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Supporting Information

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"Intermolecular Hydroacylation *via* Hydrogen-Mediated Reductive Coupling of Carboxylic Anhydrides to Styrenes and Activated Olefins: Branched Regioselectivity through the Effect of Triphenylarsine"

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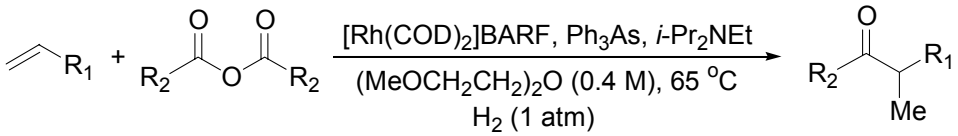
Experimental Section

General. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Diethylene glycol dimethyl ether (diglyme) was distilled from CaH_2 and degassed with Ar prior to use. Ph_3As was recrystallized from EtOH and benzoic anhydride was recrystallized from benzene and pet. ether. Chemical reagents were purchased from Aldrich and Strem chemical companies and used without further purification, unless otherwise noted. Anhydrides[1] and $[Rh(COD)_2]BARF$[2] were prepared according to the previously reported procedures. The products **1**,[3a] **2**,[3b] **3**,[3b] **4**,[3c] **5**,[3d] **10**,[3c] **12**,[3e] **19**,[3f] **25**[3g] are known and were compared with those authentic specimens.

Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still.[3] Melting points were determined on a Thomas-Hoover melting point apparatus in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/e (relative intensity). Accurate masses are reported for the molecular ion (M+1) or a suitable fragment ion.

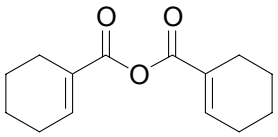
Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Gemini (300 MHz) spectrometer. Chemical Shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 300 (75 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadbrand decoupling.

Representative Procedure for the Reductive Coupling of Anhydrides or Mixed Anhydrides to Olefins



To a solution of anhydride or mixed anhydride (100 mol%), styrene (400 mol%) and *i*Pr_2NEt (200 mol%) in diglyme (0.4 M) in a test tube was added $[Rh(COD)_2]BARF$ (2 mol%) and Ph_3As (4.4 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen until complete consumption of anhydride at which point the reaction mixture was evaporated onto silica gel and the product was isolated by silica gel chromatography.

Cyclohexene-1-carboxylic anhydride



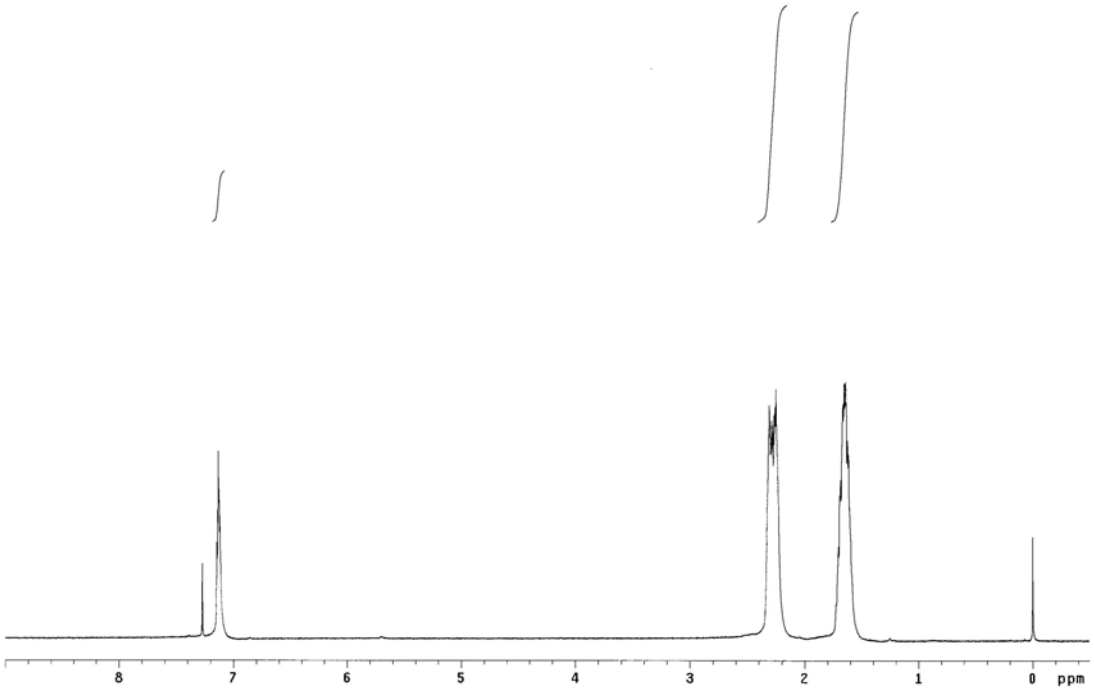
A solution of 1-cyclohexene-1-carboxylic acid (1.26 g, 10 mmol) and distilled Et_3N (1.01g, 10 mmol) in 190 mL of ethyl acetate was stirred in an ice bath. Triphosgene (0.50 g, 1.67 mmol) was added in one portion, upon which the formation of an immediate precipitate of Et_3N-HCl was observed. The reaction was allowed to mix in the ice bath for 10 min, followed by additional 30 min of stirring at room temperature. The solid (Et_3N-HCl) was filtered and washed with a small portion of (10 mL) of ethyl acetate. The filtrate was evaporated to dryness, and the resulting residue was purified by flash column chromatograph (Rf = 0.40, 10% EtOAc/hexane) to afford the product as a colorless oil (0.77 g, 66 %).

^{1}H NMR (300 MHz, $CDCl_3$): 7.13 (m, 2H), 2.31-2.25 (m, 8H), 1.69-1.62 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$): 163.8, 144.4, 130.2, 26.3, 24.0, 21.9, 21.3.

HRMS Calcd. for $C_{14}H_{18}O_3$ (M): 234.1256, Found: 234.1220.

FTIR (neat): 2936, 1769, 1711, 1642, 1422, 1270, 1167, 1055, 994, 923, 854, 714 cm^{-1}.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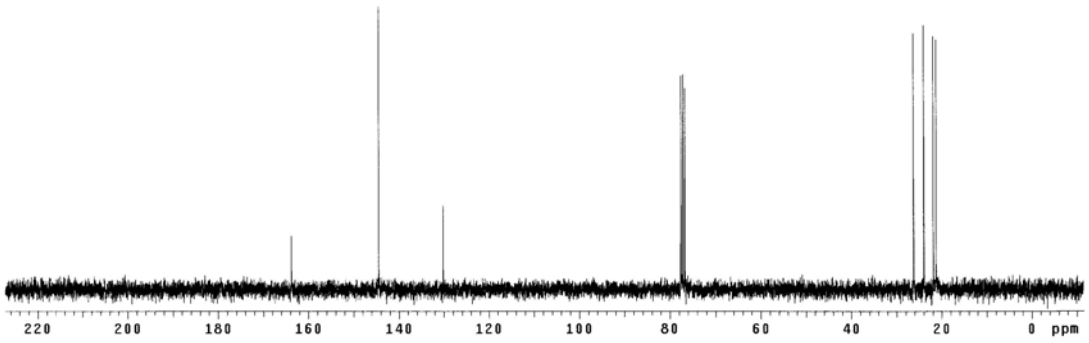
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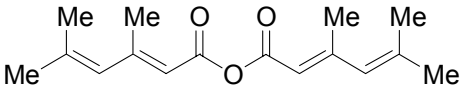
(E)-3,5-dimethyl-2,4-hexadienoic anhydride



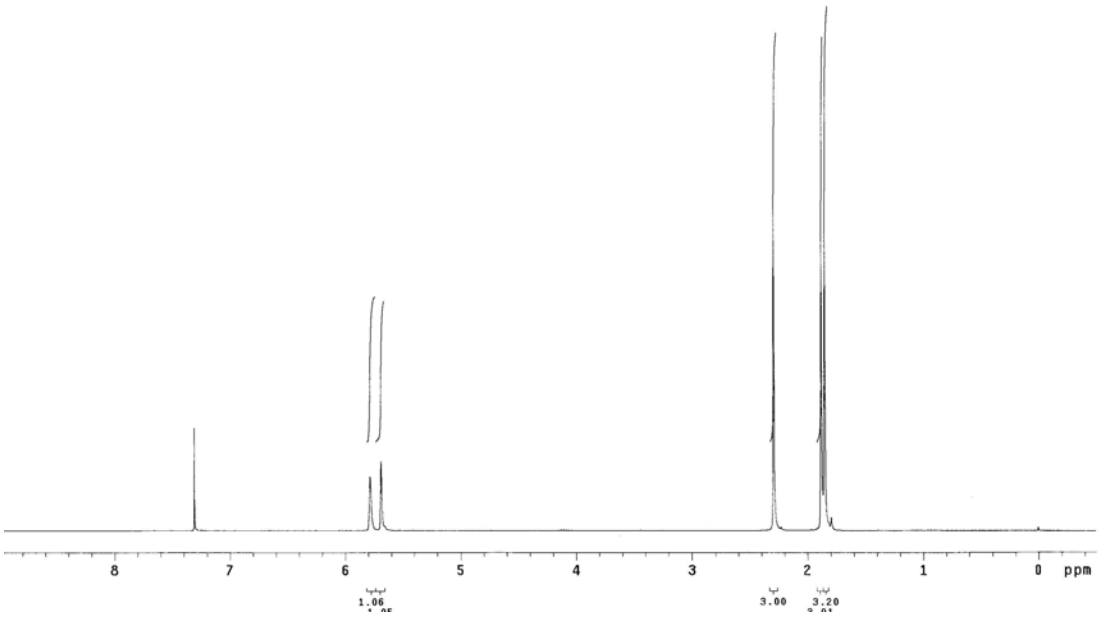
A solution of (E)-3,5-dimethyl-2,4-hexadienoic acid (1.40 g, 10 mmol) and distilled Et_3N (1.01g, 10 mmol) in 190 mL of ethyl acetate was stirred in an ice bath. Triphosgene (0.50 g, 1.67 mmol) was added in one portion, upon which the formation of an immediate precipitate of Et_3N-HCl was observed. The reaction was allowed to mix in the ice bath for 10 min, followed by additional 30 min of stirring at room temperature. The solid (Et_3N-HCl) was filtered and washed with a small portion of (10 mL) of ethyl acetate. The filtrate was evaporated to dryness, and the resulting residue was purified by flash column chromatograph (Rf = 0.50, 10% EtOAc/hexane) to afford the product as a colorless oil (1.18 g, 99 %).

^{1}H NMR (300 MHz, $CDCl_3$): 5.78 (s, 2H), 5.69 (s, 2H), 2.29 (s, 6H), 1.88 (s, 6H), 1.85 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): 162.6, 159.6, 141.0, 128.3, 116.1, 27.4, 20.3, 20.1.

HRMS Calcd. for $C_{16}H_{23}O_3$ (M): 263.1647, Found: 263.1653.

FTIR (neat): 2975, 2919, 1771, 1715, 1604, 1439, 1379, 1327, 1217, 1135, 1055, 1014, 962, 918, 878 cm^{-1}.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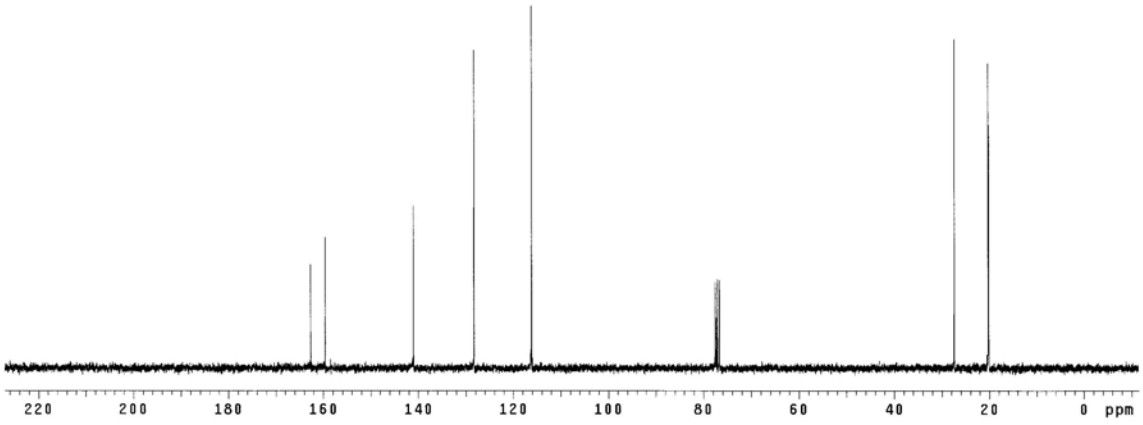
3.00
3.20


220
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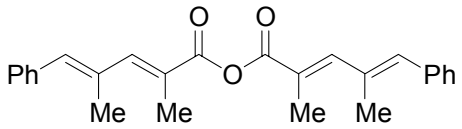
2,4-Dimethyl-5-phenyl-2,4-pentadienoic anhydride



A solution of (2E, 4E)-2,4-dimethyl-5-phenyl-2,4-pentadienoic acid (2.02 g, 10 mmol) and distilled Et_3N (1.01g, 10 mmol) in 190 mL of ethyl acetate was stirred in an ice bath. Triphosgene (0.50 g, 1.67 mmol) was added in one portion, upon which the formation of an immediate precipitate of Et_3N-HCl was observed. The reaction was allowed to mix in the ice bath for 10 min, followed by additional 30 min of stirring at room temperature. The solid (Et_3N-HCl) was filtered and washed with a small portion of (10 mL) of ethyl acetate. The filtrate was evaporated to dryness, and the resulting residue was purified by flash column chromatograph (Rf = 0.33, 10% EtOAc/hexane) to afford the product as a colorless oil (1.85 g, 96 %).

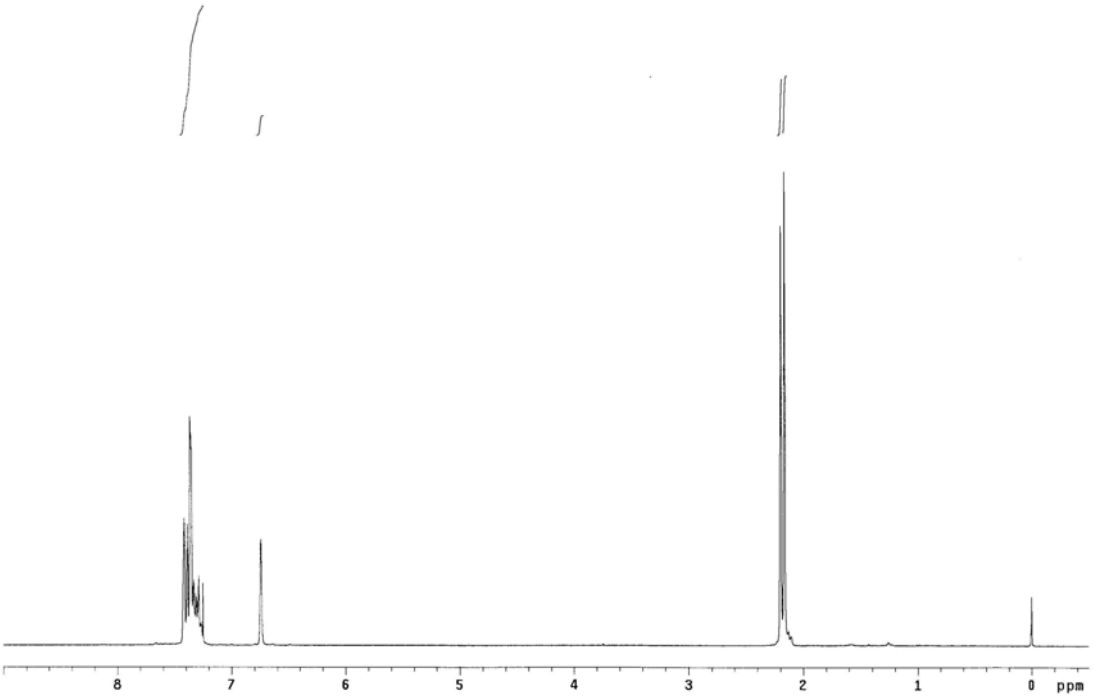
^{1}H NMR (300 MHz, $CDCl_3$): 7.42-7.29 (m, 12H), 6.74 (s, 2H), 2.20 (s, 6H), 2.17 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): 165.5, 147.4, 137.0, 136.7, 134.1, 129.5, 128.5, 127.7, 126.2, 18.4, 14.4.

