-2,4-Bis(diphenylphosphino)pentane. ((*S*,*S*)-BDPP)		-	-
(-)-2,3-Bis[(2*R*,5*R*)-2,5-dimethylphospholanyl]maleic anhydride. (Catasium MN An(R))		-	-

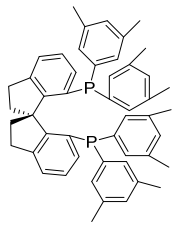
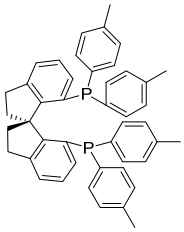
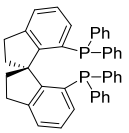
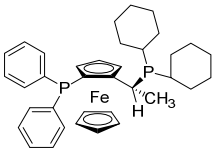
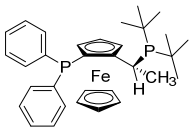
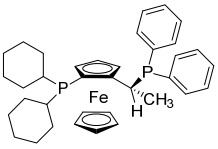
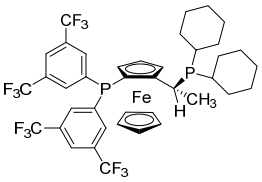
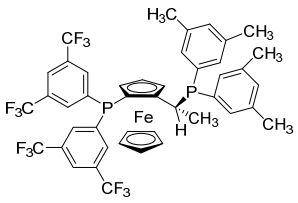
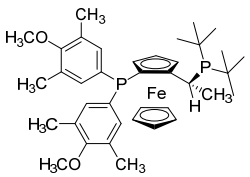
(-)-4,5-Bis[(2*R*,5*R*)-2,5-dimethylphospholanyl](1,2-dimethyl-1, 2-dihydropyridazine-3,6-dione). (Catasium MNN (R))		15	14
1-Bis(3,5-di-t-butyl-4-methoxyphenyl)phosphino-2-((2*S*, 5*S*)-2,5-di methylphospholano) ((*S*,*S*)-Me-UCAP-DTBM)		1	33
(*R*,*R*)-2,3-Bis(*tert*-butylmethylphosphino)quinoxaline. ((*R*,*R*)-QuinoxP*)		-2	18
(*R*)-1-[(*S*)-2-Diphenylphosphino)-ferrocenyl]ethyl-di-3,5-xylylphosphine.(SL-J005-1)		-16	23
(*R*)-1-[(*S*)-2-[Bis(4-fluoro-phenyl)phosphino]ferrocenyl}ethyldi-tert-butylphosphine. (SL-J014-1)		16	19
(*R*)-1-[(*S*)-2-Bis(2-methylphenyl)phosphino)ferrocenyl]ethyl di(tert-butyl)-phosphine. (SL-J211-1)		22	38
(*R*)-1-[(*S*)-2-(Bis(2-naphtyI)-phosphino)ferrocenyl]ethyl di-tert-butylphosphine. (SL-J216-1)		18	43
(*R*)-1-[(*S*)-2-(Di-1-naphtylphosphino)ferrocenyl]ethyldi-3,5-xylylphosphine. (SL-J404-1)		19	33
(*R*)-1-[(*S*)-2-Di-*tert*-butylphosphino)ferrocenyl]ethyldiphenylphosphine. (SL-J502-1)		-13	20
(*R*)-1-[(*S*)-2-Di-*tert*-butylphos-phino)ferrocenyl]ethyl-di-(2-methyl-phenyl)phosphine. (SL-J505-1)		-3	30

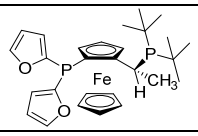
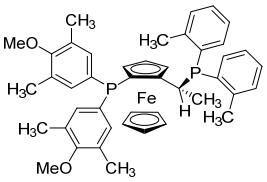
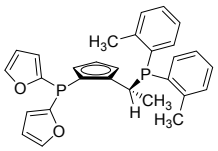
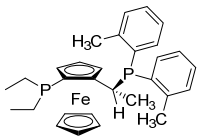
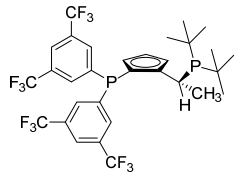
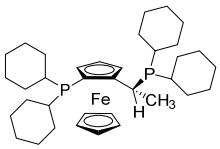
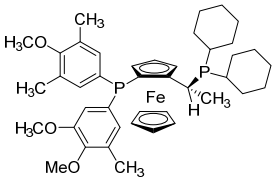
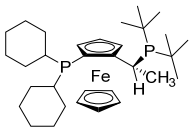
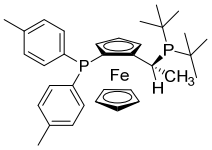
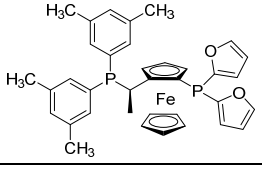
(*R*)-1-[(*S*)-2-di(*tert*-butyl)phosphino)ferrocenyl]ethyl bis(4-trifluoromethyl)-phosphine. (SL-J506-1)		-1	30
4,4-Bis(diphenylphosphine)-2,2'-5,5'-tetramethyl-3,3'-dithiophene. (-)-TMBTP		34	31
(*R*)-(+)-2,2'-Bis(di-p-tolylphosphino)-1,1'-binaphthyl. ((*R*)-Tol-Binap)		46	22
[(*R*)-4,4',5,5',6,6'-Hexamethyl 2,2'-bis[diphenylphosphino]-biphenyl. ((*R*)-Hexaphemp)		39	18
(*S*)-(-)-6,6'-Bis(diphenylphosphino)-1,1'-biphenyl-2,2'-diylbis(acetate). ((*S*)-Me-SoniPhos)		-	-
(*R*)-(+)-5,5'-Dichloro-6,6'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl. ((*R*)-Cl,MeO-Biphep)		28	37
(*R*)-(+)-5,5′-Bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole,[4(*R*)-(4,4′-bi-1,3-benzodioxole)-5,5′-diyl]bis[diphenylphosphine]. ((*R*)-SegPhos)		56	29
(*S*)-2,2'-Bis(di(3,5-di-tert-butyl-4-methoxyphenyl)phosphino)-6,6'-dimethoxy-1,1'-biphenyl. (SL-A109-2)		-18	23

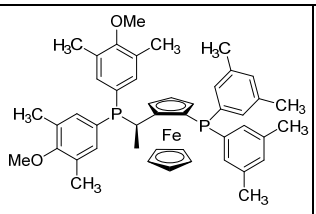
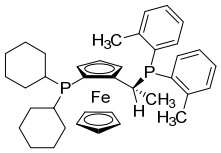
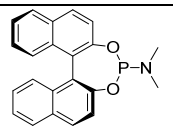
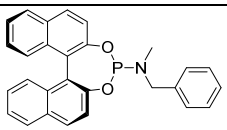
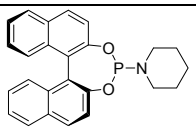
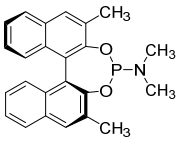
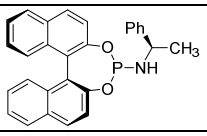
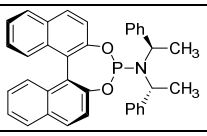
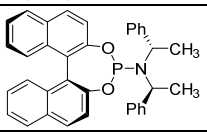
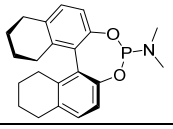
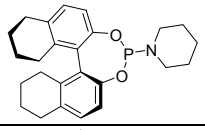
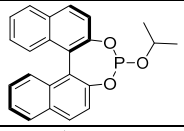
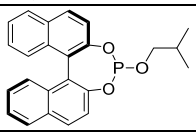
(*R*)-(+)-2,2',6,6'-Tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine. ((*R*)-P-Phos)		54	48
[(4*R*)-(4,4′-bi-1,3-benzodioxole)-5,5′-diyl]bis[bis(3,5-di-tert-butyl-4-methoxyphenyl)phosphine]. ((*R*)-DTBM-SegPhos)		52	19
(*S*)-1,13-Bis(diphenylphosphino)-7,8-dihydro-6H-dibenzo[f,h][1,5]dioxonin. (s-C_1-tunephos)		-34	27
s-C_1-tunephos		15	30
(*S*)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl. ((*S*)-Binap)		-46	29
(*R*)-(+)-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl. ((*R*)-xyl-binap)		42	27
(1*R*)-(+)-[Di(3,5-dimethylphenyl)phosphino]-2-(4-diphenylphosphino-2,5-dimethylthien-3-yl)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene ((*R*)-Catasium T2)		-2	44
[(4*R*)-(4,4-Bi-1,3-benzodioxole)-5,5-diyl]bis[bis(3,5-dimethylphenyl)phosphine] ((*R*)-DM-SegPhos)		51	26

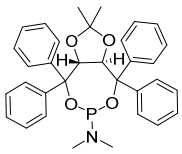
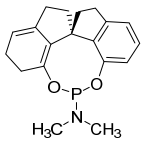
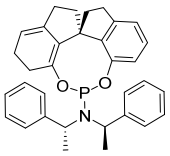
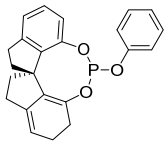
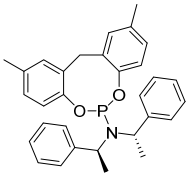
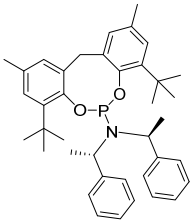
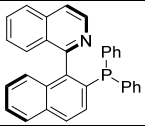
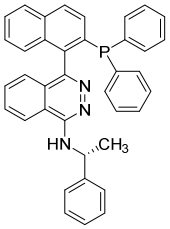
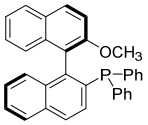
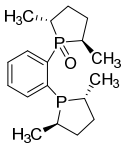
(*R*)-(-)-5,5'-Bis(diphenylphosphino)-2,2,2',2'-tetrafluoro-4,4'-bi-1,3-benzodioxole. ((*R*)-DifluoroPhos)		49	49
(S)-(-)-2,2'-Bis[di(3,5-xylyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl. (SL-A120-2)		-42	23
(*R*)-(+)-2,2''-BIS(Diphenylphosphino)-5,5'',6,6'',7,7'',8,8''-octahydro-1,1''-binaphthyl. ((*R*)-H_8-BINAP)		30	30
(*S*)-(-)-2,2',6,6'-Tetramethoxy-4,4'-bis(di(3,5-xylyl)phosphino)-3,3'-bipyridine. ((*S*)-Xylyl-P-Phos)		-44	38
(*S*)-(-)-6,6'-Bis(diphenylphosphino)-1,1'-biphenyl-2,2'-diylbis(cyclohexylcarboxylate) ((*S*)-cHex-Soniphos)		-43	28
(*R*)-(+)-2,2'-Bis(di-ptolylphosphino)-6,6'-dimethoxy-1,1'-biphenyl (SL-A102-1)		37	20
(*R*)-(+)-2,2'-Bis[di(3,5-di-i-propyl-4-dimethylaminophenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl (SL-A107-1)		9	23

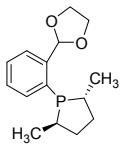
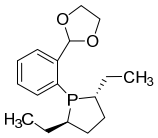
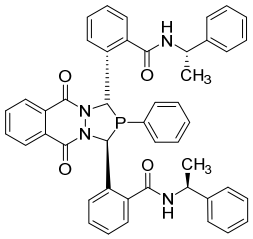
(*R*)-(+)-2,2'-Bis[di(3,4,5-trimethoxyphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl. (SL-A104-1)		58	33
(*R*)-2,2'-Bis[bis(3,5-di-*tert*-butyl phenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl. (SL-A121-1)		18	20
(*R*)-(+)-2,2'-Bis(di-2-furylphosphino)-6,6'-dimethoxy-1,1'-biphenyl. (SL-A108-1)		19	60
(*R*)-2,2'-Bis(diisopropylphosphino)-6,6'-dimethoxy-1,1'-biphenyl. (SL-A116-1)		7	19
(*R*)-2,2'-Bis(dicyclobutylphosphino)-6,6'-dimethoxy-1,1'-biphenyl. (SL-A118-1)		24	25
((*S*)-4-Isopropyl-2-[(*S*)-2-(diphenylphosphino)ferrocen-1-yl]oxazoline). SL-N003-2		-	-
((*S*)-4-Isopropyl-2-[(*S*)-2-(bis(3,5-dimethyl-4-methoxyphenyl)phosphino)ferrocen-1-yl]oxazoline). SL-N008-2		-	-
((*S*)-4-Isopropyl-2-[(*S*)-2-(bis(1-naphtyl)phosphino)ferrocen-1-yl]oxazoline). SL-N011-2		-	-
((*S*)-4-Isopropyl-2-[(*S*)-2-(bis(2-methoxyphenyl)phosphino)ferrocen-1-yl]oxazoline). SL-N012-2		41	14

(*S*)-(-)-7,7'-Bis[di(3,5-dimethylphenyl)phosphino]-1,1'-spirobiindane. ((*S*)-Xyl-SDP)		47	35
(*S*)-(-)-7,7'-Bis[di(4-methylphenyl)phosphino]-2,2',3,3'-tetrahydro-1,1'-spirobiindene. ((*S*)-Tol-SDP)		45	34
(*S*)-(-)-7,7'-Bis(diphenylphosphino)-2,2',3,3'-tetrahydro-1,1'-spirobiindene. ((*S*)-SDP)		46	29
(*R*)-(-)-1-[(*S*)-2-(Diphenylphosphino)ferrocenyl]ethyldicylcohexylphosphine. (SL-J001-1)		-24	18
(*R*)-1-[(*S*)-2-Diphenylphosphinoferrocenyl]ethyldi-tert.-butylphosphine (SL-J002-1)		0	19
(*R*)-1-[(*S*)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldiphenylphosphine. (SL-J004-1)		8	19
(*R*)-1-[(*S*)-2-Di-(3,5-bis(trifluoromethyl)phenyl-phosphino)ferrocenyl]-ethyl-dicyclohexylphosphine. (SL-J006-1)		0	33
(*R*)-1-[(*S*)-2-Di-(3,5-bis(trifluoromethyl)phenyl-phosphino)-ferrocenyl]-ethyl-di-3,5-xylylphosphine. (SL-J008-1)		-15	49
(*R*)-1-[(*S*)-2-Di-(4-methoxy-3,5-dimethylphenyl-phosphino)ferrocenyl]-ethyl-di-*tert*-butyl-phosphine. (SL-J013-1)		-4	18

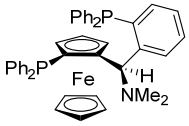
(*R*)-1-[(*S*)-2-(Di-2-furylphosphino)ferrocenyl]-ethyl-di-*tert*-butylphosphine. (SL-J212-1)		19	30
(*R*)-1-[(*S*)-2-Di-(4-methoxy-3,5-dimethylphenyl-phosphino)ferrocenyl]-ethyl-di-2-methylphenyl-phosphine. (SL-J425-1)		-5	29
(*R*)-1-[(*S*)-2-(Di-2-furylphosphino)ferrocenyl]-ethyl-di-2-methylphenylphosphine. (SL-J452-1)		10	47
(*R*)-1-[(*S*)-2-diethylphosphino)ferrocenyl]ethyl bis(2-methylphenyl)-phosphine. (SL-J503-1)		8	23
(*R*)-1-[(*S*)-2-Di-(3,5-bis(trifluoromethyl)phenyl)phosphino)ferrocenyl]ethyldi-t-butyl- phosphine. (SL-J210-1)		28	55
(*R*)-(-)-1-[(*S*)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldicyclohexylphosphine. (SL-J003-1)		19	16
(*R*)-1-[(*S*)-2-Di-(4-methoxy-3,5-dimethylphenyl-phosphino)ferrocenyl]-ethyl-dicyclohexylphosphine. (SL-J007-1)		-15	21
(*R*)-1-[(*S*)-2-(Dicyclohexylphosphino)ferrocenyl]-ethyl-di-*tert*-butylphosphine. (SL-J009-1)		7	19
(*R*)-1-{[(*S*)-2-[Bis(4-methyl-phenyl)phosphino]ferrocenyl}-ethyl-di-*tert*-butylphosphine. (SL-J012-1)		24	20
(*S*)-1-[(*R*)-2-(Di-2-furylphosphino)ferrocenyl]-ethyl-di-3,5-xylylphosphine. (SL-J015-2)		15	23

(2*R*)-1-[(1*R*)-1-[Bis(3,5-dimethylphenyl)phosphino]ethyl]-2-[bis(4-methoxy-3,5-dimethylphenyl)phosphino]ferrocene. (SL-J418-1)		-9	21
(*R*)-1-[(*S*)-2-Cyclohexylphosphino)ferrocenyl]ethyl bis(2-methylphenyl)-phosphine. (SL-J504-1)		4	19
(*R*)-(-)-[4-N,N-Dimethylamino]dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine. ((*R*)-MonoPhos)		38	32
(*S*)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a:3,4-a']dinaphthalen-4-yl)benzyl(methyl)amine. ((*S*)-N-Me-N-Bn-MonoPhos)		-12	28
(*S*)-(+)-(3,5-Dioxa-4-phosphacyclohepta[2,1-a;3,4-a']dinapthalen-4-yl)piperidine. ((*S*)-PipPhos)		-6	23
(*S*)-(+)-(2,6-Dimethyl-3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)dimethylamine. ((S)-2,6-Me-MonoPhos)		-16	27
(*S*)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)[(1*R*)-1-phenylethyl]amine. ((*S,R*)-(a-MeBn)-MonoPhos)		14	18
(*S*)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)bis[(1*R*)-1-phenylethyl]amine ((*S,R,R*)-(a-MeBn)$_2$-MonoPhos)		-12	30
(*S*)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)bis[(1*S*)-1-phenylethyl]amine. ((*S,S,S*)-(a-MeBn)$_2$-MonoPhos)		**-72**	**34**
(*S*)-(+)-(8,9,10,11,12,13,14,15-Octahydro-3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)dimethylamine. ((*S*)-H$_8$-MonoPhos)		-11	23
1-[(11b*S*)-8,9,10,11,12,13,14,15-Octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl]piperidine. ((*S*)-H$_8$-PipPhos)		-	-
(*R*)-Binaphthylisopropylphosphite. ((*R)*-BINOL-P-O^{i}Pr)		-	-
(*R*)-Binaphthylisobutylphosphite. ((*R*)-BINOL-P-O^{i}Bu)		-	-

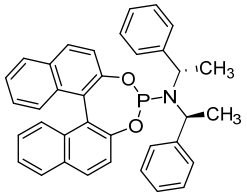
(3a*R*,8a*R*)-(-)-(2,2-Dimethyl-4,4,8,8-tetraphenyl-tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)dimethylamine. ((*R*,*R*)-TADDOL-P-NMe2)		-	-
(11a*R*)-(+)-10,11,12,13-Tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin-5-dimethylamine. ((*R*)-SIPhos)		38	38
(11a*R*)-(+)-10,11,12,13-Tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin-5-bis[(*R*)-1-phenylethyl]amine. ((*R*)-SIPhos-PE)		50	43
(11a*R*)-(+)-10,11,12,13-Tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin-5-phenoxy. ((*R*)-ShiP)		47	43
2,10-Dimethyl-N,N-bis[(1*S*)-1-phenylethyl]-12H-Dibenzo[d,g][1,3,2]dioxaphosphocin-6-amine. ((*S*,*S*)-Mikami Ligand)		5	25
4,8-Di-*tert*-butyl-2,10-dimethyl-N,N-bis[(1S)-1-phenylethyl]-12H-Dibenzo[d,g][1,3,2]dioxaphosphocin-6-amine. ((*S*,*S*)-tBu-Mikami Ligand)		32	25
(*R*)-1-(2-Diphenylphosphino-1-naphthyl)isoquinoline. ((*R*)-Quinap)		-	-
(*R*)-(+)-4-[2-(Diphenylphosphino)-1-naphthalenyl]-n-[(r)-1-phenylethyl]-1-phthalazinamine. ((*R*)-N-PINAP)		-	-
(*R*)-(+)-2-Diphenylphosphino-2'-methoxy-1,1'-binaphthyl. (*R*)-MOP		-	-
(2*R*,5*R*)-1-[2-[(2R,5R)-2,5-Dimethylphospholan-1-yl]phenyl]-2,5-dimethylphospholane 1-oxide. ((*R*,*R*)-Me-DuPhos Monoxide)		-	-

(2*S*,5*S*)-(+)-1-(2-(1,3-Dioxolan-2-yl)phenyl)-2,5-dimethylphospholane. ((*S*,*S*)-Me-RajPhos)		8	33
(2*S*,5*S*)-(-)-1-(2-(1,3-Dioxolan-2-yl)phenyl)-2,5-diethylphospholane. ((*S*,*S*)-Et-RajPhos)		13	35
2,2'-[(1*S*,3*S*)-2,3,5,10-Tetrahydro-5,10-dioxo-2-phenyl-1H-[1,2,4]diazaphospholo[1,2-b]phthalazine-1,3-diyl]bis[N-(1*S*)-1-phenylethyl]benzamide. ((*S*,*S*,*S*)-DiazaPhos-PPE)		1	30

Most promising hits (only two ligands can give more than 60% ee)

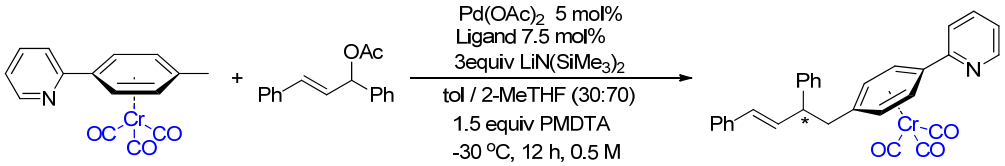


Ph-Taniaphos (SL-T001-1)
65% conv. 82% ee



(S,S,S)-(a-MeBn)2-MonoPhos
34% conv. 72% ee

7.2 24 Chiral ligand screening with an acyclic electrophile and 1c.



General Experimental for the ligand screening:

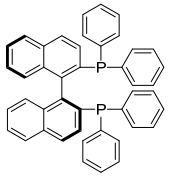
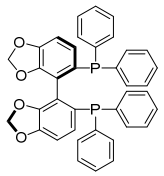
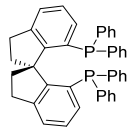
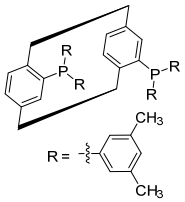
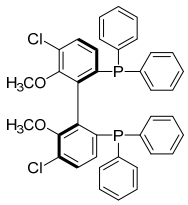
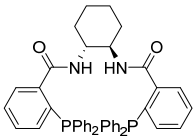
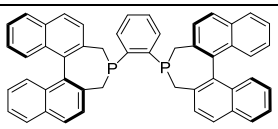
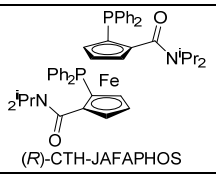
Set up:

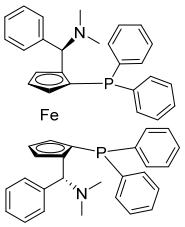
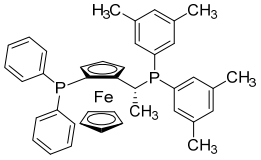
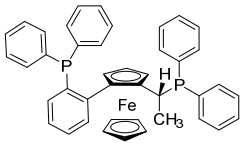
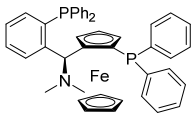
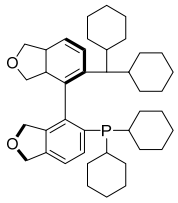
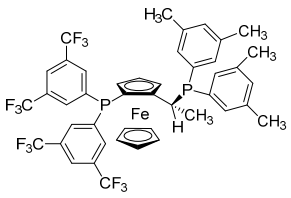
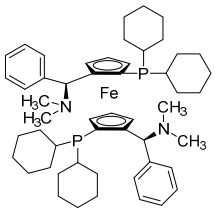
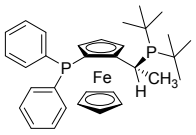
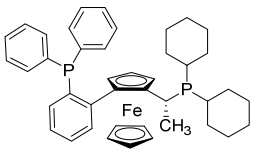
Experiments were set up inside a glovebox under a nitrogen atmosphere. A 24-well aluminum blocks containing 1 mL glass vials were predosed with $Pd(OAc)_2$ (1 μmol) and the chiral phosphine ligands (2 μmol for monodentate ligands and 1 μmol for bidentate ligands) in THF. The solvent was removed to dryness using a GeneVac. The plate was cooled down to -20 °C in glovebox fridge overnight. 3 equiv. $LiN(SiMe_3)_2$ (30 μmol), 1 equiv (2-(η^6-*p*-tolyl)pyridine)$Cr(CO)_3$ (**1c**, 10 μmol), 2 equiv **2c** (20 μmol), 1.5 equiv PMDTA (pentamethyldiethylenetriamine, 15 μmol) additive were then dosed together into each reaction vial as a solution in THF (100 μL, 0.1 M). The 24-well plates were then sealed and stirred for 12 h at -30 °C.

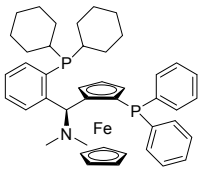
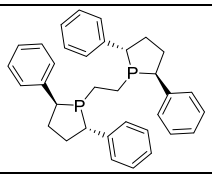
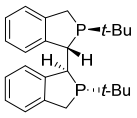
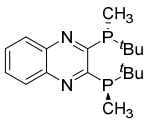
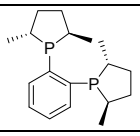
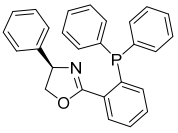
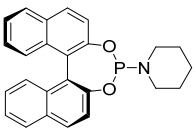
Work up:

Upon opening the plate to air, 500 μL of acetonitrile containing biphenyl (1 μmol/reaction, used as an internal standard) was added into each vial. The plates were covered again and the vials stirred for 10 min. to ensure good homogenization. Into a separate 96-well LC blocks were added 700 μL of

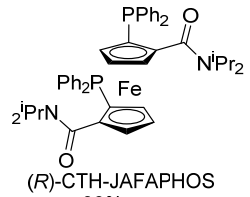
acetonitrile, followed by 25 μL of the diluted reaction mixtures. The LC blocks were then sealed with a silicon-rubber storage mat and mounted on an automated HPLC instrument for analysis.

ligand	Structure	Ee(%)	Pdt/IS
(*S*)-(−)-(1,1′-Binaphthalene-2,2′-diyl)bis(diphenylphosphine); (*S*)-Binap		60	0.87
(*R*)-(+)-5,5′-Bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole; (*R*)-segphos		76	0.46
(*S*)-(−)-7,7′-Bis(diphenylphosphino)-2,2′,3,3′-tetrahydro-1,1′-spirobiindene;(*S*)-SDP		34	0.18
(*R*)-(-)-4,12-Bis(di-3,5-xylylphosphino)[2.2]paracyclophane; (*R*)-3,5-xylyl-PHANEPHOS		38	0.29
(+)-(5,5′-Dichloro-6,6′-dimethoxy-1,1′-biphenyl)-2,2′-diyl-bis(diphenylphosphine); (*R*)-Cl,MeO-BIPHEP		60	0.28
(1*R*,2*R*)-(+)-1,2-Diaminocyclohexane-*N*,*N*′-bis(2-diphenylphosphinobenzoyl); (*R*, *R*)-DACH-phenyl Trost ligand		--	--
(*R*,*R*)-1,2-Bis[(*R*)-4,5-dihydro-3*H*-binaphtho(1,2-*c*:2′,1′-*e*)phosphepino]benzene; (*R*)-BINAPHANE		9	0.22
(*R*)-(+)-1,1'-Bis(diphenylphosphino)-2,2'-bis(N,N-diisopropylamido)ferrocene; (*R*)-CTH-JAFAPHOS		93	0.44

(S_P,S'_P)-1,1'-Bis[(*R*)-(dimethylamino)phenylmethyl]-2,2'-bis(diphenylphosphino)ferrocene; SL-M001-1		54	0.29
(2*R*)-1-[(1*R*)-1-[Bis(3,5-dimethylphenyl)phosphino]ethyl]-2-(diphenylphosphino)ferrocene; SL-J005-1		63	0.21
(*R*)-1-[(*R*)-2-(2'-Diphenylphosphinophenyl)-ferrocenyl]-ethyl-diphenylphosphine; (*R*, *R*)-SL-W002-1		65	0.49
(2*S*)-1-[(*S*)-(Dimethylamino)[2-(diphenylphosphino)phenyl]methyl]-2-(diphenylphosphino)ferrocene; (*S*, *S*)-SL-T001-1		43	0.39
(+)-((5,6),(5',6')-Bis(methylenedioxy)biphenyl-2,2'-diyl)bis(bis(cyclohexyl)phosphine); (+)-Cy-SEGPHOS		48	0.40
(1*R*)-1-[Bis[3,5-bis(trifluoromethyl)phenyl]phosphino]-2-[(1*R*)-1-[bis(3,5-dimethylphenyl)phosphino]ethyl]ferrocene; SL-J008-1		--	--
(RP,R′P)-1,1'-Bis(dicyclohexylphosphino)-2,2'-bis[(S)-α-(dimethylamino)benzyl]ferrocene; SL-M002-2		81	0.32
(*R*)-1-[(*S*)-2-Diphenylphosphinoferrocenyl]ethyldi-tert.-butylphosphine; SL-J002-1		40	0.18
(1*S*)-1-[(1*R*)-1-(Dicyclohexylphosphino)ethyl]-2-[2-(diphenylphosphino)phenyl]ferrocene; SL-W003-1		64	0.57

(1*S*)-1-(Dicyclohexylphosphino)-2-[(*R*)-[2-(dicyclohexylphosphino)phenyl](dimethylamino)methyl]ferrocene; SL-T002-1		0	0.31
1,2-Bis[(2*S*,5*S*)-2,5-diphenylphospholano]ethane(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate; (*S*,*S*)-Ph-BPE		8	0.23
(1*S*,1′*S*,2*R*,2′*R*)-2,2′-Di-*tert*-butyl-2,3,2′,3′-tetrahydro-1*H*,1′*H*(1,1′)biisophosphindolyl; (1*S*, 1′*S*, 2*R*, 2′*R*)-DuanPhos		--	--
(*R*,*R*)-(–)-2,3-Bis(*tert*-butylmethylphosphino)quinoxaline; (*R*,*R*)-QuinoxP*		--	--
(2*R*,2'*R*,5*R*,5'*R*)-2,2',5,5'-Tetramethyl-1,1'-(o-phenylene)diphospholane; (*R*,*R*)-Me-DuPhos		--	--
(*R*)-(−)-2-[2-(Diphenylphosphino)phenyl]-4-phenyl-2-oxazoline		--	--
(*S*)-(+)-(3,5-Dioxa-4-phosphacyclohepta[2,1-a:3,4-a′]dinaphthalen-4-yl)piperidine; (*S*)-PipPhos		--	--

Promising hit



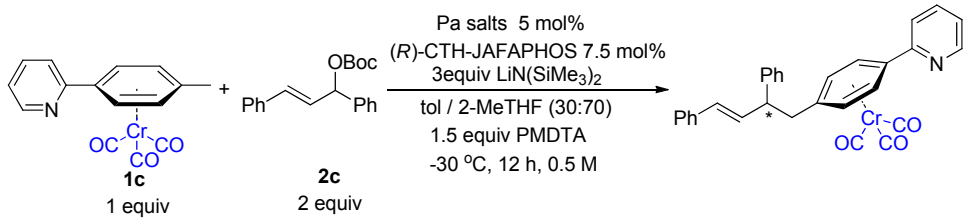
(*R*)-CTH-JAFAPHOS
93% ee

7.3 AAA in lab scale using acyclic electrophile

General Procedure D*:* To an oven-dried microwave vial equipped with a stir bar was added Pd salts (0.005 mmol) and (*R*)-CTH-JAFAPHOS (5.61 mg, 0.0075 mmol) under nitrogen atmosphere inside a glove box at room temperature. Next, 0.7 mL of dry 2-MeTHF and 0.3 mL of dry toluene were added sequentially via syringe. After the catalyst/ligand solution was stirred for 30 min at 24 °C inside the glove box, (2-(η^6-*p*-tolyl)pyridine)$Cr(CO)_3$ (30.5 mg, 0.1 mmol) was added to the reaction vial followed by $LiN(SiMe_3)_2$ (50.2 mg, 0.3 mmol). The microwave vial was sealed and removed from the

glove box. The microwave vial was cooled to -30 °C, PMDTA (33 μL, 0.15 mmol, 1.5 equiv) was added via microsyringe, and the resulting yellow solution stirred for additional 5 min. A solution of the allylic electrophile in 2-MeTHF/toluene (v/v = 0.3 mL/ 0.7 mL, 0.3 mmol) was added via syringe over 10 min under nitrogen atmosphere and the reaction mixture was stirred under nitrogen atmosphere for 12 h at –30 °C . Next, 5 drops water were added via syringe, and then the vial opened to air. The reaction mixture was passed through a short pad of silica gel and rinsed with 10 mL 10:1 ethyl acetate: methanol. The solvent was removed by rotary evaporator. The residue was purified by flash chromatography.

