Rhodium-catalyzed enantioselective cyclopropanation of electron-deficient alkenes

Supporting information

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General Methods: ^{1}H Nuclear Magnetic Resonance (^{1}H-NMR) and ^{13}C Nuclear Magnetic Resonance (^{13}C-NMR) spectra were recorded on Varian Mercury 300, INOVA 400, INOVA 600, VNMR 400 and UNITY 600 MHz. NMR spectra were recorded in deuterated chloroform ($CDCl_3$) at room temperature unless otherwise stated. The NMR data were presented as follows: chemical shift in ppm with tetramethylsilane (TMS, δ = 0.00 ppm) for ^{1}H-NMR and the residual of chloroform (δ = 77.0 ppm) for ^{13}C-NMR as internal standards, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet, br. = broad), coupling constant (*J*/Hz), integration. IR spectra were collected on a Nicolet iS10 from Thermo Scientific and reported in unit of cm^{-1}. Mass spectra were recorded on a Finnigan LTQ FTMS mass spectrometer with APCI, ESI, or NSI as ionization source. Optical rotations were measured on a Jasco *p*-2000 polarimeter (concentration in g/100mL). Melting points were measured on a MEL-TEMP of Electrothermal (uncorrected).

All reactions were performed under argon atmosphere with oven dried or flamed dried glassware. Acetonitrile, tetrahydrofuran, dichloromethane and toluene were dried by a solvent purification system (passed through activated alumina columns). Analytical TLC was performed on silica gel plates visualizing with UV light, phosphomolybdic acid or potassium permanganate stains. Flash column chromatography was performed on silica gel 60Å (230-400 mesh) from Sorbent Technologies. Unless otherwise noted, all other chemical reagents were obtained from commercial sources and used as received.

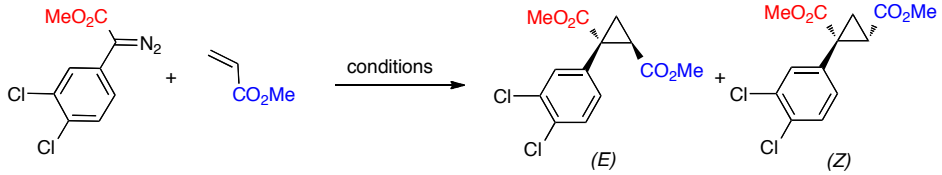
The relative configuration of the cyclopropane products generated by palladium- and rhodium-catalyzed cyclopropanation reactions:

The Wang group has previously published a palladium-catalyzed cyclopropanation reaction of methyl acrylate with aryldiazo compounds.[1] The spectral and physical property of the major diastereomer is the same as the cyclopropane generated by $Rh_2(TCPTAD)_4$ catalyzed reaction. The Wang group rendered the major diastereomer of their palladium-catalyzed reaction in a *Z*-configuration as shown in compound **SI-3**, but the major diastereomer generated from the rhodium-catalyzed reaction usually adopts a *E*-configuration as in compound **SI-2**. To clarify the stereochemistry of this reaction, both rhodium- and palladium-catalyzed reactions of diazo compound **SI-1** with methyl acrylate were performed (Table **SI-1**). The reaction catalyzed by $Pd(OAc)_2$ provided cyclopropanes as a mixture of 85:15 ratio of diastereomers (entry 1), while the $Rh_2(TCPTAD)_4$ catalyzed the reaction produced the cyclopropane as a single regioisomer with 92% ee (entry 2). The major diastereomers of those two reactions are the same based on NMR analysis (Fig. SI-1). ^{1}H-NMR showed that the signals of the methoxy groups of the major diastereomer from the palladium-catalyzed reaction are presented at relative high field (3.67 and 3.53 ppm), while those of the minor isomer are presented at 4.00 and 3.75 ppm. This result indicates that both methoxy groups of the major isomer are shielded, which would be the expected behaviors of the *E*-isomer because the aryl group would shield the methyl ester protons. This would suggest that the Wang group had incorrectly assigned the structure of the major isomer in their palladium-catalyzed

(1) Chen, S.; Ma, J.; Wang, J. *Tetrahedron Lett.* **2008**, *49*, 6781.

studies.

Table SI-1 Palladium- and rhodium-catalyzed cyclopropanations

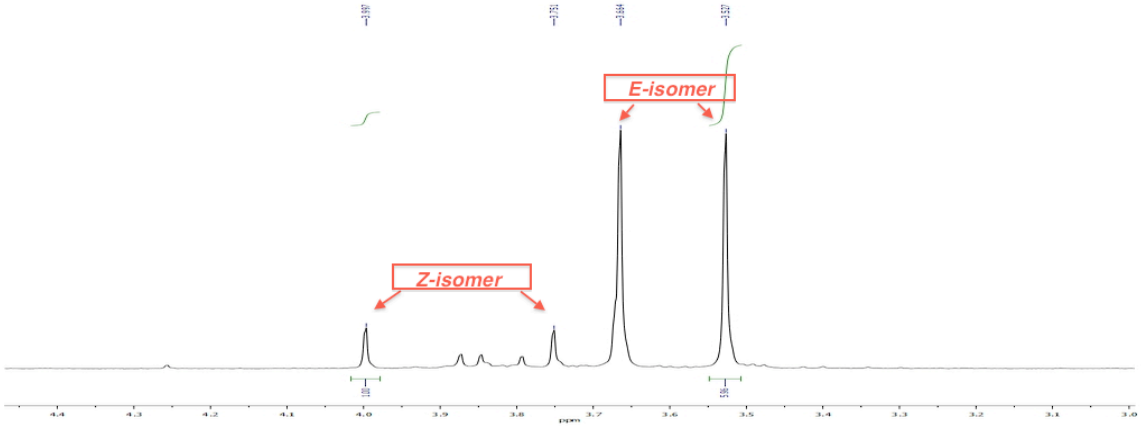


SI-1 **SI-2** **SI-3**

entry	coditions	dr[a] (*E*/*Z*)	yield[b] (%)	ee of *E*[c] (%)
1	5 mol % $Pd(OAc)_2$, PhMe, 80 °C	85:15	43	-
2	1 mol % Rh_2(*S*-TCPTAD$_4$), pentane, 36 °C	>97:3	70	92

[a] Based on crude ^{1}H-NMR. [b]Isolated yield. [c]Determined by chiral HPLC.

a) Crude ^{1}H-NMR of $Pd(OAc)_2$ catalyzed reaction of **SI-1**



b) Crude ^{1}H-NMR of Rh_2(*S*-TCPTAD)$_4$ catalyzed reaction of **SI-1**

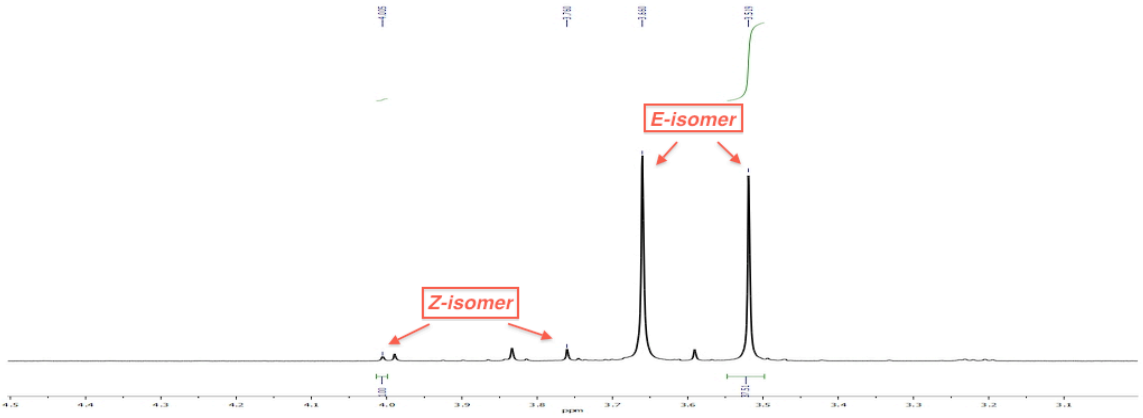
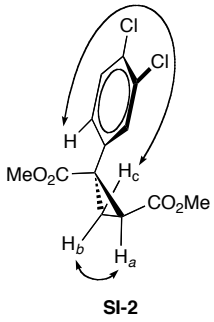


Fig. SI-1 ^{1}H-NMR of palladium- and rhodium-catalyzed reactions of **SI-1**

The stereochemical configuration of **SI-2** was further confirmed by NOE experiment (Fig. SI-2). HMQC experiment indicated that the H_a is on the carbon substituted with a methyl ester group, and protons (H_b and H_c) are on the same carbon of the cyclopropane ring. Only H_a was enhanced when H_c at 7.08 ppm was irradiated. This indicates that the cyclopropane 1.28 is in the *E* isomer because NOE enhancement of two protons (H_a and H_b) would be expected if the product was the *Z* isomer. The X-ray crystallographic structures of the analogues (**7l** and **15**) of **SI-2**, derived from the reaction of *tert*-butyl *p*-bromophenyldiazoacetate with phenyl acrylate and acrylonitrile, were obtained. Both of the two crystal structures demonstrated the $Rh_2(TCPTAD)_4$ catalyzed reaction produced cyclopropanes in *E*-configuration.



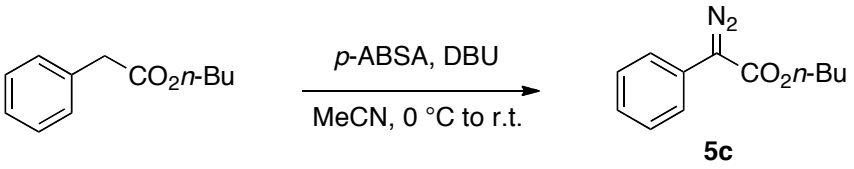
SI-2

Fig. SI-2 NOE experiment of cyclopropane **SI-2**

Synthesis of Aryldiazoacetates:

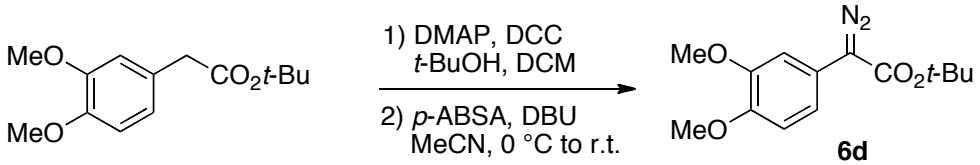
Aryldiazoacetates **1**[2]**, 4a**[2], and **4b**[3] were prepared by previously published procedures. *tert*-butyl diazo compounds **4d**, **6a-c**[4]**, 6e-g**[5] and **6h**[6] were synthesized via a modified literature procedure[4] as described for compound **6d**.

(2) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063.
(3) Peng, C.; Cheng, J.; Wang, J.; *J. Am. Chem. Soc.*, **2007,** *129*, 8708.
(4) Gao, L.; Hwang, G.; Ryu, D. H.; *J. Am. Chem. Soc.,* **2011,** *133,* 20708.
(5) Lee, E. C.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 12066.
(6) Shishkov, I. V.; Rominger, F.; Hofmann, P.; *Organometallics,* **2009**, *28*, 1049.



5c

***n*-butyl 2-diazo-2-phenylacetate (5c):** To a solution of butyl phenylaceate (5.3 g, 0.028 mol, 1 equiv) and *para*-acetamindobenzenesulfonyl azide (*p*-ABSA, 8.6 g, 0.36 mol, 1.3 equiv) in acetonitrile (40 mL) at 0 °C was added 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 6.2 mL, 0.041 mol, 1.5 equiv) in one portion. The resulting mixture was warmed up slowly in the ice-water bath to room temperature and stirred for 72 hours. The reaction was quenched with saturated ammonium chloride solution and then extracted with diethyl ether. The combined the organic layers were dried over magnesium sulfate. The solid was filtered off and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatography (silica gel, hexanes:diethyl ether = 25:1) to afford the product as a red oil (4.7 g, 62% yield). IR (neat): 2959, 2873, 2079, 1699, 1242 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.48 (d, J = 8.6 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.19-7.14 (m, 1H), 4.28 (t, J = 6.6 Hz, 2H), 1.74-1.64 (m, 2H), 1.48-1.37 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.3, 129.0, 125.8, 125.7, 124.0, 64.9, 31.0, 19.3, 13.9, the resonance resulting from the diazo carbon was not detected; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{13}H_{11}O_4N_2{}^{35}Cl_2$, 219.1128; found, 219.1128.



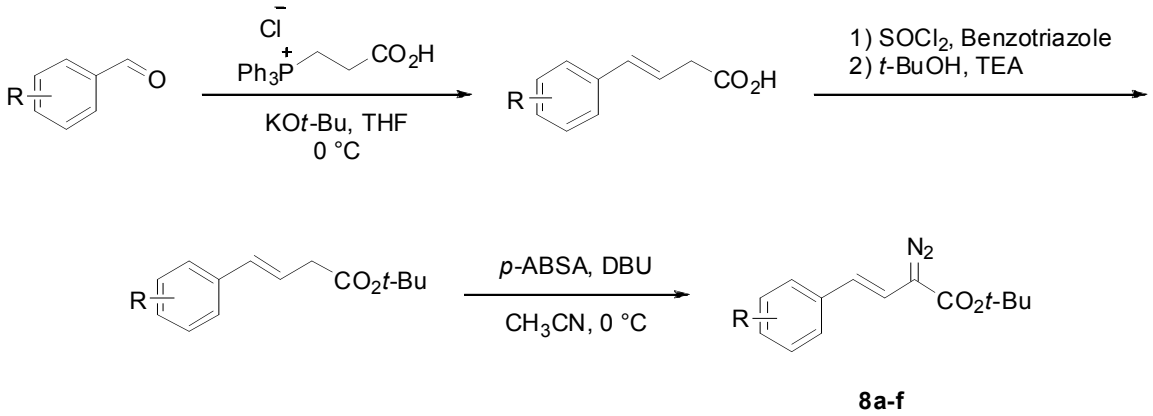
6d

***tert*-butyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (6d):** To a solution of 3,4-dimethoxyphenylacetic acid (6.1 g, 0.031 mol, 1 equiv), *tert*-butanol (9.0 g, 0.12 mol, 3.9

equiv) and 4-(dimethylamino)pyridine (DMAP, 3.0 g, 0.024 mol, 0.8 equiv) in dichloromethane (50 mL) at 0 °C was added dicyclohexylcarbodiimide (DCC, 6.7 g, 0.032 mol, 1.0 equiv) slowly. The resulting mixture was warmed up slowly in the ice-water bath to room temperature and stirred overnight. The solid was filtered off and washed with hexanes. The filtrate was concentrated in vacuo and purified by flash chromatography (silica gel, hexanes:ethyl acetate = 10:1) to afford the *tert*-butyl 3,4-dimethoxyphenylacetate as a white solid (5.8 g, 74% yield).

To a solution of *tert*-butyl 3,4-dimethoxyphenylacetate (5.8 g, 0.023 mol, 1 equiv) and *p*-ABSA (8.3 g, 0.035 mol, 1.5 equiv) in acetonitrile (30 mL) at 0 °C was added DBU (7.0 mL, 0.047 mol, 2 equiv) in one portion. The resulting mixture was warmed up slowly in the ice-water bath to room temperature and stirred for 72 hours. The reaction was quenched with saturated ammonium chloride solution and then extracted with diethyl ether. The combined the organic layers were dried over magnesium sulfate. The solid was filtered off and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatography (silica gel, hexanes:diethyl ether = 4:1) to afford the product as an orange solid (3.0 g, 47% yield). IR (neat): 2976, 2836, 2074, 1692, 1134 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.19 (d, J = 2 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 8.5, 2.0 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 1.55 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.2, 149.5, 147.2, 118.2, 116.4, 111.4, 108.4, 82.1, 56.1, 56.1, 28.6, the resonance resulting from the diazo carbon was not detected; HRMS (NSI) *m/z*: $[M+Na]^+$ calcd. for $C_{14}H_{18}O_4N_2{}^{23}Na_1$, 301.1159; found, 301.1161.

Synthesis of styryldiazoacetates:



8a-f

The styryldiazoacetates were prepared as shown in the scheme above. The procedure for the preparation of **8c** is given below. The remaining styryldiazoacetates were prepared analogously by the same procedure. Note: The aryl-3-butenoic acids and corresponding *t*-Bu esters were isolated in a form insufficiently pure for complete characterization, and were used as such in the next reaction. Thus, full characterization is presented here only for styryldiazoacetates **8a-f**.

Representative procedure for styryldiazoacetates:

(*E*)-4-(2-chlorophenyl)but-3-enoic acid: To an oven-dried flask was added (2-carboxyethyl)triphenylphosphonium chloride (26.7 g, 72 mmol, 1.2 equiv). THF (200 mL) was added, under argon, followed by 2-chlorobenzaldehyde (6.7 mL, 60 mmol, 1.0 equiv). The mixture was cooled to 0 °C and stirred vigorously. Then potassium *tert*-butoxide (16.8 g, 150 mmol, 2.5 equiv) was added in one portion. The reaction mixture was stirred for 30 minutes at 0 °C before it was warmed to room temperature, and stirred overnight. The reaction mixture was diluted with Et_2O (200 mL) and extracted with saturated aqueous sodium bicarbonate (3 x 150 mL). The combined aqueous extracts

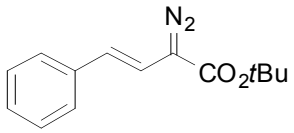
were washed with Et_2O (3 x 100 mL) and then acidified to pH = 1.0 with concentrated HCl. Et_2O (250 mL) was added and the aqueous layer removed. The ethereal layer was washed with brine, dried ($MgSO_4$) and concentrated to give the crude acid. This was purified by chromatography (10% to 15% Et_2O in pentane, with 2% acetic acid). The product so isolated was further purified by recrystallization from hexanes to give colorless needles that were pure enough for the next step: (5.5 g, ~47% yield).

(*E*)-*tert*-butyl 4-(2-chlorophenyl)but-3-enoate:[7] To a solution of the styrylacetic acid (4.0 g, 20.3 mmol, 1.0 equiv) in DCM (50 mL) was added dropwise a solution of benzotriazole (13.0 g, 16.2 mmol, 1.25 equiv) and thionyl chloride (1.9 mL, 16.2 mmol, 1.25 equiv) in DCM (17 mL) over 5 minutes. The mixture was stirred an additional 10 minutes and the precipitate filtered. The filtrate was stirred with $MgSO_4$-$7H_2O$ (5.0 g) for 10 minutes and filtered again. The filtrate was carefully poured into a solution of *tert*-butanol (50 mL) and triethylamine (5.6 mL, 40.6 mmol, 2.0 equiv). The solution was stirred under argon overnight. The reaction mixture was then washed with water (2 x 50 mL), dried ($MgSO_4$) and concentrated. The crude was purified by chromatography (3% Et_2O in pentane) to give the *tert*-butyl ester as an oil, pure enough for the next step (1.6 g, 31% yield).

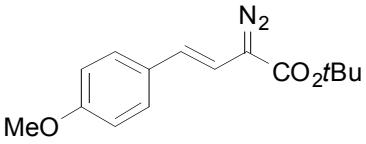
(*E*)-*tert*-butyl 4-(2-chlorophenyl)-2-diazobut-3-enoate (8c): The ester (1.6 g, 6.3 mmol, 1.0 equiv) and *p*-acetamidobenzenesulfonyl azide (2.3 g, 9.5 mmol, 1.5 equiv) were dissolved in acetonitrile (16 mL) and cooled to 0 °C. 1,8-diazobicycloundec-7-ene (1.9

(7) The *tert*-butyl esters were prepared from the corresponding acyl chloride. The acyl chloride was prepared according to a modified literature procedure: Chaudhari, S., Akamanchi, K., *Synlett*, **1999**, *11*, 1763-1765.

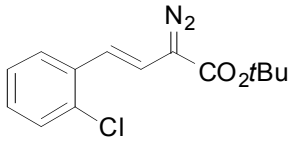
mL, 12.6 mmol, 2.0 equiv) was added dropwise. The mixture was stirred 3 hours and quenched with saturated aqueous NH_4Cl (15 mL). Et_2O (20 mL) was added, and the aqueous layer removed. The organic layer was washed with brine, dried ($MgSO_4$) and the solvents removed by rotary evaporation. The solid crude residue was dissolved in pentane (150 mL) and the solids removed by filtration. The filtrate was concentrated by rotary evaporation below room temperature. The product was collected as a red crystalline solid (1.1 g, 61% yield). (Note: diazo compounds **8b-8f** were purified by column chromatography with 3-6% Et_2O in pentane).



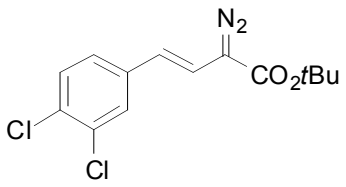
(*E*)-*tert*-butyl 2-diazo-4-phenylbut-3-enoate (8a): Following the procedure above with the *tert*-butyl ester (781 mg, 3.6 mmol, 1.0 equiv), *p*-ABSA (1.3 g, 5.4 mmol, 1.5 equiv) and DBU (1.1 mL, 7.2 mmol, 2.0 equiv), the diazo was purified by column chromatography (5% Et_2O in pentane). The red fractions were combined and concentrated below room temperature to give the product as a light red solid (520 mg, 59% yield). ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.24-7.18 (m, 1H), 6.49 (d, 1H, J = 16.3 Hz), 6.19 (d, 1H, J = 16.3 Hz), 1.56 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.5, 137.1, 128.8, 127.0, 125.9, 122.6, 112.1, 82.4, 28.5, the resonance resulting from the diazo carbon was not detected; IR (neat): 2978, 2930, 2092, 1111 cm^{-1}; HRMS (APCI) calcd. for $C_{14}H_{17}O_2N_2$ ($[M+H]^+$) 245.1285, found 245.1286.



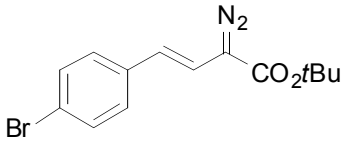
(*E*)-*tert*-butyl 2-diazo-4-(4-methoxyphenyl)but-3-enoate (8b): Following the example procedure above with the *tert*-butyl ester (833 mg, 3.4 mmol, 1.0 equiv), *p*-ABSA (1.2 g, 5.0 mmol, 1.5 equiv), and DBU (1.0 mL, 6.8 mmol, 2.0 equiv) the diazo was purified by column chromatography (5% Et_2O in pentane) to give the diazo as a red oil (692 mg, 74% yield). ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.28 (d, 2H, J = 8.6 Hz), 6.86 (d, 2H, J = 8.6 Hz), 6.28 (d, 1H, J = 16.3 Hz), 6.11 (d, 1H, J = 16.3 Hz), 3.81 (s, 3H), 1.53 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.8, 158.9, 130.0, 127.1, 122.4, 114.2, 109.4, 82.2, 55.4, 28.5; the resonance resulting from the diazo carbon was not detected; IR (film): 2977, 2070, 1693, 1245 cm^{-1}; HRMS (NSI) calcd. for $C_{15}H_{19}O_3N_2$ ($[M+H]^+$) 275.1390, found 275.1391.



(*E*)-*tert*-butyl 4-(2-chlorophenyl)-2-diazobut-3-enoate (8c): Used as the example procedure above. ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.54 (dd, 1H, J = 7.9, 1.6 Hz), 7.34 (d, 1H, J = 7.9 Hz), 7.22 (t, 1H, J = 7.9 Hz), 7.16-7.10 (m, 1H), 6.55 (d, 1H, J = 16.3 Hz), 6.50 (d, 1H, J = 16.3 Hz), 1.55 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.2, 135.1, 132.4, 129.9, 128, 126.3, 127.1, 118.3, 115.2, 82.6, 28.5; the resonance resulting from the diazo carbon was not detected; IR (neat): 2977, 2081, 1691, 1112 cm^{-1}; HRMS (NSI) calcd. for $C_{14}H_{16}O_2N_2Cl$ ($[M+H]^+$) 279.0895, found 279.0897.

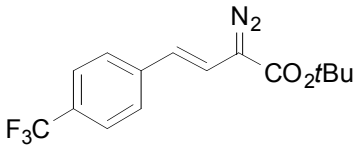


(*E*)-*tert*-butyl 2-diazo-4-(3,4-dichlorophenyl)but-3-enoate (8d): Following the example procedure above with the *tert*-butyl ester (765 mg, 2.7 mmol, 1.0 equiv), *p*-ABSA (960 mg, 4.0 mmol, 1.5 equiv) and DBU (0.81 mL, 5.4 mmol, 2.0 equiv) the diazo was purified by column chromatography (5% Et_2O in pentane). The red fractions were combined and concentrated below room temperature to give the product as a light red powder (447 mg, 53 % yield). ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.38 (s, 1H), 7.33 (d, 1H, J = 8.4 Hz), 7.13 (d, 1H, J = 8.4 Hz), 6.46 (d, 1H, J = 16.7 Hz), 6.05 (d, 1H, J = 16.7 Hz), 1.53 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.0, 137.3, 132.9, 130.6, 130.4, 127.5, 124.9, 119.9, 114.6, 82.8, 28.5; the resonance resulting from the diazo carbon was not detected; IR (neat): 2980, 2075, 1704, 1112 cm^{-1}; HRMS (NSI) calcd. for $C_{14}H_{15}O_2N_2Cl_2$ ($[M+H]^+$) 313.0505, found 313.0509.



(*E*)-*tert*-butyl 4-(4-bromophenyl)-2-diazobut-3-enoate (8e): Following the example procedure above with the *tert*-butyl ester (625 mg, 2.1 mmol, 1.0 equiv), *p*-ABSA (757 mg, 3.2 mmol, 1.5 equiv) and DBU (0.63 mL, 4.2 mmol, 2.0 equiv) the diazo was purified by column chromatography (5% Et_2O in pentane). The red fractions were combined and concentrated below room temperature to give the product as a light orange powder (275 mg, 41 % yield). ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.43 (d, 2H, J = 7.9 Hz),

7.21 (d, 2H, J = 7.9 Hz), 6.47 (d, 1H, J = 16.4 Hz), 6.11 (d, 1H, J = 16.4 Hz), 1.54 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.4, 136.2, 132.0, 127.4, 121.4, 120.7, 113.2, 82.7, 28.5; the resonance resulting from the diazo carbon was not detected; IR (neat): 2978, 2078, 1697, 1247 cm^{-1}; HRMS (NSI) calcd. for $C_{14}H_{15}O_2N_2BrNa$ ($[M+Na]^+$) 345.0209, found 345.0212.

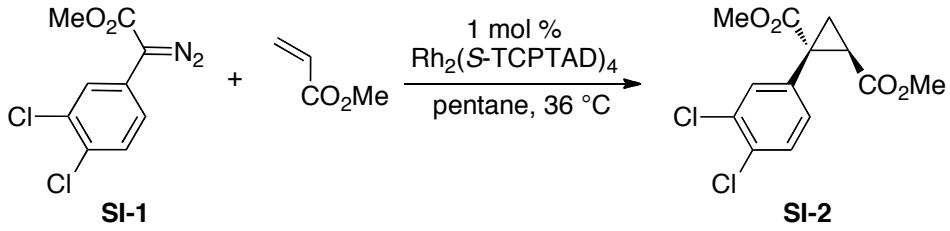


(*E*)-*tert*-butyl 2-diazo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (8f): Following the example procedure above with the *tert*-butyl ester (1.2 g, 4.1 mmol, 1.0 equiv), *p*-ABSA (1.5 g, 6.1 mmol, 1.5 equiv) and DBU (1.2 mL, 8.2 mmol, 2.0 equiv) the diazo was purified by column chromatography (10% Et_2O in pentane) to give the product as a light orange powder (760 mg, 58% yield). ^{1}H-NMR (400 MHz; $CDCl_3$) δ 7.53 (d, 2H, J = 8.2 Hz), 7.40 (d, 2H, J = 8.2 Hz), 6.58 (d, 1H, J = 16.3 Hz), 6.17 (d, 1H, J = 16.3 Hz), 1.52 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 164.1, 140.6, 128.7 (q, $^2J_{CF}$ = 31.9 Hz), 126.0, 125.8 (q, $^3J_{CF}$ = 3.8 Hz), 120.9, 115.4, 82.9, 28.5; the resonances resulting from the diazo and CF_3 carbons were not detected; IR (neat): 2998, 2076, 1692, 1107 cm^{-1}; HRMS (APCI) calcd. for $C_{15}H_{16}O_2N_2F_3$ ($[M+H]^+$) 313.1158, found 313.116;

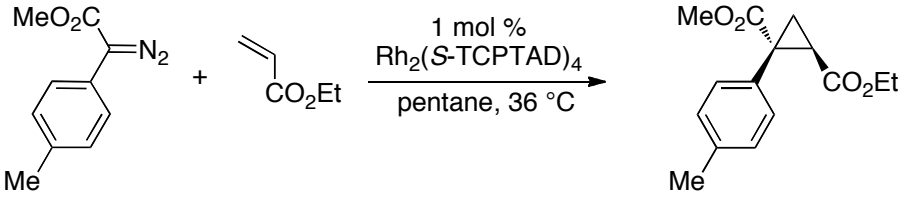
General Procedures for Cyclopropanation:

Under argon atmosphere, to a solution of alkene (5 equiv) and Rh_2(*S*-TCPTAD)$_4$ (0.01 equiv) in pentane (3-5 mL) at reflux was added a solution of diazo compound (0.5 mmol, 1 equiv) in pentane (3-5 mL) over 2 hours. The resulting mixture was stirred at reflux for

another 15 min to 1 hour before cooling down to room temperature. The volatile was removed under vacuum and the crude mixture was purified by flash chromatography.

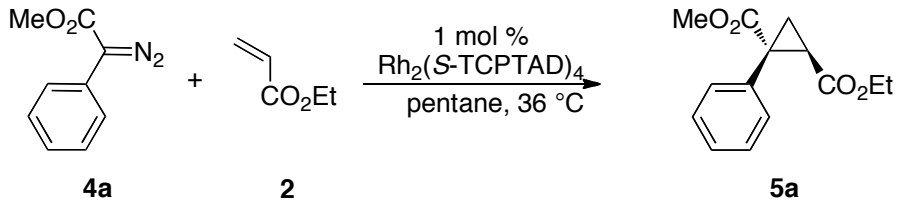


(1*R*,2*R*)-dimethyl 1-(3,4-dichlorophenyl)cyclopropane-1,2-dicarboxylate (SI-2): Following the general procedure, the reaction of methyl acrylate (0.14 ml, 1.55 mmol, 5 equiv), methyl 3,4-dichlorophenyldiazoacetate **SI-1** (71.5 mg, 0.29 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.0 mg, 0.0029 mmol, 0.01 equiv) afforded the product as a colorless oil (62.2 mg, 70% yield) after purification by flash chromatography. R_f = 0.33 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -61.3 (c 0.87, $CHCl_3$); FTIR (neat): 2953, 1726, 1475, 1436, 1260, 1207, 1207, 1165, 1135, 1095, 1032 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.3 Hz, 1H), 7.35 (d, J = 2.1 Hz, 1H), 7.08 (dd, J = 8.3, 2.1 Hz, 1H), 3.66 (s, 3H), 3.53 (s, 3H), 2.76 (dd, J = 8.5, 6.6 Hz, 1H), 1.96 (dd, J = 6.6, 4.6 Hz, 1H), 1.92 (dd, J = 8.5, 4.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.7, 169.1, 134.9, 132.5, 132.1, 132.0, 130.1, 129.8, 53.1, 52.2, 35.7, 29.5, 19.7; HRMS (ESI) *m/z*: $[M-H]^-$ calcd. for $C_{13}H_{11}O_4{}^{35}Cl_2$, 301.0040; found, 301.0040; HPLC analysis: 92% ee (AD-H, hexane, 1.0 mL/min, λ = 210 nm, t_R = 18.49 min, minor; , t_R = 20.69 min, major).



1 **2** **3**

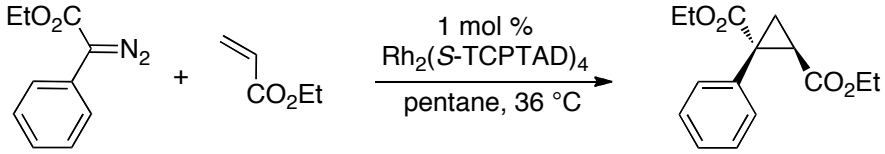
(1*R*,2*R*)-2-ethyl 1-methyl 1-(*p*-tolyl)cyclopropane-1,2-dicarboxylate (3): Following the general procedure, the reaction of ethyl acrylate (0.27 mL, 2.5 mmol, 5 equiv), methyl *p*-methylphenyldiazoacetate (95 mg, 0.50 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (11.0 mg, 0.005 mmol, 0.01 equiv) afforded the product as a colorless oil (93 mg, 71% yield) after purification by flash chromatography. R_f = 0.27 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -81.2 (c 0.99, $CHCl_3$); FTIR (neat): 2954, 1720, 1519, 1436, 1398, 1381, 1257, 1181, 1159, 1097, 1037 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 3.98-3.80 (m, 2H), 3.64 (s, 3H), 2.72 (dd, J = 8.3, 6.7 Hz, 1H), 1.99 (dd, J = 6.5, 4.4 Hz, 1H), 1.86 (dd, J = 8.5, 4.4 Hz, 1H), 1.01 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.0, 169.0, 137.3, 131.5, 130.3, 128.8, 60.8, 52.9, 36.2, 29.7, 21.2, 19.5, 13.9; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{15}H_{18}O_4{}^{23}Na_1$, 285.1097; found, 285.1098; HPLC analysis: 84% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 9.05 min, minor; t_R = 10.25 min, major).



4a **2** **5a**

(1*R*,2*R*)-2-ethyl 1-methyl 1-phenylcyclopropane-1,2-dicarboxylate (5a): Following the general procedure, the reaction of ethyl acrylate (0.16 mL, 1.47 mmol, 5 equiv),

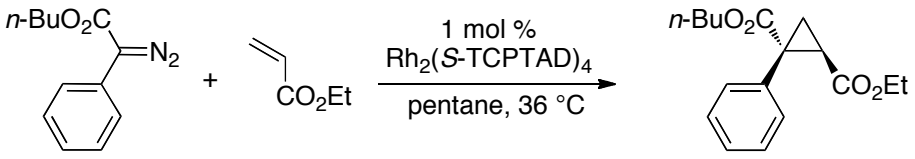
methyl phenyldiazoacetate (58.3 mg, 0.33 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.0 mg, 0.0029 mmol, 0.01 equiv) afforded the product as a colorless oil (68.2 mg, 83% yield) after purification by flash chromatography. R_f = 0.27 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -78.7 (c 1.06, $CHCl_3$); FTIR (neat): 2954, 1719, 1436, 1382, 1254, 1185, 1100, 1036 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.22 (m, 5H), 3.94-3.78 (m, 2H), 3.65 (s, 3H), 2.74 (dd, *J* = 8.5, 6.6 Hz, 1H), 2.02 (dd, *J* = 6.6, 4.5 Hz, 1H), 1.88 (dd, *J* = 8.5, 4.4 Hz, 1H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.8, 168.9, 134.6, 130.5, 128.0, 127.7, 60.8, 52.9, 36.5, 29.7, 19.4, 13.8; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{14}H_{16}O_4{}^{23}Na_1$, 271.0941; found, 271.0940; HPLC analysis: 86% ee (*SS*-Whelk, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 16.92 min, minor; t_R = 22.97 min, major).



4b **2** **5b**

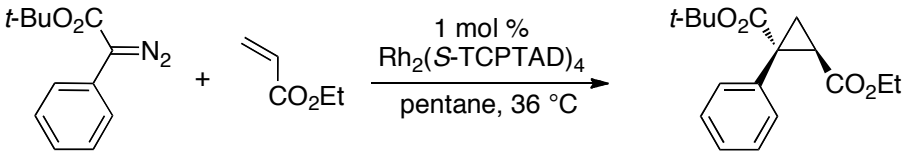
(1*R*,2*R*)-diethyl 1-phenylcyclopropane-1,2-dicarboxylate (5b): Following the general procedure, the reaction of ethyl acrylate (0.27 mL, 2.48 mmol, 5 equiv), ethyl phenyldiazoacetate (89.3 mg, 0.47 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.2 mg, 0.0049 mmol, 0.01 equiv) afforded the product as a colorless oil (95.7 mg, 78% yield) after purification by flash chromatography. R_f = 0.27 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -67.2 (c 1.06, $CHCl_3$); FTIR (neat): 2981, 1717, 1447, 1382, 1367, 1252, 1193, 1158, 1096, 1037 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 5H), 4.18-4.02 (m, 2H), 3.93-3.77 (m, 2H), 2.73 (dd, *J* = 8.5, 6.6 Hz, 1H), 2.02 (dd, *J* = 6.5, 4.5 Hz, 1H),

1.87 (dd, J = 8.5, 4.4 Hz, 1H), 1.16 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.1, 168.9, 134.6, 130.6, 127.8, 127.5, 61.6, 60.6, 36.7, 29.5, 19.03, 13.9, 13.7; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{15}H_{19}O_4$, 263.1291; found, 263.1278; HPLC analysis: 85% ee (*SS*-Whelk, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 16.11 min, minor; t_R = 22.03 min, major).



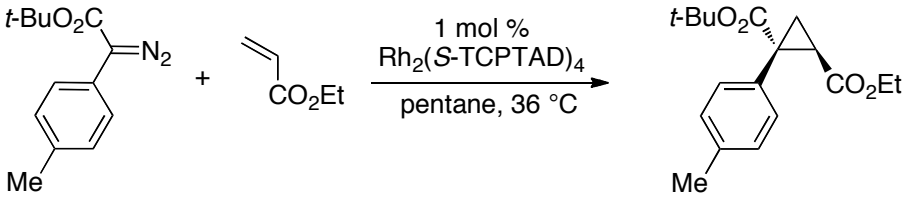
4c **2** **5c**

(1*R*,2*R*)-1-butyl 2-ethyl 1-phenylcyclopropane-1,2-dicarboxylate (5c): Following the general procedure, the reaction of ethyl acrylate (0.27 mL, 2.48 mmol, 5 equiv), *n*-butyl phenyldiazoacetate (110.0 mg, 0.50 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.5 mg, 0.0050 mmol, 0.01 equiv) afforded the product as a colorless oil (123.3 mg, 84% yield) after purification by flash chromatography. R_f = 0.30 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -64.1 (c 1.08, $CHCl_3$); FTIR (neat): 2961, 2874, 1720, 1498, 1448, 1380, 1255, 1193, 1164, 1100, 1037 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 5H), 4.13-3.96 (m, 2H), 3.94-3.78 (m, 2H), 2.73 (dd, J = 8.4, 6.6 Hz, 1H), 2.02 (dd, J = 6.5, 4.5 Hz, 1H), 1.91-1.83 (m, 1H), 1.51 (tt, J = 7.2, 6.8 Hz, 2H), 1.24 (qt, J = 7.6, 7.2 Hz, 2H), 0.97 (t, J = 7.1 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.1, 168.9, 134.7, 130.4, 127.8, 127.5, 65.4, 60.6, 36.7, 30.3, 29.4, 19.0, 18.8, 13.7, 13.5; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{22}O_4{}^{23}Na_1$, 313.1410; found, 313.1310; HPLC analysis: 81% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 9.64 min, minor; t_R = 10.74 min, major).



4d **2** **5d**

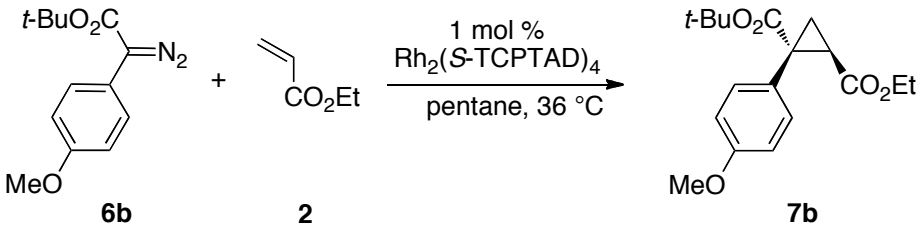
(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-phenylcyclopropane-1,2-dicarboxylate (5d): Following the general procedure, the reaction of ethyl acrylate (0.27 mL, 2.48 mmol, 5 equiv), *t*-butyl phenyldiazoacetate (114.8 mg, 0.53 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (9.8 mg, 0.0047 mmol, 0.01 equiv) afforded the product as a colorless oil (118.9 mg, 78% yield) after purification by flash chromatography. R_f = 0.30 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -61.9 (c 1.00, $CHCl_3$); FTIR (neat): 2979, 1713, 1448, 1393, 1382, 1368, 1254, 1196, 1151, 1098 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 3.92-3.78 (m, 2H), 2.66 (dd, *J* = 8.4, 6.5 Hz, 1H), 1.97 (dd, *J* = 6.4, 4.4 Hz, 1H), 1.81 (dd, *J* = 8.4, 4.4 Hz, 1H), 1.37 (s, 9H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 171.0, 169.3, 135.19, 130.5, 127.8, 127.3, 81.6, 60.6, 37.7, 29.0, 27.8, 18.7, 13.8; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{23}O_4$, 291.1591; found, 291.1592; HPLC analysis: 91% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 6.16 min, major; t_R = 6.96 min, minor).



6a **2** **7a**

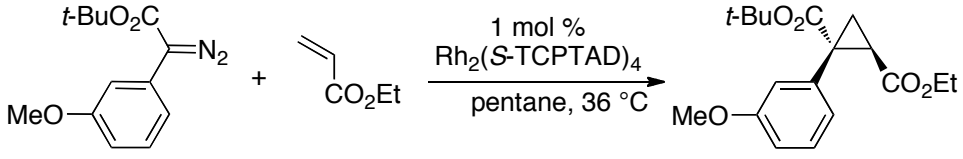
(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-(*p*-tolyl)cyclopropane-1,2-dicarboxylate (7a): Following the general procedure, the reaction of ethyl acrylate (0.16 mL, 1.47 mmol, 5

equiv), *t*-butyl *p*-methylphenyldiazoacetate (72.2 mg, 0.31 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.6 mg, 0.0031 mmol, 0.01 equiv) afforded the product as a colorless oil (57.7 mg, 61% yield) after purification by flash chromatography. R_f = 0.39 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -58.1 (c 1.02, $CHCl_3$); FTIR (neat): 2979, 1714, 1518, 1457, 1393, 1381, 1368, 1271, 1254, 1196, 1153, 1098, 1035 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 3.95-3.81 (m, 2H), 2.63 (dd, J = 8.4, 6.4 Hz, 1H), 2.31 (s, 3H), 1.94 (dd, J = 6.4, 4.4 Hz, 1H), 1.79 (dd, J = 8.4, 4.4 Hz, 1H), 1.37 (s, 9H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 169.3, 136.8, 132.0, 130.2, 128.5, 81.4, 60.6, 37.4, 28.9, 27.8, 21.1, 18.6, 13.8; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{25}O_4$, 305.1747; found, 305.1751; HPLC analysis: 89% ee (AD-H, hexane, 1.0 mL/min, λ = 230 nm, t_R = 5.39 min, minor; t_R = 6.31 min, major).



(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-(4-methoxyphenyl)cyclopropane-1,2-dicarboxylate (7b): Following the general procedure, the reaction of ethyl acrylate (0.27 mL, 2.48 mmol, 5 equiv), *t*-butyl *p*-methoxyphenyldiazoacetate (124.1 mg, 0.50 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.4 mg, 0.0049 mmol, 0.01 equiv) afforded the product as a colorless oil (143.0 mg, 89% yield) after purification by flash chromatography. R_f = 0.16 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -46.5 (c 0.97, $CHCl_3$); FTIR (neat): 2979, 1715, 1614, 1516, 1458, 1393, 1382, 1368, 1273, 1246, 1197, 1152, 1098 cm^{-1}; ^{1}H-NMR (600

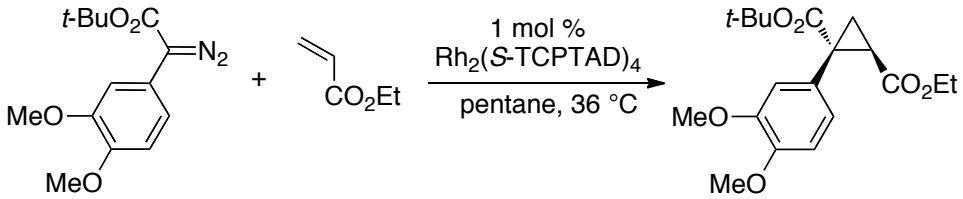
MHz, $CDCl_3$) δ 7.16 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 3.94-3.83 (m, 2H), 3.78 (s, 3H), 2.62 (dd, J = 8.3, 6.4 Hz, 1H), 1.93 (dd, J = 6.4, 4.4 Hz, 1H), 1.79 (dd, J = 8.4, 4.3 Hz, 1H), 1.37 (s, 9H), 1.00 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 169.1, 158.5, 131.3, 127.0, 113.0, 81.2, 60.4, 54.9, 36.8, 28.9, 27.6, 18.6, 13.8; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{25}O_5$, 321.1697; found, 321.1696; HPLC analysis: 88% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 230 nm, t_R = 9.88 min, minor; t_R = 11.87 min, major).



6c **2** **7c**

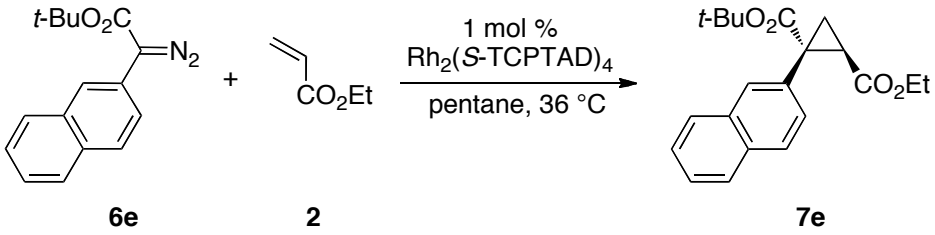
(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-(3-methoxyphenyl)cyclopropane-1,2-dicarboxylate (7c): Following the general procedure, the reaction of ethyl acrylate (0.16 mL, 1.47 mmol, 5 equiv), *t*-butyl *p*-methylphenyldiazoacetate (76.6 mg, 0.31 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.6 mg, 0.0031 mmol, 0.01 equiv) afforded the product as a colorless oil (74.4 mg, 75% yield) after purification by flash chromatography. R_f = 0.17 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -58.4 (c 1.02, $CHCl_3$); FTIR (neat): 2979, 1716, 1603, 1585, 1455, 1382, 1273, 1256, 1238, 1195, 1154, 1102 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.18 (td, J = 7.7, 0.7 Hz, 1H), 6.84 (dt, J = 7.8, 1.2, 1H), 6.80-6.77 (m, 2H), 3.92-3.84 (m, *2*H), 3.78 (s, 3H), 2.64 (dd, J = 8.4, 6.5 Hz, 1H), 1.95 (dd, J = 6.4, 4.4 Hz, 1H), 1.79 (dd, J = 8.4, 4.4 Hz, 1H), 1.37 (s, 9H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 169.2, 159.0, 136.6, 128.6, 122.9, 116.1, 112.8, 81.5, 60.6, 55.0, 37.6, 28.9, 27.7, 18.7, 13.8; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{18}H_{24}O_5{}^{23}Na_1$,

343.1516; found, 343.1517; HPLC analysis: 94% ee (AD-H, hexane, 1.0 mL/min, λ = 230 nm, t_R = 9.34 min, minor; t_R = 10.17 min, major).



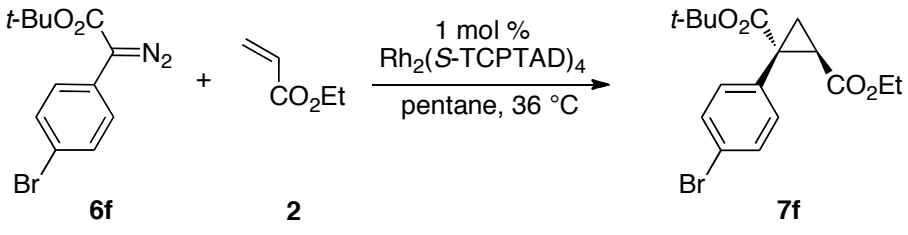
6d **2** **7d**

(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-(3,4-dimethoxyphenyl)cyclopropane-1,2-dicarboxylate (7d): Following the general procedure, the reaction of ethyl acrylate (0.27 mL, 2.47 mmol, 5 equiv), *t*-butyl 3,4-dimethoxyphenyldiazoacetate (140.5 mg, 0.50 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.8 mg, 0.0051 mmol, 0.01 equiv) afforded the product as a colorless oil (161.8 mg, 91% yield) after purification by flash chromatography. R_f = 0.23 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -52.0 (c 1.00, $CHCl_3$); FTIR (neat): 2978, 1713, 1590, 1518, 1464, 1413, 1393, 1381, 1368, 1251, 1227, 1194, 1140, 1097, 1028 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.81 (dd, J = 8.2, 1.9 Hz, 1H), 6.78-6.76 (m, 2H), 3.94-3.86 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.63 (dd, J = 8.4, 6.4 Hz, 1H), 1.95 (dd, J = 6.4, 4.4 Hz, 1H), 1.79 (dd, J = 8.4, 4.4 Hz, 1H), 1.38 (s, 9H), 1.01 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 169.1, 148.0, 148.0, 127.4, 122.5, 113.4, 110.1, 81.3, 60.5, 55.53, 55.46, 37.2, 28.9, 27.6, 18.6, 13.8; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{19}H_{26}O_6{}^{23}Na_1$, 373.1622; found, 373.1621; HPLC analysis: 93% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 19.79 min, major; t_R = 26.90 min, minor).



