

Electronic Supplementary Information

DMSO/Tf₂O-Mediated Cross-Coupling of Tryptamine with Aniline to a C3a-N1'-Linked Pyrroloindoline Alkaloid

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I. General

All melting points were measured on a Yanagimoto micro melting point apparatus, and are uncorrected. IR spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer. ¹H and ¹³C NMR spectra were measured on a JEOL JNM-AL300 (300 MHz), a JEOL JNM-AL400 (400 MHz), or a JEOL JNM-LA500 (500 MHz) spectrometer with tetramethylsilane as an internal standard. *J*-Values are given in Hertz. Mass spectra were recorded on a JEOL JMS 700 instrument with a direct inlet system. Elemental analyses were obtained using a Yanaco MT-6 elemental analyzer. Column chromatography was carried out on a silica gel [Fuji Silysia Co. Inc. (silica gel PSQ 60B)].

The following compounds were characterized by the previous reports: **10a**,¹⁾ **10b**,¹⁾ **12a**,²⁾ **12b**,³⁾ and **12c**.⁴⁾

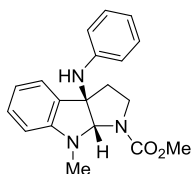
II. Experimental Procedures and Characterization Data

General procedure for the synthesis of C3a-nitrogen-substituted pyrroloindolines (Table 1)

Tf₂O (67 μL, 0.40 mmol, 1.0 equiv) was added to a solution of **10a** (93 mg, 0.40 mmol, 1.0 equiv) and DMSO (28 μL, 0.40 mmol, 1.0 equiv) in DCM (2.0 mL, 0.20 M) at -78 °C under an argon atmosphere. After stirring for 10 min, DTBP (0.18 mL, 0.80 mmol, 2.0 equiv) was added and the reaction mixture was stirred for a further 10 min. The nucleophile (1.0 equiv) was added and then the reaction mixture was warmed to 0 °C over 10 min with stirring. The reaction mixture was neutralized with saturated aqueous NaHCO₃ at 0 °C, and then extracted three times with DCM. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with *n*-hexane/AcOEt as the eluent to afford the corresponding pyrroloindoline **11**.

For Table 1

Methyl 8-methyl-3a-phenylamino-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (**11a**)



Entry 1: Aniline (37 μL); **11a** (0.12 g, 91%).

White amorphous

IR (CHCl₃): 3586, 1695, 1603, 1450 cm⁻¹.

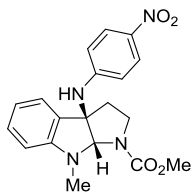
¹H NMR (300 MHz, DMSO-*d*₆, 80 °C): δ 2.11 (1H, ddd, *J* = 13.0, 7.5, 5.5 Hz), 2.39-2.55 (1H, m), 2.93 (3H, s), 3.00-3.20 (1H, m), 3.65 (3H, s), 3.82 (1H, ddd, *J* = 11.0, 7.8, 5.4 Hz), 5.53 (1H, s), 5.94 (1H, s), 6.31-6.41 (2H, m), 6.46-6.56 (2H, m), 6.61 (1H, ddd, *J* = 7.4, 7.4, 1.0 Hz), 6.88-6.98 (2H, m), 7.00 (1H, dd, *J* = 7.4, 1.0 Hz), 7.11 (1H, ddd, *J* = 7.4, 7.4, 1.0 Hz).

¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 32.6, 44.0, 51.82, 51.84, 70.8, 84.3, 106.2, 114.0, 116.3, 117.3, 122.0, 128.1, 128.6, 130.0, 145.9, 150.1, 155.1.

MS (EI): *m/z* (%) 323 (M⁺, 41), 232 (14), 231 (100), 230 (13), 171 (11), 144 (21).

HRMS (EI): *m/z* Calcd for C₁₉H₂₁N₃O₂: 323.1634; Found: 323.1632.

Methyl 8-methyl-3a-((4-nitrophenyl)amino)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11b)



Entry 2: *p*-Nitroaniline (55 mg); **11b** (0.13 g, 90%).

Yellow powder

M. p. 215-216 °C

IR (CHCl₃): 1713, 1697, 1599, 1506, 1454, 1327, 1314 cm⁻¹.

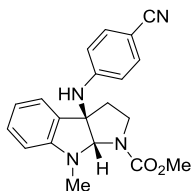
¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.21 (1H, ddd, *J* = 12.5, 7.0, 5.5 Hz), 2.54 (1H, ddd, *J* = 12.5, 7.0, 7.0 Hz), 2.98 (3H, s), 3.04-3.22 (1H, m), 3.67 (3H, s), 3.85 (1H, ddd, *J* = 12.0, 8.0, 5.5 Hz), 5.56 (1H, s), 6.42-6.51 (2H, m), 6.59 (1H, d, *J* = 7.6 Hz), 6.64 (1H, ddd, *J* = 7.6, 7.6, 1.0 Hz), 7.01 (1H, dd, *J* = 7.6, 1.0 Hz), 7.16 (1H, ddd, *J* = 7.6, 7.6, 1.0 Hz), 7.48 (1H, s), 7.82-7.92 (2H, m).

¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 32.3, 44.0, 51.9, 52.0, 70.7, 84.3, 106.5, 112.6, 117.5, 122.0, 125.0, 128.3, 129.2, 136.8, 150.1, 151.9, 154.9.

MS (EI): *m/z* (%) 368 (M⁺, 54), 232 (14), 231 (100), 171 (10), 144 (21).

HRMS (EI): *m/z* Calcd for C₁₉H₂₀N₄O₄: 368.1485; Found: 368.1479.

Methyl 3a-((4-cyanophenyl)amino)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11c)



Entry 3: *p*-Cyanoaniline (47 mg); **11c** (0.13 g, 96%).

White amorphous

IR (CHCl₃): 2218, 1697, 1607, 1518 cm⁻¹.

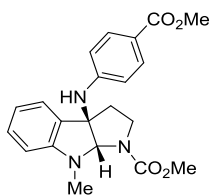
¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.17 (1H, ddd, *J* = 13.0, 7.5, 5.5 Hz), 2.43-2.57 (1H, m), 2.96 (3H, s), 3.05-3.22 (1H, m), 3.66 (3H, s), 3.77-3.92 (1H, m), 5.53 (1H, s), 6.38-6.50 (2H, m), 6.57 (1H, d, *J* = 7.6 Hz), 6.63 (1H, dd, *J* = 7.6, 7.6 Hz), 7.00 (1H, d, *J* = 7.6 Hz), 7.02 (1H, br s), 7.14 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.26-7.39 (2H, m).

¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 32.3, 39.6, 44.0, 51.9, 70.5, 84.2, 97.2, 106.4, 113.6, 117.5, 119.5, 122.0, 128.6, 129.0, 132.5, 149.6, 150.0, 154.9.

MS (EI): *m/z* (%) 348 (M⁺, 42), 232 (16), 231 (100), 171 (12), 144 (22).

HRMS (EI): *m/z* Calcd for C₂₀H₂₀N₄O₂: 348.1586; Found: 348.1587.

Methyl 3a-((4-(methoxycarbonyl)phenyl)amino)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11d)



Entry 4: *p*-Methoxycarbonylaniline (60 mg); **11d** (0.14 g, 93%).

White amorphous

IR (CHCl₃): 1705, 1697, 1607, 1520, 1452 cm⁻¹.

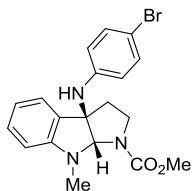
¹H NMR (400 MHz, DMSO-*d*₆, 80 °C): δ 2.17 (1H, ddd, *J* = 12.8, 7.6, 5.6 Hz), 2.42-2.58 (1H, m), 2.97 (3H, s), 3.03-3.22 (1H, m), 3.66 (3H, s), 3.71 (3H, s), 3.84 (1H, ddd, *J* = 12.0, 7.6, 5.6 Hz), 5.55 (1H, s), 6.33-6.48 (2H, m), 6.56 (1H, d, *J* = 7.6 Hz), 6.62 (1H, dd, *J* = 7.6, 7.6 Hz), 6.82 (1H, br s), 7.00 (1H, dd, *J* = 7.6, 1.2 Hz), 7.13 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.48-7.67 (2H, m).

¹³C NMR (100 MHz, DMSO-*d*₆, 80 °C): δ 32.4, 39.6, 44.0, 50.6, 51.9, 70.6, 84.4, 106.3, 112.9, 117.1, 117.4, 122.0, 128.9, 129.0, 130.0, 150.09, 150.11, 154.9, 165.8.

MS (EI): *m/z* (%) 381 (M⁺, 32), 232 (15), 231 (100), 230 (12), 171 (11), 144 (18).

HRMS (EI): *m/z* Calcd for C₂₁H₂₃N₃O₄: 381.1689; Found: 381.1689.

Methyl 3a-((4-bromophenyl)amino)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11e)



Entry 5: *p*-Bromoaniline (69 mg); **11e** (0.14 g, 89%).

Yellowish solid

M. p. 173-174 °C

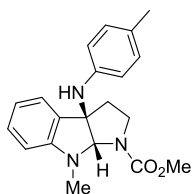
IR (CHCl₃): 1697, 1493, 1450 cm⁻¹.

¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.12 (1H, ddd, *J* = 13.0, 7.5, 5.5 Hz), 2.44 (1H, ddd, *J* = 15.0, 5.5, 5.5 Hz), 2.93 (3H, s), 3.03-3.20 (1H, m), 3.65 (3H, s), 3.81 (1H, ddd, *J* = 13.0, 7.5, 4.5 Hz), 5.50 (1H, s), 6.25 (1H, s), 6.27-6.34 (2H, m), 6.54 (1H, d, *J* = 7.6 Hz), 6.62 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 6.98 (1H, dd, *J* = 7.6, 1.2 Hz), 7.03-7.09 (2H, m), 7.12 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz).

¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 32.4, 32.5, 44.0, 51.9, 71.0, 84.3, 106.3, 107.5, 115.9, 117.3, 122.0, 128.8, 129.3, 130.7, 145.2, 150.1, 155.0.

Anal Calcd for C₁₉H₂₀N₃O₂Br: C, 56.73; H, 5.01; N, 10.45; Found: C, 56.94; H, 5.13; N, 10.22.

Methyl 8-methyl-3a-((4-methylphenyl)amino)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11f)



Entry 6: *p*-Toluidine (43 mg); **11f** (0.10 g, 74%).

Yellowish solid

M. p. 125-126 °C

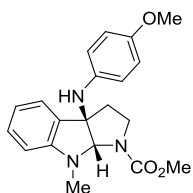
IR (CHCl₃): 1694, 1612, 1518, 1450, 1387 cm⁻¹.

¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.07 (3H, s), 2.10 (1H, ddd, *J* = 13.0, 7.5, 5.5 Hz), 2.43 (1H, ddd, *J* = 13.0, 7.5, 7.5 Hz), 2.92 (3H, s), 3.01-3.20 (1H, m), 3.65 (3H, s), 3.81 (1H, ddd, *J* = 11.5, 7.5, 5.5 Hz), 5.51 (1H, s), 5.74 (1H, s), 6.23-6.31 (2H, m), 6.52 (1H, d, *J* = 7.6 Hz), 6.60 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 6.71-6.78 (2H, m), 6.99 (1H, dd, *J* = 7.6, 1.2 Hz), 7.10 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz).

¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 19.41, 19.43, 32.6, 44.0, 51.8, 71.0, 84.3, 106.2, 114.4, 117.2, 122.0, 124.9, 128.5, 128.6, 130.3, 143.5, 150.1, 155.0.

Anal Calcd for C₂₀H₂₃N₃O₂: C, 71.19; H, 6.87; N, 12.45; Found: C, 71.03; H, 6.90; N, 12.23.

Methyl 3a-((4-methoxyphenyl)amino)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11g)



Entry 7: *p*-Anisidine (49 mg); **11g** (54 mg, 38%).

Brown amorphous

IR (CHCl₃): 1697, 1609, 1510, 1450, 1387 cm⁻¹.

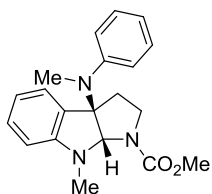
¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.09 (1H, ddd, *J* = 13.0, 7.5, 5.5 Hz), 2.40 (1H, ddd, *J* = 13.0, 7.5, 7.5 Hz), 2.90 (3H, s), 3.01-3.20 (1H, m), 3.58 (3H, s), 3.65 (3H, s), 3.80 (1H, ddd, *J* = 11.0, 7.5, 5.0 Hz), 5.47 (1H, s), 5.56 (1H, s), 6.28-6.36 (2H, m), 6.51 (1H, d, *J* = 7.6 Hz), 6.55-6.59 (2H, m), 6.61 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.00 (1H, dd, *J* = 7.6, 1.2 Hz), 7.10 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz).

¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 32.6, 44.0, 51.8, 55.0, 59.9, 71.2, 84.3, 106.2, 114.1, 115.8, 117.2, 122.1, 128.5, 130.3, 139.8, 150.2, 151.3, 155.1.

MS (EI): *m/z* (%) 353 (M⁺, 35), 232 (14), 231 (100), 230 (43), 171 (12), 144 (19).

HRMS (EI): *m/z* Calcd for C₂₀H₂₃N₃O₃: 353.1739; Found: 353.1738.

Methyl 8-methyl-3a-(methyl(phenyl)amino)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11h)



Entry 8: *N*-Methylaniline (44 μ L); **11h** (0.11 g, 83%).

Colorless oil

IR (CHCl₃): 1694, 1491, 1450, 1391 cm⁻¹.

¹H NMR (300 MHz, DMSO-*d*₆, 80 °C): δ 2.11 (1H, ddd, *J* = 12.5, 6.0, 2.5 Hz), 2.38-2.51 (1H, m), 2.68 (3H, s), 2.77 (3H, s), 2.82 (1H, ddd, *J* = 10.5, 10.5, 6.0 Hz), 3.51-3.68 (1H, m), 3.63 (3H, s), 5.47 (1H, s), 6.43 (1H, d, *J* = 7.9 Hz), 6.66 (1H, ddd, *J* = 7.4, 7.4, 1.0 Hz), 6.90-6.98 (2H, m), 6.98-7.06 (1H, m), 7.07-7.14 (2H, m), 7.14-7.24 (2H, m).

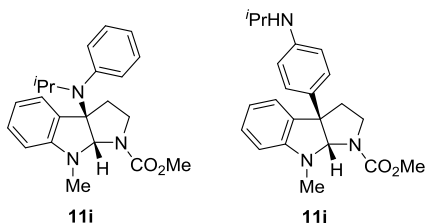
¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 32.1, 36.5, 38.5, 44.7, 51.7, 77.1, 83.0, 106.1, 116.9, 123.40, 123.42, 125.2, 127.9, 128.3, 128.9, 149.6, 150.9, 154.5.

MS (EI): *m/z* (%) 337 (M⁺, 25), 249 (12), 232 (15), 231 (100), 230 (37), 171 (23), 144 (24).

HRMS (EI): *m/z* Calcd for C₂₀H₂₃N₃O₂: 337.1790; Found: 337.1789.

Methyl 3a-(isopropyl(phenyl)amino)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11i)

Methyl 3a-(4-(isopropylamino)phenyl)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11j)



Entry 9: *N*-Isopropylaniline (58 μ L); **11i** (48 mg, 33%) and **11j** (58 mg, 40%).

11i; Colorless oil

IR (CHCl₃): 1692, 1605, 1491, 1450, 1387 cm⁻¹.

¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 0.84 (3H, d, *J* = 6.7 Hz), 0.90 (3H, d, *J* = 6.7 Hz), 1.97 (1H, ddd, *J* = 13.0, 6.3, 2.6 Hz), 2.18 (1H, ddd, *J* = 15.0, 6.3, 5.6 Hz), 2.67-2.79 (1H, m), 2.83 (3H, s), 3.40 (1H, ddd, *J* = 13.0, 6.5, 6.5 Hz), 3.48-3.59 (1H, m), 3.65 (3H, s), 5.44 (1H, s), 6.47 (1H, d, *J* = 7.6 Hz), 6.68 (1H, dd, *J* = 7.6, 7.6 Hz), 6.95-7.05 (2H, m), 7.08-7.14 (1H, m), 7.14-7.20 (1H, m), 7.21-7.34 (3H, m).

¹³C NMR (100 MHz, DMSO-*d*₆, 80 °C): δ 22.0, 23.4, 32.3, 37.2, 44.2, 48.2, 51.8, 77.7, 85.1, 106.2, 117.1, 123.3, 125.0, 127.7, 128.7, 130.6, 131.4, 143.3, 150.8, 154.7.

MS (EI): *m/z* (%) 365 (M⁺, 25), 232 (15), 231 (100), 230 (17), 171 (12), 144 (15).

HRMS (EI): *m/z* Calcd for C₂₂H₂₇N₃O₂: 365.2103; Found: 365.2101.

11j; Colorless oil

IR (CHCl₃): 1694, 1605, 1518, 1491, 1449, 1385 cm⁻¹.

¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 1.11 (6H, d, *J* = 6.4 Hz), 2.26-2.38 (1H, m), 2.41-2.57 (1H, m), 2.83-3.02 (1H, m), 2.90 (3H, s), 3.48 (1H, ddd, *J* = 13.0, 6.5, 6.5 Hz), 3.64 (3H, s), 3.83 (1H, ddd, *J* = 10.5, 7.0, 2.5 Hz), 5.01 (1H, br s), 5.40 (1H, s), 6.46 (1H, d, *J* = 7.6 Hz), 6.47-6.54 (2H, m), 6.60 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 6.90 (1H, d, *J* = 7.6 Hz), 6.95-7.02 (2H, m), 7.04 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz).

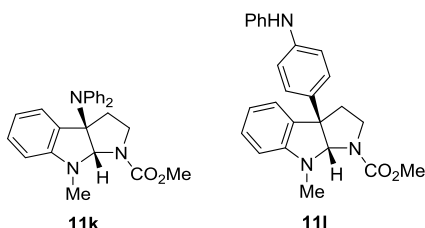
¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 22.1, 31.9, 36.9, 42.9, 45.8, 51.7, 59.0, 88.5, 105.8, 112.2, 117.1, 122.8, 126.0, 127.6, 130.4, 133.5, 146.5, 149.9, 154.7.

MS (EI): *m/z* (%) 365 (M⁺, 100), 350 (10), 278 (16), 277 (68), 263 (20).

HRMS (EI): *m/z* Calcd for C₂₂H₂₇N₃O₂: 365.2103; Found: 365.2102.

Methyl 3a-(diphenylamino)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11k)

Methyl 8-methyl-3a-(4-(phenylamino)phenyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11l)



Entry 10: Diphenylamine (68 mg); **11k** (0.12 g, 76%) and **11l** (10 mg, 6%).

11k; White amorphous

IR (CHCl₃): 1697, 1489, 1450, 1385 cm⁻¹.

¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.02 (1H, ddd, *J* = 13.0, 8.0, 5.0 Hz), 2.56 (1H, ddd, *J* = 13.0, 7.0, 7.0 Hz), 2.88-2.99 (1H, m), 2.94 (3H, s), 3.21-3.44 (1H, m), 3.67 (3H, s), 5.93 (1H, s), 6.52 (1H, d, *J* = 7.6 Hz), 6.57 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 6.76-6.84 (4H, m), 6.94-7.01 (2H, m), 7.05 (1H, dd, *J* = 7.6, 1.2 Hz), 7.09 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.13-7.25 (4H, m).

¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 32.4, 38.0, 44.2, 51.9, 75.7, 84.3, 106.3, 117.1, 122.4, 122.9, 124.9, 128.4, 128.7, 130.1, 146.3, 149.7, 154.8.

MS (EI): *m/z* (%) 399 (M⁺, 15), 311 (13), 232 (14), 231 (100), 230 (22), 171 (13), 144 (18).

HRMS (EI): *m/z* Calcd for C₂₅H₂₅N₃O₂: 399.1947; Found: 399.1945.

11l; White amorphous

IR (CHCl₃): 1715, 1651, 1645, 1557, 1539, 1506 cm⁻¹.

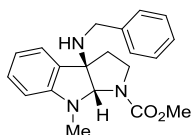
¹H NMR (300 MHz, DMSO-*d*₆, 80 °C): δ 2.38 (1H, ddd, *J* = 12.3, 6.0, 2.6 Hz), 2.45-2.59 (1H, m), 2.90-3.00 (1H, m), 2.92 (3H, s), 3.11 (1H, br s), 3.65 (3H, s), 3.86 (1H, ddd, *J* = 11.0, 7.5, 2.6 Hz), 5.46 (1H, s), 6.48 (1H, d, *J* = 7.9 Hz), 6.62 (1H, ddd, *J* = 7.3, 7.3, 1.0 Hz), 6.74-6.84 (1H, m), 6.90-7.10 (6H, m), 7.10-7.24 (4H, m).

^{13}C NMR (125 MHz, DMSO- d_6 , 80 °C): δ 31.9, 36.8, 45.8, 51.8, 59.2, 88.3, 105.9, 116.6, 116.7, 117.2, 119.3, 122.9, 126.2, 127.9, 128.6, 133.1, 134.9, 142.0, 143.3, 149.9, 154.8.

MS (EI): m/z (%) 399 (M^+ , 26), 367 (12), 312 (24), 311 (100), 219 (40), 218 (24).

HRMS (EI): m/z Calcd for $\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_2$: 399.1947; Found: 399.1945.

Methyl 3a-benzylamino-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (**11m**)



Entry 11: Benzylamine (44 μL); **11m** (40 mg, 30%).

Colorless oil

IR (CHCl_3): 1694, 1609, 1495, 1450, 1389 cm^{-1} .

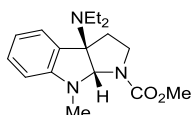
^1H NMR (300 MHz, DMSO- d_6 , 80 °C): δ 2.00-2.29 (2H, m), 2.73-3.03 (2H, m), 2.86 (3H, s), 3.38 (1H, d, $J = 13.4$ Hz), 3.50 (1H, d, $J = 13.4$ Hz), 3.65 (3H, s), 3.76 (1H, ddd, $J = 11.4, 7.5, 3.9$ Hz), 5.25 (1H, s), 6.46 (1H, d, $J = 7.9$ Hz), 6.68 (1H, t, $J = 7.3$ Hz), 7.10 (1H, td, $J = 7.7, 1.3$ Hz), 7.14-7.32 (6H, m).

^{13}C NMR (75 MHz, DMSO- d_6 , 80 °C): δ 32.5, 38.2, 44.5, 47.5, 51.6, 73.7, 84.9, 106.0, 117.0, 122.7, 125.9, 127.4, 127.5, 128.5, 129.7, 140.7, 150.9, 153.2.

MS (EI): m/z (%) 337 (M^+ , 100), 249 (10), 246 (39), 235 (14), 234 (18), 232 (40), 231 (15), 230 (12), 214 (20), 203 (11), 186 (20), 171 (14), 159 (19), 145 (21), 144 (35), 91 (22).

HRMS (EI): m/z Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_2$: 337.1790; Found: 337.1788.

Methyl 3a-diethylamino-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (**11n**)



Entry 12: Diethylamine (41 μL); **11n** (11 mg, 9%).