***Optimization of the palladium salts using (1,3-diphenylallyl) carbonate**:*



Entry	Pd salts	Yield(%)[a]	Ee(%)[b]
1[c]	$Pd(OAc)_2$	55	90
2[c]	$Pd(COD)Cl_2$	64	99
3[c]	$[Pd(ally)Cl]_2$	73	86
4[d]	$Pd(COD)Cl_2$	72	99
5[e]	$Pd(OAc)_2$	73	-38

[a] Isolated yield. [b] The ee was determined by HPLC. [c] Reactions performed using 1.0 equiv. of **1c**, 2 equiv. of **2c** and 3 equiv $LiN(SiNe_3)_2$ on a 0.1 mmol scale. [d] Reactions performed using 1.0 equiv. of **1c**, 3 equiv. of **2c** and 4 equiv $LiN(SiNe_3)_2$ on a 0.1 mmol scale. The concentration was 0.025M. [e] Reactions performed using 1.0 equiv. of **1c**, 2 equiv. of **2c** and 3 equiv $LiN(SiNe_3)_2$ on a 0.1 mmol scale. The concentration was 0.05M. Ph-Taniaphos was used instead of (*R*)-CHT-JAPAPHOS.

8. NMR Spectrum

(-)-(η^6-(2-cyclohexen-1-ylmethyl)-benzene)$Cr(CO)_3$ (3a)

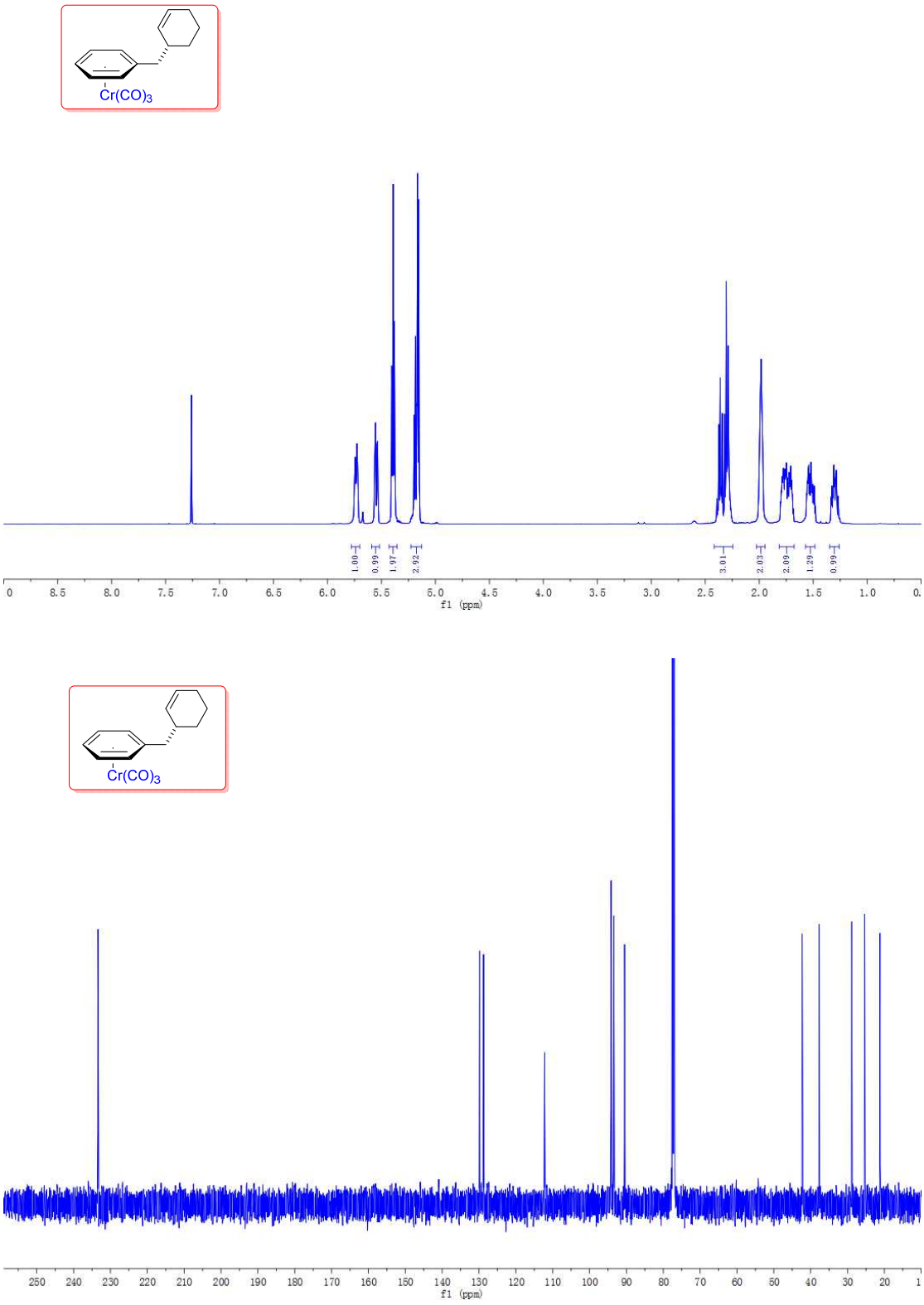


Figure S1. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3a in $CDCl_3$

(-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-tolyl)-benzene)$Cr(CO)_3$ (3b)

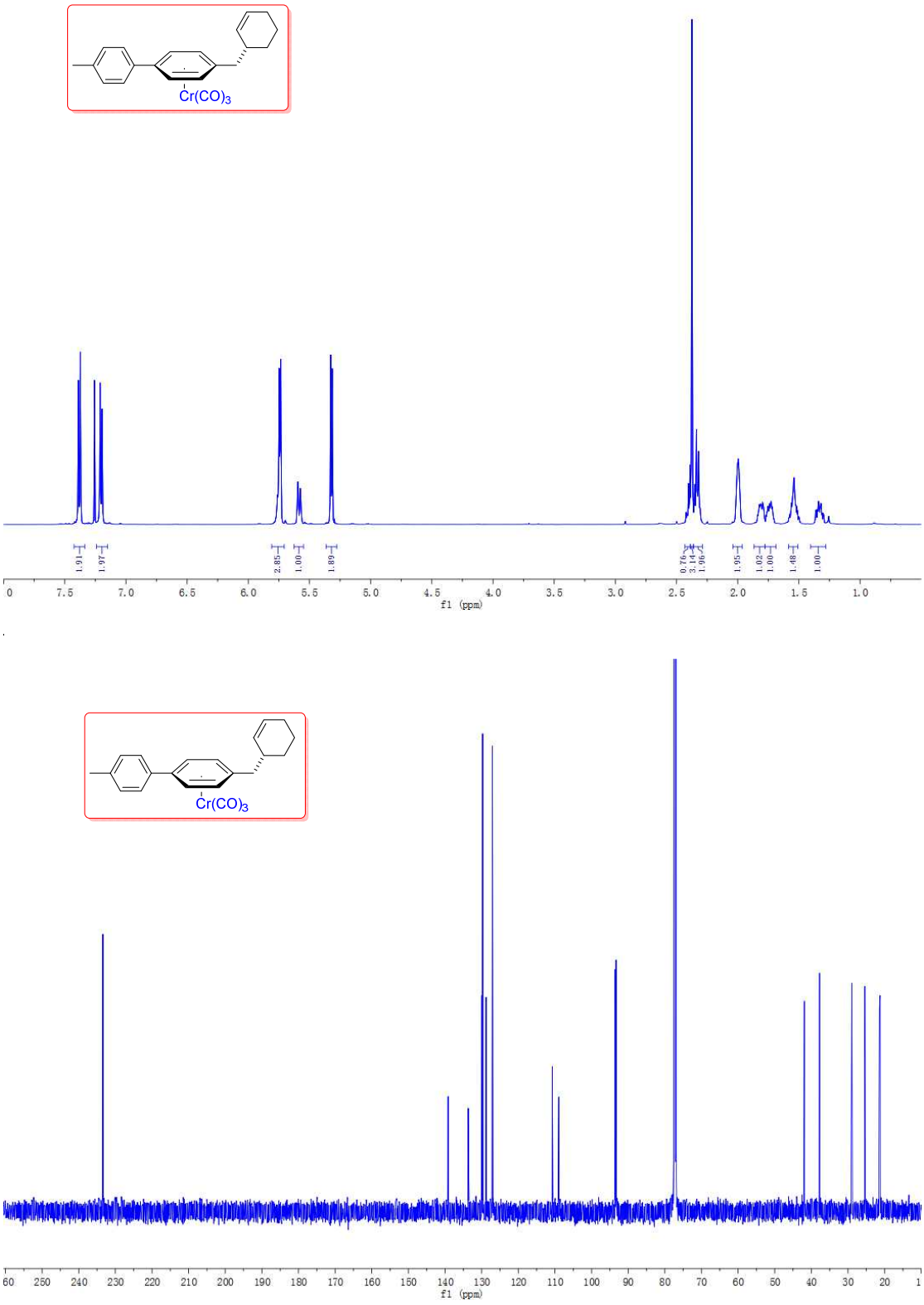


Figure S2. ^1H (500 MHz) and ^{13}C $\{^1H\}$ (125 MHz) NMR spectra of 3b in $CDCl_3$

(-)-(η^6-(2-cycloheptene-1-ylmethyl)-4-(*p*-tolyl)-benzene)$Cr(CO)_3$ (3c)

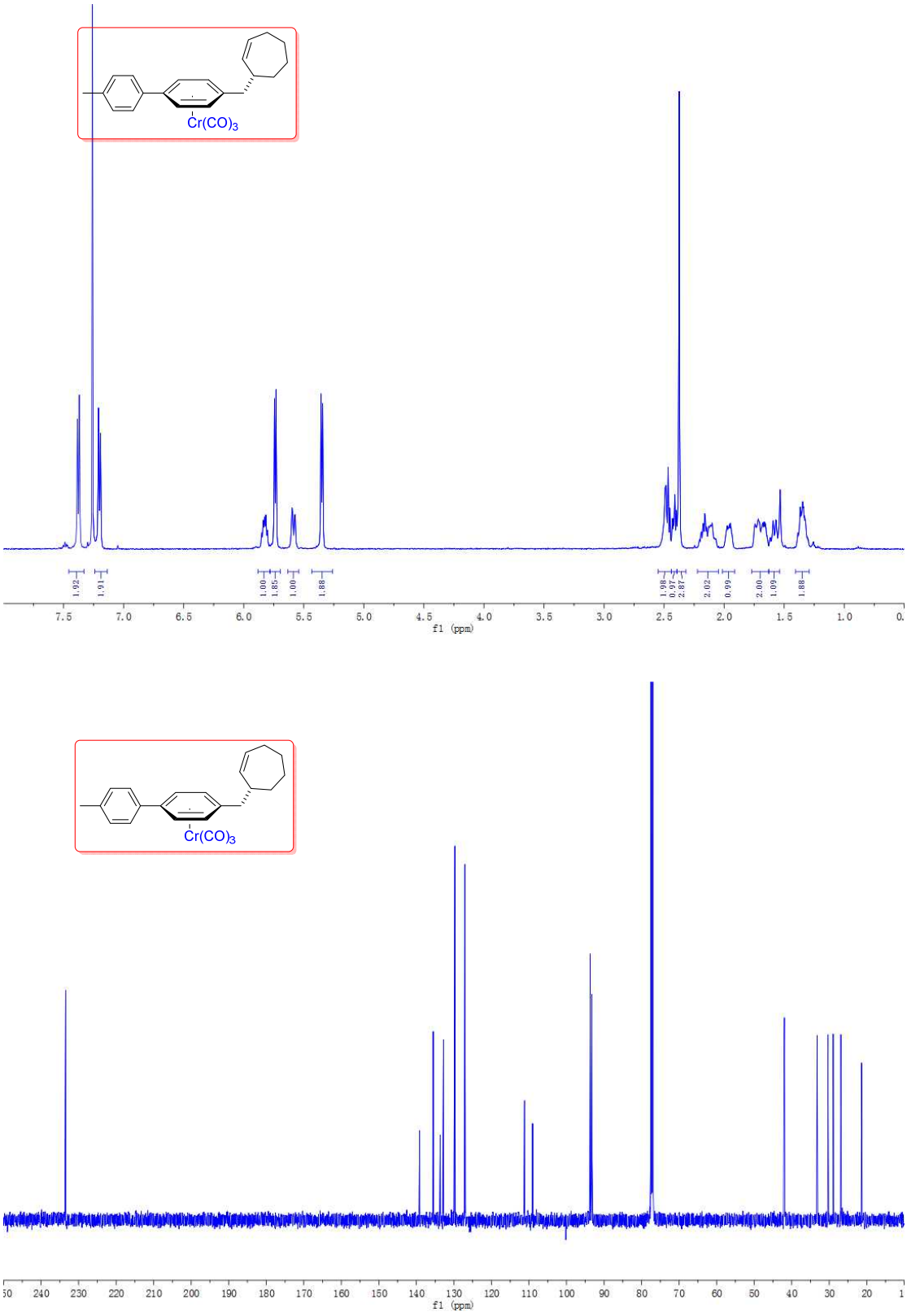


Figure S3. ^1H (500 MHz) and ^{13}C $\{^1H\}$ (125 MHz) NMR spectra of 3c in $CDCl_3$

(-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (3d)

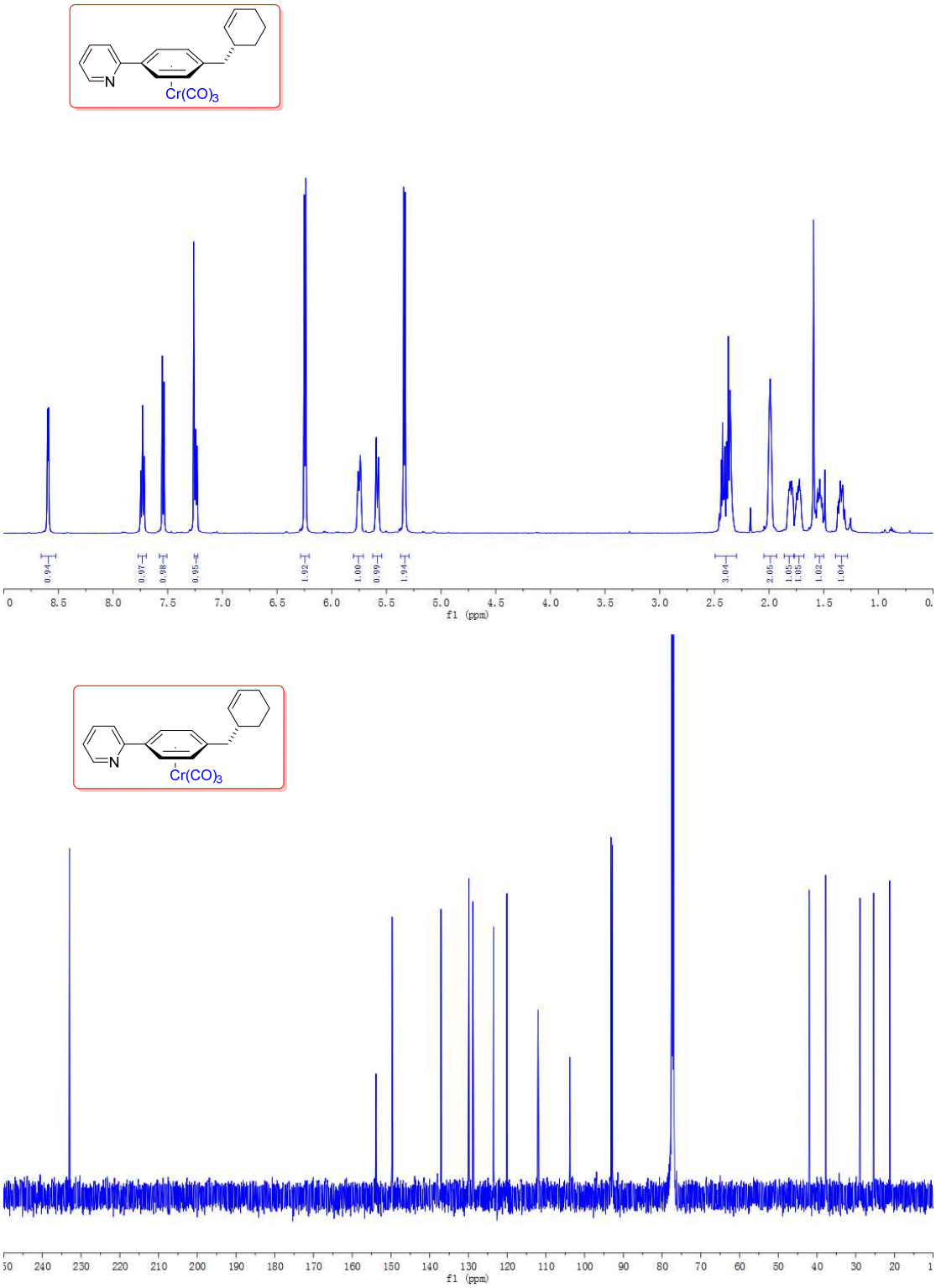


Figure S4. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3d in $CDCl_3$

(-)-(η^6-(2-cycloheptene-1-ylmethyl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (3e)

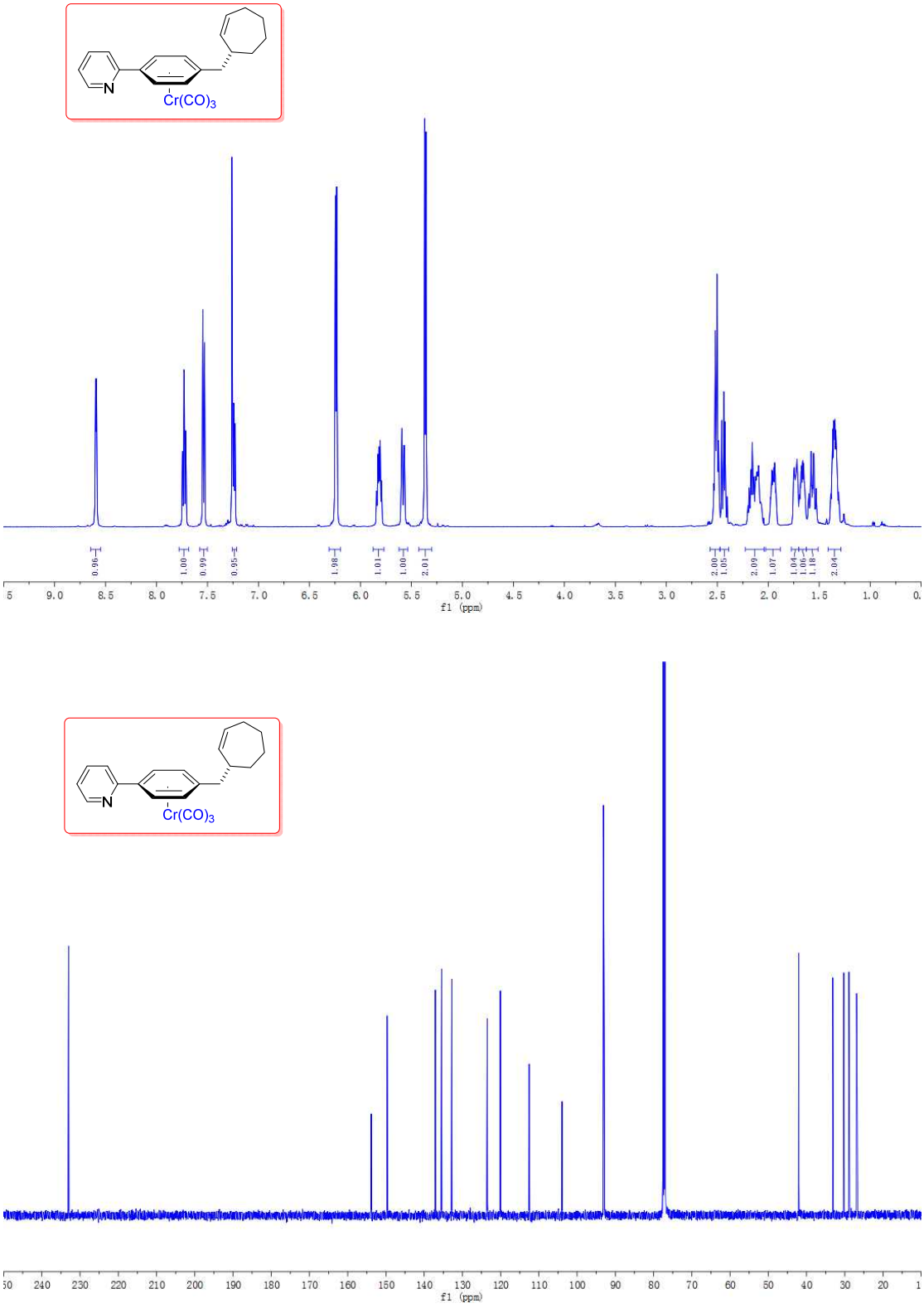


Figure S5. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3e in $CDCl_3$

(-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(2-thiophenyl)-benzene)$Cr(CO)_3$ (3f)

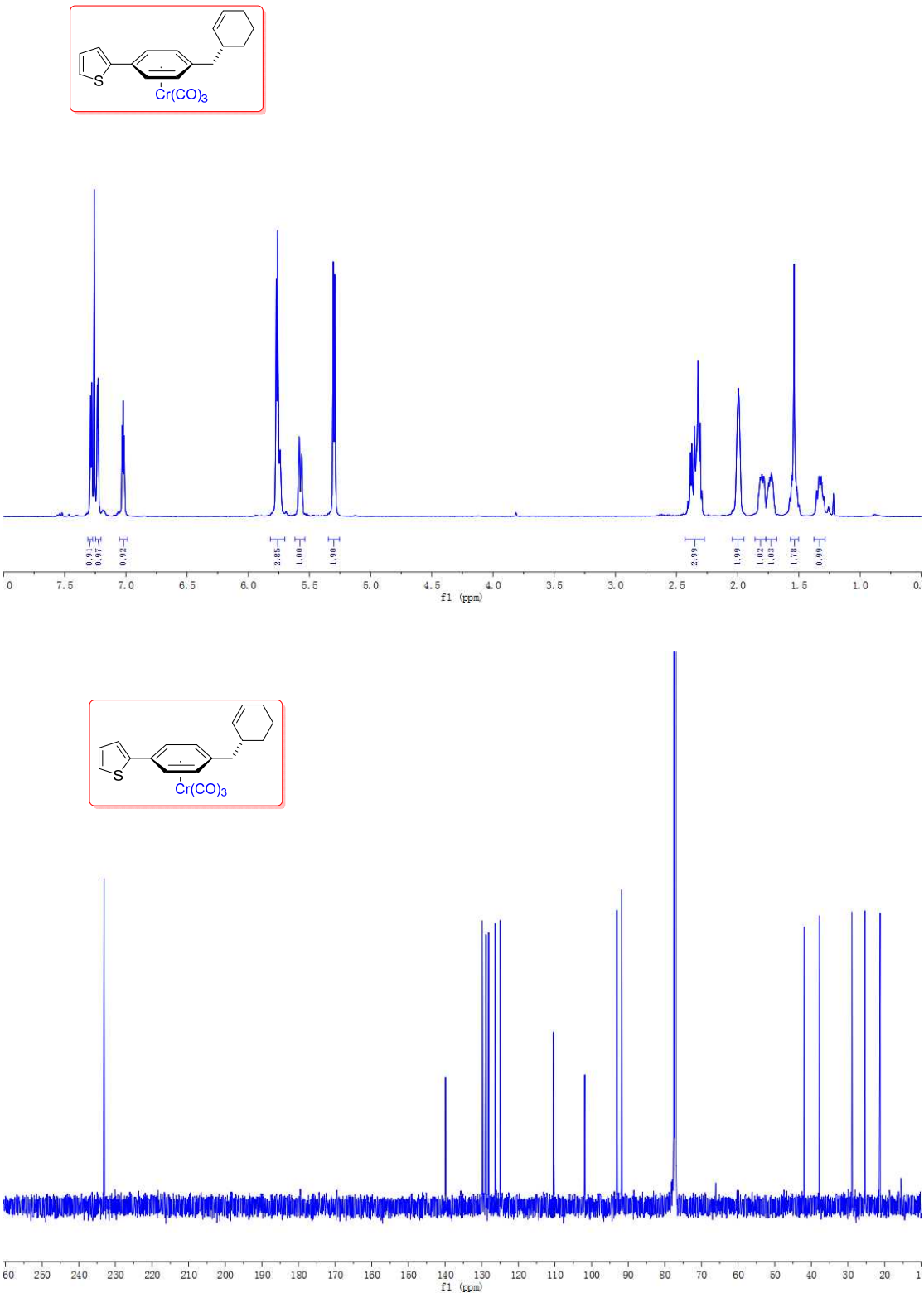


Figure S6. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3f in $CDCl_3$

(-)-(η^6-(2-cycloheptene-1-ylmethyl)-4-(2-thiophenyl)-benzene)$Cr(CO)_3$ (3g)

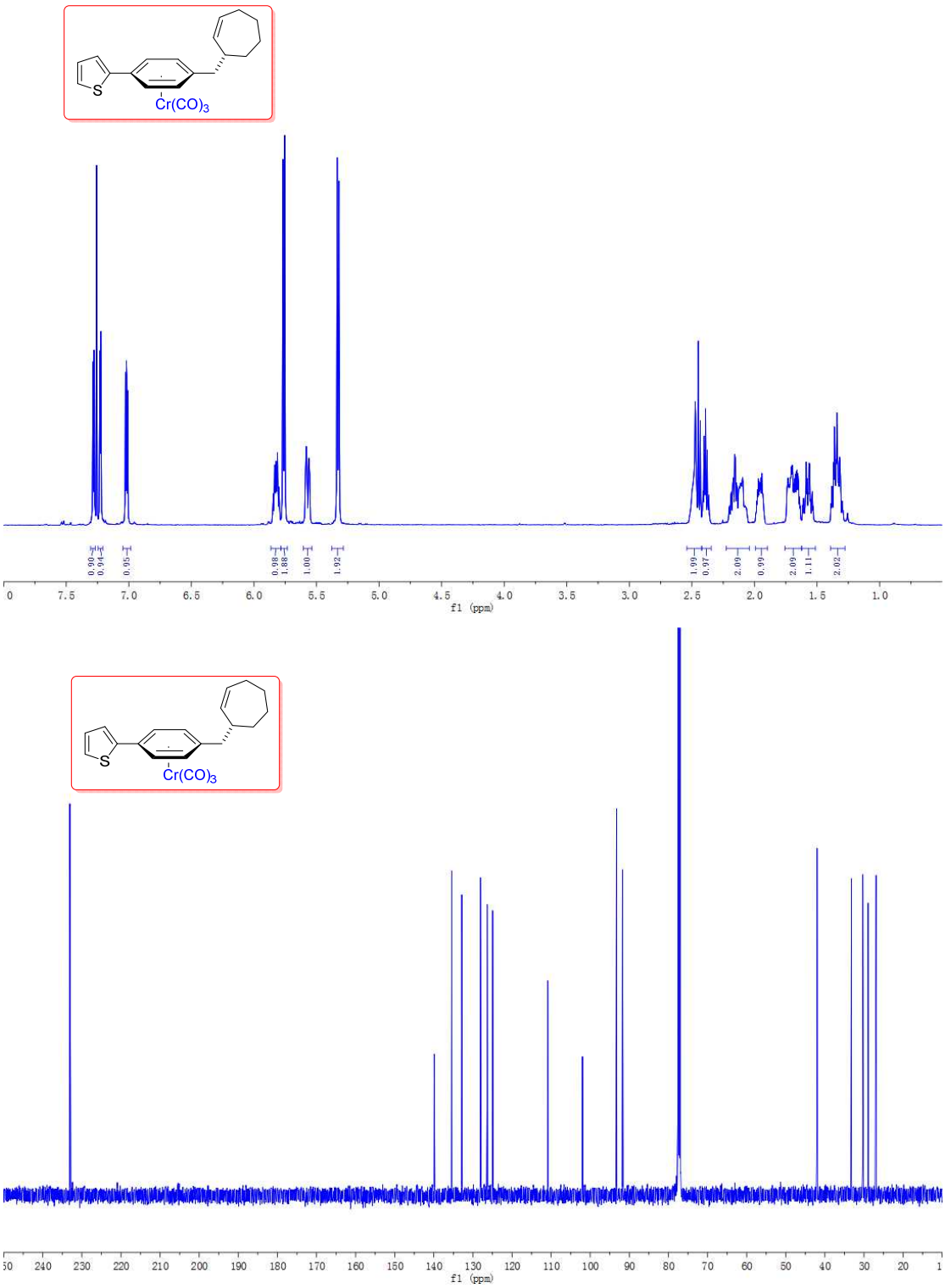


Figure S7. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3g in $CDCl_3$

(-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)$Cr(CO)_3$ (3h)

