Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Design and Preparation of Glassy Molecular Precursors by Adjusting Molecular Structures for Facile Processing of High-Performance Polymers

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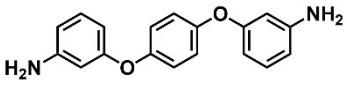
Contents

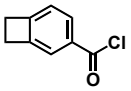
1. Structural analysis information.



3,3'-(1,4-phenylenebis(oxy))dianiline (303 mg, 35%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, J = 8.0 Hz, 2H), 7.02 (s, 4H), 6.46 – 6.37 (m, 4H), 6.34 (t, J = 2.2 Hz, 2H), 3.64 (s, 4H).

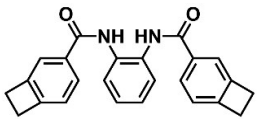
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 152.53, 147.99, 130.36, 120.56, 109.87, 108.30, 104.56.



bicyclo[4.2.0]octa-1,3,5-triene-3-carbonyl chloride (BCB-COCl)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.8, 1.6 Hz, 1H), 7.79 (s, 1H), 7.18 (d, J = 8.7 Hz, 1H), 3.25 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.78, 154.95, 146.52, 132.00, 131.22, 125.51, 123.04, 30.13, 29.35.

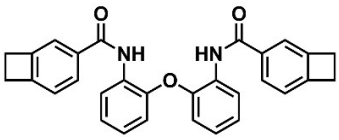


***N,N'*-(1,2-phenylene)bis(bicyclo[4.2.0]octa-1(6),2,4-triene-3-carboxamide) (*o*-1)** (287 mg, 78%)

^{1}H NMR (400 MHz, DMSO) δ 9.97 (s, 2H), 7.81 (dd, J = 7.7, 1.5 Hz, 2H), 7.69 – 7.61 (m, 4H), 7.29 (dd, J = 6.1, 3.6 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 3.19 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.50, 150.32, 145.97, 133.47, 131.83, 127.08, 126.23, 125.93, 123.11, 121.99, 29.84, 29.45.

HRMS (ESI) m/z for $C_{24}H_{21}O_2N_2$ $[M + H]^+$ calculated: 369.1598, found: 369.1598.

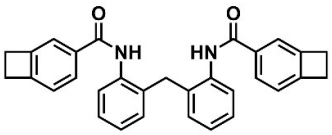


***N,N'*-(oxybis(2,1-phenylene))bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*o*-2a)** (267 mg, 58%)

^{1}H NMR (400 MHz, DMSO) δ 10.02 (s, 2H), 7.95 – 7.82 (m, 2H), 7.66 (d, J = 7.7 Hz, 2H), 7.50 (s, 2H), 7.22 – 7.10 (m, 6H), 6.95 – 6.85 (m, 2H), 3.16 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.47, 150.17, 147.94, 145.69, 133.39, 129.36, 127.31, 126.31, 125.37, 124.27, 122.85, 122.23, 118.41, 29.82, 29.39.

HRMS (ESI) m/z for $C_{30}H_{25}O_3N_2$ $[M + H]^+$ calculated: 461.1860, found: 461.1863.

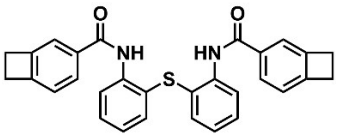


***N,N'*-(thiobis(2,1-phenylene))bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*o*-2b)** (284 mg, 62%)

^{1}H NMR (400 MHz, DMSO) δ 10.10 (s, 2H), 7.79 (dd, J = 7.7, 1.5 Hz, 2H), 7.27 (t, J = 7.7 Hz, 2H), 7.27 (m, 6H), 7.21 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 7.7 Hz, 2H), 3.92 (s, 2H), 3.19 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.63, 149.73, 145.62, 136.96, 135.78, 133.86, 130.37, 127.23, 127.08, 126.90, 126.31, 122.78, 122.17, 33.19, 30.17, 29.44.

HRMS (ESI) m/z for $C_{31}H_{27}O_2N_2$ $[M + H]^+$ calculated: 459.2067, found: 459.2071.