Colorless oil

IR (CHCl_3): 1694, 1605, 1491, 1450, 1393 cm^{-1} .

^1H NMR (300 MHz, DMSO- d_6 , 80 °C): δ 0.94 (6H, t, $J = 7.1$ Hz), 2.12 (1H, ddd, $J = 11.0, 6.0, 1.9$ Hz), 2.26 (1H, ddd, $J = 11.0, 11.0, 8.0$ Hz), 2.43-2.59 (4H, m), 2.76 (1H, ddd, $J = 11.0, 11.0, 6.0$ Hz), 2.87 (3H, s), 3.66 (3H, s), 3.75 (1H, ddd, $J = 11.0, 8.0, 1.9$ Hz), 5.21 (1H, s), 6.43 (1H, d, $J = 7.6$ Hz), 6.63 (1H, ddd, $J = 7.6, 7.6, 1.2$ Hz), 7.07-7.17 (1H, m), 7.07 (1H, dd, $J = 7.6, 1.2$ Hz).

^{13}C NMR (125 MHz, DMSO- d_6 , 80 °C): δ 15.2, 31.8, 36.9, 43.6, 44.4, 51.7, 78.4, 83.5, 105.7, 116.8, 123.3, 128.6, 129.1, 151.1, 154.5.

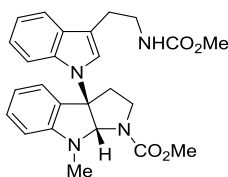
MS (EI): m/z (%) 303 (M^+ , 80), 288 (12), 232 (21), 231 (100), 202 (10), 201 (15), 171 (14), 144 (30).

HRMS (EI): m/z Calcd for $\text{C}_{17}\text{H}_{25}\text{N}_3\text{O}_2$: 303.1947; Found: 303.1946.

General procedure for the synthesis of 3a-(1-indolyl)pyrroloindolines (Table 2)

Tf₂O (1.0 equiv) was added to a solution of **10a** (1.0 equiv) and DMSO (1.0 equiv) in DCM (0.20 M) at -78 °C under an argon atmosphere. After stirring for 10 min, DTBP (2.0 equiv) was added and the reaction mixture was stirred for a further 10 min. The nucleophile (1.0 equiv) was added and then the reaction mixture was warmed to 0 °C and stirred for 10 min. Subsequently DDQ (1.0 equiv) was added to the solution and stirred 15 min under same temperature. The reaction mixture was filtrated through Celite pad, and the filtrate was washed with 10% aqueous NaHCO₃. The organic layer were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography with *n*-hexane/AcOEt (2:1 to 1:1) as an eluent to give **11**.

Methyl 3a-(3-(2-((methoxycarbonyl)amino)ethyl)-1*H*-indol-1-yl)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (**11o**)



Entry 1; **10a** (93 mg, 0.40 mmol), DMSO (28 μ L, 0.40 mmol), Tf₂O (67 μ L, 0.40 mmol), DTBP (0.18 mL, 0.80 mmol), DCM (2.0 mL), **12a** (88 mg, 0.40 mmol); **11o** (84 mg, 47%).

White amorphous

IR (CHCl₃): 1703, 1609, 1518, 1450, 1387 cm⁻¹.

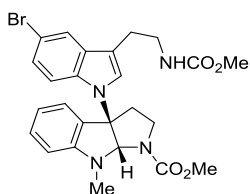
¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.58 (1H, ddd, *J* = 9.0, 4.5, 4.5 Hz), 2.78-2.87 (2H, m), 3.01 (3H, s), 3.10-3.22 (2H, m), 3.24-3.34 (2H, m), 3.53 (3H, s), 3.66 (3H, s), 3.95-4.06 (1H, m), 5.80 (1H, s), 6.59-6.67 (2H, m), 6.88 (1H, br s), 6.93-7.04 (4H, m), 7.19 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.34 (1H, s), 7.50-7.57 (1H, m).

¹³C NMR (100 MHz, DMSO-*d*₆, 80 °C): δ 24.9, 31.8, 36.9, 40.6, 44.8, 50.7, 52.0, 73.9, 85.3, 106.6, 111.1, 111.8, 117.5, 118.55, 118.62, 121.0, 122.9, 123.7, 127.6, 129.2, 129.7, 134.9, 149.9, 154.7, 156.3.

MS (EI): *m/z* (%) 448 (M⁺, 21), 232 (14), 231 (100), 230 (29), 171 (11), 144 (18).

HRMS (EI): *m/z* Calcd for C₂₅H₂₈N₄O₄: 448.2111; Found: 448.2110.

Methyl 3a-(5-bromo-3-(2-((methoxycarbonyl)amino)ethyl)-1*H*-indol-1-yl)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (**11p**)



Entry 2; **10a** (93 mg, 0.40 mmol), DMSO (28 μ L, 0.40 mmol), Tf₂O (67 μ L, 0.40 mmol), DTBP (0.18 mL, 0.80 mmol), DCM (2.0 mL), **12b** (0.12 g, 0.40 mmol); **11p** (0.19 g, 91%).

White amorphous

IR (CHCl₃): 1715, 1699, 1609, 1520, 1454, 1387 cm⁻¹.

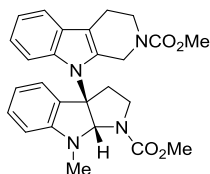
¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.54-2.65 (1H, m), 2.80 (2H, t, *J* = 7.2 Hz), 3.00 (3H, s), 3.06-3.19 (2H, m), 3.26 (2H, td, *J* = 7.2, 7.2 Hz), 3.53 (3H, s), 3.66 (3H, s), 3.94-4.06 (1H, m), 5.76 (1H, s), 6.59-6.69 (2H, m), 6.87 (1H, br s), 6.91 (1H, d, *J* = 8.6 Hz), 6.96 (1H, d, *J* = 7.6 Hz), 7.11 (1H, dd, *J* = 8.6, 2.1 Hz), 7.20 (1H, ddd, *J* = 7.6, 7.6, 1.0 Hz), 7.42 (1H, s), 7.70 (1H, d, *J* = 2.1 Hz).

¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 24.7, 31.7, 36.9, 40.6, 44.8, 50.7, 52.0, 74.0, 85.3, 106.7, 111.6, 111.7, 113.0, 117.6, 120.9, 122.9, 123.5, 125.5, 127.3, 129.9, 131.1, 133.6, 149.9, 154.6, 156.3.

MS (EI): *m/z* (%) 528 (M⁺², 7), 526 (M⁺, 6), 232 (14), 231 (100), 230 (14), 171 (10), 144 (16).

HRMS (EI): *m/z* Calcd for C₂₅H₂₇N₄O₄Br: 526.1216; Found: 526.1211.

Methyl 9-(1-(methoxycarbonyl)-8-methyl-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)-1,3,4,9-tetrahydro-2*H*-pyrido[3,4-*b*]indole-2-carboxylate (11q)



Entry 3; **10a** (46 mg, 0.20 mmol), DMSO (14 μL, 0.20 mmol), Tf₂O (34 μL, 0.20 mmol), DTBP (90 μL, 0.40 mmol), DCM (1.0 mL), **12c** (46 mg, 0.20 mmol); **11q** (55 mg, 60%).

White amorphous

IR (CHCl₃): 1694, 1609, 1449, 1381 cm⁻¹.

¹H NMR (500 MHz, DMSO-*d*₆, 80 °C): δ 2.61-2.86 (3H, m), 2.92-3.07 (1H, m), 3.03 (3H, s), 3.18 (1H, ddd, *J* = 11.5, 11.5, 8.0 Hz), 3.54 (1H, ddd, *J* = 13.5, 8.0, 5.5 Hz), 3.62 (3H, s), 3.67 (3H, s), 3.81 (1H, ddd, *J* = 13.0, 5.5, 5.5 Hz), 4.07 (1H, dd, *J* = 9.8, 8.0 Hz), 4.52 (1H, d, *J* = 16.0 Hz), 4.70 (1H, d, *J* = 16.0 Hz), 6.00 (1H, s), 6.60 (1H, d, *J* = 7.6 Hz), 6.62 (1H, d, *J* = 7.6 Hz), 7.00 (1H, dd, *J* = 7.6, 7.6 Hz), 7.02-7.10 (2H, m), 7.18 (1H, dd, *J* = 7.6, 7.6 Hz), 7.29 (1H, d, *J* = 7.6 Hz), 7.39 (1H, d, *J* = 7.6 Hz).

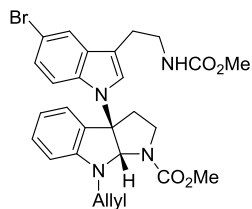
¹³C NMR (125 MHz, DMSO-*d*₆, 80 °C): δ 20.5, 30.8, 38.6, 40.7, 43.6, 44.5, 52.0, 52.1, 75.7, 84.8, 105.9, 109.8, 111.3, 117.4, 117.6, 118.9, 121.5, 123.4, 127.4, 130.0, 132.8, 136.05, 136.11, 150.0, 154.3, 155.2.

MS (EI): *m/z* (%) 460 (M⁺, 18), 232 (16), 231 (100), 230 (45), 171 (13), 144 (23).

HRMS (EI): *m/z* Calcd for C₂₆H₂₈N₄O₄: 460.2111; Found: 460.2103.

Short-step total synthesis of (±)-psychotriasine (9) (Scheme 2)

Methyl 8-allyl-3a-(5-bromo-3-(2-((methoxycarbonyl)amino)ethyl)-1*H*-indol-1-yl)-3,3a,8,8a-tetrahydro-pyrrolo[2,3-*b*]indole-1(2*H*)-carboxylate (11r)



Under argon atmosphere, to a solution of **10b** (0.16 g, 0.64 mmol, 1.0 equiv) and DMSO (45 μ L, 0.64 mmol, 1.0 equiv) in DCM (3.2 mL, 0.20 M) was added TiF_2O (0.11 mL, 0.64 mmol, 1.0 equiv). After being stirred for 10 min at -78°C , DTBP (0.29 mL, 1.3 mmol, 2.0 equiv) was added and the reaction mixture was stirred for 10 min additionally at same temperature. Subsequently, **12b** (0.19 g, 0.64 mmol, 1.0 equiv) was added to the above reaction mixture, and the mixture was stirred for 10 min at 0°C . DDQ was added to the solutions and stirred 15 min under same temperature. The reaction mixture was filtrated through Celite pad, and the filtrate was washed with 10% aqueous NaHCO_3 . The organic layer were washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography with *n*-hexane/ AcOEt (2:1 to 1:1) as an eluent to give **11r** (0.26 g, 74%) as a white amorphous.

IR (CHCl_3): 1705, 1520, 1452, 1389 cm^{-1} .

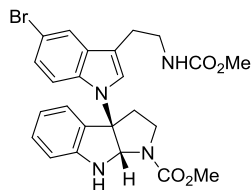
^1H NMR (500 MHz, $\text{DMSO-}d_6$, 80°C): δ 2.54-2.60 (1H, m), 2.79 (2H, dd, $J = 7.0, 7.0$ Hz), 3.11-3.22 (2H, m), 3.25 (2H, dd, $J = 14.0, 7.0$ Hz), 3.53 (3H, s), 3.63 (3H, s), 3.93-4.08 (2H, m), 4.13 (1H, dd, $J = 16.6, 5.0$ Hz), 5.11 (1H, dd, $J = 10.5, 1.5$ Hz), 5.20 (1H, dd, $J = 15.0, 1.5$ Hz), 5.80-5.94 (1H, m), 5.86 (1H, s), 6.59-6.67 (2H, m), 6.87 (1H, br s), 6.88 (1H, d, $J = 8.9$ Hz), 6.97 (1H, dd, $J = 7.8, 1.0$ Hz), 7.09 (1H, dd, $J = 8.9, 1.8$ Hz), 7.18 (1H, ddd, $J = 7.8, 7.8, 1.0$ Hz), 7.40 (1H, s), 7.70 (1H, d, $J = 1.8$ Hz).

^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, 80°C): δ 24.7, 37.0, 40.6, 44.6, 47.5, 50.7, 52.0, 74.2, 84.1, 107.0, 111.67, 111.70, 113.1, 116.2, 117.6, 121.0, 123.1, 123.4, 125.4, 127.2, 129.8, 131.2, 133.5, 133.6, 148.7, 154.4, 156.3.

MS (EI): m/z (%) 554 ($\text{M}^+ + 2$, 7), 552 (M^+ , 7), 258 (16), 257 (100), 256 (14), 216 (23).

HRMS (EI): m/z Calcd for $\text{C}_{27}\text{H}_{29}\text{N}_4\text{O}_4\text{Br}$: 552.1372; Found: 552.1371.

Methyl 3a-(5-bromo-3-(2-((methoxycarbonyl)amino)ethyl)-1H-indol-1-yl)-3,3a,8,8a-tetrahydropyrrolo-[2,3-b]indole-1(2H)-carboxylate (11s)



A solution of **11r** (0.26 g, 0.47 mmol) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (40 mg, 0.15 mmol) in EtOH (5.0 mL) and H_2O (3.8 mL) was stirred at 90 °C. After stirring for 2 hours, the reaction mixture was filtrated through Celite pad, and the filtrate was diluted with water and extracted three times with AcOEt. The organic layer were washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography with *n*-hexane/AcOEt (2:1 to 1:2) as an eluent to give **11s** (0.20 g, 87%) as a white amorphous.

IR (CHCl_3): 1715, 1697, 1454 cm^{-1} .

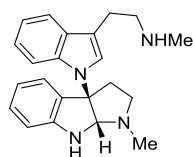
^1H NMR (500 MHz, $\text{DMSO}-d_6$, 80 °C): δ 2.66-2.75 (1H, m), 2.78 (2H, t, $J = 7.2$ Hz), 3.08-3.18 (2H, m), 3.24 (2H, dt, $J = 7.2, 7.2$ Hz), 3.53 (3H, s), 3.66 (3H, s), 3.83-3.91 (1H, m), 5.73 (1H, s), 6.63 (1H, ddd, $J = 7.6, 7.6, 1.2$ Hz), 6.68-6.74 (1H, m), 6.81 (1H, d, $J = 1.5$ Hz), 6.88 (1H, br s), 7.04 (1H, ddd, $J = 7.6, 1.2, 1.2$ Hz), 7.08-7.15 (2H, m), 7.22 (1H, d, $J = 7.6$ Hz), 7.36 (1H, s), 7.68 (1H, d, $J = 1.8$ Hz).

^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, 80 °C): δ 24.7, 36.1, 40.6, 44.4, 50.7, 51.8, 75.1, 79.1, 109.4, 111.53, 111.55, 113.2, 117.9, 120.8, 123.3, 123.4, 125.5, 126.7, 129.7, 131.0, 133.6, 149.4, 153.9, 156.2.

MS (EI): m/z (%) 514 (M^{+2} , 8), 512 (M^+ , 7), 218 (13), 217 (100), 216 (29), 157 (11), 130 (12).

HRMS (EI): m/z Calcd for $\text{C}_{24}\text{H}_{25}\text{N}_4\text{O}_4\text{Br}$: 512.1059; Found: 512.1057.

(±)-Psychotriasine (9)



To a solution of LiAlH_4 (1.0 M in THF) was added **11s** at 0 °C and the reaction mixture was heated at reflux. After 3 hours, the reaction mixture was cooled back to room temperature and carefully quenched by dropwise addition of saturated aqueous Rochelle's salt. The solution was extracted three times with DCM, washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography with AcOEt/MeOH (10:1 to 5:1) as an eluent to give **9** (53 mg, 98%) as a colorless amorphous.

IR (CHCl_3): 3428, 1485, 1458 cm^{-1} .

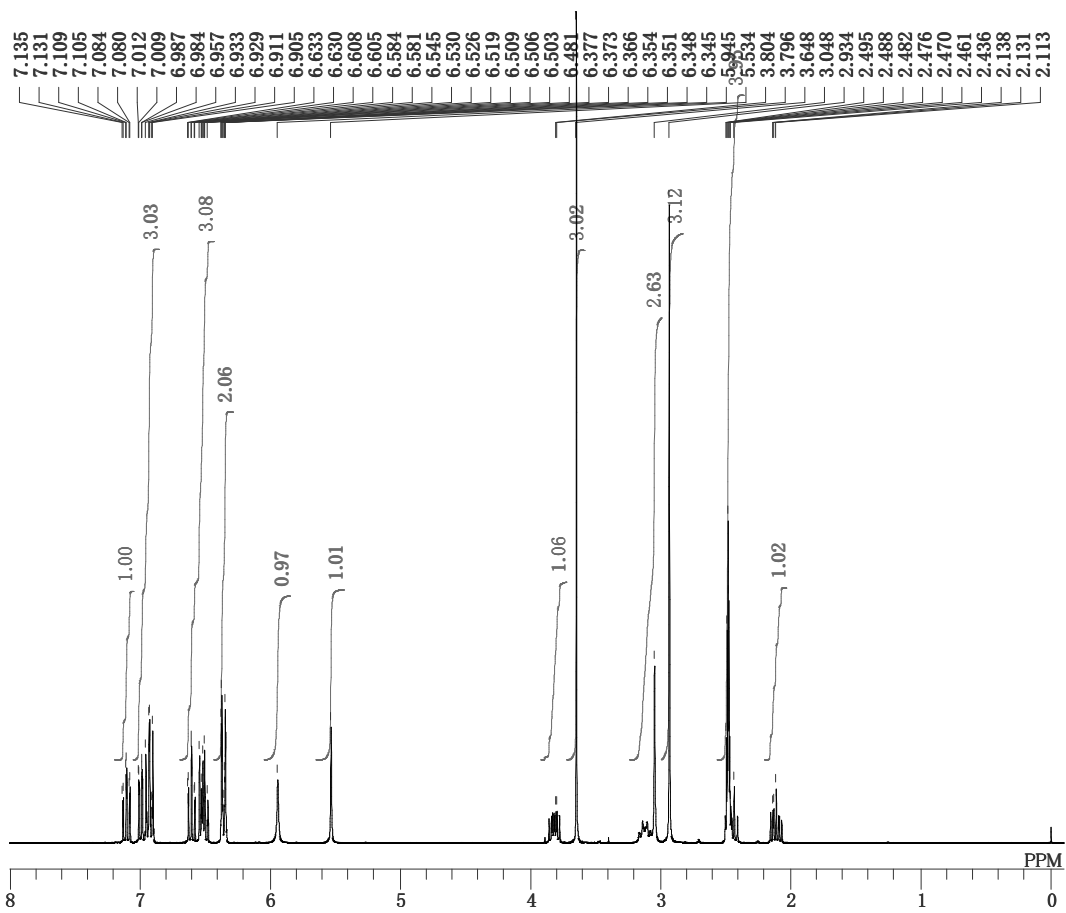
^1H NMR (500 MHz, CD_3OD): δ 2.42 (3H, s), 2.47 (3H, s), 2.47-2.51 (1H, m), 2.57-2.66 (1H, m), 2.82-3.04 (5H, m), 3.15-3.25 (1H, m), 5.22 (1H, s), 6.58 (1H, ddd, $J = 7.7, 7.7, 1.2$ Hz), 6.69 (1H, d, $J = 7.7$ Hz), 6.86 (1H, dd, $J = 7.7, 1.2$ Hz), 6.94 (1H, ddd, $J = 7.7, 7.7, 1.2$ Hz), 6.97 (1H, ddd, $J = 7.7, 7.7, 1.2$ Hz), 7.07 (1H, ddd, $J = 7.7, 7.7, 1.2$ Hz), 7.14 (1H, dd, $J = 7.7, 1.2$ Hz), 7.40 (1H, s), 7.52 (1H, dd, $J = 7.7, 1.2$ Hz).

¹³C NMR (125 MHz, CD₃OD): δ 25.8, 35.9, 36.4, 40.0, 52.2, 52.9, 77.5, 87.1, 110.1, 113.0, 113.1, 119.5, 119.7, 120.2, 122.5, 124.8, 125.1, 130.6, 130.9, 131.5, 137.8, 152.5.

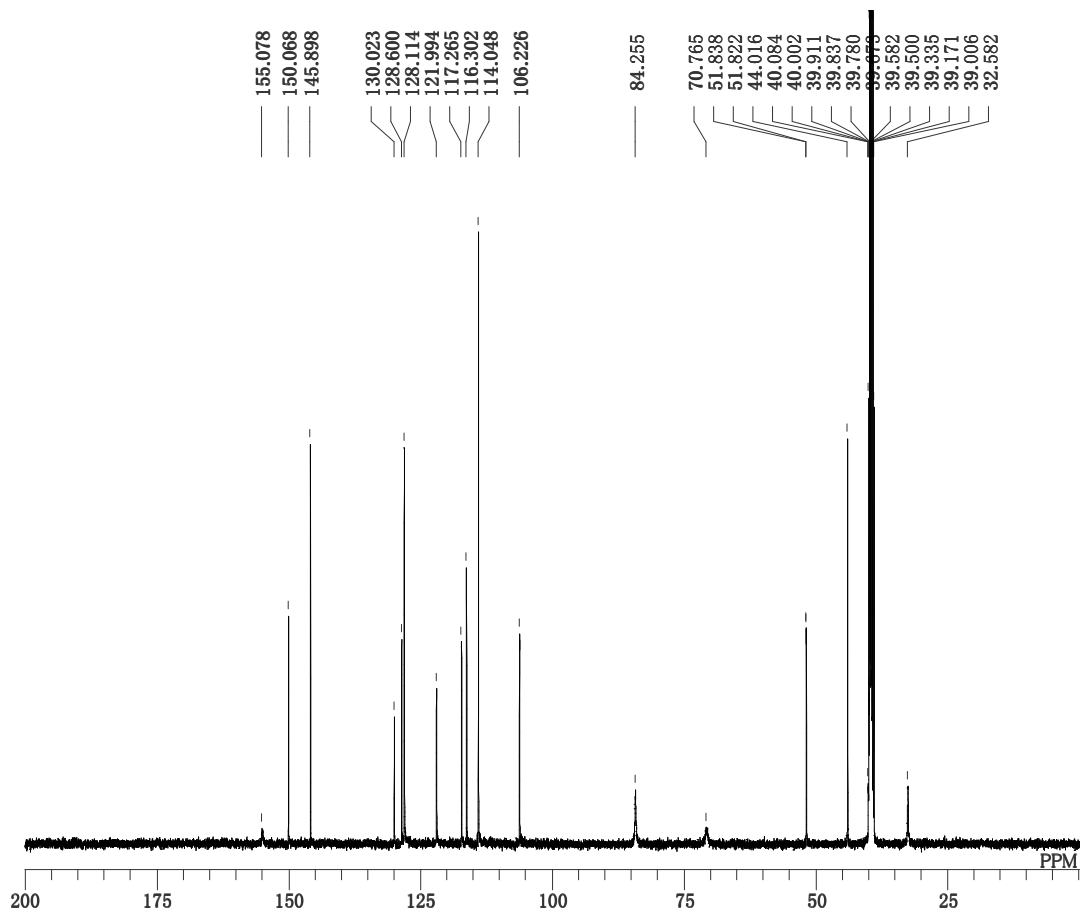
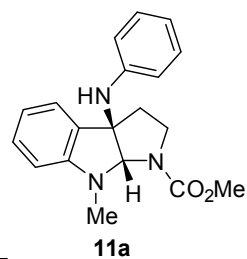
HRMS (FAB): *m/z* Calcd for C₂₂H₂₇N₄ [M+H]⁺: 347.2236; Found: 347.2239.

