Supporting information

An efficient and environmentally sustainable domino protocol for synthesis of structurally diverse spiroannulated pyrimidophenazines using Erbium doped TiO_2 nanoparticles as recyclable and reusable heterogeneous acid catalyst

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Supporting Information

Compound names and spectral details:

1. **1.1'methylspiro[benzo[a]pyrido[1',2':1,2]pyrimido[4,5-c]phenazine-16,4'-piperidine] (5aa)**

   Orange Brown semisolid, M.p. 248-250°C. ^{1}H NMR (DMSO-d_6) δ (ppm): 2.06-2.24 (m, 4H), 2.25 (s, 3H, N-CH_3), 2.27-2.50 (m, 4H), 6.94-8.30 (m, 12H, ArH).^{13}C NMR (DMSO-d_6) δ (ppm): 21.3, 37.4, 42.4, 52.4, 120.9, 123.6, 125.3, 126.0, 127.3, 128.7, 129.2, 129.8, 130.8, 131.3, 136.4, 138.5, 139.8, 140.3, 144.7, 145.7, 154.4. Anal. calcd. For $C_{27}H_{23}N_5$: C 77.67, H 5.55, N 16.77%; found: C 77.65, H 5.22, N 16.76 %.

2. **1'methylspiro[benzo[a]pyrimido[1',2':1,2]pyrimido[4,5-c]phenazine-16,4'-piperidine](5ab)**

   Rust Brown Solid, M.p. 263-265°C.^{1}H NMR (DMSO-d_6) δ (ppm): 2.07-2.24 (m, 4H), 2.25 (s, 3H, N-CH_3), 2.26-2.53 (m, 4H), 7.22-8.90 (m, 11H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 20.7, 36.8, 41.9, 51.8, 101.02, 123.26, 124.77, 125.45, 128.22, 128.79, 129.41, 129.54, 130.62, 131.52, 138.14, 139.23, 140.39, 142.95, 144.87, 155.81, 160.10. Anal. calcd. For $C_{26}H_{22}N_6$: C 77.40, H 5.25, N 17.36%; found: C 77.37, H 5.22, N 17.33 %.

3. **1'methylspiro[benzo[a]pyrizino[1',2':1,2]pyrimido[4,5-c]phenazine-16,4'-piperidine](5ac)**

Dark Orange Semisolid, M.p. 238-240°C.^{1}H NMR (DMSO-d_6) δ (ppm): 2.06-2.23 (m, 4H), 2.25 (s, 3H, N-CH_3), 2.27-2.51(m, 4H), 7.19-8.42 (m, 10H,ArH), 8.97 (s, 1H,ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 21.3, 37.4, 42.4, 52.4, 123.6, 125.3, 126.0, 127.1, 128.7, 129.1, 129.2, 129.8, 130.9, 131.4, 138.5, 139.8, 140.4, 144.7, 145.6 147.5, 154.2. Anal. calcd. For $C_{26}H_{22}N_6$: C 74.62, H 5.30, N 20.08%; found: C 74.60, H 5.27, N 20.06 %.

4. **1,1'-dimethylspiro[benzo[a]pyrido[1',2':1,2]pyrimido[4,5-*c*]phenazine-16,4'-piperidine](5ad)**

Orange Solid, M.p. 308-310°C. ^{1}H NMR (DMSO-d_6) δ (ppm): 2.05-2.24 (m, 4H), 2.25 (s, 3H, N-CH_3), 2.29 (s, 3H, CH_3), 2.28-2.52 (m, 4H), 6.96-8.28 (m, 11H,ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 21.3, 37.4, 44.2, 52.4, 120.9, 123.6, 125.3, 126.0, 127.4, 128.6, 129.2, 130.8, 131.3, 136.4, 138.5, 139.8, 142.4, 144.7, 145.7, 154.4. Anal. calcd. For $C_{28}H_{25}N_5$: C 77.93, H 5.84, N 16.23%; found: C 77.92, H 5.81, N 16.21 %.

5. **1'-methyl-1*H*-spiro[benzo[*a*]pyrino[1',6':1,2]pyrimido[4,5-*c*]phenazine-15,4'-piperidine](5ae)**

^{1}H NMR (DMSO-d_6) δ (ppm): 2.10-2.17 (m, 4H), 2.26 (s, 3H, N-CH_3), 2.22-2.54 (m, 4H), 6.17(s, 1H, NH), 7.50-8.51 (m, 8H, ArH), 8.54 (s, 1H, ArH), 9.57 (s, 1H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 21.7, 37.5, 44.5, 52.8, 116.7, 124.8, 126.1, 127.2, 128.5, 128.9, 129.5 129.7, 130.2, 132.5, 133.4, 140.2, 142.8, 144.1, 144.8, 145.3, 145.9, 150.5. Anal. calcd. For $C_{26}H_{22}N_6$: C 70.73, H 4.84, N 24.44%; found: C 70.69, H 4.80, N 24.37 %.

6. **3'4'-dihydro-2'H-spiro[benzo[a]pyrido[1',2':1,2]pyrimido[4,5-c]phenazine-16,1'-naphthalene] (5ba)**

Dark Brown Solid, M.p. 298-300°C. ^{1}H NMR (DMSO-d_6) δ (ppm): 1.71-2.85 (m, 6H), 6.45-8.33 (m, 15H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 23.3, 29.5, 38.5, 64.4, 110.7, 123.2, 124.0, 125.3, 126.2, 126.7, 127.1, 128.5, 129.2, 129.3, 129.7, 130.8, 131.2, 132.6, 133.2, 133.8, 135.7, 138.5, 139.7, 140.0, 143.0, 145.2, 145.8, 153.2,. Anal. calcd. For $C_{31}H_{22}N_4$: C 82.64, H 4.92, N 12.44%; found: C 82.63, H 4.90, N 12.42 %.

7. **3'4'-dihydro-2'H-spiro[benzo[a]pyrimido[1',2':1,2]pyrimido[4,5-c]phenazine-16,1'-naphthalene](5bb)**

Brown Solid, M.p. 278-280°C. ^{1}H NMR (DMSO-d_6) δ (ppm): 1.71-2.84 (m, 6H), 6.49-8.28 (m, 15H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 23.3, 29.3, 39.1, 64.4, 110.6, 123.4, 124.7, 125.3, 126.7, 127.0, 128.6, 129.0, 129.3, 129.7, 130.7, 131.4, 132.6, 133.9, 135.1, 135.4, 139.7, 140.0, 143.0, 145.2, 145.8, 151.1, 158.5. Anal. calcd. For $C_{30}H_{21}N_5$: C 79.80, H 4.69, N 15.51%; found: C 79.77, H 4.68, N 15.49 %.

8. **3'4'-dihydro-*2'H*-[spiro[benzo[a]pyrazino[1',2':1,2]pyrimido[4,5-c]phenazine-16,1'-naphthalene](5bc)**

Brown Solid, M.p. 253-255°C.^{1}H NMR (DMSO-d_6) δ (ppm): 1.72-2.84(m, 6H), 6.50-8.40 (m, 14H, ArH), 8.98(s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm): 23.3, 29.3, 39.1, 65.2, 121.3, 124.9, 125.3, 125.9, 126.7, 127.0, 128.6, 129.0, 129.3, 129.5, 130.6, 131.3, 132.9, 133.9, 135.2, 135.8, 139.5, 140.0, 142.3, 145.1, 145.8, 153.2, 156.6. Anal. calcd. For $C_{30}H_{21}N_5$: C 79.80, H 4.69, N 15.51%; found: C79.79, H 4.67, N 15.50 %.

9. **1-methyl-3'4'-dihydro-*2'H*-[spiro[benzo[a]pyrido[1',2':1,2]pyrimido[4,5-c]phenazine-16,1'-naphthalene](5bd)**

Dark Brown Solid, M.p. 218-220°C. ^{1}H NMR (DMSO-d_6) δ (ppm): 1.70-2.38(m, 4H), 2.46(s, 3H, CH_3), 2.80-2.86 (m, 2H), 6.37-8.79 (m, 15H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 17.2, 23.3, 29.4, 39.1, 64.4, 110.6, 123.4, 124.1, 124.7, 125.3, 126.7, 127.0, 128.6, 129.1, 129.3, 129.8, 130.8, 131.5, 132.7, 133.4, 133.9, 135.3, 135.5, 139.7, 140.0, 143.1, 145.5, 145.98, 153.5. Anal. calcd. For $C_{32}H_{24}N_4$: C 82.73, H 5.21, N 12.06%; found: C 82.71, H 5.20, N 12.03 %.

10. **3'4'-dihydro-*1H,2'H*-[spiro[benzo[a]purino[1',6':1,2]pyrimido[4,5-c]phenazine-15,1'-naphthalene](5be)**

Brown Solid, M.p.-238-240°C. ^{1}H NMR (DMSO-d_6) δ (ppm): 1.70-2.82(m, 6H) 6.18 (s, 1H, NH), 6.90-8.45(m, 12H, ArH) 8.51(s, 1H, ArH), 9.57(s, 1H, ArH),. ^{13}C NMR (DMSO-d_6) δ (ppm): 23.3, 29.3, 39.1, 64.4, 114.1, 123.4, 124.8, 125.3, 126.7, 127.0, 128.7, 129.1, 129.2, 129.5, 130.7, 131.5, 132.6, 133.9, 135.2, 135.7, 139.7, 140.0, 143.0 144.7, 145.2, 145.5, 146.4, 152.2. HRMS (ESI): m/z calcd $C_{31}H_{21}N_7$, 491.1858; found 491.5623. Anal. calcd. For $C_{31}H_{21}N_7$: C 75.75, H 4.31, N 19.95%; found: C 75.72, H 4.29, N 19.94 %.

