Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Fully Atom-economic Access to Spiro-cyclic Skeletons through Photoredox-induced Hydrogen Transfer/Giese Addition/ Dearomative Cyclization/Protonation Cascade

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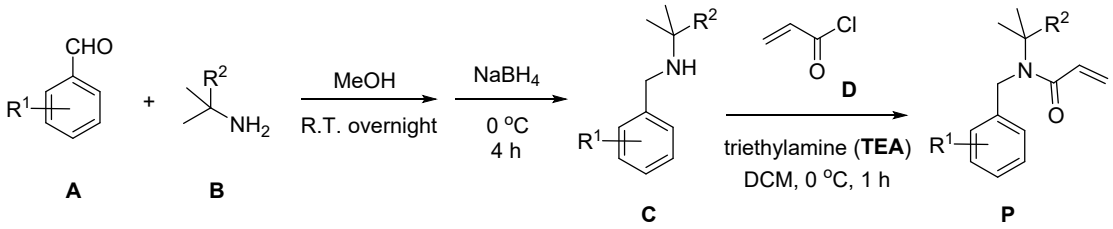
I. General information

Unless specified otherwise, all experiments were performed under N_2 atmosphere. All reagents and starting materials were purchased from commercial suppliers and used as received. FT-IR spectra were obtained with thin film samples or KBr pellets on a Bruker Vector 22 spectrometer, and data are expressed in cm^{-1}. ^1H, ^{13}C, ^{19}F spectra were recorded on Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F) and Bruker AVANCE 500 (500 MHz for ^1H; 126 MHz for ^{13}C; 471 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. The HRMS measurements were recorded on a TOF analyzer using an ESI source in the positive mode. The crystal data was collected on a Agilent Gemini E diffractometer (Mo, 50kV 40mA)and reduced by CrysAlisPro (Rigaku). Melting points were determined using a hot stage apparatus. Column chromatography was performed on silica gel (200–300 mesh) with mixtures of petroleum ether and ethyl acetate as the eluent or other solvents.

II. General procedure for preparing enamide materials

Method a:



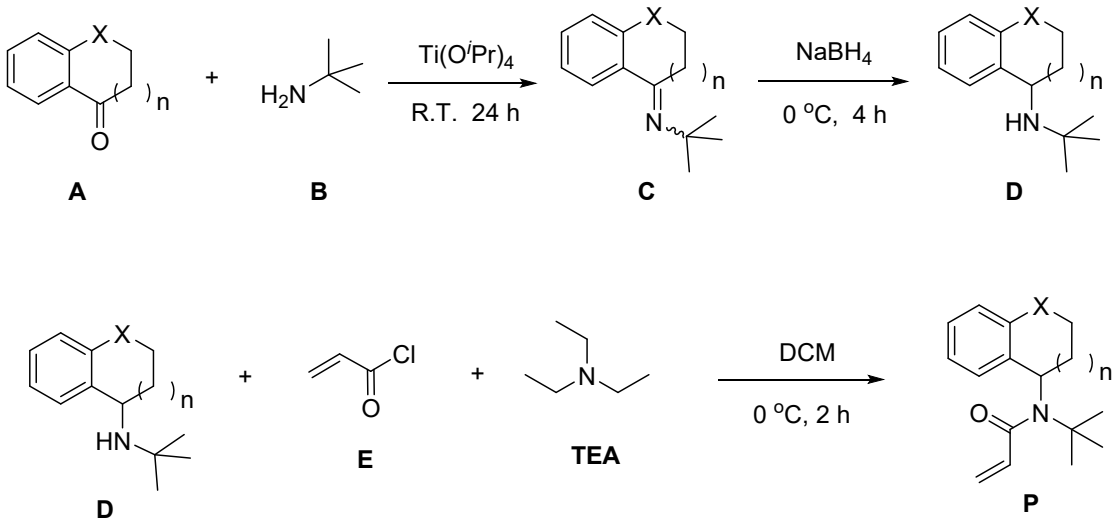
Step 1:

To a solution of commercially available compound benzaldehyde derivatives **A** (5 mmol, 1.0 eq) and the corresponding amine **B** (20 mmol, 4.0 eq) in MeOH (50 mL) was stirred at RT for overnight. After cooled the reaction solution to 0 °C, $NaBH_4$ (285 mg, 7.5 mmol, 1.5 eq) was added slowly in portions, then this reaction mixture was stirred at RT for another 4 hours. Then the reaction was quenched with water and extracted with EtOAc after removing MeOH under reduced pressure. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure to give crude product **C** which was used directly in the next step without purification.

Step 2:

To a solution of crude product **C** in CH_2Cl_2 (100 mL) was added **TEA** (760 mg, 7.5 mmol, 1.5 eq) and stirred at 0 °C for 10 mins, then acryloyl chloride **D** (452 mg, 5 mmol, 1.0 eq) was added dropwise to the reaction solution and continuously stirred for another 1 hour. The reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, concentrated, and purified by column chromatography on silica gel (15 : 1 petroleum ether : EtOAc) to give the starting material **P**.

Method b:



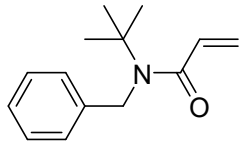
Step 1:

To a solution of commercially available compound **A** (5 mmol, 1.0 eq) and 2-methylpropan-2-amine **B** (1.46 g, 20 mmol, 4.0 eq) in $Ti(O^iPr)_4$ (20 mL) was stirred at RT for 24 hours. After cooled the reaction solution to 0 °C, MeOH (20 mL) was added dropwise and followed by $NaBH_4$ (285 mg, 7.5 mmol, 1.5 eq) slowly in portions, then this reaction mixture was stirred at RT for another 4 hours. Then the reaction was quenched by excess water and filtered with silica gel, the filter cake washed with EtOAc three times. The organic filtrate washed by H_2O and dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure to give crude product **D** which was used directly in the next step without purification.

Step 2:

To a solution of the above crude product **D** in CH_2Cl_2 (100 mL) was added **TEA** (760 mg, 7.5 mmol, 1.5 eq) and stirred at 0 °C for 10 mins, then acryloyl chloride **E** (452 mg, 5 mmol, 1.0eq) was added

dropwise to the reaction solution and continuously stirred for another 2 hours. The reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, concentrated, and purified by column chromatography on silica gel (15 : 1 petroleum ether : EtOAc) to give the starting material **P**.



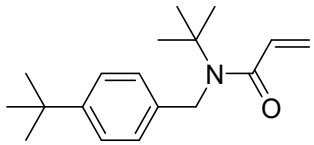
N-benzyl-N-(tert-butyl)acrylamide (**1a**)

Prepared according to **method a** which benzaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a write solid (8.6 g, 40 mmol, 80% over two steps, m.p. = 61.3 ~ 63.6 °C).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.21 (m, 3H), 6.42 – 6.26 (m, 2H), 5.56 – 5.50 (m, 1H), 4.63 (s, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 139.4, 131.5, 128.7, 127.2, 127.0, 125.7, 57.7, 48.9, 28.5.

IR (KBr, cm^{-1}): 2813, 1651, 1603, 1487, 1413, 1387, 1195, 988, 794, 747, 716.

HRMS (ESI): calcd for $C_{14}H_{20}NO^{+}$ $[M + H]^{+}$: 218.1539; found: 218.1535.



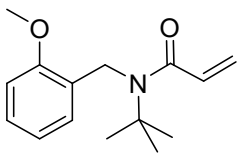
N-(tert-butyl)-N-(4-(tert-butyl)benzyl)acrylamide (**1b**)

Prepared according to **method a** which 4-(tert-butyl)benzaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a colorless viscous liquid (1.1 g, 4.1 mmol, 82% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.21 – 7.13 (m, 2H), 6.42 (dd, *J* = 16.6, 10.0 Hz, 1H), 6.32 (dd, *J* = 16.6, 2.4 Hz, 1H), 5.54 (dd, *J* = 10.0, 2.3 Hz, 1H), 4.62 (s, 2H), 1.48 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 150.0, 136.3, 131.7, 127.0, 125.7, 125.4, 57.7, 48.7, 34.5, 31.4, 28.6.

IR (KBr, cm^{-1}): 1656, 1580, 1515, 1349, 1112, 990, 882, 791, 550.

HRMS (ESI): calcd for $C_{18}H_{28}NO^{+}$ $[M + H]^{+}$: 274.2165; found: 274.2161.



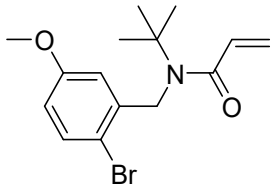
N-(tert-butyl)-N-(2-methoxybenzyl)acrylamide (**1c**)

Prepared according to **method a** which 2-methoxybenzaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a brown oil.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.20 (m, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.28 (s, 1H), 6.27 (d, *J* = 1.7 Hz, 1H), 5.47 (dd, *J* = 7.0, 5.4 Hz, 1H), 4.55 (s, 2H), 3.84 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.6, 155.8, 131.5, 127.9, 127.4, 126.9, 126.7, 120.5, 109.7, 57.4, 55.1, 44.2, 28.2.

IR(KBr, cm^{-1}): 2715, 1660, 1586, 1470 1345, 1202, 1065, 785, 731.

HRMS (ESI): calcd for $C_{15}H_{22}NO_2^+$ $[M + H]^+$: 248.1645; found: 248.1641.



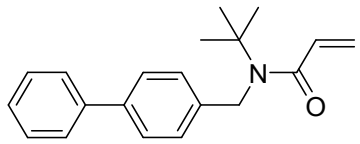
N-(2-bromo-5-methoxybenzyl)-N-(tert-butyl)acrylamide (**1d**)

Prepared according to **method a** which 2-bromo-5-methoxybenzaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a write solid (1.3 g, 4.1 mmol, 82% over two steps. m.p. = 101.1 ~ 103.6. ^{o}C).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.91 (d, *J* = 3.1 Hz, 1H), 6.73 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.38 – 6.30 (m, 1H), 6.25 (dd, *J* = 16.6, 10.0 Hz, 1H), 5.61 – 5.53 (m, 1H), 4.55 (s, 2H), 3.78 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 159.5, 139.2, 133.5, 131.1, 127.8, 114.2, 113.9, 111.6, 57.8, 55.5, 49.8, 28.4.

IR (KBr, cm^{-1}): 2718, 1655, 1584, 1354, 1295, 1194, 1054, 778, 607.

HRMS (ESI): calcd for $C_{15}H_{21}BrNO_2^+$ $[M + H]^+$: 326.0750; found: 326.0745.



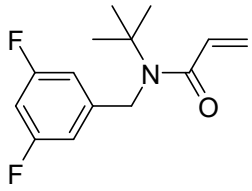
N-([1,1'-biphenyl]-4-ylmethyl)-N-(tert-butyl)acrylamide (**1e**)

Prepared according to **method a** which [1,1'-biphenyl]-4-carbaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a write solid (1.0 g, 3.6 mmol, 73% over two steps, m.p. = 75.1 ~ 77.9 ^{o}C).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.60 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.45 (dd, *J* = 16.6, 10.0 Hz, 1H), 6.36 (dd, *J* = 16.6, 2.4 Hz, 1H), 5.58 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.70 (s, 2H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 140.6, 140.1, 138.5, 131.6, 128.8, 127.5, 127.4, 127.3, 127.0, 126.2, 57.8, 48.8, 28.6.

IR (KBr, cm^{-1}): 2716, 1611, 1485, 1362, 1072, 989, 771, 697.

HRMS (ESI): calcd for $C_{20}H_{24}NO^+$ [M + H]$^+$: 294.1852; found: 294.1850.



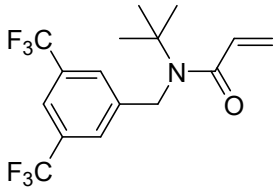
N-(tert-butyl)-N-(3,5-difluorobenzyl)acrylamide (**1f**)

Prepared according to **method a** which 3,5-difluorobenzaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a brown oil (1.0 g, 4.2 mmol, 84% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.76 – 6.70 (m, 2H), 6.69 – 6.60 (m, 1H), 6.25 (d, *J* = 6.1 Hz, 2H), 5.52 (t, *J* = 6.2 Hz, 1H), 4.55 (s, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 163.4 (dd, *J* = 249.6, 12.7 Hz), 144.2, 130.9, 127.8, 109.7 – 107.3 (dd, *J*=18.8 Hz, 7.0 Hz), 102.6 (t, *J* = 25.4 Hz), 57.8, 48.4 (t, *J* = 2.2 Hz), 28.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.6.

IR (KBr, cm^{-1}): 2716, 1622, 1456, 1363, 1196, 992, 885, 798, 777, 672.

HRMS (ESI): calcd for $C_{14}H_{18}F_2NO^+$ [M + H]$^+$: 254.1351; found: 254.1346.



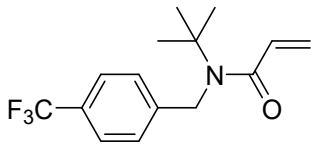
N-(3,5-bis(trifluoromethyl)benzyl)-N-(tert-butyl)acrylamide (**1g**)

Prepared according to **method a** which 3,5-bis(trifluoromethyl)benzaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a brown oil (1.4 g, 4.1 mmol, 82% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.70 (s, 2H), 6.37 – 6.31 (m, 1H), 6.26 (dd, *J* = 16.6, 9.8 Hz, 1H), 5.60 (dd, *J* = 9.8, 2.4 Hz, 1H), 4.74 (s, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 142.6, 132.3 (q, *J* = 33.4 Hz), 130.6, 128.4, 126.0 – 125.9 (m), 123.1 (d, *J* = 272.9 Hz), 121.3 (t, *J* = 4.2 Hz), 57.9, 48.4, 28.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.0.

IR (KBr, cm^{-1}): 2716, 1616, 1465, 1366, 1177, 992, 848, 796 707, 604.

HRMS (ESI): calcd for $C_{16}H_{18}F_6NO^+$ [M + H]$^+$: 354.1287; found: 354.1281.



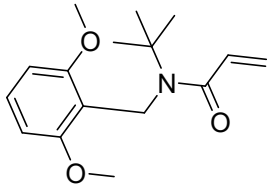
N-(tert-butyl)-N-(4-(trifluoromethyl)benzyl)acrylamide (**1h**)

Prepared according to **method a** which 4-(trifluoromethyl)benzaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a yellow oil (1.1 g, 4.0 mmol, 80% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.32 – 6.24 (m, 2H), 5.56 – 5.49 (m, 1H), 4.66 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 143.7, 131.0, 129.4 (d, *J* = 32.6 Hz), 127.7, 126.0, 125.7 (q, *J* = 3.8 Hz), 128.2 – 119.5 (m), 57.7, 48.6, 28.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.5.

IR (KBr, cm^{-1}): 2718, 1652, 1585, 1362, 1196, 1067, 883, 773.

HRMS (ESI): calcd for $C_{15}H_{19}F_3NO^+$ [M + H]$^+$: 286.1413; found: 286.1409.



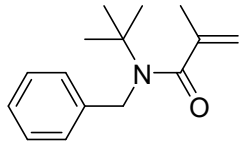
N-(tert-butyl)-N-(2,6-dimethoxybenzyl)acrylamide (**1i**)

Prepared according to **method a** which 2,6-dimethoxybenzaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a write solid (960 mg, 3.45 mmol, 69% over two steps. m.p. = 92.3 ~ 94. ^{o}C).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 8.3 Hz, 1H), 6.75 (dd, *J* = 17.0, 10.6 Hz, 1H), 6.51 (d, *J* = 8.4 Hz, 2H), 6.06 (dd, *J* = 16.9, 2.1 Hz, 1H), 5.44 (dd, *J* = 10.6, 2.1 Hz, 1H), 4.71 (s, 2H), 3.76 (s, 6H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 158.6, 134.1, 128.6, 123.0, 115.0, 103.8, 57.2, 55.2, 40.7, 28.3.

IR (KBr, cm^{-1}): 2716, 1612, 1472, 1363, 1203, 1113, 777, 724.

HRMS (ESI): calcd for $C_{16}H_{24}NO_3^+$ [M + H]$^+$: 278.1751; found: 278.1746.



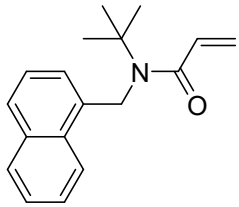
N-benzyl-N-(tert-butyl)methacrylamide (**1j**)

Prepared according to **method a** which benzaldehyde, tert-butylamine and methacryloyl chloride were used. The title compound was obtained as a off-write solid (960 mg, 3.45 mmol, 73% over two steps. m.p. = 96.0 ~ 97.9 ^{o}C).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.18 (m, 3H), 5.04 – 4.99 (m, 1H), 4.92 (p, *J* = 1.7 Hz, 1H), 4.67 (s, 2H), 1.92 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 174.7, 143.0, 140.1, 128.5, 126.9, 126.0, 113.4, 57.6, 50.7, 28.6, 20.8.

IR (KBr, cm^{-1}): 2716, 1618, 1451, 1362, 1191, 907, 779, 704.

HRMS (ESI): calcd for $C_{15}H_{22}NO^{+}$ $[M + H]^{+}$: 232.1696; found: 232.1691.



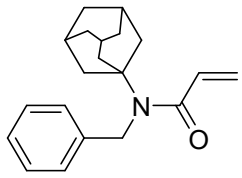
N-(tert-butyl)-N-(naphthalen-1-ylmethyl)acrylamide (**1k**)

Prepared according to **method a** which 1-naphthaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a colorless viscous liquid (970 mg, 3.6 mmol, 72% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.83 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.63 – 7.49 (m, 4H), 6.39 – 6.23 (m, 2H), 5.49 (dd, *J* = 9.7, 2.8 Hz, 1H), 5.07 (s, 2H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 134.3, 133.6, 131.4, 129.8, 129.0, 127.6, 127.3, 126.4, 126.0, 125.6, 123.6, 121.8, 57.7, 46.8, 28.3.

IR (KBr, cm^{-1}): 2716, 1615, 1483, 1362, 1196, 989, 796, 731, 601.

HRMS (ESI): calcd for $C_{18}H_{22}NO^{+}$ $[M + H]^{+}$: 268.1696; found: 268.1691.



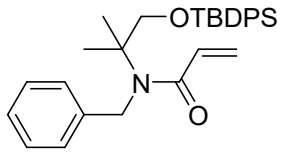
N-(adamantan-1-yl)-N-benzylacrylamide (**1l**)

Prepared according to **method a** which benzaldehyde, amantadine and acryloyl chloride were used. The title compound was obtained as a yellow solid (1.1 g, 3.9 mmol, 78% over two steps. m.p. = 138.0 ~ 139.1 ^{o}C).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.34 (m, 2H), 7.32 – 7.25 (m, 4H), 6.39 (dd, *J* = 16.6, 9.9 Hz, 1H), 6.29 (dd, *J* = 16.6, 2.6 Hz, 1H), 5.53 (dd, *J* = 10.0, 2.5 Hz, 1H), 4.67 (s, 2H), 2.26 (d, *J* = 3.4 Hz, 6H), 2.11 – 2.05 (m, 3H), 1.71 – 1.61 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 139.8, 132.1, 128.7, 127.0, 125.8, 59.2, 47.7, 39.6, 36.4, 30.1.

IR (KBr, cm^{-1}): 2716, 1647, 1606, 1452, 1361, 1196, 1105, 998, 776, 698.

HRMS (ESI): calcd for $C_{20}H_{26}NO^+$ [M + H]$^+$: 296.2009; found: 296.2005.



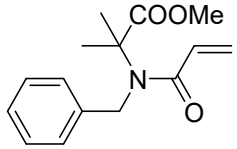
N-benzyl-N-(1-((tert-butyldiphenylsilyl)oxy)-2-methylpropan-2-yl)acrylamide (**1m**)

Prepared according to **method a** which benzaldehyde, 1-((tert-butyldiphenylsilyl)oxy)-2-methylpropan-2-amine and acryloyl chloride were used. The title compound was obtained as a colorless oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 4H), 7.44 – 7.29 (m, 8H), 7.29 – 7.21 (m, 3H), 6.38 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.30 (dd, *J* = 16.7, 2.7 Hz, 1H), 5.53 (dd, *J* = 9.8, 2.7 Hz, 1H), 4.81 (s, 2H), 4.00 (s, 2H), 1.43 (s, 6H), 1.09 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 139.7, 135.6, 133.4, 131.6, 129.6, 128.7, 127.6, 127.2, 126.9, 125.6, 68.8, 61.2, 50.2, 26.9, 24.2, 19.3.

IR (KBr, cm^{-1}): 2717, 1601, 1361, 1108, 777, 611, 505.

HRMS (ESI): calcd for $C_{30}H_{38}NO_2Si^+$ [M + H]$^+$: 472.2666; found: 472.2661.



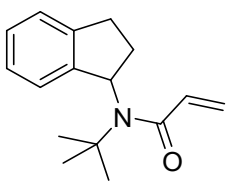
methyl 2-(N-benzylacrylamido)-2-methylpropanoate (**1n**)

Prepared according to **method a** which benzaldehyde, methyl 2-amino-2-methylpropanoate and acryloyl chloride were used. The title compound was obtained as a beige solid (1.6 g, 3.5 mmol, 70% over two steps. m.p. = 56.6 ~ 58.6 ^{o}C).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 6.40 – 6.30 (m, 2H), 5.61 (dd, *J* = 8.5, 3.8 Hz, 1H), 4.66 (s, 2H), 3.75 (s, 3H), 1.42 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.6, 167.3, 138.3, 129.1, 128.8, 128.5, 127.3, 125.8, 61.4, 52.2, 47.1, 23.6.

IR (KBr, cm^{-1}): 2718, 1660, 1613, 1355, 1284, 1200, 1066, 983, 779, 697.

HRMS (ESI): calcd for $C_{15}H_{20}NO_3^+$ [M + H]$^+$: 262.1438; found: 262.1433.



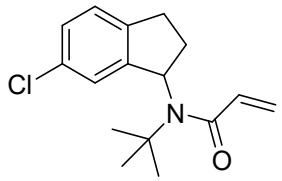
N-(tert-butyl)-N-(2,3-dihydro-1H-inden-1-yl)acrylamide (**1o**)

Prepared according to **method b** which 2,3-dihydro-1H-inden-1-one was used. The title compound was obtained as a brown oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 (q, *J* = 6.2, 5.7 Hz, 3H), 7.10 (s, 1H), 5.99 (d, *J* = 16.5 Hz, 1H), 5.83 – 5.72 (m, 1H), 5.29 (t, *J* = 8.0 Hz, 1H), 5.09 (d, *J* = 9.6 Hz, 1H), 3.08 (dd, *J* = 16.2, 10.2 Hz, 1H), 2.96 – 2.87 (m, 1H), 2.52 (q, *J* = 9.7 Hz, 1H), 2.26 (q, *J* = 11.1, 10.2 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.3, 144.8, 140.7, 132.6, 127.3, 126.9, 125.1, 124.2, 123.0, 60.2, 58.3, 34.0, 29.7, 29.5.

IR(KBr, cm^{-1}): 2719, 1650, 1480, 1354, 1133, 777, 645.

HRMS(ESI): calcd for $C_{16}H_{22}NO^{+}$ [M + H]$^{+}$: 244.1696; found: 244.1693.



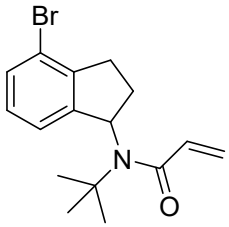
N-(tert-butyl)-N-(6-chloro-2,3-dihydro-1H-inden-1-yl)acrylamide (**1p**)

Prepared according to **method b** which 6-chloro-2,3-dihydro-1H-inden-1-one was used. The title compound was obtained as a brown oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 7.08 (m, 2H), 7.01 (s, 1H), 6.01 (d, *J* = 16.4 Hz, 1H), 5.78 (dd, *J* = 16.5, 10.2 Hz, 1H), 5.22 (t, *J* = 9.2 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 3.06 – 2.98 (m, 1H), 2.88 – 2.79 (m, 1H), 2.55 – 2.46 (m, 1H), 2.31 – 2.19 (m, 1H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 146.7, 139.2, 132.7, 132.5, 127.4, 126.1, 124.8, 123.0, 59.9, 58.3, 34.1, 29.5, 29.2.

IR(KBr, cm^{-1}): 2812, 1652, 1608, 1474, 1360, 1164, 980, 878, 736, 662.

HRMS(ESI): calcd for $C_{16}H_{21}ClNO^{+}$ [M + H]$^{+}$: 278.1306; found: 278.1302.



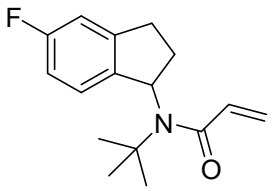
N-(4-bromo-2,3-dihydro-1H-inden-1-yl)-N-(tert-butyl)acrylamide (**1q**)

Prepared according to **method b** which 4-bromo-2,3-dihydro-1H-inden-1-one was used. The title compound was obtained as a brown oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.5 Hz, 1H), 7.03 (dd, *J* = 13.6, 5.7 Hz, 2H), 6.00 (d, *J* = 16.5 Hz, 1H), 5.85 – 5.73 (m, 1H), 5.30 (q, *J* = 11.8, 10.1 Hz, 1H), 5.15 (d, *J* = 9.8 Hz, 1H), 3.10 (dd, *J* = 16.9, 10.3 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.53 (q, *J* = 9.9, 9.3 Hz, 1H), 2.26 (p, *J* = 9.5 Hz, 1H), 1.57 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.1, 146.8, 141.1, 132.5, 130.3, 128.7, 124.8, 121.8, 120.7, 60.9, 58.3, 33.0, 31.1, 29.5.

IR(KBr, cm^{-1}): 2818, 1652, 1569, 1451, 1389, 1201, 995, 769.

HRMS(ESI): calcd for $C_{16}H_{21}BrNO^{+}$ $[M + H]^{+}$: 322.0801; found: 322.0797.



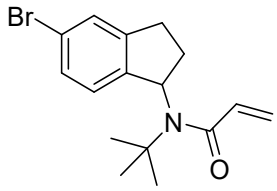
N-(tert-butyl)-N-(5-fluoro-2,3-dihydro-1H-inden-1-yl)acrylamide (**1r**)

Prepared according to **method b** which 5-fluoro-2,3-dihydro-1H-inden-1-one was used. The title compound was obtained as a brown oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.00 (s, 1H), 6.86 (dd, *J* = 22.6, 8.6 Hz, 2H), 5.98 (d, *J* = 16.5 Hz, 1H), 5.86 – 5.68 (m, 1H), 5.23 (s, 1H), 5.11 (d, *J* = 9.1 Hz, 1H), 3.06 (dd, *J* = 16.4, 10.3 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.54 (q, *J* = 10.0, 9.3 Hz, 1H), 2.33 – 2.22 (m, 1H), 1.58 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.2, 162.5 (d, *J* = 244.7 Hz), 143.1 (d, *J* = 8.1 Hz), 140.3, 132.6, 124.4, 124.1 (d, *J* = 8.8 Hz), 114.0 (d, *J* = 22.8 Hz), 112.0 (d, *J* = 22.1 Hz), 59.5, 58.3, 34.2, 29.7, 29.5. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -115.9.

IR(KBr, cm^{-1}): 2716, 1609, 1485, 1362, 1128, 976, 777, 616.

HRMS(ESI): calcd for $C_{16}H_{21}FNO^{+}$ $[M + H]^{+}$: 262.1602; found: 262.1598.



N-(5-bromo-2,3-dihydro-1H-inden-1-yl)-N-(tert-butyl)acrylamide (**1s**)

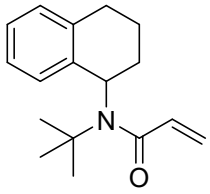
Prepared according to **method b** which 5-bromo-2,3-dihydro-1H-inden-1-one was used. The title compound was obtained as a brown oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.02 (d, *J* = 16.5 Hz, 1H), 5.89 – 5.69 (m, 1H), 5.28 – 5.06 (m, 2H), 3.07 (dd, *J* = 16.3, 10.3 Hz, 1H), 2.94 – 2.86 (m, 1H), 2.52 (q, *J* = 9.8, 9.3 Hz, 1H), 2.34 – 2.21 (m, 1H), 1.58 (s, 9H). ^{13}C NMR

(126 MHz, Chloroform-*d*) δ 168.1, 143.9, 143.2, 132.5, 130.0, 128.3, 124.8, 124.4, 121.0, 59.8, 58.3, 34.0, 29.6, 29.5.

IR(KBr, cm^{-1}): 2717, 1651, 1471, 1360, 1267, 1138, 980, 863, 772, 673.

HRMS(ESI): calcd for $C_{16}H_{21}BrNO^+$ $[M + H]^+$: 322.0801; found: 322.0796.



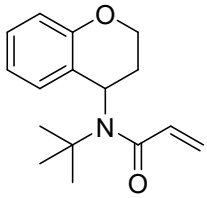
N-(tert-butyl)-N-(1,2,3,4-tetrahydronaphthalen-1-yl)acrylamide (**1t**)

Prepared according to **method b** which 3,4-dihydronaphthalen-1(2H)-one was used. The title compound was obtained as a colorless oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.19 (m, 1H), 7.18 – 7.12 (m, 2H), 7.11 – 7.08 (m, 1H), 6.09 (dd, *J* = 16.5, 2.4 Hz, 1H), 5.96 (dd, *J* = 16.5, 10.1 Hz, 1H), 5.18 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.98 (t, *J* = 9.0 Hz, 1H), 2.90 – 2.77 (m, 2H), 2.18 – 2.10 (m, 2H), 2.07 – 2.00 (m, 1H), 1.88 – 1.78 (m, 1H), 1.63 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 139.3, 136.3, 132.7, 129.1, 126.7, 126.4, 126.1, 124.8, 58.6, 55.0, 32.7, 29.4, 29.4, 23.3.

IR(KBr, cm^{-1}): 2716, 1608, 1486, 1362, 1264, 1095, 777, 612.

HRMS(ESI): calcd for $C_{17}H_{24}NO^+$ $[M + H]^+$: 258.1852; found: 258.1849.



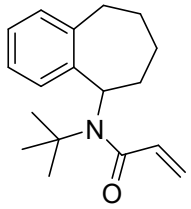
N-(tert-butyl)-N-(chroman-4-yl)acrylamide (**1u**)

Prepared according to **method b** which chroman-4-one was used. The title compound was obtained as a brown oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 – 7.11 (m, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 5.95 (dd, *J* = 16.4, 10.2 Hz, 1H), 5.23 (d, *J* = 10.1 Hz, 1H), 5.10 (dd, *J* = 11.6, 6.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.19 (t, *J* = 12.0 Hz, 1H), 2.63 – 2.53 (m, 1H), 2.08 (dd, *J* = 13.5, 6.4 Hz, 1H), 1.62 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.8, 154.6, 132.3, 128.3, 126.9, 125.6, 125.5, 121.5, 117.1, 66.4, 58.8, 50.5, 31.0, 29.4.

IR(KBr, cm^{-1}): 2718, 1606, 1487, 1360, 1215, 1112, 773, 605.

HRMS(ESI): calcd for $C_{16}H_{22}NO_2^+$ $[M + H]^+$: 260.1645; found: 260.1641.



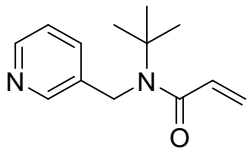
N-(tert-butyl)-N-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)acrylamide (**1v**)

Prepared according to **method b** which 6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one was used. The title compound was obtained as a brown oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.5 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.16 (d, *J* = 4.0 Hz, 2H), 6.36 (dd, *J* = 16.5, 9.9 Hz, 1H), 6.27 (dd, *J* = 16.6, 2.4 Hz, 1H), 5.42 (dd, *J* = 9.9, 2.4 Hz, 1H), 4.90 (d, *J* = 9.8 Hz, 1H), 2.89 (dd, *J* = 14.6, 6.5 Hz, 1H), 2.78 (t, *J* = 13.5 Hz, 1H), 2.10 – 1.92 (m, 4H), 1.73 (d, *J* = 13.6 Hz, 1H), 1.45 (s, 9H), 1.34 (q, *J* = 12.6 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.8, 142.5, 139.8, 134.5, 130.2, 126.7, 126.3, 126.1, 125.0, 59.3, 59.1, 39.3, 36.8, 32.2, 28.7, 27.1.

IR(KBr, cm^{-1}): 2717, 1606, 1423, 1361, 1197, 1066, 777, 610.

HRMS(ESI): calcd for $C_{18}H_{26}NO^{+}$ $[M + H]^{+}$: 272.2009; found: 272.2004.



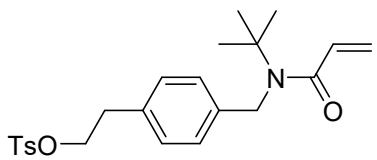
N-(tert-butyl)-N-(pyridin-3-ylmethyl)acrylamide (**1w**)

Prepared according to **method a** which nicotinaldehyde, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a brown-yellow oil (1.6 g, 3.5 mmol, 70% over two steps).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 – 8.47 (m, 2H), 7.60 – 7.49 (m, 1H), 7.33 – 7.23 (m, 1H), 6.38 – 6.26 (m, 2H), 5.56 (dd, *J* = 8.4, 3.8 Hz, 1H), 4.64 (s, 2H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 148.6, 147.7, 134.9, 133.4, 130.9, 127.7, 123.5, 57.7, 46.7, 28.5.

IR (KBr, cm^{-1}): 2715, 1647, 1507, 1361, 1195, 996, 798, 635.

HRMS (ESI): calcd for $C_{13}H_{19}N_2O^{+}$ $[M + H]^{+}$: 219.1492; found: 219.1489.



4-((N-(tert-butyl)acrylamido)methyl)phenethyl 4-methylbenzenesulfonate(**1x**)

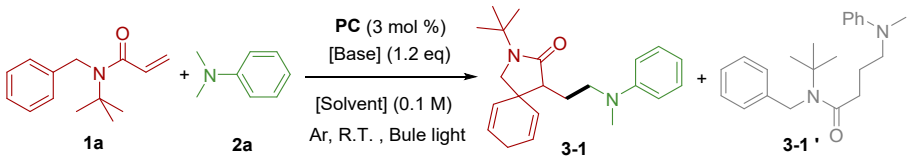
Prepared according to **method a** which 4-formylphenethyl 4-methylbenzenesulfonate, tert-butylamine and acryloyl chloride were used. The title compound was obtained as a write solid (1.3 g, 4.1 mmol, 82% over two steps. m.p. = 78.1 ~ 79.9. ^{o}C).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.16 – 7.12 (m, 4H), 6.36 (dd, *J* = 16.7, 9.7 Hz, 1H), 6.29 (dd, *J* = 16.6, 2.7 Hz, 1H), 5.56 – 5.50 (m, 1H), 4.60 (s, 2H), 4.22 (t, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.3, 144.7, 138.0, 135.0, 132.9, 131.4, 129.7, 129.2, 127.7, 127.1, 125.8, 70.3, 57.6, 48.5, 34.7, 28.4, 21.5.

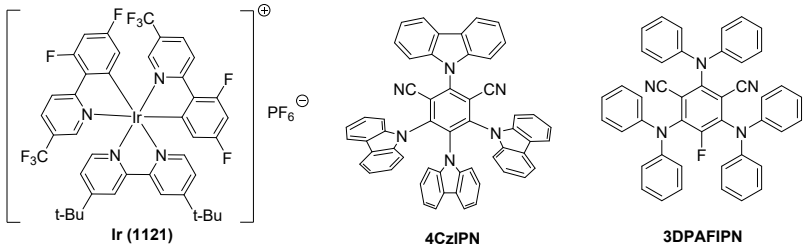
IR (KBr, cm^{-1}): 2719, 1650, 1585, 1352, 1178, 1059, 904, 779, 663.

HRMS (ESI): calcd for $C_{23}H_{30}NO_4S^+$ $[M + H]^+$: 416.1890; found: 416.1882.

III. Investigations of reaction conditions

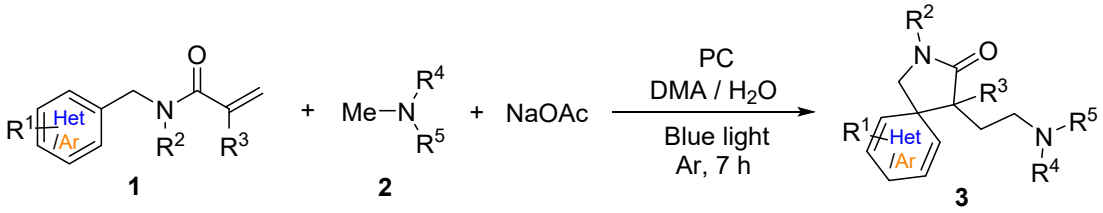


Entry	PC	Base	Solvent	Yield[b] (%)
1	Ir(1121)	NaOAc	DMA	41 (27)
2	4CzIPN	NaOAc	DMA	62 (25)
3	3DPAFIPN	NaOAc	DMA	64 (23)
4	3DPAFIPN	NaOAc	DCM	44 (5)
5	3DPAFIPN	NaOAc	MeCN	70 (15)
6[c]	3DPAFIPN	NaOAc	MeCN/H_2O	Trace (0)
7[d]	3DPAFIPN	NaOAc	DMA/H_2O	87 (9)
8[e]	3DPAFIPN	NaOAc	DMA/H_2O	84 (13)
9[f]	3DPAFIPN	NaOAc	DMA/H_2O	81 (4)
10[d]	3DPAFIPN	$K_3PO_4 \cdot 3H_2O$	DMA/H_2O	49 (10)
11[d]	3DPAFIPN	Na_2CO_3	DMA/H_2O	28 (1)
12[d]	3DPAFIPN	LiOAc	DMA/H_2O	82 (16)
13[d]	3DPAFIPN	DBU	DMA/H_2O	84 (16)
14[d, g]	3DPAFIPN	NaOAc	DMA/H_2O	75 (10)
15[d, h]	3DPAFIPN	NaOAc	DMA/H_2O	88 (8)
16[d, i]	3DPAFIPN	NaOAc	DMA/H_2O	0 (0)
17[d, j]	-	NaOAc	DMA/H_2O	0 (0)



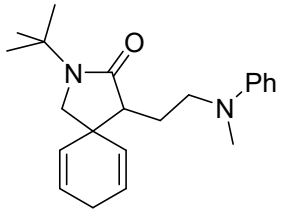
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), PC (3 mol%), Base (0.24 mmol), Visible-light irradiation with blue LEDs (2 × 15 W, 445 nm) under Argon atmosphere for 7 h. [b] Determined by ^{1}H NMR using CH_2Br_2 as the internal standard. Yield of the **3-1'** is shown in parentheses. [c] Ratio of volume is MeCN/H_2O = 8/2. [d] Ratio of volume is DMA/H_2O = 8/2. [e] Ratio of volume is DMA/H_2O = 9/1. [f] Ratio of volume is DMA/H_2O = 7/3. [g] with 1.0 equiv. of **2a**. [h] with 2.0 equiv. of **2a**. [i] without bule light. [j] without PC. DMA = *N*,*N*-dimethylacetamide. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

IV. General procedure for the dearomatization reactions



Standard Conditions:

To a 5-mL scintillation vial equipped with a stirrer bar and the requisite acrylamide **1** (0.3 mmol, 1.0 eq) was then added to the vial. The vial then charged with *N*-methyl amine **2** (0.6 mmol, 2.0 eq), sodium acetate (30 mg, 0.36 mmol, 1.2 eq) and 3DPAFIPN **(**PC**)** (6 mg, 0.009 mmol, 3 mol%), followed by made up to a total of 3.0 mL by addition of DMA and H_2O (*v* / *v* = 4 / 1). The reaction mixture was thoroughly degassed with argon via freeze-pump-thaw for 3 cycles, after degassed the vial was sealed and positioned approximately 10 cm from 2×15W blue LEDs. The mixture was stirred at room temperature for 7 hours under argon atmosphere. Afterwards, the reaction solution was washed by H_2O and extracted with EA for 3 times, the organic layer was concentrated by rotary evaporation. The crude product was purified by silica gel column chromatography (PE / EA = 20 / 1 for Ar, PE / EA = 1 / 1 for Heter and other cases) to obtain the desired product **3**. the details data of the products are summarized below.



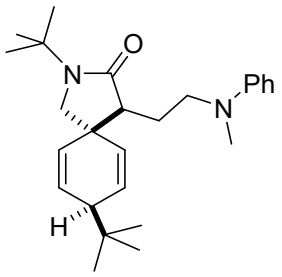
2-(tert-butyl)-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-1**)

brown oil, 73 mg, 72% yield.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 5.94 – 5.86 (m, 2H), 5.65 (dd, *J* = 10.4, 2.2 Hz, 1H), 5.53 (dd, *J* = 10.1, 2.2 Hz, 1H), 3.50 – 3.32 (m, 2H), 3.25 (d, *J* = 9.8 Hz, 1H), 3.19 (d, *J* = 9.8 Hz, 1H), 2.89 (s, 3H), 2.76 – 2.68 (m, 2H), 2.17 (t, *J* = 6.8 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.60 – 1.52 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8, 149.4, 130.1, 129.0, 127.1, 126.7, 125.6, 115.7, 112.1, 56.6, 53.8, 51.4, 51.1, 41.4, 37.6, 27.6, 26.6, 23.1.

IR(KBr, cm^{-1}): 2718, 1677, 1635, 1507, 1361, 1064, 946, 766, 606, 459.

HRMS(ESI): calcd for $C_{22}H_{31}N_2O^+$ $[M + H]^+$: 339.2431; found: 339.2426.



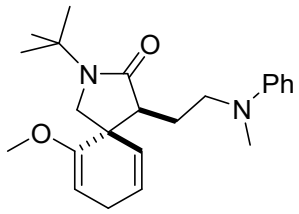
2,8-di-tert-butyl-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-2**)

Brownish yellow oil, 80 mg, 68% yield, d.r. > 20:1.

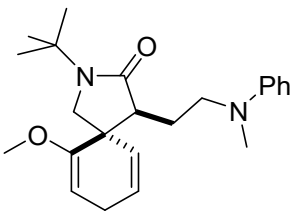
NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.9 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 5.91 (t, *J* = 12.1 Hz, 2H), 5.68 (d, *J* = 10.3 Hz, 1H), 5.57 (d, *J* = 10.2 Hz, 1H), 3.69 – 3.60 (m, 1H), 3.45 – 3.36 (m, 1H), 3.25 – 3.13 (m, 2H), 2.87 (s, 3H), 2.45 (q, *J* = 2.6 Hz, 1H), 2.18 – 2.13 (m, 1H), 1.72 – 1.59 (m, 2H), 1.39 (s, 9H), 0.91 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.6, 149.5, 131.0, 129.0, 128.9, 128.2, 128.0, 115.8, 112.3, 56.5, 53.8, 51.2, 50.8, 46.3, 41.7, 37.6, 34.0, 27.7, 23.3.

IR(KBr, cm^{-1}): 2717, 1594, 1507, 1472, 1223, 1083, 915, 749, 528.

HRMS(ESI): calcd for $C_{26}H_{39}N_2O^+$ $[M + H]^+$: 395.3057; found: 395.3051.



P1



P2

2-(tert-butyl)-6-methoxy-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-3**)

P1 41 mg, 40% yield, as a gray solid. **P2** 23 mg, 27% yield, as a brown oil. d.r. = 1.5:1

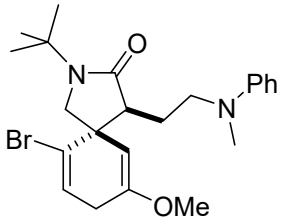
NMR:

[**P1**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 5.93 – 5.86 (m, 1H), 5.64 – 5.58 (m, 1H), 4.88 – 4.83 (m, 1H), 3.75 (d, *J* = 9.3 Hz, 1H), 3.56 (s, 3H), 3.47 – 3.38 (m, 1H), 3.32 – 3.23 (m, 1H), 3.07 (d, *J* = 9.3 Hz, 1H), 2.93 – 2.84 (m, 6H), 2.03 – 1.93 (m, 1H), 1.61 – 1.53 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.6, 152.6, 149.3, 128.9, 127.0, 124.9, 115.6, 112.1, 94.2, 54.1, 53.8, 53.6, 50.8, 46.5, 43.9, 37.6, 27.6, 26.6, 23.1.

[**P2**] NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 5.88 – 5.80 (m, 1H), 5.54 – 5.46 (m, 1H), 4.81 (t, *J* = 3.8 Hz, 1H), 2.23 (t, *J* = 6.7 Hz, 1H), 2.05 – 1.94 (m, 1H), 1.61 – 1.50 (m, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.63, 155.68, 149.41, 131.12, 128.90, 125.65, 115.61, 112.12, 92.32, 77.32, 77.00, 76.68, 55.54, 53.81, 53.44, 51.41, 50.47, 43.39, 37.56, 27.49, 26.50, 22.86.

IR(KBr, cm^{-1}): 2821, 1674, 1598, 1504, 1360, 1218, 1023, 943, 754, 692.

HRMS(ESI): calcd for $C_{23}H_{33}N_2O_2^+$ $[M + H]^+$: 369.2537; found: 369.2531.



6-bromo-2-(tert-butyl)-9-methoxy-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-4**)

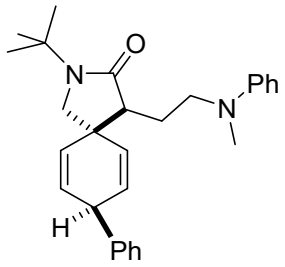
Beige solid, 90 mg, 68% yield, d.r. > 20:1, m.p. = 117.2 – 119.3 °C

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 – 7.16 (m, 2H), 6.67 – 6.62 (m, 3H), 6.22 (t, *J* = 3.8 Hz, 1H), 4.63 (s, 1H), 3.81 (d, *J* = 9.6 Hz, 1H), 3.54 (s, 3H), 3.51 – 3.43 (m, 1H), 3.35 – 3.28 (m, 1H), 3.13 (d, *J* = 9.6 Hz, 1H), 2.96 – 2.90 (m, 1H), 2.90 (s, 3H), 2.87 (t, *J* = 4.6 Hz, 2H), 1.99 – 1.90 (m,

1H), 1.61 – 1.51 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.0, 153.2, 149.2, 129.6, 129.0, 126.5, 115.8, 112.0, 94.6, 56.0, 54.3, 54.1, 50.5, 49.2, 48.5, 37.8, 31.7, 27.7, 23.1.

IR(KBr, cm^{-1}): 2717, 1594, 1471, 1218, 1026, 925, 750, 694.

HRMS(ESI): calcd for $C_{23}H_{32}BrN_2O_2^+$ $[M + H]^+$: 447.1642; found: 447.1636.



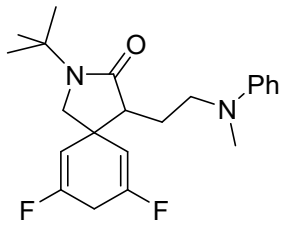
2-(tert-butyl)-4-(2-(methyl(phenyl)amino)ethyl)-8-phenyl-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-5**)

Brown oil, 75 mg, 60% yield, d.r. > 20:1.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.13 (m, 7H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 5.96 – 5.83 (m, 2H), 5.75 – 5.68 (m, 1H), 5.65 – 5.58 (m, 1H), 4.02 – 3.95 (m, 1H), 3.68 – 3.57 (m, 1H), 3.51 – 3.39 (m, 1H), 3.32 (d, *J* = 9.7 Hz, 1H), 3.24 (d, *J* = 9.8 Hz, 1H), 2.88 (s, 3H), 2.26 (dd, *J* = 8.6, 4.5 Hz, 1H), 1.86 – 1.75 (m, 1H), 1.72 – 1.60 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.2, 149.4, 143.0, 131.0, 129.7, 129.6, 129.1, 128.7, 127.7, 126.6, 126.5, 115.9, 112.3, 56.3, 53.9, 51.2, 50.7, 42.4, 41.6, 37.8, 27.8, 23.4.

IR(KBr, cm^{-1}): 2718, 1621, 1503, 1363, 1230, 1070, 909, 749, 605.

HRMS(ESI): calcd for $C_{28}H_{35}N_2O^+$ $[M + H]^+$: 415.2744; found: 415.2737.



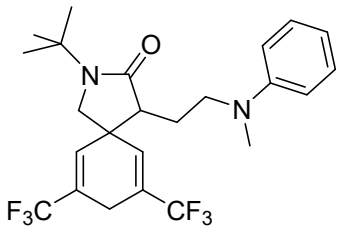
2-(tert-butyl)-7,9-difluoro-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-6**)

Brown oil, 75 mg, 67% yield.

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.5 Hz, 2H), 6.72 (d, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 6.9 Hz, 1H), 5.26 (d, *J* = 16.2 Hz, 1H), 5.13 (d, *J* = 15.4 Hz, 1H), 3.52 – 3.39 (m, 2H), 3.31 (d, *J* = 10.0 Hz, 1H), 3.24 (d, *J* = 9.8 Hz, 1H), 3.17 – 3.07 (m, 2H), 2.90 (s, 3H), 2.22 (t, *J* = 5.9 Hz, 1H), 1.88 – 1.81 (m, 1H), 1.53 – 1.46 (m, 1H), 1.39 (s, 9H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -103.7 (d, *J* = 17.3 Hz), -105.5 (d, *J* = 15.6 Hz).

IR(KBr, cm^{-1}): 2719, 1613, 1362, 1203, 1102, 1067, 858, 771, 692, 619.

HRMS(ESI): calcd for $C_{22}H_{29}F_2N_2O^+$ [M + H]$^+$: 375.2242; found: 375.2236.



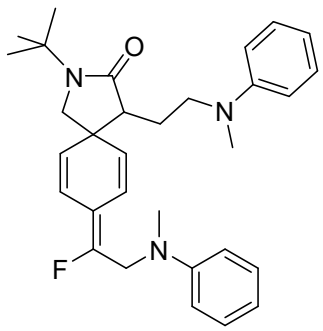
2-(tert-butyl)-4-(2-(methyl(phenyl)amino)ethyl)-7,9-bis(trifluoromethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-7**)

Brown oil, 99 mg, 70% yield.

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 7.9 Hz, 2H), 6.72 – 6.67 (m, 3H), 6.26 (s, 1H), 6.19 (s, 1H), 3.46 – 3.35 (m, 3H), 3.26 (d, *J* = 10.4 Hz, 1H), 3.03 (s, 2H), 2.86 (s, 3H), 2.41 (t, *J* = 6.7 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.47 – 1.43 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.4, 149.4, 131.3 (q, *J* = 5.5 Hz), 129.2, 128.7 (q, *J* = 5.5 Hz), 126.8 (dd, *J* = 74.9, 31.7 Hz), 127.5 – 125.9 (m), 123.8 (d, *J* = 16.0 Hz), 121.7 (d, *J* = 15.7 Hz), 116.6, 112.4, 54.6, 54.5, 50.8, 50.6, 43.1, 37.6, 27.6, 23.2, 21.6. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -69.5, -69.7.

IR(KBr, cm^{-1}): 2722, 1594, 1506, 1362, 1274, 1188, 898, 760, 660.

HRMS(ESI): calcd for $C_{24}H_{29}F_6N_2O^+$ [M + H]$^+$: 475.2179; found: 475.2173.



2-(tert-butyl)-8-(1-fluoro-2-(methyl(phenyl)amino)ethylidene)-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-8**)

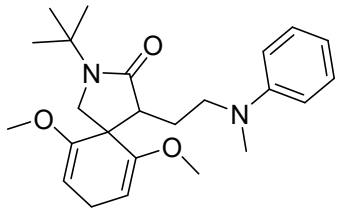
Brown oil, 32 mg, 22% yield.