III. References

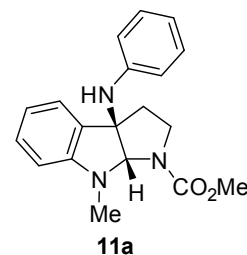
- 1) Y. Yang, X. Jiang, F.-L. Qing, *J. Org. Chem.*, 2012, **77**, 7538.
- 2) M. Somei, N. Oshikiri, M. Hasegawa, F. Yamada, *Heterocycles*, 1999, **51**, 1237
- 3) M. Hasegawa, K. Yamada, Y. Nagahama, M. Somei, *Heterocycles*, 1999, **51**, 2815
- 4) M. Somei, *JP Pat.*, 08 157 475, 1994.

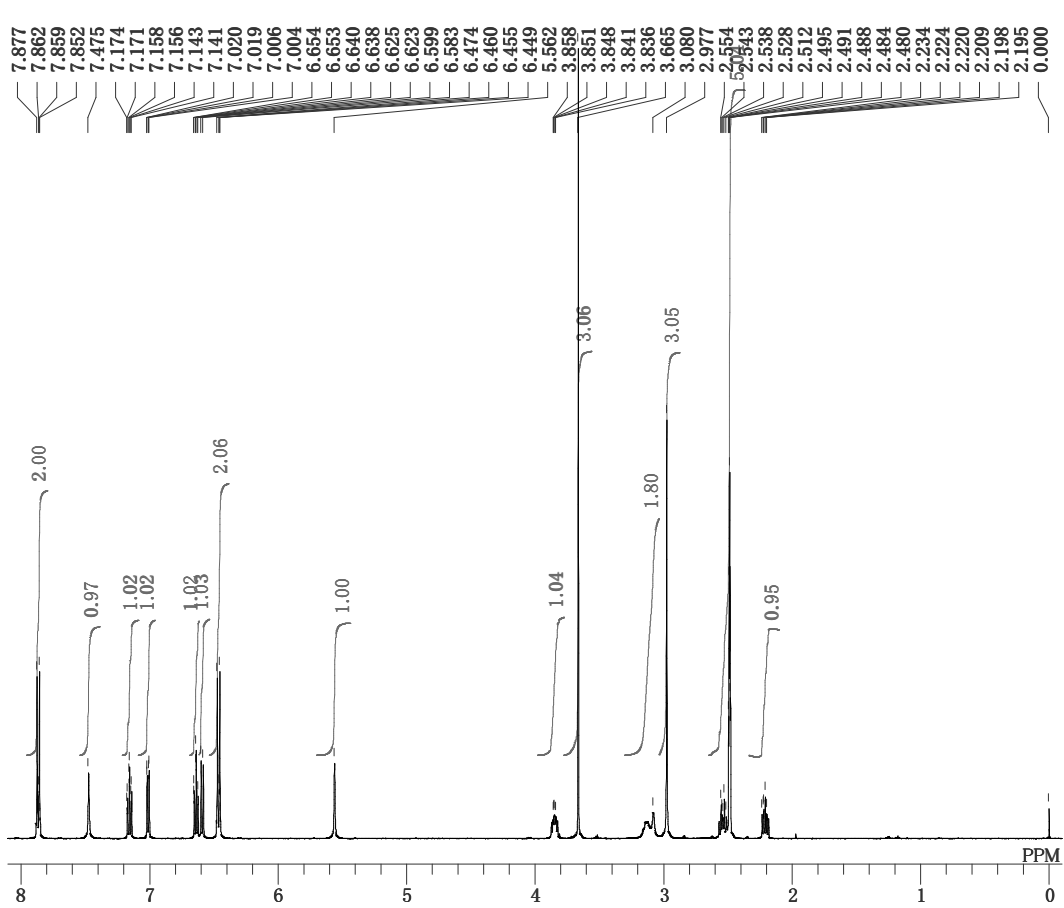


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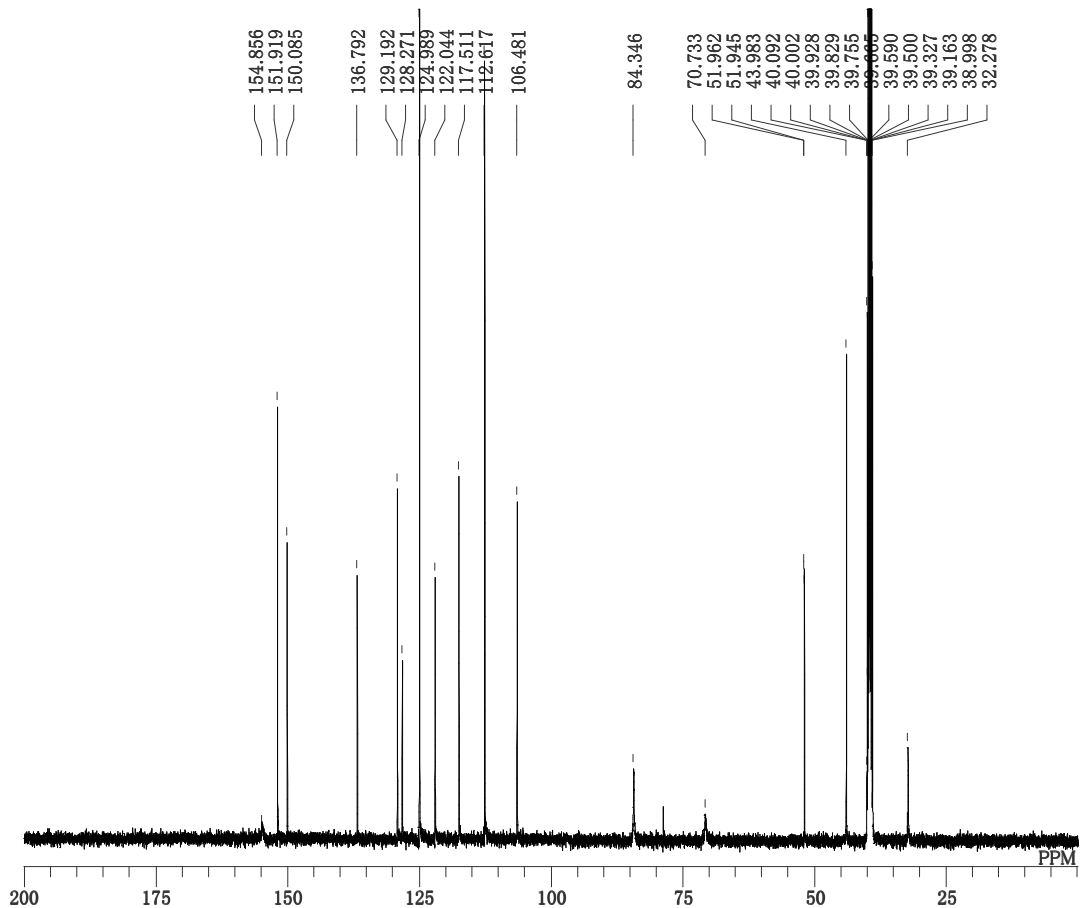
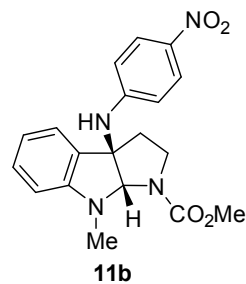


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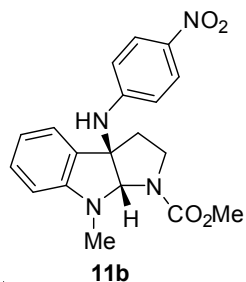


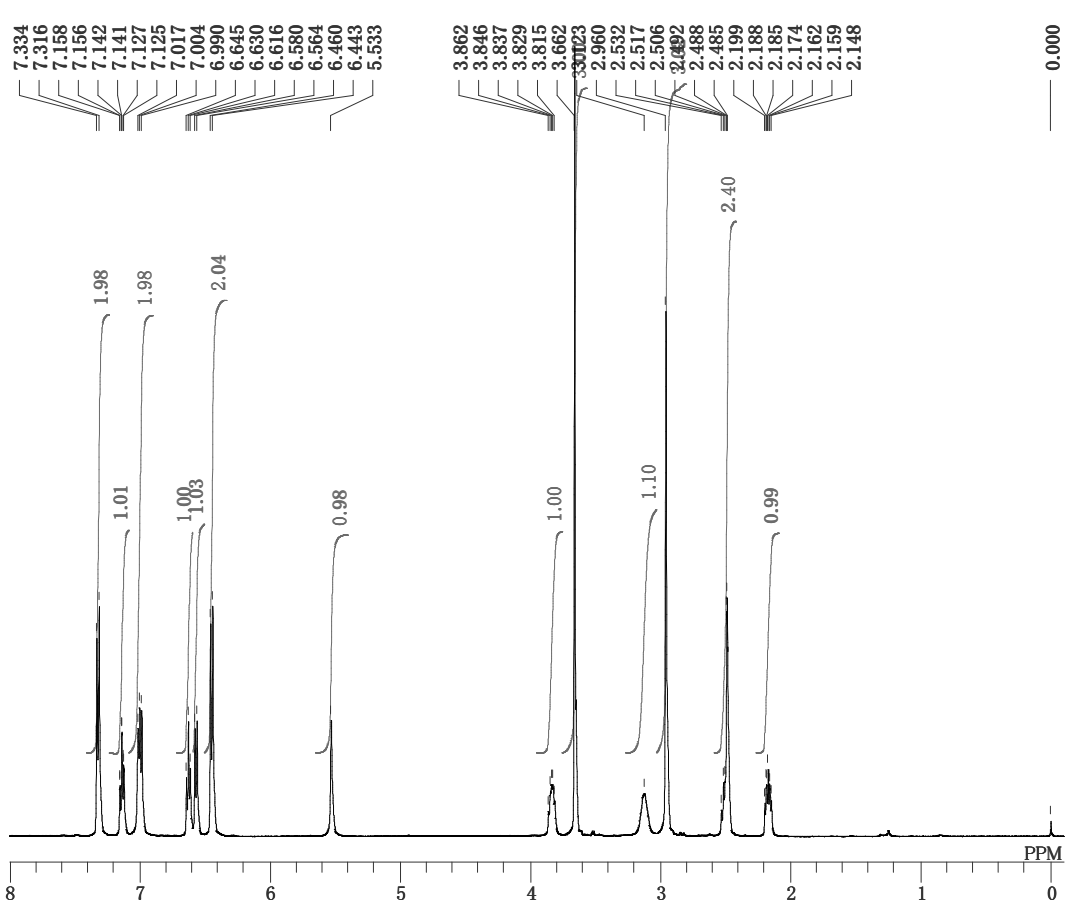


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 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 25

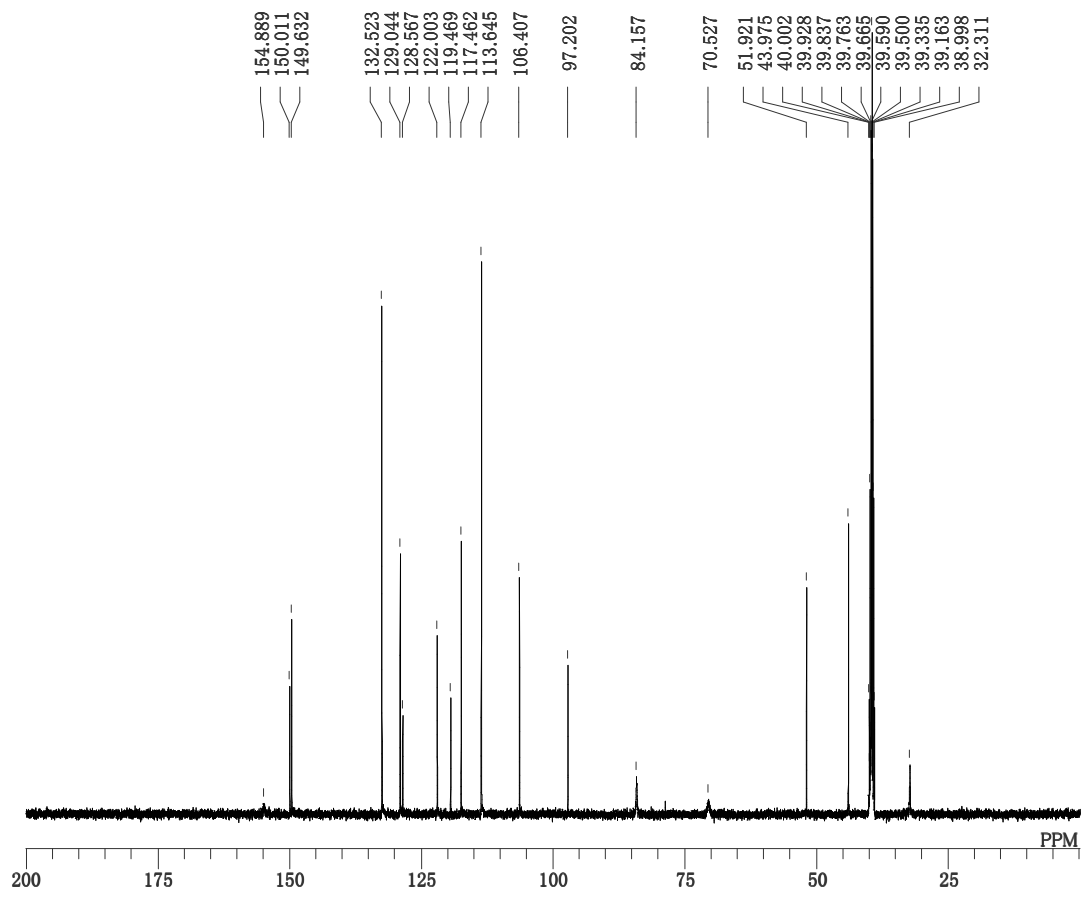
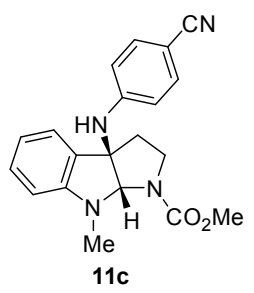


DFILE 11b C.als
 COMNT 11b C
 DATIM Tue Dec 30 13:23:08 2014
 13C
 OBNUC bcm
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 8000
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 0.12 Hz
 RGAIN 28

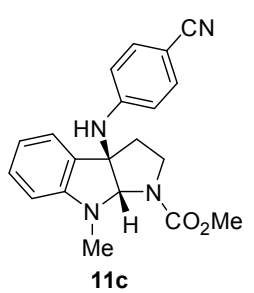


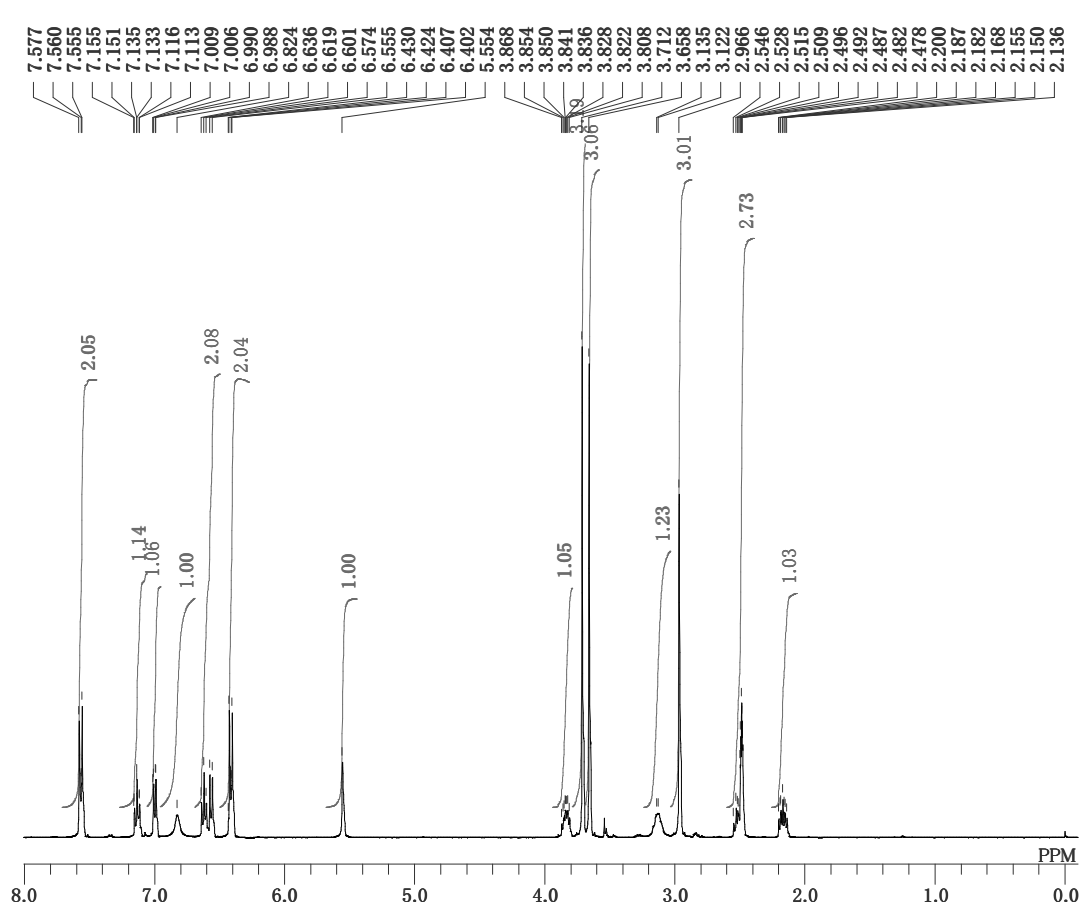


DFILE 11c H.als
 COMINT 11c H
 DATIM Wed Dec 31 03:44:10 2014
 1H
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.00 Hz
 POINT 32768
 FREQU 10000.00 Hz
 SCANS 16
 ACQTM 3.2768 sec
 PD 3.7232 sec
 PW1 5.00 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.09 Hz
 RGAIN 19

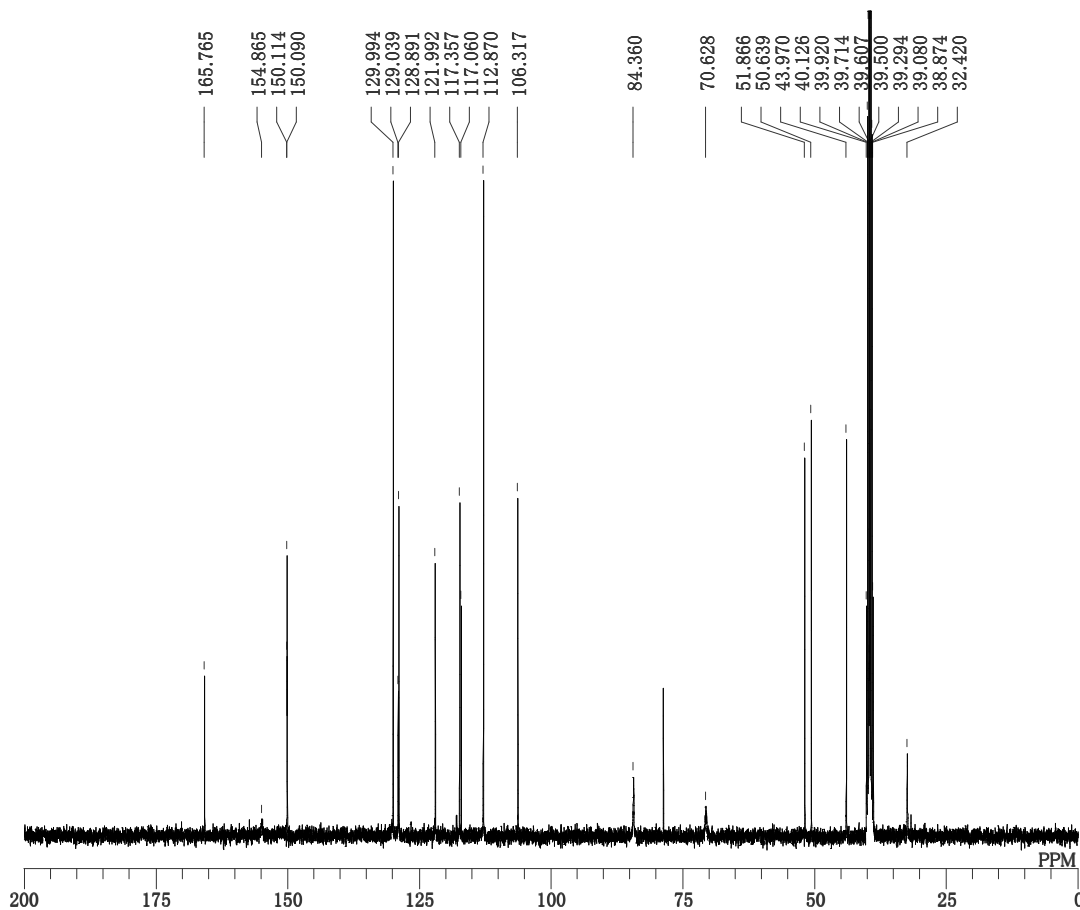
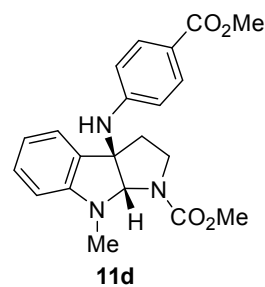


DFILE 11c C.als
 COMINT 11c C
 DATIM Wed Dec 31 04:36:38 2014
 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 1024
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 0.09 Hz
 RGAIN 28

