Supplementary Material (ESI) for Chemical Communications

Supporting Information

Phosphine-catalyzed Highly Diastereoselective [3+2] Cyclization of Isatin Derived Electron-deficient Alkenes with α-Allenic Esters

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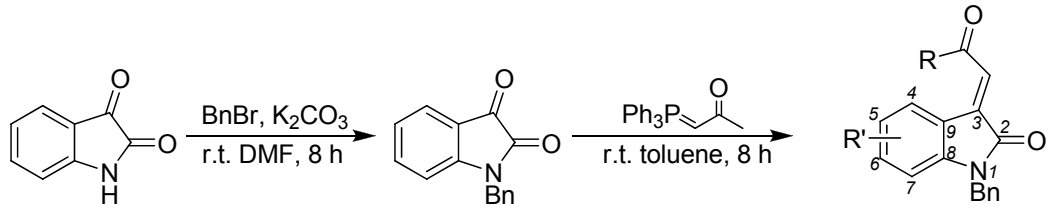
Content

General remarks. ^{1}H-NMR spectra were recorded on a 300 MHz or 400MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. ^{19}FNMR spectra were recorded at 376 MHz and 282 MHZ for a solution in $CDCl_3$ with $CFCl_3$ as the external reference. Infrared spectra were measured on a spectrometer. Mass spectra were recorded by EI method and ESI, and HRMS was measured on Kratos Analytical Concept mass spectrometer (EI or ESI). MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. All reactions were monitored by TLC with silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel at increased pressure.

Preparation of Starting Materials 1a-1p



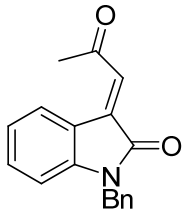
1

1a, R = Me, R' = H
1b, R = Me, R' = 4-Br
1c, R = Me, R' = 4-Cl
1d, R = Me, R' = 5-Br
1e, R = Me, R' = 5-F
1f, R = Me, R' = 5-Me
1g, R = Me, R' = 6-Br
1h. R = Me, R' = 7-CF_3
1i, R = CH_3, R' = 7-Br .
1j, R = Ph, R' = H
1k, R = Ph, R' = 5-Br
1l, R = Ph, R' = 5-F
1m, R = Ph, R' = 5-Me
1n, R = Ph, R' = 6-Br
1o, R = Ph, R'= 7-CF_3
1p, R = Ph, R' = 7-Br

Representative procedure for the preparation of (E)-1-benzyl-3-(2-oxopropylidene)-indolin-2-one

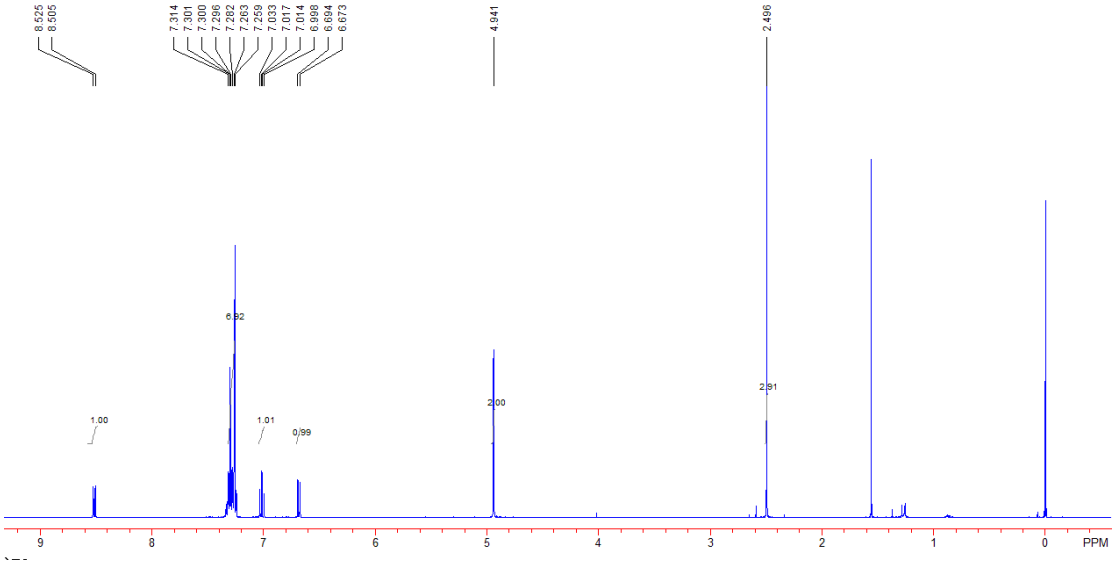
To the solution of isatin (10.0 g, 68 mmol) in DMF (50 mL) was added benzyl bromide (16.0 mL, 100 mmol), potassium carbonate (18.8 g, 100 mmol). The resulting mixture was stirred at room temperature for 8 hr. After this period, the resulting dark red mixture was poured into 200 mL of water, extracted with 200 mL of dichloromethane for twice. The organic phase was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to give N-benzylisatin as a red solid. Then 1.0 g of N-benzylisatin was mixed with the ylide in toluene

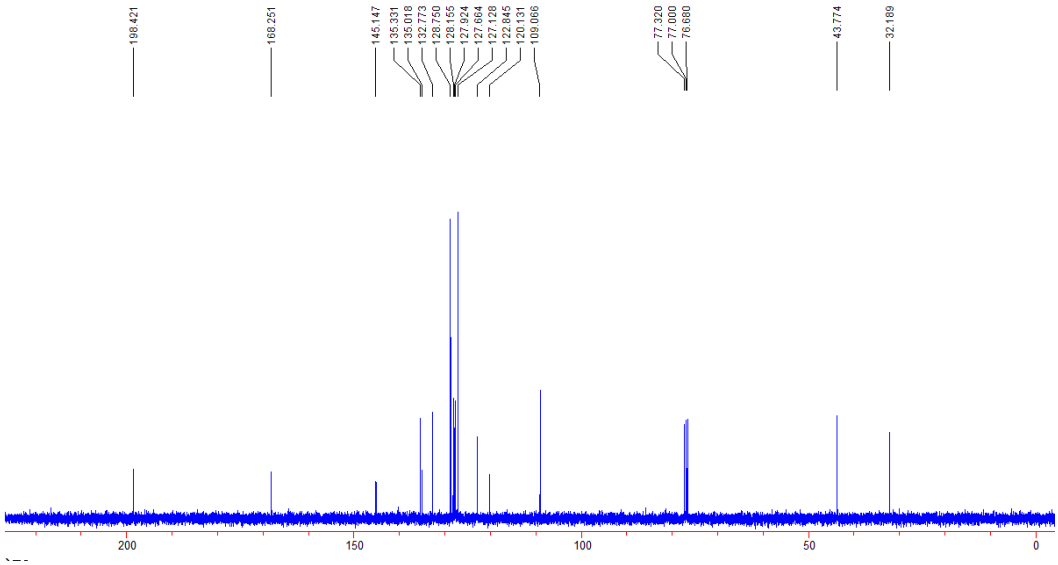
and let it to be stirred at r.t. for 8 hr. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (pentane/EtOAc = 10:1) to give **1** as orange solid (1.4 g, 75%).

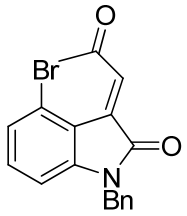


(E)-1-benzyl-3-(2-oxopropylidene)indolin-2-one 1a

Yield: 1.0 g, 75%. A Red solid. Mp: 119-121 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.50 (s, 3H), 4.94 (s, 2H), 6.68 (d, *J* = 7.6 Hz, 1H), 7.00-7.04 (m, 1H), 7.25-7.34 (m, 7H), 8.52 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 32.2, 43.8, 109.1, 120.1, 122.8, 127.1, 127.7, 127.9, 128.2, 128.8, 132.8, 135.0, 135.3, 145.1, 168.3, 198.4. IR (CH_2Cl_2) ν 3032, 2923, 1712, 1678, 1601, 1467, 1381, 1343, 877, 806, 742, 693, 615 cm^{-1}. MS (EI) *m/e* (%): 278 (13), 277 (M^+, 65), 234 (15), 207 (10), 206 (61), 91 (100), 65 (12), 43 (12). HRMS (EI) Calcd. for $C_{18}H_{15}NO_2$: 277.1103; Found: 277.1109.

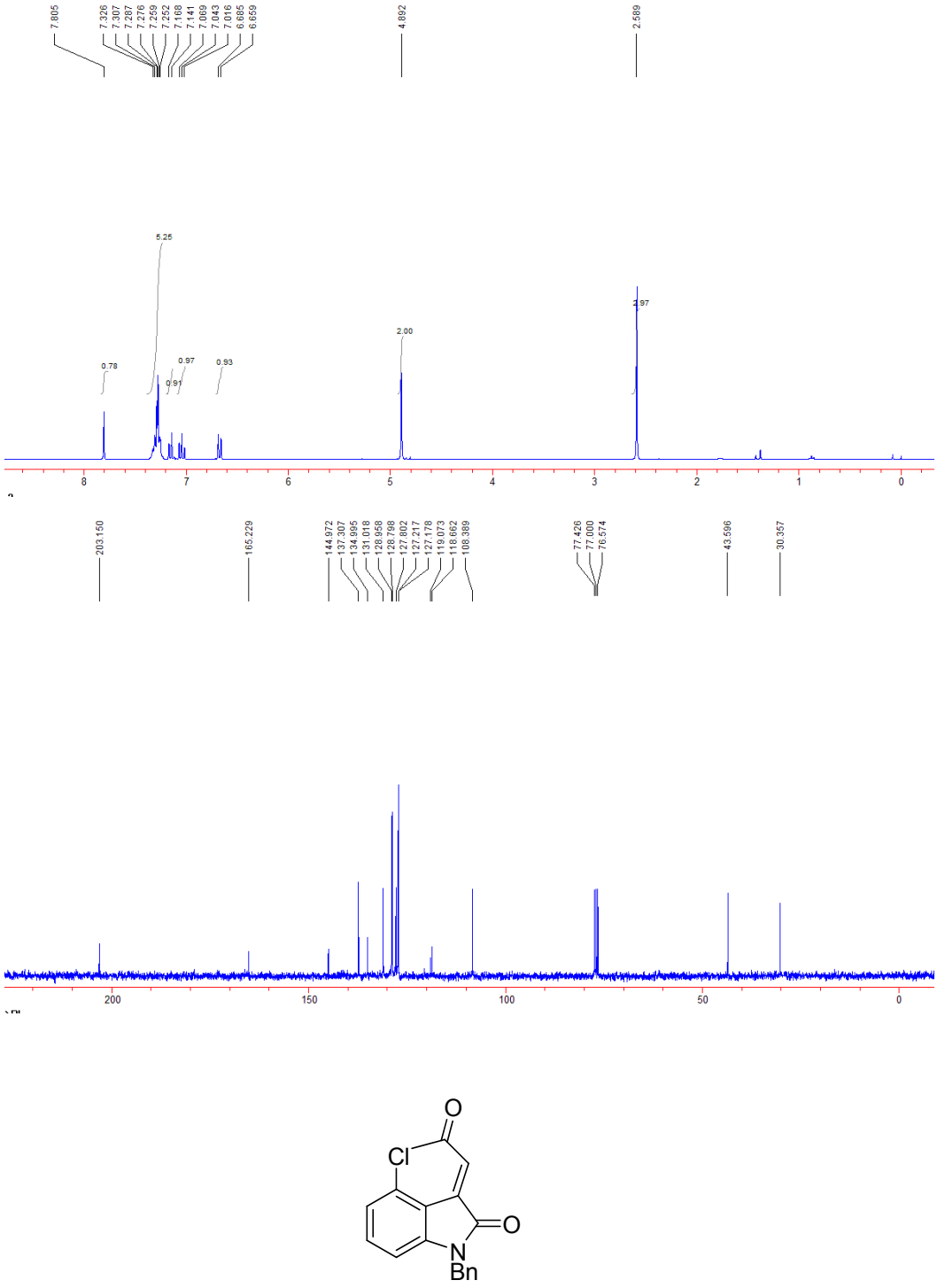






(E)-1-benzyl-4-bromo-3-(2-oxopropylidene)indolin-2-one 1b

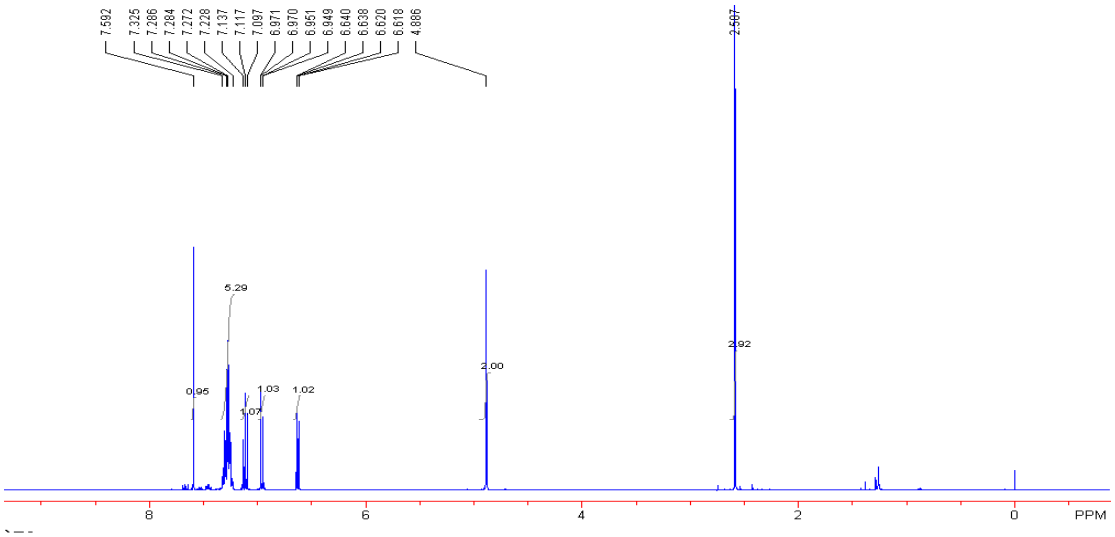
Yield: 1.2 g, 85%. A yellow solid. Mp: 160-162 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.59 (s, 3H), 4.89 (s, 2H), 6.66 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.25-7.32 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 30.4, 43.6, 108.4, 118.7, 119.1, 127.1, 127.2, 127.8, 128.8, 129.0, 131.0, 135.0, 137.3, 145.0, 165.2, 203.2. IR (CH_2Cl_2) ν 3041, 2924, 1708, 1644, 1600, 1446, 1352, 1332, 1199, 1163, 1133, 762, 720 cm^{-1}. MS (%) m/e 357 (15), 355 ($M^{+\cdot}$ 15), 286 (10), 284 (11), 276 (14), 114 (6), 92 (8), 91 (100). HRMS (EI) for $C_{18}H_{14}BrNO_2$: 355.0208; Found 355.0221.

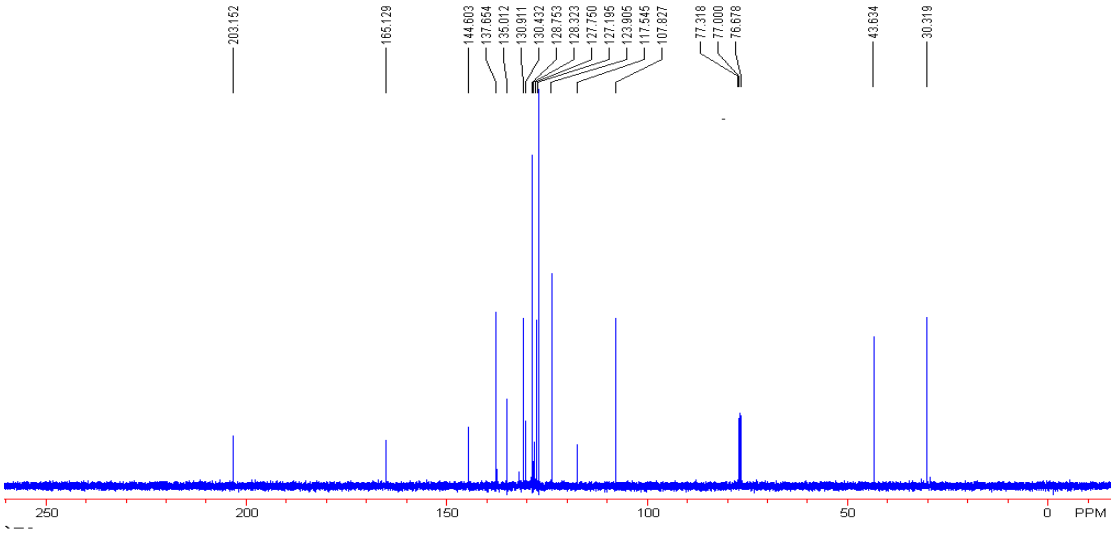


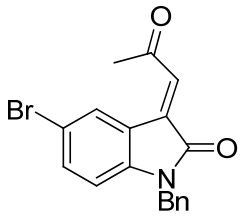
(E)-1-benzyl-4-chloro-3-(2-oxopropylidene)indolin-2-one 1c

Yield: 0.6 g, 55%. A yellow solid. Mp: 130-132 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.60 (s, 3H), 4.90 (s, 2H), 6.63 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 6.96 (dd, J_1 = 8.0 Hz, J_2 = 0.4 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 7.22-7.32 (m, 5H), 7.59 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 30.3, 43.6, 107.8, 117.6, 123.9, 127.2, 127.8, 128.3, 128.8, 130.,4 130.9, 135.0, 137.7, 144.6, 165.1, 203.2. IR (CH_2Cl_2) ν 3043, 2933, 1713, 1687, 1601, 1467, 1349, 1164, 1129, 723, 676, 617 cm^{-1}. MS (%) m/e 313(11), 311($M^{+,}$ 11), 262(20), 240(1127 183(17), 91(6100 65(11), 43(18). HRMS (EI)

for $C_{18}H_{14}ClNO_2$: 311.0713; Found: 311.0714.



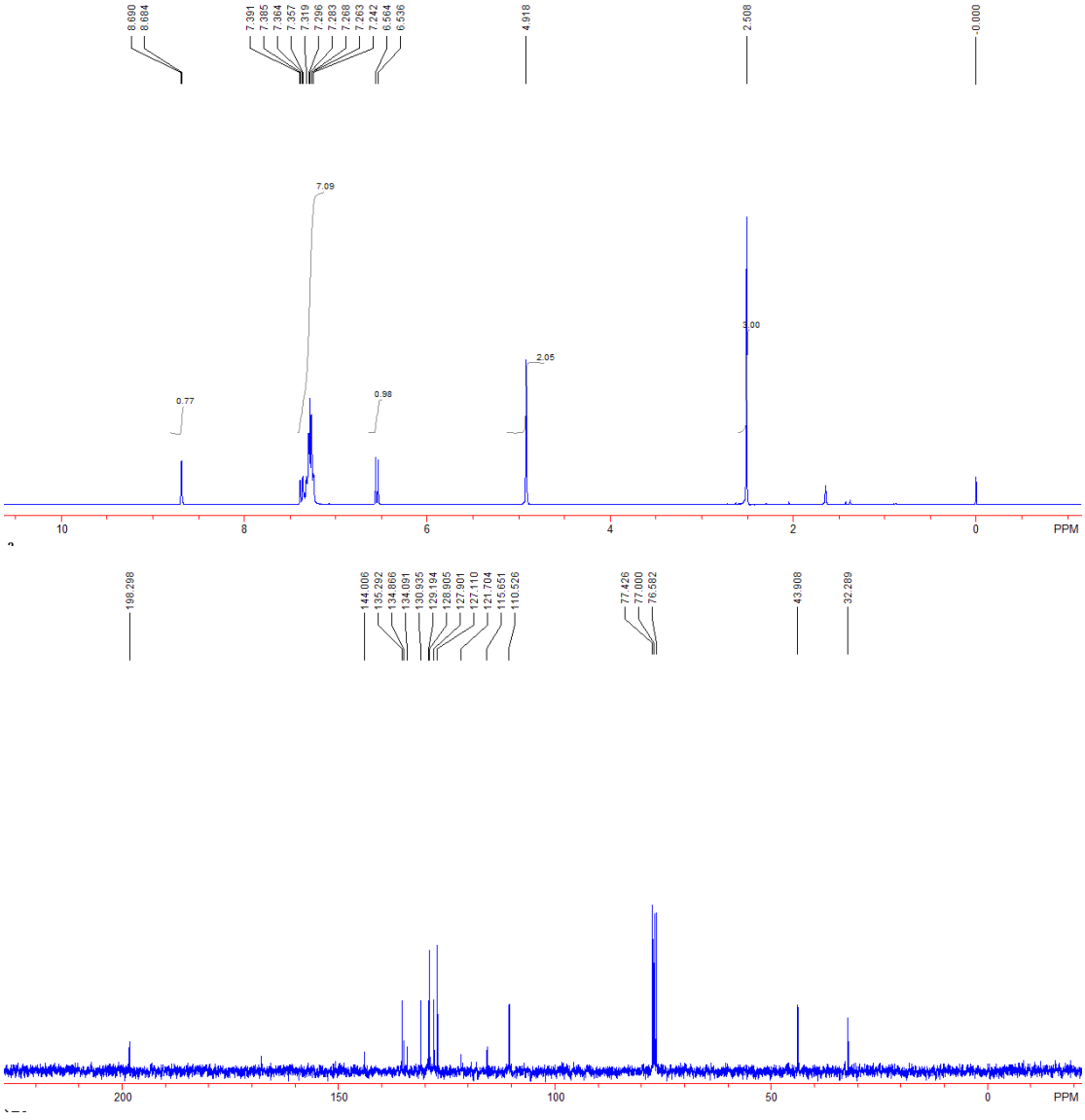


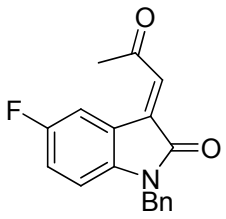


(E)-1-benzyl-5-bromo-3-(2-oxopropylidene)indolin-2-one 1d

Yield: 0.5 g, 50%. A red solid. Mp: 150-152 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.51 (s, 3H), 4.92 (s, 2H), 6.55 (d, *J* = 8.1 Hz, 1H), 7.24-7.39 (m, 7H), 8.70 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 32.1, 43.9, 110.5, 115.7, 121.7, 127.1, 127.9, 128.9, 129.2, 131.0, 134.0, 134.9, 135.3, 144.0, 167.9, 198.3. IR (CH_2Cl_2) ν 3109, 2922, 1713, 1680, 1593, 1468, 1337, 1179, 1156, 1065, 818, 731, 700 cm^{-1}. MS (%) m/e 357(22), 355($M^{+,}$ 22), 312(4), 286(13), 284(14),

204(4), 114(6), 92(7), 91(100). HRMS (EI) for $C_{18}H_{14}BrNO_2$: 355.0213; Found: 355.0199.

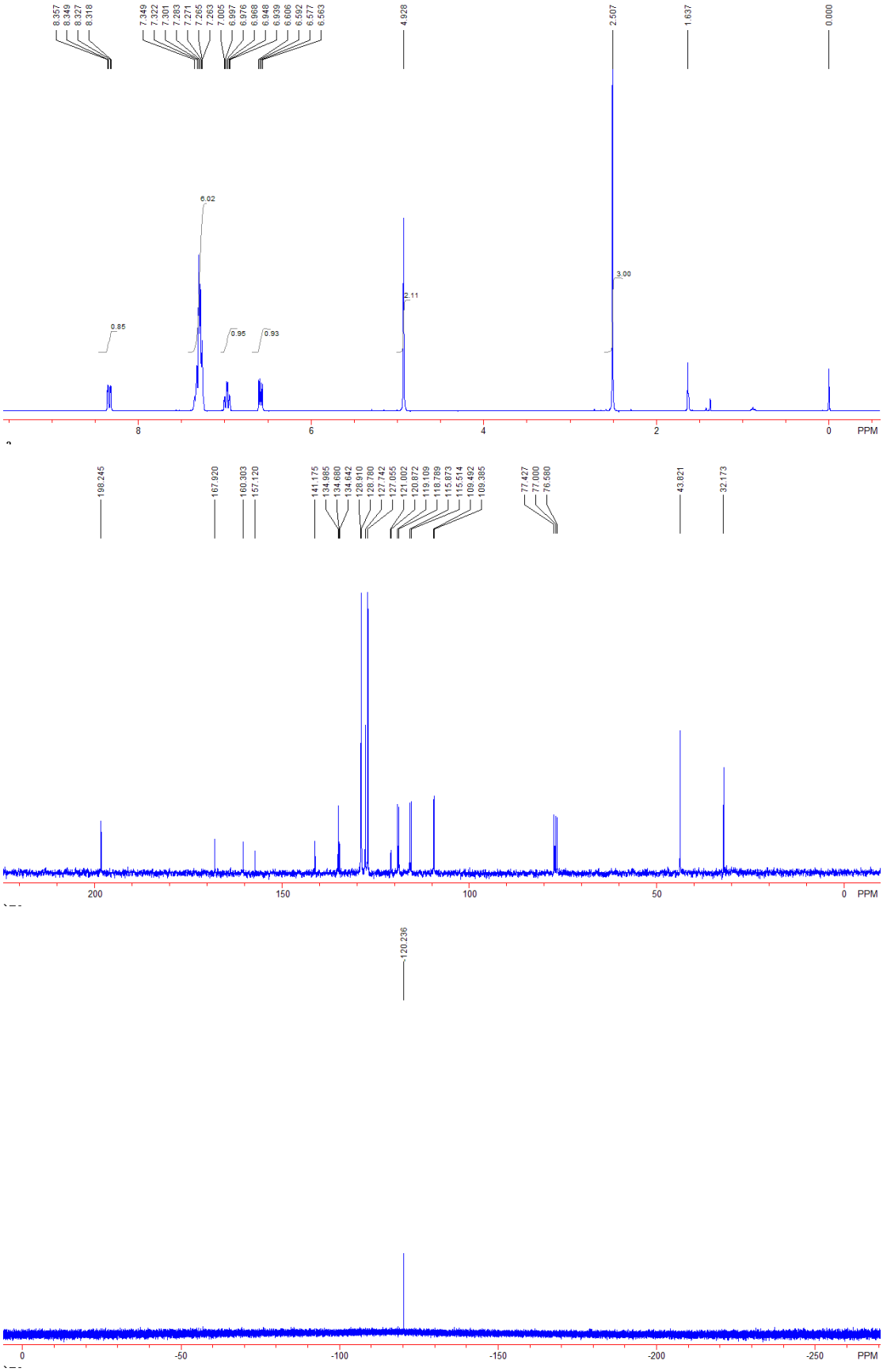


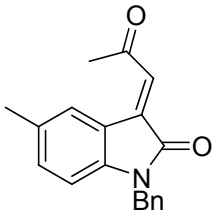


(E)-1-benzyl-5-fluoro-3-(2-oxopropylidene)indolin-2-one 1e

Yield: 0.6 g, 55%. A red solid. Mp: 130-132 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.51 (s, 3H), 4.93 (s, 2H), 6.59 (dd, J_1 = 8.7 Hz, J_2 =4.8 Hz, 1H), 6.97 (td, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1H), 7.26-7.34 (m, 6H), 8.33 (dd, J_1 = 9 Hz, J_2 = 2.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 32.2, 43.8, 109.4 (d, J = 8.0 Hz), 115.7 (d, J = 26.9 Hz), 119.0 (d, J = 24.0 Hz), 120.9 (d, J = 9.8 Hz), 127.1, 127.8, 128.8, 128.9, 134.6 (d, J = 2.8 Hz), 135.0, 141.2, 158.7 (q, J = 238.7 Hz), 167.9, 198.3. ^{19}F

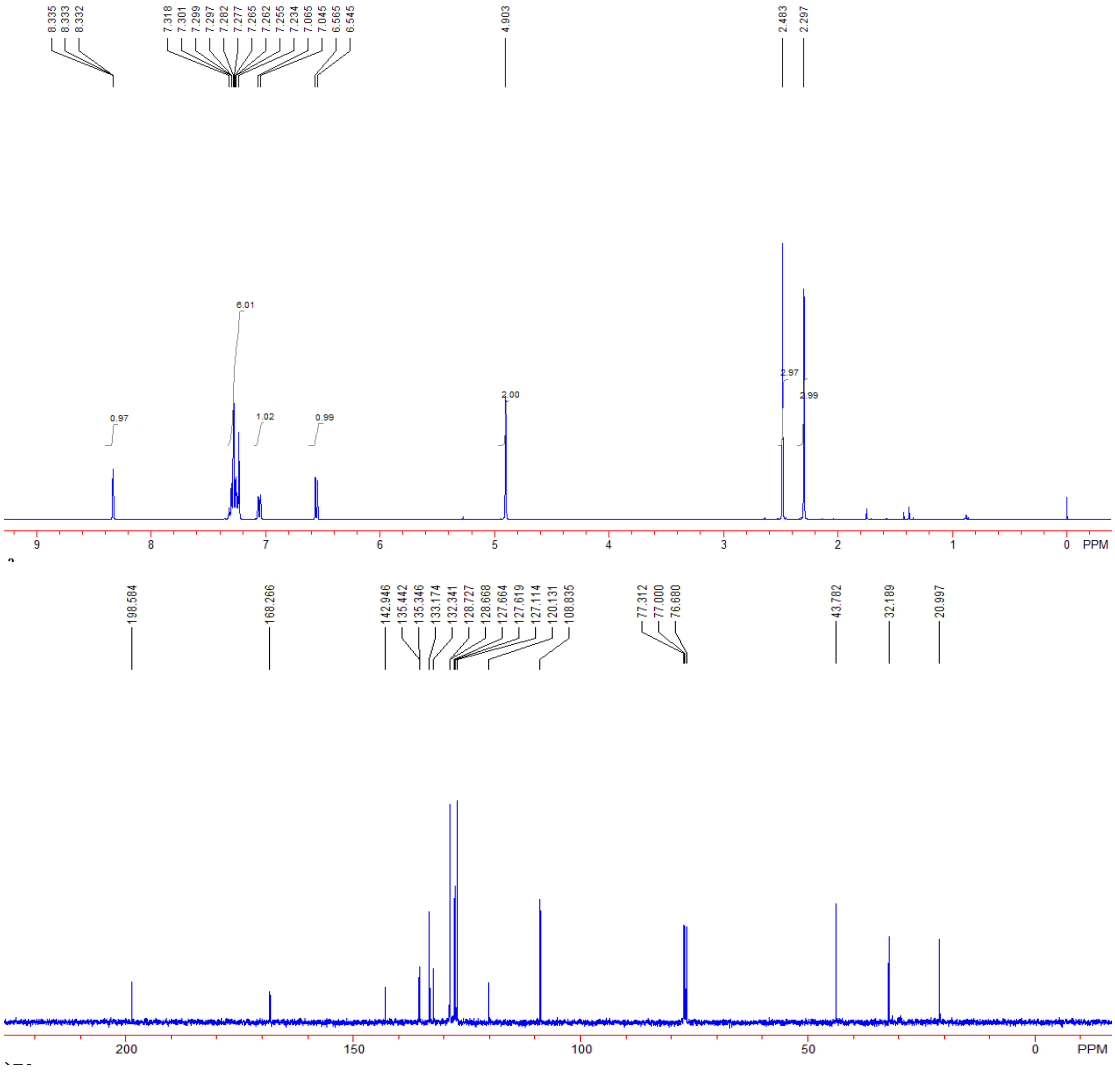
NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ -120.2. IR (CH_2Cl_2) ν 3033, 2925, 1710, 1682, 1595, 1497, 1473, 1454, 1179, 1081, 811, 721, 680 cm^{-1}. MS (%) m/e 296(10), 295($M^{+\cdot}$ 49), 252(9), 224(33), 161(3), 133(4), 92(8), 91(100). HRMS (EI) for $C_{18}H_{14}FNO_2$: 295.1009; Found: 295.1011.