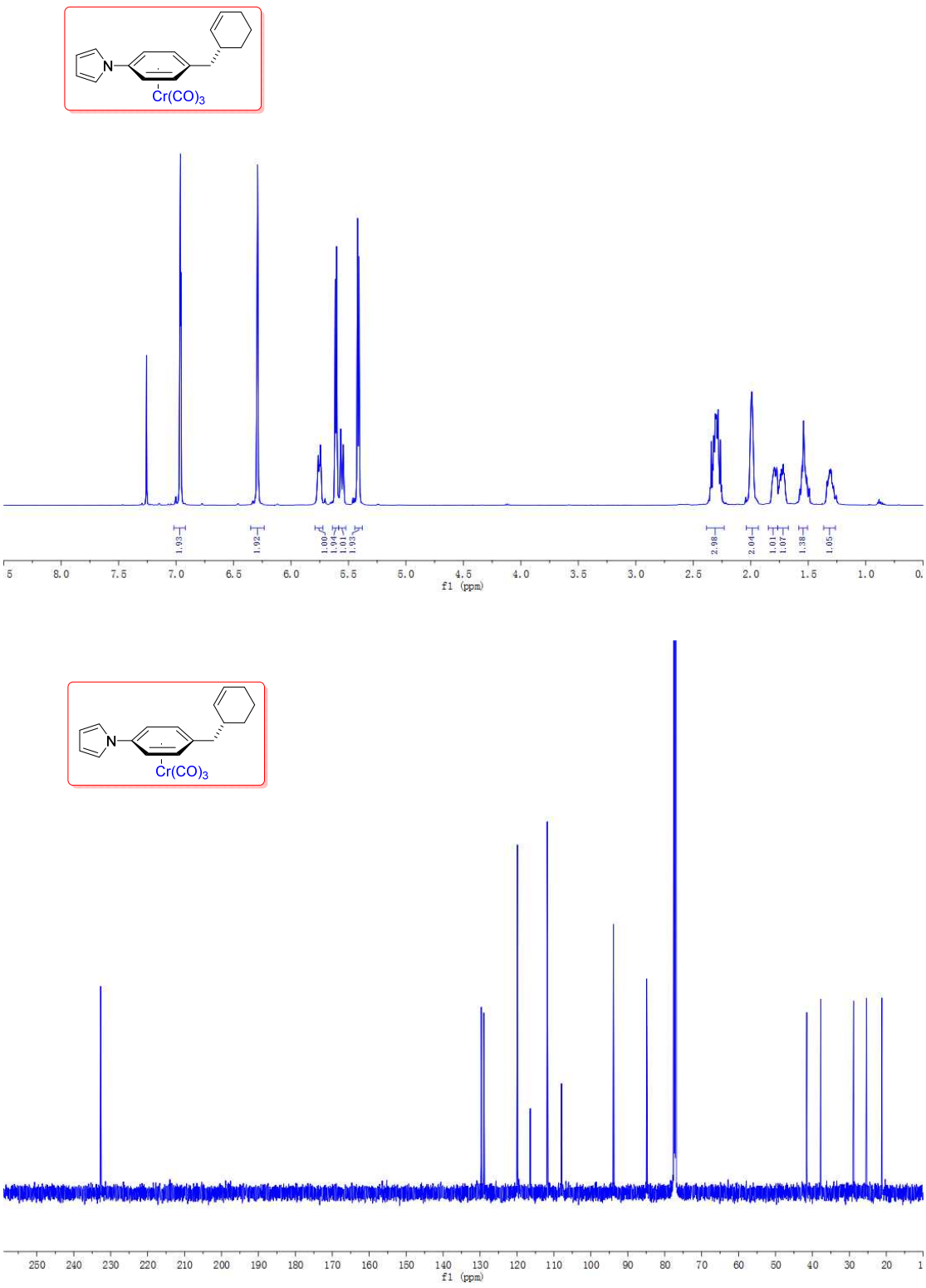


Figure S8. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3h in $CDCl_3$

(-)-(η^6-(2-cycloheptene-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)$Cr(CO)_3$ (3i)

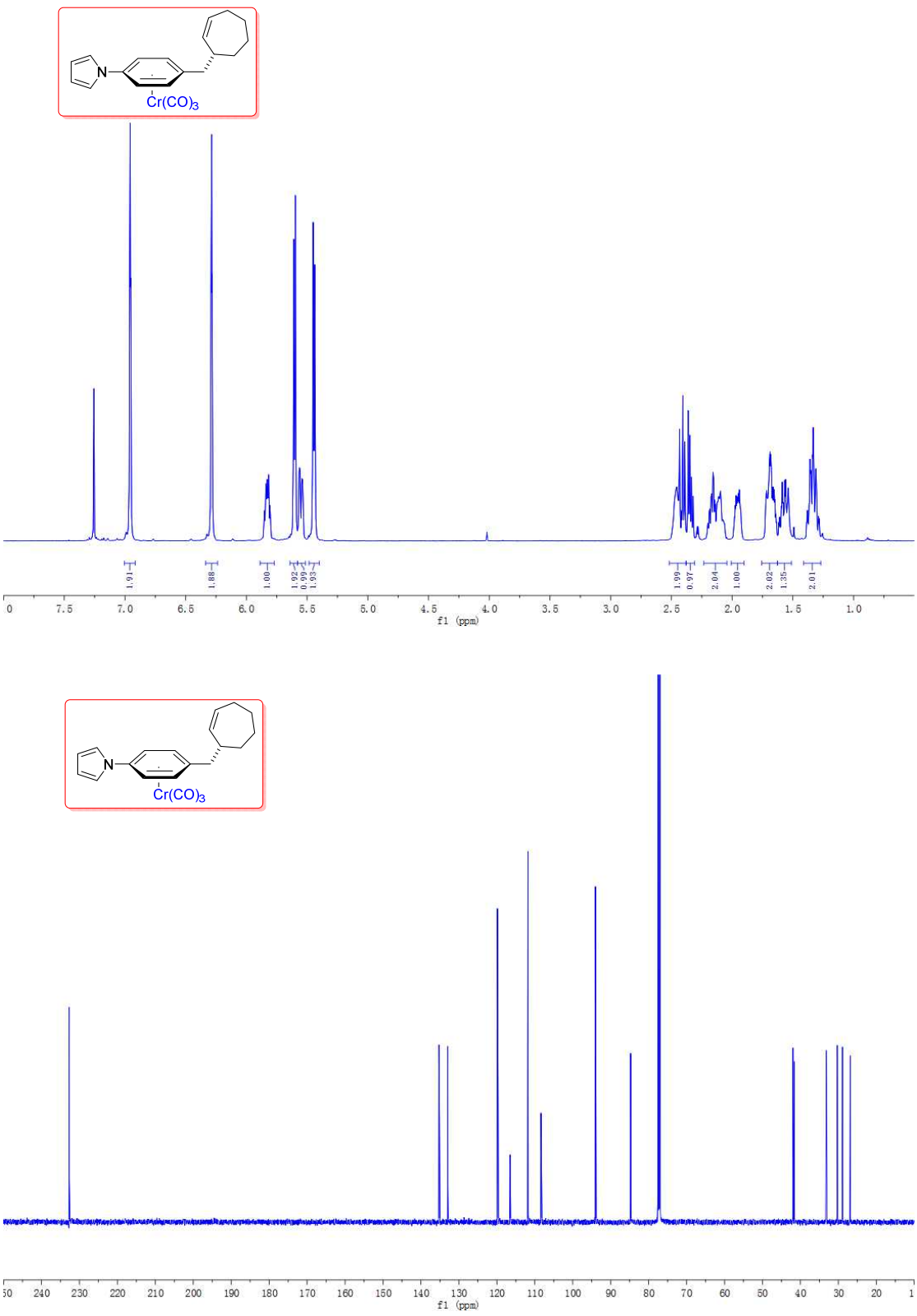


Figure S9. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3i in $CDCl_3$

(-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-chlorophenyl)-benzene)$Cr(CO)_3$ (3j)

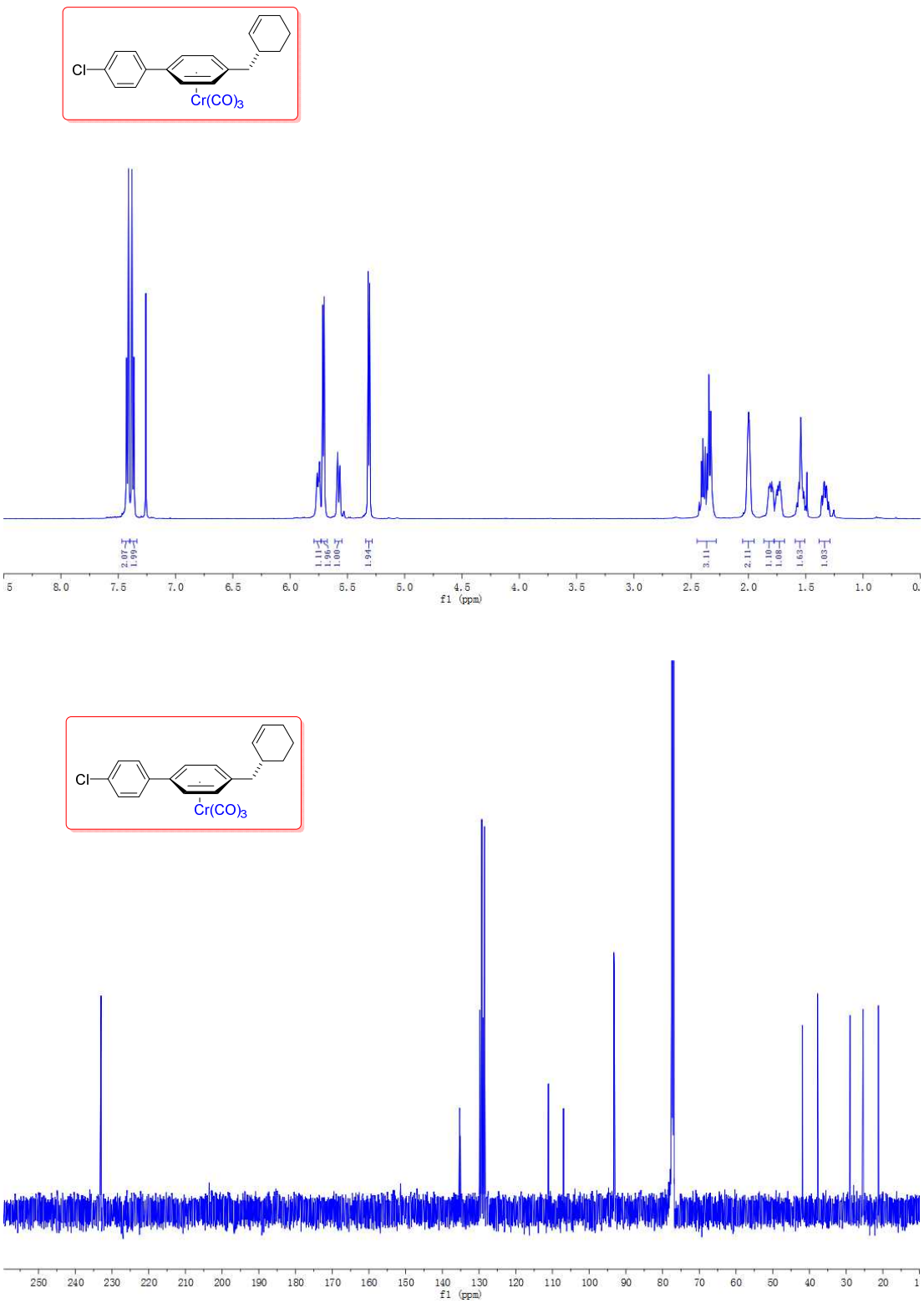


Figure S10. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3j in $CDCl_3$

(-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-trifloromethylphenyl)-benzene)$Cr(CO)_3$ (3k)

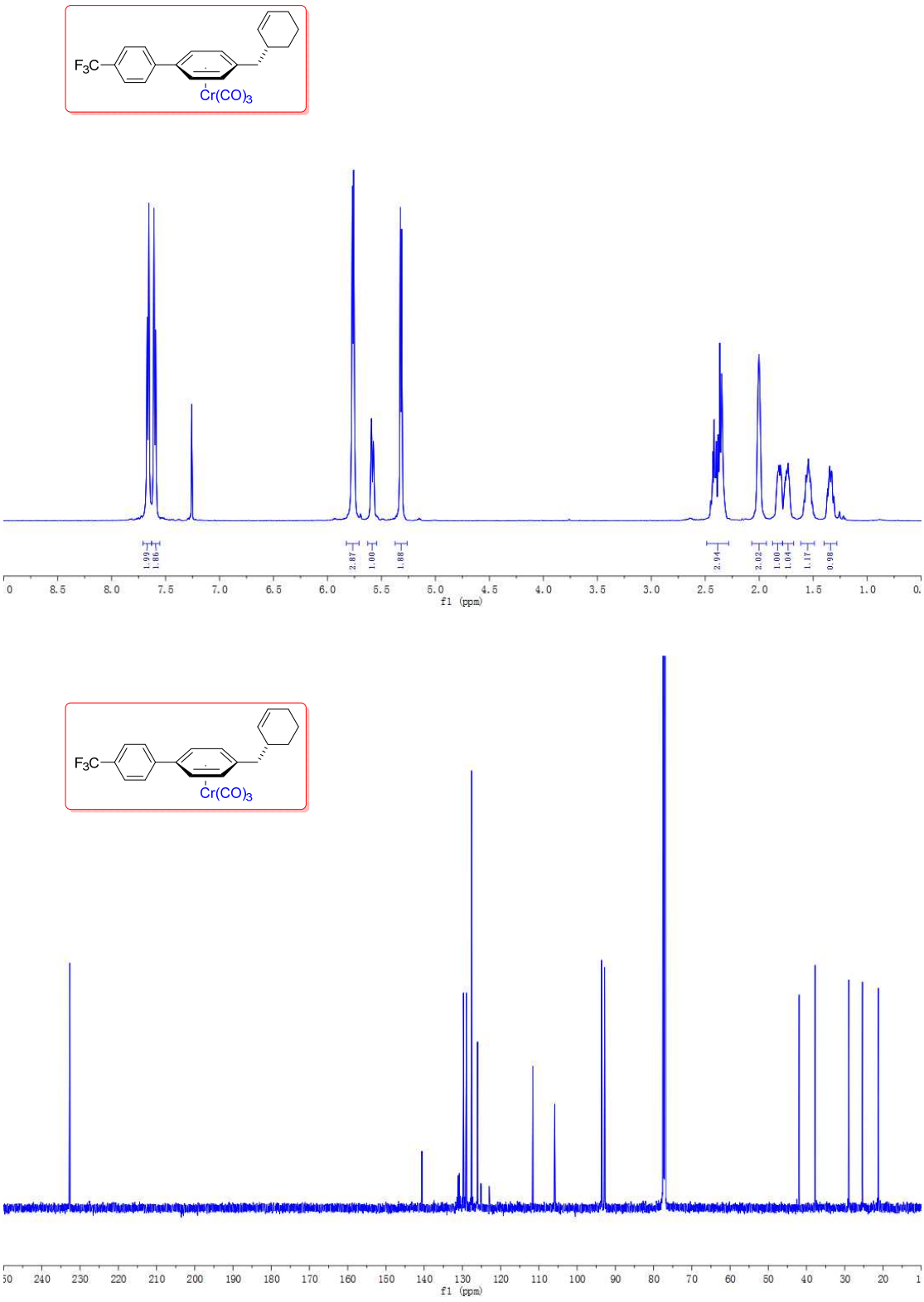


Figure S11. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3k in $CDCl_3$

(-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-chloro-benzene)$Cr(CO)_3$ (3l)

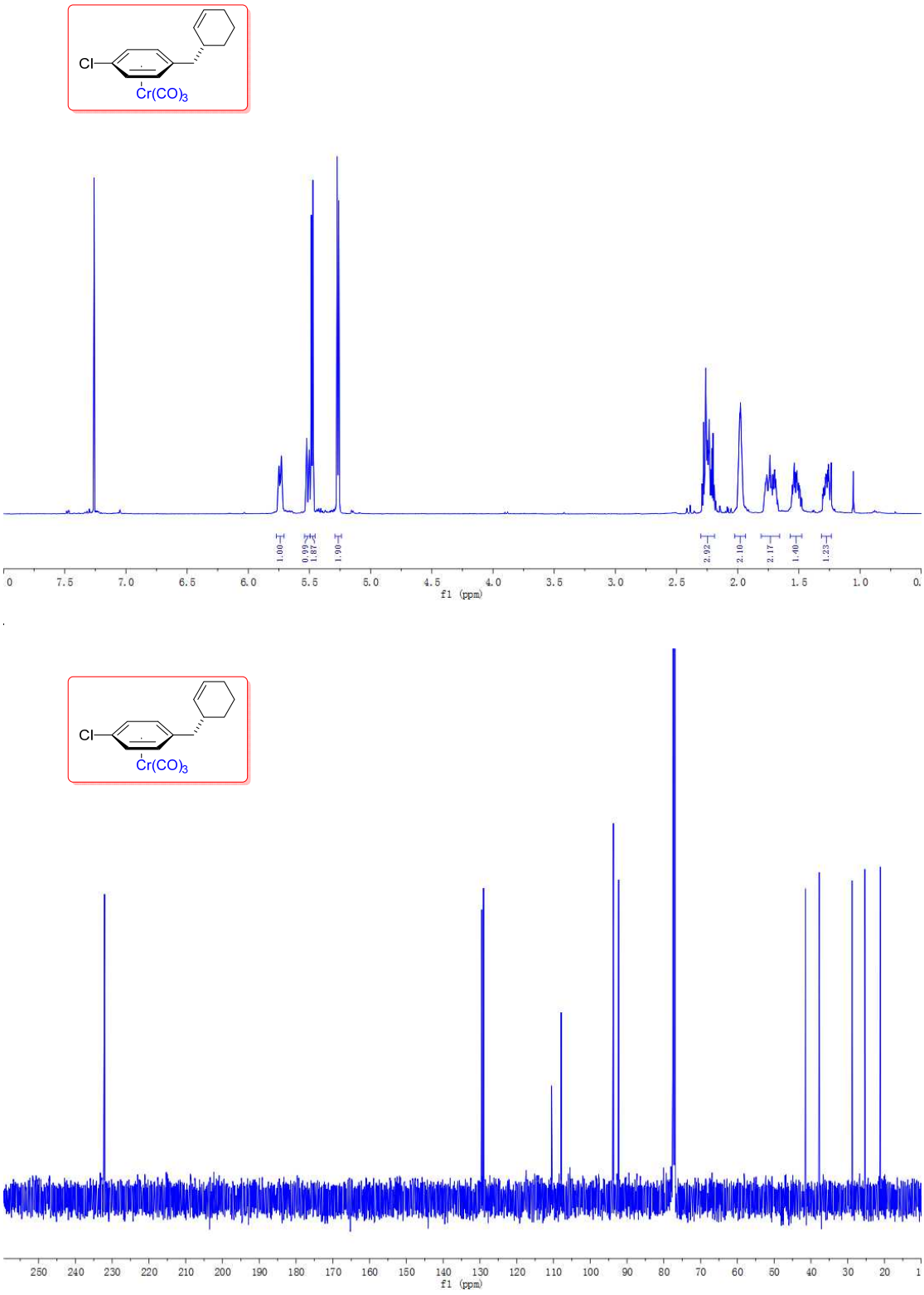


Figure S12. ^1H (500 MHz) and ^{13}C {^1H} (125 MHz) NMR spectra of 3l in $CDCl_3$

(-)-(2-cyclohexen-1-ylmethyl)-3-chlorobenzene (3m)

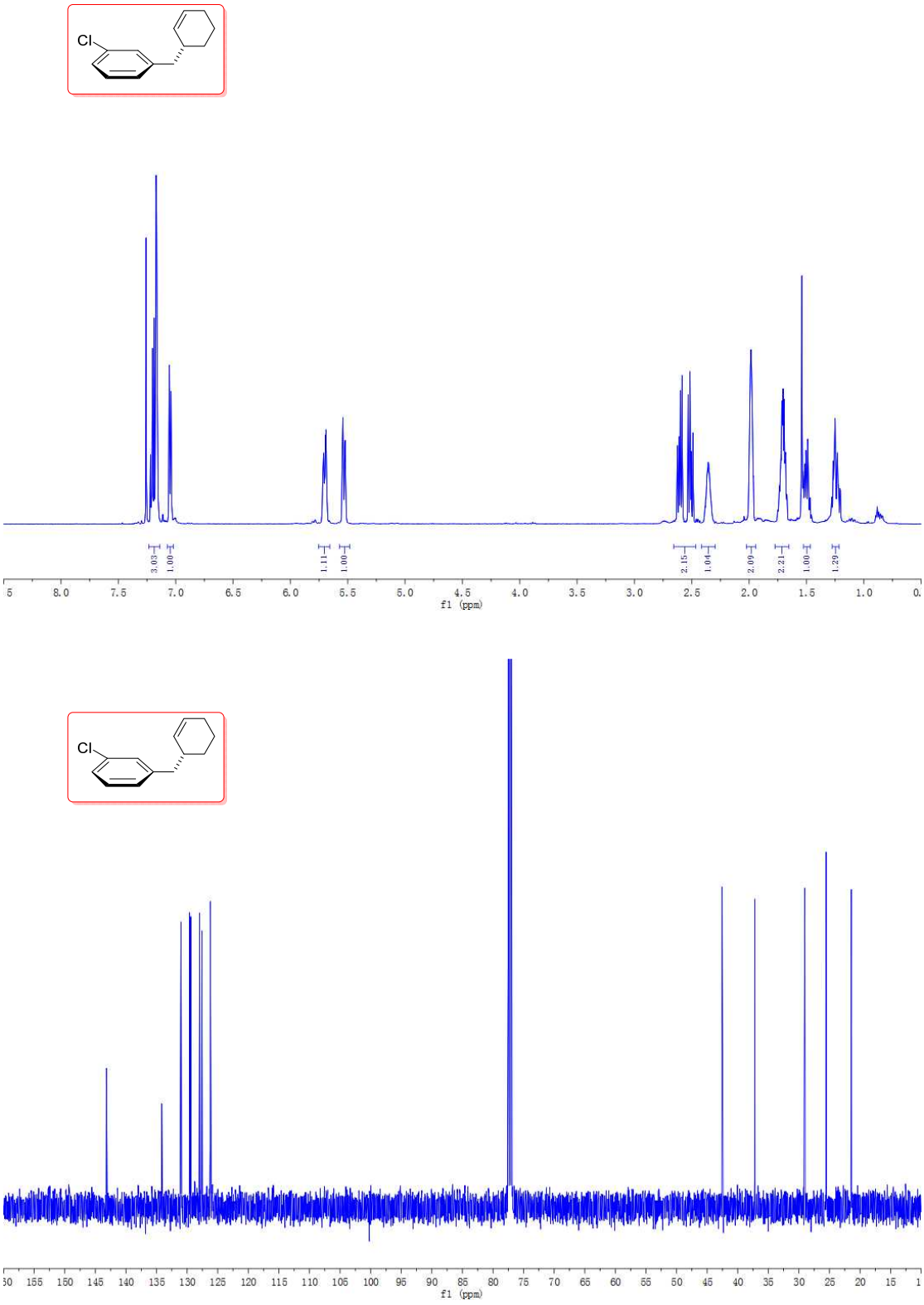


Figure S13. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3m in $CDCl_3$

(-)-(2-cyclohexen-1-ylmethyl)-3-methoxybenzene (3n)

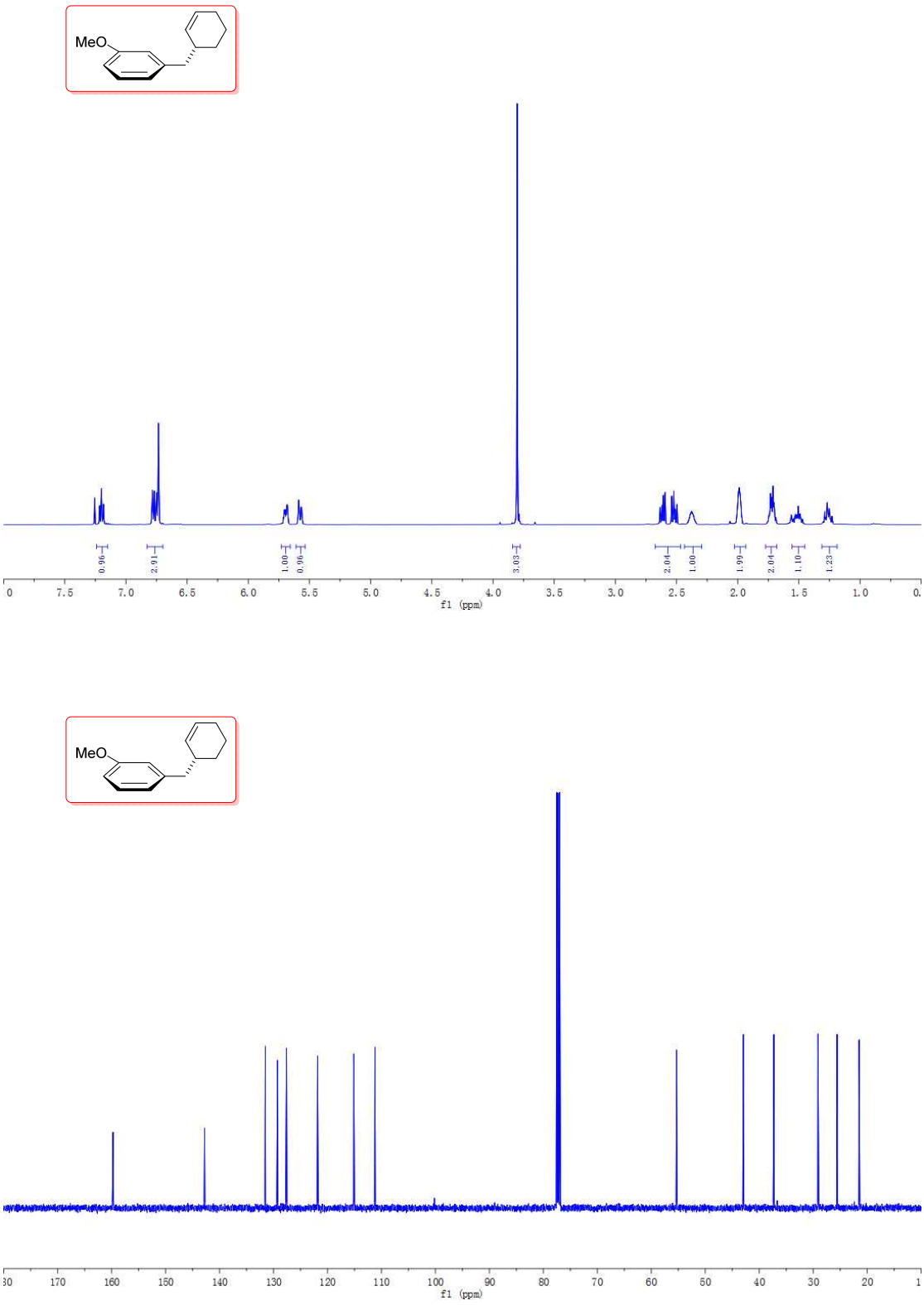


Figure S14. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3n in $CDCl_3$

(-)-(2-cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene (3o)

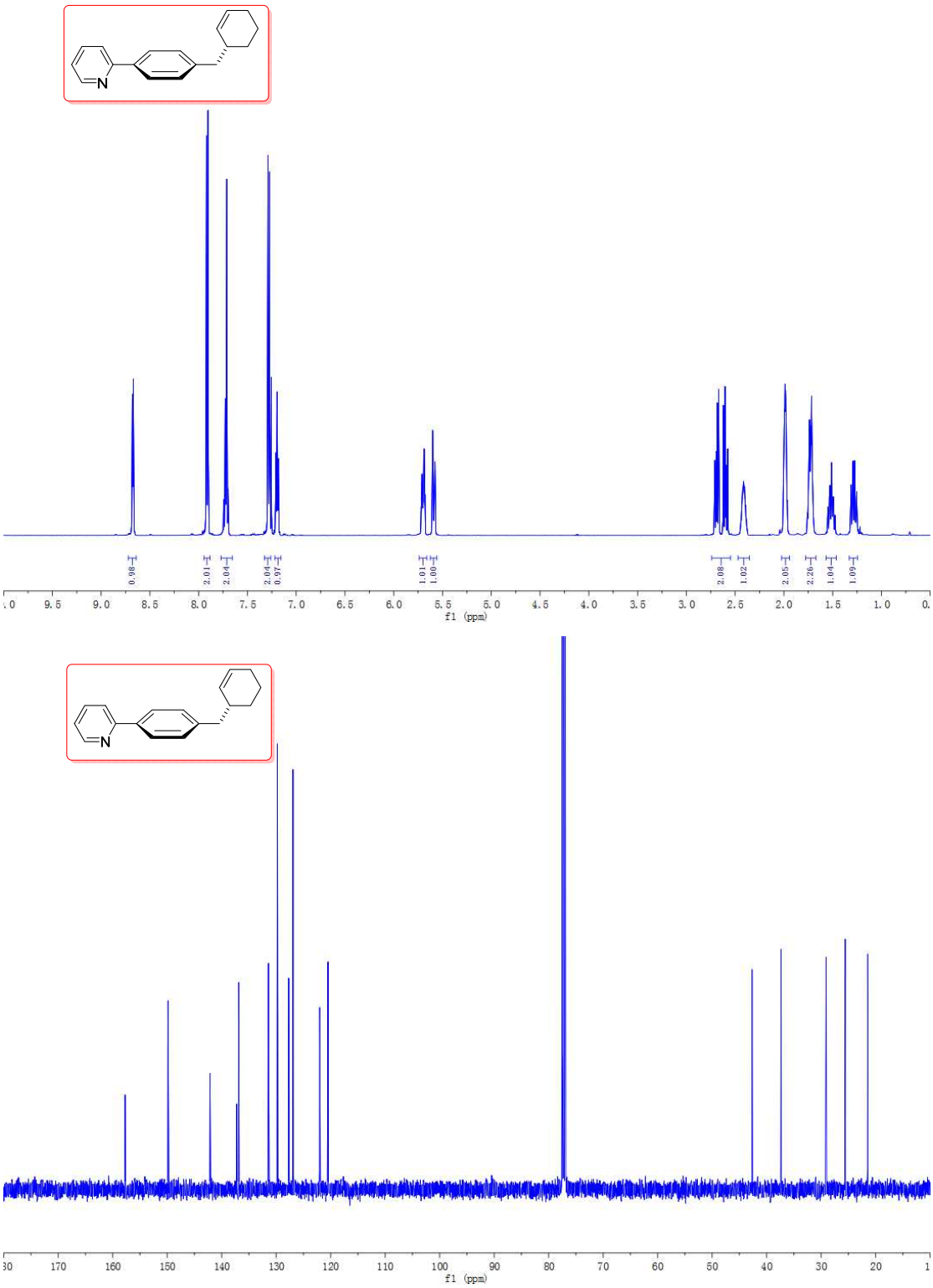


Figure S15. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3o in $CDCl_3$

(-)-3-(diphenylmethyl)-1-cyclohexene (3p)

