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Supporting information

A Highly Diastereoselective One-Pot Three-Component 1,3-Dipolar Cycloaddition of Cyclopropenes with Azomethine Ylides Generated from 11*H*-Indeno[1,2-*b*]-quinoxalin-11-ones

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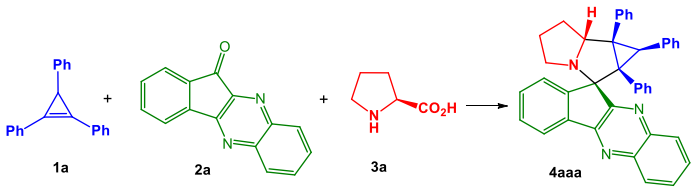
1. Experimental data

Table S1. Optimization of the reaction conditions[a]



Entry	Solvent	*T* [°C]	Time, h	Yield **4aaa** ,%[b]
1	methanol	reflux	12	80
2	ethanol	reflux	12	76
3	THF	reflux	12	49[c]
4	acetonitrile	reflux	12	61[c]
5	DMF	80	10	73
6	1,4-dioxane	80	12	43[c]
7	DMSO	80	12	67
8	ethanol	RT	72	54[c]
9	methanol	RT	72	51[c]

[a] Reaction conditions: **1a** (1 equiv.), **2a** (1 equiv.), **3a** (2 equiv.), solvent. [b] Isolated yield. [c] Unreacted **1a** and **2a** are present in the reaction mixture.

General procedure A for the one-pot three-component reaction of cyclopropenes, 11*H*-indeno[1,2-*b*]quinoxalin-11-ones, and secondary α-amino acids: A mixture of corresponding cyclopropene **1** (0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one **2** (0.3 mmol), and secondary α-amino acid **3** (0.6 mmol) was refluxed in methanol (6 mL) for 12 h until complete consumption of **1** as monitored by TLC. After cooling, the solvent was evaporated under reduced pressure. The residue was transferred into a separatory funnel using CH_2Cl_2 (5 mL), washed twice with water and brine. The washed organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated on the rotary evaporator. The resulting crude product **4** was purified by recrystallization from MeOH or by preparative thin layer chromatography (PTLC) on alumina using a mixture of hexane–CH_2Cl_2 (2:1, **4haa**, **4aac**).

(±)-(1R,1aR,2S,6aR,6bS)-1,1a,6b-Triphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline] (***4aaa***). Prepared following the general procedure **A** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol). Purified by recrystallization from MeOH. Yellow solid; yield: 133 mg (80%); mp 205–207 °C (MeOH); TLC (R_f = 0.58, SiO_2,

hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 7.5 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.82–7.71 (m, 4H), 7.66–7.58 (m, 1H), 7.56–7.48 (t, *J* = 7.5 Hz, 1H), 7.36–7.31 (m, 2H), 7.30–7.25 (m, 1H), 7.05–6.98 (m, 1H), 6.95–6.90 (m, 2H), 6.68–6.62 (m, 1H), 6.55–6.44 (m, 6H), 5.06 (t, *J* = 6.9 Hz, 1H), 3.58 (s, 1H), 3.51–3.46 (m, 1H), 2.61–2.57 (m, 1H), 2.26–2.13 (m, 1H), 2.05–1.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.1, 153.0, 145.2, 142.1, 141.9, 138.7, 137.4, 135.6, 132.5 (4C), 132.2, 131.0, 130.8 (2C), 129.8, 129.5, 129.1, 129.0, 128.6, 127.7 (2C), 126.6 (4C), 126.4, 126.2 (2C), 125.1, 122.3, 76.6, 75.0, 57.9, 48.3, 47.5, 32.7, 27.0, 26.1. IR (KBr): 3091, 3047, 2962, 2822, 1602, 1497, 1337, 1107, 758, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{40}H_{32}N_3$: 554.2591; found: 554.2602.

*Methyl (±)-(1R,1aR,2S,6aR,6bS)-1a,6b-Diphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline]-1-carboxylate (**4baa**).* Prepared following the general procedure **A** from cyclopropene **1b** (75 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol). Purified by recrystallization from MeOH. Yellow solid; yield: 111 mg (69%); mp 228–230 °C (MeOH); TLC (R_f = 0.40, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 8.05–8.00 (m, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.81–7.66 (m, 3H), 7.61–7.56 (m, 1H), 7.46–7.40 (m, 2H), 7.33–7.28 (m, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.4 Hz, 2H), 6.58 (d, *J* = 7.8 Hz, 2H), 4.97 (t, *J* = 7.0 Hz, 1H), 3.38 (s, 3H), 3.35–3.30 (m, 1H,), 3.28 (s, 1H), 2.52–2.48 (m, 1H), 2.17–2.07 (m, 1H), 1.98–1.83 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.2, 164.2, 152.9, 144.3, 142.2, 141.8, 138.7, 135.3, 132.7, 131.2, 131.0 (2C), 130.7 (2C), 129.9, 129.7, 129.2, 129.1, 128.7, 127.9 (2C), 126.9, 126.6 (2C), 126.5, 126.4, 122.4, 75.7, 74.5, 58.5, 51.2, 50.1, 47.2, 29.9, 26.8, 26.1. IR (KBr): 3077, 2947, 1746, 1605, 1446, 1327, 1162, 1136, 764, 698 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{36}H_{29}N_3NaO_2$: 558.2152; found: 558.2159.

*(±)-(1R,1aR,2S,6aR,6bS)-N-Isopropyl-1a,6b-diphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline]-1-carboxamide] (**4caa**).* Prepared following the general procedure **A** from cyclopropene **1c** (83 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol). Purified by recrystallization from MeOH. Yellow solid; yield: 128 mg (76%); mp 240–241 °C (MeOH); TLC (R_f = 0.54, SiO_2, hexane–EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34–8.25 (m, 2H), 8.06–8.00 (m, 4H), 7.79–7.66 (m, 3H), 7.62–7.56 (m, 1H), 7.50–7.44 (m, 2H), 7.39–7.33

(m, 1H), 6.92–6.84 (m, 2H), 6.79–6.73 (m, 1H), 6.68–6.61 (m, 2H), 4.98–4.90 (m, 1H), 3.75–3.65 (m, 1H), 3.49–3.40 (m, 2H), 3.18 (s, 1H), 2.56–2.47 (m, 1H), 2.16–1.80 (m, 4H), 0.56 (d, J = 6.5 Hz, 3H), 0.23 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.3, 164.4, 152.9, 144.1, 142.2, 141.8, 138.6, 134.6, 132.1 (2C), 131.6 (2C), 131.4, 130.0, 129.9, 129.6, 129.2, 129.1, 129.0, 128.7, 128.2, 127.6, 127.4 (2C), 127.2, 127.0, 122.3, 76.2, 75.0, 56.0, 48.9, 48.2, 40.8, 32.7, 26.8, 26.4, 21.7, 21.5. IR (KBr): 3429, 3051, 2967, 2863, 1646, 1526, 1465, 1444, 1366, 1338, 1180, 1155, 1124, 760, 746, 699 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{38}H_{35}N_4O$: 563.2805; found: 563.2830.

*(±)-(1R,1aR,2S,6aR,6bS)-1a,6b-Diphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]-pyrrolizine-2,11'-indeno[1,2-b]quinoxaline]-1-carbonitrile (**4daa**)*. Prepared following the general procedure **A** from cyclopropene **1d** (65 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol). Purified recrystallization from MeOH. Yellow solid; yield: 133 mg (88%); mp 249–250 °C (MeOH); TLC (R_f = 0.36, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 7.6 Hz, 2H), 8.00–7.91 (m, 3H), 7.81–7.66 (m, 3H), 7.63–7.57 (m, 1H), 7.49–7.42 (m, 2H), 7.38–7.32 (m, 1H), 6.85–6.76 (m, 3H), 6.74–6.66 (m, 2H), 5.07 (dd, J = 9.1, 5.2 Hz, 1H), 3.40 (s, 1H), 2.98–2.90 (m, 1H), 2.38–2.30 (m, 1H), 2.22–2.10 (m, 1H), 2.05–1.92 (m, 2H), 1.77–1.64 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.5, 153.1, 143.9, 142.2, 141.4, 138.3, 134.0, 131.6 (3C), 130.2, 130.1, 130.0 (2C), 129.7, 129.6, 129.2, 128.9, 128.4 (2C), 127.7, 127.6, 127.3 (2C), 125.3, 122.6, 118.8, 72.1, 71.8, 57.0, 45.5, 43.3, 26.5, 25.0, 15.1. IR (KBr): 3058, 2976, 2827, 2236, 1604, 1576, 1505, 1466, 1446, 1367, 1337, 1233, 1201, 1129, 1103, 1052, 1017, 772, 762, 747, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{35}H_{27}N_4$: 503.2230; found: 503.2251.

*(±)-(1R,1aR,2S,6aR,6bS)-1-Ethyl-1a,6b-diphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline] (**4eaa**)*. Prepared following the general procedure **A** from cyclopropene **1e** (66 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol). Purified by recrystallization from MeOH. Yellow solid; yield: 137 mg (90%); mp 219–220 °C (MeOH); TLC (R_f = 0.64, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (dd, J = 7.9, 1.6 Hz, 1H), 8.13–8.07 (m, 2H), 7.99 (dd, J = 7.9, 1.7 Hz, 1H), 7.85–7.80 (m, 2H), 7.73–7.57 (m, 4H), 7.43–7.37 (m, 2H), 7.32–7.27 (m, 1H), 6.76–6.70 (m, 1H), 6.68–6.58 (m, 4H), 4.97 (t, J = 7.1 Hz, 1H), 3.28–3.21 (m, 1H), 2.47–2.41 (m, 1H), 2.31 (t, J = 6.9 Hz, 1H), 2.16–2.05 (m, 2H), 2.03–1.81 (m, 2H), 1.58–1.39 (m, 2H), 1.11 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.0, 153.0, 146.4,

142.0, 141.9, 138.7, 138.6, 134.0, 131.3 (2C), 131.0, 130.6 (3C), 129.8, 129.5, 128.9, 128.8, 128.4, 127.8 (2C), 126.6 (2C), 126.3, 126.0, 122.3, 73.7, 73.6, 54.0, 46.8, 44.2, 30.4, 27.1, 27.0, 20.0, 14.6. IR (KBr): 3055, 2957, 2929, 2862, 1600, 1507, 1496, 1465, 1444, 1336, 1228, 1206, 1182, 1127, 1102, 761, 744, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{36}H_{32}N_3^+$: 506.2591; found 506.2600.

*(±)-(1R,1aR,2S,6aR,6bS)-1a,6b-Diphenyl-1-vinyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline] (**4faa**)*. Prepared following the general procedure **A** from cyclopropene **1f** (65 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol). Purified by recrystallization from MeOH. Yellow solid; yield: 125 mg (83%); mp > 260 °C (MeOH); TLC (R_f = 0.56, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 7.4 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 8.07–8.01 (m, 4H), 7.81–7.63 (m, 3H), 7.59–7.53 (m, 1H), 7.46–7.39 (m, 2H), 7.31–7.26 (m, 1H), 6.82–6.76 (m, 2H), 6.73–6.67 (m, 1H), 6.63–6.57 (m, 2H), 5.51 (dd, *J* = 16.7, 2.2 Hz, 1H), 5.19–5.00 (m, 3H), 3.40–3.33 (m, 1H), 3.15 (d, *J* = 10.2 Hz, 1H), 2.56–2.50 (m, 1H), 2.18–2.08 (m, 1H), 2.02–1.85 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.8, 153.1, 145.3, 142.1, 141.9, 138.6, 138.4, 137.5, 133.4, 132.2 (2C), 131.6 (3C), 131.1, 129.7, 129.6, 129.1, 128.6, 128.0 (2C), 126.7 (2C), 126.6 (2C), 126.2, 122.3, 113.1, 75.3, 74.5, 55.5, 47.5, 46.9, 32.1, 27.0, 26.1. IR (KBr): 3057, 2947, 2834, 1600, 1505, 1466, 1444, 1367, 1338, 1224, 1128, 1104, 1027, 990, 905, 762, 744, 696 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}N_3^+$: 504.2434; found 504.2446.

*(±)-(1aR,2S,6aR,6bS)-1a,6b-Diphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline] (**4gaa**)*. Prepared following the general procedure **A** from cyclopropene **1g** (58 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol). Purified recrystallization from MeOH. Yellow solid; yield: 130 mg (91%); mp 181–182 °C (MeOH); TLC (R_f = 0.56, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.1, 1.4 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 8.06–8.01 (m, 2H), 7.79–7.60 (m, 5H), 7.57–7.52 (m, 1H), 7.38–7.32 (m, 2H), 7.25–7.19 (m, 1H), 6.72–6.65 (m, 3H), 6.62–6.53 (m, 2H), 5.33–5.21 (m, 1H), 3.27–3.17 (m, 1H), 2.52–2.41 (m, 1H), 2.34 (d, *J* = 4.9 Hz, 1H), 2.16–1.94 (m, 3H), 1.86–1.74 (m, 1H), 1.64 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.5, 153.2, 142.1, 141.8, 139.0, 138.1, 136.0, 131.7 (3C), 131.0, 129.8, 129.5, 129.1 (3C), 129.0, 128.5, 128.1 (2C), 126.8 (2C), 126.2 (3C), 122.3, 73.5, 71.1, 53.2, 46.6, 41.6, 27.1, 26.3, 18.7. IR (KBr): 3049, 2950, 2826, 1599, 1498, 1444, 1337, 1156, 1019, 759, 742, 696 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{34}H_{28}N_3$: 478.2278; found: 478.2296.

*(±)-(1aR,2R,6aR,6bS)-1,1-Diphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline] (**4haa**)*. Prepared following the general procedure **A** from cyclopropene **1h** (58 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol). Purified by PTLC (Al_2O_3, hexane–CH_2Cl_2, 5:2) and subsequent crystallization from MeOH. Yellow solid; yield: 87 mg (61%); mp 196–197 °C (MeOH); TLC (R_f = 0.60, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.6 Hz, 1H), 8.15–8.08 (m, 2H), 7.75–7.64 (m, 4H), 7.53–7.48 (m, 1H), 7.36–7.23 (m, 6H), 7.16–7.09 (m, 2H), 7.04–7.01 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 4.97–4.90 (m, 1H), 2.59 (d, *J* = 7.5 Hz, 1H), 2.42 (dd, *J* = 7.4, 4.1 Hz, 1H), 2.33–2.24 (m, 1H), 2.18–2.12 (m, 1H), 2.01–1.91 (m, 3H), 1.89–1.82 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.9, 153.1, 149.3, 146.8, 142.2, 141.5, 140.1, 137.9, 132.0 (2C), 130.4, 129.9, 129.2 (2C), 129.1, 129.0, 128.5, 128.3 (2C), 128.0 (2C), 127.2 (2C), 126.4, 125.8, 121.8, 68.4, 66.2, 46.4, 44.8, 40.0, 30.0, 27.3, 23.6. IR (KBr): 3053, 2957, 2819, 1642, 1600, 1575, 1492, 1445, 1368, 1337, 1202, 1129, 1099, 772, 753, 706 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{34}H_{28}N_3^+$: 478.2278; found 478.2290.

*(±)-(1R,1aR,2S,6aR,6bS)-7',8'-Dimethyl-1,1a,6b-triphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline] (**4aba**)*. Prepared following the general procedure **A** from cyclopropene **1a** (81 mg, 0.3 mmol), 7,8-dimethyl-11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2b**) (78 mg, 0.3 mmol), and *L*-proline (69 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 131 mg (75%); mp 259–260 °C (MeOH); TLC (R_f = 0.52, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7.6 Hz, 1H), 8.12 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.79 (s, 1H), 7.77–7.72 (m, 2H), 7.62–7.56 (m, 1H), 7.53–7.47 (m, 1H), 7.39–7.32 (m, 2H), 7.29–7.24 (m, 1H), 7.04–6.96 (m, 1H), 6.95–6.90 (m, 2H), 6.67–6.61 (m, 1H), 6.52–6.46 (m, 6H), 5.09–5.02 (m, 1H), 3.60 (s, 1H), 3.50–3.41 (m, 1H), 2.62 (s, 3H), 2.63–2.54 (m, 1H), 2.52 (s, 3H), 2.24–2.14 (m, 1H), 2.04–1.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.1, 152.2, 145.0, 140.9, 140.8, 139.2, 139.0, 138.8, 137.6, 135.7, 132.6 (4C), 132.3, 130.9 (2C), 130.5, 129.4, 129.1, 128.4, 127.7 (3C), 126.6 (2C), 126.5 (2C), 126.3, 126.1, 125.0, 121.9, 76.5, 74.8, 57.9, 48.1, 47.2, 32.6, 27.0, 26.0, 20.3 (2C). IR (KBr): 3051, 3025, 2970, 2828, 1601, 1496, 1444, 1333, 1203, 1000, 745, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{36}N_3^+$: 582.2904; found 582.2927.

*(±)-(1R,1aR,2S,6aR,6bS)-7',8'-Dimethyl-1a,6b-diphenyl-1a,4,5,6,6a,6b-hexahydro-1H-spiro[cyclopropa[a]pyrrolizine-2,11'-indeno[1,2-b]quinoxaline]-1-carbonitrile (**4dba**)*. Prepared following the general procedure **A** from cyclopropene **1d** (65 mg, 0.3 mmol), 7,8-dimethyl-11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2b**) (78 mg, 0.3 mmol), and *L*-proline (**3a**) (69 mg, 0.6 mmol).

Purified by recrystallization from MeOH. Light yellow solid; yield: 132 mg (83%); mp > 260 °C (MeOH); TLC (R_f = 0.40, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01–7.97 (m, 2H), 7.95–7.91 (m, 3H), 7.78 (s, 1H), 7.68–7.63 (m, 1H), 7.59–7.55 (m, 1H), 7.49–7.42 (m, 2H), 7.37–7.32 (m, 1H), 6.85–6.76 (m, 3H), 6.72–6.68 (m, 2H), 5.05 (dd, *J* = 9.2, 5.3 Hz, 1H), 3.42 (s, 1H), 2.93–2.87 (m, 1H), 2.58 (s, 3H), 2.51 (s, 3H), 2.35–2.28 (m, 1H), 2.21–2.11 (m, 1H), 2.03–1.91 (m, 2H), 1.75–1.65 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.4, 152.2, 143.7, 140.9, 140.2, 139.9, 139.3, 138.6, 134.1, 131.6 (2C), 131.1, 130.2, 130.1, 130.0, 129.0, 128.5, 128.4 (3C), 127.6, 127.5, 127.2 (2C), 125.2, 122.2, 118.9, 71.9, 71.6, 57.0, 45.2, 43.0, 26.5, 24.9, 20.3 (2C), 15.0. IR (KBr): 3032, 2967, 2873, 2233, 1604, 1575, 1497, 1445, 1295, 1203, 1157, 1108, 1055, 746, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{37}H_{31}N_4^+$: 531.2543; found 531.2560.

*(±)-(5S,5aR,6R,6aS,6bS)-5a,6,6a-Triphenyl-1,3,5a,6,6a,6b-hexahydrospiro[cyclopropa[3,4]pyrrolo[1,2-c]thiazole-5,11'-indeno[1,2-b]quinoxaline] (**4aab**).* Prepared following the general procedure **A** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-thiaproline (**3b**) (80 mg, 0.6 mmol). Purification of the crude by recrystallization from MeOH afforded an inseparable mixture of two diastereomers in ratio 10:1. Data for the mixture of diastereomers: light yellow solid; yield: 120 mg (77%). IR (KBr): 3055, 3027, 2957, 2856, 1601, 1495, 1444, 1337, 1212, 1201, 1104, 761, 746, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{39}H_{30}N_3S$: 572.2155; found: 572.2181. NMR data for the major diastereomer **4aab**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.86–7.61 (m, 6H), 7.55–7.49 (m, 1H), 7.40–7.24 (m, 4H), 7.04–6.90 (m, 3H), 6.71–6.65 (m, 1H), 6.58–6.45 (m, 4H), 5.18 (dd, *J* = 9.9, 5.0 Hz, 1H), 4.22 (s, 1H), 3.57 (d, *J* = 4.7 Hz, 1H), 3.37 (d, *J* = 4.7 Hz, 1H), 2.97 (t, *J* = 9.3 Hz, 1H), 2.70 (dd, *J* = 8.7, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.5, 153.4, 145.3, 142.1, 141.3, 137.9, 137.0, 134.6, 132.5 (3C), 132.4, 131.8, 131.0 (2C), 129.9, 129.8, 129.6, 129.2, 128.9, 128.0 (2C), 127.0, 126.7 (2C), 126.6 (4C), 125.4, 125.3, 122.2, 76.7, 72.2, 57.9, 44.0, 43.6, 31.2, 29.2.

*(±)-(1R,2S,5S,6R)-3-Methyl-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**4aac**).* Prepared following the general procedure **A** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and sarcosine (**3c**) (53 mg, 0.6 mmol). Purified by PTLC (Al_2O_3, hexane–CH_2Cl_2, 2:1) and subsequent crystallization from MeOH. Yellow solid; yield: 78 mg (49%); mp 218–220 °C (MeOH); TLC (R_f = 0.62, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 7.2 Hz, 1H), 8.13 (d, *J* = 7.6

Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.86–7.71 (m, 4H), 7.67–7.61 (m, 1H), 7.53–7.47 (m, 1H), 7.37–7.24 (m, 4H), 7.02–6.88 (m, 3H), 6.68–6.60 (m, 1H), 6.51–6.40 (m, 5H), 4.34 (d, *J* = 9.0 Hz, 1H), 4.16 (s, 1H), 3.71 (d, *J* = 9.1 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.5, 153.7, 147.2, 141.9, 141.3, 138.2, 137.6, 135.6, 132.9 (3C), 132.5, 132.1, 131.8, 130.9 (2C), 129.7, 129.5, 129.3, 129.2, 128.7, 127.7 (2C), 126.7, 126.6 (2C), 126.4 (2C), 126.2, 125.3, 125.0, 121.9, 78.0, 67.4, 53.8, 43.3, 34.2, 33.7. IR (KBr): 3057, 3026, 2923, 1675, 1601, 1576, 1495, 1447, 1368, 1336, 1203, 1031, 759, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{38}H_{30}N_3$: 528.2434; found: 528.2434.

*(E)-2,3-Diphenylacrylaldehyde (**5**).* Obtained as a ring-opening product from cyclopropene **1j** (71 mg, 0.3 mmol). Purified by PTLC (Al_2O_3, hexane–CH_2Cl_2, 3:1) and subsequent crystallization from hexane. White solid; yield: 35 mg (56%); mp 91–92 °C (hexane) (Lit. data[1] mp 95 °C); TLC (R_f = 0.58, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 (s, 1H), 7.47–7.39 (m, 4H), 7.34–7.18 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.9, 150.1, 141.9, 134.1, 133.4, 130.7 (2C), 130.2, 129.4 (2C), 128.9 (2C), 128.5 (2C), 128.3. IR (KBr): 3054, 2848, 1688, 1626, 1597, 1446, 1414, 1198, 1094, 1070, 761, 714, 692 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{12}NaO^+$: 231.0780; found 231.0778. The NMR data are in agreement with previously reported.[1]

General procedure B for the one-pot three-component reaction of cyclopropenes, 11*H*-indeno[1,2-*b*]quinoxalin-11-ones, and primary α-amino acids: A mixture of corresponding cyclopropene **1** (0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (0.3 mmol), and primary α-amino acid **6** (0.6 mmol) was refluxed in a mixture of MeOH–H_2O (3:1, 8 mL) for 24 h until TLC showed the absence either of the starting cyclopropene **1** or of any further changes. In case of *L*-histidine (**6n**), the reaction was carried out in the presence of AcOH (0.17 mL, 3 mmol). After completion of the reaction, all volatiles were removed *in vacuo.* The residue was transferred into a separatory funnel using EtOAc (10 mL), washed twice with water and brine. The washed organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude product **6** was purified by recrystallization using an appropriate solvent (MeOH or a mixture of hexane–CH_2Cl_2) or by preparative thin layer chromatography (PTLC) on alumina using a mixture of CH_2Cl_2–hexane (2:1, **7aao**) or a mixture of CH_2Cl_2–MeOH (20:1, **7aan**, **7aar**).

*(±)-(1R,2S,4R,5S,6R)-4-Methyl-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aaa**).* Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-

alanine (**6a**) (53 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 101 mg (64%); mp 240–241 °C (MeOH); TLC (R_f = 0.30, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 7.5 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.88–7.68 (m, 5H), 7.67–7.60 (m, 1H), 7.53–7.47 (m, 1H), 7.40–7.32 (m, 2H), 7.31–7.25 (m, 1H), 7.05–6.97 (m, 1H), 6.97–6.90 (m, 2H), 6.69–6.63 (m, 1H), 6.53–6.45 (m, 5H), 5.01 (q, *J* = 6.1 Hz, 1H), 3.70 (s, 1H), 1.95 (br s, 1H, exchanges with H_2O), 1.26 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.3, 153.2, 147.5, 142.2, 141.6, 137.7, 137.3, 135.0, 133.1 (2C), 131.9, 131.8, 130.8 (3C), 129.6 (2C), 129.3, 129.1, 128.8, 127.7 (2C), 126.7 (3C), 126.6 (3C), 126.3, 125.1, 124.5, 122.1, 74.5, 64.1, 53.6, 48.9, 29.8, 15.7. IR (KBr): 3296, 3056, 3023, 2970, 2861, 1601, 1497, 1444, 1370, 1336, 1133, 1102, 760, 741, 699 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{38}H_{30}N_3$: 528.2434; found: 528.2430.

*(±)-(1R,2S,4R,5S,6R)-4-Ethyl-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aab**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-2-aminobutyric acid (**6b**) (62 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 120 mg (74%); mp > 260 °C (MeOH); TLC (R_f = 0.34, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.85–7.71 (m, 5H), 7.66–7.60 (m, 1H), 7.52–7.47 (m, 1H), 7.39–7.31 (m, 2H), 7.31–7.24 (m, 1H), 7.04–6.96 (m, 1H), 6.96–6.90 (m, 2H), 6.69–6.63 (m, 1H), 6.53–6.44 (m, 5H), 4.83 (dd, *J* = 7.4, 5.3 Hz, 1H), 3.79 (s, 1H), 1.98 (br s, 1H, exchanges with H_2O), 1.74–1.63 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 153.2, 147.7, 142.2, 141.6, 137.7, 137.4, 135.3, 133.2 (2C), 131.9, 131.7, 130.9 (3C), 129.6 (2C), 129.3, 129.1, 128.7, 127.6 (2C), 126.7 (3C), 126.5 (3C), 126.2, 125.1, 124.7, 122.1, 74.2, 69.9, 53.0, 48.2, 30.3, 24.0, 11.6. IR (KBr): 3291, 3026, 2954, 2870, 1602, 1498, 1445, 1369, 1332, 1100, 1042, 762, 741, 698 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{39}H_{32}N_3$: 542.2591; found: 542.2601.

*(±)-(1R,2S,4R,5S,6R)-1,5,6-Triphenyl-4-propyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aac**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *DL*-norvaline (**6c**) (70 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 137 mg (82%); mp > 260 °C (MeOH); TLC (R_f = 0.52, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.85–7.69 (m, 5H), 7.66–7.59 (m, 1H), 7.53–7.46 (m, 1H),

7.39–7.24 (m, 3H), 7.05–6.96 (m, 1H), 6.96–6.89 (m, 2H), 6.70–6.62 (m, 1H), 6.53–6.41 (m, 5H), 4.89 (dd, *J* = 9.0, 3.4 Hz, 1H), 3.78 (s, 1H), 2.40 (br s, 1H, exchanges with H_2O), 1.70–1.22 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.4, 153.3, 147.7, 142.2, 141.6, 137.7, 137.4, 135.2, 133.2 (2C), 131.9, 131.7, 130.9 (3C), 129.6 (2C), 129.2, 129.1, 128.7, 127.6 (2C), 126.6 (3C), 126.5 (3C), 126.2, 125.1, 124.7, 122.1, 74.3, 68.4, 53.0, 48.2, 33.4, 30.3, 20.4, 14.4. IR (KBr): 3310, 3056, 2921, 2854, 1601, 1577, 1496, 1465, 1444, 1366, 1337, 757, 744, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{40}H_{34}N_3$: 556.2747; found: 556.2766.

*(±)-(1R,2S,4R,5S,6R)-4-Butyl-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aad**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *DL*-norleucine (**6d**) (79 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 149 mg (87%); mp > 260 °C (MeOH); TLC (R_f = 0.40, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.85–7.71 (m, 5H), 7.66–7.59 (m, 1H), 7.52–7.47 (m, 1H), 7.38–7.25 (m, 3H), 7.04–6.90 (m, 3H), 6.69–6.61 (m, 1H), 6.55–6.43 (m, 5H), 4.88 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.77 (s, 1H), 2.14 (br s, 1H, exchanges with H_2O), 1.73–1.55 (m, 2H), 1.48–1.19 (m, 4H), 0.84 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.4, 153.3, 147.7, 142.2, 141.6, 137.7, 137.4, 135.2, 133.2 (2C), 131.9, 131.7, 130.9 (3C), 129.6 (2C), 129.2, 129.1, 128.7, 127.6 (2C), 126.7 (3C), 126.5 (3C), 126.2, 125.1, 124.7, 122.1, 74.3, 68.5, 53.0, 48.3, 30.9, 30.3, 29.5, 23.1, 14.1. IR (KBr): 3286, 3058, 3026, 2959, 2923, 2873, 1601, 1497, 1465, 1337, 1102, 759, 744, 699 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{41}H_{36}N_3$: 570.2904; found: 570.2902.

*(±)-(1R,2S,4R,5S,6R)-4-Hexyl-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aae**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *DL*-2-aminocaprylic acid (**6e**) (96 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 142 mg (79%); mp 200–201 °C (MeOH); TLC (R_f = 0.24, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.1 Hz, 1H), 8.18–8.13 (m, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.86–7.72 (m, 5H), 7.66–7.60 (m, 1H), 7.52–7.47 (m, 1H), 7.38–7.25 (m, 3H), 7.04–6.91 (m, 3H), 6.69–6.63 (m, 1H), 6.52–6.45 (m, 5H), 4.89 (dd, *J* = 8.4, 3.9 Hz, 1H), 3.78 (s, 1H), 2.37 (br s, 1H, exchanges with H_2O), 1.71–1.56 (m, 2H), 1.48–1.38 (m, 1H), 1.34–1.15 (m, 7H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.4, 153.3, 147.7, 142.2, 141.6, 137.7, 136.8, 137.4, 135.3, 133.2 (2C), 131.9, 131.7, 130.9 (2C), 129.6

(2C), 129.2 (2C), 128.7, 127.6 (3C), 126.7 (3C), 126.5 (2C), 126.2, 125.1, 124.7, 122.1, 74.3, 68.6, 53.0, 48.3, 31.8, 31.3, 30.3, 29.7, 27.3, 22.6, 14.0. IR (KBr): 3290, 3052, 2954, 2925, 2855, 1602, 1497, 1465, 1443, 1336, 1202, 1178, 1133, 1103, 1044, 758, 742, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{40}N_3^+$: 598.3217; found 598.3229.

*(±)-(1R,2S,4R,5S,6R)-4-Isopropyl-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aaf**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-valine (**6f**) (70 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 143 mg (86%); mp > 260 °C (MeOH); TLC (R_f = 0.50, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.03 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.84–7.72 (m, 4H), 7.65–7.60 (m, 1H), 7.51–7.47 (m, 1H), 7.35–7.22 (m, 4H), 7.06–6.92 (m, 3H), 6.68–6.62 (m, 1H), 6.53–6.45 (m, 5H), 4.98 (d, *J* = 4.4 Hz, 1H), 4.04 (s, 1H), 2.30 (br s, 1H), 1.99–1.87 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.7, 153.3, 148.2, 142.1, 141.6, 137.6, 137.3, 135.8, 133.1 (2C), 131.9, 131.7, 131.1 (3C), 129.6, 129.5, 129.2, 129.1, 128.7 (2C), 127.5 (2C), 126.6 (5C), 126.2, 125.2, 124.9, 122.0, 73.3, 72.4, 51.6, 46.5, 31.2, 29.5, 21.3, 17.8. IR (KBr): 3060, 2957, 2869, 1601, 1497, 1466, 1330, 1109, 752, 742, 696 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{40}H_{34}N_3$: 556.2747; found: 556.2769.

*(±)-(1R,2S,4R,5S,6R)-4-Isobutyl-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aag**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-leucine (**6g**) (79 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 144 mg (84%); mp > 260 °C (MeOH); TLC (R_f = 0.44, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.84–7.71 (m, 4H), 7.65–7.60 (m, 1H), 7.52–7.47 (m, 1H), 7.37–7.24 (m, 4H), 7.04–6.90 (m, 3H), 6.68–6.63 (m, 1H), 6.52–6.45 (m, 5H), 4.98 (dd, *J* = 9.5, 3.1 Hz, 1H), 3.74 (s, 1H), 2.27 (br s, 1H, exchanges with H_2O), 1.71–1.58 (m, 2H), 1.44–1.32 (m, 1H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 153.2, 147.7, 142.2, 141.7, 137.7, 137.5, 135.1, 133.2 (2C), 132.0, 131.7, 130.9 (3C), 129.7, 129.6, 129.2, 129.1, 128.7, 127.6 (2C), 126.6 (3C), 126.5 (3C), 126.2, 125.1, 124.6, 122.1, 74.4, 66.4, 52.9, 48.4, 40.1, 30.2, 25.6, 24.0, 21.7. IR (KBr): 3308, 3058, 2957, 2916, 2871, 1601, 1496, 1464, 1443, 1367, 1338, 1132, 1103, 758, 742, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{41}H_{36}N_3$: 570.2904; found: 570.2917.

*(±)-(1R,2S,4R,5S,6R)-4-(2-(Methylthio)ethyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aah**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-methionine (**6h**) (90 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 157 mg (89%); mp > 260 °C (MeOH); TLC (R_f = 0.38, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.1, 1.0 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.84–7.72 (m, 5H), 7.66–7.61 (m, 1H), 7.52–7.48 (m, 1H), 7.39–7.25 (m, 3H), 7.05–7.00 (m, 1H), 6.97–6.91 (m, 2H), 6.69–6.64 (m, 1H), 6.52–6.46 (m, 5H), 5.01 (t, *J* = 5.8 Hz, 1H), 3.83 (s, 1H), 2.75–2.43 (m, 3H), 2.04 (s, 3H), 2.02–1.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.4, 153.2, 147.5, 142.2, 141.6, 137.7, 137.1, 134.7, 137.1, 134.8, 133.2 (2C), 131.8, 131.7, 129.7, 129.6 (2C), 129.3, 129.2, 128.8, 127.8 (2C), 126.9, 126.7 (2C), 126.6 (3C), 126.3, 125.2, 124.8, 122.1, 74.2, 67.7, 52,8, 47.9, 31.9, 30.7, 30.4, 15.6. IR (KBr): 3295, 3058, 3024, 2913, 1602, 1508, 1498, 1444, 1430, 1336, 1133, 1102, 758, 740, 702 cm^{-1}. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{40}H_{34}N_3S^+$: 588.2568; found 588.2495.

*(±)-(1R,2S,4R,5S,6R)-4-Benzyl-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aai**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-phenylalanine (**6i**) (99 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 147 mg (81%); mp > 260 °C (MeOH); TLC (R_f = 0.52, SiO_2, hexane–EtOAc, 7:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 7.4 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 7.4 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.86–7.77 (m, 4H), 7.75–7.70 (m, 1H), 7.65–7.59 (m, 1H), 7.50–7.45 (m, 1H), 7.43–7.36 (m, 2H), 7.35–7.15 (m, 6H), 7.05–6.91 (m, 3H), 6.69–6.63 (m, 1H), 6.53–6.42 (m, 5H), 5.20 (dd, *J* = 8.4, 3.8 Hz, 1H), 3.87 (s, 1H), 3.00–2.86 (m, 2H), 2.33 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.6, 153.2, 147.9, 142.1, 141.5, 139.4, 137.5, 137.3, 135.0, 133.3 (2C), 131.8, 131.7, 131.0 (3C), 129.6, 129.5, 129.4 (2C), 129.2, 129.1, 128.7, 128.4 (2C), 127.8 (3C), 126.8, 126.7, 126.5 (3C), 126.3, 126.1, 125.1, 124.9, 121.9, 73.6, 68.8, 52.7, 47.5, 37.1, 30.5. IR (KBr): 3339, 3055, 2871, 1601, 1579, 1495, 1337, 1107, 1043, 758, 701 cm^{-1}. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{44}H_{34}N_3$: 604.2747; found: 604.2747.

*(±)-(1R,2S,4R,5S,6R)-1,4,5,6-Tetraphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aaj**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *DL*-2-phenylglycine (**6j**) (91 mg, 0.6 mmol). Purified by recrystallization from MeOH. Light yellow solid; yield: 163 mg (92%); mp > 260 °C (MeOH); TLC (R_f = 0.54, SiO_2, hexane–EtOAc, 7:2). ^{1}H

NMR (400 MHz, $CDCl_3$): δ = 8.44 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.32 (d, *J* = 7.7 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.87–7.82 (m, 1H), 7.79–7.74 (m, 1H), 7.71–7.66 (m, 1H), 7.56–7.50 (m, 3H), 7.35–7.23 (m, 11H), 6.97–6.83 (m, 3H), 6.71–6.65 (m, 1H), 6.54–6.40 (m, 3H), 6.13 (s, 1H), 4.16 (s, 1H), 2.63 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.0, 153.3, 148.1, 142.2, 141.6, 139.5, 137.6, 137.1, 134.6, 133.7 (2C), 131.8 (2C), 130.9 (3C), 129.6 (2C), 129.3, 129.2, 128.8, 127.8 (2C), 127.4 (6C), 126.8, 126.7, 126.4 (4C), 125.2, 125.1, 122.0, 73.6, 70.5, 52.6, 48.9, 30.4. IR (KBr): 3344, 3054, 3025, 1600, 1494, 1445, 1336, 1107, 756, 697 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{32}N_3$: 590.2591; found: 590.2594.

*(±)-4-(((1R,2S,4R,5S,6R)-1,5,6-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-yl)methyl)phenol (**7aak**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-tyrosine (**6k**) (109 mg, 0.6 mmol). Purified by recrystallization from hexane–CH_2Cl_2. Beige solid; yield: 147 mg (79%); mp > 260 °C (hexane–CH_2Cl_2); TLC (R_f = 0.24, SiO_2, hexane–EtOAc, 5:2). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.05 (s, 1H), 8.38 (d, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.89–7.68 (m, 8H), 7.57–7.51 (m, 1H), 7.44–7.38 (m, 2H), 7.32–7.27 (m, 1H), 7.00–6.85 (m, 5H), 6.69–6.53 (m, 3H), 6.52–6.40 (m, 4H), 4.83–4.75 (m, 1H), 3.99 (s, 1H), 3.72 (d, *J* = 7.4 Hz, 1H), 2.87 (dd, *J* = 13.8, 9.8 Hz, 1H), 2.68–2.60 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 165.8, 155.9, 153.4, 148.1, 141.8, 141.2, 137.9, 137.5, 135.7, 133.2 (2C), 132.9, 132.3, 131.0 (2C), 131.0 (3C), 130.3, 130.2, 130.1, 130.0, 129.8, 129.7, 129.2, 128.3 (2C), 127.2, 126.9 (4C), 126.6, 126.0, 125.5, 121.9, 115.3 (2C), 74.8, 70.8, 52.7, 48.3, 35.7, 29.6. IR (KBr): 3326, 3055, 3026, 2908, 2862, 1604, 1511, 1495, 1449, 1369, 1337, 1236, 1109, 760, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{44}H_{34}N_3O$: 620.2696; found: 620.2694.

*(±)-2,6-Diiodo-4-(((1R,2S,4R,5S,6R)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-yl)methyl)phenol (**7aal**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and 3,5-diiodo-*L*-tyrosine (**6l**) (281 mg, 0.6 mmol). Purified by recrystallization from hexane–CH_2Cl_2. Light grey solid; yield: 170 mg (65%); mp > 260 °C (hexane–CH_2Cl_2); TLC (R_f = 0.28, SiO_2, hexane–EtOAc, 5:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.84–7.69 (m, 5H), 7.66–7.61 (m, 1H), 7.54 (s, 2H), 7.51–7.45 (m, 1H), 7.41–7.28 (m, 3H), 7.05–6.99 (m, 1H), 6.97–6.91 (m, 2H), 6.69–6.63 (m, 1H), 6.52–6.40 (m, 5H), 5.76 (br s, 1H), 5.09 (dd, *J* = 7.7, 4.5 Hz, 1H), 3.83 (s, 1H), 2.85–2.72 (m, 2H), 2.28 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.4, 153.1, 152.0,

147.7, 142.1, 141.5, 139.9 (2C), 137.5, 137.0, 135.6 134.7, 133.2 (2C), 131.8, 131.5, 130.9 (2C), 129.6 (3C), 129.3, 129.1, 128.8, 127.9 (2C), 127.0, 126.7, 126.6 (4C), 126.4, 125.2, 125.0, 122.0, 82.3 (2C), 73.6, 68.6, 52.7, 47.3, 35.7, 30.5. IR (KBr): 3457, 3337, 3044, 2915, 2850, 1601, 1495, 1457, 1398, 1338, 1310, 1237, 1149, 1122, 756, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{44}H_{32}I_2N_3O$: 872.0629; found: 872.0643.

*(±)-(1R,2S,4R,5S,6R)-4-((1H-Indol-3-yl)methyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aam**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-tryptophan (**6m**) (123 mg, 0.6 mmol). Purified by recrystallization from hexane–CH_2Cl_2. Light yellow solid; yield: 112 mg (58%); mp > 260 °C (hexane–CH_2Cl_2); TLC (R_f = 0.46, SiO_2, hexane–EtOAc, 5:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 7.4 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.99–7.93 (m, 2H), 7.90–7.67 (m, 4H), 7.62–7.56 (m, 2H), 7.48–7.37 (m, 3H), 7.35–7.26 (m, 4H), 7.18–6.91 (m, 6H), 6.68–6.62 (m, 1H), 6.52–6.42 (m, 5H), 5.28 (dd, *J* = 7.7, 4.4 Hz, 1H), 3.94 (s, 1H), 3.14–3.03 (m, 2H), 2.41 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.6, 153.2, 147.9, 142.1, 141.5, 137.5, 136.3, 135.3, 133.3 (2C), 131.9, 131.7, 130.9 (2C), 129.9, 129.6, 129.5, 129.2, 129.0, 128.8, 128.6, 128.1, 127.9, 127.8 (2C), 126.8, 126.6, 126.5 (2C), 126.2, 125.8, 125.1, 124.9, 122.4, 121.9 (2C), 119.3 (2C), 113.7, 111.0, 73.8, 68.5, 52.9, 47.7, 30.3, 26.5. IR (KBr): 3425, 3056, 3026, 2920, 1602, 1495, 1455, 1365, 1337, 1104, 1032, 758, 742, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{46}H_{35}N_3^+$: 643.2856; found 643.2828.

*(±)-(1R,2S,4R,5S,6R)-4-((1H-Imidazol-4-yl)methyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**7aan**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-histidine (**6n**) (93 mg, 0.6 mmol). Purified by PTLC (Al_2O_3, CH_2Cl_2–MeOH, 20:1) and subsequent crystallization from hexane–Et_2O. Light yellow solid; yield: 61 mg (34%); mp > 260 °C (hexane–Et_2O); TLC (R_f = 0.30, SiO_2, MeOH–CH_2Cl_2, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.38 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91–7.77 (m, 3H), 7.75–7.52 (m, 6H), 7.42–7.36 (m, 2H), 7.30–7.24 (m, 1H), 6.97–6.83 (m, 4H), 6.79 (s, 1H), 6.67–6.61 (m, 1H), 6.52–6.32 (m, 5H), 4.89–4.84 (m, 1H), 3.81 (s, 1H), 2.87 (dd, *J* = 14.2, 9.1 Hz, 1H), 2.73–2.65 (m, 1H), 2.52–2.48 (m, 1H, overlapping with DMSO). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 165.7, 153.3, 148.0, 141.9, 141.3, 137.8, 137.5, 135.5, 134.8, 133.2 (2C), 132.8, 132.4, 130.9 (3C), 130.2, 130.1, 129.8 (2C), 129.7, 129.2, 128.3 (3C), 127.2, 126.9 (4C), 126.7, 125.8, 125.5, 122.0, 117.1, 74.8, 68.9, 52.8, 48.2, 29.5, 27.8. IR (KBr): 3303,

3056, 3027, 1599, 1492, 1451, 1335, 1204, 1126, 1101, 1039, 1005, 940, 750, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{41}H_{32}N_5^+$: 594.2652; found 594.2641.

*(±)-((1R,2S,4S,5S,6R)-1,5,6-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-yl)methanol (**7aao**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-serine (**6o**) (63 mg, 0.6 mmol). Purified by PTLC (Al_2O_3, CH_2Cl_2–hexane, 2:1) and subsequent crystallization from a mixture of hexane–Et_2O. Light yellow solid; yield: 98 mg (60%); mp 254–255 °C (hexane–Et_2O); TLC (R_f = 0.36, SiO_2, hexane–EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36–8.31 (m, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 8.03 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.83–7.69 (m, 4H), 7.63–7.58 (m, 1H), 7.49–7.44 (m, 1H), 7.38–7.24 (m, 4H), 7.04–6.98 (m, 1H), 6.95–6.89 (m, 2H), 6.69–6.63 (m, 1H), 6.52–6.43 (m, 5H), 5.12 (t, *J* = 5.0 Hz, 1H), 4.04 (s, 1H), 3.93–3.84 (m, 2H), 2.25–1.85 (m, 2H, exchange with H_2O). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.3, 153.1, 147.3, 142.2, 141.5, 137.6, 136.9, 134.8, 133.0 (2C), 131.8, 131.3, 130.9 (3C), 129.7, 129.5, 129.4, 129.2, 128.8, 127.9 (3C), 127.0, 126.7 (2C), 126.6 (2C), 126.4, 125.3, 124.8, 122.1, 73.8, 68.8, 63.1, 52.2, 45.4, 30.3. IR (KBr): 3338, 3055, 2871, 1601, 1579, 1495, 1337, 1107, 1043, 1035, 1021, 758, 746, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{38}H_{30}N_3O^+$: 544.2383; found 544.2407.

*(±)-((1R,2S,4S,5S,6R)-1,5,6-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-yl)methanethiol (**7aap**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-cysteine (**6p**) (73 mg, 0.6 mmol). Purified by recrystallization from hexane–CH_2Cl_2. Light yellow solid; yield: 114 mg (68%); mp 240–241 °C (hexane–CH_2Cl_2); TLC (R_f = 0.64, SiO_2, hexane–EtOAc, 5:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40–8.36 (m, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.85–7.69 (m, 4H), 7.66–7.61 (m, 1H), 7.52–7.47 (m, 1H), 7.39–7.26 (m, 4H), 7.04–6.99 (m, 1H), 6.95–6.89 (m, 2H), 6.69–6.64 (m, 1H), 6.52–6.43 (m, 5H), 5.05 (dd, *J* = 9.1, 3.2 Hz, 1H), 4.01 (s, 1H), 2.85–2.73 (m, 2H), 1.89 (br s, 1H, exchanges with H_2O), 1.44 (t, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 153.2, 147.5, 142.3, 141.5, 137.5, 136.9, 134.4, 133.1 (2C), 131.8, 131.4, 130.9 (2C), 129.7, 129.6, 129.4, 129.2, 128.8, 127.9 (3C), 127.1 (2C), 126.7 (2C), 126.6 (2C), 126.4, 125.3, 125.1, 122.0, 73.3, 69.5, 53.0, 47.1, 30.2, 26.3. IR (KBr): 3279, 3058, 2923, 2854, 2567, 1602, 1497, 1338, 1105, 761, 747, 699 cm^{-1}. HRMS (ESI): *m/z* $[M - SH]^+$ calcd for $C_{38}H_{28}N_3^+$: 526.2278; found 526.2301.

*(±)-2-((1R,2S,4R,5S,6R)-1,5,6-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-yl)ethanol (**7aaq**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *DL*-homoserine (**6q**) (71 mg, 0.6 mmol). Purified by recrystallization from MeOH–H_2O. Light yellow solid; yield: 119 mg (71%); mp > 260 °C (MeOH–H_2O); TLC (R_f = 0.50, SiO_2, hexane–EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.1, 1.1 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.95–7.92 (m, 1H), 7.85–7.69 (m, 4H), 7.65–7.61 (m, 1H), 7.52–7.48 (m, 1H), 7.38–7.24 (m, 4H), 7.04–6.91 (m, 3H), 6.69–6.64 (m, 1H), 6.52–6.45 (m, 5H), 5.09 (dd, *J* = 7.7, 3.8 Hz, 1H), 3.98–3.91 (m, 1H), 3.87 (s, 1H), 3.77–3.70 (m, 1H), 2.50–2.00 (m, 2H, exchange with H_2O), 1.98–1.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.7, 153.1, 142.2, 141.5, 137.7, 136.9, 134.6, 133.1 (2C), 131.9, 131.5, 130.9 (4C), 129.8, 129.6, 129.4, 129.2, 128.8, 127.8 (2C), 126.9, 126.7 (2C), 126.6 (3C), 126.4, 125.3, 124.7, 122.2, 74.4, 67.5, 61.6, 52.1, 47.6, 32.6, 30.3. IR (KBr): 3277, 3050, 3025, 2933, 2917, 1602, 1497, 1335, 1101, 1045, 1029, 758, 742, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{39}H_{32}N_3O^+$: 558.2540; found 558.2559.

*(±)-Amino((3-((1R,2S,4R,5S,6R)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-yl)propyl)amino)methaniminium chloride (**7aar**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-arginine hydrochloride (**6r**) (126 mg, 0.6 mmol). Purified by PTLC (Al_2O_3, CH_2Cl_2–MeOH, 20:1) and subsequent crystallization from Et_2O. Light yellow solid; yield: 115 mg (59%); mp 205–207 °C (Et_2O); TLC (R_f = 0.34, SiO_2, MeOH–CH_2Cl_2, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.42–8.34 (m, 2H), 8.03–7.99 (m, 1H), 7.93–7.80 (m, 3H), 7.75–7.62 (m, 4H), 7.57–7.52 (m, 1H), 7.41–6.85 (m, 10H), 6.68–6.62 (m, 1H), 6.51–6.43 (m, 4H), 4.66–4.59 (m, 1H), 4.02 (d, *J* = 7.4 Hz, 1H), 3.98 (s, 1H), 3.49–3.31 (m, 2H, overlapping with H_2O), 3.09–2.98 (m, 2H), 1.82–1.70 (m, 1H), 1.65–1.52 (m, 1H), 1.48–1.32 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 165.8, 157.4, 153.4, 148.0, 141.9, 141.3, 137.9, 137.4, 135.7, 133.1 (2C), 132.8, 132.4, 131.0 (2C), 130.2, 130.1, 129.8 (2C), 129.3 (2C), 128.3 (3C), 127.2, 126.9 (4C), 126.7, 126.3, 125.5, 121.9, 74.9, 68.9, 53.1, 48.5, 41.5, 29.6, 27.7, 26.9. IR (KBr): 3336, 3255, 3155, 3057, 1666, 1601, 1495, 1445, 1337, 1107, 757, 702 cm^{-1}. HRMS (ESI): *m/z* $[M - Cl]^+$ calcd for $C_{41}H_{37}N_6^+$: 613.3074; found 613.3098.

*(±)-2-((1R,2S,4R,5S,6R)-1,5,6-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-yl)acetamide (**7aas**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-asparagine (**6s**) (79 mg, 0.6 mmol). Purified by recrystallization from hexane–CH_2Cl_2. Light yellow solid, yield: 130 mg (76%); mp > 260 °C (hexane–CH_2Cl_2); TLC (R_f = 0.39,

SiO_2, CH_2Cl_2–MeOH, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.1 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.83–7.70 (m, 4H), 7.63–7.57 (m, 1H), 7.49–7.43 (m, 1H), 7.38–7.24 (m, 4H), 7.04–6.98 (m, 1H), 6.95–6.89 (m, 2H), 6.68–6.63 (m, 1H), 6.52–6.41 (m, 5H), 5.76 (s, 1H), 5.59 (s, 1H), 5.26 (dd, *J* = 9.7, 2.7 Hz, 1H), 3.89 (s, 1H), 3.16 (br s, 1H), 2.64–2.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.2, 165.2, 153.1, 147.4, 142.2, 141.5, 137.6, 137.0, 134.3, 133.1 (2C), 131.7, 131.5, 130.8 (3C), 129.7, 129.6, 129.3, 129.1, 128.8, 127.9 (3C), 127.1, 126.7 (2C), 126.6 (2C), 126.4, 125.3, 124.9, 122.0, 74.0, 64.7, 52.6, 47.1, 37.1, 30.1. IR (KBr): 3229, 3055, 3026, 1687, 1671, 1599, 1496, 1400, 1335, 1221, 1180, 1126, 949, 777, 760, 750, 703 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{39}H_{31}N_4O^+$: 571.2492; found 517.2514.

*(±)-3-((1R,2S,4R,5S,6R)-1,5,6-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-yl)propenamide (**7aat**)*. Prepared following the general procedure **B** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and *L*-glutamine (**6t**) (88 mg, 0.6 mmol). Purified by recrystallization from hexane–CH_2Cl_2. Light yellow solid; yield: 109 mg (62%); mp 249–250 °C (hexane–CH_2Cl_2); TLC (R_f = 0.32, SiO_2, CH_2Cl_2–MeOH, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.40 (d, *J* = 7.4 Hz, 1H), 8.33 (d, *J* = 7.7 Hz, 1H), 8.03–7.99 (m, 1H), 7.92–7.80 (m, 4H), 7.76–7.70 (m, 1H), 7.68–7.62 (m, 2H), 7.58–7.52 (m, 1H), 7.41–7.34 (m, 2H), 7.29–7.24 (m, 1H), 7.15 (s, 1H), 6.99–6.93 (m, 1H), 6.91–6.85 (m, 2H), 6.67–6.62 (m, 2H), 6.51–6.43 (m, 5H), 4.63–4.57 (m, 1H), 3.96–3.92 (m, 2H), 2.23–2.13 (m, 1H), 2.02–1.82 (m, 2H), 1.69–1.57 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 174.8, 165.8, 153.3, 148.1, 141.9, 141.3, 137.9, 137.4, 135.7, 133.1 (2C), 132.8, 132.4, 131.0 (3C), 130.2, 130.1, 129.8 (2C), 129.3 (2C), 128.3 (2C), 127.2, 126.9 (4C), 126.7, 126.1, 125.5, 121.9, 74.7, 68.8, 53.0, 48.4, 33.5, 29.6, 26.9. IR (KBr): 3341, 3292, 3052, 2936, 2908, 1684, 1646, 1601, 1497, 1453, 1444, 1403, 1178, 1106, 771, 759, 741, 696 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{40}H_{33}N_4O^+$: 585.2649; found 586.2676.

General procedure C for the one-pot three-component reaction of cyclopropenes, 11*H*-indeno[1,2-*b*]quinoxalin-11-ones and peptides: A mixture of corresponding cyclopropene **1** (0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (0.3 mmol), and peptide **8** (0.6 mmol) was refluxed in a mixture of MeOH–H_2O (3:1, 8 mL) in the presence of AcOH (0.17 mL, 3 mmol) for 24 h until TLC showed the absence either of starting cyclopropene **1** or of any further changes. After cooling, all volatiles were removed *in vacuo*, and acetone (5 mL) was added to the residue. Filtration to remove an excess of insoluble peptide followed by removal of the solvent under reduced pressure gave a viscous yellow oil which was crystallized from Et_2O as a beige solid.

*(±)-2-((1R,2S,4S,5S,6R)-1,5,6-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-ylcarboxamido)acetic acid (**9aaa**)*. Prepared following the general procedure **C** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and diglycine (**8a**) (79 mg, 0.6 mmol). Purified by recrystallization from Et_2O. Beige solid; yield: 142 mg (77%); mp 248–249 °C (Et_2O); TLC (R_f = 0.32, SiO_2, CH_2Cl_2–MeOH, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ =12.54 (br s, 1H), 8.46 (d, *J* = 7.5 Hz, 1H), 8.41 (d, *J* = 8.1 Hz, 1H), 8.36–8.31 (m, 1H), 8.06–7.74 (m, 5H), 7.67–7.54 (m, 3H), 7.33–7.20 (m, 3H), 6.97–6.80 (m, 3H), 6.70–6.64 (m, 1H), 6.53–6.38 (m, 6H), 5.17 (s, 1H), 4.42 (br s, 1H), 4.25 (s. 1H), 3.91 (dd, *J* = 17.4, 6.1 Hz, 1H), 3.80 (dd, *J* = 17.2, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 171.7, 170.6, 165.9, 153.4, 148.1, 142.0, 141.3, 137.4 (2C), 134.5, 133.6 (2C), 132.4 (2C), 132.1, 131.3 (2C), 130.3, 130.1, 129.8, 129.7, 129.3, 127.7 (2C), 127.1, 126.9 (3C), 126.6 (3C), 126.3, 125.5, 121.9, 74.2, 70.5, 52.0, 46.8, 41.1, 30.2. IR (KBr): 3378, 3337, 3058, 3031, 1743, 1728 1665, 1534, 1498, 1417, 1336, 1207, 1110, 760, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{40}H_{31}N_4O_3^+$: 615.2391; found 615.2388.

*(±)-2-((1R,2S,4S,5S,6R)-6-(Methoxycarbonyl)-1,5-diphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-ylcarboxamido)acetic acid (**9baa**)*. Prepared following the general procedure **C** from cyclopropene **1b** (75 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and diglycine (**8a**) (79 mg, 0.6 mmol). Purified by recrystallization from Et_2O. Beige solid; yield: 113 mg (63%); mp 183–185 °C (Et_2O); TLC (R_f = 0.32, SiO_2, CH_2Cl_2–MeOH, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6), zwitterionic form: δ = 8.40 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 7.7 Hz, 1H), 8.13–8.08 (m, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.94–7.75 (m, 6H), 7.64–7.59 (m, 1H), 7.42–7.36 (m, 2H), 7.29–7.23 (m, 1H), 6.73–6.66 (m, 1H), 6.59–6.52 (m, 5H), 5.10 (s, 1H), 4.38 (br s, 1H), 3.86 (s, 1H) 3.78 (dd, *J* = 17.4, 5.5 Hz, 1H), 3.69 (dd, *J* = 17.4, 6.0 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 171.6, 169.6 (2C), 165.1, 153.3, 147.2, 142.0, 141.2, 137.4, 134.3, 132.6, 132.5 (3C), 130.9 (2C), 130.6, 130.3, 129.9, 129.7, 129.3, 127.8 (2C), 127.2, 126.9 (3C), 126.1, 122.0, 73.8, 70.1, 52.9, 51.7, 48.2, 42.0, 27.5. IR (KBr): 3318, 3058, 2948, 1745, 1669, 1604, 1512, 1442, 1400, 1338, 1204, 1171, 773, 755, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}N_4O_5^+$: 597.2132; found 597.2138.

*(±)-2-((1R,2S,4S,5S,6R)-1,5-Diphenyl-6-vinyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-ylcarboxamido)acetic acid (**9faa**)*. Prepared following the general procedure **C** from cyclopropene **1f** (65 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and diglycine (**8a**) (79 mg, 0.6 mmol). Purified by recrystallization from Et_2O. Beige solid; yield: 156 mg (92%); mp 245–246 °C (Et_2O); TLC (R_f = 0.30, SiO_2, CH_2Cl_2–MeOH, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6), zwitterionic form: δ = 8.42–8.38 (m, 1H), 8.30 (d, *J* = 7.7

Hz, 1H), 8.17–8.12 (m, 1H), 8.03–8.00 (m, 1H), 7.97–7.75 (m, 7H), 7.61–7.56 (m, 1H), 7.43–7.37 (m, 2H), 7.26–7.21 (m, 1H), 6.73–6.65 (m, 1H), 6.62–6.56 (m, 4H), 5.56 (dd, *J* = 16.9, 2.1 Hz, 1H), 5.12 (s, 1H), 4.99 (dd, *J* = 10.2, 2.2 Hz, 1H), 4.89–4.79 (m, 1H), 4.31 (br s, 1H), 3.88 (dd, *J* = 17.4, 6.1 Hz, 1H), 3.81–3.72 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 171.8, 170.4, 165.7, 153.4, 148.2, 142.0, 141.3, 137.7, 137.3, 136.7, 133.1, 132.5 (3C), 132.1 (2C), 130.3, 130.2, 129.8, 129.7, 129.3, 128.2 (2C), 127.1 (3C), 126.9, 126.2, 121.9, 114.7, 73.6, 69.6, 49.9, 45.1, 41.4, 29.6. IR (KBr): 3372, 3334, 3057, 3029, 1743, 1727, 1654, 1605, 1539, 1509, 1432, 1337, 1208, 1110, 914, 773, 758, 745, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{36}H_{29}N_4O_3^+$: 565.2234; found 565.2257.

*(±)-2-((1R,2S,4S,5S)-1,5-Diphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-ylcarboxamido)acetic acid (**9gaa**).* Prepared following the general procedure **C** from cyclopropene **1g** (58 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and diglycine (**8a**) (79 mg, 0.6 mmol). Purified by recrystallization from Et_2O. Beige solid; yield: 116 mg (72%); mp 184–186 °C (Et_2O); TLC (R_f = 0.36, SiO_2, CH_2Cl_2–MeOH, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6), zwitterionic form: δ = 8.37 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.18–7.99 (m, 3H), 7.91–7.71 (m, 5H), 7.59–7.51 (m, 1H), 7.35–7.28 (m, 2H), 7.19–7.13 (m, 1H), 6.69–6.63 (m, 1H), 6.56–6.47 (m, 5H), 5.40 (s, 1H), 4.29 (br s, 1H), 3.78–3.65 (m, 2H), 2.71 (d, *J* = 4.8 Hz, 1H), 1.61 (d, *J* = 4.7 Hz, 1H) . ^{13}C NMR (101 MHz, DMSO-d_6): δ = 171.8, 170.8, 165.8, 153.5, 148.5, 142.1, 141.2, 138.2, 137.0, 135.9, 132.4, 131.8 (2C), 130.2 (2C), 130.1 (2C), 129.8, 129.7, 129.3, 128.3 (2C), 127.1 (2C), 126.8 (2C), 126.0, 121.9, 72.8, 66.2, 47.7, 42.0, 40.7, 16.1. IR (KBr): 3329, 3057, 3026, 2926, 1726, 1663, 31603, 1511, 1397, 1336, 1206, 1105, 759, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{34}H_{27}N_4O_3^+$: 539.2078; found 539.2099.

*(±)-2-(2-((1R,2S,4S,5S,6R)-1,5,6-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-ylcarboxamido)acetamido)acetic acid (**9aab**).* Prepared following the general procedure **C** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and triglycine (**8b**) (114 mg, 0.6 mmol). Purified by recrystallization from Et_2O. Beige solid; yield: 143 mg (71%); mp 175–176 °C (Et_2O); TLC (R_f = 0.34, SiO_2, CH_2Cl_2–MeOH, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6), zwitterionic form: δ = 8.47 (d, *J* = 7.3 Hz, 1H), 8.41 (d, *J* = 7.7 Hz, 1H), 8.38–8.32 (m, 1H), 8.05–7.73 (m, 7H), 7.62–7.53 (m, 3H), 7.34–7.18 (m, 3H), 6.98–6.82 (m, 3H), 6.70–6.65 (m, 1H), 6.53–6.37 (m, 6H), 5.19 (s, 1H), 4.40 (br s, 1H), 4.23 (s, 1H), 3.90–3.63 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 171.7, 170.3, 169.5, 165.9, 153.3, 148.0, 142.0, 141.3, 137.4, 137.3, 134.4, 133.5 (2C), 132.5 (2C), 131.9, 131.2 (2C), 130.4, 130.2, 129.9, 129.8, 129.3, 127.8 (2C), 127.2, 127.0 (3C), 126.8 (2C), 126.3 (2C), 125.6, 121.9, 74.1, 70.6, 52.1, 46.6, 42.4, 41.8, 30.1. IR (KBr): 3314, 3058, 2927, 2858, 1731, 1659, 1519, 1401,

1337, 1206, 1104, 1023, 759, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{34}N_5O_4^+$: 672.2605; found 672.2621.

*(±)-2-(2-((1R,2S,4S,5S,6R)-6-(Methoxycarbonyl)-1,5-diphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-ylcarboxamido)acetamido)acetic acid (**9bab**).* Prepared following the general procedure **C** from cyclopropene **1b** (75 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and triglycine (**8b**) (114 mg, 0.6 mmol). Purified by recrystallization from Et_2O. Beige solid; yield: 122 mg (62%); mp 175–177 °C (Et_2O); TLC (R_f = 0.40, SiO_2, CH_2Cl_2–MeOH, 10:1). ^1H NMR (400 MHz, DMSO-d_6), zwitterionic form: δ = 8.39 (d, *J* = 7.9 Hz, 1H), 8.31 (d, *J* = 7.7 Hz, 1H), 8.28–8.24 (m, 1H), 8.04–8.00 (m, 1H), 7.94–7.70 (m, 7H), 7.64–7.59 (m, 1H), 7.43–7.37 (m, 2H), 7.29–7.24 (m, 1H), 6.73–6.66 (m, 1H), 6.59–6.50 (m, 5H), 5.14 (s, 1H), 4.34 (br s, 1H), 3.85 (s, 1H), 3.81–3.61 (m, 4H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 169.8, 169.5, 168.9, 166.6, 165.1, 153.2, 147.1, 142.0, 141.1, 137.4, 134.2, 132.6, 132.4 (2C), 130.9 (2C), 130.6, 130.4, 130.0, 129.7, 129.3, 127.9 (2C), 127.3, 126.9 (4C), 126.2, 122.0, 73.7, 70.2, 52.9, 51.8, 48.2, 44.8, 42.6, 27.3. IR (KBr): 3321, 3057, 3028, 2948, 1745, 1711, 1676, 1605, 1511, 1437, 1399, 1338, 1298, 1106, 778, 754, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{38}H_{31}N_5NaO_6^+$: 676.2167; found 676.2187.

*(±)-2-(2-((1R,2S,4S,5S,6R)-1,5-Diphenyl-6-vinyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-ylcarboxamido)acetamido)acetic acid (**9fab**).* Prepared following the general procedure **C** from cyclopropene **1f** (65 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and triglycine (**8b**) (114 mg, 0.6 mmol). Purified by recrystallization from Et_2O. Beige solid; yield: 123 mg (66%); mp 234–235 °C (Et_2O); TLC (R_f = 0.28, SiO_2, CH_2Cl_2–MeOH, 10:1). ^1H NMR (400 MHz, DMSO-d_6), zwitterionic form: δ = 8.40 (d, *J* = 7.8 Hz, 1H), 8.36–8.31 (m, 1H), 8.25–8.18 (m, 1H), 8.06–7.75 (m, 9H), 7.63–7.56 (m, 1H), 7.46–7.36 (m, 2H), 7.28–7.21 (m, 1H), 6.74–6.65 (m, 1H), 6.63–6.54 (m, 4H), 5.55 (d, *J* = 16.6 Hz, 1H), 5.16 (s, 1H), 5.04–4.78 (m, 2H), 4.29 (br s, 1H), 3.88–3.68 (m, 5H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 171.8, 170.4, 169.4, 165.6, 153.4, 148.1, 142.0, 141.2, 137.7, 137.3, 136.7, 133.0, 132.6, 132.4 (2C), 132.1 (2C), 130.3, 130.2, 129.9, 129.7, 129.3, 128.3 (2C), 127.1 (3C) 126.9, 126.2, 121.9, 114.8, 73.4, 69.6, 49.9, 45.0, 42.3, 41.8, 29.5. IR (KBr): 3399, 3355, 3319, 3057, 1677, 1669, 1584, 1513, 1412, 1337, 1265, 1226, 1107, 771, 753, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{38}H_{31}N_5NaO_4^+$: 644.2268; found 644.2294.

*(±)-2-(2-((1R,2S,4S,5S)-1,5-Diphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxalin]-4-ylcarboxamido)acetamido)acetic acid (**9gab**).* Prepared following the general procedure **C** from cyclopropene **1g** (58 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**)

(70 mg, 0.3 mmol), and triglycine (**8b**) (114 mg, 0.6 mmol). Purified by recrystallization from Et_2O. Beige solid; yield: 104 mg (58%); mp 199–200 °C (Et_2O); TLC (R_f = 0.40, SiO_2, CH_2Cl_2–MeOH, 10:1). ^{1}H NMR (400 MHz, DMSO-d_6), zwitterionic form: δ = 8.37 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.24–8.18 (m, 1H), 8.05–7.98 (m, 2H), 7.92–7.72 (m, 6H), 7.60–7.54 (m, 1H), 7.36–7.28 (m, 2H), 7.20–7.14 (m, 1H), 6.69–6.64 (m, 1H), 6.56–6.48 (m, 5H), 5.48 (s, 1H), 4.26 (br s, 1H), 3.89 (dd, *J* = 16.7, 5.7 Hz, 1H), 3.82–3.72 (m, 3H), 2.73 (d, *J* = 4.6 Hz, 1H), 1.64 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 171.6, 171.1, 169.6, 165.8, 153.5, 148.4, 142.1, 141.2, 138.0, 137.0, 135.8, 132.4, 131.8 (2C), 130.2 (2C), 130.1 (3C), 129.8 (2C), 129.3, 128.4 (2C), 127.1 (2C), 126.8, 126.2, 121.9, 72.6, 66.3, 47.8, 42.2, 41.4, 40.5, 16.0. IR (KBr): 3324, 3058, 2926, 1663, 1512, 1498, 1401, 1337, 1206, 1106, 759, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{36}H_{30}N_5O_4^+$: 596.2292; found 596.2320.

General procedure D for the one-pot three-component reaction of cyclopropenes, 11*H*-indeno[1,2-*b*]quinoxalin-11-ones, and amines: A mixture of corresponding cyclopropene **1** (0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one **2** (0.3 mmol), and amine **10** (0.6 mmol) was refluxed in MeOH (6 mL) for 24 h until complete consumption of **1** as monitored by TLC. The solvent was removed under reduced pressure. The residue was recrystallized from MeOH to furnish **11** as a light yellow solid.

*Methyl (±)-(1R,2S,4R,5S,6R)-1,4,5-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline]-6-carboxylate (**11baa**)*. Prepared following the general procedure **D** from cyclopropene **1b** (75 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and benzylamine (**10a**) (64 mg, 0.6 mmol). Light yellow solid; yield: 151 mg (88%); mp > 260 °C (MeOH); TLC (R_f = 0.36, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.1 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.86–7.72 (m, 3H), 7.69–7.65 (m, 2H), 7.61–7.56 (m, 1H), 7.41–7.22 (m, 8H), 6.76–6.67 (m, 3H), 6.62–6.57 (m, 2H), 6.05 (s, 1H), 3.83 (s, 1H), 3.30 (s, 3H), 2.55 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.1, 165.1, 153.1, 147.3, 142.1, 141.5, 138.7, 137.5, 134.3, 132.3 (3C), 132.1, 130.6 (2C), 130.0, 129.6, 129.5, 129.1, 129.0, 127.9 (2C), 127.6 (3C), 127.4 (2C), 127.1, 126.7 (2C), 126.6, 125.5, 122.2, 72.9, 69.8, 53.2, 51.1, 50.6, 27.6. IR (KBr): 3312, 3054, 3030, 1743, 1600, 1575, 1508, 1442, 1339, 1187, 1167, 754, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{39}H_{30}N_3O_2^+$: 572.2333; found 572.2358.

*(±)-(1R,2S,4R,5S,6R)-N-Isopropyl-1,4,5-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline]-6-carboxamide (**11caa**)*. Prepared following the general procedure **D** from cyclopropene **1c** (83 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3

mmol), and benzylamine (**10a**) (64 mg, 0.6 mmol). Light yellow solid; yield: 108 mg (60%); mp 155–157 °C (MeOH); TLC (R_f = 0.32, SiO_2, hexane–EtOAc, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40–8.37 (m, 2H), 8.04 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.86–7.72 (m, 5H), 7.61–7.57 (m, 1H), 7.44–7.33 (m, 3H), 7.29–7.26 (m, 5H), 6.87–6.77 (m, 3H), 6.69–6.64 (m, 2H), 5.98 (s, 1H), 3.79 (s, 1H), 3.66–3.57 (m, 1H), 3.50 (d, *J* = 7.6 Hz, 1H), 2.54 (s, 1H), 0.51 (d, *J* = 6.5 Hz, 3H), 0.19 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.0, 165.0, 153.3, 142.3, 141.5, 138.4, 137.6, 133.7, 133.3 (2C), 132.3, 131.9, 131.5 (2C), 130.0, 129.5 (2C), 129.2, 128.9, 128.0 (2C), 127.9 (3C), 127.8, 127.7, 127.5 (2C), 127.4 (2C), 127.3, 125.7, 122.0, 73.0, 70.2, 50.9, 48.9, 40.7, 30.4, 21.7, 21.4. IR (KBr): 3421, 3292, 3056, 2970, 2870, 1639, 1532, 1493, 1367, 1336, 1107, 761, 705 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{41}H_{35}N_4O^+$: 599.2805; found 599.2828.