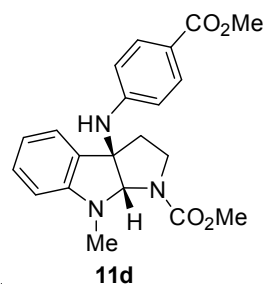


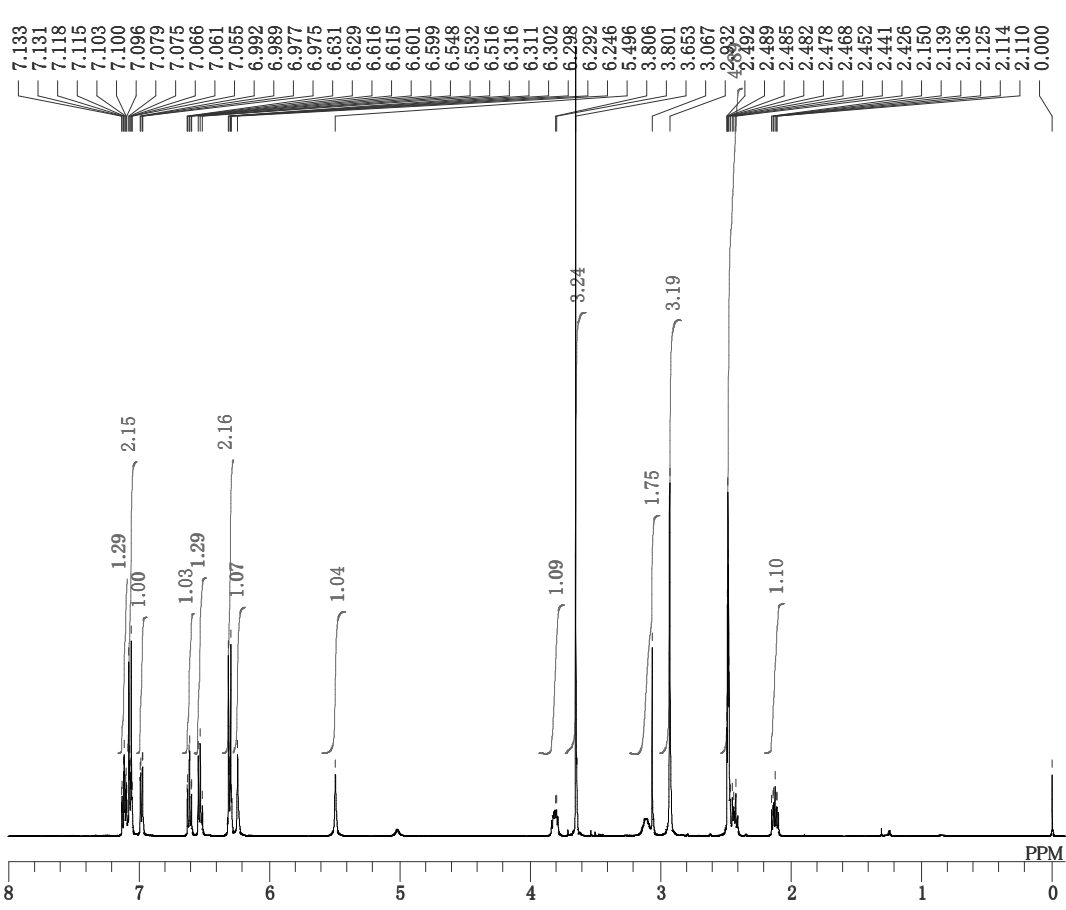


DFILE 11d H.als
COMNT 11d H
DATIM Sat Jan 10 15:27:05 2015
1H
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 80.2 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15

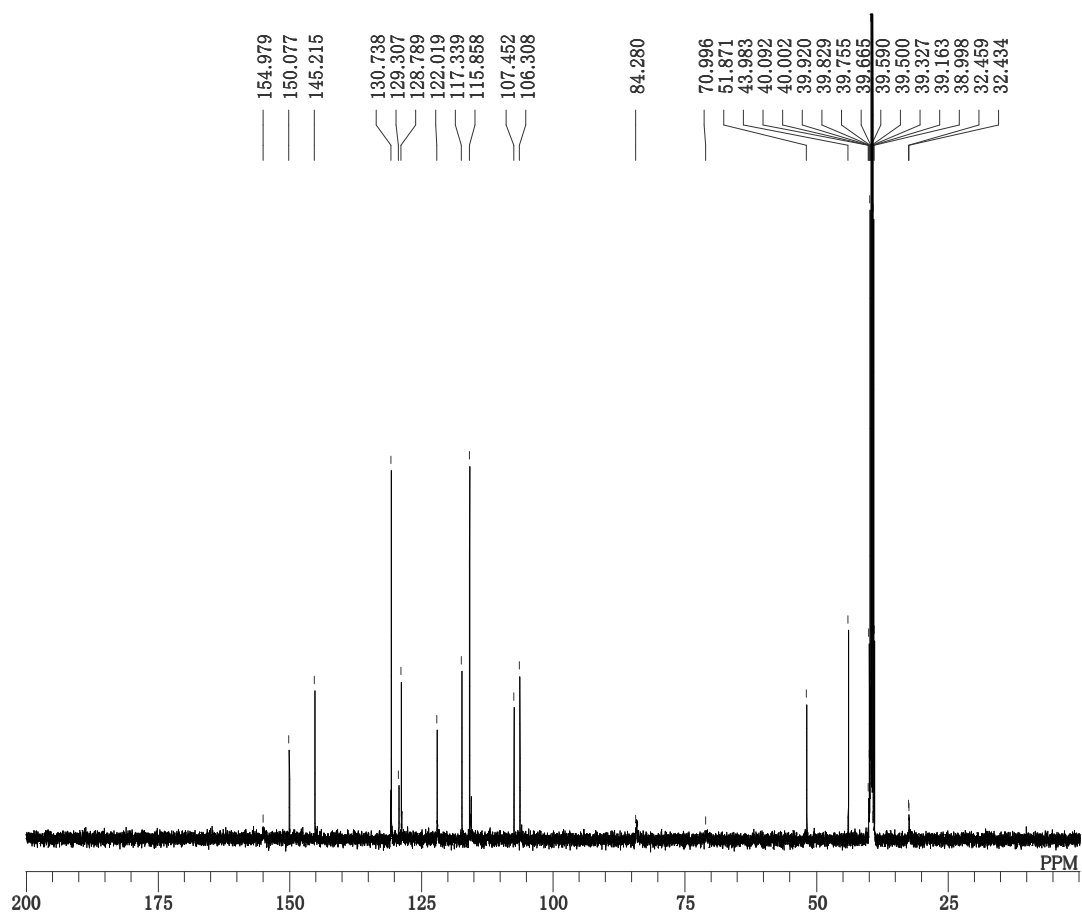
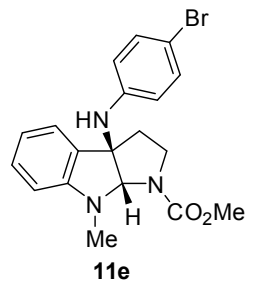


DFILE 11d C.als
COMNT 11d C
DATIM Sat Jan 10 16:45:37 2015
13C
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 1500
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 80.2 c
SLVNT DMSO
EXREF 39.50 ppm
BF 1.20 Hz
RGAIN 24

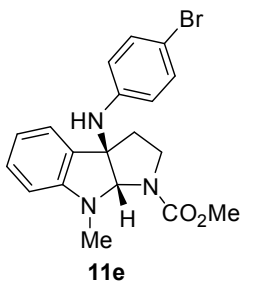


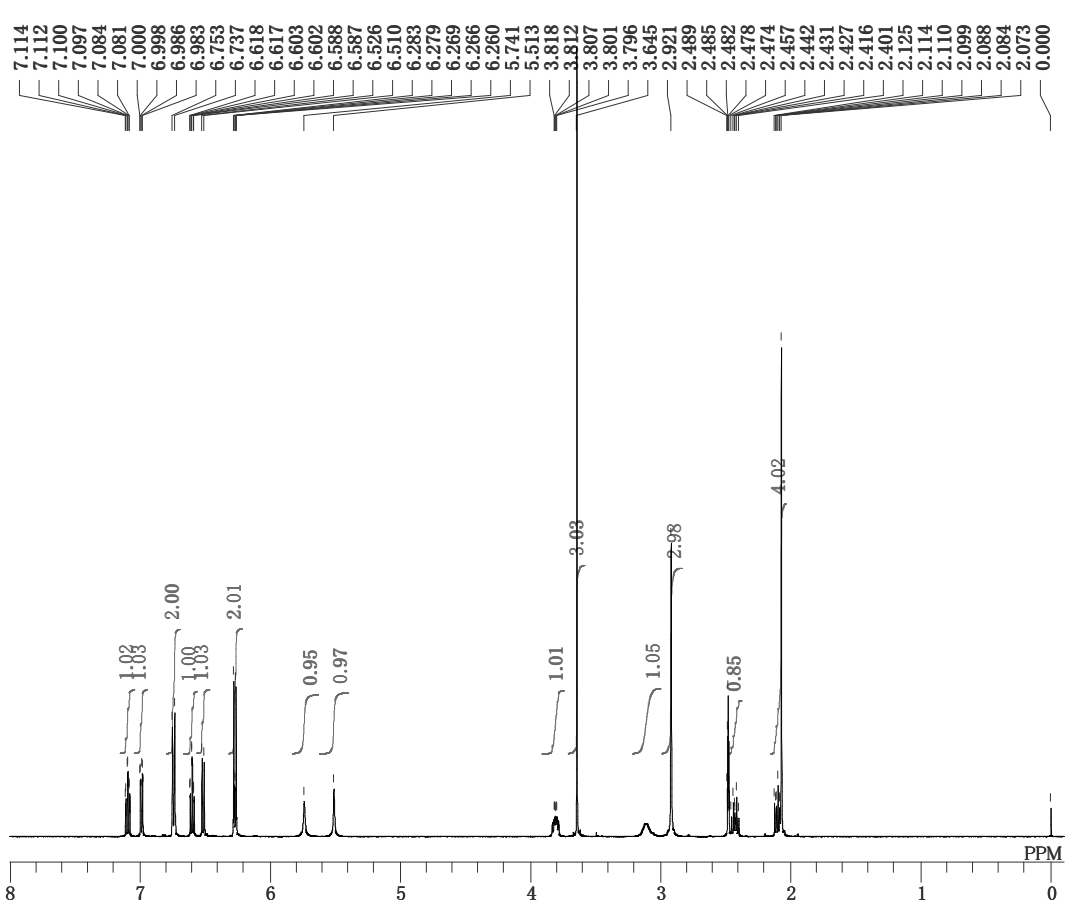


DFILE 11e H.als
 COMINT 11e H
 DATIM Mon Oct 20 23:03:57 2014
 OBNUC 1H
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.00 Hz
 POINT 32768
 FREQU 10000.00 Hz
 SCANS 16
 ACQTM 3.2768 sec
 PD 3.7232 sec
 PW1 5.00 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.09 Hz
 RGAIN 20

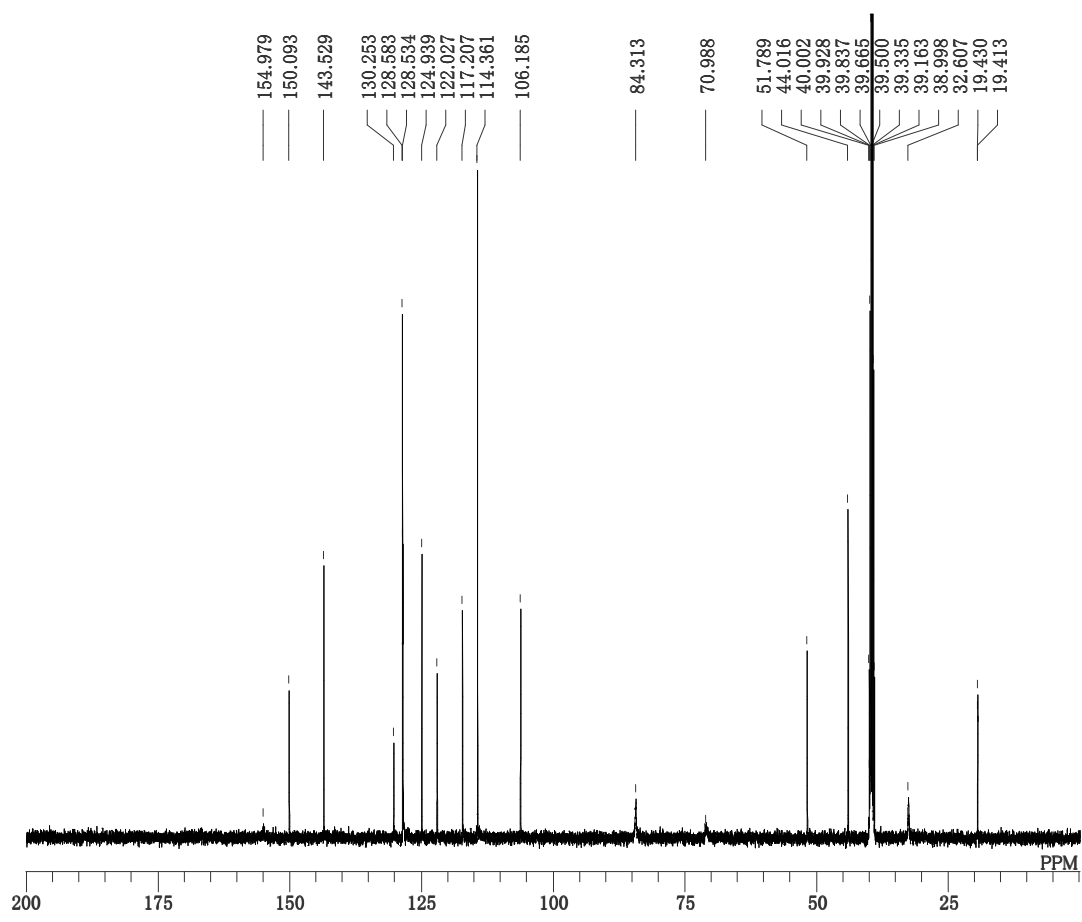
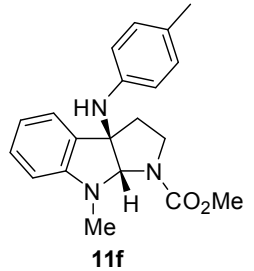


DFILE 11e C.als
 COMINT 11e C
 DATIM Tue Dec 30 05:49:27 2014
 OBNUC 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 1024
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 79.9 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 0.12 Hz
 RGAIN 27

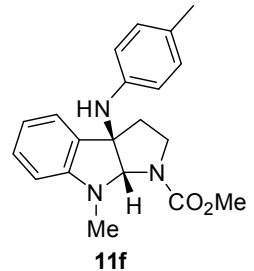


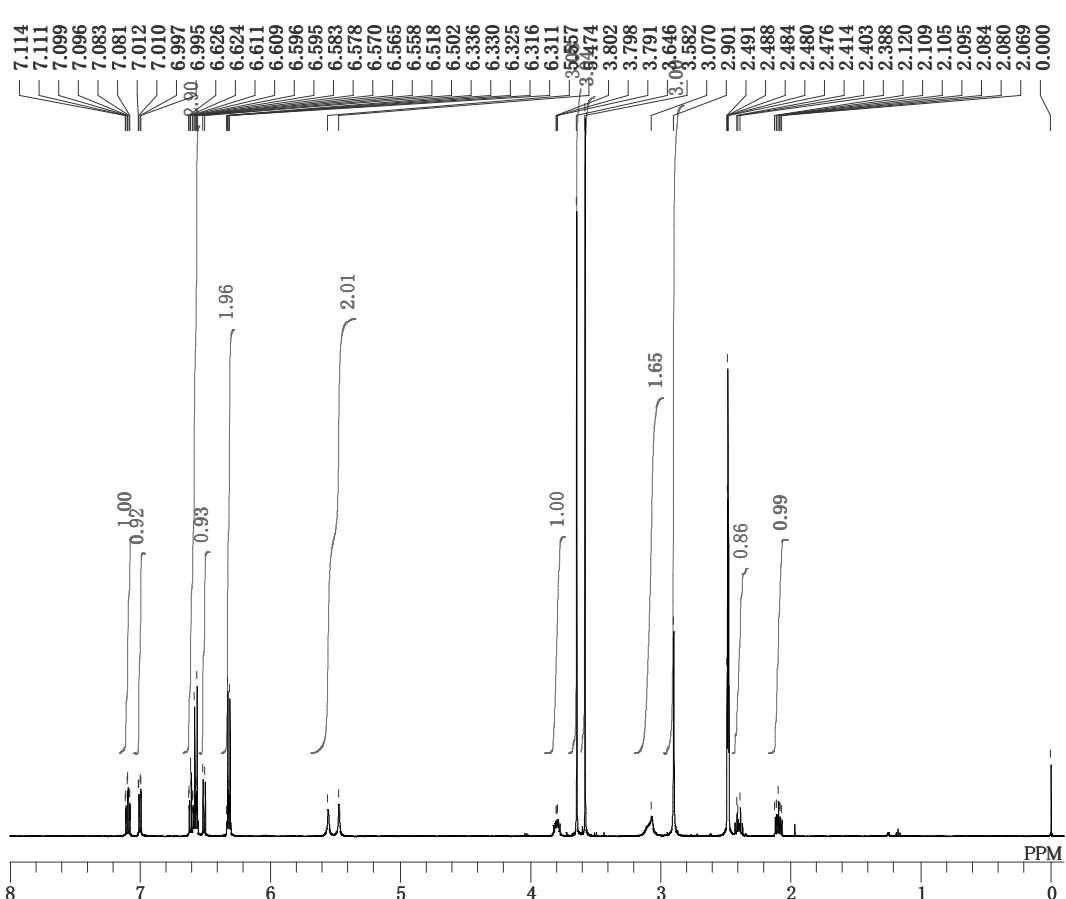


DFILE 11f H.als
COMNT 11f H
DATIM Wed Dec 31 05:16:46 2014
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 22

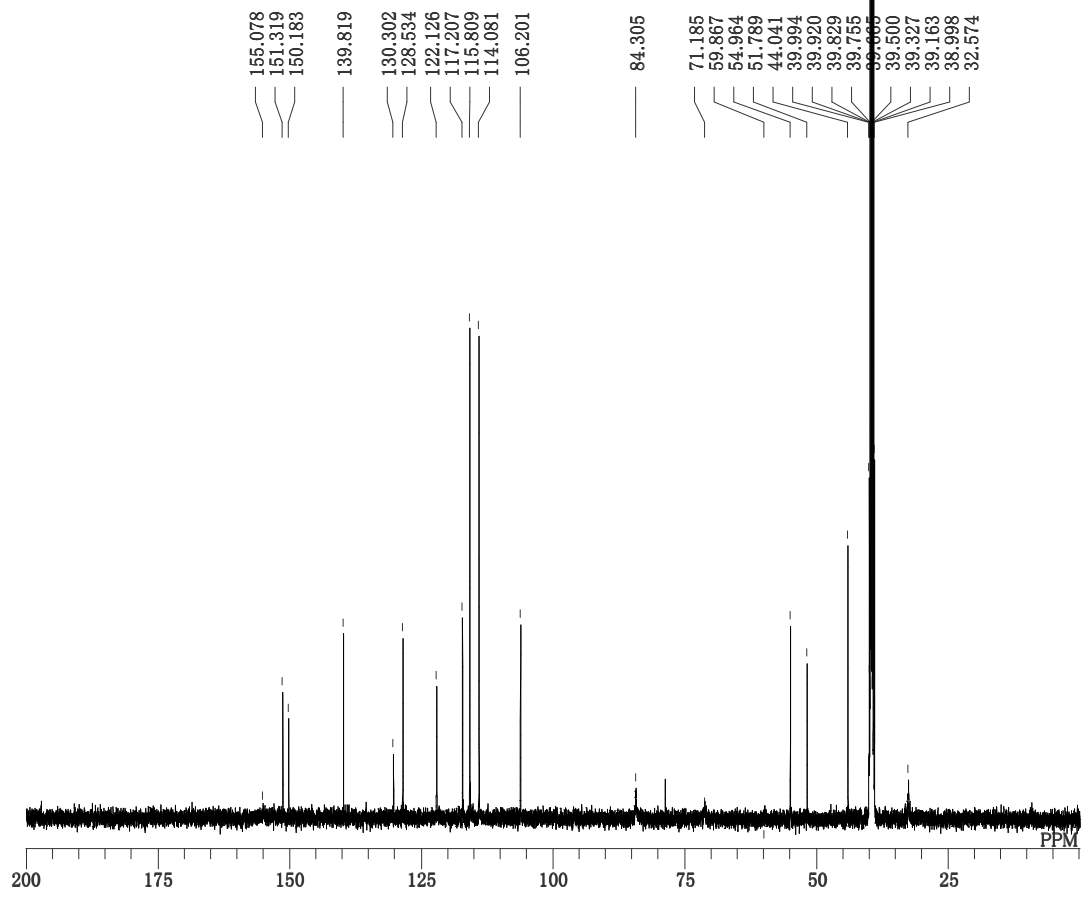
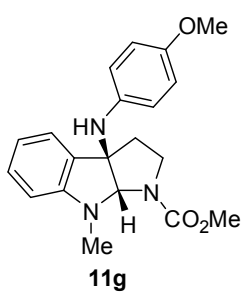


DFILE 11f C.als
COMNT 11f C
DATIM Wed Dec 31 05:58:02 2014
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 800
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 4.40 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.12 Hz
RGAIN 28

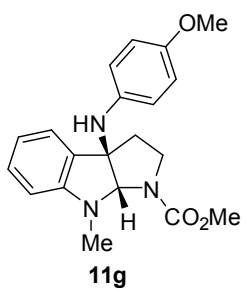


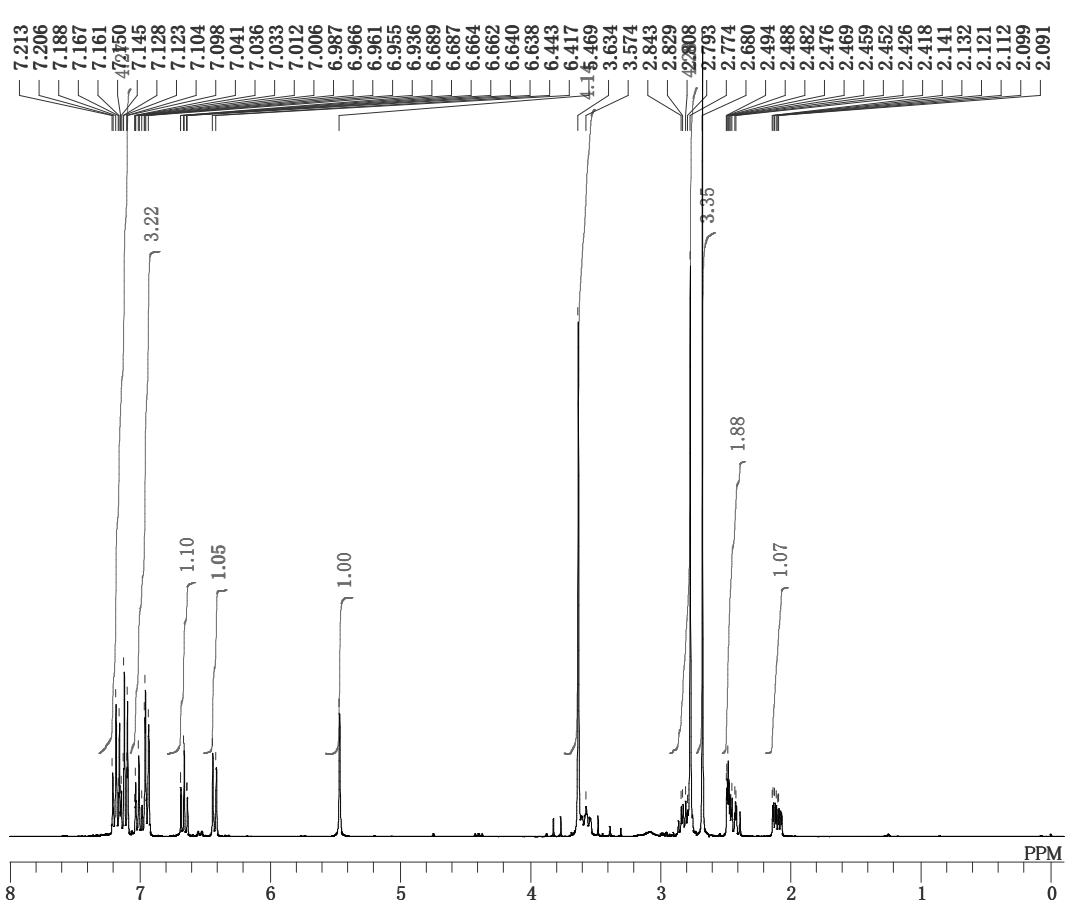


DFILE 11g H.als
COMNT 11g H
DATIM Sun Jan 4 18:33:06 2015
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 23