HRMS Calcd. for $C_{26}H_{27}O_3$ (M): 387.1960, Found: 387.1964.

FTIR (neat): 3022, 2918, 1760, 1701, 1607, 1445, 1386, 1184, 1032, 728, 698 cm^{-1}.

M.P. 97~98 ^oC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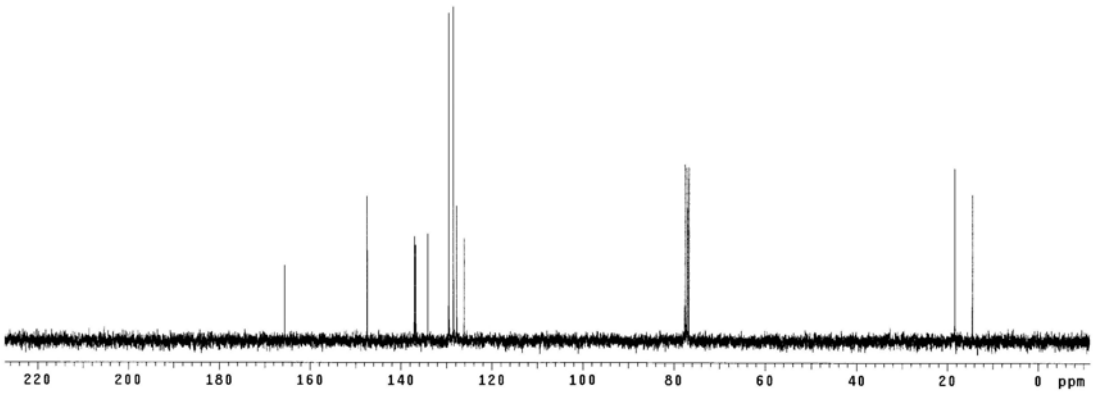
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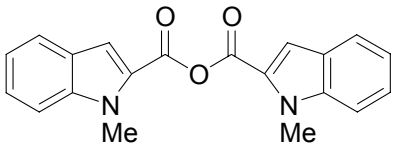
0 ppm

1-Methyl-1*H*-indole-2-carboxylic anhydride



A solution of 1-methylindole-2-carboxylic acid (1.75 g, 10 mmol) and distilled Et_3N (1.01g, 10 mmol) in 190 mL of ethyl acetate was stirred in an ice bath. Triphosgene (0.50 g, 1.67 mmol) was added in one portion, upon which the formation of an immediate precipitate of Et_3N-HCl was observed. The reaction was allowed to mix in the ice bath for 10 min, followed by additional 30 min of stirring at room temperature. The solid (Et_3N-HCl) was filtered and washed with a small portion of (10 mL) of ethyl acetate. The filtrate was evaporated to dryness, and the resulting residue was purified by flash column chromatograph (Rf = 0.48, 20% EtOAc/hexane) to afford the product as a white solid (1.5 g, 90 %).

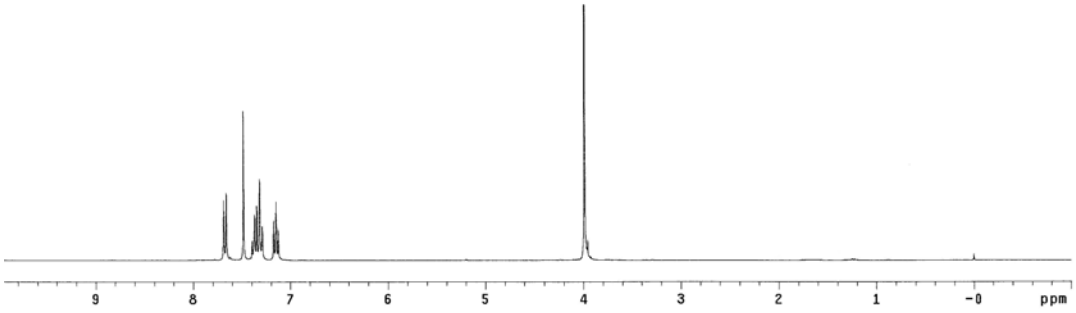
^{1}H NMR (300 MHz, $CDCl_3$): 7.67 (d, J = 8.1 Hz, 2H), 7.49 (s, 2H), 7.40-7.29 (m, 4H), 7.18-7.12 (m, 2H), 3.99 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.9, 140.6, 126.2, 125.8, 125.5, 123.0, 121.0, 113.2, 110.3, 31.4.

HRMS Calcd. for $C_{20}H_{16}N_2O_3$ (M): 332.1161, Found: 332.1166.

FTIR (neat): 2925, 1768, 1710, 1615, 1515, 1468, 1389, 1122, 1029, 741 cm^{-1}.

M.P. 142~143 ^oC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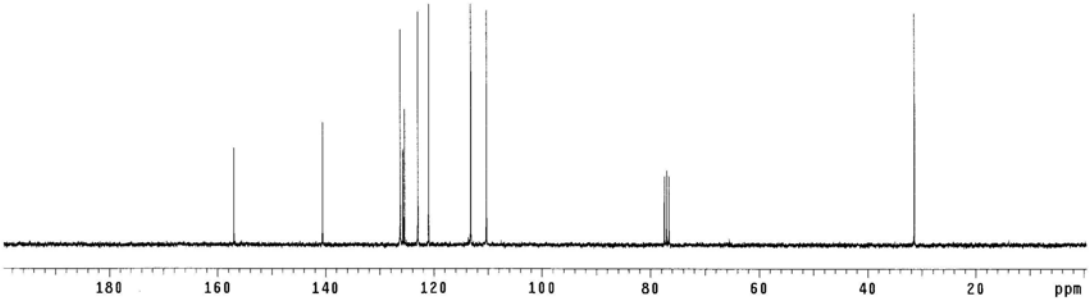
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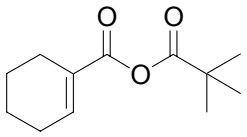
ppm

1-Cyclohexene-1-carboxylic pivalic anhydride



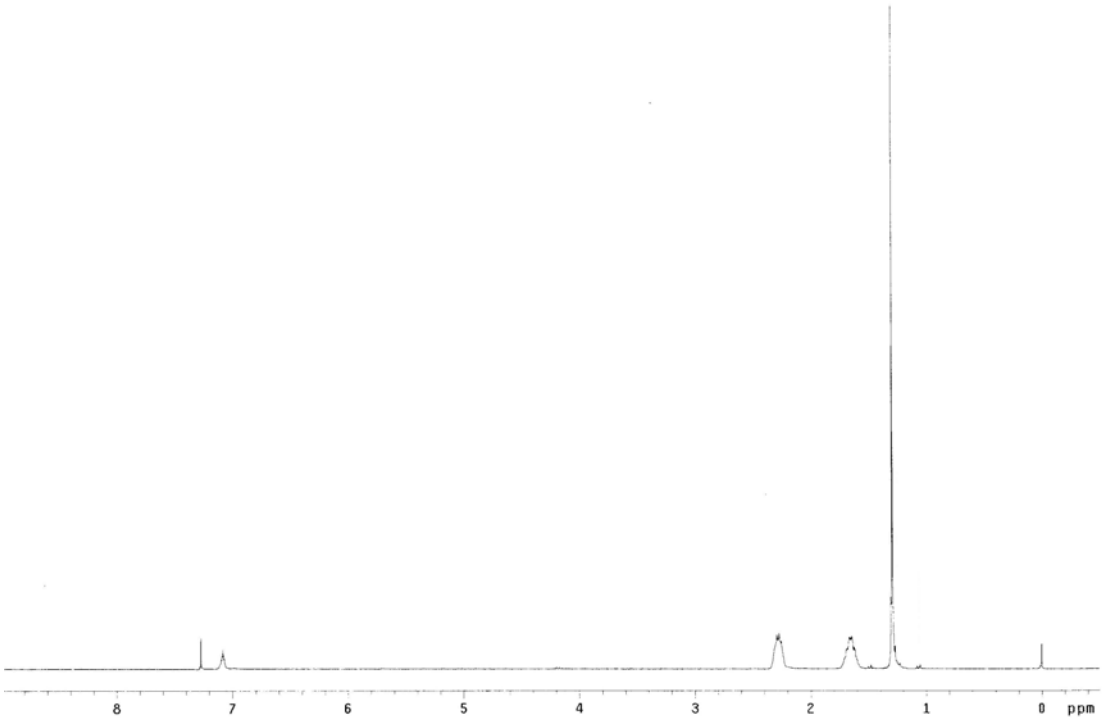
A solution of 1-cyclohexene-1-carboxylic acid (1.26 g, 10 mmol) was added dropwise distilled Et_3N (1.01 g, 10 mmol) in 20 mL of THF at – 5 ℃, and then added trimethyacetyl chloride (1.21 g, 10 mmol) in 10 mL of THF. The reaction mixture was stirred for 30 min at – 5 ℃, and this reaction mixture was allowed to warm to rt and stirred for 30 min. The resulting mixture was filtered and washed with THF and concentrated in vacuo. The resulting residue was purified by flash column chromatograph (Rf = 0.20, 2% EtOAc/hexane) to afford the product as a colorless oil (0.97 g, 46 %).

^{1}H NMR (300 MHz, $CDCl_3$): 7.04 (m, 1H), 2.23 (m, 4H), 1.61 (m, 4H), 1.25 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 174.3, 163.5, 144.8, 130.5, 40.1, 27.2, 26.8, 26.4, 24.1, 21.9, 21.3.

HRMS Calcd. for $C_{20}H_{16}N_2O_3$ (M+1): 211.1334, Found: 211.1339.

FTIR (neat): 2977, 2938, 1809, 1740, 1480, 1212, 1044, 1004, 942, 760 cm^{-1}.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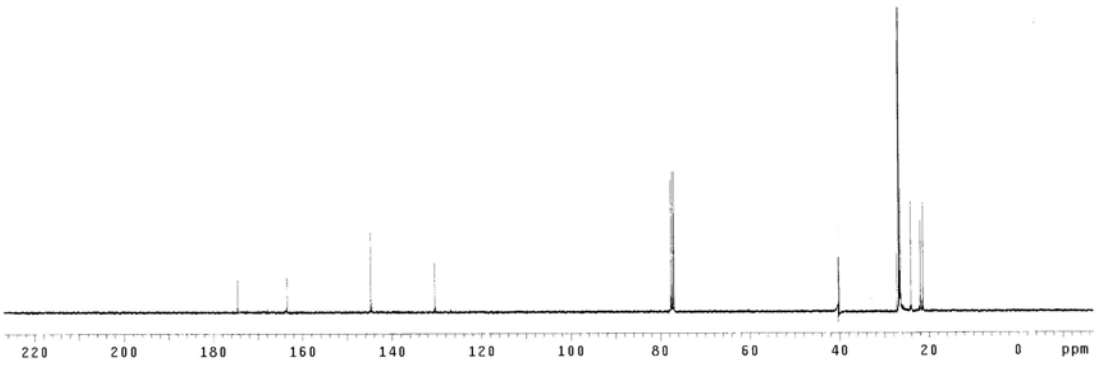
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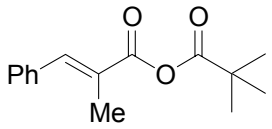
ppm

2-Methyl-3-phenyl-acrylic pivalic anhydride



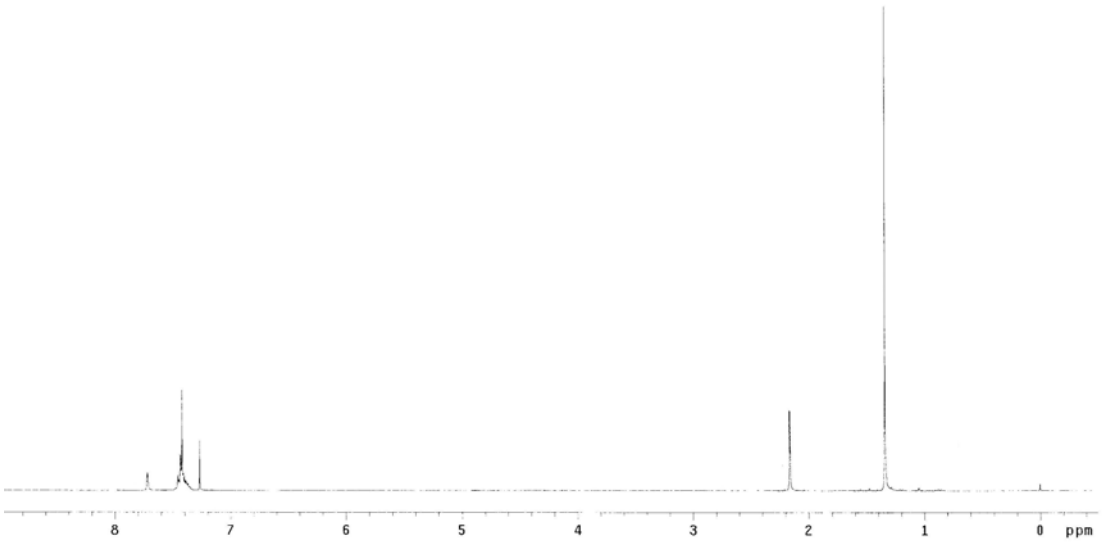
A solution of α-methylcinnamic acid (1.62 g, 10 mmol) was added dropwise distilled Et_3N (1.01 g, 10 mmol) in 20 mL of THF at – 5 ℃, and then added trimethyacetyl chloride (1.21 g, 10 mmol) in 10 mL of THF. The reaction mixture was stirred for 30 min at – 5 ℃, and this reaction mixture was allowed to warm to rt and stirred for 30 min. The resulting mixture was filtered and washed with THF and concentrated in vacuo. The resulting residue was purified by flash column chromatograph (Rf = 0.18, 2% EtOAc/hexane) to afford the product as a colorless oil (1.31 g, 53 %).

^{1}H NMR (300 MHz, $CDCl_3$): 7.72 (d, *J* = 1.8 Hz, 1H), 7.41-7.46 (m, 5H), 2.16 (d, *J* = 1.8 Hz, 3H), 1.34 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 174.3, 164.3, 142.9, 135.3, 130.2, 129.5, 128.8, 128.2, 40.4, 26.8, 14.3.

HRMS Calcd. for $C_{20}H_{16}N_2O_3$ (M): 246.1256, Found: 246.1250.