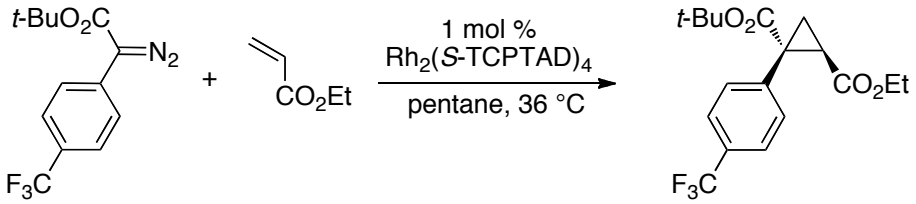
6e **2** **7e**

(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-(naphthalen-2-yl)cyclopropane-1,2-dicarboxylate (7e): Following the general procedure, the reaction of ethyl acrylate (0.27 mL, 2.47 mmol, 5 equiv), *t*-butyl 2-naphtyldiazoacetate (127.8 mg, 0.48 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.6 mg, 0.0050 mmol, 0.01 equiv) afforded the product as a colorless oil (140.2 mg, 86% yield) after purification by flash chromatography. R_f = 0.23 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -16.2 (c 0.95, $CHCl_3$); FTIR (neat): 2979, 2360, 1716, 1457, 1394, 1382, 1369, 1276, 1256, 1190, 1153, 1130 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 9.2, 4.5 Hz, 2H), 7.75-7.72 (m, 2H), 7.47-7.41 (m, 2H), 7.36 (dd, J = 8.4, 1.8 Hz, 1H), 3.89-3.71 (m, 2H), 2.73 (dd, J = 8.4, 6.4 Hz, 1H), 2.10 (dd, J = 6.4, 4.4 Hz, 1H), 1.90 (dd, J = 8.4, 4.4 Hz, 1H), 1.36 (s, 9H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 169.1, 133.0, 132.64, 132.60, 129.2, 128.5, 127.7, 127.5, 127.2, 125.7 (2xC), 81.7, 60.6, 37.8, 29.1, 27.7, 18.8, 13.7; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{21}H_{24}O_4{}^{23}Na_1$, 363.1567; found, 363.1567; HPLC analysis: 94% ee (AD-H, hexane, 1.0 mL/min, λ = 230 nm, t_R = 8.10 min, major; t_R = 9.17 min, minor).



6f **2** **7f**

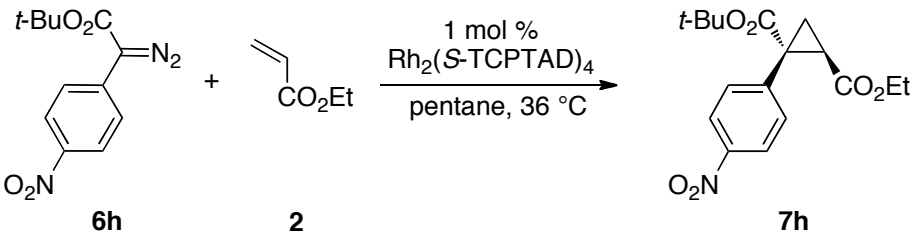
(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-(4-bromophenyl)cyclopropane-1,2-dicarboxylate (7f): Following the general procedure, the reaction of ethyl acrylate (0.27 mL, 2.47 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (151.3 mg, 0.51 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.6 mg, 0.0050 mmol, 0.01 equiv) afforded the product as a colorless oil (166.7 mg, 89% yield) after purification by flash chromatography. R_f = 0.39 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -38.4 (c 0.92, $CHCl_3$); FTIR (neat): 2979, 1715, 1490, 1394, 1381, 1368, 1276, 1254, 1197, 1150, 1094, 1033, 1011 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 3.96-3.82 (m, 2H), 2.65 (dd, J = 8.4, 6.5 Hz, 1H), 1.92 (dd, J = 6.4, 4.5 Hz, 1H), 1.82 (dd, J = 8.5, 4.5 Hz, 1H), 1.37 (s, 9H), 1.01 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.7, 168.9, 147.2, 143.0, 131.5, 123.1, 82.6, 61.1, 37.4, 29.2, 27.8, 19.1, 14.0; HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd. for $C_{17}H_{25}O_4N_1{}^{79}Br_1$, 386.0962; found, 386.0962; HPLC analysis: 93% ee (AD-H, hexane, 0.25 mL/min, λ = 230 nm, t_R = 22.13 min, minor; t_R = 24.31 min, major).



6g **2** **7g**

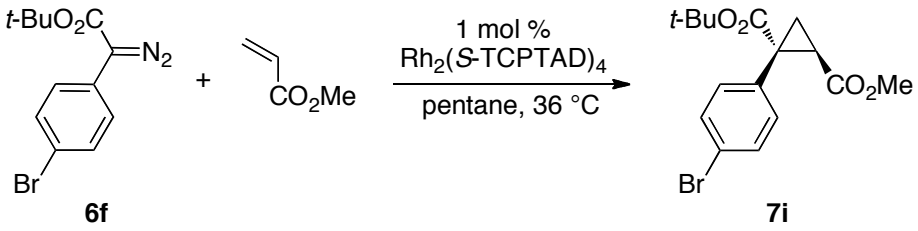
(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-(4-(trifluoromethyl)phenyl)cyclopropane-1,2-dicarboxylate (7g): Following the general procedure, the reaction of ethyl acrylate (0.16 mL, 1.47 mmol, 5 equiv), *t*-butyl *p*-trifluoromethyphenyldiazoacetate (87.5 mg, 0.31 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.1 mg, 0.0029 mmol, 0.01 equiv) afforded the product as a colorless oil (70.1 mg, 64% yield) after purification by flash

chromatography. R_f = 0.33 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -43.7 (c 0.92, $CHCl_3$); FTIR (neat): 2982, 1720, 1620, 1458, 1395, 1370, 1325, 1275, 1201, 1158, 1126, 1067, 1035, 1019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.88 (qd, J = 7.1, 2.6 Hz, 2H), 2.69 (dd, J = 8.4, 6.5 Hz, 1H), 1.98 (dd, J = 6.4, 4.5 Hz, 1H), 1.87 (dd, J = 8.5, 4.5 Hz, 1H), 1.37 (s, 9H), 0.97 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.2, 169.0, 139.4, 130.9, 129.50 (q, J = 32 Hz), 122.9 (q, J = 269 Hz), 124.8 (q, J = 4 Hz), 82.2, 60.9, 37.4, 291, 27.8, 18.8, 13.8; HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd. for $C_{18}H_{25}O_4N_1F_3$, 376.1730; found, 376.1733; HPLC analysis: 91% ee (*SS*-Whelk, 1% *i*-PrOH hexane, 1 mL/min, λ = 210 nm, t_R = 6.21 min, minor; t_R = 7.61 min, major).

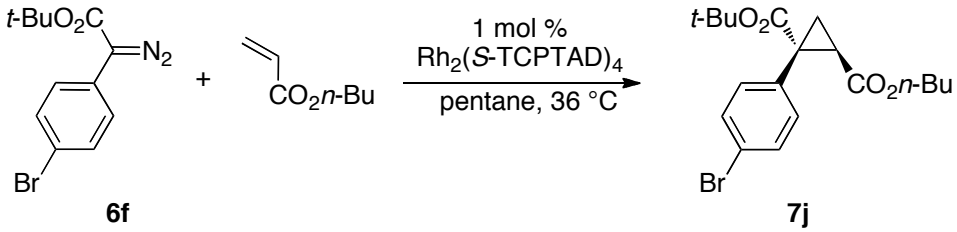


(1*R*,2*R*)-1-*tert*-butyl 2-ethyl 1-(4-nitrophenyl)cyclopropane-1,2-dicarboxylate (7h): Following the general procedure, the reaction of ethyl acrylate (0.17 mL, 1.56 mmol, 5 equiv), *t*-butyl *p*-nitrophenyldiazoacetate (75.3 mg, 0.29 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.6 mg, 0.0031 mmol, 0.01 equiv) afforded the product as a yellow oil (21.5 mg, 22% yield) after purification by flash chromatography. R_f = 0.29 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -9.5 (c 1.02, $CHCl_3$); FTIR (neat): 2980, 2358, 1719, 1603, 1522, 1457, 1394, 1382, 1369, 1348, 1294, 1257, 1200, 1154, 1096 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 3.98-3.85 (m, 2H), 2.73 (dd, J = 8.5, 6.5 Hz, 1H), 1.98 (dd, J = 6.4, 4.6 Hz, 1H), 1.92 (dd, J = 8.5, 4.6 Hz, 1H), 1.37

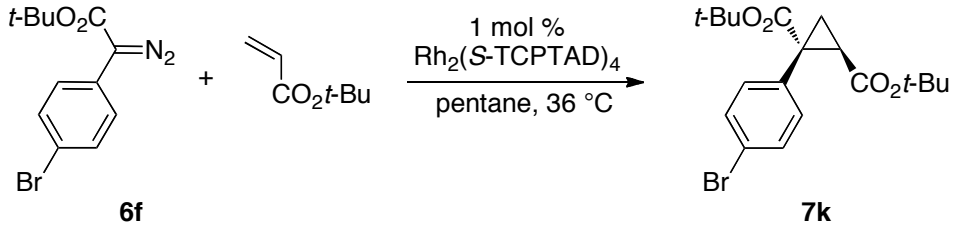
(s, 9H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.7, 168.9, 147.2, 143.0, 131.5, 123.1, 82.6, 61.1, 37.4, 29.2, 27.8, 19.1, 14.0; HRMS (ESI) *m/z*: $[M-H]^-$ calcd. for $C_{17}H_{20}O_6N_1$, 334.1296; found, 334.1297; HPLC analysis: 91% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 13.22 min, minor; t_R = 17.75 min, major).



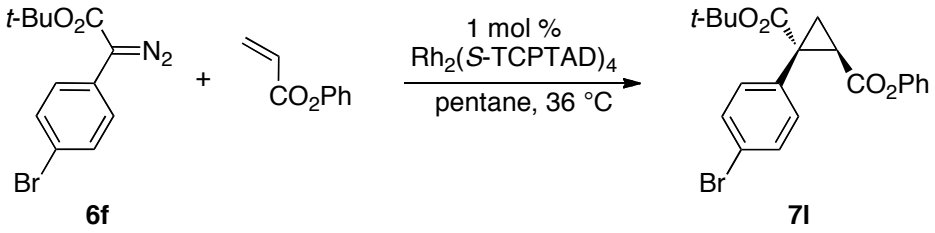
(1*R*,2*R*)-1-*tert*-butyl 2-methyl 1-(4-bromophenyl)cyclopropane-1,2-dicarboxylate (7i): Following the general procedure, the reaction of methyl acrylate (0.14 mL, 1.55 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (91.3 mg, 0.31 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.2 mg, 0.0029 mmol, 0.01 equiv) afforded the product as a colorless oil (102.2 mg, 89% yield) after purification by flash chromatography. R_f = 0.31 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -44.5 (c 1.06, $CHCl_3$); FTIR (neat): 2978, 1716, 1439, 1383, 1278, 1256, 1205, 1154, 1090, 1012 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 3.46 (s, 3H), 2.67 (dd, J = 8.4, 6.5 Hz, 1H), 1.92 (dd, J = 6.4, 4.5 Hz, 1H), 1.83 (dd, J = 8.5, 4.5 Hz, 1H), 1.36 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 169.5, 134.3, 132.1, 131.0, 121.5, 82.0, 52.0, 37.2, 28.8, 27.8, 18.8; HRMS (APCI) *m/z*: $[M-H]^-$ calcd. for $C_{16}H_{18}O_4{}^{79}Br_1$, 353.0394; found, 353.0396; HPLC analysis: 96% ee (AD-H, hexane, 0.25 mL/min, λ = 230 nm, t_R = 26.00 min, major; t_R = 32.15 min, minor).



(1*R*,2*R*)-1-*tert*-butyl 2-butyl 1-(4-bromophenyl)cyclopropane-1,2-dicarboxylate (7j): Following the general procedure, the reaction of *n*-butyl acrylate (0.22 mL, 1.53 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (94.6 mg, 0.32 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.5 mg, 0.0031 mmol, 0.01 equiv) afforded the product as a colorless oil (102.3 mg, 81% yield) after purification by flash chromatography. R_f = 0.30 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -32.3 (c 1.06, $CHCl_3$); FTIR (neat): 2961, 1718, 1490, 1457, 1395, 1369, 1277, 1256, 1200, 1155, 1094, 1070, 1012 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 3.88-3.77 (m, 2H), 2.65 (dd, J = 8.4, 6.5 Hz, 1H), 1.91 (dd, J = 6.4, 4.5 Hz, 1H), 1.82 (dd, J = 8.5, 4.4 Hz, 1H), 1.37 (s, 9H), 1.35-1.29 (m, 2H), 1.24-1.12 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 169.1, 134.5, 132.4, 131.0, 121.4, 81.9, 64.7, 37.1, 30.4, 29.0, 27.8, 18.9, 18.7, 13.5; HRMS (APCI) *m/z*: $[M-H]^-$ calcd. for $C_{19}H_{24}O_4{}^{79}Br_1$, 395.0863; found, 395.0865; HPLC analysis: 93% ee (AD-H, hexane, 1.0 mL/min, λ = 230 nm, t_R = 5.95 min, minor; t_R = 6.84 min, major).

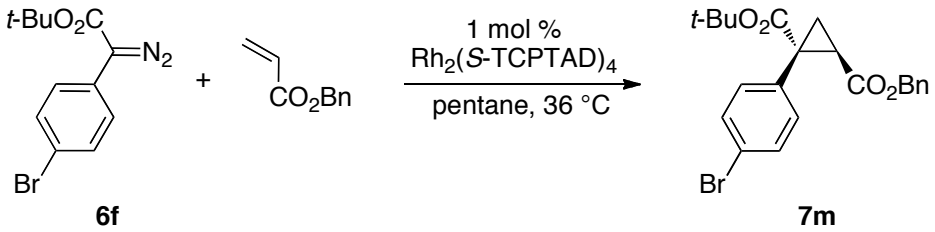


(1*R*,2*R*)-di-*tert*-butyl 1-(4-bromophenyl)cyclopropane-1,2-dicarboxylate (7k): Following the general procedure, the reaction of *t*-butyl acrylate (0.37 mL, 2.53 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (137.3 mg, 0.46 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.4 mg, 0.0049 mmol, 0.01 equiv) afforded the product as a white solid (157.1 mg, 86% yield) after purification by flash chromatography. m.p. 51-53 °C; R_f = 0.30 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -32.6 (c 0.98, $CHCl_3$); FTIR (neat): 2978, 2932, 1716, 1490, 1457, 1392, 1368, 1279, 1255, 1217, 1145, 1140, 1095, 1012 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 2.55 (dd, J = 8.4, 6.5 Hz, 1H), 1.85 (dd, J = 6.5, 4.4 Hz, 1H), 1.76 (dd, J = 8.5, 4.4 Hz, 1H), 1.37 (s, 9H), 1.19 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 168.0, 134.5, 132.4, 130.8, 121.3, 81.8, 81.0, 37.0, 30.0, 27.8, 27.7, 18.7; HRMS (ESI) *m/z*: $[M+K]^+$ calcd. for $C_{19}H_{25}O_4{}^{79}Br_1{}^{39}K_1$, 435.0568; found, 435.0569; HPLC analysis: 93% ee (AD-H, hexane, 0.25 mL/min, λ = 230 nm, t_R = 17.65 min, minor; t_R = 19.09 min, major).



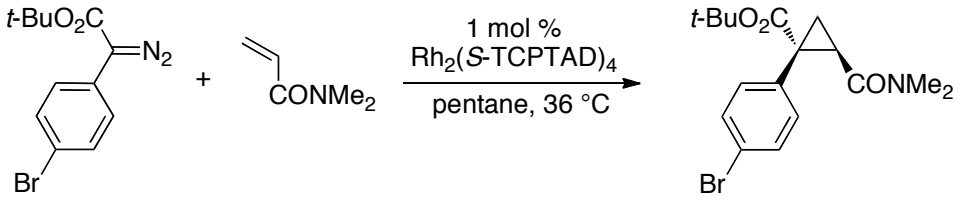
(1*R*,2*R*)-1-*tert*-butyl 2-phenyl 1-(4-bromophenyl)cyclopropane-1,2-dicarboxylate (7l): Following the general procedure, the reaction of phenyl acrylate (219.7 mg, 1.48 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (91.6 mg, 0.31 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.8 mg, 0.0032 mmol, 0.01 equiv) afforded the product as a white solid (94.6 mg, 74% yield) after purification by flash chromatography. m.p. 135-137 °C; R_f = 0.40 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -54.8 (c 1.01, $CHCl_3$); FTIR (neat): 2978,

1757, 1717, 1593, 1491, 1457, 1382, 1369, 1279, 1254, 1198, 1155, 1140, 1107, 1093, 1071, 1012 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.31-7.21 (m, 4H), 7.15 (t, J = 7.4 Hz, 1H), 6.66 (d, J = 7.7 Hz, 2H), 2.90 (dd, J = 8.4, 6.4 Hz, 1H), 2.10 (dd, J = 6.4, 4.7 Hz, 1H), 1.95 (dd, J = 8.4, 4.7 Hz, 1H), 1.40 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.2, 167.6, 150.3, 134.1, 132.4, 131.2, 129.3, 125.8, 121.8, 121.1, 82.3, 37.8, 29.0, 27.9, 19.0; HRMS (APCI) *m/z*: $[M-H]^-$ calcd. for $C_{21}H_{20}O_4{}^{79}Br_1$, 415.0550; found, 415.0551; HPLC analysis: 93% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 7.99 min, minor; t_R = 13.14 min, major).

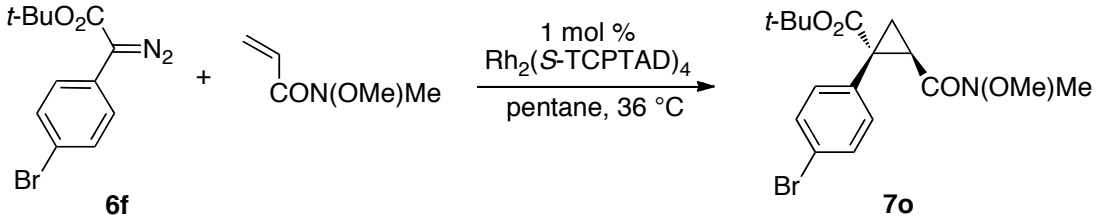


(1*R*,2*R*)-2-benzyl 1-*tert*-butyl 1-(4-bromophenyl)cyclopropane-1,2-dicarboxylate (7m): Following the general procedure, the reaction of benzyl acrylate (0.23 mL, 1.50 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (87.8 mg, 0.30 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.3 mg, 0.0030 mmol, 0.01 equiv) afforded the product as a colorless oil (59.3 mg, 47% yield) after purification by flash chromatography. R_f = 0.30 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -11.5 (c 0.91, $CHCl_3$); FTIR (neat): 2977, 1716, 1490, 1456, 1393, 1368, 1256, 1191, 1152, 1089, 1012 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 5H), 7.13-7.08 (m, 2H), 7.03 (d, J = 8.4 Hz, 2H), 4.91 (d, J = 12.1 Hz, 1H), 4.82 (d, J = 12.1 Hz, 1H), 2.70 (dd, J = 8.4, 6.5 Hz, 1H), 1.92 (dd, J = 6.4, 4.5 Hz, 1H), 1.82 (dd, J = 8.4, 4.5 Hz, 1H), 1.35 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.3, 169.0, 135.3, 134.2, 132.1, 131.1, 128.6, 128.5, 128.3, 121.5, 82.0, 66.9, 37.4,

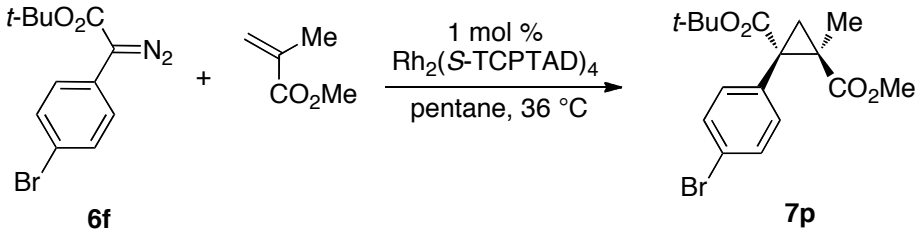
29.0, 27.8, 18.9; HRMS (APCI) *m/z*: $[M-H]^-$ calcd. for $C_{22}H_{22}O_4{}^{79}Br_1$, 429.0707; found, 429.0707; HPLC analysis: 90% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 7.69 min, minor; t_R = 13.60 min, major).



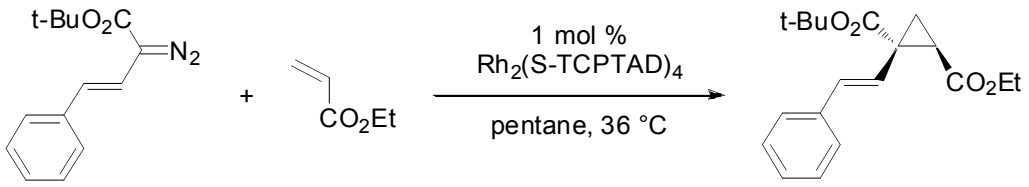
(1*R*,2*R*)-*tert*-butyl 1-(4-bromophenyl)-2-(dimethylcarbamoyl)cyclopropanecarboxylate (7n): Following the general procedure, the reaction of *N,N*-dimethylacrylamide (0.15 mL, 1.46 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (93.9 mg, 0.32 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (6.7 mg, 0.0032 mmol, 0.01 equiv) afforded the product as a white solid (62.2 mg, 52% yield) after purification by flash chromatography. m.p. 137-139 °C; R_f = 0.40 (hexanes:acetone = 2:1); $[\alpha]_D^{20}$ +41.6 (c 1.23, $CHCl_3$); FTIR (neat): 2977, 1714, 1652, 1490, 1457, 1399, 1368, 1341, 1279, 1256, 1156, 1084, 1011 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 3.21 (s, 3H), 2.79 (s, 3H), 2.78-2.74 (m, 1H), 2.13 (dd, J = 6.3, 4.3 Hz, 1H), 1.69 (dd, J = 8.5, 4.3 Hz, 1H), 1.38 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 167.1, 134.2, 131.8, 131.0, 121.3, 81.7, 37.1, 36.6, 35.5, 28.6, 27.8, 18.0; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{23}O_3N_1{}^{79}Br_1$, 368.0856; found, 368.0857; HPLC analysis: 94% ee (AD-H, 3% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 17.88 min, minor; t_R = 21.63 min, major).



(1*R*,2*R*)-*tert*-butyl 1-(4-bromophenyl)-2-(methoxy(methyl)carbamoyl)cyclopropane-carboxylate (7o): Following the general procedure, the reaction of *N,O*-dimethylacrylamide (286.5 mg, 2.49 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (156.8 mg, 0.53 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.6 mg, 0.0050 mmol, 0.01 equiv) afforded the product as a white solid (119.1 mg, 59% yield) after purification by flash chromatography. m.p. 100-102 °C; R_f = 0.20 (hexanes:ethyl acetate = 4:1); $[\alpha]_D^{20}$ +65.7 (c 1.05, $CHCl_3$); FTIR (neat): 2976, 2935, 1716, 1670, 1490, 1459, 1415, 1392, 1368, 1323, 1275, 1256, 1155, 1116, 1082, 1012 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H), 3.09-2.95 (m, 4H), 2.02 (dd, J =6.4, 4.3 Hz, 1H), 1.79 (dd, J = 8.4, 4.3 Hz, 1H), 1.38 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.0, 169.5, 134.3, 132.3, 130.9, 121.3, 81.6, 61.6, 36.9, 32.8, 27.8, 27.4, 17.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{17}H_{23}O_4N_1{}^{79}Br_1$, 384.0805; found, 384.0806; HPLC analysis: 92% ee (AD-H, 5% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 7.20 min, minor; t_R = 10.51 min, major).



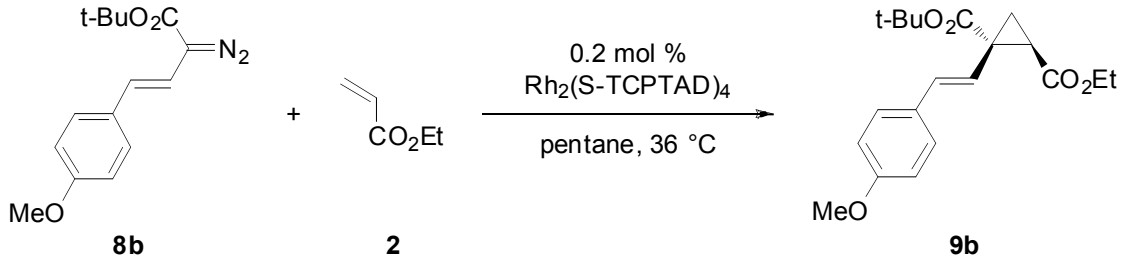
(1*S*,2*R*)-1-*tert*-butyl 2-methyl 1-(4-bromophenyl)-2-methylcyclopropane-1,2-dicarboxylate (7p): Following the general procedure, the reaction of metyl methacrylate (0.27 mL, 2.52 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (145.3 mg, 0.49 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.2 mg, 0.0049 mmol, 0.01 equiv) afforded the product as a white solid (98.6 mg, 55% yield) after purification by flash chromatography. m.p. 82-84 °C; R_f = 0.37 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ +31.0 (c 1.08, $CHCl_3$); FTIR (neat): 2976, 1717, 1489, 1457, 1436, 1394, 1368, 1320, 1275, 1254, 1195, 1158, 1116, 1101, 1073, 1011 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 3.32 (s, 3H), 2.03 (d, J = 5.2 Hz, 1H), 1.75 (d, J = 5.2 Hz, 1H), 1.50 (s, 3H), 1.38 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.4, 168.2, 135.9, 132.0, 130.7, 121.3, 82.0, 51.8, 42.2, 32.1, 27.8, 21.9, 15.7; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{21}O_4{}^{79}Br_1{}^{23}Na_1$, 391.0515; found, 391.0518; HPLC analysis: 77% ee (AD-H, hexane, 1.0 mL/min, λ = 230 nm, t_R = 5.20 min, major; t_R = 5.74 min, minor).



8a **2** **9a**

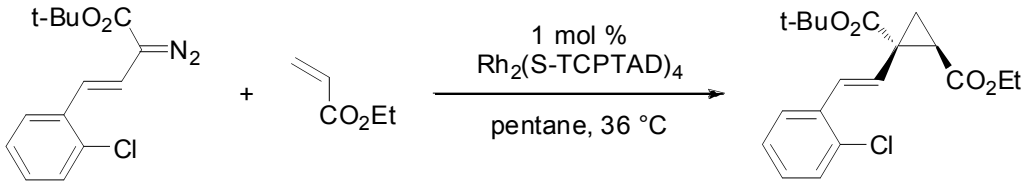
(1*S*,2*R*)-1-*tert*-butyl 2-ethyl 1-((*E*)-styryl)cyclopropane-1,2-dicarboxylate (9a): Prepared using the standard conditions with ethyl acrylate (0.27 mL, 2.5 mmol, 5.0 equiv), Rh_2(*S*-TCPTAD)$_4$ (11 mg, 1 mol %), in pentane (3 mL) and diazo **8a** (122 mg, 0.5 mmol, 1.0 equiv) in pentane (3 mL). The product was purified by column chromatography (8% Et_2O in pentane) to give the product as a green tinged oil (131 mg, 89% yield) in 97% ee. $[\alpha]_D^{20}$: -70.6 (c. 2.0, $CHCl_3$); ^{1}H-NMR (600 MHz; $CDCl_3$) δ 7.36

(d, 2H, J = 7.5 Hz), 7.29 (t, 2H, J = 7.5 Hz), 7.21 (t, 1H, J = 7.5 Hz), 6.53 (d, 1H, J = 16.1 Hz), 6.38 (d, 1H, J = 16.1 Hz), 4.09-4.01 (m, 2H), 2.50-2.47 (m, 1H), 1.90-1.87 (m, 1H), 1.74 (dd, 1H, J = 8.5, 4.6 Hz), 1.47 (s, 9H), 1.15 (t, 3H, J = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.0, 169.0, 137.1, 133.5, 128.6, 127.7, 126.6, 122.1, 82.0, 61.1, 34.2, 31, 28.2, 18.2, 14.4; IR (film): 2979, 1716, 1251, 1142 cm^{-1}; HRMS (NSI) calcd. for $C_{19}H_{24}O_4Na$ ([M+Na]$^+$) 339.1567, found 339.1568; The ee was determined by chiral HPLC: AD-H column, 1 mL/min, 0.7 % iPrOH in hexanes. Major: 6.5 min, Minor: 8.1 min, 97 % ee.



(1*S*,2*R*)-1-*tert*-butyl 2-ethyl 1-((*E*)-4-methoxystyryl)cyclopropane-1,2-dicarboxylate (9b): Prepared using the standard conditions with ethyl acrylate (0.27 mL, 2.5 mmol, 5.0 equiv), Rh_2(*S*-TCPTAD)$_4$ (1.1 mg, 0.1 mol %), in pentane (3 mL) and diazo **8b** (137 mg, 0.5 mmol, 1.0 equiv) in pentane (3 mL). After the diazo addition was complete another 1.1 mg (0.1 mol %) of the rhodium catalyst was added, and the mixture stirred at reflux for 1 hour before removing volatiles. The product was purified by column chromatography (10% Et_2O in pentane) to give the product as a yellowish oil (134 mg, 77% yield) in 97% ee. $[\alpha]_D^{20}$: -62.2 (c. 1.8, $CHCl_3$); ^{1}H-NMR (600 MHz; $CDCl_3$) δ 7.29 (d, 2H, J = 8.6 Hz), 6.82 (d, 2H, J = 8.6 Hz), 6.46 (d, 1H, J = 16.0 Hz), 6.23 (d, 1H, J = 16.0 Hz), 4.10-4.02 (m, 2H), 3.79 (s, 3H), 2.46 (dd, 1H, J = 8.5, 6.7 Hz), 1.87 (dd, 1H, J

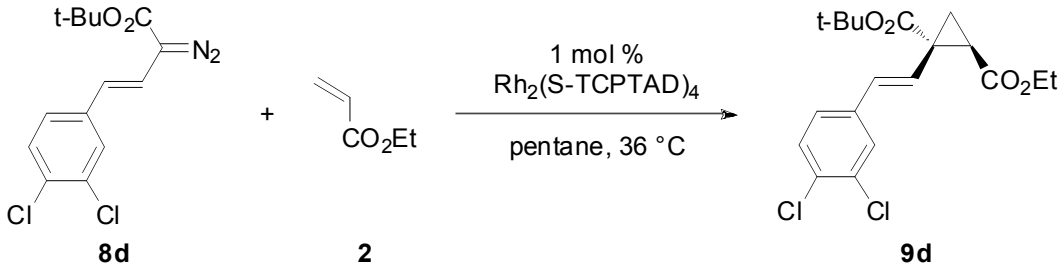
= 6.7, 4.7 Hz), 1.71 (dd, 1H, *J* = 8.5, 4.7 Hz), 1.46 (s, 9H), 1.14 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 169.0, 159.3, 123.9, 129.9, 127.7, 119.7, 114.0, 81.9, 61.0, 55.4, 34.3, 30.9, 28.1, 18.1, 14.4; IR (neat): 2979, 1715, 1511, 1246 cm^{-1}; HRMS (NSI) calcd. for $C_{20}H_{27}O_5$ ($[M+H]^+$) 347.1853, found 347.1856; The ee was determined by chiral HPLC: ADH column, 0.8 mL/min, 1 % iPrOH in hexanes. Major: 13.2 min, Minor: 14.0 min, 97 % ee.



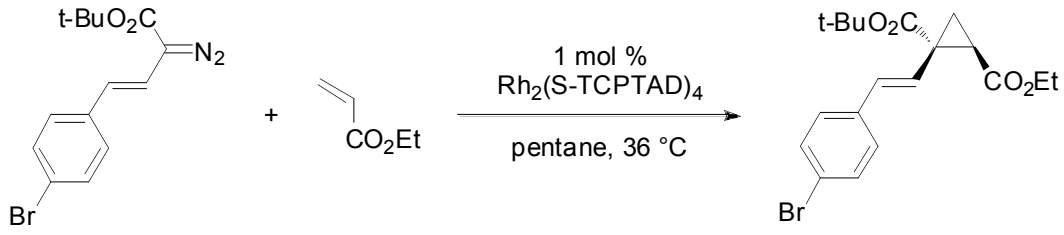
8c **2** **9c**

(1*S*,2*R*)-1-*tert*-butyl 2-ethyl 1-((*E*)-2-chlorostyryl)cyclopropane-1,2-dicarboxylate (9c): Prepared using the standard conditions with ethyl acrylate (0.27 mL, 2.5 mmol, 5.0 equiv), Rh_2(*S*-TCPTAD)$_4$ (11 mg, 1 mol %), in pentane (3 mL) and diazo **8c** (139 mg, 0.5 mmol, 1.0 equiv) in pentane (3 mL). The product was purified by column chromatography (6% Et_2O in pentane) to give the product as a yellowish oil (141 mg, 81% yield) in 91% ee. $[\alpha]_D^{20}$: -66.2 (c. 1.5, $CHCl_3$); ^{1}H-NMR (600 MHz; $CDCl_3$) *δ* 7.49 (dd, 1H, *J* = 7.6, 1.7 Hz), 7.33 (dd, 1H, *J* = 7.6, 1.4 Hz), 7.2 (td, 1H, *J* = 7.6, 1.4 Hz), 7.16 (td, 1H, *J* = 7.6, 1.7 Hz), 6.69 (d, 1H, *J* = 16.0 Hz), 6.36 (d, 1H, *J* = 16.0 Hz), 4.13-4.06 (m, 2H), 2.52 (d, 1H, *J* = 8.6, 6.7 Hz), 1.90 (dd, 1H, *J* = 6.7, 4.8 Hz), 1.78 (dd, 1H, *J* = 8.6, 4.8 Hz), 1.49 (s, 9H), 1.19 (t, 3H, *J* = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ* 170.7, 169.1, 135.4, 133.2, 129.9, 129.8, 128.8, 127.0, 125.4, 82.2, 61.2, 34.4, 30.9, 28.2, 18.9, 14.5; IR (neat): 2979, 1716, 1250, 1143 cm^{-1}; HRMS (NSI) calcd. for $C_{19}H_{24}O_4Cl$

([M+H]$^+$) 351.1358, found 351.1362; The ee was determined by chiral HPLC: ADH column, 1 mL/min, 0.7 % iPrOH in hexanes. Major: 5.7 min, Minor: 6.3 min, 91 % ee.

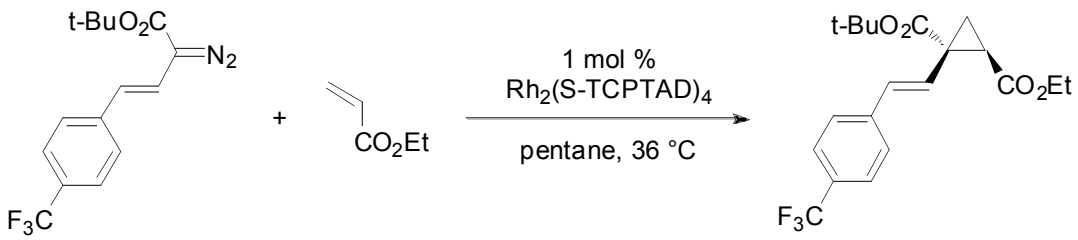


(1*S*,2*R*)-1-*tert*-butyl 2-ethyl 1-((*E*)-3,4-dichlorostyryl)cyclopropane-1,2-dicarboxylate (9d): Prepared using the standard conditions with ethyl acrylate (0.27 mL, 2.5 mmol, 5.0 equiv), Rh_2(*S*-TCPTAD)$_4$ (11 mg, 1 mol %), in pentane (3 mL) and diazo **8d** (157 mg, 0.5 mmol, 1.0 equiv) in pentane (3 mL). The product was purified by column chromatography (6% Et_2O in pentane) to give the product as a yellowish oil (149 mg, 77% yield) in 98% ee. $[\alpha]_D^{20}$: -60.8 (c. 1.5, $CHCl_3$); ^{1}H-NMR (600 MHz; $CDCl_3$) δ 7.42 (d, 1H, J = 1.9 Hz), 7.34 (d, 1H, J = 8.6 Hz), 7.17 (dd, 1H, J = 8.6, 1.9 Hz), 6.45 (d, 1H, J = 16.2 Hz), 6.38 (d, 1H, J = 16.2 Hz), 4.12-4.03 (m, 2H), 2.49 (dd, 1H, J = 8.5, 6.7 Hz), 1.84 (dd, 1H, J = 6.7, 4.7 Hz), 1.76 (dd, 1H, J = 8.5, 4.7 Hz), 1.46 (s, 9H), 1.17 (t, 3H, J = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.5, 168.9, 137.2, 132.8, 131.3, 131.2, 130.6, 128.2, 125.7, 124.4, 82.3, 61.2, 34.1, 31.0, 28.1, 18.5, 14.5; IR (neat): 2979, 1716, 1184, 1131 cm^{-1}; HRMS (NSI) calcd. for $C_{19}H_{23}O_4Cl_2$ ([M+H]$^+$) 385.0968, found 385.0974; The ee was determined by chiral HPLC: SS Whelk column, 1 mL/min, 1 % iPrOH in hexanes. Major: 15.2 min, Minor: 11.5 min, 98 % ee.



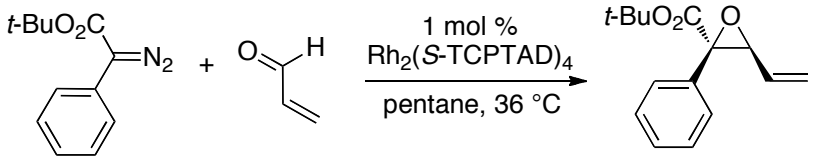
8e **2** **9e**

(1*S*,2*R*)-1-*tert*-butyl 2-ethyl 1-((*E*)-4-bromostyryl)cyclopropane-1,2-dicarboxylate (9e): Prepared using the standard conditions with ethyl acrylate (0.22 mL, 2.0 mmol, 5.0 equiv), Rh_2(*S*-TCPTAD)$_4$ (8 mg, 1 mol %), in pentane (3 mL) and diazo **8e** (129 mg, 0.4 mmol, 1.0 equiv) in pentane (3 mL). The product was purified by column chromatography (5% Et_2O in pentane) to give the product as a yellowish oil (136 mg, 86% yield) in 98% ee. $[\alpha]_D^{20}$: -49.3 (c. 1.8, $CHCl_3$); ^{1}H-NMR (600 MHz; $CDCl_3$) δ 7.42 (d, 2H, J = 8.4 Hz), 7.23 (d, 2H, J = 8.4 Hz), 6.49 (d, 1H, J = 15.7 Hz), 6.38 (d, 1H, J = 15.7 Hz), 4.11-4.02 (m, 2H), 2.50 (dd, 1H, J = 8.4, 6.7 Hz), 1.87 (dd, 1H, J = 6.7, 4.8 Hz), 1.76 (dd, 1H, J = 8.6, 4.8 Hz), 1.47 (s, 9H), 1.16 (t, 3H, J = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 169.0, 136.1, 132.3, 131.8, 128.1, 123.0, 121.5, 82.1, 61.2, 34.2, 31.0, 28.2, 18.4, 14.5; IR (neat): 2978, 1716, 1250, 1411 cm^{-1}; HRMS (NSI) calcd. for $C_{19}H_{23}O_4BrNa$ ([M+Na]$^+$) 417.0672, found 417.0674; The ee was determined by chiral HPLC: SS Whelk column, 1 mL/min, 1 % iPrOH in hexanes. Major: 16.8 min, Minor: 12.7 min, 98 % ee.



8f **2** **9f**

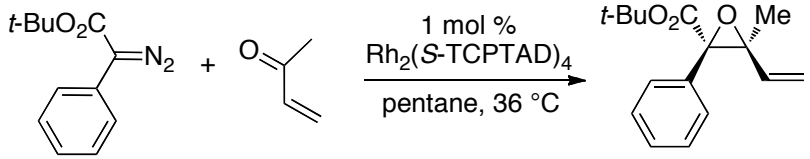
(1*S*,2*R*)-1-*tert*-butyl 2-ethyl 1-((*E*)-4-(trifluoromethyl)styryl)cyclopropane-1,2-dicarboxylate (9f): Prepared using the standard conditions with ethyl acrylate (0.27 mL, 2.5 mmol, 5.0 equiv), Rh_2(*S*-TCPTAD)$_4$ (11 mg, 1 mol %), in pentane (3 mL) and diazo **8f** (156 mg, 0.5 mmol, 1.0 equiv) in pentane (3 mL). The product was purified by column chromatography (5% Et_2O in pentane) to give the product as a pale yellow oil (164 mg, 85% yield) in 95% ee. $[\alpha]_D^{20}$: -59.4 (c. 1.62, $CHCl_3$); ^{1}H-NMR (600 MHz; $CDCl_3$) δ 7.51 (d, 2H, J = 8.2 Hz), 7.42 (d, 2H, J = 8.2 Hz), 6.57 (d, 1H, J = 16.1 Hz), 6.47 (d, 1H, J = 16.1 Hz), 4.12-4.03 (m, 2H), 2.50 (dd, 1H, J = 8.5, 6.7 Hz), 1.86 (dd, 1H, J = 6.7, 4.7 Hz), 1.76 (dd, 1H, J = 8.5, 4.7 Hz), 1.45 (s, 9H), 1.14 (t, 3H, J = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 168.9, 140.6, 132.1, 129.4 ($^2J_{CF}$ = 32.3 Hz), 126.7, 125.6 ($^3J_{CF}$ = 3.8 Hz), 125.1, 124.4 ($^1J_{CF}$ = 272 Hz), 82.3, 61.2, 34.1, 31.1, 28.1, 18.5, 14.4; IR (neat): 2981, 1717, 1322, 1121 cm^{-1}; HRMS (APCI) calcd. for $C_{20}H_{24}O_4F_3$ ($[M+H]^+$) 385.1621, found 385.1626; The ee was determined by chiral HPLC: SS Whelk column, 1 mL/min, 1 % iPrOH in hexanes. Major: 10.9 min, Minor: 8.3 min, 95 % ee.



4d **10** **12**

***tert*-butyl 2-phenyl-3-vinyloxirane-2-carboxylate (12):** Following the general procedure, the reaction of methyl methacrylate (0.07 mL, 1.03 mmol, 5 equiv), *t*-butyl phenyldiazoacetate (46.0 mg, 0.21 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (4.4 mg, 0.0021 mmol, 0.01 equiv) afforded the product as a colorless oil (16.4 mg, 32% yield) after purification by flash chromatography. R_f = 0.39 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -

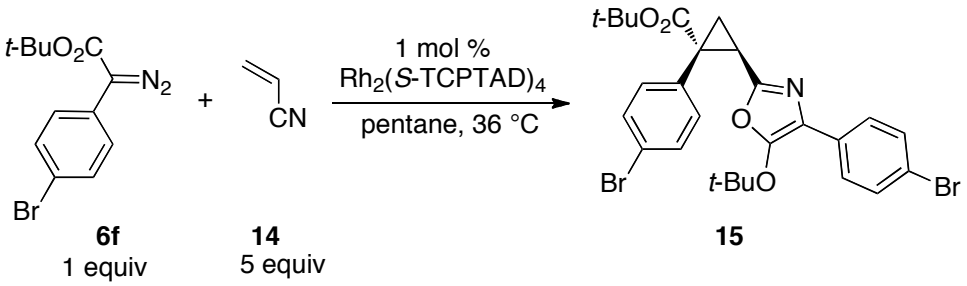
3.3 (c 0.69, $CHCl_3$); FTIR (neat): 2980, 2108, 1742, 1727, 1450, 1394, 1369, 1333, 1258, 1206, 1190, 1156, 1106 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.0, 1.3 Hz, 2H), 7.39-7.31 (m, 3H), 5.78 (ddd, J = 17.3, 10.5, 7.4 Hz, 1H), 5.60 (d, J = 17.1 Hz, 1H), 5.44 (d, J = 10.6 Hz, 1H), 3.50 (d, J = 7.4 Hz, 1H), 1.49 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.4, 135.2, 131.4, 128.4, 128.3, 126.3, 121.9, 83.0, 65.3, 28.0, 27.7; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{15}H_{18}O_3{}^{23}Na_1$, 269.1148; found, 269.1147; HPLC analysis: 15% ee (OD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 230 nm, t_R = 4.42 min, minor; t_R = 4.90 min, major).



4d **11** **13**

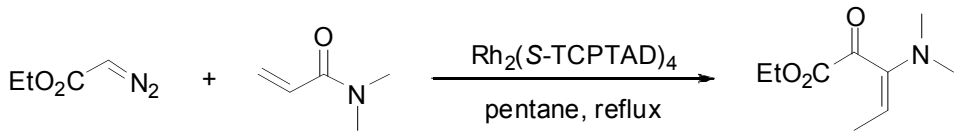
***tert*-butyl 3-methyl-2-phenyl-3-vinyloxirane-2-carboxylate (13):** Following the general procedure, the reaction of 3-buten-2-one (0.20 mL, 2.44 mmol, 5 equiv), *t*-butyl phenyldiazoacetate (108.9 mg, 0.50 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (10.5 mg, 0.0050 mmol, 0.01 equiv) afforded the product as a colorless oil (34.3 mg, 26% yield) after purification by flash chromatography. R_f = 0.39 (hexanes:ethyl acetate = 10:1); R_f = 0.38 (hexanes:ethyl acetate = 10:1); FTIR (neat): 2927, 2854, 2358, 1725, 1455, 1393, 1369, 1250, 1158, 1084, 1069, 1031, 1010 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.9, 1.7 Hz, 2H), 7.38-7.29 (m, 3H), 5.31 (dd, J = 17.2, 1.8 Hz, 1H), 5.22 (dd, J = 17.2, 10.4 Hz, 1H), 5.13 (dd, J = 10.4, 1.8 Hz, 1H), 1.60 (s, 3H), 1.57 (s, 9H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 167.6, 135.8, 133.9, 128.0, 127.9, 127.7, 119.1, 82.7, 69.9, 65.0, 28.0, 17.1; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{16}H_{20}O_3{}^{23}Na_1$, 283.1305; found,

283.1305. HPLC analysis: <5% ee (AD-H, hexane, 0.25 mL/min, λ = 210 nm, t_R = 20.96 min, minor; t_R = 22.02 min, major).



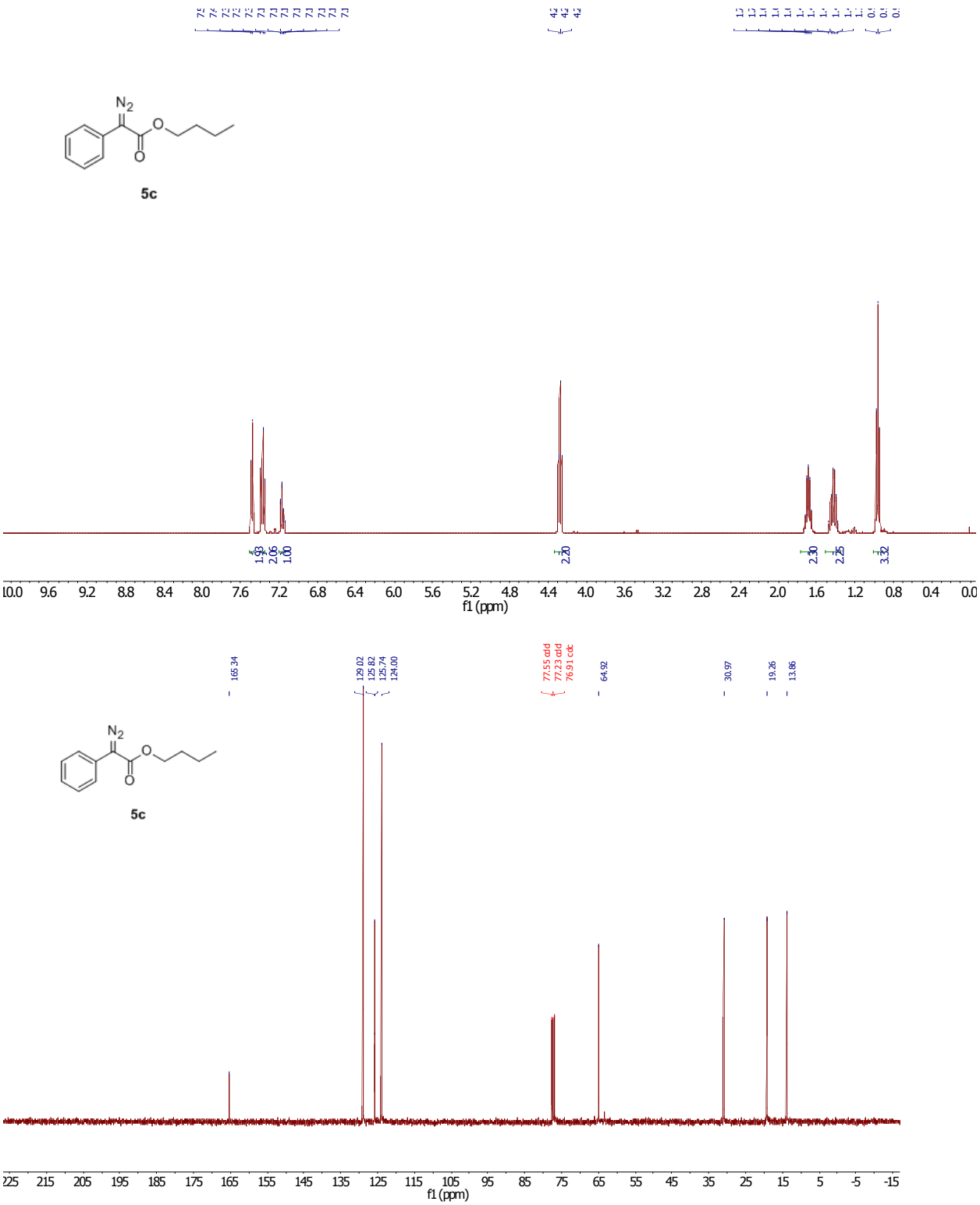
(1*R*,2*R*)-*tert*-butyl 1-(4-bromophenyl)-2-(4-(4-bromophenyl)-5-(*tert*-butoxy)oxazol-2-yl)cyclopropanecarboxylate (15): Following the general procedure, the reaction of acrylonitrile (0.165 mL, 2.5 mmol, 5 equiv), *t*-butyl *p*-bromophenyldiazoacetate (149 mg, 0.50 mmol, 1 equiv) and Rh_2(*S*-TCPTAD)$_4$ (11.0 mg, 0.005 mmol, 0.01 equiv) afforded the product as a white solid (142 mg, 96% yield) after purification by flash chromatography. m.p. 133-135 °C; R_f = 0.39 (hexanes:ethyl acetate = 10:1); $[\alpha]_D^{20}$ -87.0 (c 1.02, $CHCl_3$); FTIR (neat): 2977, 2932, 1715, 1636, 1584, 1489, 1394, 1369, 1303, 1254, 1152, 1097, 1071, 1012 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 3.13 (dd, J = 9.2, 6.8 Hz, 1H), 2.09 (dd, J = 9.2, 4.8 Hz, 1H), 2.01 (dd, J = 6.8, 4.9 Hz, 1H), 1.39 (s, 9H), 1.05 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.2, 151.6, 151.1, 134.6, 132.5, 131.3, 131.1, 130.2, 126.5, 121.5, 120.0, 119.3, 86.0, 81.8, 36.7, 27.9, 27.8, 25.2, 18.5; HRMS (APCI) *m/z*: $[M+H]^+$ calcd. for $C_{27}H_{24}O_4{}^{23}Na_1$, 590.0536; found, 590.0541; HPLC analysis: 97% ee (AD-H, 1% *i*-PrOH in hexane, 1.0 mL/min, λ = 210 nm, t_R = 5.77 min, major; t_R = 6.29 min, minor).