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.2 (t, *J* = 8.0 Hz, 2H), 7.2 (t, *J* = 8.0 Hz, 2H), 6.8 (dd, *J* = 16.9, 8.0 Hz, 3H), 6.7 (d, *J* = 11.3 Hz, 1H), 6.6 (dd, *J* = 15.0, 7.7 Hz, 3H), 6.4 (d, *J* = 10.1 Hz, 1H), 5.8 (d, *J* = 10.4 Hz, 1H), 5.7 (d, *J* = 10.1 Hz, 1H), 4.2 (d, *J* = 3.2 Hz, 1H), 4.2 (d, *J* = 2.3 Hz, 1H), 3.5 – 3.4 (m, 1H), 3.3 – 3.3 (m, 2H), 3.2 (d, *J* = 9.9 Hz, 1H), 2.9 (s, 3H), 2.8 (s, 3H), 2.3 (t, *J* = 6.9 Hz, 1H), 2.0 – 1.9 (m, 1H), 1.5 – 1.5 (m, 1H), 1.4 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.3, 155.7, 153.6, 149.3, 132.6, 129.5, 129.5, 129.1, 129.0, 121.9, 121.8, 120.2, 117.8, 115.9, 113.5, 113.4, 113.4,

112.3, 112.3, 55.5, 55.5, 54.0, 51.3, 51.3, 50.8, 49.9 (d, J = 26.8 Hz), 44.4, 38.2, 37.6, 27.7, 23.5. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.8.

IR(KBr, cm^{-1}): 2718, 1604, 1509, 1362, 1203, 1047, 943, 809, 691.

HRMS(ESI): calcd for $C_{31}H_{39}FN_3O^+$ [M + H]$^+$: 488.3072; found: 488.3066.



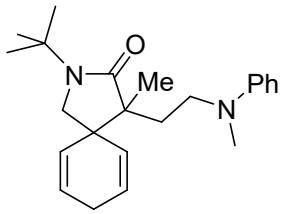
2-(tert-butyl)-6,10-dimethoxy-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-9**)

Brown oil, 60 mg, 50% yield.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (t, J = 8.0 Hz, 2H), 6.69 – 6.58 (m, 3H), 4.86 – 4.78 (m, 2H), 3.69 (d, J = 9.5 Hz, 1H), 3.55 (s, 3H), 3.46 (s, 3H), 3.45 – 3.32 (m, 1H), 3.28 (d, J = 9.5 Hz, 1H), 3.24 – 3.11 (m, 1H), 2.92 – 2.87 (m, 3H), 2.86 (s, 3H), 2.06 – 1.95 (m, 1H), 1.55 – 1.42 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8, 155.2, 152.6, 149.4, 128.9, 115.6, 112.1, 93.8, 92.0, 54.6, 53.9, 52.1, 51.3, 46.1, 45.6, 37.6, 27.5, 24.1, 23.0.

IR(KBr, cm^{-1}): 2717, 1601, 1506, 1413, 1265, 1161, 991, 742, 612.

HRMS(ESI): calcd for $C_{24}H_{35}N_2O_3^+$ [M + H]$^+$: 399.2642; found: 399.2638.



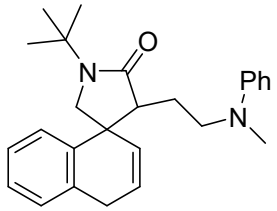
2-(tert-butyl)-4-methyl-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-10**)

brown oil, 70 mg, 67% yield.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, J = 7.8 Hz, 2H), 6.69 – 6.62 (m, 3H), 5.91 (t, J = 10.0 Hz, 2H), 5.68 (d, J = 10.3 Hz, 1H), 5.62 (d, J = 10.1 Hz, 1H), 3.53 – 3.42 (m, 1H), 3.38 – 3.27 (m, 1H), 3.21 (s, 2H), 2.87 (s, 3H), 2.72 (s, 2H), 1.84 – 1.73 (m, 1H), 1.64 – 1.55 (m, 1H), 1.41 (s, 9H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.8, 149.0, 129.0, 127.7, 126.3, 126.1, 115.6, 111.9, 54.8, 53.6, 50.6, 47.7, 43.1, 37.6, 29.1, 27.5, 26.8, 16.2.

IR(KBr, cm^{-1}): 2719, 1600, 1509, 1392, 1058, 948, 816, 694.

HRMS(ESI): calcd for $C_{23}H_{33}N_2O^+$ [M + H]$^+$: 353.2587; found: 353.2582.



rac-**P**

2-(tert-butyl)-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-11**)

Brown yellow oil, 40 mg (**P1**, small polarity), 35% yield and 41mg (**P2**, big polarity), 35% yield, d.r. = 1:1.

NMR:

[**P1**] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.13 (m, 3H), 7.11 (dd, *J* = 9.0, 7.2 Hz, 2H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 2H), 6.10 – 6.03 (m, 1H), 5.80 – 5.74 (m, 1H), 3.75 (d, *J* = 9.9 Hz, 1H), 3.48 (t, *J* = 3.1 Hz, 2H), 3.38 (d, *J* = 9.9 Hz, 1H), 3.10 – 2.97 (m, 2H), 2.83 (t, *J* = 6.7 Hz, 1H), 2.69 (s, 3H), 2.03 – 1.94 (m, 1H), 1.56 – 1.50 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.3, 149.3, 137.0, 134.6, 128.9, 128.8, 127.6, 126.7, 126.6, 126.1, 124.9, 115.8, 112.1, 59.1, 54.0, 53.2, 51.0, 43.6, 37.4, 29.8, 27.7, 23.5.

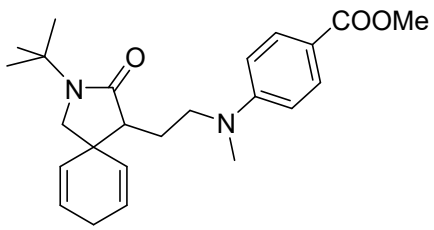
[**P2**] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.1 Hz, 1H), 7.25 (dd, *J* = 6.7, 1.2 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.09 – 7.04 (m, 2H), 6.58 (t, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 8.2 Hz, 2H), 6.03 – 5.97 (m, 1H), 5.69 – 5.65 (m, 1H), 3.63 (d, *J* = 10.2 Hz, 1H), 3.53 (d, *J* = 10.2 Hz, 1H), 3.45 (t, *J* = 3.1 Hz, 2H), 3.28 – 3.21 (m, 1H), 3.19 – 3.12 (m, 1H), 2.73 (s, 3H), 2.51 (dd, *J* = 7.9, 6.1 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.46 (s, 9H), 1.39 – 1.32 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.4, 149.2, 137.8, 133.5, 132.8, 128.9, 128.8, 127.0, 126.9, 125.9, 125.0, 115.6, 111.9, 59.2, 54.3, 53.4, 50.9, 42.3, 37.5, 29.8, 27.6, 23.7.

IR(KBr, cm^{-1}):

[**P1**] 2719, 1681, 1599, 1456, 1396, 1268, 1194, 1035, 951, 753, 694.

[**P2**] 2720, 1593, 1504, 1363, 1298, 1223, 1155, 1035, 990, 750, 696.

HRMS(ESI): calcd for $C_{26}H_{33}N_2O^+$ [M + H]$^+$: 389.2587; found: 389.2581.



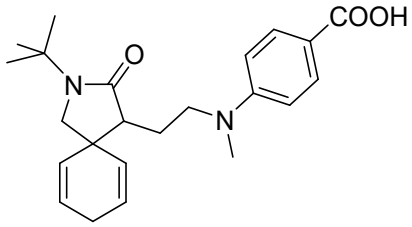
methyl 4-((2-(2-(tert-butyl)-3-oxo-2-azaspiro[4.5]deca-6,9-dien-4-l)ethyl)(methyl)amino)benzoate (**3-12**)

Brown oil, 82 mg, 59% yiled.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 5.94 – 5.84 (m, 2H), 5.66 – 5.59 (m, 1H), 5.53 – 5.47 (m, 1H), 3.82 (s, 3H), 3.54 – 3.37 (m, 2H), 3.26 – 3.15 (m, 2H), 2.95 (s, 3H), 2.70 (s, 2H), 2.11 (t, *J* = 6.8 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.59 – 1.49 (m, 1H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.5, 167.4, 152.3, 131.2, 129.9, 127.0, 127.0, 125.8, 116.3, 110.4, 56.6, 53.9, 51.3, 51.3, 50.7, 41.4, 37.7, 27.6, 26.6, 23.2.

IR(KBr, cm^{-1}): 2711, 1674, 1529, 1470, 1366, 1227, 1111, 974, 768, 592.

HRMS(ESI): calcd for $C_{24}H_{33}N_2O_3^+$ $[M + H]^+$: 397.2486; found: 397.2482.



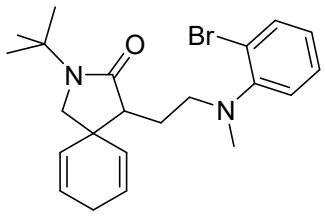
4-((2-(2-(tert-butyl)-3-oxo-2-azaspiro[4.5]deca-6,9-dien-4-yl)ethyl)(methyl)amino)benzoic acid (**3-13**)

Brown oil, 75 mg, 66% yield.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 5.90 (t, *J* = 7.9 Hz, 2H), 5.63 (d, *J* = 10.3 Hz, 1H), 5.51 (d, *J* = 9.1 Hz, 1H), 3.53 – 3.38(m, 2H), 3.25 (d, *J* = 9.8 Hz, 1H), 3.18 (d, *J* = 9.8 Hz, 1H), 2.97 (s, 3H), 2.71 (s, 2H), 2.14 (t, *J* = 6.7 Hz, 1H), 1.97 – 1.84 (m, 1H), 1.61 – 1.51 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.6, 172.1, 152.8, 131.9, 129.9, 127.0, 126.9, 125.9, 115.5, 110.4, 56.6, 53.9, 51.3, 50.7, 41.4, 37.7, 27.6, 26.6, 23.2.

IR(KBr, cm^{-1}): 2702, 1670, 1532, 1389, 1184, 945, 831, 739, 561.

HRMS(ESI): calcd for $C_{23}H_{31}N_2O_3^+$ $[M + H]^+$: 383.2329; found: 383.2324.



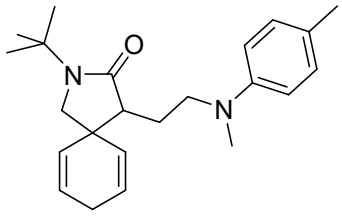
4-(2-((2-bromophenyl)(methyl)amino)ethyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-14**)

Brown oil, 83 mg, 67% yield.

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.04 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.86 – 6.82 (m, 1H), 5.81 – 5.76 (m, 1H), 5.66 – 5.61 (m, 1H), 5.57 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.48 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.20 (d, *J* = 9.8 Hz, 1H), 3.12 (d, *J* = 9.7 Hz, 1H), 3.11 – 3.00 (m, 2H), 2.70 (s, 3H), 2.63 – 2.53 (m, 2H), 2.37 (dd, *J* = 7.9, 5.8 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.51 – 1.44 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.2, 151.2, 133.6, 130.3, 127.8, 127.0, 126.0, 125.5, 123.8, 122.2, 120.4, 56.6, 53.7, 53.3, 50.8, 41.4, 41.3, 27.7, 26.6, 23.6.

IR(KBr, cm^{-1}): 2724, 1597, 1473, 1361, 1117, 1028, 917, 764, 567.

HRMS(ESI): calcd for $C_{22}H_{30}BrN_2O^+$ [M + H]$^+$: 417.1536; found: 417.1530.



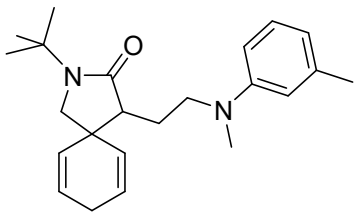
2-(tert-butyl)-4-(2-(methyl(p-tolyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-15**)

Brown oil, 72 mg, 69% yield.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.00 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 5.93 – 5.85 (m, 2H), 5.67 – 5.61 (m, 1H), 5.55 – 5.49 (m, 1H), 3.47 – 3.38 (m, 1H), 3.37 – 3.28 (m, 1H), 3.26 – 3.16 (m, 2H), 2.85 (s, 3H), 2.76 – 2.68 (m, 2H), 2.24 (s, 3H), 2.17 (t, *J* = 6.8 Hz, 1H), 1.94 – 1.86 (m, 1H), 1.60 – 1.49 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.9, 147.4, 130.2, 129.5, 127.2, 126.7, 125.6, 125.0, 112.5, 56.6, 53.8, 51.4, 51.4, 41.4, 37.7, 27.6, 26.6, 23.0, 20.1.

IR(KBr, cm^{-1}): 2811, 1683, 1611, 1521, 1362, 1224, 775.

HRMS(ESI): calcd for $C_{23}H_{33}N_2O^+$ [M + H]$^+$: 353.2587; found: 353.2583.



2-(tert-butyl)-4-(2-(methyl(m-tolyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-16**)

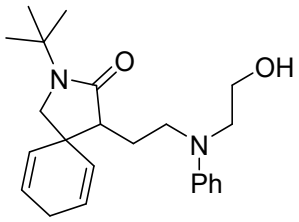
Brown oil, 73 mg, 70% yield.

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 7.12 – 7.04 (m, 1H), 6.56 – 6.49 (m, 2H), 6.48 (d, *J* = 8.1 Hz, 1H), 5.95 – 5.84 (m, 2H), 5.70 – 5.61 (m, 1H), 5.57 – 5.49 (m, 1H), 3.53 – 3.41 (m, 1H), 3.38 – 3.26 (m, 1H), 3.28 – 3.15 (m, 2H), 2.88 (s, 3H), 2.76 – 2.69 (m, *J* = 2.0 Hz, 2H), 2.29 (s, 3H), 2.17 (t, *J*

= 6.8 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.62 – 1.51 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.9, 149.5, 138.6, 130.2, 128.8, 127.2, 126.7, 125.6, 116.7, 112.9, 109.4, 56.6, 53.8, 51.4, 51.1, 41.4, 37.6, 27.7, 26.6, 23.2, 21.8.

IR(KBr, cm^{-1}): 2782, 1682, 1600, 1500, 1356, 1225, 1086, 769.

HRMS(ESI): calcd for $C_{23}H_{33}N_2O^+$ [M + H]$^+$: 353.2587; found: 353.2583.



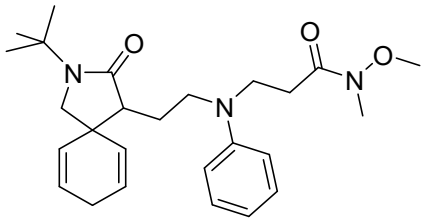
2-(tert-butyl)-4-(2-((2-hydroxyethyl)(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-17**)

Brown oil, 75 mg, 68% yield.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.17 (m, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 5.95 – 5.86 (m, 2H), 5.68 – 5.62 (m, 1H), 5.57 – 5.50 (m, 1H), 3.77 (t, *J* = 6.1 Hz, 2H), 3.53 – 3.40 (m, 4H), 3.30 – 3.17 (m, 2H), 2.77 – 2.68 (m, 2H), 2.17 (t, *J* = 6.7 Hz, 1H), 1.97 – 1.86 (m, 1H), 1.65 – 1.55 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8, 148.3, 129.9, 129.0, 127.0, 126.9, 125.7, 116.1, 112.4, 59.9, 56.6, 53.8, 52.7, 51.6, 49.9, 41.4, 27.6, 26.5, 23.4.

IR(KBr, cm^{-1}): 2832, 1664, 1598, 1506, 1361, 1226, 775.

HRMS(ESI): calcd for $C_{23}H_{33}N_2O_2^+$ [M + H]$^+$: 369.2537; found: 369.2534.



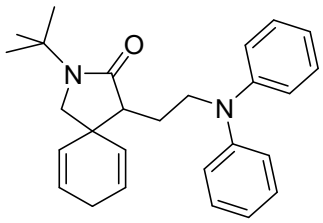
3-((2-(2-(tert-butyl)-3-oxo-2-azaspiro[4.5]deca-6,9-dien-4-yl)ethyl)(phenyl)amino)-N-methoxy-N-methylpropanamide (**3-18**)

Brown oil, 81 mg, 62% yield.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 6.62 (t, *J* = 7.1 Hz, 1H), 5.92 – 5.84 (m, 2H), 5.63 (d, *J* = 10.1 Hz, 1H), 5.51 (d, *J* = 8.7 Hz, 1H), 3.66 – 3.56 (m, 5H), 3.54 – 3.42 (m, 1H), 3.43 – 3.31 (m, 1H), 3.27 – 3.16 (m, 2H), 3.16 (s, 3H), 2.73 – 2.63 (m, 4H), 2.15 (t, *J* = 6.7 Hz, 1H), 1.97 – 1.83 (m, 1H), 1.60 – 1.51 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7, 147.4, 130.0, 129.1, 127.0, 126.8, 125.6, 115.5, 111.8, 61.2, 56.5, 53.7, 51.5, 49.3, 45.9, 41.4, 27.6, 26.5, 23.9.

IR(KBr, cm^{-1}): 2710, 1620, 1502, 1359, 1214, 1043, 992, 872, 744, 569.

HRMS(ESI): calcd for $C_{26}H_{38}N_3O_3^+$ $[M + H]^+$: 440.2908; found: 440.2904.



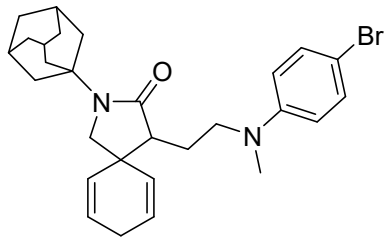
2-(tert-butyl)-4-(2-(diphenylamino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-19**)

Brown oil, 72 mg, 60% yield.

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.7 Hz, 4H), 6.98 (d, *J* = 7.8 Hz, 4H), 6.90 (t, *J* = 7.2 Hz, 2H), 5.85 (dd, *J* = 18.5, 10.2 Hz, 2H), 5.64 (d, *J* = 10.1 Hz, 1H), 5.48 (d, *J* = 9.4 Hz, 1H), 3.88 – 3.73 (m, 2H), 3.26 – 3.14 (m, 2H), 2.66 (s, 2H), 2.20 (t, *J* = 6.8 Hz, 1H), 2.09 – 1.98 (m, 1H), 1.73 – 1.61 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7, 147.8, 130.2, 129.2, 127.2, 126.8, 125.8, 121.0, 120.9, 56.7, 53.9, 51.7, 50.6, 41.4, 27.7, 26.6, 24.2.

IR(KBr, cm^{-1}): 2720, 1681, 1594, 1494, 1392, 1244, 1067, 988, 878, 696.

HRMS(ESI): calcd for $C_{27}H_{33}N_2O^+$ $[M + H]^+$: 401.2587; found: 401.2582.



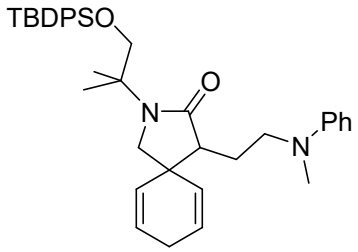
2-(adamantan-1-yl)-4-(2-((4-bromophenyl)(methyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-20**)

Brown oil, 97 mg, 66% yield.

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 9.1 Hz, 2H), 6.56 (d, *J* = 9.1 Hz, 2H), 5.92 – 5.83 (m, 2H), 5.67 – 5.60 (m, 1H), 5.53 – 5.45 (m, 1H), 3.39 (dd, *J* = 9.3, 6.7 Hz, 2H), 3.21 (s, 2H), 2.85 (s, 3H), 2.69 (d, *J* = 5.5 Hz, 2H), 2.09 (d, *J* = 9.6 Hz, 10H), 1.89 – 1.76 (m, 1H), 1.70 (d, *J* = 13.8 Hz, 7H), 1.56 – 1.42 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7, 148.3, 131.6, 130.0, 127.2, 126.9, 125.6, 113.7, 107.5, 55.5, 55.1, 51.6, 51.1, 41.6, 39.7, 37.7, 36.3, 29.6, 26.7, 22.9.

IR(KBr, cm^{-1}): 2710, 1670, 1594, 1455, 1345, 1196, 923, 802, 578.

HRMS(ESI): calcd for $C_{28}H_{36}BrN_2O^+$ $[M + H]^+$: 495.2006; found: 495.2001.



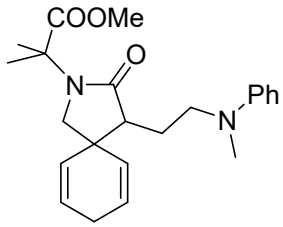
2-(1-((tert-butyldiphenylsilyl)oxy)-2-methylpropan-2-yl)-4-(2-(methyl(phenyl)amino)ethyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-21**)

Brown oil, 100 mg, 60% yield.

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.3 Hz, 4H), 7.46 – 7.39 (m, 6H), 7.22 (t, *J* = 7.6 Hz, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 5.93 – 5.84 (m, 2H), 5.76 (d, *J* = 10.2 Hz, 1H), 5.53 (d, *J* = 9.9 Hz, 1H), 3.99 (d, *J* = 10.0 Hz, 1H), 3.81 (d, *J* = 10.0 Hz, 1H), 3.46 (t, *J* = 8.0 Hz, 2H), 3.40 (d, *J* = 9.6 Hz, 1H), 3.34 (d, *J* = 9.6 Hz, 1H), 2.93 (s, 3H), 2.74 (s, 2H), 2.16 (t, *J* = 6.7 Hz, 1H), 1.99 – 1.90 (m, 1H), 1.64 – 1.55 (m, 1H), 1.39 (s, 6H), 1.12 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.9, 149.3, 135.6, 133.4, 130.2, 129.6, 129.0, 127.6, 127.5, 126.8, 125.3, 115.7, 112.1, 68.5, 57.8, 57.6, 51.4, 51.1, 41.7, 37.7, 26.9, 26.6, 23.4, 23.1, 19.3.

IR(KBr, cm^{-1}): 2715, 1602, 1504, 1392, 1194, 994, 817, 612.

HRMS(ESI): calcd for $C_{38}H_{49}N_2O_2Si^+$ $[M + H]^+$: 593.3558; found: 593.3550.



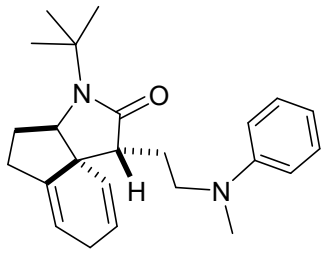
methyl 2-methyl-2-(4-(2-(methyl(phenyl)amino)ethyl)-3-oxo-2-azaspiro[4.5]deca-6,9-dien-2-yl)propanoate (**3-22**)

Brown oil, 41 mg, 36% yield.

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 7.7 Hz, 2H), 6.65 (t, *J* = 7.0 Hz, 1H), 5.91 (dd, *J* = 9.1, 3.3 Hz, 2H), 5.70 (d, *J* = 10.3 Hz, 1H), 5.57 (d, *J* = 10.0 Hz, 1H), 3.74 (s, 3H), 3.52 – 3.44 (m, 1H), 3.38 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.33 (d, *J* = 9.2 Hz, 1H), 3.20 (d, *J* = 9.4 Hz, 1H), 2.87 (s, 3H), 2.73 (s, 2H), 2.23 (t, *J* = 6.9 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.61 – 1.54 (m, 1H), 1.49 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.7, 174.4, 149.4, 129.7, 129.0, 127.1, 127.0, 125.8, 115.8, 112.2, 58.1, 55.7, 52.4, 50.9, 50.2, 42.3, 37.6, 26.6, 23.9, 23.4, 22.9.

IR(KBr, cm^{-1}): 2718, 1613, 1508, 1362, 1199, 947, 850, 696.

HRMS(ESI): calcd for $C_{23}H_{31}N_2O_3^+$ $[M + H]^+$: 383.2329; found: 383.2323.



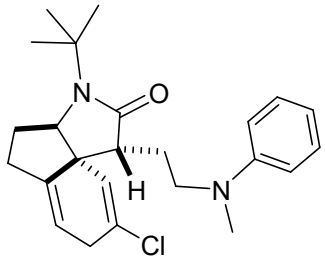
3-(tert-butyl)-1-(2-(methyl(phenyl)amino)ethyl)-3a,4,5,7-tetrahydro-1H-indeno[1,7a-b]pyrrol-2(3H)-one (**3-23**)

Brown oil, 75mg, 69 % yield (d.r. > 20:1).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.01 – 5.95 (m, 1H), 5.71 (d, *J* = 9.9 Hz, 1H), 5.59 (s, 1H), 3.64 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.38 – 3.21 (m, 2H), 2.87 (s, 3H), 2.76 – 2.70 (m, 2H), 2.73 – 2.64 (m, 2H), 2.47 (dd, *J* = 8.1, 5.8 Hz, 1H), 2.35 (dd, *J* = 14.6, 9.8 Hz, 1H), 2.08 – 1.91 (m, 2H), 1.80 – 1.74 (m, 1H), 1.50 (dd, *J* = 16.1, 7.3 Hz, 2H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7, 149.4, 140.7, 128.9, 126.7, 126.4, 117.7, 115.8, 112.2, 65.8, 53.8, 51.2, 50.4, 47.3, 37.7, 31.0, 30.0, 28.2, 27.4, 23.9.

KR(KBr, cm^{-1}): 2718, 1601, 1505, 1362, 1221, 1118, 948, 693.

HRMS(ESI): calcd for $C_{24}H_{33}N_2O^+$ $[M + H]^+$: 365.2587; found: 365.2583.



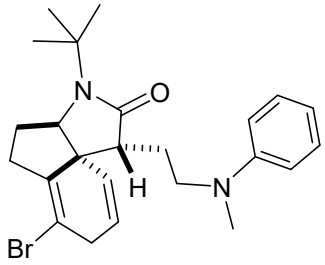
3-(tert-butyl)-8-chloro-1-(2-(methyl(phenyl)amino)ethyl)-3a,4,5,7-tetrahydro-1H-indeno[1,7a-b]pyrrol-2(3H)-one (**3-24**)

Brown oil, 75 mg, 63 % yield (d.r. = 2.33:1).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.17 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 3H), 6.65 (d, *J* = 7.2 Hz, 2H), 5.82 (d, *J* = 1.7 Hz, 1H), 5.54 – 5.48 (m, 1H), 3.70 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.37 – 3.21 (m, 2H), 3.15 – 3.10 (m, 0.3H), 3.10 – 3.05 (m, 0.7H), 2.98 – 2.92 (m, 0.7H), 2.93 – 2.88 (m, 0.3H), 2.88 (s, 3H), 2.73 – 2.61 (m, 1H), 2.50 (dd, *J* = 8.7, 5.4 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.13 – 1.95 (m, 2H), 1.85 – 1.72 (m, 1H), 1.63 – 1.50 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 149.3, 140.4, 132.3, 129.1, 123.9, 116.8, 116.0, 112.3, 65.2, 54.0, 53.7, 51.1, 47.4, 37.7, 34.7, 31.6, 29.5, 28.2, 24.0.

KR(KBr, cm^{-1}): 2718, 1601, 1505, 1362, 1221, 1118, 948, 756, 693.

HRMS(ESI): calcd for $C_{24}H_{32}ClN_2O^+$ [M + H]$^+$: 399.2198; found: 399.2193.



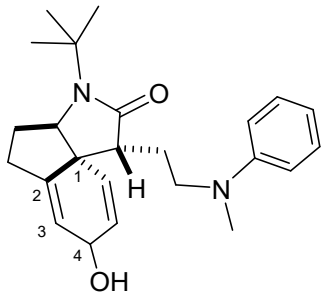
6-bromo-3-(tert-butyl)-1-(2-(methyl(phenyl)amino)ethyl)-3a,4,5,7-tetrahydro-1H-indeno[1,7a-b]pyrrol-2(3H)-one (**3-25**)

Brown oil, 96 mg, 73 % yield (d.r. > 20:1).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 7.8 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.67 (t, *J* = 7.1 Hz, 1H), 5.87 – 5.79 (m, 1H), 5.68 (d, *J* = 9.7 Hz, 1H), 3.71 (dd, *J* = 8.8, 5.8 Hz, 1H), 3.46 – 3.36 (m, 1H), 3.32 – 3.22 (m, 1H), 3.18 (d, *J* = 22.2 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.87 (s, 3H), 2.71 – 2.61 (m, 2H), 2.49 (t, *J* = 6.7 Hz, 1H), 2.21 – 2.09 (m, 1H), 1.99 – 1.88 (m, 1H), 1.87 – 1.77 (m, 1H), 1.53 – 1.45 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.0, 149.4, 139.4, 129.1, 126.2, 126.2, 116.1, 114.0, 112.4, 65.2, 55.1, 53.9, 51.1, 47.5, 37.7, 37.5, 30.7, 30.2, 28.2, 23.7.

IR(KBr, cm^{-1}): 2718, 1678, 1605, 1506, 1362, 1222, 1039, 749, 645.

HRMS(ESI): calcd for $C_{24}H_{32}BrN_2O^+$ [M + H]$^+$: 443.1693; found: 443.1688.



3-(tert-butyl)-7-hydroxy-1-(2-(methyl(phenyl)amino)ethyl)-3a,4,5,7-tetrahydro-1H-indeno[1,7a-b]pyrrol-2(3H)-one (**3-26**)

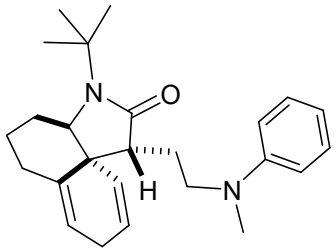
Brown oil, 67 mg, 59 % yield (From 4-F) (d.r. > 20:1); 78 mg, 68 % yield (From 4-Br) (d.r. > 20:1)

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 7.4 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.65 (t, *J* = 6.9 Hz, 1H), 6.01 (dd, *J* = 9.9, 4.4 Hz, 1H), 5.86 (d, *J* = 9.9 Hz, 1H), 5.78 (s, 1H), 4.55 (t, *J* = 4.9 Hz, 1H), 3.60 (dd, *J* = 8.7, 4.1 Hz, 1H), 3.56 – 3.48 (m, 1H), 3.46 – 3.38 (m, 1H), 2.87 (s, 3H), 2.78 – 2.69 (m, 1H), 2.49 (t, *J* = 6.3 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.12 – 2.03 (m, 1H), 1.84 – 1.78 (m, 2H), 1.56 – 1.50 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.7, 149.5, 129.1, 129.0,

129.0, 121.7, 121.6, 116.2, 116.2, 112.7, 64.4, 63.1, 63.0, 54.0, 51.4, 51.0, 51.0, 46.0, 38.2, 38.2, 31.6, 30.1, 28.3, 23.8.

IR(KBr, cm^{-1}): 2967, 1659, 1594, 1507, 1358, 1001, 876, 692.

HRMS(ESI): calcd for $C_{24}H_{33}N_2O_2^+$ $[M + H]^+$: 381.2537; found: 381.2532.



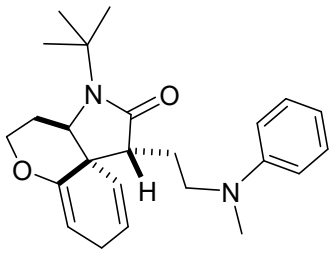
3-(tert-butyl)-1-(2-(methyl(phenyl)amino)ethyl)-3,3a,4,5,6,8-hexahydrobenzo[d]indol-2(1H)-one (**3-27**)

Brown oil, 83 mg, 73 % yield (d.r. > 20:1).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 5.88 (dd, *J* = 10.1, 4.4 Hz, 1H), 5.63 (t, *J* = 3.5 Hz, 1H), 5.58 – 5.51 (m, 1H), 3.41 (t, *J* = 7.9 Hz, 2H), 3.30 (dd, *J* = 10.6, 5.9 Hz, 1H), 2.88 (s, 3H), 2.74 (d, *J* = 6.5 Hz, 1H), 2.72 – 2.67 (m, 2H), 2.22 – 2.12 (m, 3H), 1.94 – 1.84 (m, 1H), 1.79 – 1.73 (m, 1H), 1.55 – 1.46 (m, 2H), 1.43 (s, 9H), 1.28 – 1.22 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 149.5, 136.5, 128.9, 128.0, 126.2, 121.9, 115.8, 112.2, 63.0, 53.7, 51.2, 45.7, 45.6, 37.6, 32.0, 31.9, 28.1, 27.1, 24.1, 23.3.

IR(KBr, cm^{-1}): 2711, 1675, 1504, 1394, 1266, 1027, 954, 750, 698.

HRMS(ESI): calcd for $C_{25}H_{35}N_2O^+$ $[M + H]^+$: 379.2744; found: 379.2738



3-(tert-butyl)-1-(2-(methyl(phenyl)amino)ethyl)-3,3a,4,5-tetrahydro-8H-chromeno[4,4a-b]pyrrol-2(1H)-one (**3-28**)

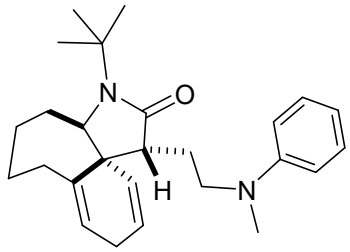
White solid, 80 mg, 70 % yield (d.r. = 6.62:1).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.15 (m, 2H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 5.92 – 5.83 (m, 1H), 5.56 – 5.48 (m, 1H), 5.47 – 5.40 (m, 1H), 4.15 – 4.06 (m, 1H), 3.60 – 3.46 (m, 3H), 3.43 – 3.30 (m, 1H), 2.89 (s, 4H), 2.86 (t, *J* = 6.6 Hz, 5H), 2.83 – 2.68 (m, 2H), 2.09 –

1.84 (m, 4H), 1.60 – 1.48 (m, 1H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 151.7, 149.2, 128.9, 126.6, 115.6, 112.1, 108.1, 66.7, 59.6, 53.9, 51.3, 46.0, 43.7, 37.7, 31.6, 28.1, 26.7, 23.1.

IR(KBr, cm^{-1}): 2824, 1667, 1598, 1507, 1359, 1219, 1073, 950, 751, 690.

HRMS(ESI): calcd for $C_{24}H_{33}N_2O_2^+$ $[M + H]^+$: 381.2537; found: 381.2531



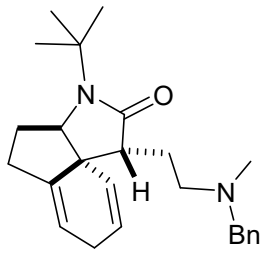
3-(tert-butyl)-1-(2-(methyl(phenyl)amino)ethyl)-3a,4,5,6,7,9-hexahydro-1H-benzo[2,3]cyclohepta[1,2-b]pyrrol-2(3H)-one (**3-29**)

Brown oil, 100 mg, 85 % yield (d.r. = 1.27:1).

NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.68 (d, *J* = 8.1 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 5.88 – 5.81 (m, 1H), 5.76 – 5.69 (m, 1H), 5.61 – 5.53 (m, 1H), 3.54 – 3.42 (m, 1H), 3.36 – 3.24 (m, 1H), 3.20 (dd, *J* = 10.7, 4.2 Hz, 1H), 2.92 – 2.83 (m, 4H), 2.77 – 2.66 (m, 2H), 2.42 – 2.29 (m, 1H), 2.14 – 2.08 (m, 1H), 1.96 – 1.83 (m, 2H), 1.73 – 1.62 (m, 3H), 1.61 – 1.48 (m, 2H), 1.43 (s, 9H), 1.36 – 1.26 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.6, 149.4, 135.4, 129.5, 128.9, 125.9, 124.6, 115.7, 112.1, 69.0, 53.9, 51.0, 47.6, 45.4, 37.5, 29.4, 29.2, 28.1, 27.6, 27.3, 23.2, 20.0.

IR(KBr, cm^{-1}): 2818, 1739, 1625, 1398, 1259, 1032, 989, 860, 752, 695.

HRMS(ESI): calcd for $C_{26}H_{37}N_2O^+$ $[M + H]^+$: 393.2900; found: 393.2894



1-(2-(benzyl(methyl)amino)ethyl)-3-(tert-butyl)-3a,4,5,7-tetrahydro-1H-indeno[1,7a-b]pyrrol-2(3H)-one (**3-30**)

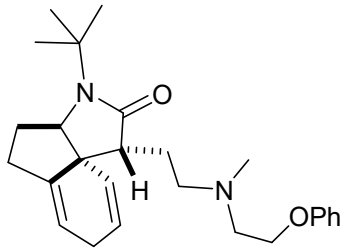
Brown oil, 85 mg, 75 % yield (d.r. > 20:1)

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.18 (m, 5H), 5.86 – 5.80 (m, 1H), 5.62 (dd, *J* = 9.9, 2.7 Hz, 1H), 5.47 – 5.42 (m, 1H), 3.59 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.47 (d, *J* = 13.0 Hz, 1H), 3.36 (d,

J = 13.0 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.63 – 2.54 (m, 2H), 2.45 – 2.39 (m, 1H), 2.35 – 2.27 (m, 3H), 2.12 (s, 3H), 2.07 – 1.94 (m, 3H), 1.78 – 1.71 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.1, 140.8, 139.3, 129.0, 128.0, 126.7, 126.4, 126.3, 117.3, 65.8, 62.1, 55.0, 53.7, 50.2, 47.0, 41.7, 30.9, 30.1, 28.2, 27.2, 24.3.

IR(KBr, cm^{-1}): 2823, 1601, 1461, 1389, 1264, 1133, 978, 815, 649.

HRMS(ESI): calcd for $C_{25}H_{35}N_2O^+$ $[M + H]^+$: 379.2744; found: 379.2738



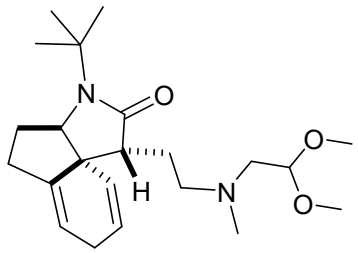
3-(tert-butyl)-1-(2-(methyl(2-phenoxyethyl)amino)ethyl)-3a,4,5,7-tetrahydro-1H-indeno[1,7a-b]pyrrol-2(3H)-one (**3-31**)

Brown oil, 86 mg, 70 % yield (d.r. > 20:1).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.9 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.91 (d, *J* = 9.7 Hz, 1H), 5.65 (d, *J* = 9.8 Hz, 1H), 5.51 (s, 1H), 4.01 (t, *J* = 6.0 Hz, 2H), 3.60 (dd, *J* = 9.1, 4.5 Hz, 1H), 2.76 (t, *J* = 6.0 Hz, 2H), 2.74 – 2.69 (m, 1H), 2.67 (s, 2H), 2.61 (dd, *J* = 9.0, 5.0 Hz, 1H), 2.47 – 2.40 (m, 2H), 2.34 – 2.28 (m, 4H), 2.04 – 1.93 (m, 2H), 1.78 – 1.70 (m, 1H), 1.40 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.0, 141.0, 129.3, 126.6, 126.3, 120.5, 117.4, 114.5, 65.9, 65.8, 56.1, 55.6, 53.8, 50.4, 46.9, 42.5, 30.9, 30.0, 28.3, 27.3, 24.2.

IR(KBr, cm^{-1}): 2719, 1612, 1496, 1361, 1233, 1070, 885, 771, 691.

HRMS(ESI): calcd for $C_{26}H_{37}N_2O_2^+$ $[M + H]^+$: 409.2850; found: 409.2845.



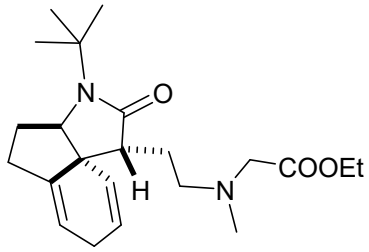
3-(tert-butyl)-1-(2-((2,2-dimethoxyethyl)(methyl)amino)ethyl)-3a,4,5,7-tetrahydro-1H-indeno[1,7a-b]pyrrol-2(3H)-one (**3-32**)

Brown oil, 77 mg, 69 % yield (d.r. > 20:1)

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.87 (d, *J* = 9.7 Hz, 1H), 5.61 (d, *J* = 9.8 Hz, 1H), 5.50 (s, 1H), 4.39 (t, *J* = 5.2 Hz, 1H), 3.57 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.29 (s, 6H), 2.74 – 2.67 (m, 1H), 2.65 (s, 2H), 2.51 (dd, *J* = 8.9, 5.0 Hz, 1H), 2.43 (d, *J* = 5.2 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 2.33 – 2.24 (m, 2H), 2.20 (s, 3H), 2.01 – 1.84 (m, 2H), 1.76 – 1.67 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.9, 140.9, 126.5, 126.2, 117.4, 102.7, 65.7, 58.5, 56.2, 53.7, 53.1, 53.0, 50.3, 47.0, 42.6, 30.9, 30.0, 28.2, 27.3, 23.9.

IR(KBr, cm^{-1}): 2832, 1603, 1470, 1361, 1209, 1070, 822, 771, 652.

HRMS(ESI): calcd for $C_{22}H_{37}N_2O_3^+$ $[M + H]^+$: 377.2799; found: 377.2794.



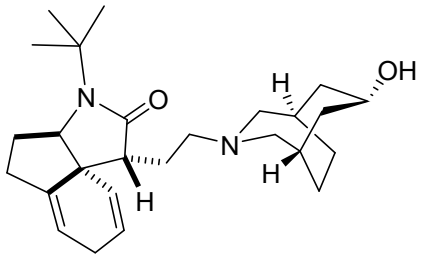
ethyl N-(2-(3-(tert-butyl)-2-oxo-2,3,3a,4,5,7-hexahydro-1H-indeno[1,7a-b]pyrrol-1-yl)ethyl)-N-methylglycinate (**3-33**)

Brown oil, 81 mg, 72 % yield (d.r. > 20:1)

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.91 – 5.86 (m, 1H), 5.62 (d, *J* = 9.9 Hz, 1H), 5.51 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.58 (dd, *J* = 9.2, 4.5 Hz, 1H), 3.17 (d, *J* = 3.7 Hz, 2H), 2.77 – 2.67 (m, 1H), 2.69 – 2.64 (m, 2H), 2.56 (dd, *J* = 9.0, 5.0 Hz, 1H), 2.52 – 2.39 (m, 2H), 2.35 – 2.26 (m, 4H), 2.05 – 1.95 (m, 1H), 1.95 – 1.85 (m, 1H), 1.78 – 1.68 (m, 1H), 1.45 – 1.32 (m, 10H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.0, 171.1, 141.0, 126.5, 126.3, 117.3, 65.7, 60.2, 58.1, 54.6, 53.7, 50.3, 46.9, 41.9, 30.9, 30.0, 28.2, 27.3, 24.3, 14.2.

IR(KBr, cm^{-1}): 2835, 1737, 1595, 1460, 1360, 1184, 1038, 769, 681, 570.

HRMS(ESI): calcd for $C_{22}H_{35}N_2O_3^+$ $[M + H]^+$: 375.2642; found: 375.2638



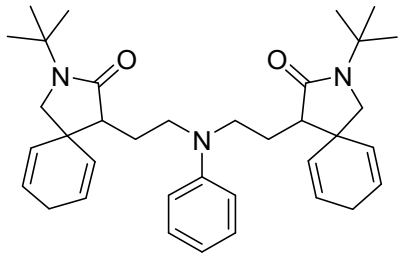
3-(tert-butyl)-1-(2-(7-hydroxy-3-azabicyclo[3.3.2]decan-3-yl)ethyl)-3a,4,5,7-tetrahydro-1H-indeno[1,7a-b]pyrrol-2(3H)-one (**3-34**)

Brown oil, 80 mg, 70 % yield (d.r. > 20:1).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.87 (d, *J* = 9.7 Hz, 1H), 5.61 (d, *J* = 9.6 Hz, 1H), 5.50 (s, 1H), 3.96 (s, 1H), 3.56 (dd, *J* = 8.4, 3.7 Hz, 1H), 3.11 (s, 2H), 2.72 – 2.62 (m, 4H), 2.36 – 2.23 (m, 3H), 2.09 – 1.93 (m, 6H), 1.87 – 1.79 (m, 3H), 1.79 – 1.68 (m, 2H), 1.59 (d, *J* = 14.3 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.3, 140.7, 126.4, 126.4, 117.3, 65.7, 64.7, 58.3, 57.9, 53.7, 50.4, 49.8, 47.1, 38.9, 30.9, 30.0, 28.2, 27.3, 26.2, 26.1, 25.8.

IR(KBr, cm^{-1}): 2831, 1594, 1357, 1073, 953, 896, 772, 693.

HRMS(ESI): calcd for $C_{24}H_{37}N_2O_2^+$ [M + H]$^+$: 385.2850; found: 385.2845.



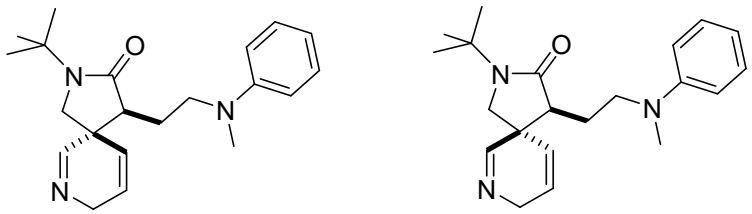
4,4'-((phenylazanediyl)bis(ethane-2,1-diyl))bis(2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one) (**3-35**)

Brown oil, 48mg, 58 yield (d.r. = 1.44:1).

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.12 (q, *J* = 7.4 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 1.18H), 6.66 (d, *J* = 8.1 Hz, 0.82H), 6.56 (t, *J* = 6.9 Hz, 1H), 5.93 – 5.82 (m, 4H), 5.63 (t, *J* = 9.3 Hz, 2H), 5.51 (d, *J* = 9.9 Hz, 2H), 3.42 – 3.28 (m, 4H), 3.23 (d, *J* = 9.8 Hz, 2H), 3.17 (d, *J* = 9.8 Hz, 2H), 2.76 – 2.64 (m, 4H), 2.12 (q, *J* = 6.4 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.57 – 1.49 (m, 2H), 1.38 (s, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.8, 174.7, 148.1, 130.2, 130.0, 128.9, 128.9, 127.2, 127.1, 126.8, 126.6, 125.6, 114.8, 111.7, 111.7, 56.6, 53.7, 51.8, 51.6, 48.7, 48.7, 41.4, 41.3, 27.6, 27.6, 26.6, 23.7, 23.7.

IR(KBr, cm^{-1}): 2814, 1615, 1463, 1264, 1037, 916, 791, 640.

HRMS(ESI): calcd for $C_{36}H_{50}N_3O_2^+$ [M + H]$^+$: 556.3898; found: 556.3893



2-(tert-butyl)-4-(2-(methyl(phenyl)amino)ethyl)-2,7-diazaspiro[4.5]deca-6,9-dien-3-one (**3-36**)

Brown oil, 70 mg, 69% yield, d.r. = 1:1.

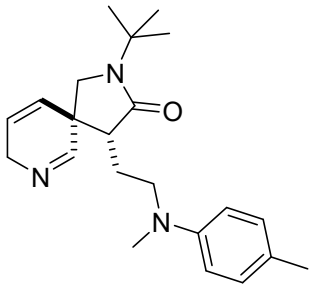
NMR:

[**P1**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (q, *J* = 2.7 Hz, 1H), 7.19 (dd, *J* = 8.8, 7.2 Hz, 2H), 6.70 (d, *J* = 7.8 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.00 – 5.92 (m, 1H), 5.60 – 5.53 (m, 1H), 4.26 – 4.13 (m, 2H), 3.53 – 3.43 (m, 2H), 3.33 (d, *J* = 10.5 Hz, 1H), 3.23 (d, *J* = 10.4 Hz, 1H), 2.87 (s, 3H), 2.26 (dd, *J* = 7.7, 5.9 Hz, 1H), 2.00 – 1.90 (m, 1H), 1.59 – 1.49 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 161.7, 149.3, 129.1, 127.6, 125.9, 116.1, 112.3, 54.2, 53.5, 50.9, 50.1, 50.0, 40.6, 37.7, 27.6, 23.3.

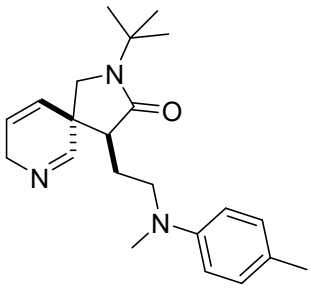
[**P2**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (q, *J* = 2.7 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.05 – 5.97 (m, 1H), 5.78 – 5.69 (m, 1H), 4.23 (q, *J* = 2.5 Hz, 2H), 3.50 – 3.35 (m, 3H), 3.21 (d, *J* = 10.1 Hz, 1H), 2.90 (s, 3H), 2.41 (t, *J* = 6.8 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.58 – 1.50 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.6, 163.4, 149.3, 129.1, 126.4, 123.7, 116.2, 112.3, 54.1, 53.6, 50.8, 50.0, 48.9, 41.2, 37.7, 27.6, 23.3.

IR(KBr, cm^{-1}): 1684, 1600, 1506, 1403, 1364, 1225, 945, 749.

HRMS(ESI): calcd for $C_{21}H_{30}N_3O^+$ $[M + H]^+$: 340.2383; found: 340.2378.



P1



P2

2-(tert-butyl)-4-(2-(methyl(p-tolyl)amino)ethyl)-2,7-diazaspiro[4.5]deca-6,9-dien-3-one (**3-37**)

Brown oil, 76 mg, 71% yield. (d.r. = 1:1).

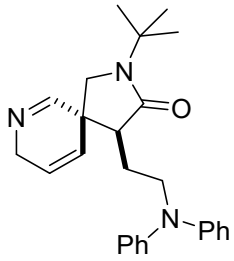
NMR:

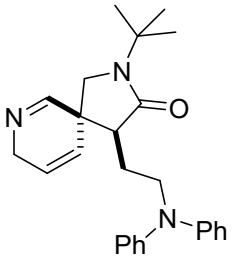
[**P1**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 5.97 (d, *J* = 10.3 Hz, 1H), 5.57 (dd, *J* = 10.5, 2.3 Hz, 1H), 4.27 – 4.15 (m, 2H), 3.43 (t, *J* = 7.6 Hz, 2H), 3.33 (d, *J* = 10.4 Hz, 1H), 3.23 (d, *J* = 10.4 Hz, 1H), 2.83 (s, 3H), 2.28 (t, *J* = 6.8 Hz, 1H), 2.23 (s, 3H), 2.00 – 1.91 (m, 1H), 1.57 – 1.49 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 161.7, 147.4, 129.6, 127.5, 125.9, 125.4, 112.7, 54.2, 53.5, 51.2, 50.0, 40.6, 37.8, 27.6, 23.2, 20.1.

[**P2**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (q, *J* = 2.7 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 6.03 – 5.94 (m, 1H), 5.75 – 5.66 (m, 1H), 4.21 (q, *J* = 2.5 Hz, 2H), 3.43 (d, *J* = 10.0 Hz, 1H), 3.41 – 3.27 (m, 2H), 3.18 (d, *J* = 10.0 Hz, 1H), 2.83 (s, 3H), 2.40 (t, *J* = 6.8 Hz, 1H), 2.23 (s, 3H), 1.97 – 1.87 (m, 1H), 1.56 – 1.46 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.6, 163.5, 147.3, 129.6, 126.4, 125.4, 123.7, 112.8, 54.1, 53.6, 51.1, 50.0, 48.9, 41.2, 37.9, 27.6, 23.2, 20.1.

IR(KBr, cm^{-1}): 2703, 1686, 1650, 1520, 1476, 1363, 1221, 989, 803, 732.

HRMS(ESI): calcd for $C_{22}H_{32}N_3O^+$ [M + H]$^+$: 354.2540; found: 354.2535.


P1 (cis)


P2 (trans)

2-(tert-butyl)-4-(2-(diphenylamino)ethyl)-2,7-diazaspiro[4.5]deca-6,9-dien-3-one **(3-38)**

Brown oil, 81 mg, 67% yield. (d.r. = 1:1).

