CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Scope and Mechanism of the Pd^{II}-Catalyzed Arylation/Carboalkoxylation of Unactivated Olefins with Indo

Cong Liu and Ross A. Widenhoefer*

P. M. Gross Chemical Laboratory, Duke University, Durham, NC 27708–0346; rwidenho@chem.duke.edu

Experimental procedures and analytical, spectroscopic, and structural data for new compounds (45 pages).

General Experimental Methods. NMR spectra were obtained on a Varian spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR in $CDCl_3$ unless otherwise noted. IR spectra were obtained on a Bomen MB-100 FT-IR spectrometer. Gas chromatography was performed on a Hewlett-Pakard 5890 gas chromatography equipped with a 25 m polydimethylsiloxane capillary column. Flash column chromatography was performed employing 200-400 mesh silica gel (EM). Thin layer chromatography (TLC) was performed on silica gel 60 F_{254}. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ) or by Robertson Microlit Laboratories (Madison, NJ).

Anhydrous methanol (Aldrich) was stored in an inert atmosphere glovebox. Anhydrous THF (Fischer) was distilled over sodium benzophenone ketyl prior to use. $PdCl_2(CH_3CN)_2$ (**2**), $PdCl_2(PPh_3)_2$, $CuCl_2$ (Strem), methyl isobutyrate, *trans*-1-bromo-2-pentene, *cis*-1-bromo-2-pentene, ethyl 6-heptenoate, $Pd(OAc)_2$, 1,2-dimethylindole, 2-phenylindole, 3-methylstyrene, 2-methylstyrene, 4-methoxystyrene, 4-chlorostyrene, 2-vinylnaphthalene (Aldrich), 4-fluoro-2-methylaniline, styrene, 4-methylstyrene, 2-methylindole (Acros), 5-methoxy-2-methylindole, 5-chloro-2-methylindole (Alfa Aesar), and methyl 5-hexenoate (TCI) were used as received. *N*-Trimethylsilyl-*o*-toluidine (**S1**)[1], 1-methyl-2-(4-pentenyl)indole (**5**),[2] 2-(4-pentenyl)indole (**8**),[2] 5-methoxy-1-methyl-2-(4-pentenyl)indole (Table 2, entry 3),[2] *N*-trimethylsilyl-4-fluoro-*o*-toluidine,[1] 2-(1,1-dimethyl-4-pentenyl)-1-methylindole (Table 2, entry 5),[2] 2-(2,2-dicarbomethoxy-4-pentenyl)-1-methylindole (Table 2, entry 6),[2] *N*-allyl-*N*-methyl-1-methylindole-2-carboxamide (Table 2, entry 7),[3] 1-methyl-2-(4-methyl-4-pentenyl)indole (Table 2, entry 8),[2] *cis*-2-(2,2-dicarbomethoxy-4-heptenyl)-1-methylindole (Table 2, entry 9),[2] dimethyl

2-(2-cyclohexenyl)-2-(1-methyl-2-indolylmethyl)malonate (Table 2, entry 10),[2] 1-methyl-2-(3-butenyl)indole (Table 2, entry 11),[2] 3-(1-methyl-3-indolyl)propionaldehyde,[4] 3-(4-pentenyl)indole (**16**),[5] 1-(4-pentenyl)pyrrole (**25**) were synthesized employing published procedures.[6]

Alkenyl Indoles

5-Fluoro-2-(4-pentenyl)indole (Table 2, entry 4). 5-Fluoro-2-(4-pentenyl)indole was isolated in 29% yield as a pale yellow oil from the reaction of *N*-trimethylsilyl-4-fluoro-*o*-toluidine and methyl 5-hexenoate employing a procedure similar to that used to synthesize **8**.[2] TLC (hexanes-CH_2Cl_2 = 1:1): R_f = 0.50. ^{1}H NMR: δ 7.84 (s, 1 H), 7.20-7.17 (m, 2 H), 6.87 (dt, *J* = 2.6, 9.2 Hz, 1 H), 6.23-6.22 (m, 1 H), 5.85 (tdd, *J* = 6.6, 10.4, 17.2 Hz, 1 H), 5.11-5.03 (m, 2 H), 2.76 (t, *J* = 7.2 Hz, 2 H), 2.17 (q, *J* = 7.2 Hz, 2 H), 1.83 (quintet, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 158.2 (d, $^1J_{CF}$ = 232 Hz), 141.8, 138.4, 132.6, 129.6 (d, $^3J_{CF}$ = 10 Hz), 115.6, 111.0 (d, $^3J_{CF}$ = 10 Hz), 109.3 (d, $^2J_{CF}$ = 26 Hz), 105.0 (d, $^2J_{CF}$ = 24 Hz), 100.2, 33.5, 28.5, 27.9. IR (neat, cm^{-1}): 3415, 2932, 1585, 1485, 1453, 1416, 1313, 1167, 1105, 953. Anal. calcd (found) for $C_{13}H_{14}FN$: C, 76.82 (76.80); H, 6.94 (6.78).

***trans*-2-(1,1-Dimethyl-3-hexenyl)indole [(*E*)-11]**. Methyl isobutyrate (3.06 g, 30.0 mmol) was added to a solution of LDA [generated from *n*-BuLi and diisopropylamine] in THF at –78 °C. The resulting solution was stirred for 30 min and treated with *trans*-1-bromo-2-pentene (4.00 g, 30.0 mmol). The resulting mixture was warmed to room temperature, stirred for 4 h, and quenched with saturated aqueous NH_4Cl. The layers were separated and the aqueous layer was extracted with ether (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$) and

concentrated under vacuum. Column chromatography of the residue (SiO_2; hexanes–EtOAc = 10:1) gave methyl *trans*-2,2-dimethyl-4-heptenoate (**S2**) (3.82 g, 75%) as a colorless oil.

A solution of *n*-BuLi in hexanes (2.5 M, 15.0 mL, 37.5 mmol) was added dropwise to a solution of **S1** (2.69 g, 15.0 mmol) in hexanes (50 mL) at 0 °C. The resulting orange solution was refluxed for 6 h, cooled to –78 ºC, and treated with a solution of **S2** (2.55 g, 15.0 mmol) in THF (10 mL). The resulting mixture was warmed to room temperature, stirred for 1 h, and quenched with brine. The layers were separated and the aqueous layer was extracted with ether (2 × 30 mL). The combined ether extracts were dried ($MgSO_4$) and concentrated under vacuum. Column chromatography of the residue (SiO_2; hexanes–CH_2Cl_2 = 10:1) gave (*E*)-**11** (2.42 g, 71%) as a pale yellow oil.

For S2: TLC (hexanes-EtOAc = 10:1): R_f = 0.61. ^{1}H NMR: δ 5.46 (ttd, *J* = 1.2, 6.2, 15.2 Hz, 1 H), 5.29 (ttd, *J* = 1.6, 7.2, 14.8 Hz, 1 H), 3.64 (s , 3 H), 2.17 (dd, *J* = 0.8, 7.2 Hz, 2 H), 1.98 (quint, *J* = 7.2 Hz, 2 H), 1.13 (s, 6 H), 0.94 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 178.5, 136.1, 124.7, 51.9, 43.9, 43.0, 26.0, 25.1, 14.3. IR (neat, cm^{-1}): 2968, 1733, 1433, 1200, 1135, 990, 867, 713. Anal. calcd (found) for $C_{10}H_{18}O_2$: C, 70.55 (70.61); H, 10.66 (10.83).

For (*E*)-11: TLC (hexanes-CH_2Cl_2 = 1:1): R_f = 0.65. ^{1}H NMR: δ 8.00 (s, 1 H), 7.58 (dd, *J* = 0.8, 8.2 Hz, 1 H), 7.34 (dd, *J* = 0.8, 7.6 Hz, 1 H), 7.19-7.09 (m, 2 H), 6.30 (m, 1 H), 5.53 (ttd, *J* = 1.4, 7.2, 15.0 Hz, 1 H), 5.32 (ttd, *J* = 1.2, 7.0, 15.2 Hz, 1 H), 2.35 (dd, *J* = 1.2, 7.2 Hz, 2 H), 2.02 (quint, *J* = 7.8 Hz, 2 H), 1.38 (s, 6 H), 0.98 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 147.9, 136.1, 136.0, 128.8, 125.4, 121.3, 120.3, 119.8, 110.7, 98.3, 46.8, 35.4, 28.0, 26.0, 14.3. IR (neat, cm^{-1}): 3424, 2962, 2929, 1455, 1294, 969, 784, 749, 693. Anal. calcd (found) for $C_{16}H_{21}N$: C, 84.53 (84.37); H, 9.31 (9.22).

***cis*-2-(1,1-Dimethyl-3-hexenyl)indole [(*Z*)-11]**. *cis*-2,2-Dimethyl-4-heptenoate (**S3**) was isolated in 53% yield as a colorless oil from the reaction of methyl isobutyrate and *cis*-1-bromo-2-pentene employing a procedure similar to that used to synthesize **S2**. (*Z*)-**11** was isolated in 66% yield as a pale yellow oil from the reaction of **S1** and **S3** employing a procedure similar to that used to synthesize **8**.

For S3: TLC (hexanes-EtOAc = 10:1): R_f = 0.60. ^{1}H NMR: δ 5.46 (ttd, *J* = 1.6, 7.2, 10.8 Hz, 1 H), 5.25 (ttd, *J* = 1.6, 7.0, 10.8 Hz, 1 H), 3.65 (s, 3 H), 2.26 (d, *J* = 7.6 Hz, 2 H), 2.03 (quint, *J* = 7.2 Hz, 2 H), 1.17 (s, 6 H), 0.94 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 178.5, 134.7, 124.3, 52.0, 42.8, 38.0, 25.1, 20.9, 14.5. IR (neat, cm^{-1}): 2966, 2874, 1734, 1433, 1198, 1142, 867. Anal. calcd (found) for $C_{10}H_{18}O_2$: C, 70.55 (70.50); H, 10.66 (10.83).

For (*Z*)-11: TLC (hexanes-CH_2Cl_2 = 1:1): R_f = 0.67. ^{1}H NMR: δ 8.00 (s, 1 H), 7.57 (dd, *J* = 0.8, 8.0 Hz, 1 H), 7.32 (dd, *J* = 0.8, 7.6 Hz, 1 H), 7.17-7.07 (m, 2 H), 6.30-6.29 (m, 1 H), 5.48 (ttd, *J* = 1.6, 7.2, 10.8 Hz, 1 H), 5.30 (ttd, *J* = 1.6, 7.0, 10.8 Hz, 1 H), 2.41 (d, *J* = 8.2 Hz, 2 H), 2.03 (quint, *J* = 7.6 Hz, 2 H), 1.40 (s, 6 H), 0.94 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 147.6, 136.0, 134.5, 1286, 125.1, 121.3, 120.2, 119.8, 110.6, 98.3, 40.8, 35.5, 28.0, 20.9, 14.3. IR (neat, cm^{-1}): 3424, 2963, 1460, 1296, 784. Anal. calcd (found) for $C_{16}H_{21}N$: C, 84.53 (84.40); H, 9.31 (9.48).

2-(5-Hexenyl)-1-methylindole (13). 2-(5-Hexenyl)indole (**S4**) was isolated in 50% yield as a pale yellow oil from the reaction of **S1** and ethyl 6-heptenoate employing a procedure similar to that used to synthesize **8**. **13** was isolated in 74% yield as a colorless oil from the reaction of **S4** and methyl iodide employing a procedure similar to that used to synthesize **5**.

For S4: TLC (hexanes-CH_2Cl_2 = 1:1): R_f = 0.56. ^{1}H NMR: δ 7.79 (s, 1 H), 7.59-7.57 (m, 1 H), 7.32-7.29 (m, 1 H), 7.09-7.03 (m, 2 H), 6.29-6.27 (m, 1 H), 5.85 (tdd, *J* = 6.6, 10.4,

17.2 Hz, H), 5.10-5.00 (m, 2 H), 2.77 (t, *J* = 7.6 Hz, 2 H), 2.15 (q, *J* = 7.6 Hz, 2 H), 1.77 (quint, *J* = 7.6 Hz, 2 H), 1.54 (quint, *J* = 7.6 Hz, 2 H). $^{13}C\{^{1}H\}$ NMR: δ 147.1, 138.9, 136.1, 129.1, 121.2, 120.0, 119.9, 115.0, 110.6, 99.8, 33.8, 28.9, 28.8, 28.4. IR (neat, cm^{-1}): 3404, 2930, 1550, 1457, 1414, 1287, 909, 779, 748. Anal. calcd (found) for $C_{14}H_{17}N$: C, 84.37 (84.25); H, 8.60 (8.42).

For 13: TLC (hexanes-CH_2Cl_2 = 5:1): R_f = 0.38. ^{1}H NMR: δ 7.62-7.60 (m, 1 H), 7.34-7.32 (m, 1 H), 7.25-7.21 (m, 2 H), 6.33-6.31 (m, 1 H), 5.90 (tdd, *J* = 6.6, 10.4, 17.2 Hz, 1 H), 5.14-5.03 (m, 2 H), 3.70 (s, 3 H), 2.80 (t, *J* = 7.6 Hz, 2 H), 2.20 (q, *J* = 7.6 Hz, 2 H), 1.81 (quint, *J* = 7.6 Hz, 2 H), 1.61 (quint, *J* = 7.6 Hz, 2 H). $^{13}C\{^{1}H\}$ NMR: δ 141.5, 138.9, 137.6, 128.2, 120.8, 120.1, 119.5, 115.0, 109.0, 99.0, 33.9, 29.7, 28.9, 28.4, 27.0. IR (neat, cm^{-1}): 2931, 1546, 1468, 909, 770, 746. Anal. calcd (found) for $C_{15}H_{19}N$: C, 84.46 (84.22); H, 8.98 (8.84).

3-(3-Butenyl)-1-methylindole (18). *n*-BuLi (2.5 M solution in hexanes, 4.4 mL, 11 mmol) was added dropwise to a mixture of Ph_3PCH_3Br (3.93 g, 11.0 mmol) in THF (50 mL) at 0 °C. The resulting mixture was stirred for 1 h and treated with a solution of 3-(1-methyl-3-indolyl)propionaldehyde (0.79 g, 4.2 mmol) in THF (10 mL). The resulting mixture was warmed to room temperature, stirred for 2.5 h, and quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with ether (3 × 30 mL) and the layers were separated. The combined ether extracts were dried ($MgSO_4$) and concentrated under vacuum. Column chromatography of the residue (SiO_2; hexanes–EtOAc = 5:1) gave **18** (0.70 g, 90%) as a pale yellow oil. TLC (hexanes-EtOAc = 2:1): R_f = 0.71. ^{1}H NMR: δ 7.70-7.68 (m, 1 H), 7.42-7.28 (m, 2 H), 7.19 (dt, *J* = 0.8, 7.6 Hz, 1 H), 6.90 (s, 1 H), 6.03 (tdd, *J* = 6.6, 10.4, 17.2 Hz, 1 H), 5.21-5.07 (m, 2 H), 3.79 (s, 3 H), 2.94 (t, *J* = 7.2 Hz, 2 H), 2.58 (q, *J* = 7.2 Hz, 2 H). $^{13}C\{^{1}H\}$ NMR: δ 139.2, 137.3, 128.2, 126.4, 121.8, 119.3, 118.8, 114.9, 109.4, 34.9, 32.8, 25.0. IR

(neat, cm^{-1}): 3060, 2913, 1640, 1470, 1376, 1322, 910. Anal. calcd (found) for $C_{13}H_{15}N$: C, 84.28 (84.01); H, 8.16 (8.06).

Dimethyl 2-allyl-2-(1-methyl-3-indolyl)malonate (31-d_0). A solution of 2-(1-methyl-3-indolyl)malonate[7] (1.80 g, 6.90 mmol) in THF (5 mL) was added to a suspension of NaH (0.17 g, 7.0 mmol) in THF (35 mL) at room temperature. The resulting mixture was refluxed 1 h to form a colorless solution that was cooled to room temperature and treated with propargyl bromide (1.2 g, 8.3 mmol). The resulting mixture was refluxed for 1.5 h, cooled to room temperature, and quenched with saturated aqueous NH_4Cl. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed (brine), dried ($MgSO_4$), and concentrated under vacuum. Column chromatography of the residue (SiO_2; hexanes–EtOAc = 5:1 → 1:1) gave dimethyl 2-(1-methyl-3-indolyl)-2-(2-propynyl)malonate (**S5**) (1.73 g, 84%) as a pale yellow solid.

A solution of **S5** (0.45 g, 1.5 mmol) in CH_2Cl_2 (2 mL) was added to a suspension of Cp_2ZrHCl (0.58 g, 2.2 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The resulting mixture was stirred for 1 h and quenched with water (5 mL). The resulting mixture was filtered through a pad of silica gel and eluted with CH_2Cl_2 (5 × 20 mL). The combined filtrate was concentrated under vacuum and chromatographed (SiO_2; hexanes–EtOAc = 5:1) to give **31**-d_0 (0.34 g, 75%) as a white solid.

For S5: mp 111-113 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.55. ^{1}H NMR: δ 7.55-7.52 (m, 1 H), 7.49 (br s, 1 H), 7.31-7.29 (m, 1 H), 7.24-7.20 (m, 1 H), 7.11-7.07 (m, 1 H), 3.99 (s, 9 H), 3.32 (d, J = 2.8 Hz, 2 H), 2.44 (t, J = 2.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 170.4, 137.3, 129.0, 126.3, 122.0, 120.3, 119.8, 109.8, 109.0, 79.9, 71.8, 57.7, 53.3, 33.2, 26.8. IR (neat, cm^{-1}): 3282, 2952, 1742, 1732, 1434, 1238, 1074, 743. Anal. calcd (found) for $C_{17}H_{17}NO_4$: C, 68.21 (68.12); H, 5.72 (5.80).