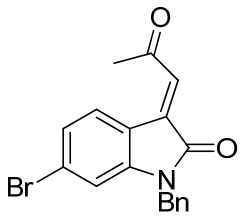




(E)-1-benzyl-5-methyl-3-(2-oxopropylidene)indolin-2-one 1f

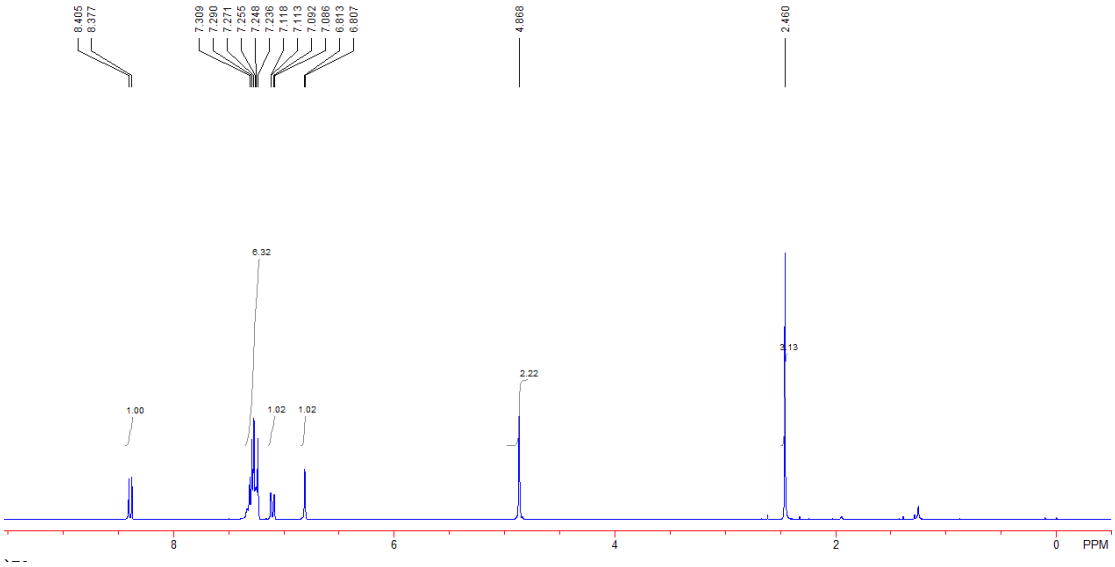
Yield: 0.7 g, 60%. A red solid. Mp: 132-134 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.80 (s, 3H), 2.48 (s, 3H), 4.90 (s, 2H), 6.56 (d, J = 8.4Hz), 7.06 (d, J = 8.0 Hz, 1H), 7.23-7.32 (m, 6H), 8.33-8.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.0, 32.2, 43.8, 108.8, 120.1, 127.1, 127.6, 127.7, 128.7, 128.7, 132.3, 135.2, 135.3, 135.4, 142.9, 168.3, 198.6. IR (CH_2Cl_2) ν 2922, 2853, 1708, 1682, 1625, 1603, 1588, 1483, 1455, 1437, 1363, 1342, 1312, 1190, 1115, 1082, 1011, 813, 736, 701, 639 cm^{-1}. MS (EI) *m/e* (%): 291 (M^+, 59.1), 248 (13.6), 220 (51.9), 91 (100.0), 65 (12.1), 43 (19.0). HRMS (EI) Calcd. for $C_{19}H_{17}NO_2$: 291.1259; Found: 291.1258.

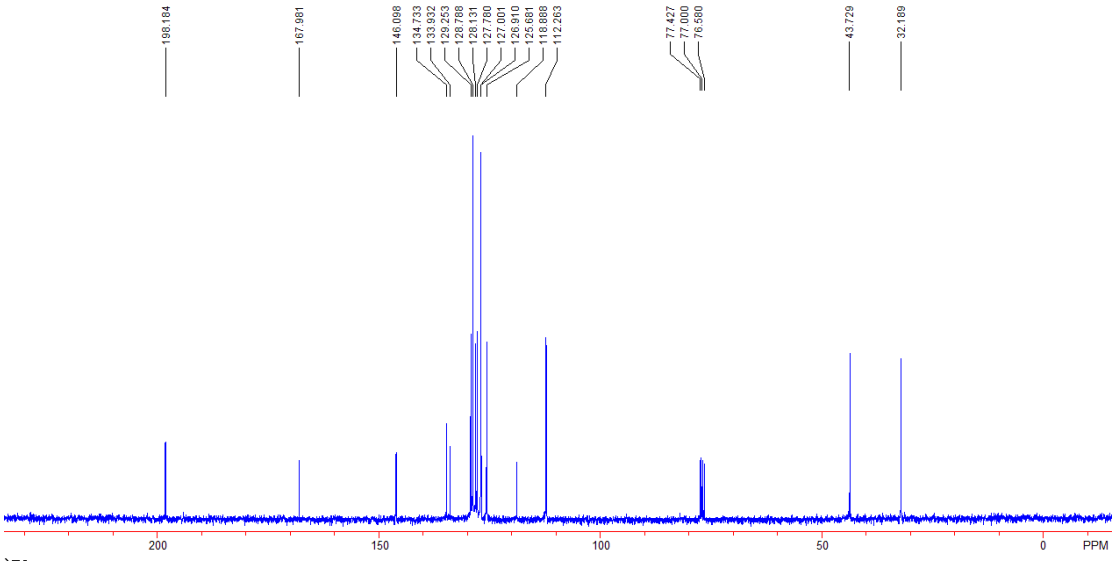


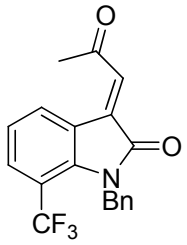


(E)-1-benzyl-6-bromo-3-(2-oxopropylidene)indolin-2-one 1g

Yield: 0.6 g, 55%. A red solid. Mp: 150-152 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.46 (s, 3H), 4.87 (s, 2H), 6.81 (d, J = 1.8 Hz, 1H), 7.10 (dd, J_1 = 7.8 Hz, J_2 = 1.8Hz, 1H), 7.24-7.31 (m, 6H), 8.39 (d, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 32.2, 43.7, 112.3, 118.9, 125.7, 126.9, 127.0, 127.8, 128.1, 128.8, 129.3, 134.0, 134.7, 146.1, 168.0, 198.1. IR (CH_2Cl_2) ν 2991, 2990, 1717, 1680, 1595, 1468, 1432, 1347, 1184, 1071, 851, 745, 632 cm^{-1}. MS (%) m/e 357(20), 355(M^{+}, 21), 286(15), 284(16), 92(7), 91(100), 65(11), 43(12). HRMS (EI) for $C_{18}H_{14}NO_2Br$: 355.0208; Found: 355.0203.

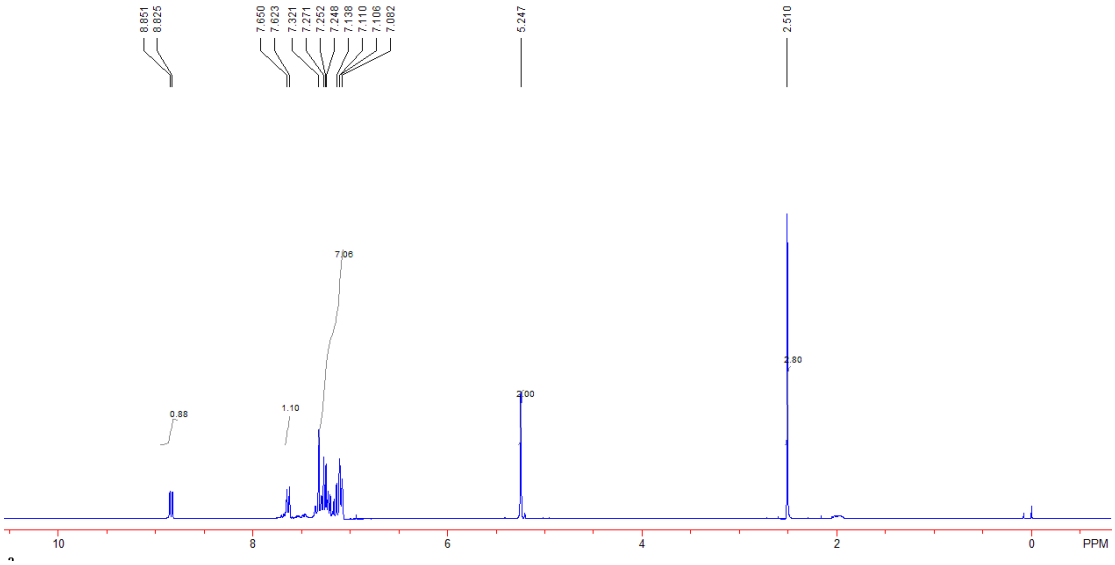






(E)-1-benzyl-7-trifluoromethyl-3-(2-oxopropylidene)indolin-2-one 1h

Yield: 1.0 g, 90%. A red solid. Mp: 139-141 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.51 (s, 3H), 5.25 (s, 2H), 7.08-7.65 (m, 7H), 7.64 (d, J = 8.1 Hz, 1H), 8.84 (d, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.6, 45.8 (q, J = 5.5 Hz), 112.8 (q, J = 32.8 Hz), 122.3, 122.6, 123.0 (q, J = 270.0 Hz), 125.6, 126.9, 128.3, 129.8, 130.3 (q, J = 6.4 Hz), 131.3, 131.9 (q, J = 2.9 Hz), 135.9, 142.9 (q, J = 1.6 Hz), 169.4, 198.5. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ -55.1. IR (CH_2Cl_2) ν 3095, 2955, 1719, 1685, 1584, 1449, 1427, 1340, 1323, 1180, 1116, 810, 737, 695 cm^{-1}. MS (%) m/e 346(7), 345($M^{+\cdot}$, 33), 274(21), 254(24), 92(8), 91(100), 65(12), 43(10). HRMS (EI) for $C_{19}H_{14}NO_2F_3$: 345.0977; Found: 345.0981.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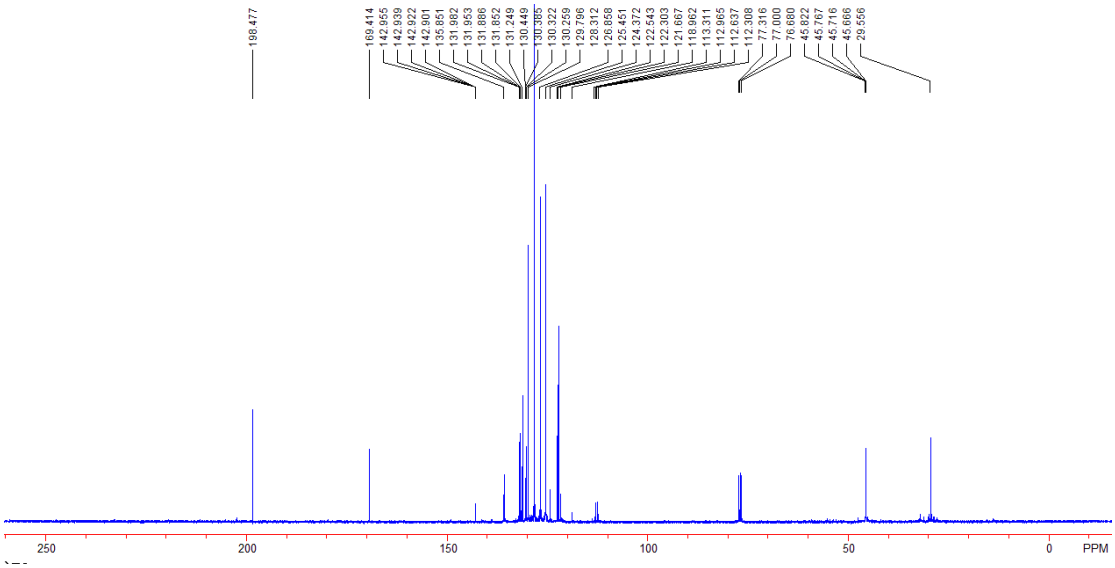
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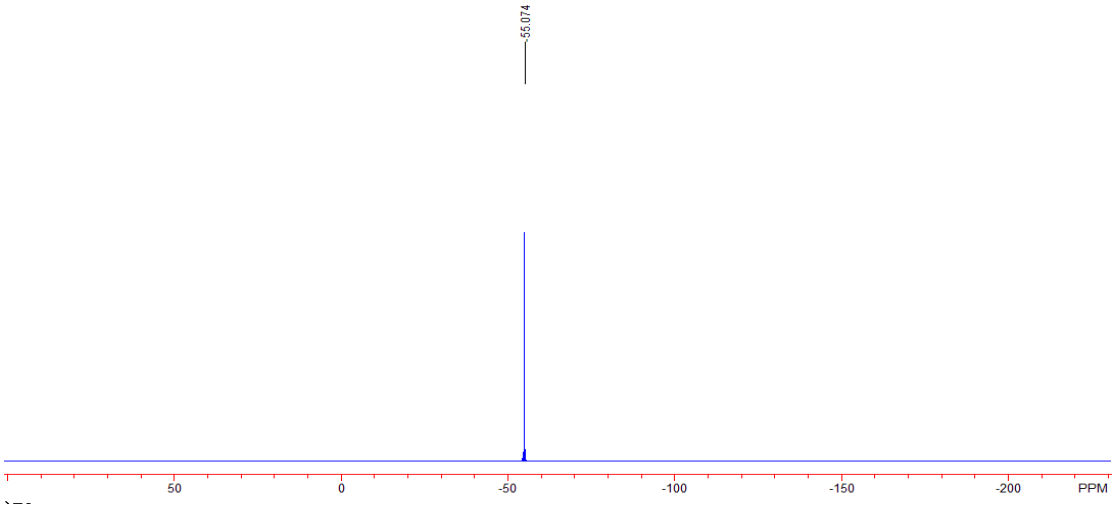
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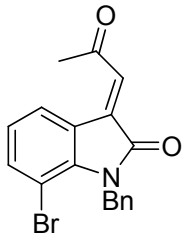
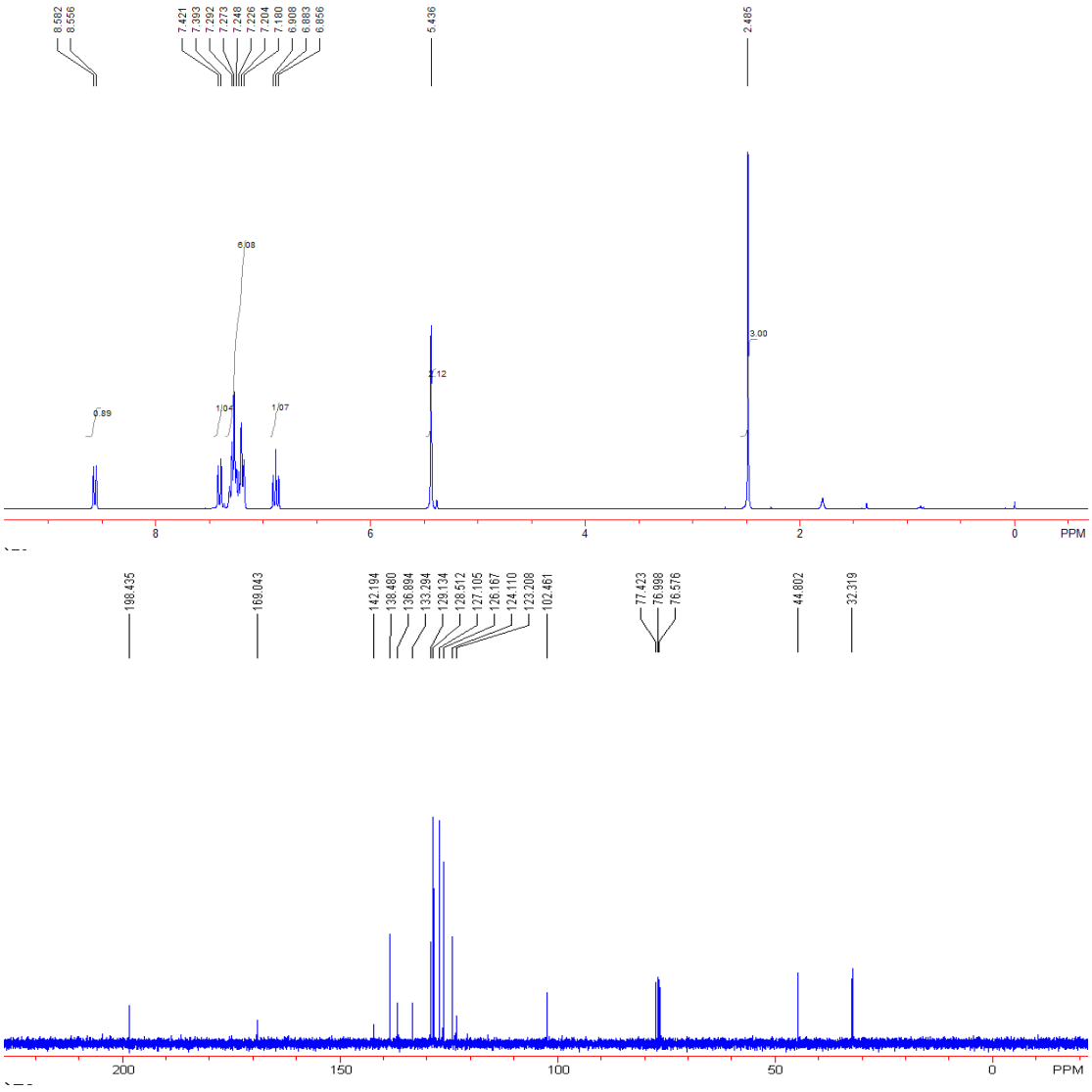
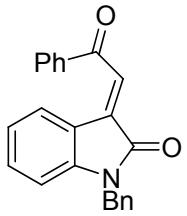


(E)-1-benzyl-7-bromo-3-(2-oxopropylidene)indolin-2-one 1i

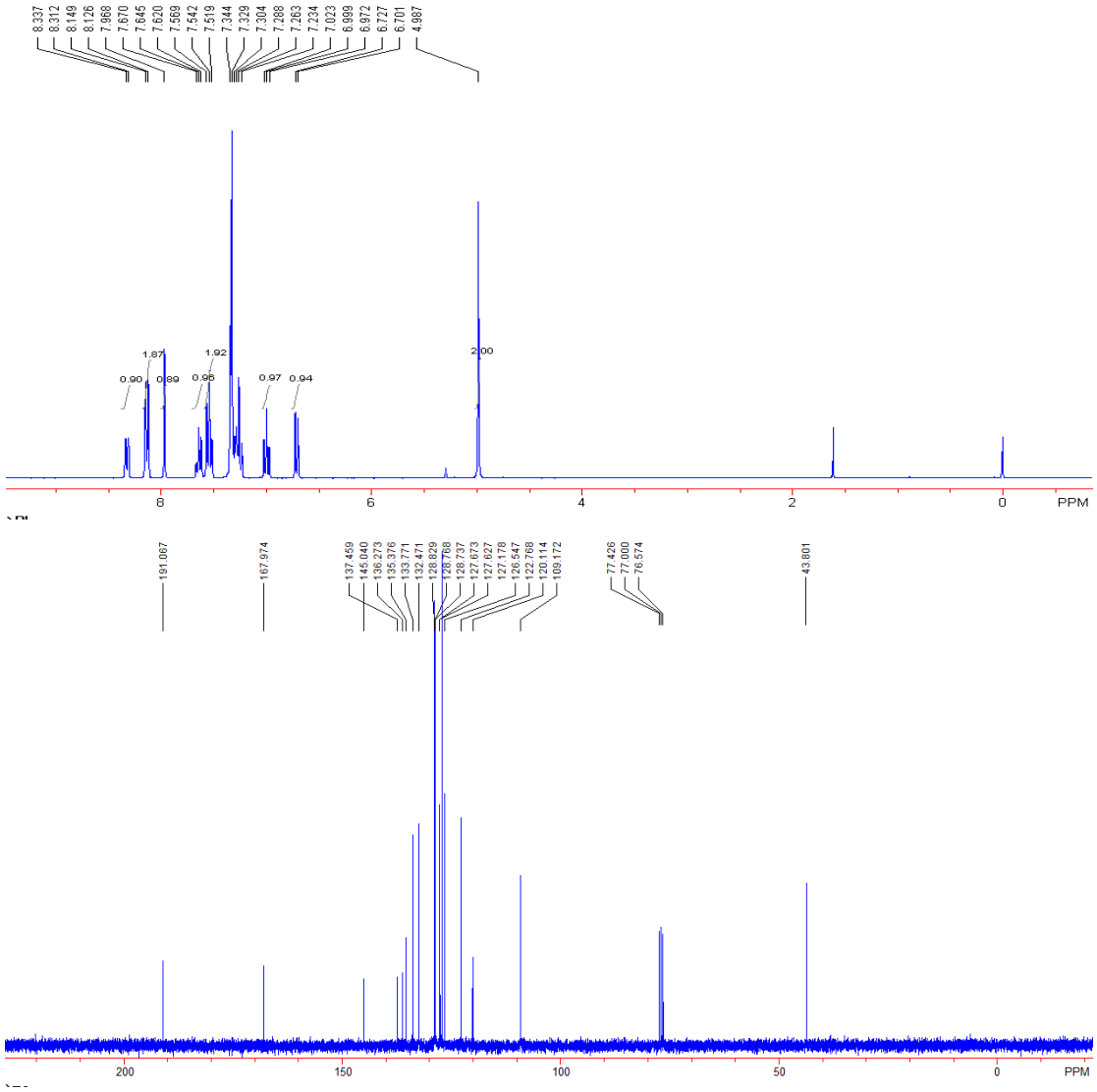
Yield: 0.8 g, 75%. A red solid. Mp: 131-133 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.48 (s, 3H), 5.44 (s, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 7.18-7.39 (m, 6H), 7.41 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 32.3, 44.8, 102.5, 123.2, 124.1, 126.2, 127.1, 128.5, 129.1, 133.2, 136.9, 138.5, 142.2, 169.0, 198.5. IR (CH_2Cl_2) ν 3102, 2924, 1707, 1680, 1589, 1439, 1362, 1337, 1188, 1164, 1116, 1078, 764, 724, 645 cm^{-1}. MS (%) m/e 357(22), 355($M^{+,}$ 22), 286(29), 284(29), 204(13), 91(100), 65(12), 43(14). HRMS (EI) for $C_{18}H_{14}NO_2Br$: 355.0208; Found: 355.0201.

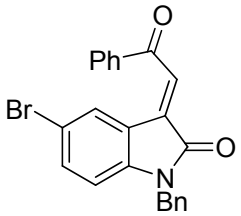




(E)-1-benzyl-3-(2-oxo-2-phenylethylidene)indolin-2-one 1j

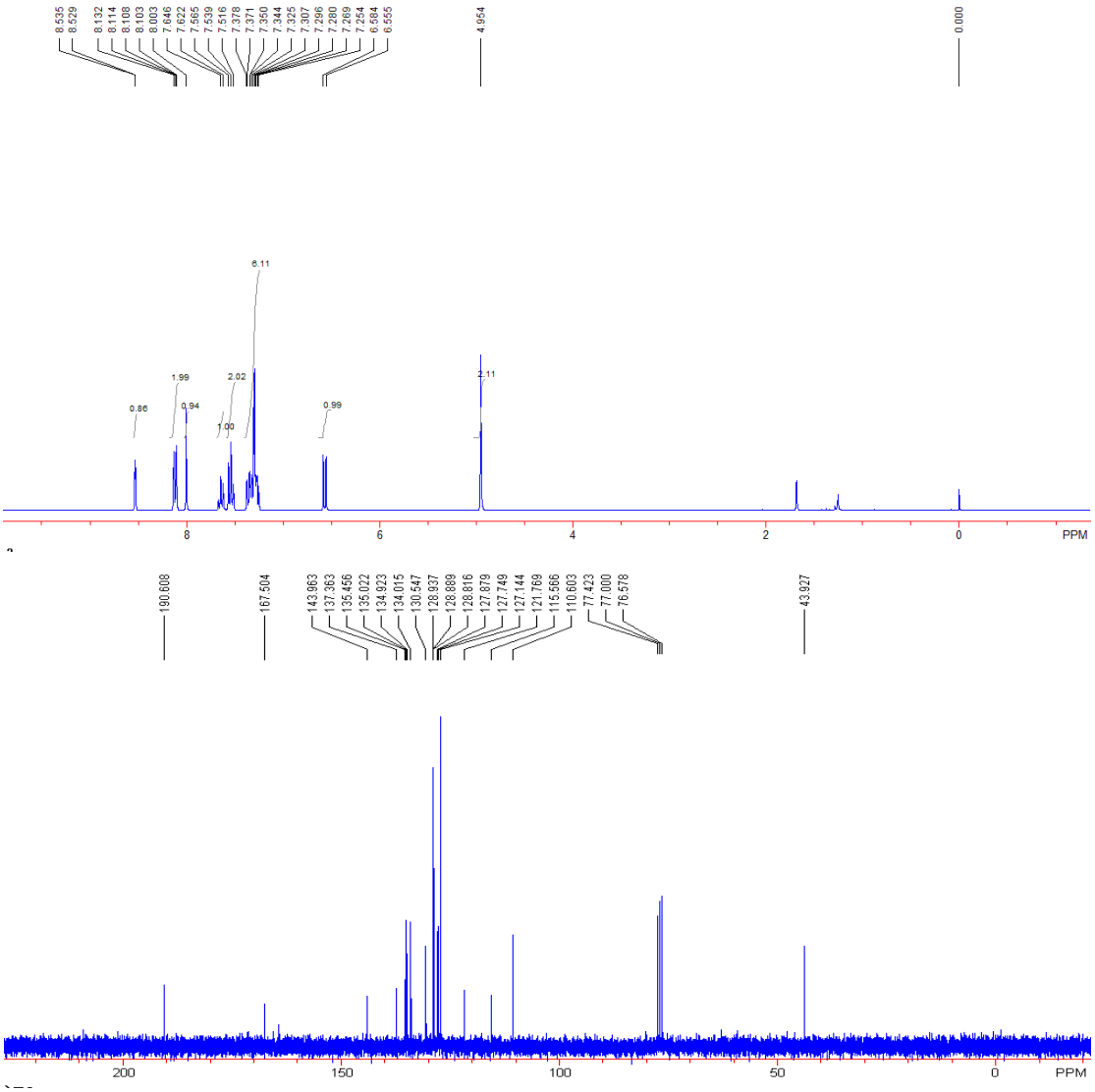
Yield: 1.1 g, 55%. A red solid. Mp: 136-138 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.98 (s, 2H,), 6.71 (d, *J* = 8.1 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.23-7.34 (m, 6H), 7.51-7.56 (m, 2H), 7.61-7.66 (m, 1H), 7.96 (s, 1H), 8.13 (d, *J* = 7.2 Hz, 2H), 8.32 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 43.8, 109.2, 120.1, 122.8, 126.6, 127.2, 128.7, 128.8, 128.8, 132.5, 135.4, 136.3, 137.5, 145.0, 168.0, 191.1; IR (CH_2Cl_2) ν 3068, 2923, 1708, 1655, 1593, 1467, 1451, 1346, 1224, 1188, 1003, 702, 684, 642, 616 cm^{-1}. MS (EI) *m/e* (%): 339 (M^+, 73), 234 (25) 206 (55), 105 (21), 91 (100), 77 (31), 65 (12); HRMS (EI) Calcd. for $C_{23}H_{17}NO_2$: 339.1259; Found: 339.1261.