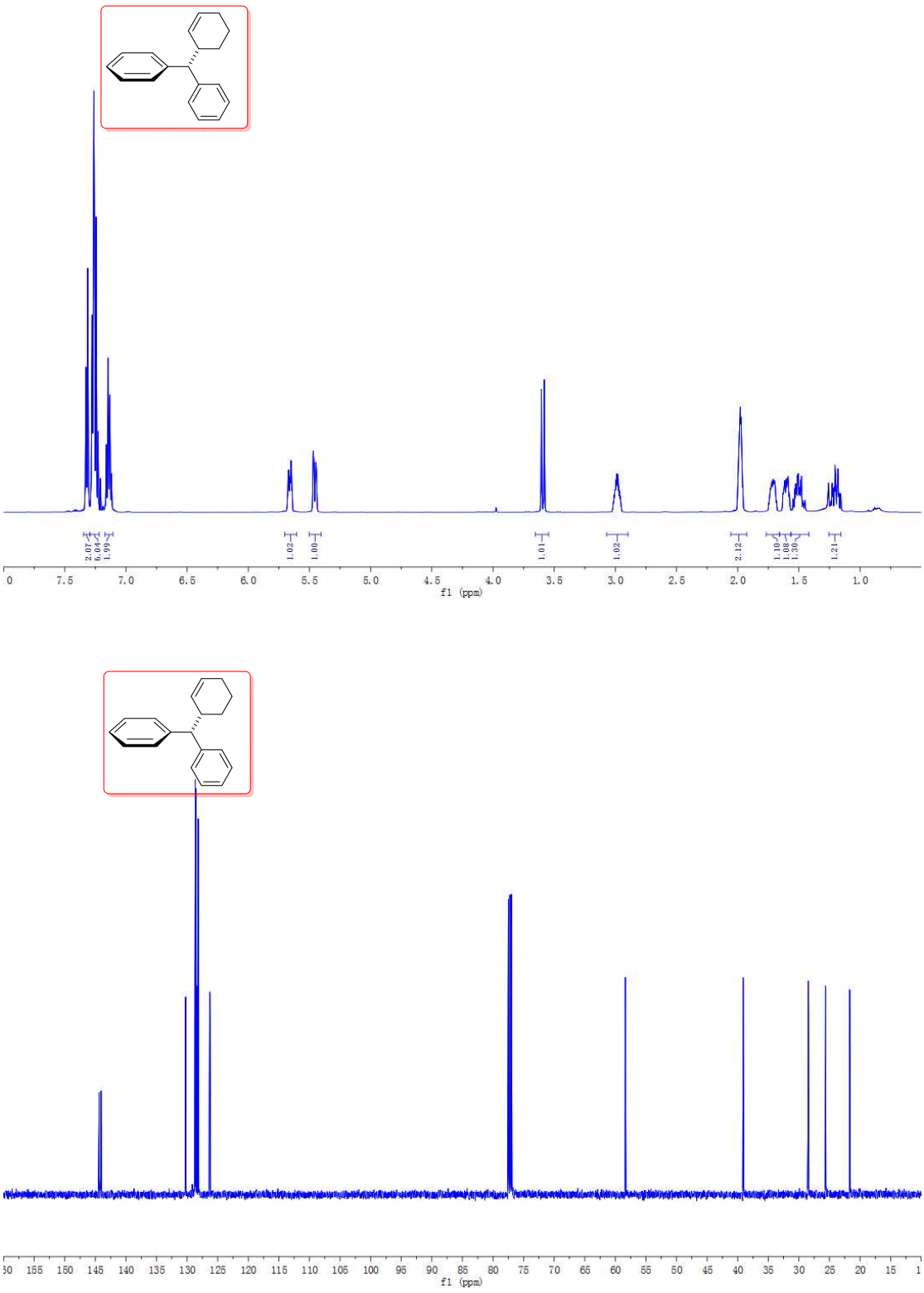


Figure S16. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3p in $CDCl_3$

(-)-4-(cyclohex-2-en-1-yl(phenyl)methyl)morpholine (3q)

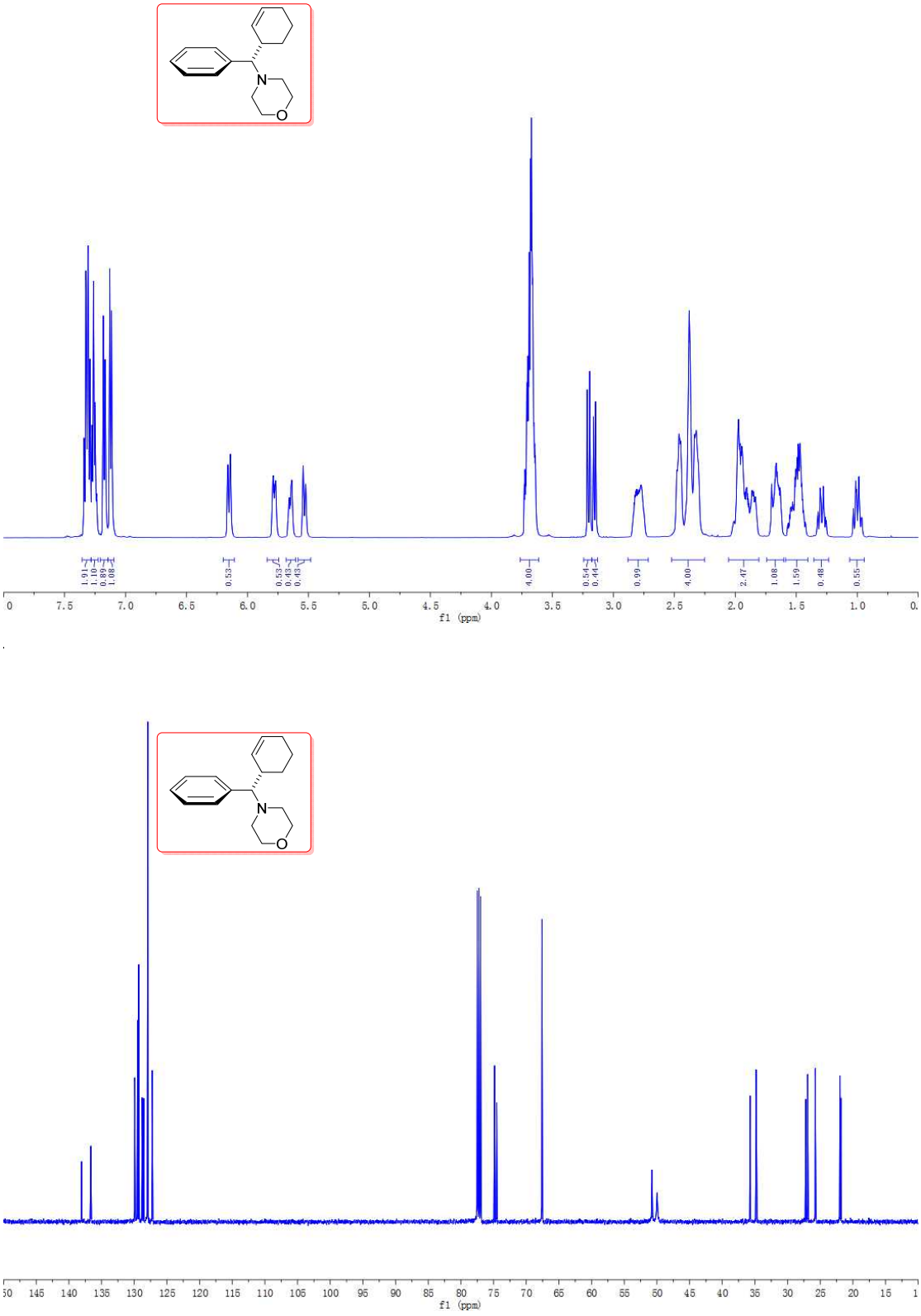


Figure S17. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3q in $CDCl_3$

(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-4-(2-pyridyl)-benzene)Cr(CO)$_3$ (3r)

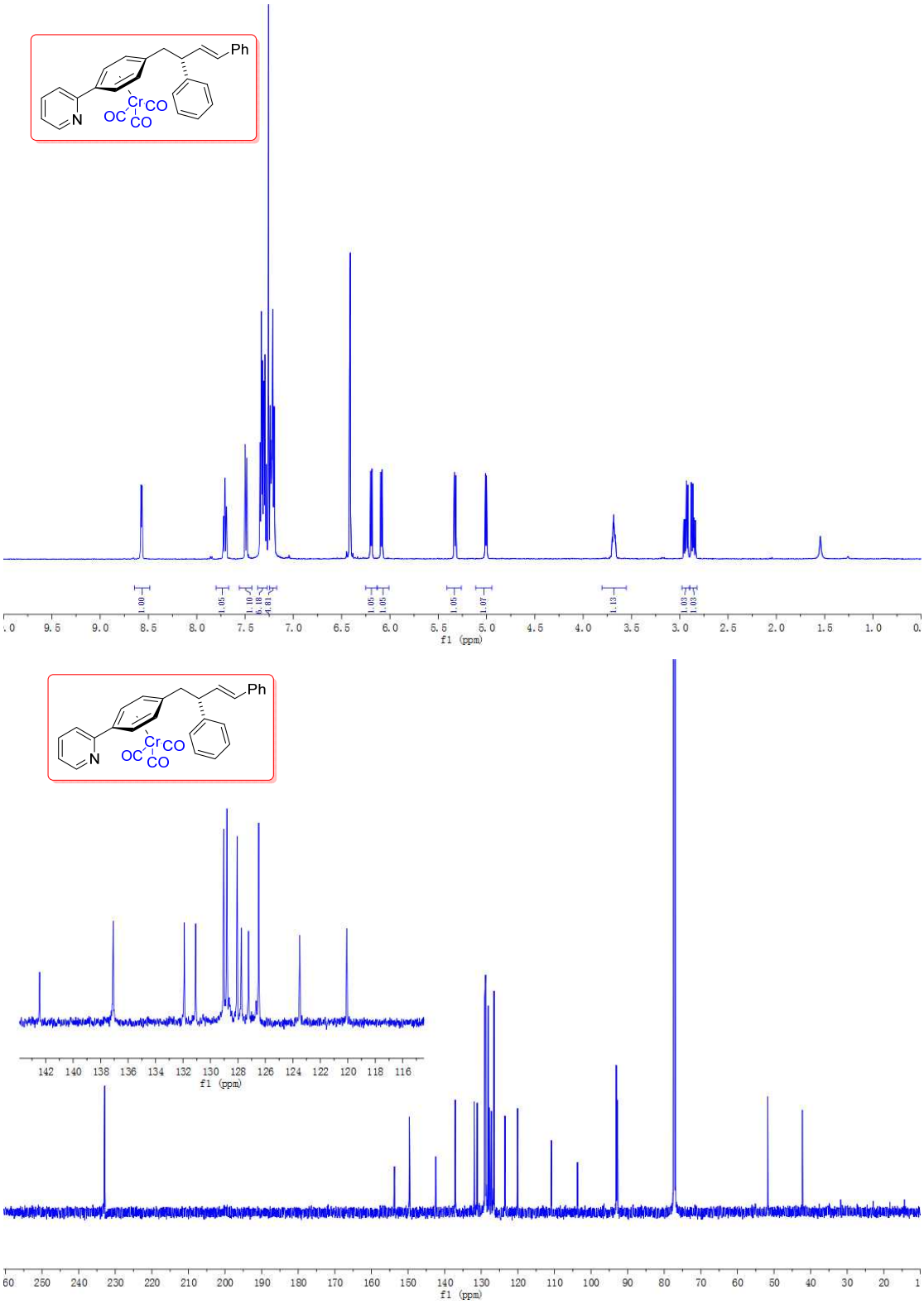


Figure S18. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3r in $CDCl_3$

(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(2-thiophenyl)-benzene)Cr(CO)$_3$ (3s)

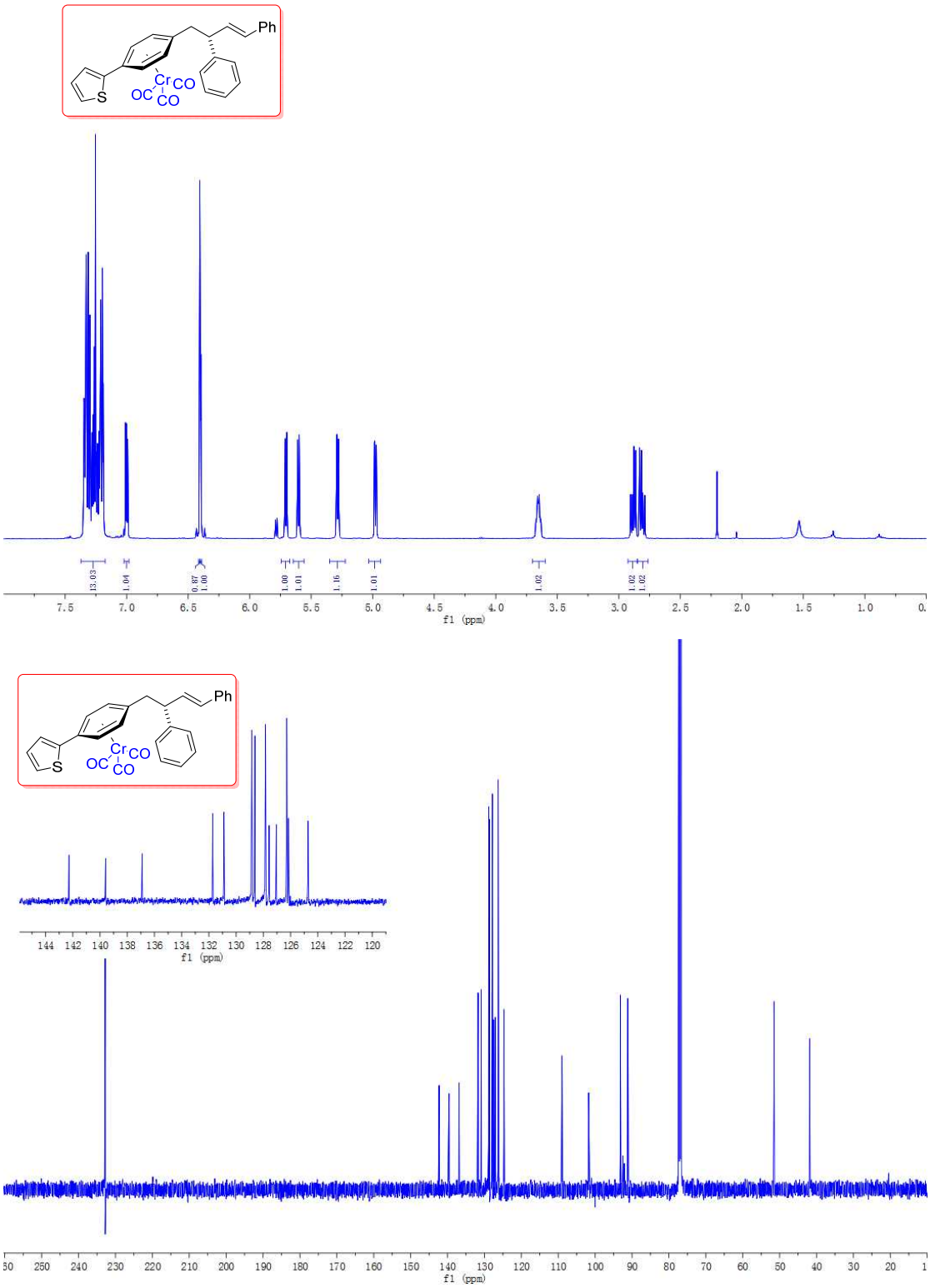


Figure S19. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3s in $CDCl_3$

(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(*p*-trifloromethylphenyl)-benzene)Cr(CO)$_3$ (3t)

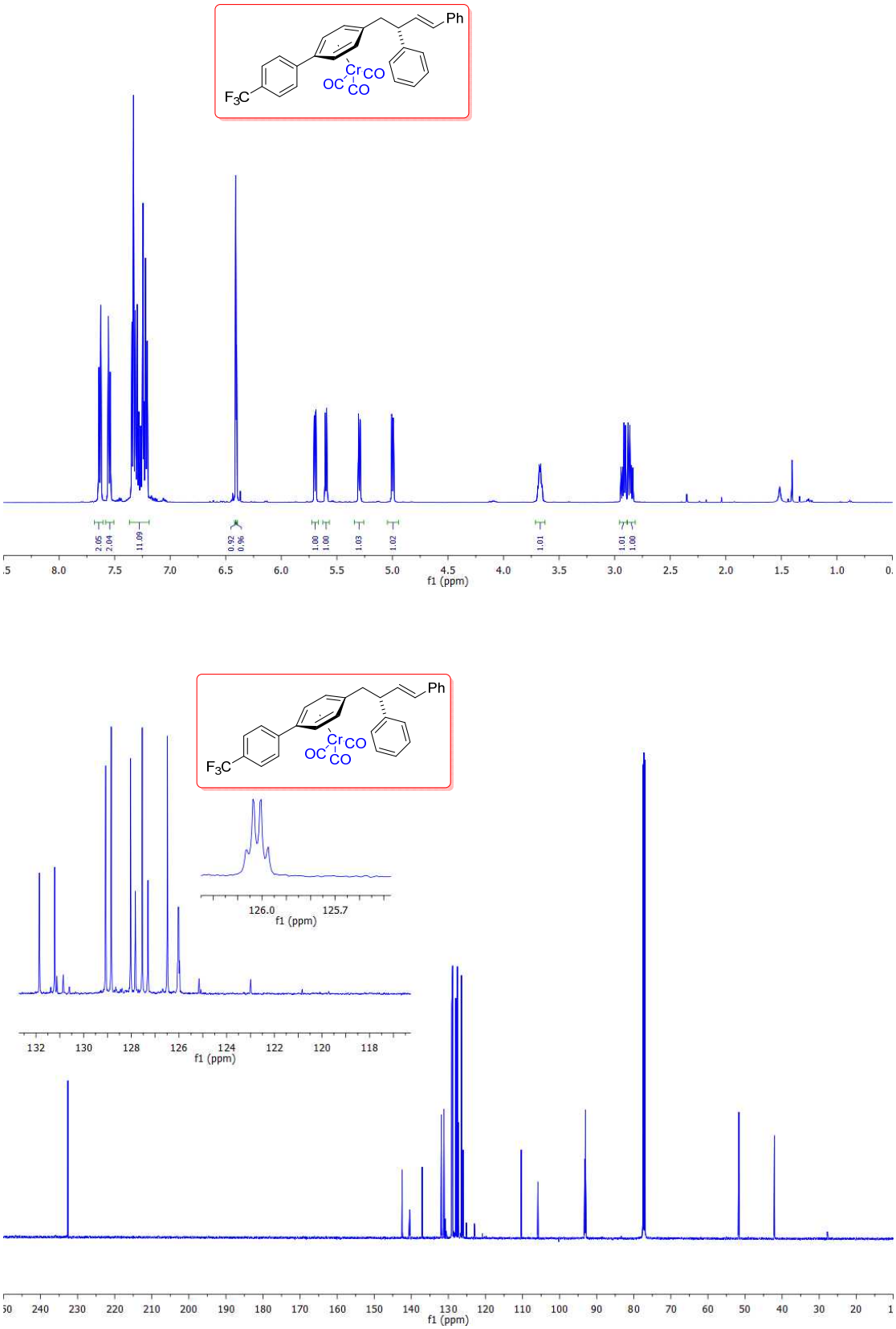


Figure S20 ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3t in $CDCl_3$

(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(*p*-chlorophenyl)-benzene)Cr(CO)$_3$ (3u)

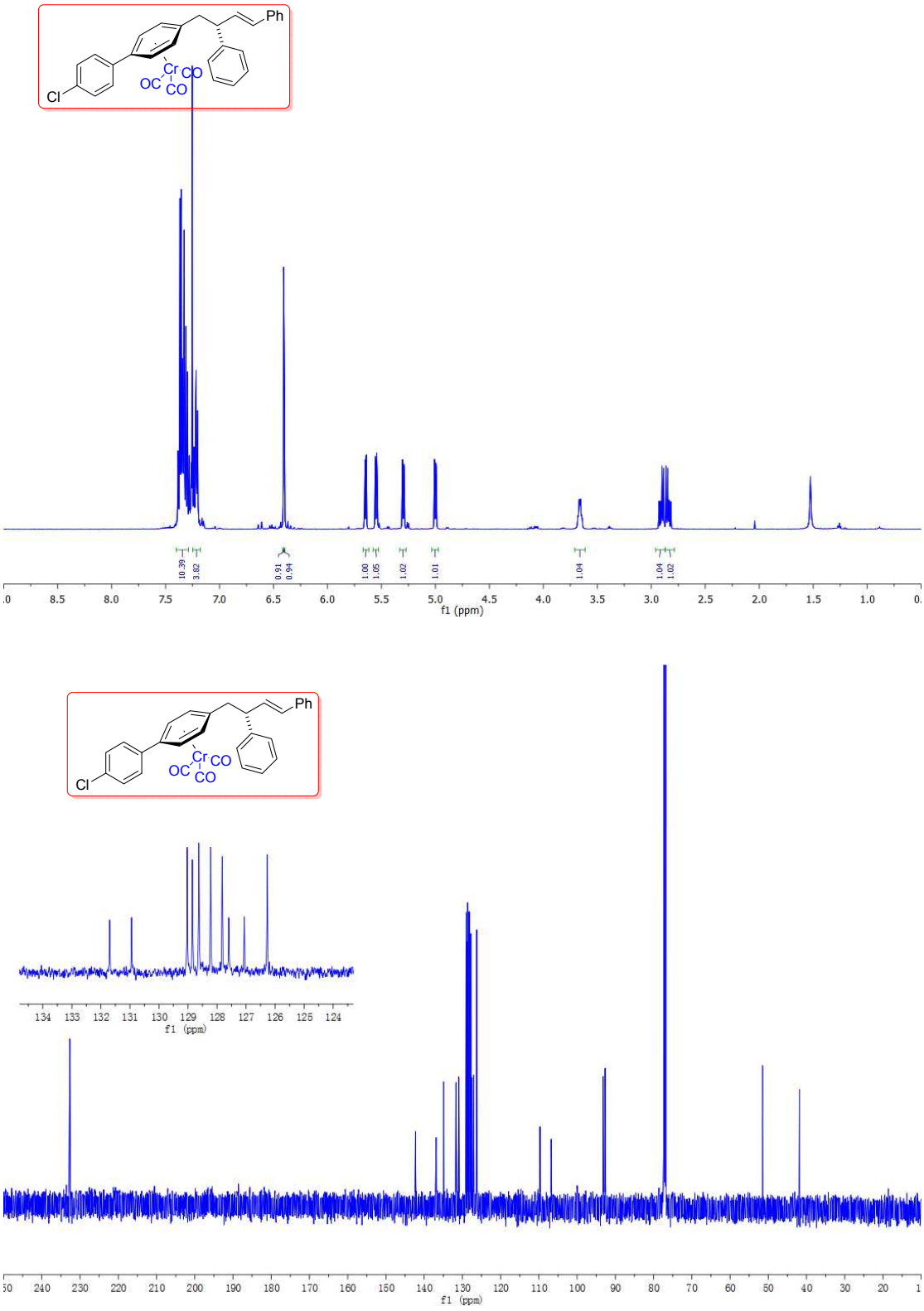


Figure S21. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3u in $CDCl_3$

(*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(*p*-fluorophenyl)-benzene)Cr(CO)$_3$ (3v)

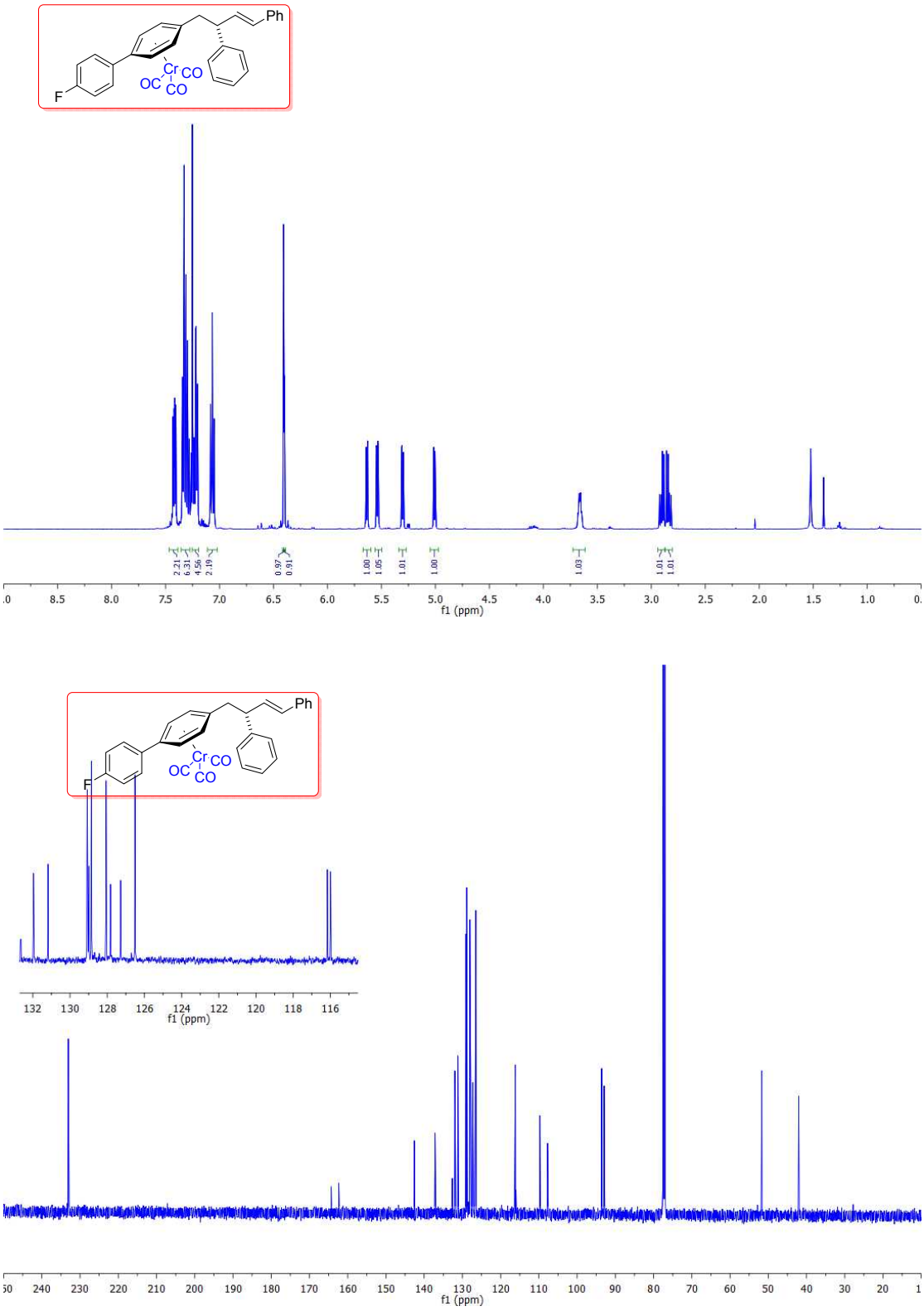


Figure S22. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3v in $CDCl_3$

(*E*)-(η^6-(2-ethylhex-3-en-1-yl)-4-(2-pyridyl)-benzene)Cr(CO)$_3$ (3w)

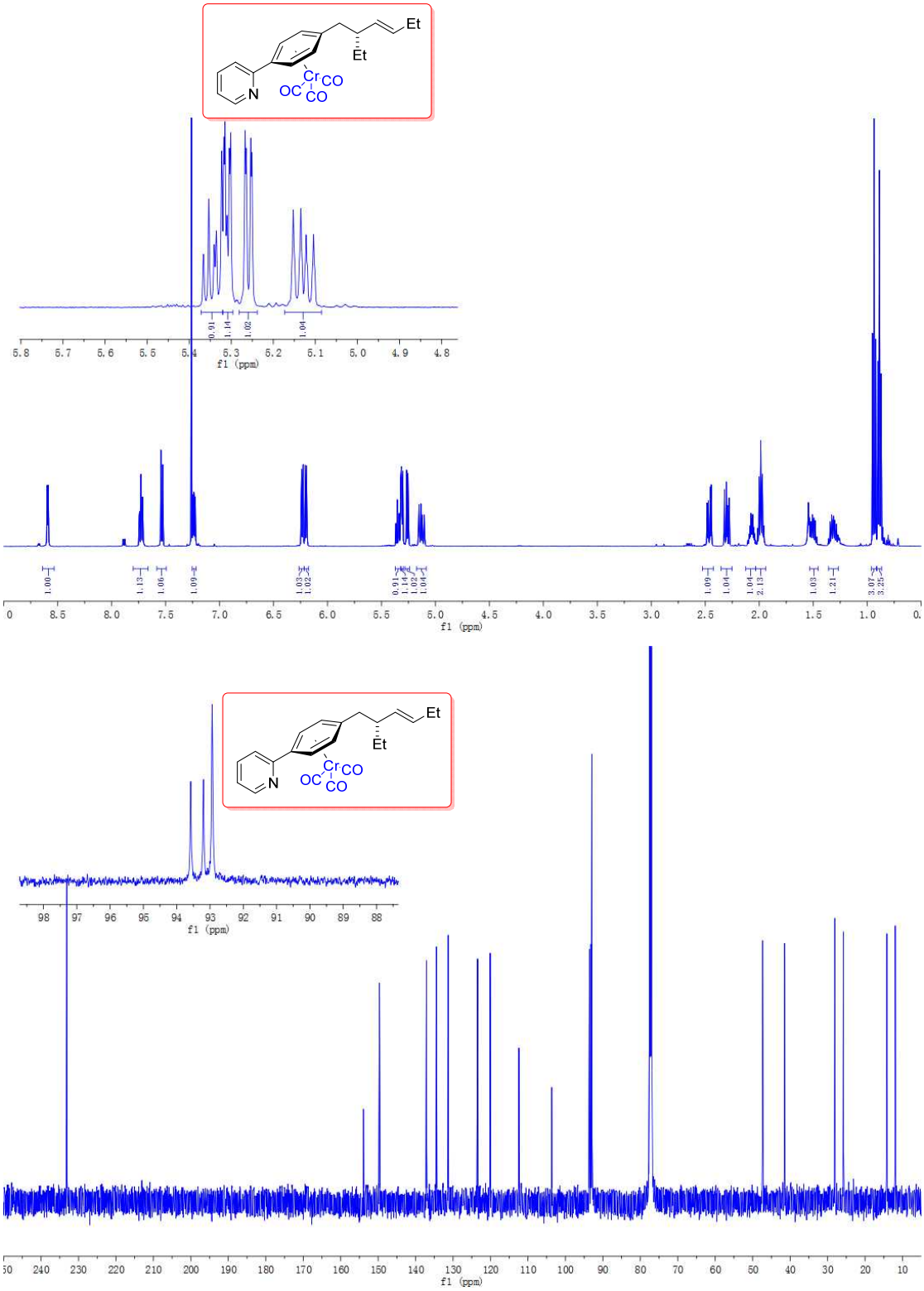


Figure S23. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3w in $CDCl_3$

***cis*-(η^6-(5-phenyl-2-cyclohexen-1-ylmethyl)-benzene)Cr(CO)$_3$ (3x)**

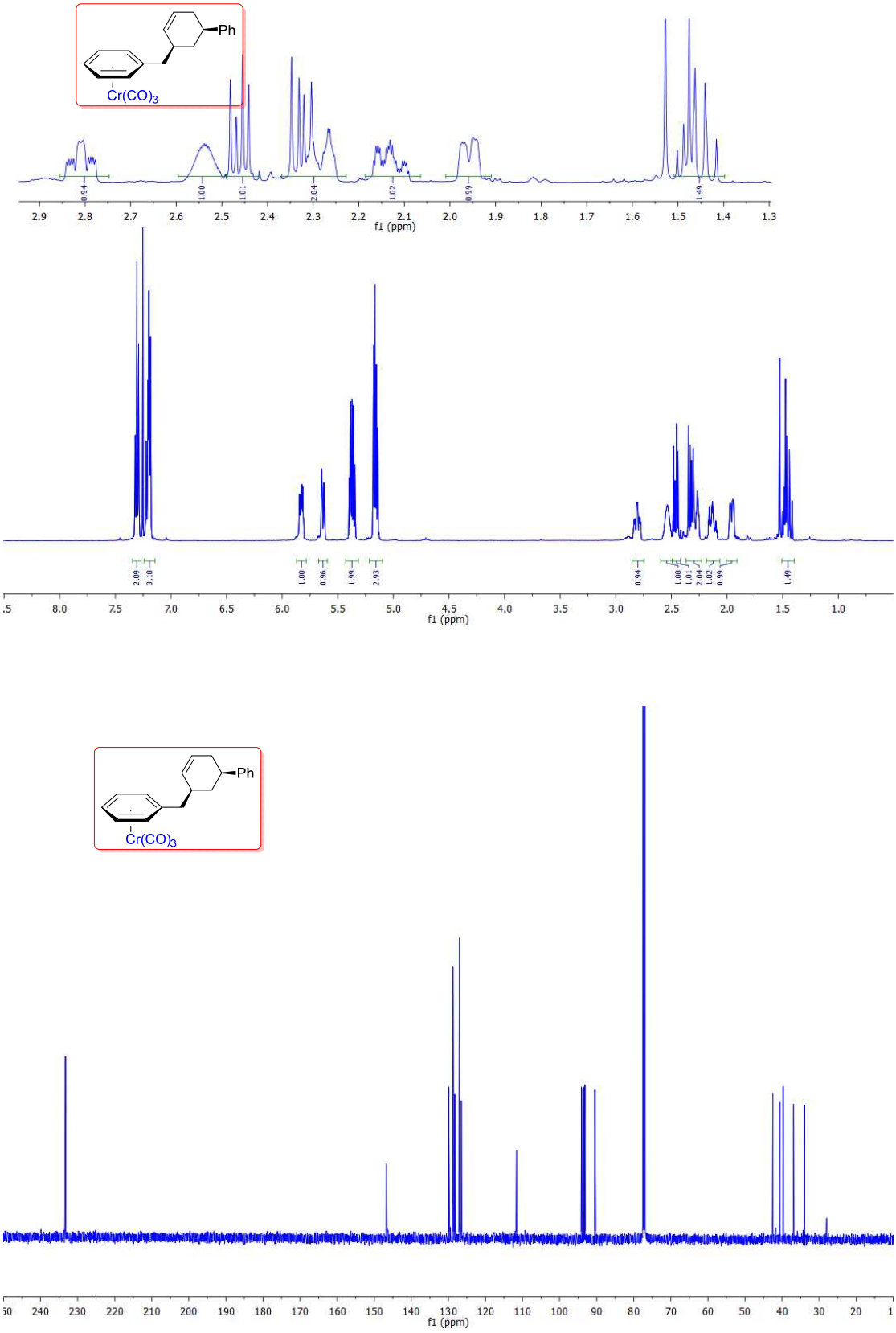


Figure S24. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3x in $CDCl_3$

(*E*)-2-(4-(2,4-diphenylbut-3-en-1-yl)phenyl)pyridine (3y)