For 31-d_0: mp 82-84 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.63. ^{1}H NMR: δ 7.56-7.54 (m, 1 H), 7.46 (br s, 1 H), 7.30-7.28 (m, 1 H), 7.23-7.19 (m, 1 H), 7.11-7.06 (m, 1 H), 5.72 (ttd, J = 7.2, 10.0, 17.2, 1 H), 5.08-4.99 (m, 2 H), 3.76 (s, 3 H), 3.71 (s, 6 H), 3.16 (td, *J* = 1.2, 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 171.3, 137.3, 133.6, 128.7, 126.4, 122.0, 120.5, 119.7, 118.6, 110.1, 109.7, 58.4, 52.9, 40.5, 33.2. IR (neat, cm^{-1}): 2951, 1727, 1433, 742. Anal. calcd (found) for $C_{17}H_{19}NO_4$: C, 67.76 (67.80); H, 6.36 (6.43)

(*Z*)-Dimethyl 2-(3-deuterioallyl)-2-(1-methyl-3-indolyl)malonate [(*Z*)-31]. A solution of **S5** (0.60 g, 2.0 mmol) in THF (5 mL) was added to a mixture of sodium methoxide (30 mg, 0.5 mmol) in CH_3OD (5 mL) at room temperature. The resulting mixture was stirred for 0.5 h and concentrated under vacuum. The residue was dissolved in CH_3OD/THF (1/1, 5 mL), stirred at room temperature for 0.5 h, and concentrated under vacuum. The preceding two steps were performed in triplicate, the resulting residue was treated with D_2O (5 mL), and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed (D_2O), dried ($MgSO_4$), and concentrated under vacuum to give crude dimethyl 2-(1-methyl-3-indolyl)-2-(3-deuterio-2-propynyl)malonate (**S5**-d_1) (0.58 g, 96%) as a white solid that was used in the following step without further purification. Compound (*Z*)-**31** was isolated in 77% yield as a white solid from **S5**-d_1 employing a procedure similar to that used to synthesize **31**-d_0 from **S5**.

For S5-d_1: TLC (hexanes-EtOAc = 2:1): R_f = 0.55. ^{1}H NMR: δ 7.54-7.51 (m, 1 H), 7.49 (br s, 1 H), 7.31-7.28 (m, 1 H), 7.24-7.18 (m, 1 H), 7.11-7.06 (m, 1 H), 3.77 (s, 3 H), 3.76 (s, 6 H), 3.13 (s, 2 H). ^{13}C{^{1}H} NMR: δ 170.3, 137.2, 128.9, 126.2, 121.9, 120.2, 119.8, 109.7, 109.0, 79.4 (m), 71.6 (t, *J* = 38.1 Hz, IS = 246 ppb), 57.7, 53.2, 33.2, 26.7. HRMS calcd (found) for $C_{17}H_{16}DNO_4$ (M^+): 300.1219 (300.1219).

For (*Z*)-31: ^{1}H NMR: δ 7.55-7.53 (m, 1 H), 7.45 (br s, 1 H), 7.30-7.28 (m, 1 H), 7.23-7.19 (m, 1 H), 7.10-7.06 (m, 1 H), 5.74-5.68 (m, 1 H), 5.00-4.97 (m, 1 H), 3.76 (s, 3 H), 3.71 (s, 6 H), 3.16 (dd, *J* = 1.2, 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 171.3, 137.3, 133.6, 128.7, 126.4, 122.0, 120.5, 119.7, 118.4 (t, *J* = 23.2 Hz, IS = 264 ppb), 110.1, 109.7, 58.4, 52.9, 40.5, 33.2. HRMS calcd (found) for $C_{17}H_{18}DNO_4$ (MH^+): 302.1376 (302.1378).

(*E*)-Dimethyl 2-(3-deuterioallyl)-2-(1-methyl-3-indolyl)malonate [(*E*)-31]. Compound (*E*)-**31** was isolated in 72% yield as a white solid from sequential reaction of **S5** with Cp_2ZrHCl and H_2O employing a procedure similar to that used to synthesize **31**-d_0 from **S5**. ^{1}H NMR: δ 7.55-7.53 (m, 1 H), 7.45 (br s, 1 H), 7.29-7.27 (m, 1 H), 7.23-7.18 (m, 1 H), 7.10-7.06 (m, 1 H), 5.75-5.68 (m, 1 H), 5.07-5.00 (m, 1 H), 3.76 (s, 3 H), 3.71 (s, 6 H), 3.16 (dd, *J* = 1.6, 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 171.3, 137.3, 133.5, 128.7, 126.4, 122.0, 120.5, 119.7, 118.4 (t, *J* = 25.1 Hz, IS = 254 ppb), 110.1, 109.8, 58.4, 52.9, 40.5, 33.2. HRMS calcd (found) for $C_{17}H_{18}DNO_4$ (MH^+): 302.1376 (302.1381).

Polycyclic Indoles

Methyl (2,3,4,9-tetrahydro-4-carbazolyl)acetate (9).[8] Pale yellow oil, 83%. TLC (hexanes-EtOAc = 2:1): R_f = 0.62. ^{1}H NMR: δ 7.82 (s, 1 H), 7.56 (d, *J* = 7.6 Hz, 1 H), 7.24 (dd, *J* = 0.8, 7.6 Hz, 1 H), 7.17-7.09 (m, 2 H), 3.76 (s, 3 H), 3.60-3.57 (m, 1 H), 3.04 (dd, *J* = 4.0, 15.2 Hz, 1 H), 2.70-2.64 (m, 2 H), 2.47 (dd, *J* = 10.4, 14.8 Hz, 1 H), 2.00-1.79 (m, 4 H). ^{13}C{^{1}H} NMR: δ 174.1, 136.0, 134.9, 127.0, 121.2, 119.4, 118.3, 112.1, 110.9, 51.9, 39.9, 29.3, 28.7, 23.4, 19.6. IR (neat, cm^{-1}): 3399, 2932, 1733, 1464, 1434, 1326, 1283, 1168, 1072, 1012, 741

Methyl (6-methoxy-9-methyl-2,3,4,9-tetrahydro-4-carbazolyl)acetate (Table 2, entry 3). Pale yellow oil, 86%. TLC (hexanes-EtOAc = 2:1): R_f = 0.57. ^{1}H NMR: δ 7.16 (d, J = 9.2 Hz, 1 H), 7.00 (d, J = 2.4 Hz, 1 H), 6.84 (dd, J = 2.4, 8.4 Hz, 1 H), 3.88 (s, 3 H), 3.75 (s, 3 H), 3.58 (s, 3 H), 3.58-3.54 (m, 1 H), 2.97 (dd, J = 4.0, 15.2 Hz, 1 H), 2.76-2.60 (m, 2 H), 2.44 (dd, J = 10.4, 14.8 Hz, 1 H), 1.98-1.74 (m, 4 H). ^{13}C{^{1}H} NMR: δ 173.9, 153.9, 137.0, 132.4, 126.6, 111.1, 110.4, 109.5, 100.9, 56.3, 51.7, 39.8, 29.2, 28.5, 22.4, 19.3. IR (neat, cm^{-1}): 2934, 1732, 1621, 1579, 1484, 1415, 1281, 1254, 1223, 1153, 1080, 793. Anal. calcd (found) for $C_{17}H_{21}NO_3$: C, 71.06 (71.16); H, 7.37 (7.45).

Methyl (6-fluoro-2,3,4,9-tetrahydro-4-carbazolyl)acetate (Table 2, entry 4). Colorless oil, 74%. TLC (hexanes-EtOAc = 2:1): R_f = 0.45. ^{1}H NMR (Figure S1): δ 7.78 (s, 1 H), 7.19-7.14 (m, 2 H), 6.85 (dt, J = 2.6, 9.0 Hz, 1 H), 3.73 (s, 3 H), 3.52-3.46 (m, 1 H), 2.92 (dd, J = 4.0, 15.2 Hz, 1 H), 2.720-2.66 (m, 2 H), 2.42 (dd, J = 10.4, 14.8 Hz, 1 H), 1.97-1.75 (m, 4 H). ^{13}C{^{1}H} NMR (Figure S2): δ 173.8, 158.0 (d, $^1J_{CF}$ = 233 Hz), 136.9, 132.5, 127.5 (d, $^3J_{CF}$ = 10 Hz), 112.8, 111.3 (d, $^3J_{CF}$ = 10 Hz), 109.3 (d, $^2J_{CF}$ = 26 Hz), 103.6 (d, $^2J_{CF}$ = 24 Hz), 51.9, 39.8, 29.2, 28.8, 23.6, 19.6. IR (neat, cm^{-1}): 3409, 2936, 1713, 1583, 1484, 1453, 1317, 1290, 1169, 1128, 797. HRMS calcd (found) for $C_{15}H_{16}FNO_2$ (M^+): 261.1165 (261.1159).

Methyl (1,1,9-trimethyl-2,3,4,9-tetrahydro-4-carbazolyl)acetate (Table 2, entry 5). Pale yellow oil, 84%. TLC (hexanes-EtOAc = 2:1): R_f = 0.74. ^{1}H NMR: δ 7.60 (d, J = 7.6 Hz, 1 H), 7.32 (d, J = 8.0 Hz, 1 H), 7.25 (t, J = 7.6 Hz, 1 H), 7.15 (t, J = 7.4 Hz, 1 H), 3.86 (s, 3 H), 3.80 (s, 3 H), 3.65-3.60 (m, 1 H), 3.02 (dd, J = 3.6, 15.2 Hz, 1 H), 2.53 (dd, J = 11.2, 15.2 Hz, 1 H), 2.10 (ddt, J = 2.4, 5.2, 12.8 Hz, 1 H), 1.95 (dt, J = 2.0, 13.6 Hz, 1 H), 1.83-1.78 (m, 1 H), 1.67 (ddd, J = 2.4, 5.6, 13.2 Hz, 1 H), 1.54 (s, 3 H), 1.43 (s, 3 H). ^{13}C{^{1}H} NMR: δ 173.9, 142.7, 137.9, 126.1, 121.4, 119.2, 118.5, 111.5, 109.0, 51.8, 39.7, 38.4, 32.5, 32.2, 29.7, 29.2,

27.7, 25.1. IR (neat, cm^{-1}): 2932, 1747, 1727, 1470, 1285, 1165, 1015, 742. Anal. calcd (found) for $C_{18}H_{23}NO_2$: C, 75.76 (75.60); H, 8.12 (8.12).

Methyl (2,2-dicarbomethoxy-9-methyl-2,3,4,9-tetrahydro-4-carbazolyl)acetate (Table 2, entry 6). Pale yellow oil, 87%. TLC (hexanes-EtOAc = 2:1): R_f = 0.43. ^{1}H NMR: δ 7.51 (d, *J* = 8.0 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 7.08 (t, *J* = 7.8 Hz, 1 H), 3.80 (s, 3 H), 3.75 (s, 3 H), 3.69 (s, 3 H), 3.67 (s, 3 H), 3.70-3.63 (m, 1 H), 3.45 (d, *J* = 16.4 Hz, 1 H), 3.31 (dd, *J* = 3.6, 15.8 Hz, 1 H), 3.20 (d, *J* = 16.0 Hz, 1 H), 2.86 (dd, *J* = 6.0, 13.6 Hz, 1 H), 2.32 (dd, *J* = 10.4, 15.8 Hz, 1 H), 2.05 (dd, *J* = 8.8, 13.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.1, 172.2, 170.9, 137.8, 133.4, 125.9, 121.3, 119.3, 119.0, 109.6, 109.3, 54.4, 53.2, 51.9, 51.7, 40.3, 35.4, 29.5, 28.6, 28.4. IR (neat, cm^{-1}): 2953, 1747, 1722, 1085, 1018, 738. Anal. calcd (found) for $C_{20}H_{23}NO_6$: C, 64.33 (64.48); H, 6.21 (6.29).

Methyl (2,9-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-β-carbolin-4-yl-acetate (Table 2, entry 7). Colorless oil, 91%. TLC (hexanes-EtOAc = 10:1): R_f = 0.21. ^{1}H NMR: δ 7.61 (td, *J* = 0.8, 8.0 Hz, 1 H), 7.37-7.30 (m, 2 H), 7.14 (dt, *J* = 1.0, 8.0 Hz, 1 H), 4.11 (s, 3 H), 3.94 (dd, *J* = 4.8, 12.8 Hz, 1 H), 3.68 (s, 3 H), 3.67-3.63 (X portion of ABX, partially obscured, 1 H), 3.46 (dd, *J* = 6.4, 12.8 Hz, 1 H), 3.12 (s, 3 H), 2.68, 2.66 (AB portion of ABX, J_{AB} = 15.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 172.8, 161.8, 139.4, 126.3, 124.9, 123.2, 120.8, 120.5, 120.3, 110.6, 54.3, 52.1, 37.3, 34.7, 31.5, 29.1. IR (neat, cm^{-1}): 2948, 1727, 1649, 1493, 1440, 1248, 1165, 1082, 742. Anal. calcd (found) for $C_{16}H_{18}N_2O_3$: C, 67.12 (66.98); H, 6.34 (6.38).

Methyl (4,9-dimethyl-2,3,4,9-tetrahydro-4-carbazolyl)acetate (Table 2, entry 8). Pale yellow solid, 87%. mp 85-87 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.72. ^{1}H NMR: δ 7.68 (d, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 1 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 7.09 (t, *J* = 7.6 Hz, 1 H), 3.66 (s, 3 H), 3.61 (s, 3 H), 3.04 (d, *J* = 13.6 Hz, 1 H), 2.70 (dd, *J* = 5.6, 12.0 Hz, 2 H), 2.65

(d, *J* = 13.6 Hz, 1 H), 2.16-2.08 (m, 1 H), 1.97 (quint, *J* = 6.0 Hz, 2 H), 1.75-1.69 (m, 1 H), 1.60 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.0, 137.2, 135.6, 125.7, 120.6, 119.8, 118.8, 116.0, 109.1, 51.5, 45.6, 36.8, 35.0, 29.3, 27.2, 22.6, 19.7. IR (neat, cm^{-1}): 2933, 1727, 1469, 1433, 1412, 1373, 1314, 1092, 1018. Anal. calcd (found) for $C_{17}H_{21}NO_2$: C, 75.25 (75.03); H, 7.80 (7.55).

2,2-Dicarbomethoxy-4-(1-carbomethoxypropyl)-9-methyl-1,3,4,9-tetrahydrocarbazole (Table 2, entry 9). White solid, 62%. mp 174-176 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.41. ^{1}H NMR: δ 7.57 (d, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 7.07 (t, *J* = 7.6 Hz, 1 H), 3.93-3.91 (m, 1 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.66 (s, 3 H), 3.620 (s, 3 H), 3.52 (d, *J* = 16.0 Hz, 1 H), 3.35 (br d, *J* = 11.2 Hz, 1 H), 3.07 (d, *J* = 15.8 Hz, 1 H), 2.45 (dd, *J* = 5.0, 13.0 Hz, 1 H), 2.02 (dd, *J* = 11.2, 14.8 Hz, 1 H), 1.69-1.60 (m, 1 H), 1.06-0.97 (m, 1 H). $^{13}C\{^{1}H\}$ NMR: δ 175.6, 172.3, 170.7, 137.9, 134.4, 126.1, 121.2, 119.3, 109.3, 108.8, 55.0, 53.4, 53.1, 52.0, 49.6, 34.6, 30.9, 29.6, 28.3, 18.4, 13.5. IR (neat, cm^{-1}): 2952, 1730, 1469, 1437, 1048, 737. Anal. calcd (found) for $C_{22}H_{27}NO_6$: C, 65.82 (65.81); H, 6.78 (6.70).

1,5,5-Tricarbomethoxy-7-methyl-2,3,4a,6,7,11c-hexahydro-1*H*,4*H*-benzo[c]carbazole (Table 2, entry 10). White solid, 45%. mp 174-176 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.41. ^{1}H NMR: δ 7.55 (d, *J* = 8.0 Hz, 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 7.04 (t, *J* = 7.8 Hz, 1 H), 3.93-3.91 (m, 1 H), 3.90-3.88 (m, 1 H), 3.84 (s, 3 H), 3.80 (s, 3 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 3.55 (d, *J* = 17.6 Hz, 1 H), 3.11 (dd, *J* = 2.6, 17.4 Hz, 1 H), 3.08 (td, *J* = 3.8, 12.8 Hz, 1 H), 2.01 (br d, *J* = 13.6 Hz, 1 H), 1.59-1.22 (m, 5 H). $^{13}C\{^{1}H\}$ NMR: δ 175.6, 171.0, 170.4, 137.9, 133.7, 126.1, 120.9, 119.4, 119.1, 109.3, 107.3, 59.2, 53.3, 52.1, 42.3, 42.2, 37.4, 33.8, 29.6, 24.6, 23.7, 23.1, 22.2. IR (neat, cm^{-1}): 2950, 1732,

1469, 1433, 1260, 1048, 911, 737. Anal. calcd (found) for $C_{23}H_{27}NO_6$: C, 66.81 (67.06); H, 6.58 (6.68).