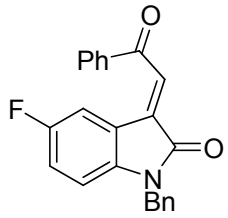




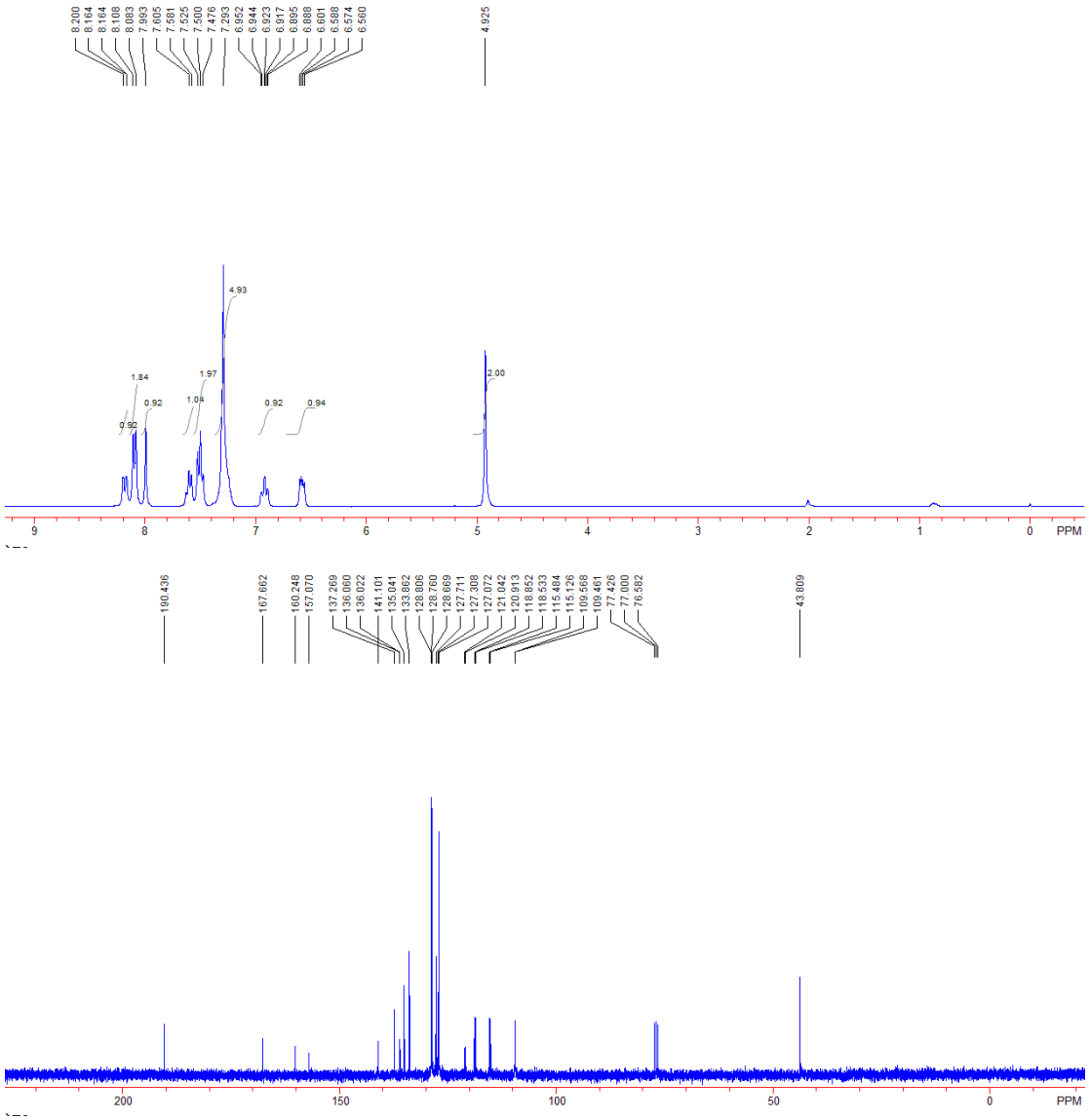
(E)-1-benzyl-5-bromo-3-(2-oxo-2-phenylethylidene)indolin-2-one 1k

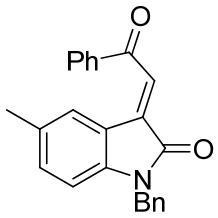
Yield: 0.9 g, 70%. A red solid. Mp: 170-172 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.96 (s, 2H), 6.57 (d, *J* = 8.7 Hz, 1H), 7.25-7.38 (m, 6H), 7.51-7.65 (m, 3H), 8.00 (s, 1H), 8.53. (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 43.9, 110.6, 115.6, 121.8, 127.2, 127.8, 127.9, 128.8, 128.9, 129.0 130.6, 134.0, 134.9, 135.0, 135.6, 137.4, 144.0, 167.5, 190.6. IR (CH_2Cl_2) ν 3106, 2923, 1712, 1656, 1594, 1462, 1451, 1346, 1224, 1009, 798, 698, 679, 642, 616 cm^{-1}. MS (EI) *m/e* (%): 419 (23), 417 (M^+,23), 286 (12), 284 (12), 105 (19), 91 (100), 77 (21), 65 (9); HRMS (EI) Calcd. for $C_{23}H_{16}BrNO_2$: 417.0364; Found: 417.0360.





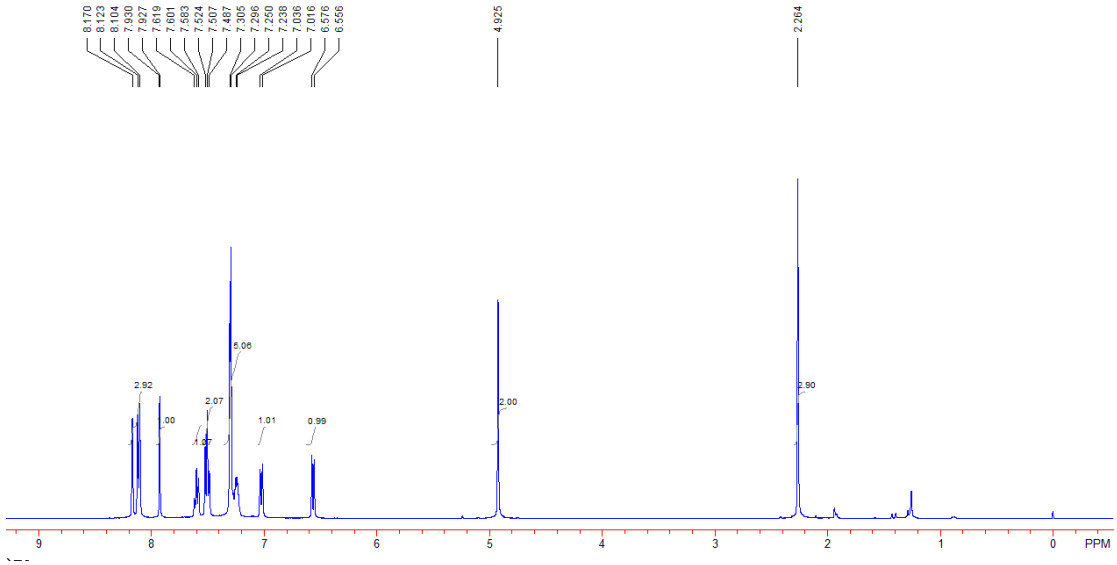
Yield: 0.7 g, 55%. A red solid. Mp: 135-137 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.93 (s, 3H), 6.58 (dd, J_1 = 8.1 Hz, J_2 = 3.9 Hz, 1H), 6.89-6.92 (m, 1H), 7.29 (brs, 5H), 7.48-7.61 (m, 3H), 8.00 (s, 1H), 8.05 (d, J = 7.5 Hz, 2H), 8.19 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 43.8, 109.5 (d, J = 8.0 Hz), 115.3 (d, J = 26.9 Hz), 118.7 (d, J = 23.9 Hz), 121.0 (d, J = 9.7 Hz), 127.1, 127.3, 127.7, 128.6, 128.7, 128.8, 133.9, 135.1, 136.0 (d, J = 2.8 Hz), 137.3, 141.1, 158.7 (d, J = 238.3Hz), 167.7, 190.4. IR (CH_2Cl_2) ν 3031, 2924, 1700, 1650, 1574, 1466, 1445, 1333, 1255, 1199, 966, 702, 684, 642, 616 cm^{-1}. MS (EI) *m/e* (%): 358 (13), 357 (M^+, 13), 252 (16), 224 (34), 105 (16), 91 (100), 77 (22), 65 (10); HRMS (EI) Calcd. for $C_{23}H_{16}FNO_2$: 357.1165; Found: 357.1157.

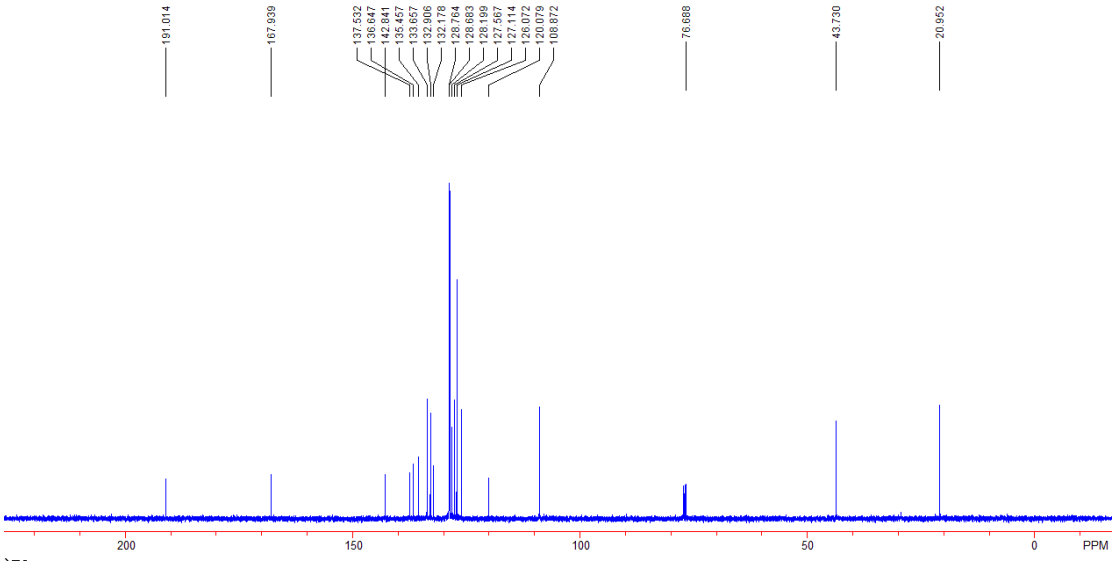


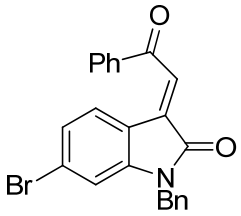


(E)-1-benzyl-5-methyl-3-(2-oxo-2-phenylethylidene)indolin-2-one 1m

Yield: 1.0 g, 75%. A red solid. Mp: 160-162 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.26 (s, 3H), 4.92 (s, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.24-7.31 (m, 5H), 7.49-7.52 (m, 2H), 7.58-7.62 (m, 1H), 7.93 (s, 1H), 8.11 (d, *J* = 7.6 Hz), 8.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.0, 43.7, 108.9, 120.1, 126.1, 127.1, 127.6, 128.2, 128.7. 128.8, 132.2, 132.9, 133.7, 135.5, 136.7, 137.5, 142.8, 167.9, 191.0; IR (CH_2Cl_2) ν 3058, 2924, 1706, 1655, 1588, 1474, 1365, 1336, 1231, 1183, 1015, 813, 684, 642, 616 cm^{-1}. MS (EI) *m/e* (%): 353 (M^+, 73), 220 (54), 105 (25), 91 (100), 77 (30), 65 (11), 57 (5); HRMS (EI) Calcd. for $C_{24}H_{19}NO_2$: 353.1416; Found: 353.1414.

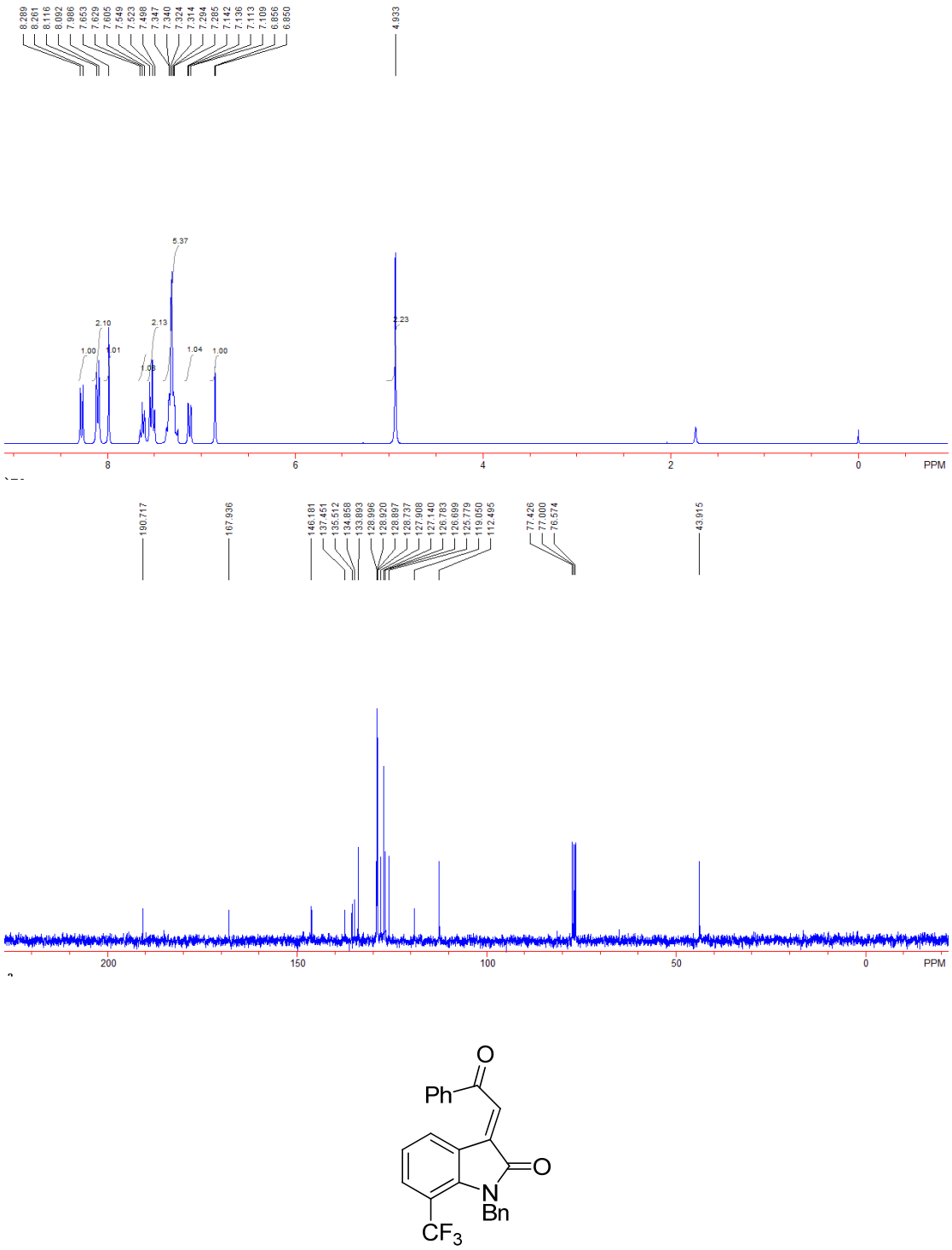






(E)-1-benzyl-6-bromo-3-(2-oxo-2-phenylethylidene)indolin-2-one 1n

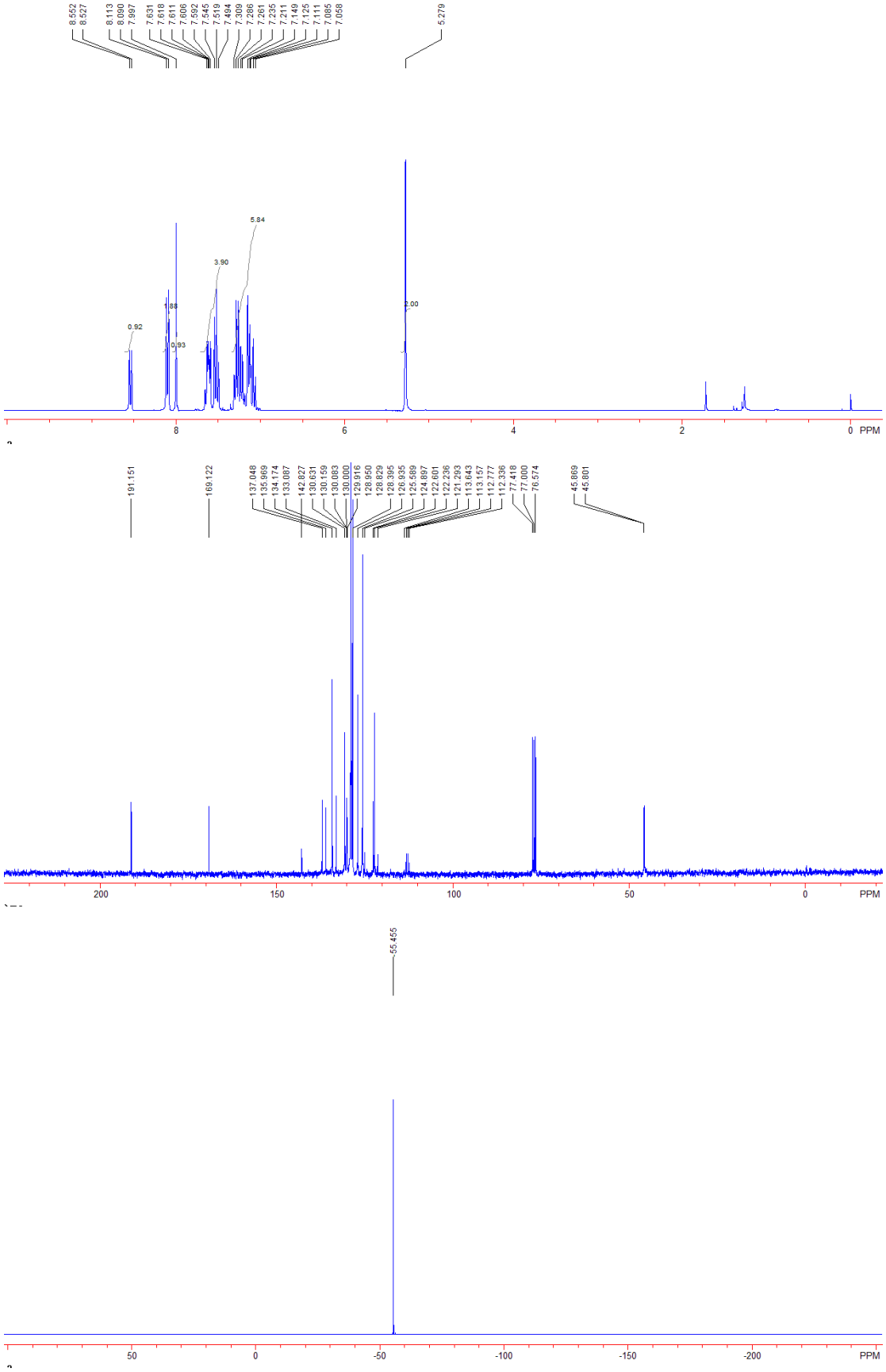
Yield: 0.64 g, 40%. A red solid. Mp: 180-182 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 4.93 (s, 2H), 4.92 (s, 2H), 6.85 (d, J = 1.8 Hz, 1H), 7.13 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 1H), 7.29-7.35 (m, 5H), 7.52 (t, J = 6.0 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.97 (s, 1H), 8.11 (d, J = 7.2 Hz), 8.28 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.9, 112.5, 119.1, 125.8, 126.7, 126.8, 127.1, 127.9. 128.7, 128.8, 128.9, 133.9, 134.9, 135.5, 137.4, 146.2, 168.0, 190.1; IR (CH_2Cl_2) ν 2924, 2853, 1718, 1651, 1612, 1584, 1449, 1363, 1346, 1228, 1107, 866, 825, 700, 647 cm^{-1}. MS (EI) *m/e* (%):419(24), 417 (M^+, 23), 286 (15), 284 (15), 105 (20), 91 (100), 77 (24), 65 (10); HRMS (EI) Calcd. for $C_{23}H_{16}NO_2Br$: 417.0364; Found: 417.0365.

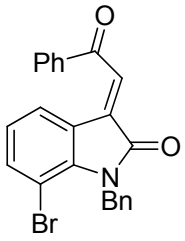


(E)-1-benzyl-7-trifluoromethyl-3-(2-oxo-2-phenylethylidene)indolin-2-one 1o

Yield: 0.4 g, 30%. A red solid. Mp: 141-143 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 5.28 (s, 2H), 7.01-7.31 (m, 6H), 7.49-7.63 (m, 4H), 7.80 (s, 1H), 8.10 (d, J = 6.9 Hz, 1H), 7.97 (s, 1H), 8.54 (d, J = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 45.8 (q, J = 5.1 Hz), 113.0 (q, J = 28.5 Hz), 122.2, 122.6, 123.1 (q, J = 270.3 Hz), 125.6, 126.9, 128.4, 128.8, 129.0, 130.0 (q, J = 6.2 Hz), 130.6, 133.1, 134.2, 136.0, 137.1, 142.9, 169.1, 191.2. IR (CH_2Cl_2) ν 3103, 3033, 1717, 1662, 1585, 1448, 1428, 1340, 1250, 1162, 1113, 1011, 788, 68594, 634 cm^{-1}. ^{19}F NMR ($CDCl_3$, 282 MHz,

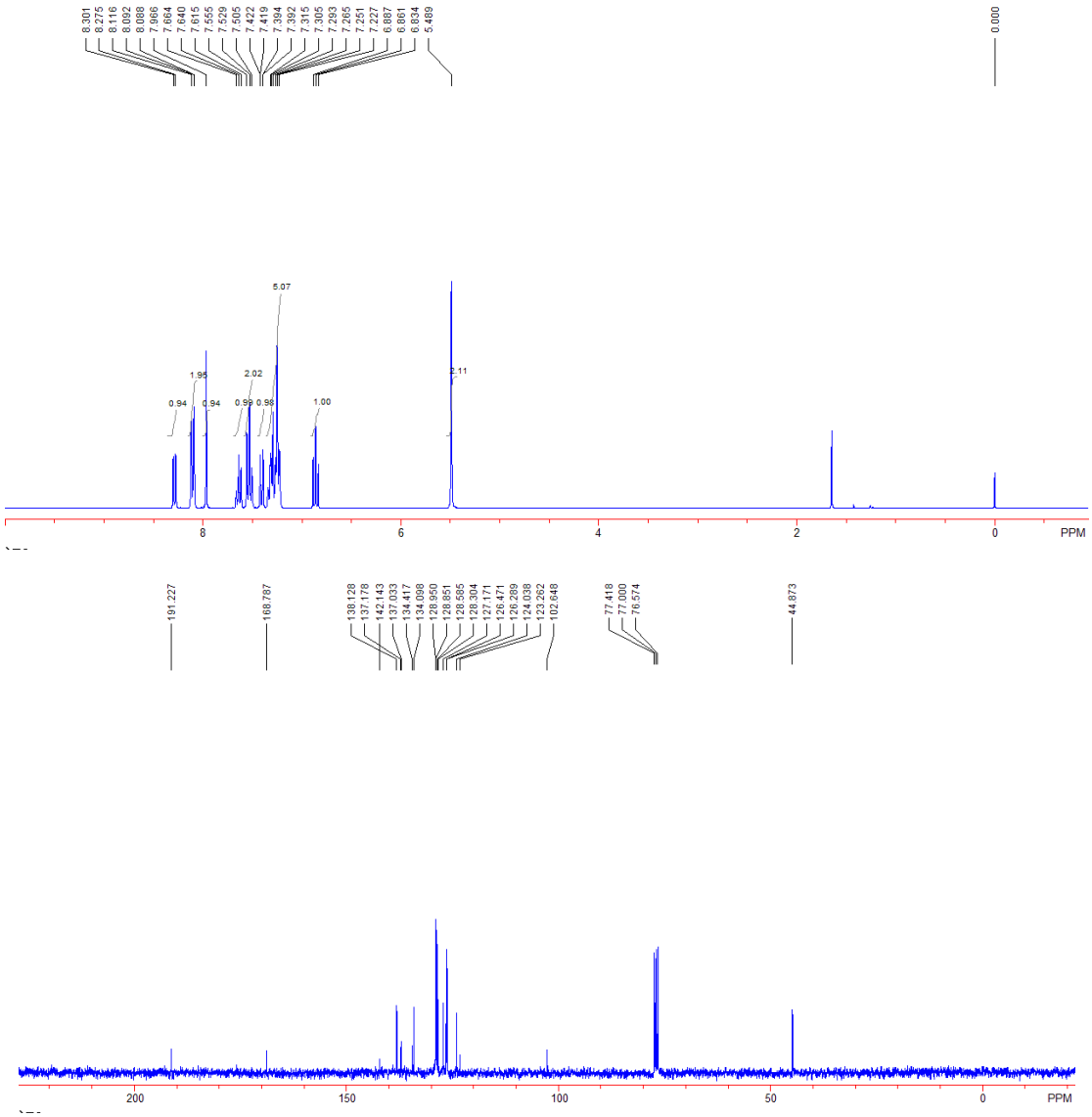
$CFCl_3$): δ -55.45. MS (EI) *m/e* (%):408 (11), 407 (M^+, 40), 274 (19), 254 (20), 105 (20), 91 (100), 77 (22), 65 (10). HRMS (EI) Calcd. for $C_{24}H_{16}NO_2F_3$: 407.1133; Found: 407.1132.





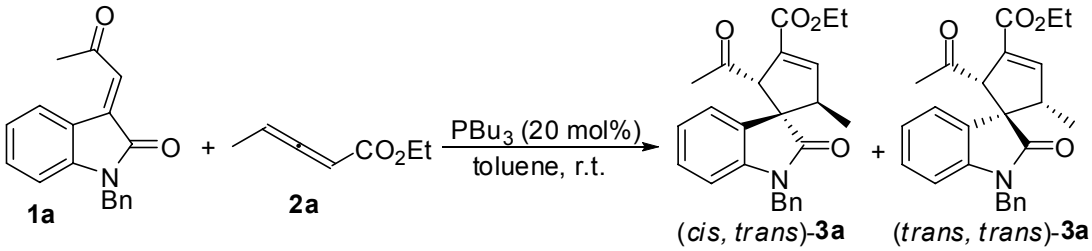
(E)-1-benzyl-7-bromo-3-(2-oxo-2-phenylethylidene)indolin-2-one 3p

Yield: 0.7 g, 55%. A red solid. Mp: 175-177 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 5.48 (s, 2H), 6.86 (t, *J* = 7.8 Hz, 1H), 7.22-7.42 (m, 6H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.97 (s, 1H), 8.11 (d, *J* = 6.0 Hz, 1H), 8.29 (d, *J* = 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 44.8, 102.7, 123.3, 124.0, 126.1, 126.5, 127.2, 128.3. 128.6, 128.8, 128.9, 134.1, 134.4, 135.5, 137.0, 142.2, 168.8, 191.2. IR (CH_2Cl_2) ν 3087, 2925, 1705, 1657, 1595, 1439, 1331, 1231, 1162, 1115, 1007, 758, 703, 685, 648 cm^{-1}. MS (EI) *m/e* (%): 419 (25), 417 (M^+, 25), 286 (28), 284 (28), 204 (11), 105 (28), 91 (100), 77 (30). HRMS (EI) Calcd. for $C_{23}H_{16}NO_2Br$: 417.0364; Found: 417.0361.



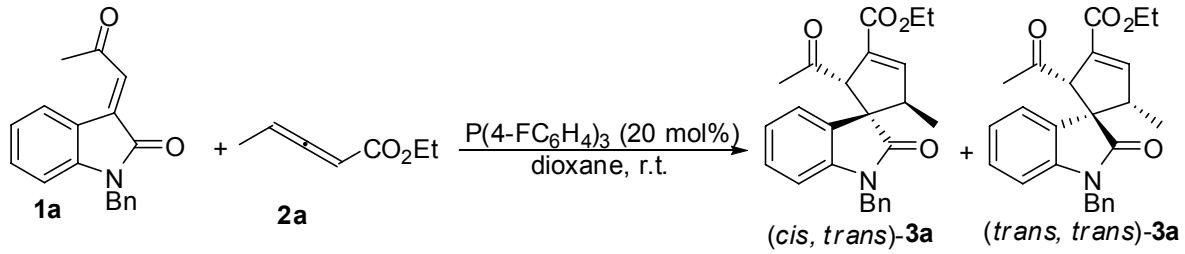
Representative procedure for the preparation of 3a-3p

General Procedure A:



To a solution of **1a** (28.0 mg, 0.1 mmol) and **2a** (25.2 mg, 0.2 mmol) in degassed toluene (1.0 mL) under Ar was added catalyst (5.0 μL, 20 mol%). The reaction mixture was stirred at r.t. for 8 h. It was then concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (pentane/EtOAc = 10:1 to 4:1). The pure product **3a** was then obtained (as a mixture of (*trans,trans*)/(*cis,trans*) diastereoisomers with 1/4) as colorless solid (30.0 mg, 76.0%).

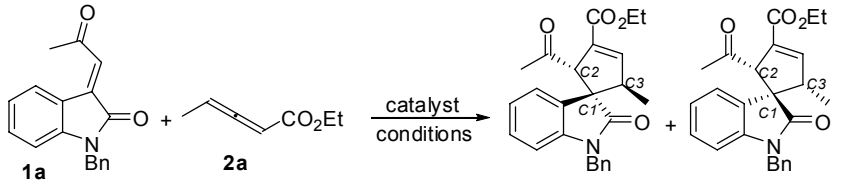
General Procedure B:



To a solution of **1a** (28.0 mg, 0.1 mmol) and **2a** (31.5 mg, 0.25 mmol) in degassed dioxane (1.0 mL) under Ar was added catalyst (5.1 mg, 20 mol%). The reaction mixture was stirred at r.t. for 8 h. It was then concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (pentane/EtOAc = 10:1 to 4:1). The pure product **3a** was then obtained (as a mixture of (*trans,trans*)/(*cis,trans*) diastereoisomers with 20/1) as colorless solid (29.0 mg, 73.0%).