Experimental data for compound 18

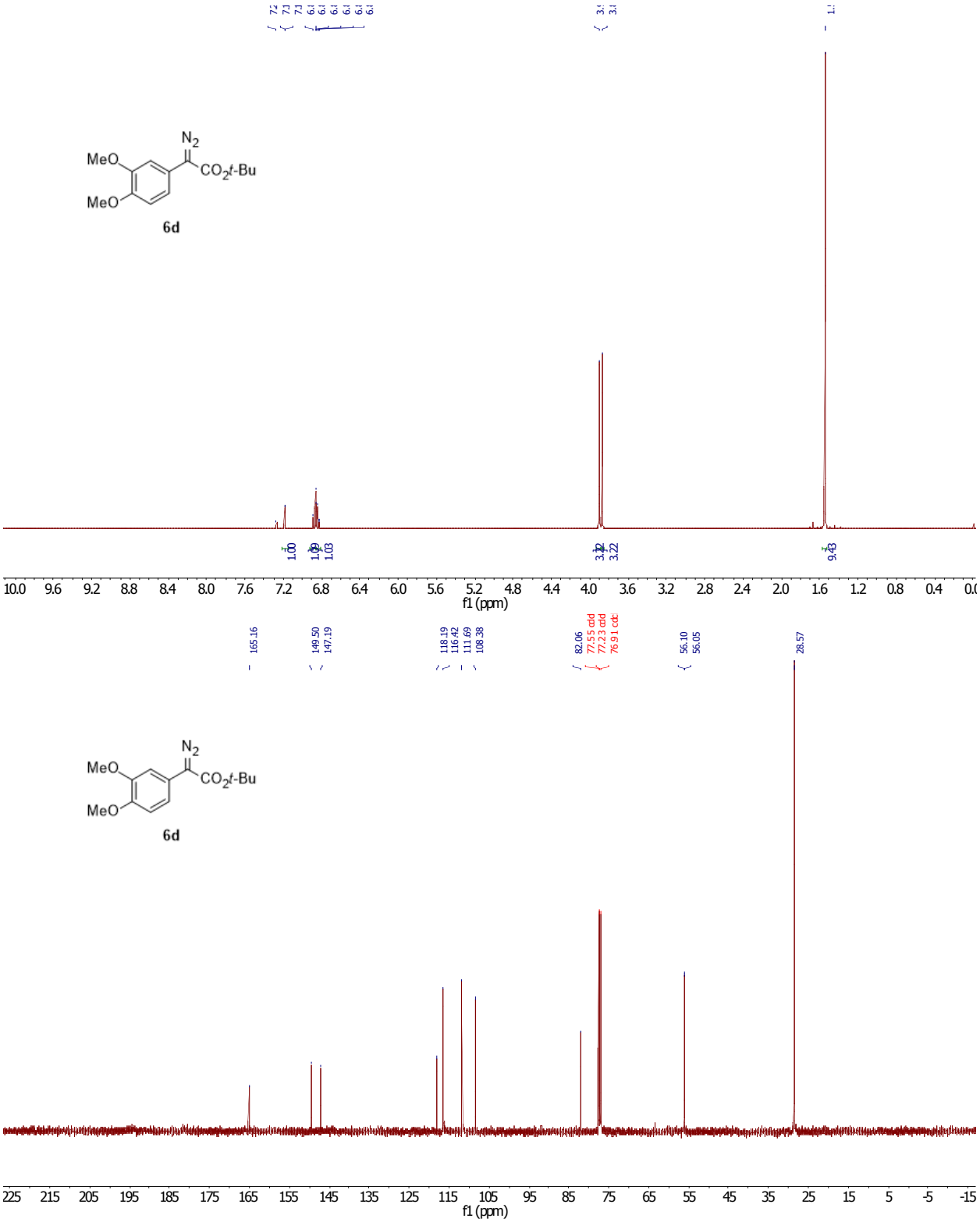


16 **17** **18**

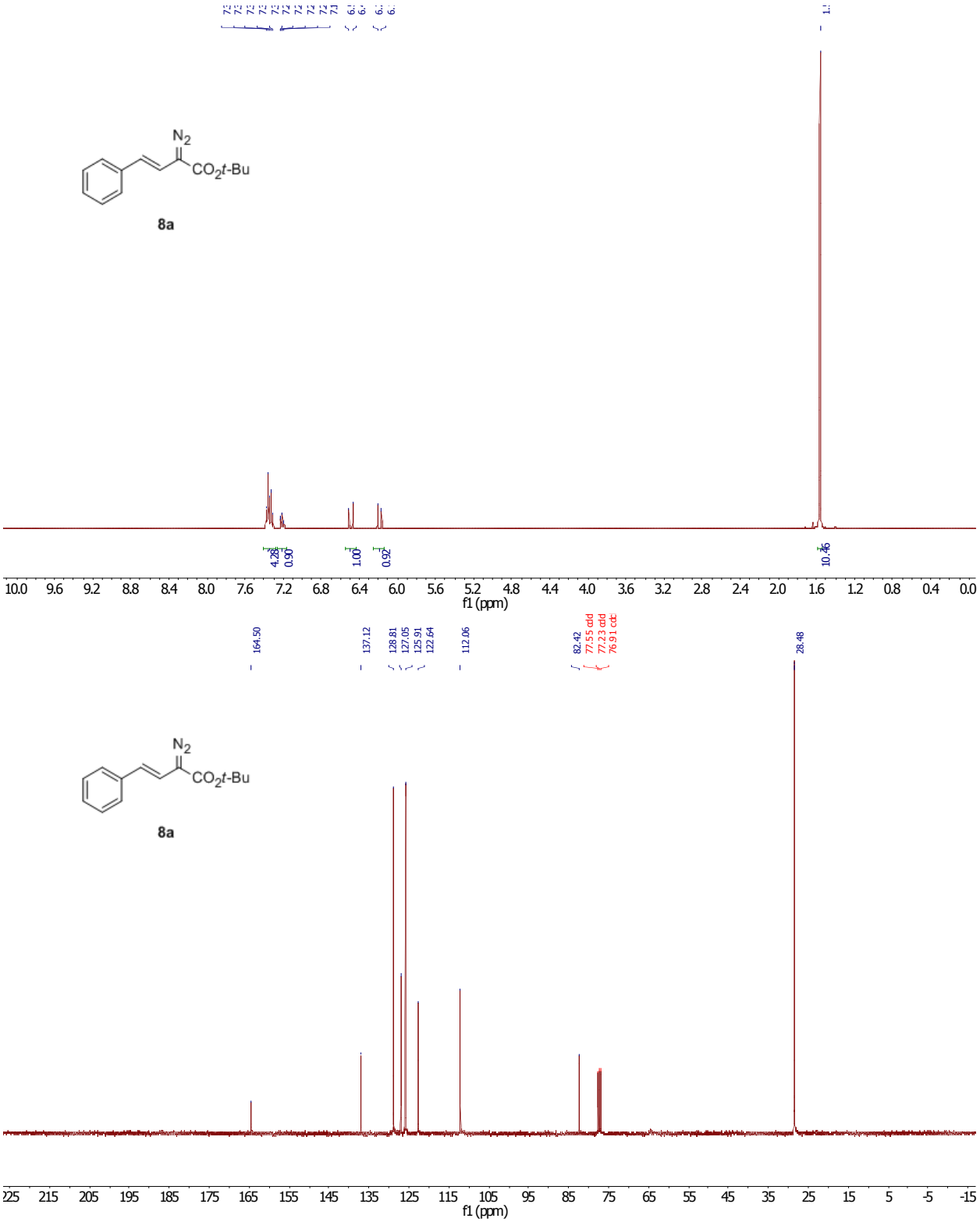
(*E*)-ethyl 3-(dimethylamino)-2-oxopent-3-enoate (18): To a solution of *N,N*-dimethylacrylamide **18** (0.26 mL, 2.5 mmol, 5.0 equiv) and Rh_2(*S*-TCPTAD)$_4$ (11 mg, 1 mol %) in pentane (3 mL) at reflux was added a solution of ethyl diazoacetate (80% pure by mass with DCM, 72 mg, 0.5 mmol) in pentane (3 mL) over 2 hours. The mixture was stirred for an additional hour at reflux and allowed to cool to room temperature. To isolate the product, the pentane was removed under reduced pressure and the crude reside purified by column chromatography (6% Et_2O in pentane) to give the product as a yellow oil (36 mg, 39 % yield). ^{1}H-NMR (400 MHz; $CDCl_3$) δ 6.28 (q, 1H, J = 7.1 Hz), 4.32 (q, 2H, J = 7.2 Hz), 2.68 (s, 6H), 1.94 (d, 3H, J = 7.1 Hz), 1.35 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 187.9, 165.5, 147.4, 138.9, 62.1, 42.7, 14.2; IR (neat): 2981, 2938, 1733, 1675, 1176, 1021 cm^{-1}; HRMS (APCI) calcd. for $C_9H_{16}O_3N$ ($[M+H]^+$) 186.1125, found 186.1125.



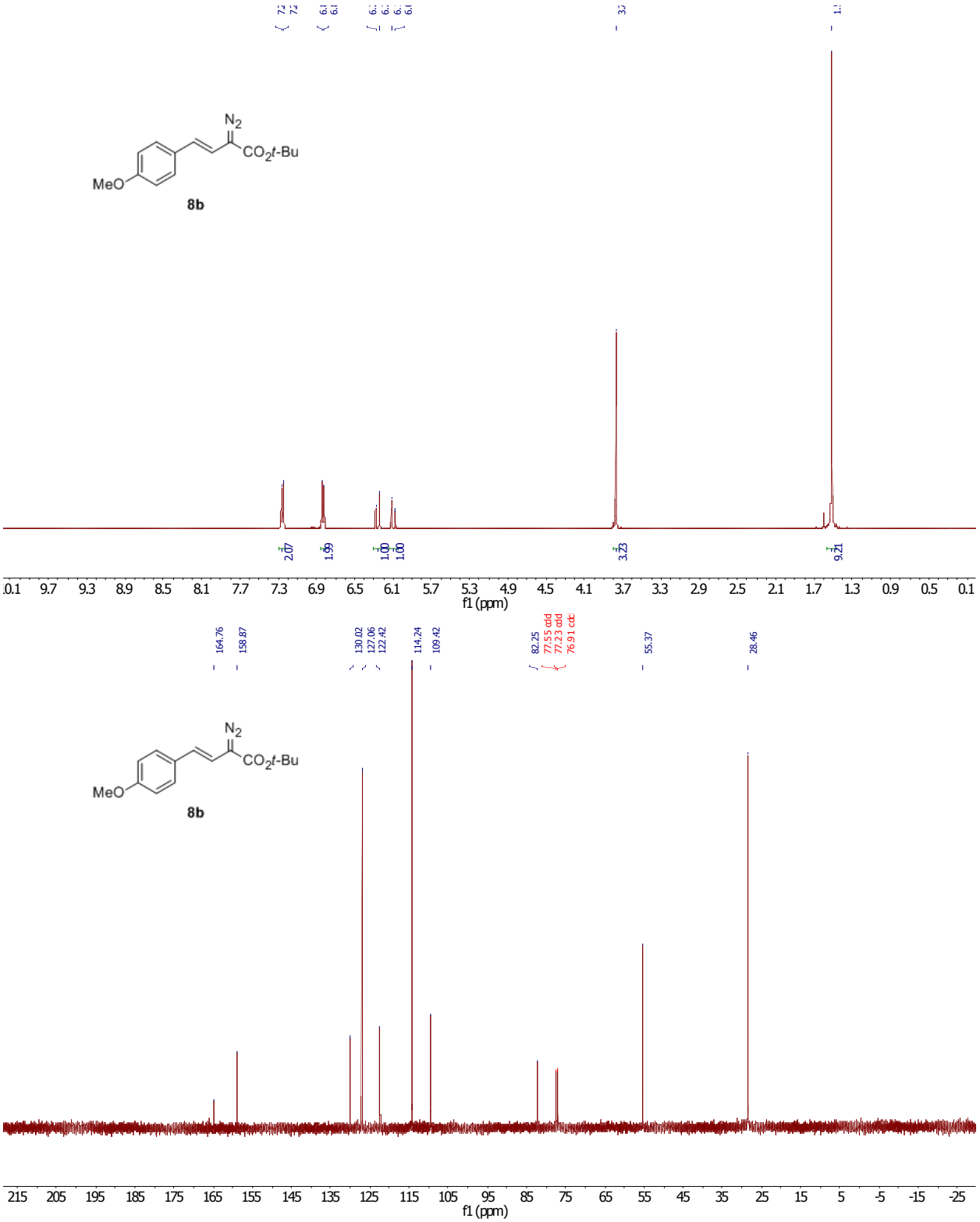
^{1}H- and ^{13}C-NMR spectra of compound **5c**



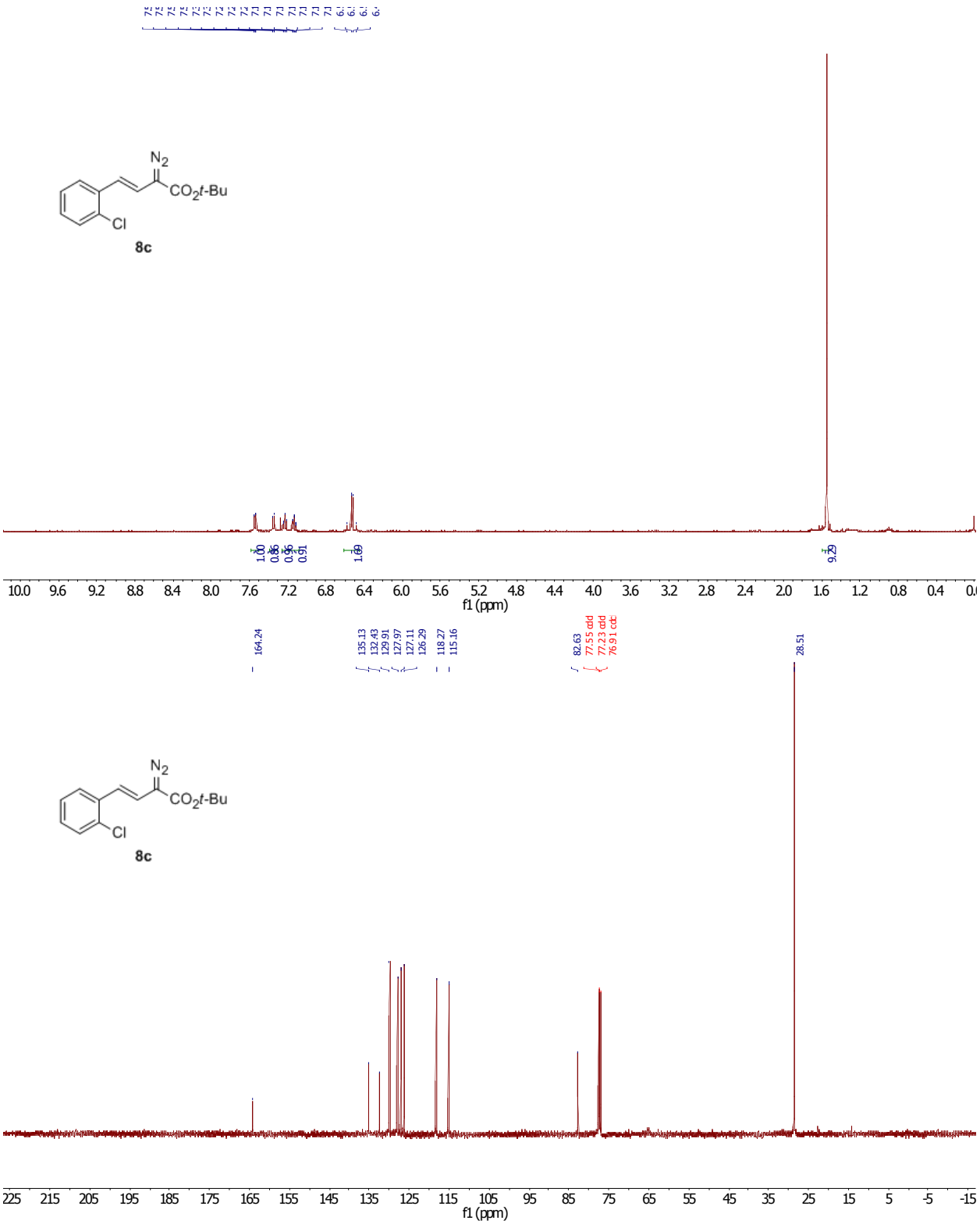
^{1}H- and ^{13}C-NMR spectra of compound **6d**



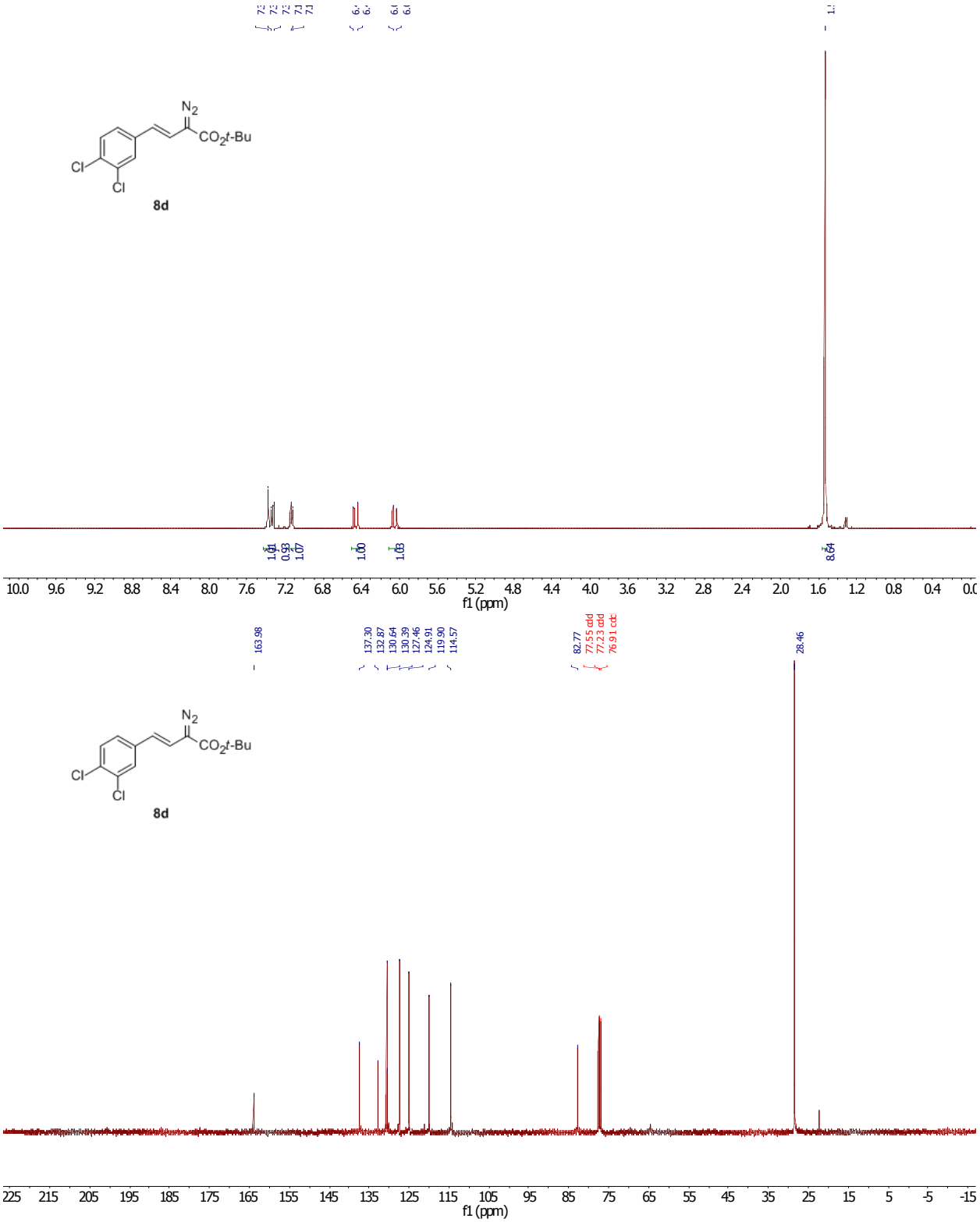
^{1}H- and ^{13}C-NMR spectra of compound **8a**



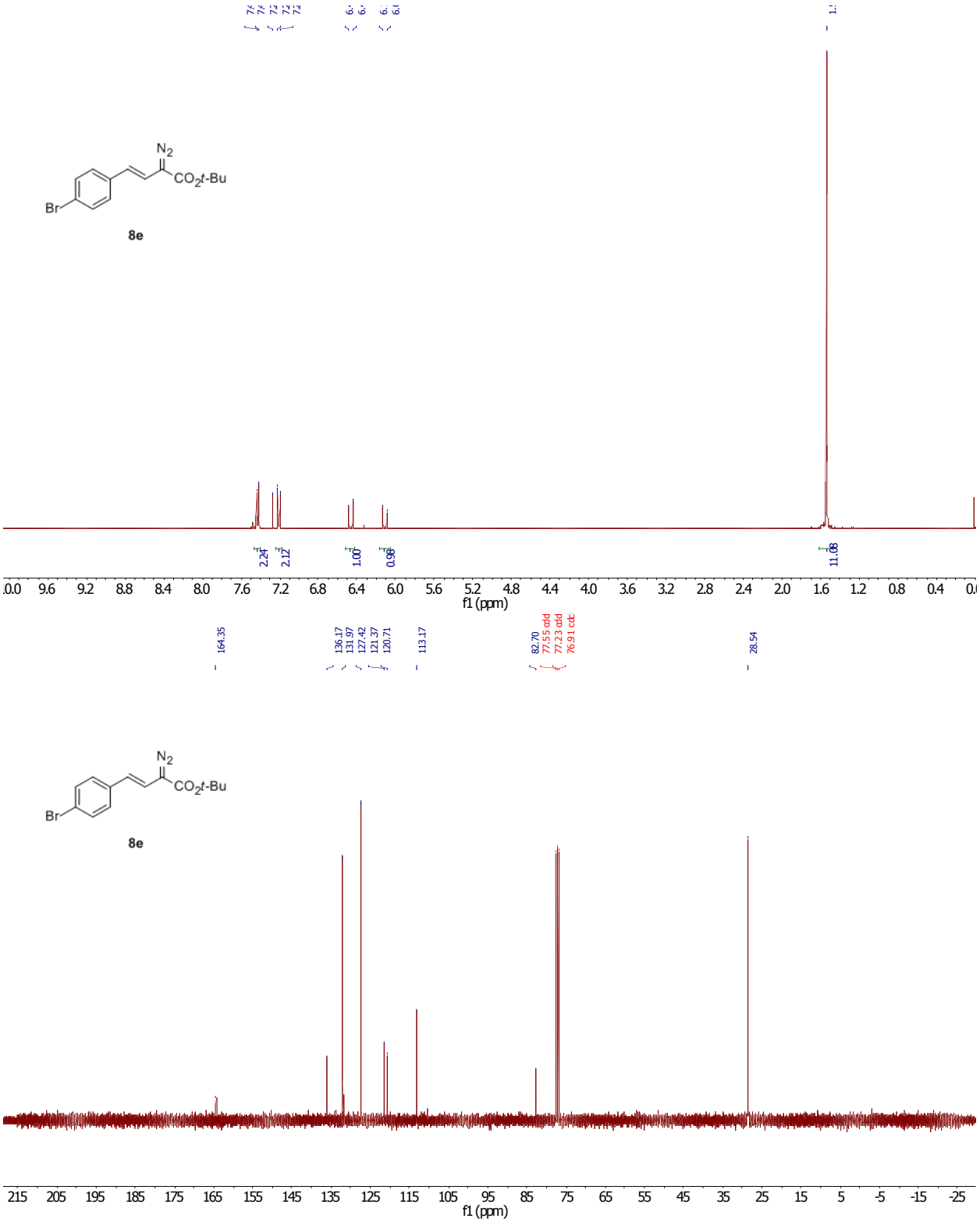
^{1}H- and ^{13}C-NMR spectra of compound **8b**



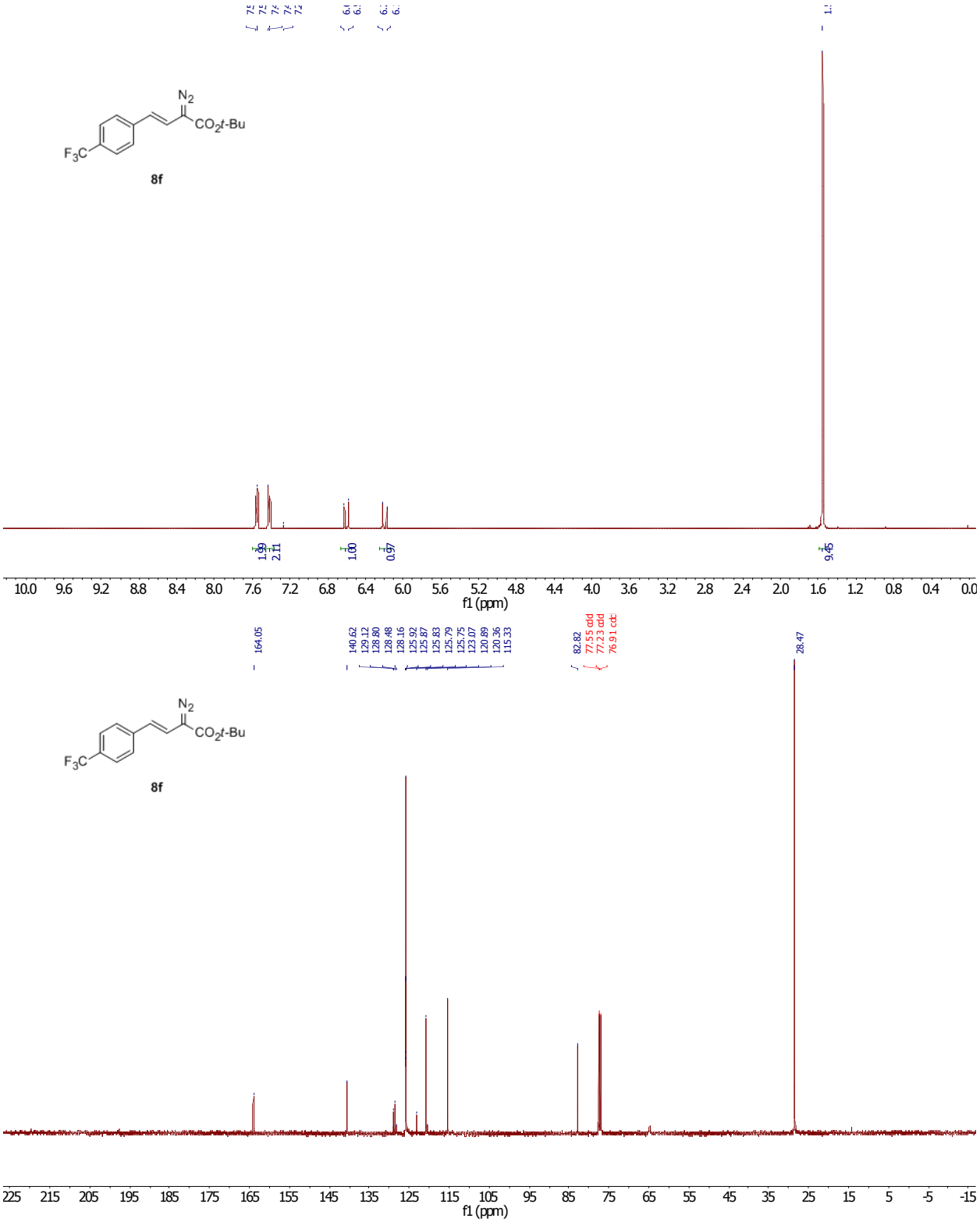
^{1}H- and ^{13}C-NMR spectra of compound **8c**



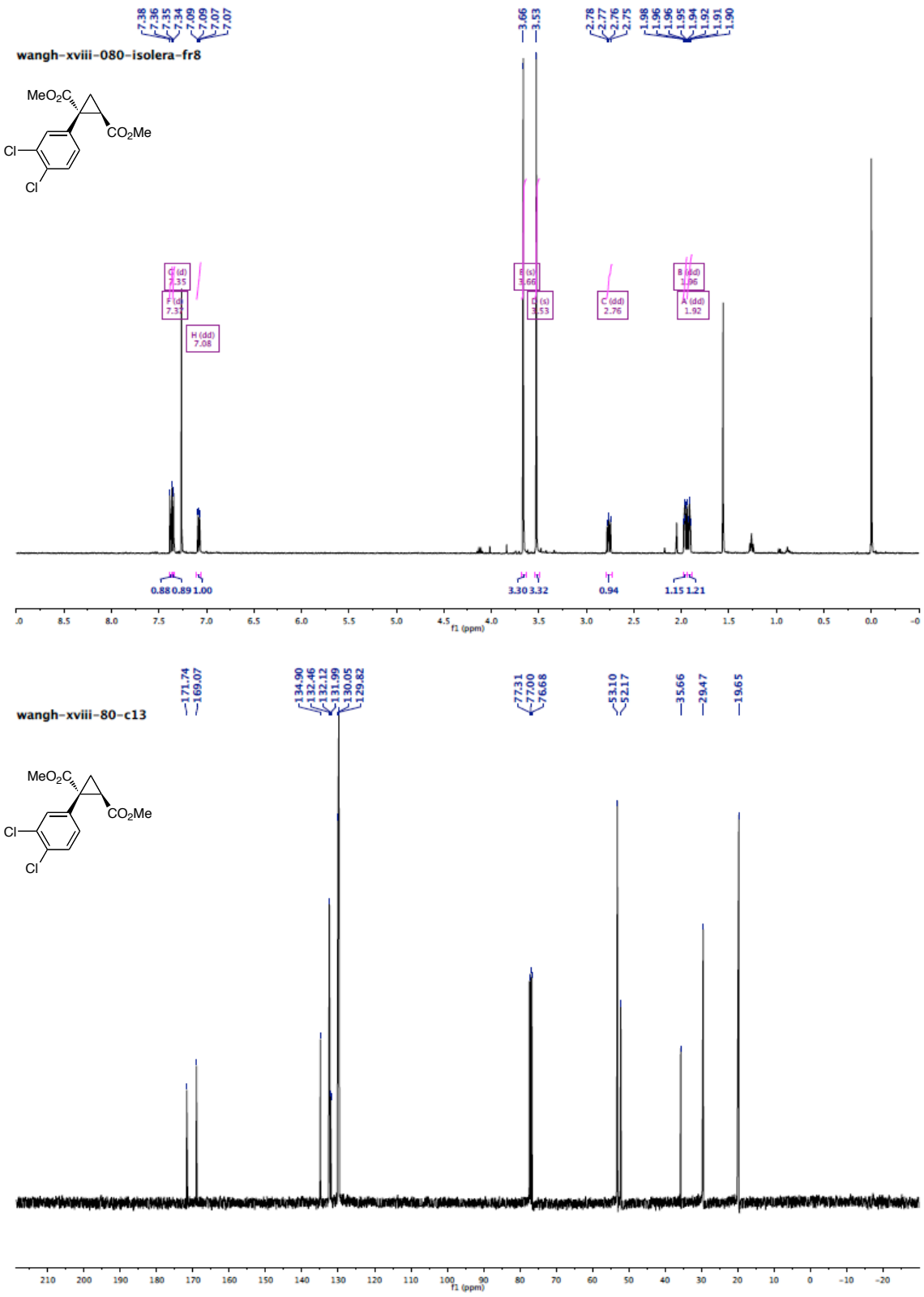
^{1}H- and ^{13}C-NMR spectra of compound **8d**



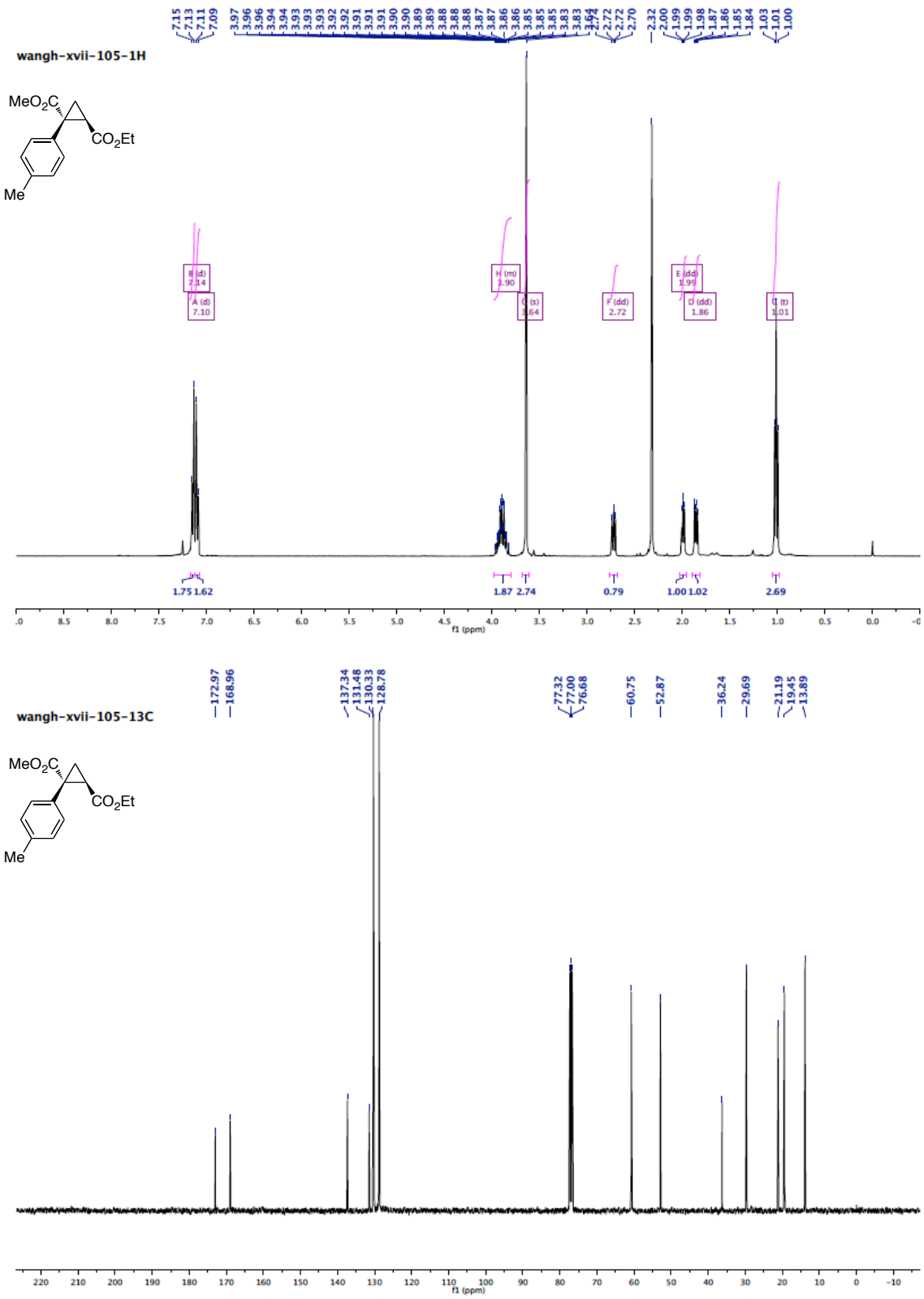
^{1}H- and ^{13}C-NMR spectra of compound **8e**



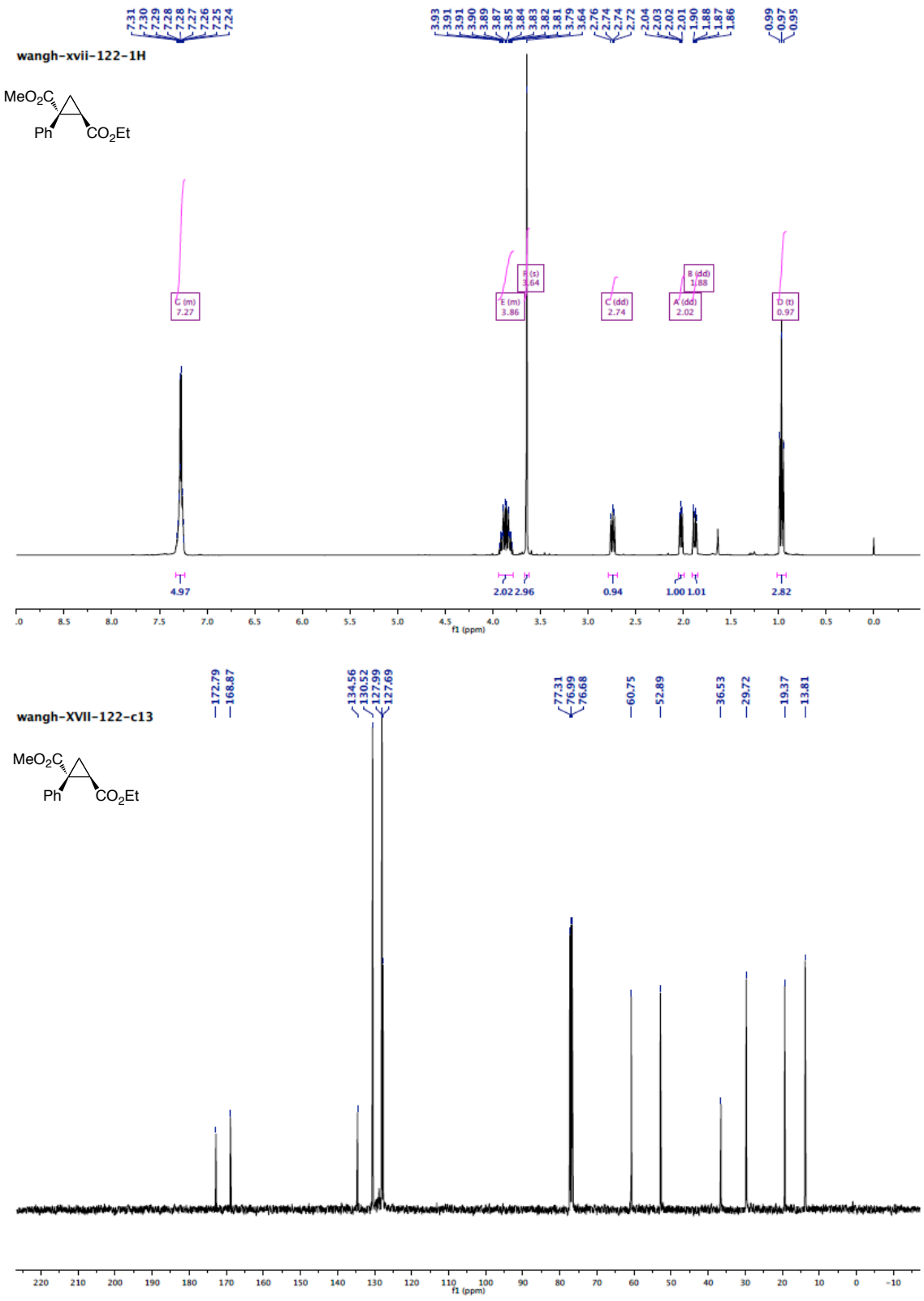
^{1}H- and ^{13}C-NMR spectra of compound **8f**



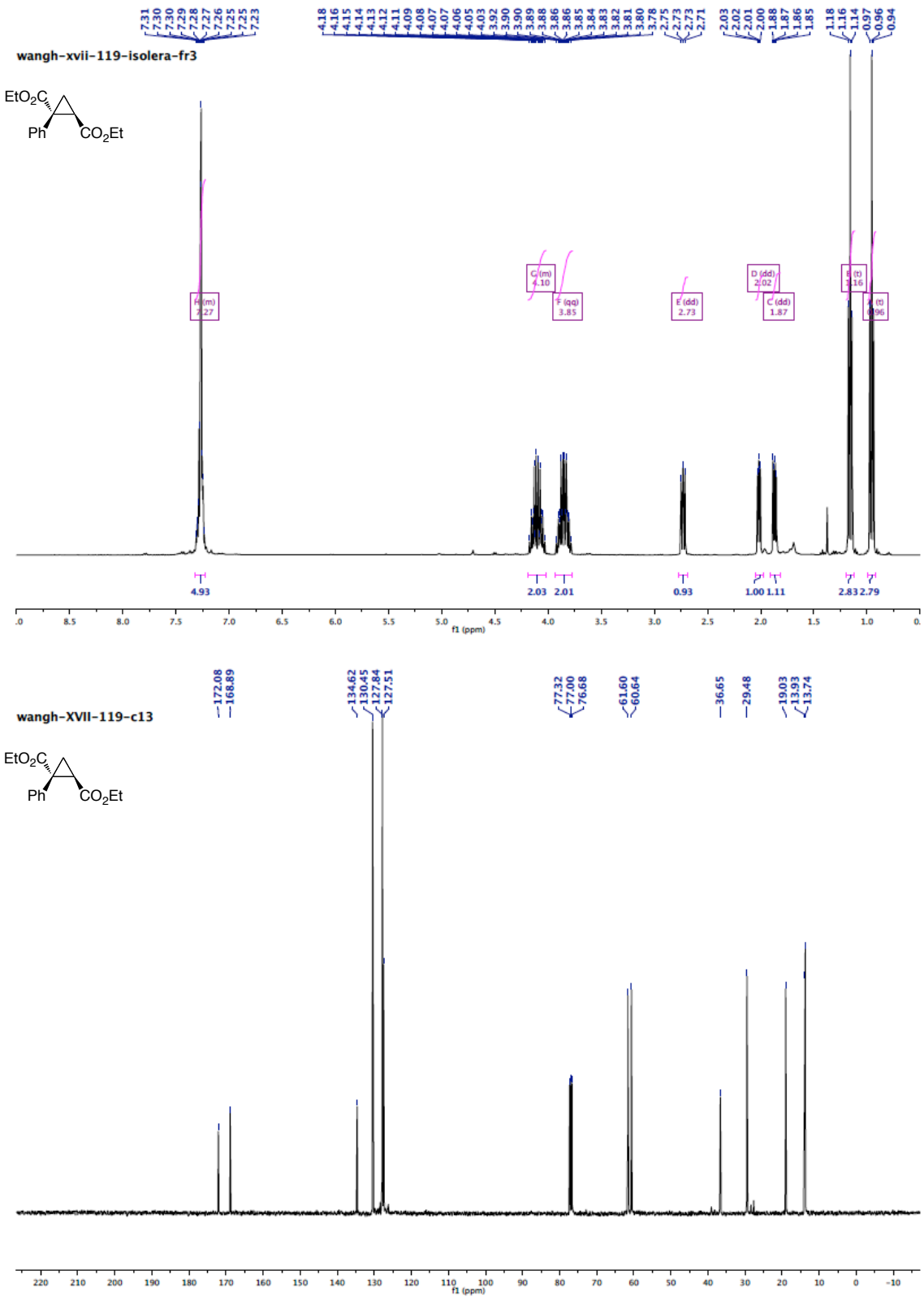
^{1}H- and ^{13}C-NMR spectra of compound **SI-2**



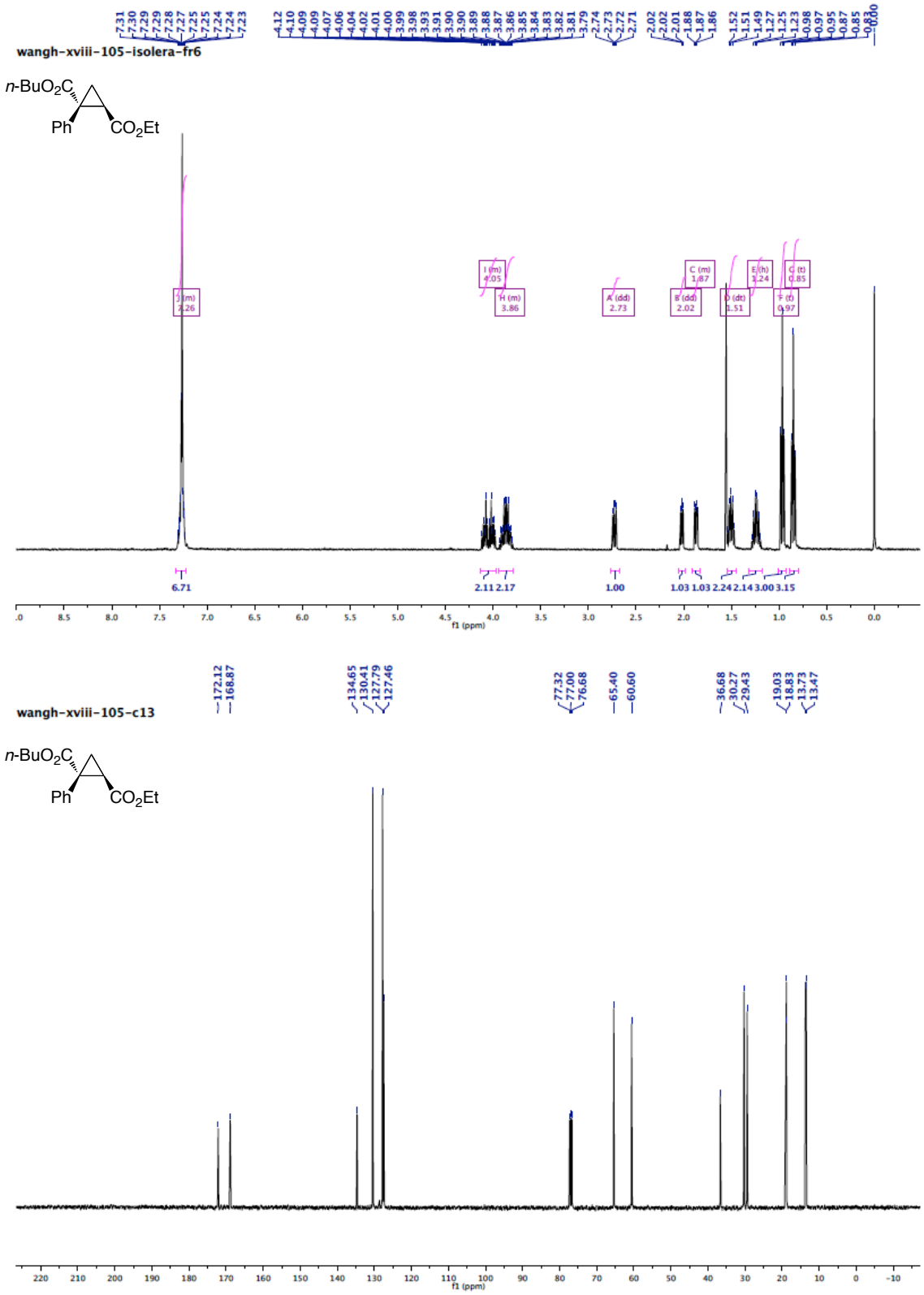
^{1}H- and ^{13}C-NMR spectra of compound **3**