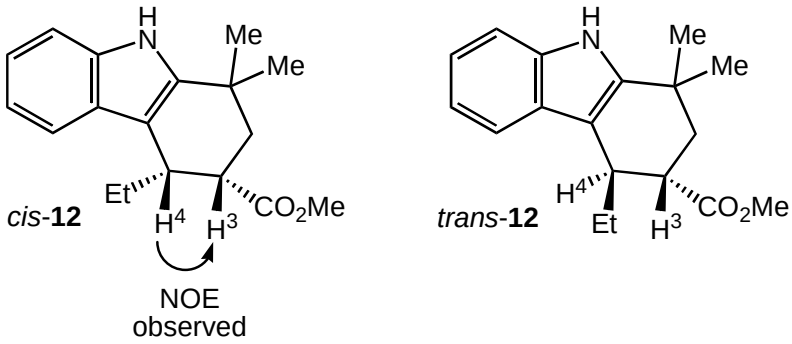
3-Carbomethoxy-9-methyl-2,3,4,9-tetrahydrocarbazole (10).[7] Pale yellow oil, 76%. TLC (hexanes-EtOAc = 2:1): R_f = 0.61. ^{1}H NMR: δ 7.48 (d, *J* = 8.0 Hz, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.20 (dt, *J* = 0.8, 7.6 Hz, 1 H), 7.11 (dt, *J* = 0.8, 7.8 Hz, 1 H), 3.75 (s, 3 H), 3.63 (s, 3 H), 3.10 (dd, *J* = 5.4, 15.0 Hz, 1 H), 2.96-2.70 (m, 4 H), 2.38-2.33 (m, 1 H), 2.47 (dtd, *J* = 6.0, 10.4, 13.2 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 176.3, 137.3, 134.9, 127.1, 121.1, 119.1, 118.0, 108.9, 107.7, 82.1, 40.4, 29.4, 26.0, 24.4, 21.5. IR (neat, cm^{-1}): 2934, 1731, 1470, 1434, 1416, 1379, 1281, 1166, 1080, 1014, 739.

***cis*-3-Carbomethoxy-4-ethyl-1,1-dimethyl-2,3,4,9-tetrahydrocarbazole (*cis*-12)**. White solid, 92%. mp 64-67 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.68. ^{1}H NMR (Figure S3): δ 7.96 (s, 1 H), 7.57 (dd, *J* = 0.8, 8.0 Hz, 1 H), 7.32 (dd, *J* = 0.8, 8.4 Hz, 1 H), 7.19-7.10 (m, 2 H), 3.82 (s, 3 H), 3.43 (td, *J* = 4.8, 8.8 Hz, 1 H), 3.08 (ddd, *J* = 2.6, 5.0, 13.2 Hz, 1 H), 2.23 (t, *J* = 13.6 Hz, 1 H), 1.94 (dd, *J* = 2.2, 13.8 Hz, 1 H), 1.70-1.55 (m, 2 H), 1.45 (s, 3 H), 1.30 (s, 3 H), 1.06 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S4): δ 175.9, 141.2, 136.3, 127.8, 121.5, 119.5, 119.4, 112.6, 110.9, 51.9, 42.9, 36.4, 36.3, 32.0, 30.3, 29.7, 26.7, 13.8. IR (neat, cm^{-1}): 3406, 2958, 1727, 1713, 1455, 1430, 1140, 1013, 908, 734. HRMS calcd (found) for $C_{18}H_{23}NO_2$ (M^+): 285.1729 (285.1722).

***trans*-3-Carbomethoxy-4-ethyl-1,1-dimethyl-2,3,4,9-tetrahydrocarbazole (*trans*-12)**. Pale yellow viscous oil, 84%. TLC (hexanes–EtOAc = 2:1): R_f = 0.66. ^{1}H NMR (Figure S5): δ 7.96 (s, 1 H), 7.62 (d, *J* = 8.0 Hz, 1 H), 7.32 (dd, *J* = 0.8, 8.2 Hz, 1 H), 7.18-7.08 (m, 2 H), 3.80 (s, 3 H), 3.55 (ddd, *J* = 3.0, 6.6, 9.2 Hz, 1 H), 2.96 (ddd, *J* = 2.4, 9.2, 12.4 Hz, 1 H), 2.24-2.13 (m, 1 H), 2.02 (t, *J* = 13.2 Hz, 1 H), 1.97-1.89 (m, 2 H), 1.39 (s, 3 H), 1.37 (s, 3 H), 0.83 (t, *J* =

7.6 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (Figure S6): δ 177.1, 141.8, 136.4, 127.3, 121.3, 119.8, 119.5, 111.0, 109.7, 52.1, 42.7, 42.1, 36.9, 31.7, 29.4, 29.3, 25.2, 9.3. IR (neat, cm^{-1}): 3391, 2961, 1717, 1455, 1455, 1167, 908, 740. HRMS calcd (found) for $C_{18}H_{23}NO_2$ (M^+): 285.1729 (285.1732).

The stereochemistry of *cis*-**12** and *trans*-**12** were established by ^{1}H NOE analysis. In particular, irradiation of H_4 led to the enhancement of H_3 in *cis*-**12** but not in *trans*-**12**. The stereochemistry of *cis*-**12** was confirmed via X-ray crystallographic analysis (Tables S1-S4, Figure S7).



Methyl (5-methyl-5,6,7,8,9,10-hexahydro-cyclohepta[b]indol-10-yl)acetate (14). Pale yellow oil, 74%. TLC (hexanes-EtOAc = 2:1): R_f = 0.70. ^{1}H NMR: δ 7.60 (d, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* = 8.0 Hz, 1 H), 7.19 (dt, *J* = 1.0, 7.6 Hz, 1 H), 7.12 (dt, *J* = 0.8, 7.6 Hz, 1 H), 3.93-3.88 (m, 1 H), 3.67 (s, 3 H), 3.65 (s, 3 H), 3.03 (ddd, *J* = 2.4, 6.2, 16.0 Hz, 1 H), 2.81 (ddd, *J* = 2.4, 12.0, 15.6 Hz, 1 H), 2.68 (d, J = 8.0 Hz, 2 H), 2.13-1.59 (m, 6 H). $^{13}C\{^{1}H\}$ NMR: δ 173.7, 138.7, 136.1, 127.4, 120.8, 119.1, 118.0, 115.4, 109.1, 51.8, 38.8, 31.9, 31.8, 29.7, 27.7, 25.9, 25.6. IR (neat, cm-1): 2922, 2852, 1730, 1470, 1434, 1382, 1360, 1285, 1165, 1015, 739. Anal. calcd (found) for $C_{17}H_{21}NO_2$: C, 75.25 (75.24); H, 7.80 (7.75).

Methyl (2,3,4,9-tetrahydro-1-carbazolyl)acetate (17). Pale yellow oil, 85%. TLC (hexanes–EtOAc = 5:1): R_f = 0.64. ^{1}H NMR: δ 8.74 (s, 1 H), 7.51 (dd, J = 0.8, 8.4 Hz, 1 H), 7.33 (td, *J* = 0.8, 8.2 Hz, 1 H), 7.17 (dt, *J* = 1.0, 7.6 Hz, 1 H), 7.11 (dt, *J* = 1.0, 7.6 Hz, 1 H), 3.80 (s, 3 H), 3.43-3.36 (m, 1 H), 2.76-2.63 (m, 4 H), 2.13-2.06 (m, 1 H), 2.00-1.82 (m, 2 H), 1.72-1.65 (m, 1 H). ^{13}C{^{1}H} NMR: δ 175.3, 136.5, 135.9, 127.5, 121.6, 119.3, 118.3, 111.1, 110.5, 52.3, 40.6, 30.9, 30.2, 21.7, 21.3. IR (neat, cm^{-1}): 3406, 2930, 2846, 1727, 1466, 1363, 1329, 1009, 741. Anal. calcd (found) for $C_{15}H_{17}NO_2$: C, 74.05 (73.90); H, 7.04 (7.07).

2-Carbomethoxy-9-methyl-2,3,4,9-tetrahydrocarbazole (19).[9] Pale yellow solid, 58%. TLC (hexanes-EtOAc = 2:1): R_f = 0.61. ^{1}H NMR: δ 7.50 (d, *J* = 7.6 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 7.15 (dt, *J* = 0.8, 7.8 Hz, 1 H), 7.13 (dt, *J* = 1.0, 7.8 Hz, 1 H), 3.81 (s, 3 H), 3.66 (s, 3 H), 3.04-2.75 (m, 5 H), 2.40-2.34 (m, 1 H), 2.47 (dtd, *J* = 5.6, 10.8, 13.2 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 175.9, 137.3, 134.0, 127.0, 121.1, 119.1, 118.1, 108.9, 108.8, 52.2, 40.6, 29.4, 26.6, 24.9, 20.7. IR (neat, cm^{-1}): 2948, 2846, 1742, 1732, 1470, 1380, 1168, 1380, 1168, 1011, 739. Anal. calcd (found) for $C_{15}H_{17}NO_2$: C, 74.05 (73.96); H, 7.04 (7.17).

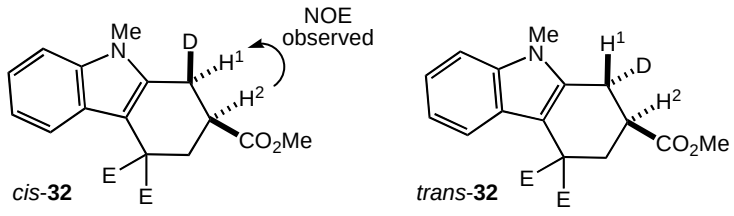
32-*d*$_0$. White solid, 41%. mp 168-170 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.30. ^{1}H NMR: δ 7.53 (d, *J* = 8.0 Hz, 1 H), 7.26 (d, *J* = 8.8 Hz, 1 H), 7.18 (dd, *J* = 6.8, 8.0 Hz, 1 H), 7.10 (dd, *J* = 6.8, 8.0 Hz, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.71 (s, 3 H), 3.62 (s, 3 H), 3.28-3.21 (m, 1 H), 3.11-3.06 (m, 2 H), 2.90 (dd, *J* = 11.6, 16.4 Hz, 1 H), 2.12 (t, *J* = 13.0 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 174.8, 172.3, 171.4, 137.6, 136.1, 126.0, 121.6, 120.7, 120.0, 109.2, 105.0, 54.8, 53.2, 52.9, 52.5, 37.7, 33.9, 29.5, 24.9. IR (neat, cm^{-1}): 2950, 17257, 1434, 741. HRMS calcd (found) for $C_{19}H_{21}NO_6$ (M^+): 359.1369 (359.1368).

***cis*-32**. White solid, 37%. TLC (hexanes-EtOAc = 2:1): R_f = 0.30. ^{1}H NMR: δ 7.53 (d, *J* = 8.0 Hz, 1 H), 7.26 (d, *J* = 8.8 Hz, 1 H), 7.18 (dd, *J* = 6.8, 8.0 Hz, 1 H), 7.10 (dd, *J* = 6.8, 8.0

Hz, 1 H), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.71 (s, 3 H), 3.62 (s, 3 H), 3.24 (ddd, *J* = 2.7, 5.5, 12.5 Hz, 1 H), 3.07 (dd, *J* = 2.8, 12.8 Hz, 1 H), 3.06 (d, *J* = 5.3 Hz, 1 H), 2.12 (t, *J* = 12.8 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR: δ 174.8, 172.4, 171.5, 137.6, 136.1, 126.1, 121.6, 120.7, 120.0, 109.2, 105.1, 54.9, 53.2, 52.9, 52.5, 37.6, 33.9, 29.6, 24.5 (t, *J* = 19.9 Hz, IS = 338 ppb). HRMS calcd (found) for $C_{19}H_{20}DNO_6$ (MH^+): 361.1494 (361.1507).

***trans*-32**. White solid, 34%. TLC (hexanes-EtOAc = 2:1): R_f = 0.30. ^{1}H NMR: δ 7.52 (d, *J* = 8.0 Hz, 1 H), 7.26 (d, *J* = 8.8 Hz, 1 H), 7.18 (dd, *J* = 6.8, 8.0 Hz, 1 H), 7.09 (dd, *J* = 6.8, 8.0 Hz, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.70 (s, 3 H), 3.63 (s, 3 H), 3.23 (dt, *J* = 2.6, 11.6 Hz, 1 H), 3.07 (dd, *J* = 2.8, 13.0 Hz, 1 H), 2.87 (d, *J* = 11.6 Hz, 1 H), 2.11 (t, *J* = 13.0 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR: δ 174.8, 172.4, 171.5, 137.6, 136.1, 126.1, 121.6, 120.7, 120.0, 109.2, 105.1, 54.9, 53.2, 52.9, 52.5, 37.6, 33.9, 29.6, 24.6 (t, *J* = 22.3 Hz, IS = 270 ppb). HRMS calcd (found) for $C_{19}H_{20}DNO_6$ (MH^+): 361.1494 (361.1502).

The stereochemistries of *cis*-**32** and *trans*-**32** were established by ^{1}H NMR and ^{1}H NOE analysis. In particular, $J_{H1\text{-}H2}$ for *cis*-**32** was 5.4 Hz, consistent with a syn relationship whereas $J_{H1\text{-}H2}$ for *trans*-**32** was 11.6 Hz, consistent with an anti relationship. More importantly, irradiation of H^2 led to enhancement of H^1 in *cis*-**32** but not in *trans*-**32.**



II. Cyclization/carboalkoxylation in THF

9. THF (4 mL), methanol (180 μL, 5.0 mmol), and a solution of **8** (99 mg, 0.50 mmol) in

THF (1.0 mL) were added sequentially to a flask containing **2** (6.5 mg, 0.025 mmol) and $CuCl_2$ (200 mg, 1.5 mmol) under CO (1 atm). The resulting suspension was stirred for 30 min and concentrated under vacuum. Column chromatography of the residue (SiO_2; hexanes–EtOAc = 5:1) gave **9** (106 mg, 83%) as a pale yellow oil.

Indole derivatives **20**-**24** were synthesized employing a procedure similar to that used to synthesize **9** in THF.

Ethyl (2,3,4,9-tetrahydro-4-carbazolyl)acetate (**20**). Pale yellow oil, 73%. TLC (hexanes-EtOAc = 2:1): R_f = 0.58. ^{1}H NMR: δ 7.78 (s, 1 H), 7.52 (d, *J* = 8.4 Hz, 1 H), 7.26-7.23 (m, 1 H), 7.14-7.06 (m, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 3.58-3.52 (m, 1 H), 2.99 (dd, *J* = 4.0, 15.2 Hz, 1 H), 2.69-2.66 (m, 2 H), 2.41 (dd, *J* = 10.4, 14.8 Hz, 1 H), 2.00-1.74 (m, 4 H), 1.29 (t, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 173.6, 136.0, 134.9, 127.1, 121.3, 119.5, 118.4, 112.4, 110.9, 60.6, 40.2, 29.3, 28.7, 23.5, 19.7, 14.6. IR (neat, cm^{-1}): 3399, 2932, 1729, 1713, 1463, 1370, 1326, 1301, 1281, 1177, 1071, 1030, 741. Anal. calcd (found) for $C_{16}H_{19}NO_2$: C, 74.68 (74.40); H, 7.44 (7.65).

***n*-Octyl (2,3,4,9-tetrahydro-4-carbazolyl)acetate** (**21**). Pale yellow oil, 82%. TLC (hexanes-EtOAc = 2:1): R_f = 0.75. ^{1}H NMR: δ 7.78 (s, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 7.26-7.24 (m, 1 H), 7.14-7.06 (m, 1 H), 4.14 (t, *J* = 6.2 Hz, 2 H), 3.58-3.53 (m, 1 H), 2.99 (dd, *J* = 4.0, 15.2 Hz, 1 H), 2.69-2.67 (m, 2 H), 2.42 (dd, *J* = 10.4, 14.8 Hz, 1 H), 1.98-1.73 (m, 4 H), 1.68-1.62 (m, 2 H), 1.39-1.26 (m, 10 H), 0.91 (t, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 173.7, 136.1, 134.9, 127.1, 121.3, 119.5, 118.4, 112.4, 110.9, 64.9, 40.3, 32.1, 29.5, 29.4, 28.9, 28.8, 26.2, 23.5, 23.0, 19.7, 14.4. IR (neat, cm^{-1}): 3402, 2925, 2855, 1713, 1454, 739. Anal. calcd (found) for $C_{22}H_{31}NO_2$: C, 77.38 (77.13); H, 9.15 (9.23).

Isopropyl (2,3,4,9-tetrahydro-4-carbazolyl)acetate (**22**). Pale yellow oil, 75%. TLC

(hexanes-EtOAc = 2:1): R_f = 0.61. ^{1}H NMR (Figure S8): δ 7.79 (s, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.26-7.23 (m, 1 H), 7.15-7.06 (m, 1 H), 5.10 (septet, *J* = 7.6 Hz, 1 H), 3.58-3.53 (m, 1 H), 2.99 (dd, *J* = 4.0, 15.2 Hz, 1 H), 2.70-2.62 (m, 2 H), 2.39 (dd, *J* = 10.4, 14.8 Hz, 1 H), 2.00-1.76 (m, 4 H), 1.29 (d, *J* = 6.4 Hz, 3 H), 1.26 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S9): δ 173.2, 136.0, 134.9, 127.1, 121.3, 119.4, 118.5, 112.4, 110.8, 67.9, 40.6, 29.4, 28.7, 23.5, 22.3, 22.1, 19.8. IR (neat, cm^{-1}): 3402, 2978, 2934, 1729, 1453, 1372, 1107, 741. HRMS calcd (found) for $C_{17}H_{21}NO_2$ (M^+): 271.1572 (271.1568).