Optimization of the reaction conditions

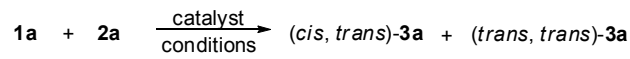
Table SI-1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	yield (%)[b]	(*cis, trans*): (*trans, trans*)[c]
1	PBu_3	toluene	76	4:1
2	PBu_3	n-Bu_2O	71	4:1
3	PBu_3	^{t}BuOMe	56	4:1
4	PBu_3	DCM	<5	4:1
5	PBu_3	Et_2O	50[d]	9:1
6	PBu_3	THF	<5	4:1
7	PBu_3	MeCN	complex	–
8	PBu_3	DMF	complex	–
9	PMe_3	toluene	-[e]	–
10	P^tBu_3	toluene	-[e]	–
11	PBu_3[f]	toluene	50	–

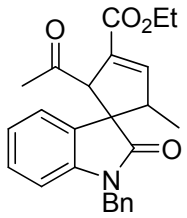
[a]The reaction was carried out on a 0.1 mmol scale with 20 mol% catalyst under Ar in solvent (1.0 mL) at rt for 8 h, and the ratio of **1a/2a** was 1.0/2.0. [b]Isolated yield. [c]The diastereomeric ratio of (*cis*, *trans*)/(*trans*, *trans*) was determined by ^{1}H NMR spectroscopic data. [d]The reaction time was prolonged to 48 h. [e]No reaction occurred. [f]10 mol% of the catalyst was used and the reaction time was prolonged to 48 h.

Table SI-2. Optimization of Reaction Conditions[a]



entry	catalyst	solvent	yield (%)[b]	(*cis*, *trans*): (*trans*, *trans*)[c]
1	$PPhMe_2$	toluene	79	1:1.5
2	PPh_2Me	toluene	67	1:10
3	PPh_3	toluene	52	1:20
4	$P(MeO)Ph_2$	toluene	-[d]	–
5	$P(4\text{-}MeOC_6H_4)_3$	toluene	67	1:11
6	$P(4\text{-}MeC_6H_4)_3$	toluene	67	1:20
7	$P(4\text{-}FC_6H_4)_3$	toluene	57	<1:20
8	$P(4\text{-}FC_6H_4)_3$	Et_2O	71	<1:20
9	$P(4\text{-}FC_6H_4)_3$	DCM	50	1:19
10	$P(4\text{-}FC_6H_4)_3$	MeCN	54	<1:20
11	$P(4\text{-}FC_6H_4)_3$	THF	50	1:20
12[e]	$P(4\text{-}FC_6H_4)_3$	Et_2O	76	<1:20
13	$P(4\text{-}FC_6H_4)_3$	dioxane	73	<1:20

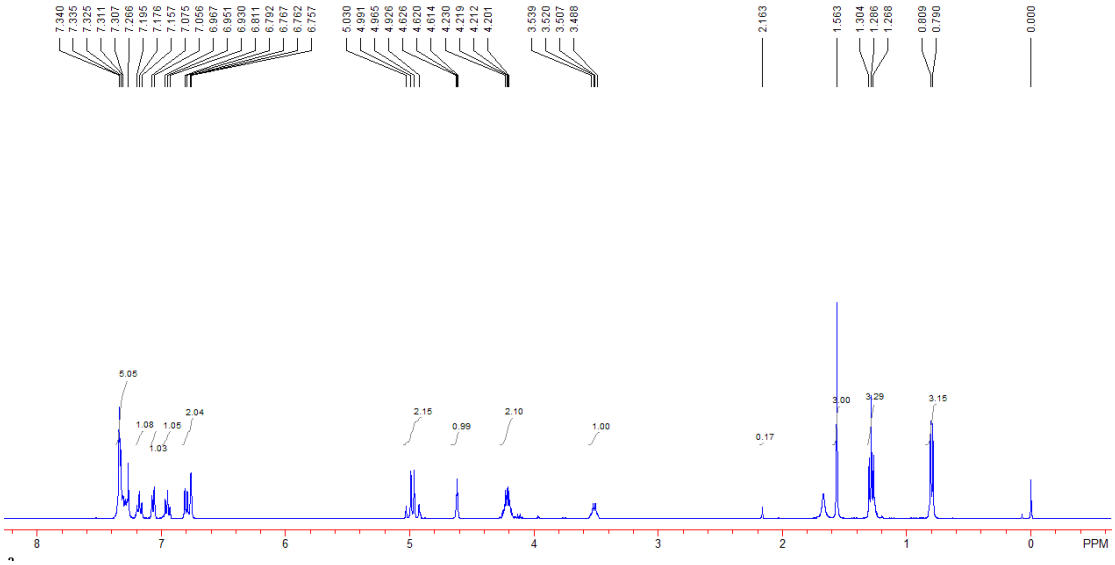
[a]The reaction was carried out on a 0.1 mmol scale with 20 mol% catalyst under Ar in solvent (1.0 mL) at rt for 8 h, and the ratio of **1a/2a** was 1.0/2.0. [b]Isolated yield. [c]The diastereomeric ratio of (*cis*, *trans*)/(*trans*, *trans*) was determined by ^{1}H NMR spectroscopic data. [d]No reaction occurred. [e]**2a** (2.5 equiv) was used.

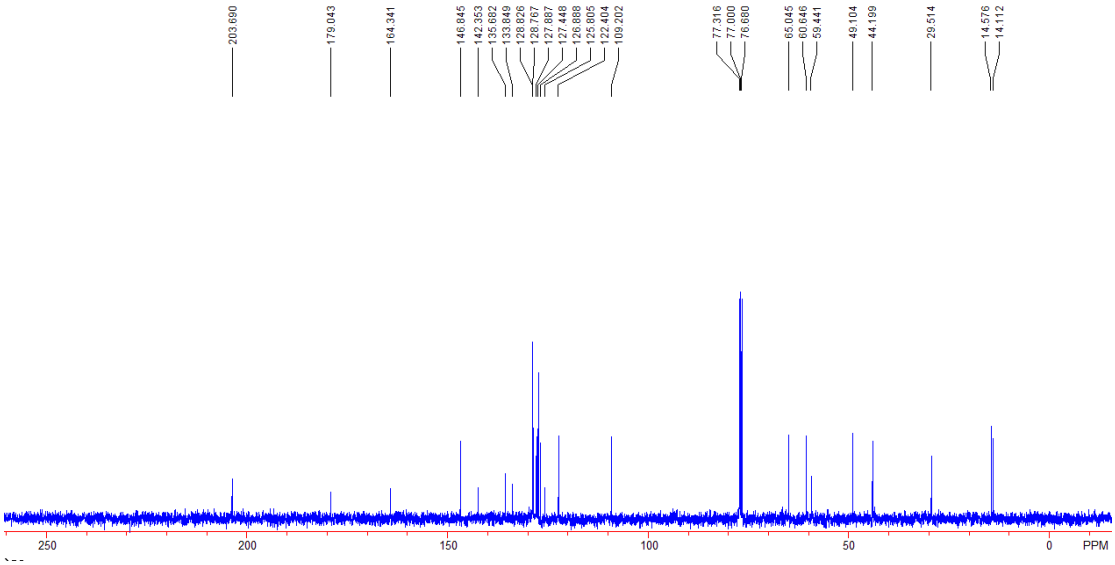


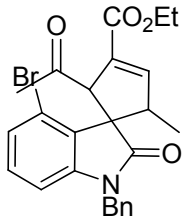
Compound 3a

(*trans,trans*) : (*cis,trans*) > 20 : 1

Yield: 29 mg, 73%. A colorless solid. Mp: 133-135 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.80 (d, *J* = 7.6 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.56 (s, 3H), 2.16 (s, 0.17H), 3.48-3.54 (m, 1H), 4.20-4.23 (m, 2H), 4.62 (t, *J* = 2.4 Hz, 1H), 4.94 (d, *J* = 26.0 Hz, 1H), 5.01 (d, *J* = 26.0 Hz), 6.76-6.81 (m, 2H), 6.93-6.97 (m, 1H), 7.06 (d, *J* = 7.6 Hz), 7.18 (t, *J* = 7.6 Hz, 1H), 7.26-7.34 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.6, 29.5, 44.2, 49.1, 59.5, 60.7, 65.1, 109.2, 122.4, 125.8, 126.8, 127.5, 127.9, 128.8, 133.9, 135.7, 142.4, 146.9, 164.3, 179.1, 203.7. IR (CH_2Cl_2) ν 3087, 2978, 1708, 1611, 1487, 1466, 1361, 1169, 800, 750, 696 cm^{-1}. MS (ESI) *m/e* 426 (M +23, 100). HRMS (ESI) Calcd. for $C_{25}H_{25}NO_4Na^{+1}$ requires 426.1675, Found: 426.1685.



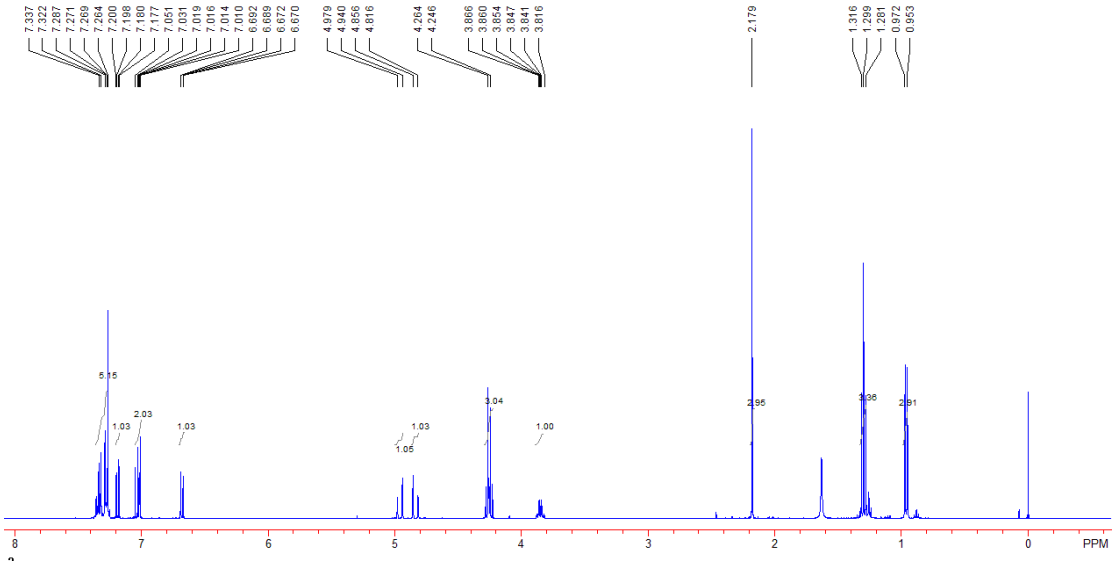


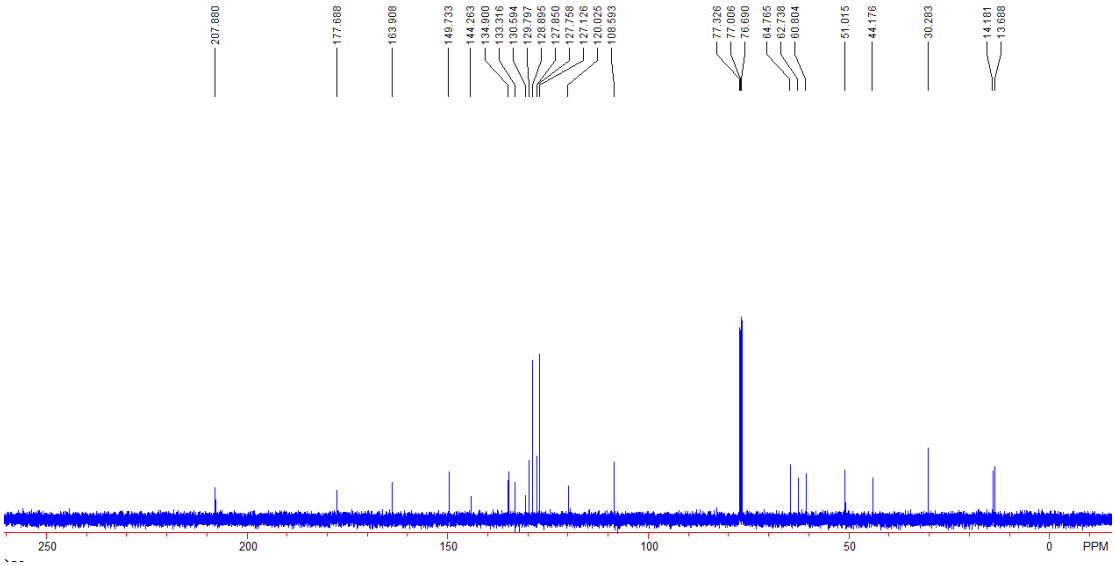


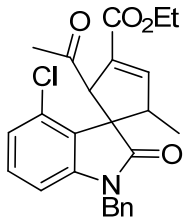
Compound 3b

(*cis,trans*) : (*trans,trans*) > 20 : **1**

Yield: 19 mg, 40%. A colorless solid. Mp: 85-87 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.96 (d, J = 7.6 Hz, 3H), 1.30 (t, J = 6.8 Hz, 3H), 2.17 (s, 3H), 3.81-3.87 (m, 1H), 4.24-4.26 (m, 3H), 4.83 (d, J = 15.6 Hz, 1H), 4.95 (d, J = 15.6 Hz, 1H), 6.68 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.01-7.05 (m, 2H), 7.19 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.26-7.33 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.7, 14.2, 30.3, 44.2, 51.0, 60.8, 62.7, 64.8, 108.6, 120.0, 127.1, 127.8, 128.9, 129.8, 130.6, 133.3, 134.9, 144.2, 149.7, 163.9, 177.8, 207.8. IR (CH_2Cl_2) ν 2979, 2928, 1704, 1601, 1451, 1336, 1252, 1193, 1252, 1116, 775, 698 cm^{-1}. MS (ESI) *m/e* 504 (M +23, 100). HRMS (ESI) Calcd. for $C_{25}H_{24}NO_4BrNa^{+1}$ requires 504.0781, Found: 504.0793.





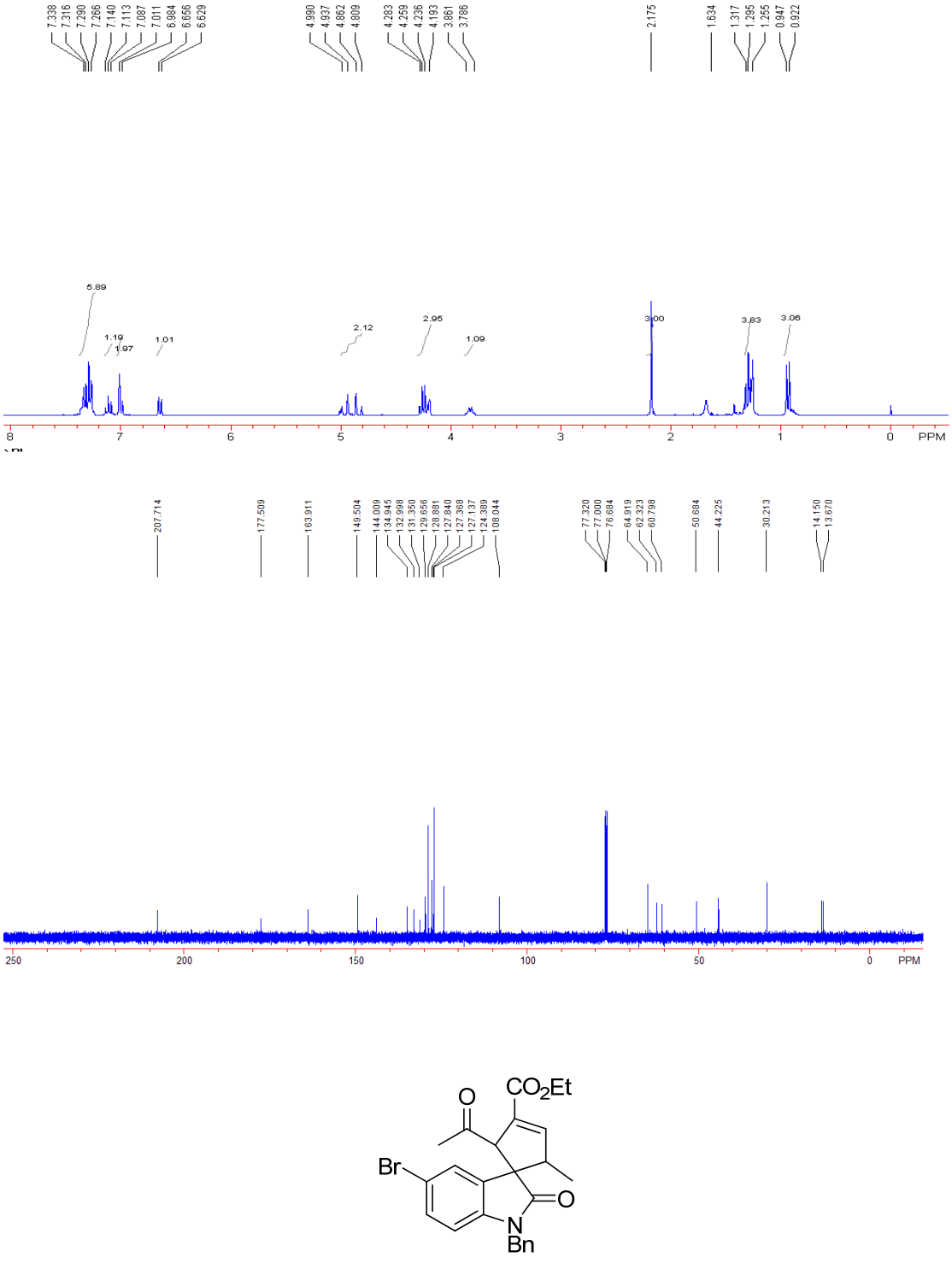


Compound 3c

(*cis,trans*) : (*trans,trans*) > 20 : **1**

Yield: 19 mg, 40%. A colorless solid. Mp: 79-81 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.93 (d, *J* = 7.5 Hz, 3H), 1.30 (t, *J* = 6.6 Hz, 3H), 2.18 (s, 3H), 3.79-3.86 (m, 1H), 4.19-4.28 (m, 3H), 4.84 (d, *J* = 15.9 Hz, 1H), 4.96 (d, *J* = 15.9 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.99-7.01 (m, 2H), 7.11 (t, *J* = 8.1 Hz, 1H), 7.27-7.34 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.7, 14.2, 30.2, 44.2, 50.6, 60.8, 62.3, 64.9, 108.1, 124.4, 127.1, 127.4, 127.8, 128.8, 130.0, 131.4, 133.0, 135.0, 144.0,

149.5, 163.9, 177.5, 207.7. IR (CH_2Cl_2) ν 2979, 2929, 1705, 1604, 1582, 1453, 1336, 1253, 1117, 1051, 777, 727, 698 cm^{-1}. MS (ESI) *m/e* 460 (M+23, 100). HRMS (ESI) Calcd. for $C_{25}H_{24}NO_4ClNa^{+1}$ requires 460.1286, Found: 460.1288.

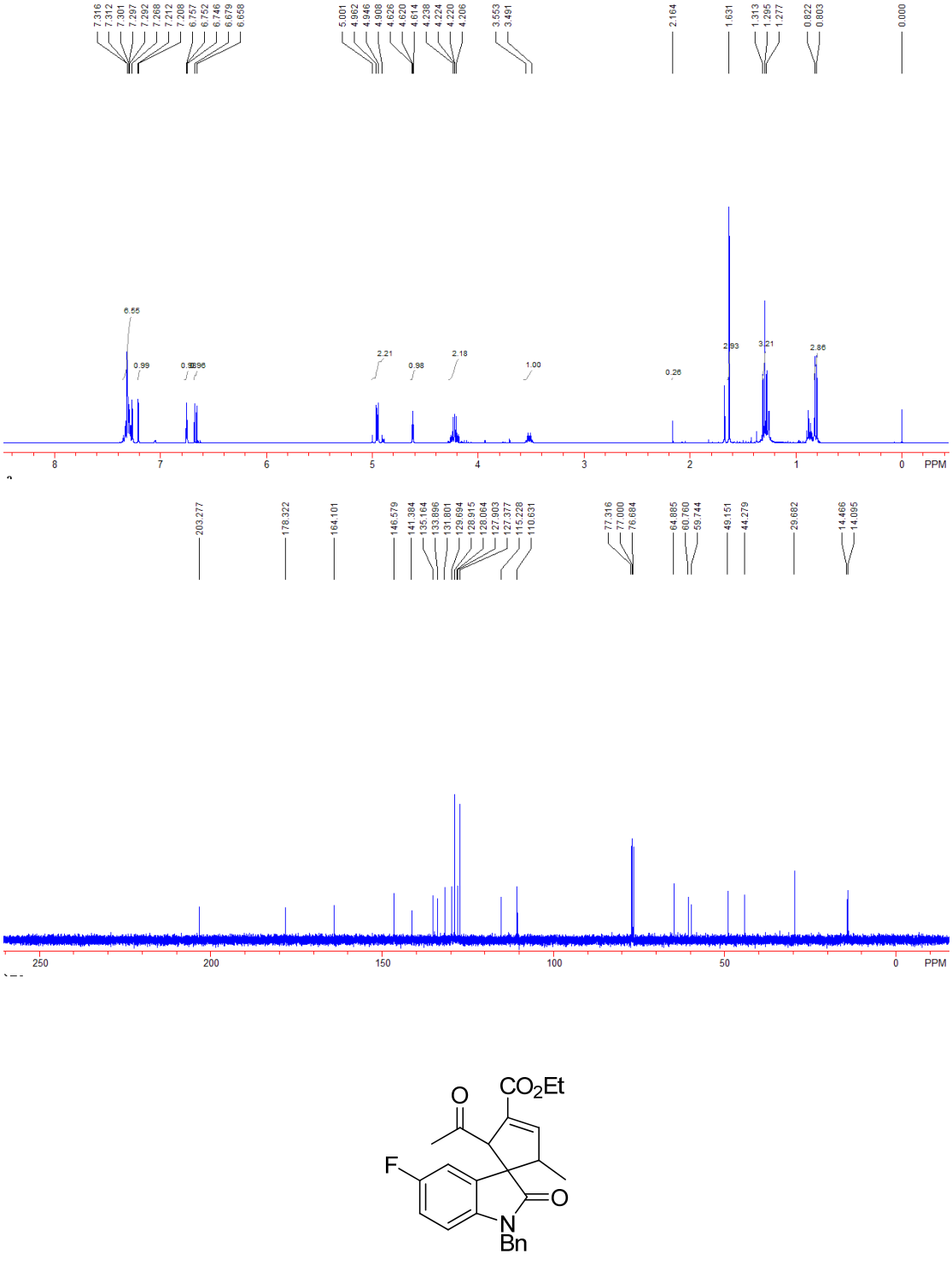


Compound 3d

(*trans,trans*) : (*cis,trans*) = 20 : 1

Yield: 36 mg, 74%. A colorless solid. Mp: 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.81 (d, *J* = 7.6 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.63 (s, 3H), 2.17 (s, 0.26H), 3.49-3.55 (m, 1H),

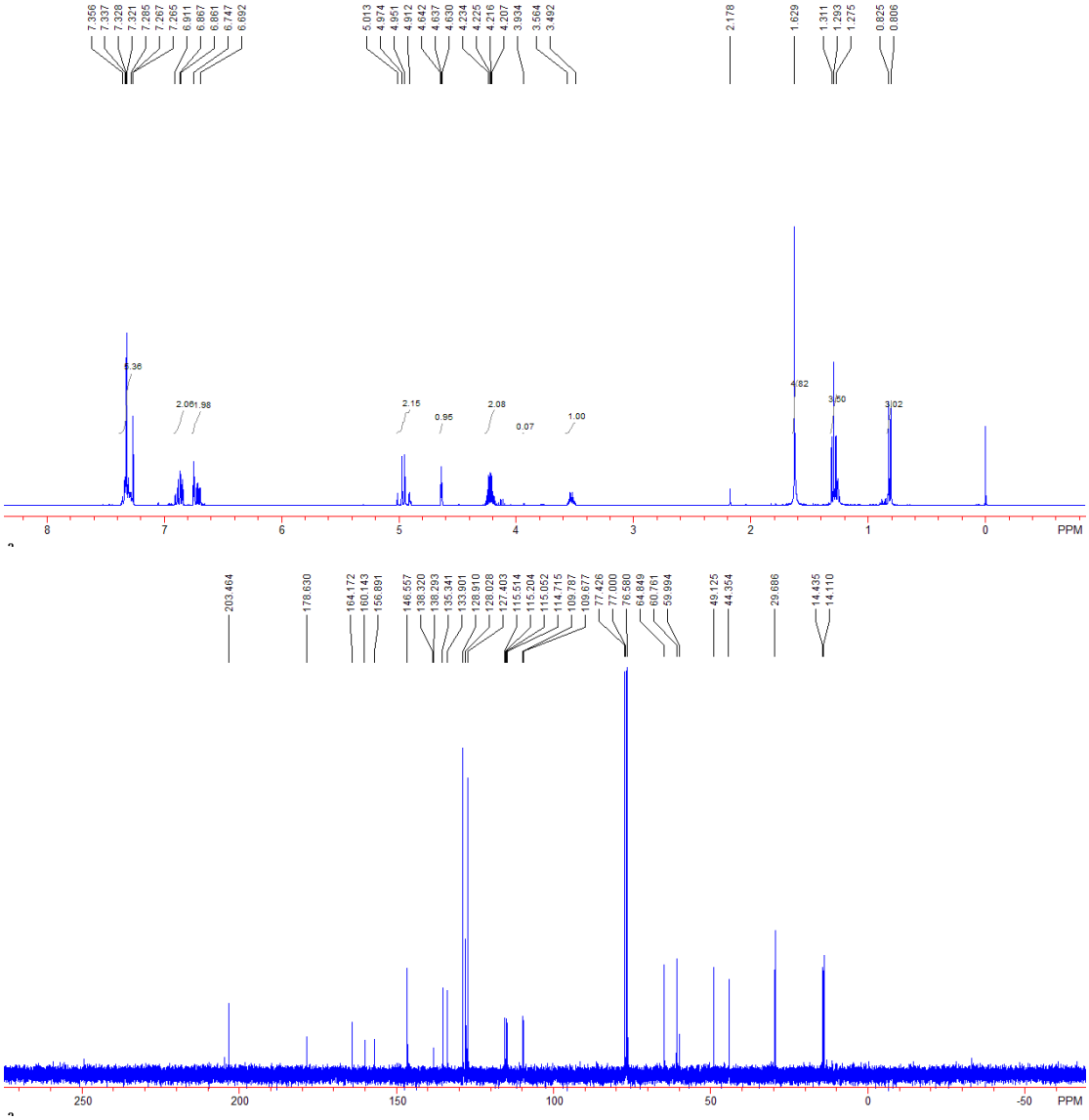
4.21-4.24 (m, 2H), 4.62 (t, J = 2.4 Hz, 1H), 4.93 (d, J = 15.6 Hz, 1H), 4.97 (d, J = 15.6 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.75 (t, J = 2 Hz, 1H), 7.21 (d, J = 1.6 Hz, 1H), 7.21-7.32 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.5, 30.0, 44.3, 49.2, 59.8, 60.8, 64.9, 110.6, 115.2, 127.4, 127.9, 128.1, 128.9, 129.7, 131.8, 133.9, 135.2, 141.4, 146.6, 164.1, 178.3, 203.3. IR (CH_2Cl_2) ν 2973, 2923, 1703, 1678, 1484, 1445, 1373, 1301, 1247, 1174, 819, 733, 690 cm^{-1}. MS (ESI) *m/e* 504 (M+23, 100). HRMS (ESI) Calcd. for $C_{25}H_{24}NO_4BrNa^{+1}$ requires 504.0781, Found: 504.0799.

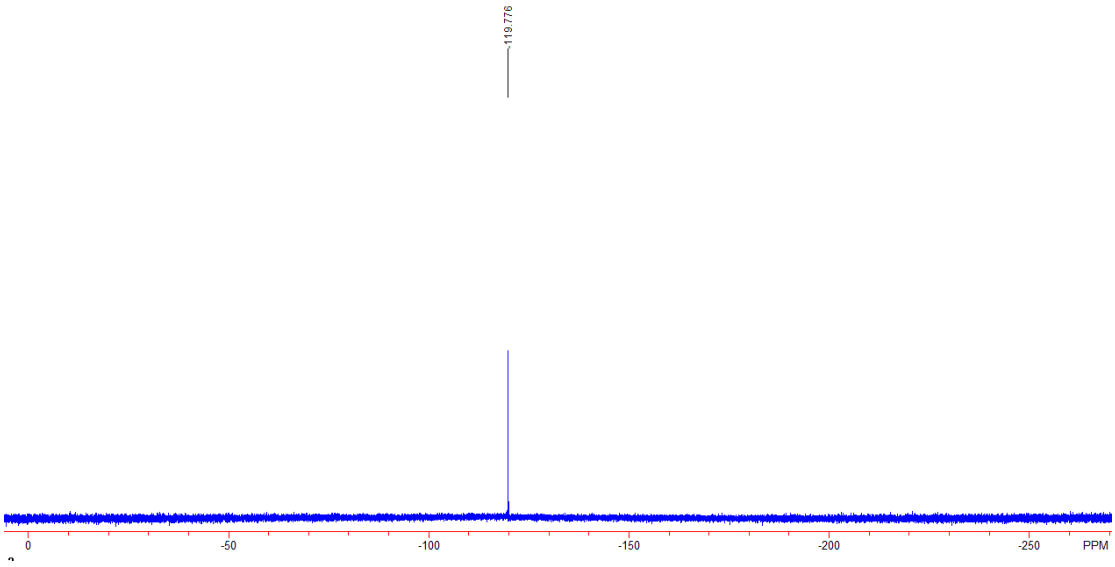


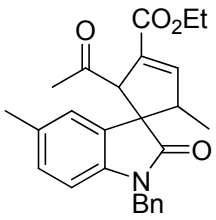
Compound 3e

(*trans,trans*) : (*cis,trans*) = 14 : 1

Yield: 33 mg, 78%. A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.81 (d, J = 7.6 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.63 (s, 3H), 2.18 (s, 0.22H), 3.48-3.57 (m, 1H), 3.98 (s, 0.07H), 4.21-4.24 (m, 2H), 4.64 (t, J = 2.0 Hz, 1H), 4.93 (d, J = 15.6 Hz, 1H), 5.00 (d, J = 15.6 Hz, 1H), 6.69-6.91 (m, 4H), 7.26-7.36 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.4, 29.7, 44.4, 49.1, 59.8, 60.0, 60.7, 64.9, 109.7 (d, J = 11.0 Hz), 114.9 (d, J = 33.7 Hz), 115.4 (d, J = 31.0 Hz), 127.4, 128.0, 128.9, 133.9, 135.4, 138.2 (d, J = 2.7 Hz), 146.6, 158.5 (d, J = 324.0 Hz), 164.2, 178.6, 203.5. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ -119.8. IR (CH_2Cl_2) ν 2978, 2929, 1705, 1486, 1451, 1339, 1251, 1169, 1121, 1025, 862, 730 cm^{-1}. MS (ESI) *m/e* 444 (M+23, 100). HRMS (ESI) Calcd. for $C_{25}H_{24}NO_4FNa^{+1}$ requires 444.1582, Found: 444.1585.