*(±)-(1R,2S,4R,5S,6R)-1,4,5-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline]-6-carbonitrile (**11daa**)*. Prepared following the general procedure **D** from cyclopropene **1d** (65 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and benzylamine (**10a**) (64 mg, 0.6 mmol). Light yellow solid; yield: 139 mg (86%); mp > 260 °C (MeOH); TLC (R_f = 0.32, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 8.09–8.05 (m, 1H), 8.03–7.99 (m, 3H), 7.87–7.72 (m, 3H), 7.63–7.58 (m, 1H), 7.49–7.43 (m, 2H), 7.40–7.22 (m, 6H), 6.85–6.78 (m, 3H), 6.72–6.66 (m, 2H), 6.17 (s, 1H), 3.65 (s, 1H), 2.55 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.1, 152.9, 146.3, 142.1, 141.3, 137.9, 137.4, 133.2, 132.2, 131.4 (4C), 130.4, 129.9 (2C), 129.5, 129.3, 129.2, 128.5 (2C), 128.3 (2C), 128.1, 128.0, 127.8, 127.4 (2C), 126.8 (2C), 125.0, 122.5, 118.7, 71.8, 67.6, 51.8, 48.6, 13.0. IR (KBr): 3286, 3057, 3028, 2238, 1604, 1578, 1505, 1497, 1449, 1337, 1104, 1055, 756, 701 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{38}H_{27}N_4^+$: 539.2230; found 539.2246.

*(±)-(1R,2S,4R,5S,6R)-6-Ethyl-1,4,5-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11eaa**)*. Prepared following the general procedure **D** from cyclopropene **1e** (66 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and benzylamine (**10a**) (64 mg, 0.6 mmol). Light yellow solid; yield: 151 mg (93%); mp 209–210 °C (MeOH); TLC (R_f = 0.58, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 8.03 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.99–7.95 (m, 2H), 7.80–7.68 (m, 3H), 7.64–7.59 (m, 1H), 7.44–7.38 (m, 2H), 7.34–7.25 (m, 6H), 6.74–6.66 (m, 3H), 6.62–6.57 (m, 2H), 5.95 (s, 1H), 2.76 (t, *J* = 6.8 Hz, 1H), 2.40 (br s, 1H), 1.57–1.45 (m, 1H), 1.27–1.16 (m, 1H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.9, 153.3, 149.3, 142.1, 141.6, 140.2, 137.9, 137.7, 134.1, 132.2 (2C), 131.9, 130.7 (2C), 129.6, 129.5, 129.1

(2C), 128.6, 127.9 (2C), 127.8 (2C), 127.3 (2C), 127.2, 126.7 (2C), 126.5, 126.0, 125.2, 122.2, 72.6, 69.5, 48.1, 45.7, 27.6, 20.3, 14.6. IR (KBr): 3293, 3051, 2974, 2851, 1600, 1496, 1335, 1101, 761, 699 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{39}H_{32}N_3^+$: 542.2591; found 542.2601.

*(±)-(1R,2S,4R,5S,6R)-1,4,5-Triphenyl-6-vinyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11faa**)*. Prepared following the general procedure **D** from cyclopropene **1f** (65 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and benzylamine (**10a**) (64 mg, 0.6 mmol). Light yellow solid; yield: 128 mg (79%); mp 238–239 °C (MeOH); TLC (R_f = 0.56, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.99–7.92 (m, 3H), 7.85–7.68 (m, 3H), 7.58–7.53 (m, 1H), 7.41–7.25 (m, 8H), 6.77–6.71 (m, 3H), 6.64–6.59 (m, 2H), 6.11 (s, 1H), 5.41 (dd, *J* = 16.8, 2.3 Hz, 1H), 5.06 (dt, *J* = 16.8, 10.3 Hz, 1H), 4.96 (dd, *J* = 10.1, 2.4 Hz, 1H), 3.66 (d, *J* = 10.5 Hz, 1H), 2.51 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.7, 153.4, 148.2, 142.3, 141.5, 139.7, 137.9, 137.5, 136.7, 133.0, 132.6 (2C), 132.1 (2C), 131.9, 129.6 (2C), 129.3, 129.2, 128.8, 127.9 (4C), 127.3 (3C), 126.8 (3C), 126.4, 125.3, 122.0, 113.5, 73.1, 69.5, 50.3, 47.1, 29.9. IR (KBr): 3372, 3055, 1601, 1448, 1335, 1101, 904, 754, 698 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{39}H_{30}N_3^+$: 540.2434; found 540.2452.

*(±)-(1R,2S,4R,5S)-1,4,5-Triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11gaa**)*. Prepared following the general procedure **D** from cyclopropene **1g** (58 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and benzylamine (**10a**) (64 mg, 0.6 mmol). Light yellow solid; yield: 103 mg (67%); mp 195–196 °C (MeOH); TLC (R_f = 0.50, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.08–8.04 (m, 1H), 8.01–7.97 (m, 1H), 7.85–7.72 (m, 4H), 7.71–7.65 (m, 1H), 7.56–7.51 (m, 1H), 7.48–7.44 (m, 2H), 7.37–7.19 (m, 6H), 6.73–6.63 (m, 3H), 6.60–6.55 (m, 2H), 6.37 (s, 1H), 2.67 (d, *J* = 4.7 Hz, 1H), 2.21 (br s, 1H), 1.59 (d, *J* = 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.6, 153.5, 148.3, 142.3, 141.5, 140.5, 138.1, 137.3, 135.8, 131.7, 131.5 (2C), 130.3 (2C), 129.7, 129.6, 129.4, 129.2, 128.8, 128.1 (2C), 128.0 (2C), 127.2 (3C), 126.9 (2C), 126.6, 126.3, 125.0, 122.1, 72.6, 66.3, 47.9, 42.7, 16.0. IR (KBr): 3332, 3285, 3052, 1602, 1494, 1447, 1366, 1337, 1106, 1031, 758, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{37}H_{28}N_3^+$: 514.2278; found 514.2297.

*(±)-(1R,2S,4R,5S,6R)-7',8'-Dimethyl-1,4,5,6-tetraphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11aba**)*. Prepared following the general procedure **D** from cyclopropene **1a** (81 mg, 0.3 mmol), 7,8-dimethyl-11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2b**) (78 mg, 0.3 mmol), and benzylamine (**10a**) (64 mg, 0.6 mmol). Light yellow solid; yield: 167 mg

(90%); mp > 260 °C (MeOH); TLC (R_f = 0.52, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 7.7 Hz, 1H), 8.17 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.80 (s, 1H), 7.67–7.62 (m, 1H), 7.57–7.46 (m, 3H), 7.36–7.22 (m, 9H), 6.97–6.83 (m, 3H), 6.70–6.65 (m, 1H), 6.54–6.47 (m, 3H), 6.44–6.40 (m, 2H), 6.12 (s, 1H), 4.16 (s, 1H), 2.65 (s, 3H), 2.60 (br s, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.0, 152.3, 147.8, 140.8, 140.4, 139.6, 139.1, 137.8, 137.2, 134.6, 133.8 (2C), 132.5, 131.8, 131.4, 131.0 (3C), 129.5, 128.9, 128.4, 128.0, 127.8, 127.4 (4C), 127.3, 127.0, 126.7, 126.6 (2C), 126.4 (2C), 126.3, 125.2, 125.0, 121.8, 73.6, 70.4, 52.6, 48.9, 30.4, 20.4, 20.3. IR (KBr): 3346, 3052, 3029, 2878, 1600, 1572, 1496, 1420, 1335, 1106, 1024, 759, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{45}H_{36}N_3^+$: 618.2904; found 618.2926.

*(±)-(1R,2S,4R,5S,6R)-1,5,6-Triphenyl-4-(p-tolyl)-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11aab**).* Prepared following the general procedure **D** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and 4-xylylamine (**10b**) (73 mg, 0.6 mmol). Light yellow solid; yield: 168 mg (93%); mp > 260 °C (MeOH); TLC (R_f = 0.50, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.32 (d, *J* = 7.7 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.87–7.81 (m, 1H), 7.79–7.74 (m, 1H), 7.70–7.65 (m, 1H), 7.59–7.49 (m, 3H), 7.31–7.20 (m, 6H), 7.09–7.04 (m, 2H), 6.97–6.92 (m, 1H), 6.89–6.84 (m, 2H), 6.71–6.65 (m, 1H), 6.53–6.47 (m, 3H), 6.45–6.41 (m, 2H), 6.10 (s, 1H), 4.15 (s, 1H), 2.60 (br s, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.0, 153.3, 148.1, 142.2, 141.6, 137.6, 137.2, 136.9, 136.4, 134.7, 133.7 (2C), 131.8 (2C), 131.0 (2C), 129.6 (3C), 129.3, 129.2, 128.8, 128.6 (2C), 127.4 (2C), 127.3 (2C), 126.7 (3C), 126.4 (3C), 126.3, 125.2, 125.0, 122.0, 73.6, 70.3, 52.6, 48.9, 30.5, 21.1. IR (KBr): 3358, 3057, 3026, 2866, 1601, 1573, 1495, 1444, 1333, 1106, 757, 698 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{44}H_{34}N_3^+$: 604.2747; found 604.2770.

*(±)-(1R,2S,4R,5S,6R)-4-(4-Methoxyphenyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11aac**).* Prepared following the general procedure **D** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and 4-methoxybenzylamine (**10c**) (82 mg, 0.6 mmol). Light yellow solid; yield: 158 mg (85%); mp > 260 °C (MeOH); TLC (R_f = 0.40, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.31 (d, *J* = 7.6 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.87–7.81 (m, 1H), 7.79–7.73 (m, 1H), 7.70–7.65 (m, 1H), 7.59–7.49 (m, 3H), 7.30–7.24 (m, 7H), 6.98–6.78 (m, 5H), 6.70–6.65 (m, 1H), 6.55–6.40 (m, 4H), 6.09 (s, 1H), 4.14 (s, 1H), 3.79 (s, 3H), 2.60 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 159.0, 153.3, 148.1, 142.2, 141.6, 137.6, 137.2, 134.7, 133.7 (2C), 131.8, 131.6 (2C), 130.9 (3C), 129.6 (2C), 129.3, 129.2, 128.8, 128.4 (2C), 127.4 (3C), 126.7 (3C), 126.4 (3C), 125.2, 125.1, 122.0, 113.2

(2C), 73.6, 70.0, 55.2, 52.5, 49.0, 30.4. IR (KBr): 3347, 3059, 3026, 2927, 2834, 1610, 1510, 1496, 1443, 1334, 1244, 1170, 1107, 1042, 757, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{44}H_{34}N_3O^+$: 620.2696; found 620.2712.

*(±)-(1R,2S,4R,5S,6R)-4-(4-Fluorophenyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11aad**)*. Prepared following the general procedure **D** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and 4-fluorobenzylamine (**10d**) (75 mg, 0.6 mmol). Light yellow solid; yield: 175 mg (96%); mp > 260 °C (MeOH); TLC (R_f = 0.50, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.31 (d, *J* = 7.7 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.87–7.82 (m, 1H), 7.80–7.74 (m, 1H), 7.71–7.65 (m, 1H), 7.55–7.49 (m, 3H), 7.31–7.25 (m, 7H), 6.98–6.92 (m, 3H), 6.89–6.83 (m, 2H), 6.71–6.66 (m, 1H), 6.54–6.47 (m, 2H), 6.42–6.38 (m, 2H), 6.11 (s, 1H), 4.11 (s, 1H), 2.60 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.9, 163.5, 161.1, 153.2, 148.0, 142.3, 141.5, 137.6, 136.9, 135.2, 134.4, 133.7 (2C), 131.8, 131.6, 130.9 (2C), 129.7, 129.5, 129.4, 129.2, 128.9, 128.7 (2C), 127.5 (2C), 126.9, 126.7 (2C), 126.5 (3C), 126.4, 125.2, 125.1, 122.0, 114.7, 114.5, 73.5, 69.7, 52.6, 48.9, 30.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –115.7. IR (KBr): 3347, 3058, 2876, 1602, 1506, 1443, 1366, 1334, 1221, 1153, 1107, 757, 698 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{31}FN_3^+$: 608.2497; found 608.2518.

*(±)-(1R,2S,4R,5S,6R)-4-(4-Chlorophenyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11aae**)*. Prepared following the general procedure **D** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and 4-chlorobenzylamine (**10e**) (85 mg, 0.6 mmol). Light yellow solid; yield: 146 mg (78%); mp > 260 °C (MeOH); TLC (R_f = 0.56, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 7.4 Hz, 1H), 8.36–8.30 (m, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.98–7.93 (m, 1H), 7.88–7.83 (m, 1H), 7.81–7.75 (m, 1H), 7.71–7.63 (m, 1H), 7.56–7.47 (m, 3H), 7.32–7.18 (m, 9H), 6.98–6.92 (m, 1H), 6.89–6.83 (m, 2H), 6.71–6.66 (m, 1H), 6.54–6.47 (m, 2H), 6.41–6.37 (m, 2H), 6.12 (s, 1H), 4.11 (s, 1H), 2.48 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.8, 153.2, 147.9, 142.1, 141.5, 137.5, 136.8, 134.2, 133.7 (2C), 133.1, 131.9, 130.9 (3C), 129.8, 129.5 (4C), 129.2, 128.9, 128.6 (2C), 128.0 (3C), 127.6 (2C), 127.0, 126.8 (2C), 126.5 (3C), 125.3, 125.2, 122.1, 73.5, 69.7, 52.5, 48.7, 30.4. IR (KBr): 3344, 3055, 2871, 1601, 1491, 1443, 1331, 1107, 1093, 1011, 758, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{31}ClN_3^+$: 624.2201; found 624.2200.

*(±)-(1R,2S,4S,5S,6R)-4-(2,4-Dichlorophenyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11aaf**).* Prepared following the general procedure **D** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and 2,4-dichlorobenzylamine (**10f**) (106 mg, 0.6 mmol). Light yellow solid; yield: 176 mg (89%); mp > 260 °C (MeOH); TLC (R_f = 0.52, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.25–8.21 (m, 2H), 8.06 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.88–7.83 (m, 1H), 7.80–7.75 (m, 1H), 7.67–7.60 (m, 3H), 7.53–7.48 (m, 1H), 7.36 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.26–7.21 (m, 4H), 7.05–7.00 (m, 1H), 6.96–6.91 (m, 2H), 6.73–6.67 (m, 1H), 6.65 (s, 1H), 6.55–6.46 (m, 6H), 4.32 (s, 1H), 2.80 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 153.2, 147.5, 142.3, 141.5, 137.6, 136.7, 136.2, 135.7, 133.6 (3C), 133.5, 131.8, 131.2, 131.0 (2C), 130.0, 129.7 (3C), 129.5, 129.3, 129.2, 128.9, 127.6 (3C), 127.1, 127.0, 126.7 (4C), 126.5, 125.4, 125.2, 122.0, 73.5, 65.4, 51.4, 47.3, 30.9. IR (KBr): 3341, 3061, 3025, 1602, 1585, 1495, 1465, 1446, 1386, 1365, 1335, 1104, 757, 699 cm^{-1}. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{43}H_{30}Cl_2N_3^+$: 658.1811; found 658.1840.

*(±)-(1R,2S,4S,5S,6R)-1,5,6-Triphenyl-4-(pyridin-3-yl)-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11aag**).* Prepared following the general procedure **D** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and 3-picolylamine (**10g**) (65 mg, 0.6 mmol). Light yellow solid; yield: 167 mg (94%); mp > 260 °C (MeOH); TLC (R_f = 0.32, SiO_2, hexane–EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61–8.57 (m, 1H), 8.53–8.49 (m, 1H), 8.44 (d, *J* = 8.2 Hz, 1H), 8.31 (d, *J* = 7.7 Hz, 1H), 8.08–8.02 (m, 1H), 7.97–7.93 (m, 1H), 7.88–7.82 (m, 1H), 7.80–7.75 (m, 1H), 7.72–7.67 (m, 1H), 7.60–7.50 (m, 4H), 7.32–7.25 (m, 5H), 7.23–7.18 (m, 1H), 6.98–6.92 (m, 1H), 6.89–6.83 (m, 2H), 6.72–6.66 (m, 1H), 6.55–6.47 (m, 2H), 6.42–6.38 (m, 2H), 6.16 (s, 1H), 4.12 (s, 1H), 2.60 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.7, 153.3, 148.5, 147.7, 142.5, 141.5, 137.6, 136.5, 135.3 (2C), 133.9, 133.5 (2C), 131.9 (2C), 131.4, 130.9 (2C), 129.8, 129.5 (3C), 129.3, 129.0, 127.8 (2C), 127.2, 126.8 (2C), 126.5 (4C), 125.3, 125.2, 123.0, 122.0, 73.5, 68.4, 52.7, 48.7, 30.4. IR (KBr): 3308, 3058, 3025, 2841, 1601, 1495, 1446, 1336, 1205, 1118, 752, 709, 698 cm^{-1}. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{42}H_{31}N_4^+$: 591.2543; found 591.2555.

*(±)-(1R,2S,4S,5S,6R)-4-(Furan-2-yl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-b]quinoxaline] (**11aah**).* Prepared following the general procedure **D** from cyclopropene **1a** (81 mg, 0.3 mmol), 11*H*-indeno[1,2-*b*]quinoxalin-11-one (**2a**) (70 mg, 0.3 mmol), and furfurylamine (**10h**) (58 mg, 0.6 mmol). Light yellow solid; yield: 151 mg (87%); mp > 260 °C (MeOH); TLC (R_f = 0.30, SiO_2, hexane–EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.25 (d, *J* = 7.7 Hz, 1H), 8.06 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.95 (d, *J*

= 7.5 Hz, 1H), 7.87–7.81 (m, 1H), 7.79–7.74 (m, 1H), 7.68–7.62 (m, 3H), 7.54–7.49 (m, 1H), 7.40 (s, 1H), 7.32–7.21 (m, 3H), 7.04–6.99 (m, 1H), 6.96–6.91 (m, 2H), 6.72–6.66 (m, 1H), 6.55–6.49 (m, 6H), 6.31–6.28 (m, 2H), 6.09 (s, 1H), 4.27 (s, 1H), 2.95 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.3, 153.3, 153.2, 147.1, 142.3, 142.2, 141.5, 137.7, 137.0, 134.3, 133.1 (2C), 132.5, 131.8, 131.5, 131.0 (2C), 129.8, 129.6, 129.4, 129.2, 128.9, 127.6 (3C), 126.8 (3C), 126.6 (2C), 126.4, 125.3, 124.8, 122.1, 110.0, 107.5, 74.0, 66.2, 52.3, 47.5, 30.8. IR (KBr): 3295, 3057, 3029, 1603, 1501, 1335, 1187, 1074, 756, 700 cm^{-1}. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{41}H_{30}N_3O^+$: 580.2383; found 580.2380.

General procedure E for oxidation of 3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-*b*]quinoxalines] to 3-azaspiro[bicyclo[3.1.0]hex-3-ene-2,11'-indeno[1,2-b]quinoxalines]: A 50 mL round-bottom two-necked flask equipped with a magnetic stirbar was charged with corresponding 3-azaspiro[bicyclo[3.1.0]hexane-2,11'-indeno[1,2-*b*]quinoxaline] **11** (1.0 mmol) and dry toluene (25 mL). The suspension was heated and stirred at 80 °C under an argon atmosphere until the starting amine **11** dissolved completely. DDQ (3.0 or 6.0 mmol) was then added in one portion to the obtained solution, and the mixture was allowed to reflux for 1 h or 5 h. After cooling, the reaction mixture was quenched with aqueous saturated potassium carbonate and transferred into a separatory funnel. The aqueous layer was removed and the organic one was washed three times with saturated K_2CO_3 and twice with H_2O to remove completely the resulting hydroquinone. Further, the organic layer was collected, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The resulting crude product **12** was purified by recrystallization from MeOH.

*(±)-(1R,2S,5S,6S)-1,4,5,6-Tetraphenyl-3-azaspiro[bicyclo[3.1.0]hex-3-ene-2,11'-indeno[1,2-b]quinoxaline] (**12a**)*. Prepared following the general procedure **E** from compound **11aaa** (**7aaj**) (1.0 mmol, 590 mg) and DDQ (3.0 mmol, 681 mg) at reflux for 1 h. Beige solid; yield: 482 mg (82%); mp > 260 °C (MeOH); TLC (R_f = 0.48, SiO_2, hexane–EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.12–8.03 (m, 3H), 7.97–7.86 (m, 2H), 7.82–7.57 (m, 6H), 7.38–7.21 (m, 6H), 7.14–6.99 (m, 4H), 6.72–6.60 (m, 3H), 6.55–6.49 (m, 2H), 6.03–5.90 (m, 1H), 3.58 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.2, 160.5, 153.7, 147.0, 142.6, 141.7, 138.7, 135.3, 133.5, 133.3 (2C), 132.1, 131.9, 131.3, 131.0 (4C), 130.5, 129.9, 129.6 (2C), 129.3 (2C), 129.1, 128.7, 128.1 (2C), 127.9 (2C), 127.5, 127.0 (4C), 126.7, 126.2, 125.2, 122.6, 86.4, 53.7, 51.9, 41.0. IR (KBr): 3057, 3032, 1599, 1570, 1495, 1447, 1329, 1302, 1265, 1069, 1026, 760, 698 cm^{-1}. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{43}H_{30}N_3^+$: 588.2434; found 588.2441.

*(±)-(1R,2S,5S,6S)-1,5,6-Triphenyl-4-(p-tolyl)-3-azaspiro[bicyclo[3.1.0]hex-3-ene-2,11'-indeno[1,2-b]quinoxaline] (**12b**)*. Prepared following the general procedure **E** from compound **11aab** (1.0 mmol, 604 mg) and DDQ (3.0 mmol, 681 mg) at reflux for 1 h. Beige solid; yield: 548 mg (91%); mp > 260 °C (MeOH); TLC (R_f = 0.56, SiO_2, hexane–EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.11–7.99 (m, 3H), 7.96–7.85 (m, 2H), 7.78–7.56 (m, 6H), 7.36–7.23 (m, 3H), 7.14–6.98 (m, 6H), 6.70–6.59 (m, 3H), 6.54–6.48 (m, 2H), 6.02–5.88 (m, 1H), 3.55 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 184.0, 160.7, 153.8, 147.3, 142.6, 141.7, 140.7, 138.7, 135.5, 133.3 (2C), 132.4, 131.9, 131.4, 131.0 (3C), 130.8, 129.8, 129.6 (2C), 129.3 (3C), 129.1, 128.8 (2C), 128.7, 127.9 (3C), 127.4, 127.0 (3C), 126.6, 126.2, 125.2, 122.5, 86.4, 53.7, 52.0, 40.9, 21.5. IR (KBr): 3059, 3029, 1605, 1585, 1555, 1495, 1367, 1320, 1298, 1182, 1071, 823, 756, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{44}H_{32}N_3^+$: 602.2591; found 602.2589.

*(±)-(1R,2S,5S,6S)-4-(4-Methoxyphenyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hex-3-ene-2,11'-indeno[1,2-b]quinoxaline] (**12c**)*. Prepared following the general procedure **E** from compound **11aac** (1.0 mmol, 620 mg) and DDQ (3.0 mmol, 681 mg) at reflux for 1 h. Beige solid; yield: 537 mg (87%); mp > 260 °C (MeOH); TLC (R_f = 0.30, SiO_2, hexane–EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 7.5 Hz, 1H), 8.13–7.85 (m, 5H), 7.81–7.56 (m, 6H), 7.38–7.24 (m, 3H), 7.13–6.99 (m, 4H), 6.80–6.75 (m, 2H), 6.71–6.61 (m, 3H), 6.55–6.48 (m, 2H), 6.03–5.89 (m, 1H), 3.77 (s, 3H), 3.56 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.4, 161.4, 160.8, 153.7, 147.4, 142.6, 141.7, 138.7, 135.5, 133.3 (2C), 132.6, 131.9, 131.4, 131.1, 131.0 (4C), 129.8 (2C), 129.6, 129.5, 129.1, 128.7, 127.9 (2C), 127.5, 127.0 (4C), 126.6, 126.2 (2C), 125.2, 122.5, 113.5 (2C), 86.2, 55.2, 53.5, 52.0, 40.9. IR (KBr): 3053, 2918, 2849, 1607, 1589, 1510, 1497, 1323, 1302, 1258, 1171, 1030, 833, 768, 754, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{44}H_{32}N_3O^+$: 618.2540; found 618.2554.

*(±)-(1R,2S,5S,6S)-4-(4-Fluorophenyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hex-3-ene-2,11'-indeno[1,2-b]quinoxaline] (**12d**)*. Prepared following the general procedure **E** from compound **11aad** (1.0 mmol, 608 mg) and DDQ (6 mmol, 1.362 g) at reflux for 5 h. Beige solid; yield: 442 mg (73%); mp > 260 °C (MeOH); TLC (R_f = 0.56, SiO_2, hexane–EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 7.1 Hz, 1H), 8.13–7.56 (m, 12H), 7.39–7.29 (m, 2H), 7.16–6.94 (m, 6H), 6.75–6.47 (m, 5H), 6.02–5.86 (m, 1H), 3.55 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.1, 160.4, 153.6, 146.9, 142.6, 141.5, 138.7, 135.2, 133.2 (2C), 132.0, 131.9, 131.5, 131.4, 131.2, 131.0 (3C), 129.9 (2C), 129.6 (4C), 129.1, 128.7, 128.0 (2C), 127.6, 127.0 (4C), 126.7, 126.3, 125.1, 122.6, 115.3, 115.1, 86.4, 53.5, 52.0, 40.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –109.4. IR

(KBr): 3059, 3028, 2852, 1603, 1573, 1508, 1497, 1335, 1231, 1158, 1070, 839, 757, 702 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{29}FN_3^+$: 606.2340; found 606.2352.

(±)-(1R,2S,5S,6S)-4-(4-Chlorophenyl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hex-3-ene-2,11'-indeno[1,2-b]quinoxaline] ***(12e)***. Prepared following the general procedure **E** from compound **11aae** (1.0 mmol, 624 mg) and DDQ (6.0 mmol, 1.362 g) at reflux for 5 h. Beige solid; yield: 361 mg (58%); mp > 260 °C (MeOH); TLC (R_f = 0.70, SiO_2, hexane–EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.13–8.02 (m, 3H), 7.96–7.81 (m, 2H), 7.79–7.57 (m, 6H), 7.36–7.21 (m, 5H), 7.14–6.99 (m, 4H), 6.71–6.49 (m, 5H), 6.01–5.88 (m, 1H), 3.54 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.1, 160.3, 146.9, 142.6, 141.6, 138.7, 136.6, 135.1, 133.2 (2C), 131.9 (4C), 131.1, 131.0 (4C), 130.6 (3C), 130.0, 129.7, 129.6, 129.1, 128.8, 128.4 (2C), 128.0 (2C), 127.7, 127.1, 127.0 (4C), 126.3, 125.1, 86.5, 53.5, 52.0, 41.0. IR (KBr): 3057, 3026, 1591, 1495, 1333, 1300, 1090, 758, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{29}ClN_3^+$: 622.2045; found 622.2055.

(±)-(1R,2S,5S,6S)-4-(Furan-2-yl)-1,5,6-triphenyl-3-azaspiro[bicyclo[3.1.0]hex-3-ene-2,11'-indeno[1,2-b]quinoxaline] ***(12f)***. Prepared following the general procedure **E** from compound **11aah** (1.0 mmol, 580 mg) and DDQ (3.0 mmol, 681 mg) at reflux for 1 h. Beige solid; yield: 445 mg (77%); mp > 260 °C (MeOH); TLC (R_f = 0.20, SiO_2, hexane–EtOAc, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (dd, *J* = 8.2, 1.7 Hz, 1H), 8.11–8.07 (m, 2H), 8.03–7.99 (m, 1H), 7.76–7.55 (m, 5H), 7.49–7.37 (m, 4H), 7.24–7.17 (m, 1H), 7.10–7.04 (m, 1H), 7.00–6.93 (m, 2H), 6.70–6.65 (m, 1H), 6.60–6.45 (m, 5H), 6.32–6.29 (m, 1H), 6.05–6.00 (m, 1H), 5.93 (d, *J* = 6.1 Hz, 1H), 3.47 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 160.5, 153.7, 148.2, 146.9, 145.1, 142.6, 141.7, 138.7, 135.1, 132.1, 131.9, 131.4, 131.0, 130.9 (4C), 129.9, 129.6 (2C), 129.0, 128.7 (2C), 128.2 (2C), 127.0 (2C), 126.9 (3C), 126.7, 126.1, 125.3, 122.5, 116.3, 111.7, 86.4, 52.8, 52.3, 40.5. IR (KBr): 3062, 3028, 2921, 2851, 1601, 1495, 1476, 1335, 1162, 1068, 1031, 1006, 968, 758, 700 cm^{-1}. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{41}H_{28}N_3O^+$: 578.2227; found 578.2228.

2. Copies of NMR spectra

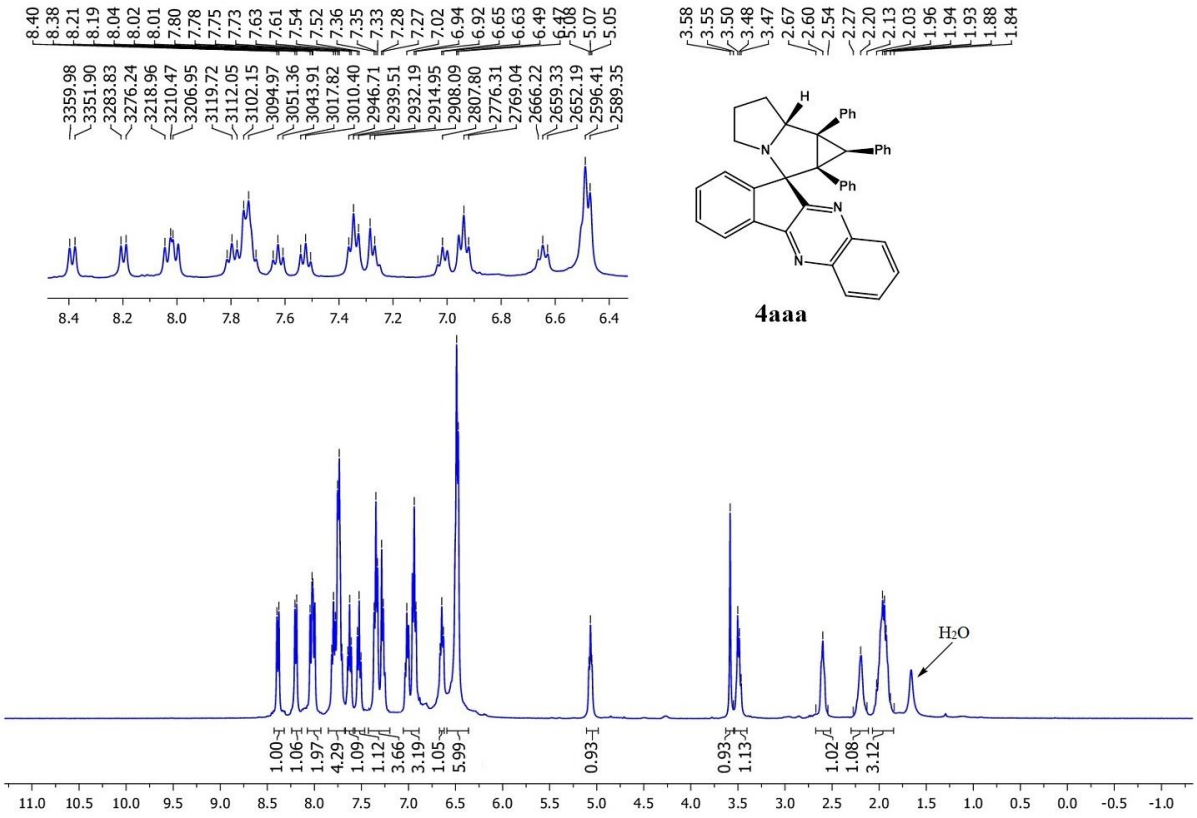


Figure S1. ^{1}H NMR spectrum of compound **4aaa** ($CDCl_3$, 400 MHz)

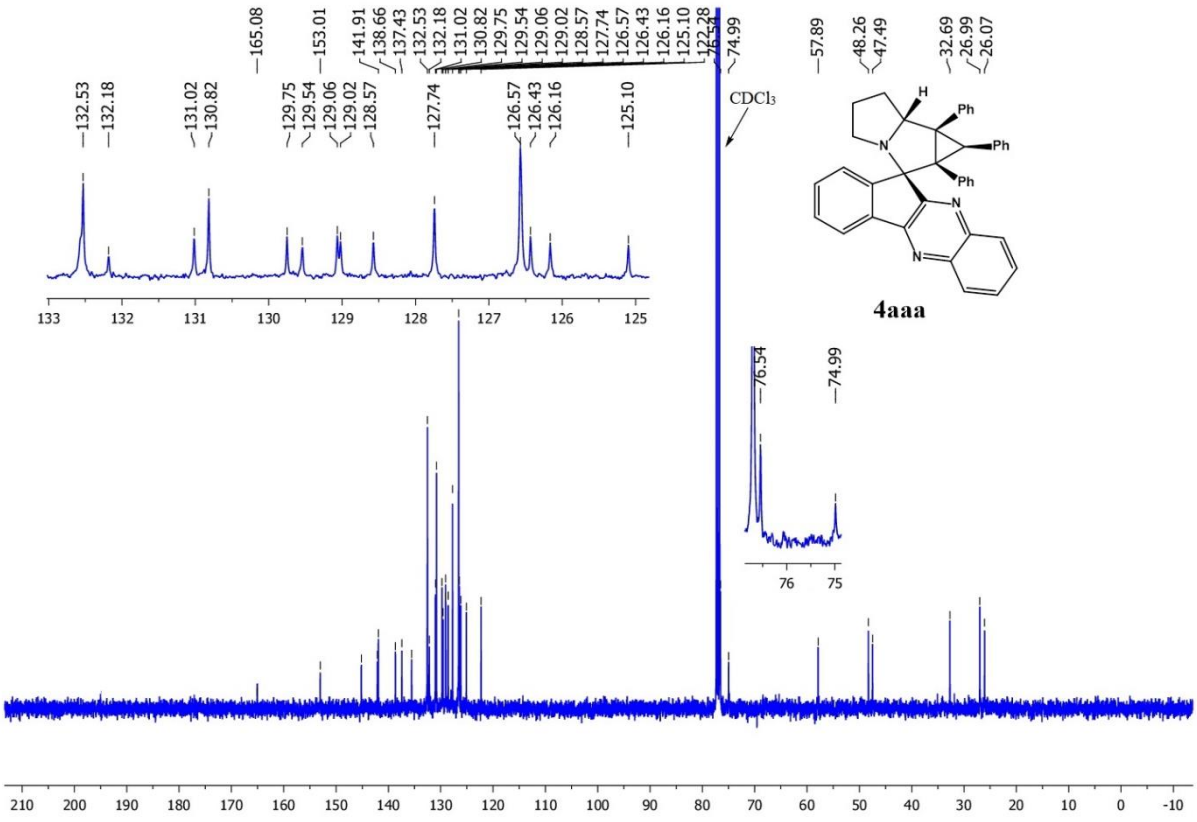


Figure S2. ^{13}C NMR spectrum of compound **4aaa** ($CDCl_3$, 101 MHz)

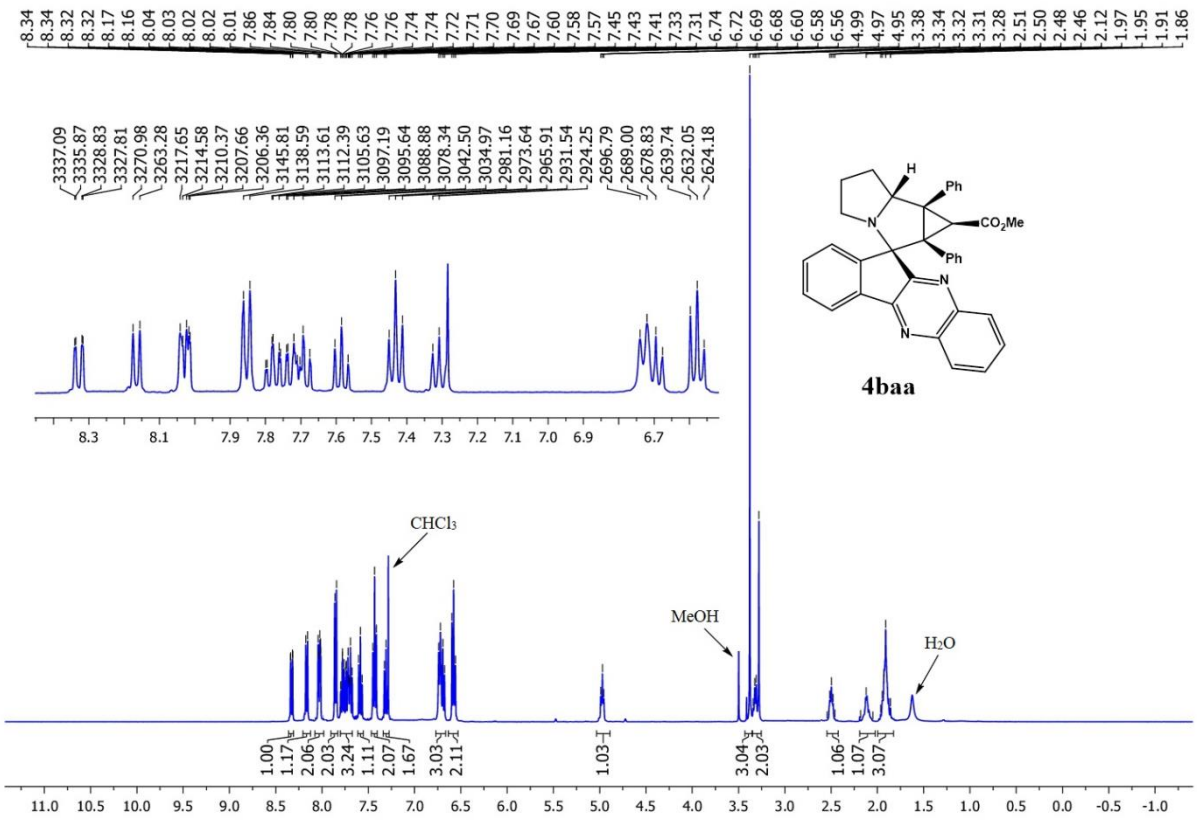


Figure S3. ^{1}H NMR spectrum of compound **4baa** ($CDCl_3$, 400 MHz)

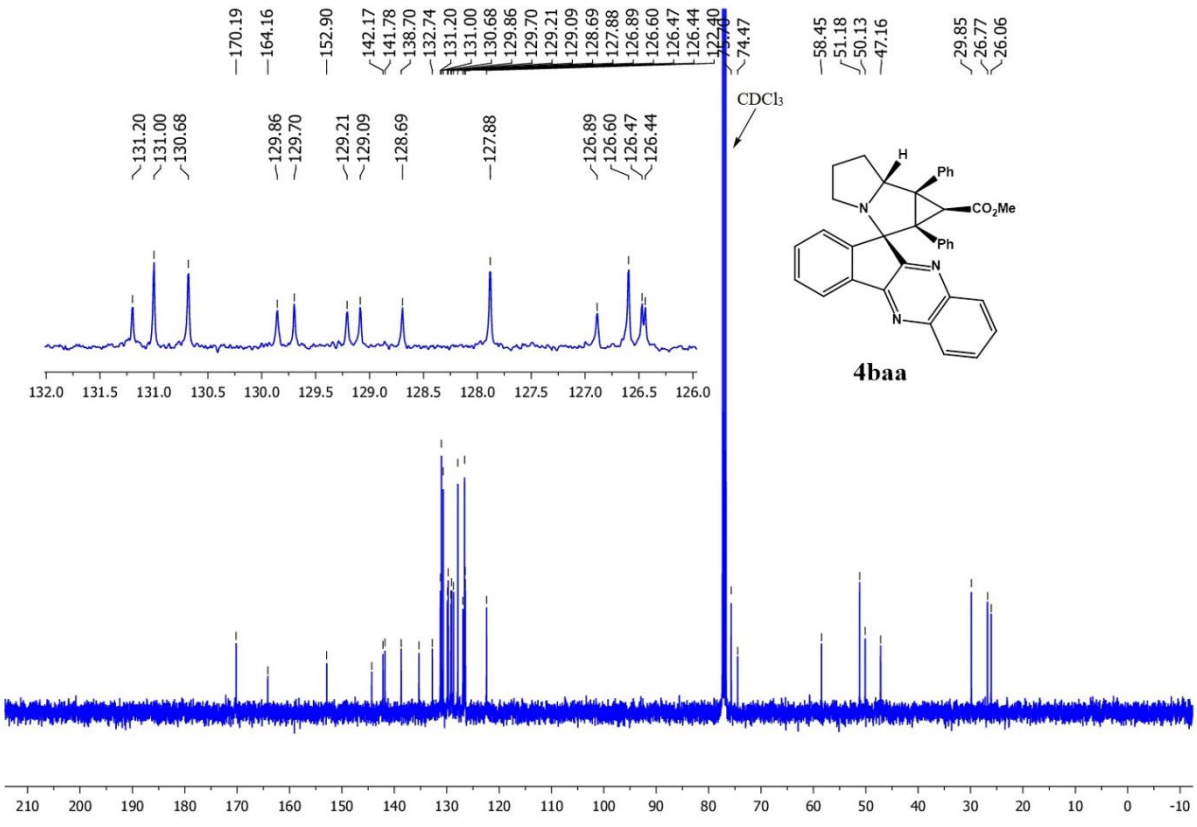


Figure S4. ^{13}C NMR spectrum of compound **4baa** ($CDCl_3$, 101 MHz)

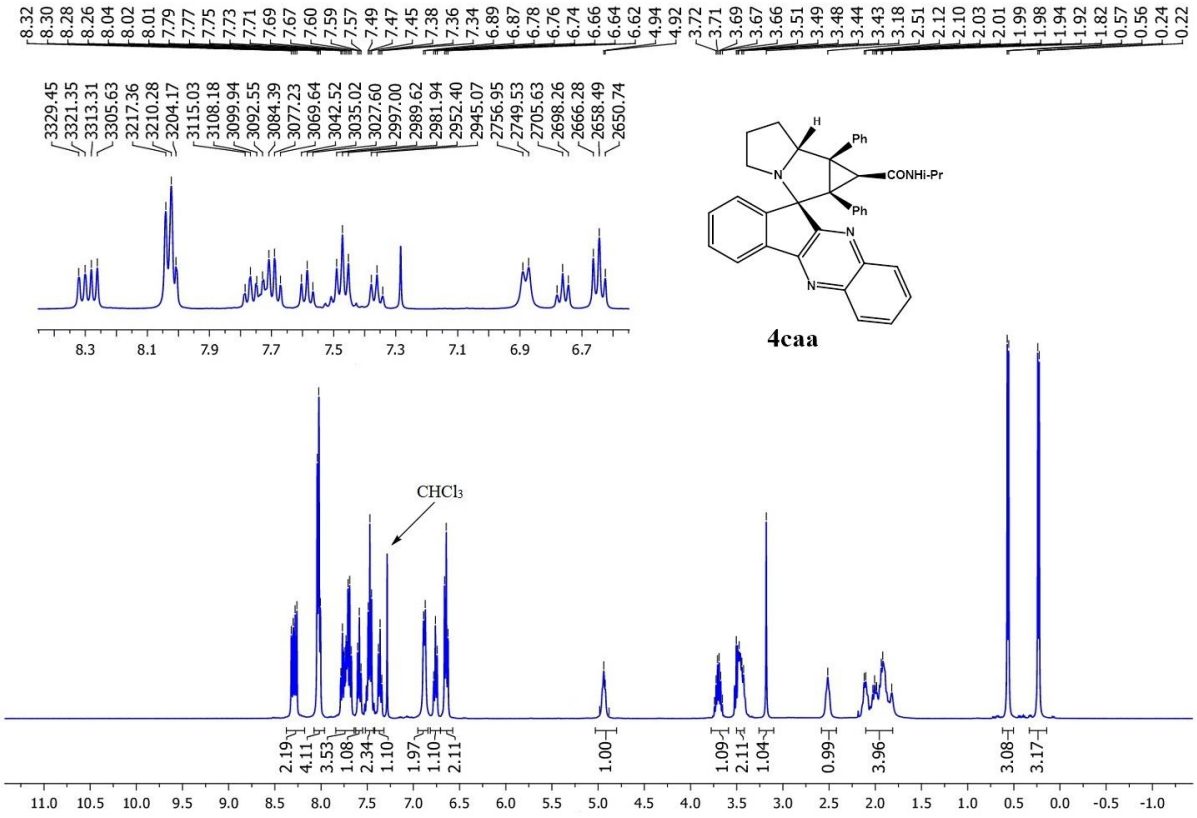


Figure S5. ^{1}H NMR spectrum of compound **4caa** ($CDCl_3$, 400 MHz)

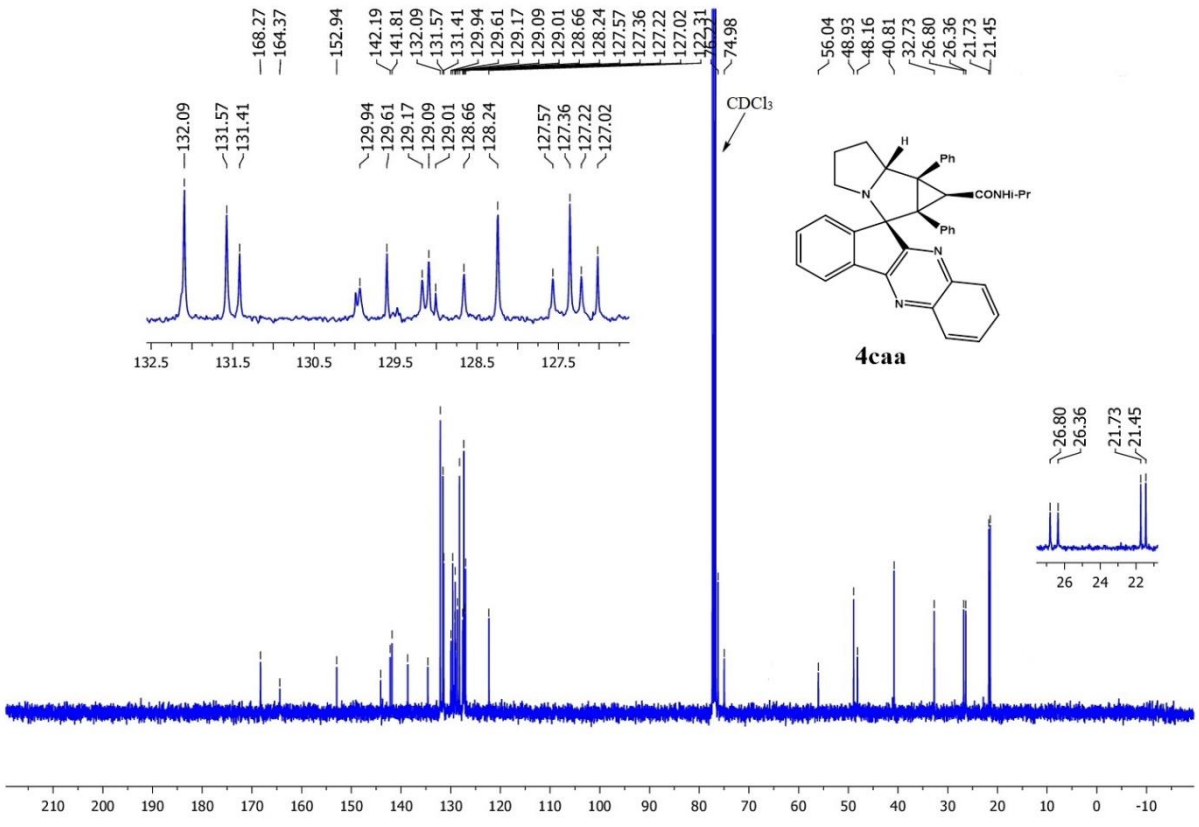


Figure S6. ^{13}C NMR spectrum of compound **4caa** ($CDCl_3$, 101 MHz)

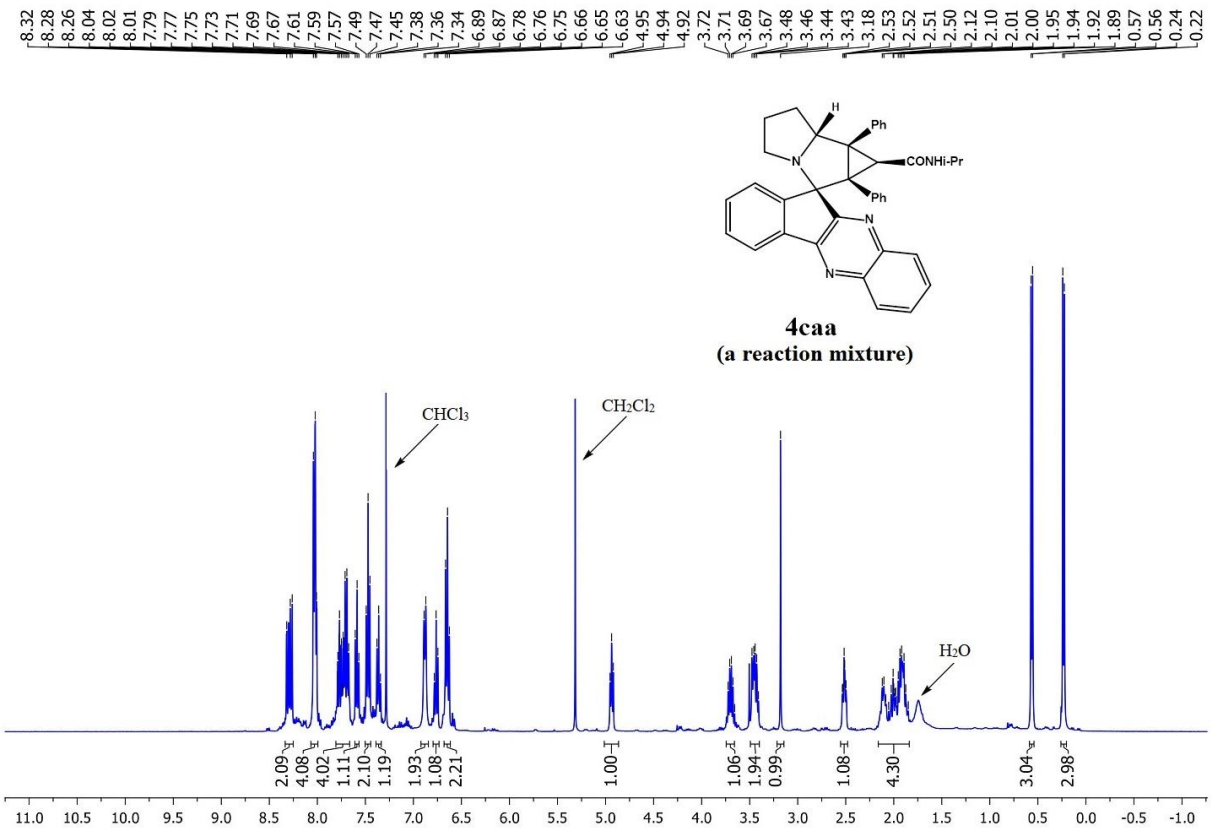


Figure S7. ^{1}H NMR spectrum of the crude reaction mixture for **4caa** ($CDCl_3$, 400 MHz)

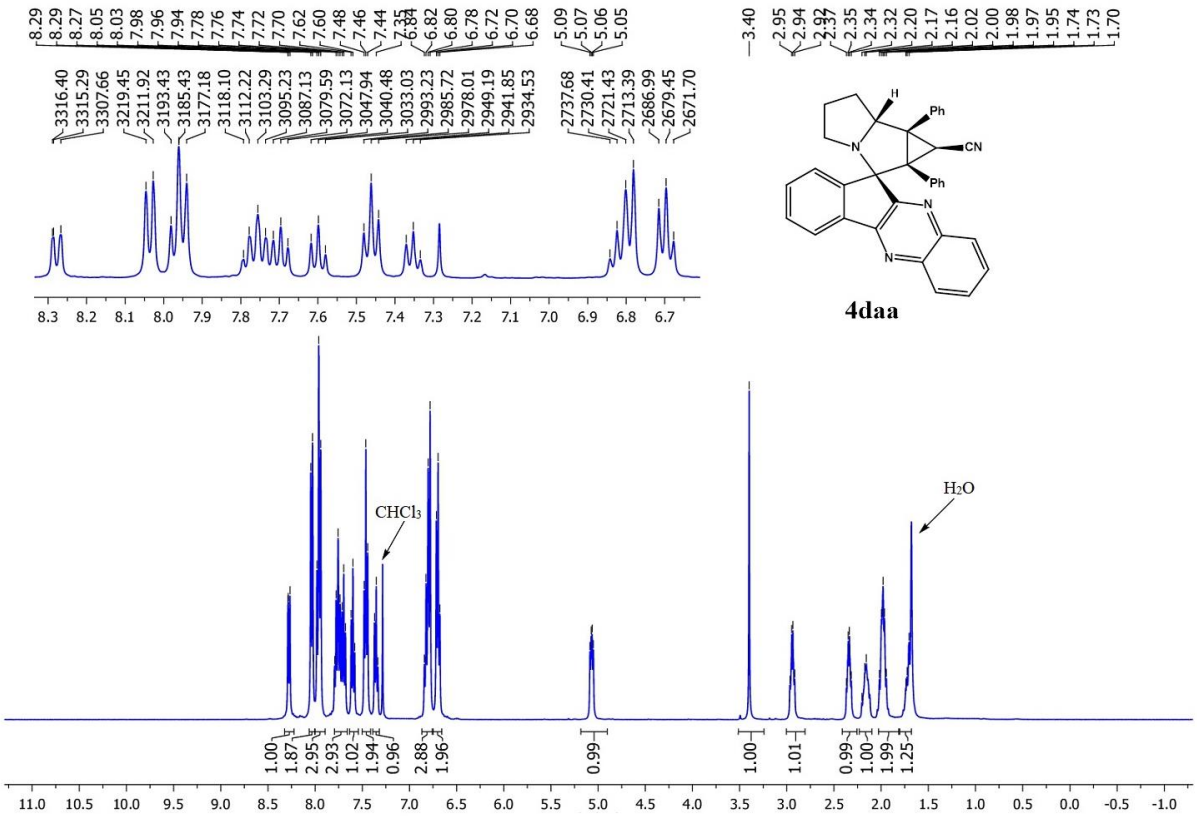


Figure S8. ^{1}H NMR spectrum of compound **4daa** ($CDCl_3$, 400 MHz)

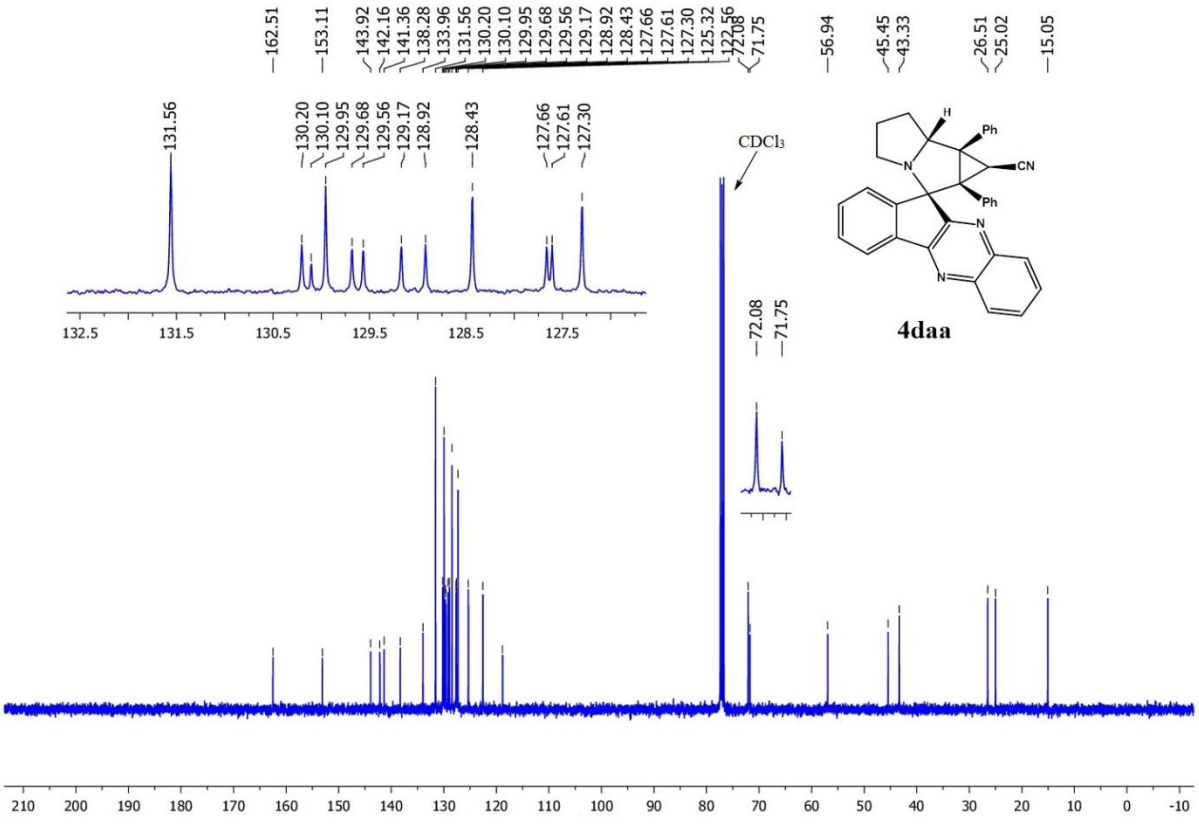


Figure S9. ^{13}C NMR spectrum of compound **4daa** ($CDCl_3$, 101 MHz)

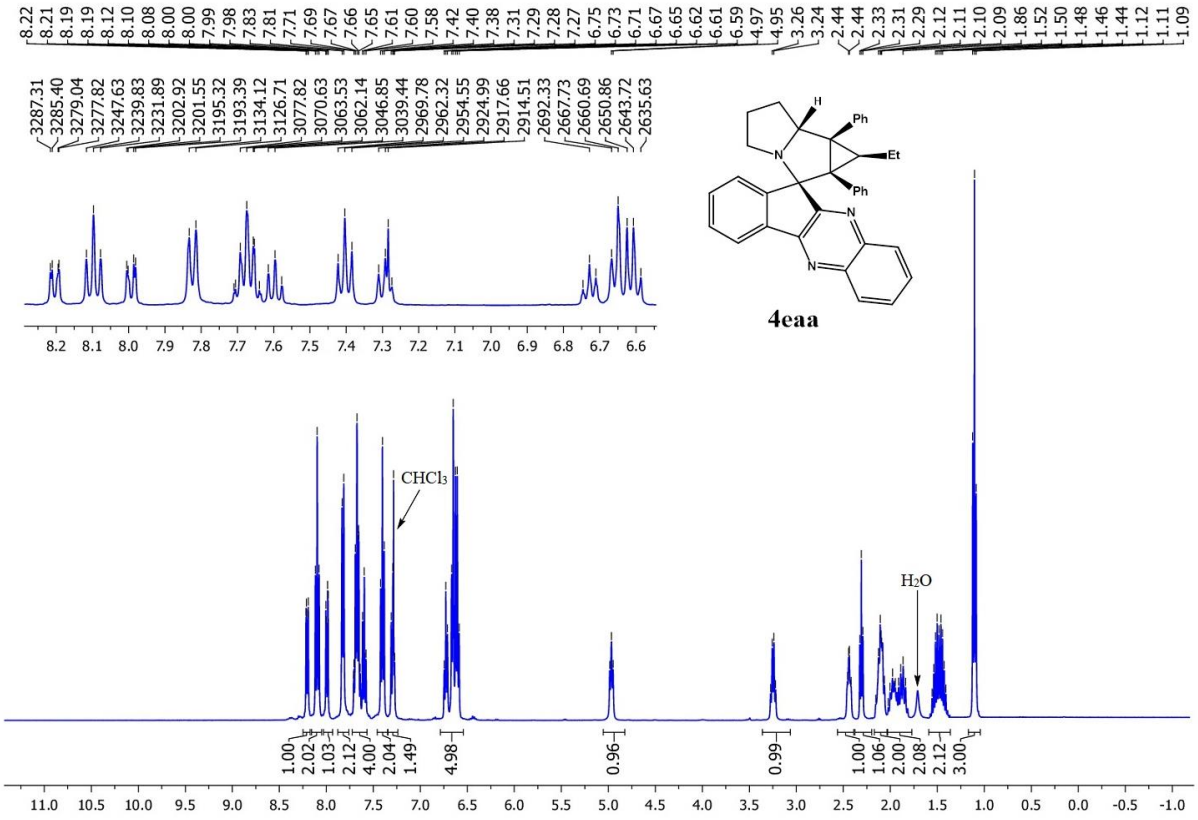


Figure S10. ^{1}H NMR spectrum of compound **4eaa** ($CDCl_3$, 400 MHz)

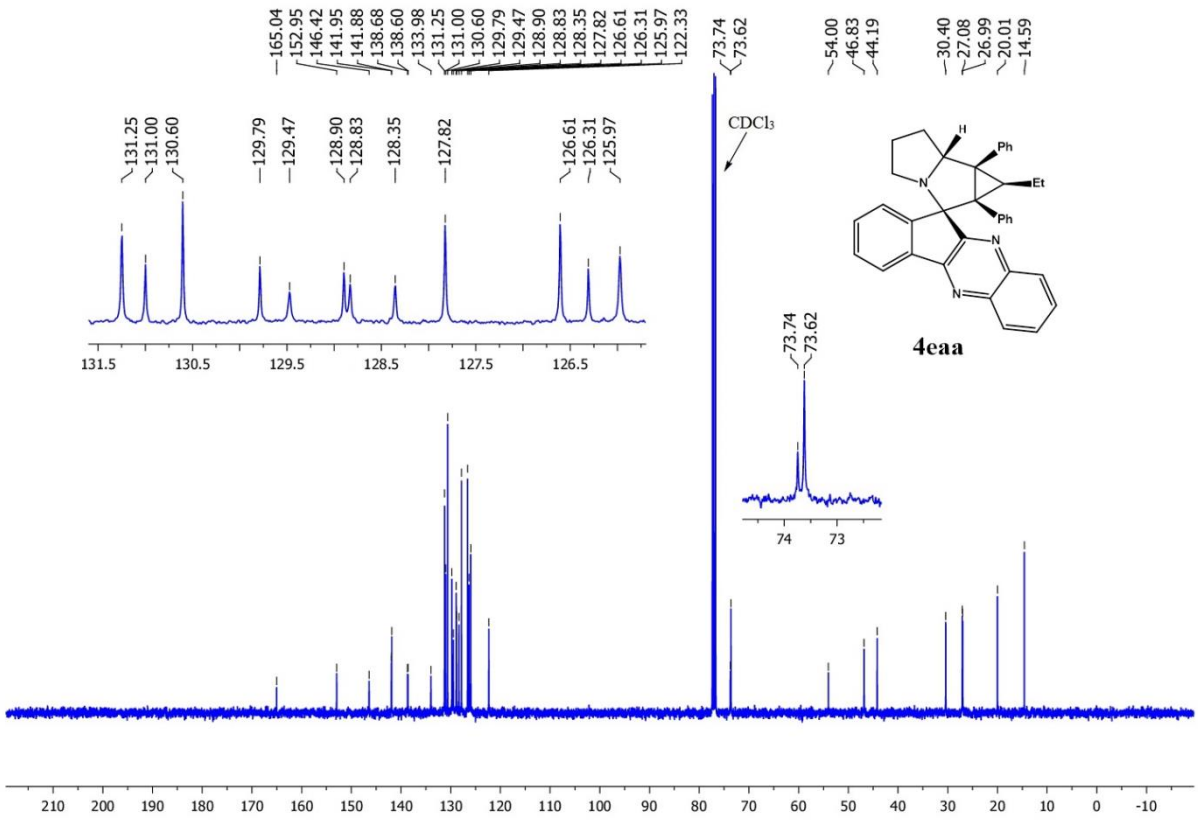


Figure S11. ^{13}C NMR spectrum of compound **4eaa** ($CDCl_3$, 101 MHz)

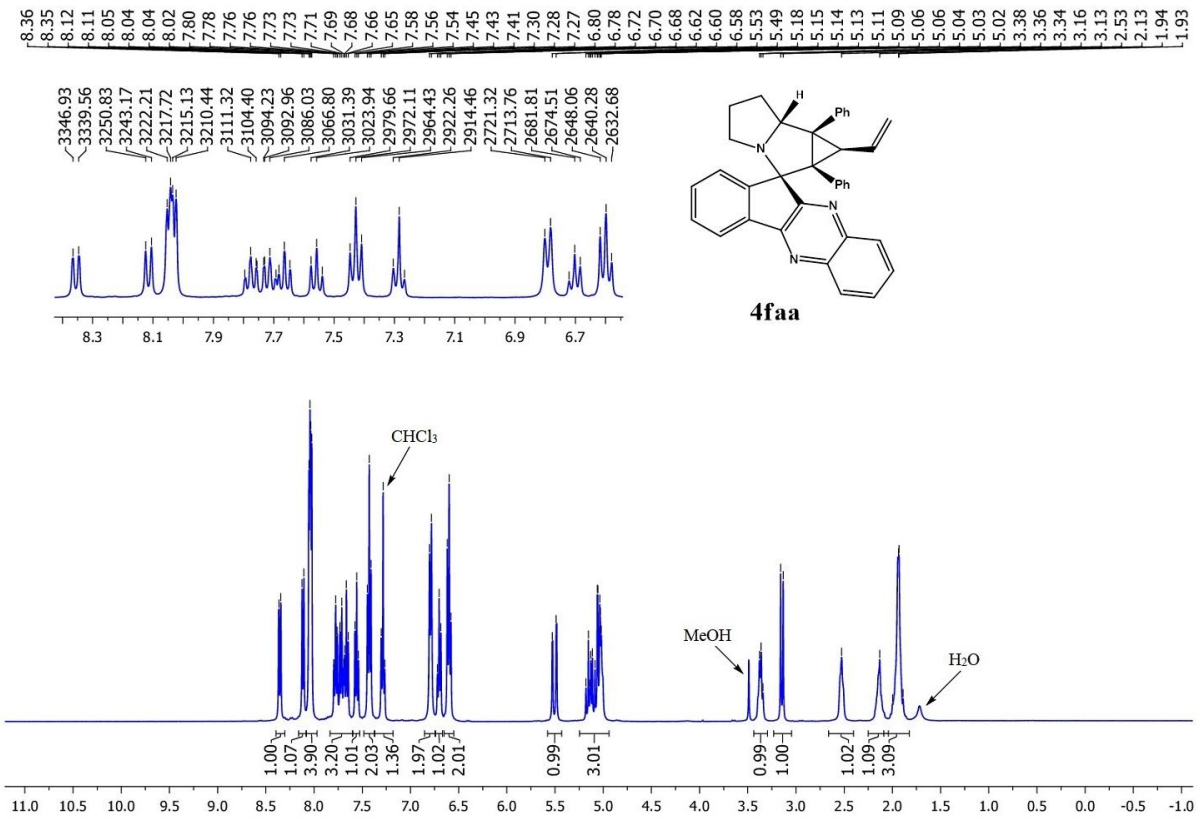


Figure S12. ^{1}H NMR spectrum of compound **4faa** ($CDCl_3$, 400 MHz)

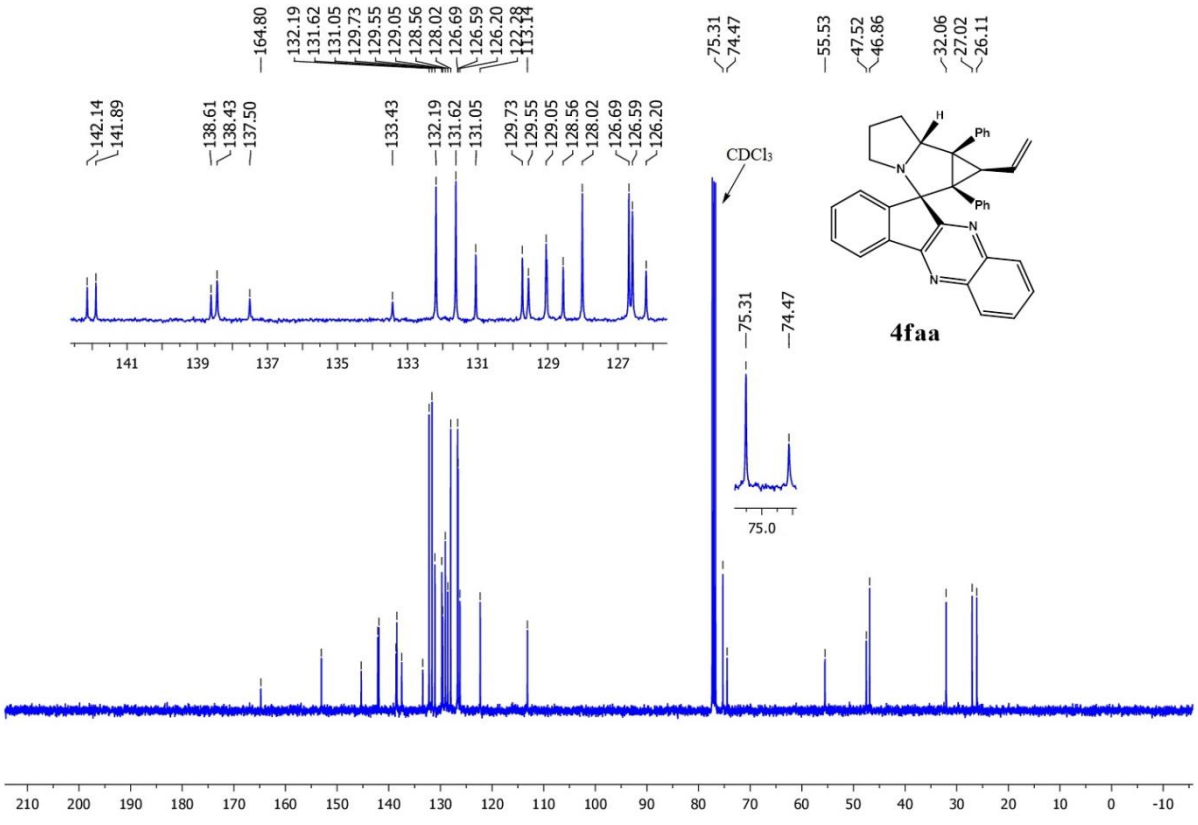


Figure S13. ^{13}C NMR spectrum of compound **4faa** ($CDCl_3$, 101 MHz)

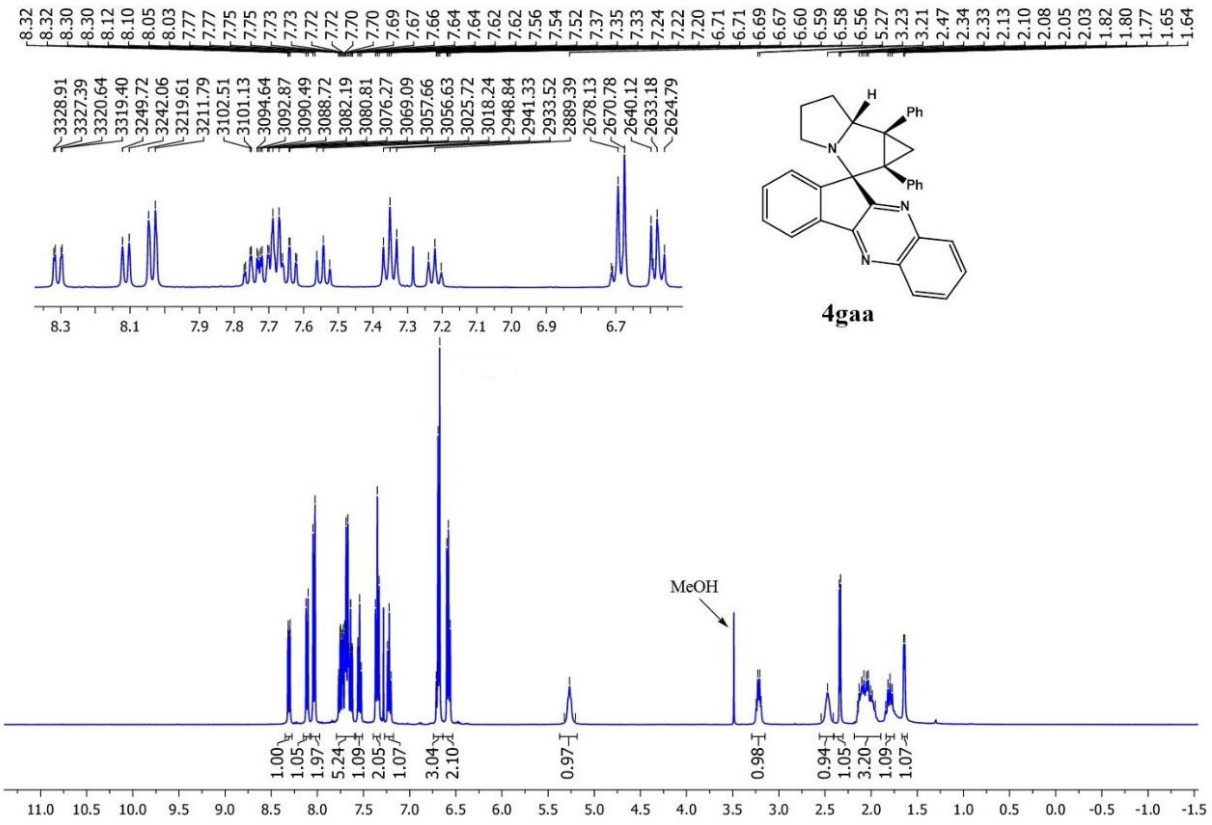


Figure S14. ^{1}H NMR spectrum of compound **4gaa** ($CDCl_3$, 400 MHz)