Cyclohexyl (2,3,4,9-tetrahydro-4-carbazolyl)acetate (**23**). Pale yellow oil, 73%. TLC (hexanes-EtOAc = 2:1): R_f = 0.71. ^{1}H NMR (Figure S10): δ 7.78 (s, 1 H), 7.56 (d, *J* = 7.6 Hz, 1 H), 7.29-7.27 (m, 1 H), 7.15-7.07 (m, 2 H), 4.86 (tt, *J* = 3.6, 8.8 Hz, 1 H), 3.59-3.52 (m, 1 H), 2.99 (dd, *J* = 4.0, 15.2 Hz, 1 H), 2.72-2.69 (m, 2 H), 2.41 (dd, *J* = 10.4, 14.8 Hz, 1 H), 1.99-1.69 (m, 8 H), 1.58-1.27 (m, 6 H). ^{13}C{^{1}H} NMR (Figure S11): δ 173.1, 136.1, 134.9, 127.1, 121.3, 119.5, 118.5, 112.5, 110.9, 72.8, 40.6, 32.0, 31.9, 29.5, 28.7, 25.7, 24.0, 23.5, 19.8. IR (neat, cm^{-1}): 3403, 2935, 1725, 1453, 1281, 1182, 1014, 908, 741. HRMS calcd (found) for $C_{20}H_{25}NO_2$ (M^+): 311.1885 (311.1887).

4-Chlorobutyl 2-(9-methyl-2,3,4,9-tetrahydro-4-carbazolyl)acetate (24). Pale yellow oil, 65%. TLC (hexanes-EtOAc = 5:1): R_f = 0.45. ^{1}H NMR: δ 7.53 (br d, *J* = 8.0 Hz, 1 H), 7.27 (br d, *J* = 8.0 Hz, 1 H), 7.19-7.15 (m, 1 H), 7.10-7.06 (m, 1 H), 4.17-4.15 (m, 2 H), 3.62 (s, 3 H), 3.58-3.54 (m, 3 H), 2.98 (dd, *J* = 4.2, 15.0 Hz, 1 H), 2.78-2.63 (m, 2 H), 2.44 (dd, *J* = 10.2, 15.0 Hz, 1 H), 2.00-1.77 (m, 8 H). ^{13}C{^{1}H} NMR: δ 173.5, 137.2, 136.4, 126.5, 121.0, 119.1, 118.4, 111.5, 109.0, 63.8, 44.8, 40.4, 29.5, 29.3, 28.6, 26.4, 22.4, 19.6. IR (neat, cm^{-1}): 2934, 1729, 1470, 1165, 739. Anal. calcd (found) for $C_{19}H_{25}ClNO_2$: C, 68.15 (68.07); H, 7.53 (7.50).

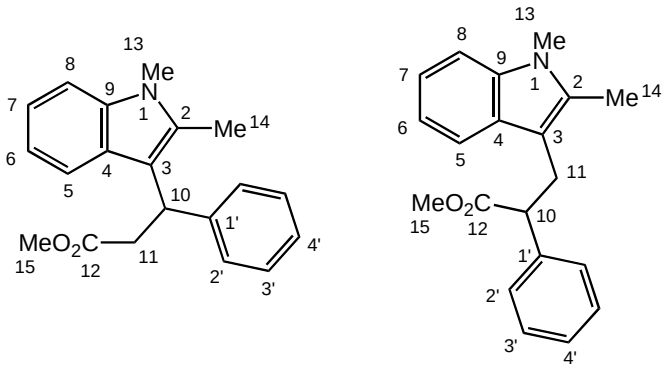
Methyl 2-(3-ethyl-5,6,7,8-tetrahydroindolizin-8-yl)acetate (28). Pale yellow oil, 52%. TLC (hexanes-EtOAc = 5:1): R_f = 0.41. ^{1}H NMR (Figure S12): δ 5.87-5.83 (m, 2 H), 3.90-3.85 (m, 1 H), 3.72 (s, 3 H), 3.70-3.62 (m, 1 H), 3.36-3.29 (m, 1 H), 2.85 (dd, *J* = 5.2, 15.4 Hz, 1 H), 2.59-2.43 (m, 3 H), 2.12-2.03 (m, 2 H), 1.98-1.87 (m, 1 H), 1.47 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S13): δ 173.2, 133.8, 131.3, 103.8, 102.8, 103.8, 51.8, 42.8, 40.5, 31.9, 27.5, 22.7, 19.7, 12.8. IR (neat, cm^{-1}): 2938, 2870, 1738, 1731, 1279, 1156, 1019, 747. HRMS calcd (found) for $C_{13}H_{19}NO_2$ (M^+): 221.1416 (221.1418).

3-Chloro-1-methyl-2-(4-pentenyl)indole (7). A solution of **5** (0.30, 1.5 mmol) in methanol (2.0 mL) was added to a flask containing a suspension of $CuCl_2$ (0.60 g, 4.5 mmol) in methanol (8.0 mL) under CO (1 atm). The resulting suspension was stirred for 45 min and concentrated under vacuum. Column chromatography of the residue (SiO_2; hexanes–EtOAc = 10:1) gave **7** (0.27 g, 77%) as a pale yellow oil. TLC (hexanes-EtOAc = 5:1): R_f = 0.66. ^{1}H NMR: δ 7.62-7.59 (m, 1 H), 7.31-7.18 (m, 3 H), 5.89 (tdd, *J* = 6.8, 10.4, 16.4 Hz, 1 H), 5.14-5.04 (m, 2 H), 3.70 (s, 3 H), 2.87 (t, *J* = 7.6 Hz, 2 H), 2.21 (q, *J* = 7.2 Hz, 2 H), 1.76 (quint, *J* = 7.2 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 138.3, 136.4, 135.9, 125.6, 122.1, 120.2, 117.8, 115.5, 109.3, 102.9, 33.5, 30.3, 28.5, 24.0.

Intermolecular Arylation of Vinyl Arenes with Indoles

Regiochemistry of methyl 3-(1,2-dimethyl-3-indolyl)-3-phenylpropanate (28). The C and H atoms of **29** were assigned on the basis of the ^{1}H-^{1}H COSY (Figure S14) and HMQC (Figure S15) spectroscopy, respectively. The structure was assigned as that of **29** on the basis of the HMBC spectrum (Figure S16). In particular, the HMBC spectrum of **29** displayed 3-bond couplings between H(11) and C(3) and between H(11) and C(1'), with no 4-bond couplings

between H(11) and either C(2), C(4), or C(2'). The failure to observe coupling between H(11) and either C(2) or C(4) argue against regioisomer **29'**, which would be expected to display couplings between H(11) and both C(2) and C(4).



Methyl 3-(1,2-dimethy-3-indolyl)-3-*p*-tolylpropanoate (Table 6, entry 1). Pale yellow oil, 78%. TLC (hexanes-EtOAc = 5:1): R_f = 0.36. ^{1}H NMR: δ 7.47 (br d, *J* = 7.6 Hz, 1 H), 7.24-7.21 (m, 3 H), 7.11 (dt, *J* = 0.8, 7.8 Hz, 1 H), 7.05 (br d, *J* = 8.0 Hz, 2 H), 7.01-6.97 (m, 1 H), 4.84 (t, *J* = 7.8 Hz, 1 H), 3.63 (s, 3 H), 3.58 (s, 3 H), 3.33 (dd, *J* = 7.2, 15.6 Hz, 1 H), 3.19 (dd, *J* = 8.4, 15.6 Hz, 1 H), 2.41 (s, 3 H), 2.28 (s, 3 H). ^{13}C{^{1}H} NMR: δ 173.3, 141.2, 137.1, 135.7, 133.7, 129.3, 127.5, 126.7, 120.6, 119.4, 119.0, 112.9, 109.0, 51.8, 39.80, 38.0, 29.8, 21.2, 10.9. IR (neat, cm^{-1}): 2953, 1738, 1731, 1513, 1470, 1434, 1254, 1159, 739. Anal. calcd (found) for $C_{21}H_{23}NO_2$: C, 78.47 (78.12); H, 7.21 (7.22).

Methyl 3-(1,2-dimethyl-3-indolyl)-3-*m*-tolylpropanoate (Table 6, entry 2). Pale yellow oil, 76%. TLC (hexanes-EtOAc = 5:1): R_f = 0.41. ^{1}H NMR: δ 7.55 (br d, *J* = 8.0 Hz, 1 H), 7.27 (d, *J* = 8.0 Hz, 1 H), 7.23-7.15 (m, 4 H), 7.08-7.01 (m, 2 H), 4.92 (t, *J* = 7.8 Hz, 1 H), 3.65 (s, 3 H), 3.61 (s, 3 H), 3.40 (dd, *J* = 7.0, 15.8 Hz, 1 H), 3.27 (dd, *J* = 8.4, 15.6 Hz, 1 H), 2.47

(s, 3 H), 2.34 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.3, 144.1, 138.0, 137.1, 133.7, 128.5, 128.4, 127.0, 126.7, 124.5, 120.5, 119.4, 119.0, 112.8, 108.9, 51.8, 39.7, 38.3, 29.7, 21.8, 10.9. IR (neat, cm^{-1}): 2953, 1742, 1722, 1470, 1367, 1161, 739. Anal. calcd (found) for $C_{21}H_{23}NO_2$: C, 78.47 (78.30); H, 7.21 (7.21).

Methyl 3-(1,2-dimethy-3-indolyl)-3-*o*-tolylpropanoate (Table 6, entry 3). Pale yellow oil, 44%. TLC (hexanes-EtOAc = 5:1): R_f = 0.32. ^{1}H NMR: δ 7.63 (br d, *J* = 7.6 Hz, 1 H), 7.55 (br d, *J* = 7.6 Hz, 1 H), 7.31-7.26 (m, 2 H), 7.20-7.13 (m, 3 H), 7.06-7.02 (m, 1 H), 4.99 (t, *J* = 7.8 Hz, 1 H), 3.65 (s, 3 H), 3.62 (s, 3 H), 3.29 (d, *J* = 7.2 Hz, 1 H), 2.43 (s, 3 H), 2.28 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.1, 141.6, 137.0, 133.7, 131.1, 126.9, 126.5, 126.4, 125.9, 120.5, 119.2, 119.0, 111.3, 108.9, 51.8, 39.7, 35.9, 29.7, 20.0, 10.9. IR (neat, cm^{-1}): 2953, 1737, 1731, 1470, 739. Anal. calcd (found) for $C_{21}H_{23}NO_2$: C, 78.47 (78.23); H, 7.21 (7.28).

Methyl 3-(1,2-dimethyl-3-indolyl)-3-(4-methoxyphenyl)propanoate (Table 6, entry 4). Pale yellow oil, 40%. TLC (hexanes-EtOAc = 5:1): R_f = 0.29. ^{1}H NMR: δ 7.44 (br d, *J* = 8.0 Hz, 1 H), 7.25-7.21 (m, 3 H), 7.12-7.09 (m, 1 H), 7.00-6.96 (m, 1 H), 6.80-6.76 (m, 2 H), 4.82 (t, *J* = 7.8 Hz, 1 H), 3.73 (s, 3 H), 3.62 (s, 3 H), 3.55 (s, 3 H), 3.31 (dd, *J* = 7.6, 15.6 Hz, 1 H), 3.16 (dd, *J* = 8.4, 15.6 Hz, 1 H), 2.40 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.3, 158.0, 137.1, 136.3, 133.7, 128.6, 120.6, 119.4, 119.0, 113.9, 113.0, 109.0, 55.5, 51.8, 40.0, 37.6, 29.8, 10.9. IR (neat, cm^{-1}): 2953, 1737, 1610, 1512, 1470, 1366, 1247, 1033, 831, 740. Anal. calcd (found) for $C_{21}H_{23}NO_3$: C, 74.75 (74.59); H, 6.87 (6.99).

Methyl 3-(4-chlorophenyl)-3-(1,2-dimethyl-3-indolyl)propanoate (Table 6, entry 5). Pale yellow oil, 50%. TLC (hexanes-EtOAc = 5:1): R_f = 0.32. ^{1}H NMR: δ 7.42 (br d, *J* = 8.0 Hz, 1 H), 7.27-7.19 (m, 5 H), 7.15-7.11 (m, 1 H), 7.02-6.98 (m, 1 H), 4.85 (t, *J* = 7.6 Hz, 1 H), 3.63 (s, 3 H), 3.57 (s, 3 H), 3.32 (dd, *J* = 7.8, 15.8 Hz, 1 H), 3.17 (dd, *J* = 7.6, 15.6 Hz, 1 H), 2.41

(s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.0, 142.7, 137.1, 133.8, 132.0, 129.0, 128.7, 126.5, 120.8, 119.2, 112.3, 109.1, 51.9, 39.6, 37.9, 29.8, 10.9. IR (neat, cm^{-1}): 2953, 1737, 1727, 1492, 1470, 1433, 1400, 1366, 1254, 1160, 1013, 739. Anal. calcd (found) for $C_{20}H_{20}ClNO_2$: C, 70.27 (70.48); H, 5.90 (5.87).

Methyl 3-(1,2-dimethyl-3-indolyl)-3-(-2-naphthalenyl)propanoate (Table 6, entry 6). Pale yellow oil, 58%. TLC (hexanes-EtOAc = 5:1): R_f = 0.27. ^{1}H NMR: δ 7.85-7.70 (m, 4 H), 7.54-7.42 (m, 4 H), 7.25 (br d, *J* = 8.0 Hz, 1 H), 7.14 (dd, *J* = 8.0, 8.8 Hz, 1 H), 7.01 (dd, *J* = 8.0, 9.2 Hz, 1 H), 5.08 (t, *J* = 7.6 Hz, 1 H), 3.63 (s, 3 H), 3.61 (s, 3 H), 3.52 (dd, *J* = 6.8, 15.6 Hz, H), 3.32 (dd, *J* = 8.6, 15.8 Hz, 1 H), 2.46 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.2, 141.7, 137.1, 133.9, 133.6, 132.3, 128.2, 128.1, 127.8, 127.2, 126.8, 126.2, 125.6, 124.8, 120.7, 119.3, 119.1, 112.6, 109.0, 51.9, 39.5, 38.4, 29.8, 10.9. IR (neat, cm^{-1}): 3050, 1732, 1470, 1434, 1407, 1366, 1268, 1160, 908, 856, 819. Anal. calcd (found) for $C_{24}H_{23}NO_2$: C, 80.64 (80.38); H, 6.49 (6.46).

Methyl 3-(2-methyl-3-indolyl)-3-*p*-tolylpropanoate (Table 6, entry 7). White solid, 71%. mp 109-111 °C. TLC (hexanes-EtOAc = 5:1): R_f = 0.21. ^{1}H NMR: δ 7.83 (s, 1 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 7.28-7.03 (m, 7 H), 4.86 (t, *J* = 7.6 Hz, 1 H), 3.58 (s, 3 H), 3.37 (dd, *J* = 7.0, 15.4 Hz, 1 H), 3.25 (dd, *J* = 8.6, 15.4 Hz, 1 H), 2.35 (s, 3 H), 2.32 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.4, 140.9, 135.8, 135.6, 131.9, 129.3, 127.6, 127.5, 120.9, 119.4, 119.3, 113.3, 110.7, 51.8, 39.7, 37.7, 21.2, 12.3. IR (neat, cm^{-1}): 3404, 2948, 1722, 1512, 1460, 1434, 1358, 1161, 909, 816, 740. Anal. calcd (found) for $C_{20}H_{21}NO_2$: C, 78.15 (78.53); H, 6.89 (7.01).

Methyl 3-(5-methoxy-2-methyl-3-indolyl)-3-*p*-tolylpropanoate (Table 6, entry 8). Yellow viscous oil, 63%. TLC (hexanes–EtOAc = 2:1): R_f = 0.46. ^{1}H NMR: δ 7.76 (s, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.8 Hz, 3 H), 6.89 (d, *J* = 4.0 Hz, 1 H), 6.71 (dd, *J* = 4.8, 8.8 Hz, 1 H), 4.78 (t, *J* = 7.6 Hz, 1 H), 3.76 (s, 3 H), 3.56 (s, 3 H), 3.28 (dd, *J* = 7.2, 15.6 Hz, 1

H), 3.16 (dd, *J* = 8.6, 15.4 Hz, 1 H), 2.31 (s, 3 H), 2.28 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.4, 153.8, 140.8, 135.8, 132.8, 130.8, 129.3, 128.2, 127.5, 113.3, 111.1, 110.2, 102.1, 56.2, 51.9, 39.5, 37.6, 21.2, 12.5. IR (neat, cm^{-1}): 3403, 2953, 1732, 1586, 1512, 1484, 1216, 1032, 909, 731. Anal. calcd (found) for $C_{21}H_{23}NO_3$: C, 74.75 (74.81); H, 6.87 (6.77).

Methyl 3-(5-chloro-2-methyl-3-indolyl)-3-*p*-tolylpropanoate (Table 6, entry 9). Pale yellow oil, 65%. TLC (hexanes–EtOAc = 2:1): R_f = 0.47. ^{1}H NMR: δ 7.92 (s, 1 H), 7.41 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.09-6.97 (m, 4 H), 4.76 (t, *J* = 7.8 Hz, 1 H), 3.56 (s, 3 H), 3.29 (dd, *J* = 6.8, 15.6 Hz, 1 H), 3.16 (dd, *J* = 8.8, 15.4 Hz, 1 H), 2.29 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.3, 140.4, 136.0, 134.0, 133.6, 129.4, 128.7, 127.3, 125.0, 121.2, 118.6, 113.2, 111.6, 51.9, 39.5, 37.5, 21.2, 12.4. IR (neat, cm^{-1}): 3410, 1726, 1435, 1304, 1160, 796, 732. Anal. calcd (found) for $C_{20}H_{20}ClNO_2$: C, 70.27 (70.30); H, 5.90 (5.92).