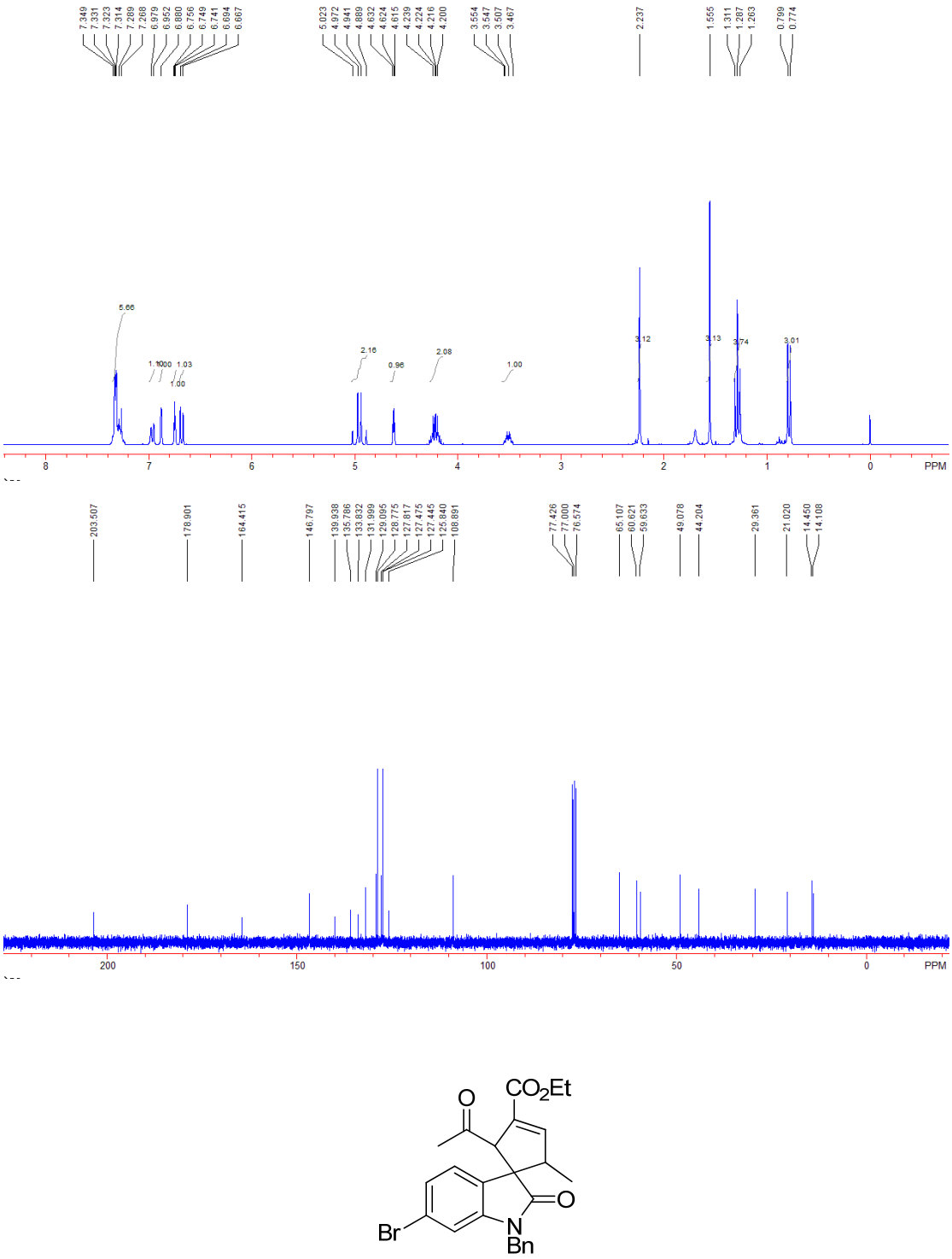




Compound 3f

(*trans,trans*) *:* (*cis,trans*) > 20 : **1**

Yield: 30 mg, 75%. A colorless solid. Mp: 105-107 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.76 (d, *J* = 6 Hz, 3H), 1.29 (t, *J* = 8.1 Hz, 3H), 1.56 (s, 3H), 2.16 (s, 0.05), 2.24 (s, 3H), 3.47-3.56 (m, 1H), 4.20-4.24 (m, 2H), 4.63 (t, *J* = 2.4 Hz, 1H), 4.92 (d, *J* = 15.3 Hz, 1H), 5.01 (d, *J* = 15.3 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 6.75 (t, *J* = 2.1 Hz, 1H), 6.88 (s, 1H), 6.97 (d, *J* = 8.1 Hz), 7.27-7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 14.1, 14.5, 21.0, 29.4, 44.2, 49.1, 59.6, 60.6, 65.1, 108.9, 125.8, 127.3, 127.5, 127.9, 128.8, 129.0, 132.0, 133.8, 135.8, 140.0, 146.8, 164.4, 178.9, 203.5. IR (CH_2Cl_2) ν 2961, 2870, 1704, 1495, 1447, 1364, 1243, 1164, 807, 753, 730, 695, 666 cm^{-1}. MS (ESI) *m/e* 502 (M+23, 100). HRMS (ESI) Calcd. for $C_{26}H_{27}NO_4Na^{+1}$ requires 440.1832, Found: 440.1837.

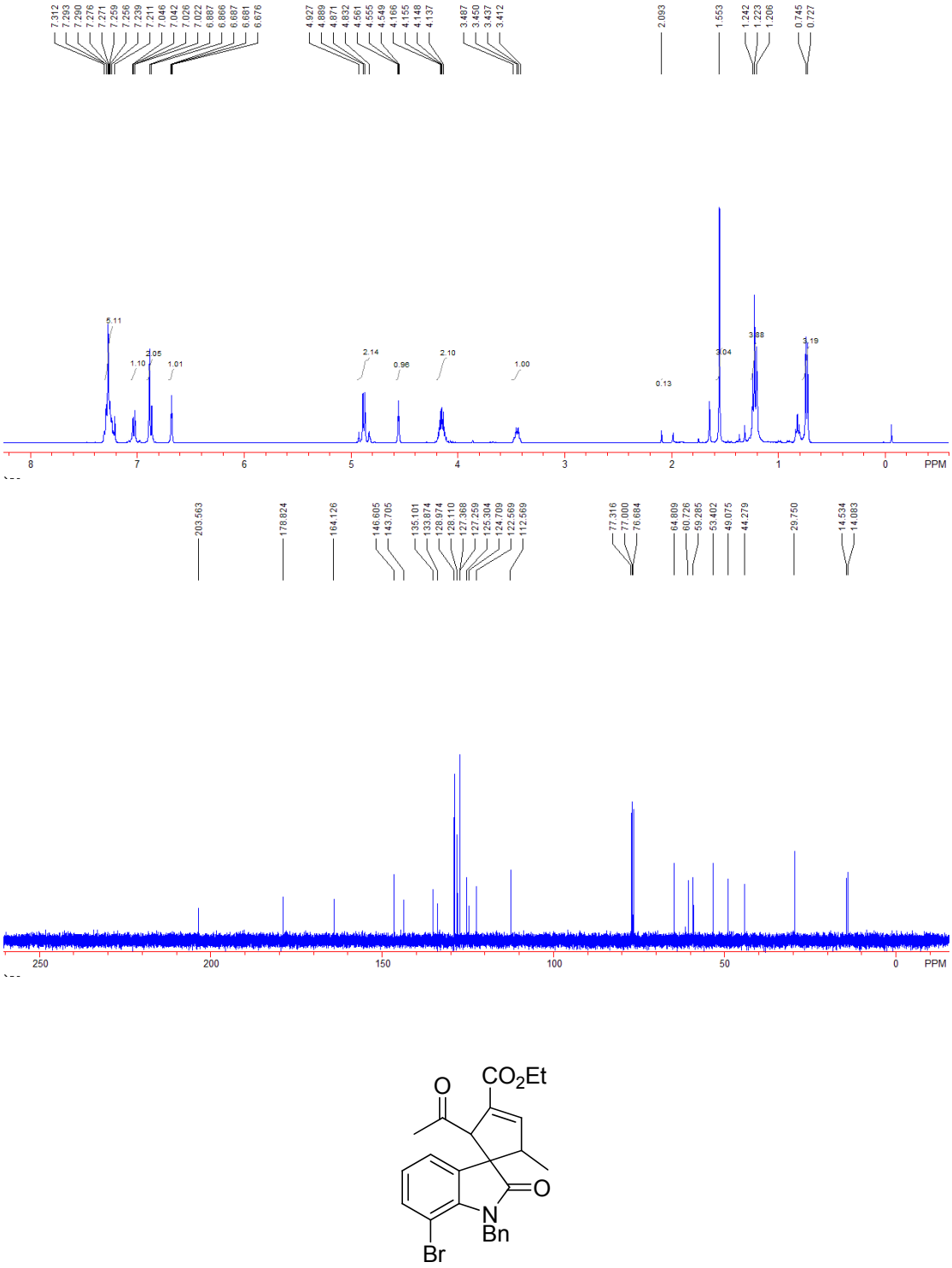


Compound 3g

(*trans,trans*) : (*cis,trans*) = 20 : **1**

Yield: 38 mg, 78%. A colorless solid. Mp: 160-162 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.80 (d, J = 7.2 Hz, 3H), 1.28 (t, J = 7.6 Hz, 3H), 1.61 (s, 3H), 2.14 (s, 0.13H), 3.49-3.51 (m, 1H), 4.19-4.23 (m, 2H), 4.61 (t, J = 2.4 Hz, 1H), 4.84 (d, J = 15.2 Hz, 1H), 4.90 (d, J = 15.2 Hz), 6.74 (d, J = 2.4 Hz, 1H), 7.10 (dd, J_1 = 8 Hz, J_2 = 1.6 Hz, 2H), 7.31-7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.5, 29.8, 44.3, 49.1, 53.4, 59.2, 60.7, 64.8, 112.7, 122.6, 124.7, 125.3,

127.2, 127.4, 128.1, 130.0, 135.1, 143.7, 146.6, 164.1, 178.8, 203.6. IR (CH_2Cl_2) ν 2964, 2925, 1708, 1600, 1483, 1429, 1370, 1301, 1250, 1172, 1124, 1026, 842, 732, 698 cm^{-1}. MS (ESI) *m/e* 504 (M+23, 100). HRMS (ESI) Calcd. for $C_{25}H_{24}BrNO_4Na^{+1}$ requires 504.0781, Found: 504.0799.

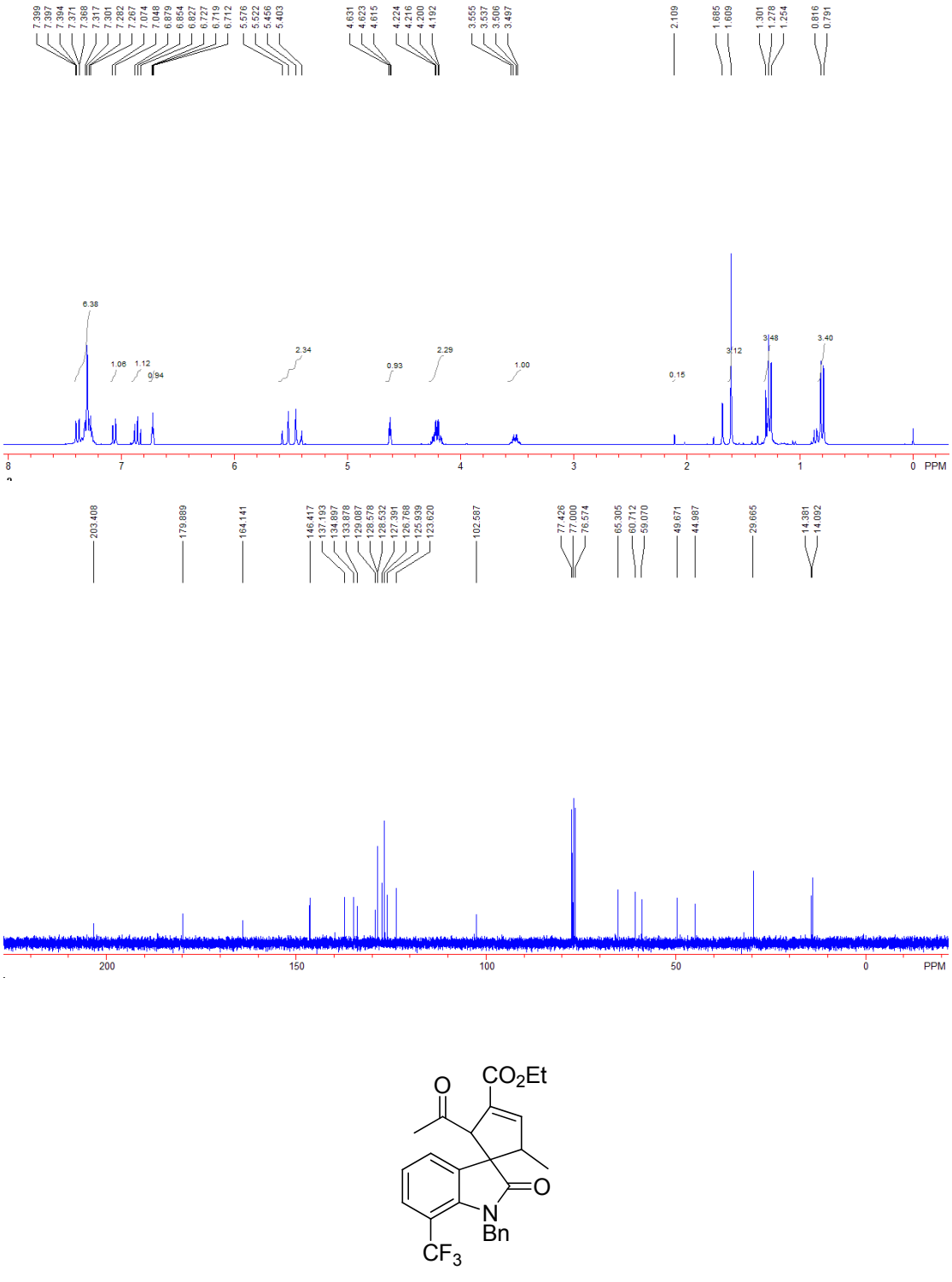


Compound 3h

(*trans,trans*) : (*cis,trans*) > 20 : 1

Yield: 45 mg, 92%. A colorless solid. Mp: 111-113 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.80 (d, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.61 (s, 3H), 2.11 (s, 0.15H), 3.46-3.53 (m, 1H),

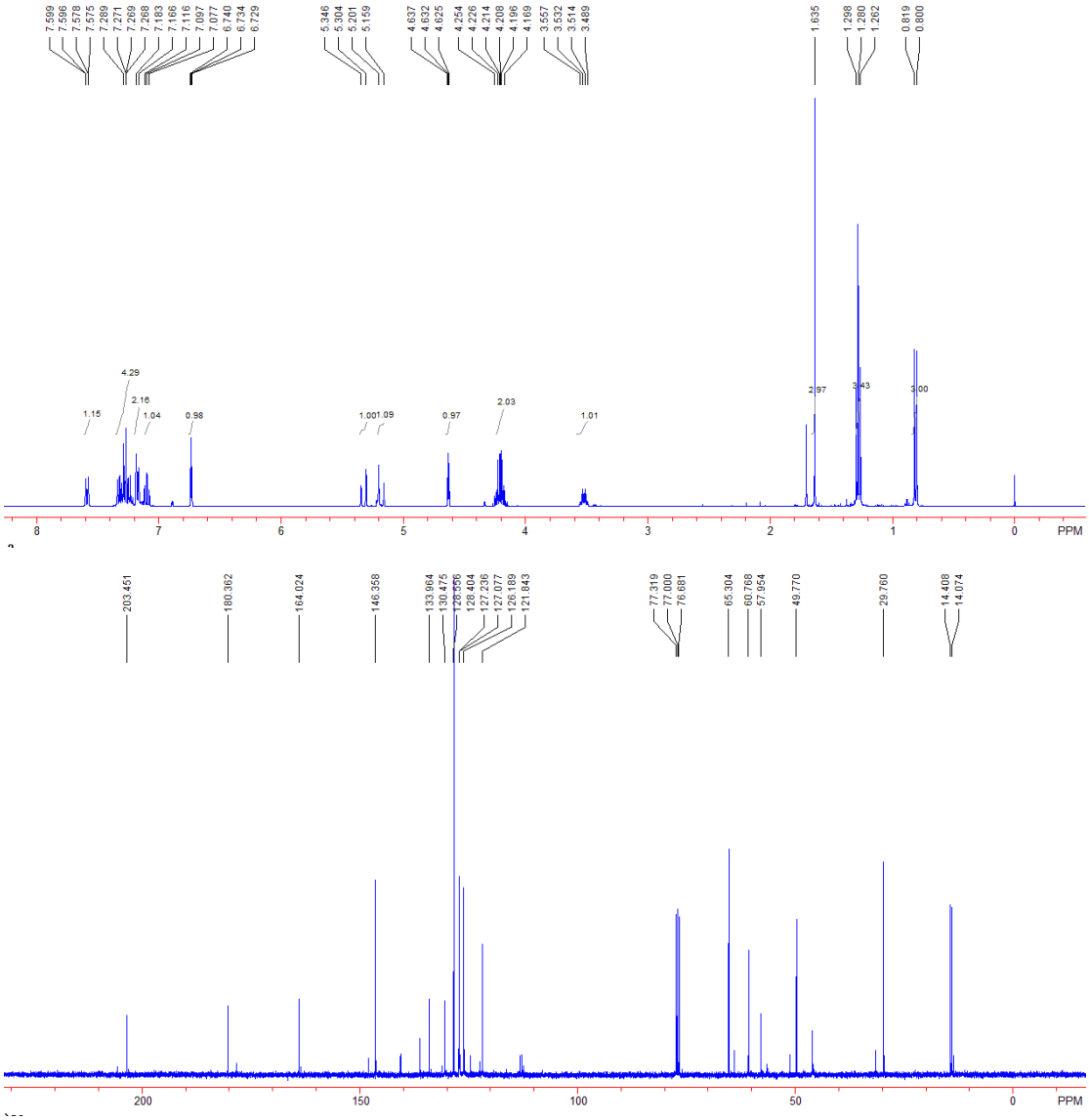
4.19-4.22 (m, 2H), 4.62 (t, J = 2.4 Hz, 1H), 5.43 (d, J = 16.2 Hz, 1H), 5.73 (d, J = 16.2 Hz, 1H), 6.72 (d, J = 2.4 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.27-7.40 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 14.1, 14.4, 30.0, 45.0, 50.0, 59.1, 60.7, 65.3, 102.6, 123.6, 126.0, 126.8, 127.4, 128.6, 129.1, 133.9, 134.9, 137.2, 139.9, 146.4, 164.1, 179.9, 203.5. IR (CH_2Cl_2) ν 2963, 2923, 1710, 1447, 1340, 1240, 1165, 1076, 1017, 753, 725, 696 cm^{-1}. MS (ESI) *m/e* 504 (M+23, 100). HRMS (ESI) Calcd. for $C_{25}H_{24}BrNO_4Na^{+1}$ requires 504.0781, Found: 504.0781.

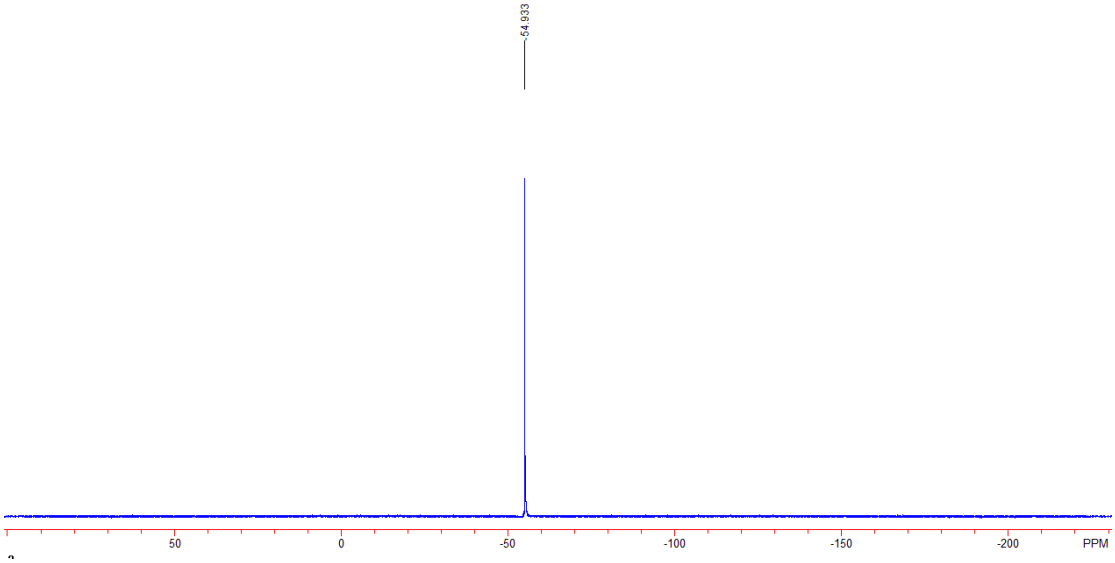


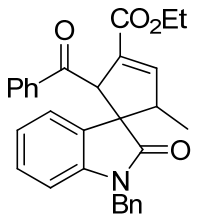
Compound 3i

(*trans,trans*) : (*cis,trans*) > 20 : 1

Yield: 28 mg, 60%. A colorless solid. Mp: 118-120 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.81 (d, J = 7.6 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H), 1.64 (s, 3H), 2.11 (s, 0.15H), 3.49-3.56 (m, 1H), 4.17-4.26 (m, 2H), 4.63 (t, J = 2.0 Hz, 1H), 5.17 (d, J = 16.8 Hz, 1H), 5.32 (d, J = 16.8 Hz, 1H), 6.74 (d, J = 2.4 Hz, 1H), 7.10 (t, J = 8.8 Hz, 1H), 7.17 (d, J = 6.8 Hz, 1H), 7.27-7.29 (m, 4H), 7.58 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.4, 29.8, 46.2, 49.8, 58.0, 60.8, 65.3, 113.0 (q, J = 32.6 Hz), 121.9, 123.2 (q, J = 270 Hz), 126.2, 127.1 (q, J = 6.9 Hz), 127.2, 128.4, 128.6, 130.5, 133.9, 136.2, 140.6, 146.4, 164.0, 180.4, 203.5. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ -54.9. IR (CH_2Cl_2) ν 2978, 2929, 1715, 1594, 1452, 1437, 1332, 1241, 1162, 1118, 1081, 696 cm^{-1}. MS (ESI) *m/e* 494 (M+23, 100). HRMS (ESI) Calcd. for $C_{26}H_{24}F_3NO_4Na^{+1}$ requires 494.1549, Found: 494.1564.



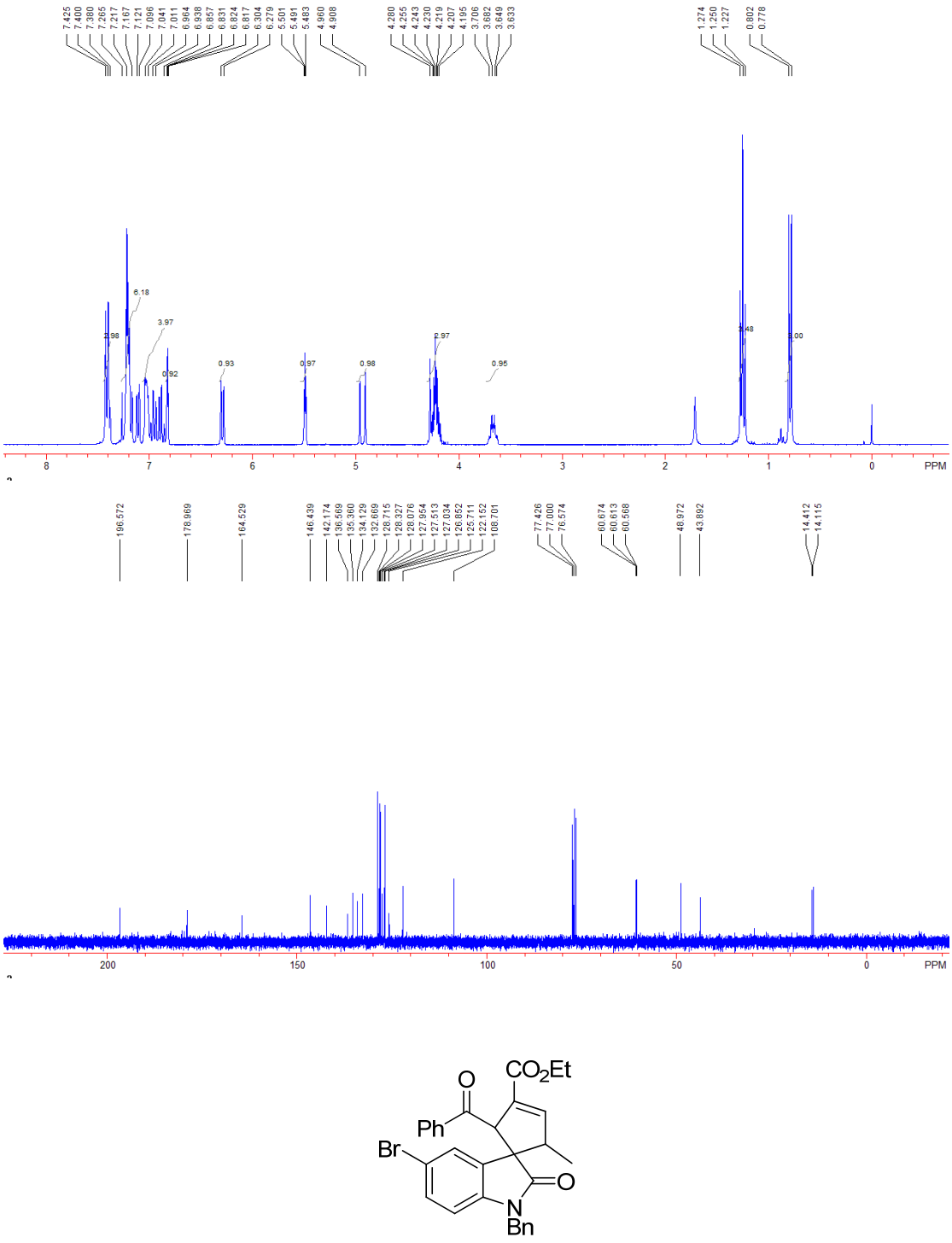




Compound 3j

(*trans,trans*) *:* (*cis,trans*) > 20 : **1**

Yield: 32 mg, 69%. A colorless solid. Mp: 144-146 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.79 (d, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 3.62-3.71 (m, 1H), 4.20-4.27 (m, 2H), 4.26 (d, J = 15.6 Hz, 1H), 4.93 (d, J = 15.6 Hz, 1H), 5.49 (t, J = 3.0 Hz, 1H), 6.29 (d, J = 7.5 Hz, 1H), 6.83 (t, J = 2.1 Hz, 1H), 6.86-7.04 (m, 4H), 7.10-7.27 (m, 6H), 7.38-7.43 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 14.1, 14.4, 43.9, 49.0, 60.5, 60.6, 60.7, 108.7, 122.1, 125.7, 126.8, 127.0, 128.0, 128.1, 128.3, 128.7, 132.7, 134.1, 135.4, 136.6, 142.2, 146.4, 164.5, 179.0, 196.6. IR (CH_2Cl_2) ν 2978, 2830, 1719, 1607, 1467, 1365, 1349, 1236, 1127, 759, 742, 696 cm^{-1}. MS (ESI) *m/e* 488 (M+23, 100). HRMS (ESI) Calcd. for $C_{30}H_{27}NO_4Na^{+1}$ requires 488.1832, Found: 488.1846.