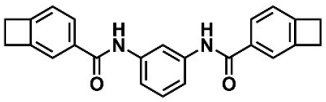


***N,N'*-(methylenebis(2,1-phenylene))bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*o*-2c)** (305 mg, 64%)

^{1}H NMR (400 MHz, DMSO) δ 9.84 (s, 2H), 7.80 – 7.70 (m, 4H), 7.57 (s, 2H), 7.41 – 7.31 (m, 2H), 7.24 – 7.15 (m, 2H), 3.19 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.33, 150.20, 145.86, 138.34, 133.33, 132.46, 129.48, 128.76, 127.23, 126.79, 126.17, 122.98, 122.10, 29.84, 29.47.

HRMS (ESI) m/z for $C_{30}H_{25}O_2N_2S$ $[M + H]^+$ calculated: 477.1631, found: 477.1633.

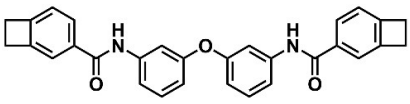


***N,N′*-(1,3-phenylene)bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*m*-1)** (265 mg, 72%)

^{1}H NMR (400 MHz, DMSO) δ 10.19 (s, 2H), 8.32 (t, J = 2.0 Hz, 1H), 7.83 (dd, J = 7.7, 1.5 Hz, 2H), 7.69 (t, J = 1.2 Hz, 2H), 7.48 (dd, J = 8.1, 2.0 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.24 (dd, J = 7.6, 1.0 Hz, 2H), 3.21 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.49, 149.85, 145.65, 139.94, 134.26, 128.92, 127.32, 122.85, 122.23, 116.32, 113.30, 29.83, 29.47.

HRMS (ESI) m/z for $C_{24}H_{21}O_2N_2$ $[M + H]^+$ calculated: 369.1598, found: 369.1599.

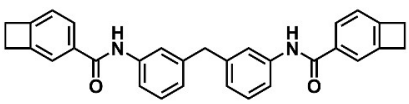


***N,N′*-(oxybis(3,1-phenylene))bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*m*-2a)** (281 mg, 61%)

^{1}H NMR (400 MHz, DMSO) δ 10.23 (s, 1H), 7.78 (d, J = 7.7 Hz, 1H), 7.67 – 7.54 (m, 2H), 7.36 (t, J = 8.1 Hz, 1H), 7.22 (d, J = 7.7 Hz, 1H), 6.79 (dd, J = 8.1, 1.5 Hz, 1H), 3.20 (s, 4H).

^{13}C NMR (101 MHz, DMSO) δ 166.66, 157.29, 150.02, 145.69, 141.42, 134.06, 130.39, 127.31, 122.90, 122.20, 115.52, 114.25, 110.70, 29.84, 29.46.

HRMS (ESI) m/z for $C_{30}H_{25}O_3N_2$ $[M + H]^+$ calculated: 461.1860, found: 461.1866.

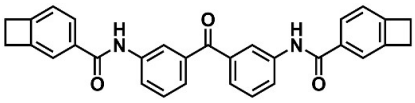


***N,N′*-(methylenebis(3,1-phenylene))bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*m*-2b)** (321 mg, 70%)

^{1}H NMR (400 MHz, DMSO) δ 10.10 (s, 2H), 7.79 (dd, J = 7.7, 1.4 Hz, 2H), 7.65 (s, 4H), 7.64 (s, 2H), 7.27 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 7.6 Hz, 2H), 3.93 (s, 2H), 3.20 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.47, 149.83, 145.64, 142.01, 139.93, 134.24, 129.06, 127.26, 124.49, 122.85, 122.18, 121.03, 118.55, 41.96, 29.82, 29.45.

HRMS (ESI) m/z for $C_{31}H_{27}O_2N_2$ $[M + H]^+$ calculated: 459.2067, found: 459.2070.

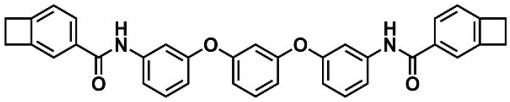


***N,N′*-(carbonylbis(3,1-phenylene))bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*m*-2c)** (392 mg, 83%)

^{1}H NMR (400 MHz, DMSO) δ 10.40 (s, 2H), 8.23 (s, 2H), 8.16 (d, J = 7.0 Hz, 2H), 7.83 (d, J = 7.7 Hz, 2H), 7.69 (s, 2H), 7.56 (t, J = 7.9 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 3.21 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 196.05, 166.77, 150.16, 145.75, 140.05, 137.95, 133.88, 129.37, 127.36, 125.14, 124.53, 122.94, 122.24, 121.60, 29.87, 29.46.