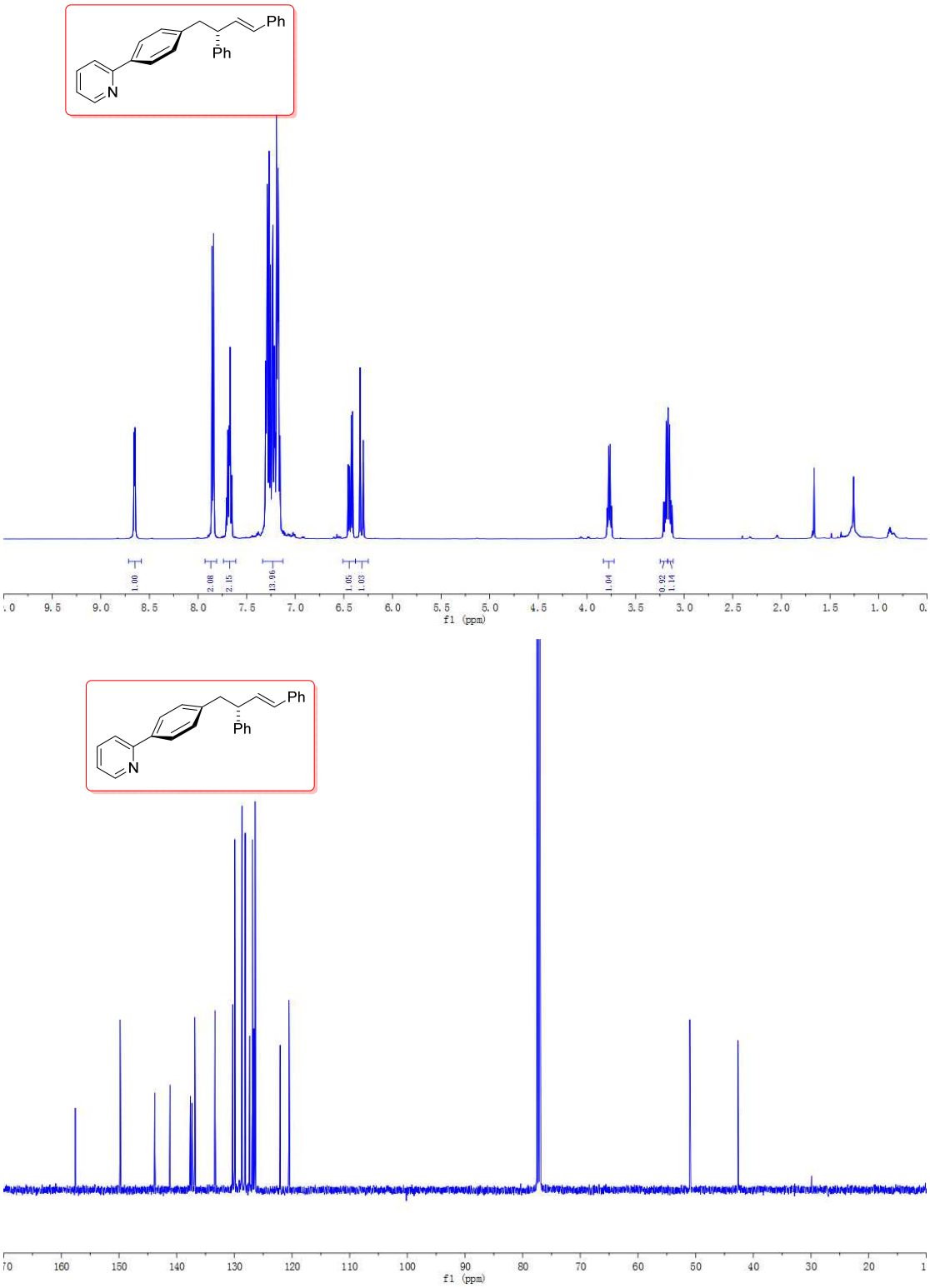


Figure S25. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 3y in $CDCl_3$

(+)-2-phenyl-3-(4-(pyridin-2-yl)phenyl)propanoic acid (4)

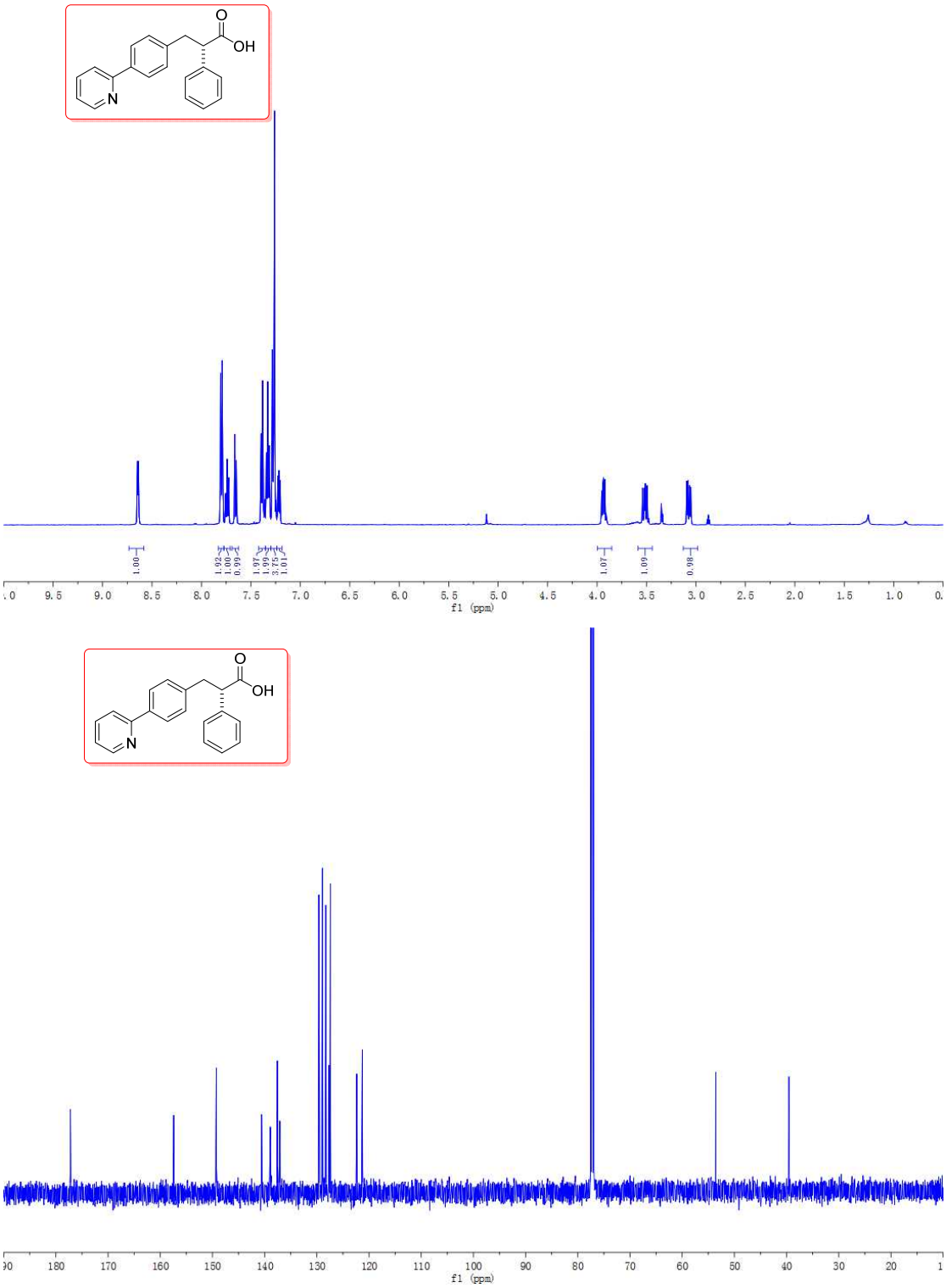
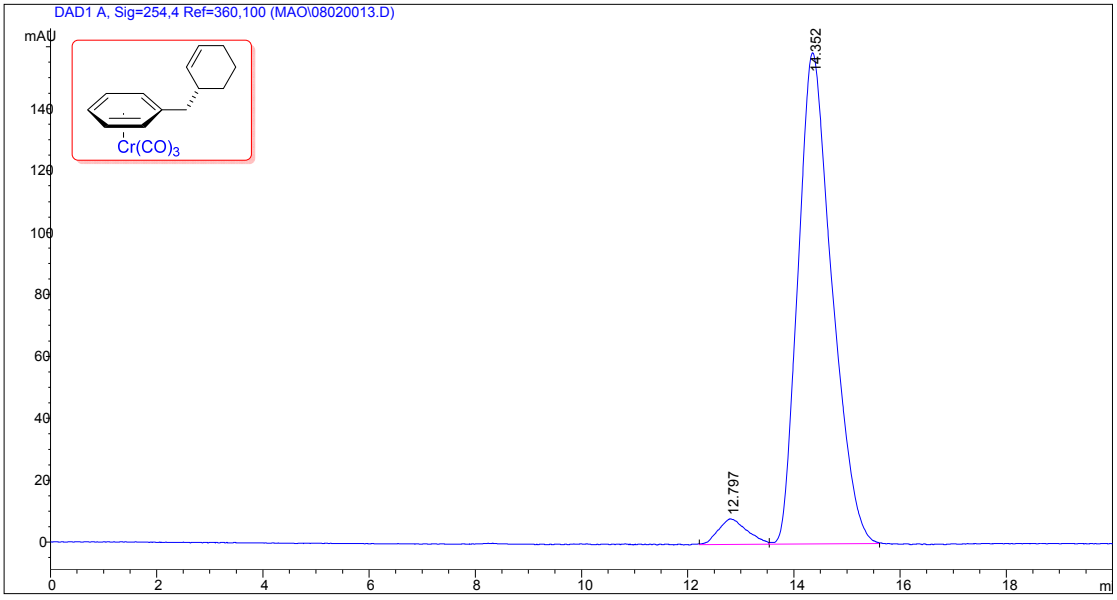


Figure S26. ^{1}H (500 MHz) and ^{13}C {^{1}H} (125 MHz) NMR spectra of 4 in $CDCl_3$

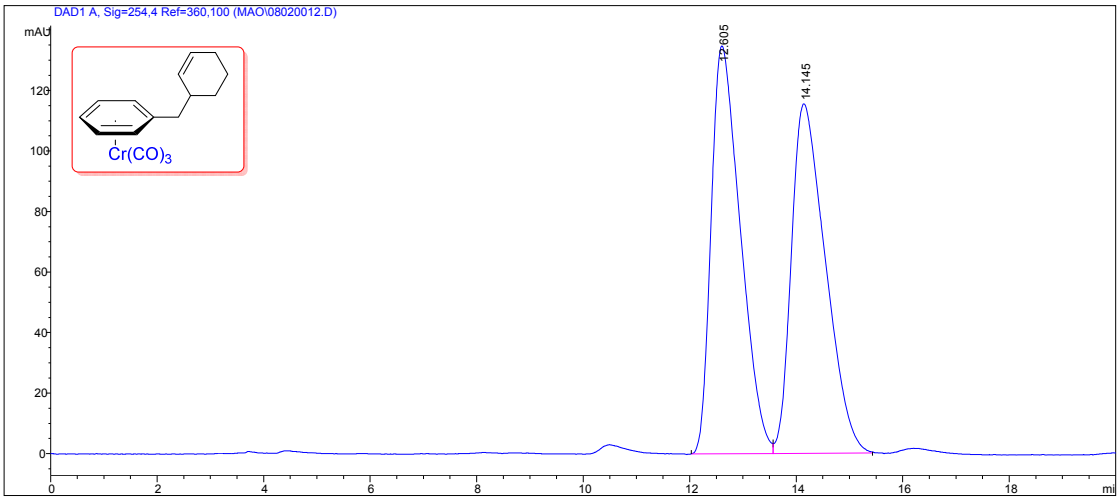
9. HPLC and SFC Chromatography of the Products

Figure S27. HPLC Chromatography of (-)-(η^6-(2-cyclohexen-1-ylmethyl)-benzene)$Cr(CO)_3$ (**3a**) (Daicel Chiralcel OD-H column, 1% isopropanol in hexanes, 1 mL/min, 254 nm)



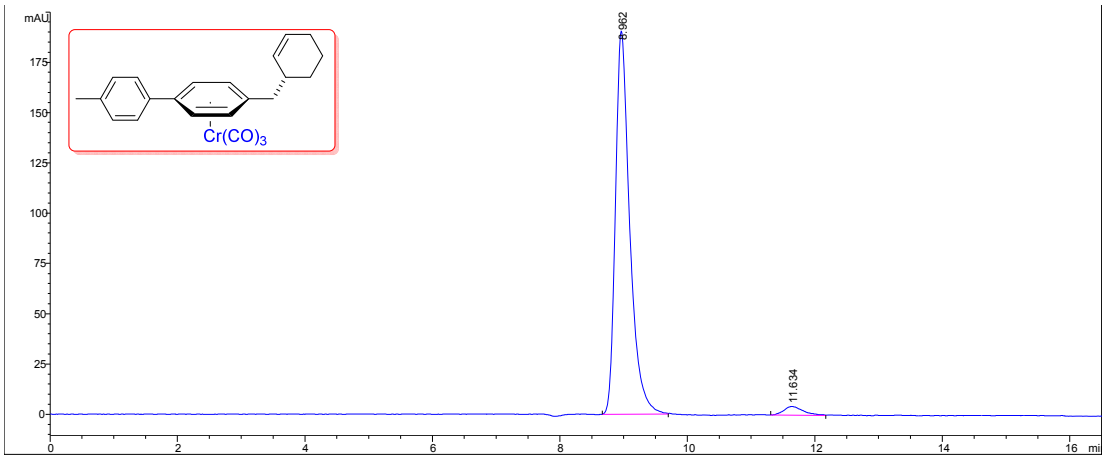
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.797 BV	0.4516	308.34775	8.21995	4.2157
2	14.352 VB	0.6213	7005.96045	158.63341	95.7843
Totals :			7314.30820	166.85336	

Figure S28. HPLC Chromatography of Racemic-(η^6-(2-cyclohexen-1-ylmethyl)-benzene)$Cr(CO)_3$ (**3a**) (Daicel Chiralcel OD-H column, 1% isopropanol in hexanes, 1 mL/min, 254 nm)



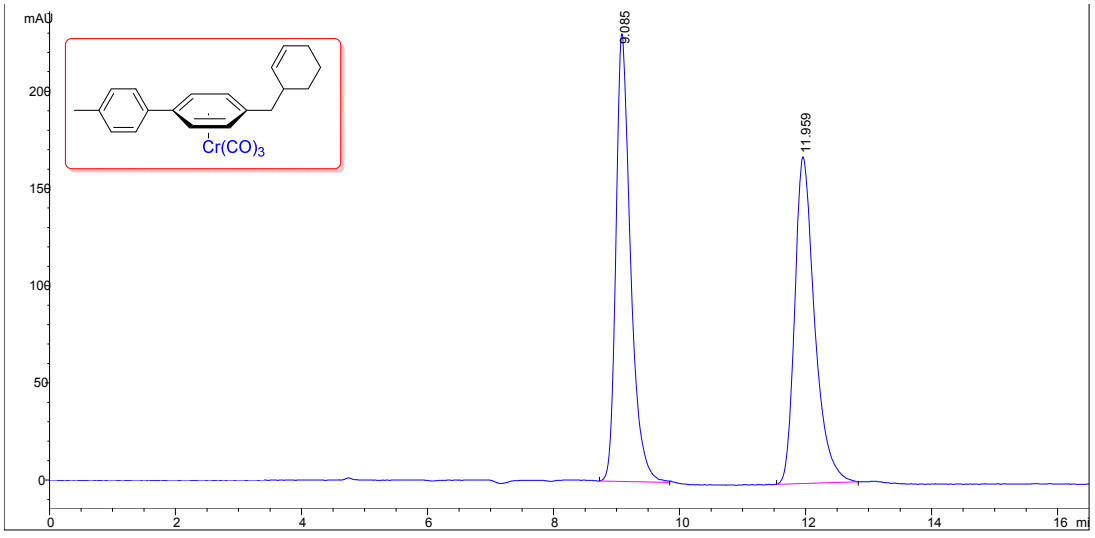
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.605 BV	0.5606	5137.38672	134.79625	50.0301
2	14.145 VB	0.6383	5131.19971	115.49967	49.9699
Totals :			1.02686e4	250.29592	

Figure S29. HPLC Chromatography of (-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(p-tolyl)-benzene)$Cr(CO)_3$ (**3b**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 0.8 mL/min, 254 nm)



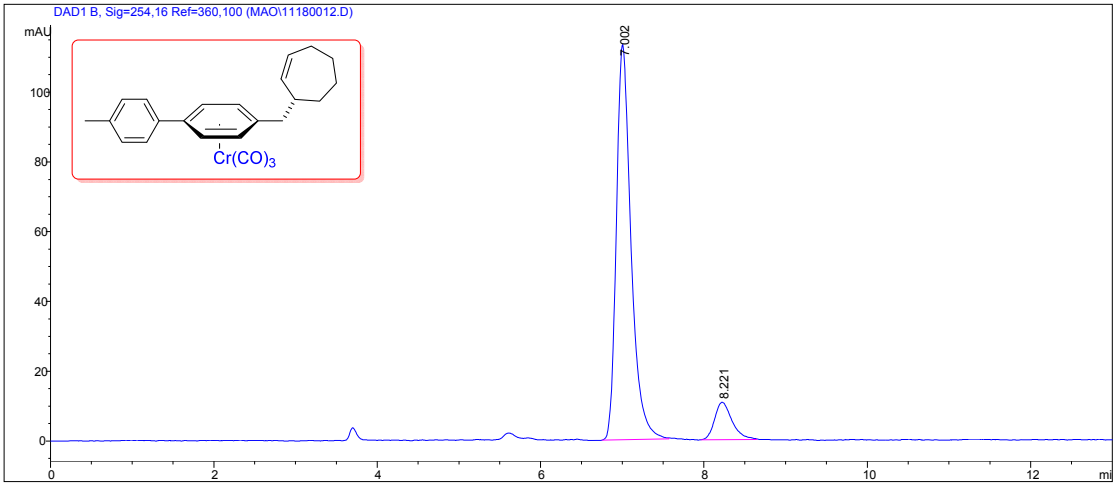
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.962 BB	0.2346	2981.94141	190.54967	97.0998
2	11.634 BB	0.2622	89.06477	4.29066	2.9002
Totals :			3071.00617	194.84033	

Figure S30. HPLC Chromatography of Racemic-(η^6-(2-cyclohexen-1-ylmethyl)-4-(p-tolyl)-benzene)$Cr(CO)_3$ (**3b**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 0.8 mL/min, 254 nm)



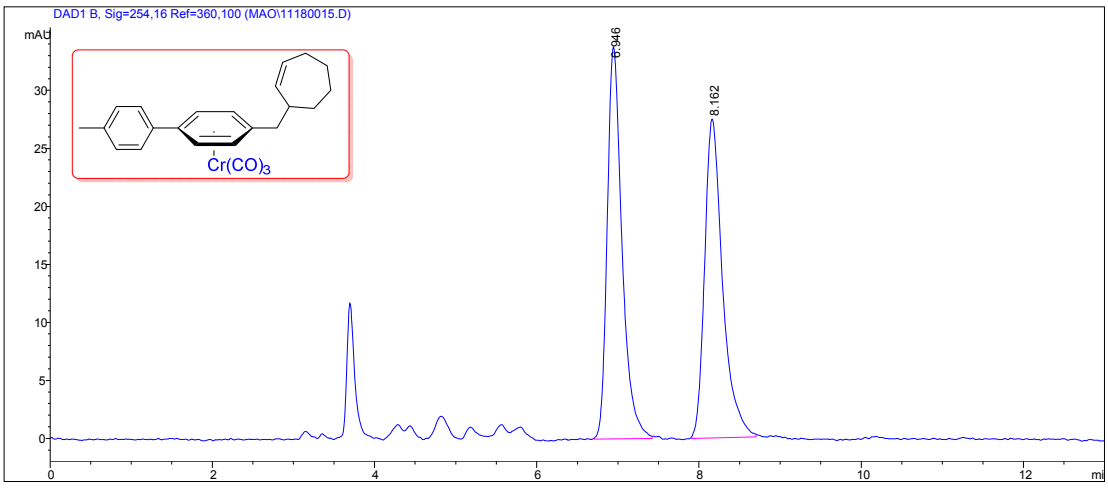
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.085 PB	0.2424	3722.02588	230.45227	50.2085
2	11.959 BB	0.3323	3691.10767	168.04063	49.7915
Totals :			7413.13354	398.49290	

Figure S31. HPLC Chromatography of (-)-(η^6-(2-cycloheptene-1-ylmethyl)-4-(*p*-tolyl)-benzene)$Cr(CO)_3$ (**3c**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



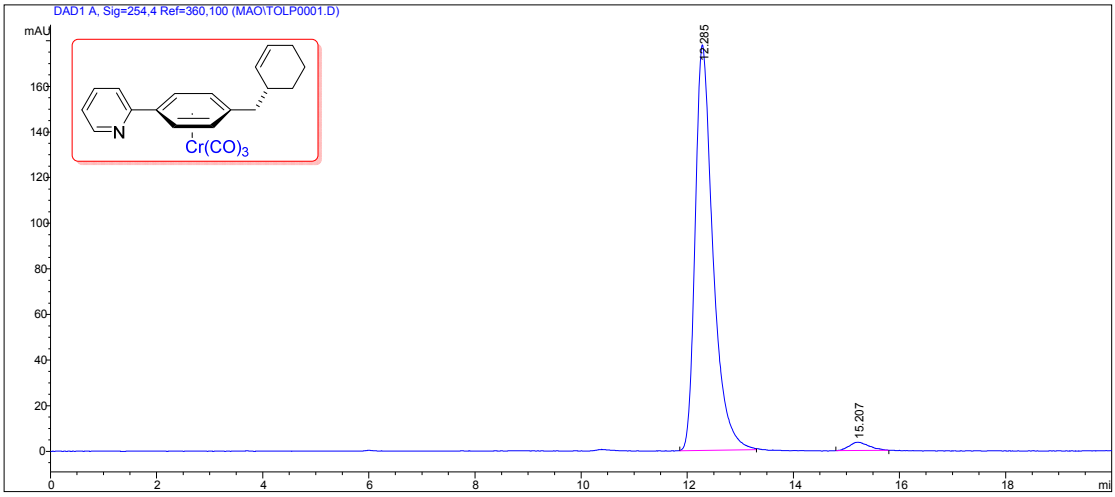
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.002 MM	0.2093	1426.26880	113.57224	90.7723
2	8.221 MM	0.2328	144.99117	10.37832	9.2277
Totals :			1571.25996	123.95055	

Figure S32. HPLC Chromatography of Racemic-(η^6-(2-cycloheptene-1-ylmethyl)-4-(*p*-tolyl)-benzene)$Cr(CO)_3$ (**3c**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



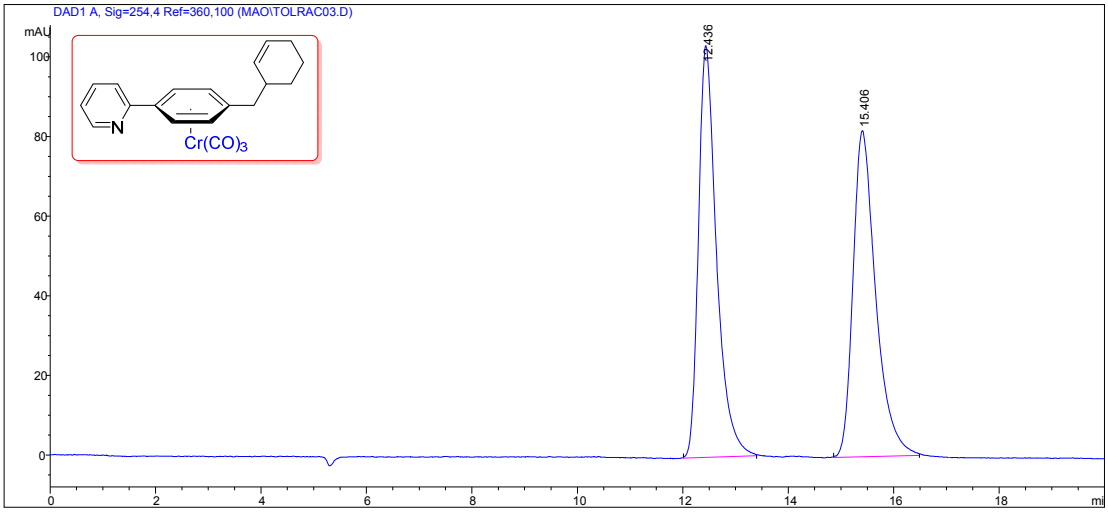
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.946 BB	0.1917	428.11591	33.81565	50.3155
2	8.162 BB	0.2315	422.74731	27.48004	49.6845
Totals :			850.86322	61.29569	

Figure S33. HPLC Chromatography of (-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (**3d**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



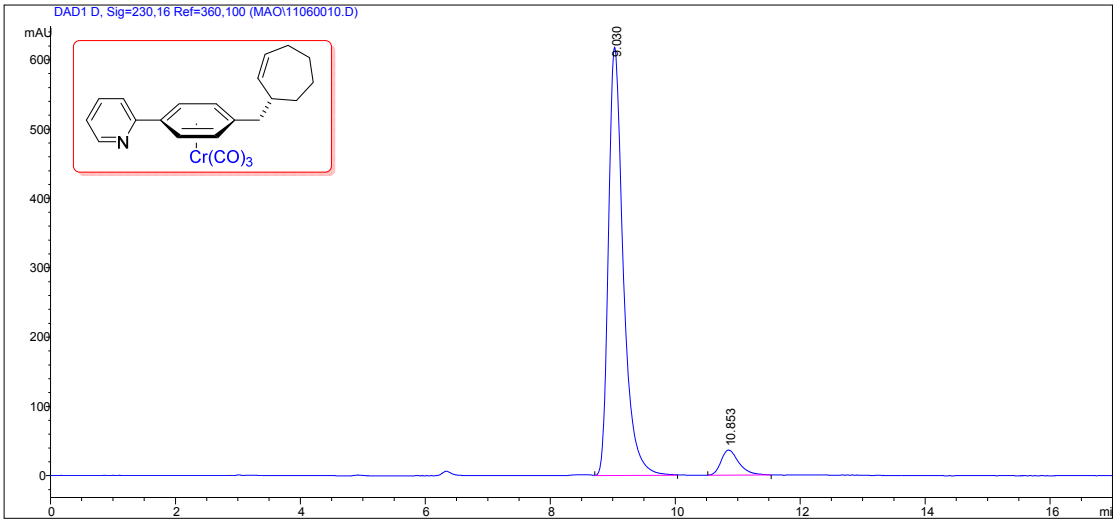
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.285 BB	0.3494	4134.89014	177.75035	97.7503
2	15.207 BB	0.3128	95.16547	3.61910	2.2497
Totals :			4230.05561	181.36945	

Figure S34. HPLC Chromatography of Racemic-(η^6-(2-cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (**3d**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



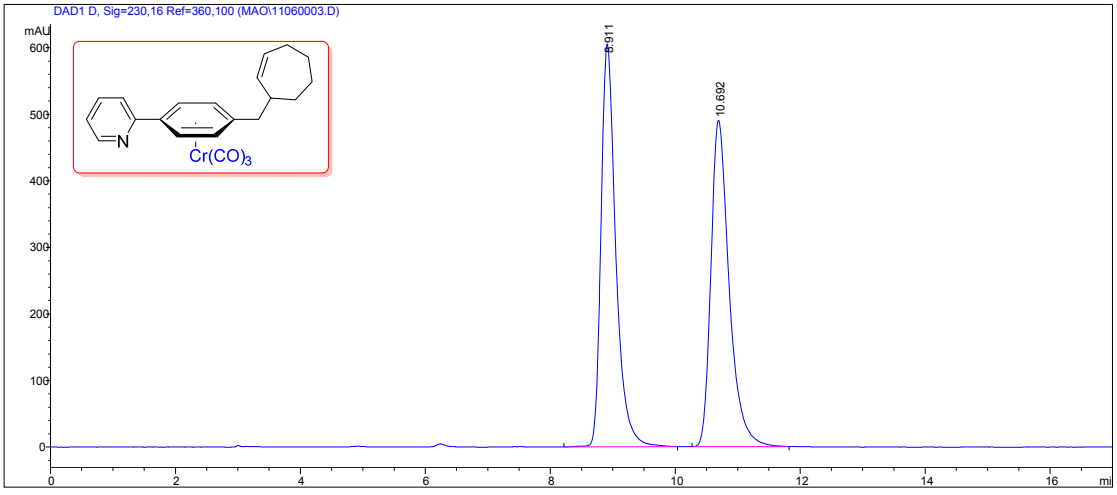
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.436 BB	0.3628	2470.47583	103.36775	50.2543
2	15.406 BB	0.4446	2445.47583	81.83861	49.7457
Totals :			4915.95166	185.20636	

Figure S35. HPLC Chromatography of (-)-(η^6-(2-cycloheptene-1-ylmethyl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (**3e**) (Daicel Chiralpak AD-H column, 10% isopropanol in hexanes, 1 mL/min, 230 nm)