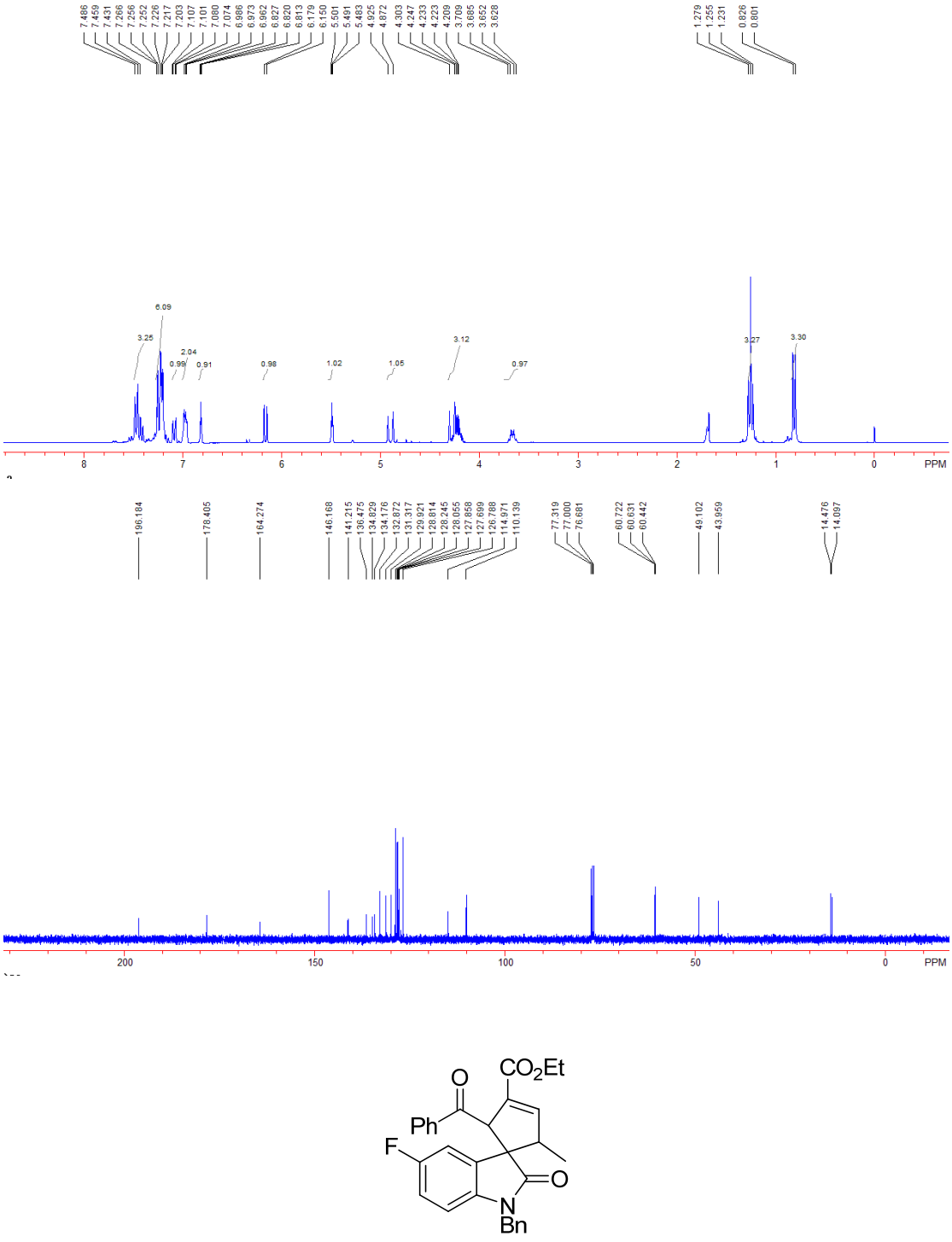


Compound 3k

(*trans,trans*) *:* (*cis,trans*) > 20 : **1**

Yield: 45 mg, 82%. A colorless solid. Mp: 197-199 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.81 (d, J = 7.5 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 3.63-3.71 (m, 1H), 4.21-4.31 (m, 2H), 4.29 (d, J = 15.9 Hz, 1H), 4.90 (d, J = 15.9 Hz, 1H), 5.49 (t, J = 3.0 Hz, 1H), 6.17 (d, J = 8.7 Hz, 1H), 6.82 (t, J = 2.1 Hz, 1H), 6.96-6.99 (m, 2H), 7.09 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 7.25-7.27 (m, 6H), 7.43-7.48 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.5, 44.0, 49.1, 60.5, 60.6, 60.7, 110.1, 115.0,

126.8, 127.8, 127.9, 128.1, 128.3, 128.8, 129.9, 131.3, 132.8, 134.2, 134.8, 136.5, 141.2, 146.2, 164.3, 178.4, 196.2. IR (CH_2Cl_2) ν 2973, 2956, 1703, 1678, 1484, 1338, 1218, 1174, 1079, 819, 690, 659 cm^{-1}. MS (ESI) *m/e* 504 (M+23, 100). HRMS (ESI) Calcd. for $C_{30}H_{26}NO_4BrNa^{+1}$ requires 566.0937, Found: 566.0950.

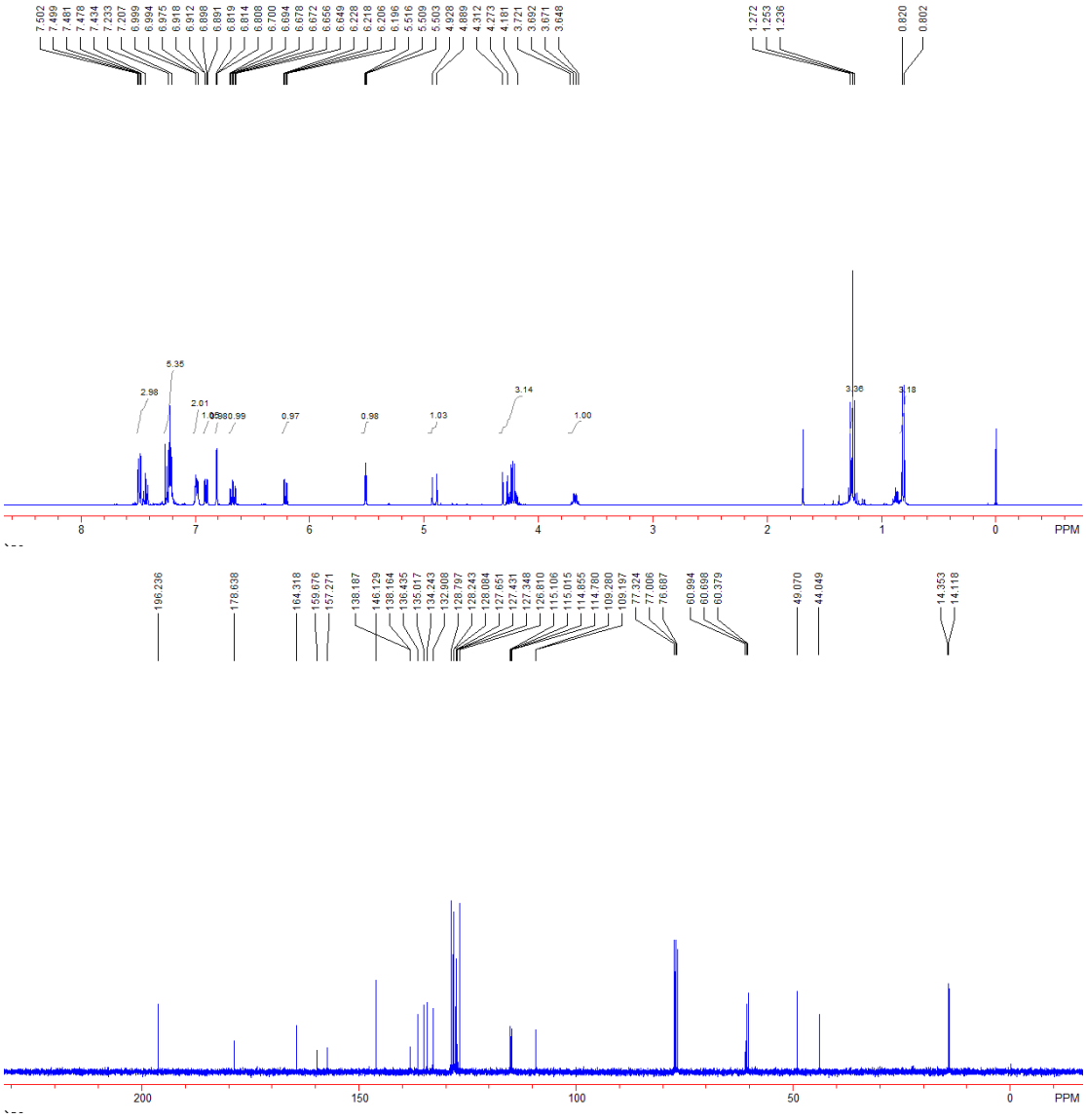


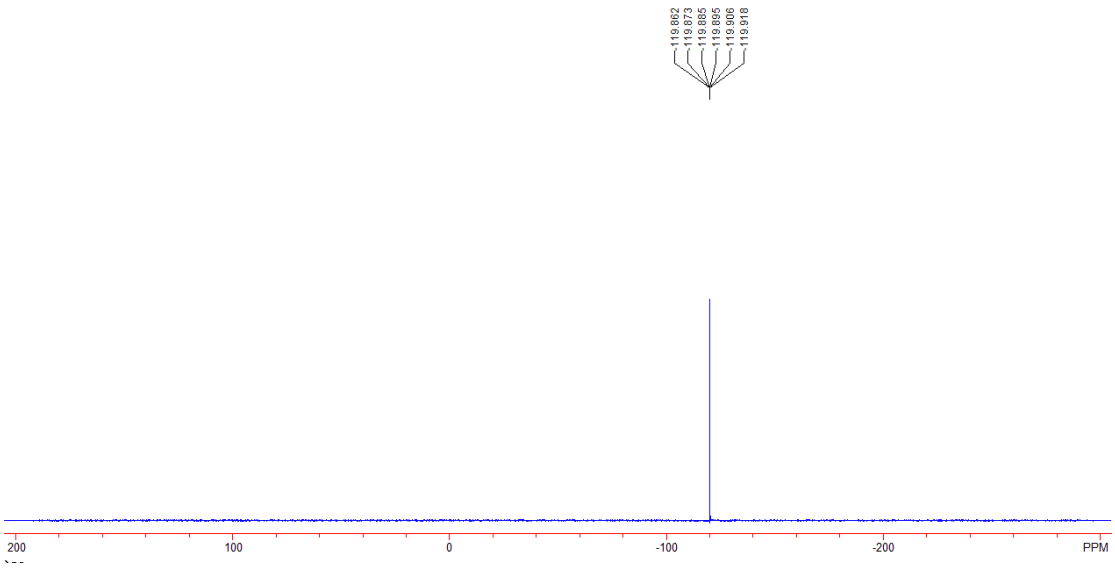
Compound 3l

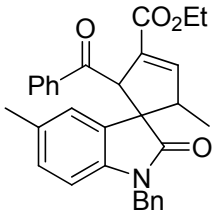
(*trans,trans*) : (*cis,trans*) > 20 : 1

Yield: 45 mg, 99%. A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.81 (d, *J* = 7.5 Hz, 3H),

1.25 (t, J = 7.6 Hz, 3H), 3.65-3.72 (m, 1H), 4.18-4.27 (m, 2H), 4.29 (d, J = 15.6 Hz, 1H), 4.90 (d, J = 15.6 Hz, 1H), 5.50 (t, J = 2.8 Hz, 1H), 6.21 (q, J = 4.0 Hz, 1H), 6.67 (td, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.82 (t, J = 2.0 Hz,1H), 6.91 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.98-7.00 (m, 2H), 7.20-7.26 (m, 5H), 7.43-7.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.4, 44.1, 49.1, 60.4, 60.7, 61.0, 109.2 (d, J = 8.3 Hz), 114.8 (d, J = 7.5 Hz), 115.1 (d, J = 9.1 Hz), 126.8, 127.4 (d, J = 8.3 Hz), 127.7, 128.1, 128.3, 128.8, 132.9, 134.3, 135.1, 136.4, 138.1 (d, J = 2.3 Hz), 146.1, 158.5 (d, J = 40.5 Hz), 164.3, 178.6, 196.2. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ -119.8. IR(CH_2Cl_2) ν 2977, 2927, 1707, 1682, 1488, 1450, 1342, 1253, 1172, 1035, 862, 753, 695 cm^{-1}. MS (ESI) *m/e* 506 (M+23, 100). HRMS (ESI) Calcd. for $C_{30}H_{26}NO_4FNa^{+1}$ requires 506.1738, Found: 506.1743.



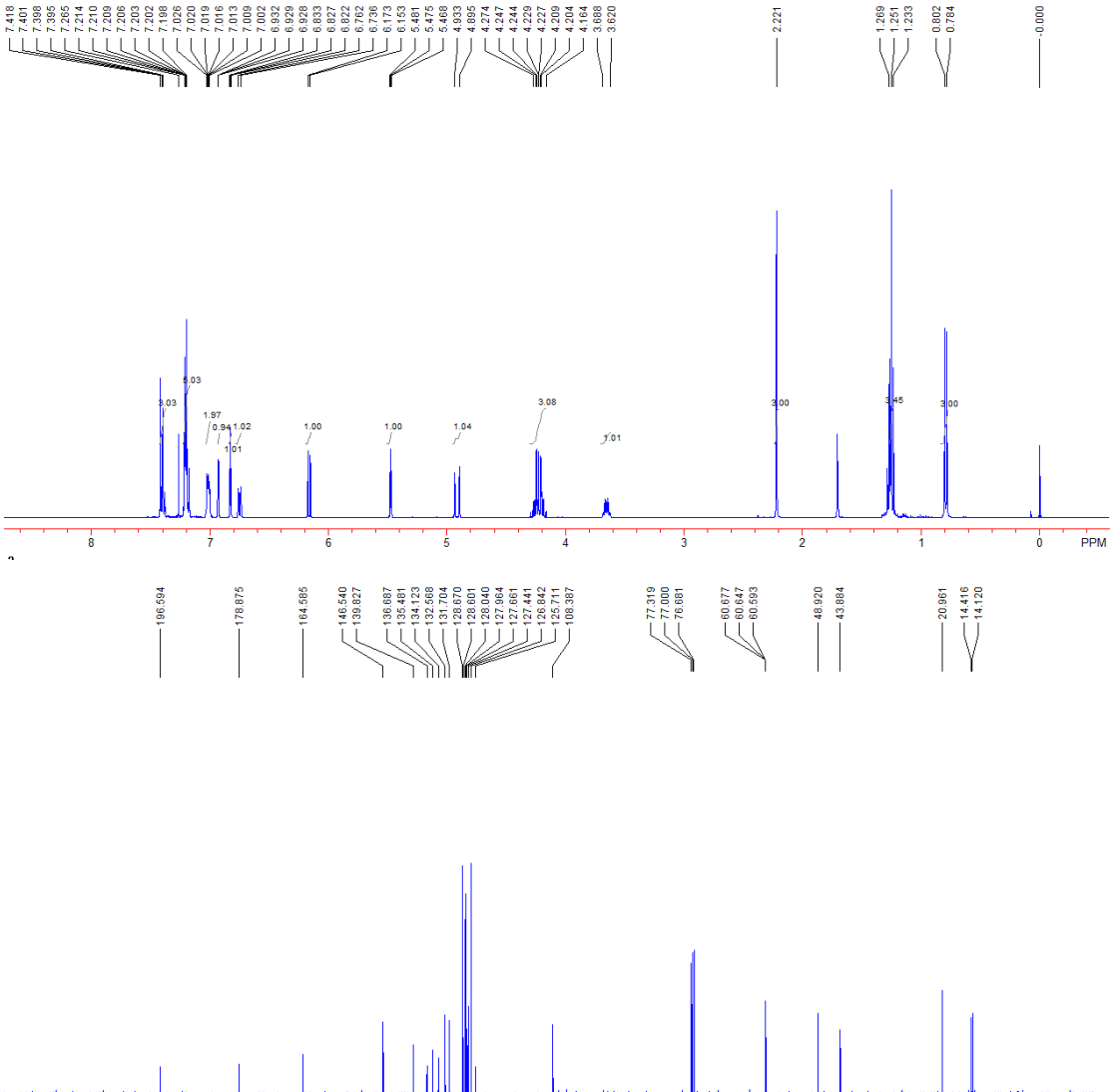


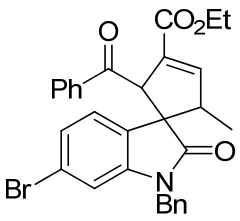


Compound 3m

(*trans,trans*) *:* (*cis,trans*) > 20 : **1**

Yield: 40 mg, 83%. A colorless solid. Mp: 128-130 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.79 (d, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.22 (s, 3H), 3.62-3.69 (m, 1H), 4.16-4.27 (m, 3H), 4.91 (d, *J* = 15.2 Hz, 1H), 5.47 (t, *J* = 2.4 Hz, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 6.73-6.76 (m, 1H), 6.83 (t, *J* = 2.4 Hz, 1H), 6.92-6.93 (m, 1H), 7.00-7.03 (m, 2H), 7.19-7.21 (m, 5H), 7.39-7.41 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 14.1, 14.4, 20.9, 43.9, 60.5, 60.6, 60.7, 108.4, 125.7, 126.8, 127.4, 127.6, 127.9, 128.0, 128.6, 128.7, 131.7, 132.6, 134.1, 135.5, 136.6, 139.8, 146.5, 164.6, 178.9, 196.6. IR (CH_2Cl_2) ν 2961, 2870, 1704, 1618, 1495, 1364, 1192, 1077, 807, 730, 695, 666 cm^{-1}. MS (ESI) *m/e* 502 (M+23, 100). HRMS (ESI) Calcd. for $C_{31}H_{29}NO_4Na^{+1}$ requires 502.1988, Found: 502.1997.



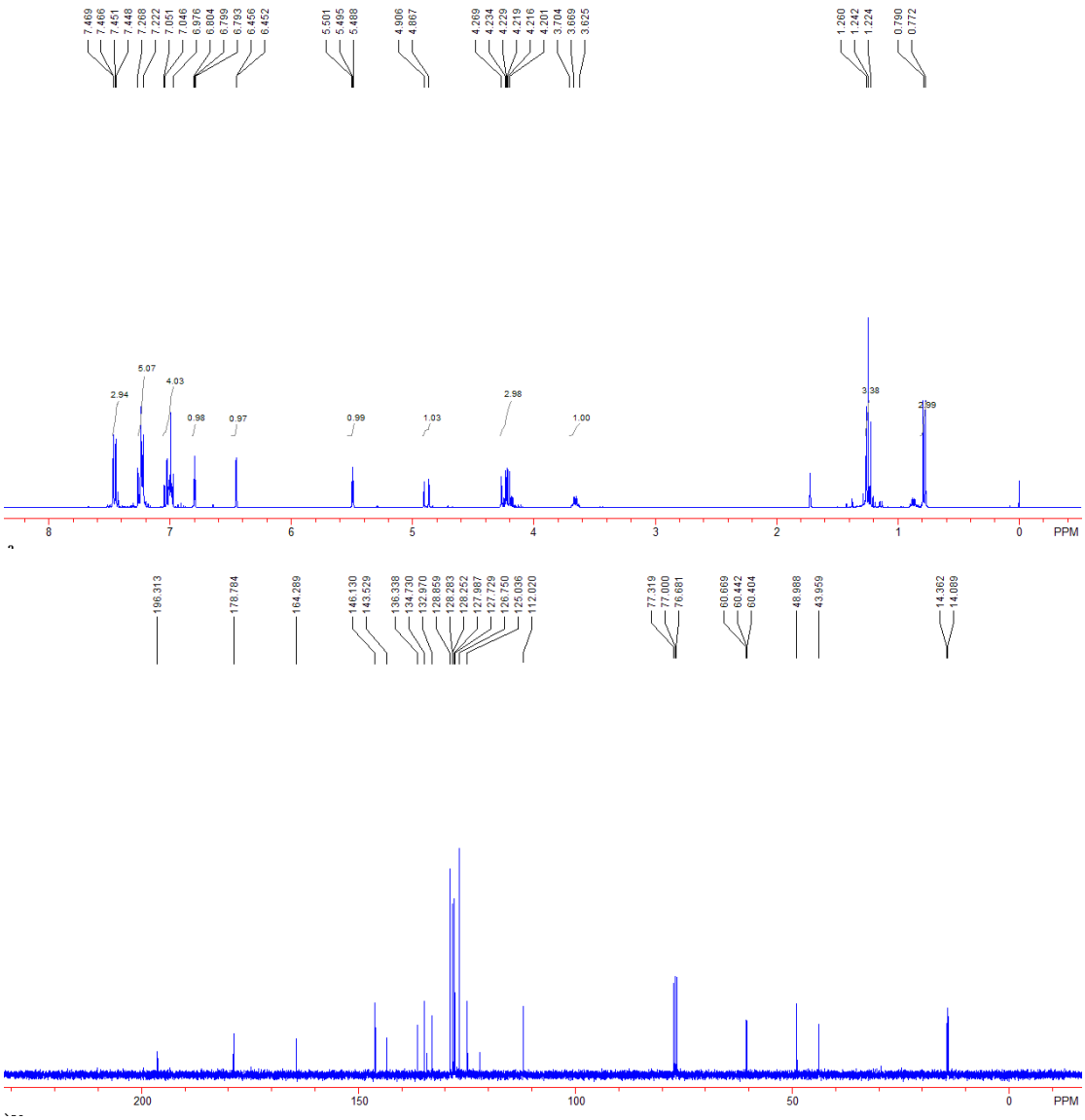


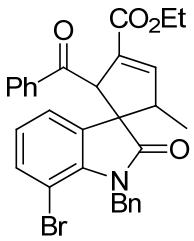
Compound 3n

(*trans,trans*) *:* (*cis,trans*) > 20 : **1**

Yield: 48 mg, 99%. A colorless solid. Mp: 180-182 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.78 (d, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 3.63-3.70 (m, 1H), 4.20-4.23 (m, 2H), 4.24 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 5.50 (t, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 1.6 Hz, 1H), 6.79 (t, *J* = 2.0 Hz, 1H), 6.97-7.01 (m, 4H), 7.22-7.26 (m, 1H), 7.20-7.27 (m, 5H), 7.45-7.48 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.4, 44.0, 49.0, 60.4, 60.5, 60.7, 112.0, 125.0, 126.8, 127.8,

127.9, 128.2, 128.3, 128.9, 133.0, 134.8, 136.3, 143.5, 146.1, 164.3, 178.8, 196.3. IR (CH_2Cl_2) ν 3031, 2931, 1710, 1682, 1599, 1482, 1371, 1252, 1124, 954, 841, 737, 668 cm^{-1}. MS (ESI) *m/e* 504 (M+23, 100). HRMS (ESI) Calcd. for $C_{30}H_{26}NO_4BrNa^{+1}$ requires 566.0937, Found: 566.0942.



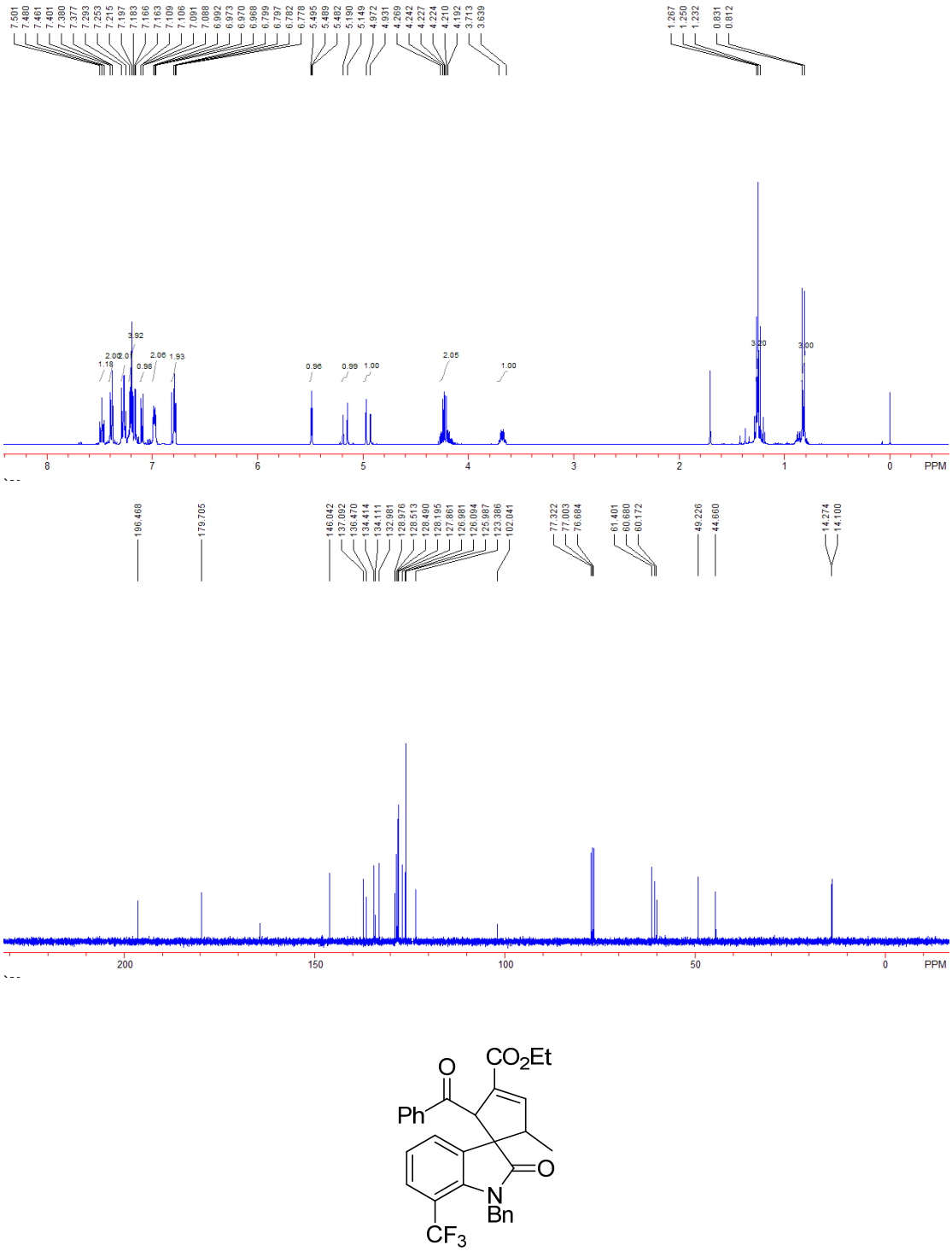


Compound 3o

(*trans,trans*) *:* (*cis,trans*) > 20 : 1

Yield: 44 mg, 80%. A colorless solid. Mp: 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.82 (d, *J* = 7.6 Hz, 3H), 1.25 (t, *J* = 6.8 Hz, 3H), 3.64-3.71 (m, 1H), 4.20-4.27 (m, 2H), 4.95 (d, *J* = 16.4

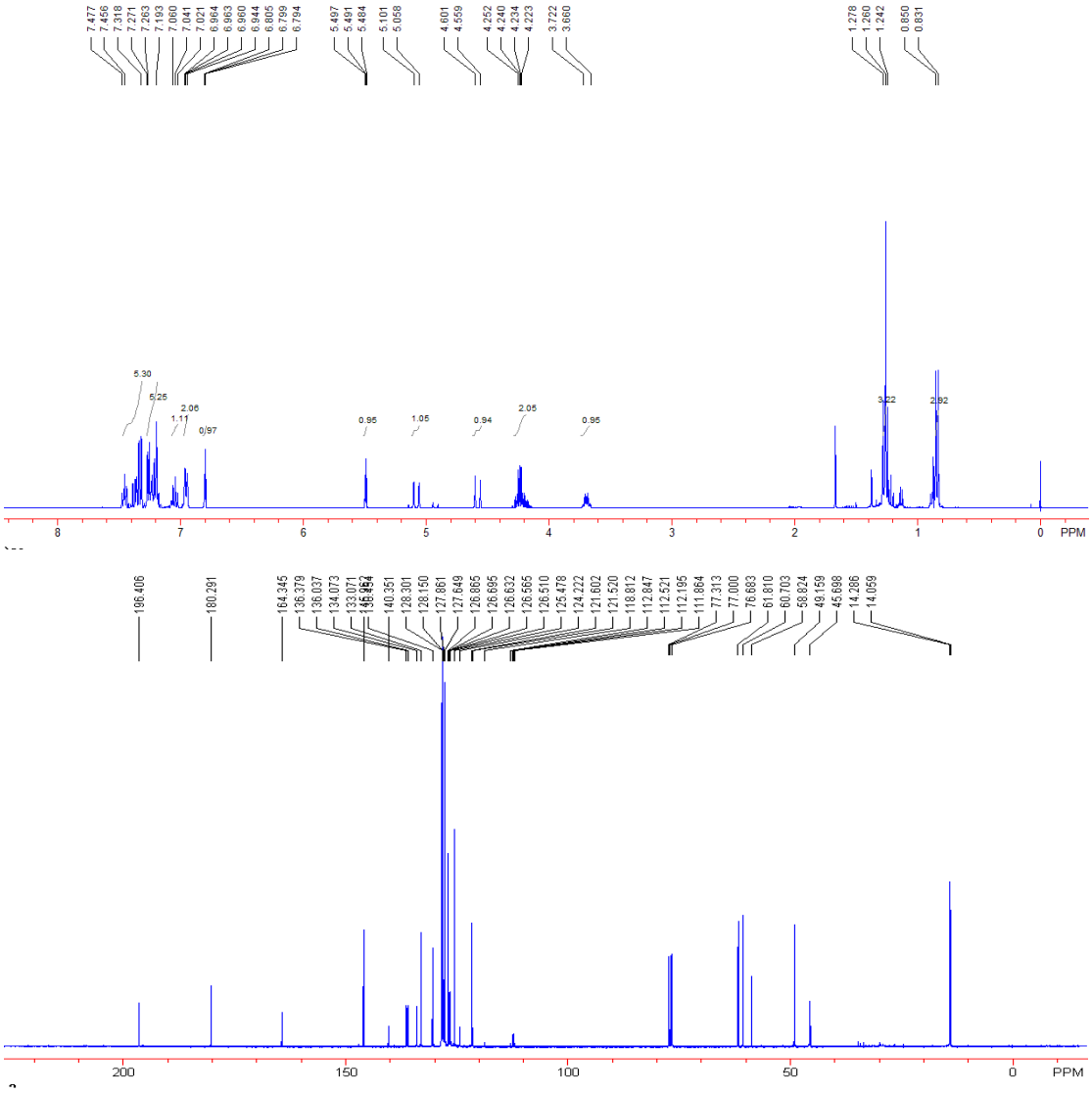
Hz, 1H), 5.16 (d, J = 16.4 Hz, 1H), 5.49 (t, J = 2.4 Hz, 1H), 6.78-6.80 (m, 2H), 6.97-7.00 (m, 2H), 7.09 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.16-7.29 (m, 7H), 7.38-7.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.3, 44.7, 49.2, 60.2, 60.7, 61.4, 102.1, 123.4, 126.0, 126.1, 127.0, 127.9, 128.2, 129.0, 133.0, 134.1, 134.4, 136.5, 137.1, 139.8, 146.1, 164.4, 179.7, 196.5. IR (CH_2Cl_2) ν 3058, 2924, 1705, 1682, 1577, 1462, 1368, 1218, 1110, 749, 726, 689 cm^{-1}. MS (ESI) *m/e* 566 (M+23, 100). HRMS (ESI) Calcd. for $C_{30}H_{26}NO_4BrNa^{+1}$ requires 566.0937, Found: 566.0949.