11. ***2H*-spiro[acenaphthylene-1,16'-benzo[a]pyrido[1',2':1,2]pyrimido[4,5-c]phenazin]-2-one (5ca)**

Dark Brown Solid, M.p. 288-290°C. ^{1}H NMR (DMSO-d_6) δ (ppm): 7.61-8.37 (m, 18H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 79.2, 121.7, 123.4, 124.47, 125.3, 127.3, 128.6, 128.9, 129.2, 129.4, 129.8, 130.6, 130.7, 131.0, 131.4, 132.3, 132.5, 132.8, 133.9, 139.7, 140.0, 142.1, 143.0, 143.3, 144.8, 145.3, 145.8, 151.2,

153.3, 198.8. Anal. calcd. For $C_{33}H_{18}N_4O$: C 81.47, H 3.73, N 11.52, O 3,29%; found: C 81.45, H 3.71, N 11.50, O 3.27 %.

12. ***2H*-spiro[acenaphthylene-1,16'-benzo[a]pyrimido[1',2':1,2]pyrimido[4,5-c]phenazin]-2-one (5cb)**

Brown Solid, M.p. 273-275^oC. ^1H NMR (DMSO-d_6) δ (ppm): 7.68-8.42 (m, 17H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 79.2, 121.7, 123.4, 125.3, 127.3, 128.6, 128.9, 129.2, 129.4, 129.7, 130.6, 130.7, 131.0, 131.4, 132.2, 132.4, 132.7, 133.9, 139.7, 140.0, 143.0, 143.3, 144.8, 145.3, 145.8, 151.8,157.4, 198.0. Anal. calcd. For $C_{32}H_{17}N_5O$: C 78.84, H 3.51, N 14.37, O 3.28%; found: C 78.83, H 3.49, N 14.35, O 3.25 %.

13. ***2H*-spiro[acenaphthylene-1,16'-benzo[a]pyrazino[1',2':1,2]pyrimido[4,5-c]phenazin]-2-one (5cc)**

Brown Semisolid, M.p.-283-285^oC. ^1H NMR (DMSO-d_6) δ (ppm): 7.70-8.45 (m, 16H, ArH), 8.97(s, 1H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 79.2, 123.4, 125.3, 125.7, 127.3, 128.7, 128.9, 129.3, 129.6, 130.0, 130.5, 130.5, 130.9, 131.0, 131.4, 132.4, 132.5, 132.8, 133.9, 139.7, 140.0, 143.0, 143.3, 144.7, 145.6, 145.8, 151.1, 153.4, 198.0. Anal. calcd. For $C_{32}H_{17}N_5O$: C 78.84, H 3.51, N 14.37, O 3.28%; found: C 78.82, H 3.48, N 14.36, O 3.26 %.

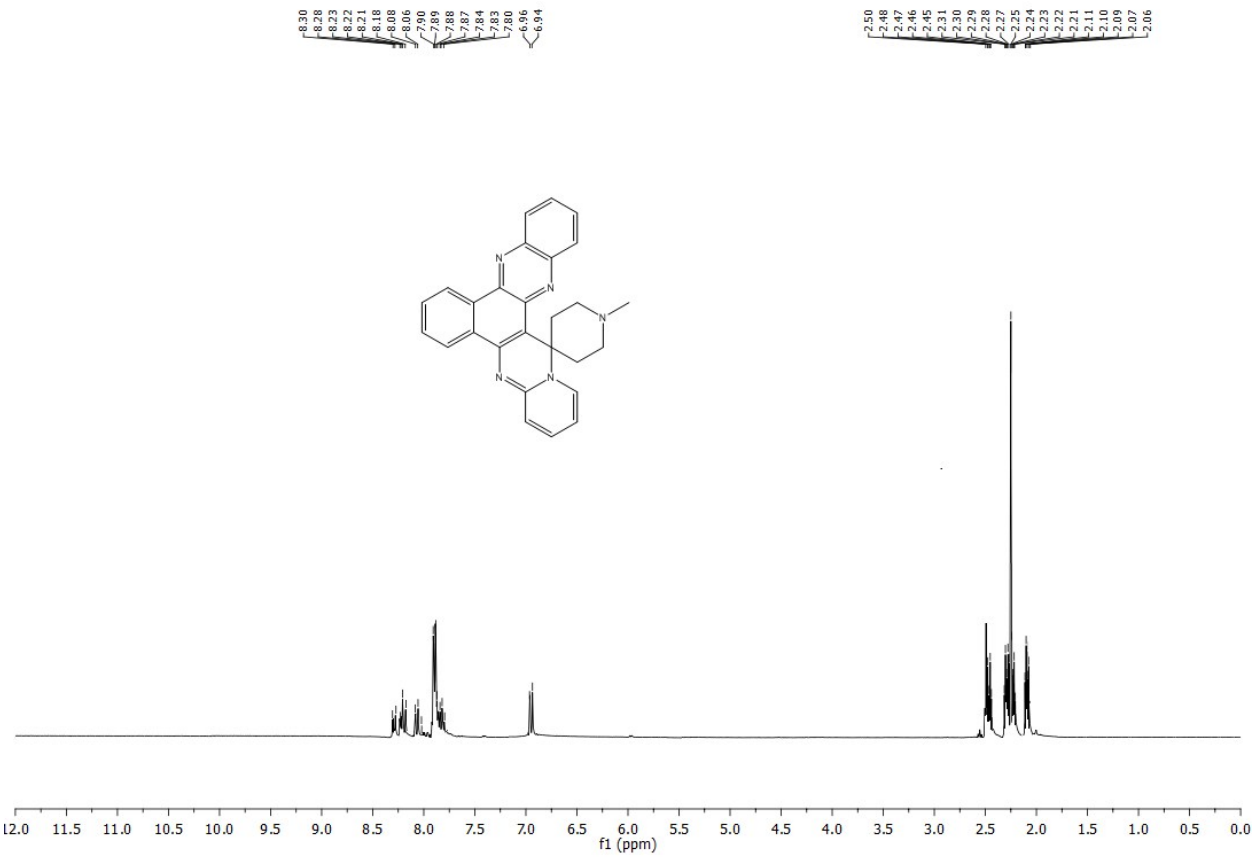
14. **1'-methyl-*2H*-spiro[acenaphthylene-1,16'benzo[a]pyrido[1',2':1,2]pyrimido[4,5-c]phenazin]-2-one (5cd)**

Orange Semisolid, M.p.-233-235^oC. ^1H NMR (DMSO-d_6) δ (ppm): 2.24 (s, 3H, CH_3), 7.73-8.40 (m, 17H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 21.3, 79.2, 121.7, 122.4, 123.4, 124.3, 125.4, 126.0, 128.6, 128.8, 129.0, 129.3, 129.9, 130.2, 130.8, 131.0, 131.2, 131.9, 132.8, 133.8, 138.7, 139.7, 140.6, 142.2, 143.4, 144.8, 145.3, 145.8, 147.7, 154.7, 198.0. Anal. calcd. For $C_{34}H_{20}N_4O$: C 81.58, H 4.03, N 11.19, O 3.20%; found: C 81.56, H 4.01, N 11.17, O 3.19 %.

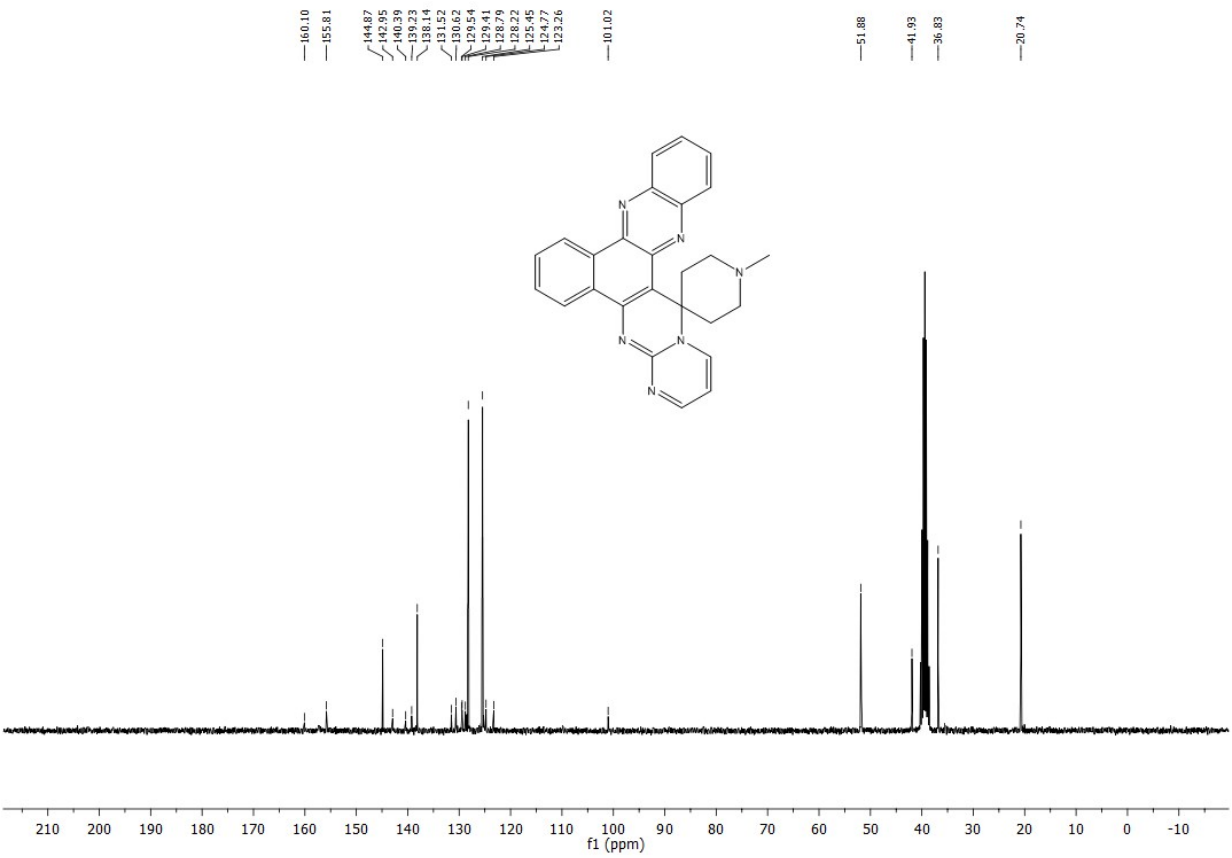
15. ***1H,2H*-spiro[acenaphthylene-1,15'-benzo[a]purino[1',6':1,2]pyrimido[4,5-c]phenazin]-2-one (5ce)**

Orange Semisolid, M.p.-238-240^oC. ^1H NMR (DMSO-d_6) δ (ppm): 6.18(s, 1H, NH), 7.86-8.53 (m, 14H, ArH), 8.5 (s, 1H, ArH), 9.58 (s, 1H, ArH). ^{13}C NMR (DMSO-d_6) δ (ppm): 79.2, 121.4, 123.7, 124.8, 125.4, 128.0, 128.2, 128.4, 128.7, 129.0, 129.3, 129.4, 129.7, 129.9, 130.2, 130.7, 131.5, 132.2, 132.7, 133.5, 138.3, 139.6, 141.9, 143.4, 144.5, 144.9, 149.0, 150.7, 152.0, 198.1. Anal. calcd. For $C_{33}H_{17}N_7O$: C 75.13, H 3.25, N 18.59, O 3.03%; found: C 75.11, H 3.23, N 18.58, O 3.01 %.