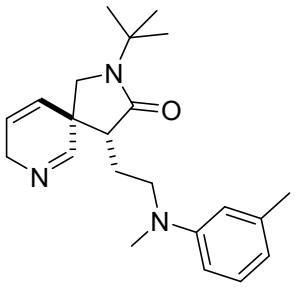
NMR:

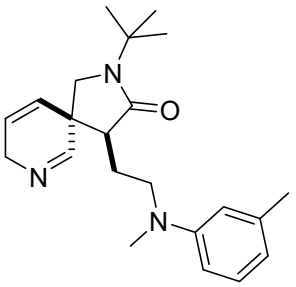
[**P1**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.22 (t, *J* = 7.8 Hz, 4H), 6.97 (d, *J* = 8.0 Hz, 4H), 6.91 (t, *J* = 7.4 Hz, 2H), 5.90 – 5.80 (m, 1H), 5.52 – 5.43 (m, 1H), 4.15 (d, *J* = 23.3 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.97 – 3.81 (m, 2H), 3.32 (d, *J* = 10.3 Hz, 1H), 3.21 (d, *J* = 10.4 Hz, 1H), 2.31 (t, *J* = 6.7 Hz, 1H), 2.07 – 2.00 (m, 1H), 1.64 – 1.56 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 161.6, 147.6, 129.2, 127.5, 125.6, 121.1, 120.9, 54.2, 53.5, 50.2, 50.1, 49.9, 40.6, 27.6, 24.1.

[**P2**] NMR: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.25 (t, *J* = 7.7 Hz, 4H), 6.99 (d, *J* = 8.0 Hz, 4H), 6.94 (t, *J* = 7.3 Hz, 2H), 6.00 – 5.92 (m, 1H), 5.75 – 5.68 (m, 1H), 4.20 (d, *J* = 22.4 Hz, 1H), 4.08 (d, *J* = 23.5 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.81 – 3.72 (m, 1H), 3.45 (d, *J* = 10.1 Hz, 1H), 3.20 (d, *J* = 10.1 Hz, 1H), 2.44 (t, *J* = 6.9 Hz, 1H), 2.13 – 2.02 (m, 1H), 1.67 – 1.58 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 163.3, 147.6, 129.2, 126.4, 123.5, 121.1, 120.8, 54.1, 53.6, 50.1, 49.9, 48.9, 41.1, 27.5, 24.2.

IR(KBr, cm^{-1}): 2805, 1687, 1643, 1590, 1496, 1364, 1246, 1188, 1068, 992, 749, 697.

HRMS(ESI): calcd for $C_{26}H_{32}N_3O^+$ [M + H]$^+$: 402.2540; found: 402.2535.


P1


P2

2-(tert-butyl)-4-(2-(methyl(m-tolyl)amino)ethyl)-2,7-diazaspiro[4.5]deca-6,9-dien-3-one (**3-39**)

Brown oil, 75 mg, 70% yield. (d.r. = 1:1).

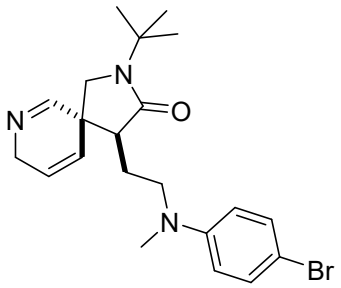
NMR:

[**P1**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.57 – 6.45 (m, 3H), 5.97 (d, *J* = 10.3 Hz, 1H), 5.57 (d, *J* = 10.3 Hz, 1H), 4.26 – 4.11 (m, 2H), 3.52 – 3.40 (m, 2H), 3.33 (d, *J* = 10.5 Hz, 1H), 3.23 (d, *J* = 10.4 Hz, 1H), 2.86 (s, 3H), 2.32 – 2.25 (m, 4H), 2.01 – 1.91 (m, 1H), 1.59 – 1.50 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 161.7, 149.5, 138.7, 128.9, 127.5, 125.9, 117.0, 113.0, 109.5, 54.2, 53.5, 50.9, 50.0, 50.0, 40.6, 37.6, 27.6, 23.3, 21.8.

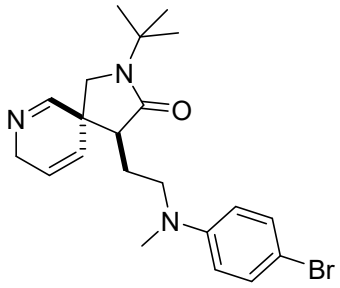
[**P2**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (q, *J* = 2.7 Hz, 1H), 7.08 (dd, *J* = 9.1, 7.3 Hz, 1H), 6.52 (d, *J* = 6.0 Hz, 3H), 6.50 (d, *J* = 7.5 Hz, 1H), 6.03 – 5.94 (m, 1H), 5.76 – 5.67 (m, 1H), 4.22 (q, *J* = 2.5 Hz, 2H), 3.43 (d, *J* = 10.0 Hz, 1H), 3.38 (t, *J* = 7.8 Hz, 2H), 3.18 (d, *J* = 10.0 Hz, 1H), 2.86 (s, 3H), 2.39 (t, *J* = 6.9 Hz, 1H), 2.29 (s, 3H), 1.97 – 1.87 (m, 1H), 1.56 – 1.48 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.5, 163.7, 149.3, 138.6, 128.9, 126.3, 123.6, 117.1, 113.0, 109.5, 54.1, 53.6, 50.7, 49.9, 48.9, 41.2, 37.7, 27.6, 23.3, 21.8.

IR(KBr, cm^{-1}): 2713, 1686, 1646, 1499, 1363, 1224, 1180, 994, 769, 726.

HRMS(ESI): calcd for $C_{22}H_{32}N_3O^+$ $[M + H]^+$: 354.2540; found: 354.2535.



P1 (cis)



P2 (trans)

4-(2-((4-bromophenyl)(methyl)amino)ethyl)-2-(tert-butyl)-2,7-diazaspiro[4.5]deca-6,9-dien-3-one (**3-40**)

Brown oil, 90 mg, 72% yield, d.r. = 1:1.

NMR:

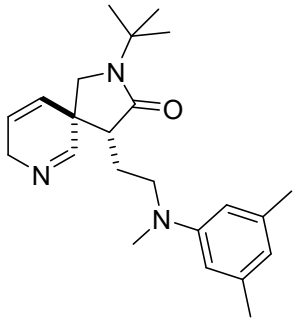
[**P1**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 9.2 Hz, 2H), 6.03 – 5.93 (m, 1H), 5.56 (dd, *J* = 10.3, 2.3 Hz, 1H), 4.25 – 4.11 (m, 2H), 3.56 – 3.46 (m, 1H), 3.46 – 3.37 (m, 1H), 3.34 (d, *J* = 10.4 Hz, 1H), 3.24 (d, *J* = 10.5 Hz, 1H), 2.85 (s, 3H), 2.25 – 2.18 (m, 1H), 1.96 – 1.87 (m, 1H), 1.57 – 1.48 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.8, 161.5, 148.1, 131.6, 127.6, 125.7, 113.7, 107.8, 54.2, 53.4, 50.7, 49.9, 40.5, 37.7, 27.6, 23.0.

[**P2**] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.18 (d, *J* = 9.0 Hz, 2H), 6.50 (d, *J* = 9.2 Hz, 2H), 5.96 – 5.87 (m, 1H), 5.67 – 5.59 (m, 1H), 4.18 – 4.08 (m, 2H), 3.41 – 3.32 (m, 2H), 3.29 – 3.22 (m, 1H), 3.12 (d, *J* = 10.1 Hz, 1H), 2.77 (s, 3H), 2.28 (t, *J* = 6.8 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.45 –

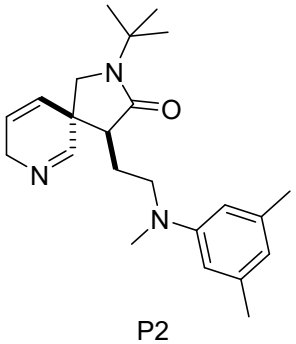
1.38 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.4, 163.3, 148.2, 131.7, 126.5, 123.6, 113.9, 108.0, 54.2, 53.6, 50.7, 50.0, 48.8, 41.2, 37.8, 27.6, 23.2.

IR(KBr, cm^{-1}): 1677, 1599, 1501, 1362, 1075, 774.

HRMS(ESI): calcd for $C_{21}H_{29}N_3BrO^+$ [M + H]$^+$: 418.1489; found: 418.1484.



P1



P2

2-(tert-butyl)-4-(2-((3,5-dimethylphenyl)(methyl)amino)ethyl)-2,7-diazaspiro[4.5]deca-6,9-dien-3-one (**3-41**)

Brown oil, 76 mg, 69% yield. (d.r. = 1:1).

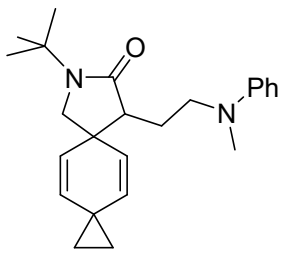
NMR:

[**P1**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 3.0 Hz, 1H), 6.35 (s, 3H), 6.01 – 5.93 (m, 1H), 5.62 – 5.54 (m, 1H), 4.25 – 4.14 (m, 2H), 3.55 – 3.43 (m, 1H), 3.45 – 3.35 (m, 1H), 3.33 (d, *J* = 10.4 Hz, 1H), 3.23 (d, *J* = 10.4 Hz, 1H), 2.85 (s, 3H), 2.31 – 2.26 (m, 2H), 2.25 (s, 6H), 2.01 – 1.89 (m, 1H), 1.60 – 1.50 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 161.9, 149.7, 138.6, 127.4, 126.0, 118.2, 110.3, 54.2, 53.5, 50.9, 50.0, 49.9, 40.7, 37.6, 27.6, 23.5, 21.7.

[**P2**] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 3.2 Hz, 1H), 6.34 (s, 3H), 6.03 – 5.96 (m, 1H), 5.76 – 5.69 (m, 1H), 4.22 (q, *J* = 2.5 Hz, 2H), 3.43 (d, *J* = 10.0 Hz, 1H), 3.41 – 3.27 (m, 2H), 3.18 (d, *J* = 10.0 Hz, 1H), 2.85 (s, 3H), 2.40 (t, *J* = 6.8 Hz, 1H), 2.25 (s, 6H), 1.96 – 1.87 (m, 1H), 1.56 – 1.47 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.6, 163.7, 149.5, 138.5, 126.3, 123.7, 118.2, 110.3, 54.1, 53.6, 50.7, 49.9, 48.9, 41.2, 37.7, 27.6, 23.4, 21.7.

IR(KBr, cm^{-1}): 2709, 1687, 1644, 1598, 1484, 1400, 1227, 992, 765, 727.

HRMS(ESI): calcd for $C_{23}H_{34}N_3O^+$ [M + H]$^+$: 368.2696; found: 368.2691.



8-(tert-butyl)-10-(2-(methyl(phenyl)amino)ethyl)-8-azadispiro[2.2.4^{6}.2^{3}]dodeca-4,11-dien-9-one (**3-42**)

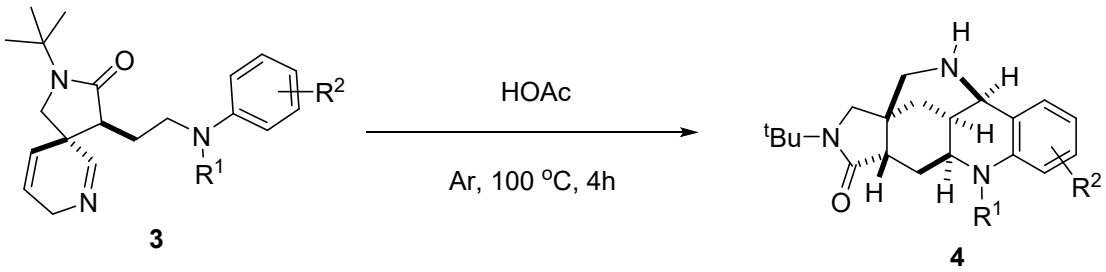
Brown oil, 70 mg, 64% yield.

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 5.59 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.46 (dd, *J* = 9.8, 2.1 Hz, 1H), 5.27 – 5.19 (m, 2H), 3.61 – 3.53 (m, 1H), 3.34 – 3.27 (m, 1H), 3.26 (s, 2H), 2.90 (s, 3H), 2.18 (dd, *J* = 7.8, 6.0 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.69 – 1.60 (m, 1H), 1.39 (s, 9H), 0.93 – 0.84 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.7, 149.3, 134.3, 133.2, 128.9, 128.6, 125.5, 115.7, 112.2, 57.0, 53.8, 51.8, 51.0, 42.4, 37.6, 27.6, 23.2, 20.8, 16.6, 16.3.

IR(KBr, cm^{-1}): 2720, 1601, 1505, 1362, 1239, 1046, 925, 747, 649.

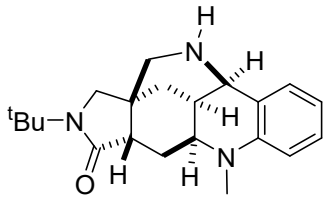
HRMS(ESI): calcd for $C_{24}H_{33}N_2O^+$ $[M + H]^+$: 365.2587; found: 365.2582.

V. Synthesis of multicyclic *N*-containing skeletons



3 **4**

To a solution of **3** (0.1 mmol, 1.0 eq) in HOAc (2 mL) was stirred at 100 °C under argon atmosphere for 4 hours. Then the reaction was quenched with water and adjusted pH to 7 - 8, followed by extracting with EtOAc for 3 times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure to give crude product **4**, which was purified by silica gel column chromatography (PE / EA = 2 / 1 ~ 1 / 1) to obtain product **4**. the details data of the products are summarized below.



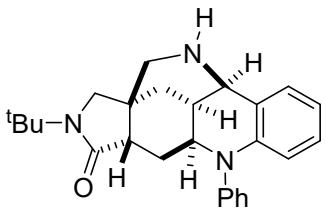
2-(tert-butyl)-5-methyl-1,2,4,4a,5,10,10a,11-octahydro-10,11a-(epiminomethano)pyrrolo[3,4-b]acridin-3(3aH)-one (**4-1**)

White solid, 20.3 mg, 60% yield, m.p. = 207.9 – 209.2 °C.

NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.14 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 3.85 (d, *J* = 3.1 Hz, 1H), 3.35 – 3.28 (m, 1H), 3.09 – 3.04 (m, 2H), 2.98 (d, *J* = 9.5 Hz, 1H), 2.97 – 2.93 (m, 4H), 2.54 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.48 (d, *J* = 9.9 Hz, 1H), 2.18 (p, *J* = 4.0 Hz, 1H), 1.98 – 1.90 (m, 1H), 1.87 – 1.82 (m, 1H), 1.70 – 1.64 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.2, 143.4, 129.5, 128.9, 123.4, 115.5, 111.0, 56.7, 55.0, 54.0, 53.7, 53.3, 49.1, 36.8, 35.5, 34.5, 31.7, 27.7, 25.5.

IR(KBr, cm^{-1}): 2830, 1598, 1356, 1088, 774, 742, 530.

HRMS(ESI): calcd for $C_{21}H_{30}N_3O^+$ $[M + H]^+$: 340.2383; found: 340.2380.



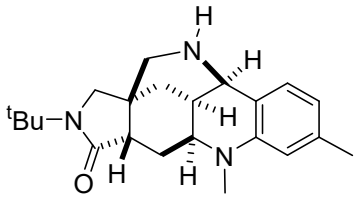
2-(tert-butyl)-5-phenyl-1,2,4,4a,5,10,10a,11-octahydro-10,11a-(epiminomethano)pyrrolo[3,4-b]acridin-3(3aH)-one (**4-2**)

White solid, 30.5 mg, 76% yield.

NMR: ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.45 (t, J = 7.4 Hz, 3H), 7.31 (d, J = 7.9 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.10 (t, J = 7.9 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.62 (d, J = 8.5 Hz, 1H), 4.58 (d, J = 5.0 Hz, 1H), 3.75 – 3.67 (m, 1H), 3.47 (d, J = 12.4 Hz, 1H), 3.42 – 3.35 (m, 2H), 3.34 – 3.26 (m, 2H), 2.71 (d, J = 8.5 Hz, 2H), 2.54 (dd, J = 15.6, 7.6 Hz, 1H), 2.10 – 2.00 (m, 2H), 1.93 (d, J = 13.9 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 173.8, 146.0, 142.6, 130.5, 130.1, 129.7, 126.7, 125.7, 118.0, 116.4, 116.3, 56.1, 54.2, 52.2, 51.7, 50.4, 47.2, 33.0, 31.1, 30.1, 26.5, 24.4.

IR(KBr, cm^{-1}): 2830, 1596, 1358, 1241, 1071, 774, 543.

HRMS(ESI): calcd for $C_{26}H_{32}N_3O$ $[M + H]^+$: 402.2540; found: 402.2536.



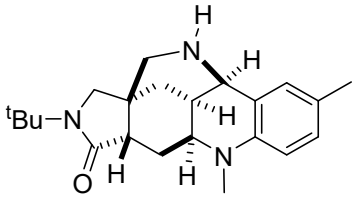
2-(tert-butyl)-5,7-dimethyl-1,2,4,4a,5,10,10a,11-octahydro-10,11a-(epiminomethano)pyrrolo[3,4-b]acridin-3(3aH)-one (**4-3**)

White-off solid, 24.4 mg, 69% yield.

NMR: ^{1}H NMR (500 MHz, Chloroform-d) δ 6.97 (d, J = 7.6 Hz, 1H), 6.44 (d, J = 7.8 Hz, 1H), 6.38 (s, 1H), 3.84 (s, 1H), 3.36 – 3.23 (m, 1H), 3.06 (d, J = 10.4 Hz, 2H), 3.00 – 2.90 (m, 5H), 2.53 (dd, J = 14.0, 7.5 Hz, 1H), 2.48 (d, J = 9.3 Hz, 1H), 2.28 (s, 3H), 2.16 (s, 1H), 1.92 (q, J = 10.1 Hz, 1H), 1.84 (d, J = 13.6 Hz, 1H), 1.69 (t, J = 14.3 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-d) δ 175.2, 143.3, 138.7, 129.5, 120.6, 116.4, 111.6, 56.7, 54.9, 53.7, 53.6, 53.3, 49.1, 36.8, 35.5, 34.6, 31.9, 27.7, 25.4, 21.7.

IR(KBr, cm^{-1}): 2732, 1675, 1607, 1510, 1360, 1221, 1143, 963, 784.

HRMS(ESI): calcd for $C_{22}H_{32}N_3O^+$ $[M + H]^+$: 354.2540; found: 354.2536.



2-(tert-butyl)-5,8-dimethyl-1,2,4,4a,5,10,10a,11-octahydro-10,11a-(epiminomethano)pyrrolo[3,4-b]acridin-3(3aH)-one (**4-4**)

White-off solid, 25 mg, 71% yield.

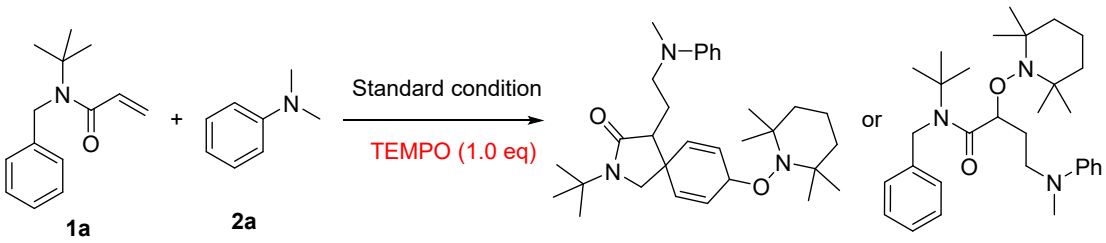
NMR: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.97 (d, *J* = 8.7 Hz, 1H), 6.94 (s, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 1H), 3.30 (p, *J* = 6.0 Hz, 1H), 3.11 – 3.04 (m, 2H), 3.01 – 2.94 (m, 2H), 2.93 (s, 3H), 2.24 – 2.16 (m, 4H), 1.94 – 1.76 (m, 6H), 1.73 – 1.66 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.1, 141.2, 130.3, 129.6, 124.7, 123.0, 111.3, 56.6, 54.7, 53.8, 53.7, 53.2, 48.9, 36.8, 35.4, 34.5, 31.9, 27.7, 24.9, 20.0.

IR(KBr, cm^{-1}): 2832, 1674, 1606, 1510, 1361, 1211, 1108, 993, 774.

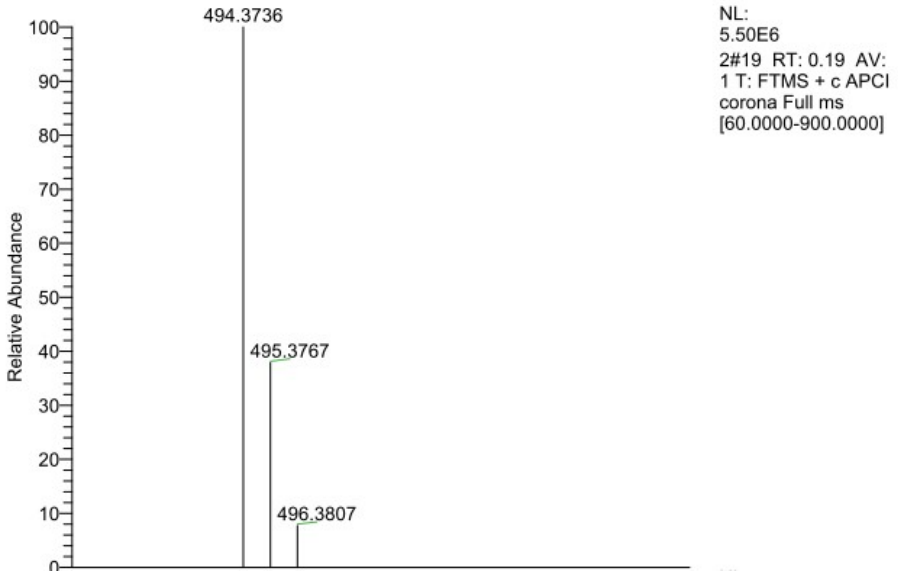
HRMS(ESI): calcd for $C_{22}H_{32}N_3O^+$ $[M + H]^+$: 354.2540; found: 354.2536.

VI. Mechanism studies

vii-1. Radical trapping experiment



HRMS(ESI): calcd for C31H48N3O2$^+$ [M + H]$^+$: 494.3741; found: 494.3736.



vii-2. Electrochemical measurements

In a nitrogen atmosphere, a standard three-electrode cell configuration was used to collect cyclic voltammograms (CVs) at room temperature with a CHI660e electrochemical workstation. A 3 mm glassy carbon electrode, an Ag/AgCl (3 M KCl) electrode, and a platinum sheet auxiliary electrode were used as the working electrode, reference electrode, and counter electrode, respectively. The electrolyte cell contains 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) and 1 mM substrates in MeCN. The scan rate is 0.1 V/s and the range is -2.0 V to 2.0 V. For comparison with reported redox potentials of the photosensitizers, the reference electrode potential was converted to the saturated calomel electrode (SCE) scale. According to the CVs results about **1a** (Fig S1) and **2a** (Fig S2), it's clear that the single electron transfer between **2a** and 3DPAFIPN (Ep/2 = +1.09 V vs SCE)[1] could be smoothly occurred, while **1a** substrate can neither be oxidized nor reduced.

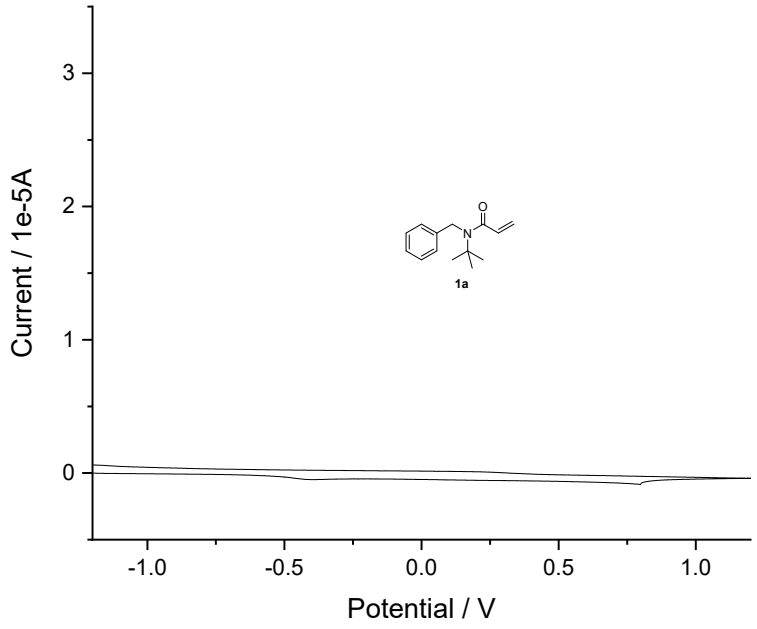


Fig S1 Cyclic voltammogram of **1a** in MeCN

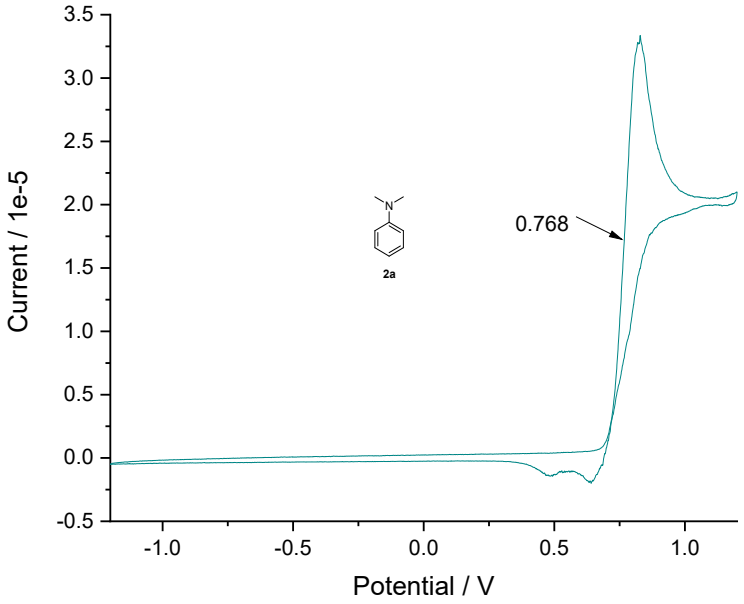


Fig S2 Cyclic voltammogram of **2a** in MeCN

vii-3. Stern–Volmer luminescence quenching studies

Stern-Volmer experiments were conducted on a Hitachi F7000 Fluorescence Spectrophotometer. Each component was prepared in DCE prior to each set of experiments. The solutions were irradiated at 365 nm and the luminescence measured at 470 nm. Linear regression of I^0/I against concentration was performed in Origin.

species	Concentration (mM)
3DPAFIPN	0.01
2a	varied
1a	varied

substrate (mM)		0.03	0.06	0.09	0.12	0.15
I_0/I_1	**2a**	1.606	2.194	2.576	3.030	3.731
	1a	0.992	1.051	1.073	0.964	1.008

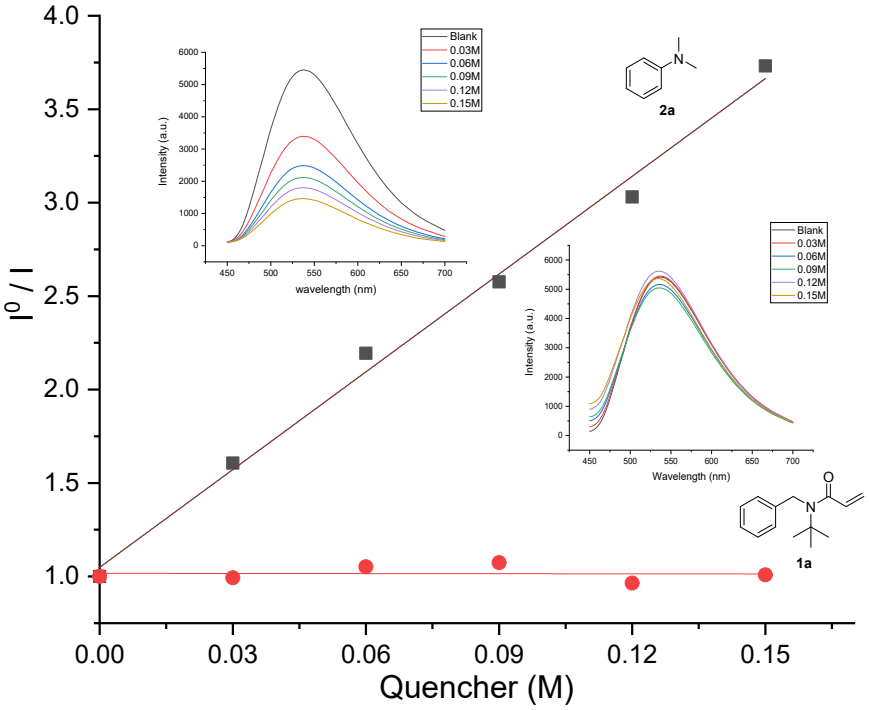
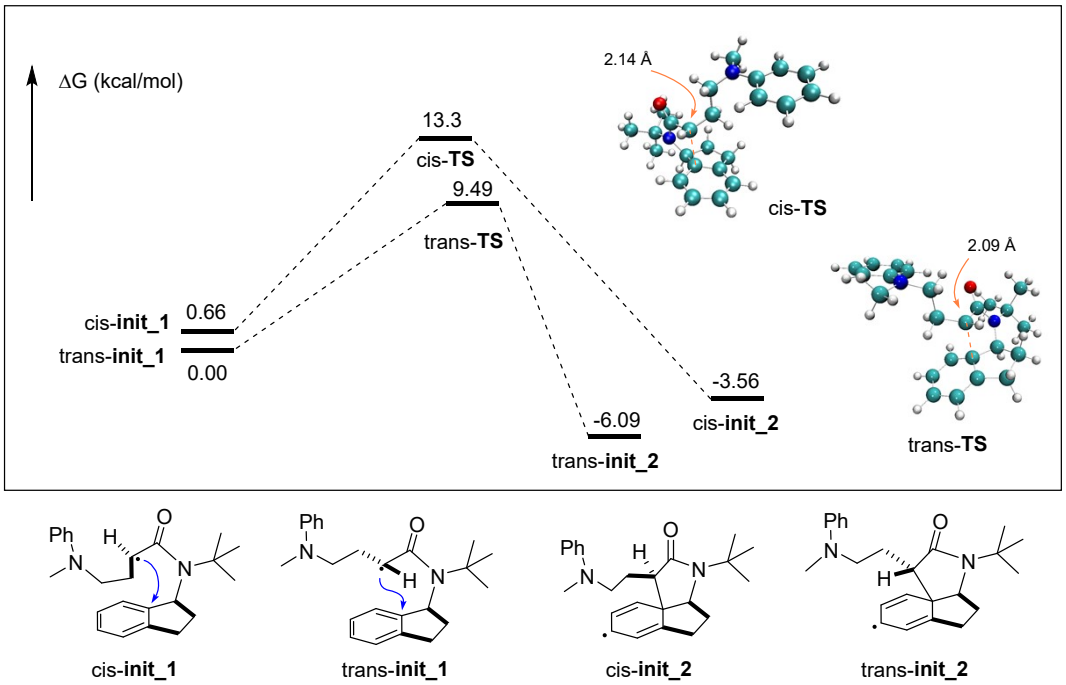


Fig S3 Stern-Volmer experiments for **1a** and **2a**

VII. Computational details

All calculations were carried out with the Gaussian 09 programs.[2] The geometries of all the species were fully optimized by using density functional theory (DFT) of the B3LYP functional[3] with the dispersion correction (Grimme's D3).[4] For these optimizations, the basis set was used 6-31G(d,p) for all the atoms. Vibrational frequency calculations done at the B3LYP-D3/6-31G(d,p) level of theory were used to characterize all the stationary points as either minima (the number of imaginary frequencies (NIMAG=0) or transition states (NIMAG=1)). In order to get more accurate electronic energies, the single point energy was calculated under M062x/SMD/6-311G(d,p) level in *N,N*-dimethylacetamide with SMD[5] model. The 3D images of the calculated structures were prepared using VMD program. [6]



cis-**init_1**

C	0.20376000	3.36445700	-0.18513700
C	0.84956000	2.91839500	-1.34138900
C	0.35600000	1.81748100	-2.04990000
C	-0.78186300	1.14211100	-1.60234400
C	-1.40899000	1.58002200	-0.43863100
C	-0.93301600	2.69226100	0.26053700
C	-2.65788100	1.02294000	0.22342600

C	-2.69353200	1.73432300	1.60882200
C	-1.80871300	2.99780600	1.45767900
N	-2.78458000	-0.44116500	0.25005200
C	-4.05812300	-1.08816500	-0.21965300
C	-3.90045200	-1.55246500	-1.67802100
C	-4.40273600	-2.26960400	0.70856400
C	-5.24032800	-0.10527500	-0.13320400
C	-1.65832600	-1.23926600	0.43642600
O	-1.61733900	-2.42730600	0.06615600
C	-0.49437000	-0.67670600	1.10419500
C	0.78539600	-1.42705300	1.09286900
C	1.36372800	-1.58507900	-0.35205000
N	2.77994000	-1.88923500	-0.37626200
C	3.70011400	-0.88296600	-0.08602700
C	3.15747700	-3.27354700	-0.15406400
C	5.05933300	-1.18438400	0.14688900
C	5.98436200	-0.17260000	0.39143800
C	5.59712200	1.16623900	0.42723900
C	4.25242400	1.47292400	0.21631900
C	3.31475800	0.47614500	-0.02989700
H	0.58970100	4.22002700	0.36216100
H	1.74470800	3.42383300	-1.68996100
H	0.86937000	1.47871100	-2.94424400
H	-1.15634100	0.27214400	-2.13362000
H	-3.49885600	1.38872400	-0.36438600
H	-2.28566900	1.06148100	2.36667800
H	-3.71644000	1.97050100	1.91208600

H	-1.23006700	3.21975800	2.36041500
H	-2.42471500	3.88375400	1.25606000
H	-3.09664500	-2.28406100	-1.75512100
H	-3.66981900	-0.69796800	-2.32410200
H	-4.83100700	-2.00449600	-2.03733100
H	-3.62913800	-3.03304700	0.68730100
H	-5.34905300	-2.71618800	0.38845800
H	-4.52386200	-1.91326100	1.73661000
H	-5.20702300	0.68172100	-0.89149900
H	-5.31367500	0.35700800	0.85559700
H	-6.16110400	-0.66827400	-0.30569000
H	0.64091200	-2.43521600	1.49938800
H	1.52479100	-0.90807200	1.70828800
H	1.18316200	-0.67393100	-0.92243300
H	0.81531000	-2.38234500	-0.85527100
H	2.30722900	-3.91155900	-0.39944200
H	3.45369900	-3.47637000	0.88650600
H	3.99042000	-3.56301600	-0.80418400
H	5.40060200	-2.21157100	0.13333800
H	7.02298500	-0.44274300	0.56075800
H	6.32265100	1.94913200	0.62177400
H	3.91509500	2.50543300	0.24879700
H	2.28382900	0.76680900	-0.17664500
H	-0.51406700	0.30635700	1.54941900

trans-**init_1**

C	-2.67313400	-3.57301400	0.54112900

C	-1.75360500	-3.65870600	1.58933200
C	-1.21398200	-2.49980000	2.15730000
C	-1.58177200	-1.24180300	1.67828600
C	-2.48259900	-1.16320500	0.61722000
C	-3.03750500	-2.31761200	0.05849000
C	-3.05210000	0.07899400	-0.04730400
C	-3.74981700	-0.47471800	-1.32207100
C	-4.02554300	-1.97096400	-1.03461100
N	-2.11177500	1.19164900	-0.26771900
C	-2.54340800	2.57219200	0.12654800
C	-2.28551200	2.79192400	1.62644100
C	-1.79255900	3.61760000	-0.72037500
C	-4.04079800	2.76097000	-0.18539300
C	-0.75455700	0.90627100	-0.38361500
O	0.12841400	1.67604800	0.04003600
C	-0.36950800	-0.32891800	-1.04652000
C	1.02602700	-0.81223500	-0.93187900
C	2.01540700	0.00425700	-1.82533400
N	3.40553900	-0.35240300	-1.62556700
C	4.04669000	0.01508600	-0.44009900
C	3.90109300	-1.50268300	-2.35886800
C	5.30379700	-0.52862200	-0.10040700
C	5.96472900	-0.12924100	1.05845000
C	5.39888300	0.80697400	1.92190500
C	4.14723700	1.33483700	1.60254200
C	3.47091200	0.95189200	0.44851900
H	-3.09277400	-4.47541300	0.10485800

H	-1.45386300	-4.63219000	1.96531300
H	-0.49955300	-2.57902100	2.97072100
H	-1.14928800	-0.34054700	2.10208500
H	-3.81914700	0.46034500	0.63091300
H	-3.06948900	-0.36305200	-2.17050100
H	-4.65618000	0.08454100	-1.56496700
H	-3.91618200	-2.60058000	-1.92384700
H	-5.05238800	-2.11577200	-0.67378900
H	-1.21876200	2.70014600	1.83546300
H	-2.82871900	2.05162200	2.22451700
H	-2.62398000	3.78634300	1.93563100
H	-0.72571000	3.61573900	-0.51398700
H	-2.19587600	4.61039100	-0.49984800
H	-1.94679800	3.41695000	-1.78545400
H	-4.70022300	2.16758000	0.45236500
H	-4.25702600	2.52166100	-1.23055900
H	-4.29950200	3.80980100	-0.01905000
H	1.08903400	-1.87029500	-1.20531300
H	1.37093700	-0.70604400	0.10181800
H	1.86790500	1.06355700	-1.61458300
H	1.77211800	-0.15418900	-2.87959100
H	3.26962600	-1.66094700	-3.23475100
H	3.90274100	-2.42764300	-1.76162500
H	4.92287400	-1.33084400	-2.71426400
H	5.77463300	-1.26286600	-0.74144900
H	6.93409600	-0.56424300	1.28560600
H	5.91616900	1.11164900	2.82581900

H	3.67614300	2.05581800	2.26473200
H	2.48991000	1.36955100	0.25882500
H	-1.07464400	-0.86201900	-1.67048900

cis-**TS**

C	0.22422600	3.28532500	0.64955400
C	0.03600400	3.95406700	-0.56928000
C	-1.00706900	3.57060500	-1.43265500
C	-1.81363400	2.48761600	-1.12923900
C	-1.51033900	1.69189600	0.01631000
C	-0.57685700	2.20071500	0.96673100
C	-2.48495900	0.74559200	0.70854100
C	-1.78025300	0.39411500	2.05632000
C	-0.66604400	1.45151400	2.27581700
N	-2.79313500	-0.41625500	-0.13244100
C	-4.01228300	-1.25689100	0.08876700
C	-4.66137300	-1.56309500	-1.27278600
C	-3.61653800	-2.55798400	0.81079100
C	-5.03807200	-0.50184600	0.94548400
C	-1.75155100	-0.87984900	-0.89408100
O	-1.74534000	-1.95257100	-1.50551300
C	-0.55932800	0.02696000	-0.93375900
C	0.68465700	-0.44488800	-0.23686500
C	1.49030300	-1.44177600	-1.10495500
N	2.69004700	-1.94247100	-0.44974600
C	3.75797700	-1.07927000	-0.20822700
C	2.51245800	-3.09029900	0.42155700

C	4.75816300	-1.39972500	0.73509700
C	5.84411700	-0.55294000	0.94334400
C	5.97272500	0.64205800	0.23809400
C	4.98386200	0.97490800	-0.68847400
C	3.89492400	0.13935000	-0.91108500
H	0.97019700	3.64132600	1.35521000
H	0.66191800	4.80366300	-0.82224500
H	-1.19074000	4.14333400	-2.33692500
H	-2.62293300	2.18784900	-1.78901600
H	-3.41302000	1.28562800	0.89806600
H	-1.35249200	-0.60738700	1.97234100
H	-2.49125800	0.36621200	2.88605200
H	0.28603800	0.98602900	2.55553100
H	-0.92365000	2.14065800	3.08896800
H	-3.98169200	-2.12641100	-1.90971600
H	-4.93034900	-0.63067500	-1.77909500
H	-5.57464600	-2.14677700	-1.12100800
H	-2.88414400	-3.11086900	0.22236000
H	-4.49901400	-3.18894000	0.95623200
H	-3.19201900	-2.33782600	1.79541400
H	-5.36634000	0.42585500	0.46738600
H	-4.66177500	-0.27127300	1.94600500
H	-5.91739800	-1.13996800	1.06569700
H	0.43969000	-0.93522000	0.71167300
H	1.32125300	0.41506000	0.00017700
H	1.75608500	-0.96904600	-2.05550100
H	0.85156800	-2.29013700	-1.35617100

H	1.64577800	-3.65856600	0.08087000
H	2.35283100	-2.81530100	1.47639500
H	3.38412100	-3.75129300	0.37544700
H	4.69238100	-2.31307800	1.31179200
H	6.59517900	-0.83575400	1.67567700
H	6.81830100	1.30001600	0.40850900
H	5.05420100	1.90253400	-1.24953900
H	3.15085400	0.43820400	-1.63814800
H	-0.38128000	0.44684900	-1.92301600

trans-**TS**

C	1.80256800	3.66626300	0.54128600
C	0.90332400	3.62841100	1.61939900
C	0.60718600	2.40482900	2.25078000
C	1.14475500	1.21959800	1.78498200
C	1.91757700	1.22634700	0.58225500
C	2.34722400	2.48832700	0.06232100
C	2.92751800	0.14655300	0.18701900
C	3.69641600	0.77414300	-1.01639000
C	3.43879500	2.30526700	-0.96799200
N	2.23549900	-1.11087600	-0.10314500
C	2.83968100	-2.45989700	0.11399700
C	2.06666600	-3.18434900	1.22999700
C	2.77644200	-3.25453700	-1.20286800
C	4.31206700	-2.33085000	0.52952100
C	0.95122600	-0.96364000	-0.56110900
O	0.14991700	-1.89358600	-0.71460300

C	0.59027500	0.45936600	-0.83107000
C	-0.82653700	0.87934900	-0.59786200
C	-1.77913400	0.41140900	-1.72718300
N	-3.18312400	0.65418100	-1.43747200
C	-3.82619200	-0.12578200	-0.47377400
C	-3.67870800	1.99397900	-1.69238500
C	-5.08761400	0.24908100	0.03602900
C	-5.75058500	-0.55058800	0.96392300
C	-5.18331500	-1.73614500	1.42678200
C	-3.92767700	-2.10470700	0.94167200
C	-3.24972500	-1.32174600	0.01286100
H	2.09683500	4.62129200	0.11352100
H	0.47350800	4.54973400	1.99860000
H	-0.03707900	2.39697800	3.12485400
H	0.92065600	0.27449000	2.27113900
H	3.60929100	-0.01668500	1.02293400
H	3.30950500	0.33924800	-1.94140800
H	4.76218400	0.53645000	-0.97674500
H	3.15551300	2.70026500	-1.95125000
H	4.33908900	2.85402700	-0.66703400
H	1.02013100	-3.30448800	0.95107900
H	2.12129100	-2.61077300	2.16124400
H	2.50364900	-4.17162200	1.41108600
H	1.74586000	-3.36627500	-1.53771200
H	3.20919300	-4.24905100	-1.05706400
H	3.35042900	-2.74266200	-1.98209900
H	4.43076800	-1.86686400	1.51249100

H	4.89742000	-1.76577800	-0.20148800
H	4.73926500	-3.33509400	0.59125500
H	-0.87373800	1.97119800	-0.51051200
H	-1.18452500	0.46482600	0.34812300
H	-1.61918100	-0.65141000	-1.90937800
H	-1.53249700	0.93272400	-2.65797800
H	-3.04530800	2.46603400	-2.44565300
H	-3.68335700	2.63318500	-0.79552900
H	-4.69920300	1.96607400	-2.08962700
H	-5.56012600	1.16594200	-0.29244200
H	-6.72306300	-0.23252700	1.32975000
H	-5.70197500	-2.35357900	2.15290800
H	-3.45526000	-3.01739800	1.29425900
H	-2.26772400	-1.63963400	-0.31491700
H	1.05909400	0.87284200	-1.72439300

cis-**init_2**

C	1.40682300	3.67089600	0.39128100
C	0.81183300	3.73487400	1.67450600
C	0.71077300	2.55613500	2.46031700
C	1.06127200	1.33632700	1.95758400
C	1.41423500	1.16633800	0.50924800
C	1.75396900	2.46809300	-0.15845600
C	2.65560300	0.27124800	0.22443200
C	3.26155300	0.81333500	-1.10619300
C	2.66043200	2.22957500	-1.33874200
N	2.12393800	-1.08689700	0.15176500

C	2.95957300	-2.32084300	0.15596500
C	2.35105100	-3.32765300	1.14766900
C	3.00085400	-2.91679900	-1.26244500
C	4.38394800	-1.98139900	0.61311500
C	0.79444900	-1.09951800	-0.16804000
O	0.13291100	-2.09802400	-0.45448500
C	0.25078700	0.32463800	-0.15964400
C	-0.21579600	0.74947000	-1.56210800
C	-1.60759800	0.19450700	-1.89664600
N	-2.63856700	0.72192400	-1.00524100
C	-3.51053200	-0.14574400	-0.33065800
C	-3.11163600	2.04722800	-1.35218100
C	-4.83658600	0.23076600	-0.04185800
C	-5.67942100	-0.61870400	0.67469500
C	-5.23756500	-1.86416000	1.11278400
C	-3.92433000	-2.24435000	0.82592100
C	-3.06610600	-1.40638200	0.12286900
H	1.65735000	4.59424800	-0.12645500
H	3.37537200	0.35646900	1.03937800
H	2.99512800	0.13716700	-1.92211500
H	4.35313200	0.84375100	-1.05931500
H	2.11161100	2.25844300	-2.28841200
H	3.43142000	3.00383800	-1.40504600
H	1.33989700	-3.60135600	0.84903200
H	2.31735900	-2.89454900	2.15224900
H	2.96899100	-4.23016200	1.18279800
H	1.99014800	-3.13416600	-1.60983300

H	3.58012700	-3.84545400	-1.26262200
H	3.47642700	-2.22113500	-1.96081100
H	4.39787700	-1.57723100	1.62943500
H	4.87551300	-1.26949100	-0.05552800
H	4.97738100	-2.89940000	0.61243100
H	0.49099200	0.41859900	-2.33236000
H	-0.23920300	1.84335600	-1.60168100
H	-1.58876300	-0.89182900	-1.83051700
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H	-3.51110200	2.55576400	-0.47068000
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H	-3.55139800	-3.20740700	1.16345900
H	-2.04494900	-1.72637400	-0.05266900
H	0.98826000	0.43622400	2.56264700
H	0.52334600	4.69284400	2.09311200
H	0.36804700	2.63568300	3.48818400
H	-0.63088500	0.36450500	0.48622600

trans-**init_2**

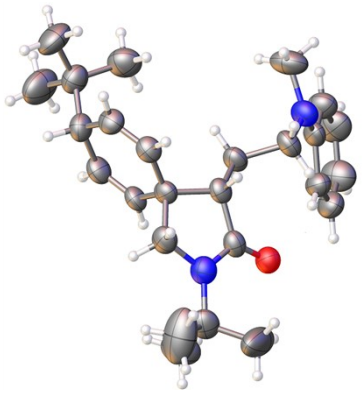
C	2.12436500	3.61037100	0.38516600
C	1.38411900	3.72929600	1.58899500
C	0.95368100	2.56035800	2.27057300
C	1.13991800	1.31530500	1.74067800

C	1.70573300	1.13824400	0.36657000
C	2.32540500	2.38719300	-0.18674500
C	2.84252100	0.07497700	0.25036700
C	3.77794900	0.58862700	-0.89221400
C	3.27422800	2.00878600	-1.29109600
N	2.14479400	-1.18200600	-0.01027500
C	2.75029700	-2.53631300	0.13314100
C	1.89388600	-3.36282000	1.10808700
C	2.80459600	-3.21165200	-1.24846500
C	4.17270800	-2.41742200	0.69557200
C	0.88014000	-0.98573100	-0.49012400
O	0.07998700	-1.86549500	-0.80386300
C	0.63078200	0.51753400	-0.60543800
C	-0.81674500	0.93995100	-0.37104300
C	-1.72848600	0.58339500	-1.55698100
N	-3.14106000	0.82582400	-1.30229900
C	-3.83552000	-0.02545600	-0.44096100
C	-3.60456800	2.19234500	-1.45383600
C	-5.10775000	0.32896600	0.05697800
C	-5.82030200	-0.53807200	0.88197200
C	-5.29442600	-1.77438400	1.25146700
C	-4.02935500	-2.12517000	0.77780300
C	-3.30205900	-1.27492100	-0.04891600
H	2.58394400	4.49508300	-0.04935300
H	3.39110900	0.01035300	1.19042200
H	3.75489700	-0.10168500	-1.73862800
H	4.81122000	0.63371100	-0.53806600

H	2.76047500	1.96537800	-2.26133400
H	4.08695200	2.73197900	-1.40286300
H	0.87763400	-3.46950600	0.72954400
H	1.85648700	-2.87384300	2.08675400
H	2.33199500	-4.35735300	1.23773700
H	1.80408100	-3.28588200	-1.67545700
H	3.22357000	-4.21853100	-1.15681200
H	3.44074200	-2.63900700	-1.93099500
H	4.18085400	-1.98960700	1.70194000
H	4.82196300	-1.81667900	0.05274700
H	4.60461200	-3.41952400	0.75973200
H	-0.84727900	2.02090700	-0.19438100
H	-1.20321000	0.46085300	0.53261300
H	-1.58000000	-0.46149300	-1.83081300
H	-1.44092200	1.17829900	-2.43160800
H	-2.93439900	2.71768800	-2.13685500
H	-3.63465700	2.74962000	-0.50419700
H	-4.60894200	2.22018700	-1.89040500
H	-5.54938100	1.28328700	-0.19999900
H	-6.79918500	-0.23282200	1.24168400
H	-5.85184800	-2.44453400	1.89774600
H	-3.58897800	-3.07799800	1.05856300
H	-2.31680500	-1.58496600	-0.37415500
H	0.81706600	0.42563300	2.27450300
H	1.21798700	4.70602700	2.02986900
H	0.48477200	2.66341800	3.24530900
H	0.91250300	0.78780100	-1.63363100

VIII. Crystallographic data

The crystal data was collected on a Agilent Gemini E diffractometer (Mo, 50kV 40 mA) and reduced by CrysAlisPro (Rigaku). The structures were solved by direct methods using SHELXS-97. Refinements were performed with SHELXL-2013 using full matrix least-squares calculations on F2, with anisotropic displacement parameters for all the nonhydrogen atoms.