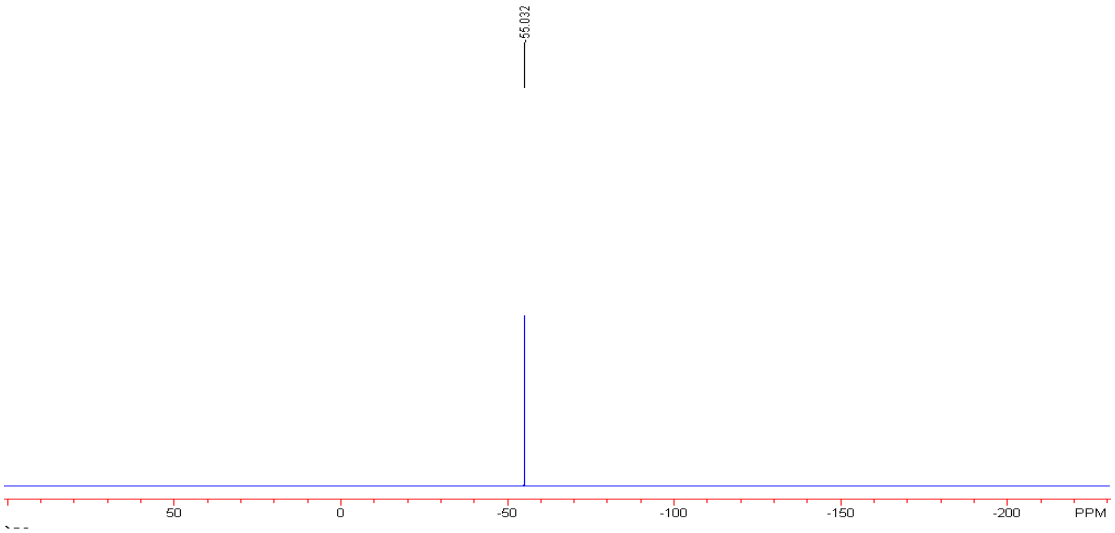


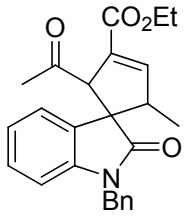
Compound 3p

(*trans,trans*) : (*cis,trans*) > 20 : 1

Yield: 50 mg, 93%. A colorless solid. Mp: 129-131 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.84 (d, *J* = 7.6 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 3.60-3.72 (m, 1H), 4.20-4.23 (m, 2H), 4.58 (d, *J* = 17.3 Hz, 1H), 5.07 (d, *J* = 17.3 Hz, 1H), 5.50 (t, *J* = 2.4 Hz, 1H), 6.79 (d, *J* = 1.6 Hz, 1H), 6.95-6.97 (m, 2H), 6.97-7.01 (m, 4H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.19-7.31 (m, 5H), 7.31-7.48 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 14.3, 45.9, 49.1, 58.8, 60.7, 61.8, 112.4 (q, *J* = 32.6 Hz), 121.6, 122.8 (q, *J* = 270.2 Hz), 125.5, 126.5 (q, *J* = 6.7 Hz), 126.9, 127.5, 127.9, 128.2, 130.5, 133.1, 134.1, 136.0, 136.4, 140.4, 146.0, 164.3, 180.3, 196.4. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ -55.03. IR (CH_2Cl_2) ν 3090, 2928, 1714, 1687, 1450, 1438, 1226, 1132, 1095, 1054, 725, 708, 693 cm^{-1}. MS (ESI) *m/e* 556 (M+23, 100). HRMS (ESI) Calcd. for $C_{31}H_{26}NO_4F_3Na^{+1}$ requires 556.1706, Found: 556.1695.



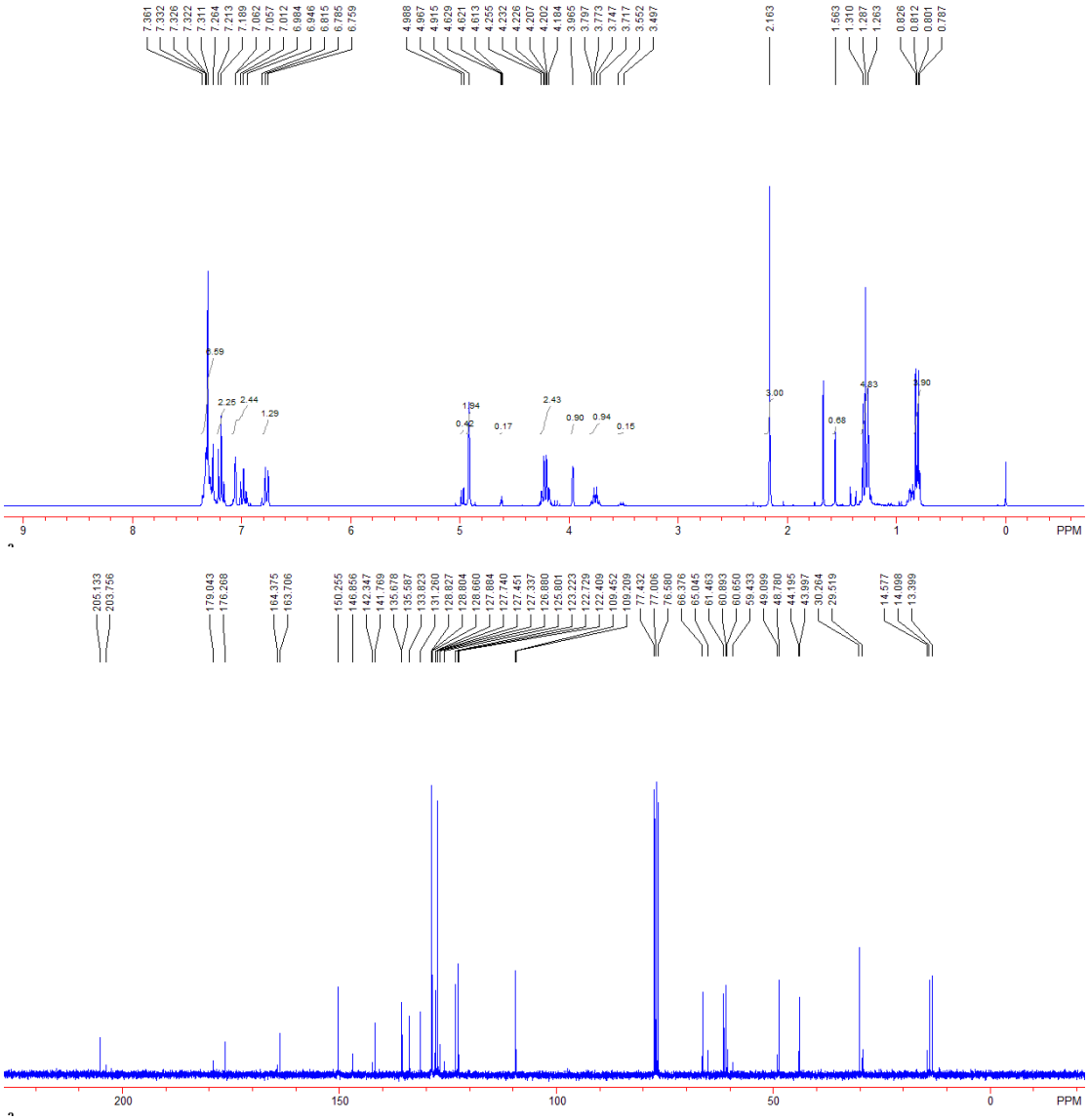


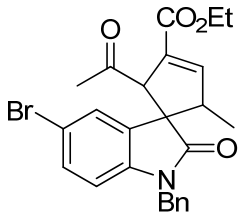


Compound 3a

(*trans,trans*) *:* (*cis,trans*) = 1 : **4**

Yield: 29 mg, 76%. A colorless solid. Mp: 133-135 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.80 (d, *J* = 7.5 Hz, 0.68H), 0.81 (d, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 6.9 Hz, 4.8H), 1.56 (s, 0.68H), 2.16 (s, 3H), 3.49-3.55 (m, 0.15H), 3.72-3.80 (m, 1H), 3.97 (s, 1H), 4.19-4.26 (m, 2.43H), 4.62 (t, *J* = 2.4 Hz, 0.15H), 4.92-4.99 (m, 2.42H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.95-7.06 (m, 2.42H), 6.97-7.00 (m, 2H), 7.19-7.36 (m, 8.8H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.4, 14.1, 14.6, 29.5, 30.3, 44.0, 44.2, 48.8, 49.1, 59.4, 60.7, 60.9, 61.5, 65.1, 66.4, 109.2, 109.5, 122.4, 122.7, 123.2, 125.8, 126.9, 126.1, 127.3, 127.5, 127.7, 127.9, 128.7, 128.7, 128.8, 128.8, 131.2, 133.8, 135.6, 135.7, 141.8, 142.4, 146.9, 150.3, 163.7, 164.4, 176.3, 179.1, 203.8, 205.1. IR (CH_2Cl_2) ν 2963, 2925, 1703, 1610, 1486, 1466, 1348, 1346, 1238, 1121, 950, 755, 689 cm^{-1}. MS (ESI) *m/e* 404 (M^+, 100). HRMS (ESI) Calcd. for $C_{25}H_{26}NO_4^{+1}$ requires 404.1857, Found: 404.1857.



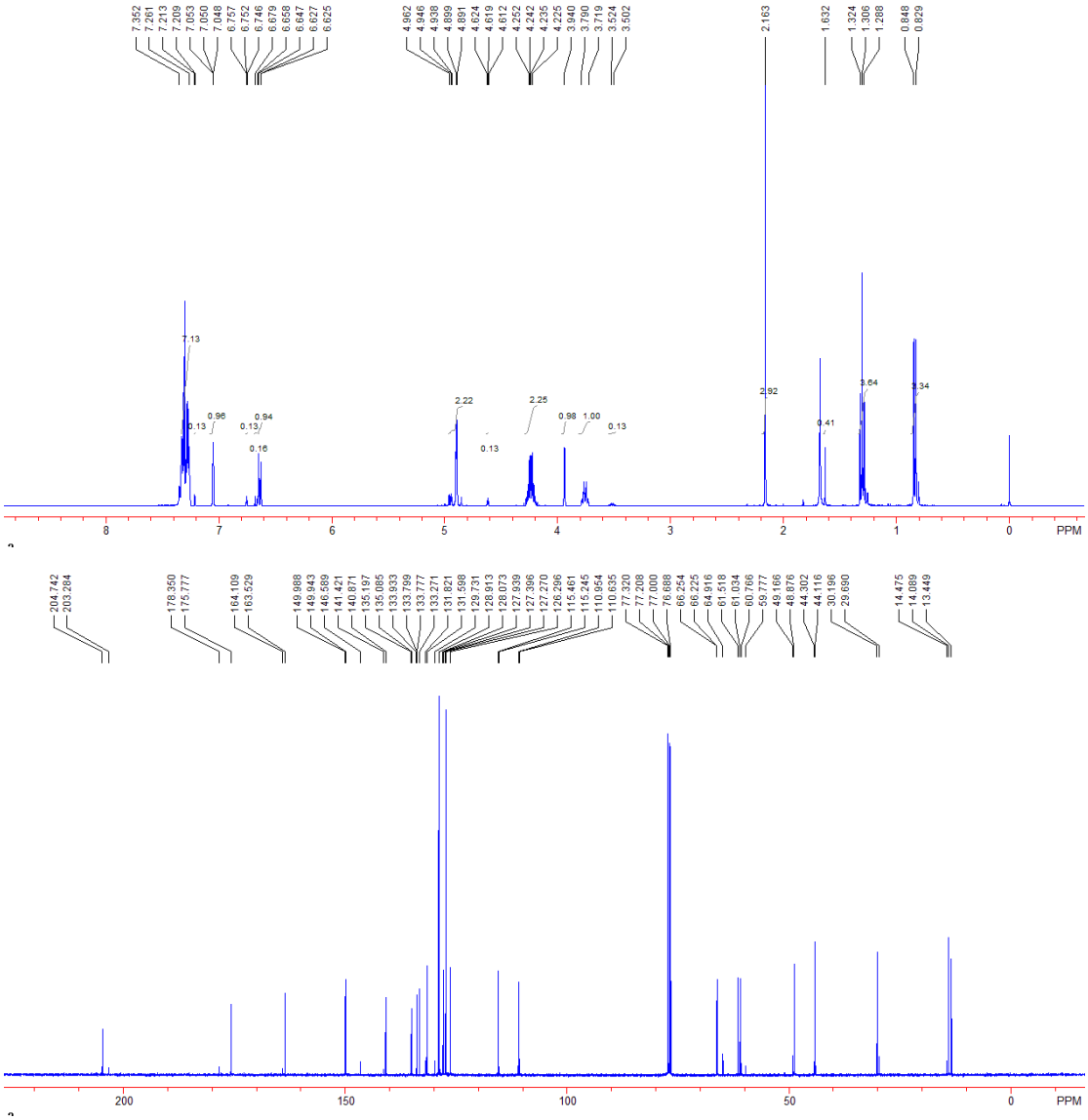


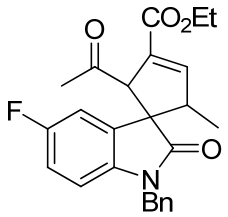
Compound 3d

(*trans,trans*) *:* (*cis,trans*) = 1 : **7**

Yield: 37 mg, 74%. A colorless solid. Mp: 155-157 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.84 (d, *J* = 7.6 Hz, 3.3H), 1.31 (t, *J* = 7.2 Hz, 3.6H), 1.63 (s, 0.68H), 2.16 (s, 3H), 3.50-3.53 (m, 0.13H), 3.72-3.80 (m, 1H), 3.94 (s, 1H), 4.23-4.25 (m, 2.25H), 4.62 (t, *J* = 2.4 Hz, 0.13H), 4.89-4.96 (m, 2.22H), 6.63-6.68 (m, 1.13H), 6.75 (t, *J* = 2.0 Hz, 0.13H), 7.04-7.05 (m, 1H), 7.21 (d, *J* = 1.6 Hz, 0.13H), 7.21-7.35 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.5, 14.1, 14.5, 29.7, 30.2, 44.1,

44.3, 48.9, 49.2, 59.8, 60.8, 61.0, 61.5, 65.0, 66.2, 66.3, 110.6, 111.0, 115.3, 115.5, 126.3, 127.2, 127.3, 128.0, 128.1, 128.9, 129.7, 131.6, 131.8, 133.3, 133.7, 133.8, 134.0, 140.9, 141.4, 146.6, 149.9, 150.0, 163.5, 164.1, 175.8, 178.4, 203.3, 204.8. IR (CH_2Cl_2) ν 2982, 2929, 1705, 1604, 1477, 1355, 1299, 1252, 1121, 942, 824, 745, 695 cm^{-1}. MS (ESI) *m/e* 482 (M^+, 100). HRMS (ESI) Calcd. for $C_{25}H_{25}NO_4Br^{+1}$ requires 482.0962, Found: 482.0967.

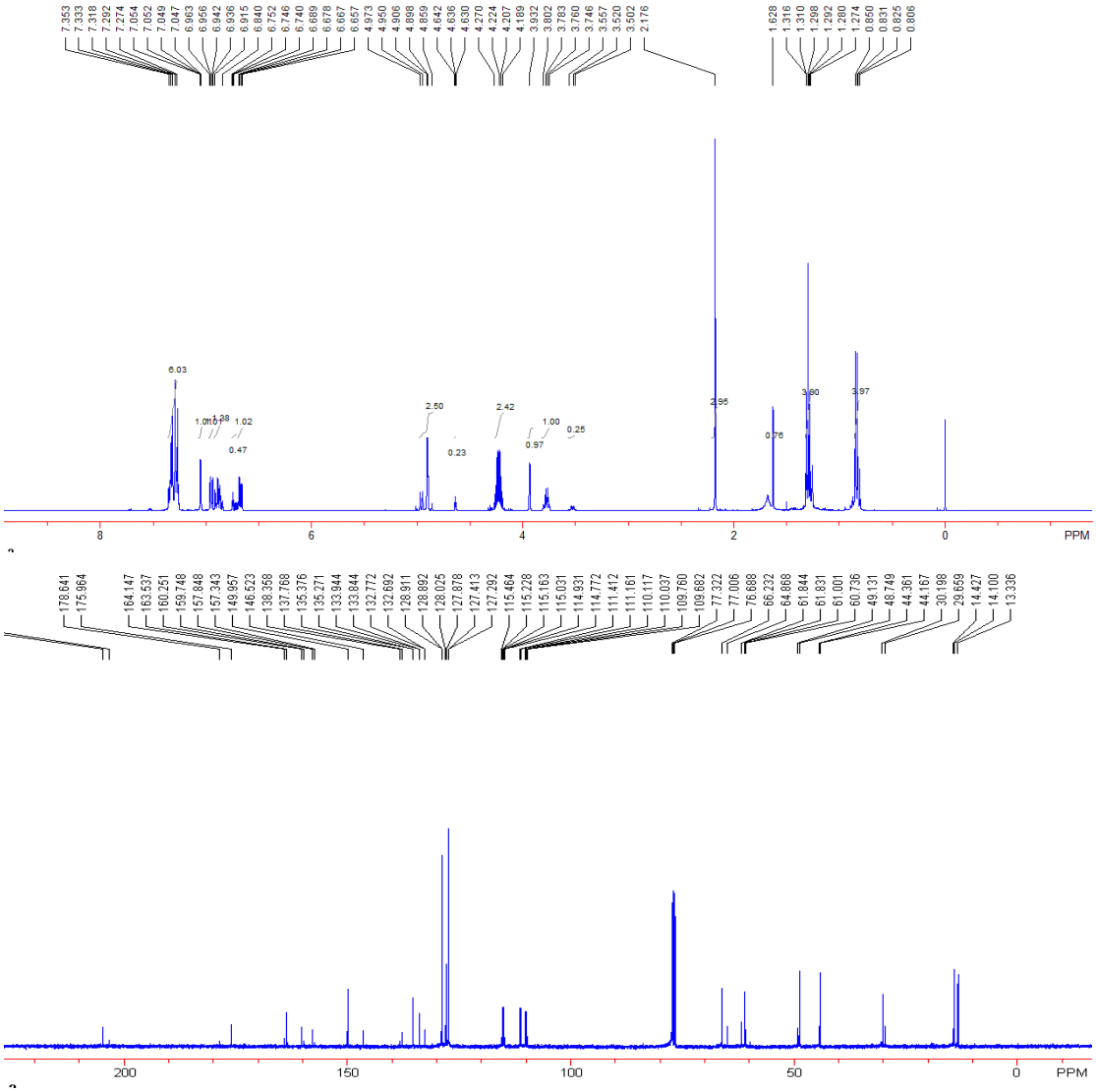


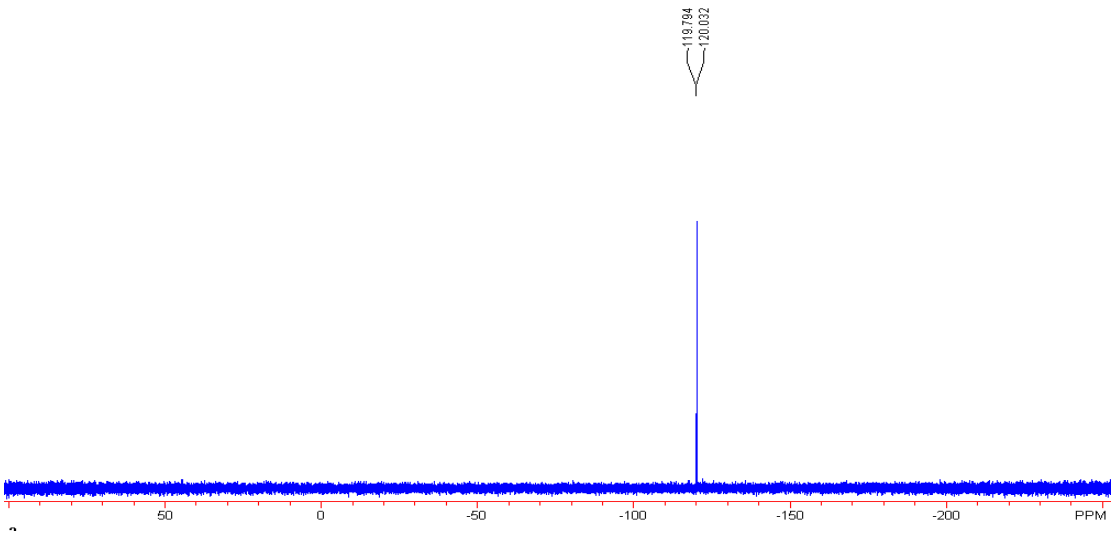


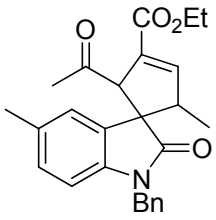
Compound 3f

(*trans,trans*) *:* (*cis,trans*) = 1 : 4

Yield: 31 mg, 76%. A colorless solid. Mp: 150-152 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.81 (d, *J* = 7.6 Hz, 0.76H), 0.84 (d, J = 7.6 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 0.76H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.63 (s, 0.76H), 2.18 (s, 3H), 3.50-3.56 (m, 0.25H), 3.75-3.80 (m, 1H), 3.97 (s, 1H), 4.19-4.27 (m, 2.42H), 4.64 (t, *J* = 2.4 Hz, 0.23H), 4.86-4.97 (m, 2.50H), 6.67 (q, *J* = 4.4 Hz, 1H), 6.74-6.75 (m, 0.47H), 6.80-6.92 (m, 1.38H), 6.95 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 7.05-7.06 (m, 1H), 7.28-7.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.3, 14.1, 14.4, 29.7, 30.2, 44.2, 44.4, 48.7, 49.1, 60.7, 61.0, 61.8, 61.9, 64.9, 66.2, 109.7 (d, *J* = 8.2 Hz), 110.1 (d, *J* = 8.2 Hz), 111.3 (d, *J* = 25.3 Hz), 114.9 (d, *J* = 25.3), 115.1 (d, *J* = 23.1 Hz), 115.4 (d, *J* = 23.1 Hz), 127.3, 127.4, 127.9, 128.0, 128.8, 128.9, 132.7 (d, *J* = 8.2 Hz), 133.8, 133.9, 135.3, 135.4, 137.8, 138.4, 146.5, 149.9, 159.1 (d, *J* = 266.2 Hz), 158.5 (d, *J* = 266.2 Hz), 163.5, 164.1, 176.0, 178.6, 203.4, 204.7. ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$): δ -120.0, -119.8. IR (CH_2Cl_2) ν 2973, 2926, 1706, 1488, 1453, 1360, 1335, 1239, 1162, 820, 746, 659 cm^{-1}. MS (ESI) *m/e* 422 (M^+, 100). HRMS (ESI) Calcd. for $C_{25}H_{25}NO_4F^{+1}$ requires 422.1762, Found: 422.1763.



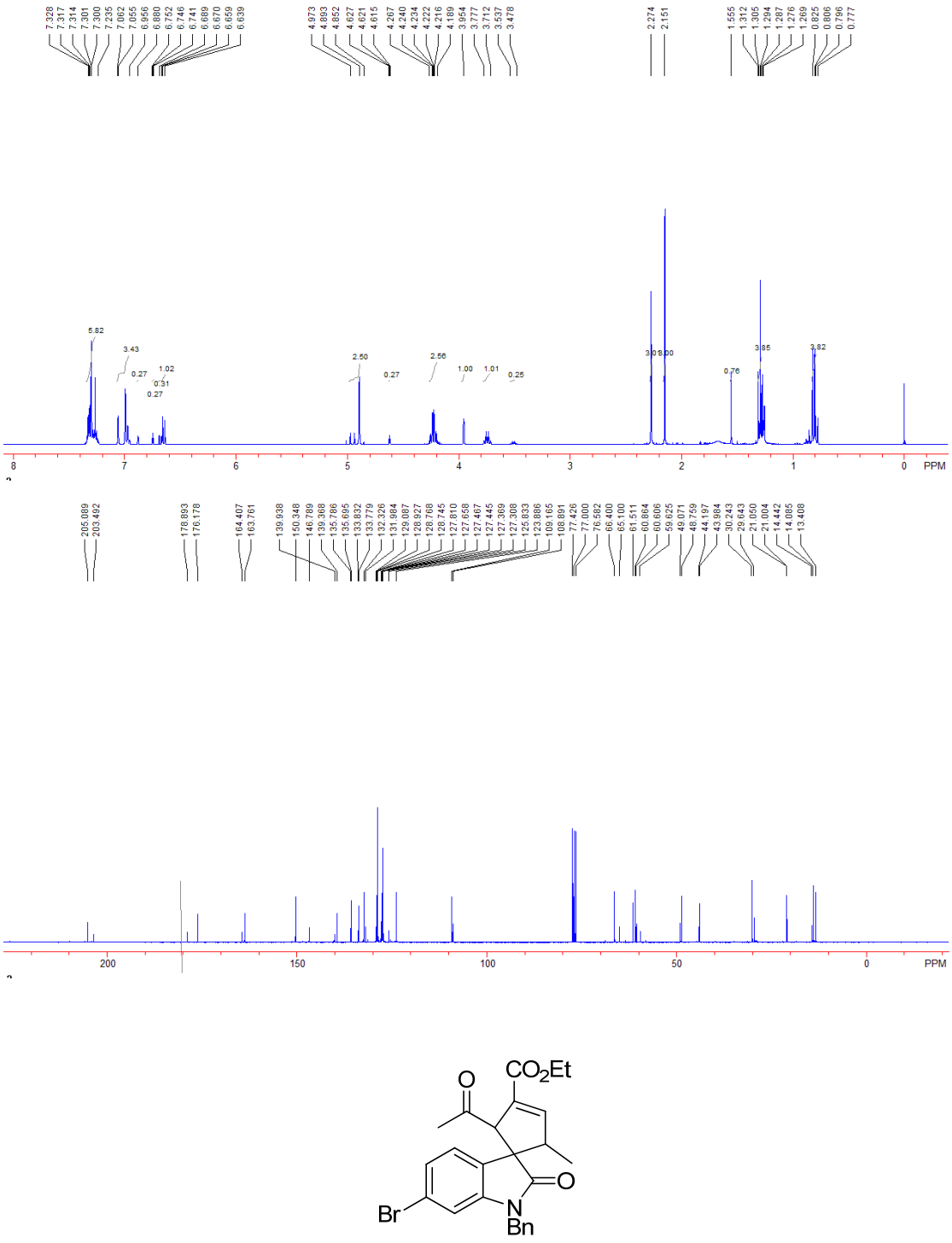




Compound 3g

(*trans,trans*) *:* (*cis,trans*) = 1 : **4**

Yield: 35 mg, 85%. A colorless solid. Mp: 87-99 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.79 (d, *J* = 7.6 Hz, 0.76H), 0.81 (d, *J* = 7.6 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 0.78H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.56 (s, 0.78H), 2.15 (s, 3H), 2.28 (s, 3H), 3.48-3.58 (m, 0.25H), 3.71-3.78 (m, 1H), 3.96 (s, 1H), 4.19-4.27 (m, 2.52H), 4.62 (t, *J* = 2.4 Hz, 0.27H), 4.85-4.97 (m, 2.50H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.6 Hz. 0.31H), 6.74 (t, *J* = 2.4 Hz, 0.27H), 6.88 (s, 0.27H), 6.96-7.02 (m, 3.43H), 7.24-7.33 (m, 5.8H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.4, 14.1, 14.4, 21.0, 21.1, 29.7, 30.3, 44.0, 44.2, 48.8, 49.1, 59.6, 60.6, 60.8, 61.5, 65.1, 66.4, 108.9, 109.2, 123.9, 125.9, 127.1, 127.3, 127.4, 127.5, 127.7, 127.8, 128.8, 128.9, 128.9, 129.0, 132.0, 132.3, 133.8, 133.9, 135.7, 135.8, 139.4, 140.0, 146.8, 150.4, 163.8, 164.4, 176.2, 178.9, 203.5, 205.1. IR (CH_2Cl_2) ν 2962, 2922, 1703, 1493, 1454, 1338, 1242, 1221, 1121, 1024, 808, 698 cm^{-1}. MS (ESI) *m/e* 418 (M^+, 100). HRMS (ESI) Calcd. for $C_{26}H_{28}NO_4^{+1}$ requires 418.2012, Found: 418.2013.