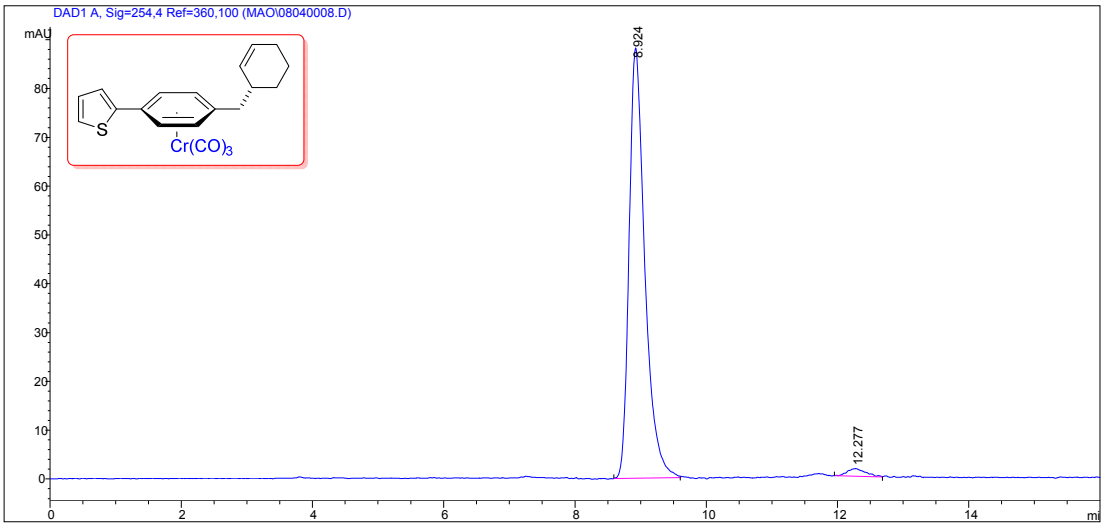
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.030 VB	0.2503	1.01821e4	617.63788	93.3338
2	10.853 BB	0.3025	727.23602	36.18559	6.6662
Totals :			1.09094e4	653.82347	

Figure S36. HPLC Chromatography of Racemic (η^6-(2-cycloheptene-1-ylmethyl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (**3e**) (Daicel Chiralpak AD-H column, 10% isopropanol in hexanes, 1 mL/min, 230 nm)



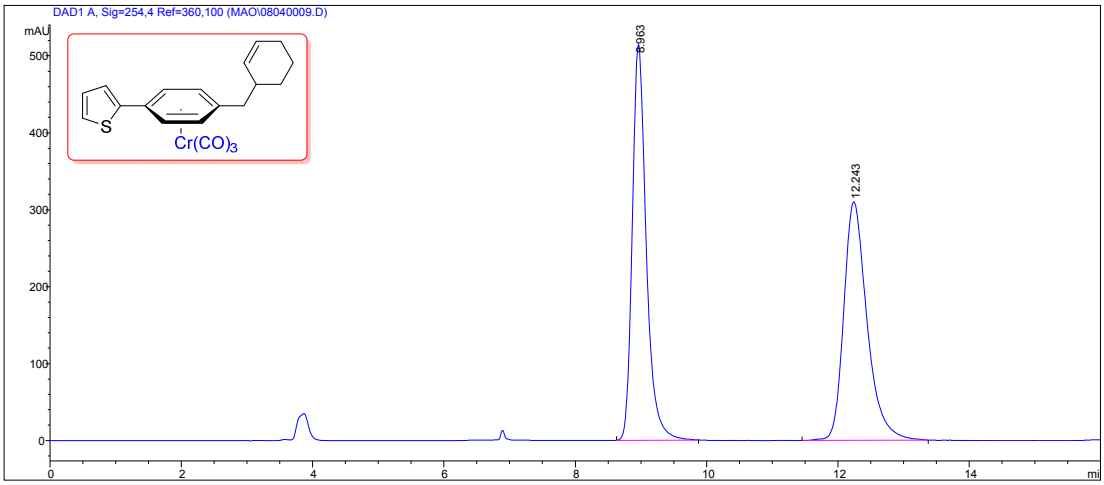
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.911 PB	0.2503	9975.95996	605.27020	50.0167
2	10.692 BB	0.3071	9969.29004	490.60995	49.9833
Totals :			1.99453e4	1095.88016	

Figure S37. HPLC Chromatography of (-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(2-thiophenyl)-benzene)$Cr(CO)_3$ (**3f**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



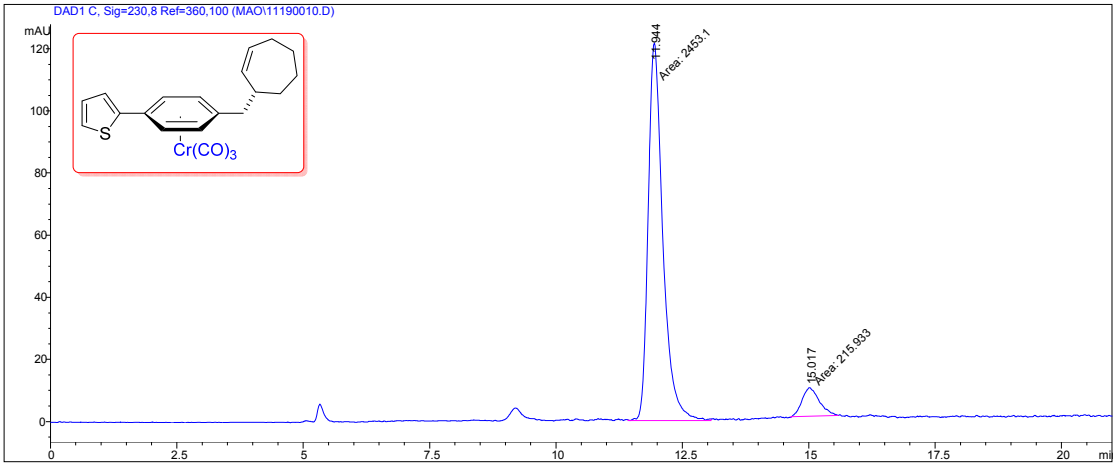
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.924 BB	0.2501	1465.99377	88.10648	97.8950
2	12.277 PV	0.2486	31.52340	1.59488	2.1050
Totals :			1497.51717	89.70136	

Figure S38. HPLC Chromatography of Racemic (η^6-(2-cyclohexen-1-ylmethyl)-4-(2-thiophenyl)-benzene)$Cr(CO)_3$ (**3f**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



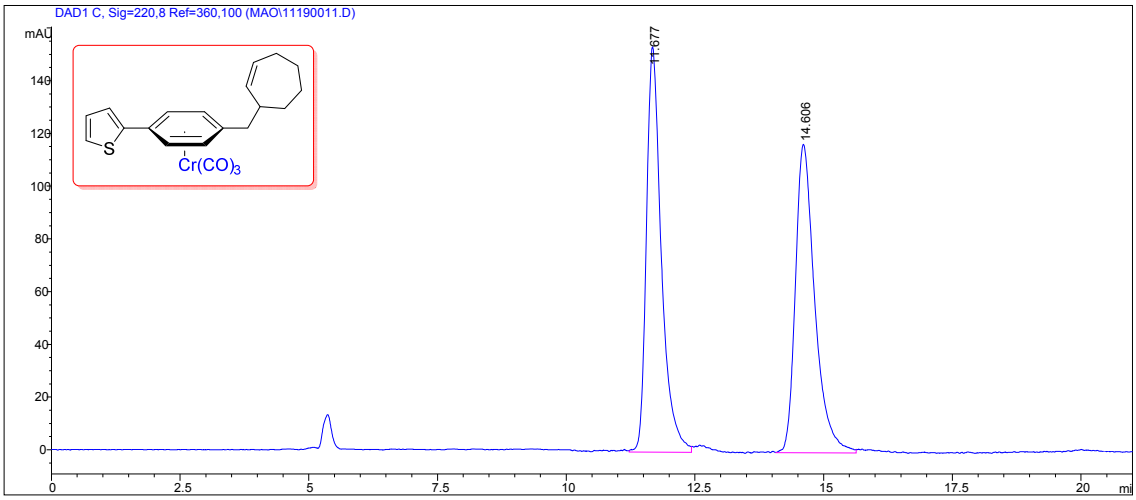
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.963 BB	0.2268	7618.07715	514.41003	49.9194
2	12.243 BB	0.3716	7642.67090	309.97571	50.0806
Totals :			1.52607e4	824.38574	

Figure S39. HPLC Chromatography of (-)-(η^6-(2-cycloheptene-1-ylmethyl)-4-(2-thiophenyl)-benzene)$Cr(CO)_3$ (**3g**) (Daicel Chiralpak AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



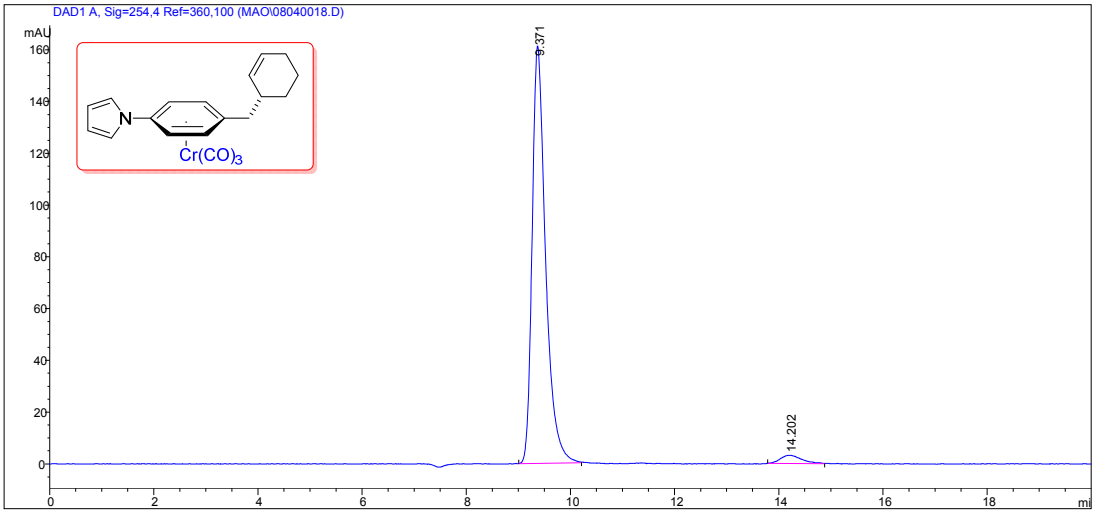
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.944 MM	0.3363	2451.35645	121.48005	91.4745
2	15.017 MM	0.4030	228.46703	9.44778	8.5255
Totals :			1571.25996	123.95055	

Figure S40. HPLC Chromatography of Racemic (η^6-(2-cycloheptene-1-ylmethyl)-4-(2-thiophenyl)-benzene)$Cr(CO)_3$ (**3g**) (Daicel Chiralpak AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



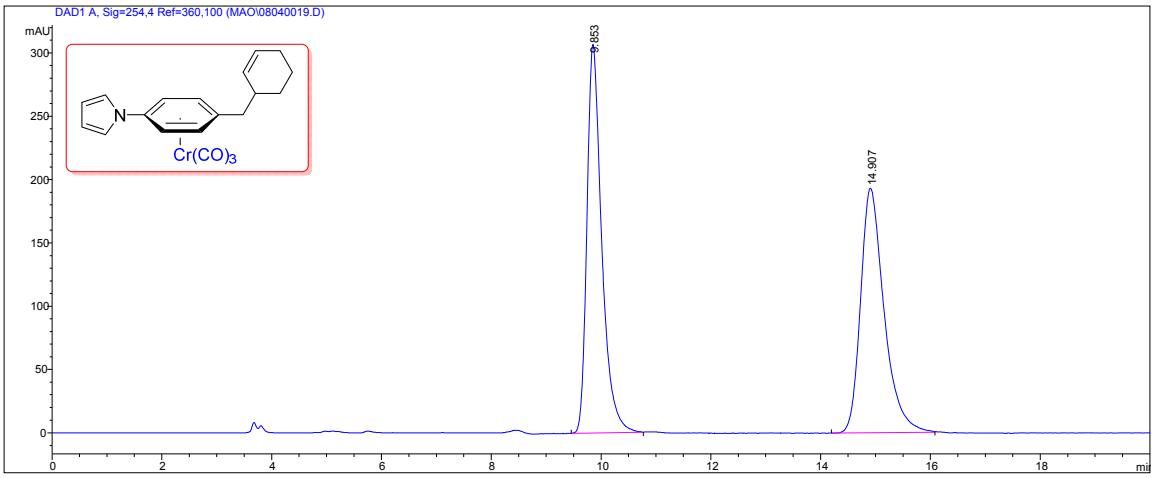
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.677 BB	0.3039	3110.29224	153.79663	50.3645
2	14.606 VB	0.3855	3065.26880	117.04102	49.6355
Totals :			6175.56104	270.83765	

Figure S41. HPLC Chromatography of (-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)$Cr(CO)_3$ (**3h**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



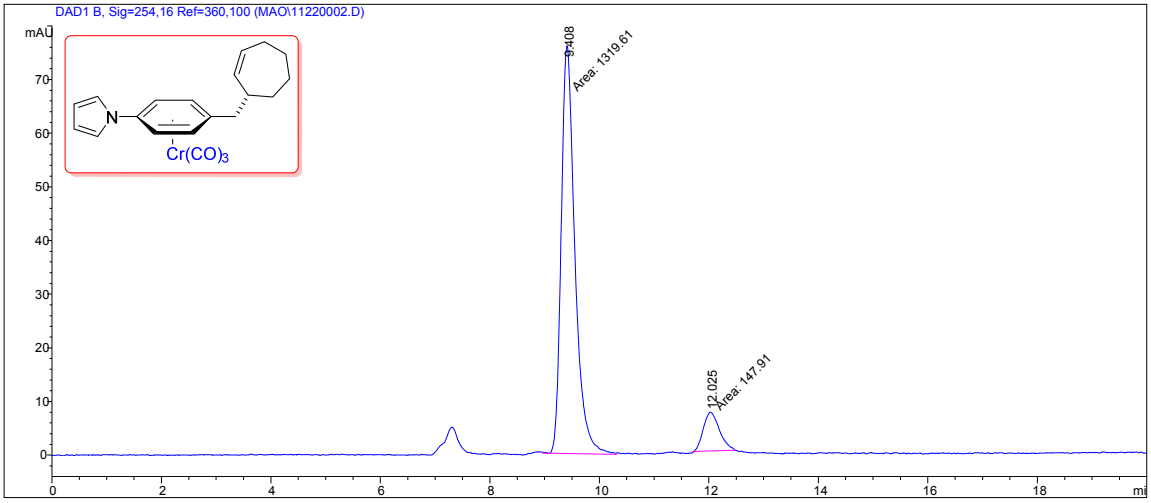
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.371 BB	0.2718	2900.85962	161.28438	96.9723
2	14.202 BB	0.3399	90.57287	3.18405	3.0277
Totals :			2991.43249	164.46843	

Figure S42. HPLC Chromatography of Racemic (η^6-(2-cyclohexen-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)$Cr(CO)_3$ (**3h**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



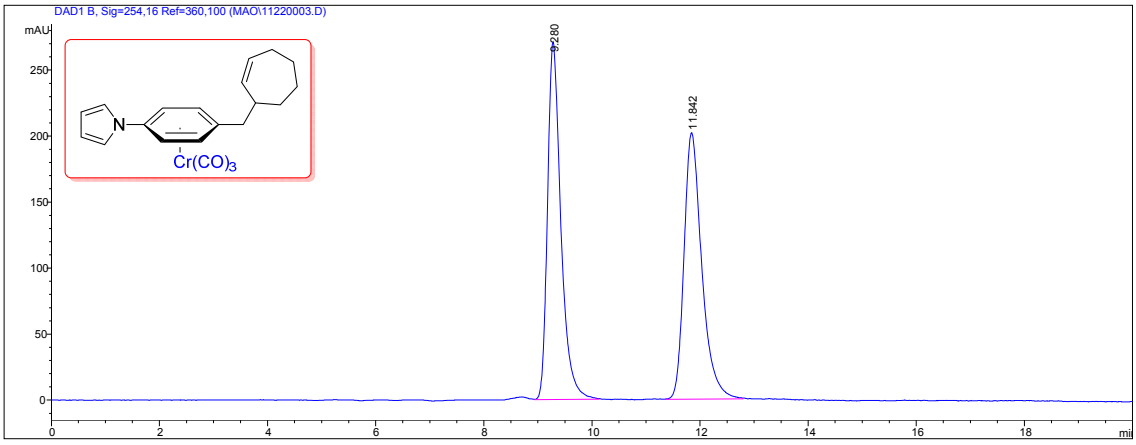
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.853 PB	0.2782	5743.46289	307.05627	50.0461
2	14.907 PB	0.4483	5732.87549	193.14444	49.9539
Totals :			1.14763e4	500.20071	

Figure S43. HPLC Chromatography of (-)-(η^6-(2-cycloheptene-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)$Cr(CO)_3$ (**3i**) (Daicel Chiralpak AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



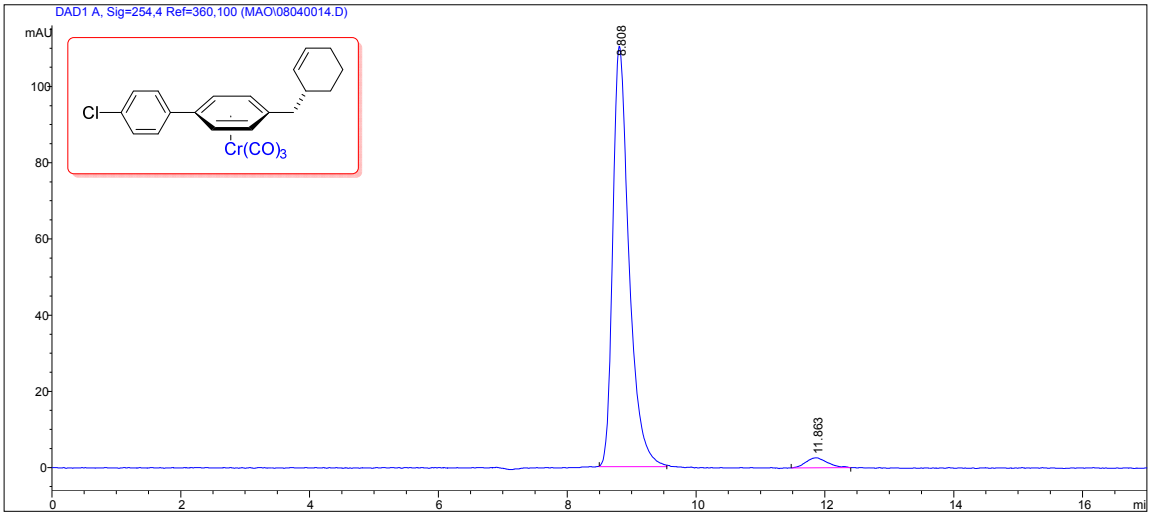
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.408 MM	0.2895	1319.61414	75.96938	89.9211
2	12.025 MM	0.3417	147.90999	7.21384	10.0789
Totals :			1467.52412	83.18322	

Figure S44. HPLC Chromatography of Racemic (η^6-(2-cycloheptene-1-ylmethyl)-4-(*N*-pyrrolyl)-benzene)$Cr(CO)_3$ (**3i**) (Daicel Chiralpak AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



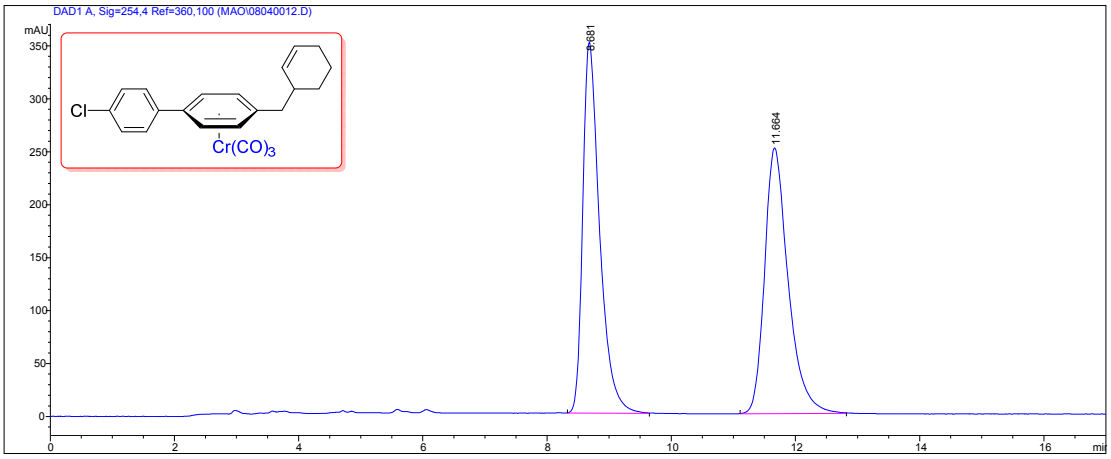
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.280 VB	0.2581	4647.25879	270.92712	50.2281
2	11.842 BB	0.3421	4605.05029	201.90938	49.7719
Totals :			9252.30908	472.83650	

Figure S45. HPLC Chromatography of (-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-chlorophenyl)-benzene)$Cr(CO)_3$ (**3j**) (Daicel Chiralpak AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



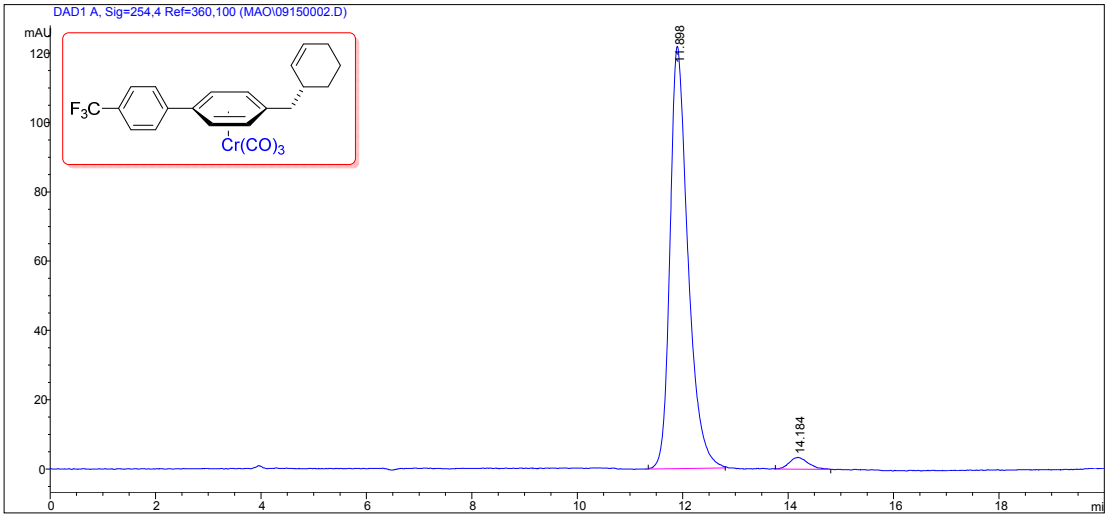
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.808 BB	0.2661	1930.96094	110.35913	96.8269
2	11.863 PB	0.2964	63.27964	2.69062	3.1731
Totals :			1994.24058	113.04975	

Figure S46. HPLC Chromatography of Racemic (η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-chlorophenyl)-benzene)$Cr(CO)_3$ (**3j**) (Daicel Chiralpak AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



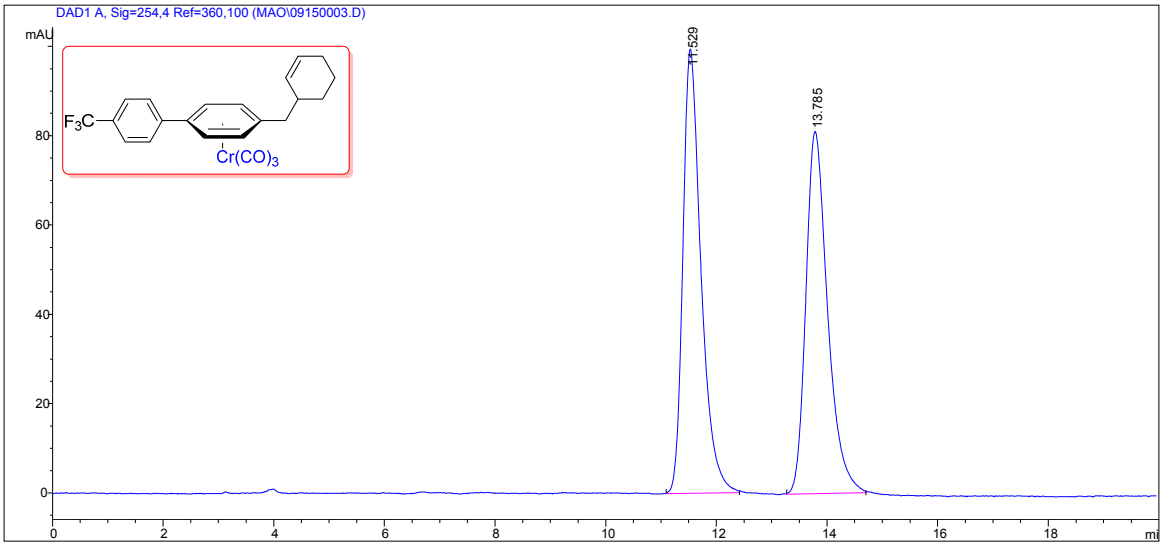
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.681 BB	0.2844	6610.35059	349.97873	49.9269
2	11.664 BB	0.3984	6629.70947	250.78882	50.0731
Totals :			1.32401e4	600.76755	

Figure S47. HPLC Chromatography of (-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-trifloromethylphenyl)-benzene)$Cr(CO)_3$ (**3k**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



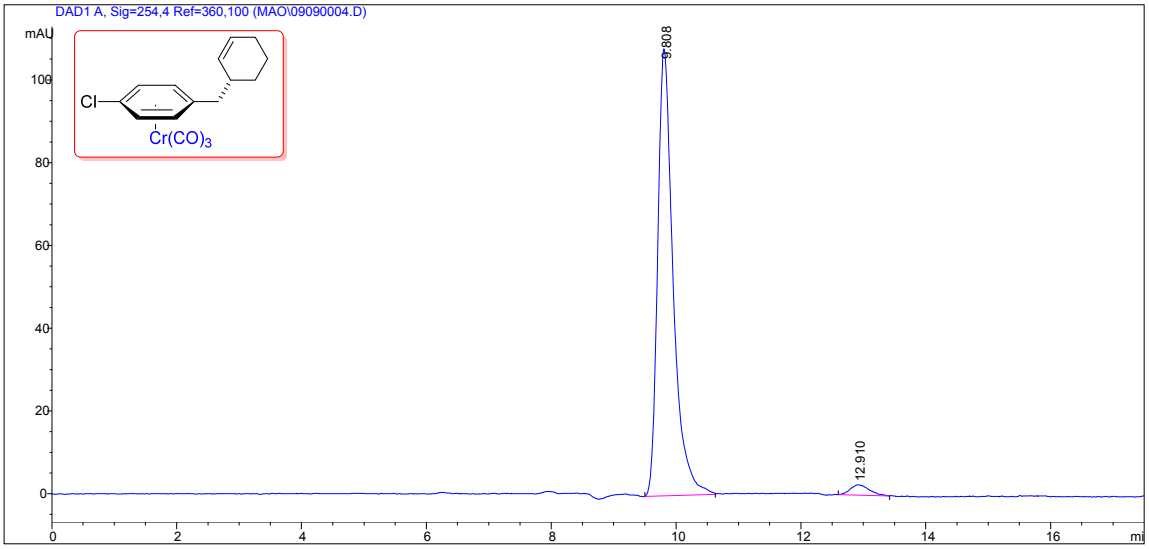
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.898 BB	0.3549	2893.36670	121.88882	97.1506
2	14.184 PB	0.3032	84.86157	3.39969	2.8494
Totals :			2978.22827	125.28851	

Figure S48. HPLC Chromatography of Racemic (η^6-(2-cyclohexen-1-ylmethyl)-4-(*p*-trifloromethylphenyl)-benzene)$Cr(CO)_3$ (**3k**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 1 mL/min, 254 nm)



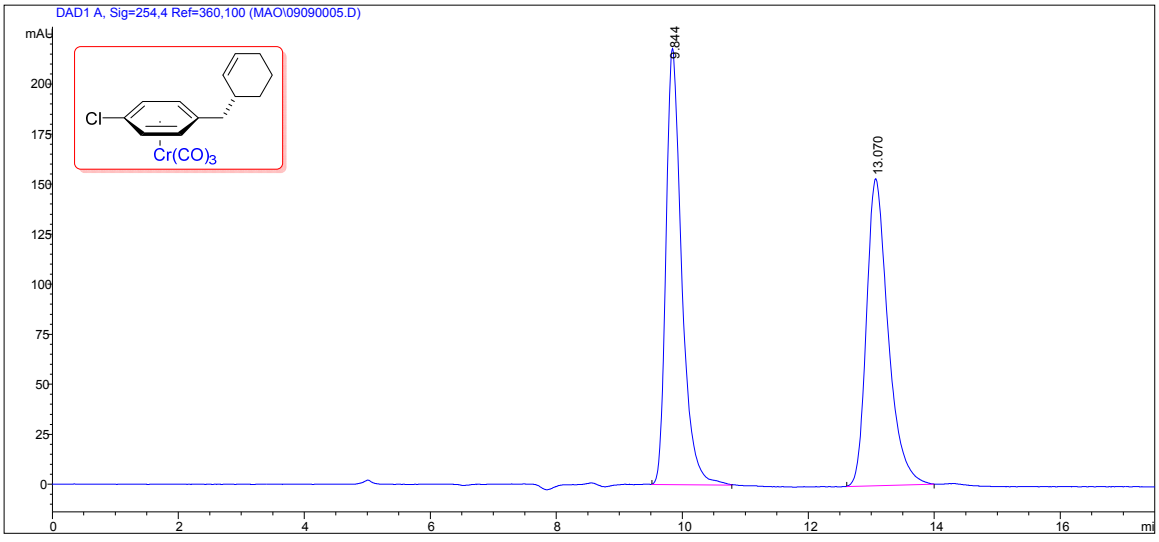
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.529 BB	0.3380	2267.95459	99.46400	50.6349
2	13.785 BB	0.4121	2211.07593	81.10450	49.3651
Totals :			4479.03052	180.56850	

Figure S49. HPLC Chromatography of (-)-(η^6-(2-cyclohexen-1-ylmethyl)-4-chloro-benzene)$Cr(CO)_3$ (**3l**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 0.8 mL/min, 254 nm)