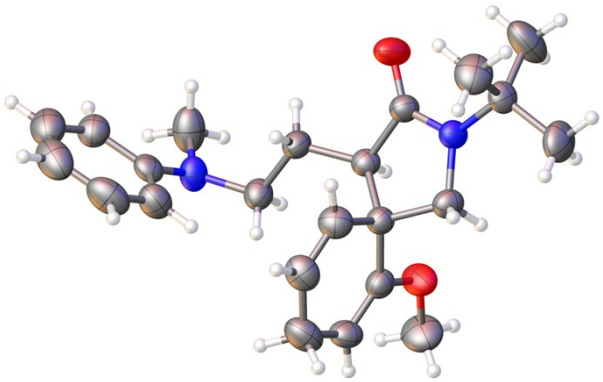


X-ray crystallographic data for **3-2** (CCDC 2310087)

Crystal data and structure refinement

Identification code	exp_13794_auto
Empirical formula	$C_{26}H_{38}N_2O$
Formula weight	394.58
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.1618(17)
b/Å	12.6995(9)
c/Å	18.3176(14)
α/°	90
β/°	100.330(8)
γ/°	90
Volume/Å^3	4843.0(6)
Z	8
ρ_{calc}g/cm^3	1.082
μ/mm^{-1}	0.065
F(000)	1728.0
Crystal size/mm^3	0.18 × 0.12 × 0.07
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.562 to 48.996

Index ranges	$-24 \leq h \leq 21$, $-9 \leq k \leq 14$, $-21 \leq l \leq 21$
Reflections collected	18399
Independent reflections	7997 [R_{int} = 0.0542, R_{sigma} = 0.1373]
Data/restraints/parameters	7997/17/519
Goodness-of-fit on F^2	0.955
Final R indexes [I>=2σ (I)]	R_1 = 0.0908, wR_2 = 0.2398
Final R indexes [all data]	R_1 = 0.1890, wR_2 = 0.3041
Largest diff. peak/hole / e $Å^{-3}$	0.74/-0.59

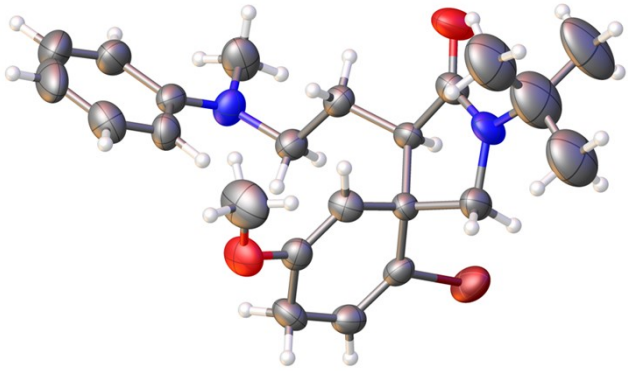


X-ray crystallographic data for **3-3-**major (CCDC 2189219)

Crystal data and structure refinement

Identification code	exp_11661
Empirical formula	$C_{23}H_{32}N_2O_2$
Formula weight	368.50
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.8978(19)
b/Å	9.9999(9)
c/Å	14.9001(18)
α/°	90
β/°	93.852(13)
γ/°	90

Volume/Å^3	2066.1(4)
Z	4
ρ_{calc}g/cm^3	1.185
μ/mm^{-1}	0.075
F(000)	800.0
Crystal size/mm^3	0.2 × 0.18 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.15 to 48.998
Index ranges	-16 ≤ h ≤ 15, -11 ≤ k ≤ 8, -13 ≤ l ≤ 17
Reflections collected	7792
Independent reflections	3424 [R_{int} = 0.0316, R_{sigma} = 0.0529]
Data/restraints/parameters	3424/0/249
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0668, wR_2 = 0.1217
Final R indexes [all data]	R_1 = 0.1093, wR_2 = 0.1404
Largest diff. peak/hole / e Å^{-3}	0.17/-0.15

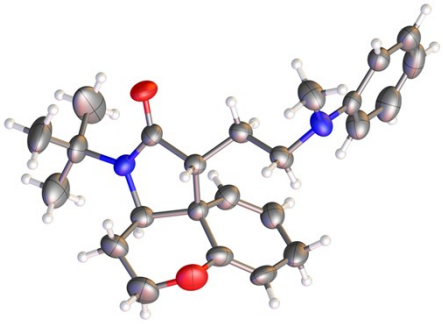


X-ray crystallographic data for **3-4** (CCDC 2141716)

Crystal data and structure refinement

Identification code	exp_10035
Empirical formula	$C_{23}H_{31}BrN_2O_2$
Formula weight	446.40

Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.2363(17)
b/Å	12.6108(8)
c/Å	13.0773(13)
α/°	90
β/°	104.172(11)
γ/°	90
Volume/Å^3	2276.3(4)
Z	4
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	1.825
F(000)	932.0
Crystal size/mm^3	0.28 × 0.2 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.374 to 49
Index ranges	$-16 \leq h \leq 16$, $-14 \leq k \leq 11$, $-10 \leq l \leq 15$
Reflections collected	9067
Independent reflections	3741 [R_{int} = 0.0420, R_{sigma} = 0.0689]
Data/restraints/parameters	3741/1/246
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0637, wR_2 = 0.1401
Final R indexes [all data]	R_1 = 0.1029, wR_2 = 0.1619
Largest diff. peak/hole / e Å^{-3}	1.30/-0.86

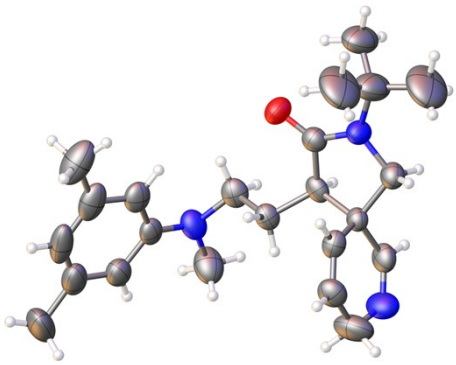


X-ray crystallographic data for **3-28** (2182835)

Crystal data and structure refinement

Identification code	exp_10391
Empirical formula	$C_{24}H_{32}N_2O_2$
Formula weight	380.51
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.2226(17)
b/Å	13.177(2)
c/Å	12.2423(16)
α/°	90
β/°	91.432(11)
γ/°	90
Volume/Å^3	2132.3(5)
Z	4
ρ_{calc}g/cm^3	1.185
μ/mm^{-1}	0.075
F(000)	824.0
Crystal size/mm^3	0.22 × 0.14 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.364 to 53.998

Index ranges	$-16 \leq h \leq 12$, $-16 \leq k \leq 15$, $-13 \leq l \leq 15$
Reflections collected	10492
Independent reflections	4595 [R_{int} = 0.0505, R_{sigma} = 0.0973]
Data/restraints/parameters	4595/0/257
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0774, wR_2 = 0.1225
Final R indexes [all data]	R_1 = 0.1705, wR_2 = 0.1572
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.18

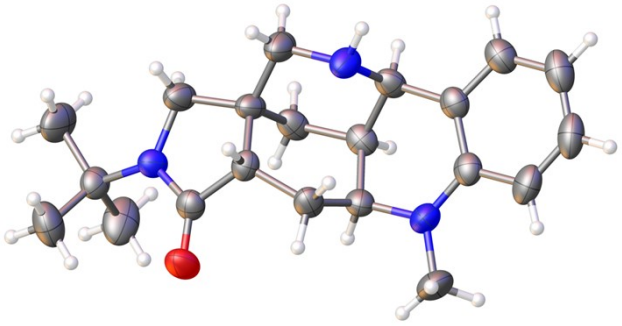


X-ray crystallographic data for *trans*-**3-41** (CCDC 2207806)

Crystal data and structure refinement

Identification code	exp_11890
Empirical formula	$C_{23}H_{33}N_3O$
Formula weight	367.52
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.9111(8)
b/Å	17.4811(13)
c/Å	12.6792(13)
α/°	90
β/°	95.028(9)
γ/°	90

Volume/Å^3	2188.3(3)
Z	4
ρ_{calc}g/cm^3	1.116
μ/mm^{-1}	0.069
F(000)	800.0
Crystal size/mm^3	0.31 × 0.18 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.978 to 49.996
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 20, -15 ≤ l ≤ 14
Reflections collected	9602
Independent reflections	3802 [R_{int} = 0.0425, R_{sigma} = 0.0734]
Data/restraints/parameters	3802/0/238
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0993, wR_2 = 0.2205
Final R indexes [all data]	R_1 = 0.1693, wR_2 = 0.2649
Largest diff. peak/hole / e Å^{-3}	0.53/-0.58



X-ray crystallographic data for **4-1** (CCDC 2207807)

Crystal data and structure refinement

Identification code	exp_11891
Empirical formula	$C_{21}H_{29}N_3O$
Formula weight	339.47
Temperature/K	293(2)

Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.5960(10)
b/Å	9.6411(12)
c/Å	14.4759(16)
α/°	90
β/°	90.818(13)
γ/°	90
Volume/Å^3	920.5(2)
Z	2
ρ_{calc}g/cm^3	1.225
μ/mm^{-1}	0.076
F(000)	368.0
Crystal size/mm^3	0.32 × 0.22 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.076 to 58.878
Index ranges	$-5 \leq h \leq 9$, $-13 \leq k \leq 13$, $-18 \leq l \leq 19$
Reflections collected	7820
Independent reflections	4069 [R_{int} = 0.0383, R_{sigma} = 0.0771]
Data/restraints/parameters	4069/1/233
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1051
Final R indexes [all data]	R_1 = 0.0950, wR_2 = 0.1209
Largest diff. peak/hole / e Å^{-3}	0.20/-0.29
Flack parameter	-0.3(10)

IX. Reference

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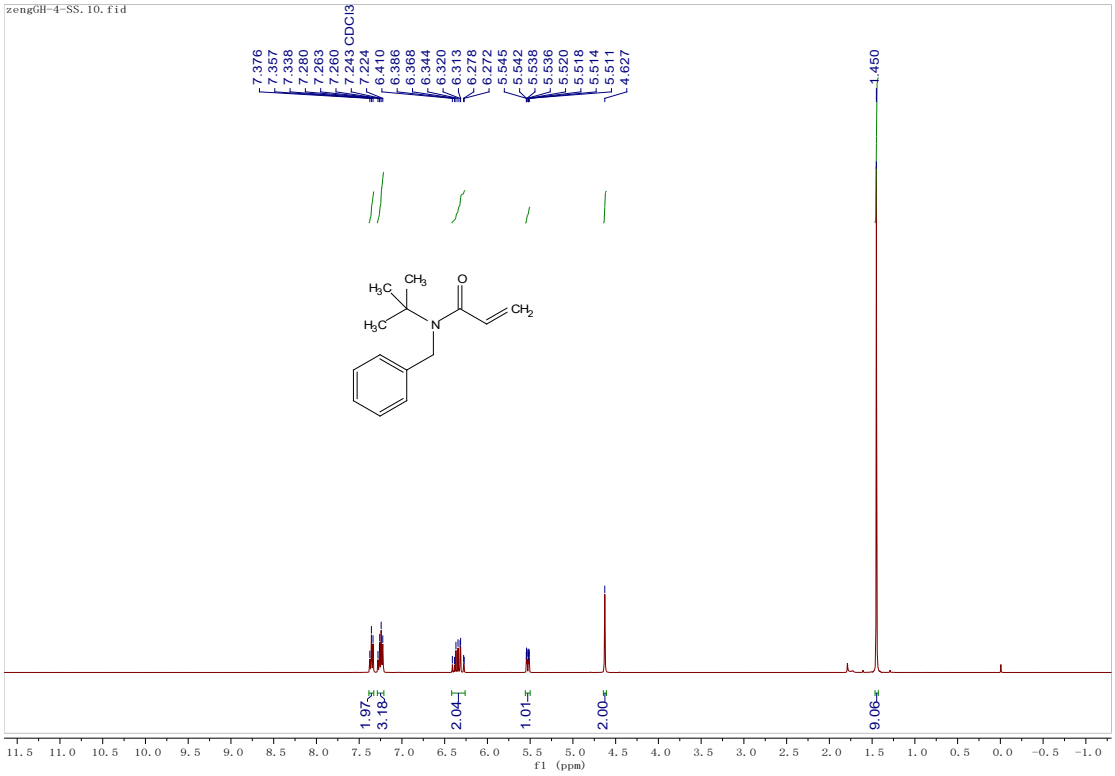
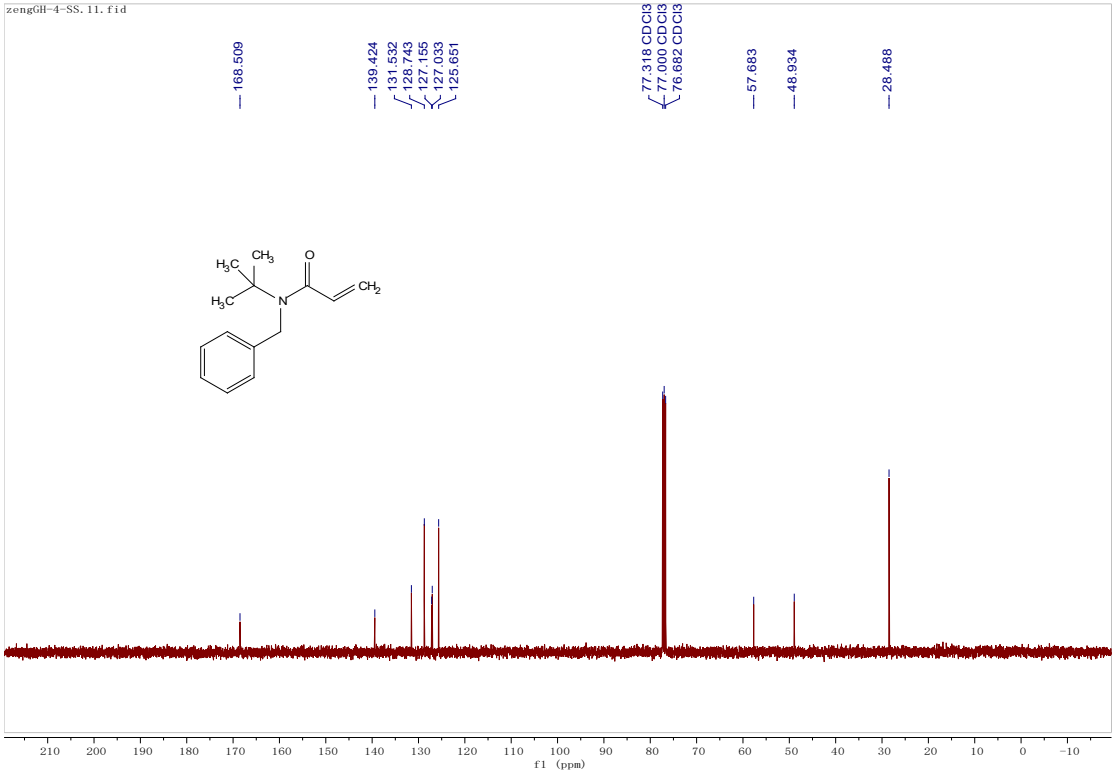
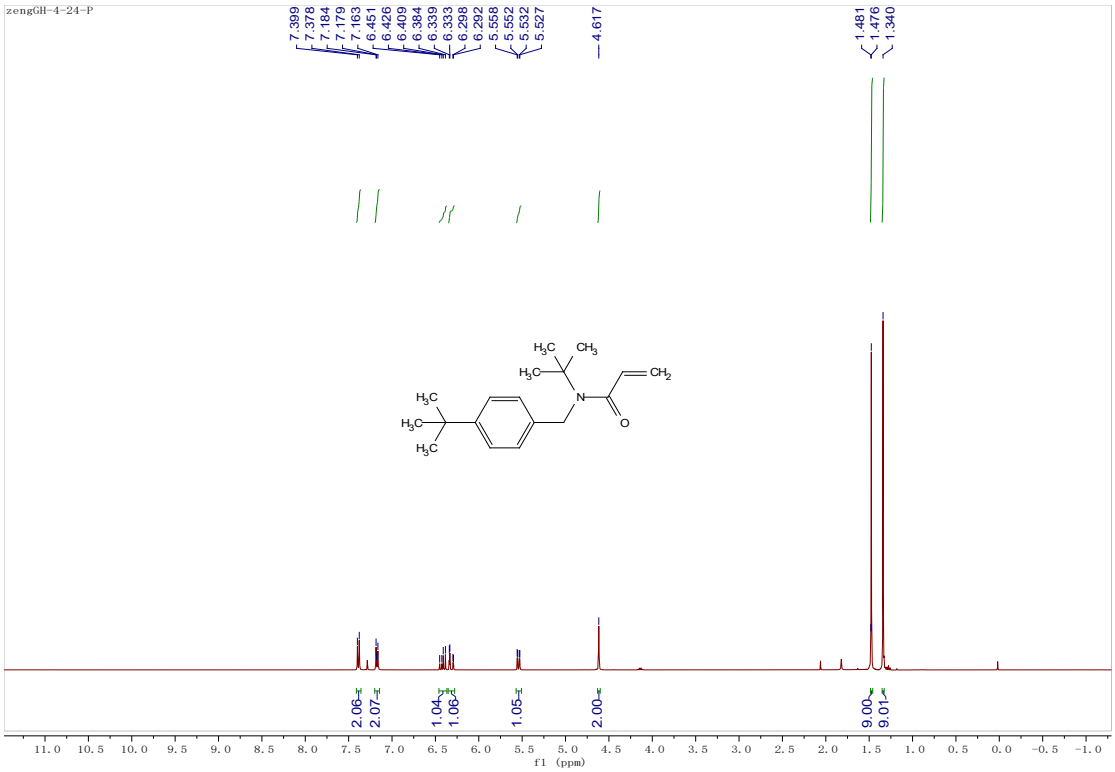
X. NMR Spectra



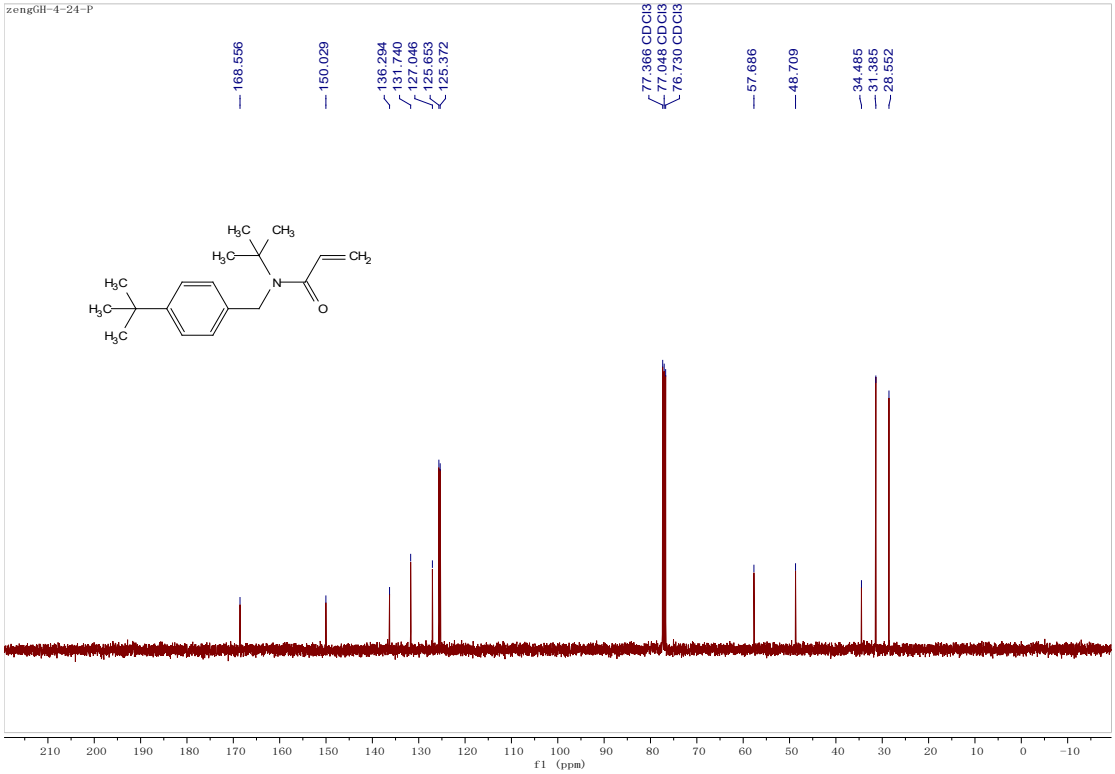
^{1}H NMR of **1a**



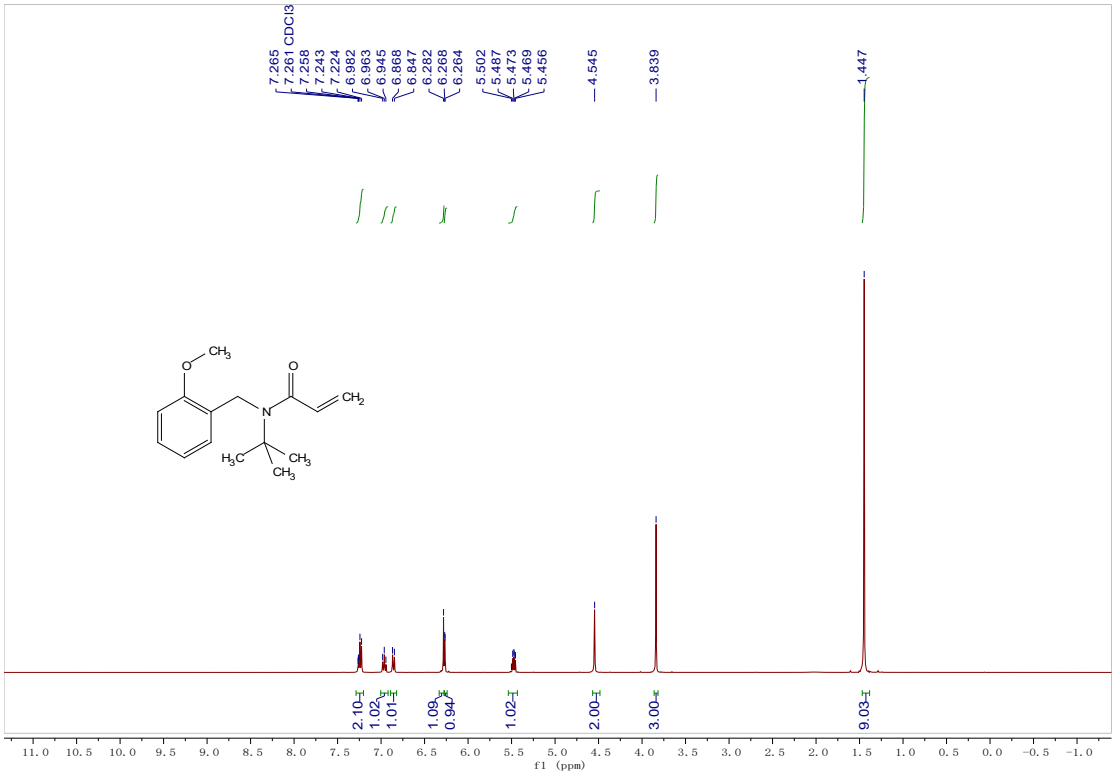
^{13}C NMR of **1a**



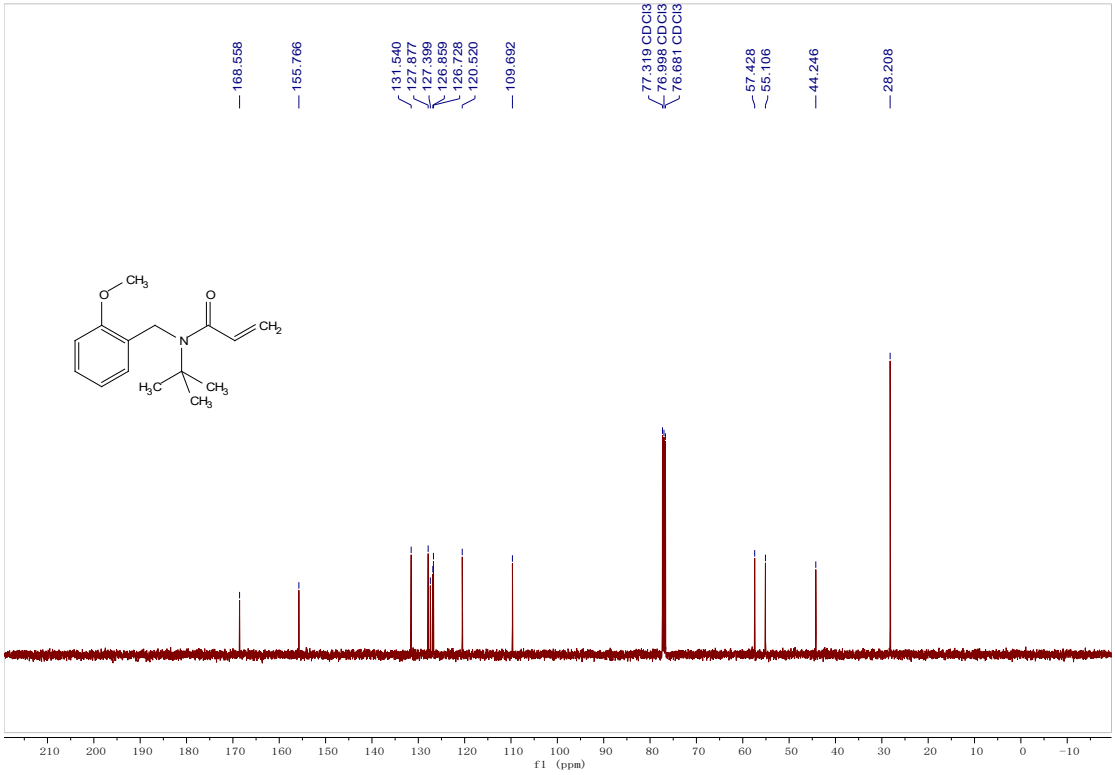
^{1}H NMR of **1b**



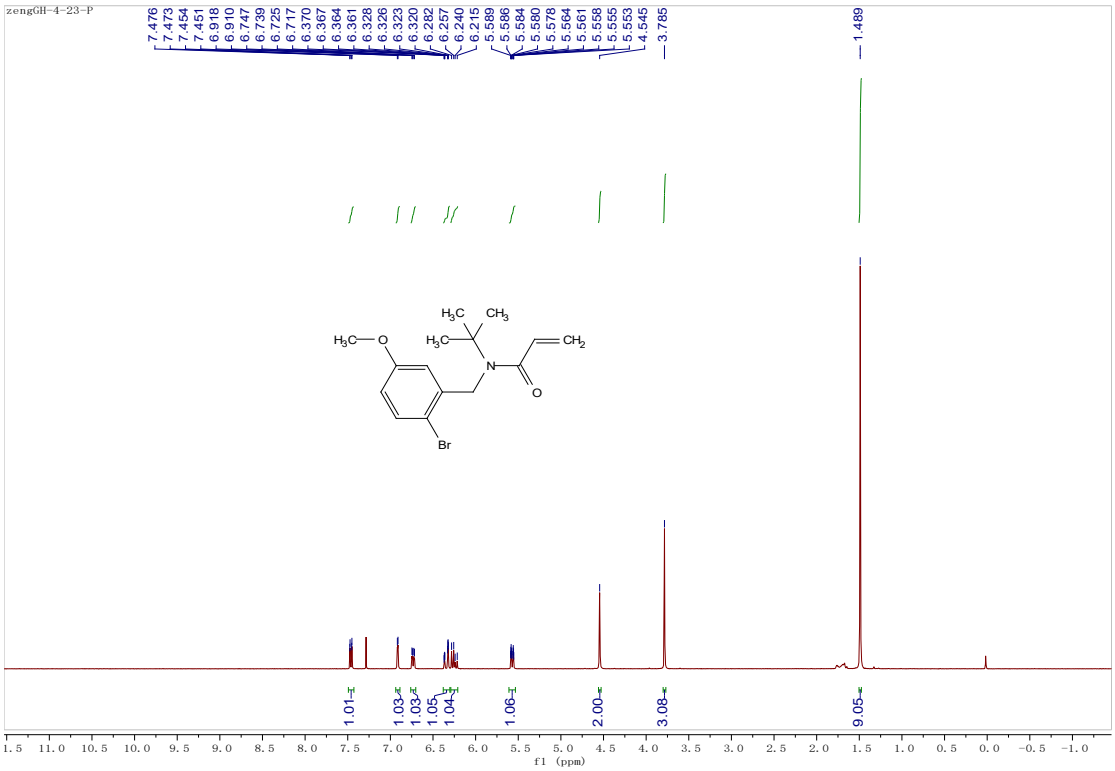
^{13}C NMR of **1b**



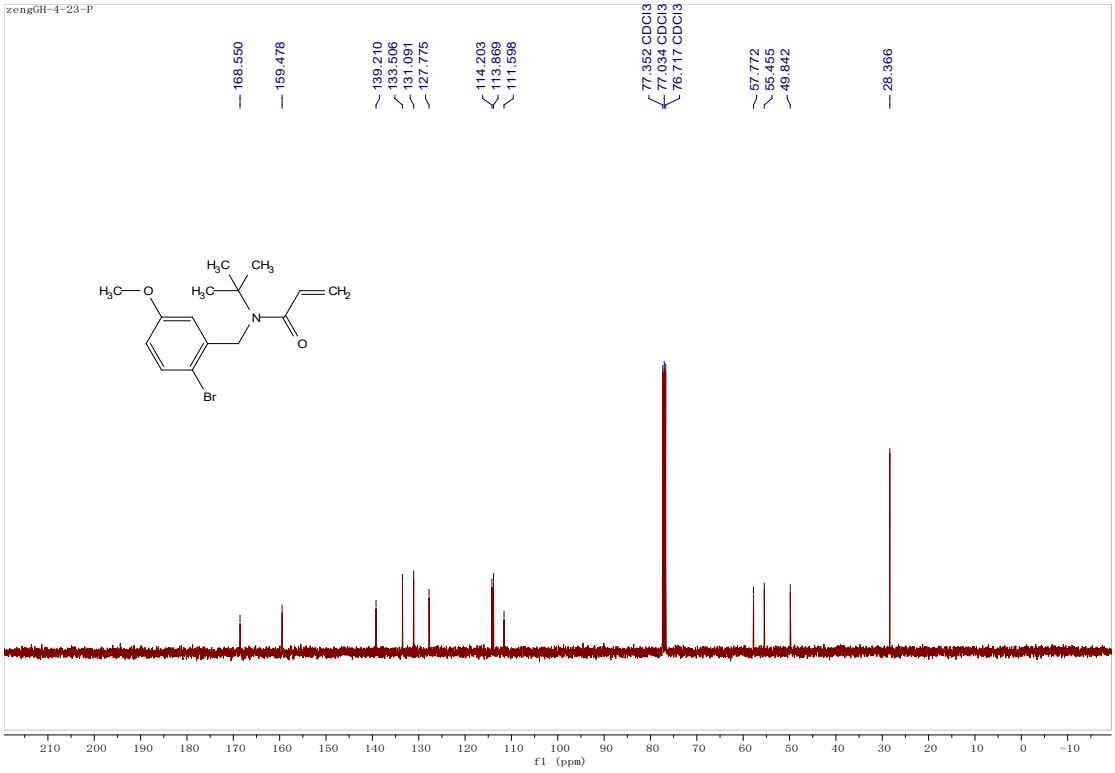
^{1}H NMR of **1c**



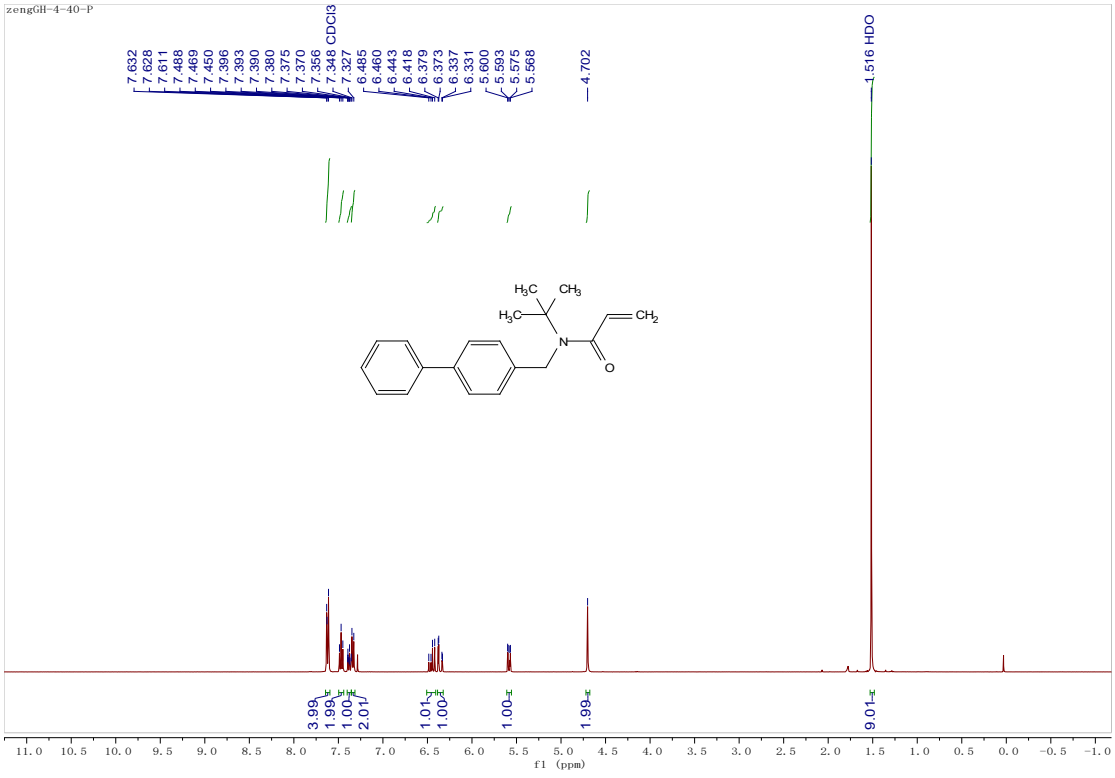
^{13}C NMR of **1c**



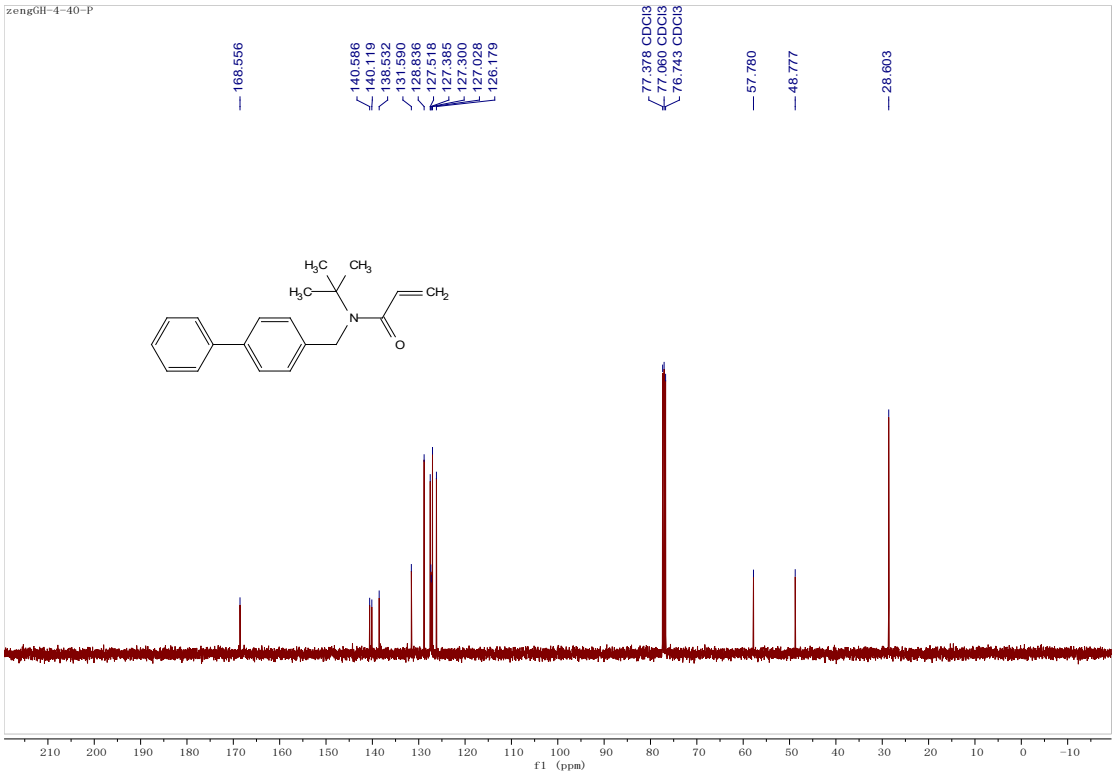
^{1}H NMR of **1d**



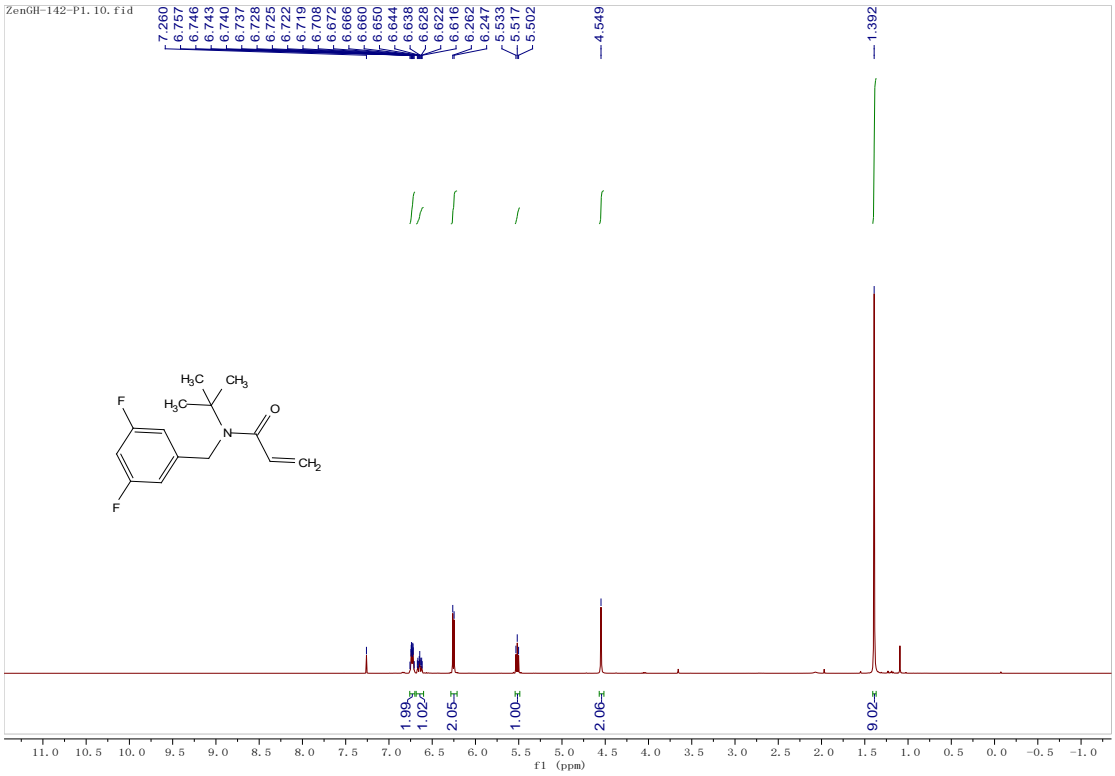
^{13}C NMR of **1d**


zengGH-4-40-P
7.632
7.628
7.611
7.488
7.469
7.450
7.396
7.393
7.390
7.380
7.375
7.370
7.356
7.348 CDCl3
7.327
6.485
6.460
6.443
6.418
6.379
6.373
6.337
6.331
5.600
5.593
5.575
5.568
4.702
1.516 HDO
H3C
CH3
H3C
CH2
N
O
3.99
1.99
1.00
2.01
1.01
1.00
1.00
1.99
9.01
f1 (ppm)

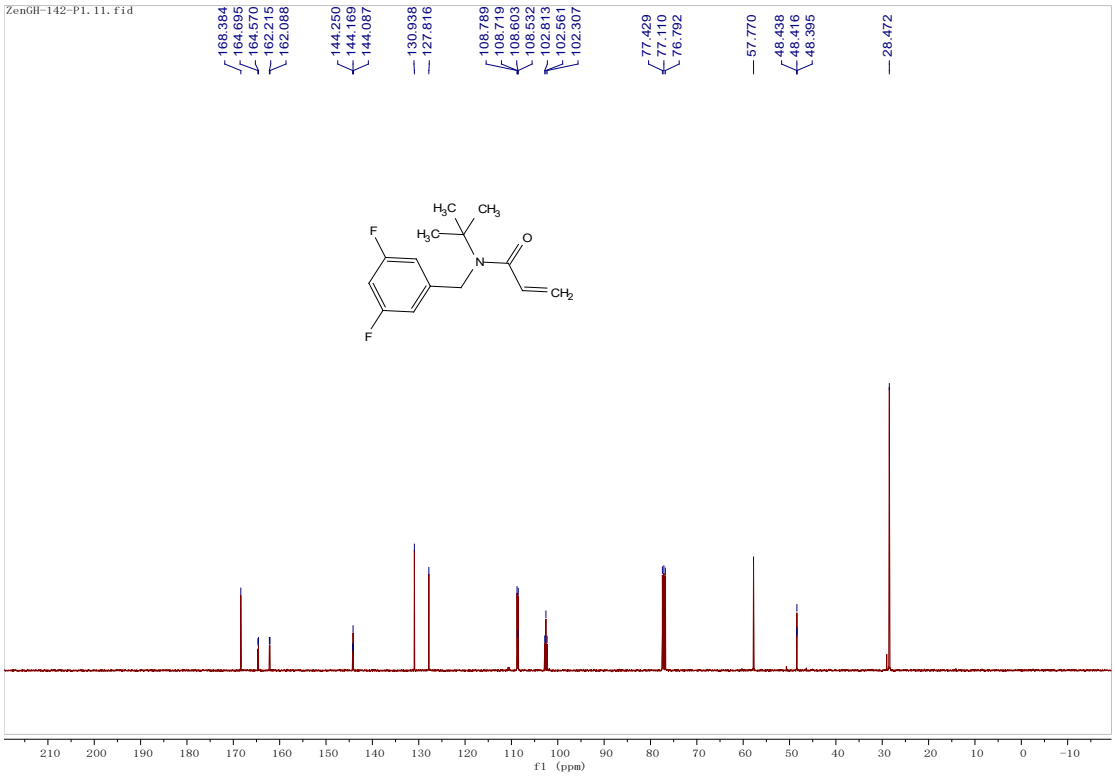
^{1}H NMR of **1e**


zengGH-4-40-P
168.556
140.586
140.119
138.532
131.590
128.836
127.518
127.385
127.300
127.028
126.179
77.378 CDCl3
77.060 CDCl3
76.743 CDCl3
57.780
48.777
28.603
H3C
CH3
H3C
CH2
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

^{13}C NMR of **1e**

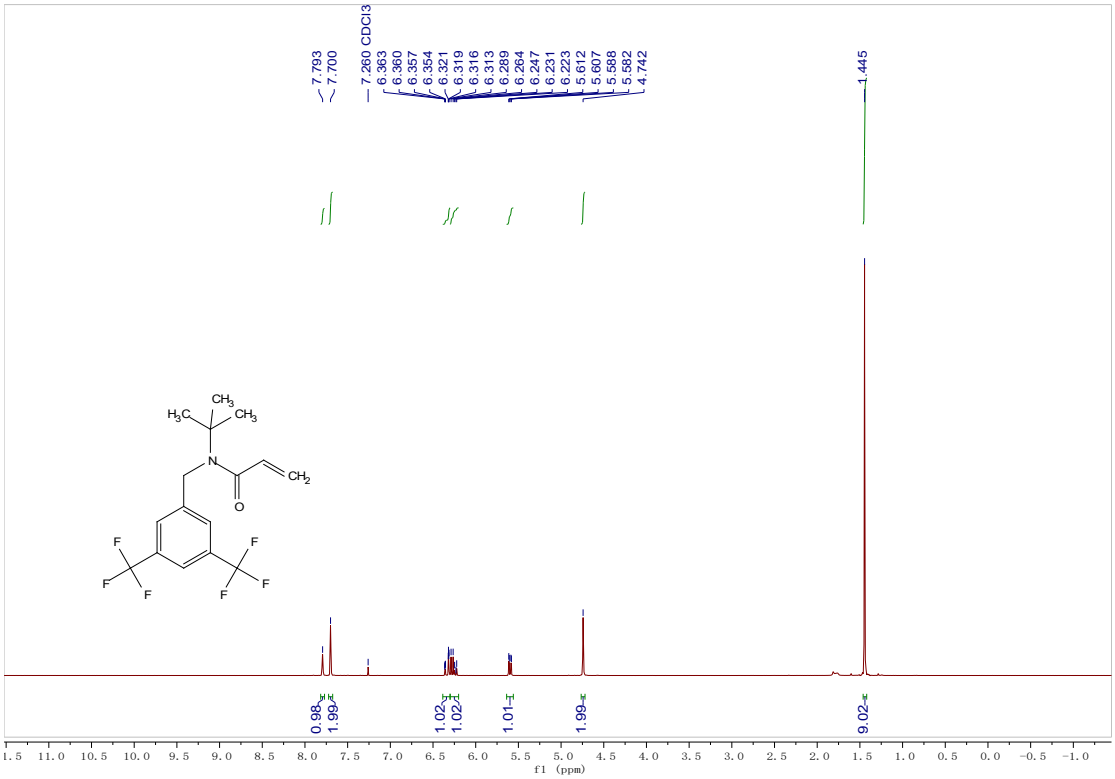


^{1}H NMR of **1f**

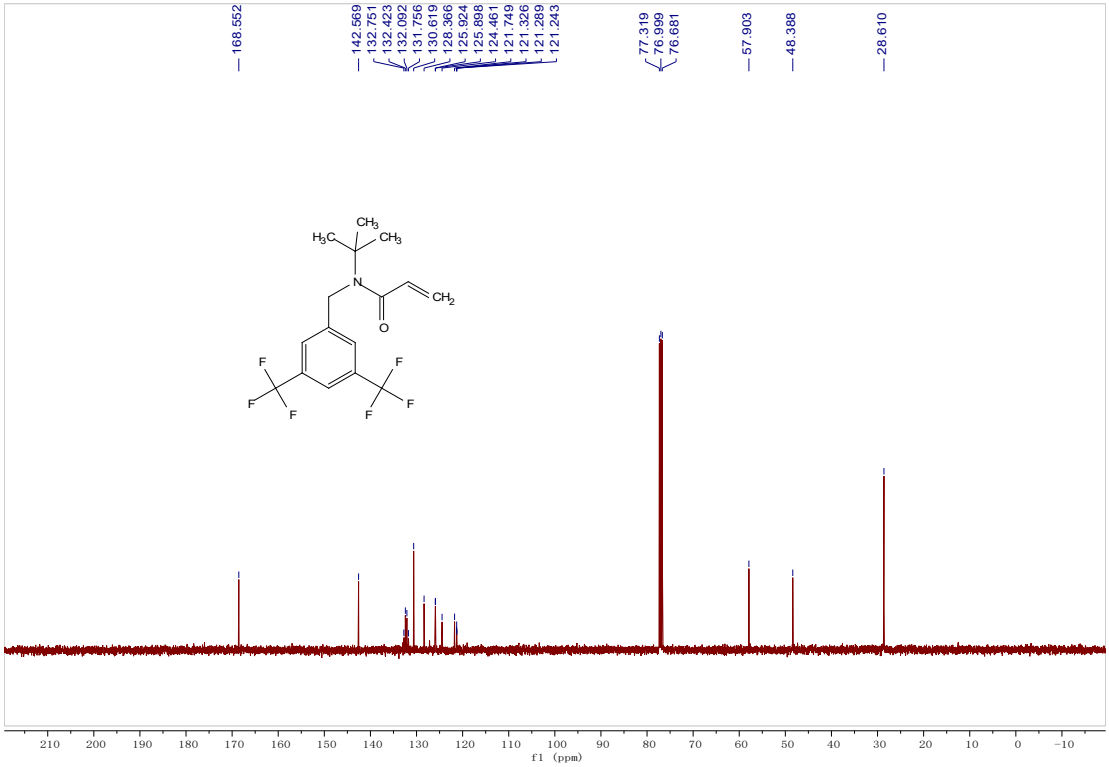


^{13}C NMR of **1f**

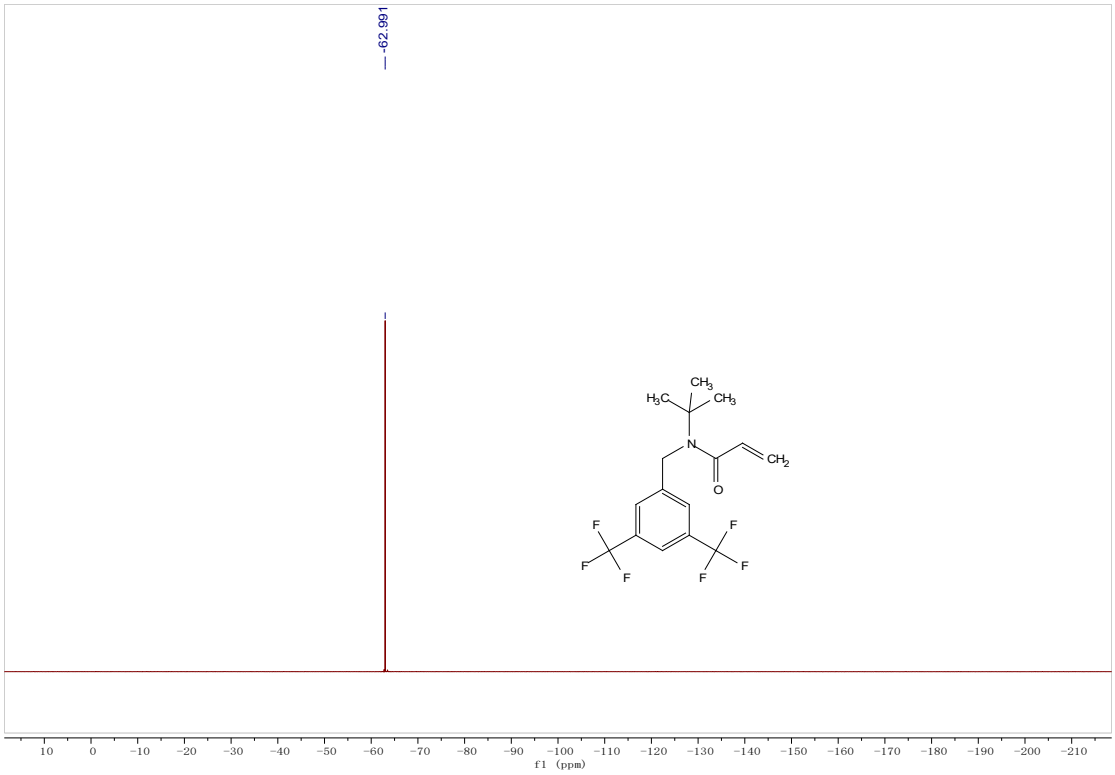
^{19}F NMR of **1f**



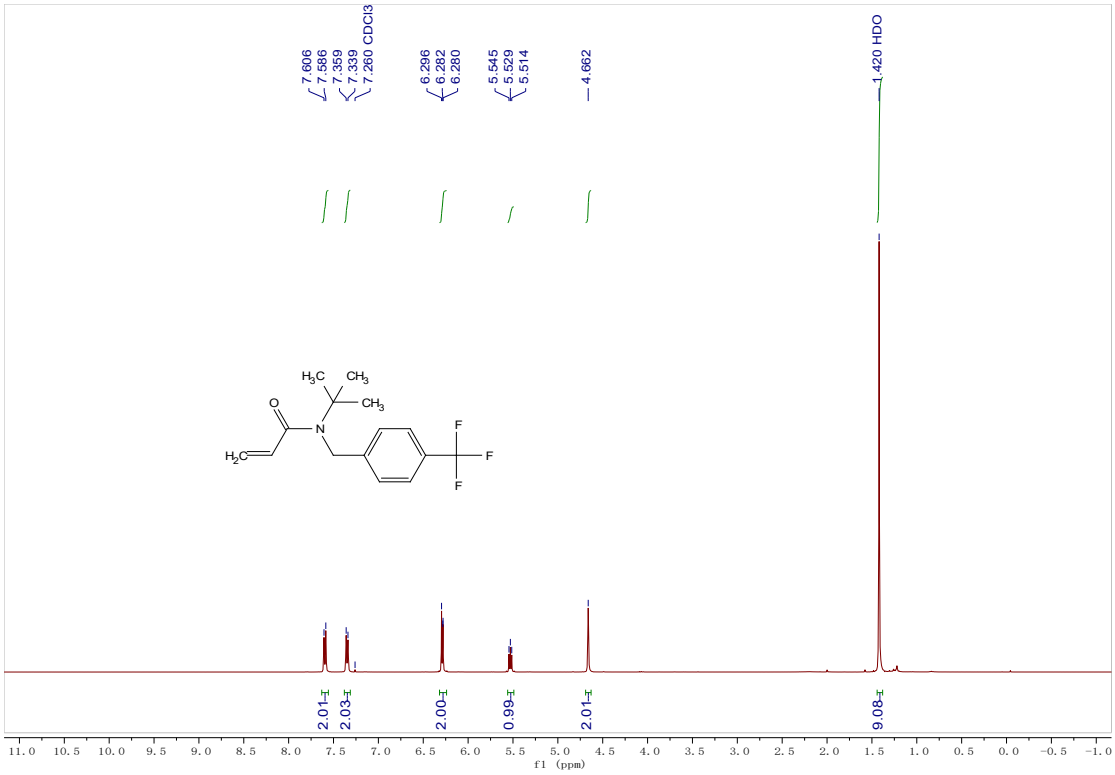
^{1}H NMR of **1g**



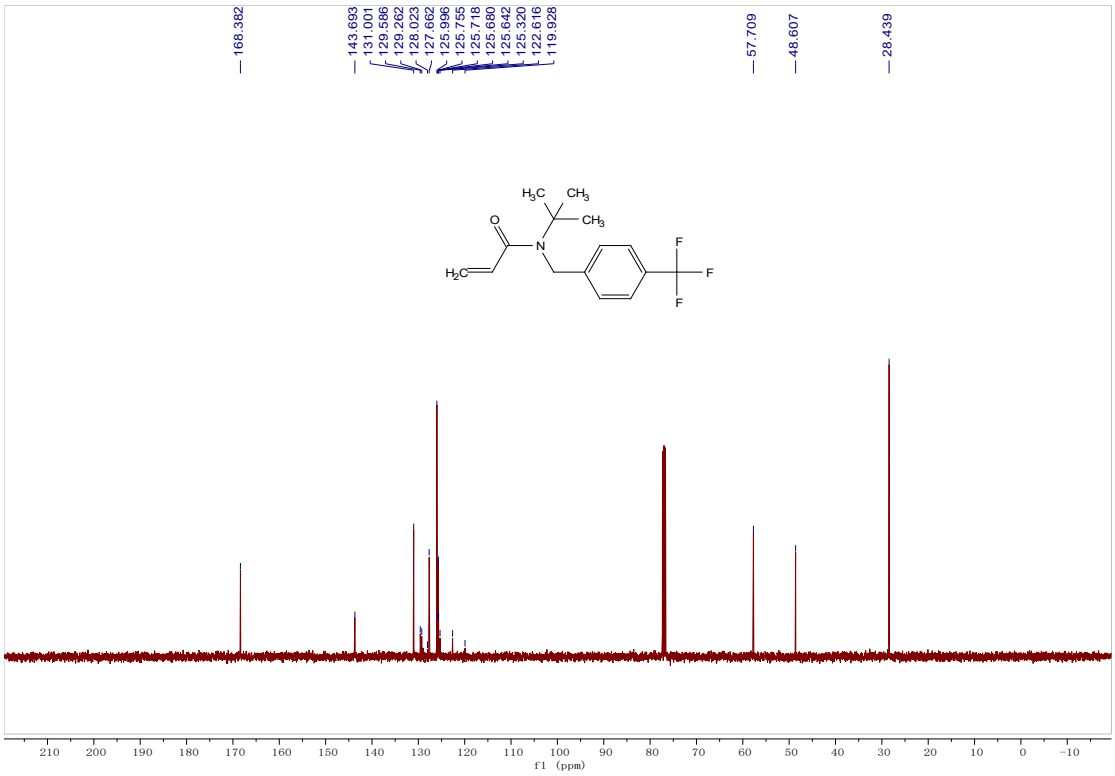
^{13}C NMR of **1g**



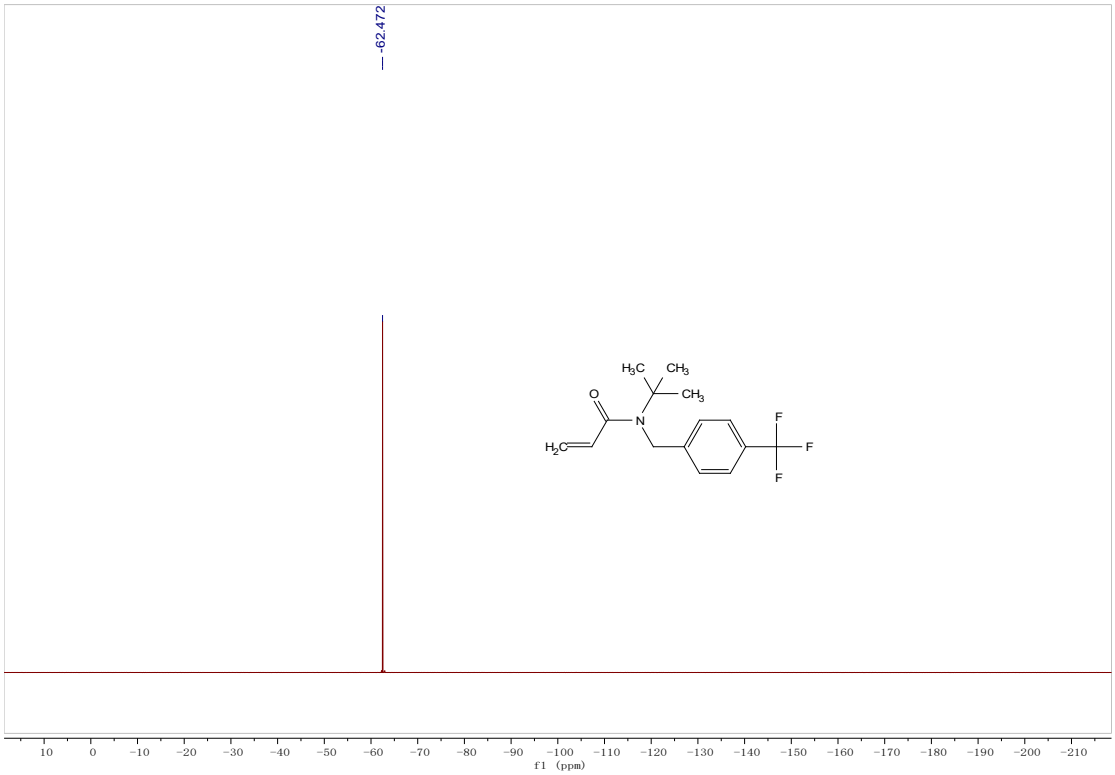
^{19}F NMR of **1g**


7.606
7.586
7.359
7.339
7.260 CDCl3
6.296
6.282
6.280
5.545
5.529
5.514
4.662
1.420 HDO
H3C
CH3
CH3
O
N
H2C
F
F
F
2.01
2.03
2.00
0.99
2.01
9.08
f1 (ppm)