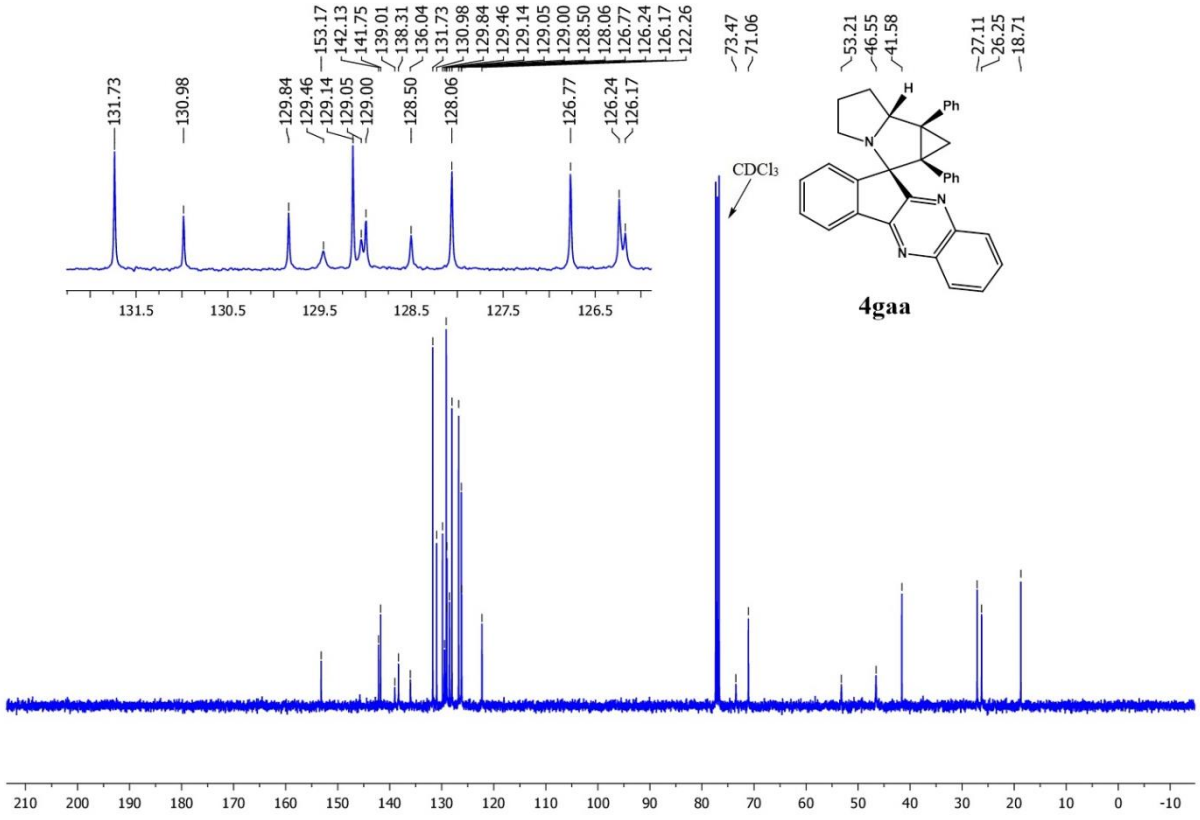


Figure S15. ^{13}C NMR spectrum of compound **4gaa** ($CDCl_3$, 101 MHz)

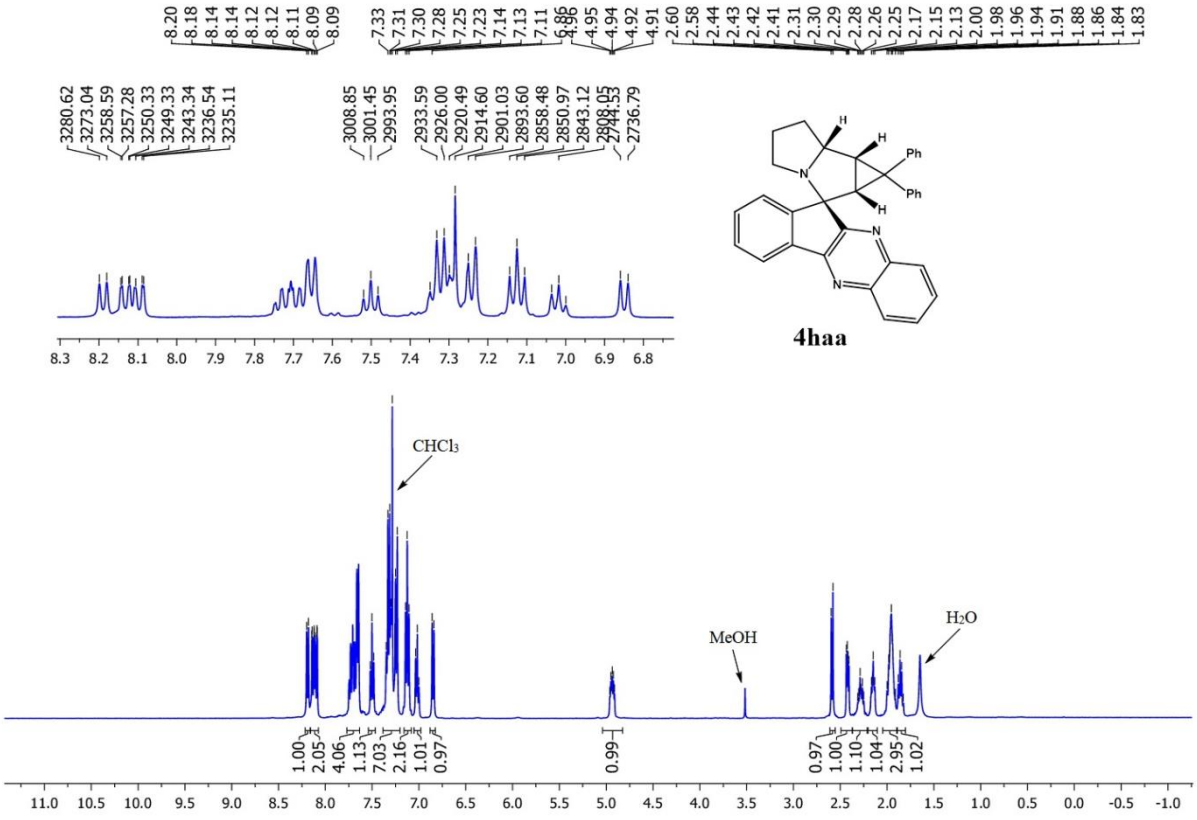


Figure S16. ^{1}H NMR spectrum of compound **4haa** ($CDCl_3$, 400 MHz)

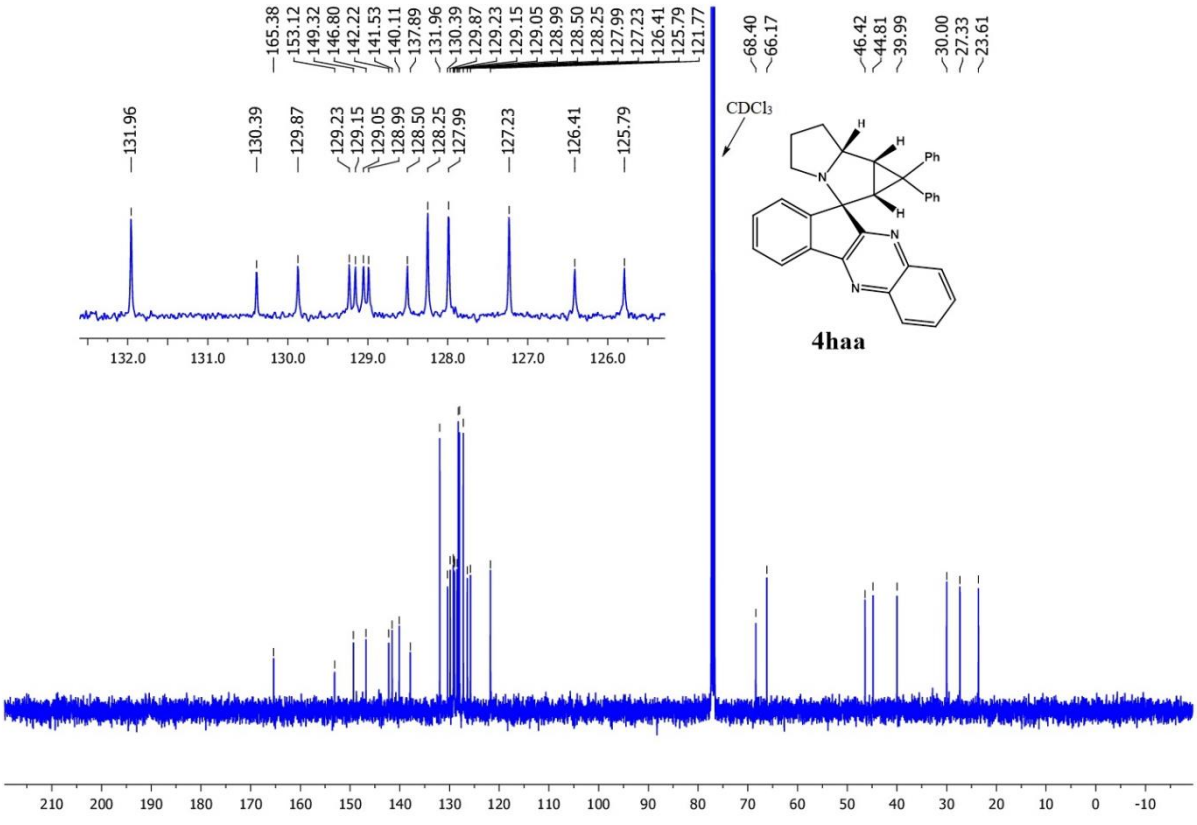


Figure S17. ^{13}C NMR spectrum of compound **4haa** ($CDCl_3$, 101 MHz)

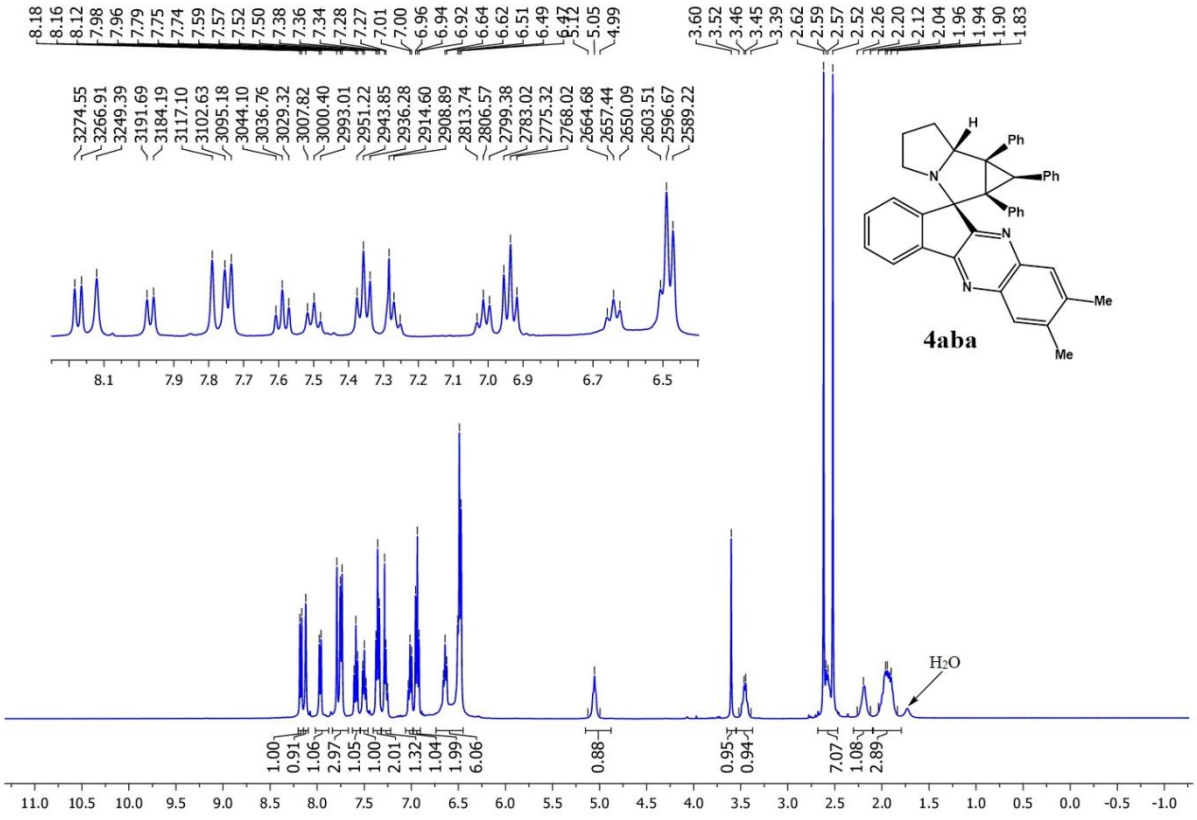


Figure S18. ^{1}H NMR spectrum of compound **4aba** ($CDCl_3$, 400 MHz)

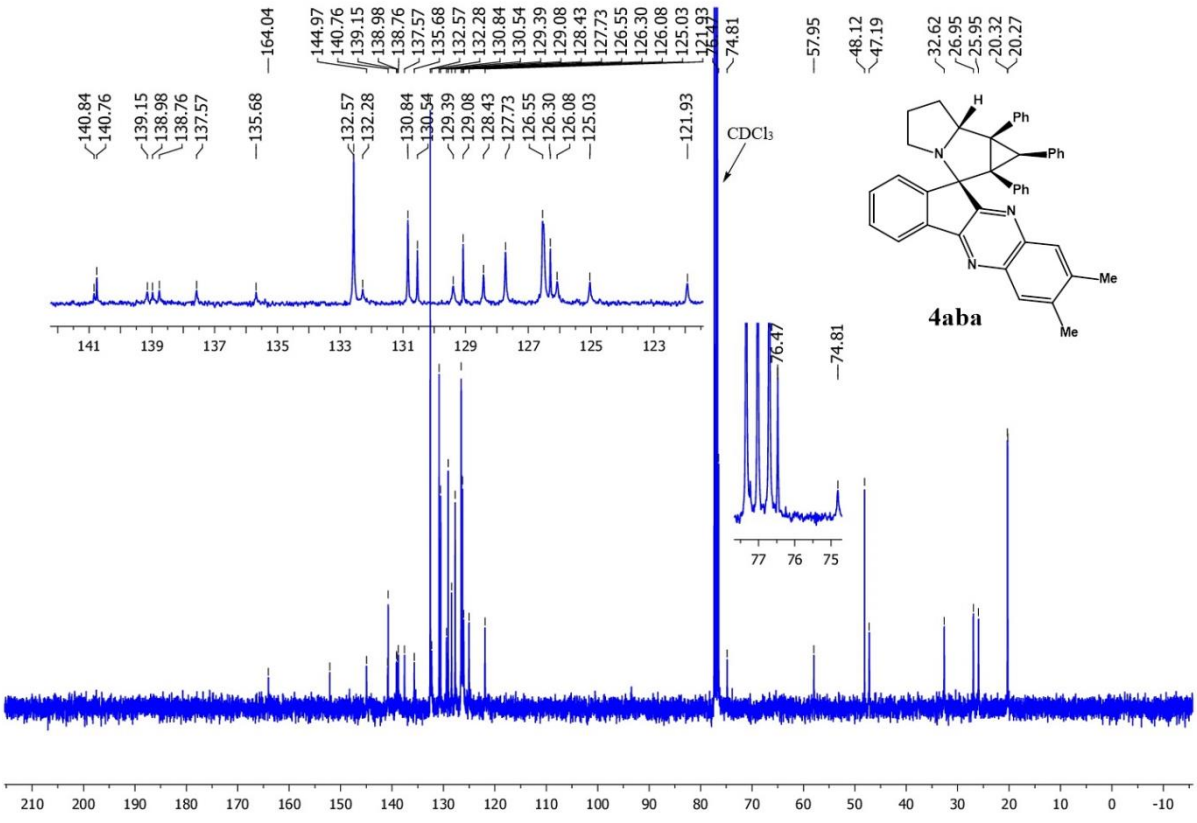


Figure S19. ^{13}C NMR spectrum of compound **4aba** ($CDCl_3$, 101 MHz)

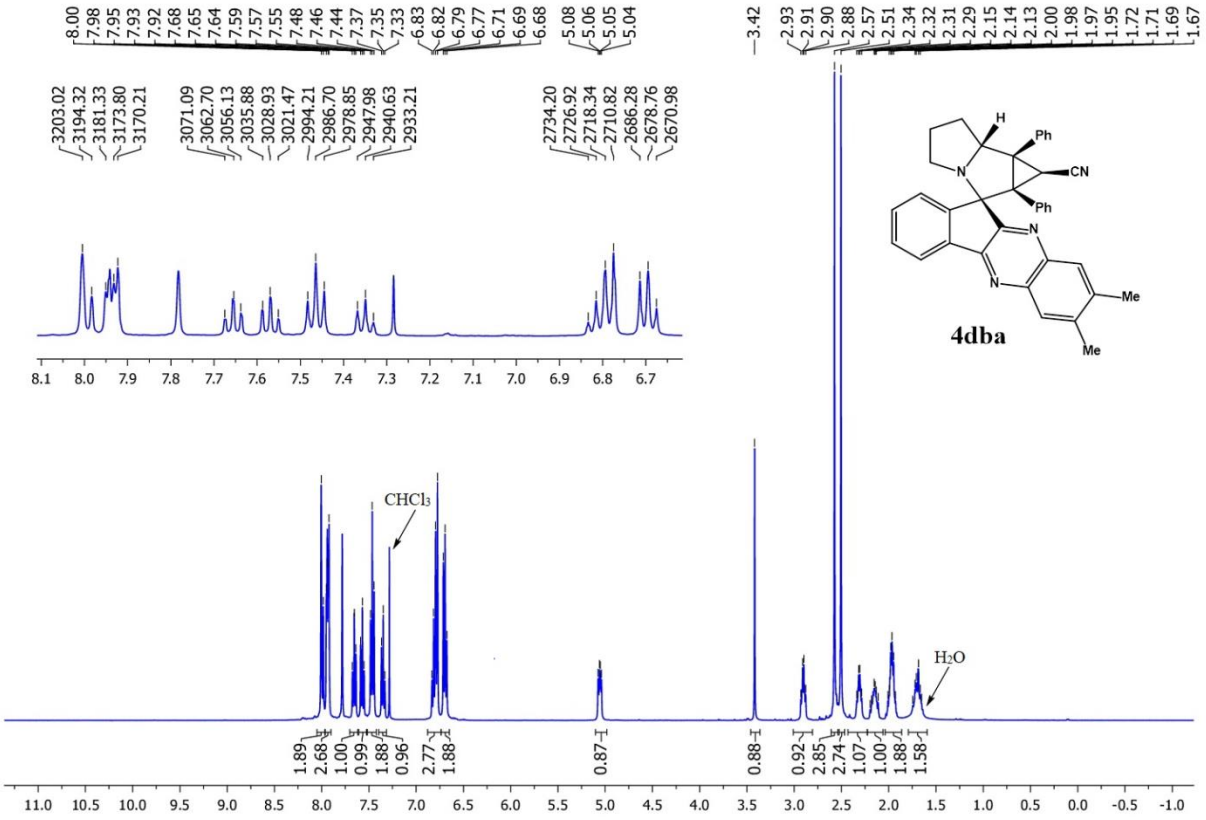


Figure S20. ^{1}H NMR spectrum of compound **4dba** ($CDCl_3$, 400 MHz)

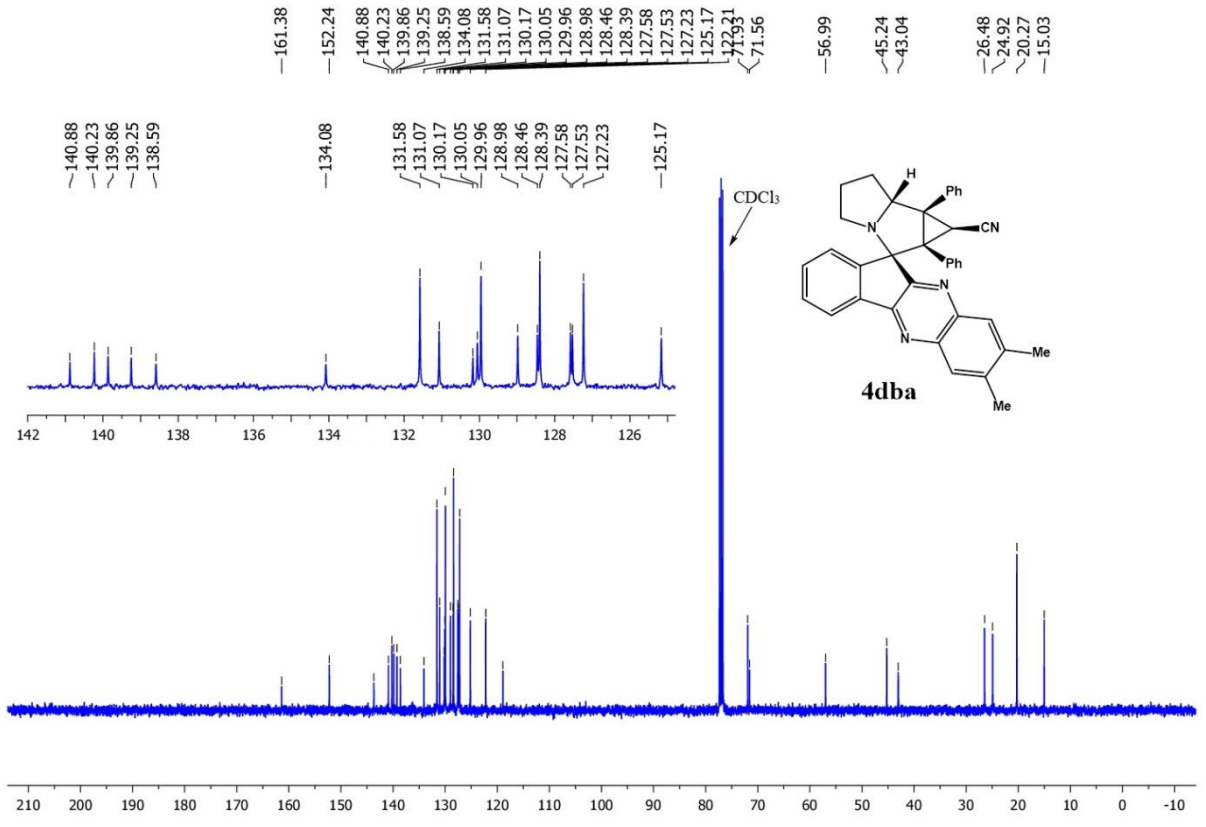


Figure S21. ^{13}C NMR spectrum of compound **4dba** ($CDCl_3$, 101 MHz)

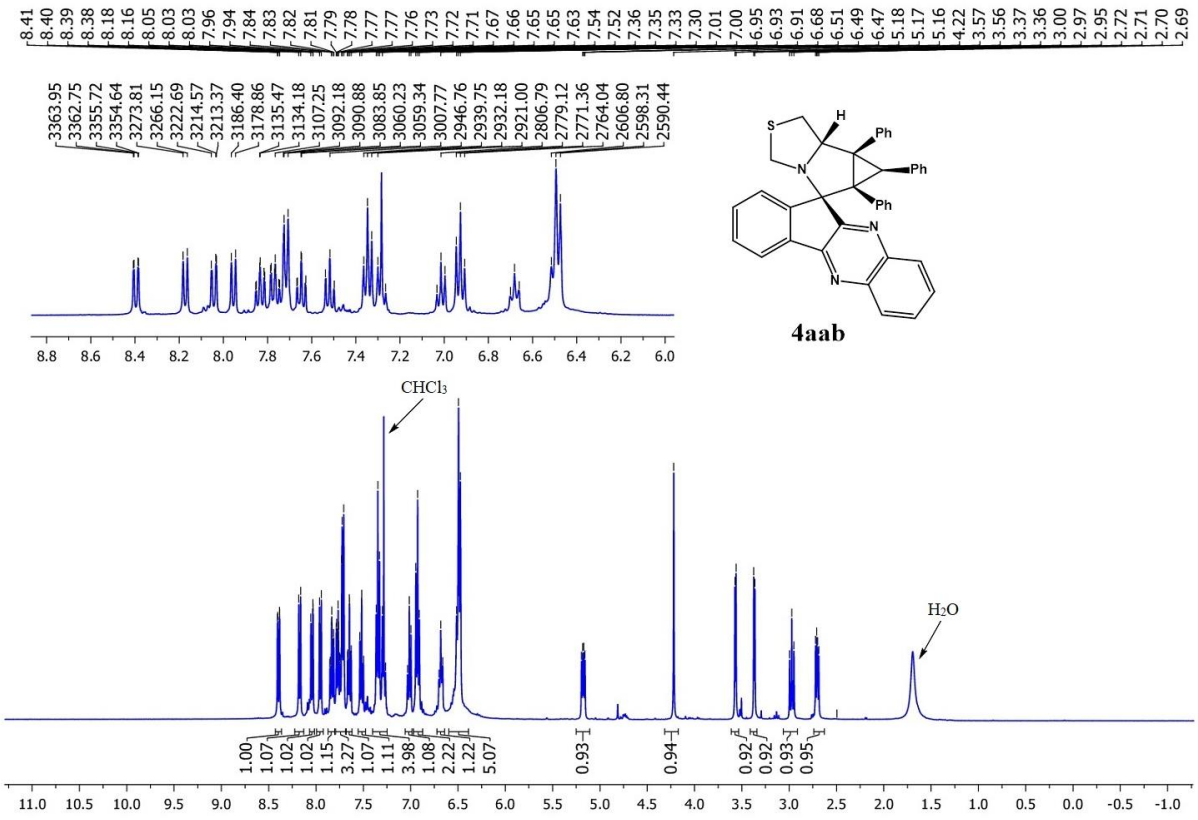


Figure S22. ^{1}H NMR spectrum of compound **4aab** ($CDCl_3$, 400 MHz)

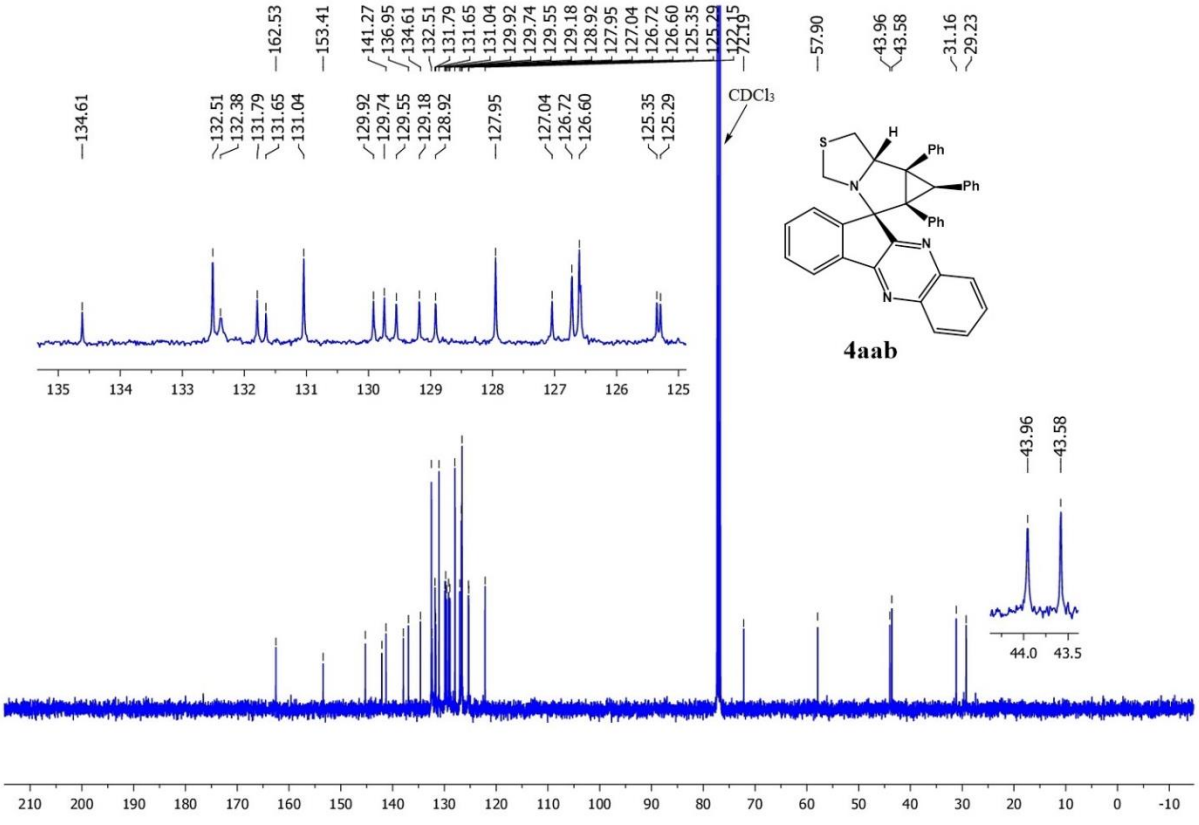


Figure S23. ^{13}C NMR spectrum of compound **4aab** ($CDCl_3$, 101 MHz)

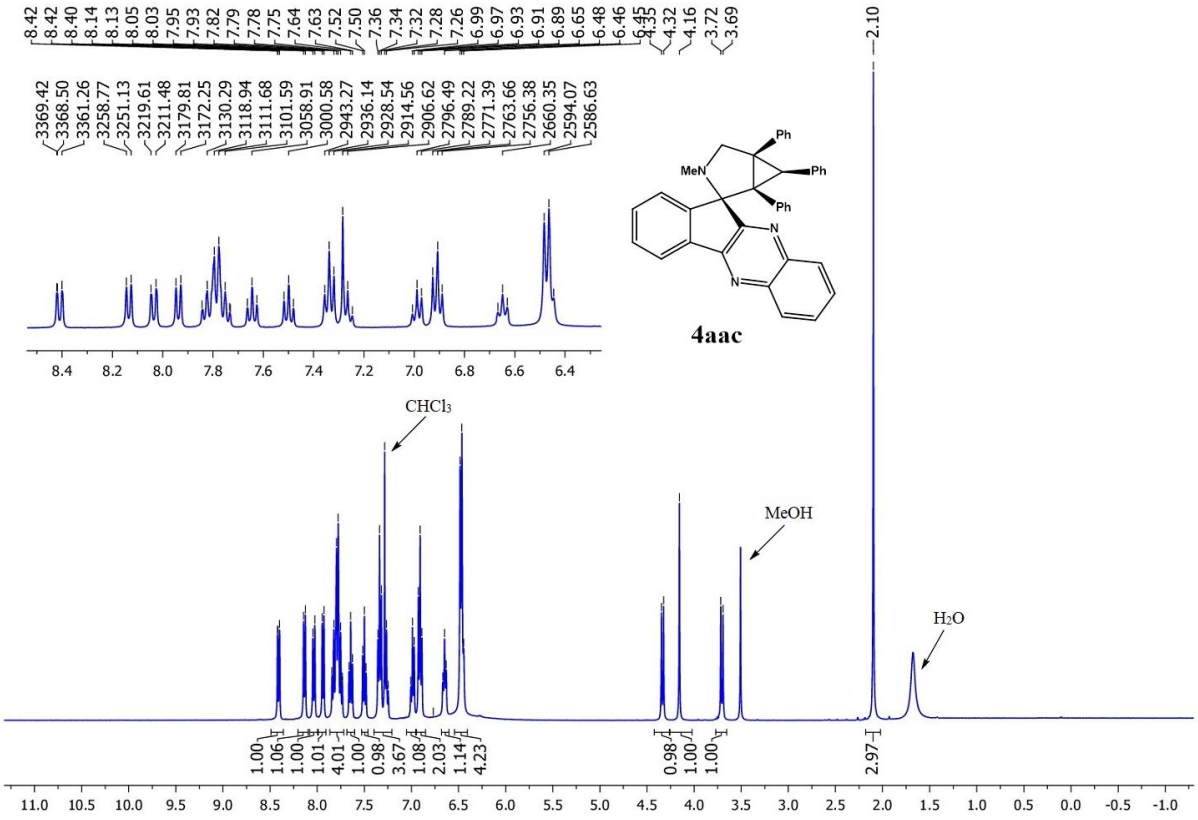


Figure S24. ^{1}H NMR spectrum of compound **4aac** ($CDCl_3$, 400 MHz)

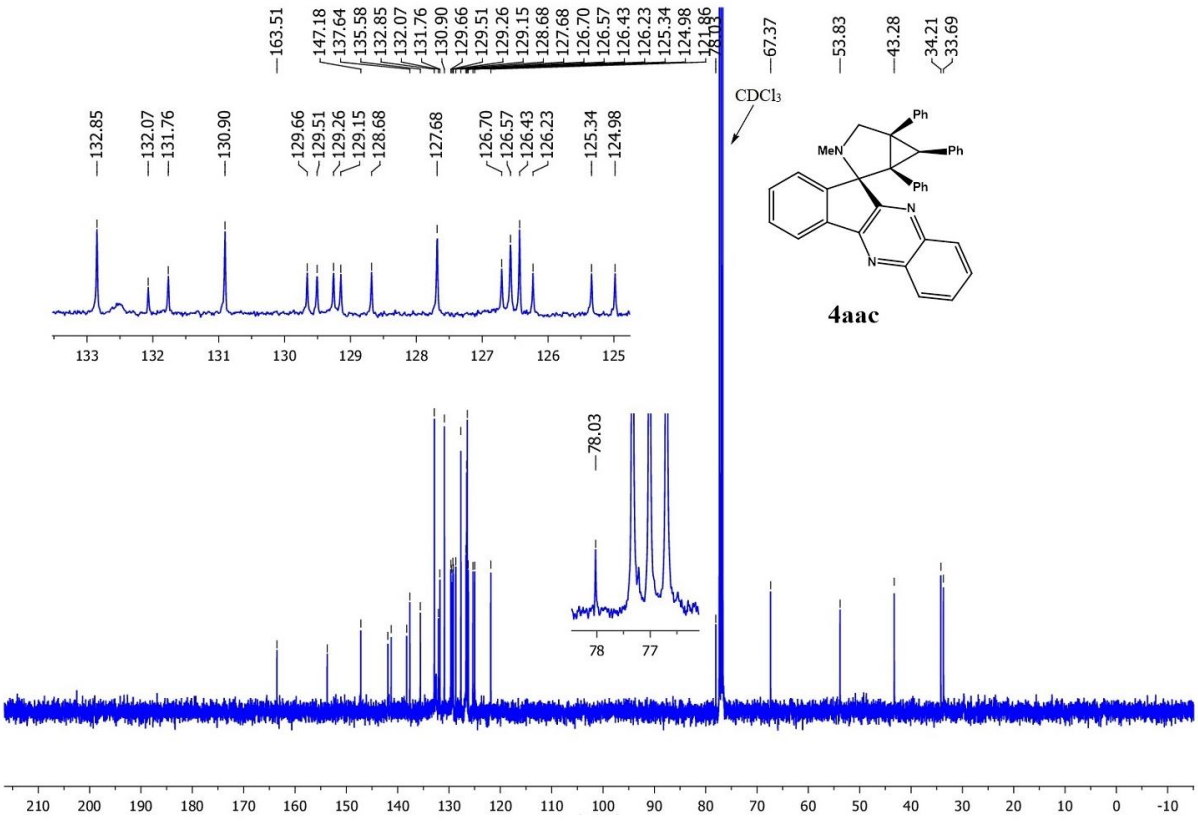


Figure S25. ^{13}C NMR spectrum of compound **4aac** ($CDCl_3$, 101 MHz)

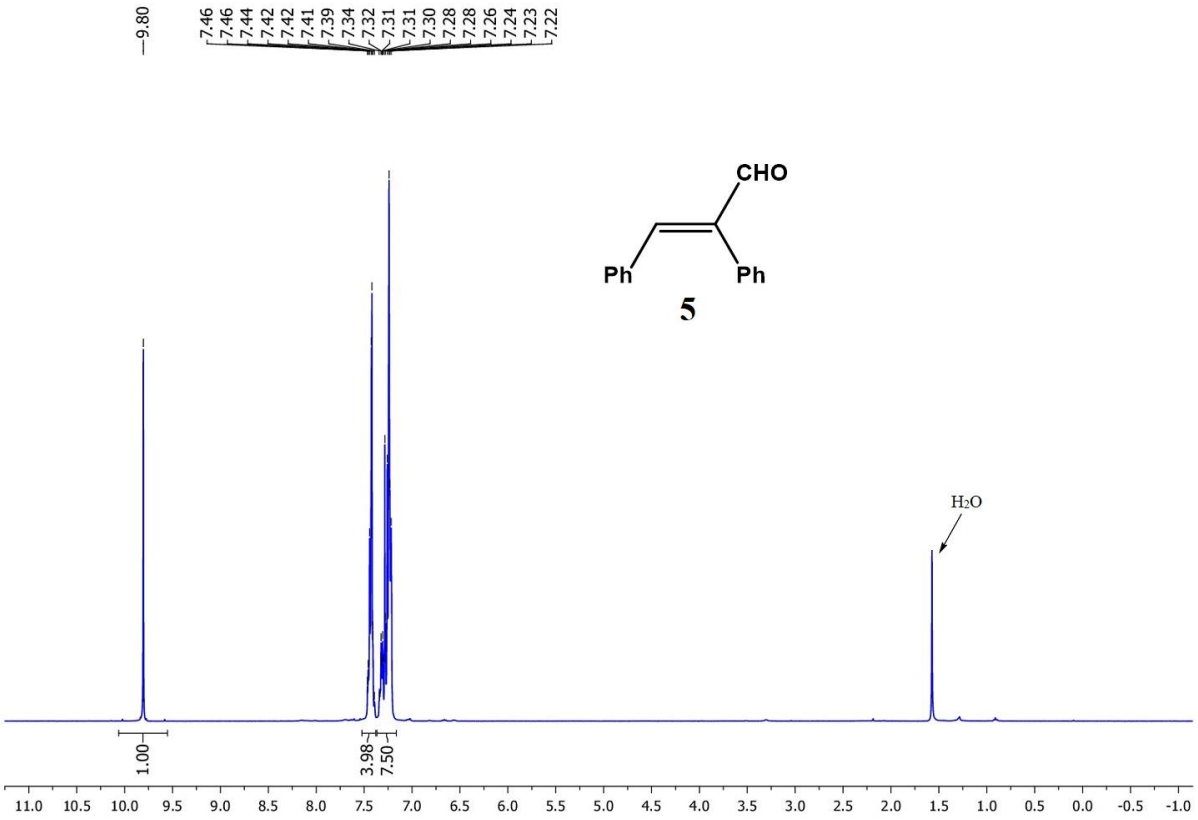


Figure S26. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400 MHz)

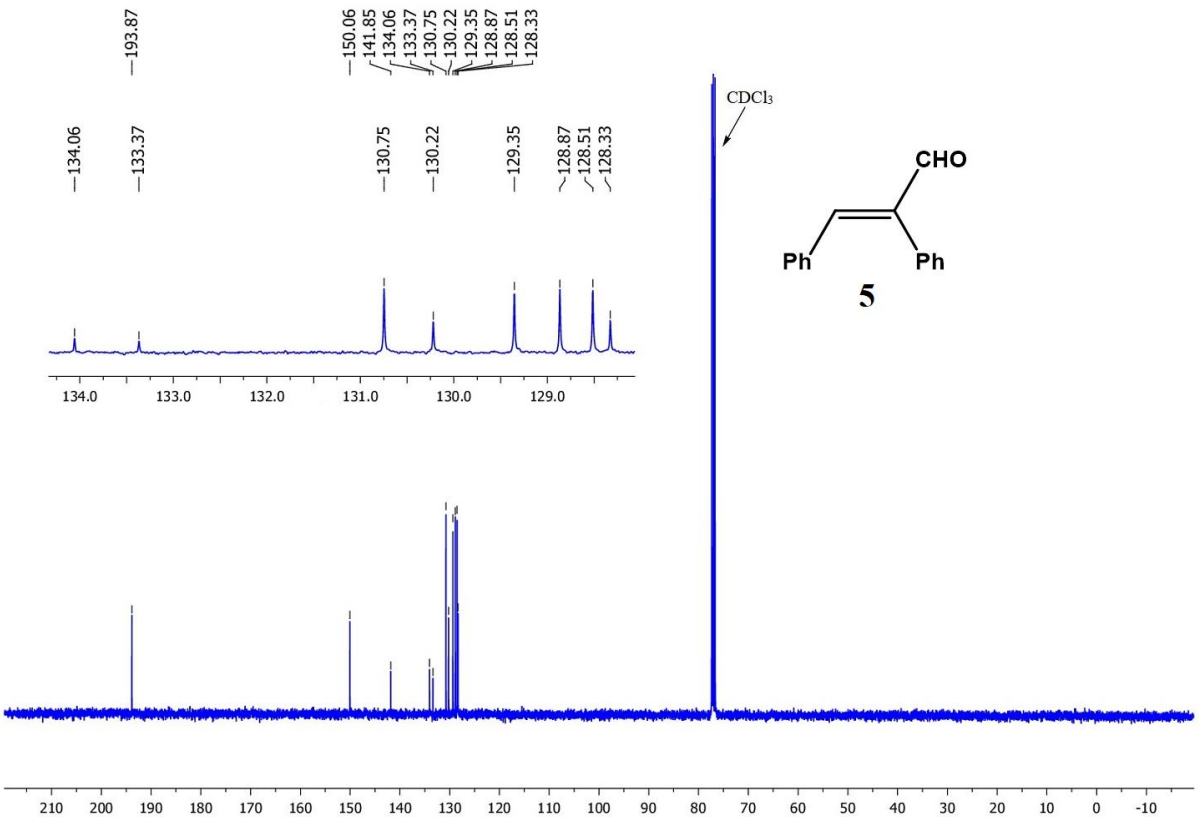


Figure S27. ^{13}C NMR spectrum of compound **5** ($CDCl_3$, 101 MHz)

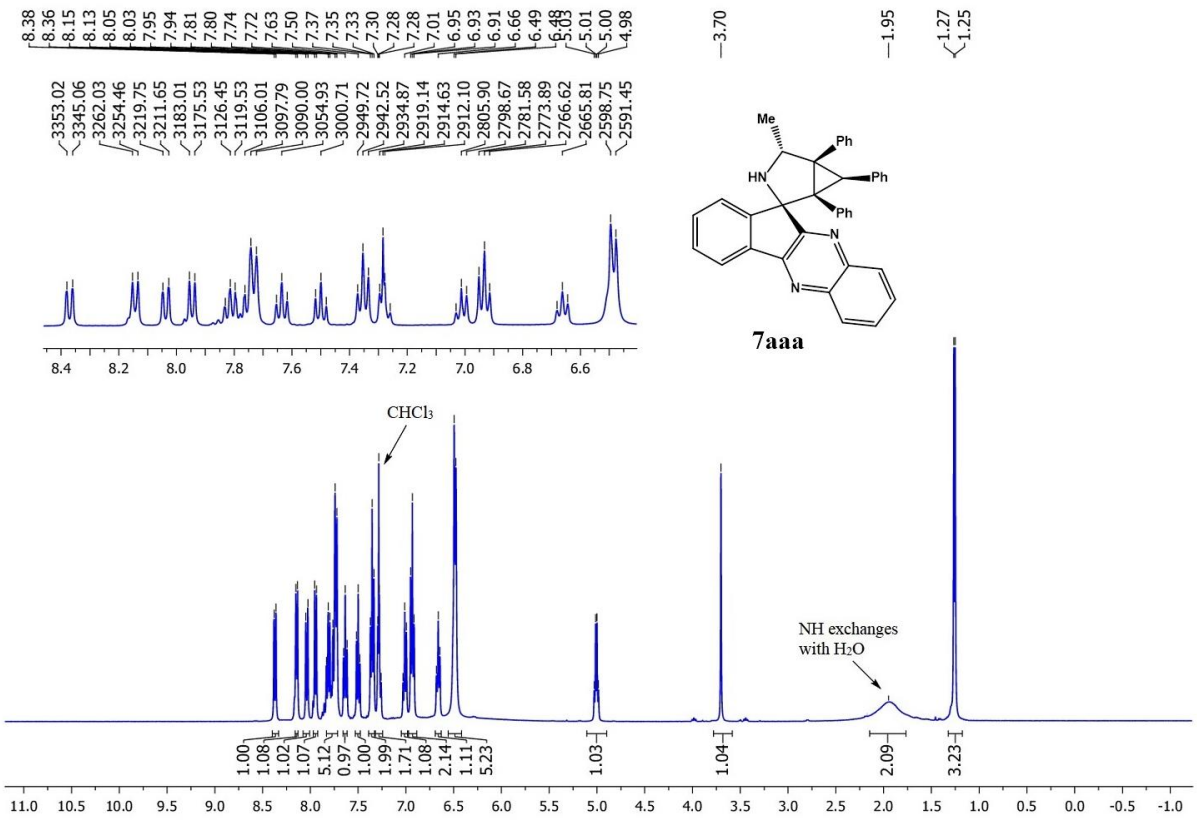


Figure S28. ^{1}H NMR spectrum of compound **7aaa** ($CDCl_3$, 400 MHz)

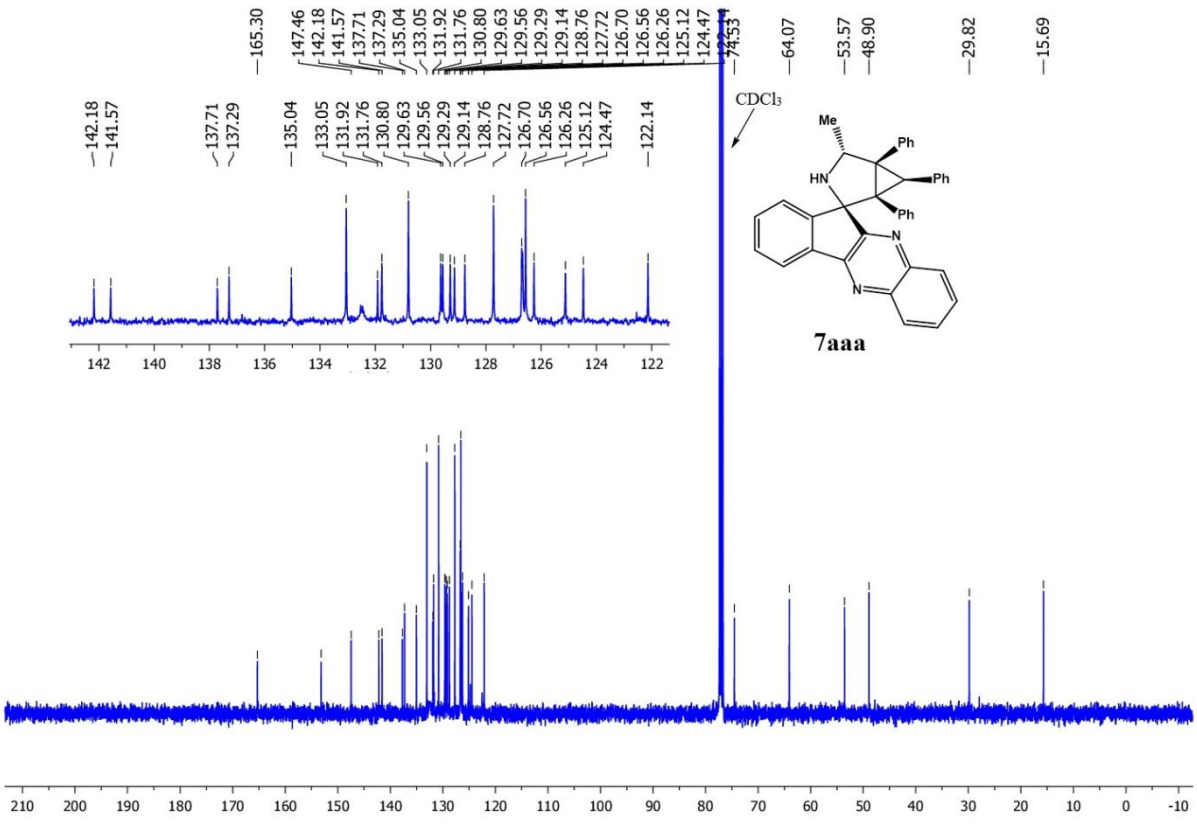


Figure S29. ^{13}C NMR spectrum of compound **7aaa** ($CDCl_3$, 101 MHz)

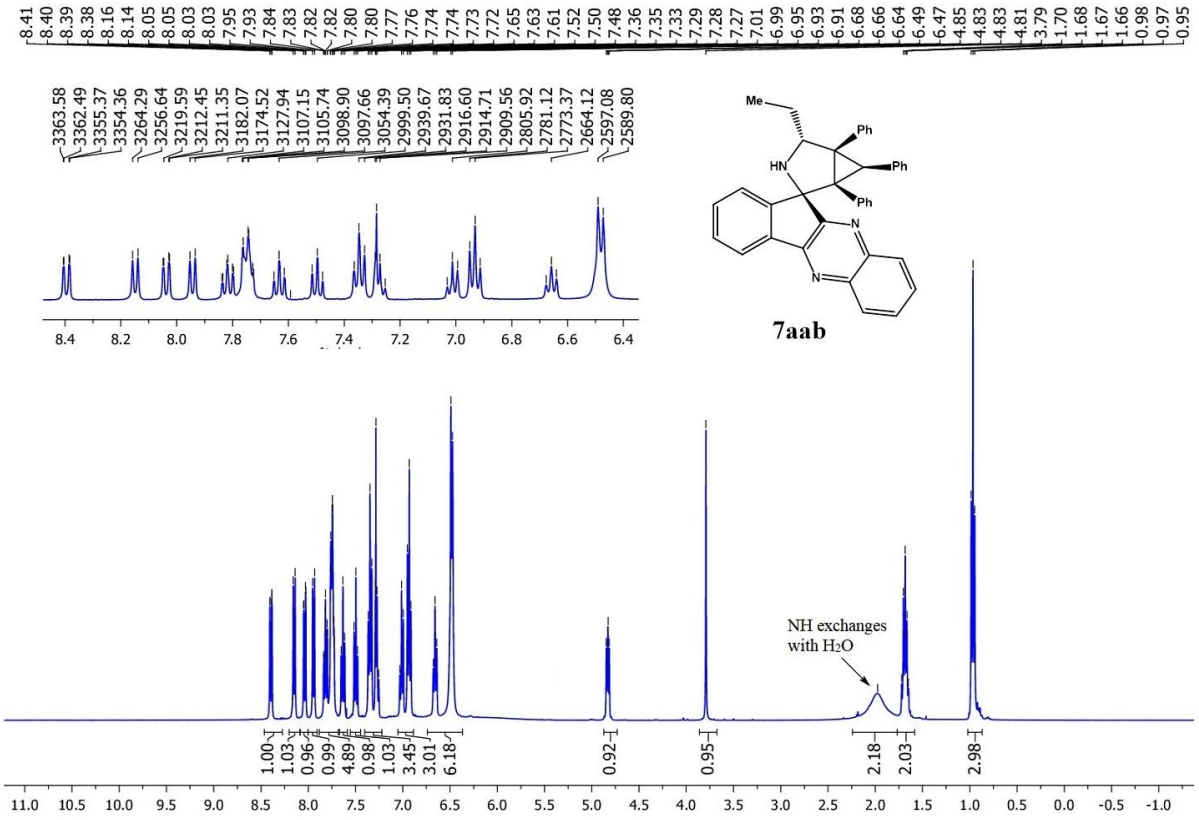


Figure S30. ^{1}H NMR spectrum of compound **7aab** ($CDCl_3$, 400 MHz)

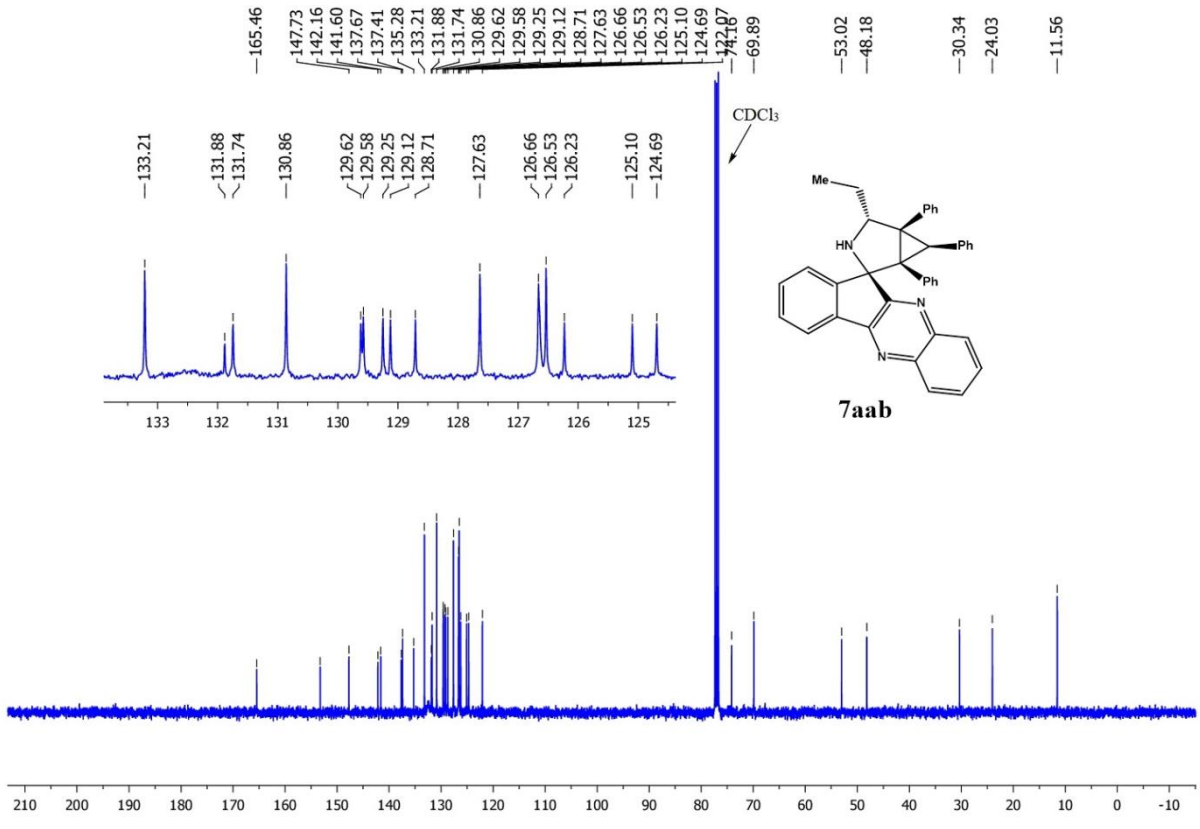


Figure S31. ^{13}C NMR spectrum of compound **7aab** ($CDCl_3$, 101 MHz)

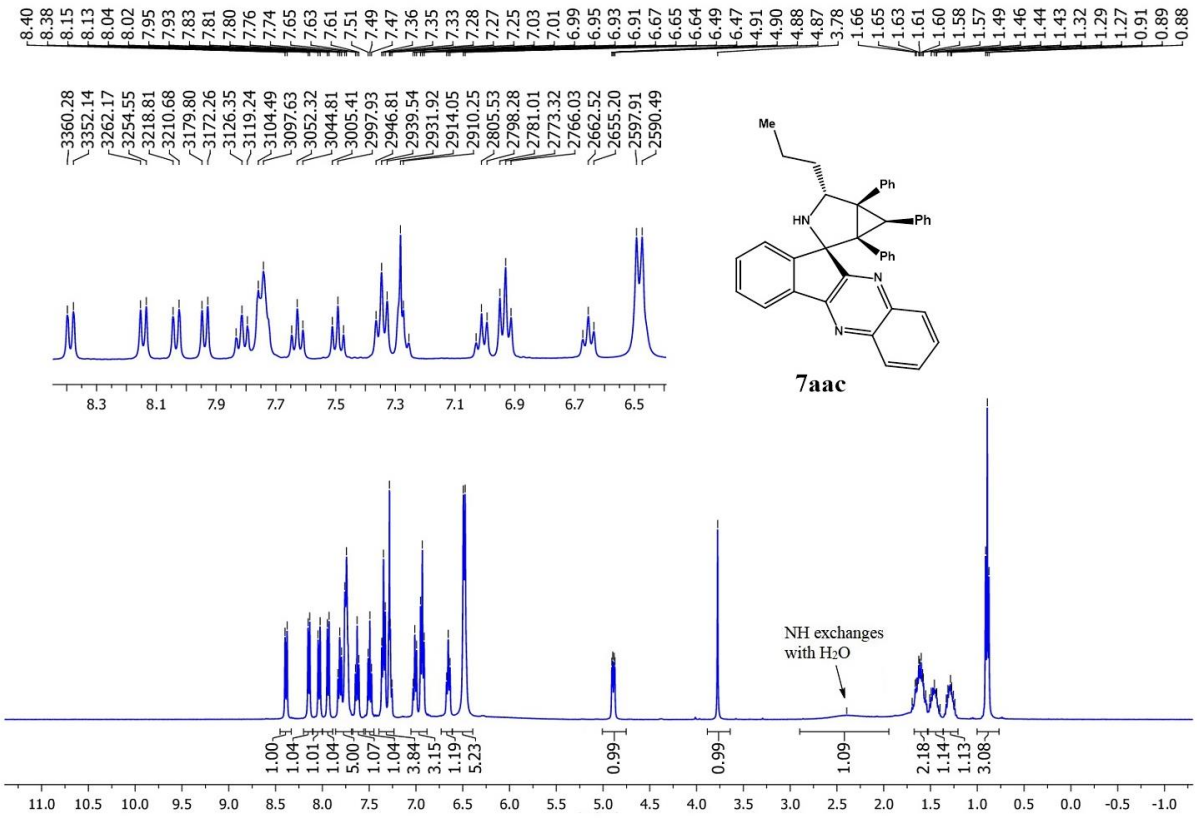


Figure S32. ^{1}H NMR spectrum of compound **7aac** ($CDCl_3$, 400 MHz)

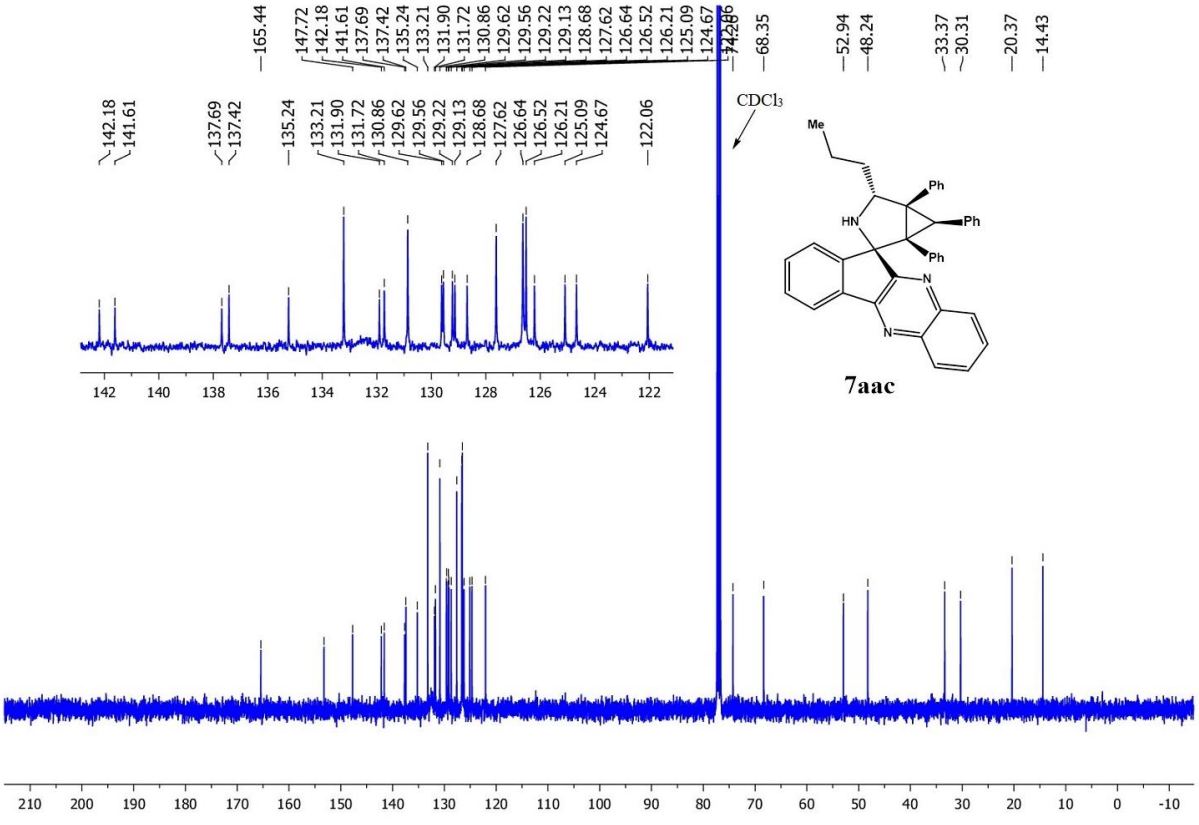


Figure S33. ^{13}C NMR spectrum of compound **7aac** ($CDCl_3$, 101 MHz)

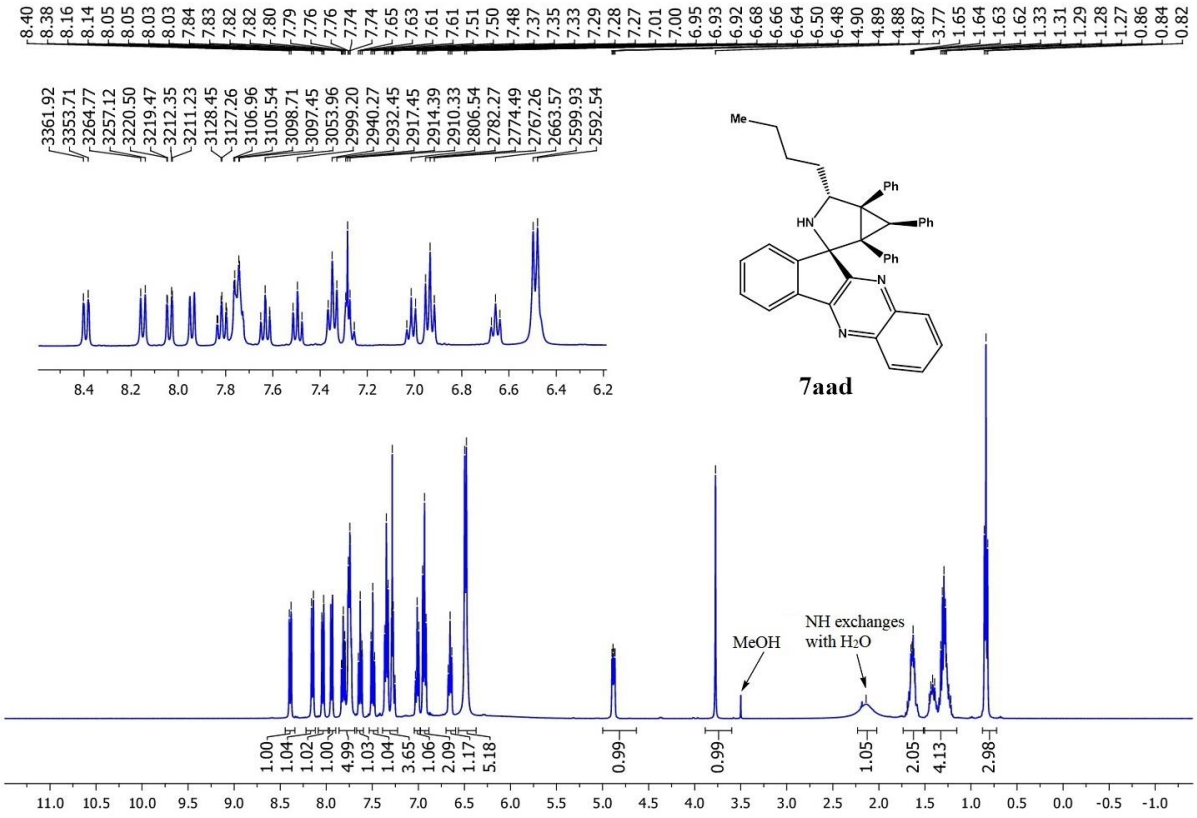


Figure S34. ^{1}H NMR spectrum of compound **7aad** ($CDCl_3$, 400 MHz)

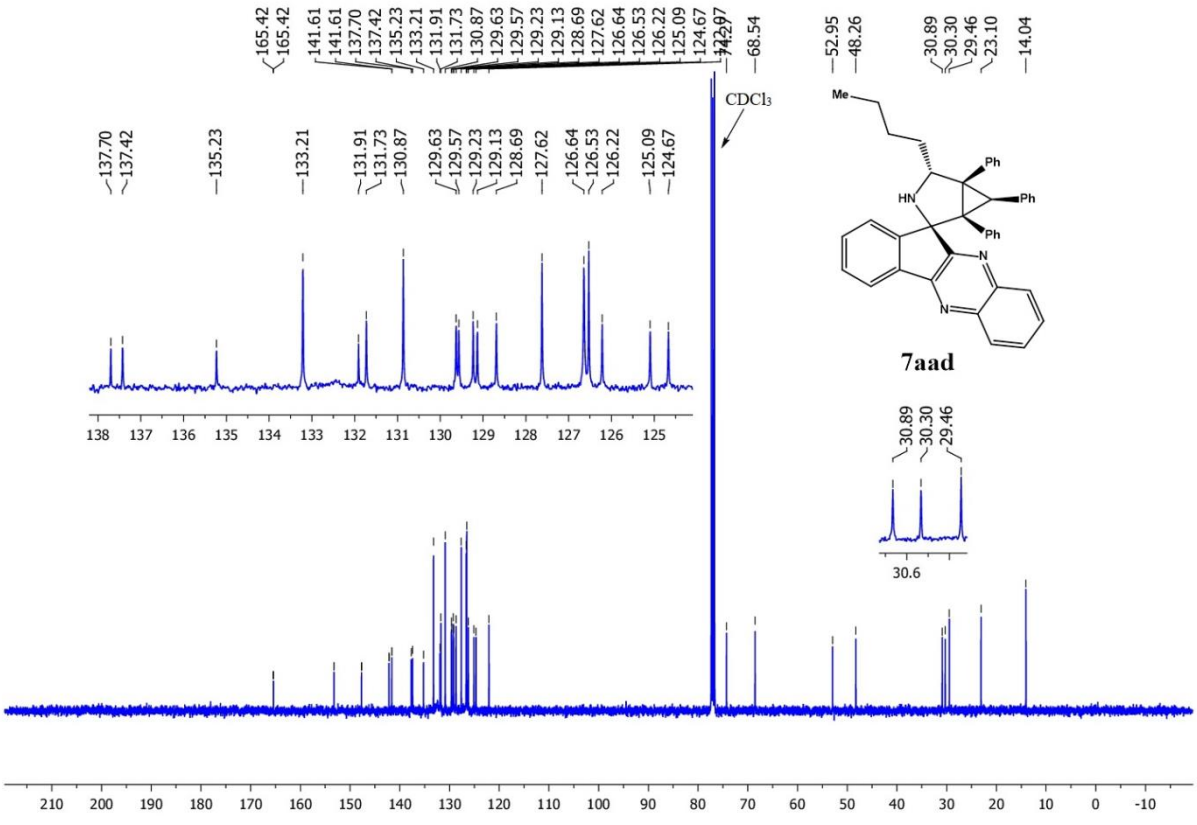


Figure S35. ^{13}C NMR spectrum of compound **7aad** ($CDCl_3$, 101 MHz)

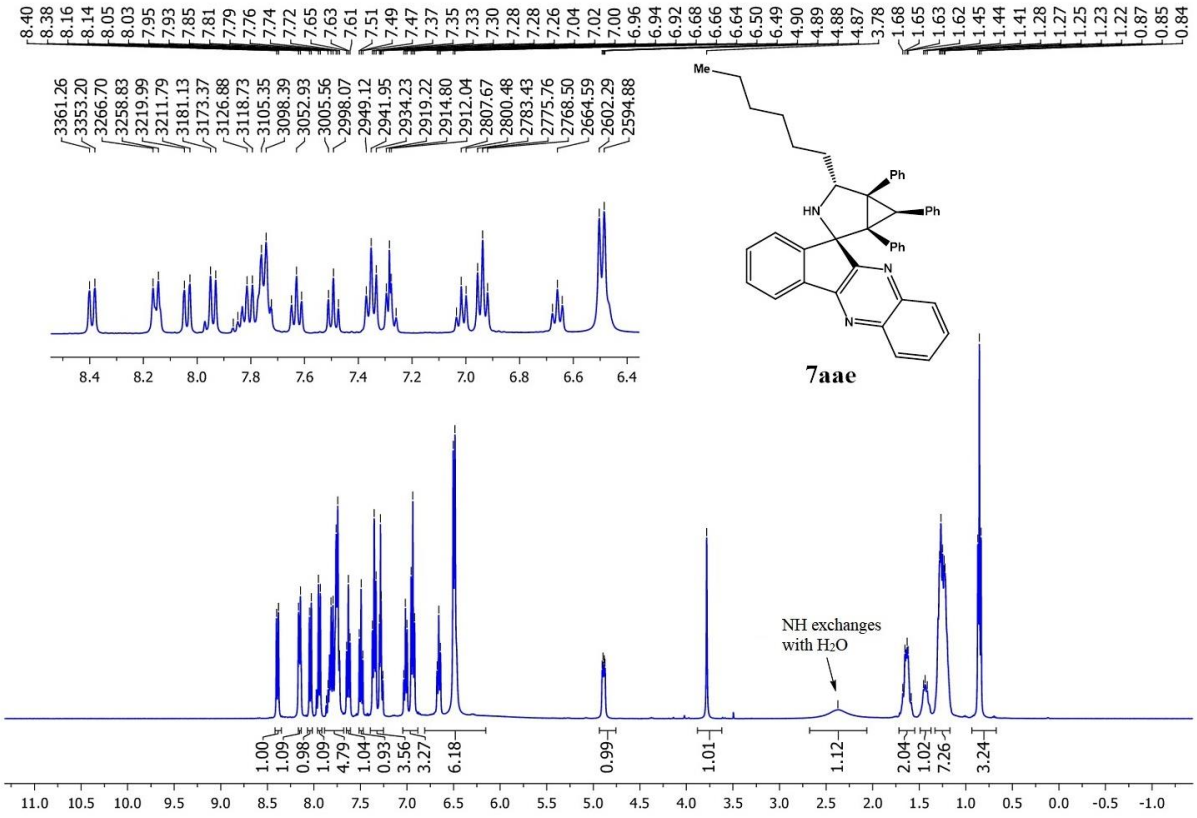


Figure S36. ^{1}H NMR spectrum of compound **7aae** ($CDCl_3$, 400 MHz)

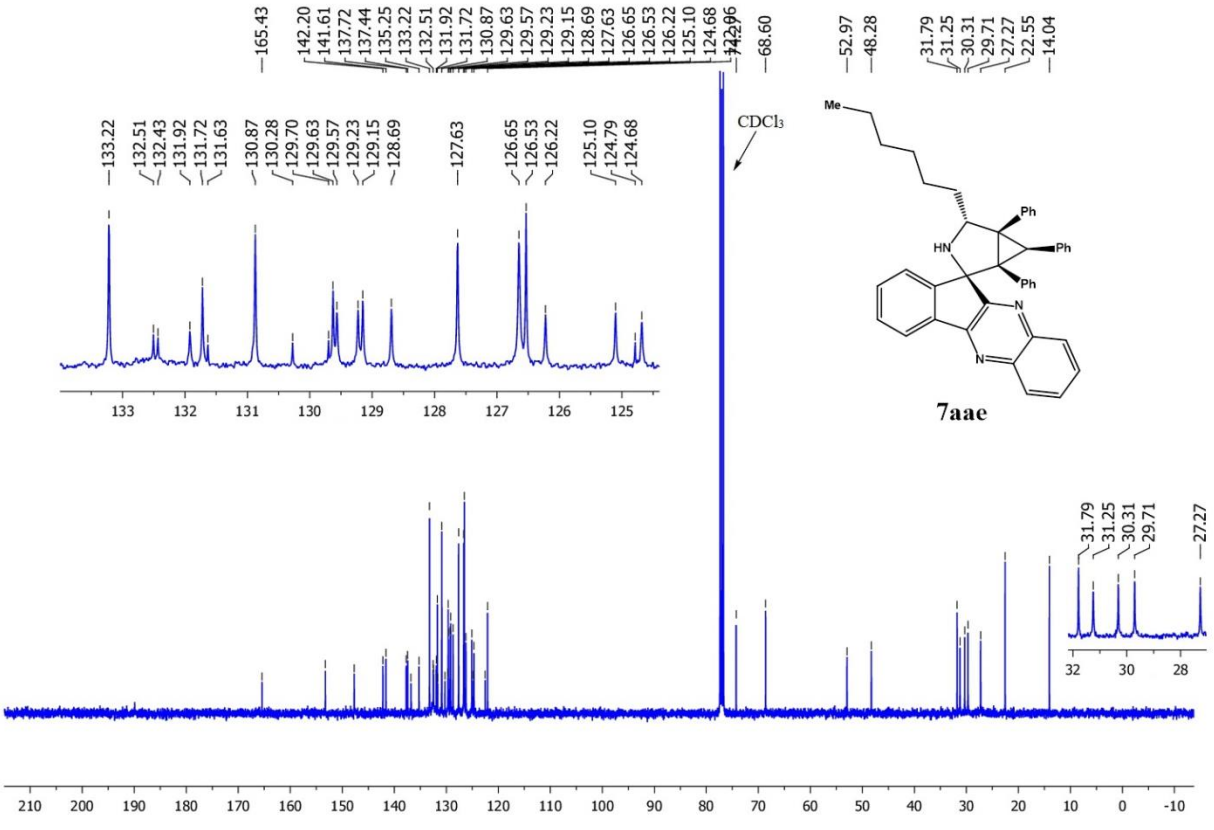


Figure S37. ^{13}C NMR spectrum of compound **7aae** ($CDCl_3$, 101 MHz)