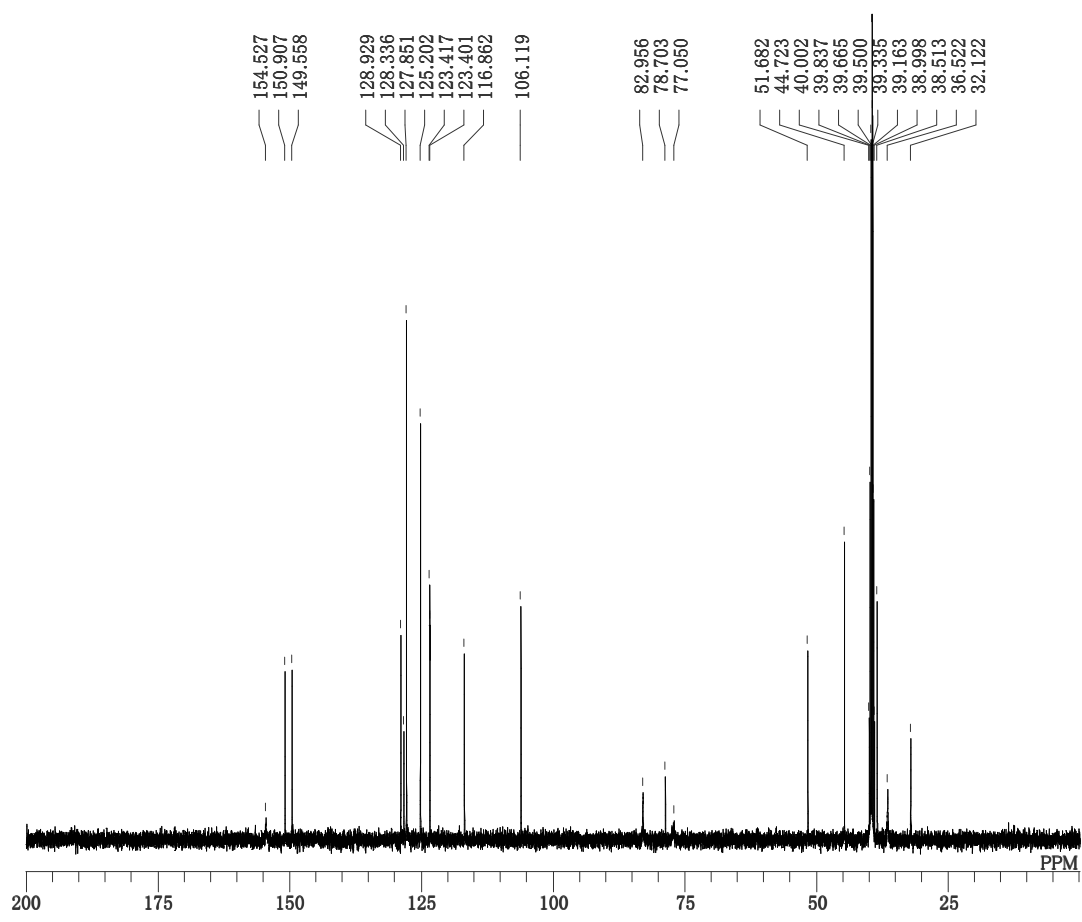
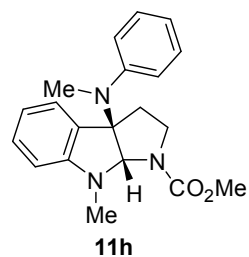


DFILE 11g C.als
COMNT 11g C
DATIM Mon Jan 5 04:09:04 2015
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 3000
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 4.40 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 39.50 ppm
BF 2.00 Hz
RGAIN 27

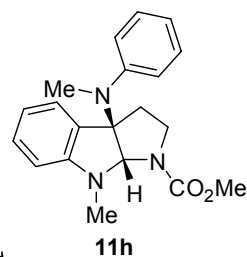


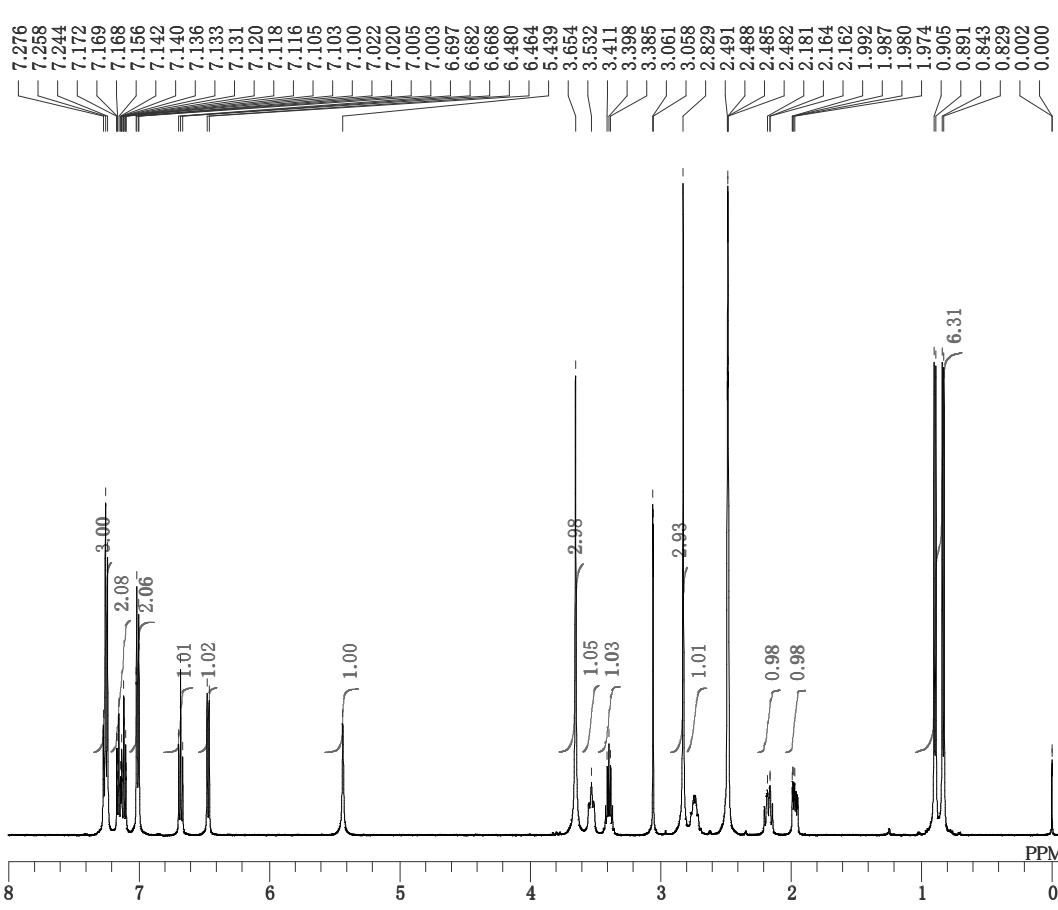


DFILE 11h H.als
 COMNT 11h H
 DATIM Mon Jan 19 16:50:28 2015
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.00 Hz
 POINT 32768
 FREQU 6006.01 Hz
 SCANS 8
 ACQTM 5.4559 sec
 PD 1.5440 sec
 PW1 5.30 usec
 IRNUC 1H
 CTEMP 80.4 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 13

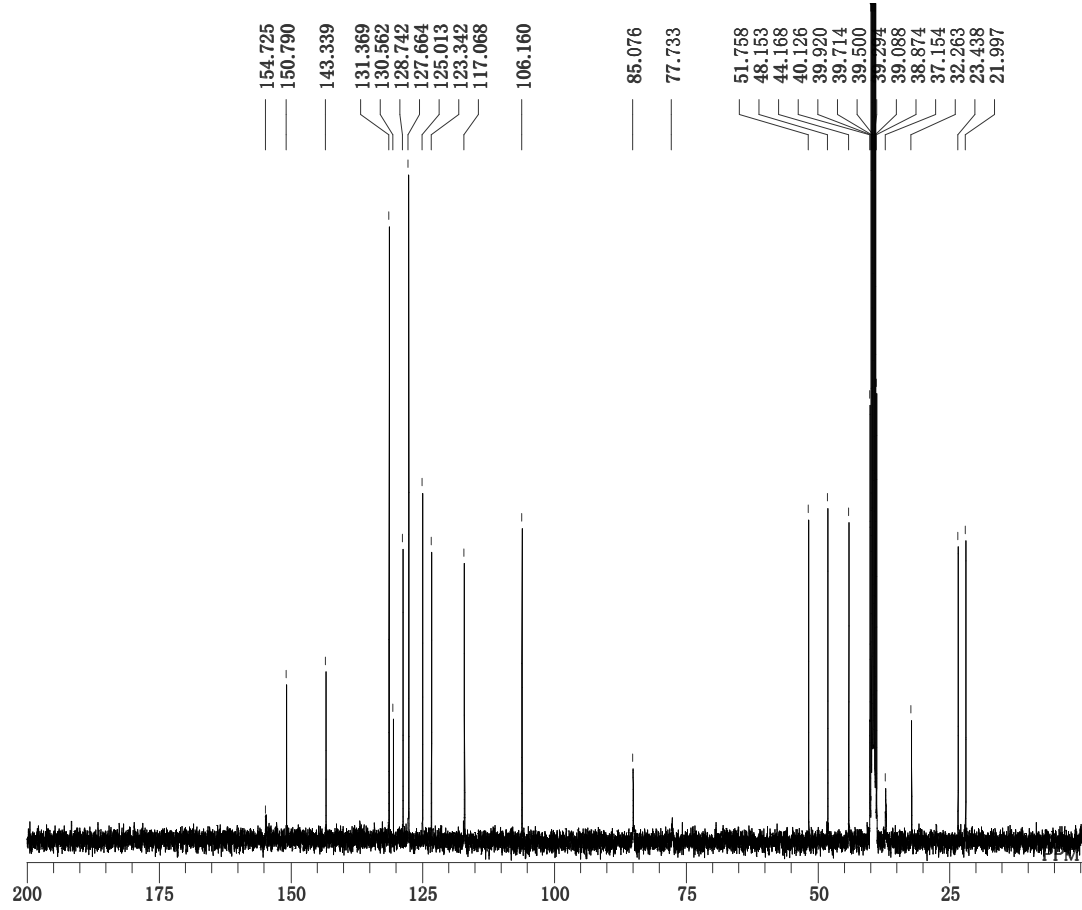
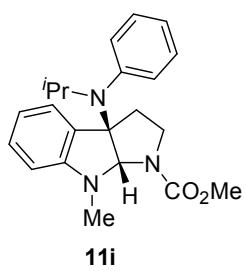


DFILE 11h C.als
 COMNT 11h C
 DATIM Wed Jan 16 21:56:11 2013
 OBNUC 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 128
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 5.40 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 0.12 Hz
 RGAIN 28

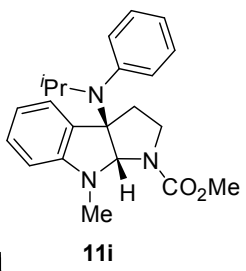


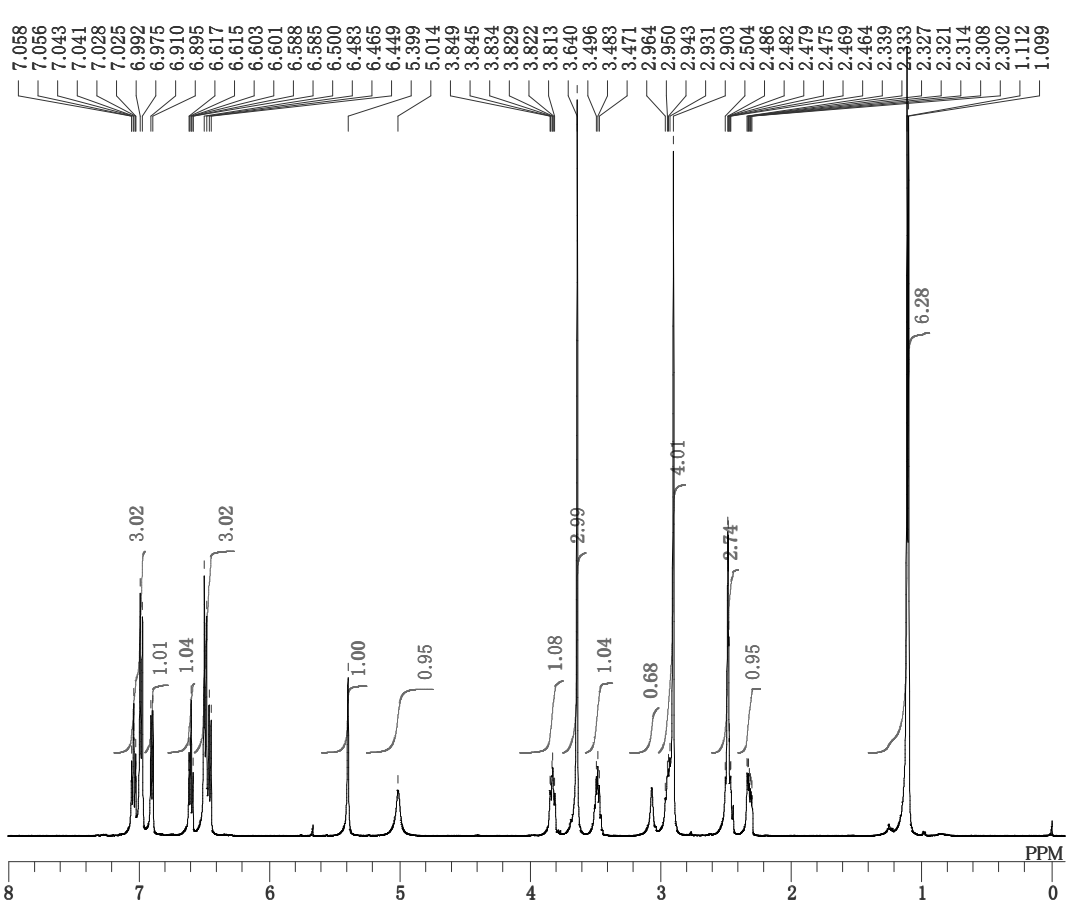


DFILE 11i H.als
 COMINT 11i H
 DATIM Sat Nov 15 21:16:15 2014
 1H
 OBNUC non
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.00 Hz
 POINT 32768
 FREQU 10000.00 Hz
 SCANS 16
 ACQTM 3.2768 sec
 PD 3.7232 sec
 PW1 5.00 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.09 Hz
 RGAIN 23

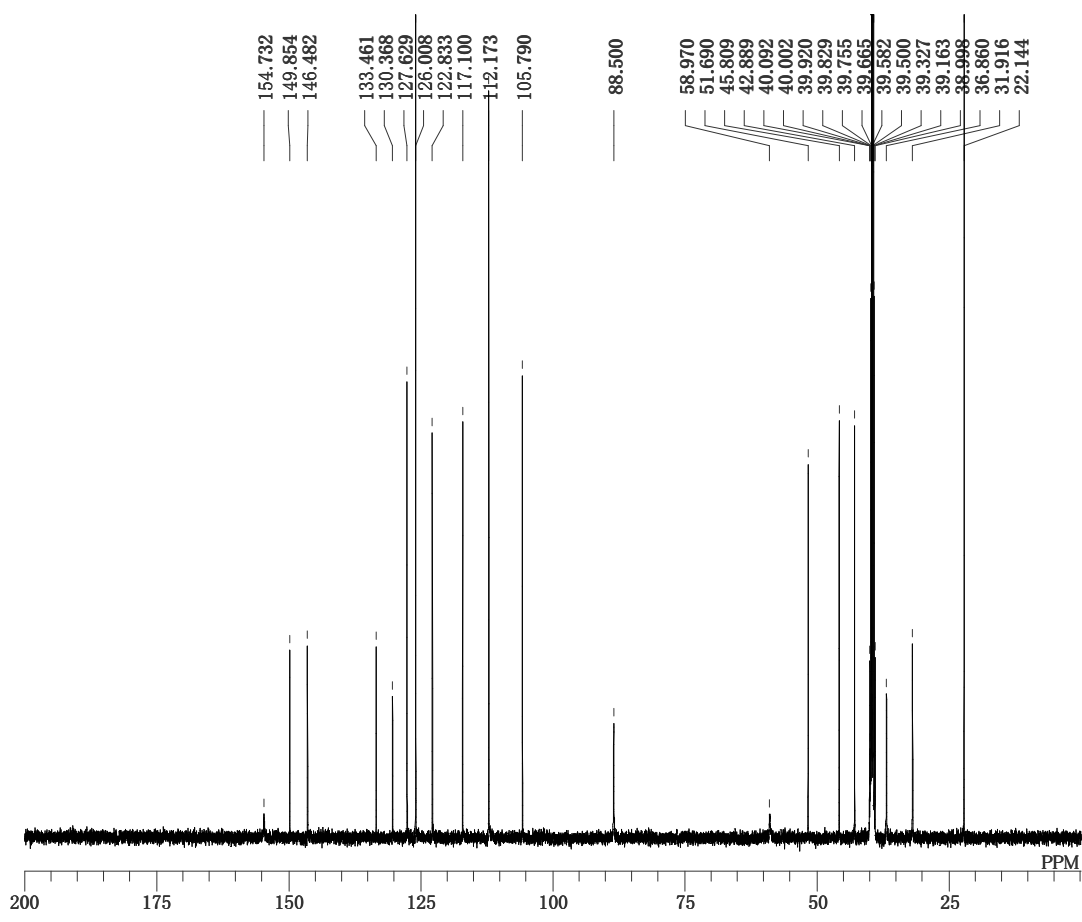
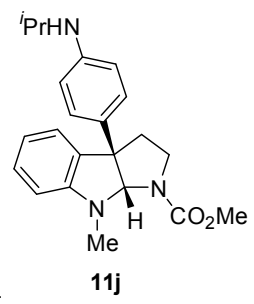


DFILE 11i C.als
 COMINT 11i C
 DATIM Thu Jan 29 23:11:29 2015
 13C
 OBNUC BCM
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
 SCANS 3000
 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 6.00 usec
 IRNUC 1H
 CTEMP 80.2 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 1.20 Hz
 RGAIN 24

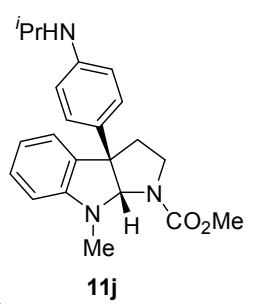


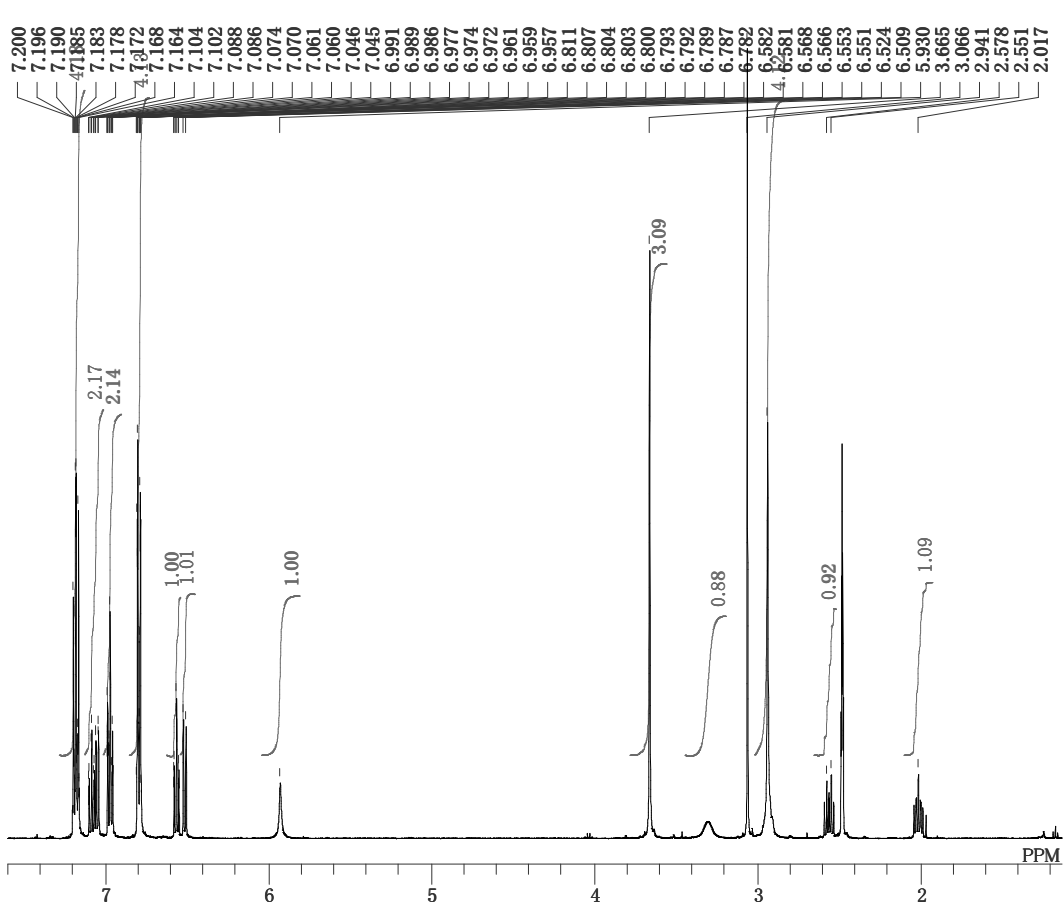


DFILE 11j H.als
 COMNT 11j H
 DATIM Sun Nov 16 21:05:42 2014
 OBNUC 1H
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.00 Hz
 POINT 32768
 FREQU 10000.00 Hz
 SCANS 8
 ACQTM 3.2768 sec
 PD 3.7232 sec
 PW1 5.00 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.09 Hz
 RGAIN 18