Methyl 3-(2-pheny-3-indolyl)-3-*p*-tolylpropanoate (Table 6, entry 10). Pale yellow oil, 77%. TLC (hexanes-EtOAc = 5:1): R_f = 0.31. ^{1}H NMR: δ 8.10 (s, 1 H), 7.58-7.04 (m, 13 H), 5.02 (t, *J* = 7.6 Hz, 1 H), 3.47 (s, 3 H), 3.33 (dd, *J* = 7.4, 15.4 Hz, 1 H), 3.22 (dd, *J* = 8.6, 15.6 Hz, 1 H), 2.29 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.1, 141.1, 136.5, 135.9, 133.3, 129.4, 129.1, 129.0, 128.3, 127.8, 127.6, 122.3, 121.0, 119.9, 114.3, 111.4, 51.8, 40.4, 37.9, 21.3. IR (neat, cm^{-1}): 3401, 1727, 1512, 1487, 1454, 1160, 909, 810, 765, 739, 699. Anal. calcd (found) for $C_{25}H_{23}NO_2$: C, 81.27 (81.03); H, 6.27 (6.41)

Dimethyl 2-((3-(2-carbomethoxy-1-*p*-tolylethyl)-1-methyl-2-indolyl)methyl)malonate (Table 6, entry 11). White solid, 63%. mp = 144-146 °C. TLC (hexanes-EtOAc = 2:1): R_f = 0.36. ^{1}H NMR: δ 7.44 (d, *J* = 8.0 Hz, 1 H), 7.26 (d, *J* = 8.0 Hz, 1 H), 7.20-7.16 (m, 3 H), 7.05-6.99 (m, 3 H), 4.83 (t, *J* = 7.6 Hz, 1 H), 3.71 (s, 3 H), 3.69 (s, 3 H), 3.67-3.59 (m, 2 H), 3.57 (s, 3 H), 3.55 (s, 3 H), 3.47 (dd, *J* = 6.6, 15.2 Hz, 1 H), 3.33 (dd, *J* = 6.8, 16.0 Hz, 1 H), 3.17 (dd, *J* =

8.4, 15.6 Hz, 1 H), 2.28 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 173.2, 169.3, 169.2, 140.7, 137.8, 135.8, 133.5, 129.3, 127.6, 126.5, 121.4, 120.5, 119.4, 114.4, 109.6, 53.0, 52.1, 51.9, 40.5, 37.9, 30.1, 24.0, 21.2. IR (neat, cm^{-1}): 2948, 1737, 1732, 1513, 1469, 742. Anal. calcd (found) for $C_{26}H_{29}NO_6$: C, 69.16 (68.90); H, 6.47 (6.43).

Part II. Mechanism

Stoichiometric reaction of 5 with 2 in the presence of $CuCl_2$ (Table 7, entry 3). A solution of **5** (50 mg, 0.25 mmol) and eicosane (20 mg, internal standard) in methanol/THF (5:3, 2 mL) was added to a flask containing a suspension of **2** (65 mg, 0.25 mmol) and $CuCl_2$ (34 mg, 0.25 mmol) in THF (1.0 mL) under CO (1 atm). Aliquats were removed periodically via syringe, diluted with EtOAc, filtered through a plug of silica gel, and analyzed by GC. After 5 min, 98% of **5** had been consumed to form **6** in 37% yield. After 180 min, **6** accounted for 97% of the reaction mixture. The remaining stoichiometric reactions depicted in Table 7 were performed in an analogous fashion.

NMR studies

$[PdCl(\mu\text{-}Cl)CO]_2$ (33) and $[PdCl(\mu\text{-}Cl)^{13}CO]_2$ [33-($^{13}CO)_2$]. A suspension of **2** (26 mg, 0.10 mmol) in methanol-d_4 (1.0 mL) under CO (1 atm) was stirred for 5 min to form **33**-($^{13}CO)_2$ as a yellow suspension that was characterized without isolation by ^{13}C NMR spectroscopy. $^{13}C\{^{1}H\}$ NMR (methanol-d_4): δ = 165.5. $[PdCl(\mu\text{-}Cl)CO]_2$ (**33**) was synthesized from the analogous reaction of **2** and CO in chloroform and was characterized without isolation by IR spectroscopy. IR ($CHCl_3$, cm^{-1}): 2166.

Reaction of 33 and 33-(^{13}CO)$_2$ with CuCl$_2$. $CuCl_2$ (0.13 g, 1.0 mmol) was added to a suspension of **33**-(^{13}CO)$_2$ in methanol-d_4 (1.0 mL) under ^{13}CO and the resulting suspension was agitated for 2 min. ^{13}C NMR spectroscopy of the resulting green solution displayed a ~4:1 ratio of resonances at $\delta = 165$ and $\delta = 173$. The corresponding solution generated from reaction of **33** with $CuCl_2$ in chloroform under CO was analyzed by IR spectroscopy. IR ($CHCl_3$, cm^{-1}): 2166.

Reaction of 33-(^{13}CO)$_2$ with CuCl$_2$ and 5. A solution of **5** (50 mg, 0.25 mmol) in methanol-d_4/THF (1 mL, 1:1) was added to a green solution formed by reaction of **2** (65 mg, 0.25 mmol) with $CuCl_2$ (50 mg, 0.38 mmol) in methanol-d_4/THF (1:1, 2.0 mL) under ^{13}CO (1 atm). The resulting solution was stirred for 2.5 min and analyzed periodically by ^{13}C NMR spectroscopy. In addition to the resonance corresponding to the carbonyl peak of **33**-(^{13}CO)$_2$ (δ = 175.4), carbonyl resonances at δ = 210.5, 173.5, and 164.5 along with a small peak at δ = 126.2 corresponding to $^{13}CO_2$ were observed throughout complete conversion of **5** to **6**. In a second experiment, a solution of **5** (50 mg, 0.25 mmol) in methanol-d_4/THF (1:1, 1 mL) was added to a suspension of **2** (3.3 mg, 1.3×10^{-2} mmol) and $CuCl_2$ (0.10 g, 0.75 mmol) in methanol-d_4/THF (1:1, 2 mL) under ^{13}CO (1 atm). The resulting mixture was stirred for 3.5 min and then analyzed periodically by ^{13}C NMR spectroscopy. In addition to the resonance corresponding to the carbonyl peak of **33**-(^{13}CO)$_2$ (δ = 175.4) carbonyl resonances at δ = 173.5, 164.5 and 126.2 ($^{13}CO_2$) were observed throughout complete conversion of **5** to **6**.

Figure S1. ^{1}H NMR spectrum of methyl (6-fluoro-2,3,4,9-tetrahydro-4-carbazolyl)acetate (Table 2, entry 4).

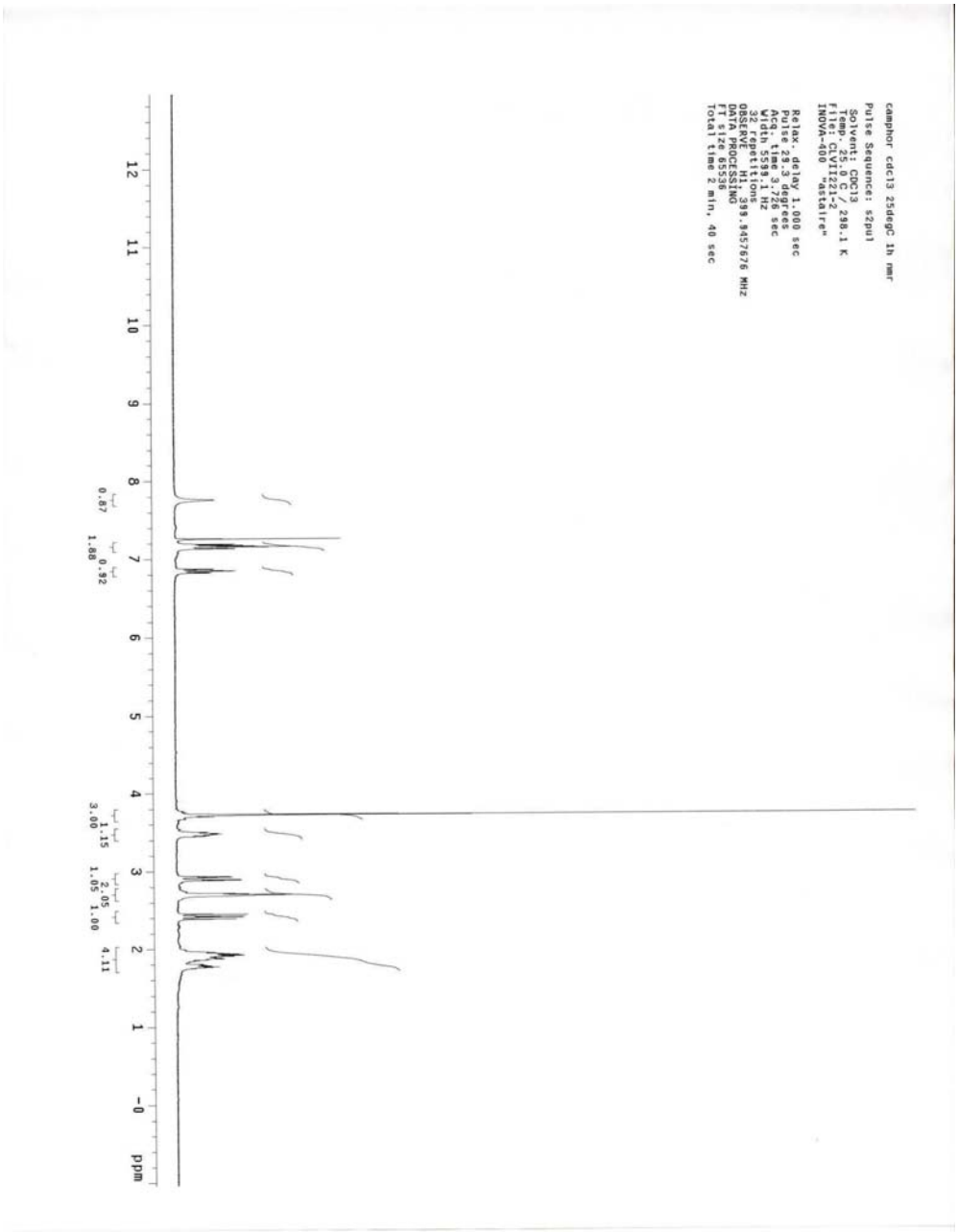


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (6-fluoro-2,3,4,9-tetrahydro-4-carbazolyl)acetate (Table 2, entry 4).

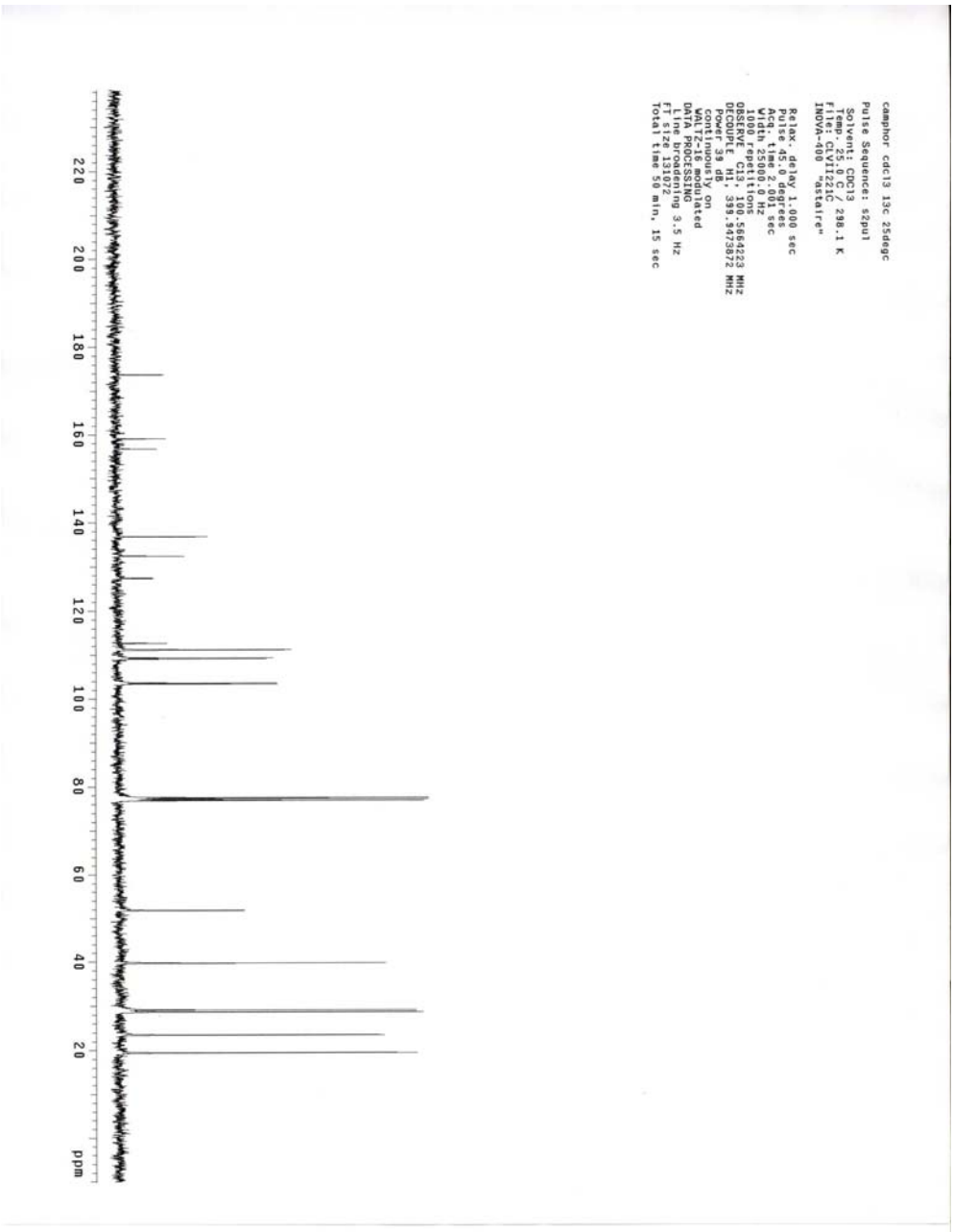


Figure S3. ^{1}H NMR spectrum of *cis*-**12** in $CDCl_3$.

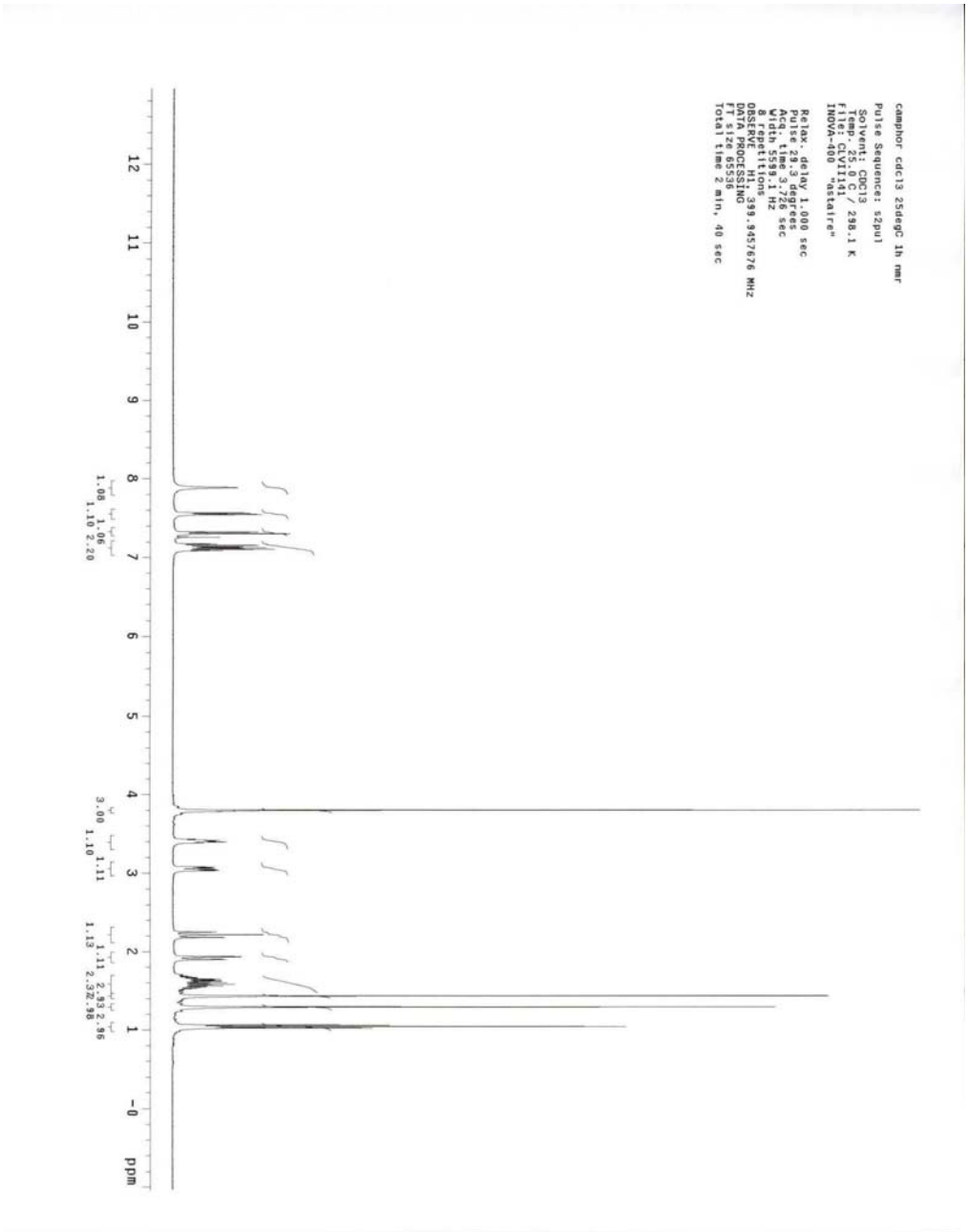


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of *cis*-**12** in $CDCl_3$.