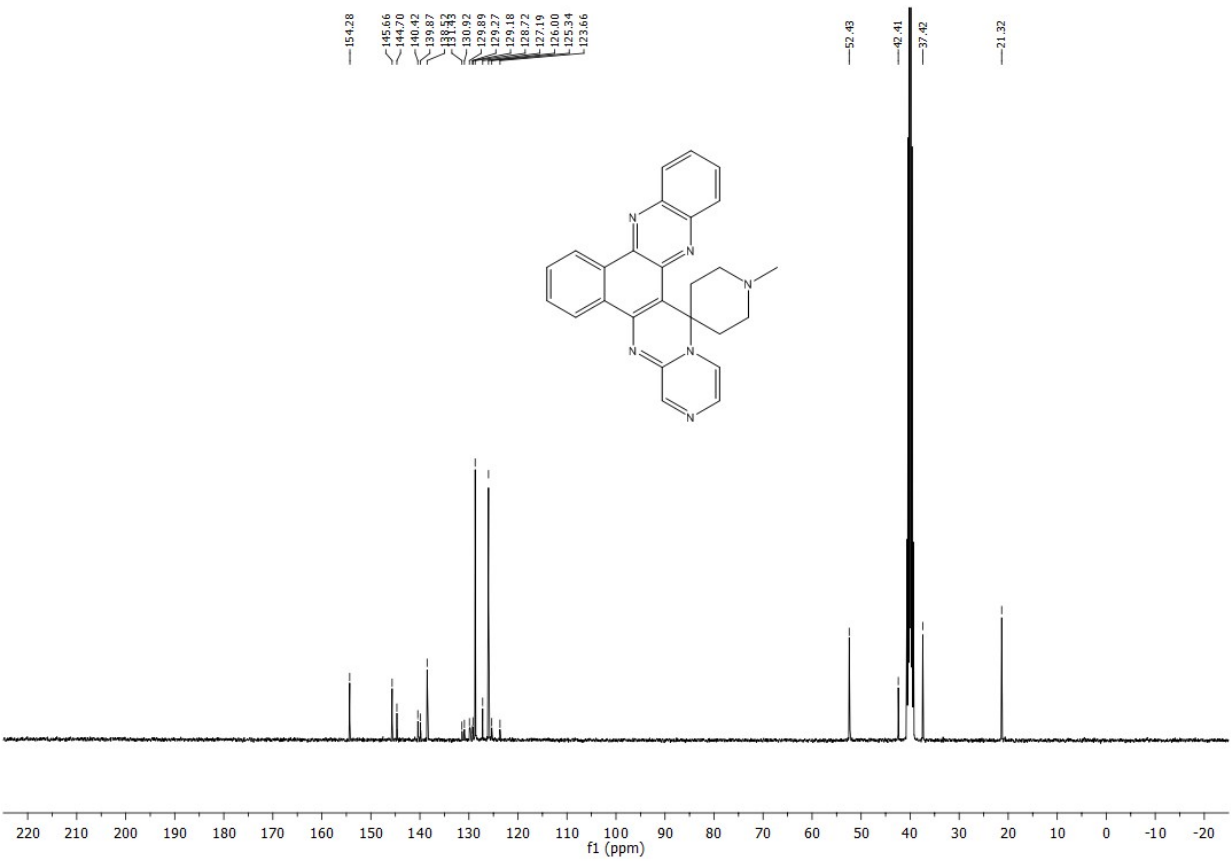
Copies of ^{1}H and ^{13}C NMR



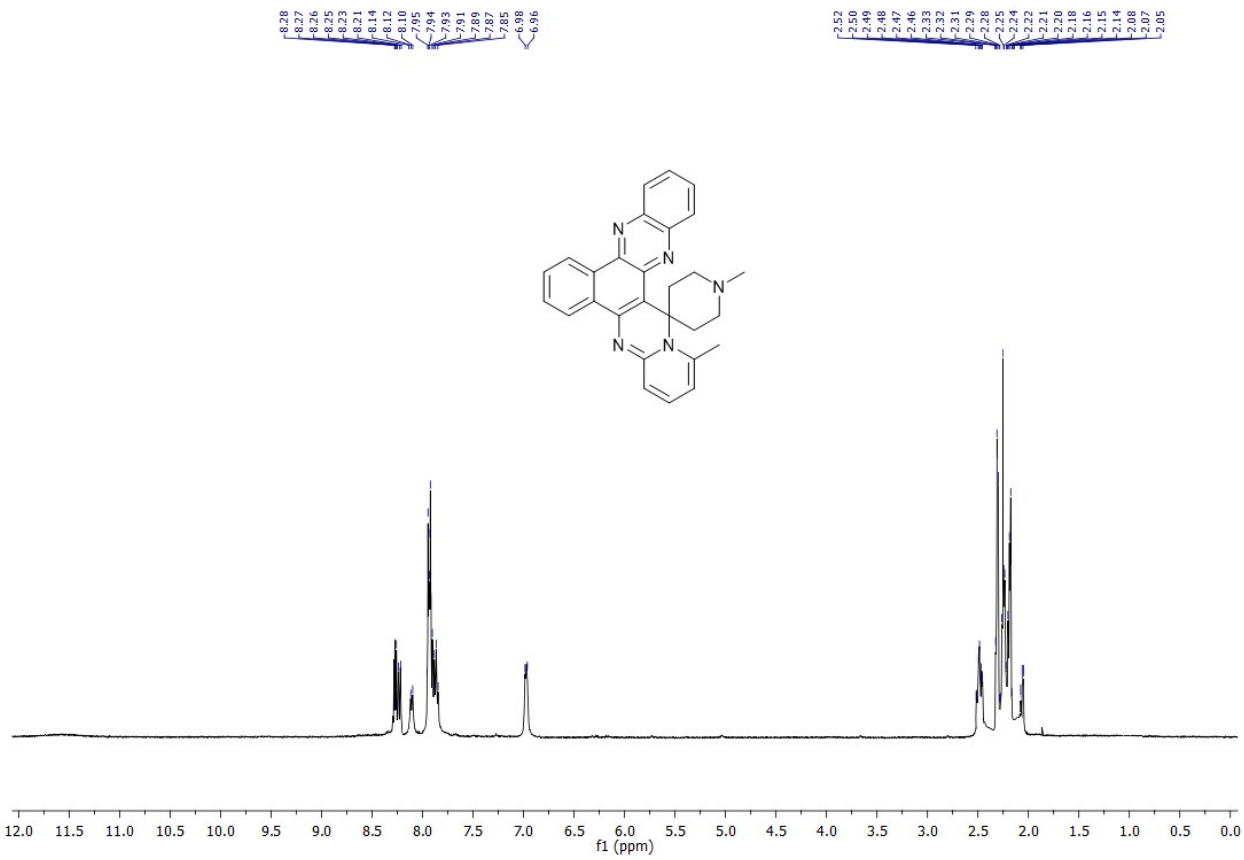
^{1}H spectra of (5aa)



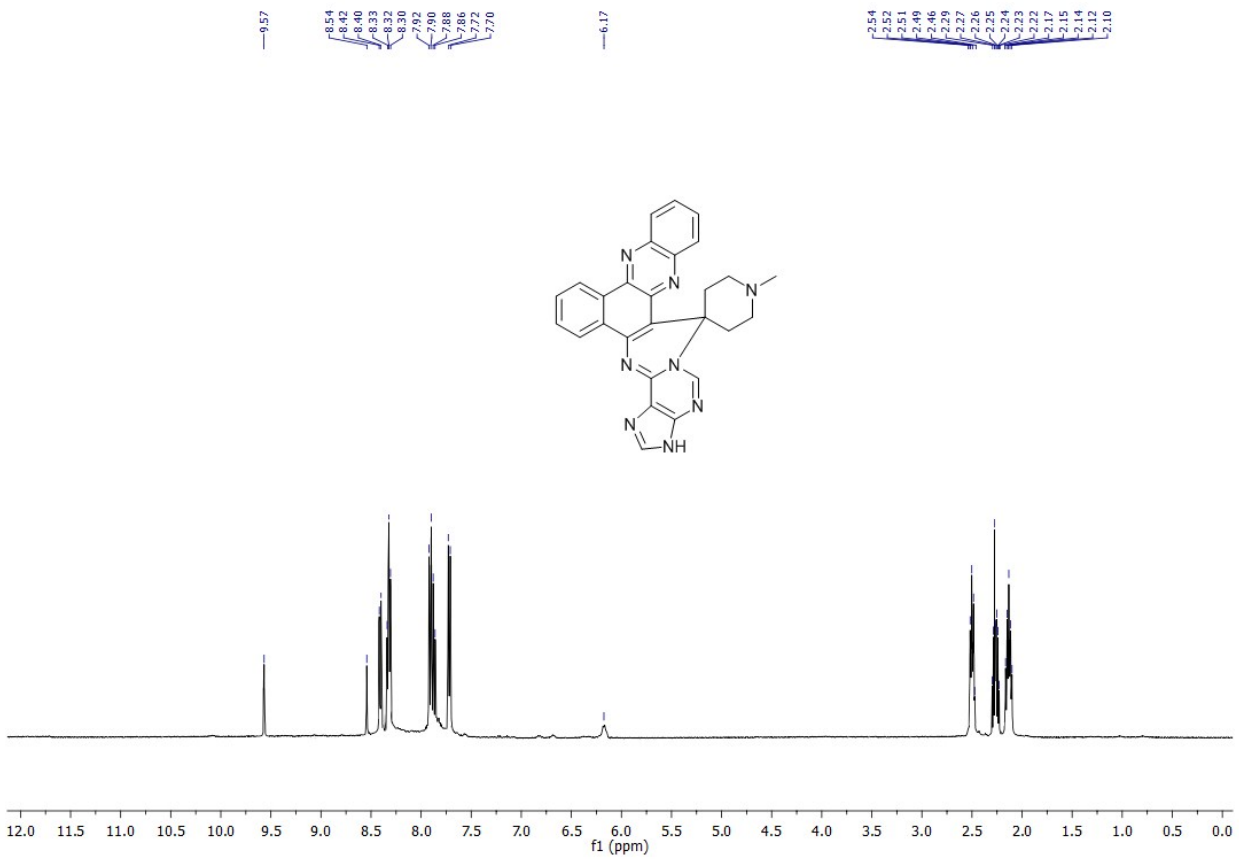
^{13}C spectra of (5ab)



