Supporting Information

Rh-catalyzed Intermolecular Reactions of Alkynes with α-Diazoesters that Possess β-hydrogens: Ligand based Control over Divergent Pathways

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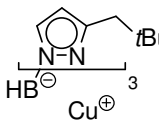
Experimental Procedures

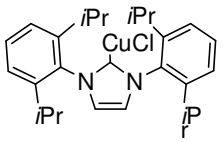
General Considerations

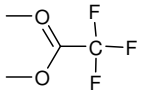
All reactions were carried out in glassware that was flame-dried under vacuum and cooled under nitrogen. CH_2Cl_2 was dried with columns packed with activated neutral alumina. Unless noted otherwise chromatography was performed on silica gel (ICN SiliTech 32-62D, 60Å) that was deactivated by treating with $EtSiCl_3$[1]. For ^{13}C NMR, multiplicities were distinguished using a ATP pulse sequence: typical methylene and quartenary carbons appear 'up' (u); methane and methyl carbons 'down'(dn). Exceptions are methine carbons of cyclopropenes, which have usually the same phase as 'normal' methylenes and quaternary carbons. The abbreviation 'app' stands for apparent (e.g. 'app t' = apparent triplet). NMR yields were determined by using mesitylene (Aldrich) as a standard. Reagents were used directly as purchased from commercial sources. Ethyl 2-diazopropanoate[2], ethyl 2-diazobutanoate[3], and ethyl 2-diazohydrocinnamate[3] were prepared according to literature protocols. The rhodium catalysts $Rh_2(piv)_4$[4] (piv = pivalate), $Rh_2(O_2CCMe_2Ph)_4$[5] and $Rh_2(TPA)_4$[5] (TPA = triphenylacetate) were also prepared by methods in the literature.

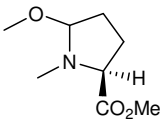
For the cyclopropenation reactions of ethyl 2-diazopropanoate and ethyl 2-diazobutanoate with phenylacetylene a variety of different Rh- and Cu-catalysts was screened. Reaction of ethyl 2-diazopropanoate with 4 equiv of phenylacetylene using Cu-catalyst (I)[6] (2.8 mol%, rt) did not give any cyclopropenation product. For the formation of ethyl 2-phenyl-1-ethyl-cycloprop-2-ene-1-carboxylate (**2a**) ethyl α-diazobutanoate was reacted with 4 equiv of phenylacetylene at -78°C using following Rh- and Cu-catalyst: $Rh_2(TFA)_4$ (0.5 mol%), Rh_2(*S*-DOSP)$_4$ (1.0 mol%), Rh_2(5*S*-MEPY)$_4$ (0.5 mol%), Rh_2(4*S*-MEOX)$_4$ (0.5 mol%), Rh_2(*S*-PTPA)$_4$ (0.5 mol%), and Cu-catalyst (II)[7] (4 mol%, rt). None of these catalysts gave the desired cyclopropene (**2a**).

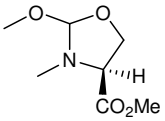
List of abbreviations of the screened Rh- and Cu catalyst:

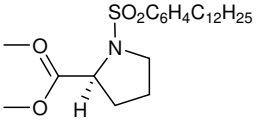
Copper hydrotris(1-neopentylpyrazol-1-yl)borate  (I)

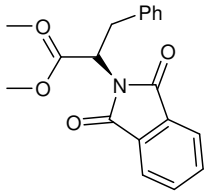
1,3-bis(diisopropylphenyl)imidazol-2-ylidene copper chloride  (II)

$Rh_2(TFA)_4$ Dirhodium(II) tetrakis(trifluoroacetate) 

$Rh_2(5S\text{-MEPY})_4$
Dirhodium(II) tetrakis(methyl 2-oxopyrrolidine-5(*S*)-carboxylate) 

$Rh_2(4S\text{-MEOX})_4$
Dirhodium(II) tetrakis(methyl 2-oxooxazolidin-4(*S*)-carboxylate) 

$Rh_2(S\text{-DOSP})_4$
Dirhodium(II) tetrakis((*S*)-*N*-(dodecylbenzenesulfonyl)prolinate) 

$Rh_2(S\text{-PTPA})_4$
Dirhodium(II) tetrakis(*N*-phthaloyl-L-phenylalanate) 

[1] **Deactivated Silica Gel:** Flash silica gel (100 g, ICN SiliTech 32-62D, 60 Å) was suspended in 200 mL of dry chloroform in a round bottomed flask under a N_2 atmosphere. The flask was chilled by an ice bath. Ethyltrichlorosilane (5.1 g, 31 mmol) was added via syringe. After the addition was completed, the flask was closed and shaken vigorously to mix (HCl is formed). The mixture was allowed to sit at rt with occasional shaking until the next day (suspension becomes yellow). The silica gel was filtered on a Buchner funnel and washed twice with 200

mL portions of chloroform and three times with 200 mL portions of methanol. The silica gel was transferred to a round bottomed flask, and was dried by heating (40°C oil bath) under vacuum.

[2] Bachmann, S., Fielenbach, D., Jørgensen, K. A., *Org. Biomol. Chem.*, **2004**, 2, 3044-3049.

[3] Taber, D. F., Sheth, R. B., Joshi, P. V., *J. Org. Chem.*, **2005**, 70, 2851-2854.

[4] Cotton, F. A., Felthouse, T. R., *Inorg. Chem.*, **1980**, 19, 323-328.

[5] Hashimoto, S. Watanabe, N., Ikegami, S., *Tetrahedron Lett.*, **1992**, 33, 2709-2712.

[6] Diaz-Requejo, M. M., Mairena, M. A., Belderrain, T. R., Nicasio, M. C., Trofimenko, S., Pérez, P.J., *Chem. Commun.*, **2001**, 1804-1805.

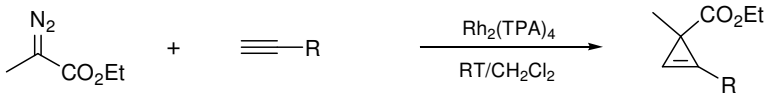
[7] Jurkauskas, V., Sadighi, J. P., Buchwald, S. L., *Org. Lett.*, **2003**, 5, 2417-2420.

Synthetic Procedures

Tetrkis(dimethylphenylcarboxylato)dirhodium(II)·2MeCO$_2$Et

A mixture of $Rh_2(OAc)_4$ (0.10 g, 0.23 mmol) and dimethylphenylacetic acid (0.37 g, 2.26 mmol) was heated at 130°C for 4h. After allowing the mixture to cool to rt, CH_2Cl_2 was added and the dark green solution was washed with saturated aqueous $NaHCO_3$ and water. The solvent was removed and the residue was chromatographed on silica gel (30% ethyl acetate/hexane) to give 104 mg (53%) of the crude compound. Further recrystallization (hexane/ethyl acetate) gave $Rh_2(O_2CCMe_2Ph)_4 \cdot 2CH_3COOEt$ as dark green crystals, mp > 300°C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.21-7.04 (m, 20H), 4.12 (q, J=7.2 Hz, 4H), 2.03 (s, 6H), 1.27 (s, 24H), 1.24 (t, J=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 196.8, 171.6, 145.4, 128.1, 126.3, 125.7, 60.5, 48.4, 26.9, 21.0, 14.2.

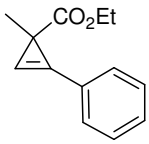
General procedure I for the synthesis of cyclopropenes 1a-c:



In a dry round bottomed flask, $Rh_2(TPA)_4$ (5.3 mg, 0.0039 mmol) and 2.34 mmol of alkyne were dissolved in 5 mL anhydrous CH_2Cl_2 at rt under a nitrogen atmosphere. Ethyl 2-diazopropanoate (100 mg, 0.78 mmol) was dissolved in 3 mL CH_2Cl_2 and added to the reaction mixture via syringe pump at a rate of 1mL/h. After the addition was complete 94 mg (0.78 mmol) of mesitylene was added to the reaction mixture, and a ^{1}H NMR spectrum was taken to estimate the yield. The solvent was subsequently removed and the residue was chromatographed on deactivated silica gel (eluting first with 100% pentane, then with a gradient up to 10% Et_2O in pentane).

Stability note: Compounds **1a-c** are moderately stable compounds. While they can be chromatographed on deactivated silica gel, they decompose over the course of several days at rt. Thus, they should be stored in the freezer under nitrogen atmosphere and used within several days of preparation.

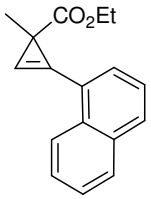
Ethyl 2-phenyl-1-methyl-cycloprop-2-ene-1-carboxylate (1a)



Following the general procedure I, 102 mg (65%) of **1a** was obtained as a colorless oil. The purity was measured to be ≥ 94% by ^{1}H NMR and GC. ^{1}H NMR (Acetone-d_6, 400 MHz, δ): 7.56-7.37 (m, 5H), 7.21 (s, 1H), 4.03 (q, J=7.3 Hz, 2H), 1.48 (s, 3H), 1.12 (t, J=7.3 Hz, 3H);

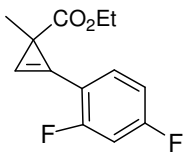
^{13}C NMR (Acetone-d_6, 100 MHz, δ): 176.1(u), 130.2(dn), 130.0(dn), 129.6(dn), 127.1(u), 119.5(u), 103.6(u), 60.5(u), 25.0(u), 20.3(dn), 14.5(dn); IR (neat, cm^{-1}): 2978, 1711, 1487, 1446, 1367, 1251, 1209, 1171, 1108, 1072, 1026, 973, 943, 886, 863, 790, 765, 697; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{13}H_{15}O_2$, 203.1072; found, 203.1068.

Ethyl 2-(α-naphthyl)-1-methyl-cycloprop-2-ene-1-carboxylate (1b)



Following the general procedure I, 121 mg (62%) of **1b** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.45-8.38 (m, 1H), 7.97-7.85 (m, 2H), 7.73-7.49 (m, 4H), 7.33 (s, 1H), 4.16 (q, J=7.2 Hz, 2H), 1.66 (s, 3H), 1.22 (t, J=7.2 Hz, 3H); ^{13}C NMR (Acetone-d_6, 100 MHz, δ): 176.4(u), 134.7(u), 133.0(u), 131.2(dn), 130.0(dn), 129.5(dn), 128.2(dn), 127.5(dn), 126.5(dn), 125.4(dn), 123.5(u). 117.9(u), 106.6(u), 60.8(u), 23.7(u), 20.6(dn), 14.7(dn); IR (neat, cm^{-1}): 2977, 1706, 1588, 1508, 1445, 1392, 1367, 1269, 1249, 1217, 1169, 1108, 1047, 1024, 977, 939, 895, 863, 801, 773, 738, 697, 666, 634; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{17}H_{16}O_2$, 252.1150; found, 252.1159.

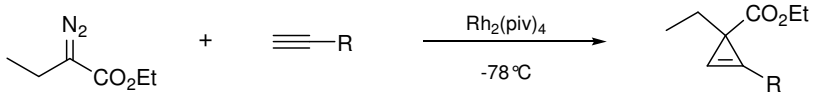
Ethyl 2-(2,4-difluorphenyl)-1-methyl-cycloprop-2-ene-1-carboxylate (1c)



Following the general procedure I, 113 mg (61%) of **1c** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. ^{1}H NMR (Acetone-d_6, 400 MHz, δ):

7.64-7.56 (m, 1H), 7.40 (s, 1H), 7.25-7.10 (m, 2H), 4.05 (q, J=7.2 Hz, 2H), 1.47 (s, 3H), 1.14 (t, J=7.2 Hz, 3H); ^{13}C NMR (Acetone-d_6, 100 MHz, δ): 175.8(u), 164.6(u) (dd, ^{1}J(CF)=252 Hz, ^{3}J(CF)=12 Hz), 162.4(u) (dd, ^{1}J(CF)=255 Hz, ^{3}J(CF)=12 Hz), 133.1(dn) (dd, ^{3}J(CF)=10 Hz, ^{3}J(CF)=4 Hz), 113.4(u), 112.9(dn) (dd, ^{2}J(CF)=22 Hz, ^{4}J(CF)=4 Hz), 112.3(u) (dd, ^{2}J(CF)=19 Hz, ^{4}J(CF)=4 Hz), 106.1(u) (app t, ^{3}J(CF)=4 Hz), 105.3(dn) (dd, ^{2}J(CF)=26 Hz, ^{2}J(CF)=24 Hz), 60.7(u), 24.4(u), 20.6(dn), 14.5(dn); IR (neat, cm^{-1}): 2979, 1713, 1610, 1591, 1497, 1463, 1429, 1368, 1272, 1172, 1142, 1111, 1098, 1027, 969, 851, 818, 786, 732, 683, 626; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{13}H_{12}O_2F_2$, 239.0884; found, 239.0891.

General Procedure II for the synthesis of cyclopropenes 2a-h:

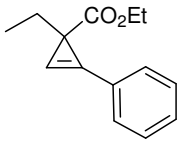


In a dry round bottomed flask $Rh_2(piv)_4$ (2 mg, 0.0035 mmol) and 2.10 mmol of alkyne were dissolved in 5 mL anhydrous CH_2Cl_2 and cooled by a bath of dry ice/acetone (-78°C) under a nitrogen atmosphere. Ethyl 2-diazobutanoate (100 mg, 0.70 mmol) was dissolved in 3 mL CH_2Cl_2 and added to the reaction mixtures via syringe pump at a rate of 1mL/h. After the addition was complete, the cold bath was removed and 84 mg (0.70 mmol) of mesitylene was added to the reaction mixture. A ^{1}H NMR spectrum was taken to estimate the yield. The solvent was removed subsequently and the residue was chromatographed on deactivated silica gel (eluting first with 100% hexane, then with a gradient up to 10% Et_2O in hexane).

Stability note: Compounds **2a**, **2b**, **2c**, **2d**, **2g**, and **2h** are moderately stable compounds. While they can be chromatographed on deactivated silica gel, they decompose over the course of several days at rt. Thus, they should be stored in the freezer under nitrogen atmosphere and used within several days of preparation. Cyclopropenes **2e** and **2f** are unstable and start

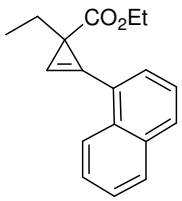
decomposing even on deactivated silica gel. Therefore it was not possible to isolate **2e** with a purity greater than 85% (by ^{1}H NMR). The isolated yield for **2f** (40%) is significantly lower then the NMR yield (72%) due to its instability.