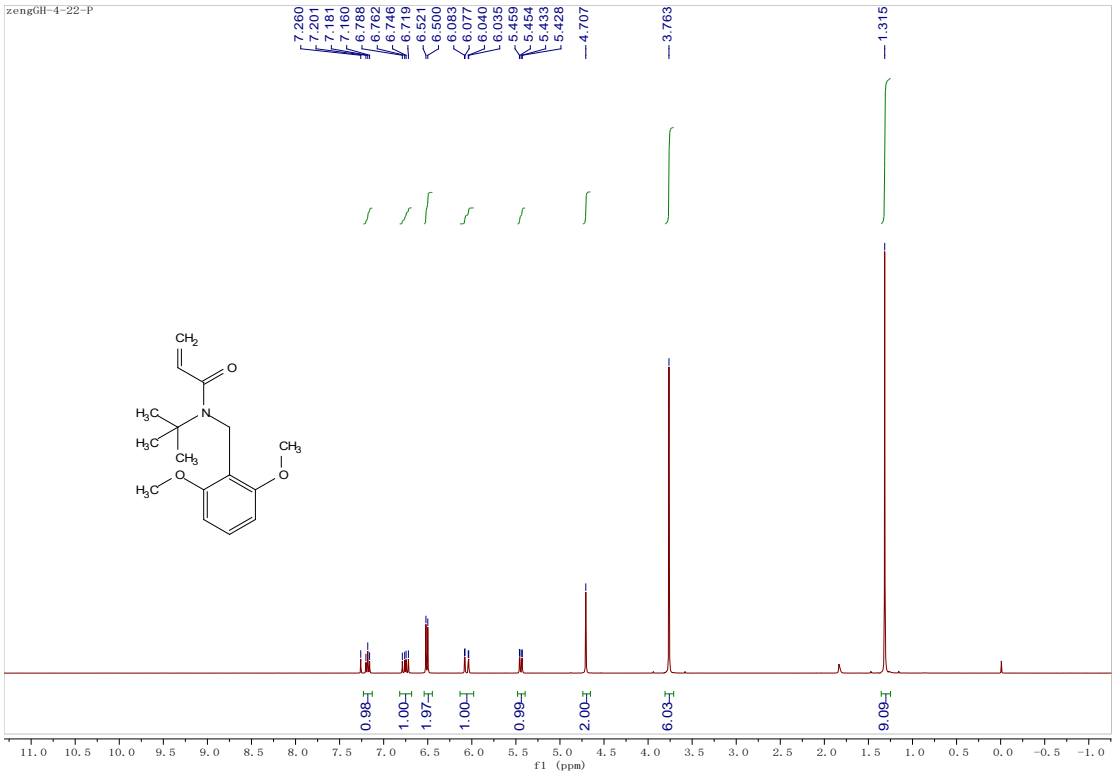
^{1}H NMR of **1h**



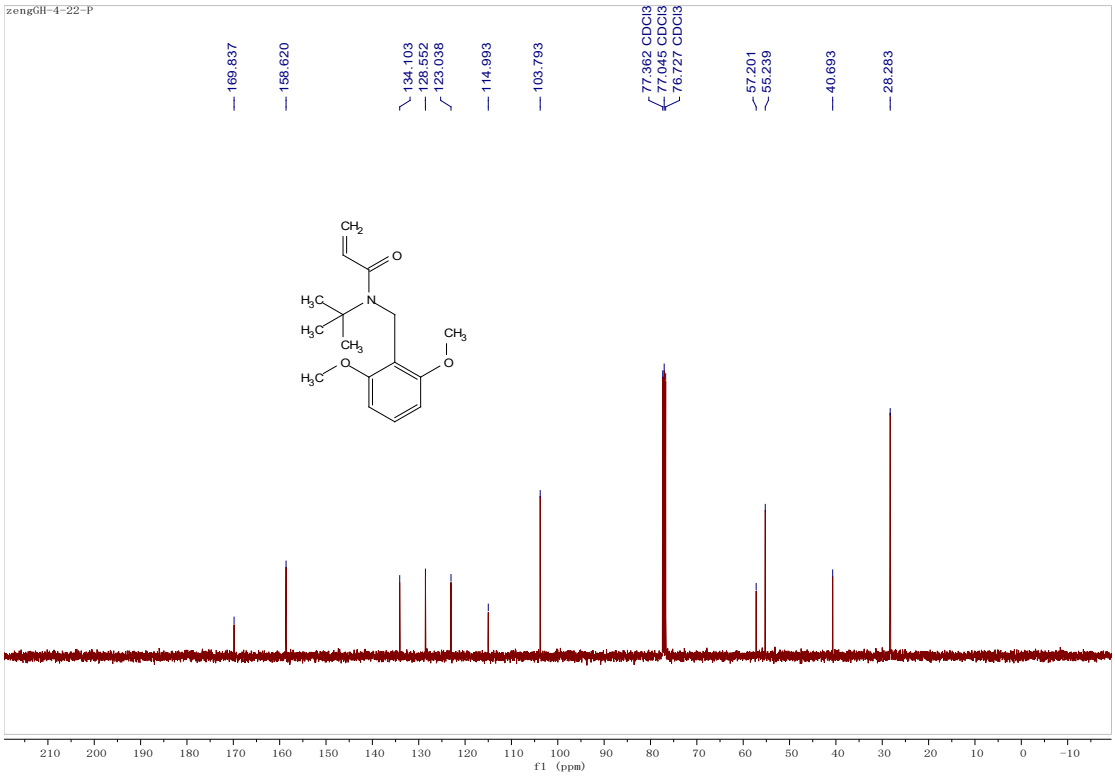
^{13}C NMR of **1h**



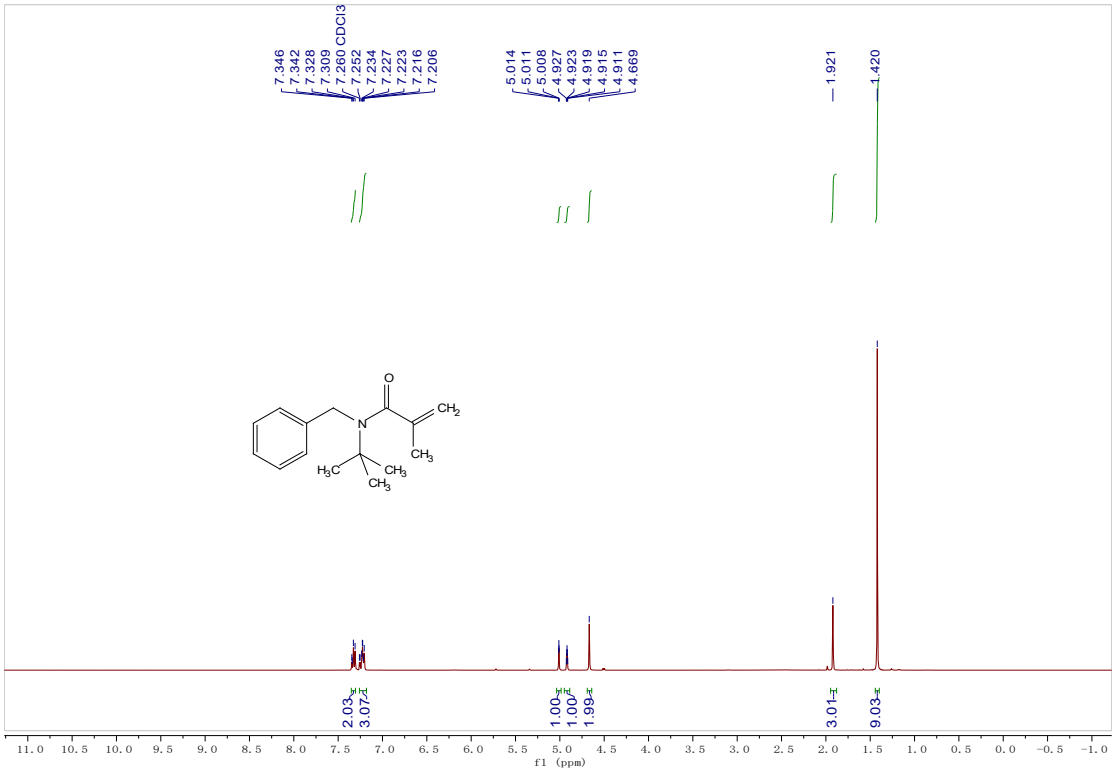
^{19}F NMR of **1h**



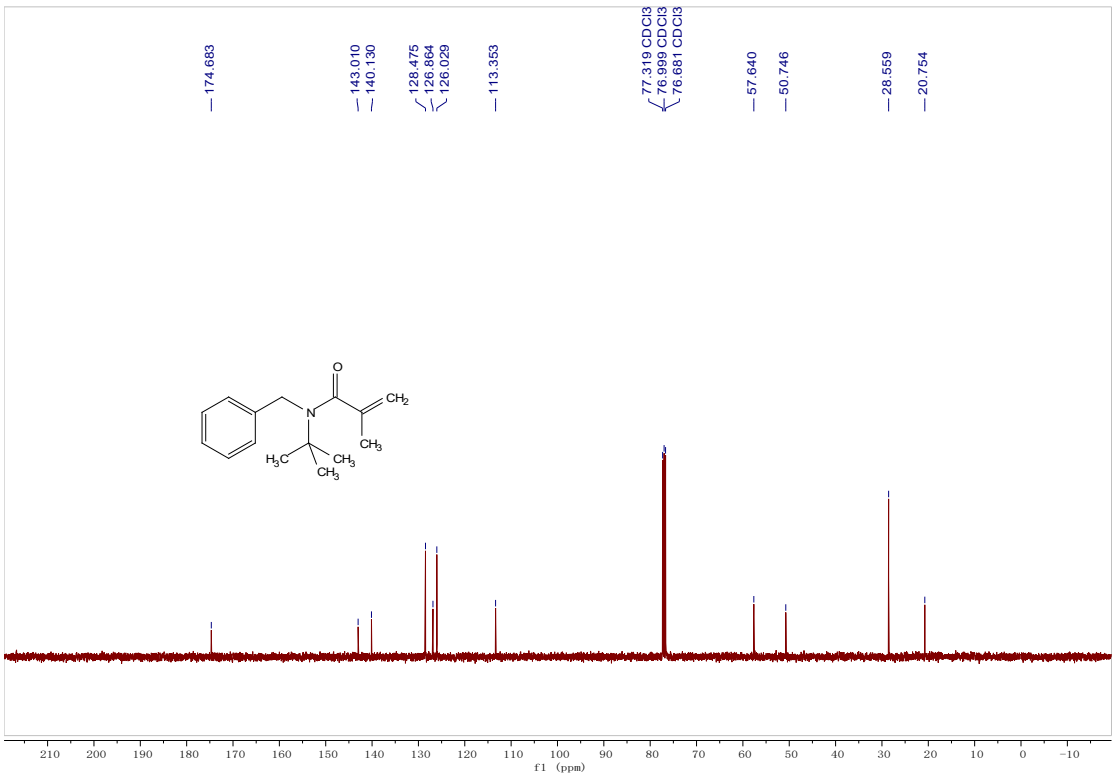
^{1}H NMR of **1i**



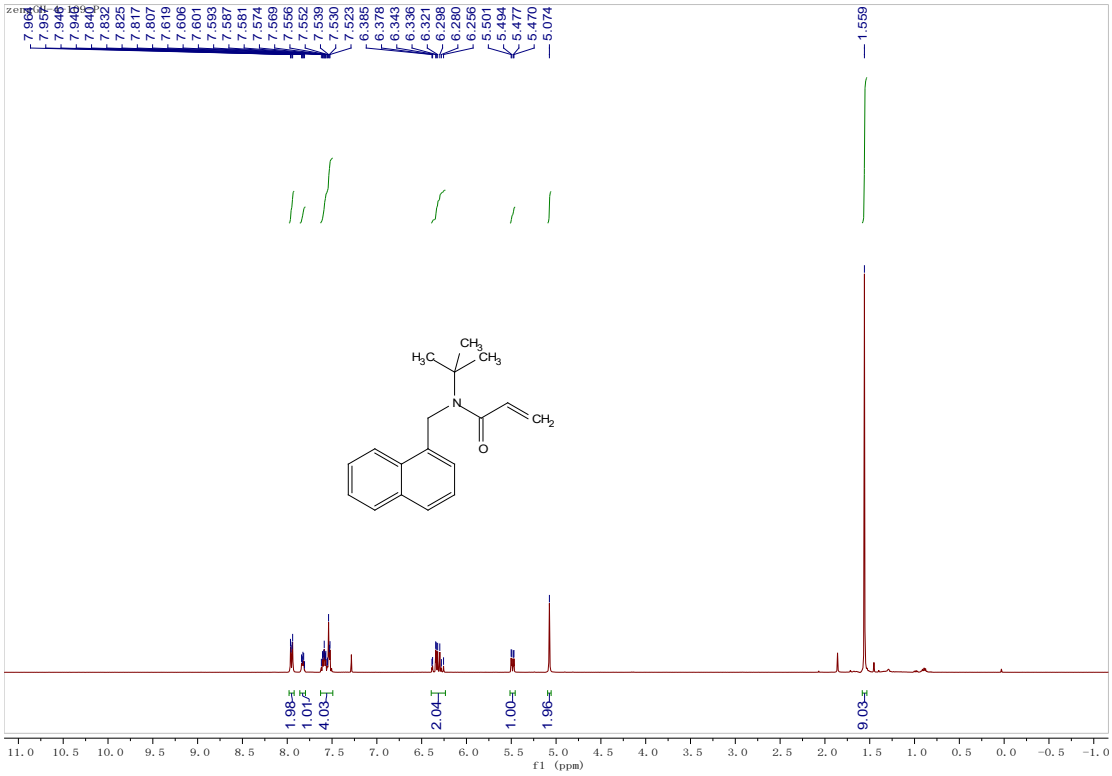
^{13}C NMR of **1i**



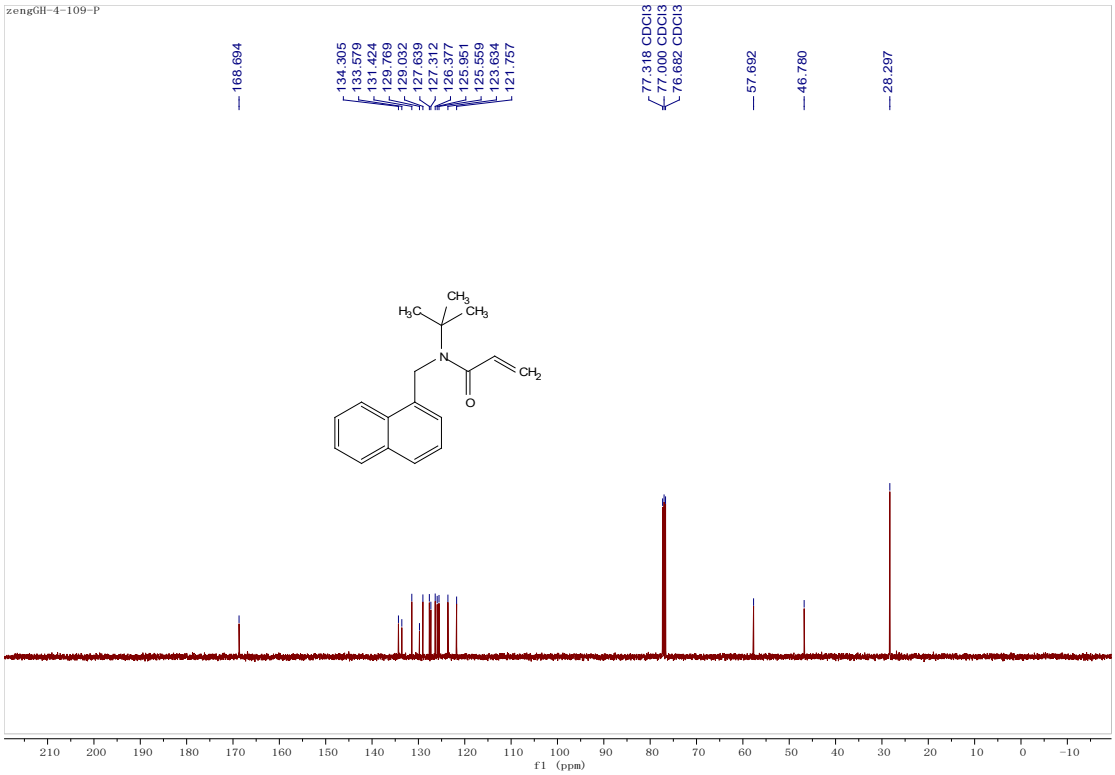
^{1}H NMR of **1j**



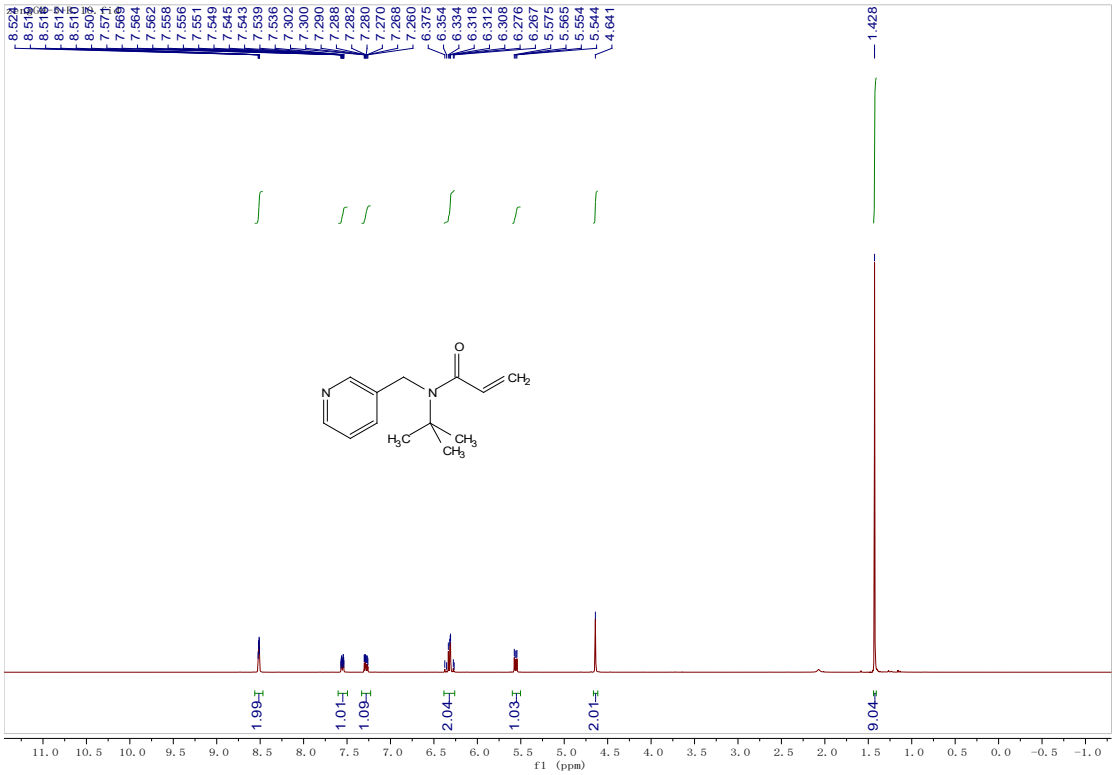
^{13}C NMR of **1j**


7.963
7.957
7.946
7.944
7.840
7.832
7.825
7.817
7.807
7.619
7.606
7.601
7.593
7.587
7.581
7.574
7.569
7.556
7.552
7.539
7.530
7.523
6.385
6.378
6.343
6.336
6.321
6.298
6.280
6.256
5.501
5.494
5.477
5.470
5.074
1.559
1.98
1.01
4.03
2.04
1.00
1.96
9.03
f1 (ppm)

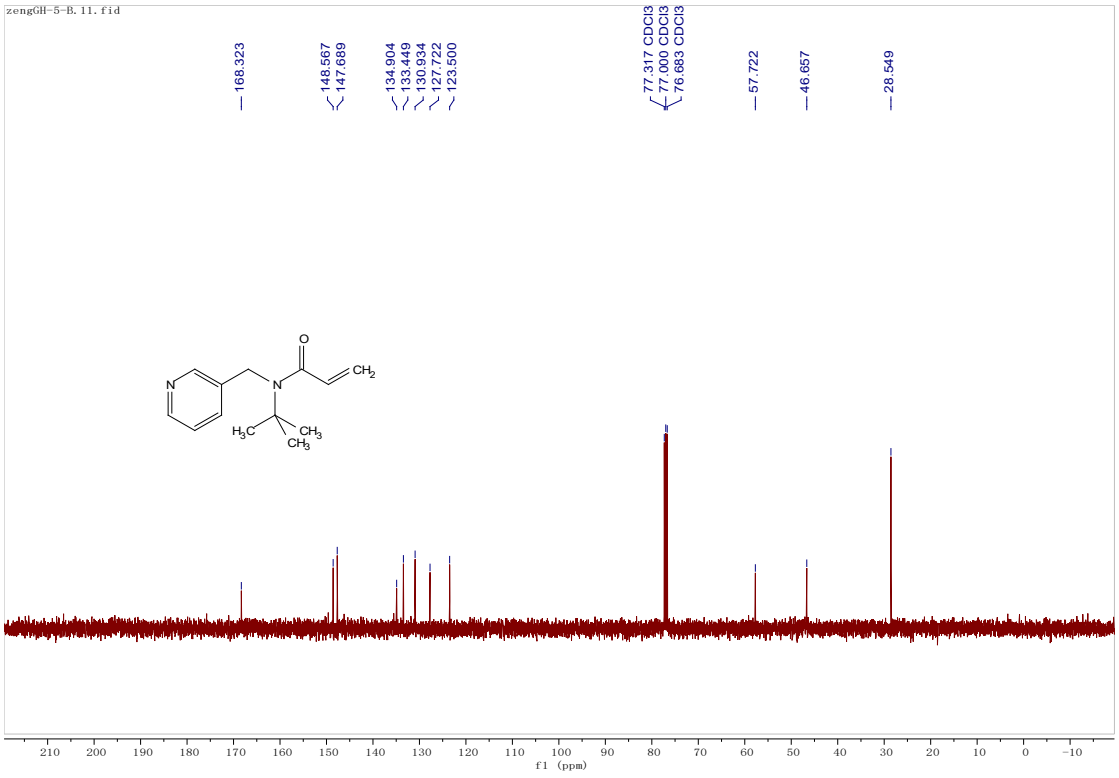
^{1}H NMR of **1k**


zengGH-4-109-P
168.694
134.305
133.579
131.424
129.769
129.032
127.639
127.312
126.377
125.951
125.559
123.634
121.757
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
57.692
46.780
28.297
f1 (ppm)

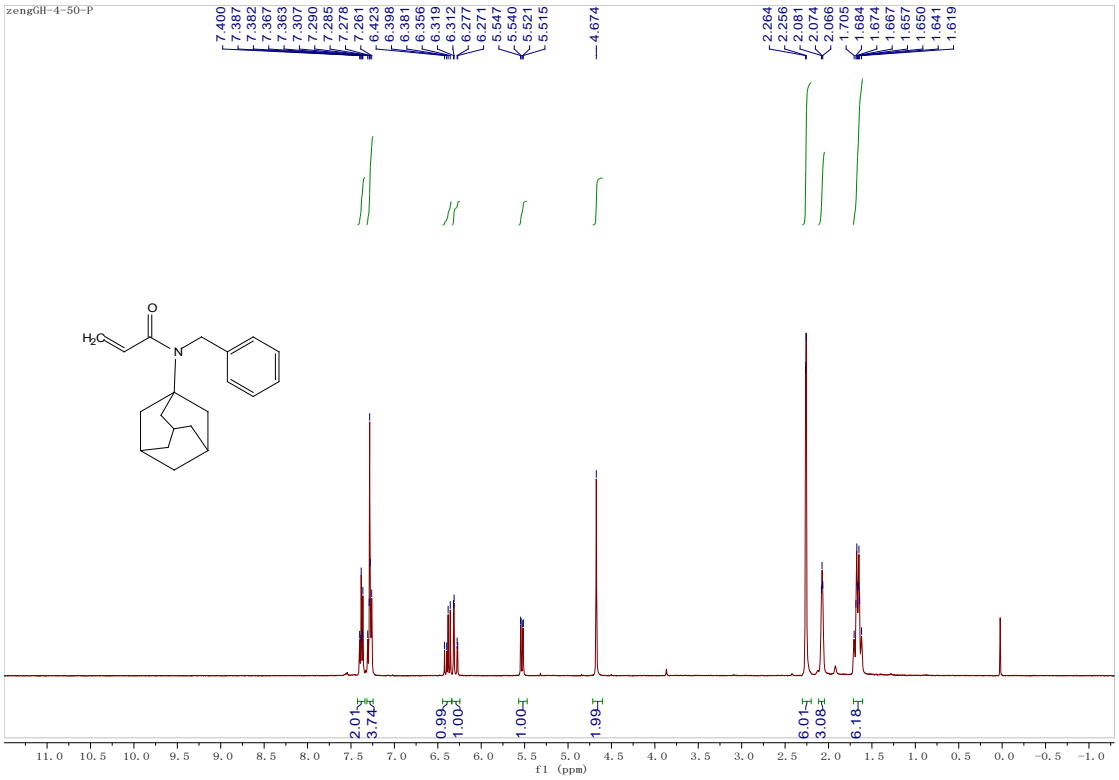
^{13}C NMR of **1k**



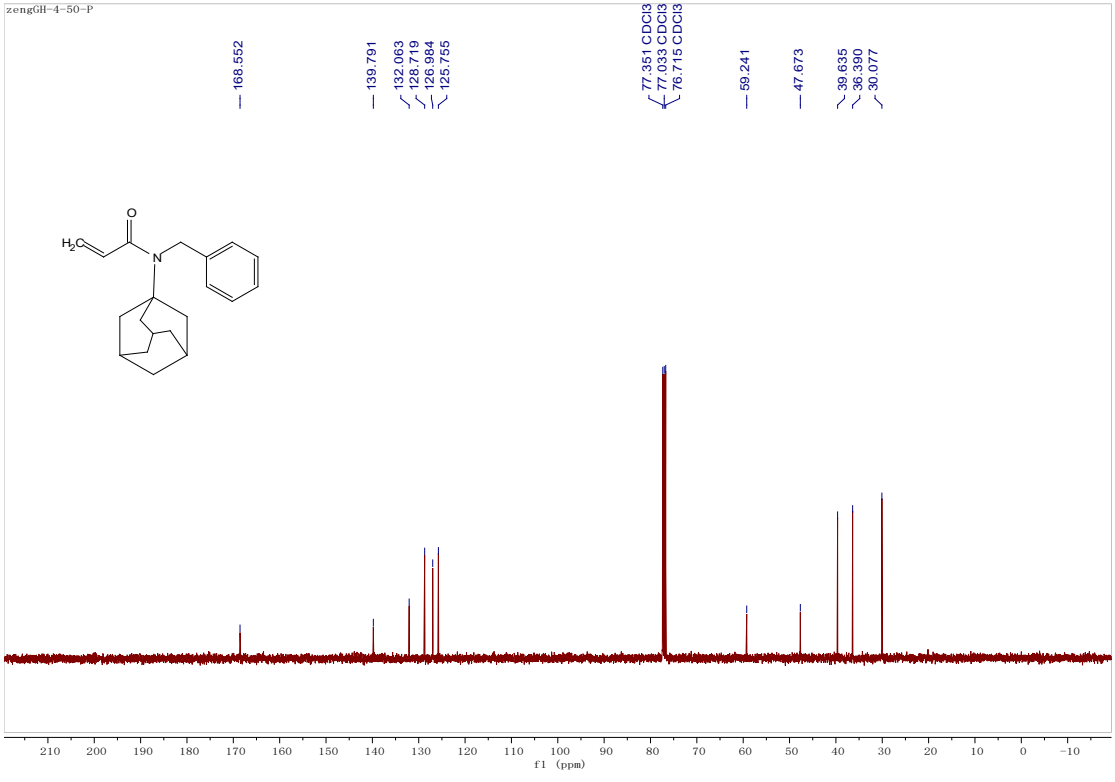
^{1}H NMR of **1l**


zengGH-5-B.11.fid
168.323
148.567
147.689
134.904
133.449
130.934
127.722
123.500
77.317 CDCl3
77.000 CDCl3
76.683 CDCl3
57.722
46.657
28.549
O
N
N
CH2
H3C
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

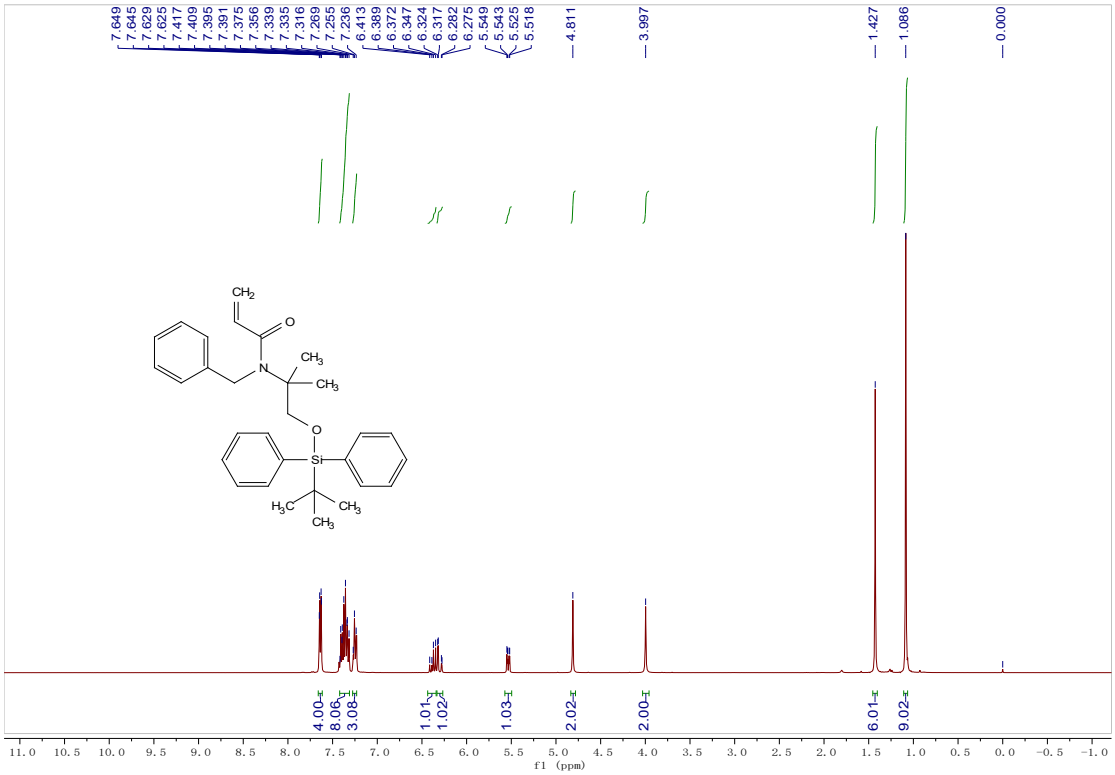
^{13}C NMR of **1l**


zengGH-4-50-P
7.400
7.387
7.382
7.367
7.363
7.307
7.290
7.285
7.278
7.261
6.423
6.398
6.381
6.356
6.319
6.312
6.277
6.271
5.547
5.540
5.521
5.515
4.674
2.264
2.256
2.081
2.074
2.066
1.705
1.684
1.674
1.667
1.657
1.650
1.641
1.619
2.01
3.74
0.99
1.00
1.00
1.99
6.01
3.08
6.18
f1 (ppm)

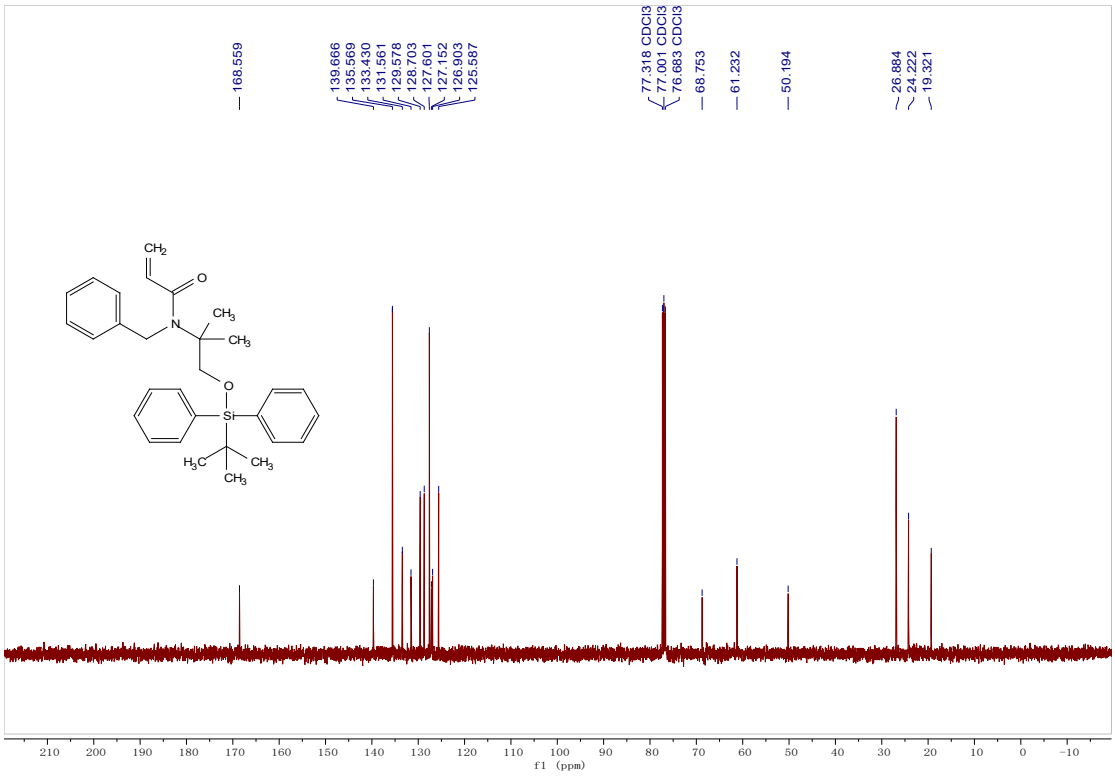
^{1}H NMR of **1m**


zengGH-4-50-P
168.552
139.791
132.063
128.719
126.984
125.755
77.351 CDCl3
77.033 CDCl3
76.715 CDCl3
59.241
47.673
39.635
36.390
30.077
f1 (ppm)

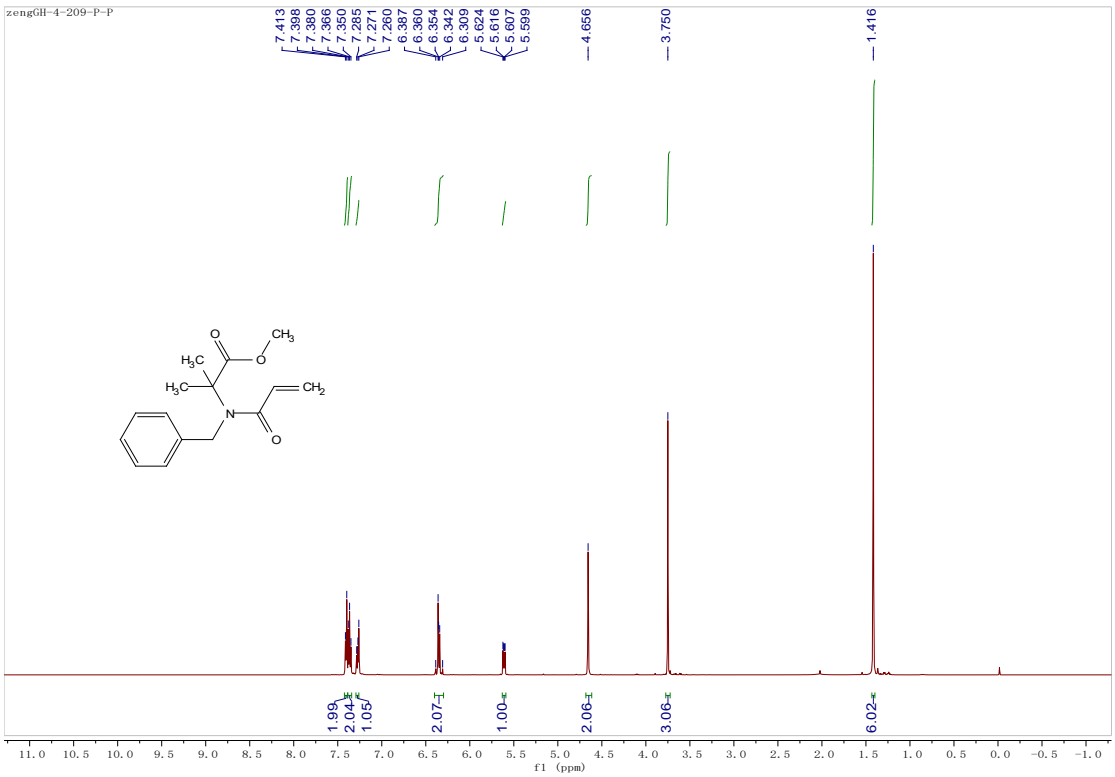
^{13}C NMR of **1m**



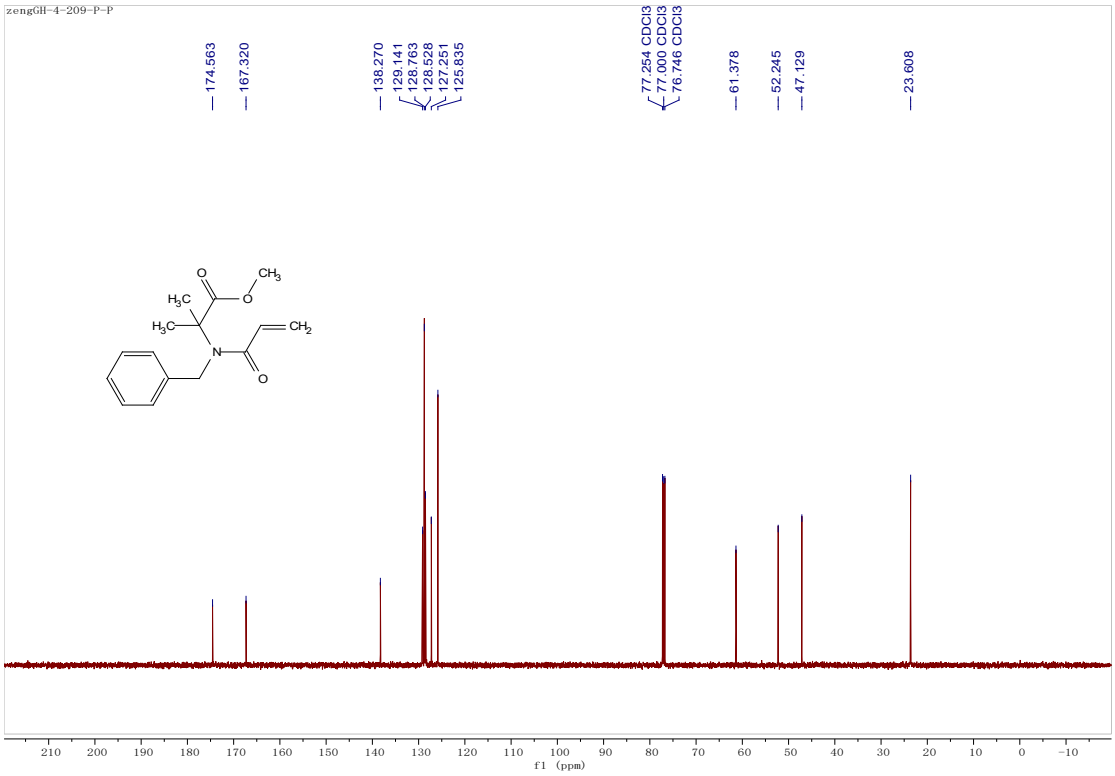
^{1}H NMR of **1n**



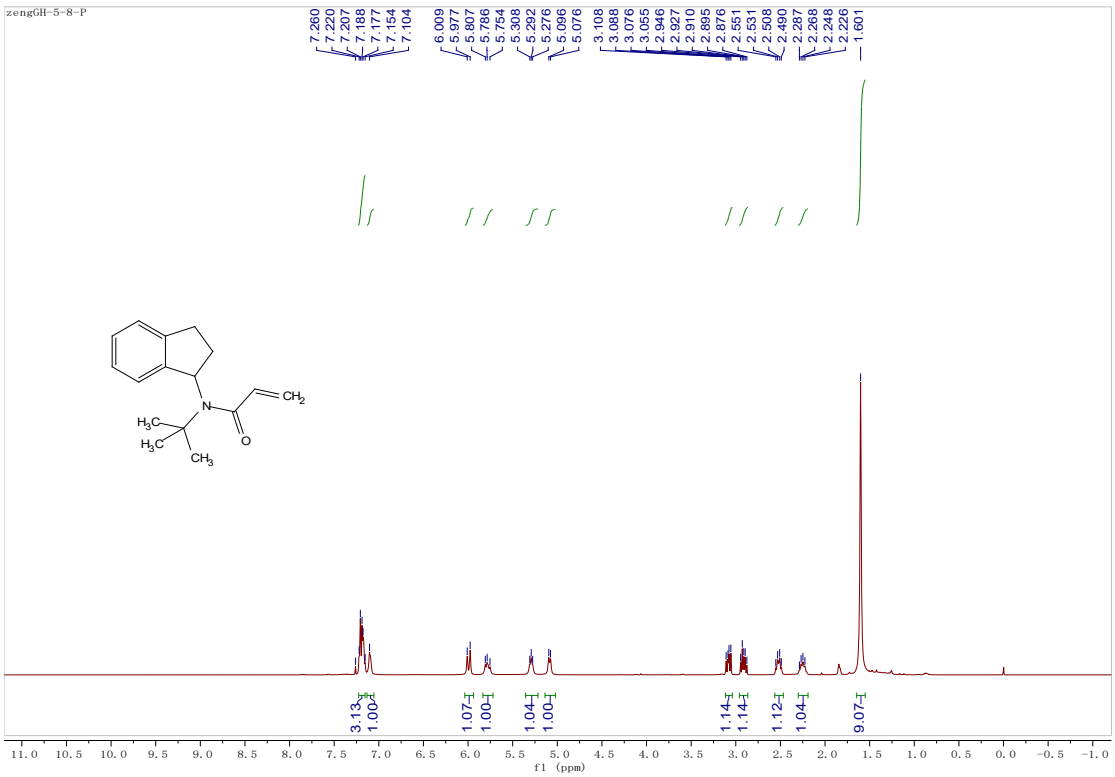
^{13}C NMR of **1n**



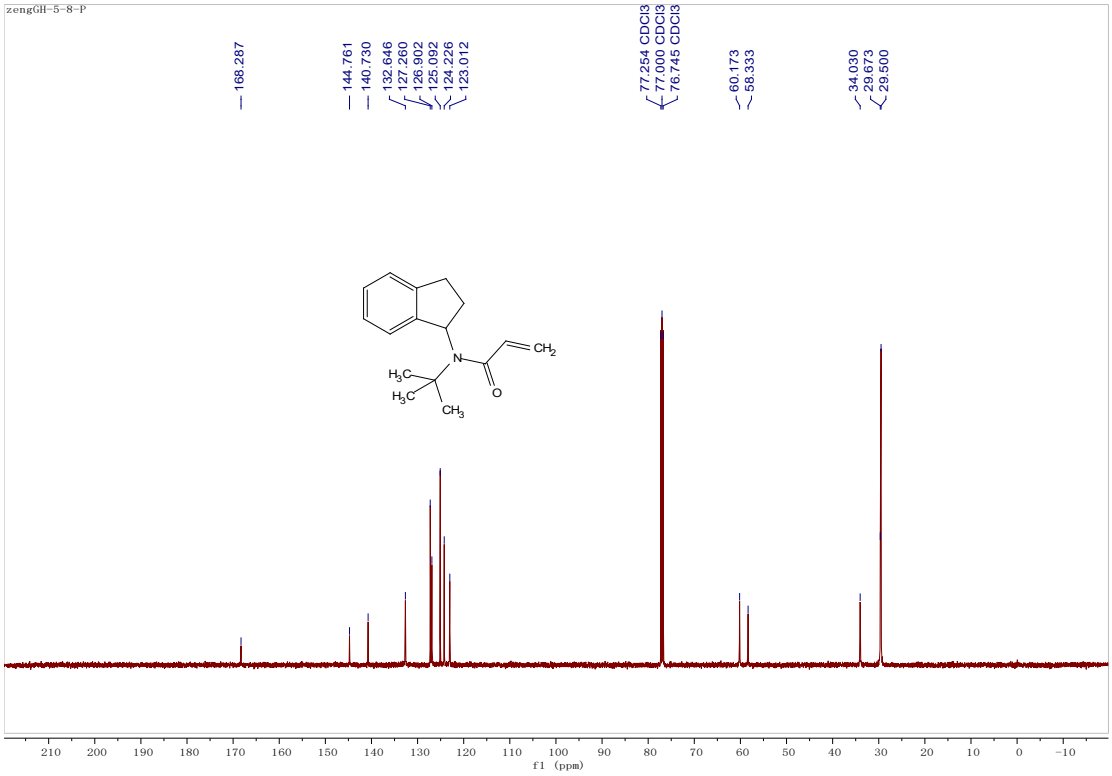
^{1}H NMR of **1o**



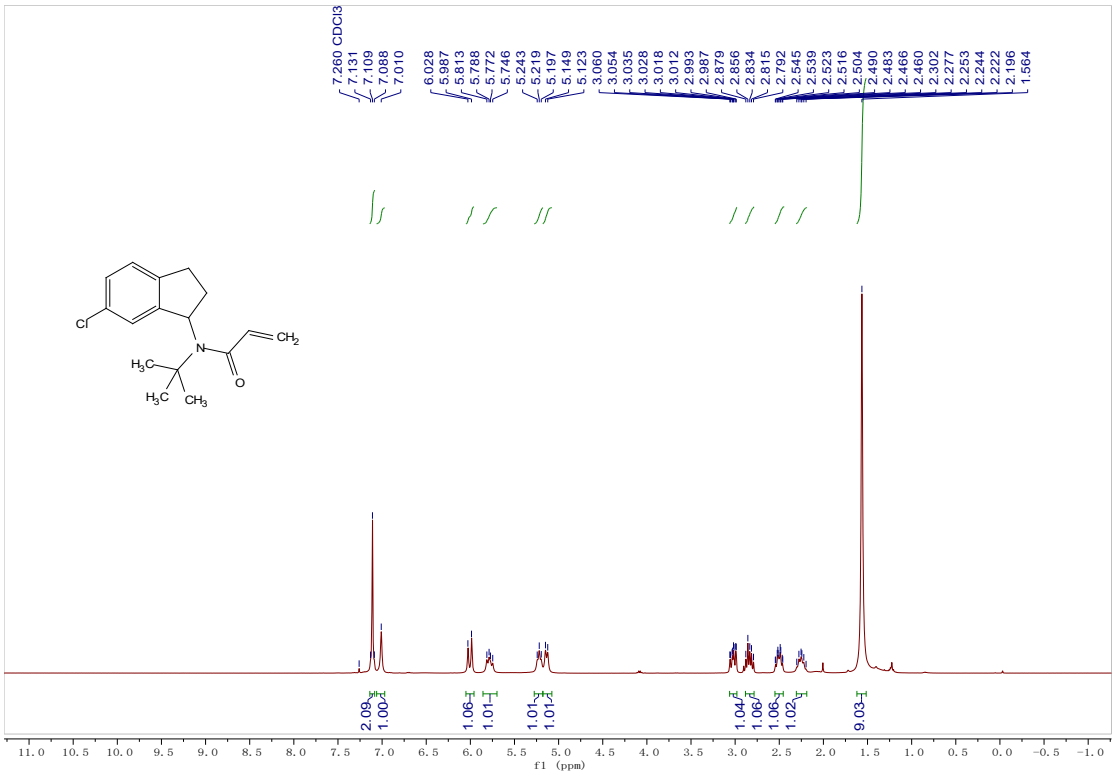
^{13}C NMR of **1o**



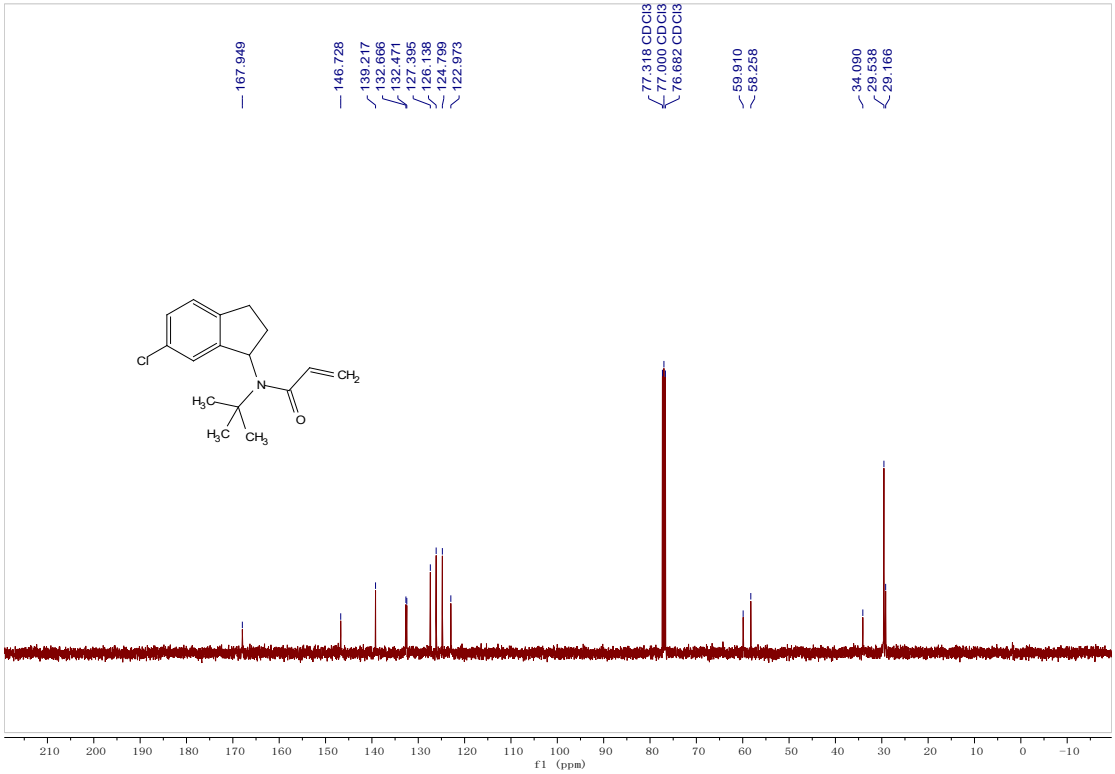
^{1}H NMR of **1p**


zengGH-5-8-P
168.287
144.761
140.730
132.646
127.260
126.902
125.092
124.226
123.012
77.254 CDCl3
77.000 CDCl3
76.745 CDCl3
60.173
58.333
34.030
29.673
29.500
CH2
N
O
H3C
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