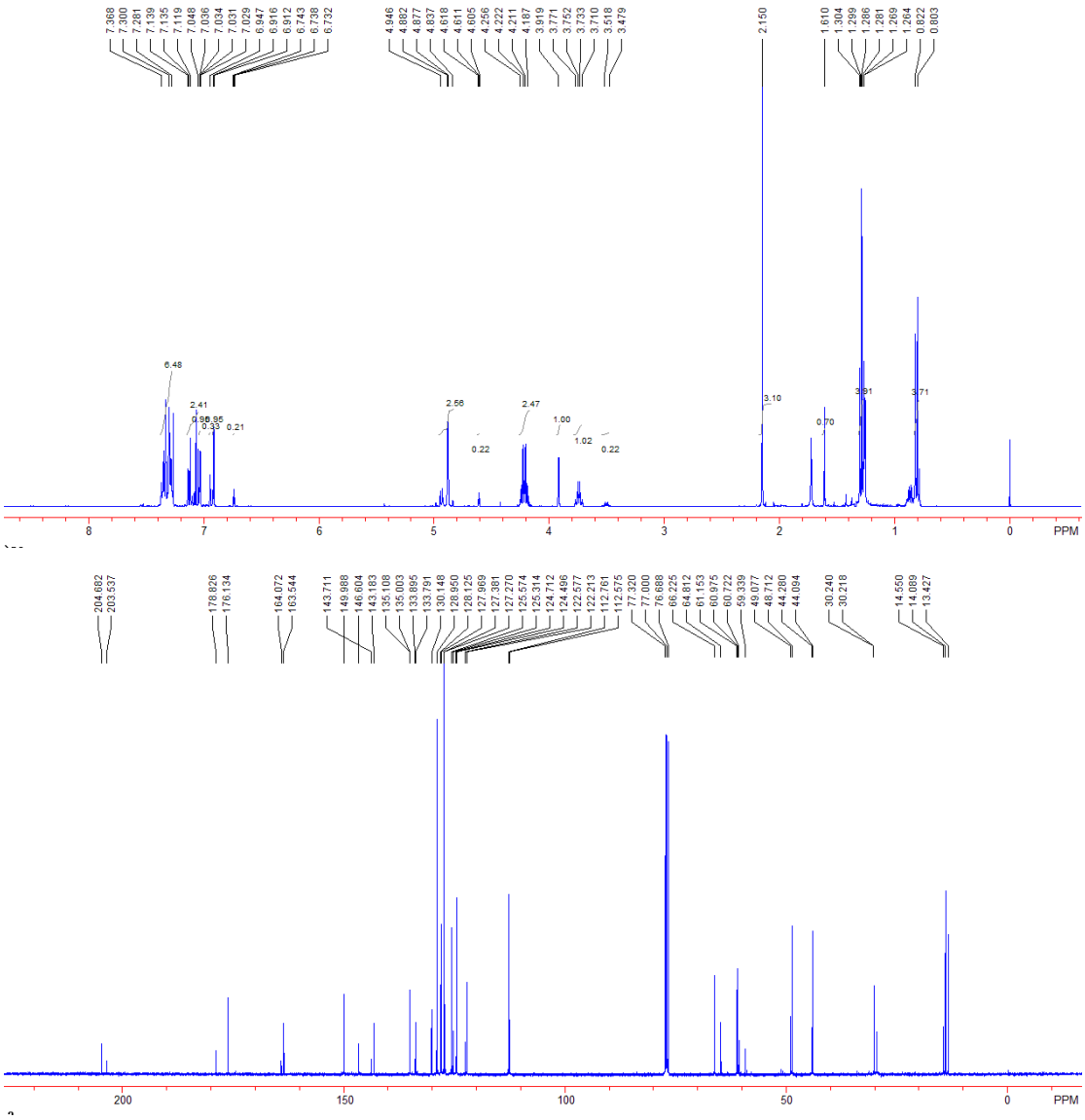


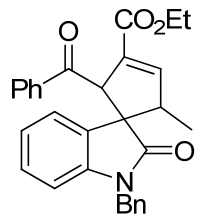
Compound 3g

***(trans,trans) : (cis,trans)* = 1 : 4**

Yield: 31 mg, 70%. A colorless solid. Mp: 150-152 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.81 (d, J = 7.6 Hz, 3.7H), 1.28 (t, J = 7.2 Hz, 0.78H), 1.30 (t, J = 7.2 Hz, 3H),1.61 (s, 0.70H), 2.15 (s, 3H), 3.48-3.52 (m, 0.22H), 3.71-3.78 (m, 1H), 3.92 (s, 1H), 4.19-4.26 (m, 2.47H), 4.61 (t, J = 2.4 Hz, 0.22H), 4.84-4.95 (m, 2.56H), 6.74 (t, J = 2.0 Hz, 0.21H), 6.91 (d, J = 1.6 Hz, 1H), 7.03 (dd, J_1 = 2.0 Hz, J_2 = 1.6 Hz, 1H), 7.02-7.14 (m, 2.41H), 7.28-7.37 (m, 6.48H). ^{13}C NMR (100 MHz,

$CDCl_3$, TMS): δ 13.4, 14.1, 14.5, 30.2, 30.3, 44.1, 44.3.48.7, 49.1, 59.3, 60.7, 60.9, 61.1, 64.8, 66.2, 112.6, 112.7, 122.2, 122.6, 124.5, 124.7, 125.3., 125.5, 127.3, 127.4, 127.9, 128.1, 128.9, 130.1, 133.7, 135.0, 135.1, 143.1, 143.7, 146.6, 149.9, 163.6, 164.1, 176.1, 178.8, 203.5, 204.7. IR (CH_2Cl_2) ν 2958, 2924, 1699, 1607, 1484, 1466, 1336, 1255, 1119, 731, 714 cm^{-1}. MS (ESI) *m/e* 526 (M+23, 100). HRMS (ESI) Calcd. for $C_{25}H_{24}NO_4BrNa^{+1}$ requires 504.0781, Found: 504.0783.

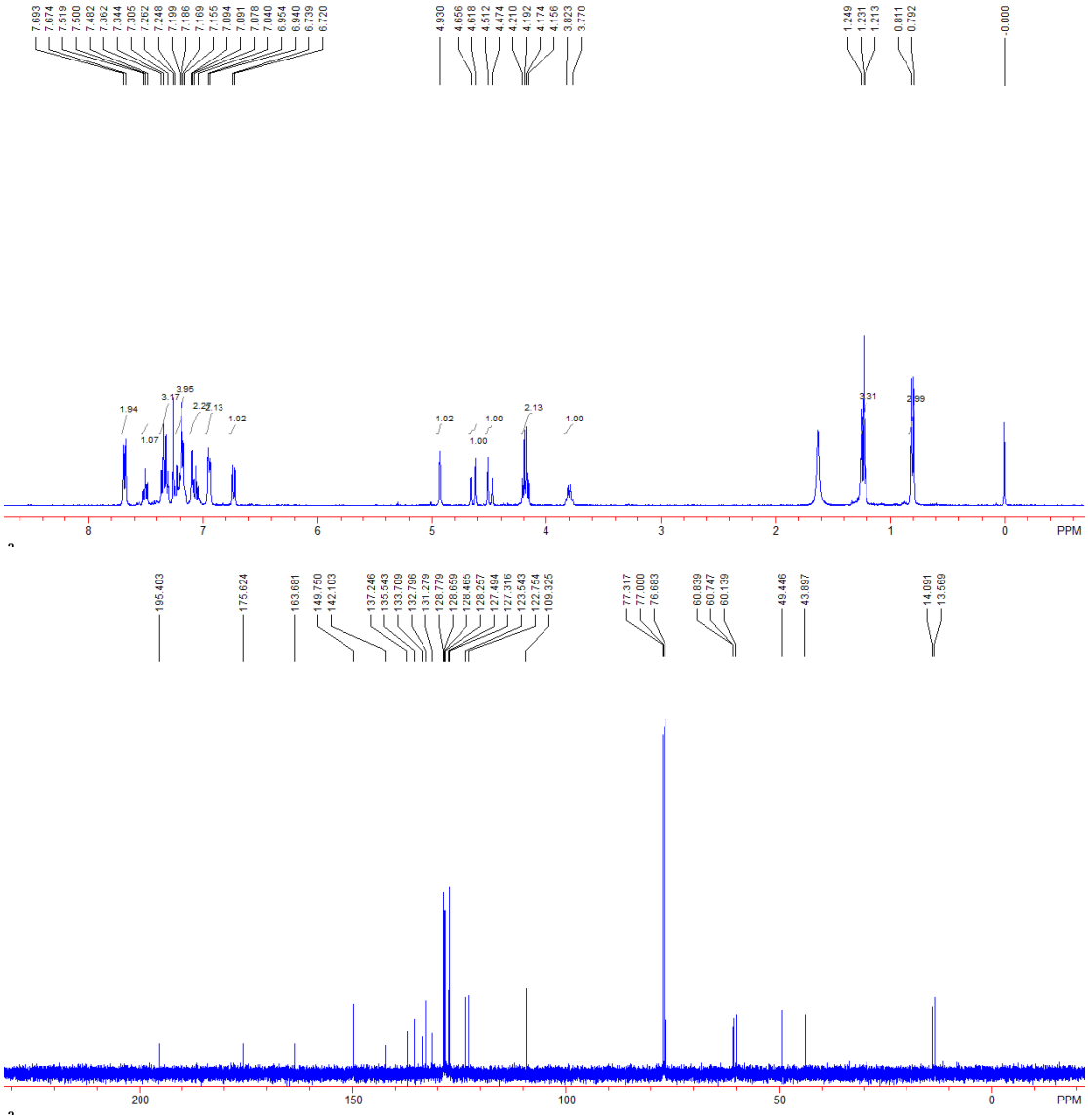


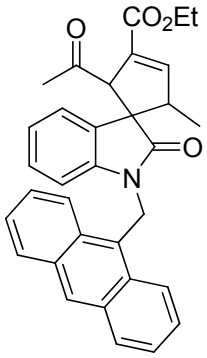


Compound 3j

***(trans,trans) : (cis,trans)* = 1 : 2**

Yield: 32 mg, 70%. A colorless solid. Mp: 140-142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.80 (d, J = 7.6 Hz, 3 H), 1.23 (t, J = 7.2 Hz, 3H), 3.77-3.82 (m, 1H), 4.18 (q, J = 7.2 Hz, 1H), 3.96 (s, 1H), 4.18-4.26 (m, 2.65H), 4.57 (dd, J_1 = 57.6 Hz, J_2 = 15.2 Hz, 2H), 4.93 (s, 1H), 6.72 (d, J= 7.6 Hz, 1H), 6.94-6.96 (m, 2H), 6.71-6.78 (m, 3H), 7.04-7.09 (m, 2H), 7.15-7.19 (m, 4H), 7.31-7.36 (m, 3H), 7.50. (t, J = 7.6 Hz, 1Hz), 7.67-7.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.5, 14.1, 43.8, 49.4, 60.1, 60.7, 60.8, 109.3, 122.7, 123.5, 127.3, 127.4, 128.3, 128.4, 128.6, 128.7, 131.3, 132.7, 133.7, 135.5, 137.3, 142.1, 149.8, 163.7, 175.6, 195.4. IR (CH_2Cl_2) ν 2977, 1873, 1740, 148, 1486, 1350, 1236, 1023, 707, 630, 618 cm^{-1}. MS (ESI) *m/e* 526 (M+23, 100). HRMS (ESI) Calcd. for $C_{30}H_{27}NO_4Na^{+1}$ requires 488.1832, Found: 488.1846.

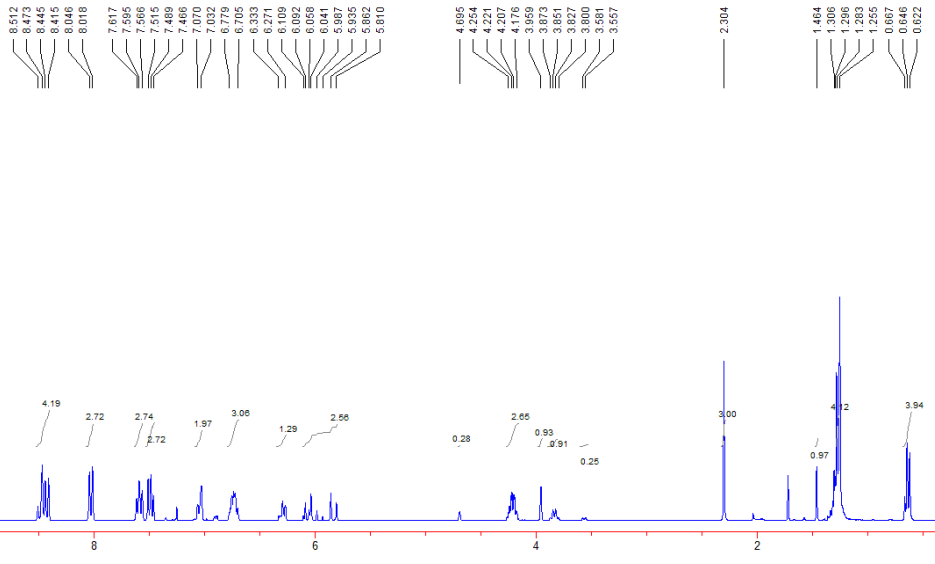


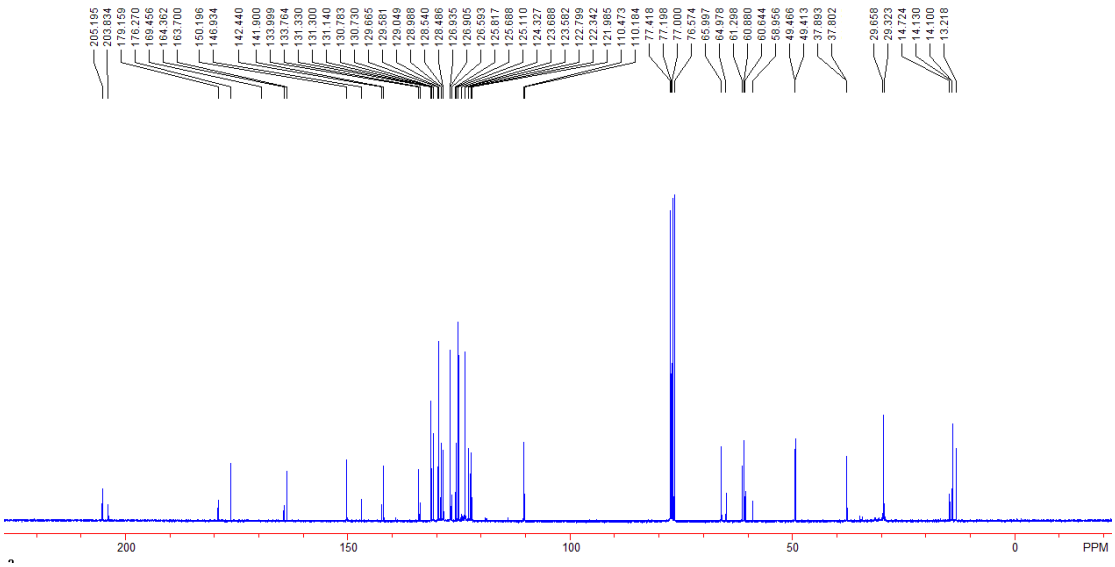


Compound 3q

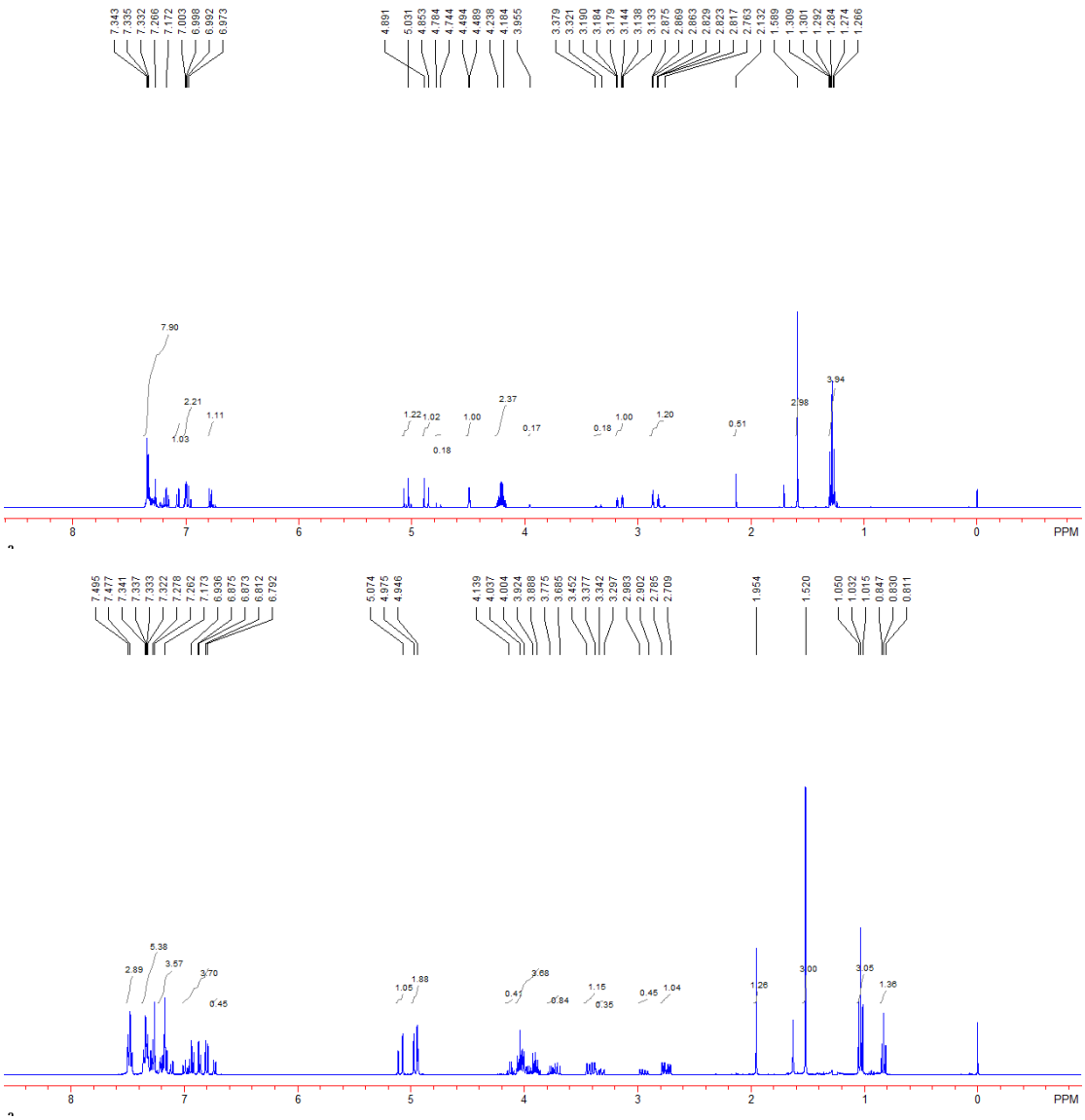
***(trans,trans) : (cis,trans)* = 1 : 3**

Yield: 46 mg, 91%. A colorless solid. Mp: 134-136 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.64 (d, J = 7.2 Hz, 3.94H), 1.25-1.30 (m, 4.12H), 1.47 (s, 0.97H), 2.31 (s, 3H), 3.55-3.58 (m, 0.25H), 3.80-3.87 (m, 1H), 3.96 (s, 1H), 4.18-4.26 (m, 2.65H), 4.70 (s, 0.28H), 5.95 (dd, J_1 = 69.0 Hz, J_2 = 15.3 Hz, 2H), 6.02 (dd, J_1 = 69.0 Hz, J_2 = 15.3 Hz, 0.56H), 6.27-6.33 (m, 1.29H), 6.71-6.78 (m, 3H), 7.03-7.07 (m, 2H), 7.49 (t, J = 7.8 Hz, 2.72H), 7.60 (t, J = 6.6 Hz, 2.72H), 8.03 (d, J = 8.4 Hz, 2.72 Hz), 8.42-8.51 (m, 4.19H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 13.2, 14.1, 14.2, 14.7, 29.3, 29.6, 37.8, 37.9, 49.4, 49.5, 58.9, 60.6, 60.8, 61.2, 64.9, 65.9, 110.2, 110.4, 121.3, 122.4, 123.6, 123.7, 124.3, 125.1, 125.7, 125.8, 126.5, 126.9, 128.4, 128.5, 128.9, 129.0, 129.6, 129.7, 130.7, 131.2, 131.3, 133.7, 141.9, 142.4, 146.9, 150.2, 163.7, 164.4, 169.5, 176.3, 179.2, 2033.8, 205.2. IR (CH_2Cl_2) ν 2958, 2924, 1699, 1607, 1484, 1466, 1336, 1211, 1119, 968, 886, 731 cm^{-1}. MS (ESI) *m/e* 526 (M+23, 100). HRMS (ESI) Calcd. for $C_{33}H_{29}NO_4Na^{+1}$ requires 526.1989, Found: 526.1996.

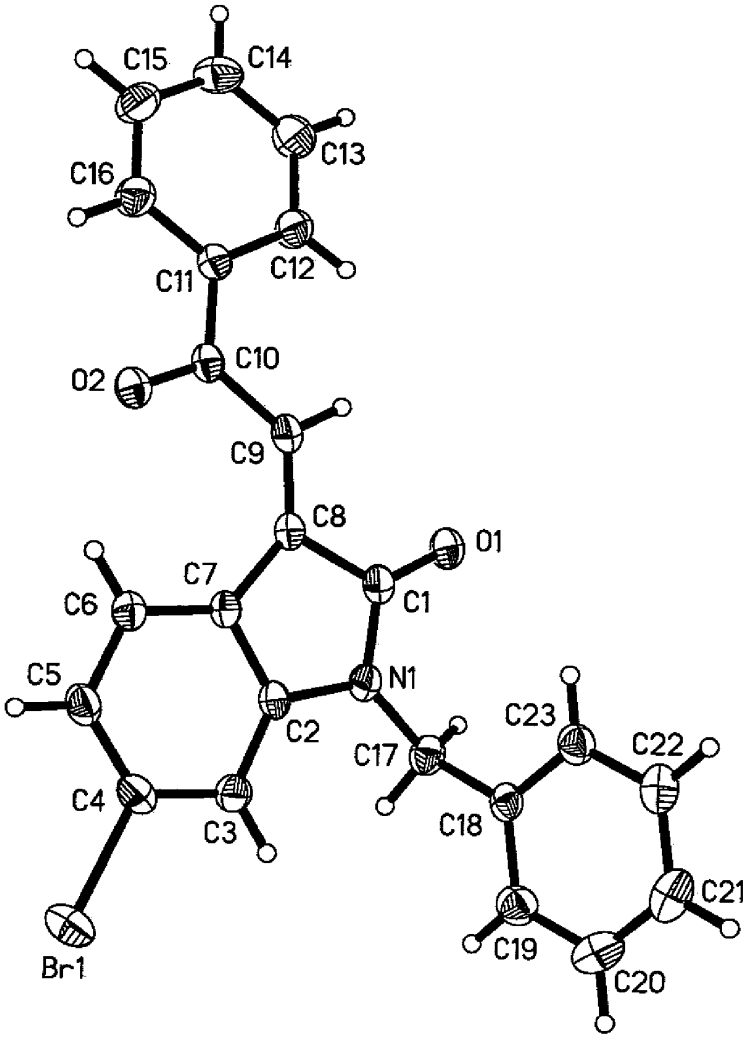



205.195
203.834
179.159
176.270
169.456
164.362
163.700
150.196
146.934
142.440
141.900
133.999
133.764
131.330
131.300
131.140
130.783
130.730
129.665
129.581
129.049
128.868
128.540
128.486
126.935
126.905
126.593
125.817
125.688
125.110
124.327
123.688
123.562
122.799
122.342
121.985
110.473
110.184
77.418
77.198
77.000
76.574
65.997
64.978
61.298
60.880
60.644
58.956
49.466
49.413
37.893
37.802
29.658
29.323
14.724
14.130
14.100
13.218
200
150
100
50
0
PPM

The spectroscopic data of the two separated products of 2,3-butadienoate with **1a** is as following, each of which contains two diastereoisomers along with the ratio of 1 : 0.2 and 1 : 0.4.

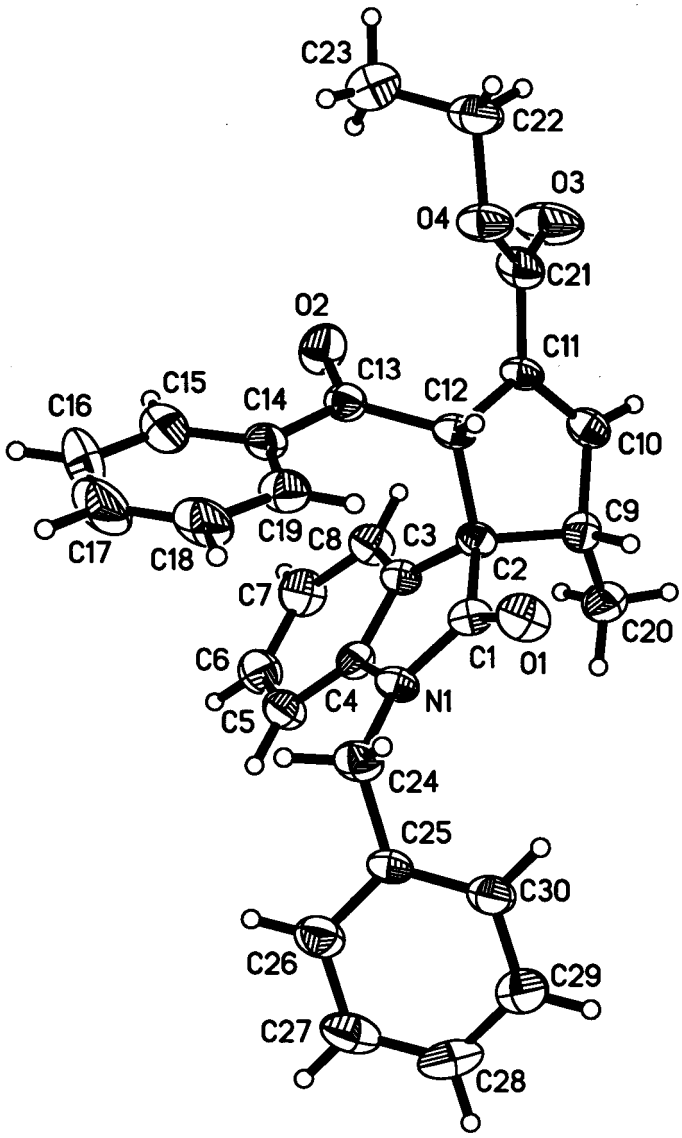


X-ray Crystal Structure of 1n



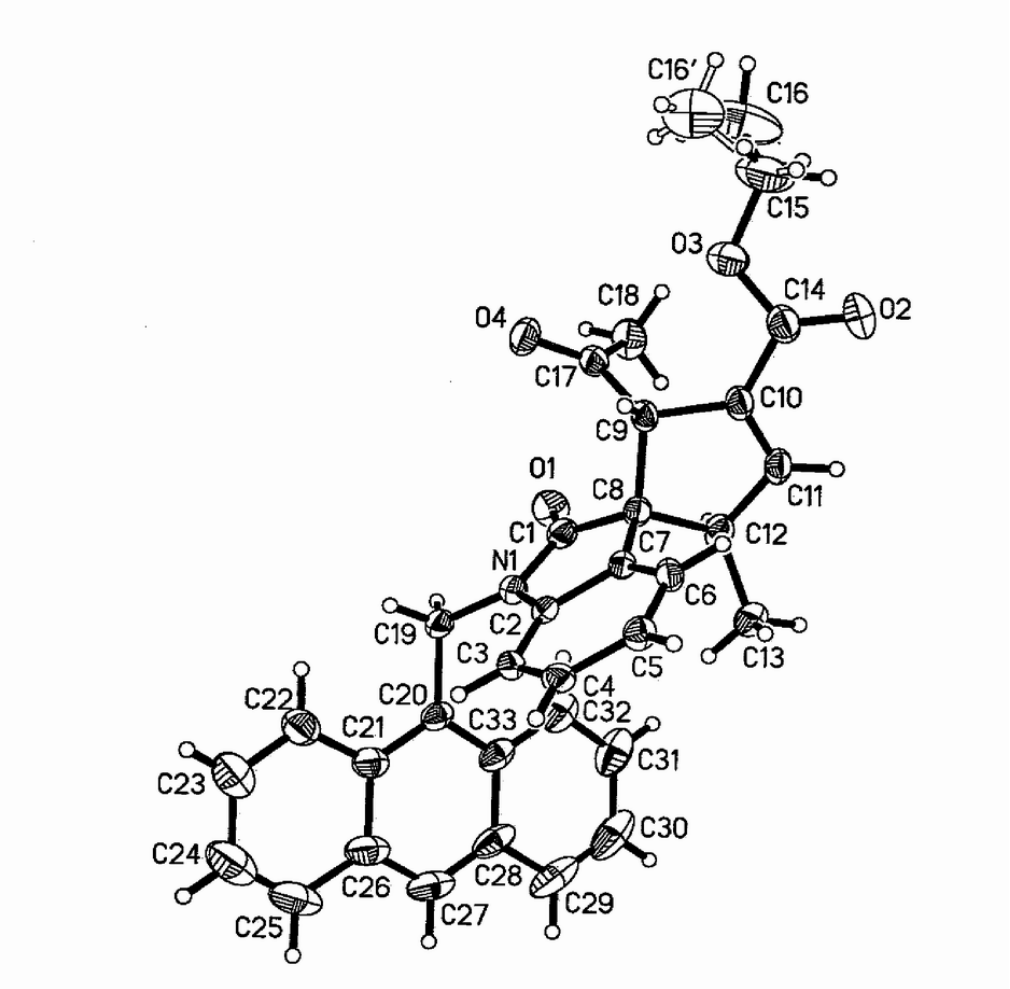
The crystal data of **1n** have been deposited in CCDC with number 792765. Empirical Formula: $C_{23}H_{16}BrNO_2$; Formula Weight: 418.28; Crystal Color, Habit: colorless; Crystal Dimensions: 0.401 x 0.256 x 0.147 mm; Crystal System: Monoclinic; Lattice Parameters: a = 8.2650(17)Å, b = 13.415(3)Å, c = 16.413(3)Å, $\alpha = 90^o$, $\beta = 92.032(4)^o$, $\gamma = 90^o$, V = 1818.6(6)Å^3; Space group: P2(1)/n; Z = 4; D_{calc} = 1.528 g/cm^3; F_{000} = 848; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0397, 0.0954.

X-ray Crystal Structure of (*trans,trans*)-3j



The crystal data of (*trans,trans*)-**3j** have been deposited in CCDC with number 783106. Empirical Formula: $C_{30}H_{27}NO_4$; Formula Weight: 465.53; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.390 x 0.318 x 0.157 mm; Crystal System: Triclinic; Lattice Parameters: a = 10.5001(12)Å, b = 10.6998(11)Å, c = 24.381(3)Å, α = 81.545(2)^o, β = 83.868(2)^o, γ = 64.481(2)^o, V = 2442.2(5)Å^3; Space group: P-1; Z = 4; D_{calc} = 1.266 g/cm^3; F_{000} = 984; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0598, 0.1252.

X-ray Crystal Structure of (*cis,trans*)-3q



The crystal data of (*cis,trans*)-**3q** have been deposited in CCDC with number 789405. Empirical Formula: $C_{33}H_{29}NO_4$; Formula Weight: 503.57; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.415 x 0.360 x 0.301 mm; Crystal System: Triclinic; Lattice Parameters: a = 7.5777(9)Å, b = 12.4273(15)Å, c = 14.6322(18)Å, α = 81.787(2)^o, β = 77.390(2)^o, γ = 80.671(2)^o, V = 1318.6(3)Å^3; Space group: P-1; Z = 4; D_{calc} = 1.268 g/cm^3; F_{000} = 532; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0591, 0.1536.