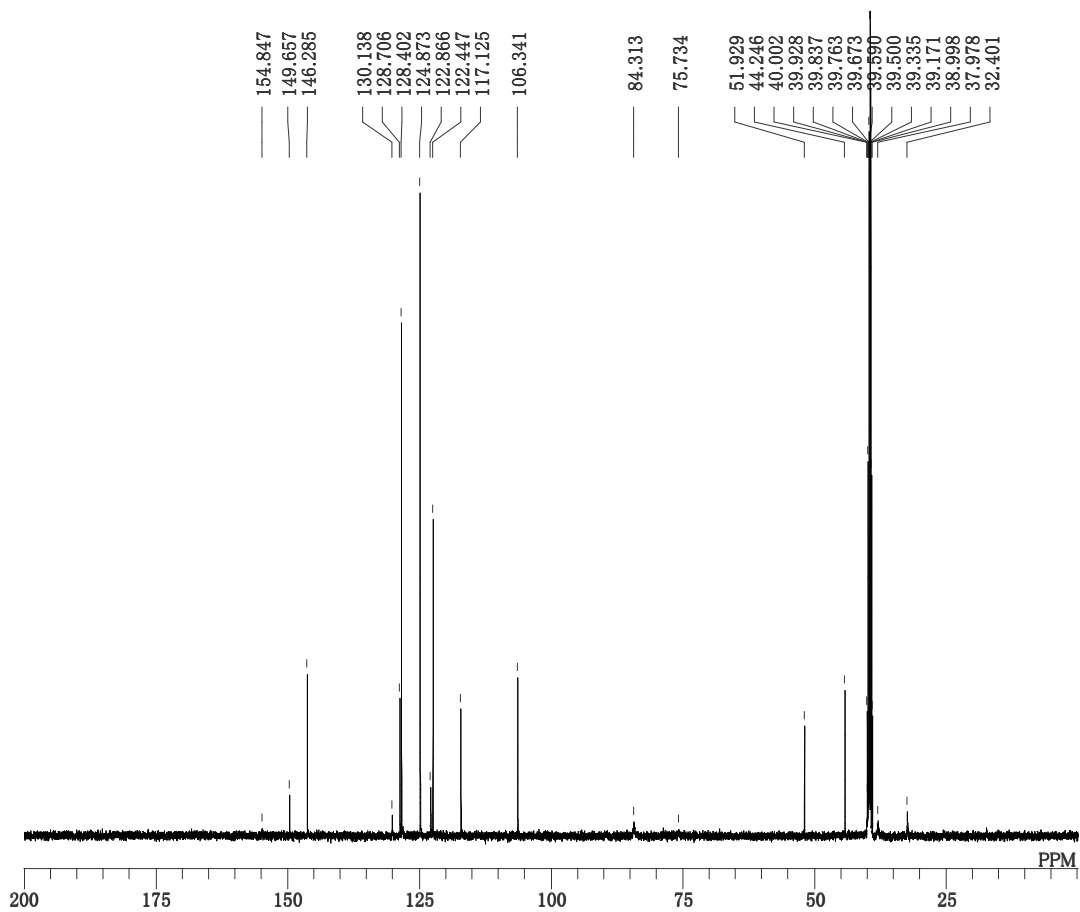
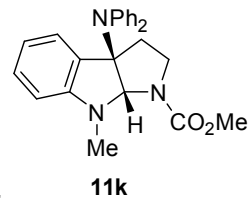


DFILE 11j C.als
 COMNT 11j C
 DATIM Sun Nov 16 22:27:00 2014
 OBNUC 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 1600
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 0.09 Hz
 RGAIN 28

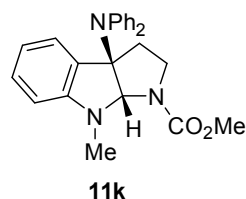


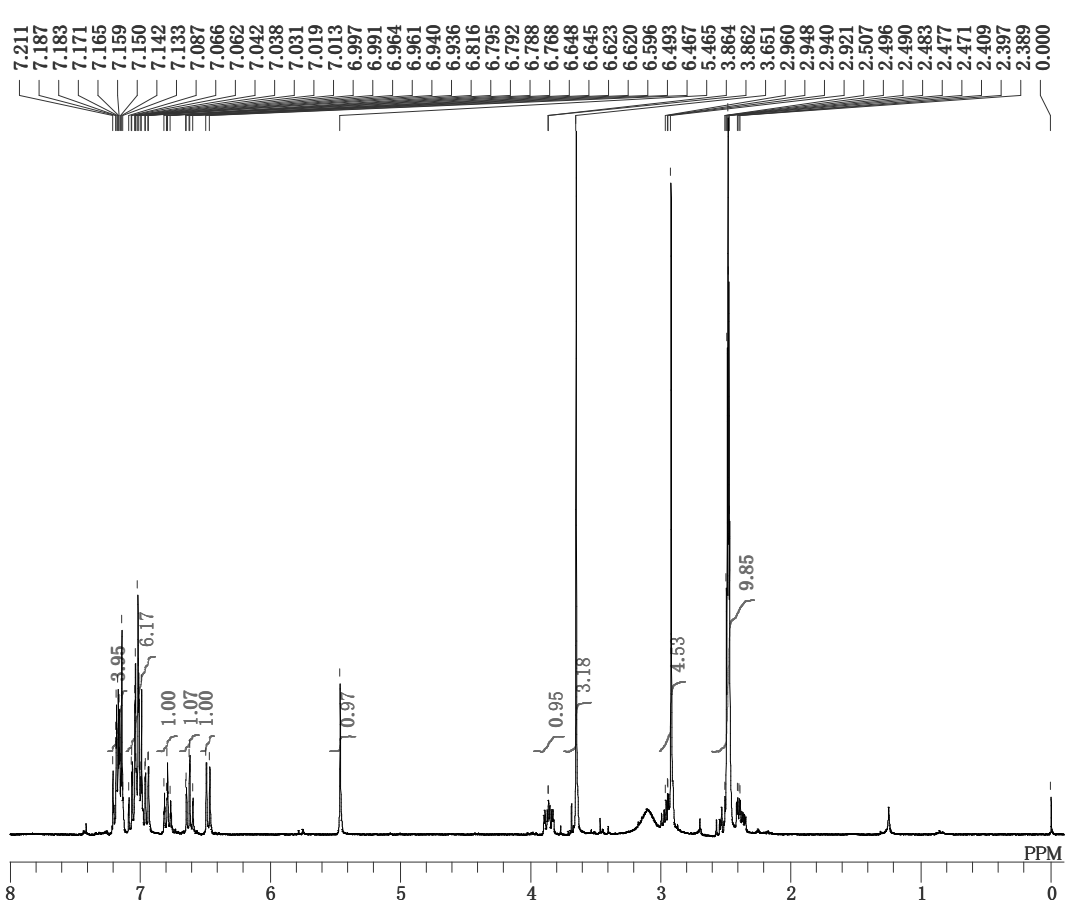


DFILE 11k H.als
COMNT 11k H
DATIM Sun Feb 23 04:37:15 2014
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 21

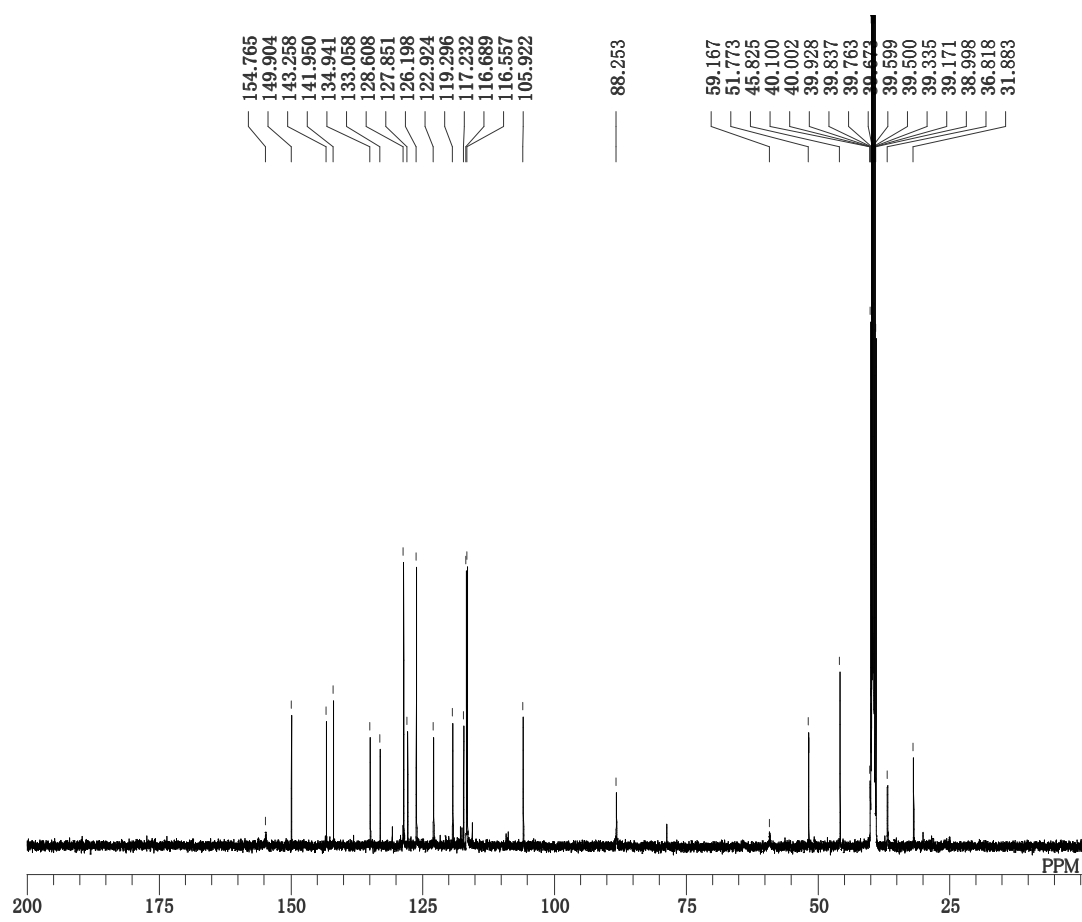
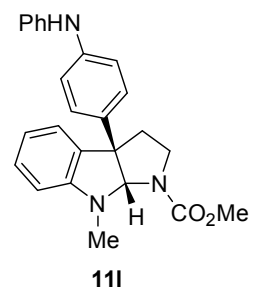


DFILE 11k C.als
COMNT 11k C
DATIM Sun Feb 23 05:42:27 2014
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 1024
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 4.40 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.12 Hz
RGAIN 27

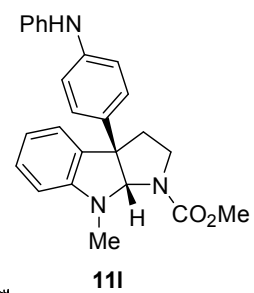


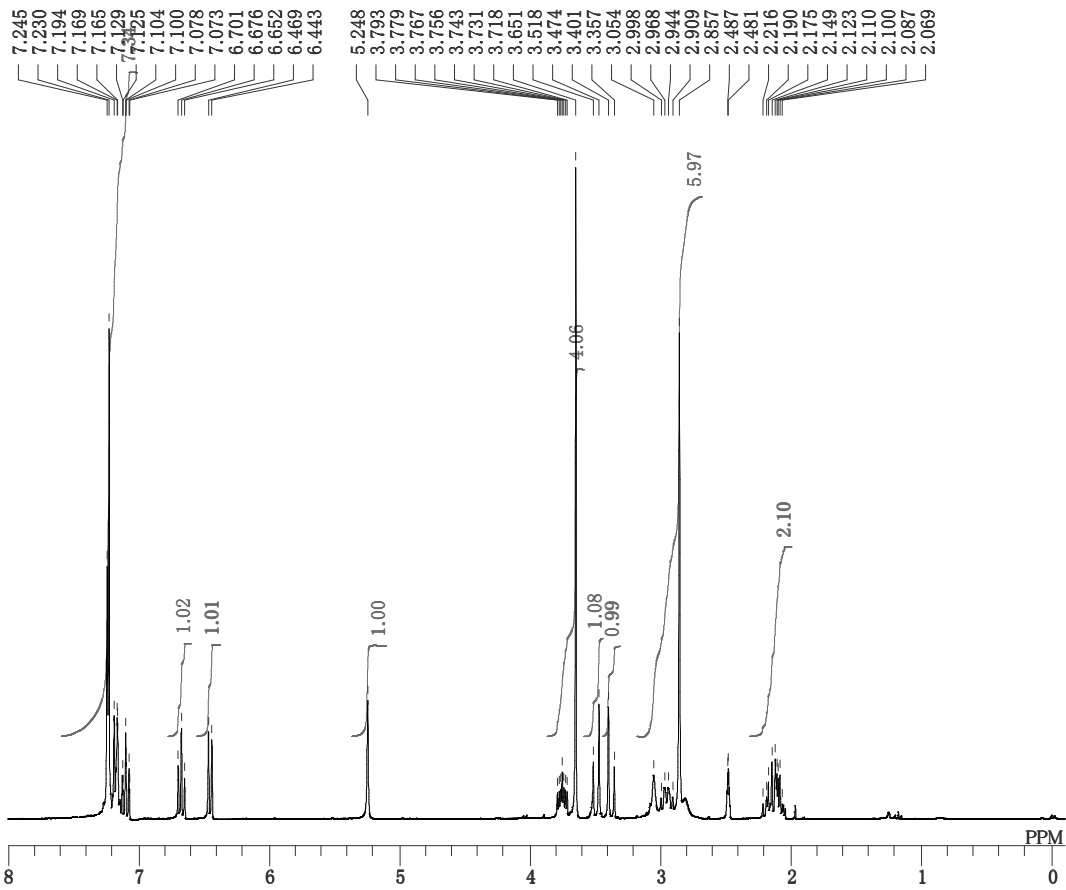


DFILE 11I H.als
 COMNT 11I H
 DATIM Mon Jan 19 17:03:00 2015
 OBNUC 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.00 Hz
 POINT 32768
 FREQU 6006.01 Hz
 SCANS 16
 ACQTM 5.4559 sec
 PD 1.5440 sec
 PW1 5.30 usec
 IRNUC 1H
 CTEMP 80.5 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

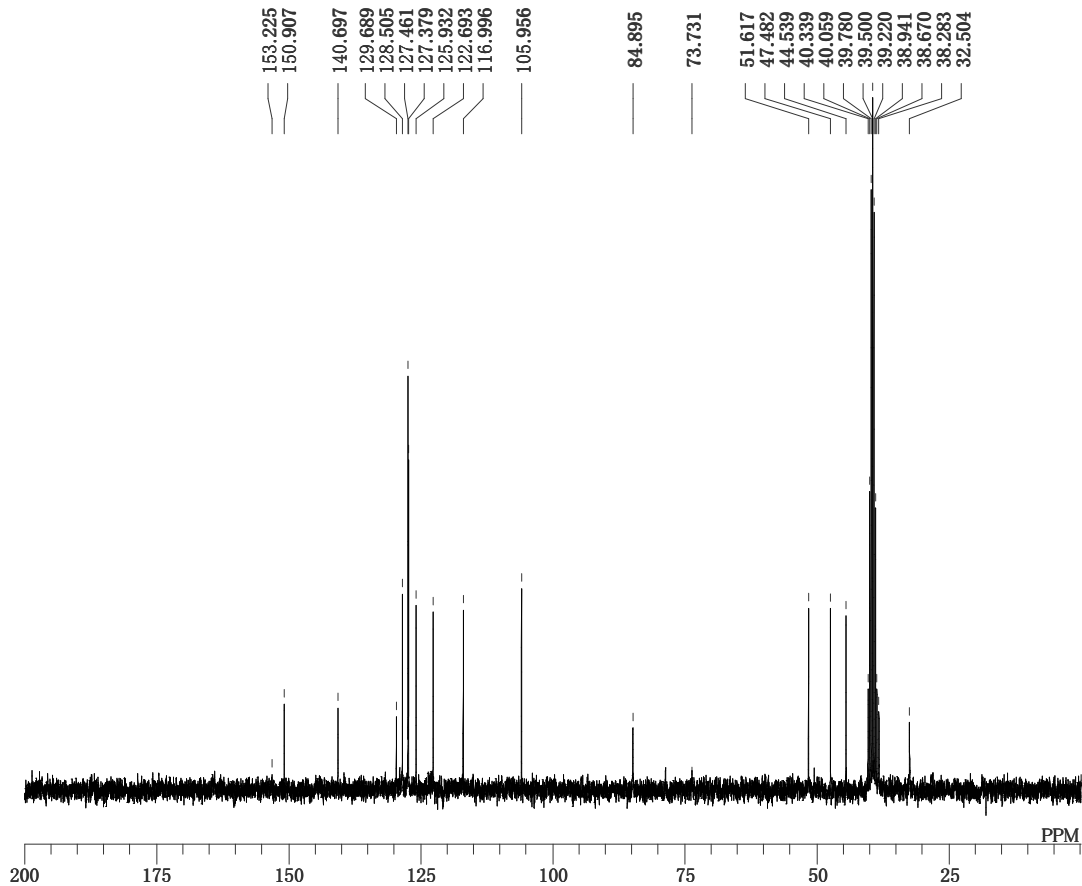
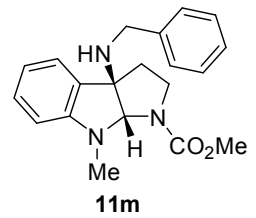


DFILE 11I C.als
 COMNT 11I C
 DATIM Sat Jan 10 14:47:44 2015
 OBNUC 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 10000
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 79.9 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 1.20 Hz
 RGAIN 27

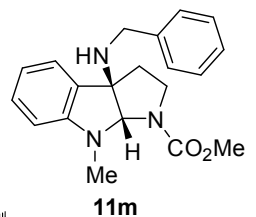


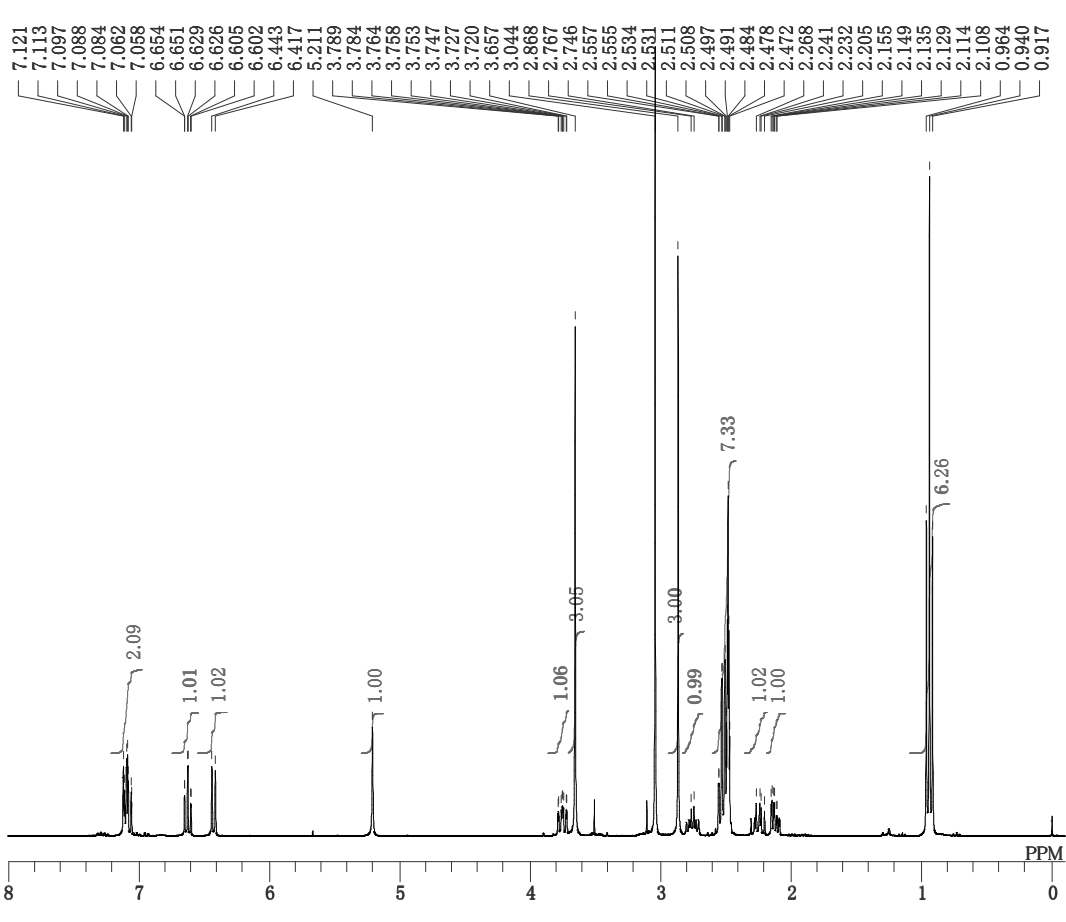


DFILE 11m H.als
 COMNT 11m H
 DATIM Sat Jan 11 10:22:01 2014
 1H
 EXMOD NON
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.00 Hz
 POINT 32768
 FREQU 6006.01 Hz
 SCANS 16
 ACQTM 5.4559 sec
 PD 1.5440 sec
 PW1 5.30 usec
 IRNUC 1H
 CTEMP 81.0 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 14

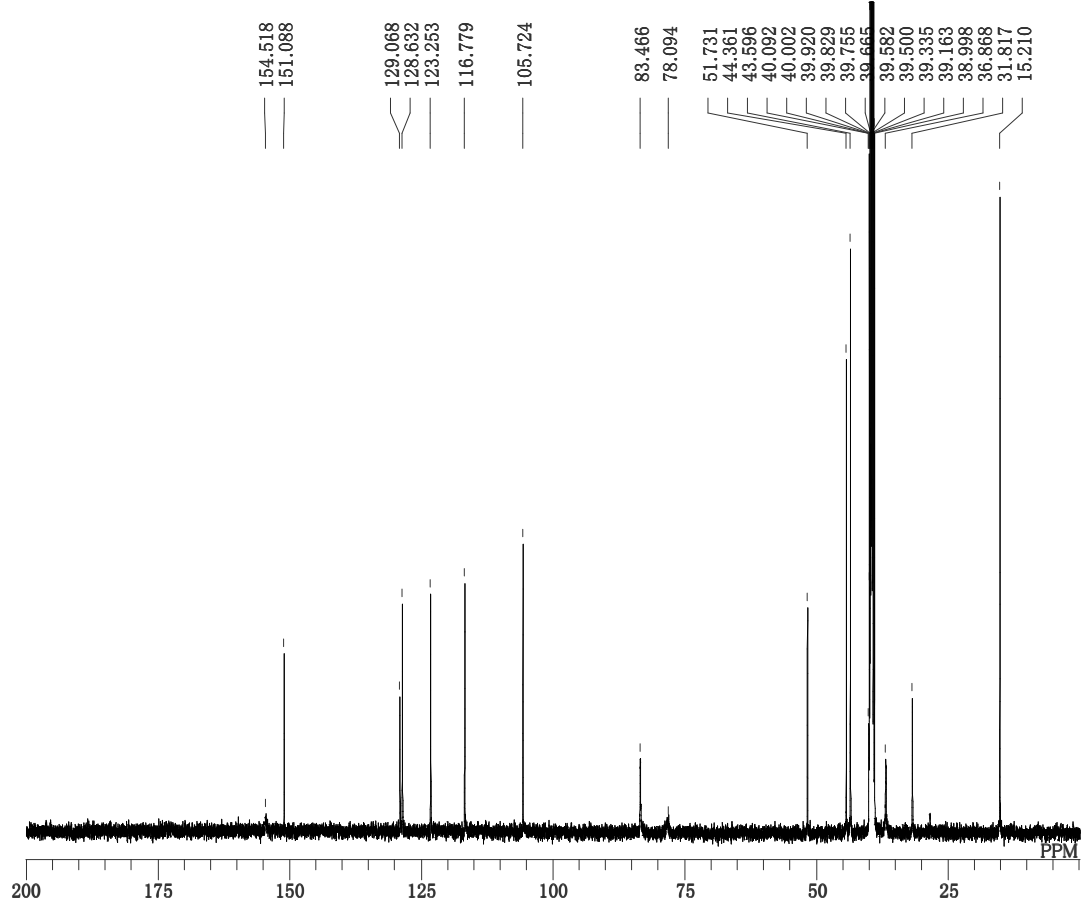
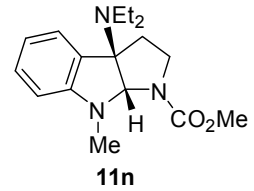