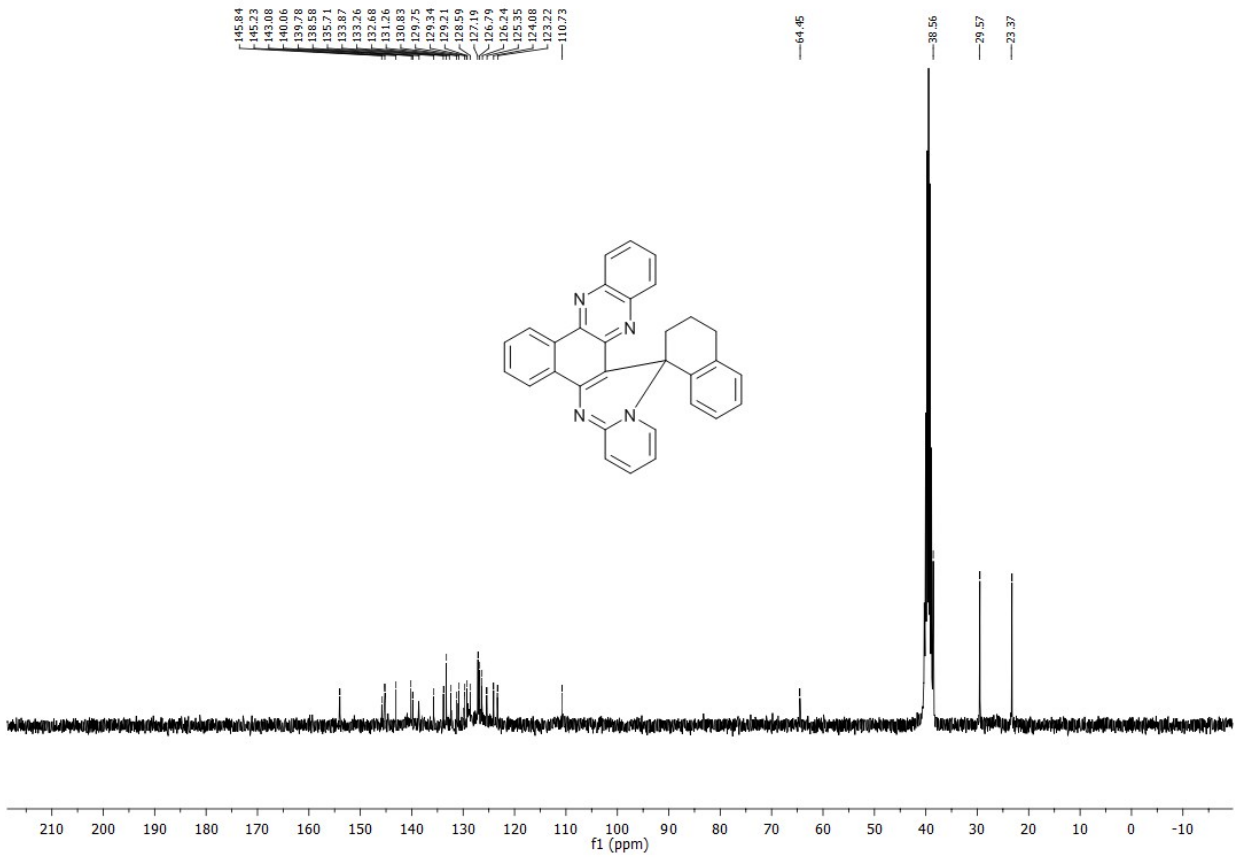
^{13}C spectra of (5ac)



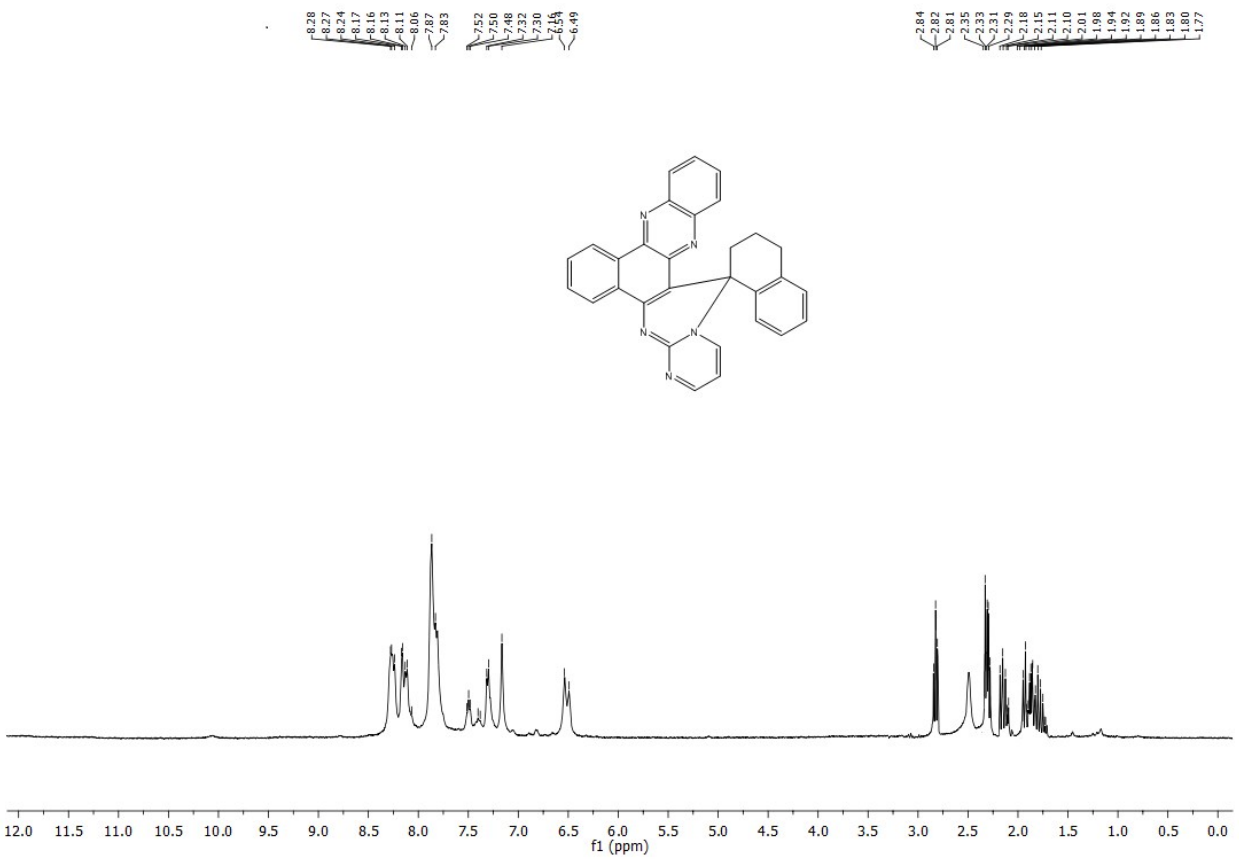
^{1}H spectra of (5ad)



^{1}H spectra of (5ae)



^{13}C spectra of (5ba)