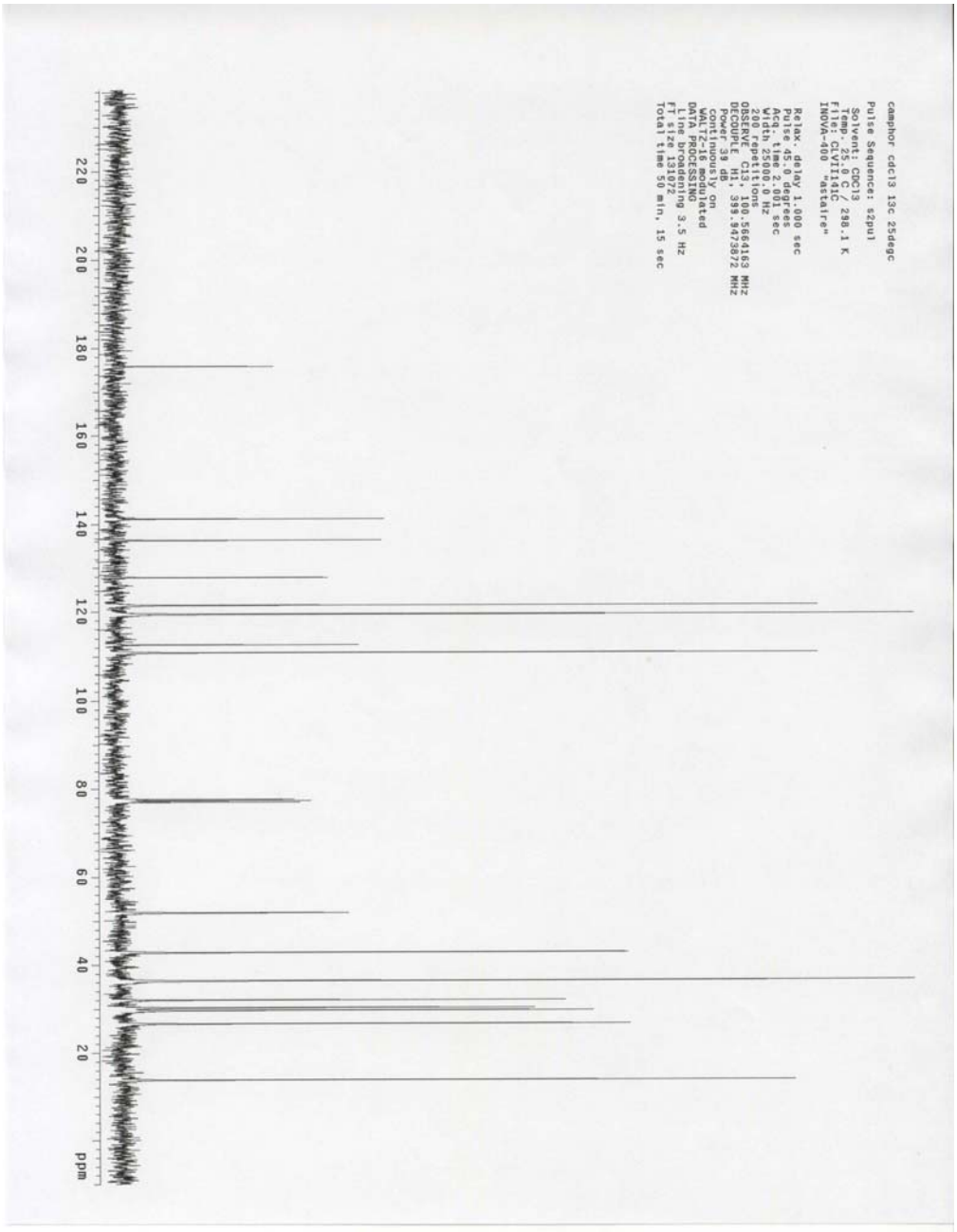


Figure S5. ^{1}H NMR spectrum of *trans*-**12** in $CDCl_3$.

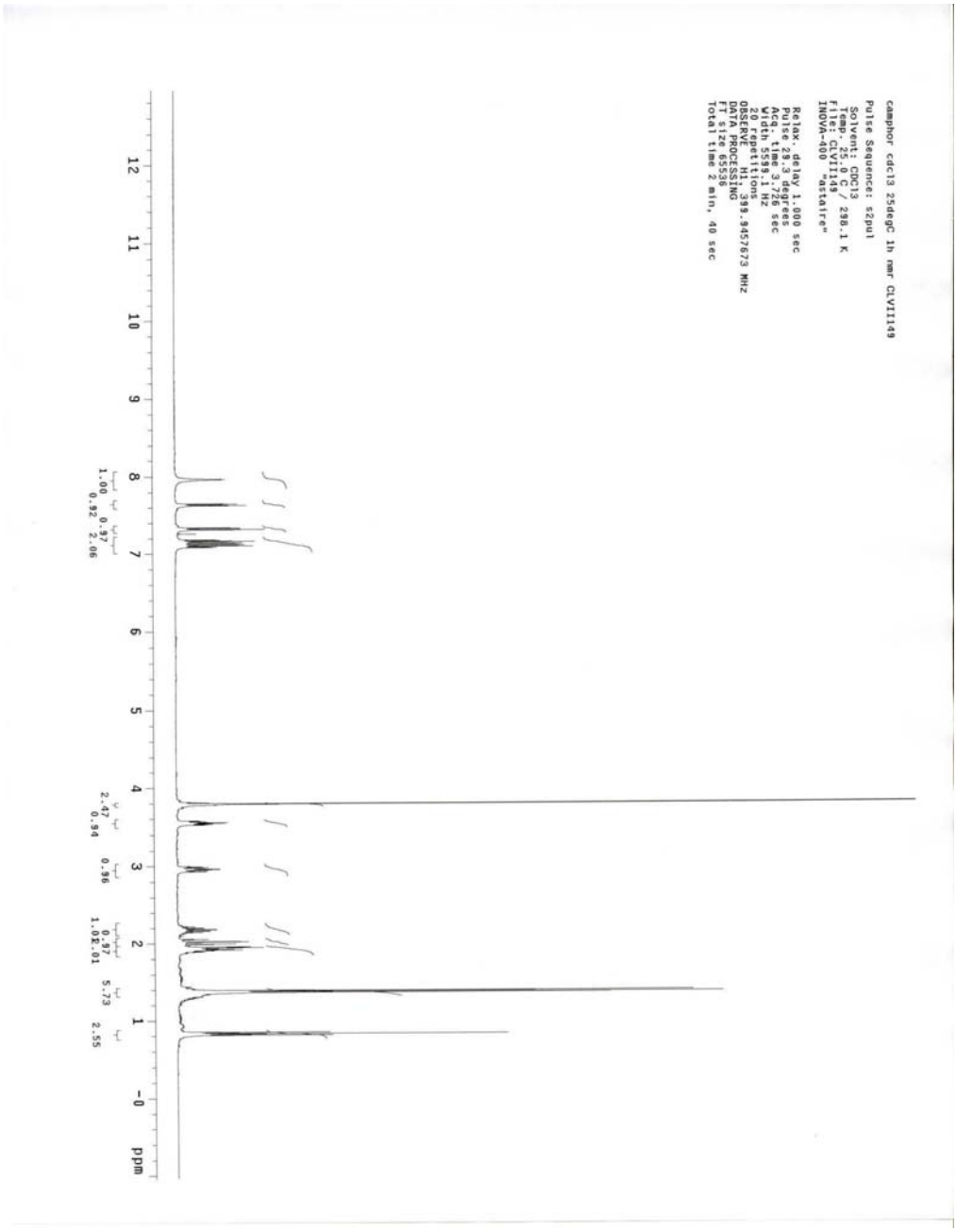


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of *trans*-**12** in $CDCl_3$.

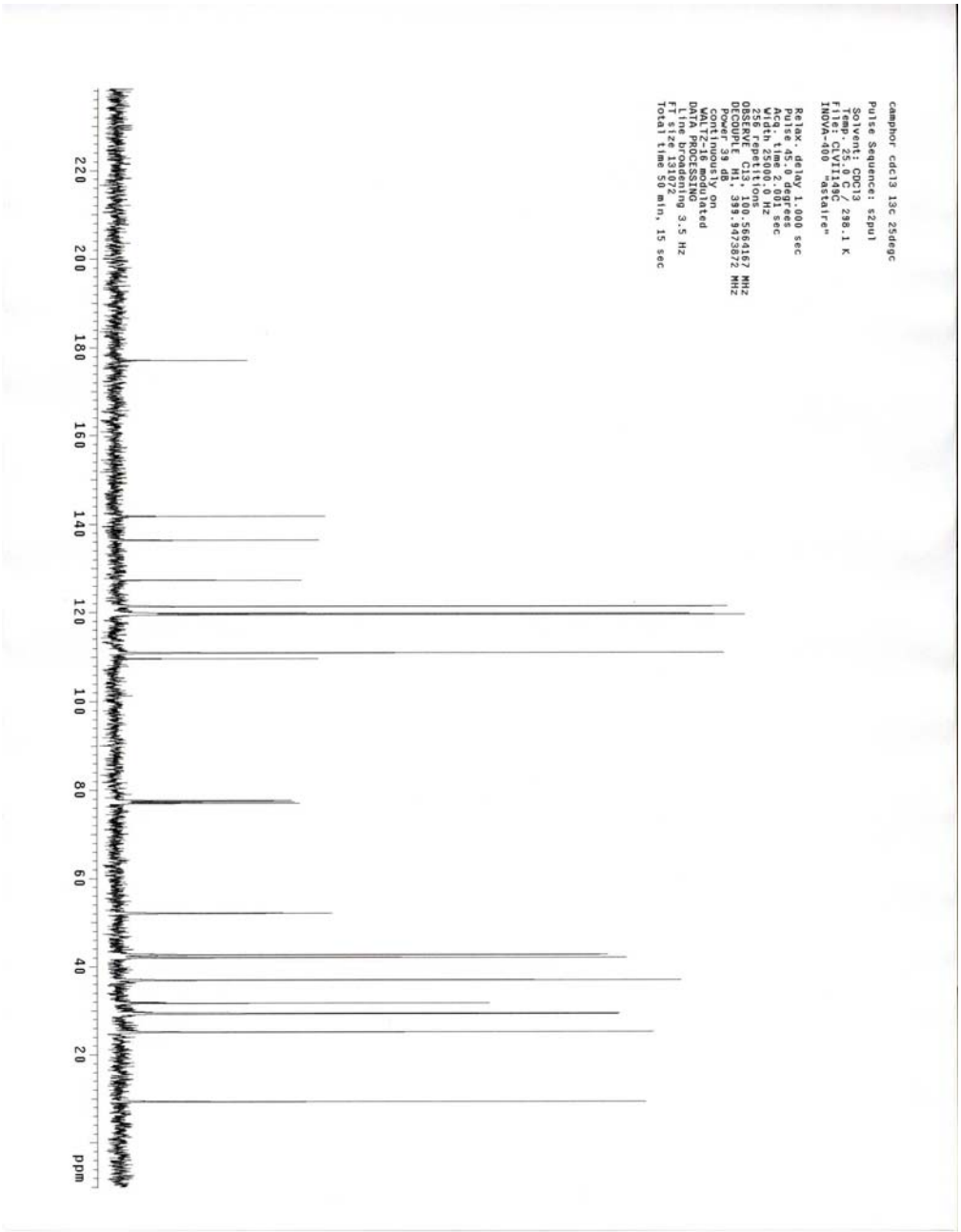


Figure S7. X-ray crystal structure of *cis*-**12**.

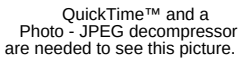


Figure S8. ^{1}H NMR spectrum of **22** in $CDCl_3$.

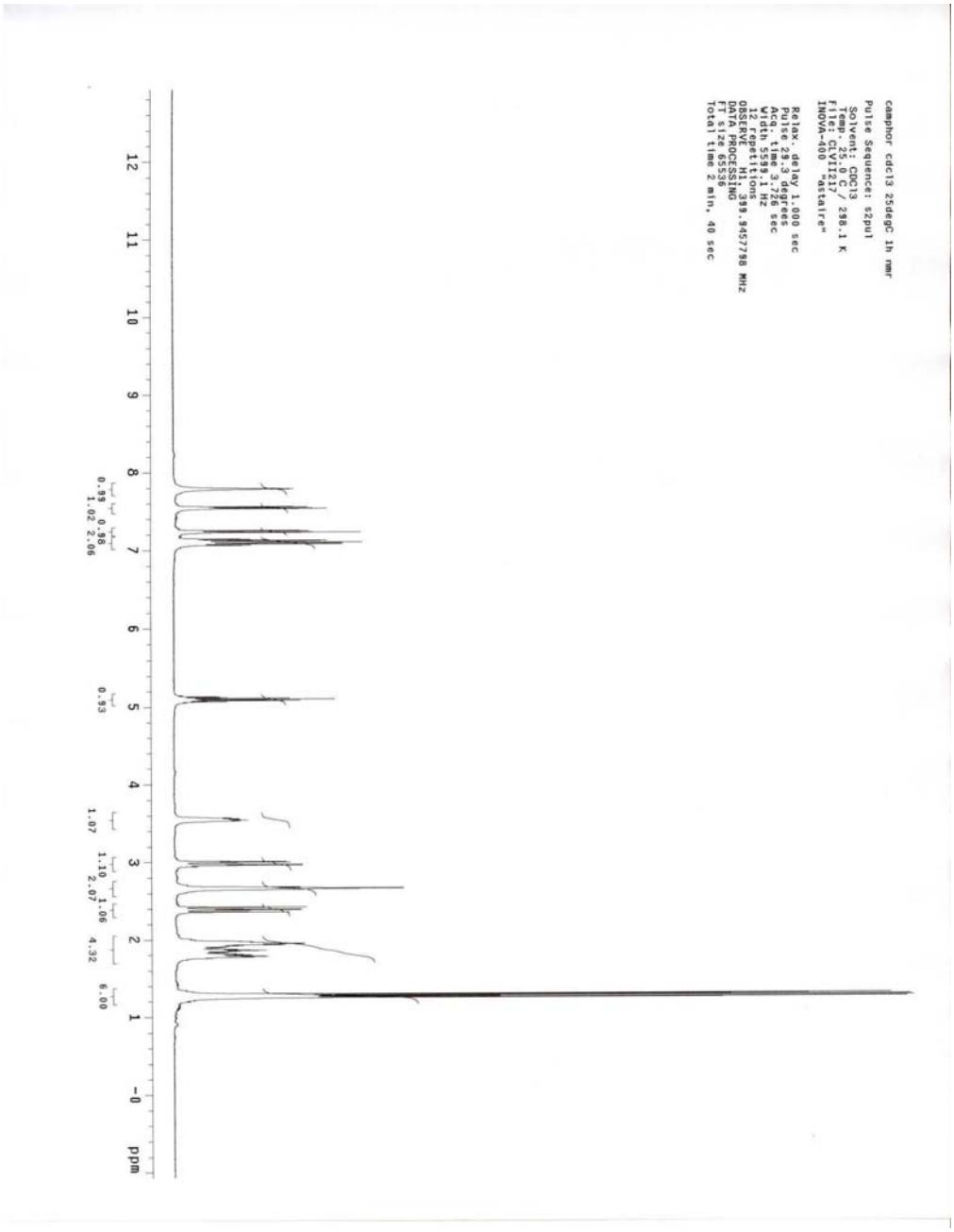


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **22** in $CDCl_3$.