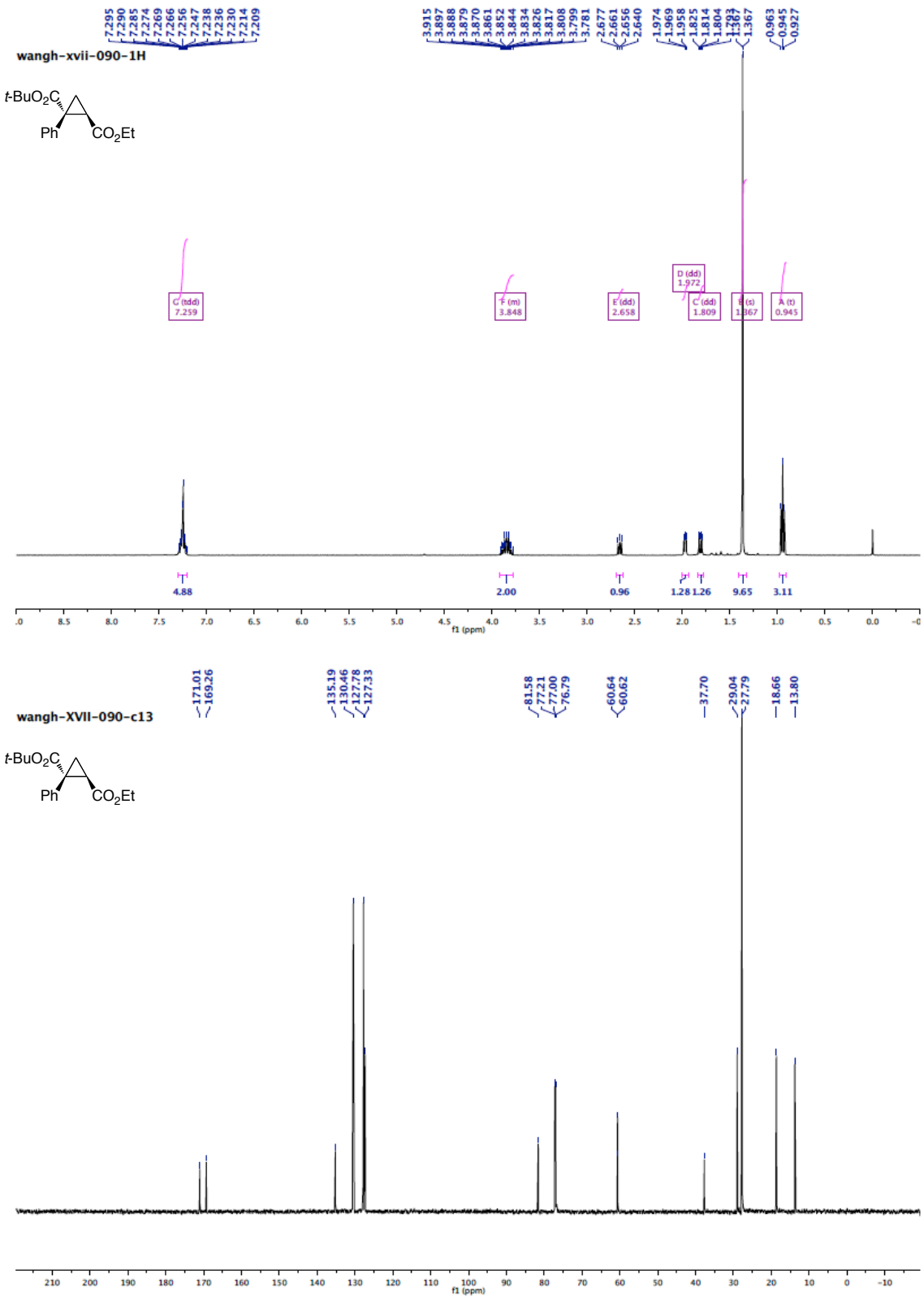
^{1}H- and ^{13}C-NMR spectra of compound **5a**



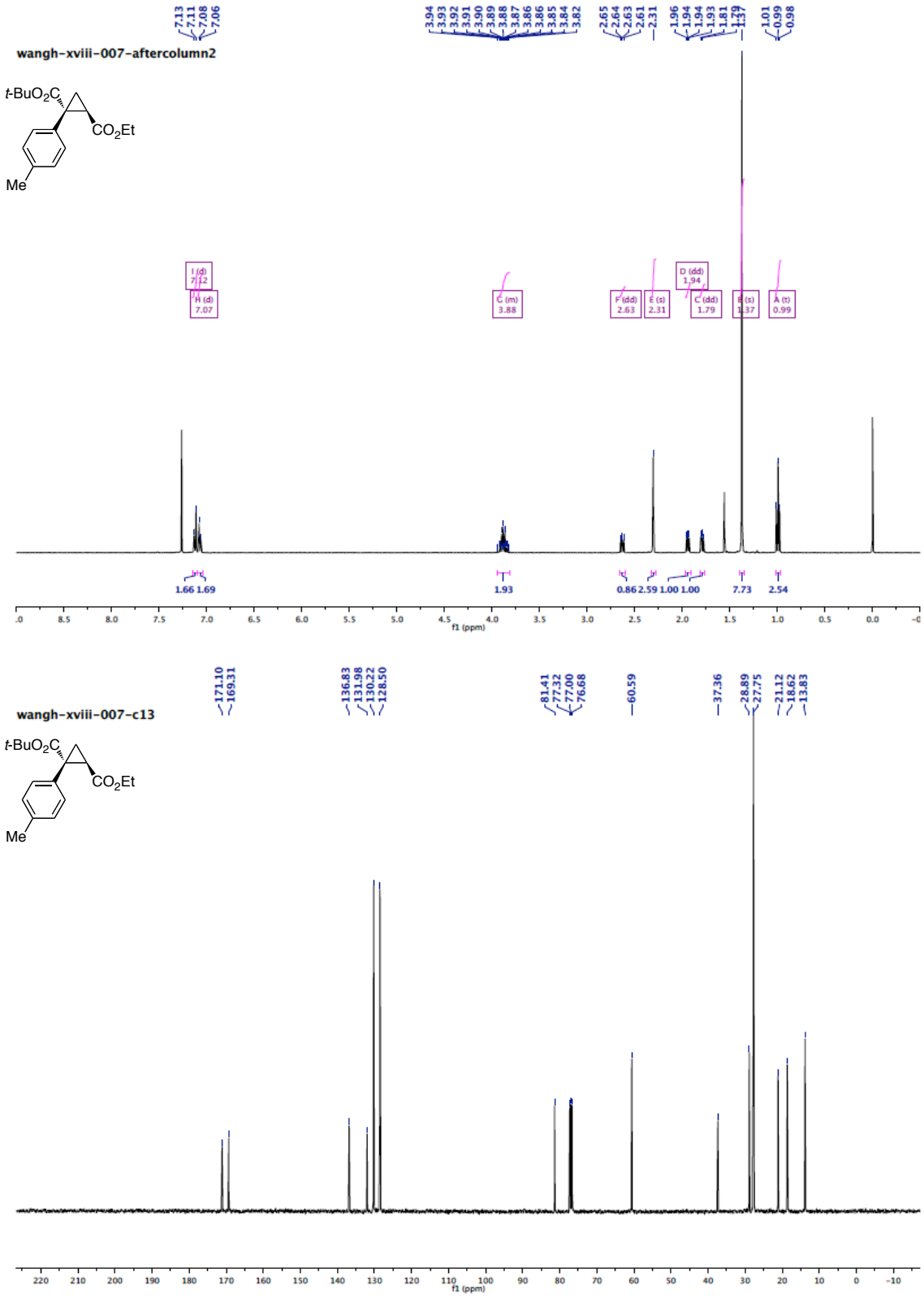
^{1}H- and ^{13}C-NMR spectra of compound **5b**



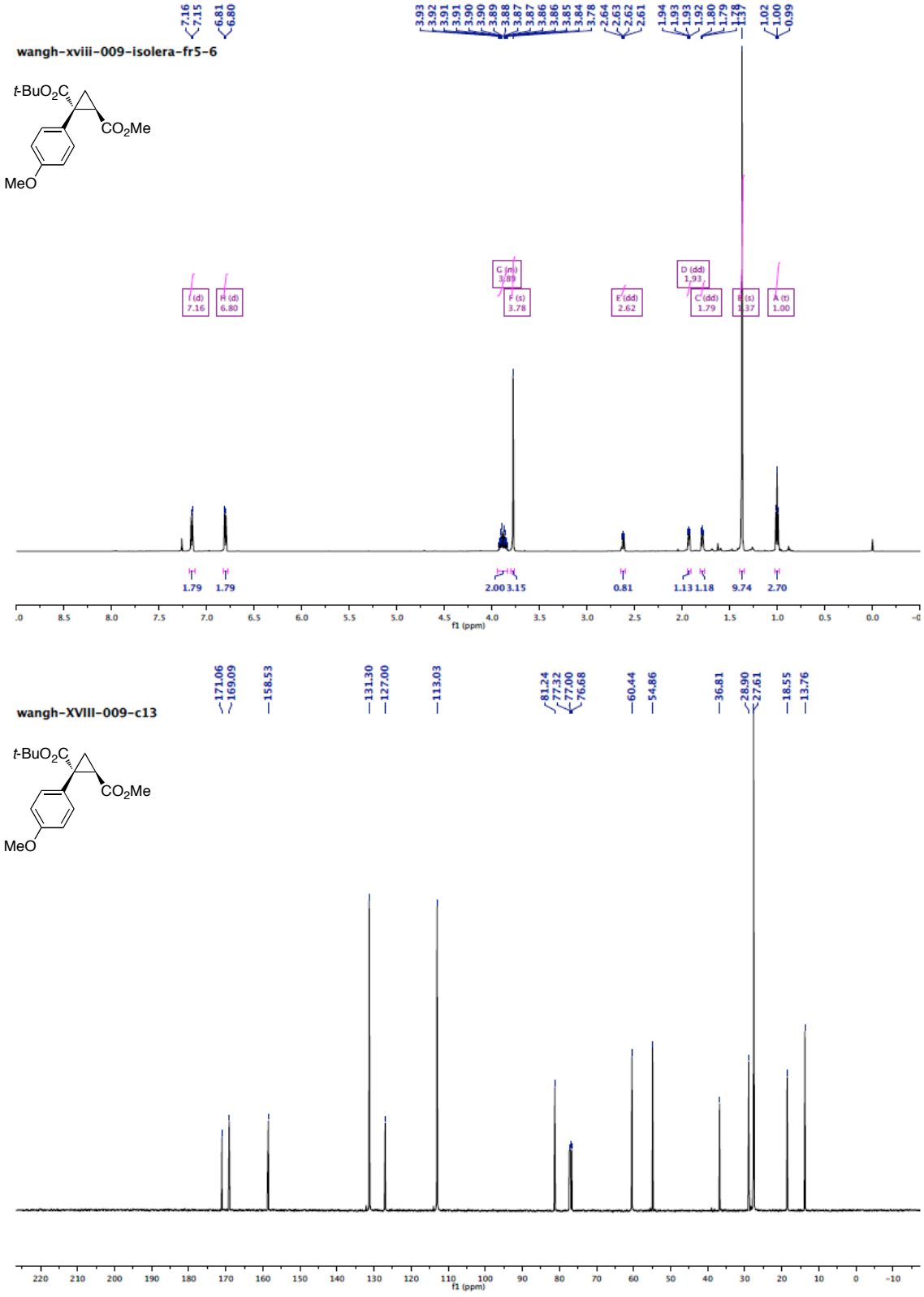
^{1}H- and ^{13}C-NMR spectra of compound **5c**



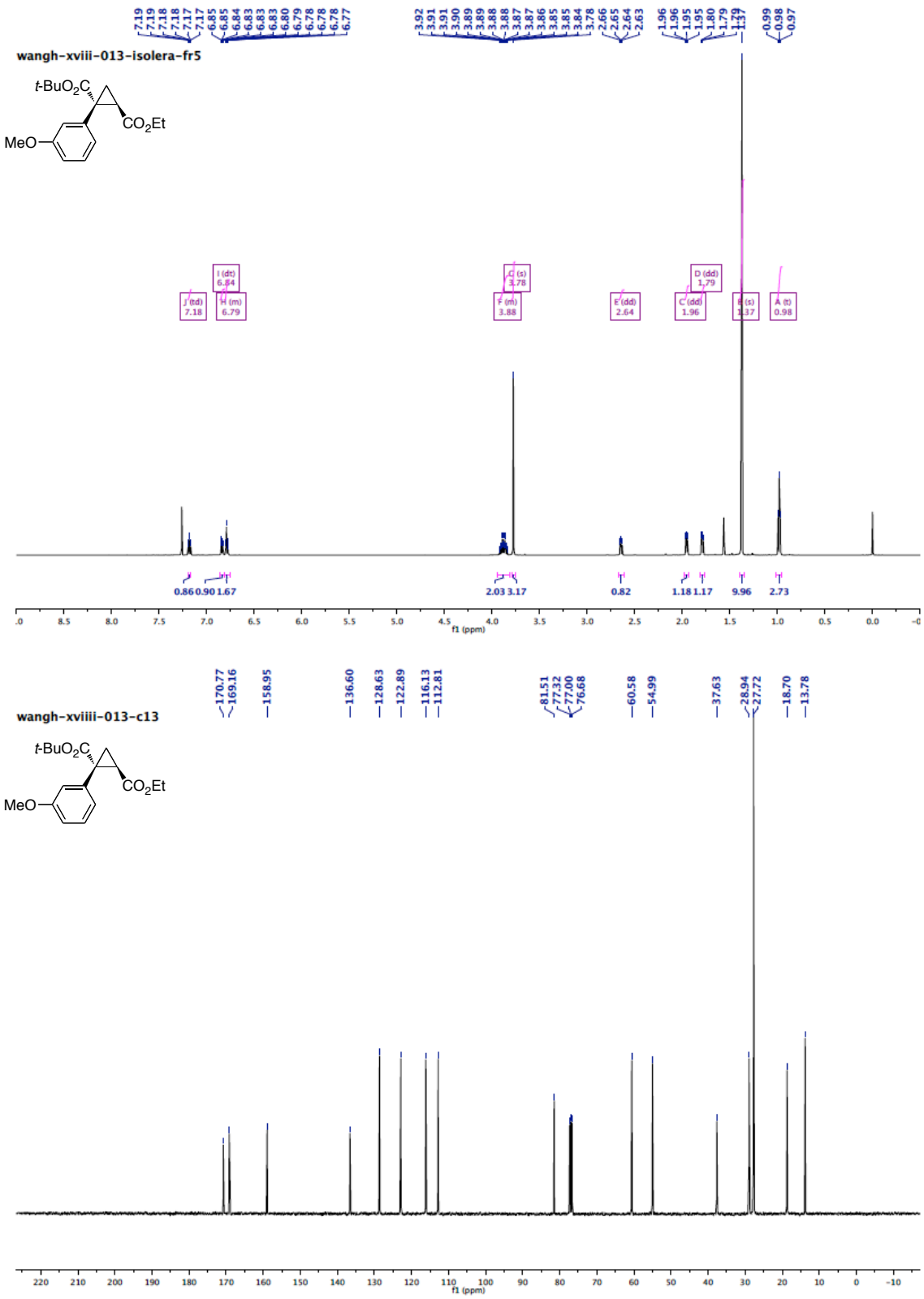
^{1}H- and ^{13}C-NMR spectra of compound **5d**



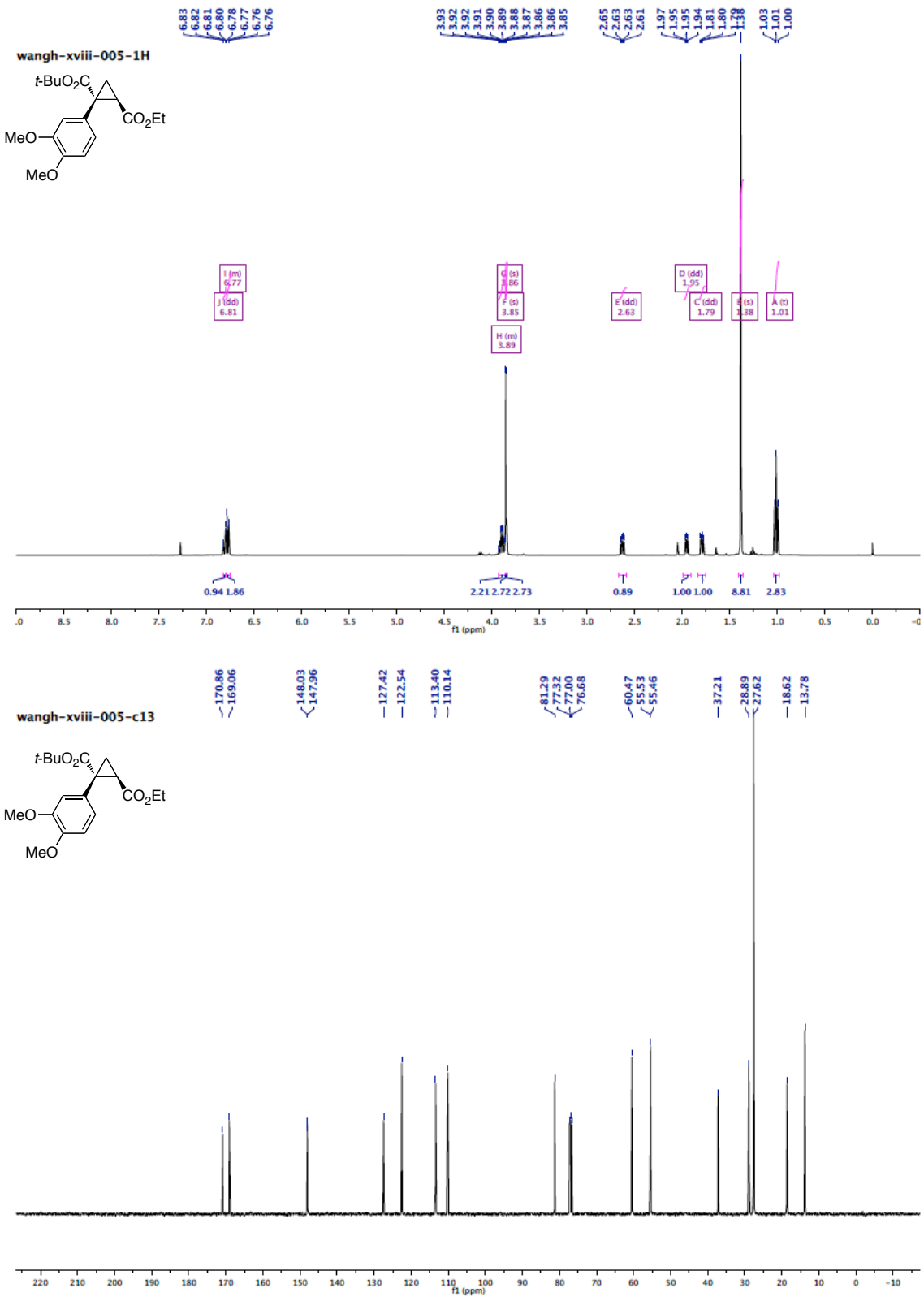
^{1}H- and ^{13}C-NMR spectra of compound **7a**



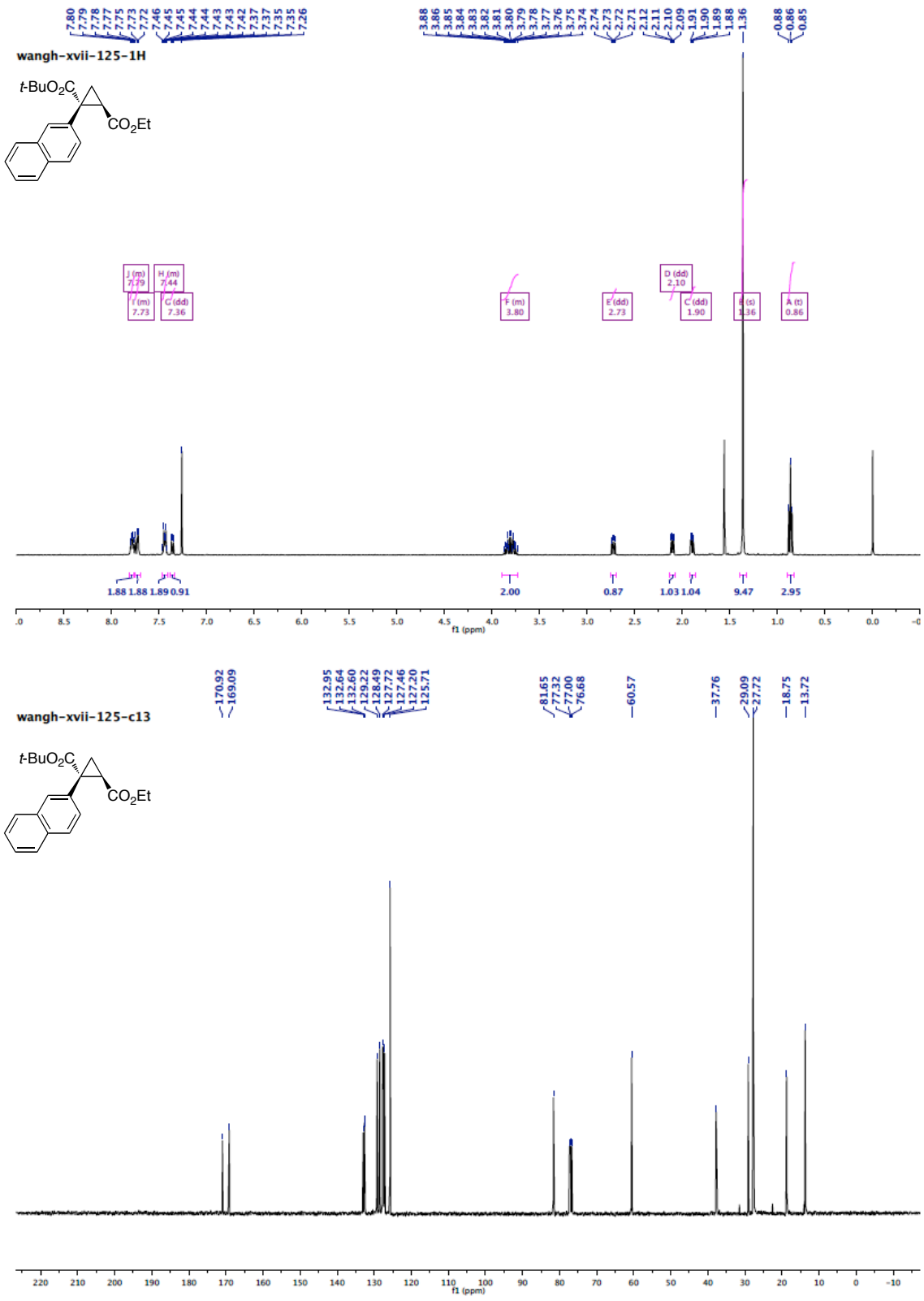
^{1}H- and ^{13}C-NMR spectra of compound **7b**



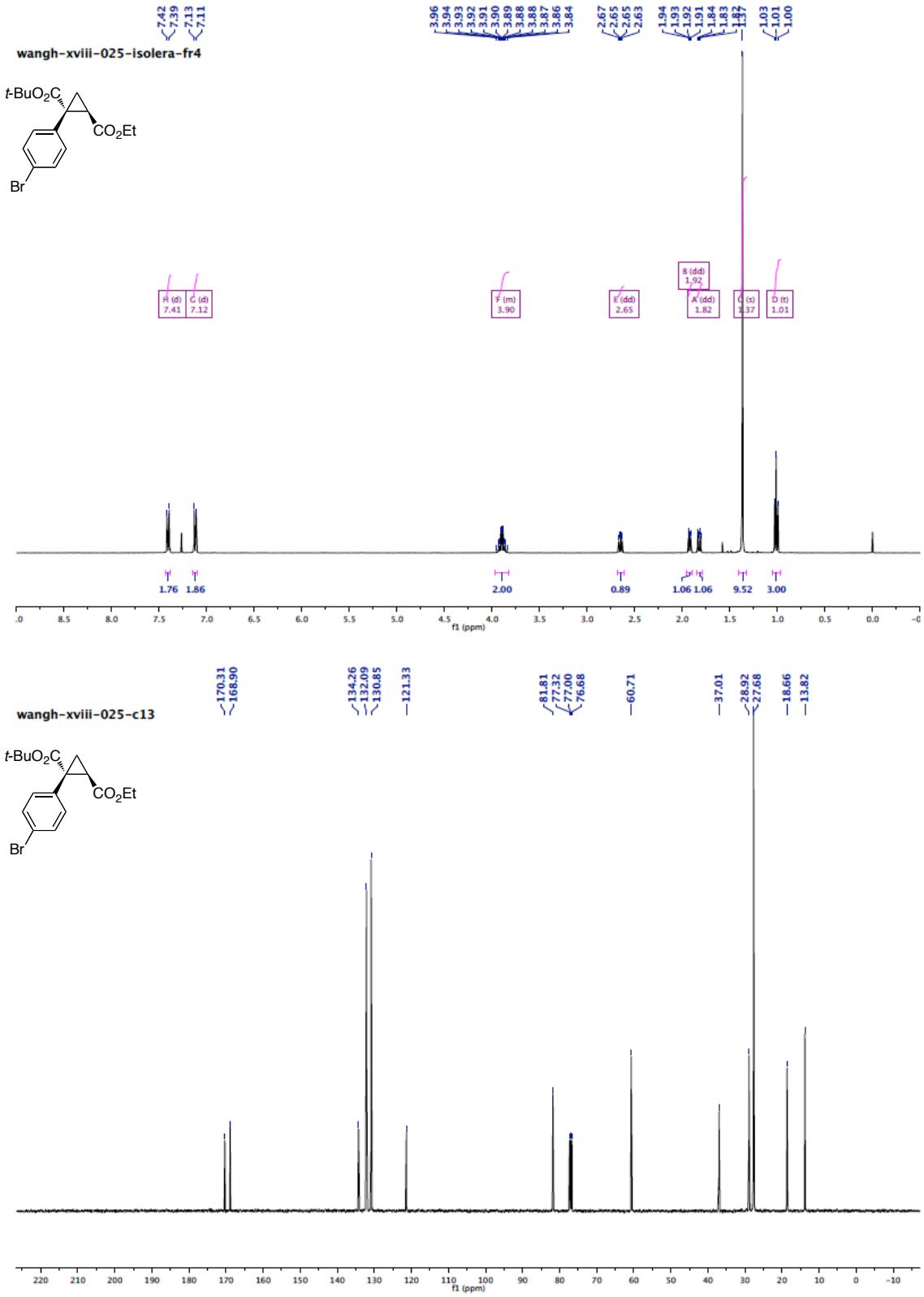
^{1}H- and ^{13}C-NMR spectra of compound **7c**



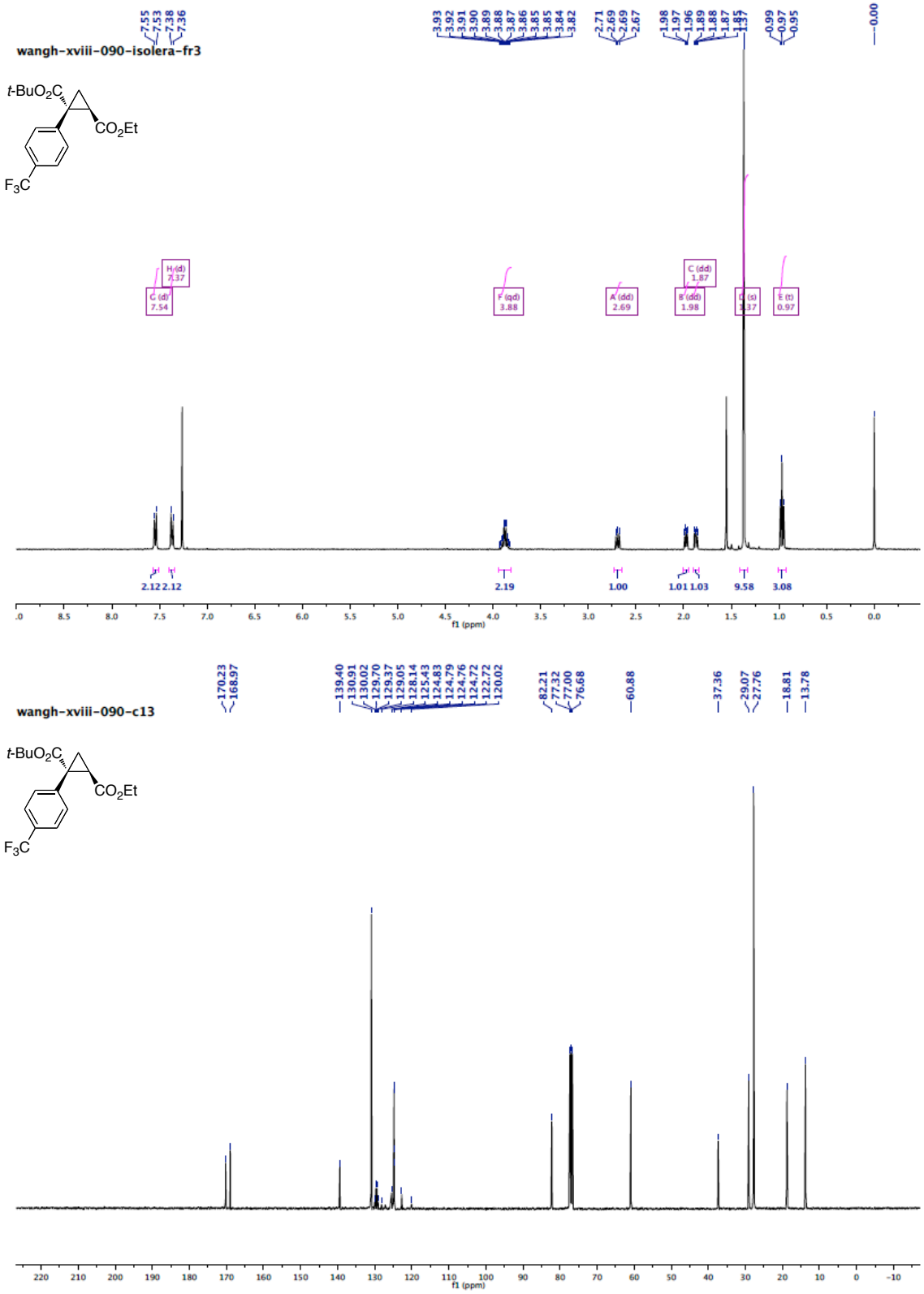
^{1}H- and ^{13}C-NMR spectra of compound **7d**



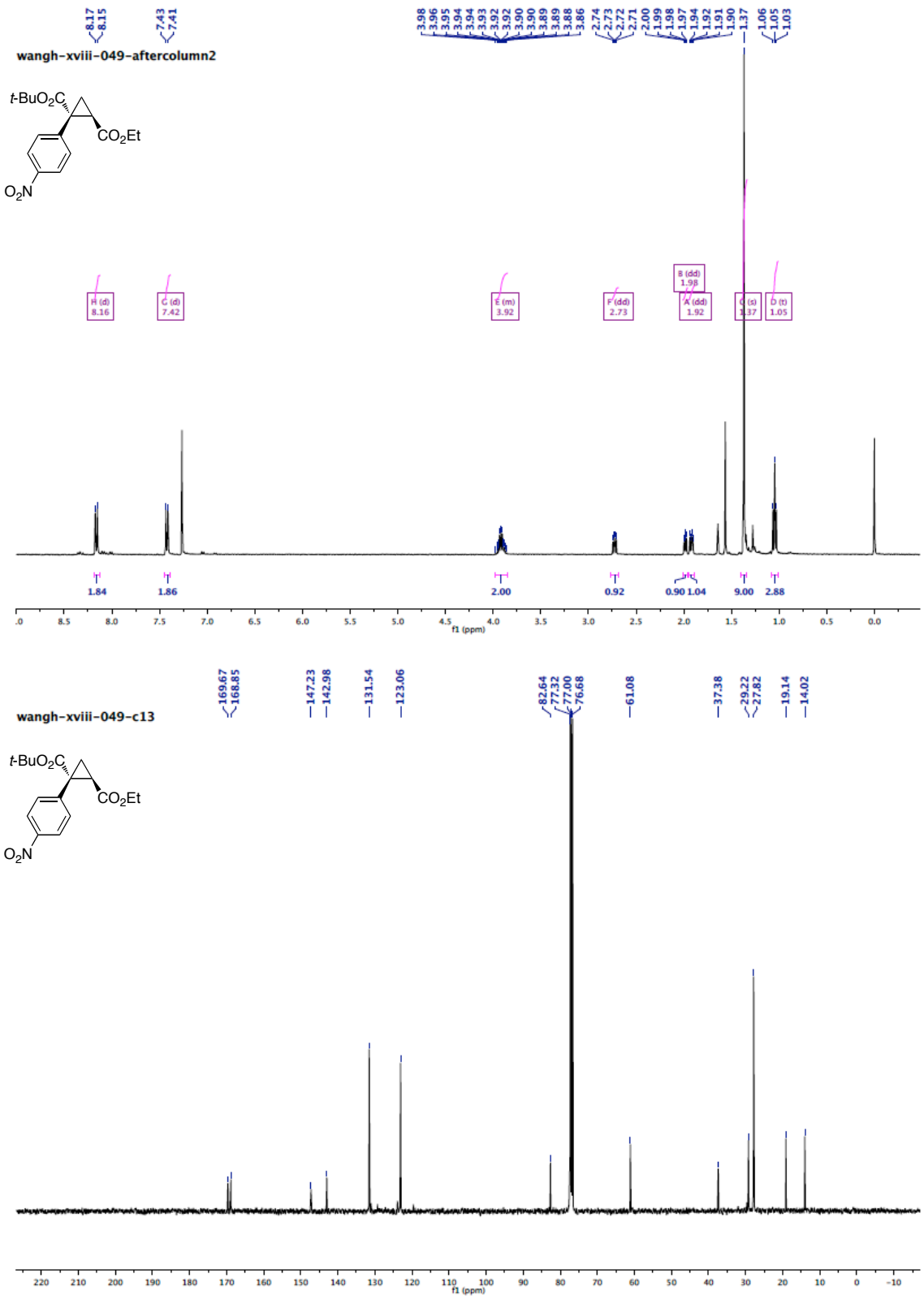
^{1}H- and ^{13}C-NMR spectra of compound **7e**



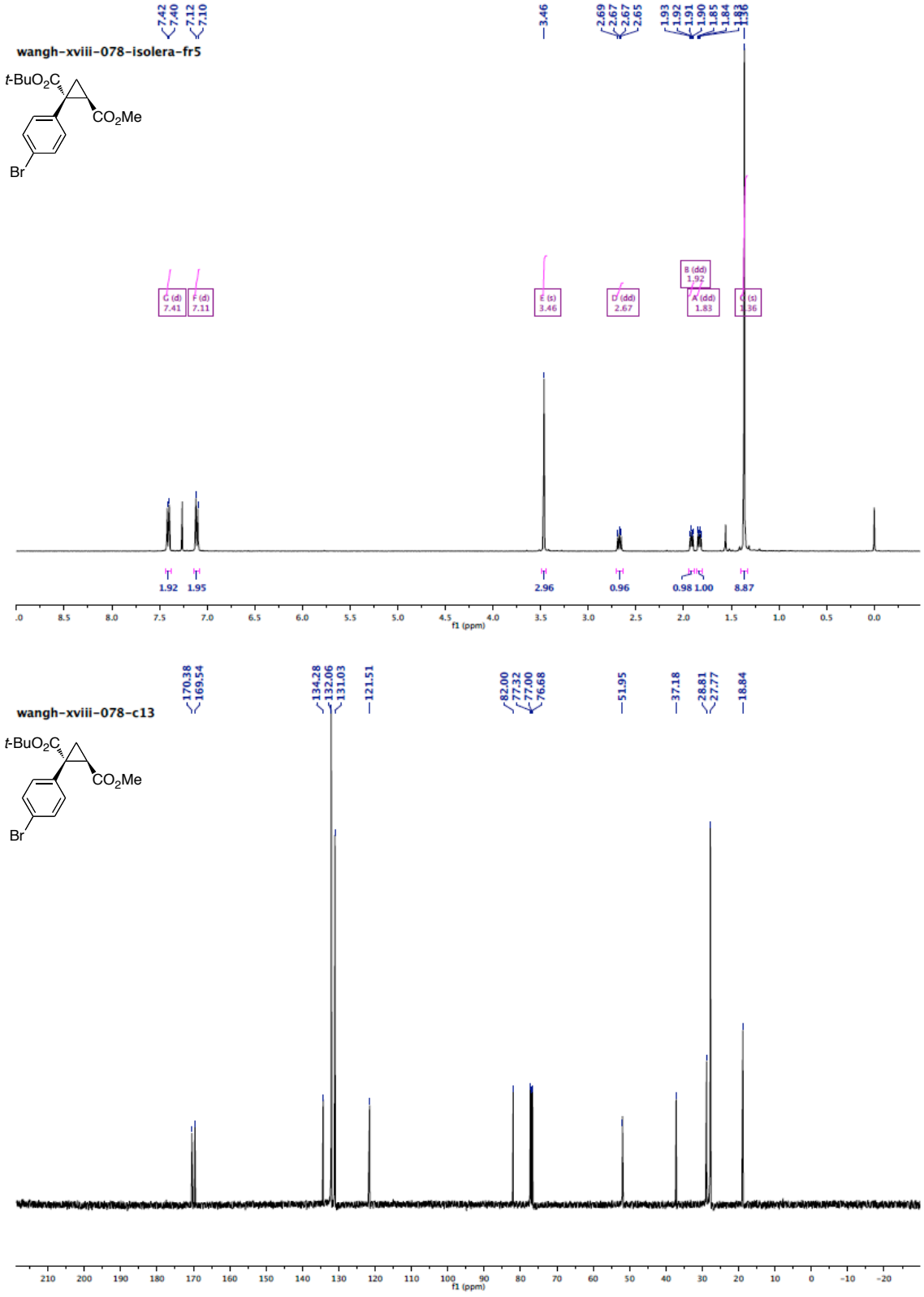
^{1}H- and ^{13}C-NMR spectra of compound **7f**



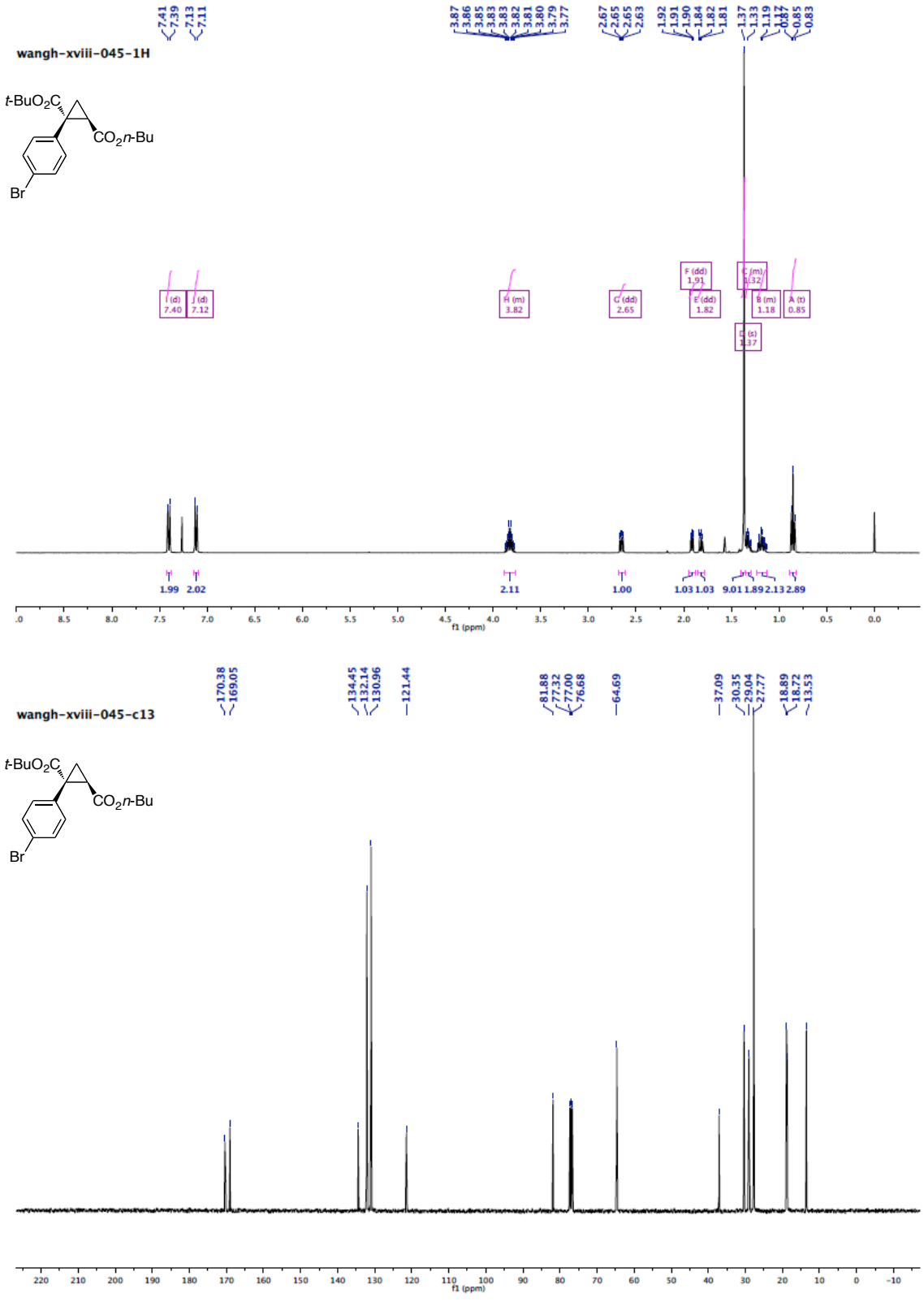
^{1}H- and ^{13}C-NMR spectra of compound **7g**



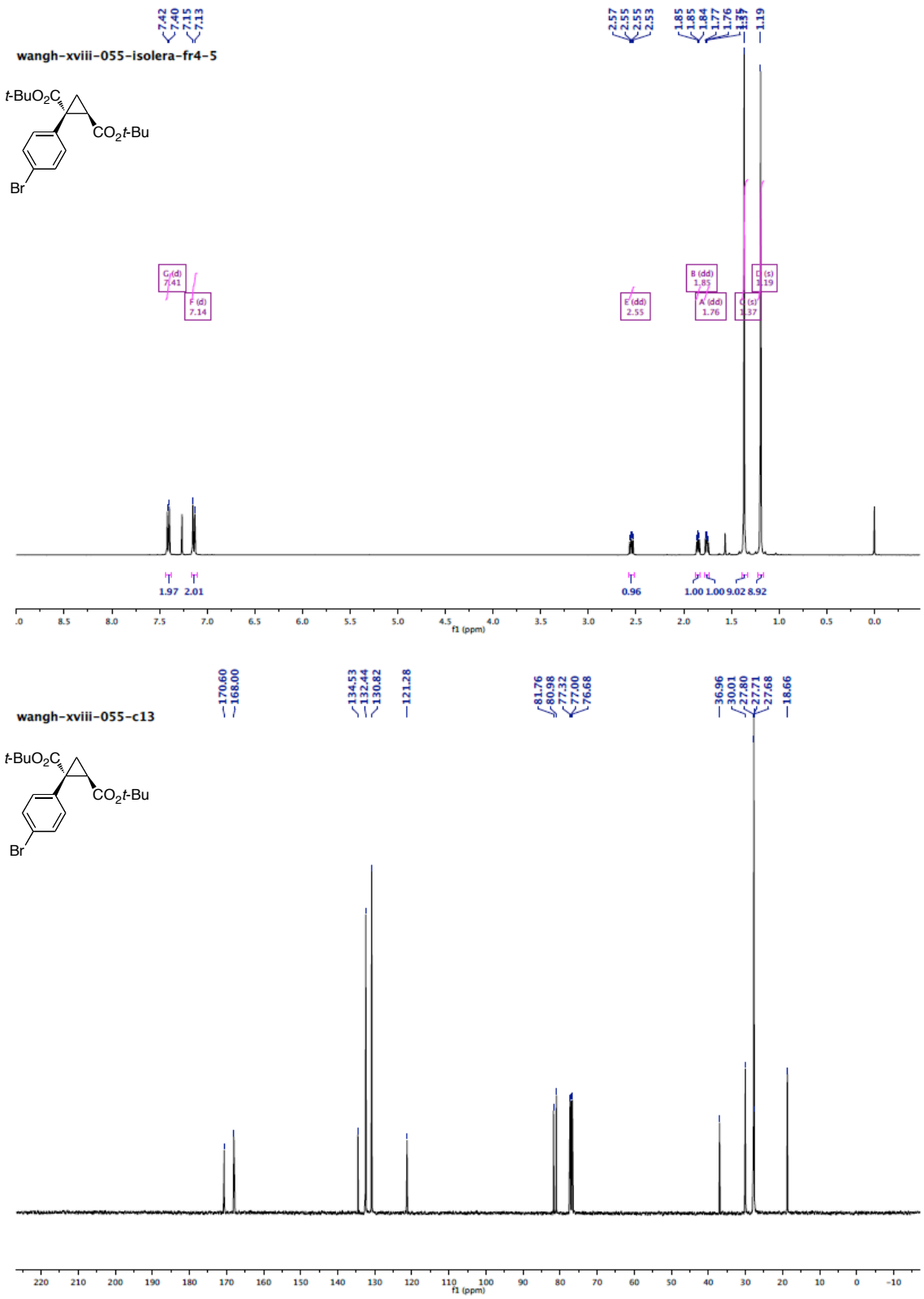
^{1}H- and ^{13}C-NMR spectra of compound **7h**



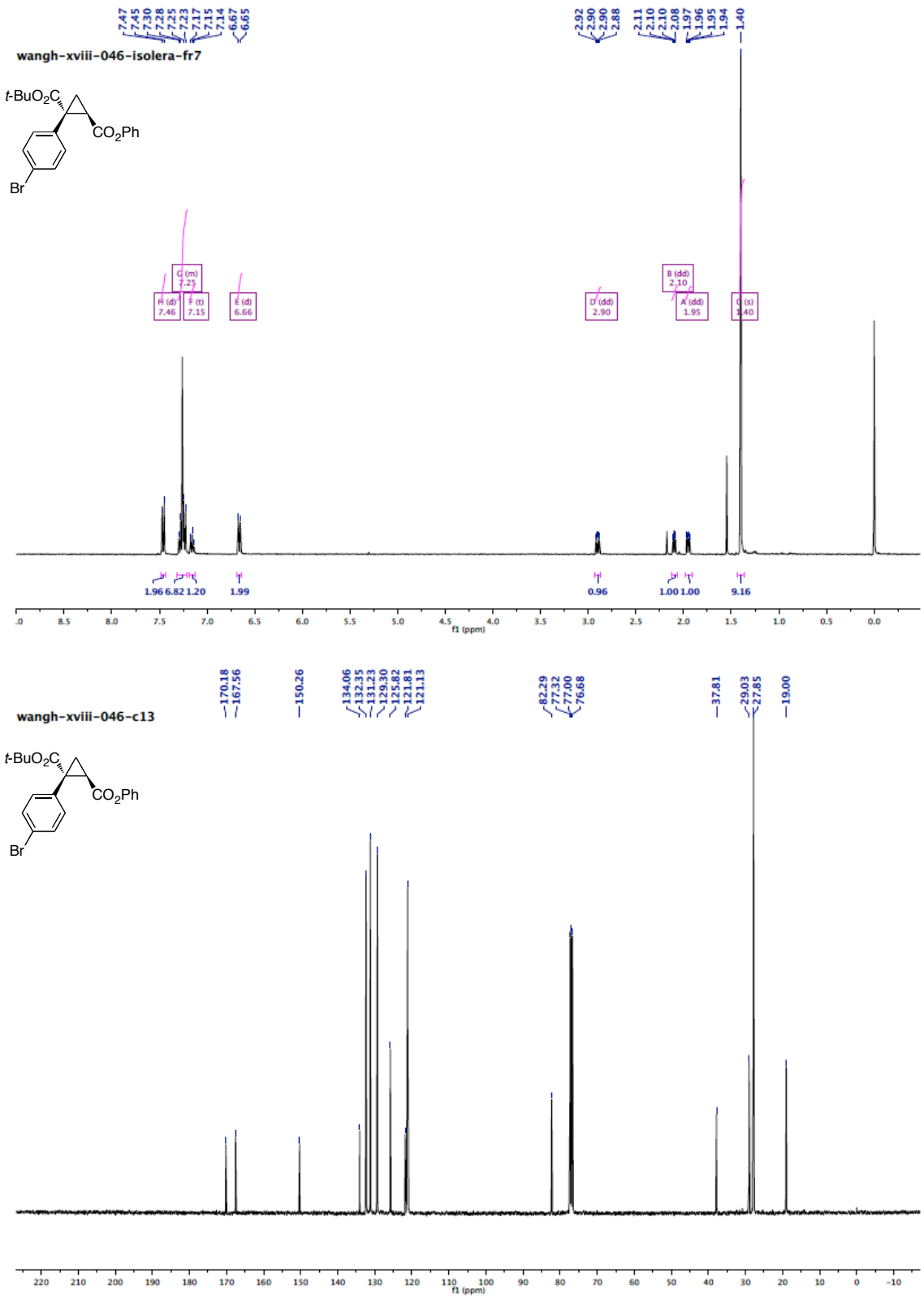
^{1}H- and ^{13}C-NMR spectra of compound **7i**



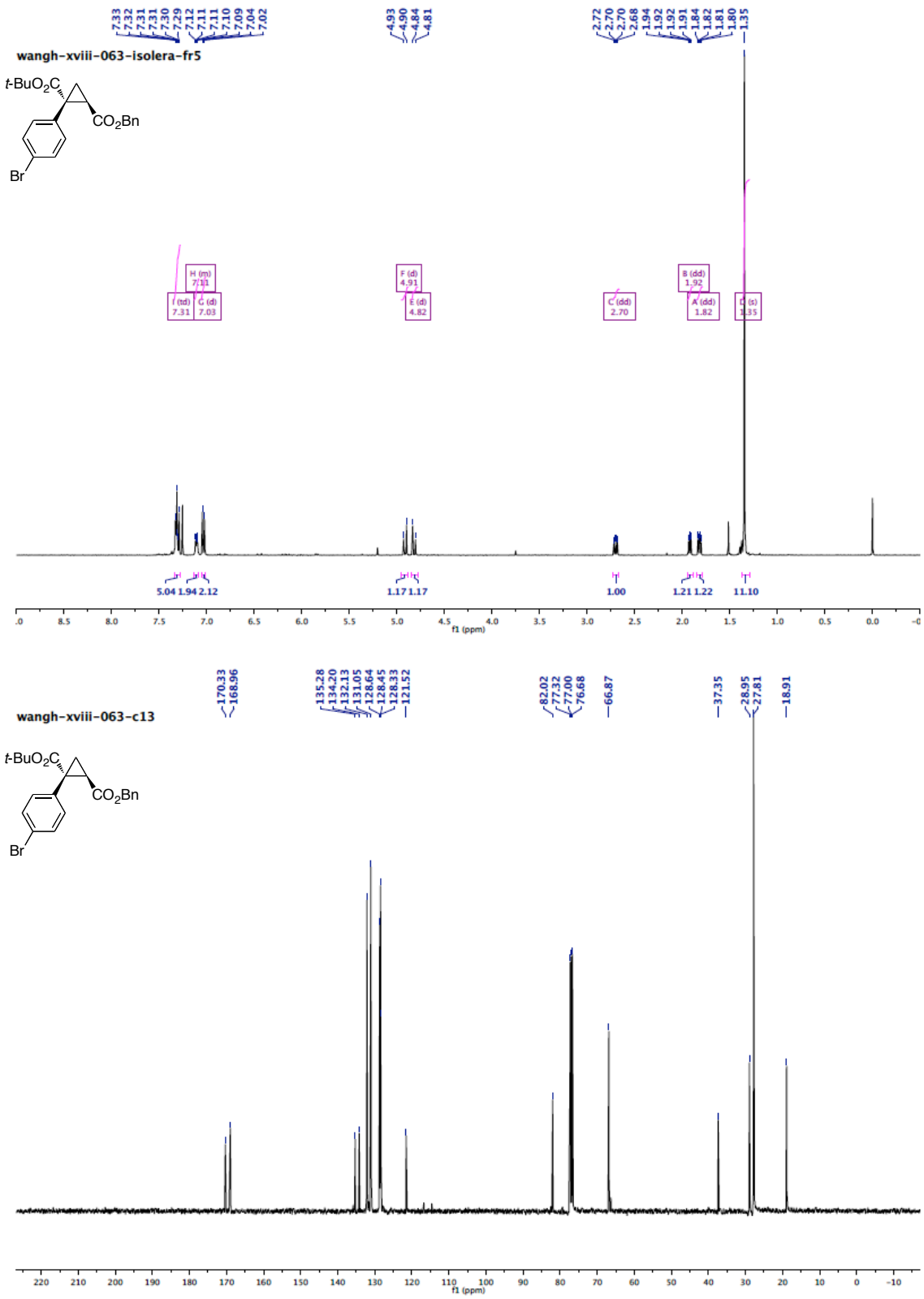
^{1}H- and ^{13}C-NMR spectra of compound **7j**