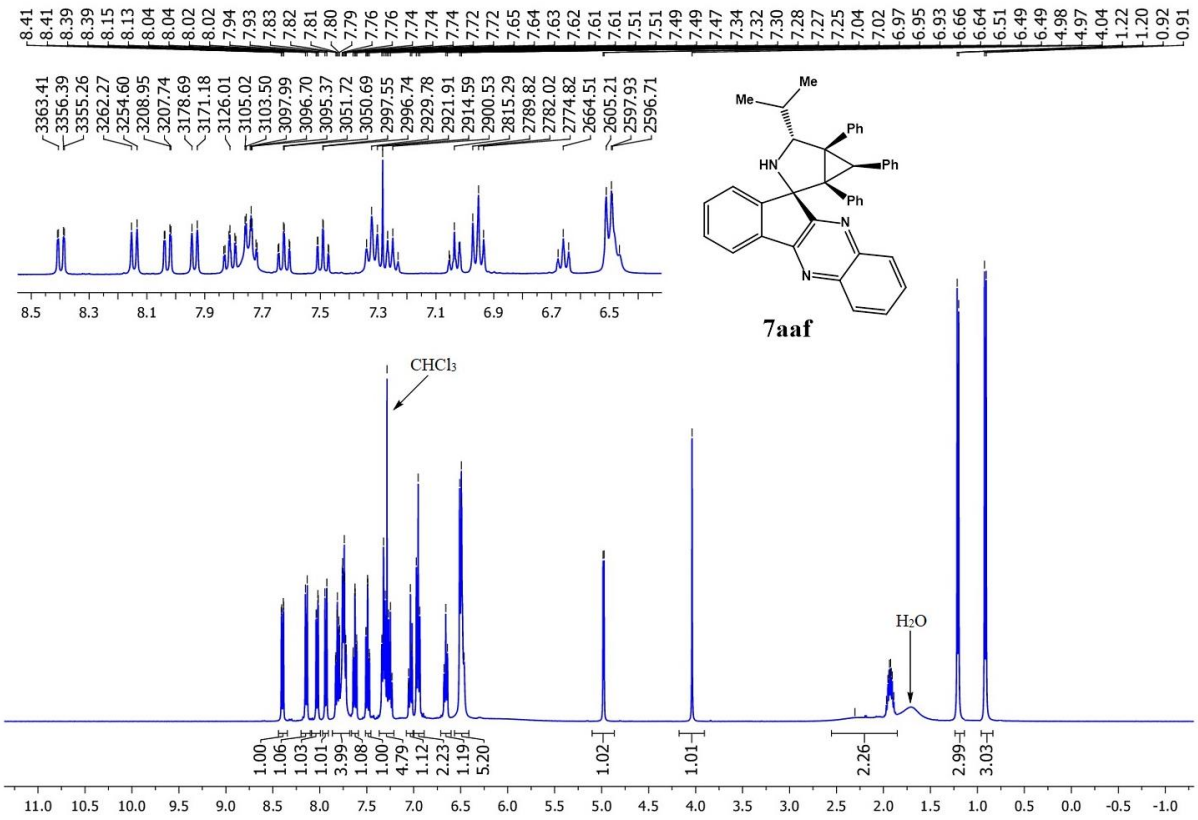


Figure S38. ^{1}H NMR spectrum of compound **7aaf** ($CDCl_3$, 400 MHz)

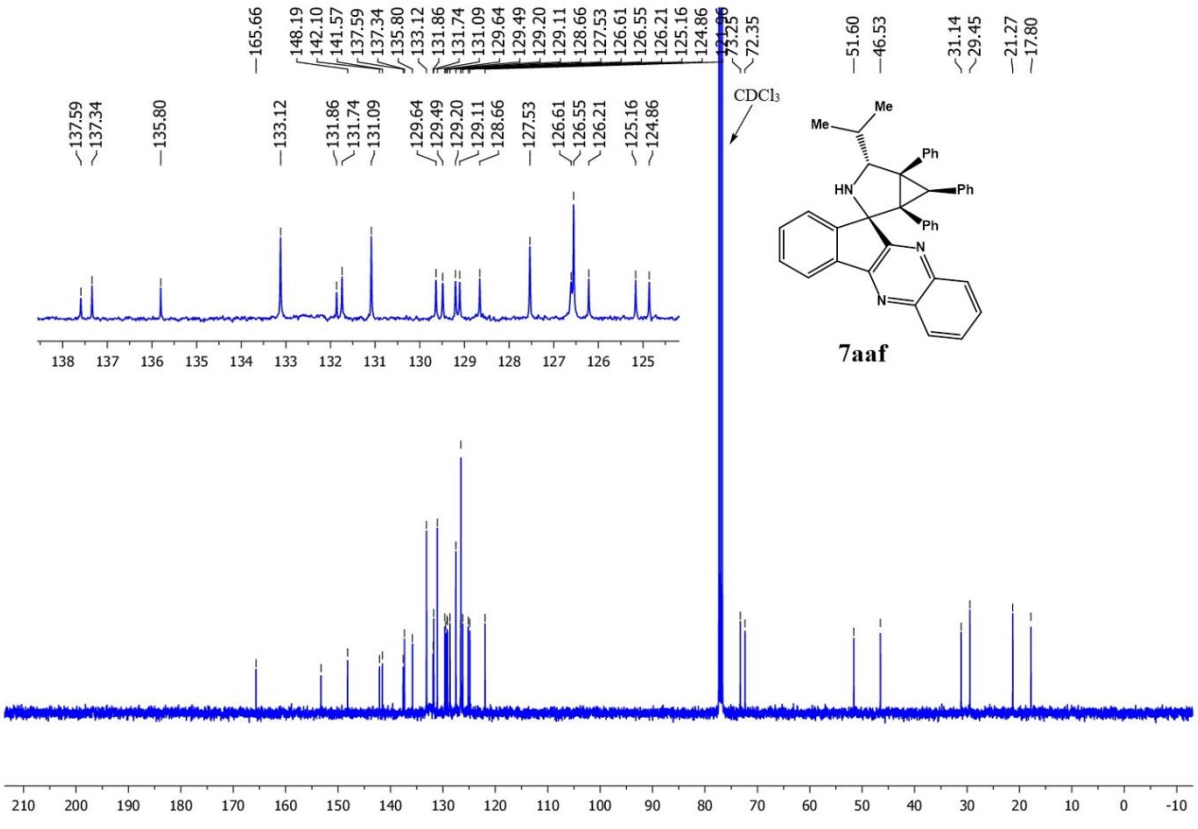


Figure S39. ^{13}C NMR spectrum of compound **7aaf** ($CDCl_3$, 101 MHz)

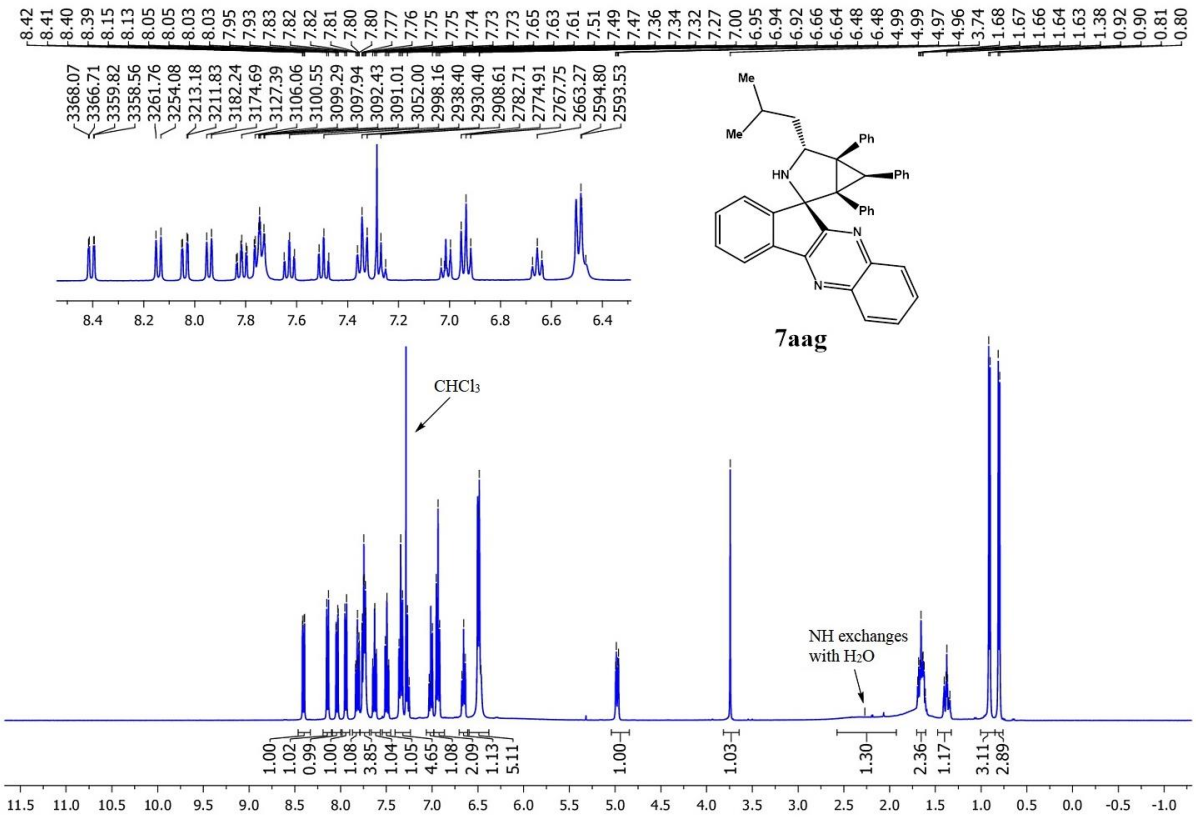


Figure S40. ^{1}H NMR spectrum of compound **7aag** ($CDCl_3$, 400 MHz)

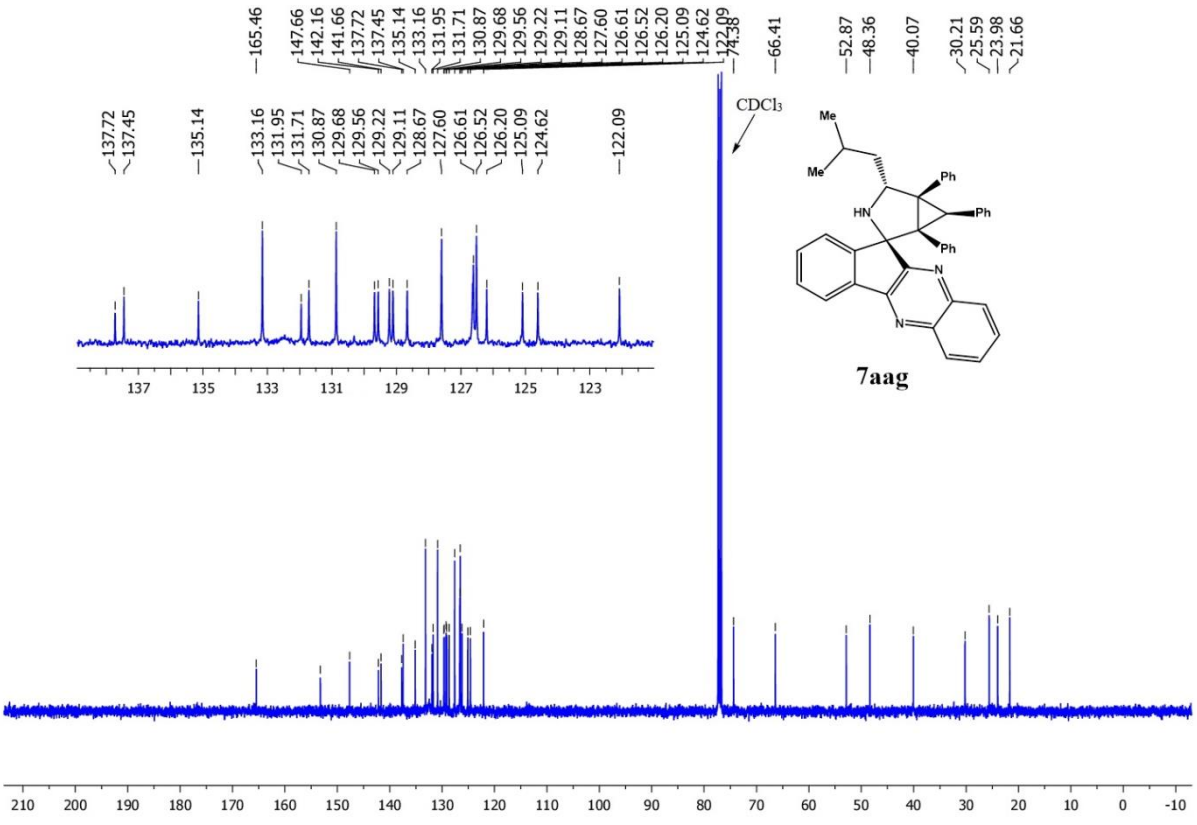


Figure S41. ^{13}C NMR spectrum of compound **7aag** ($CDCl_3$, 101 MHz)

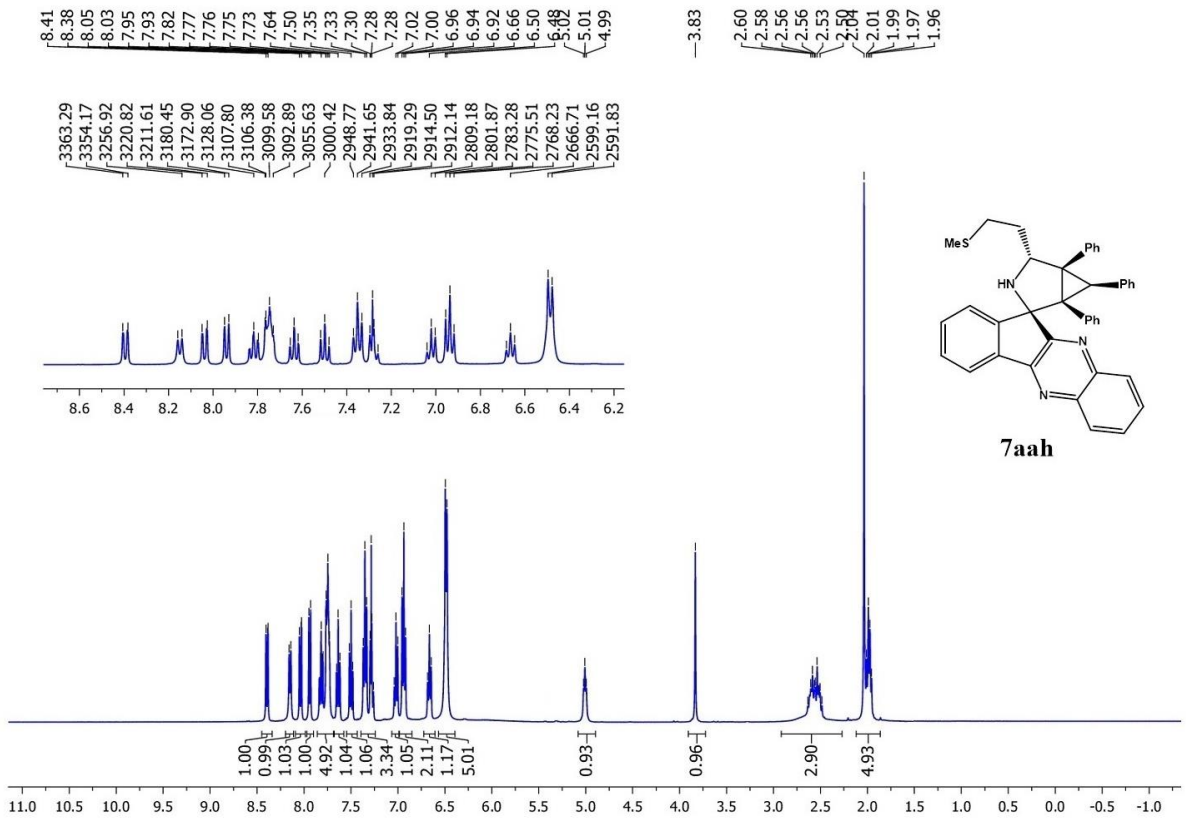


Figure S42. ^{1}H NMR spectrum of compound **7aah** ($CDCl_3$, 400 MHz)

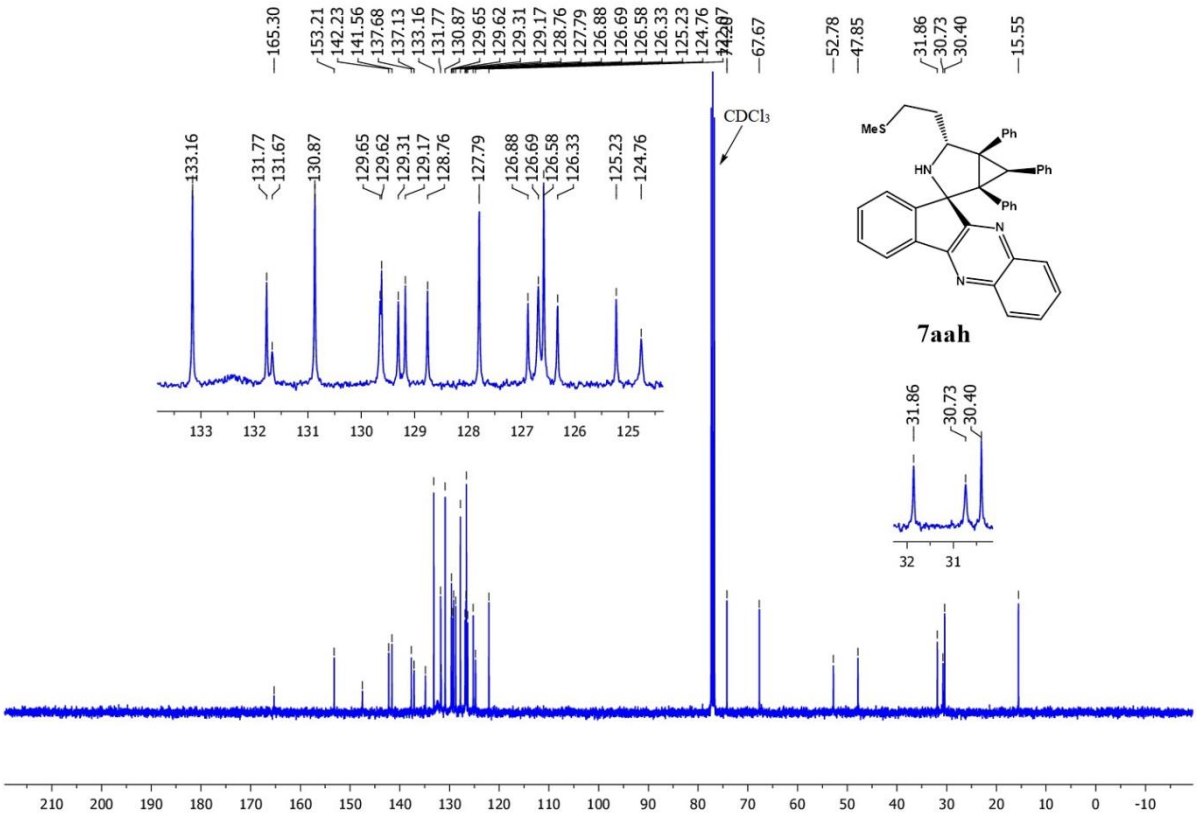


Figure S43. ^{13}C NMR spectrum of compound **7aah** ($CDCl_3$, 101 MHz)

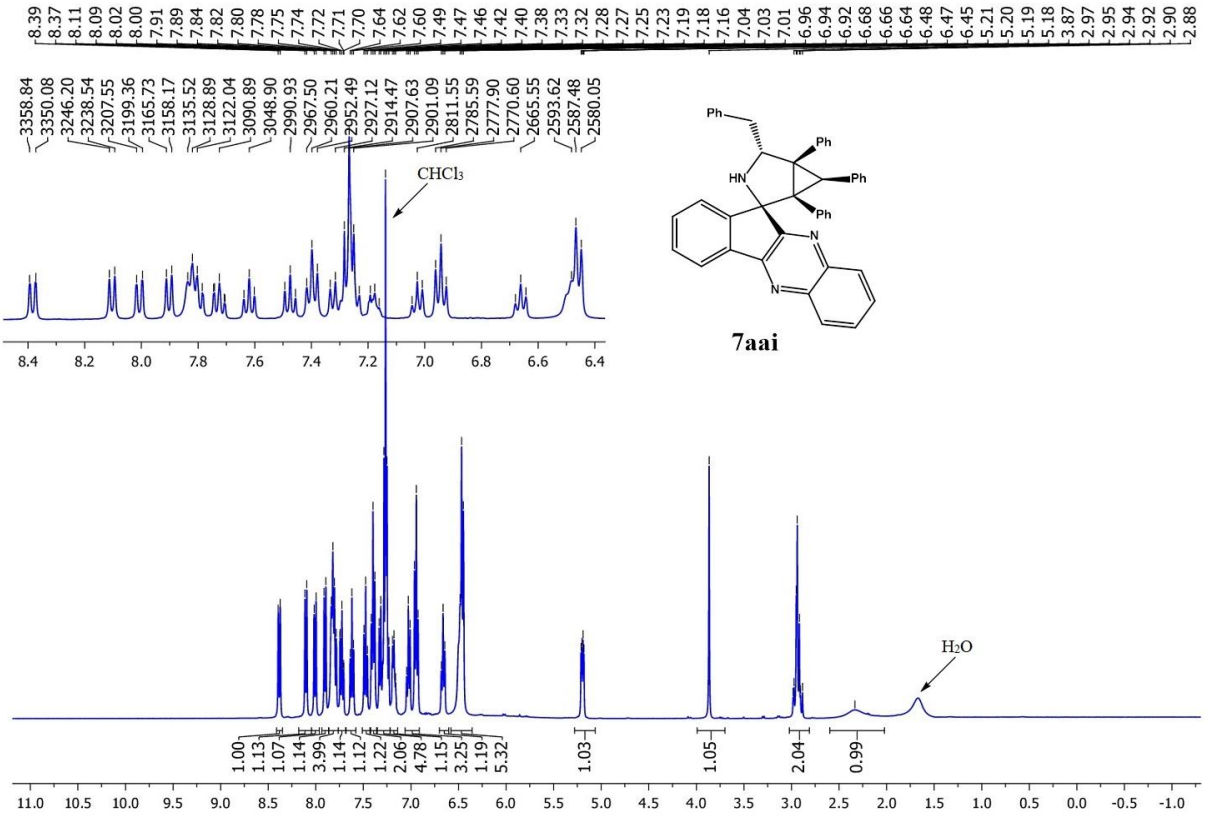


Figure S44. ^{1}H NMR spectrum of compound **7aai** ($CDCl_3$, 400 MHz)

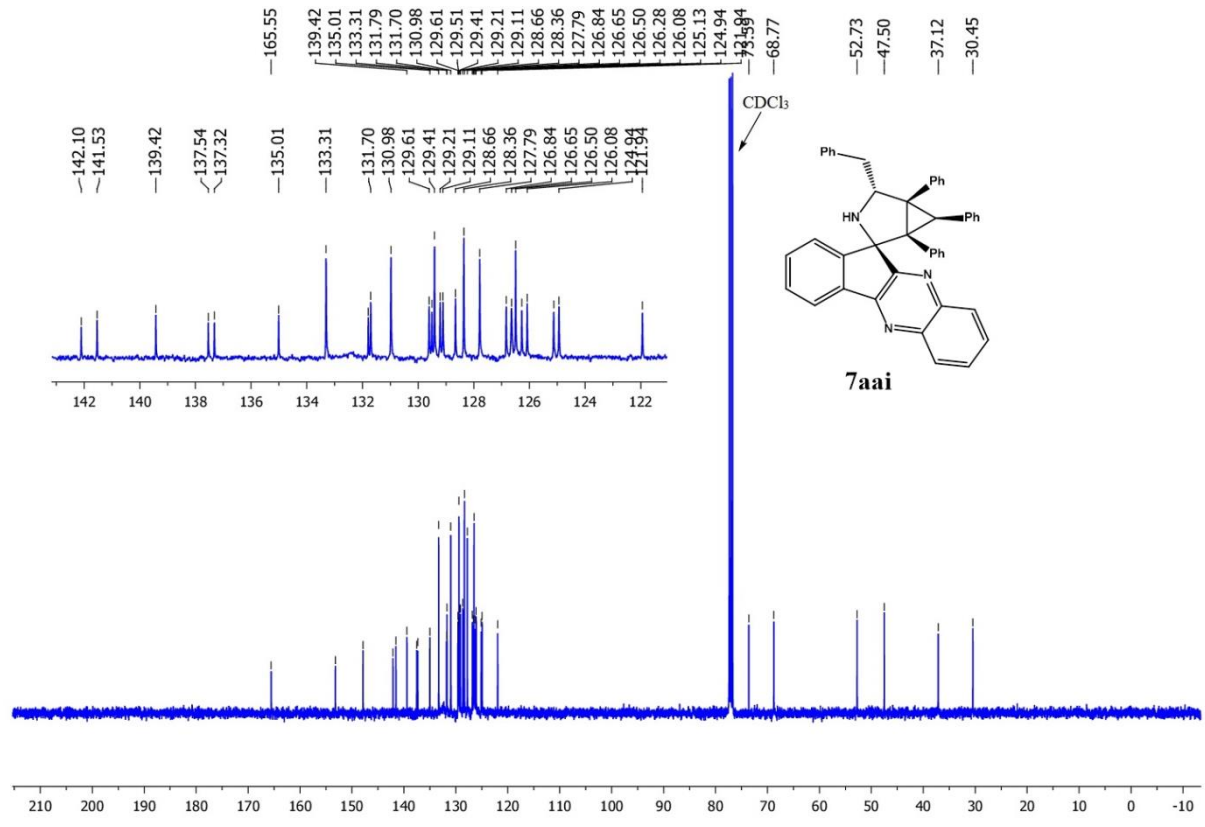


Figure S45. ^{13}C NMR spectrum of compound **7aai** ($CDCl_3$, 101 MHz)

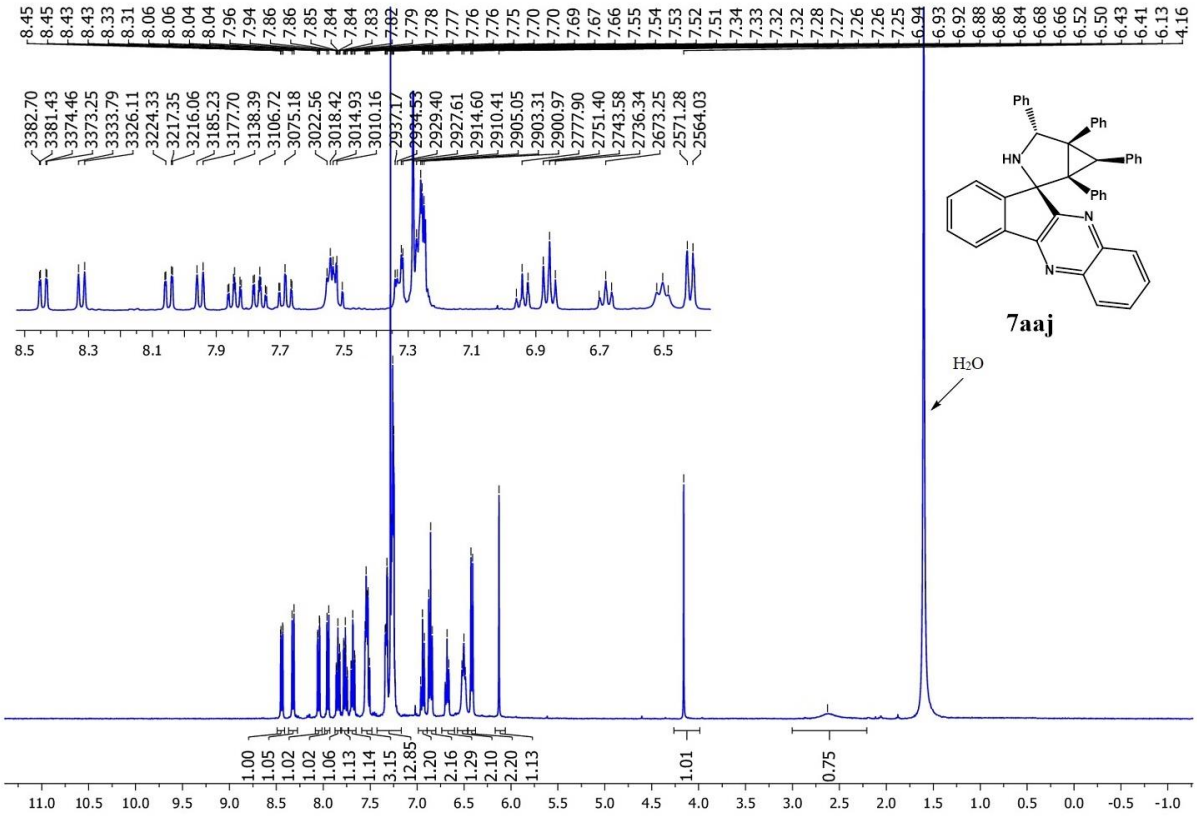


Figure S46. ^{1}H NMR spectrum of compound **7aaj** ($CDCl_3$, 400 MHz)

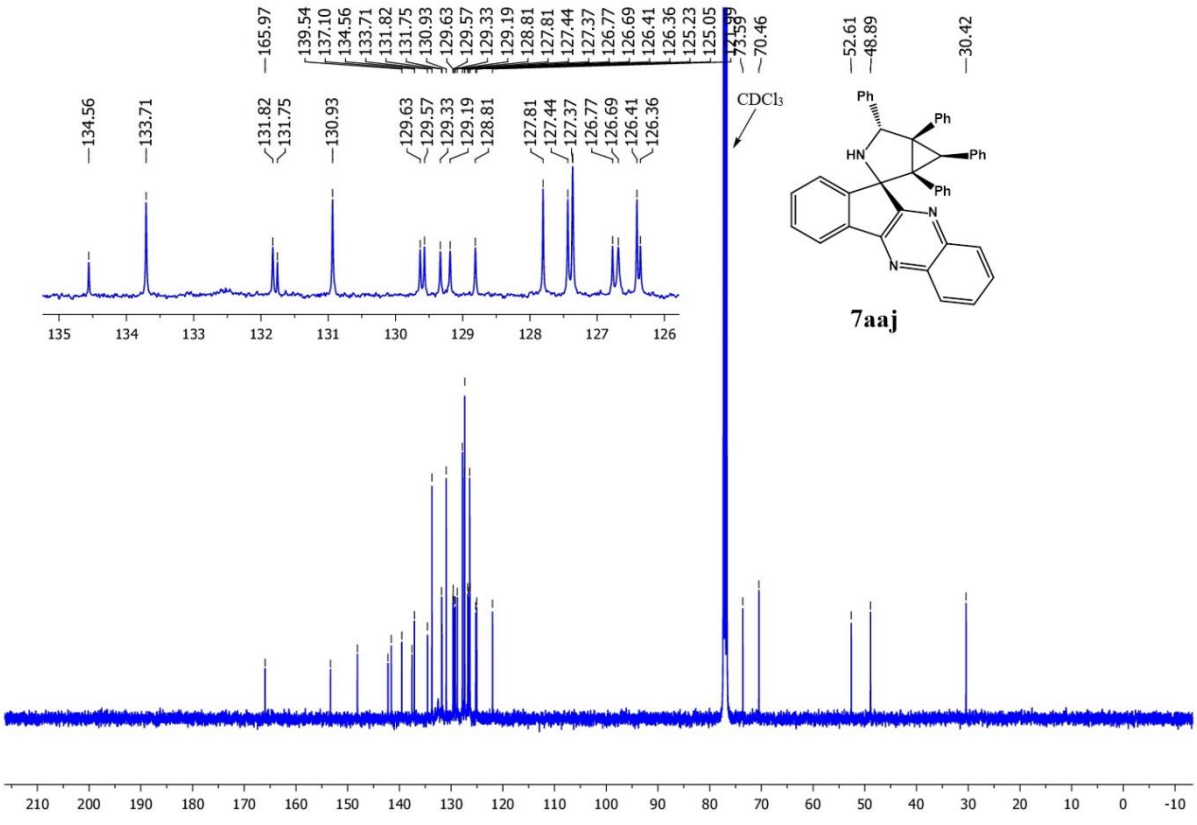


Figure S47. ^{13}C NMR spectrum of compound **7aaj** ($CDCl_3$, 101 MHz)

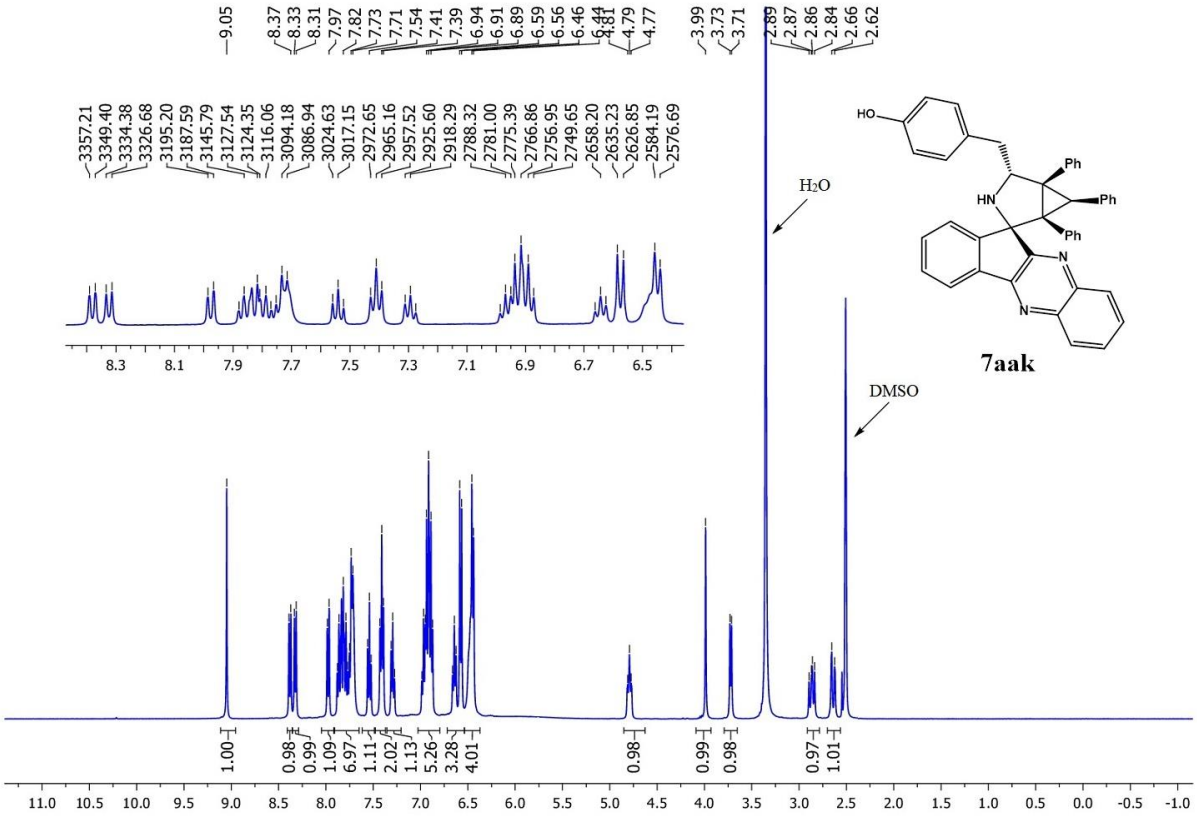


Figure S48. ^{1}H NMR spectrum of compound **7aak** (DMSO-d_6, 400 MHz)

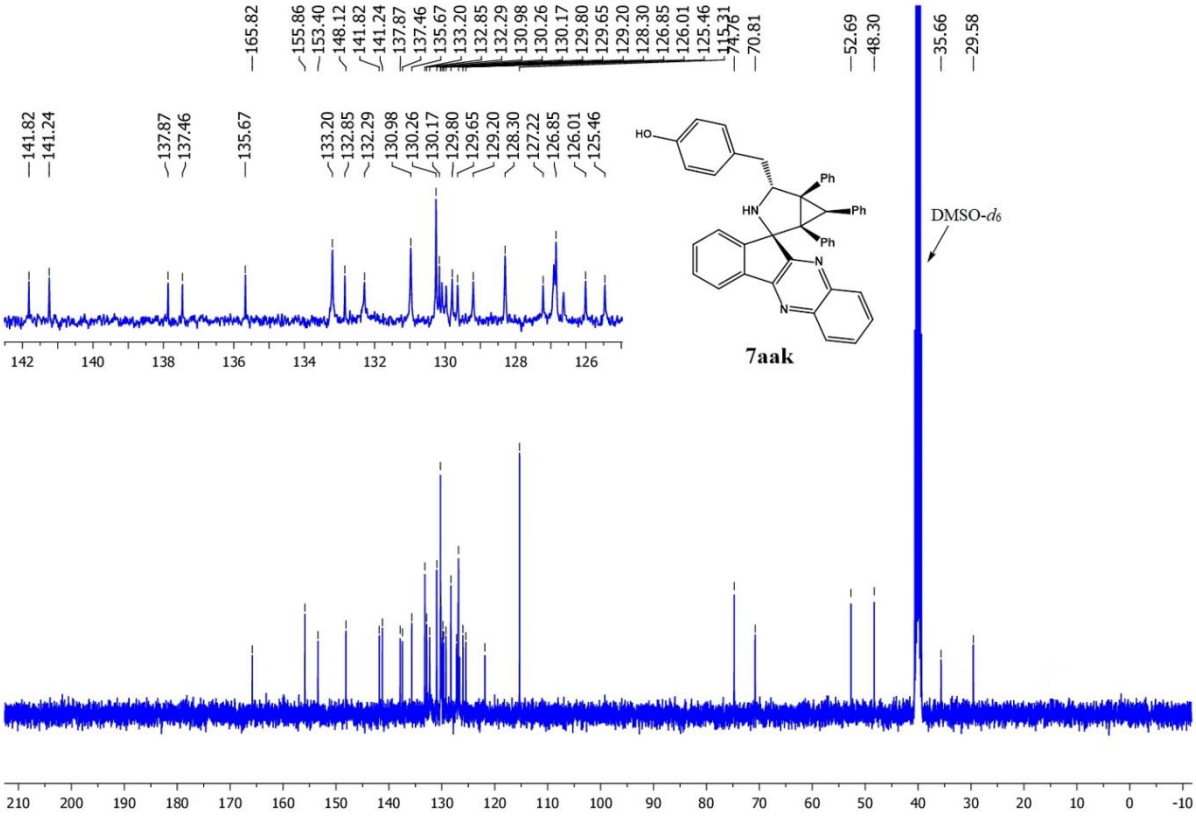


Figure S49. ^{13}C NMR spectrum of compound **7aak** (DMSO-d_6, 101 MHz)

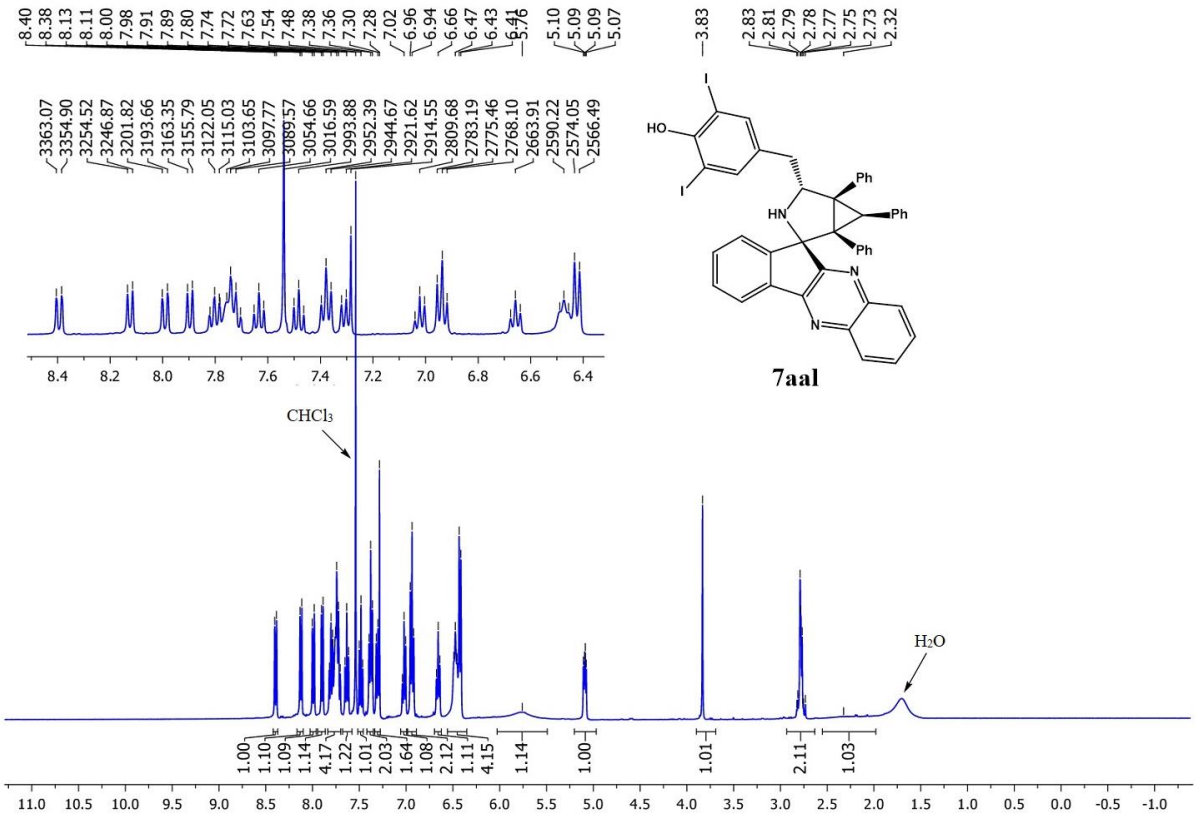


Figure S50. ^{1}H NMR spectrum of compound **7aal** ($CDCl_3$, 400 MHz)

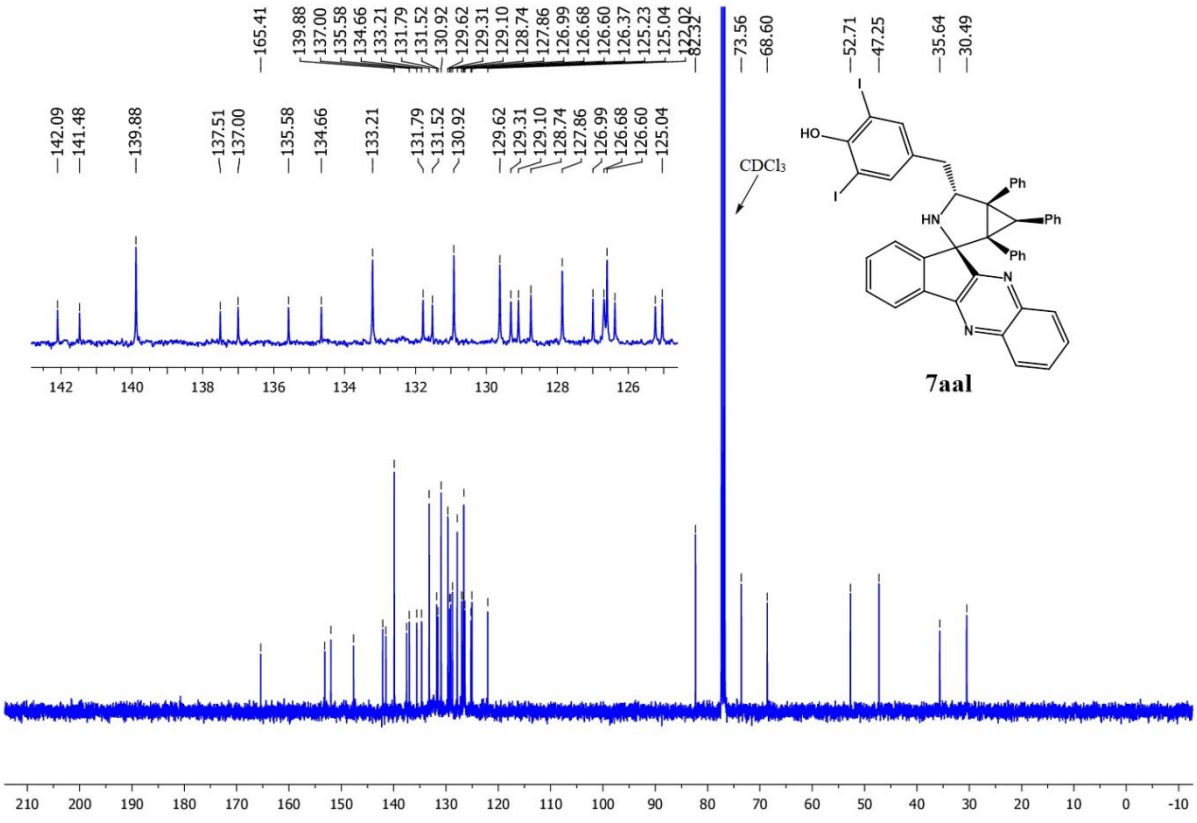


Figure S51. ^{13}C NMR spectrum of compound **7aal** ($CDCl_3$, 101 MHz)

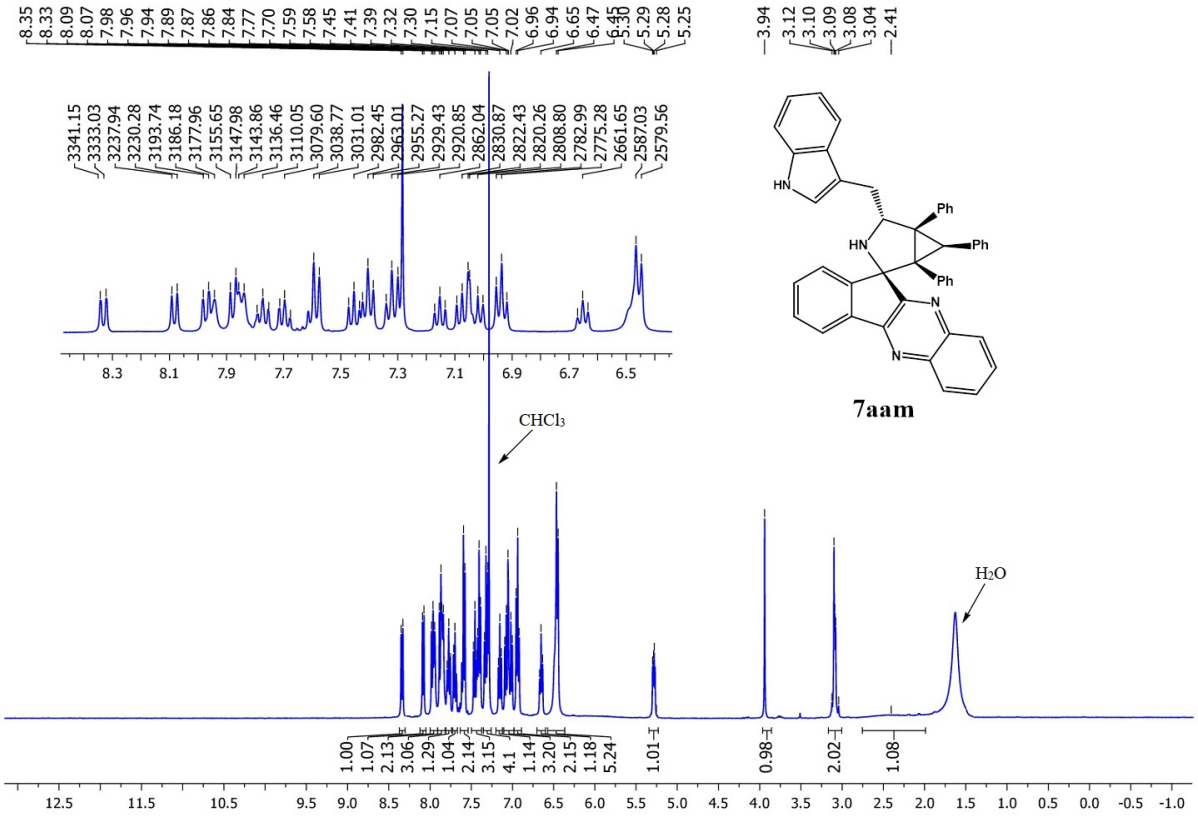


Figure S52. ^{1}H NMR spectrum of compound **7aam** ($CDCl_3$, 400 MHz)

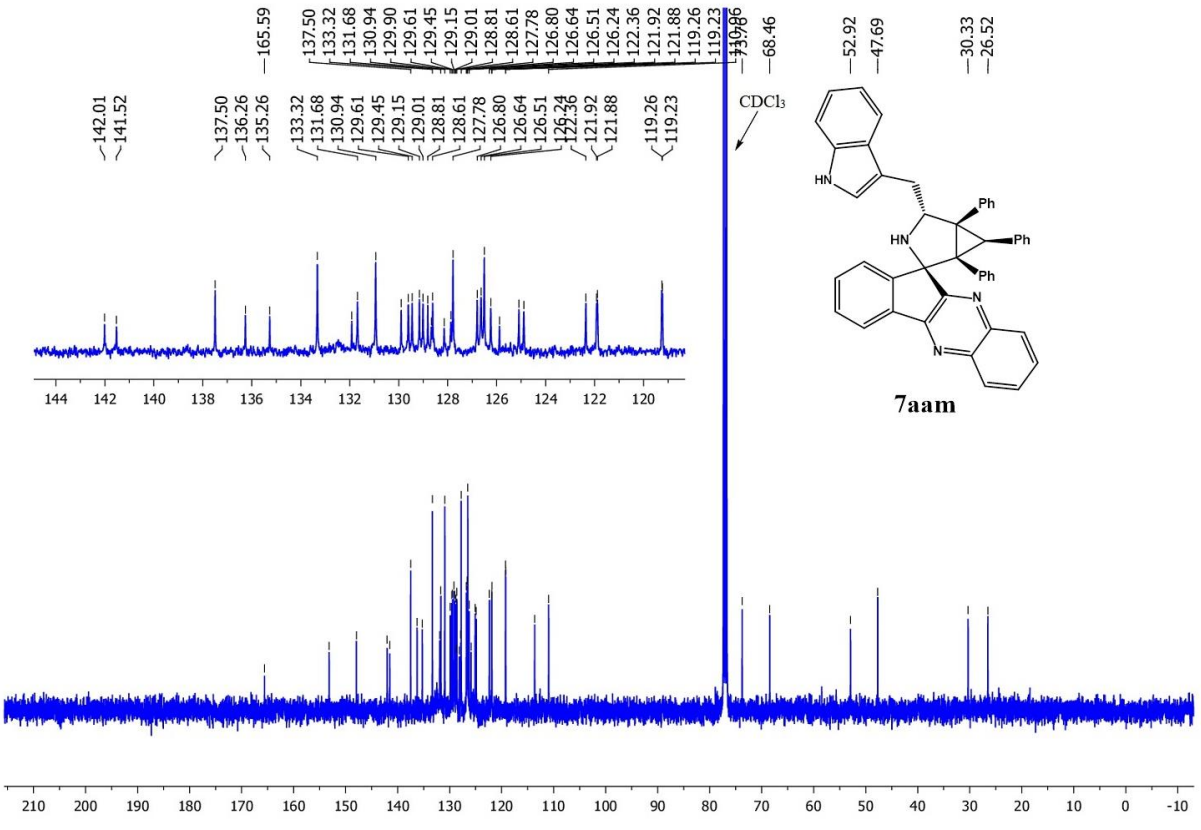


Figure S53. ^{13}C NMR spectrum of compound **7aam** ($CDCl_3$, 101 MHz)

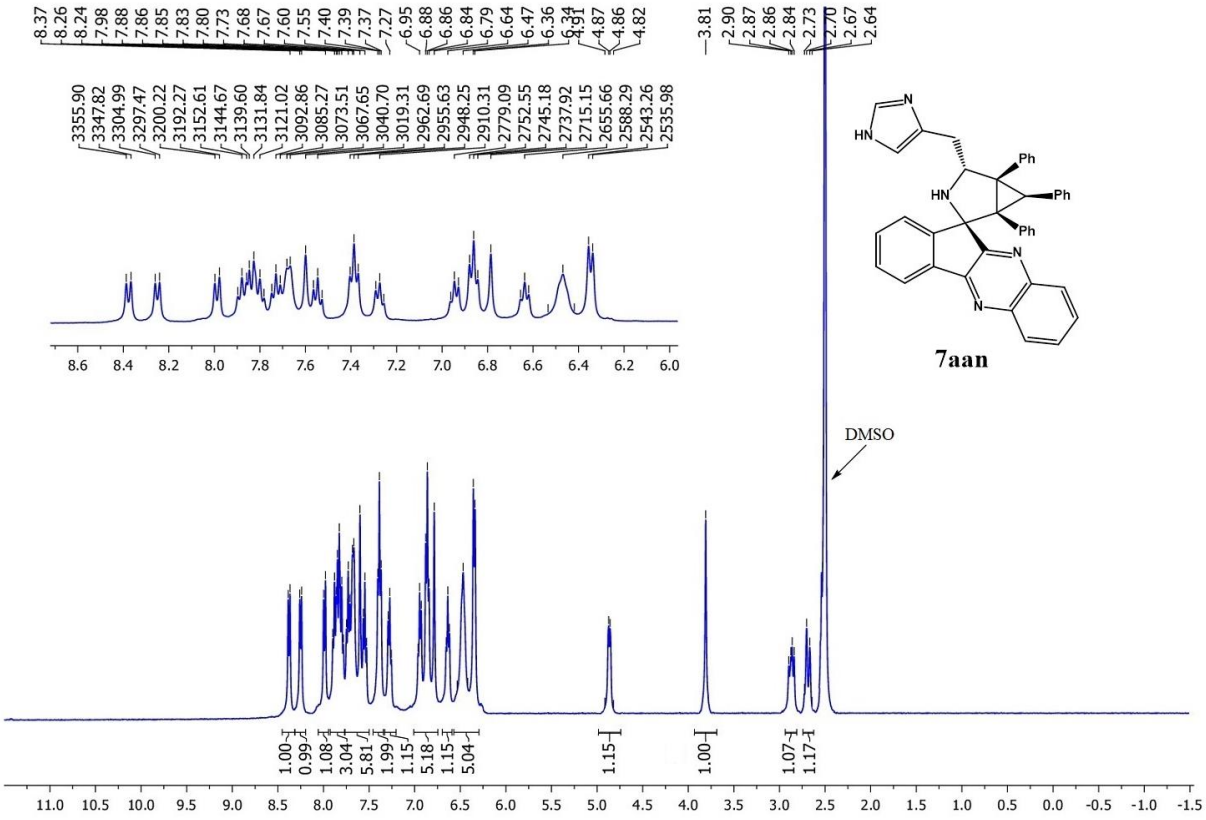


Figure S54. ^{1}H NMR spectrum of compound **7aan** (DMSO-d_6, 400 MHz)

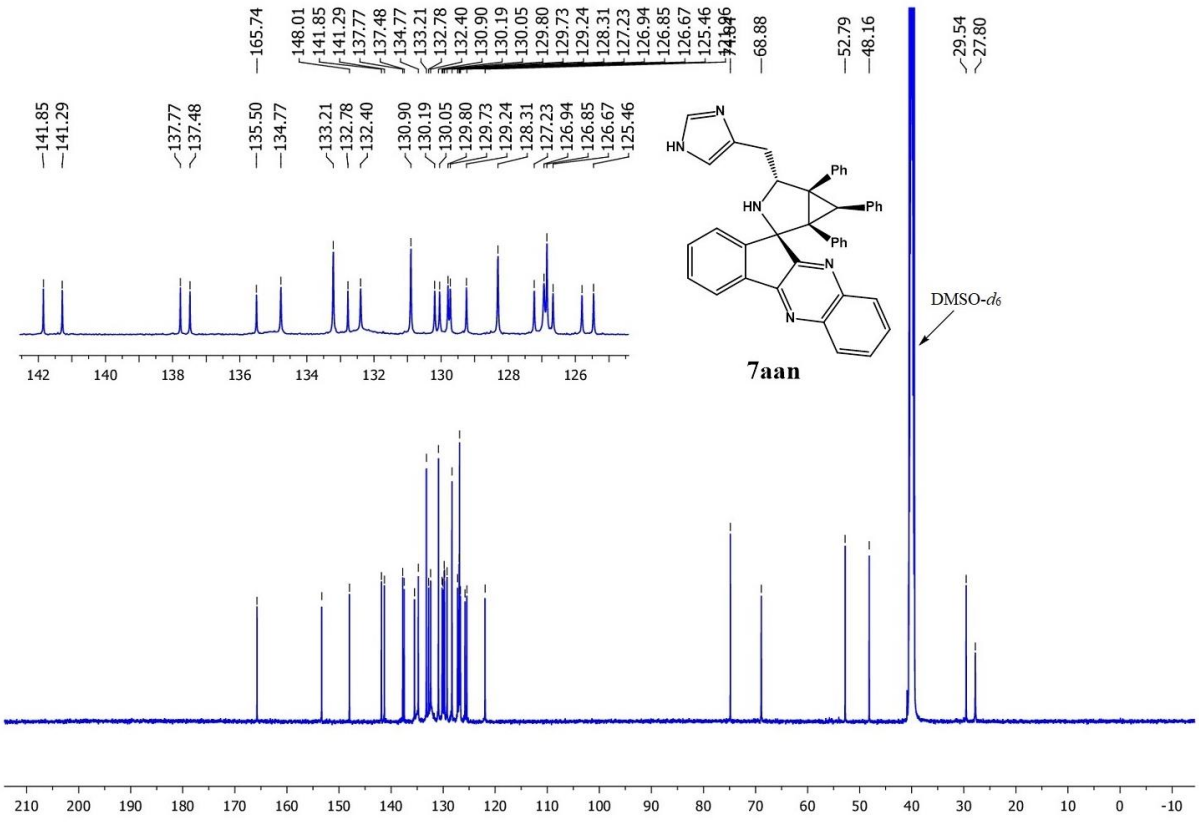


Figure S55. ^{13}C NMR spectrum of compound **7aan** (DMSO-d_6, 101 MHz)

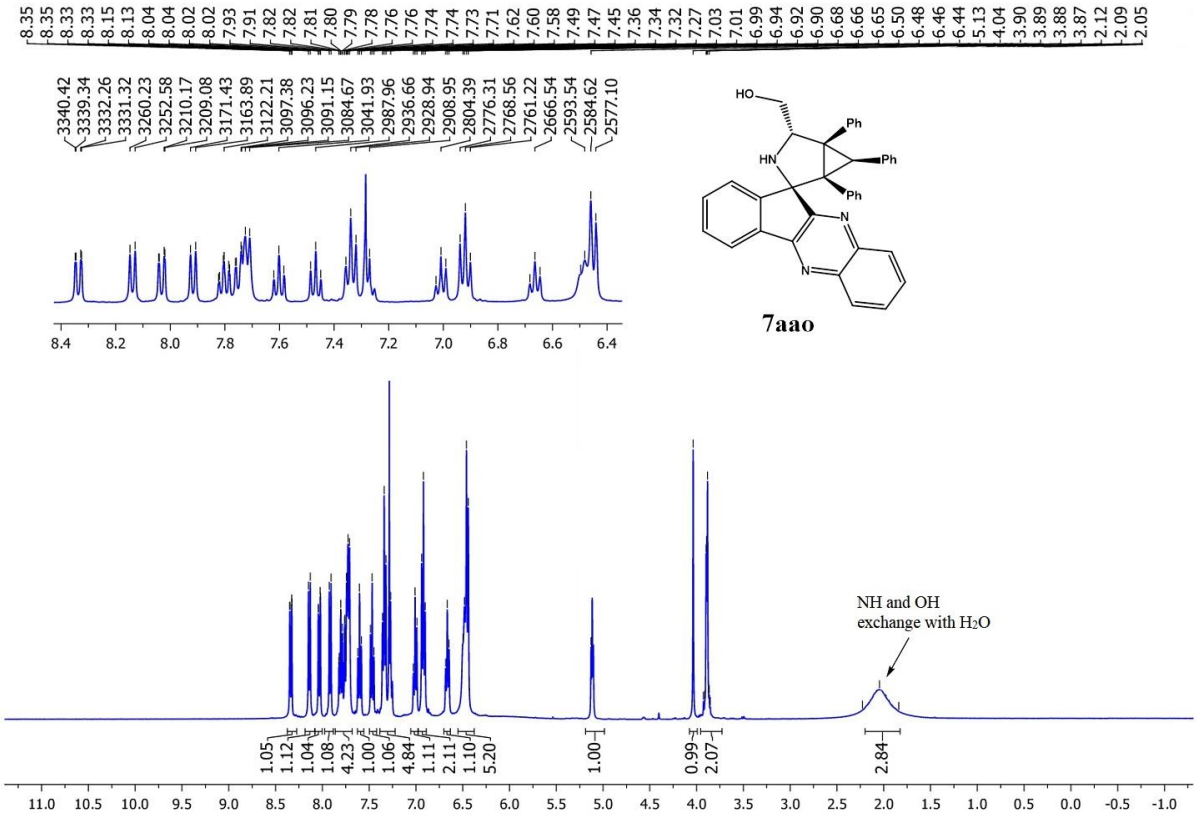


Figure S56. ^{1}H NMR spectrum of compound **7aao** ($CDCl_3$, 400 MHz)

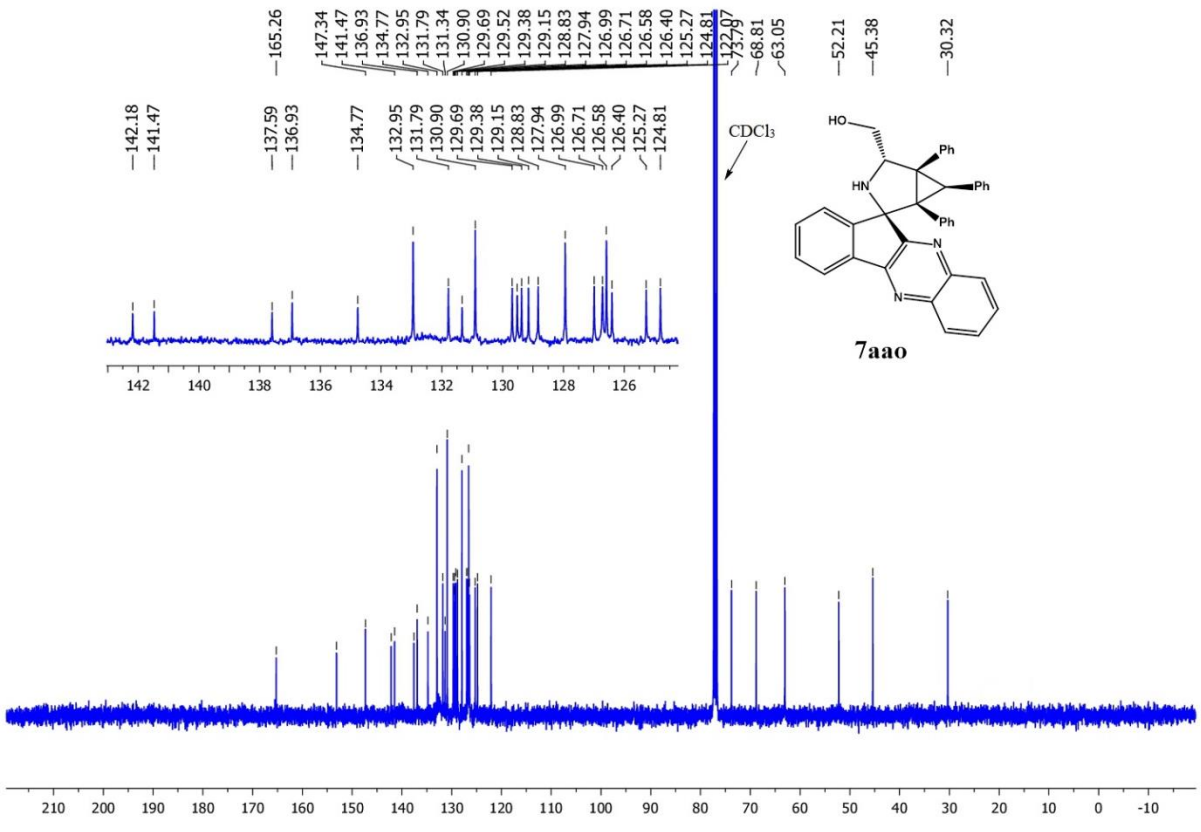


Figure S57. ^{13}C NMR spectrum of compound **7aao** ($CDCl_3$, 101 MHz)

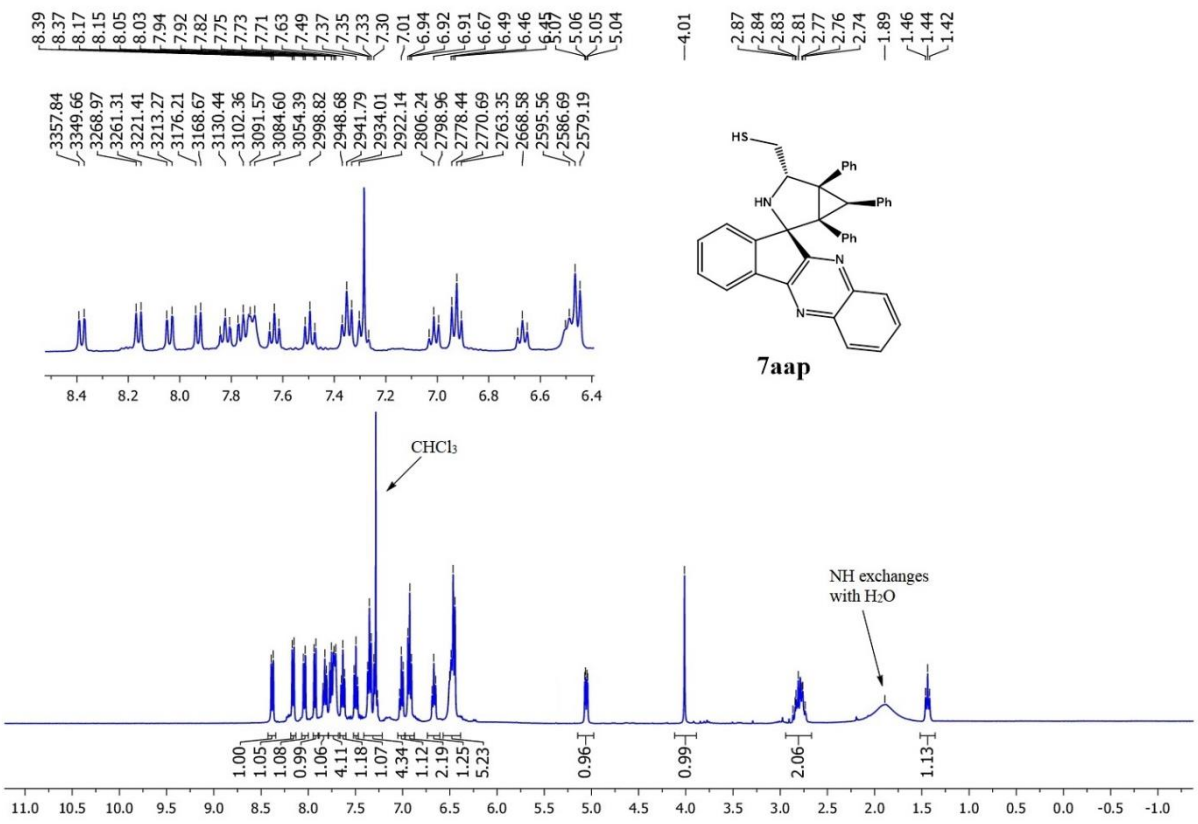


Figure S58. ^{1}H NMR spectrum of compound **7aap** ($CDCl_3$, 400 MHz)

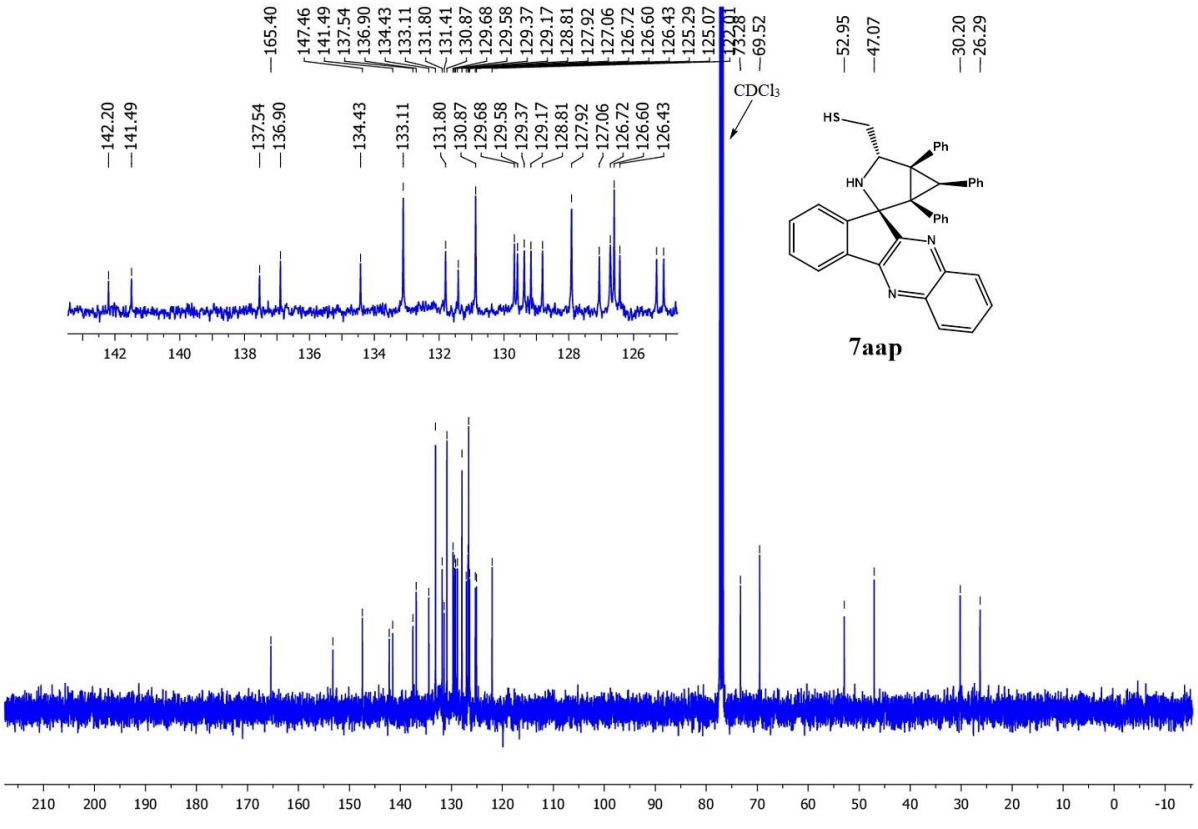


Figure S59. ^{13}C NMR spectrum of compound **7aap** ($CDCl_3$, 101 MHz)