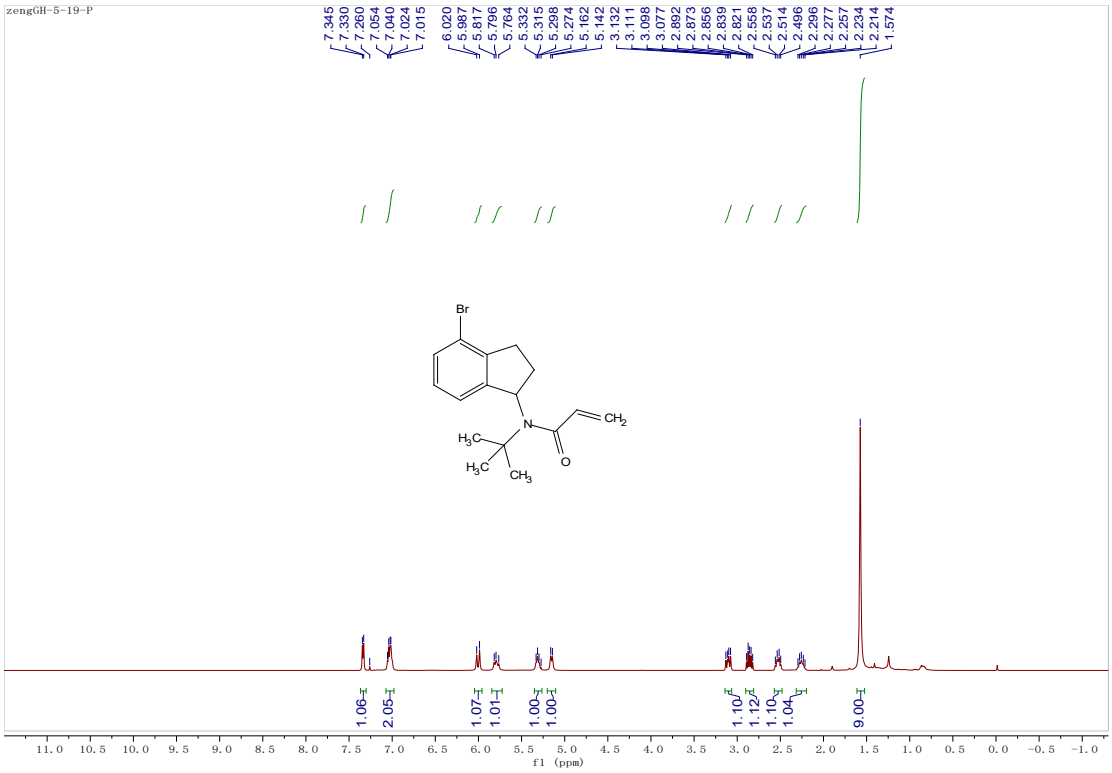
^{13}C NMR of **1p**



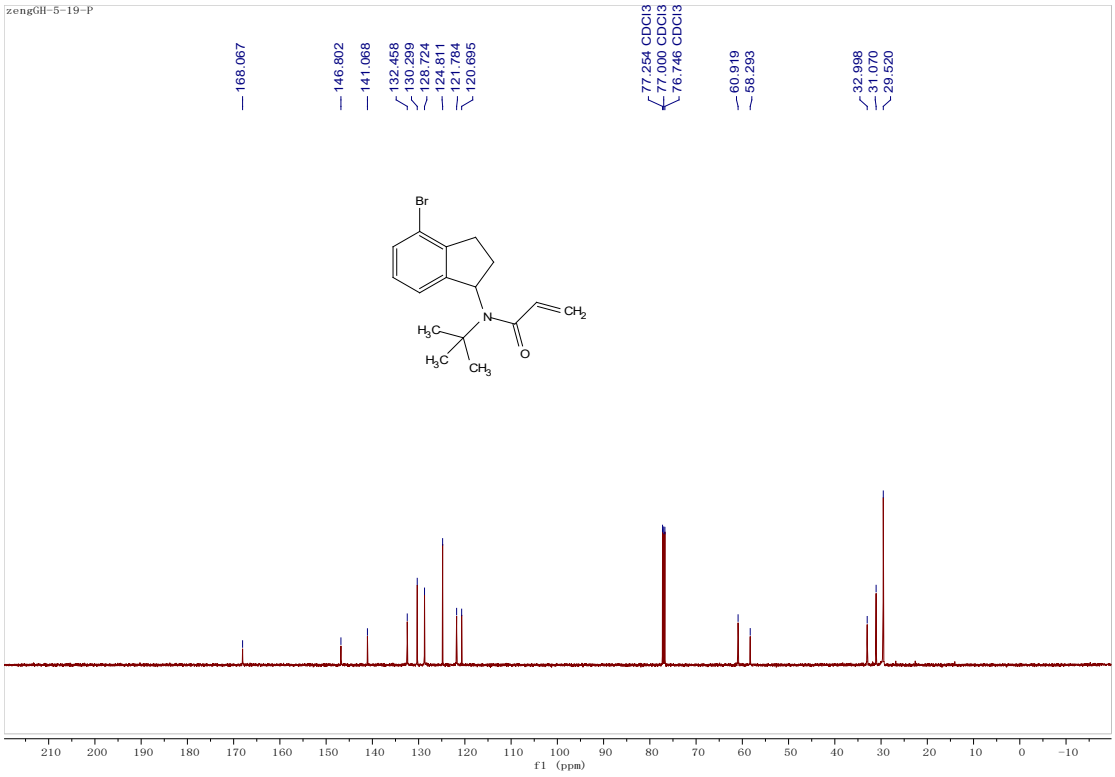
^{1}H NMR of **1q**



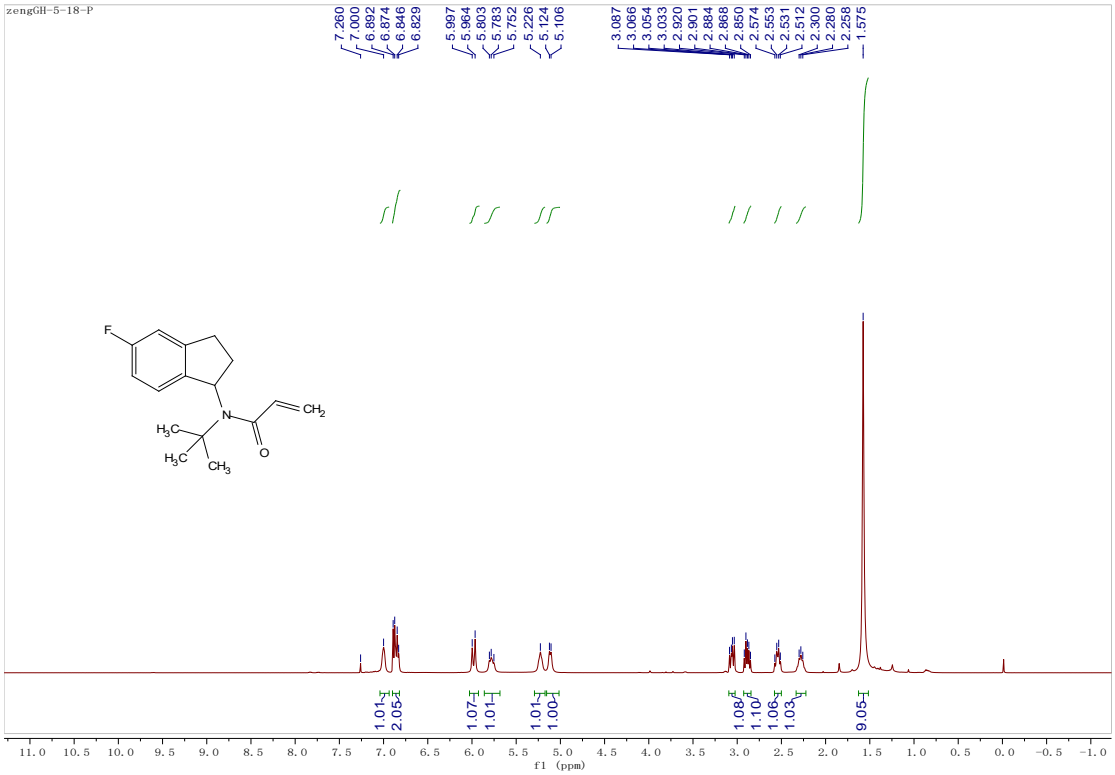
^{13}C NMR of **1q**


zengGH-5-19-P
7.345
7.330
7.260
7.054
7.040
7.024
7.015
6.020
5.987
5.817
5.796
5.764
5.332
5.315
5.298
5.274
5.162
5.142
3.132
3.111
3.098
3.077
2.892
2.873
2.856
2.839
2.821
2.558
2.537
2.514
2.496
2.296
2.277
2.257
2.234
2.214
1.574
Br
N
CH2
O
H3C
H3C
CH3
1.06
2.05
1.07
1.01
1.00
1.00
1.10
1.12
1.10
1.04
9.00
f1 (ppm)

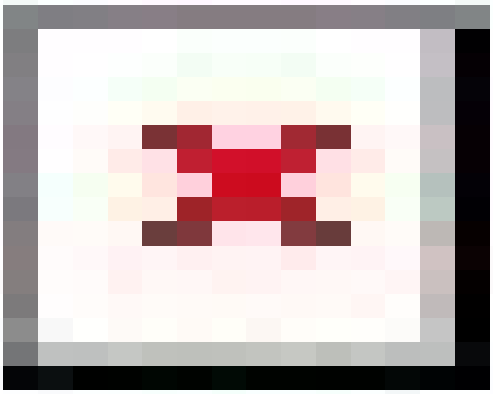
^{1}H NMR of **1r**


zengGH-5-19-P
168.067
146.802
141.068
132.458
130.299
128.724
124.811
121.784
120.695
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
60.919
58.293
32.998
31.070
29.520
Br
N
CH2
O
H3C
H3C
CH3
f1 (ppm)

^{13}C NMR of **1r**



^{1}H NMR of **1s**



^{13}C NMR of **1s**

^{19}F NMR of **1s**

^{1}H NMR of **1t**

^{13}C NMR of **1t**

^{1}H NMR of **1u**

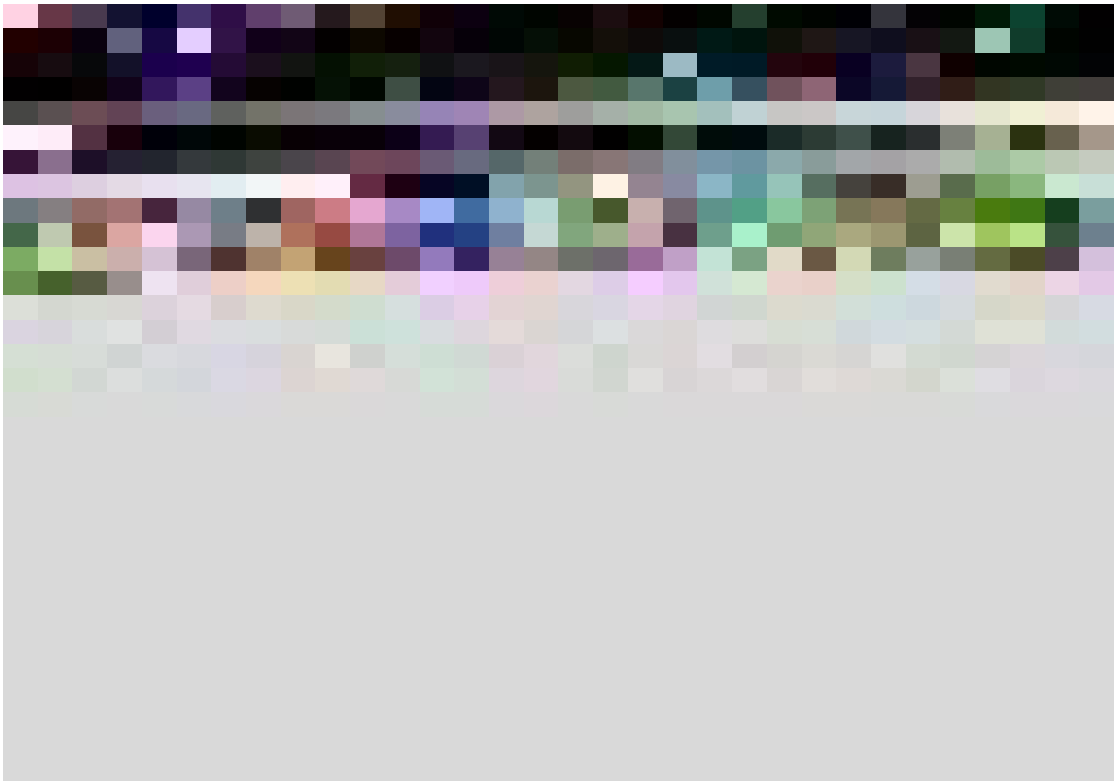
^{13}C NMR of **1u**

^{1}H NMR of **1v**

^{13}C NMR of **1v**

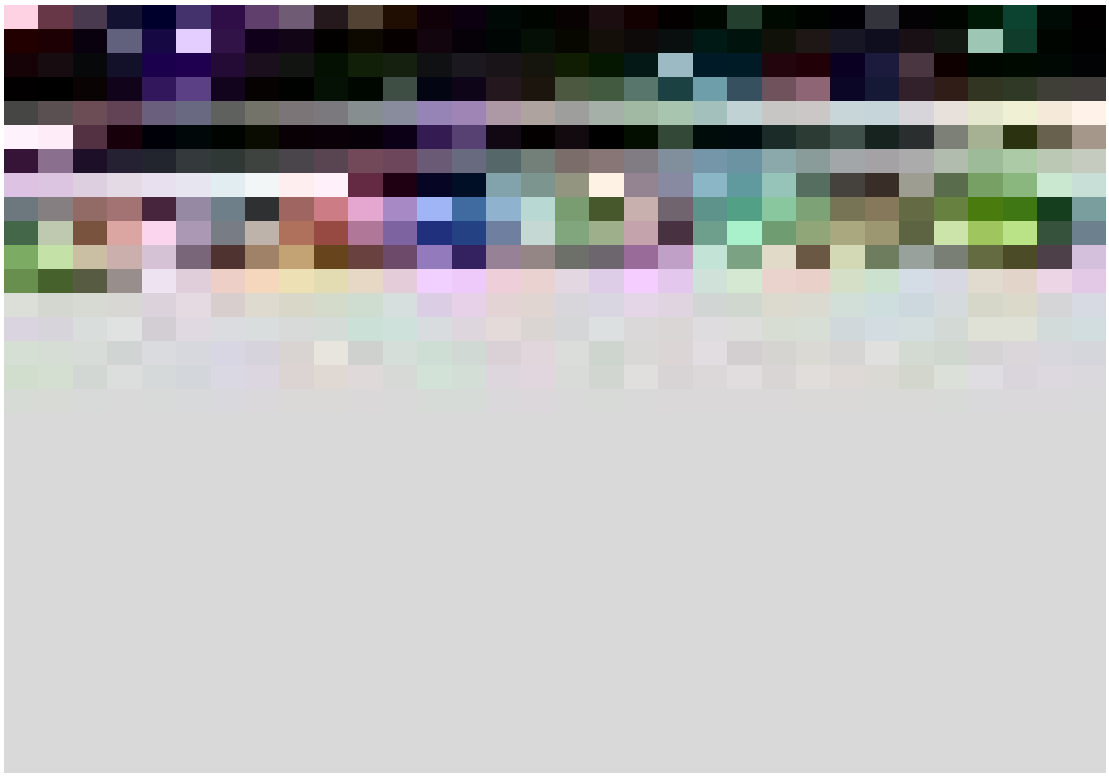
^{1}H NMR of **1w**

^{13}C NMR of **1w**

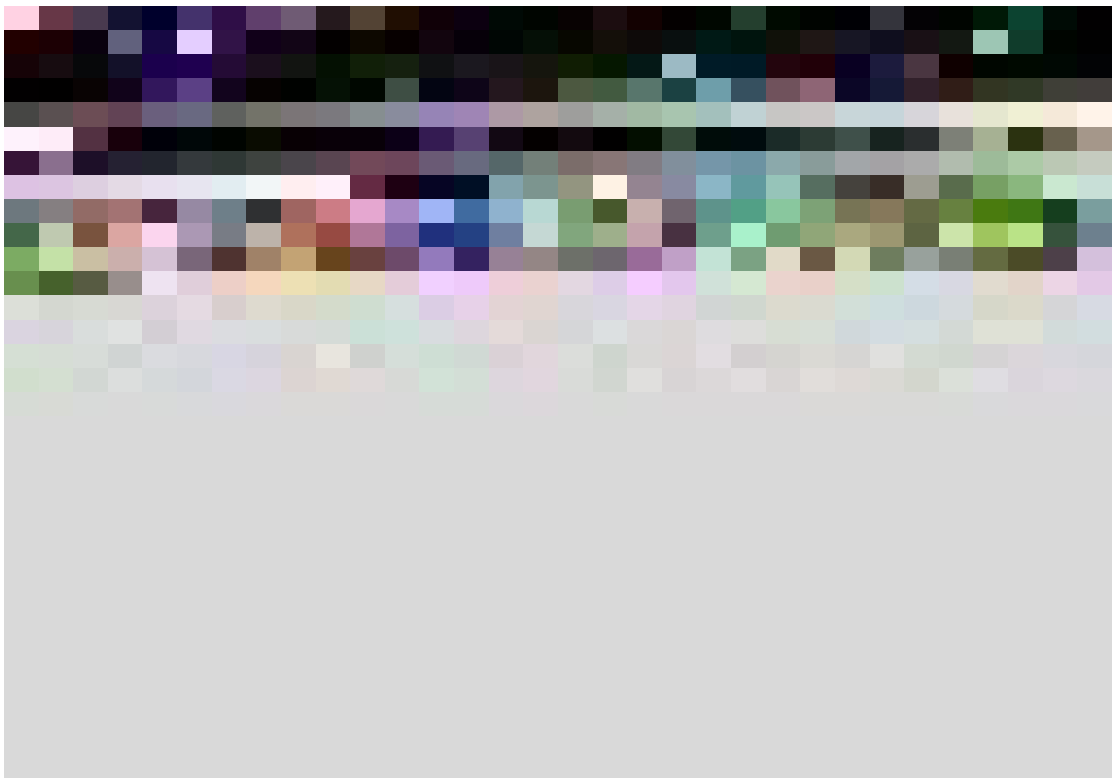


^{1}H NMR of **1x**

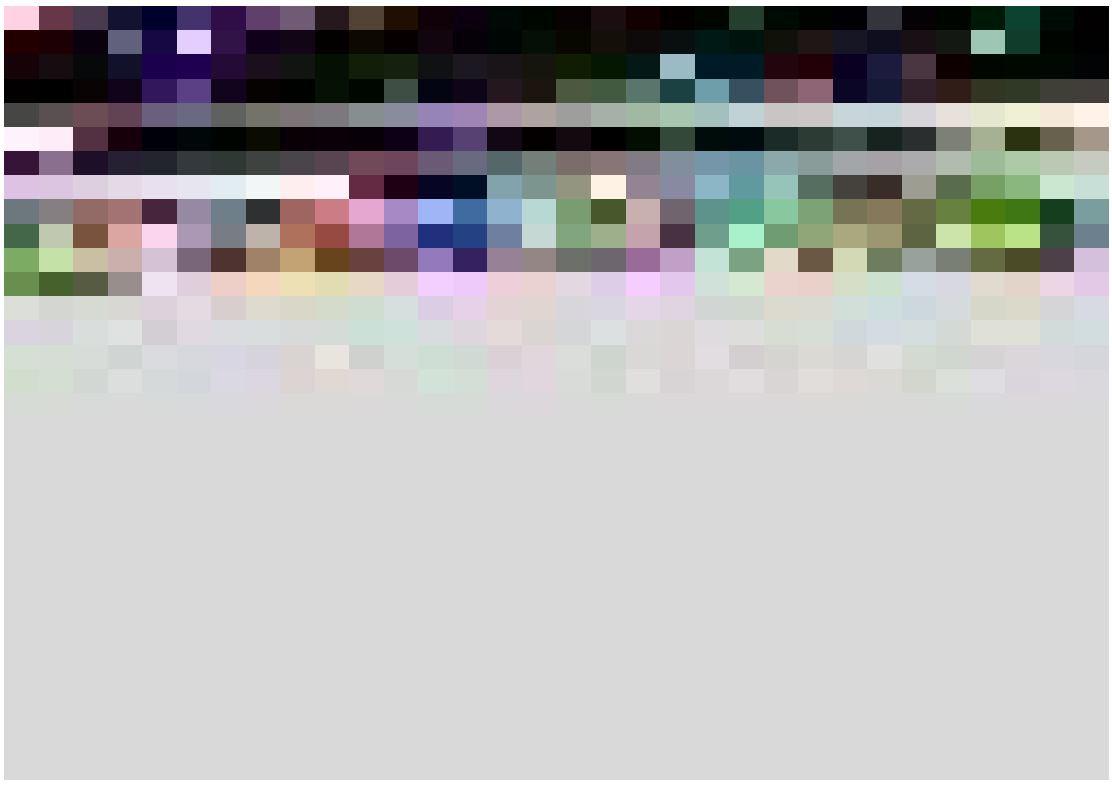
^{13}C NMR of **1x**



^{1}H NMR of **3-1**

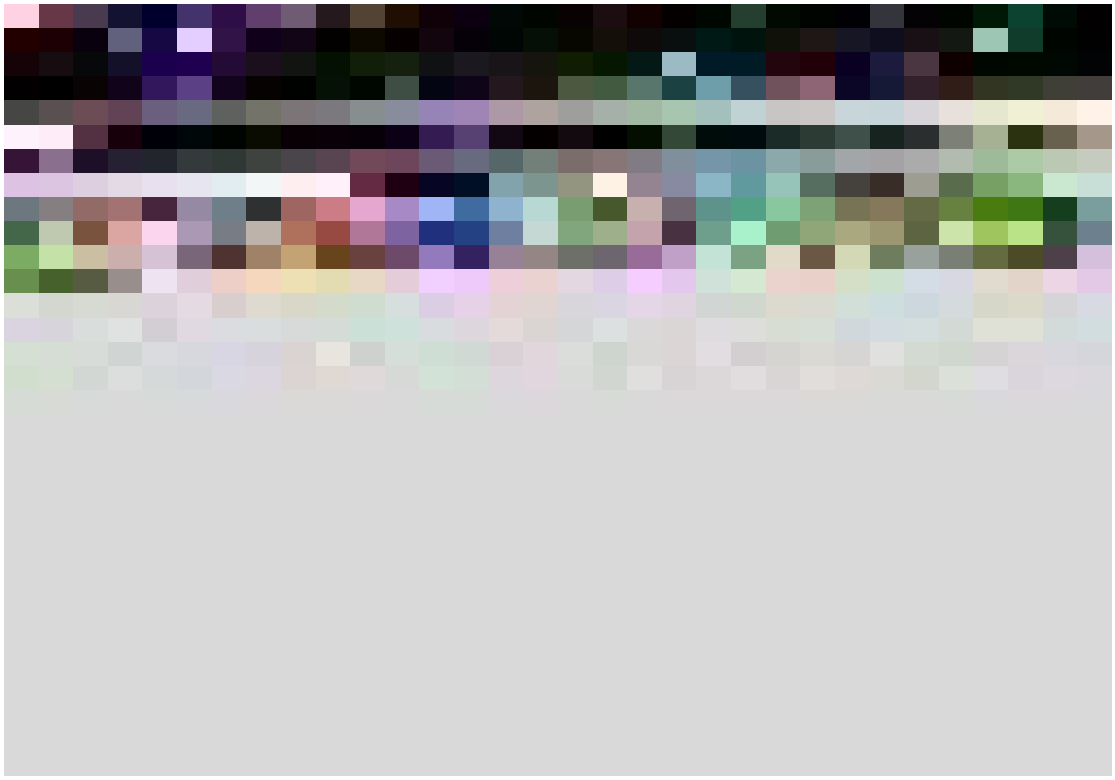


^{13}C NMR of **3-1**



^{1}H NMR of **3-2**

^{13}C NMR of **3-2**

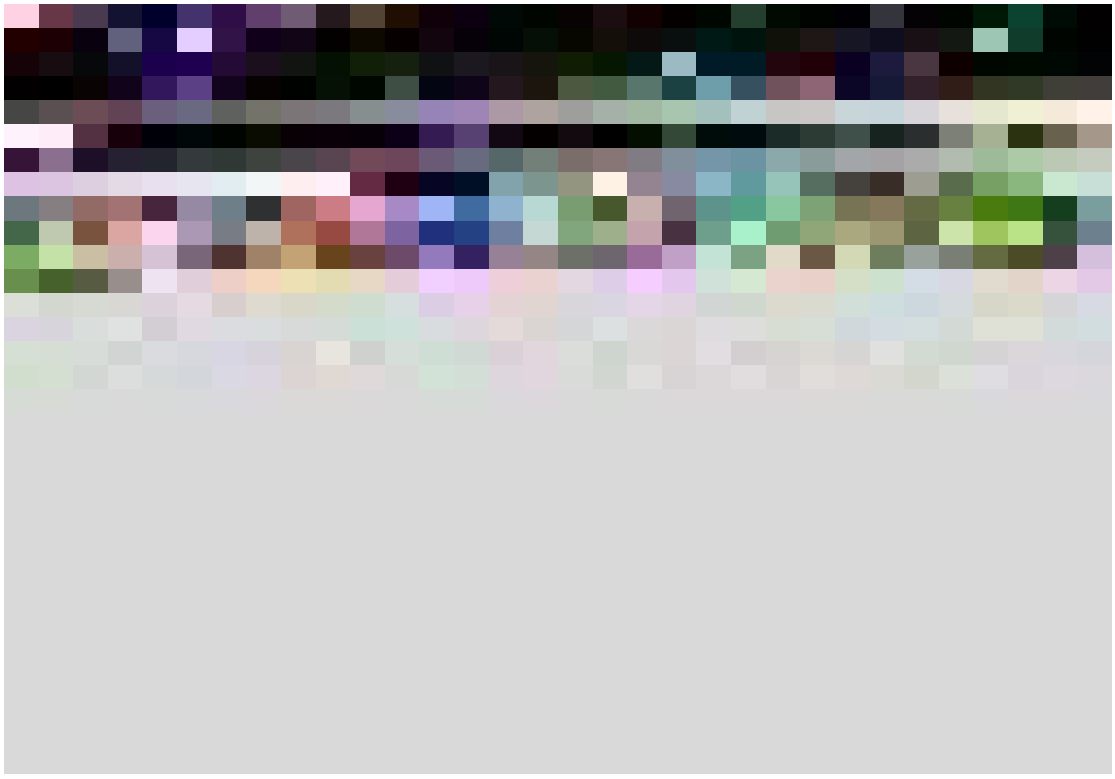


^{1}H NMR of **3-3** (P1, trans)

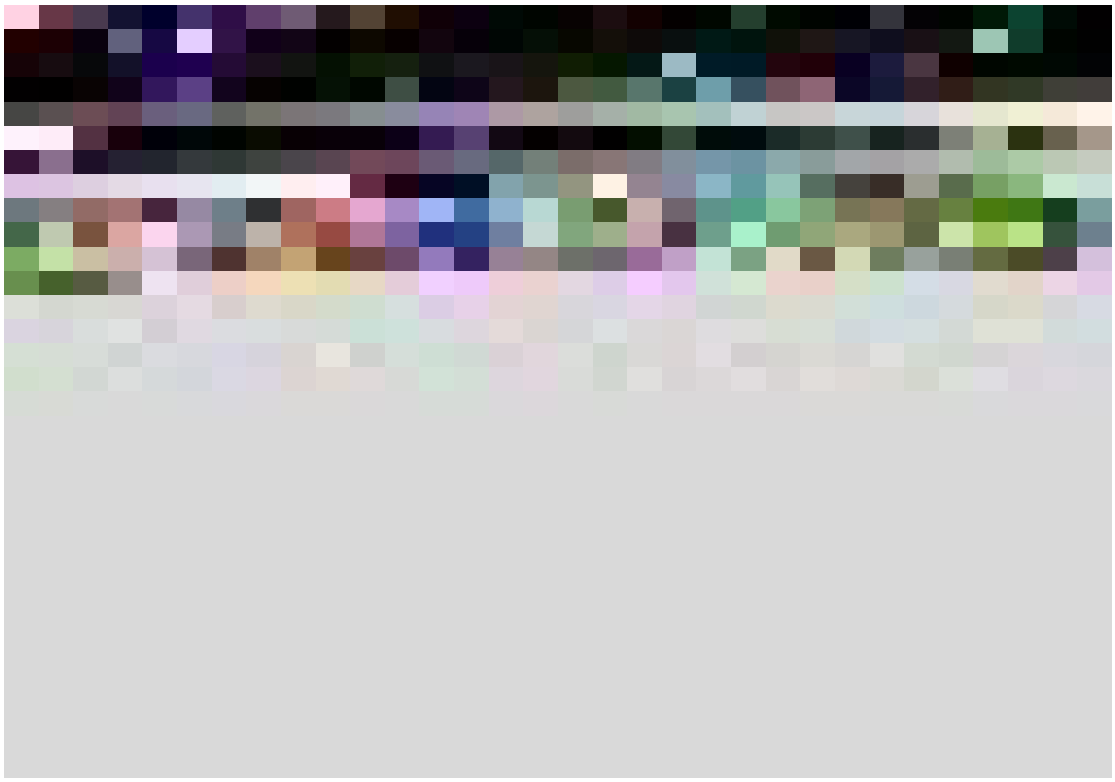
^{13}C NMR of **3-3** (P1, trans)

^{1}H NMR of **3-3** (P2, cis)

^{13}C NMR of **3-3** (P2, cis)