FTIR (neat): 2977, 1796, 1721, 1631, 1480, 1209, 1043, 1015, 697 cm^{-1}.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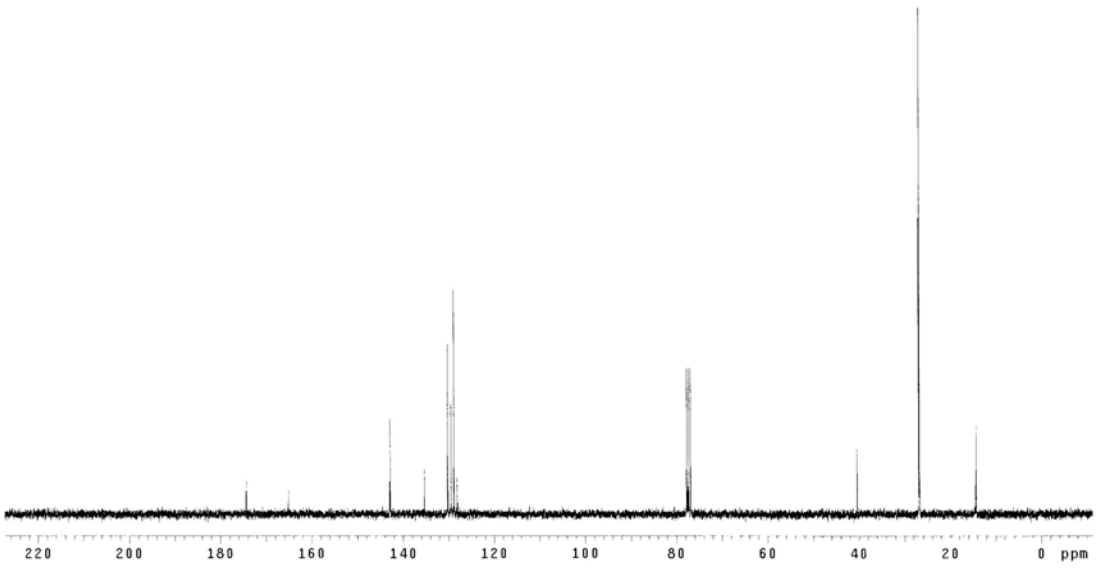
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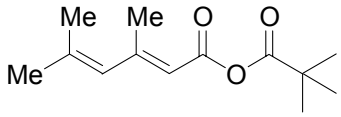
3,5-Dimethyl-hexa-2,4-dienoic pivalic anhydride



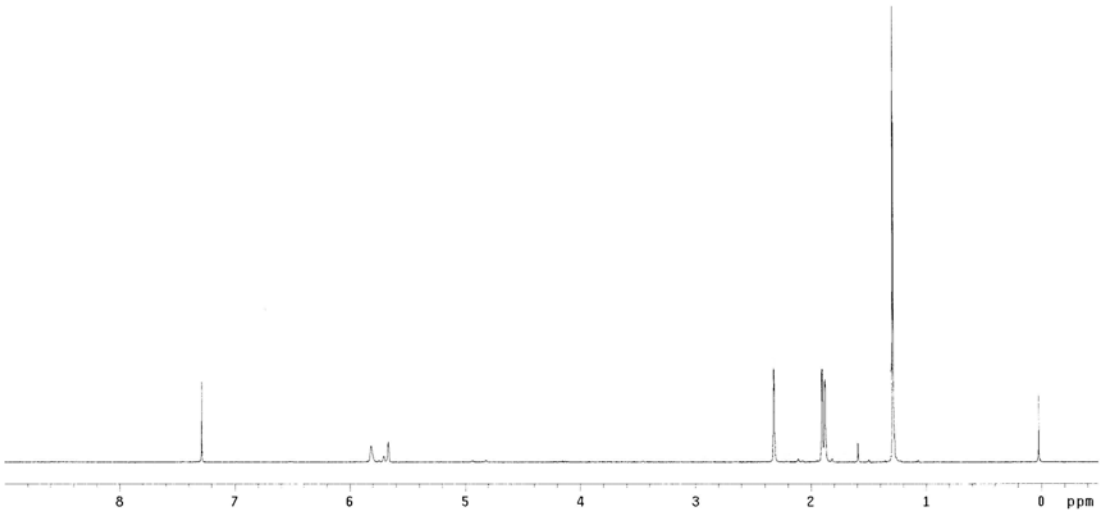
A solution of (E)-3,5-dimethyl-2,4-hexadienoic acid (1.40 g, 10 mmol) was added dropwise distilled Et_3N (1.01 g, 10 mmol) in 20 mL of THF at – 5 ℃, and then added trimethyacetyl chloride (1.21 g, 10 mmol) in 10 mL of THF. The reaction mixture was stirred for 30 min at – 5 ℃, and this reaction mixture was allowed to warm to rt and stirred for 30 min. The resulting mixture was filtered and washed with THF and concentrated in vacuo. The resulting residue was purified by flash column chromatograph (Rf = 0.24, 2% EtOAc/hexane) to afford the product as a colorless oil (1.79 g, 80 %).

^{1}H NMR (300 MHz, $CDCl_3$): 5.82 (s, 1H), 5.67 (s, 1H), 2.32 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 174.5, 162.9, 159.9, 141.2, 128.5, 116.4, 49.9, 27.7, 26.8, 20.5, 20.4.

HRMS Calcd. for $C_{20}H_{16}N_2O_3$ (M+1): 225.1491, Found: 225.1492.

FTIR (neat): 2976, 2936, 1795, 1728, 1606, 1480, 1447, 1396, 1378, 1223, 1050, 1011, 938, 758 cm^{-1}.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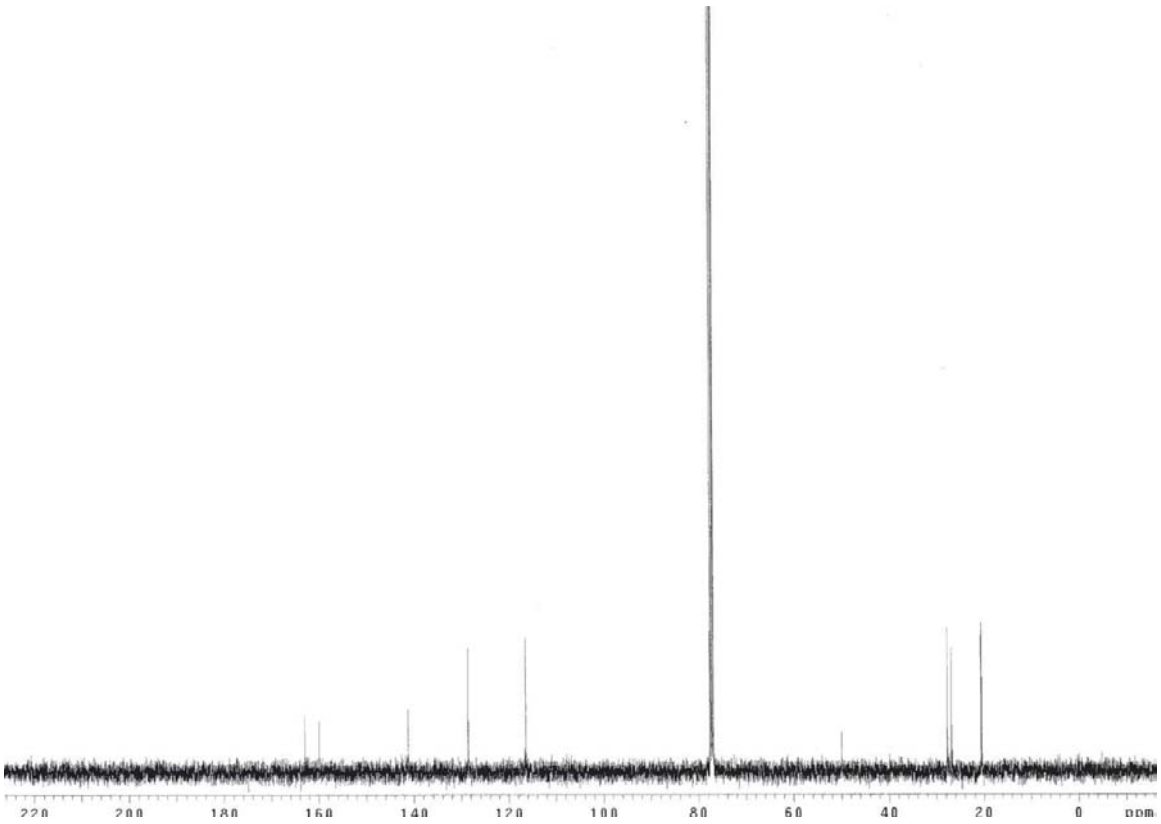
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200
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100
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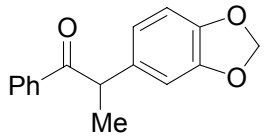
60
40
20
0
ppm

2-Benzo[1,3]dioxol-5-yl-1-phenyl-propan-1-one (6)



6

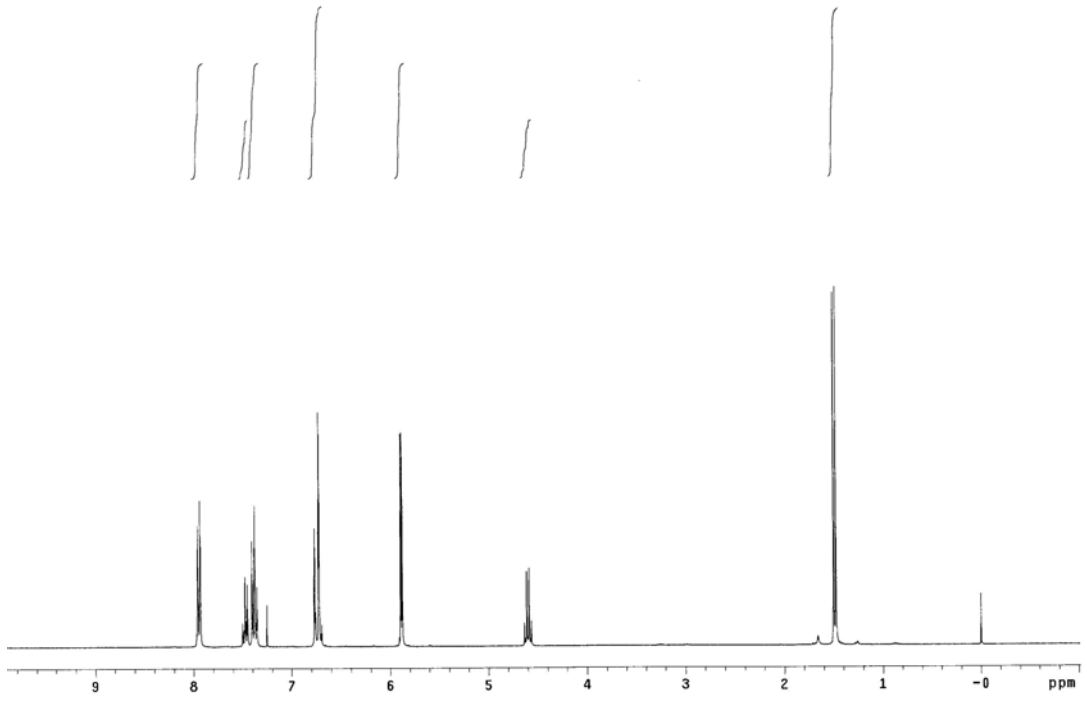
To a solution of benzoic anhydride (68.0 mg, 0.30 mmol, 100 mol%), 5-vinylbenzo[1,3]dioxole[4a] (178 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (7.1 mg, 0.006 mmol, 2 mol%) and Ph_3As (4.0 mg, 0.0132 mmol, 4.4 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.42, 10% EtOAc/hexane) to afford 53.4 mg as a colorless oil (70 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.96-7.93 (m, 2H), 7.50-7.45 (m, 1H), 7.41-7.35 (m, 2H), 6.77-6.70 (m, 3H), 5.89 (dd, *J* = 4.8, 1.5 Hz, 2H), 4.60 (q, *J* = 6.9 Hz, 1H), 1.49 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 200.2, 148.0, 146.5, 136.4, 135.2, 132.8, 128.7, 128.5, 121.0, 108.6, 108.1, 101.0, 47.4, 19.5.

HRMS Calcd. for $C_{16}H_{15}O_3$ (M+1): 255.1021, Found: 255.1024.

FTIR (neat): 2927, 1682, 1596, 1504, 1485, 1448, 1247, 1039, 957, 806, 696 cm^{-1}.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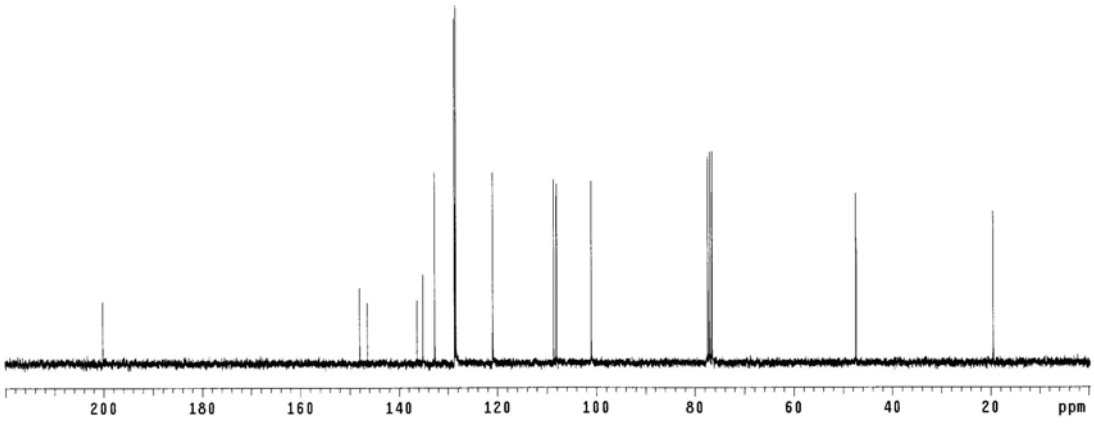
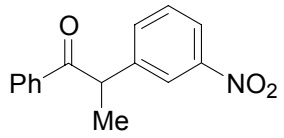

200
180
160
140
120
100
80
60
40
20
ppm

2-(3-Nitrophenyl)-1-phenyl-propan-1-one (7)



7

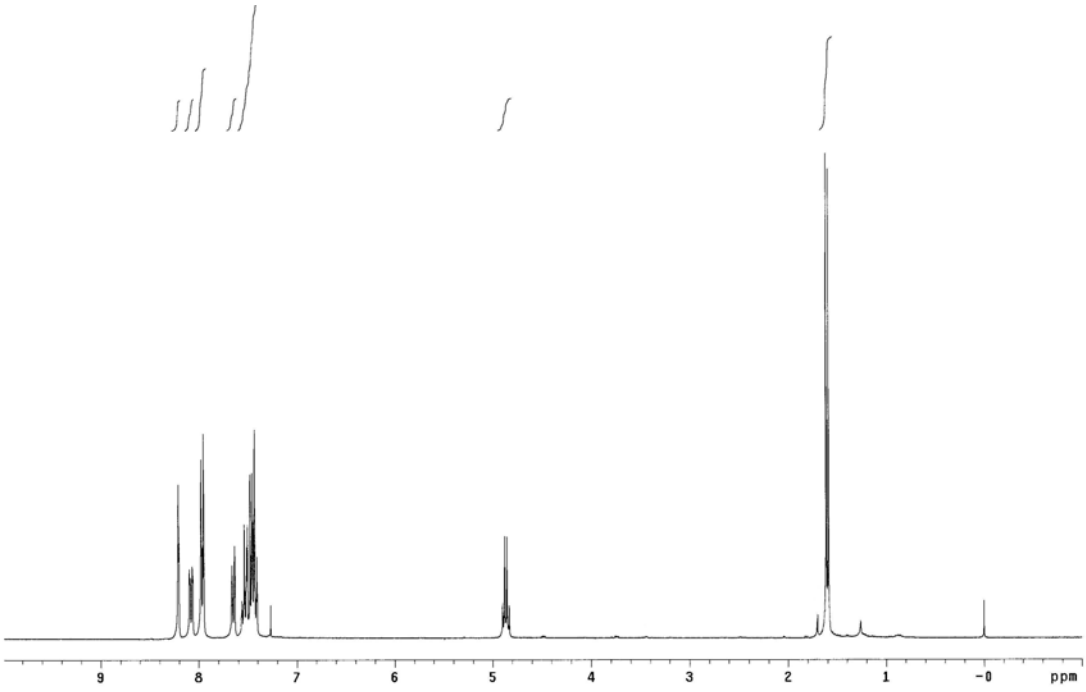
To a solution of benzoic anhydride (68.0 mg, 0.30 mmol, 100 mol%), 3-nitrostyrene (167.0 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (7.1 mg, 0.006 mmol, 2 mol%) and Ph_3As (4.0 mg, 0.0132 mmol, 4.4 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.38, 10% EtOAc/hexane) to afford 63.0 mg as a yellowish oil (82 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.20 (t, *J* = 2.1 Hz, 1H), 8.10-8.06 (m, 1H), 7.98-7.95 (m, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.57-7.41 (m, 4H), 4.86 (q, *J* = 6.9 Hz, 1H), 1.59 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 199.3, 148.5, 143.1, 135.7, 134.0, 133.3, 129.8, 128.7, 128.6, 122.9, 122.1, 46.9, 19.4.

HRMS Calcd. for $C_{15}H_{14}NO_3$ (M+1): 256.0974, Found: 256.0974.