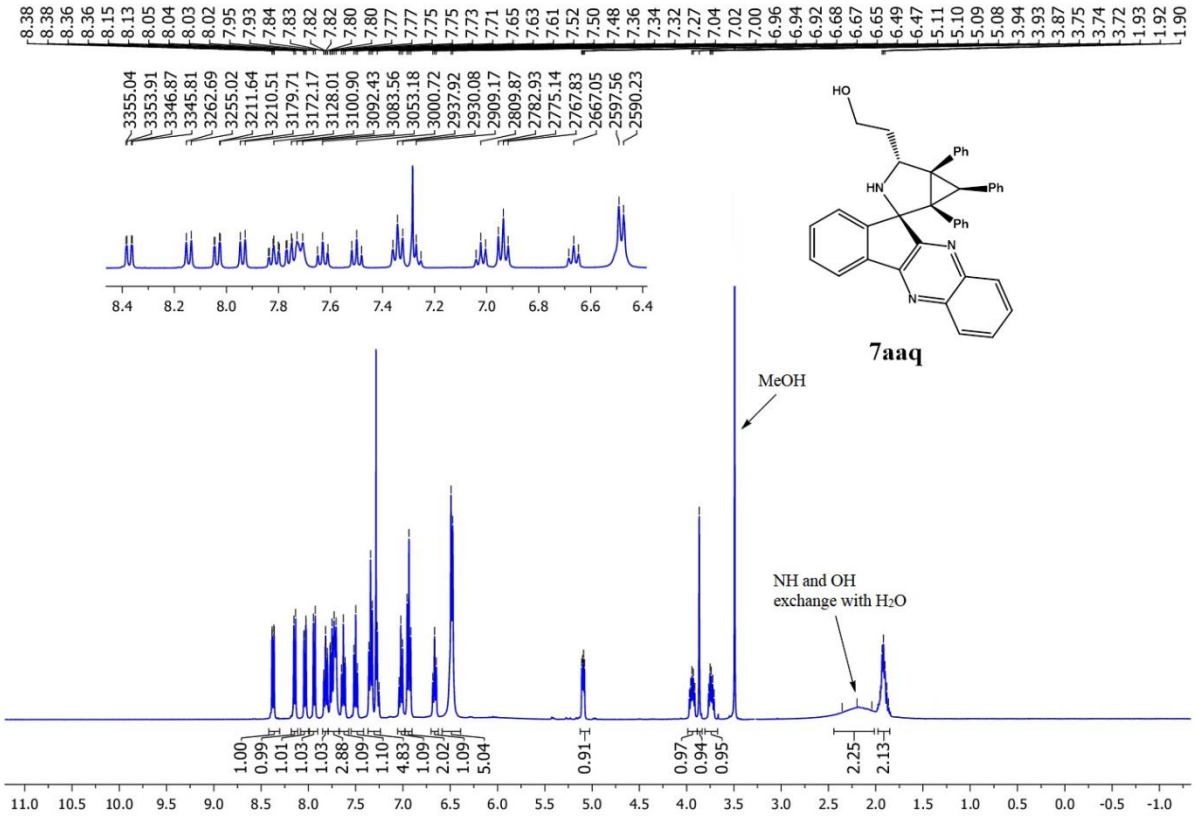


Figure S60. ^{1}H NMR spectrum of compound **7aaq** ($CDCl_3$, 400 MHz)

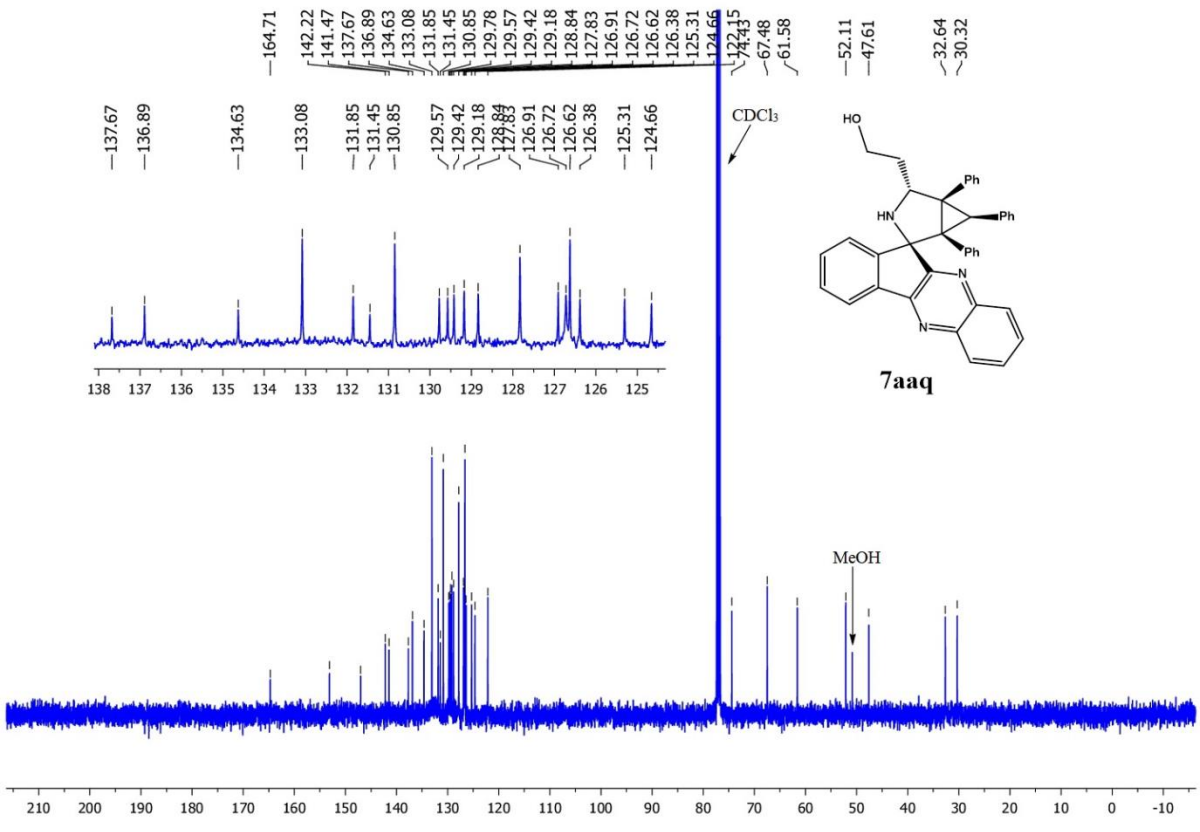


Figure S61. ^{13}C NMR spectrum of compound **7aaq** ($CDCl_3$, 101 MHz)

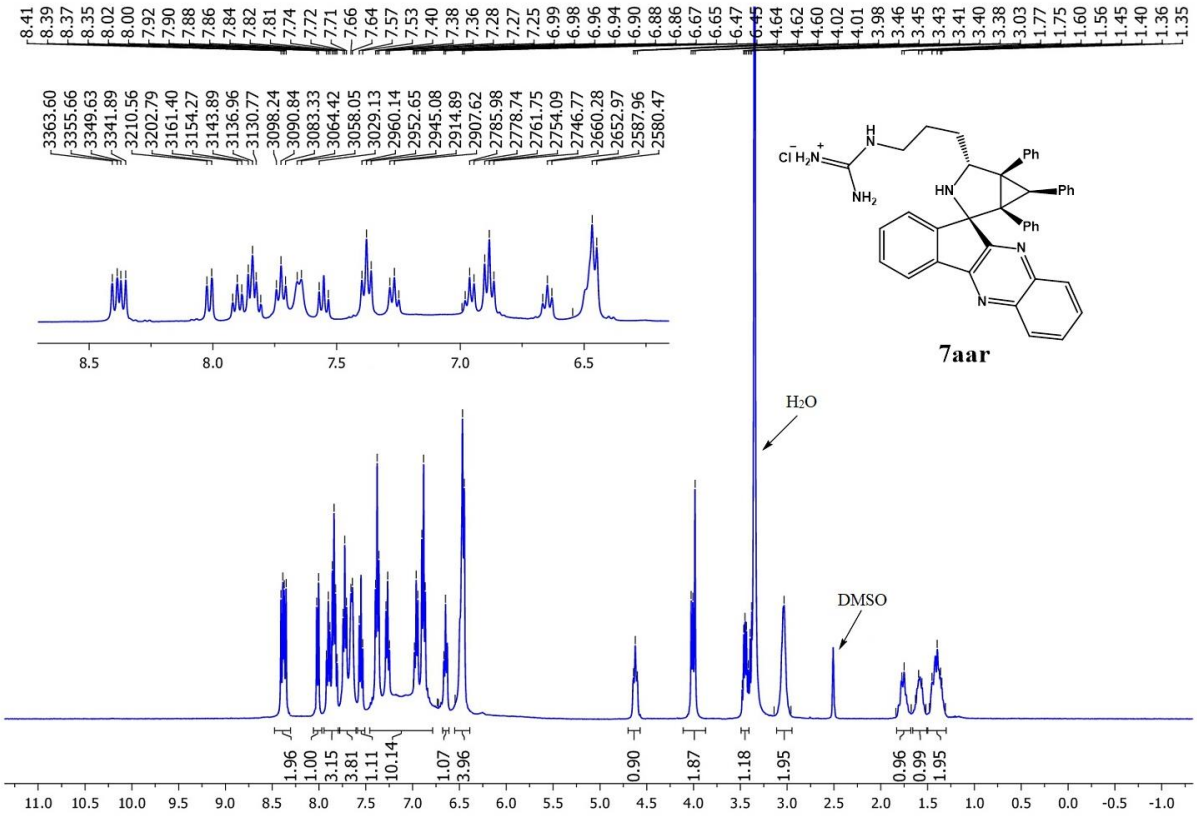


Figure S62. ^{1}H NMR spectrum of compound **7aar** (DMSO-d_6, 400 MHz)

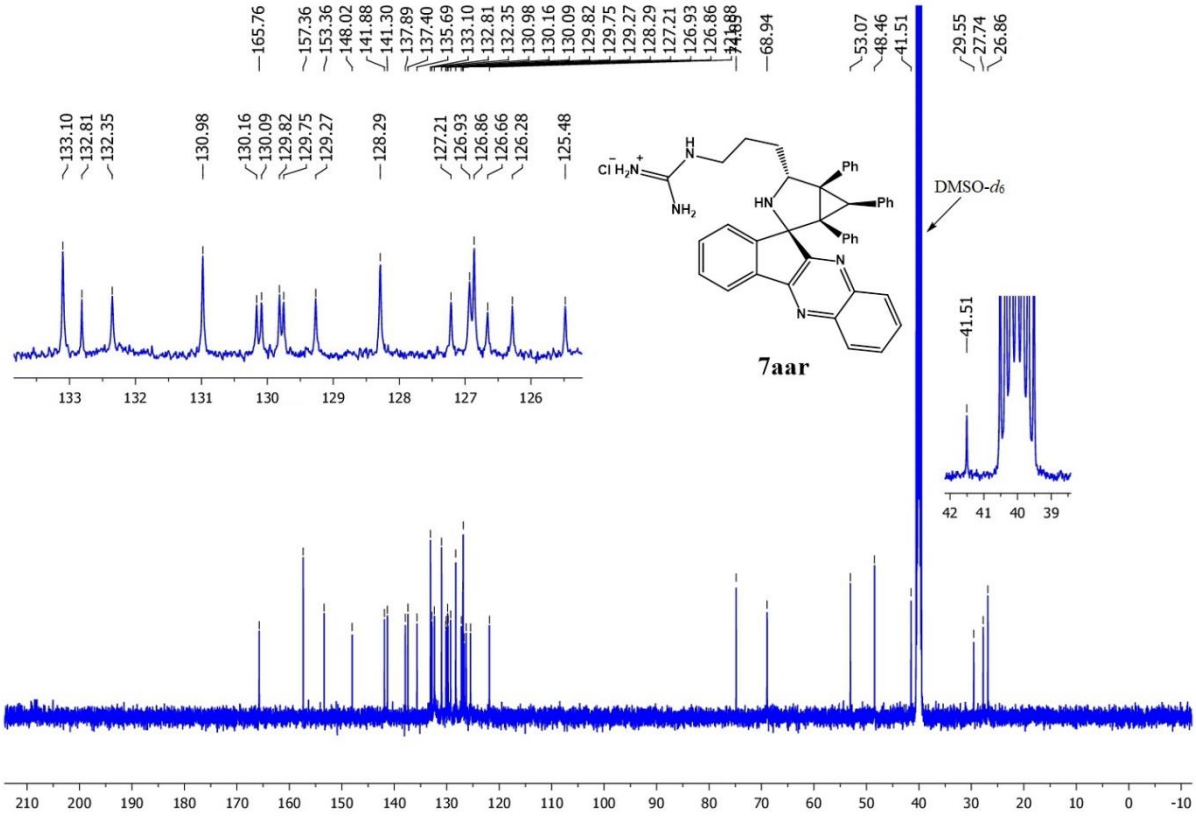


Figure S63. ^{13}C NMR spectrum of compound **7aar** (DMSO-d_6, 101 MHz)

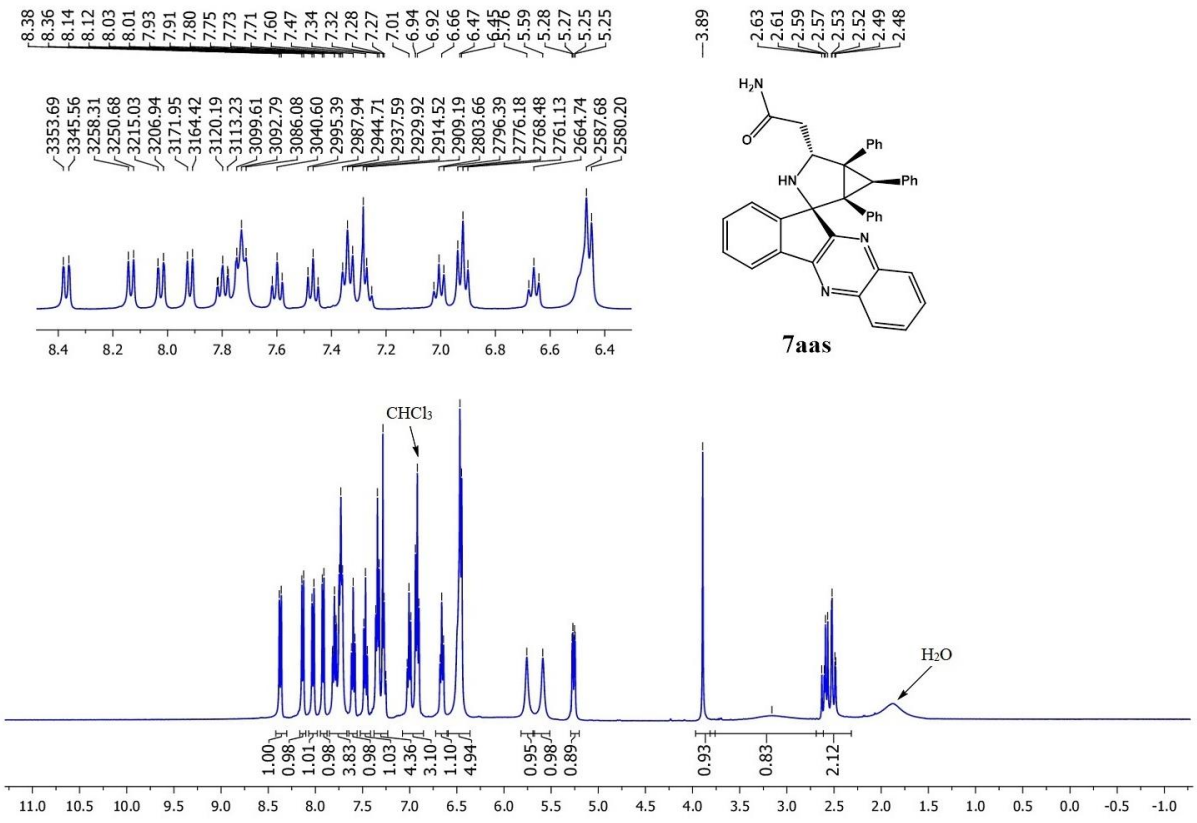


Figure S64. ^{1}H NMR spectrum of compound **7aas** ($CDCl_3$, 400 MHz)

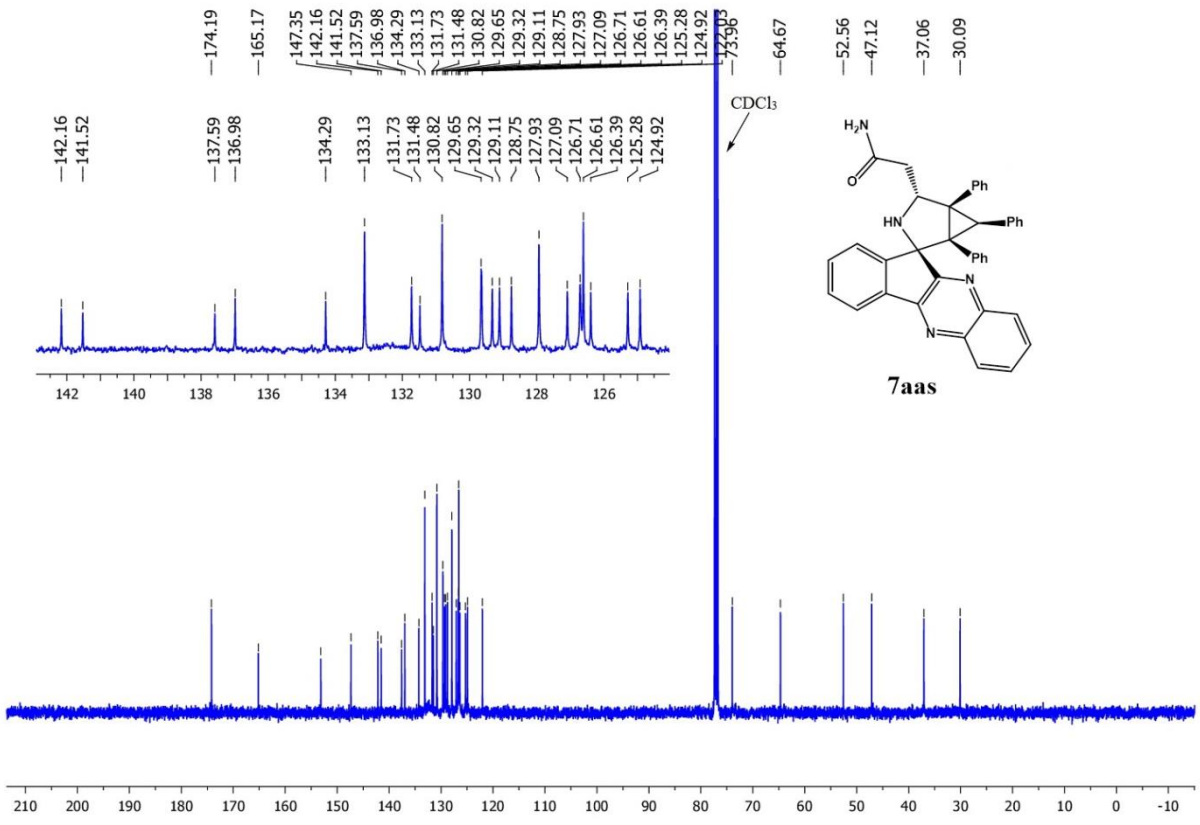


Figure S65. ^{13}C NMR spectrum of compound **7aas** ($CDCl_3$, 101 MHz)

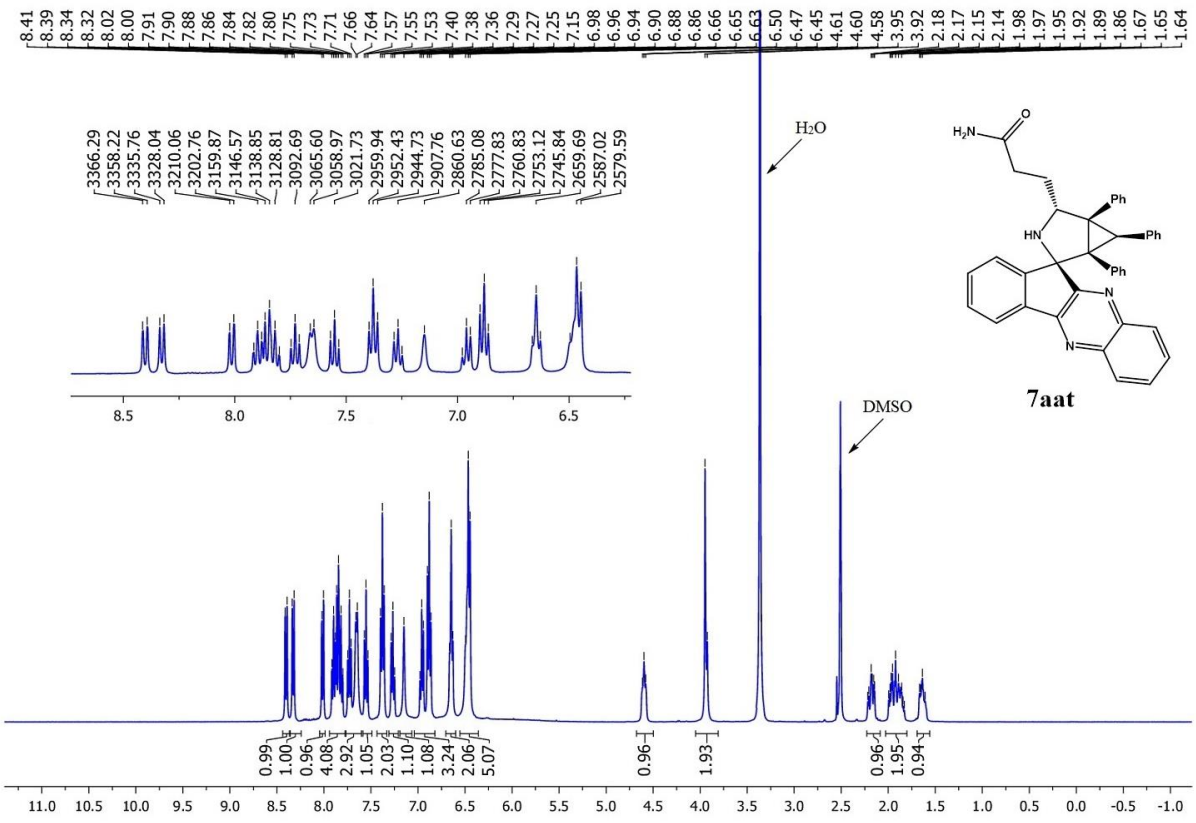


Figure S66. ^{1}H NMR spectrum of compound **7aat** (DMSO-d_6, 400 MHz)

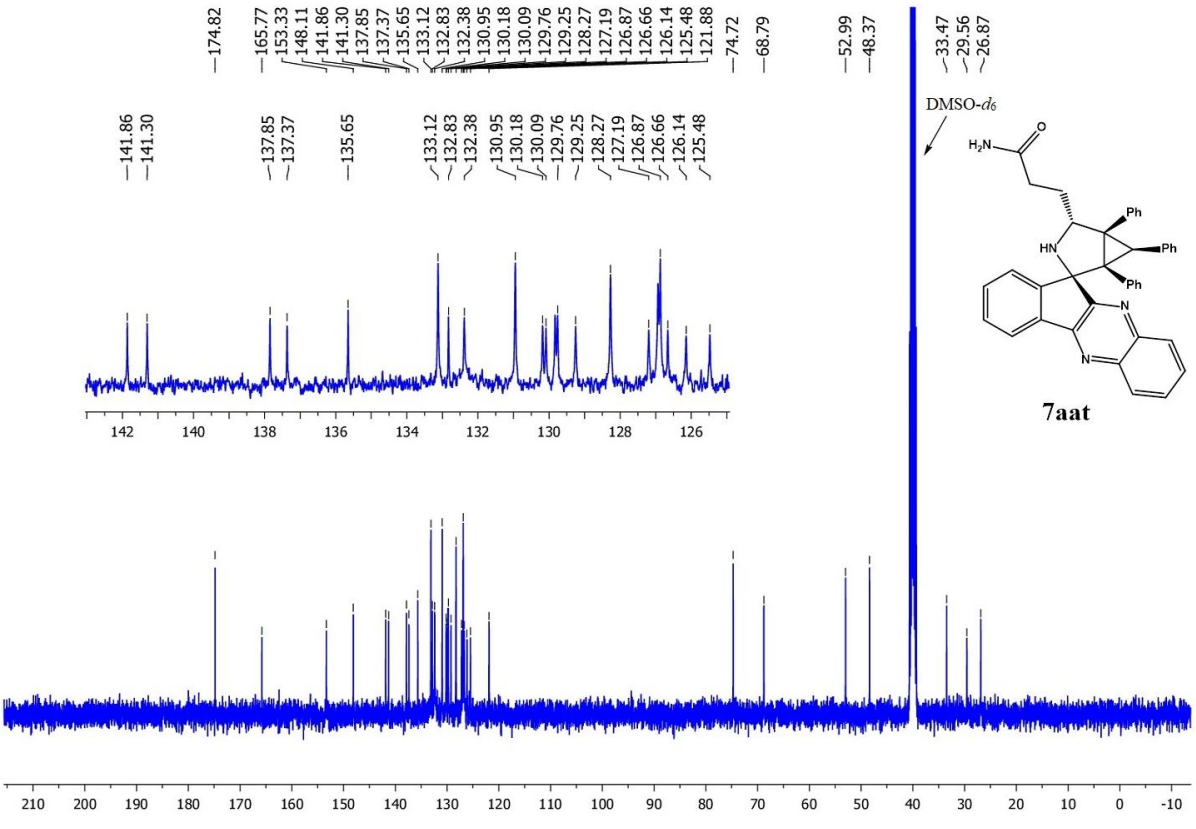


Figure S67. ^{13}C NMR spectrum of compound **7aat** (DMSO-d_6, 101 MHz)

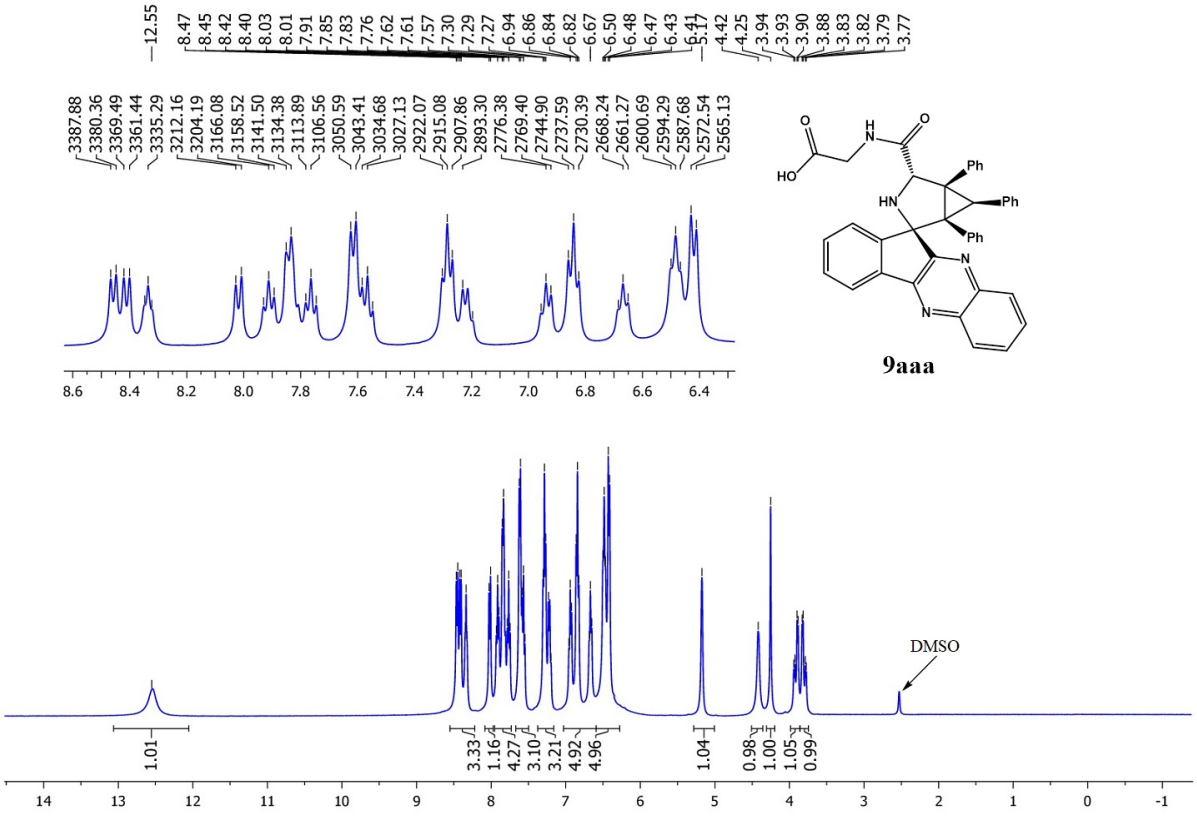


Figure S68. ^{1}H NMR spectrum of compound **9aaa** (DMSO-d_6, 400 MHz)

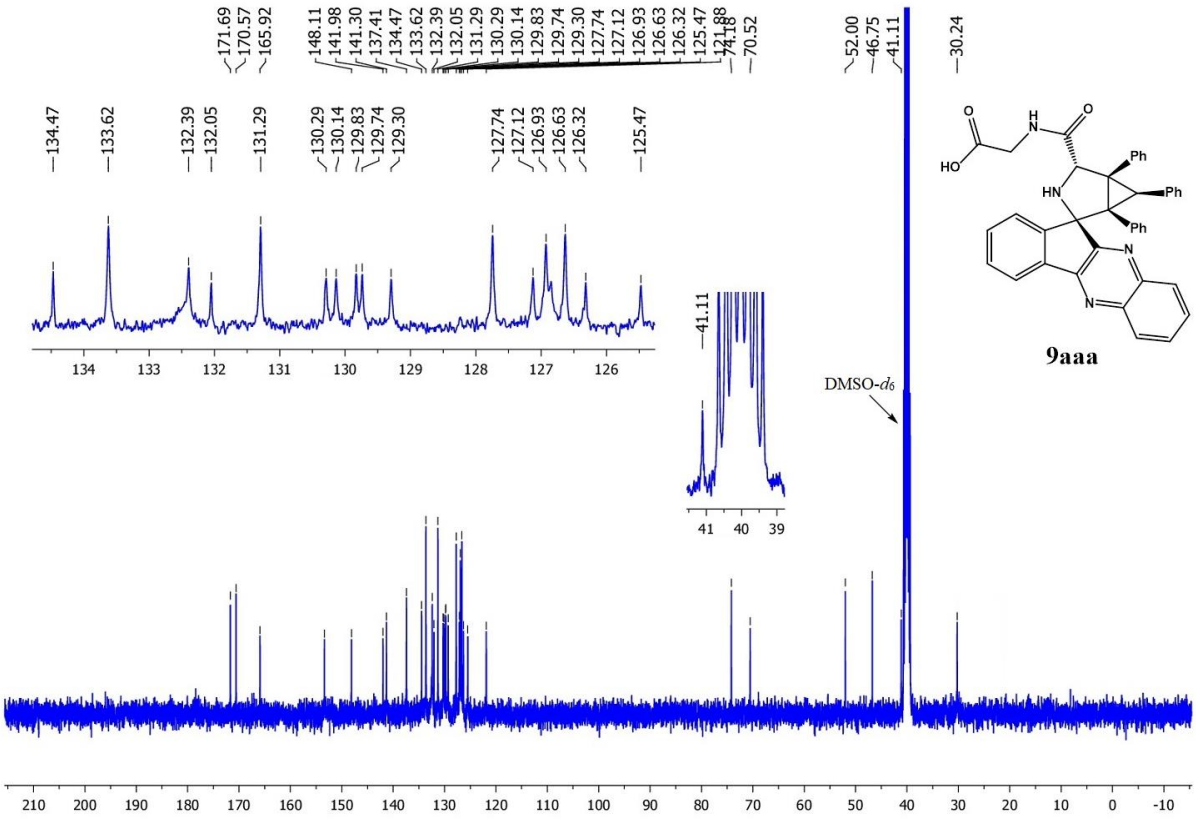


Figure S69. ^{13}C NMR spectrum of compound **9aaa** (DMSO-d_6, 101 MHz)

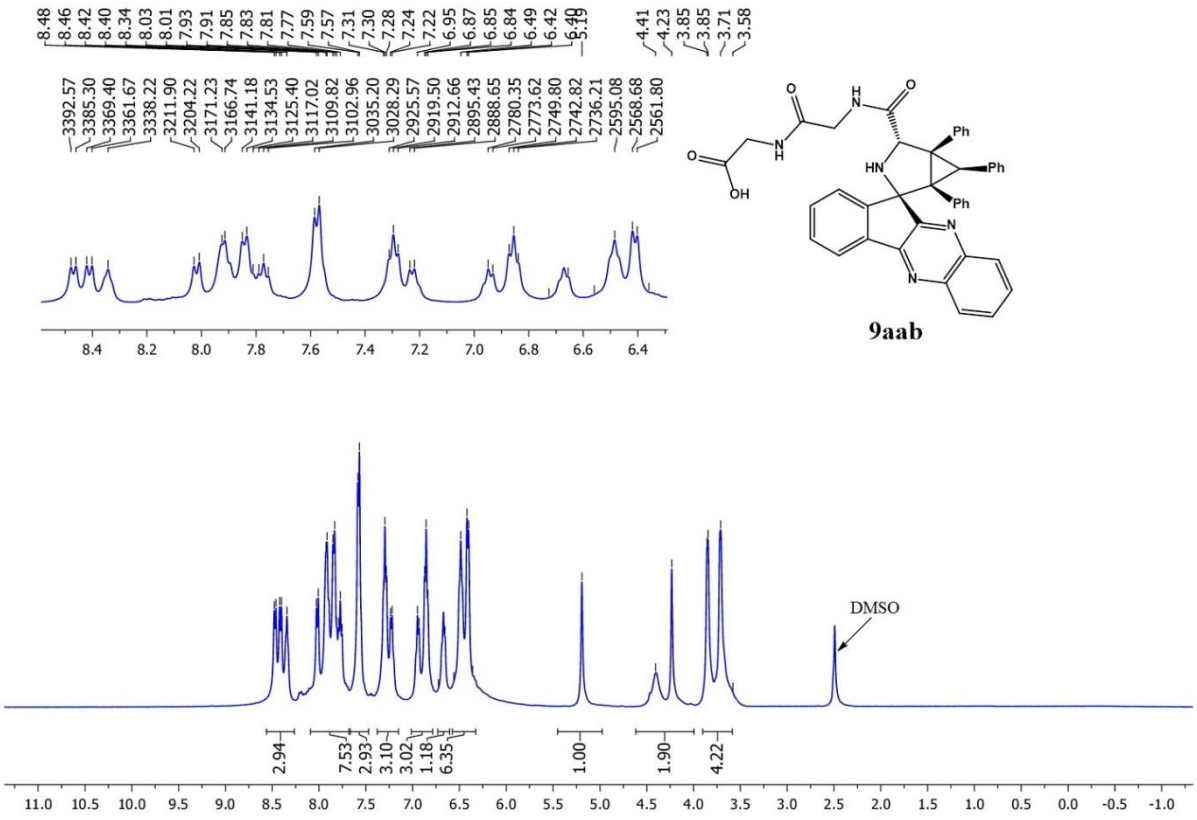


Figure S70. ^{1}H NMR spectrum of compound **9aab** (DMSO-d_6, 400 MHz)

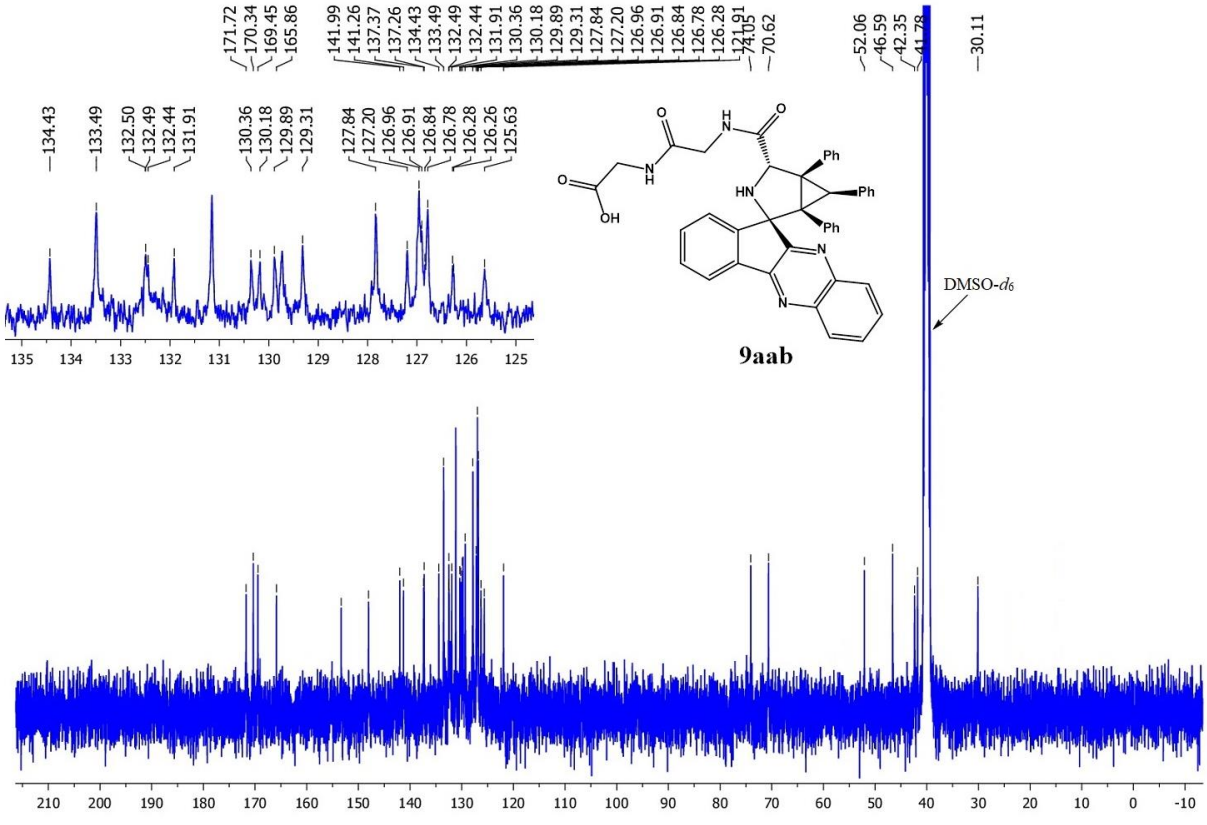


Figure S71. ^{13}C NMR spectrum of compound **9aab** (DMSO-d_6, 101 MHz)

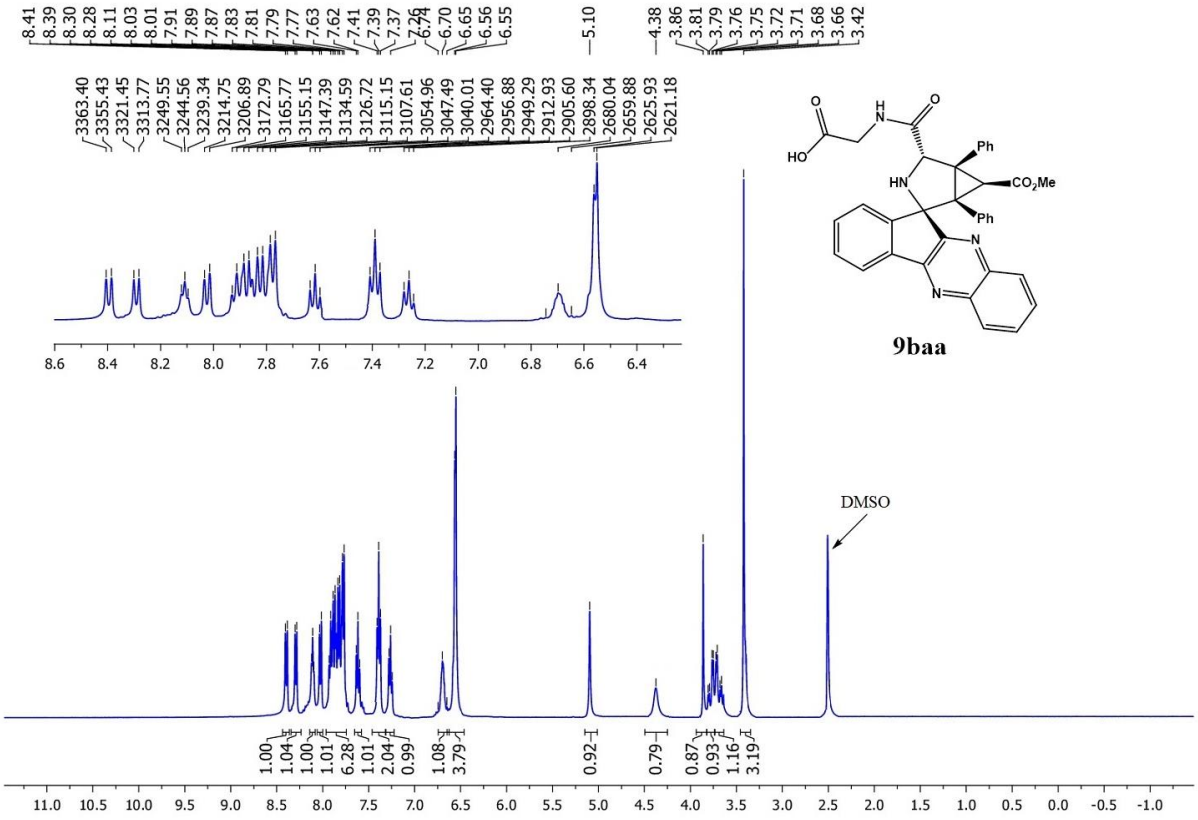


Figure S72. ^{1}H NMR spectrum of compound **9baa** (DMSO-d_6, 400 MHz)

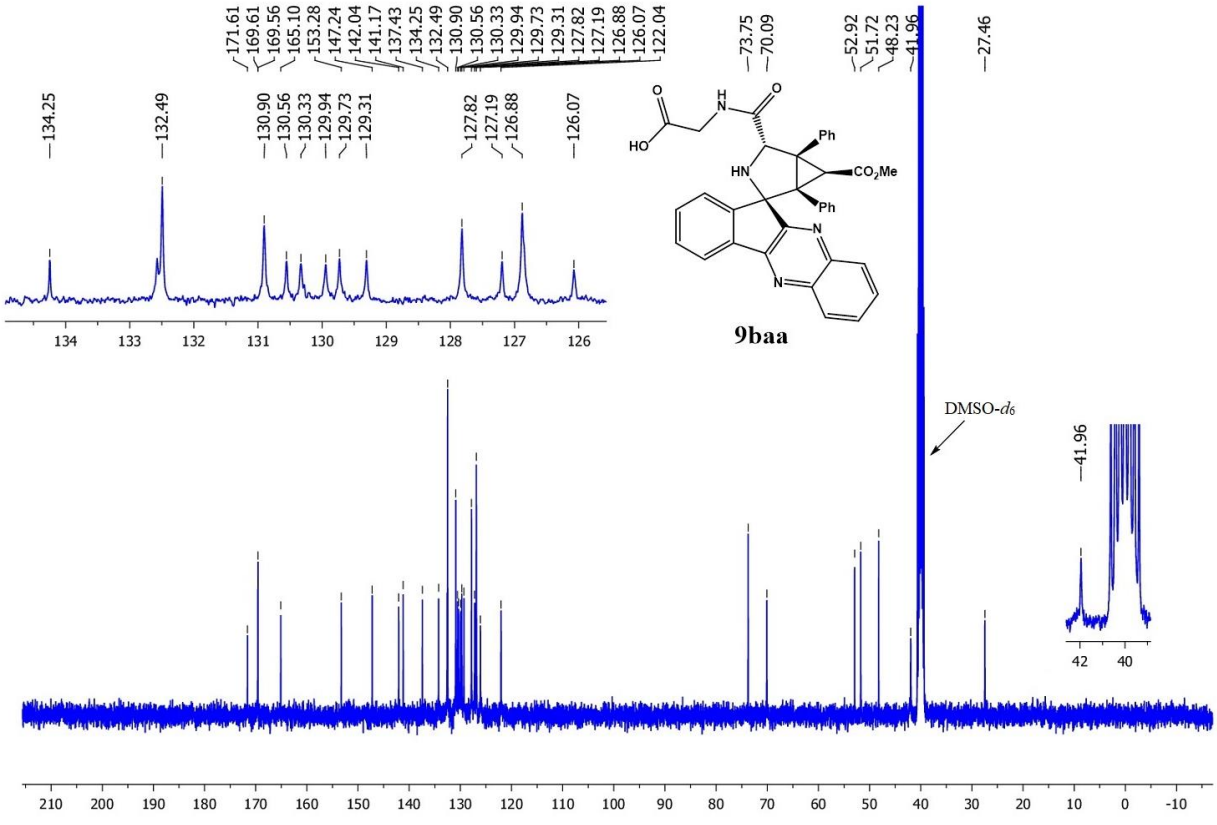


Figure S73. ^{13}C NMR spectrum of compound **9baa** (DMSO-d_6, 101 MHz)

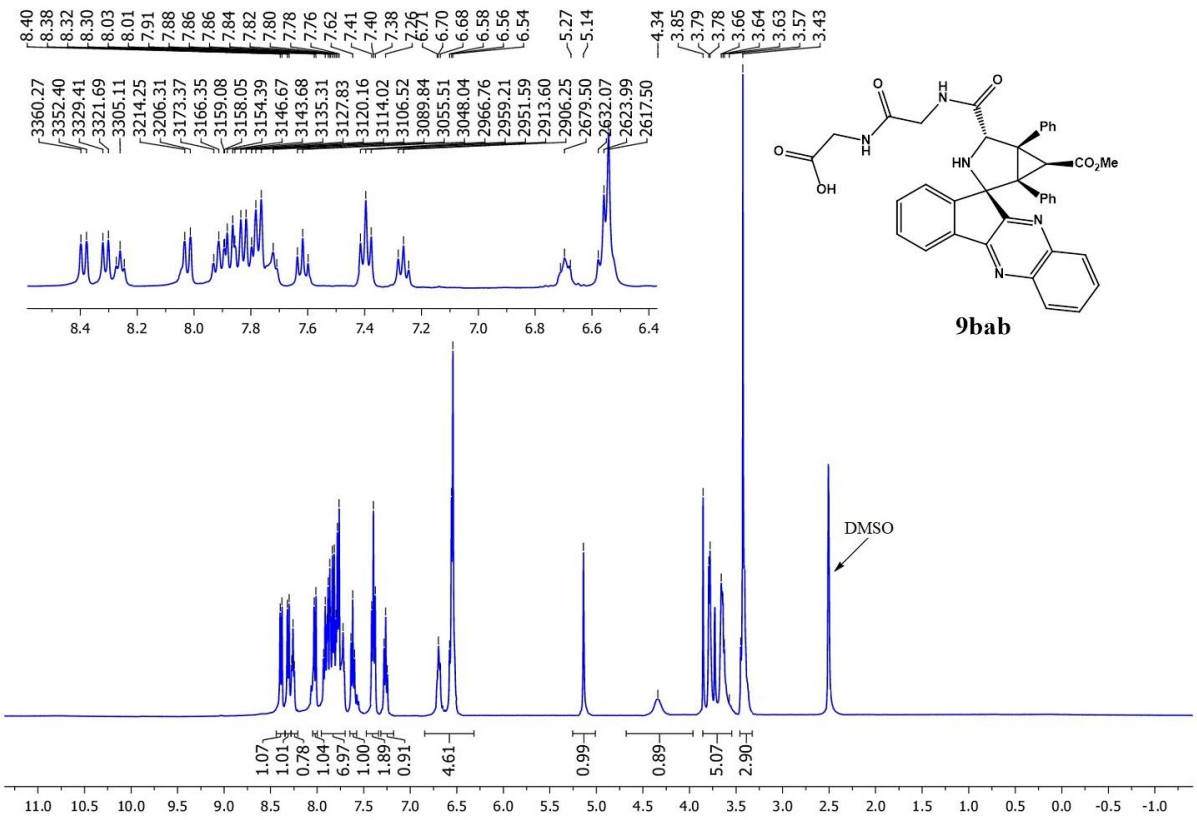


Figure S74. ^{1}H NMR spectrum of compound **9bab** (DMSO-d_6, 400 MHz)

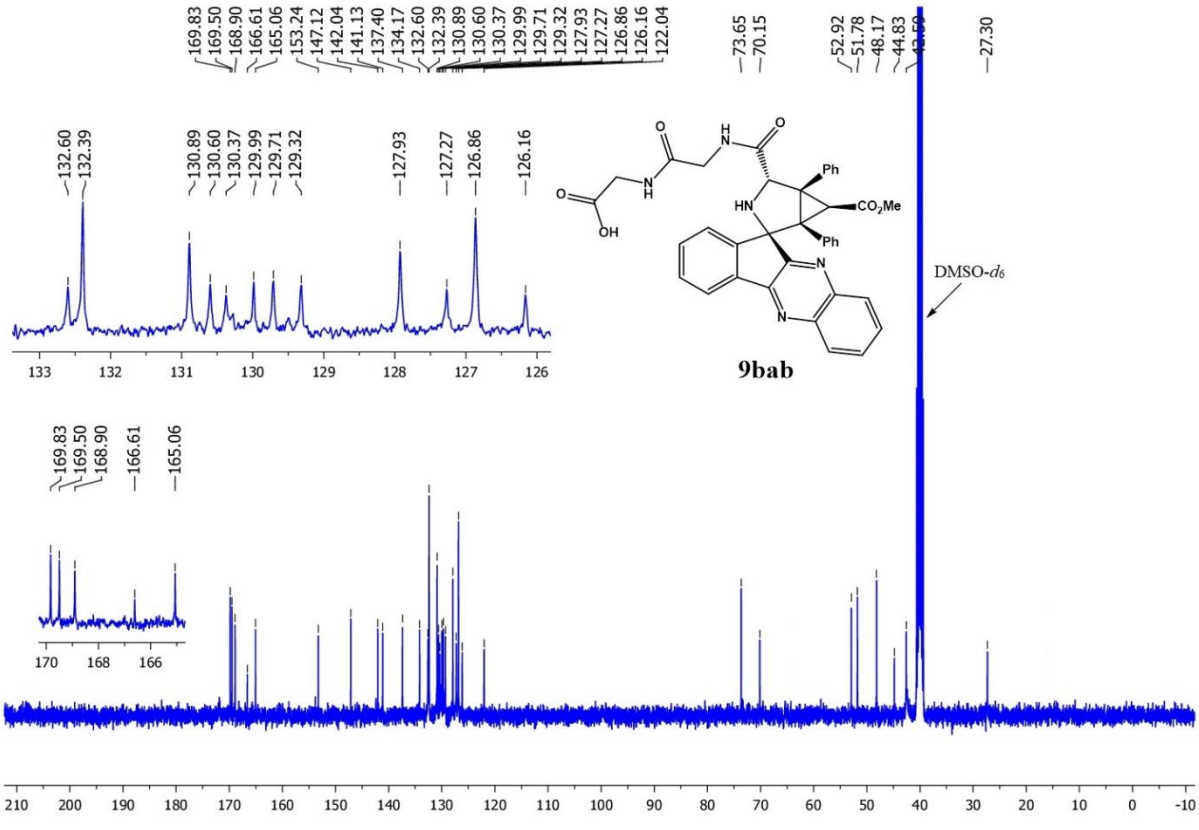


Figure S75. ^{13}C NMR spectrum of compound **9bab** (DMSO-d_6, 101 MHz)

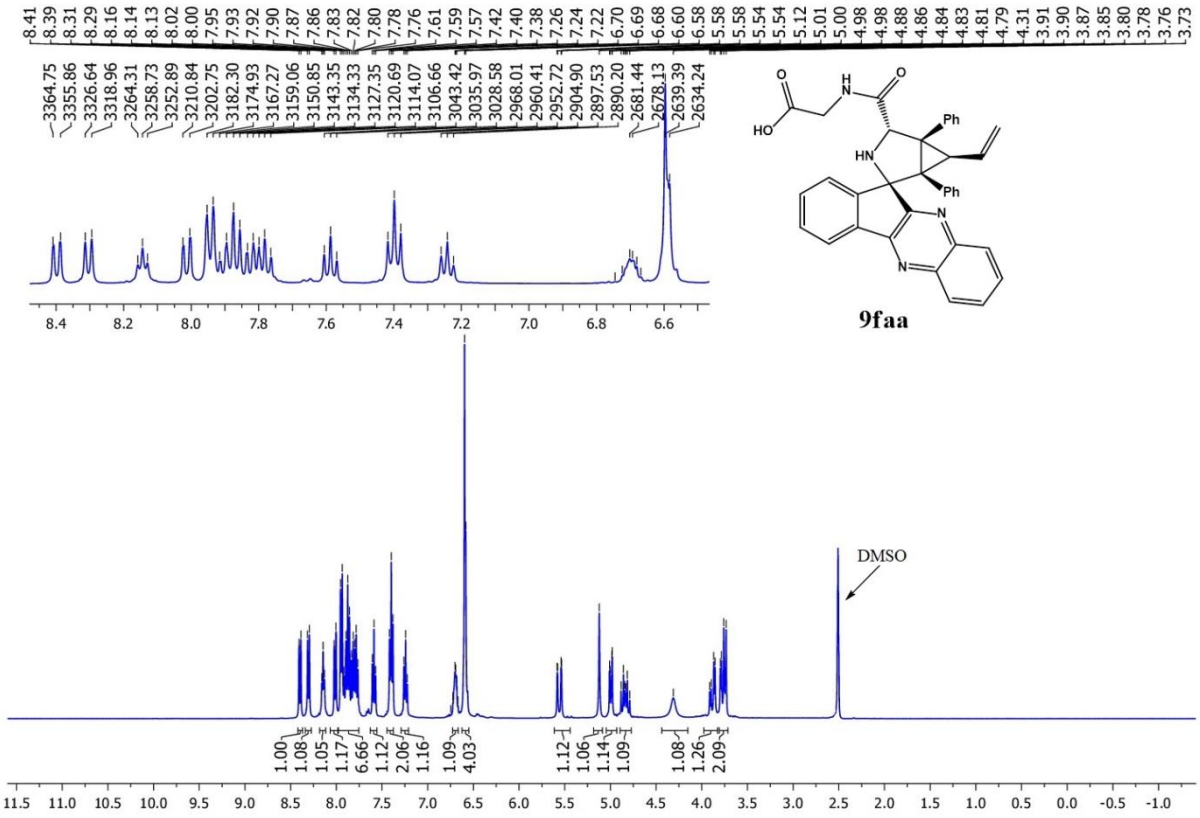


Figure S76. ^{1}H NMR spectrum of compound **9faa** (DMSO-d_6, 400 MHz)

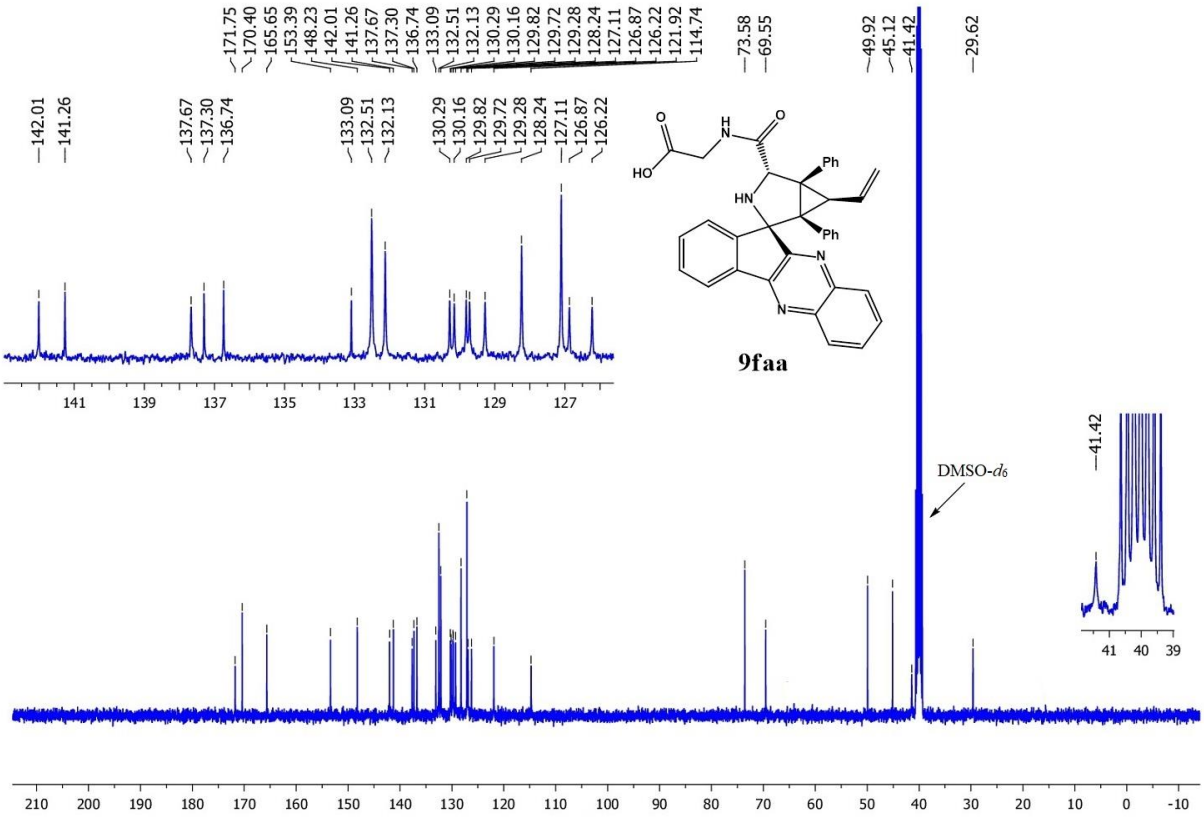


Figure S77. ^{13}C NMR spectrum of compound **9faa** (DMSO-d_6, 101 MHz)

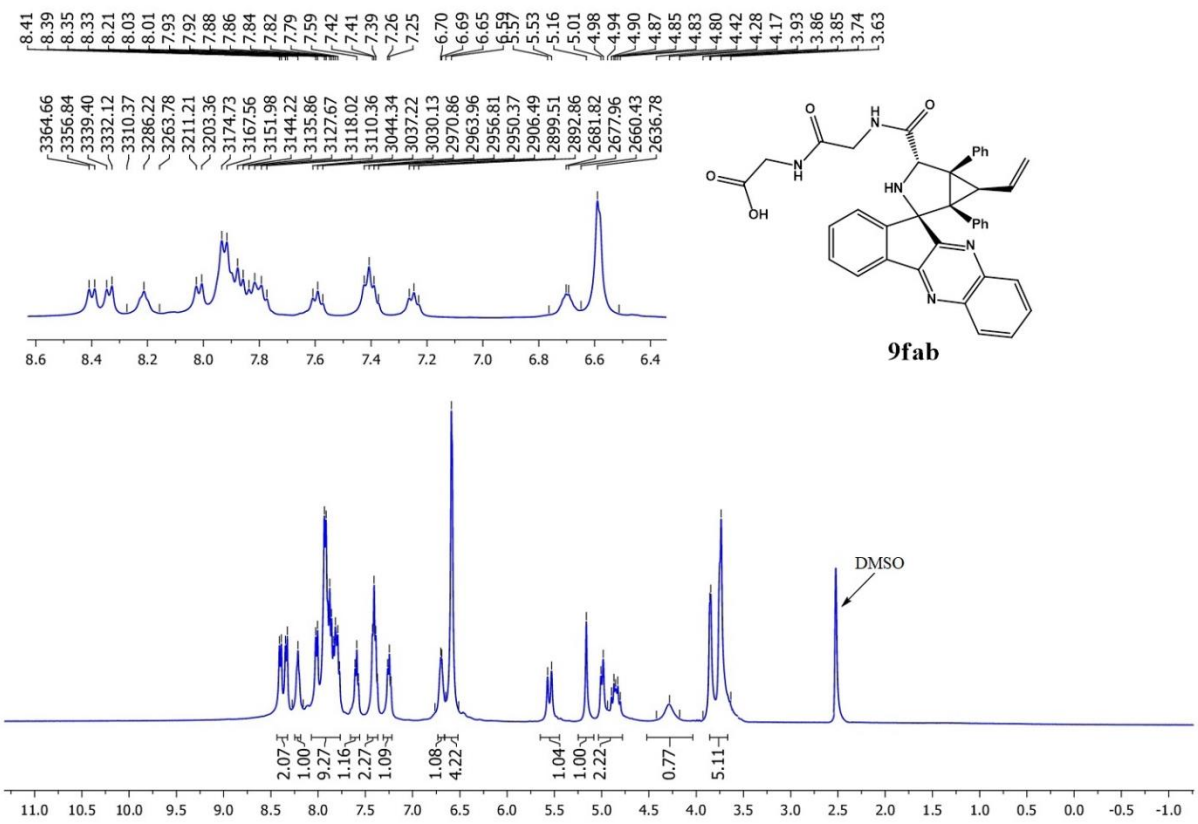


Figure S78. ^{1}H NMR spectrum of compound **9fab** (DMSO-d_6, 400 MHz)

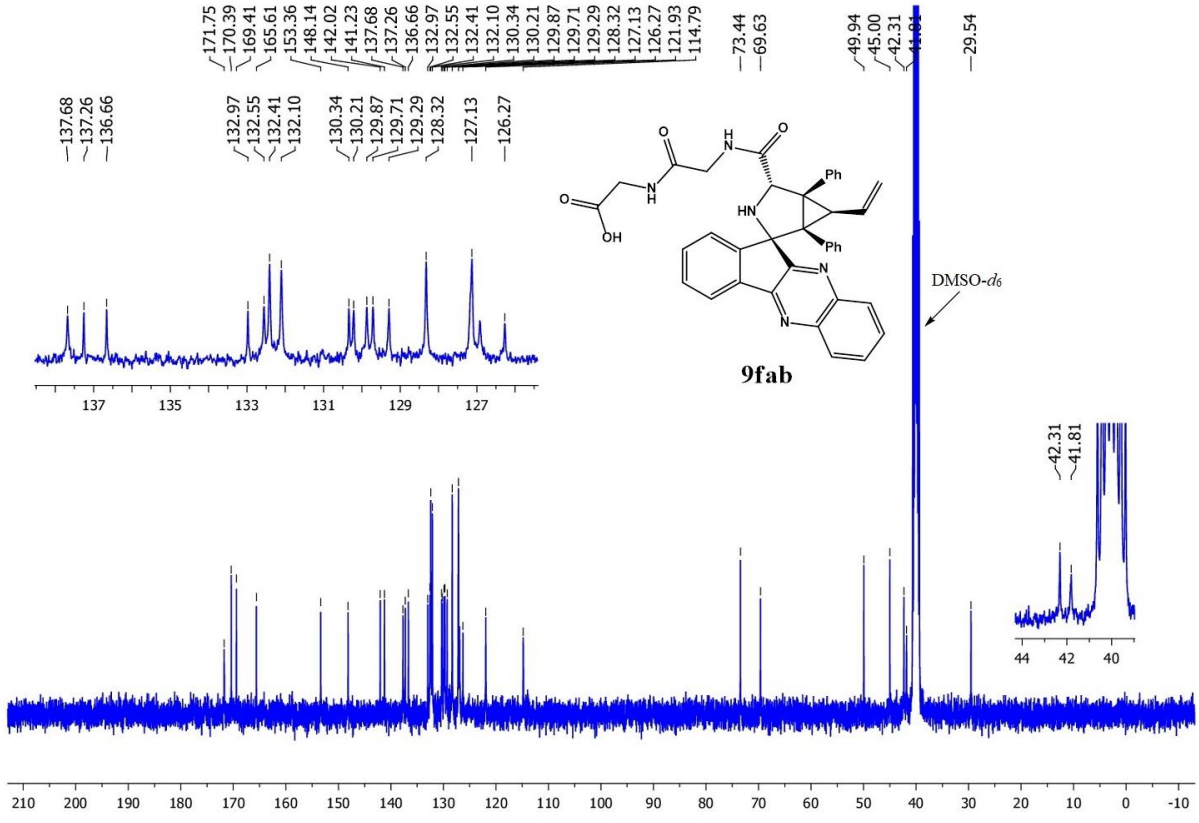


Figure S79. ^{13}C NMR spectrum of compound **9fab** (DMSO-d_6, 101 MHz)

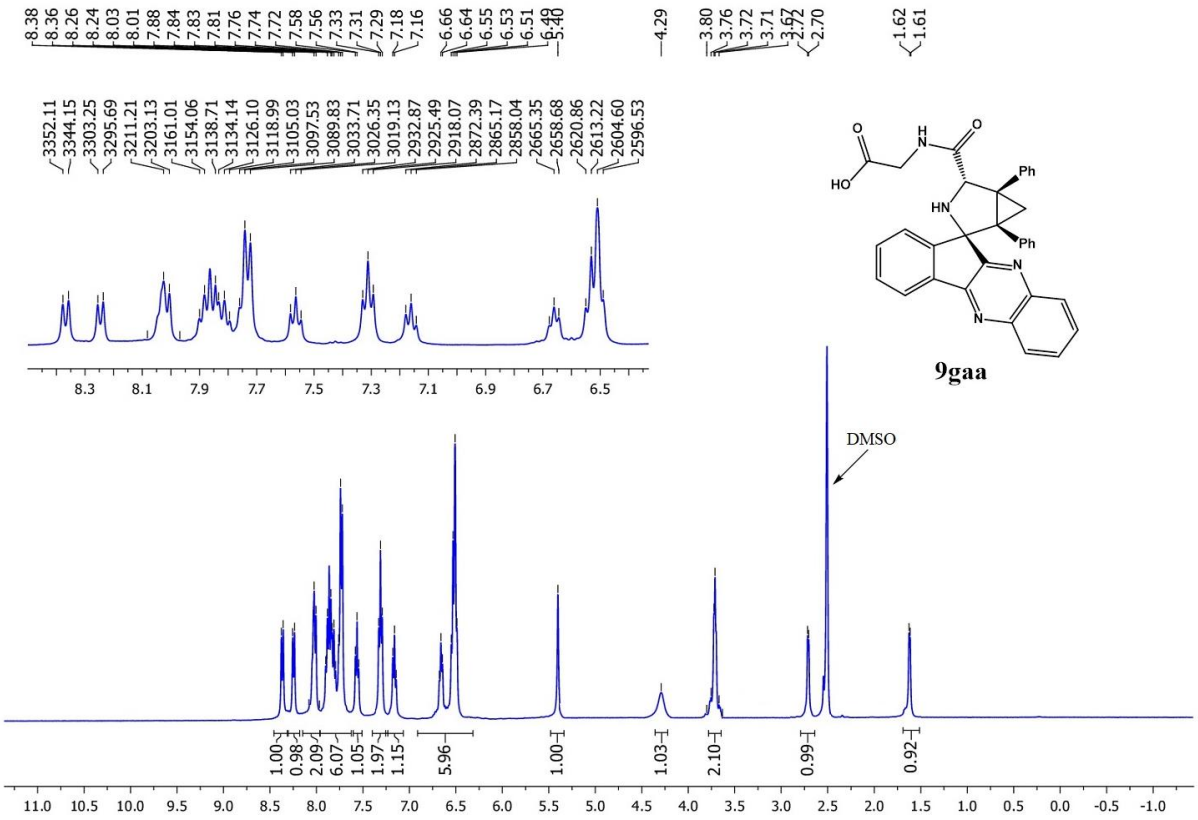


Figure S80. ^{1}H NMR spectrum of compound **9gaa** (DMSO-d_6, 400 MHz)

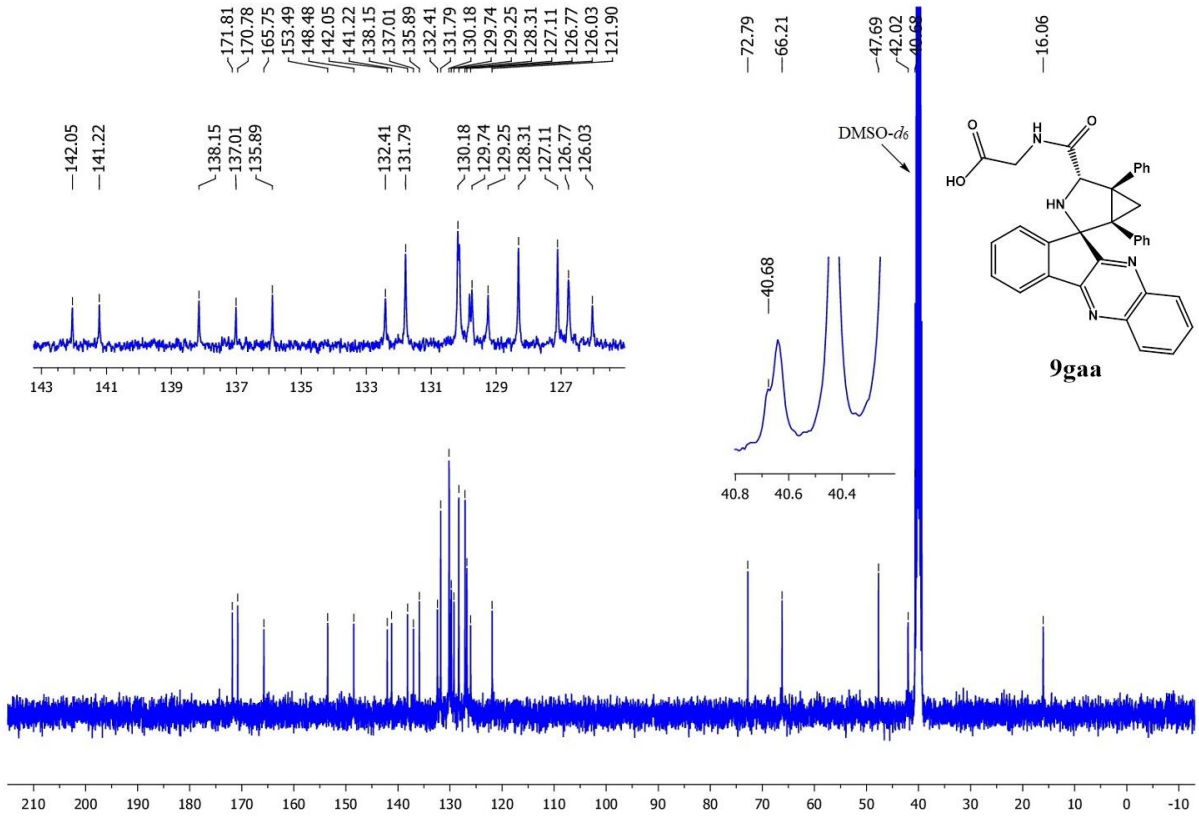


Figure S81. ^{13}C NMR spectrum of compound **9gaa** (DMSO-d_6, 101 MHz)

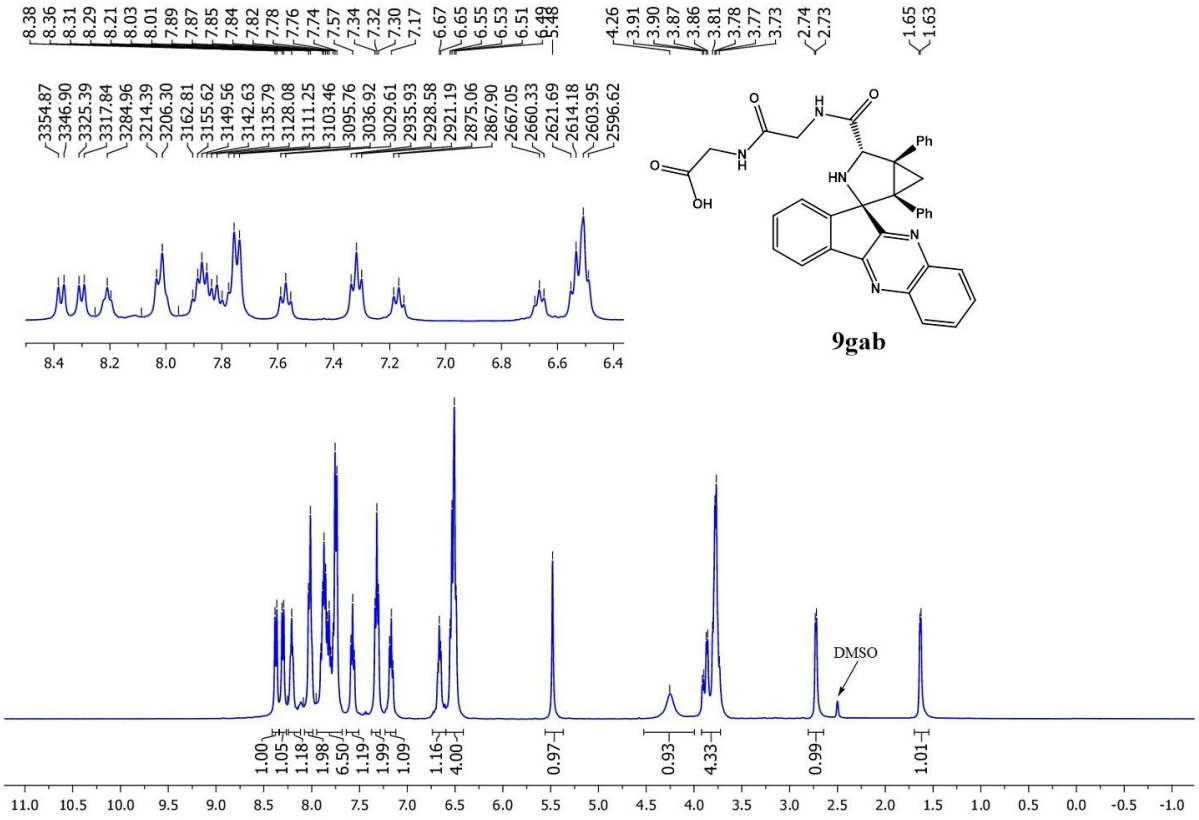


Figure S82. ^{1}H NMR spectrum of compound **9gab** (DMSO-d_6, 400 MHz)