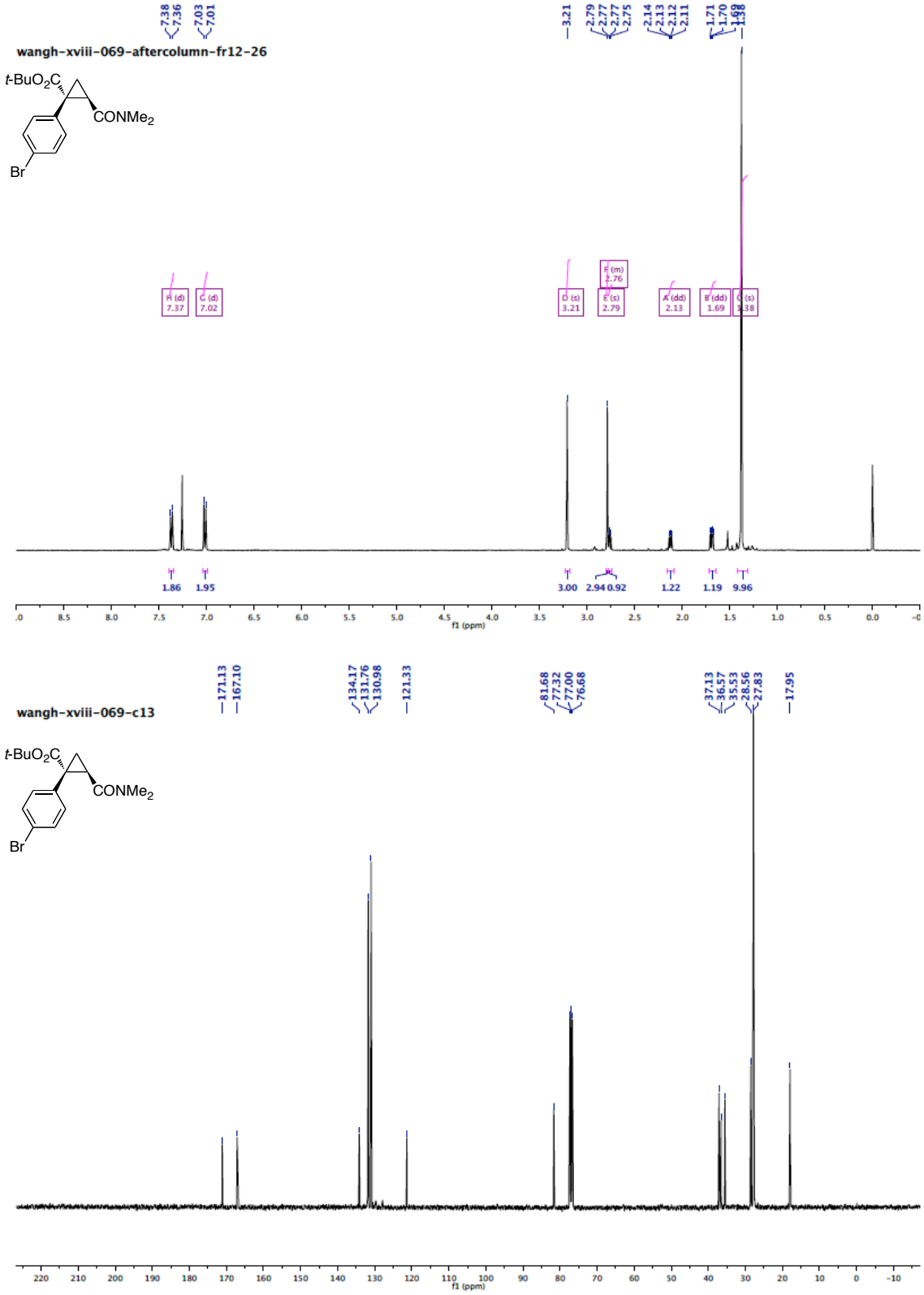
^{1}H- and ^{13}C-NMR spectra of compound **7k**



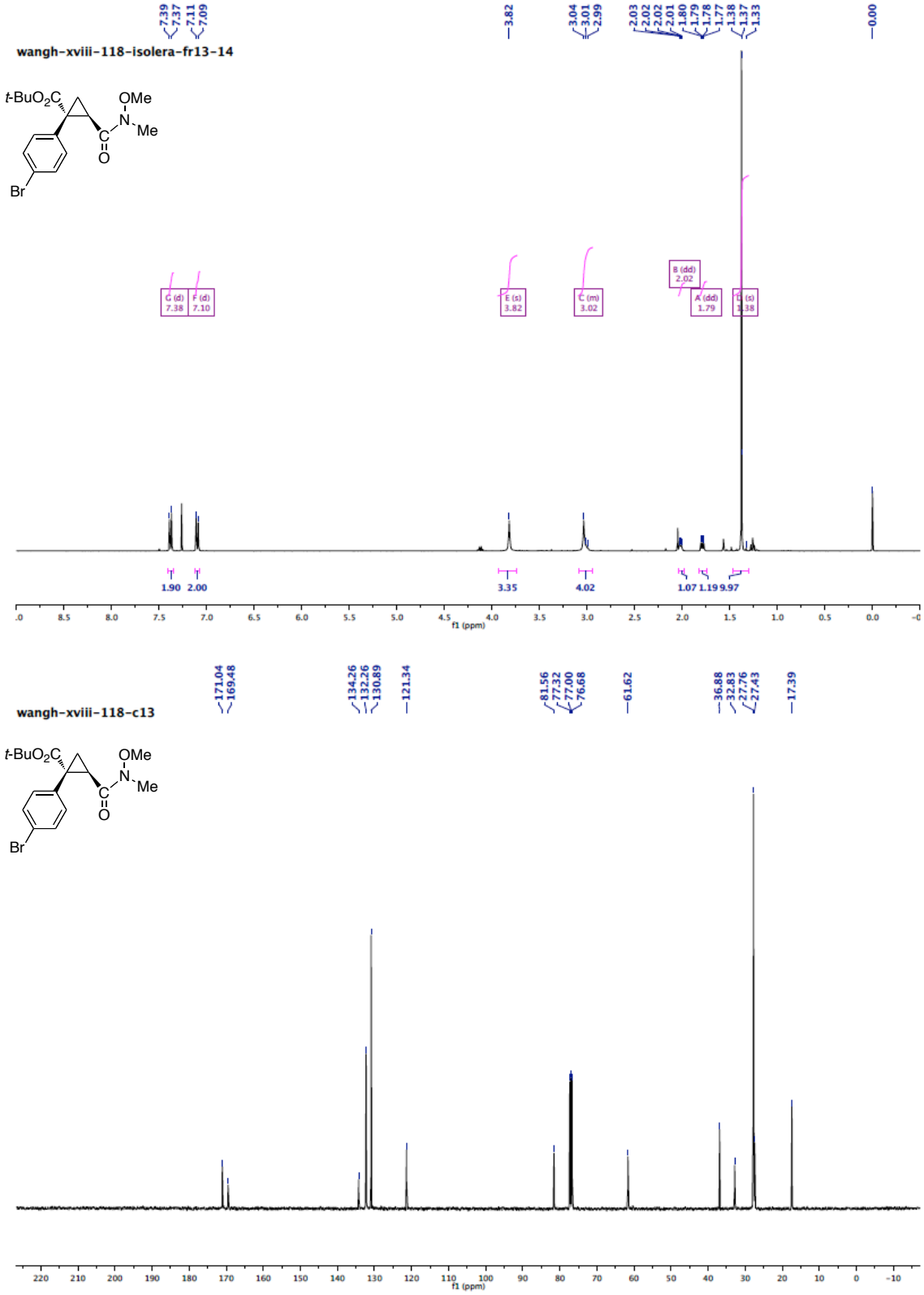
^{1}H- and ^{13}C-NMR spectra of compound **7l**



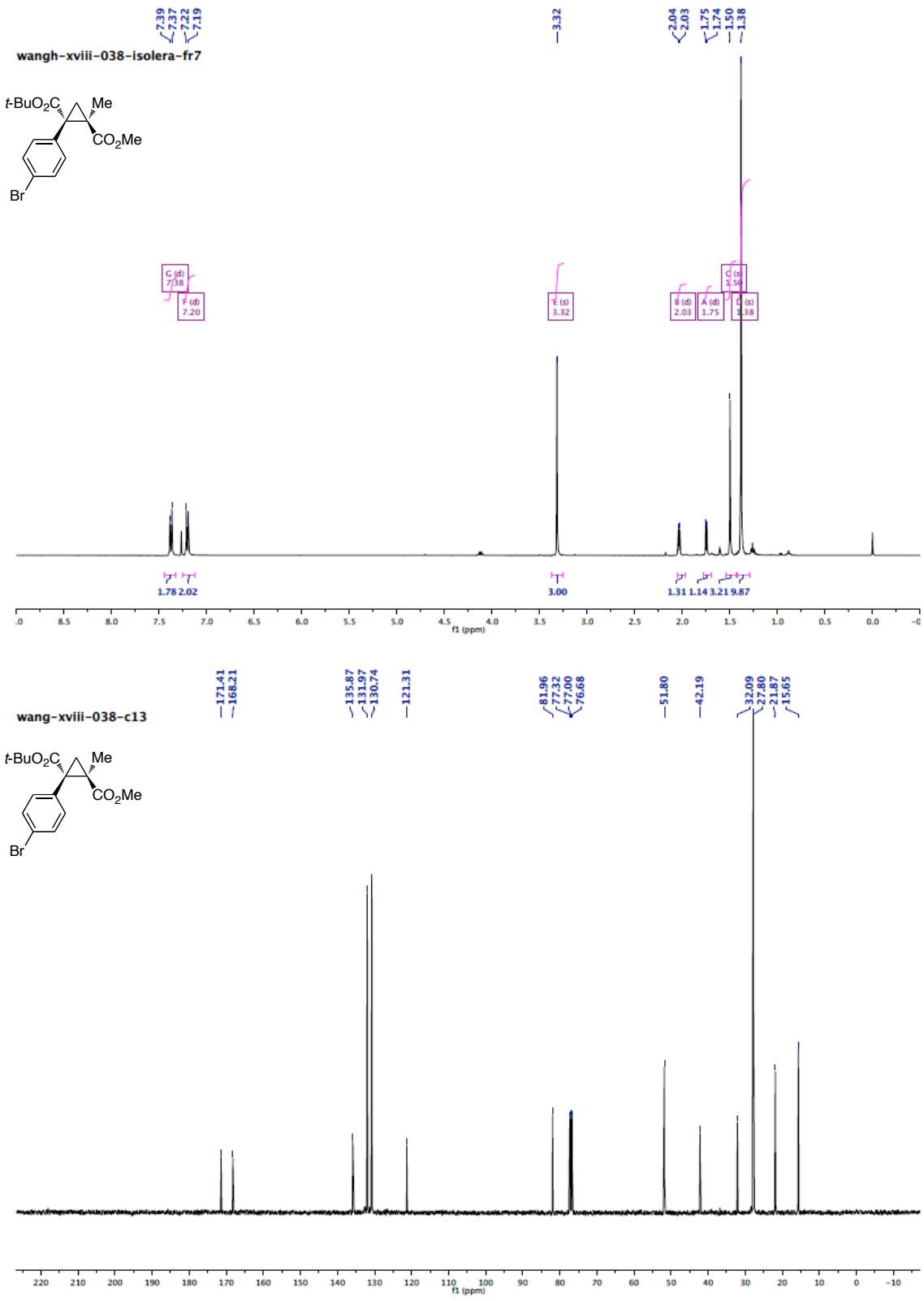
^{1}H- and ^{13}C-NMR spectra of compound **7m**



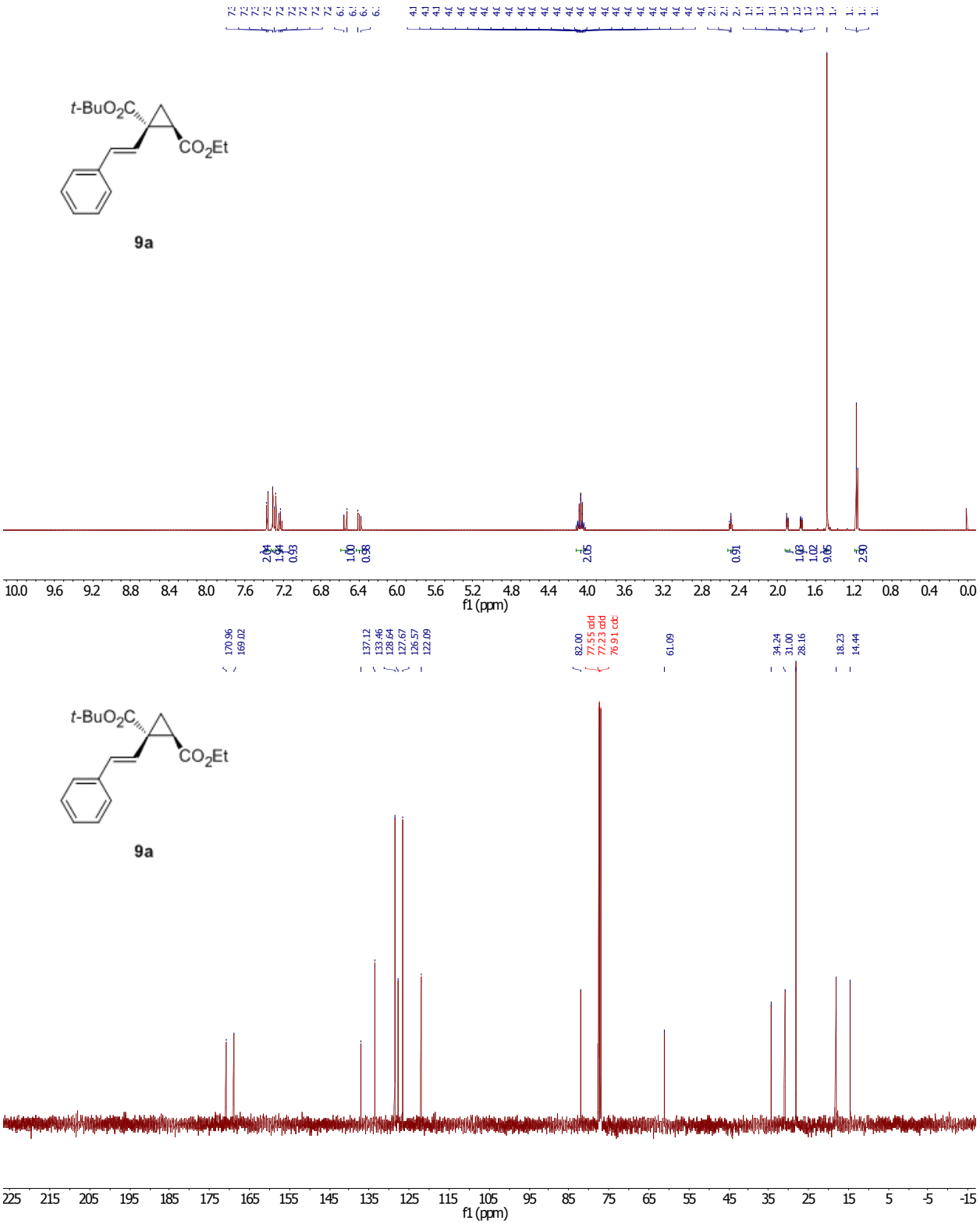
^{1}H- and ^{13}C-NMR spectra of compound **7n**



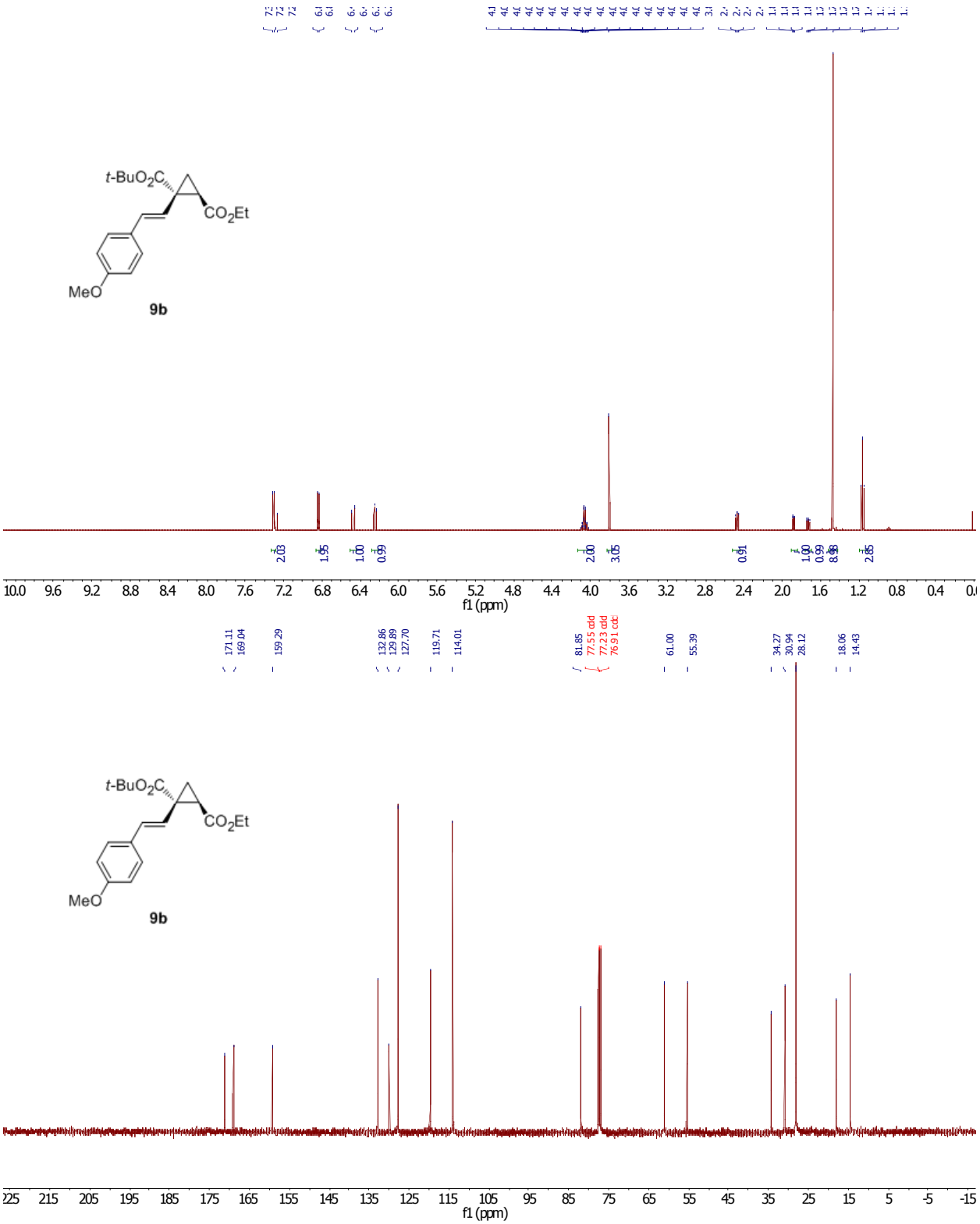
^{1}H- and ^{13}C-NMR spectra of compound **7o**



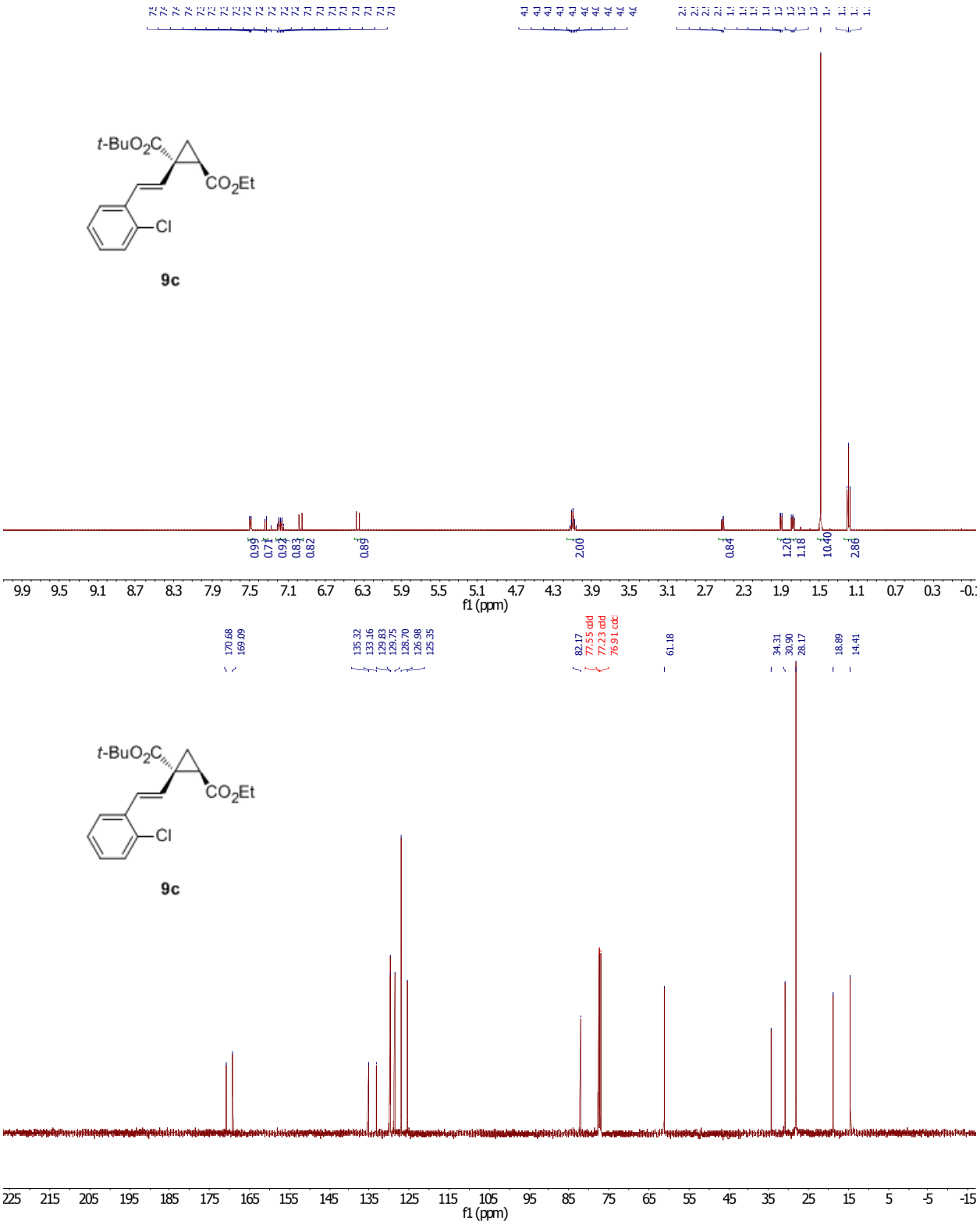
^{1}H- and ^{13}C-NMR spectra of compound **7p**



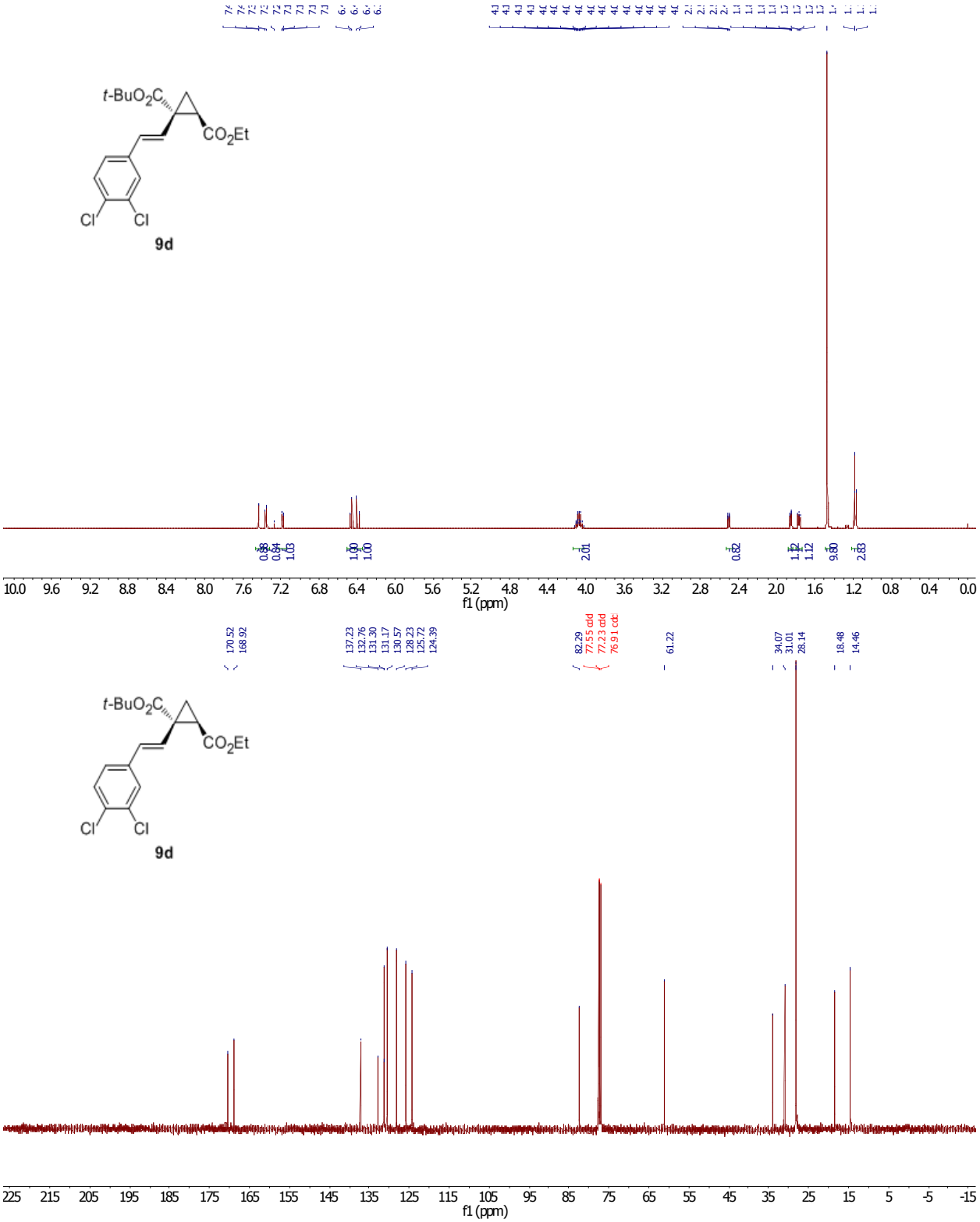
^{1}H- and ^{13}C-NMR spectra of compound **9a**



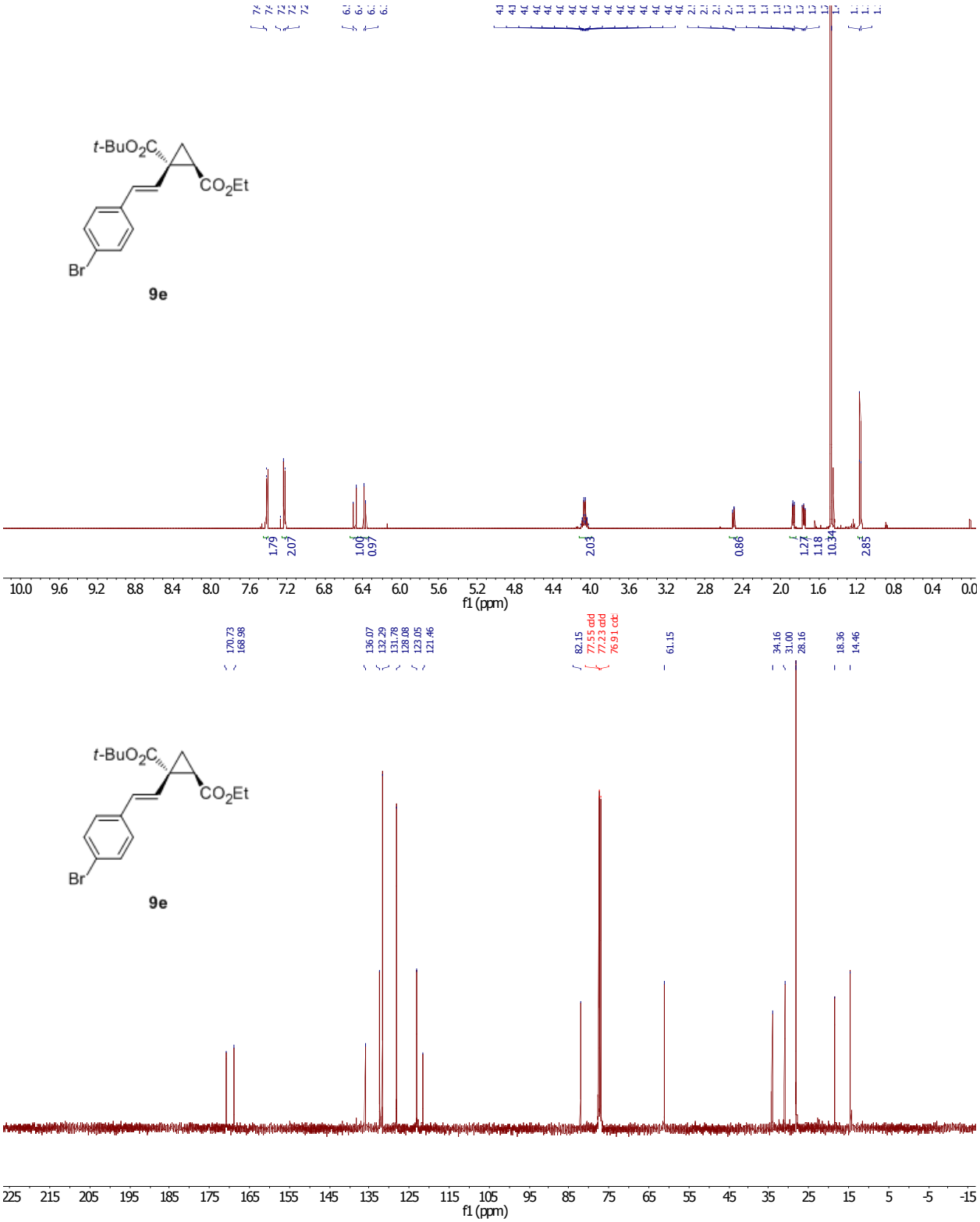
^{1}H- and ^{13}C-NMR spectra of compound **9b**



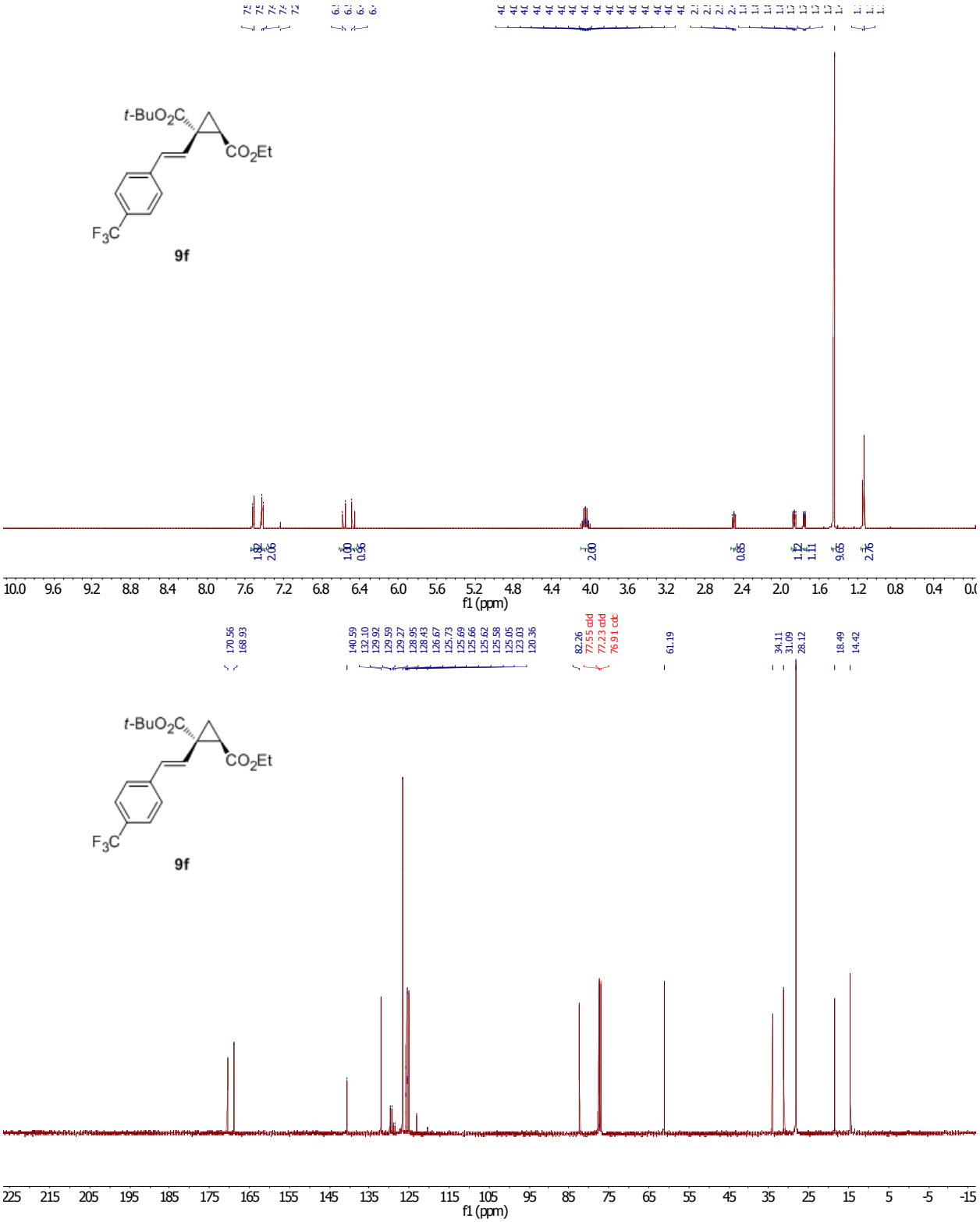
^{1}H- and ^{13}C-NMR spectra of compound **9c**



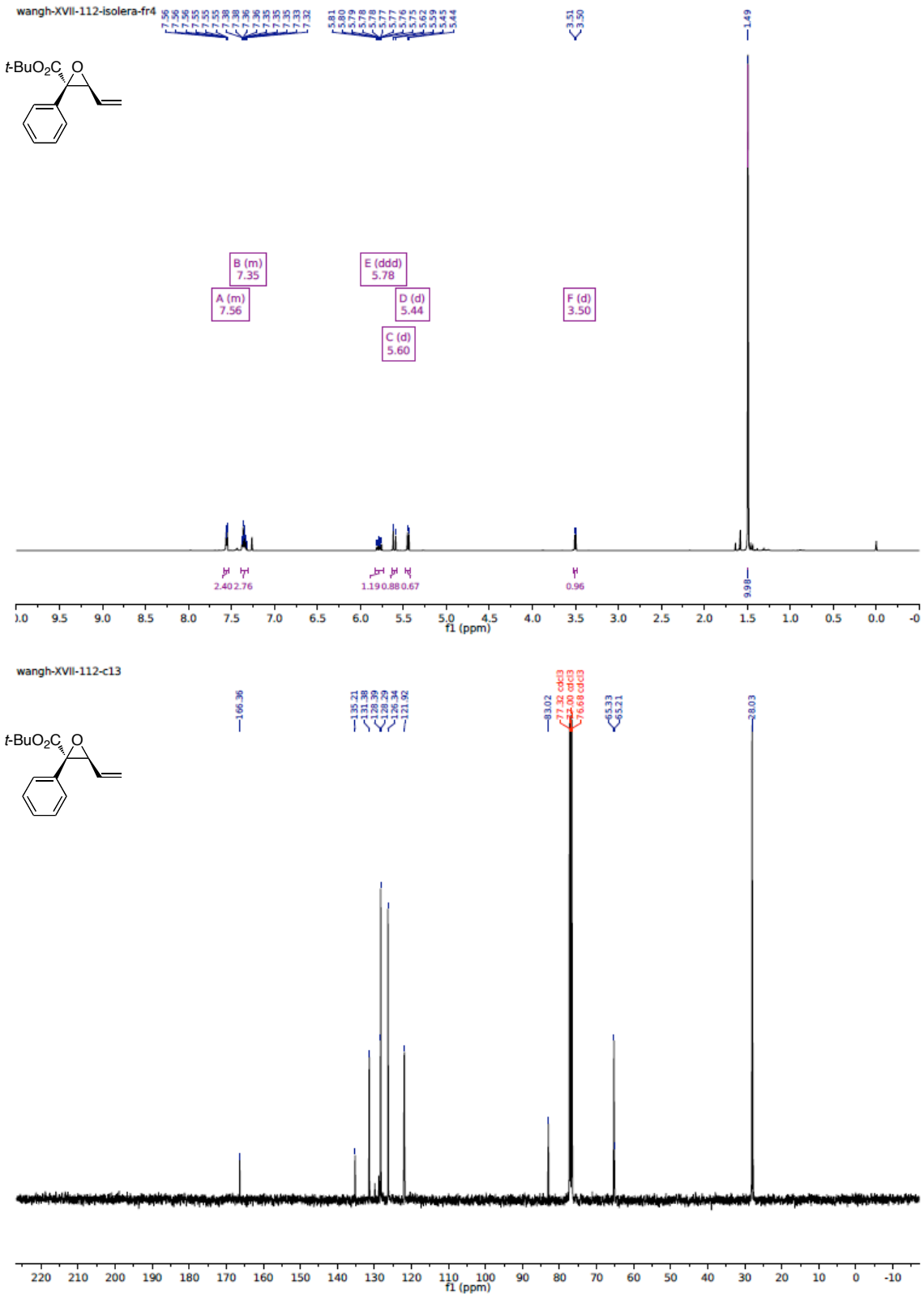
^{1}H- and ^{13}C-NMR spectra of compound **9d**



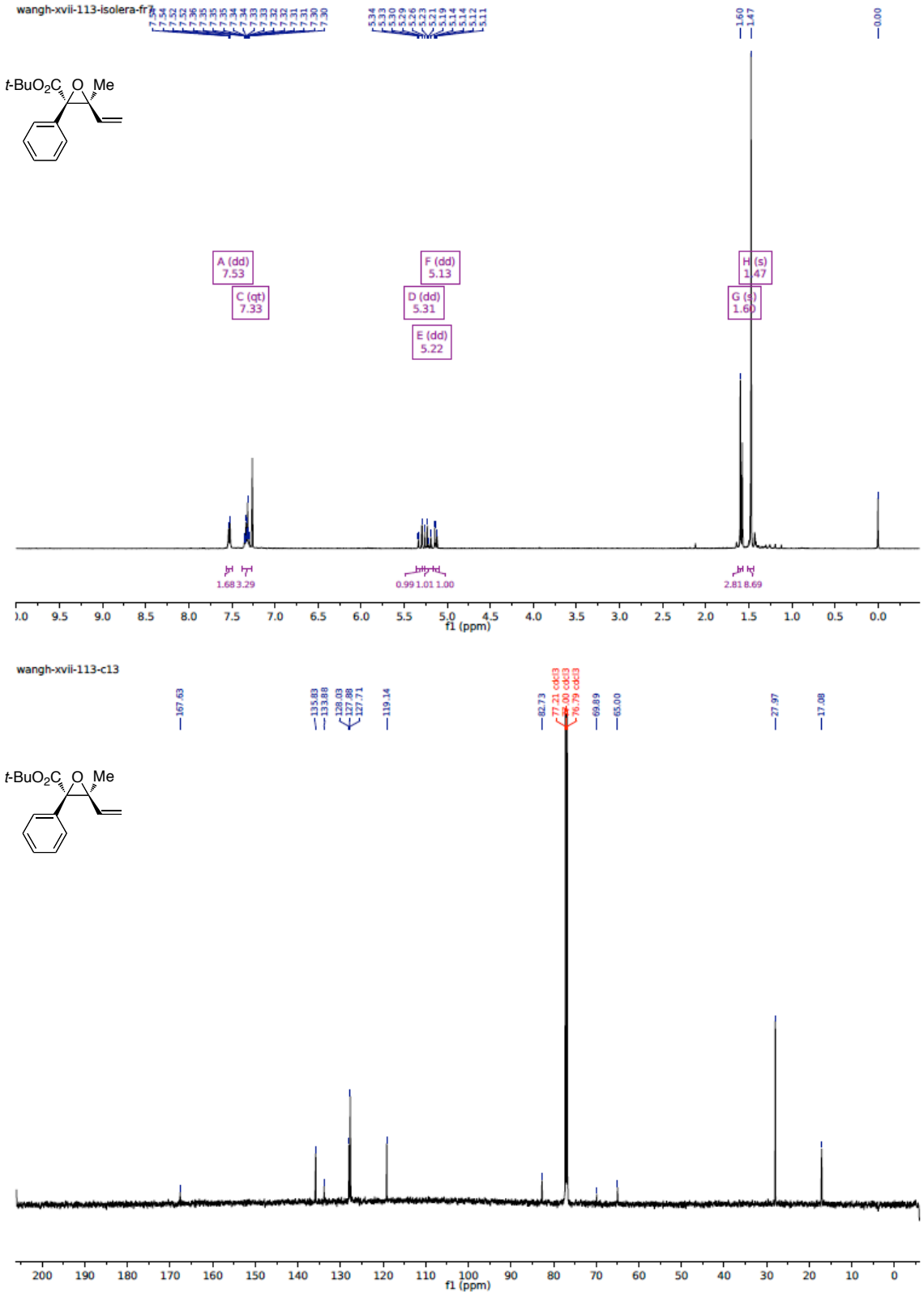
^{1}H- and ^{13}C-NMR spectra of compound **9e**



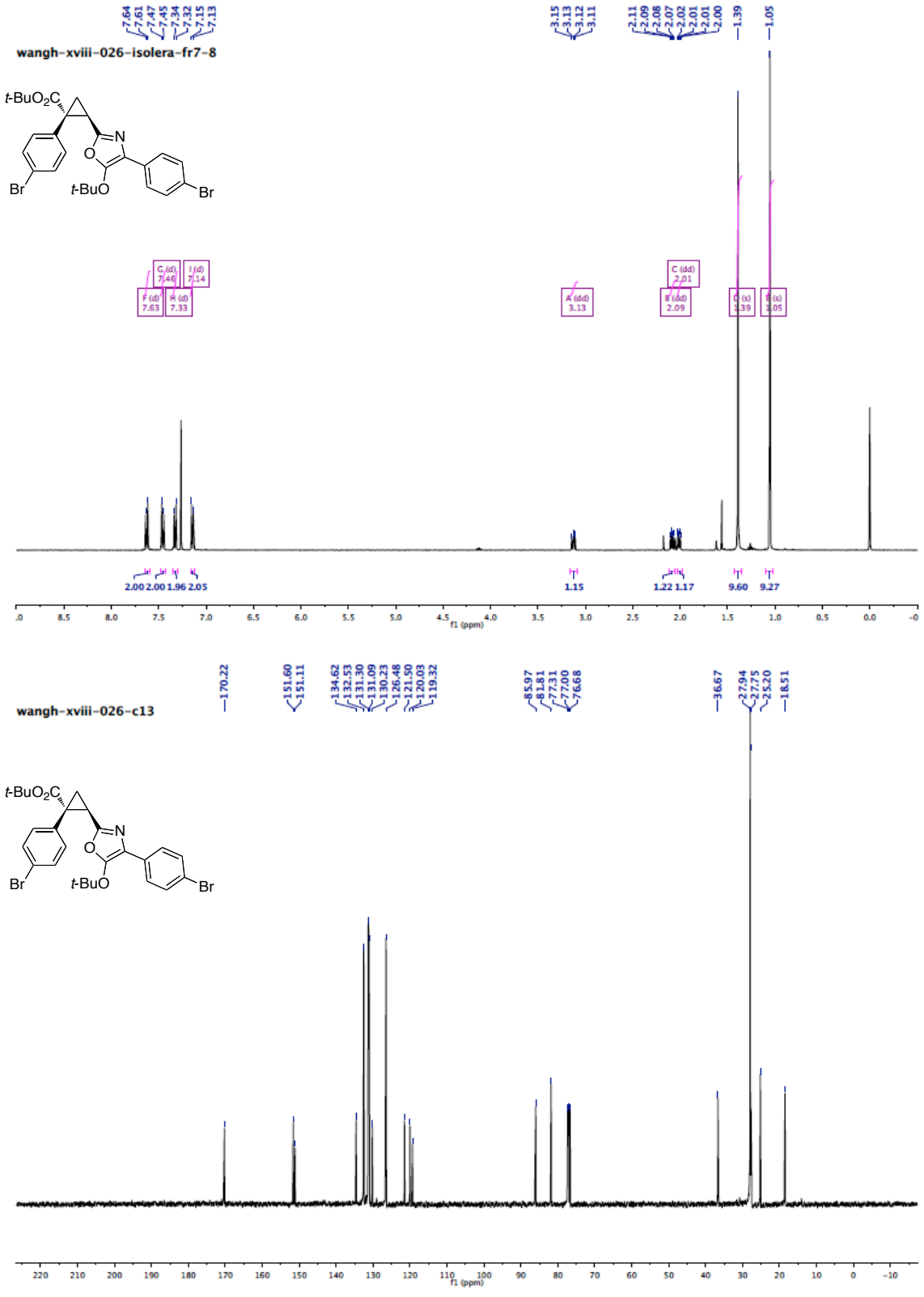
^{1}H- and ^{13}C-NMR spectra of compound **9f**



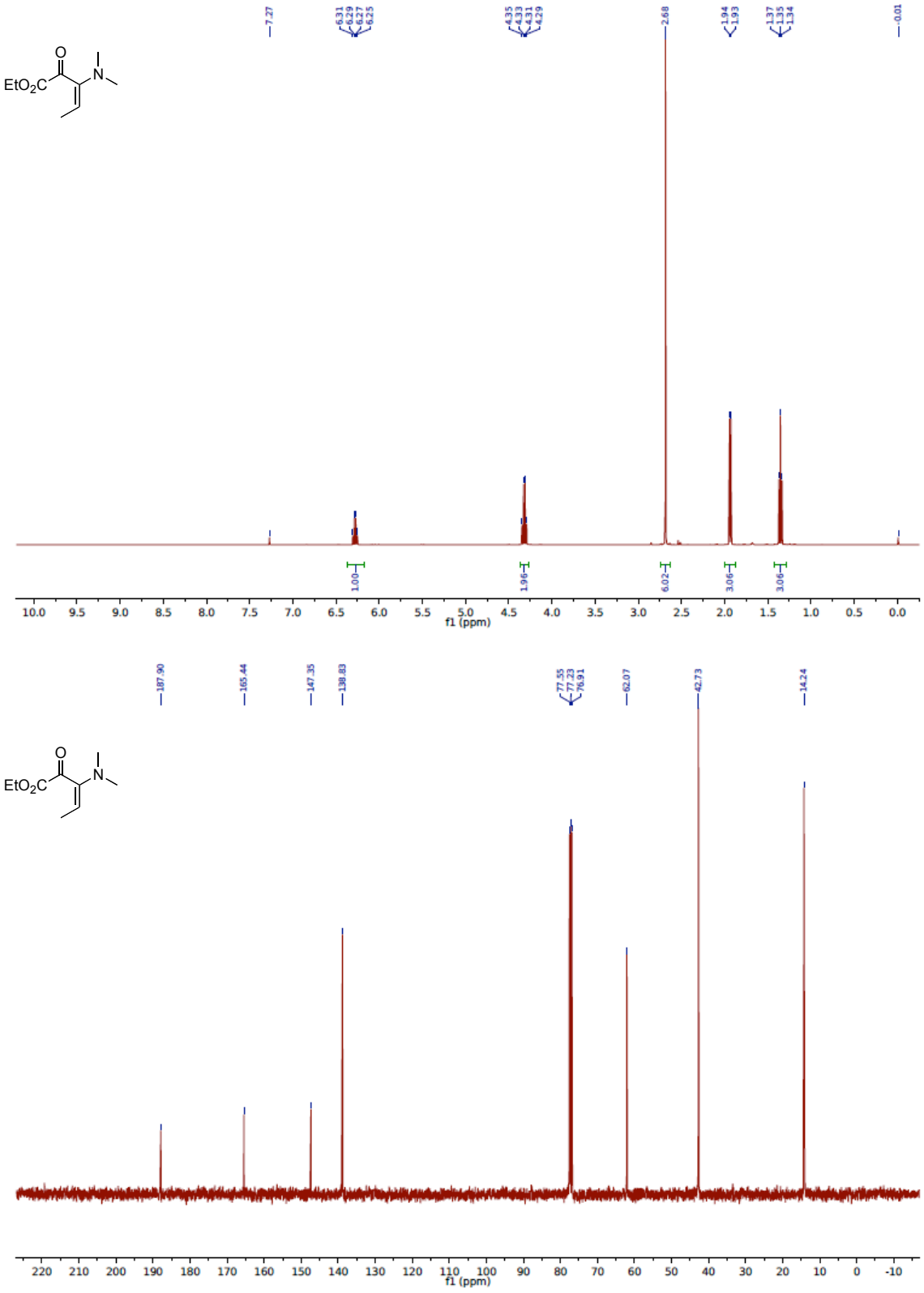
^{1}H- and ^{13}C-NMR spectra of compound **12**