FTIR (neat): 3067, 2978, 2933, 1684, 1529, 1448, 1350, 1221, 1100, 957, 792, 688 cm^{-1}.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4
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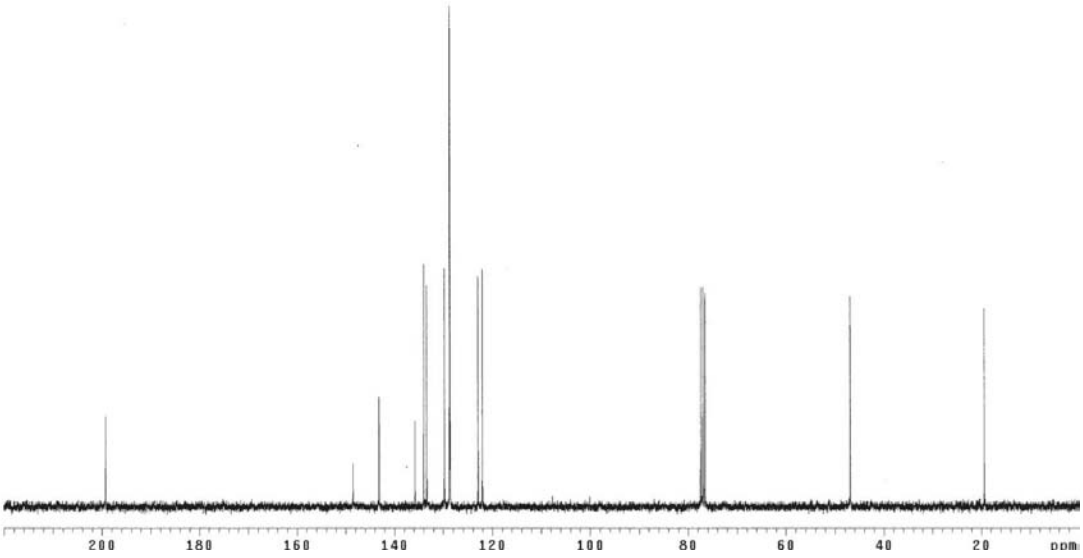
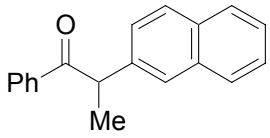
2
1
-0
ppm


200
180
160
140
120
100
80
60
40
20
ppm

2-Naphthalen-2-yl-1-phenyl-propan-1-one (8)



8

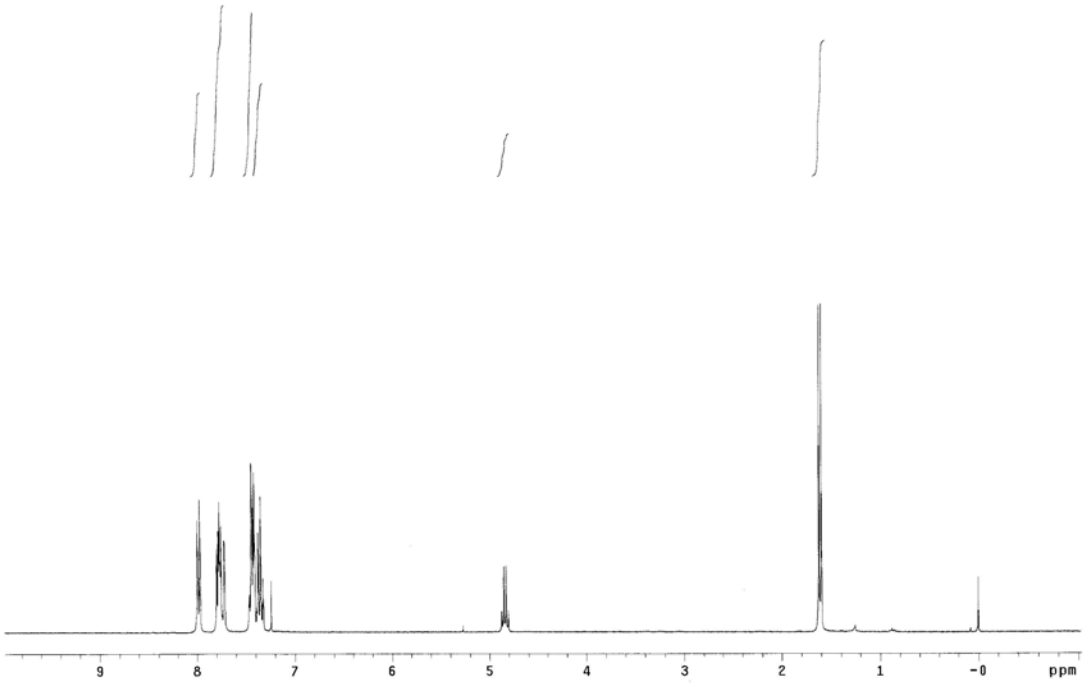
To a solution of benzoic anhydride (68.0 mg, 0.30 mmol, 100 mol%), 2-vinylnaphthalene (185 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (7.1 mg, 0.006 mmol, 2 mol%) and Ph_3As (4.0 mg, 0.0132 mmol, 4.4 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.46, 10% EtOAc/hexane) to afford 58.0 mg as a yellowish oil (75 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.01-7.97 (m, 2H), 7.80-7.74 (m, 3H), 7.72 (m, 1H), 7.47-7.7.41 (m, 4H), 7.39-7.32 (m, 2H), 4.84 (q, J = 6.9 Hz, 1H), 1.61 (d, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 200.2, 139.0, 136.4, 133.7, 132.8, 132.3, 128.8, 128.5, 127.7, 127.6, 126.4, 126.2, 125.9, 125.8, 48.0, 19.5.

HRMS Calcd. for $C_{19}H_{17}O$ (M+1): 261.1279, Found: 261.1281.

FTIR (neat): 3056, 2973, 2929, 1682, 1597, 1448, 1217, 958, 730, 689 cm^{-1}.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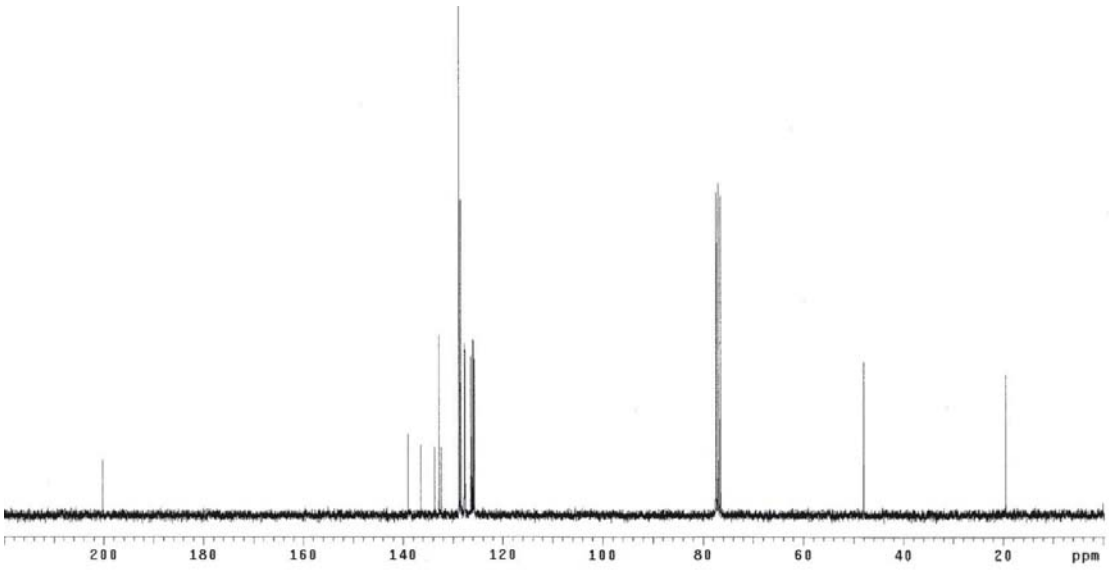
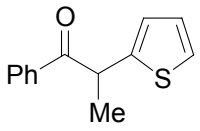
5
4
3
2
1
-0
ppm


200
180
160
140
120
100
80
60
40
20
ppm

1-Phenyl-1-thiophen-2-yl-propan-1-one (9)



9

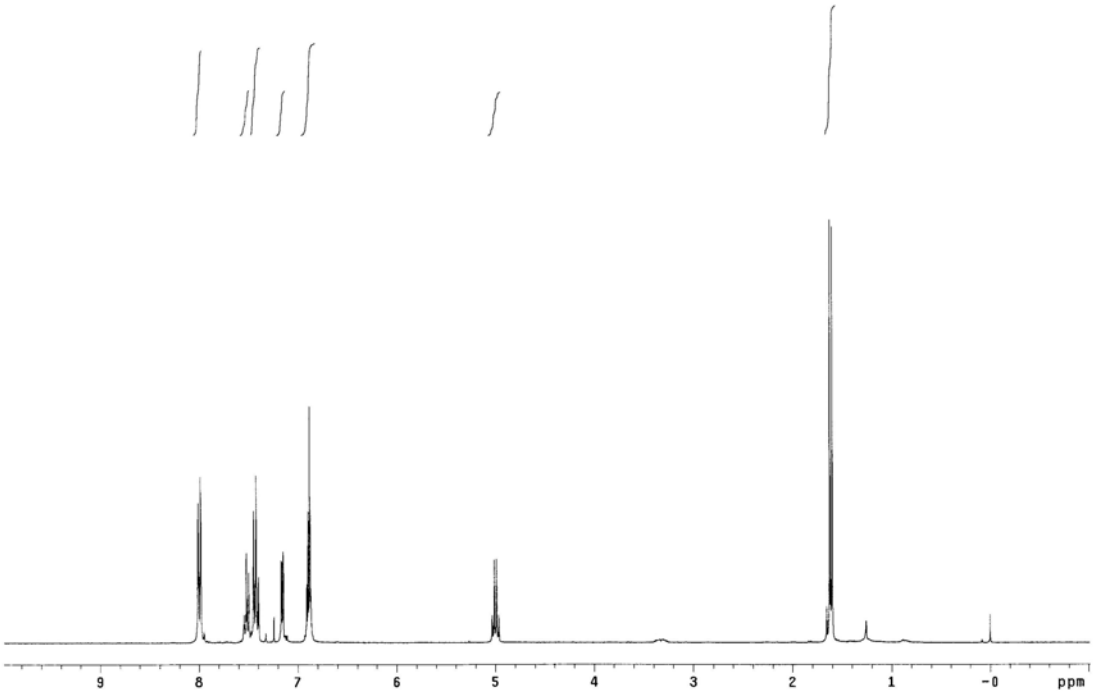
To a solution of benzoic anhydride (68.0 mg, 0.30 mmol, 100 mol%), 2-vinylthiophene[4b] (132 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (7.1 mg, 0.006 mmol, 2 mol%) and Ph_3As (4.0 mg, 0.0132 mmol, 4.4 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.58, 10% EtOAc/hexane) to afford 48.0 mg as a yellowish oil (74 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.01-7.98 (m, 2H), 7.55-7.49 (m, 1H), 7.45-7.40 (m, 2H), 7.17-7.15 (m, 1H), 6.91-6.87 (m, 2H), 5.00 (q, *J* = 6.9 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 199.1, 143.6, 135.9, 133.1, 128.7, 128.6, 126.9, 124.9, 124.5, 42.2, 20.2.

HRMS Calcd. for $C_{13}H_{13}OS$ (M+1): 217.0687, Found: 217.0685.

FTIR (neat): 3066, 2977, 2931, 1683, 1596, 1448, 1329, 1228, 946, 833, 689 cm^{-1}.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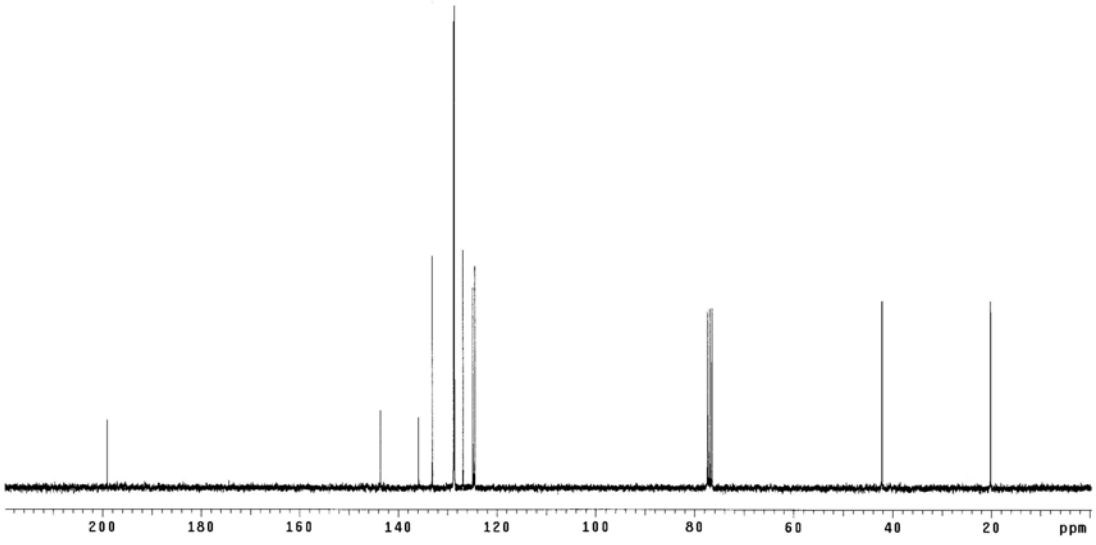
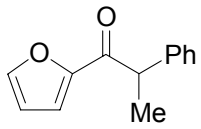
6
5
4
3
2
1
-0
ppm


200
180
160
140
120
100
80
60
40
20
ppm

1-Furan-2-yl-2-phenyl-propan-1-one (11)



11

To a solution of 2-furoic anhydride[5a] (61.9 mg, 0.30 mmol, 100 mol%), styrene (125 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.33, 10% EtOAc/hexane) to afford 37.8 mg as a colorless oil (63 % yield).

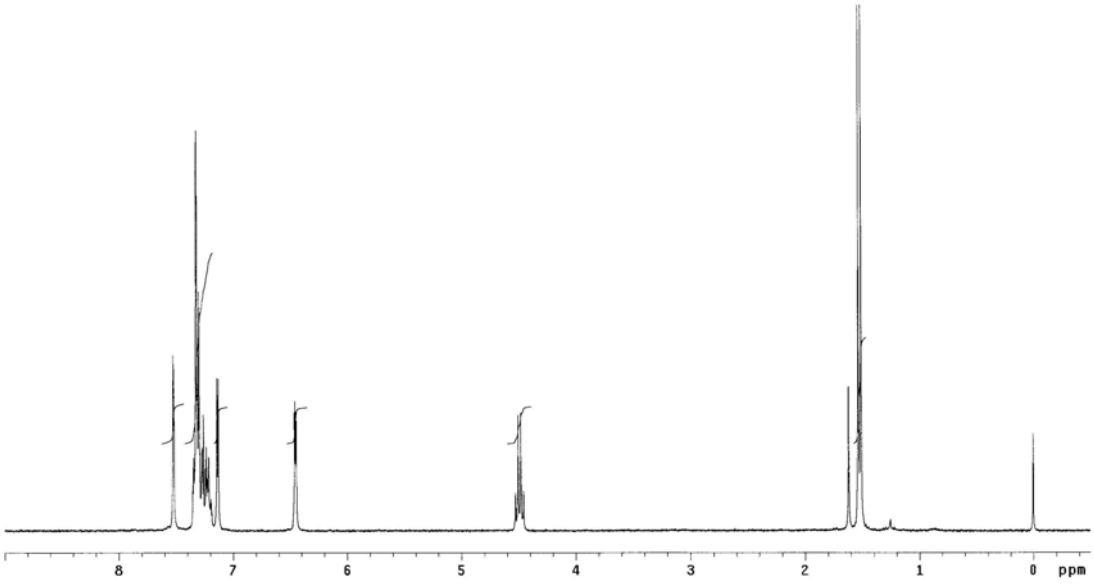
^{1}H NMR (300 MHz, $CDCl_3$): 7.52 (d, *J* = 1.5 Hz, 1H), 7.35-7.19 (m, 5H), 7.14 (d, *J* = 3.6 Hz, 1H), 6.45 (dd, *J* = 3.6, 1.5 Hz, 1H), 4.49 (q, *J* = 6.9 Hz, 1H), 1.53 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 189.7, 152.4, 146.6, 141.1, 129.0, 128.1, 127.3, 118.1, 112.4, 48.2, 18.6.

HRMS Calcd. for $C_{13}H_{13}O_2$ (M+1): 201.0916, Found: 201.0921.

FTIR (neat): 3132, 2977, 2931, 1673, 1565, 1465, 1390, 1330, 1262, 1160, 1015, 962, 885, 761, 699 cm^{-1}.