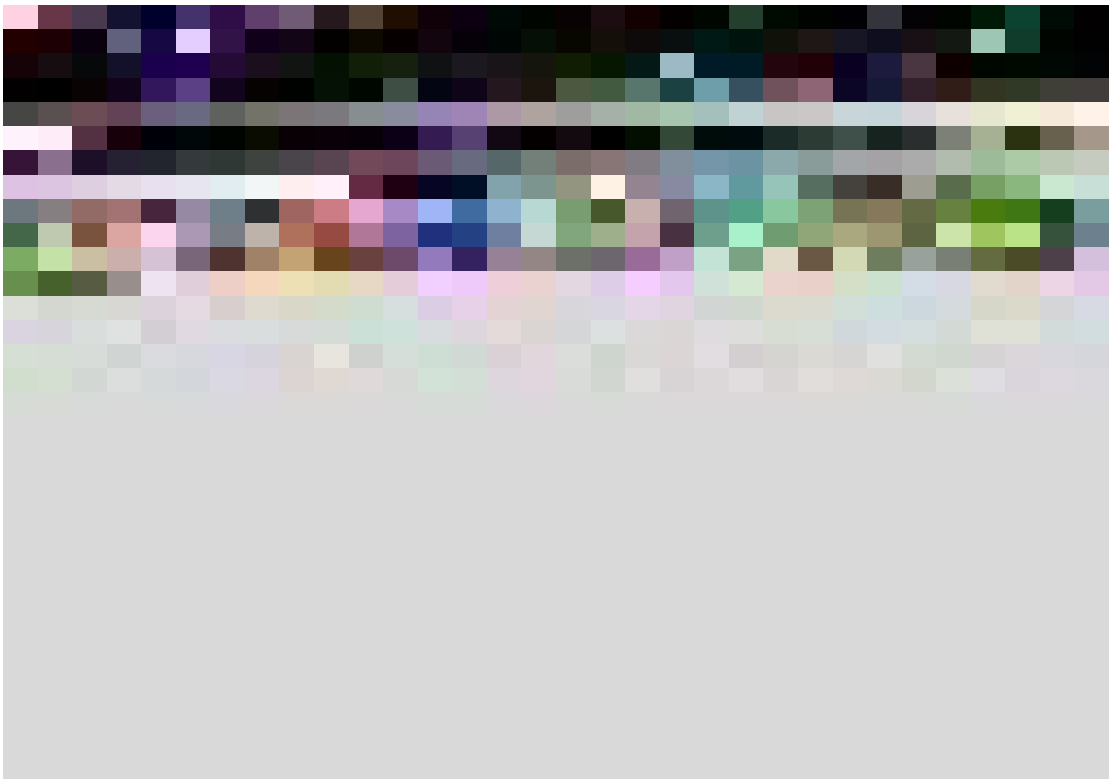
^{1}H NMR of **3-4**



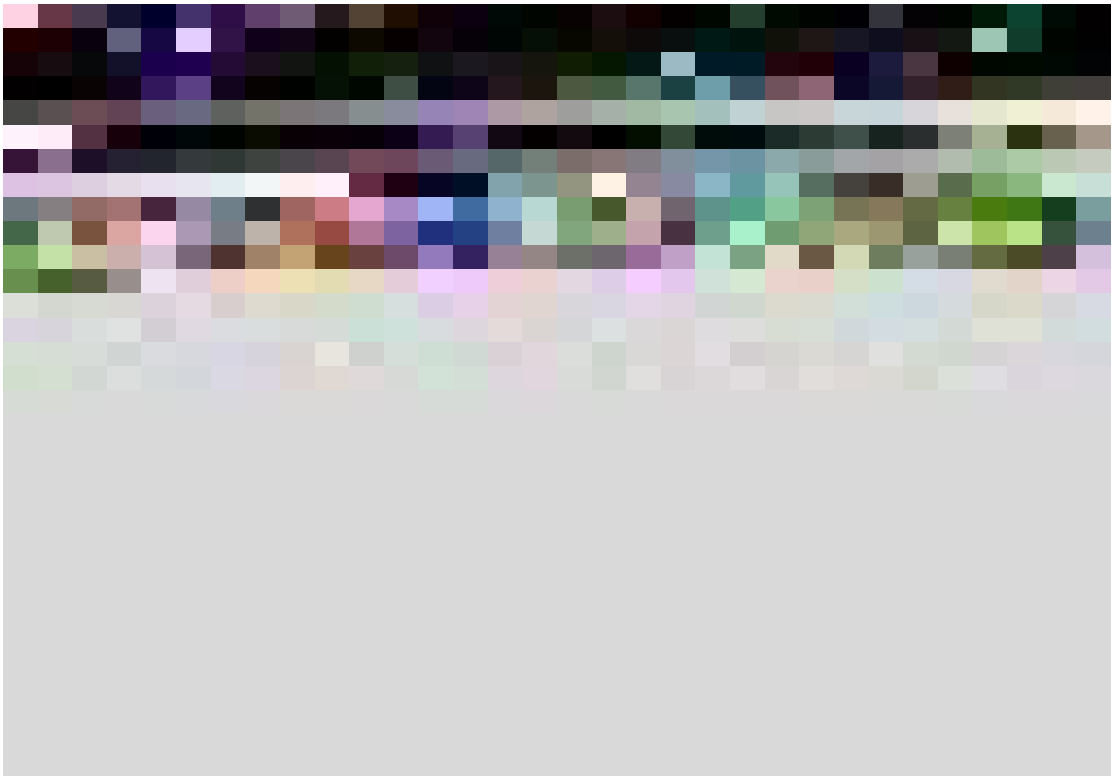
^{13}C NMR of **3-4**

^{1}H NMR of **3-5**

^{13}C NMR of **3-5**

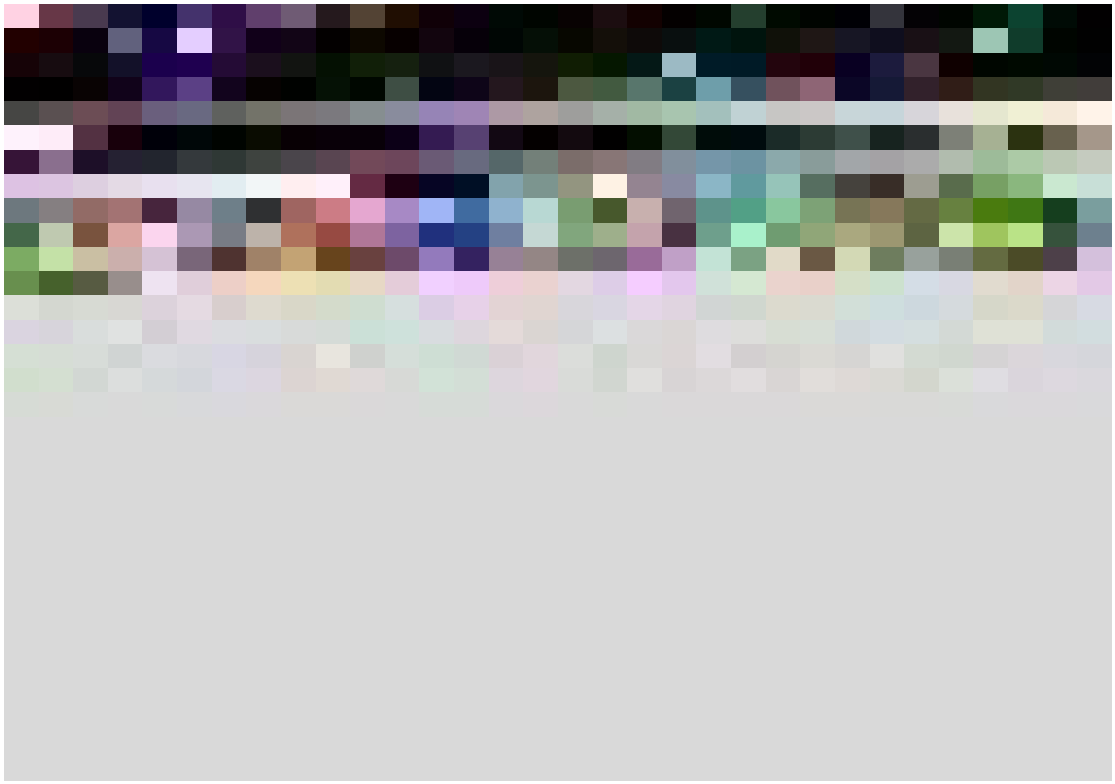


^{1}H NMR of **3-6**



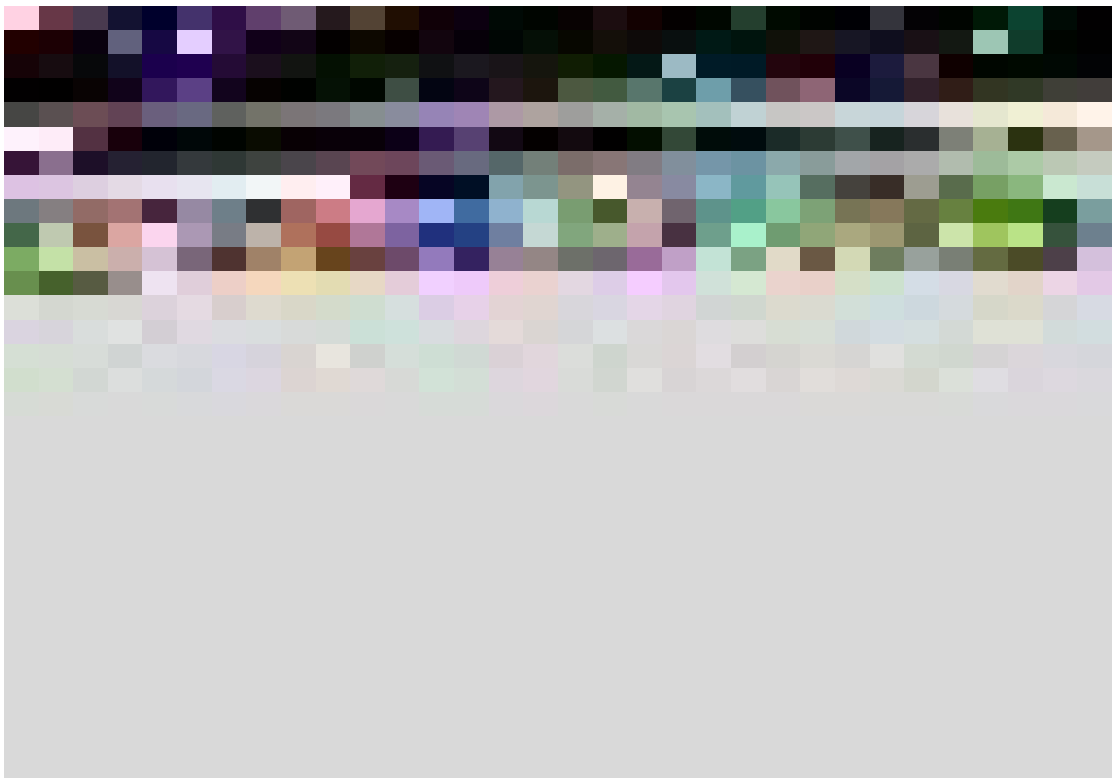
^{13}C NMR of **3-6**

^{19}F NMR of **3-6**



^{1}H NMR of **3-7**

^{13}C NMR of **3-7**

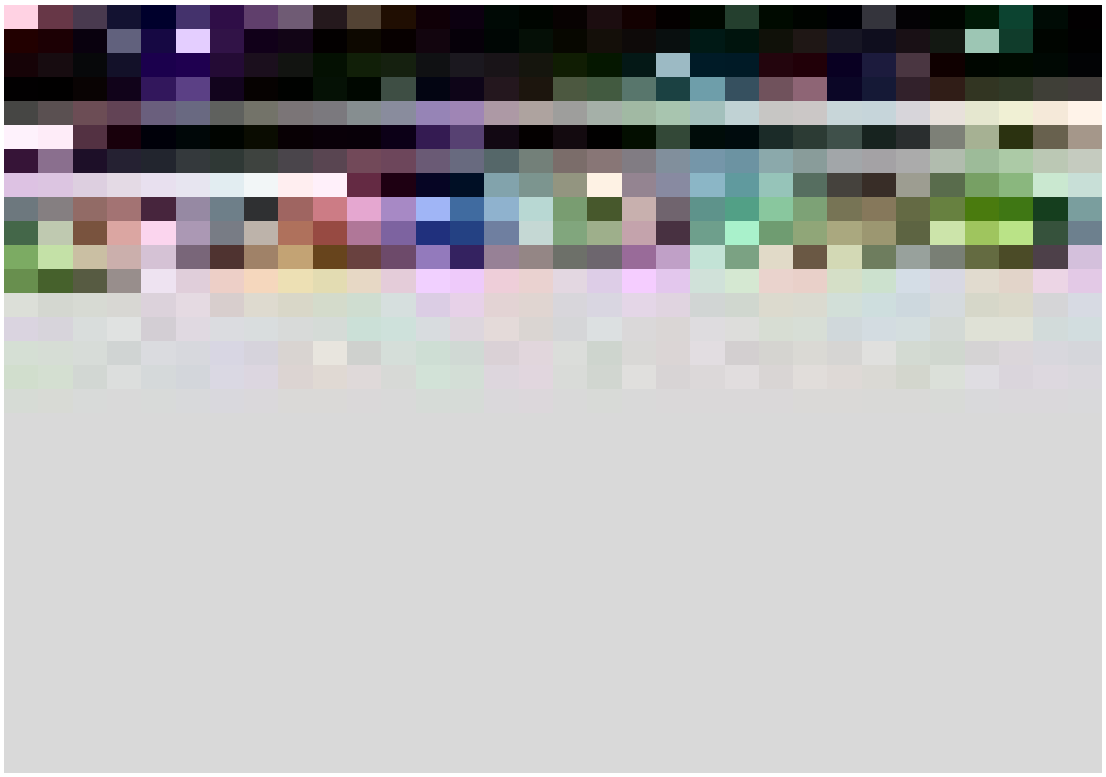


^{19}F NMR of **3-7**

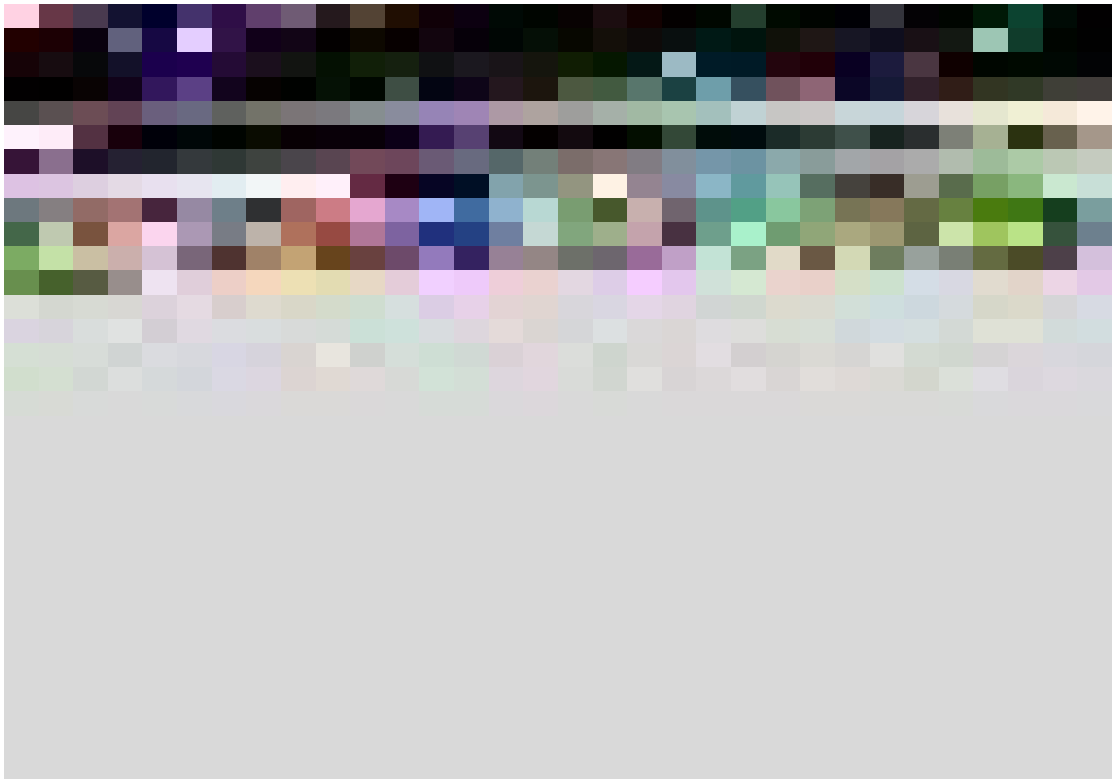
^{1}H NMR of **3-8**

^{13}C NMR of **3-8**

^{19}F NMR of **3-8**

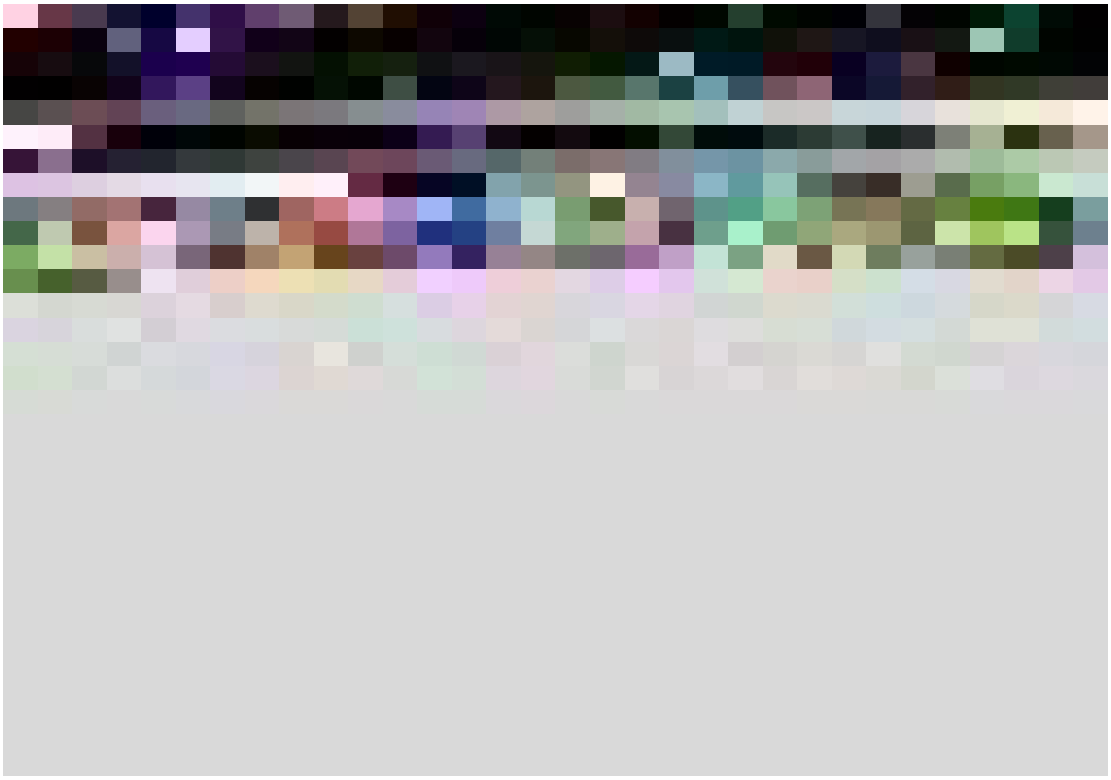


^{1}H NMR of **3-9**



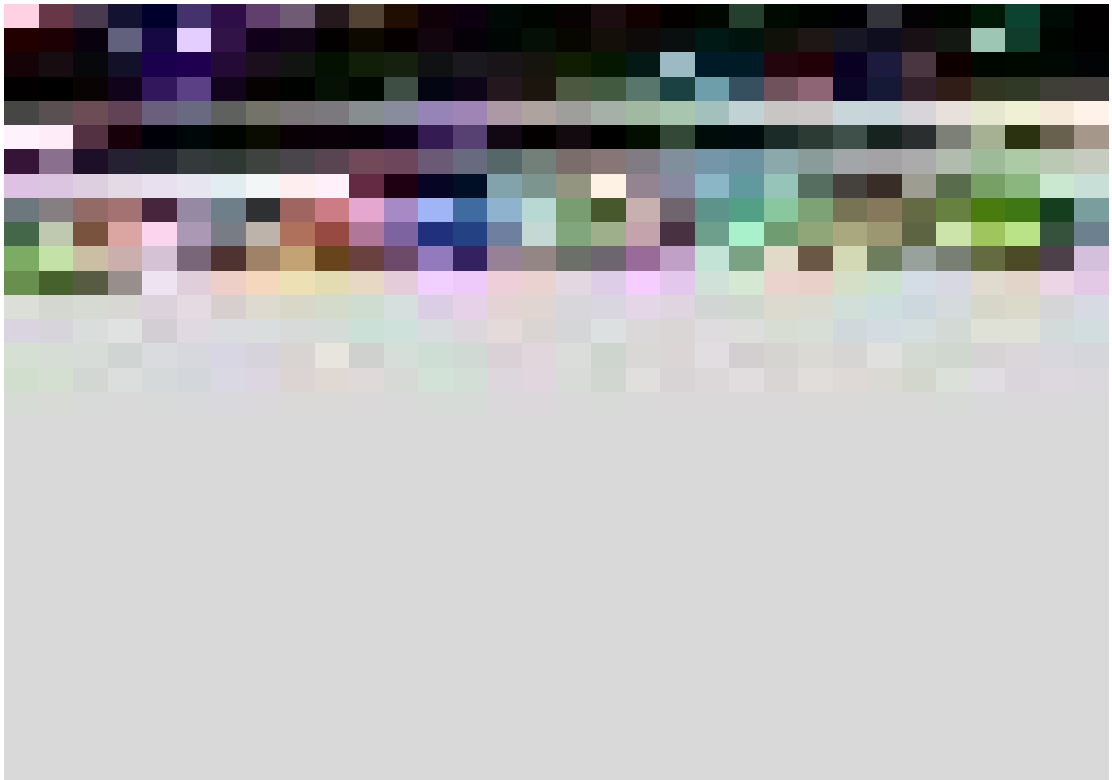
^{13}C NMR of **3-9**

^{1}H NMR of **3-10**



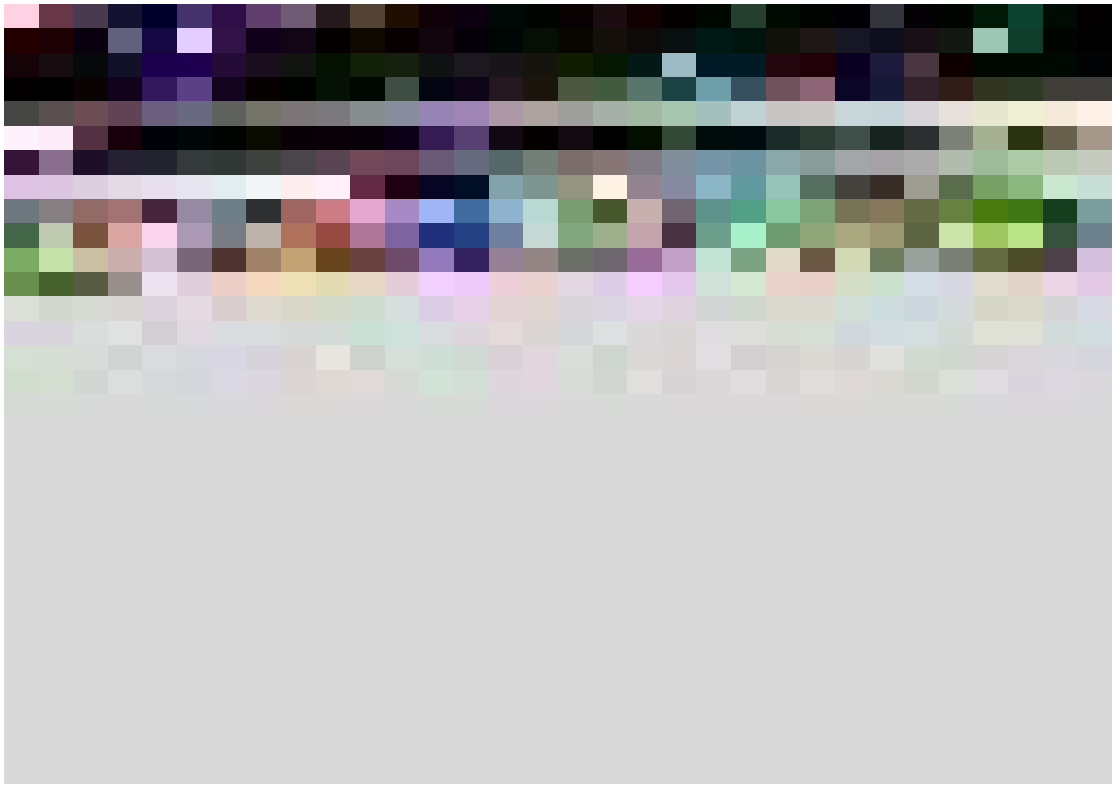
^{13}C NMR of **3-10**

^{1}H NMR of **3-11** (small polarity)



^{13}C NMR of **3-11** (small polarity)

^{1}H NMR of **3-11** (big polarity)



^{1}H NMR of **3-11** (big polarity)