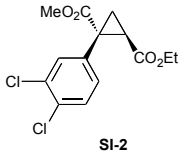
^{1}H- and ^{13}C-NMR spectra of compound **13**



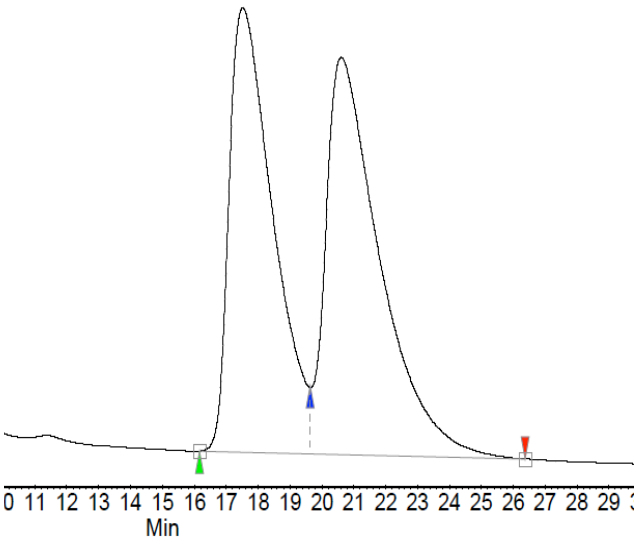
^{1}H- and ^{13}C-NMR spectra of compound **15**



^{1}H- and ^{13}C-NMR spectra of compound **18**



SI-2



#	Time (Min)	Area (%)
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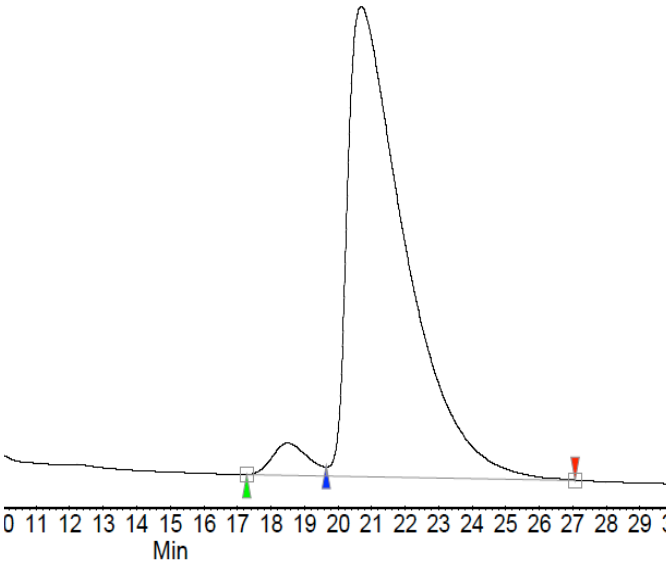
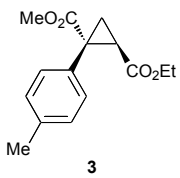
2	20.61	52.531



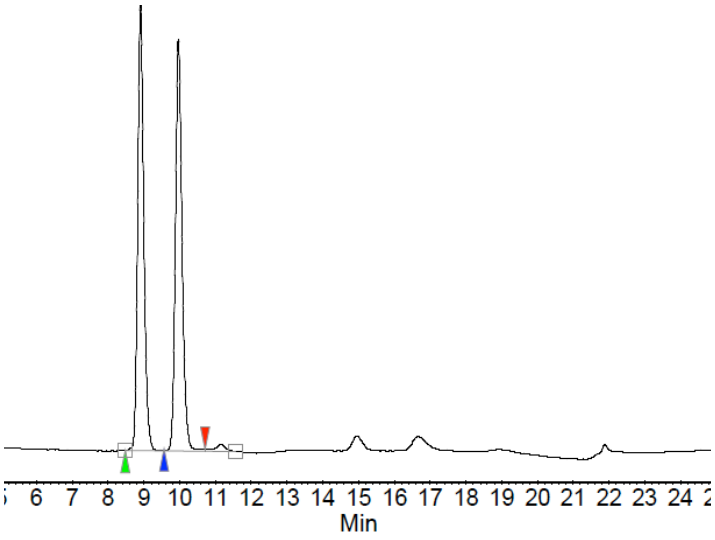
#	Time (Min)	Area (%)
1	18.49	4.057
2	20.69	95.943

92% ee

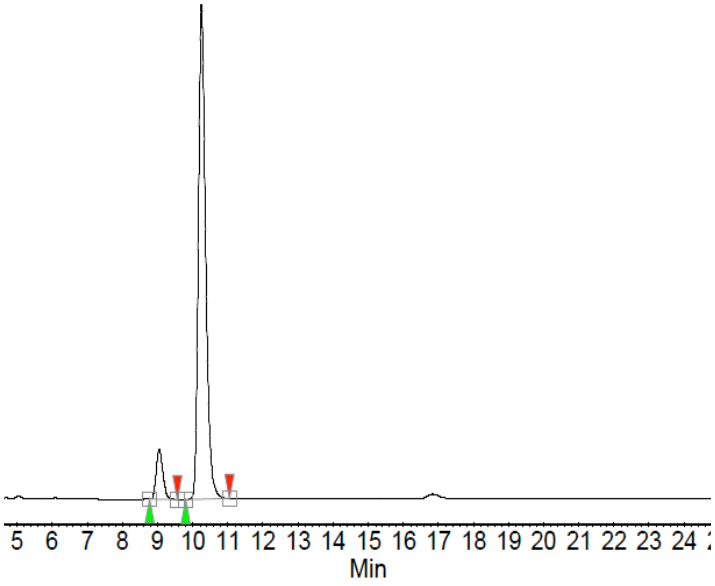
HPLC traces of compound **SI-2**



3



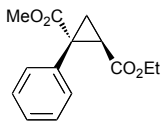
#	Time (Min)	Area (%)
1	8.93	49.786
2	10.37	50.214



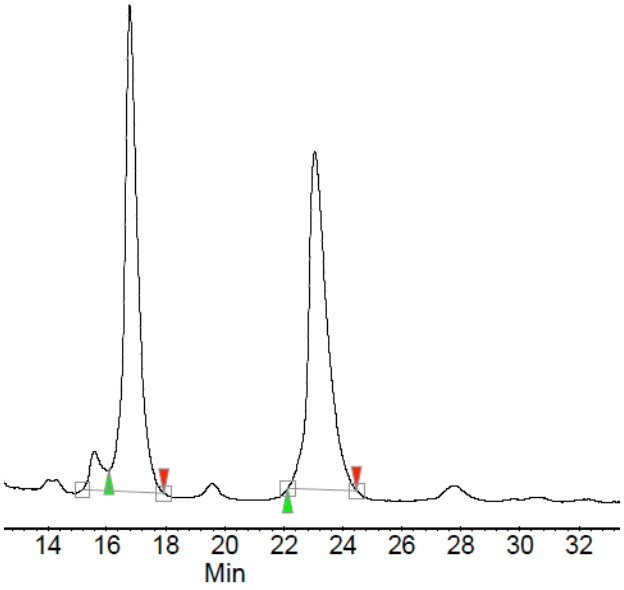
#	Time (min)	Area (%)
1	9.05	8.216
2	10.25	91.784

84% ee

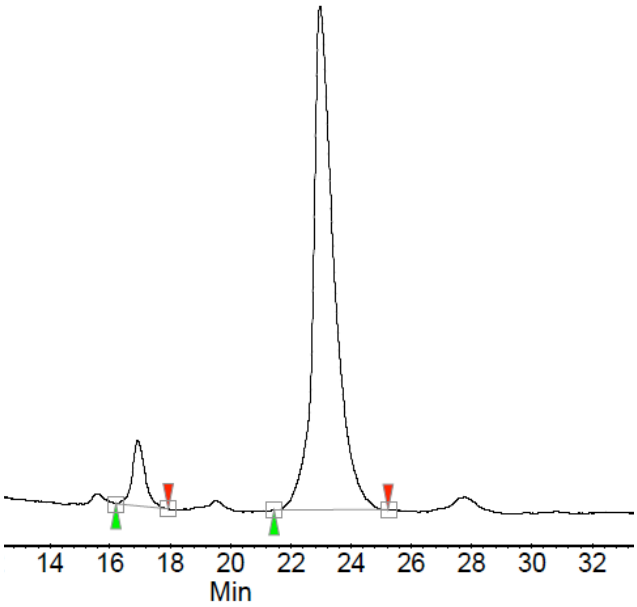
HPLC traces of compound **3**



5a



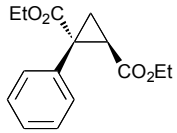
#	Time (Min)	Area (%)
1	16.78	51.028
2	23.05	48.972



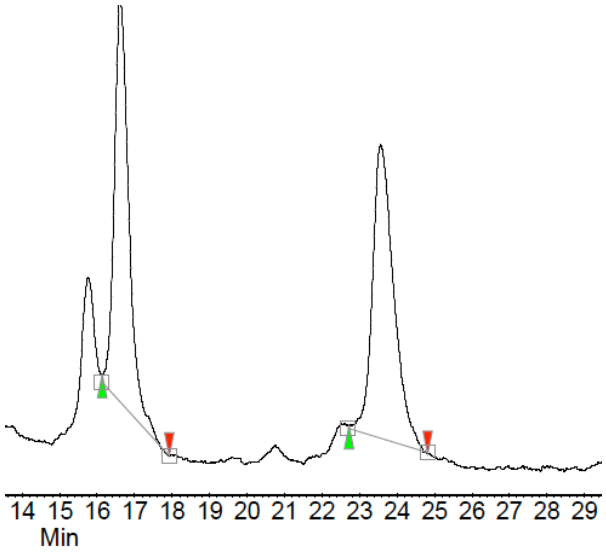
#	Time (Min)	Area (%)
1	16.92	7.252
2	22.97	92.748

85% ee

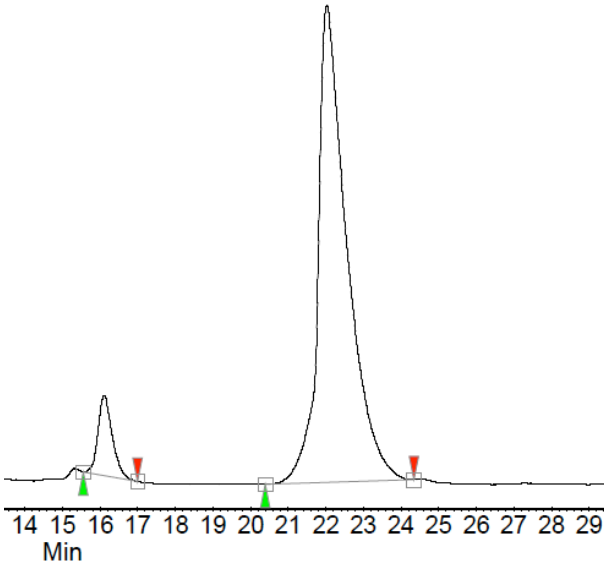
HPLC traces of compound **5a**



5b



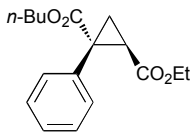
#	Time (Min)	Area (%)
1	16.62	48.403
2	23.57	51.597



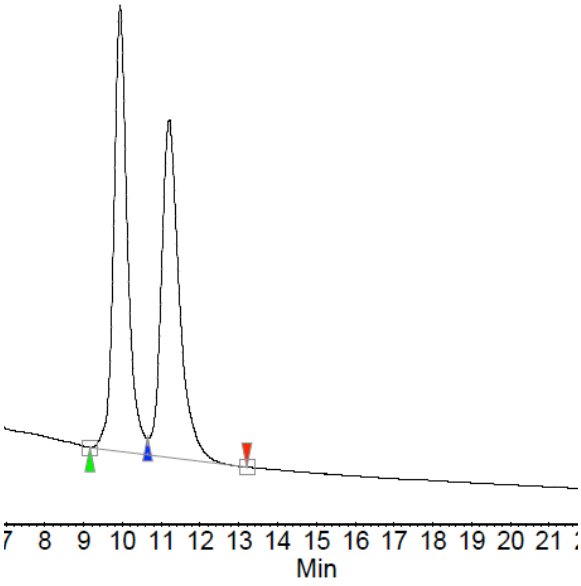
#	Time (Min)	Area (%)
1	16.11	7.649
2	22.03	92.351

85% ee

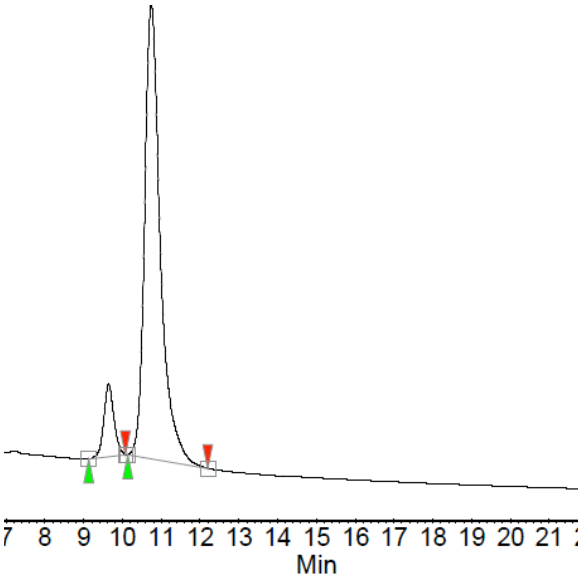
HPLC traces of compound **5b**



5c



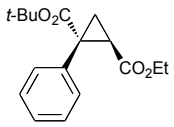
#	Time (Min)	Area (%)
1	9.93	50.070
2	11.20	49.930



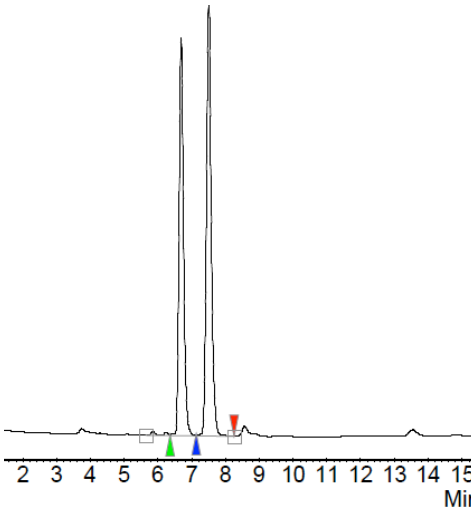
#	Time (Min)	Area (%)
1	9.64	9.332
2	10.74	90.668

81% ee

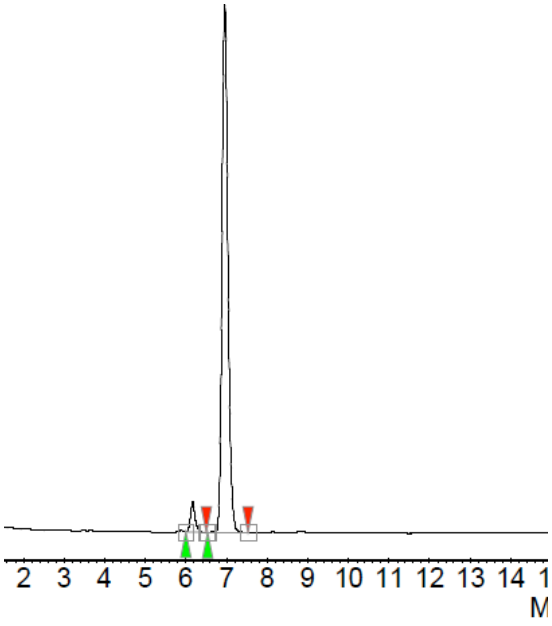
HPLC traces of compound **5c**



5d



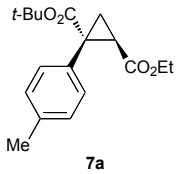
#	Time (Min)	Area (%)
1	6.69	44.632
2	7.50	55.368



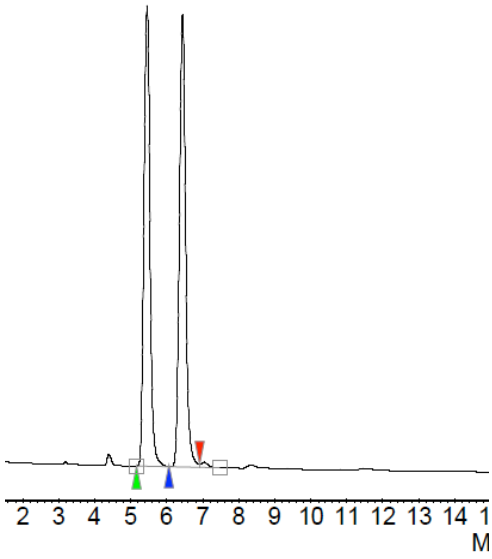
#	Time (Min)	Area (%)
1	6.16	4.415
2	6.96	95.585

91% ee

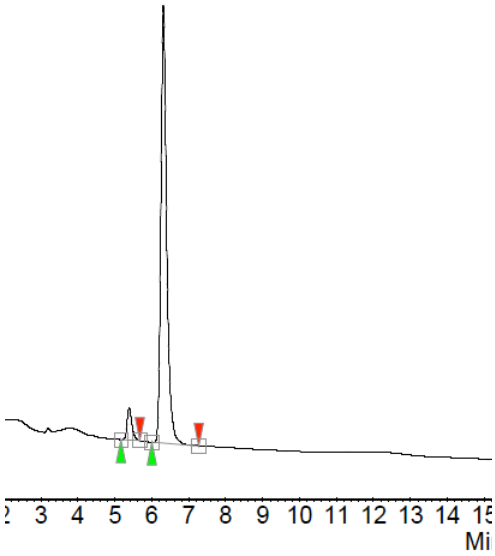
HPLC traces of compound **5d**



7a



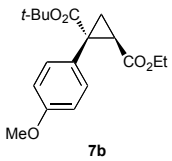
#	Time (Min)	Area (%)
1	5.45	50.027
2	6.44	49.973



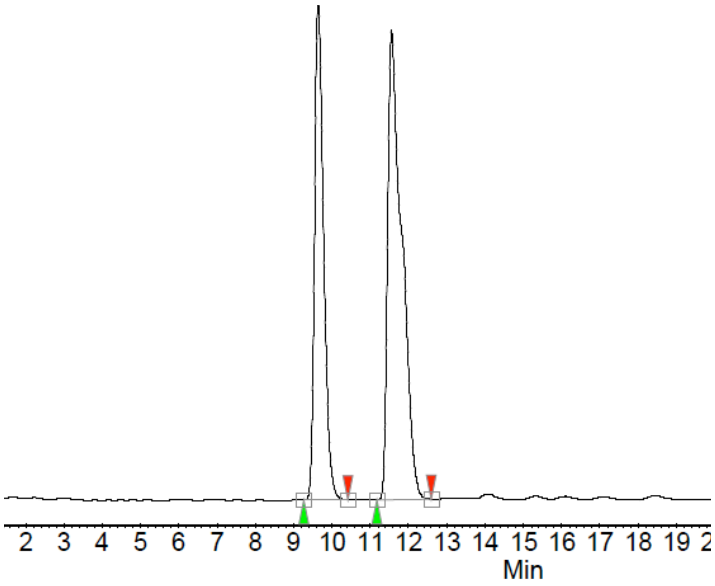
#	Time (Min)	Area (%)
1	5.39	5.616
2	6.31	94.384

89% ee

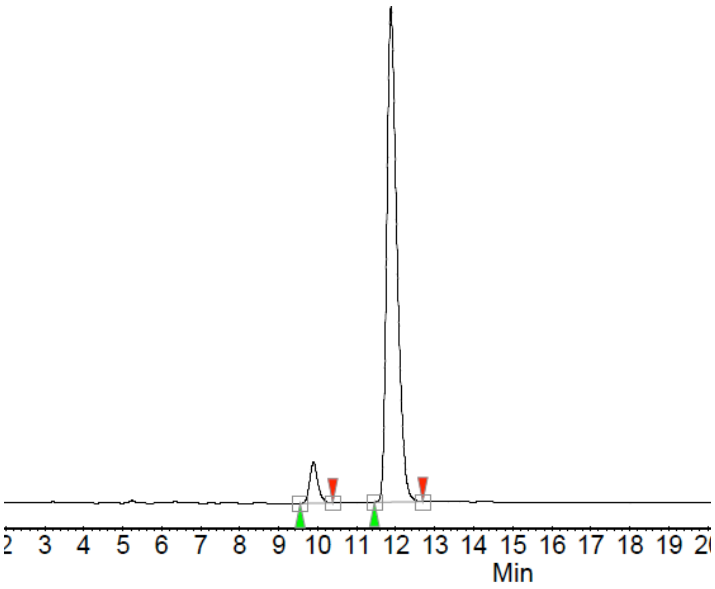
HPLC traces of compound **7a**



7b



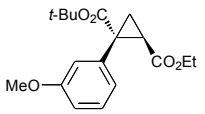
#	Time (Min)	Area (%)
1	9.64	40.332
2	11.56	59.668



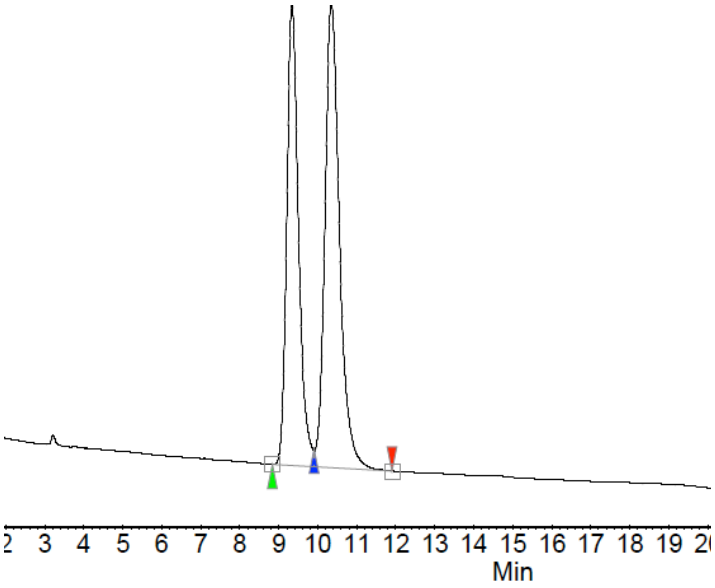
#	Time (Min)	Area (%)
1	9.89	6.137
2	11.87	93.863

88% ee

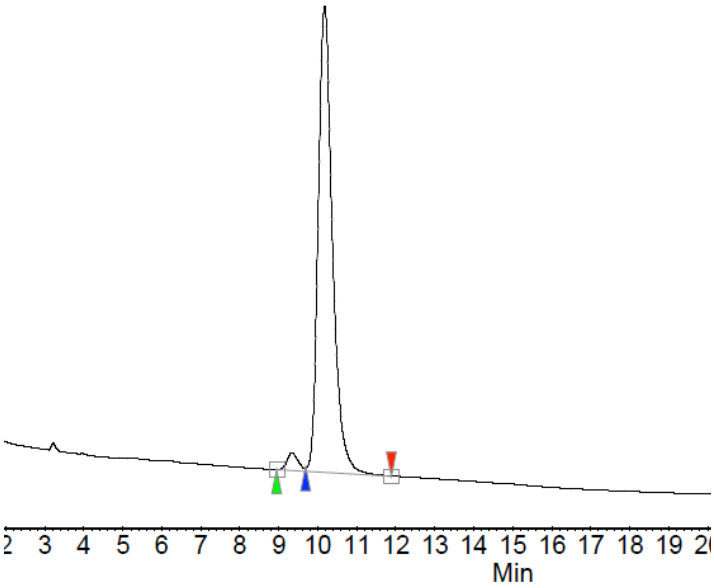
HPLC traces of compound **7b**



7c



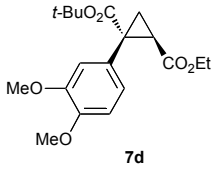
#	Time (Min)	Area (%)
1	9.34	44.342
2	10.35	55.658



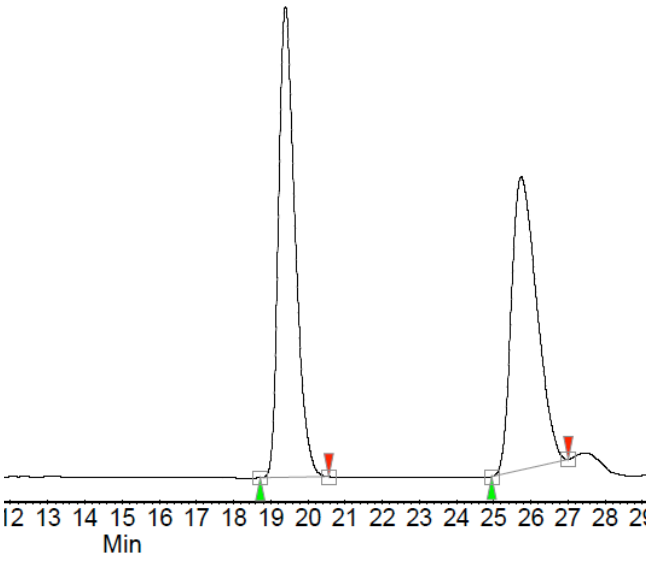
#	Time (Min)	Area (%)
1	9.34	2.845
2	10.17	97.155

94% ee

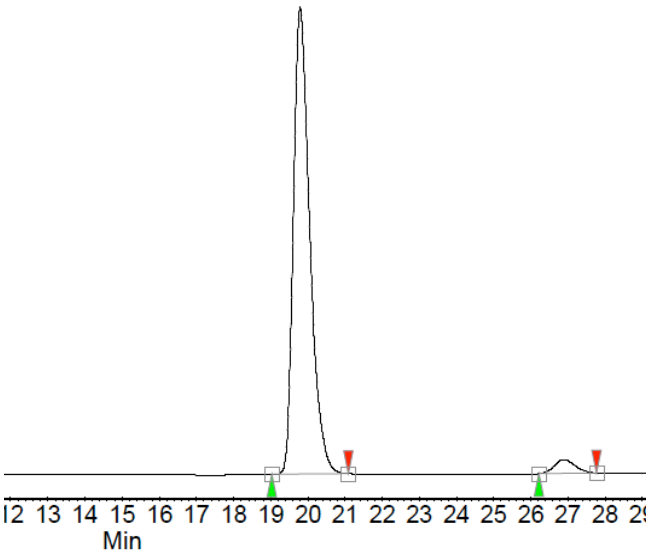
HPLC traces of compound **7c**



7d



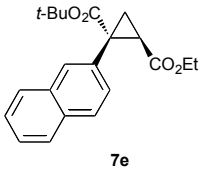
#	Time (Min)	Area (%)
1	19.39	51.239
2	25.74	48.761



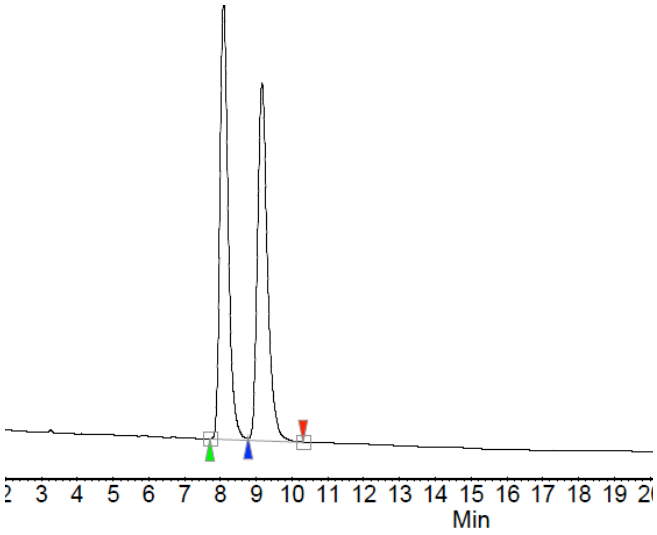
#	Time (Min)	Area (%)
1	19.79	96.280
2	26.90	3.720

93% ee

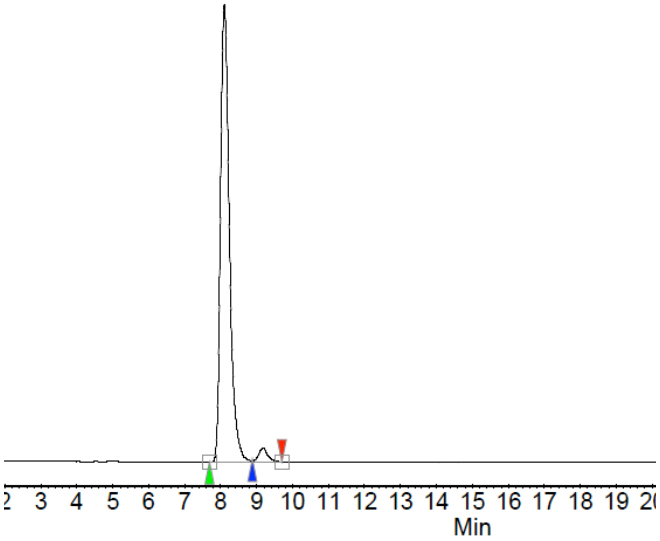
HPLC traces of compound **7d**



7e



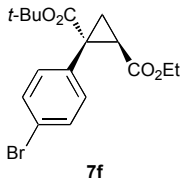
#	Time (Min)	Area (%)
1	8.08	50.350
2	9.16	49.650



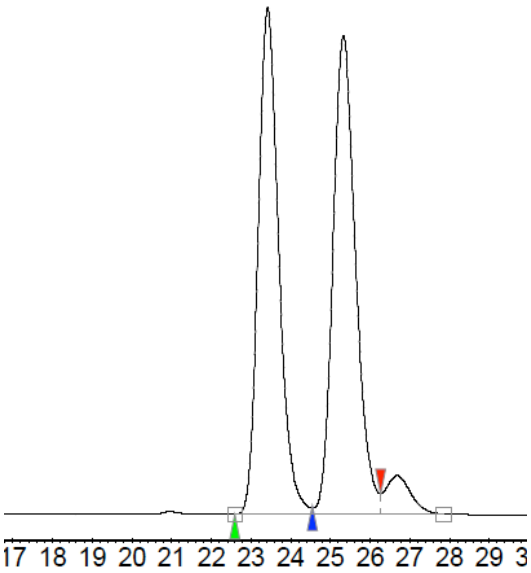
#	Time (Min)	Area (%)
1	8.10	96.956
2	9.17	3.044

94% ee

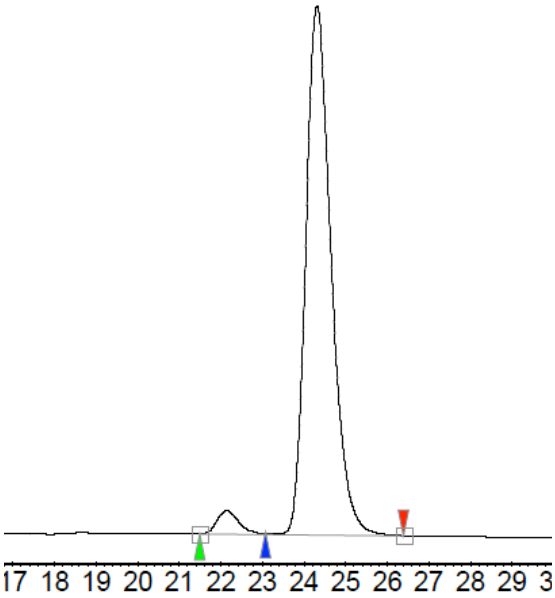
HPLC traces of compound **7e**



7f



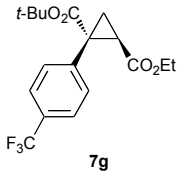
#	Time (Min)	Area (%)
1	23.42	49.036
2	25.33	50.964



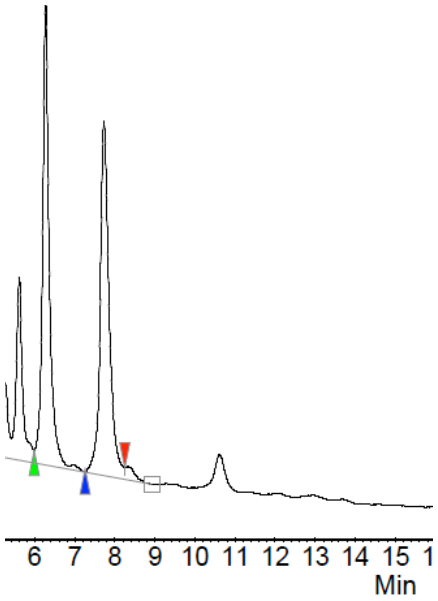
#	Time (Min)	Area (%)
1	22.13	3.714
2	24.31	96.286

93% ee

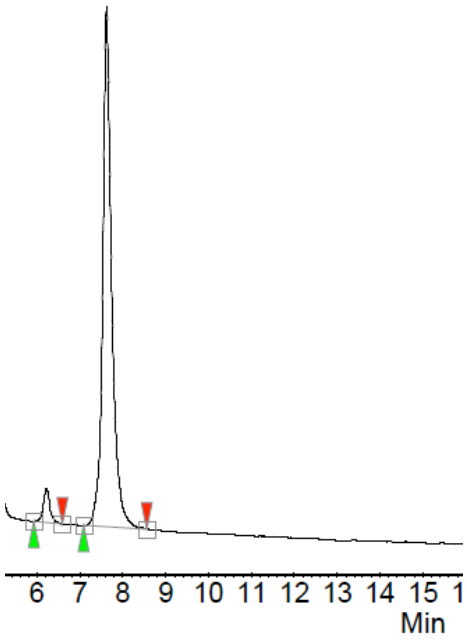
HPLC traces of compound **7f**



7g



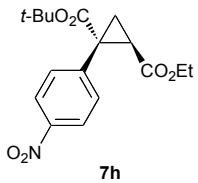
#	Time (Min)	Area (%)
1	6.26	50.316
2	7.72	49.684



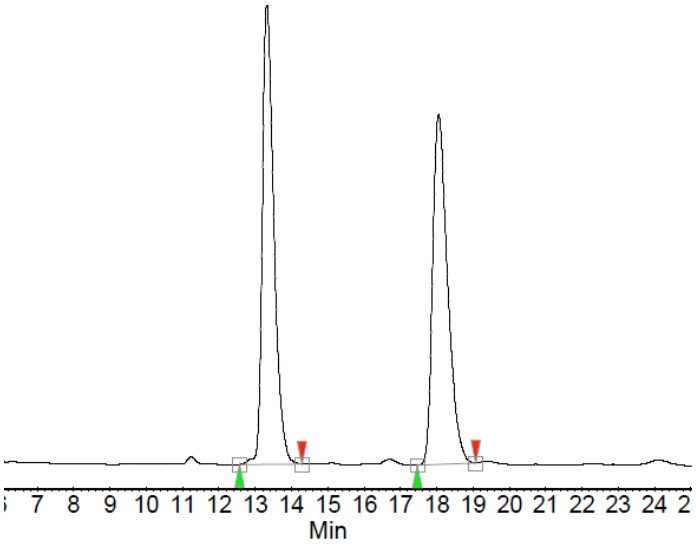
#	Time (Min)	Area (%)
1	6.21	4.430
2	7.61	95.570

91% ee

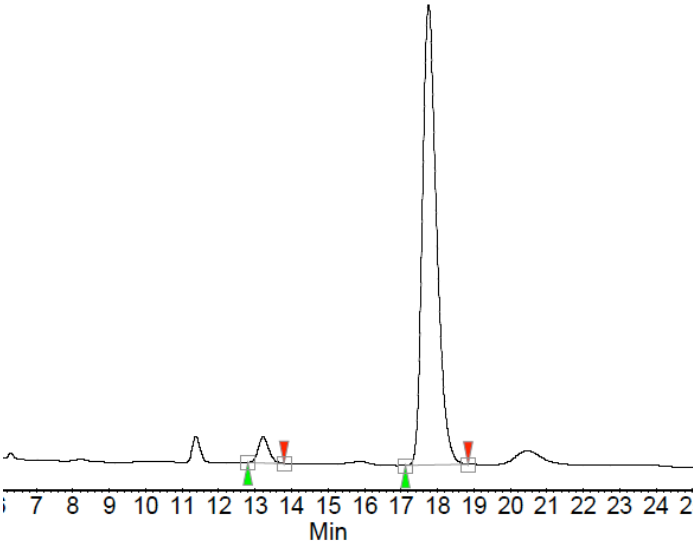
HPLC traces of compound **7g**



7h



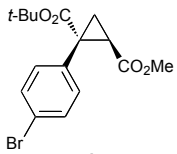
#	Time (Min)	Area (%)
1	13.32	50.448
2	18.05	49.552



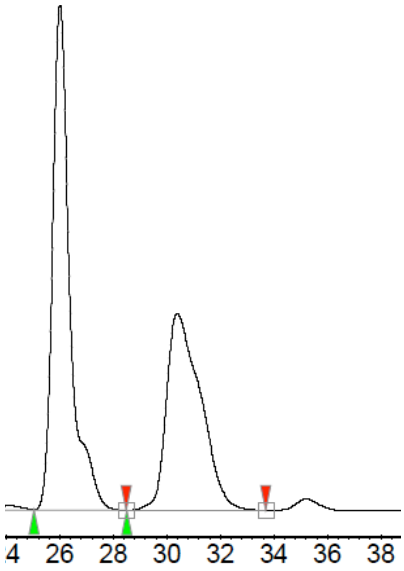
#	Time (Min)	Area (%)
1	13.22	4.051
2	17.75	95.949

92% ee

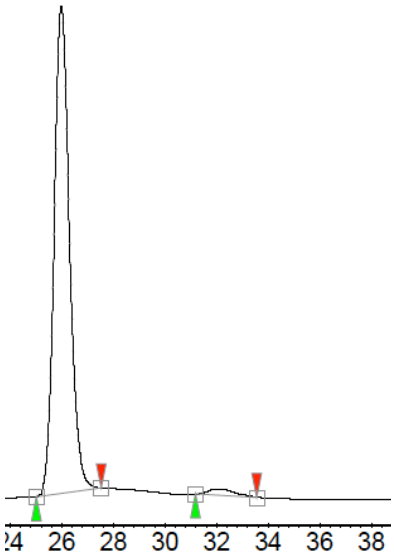
HPLC traces of compound **7h**



7i



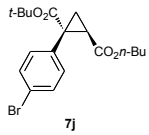
#	Time (Min)	Area (%)
1	26.03	56.659
2	30.40	43.341



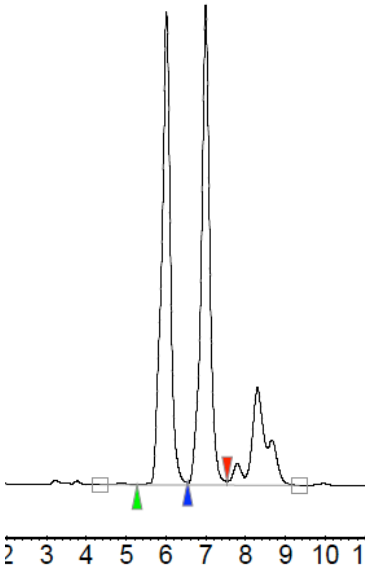
#	Time (Min)	Area (%)
1	26.00	97.721
2	32.15	2.279

95% ee

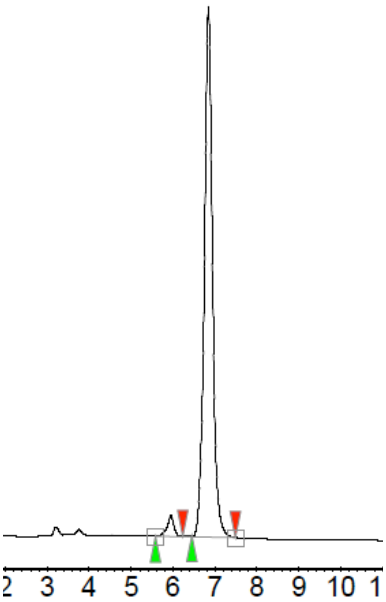
HPLC traces of compound **7i**



7j



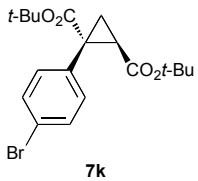
#	Time (Min)	Area (%)
1	6.01	50.173
2	6.99	49.827



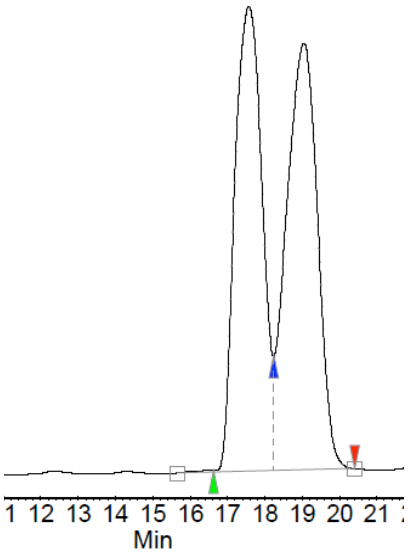
#	Time (Min)	Area (%)
1	5.95	3.430
2	6.84	96.570

93% ee

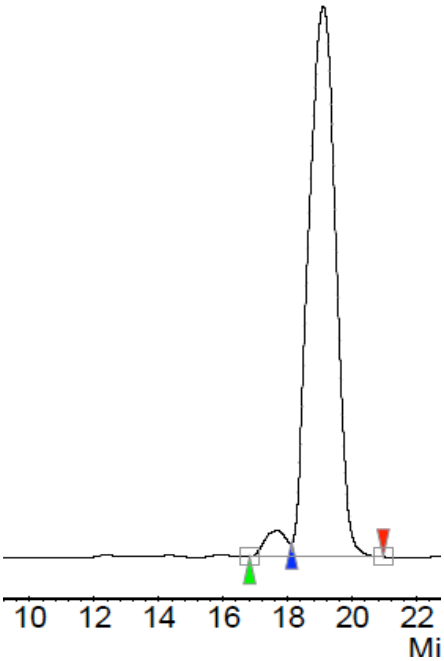
HPLC traces of compound **7j**



7k



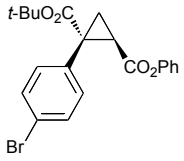
#	Time (Min)	Area (%)
1	17.57	48.736
2	19.05	51.264



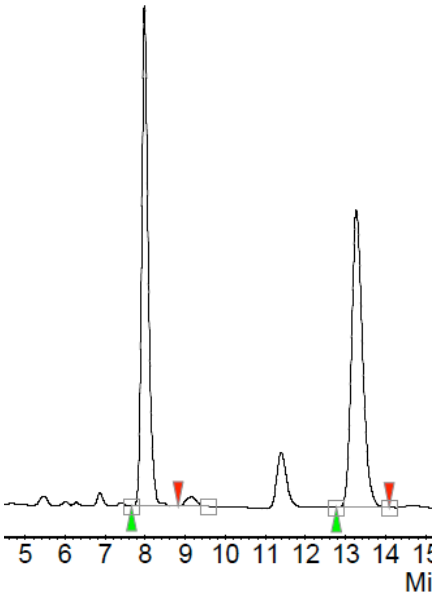
#	Time (Min)	Area (%)
1	17.65	3.665
2	19.09	96.335

93% ee

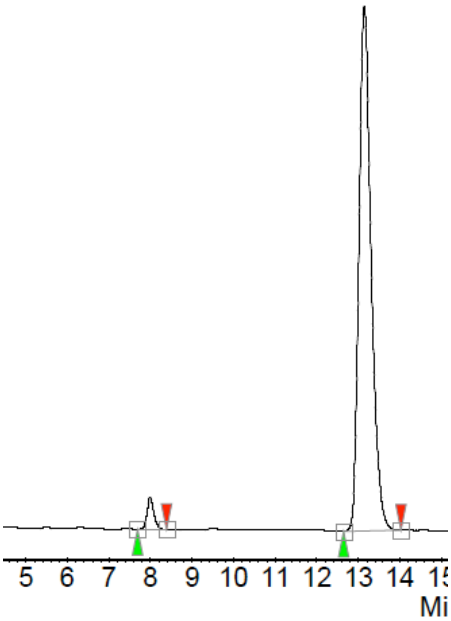
HPLC traces of compound **7k**



7l



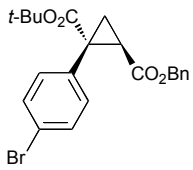
#	Time (Min)	Area (%)
1	7.98	50.355
2	13.27	49.645



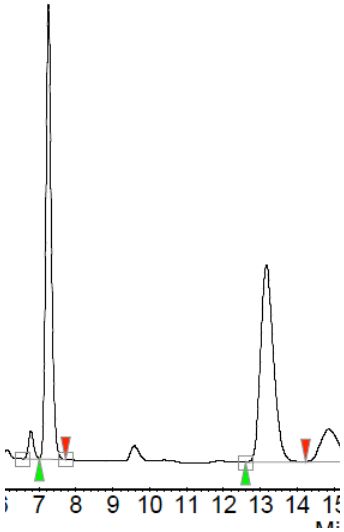
#	Time (Min)	Area (%)
1	7.99	3.389
2	13.14	96.611

93% ee

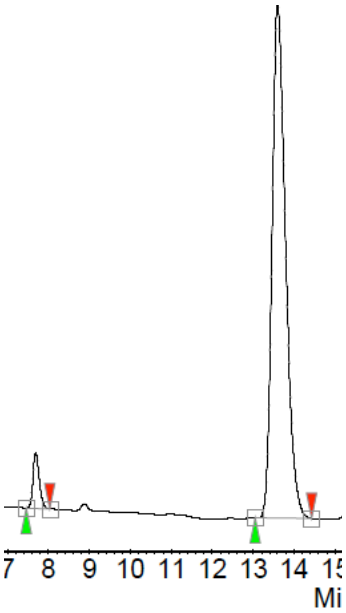
HPLC traces of compound **7l**



7m



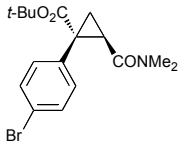
#	Time (Min)	Area (%)
1	7.25	50.033
2	13.16	49.967



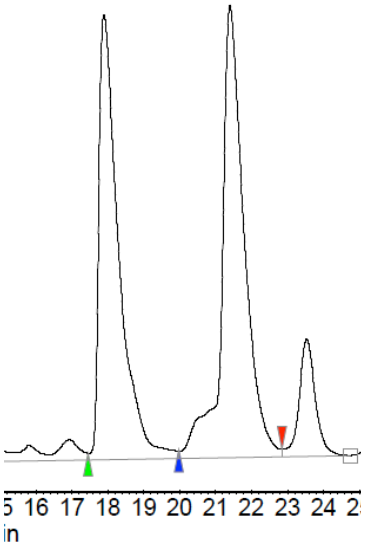
#	Time (Min)	Area (%)
1	7.69	4.829
2	13.60	95.171

90% ee

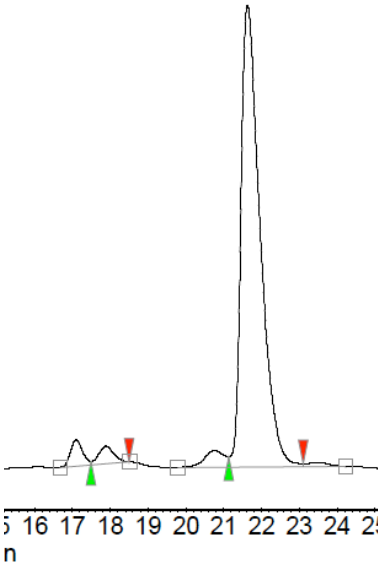
HPLC traces of compound **7m**



7n



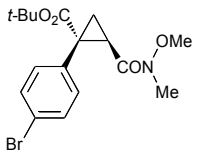
#	Time (Min)	Area (%)
1	17.89	46.440
2	21.40	53.560



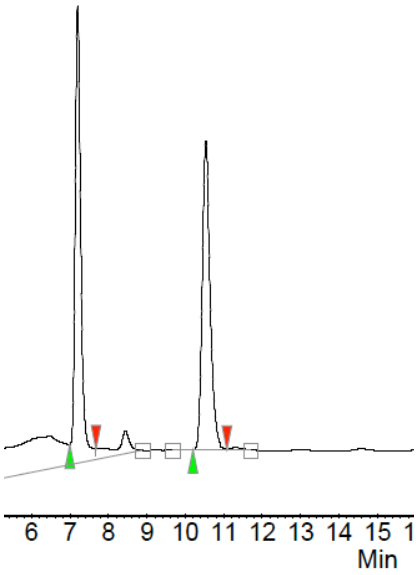
#	Time (Min)	Area (%)
1	17.88	2.910
2	21.63	97.090

94% ee

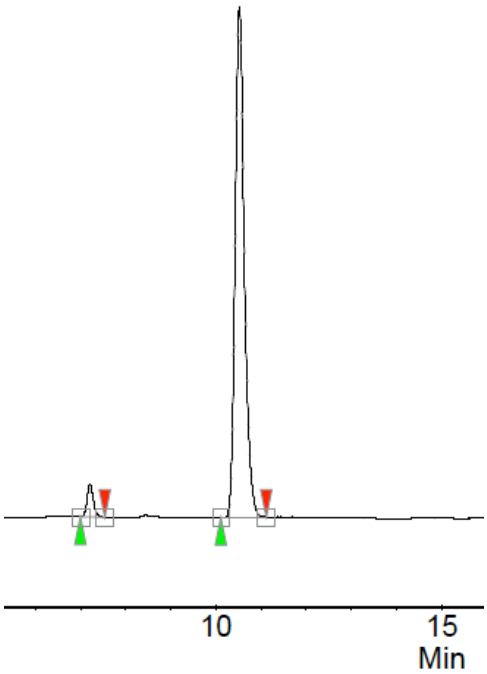
HPLC traces of compound **7n**



7o



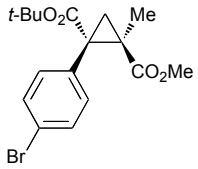
#	Time (Min)	Area (%)
1	7.19	51.860
2	10.53	48.140