M.P. 54~55 ^oC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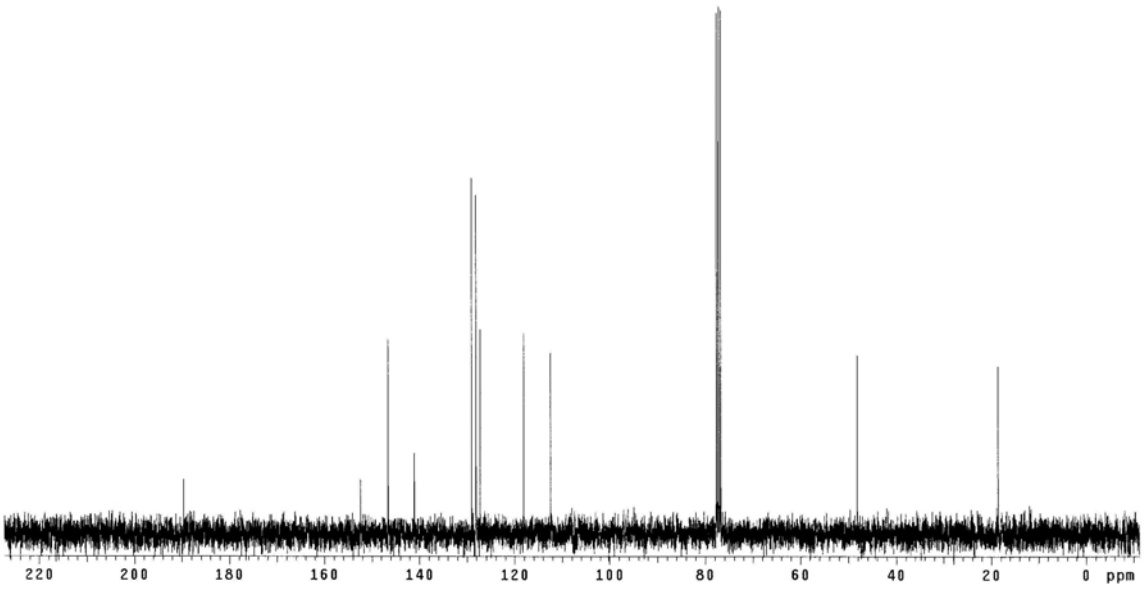
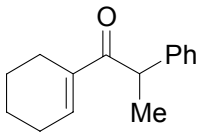
0 ppm


220
200
180
160
140
120
100
80
60
40
20
0 ppm

1-Cyclohex-1-enyl-2-phenyl-propan-1-one (13)



13

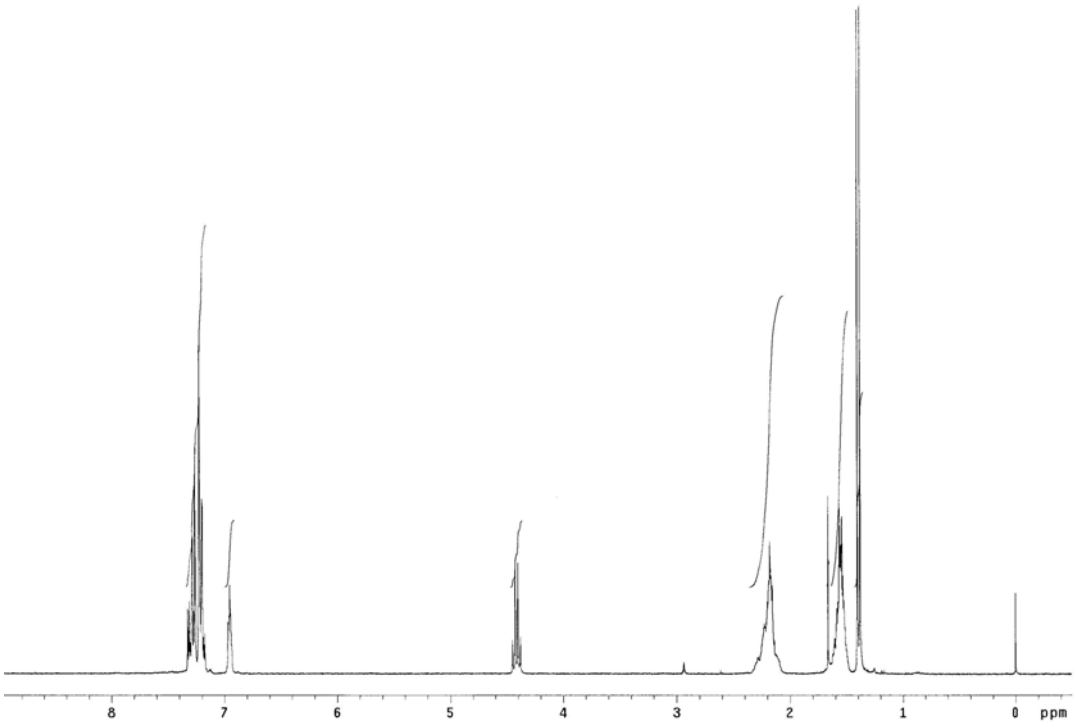
To a solution of cyclohexene-1-carboxylic anhydride (70.3 mg, 0.30 mmol, 100 mol%), styrene (125 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.20, 2% EtOAc/hexane) to afford 54.0 mg as a colorless oil (84 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.32-7.17 (m, 5H), 6.97-6.93 (m, 1H), 4.41 (q, *J* = 6.9 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 201.7, 142.6, 140.7, 138.7, 129.0, 127.8, 126.8, 46.2, 26.4, 23.8, 22.2, 21.7, 19.9.

HRMS Calcd. for $C_{15}H_{19}O$ (M+1): 215.1436, Found: 215.1440.

FTIR (neat) 2931, 2861, 1663, 1635, 1492, 1451, 1381, 1269, 1208, 1063, 978, 879, 753, 700 cm^{-1}.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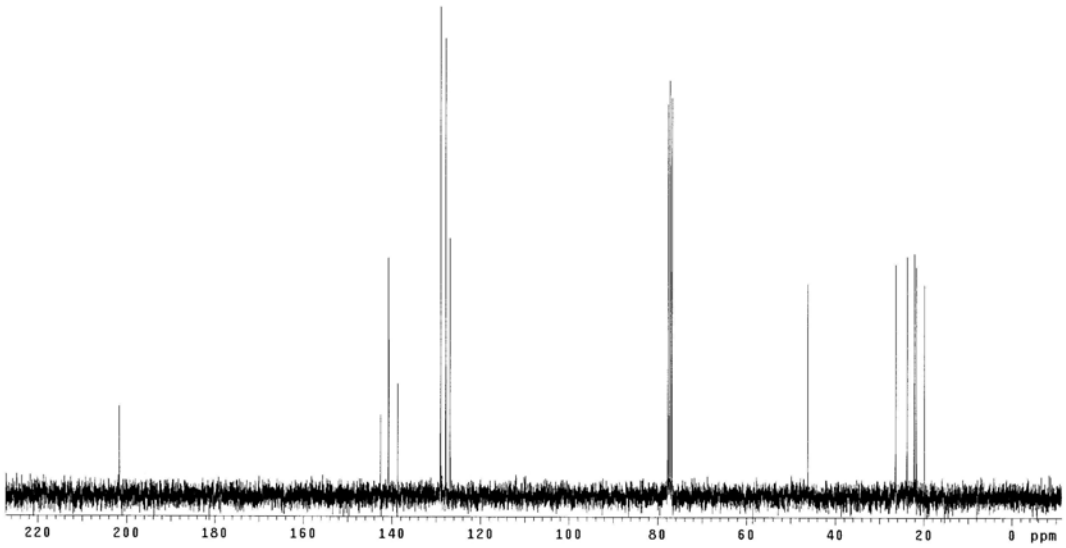
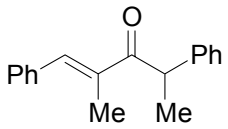

220
200
180
160
140
120
100
80
60
40
20
0 ppm

2-Methyl-1,4-diphenyl-pen-1-en-3-one (14)



14

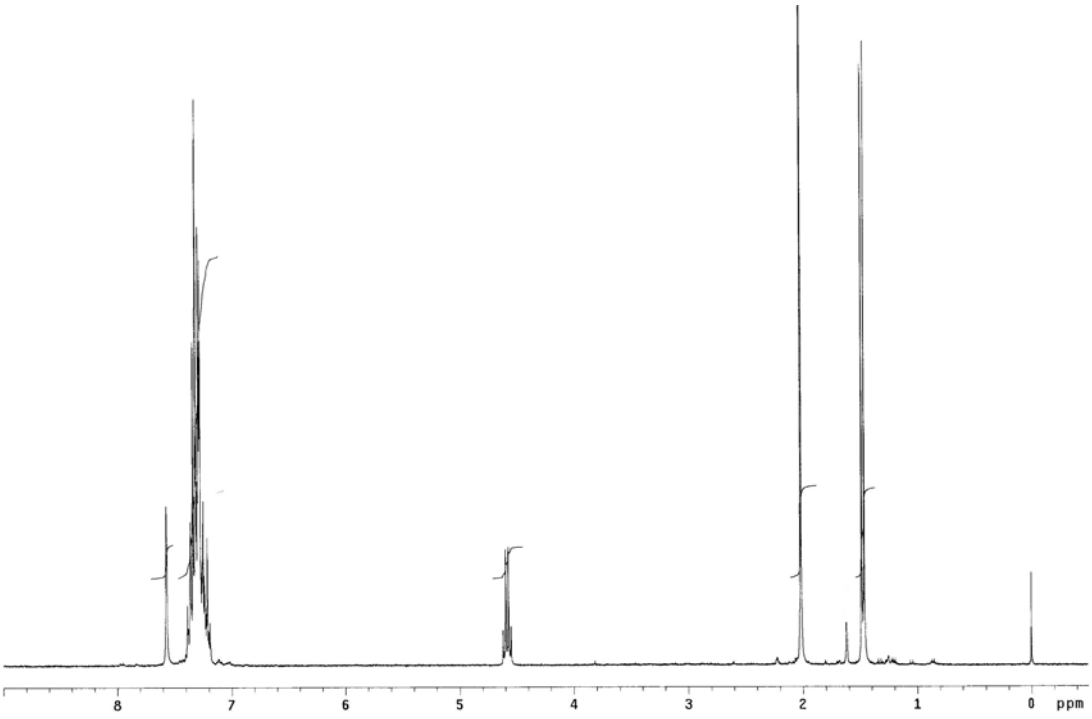
To a solution of α-methylcinnamic anhydride[5b] (91.9 mg, 0.30 mmol, 100 mol%), styrene (125 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.18, 2% EtOAc/hexane) to afford 54.8 mg as a colorless oil (73 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.57 (s, 1H), 7.39-7.19 (m, 10H), 4.59 (q, *J* = 6.9 Hz, 1H), 2.02 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 202.8, 142.4, 139.5, 136.8, 136.2, 129.9, 129.2, 128.7, 128.6, 127.8, 127.0, 47.0, 20.1, 13.9.

HRMS Calcd. for $C_{18}H_{19}O$ (M+1): 251.1436, Found: 251.1442.

FTIR (neat) 3059, 2973, 2929, 1664, 1625, 1491, 1450, 1370, 1212, 1027, 927, 744, 698 cm^{-1}.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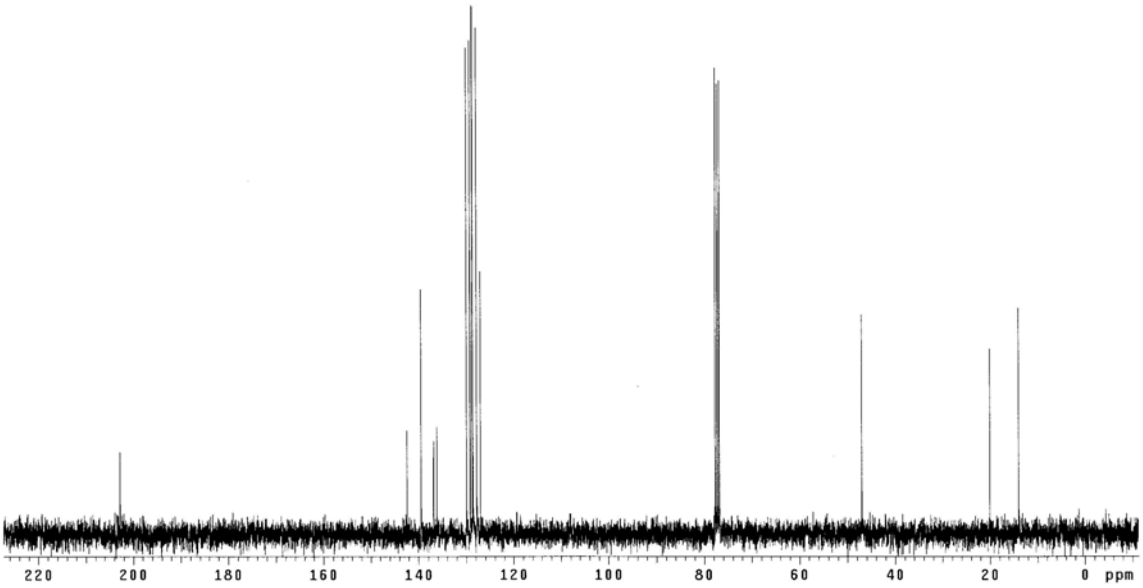
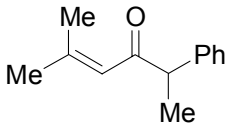
0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

5-Methyl-2-phenyl-hex-4-en-3-one (15)



15

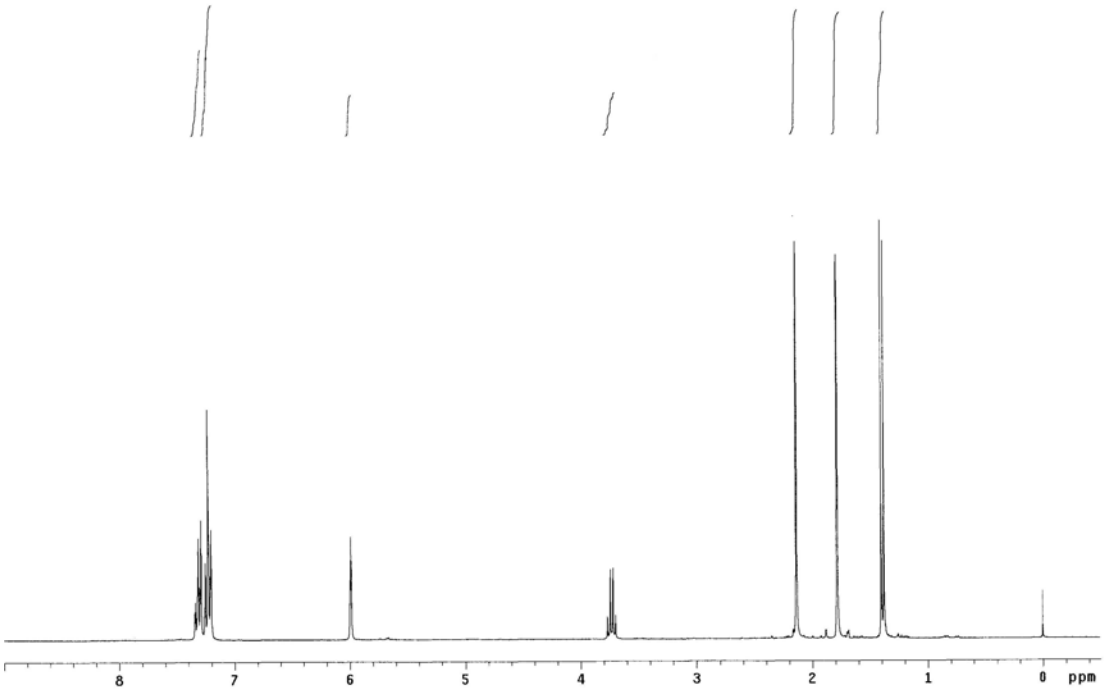
To a solution of 3-methylcrotonic anhydride (54.7 mg, 0.30 mmol, 100 mol%), styrene (125 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.20, 2% EtOAc/hexane) to afford 52.5 mg as a colorless oil (93 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.34-7.29 (m, 2H), 7.26-7.20 (m, 3H), 5.99 (septet, *J* = 1.2 Hz, 1H), 3.73 (q, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 1.2 Hz, 3H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.39 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 200.3, 156.1, 141.2, 128.7, 127.9, 126.8, 123.0, 53.5, 27.7, 20.8, 17.5.

HRMS Calcd. for $C_{13}H_{17}O$ (M+1): 189.1279, Found: 189.1272.