DFILE 11m C.als
 COMNT 11m C
 DATIM Fri Dec 06 10:07:00 2013
 13C
 EXMOD BCM
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFIN 1840.00 Hz
 POINT 32768
 FREQU 20356.23 Hz
 SCANS 400
 ACQTM 1.6097 sec
 PD 1.3900 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 81.1 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 1.20 Hz
 RGAIN 24

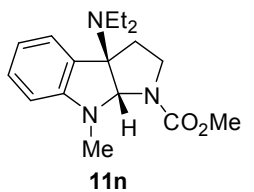


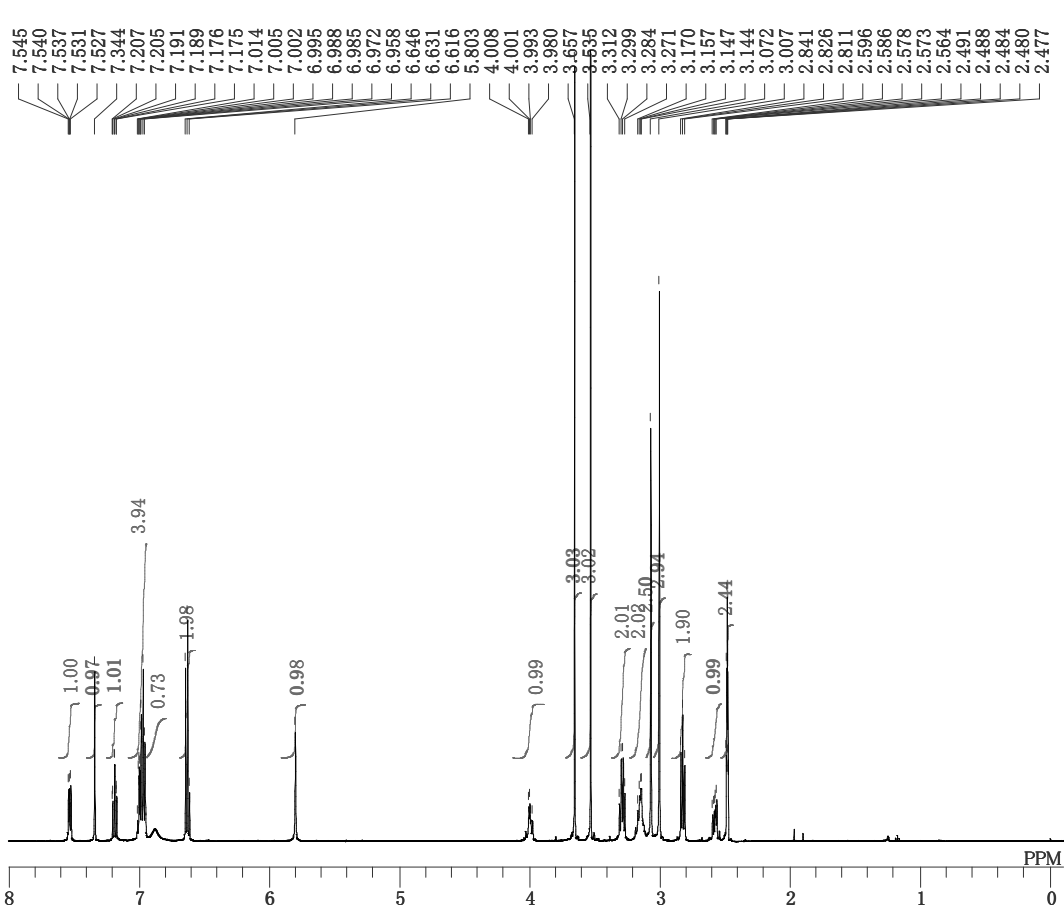


DFILE 11n H.als
 COMINT 11n H
 DATIM Thu Dec 26 10:36:31 2013
 1H
 OBNUC NON
 EXMOD
 OBFRQ 300.40 MHz
 OBSET 130.00 KHz
 OBFIN 1150.00 Hz
 POINT 32768
 FREQU 6006.01 Hz
 SCANS 32
 ACQTM 5.4559 sec
 PD 1.5440 sec
 PW1 5.30 usec
 IRNUC 1H
 CTEMP 81.0 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 17

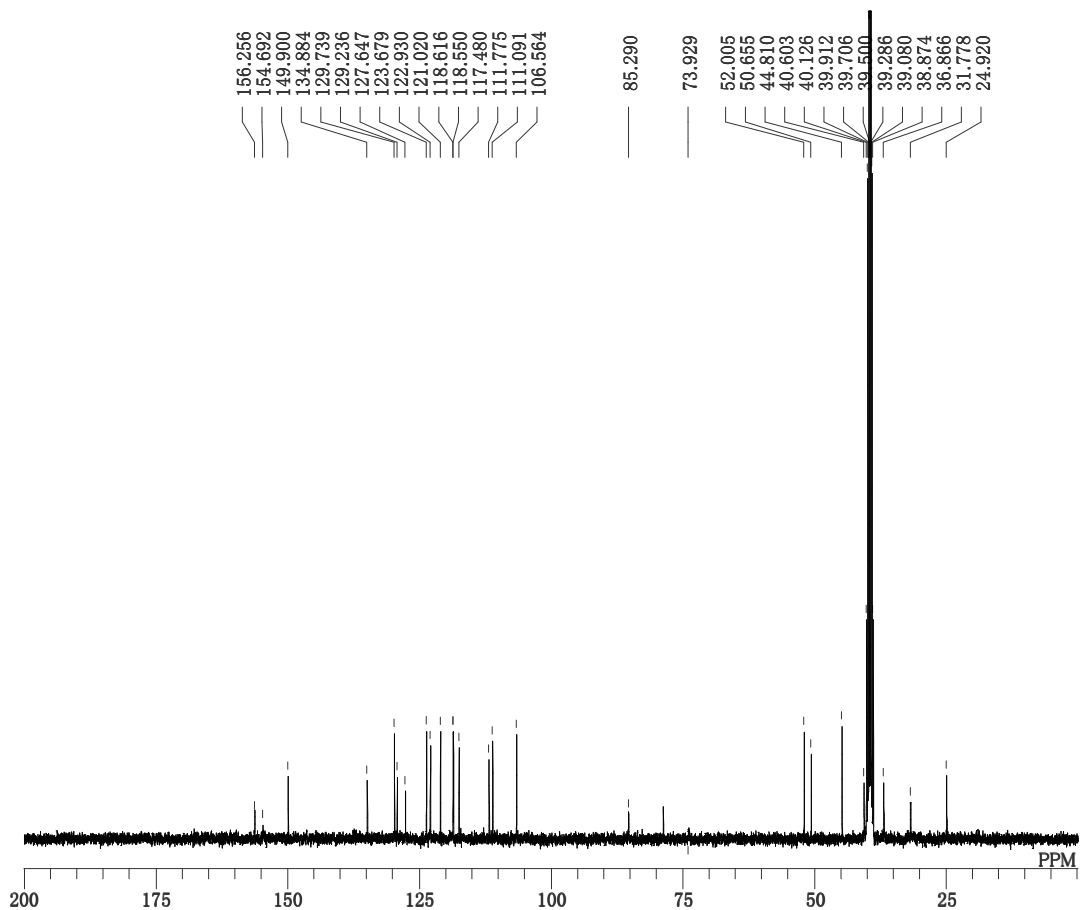
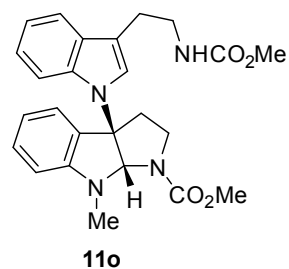


DFILE 11n C.als
 COMINT 11n C
 DATIM Mon Jan 5 14:31:45 2015
 13C
 OBNUC bcm
 EXMOD
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 12000
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 1.20 Hz
 RGAIN 27

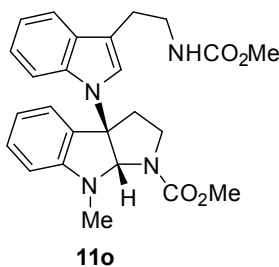


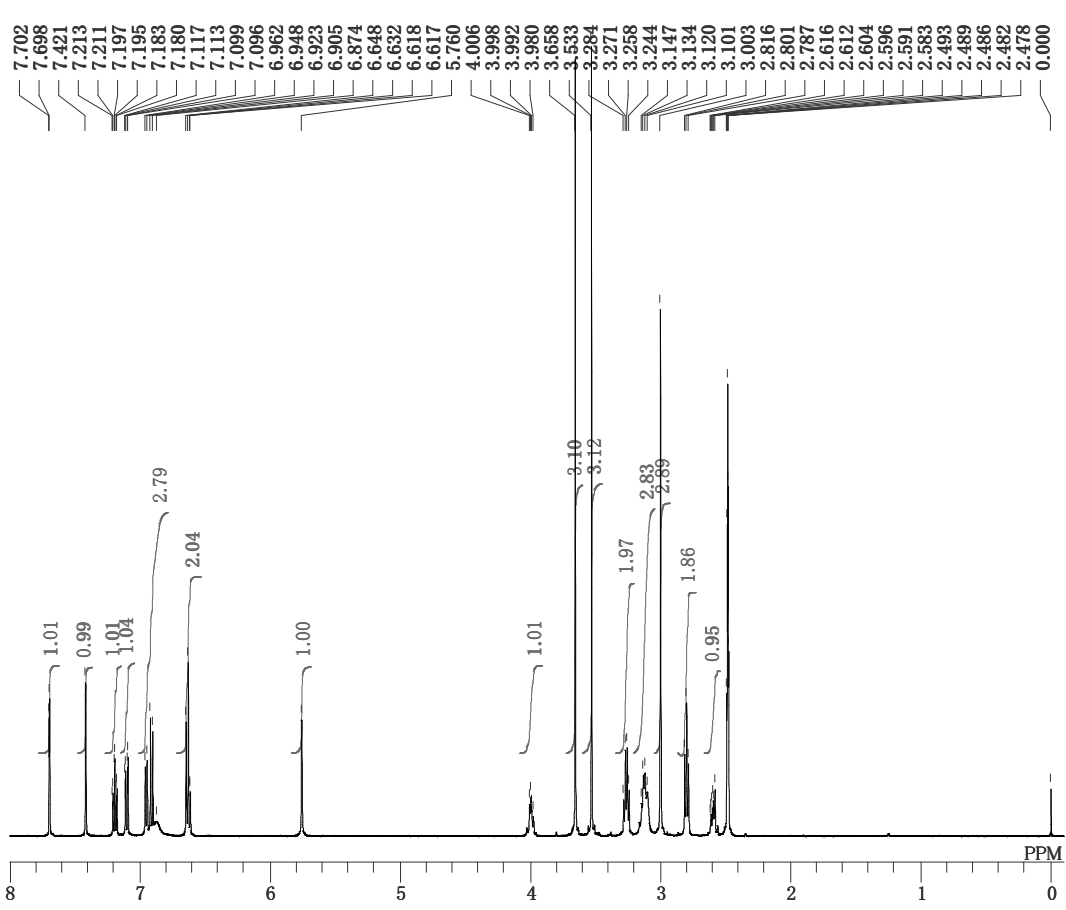


DFILE 11o H.als
COMNT 11o H
DATIM Mon Jan 21 19:50:22 2013
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23

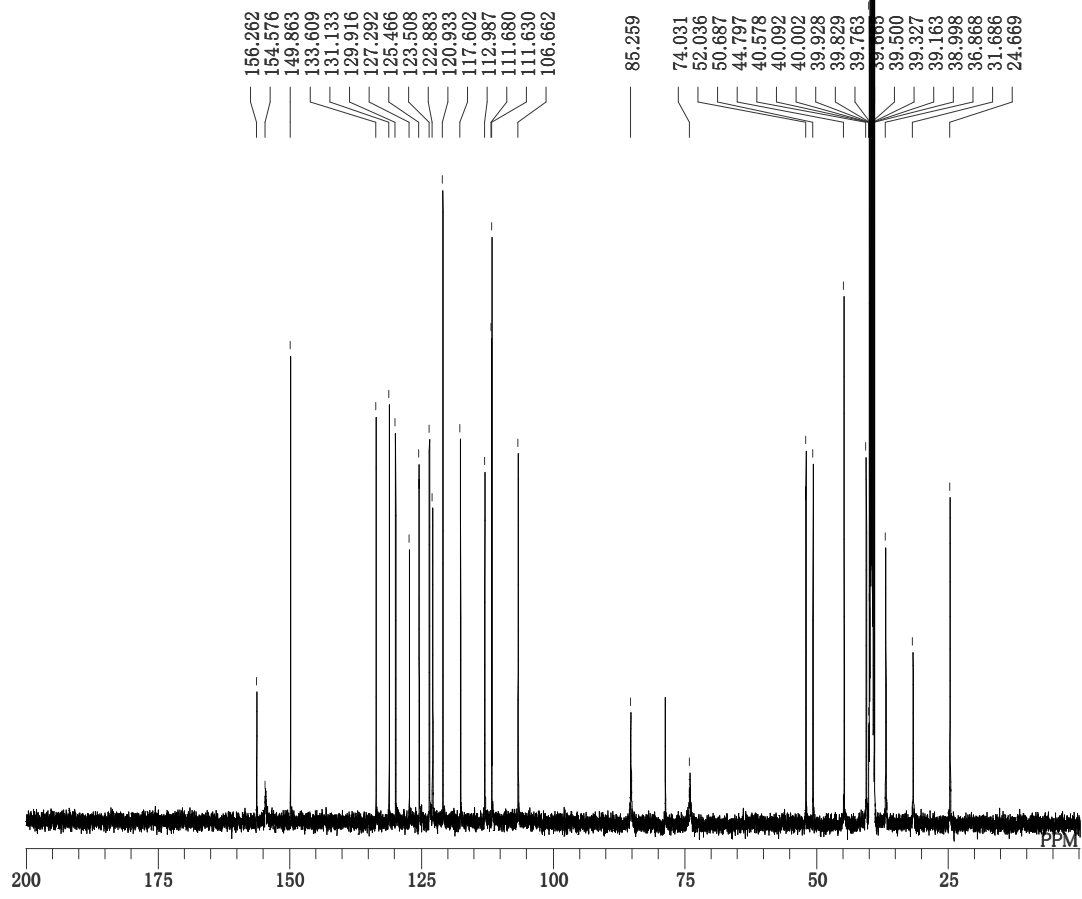
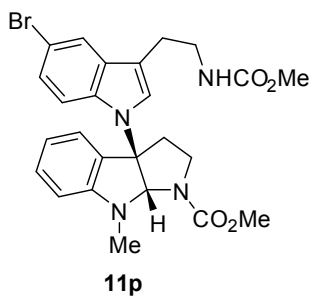


DFILE 11o C.als
COMNT 11o C
DATIM Thu Jan 31 00:27:48 2013
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 3200
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.00 usec
IRNUC 1H
CTEMP 80.2 c
SLVNT DMSO
EXREF 39.50 ppm
BF 1.20 Hz
RGAIN 24

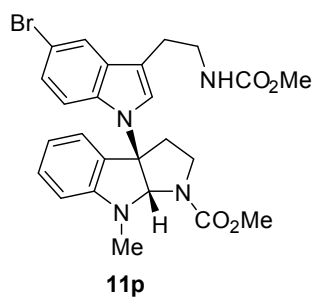


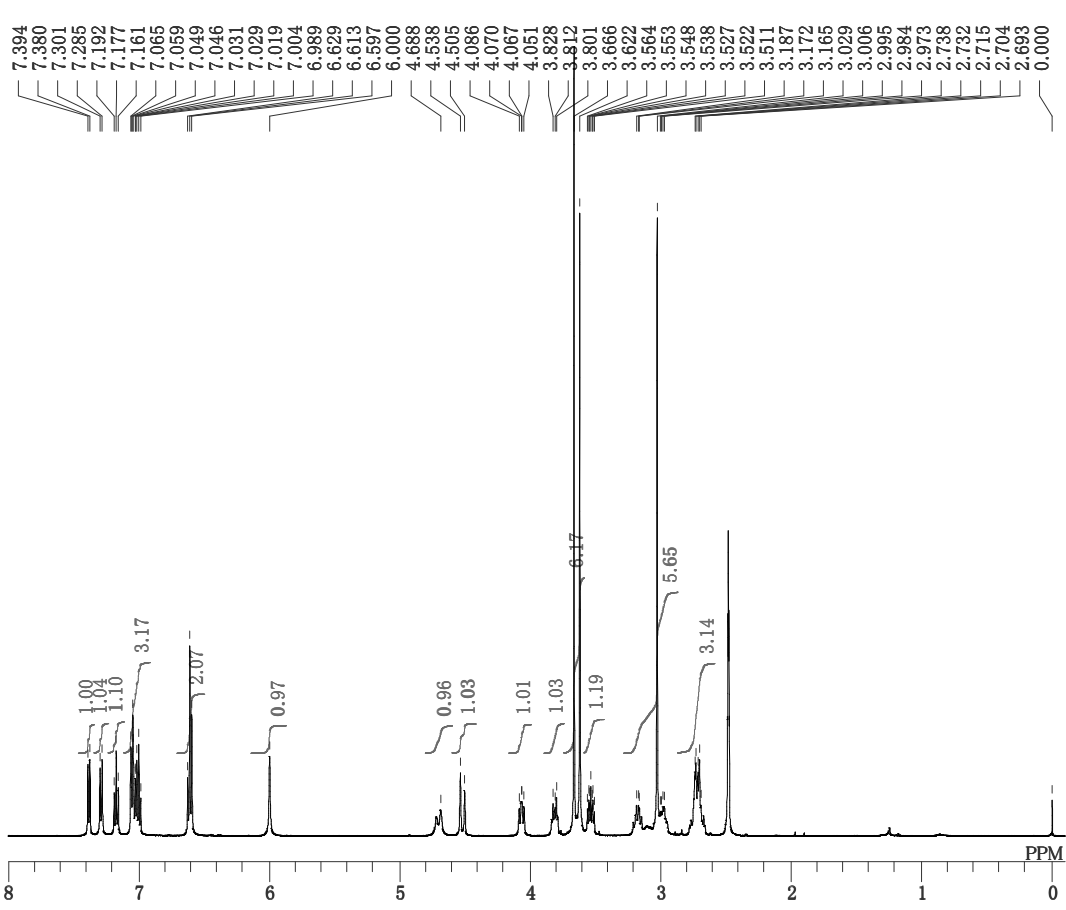


DFILE 11p H.als
 COMNT 11p H
 DATIM Wed Dec 31 06:36:02 2014
 OBNUC 1H
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.00 Hz
 POINT 32768
 FREQU 10000.00 Hz
 SCANS 16
 ACQTM 3.2768 sec
 PD 3.7232 sec
 PW1 5.00 usec
 IRNUC 1H
 CTEMP 79.9 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 24

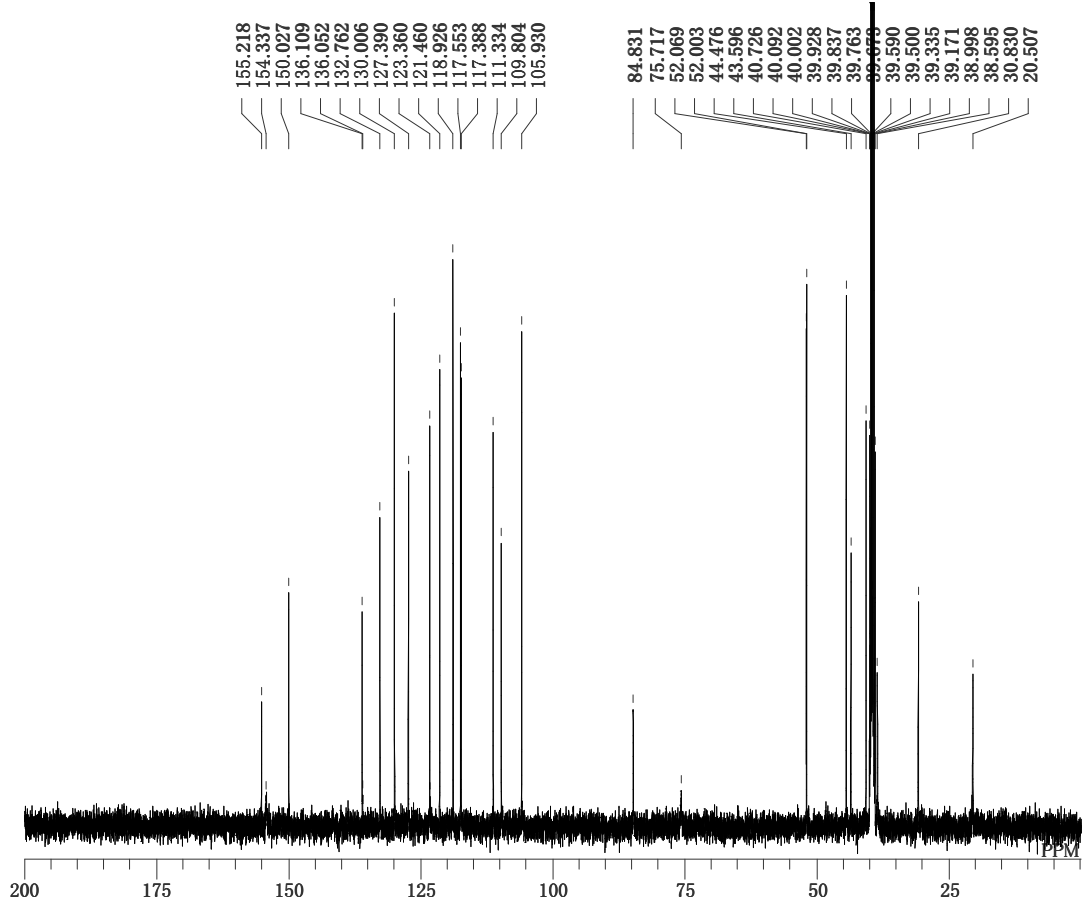
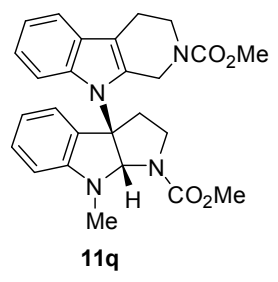


DFILE 11p C.als
 COMNT 11p C
 DATIM Wed Dec 31 14:57:20 2014
 OBNUC 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 10000
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 0.12 Hz
 RGAIN 27