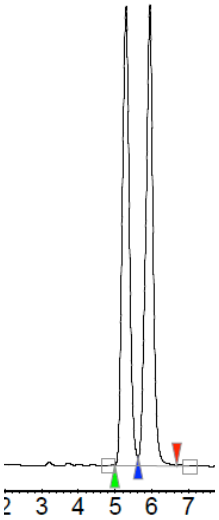
#	Time (Min)	Area (%)
1	7.20	4.155
2	10.51	95.845

92% ee

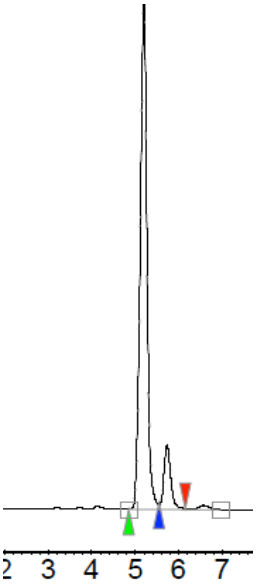
HPLC traces of compound **7o**



7p



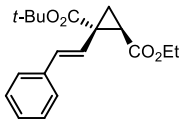
#	Time (Min)	Area (%)
1	5.29	49.476
2	5.95	50.524



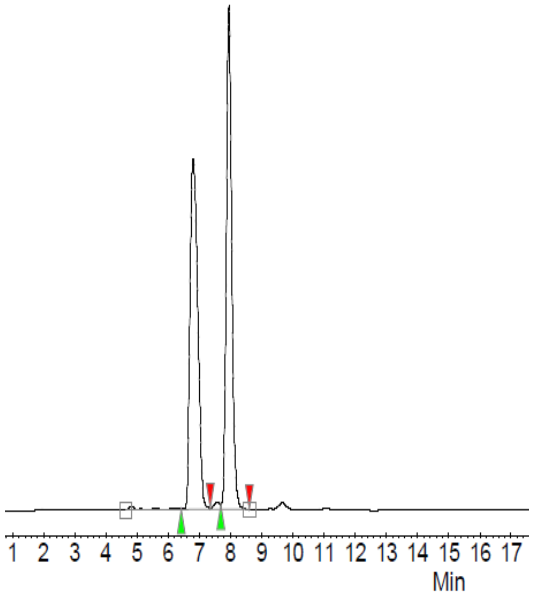
#	Time (Min)	Area (%)
1	5.20	88.355
2	5.74	11.645

77% ee

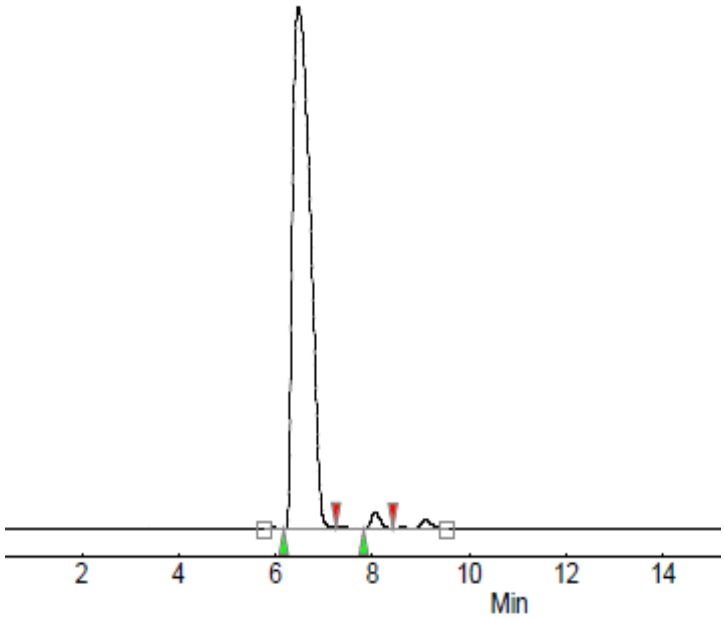
HPLC traces of compound **7p**



9a



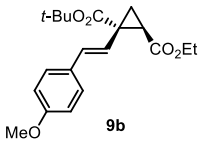
1	6.80 min	50.008
2	7.95 min	49.992



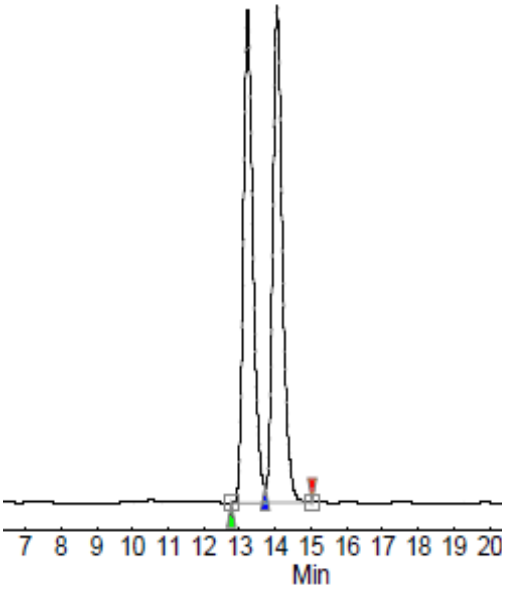
1	6.48 min	98.307
2	8.06 min	1.693

97% ee

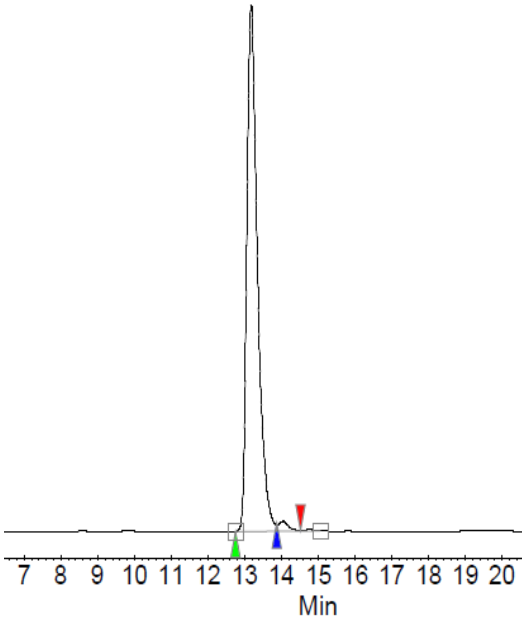
HPLC traces of compound **9a**



9b



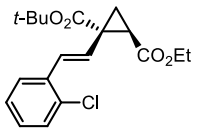
#	Time (Min)	Area (%)
1	13.22	49.641
2	14.05	50.359



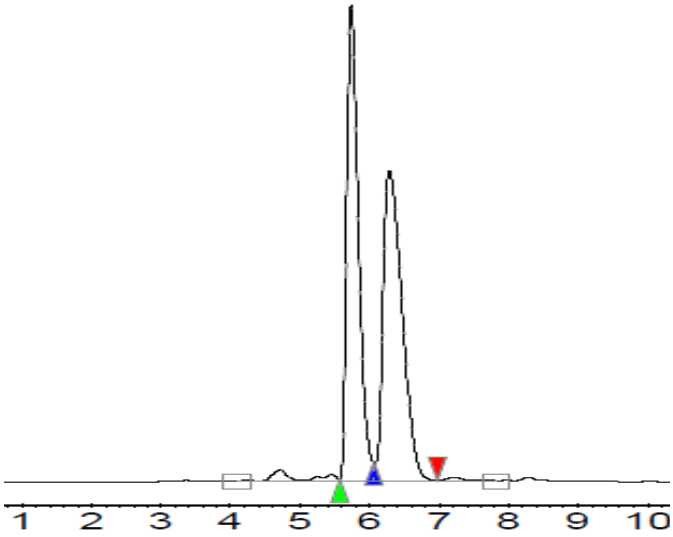
#	Time (Min)	Area (%)
1	13.17	98.276
2	14.04	1.724

97% ee

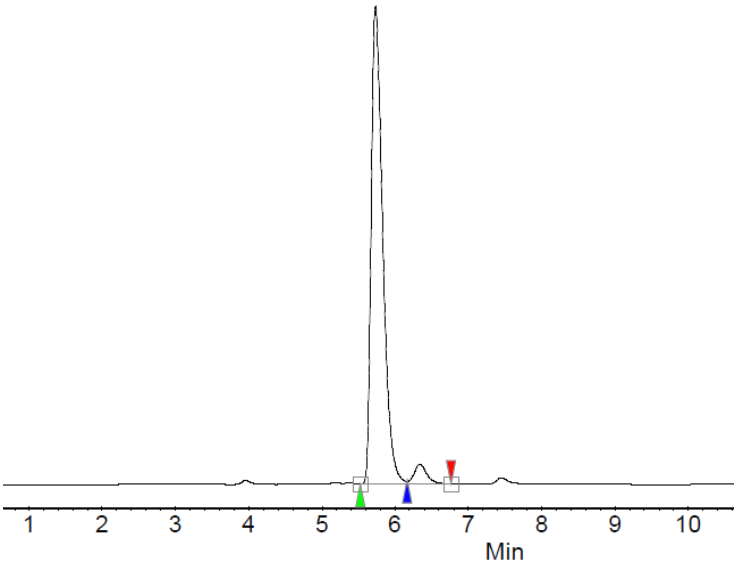
HPLC traces of compound **9b**



9c



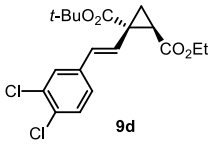
#	Time (Min)	Area (%)
1	5.73	48.025
2	6.29	51.975



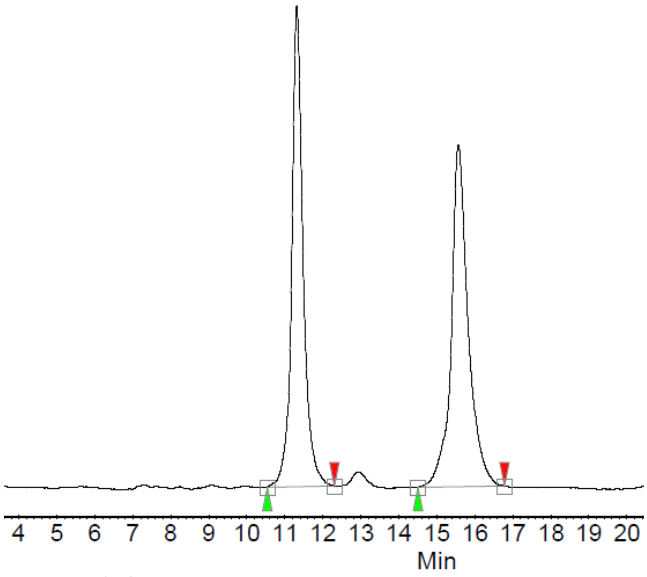
#	Time (Min)	Area (%)
1	5.73 min	95.542
2	6.34 min	4.458

91% ee

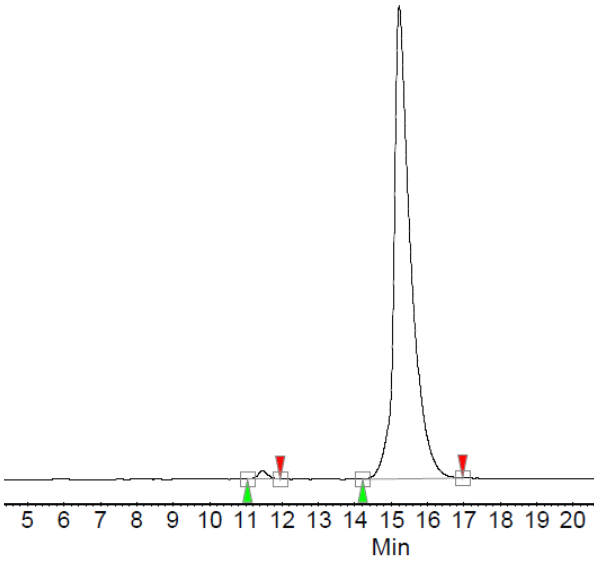
HPLC traces of compound **9c**



9d



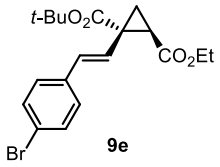
#	Time (Min)	Area (%)
1	11.31	48.264
2	15.57	51.736



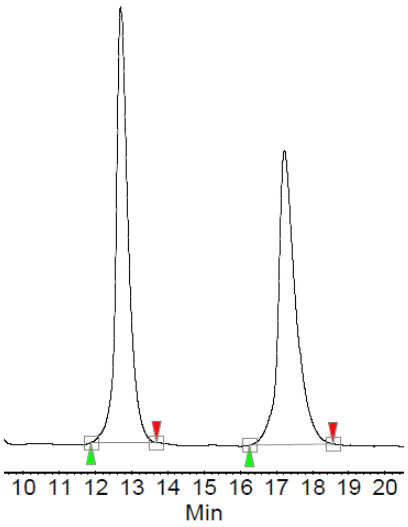
#	Time (Min)	Area (%)
1	11.46 min	0.975
2	15.22 min	99.025

98% ee

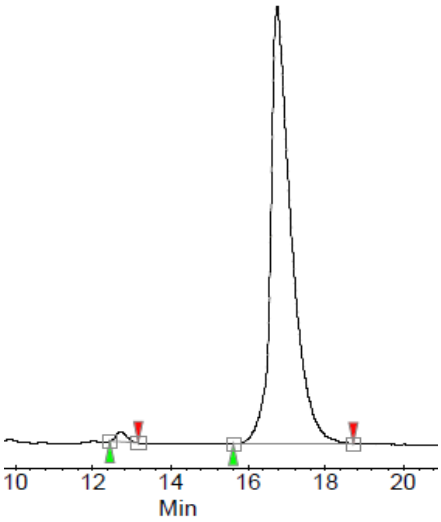
HPLC traces of compound **9d**



9e



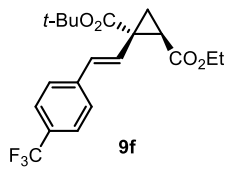
#	Time (Min)	Area (%)
1	12.69	50.599
2	17.22	49.401



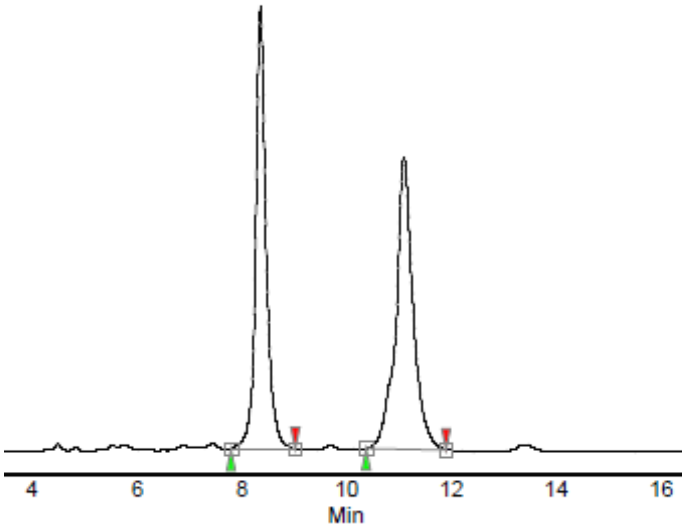
#	Time (Min)	Area (%)
1	12.72 min	1.175
2	16.74 min	98.825

98% ee

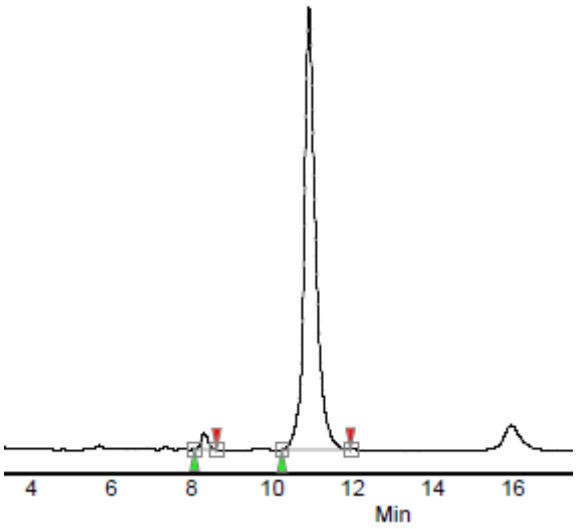
HPLC traces of compound **9e**



9f



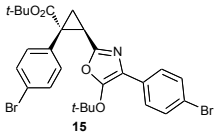
#	Time (Min)	Area (%)
1	8.35	47.773
2	11.09	52.227



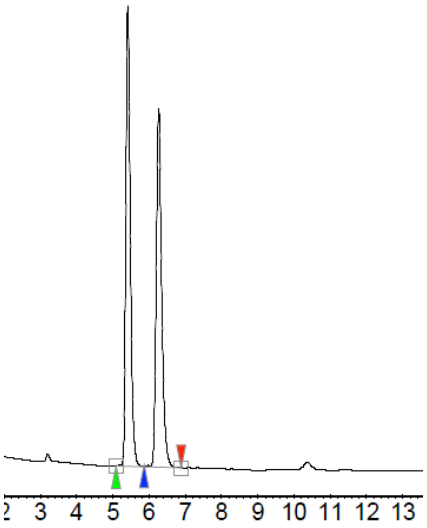
#	Time (Min)	Area (%)
1	8.32	2.322
2	10.91	97.678

95% ee

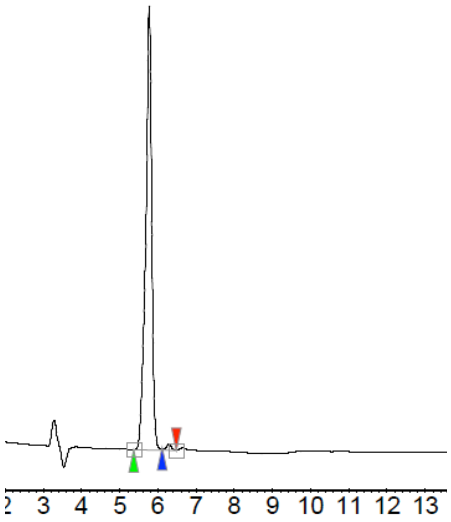
HPLC traces of compound **9f**



15



#	Time (Min)	Area (%)
1	5.41	50.377
2	6.26	49.623



#	Time (Min)	Area (%)
1	5.77	98.650
2	6.29	1.350

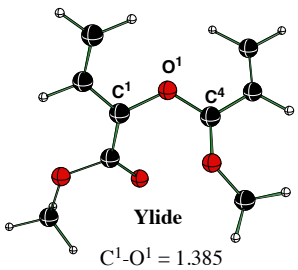
97% ee

HPLC traces of compound **15**

Computational data:

1. Completed Ref. 20:

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.



	Ylide	TS_EP	Epoxide
a:	C^1-O^1 = 1.385 C^4-O^1 = 1.303 C^1-C^4 = 2.370	C^1-O^1 = 1.427 C^4-O^1 = 1.325 C^1-C^4 = 2.216	C^1-O^1 = 1.423 C^4-O^1 = 1.386 C^1-C^4 = 1.520
b:	C^1-O^1 = 1.409 C^4-O^1 = 1.319 C^1-C^4 = 2.381	C^1-O^1 = 1.450 C^4-O^1 = 1.330 C^1-C^4 = 2.159	C^1-O^1 = 1.413 C^4-O^1 = 1.415 C^1-C^4 = 1.507
c:	C^1-O^1 = 1.366 C^4-O^1 = 1.316 C^1-C^4 = 2.387	C^1-O^1 = 1.398 C^4-O^1 = 1.353 C^1-C^4 = 2.149	C^1-O^1 = 1.409 C^4-O^1 = 1.425 C^1-C^4 = 1.507

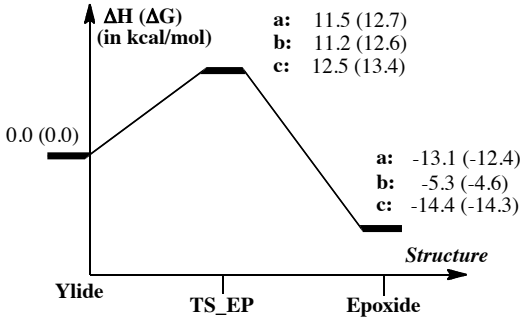


Fig. SI-3 Calculated (in gas phase) structures, important geometry parameters (in Å), and relative energies of the epoxidation reaction of (a) acrylate, (b) acrylamide and (c) methyl vinyl ketone with carbenoid $C(CH{=}CH_2)(CO_2Me)$.

3. Cartesian coordinates (in Å) of all reported reactants, intermediates, transition states and products of the reaction of vinyldiazoacetate with methyl acarylate (R = OMe), *N*,*N*-dimethylacrylamide (R = NMe_2), and methyl vinyl ketone (R = Me).

R = OMe

Reactant, SUB

O	0.62240700	1.60135500	-0.00007500
C	0.07666200	0.52773000	-0.00004800
C	0.81057200	-0.76376600	-0.00004300
C	2.14206700	-0.76553200	0.00008200
O	-1.28142600	0.49519100	-0.00005800
C	-1.99287500	-0.73689300	0.00009600
H	0.26320100	-1.70006400	-0.00015000
H	2.68752600	0.17308600	0.00019600
H	2.71196600	-1.68754100	0.00008300
H	-1.78065300	-1.32958800	0.89464600
H	-1.78084700	-1.32969700	-0.89442900
H	-3.04759900	-0.46779900	0.00019400

Reactant, CARB

C	-2.16041200	0.88293300	0.16570700
C	-3.16992000	-0.17310900	0.37252700
O	-3.65255200	-0.65377300	-0.77721200
C	-4.51125400	-1.79451400	-0.64347000
O	-3.48809700	-0.54543600	1.47948200
C	-2.62279900	2.22569100	0.12839200
C	-1.88864700	3.25003900	-0.36106500
O	-0.30601400	-0.61947400	1.94289900
C	0.72828600	-1.22225400	2.34977600
O	1.83488300	-1.36037000	1.77458900
Rh	2.05879700	-0.49863100	-0.09324700
O	2.61896600	1.28944800	0.80909400
C	1.72591700	2.11325900	1.11241200
O	0.47216300	2.02443600	0.94483900
O	1.33131600	-2.23092400	-0.97254500
C	0.08988100	-2.35822200	-1.08758700
O	-0.82732700	-1.54781800	-0.76416500
O	2.15710500	0.39501900	-1.96153900
C	1.13887400	0.99233700	-2.37916500
O	0.01527600	1.13636700	-1.81131300
Rh	-0.27802800	0.28418800	0.07768900
H	-3.95975500	-2.62538200	-0.19964400
H	-4.82856900	-2.04455100	-1.65291200
H	-5.37319100	-1.56070500	-0.01670300
H	-0.88857000	3.08847900	-0.74261900
H	-2.30528200	4.24936900	-0.43178300
H	-3.64645800	2.42099200	0.45508200
H	2.06080600	3.04733900	1.59061300
H	-0.26507700	-3.30152200	-1.53254500
H	1.21653500	1.46118000	-3.37280900
H	0.62964100	-1.68203800	3.34525400

PC, Pre-reaction Complex

Rh	-2.70291200	0.50321000	-0.44484000
O	-1.77771300	2.09754700	-1.38015200
O	-2.45370800	-0.63444700	-2.16842300
O	-3.51812400	-1.13984000	0.52797400
O	-2.76563600	1.59629500	1.32560300
Rh	-0.47408600	-0.29387800	0.26360100
C	-1.76060000	1.56852000	2.07496900
O	-0.67614700	0.93038000	1.93086300
C	-2.74525300	-1.87850400	1.18029100
O	-1.48734900	-1.79415900	1.30635600
C	-0.52263200	2.12400000	-1.35984400
O	0.28248500	1.31791100	-0.81485300
O	-0.45451500	-1.46208300	-1.47204900
C	-1.42380800	-1.33910900	-2.27789100
H	-1.33996900	-1.94292700	-3.19554200
H	-0.04390700	2.96426700	-1.88854000
H	-3.20714800	-2.71842000	1.72298900
H	-1.81477800	2.17889900	2.99033200
C	1.30937200	-0.96325500	0.76273700
C	2.13726500	-1.36754500	-0.39668700
O	2.57072600	-0.62549500	-1.24814600
O	2.29073900	-2.70575100	-0.40979600
C	2.90475000	-3.22706500	-1.59366400
H	3.93742000	-2.88071900	-1.67698700
H	2.87564000	-4.30945900	-1.49210100
H	2.35017400	-2.90851400	-2.47832900
C	1.84401100	-1.11730900	2.06867400
H	2.92184900	-1.25011900	2.16661800
C	1.06814200	-1.15720100	3.17415100
H	1.50287300	-1.33089100	4.15297400
H	-0.00809300	-1.05987000	3.10846600
O	2.84375300	1.64741500	1.32944100
C	3.69414100	1.44417700	0.49848800
C	3.88563200	2.27790100	-0.71006300
H	4.71750100	2.07958400	-1.37622200
C	3.02624100	3.25756900	-0.97880300
H	2.18241700	3.43719400	-0.32063700
H	3.13502700	3.88539000	-1.85645100
O	4.53894100	0.39254000	0.70134300
C	5.48398500	0.01137400	-0.29630500
H	6.26403200	0.76792400	-0.42347600
H	4.99040000	-0.19126200	-1.25011000
H	5.94636500	-0.90484300	0.07117000

TS_CP

C	-1.54385900	4.27563900	0.65713400
O	-1.67696100	2.87558300	0.91985700
C	-1.70731600	2.09696500	-0.18153300
C	-1.58276000	0.66307700	0.22833800
C	-2.31616800	0.24070400	1.40434400
C	-2.28208000	-1.00859400	1.88845600
O	-1.74643700	2.52588100	-1.31026200

Rh	0.39714200	0.02990200	-0.00116700
O	0.00129800	-2.00411400	-0.21407000
C	0.98664700	-2.80242700	-0.25027300
O	2.20855000	-2.53723700	-0.19507300
Rh	2.79522400	-0.54188300	-0.04591100
O	2.71888300	-0.36215500	-2.10968900
C	1.63252700	-0.02278400	-2.63576900
O	0.52499100	0.21360700	-2.07077500
O	0.53039000	-0.22709200	2.07193300
C	1.65218400	-0.49771800	2.58778600
O	2.75686200	-0.67714900	2.01971800
O	1.03073700	2.01922900	0.18367400
C	2.26929500	2.27053900	0.17687700
O	3.23552100	1.47327000	0.09986800
H	-0.64612700	4.46273700	0.06538300
H	-1.46987500	4.75466800	1.63092400
H	-2.41284000	4.64861900	0.11183600
H	-1.70481800	-1.78694900	1.40035000
H	-2.84281000	-1.28075500	2.77642400
H	-2.91695800	0.99512800	1.91271600
H	0.71796400	-3.86633400	-0.34384400
H	2.52671900	3.33918700	0.25166400
H	1.64976100	-0.58790100	3.68555300
H	1.62956100	0.08494400	-3.73130200
C	-2.30284300	-0.34367300	-1.48004000
H	-2.03814200	-1.35650200	-1.19778700
C	-3.58360700	0.10409700	-1.31225800
H	-1.63950600	0.17160500	-2.16298400
C	-4.61314500	-0.60829100	-0.55393000
H	-3.87473400	1.08875800	-1.66247800
O	-5.66528800	-0.12064100	-0.20076300
O	-4.25443200	-1.88573000	-0.28096300
C	-5.21124400	-2.62282000	0.48130300
H	-4.77212000	-3.60499300	0.64321000
H	-5.40909700	-2.12768800	1.43427300
H	-6.15218500	-2.71127900	-0.06569800

TS_EP

Rh	-2.80768600	-0.20894900	0.32364700
O	-2.36933200	0.07906900	2.32843000
O	-2.96941200	1.84087400	0.06945500
O	-3.12628300	-0.48487400	-1.70209300
O	-2.53674800	-2.24613200	0.55475200
Rh	-0.44431500	-0.02233500	-0.14755200
C	-1.37087500	-2.70106600	0.40771600
O	-0.31221000	-2.07713900	0.12777400
C	-2.12315500	-0.46273000	-2.46423200
O	-0.91022200	-0.29945900	-2.16419600
C	-1.15888200	0.24256600	2.63883300
O	-0.14777500	0.25440400	1.88740800
O	-0.75507100	2.02354100	-0.39755800
C	-1.92163800	2.47134100	-0.22937900
H	-2.03807100	3.55866100	-0.36262200
H	-0.95660200	0.39569000	3.71069500
H	-2.33474200	-0.60591000	-3.53574600
H	-1.26185800	-3.78876500	0.54055200
C	2.16054300	-0.07097700	-0.41914200
C	2.11257300	1.38937900	-0.29439500
O	2.10524600	2.03368200	0.73523900
O	2.08696000	1.96519200	-1.52621100
C	1.94384800	3.38521500	-1.50790500
H	2.81401200	3.85609700	-1.04396900
H	1.86500600	3.68631700	-2.55100700
H	1.04653800	3.66826000	-0.95692200
C	2.09646800	-0.77326000	-1.67374100
H	1.96549900	-0.11507800	-2.52611700
C	2.14360900	-2.10165600	-1.85816400
H	2.04658300	-2.51592400	-2.85445600
H	2.23214700	-2.79659500	-1.03330700
O	2.36426700	-0.82026200	0.79230800
C	3.68981800	-0.68802500	0.65325000
C	4.43569600	0.26352500	1.41602000
H	5.49181500	0.37084100	1.19319600
C	3.86381400	0.97661700	2.40275500
H	2.81665500	0.85305400	2.64621500
H	4.44587600	1.68089900	2.98588600
O	4.25951900	-1.70045400	0.01501100
C	5.60741000	-1.55811100	-0.43880400
H	5.78957100	-2.41436200	-1.08392700
H	5.72410300	-0.63577200	-1.01326100
H	6.30662300	-1.57406300	0.40109300

TS_YL

Rh	2.77139100	-0.35997600	-0.29199100
O	2.12840500	-1.84340000	-1.59455000
O	2.65044800	1.02386400	-1.84210200
O	3.28232700	1.15536600	1.03329600
O	2.72739200	-1.71040200	1.28977800
Rh	0.39978200	0.13867900	0.19691400
C	1.64897900	-1.84587000	1.91553000
O	0.54097200	-1.26459000	1.73229300
C	2.35390500	1.78154900	1.59747400
O	1.10436800	1.62553300	1.48132600
C	0.89261300	-2.00682100	-1.72797000
O	-0.05969400	-1.39600900	-1.16288700
O	0.46392200	1.47874000	-1.41452200
C	1.55500900	1.59829900	-2.04389700
H	1.52776800	2.31022200	-2.88547500
H	0.58278400	-2.79493100	-2.43543200
H	2.65704500	2.58063400	2.29327200
H	1.65673100	-2.57228000	2.74449200
C	-1.50449400	0.63130600	0.68784300
C	-2.20833900	1.29323600	-0.44218900
O	-2.77225400	0.77309400	-1.37824500
O	-2.03462000	2.62602700	-0.31432700
C	-2.40891800	3.39230400	-1.46252200
H	-3.48213700	3.31014800	-1.64756200
H	-2.14070000	4.42077400	-1.23117300
H	-1.86642900	3.04271000	-2.34217300
C	-1.77255900	1.07795600	2.03647800
H	-1.98900500	2.14622500	2.09550900
C	-1.73458200	0.34389900	3.15178700

H	-1.92450100	0.79707900	4.11765400
H	-1.54264300	-0.72144600	3.11723200
O	-2.37505300	-1.17664300	0.61334900
C	-3.55070700	-1.22686200	0.25425900
C	-4.02458400	-2.28079000	-0.64651000
H	-5.07210200	-2.56421900	-0.62071200
C	-3.16135000	-2.84066400	-1.49532800
H	-2.12974700	-2.49698200	-1.52064700
H	-3.47217800	-3.61636300	-2.18651700
O	-4.39848400	-0.31082500	0.72329600
C	-5.67887900	-0.15727200	0.10246300
H	-6.35136200	-0.97289300	0.38033800
H	-5.57633300	-0.09786300	-0.98270000
H	-6.07835500	0.77989700	0.48419900

YL

Rh	2.76509000	-0.31211700	-0.25616200
O	2.19081800	-1.78893300	-1.60371300
O	2.65090300	1.09706200	-1.78321500
O	3.18640100	1.19492200	1.10958200
O	2.70218100	-1.69100700	1.30281900
Rh	0.37530700	0.09706600	0.17805900
C	1.60991800	-1.87453100	1.89513300
O	0.49072700	-1.32527600	1.68921200
C	2.22059800	1.78571100	1.65242900
O	0.98185600	1.59397300	1.49554900
C	0.96729900	-2.00556100	-1.76244600
O	-0.02009900	-1.44481500	-1.20346800
O	0.44076000	1.47519900	-1.40386300
C	1.54197600	1.64455900	-1.99917200
H	1.52005200	2.37737900	-2.82335500
H	0.70896100	-2.79636300	-2.48789900
H	2.48220700	2.58449500	2.36546800
H	1.62158400	-2.61699000	2.70975000
C	-1.74741500	0.41517300	0.70012100
C	-2.21735000	1.28343400	-0.39417800
O	-2.74538300	0.89392600	-1.42310500
O	-1.93543400	2.57178600	-0.13928000
C	-2.11308000	3.45597800	-1.24764600
H	-3.15644400	3.46916600	-1.57029600
H	-1.81574700	4.43940400	-0.88931100
H	-1.48022300	3.14433500	-2.07976900
C	-1.81077300	0.84468100	2.08549000
H	-1.49534300	1.87421400	2.22591600
C	-2.13983000	0.08547200	3.13468800
H	-2.10916200	0.48364400	4.14127200
H	-2.41654000	-0.95784600	3.02396500
O	-2.29875700	-0.94919300	0.49964500
C	-3.50679300	-1.09242400	0.10648300
C	-3.84249900	-2.26039500	-0.67013800
H	-4.88100700	-2.57258500	-0.68775800
C	-2.89154300	-2.89858300	-1.36422200
H	-1.86936000	-2.52268100	-1.36547900
H	-3.13082300	-3.77803000	-1.95159800
O	-4.38755900	-0.21250300	0.49403100
C	-5.64968600	-0.13273100	-0.19192300
H	-6.29156300	-0.96906600	0.09151000
H	-5.48429100	-0.10811500	-1.26948100
H	-6.09644200	0.80053300	0.14046200

R = NMe_2

Reactant, SUB

O	0.07103800	1.89727100	-0.03922800
C	-2.25344400	-0.60692200	0.44110800
C	-1.61198200	0.30064300	-0.29132100
C	-0.18859800	0.70303800	-0.12197400
N	0.77499800	-0.26847700	-0.01194000
C	0.60149600	-1.67042400	-0.32607800
C	2.13305400	0.13230300	0.29206900
H	-3.32777600	-0.73771200	0.36807800
H	-1.73813800	-1.23388900	1.16345500
H	-2.16308900	0.95321800	-0.96346500
H	0.66866800	-2.29858600	0.57107900
H	-0.35951800	-1.84646700	-0.80264400
H	1.39128900	-1.99069000	-1.01480100
H	2.52347300	-0.46600600	1.12171800
H	2.78933200	-0.01537200	-0.57362900
H	2.13931100	1.18484900	0.56478400

PC, Pre-reaction Complex

Rh	2.79035400	-0.64814400	-0.40444500
O	1.77219800	-2.31675000	-1.08448700
O	2.62478700	0.19895400	-2.29215400
O	3.70247000	1.07658600	0.29914300
O	2.78491700	-1.42938200	1.52672500
Rh	0.60975600	0.39562600	0.13324900
C	1.82089100	-1.15616100	2.27714500
O	0.79511300	-0.45230400	2.03258400
C	2.97294700	1.99731500	0.73233800
O	1.70832800	2.03900200	0.80446900
C	0.52111100	-2.29701500	-0.99941600
O	-0.23343400	-1.38421900	-0.55913000
O	0.61896500	1.15313900	-1.80683000
C	1.60434100	0.87999500	-2.55186400
H	1.54610800	1.30623600	-3.56578400
H	-0.00641000	-3.19773100	-1.35492500
H	3.48486400	2.89823800	1.10558100
H	1.85517300	-1.57972400	3.29401300
C	-1.12576100	1.24609000	0.51645700
C	-2.08431100	1.33129100	-0.61585500
O	-2.33721300	0.43148100	-1.38362500
O	-2.61963500	2.56496600	-0.69381800
C	-3.56354600	2.74395700	-1.75396600
H	-4.45747000	2.14756800	-1.55769600
H	-3.80801100	3.80365200	-1.76152700
H	-3.13171200	2.43966400	-2.70935000
C	-1.54905800	1.79940500	1.75790300
H	-2.60135300	2.07121900	1.84669100
C	-0.71484600	2.02666500	2.79767700
H	-1.08122300	2.48647600	3.71024900
H	0.33943900	1.78870400	2.74202900

O	-4.24600300	0.12446600	1.14556300
C	-3.77746000	-0.94440300	0.75081000
C	-2.70188800	-1.63207400	1.51267900
H	-2.13393200	-2.43013200	1.05094600
C	-2.41388000	-1.24738400	2.75414700
H	-2.96727400	-0.43619100	3.21747900
H	-1.62337200	-1.71690200	3.32772400
N	-4.24295600	-1.56030700	-0.38118900
C	-3.54602000	-2.63357900	-1.06578100
H	-4.24868100	-3.13023600	-1.73799900
H	-3.17753200	-3.38565500	-0.36987600
H	-2.70890200	-2.24466100	-1.65801300
C	-5.22728300	-0.86631000	-1.18578800
H	-4.75262800	-0.38245400	-2.04809200
H	-5.97300100	-1.57857200	-1.54990200
H	-5.71369300	-0.10830300	-0.57585800

TS_CP

C	-2.06411400	3.77508500	0.56930600
O	-1.97314400	2.37321400	0.83202400
C	-1.80451100	1.60434900	-0.26943100
C	-1.45558200	0.21505100	0.15475900
C	-2.14361800	-0.32807900	1.30391100
C	-1.99359700	-1.59031000	1.73152100
O	-1.86199400	2.03510900	-1.39734400
Rh	0.60790100	-0.05563300	-0.00483500
O	0.59184000	-2.13049300	-0.25620500
C	1.70644900	-2.73332500	-0.27511900
O	2.85872700	-2.25034700	-0.18006600
Rh	3.06965900	-0.19579900	0.01866500
O	3.02223200	0.00902400	-2.04634000
C	1.90779600	0.16455800	-2.59979500
O	0.75977400	0.19428100	-2.06848600
O	0.71277500	-0.33886500	2.06680400
C	1.84971600	-0.42538900	2.61234500
O	2.98504700	-0.38584500	2.07890700
O	0.86403900	2.00574200	0.23075400
C	2.03643600	2.47847400	0.26209700
O	3.13222600	1.87273700	0.19987300
C	-1.95817300	-1.00793800	-1.53442600
C	-3.25333500	-0.58349800	-1.50107600
C	-4.22617500	-1.25130100	-0.61605400
H	-1.17980600	4.11580900	0.02785100
H	-2.12748400	4.25759400	1.54244200
H	-2.95155100	3.99883000	-0.02771500
H	-1.33619600	-2.28495600	1.21812100
H	-2.54116200	-1.96414200	2.58945500
H	-2.82761600	0.33696300	1.83323000
H	1.64246000	-3.82650500	-0.39215700
H	2.09100000	3.57480400	0.35912500
H	1.83197700	-0.55365600	3.70646600
H	1.91753800	0.29135800	-3.69365500
H	-1.68634000	-1.94560600	-1.06147600
H	-1.25972500	-0.58179000	-2.24321300
H	-3.53473500	0.28986400	-2.07721200
N	-5.25635900	-0.48193500	-0.12718000
O	-4.09901100	-2.43757400	-0.32494700
C	-5.30074000	0.96658700	-0.15298200
C	-6.19850600	-1.10022800	0.78220800
H	-5.94164300	-0.88098200	1.82689600
H	-7.20316100	-0.71400700	0.58909000
H	-6.18155700	-2.17807300	0.64024200
H	-5.10432000	1.37791000	0.84629000
H	-4.56319600	1.38615400	-0.83324700
H	-6.29256100	1.30835000	-0.46599300

TS_EP

Rh	-2.91593200	-0.30352900	0.35410900
O	-2.45287400	0.06456400	2.33721700
O	-3.18755600	1.72520700	0.05287200
O	-3.27822300	-0.65290600	-1.65070000
O	-2.53283100	-2.31850600	0.63283400
Rh	-0.58032000	-0.01390200	-0.18450800
C	-1.35212700	-2.72189200	0.46316500
O	-0.33328800	-2.05671400	0.13271500
C	-2.29957700	-0.59451100	-2.44350100
O	-1.09036000	-0.35774900	-2.18322700
C	-1.24128900	0.28370400	2.61191900
O	-0.25206200	0.31167200	1.83425500
O	-0.99452800	2.00408200	-0.46138400
C	-2.17719500	2.39967500	-0.27858700
H	-2.34813300	3.47731500	-0.43001400
H	-1.01775800	0.47496200	3.67303300
H	-2.53478900	-0.77557600	-3.50429100
H	-1.18806000	-3.79927200	0.62362100
C	2.13244000	0.27452800	-0.39415900
C	1.95380800	1.71700100	-0.18324000
O	1.88436000	2.28444100	0.88512200
O	1.89389600	2.37362900	-1.37305300
C	1.64298200	3.77239500	-1.25606400
H	2.46325500	4.27186900	-0.73522200
H	1.56148700	4.14507300	-2.27562700
H	0.71587700	3.94859700	-0.70837800
C	1.97856000	-0.34692700	-1.68563200
H	1.86796600	0.37509600	-2.48827500
C	1.96896400	-1.65632900	-1.97908700
H	1.84350700	-1.98052400	-3.00516900
H	1.96593200	-2.42208600	-1.21766800
O	2.35319500	-0.50490700	0.78083400
C	3.68092500	-0.38330800	0.49422600
C	4.47887500	0.63111700	1.14991800
H	5.49672500	0.75446500	0.79308200
C	4.04742400	1.32474500	2.21090700
H	3.04619500	1.19193900	2.59876000
H	4.69870000	2.03497600	2.70742300
N	4.26765700	-1.46241500	-0.09405700
C	5.60337000	-1.35322400	-0.64136500
C	3.86195300	-2.80070700	0.30840000
H	3.92164800	-3.48036700	-0.54426700
H	4.52133500	-3.17436200	1.10421100
H	2.83888700	-2.78121600	0.67981100
H	5.74142000	-2.14520600	-1.37978700

H	5.72647400	-0.39718800	-1.15062500
H	6.38454800	-1.45731700	0.12447900

TS_YL

Rh	-2.84975000	0.35648600	-0.34106300
O	-2.14034800	1.70261900	-1.75612800
O	-2.77193800	-1.15798400	-1.76683300
O	-3.42627800	-1.02328600	1.09642800
O	-2.77344100	1.83300700	1.11686500
Rh	-0.49771100	-0.17536200	0.20686500
C	-1.69512600	1.99158200	1.73789900
O	-0.60092200	1.37019000	1.61145200
C	-2.52451300	-1.63032200	1.72250500
O	-1.26992600	-1.52488600	1.61034400
C	-0.89694500	1.79986800	-1.89272200
O	0.02451400	1.20012200	-1.26853500
O	-0.60535500	-1.64593600	-1.28005100
C	-1.69530800	-1.78262300	-1.90843400
H	-1.68463900	-2.56420500	-2.68566900
H	-0.54523900	2.50940800	-2.66094900
H	-2.86315800	-2.35828000	2.47762100
H	-1.68901200	2.78527700	2.50279300
C	1.38893000	-0.71423800	0.71158900
C	2.07138200	-1.35370500	-0.43612100
O	2.55884100	-0.80642100	-1.39848500
O	1.99233600	-2.70056000	-0.29956600
C	2.36662700	-3.43782900	-1.46498600
H	3.42367600	-3.28282200	-1.69678700
H	2.17974800	-4.48305400	-1.22800200
H	1.76634100	-3.12548000	-2.32101700
C	1.57867400	-1.22063200	2.05287900
H	1.70918700	-2.30407900	2.08798600
C	1.54356700	-0.51424900	3.18658800
H	1.65252600	-1.00403200	4.14716100
H	1.42890800	0.56306600	3.17066400
O	2.38719000	1.04602700	0.83425500
C	3.37047900	1.36418900	0.12560600
C	3.35473400	2.65219200	-0.58736700
H	4.27422100	3.01740300	-1.03175100
C	2.25000400	3.39711800	-0.60809000
H	1.34031100	3.03271200	-0.14396400
H	2.23681000	4.37252000	-1.08183300
N	4.50637200	0.62428700	0.09553000
C	5.47166900	0.66550000	-0.98569700
H	6.47568700	0.87502700	-0.60330600
H	5.20422300	1.41023900	-1.72934400
H	5.48424600	-0.30746800	-1.48849100
C	4.67053200	-0.49267200	1.00334000
H	4.43176600	-1.44841500	0.52040900
H	5.71510800	-0.53090100	1.32477100
H	4.02481100	-0.36569000	1.86999500

YL

Rh	2.85202500	-0.31605100	-0.29827600
O	2.21129900	-1.58649000	-1.82111200
O	2.80591900	1.28676100	-1.62543500
O	3.33976300	0.98739200	1.24220800
O	2.74185000	-1.88552200	1.06206400
Rh	0.48171300	0.12602700	0.19029500
C	1.64095600	-2.11607300	1.62086500
O	0.53811200	-1.51440800	1.48575300
C	2.39829100	1.54148900	1.86313700
O	1.15366100	1.41628200	1.69459800
C	0.97633800	-1.71432900	-2.00425300
O	0.01788000	-1.18242400	-1.37443900
O	0.61541100	1.70088900	-1.18158800
C	1.72074600	1.90333400	-1.75764400
C	-1.70364000	0.46604600	0.72610300
C	-2.07625000	1.30950400	-0.41040800
O	-2.51414700	0.91407500	-1.47781000
O	-1.84474300	2.61493600	-0.13858200
C	-1.97052400	3.48636800	-1.26122300
C	-1.66371300	0.95169100	2.08874800
C	-1.98878900	0.25562000	3.18666400
O	-2.24979200	-0.88583200	0.64098600
C	-3.32928300	-1.22530800	-0.00034600
C	-3.31365900	-2.56507400	-0.56232600
C	-2.19609400	-3.29708500	-0.59604400
N	-4.43702600	-0.48873600	-0.04969800
H	1.72737600	2.74190100	-2.47436100
H	0.67830900	-2.38710200	-2.82677300
H	2.69559900	2.23348800	2.66823800
H	1.62849800	-2.96340200	2.32674900
H	-3.00405200	3.51204800	-1.61809100
H	-1.67166200	4.47088400	-0.90615200
H	-1.31951600	3.15899600	-2.07239500
H	-1.29057900	1.96657700	2.17624900
H	-1.87526700	0.68886600	4.17249800
H	-2.32379800	-0.77523100	3.13263200
H	-4.26130100	-2.97728100	-0.88982100
H	-1.25045700	-2.88389600	-0.26460400
H	-2.21618400	-4.31959700	-0.95563100
C	-5.42298200	-0.66499900	-1.10771400
C	-4.68410700	0.64470300	0.82835300
H	-5.65291900	0.31899300	-1.52257400
H	-5.02345300	-1.27394500	-1.91401400
H	-6.34429500	-1.10834700	-0.71815400
H	-5.74018900	0.61806100	1.10824000
H	-4.07539900	0.57795100	1.72913600
H	-4.48515900	1.59267800	0.31925400

R = Me

Reactant, SUB

O	0.40199300	1.38149400	-0.00003300
C	0.44310200	0.16663500	0.00000100
C	-0.79507800	-0.66192500	0.00006000
C	-2.00533500	-0.10564200	-0.00000500
C	1.74021700	-0.59483000	-0.00001100
H	-0.67755000	-1.74406300	0.00011400
H	-2.10122400	0.97650500	-0.00015300
H	-2.91388100	-0.69664100	-0.00003400
H	1.79514300	-1.24910100	0.87587400

H	1.79481800	-1.24976900	-0.87541400
H	2.58931600	0.08568600	-0.00039500

PC, Pre-reaction Complex

Rh	-2.39308300	0.38006600	-0.50338900
O	-1.43663100	1.56992600	-1.90668400
O	-2.32249100	-1.22935500	-1.82537600
O	-3.22777400	-0.84773100	0.94973200
O	-2.27766100	1.94267400	0.86500200
Rh	-0.16751900	-0.33774800	0.29682900
C	-1.21526400	2.08269900	1.51362700
O	-0.17199600	1.36344300	1.50258800
C	-2.45320200	-1.39470700	1.76770000
O	-1.18747600	-1.35063800	1.81213800
C	-0.18931500	1.47489400	-1.98448100
O	0.60042800	0.77491400	-1.28709800
O	-0.35195100	-1.98052800	-0.97546600
C	-1.35556100	-2.02237900	-1.74686300
C	1.60989100	-0.95106700	0.89089200
C	2.35345800	-1.72606400	-0.12771800
O	2.81031400	-1.27148500	-1.14900500
O	2.39668600	-3.02580600	0.21743600
C	2.91798800	-3.89606300	-0.79489900
C	2.20938300	-0.74677400	2.16232200
C	1.50279600	-0.39444900	3.25809100
O	3.46657600	1.35088900	0.59943800
C	3.28009900	1.98019000	-0.42842400
C	2.46695500	3.22849200	-0.43258700
C	1.93756300	3.71903100	0.68600700
C	3.85141800	1.56138400	-1.75038400
H	-1.36884500	-2.88075300	-2.43735800
H	0.30116800	2.08058600	-2.76426700
H	-2.92089000	-1.99792200	2.56172100
H	-1.16742400	2.94912400	2.19366500
H	3.95401100	-3.64246600	-1.02553500
H	2.85269400	-4.90098100	-0.38449600
H	2.31989200	-3.81299100	-1.70458700
H	3.28033700	-0.92821000	2.25560600
H	1.98547900	-0.30748000	4.22605600
H	0.43258000	-0.23727100	3.21025300
H	2.32514100	3.73226600	-1.38752100
H	2.09001500	3.19604100	1.62630100
H	1.34601700	4.62825200	0.69697300
H	3.03925500	1.17255300	-2.37293900
H	4.29146200	2.41541000	-2.27440100
H	4.58477200	0.76800800	-1.62558800