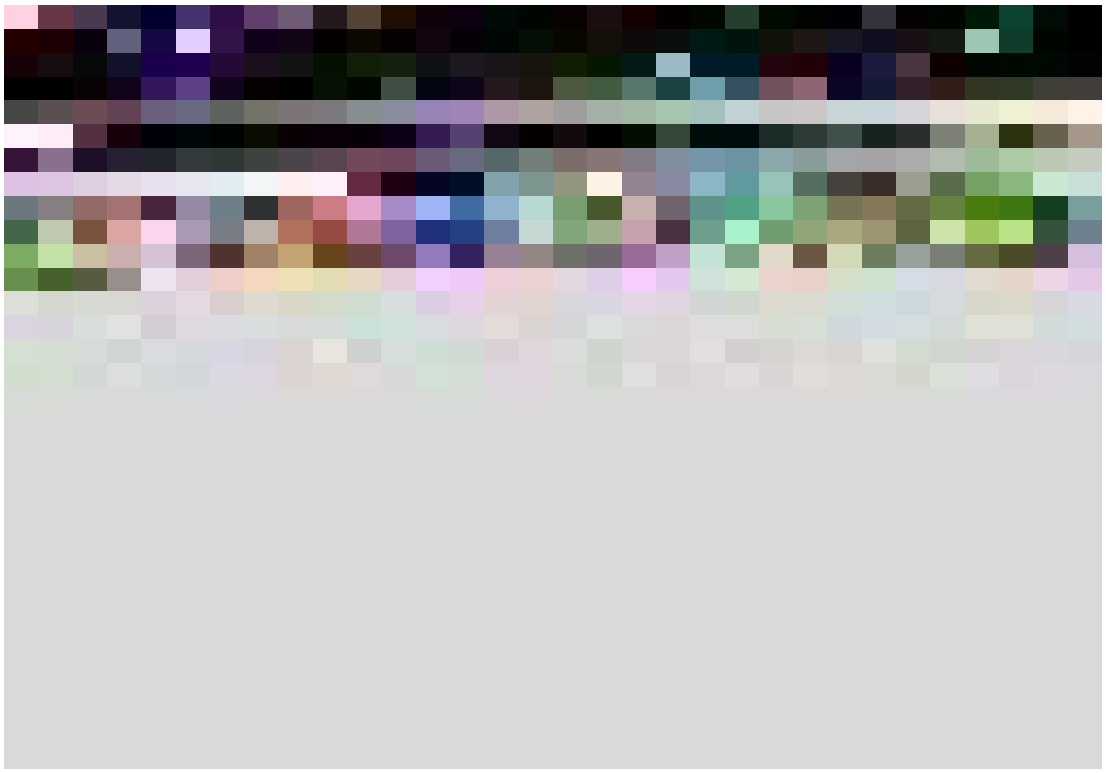
^{1}H NMR of **3-12**

^{13}C NMR of **3-12**

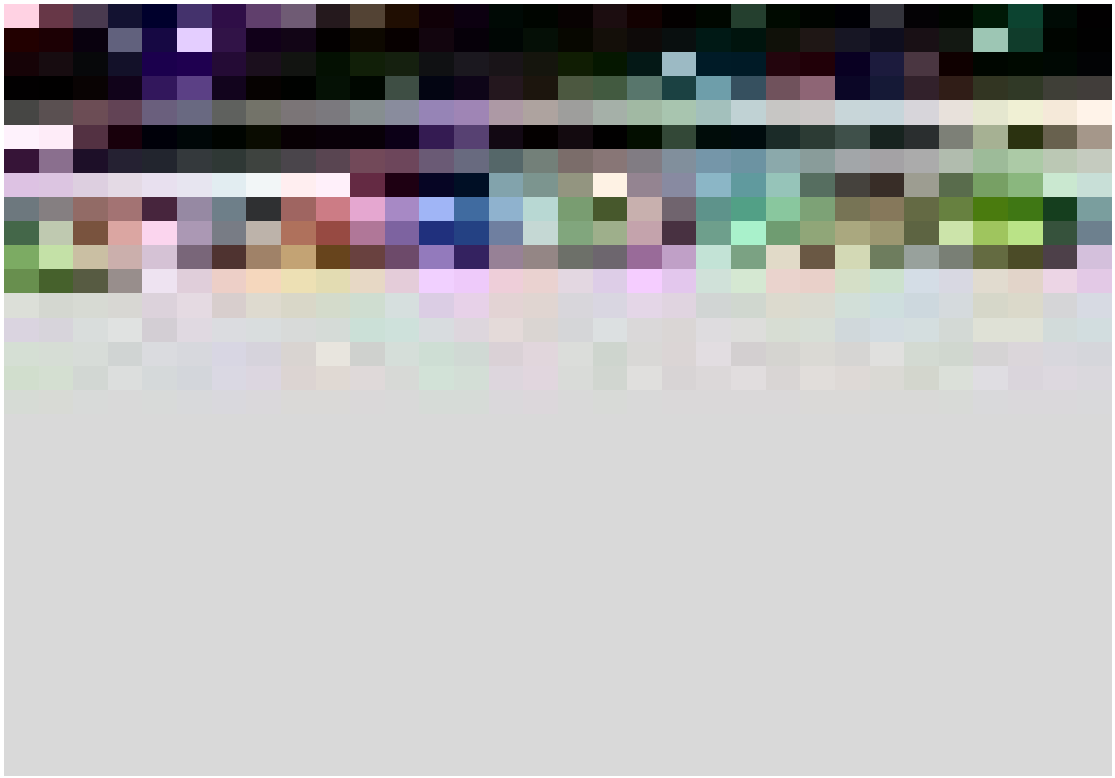
^{1}H NMR of **3-13**

^{13}C NMR of **3-13**

^{1}H NMR of **3-14**

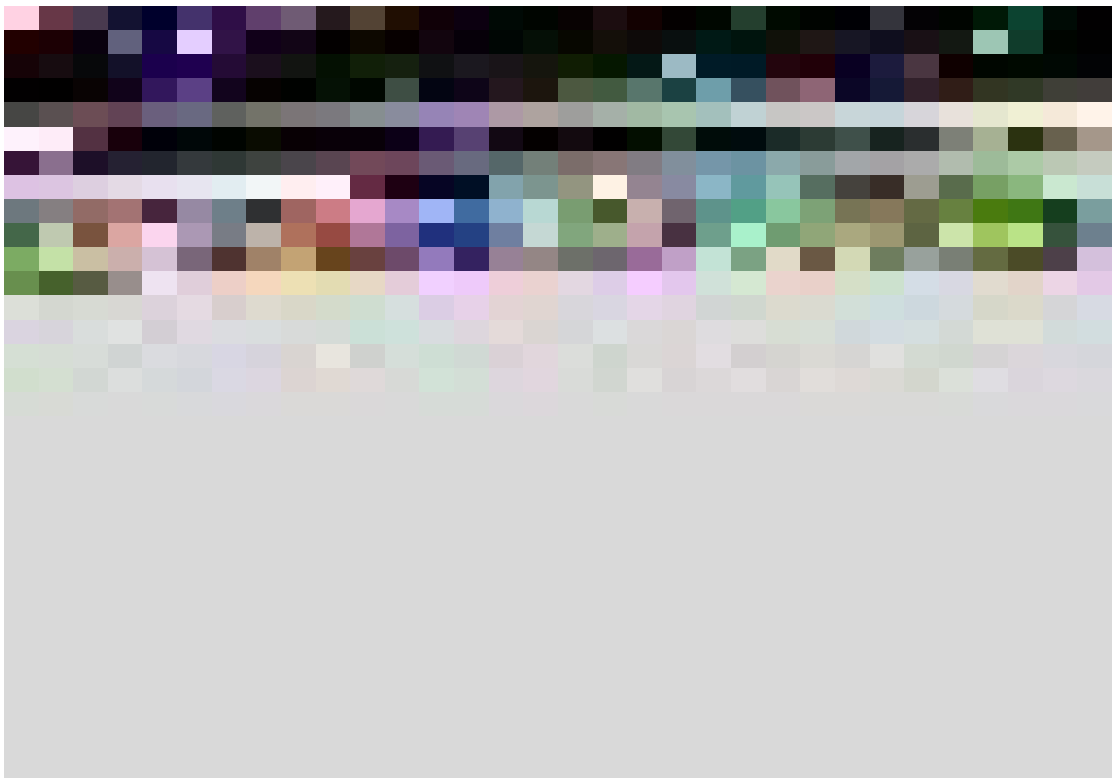


^{13}C NMR of **3-14**



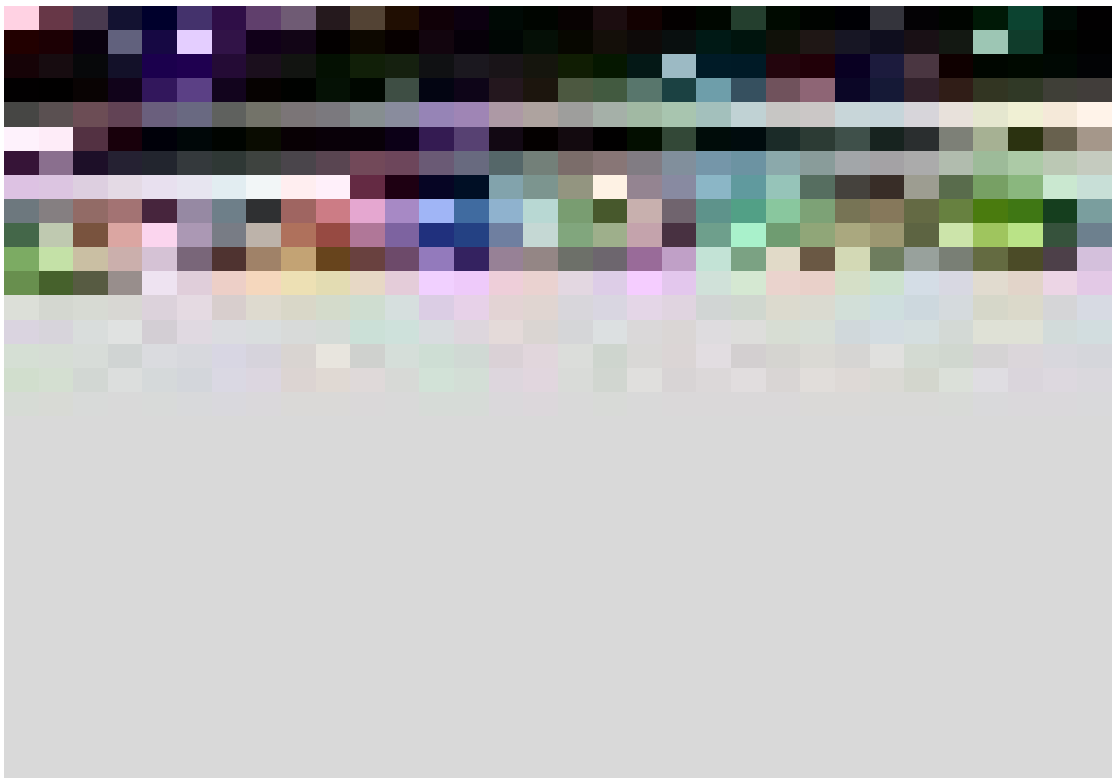
^{1}H NMR of **3-15**

^{13}C NMR of **3-15**



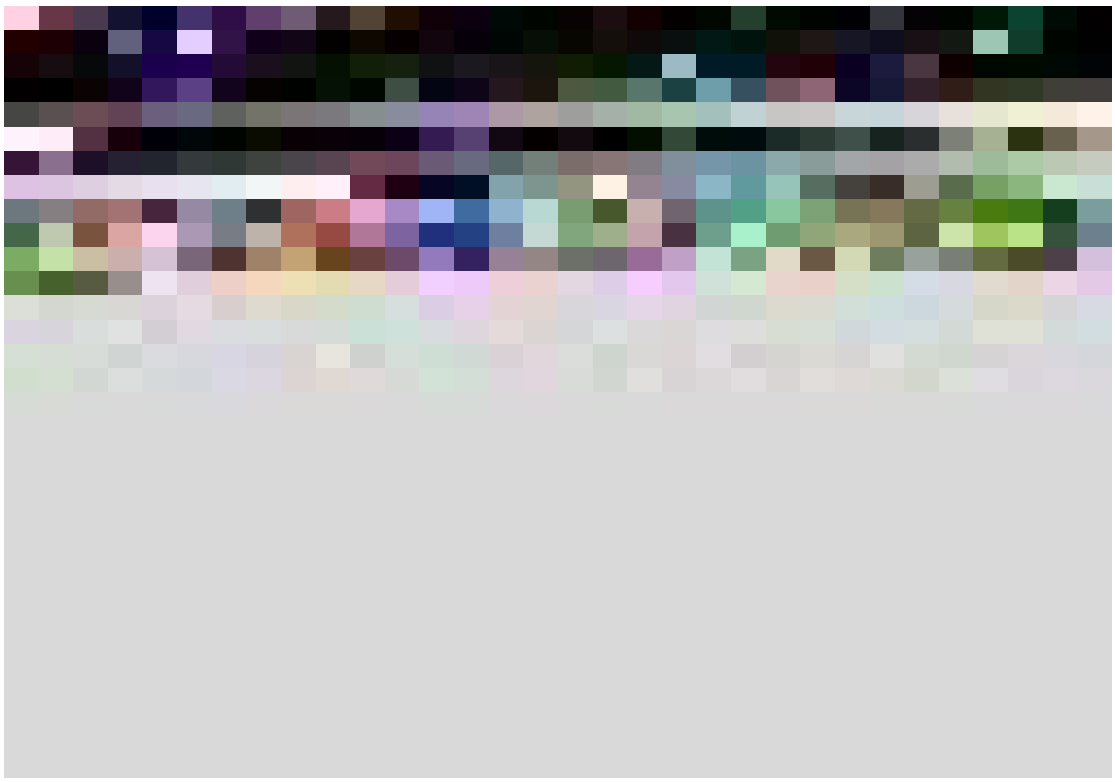
^{1}H NMR of **3-16**

^{13}C NMR of **3-16**

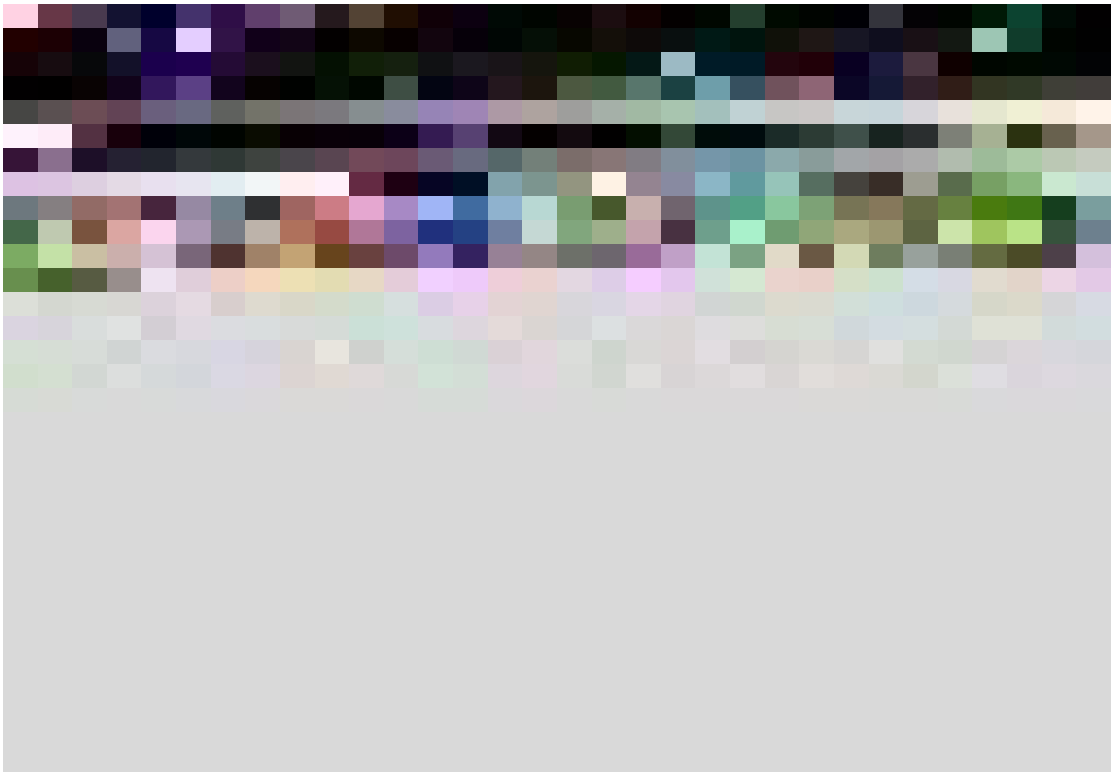


^{1}H NMR of **3-17**

^{13}C NMR of **3-17**

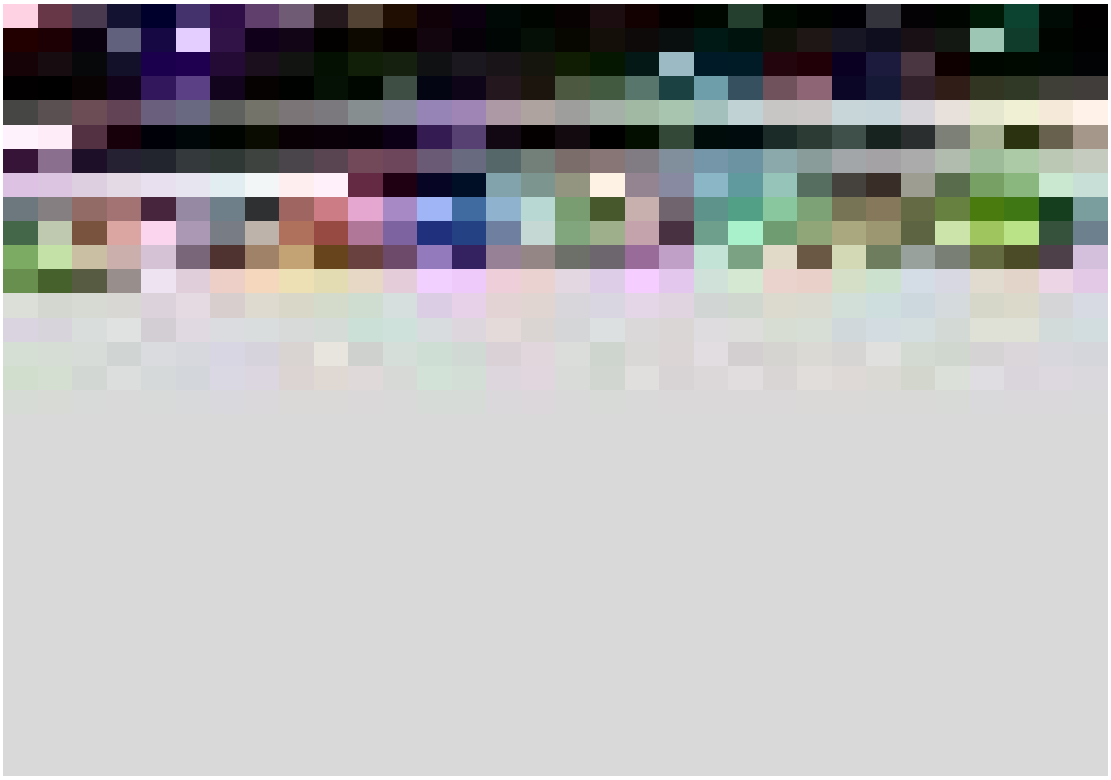


^{1}H NMR of **3-18**



^{13}C NMR of **3-18**

^{1}H NMR of **3-19**



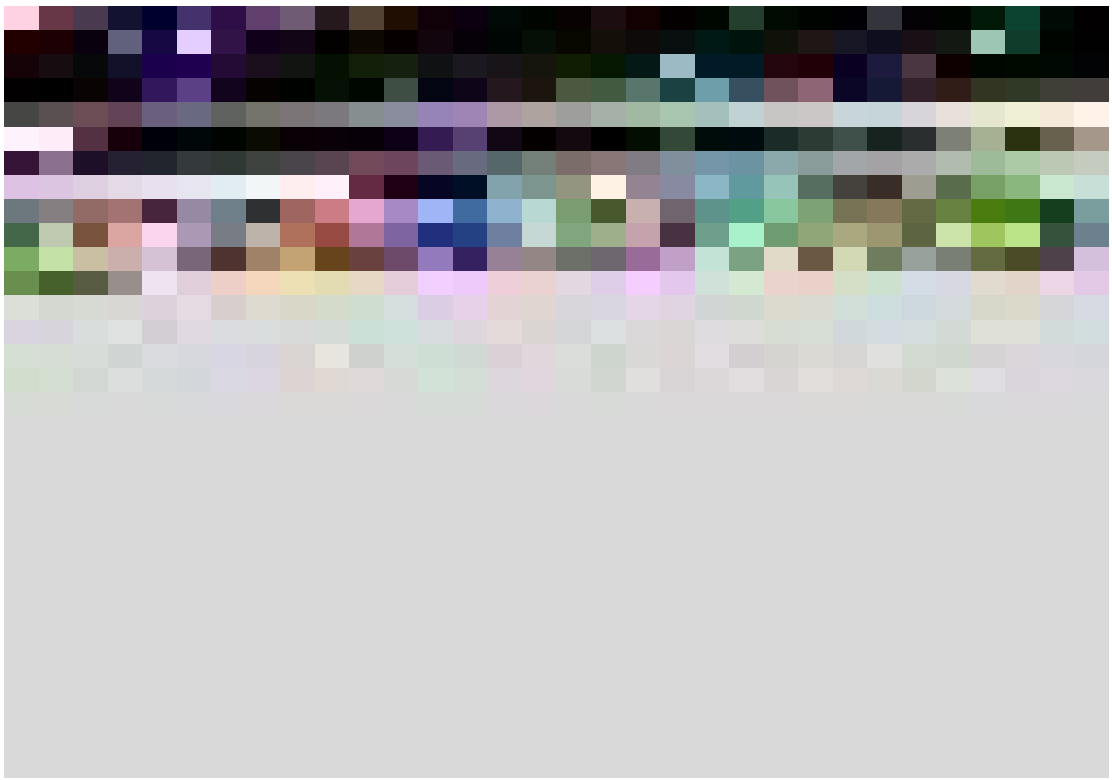
^{1}H NMR of **3-19**

^{1}H NMR of **3-20**

^{13}C NMR of **3-20**

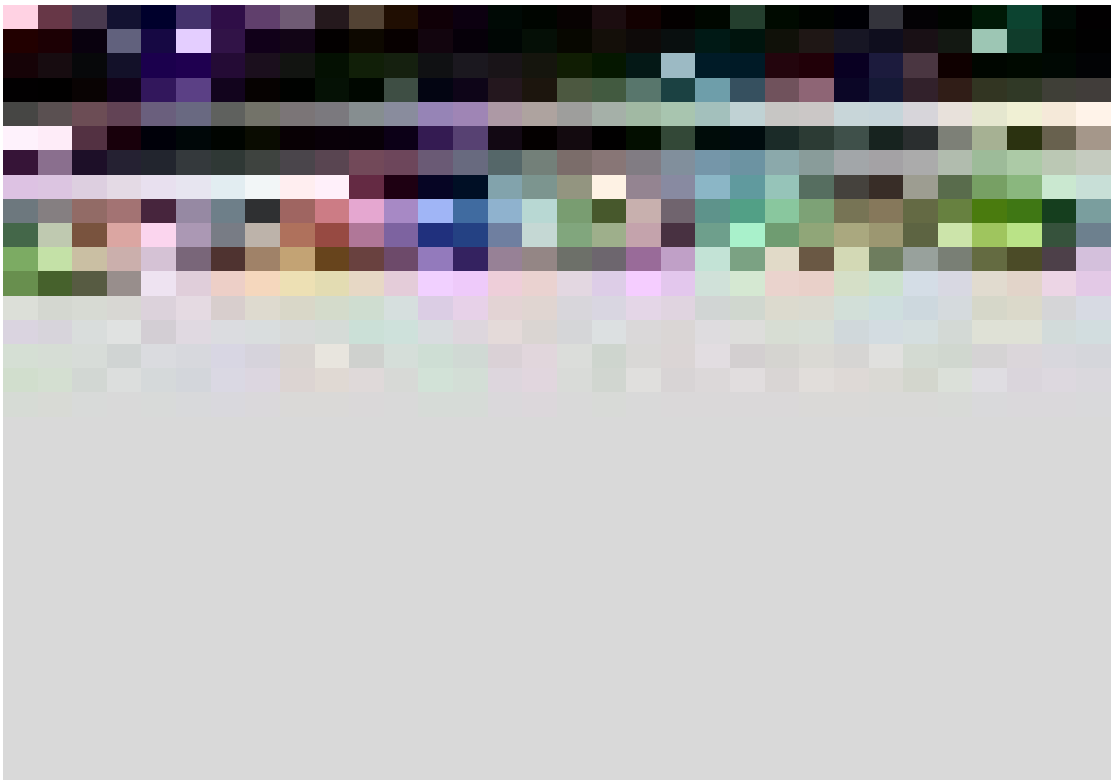
^{1}H NMR of **3-21**

^{13}C NMR of **3-21**



^{1}H NMR of **3-22**

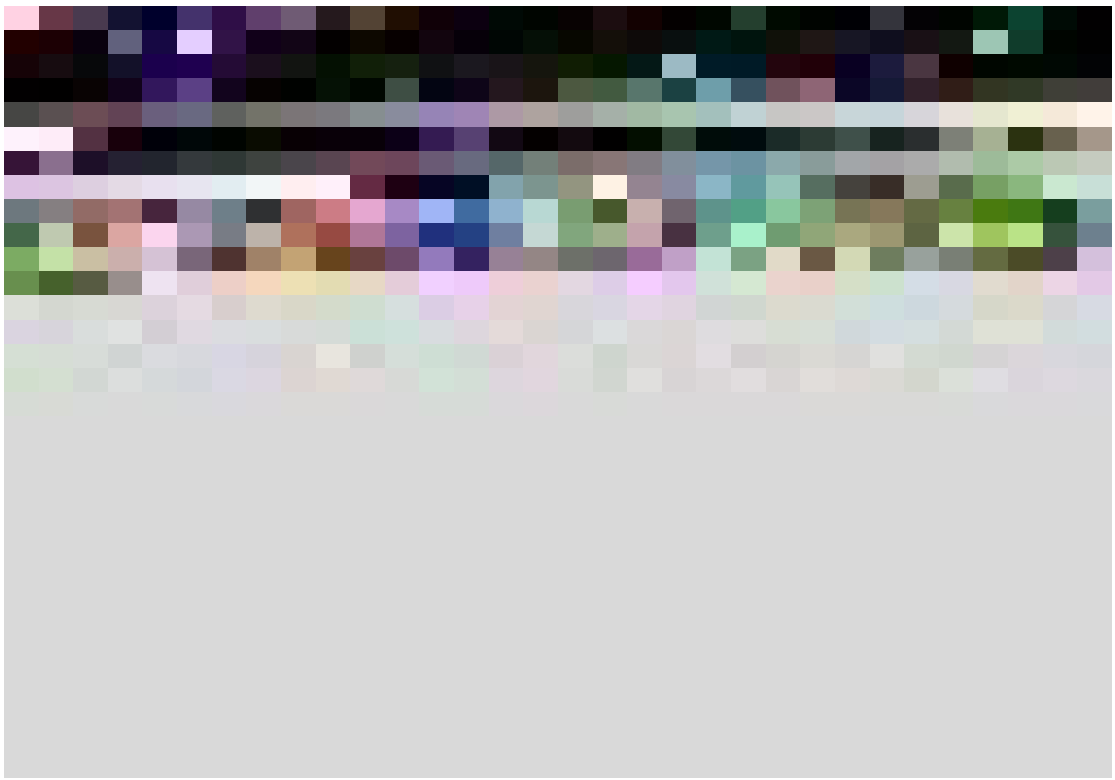
^{13}C NMR of **3-22**



^{1}H NMR of **3-23**

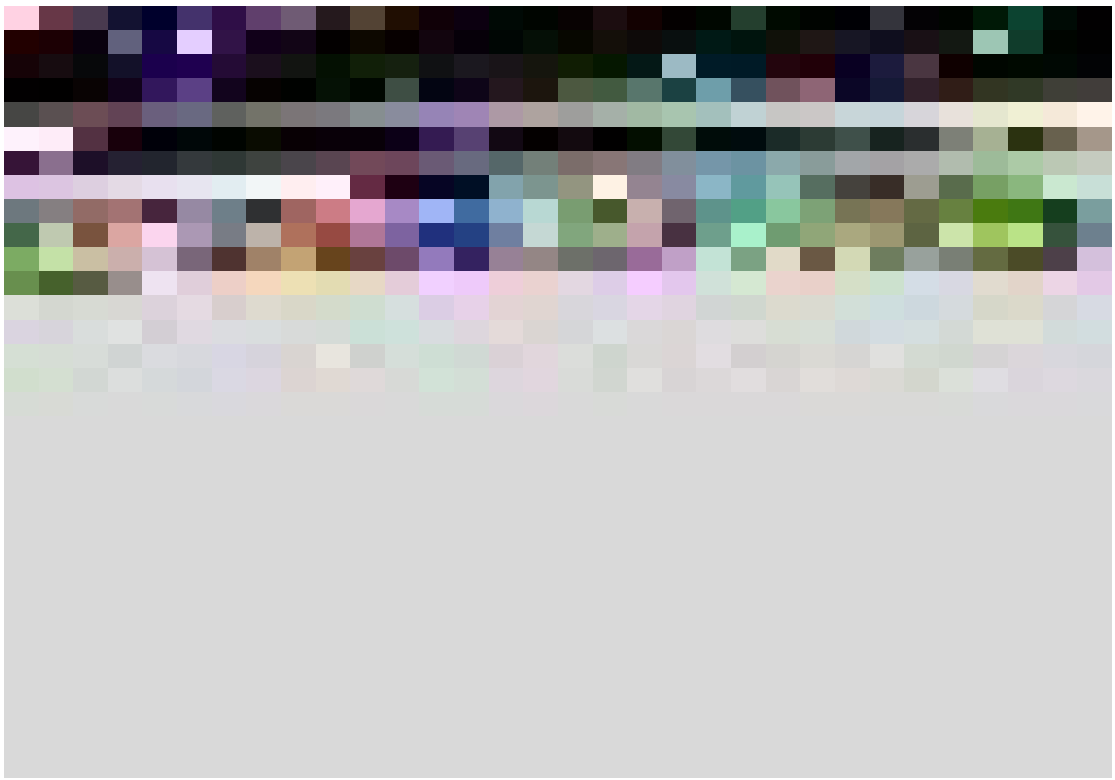
^{13}C NMR of **3-23**

^{1}H NMR of **3-24**



^{13}C NMR of **3-24**

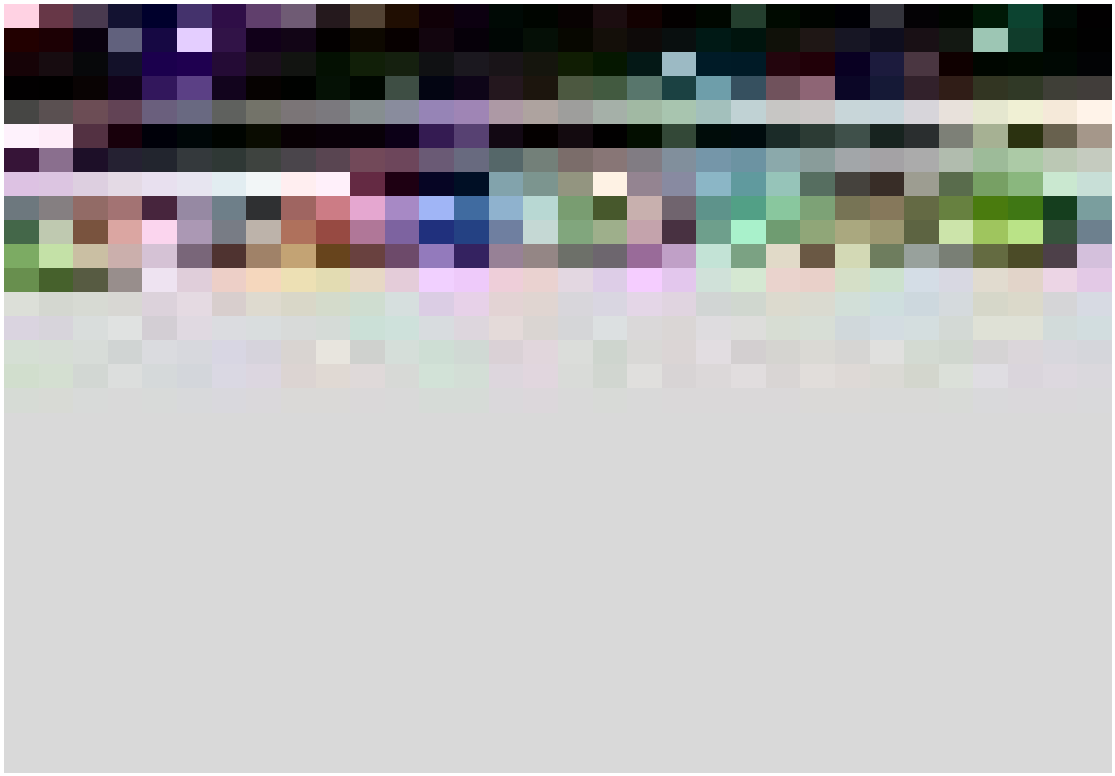
^{1}H NMR of **3-25**



^{13}C NMR of **3-25**

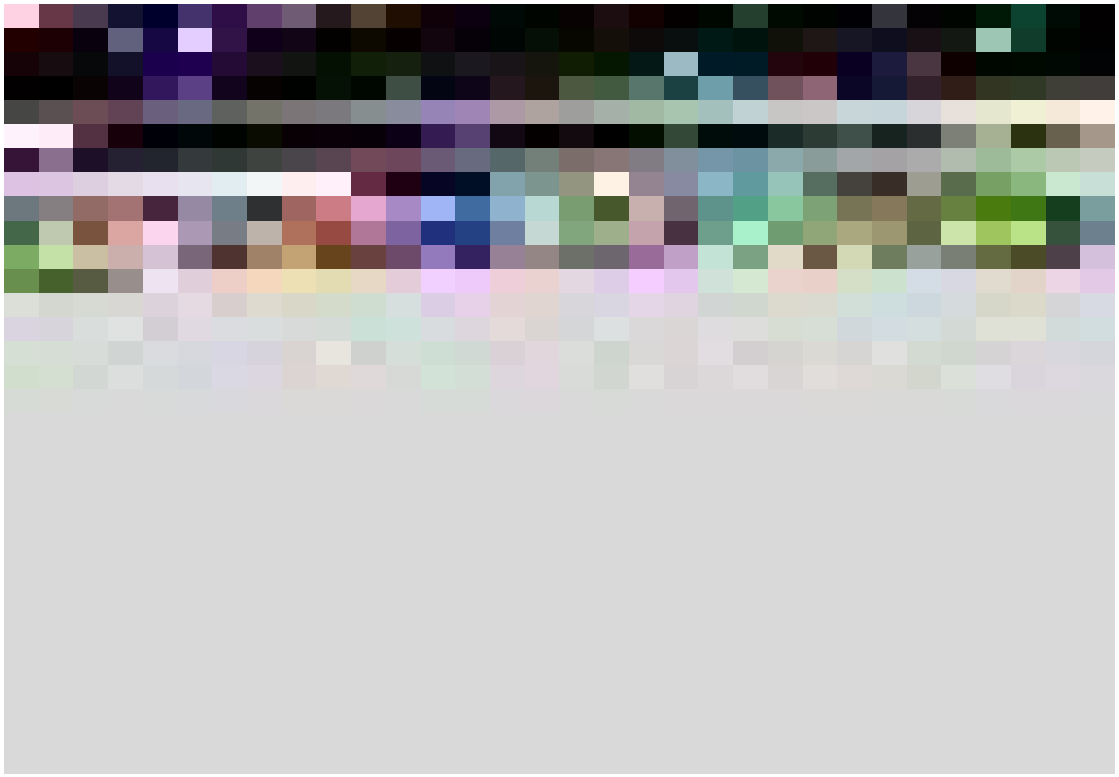
^{1}H NMR of **3-26**

^{13}C NMR of **3-26**



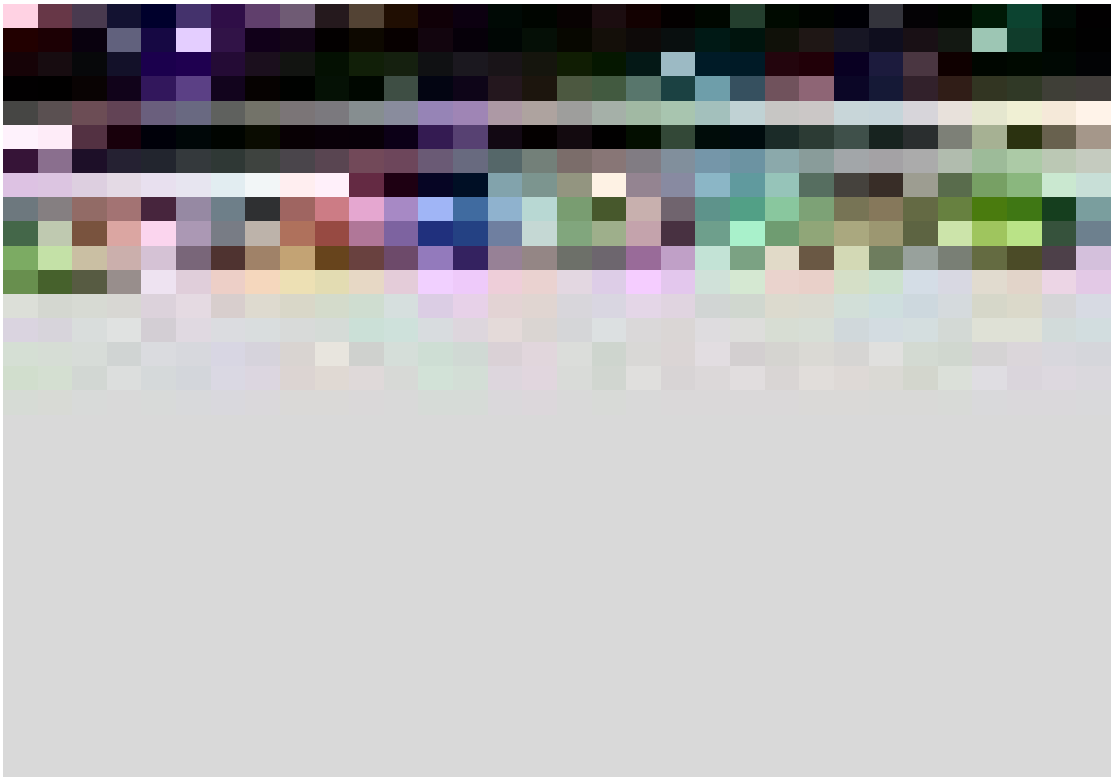
^{1}H NMR of **3-27**

^{13}C NMR of **3-27**



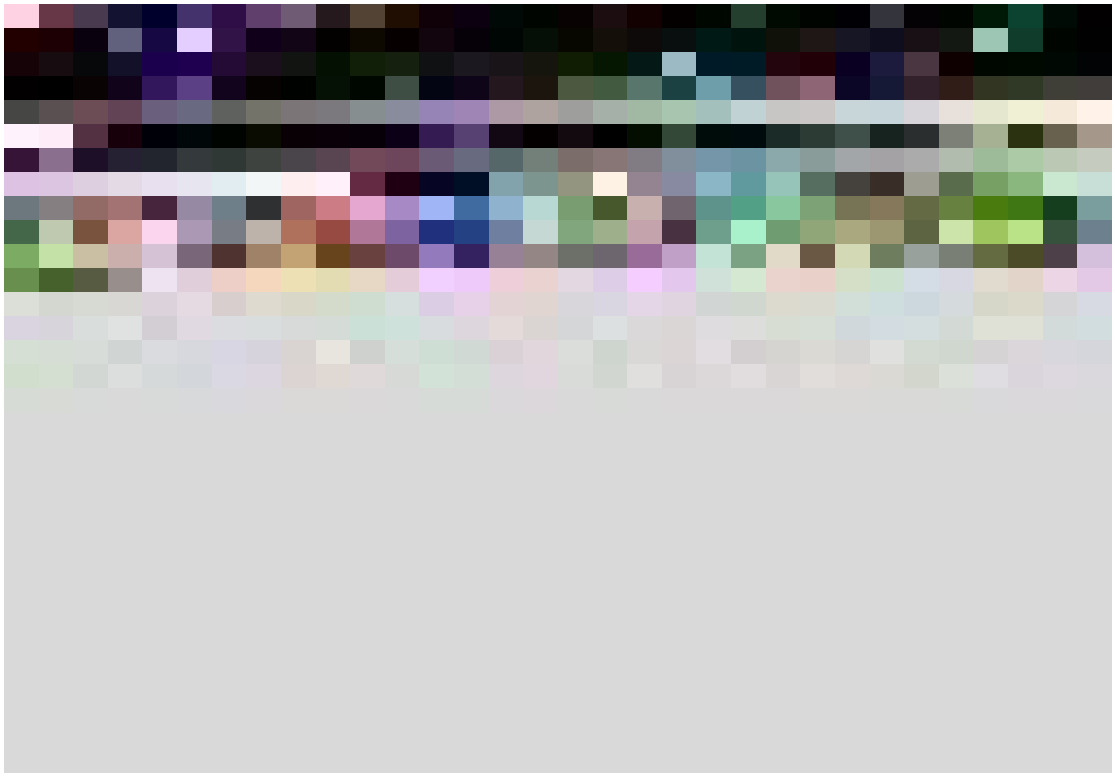
^{1}H NMR of **3-28**

^{13}C NMR of **3-28**

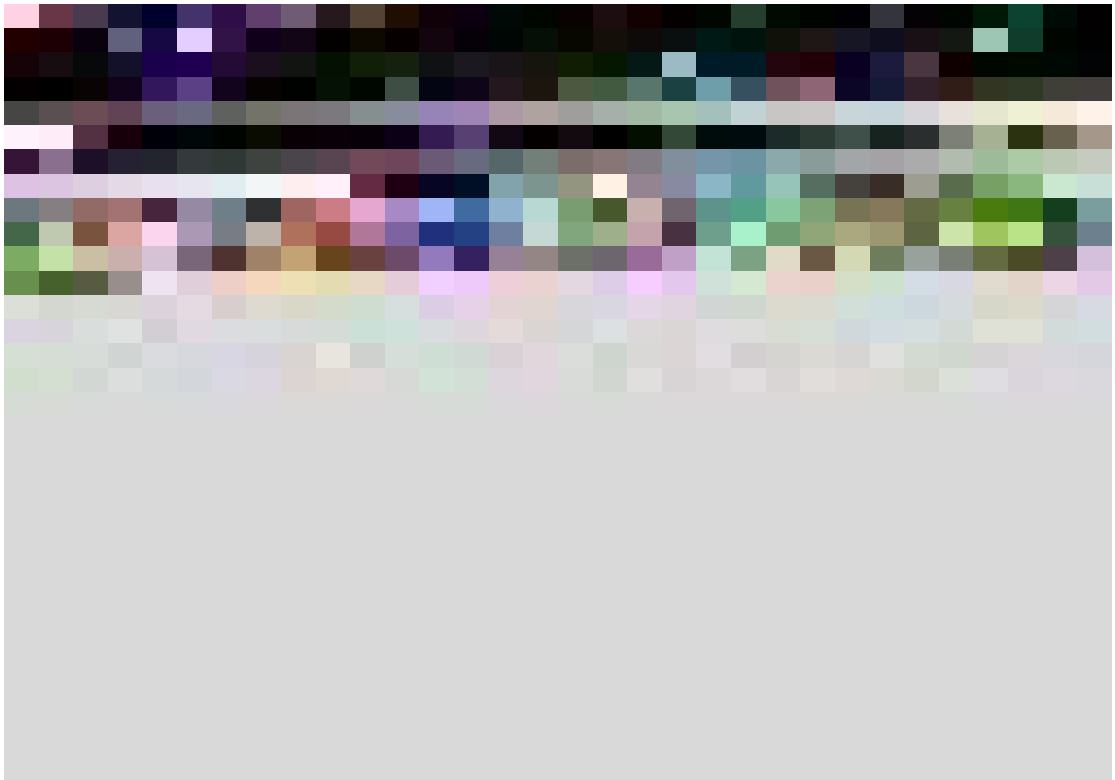


^{1}H NMR of **3-29**

^{13}C NMR of **3-29**

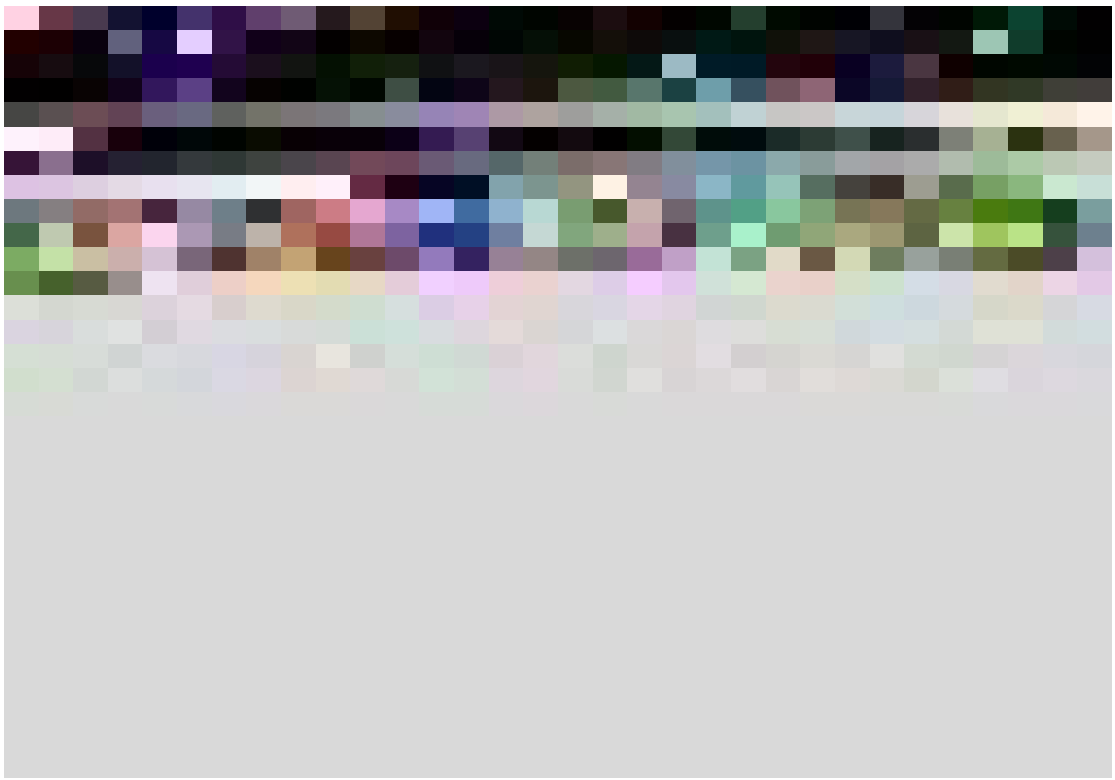


^{1}H NMR of **3-30**

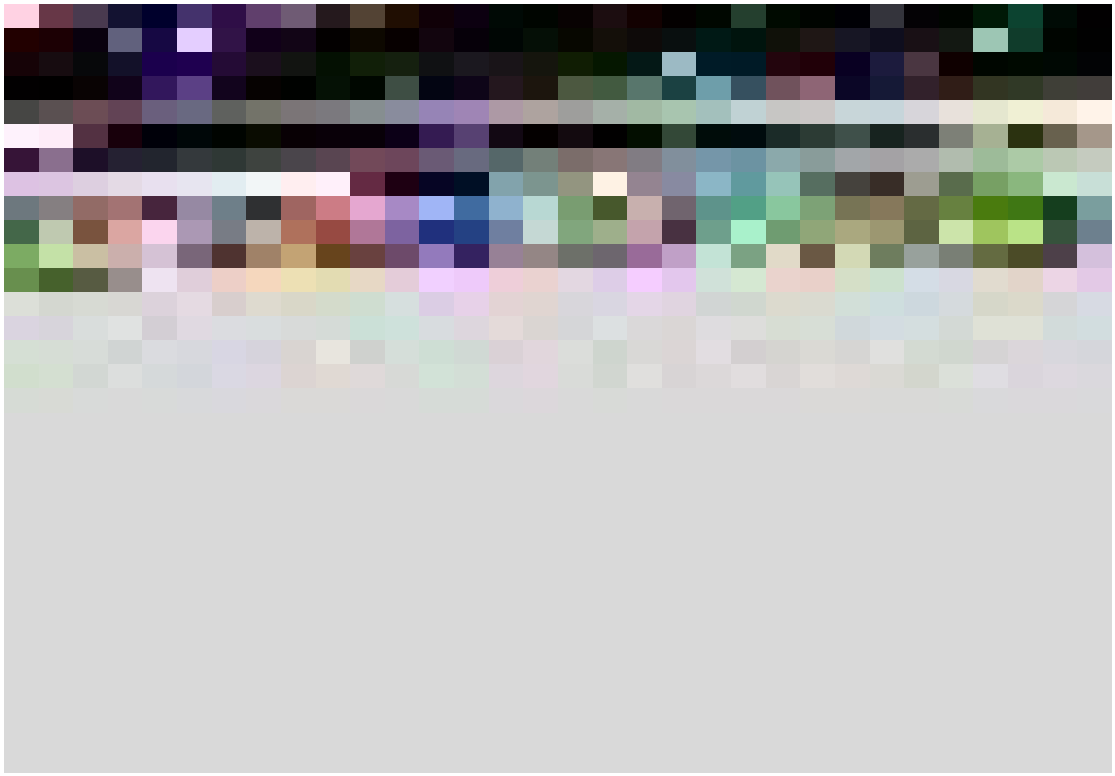


^{13}C NMR of **3-30**

^{1}H NMR of **3-31**

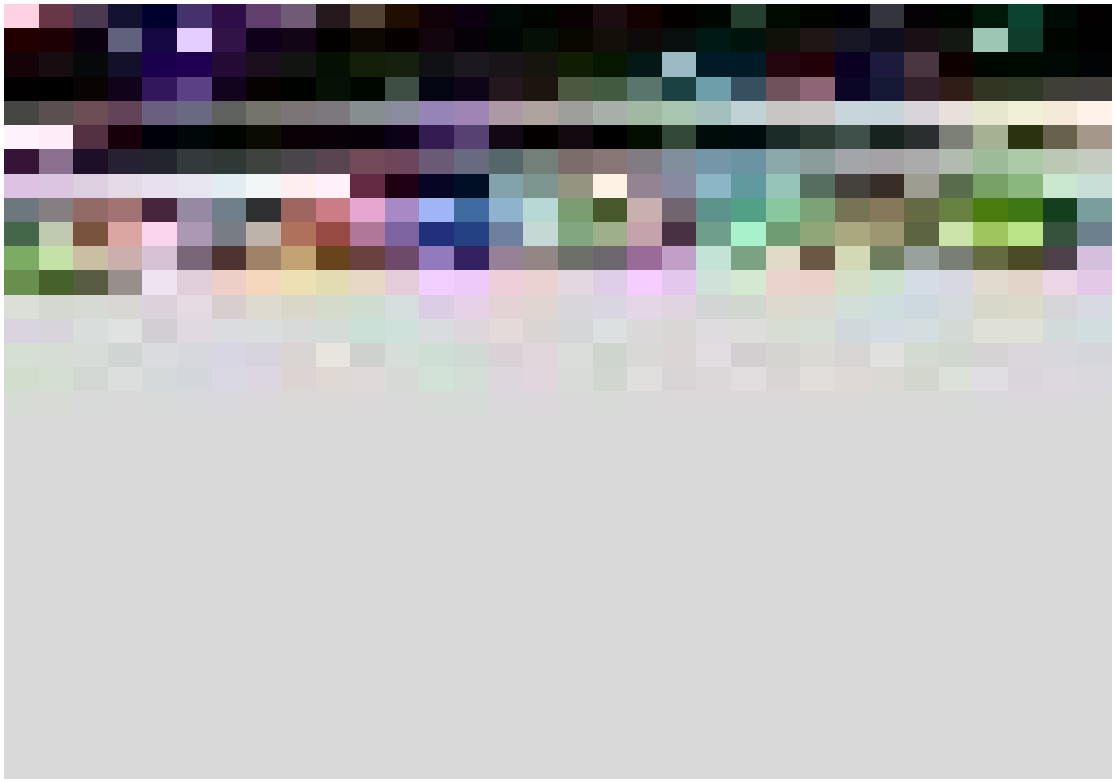


^{13}C NMR of **3-31**

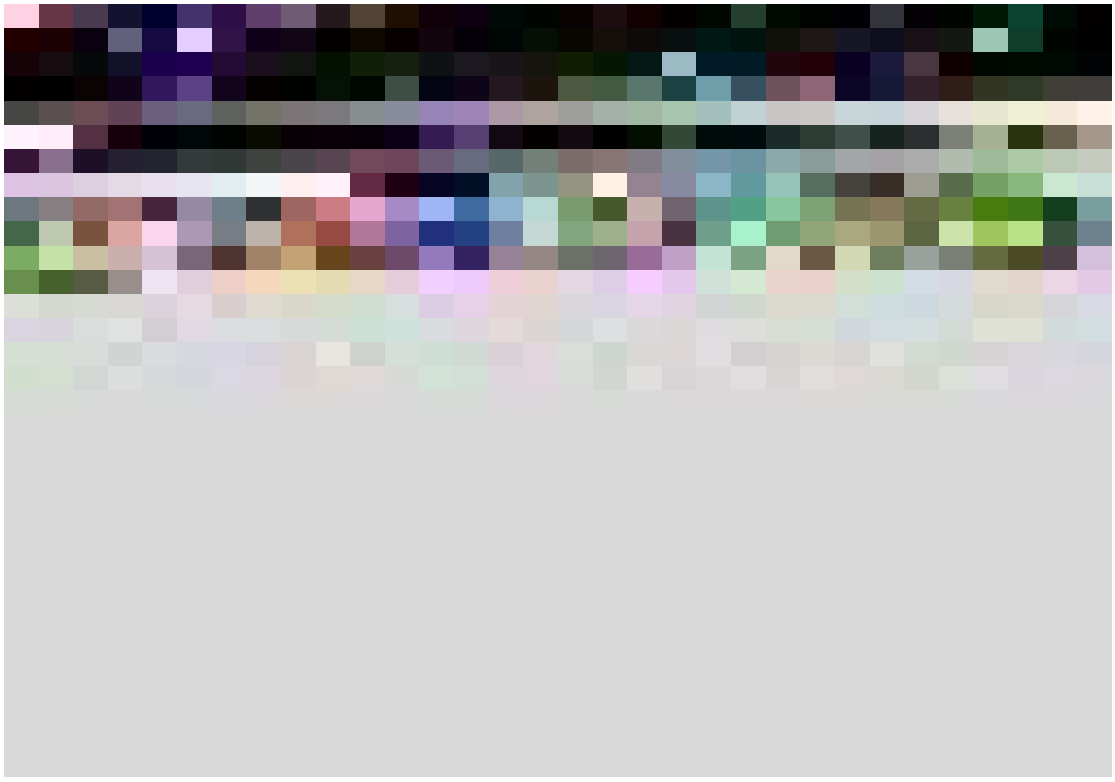


^{1}H NMR of **3-32**

^{13}C NMR of **3-32**

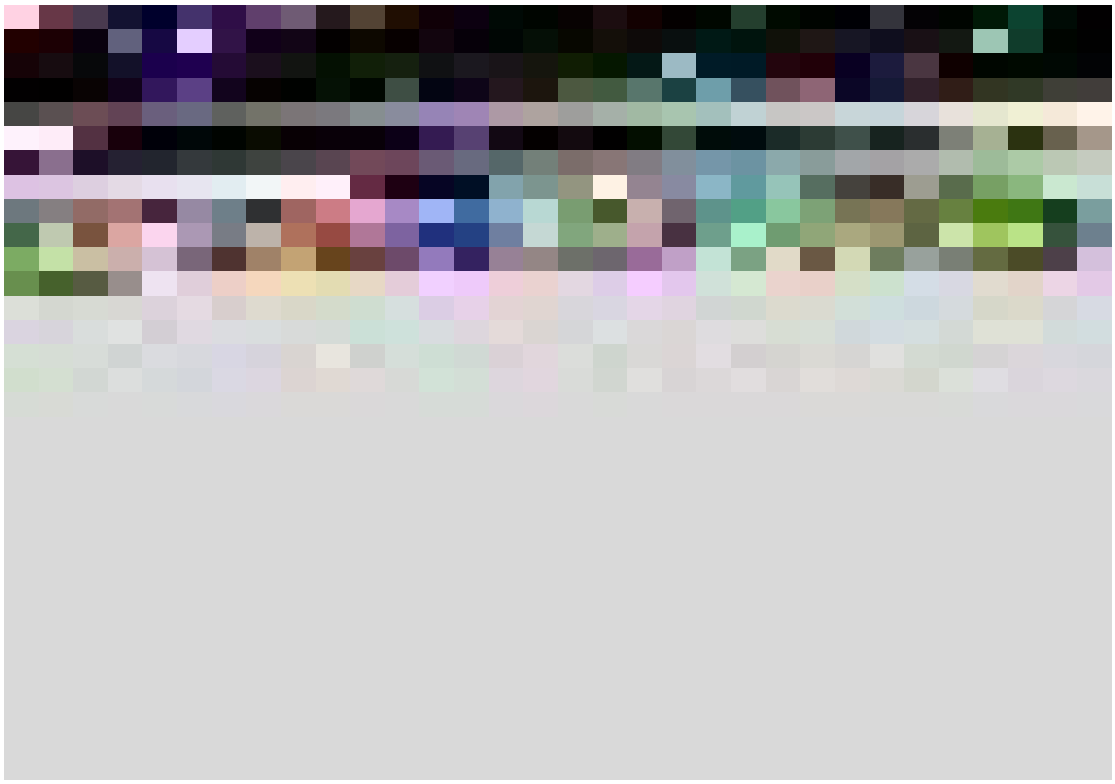


^{1}H NMR of **3-33**



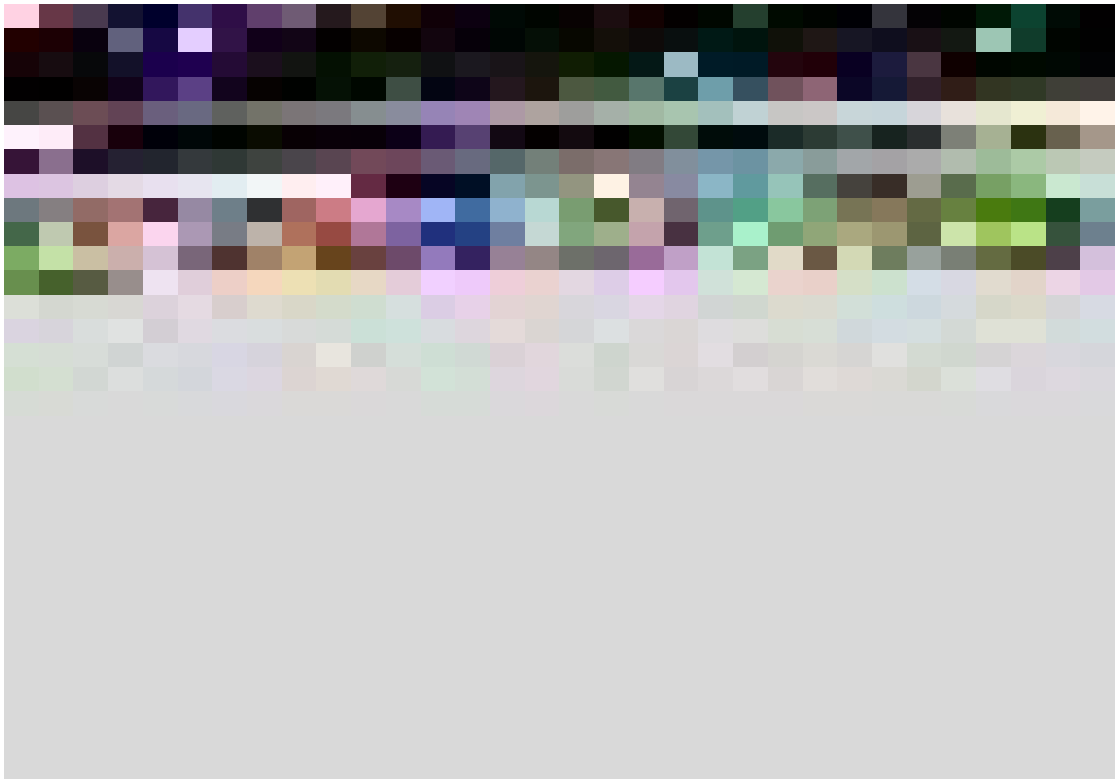
^{13}C NMR of **3-33**

^{1}H NMR of **3-34**



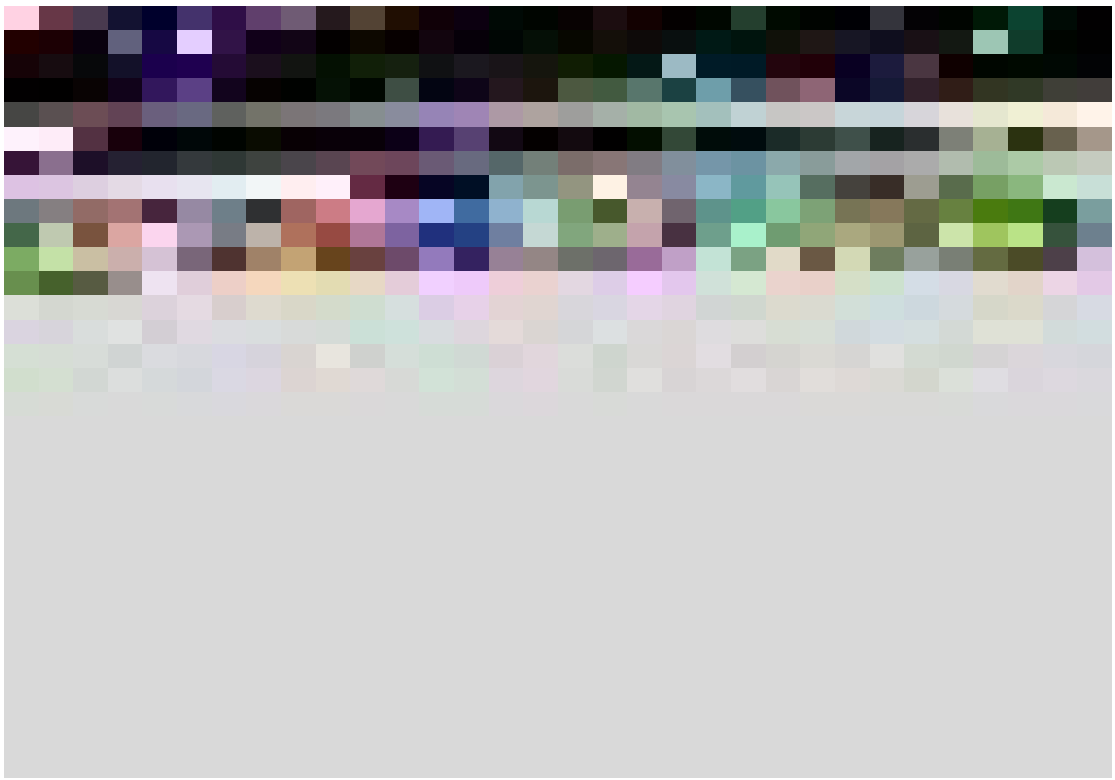
^{13}C NMR of **3-34**

^{1}H NMR of **3-35**



^{13}C NMR of **3-35**

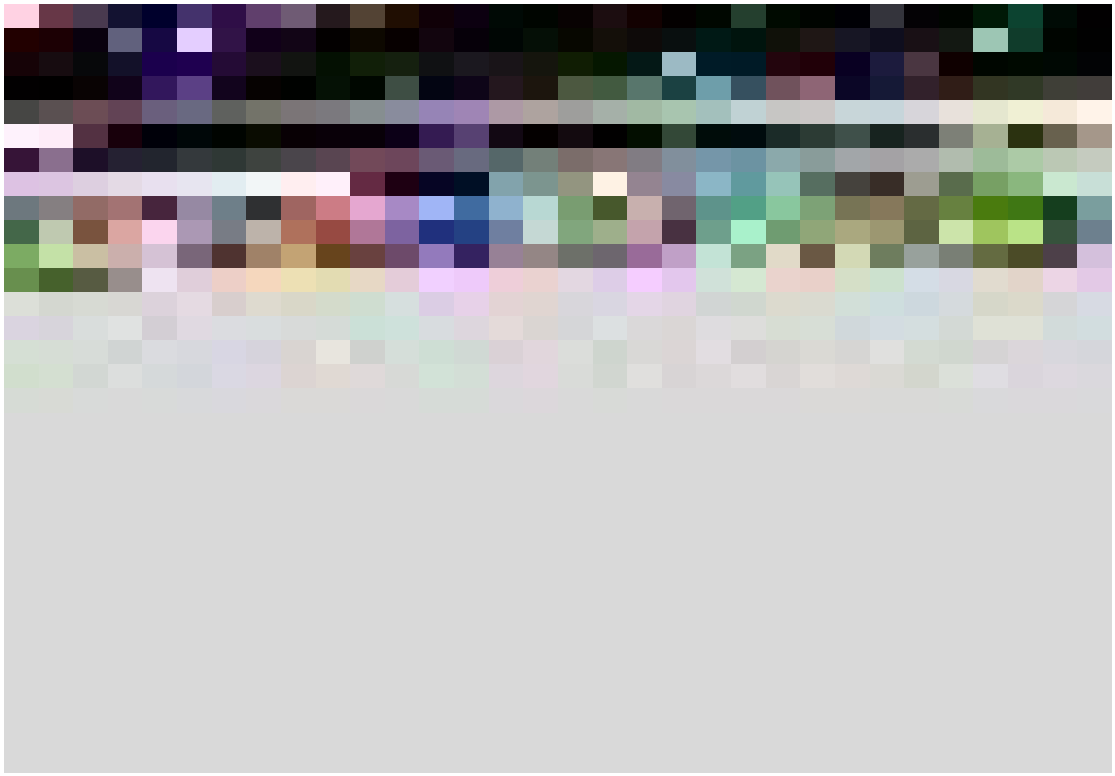
^{1}H NMR of **3-36** (cis)



^{13}C NMR of **3-36** (cis)

^{1}H NMR of **3-36** (trans)

^{13}C NMR of **3-36** (trans)



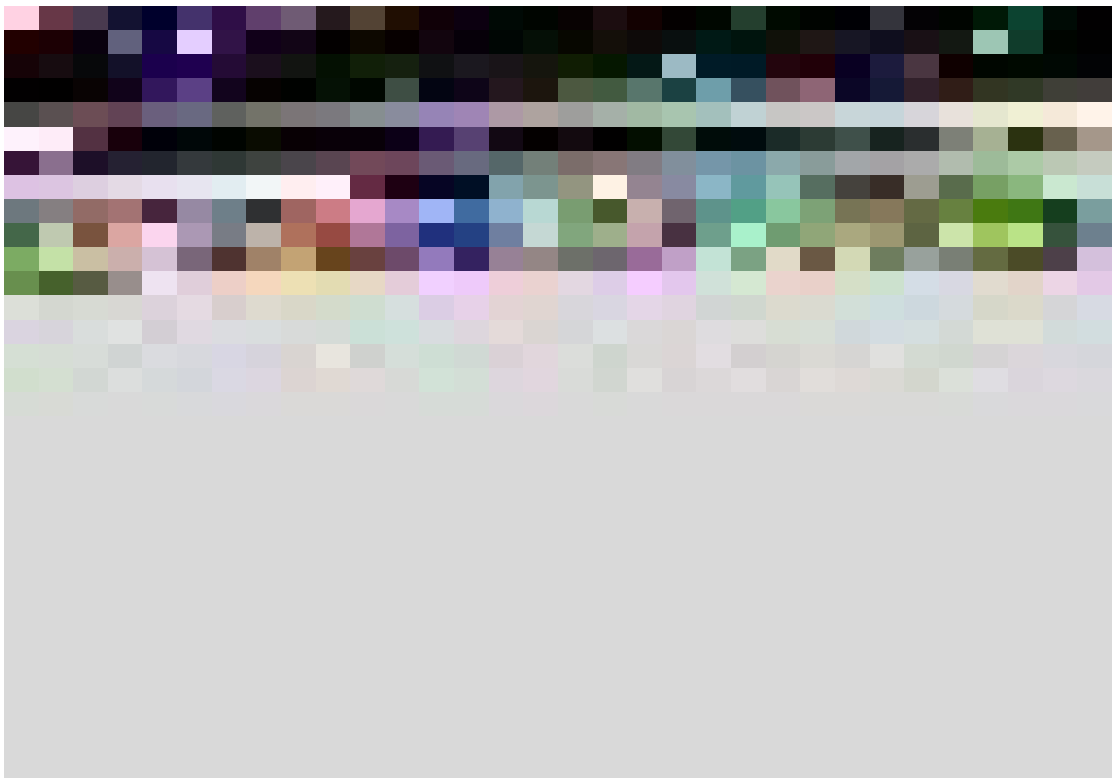
^{1}H NMR of **3-37** (cis)

^{13}C NMR of **3-37** (cis)

^{1}H NMR of **3-37** (trans)

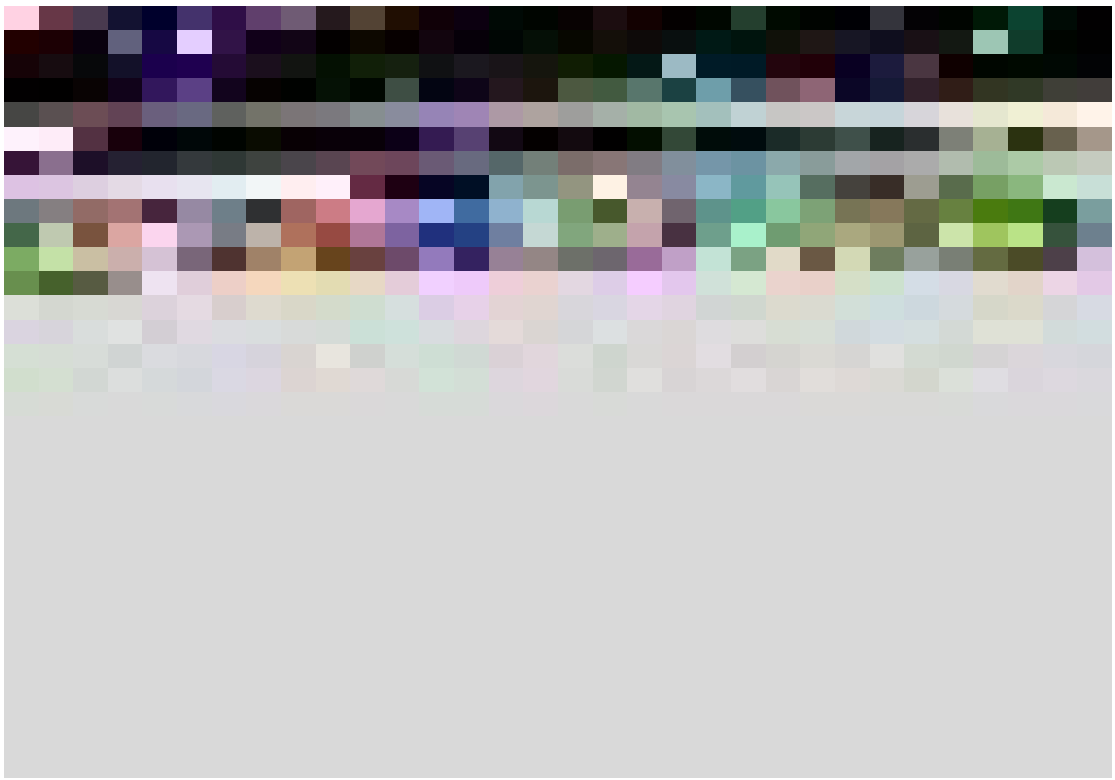
^{13}C NMR of **3-37** (trans)

^{1}H NMR of **3-38** (cis)

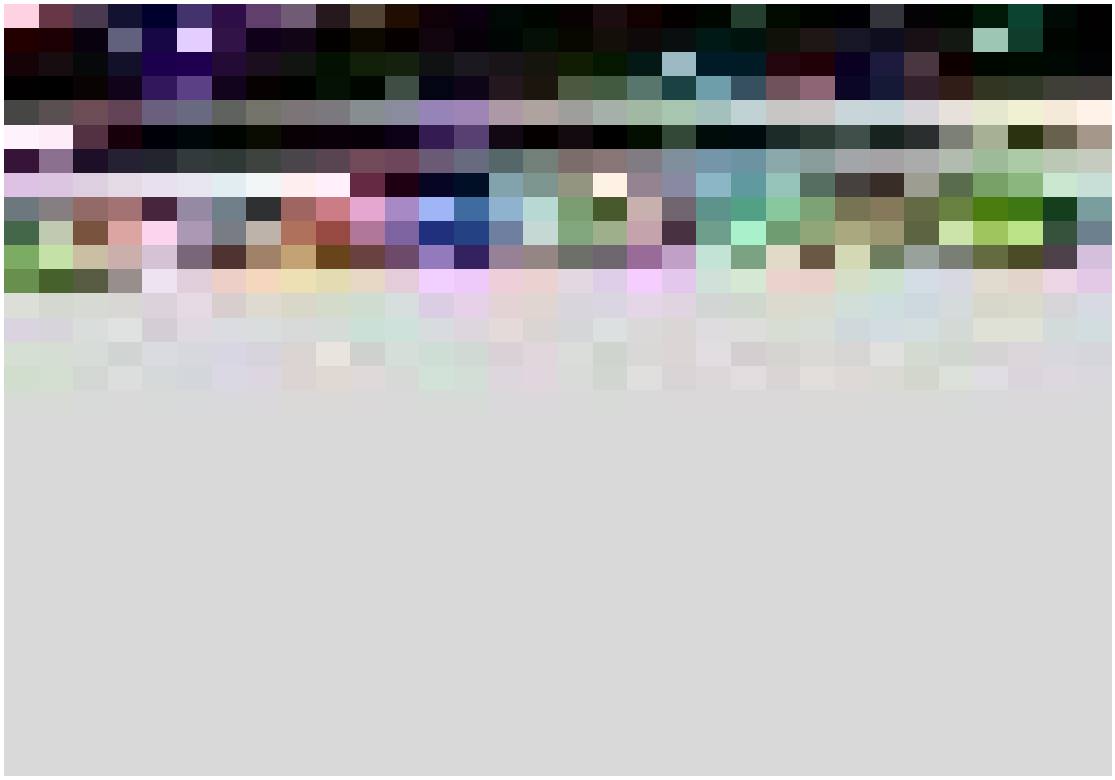


^{13}C NMR of **3-38** (cis)

^{1}H NMR of **3-38** (trans)

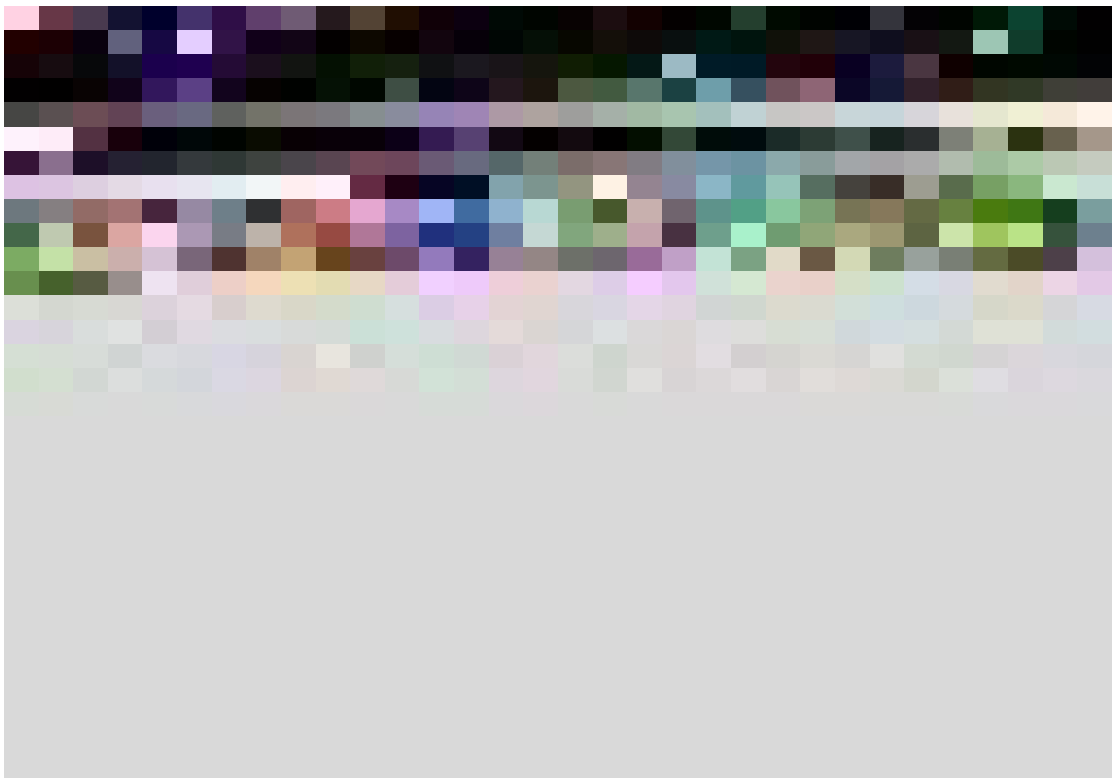


^{13}C NMR of **3-38** (trans)



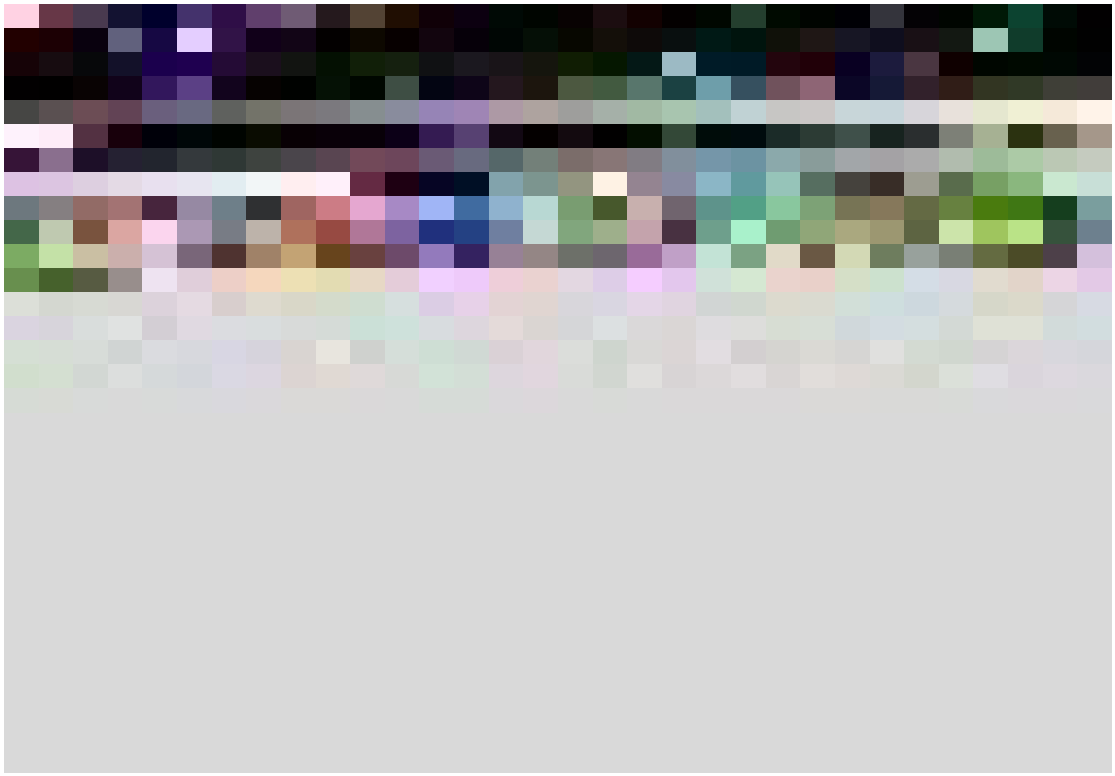
^{1}H NMR of **3-39** (cis)

^{13}C NMR of **3-39** (cis)



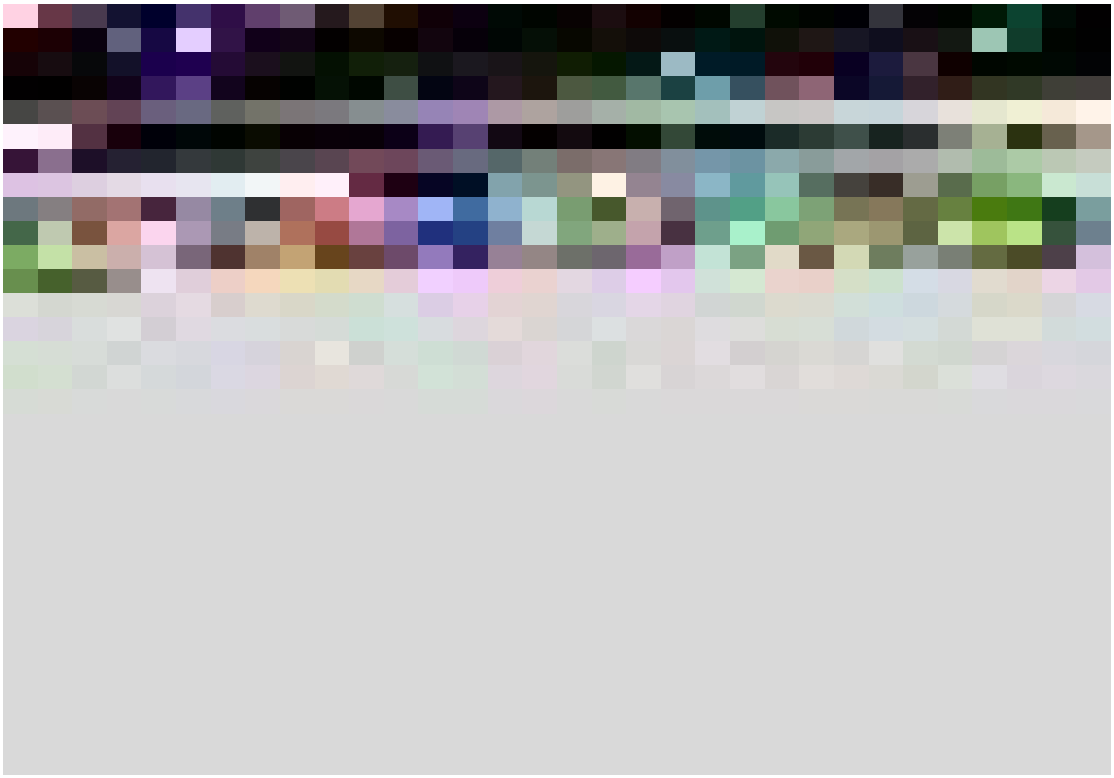
^{1}H NMR of **3-39** (trans)

^{13}C NMR of **3-39** (trans)



^{1}H NMR of **3-40** (cis)

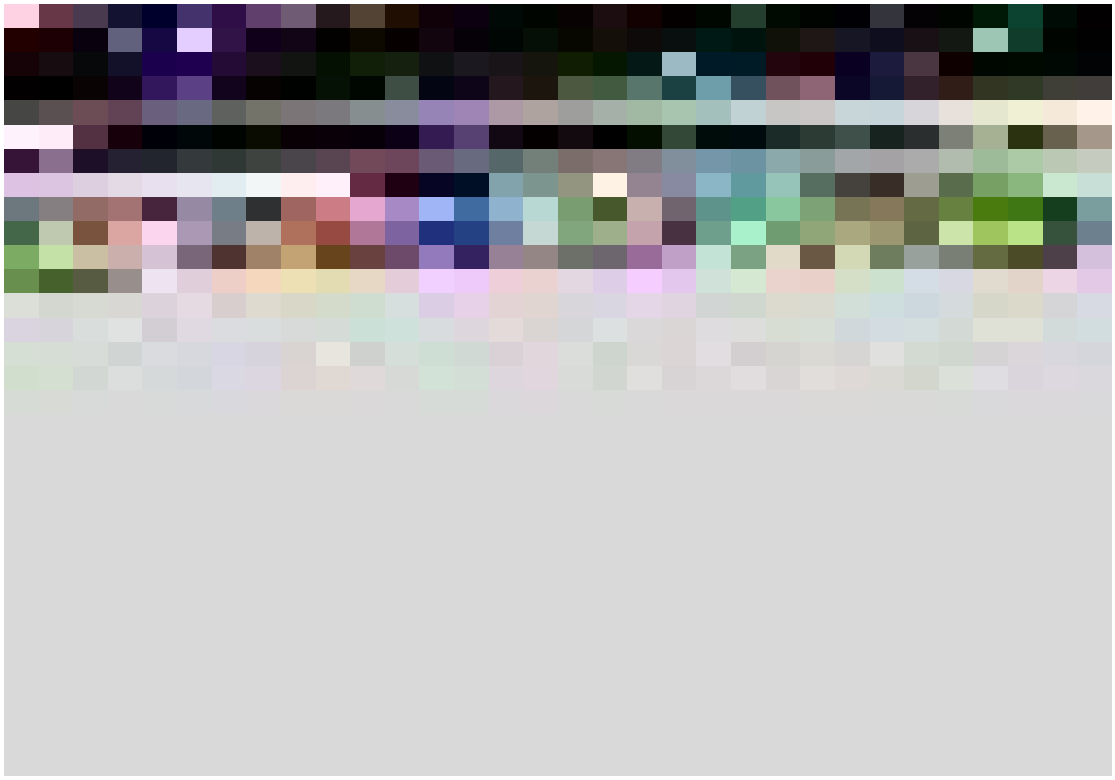
^{13}C NMR of **3-40** (cis)



^{1}H NMR of **3-40** (trans)

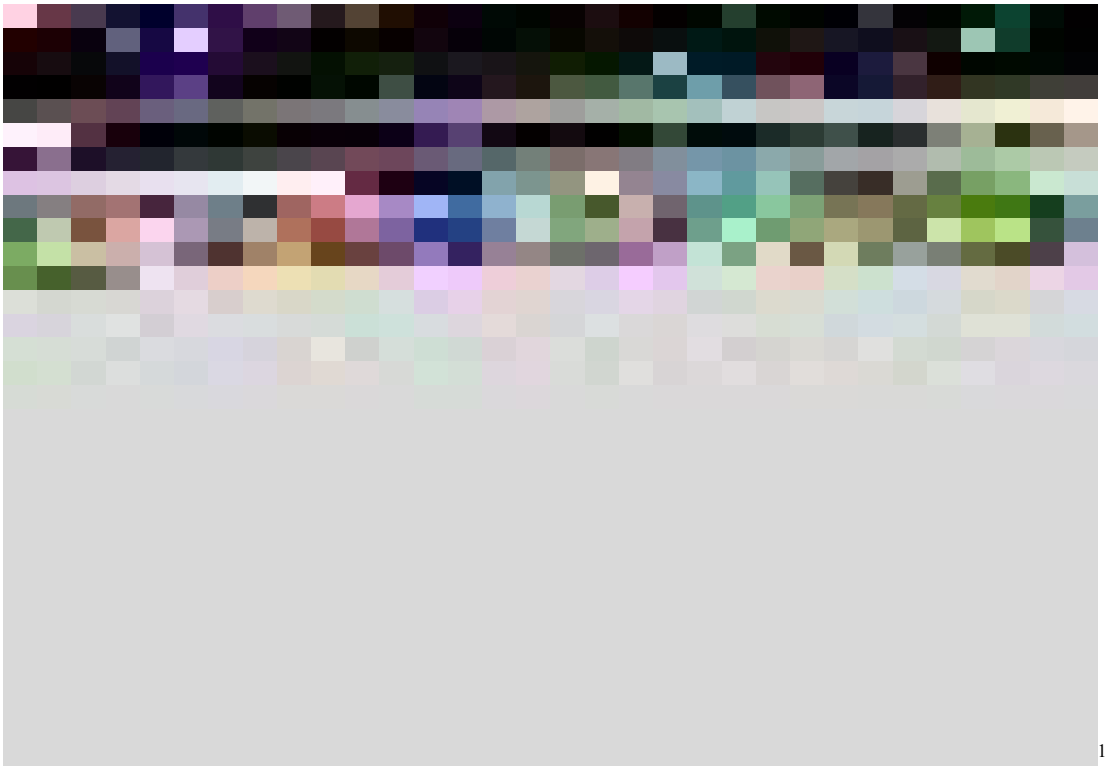
^{13}C NMR of **3-40** (trans)

^{1}H NMR of **3-41** (cis)



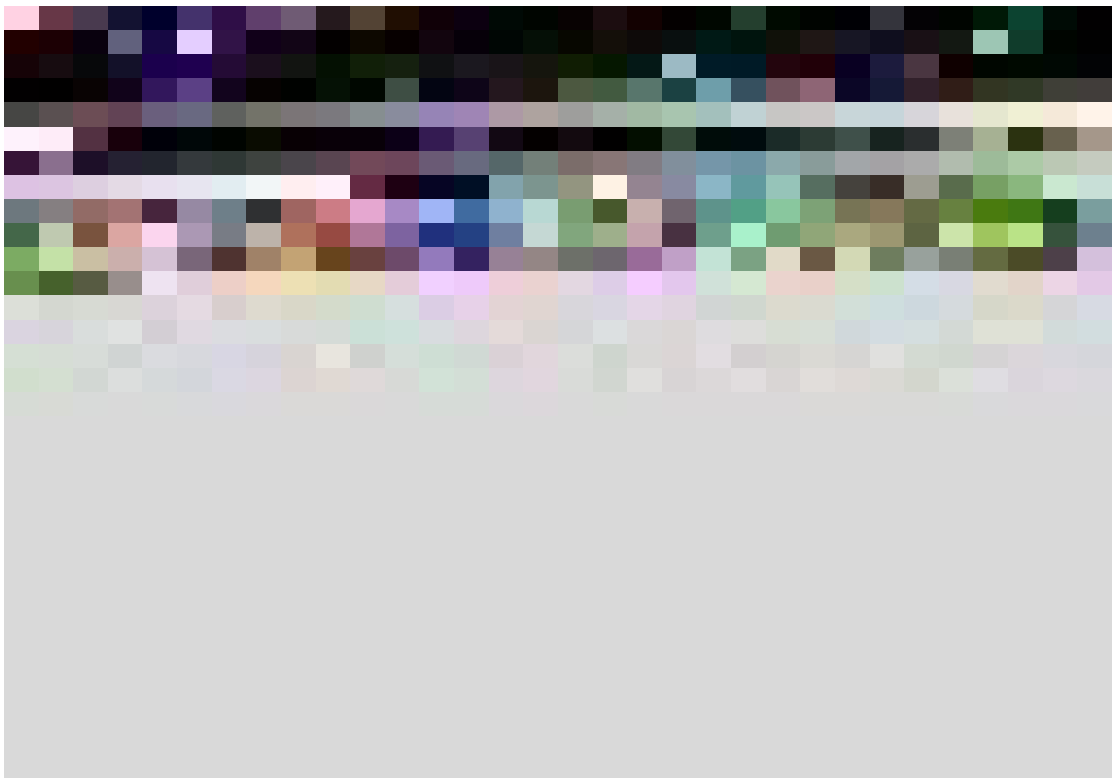
^{13}C NMR of **3-41** (cis)

^{1}H NMR of **3-41** (trans)



^{3}C NMR of **3-41** (trans)

^{1}H NMR of **3-42**

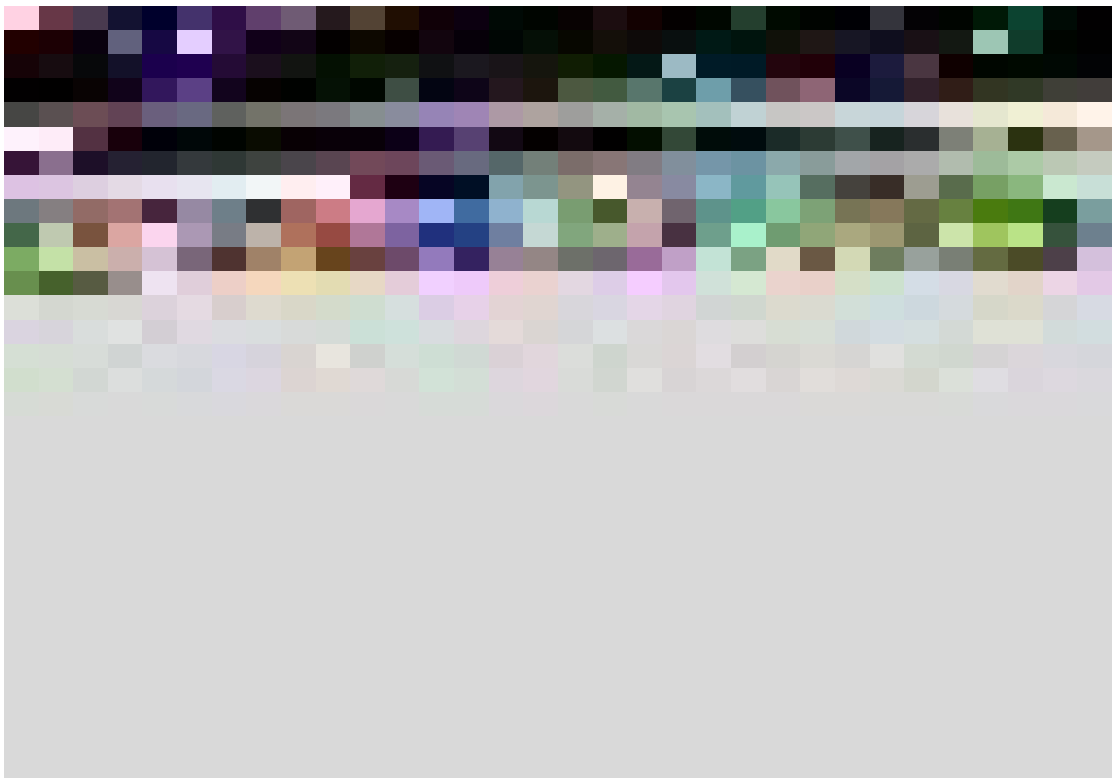


^{13}C NMR of **3-42**

^{1}H NMR of **4-1**

^{13}C NMR of **4-1**

^{1}H NMR of **4-2**



^{13}C NMR of **4-2**

^{1}H NMR of **4-3**

^{13}C NMR of **4-3**

^{1}H NMR of **4-4**

^{13}C NMR of **4-4**