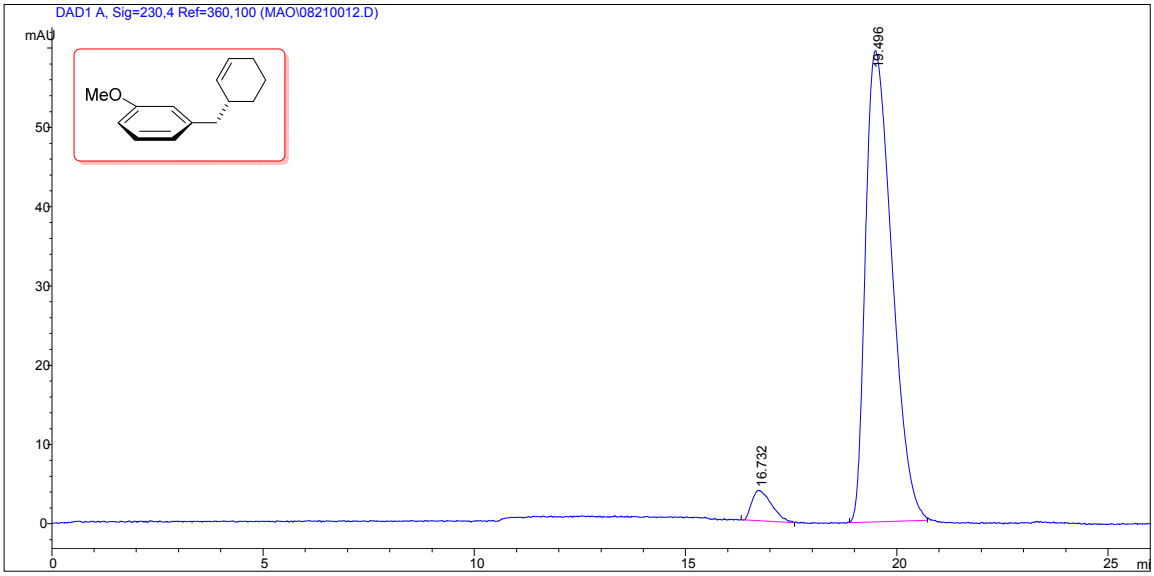
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.808 PB	0.2569	1857.87256	107.89856	97.1465
2	12.910 BB	0.2732	54.57198	2.53466	2.8535
Totals :			1912.44454	110.43322	

Figure S50. HPLC Chromatography of Racemic (η^6-(2-cyclohexen-1-ylmethyl)-4-chloro-benzene)$Cr(CO)_3$ (**3l**) (Daicel Chiralpak AD-H column, 5% isopropanol in hexanes, 0.8 mL/min, 254 nm)



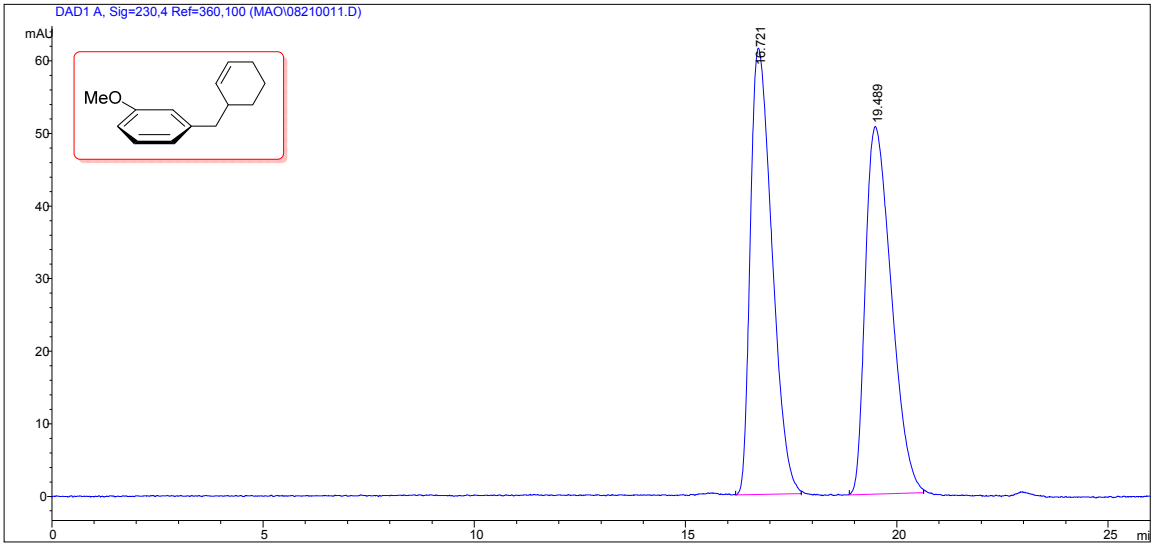
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.844 BB	0.2609	3788.56763	217.88593	50.8900
2	13.070 BB	0.3598	3656.06006	153.51476	49.1100
Totals :			7444.62769	371.40068	

Figure S51. HPLC Chromatography of (-)-(2-cyclohexen-1-ylmethyl)-3-methoxybenzene **(3n)** (Daicel Chiralcel OJ-H column, 1% isopropanol in hexanes, 0.5 mL/min, 230 nm)



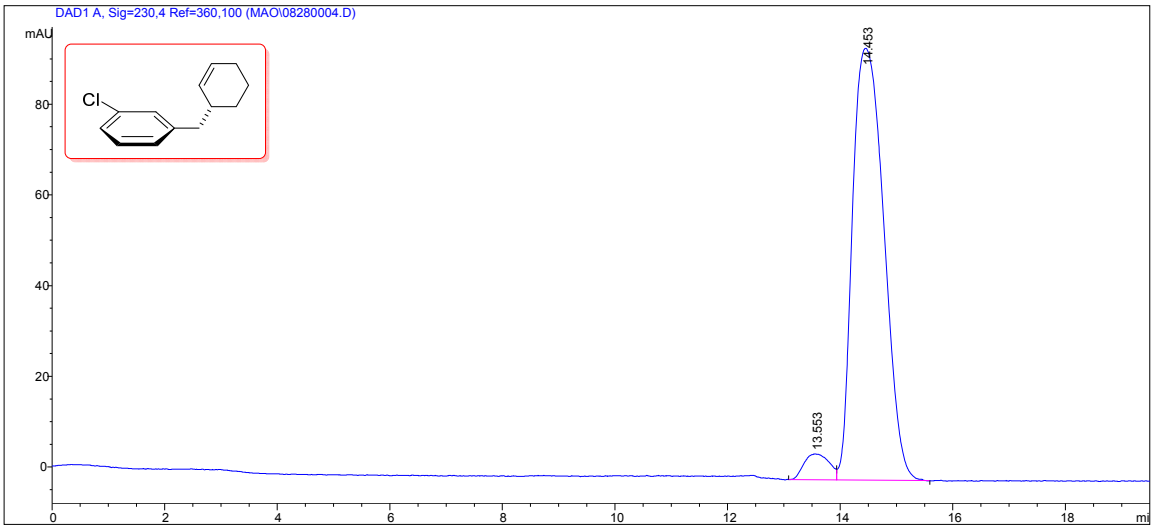
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.732 BB	0.3920	123.76182	3.81944	4.5753
2	19.496 BB	0.6349	2581.21509	59.40750	95.4247
Totals :			2704.97691	63.22694	

Figure S52. HPLC Chromatography of Racemic (2-cyclohexen-1-ylmethyl)-3-methoxybenzene **(3n)** (Daicel Chiralcel OJ-H column, 1% isopropanol in hexanes, 0.5 mL/min, 230 nm)



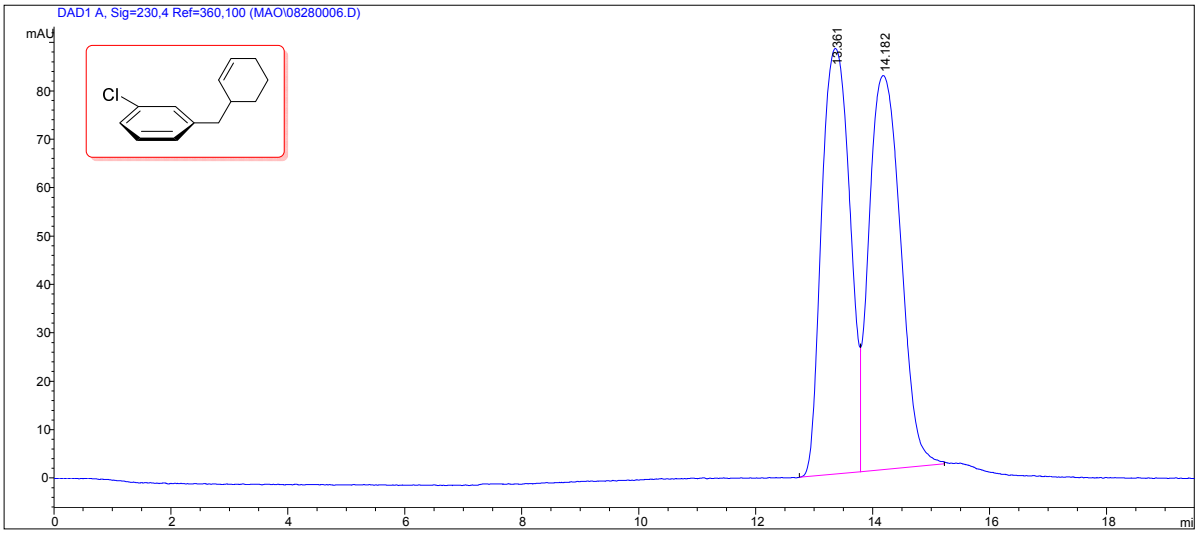
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.721 PB	0.5275	2188.95581	61.46886	50.2959
2	19.489 BB	0.6343	2163.19702	50.64337	49.7041
Totals :			4352.15283	112.11223	

Figure S53. HPLC Chromatography of (-)-(2-cyclohexen-1-ylmethyl)-3-chlorobenzene **(3m)** (Daicel Chiralcel OJ-H column, 0.5% isopropanol in hexanes, 0.4 mL/min, 230 nm)



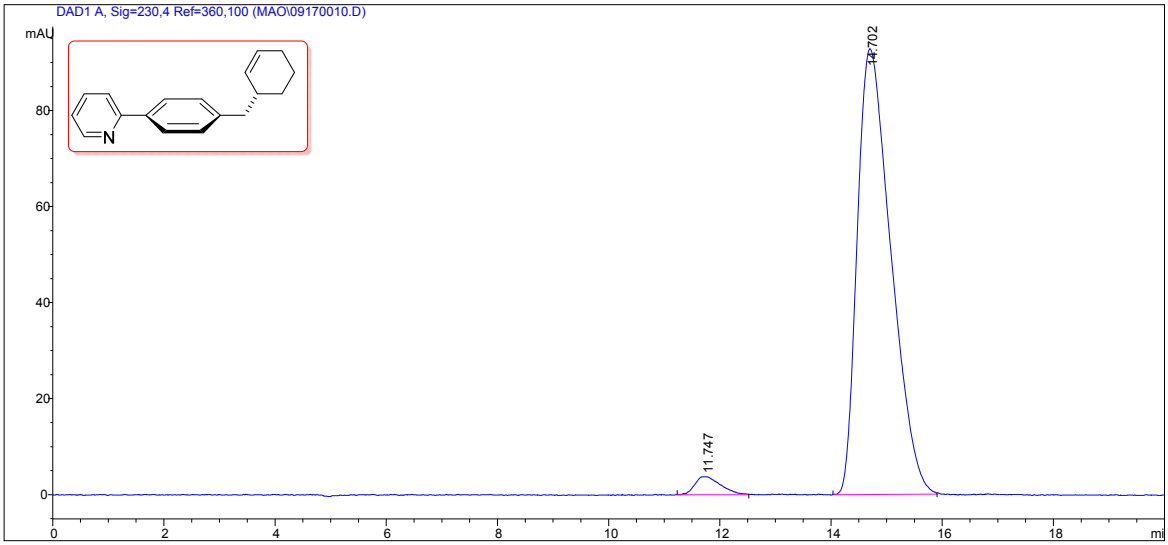
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.553 PV	0.3762	179.12894	5.73759	4.6344
2	14.453 VP	0.6217	3686.04956	95.19756	95.3656
Totals :			3865.17850	100.93515	

Figure S54. HPLC Chromatography of Racemic (2-cyclohexen-1-ylmethyl)-3-chlorobenzene **(3m)** (Daicel Chiralcel OJ-H column, 0.5% isopropanol in hexanes, 0.4 mL/min, 230 nm)



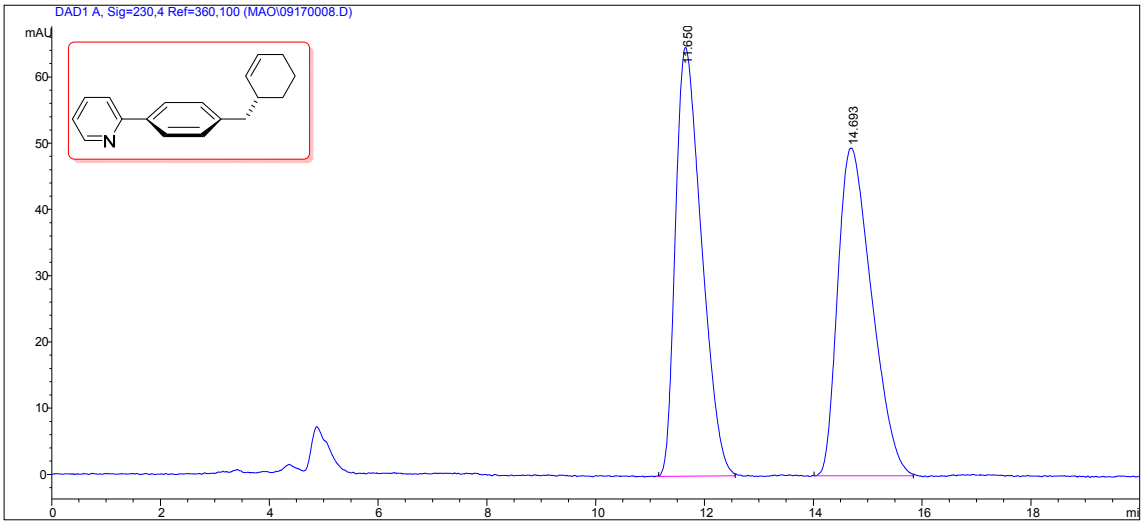
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.361 PV	0.5401	2955.41602	87.94601	49.0507
2	14.182 VB	0.5959	3069.81128	81.42049	50.9493
Totals :			6025.22729	169.36650	

Figure S55. HPLC Chromatography of (-)-(2-cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene **(3o)** (Daicel Chiralcel OD-H column, 5% isopropanol in hexanes, 1 mL/min, 230 nm)



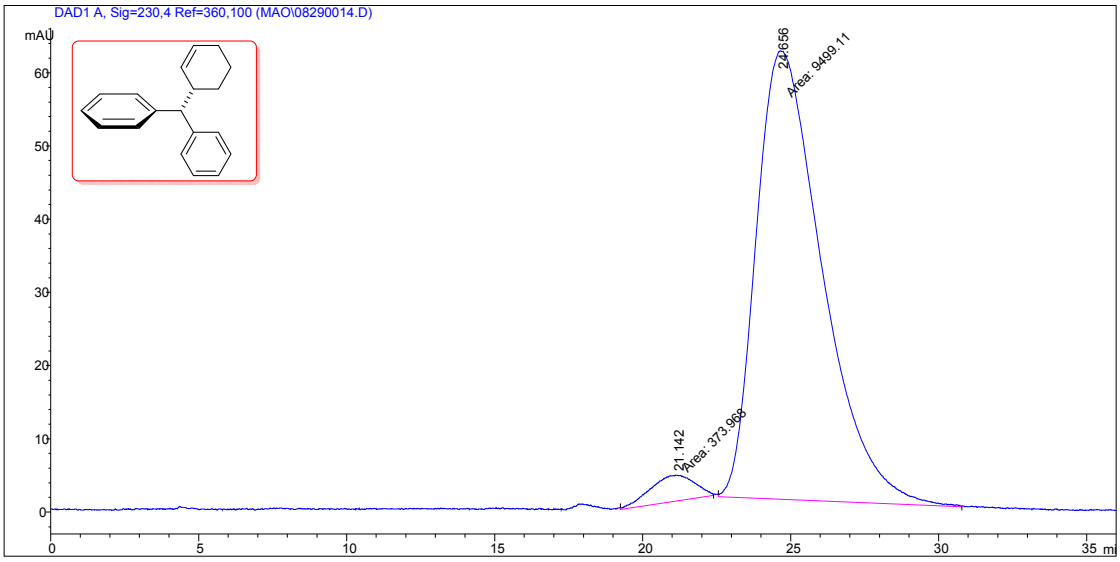
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.747 BB	0.3842	122.22953	3.77035	3.0405
2	14.702 BB	0.6178	3897.75439	92.83849	96.9595
Totals :			4019.98392	96.60884	

Figure S56. HPLC Chromatography of Racemic (2-cyclohexen-1-ylmethyl)-4-(2-pyridyl)-benzene **(3o)** (Daicel Chiralcel OD-H column, 5% isopropanol in hexanes, 1 mL/min, 230 nm)



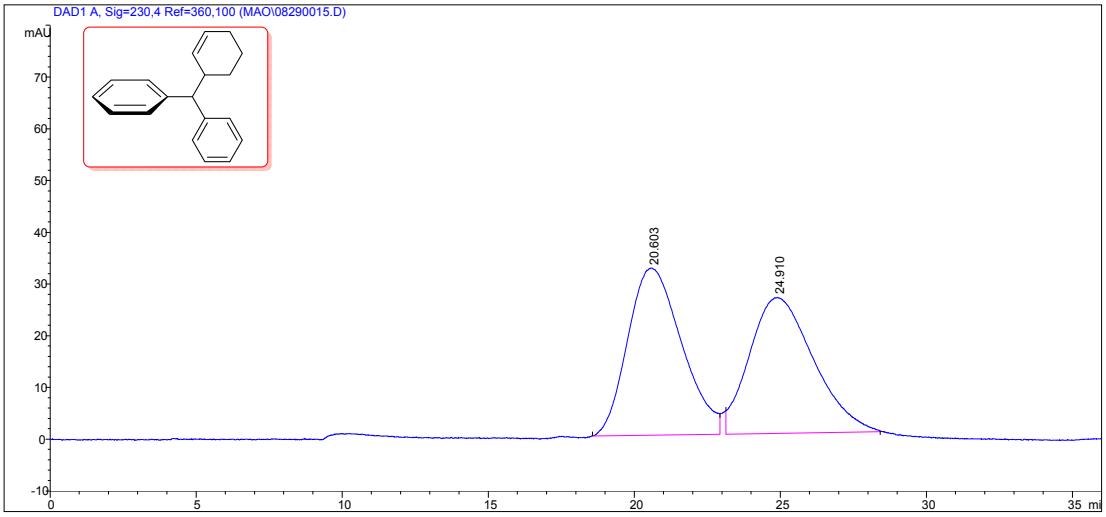
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.650 BB	0.4899	2150.46533	64.68620	50.1051
2	14.693 BB	0.6110	2141.44702	49.47689	49.8949
Totals :			4291.91235	114.16308	

Figure S57. HPLC Chromatography of (-)-3-(diphenylmethyl)-1-cyclohexene (**3p**) (Daicel Chiralcel OJ-H column, 3% isopropanol in hexanes, 0.8 mL/min, 230 nm)



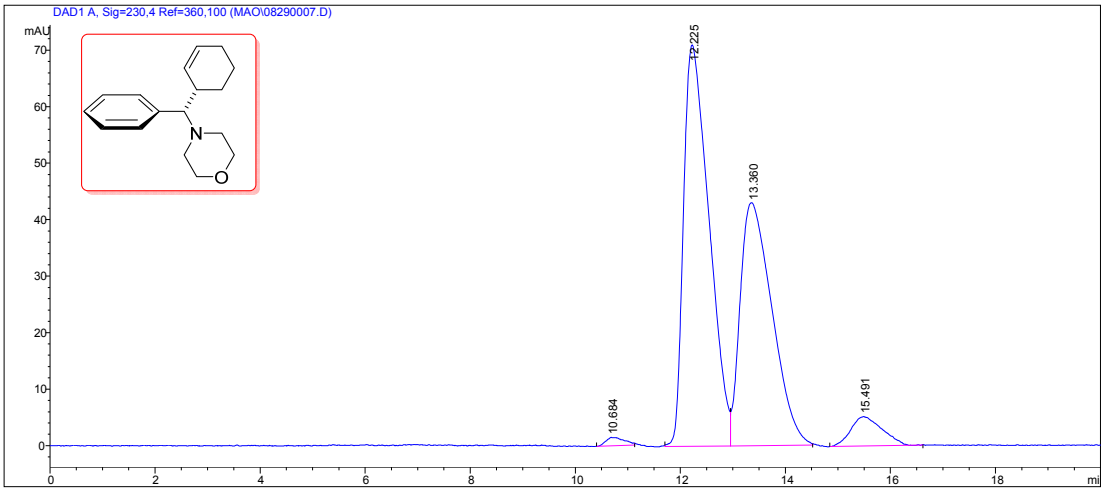
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.142 MM	1.7571	373.96790	3.54730	3.7878
2	24.656 MM	2.5846	9499.11230	61.25507	96.2122
Totals :			9873.08020	64.80237	

Figure S58. HPLC Chromatography of Reacmic 3-(diphenylmethyl)-1-cyclohexene (**3p**) (Daicel Chiralcel OJ-H column, 3% isopropanol in hexanes, 0.8 mL/min, 230 nm)



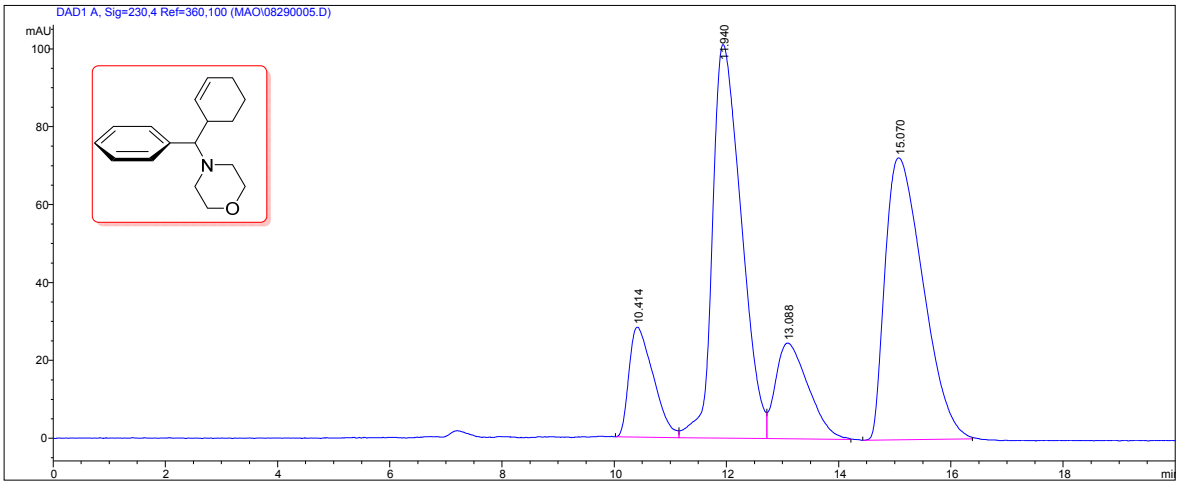
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.603 BV	1.5083	4142.06152	32.29613	50.9203
2	24.910 BB	1.7871	3992.33179	26.23972	49.0797
Totals :			8134.39331	58.53584	

Figure S59. HPLC Chromatography of 4-(cyclohex-2-en-1-yl(phenyl)methyl)morpholine (**3q**) (Daicel Chiralcel OD-H column, 2% isopropanol in hexanes, 0.6 mL/min, 230 nm)



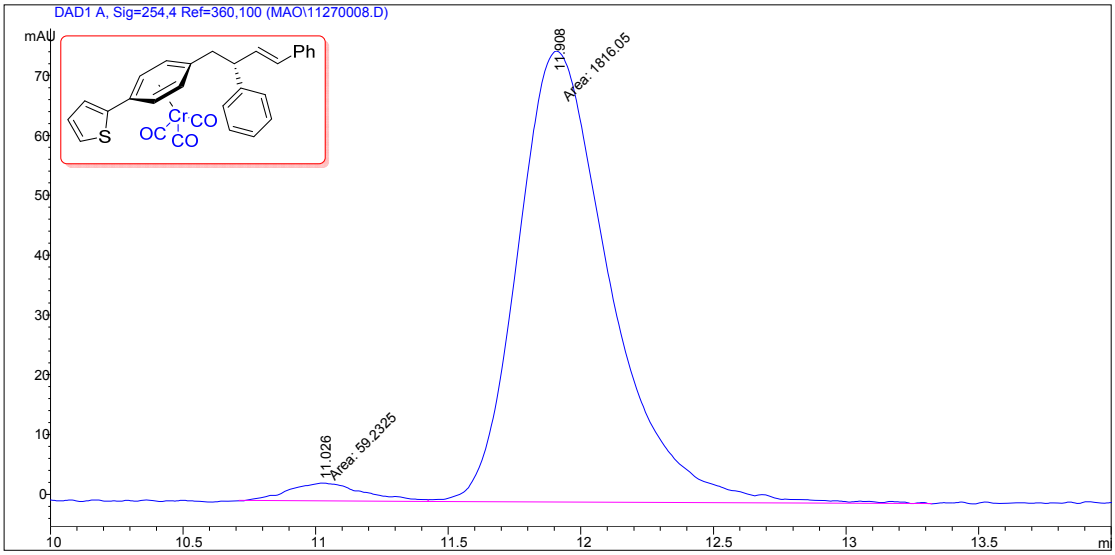
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.684 BB	0.2957	35.77865	1.47155	0.8021
2	12.225 BV	0.4847	2391.06177	71.03177	53.6054
3	13.360 VB	0.5868	1816.64355	43.00996	40.7275
4	15.491 PB	0.4949	216.99867	5.22151	4.8649
Totals :			4460.48265	120.73479	

Figure S60. HPLC Chromatography of Racemic 4-(cyclohex-2-en-1-yl(phenyl)methyl)morpholine (**3q**) (Daicel Chiralcel OD-H column, 2% isopropanol in hexanes, 0.6 mL/min, 230 nm)



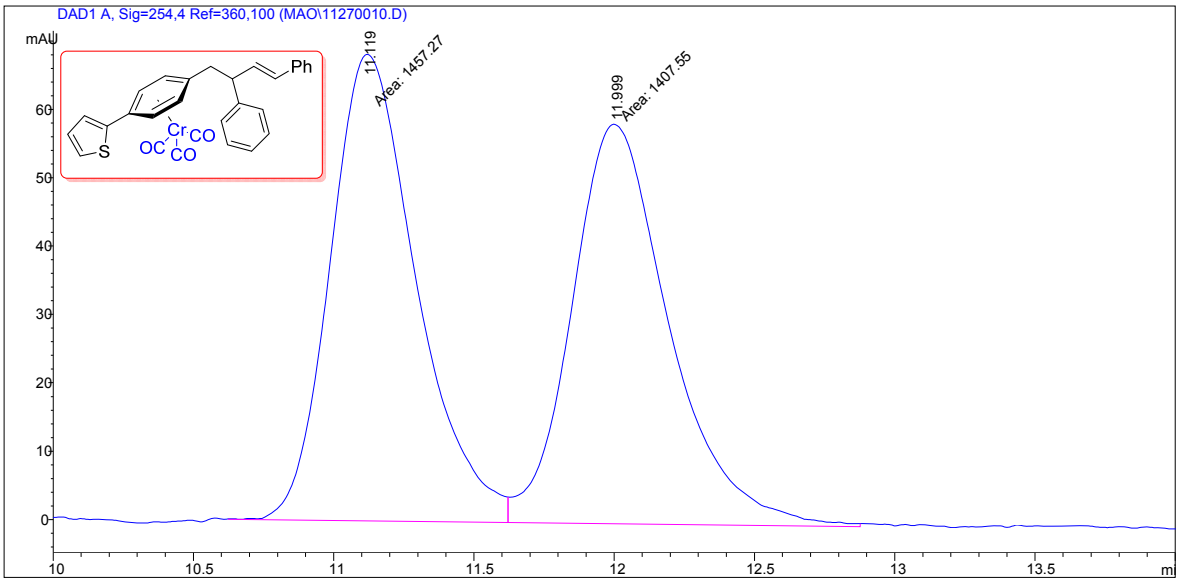
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.414 PV	0.4317	851.62494	28.25228	9.6247
2	11.940 VV	0.5279	3601.92896	101.03686	40.7074
3	13.088 VB	0.5497	997.35944	24.56438	11.2717
4	15.070 PB	0.6918	3397.42139	72.35164	38.3962
Totals :			8848.33472	226.20515	

Figure S61. HPLC Chromatography of (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(2-thiophenyl)-benzene)$Cr(CO)_3$ (**3s**) (Daicel Chiralcel AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



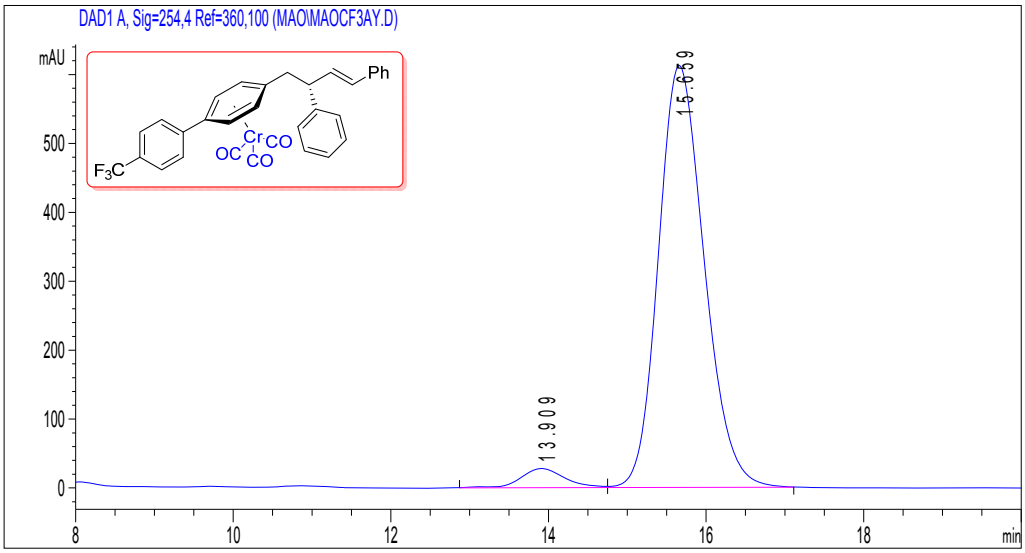
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.026 MF	0.3280	59.23249	3.00956	3.1586
2	11.908 FM	0.4014	1816.04700	75.39764	96.8414
Totals :			1875.27949	78.40720	

Figure S62. HPLC Chromatography of Racemic (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(2-thiophenyl)-benzene)$Cr(CO)_3$ (**3s**) (Daicel Chiralcel AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



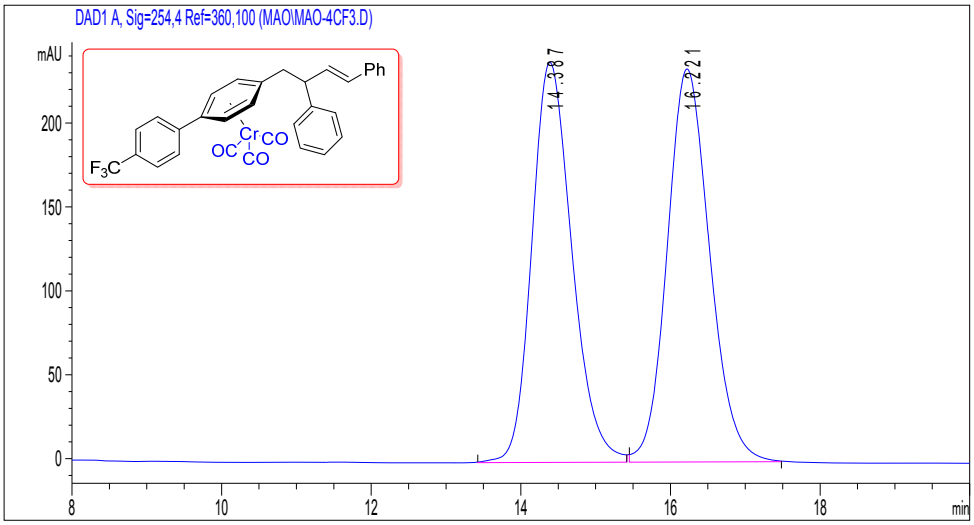
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.119 MF	0.3556	1457.26794	68.30312	50.8678
2	11.999 FM	0.4012	1407.54651	58.47522	49.1322
Totals :			2864.81445	126.77834	