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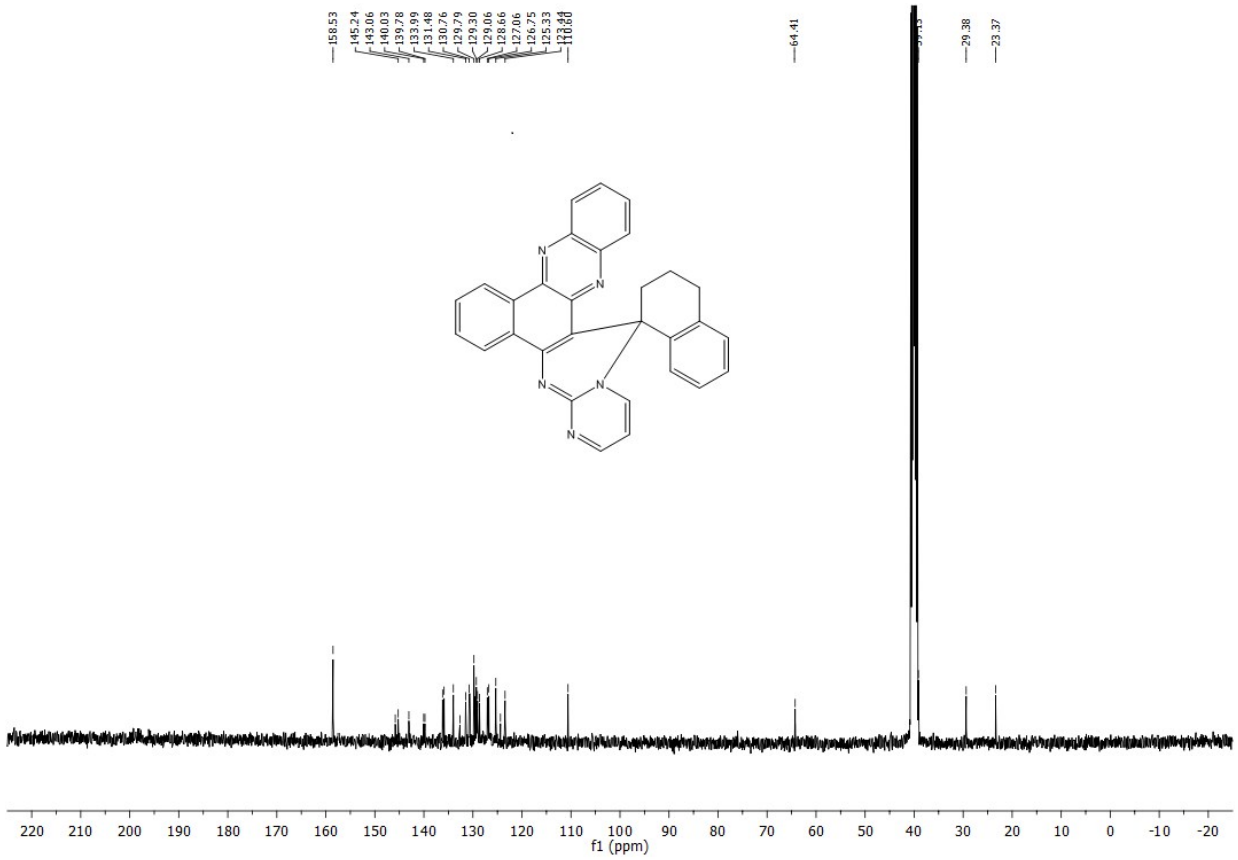

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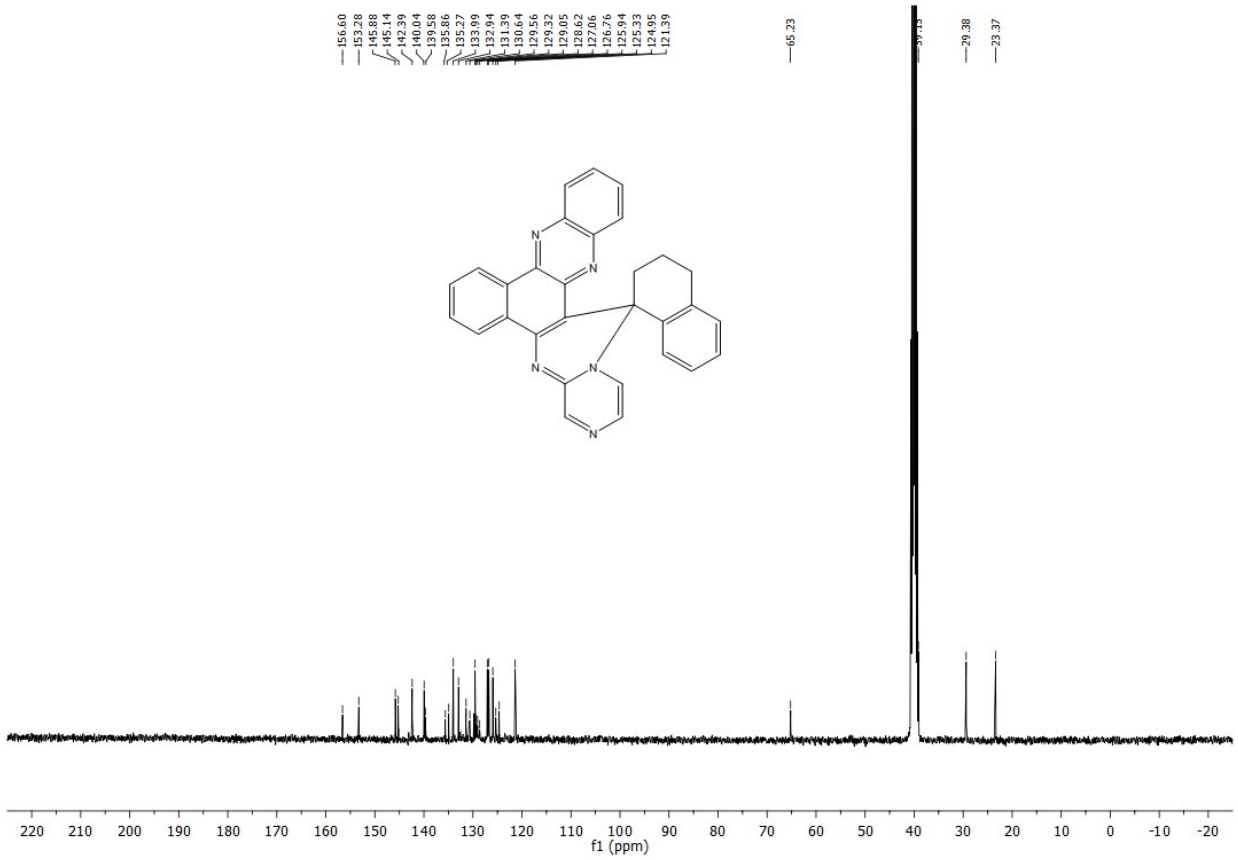
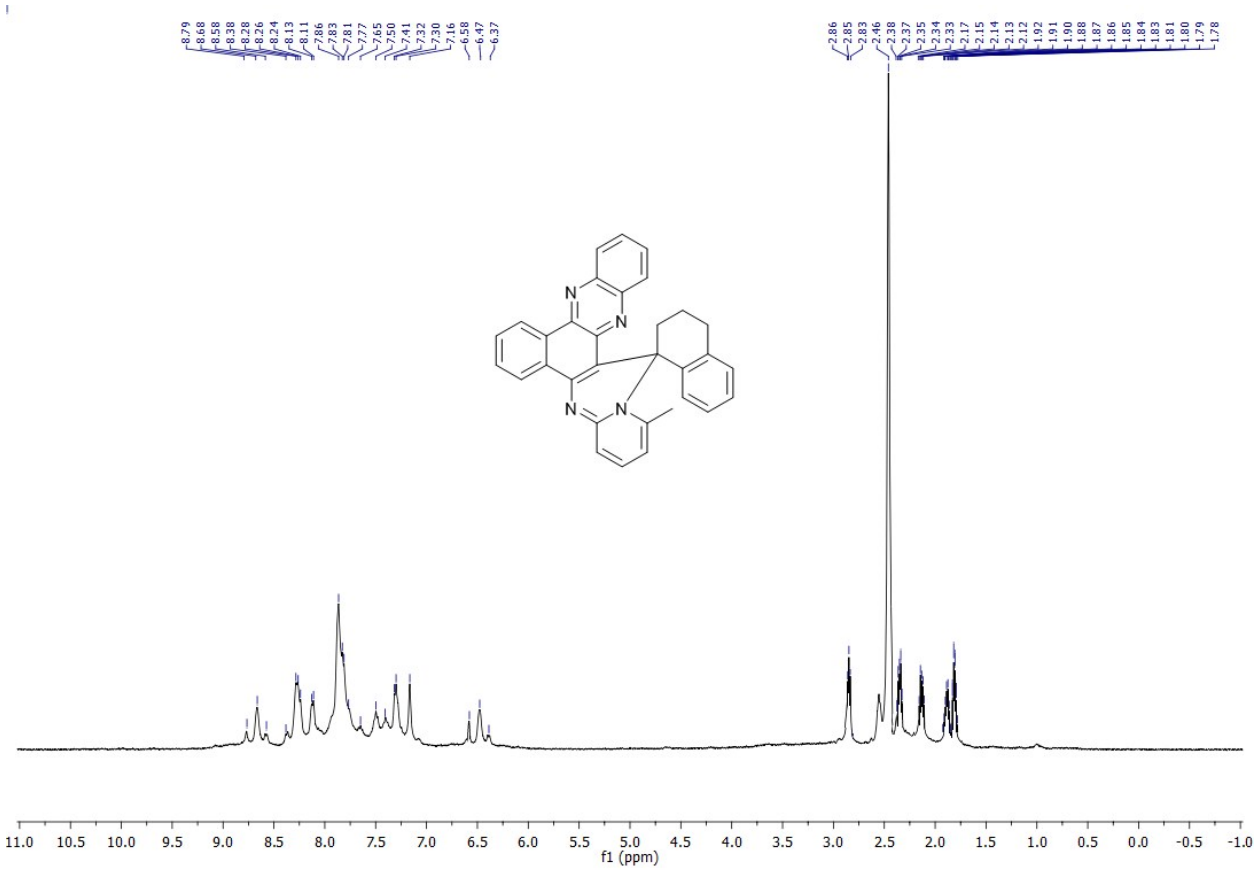


^{13}C spectra of (5bc)