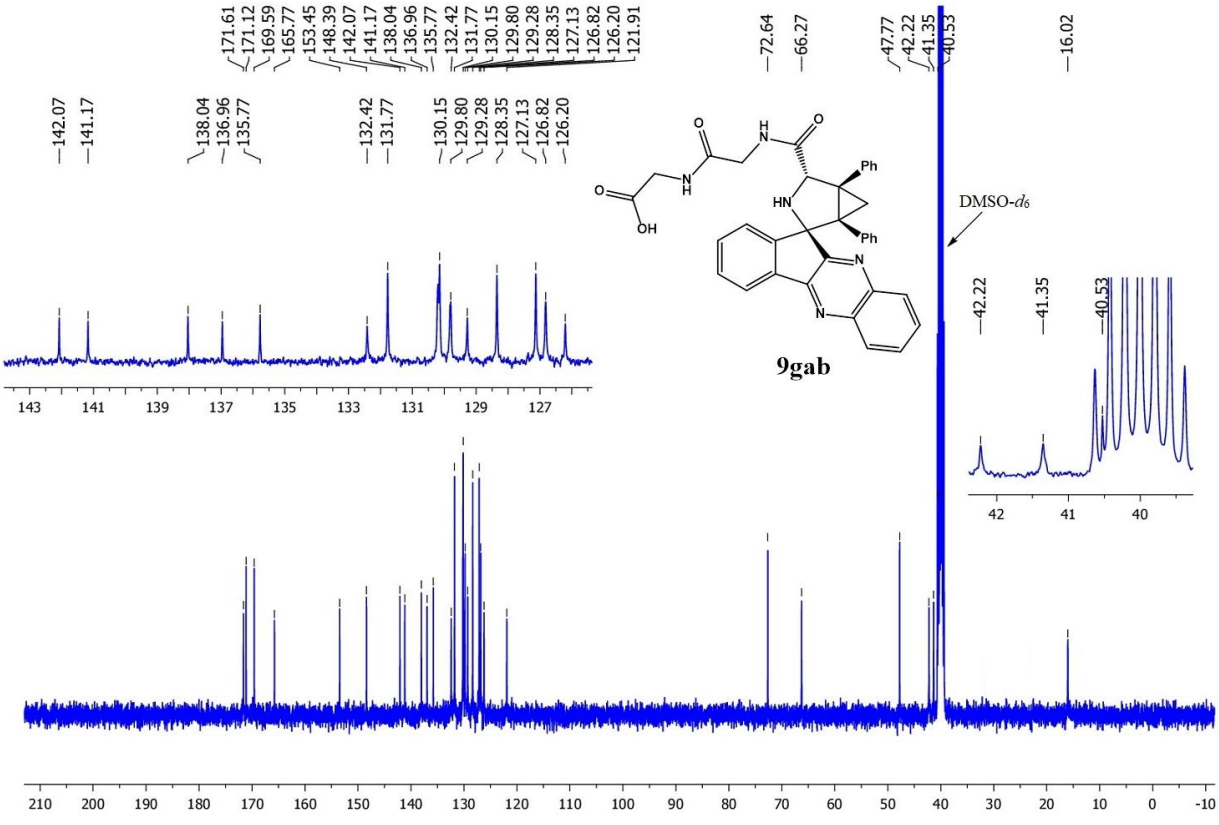


Figure S83. ^{13}C NMR spectrum of compound **9gab** (DMSO-d_6, 101 MHz)

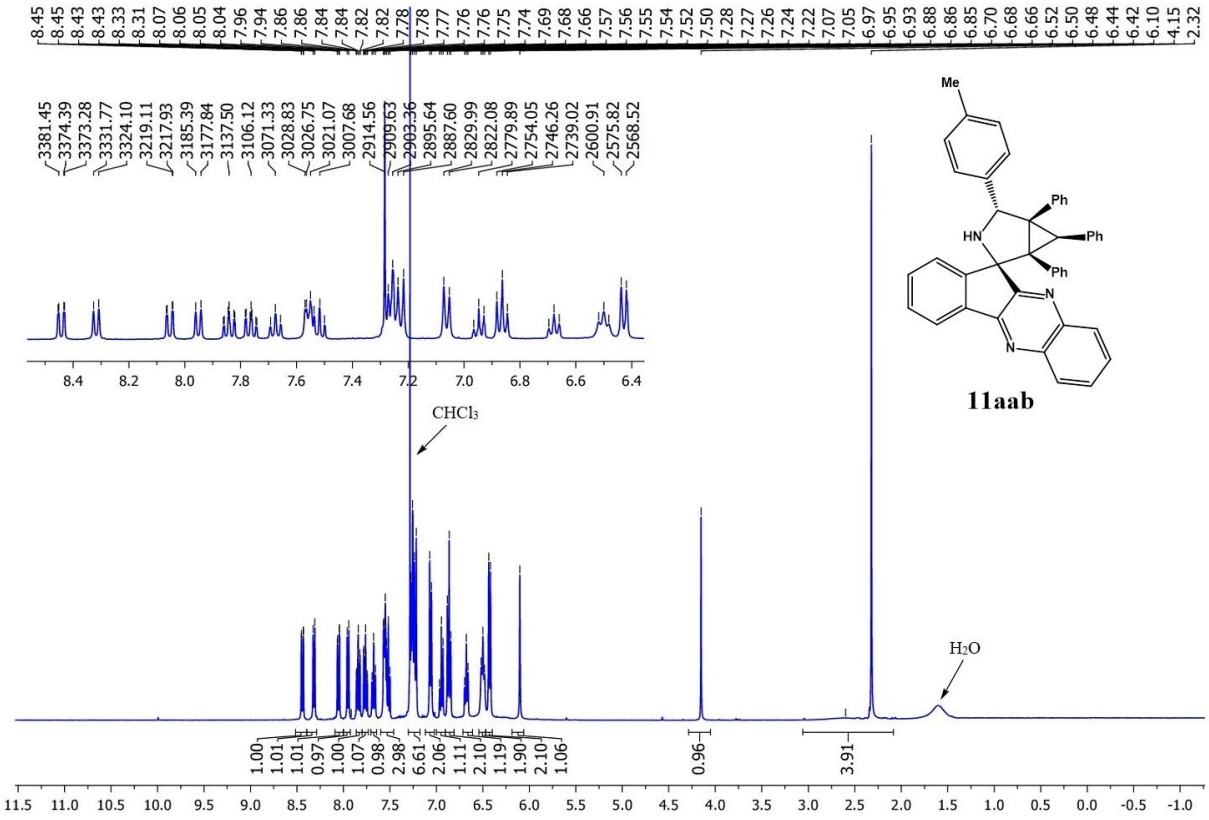


Figure S84. ^{1}H NMR spectrum of compound **11aab** ($CDCl_3$, 400 MHz)

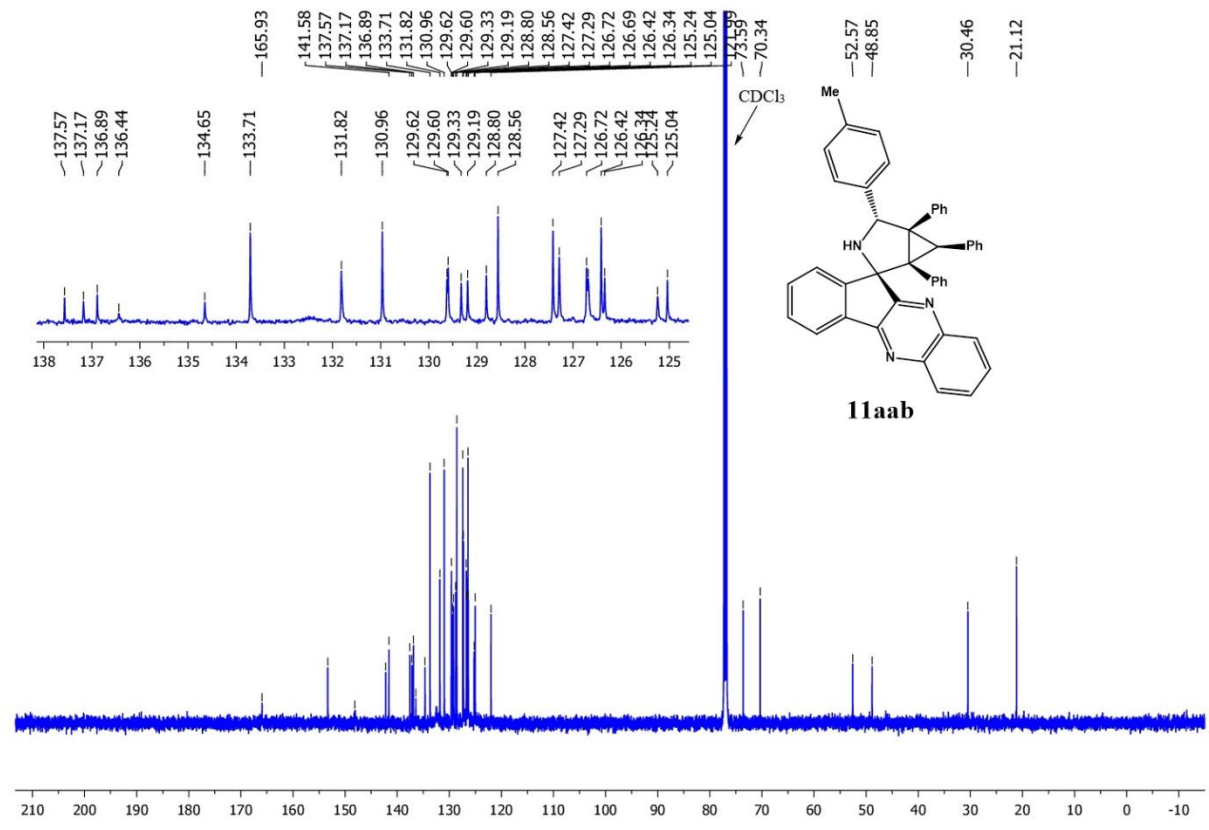


Figure S85. ^{13}C NMR spectrum of compound **11aab** ($CDCl_3$, 101 MHz)

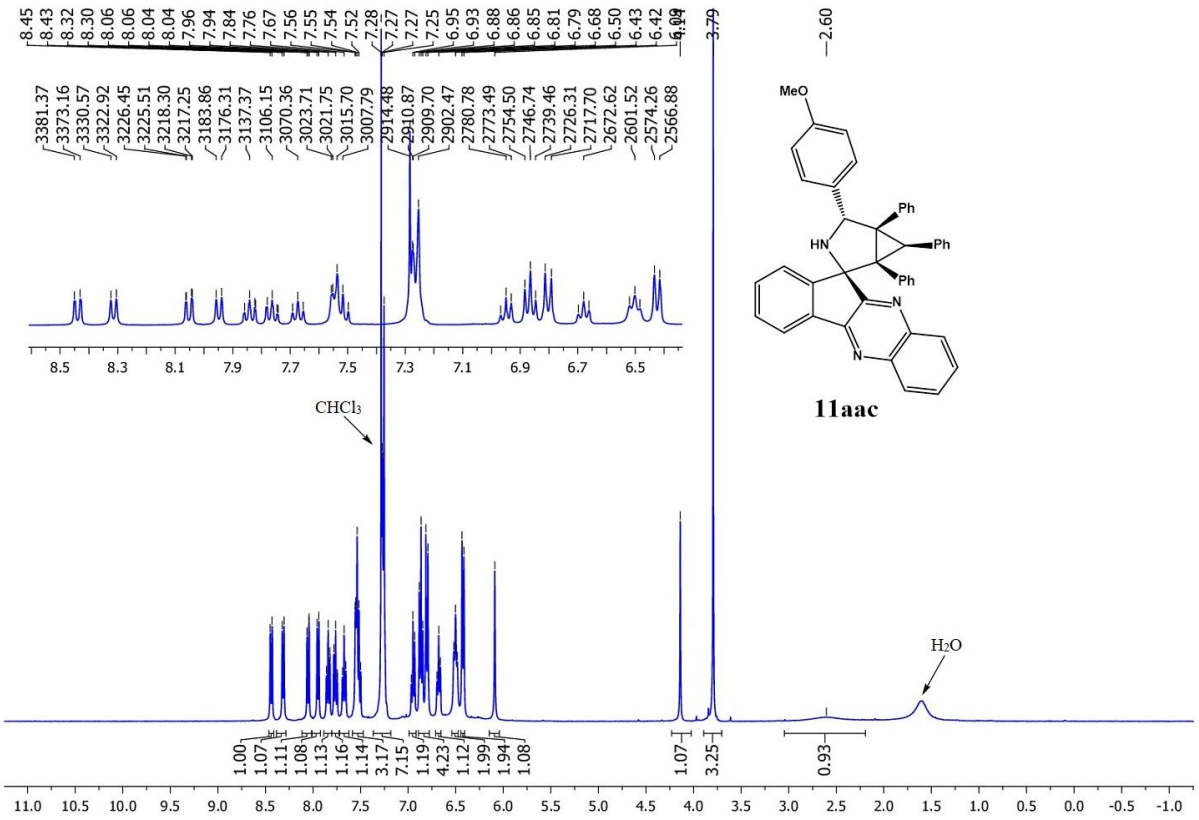


Figure S86. ^{1}H NMR spectrum of compound **11aac** ($CDCl_3$, 400 MHz)

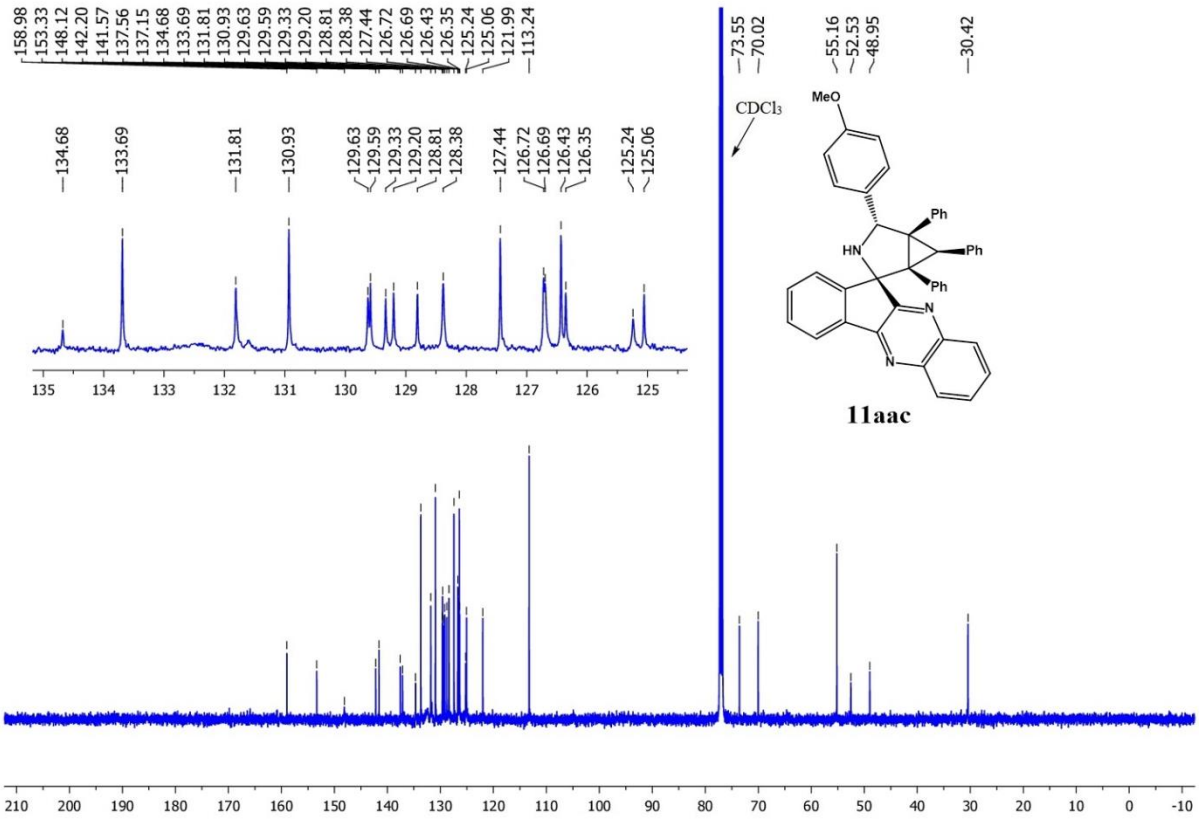


Figure S87. ^{13}C NMR spectrum of compound **11aac** ($CDCl_3$, 101 MHz)

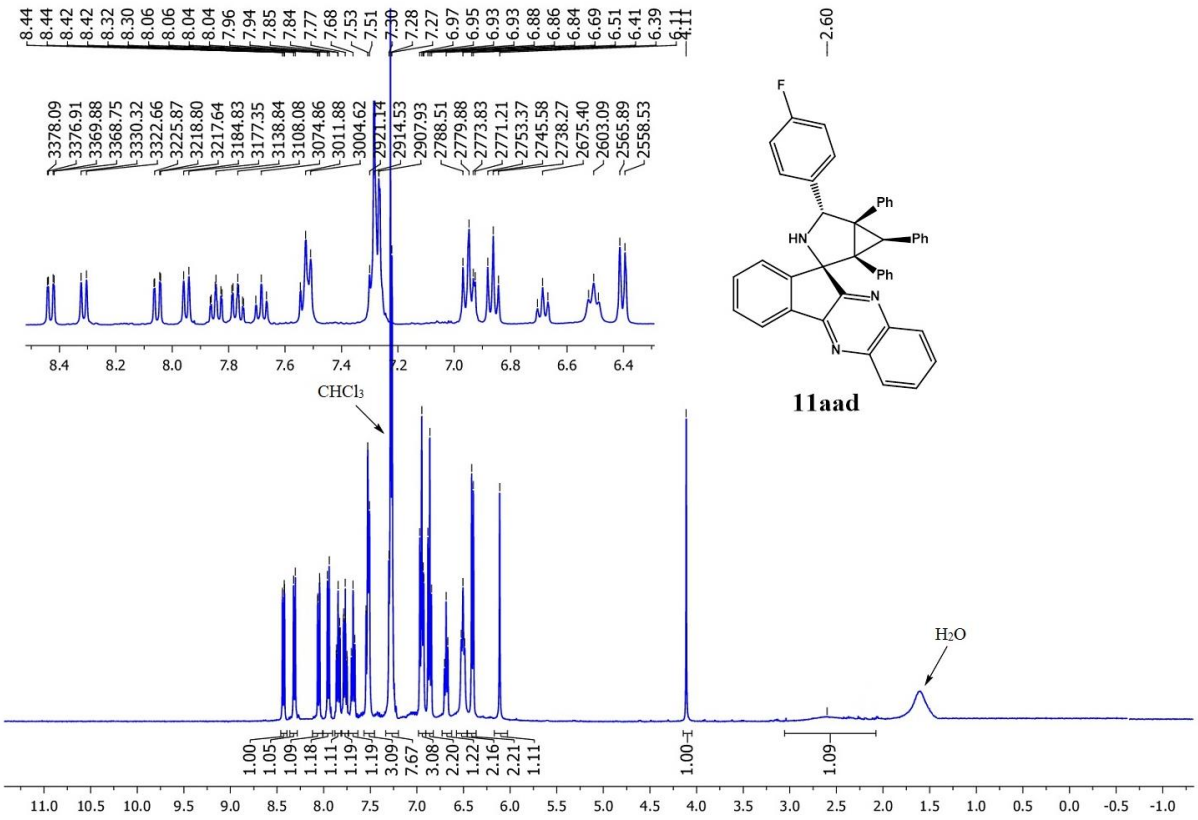


Figure S88. ^{1}H NMR spectrum of compound **11aad** ($CDCl_3$, 400 MHz)

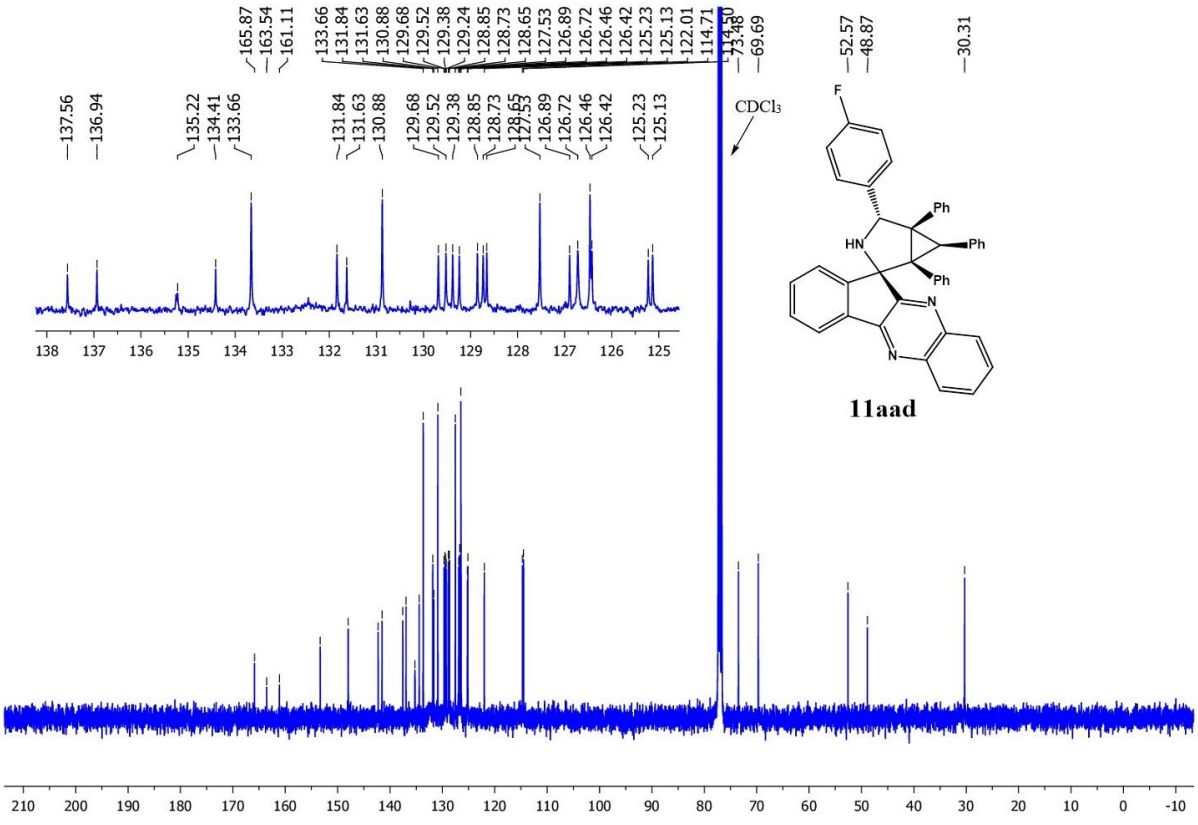


Figure S89. ^{13}C NMR spectrum of compound **11aad** ($CDCl_3$, 101 MHz)

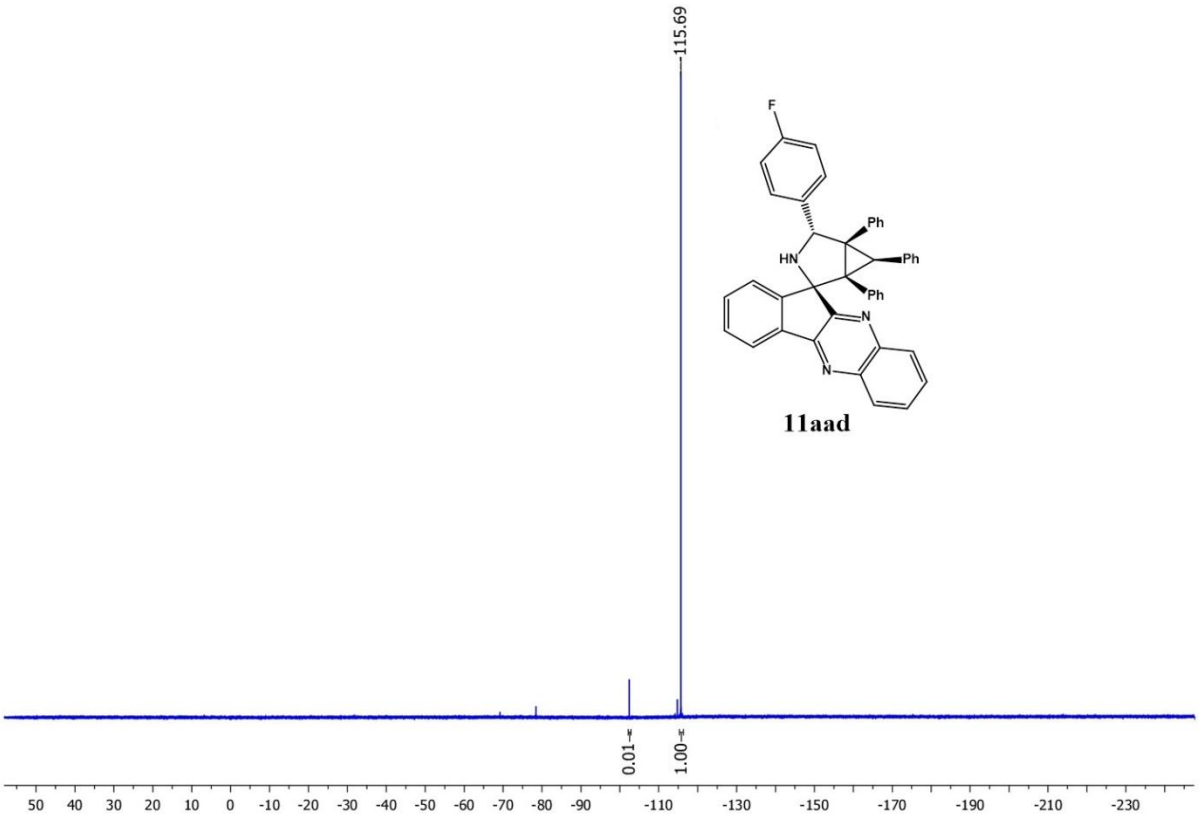


Figure S90. ^{19}F NMR spectrum of compound **11aad** ($CDCl_3$, 376 MHz)

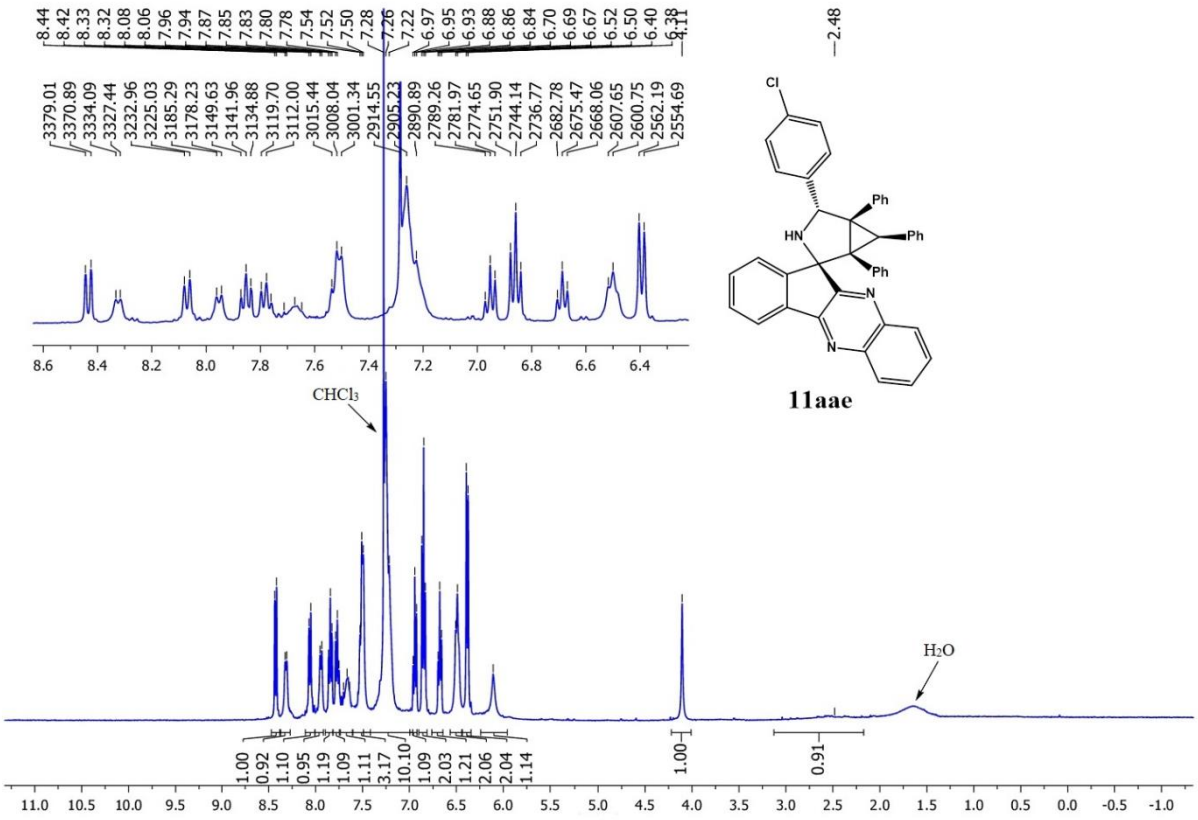


Figure S91. ^{1}H NMR spectrum of compound **11aae** ($CDCl_3$, 400 MHz)

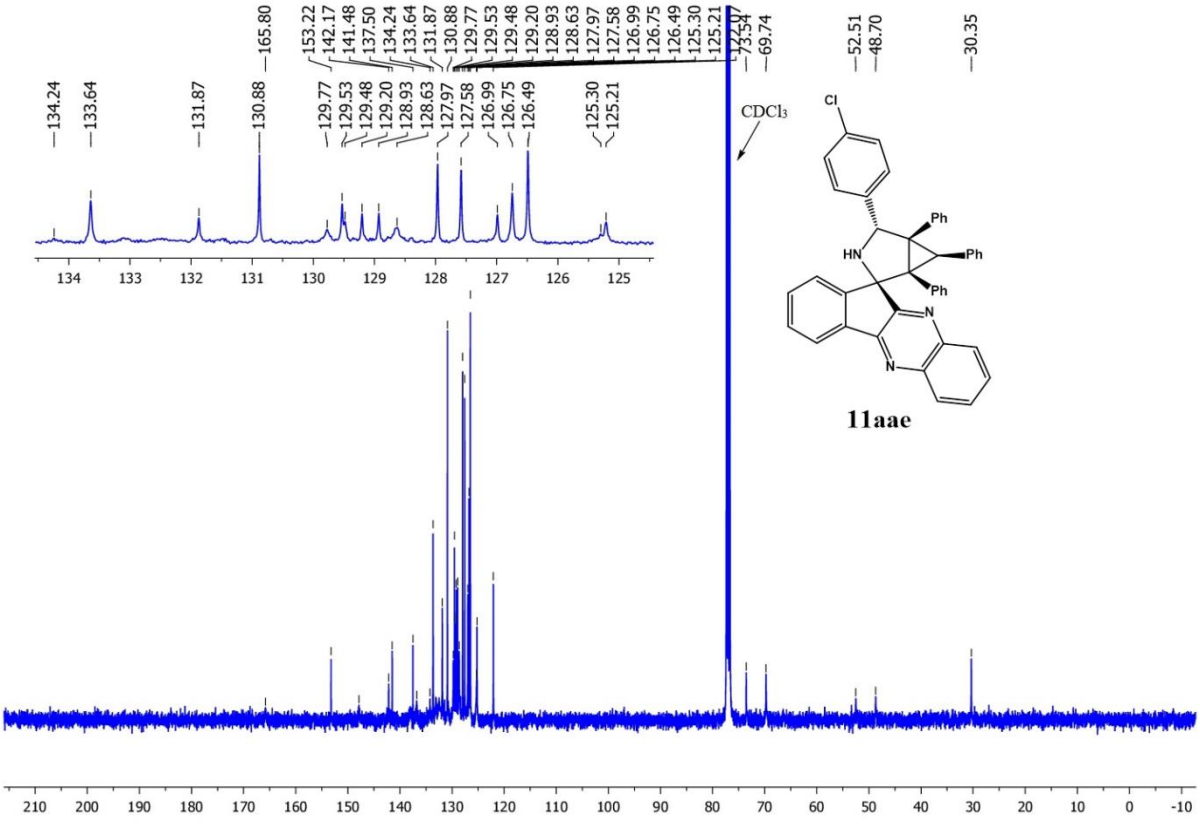


Figure S92. ^{13}C NMR spectrum of compound **11aae** ($CDCl_3$, 101 MHz)

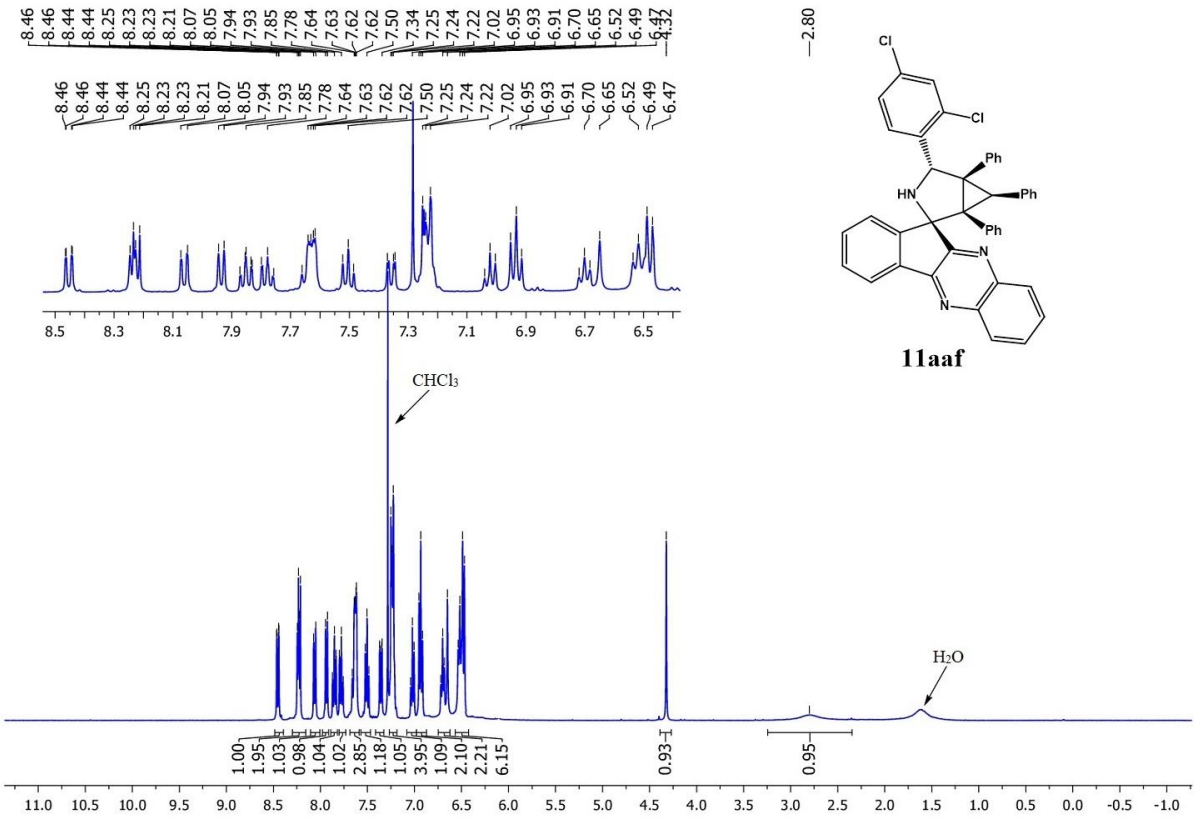


Figure S93. ^{1}H NMR spectrum of compound **11aaf** ($CDCl_3$, 400 MHz)

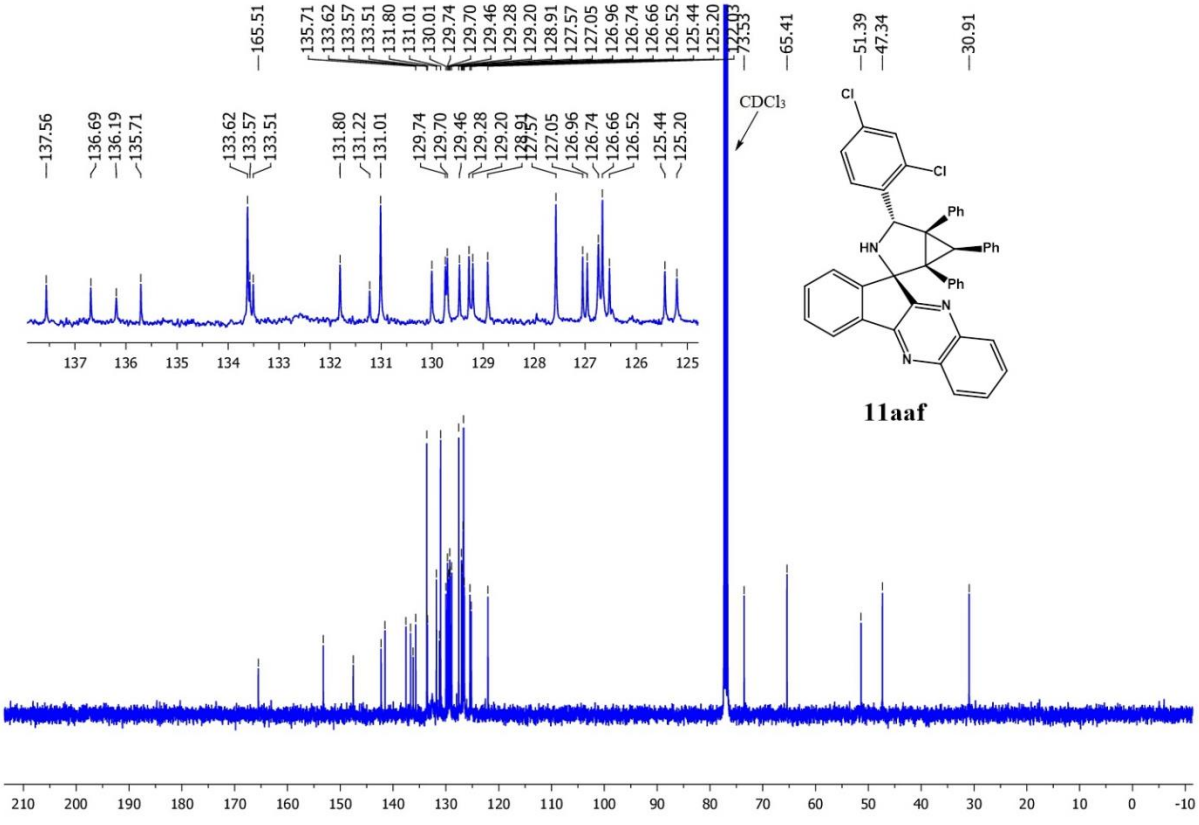


Figure S94. ^{13}C NMR spectrum of compound **11aaf** ($CDCl_3$, 101 MHz)

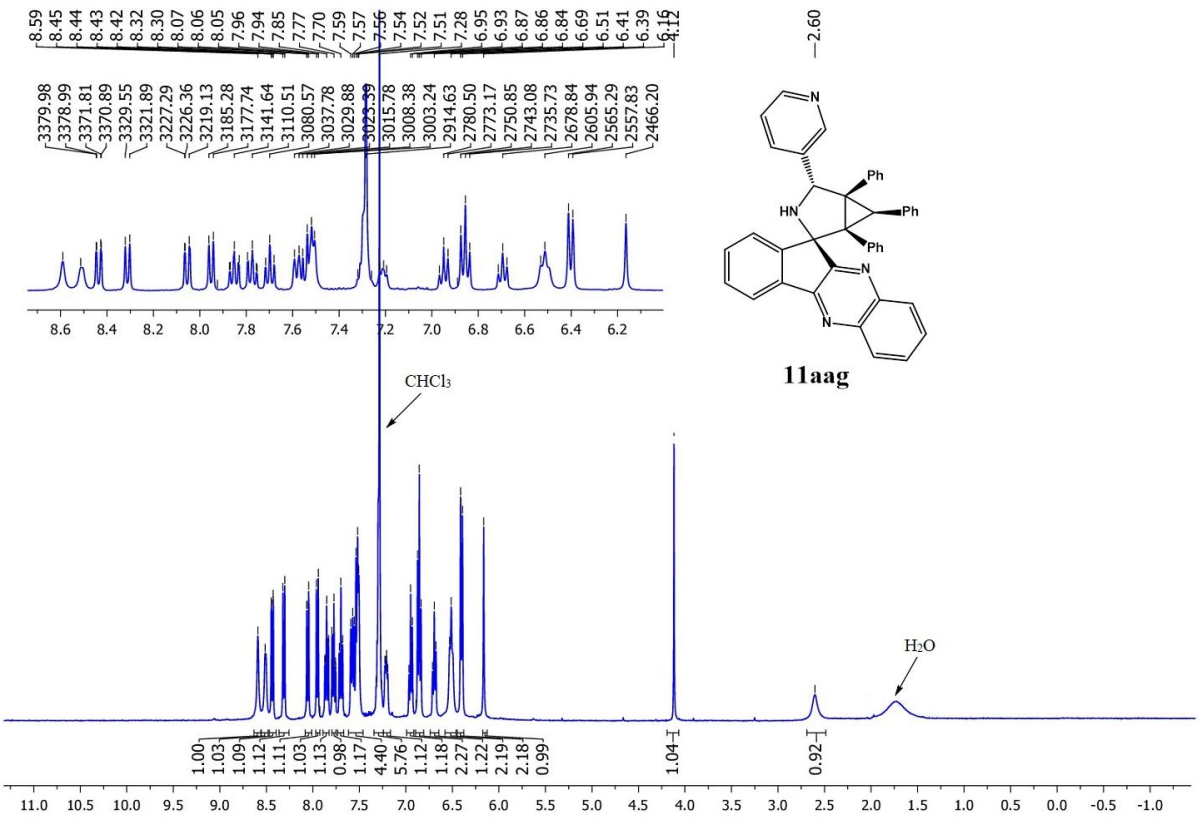


Figure S95. ^{1}H NMR spectrum of compound **11aag** ($CDCl_3$, 400 MHz)

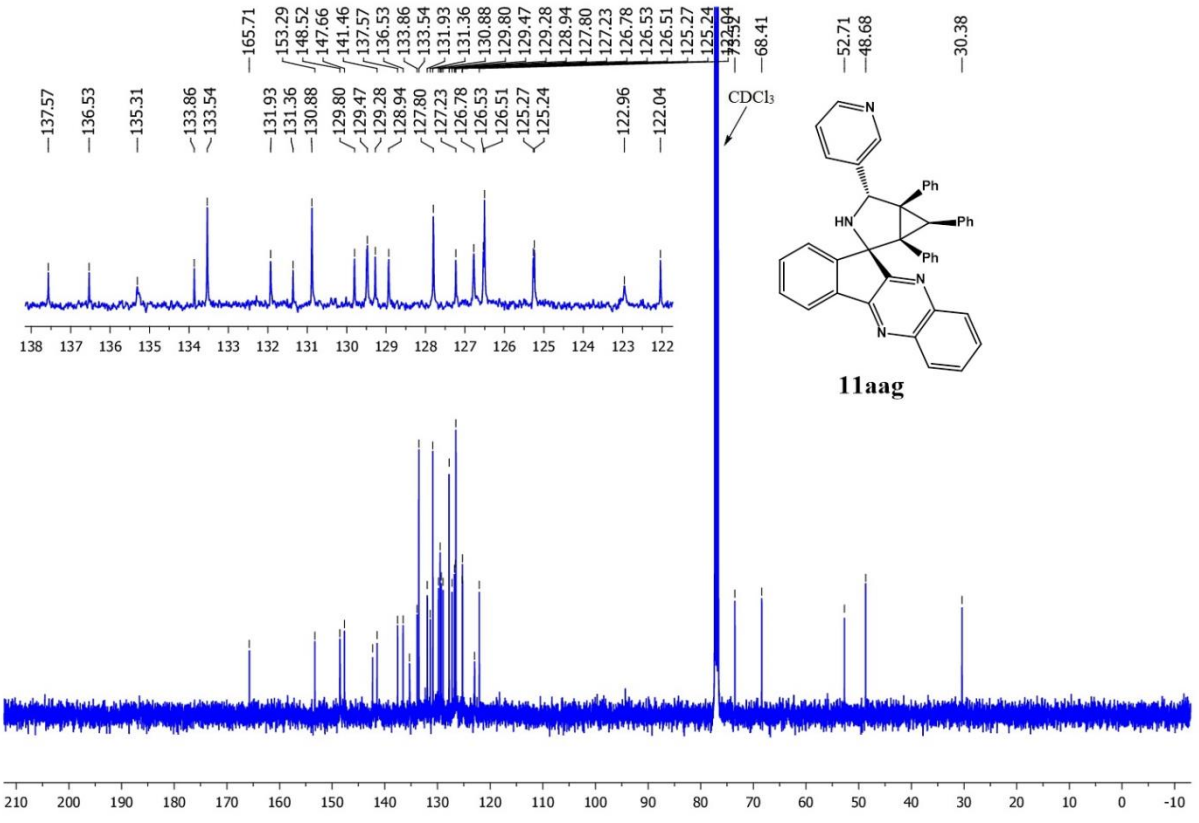


Figure S96. ^{13}C NMR spectrum of compound **11aag** ($CDCl_3$, 101 MHz)

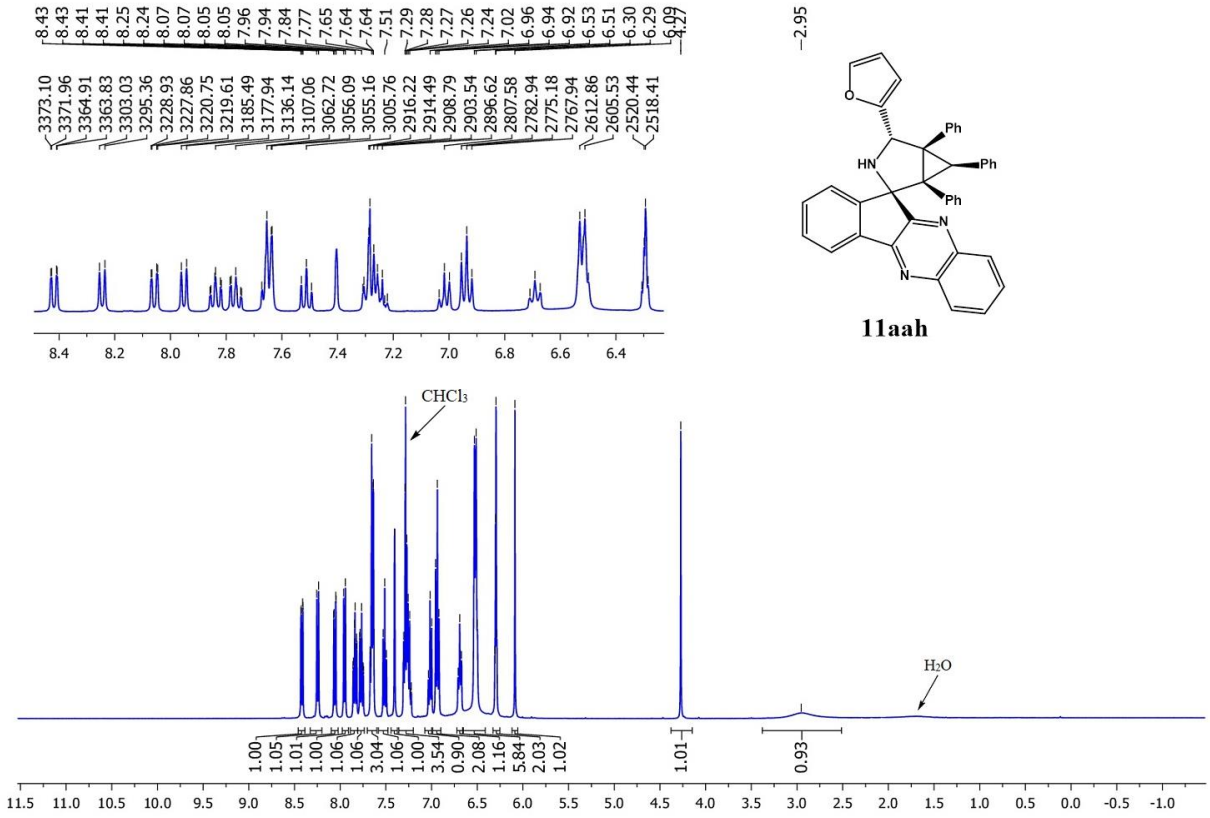


Figure S97. ^{1}H NMR spectrum of compound **11aah** ($CDCl_3$, 400 MHz)

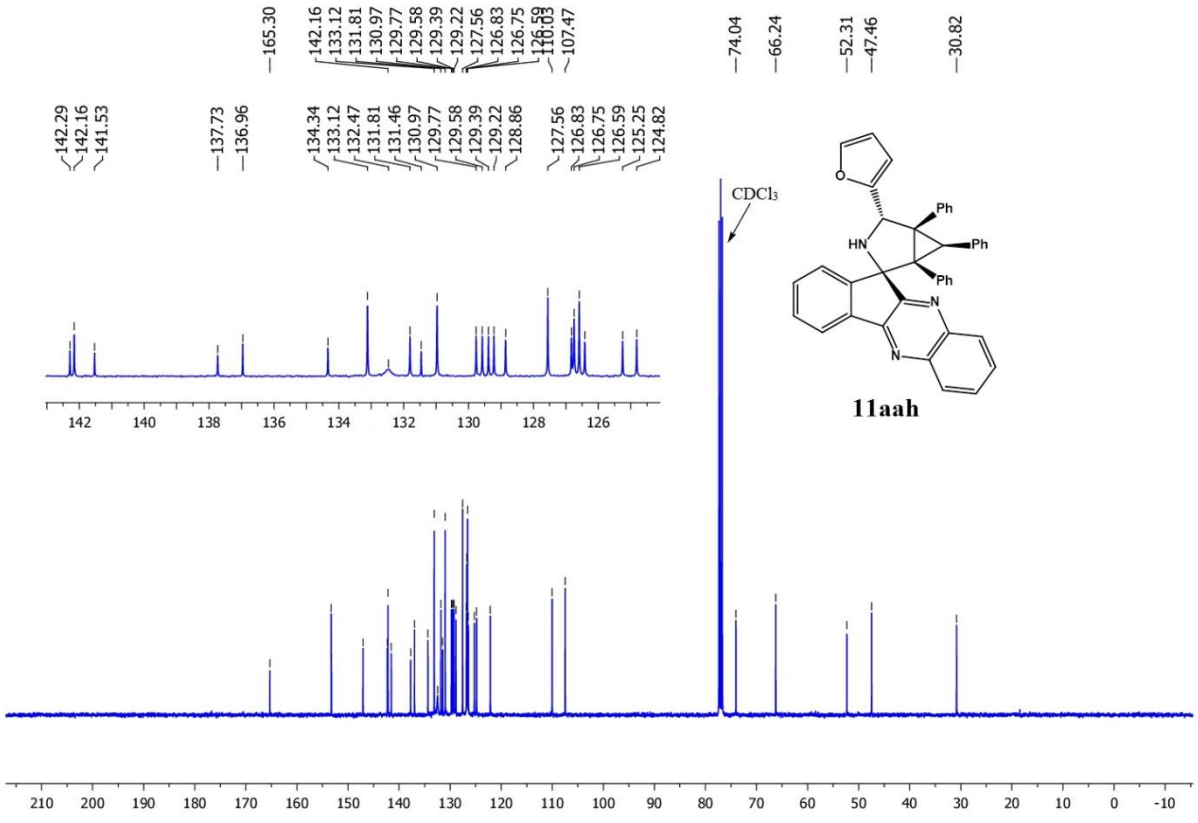


Figure S98. ^{13}C NMR spectrum of compound **11aah** ($CDCl_3$, 101 MHz)

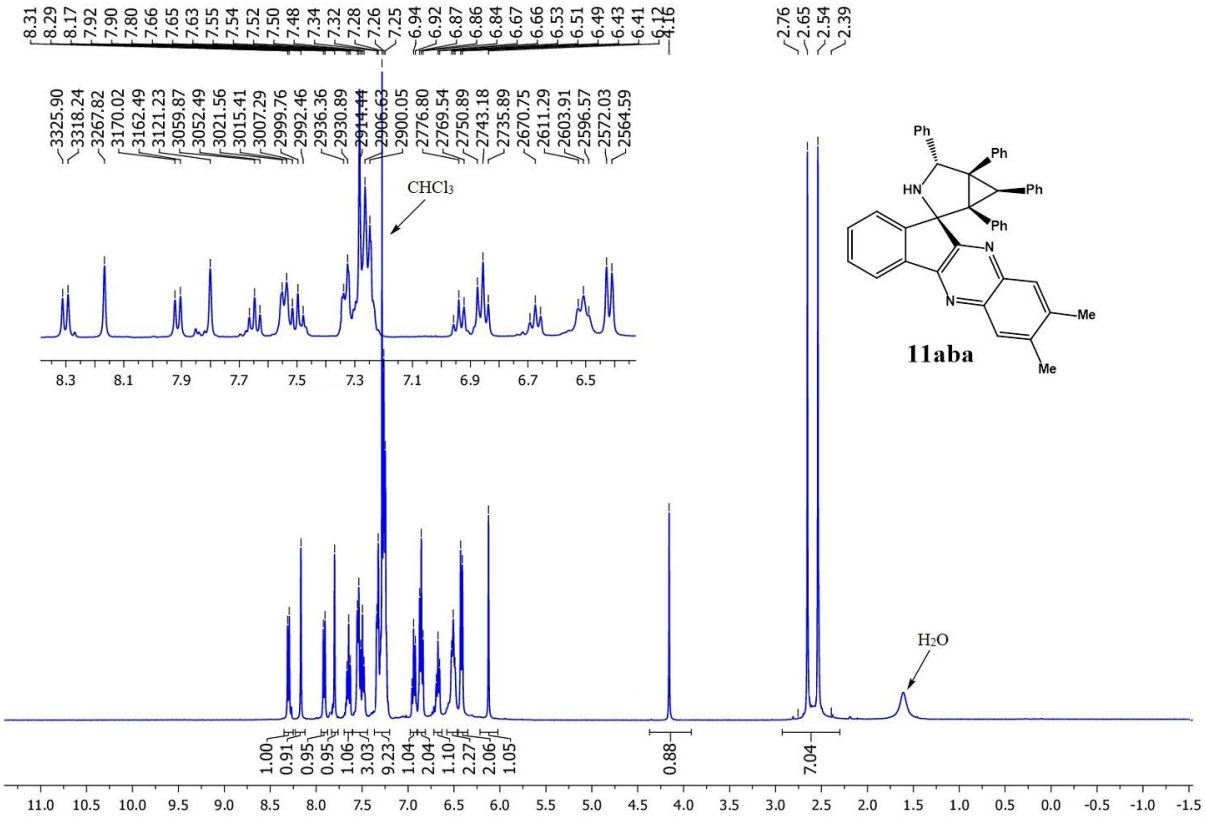


Figure S99. ^{1}H NMR spectrum of compound **11aba** ($CDCl_3$, 400 MHz)

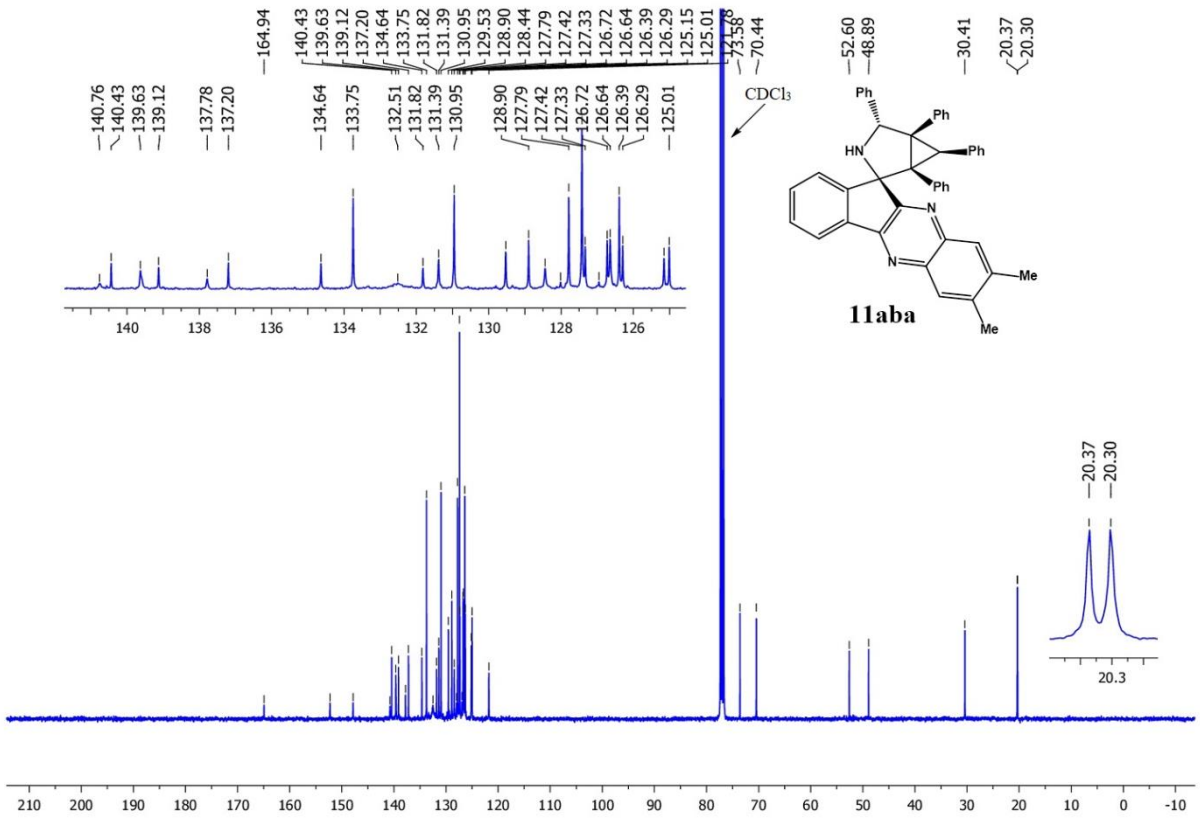


Figure S100. ^{13}C NMR spectrum of compound **11aba** ($CDCl_3$, 101 MHz)

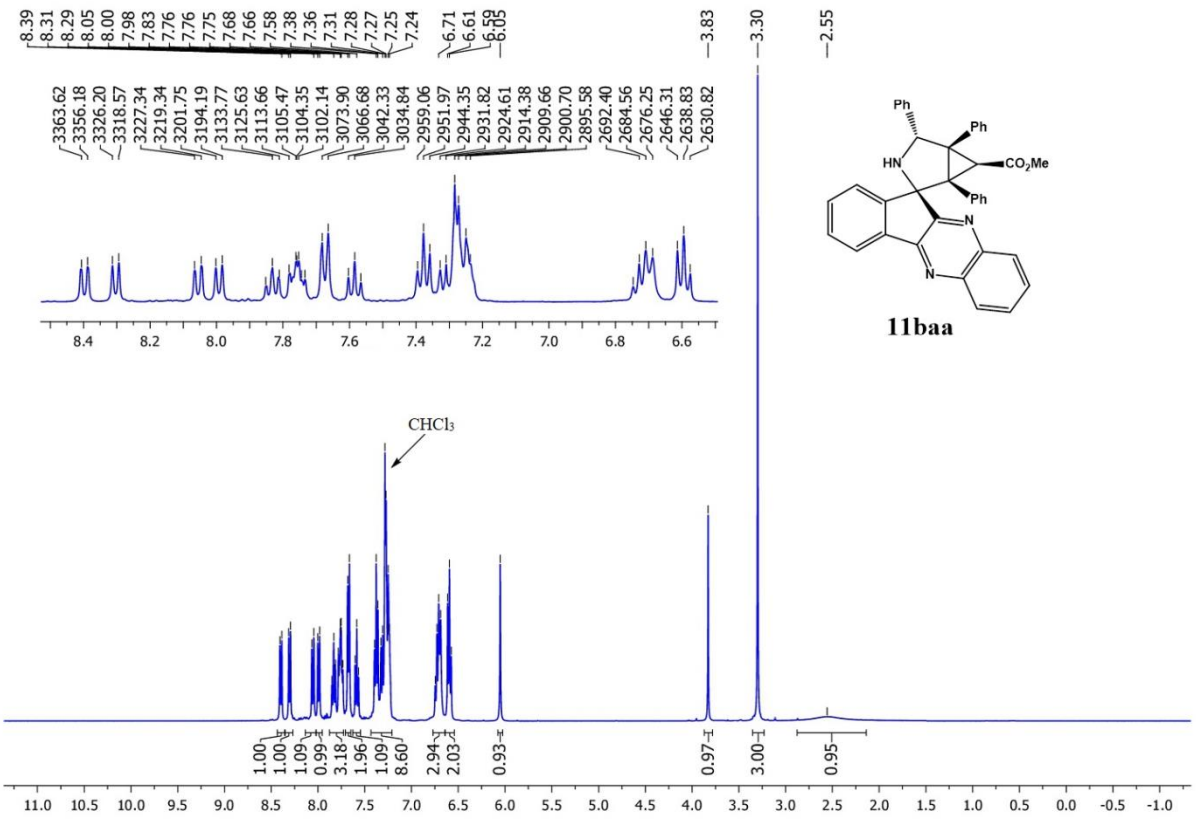


Figure S101. ^{1}H NMR spectrum of compound **11baa** ($CDCl_3$, 400 MHz)

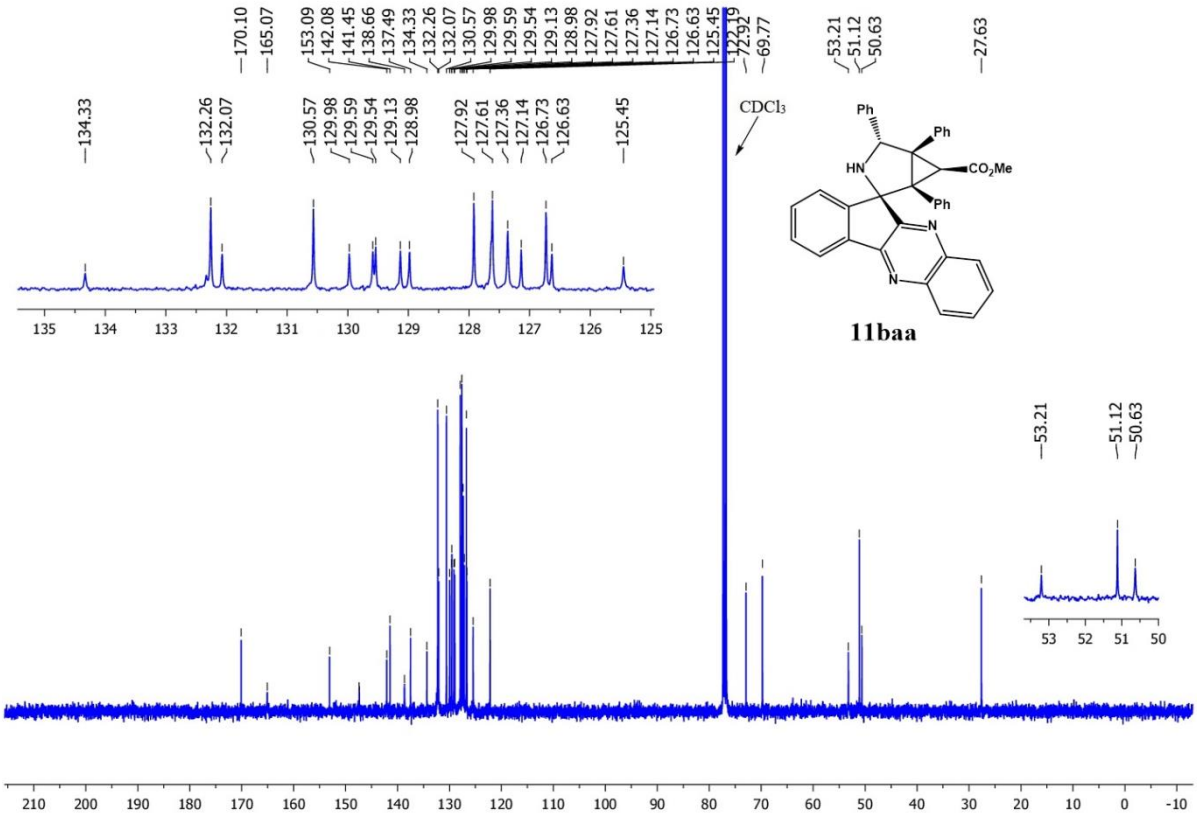


Figure S102. ^{13}C NMR spectrum of compound **11baa** ($CDCl_3$, 101 MHz)

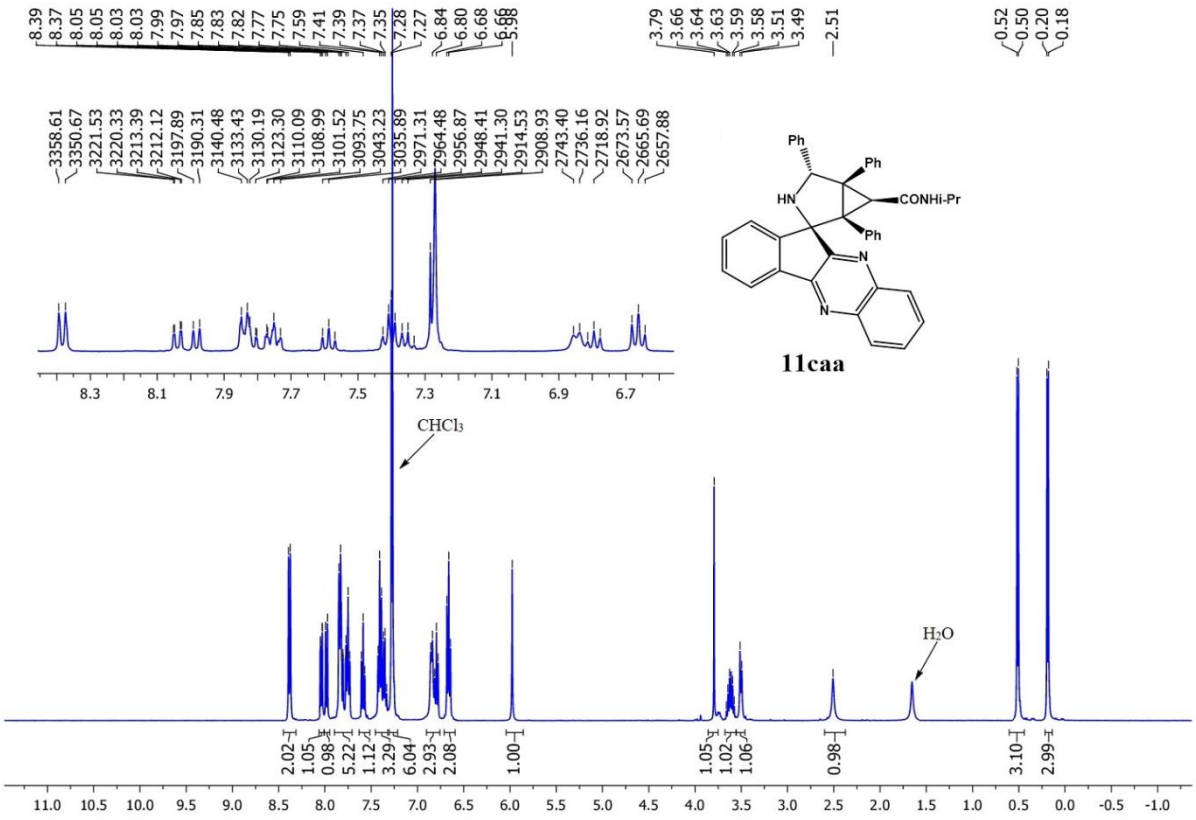


Figure S103. ^{1}H NMR spectrum of compound **11caa** ($CDCl_3$, 400 MHz)

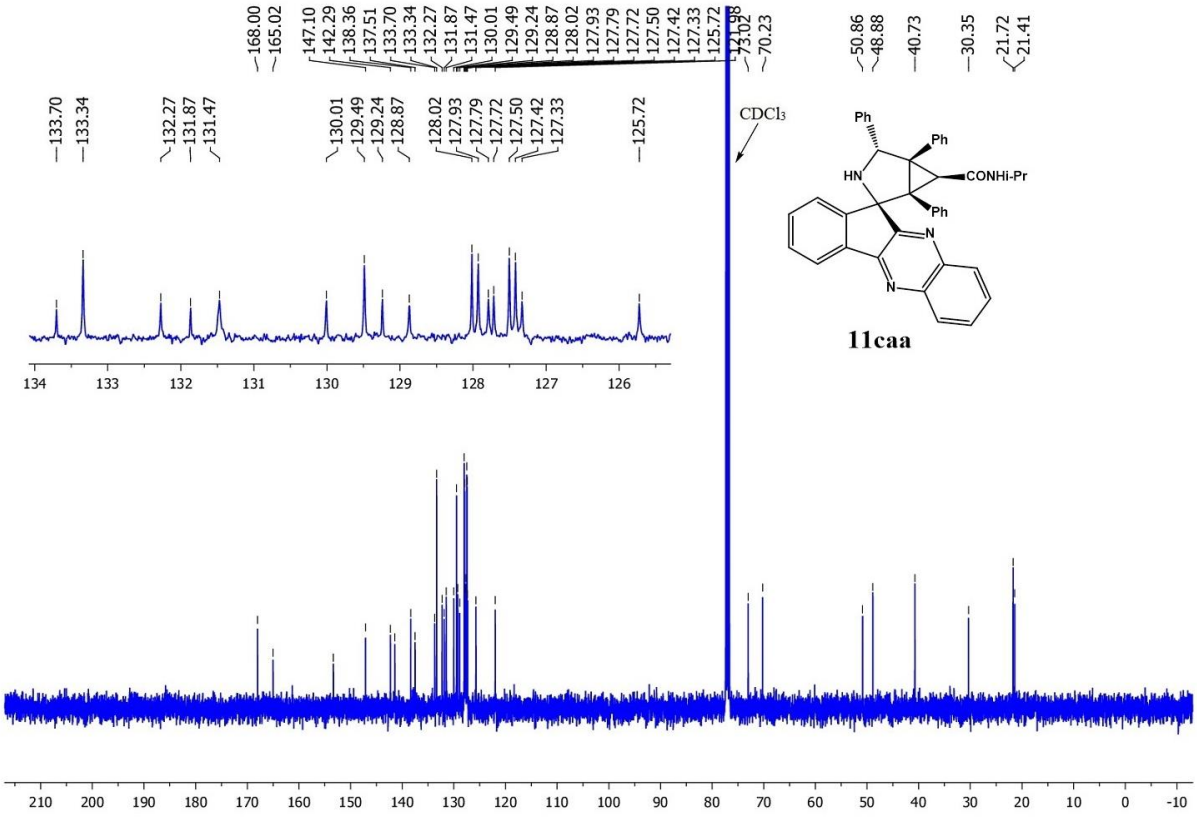


Figure S104. ^{13}C NMR spectrum of compound **11caa** ($CDCl_3$, 101 MHz)

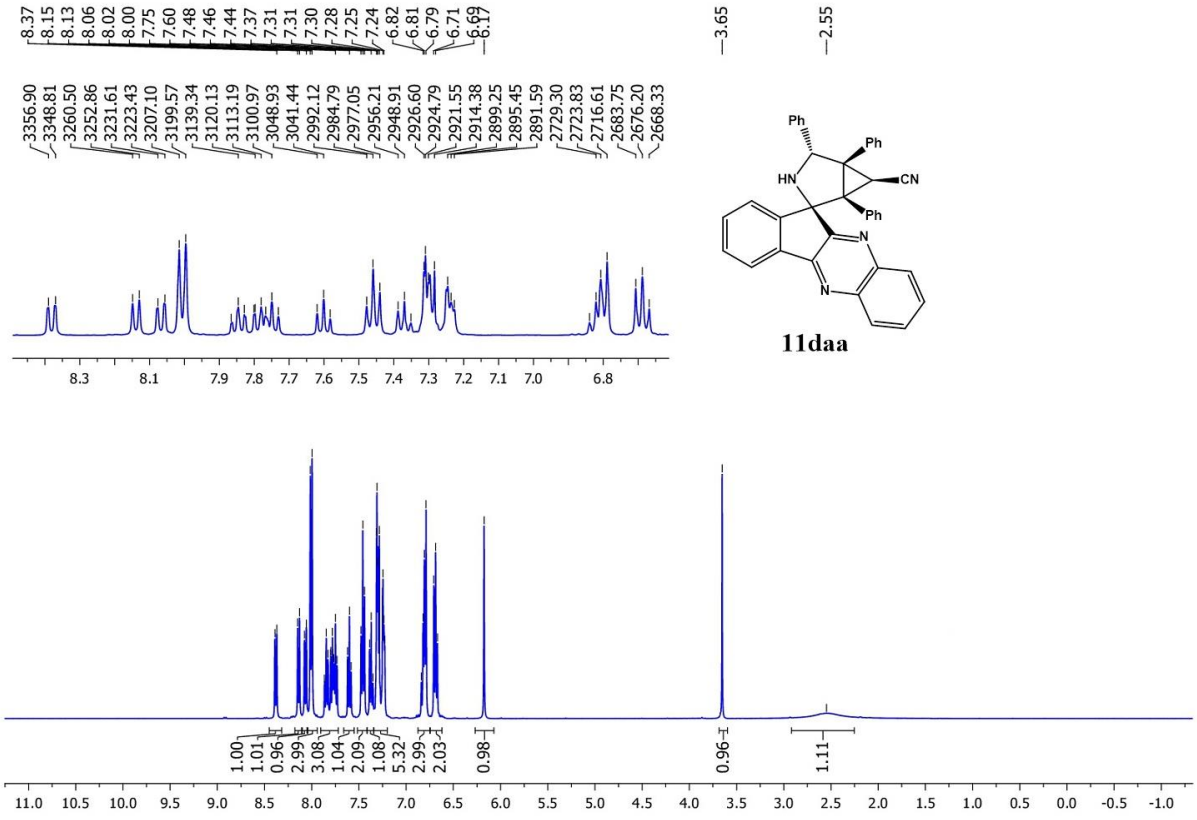


Figure S105. ^{1}H NMR spectrum of compound **11daa** ($CDCl_3$, 400 MHz)

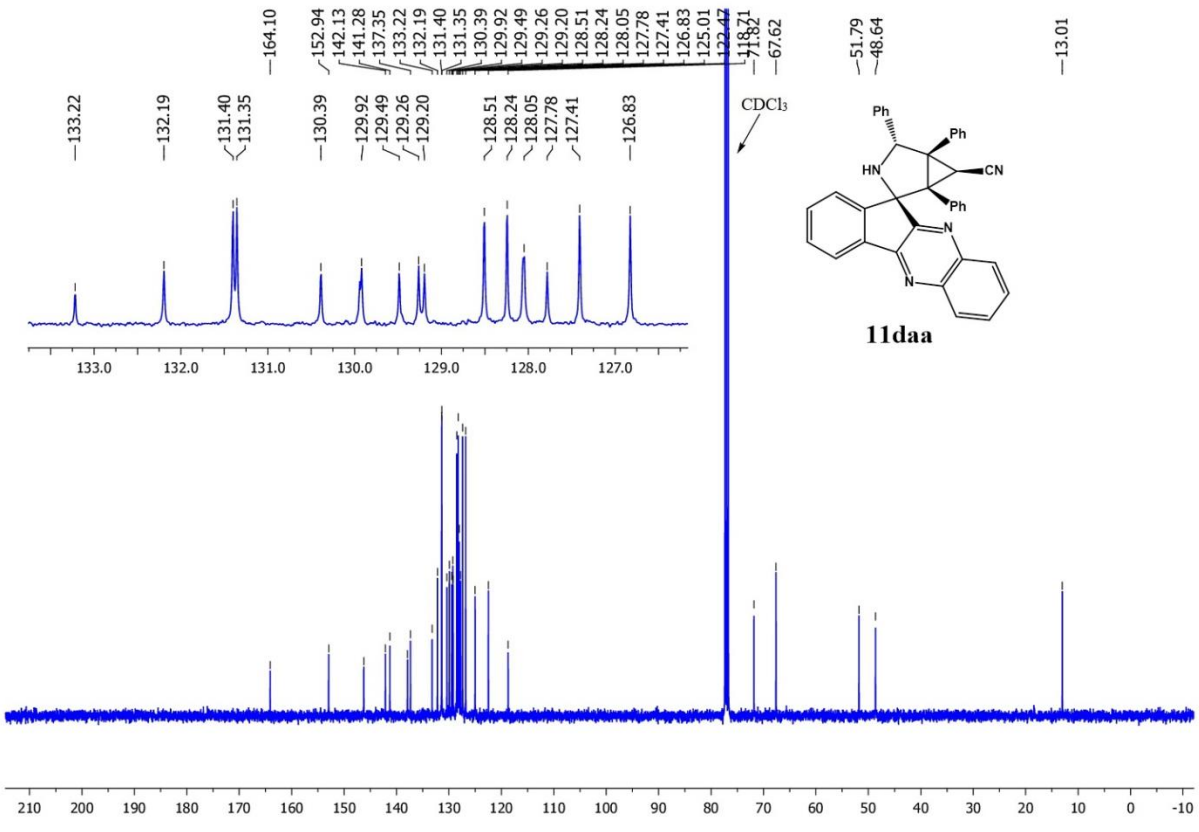


Figure S106. ^{13}C NMR spectrum of compound **11daa** ($CDCl_3$, 101 MHz)

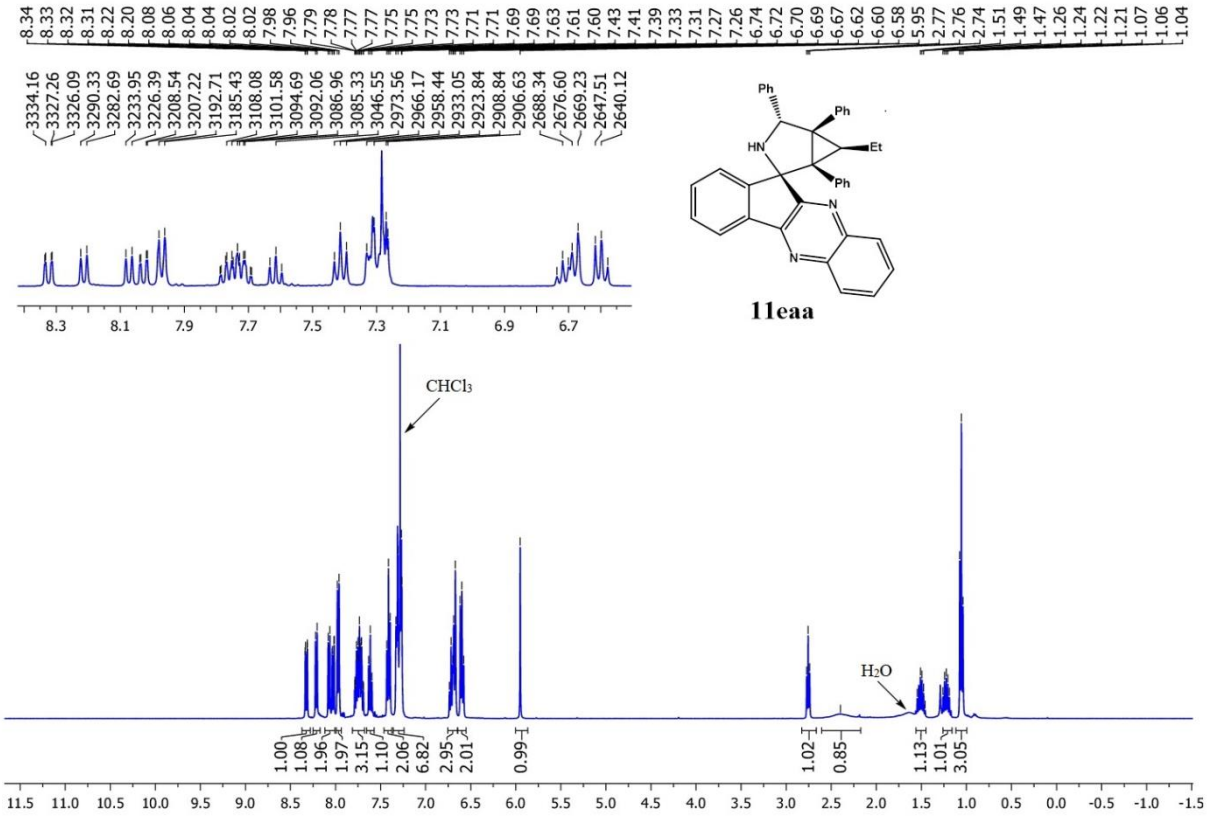


Figure S107. ^{13}C NMR spectrum of compound **11eaa** ($CDCl_3$, 400 MHz)

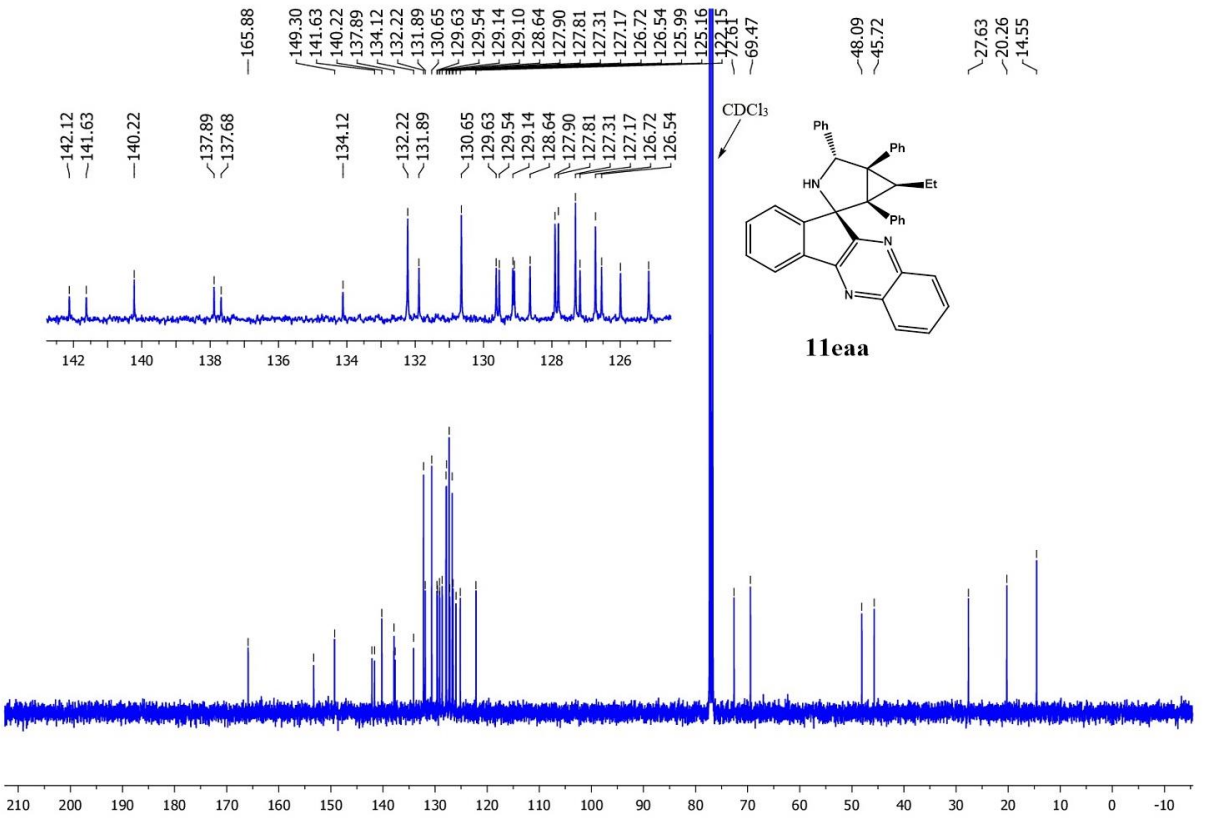


Figure S108. ^{1}H NMR spectrum of compound **11eaa** ($CDCl_3$, 101 MHz)

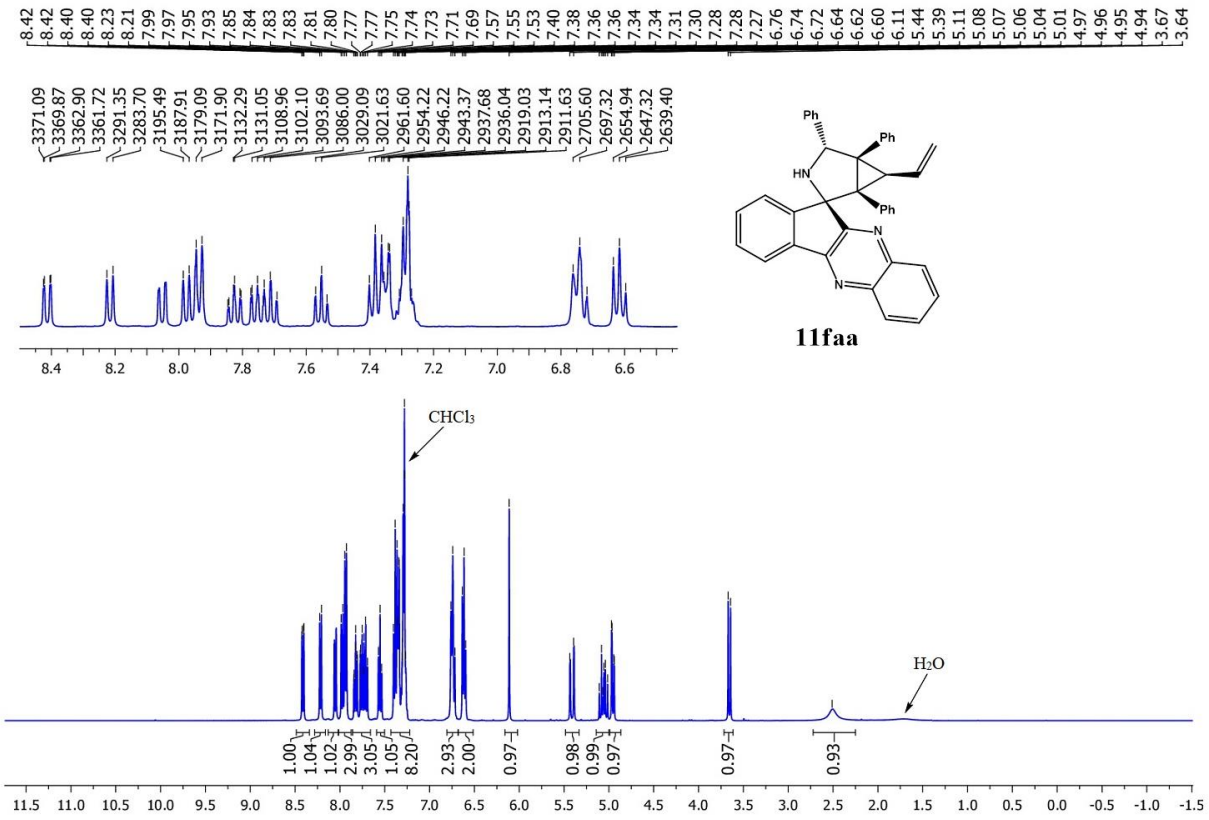


Figure S109. ^{1}H NMR spectrum of compound **11faa** ($CDCl_3$, 400 MHz)

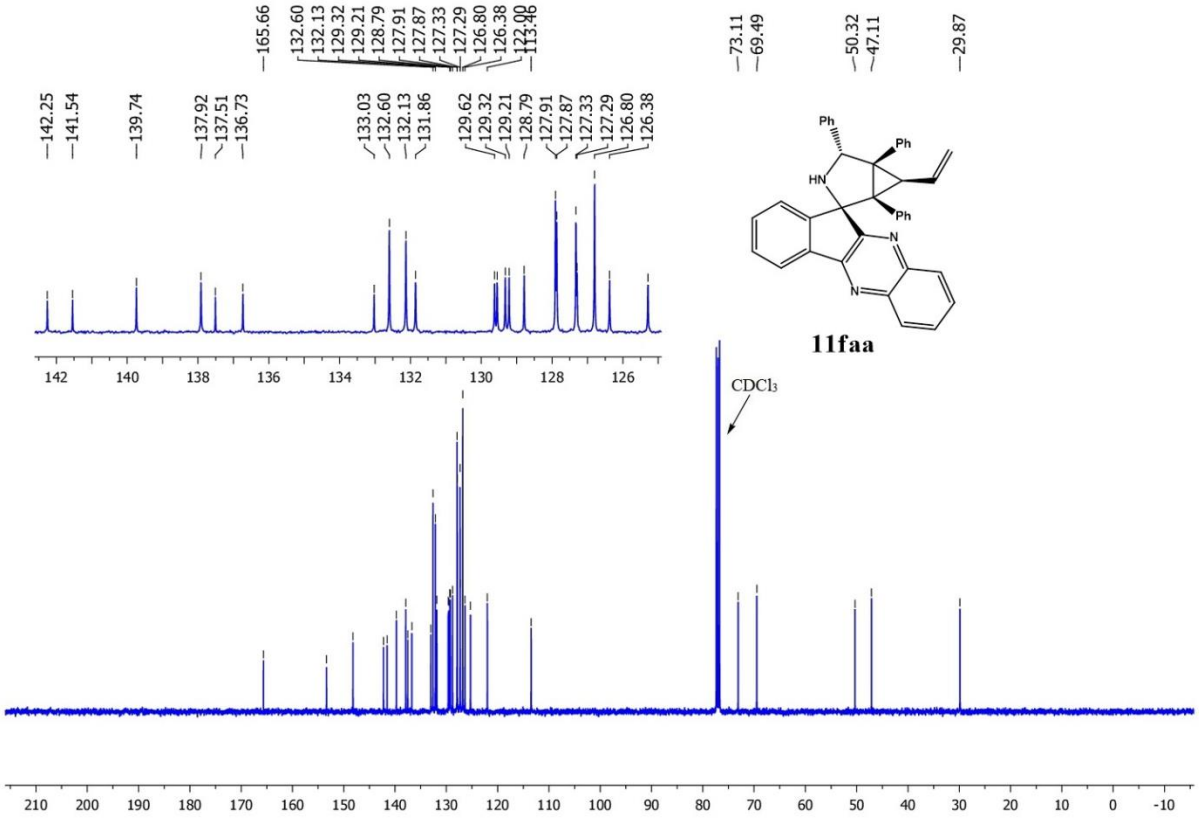


Figure S110. ^{13}C NMR spectrum of compound **11faa** ($CDCl_3$, 101 MHz)

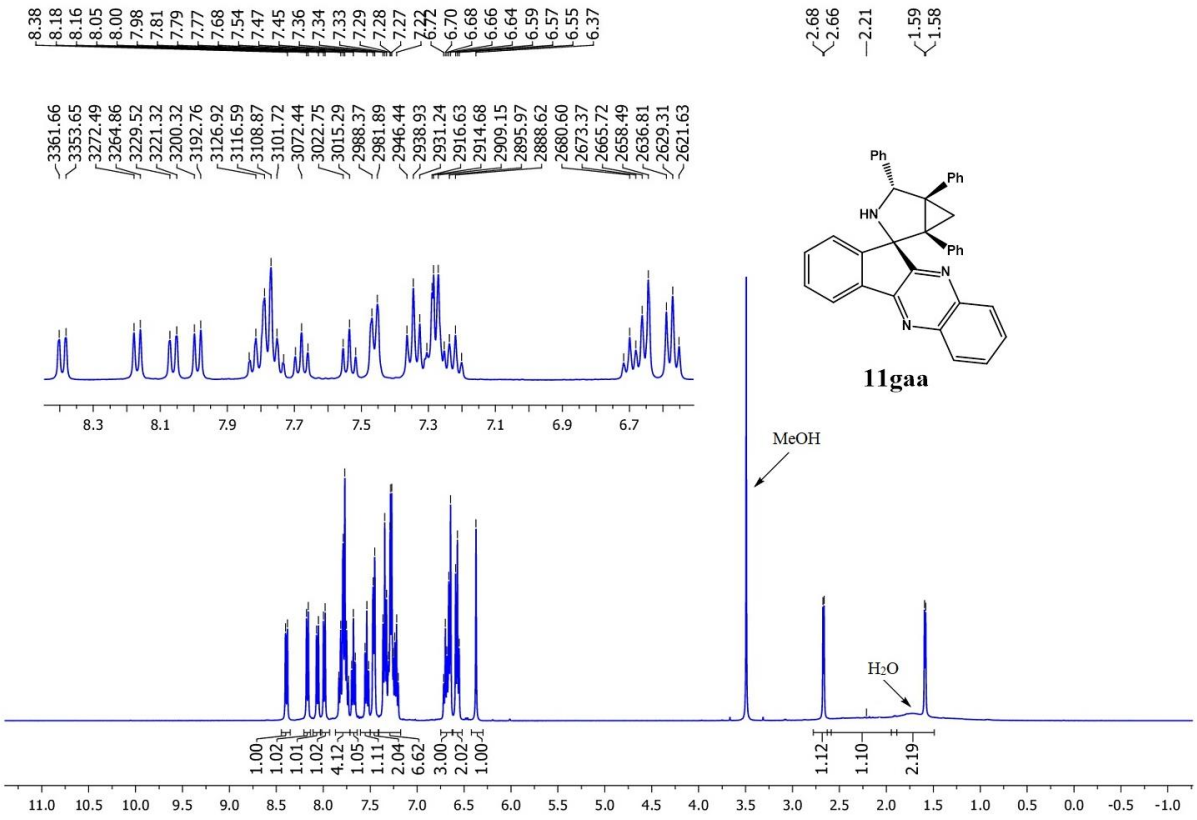


Figure S111. ^{1}H NMR spectrum of compound **11gaa** ($CDCl_3$, 400 MHz)

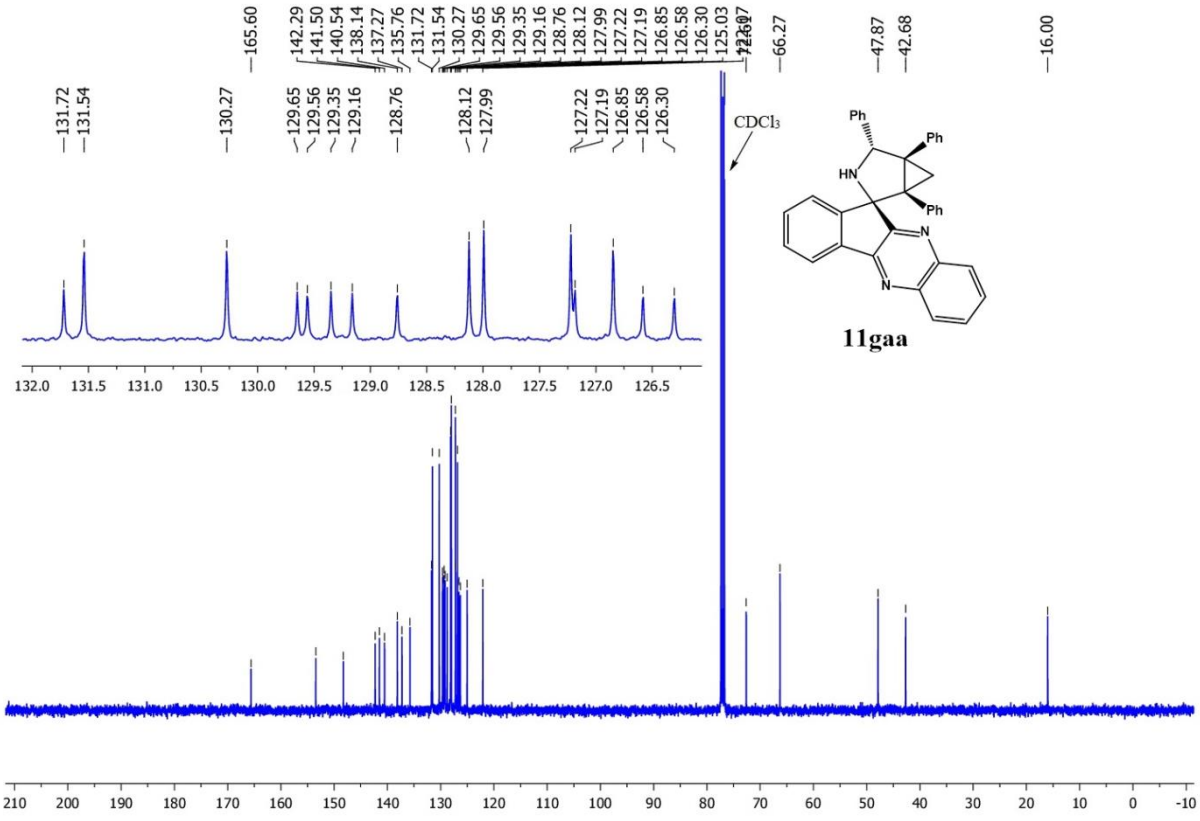


Figure S112. ^{13}C NMR spectrum of compound **11gaa** ($CDCl_3$, 101 MHz)

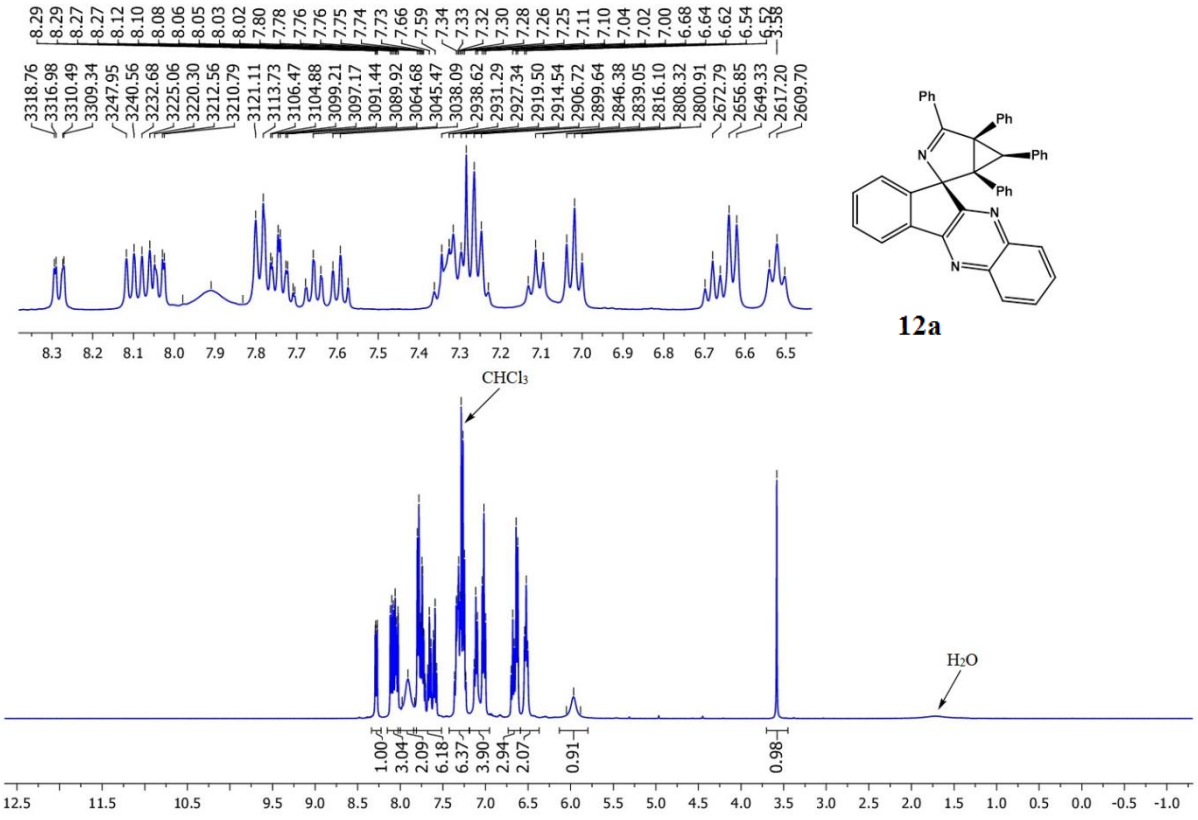


Figure S113. ^{1}H NMR spectrum of compound **12a** ($CDCl_3$, 400 MHz)

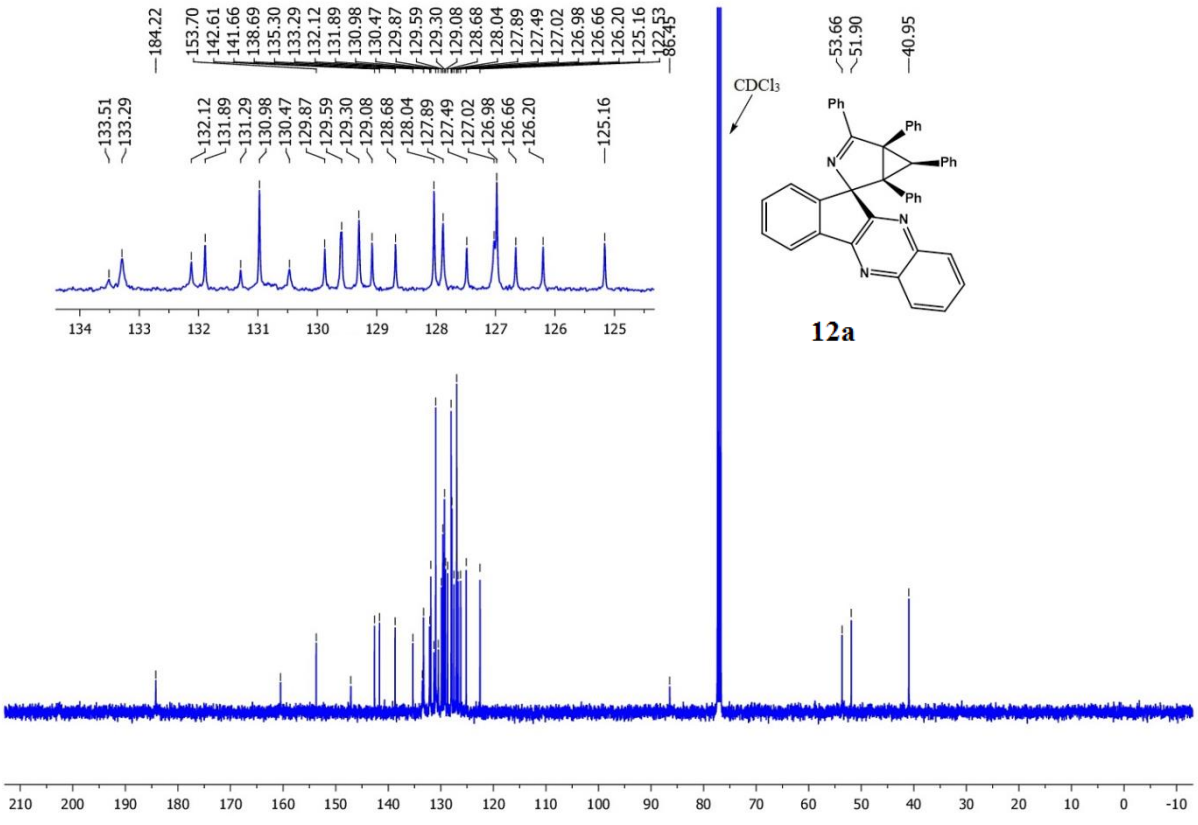


Figure S114. ^{13}C NMR spectrum of compound **12a** ($CDCl_3$, 101 MHz)

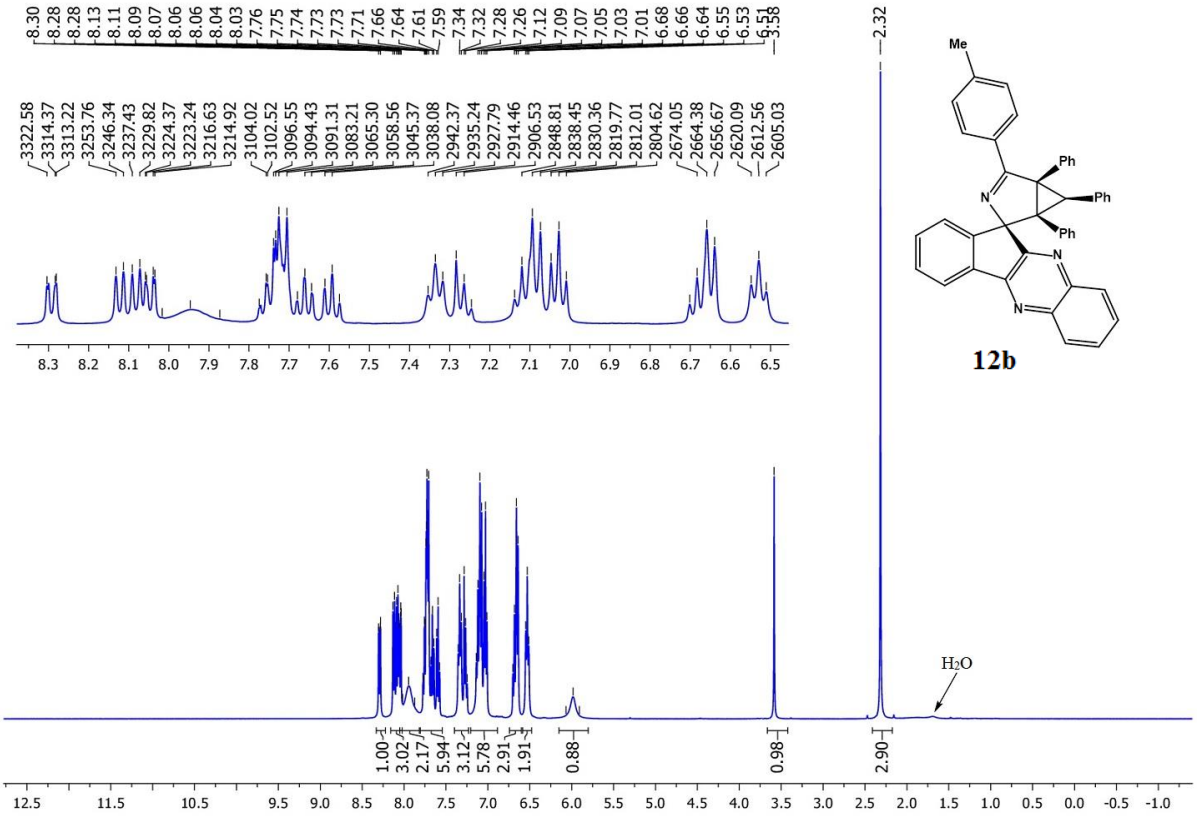


Figure S115. ^{1}H NMR spectrum of compound **12b** ($CDCl_3$, 400 MHz)

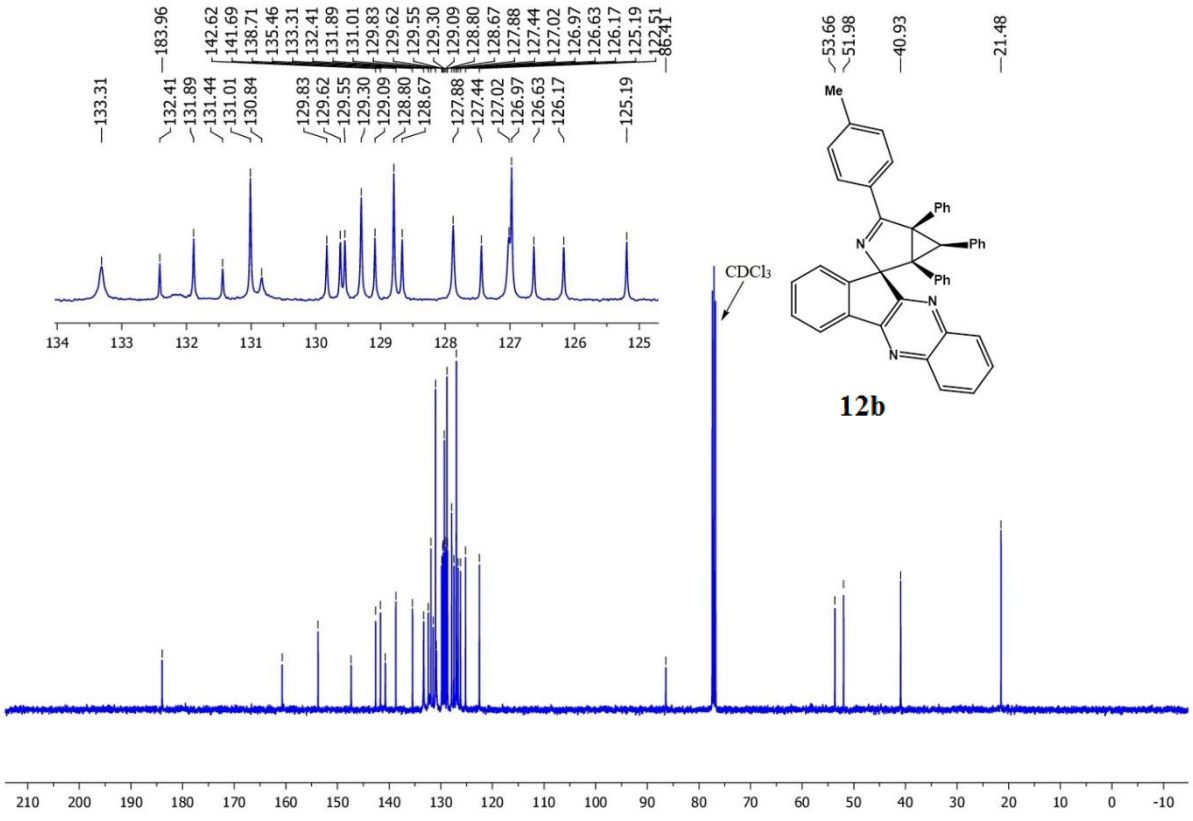


Figure S116. ^{13}C NMR spectrum of compound **12b** ($CDCl_3$, 101 MHz)

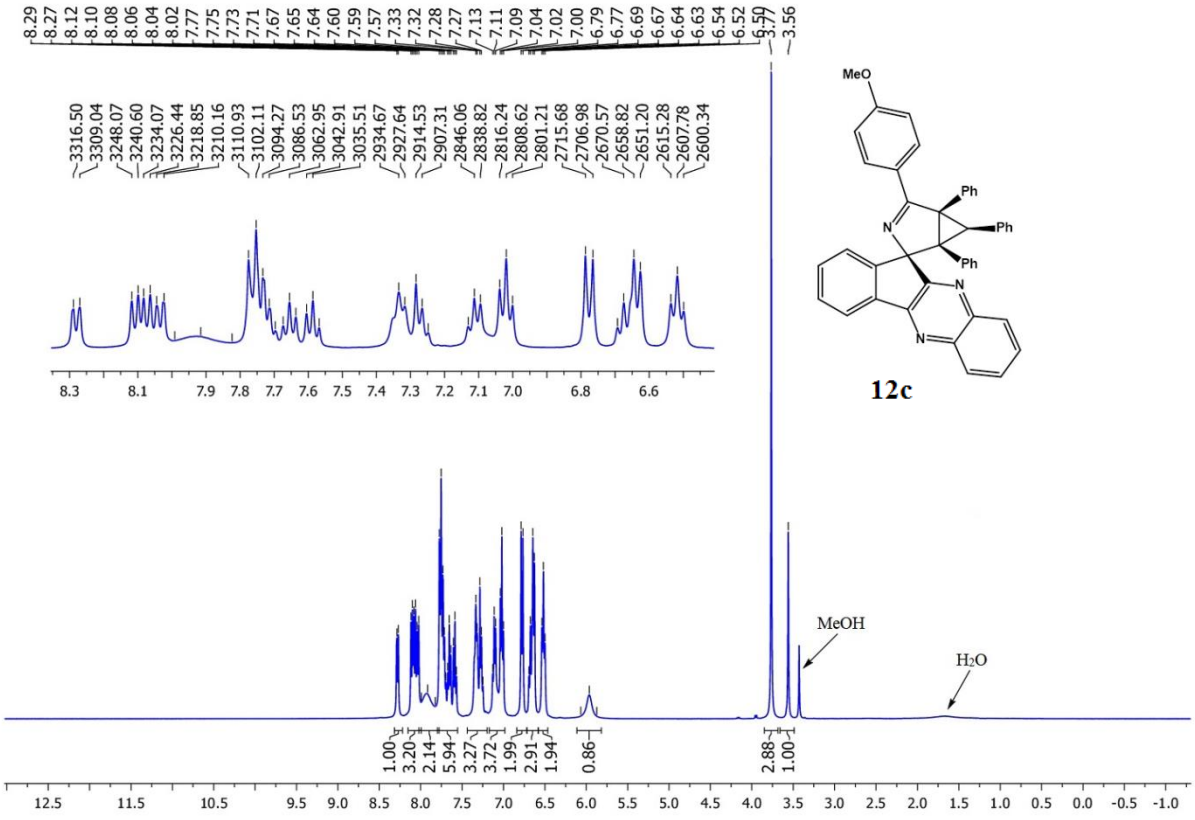


Figure S117. ^{1}H NMR spectrum of compound **12c** ($CDCl_3$, 400 MHz)

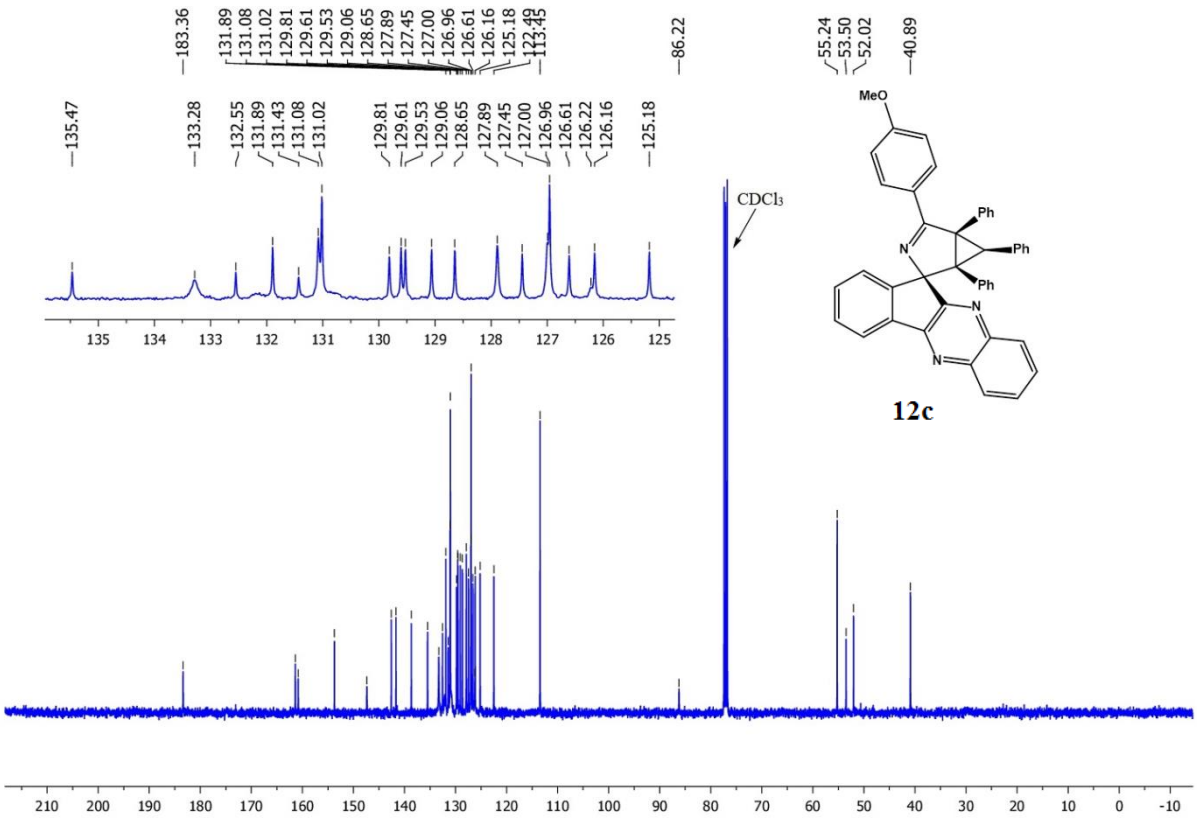


Figure S118. ^{13}C NMR spectrum of compound **12c** ($CDCl_3$, 101 MHz)

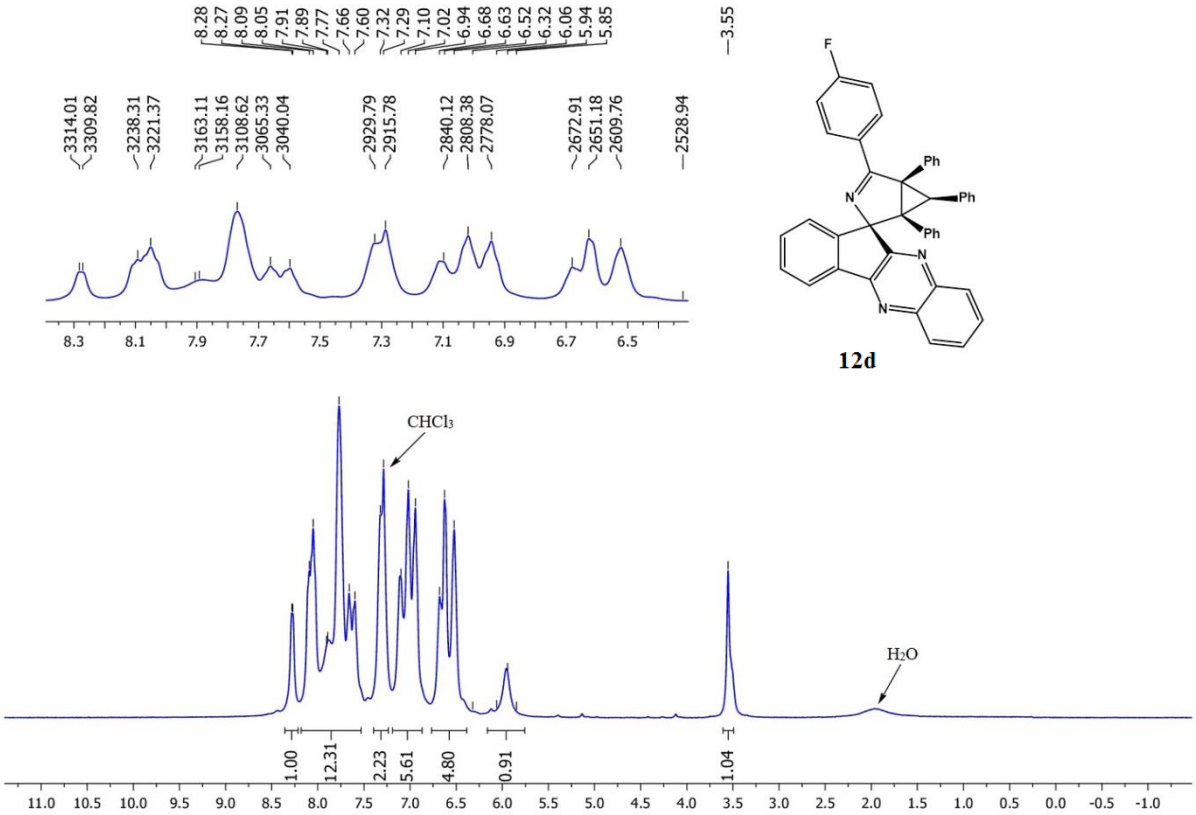


Figure S119. ^{1}H NMR spectrum of compound **12d** ($CDCl_3$, 400 MHz)

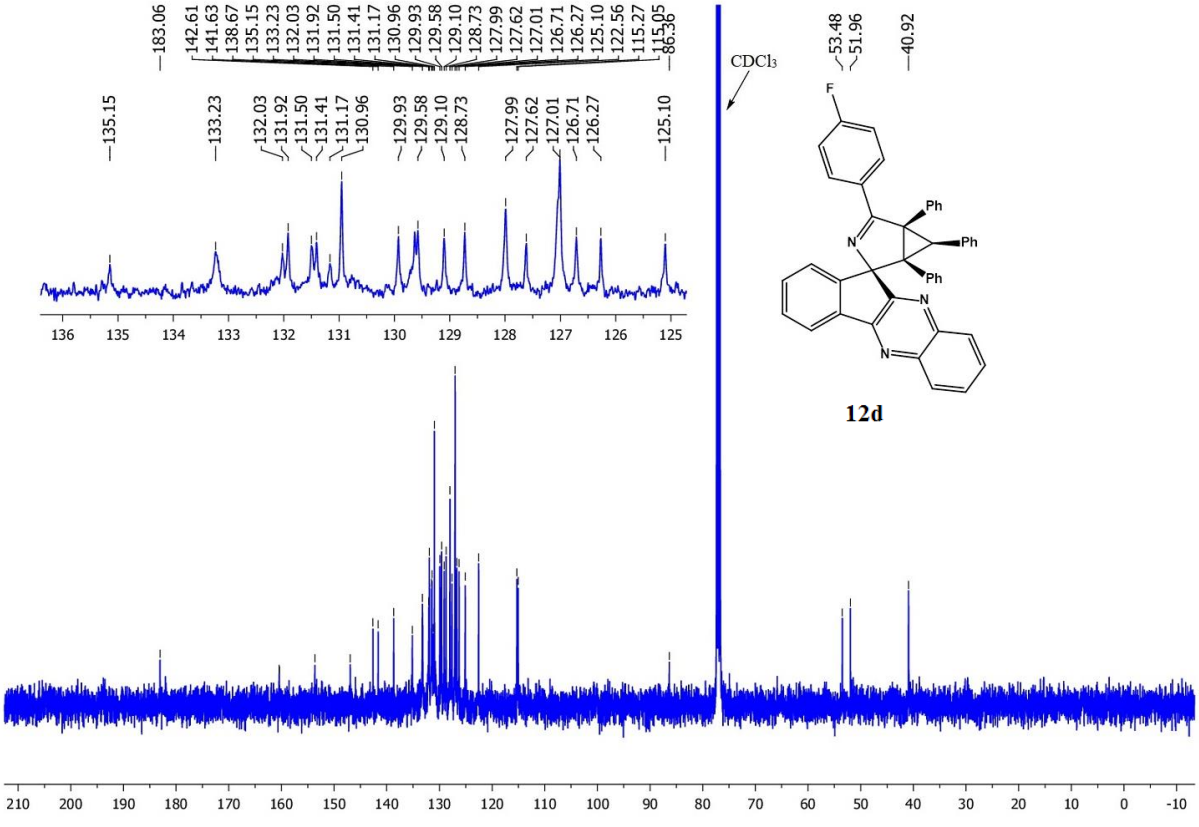


Figure S120. ^{13}C NMR spectrum of compound **12d** ($CDCl_3$, 101 MHz)

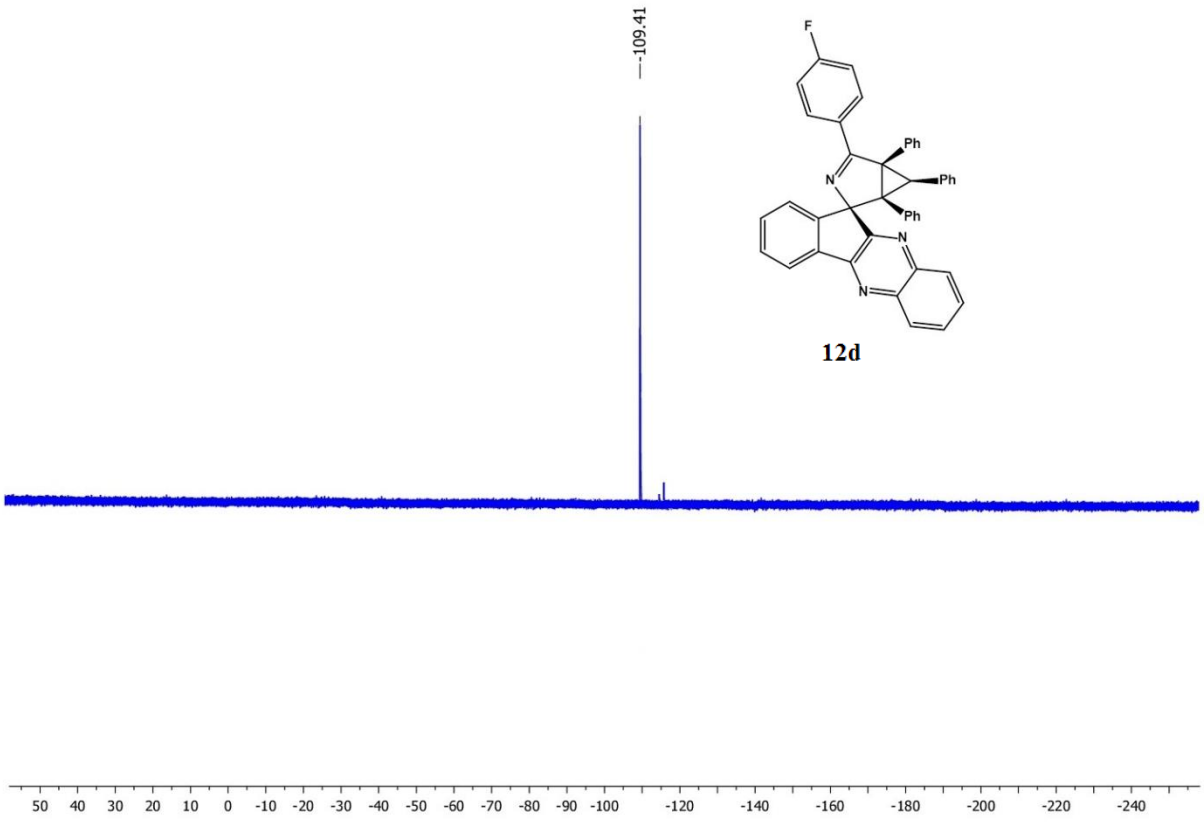


Figure S121. ^{19}F NMR spectrum of compound **12d** ($CDCl_3$, 376 MHz)

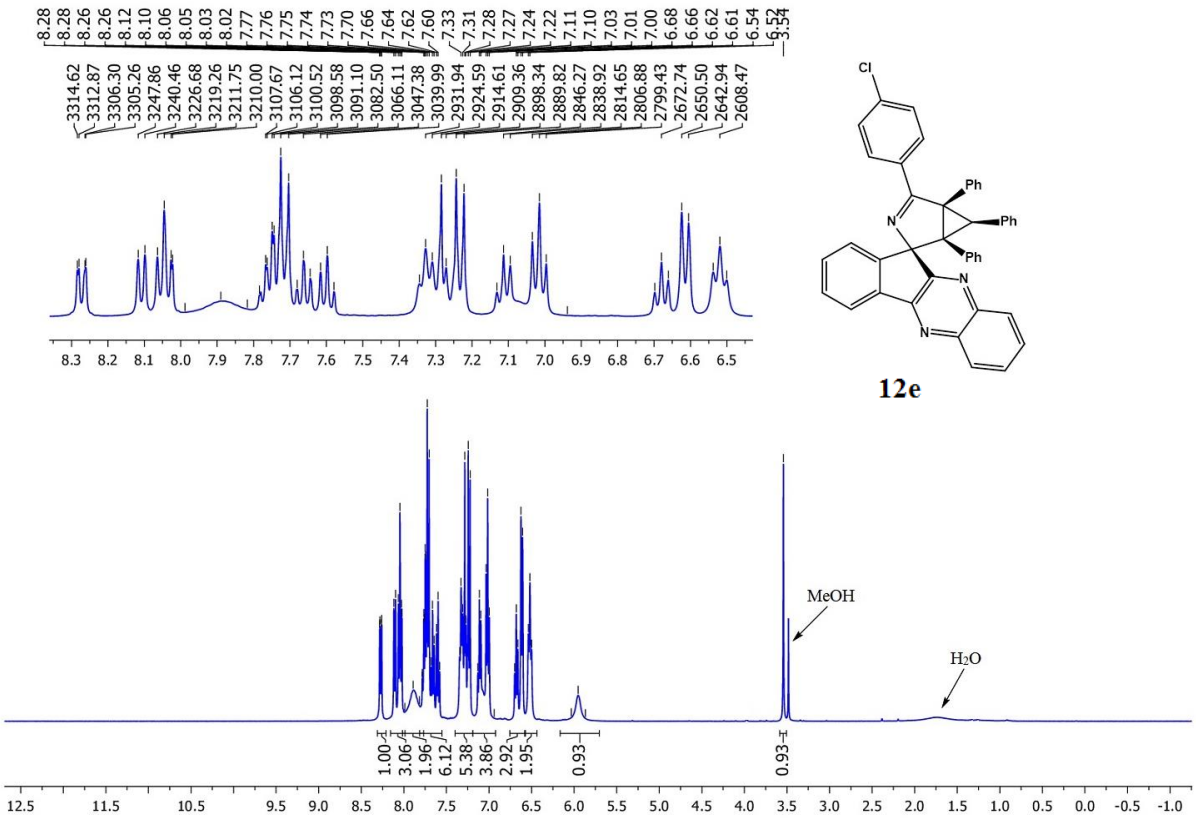


Figure S122. ^{1}H NMR spectrum of compound **12e** ($CDCl_3$, 400 MHz)

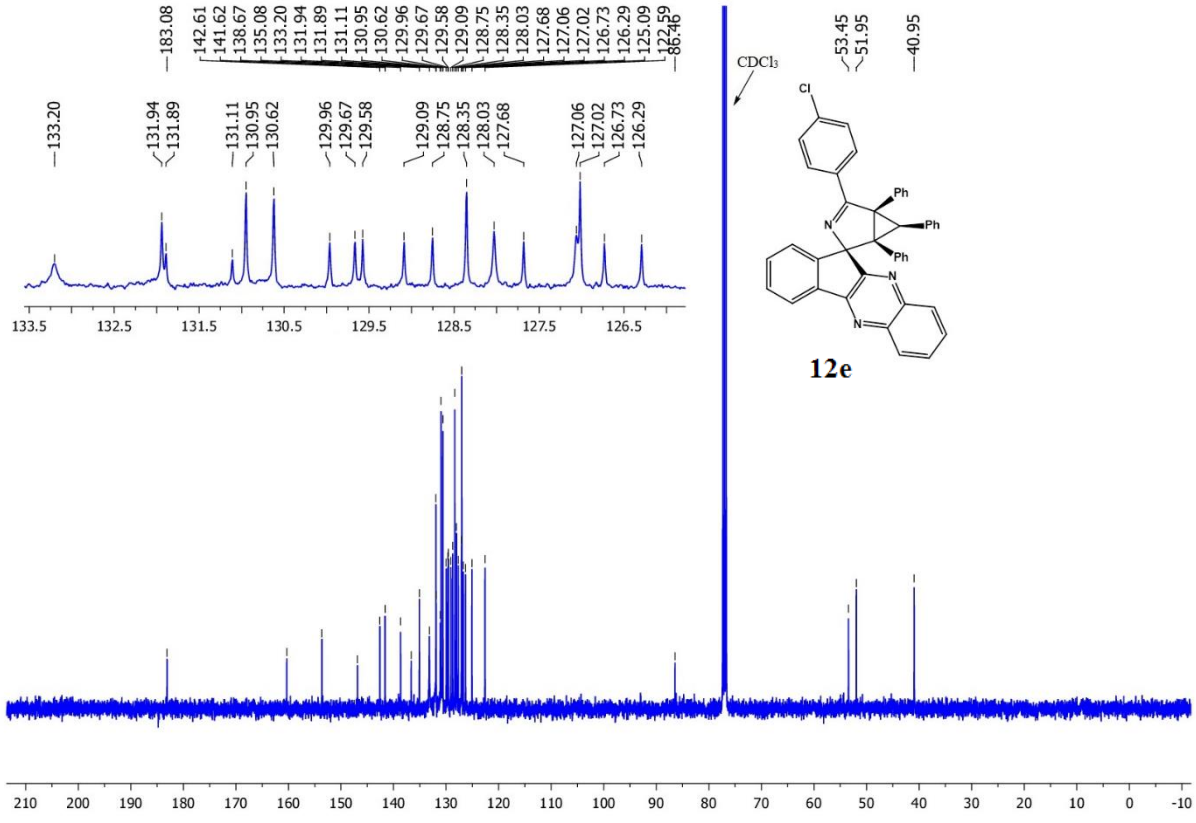


Figure S123. ^{13}C NMR spectrum of compound **12e** ($CDCl_3$, 101 MHz)

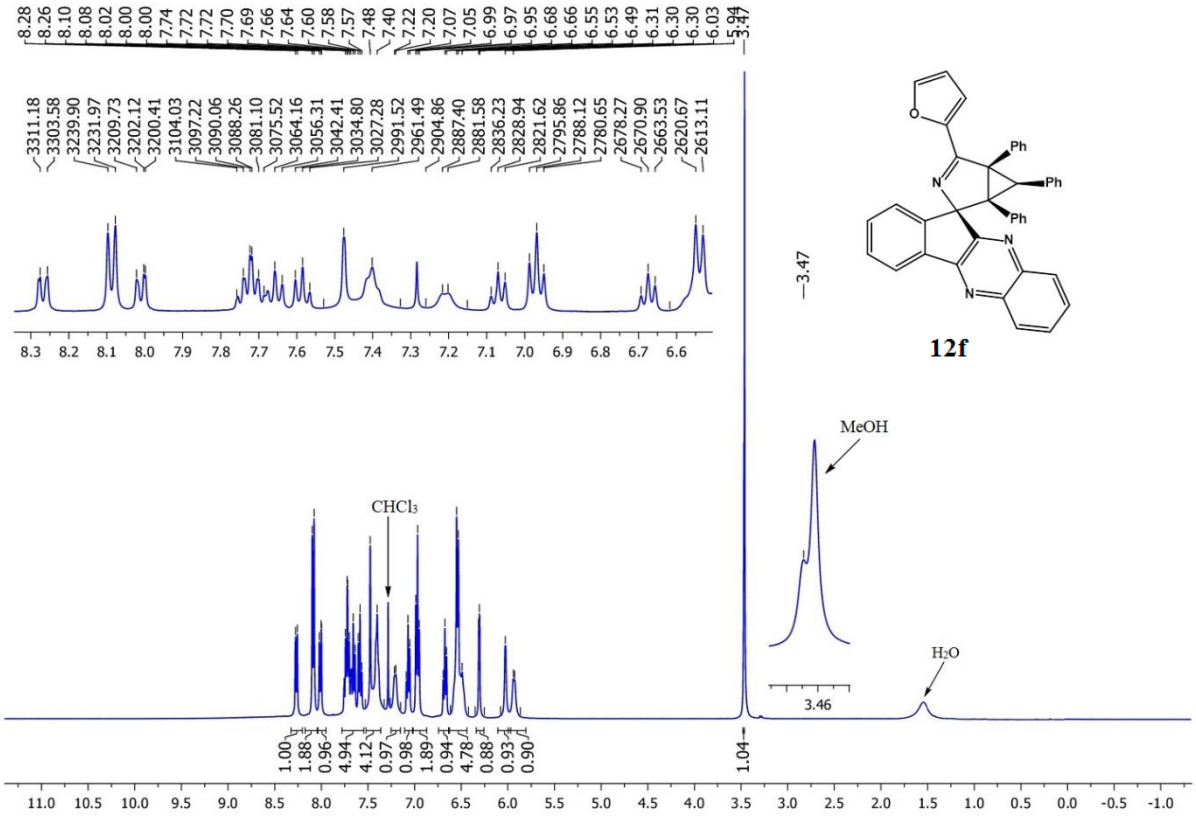


Figure S124. ^{1}H NMR spectrum of compound **12f** ($CDCl_3$, 400 MHz)

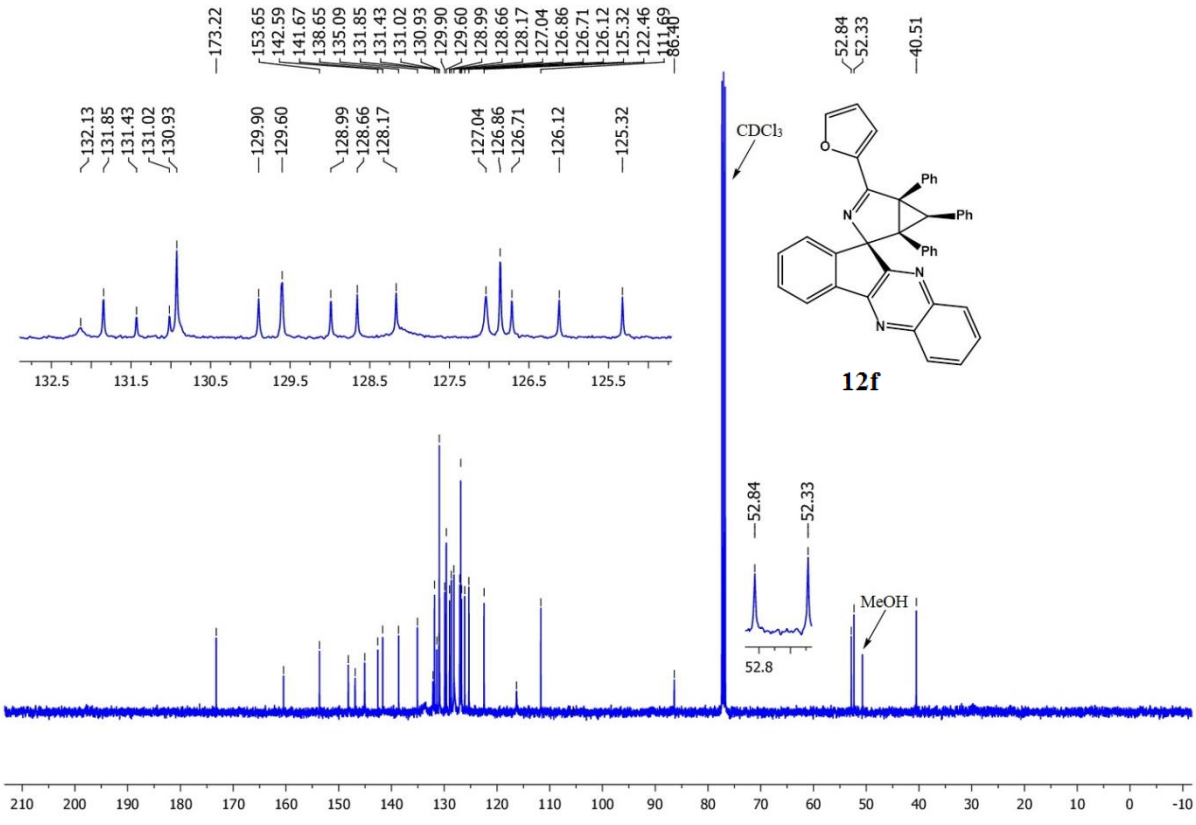


Figure S125. ^{13}C NMR spectrum of compound **12f** ($CDCl_3$, 101 MHz)

3. Bioassay details

Table S2. Evaluation of proliferative activity and viability of K562 cells by flow cytometry

Compound	Number of cells					
	24 h		48 h		72 h	
	experiment	average	experiment	average	experiment	average
Imatinib mesylate	11393	11124	13125	13347	6683	7913
	9922		13324		7133	
	12058		13593		9924	
4aab	18349	20590	38307	36879	76373	66450
	22336		34489		61945	
	21085		37843		61032	
4caa	13151	13926	12660	12667	9608	8765
					8515	
	14702		12674		8172	
7aac	10740	13060	20517	14872	24180	33150
	14408		14290		33597	
	14033		9810		41673	
7aad	14856	15465	27750	27532	67666	52383
	15727		26203		49934	
	15814		28645		39551	
7aae	13045	13018	31276	30044	53820	56804
	12457		29482		55055	
	13553		29375		61539	
7aag	9763	9110	20193	16203	30943	34298
	8850		14778		35736	
	8718		13640		36215	
7aak	10740	10458	23019	20682	28996	33209
	9925		18975		35974	
	10710		20053		34659	
7aao	9796	9204	9337	9767	13054	12116
	8991		9556		11047	
	8827		10410		12247	
7aar	15209	13384	15857	16444	21334	19259
	14982		14158		15952	

	9961		19319		20492	
7aas	8347	8201	7177	7378	3758	4253
	7962		7403		4414	
	8295		7555		4587	
7aat	8210	7511	7285	6671	4439	4577
	7165		6759		4592	
	7158		5969		4700	
9aaa	9126	9252	10005	10476	9480	10728
	8993		11677		10587	
	9639		9746		12119	
9aab	10458	11473	27269	28577	62359	61986
	12102		28671		61613	
	11860		29731			
9baa	16260	15509	32843	33320	72172	69265
	13321		35047		62799	
	16948		32071		72824	
Control	13593	14646	32206	32702	71334	70961
	14755		32657		69851	
	15590		33243		71699	

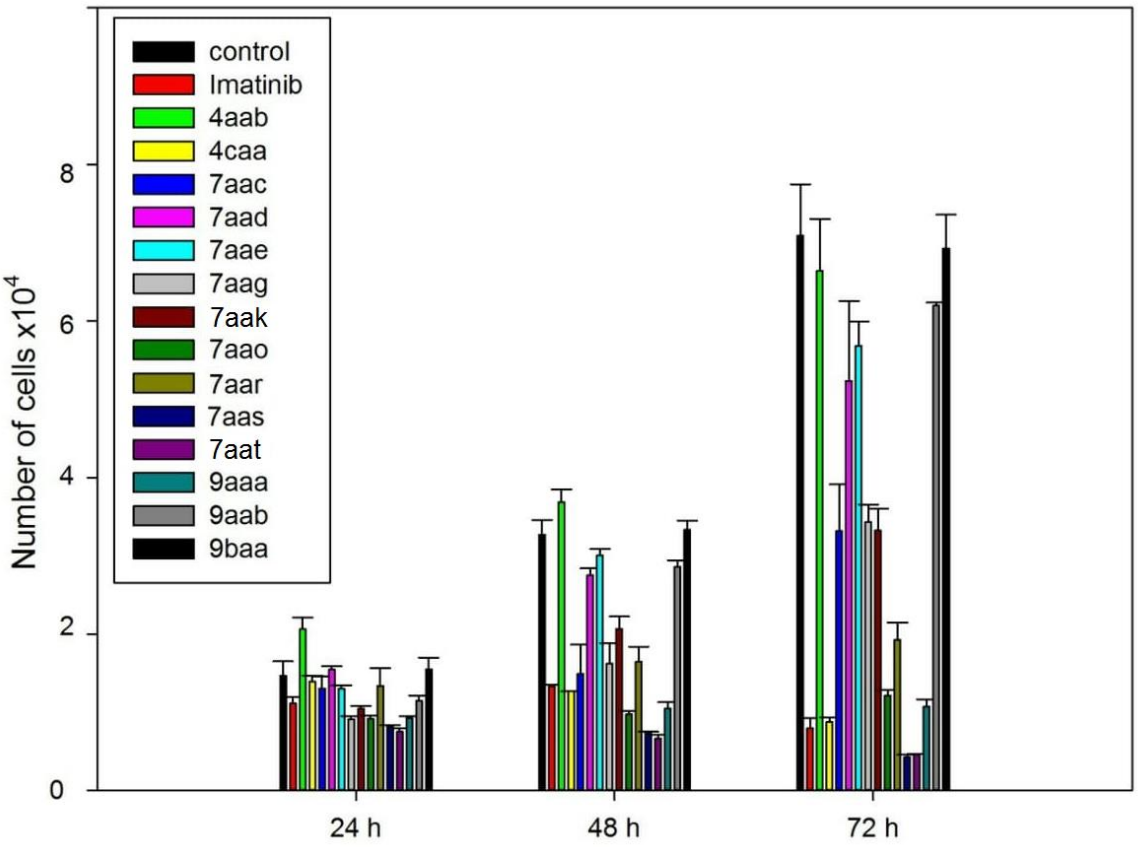


Figure S126. Cytotoxicity of selected compounds against human leukemia K562 cell line [at 25 μM for the tested compounds (10 μM for **7aar**) and 10 μM for Imatinib]

BECKMAN COULTER INC. 7aao 24h

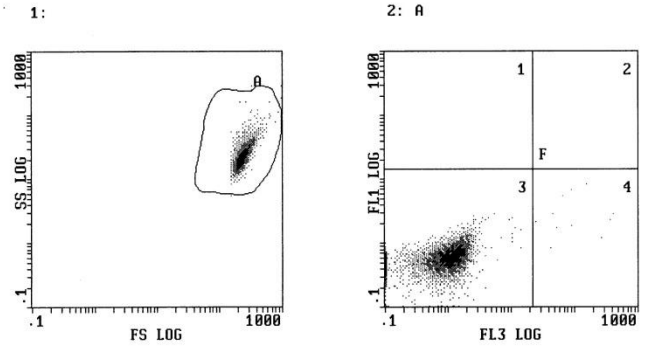
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

25Jan17 09:38:32
k562 cell cycle new custom
Z0006726
5 24h-1

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 9030 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.9	9023	241.8	23.2	226.0	19.6	155	22.72	41.65
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.00	0	****	****	****	****	**	**	**
	F3	F	99.6	8991	0.810	0.543	0.102	0.402	56	88.54	47.39
	F4	F	0.35	32	88.1	2.72	46.4	2.80	2	111.80	65.39

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Figure S127. Cytotoxicity of **7aao** against human leukemia K562 cell line, 24 h

BECKMAN COULTER INC.

7aao 48h

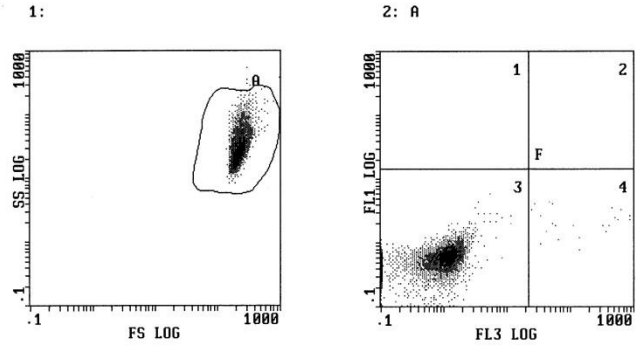
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

26Jan17 08:11:52
k562 cell cycle new custom
Z0006816
5 48h-1

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 9646 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.6	9611	230.2	33.2	226.0	21.0	99	21.99	60.13
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.00	0	****	****	****	****	**	**	**
	F3	F	99.4	9556	0.767	0.512	0.102	0.432	71	90.39	48.33
	F4	F	0.57	55	124.1	2.60	22.6	2.80	1	132.82	50.04

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Figure S128. Cytotoxicity of **7aao** against human leukemia K562 cell line, 48 h

BECKMAN COULTER INC.