FTIR (neat): 3026, 2975, 2931, 1683, 1621, 1493, 1451, 1379, 1207, 1131, 1023, 883, 848, 700 cm^{-1}.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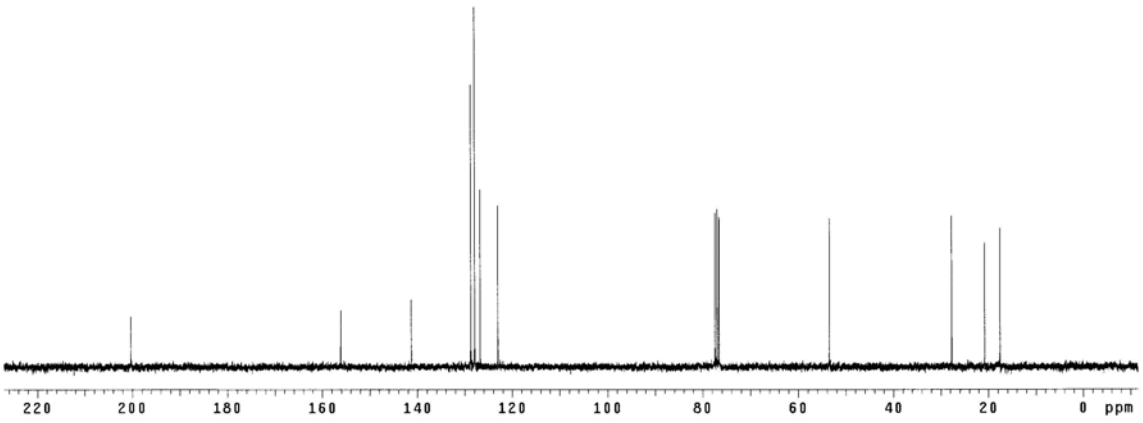
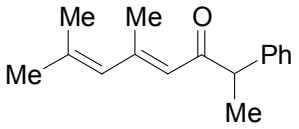
0 ppm


220
200
180
160
140
120
100
80
60
40
20
0 ppm

(E)-5,7-Dimethyl-2-phenyl-octa-4,6-dien-3-one (16)



16

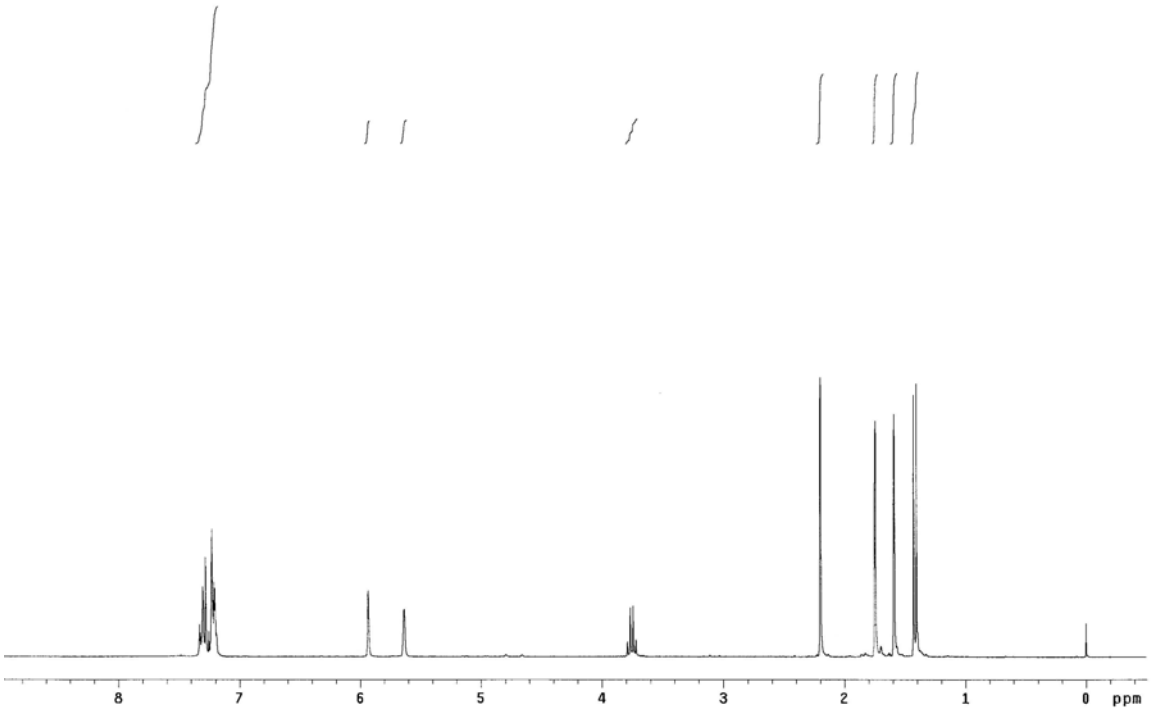
To a solution of (E)-3,5-dimethyl-2,4-hexadienoic anhydride (78.7 mg, 0.30 mmol, 100 mol%), styrene (125 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.20, 2% EtOAc/hexane) to afford 50.0 mg as a colorless oil (74 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.33-7.28 (m, 2H), 7.24-7.19 (m, 3H), 5.94 (s, 1H), 5.64 (s, 1H), 3.75 (q, J = 6.9 Hz, 1H), 2.20 (d, J = 0.9 Hz, 3H), 1.74 (d, J = 1.2 Hz, 3H), 1.59 (d, J = 0.9 Hz, 3H), 1.42 (d, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 200.8, 153.5, 141.5, 139.5, 129.1, 128.9, 128.1, 126.9, 124.3, 54.1, 27.4, 20.2, 20.0, 17.5.

HRMS Calcd. for $C_{16}H_{21}O$ (M+1): 229.1592, Found: 229.1590.

FTIR (neat): 2972, 2930, 1679, 1597, 1451, 1375, 1128, 1046, 905, 862, 699 cm^{-1}.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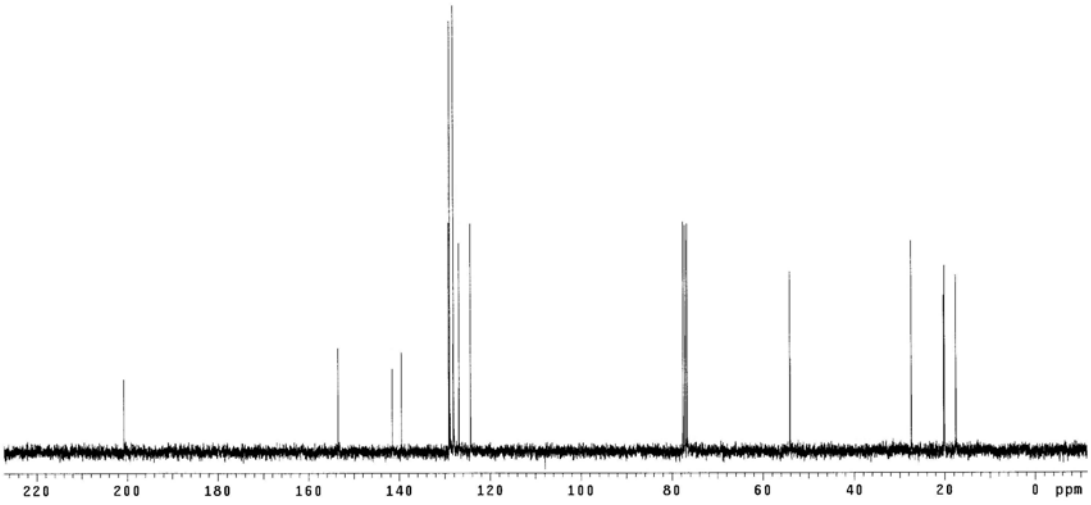
220
200
180
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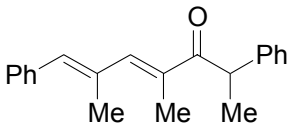
120
100
80
60
40
20
0
ppm

4,6-Dimethyl-2,7-diphenyl-hepta-4,6-dien-3-one (17)



17

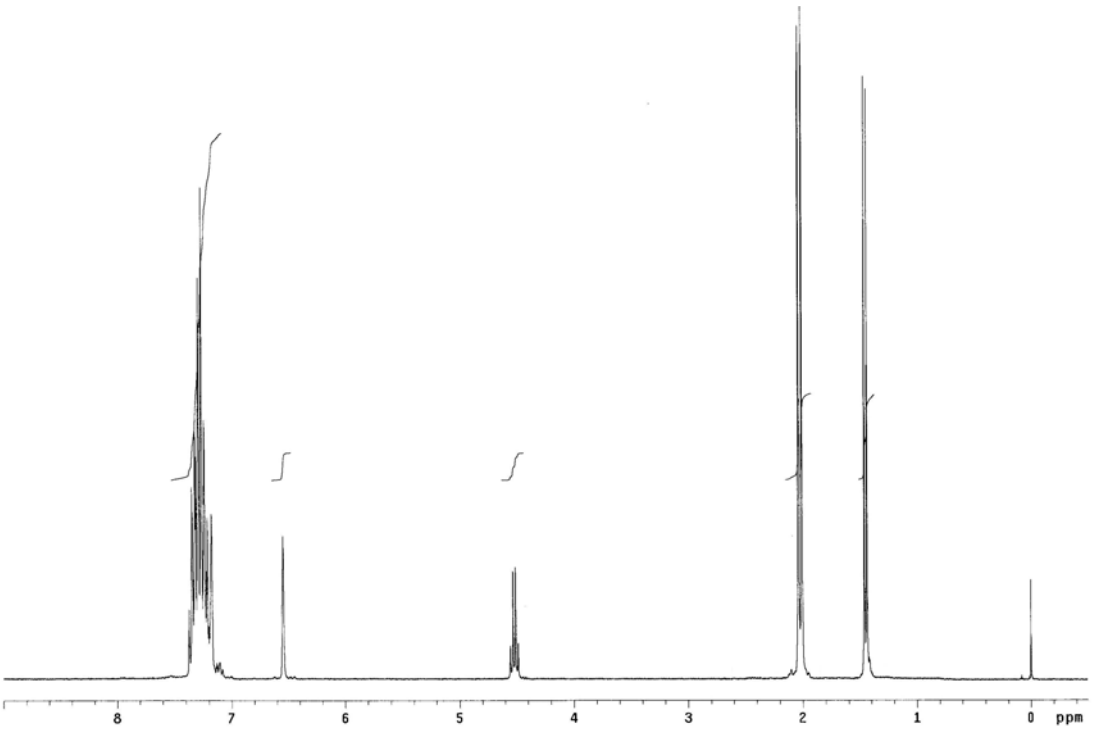
To a solution of 2,4-Dimethyl-5-phenyl-2,4-pentadienoic anhydride (116 mg, 0.30 mmol, 100 mol%), styrene (125 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.15, 2% EtOAc/hexane) to afford 74.1 mg as a colorless oil (85 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.37-7.20 (m, 10H), 7.20 (s, 1H), 6.55 (1H), 4.52 (q, J = 6.9 Hz, 1H), 2.04 (s, 3H), 2.01 (s, 3H), 1.45 (d, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 202.8, 144.0, 142.3, 137.0, 135.2, 134.9, 134.5, 129.3, 128.9, 128.4, 127.7, 127.4, 126.8, 46.7, 19.9, 18.6, 14.0.

HRMS Calcd. for $C_{21}H_{23}O$ (M+1): 291.1749, Found: 291.1749.

FTIR (neat) 3024, 2972, 2929, 1662, 1601, 1491, 1451, 1370, 1215, 1038, 752, 699 cm^{-1}.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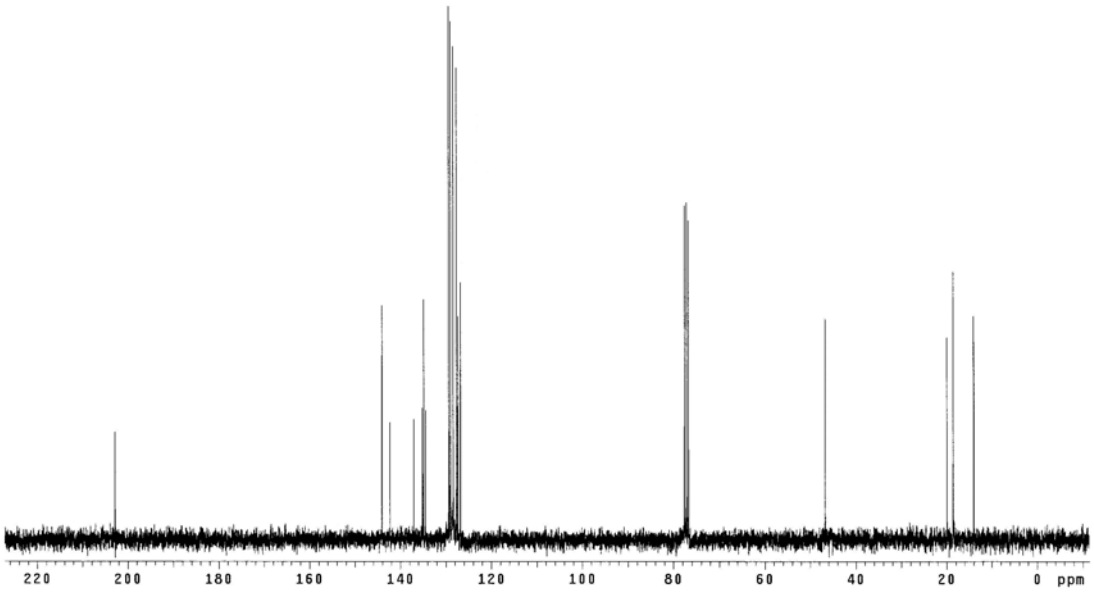
220
200
180
160
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120
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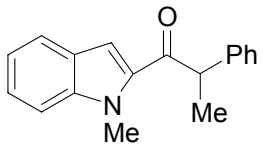
80
60
40
20
0
ppm

1-(1-Methyl-1*H*-indol-2-yl)-2-phenyl-propan-1-one (18)



18

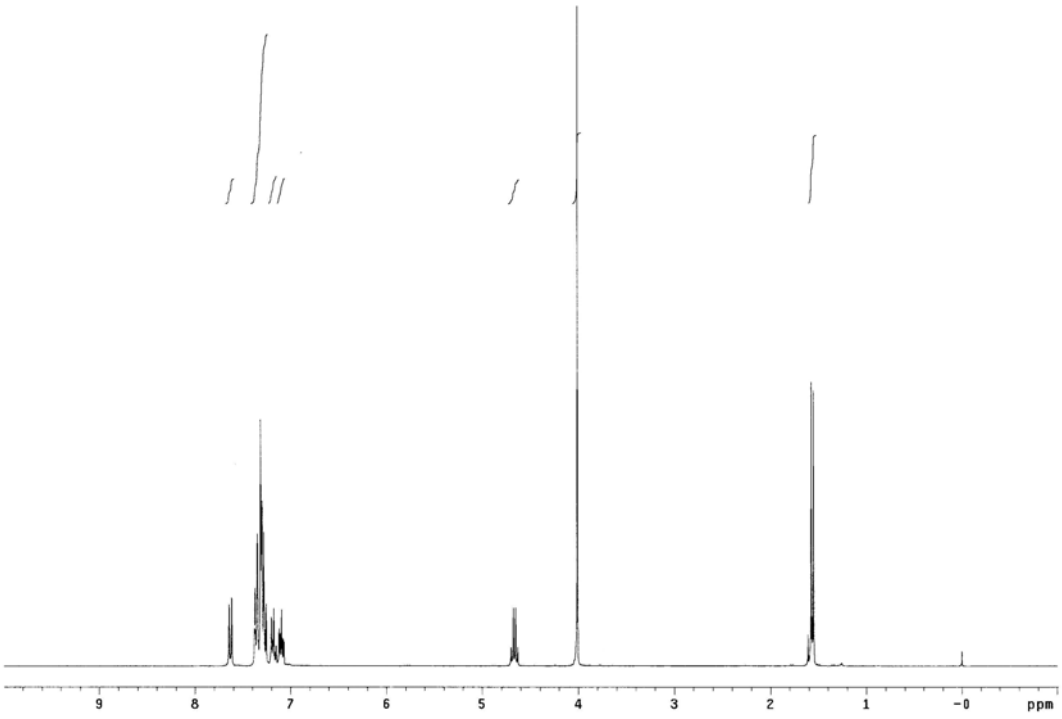
To a solution of 1-Methyl-1*H*-indole-2-carboxylic anhydride (66.5 mg, 0.30 mmol, 100 mol%), styrene (125 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.56, 10% EtOAc/hexane) to afford 72.7 mg as a colorless oil (92 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (d, *J* = 7.8 Hz, 1H), 7.38-7.25 (m, 7H), 7.20-7.15 (m, 1H), 7.12-7.07 (m, 1H), 4.66 (q, *J* = 6.9 Hz, 1H), 4.01 (s, 3H), 1.56 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 194.4, 141.8, 140.1, 134.3, 128.8, 127.6, 126.8, 125.8, 125.7, 122.9, 120.6, 111.8, 110.2, 48.9, 32.2, 19.0.