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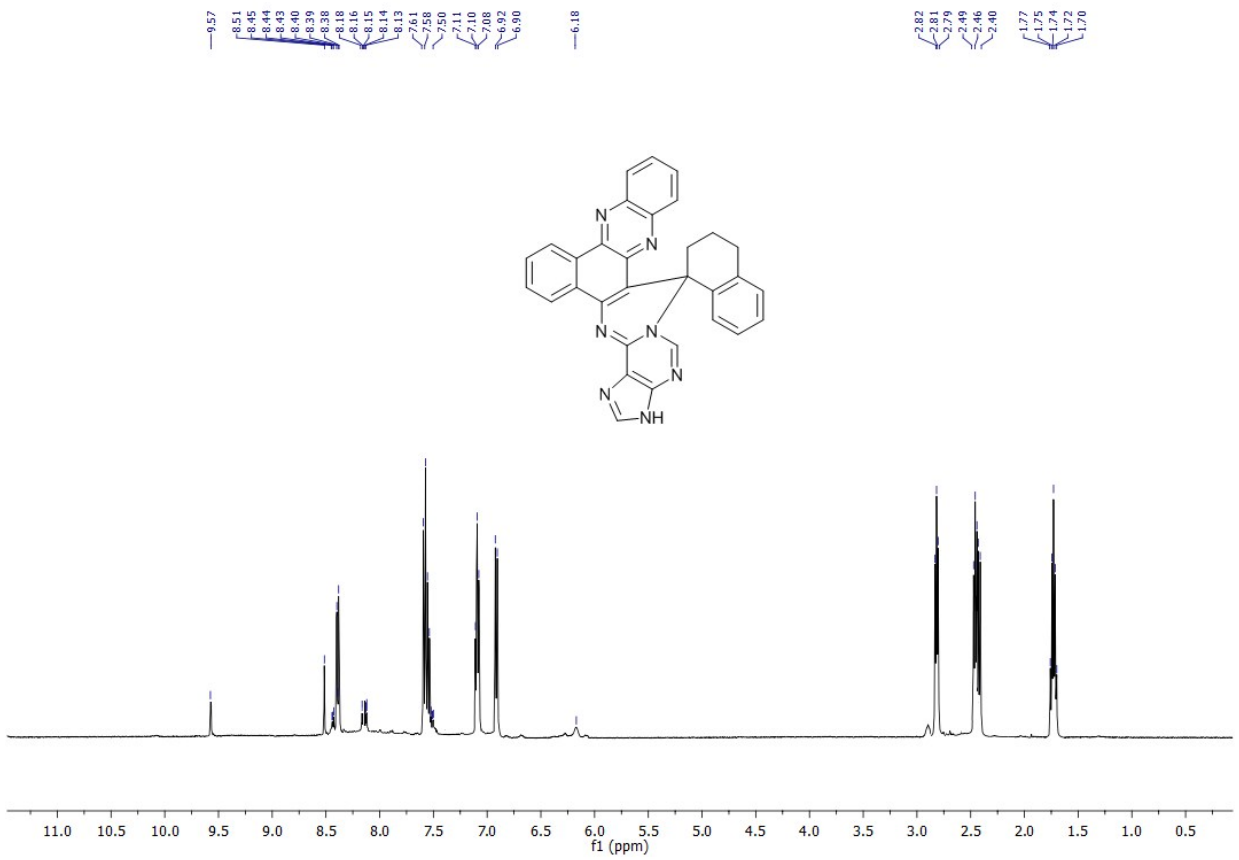
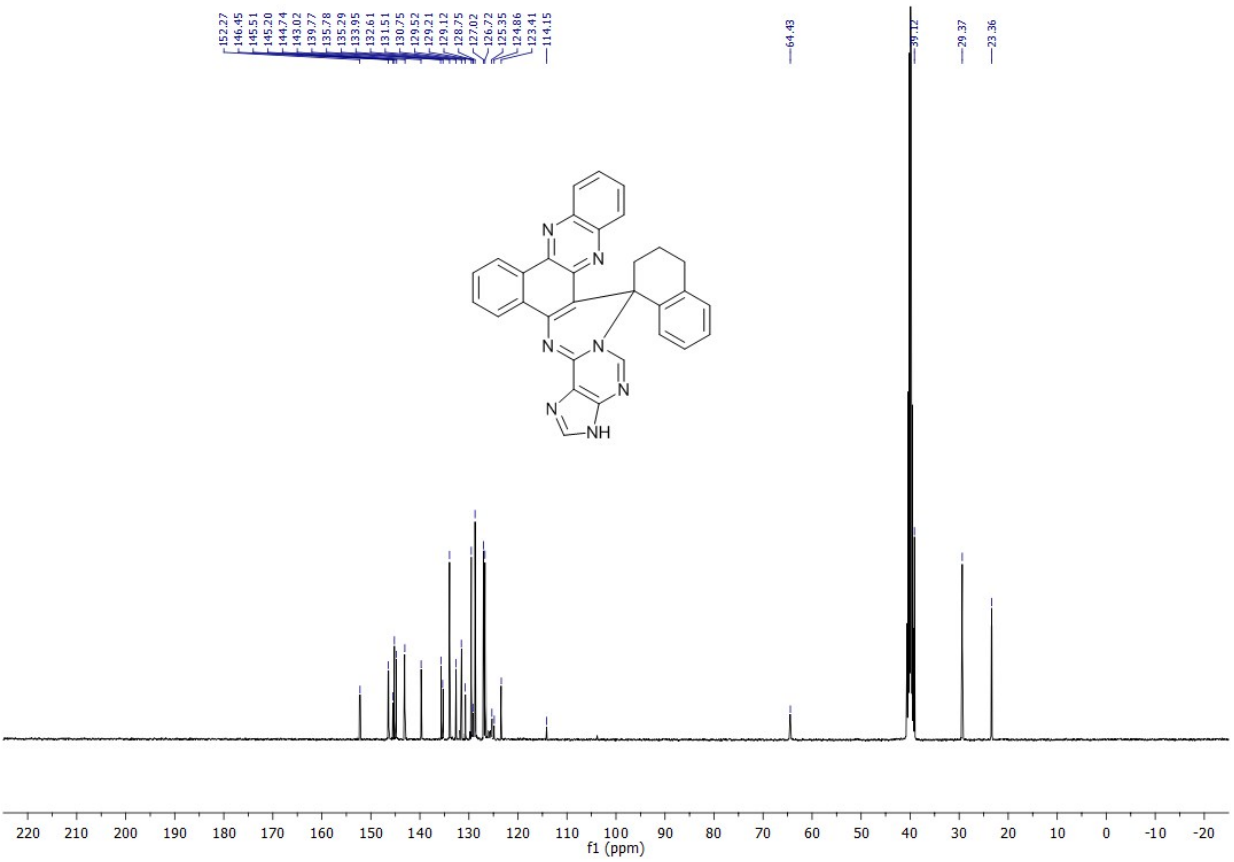
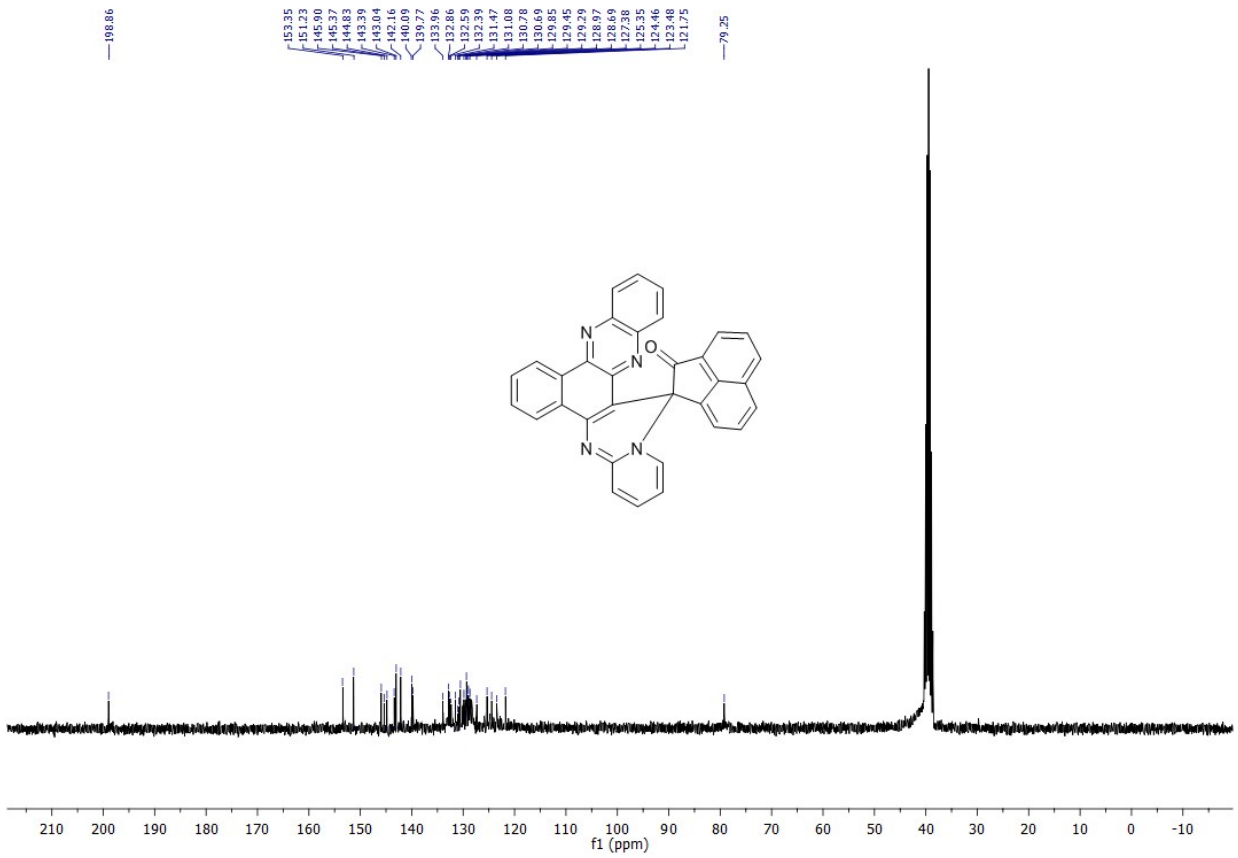