7aao 72h

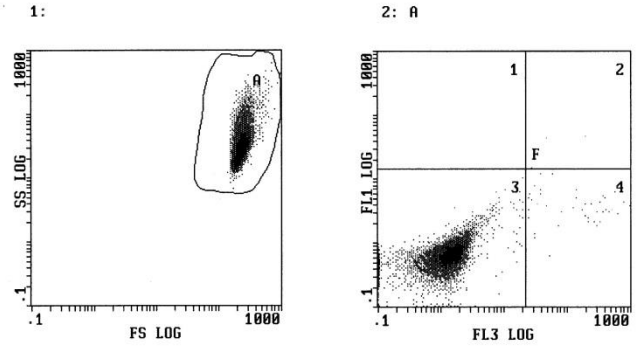
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

27Jan17 09:04:50
k562 cell cycle new custom
Z0006881
5 72h-2

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 12386 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	100	12383	241.1	38.8	226.0	26.1	97	24.73	70.93
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.06	7	101.4	45.0	28.0	14.7	1	78.36	56.44
	F3	F	98.9	12247	1.13	0.582	1.47	0.715	65	81.82	51.52
	F4	F	1.04	129	112.6	3.57	28.0	6.65	3	121.73	58.50

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Figure S129. Cytotoxicity of **7aao** against human leukemia K562 cell line, 72 h

BECKMAN COULTER INC. 7aas 24h

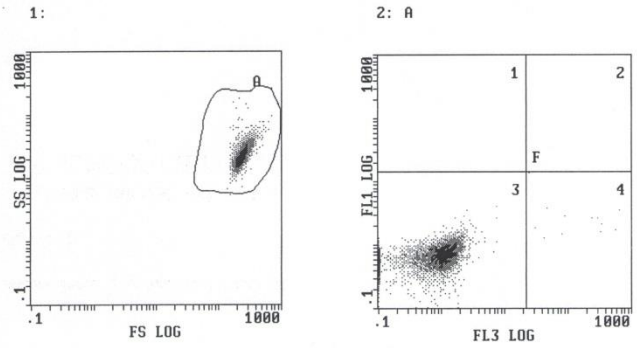
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

25Jan17 09:34:24
k562 cell cycle new custom
Z0006724
4 24h-2

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 8348 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.9	8337	244.8	22.8	210.3	16.9	154	22.08	37.76
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.00	0	****	****	****	****	**	**	**
	F3	F	99.5	8295	0.726	0.622	0.102	0.619	71	91.05	45.56
	F4	F	0.50	42	206.4	2.93	348.0	2.10	2	116.90	53.13

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Figure S130. Cytotoxicity of **7aas** against human leukemia K562 cell line, 24 h

BECKMAN COULTER INC. 7aas 48h

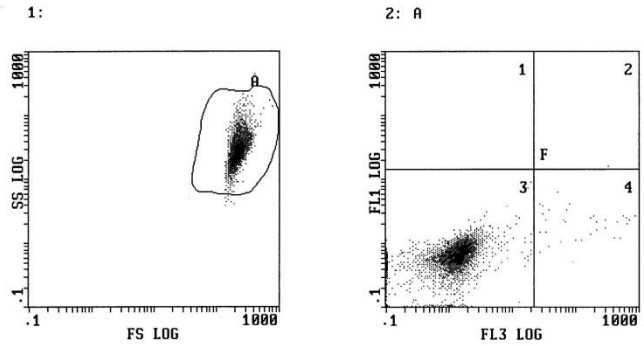
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

26Jan17 08:06:37
k562 cell cycle new custom
Z0006813
4 48h-1

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 7531 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.6	7498	226.5	28.7	195.7	19.6	85	22.48	54.66
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.01	1	323.8	15.8	323.8	15.8	1	0.00	0.00
	F3	F	98.7	7403	1.09	0.561	0.102	0.102	41	88.56	56.42
	F4	F	1.25	94	123.5	2.04	464.0	2.10	3	125.62	52.12

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Figure S131. Cytotoxicity of **7aas** against human leukemia K562 cell line, 48 h

BECKMAN COULTER INC. 7aas 72h

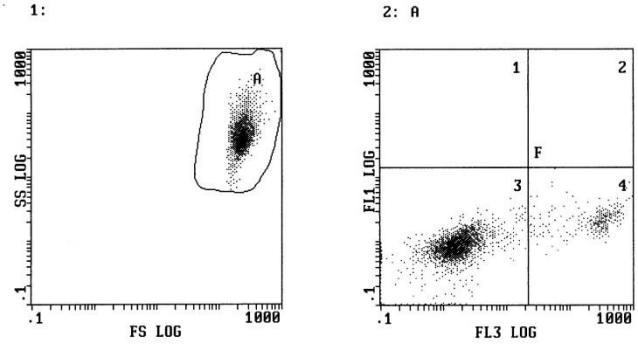
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

27Jan17 09:11:18
k562 cell cycle new custom
Z0006883
4 72h-1

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 5305 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	100	5303	238.0	45.5	242.8	37.4	44	26.26	60.59
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.02	1	32.4	22.6	32.4	22.6	1	0.00	0.00
	F3	F	83.2	4414	1.63	0.802	1.58	0.825	24	90.32	55.26
	F4	F	16.7	888	216.0	2.12	280.4	1.82	10	94.67	40.12

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Figure S132. Cytotoxicity of **7aas** against human leukemia K562 cell line, 72 h

BECKMAN COULTER INC. 7aat 24h

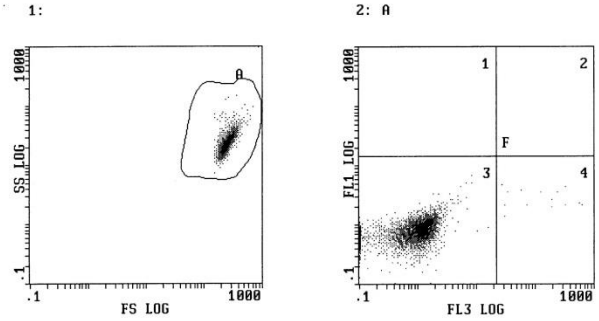
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

25Jan17 09:26:46
k562 cell cycle new custom
Z0006720
3 24h-1

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 7212 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.9	7206	254.9	23.4	260.9	22.6	131	22.72	38.37
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.01	1	66.5	24.3	66.5	24.3	1	0.00	0.00
	F3	F	99.4	7165	0.791	0.724	0.102	0.576	57	90.93	44.92
	F4	F	0.56	40	114.5	2.49	34.8	1.69	2	123.95	49.95

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Figure S133. Cytotoxicity of **7aat** against human leukemia K562 cell line, 24 h

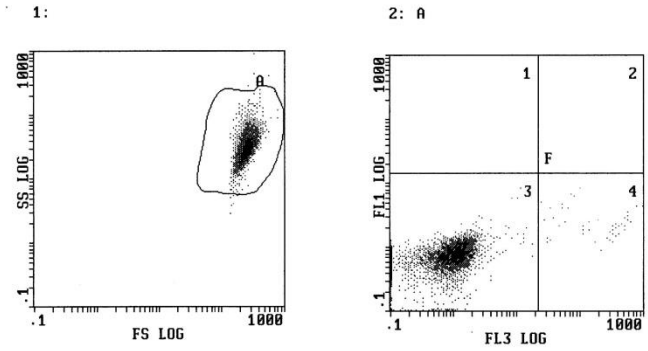
BECKMAN COULTER INC. 7aat 48h

COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

26Jan17 08:01:19
k562 cell cycle new custom
Z0006810
3 48h-1
Stop Time: 50 seconds, 6907 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.5	6875	249.3	30.7	260.9	28.0	86	24.12	52.53
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.01	1	210.3	16.9	210.3	16.9	1	0.00	0.00
	F3	F	98.3	6759	0.736	0.638	0.102	0.102	60	97.54	56.82
	F4	F	1.67	115	192.8	2.16	301.3	1.27	2	111.08	50.11

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Figure S134. Cytotoxicity of **7aat** against human leukemia K562 cell line, 48 h

BECKMAN COULTER INC. 7aat 72h

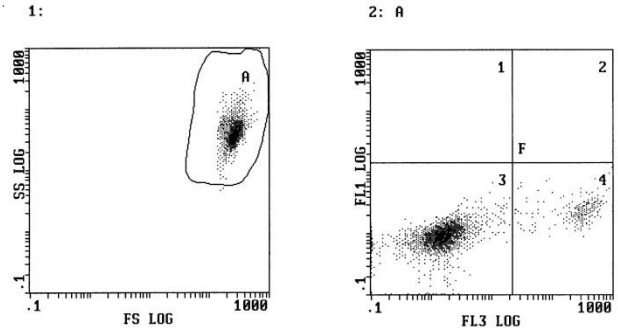
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

27Jan17 09:17:26
k562 cell cycle new custom
Z0006886
3 72h-1

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 5339 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.9	5333	254.0	41.6	260.9	30.1	63	26.11	49.80
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.00	0	****	****	****	****	**	**	**
	F3	F	86.1	4592	1.45	0.849	1.82	0.953	31	88.59	50.52
	F4	F	13.9	741	237.2	2.28	348.0	1.96	9	90.55	41.48

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Figure S135. Cytotoxicity of **7aat** against human leukemia K562 cell line, 72 h

BECKMAN COULTER INC. 9aaa 24h

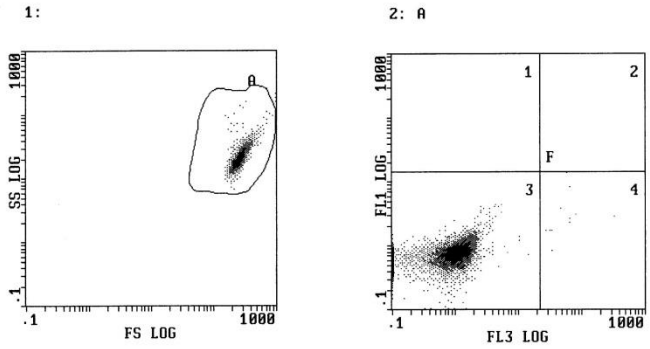
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

25Jan17 09:42:49
k562 cell cycle new custom
Z0006728
6 24h

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 9175 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.9	9164	266.2	20.7	260.9	19.6	183	23.81	36.78
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.00	0	****	****	****	****	**	**	**
	F3	F	99.6	9126	0.727	0.684	0.102	0.536	78	92.25	43.88
	F4	F	0.41	38	68.0	2.52	32.4	1.69	2	92.73	59.51

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Figure S136. Cytotoxicity of **9aaa** against human leukemia K562 cell line, 24 h

BECKMAN COULTER INC.

9aaa 48h

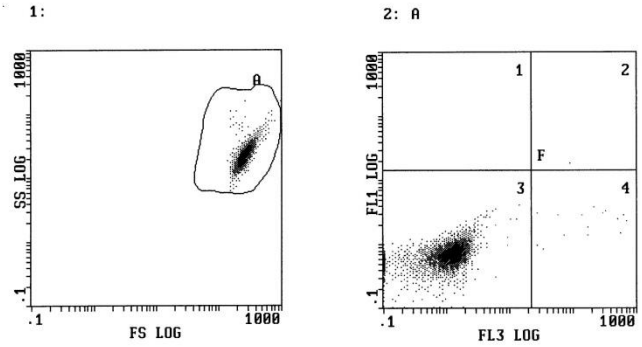
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

26Jan17 08:15:59
k562 cell cycle new custom
Z0006818
6 48h

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 10067 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	99.9	10059	261.4	21.7	242.8	19.6	179	24.00	37.51
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.01	1	88.7	18.2	88.7	18.2	1	0.00	0.00
	F3	F	99.5	10005	0.927	0.635	1.10	0.619	54	82.91	43.85
	F4	F	0.53	53	125.4	2.43	348.0	1.96	2	124.84	53.31

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Figure S137. Cytotoxicity of **9aaa** against human leukemia K562 cell line, 48 h

BECKMAN COULTER INC. 9aaa 72h

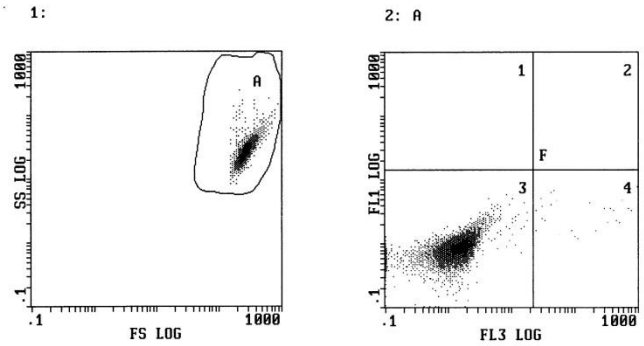
COULTER(R) EPICS(R) Acquisition Flow Cytometry Report

27Jan17 08:56:22
k562 cell cycle new custom
Z0006877
6 72h-1

OP ID: 0

Initial cytosett. from prot. k562 cell cycle new custom

Stop Time: 50 seconds, 10672 events



Stats: Not Normalized, Listgating: Disabled

Hist	Region	ID	%	Count	Mn X	Mn Y	PkPosX	PkPosY	PkCnt	FPCVX	FPCVY
1	A	A	100	10671	273.5	26.6	242.8	22.6	181	26.25	40.30
2	F1	F	0.00	0	****	****	****	****	**	**	**
	F2	F	0.00	0	****	****	****	****	**	**	**
	F3	F	99.2	10587	1.22	0.782	1.58	0.825	77	74.29	43.69
	F4	F	0.79	84	116.6	3.05	30.1	4.99	2	128.43	57.89

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Figure S138. Cytotoxicity of **9aaa** against human leukemia K562 cell line, 72 h

4. X-ray crystallographic data for compounds 4faa, 7aaq, 11baa, 12a and 12c

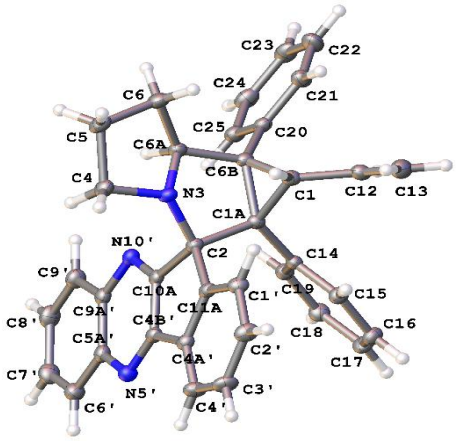

Figure S139. ORTEP representation of the molecular structure of **4faa** (CCDC 1556702). Thermal ellipsoids are drawn at 50% probability level.

Table S3. Crystal data and structure refinement for compound **4faa**

Empirical formula	$C_{36}H_{29}N_3$
Formula weight	503.62
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	16.4746(7)
b/Å	9.1306(3)
c/Å	19.2167(8)
α/°	90
β/°	113.764(5)
γ/°	90
Volume/Å^3	2645.56(19)
Z	4
ρ_{calc} g/cm^3	1.264
μ/mm-1	0.074
F(000)	1064.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.246 to 54.99
Index ranges	-21 ≤ h ≤ 21, -11 ≤ k ≤ 11, -24 ≤ l ≤ 13
Reflections collected	17160
Independent reflections	6077 [R_{int} = 0.0248, R_{sigma} = 0.0294]
Data/restraints/parameters	6077/0/352
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.0952
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.1024
Largest diff. peak/hole / e Å^{-3}	0.31/-0.22

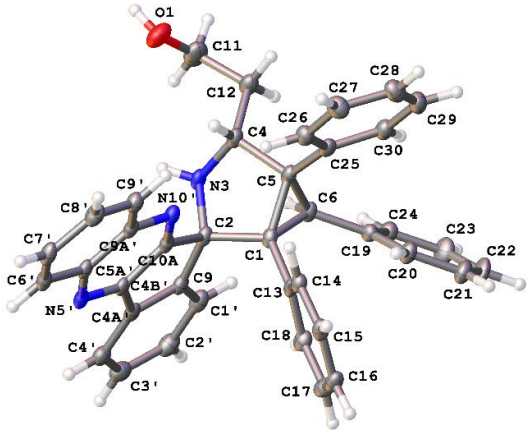

Figure S140. ORTEP representation of the molecular structure of **7aaq** MeOH solvate (CCDC 1556703). Thermal ellipsoids are drawn at 50% probability level.

Table S4. Crystal data and structure refinement for compound **7aaq**

Empirical formula	$C_{40.35}H_{35.05}N_3O_{1.68}$
Formula weight	588.76
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.0006(3)
b/Å	13.4106(7)
c/Å	13.9272(4)
α/°	73.859(4)
β/°	78.251(3)
γ/°	71.617(4)
Volume/Å^3	1519.94(12)
Z	2
ρ_{calc} g/cm^3	1.286
μ/mm^{-1}	0.616
F(000)	623.0
Crystal size/mm^3	0.25 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.662 to 139.972
Index ranges	$-10 \leq h \leq 10$, $-16 \leq k \leq 16$, $-12 \leq l \leq 16$
Reflections collected	10039
Independent reflections	5735 [R_{int} = 0.0334, R_{sigma} = 0.0426]
Data/restraints/parameters	5735/1/432
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0478, wR_2 = 0.1249
Final R indexes [all data]	R_1 = 0.0600, wR_2 = 0.1337
Largest diff. peak/hole / e Å^{-3}	0.53/-0.31

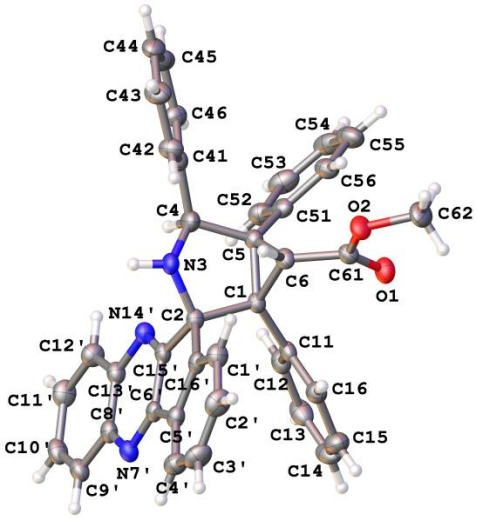

Figure S141. ORTEP representation of the molecular structure of **11baa** (CCDC 1582653). Thermal ellipsoids are drawn at 50% probability level.

Table S5. Crystal data and structure refinement for compound **11baa**

Empirical formula	$C_{39}H_{29}N_3O_2$
Formula weight	571.65
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.8591(3)
b/Å	17.6789(6)
c/Å	16.9614(6)
α/°	90
β/°	96.753(3)
γ/°	90
Volume/Å^3	2935.83(17)
Z	4
ρ_{calc} g/cm^3	1.293
μ/mm^{-1}	0.080
F(000)	1200.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.554 to 55
Index ranges	$-12 \le h \le 11$, $-22 \le k \le 21$, $-16 \le l \le 22$
Reflections collected	14357
Independent reflections	6716 [R_{int} = 0.0246, R_{sigma} = 0.0400]
Data/restraints/parameters	6716/0/438
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0520, wR_2 = 0.1152
Final R indexes [all data]	R_1 = 0.0712, wR_2 = 0.1249
Largest diff. peak/hole / e Å^{-3}	0.29/-0.23

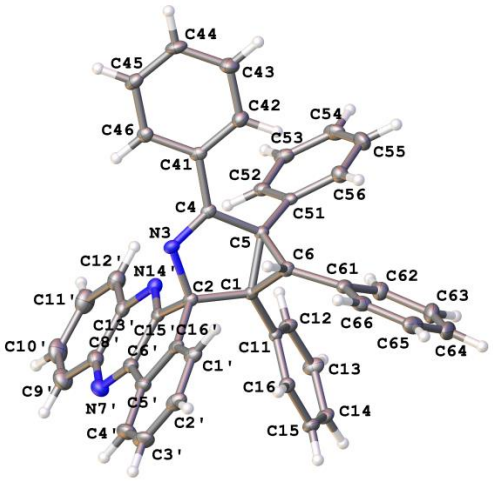

Figure S142. ORTEP representation of the molecular structure of **12a** (CCDC 1582655). Thermal ellipsoids are drawn at 50% probability level.

Table S6. Crystal data and structure refinement for compound **12a**

Empirical formula	$C_{43}H_{29}N_3$
Formula weight	587.69
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.7752(5)
b/Å	18.4617(8)
c/Å	18.0848(9)
α/°	90
β/°	102.389(5)
γ/°	90
Volume/Å^3	3187.7(3)
Z	4
ρ_{calc} g/cm^3	1.225
μ/mm^{-1}	0.072
F(000)	1232.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.712 to 55
Index ranges	$-12 \le h \le 12$, $-23 \le k \le 23$, $-23 \le l \le 23$
Reflections collected	21229
Independent reflections	7299 [R_{int} = 0.0287, R_{sigma} = 0.0339]
Data/restraints/parameters	7299/0/415
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0427, wR_2 = 0.0926
Final R indexes [all data]	R_1 = 0.0534, wR_2 = 0.0987
Largest diff. peak/hole / e Å^{-3}	0.33/-0.21

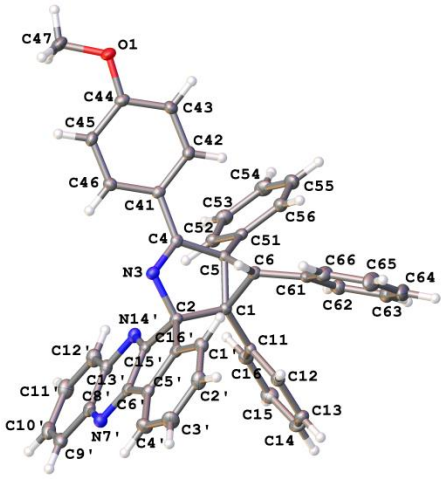

Figure S143. ORTEP representation of the molecular structure of **12c** (CCDC 1582654). Thermal ellipsoids are drawn at 50% probability level.

Table S7. Crystal data and structure refinement for compound **12c**

Empirical formula	$C_{44}H_{31}N_3O$
Formula weight	617.72
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.9057(3)
b/Å	18.2185(5)
c/Å	17.9256(5)
α/°	90
β/°	94.694(3)
γ/°	90
Volume/Å^3	3224.13(16)
Z	4
ρ_{calc} g/cm^3	1.273
μ/mm^{-1}	0.077
F(000)	1296.0
Crystal size/mm^3	0.2 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.894 to 54.996
Index ranges	$-12 \leq h \leq 12$, $-23 \leq k \leq 13$, $-18 \leq l \leq 23$
Reflections collected	15480
Independent reflections	7300 [R_{int} = 0.0252, R_{sigma} = 0.0391]
Data/restraints/parameters	7300/0/434
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.0951
Final R indexes [all data]	R_1 = 0.0596, wR_2 = 0.1036
Largest diff. peak/hole / e Å^{-3}	0.35/-0.23

5. Computational data

Table S8. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **Ox-1** lactone

Atom	X	Y	Z
C	-4.397571000000	0.585281000000	-0.317279000000
C	-4.507200000000	-0.804071000000	-0.442638000000
C	-3.365607000000	-1.599809000000	-0.543157000000
C	-2.124784000000	-0.970046000000	-0.536404000000
C	-2.010958000000	0.425730000000	-0.454406000000
C	-3.148494000000	1.213710000000	-0.317825000000
C	-0.775095000000	-1.563068000000	-0.520563000000
C	0.174399000000	-0.494041000000	-0.419313000000
C	-0.550053000000	0.852291000000	-0.491079000000
N	-0.438088000000	-2.818638000000	-0.532650000000
C	0.914225000000	-3.049553000000	-0.428495000000
C	1.852397000000	-1.987643000000	-0.303871000000
N	1.450660000000	-0.668495000000	-0.302121000000
C	1.380868000000	-4.387873000000	-0.431913000000
C	2.725600000000	-4.652902000000	-0.314824000000
C	3.658958000000	-3.593487000000	-0.188007000000
C	3.231611000000	-2.285825000000	-0.181427000000
N	-0.116472000000	1.571193000000	-1.674735000000
C	1.098920000000	2.273475000000	-1.221753000000
C	0.830522000000	2.488677000000	0.271008000000
O	-0.196587000000	1.683382000000	0.644972000000
C	-1.012616000000	2.649469000000	-2.142035000000
C	-0.055191000000	3.534438000000	-2.933381000000
C	1.191897000000	3.580871000000	-2.030119000000
O	1.375057000000	3.238500000000	1.035746000000
H	-5.304837000000	1.191776000000	-0.211844000000
H	-5.499197000000	-1.271015000000	-0.443059000000
H	-3.429852000000	-2.692397000000	-0.608361000000

H	-3.077750000000	2.300628000000	-0.199042000000
H	0.637094000000	-5.187384000000	-0.528302000000
H	3.081564000000	-5.689824000000	-0.317967000000
H	4.727265000000	-3.821099000000	-0.094382000000
H	3.930685000000	-1.446759000000	-0.085362000000
H	1.991376000000	1.630271000000	-1.306401000000
H	-1.847459000000	2.237059000000	-2.732697000000
H	-1.428339000000	3.231277000000	-1.288444000000
H	-0.475929000000	4.531035000000	-3.142105000000
H	0.185692000000	3.046581000000	-3.894155000000
H	2.129368000000	3.638015000000	-2.604251000000
H	1.165973000000	4.444197000000	-1.341941000000

Table S9. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **Ox-1** to **I-1**

Atom	X	Y	Z
C	1.772757000	-2.354930000	-0.385284000
C	0.810210000	-3.190948000	-0.958303000
C	-0.439018000	-2.687988000	-1.329077000
C	-0.693237000	-1.343095000	-1.104035000
C	0.264398000	-0.493148000	-0.515889000
C	1.514810000	-0.999445000	-0.160281000
C	-1.909474000	-0.567095000	-1.403263000
C	-1.682220000	0.794117000	-1.010904000
C	-0.287673000	0.886260000	-0.451505000
N	-3.027269000	-0.989171000	-1.913055000
C	-3.997900000	-0.025316000	-2.047827000
C	-3.778980000	1.319595000	-1.640355000
N	-2.577689000	1.724763000	-1.107712000
C	-5.251897000	-0.387390000	-2.598814000
C	-6.245021000	0.554653000	-2.732192000
C	-6.027497000	1.894607000	-2.322059000

C	-4.818059000	2.271727000	-1.786493000
N	0.120760000	1.872665000	0.313467000
C	-0.149901000	3.204100000	-0.217082000
C	0.275962000	3.100900000	-1.743534000
O	0.348807000	1.917522000	-2.192165000
C	1.395948000	1.899528000	1.048215000
C	1.363975000	3.286564000	1.685438000
C	0.716383000	4.169607000	0.604816000
O	0.486624000	4.166659000	-2.328971000
H	2.750603000	-2.765067000	-0.108456000
H	1.041488000	-4.249998000	-1.121371000
H	-1.204894000	-3.324971000	-1.786414000
H	2.297054000	-0.372541000	0.274727000
H	-5.393631000	-1.429962000	-2.906259000
H	-7.214404000	0.270583000	-3.158403000
H	-6.830469000	2.632196000	-2.434778000
H	-4.621312000	3.300473000	-1.462931000
H	-1.226682000	3.430247000	-0.209878000
H	1.441199000	1.068069000	1.769600000
H	2.230675000	1.813473000	0.322504000
H	2.370340000	3.624508000	1.977817000
H	0.731393000	3.256112000	2.589675000
H	0.122173000	4.987351000	1.041143000
H	1.469156000	4.619853000	-0.064313000

Table S10. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **I-1** pyrrolidinium carboxylate

Atom	X	Y	Z
C	-3.536576000	0.811851000	-2.786317000
C	-4.118231000	-0.297178000	-2.168727000
C	-3.406747000	-1.033662000	-1.217250000
C	-2.121928000	-0.622893000	-0.902691000

C	-1.527923000	0.509202000	-1.501660000
C	-2.240811000	1.227828000	-2.465061000
C	-1.155190000	-1.248029000	0.016819000
C	0.056812000	-0.482387000	-0.012814000
C	-0.165171000	0.675637000	-0.935994000
N	-1.307926000	-2.324428000	0.728285000
C	-0.202087000	-2.695296000	1.454079000
C	1.011795000	-1.953873000	1.399386000
N	1.126217000	-0.816117000	0.642036000
C	-0.269463000	-3.853922000	2.266703000
C	0.831376000	-4.255237000	2.986633000
C	2.043428000	-3.520043000	2.925635000
C	2.133933000	-2.390653000	2.147725000
N	0.691374000	1.603147000	-1.189289000
C	1.933489000	1.780062000	-0.446618000
C	1.547460000	2.333571000	1.016419000
O	0.391233000	2.084647000	1.398055000
C	0.438964000	2.773826000	-2.063575000
C	1.607657000	3.721723000	-1.774030000
C	2.714824000	2.793794000	-1.267195000
O	2.487714000	2.922416000	1.576317000
H	-4.101022000	1.369786000	-3.541800000
H	-5.136895000	-0.596924000	-2.440674000
H	-3.835994000	-1.917493000	-0.731821000
H	-1.823374000	2.089720000	-2.989104000
H	-1.215833000	-4.406059000	2.294269000
H	0.776264000	-5.152762000	3.613781000
H	2.910367000	-3.857162000	3.505471000
H	3.055082000	-1.799989000	2.083844000
H	2.427439000	0.810970000	-0.292718000
H	-0.542758000	3.203499000	-1.807059000

H	0.426931000	2.420756000	-3.110415000
H	1.883894000	4.299161000	-2.669364000
H	1.321420000	4.430915000	-0.977086000
H	3.244559000	2.305612000	-2.104790000
H	3.441862000	3.301105000	-0.616459000

Table S11. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **I-1** to **D-1**

Atom	X	Y	Z
C	-3.392189000	0.407158000	-2.348981000
C	-3.971525000	-0.719263000	-1.756863000
C	-3.241810000	-1.472928000	-0.837107000
C	-1.949873000	-1.068747000	-0.527447000
C	-1.353690000	0.079910000	-1.101926000
C	-2.092727000	0.816446000	-2.036874000
C	-0.978840000	-1.708923000	0.366905000
C	0.239765000	-0.931802000	0.334779000
C	0.014837000	0.210506000	-0.554369000
N	-1.127129000	-2.789518000	1.073483000
C	-0.020189000	-3.162415000	1.798878000
C	1.187625000	-2.412309000	1.757783000
N	1.307293000	-1.267857000	1.009650000
C	-0.087602000	-4.328377000	2.602145000
C	1.006419000	-4.733581000	3.330670000
C	2.213135000	-3.989555000	3.285160000
C	2.302500000	-2.853066000	2.516053000
N	0.918212000	1.139763000	-0.813207000
C	2.129168000	1.270495000	-0.197918000
C	1.537308000	2.103926000	1.584321000
O	0.480556000	1.616160000	1.857962000
C	0.662414000	2.291768000	-1.719407000
C	1.851049000	3.227398000	-1.478908000

C	2.943988000	2.306504000	-0.922131000
O	2.431123000	2.846713000	1.877794000
H	-3.965886000	0.987328000	-3.081506000
H	-4.993392000	-1.012381000	-2.023306000
H	-3.659651000	-2.370324000	-0.365410000
H	-1.689876000	1.694468000	-2.546141000
H	-1.032685000	-4.883993000	2.615759000
H	0.949463000	-5.636521000	3.949855000
H	3.078367000	-4.324520000	3.869311000
H	3.222597000	-2.258904000	2.465939000
H	2.541924000	0.364026000	0.254626000
H	-0.306334000	2.742298000	-1.454041000
H	0.618357000	1.899479000	-2.750989000
H	2.141170000	3.754692000	-2.400340000
H	1.580905000	3.979863000	-0.716952000
H	3.546389000	1.845160000	-1.728631000
H	3.623726000	2.824961000	-0.227542000

Table S12. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **D-1** azomethine ylide (S-shaped)

Atom	X	Y	Z
C	2.761479000	-0.194450000	-0.030349000
C	2.733290000	-1.615394000	-0.134261000
C	3.952039000	-2.336978000	-0.213260000
C	5.160539000	-1.680474000	-0.190557000
C	5.193038000	-0.265699000	-0.085903000
C	4.025529000	0.457208000	-0.007671000
N	1.624219000	0.560265000	0.049903000
C	0.491000000	-0.126166000	0.020354000
C	0.476000000	-1.585874000	-0.082605000
N	1.549969000	-2.315160000	-0.158452000
C	-0.859069000	0.318101000	0.067258000

C	-1.733598000	-0.846805000	0.024468000
C	-0.917403000	-2.012392000	-0.074747000
C	-3.129517000	-1.037433000	0.086005000
C	-3.649790000	-2.329596000	0.028536000
C	-2.829495000	-3.462453000	-0.084497000
C	-1.447679000	-3.299107000	-0.130790000
N	-1.217601000	1.658111000	0.128768000
C	-2.639121000	2.085616000	0.046665000
C	-2.553823000	3.600838000	-0.164267000
C	-1.145245000	3.976964000	0.328277000
C	-0.417007000	2.674285000	0.272678000
H	3.887523000	-3.429371000	-0.292615000
H	6.098142000	-2.245157000	-0.252758000
H	6.158698000	0.254315000	-0.067225000
H	4.031502000	1.551154000	0.073613000
H	-3.828443000	-0.203181000	0.190159000
H	-4.738557000	-2.458605000	0.077723000
H	-3.274384000	-4.463041000	-0.127707000
H	-0.769104000	-4.158490000	-0.206625000
H	-3.119096000	1.551353000	-0.786845000
H	-3.127811000	1.799472000	0.994451000
H	-3.353823000	4.130412000	0.373892000
H	-2.650528000	3.831276000	-1.238152000
H	-1.144251000	4.350177000	1.371502000
H	-0.654553000	4.747234000	-0.290292000
H	0.658596000	2.493237000	0.365458000

Table S13. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **Ox-2** lactone

Atom	X	Y	Z
C	-4.337623000	0.656510000	-0.412043000
C	-4.471600000	-0.727262000	-0.252259000

C	-3.342452000	-1.541971000	-0.168136000
C	-2.091389000	-0.935113000	-0.228010000
C	-1.950267000	0.452354000	-0.354359000
C	-3.076886000	1.259475000	-0.468382000
C	-0.753530000	-1.550832000	-0.255859000
C	0.221161000	-0.506017000	-0.387216000
C	-0.471087000	0.855035000	-0.345975000
N	-0.447661000	-2.815258000	-0.236835000
C	0.892733000	-3.084600000	-0.371245000
C	1.853229000	-2.049585000	-0.539850000
N	1.487890000	-0.722234000	-0.545392000
C	1.325002000	-4.434692000	-0.360450000
C	2.658324000	-4.734890000	-0.514237000
C	3.614736000	-3.701626000	-0.687245000
C	3.220690000	-2.384267000	-0.701221000
N	-0.136810000	1.678942000	0.804665000
C	-0.356540000	3.056193000	0.330802000
C	-0.109439000	2.947067000	-1.176397000
O	-0.134580000	1.636965000	-1.522350000
C	1.284086000	1.652946000	1.227329000
C	1.419666000	2.978191000	1.967262000
C	0.659869000	3.958178000	1.056761000
O	0.095776000	3.824003000	-1.971907000
H	-5.235548000	1.279566000	-0.500080000
H	-5.472034000	-1.173431000	-0.209235000
H	-3.423973000	-2.631198000	-0.071750000
H	-2.999745000	2.342925000	-0.616653000
H	0.564707000	-5.213356000	-0.229726000
H	2.988440000	-5.780389000	-0.505738000
H	4.673245000	-3.958749000	-0.810545000
H	3.936529000	-1.564296000	-0.831784000

H	-1.399419000	3.385230000	0.488233000
H	1.484609000	0.766473000	1.851554000
H	1.967181000	1.623914000	0.351505000
H	2.470888000	3.265802000	2.129073000
H	0.921072000	2.904729000	2.949878000
H	0.160958000	4.762777000	1.618223000
H	1.328692000	4.429989000	0.315493000

Table S14. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **Ox-2** to **I-2**

Atom	X	Y	Z
C	-4.326884000	0.636725000	-0.080358000
C	-4.462398000	-0.700016000	-0.465678000
C	-3.334630000	-1.511062000	-0.602266000
C	-2.090179000	-0.948003000	-0.355773000
C	-1.939413000	0.403071000	0.008576000
C	-3.071056000	1.201654000	0.160200000
C	-0.767234000	-1.596019000	-0.371312000
C	0.211132000	-0.626211000	0.027460000
C	-0.482483000	0.686468000	0.212074000
N	-0.473475000	-2.827838000	-0.662798000
C	0.860594000	-3.140708000	-0.554914000
C	1.829268000	-2.178110000	-0.154922000
N	1.478002000	-0.882532000	0.138153000
C	1.279521000	-4.462201000	-0.845865000
C	2.607638000	-4.804565000	-0.738445000
C	3.572110000	-3.844510000	-0.338875000
C	3.191583000	-2.554586000	-0.052610000
N	0.056874000	1.737810000	0.786396000
C	-0.373190000	3.025950000	0.253760000
C	-0.357137000	2.818791000	-1.324534000
O	-0.311696000	1.611077000	-1.698928000

C	1.490793000	1.830227000	1.135477000
C	1.594125000	3.256441000	1.664337000
C	0.661229000	4.054827000	0.739730000
O	-0.386782000	3.847400000	-2.005927000
H	-5.221345000	1.259364000	0.037493000
H	-5.460164000	-1.113534000	-0.652466000
H	-3.413602000	-2.567327000	-0.884788000
H	-3.014396000	2.249000000	0.466349000
H	0.514864000	-5.185330000	-1.152401000
H	2.927248000	-5.828838000	-0.963768000
H	4.625698000	-4.136457000	-0.259803000
H	3.912877000	-1.789672000	0.257912000
H	-1.398793000	3.291513000	0.548045000
H	1.759252000	1.043922000	1.856138000
H	2.089264000	1.683229000	0.214468000
H	2.632835000	3.622130000	1.651773000
H	1.227022000	3.289245000	2.705337000
H	0.186133000	4.902130000	1.257553000
H	1.195697000	4.454039000	-0.138900000

Table S15. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **I-2** pyrrolidinium carboxylate

Atom	X	Y	Z
C	-4.091344000	0.719807000	-0.400888000
C	-4.273874000	-0.664492000	-0.453747000
C	-3.179305000	-1.527365000	-0.357393000
C	-1.923783000	-0.968424000	-0.180650000
C	-1.728900000	0.426694000	-0.089804000
C	-2.822664000	1.282249000	-0.234984000
C	-0.620057000	-1.649461000	-0.099130000
C	0.396562000	-0.650022000	0.061178000
C	-0.282549000	0.680740000	0.141365000

N	-0.367252000	-2.921671000	-0.164620000
C	0.965103000	-3.248871000	-0.078507000
C	1.973778000	-2.256380000	0.075797000
N	1.663193000	-0.921076000	0.152574000
C	1.341592000	-4.612036000	-0.146533000
C	2.668945000	-4.964953000	-0.064764000
C	3.673498000	-3.975026000	0.088486000
C	3.333887000	-2.644487000	0.157786000
N	0.310258000	1.761359000	0.516155000
C	-0.321634000	3.068564000	0.700588000
C	-0.444173000	3.769375000	-0.737519000
O	-0.812242000	2.999227000	-1.644148000
C	1.772088000	1.857811000	0.795520000
C	1.992176000	3.337580000	1.110749000
C	0.630914000	3.798202000	1.634627000
O	-0.182156000	4.982247000	-0.751305000
H	-4.956219000	1.383840000	-0.511510000
H	-5.280955000	-1.074460000	-0.592381000
H	-3.293039000	-2.615386000	-0.425456000
H	-2.697902000	2.365252000	-0.280677000
H	0.547116000	-5.357499000	-0.265624000
H	2.957117000	-6.021432000	-0.118465000
H	4.725200000	-4.277188000	0.152145000
H	4.086399000	-1.856521000	0.276488000
H	-1.336458000	2.927272000	1.106764000
H	1.987929000	1.198727000	1.654559000
H	2.329538000	1.477224000	-0.072696000
H	2.232103000	3.892331000	0.186821000
H	2.816393000	3.472702000	1.827923000
H	0.476327000	3.487206000	2.683499000
H	0.477003000	4.881921000	1.534790000

Table S16. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **I-2** to **D-2**

Atom	X	Y	Z
C	-4.258637000	0.660294000	-0.472371000
C	-4.423218000	-0.713348000	-0.674253000
C	-3.313353000	-1.557963000	-0.637009000
C	-2.068360000	-1.001829000	-0.375383000
C	-1.885009000	0.382425000	-0.140869000
C	-3.004474000	1.221621000	-0.216532000
C	-0.764727000	-1.668412000	-0.312092000
C	0.239233000	-0.666928000	-0.027414000
C	-0.449455000	0.627540000	0.105886000
N	-0.499156000	-2.931372000	-0.473315000
C	0.827672000	-3.264271000	-0.353497000
C	1.818460000	-2.286311000	-0.065403000
N	1.505199000	-0.961568000	0.102288000
C	1.213566000	-4.618390000	-0.517909000
C	2.534706000	-4.982199000	-0.398274000
C	3.523805000	-4.007233000	-0.108037000
C	3.173935000	-2.687107000	0.054761000
N	0.130370000	1.742925000	0.518252000
C	-0.447026000	2.963200000	0.698766000
C	-0.538696000	3.632953000	-1.282804000
O	-0.834099000	2.670308000	-1.923656000
C	1.601900000	1.824972000	0.768085000
C	1.862547000	3.321192000	0.937568000
C	0.515009000	3.876061000	1.410473000
O	-0.288667000	4.798685000	-1.209603000
H	-5.131229000	1.322043000	-0.527311000
H	-5.420430000	-1.121241000	-0.875591000
H	-3.402513000	-2.636825000	-0.812400000

H	-2.934391000	2.306937000	-0.120093000
H	0.426920000	-5.349157000	-0.740258000
H	2.828864000	-6.030564000	-0.526476000
H	4.572851000	-4.311845000	-0.014108000
H	3.917534000	-1.913098000	0.278839000
H	-1.519657000	2.977598000	0.908202000
H	1.804961000	1.238701000	1.681495000
H	2.136546000	1.350942000	-0.065502000
H	2.121404000	3.768513000	-0.038882000
H	2.690862000	3.508904000	1.637913000
H	0.399314000	3.796471000	2.509131000
H	0.356348000	4.924879000	1.113281000

Table S17. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **D-2** azomethine ylide (W-shaped)

Atom	X	Y	Z
C	2.748933000	-0.185588000	-0.175497000
C	2.734466000	-1.604806000	-0.043717000
C	3.960922000	-2.315609000	0.033092000
C	5.162634000	-1.650037000	-0.018329000
C	5.182310000	-0.236062000	-0.151394000
C	4.008771000	0.475528000	-0.227964000
N	1.608278000	0.559408000	-0.253831000
C	0.479711000	-0.128116000	-0.189948000
C	0.476635000	-1.587610000	-0.062519000
N	1.558018000	-2.309238000	0.009177000
C	-0.882640000	0.296440000	-0.247088000
C	-1.737083000	-0.871755000	-0.146210000
C	-0.911536000	-2.027968000	-0.031922000
C	-3.133232000	-1.051189000	-0.084542000
C	-3.649595000	-2.337915000	0.066668000
C	-2.821817000	-3.467589000	0.154967000

C	-1.438158000	-3.308773000	0.111347000
N	-1.292588000	1.611282000	-0.406486000
C	-0.352789000	2.736270000	-0.122919000
C	-1.277263000	3.950543000	-0.020282000
C	-2.520900000	3.546748000	-0.831028000
C	-2.445224000	2.054292000	-0.809207000
H	3.906441000	-3.406755000	0.134601000
H	6.105830000	-2.205549000	0.042403000
H	6.143686000	0.290530000	-0.193304000
H	4.002490000	1.567603000	-0.330924000
H	-3.832664000	-0.210590000	-0.126677000
H	-4.738388000	-2.465721000	0.117617000
H	-3.263532000	-4.464427000	0.265224000
H	-0.759118000	-4.167151000	0.193521000
H	0.214943000	2.501933000	0.788910000
H	0.358607000	2.784213000	-0.963666000
H	-0.794248000	4.863566000	-0.399465000
H	-1.556353000	4.118687000	1.033638000
H	-2.477061000	3.896130000	-1.881546000
H	-3.467797000	3.917780000	-0.404295000
H	-3.216908000	1.364919000	-1.159058000

Table S18. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **D-1** to **D-2**

Atom	X	Y	Z
C	2.692001000	-0.185048000	0.210059000
C	2.695664000	-1.612574000	0.134943000
C	3.923104000	-2.317618000	0.254386000
C	5.108905000	-1.648260000	0.441987000
C	5.111076000	-0.229315000	0.519522000
C	3.938948000	0.478669000	0.407470000
N	1.558148000	0.560050000	0.100637000

C	0.449198000	-0.147287000	-0.086916000
C	0.453402000	-1.619638000	-0.147493000
N	1.540244000	-2.331976000	-0.043709000
C	-0.883557000	0.269777000	-0.249508000
C	-1.735595000	-0.876751000	-0.370941000
C	-0.925139000	-2.052758000	-0.324715000
C	-3.130063000	-1.013871000	-0.524263000
C	-3.671034000	-2.290682000	-0.627786000
C	-2.865652000	-3.447157000	-0.585967000
C	-1.487209000	-3.326144000	-0.433718000
N	-1.301389000	1.628687000	-0.141502000
C	-1.526262000	2.267891000	1.181862000
C	-2.129654000	3.631801000	0.822060000
C	-1.742422000	3.839549000	-0.657540000
C	-1.402188000	2.463383000	-1.110040000
H	3.880914000	-3.412492000	0.191141000
H	6.050358000	-2.202647000	0.532849000
H	6.058191000	0.303508000	0.670309000
H	3.920368000	1.574277000	0.463994000
H	-3.778587000	-0.129081000	-0.563097000
H	-4.756981000	-2.401080000	-0.746575000
H	-3.328062000	-4.437090000	-0.672679000
H	-0.839536000	-4.211839000	-0.395566000
H	-2.181967000	1.613921000	1.777850000
H	-0.536877000	2.325616000	1.670673000
H	-1.752519000	4.435149000	1.471698000
H	-3.227040000	3.595454000	0.919417000
H	-0.836115000	4.462726000	-0.788602000
H	-2.533810000	4.285302000	-1.282122000
H	-1.207196000	2.131735000	-2.137986000

Table S19. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **D-1** to **4gaa** (**TS_1**-*endo*)

Atom	X	Y	Z
C	2.520346000	-0.512778000	0.074966000
C	2.348728000	-1.900987000	-0.184600000
C	3.481239000	-2.754131000	-0.197353000
C	4.739795000	-2.252014000	0.041976000
C	4.913335000	-0.868365000	0.300520000
C	3.830545000	-0.019255000	0.314457000
N	1.464327000	0.360979000	0.126313000
C	0.283944000	-0.179031000	-0.082224000
C	0.119125000	-1.603296000	-0.349406000
N	1.106475000	-2.447097000	-0.404437000
C	-1.029822000	0.419776000	-0.076246000
C	-2.000601000	-0.631121000	-0.376326000
C	-1.309320000	-1.860572000	-0.521881000
C	-3.404375000	-0.639195000	-0.440997000
C	-4.064406000	-1.848088000	-0.658924000
C	-3.365488000	-3.056087000	-0.809663000
C	-1.974750000	-3.064704000	-0.736991000
N	-1.256409000	1.766606000	-0.033692000
C	-2.492631000	2.440063000	-0.507543000
C	-2.086218000	3.917624000	-0.512868000
C	-0.987417000	4.006754000	0.562359000
C	-0.428250000	2.610015000	0.582161000
H	3.309915000	-3.819000000	-0.397404000
H	5.610562000	-2.918052000	0.034173000
H	5.918983000	-0.474250000	0.490951000
H	3.945006000	1.054564000	0.509798000
H	-3.994930000	0.273860000	-0.316689000
H	-5.160425000	-1.851691000	-0.708767000

H	-3.916623000	-3.988566000	-0.977413000
H	-1.399267000	-3.994211000	-0.832517000
H	-2.756322000	2.042345000	-1.501455000
H	-3.328329000	2.247681000	0.185218000
H	-2.944636000	4.577977000	-0.314846000
H	-1.664716000	4.181195000	-1.498140000
H	-1.409080000	4.243360000	1.560269000
H	-0.220020000	4.765024000	0.337324000
H	0.626394000	2.338491000	0.663322000
C	-0.804263000	0.407276000	2.482827000
C	-1.979914000	1.274502000	2.787047000
C	-0.545818000	1.720525000	2.647024000
H	-2.446700000	1.204387000	3.785848000
H	-2.689931000	1.527704000	1.981558000
C	-0.337409000	-0.949226000	2.703436000
C	-1.240394000	-2.023062000	2.656343000
C	1.025342000	-1.210256000	2.933261000
C	-0.787880000	-3.331010000	2.828350000
C	1.473392000	-2.516562000	3.101261000
C	0.568814000	-3.581569000	3.043259000
H	-2.302152000	-1.817140000	2.462313000
H	1.731606000	-0.371761000	2.973747000
H	-1.500155000	-4.164288000	2.781502000
H	2.540485000	-2.709211000	3.270390000
H	0.924041000	-4.611578000	3.169831000
C	0.382090000	2.638407000	3.310625000
C	-0.101539000	3.641514000	4.162061000
C	1.764908000	2.542808000	3.082598000
C	0.783324000	4.515785000	4.794572000
C	2.644616000	3.419702000	3.713291000
C	2.157503000	4.407850000	4.573913000

H	-1.183645000	3.725084000	4.329181000
H	2.137168000	1.778020000	2.385548000
H	0.394192000	5.292674000	5.464235000
H	3.722685000	3.334554000	3.528654000
H	2.851241000	5.098381000	5.068539000

Table S20. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **4gaa** cycloadduct

Atom	X	Y	Z
C	2.702428000	-0.569154000	-0.178022000
C	2.512094000	-1.882859000	-0.688422000
C	3.643747000	-2.650447000	-1.065716000
C	4.909637000	-2.127033000	-0.944536000
C	5.098109000	-0.815069000	-0.440435000
C	4.017183000	-0.052057000	-0.063720000
N	1.640322000	0.214202000	0.217693000
C	0.475460000	-0.337690000	0.078128000
C	0.283646000	-1.654349000	-0.460437000
N	1.259486000	-2.431199000	-0.834651000
C	-0.865025000	0.297977000	0.445813000
C	-1.842733000	-0.787361000	-0.003192000
C	-1.164815000	-1.915768000	-0.494394000
C	-3.231774000	-0.821059000	0.111720000
C	-3.916455000	-1.968125000	-0.300616000
C	-3.231345000	-3.078874000	-0.807629000
C	-1.840595000	-3.063674000	-0.901638000
N	-0.963871000	1.611436000	-0.173877000
C	-2.147666000	2.092799000	-0.884113000
C	-1.890100000	3.601335000	-0.927508000
C	-1.309296000	3.882382000	0.467268000
C	-0.464024000	2.631785000	0.764505000
H	3.467155000	-3.660344000	-1.454403000

H	5.780476000	-2.724119000	-1.239574000
H	6.112798000	-0.409764000	-0.350864000
H	4.136378000	0.964754000	0.329543000
H	-3.789990000	0.025014000	0.528544000
H	-5.009589000	-1.999517000	-0.217992000
H	-3.792559000	-3.966839000	-1.121481000
H	-1.280111000	-3.927726000	-1.278604000
H	-2.221179000	1.638184000	-1.889320000
H	-3.106919000	1.892038000	-0.358159000
H	-2.802127000	4.181069000	-1.146547000
H	-1.138520000	3.825251000	-1.706545000
H	-2.129477000	3.958808000	1.206363000
H	-0.721762000	4.813773000	0.515603000
H	0.612968000	2.820273000	0.586034000
C	-0.910948000	0.547620000	1.974529000
C	-1.997779000	1.489790000	2.428253000
C	-0.612510000	2.023664000	2.170827000
H	-2.315326000	1.371486000	3.470994000
H	-2.795530000	1.780004000	1.734406000
C	-0.496224000	-0.575639000	2.878081000
C	-1.482317000	-1.433588000	3.382686000
C	0.846063000	-0.835335000	3.185401000
C	-1.139528000	-2.528585000	4.175828000
C	1.190734000	-1.927244000	3.983599000
C	0.200304000	-2.777466000	4.478434000
H	-2.535427000	-1.231447000	3.143109000
H	1.625412000	-0.171641000	2.793583000
H	-1.923909000	-3.191586000	4.560955000
H	2.245013000	-2.115353000	4.220959000
H	0.473779000	-3.636632000	5.103038000
C	0.261136000	2.555609000	3.262215000

C	-0.272518000	3.100024000	4.433689000
C	1.655068000	2.534967000	3.098825000
C	0.566478000	3.606949000	5.429570000
C	2.493196000	3.040925000	4.090382000
C	1.950415000	3.578870000	5.260941000
H	-1.361378000	3.134297000	4.566442000
H	2.074807000	2.094802000	2.182471000
H	0.132284000	4.030456000	6.343539000
H	3.581094000	3.012412000	3.951597000
H	2.609690000	3.976074000	6.042363000

Table S21. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **D-1** to **4gaa'** (**TS$_2$**-*exo*)

Atom	X	Y	Z
C	2.120401000	-0.715195000	0.299704000
C	1.811455000	-2.100425000	0.406942000
C	2.856259000	-3.036549000	0.616927000
C	4.162745000	-2.618229000	0.714666000
C	4.474733000	-1.238819000	0.600969000
C	3.479371000	-0.311394000	0.397412000
N	1.155917000	0.239719000	0.109757000
C	-0.078632000	-0.217129000	0.054123000
C	-0.377182000	-1.642480000	0.111612000
N	0.522666000	-2.563364000	0.289472000
C	-1.329890000	0.483295000	-0.131878000
C	-2.382767000	-0.523412000	-0.307990000
C	-1.812271000	-1.807135000	-0.104779000
C	-3.762999000	-0.450960000	-0.563749000
C	-4.513404000	-1.626748000	-0.602633000
C	-3.934109000	-2.883185000	-0.383233000
C	-2.566739000	-2.975281000	-0.132769000
N	-1.447313000	1.834534000	-0.247270000

C	-2.703359000	2.497881000	-0.643760000
C	-2.372939000	3.999593000	-0.631223000
C	-0.960579000	4.112498000	-0.013425000
C	-0.586349000	2.694353000	0.308607000
H	2.578696000	-4.095048000	0.693886000
H	4.965295000	-3.347063000	0.877549000
H	5.518646000	-0.911003000	0.677151000
H	3.699877000	0.759423000	0.307440000
H	-4.276765000	0.496919000	-0.740926000
H	-5.588869000	-1.558305000	-0.808603000
H	-4.554089000	-3.786624000	-0.414745000
H	-2.076042000	-3.941241000	0.040772000
H	-3.014632000	2.119724000	-1.631655000
H	-3.481859000	2.234821000	0.094928000
H	-3.119146000	4.552115000	-0.038597000
H	-2.389932000	4.406249000	-1.654562000
H	-0.941552000	4.743066000	0.892278000
H	-0.230342000	4.540551000	-0.723489000
H	0.440822000	2.355133000	0.467892000
C	-1.099336000	0.854431000	2.486147000
C	-1.009222000	2.206147000	2.434984000
C	0.222212000	1.438668000	2.864214000
C	-1.861815000	-0.325047000	2.839355000
C	-3.265351000	-0.373407000	2.762665000
C	-1.165434000	-1.476095000	3.245438000
C	-3.948362000	-1.536526000	3.101576000
C	-1.853026000	-2.639087000	3.588531000
C	-3.246505000	-2.673166000	3.517072000
H	-3.818383000	0.510868000	2.421046000
H	-0.067410000	-1.442226000	3.281993000
H	-5.043157000	-1.562710000	3.033413000

H	-1.295471000	-3.528843000	3.906205000
H	-3.789902000	-3.588707000	3.780682000
H	0.503362000	1.415017000	3.933820000
H	1.077546000	1.377514000	2.169265000
C	-1.698123000	3.399471000	2.937992000
C	-3.081979000	3.581154000	2.790382000
C	-0.948604000	4.402820000	3.570201000
C	-3.698087000	4.739698000	3.261169000
C	-1.567648000	5.557738000	4.047952000
C	-2.943663000	5.732801000	3.890637000
H	-3.684103000	2.803424000	2.303844000
H	0.134799000	4.263764000	3.681965000
H	-4.780720000	4.867046000	3.138071000
H	-0.968418000	6.331591000	4.543437000
H	-3.430274000	6.643456000	4.259996000

Table S22. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **4gaa'** cycloadduct

Atom	X	Y	Z
C	2.280576000	-1.313428000	0.681717000
C	1.757230000	-2.565453000	0.258001000
C	2.626985000	-3.681480000	0.154571000
C	3.961779000	-3.551112000	0.459028000
C	4.484158000	-2.300843000	0.878819000
C	3.660706000	-1.204435000	0.987727000
N	1.483141000	-0.198343000	0.803056000
C	0.233453000	-0.380782000	0.504083000
C	-0.286999000	-1.642127000	0.059414000
N	0.431548000	-2.722362000	-0.064321000
C	-0.876798000	0.676226000	0.574711000
C	-2.071243000	-0.128861000	0.018923000
C	-1.716296000	-1.462855000	-0.234357000

C	-3.393157000	0.262869000	-0.180143000
C	-4.323584000	-0.672642000	-0.640686000
C	-3.952165000	-1.998380000	-0.893860000
C	-2.635954000	-2.406200000	-0.686780000
N	-0.465107000	1.909005000	-0.096496000
C	-0.746137000	2.040046000	-1.522840000
C	-2.063868000	2.847089000	-1.645845000
C	-2.263498000	3.514338000	-0.264285000
C	-1.024091000	3.091536000	0.572304000
H	2.196537000	-4.634685000	-0.174685000
H	4.629584000	-4.416859000	0.376779000
H	5.550534000	-2.211784000	1.117525000
H	4.036366000	-0.225952000	1.309491000
H	-3.719540000	1.285344000	0.037779000
H	-5.363537000	-0.362164000	-0.798478000
H	-4.700591000	-2.715383000	-1.251183000
H	-2.316790000	-3.439316000	-0.870056000
H	0.084272000	2.588789000	-2.005972000
H	-0.802524000	1.042459000	-1.994767000
H	-2.910022000	2.184481000	-1.895215000
H	-1.992123000	3.596563000	-2.451870000
H	-3.197226000	3.189272000	0.230946000
H	-2.327527000	4.610358000	-0.363872000
H	-0.269971000	3.905221000	0.528934000
C	-1.115753000	1.124968000	2.035680000
C	-1.222920000	2.653336000	2.022902000
C	0.010530000	1.958985000	2.575223000
C	-1.852850000	0.165531000	2.920407000
C	-3.248175000	0.181633000	3.035661000
C	-1.125030000	-0.812017000	3.607788000
C	-3.903145000	-0.764014000	3.822747000

C	-1.778666000	-1.764159000	4.392602000
C	-3.169499000	-1.741512000	4.500384000
H	-3.820671000	0.959330000	2.513368000
H	-0.028794000	-0.817711000	3.524574000
H	-4.996111000	-0.737001000	3.911415000
H	-1.197069000	-2.526707000	4.924842000
H	-3.685702000	-2.486042000	5.118776000
H	0.120918000	1.974542000	3.666635000
H	0.934701000	2.009782000	1.990660000
C	-2.045357000	3.477110000	2.967828000
C	-2.341390000	3.031016000	4.266813000
C	-2.466417000	4.765403000	2.608130000
C	-3.066341000	3.826453000	5.152312000
C	-3.187074000	5.565880000	3.496510000
C	-3.501394000	5.097408000	4.770448000
H	-1.997322000	2.045093000	4.600008000
H	-2.212925000	5.168309000	1.622676000
H	-3.288885000	3.447591000	6.157528000
H	-3.500131000	6.569790000	3.184612000
H	-4.070997000	5.722449000	5.468629000

Table S23. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **D**-**2** to **4gaa''** (**TS**$_{3}$-*exo*)

Atom	X	Y	Z
C	2.732014000	0.237834000	0.941144000
C	2.681537000	-1.146820000	1.272481000
C	3.858824000	-1.800471000	1.722251000
C	5.042038000	-1.110561000	1.837423000
C	5.095486000	0.269173000	1.506459000
C	3.969503000	0.926358000	1.070171000

N	1.632694000	0.925609000	0.504039000
C	0.527555000	0.216413000	0.410055000
C	0.490620000	-1.203446000	0.737019000
N	1.523138000	-1.872858000	1.163211000
C	-0.777471000	0.582991000	-0.088740000
C	-1.634830000	-0.599979000	-0.002128000
C	-0.863010000	-1.688071000	0.481994000
C	-2.991031000	-0.822106000	-0.286663000
C	-3.524385000	-2.099266000	-0.099576000
C	-2.742131000	-3.169083000	0.357296000
C	-1.396568000	-2.961189000	0.655305000
N	-1.157644000	1.854329000	-0.422544000
C	-0.543240000	3.091063000	0.134549000
C	-0.907717000	4.153857000	-0.904542000
C	-2.210818000	3.620091000	-1.524048000
C	-2.029256000	2.136982000	-1.385751000
H	3.782373000	-2.866623000	1.968653000
H	5.947563000	-1.622438000	2.183967000
H	6.043626000	0.812367000	1.600019000
H	3.988546000	1.991485000	0.809041000
H	-3.653345000	-0.019616000	-0.628728000
H	-4.586645000	-2.265562000	-0.318598000
H	-3.190853000	-4.161222000	0.482739000
H	-0.755985000	-3.773225000	1.022569000
H	-1.026550000	3.281443000	1.110968000
H	0.533444000	2.933997000	0.291136000
H	-0.123482000	4.204814000	-1.681015000
H	-1.017128000	5.151387000	-0.452503000
H	-2.359121000	3.913667000	-2.577377000
H	-3.104300000	3.944575000	-0.955320000
H	-2.772712000	1.400361000	-1.693224000

C	0.610955000	1.464502000	-2.711203000
C	-0.199206000	0.220711000	-2.594404000
C	-0.838378000	1.298642000	-3.097255000
H	0.857745000	2.024778000	-1.791113000
H	1.386862000	1.522985000	-3.495551000
C	-0.035609000	-1.218105000	-2.604284000
C	-1.098604000	-2.071741000	-2.947332000
C	1.196476000	-1.778301000	-2.232793000
C	-0.927766000	-3.451906000	-2.923095000
C	1.365218000	-3.162232000	-2.211816000
C	0.304094000	-4.001971000	-2.554065000
H	-2.067586000	-1.640210000	-3.225223000
H	2.019783000	-1.108424000	-1.944807000
H	-1.765612000	-4.108809000	-3.187549000
H	2.331192000	-3.588563000	-1.913709000
H	0.435554000	-5.090753000	-2.531585000
C	-1.717490000	1.722954000	-4.187554000
C	-1.359594000	2.826178000	-4.976661000
C	-2.930608000	1.065739000	-4.447489000
C	-2.184131000	3.245859000	-6.020390000
C	-3.754739000	1.490473000	-5.488039000
C	-3.382898000	2.578880000	-6.281314000
H	-0.419354000	3.351232000	-4.761676000
H	-3.232566000	0.215378000	-3.820924000
H	-1.889195000	4.105966000	-6.633886000
H	-4.698487000	0.966288000	-5.681805000
H	-4.032371000	2.911260000	-7.099905000

Table S24. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **4gaa''** cycloadduct

Atom	X	Y	Z
C	2.918144000	0.023869000	0.609658000

C	2.773178000	-1.295453000	1.116204000
C	3.905282000	-1.962438000	1.648876000
C	5.129398000	-1.335804000	1.678424000
C	5.272776000	-0.017435000	1.176234000
C	4.189234000	0.648834000	0.651091000
N	1.855446000	0.710339000	0.063717000
C	0.720161000	0.080544000	0.083379000
C	0.576222000	-1.256041000	0.610508000
N	1.562842000	-1.945606000	1.106038000
C	-0.592897000	0.524357000	-0.557963000
C	-1.533776000	-0.591148000	-0.101553000
C	-0.835464000	-1.651677000	0.485119000
C	-2.912781000	-0.662836000	-0.259107000
C	-3.568759000	-1.832982000	0.133477000
C	-2.857999000	-2.910705000	0.679917000
C	-1.479114000	-2.825008000	0.873893000
N	-1.103088000	1.858052000	-0.300377000
C	-0.351543000	2.865665000	0.454076000
C	-1.061580000	4.160494000	0.053181000
C	-1.330884000	3.941289000	-1.442474000
C	-1.684300000	2.447426000	-1.521539000
H	3.763607000	-2.980016000	2.031608000
H	6.001596000	-1.855588000	2.092268000
H	6.254292000	0.470272000	1.206329000
H	4.272444000	1.667092000	0.253192000
H	-3.472891000	0.180076000	-0.685319000
H	-4.655975000	-1.911898000	0.010809000
H	-3.395254000	-3.820673000	0.972110000
H	-0.911110000	-3.647276000	1.325737000
H	-0.404673000	2.666848000	1.541208000
H	0.720794000	2.905485000	0.172228000

H	-0.455454000	5.057942000	0.261076000
H	-2.016368000	4.249935000	0.603501000
H	-0.407258000	4.132148000	-2.021194000
H	-2.127208000	4.588254000	-1.845737000
H	-2.787253000	2.317215000	-1.533035000
C	0.410217000	1.586117000	-2.657511000
C	-0.400447000	0.445024000	-2.106194000
C	-1.094706000	1.659858000	-2.699251000
H	0.944560000	2.231419000	-1.949047000
H	0.939708000	1.382269000	-3.595220000
C	-0.281475000	-0.920912000	-2.708492000
C	-1.403666000	-1.675438000	-3.071260000
C	0.987101000	-1.507807000	-2.797924000
C	-1.260182000	-2.994348000	-3.502280000
C	1.133480000	-2.828168000	-3.225849000
C	0.007606000	-3.575594000	-3.574280000
H	-2.400941000	-1.225837000	-3.000198000
H	1.869082000	-0.915783000	-2.513903000
H	-2.147868000	-3.575475000	-3.780432000
H	2.132865000	-3.276378000	-3.284009000
H	0.118214000	-4.614927000	-3.906960000
C	-1.854107000	1.629063000	-3.990202000
C	-1.268576000	2.036073000	-5.193182000
C	-3.190363000	1.201515000	-4.007345000
C	-1.993314000	2.005931000	-6.387134000
C	-3.916441000	1.170110000	-5.196004000
C	-3.317905000	1.571261000	-6.393197000
H	-0.230217000	2.390139000	-5.195810000
H	-3.668004000	0.877799000	-3.072069000
H	-1.515992000	2.328882000	-7.320520000
H	-4.958019000	0.826331000	-5.188974000

H	-3.887108000	1.545736000	-7.330235000

Table S25. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized TS from **D-2** to **4gaa'''** (**TS$_4$-*endo***)

Atom	X	Y	Z
C	-4.446265000	-1.405247000	-0.202992000
C	-3.897648000	-2.697932000	0.022986000
C	-4.765025000	-3.816481000	0.124806000
C	-6.125931000	-3.657700000	0.012029000
C	-6.675907000	-2.368779000	-0.216887000
C	-5.855796000	-1.270480000	-0.326256000
N	-3.668009000	-0.282023000	-0.274638000
C	-2.379829000	-0.481482000	-0.117436000
C	-1.825569000	-1.811299000	0.090561000
N	-2.546861000	-2.892872000	0.159740000
C	-1.284681000	0.466674000	-0.031364000
C	-0.043372000	-0.307857000	0.060359000
C	-0.373357000	-1.682670000	0.178657000
C	1.315464000	0.044293000	-0.002806000
C	2.283244000	-0.954746000	0.109678000
C	1.939040000	-2.303638000	0.279671000
C	0.596045000	-2.673925000	0.300942000
N	-1.413334000	1.814419000	-0.186510000
C	-2.690525000	2.432671000	-0.609882000
C	-2.399567000	3.941228000	-0.635049000
C	-1.012471000	4.114505000	0.024000000
C	-0.603982000	2.713710000	0.375473000
H	-4.308117000	-4.797634000	0.302926000
H	-6.791017000	-4.525198000	0.098072000
H	-7.762821000	-2.251480000	-0.305910000
H	-6.257661000	-0.264757000	-0.499426000
H	1.641275000	1.076921000	-0.166315000

H	3.342214000	-0.672096000	0.058906000
H	2.725107000	-3.061521000	0.374283000
H	0.289521000	-3.723151000	0.397306000
H	-2.987887000	2.009395000	-1.582602000
H	-3.466491000	2.144203000	0.119247000
H	-3.179064000	4.493206000	-0.085879000
H	-2.390896000	4.316079000	-1.670846000
H	-1.042456000	4.752060000	0.925032000
H	-0.275023000	4.561832000	-0.666488000
H	0.425604000	2.439625000	0.614062000
C	-1.191607000	0.865250000	2.539960000
C	-1.056917000	2.213217000	2.508078000
C	0.151786000	1.400161000	2.910756000
C	-1.993246000	-0.281437000	2.917315000
C	-3.397517000	-0.281389000	2.827669000
C	-1.340895000	-1.443091000	3.363333000
C	-4.124813000	-1.412869000	3.182415000
C	-2.073901000	-2.572663000	3.725273000
C	-3.466328000	-2.562521000	3.632531000
H	-3.913310000	0.610442000	2.449225000
H	-0.243884000	-1.444960000	3.416039000
H	-5.219061000	-1.406505000	3.092544000
H	-1.552284000	-3.472821000	4.073261000
H	-4.043775000	-3.454473000	3.904918000
H	0.449980000	1.350914000	3.974743000
H	1.003872000	1.317408000	2.211218000
C	-1.702507000	3.429778000	3.007624000
C	-3.073410000	3.669763000	2.824046000
C	-0.926605000	4.399341000	3.659886000
C	-3.652189000	4.851262000	3.284116000
C	-1.509382000	5.577458000	4.126683000

C	-2.872902000	5.809761000	3.937115000
H	-3.691465000	2.921746000	2.311380000
H	0.147195000	4.216081000	3.796261000
H	-4.724557000	5.025246000	3.132662000
H	-0.890835000	6.324775000	4.638934000
H	-3.329765000	6.739153000	4.297709000

Table S26. Cartesian coordinates (in Å) of M11/cc-pVDZ optimized **4gaa'''** cycloadduct

Atom	X	Y	Z
C	-4.303541000	-0.834492000	-0.078332000
C	-4.046082000	-2.221652000	-0.259431000
C	-5.120901000	-3.090633000	-0.577181000
C	-6.397614000	-2.596646000	-0.708369000
C	-6.653911000	-1.213677000	-0.527530000
C	-5.628079000	-0.350143000	-0.218740000
N	-3.298580000	0.052845000	0.239169000
C	-2.120991000	-0.477301000	0.355141000
C	-1.861363000	-1.875136000	0.157324000
N	-2.781640000	-2.747343000	-0.139256000
C	-0.830205000	0.269704000	0.695900000
C	0.194344000	-0.863800000	0.636512000
C	-0.418440000	-2.094005000	0.346427000
C	1.562374000	-0.828415000	0.904071000
C	2.293859000	-2.018333000	0.843998000
C	1.675010000	-3.235519000	0.534797000
C	0.303576000	-3.283895000	0.289756000
N	-0.660565000	1.382164000	-0.227277000
C	0.584801000	1.691936000	-0.926159000
C	0.326563000	3.127077000	-1.392554000
C	-0.394501000	3.750338000	-0.186466000
C	-1.253562000	2.596514000	0.359753000

H	-4.892523000	-4.154523000	-0.711973000
H	-7.224812000	-3.273006000	-0.954195000
H	-7.676652000	-0.833513000	-0.634422000
H	-5.798009000	0.723329000	-0.072971000
H	2.068599000	0.106588000	1.168540000
H	3.371047000	-1.996879000	1.048382000
H	2.271903000	-4.154270000	0.495668000
H	-0.207661000	-4.226996000	0.062374000
H	1.490402000	1.663429000	-0.280829000
H	0.755416000	0.991168000	-1.764272000
H	-0.343560000	3.113609000	-2.271251000
H	1.253046000	3.657039000	-1.668980000
H	-0.989900000	4.639943000	-0.451605000
H	0.344912000	4.053292000	0.579568000
H	-2.310043000	2.678703000	0.037297000
C	-0.939820000	0.906658000	2.104904000
C	-1.233738000	2.385848000	1.880588000
C	0.119412000	1.931283000	2.390349000
C	-1.495240000	0.055274000	3.205523000
C	-2.875229000	-0.058888000	3.419950000
C	-0.617696000	-0.668846000	4.020601000
C	-3.366025000	-0.881572000	4.433593000
C	-1.107353000	-1.495134000	5.033525000
C	-2.483186000	-1.602071000	5.241634000
H	-3.561720000	0.517736000	2.786776000
H	0.464669000	-0.575618000	3.854799000
H	-4.447900000	-0.957414000	4.598220000
H	-0.409271000	-2.057667000	5.665569000
H	-2.870149000	-2.247778000	6.039479000
H	0.345435000	2.121264000	3.446170000
H	0.974728000	2.034316000	1.712202000

C	-2.136794000	3.204976000	2.748278000
C	-2.156712000	3.046361000	4.144273000
C	-2.969608000	4.182119000	2.185387000
C	-2.993972000	3.822535000	4.942615000
C	-3.806187000	4.963733000	2.985704000
C	-3.826347000	4.785671000	4.367654000
H	-1.511886000	2.296790000	4.620110000
H	-2.965899000	4.351473000	1.102530000
H	-2.993409000	3.673818000	6.029497000
H	-4.445409000	5.722807000	2.518155000
H	-4.483269000	5.397845000	4.997117000

6. References

1. Data for (*E*)-2,3-Diphenylacrylaldehyde (**5**): (a) K. Alder, J. Haydn, K. Heimbach, K. Neufang, *Liebigs Chem.*, 1954, **586**, 128; (b) G. A. Molander, T. Fumagalli, *J. Org. Chem.*, 2006, **71**, 5743; (c) R. J. Kulawiec, J. H. Kim, *J. Org. Chem.*, 1996, **61**, 7656.