HRMS Calcd. for $C_{18}H_{18}NO$ (M+1): 264.1388, Found: 264.1391.

FTIR (neat): 3060, 2972, 2930, 1660, 1614, 1512, 1464, 1389, 1319, 1199, 1166, 957, 752 cm^{-1}.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5
4
3
2
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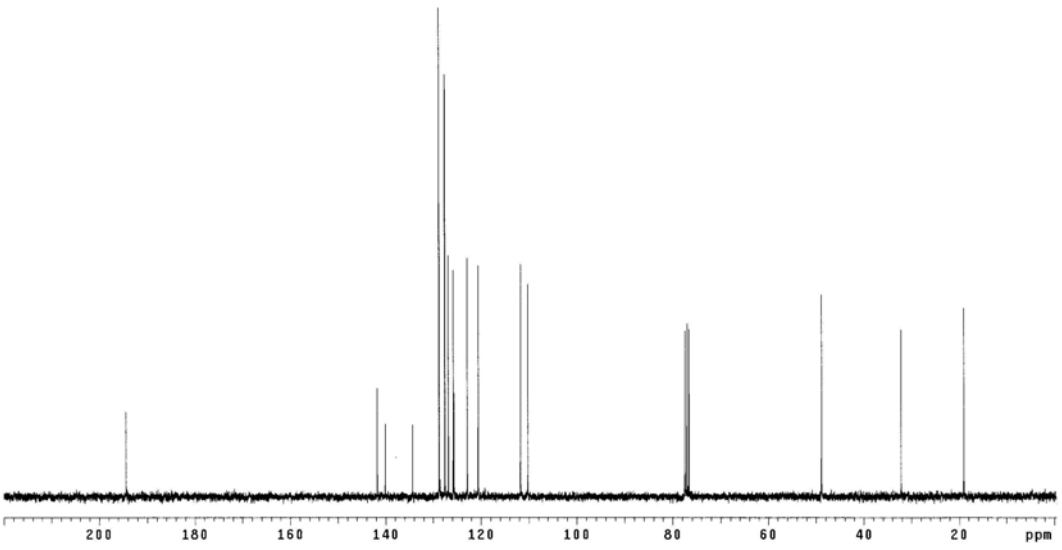
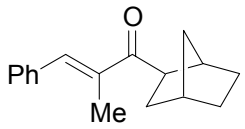
-0
ppm


200
180
160
140
120
100
80
60
40
20
ppm

1-Bicyclo[2.2.1]hept-2-yl-2-methyl-3-phenyl-propenone (20)



20

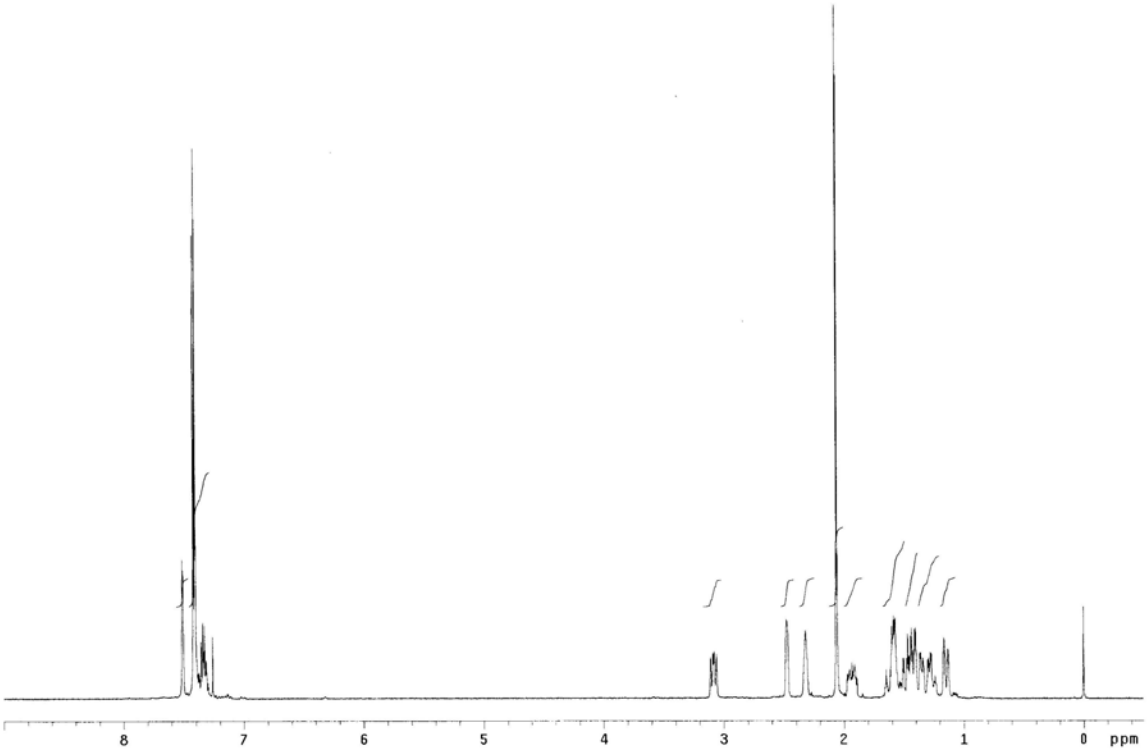
To a solution of α-Methylcinnamic anhydride[5c] (91.9 mg, 0.30 mmol, 100 mol%), 2-norbornene (113 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.25, 2% EtOAc/hexane) to afford 67.1 mg as a colorless oil (93 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.51 (m, 1H), 7.42-7.40 (m, 2H), 7.36-7.31 (m, 3H), 3.08 (dd, *J* = 8.7, 5.4 Hz, 1H), 2.47 (s, 1H), 2.32 (s, 1H), 2.06 (s, 3H), 1.97-1.91 (m, 1H), 1.61-1.51 (m, 2H), 1.47-1.41 (m, 2H), 1.37-1.24 (m, 2H), 1.71-1.13 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 204.1, 138.3, 137.0, 136.5, 129.9, 128.7, 128.5, 48.6, 41.5, 36.6, 36.5, 34.9, 30.0, 29.2, 13.9.

HRMS Calcd. for $C_{17}H_{21}O$ (M+1): 241.1592, Found 241.1597.

FTIR (neat): 2953, 2869, 1663, 1624, 1449, 1364, 1311, 1212, 1076, 1051, 1009, 926, 754, 697 cm^{-1}.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4
3
2
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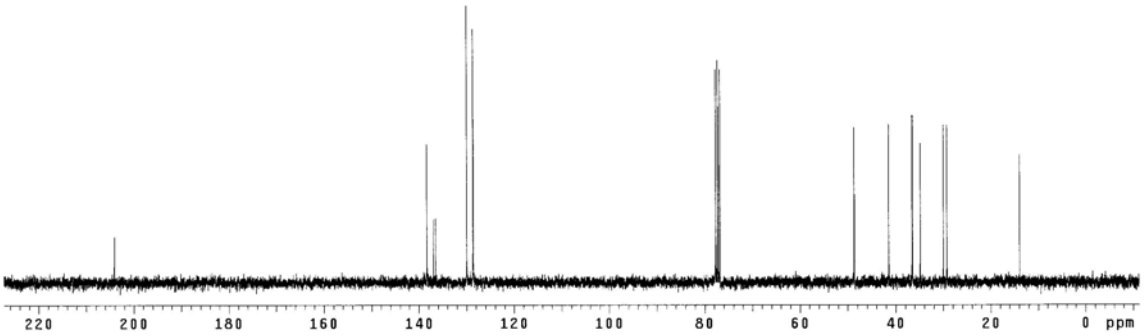
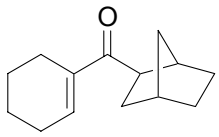
0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

Bicyclo[2.2.1]hept-2-yl-cyclohex-1-enyl-methanone (21)



21

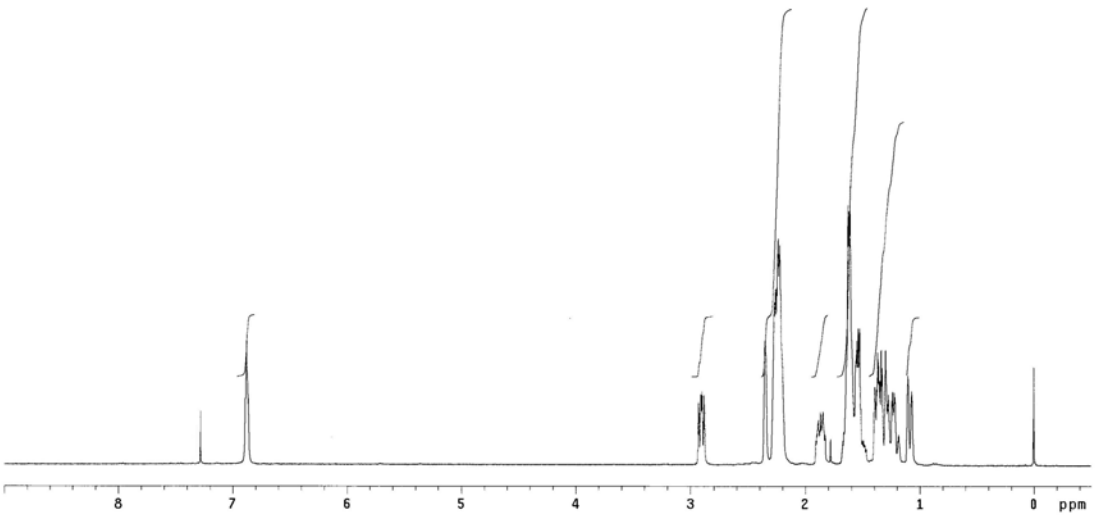
To a solution of Cyclohexene-1-carboxylic anhydride (70.3 mg, 0.30 mmol, 100 mol%), 2-norbornene (113 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.25, 2% EtOAc/hexane) to afford 55.8 mg as a colorless oil (91 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 6.85 (m, 1H), 2.85 (dd, J = 9.0, 5.7 Hz, 1H), 2.35 (s, 1H), 2.27-2.21 (m, 5H), 1.89-1.84 (m, 1H), 1.64-1.53 (m, 6H), 1.40-1.33 (m, 2H), 1.30-1.27 (m, 1H), 1.25-1.22 (m, 1H), 1.11-1.07 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 203.1, 139.3, 138.6, 48.0, 41.5, 36.4, 36.3, 34.3, 30.0, 29.2, 26.3, 23.8, 22.3, 21.9.

HRMS Calcd. for $C_{14}H_{21}O$ (M+1): 2051592, Found 205.1589.

FTIR (neat): 2947, 2868, 1664, 1636, 1451, 1383, 1343, 1312, 1268, 1194, 995, 920, 699 cm^{-1}.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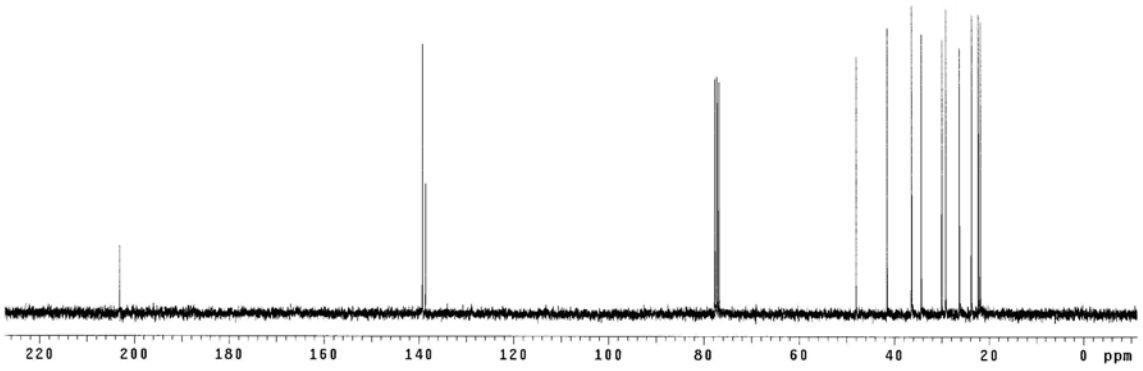
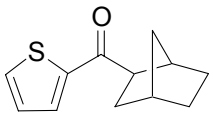

220
200
180
160
140
120
100
80
60
40
20
0
ppm

Bicyclo[2.2.1]hept-2-yl-thiophen-2-yl-methanone (22)



22

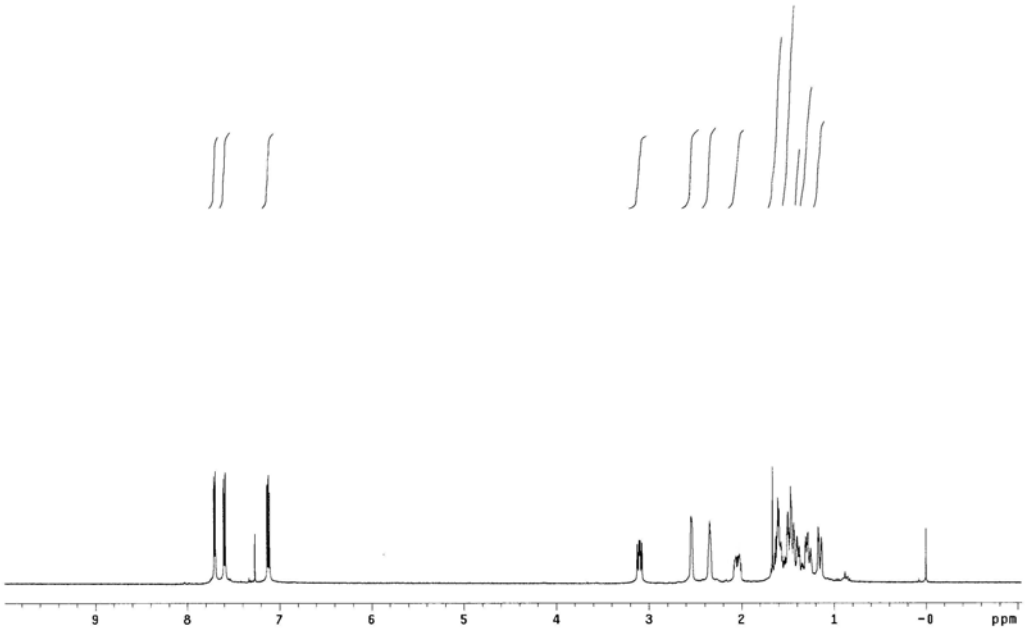
To a solution of thiophene-2-carboxylic anhydride[5d] (71.5 mg, 0.30 mmol, 100 mol%), 2-norbornene (113 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [Rh(COD)$_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.59, 10% EtOAc/hexane) to afford 42.7 mg as a colorless oil (69 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.70 (dd, *J* = 3.6, 0.9 Hz, 1H), 7.60 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.12 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.10 (dd, *J* = 8.6, 5.4 Hz, 1H), 2.55 (s, 1H), 2.35 (s, 1H), 2.09-2.01 (m, 1H), 1.68-1.56 (m, 2H), 1.54-1.37 (m, 3H), 1.31-1.25 (m, 1H), 1.18-1.13 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 194.7, 144.3, 132.9, 131.4, 127.9, 50.7, 41.8, 36.2, 36.1, 33.6, 29.8, 28.9.

HRMS Calcd. for $C_{12}H_{15}OS$ (M+1): 207.0844, Found 207.0844.