Ethyl 2-phenyl-1-ethyl-cycloprop-2-ene-1-carboxylate (2a)



Following the general procedure II, 89 mg (59%) of **2a** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.52-7.46 (m, 2H), 7.42-7.31 (m, 3H), 6.95 (s, 1H), 4.09 (q, J=7.0 Hz, 2H), 2.15-2.05 (m, 1H), 1.95-1.85 (m, 1H), 1.17 (t, J=7.0 Hz, 3H), 0.78 (t, J=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 176.3(u), 129.5(dn), 129.4(dn), 128.6(dn), 126.6(u), 117.9(u), 100.9(u), 60.3(u), 30.7(u), 24.8(u), 14.3(dn), 11.5(dn); IR (neat, cm^{-1}): 3132, 2964, 2933, 2873, 1711, 1487, 1447, 1367, 1293, 1237, 1202, 1171, 1126, 1090, 1036, 1003, 957, 765, 698; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{14}H_{16}O_2$, 216.1150; found, 216.1152.

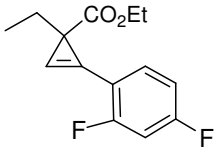
Ethyl 2-(α–naphthyl)-1-ethyl-cycloprop-2-ene-1-carboxylate (2b)



Following the general procedure II, 186 mg (51%) of **2b** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.46-8.35 (m, 1H), 7.92-7.81 (m, 2H), 7.66-7.44 (m, 4H), 7.29 (s, 1H), 4.12 (q, J=7.2 Hz, 2H), 2.33-2.18 (m, 1H), 2.06-1.92 (m, 1H), 1.17 (t, J=7.2 Hz, 3H), 0.82 (t, J=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 176.3(u), 133.5(u), 132.2(u), 130.2(dn), 129.2(dn), 128.5(dn), 127.1(dn), 126.4(dn),

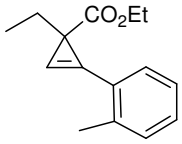
125.4(dn), 124.6(dn), 123.1(u), 116.2(u), 103.2(u), 60.4(u), 29.3(u), 24.7(u), 14.3(dn), 11.3(dn); IR (neat, cm^{-1}): 3127, 2963, 1708, 1589, 1508, 1458, 1369, 1334, 1293, 1237, 1215, 1169, 1125, 1089, 1035, 961, 900, 863, 802, 773, 699, 664, 630; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{18}H_{18}O_3$, 266.1304; found, 266.1304.

Ethyl 2-(2,4-difluorphenyl)-1-ethyl-cycloprop-2-ene-1-carboxylate (2c)



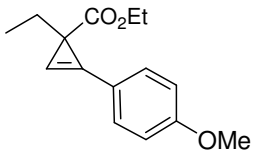
Following the general procedure II, 76 mg (43%) of **2c** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.44-7.36 (m, 1H), 7.08 (s, 1H), 6.96-6.85 (m, 2H), 4.12 (m, 2H), 2.15-2.03 (m, 1H), 1.97-1.85 (m, 1H), 1.20 (t, J=7.2 Hz, 3H), 0.77 (t, J=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 175.9(u), 163.8(u) (dd, ^{1}J(CF)=253 Hz, ^{3}J(CF)= 12 Hz), 161.7(u) (dd, ^{1}J(CF)=255 Hz, ^{3}J(CF)=12 Hz), 131.8 (dn) (dd ^{3}J(CF)=10 Hz, ^{3}J(CF)=4 Hz), 111.8 (dn) (dd, ^{2}J(CF)=22 Hz, ^{4}J(CF)=4 Hz), 111.7 (u) (d, ^{4}J(CF)=4 Hz), 111.6 (u), 104.5 (u), (dd, ^{2}J(CF)= 26 Hz, ^{2}J(CF)=24 Hz), 103.3 (u) (app t, ^{3}J(CF)=4 Hz), 60.5(u), 29.9(u), 24.8(u), 14.3(dn), 11.3(dn); IR (neat, cm^{-1}): 3137, 2966, 2934, 2875, 1778, 1713, 1609, 1592, 1497, 1463, 1429, 1368, 1296, 1271, 1235, 1141, 1127, 1097, 1037, 968, 851, 818, 775, 732, 685, 624; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{14}H_{14}O_2F_2$, 252.0962; found, 252.0962.

Ethyl 2-*o*-toluene-1-ethyl-cycloprop-2-ene-1-carboxylate (2d)



Following the general procedure II, 103 mg (64%) of **2d** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.34-7.18 (m, 4H), 7.13 (s, 1H), 4.12 (q, J=7.2 Hz, 2H), 2.46 (s, 3H), 2.22-2.10 (m, 1H), 1.94-1.81 (m, 1H), 1.20 (t, J=7.2 Hz, 3H), 0.78 (t, J=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 176.5(u), 139.6(u), 130.3(dn), 130.1(dn), 129.4(dn), 126.0(dn), 125.4(u), 116.9(u), 102.8(u), 60.4(u), 29.8(u), 24.9(u), 20.0(dn), 14.4(dn), 11.4(dn); IR (neat, cm^{-1}): 3131, 2962, 2931, 2873, 1710, 1460, 1367, 1293, 1236, 1209, 1125, 1089, 1038, 1007, 962, 899, 865; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{15}H_{18}O_2$, 230.1309; found, 230.1309.

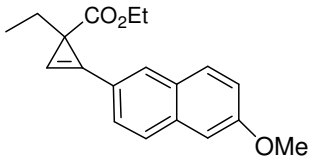
Ethyl 2-*p*-methoxy-phenyl-1-ethyl-cycloprop-2-ene-1-carboxylate (2e)



Following the general procedure II, 84 mg (49%) of **2e** was obtained as a colorless oil. The purity was measured to be 85% by ^{1}H NMR. Due to the instability of this compound it was not possible to obtain this cyclopropene in better purity or yield, although the yield as estimated by crude ^{1}H NMR was 67%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.49-7.43 (m, 2H), 6.97-6.89 (m, 2H), 6.81 (s, 1H), 4.11 (q, J=7.2 Hz, 2H), 3.83 (s, 3H), 2.16-2.02 (m, 1H), 1.97-1.84 (m, 1H), 1.19 (t, J=7.2 Hz, 3H), 0.79 (t, J=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 176.6(u), 160.5(u), 131.1(dn), 119.2(u), 117.2(u), 114.2(dn), 97.9(u), 60.3(u), 55.3(dn), 30.5(u), 24.9(u), 14.3(dn), 11.5(dn); IR (neat, cm^{-1}): 3134, 2963, 2934, 2840, 1769, 1709,

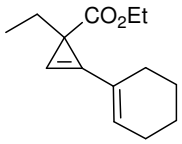
1604, 1576, 1505, 1462, 1417, 1367, 1298, 1247, 1166, 1225, 1091, 1030, 954, 898, 834, 773, 730, 681, 614; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{15}H_{19}O_3$, 247.1334; found, 247.1333.

Ethyl 2-(6-methoxy-2-naphthyl)-1-ethyl-cycloprop-2-ene-1-carboxylate (2f)



Following the general procedure II, 82 mg (40%) of **2f** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.86-7.80 (m, 1H), 7.77-7.69 (m, 2H), 7.62-7.54 (m, 1H), 7.19-7.07 (m, 2H), 6.96 (s, 1H), 4.11 (q, J=6.8 Hz, 2H), 3.91 (s, 3H), 2.23-2.09 (m, 1H), 2.04-1.91 (m, 1H), 1.17 (t, J=6.8 Hz, 3H), 0.81 (t, J= 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 176.5(u), 158.6(u), 135.1(u), 129.9(dn), 129.2(dn), 128.6(u), 127.3(dn), 127.1(dn), 121.9(u), 119.4(dn), 118.1(u), 105.9(dn), 100.1(u), 60.4(u), 55.3(dn), 30.9(u), 24.9(u), 14.3(dn), 11.5(dn); IR (neat, cm^{-1}): 3132, 2961, 1770, 1708, 1626, 1602, 1502, 1479, 1462, 1412, 1389, 1335, 1293, 1264, 1228, 1194, 1167, 1124, 1090, 1030, 959, 853, 809, 776, 701, 664; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{19}H_{20}O_3$, 296.1420; found, 296.1420.

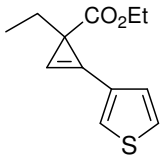
Ethyl 2-(1-cyclohexene)-1-ethyl-cycloprop-2-ene-1-carboxylate (2g)



General procedure II was followed on one-half scale. 51 mg (66%) of **2g** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 6.55 (s, 1H), 5.99 (s, 1H), 4.15-4.02 (m, 2H), 2.37-2.10 (m, 4H), 2.06-1.93 (m, 1H), 1.78-1.53 (m, 5H), 1.19 (t, J=7.2 Hz, 3H), 0.73 (t, J= 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100

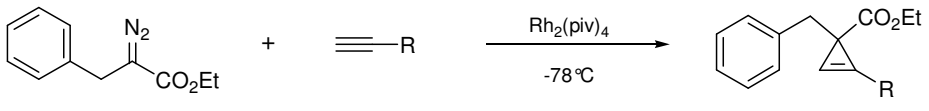
MHz, δ): 176.6(u), 134.5(dn), 125.4(u), 119.2(u), 98.1(u), 60.2(u), 30.5(u), 26.8(u), 25.6(u), 24.8(u), 22.2(u), 21.8(u), 14.4(dn), 11.4(dn); IR (neat, cm^{-1}): 2931, 2864, 2359, 1769, 1711, 1449, 1366, 1292, 1253, 1232, 1172, 1124, 1090, 1038, 958, 919, 847, 799, 774, 682; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{14}H_{20}O_2$, 220.1463; found, 220.1462.

Ethyl 2-(3-thiophene)-1-ethyl-cycloprop-2-ene-1-carboxylate (2h)



Following the general procedure II, 101 mg (65%) of **2h** was obtained as a colorless oil. The purity was measured to be 93 % by ^1H NMR and GC. ^1H NMR ($CDCl_3$, 400 MHz, δ): 7.31-7.34 (m, 1H), 7.29-7.25 (m, 1H), 7.21-7.16 (m, 1H), 6.72 (s, 1H), 4.04 (q, J=7.2 Hz, 2H), 2.03-2.91 (m, 1H), 2.91-1.79 (m, 1H), 1.12 (t, J=7.2 Hz, 3H), 0.81 (t, J= 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 176.2(u), 128.0(u), 128.0(dn), 127.2(dn), 126.4(dn), 112.7(u), 98.5(u), 60.4(u), 30.7(u), 25.1(u), 14.3(dn), 11.5(dn); IR (neat, cm^{-1}): 3109, 2964, 2931, 2873, 1776, 1709, 1461, 1367, 1292, 1239, 1222, 1125, 1089, 1036, 1005, 954, 854, 786, 695; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{12}H_{14}O_2S$, 222.0715; found, 222.0722.

General Procedure III for the synthesis 2-subtituted of cyclopropenes (3a-e)

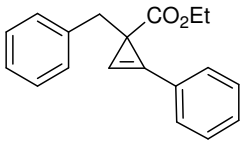


In a dry round bottomed flask $Rh_2(piv)_4$ (1.2 mg, 0.0020 mmol) and 1.50 mmol of alkyne were dissolved in 5 mL anhydrous CH_2Cl_2 and cooled by a bath of dry ice/acetone (-78°C) under a nitrogen atmosphere. Ethyl 2-diazohydrocinnamate (100 mg, 0.49 mmol) was

dissolved in 3 mL CH_2Cl_2 and added to the reaction mixtures via syringe pump at a rate of 1mL/h. After the addition was complete, the cold bath was removed and 60 mg (0.49 mmol) of mesitylene was added to the reaction mixture. A ^{1}H NMR spectrum was taken to estimate the yield. The solvent was removed and the residue was chromatographed on deactivated silica gel (eluting first with 100% hexane, then with a gradient up to 10% Et_2O in hexane).

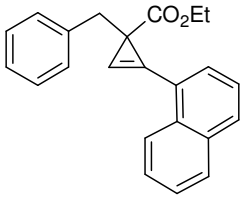
Stability note: Compounds **3a-e** are moderately stable compounds. While they can be chromatographed on deactivated silica gel, they decompose over the course of several days at rt. Thus, they should be stored in the freezer under nitrogen atmosphere and used within several days of preparation.

Ethyl 2-phenyl-1-benzyl-cycloprop-2-ene-1-carboxylate (3a)



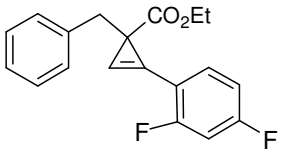
General procedure III was followed on 4x scale. Thus, 400 mg (1.96 mmol) of ethyl 2-diazohydrocinnamate gave 410 mg (75%) of **3a** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and HPLC. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.50-7.30 (m, 5H), 7.3-7.1 (m, 5H), 6.87 (s, 1H), 4.15 (q, J=7.2 Hz, 2H), 3.65 (d, J=14 Hz, 1H), 3.08 (d, J=14 Hz, 1H), 1.21 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 175.9(u), 139.9(u), 129.7(dn), 129.6(dn), 129.5(dn), 128.7(dn), 128.1(dn), 126.1(u), 125.9(dn), 117.5(u), 100.8(u), 60.7(u), 38.9(u), 31.0(u), 14.4(dn); IR (neat, cm^{-1}): 1712, 1494, 1447, 1367, 1263, 1197, 1145, 1083, 1053, 1027, 965, 912, 766, 698, 629; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{19}H_{18}O_2$, 278.1297; found, 278.1297.

Ethyl 2-(α–naphthyl)-1-benzyl-cycloprop-2-ene-1-carboxylate (3b)



Following the general procedure III, 116 mg (72%) of **3b** was obtained as a colorless oil. The purity was measured to be 95% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.34-8.24 (m, 1H), 7.92-7.84 (m, 2H), 7.62-7.43 (m, 4H), 7.23-7.10 (m, 6H), 4.11 (q, J=7.2 Hz, 2H), 3.77 (d, J= 14 Hz, 1H), 3.04 (d, J=14 Hz, 1H), 1.17 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 175.9(u), 139.9(u), 133.6(u), 132.3(u), 130.5(dn), 129.5(dn), 129.5(dn), 128.5(dn), 128.2(dn), 127.2(dn), 126.5(dn), 125.9(dn), 125.4 (dn), 124.7(dn), 122.6(u), 115.9(u), 103.1(u), 61.0(u), 38.9(u), 29.6(u), 14.3(dn); IR (neat, cm^{-1}): 2980, 1771, 1707, 1603, 1588, 1508, 1495, 1453, 1392, 1367, 1259, 1217, 1144, 1084, 1046, 926, 863, 801, 774, 751, 699, 635; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{23}H_{20}O_2$, 328.1463; found, 328.1474.

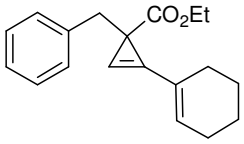
Ethyl 2-(2,4-difluorphenyl)-1-benzyl-cycloprop-2-ene-1-carboxylate (3c)



Following the general procedure III, 79 mg (51%) of **3c** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.26-7.05 (m, 6H), 6.96 (s, 1H), 6.89-6.81 (m, 2H), 4.13 (m, 2H), 3.46 (d, J=14 Hz, 1H), 3.12 (d, J= 14 Hz, 1H), 1.19 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 175.9(u), 163.8(u) (dd, ^{1}J(CF)=252 Hz, ^{3}J(CF)= 12 Hz), 161.7(u) (dd, ^{1}J(CF)=255 Hz, ^{3}J(CF)=12Hz), 139.5(u), 131.9(dn) (dd, ^{3}J(CF)=11 Hz, ^{3}J(CF)=4 Hz), 129.5(dn), 128.1(dn), 125.9(dn), 111.6(dn) (dd, ^{2}J(CF)=22 Hz, ^{4}J(CF)=4 Hz), 111.2(u) (dd, ^{2}J(CF)=14 Hz, ^{4}J(CF)=4 Hz), 111.1(u), 104.5(dn)

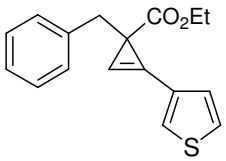
(dd, ^{2}J(CF=25 Hz, ^{2}J(CF)=24 Hz), 103.5(u) (app t, ^{3}J(CF)=4 Hz), 60.8(u), 39.0(u), 30.2(u), 14.2(dn); IR (neat, cm^{-1}): 1713, 1609, 1591, 1497, 1429, 1268, 1189, 1142, 1098, 1084, 1053, 969, 852, 818, 781, 754, 732, 701, 626; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{19}H_{17}O_2F_2$, 315.1197; found, 315.1193.

Ethyl 2-(1-cyclohexene)-1-benzyl-cycloprop-2-ene-1-carboxylate (3d)



Following the general procedure III, 66 mg (48%) of **3d** was obtained as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR. ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.29-7.22 (m, 2H), 7.21-7.13 (m, 2H), 7.10-7.03 (m, 1H), 6.23 (s, 1H), 6.02-5.95 (m, 1H), 4.02 (q, J=7.2 Hz, 2H), 3.80 (d, J=14 Hz, 1H), 3.05 (d, J=14 Hz, 1H), 2.16-2.03 (m, 1H), 2.03-1.92 (m, 1H), 1.89-1.80 (m, 2H), 1.42-1.24 (m, 4H), 0.95 (t, J=7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 175.4(u), 141.0(u), 135.0(dn), 129.9(dn), 128.7(dn), 126.1(dn), 125.6(u), 119.1(u), 99.0(u), 60.3(u), 39.5(u), 31.1(u), 27.0(u), 25.7(u), 22.4(u), 22.0(u), 14.4(dn); IR (neat, cm^{-1}): 2928, 2860, 1768, 1710, 1495, 1452, 1366, 1260, 1226, 1140, 1082, 1053, 971, 918, 846, 801, 750, 699; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{19}H_{22}O_2$, 282.1619; found, 282.1624.

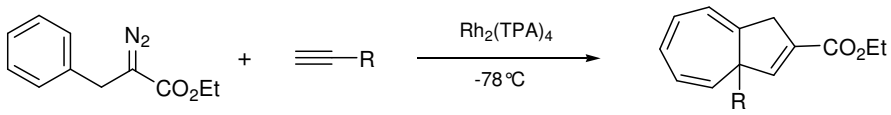
Ethyl 2-(3-thiophene)-1-benzyl-cycloprop-2-ene-1-carboxylate (3e)



Following the general procedure III, 63 mg (45%) of **3e** was obtained as a colorless oil. The purity was measured to be ~ 92% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.33-7.28 (m, 2H), 7.22-7.07 (m, 6H), 6.70 (s, 1H), 4.11 (q, J=7.2 Hz, 2H), 3.42(d, J=14 Hz, 1H), 3.94 (d,

J=14 Hz, 1H), 1.17 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 175.7(u), 140.0(u), 129.5(dn), 128.1(dn), 128.1(dn), 127.6(dn), 127.5(u), 126.3(dn), 125.9(dn), 112.2(u), 98.5(u), 60.7(u), 39.1(u), 31.0(u), 14.3(dn); IR (neat, cm^{-1}): 2975, 1711, 1495, 1453, 1368, 1263, 1219, 1145, 1084, 1049, 978, 863, 788, 749, 698; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{17}H_{17}O_2S$, 285.0949; found, 285.0948.

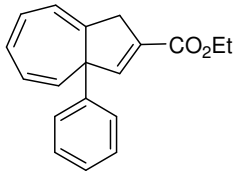
General Procedure IV for the synthesis of bicyclic compounds 4a and 4b



In a dry round bottomed flask under a nitrogen atmosphere, $Rh_2(TPA)_4$ (3.3 mg, 0.0024 mmol) and 1.50 mmol of alkyne were dissolved in 5 mL anhydrous CH_2Cl_2 and cooled by a bath of dry ice/acetone (-78°C). Ethyl 2-diazohydrocinnamate (100 mg, 0.49 mmol) was dissolved in 3 mL CH_2Cl_2 and added to the reaction mixture via syringe pump at a rate of 1mL/h. After the addition was complete, the cold bath was removed and 60 mg (0.49 mmol) mesitylene was added to the reaction mixture. A ^{1}H NMR spectrum was taken to estimate the yield. The solvent was removed and the residue was chromatographed on deactivated silica gel (eluting first with 100% hexane, then with a gradient up to 10% Et_2O in hexane).

Stability note: Crystals of **4a** were stored under nitrogen in the freezer, where, even after several months, no decomposition proceeds. However, at rt in solution **4a** decomposes within several days. Compound **4b** decomposes, even when stored in the freezer under nitrogen atmosphere within a few days.

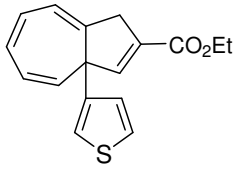
Ethyl 3-phenyl-1,3-dihydroazulene-2-carboxylate (4a)



Following the general procedure IV, 67 mg (49 %) of **4a** was obtained as colorless crystals, mp. 89°C. The purity was measured to be ≥95% by ^{1}H NMR. ^{1}H NMR (Acetone-d_6, 400 MHz, δ): 7.17-7.03 (m, 5H), 6.83-6.79 (m, 1H), 6.52-6.47 (m, 1H), 6.34-6.26 (m, 2H), 6.25-6.18 (m, 1H), 5.70-5.64 (m, 1H), 4.16 (q, J=7.1 Hz, 2H), 3.89-3.58 (m, 2H)[a], 1.24 (t, J=7.1 Hz, 3H); ^{13}C NMR (Acetone-d_6, 100 MHz, δ): 165.0(u), 149.8(dn), 143.0(u), 142.9(u), 133.4(u), 130.2(dn), 129.4(dn), 128.4(dn), 127.7(dn), 127.3(dn), 126.6(dn), 126.3(dn), 121.4(dn), 61.9(u), 60.9(u), 40.0(u), 14.6(dn); IR (neat, cm^{-1}): 3019, 1704, 1647, 1491, 1464, 1146, 1385, 1369, 1310, 1265, 1233, 1217, 1183, 1151, 1110, 1077, 1015, 937, 898, 881, 859, 840, 769, 745, 723, 694, 622; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{19}H_{18}O_2$, 278.1307; found,278.1303.

[a] AB-Spinsystem: δ_a=3.84 ppm, δ_b=3.64 ppm, J(AB)=24 Hz

Ethyl 3-(thiophen-3-yl)-1,3-dihydroazulene-2-carboxylate (4b)

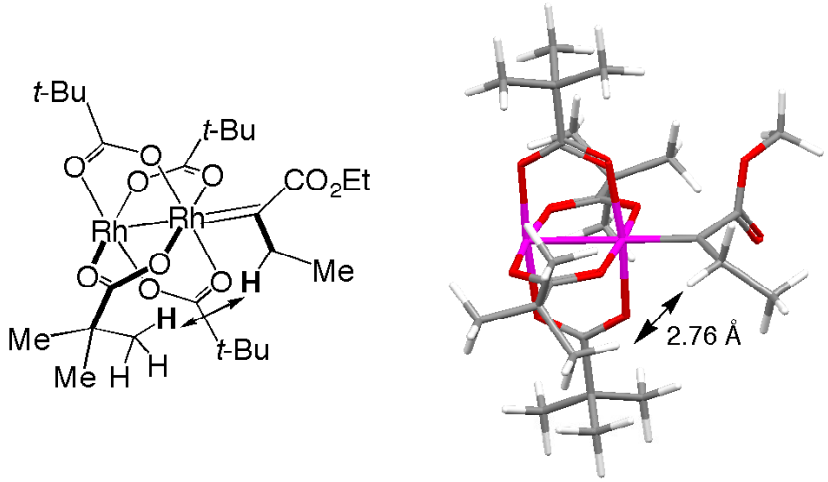


Following the general procedure IV, 92 mg (66 %) of **4b** was obtained as a colorless oil. The purity was measured to be ≥95% by ^{1}H NMR. ^{1}H NMR (Acetone-d_6, 400 MHz, δ): 7.26-6.92 (m, 1H), 6.92-6.79 (m, 3H), 6.46-6.39 (m, 1H), 6.36-6.22 (m, 3H), 5.67-5.58 (m, 1H), 4.19 (q, J=7.1 Hz, 2H), 3.87-3.55 (m, 2H)[a], 1.27 (t, J=7.1 Hz, 3H); ^{13}C NMR(Acetone-d_6, 100 MHz,

δ): 165.0(u), 148.6(dn), 143.2(u), 142.5(u), 133.8(u), 129.9(dn), 129.3(dn), 127.8(dn), 126.5(dn), 126.3(dn), 125.6(dn), 121.8(dn), 121.1(dn), 61.0(u), 59.0(u), 29.4(u), 14.6(dn); IR (neat, cm^{-1}): 2977, 1712, 1650, 1371, 1327, 1311, 1257, 1234, 1144, 1092, 1067, 1016, 899, 854, 839, 783, 743, 724, 695, 652; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{17}H_{17}O_2S$, 285.0949; found, 285.0942.

[a] AB-Spinsystem: δ_a=3.82 ppm, δ_b= 3.61 ppm, J(AB)= 20 Hz

DFT calculated structure of 5.



The DFT optimized structure shows that the closest distance from the β-hydrogen to the hydrogens of the t-Bu groups is 2.76 Å.

Quantum chemistry calculations were carried out using the Gaussian03 program system utilizing gradient geometry optimization. Calculations were performed using the B3LYP hybrid density functional in combination with the Los Alamos effective core potential coupled with a double-ς LANL2DZ basis set for Rh, an all-electron 6-31G(d) basis set for the rest of the atoms. The GEN (allows different user-specified basis sets for different atoms to be

used) and PSEUDO=READ (requests that a model potential, LANL2DZ, be substituted for the core electrons) keywords have been used to perform these calculations in utilizing the Gaussian program.

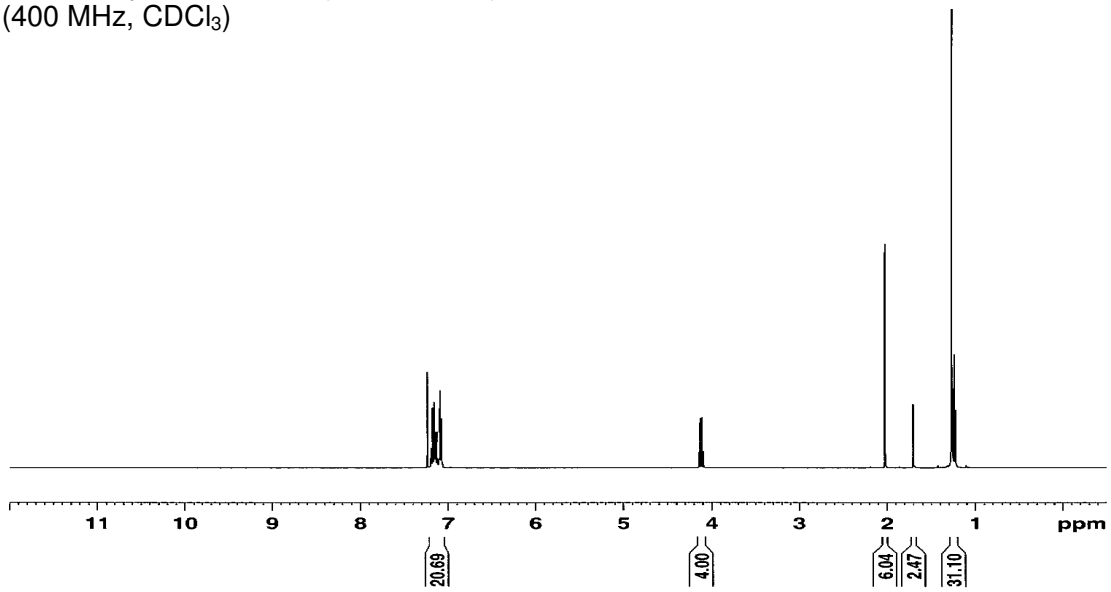
E: -1950.606934 a.u.

XYZ coordinates for **5**:

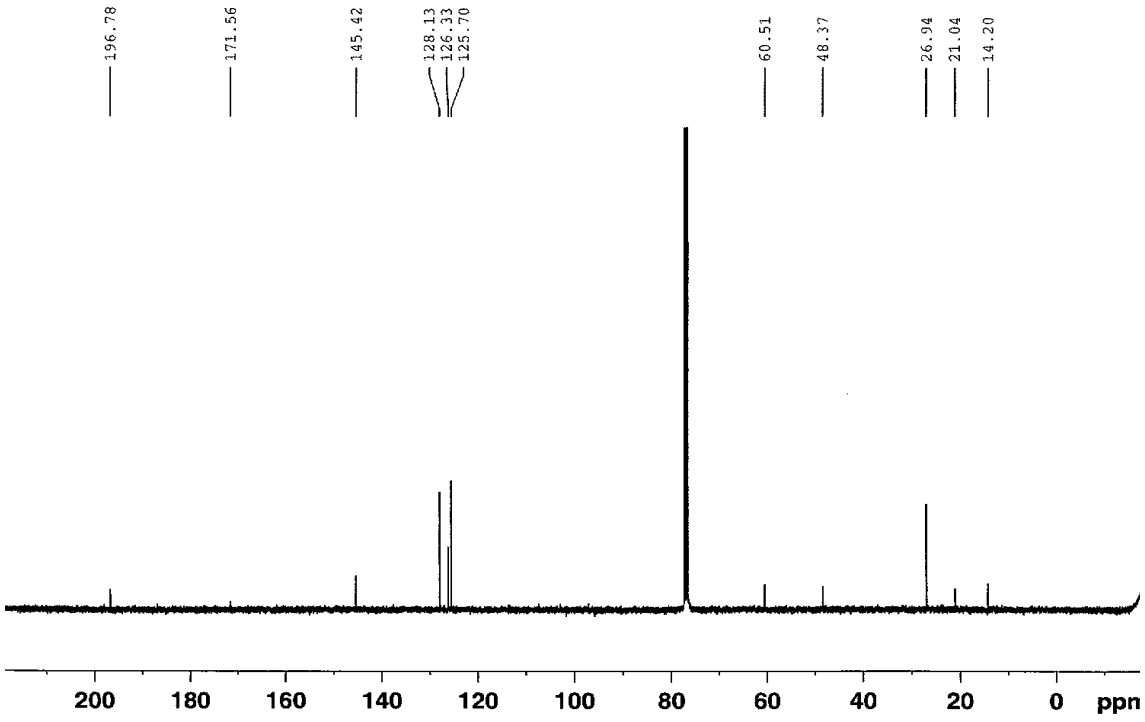
C	-0.906016	-4.719369	0.342296
O	0.742025	1.934048	0.441805
O	1.882950	-0.738851	0.066585
C	0.444799	-0.125951	2.534040
O	-1.263331	-1.784094	-1.686390
O	-2.373012	0.896409	-1.239160
O	0.257982	2.066449	-1.765883
O	-0.759991	-1.936514	0.515329
O	-1.897285	0.731764	0.970344
Rh	-0.515998	0.145350	-1.788287
Rh	0.018426	-0.011984	0.609993
C	-4.718573	0.669745	1.379546
C	2.150830	-0.901700	-1.173535
C	3.512918	-1.532432	-1.520085
C	4.149223	-0.743690	-2.682478
C	4.451336	-1.534333	-0.302239
C	-2.661736	1.024568	-0.015992
C	-4.041997	1.602235	0.352462
C	-4.925145	1.732969	-0.899221
O	1.384249	-0.623670	-2.140786
C	1.321135	3.952891	-0.733496
C	2.722390	3.809996	-1.374330
C	1.448459	4.552544	0.676675
C	0.435242	4.853721	-1.617206
C	-1.966875	-4.407386	-1.928337
C	-1.818481	-3.819341	-0.515184
C	-3.208677	-3.696984	0.152962
C	-1.225280	-2.399682	-0.583039
C	0.711431	2.538984	-0.683619
C	-3.811938	2.994188	0.984199
C	3.230060	-2.985771	-1.968891
C	1.820252	-0.488533	2.942927
O	2.116682	-1.655030	3.121086
O	2.640911	0.559647	3.076649
C	-0.539414	0.101237	3.621912
C	4.007405	0.240653	3.415467
C	-0.536799	-0.944554	4.760335
H	-0.786419	-4.318912	1.351950
H	0.090847	-4.811470	-0.104665
H	-1.337452	-5.724936	0.411995

H	-5.699632	1.072554	1.657476
H	-4.115213	0.572135	2.286132
H	-4.872709	-0.332807	0.963296
H	5.099653	-1.208541	-2.970104
H	4.355800	0.293217	-2.391509
H	3.489508	-0.726261	-3.553399
H	5.402484	-2.009048	-0.571111
H	4.014448	-2.080071	0.538647
H	4.664969	-0.512523	0.031298
H	-4.468454	2.391314	-1.643306
H	-5.900135	2.149070	-0.618611
H	-5.090499	0.760574	-1.373716
H	2.652566	3.376575	-2.376928
H	3.371327	3.170602	-0.764382
H	3.196577	4.795305	-1.454768
H	0.469717	4.642198	1.160270
H	1.888895	5.554706	0.611611
H	2.083177	3.935551	1.318396
H	-0.566692	4.967562	-1.186572
H	0.326590	4.437443	-2.621501
H	0.883068	5.851407	-1.696050
H	-2.616504	-3.788925	-2.553191
H	-2.399634	-5.412863	-1.863526
H	-0.996756	-4.484584	-2.430244
H	-3.875080	-3.057638	-0.437842
H	-3.125966	-3.274763	1.159552
H	-3.671919	-4.687601	0.230695
H	-3.326726	3.674290	0.274166
H	-3.182481	2.922190	1.876294
H	-4.773217	3.436785	1.270866
H	4.169269	-3.478905	-2.246354
H	2.559590	-3.004044	-2.833435
H	2.769902	-3.565459	-1.160041
H	-1.538755	0.224043	3.198752
H	-0.247878	1.082839	4.045124
H	4.507826	1.202593	3.521777
H	4.463046	-0.346230	2.615247
H	4.048414	-0.322507	4.351110
H	-1.289368	-0.664179	5.503921
H	0.434663	-1.012092	5.257236
H	-0.786852	-1.935337	4.371024

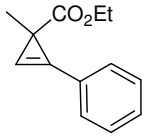
^{1}H NMR spectrum of $Rh_2(O_2CCMe_2Ph)_4*2CH_3COOEt$
(400 MHz, $CDCl_3$)



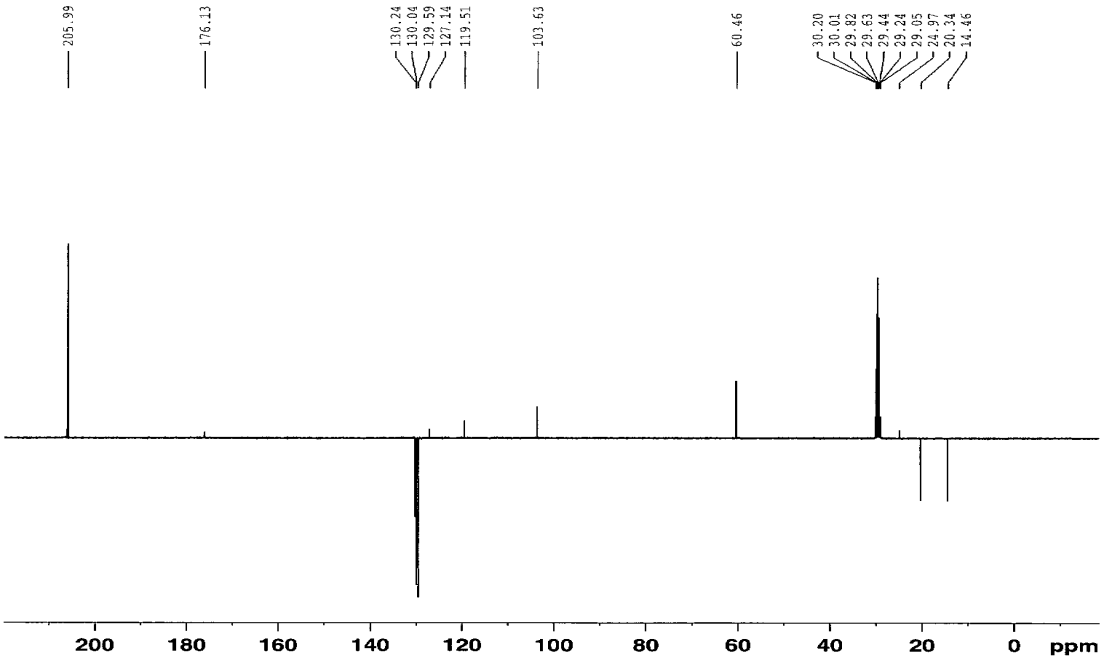
^{13}C NMR spectrum of $Rh_2(O_2CCMe_2Ph)_4*2CH_3COOEt$
(100 MHz, $CDCl_3$)



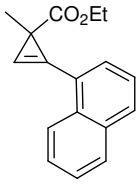
^{1}H NMR spectrum of **1a**
(400 MHz, Acetone-d_6)



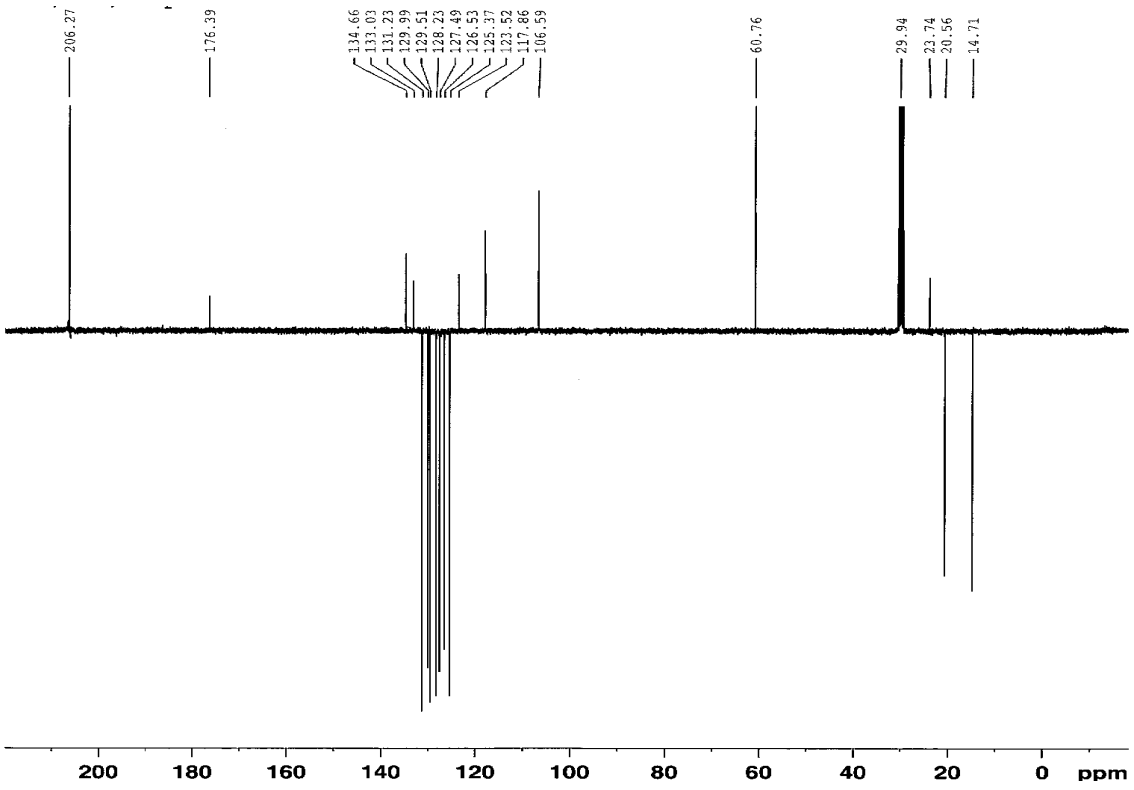
^{13}C NMR spectrum of **1a**
(100 MHz, Acetone-d_6)



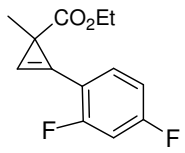
^{1}H NMR spectrum of **1b**
(400 MHz, $CDCl_3$)



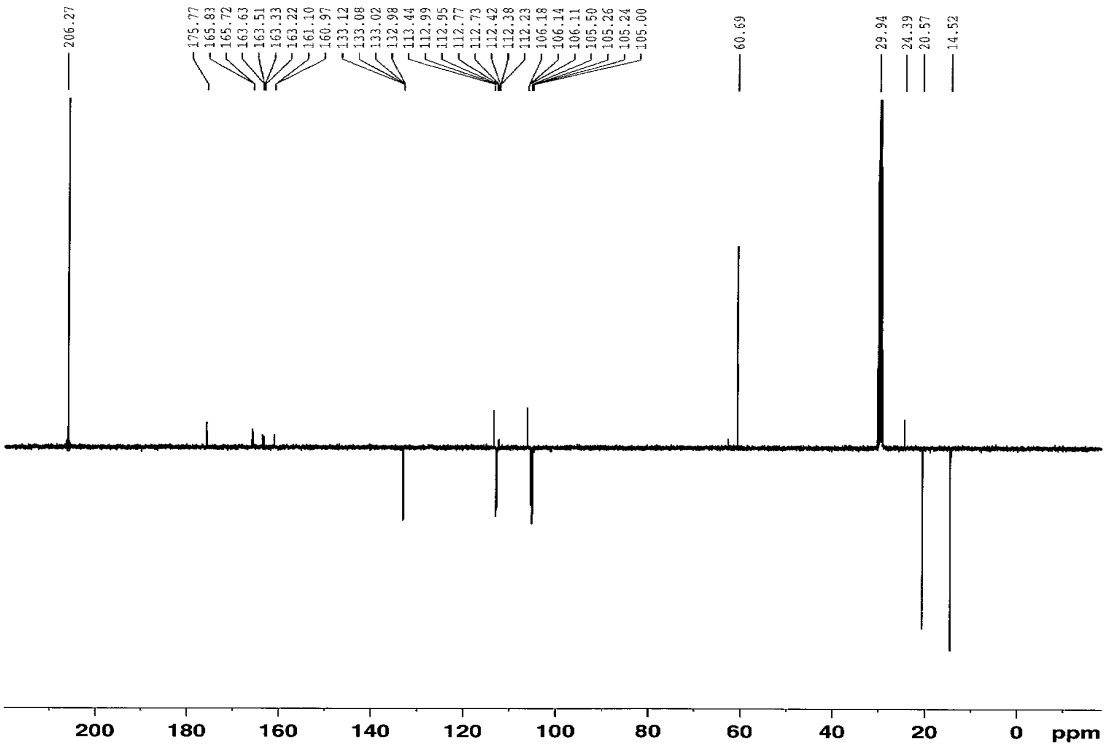
^{13}C NMR spectrum of **1b**
(100 MHz, Acetone-d_6)



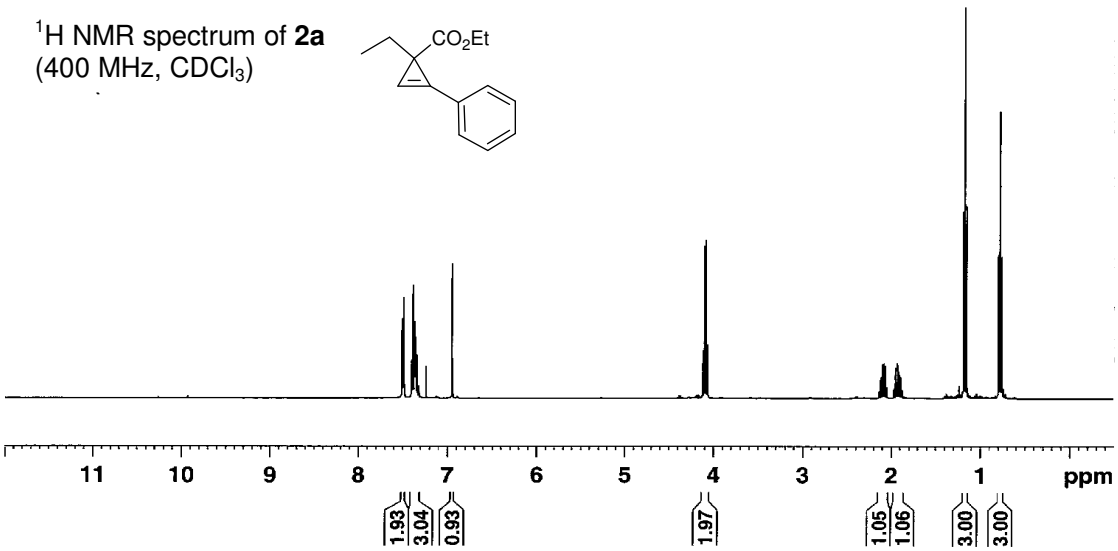
^{1}H NMR spectrum of **1c**
(400 MHz, Acetone-d_6)



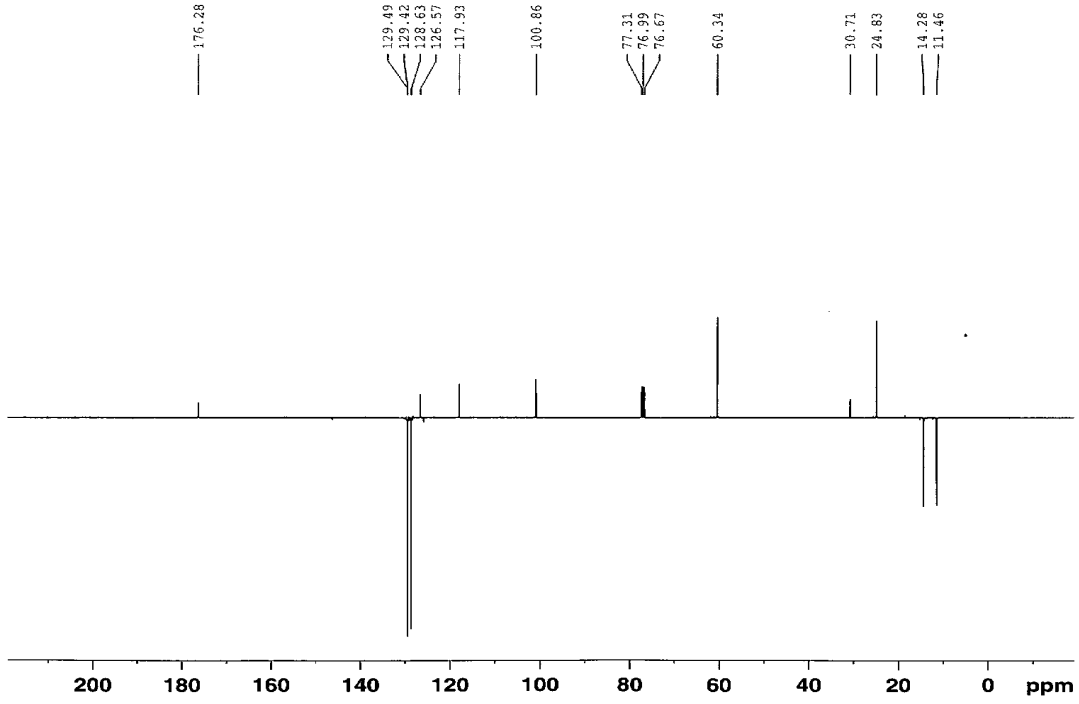
^{13}C NMR spectrum of **1c**
(100 MHz, Acetone-d_6)



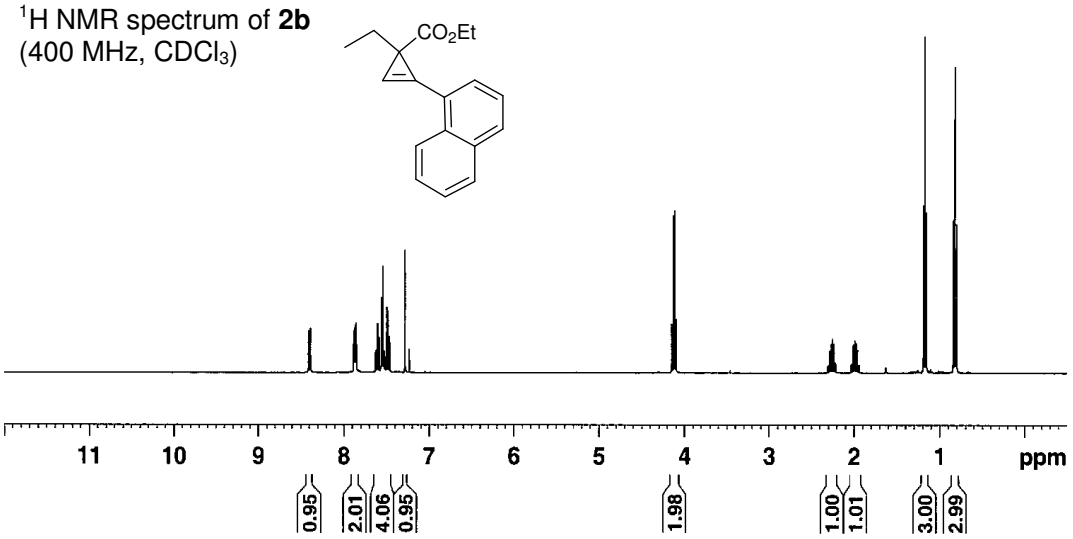
^{1}H NMR spectrum of **2a**
(400 MHz, $CDCl_3$)



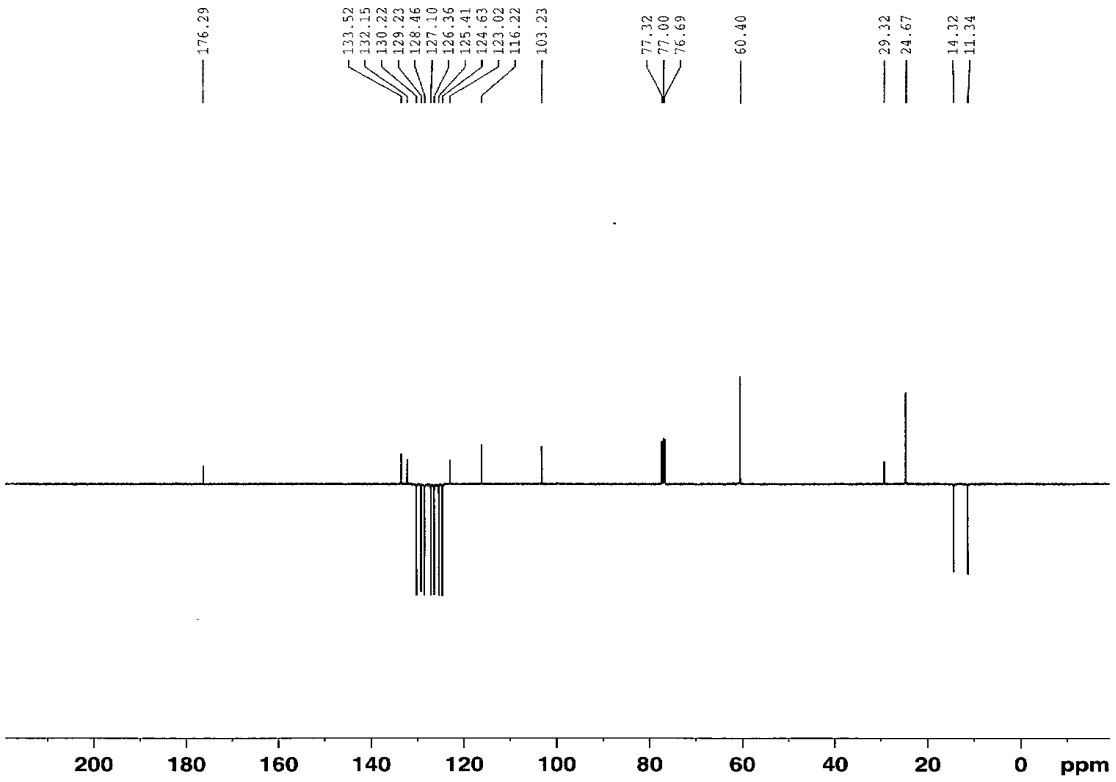
^{13}C NMR spectrum of **2a**
(100 MHz, $CDCl_3$)



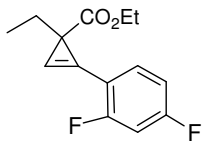
^{1}H NMR spectrum of **2b**
(400 MHz, $CDCl_3$)



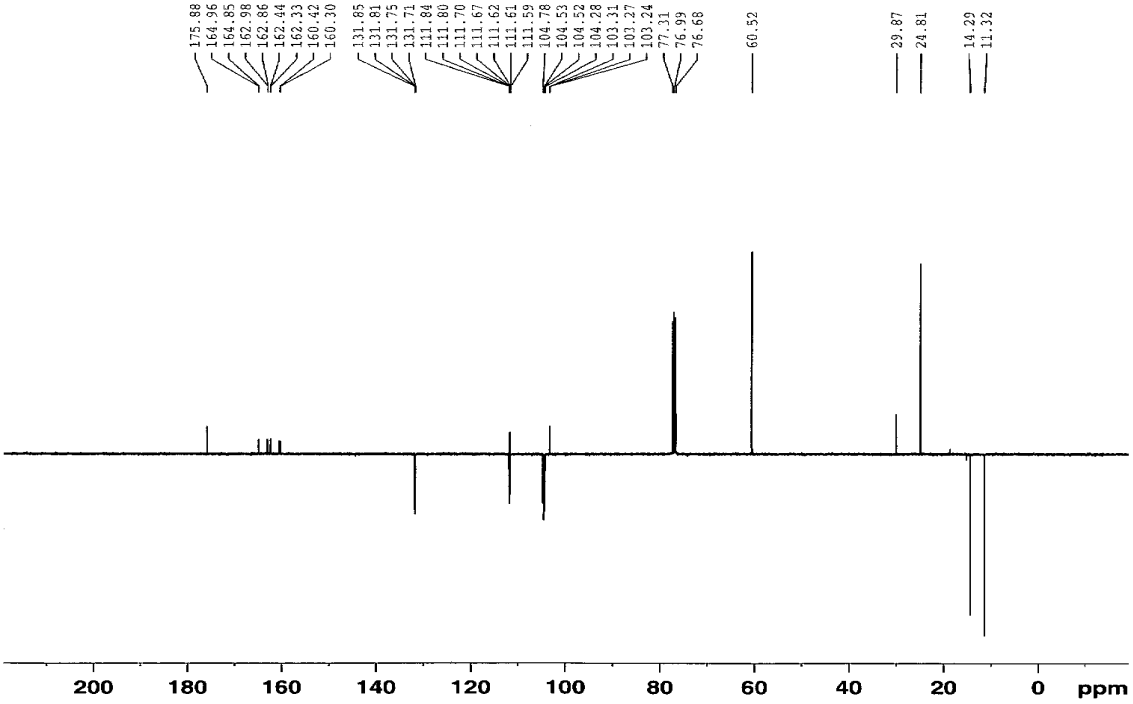
^{1}H NMR spectrum of **2b**
(100 MHz, $CDCl_3$)



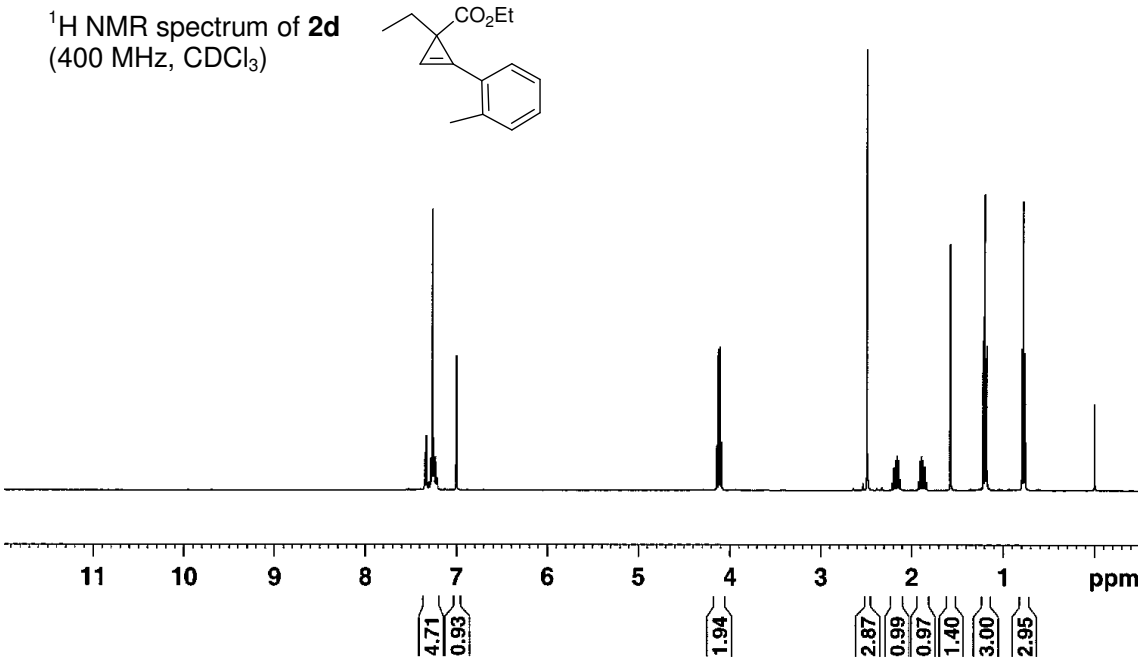
^{1}H NMR spectrum of **2c**
(400 MHz, $CDCl_3$)



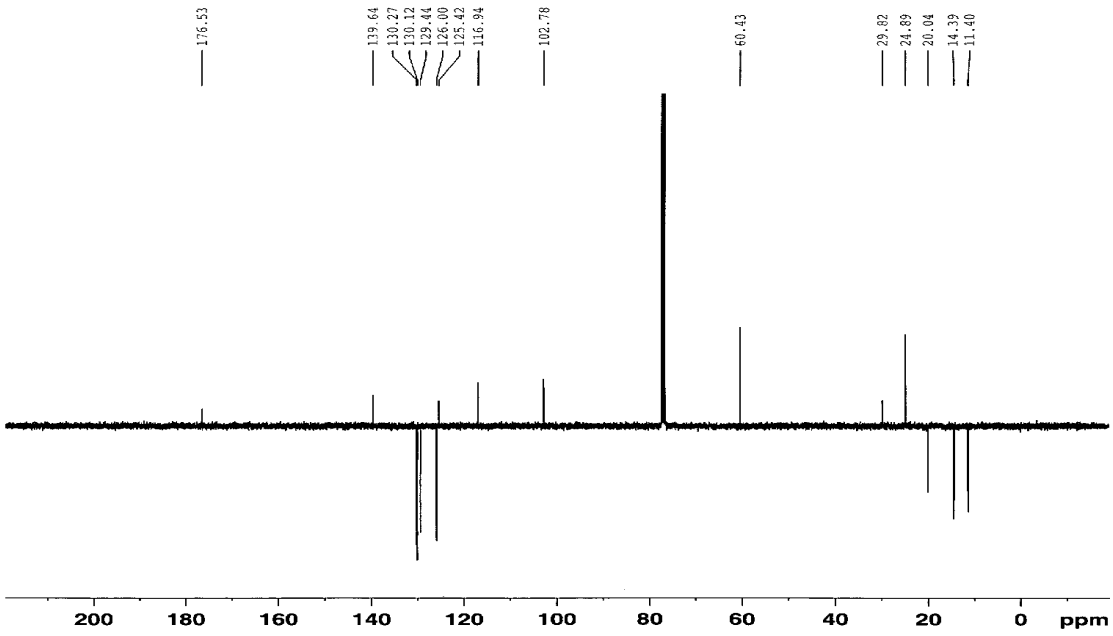
^{13}C NMR spectrum of **2c**
(100 MHz, $CDCl_3$)



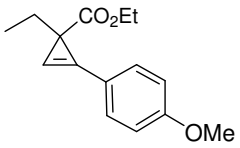
^{1}H NMR spectrum of **2d**
(400 MHz, $CDCl_3$)

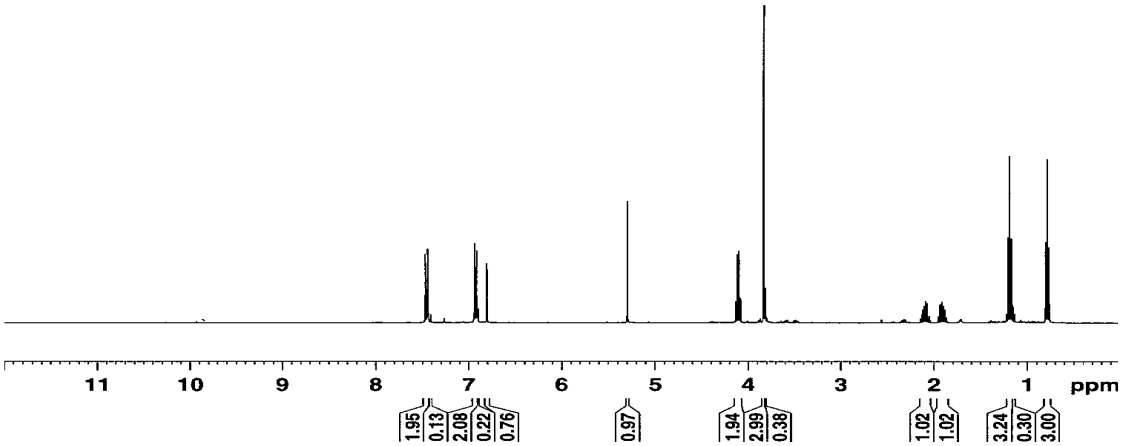


^{13}C NMR spectrum of **2d**
(100 MHz, $CDCl_3$)

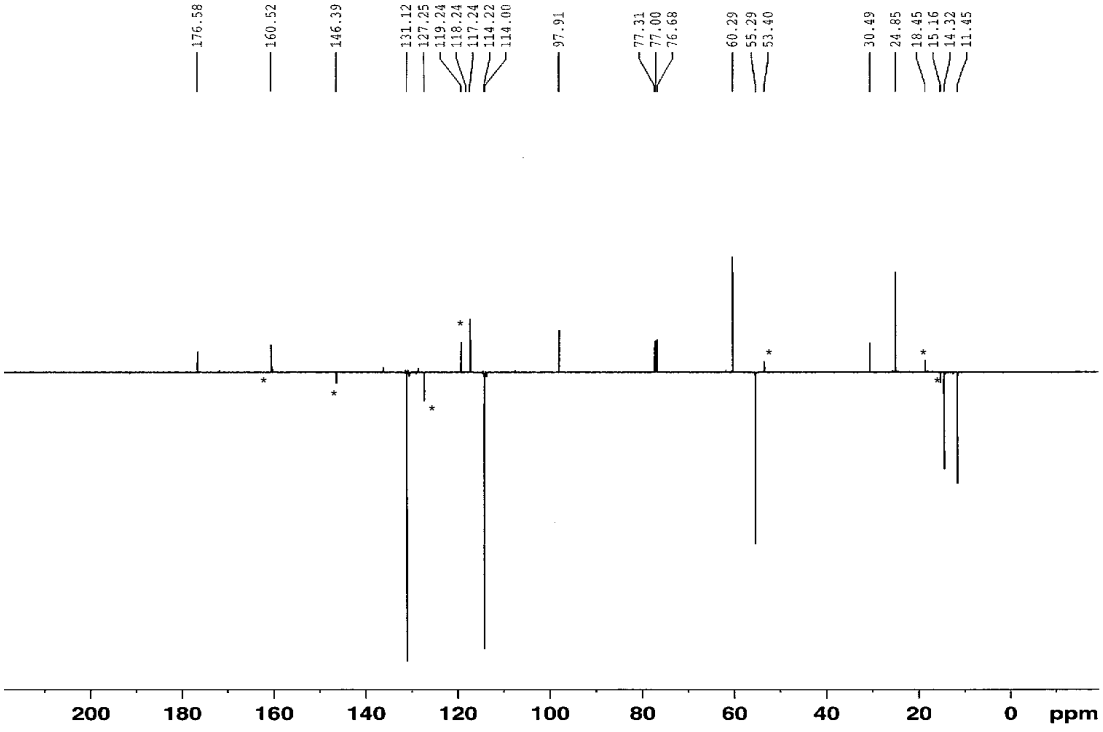


^{1}H NMR spectrum of **2e**
(400 MHz, $CDCl_3$)
85% purity

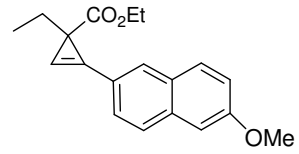




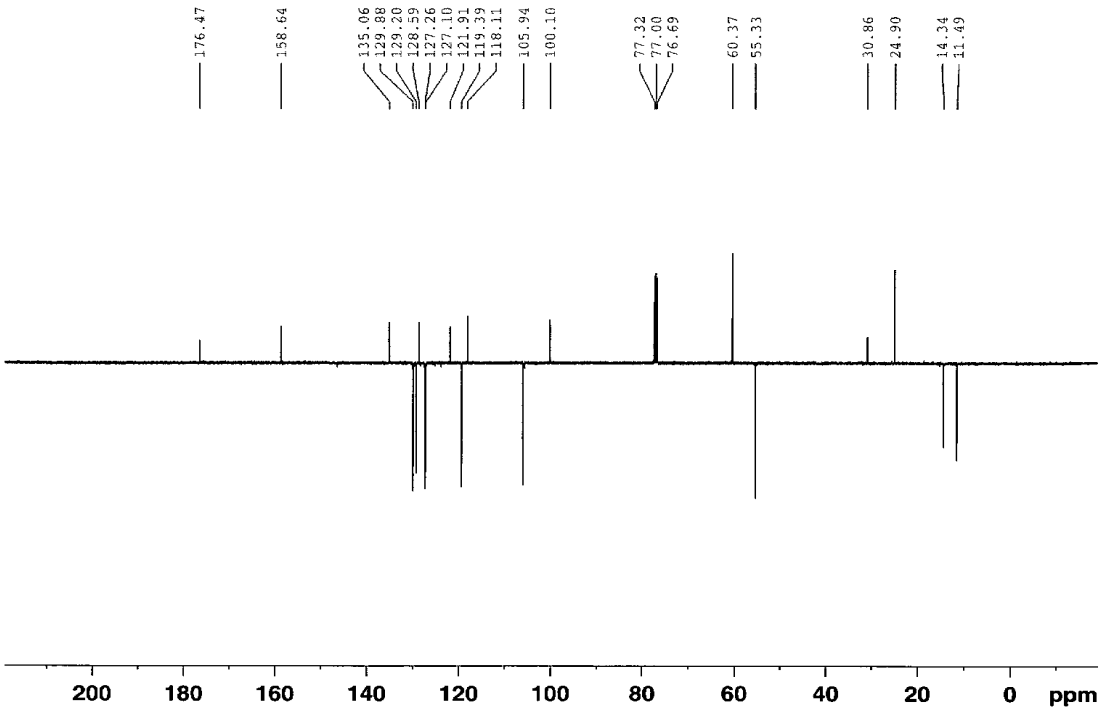
^{13}C NMR spectrum of **2e**
(100 MHz, $CDCl_3$)
impurities are marked by *



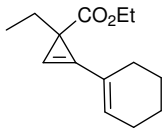
^{1}H NMR spectrum of **2f**
(400 MHz, $CDCl_3$)



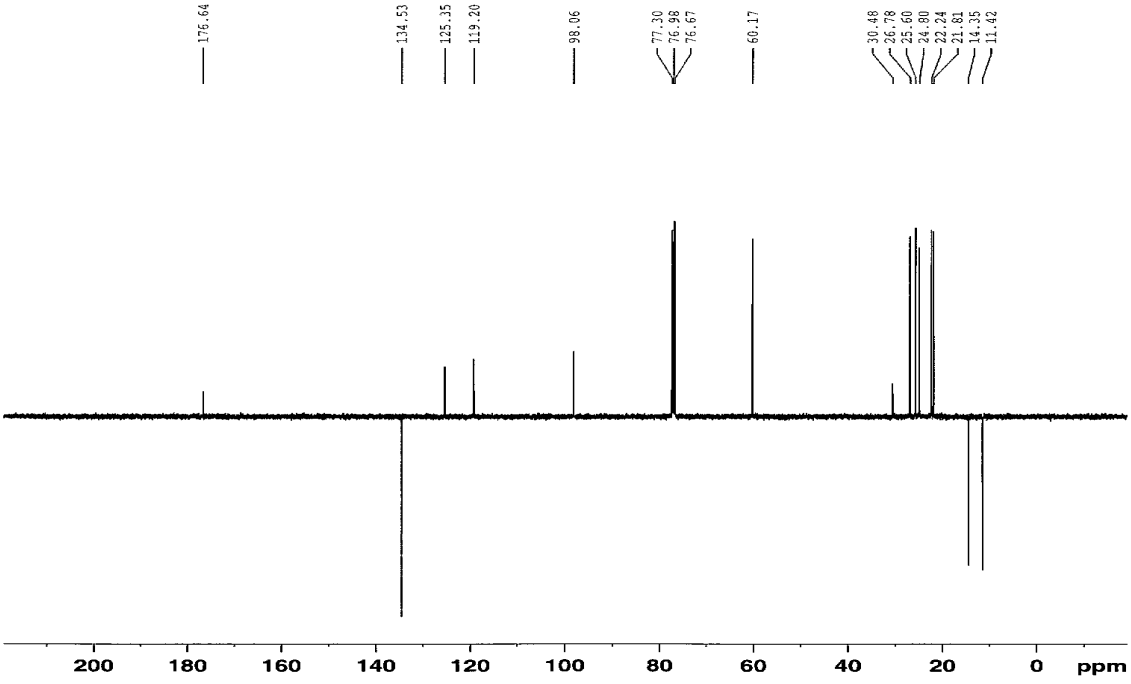
^{13}C NMR spectrum of **2f**
(100 MHz, $CDCl_3$)



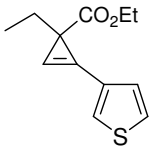
^{1}H NMR spectrum of **2g**
(400 MHz, $CDCl_3$)



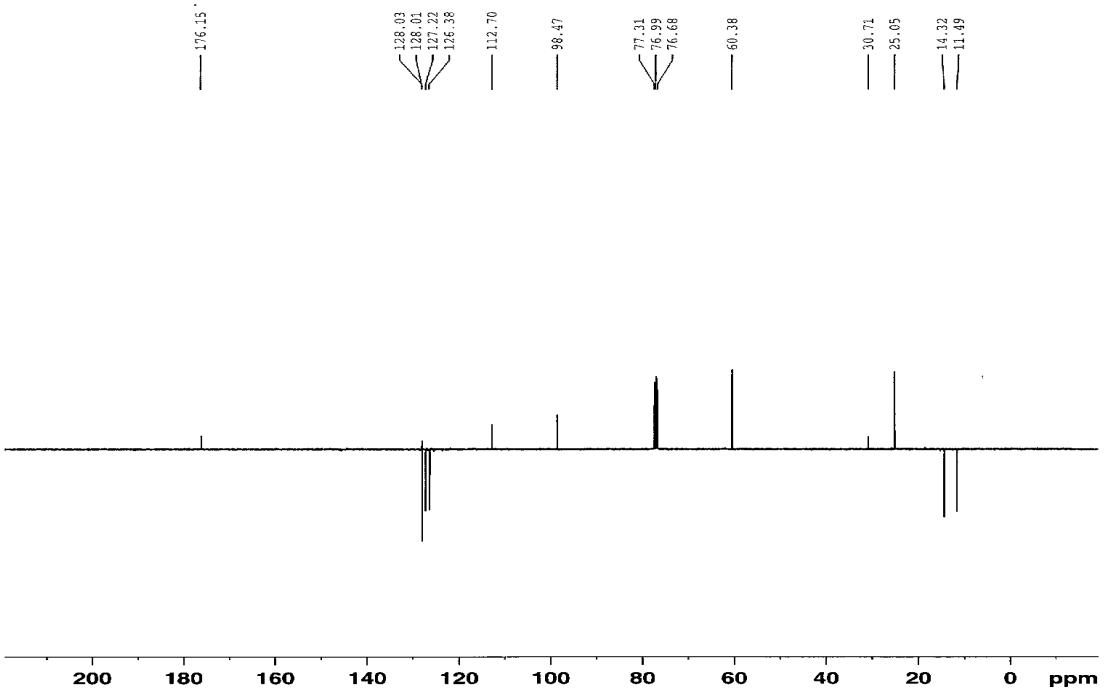
^{13}C NMR spectrum of **2g**
(100 MHz, $CDCl_3$)



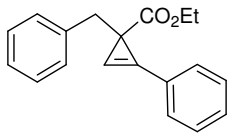
^{1}H NMR spectrum of **2h**
(400 MHz, $CDCl_3$)

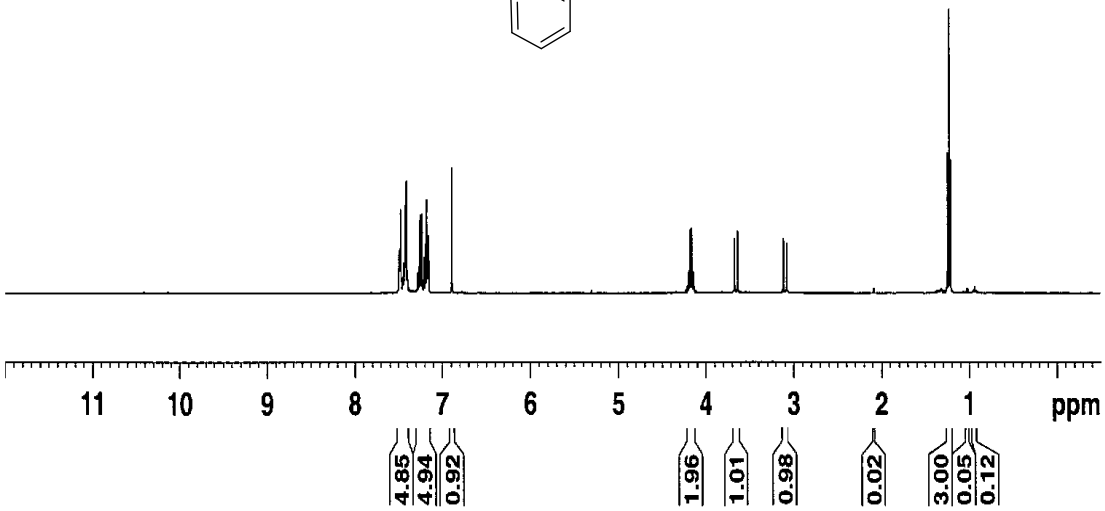


^{13}C NMR spectrum of **2h**
(100 MHz, $CDCl_3$)

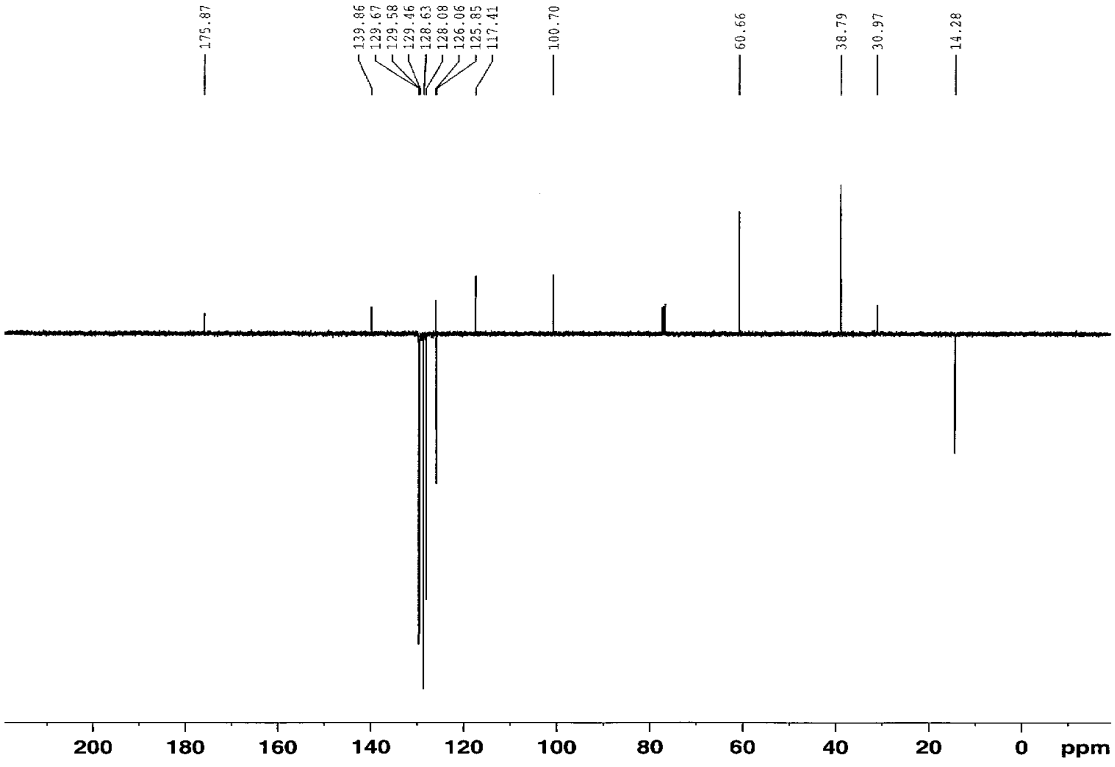


^{1}H NMR spectrum of **3a**
(400 MHz, $CDCl_3$)

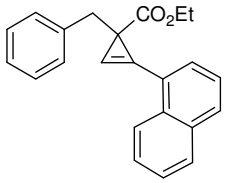


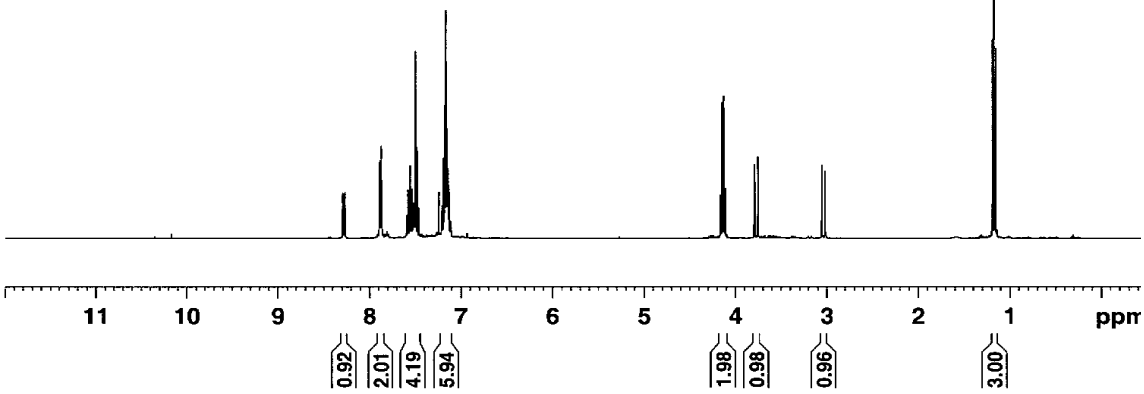


^{13}C NMR spectrum of **3a**
(100 MHz, $CDCl_3$)

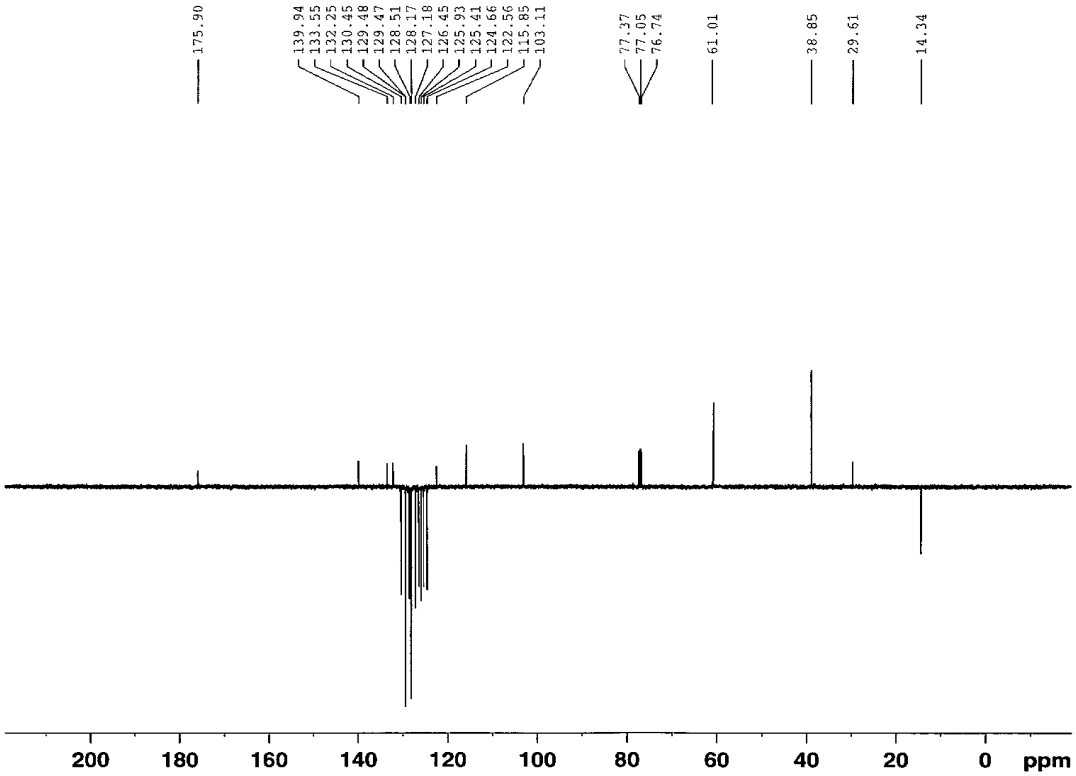


^{1}H NMR spectrum of **3b**
(400 MHz, $CDCl_3$)

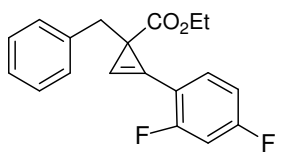


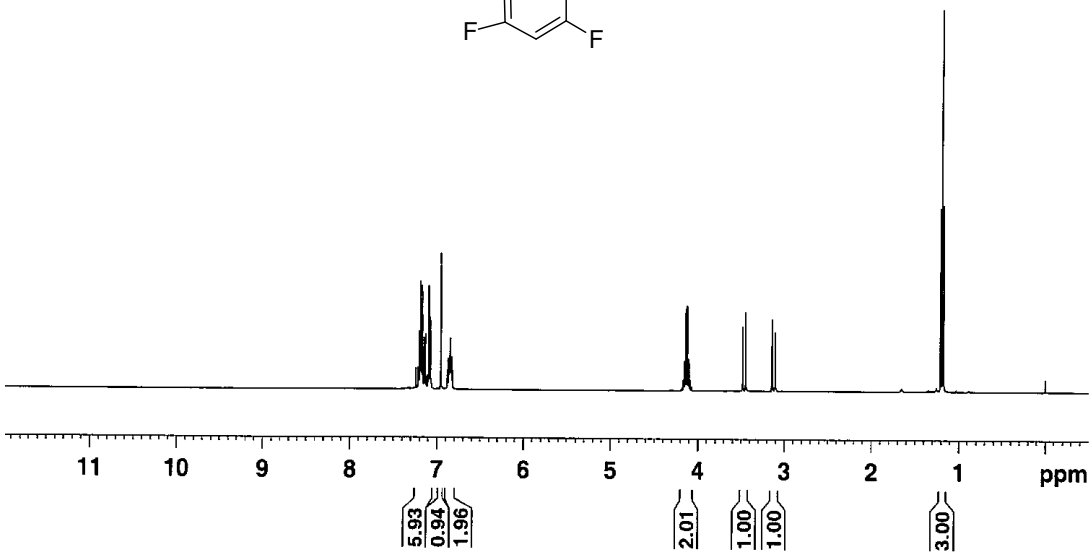


^{13}C NMR spectrum of **3b**
(100 MHz, $CDCl_3$)