Figure S63. HPLC Chromatography of (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-4-(4-trifluorophenyl)-benzene)$Cr(CO)_3$ (**3t**) (Daicel Chiralcel AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



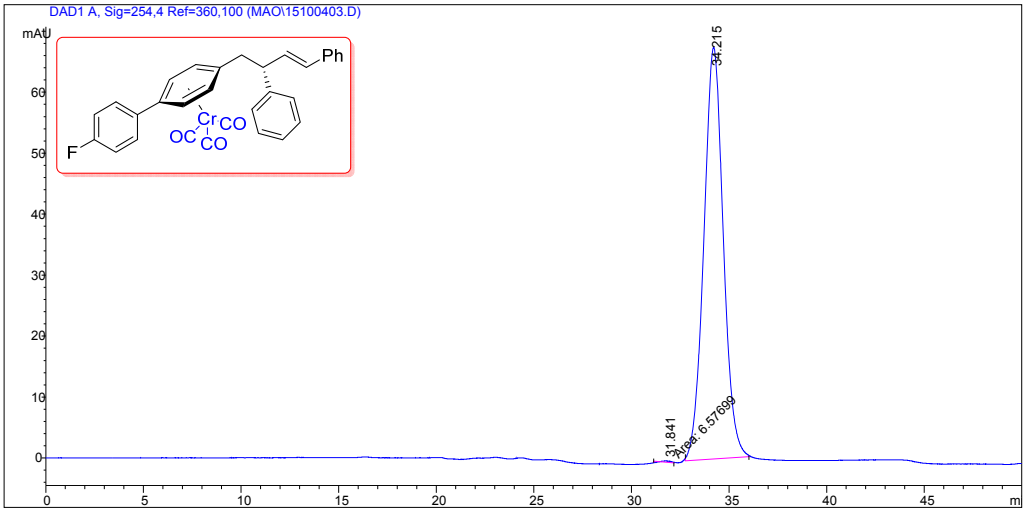
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.909 BV	0.5909	1101.54919	28.00648	4.2678
2	15.659 VB	0.6267	2.47091e4	612.38318	95.7322
Totals :			2.58106e4	640.38966	

Figure S64. HPLC Chromatography of Racemic (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-4-(4-trifluorophenyl)-benzene)$Cr(CO)_3$ (**3t**) (Daicel Chiralcel AD-H column, 10% isopropanol in hexanes, 1 mL/min, 254 nm)



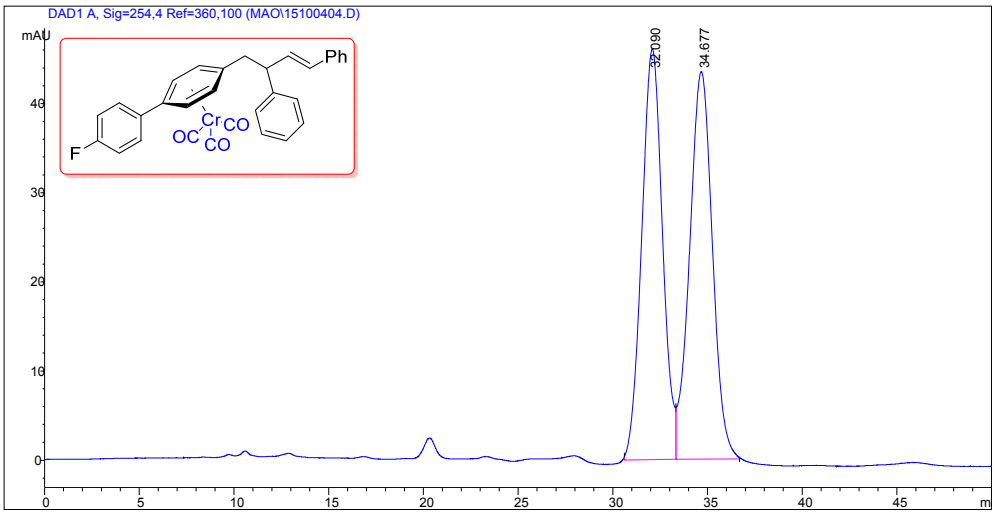
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.387 BB	0.5715	8861.02441	238.47751	48.9564
2	16.221 BB	0.6081	9238.81348	234.24826	51.0436
Totals :			1.80998e4	472.72577	

Figure S65. HPLC Chromatography of Racemic (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(4-fluorophenyl)-benzene)$Cr(CO)_3$ (**3v**) (Daicel Chiralpak IB column, 5% isopropanol in hexanes, 0.4 mL/min, 254 nm)



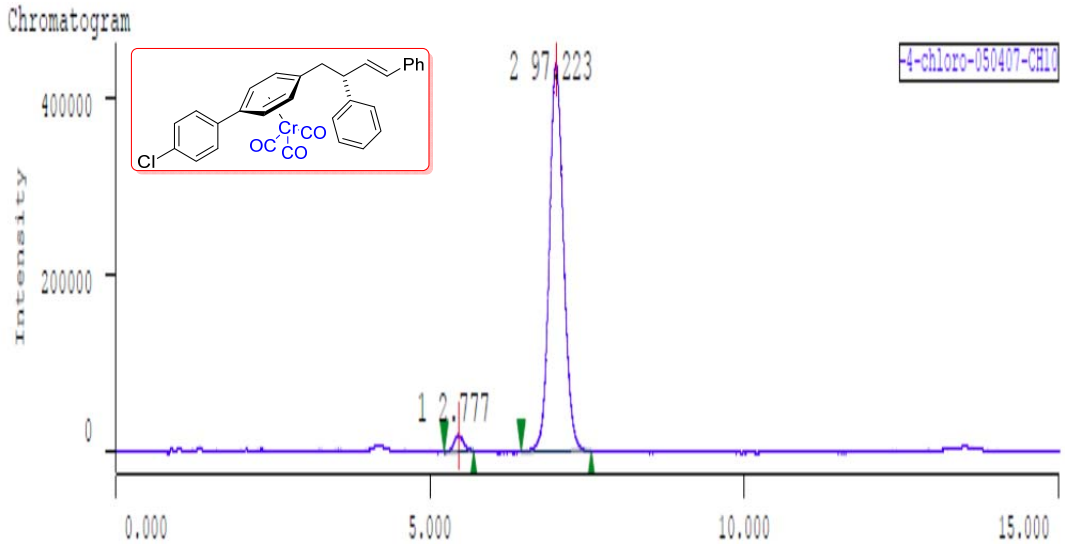
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.841 MM	0.5225	6.57699	2.09774e-1	0.1406
2	34.215 BB	0.9814	4672.25195	67.51069	99.8594
Totals :			4678.82894	67.72046	

Figure S66. HPLC Chromatography of Racemic (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(4-fluorophenyl)-benzene)$Cr(CO)_3$ (**3v**) (Daicel Chiralpak IB column, 5% isopropanol in hexanes, 0.4 mL/min, 254 nm)



Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.090 BV	1.0665	3500.08691	46.06406	48.9629
2	34.677 VB	1.1773	3648.36597	43.46463	51.0371
Totals :			7148.45288	89.52869	

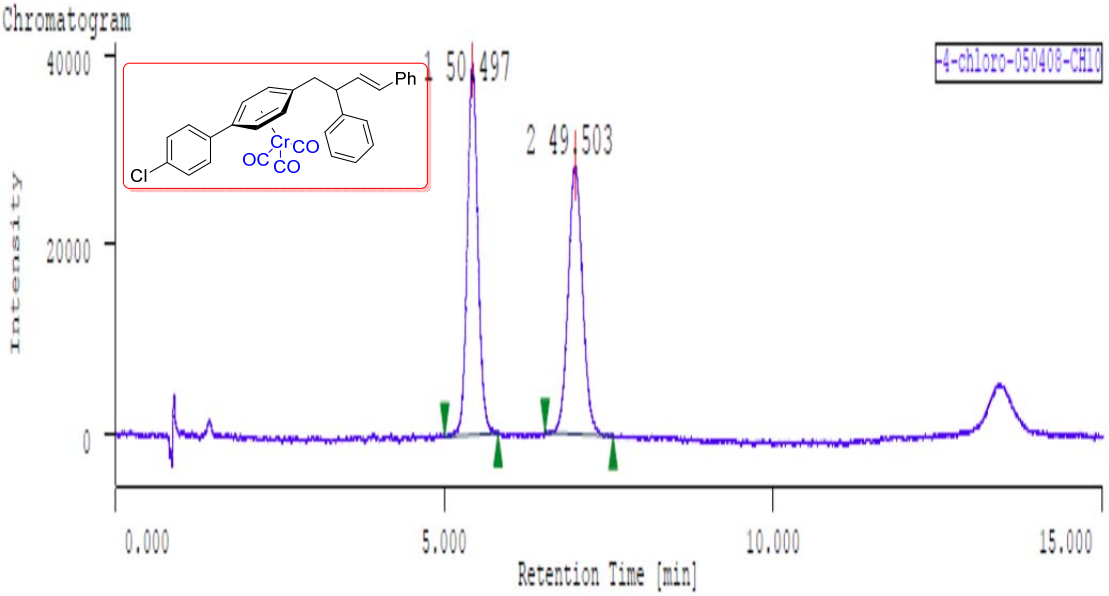
Figure S67. SFC Chromatography of (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(4-chlorophenyl)-benzene)$Cr(CO)_3$ (**3u**) (Daicel Chiralcel AD-H column, 10% methanol in CO_2, 4 mL/min, 254 nm)



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Symmetry Factor
1	10	5.453	197312	18078	2.777	1.125
2	10	7.003	6908092	439196	97.223	1.103

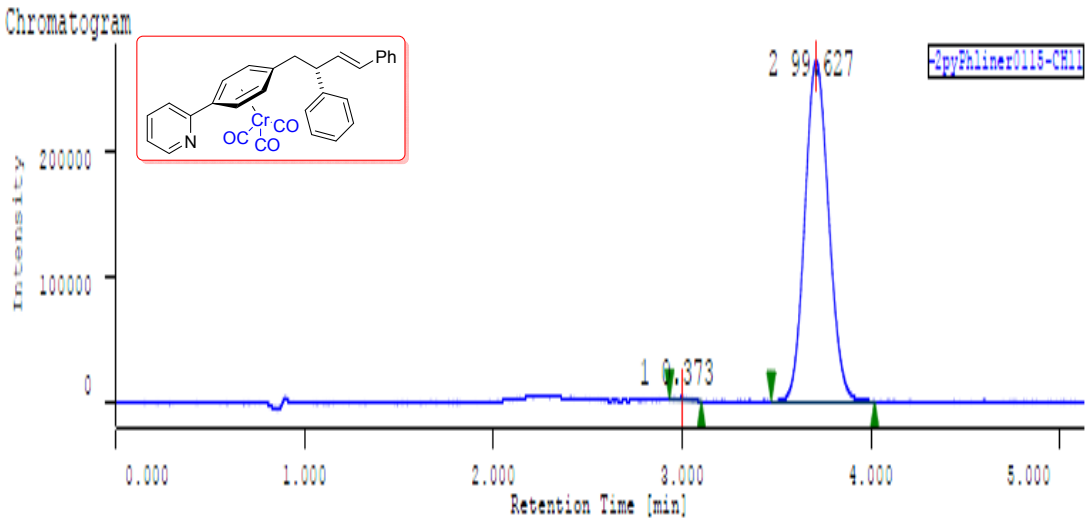
Figure S68. HPLC Chromatography of Racemic (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-(4-chlorophenyl)-benzene)$Cr(CO)_3$ (**3u**) (Daicel Chiralcel AD-H column, 10% methanol in CO_2, 4 mL/min, 254 nm)



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Symmetry Factor
1	10	5.430	440572	39135	50.497	1.084
2	10	6.985	431900	28220	49.503	1.080

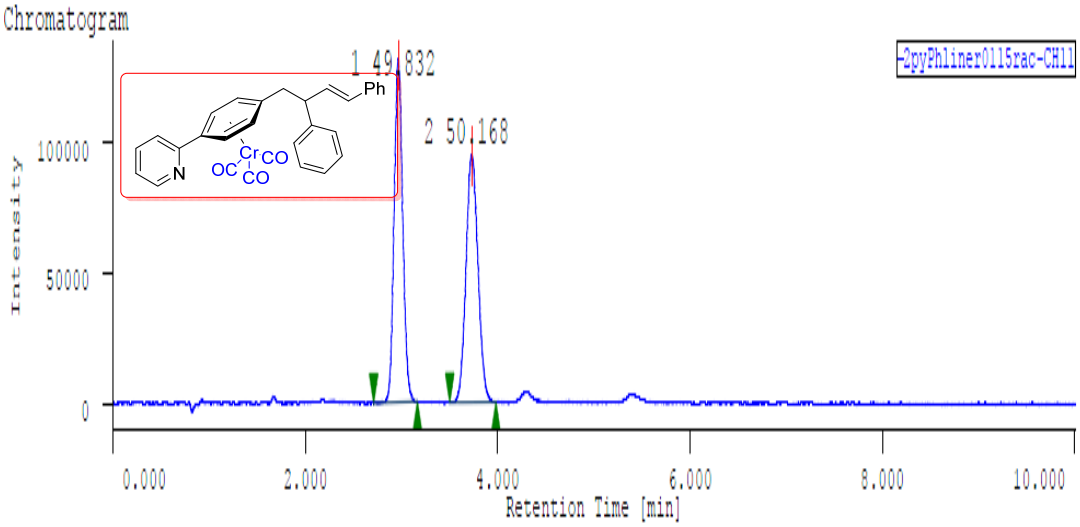
Figure S69. SFC Chromatography of (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (**3r**) (Daicel Chiralcel AD-H column, 30% methanol in CO_2, 4 mL/min, 270 nm)



Peak Information

#	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Symmetry Factor
1	11	2.997	8917	1894	0.373	1.217
2	11	3.708	2382891	271270	99.627	1.097

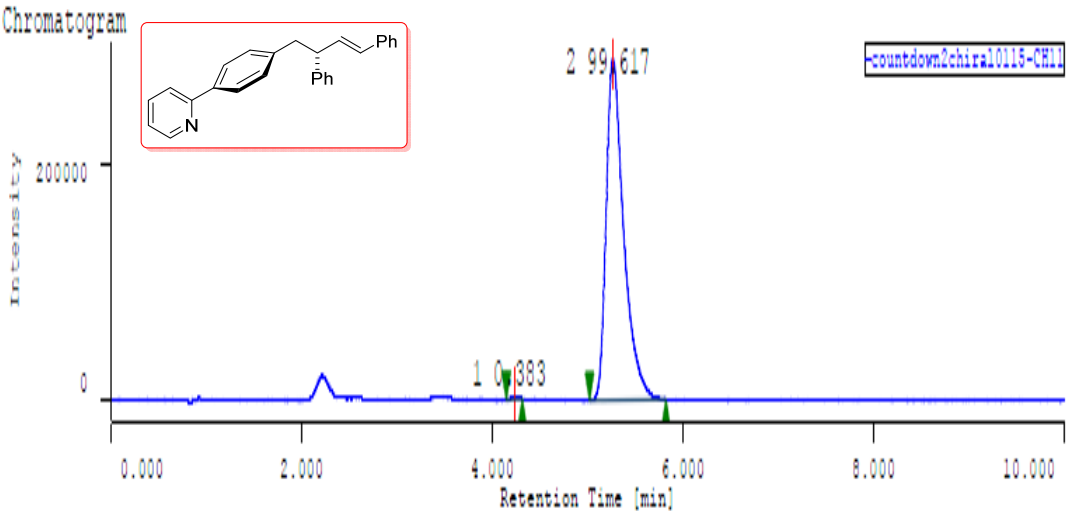
Figure S70. SFC Chromatography of Racemic (*E*)-(η^6-(2,4-diphenylbut-3-en-1-yl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (**3r**) (Daicel Chiralcel AD-H column, 30% methanol in CO_2, 4 mL/min, 270 nm)



Peak Information

#	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Symmetry Factor
1	11	2.965	821990	131149	49.832	1.091
2	11	3.728	827523	94586	50.168	1.073

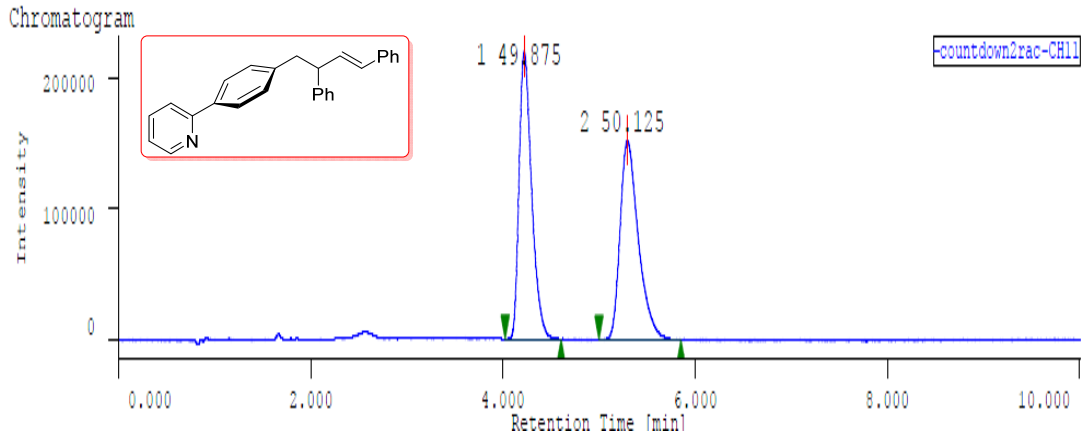
Figure S71. SFC Chromatography of (E)-2-(4-(2,4-diphenylbut-3-en-1-yl)phenyl)pyridine **(3y)** (Daicel Chiralcel AD-H column, 30% methanol in CO_2, 4 mL/min, 270 nm)



Peak Information

#	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Symmetry Factor
1	11	4.225	14258	2738	0.383	1.035
2	11	5.263	3713172	289935	99.617	1.571

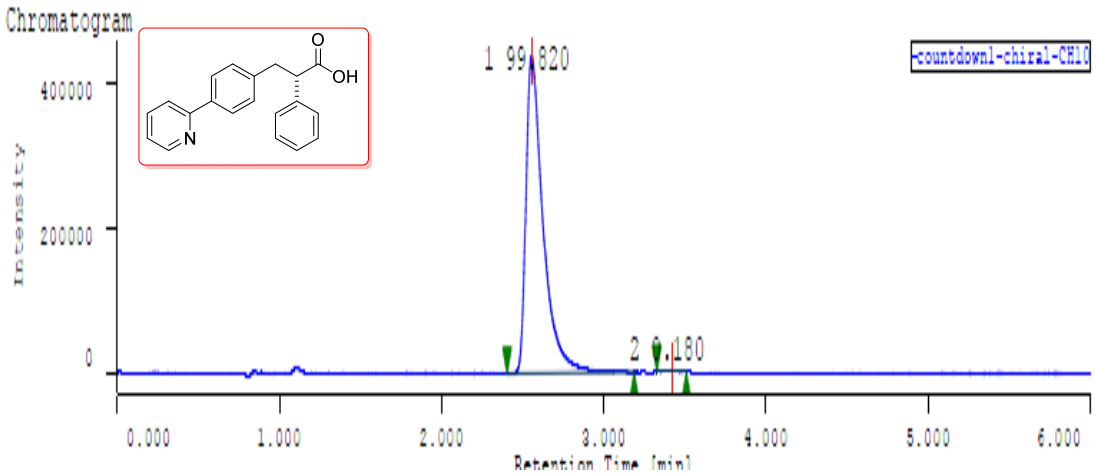
Figure S72. SFC Chromatography of Racemic (*E*)-2-(4-(2,4-diphenylbut-3-en-1-yl)phenyl)pyridine **(3y)** (Daicel Chiralcel AD-H column, 30% methanol in CO_2, 4 mL/min, 270 nm)



Peak Information

#	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Symmetry Factor
1	11	4.218	1986421	218624	49.875	1.407
2	11	5.290	1996366	150985	50.125	1.459

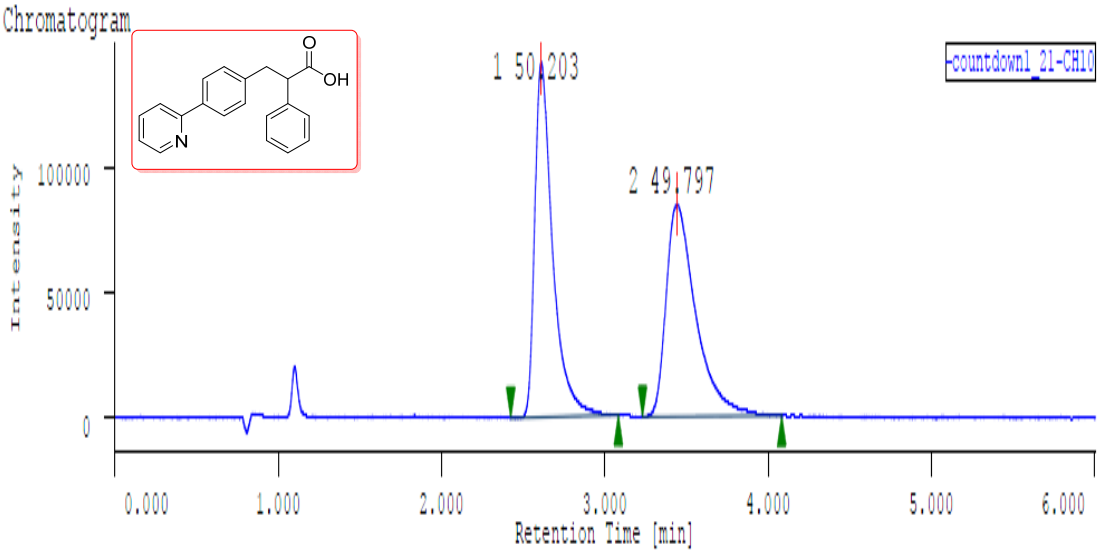
Figure S73. SFC Chromatography of (-)-2-phenyl-3-(4-(pyridin-2-yl)phenyl)propanoic acid (**4**) (Daicel Chiralpak IA column, 30% methanol in CO_2, 4 mL/min, 254 nm)



Peak Information

#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Symmetry Factor
1	10	2.557	3242453	439858	99.820	1.920
2	10	3.420	5858	997	0.180	0.969

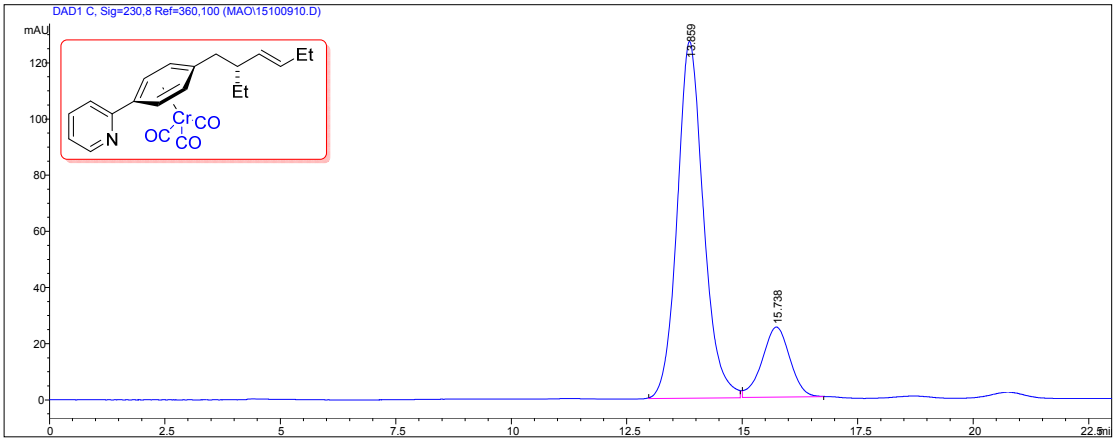
Figure S74. SFC Chromatography of Racemic 2-phenyl-3-(4-(pyridin-2-yl)phenyl)propanoic acid (**4**) (Daicel Chiralpak IA column, 30% methanol in CO_2, 4 mL/min, 254 nm)



Peak Information

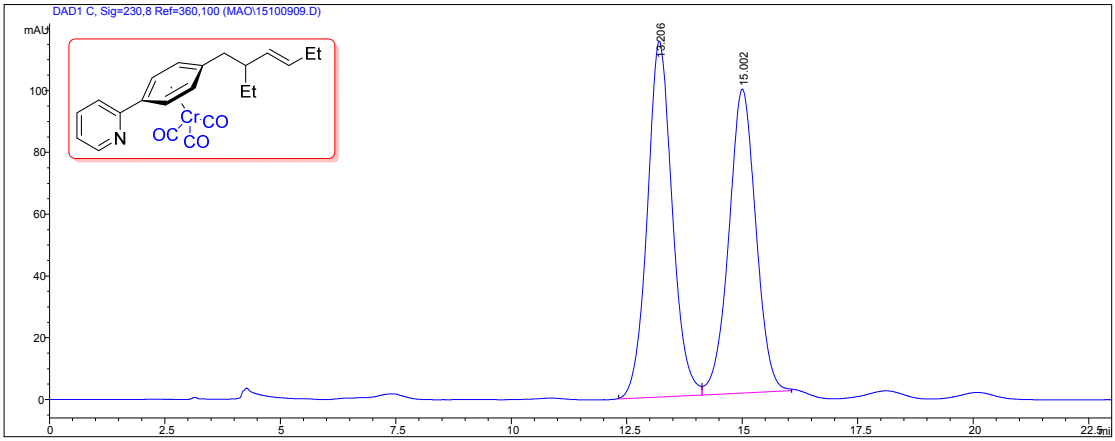
#	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Symmetry Factor
1	10	2.610	1073309	140784	50.203	1.772
2	10	3.440	1064645	84240	49.797	1.768

Figure S75. HPLC Chromatography of (*E*)-(η^6-(2-ethylhex-3-en-1-yl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (**3w**) (Daicel Chiralpak IB column, 1% isopropanol in hexanes, 1 mL/min, 230 nm)



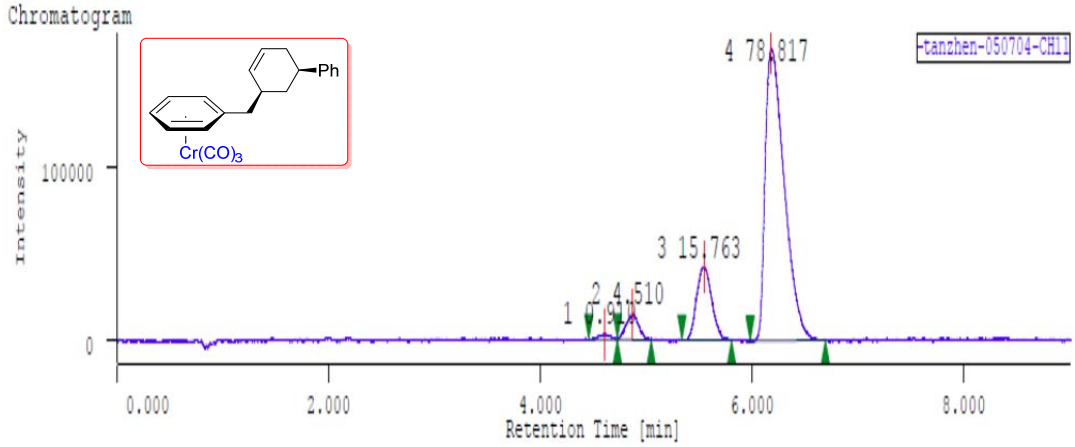
Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.859 BB	0.5965	5013.58496	127.01143	82.7532
2	15.738 BB	0.6381	1044.89441	24.97523	17.2468
Totals :			6058.47937	151.98665	

Figure S76. HPLC Chromatography of Racemic (*E*)-(η^6-(2-ethylhex-3-en-1-yl)-4-(2-pyridyl)-benzene)$Cr(CO)_3$ (**3w**) (Daicel Chiralpak IB column, 1% isopropanol in hexanes, 1 mL/min, 230 nm)



Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.206 BV	0.5676	4320.83545	115.18378	51.8978
2	15.002 VB	0.6231	4004.82471	98.33588	48.1022
Totals :			8325.66016	213.51966	

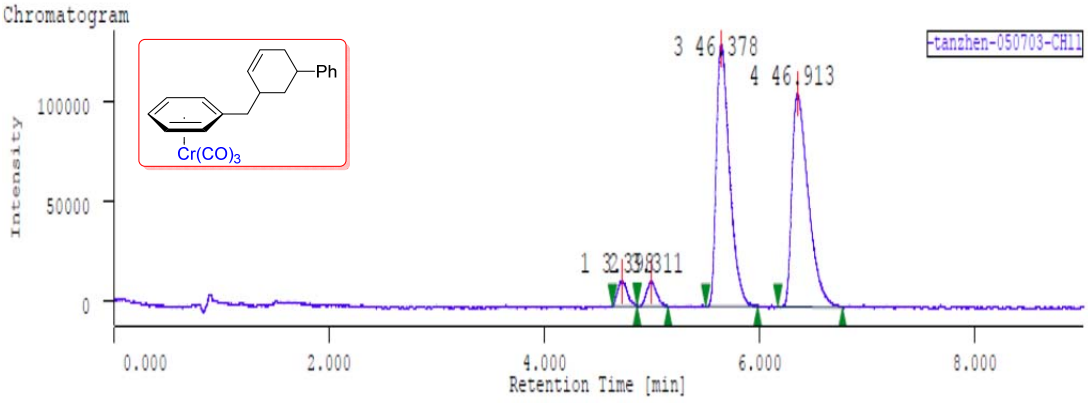
Figure S77. SFC Chromatography of (η^6-(5-phenyl-2-cyclohexen-1-ylmethyl)-benzene)$Cr(CO)_3$ (**3x**) (Daicel Chiralpak IA column, 10% methanol in CO_2, 4 mL/min, 270 nm)



Peak Information

#	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Symmetry Factor
1	11	4.605	24159	3083	0.910	N/A
2	11	4.868	119792	14244	4.510	1.008
3	11	5.542	418647	42068	15.763	1.121
4	11	6.178	2093342	167512	78.817	1.852

Figure S78. SFC Chromatography of racemic (η^6-(5-phenyl-2-cyclohexen-1-ylmethyl)-benzene)$Cr(CO)_3$ (**3x**) (Daicel Chiralpak IA column, 10% methanol in CO_2, 4 mL/min, 270 nm)



Peak Information

#	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Symmetry Factor
1	11	4.722	82346	12742	3.398	1.237
2	11	4.990	80243	12377	3.311	1.144
3	11	5.640	1123865	131826	46.378	1.604
4	11	6.347	1136824	107196	46.913	1.804

10. References

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