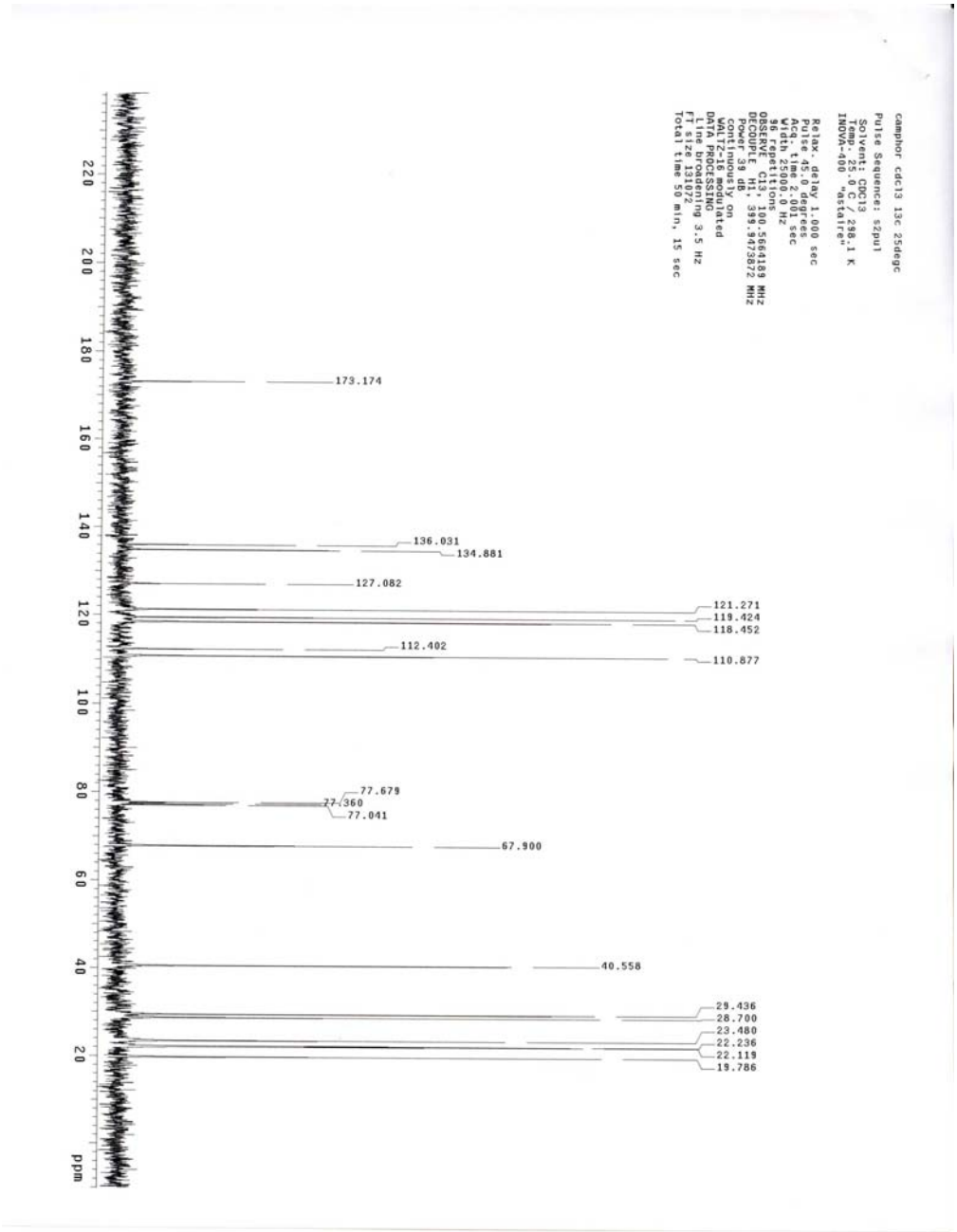


Figure S10. ^{1}H NMR spectrum of **23** in $CDCl_3$.

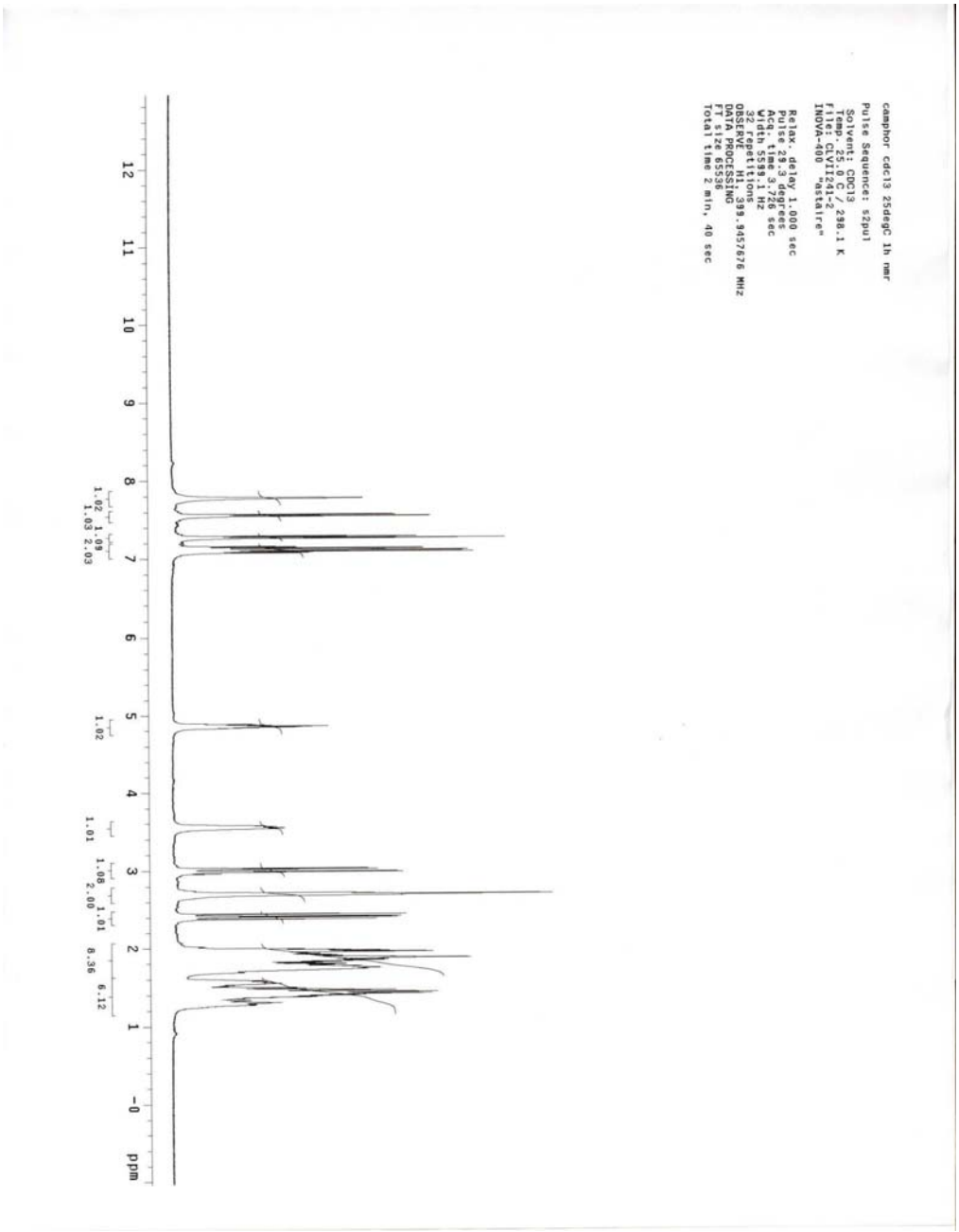


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **23** in $CDCl_3$.

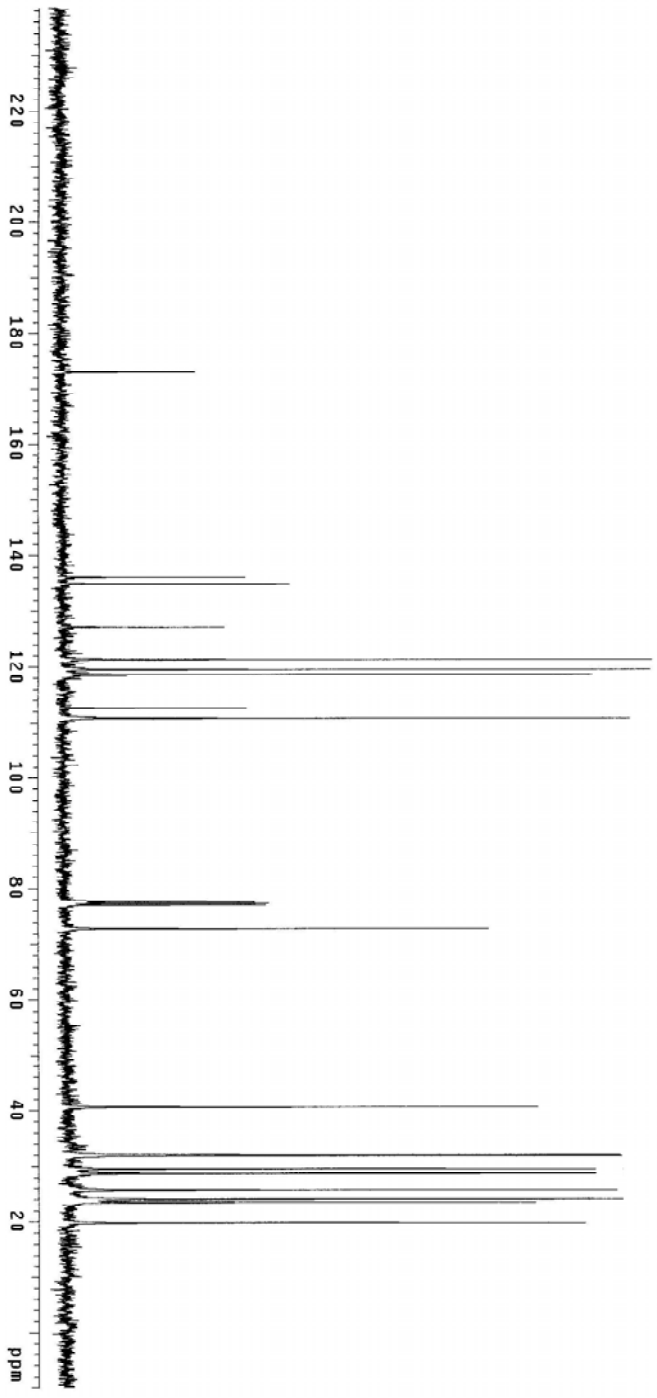


Figure S12. ^{1}H NMR spectrum of **28** in $CDCl_3$.

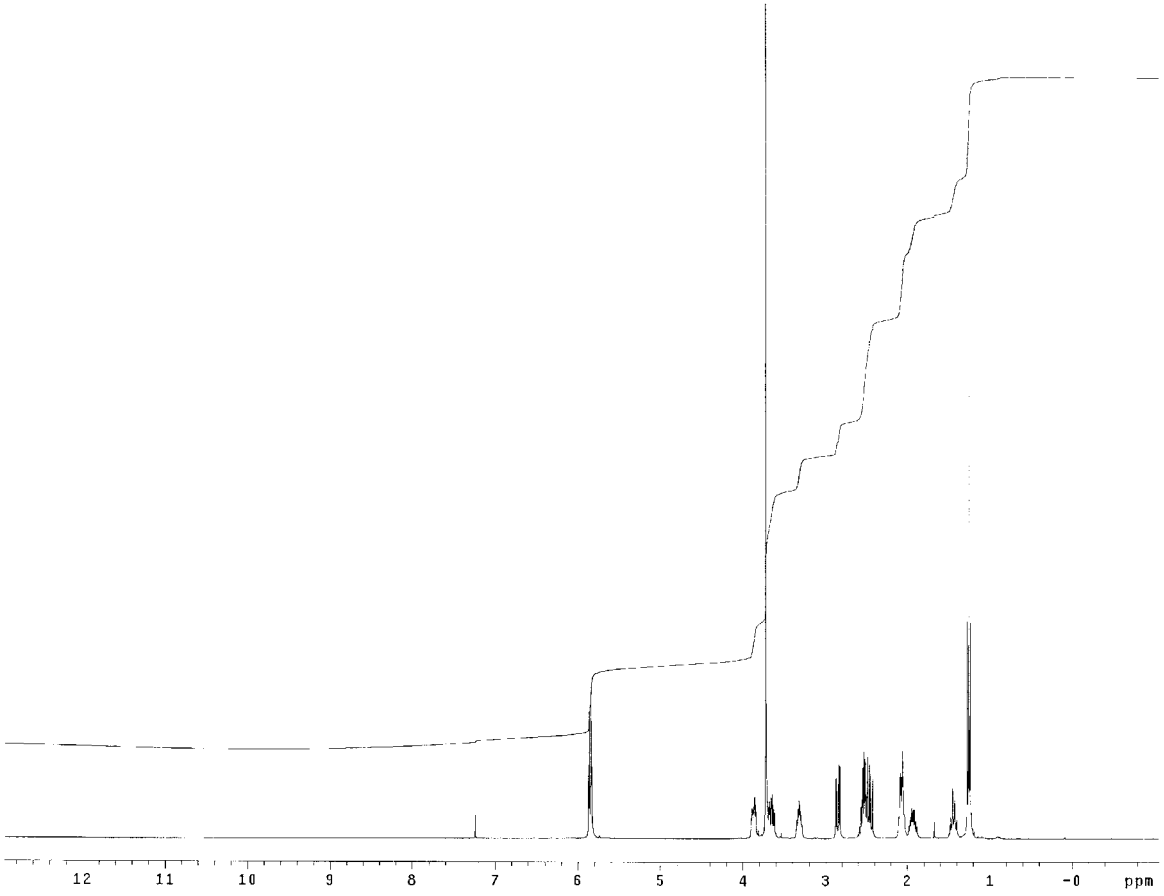


Figure S13. ^{13}C NMR spectrum of **28** in $CDCl_3$.

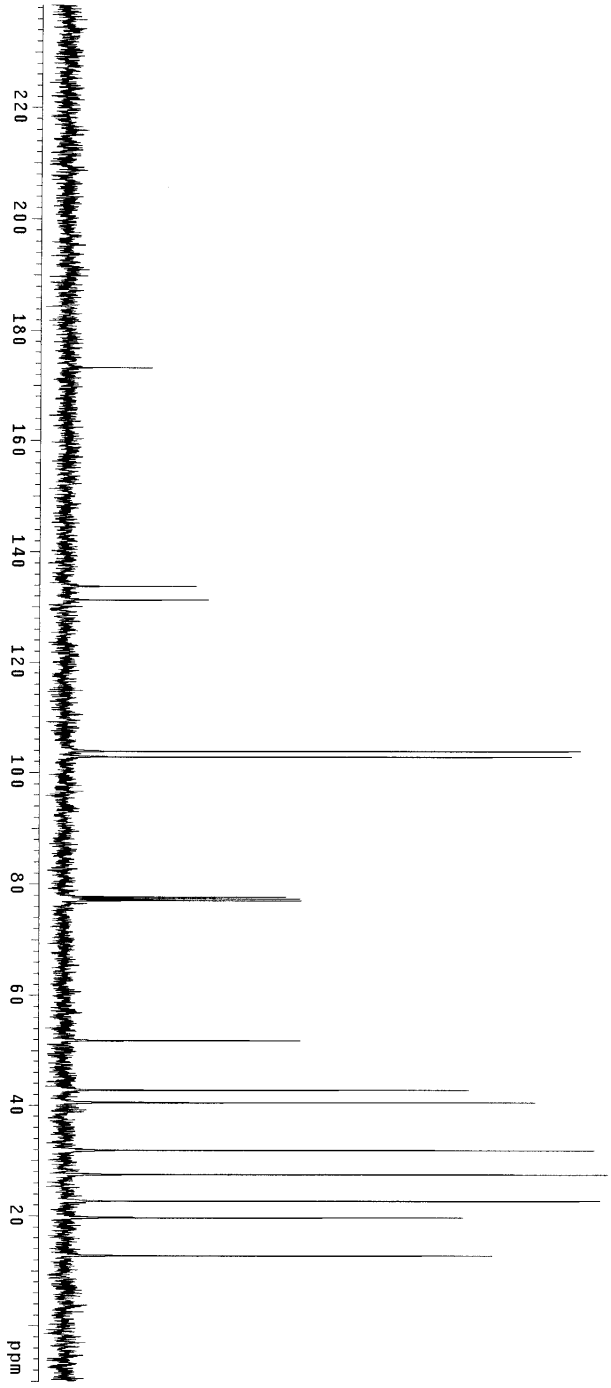


Figure S14. ^{1}H-^{1}H COSY spectrum of **29** in $CDCl_3$.