FTIR (neat): 3089, 2954, 2869, 1658, 1518, 1415, 1357, 1233, 1054, 849, 720 cm^{-1}.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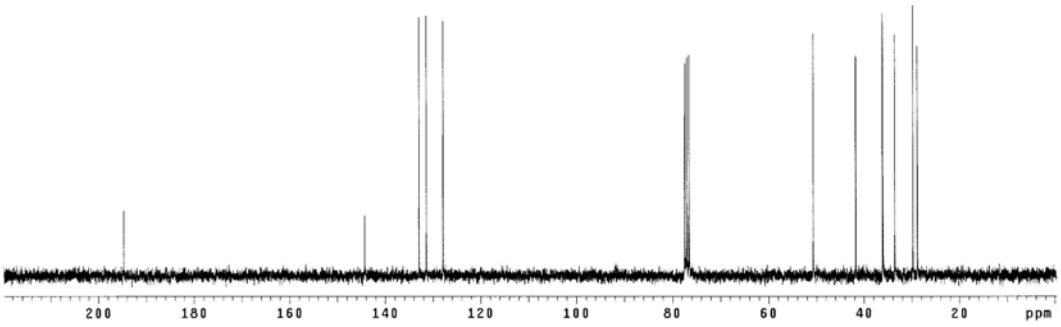
ppm


200
180
160
140
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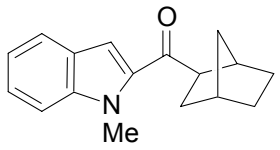
100
80
60
40
20
ppm

Bicycl[2.2.1]hept-2-yl-(1-methyl-1H-indol-2-yl)-methanone (23)



23

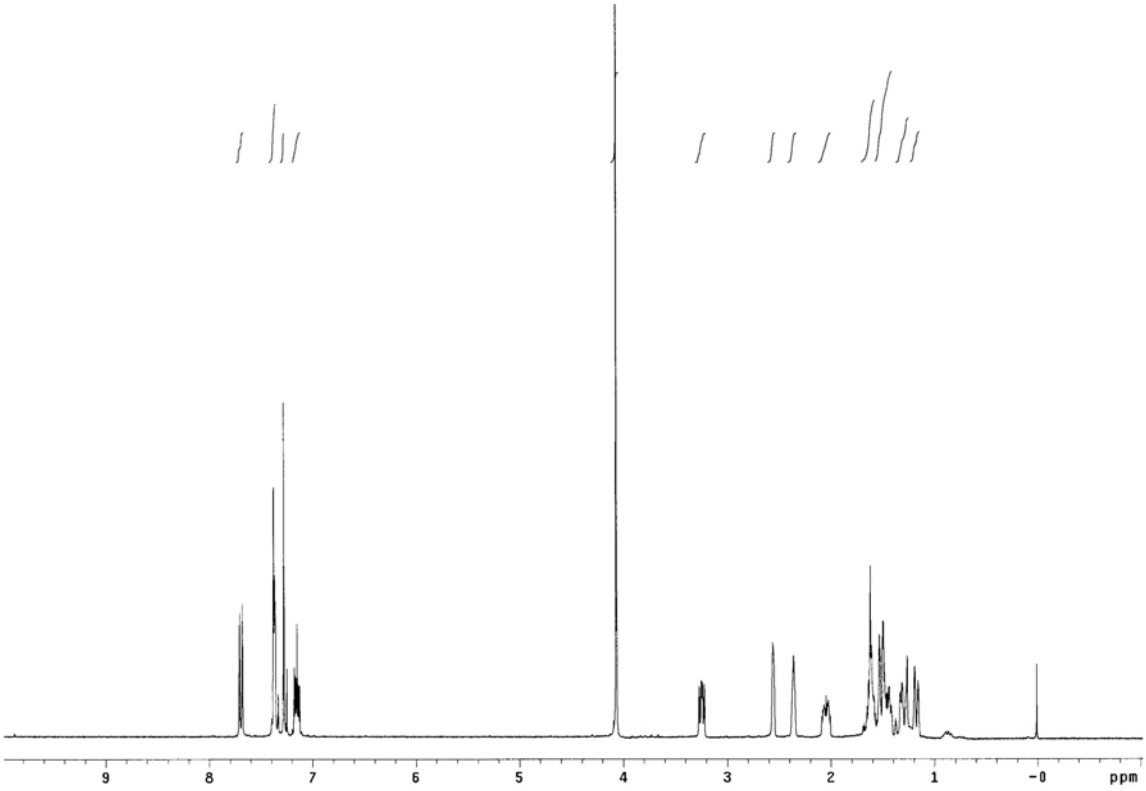
To a solution of 1-Methyl-1*H*-indole-2-carboxylic anhydride (66.5 mg, 0.30 mmol, 100 mol%), 2-norbornene (113 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.66, 10% EtOAc/hexane) to afford 56.2 mg as a colorless oil (74 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.69 (d, *J* = 8.1 Hz, 1H), 7.38-7.36 (m, 2H), 7.28 (s, 1H), 7.18-7.13 (m, 1H), 4.07 (s, 3H), 3.24 (dd, *J* = 8.6, 5.4 Hz, 1H), 2.56 (s, 1H), 2.36 (s, 1H), 2.09-2.01 (m, 1H), 1.69-1.58 (m, 2H), 1.56-1.42 (m, 3H), 1.34-1.26 (m, 1H), 1.20-1.16 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 196.2, 139.9, 134.7, 125.8, 125.5, 122.7, 120.5, 110.7, 110.3, 50.9, 42.2, 36.2, 36.1, 34.0, 32.2, 29.9, 28.9.

HRMS Calcd. for $C_{17}H_{20}NO$ (M+1): 254.1545, Found 254.1549.

FTIR (neat): 3057, 2952, 2868, 1660, 1512, 1464, 1391, 1190, 992, 744 cm^{-1}.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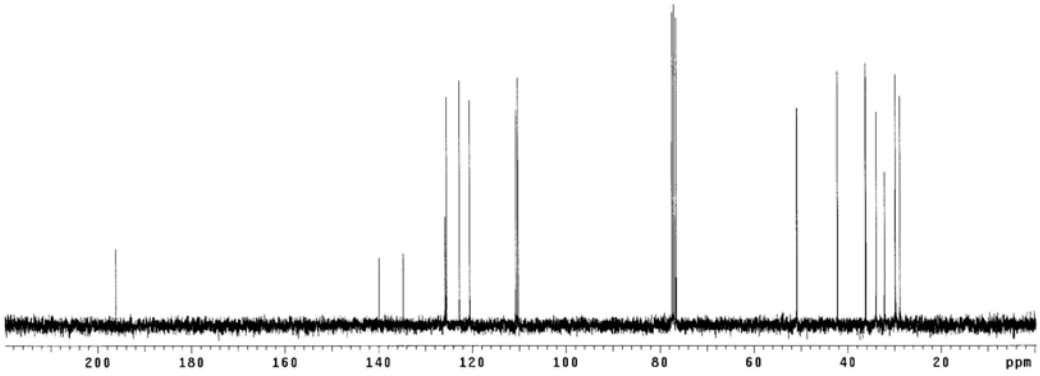
-0
ppm


200
180
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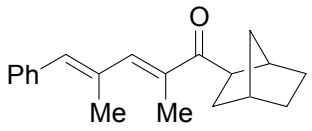
140
120
100
80
60
40
20
ppm

1-Bicyclo[2.2.1]hept-2-yl-2,4-dimethyl-5-phenyl-penta-2,4-dien-1-one (24)



24

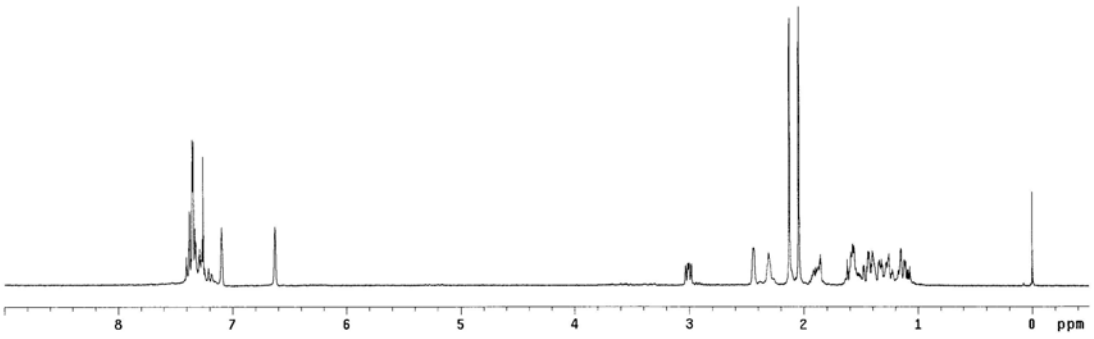
To a solution of 2,4-Dimethyl-5-phenyl-2,4-pentadienoic anhydride (116 mg, 0.30 mmol, 100 mol%), 2-norbornene (113 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.20, 2% EtOAc/hexane) to afford 51.3 mg as a colorless oil (61 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.40-7.32 (m, 2H), 7.29 (m, 3H), 7.09 (s, 1H), 6.63 (s, 1H), 3.01 (dd, J = 8.8, 5.7 Hz, 1H), 2.44 (s, 1H), 2.31 (s, 1H), 2.12 (s, 3H), 2.04 (s, 3H), 1.91-1.85 (m, 1H), 1.59-1.55 (m, 2H), 1.48-1.31(m, 3H), 1.28-1.23 (m, 1H), 1.17-1.11 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 204.2, 142.9, 137.2, 135.3, 134.7, 134.4, 129.4, 128.4, 127.3, 48.5, 41.3, 36.4, 36.3, 34.8, 29.9, 29.1, 18.8, 13.9.

HRMS Calcd. for $C_{20}H_{25}O$ (M+1): 281.1905, Found: 281.1902.

FTIR (neat): 2952, 2869, 1706, 1660, 1606, 1449, 1363, 1217, 1075, 1052, 921, 746, 698 cm^{-1}.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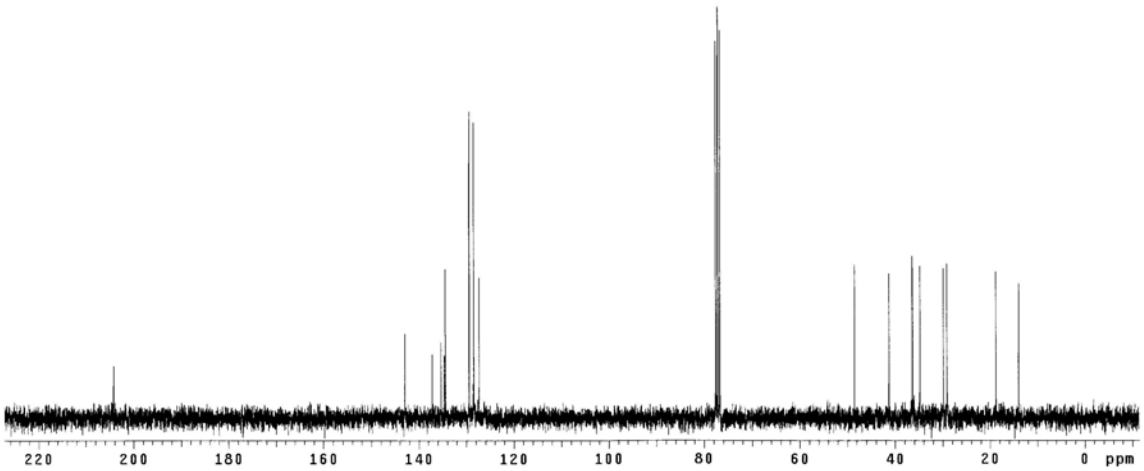
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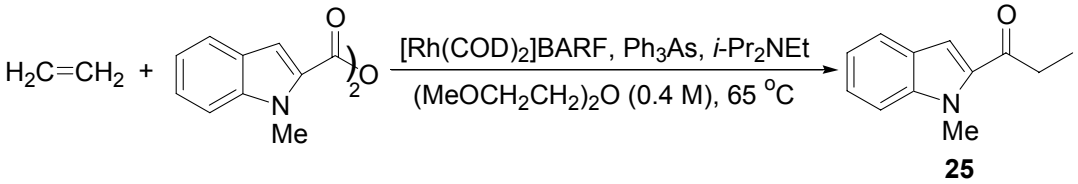
40
20
0
ppm

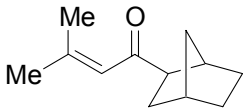
Reductive Coupling of Anhydride to Ethylene



25

To a solution of 1-Methyl-1*H*-indole-2-carboxylic anhydride (66.5 mg, 0.30 mmol, 100 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by mixture of ethylene and hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of ethylene and hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.50, 10% EtOAc/hexane) to afford 23.6 mg of 1-(1-methyl-1*H*-indol-2-yl)-propan-1-one[3g] as a white solid (44 % yield).

1-Bicyclo[2.2.1]hept-2-yl-3-methyl-but-2-en-1-one (26)



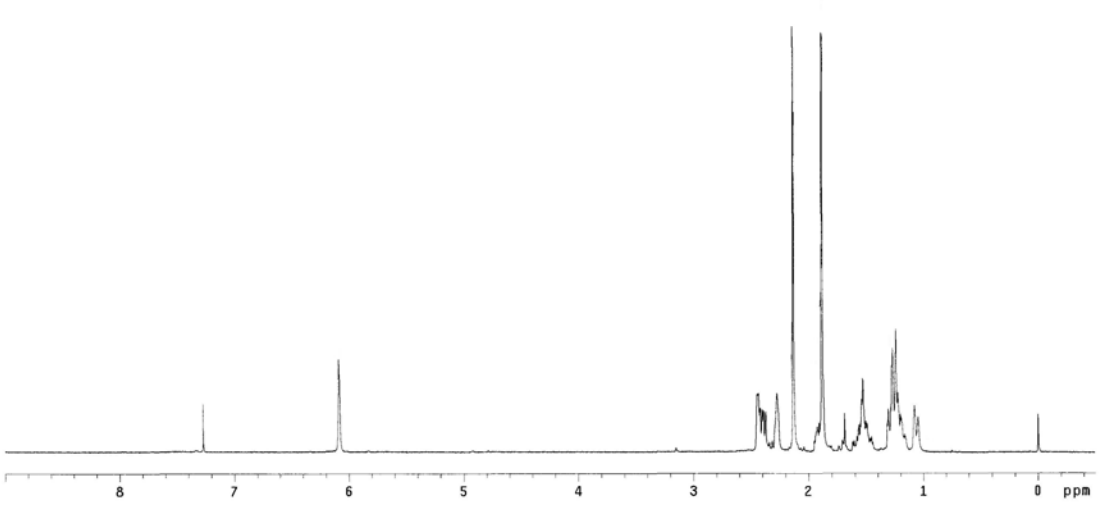
26

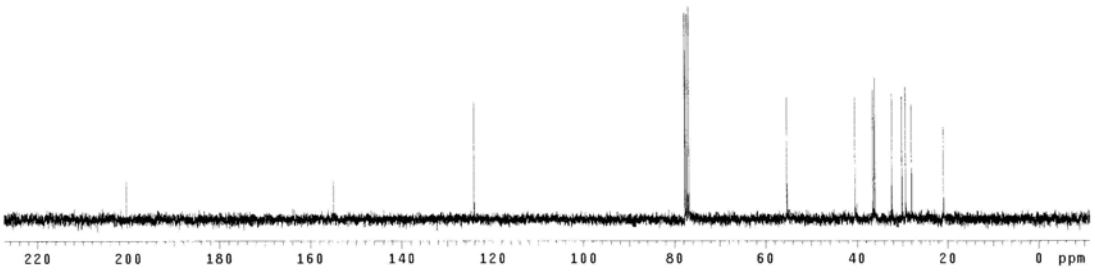
To a solution of 2,4-Dimethyl-5-phenyl-2,4-pentadienoic anhydride[6] (55.3 mg, 0.30 mmol, 100 mol%), 2-norbornene (113 mg, 1.2 mmol, 400 mol%) and *i*Pr_2NEt (77.5 mg, 0.60 mmol, 200 mol%) in diglyme (0.75 mL, 0.4 M) was added [$Rh(COD)_2$]BARF (17.8 mg, 0.015 mmol, 5 mol%) and Ph_3As (11.0 mg, 0.036 mmol, 12 mol%). The system was purged with argon gas followed by hydrogen gas. The reaction was allowed to stir at 65 ℃ under 1 atm of hydrogen for 10 hours. The title compound was purified by flash column chromatography (Rf = 0.22, 2% EtOAc/hexane) to afford 33.2 mg as a colorless oil (62 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 6.01 (s, 1H), 2.44-2.37 (m, 2H), 2.28 (s, 1H), 2.13 (s, 3H), 1.93 (m, 1H), 1.88 (s, 3H), 1.57-1.50 (m, 2H), 1.32-1.20 (m, 4H), 1.08-1.05 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 202.3, 154.9, 124.1, 55.3, 40.4, 36.5, 36.1, 32.3, 30.1, 29.3, 27.9, 20.9.

FTIR (neat): 3164, 2952, 2869, 1657, 1584, 1451, 1373, 1311, 1223, 1084, 1029, 801, 694 cm^{-1}.


8
7
6
5
4
3
2
1
0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

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