HRMS (ESI) m/z for $C_{31}H_{25}O_3N_2$ $[M + H]^+$ calculated: 473.1860, found: 473.1866.

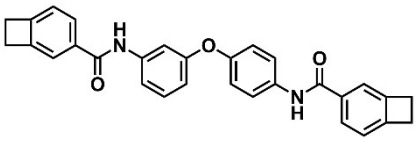


***N,N′*-((1,3-phenylenebis(oxy))bis(3,1-phenylene))bis(bicyclo[4.2.0]octa-1(6),2,4-triene-3-carboxamide) (*m*-3)** (304 mg, 55%)

^{1}H NMR (400 MHz, DMSO) δ 10.22 (s, 2H), 7.78 (dd, J = 7.7, 1.5 Hz, 2H), 7.64 (s, 2H), 7.62 (t, J = 2.2 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.41 (t, J = 8.2 Hz, 1H), 7.35 (t, J = 8.1 Hz, 2H), 7.22 (d, J = 6.7 Hz, 2H), 6.80 (dd, J = 8.3, 2.4 Hz, 4H), 6.70 (t, J = 2.3 Hz, 1H), 3.20 (s,8H).

^{13}C NMR (101 MHz, DMSO) δ 166.68, 158.50, 156.72, 150.03, 145.70, 141.45, 134.05, 131.60, 130.44, 127.30, 122.90, 122.19, 115.88, 114.35, 113.73, 110.94, 109.34, 29.85, 29.45.

HRMS (ESI) m/z for $C_{36}H_{29}O_4N_2$ $[M + H]^+$ calculated: 553.2122, found: 553.2128.

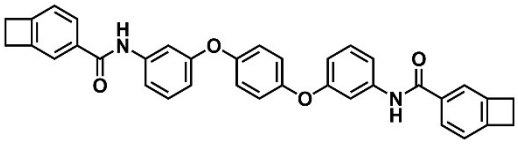


***N*-(3-(4-(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamido)phenoxy)phenyl)bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide (*mp*-2)** (336 mg, 73%)

^{1}H NMR (400 MHz, DMSO) δ 10.19 (s, 2H), 7.82 (d, J = 9.0 Hz, 3H), 7.78 (d, J = 6.2 Hz, 1H), 7.66 (d, J = 15.4 Hz, 2H), 7.55 (d, J = 6.2 Hz, 1H), 7.51 (t, J = 2.2 Hz, 1H), 7.33 (t, J = 8.1 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.07 (d, J = 9.0 Hz, 2H), 6.74 (dd, J = 9.1, 2.5 Hz, 1H), 3.21 (s, 4H), 3.20 (s, 4H).

^{13}C NMR (101 MHz, DMSO) δ 166.64, 166.40, 158.15, 152.23, 149.98, 149.85, 145.68, 141.34, 135.81, 134.24, 134.10, 130.29, 127.30, 127.25, 122.89, 122.35, 122.19, 122.15, 120.01, 115.00, 113.38, 109.74, 29.84, 29.46.

HRMS (ESI) m/z for $C_{30}H_{25}O_3N_2$ $[M + H]^+$ calculated: 461.1860, found: 461.1856.

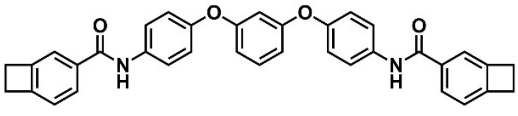


***N,N′*-((1,4-phenylenebis(oxy))bis(3,1-phenylene))bis(bicyclo[4.2.0]octa-1(6),2,4-triene-3-carboxamide) (*mp*-3a)** (409 mg, 74%)

^{1}H NMR (400 MHz, DMSO) δ 10.22 (s, 2H), 7.78 (d, J = 7.7 Hz, 2H), 7.65 (s, 2H), 7.58 (d, J = 7.9 Hz, 4H), 7.34 (t, J = 7.9 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 7.11 (s, 4H), 6.76 (d, J = 8.4 Hz, 2H), 3.20 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.67, 157.80, 152.63, 150.02, 145.69, 141.41, 134.07, 130.39, 127.32, 122.90, 122.21, 121.03, 115.30, 113.61, 110.15, 29.85, 29.46.