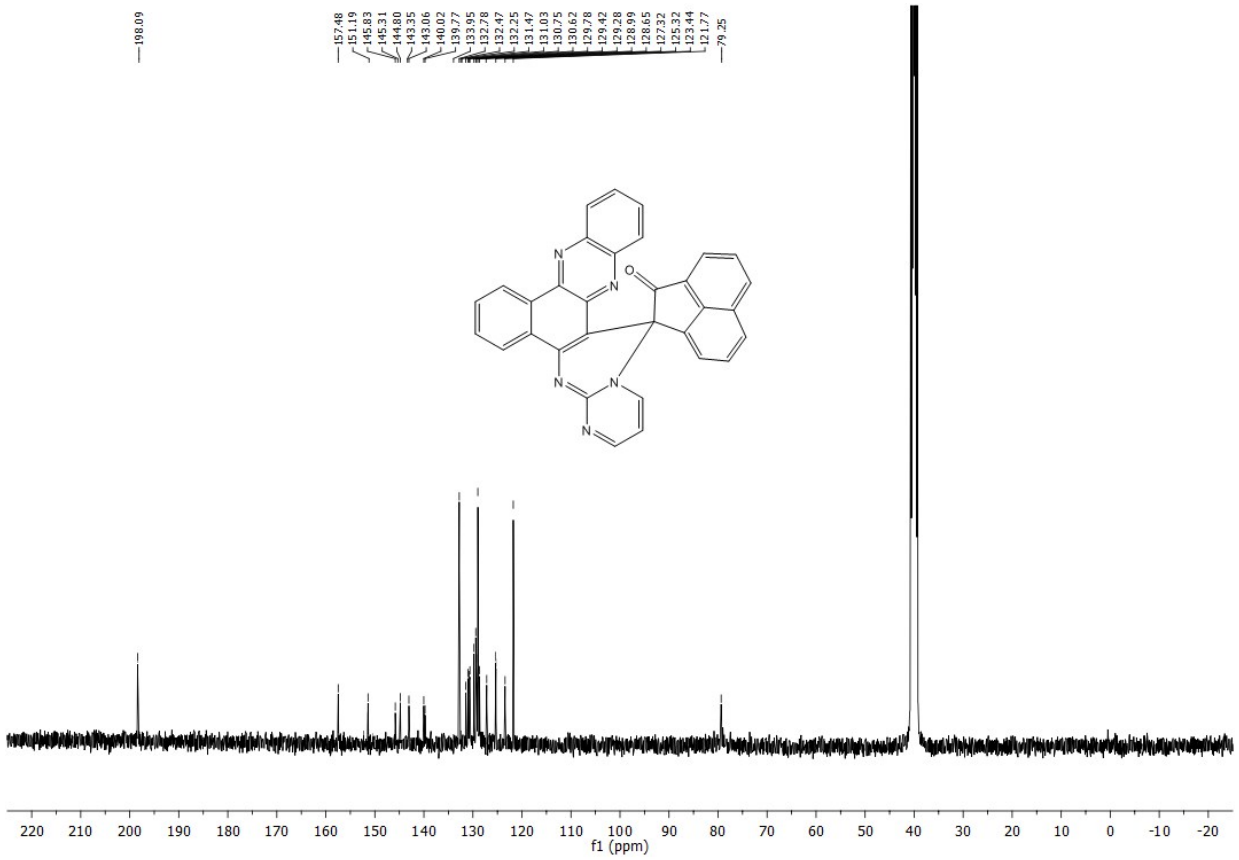
^{1}H spectra of (5be)



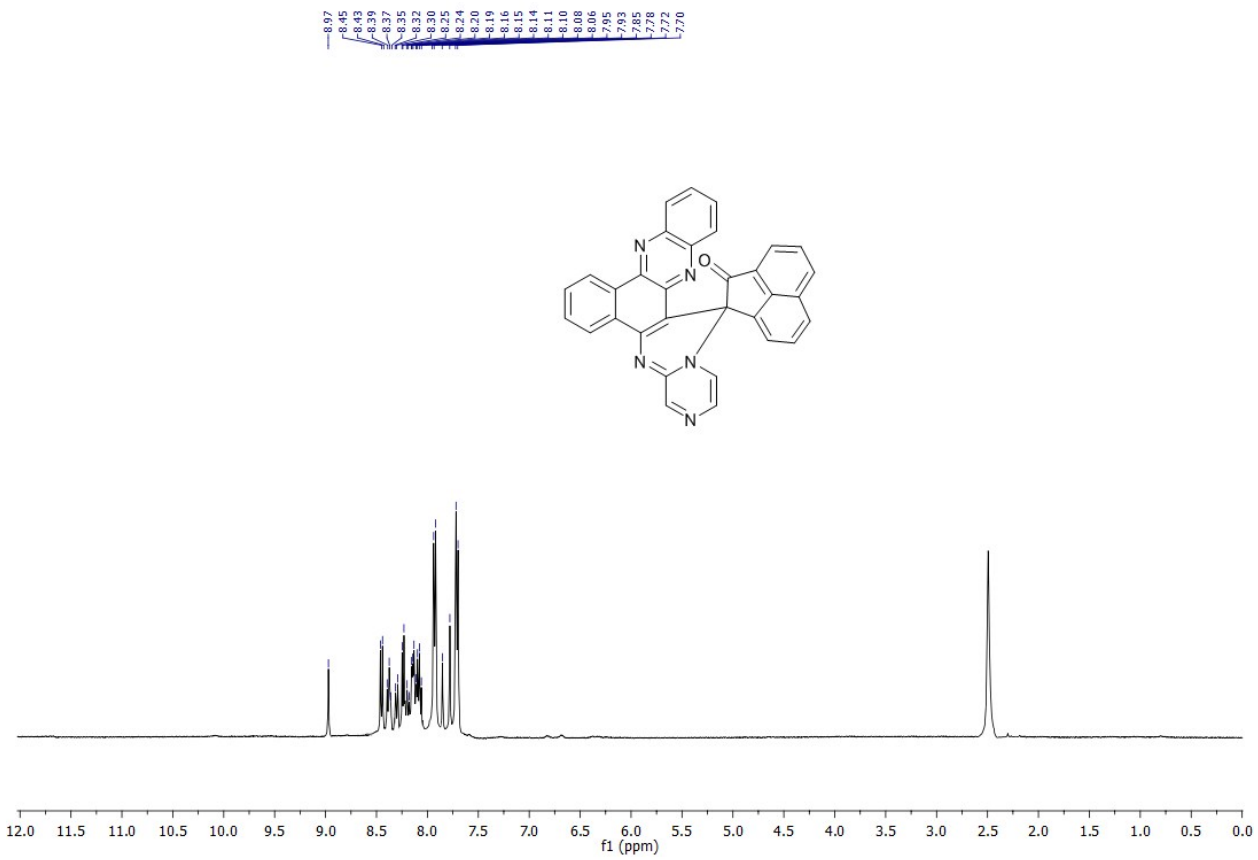
^{13}C spectra of (5be)



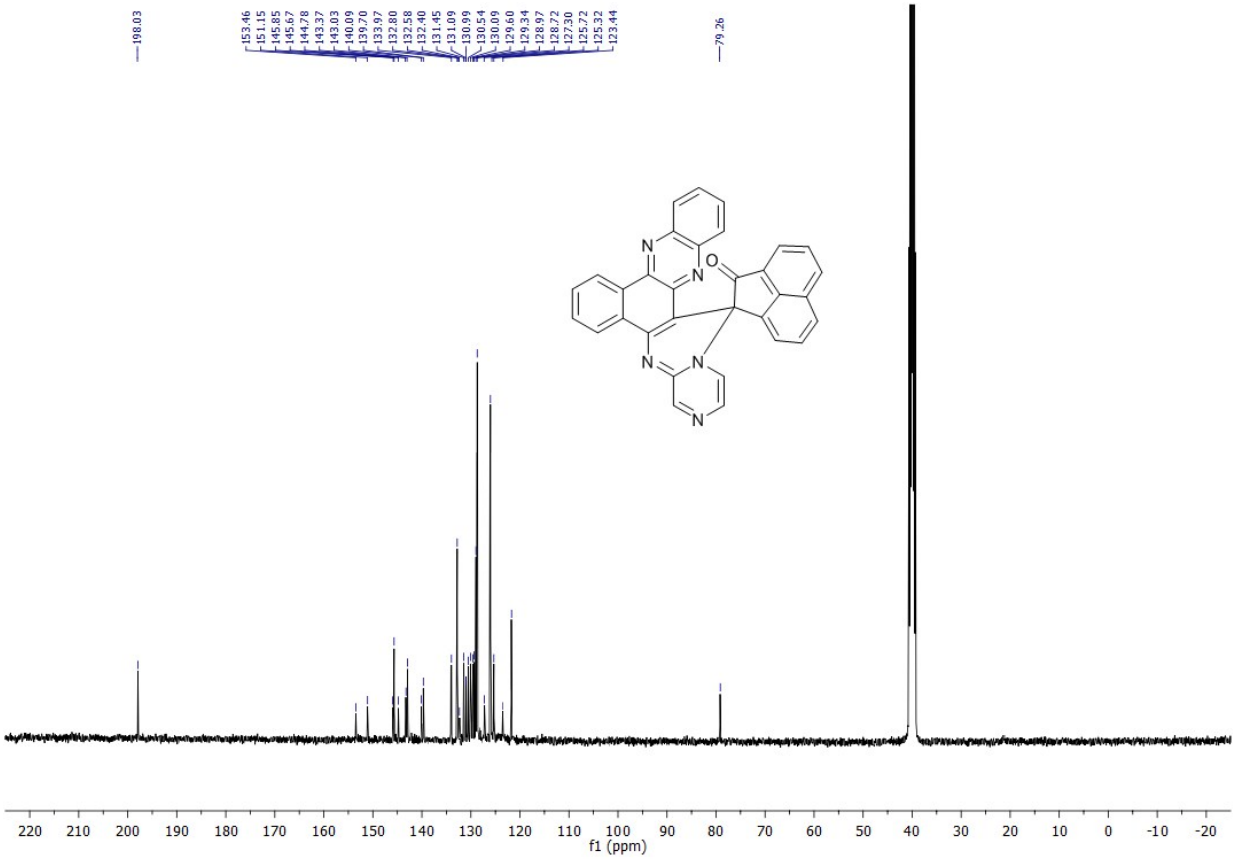
^{13}C spectra of (5ca)



^{13}C spectra of (5cb)



^{1}H spectra of (5cc)