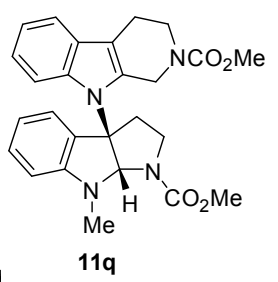


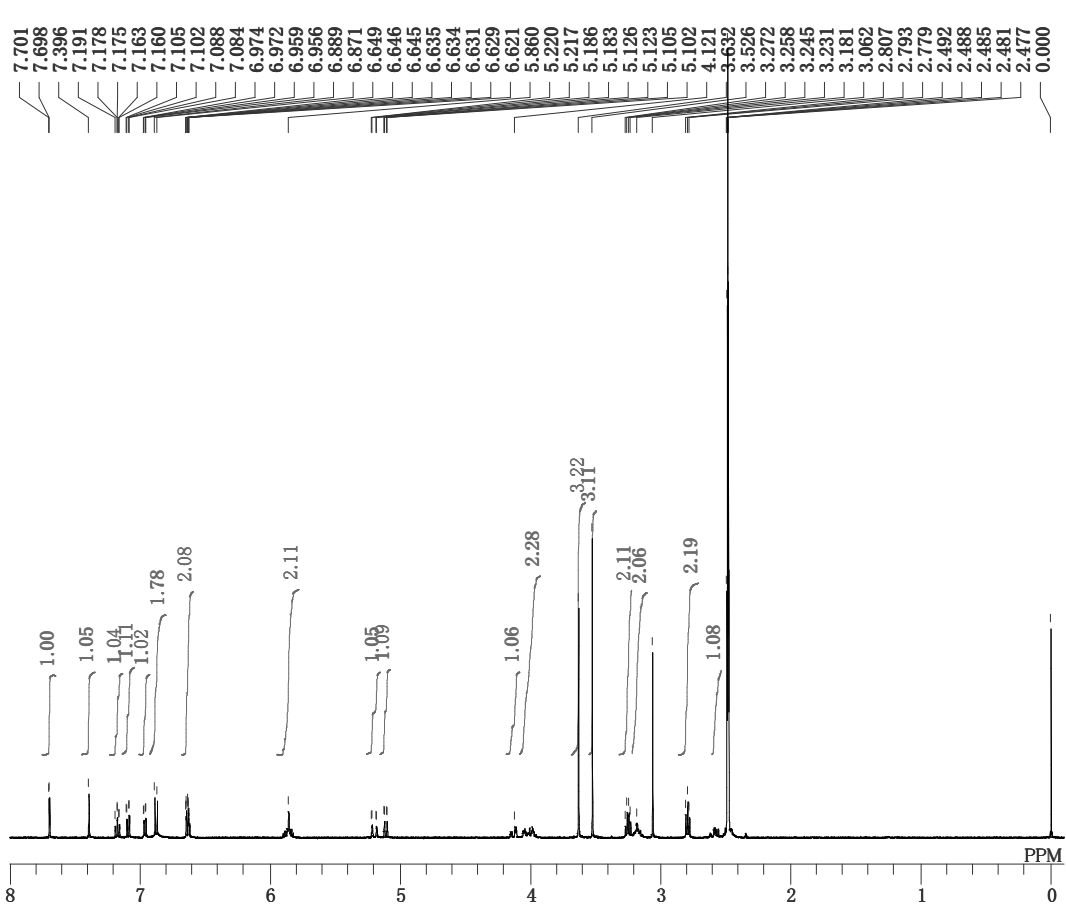


DFILE 11q H.als
 COMNT 11q H
 DATIM Tue Nov 25 23:09:21 2014
 1H
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.00 Hz
 POINT 32768
 FREQU 10000.00 Hz
 SCANS 8
 ACQTM 3.2768 sec
 PD 3.7232 sec
 PW1 5.00 usec
 IRNUC 1H
 CTEMP 80.1 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.09 Hz
 RGAIN 19

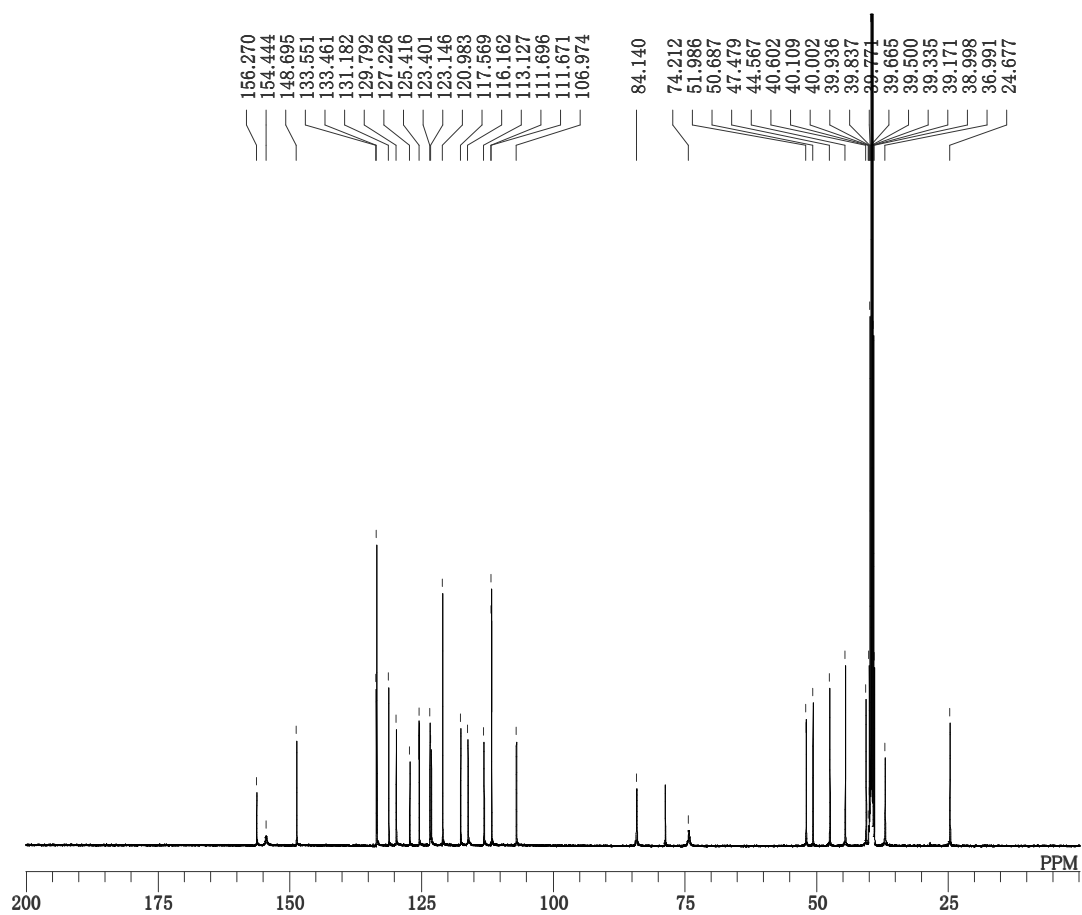
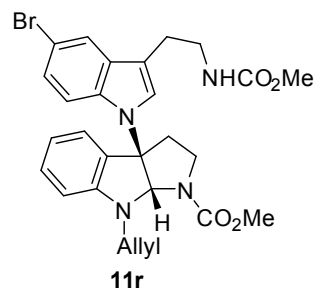


DFILE 11q C.als
 COMNT 11q C
 DATIM Wed Nov 26 00:01:45 2014
 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 1024
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 80.0 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 0.12 Hz
 RGAIN 27

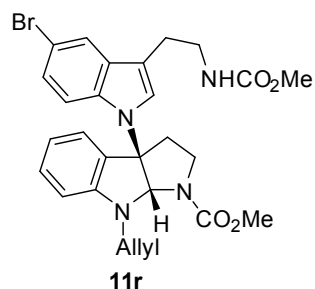


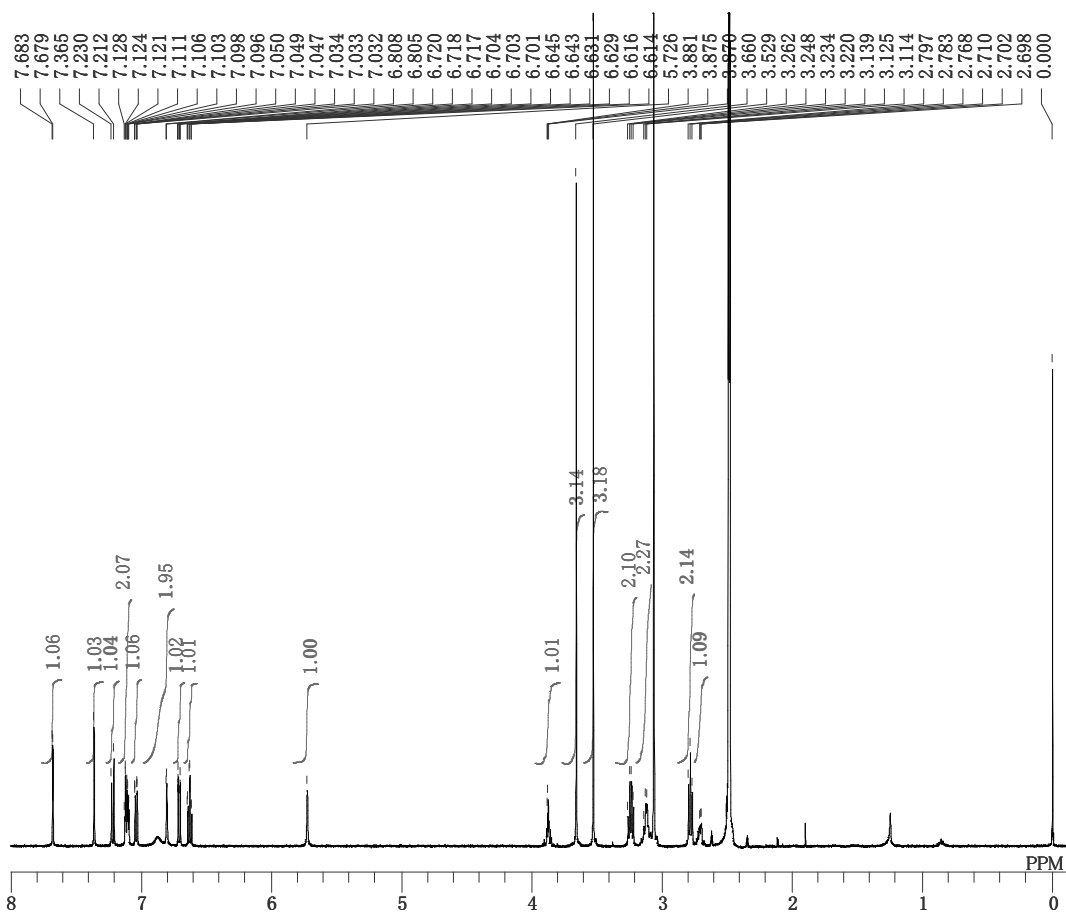


DFILE 11r H.als
COMNT 11r H
DATIM Sun Dec 16 18:55:23 2012
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 8
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.01 Hz
RGAIN 25

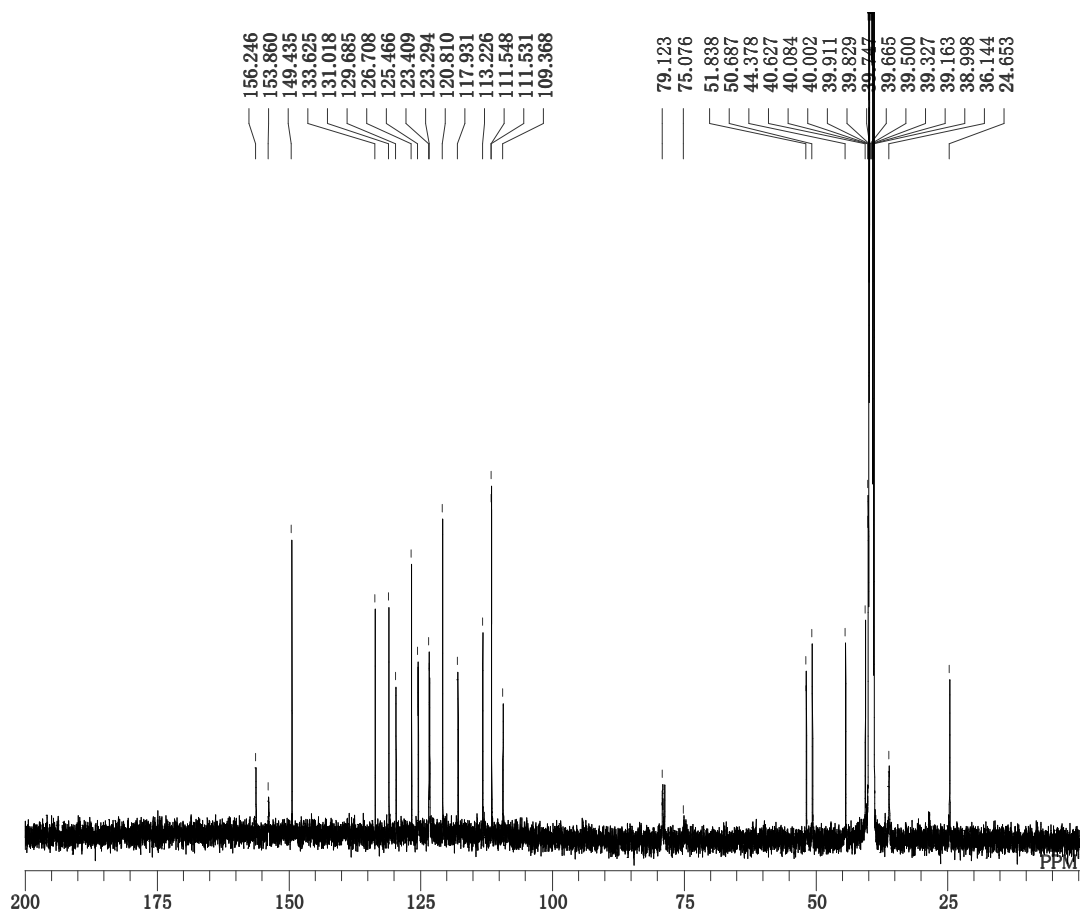
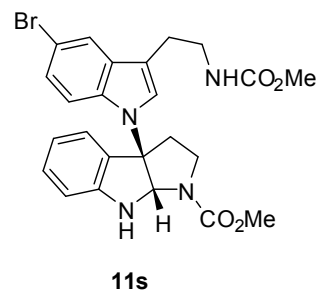


DFILE 11r C.als
COMNT 11r C
DATIM Sat Jan 3 14:12:06 2015
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 70000
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 4.40 usec
IRNUC 1H
CTEMP 80.0 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.09 Hz
RGAIN 28

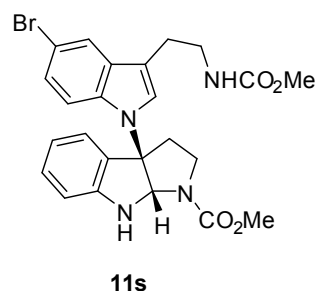


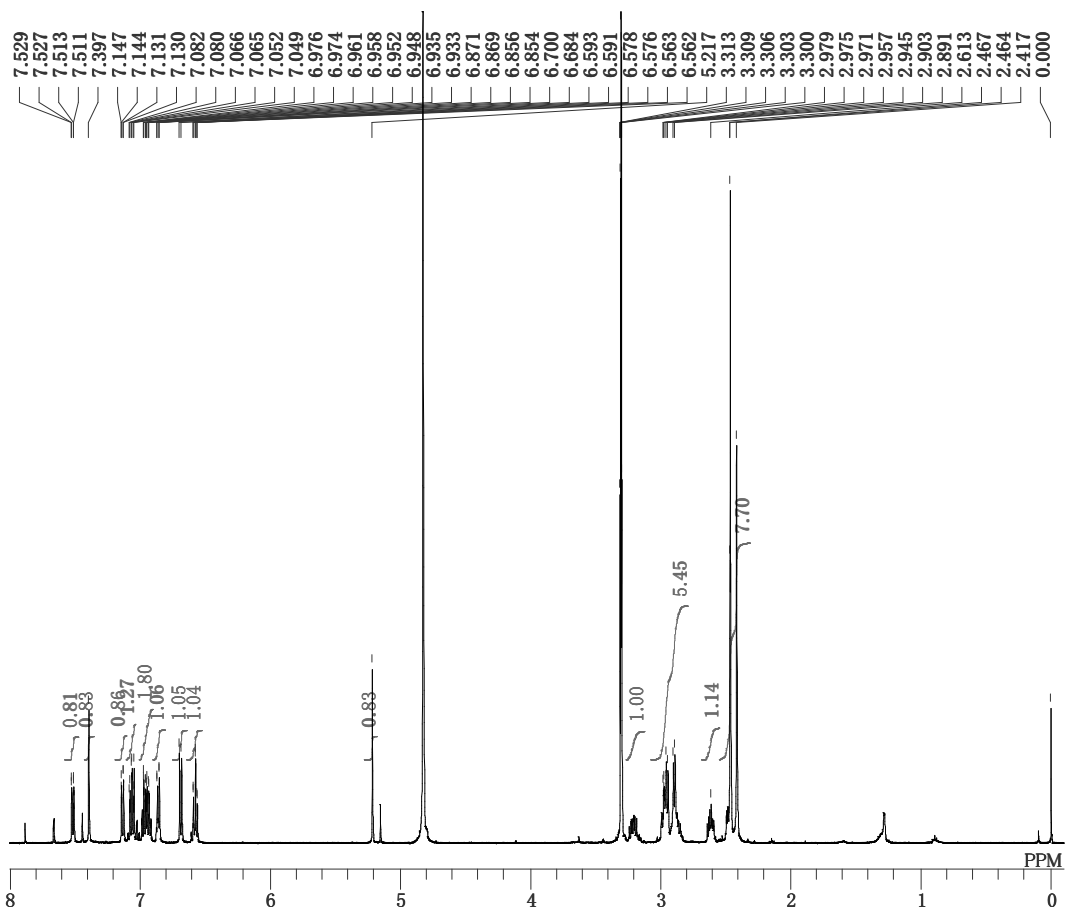


DFILE 11s H.als
 COMNT 11s H
 DATIM Wed Jan 7 02:06:22 2015
 OBNUC 1H
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.00 Hz
 POINT 32768
 FREQU 10000.00 Hz
 SCANS 32
 ACQTM 3.2768 sec
 PD 3.7232 sec
 PW1 5.00 usec
 IRNUC 1H
 CTEMP 79.9 c
 SLVNT DMSO
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 26

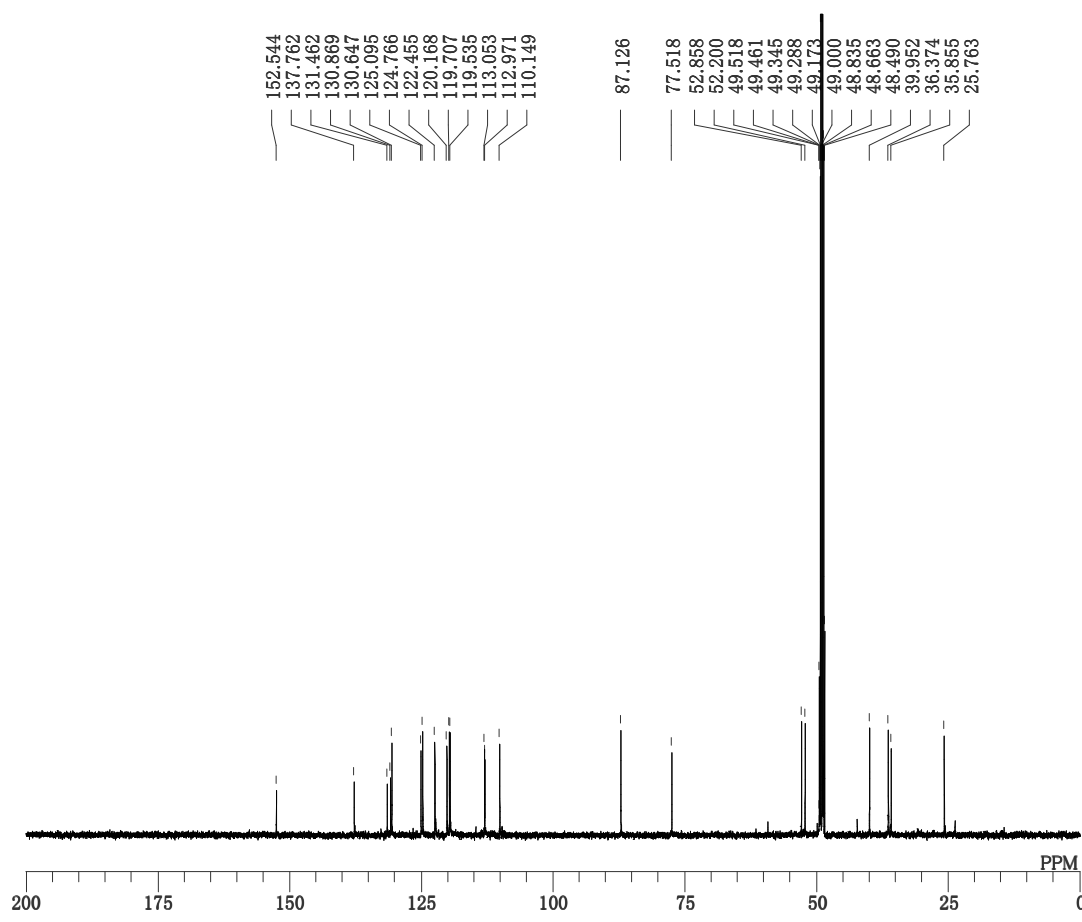
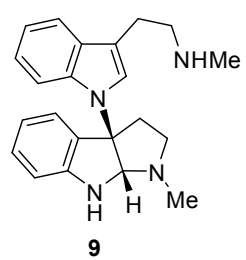


DFILE 11s C.als
 COMNT 11s C
 DATIM Thu Jan 8 19:47:51 2015
 OBNUC 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 50000
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 4.40 usec
 IRNUC 1H
 CTEMP 79.9 c
 SLVNT DMSO
 EXREF 39.50 ppm
 BF 1.20 Hz
 RGAIN 27





DFILE 9 H.als
 COMNT 9 H
 DATIM Wed Jan 7 01:34:03 2015
 OBNUC 1H
 EXMOD non
 OBFRQ 500.00 MHz
 OBSET 160.00 KHz
 OBFIN 2160.00 Hz
 POINT 32768
 FREQU 10000.00 Hz
 SCANS 16
 ACQTM 3.2768 sec
 PD 3.7232 sec
 PW1 5.00 usec
 IRNUC 1H
 CTEMP 27.9 c
 SLVNT CD3OD
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 22



DFILE 9 C.als
 COMNT 9 C
 DATIM Fri May 10 14:44:13 2013
 OBNUC 13C
 EXMOD bcm
 OBFRQ 125.65 MHz
 OBSET 120.00 KHz
 OBFIN 7958.00 Hz
 POINT 32768
 FREQU 33898.30 Hz
 SCANS 800
 ACQTM 0.9667 sec
 PD 2.0333 sec
 PW1 11.75 usec
 IRNUC 1H
 CTEMP 27.9 c
 SLVNT CD3OD
 EXREF 49.00 ppm
 BF 1.20 Hz
 RGAIN 27