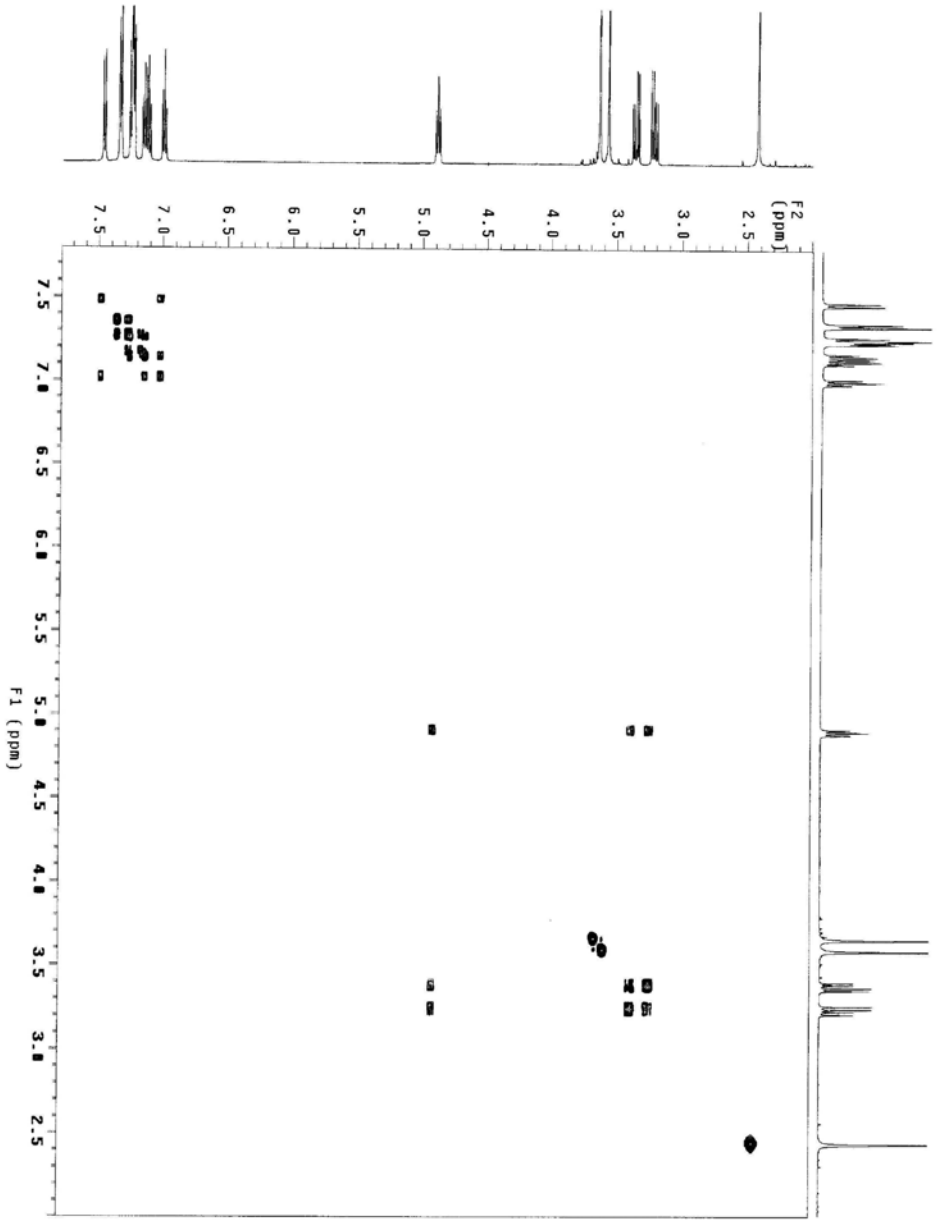


Figure S15. ^{1}H-^{13}C HMQC spectrum of **29** in $CDCl_3$.

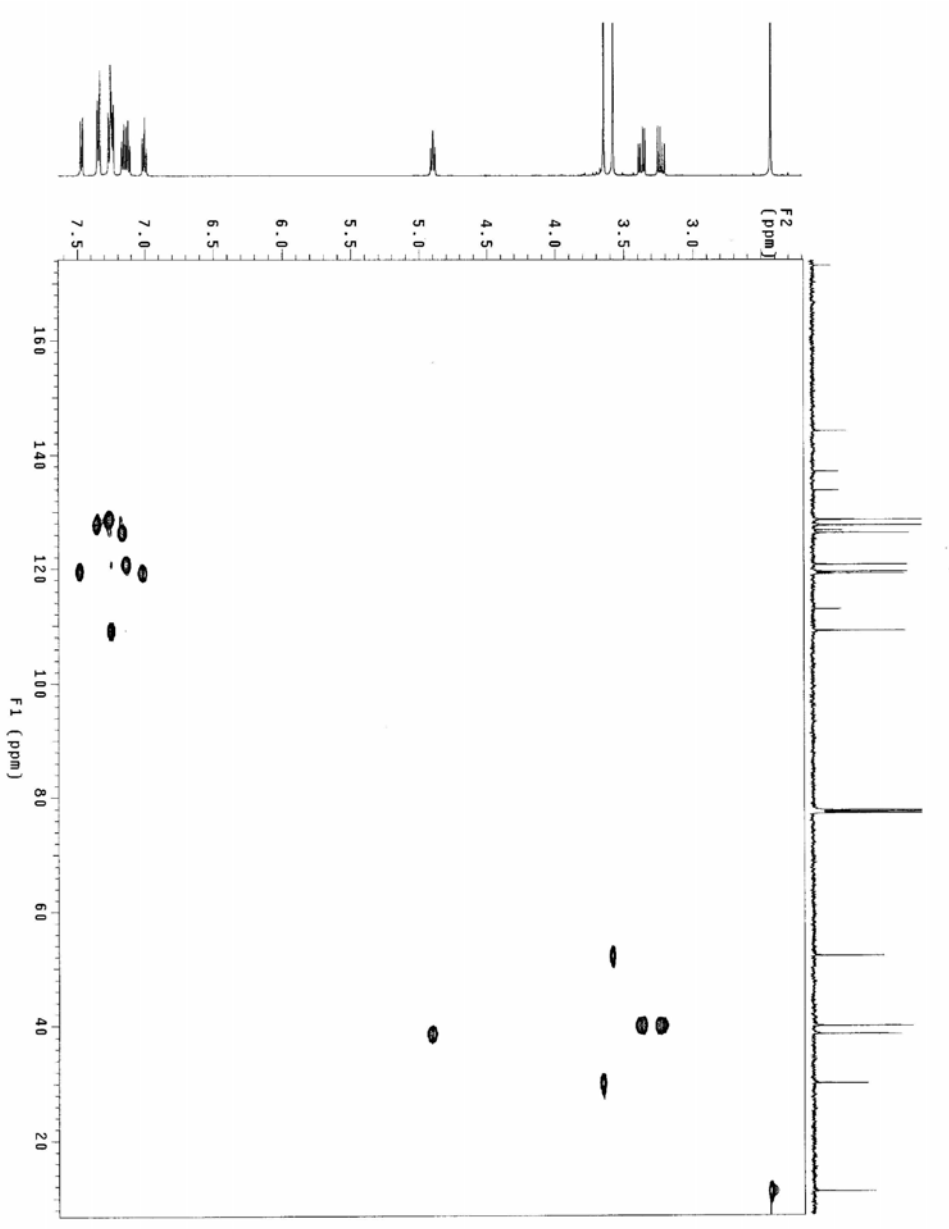


Figure S16. ^{1}H-^{13}C HMBC spectrum of **29** in $CDCl_3$.

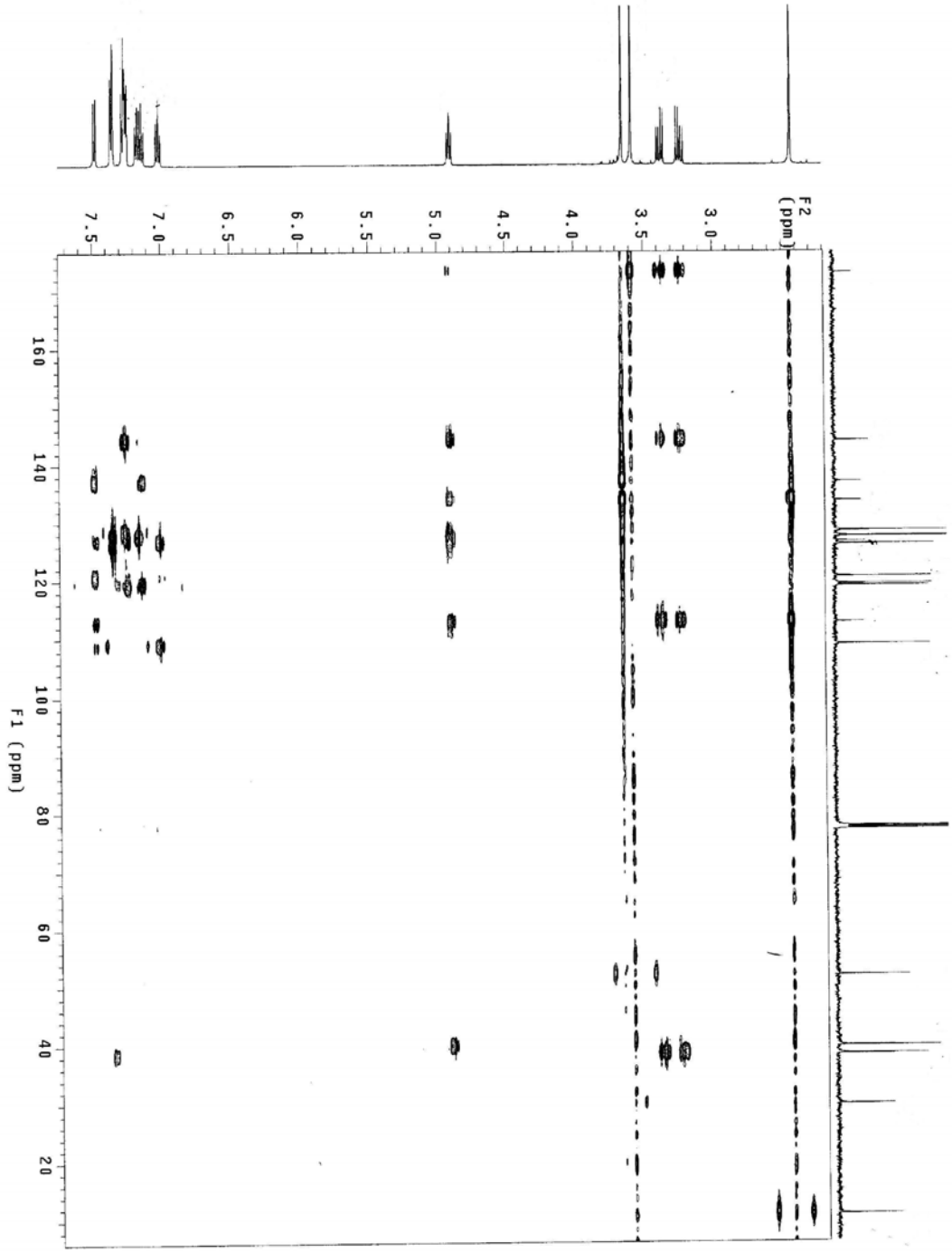


Table S1. X-ray crystal data and collection and refinement of parameters for *cis*-**12**.

empirical formula	$C_{18}H_{23}NO_2$
fw	285.38
crystal size (mm)	0.30 × 0.30 × 0.20
crystal system	Orthorhombic
space group	P bca
a (Å)	9.4635(4)
b (Å)	16.8018(7)
c (Å)	20.2194(9)
V (Å^3)	3214.96(24)
Z	8
scan mode	w
2θ limits (deg)	5.00 < 2*q* < 50.00
D_c (mg*cm^{-3})	1.179
unique reflections	2842
data with Inet > 2.5σ(I)	2151
F(000)	1232.69
R_f	0.044
R_w	0.049
GoF	1.9942
No. of parameters	191
max ² /σ	0.000
largest resid density (e/Å^3)	0.230

Table S2. Bond lengths for *cis*-**12**.

C(1)-C(2)	1.4440(23)	C(10)-C(11)	1.542(3)
C(1)-C(9)	1.3682(24)	C(10)-C(14)	1.532(3)
C(1)-C(13)	1.5084(24)	C(10)-C(15)	1.539(3)
C(2)-C(3)	1.4059(25)	C(11)-C(12)	1.528(3)
C(2)-C(7)	1.4152(25)	C(12)-C(13)	1.5555(24)
C(3)-C(4)	1.373(3)	C(12)-C(16)	1.5039(25)
C(4)-C(5)	1.398(3)	C(13)-C(20)	1.537(3)
C(5)-C(6)	1.374(3)	C(16)-O(17)	1.2106(22)
C(6)-C(7)	1.394(3)	C(16)-O(18)	1.3348(22)
C(7)-N(8)	1.3780(22)	O(18)-C(19)	1.4540(24)
N(8)-C(9)	1.3784(22)	C(20)-C(21)	1.516(3)
C(9)-C(10)	1.5055(24)		

Table S3. Bond angles for *cis*-**12**.

C(2)-C(1)-C(9)	106.86(15)	C(9)-C(10)-C(14)	111.80(15)
C(2)-C(1)-C(13)	129.69(15)	C(9)-C(10)-C(15)	108.65(15)
C(9)-C(1)-C(13)	123.41(15)	C(11)-C(10)-C(14)	109.22(15)
C(1)-C(2)-C(3)	135.27(16)	C(11)-C(10)-C(15)	110.81(15)
C(1)-C(2)-C(7)	106.48(15)	C(14)-C(10)-C(15)	109.02(15)
C(3)-C(2)-C(7)	118.23(16)	C(10)-C(11)-C(12)	113.41(14)
C(2)-C(3)-C(4)	119.24(17)	C(11)-C(12)-C(13)	111.80(14)
C(3)-C(4)-C(5)	121.33(17)	C(11)-C(12)-C(16)	112.07(14)
C(4)-C(5)-C(6)	121.27(17)	C(13)-C(12)-C(16)	110.86(14)
C(5)-C(6)-C(7)	117.65(18)	C(1)-C(13)-C(12)	107.30(14)
C(2)-C(7)-C(6)	122.26(16)	C(1)-C(13)-C(20)	113.68(14)
C(2)-C(7)-N(8)	107.83(15)	C(12)-C(13)-C(20)	111.59(14)
C(6)-C(7)-N(8)	129.91(17)	C(12)-C(16)-O(17)	126.08(16)
C(7)-N(8)-C(9)	108.94(14)	C(12)-C(16)-O(18)	111.16(15)
C(1)-C(9)-N(8)	109.87(15)	O(17)-C(16)-O(18)	122.75(17)
C(1)-C(9)-C(10)	127.40(16)	C(16)-O(18)-C(19)	116.56(15)
N(8)-C(9)-C(10)	122.54(15)	C(13)-C(20)-C(21)	114.69(15)
C(9)-C(10)-C(11)	107.33(1		

Table S4. Atomic coordinates for *cis*-**12**.

	x	y	z	Biso
C1	0.02874(17)	0.79392(10)	0.11622(9)	1.68(7)
C2	-0.05462(18)	0.72554(10)	0.09752(9)	1.81(7)
C3	-0.19807(19)	0.71188(11)	0.08345(10)	2.31(8)
C4	-0.24171(20)	0.63628(12)	0.06763(11)	2.90(9)
C5	-0.14632(22)	0.57284(12)	0.06497(11)	3.22(10)
C6	-0.00548(22)	0.58352(11)	0.07885(10)	2.79(9)
C7	0.03926(19)	0.66002(10)	0.09542(9)	2.01(7)
N8	0.17156(15)	0.68707(9)	0.11287(8)	2.02(6)
C9	0.16402(18)	0.76754(10)	0.12567(9)	1.77(8)
C10	0.28773(18)	0.81435(11)	0.15173(10)	2.09(7)
C11	0.24555(19)	0.90297(10)	0.15059(10)	2.19(8)
C12	0.09426(18)	0.91798(10)	0.17392(9)	1.89(7)
C13	-0.01612(17)	0.87909(10)	0.12696(9)	1.73(7)
C14	0.42010(20)	0.80247(12)	0.10921(11)	3.05(10)
C15	0.31926(22)	0.78672(12)	0.22280(11)	3.09(9)
C16	0.06414(19)	1.00519(11)	0.18294(9)	2.00(7)
O17	0.13272(13)	1.05963(7)	0.16040(7)	2.70(6)
O18	-0.05199(14)	1.01646(8)	0.21922(7)	3.09(6)
C19	-0.09264(24)	1.09858(12)	0.23161(12)	3.71(10)
C20	-0.03301(19)	0.92675(11)	0.06259(9)	2.04(8)
C21	-0.13613(21)	0.89125(11)	0.01339(10)	2.60(8)
H3	-0.264	0.755	0.085	3.1
H4	-0.340	0.627	0.058	3.7
H5	-0.180	0.521	0.053	4.0
H6	0.060	0.540	0.077	3.6
H8	0.255	0.655	0.116	2.8
H11a	0.253	0.922	0.106	3.0
H11b	0.309	0.932	0.178	3.0
H12	0.085	0.893	0.216	2.7
H13	-0.106	0.879	0.149	2.5
H14a	0.401	0.819	0.065	3.8
H14b	0.496	0.833	0.127	3.8
H14c	0.446	0.747	0.109	3.8
H15a	0.236	0.794	0.249	3.9
H15b	0.345	0.731	0.223	3.9
H15c	0.396	0.818	0.241	3.9
H19a	-0.177	1.100	0.258	4.5
H19b	-0.018	1.125	0.255	4.5
H19c	-0.110	1.125	0.190	4.5
H20a	0.058	0.930	0.042	2.8
H20b	-0.065	0.979	0.073	2.8
H21a	-0.141	0.924	-0.026	3.4

Table S4. Continued.

H21b	-0.105	0.839	0.002	3.4
H21c	-0.228	0.888	0.034	3.4

[a] Biso is the Mean of the Principal Axes of the Thermal Ellpsoid.

References

[1] Smith, A. B. III; Visnick, M.; Haseltine, J. N.; Sprengeler, P. A. *Tetrahedron* **1986**, *42*, 2957.

[2] Liu, C.; Han, X.; Wang, X.; Widenhoefer, R. *J. Am. Chem. Soc.* **2004**, *126*, 3700.

[3] Abbiati, G.; Beccalli, E. M.; Broggini, G.; Zoni, C. *J. Org. Chem.* **2003**, *68*, 7625.

[4] Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc*. **2003**, *125*, 9578.

[5] Youn, S. W.; Pastine, S. J.; Sames, D. *Org. Lett.* **2004**, *6*, 581.

[6] Banwell, M. G.; Beck, D. A. S.; Smith, J. A.; *Org. Biomol. Chem.* **2004**, *2*,157.

[7] Gibe, R.; Kerr, M. A. *J. Org. Chem.* **2002**, *67*, 6247.

[8] Rodriguez, J. G. T. F.; Esteban-Calderon, C.; Martinez-Ripoll, M. *J. Chem. Soc., Perkin Trans 1* **1989,** 11, 2117.

[9] Marinelli, E. R., *Tetrahedron Lett.* **1982,** 23, 2745.