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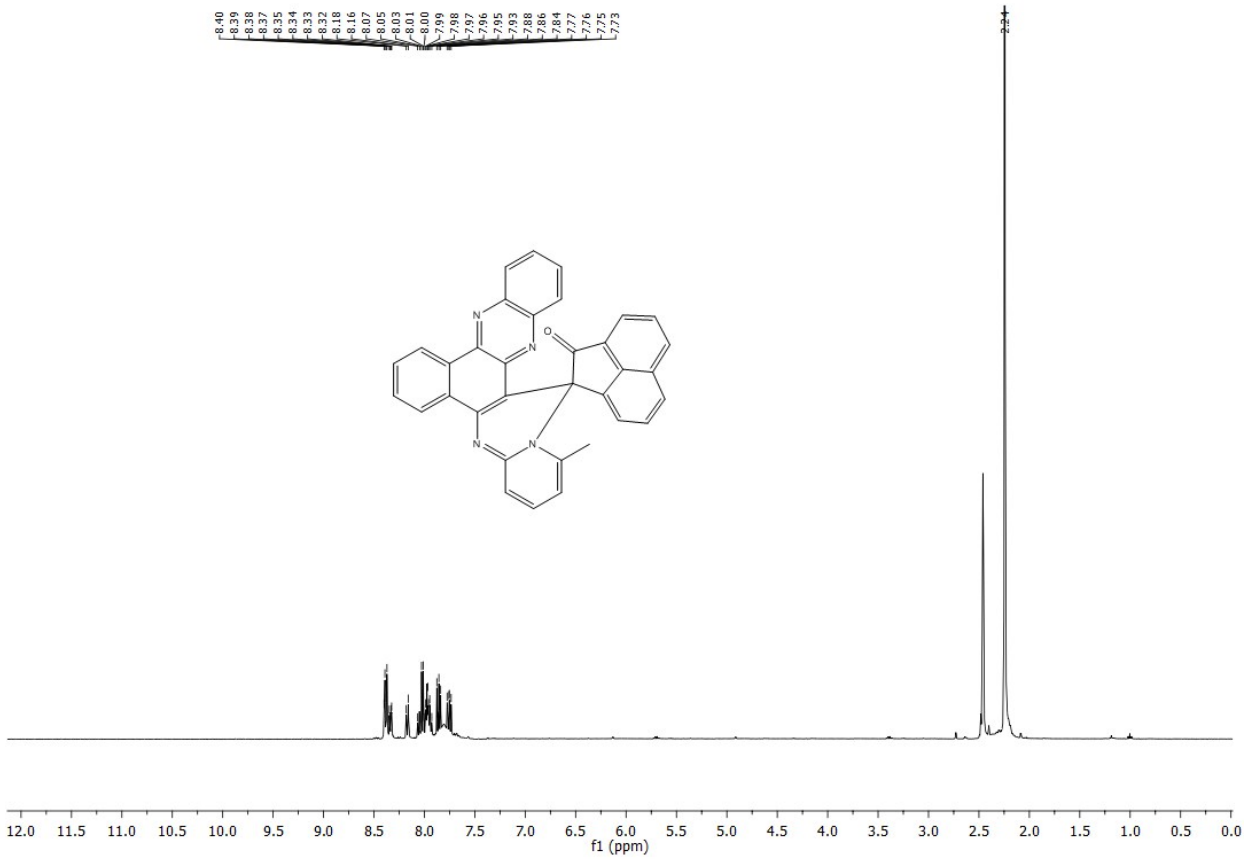
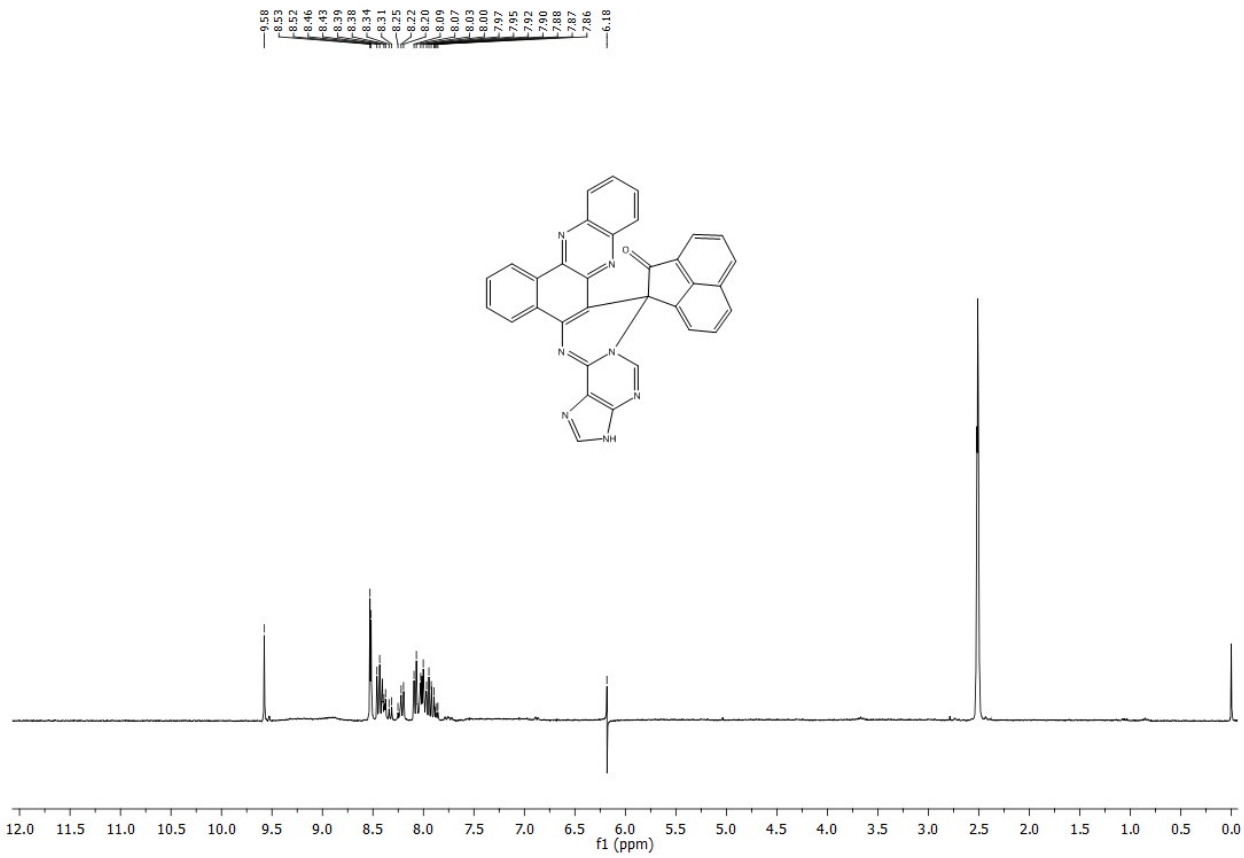
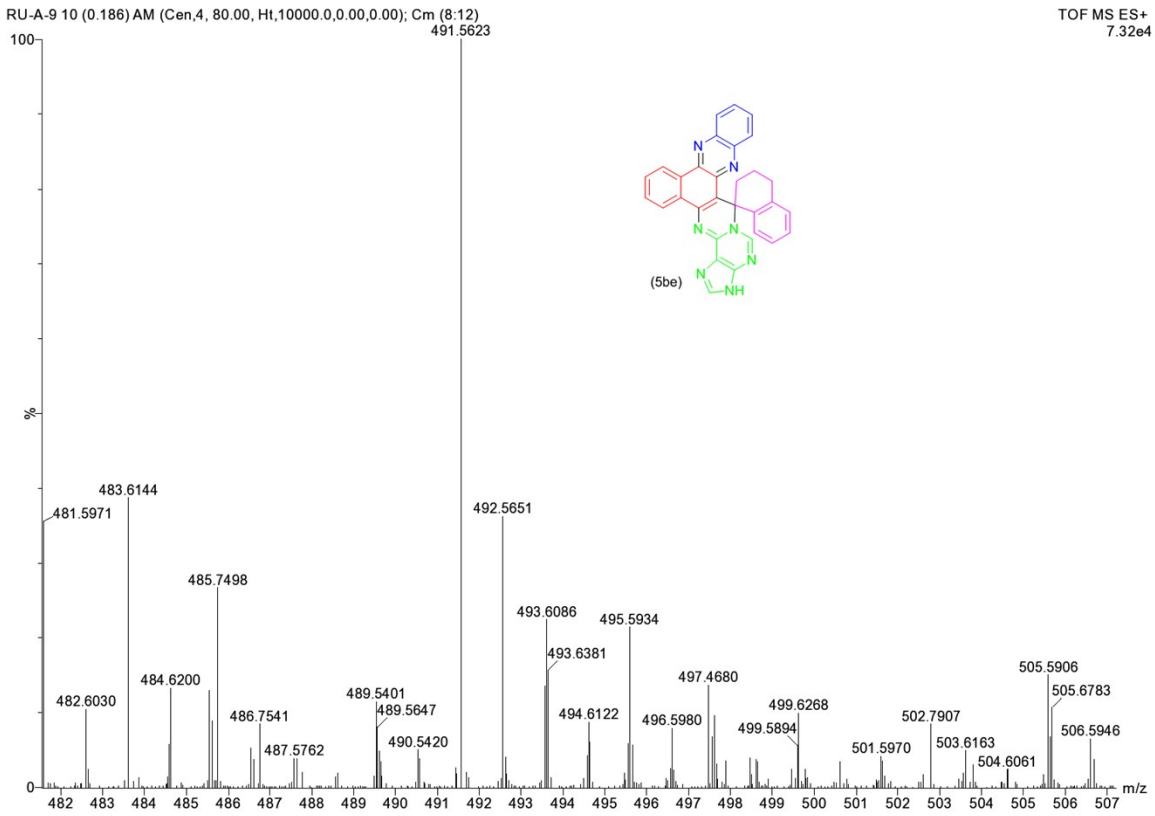


^{1}H spectra of (5cd)



^{1}H spectra of (5ce)



HR-MS Spectrum of (5be)