TS_CP

C	-2.19580800	3.93518100	0.52798800
O	-2.14788600	2.54922900	0.87745600
C	-2.09702400	1.70593100	-0.17694100
C	-1.76037900	0.33271800	0.30525100
C	-2.39963100	-0.13440400	1.50195100
C	-2.25150400	-1.38815100	1.96566100
O	-2.22886400	2.05667500	-1.32548400
Rh	0.27346300	-0.04693600	0.01329400
O	0.19083900	-2.13169400	-0.09033700
C	1.28683500	-2.76687200	-0.13845700
O	2.45414800	-2.31141200	-0.14424100
Rh	2.72645700	-0.25271200	-0.07958600
O	2.57772500	-0.16340300	-2.14452400
C	1.43926000	-0.02781900	-2.65332600
O	0.32022900	0.05271100	-2.06852800
O	0.48237900	-0.19096300	2.08700000
C	1.64156500	-0.28513400	2.58283900
O	2.74887100	-0.32207000	1.99394100
O	0.60009000	2.01957100	0.07747800
C	1.78457300	2.45899400	0.03564000
O	2.86059200	1.81774200	-0.02256700
C	-2.41397400	-0.91182100	-1.31389600
C	-3.74221800	-0.59707900	-1.20941100
C	-4.65159500	-1.36770000	-0.35985100
H	-1.34090300	4.19269900	-0.09988100
H	-2.16038800	4.48113500	1.46833000
H	-3.11498200	4.16523500	-0.01449400
H	-1.61807800	-2.10397500	1.45295600
H	-2.77157400	-1.72775700	2.85398700
H	-3.06031000	0.55741500	2.02594100
H	1.18829300	-3.86278000	-0.18101300
H	1.87269100	3.55719900	0.05429900
H	1.67282400	-0.34262000	3.68234600
H	1.39729200	0.02802000	-3.75200000
H	-2.06096700	-1.85101600	-0.89889200
H	-1.79178000	-0.42163000	-2.05201400
H	-4.12270200	0.28982100	-1.71091300
C	-6.07935600	-0.90004600	-0.29849900
O	-4.25078500	-2.31613600	0.30730800
H	-6.70053000	-1.61901200	0.23287300
H	-6.12394600	0.06106900	0.22675800
H	-6.48451300	-0.72441400	-1.29885700

TS_EP

Rh	-2.63153600	-0.06730100	0.38986000
O	-2.06294200	-0.03091700	2.38524800
O	-2.59272000	2.00688500	0.34661800
O	-3.08123100	-0.09826000	-1.63118100
O	-2.54625000	-2.13895500	0.40166400
Rh	-0.28184700	-0.05585500	-0.20178900
C	-1.44325800	-2.68272400	0.13058400
O	-0.34368800	-2.13529200	-0.15385700
C	-2.12152100	-0.08765700	-2.44658700
O	-0.88406700	-0.06990900	-2.20700800
C	-0.82962200	-0.02697100	2.63870200
O	0.14101700	-0.03892800	1.83454200
O	-0.39598600	2.02669100	-0.22681800
C	-1.50287600	2.56252400	0.05194200
H	-1.51590500	3.66399800	0.03366900
H	-0.56145600	-0.01160000	3.70699500
H	-2.40042000	-0.09601800	-3.51219800
H	-1.43692200	-3.78403900	0.14288600
C	2.26113900	-0.22529100	-0.57038100
C	2.40913200	1.20172200	-0.24055600

O	2.46485900	1.69147000	0.86936400
O	2.44544200	1.94547500	-1.37701900
C	2.43977800	3.35591100	-1.15599700
H	3.36034500	3.67246500	-0.65999200
H	2.37044700	3.80953900	-2.14296000
H	1.58599400	3.64024800	-0.54025400
C	2.05806600	-0.71770500	-1.89771400
H	1.88810200	0.05029400	-2.64399400
C	2.01952900	-2.01836200	-2.24811200
H	1.79511100	-2.31144700	-3.26606200
H	2.14678300	-2.80575400	-1.51399500
O	2.49354500	-1.16468700	0.46954500
C	3.85217600	-1.03158500	0.47945500
C	4.44512400	-0.37981600	1.58696600
H	5.52879900	-0.30194000	1.58660500
C	3.71466000	0.11487000	2.61246400
H	2.63450900	0.03270900	2.61238300
H	4.19402900	0.59631100	3.45756100
C	4.66424400	-1.80635900	-0.48139300
H	4.59728300	-2.87156800	-0.22564500
H	4.29966100	-1.73045100	-1.51176600
H	5.71259700	-1.51066900	-0.43146600

TS_YL

Rh	2.59252600	-0.35705700	-0.30554900
O	1.92844200	-1.67623200	-1.76505600
O	2.52887900	1.19261900	-1.69400100
O	3.11948800	0.99510200	1.17979900
O	2.49857600	-1.87249300	1.11083200
Rh	0.22856200	0.14389000	0.20924500
C	1.41251000	-2.05004500	1.71233300
O	0.32014700	-1.42460300	1.58871600
C	2.19882300	1.57969900	1.79902100
O	0.94743500	1.46784000	1.65404300
C	0.68961100	-1.79805200	-1.91989700
O	-0.25323600	-1.23067000	-1.29732900
O	0.34589300	1.64077200	-1.24598000
C	1.44770300	1.80674600	-1.84629500
H	1.44395400	2.60640700	-2.60483500
H	0.36661200	-2.50004000	-2.70746000
H	2.51234700	2.29111900	2.58005100
H	1.39685400	-2.86530800	2.45394900
C	-1.67575200	0.64539300	0.68898300
C	-2.34038500	1.35240300	-0.43630000
O	-2.84763900	0.86692100	-1.42075100
O	-2.20743500	2.68240100	-0.23284900
C	-2.52946600	3.49672300	-1.36433200
H	-3.59261500	3.42242300	-1.60255700
H	-2.27424400	4.51462400	-1.07803200
H	-1.94679400	3.18399900	-2.23176200
C	-1.98333600	1.03826300	2.04713000
H	-2.29707700	2.07942200	2.14705200
C	-1.87290700	0.26903800	3.13571800
H	-2.10468300	0.66373000	4.11828400
H	-1.56980100	-0.76896100	3.06144800
O	-2.56569500	-1.15680300	0.51023600
C	-3.74165700	-1.27322400	0.14949500
C	-4.12936800	-2.46387200	-0.62017700
H	-5.18981200	-2.69330100	-0.69366500
C	-3.20594100	-3.17749400	-1.26781700
H	-2.16218300	-2.88108500	-1.20864600
H	-3.47014700	-4.03338200	-1.87847000
C	-4.81464800	-0.28469700	0.46595600
H	-5.62152200	-0.79508300	1.00156000
H	-4.44725900	0.53988600	1.07435000
H	-5.24253600	0.10395300	-0.46179600

YL

Rh	2.56693600	-0.27955000	-0.25344100
O	1.99476000	-1.49121100	-1.85028000
O	2.53235900	1.37865200	-1.50851700
O	2.97972700	0.95826300	1.36221700
O	2.44595500	-1.91146900	1.02942600
Rh	0.18185000	0.09197900	0.18025400
C	1.33378400	-2.18930100	1.54312000
O	0.22503700	-1.60071900	1.39967400
C	2.00780400	1.45791900	1.98271400
O	0.77200400	1.31411000	1.76884100
C	0.76865200	-1.63553800	-2.07806300
O	-0.21801500	-1.14999300	-1.45520000
O	0.32682800	1.73891400	-1.09983600
C	1.44180900	1.98749600	-1.63712700
H	1.45399800	2.86137900	-2.30956900
H	0.51110000	-2.27678000	-2.93784100
H	2.26445300	2.11177200	2.83199700
H	1.31668400	-3.06745000	2.20935000
C	-2.02613200	0.40887100	0.66116900
C	-2.34707300	1.40293000	-0.37199600
O	-2.68511000	1.14580100	-1.51232900
O	-2.14973500	2.65303900	0.09226900
C	-2.19459000	3.67424800	-0.90748800
H	-3.18916000	3.73270300	-1.35531200
H	-1.95783000	4.60213600	-0.39080000
H	-1.45962100	3.47002100	-1.68665800
C	-2.08590200	0.69011300	2.08010400
H	-1.74018600	1.68490800	2.34053400
C	-2.47649100	-0.16760500	3.03198000
H	-2.45612600	0.11712700	4.07639000
H	-2.79001200	-1.18056500	2.80267600
O	-2.47083900	-0.92194200	0.35208600
C	-3.59021100	-1.19364300	-0.22814000
C	-3.69686900	-2.52349400	-0.76328100
H	-4.68766900	-2.82942200	-1.08541800
C	-2.64123400	-3.34542800	-0.88691000
H	-1.64659800	-3.01358900	-0.60818900
H	-2.75698100	-4.34684700	-1.28480500
C	-4.73846700	-0.26971800	-0.26927700
H	-5.65547100	-0.84082500	-0.10498100
H	-4.64930200	0.51822900	0.47958600
H	-4.80691300	0.20921600	-1.25119400

X-ray crystallography data:

1. X-ray crystallographic structure of product 7l

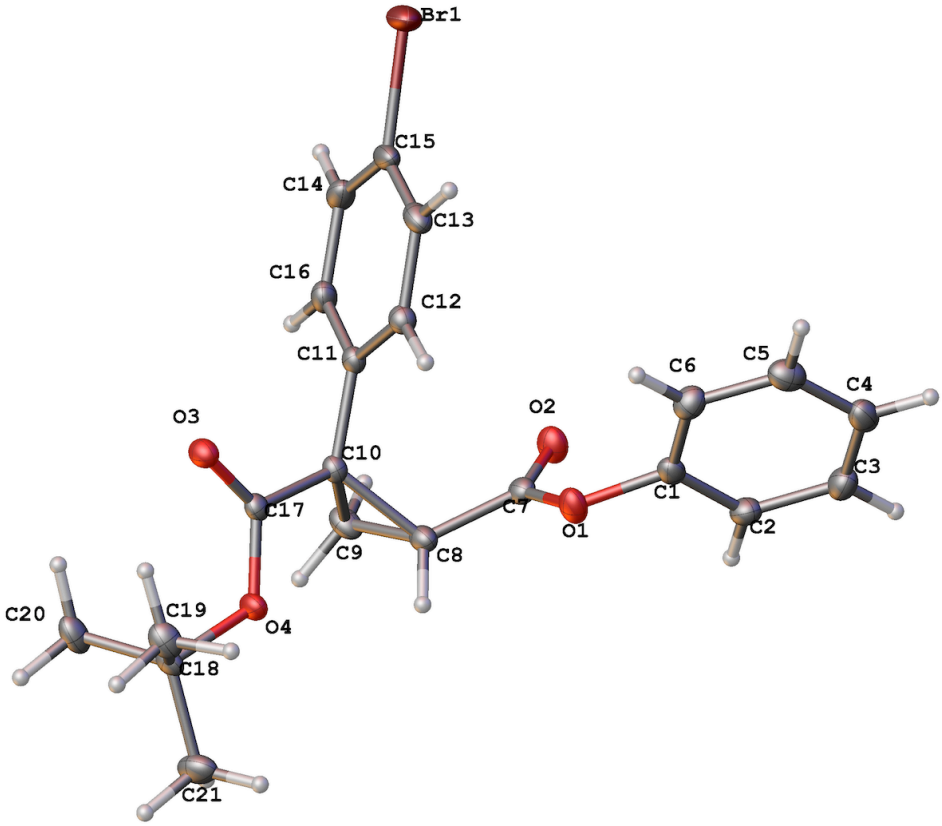


Table 1. Crystal data and structure refinement for product **7l**

Identification code	HW-XVIII-046	
Empirical formula	C21 H21 Br O4	
Formula weight	417.29	
Temperature	173.2 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.0402(2) Å	α= 90°.
	b = 15.4144(4) Å	β= 90°.
	c = 20.7290(8) Å	γ = 90°.
Volume	1930.00(11) Å^3	
Z	4	
Density (calculated)	1.436 Mg/m^3	
Absorption coefficient	2.152 mm^{-1}	
F(000)	856	
Crystal size	0.472 x 0.451 x 0.346 mm^3	
Theta range for data collection	1.65 to 30.99°.	
Index ranges	-8<=h<=8, -21<=k<=21, -15<=l<=29	
Reflections collected	21661	
Independent reflections	6098 [R(int) = 0.0482]	
Completeness to theta = 30.99°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7464 and 0.5354	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6098 / 0 / 238	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R_1 = 0.0382, wR_2 = 0.0836	
R indices (all data)	R_1 = 0.0604, wR_2 = 0.0916	
Absolute structure parameter	0.006(7)	
Largest diff. peak and hole	0.349 and -0.357 e.Å^{-3}	

Table 2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for product **7l**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Br(1)	-1109(1)	2618(1)	3356(1)	70(1)
C(1)	1296(3)	6901(1)	4382(1)	30(1)
C(2)	2868(3)	7495(1)	4195(1)	34(1)
C(3)	2435(4)	8010(2)	3664(1)	40(1)
C(4)	472(4)	7923(1)	3328(1)	40(1)
C(5)	-1062(4)	7314(2)	3522(1)	41(1)
C(6)	-670(3)	6797(2)	4055(1)	37(1)
C(7)	3213(3)	5848(1)	5026(1)	28(1)
C(8)	3116(3)	5493(1)	5690(1)	29(1)
C(9)	4540(3)	4747(2)	5872(1)	34(1)
C(10)	2112(3)	4579(1)	5764(1)	24(1)
C(11)	1386(3)	4113(1)	5169(1)	24(1)
C(12)	-535(3)	4373(1)	4852(1)	28(1)
C(13)	-1282(4)	3930(2)	4311(1)	36(1)
C(14)	-49(4)	3241(2)	4079(1)	39(1)
C(15)	1884(4)	2982(2)	4372(1)	41(1)
C(16)	2591(4)	3420(1)	4921(1)	33(1)
C(17)	718(3)	4419(1)	6353(1)	24(1)
C(18)	492(3)	4800(1)	7512(1)	28(1)
C(19)	-2022(3)	4875(2)	7540(1)	38(1)
C(20)	1273(4)	3924(2)	7740(1)	40(1)
C(21)	1588(4)	5528(2)	7879(1)	45(1)
O(1)	1555(2)	6435(1)	4961(1)	36(1)
O(2)	4465(2)	5656(1)	4605(1)	38(1)
O(3)	-716(2)	3876(1)	6375(1)	32(1)
O(4)	1295(2)	4945(1)	6840(1)	30(1)

Table 3. Bond lengths [Å] and angles [°] for product **7l**

Br(1)-C(14)	1.891(2)
O(1)-C(1)	1.406(2)
O(1)-C(7)	1.357(2)
O(2)-C(7)	1.193(2)
O(3)-C(17)	1.205(2)
O(4)-C(17)	1.341(2)
O(4)-C(18)	1.492(2)
C(1)-C(2)	1.375(3)
C(1)-C(6)	1.377(3)
C(2)-C(3)	1.382(3)
C(3)-C(4)	1.382(3)
C(4)-C(5)	1.380(3)
C(5)-C(6)	1.383(3)
C(7)-C(8)	1.482(3)
C(8)-C(9)	1.484(3)
C(8)-C(10)	1.542(3)
C(9)-C(10)	1.506(3)
C(10)-C(11)	1.493(3)
C(10)-C(17)	1.503(3)
C(11)-C(12)	1.393(3)
C(11)-C(16)	1.392(3)
C(12)-C(13)	1.387(3)
C(13)-C(14)	1.384(3)
C(14)-C(15)	1.375(3)
C(15)-C(16)	1.391(3)
C(18)-C(19)	1.524(3)
C(18)-C(20)	1.507(3)
C(18)-C(21)	1.509(3)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-H(4)	0.9500
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(8)-H(8)	1.0000

C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(1)-O(1)-C(7)	120.49(14)
C(17)-O(4)-C(18)	121.84(14)
O(1)-C(1)-C(2)	120.24(16)
O(1)-C(1)-C(6)	117.17(17)
C(2)-C(1)-C(6)	122.28(18)
C(1)-C(2)-C(3)	118.48(18)
C(2)-C(3)-C(4)	120.6(2)
C(3)-C(4)-C(5)	119.6(2)
C(4)-C(5)-C(6)	120.7(2)
C(1)-C(6)-C(5)	118.3(2)
O(1)-C(7)-O(2)	124.08(17)
O(1)-C(7)-C(8)	108.05(15)
O(2)-C(7)-C(8)	127.84(18)
C(7)-C(8)-C(9)	119.97(17)
C(7)-C(8)-C(10)	116.49(16)
C(9)-C(8)-C(10)	59.67(13)
C(8)-C(9)-C(10)	62.06(13)
C(8)-C(10)-C(9)	58.27(13)
C(8)-C(10)-C(11)	118.17(16)
C(8)-C(10)-C(17)	116.82(16)

C(9)-C(10)-C(11)	119.46(16)
C(9)-C(10)-C(17)	116.94(16)
C(11)-C(10)-C(17)	115.33(16)
C(10)-C(11)-C(12)	119.84(16)
C(10)-C(11)-C(16)	121.38(17)
C(12)-C(11)-C(16)	118.78(17)
C(11)-C(12)-C(13)	120.79(19)
C(12)-C(13)-C(14)	118.9(2)
Br(1)-C(14)-C(13)	118.86(17)
Br(1)-C(14)-C(15)	119.31(17)
C(13)-C(14)-C(15)	121.8(2)
C(14)-C(15)-C(16)	118.7(2)
C(11)-C(16)-C(15)	121.0(2)
O(3)-C(17)-O(4)	125.32(16)
O(3)-C(17)-C(10)	123.17(16)
O(4)-C(17)-C(10)	111.51(15)
O(4)-C(18)-C(19)	110.37(15)
O(4)-C(18)-C(20)	109.01(15)
O(4)-C(18)-C(21)	102.51(16)
C(19)-C(18)-C(20)	111.58(18)
C(19)-C(18)-C(21)	111.20(18)
C(20)-C(18)-C(21)	111.79(17)
C(1)-C(2)-H(2)	121.00
C(3)-C(2)-H(2)	121.00
C(2)-C(3)-H(3)	120.00
C(4)-C(3)-H(3)	120.00
C(3)-C(4)-H(4)	120.00
C(5)-C(4)-H(4)	120.00
C(4)-C(5)-H(5)	120.00
C(6)-C(5)-H(5)	120.00
C(1)-C(6)-H(6)	121.00
C(5)-C(6)-H(6)	121.00
C(7)-C(8)-H(8)	116.00
C(9)-C(8)-H(8)	116.00
C(10)-C(8)-H(8)	116.00
C(8)-C(9)-H(9A)	118.00

C(8)-C(9)-H(9B)	118.00
C(10)-C(9)-H(9A)	118.00
C(10)-C(9)-H(9B)	118.00
H(9A)-C(9)-H(9B)	115.00
C(11)-C(12)-H(12)	120.00
C(13)-C(12)-H(12)	120.00
C(12)-C(13)-H(13)	121.00
C(14)-C(13)-H(13)	121.00
C(14)-C(15)-H(15)	121.00
C(16)-C(15)-H(15)	121.00
C(11)-C(16)-H(16)	120.00
C(15)-C(16)-H(16)	119.00
C(18)-C(19)-H(19A)	110.00
C(18)-C(19)-H(19B)	110.00
C(18)-C(19)-H(19C)	109.00
H(19A)-C(19)-H(19B)	109.00
H(19A)-C(19)-H(19C)	109.00
H(19B)-C(19)-H(19C)	109.00
C(18)-C(20)-H(20A)	109.00
C(18)-C(20)-H(20B)	110.00
C(18)-C(20)-H(20C)	109.00
H(20A)-C(20)-H(20B)	109.00
H(20A)-C(20)-H(20C)	109.00
H(20B)-C(20)-H(20C)	109.00
C(18)-C(21)-H(21A)	110.00
C(18)-C(21)-H(21B)	109.00
C(18)-C(21)-H(21C)	109.00
H(21A)-C(21)-H(21B)	109.00
H(21A)-C(21)-H(21C)	109.00
H(21B)-C(21)-H(21C)	110.00

Table 4. Anisotropic displacement parameters ($Å^2x10^3$) for product **7l**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	132(1)	49(1)	30(1)	-4(1)	-15(1)	-37(1)
C(1)	40(1)	26(1)	22(1)	-3(1)	4(1)	3(1)
C(2)	39(1)	32(1)	32(1)	-4(1)	0(1)	-6(1)
C(3)	51(1)	31(1)	38(1)	2(1)	6(1)	-6(1)
C(4)	56(1)	32(1)	31(1)	0(1)	0(1)	8(1)
C(5)	40(1)	44(1)	39(1)	-6(1)	-6(1)	6(1)
C(6)	36(1)	34(1)	42(1)	0(1)	6(1)	-4(1)
C(7)	31(1)	26(1)	27(1)	0(1)	2(1)	-8(1)
C(8)	32(1)	32(1)	22(1)	0(1)	1(1)	-7(1)
C(9)	25(1)	51(1)	26(1)	2(1)	-3(1)	-3(1)
C(10)	24(1)	26(1)	21(1)	2(1)	1(1)	2(1)
C(11)	28(1)	24(1)	20(1)	2(1)	3(1)	-1(1)
C(12)	28(1)	30(1)	26(1)	2(1)	0(1)	-2(1)
C(13)	40(1)	43(1)	26(1)	6(1)	-7(1)	-12(1)
C(14)	63(1)	34(1)	20(1)	1(1)	0(1)	-20(1)
C(15)	68(2)	26(1)	28(1)	-2(1)	11(1)	-2(1)
C(16)	44(1)	28(1)	28(1)	5(1)	2(1)	3(1)
C(17)	26(1)	26(1)	21(1)	3(1)	-2(1)	2(1)
C(18)	31(1)	36(1)	17(1)	0(1)	1(1)	0(1)
C(19)	33(1)	47(2)	33(1)	2(1)	3(1)	9(1)
C(20)	44(1)	48(1)	27(1)	8(1)	0(1)	15(1)
C(21)	51(1)	52(2)	32(1)	-13(1)	8(1)	-11(1)
O(1)	45(1)	38(1)	26(1)	5(1)	10(1)	6(1)
O(2)	40(1)	41(1)	32(1)	4(1)	11(1)	3(1)
O(3)	34(1)	37(1)	26(1)	0(1)	2(1)	-7(1)
O(4)	39(1)	33(1)	20(1)	-1(1)	4(1)	-8(1)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for product **7l**

	x	y	z	U(eq)
H(2)	4221	7549	4425	41
H(3)	3496	8427	3529	48
H(4)	180	8281	2965	47
H(5)	-2402	7249	3287	49
H(6)	-1731	6380	4192	44
H(8)	2770	5917	6041	35
H(9A)	5094	4724	6322	41
H(9B)	5591	4526	5545	41
H(12)	-1343	4858	5007	34
H(13)	-2617	4098	4103	44
H(15)	2721	2512	4202	49
H(16)	3917	3243	5130	40
H(19A)	-2486	5420	7339	57
H(19B)	-2508	4866	7991	57
H(19C)	-2690	4386	7309	57
H(20A)	512	3468	7496	60
H(20B)	942	3858	8201	60
H(20C)	2874	3874	7672	60
H(21A)	3195	5496	7820	68
H(21B)	1235	5475	8339	68
H(21C)	1044	6086	7717	68

Table 6. Torsion angles [°] for product **7l**

C(7)-O(1)-C(1)-C(2)	-66.8(2)
C(7)-O(1)-C(1)-C(6)	119.4(2)
C(1)-O(1)-C(7)-O(2)	-3.7(3)
C(1)-O(1)-C(7)-C(8)	177.80(16)
C(17)-O(4)-C(18)-C(19)	-62.5(2)
C(18)-O(4)-C(17)-O(3)	11.9(3)
C(18)-O(4)-C(17)-C(10)	-167.44(15)
C(17)-O(4)-C(18)-C(20)	60.4(2)
C(17)-O(4)-C(18)-C(21)	179.01(16)
O(1)-C(1)-C(6)-C(5)	173.34(19)
C(2)-C(1)-C(6)-C(5)	-0.3(3)
C(6)-C(1)-C(2)-C(3)	0.8(3)
O(1)-C(1)-C(2)-C(3)	-172.64(18)
C(1)-C(2)-C(3)-C(4)	-0.5(3)
C(2)-C(3)-C(4)-C(5)	-0.3(3)
C(3)-C(4)-C(5)-C(6)	0.9(4)
C(4)-C(5)-C(6)-C(1)	-0.6(3)
O(1)-C(7)-C(8)-C(10)	102.99(19)
O(2)-C(7)-C(8)-C(9)	-6.8(3)
O(1)-C(7)-C(8)-C(9)	171.65(17)
O(2)-C(7)-C(8)-C(10)	-75.4(3)
C(9)-C(8)-C(10)-C(11)	-108.95(19)
C(7)-C(8)-C(9)-C(10)	-105.0(2)
C(7)-C(8)-C(10)-C(9)	110.80(19)
C(9)-C(8)-C(10)-C(17)	106.52(18)
C(7)-C(8)-C(10)-C(17)	-142.68(17)
C(7)-C(8)-C(10)-C(11)	1.9(2)
C(8)-C(9)-C(10)-C(17)	-106.31(19)
C(8)-C(9)-C(10)-C(11)	106.75(19)
C(17)-C(10)-C(11)-C(16)	-108.5(2)
C(8)-C(10)-C(17)-O(3)	154.48(18)
C(8)-C(10)-C(11)-C(12)	-73.5(2)
C(8)-C(10)-C(11)-C(16)	106.5(2)
C(9)-C(10)-C(11)-C(12)	-141.04(19)

C(9)-C(10)-C(11)-C(16)	39.0(3)
C(17)-C(10)-C(11)-C(12)	71.5(2)
C(11)-C(10)-C(17)-O(4)	-171.70(15)
C(9)-C(10)-C(17)-O(3)	-139.4(2)
C(9)-C(10)-C(17)-O(4)	40.0(2)
C(8)-C(10)-C(17)-O(4)	-26.2(2)
C(11)-C(10)-C(17)-O(3)	9.0(3)
C(16)-C(11)-C(12)-C(13)	2.3(3)
C(10)-C(11)-C(16)-C(15)	179.01(19)
C(10)-C(11)-C(12)-C(13)	-177.72(18)
C(12)-C(11)-C(16)-C(15)	-1.0(3)
C(11)-C(12)-C(13)-C(14)	-1.9(3)
C(12)-C(13)-C(14)-Br(1)	178.29(16)
C(12)-C(13)-C(14)-C(15)	0.3(3)
C(13)-C(14)-C(15)-C(16)	1.0(3)
Br(1)-C(14)-C(15)-C(16)	-177.02(16)
C(14)-C(15)-C(16)-C(11)	-0.6(3)

Table 7. Hydrogen bonds for product **7l** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...O(1)#1	0.9500	2.4600	3.277(2)	144.00
C(8)-H(8)...O(4)	1.0000	2.4000	2.758(2)	100.00
C(19)-H(19C)...O(3)	0.9800	2.4100	2.971(3)	116.00
C(20)-H(20A)...O(3)	0.9800	2.5200	3.075(2)	116.00

Symmetry transformations used to generate equivalent atoms:
#1 1/2+x, 3/2-y, 1-z

2. X-ray crystallographic structure of 15

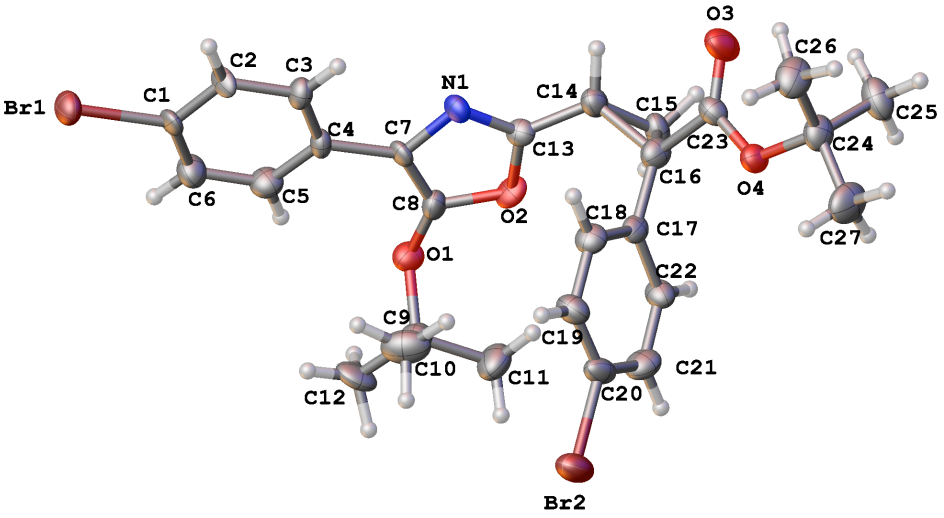


Table 1. Crystal data and structure refinement for product **15**

Identification code	hwxviii026	
Empirical formula	C27 H29 Br2 N O4	
Formula weight	591.33	
Temperature	173.2 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.4731(3) Å	α= 90º.
	b = 9.8670(4) Å	β= 90º.
	c = 41.1040(18) Å	γ= 90º.
Volume	2625.3(2) Å ^{3}	
Z	4	
Density (calculated)	1.496 Mg/m^3	
Absorption coefficient	3.120 mm^{-1}	
F(000)	1200	
Crystal size	0.366 x 0.335 x 0.098 mm^3	
Theta range for data collection	1.98 to 27.54º.	
Index ranges	-6<=h<=8, -12<=k<=12, -53<=l<=53	
Reflections collected	22383	
Independent reflections	6020 [R(int) = 0.0625]	
Completeness to theta = 27.54º	99.4 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8326 and 0.4559	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6020 / 0 / 313	
Goodness-of-fit on F^2	1.140	
Final R indices [I>2sigma(I)]	R_1 = 0.0687, wR_2 = 0.1594	
R indices (all data)	R_1 = 0.0782, wR_2 = 0.1629	
Absolute structure parameter	0.102(19)	
Largest diff. peak and hole	1.210 and -1.426 e.Å^{-3}	

Table 2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for product **15**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Br(1)	-1110(1)	5372(1)	7783(1)	37(1)
Br(2)	5422(2)	6904(1)	5278(1)	50(1)
C(1)	1333(10)	5373(8)	7522(2)	28(1)
C(2)	2082(10)	4156(7)	7412(2)	26(2)
C(3)	3865(11)	4150(7)	7214(2)	29(1)
C(4)	4826(9)	5348(7)	7141(1)	24(1)
C(5)	4070(13)	6572(7)	7265(2)	36(2)
C(6)	2329(13)	6570(8)	7458(2)	38(2)
C(7)	6733(9)	5332(7)	6941(2)	23(1)
C(8)	7801(12)	6389(8)	6813(2)	30(2)
C(9)	6894(13)	8525(8)	6555(2)	36(2)
C(10)	5237(16)	7756(10)	6377(2)	55(3)
C(11)	8771(16)	8802(9)	6338(2)	51(2)
C(12)	6110(16)	9840(7)	6704(2)	47(2)
C(13)	9345(10)	4496(7)	6681(2)	25(1)
C(14)	10887(12)	3612(7)	6541(2)	31(2)
C(15)	11247(13)	3632(7)	6168(2)	32(2)
C(16)	12771(11)	4242(8)	6400(2)	33(2)
C(17)	9858(11)	4449(6)	5960(2)	28(1)
C(18)	7821(12)	4050(7)	5913(2)	32(2)
C(19)	6520(12)	4789(8)	5714(2)	36(2)
C(20)	7237(14)	5903(8)	5554(2)	35(2)
C(21)	9228(14)	6347(8)	5595(2)	40(2)
C(22)	10522(12)	5627(7)	5799(2)	31(2)
C(23)	11998(11)	2288(7)	6033(2)	29(2)
C(24)	12648(14)	1144(8)	5514(2)	37(2)
C(25)	14979(13)	1012(9)	5563(2)	45(2)
C(26)	11565(16)	-150(9)	5604(2)	51(2)
C(27)	12194(18)	1565(10)	5175(2)	56(3)

N(1)	7718(9)	4128(6)	6850(1)	26(1)
O(1)	7649(8)	7723(5)	6840(1)	32(1)
O(2)	9503(8)	5873(5)	6646(1)	30(1)
O(3)	12720(11)	1406(6)	6198(1)	48(2)
O(4)	11879(8)	2296(5)	5712(1)	31(1)

Table 3. Bond lengths [Å] and angles [º] for product **15**

Br(1)-C(1)	1.911(7)
Br(2)-C(20)	1.909(8)
O(1)-C(8)	1.325(9)
O(1)-C(9)	1.495(9)
O(2)-C(8)	1.394(9)
O(2)-C(13)	1.370(8)
O(3)-C(23)	1.199(9)
O(4)-C(23)	1.320(9)
O(4)-C(24)	1.486(9)
N(1)-C(7)	1.399(9)
N(1)-C(13)	1.312(9)
C(1)-C(2)	1.372(10)
C(1)-C(6)	1.371(11)
C(2)-C(3)	1.412(10)
C(3)-C(4)	1.369(10)
C(4)-C(5)	1.399(10)
C(4)-C(7)	1.484(8)
C(5)-C(6)	1.379(12)
C(7)-C(8)	1.357(10)
C(9)-C(10)	1.504(13)
C(9)-C(11)	1.533(13)
C(9)-C(12)	1.521(11)
C(13)-C(14)	1.446(10)
C(14)-C(15)	1.551(10)
C(14)-C(16)	1.486(10)
C(15)-C(16)	1.499(10)
C(15)-C(17)	1.478(10)
C(15)-C(23)	1.517(10)
C(17)-C(18)	1.390(10)
C(17)-C(22)	1.406(9)
C(18)-C(19)	1.382(11)
C(19)-C(20)	1.362(11)
C(20)-C(21)	1.371(13)
C(21)-C(22)	1.381(11)

C(24)-C(25)	1.528(12)
C(24)-C(26)	1.503(12)
C(24)-C(27)	1.482(12)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(14)-H(14)	1.0000
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(8)-O(1)-C(9)	119.0(6)
C(8)-O(2)-C(13)	104.6(5)
C(23)-O(4)-C(24)	121.7(6)
C(7)-N(1)-C(13)	105.8(6)

Br(1)-C(1)-C(2)	118.5(5)
Br(1)-C(1)-C(6)	119.8(6)
C(2)-C(1)-C(6)	121.6(7)
C(1)-C(2)-C(3)	118.9(6)
C(2)-C(3)-C(4)	119.6(6)
C(3)-C(4)-C(5)	120.5(6)
C(3)-C(4)-C(7)	119.4(6)
C(5)-C(4)-C(7)	120.1(6)
C(4)-C(5)-C(6)	119.6(7)
C(1)-C(6)-C(5)	119.8(7)
N(1)-C(7)-C(4)	122.4(6)
N(1)-C(7)-C(8)	108.5(6)
C(4)-C(7)-C(8)	129.1(6)
O(1)-C(8)-O(2)	117.6(6)
O(1)-C(8)-C(7)	133.9(7)
O(2)-C(8)-C(7)	108.2(6)
O(1)-C(9)-C(10)	110.3(6)
O(1)-C(9)-C(11)	107.0(6)
O(1)-C(9)-C(12)	104.2(6)
C(10)-C(9)-C(11)	111.8(7)
C(10)-C(9)-C(12)	112.8(8)
C(11)-C(9)-C(12)	110.3(7)
O(2)-C(13)-N(1)	112.9(6)
O(2)-C(13)-C(14)	120.3(6)
N(1)-C(13)-C(14)	126.8(6)
C(13)-C(14)-C(15)	119.4(6)
C(13)-C(14)-C(16)	118.0(6)
C(15)-C(14)-C(16)	59.1(5)
C(14)-C(15)-C(16)	58.3(5)
C(14)-C(15)-C(17)	119.1(6)
C(14)-C(15)-C(23)	113.4(6)
C(16)-C(15)-C(17)	123.3(6)
C(16)-C(15)-C(23)	111.9(6)
C(17)-C(15)-C(23)	117.5(6)
C(14)-C(16)-C(15)	62.6(5)
C(15)-C(17)-C(18)	120.2(6)

C(15)-C(17)-C(22)	122.5(7)
C(18)-C(17)-C(22)	117.3(6)
C(17)-C(18)-C(19)	120.8(7)
C(18)-C(19)-C(20)	120.2(7)
Br(2)-C(20)-C(19)	119.6(6)
Br(2)-C(20)-C(21)	119.0(6)
C(19)-C(20)-C(21)	121.3(7)
C(20)-C(21)-C(22)	118.6(7)
C(17)-C(22)-C(21)	121.8(7)
O(3)-C(23)-O(4)	126.4(7)
O(3)-C(23)-C(15)	123.5(7)
O(4)-C(23)-C(15)	109.9(6)
O(4)-C(24)-C(25)	108.8(6)
O(4)-C(24)-C(26)	110.9(7)
O(4)-C(24)-C(27)	103.7(7)
C(25)-C(24)-C(26)	110.8(7)
C(25)-C(24)-C(27)	110.2(8)
C(26)-C(24)-C(27)	112.2(7)
C(1)-C(2)-H(2)	121.00
C(3)-C(2)-H(2)	121.00
C(2)-C(3)-H(3)	120.00
C(4)-C(3)-H(3)	120.00
C(4)-C(5)-H(5)	120.00
C(6)-C(5)-H(5)	120.00
C(1)-C(6)-H(6)	120.00
C(5)-C(6)-H(6)	120.00
C(9)-C(10)-H(10A)	109.00
C(9)-C(10)-H(10B)	109.00
C(9)-C(10)-H(10C)	110.00
H(10A)-C(10)-H(10B)	109.00
H(10A)-C(10)-H(10C)	109.00
H(10B)-C(10)-H(10C)	109.00
C(9)-C(11)-H(11A)	110.00
C(9)-C(11)-H(11B)	109.00
C(9)-C(11)-H(11C)	110.00
H(11A)-C(11)-H(11B)	109.00

H(11A)-C(11)-H(11C)	110.00
H(11B)-C(11)-H(11C)	109.00
C(9)-C(12)-H(12A)	109.00
C(9)-C(12)-H(12B)	109.00
C(9)-C(12)-H(12C)	110.00
H(12A)-C(12)-H(12B)	109.00
H(12A)-C(12)-H(12C)	109.00
H(12B)-C(12)-H(12C)	109.00
C(13)-C(14)-H(14)	116.00
C(15)-C(14)-H(14)	116.00
C(16)-C(14)-H(14)	116.00
C(14)-C(16)-H(16A)	118.00
C(14)-C(16)-H(16B)	118.00
C(15)-C(16)-H(16A)	117.00
C(15)-C(16)-H(16B)	117.00
H(16A)-C(16)-H(16B)	115.00
C(17)-C(18)-H(18)	120.00
C(19)-C(18)-H(18)	120.00
C(18)-C(19)-H(19)	120.00
C(20)-C(19)-H(19)	120.00
C(20)-C(21)-H(21)	121.00
C(22)-C(21)-H(21)	121.00
C(17)-C(22)-H(22)	119.00
C(21)-C(22)-H(22)	119.00
C(24)-C(25)-H(25A)	110.00
C(24)-C(25)-H(25B)	110.00
C(24)-C(25)-H(25C)	109.00
H(25A)-C(25)-H(25B)	110.00
H(25A)-C(25)-H(25C)	109.00
H(25B)-C(25)-H(25C)	109.00
C(24)-C(26)-H(26A)	109.00
C(24)-C(26)-H(26B)	109.00
C(24)-C(26)-H(26C)	110.00
H(26A)-C(26)-H(26B)	109.00
H(26A)-C(26)-H(26C)	109.00
H(26B)-C(26)-H(26C)	110.00

C(24)-C(27)-H(27A)	110.00
C(24)-C(27)-H(27B)	109.00
C(24)-C(27)-H(27C)	110.00
H(27A)-C(27)-H(27B)	109.00
H(27A)-C(27)-H(27C)	109.00
H(27B)-C(27)-H(27C)	109.00

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2x10^3$) for product **15**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	26(1)	39(1)	47(1)	2(1)	10(1)	0(1)
Br(2)	63(1)	46(1)	42(1)	7(1)	-2(1)	21(1)
C(1)	16(3)	35(4)	35(3)	5(3)	2(3)	12(3)
C(2)	11(3)	22(3)	46(4)	-1(3)	3(3)	-5(2)
C(3)	22(3)	37(4)	30(3)	-2(3)	4(3)	-2(3)
C(4)	18(3)	32(3)	23(3)	-4(3)	3(2)	2(3)
C(5)	38(4)	29(4)	42(4)	3(3)	1(4)	-5(3)
C(6)	37(4)	31(4)	44(4)	-3(3)	7(4)	2(3)
C(7)	13(3)	26(3)	31(3)	0(3)	-1(2)	6(3)
C(8)	29(4)	36(4)	24(3)	0(3)	6(3)	3(3)
C(9)	43(4)	26(4)	38(4)	4(3)	5(3)	0(3)
C(10)	57(6)	50(6)	58(5)	12(4)	-24(5)	-12(5)
C(11)	59(6)	42(5)	51(5)	7(4)	20(5)	-5(5)
C(12)	58(5)	24(4)	59(5)	0(3)	-8(5)	16(4)
C(13)	20(3)	23(3)	31(3)	0(3)	-3(2)	-6(3)
C(14)	33(4)	32(4)	28(3)	-3(3)	1(3)	7(3)
C(15)	41(4)	28(4)	29(3)	-5(3)	2(3)	-1(3)
C(16)	24(4)	41(4)	35(4)	-9(3)	1(3)	6(3)
C(17)	38(4)	18(3)	27(3)	-5(3)	7(3)	1(3)
C(18)	33(4)	25(4)	37(4)	1(3)	1(3)	-8(3)
C(19)	31(4)	30(4)	46(4)	2(3)	-4(3)	3(3)
C(20)	49(5)	31(4)	24(3)	-1(3)	-4(3)	14(4)
C(21)	52(6)	29(4)	40(4)	5(3)	4(4)	-7(4)
C(22)	29(3)	22(3)	42(4)	3(3)	4(3)	-2(3)
C(23)	26(3)	24(4)	37(4)	-2(3)	-1(3)	2(3)
C(24)	42(5)	34(4)	36(4)	-10(3)	5(4)	-1(4)
C(25)	33(5)	39(4)	64(6)	-16(4)	4(4)	-1(4)
C(26)	63(6)	34(5)	55(5)	-11(4)	12(4)	-7(4)
C(27)	85(7)	45(5)	37(5)	-14(4)	11(5)	1(5)

N(1)	17(3)	26(3)	35(3)	0(2)	-1(2)	2(2)
O(1)	38(3)	25(3)	33(3)	-2(2)	1(2)	-2(2)
O(2)	26(2)	32(3)	31(2)	1(2)	1(2)	-16(2)
O(3)	64(4)	43(3)	39(3)	-4(3)	1(3)	24(3)
O(4)	36(3)	27(3)	29(3)	-3(2)	2(2)	5(2)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for product **15**

	x	y	z	U(eq)
H(2)	1413	3331	7468	31
H(3)	4395	3320	7132	35
H(5)	4751	7399	7216	44
H(6)	1822	7395	7546	45
H(10A)	5831	6935	6281	83
H(10B)	4663	8329	6204	83
H(10C)	4137	7505	6529	83
H(11A)	9828	9285	6463	76
H(11B)	8347	9357	6152	76
H(11C)	9337	7941	6259	76
H(12A)	4723	9698	6793	71
H(12B)	6058	10544	6536	71
H(12C)	7045	10126	6879	71
H(14)	11086	2718	6651	37
H(16A)	14099	3762	6431	40
H(16B)	12873	5243	6406	40
H(18)	7318	3260	6018	38
H(19)	5120	4520	5689	43
H(21)	9707	7134	5485	49
H(22)	11897	5937	5831	37
H(25A)	15663	1845	5491	68
H(25B)	15498	242	5437	68
H(25C)	15272	864	5795	68
H(26A)	12023	-442	5820	76
H(26B)	11898	-854	5444	76
H(26C)	10069	2	5607	76
H(27A)	10728	1800	5155	83
H(27B)	12514	817	5026	83
H(27C)	13039	2355	5118	83

Table 6. Torsion angles [º] for product **15**

C(8)-O(1)-C(9)-C(11)	-85.1(8)
C(8)-O(1)-C(9)-C(12)	158.1(7)
C(8)-O(1)-C(9)-C(10)	36.7(9)
C(9)-O(1)-C(8)-C(7)	-109.2(9)
C(9)-O(1)-C(8)-O(2)	78.3(8)
C(13)-O(2)-C(8)-C(7)	0.6(7)
C(13)-O(2)-C(8)-O(1)	175.0(6)
C(8)-O(2)-C(13)-C(14)	-179.2(6)
C(8)-O(2)-C(13)-N(1)	0.4(7)
C(23)-O(4)-C(24)-C(25)	-63.4(8)
C(23)-O(4)-C(24)-C(27)	179.4(7)
C(23)-O(4)-C(24)-C(26)	58.7(9)
C(24)-O(4)-C(23)-O(3)	0.7(12)
C(24)-O(4)-C(23)-C(15)	175.8(6)
C(7)-N(1)-C(13)-C(14)	178.4(6)
C(7)-N(1)-C(13)-O(2)	-1.2(7)
C(13)-N(1)-C(7)-C(8)	1.6(7)
C(13)-N(1)-C(7)-C(4)	-179.0(6)
Br(1)-C(1)-C(2)-C(3)	178.9(5)
Br(1)-C(1)-C(6)-C(5)	-178.8(6)
C(6)-C(1)-C(2)-C(3)	-3.2(11)
C(2)-C(1)-C(6)-C(5)	3.3(12)
C(1)-C(2)-C(3)-C(4)	1.1(10)
C(2)-C(3)-C(4)-C(7)	178.3(6)
C(2)-C(3)-C(4)-C(5)	0.9(10)
C(3)-C(4)-C(7)-C(8)	172.6(7)
C(3)-C(4)-C(7)-N(1)	-6.7(9)
C(3)-C(4)-C(5)-C(6)	-0.8(11)
C(5)-C(4)-C(7)-N(1)	170.7(6)
C(5)-C(4)-C(7)-C(8)	-10.1(10)
C(7)-C(4)-C(5)-C(6)	-178.2(7)
C(4)-C(5)-C(6)-C(1)	-1.3(12)
C(4)-C(7)-C(8)-O(1)	6.2(13)
N(1)-C(7)-C(8)-O(2)	-1.4(8)

C(4)-C(7)-C(8)-O(2)	179.3(6)
N(1)-C(7)-C(8)-O(1)	-174.5(8)
O(2)-C(13)-C(14)-C(16)	8.4(9)
N(1)-C(13)-C(14)-C(15)	120.4(8)
O(2)-C(13)-C(14)-C(15)	-60.1(9)
N(1)-C(13)-C(14)-C(16)	-171.2(7)
C(16)-C(14)-C(15)-C(23)	102.1(7)
C(13)-C(14)-C(15)-C(16)	106.9(7)
C(13)-C(14)-C(15)-C(17)	-6.3(10)
C(13)-C(14)-C(16)-C(15)	-109.3(7)
C(16)-C(14)-C(15)-C(17)	-113.2(7)
C(13)-C(14)-C(15)-C(23)	-151.0(7)
C(23)-C(15)-C(16)-C(14)	-104.8(6)
C(17)-C(15)-C(16)-C(14)	106.1(8)
C(23)-C(15)-C(17)-C(22)	-105.9(8)
C(14)-C(15)-C(23)-O(3)	-17.1(11)
C(14)-C(15)-C(17)-C(18)	-70.5(9)
C(14)-C(15)-C(17)-C(22)	110.9(8)
C(16)-C(15)-C(17)-C(18)	-139.8(7)
C(16)-C(15)-C(17)-C(22)	41.6(10)
C(23)-C(15)-C(17)-C(18)	72.8(9)
C(17)-C(15)-C(23)-O(4)	22.4(9)
C(16)-C(15)-C(23)-O(3)	46.6(10)
C(16)-C(15)-C(23)-O(4)	-128.6(6)
C(14)-C(15)-C(23)-O(4)	167.7(6)
C(17)-C(15)-C(23)-O(3)	-162.4(7)
C(22)-C(17)-C(18)-C(19)	0.1(10)
C(15)-C(17)-C(22)-C(21)	177.2(7)
C(15)-C(17)-C(18)-C(19)	-178.6(7)
C(18)-C(17)-C(22)-C(21)	-1.4(10)
C(17)-C(18)-C(19)-C(20)	1.8(11)
C(18)-C(19)-C(20)-Br(2)	179.6(6)
C(18)-C(19)-C(20)-C(21)	-2.3(12)
C(19)-C(20)-C(21)-C(22)	1.0(12)
Br(2)-C(20)-C(21)-C(22)	179.1(6)
C(20)-C(21)-C(22)-C(17)	0.9(11)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for product **15**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3)...N(1)	0.9500	2.5700	2.909(9)	101.00
C(5)-H(5)...O(1)	0.9500	2.4500	3.115(9)	127.00
C(11)-H(11C)...O(2)	0.9800	2.5900	3.191(10)	120.00
C(14)-H(14)...O(3)	1.0000	2.5000	2.850(9)	100.00
C(16)-H(16B)...O(2)	0.9900	2.4700	2.844(9)	102.00
C(25)-H(25C)...O(3)	0.9800	2.4000	3.018(10)	120.00
C(26)-H(26A)...O(3)	0.9800	2.4400	2.981(10)	114.00

Symmetry transformations used to generate equivalent atoms: