Enhancement of Cyclopropanation Chemistry in the Silver-Catalyzed Reactions of Aryldiazoacetates

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Supporting Information

A: General Information:

^{1}H NMR spectra were recorded on either a 400 or 500 MHz Varian spectrometer or a 300 MHz Gemini spectrometer, and ^{13}C NMR at either 75 or 125 MHz with the sample solvent being $CDCl_3$ unless otherwise noted. All coupling constants are rounded to the nearest half integer. Mass spectral determinations were carried out by GC-MS (EI), LC-MS (ESI) in the Instrument Center, Department of Chemistry, University at Buffalo. IR spectra were obtained using a Thermo-Nicolet Avatar 330 FTIR. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross GA. Analytical TLC was performed on Whatman 0.25 mm aluminum backed silica gel (60F-254) plates using UV light and/or phosphomolybdic acid (PMA) stain for visualization. Glassware was dried in an oven (90 °C) overnight then flame dried under vacuum prior to use. Reactions were conducted under argon atmosphere unless otherwise stated. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). The reaction solvent (CH_2Cl_2) was dried by passing through activated A2 alumina columns (Grubbs type solvent purifier) and degassed (by bubbling argon gas through for 5-10 min) prior to use.

Starting Materials:

The following starting materials: methyl phenyldiazoacetate (**1**)[1,2] and methyl phenylvinyldiazoacetate (**7**)[3] were synthesized according to the literature. All other materials were purchased from Aldrich, Acros, or TCI and used as received.

B: General Procedure:

Silver catalysis:

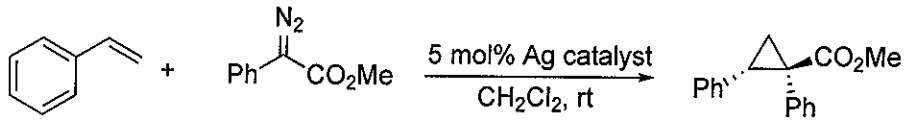
In a rigorously dried round bottom flask covered in aluminum foil to exclude light, the catalyst, $AgSbF_6$, was added directly into the flask (0.03 mmol, 10 mol %), then dissolved in 5-8 mL of CH_2Cl_2. The alkene substrate (1.5-3 mmol, 5-10 equiv) was added and the entire solution was heated to reflux under argon. The diazoacetate (0.3 mmol, 1 equiv) was dissolved in 3 mL of CH_2Cl_2 and added to the reaction at the top of the reflux condenser over 3 h *via* syringe pump addition. The solution was refluxed for 1 h after addition was completed and then continued until periodic TLC analysis (20% EtOAc/Hexanes, UV then PMA visualization) showed that all diazoacetate had been consumed. The reaction was concentrated under reduced pressure, analyzed by crude ^1H NMR spectroscopy and purified by flash column chromatography.

Rhodium catalysis:

To a rigorously dried round bottom flask was added $Rh_2(OAc)_4$ (0.003 mmol, 1 mol %), and dissolved in 5-8 mL of CH_2Cl_2. The alkene substrate (1.5 mmol, 5 equiv) was added and the entire solution was heated to reflux under Argon. The diazoacetate (0.3 mmol, 1 equiv) was dissolved in 3 mL of CH_2Cl_2 and added to the reaction at the top of the reflux condenser over 3 h *via* syringe pump addition. The solution was refluxed for 1 h after addition completed and then continued until periodic TLC analysis (20% EtOAc/Hexanes, UV then PMA visualization) showed that all diazoacetate had been consumed. The reaction was concentrated under reduced pressure, analyzed by crude ^1H NMR spectroscopy and purified by flash column chromatography.

C: Results for Silver Catalyzed Reaction:

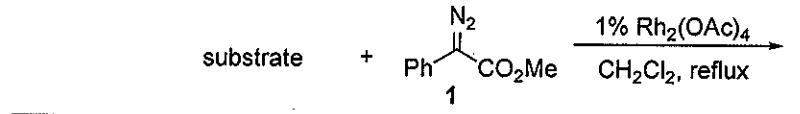
Table 3: *Summary of the evaluation of silver catalysts for the reaction of methyl phenyldiazoacetate with styrene*



Catalyst	Yield (%)
$AgSbF_6$	91
$AgBF_4$	85
$AgCO_2Ph$	75
$AgNTf_2$	70
$AgNO_3$	67
$Ag(O_2CCF_3)$	64
Ag(OAc)	29
$Ag_2(SO_4)$	NR

D: Results for Rhodium Catalyzed Reactions:

Table 4: *Rhodium catalyzed reactions with methyl phenyldiazoacetate.*



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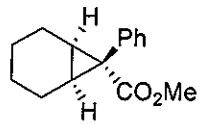
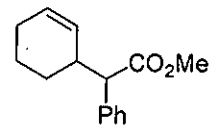
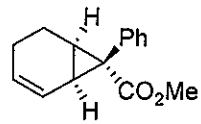
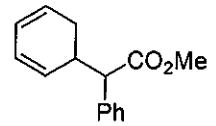
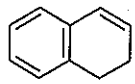
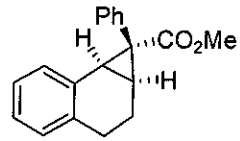
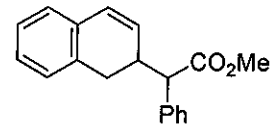
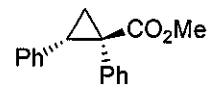
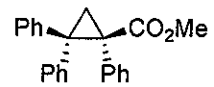
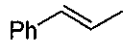
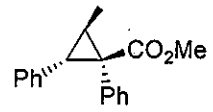
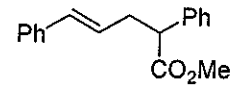
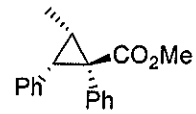
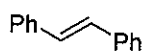
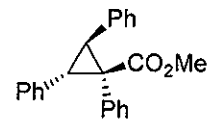
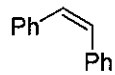
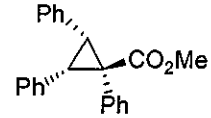
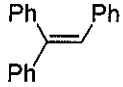
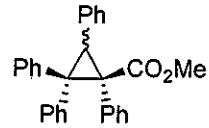
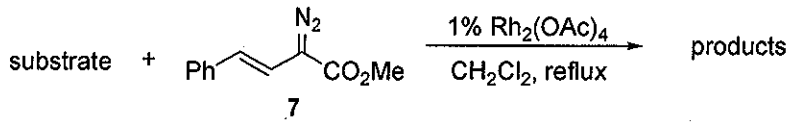
1				**A:B** = 1:2.2	44[a]
2				**A:B** = 1:1.8	44[a]
3				**A:B** = 1:1.3	60[a]
4					93
5					82
6				**A:B** = 1:>20	4[b]
7					46
8					<1
9					<1
10					<1

[a] combined yield
[b] only C-H insesrtion product was formed

Table 5: *Rhodium catalyzed reactions with methyl phenylvinyldiazoacetate.*



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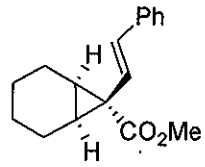
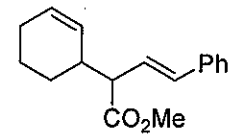
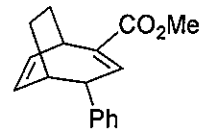
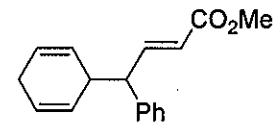
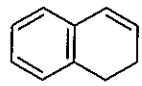
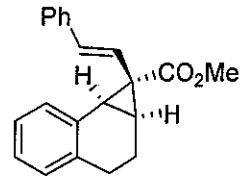
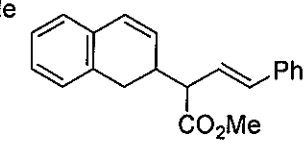
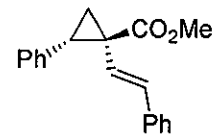
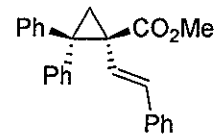
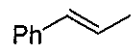
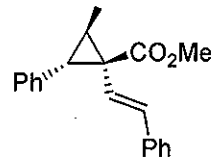
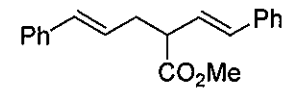
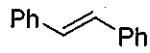
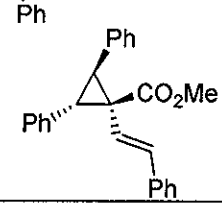
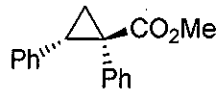
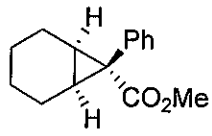
1				**A:B** = 1:1	22
2				**A:B** = 2:1	36[a]
3				**A:B** = 2:1	52[a]
4					78
5					64
6				**A:B** = 2:1	<5
7					<1

[a] combined yield

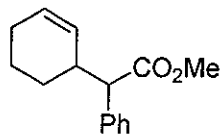
E: Compound Characterization:



(±)-(1*R*,2*S*)-Methyl 1,2-diphenylcyclopropanecarboxylate (2):[4,5] *Ag*: Methyl phenyldiazoacetate (**1**) (92.3 mg, 0.524 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (18.5 mg, 0.053 mmol, 10 mol%) and 0.6 mL (5.2 mmol, 10 equiv) styrene in 5 mL of CH_2Cl_2. **2** was isolated as a white solid (127.3 mg, 0.504 mmol, 96% yield) upon purification by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient). *Rh:* Methyl phenyldiazoacetate (**1**) (89.9 mg, 0.51 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 1 h to a refluxing solution of $Rh_2(OAc)_4$ (2.6 mg, 0.0058 mmol, 1 mol%) and styrene (0.6 mL, 5.2 mmol, 10 equiv) in 5 mL of CH_2Cl_2. **2** was isolated as a white solid (119.8 mg, 0.475 mmol, 93% yield) upon purification by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient). R_f = 0.39 (20% ethyl acetate/hexanes); mp 59.5-61.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.09 (m, 3H), 7.03-7.00 (m, 5H), 6.76-6.74 (m, 2H), 3.63 (s, 3H), 3.11 (dd, *J* = 7.0, 9.5 Hz, 1H), 2.13 (dd, *J* = 5.0, 9.5 Hz, 1H), 1.86 (dd, *J* = 5.0, 7.0 Hz, 1H); The spectroscopic data and stereochemical assignment is consistent with previously reported results.[4,5]

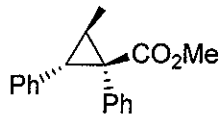


(±)-(1*S*,6*R*,7*R*)-Methyl 7-phenylbicyclo[4.1.0]heptane-7-carboxylate (3):[6,7] *Ag*: Methyl phenyldiazoacetate (**1**) (53.9 mg, 0.305 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (13.2 mg, 0.038 mmol, 12 mol%) and 0.31 mL (3.06 mmol, 10 equiv) cyclohexene in 8 mL of CH_2Cl_2. Purification by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) gave **3** as a white solid (61.7 mg, 0.268 mmol, 88% yield). R_f = 0.38 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 3.53 (s, 3H), 2.01-1.94 (m, 4H), 1.76-1.69 (m, 2H), 1.07-1.03 (m, 2H), 0.59-0.56 (m, 2H). The spectroscopic data and stereochemical assignment is consistent with previously reported results.[6,7]

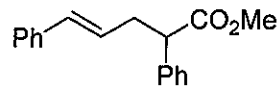


(±)-Methyl 2-(cyclohex-2-enyl)-2-phenylacetate (4):[6,7] *Rh:* Methyl phenyldiazoacetate (**1**) (54.2 mg, 0.307 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $Rh_2(OAc)_4$ (1.7 mg, 0.0038 mmol, 1 mol%) and cyclohexene (0.31 mL, 3.06 mmol, 10 equiv) in 8 mL of CH_2Cl_2. The products were purified by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient) to obtain a clear oil (31.3 mg, 0.136 mmol, 44% yield) consisting of mixture of

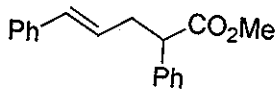
cyclopropane **3** and cyclohexene **4** in a ratio of 1:2.6. R_f = 0.44 (20 % ethyl acetate/hexanes). Product **4** is a mixture of diastereomers in a 1:1.3 ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 5H), 5.80-5.77 (m, 1H, DS1), 5.66-5.62 (m, 1H), 5.16-5.14 (m, 1H, DS2), 3.66 (s, 3H), 3.32 (d, *J*=11 Hz, 1H), 2.89-2.86 (m, 1H), 2.0-0.8 (m, 6H). The spectroscopic data is consistent with previously reported results.[6,7]



(±)-(1*R*,2*R*,3*S*)-Methyl 2-methyl-1,3-diphenylcyclopropanecarboxylate (5): *Ag*: Methyl phenyldiazoacetate (**1**) (54.1 mg, 0.307 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (12.4 mg, 0.036 mmol, 12 mol%) and *trans*-β-methylstyrene (0.2 mL, 1.54 mmol, 5 equiv) in 8 mL of CH_2Cl_2. Purification by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient) gave the title compound **5** as a white solid (65.4 mg, 0.246 mmol, 80% yield). mp 82.5-85 °C; R_f = 0.42 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-7.12 (m, 3H), 7.06-6.99 (m, 5H), 6.76-6.74 (m, 2H), 3.64 (s, 3H), 3.08 (d, *J*=8.0 Hz, 1H), 2.27-2.24 (m, 1H), 1.47 (d, *J*=6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 137.0, 136.4, 131.3, 127.9, 127.8, 127.6, 126.9, 126.0, 52.3, 42.4, 37.7, 27.3, 12.9; FTIR (film) 3028, 2951, 1717, 1433, 1253, 1214, 1169 cm^{-1}. Anal. calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.06; H, 6.80. Stereochemical assignment is based on analogy to previous work by Davies.[4]



(±)- (*E*)-Methyl 2,5-diphenylpent-4-enoate (6): *Rh:* Methyl phenyldiazoacetate (**1**) (56.3 mg, 0.32 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $Rh_2(OAc)_4$ (1.5 mg, 0.0034 mmol, 1 mol%) and *trans-β*-methylstyrene (0.2 mL, 1.54 mmol, 4.8 equiv) in 8 mL of CH_2Cl_2. The products were purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) to obtain **6** as a colorless oil (3.1 mg, 0.012 mmol, 4% yield). R_f = 0.42 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 10H), 6.43 (d, *J*=15.5 Hz, 2H), 6.1 (ddd, *J*=15.5, 7.5, 7.5 Hz, 1H), 3.71 (dd, *J*=8.5, 7.5 Hz, 1H) 3.66 (s, 3H), 3.01-2.95 (m, 1H), 2.69-2.64 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 138.6, 137.4, 132.3, 128.7, 128.5, 127.9, 127.4, 127.2, 126.9, 126.1, 52.0, 51.8, 37.0; FTIR (film) 3028, 2951, 2924, 1735, 1495, 1454, 1434, 1160 cm^{-1}; LRMS (ESI) *m/z* (relative intensity): 267 (66); HRMS (EI) *m/z* calcd for $[C_{18}H_{19}O_2]^+$ ($[M+H]^+$): 267.1380. Found: 267.1372.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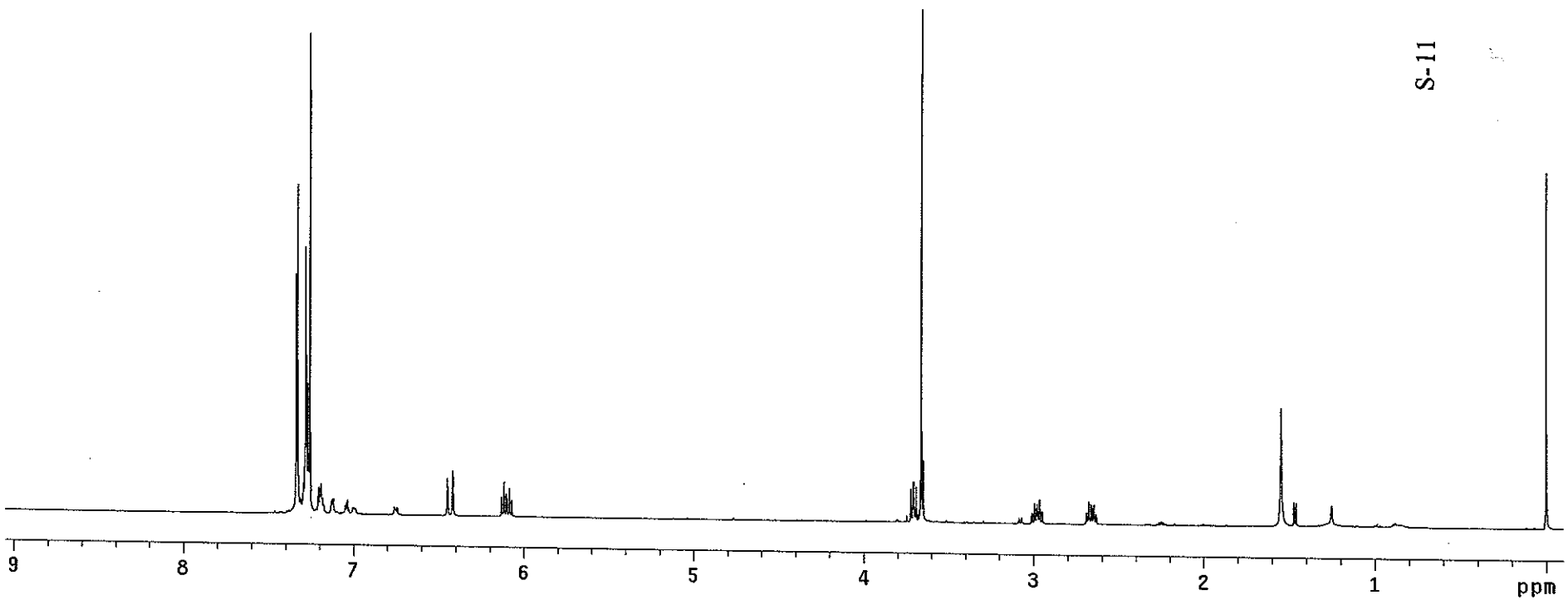
Ph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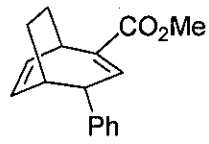
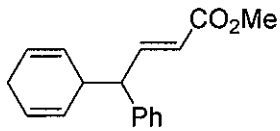
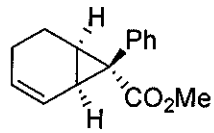


(±)-(2*E*)-Methyl 4-phenylbicyclo[3.2.2]nona-2,6-diene-2-carboxylate (8):[8] *Ag*: Methyl phenylvinyldiazoacetate (**7**) (84.6 mg, 0.418 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (15.6 mg, 0.045 mmol, 10 mol%) and 1,3-cyclohexadiene (0.4 mL, 4.3 mmol, 10 equiv) in 8 mL of CH_2Cl_2. The crude mixture was purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) to obtain a clear oil (89.8 mg, 0.353 mmol, 67% yield) as a combination of cyclopropanation/cope product **8** and C–H/cope product **9** in a 5.4:1 ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 -7.17 (m, 3H), 7.14 (d, *J*=7.0 Hz, 2H), 6.73 (d, *J*=4.0 Hz, 1H), 6.43 (dd, *J*=8.0, 8.0 Hz, 1H), 5.64 (dd, *J*=8.0, 7.5 Hz, 1H), 3.74 (s, 3H), 3.66 (dd, *J*=4.0, 4.0 Hz, 1H), 3.56-3.53 (m, 1H), 2.73 (m, 1H), 2.10-2.05 (m, 1H), 1.98-1.93 (m, 2H), 1.83-1.76 (m, 1H). The spectroscopic data is consistent with previously reported results.[8]

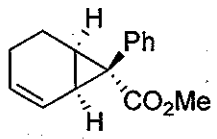


(±)- (2*E*)-Methyl 4-(cyclohexa-2,5-dienyl)-4-phenylbut-2-enoate (9):[8] *Rh:* Methyl phenylvinyldiazoacetate (**7**) (102.9 mg, 0.509 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 2 h to a refluxing solution of $Rh_2(OAc)_4$ (2.3 mg, 0.0052 mmol, 1 mol%) and 1,3-cyclohexadiene (0.5 mL, 4.3 mmol, 8 equiv) in 8 mL of CH_2Cl_2. The crude product was purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl

acetate/hexanes gradient) to obtain a colorless oil (46.3 mg, 0.182 mmol, 36% yield) as a mixture of the combined cyclopropanation/cope product **8** and C–H/cope product **9** in a 2:1 ratio. R_f = 0.39 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.13 (m, 6 H), 5.84 (d, *J* = 15.5 Hz, 1H), 5.81-5.78 (m, 1H), 5.75-5.72(m, 1H), 5.68-5.65 (m, 1H), 5.46-5.44 (m, 1H), 3.72 (s, 3H), 3.41 (dd, *J*=8.0, 8.5 Hz, 1H), 3.22-3.20 (m, 1H), 2.61-2.59 (m, 2H). The spectroscopic data is consistent with previously reported results.[8]



(±)-(1*S*,6*R*,7*S*)-Methyl 7-phenylbicyclo[4.1.0]hept-2-ene-7-carboxylate (Table 1, Entry 2): *Ag*: Methyl phenyldiazoacetate (**1**) (55.4 mg, 0.314 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (12.0 mg, 0.035 mmol, 11 mol%) and 1,3-cyclohexadiene (0.3 mL, 3.2 mmol, 10 equiv) in 8 mL of CH_2Cl_2. The crude material was purified by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient) to give the title compound as a white solid (56.7 mg, 0.248 mmol, 79% yield). mp 91.5-95 °C; R_f = 0.37 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.21 (m, 5H), 6.03-6.00 (m, 1H), 5.43-5.39 (m, 1H), 3.57 (s, 3H), 2.37-2.27 (m, 2H), 2.00-1.94 (m, 1H), 1.85-1.80 (m, 1H), 1.60-1.53 (m, 1H), 0.47-0.40 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 134.7, 128.4, 127.7, 126.9, 122.6, 52.4, 40.3, 27.6, 25.6, 21.0, 16.7; FTIR (film) 3032, 2930, 1707, 1429, 1237, 1201, 1061, 1022 cm^{-1}. LRMS (ESI) *m/z* (relative intensity): 251 (100); HRMS (ESI) *m/z* calcd for $[C_{15}H_{16}O_2Na]^+$ ($[M+Na]^+$): 251.1043. Found: 251.1044. Stereochemical assignment is based on analogy to previously reported results by Davies.[4,8]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H

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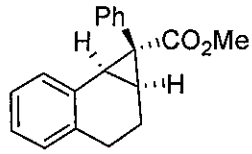
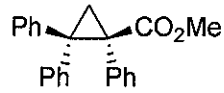
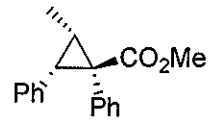


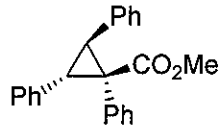
(±)- (1*R*,1α*S*,7β*S*)- Methyl 1α,2,3,7β- tetrahydro-1- phenyl-1H-cyclopropa[*a*]naphthalene-1-carboxylate (Table 1, Entry 3): *Ag*: Methyl phenyldiazoacetate (**1**) (54.4 mg, 0.308 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (11.2 mg, 0.032 mmol, 10 mol%) and 1,2-dihydronaphthalene (0.4 mL, 3.06 mmol, 10 equiv) in 8 mL of CH_2Cl_2. The crude compound was purified by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient) to give the title compound as a white solid (69.3 mg, 0.249 mmol, 80% yield). mp 114-116.5 °C; R_f = 0.36 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J*=7.5 Hz, 1H), 7.18-7.13 (m, 2H), 7.10-7.03 (m, 3H), 6.96-6.94 (m, 2H), 6.70 (d, *J*=7.5 Hz, 2H), 3.60 (s, 3H), 3.04 (d, *J*=9.0 Hz, 1H), 2.58-2.55 (m, 1H), 2.18-2.13 (m, 2H), 2.00-1.93 (m, 1H), 1.07-1.00 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 135.3, 134.7, 133.0, 130.8, 130.1, 128.3, 127.8, 126.9, 126.4, 125.9, 52.6, 39.0, 31.0, 28.3, 25.3, 18.1; FTIR (film) 3027, 2928, 2856, 1713, 1494, 1434, 1236, 1204 cm^{-1}; Anal. calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.95; H, 6.63. Stereochemical assignment is based on analogy to previously reported results by Davies.[4,9]



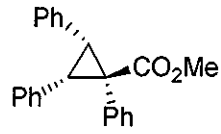
(±)-(*S*)-Methyl 1,2,2-triphenylcyclopropanecarboxylate (Table 1, Entry 5)[5,10,11]**:** *Ag*: Methyl phenyldiazoacetate (**1**) (53.6 mg, 0.30 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (17.4 mg, 0.05 mmol, 17 mol%) and 1,1-diphenylethylene (0.27 mL, 1.53 mmol, 5 equiv) in 8 mL of CH_2Cl_2. Purification by flash column chromatography (5% ethyl acetate/hexanes to 20% ethyl acetate/hexanes gradient) gave the title compound as a colorless oil (82 mg, 0.249 mmol, 82% yield). *Rh*: Methyl phenyldiazoacetate (**1**) (53.4 mg, 0.303 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $Rh_2(OAc)_4$ (1.5 mg, 0.0034 mmol, 1 mol%) and 1,1-diphenylethylene (0.27 mL, 1.53 mmol, 5 equiv) in 8 mL of CH_2Cl_2. The products were purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) to give the title compound as a colorless oil (81.1 mg, 0.247 mmol, 82% yield). R_f = 0.29 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J*=7.5 Hz, 2H), 7.35-7.23 (m, 5H), 7.12 (m, 3H), 6.95 (m, 5H), 3.35 (s, 3H), 2.69 (d, *J*=5.5 Hz, 1H), 2.43 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 142.0, 139.6, 135.7, 131.9 (2C), 130.0, 128.7, 128.3, 127.5, 127.4, 126.9, 126.1, 52.1, 44.4, 43.1, 22.8; FTIR (film) 3025, 1722, 1495, 1449, 1302, 1216, 1140 cm^{-1}; LRMS (EI) *m/z* (relative intensity): 269.1 (100), 191.1 (85), 328.1 (56); HRMS (EI) *m/z* calcd for $[C_{23}H_{20}O_2]^+$ ($[M^+]$): 328.1458. Found: 328.1459. The spectroscopic data and stereochemical assignment is consistent with previously reported results.[5,10,11]



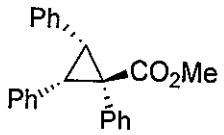
(±)-(1*R*,2*S*,3*S*)-Methyl 2-methyl-1,3-diphenylcyclopropanecarboxylate (Table 1, Entry 7): *Ag*: Methyl phenyldiazoacetate (**1**) (55.2 mg, 0.313 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (11.1 mg, 0.032 mmol, 10 mol%) and *cis*-β-methylstyrene (0.2 mL, 1.54 mmol, 5 equiv) in 7 mL of CH_2Cl_2. This compound was purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) to obtain the title compound as a white solid (71.8 mg, 0.27 mmol, 86% yield). *Rh:* Methyl phenyldiazoacetate (**1**) (53.3 mg, 0.302 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $Rh_2(OAc)_4$ (1.8 mg, 0.004 mmol, 1 mol%) and *cis*-β-methylstyrene (0.2 mL, 1.54 mmol, 5 equiv) in 7 mL of CH_2Cl_2. The product was purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) to obtain the title compound as a white solid (37 mg, 0.139 mmol, 46% yield). mp 82-84 °C; R_f = 0.36 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.23 (m, 3H), 7.12-7.08 (m, 3H), 7.05-7.02 (m, 2H), 6.77-6.75 (m, 2H), 3.60 (s, 3H), 3.10 (d, *J*=10.0 Hz, 1H), 2.39-2.36 (m, 1H), 1.26 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 136.1, 133.1, 132.2, 130.3, 127.8, 127.4, 127.2, 125.9, 52.7, 38.0, 36.5, 27.8, 10.8; FTIR (film) 3028, 2951, 1714, 1497, 1446, 1433, 1240, 1223, 1056 cm^{-1}; Anal. calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.00; H, 6.84. Stereochemical assignment is based on analogy to previous work by Davies.[4]



(±)-(2*S*,3*S*)-Methyl 1,2,3-triphenylcyclopropanecarboxylate (Table 1, Entry 8): *Ag*: Methyl phenyldiazoacetate (**1**) (57.2 mg, 0.324 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (13.3 mg, 0.038 mmol, 12 mol%) and *trans*-stilbene (0.2736 mg, 1.52 mmol, 4.75 equiv) in 8 mL of CH_2Cl_2. The title compound was obtained as a white solid (89.7 mg, 0.273 mmol, 84% yield) following purification by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient). mp 141-144 °C; R_f = 0.31 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J*=7.0 Hz, 2H), 7.35 (t, *J*=7.0 Hz, 2H), 7.28 (m, 1H), 7.19 (m, 5H). 7.13-7.09 (m, 3H), 6.94 (br d, *J*=7.0 Hz, 2H), 3.86 (d, *J*=8.0 Hz, 1H), 3.54 (d, *J*=8.0 Hz, 1H), 3.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 136.4, 136.2, 135.7, 131.2, 128.9, 128.2 (2C), 127.9 (2C), 127.2, 120.0, 126.4, 52.2, 46.0, 36.7, 34.7; FTIR (film) 3061, 3028, 2949, 1721, 1497, 1252 cm^{-1}; Anal. calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.08; H, 6.15. Stereochemical assignment is based on analogy to previous work by Davies.[4]



(±)-(1*S*,2*R*,3*S*)-Methyl 1,2,3-triphenylcyclopropanecarboxylate (Table 1, Entry 9): *Ag*: Methyl phenyldiazoacetate (**1**) (55.2 mg, 0.313 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (12.9 mg, 0.037 mmol, 12 mol%) and *cis*-stilbene (0.27 mL, 1.53 mmol, 4.9 equiv) in 8 mL of CH_2Cl_2. Purification by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient) gave the title compound as a colorless oil (55.4 mg, 0.169 mmol, 54% yield). R_f = 0.39 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.06 (m, 11H), 6.88 (d, *J*=7.5 Hz, 4H), 3.68 (s, 3H), 3.55 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 134.3, 133.5, 132.2, 131.7, 128.2, 127.4, 127.1, 126.3, 53.0, 40.4, 36.5; FTIR (film) 3059, 3028, 2949, 1713, 1497, 1231 cm^{-1}; LRMS (ESI) *m/z* (relative intensity): 269 (100), 328 (88); HRMS (EI) *m/z* calcd for $[C_{23}H_{20}O_2]^+$ ($[M^+]$): 328.1458. Found: 328.1468. Stereochemical assignment is based on analogy to previous work by Davies and from the symmetric nature of the ^{1}H NMR spectrum.[4]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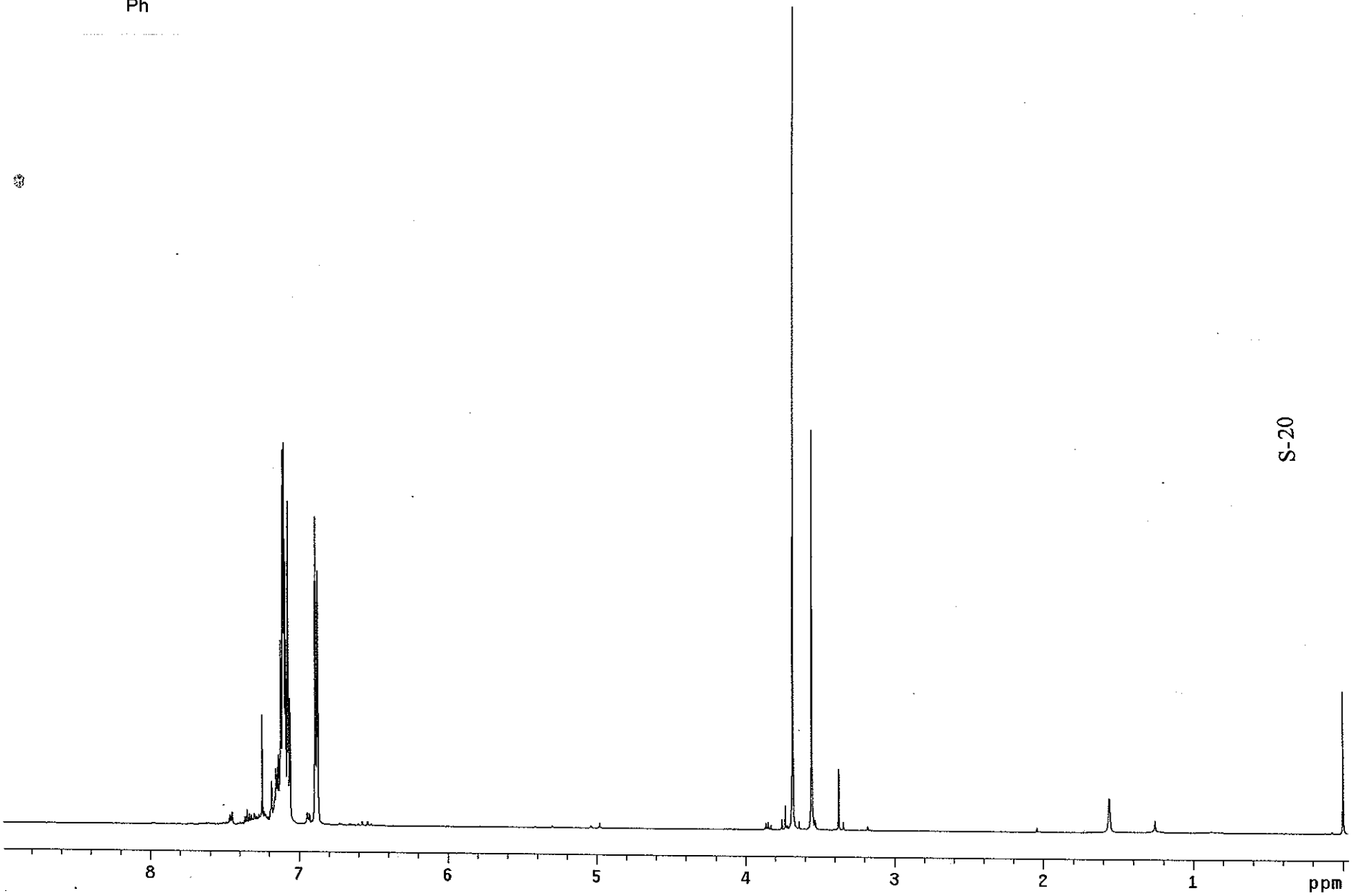
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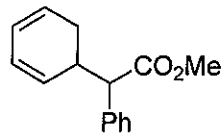
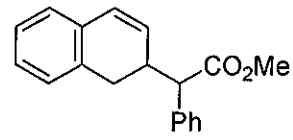
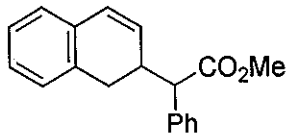


(±)-Methyl 2-(cyclohexa-2,4-dienyl)-2-phenylacetate (Table 3, Entry 2B): *Rh:* Phenyldiazoacetate (**1**) (54.8 mg, 0.311 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $Rh_2(OAc)_4$ (1.8 mg, 0.0038 mmol, 1 mol%) and 1,3-cyclohexadiene (0.3 mL, 3.2 mmol, 10 equiv) in 8 mL of CH_2Cl_2. Purification by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) gave a clear oil (39.6 mg, 0.137 mmol, 44% yield) consisting of mixture of cyclopropane (**Table 3, Entry 2A**) and the title compound in a ratio of 1:1.8. $R_f = 0.41$ (20% ethyl acetate/hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.20 (m, 5H), 5.94-5.91 (m, 1H), 5.85-5.82 (m, 1H), 5.80-5.78 (m, 1H), 5.26-5.23 (dd, *J*=4.0, 9.5 Hz, 1H), 3.65 (s, 3H), 3.10-3.00 (m, 1H), 2.45-2.38 (m, 1H), 2.13-2.00 (m, 2H). The spectroscopic data is consistent with previously reported results.[8]



(±)-Methyl 2-(1,2-dihydronaphthalen-2-yl)-2-phenylacetate (Table 3, Entry 3B): *Rh:* Methyl phenyldiazoacetate (**1**) (53.8 mg, 0.305 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $Rh_2(OAc)_4$ (1.5 mg, 0.0034 mmol, 1 mol%) and 1,2-dihydronaphthalene (0.4 mL, 3.06 mmol, 10 equiv) in 8 mL of CH_2Cl_2. The crude products were purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) to obtain a colorless oil (50.8 mg, 0.183 mmol, 60% yield) consisting of mixture of cyclopropane and C–H insertion product (title compound) in a ratio of 1:1. R_f = 0.43 (20% ethyl acetate/hexanes). The title compound is in a 1:1 mixture of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ (DS1) 7.42-6.89 (m, 9H), 6.54 (d, *J*=9.5 Hz, 1H), 6.09 (dd, *J*=5.0, 9.5 Hz, 1H), 3.63 (s, 3H), 3.40 (d, *J*=5.5 Hz, 1H), 3.28-3.17 (m, 1H), 2.74-2.63 (m, 1H), 2.32 (dd, *J*=5.5, 16.0 Hz, 1H) ; (DS2) 7.42-6.89 (m, 9H), 6.38 (d, *J*=9.5 Hz, 1H), 5.47 (dd, *J*=4.0, 9.5 Hz, 1H), 3.68 (s, 3H), 3.50 (d, *J*=11.5 Hz, 1H), 3.12-3.00 (m, 1H), 3.05-2.97 (m, 1H), 2.74-2.63 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (DS1) 173.7, 137.0, 133.5, 129.5, 128.7 (2C), 128.6, 128.2, 128.0, 127.5, 127.3, 126.7, 125.9, 54.8, 52.0, 36.9, 32.9; (DS2) 173.7, 137.4, 133.8, 130.5, 128.7, 128.6, 128.5, 128.3, 128.1, 127.5, 127.3, 126.7, 126.0, 54.2, 52.0, 36.7, 30.7; FTIR (film) 3032, 2949, 1731, 1490, 1454, 1151 cm^{-1}; LRMS (ESI) *m/z* (relative intensity): 301 (100); HRMS (ESI) *m/z* calcd for $[C_{19}H_{18}O_2Na]^+$ ($[M+Na]^+$): 301.1199. Found: 301.1202.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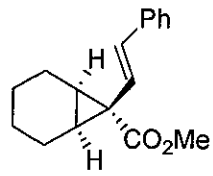
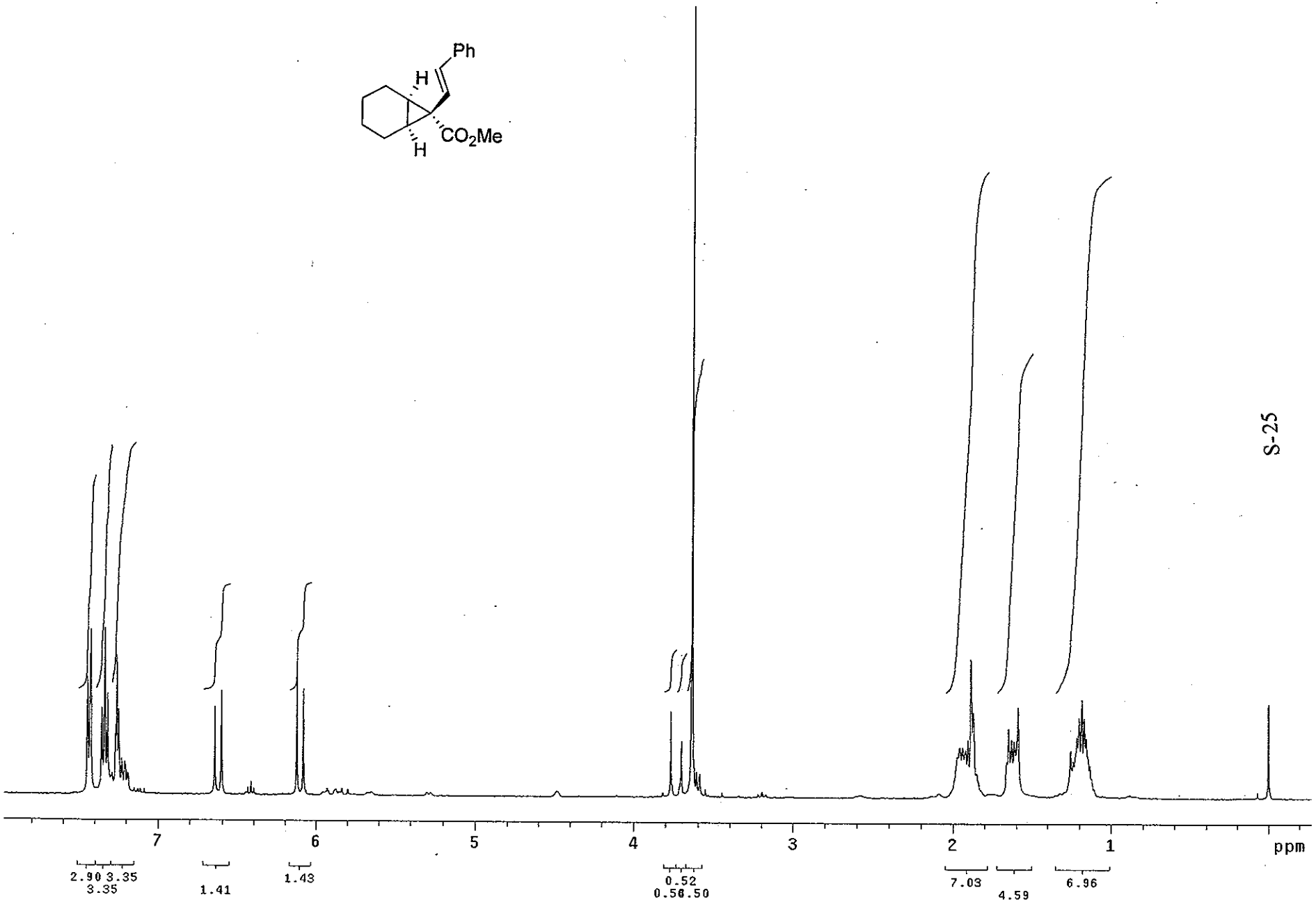


(±)-(1*S*,6*R*,7*R*)-Methyl 7-styrylbicyclo[4.1.0]heptane-7-carboxylate (Table 2, Entry 1): *Ag*: Methyl phenylvinyldiazoacetate (7) (87.2 mg, 0.43 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (18.6 mg, 0.05 mmol, 12 mol%) and cyclohexene (0.38 mL, 4.2 mmol, 10 equiv) in 8 mL of CH_2Cl_2. Purification by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient gave the title compound as a colorless oil (46.9 mg, 0.183mmol, 43% yield). R_f = 0.47 (20% ethyl acetate/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.25 (m, 5H), 6.63 (d, *J*=16.5 Hz, 1H), 6.10 (d, *J*=16.5 Hz, 1H), 3.69 (s, 3H), 1.96-2.87 (m, 4H), 1.65-1.59 (m, 2H), 1.22-1.15 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 137.5, 137.1, 128.5, 127.5, 126.1, 121.9, 52.1, 30.3, 25.1, 21.2, 19.3; FTIR (film) 3023, 2934, 2856, 1713, 1447, 1433, 1236, 1173 cm^{-1}; LRMS (EI) *m/z* (relative intensity): 256 (100); HRMS (EI) *m/z* calcd for $[C_{17}H_{20}O_2]^+$ ($[M^+]$): 256.1458. Found: 256.1462. The stereochemical assignment is based on analogy to previous work by Davies and Müller.[4,6,7]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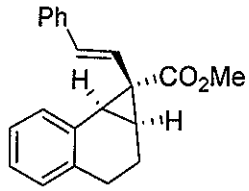
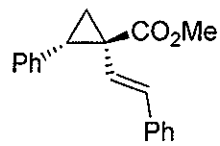
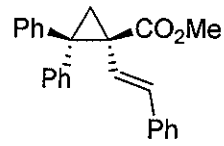
0.56.50
7.03
4.59
6.96



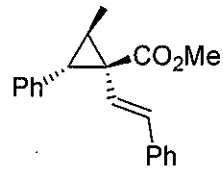
(±)-(1*R*,1α*S*,7β*S*)-Methyl-1α,2,3,7β-tetrahydro-1-styryl-1H-cyclopropa[*a*]naphthalene-1-carboxylate (Table 2, Entry 3A): *Ag*: Methyl phenylvinyldiazoacetate (**7**) (63.5 mg, 0.314 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (10.8 mg, 0.031 mmol, 10 mol%) and 1,2-dihydronaphthalene (0.2 mL, 1.53 mmol, 4.9 equiv) in 8 mL of CH_2Cl_2. The title compound (54.1 mg, 0.178 mmol, 57% yield) was obtained upon purification by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient). mp 76-78 °C; R_f = 0.38 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J*=7.5 Hz, 1H), 7.23-7.08 (m, 7H), 6.95 (d, *J*=7.5 Hz, 1H), 6.17 (d, *J*=16.5 Hz, 1H), 5.97 (d, *J*=16.5 Hz, 1H), 3.70 (s, 3H), 2.94 (d, *J*=9 Hz, 1H), 2.63-2.56 (m, 1H), 2.44-2.35 (m, 2H), 2.10-2.04 (m, 1H), 2.03-2.00 (m, 1H). The spectroscopic data and stereochemical assignment is consistent with previously reported results.[9]



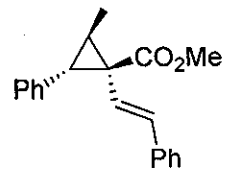
(±)-(1*S*,2*S*)-Methyl 2-phenyl-1-styrylcyclopropanecarboxylate (Table 2, Entry 4): *Ag*: Methyl phenylvinyldiazoacetate (7) (107.7 mg, 0.53 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (18.0 mg, 0.052 mmol, 10 mol%) and styrene (0.6 mL, 5.2 mmol, 10 equiv) in 5 mL of CH_2Cl_2. The crude mixture was purified by flash column chromatography (5% diethyl ether/pentane to 15% diethyl ether/pentane gradient) to obtain the title compound as a white solid (121.4 mg, 0.436 mmol, 82% yield). *Rh:* Methyl phenylvinyldiazoacetate (7) (102.5 mg, 0.507 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 1 h to a refluxing solution of $Rh_2(OAc)_4$ (2.4 mg, 0.0054 mmol, 1 mol%) and styrene (0.6 mL, 5.2 mmol, 10 equiv) in 5 mL of CH_2Cl_2. The product was purified by flash column chromatography (5% diethyl ether/pentane to 15% diethyl ether/pentane gradient) to obtain the title compound as a white solid (110.8 mg, 0.398 mmol, 78% yield). mp 63-65 °C; R_f = 0.405 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.13 (m, 10H), 6.34 (d, *J*=16 Hz, 1H), 6.13 (d, *J*=16 Hz, 1H), 3.74 (s, 3H), 3.00 (dd, *J*=7.0, 9.0 Hz, 1H), 2.02 (dd, *J*=9.0, 5.0, Hz, 1H) 1.82 (dd *J*=5.0, 7.0 Hz, 1H). The spectroscopic data and stereochemical assignment is consistent with previously reported results.[4]



(±)-(*S*)-Methyl 2,2-diphenyl-1-styrylcyclopropanecarboxylate (Table 2, Entry 5): *Ag*: Methyl phenylvinyldiazoacetate (**7**) (60.6 mg, 0.30 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h at room temperature to a solution of $AgSbF_6$ (13.1 mg, 0.038 mmol, 13 mol%) and 1,1-diphenylethylene (0.3 mL, 1.69 mmol, 5.6 equiv) in 5 mL of CH_2Cl_2. The crude mixture was purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) to obtain the title compound as a white solid (59.6 mg, 0.168 mmol, 56% yield). *Rh:* Methyl phenylvinyldiazoacetate (**7**) (103.4 mg, 0.511 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 2 h to a refluxing solution of $Rh_2(OAc)_4$ (2.5 mg, 0.0056 mmol, 1 mol%) and 1,1-diphenylethylene (0.45 mL, 1.53 mmol, 5 equiv) in 8 mL of CH_2Cl_2. The crude mixture was purified by flash column chromatography (5% ethyl acetate/hexanes to 15% ethyl acetate/hexanes gradient) to obtain the title compound as a white solid (116.8 mg, 0.329 mmol, 64 % yield). mp 91.5-94 °C; R_f = 0.41 (20% ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.39 (m, 5H), 7.24-7.09 (m, 10H), 6.46 (d, *J*=16.0 Hz, 1H), 6.18 (d, *J*=16.0 Hz, 1H), 3.39 (s, 3H), 2.62 (d, *J*=5.5 Hz, 1H), 2.05 (d, *J*=5.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 142.1, 140.8, 137.3, 130.9, 129.9, 128.8, 128.3 (3C), 127.1, 126.8 (2C), 126.7, 126.1, 51.8, 47.1, 38.9, 22.6; FTIR (film) 3025, 2948, 1730, 1493, 1447, 1237, 1125 cm^{-1}; Anal. calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.42; H, 6.27. The stereochemical assignment is based on analogy to previously reported results.[5,10,11]



(±)-(1*R*,2*R*,3*S*)-Methyl 2-methyl-3-phenyl-1-styrylcyclopropanecarboxylate (Table 2, Entry 6): *Ag*: Methyl phenylvinyldiazoacetate (**7**) (61 mg, 0.301 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (10.8 mg, 031 mmol, 10 mol%) and *trans*-*β*-methylstyrene (0.2 mL, 1.54 mmol, 5.1 equiv) in 8 mL of CH_2Cl_2. Purification by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient) gave the title compound as a colorless oil (57.3 mg, 0.196 mmol, 65% yield). R_f = 0.39 (20% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.11 (m, 10H), 6.35 (d, *J*=16 Hz, 1H), 5.95 (d, *J*=16 Hz, 1H), 3.77 (s, 3H), 3.02 (d, *J*=8 Hz, 1H), 2.15 (m, 1H), 1.43 (d, *J*=6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 132.6, 128.9, 128.8, 128.6, 128.4, 128.0, 127.2, 126.5, 126.1, 126.0, 52.2, 39.4, 38.8, 27.4, 12.8; FTIR (film) 3026, 2951, 1719, 1449, 1434, 1241, 1154 cm^{-1}; LRMS (ESI) *m/z* (relative intensity): 315 (100); HRMS (ESI) *m/z* calcd for $[C_{25}H_{22}O_2Na]^+$ ($[M+Na]^+$): 315.1356. Found: 315.1350. The stereochemical assignment is based on analogy to previously reported results.[4]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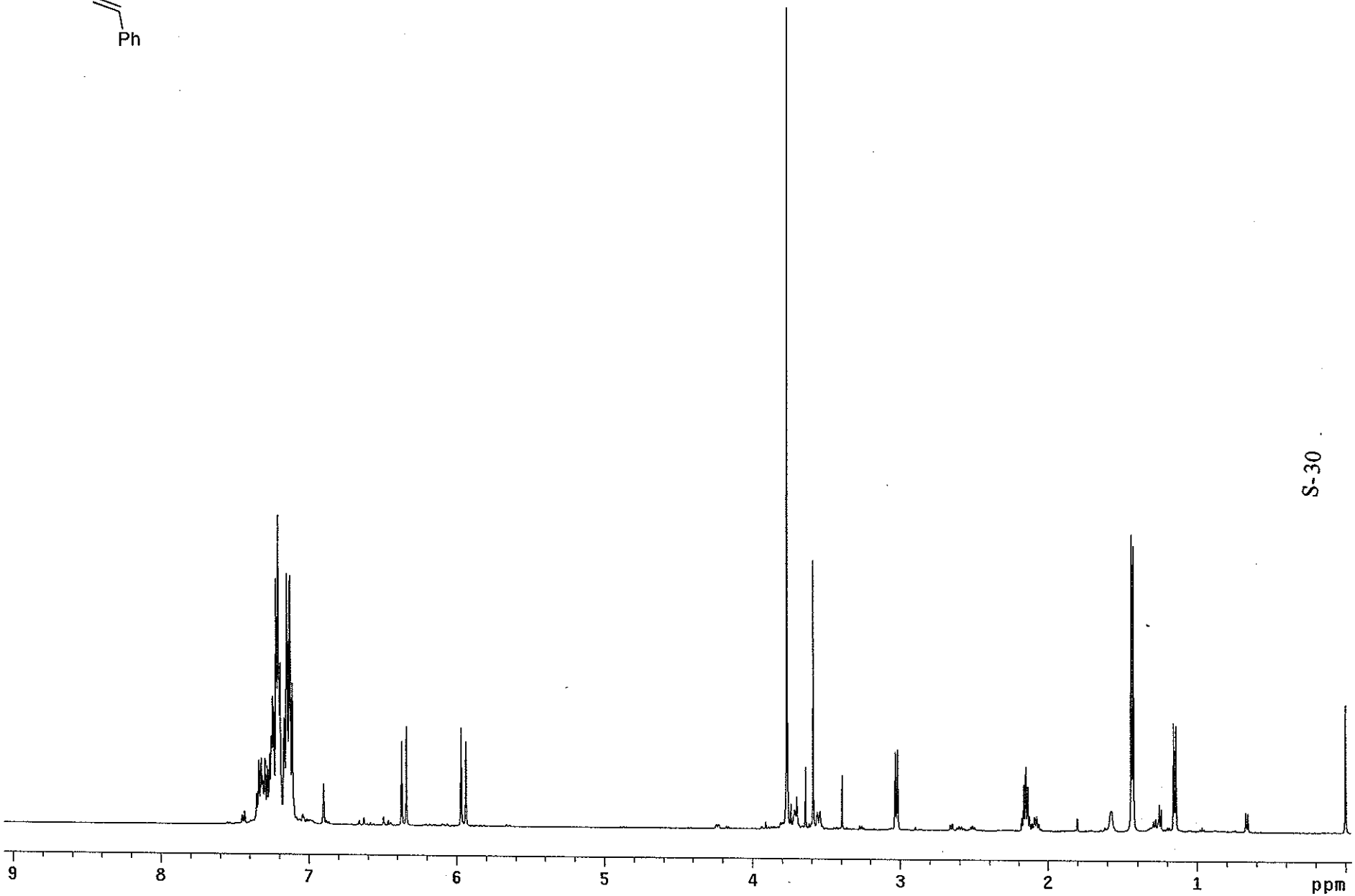
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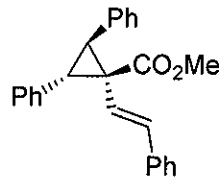
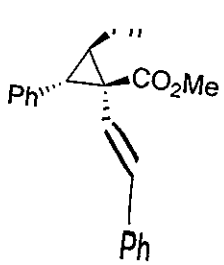


(±)-(2*S*,3*S*)-Methyl 2,3-diphenyl-1-styrylcyclopropanecarboxylate (Table 2, Entry 7): *Ag*: Methyl phenylvinyldiazoacetate (**7**) (115.3 mg, 0.57 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 3 h to a refluxing solution of $AgSbF_6$ (18.6 mg, 0.054 mmol, 10 mol%) and *trans*-stilbene (0.4741 g, 2.63 mmol, 4.6 equiv) in 8 mL of CH_2Cl_2. A light yellow oil (69.3 mg, 0.196 mmol, 34% yield) was obtained upon purification by flash column chromatography (2% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient). R_f = 0.37 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.16 (m, 15H), 6.52 (d, *J*=16 Hz, 1H), 6.08 (d, *J*=16 Hz, 1H), 3.83 (d, *J*=8.0 Hz, 1H), 3.37 (d, *J*=8.0 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 137.0, 136.2, 135.8, 132.9, 129.2, 128.9, 128.4, 128.3, 128.2, 127.4, 127.0, 126.9, 126.2, 125.4, 52.0, 41.4, 37.4, 36.1; FTIR (film) 3026, 2949, 1725, 1603, 1497, 1254 cm^{-1}; LRMS (ESI) *m/z* (relative intensity): 355 (100), 377 (12); HRMS (EI) *m/z* calcd for $[C_{25}H_{22}NaO_2]^+$ ($[M+Na]^+$): 377.1512. Found: 377.1518. The stereochemical assignment is based on analogy to previously reported results.[4]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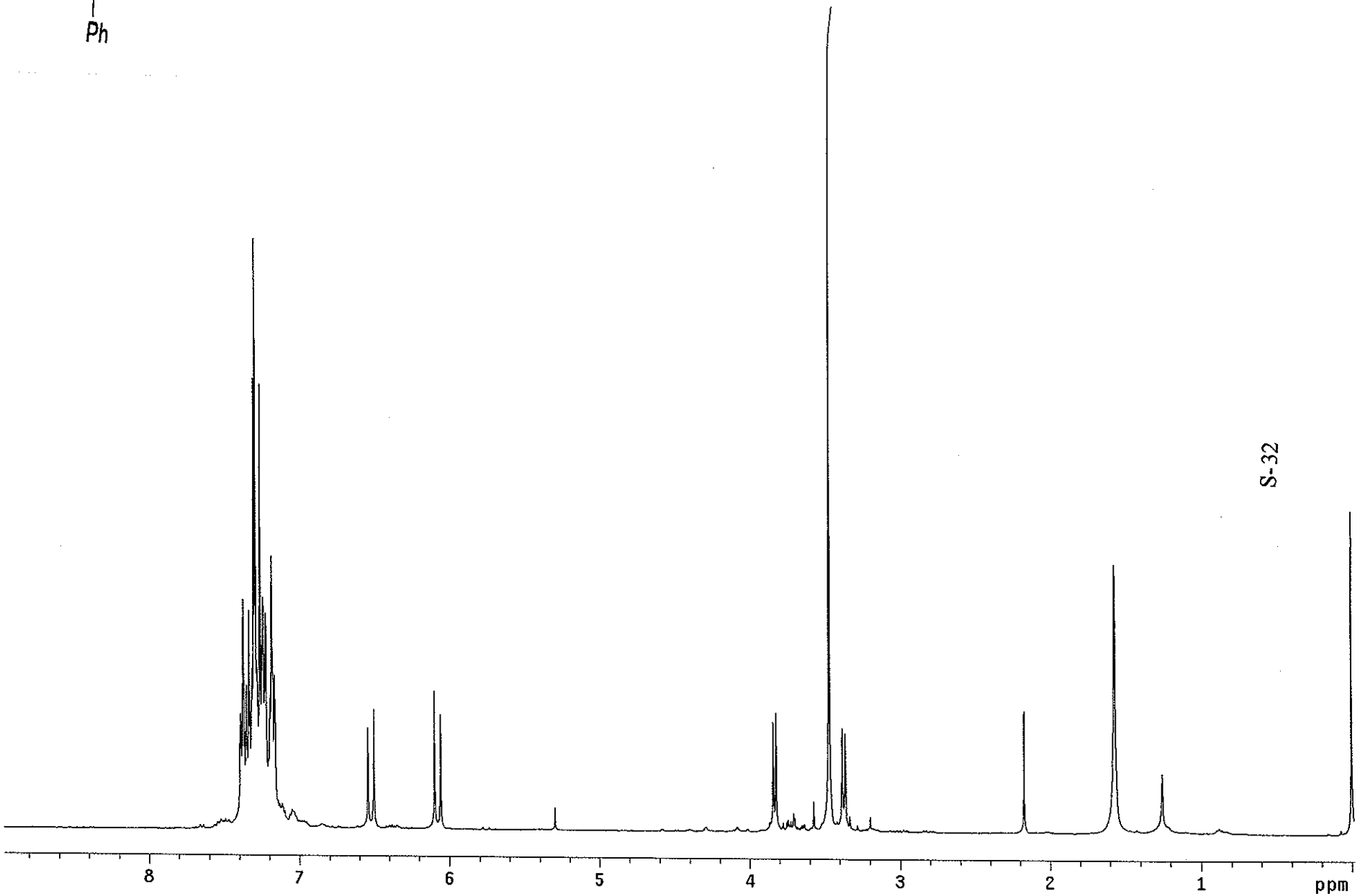
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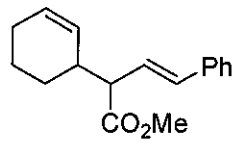
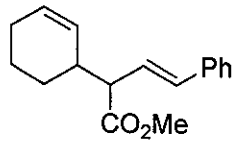


(±)- (3*E*)-Methyl 2-(cyclohex-2-enyl)-4-phenylbut-3-enoate (Table 4, Entry 1B): *Rh:* Methyl phenylvinyldiazoacetate (**7**) (107.8 mg, 0.533 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 2 h to a refluxing solution of $Rh_2(OAc)_4$ (2.3 mg, 0.0052 mmol, 1 mol%) and cyclohexene (0.5 mL, 4.9 mmol, 9 equiv) in 8 mL of CH_2Cl_2. The crude product were purified by flash column chromatography (5% ethyl acetate/pentane to 10% ethyl acetate/pentane gradient) to obtain the title compound as a colorless oil (29.7 mg, 0.116 mmol, 22% yield) as a combination of cyclopropane and cyclohexene (title compound). R_f = 0.51 (20% ethyl acetate/hexanes) as a 2:1 mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.21 (m, 5H), 6.47 (d, *J*=15.5 Hz, 1H), 6.24-6.15 (m, 1H), 5.78-5.74 (m, 1H), 5.65 (br d, DS1, *J*=10.0 Hz, 1H), 5.50 (br d, DS2, *J*=9.0 Hz, 1H), 3.71 (s, 3H), 3.03-2.99 (m, 1H), 2.61-2.59 (m, 1H), 1.98 (m, 2H), 1.78-1.71 (m, 2H), 1.56-1.33 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 133.6, 133.2, 129.0, 128.5, 127.8, 127.6, 126.4, 126.2, 55.4, 51.8, 38.0, 27.4, 25.1, 21.4; FTIR (film) 3024, 2926, 2858, 1732, 1434, 1156 cm^{-1}; LRMS (ESI) *m/z* (relative intensity): 176 (100), 256 (13); HRMS (EI) *m/z* calcd for $[C_{17}H_{20}O_2]^+$ ($[M^+]$): 256.1458. Found: 256.1467.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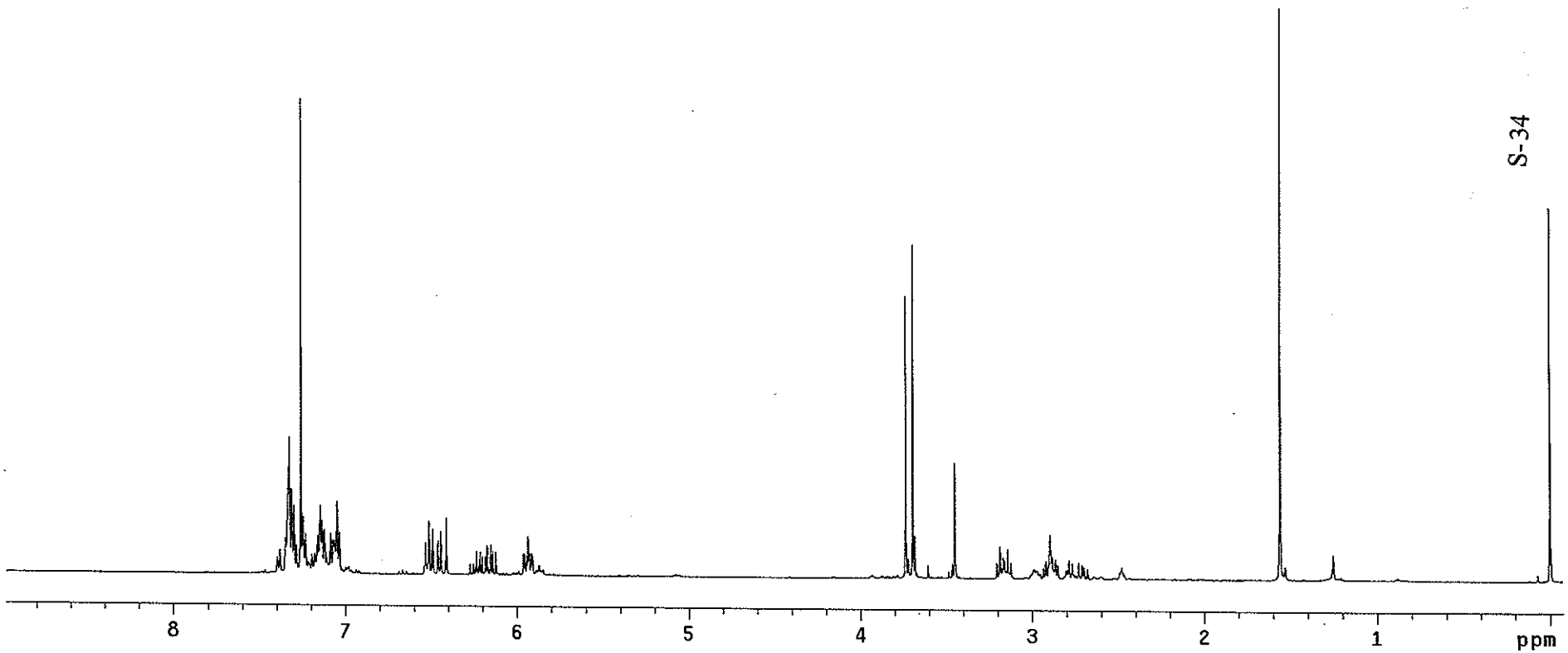
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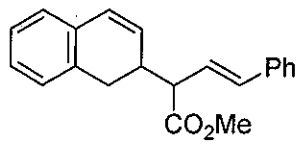

(±)-(3*E*)-Methyl 2-(1,2-dihydronaphthalen-2-yl)-4-phenylbut-3-enoate (Table 4, Entry 3B):[9] *Rh:* Methyl phenylvinyldiazoacetate (**7**) (101.7 mg, 0.5 mmol, 1 equiv) in 3 mL CH_2Cl_2 was added over 2 h to a refluxing solution of $Rh_2(OAc)_4$ (2.4 mg, 0.0054 mmol, 1 mol%) and 1,2-dihydronaphthalene (0.34 mL, 2.6 mmol, 5 equiv) in 8 mL of CH_2Cl_2. The crude product was purified by flash column chromatography (5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes gradient) to obtain a colorless oil (79.8 mg, 0.262 mmol, 52% yield) consisting of mixture of cyclopropane and C–H insertion product (title compound) in a ratio of 2:1. The title compound was isolated as inseparable mixture of C–H/Cope rearrangement diastereomers (1:1.3). R_f = 0.38 (20% ethyl acetate/hexanes). DS1 reported in the literature[9]: ^{1}H NMR DS2 (500 MHz, $CDCl_3$) δ 7.39-7.03 (m, 9H), 6.50 (d, *J*=10 Hz, 1H), 6.45 (d, *J*=16 Hz, 1H), 6.21 (dd, *J*=16.0, 10.0 Hz, 1H), 5.96 (dd, *J*=10.0, 4.0 Hz, 1H), 3.74 (s, 3H), 3.18 (dd, *J*=9.5, 9.5 Hz, 1H), 3.00-2.85 (m, 2H), 2.81-2.67 (m, 1H). The spectroscopic data is consistent with previously reported results.[9]

F: References

(1) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063-3070.

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