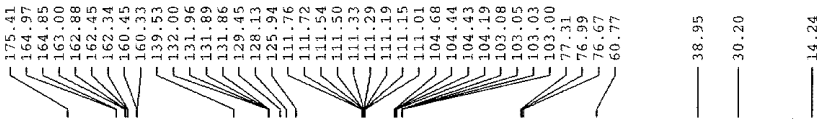


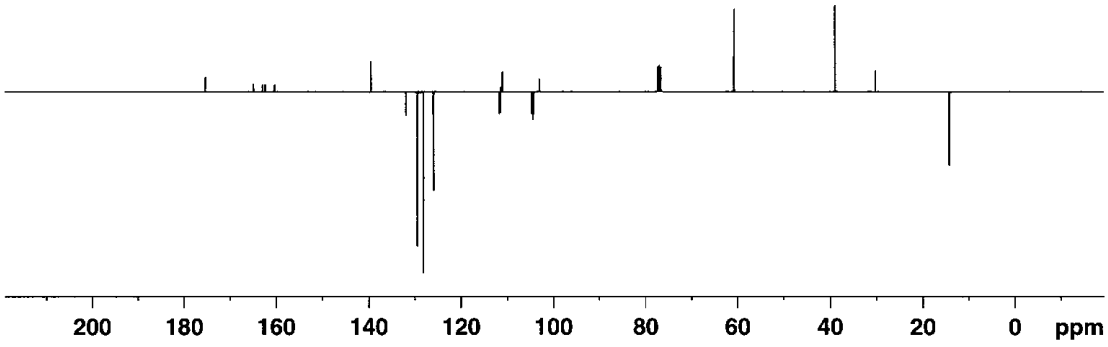
^{1}H NMR spectrum of **3c**
(400 MHz, $CDCl_3$)



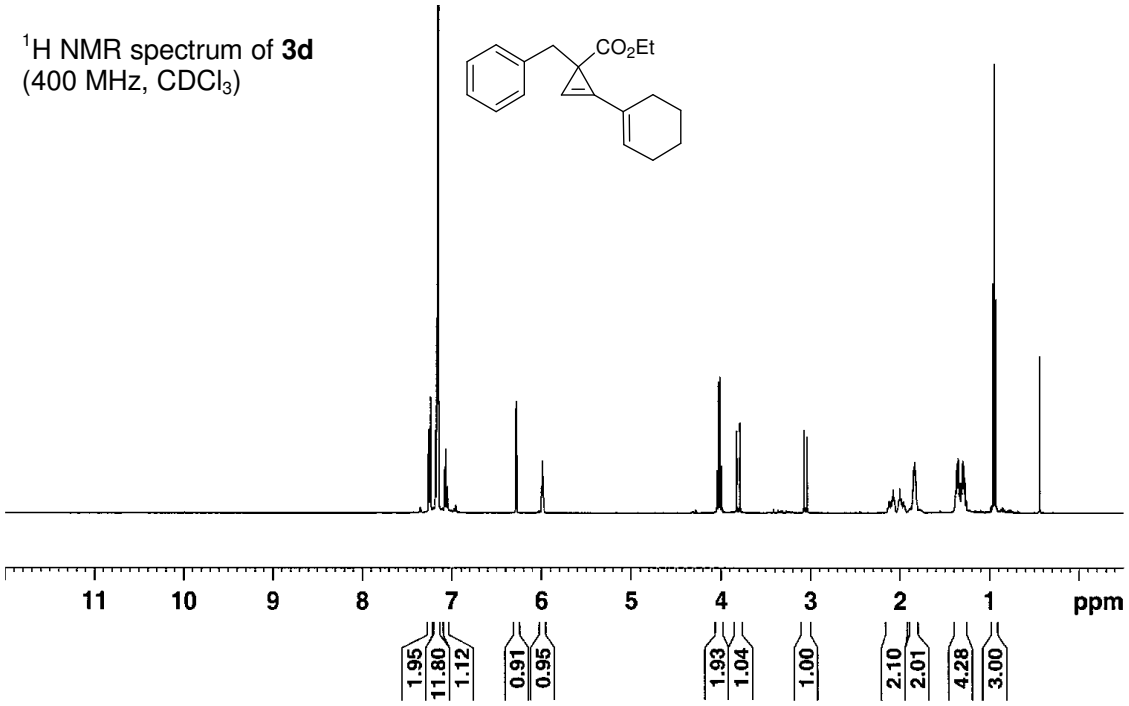


^{13}C NMR spectrum of **3c**
(100 MHz, $CDCl_3$)

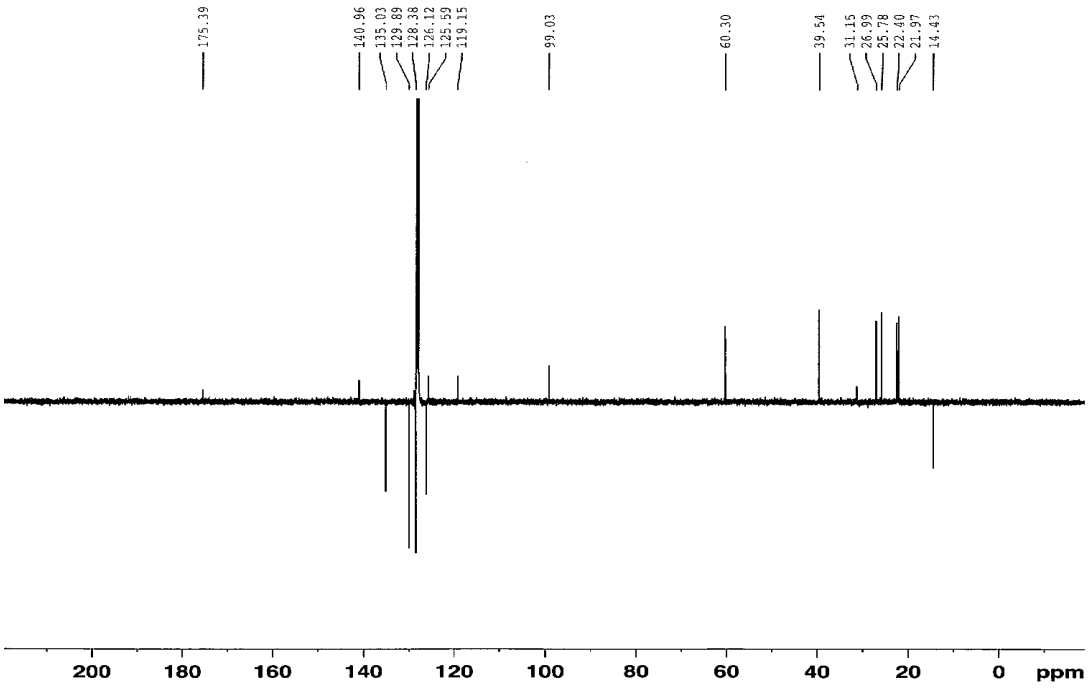




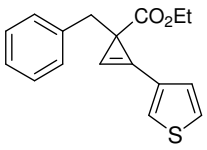
^{1}H NMR spectrum of **3d**
(400 MHz, $CDCl_3$)



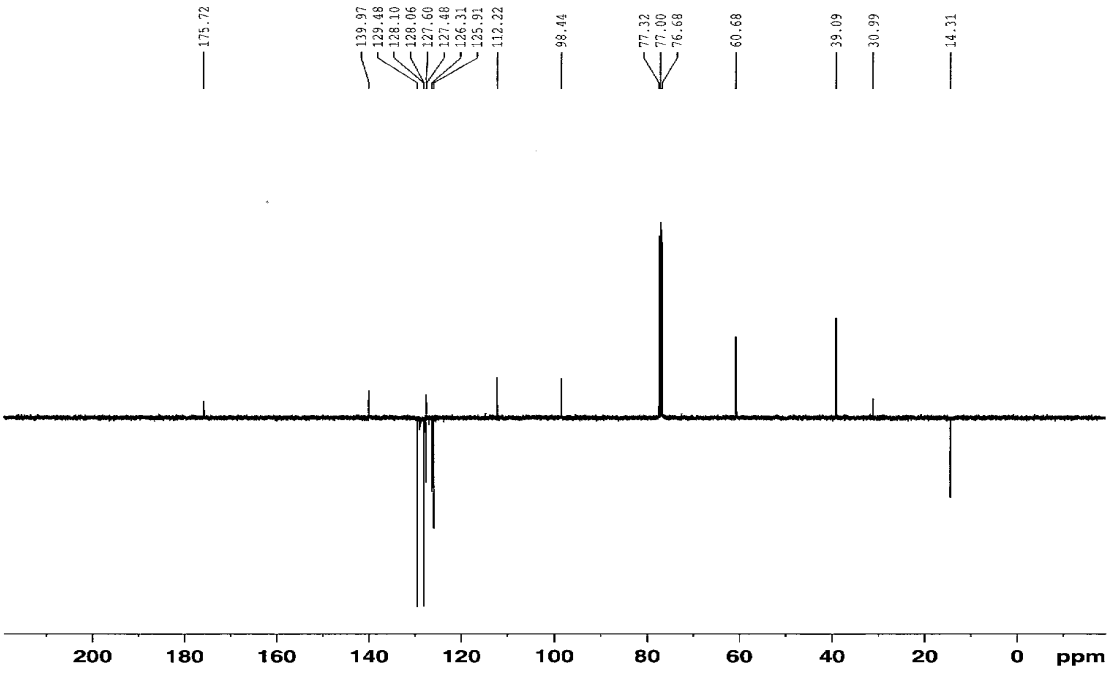
^{13}C NMR spectrum of **3d**
(100 MHz, $CDCl_3$)



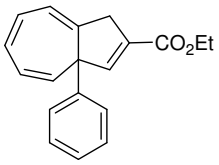
^{1}H NMR spectrum of **3e**
(400 MHz, $CDCl_3$)
92% purity



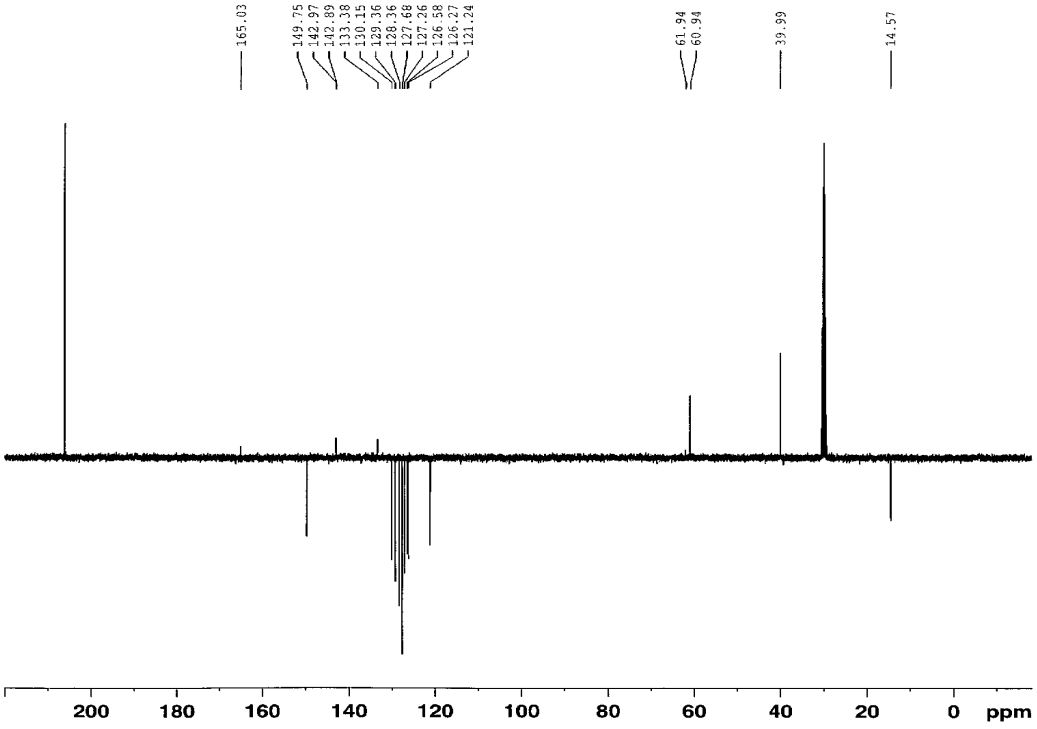
^{13}C NMR spectrum of **3e**
(100 MHz, $CDCl_3$)



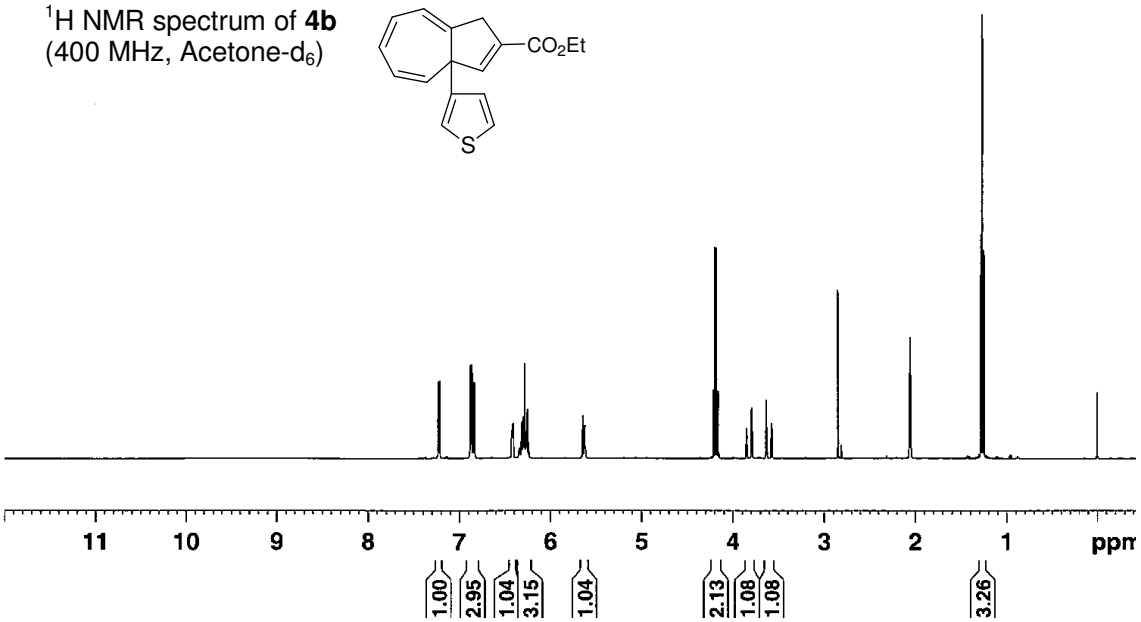
^{1}H NMR spectrum of **4a**
(400 MHz, Acetone-d_6)



^{13}C NMR spectrum of **4a**
(100 MHz, Acetone-d_6)



^{1}H NMR spectrum of **4b**
(400 MHz, Acetone-d_6)



^{13}C NMR spectrum of **4b**
(400 MHz, Acetone-d_6)