HRMS (ESI) m/z for $C_{36}H_{28}O_4N_2Na$ $[M + Na]^+$ calculated: 575.1941, found: 575.1951.

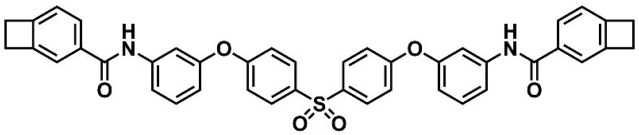


***N,N′*-((1,3-phenylenebis(oxy))bis(4,1-phenylene))bis(bicyclo[4.2.0]octa-1(6),2,4-triene-3-carboxamide) (*mp*-3b)** (414 mg, 75%)

^{1}H NMR (400 MHz, DMSO) δ 10.17 (s, 2H), 7.80 (t, J = 9.6 Hz, 6H), 7.67 (s, 2H), 7.24 (d, J = 8.6 Hz, 2H), 7.03 (s, 4H), 7.02 (s, 4H), 3.21 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 167.69, 153.11, 153.06, 149.85, 145.69, 135.89, 134.21, 127.24, 122.90, 122.41, 122.15, 120.26, 119.13, 29.84, 29.47.

HRMS (ESI) m/z for $C_{36}H_{29}O_4N_2$ $[M + H]^+$ calculated: 553.2122, found: 553.2131.

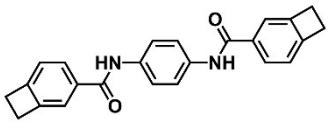


***N,N′*-(((sulfonylbis(4,1-phenylene))bis(oxy))bis(3,1-phenylene))bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*mp*-4)** (616 mg, 89%)

^{1}H NMR (400 MHz, DMSO) δ 10.27 (s, 2H), 7.95 (d, *J* = 8.9 Hz, 4H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 4H), 7.41 (t, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 4H), 6.87 (d, *J* = 8.1 Hz, 2H), 3.18 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.72, 161.75, 155.12, 150.12, 145.73, 141.70, 135.73, 133.94, 130.85, 130.37, 127.31, 122.92, 122.19, 118.52, 117.02, 115.50, 111.93, 29.85, 29.45.

HRMS (ESI) m/z for $C_{42}H_{33}O_6N_2S$ $[M + H]^+$ calculated: 693.2054, found: 693.2065.

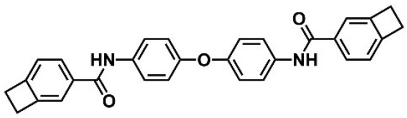


***N,N′*-(1,4-phenylene)bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*p*-1)** (298 mg, 81%)

^{1}H NMR (400 MHz, DMSO) δ 10.14 (s, 2H), 7.82 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.74 (s, 4H), 7.68 (s, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 3.21 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.27, 149.79, 145.67, 135.45, 134.28, 127.23, 122.89, 122.15, 120.96, 29.84, 29.47.

HRMS (ESI) m/z for $C_{24}H_{21}O_2N_2$ $[M + H]^+$ calculated: 369.1598, found: 369.1602.

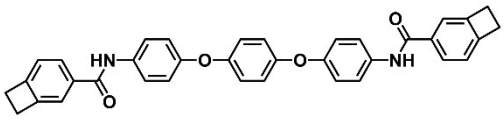


***N,N′*-(oxybis(4,1-phenylene))bis(bicyclo[4.2.0]octa-1,3,5-triene-3-carboxamide) (*p*-2)** (341 mg, 74%)

^{1}H NMR (400 MHz, DMSO) δ 10.16 (s, 2H), 7.85 – 7.75 (m, 6H), 7.67 (s, 2H), 7.24 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 9.0 Hz, 4H), 3.21 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.33, 153.22, 149.83, 145.69, 135.32, 134.23, 127.23, 122.89, 122.41, 122.14, 119.02, 29.84, 29.47.

HRMS (ESI) m/z for $C_{30}H_{25}O_3N_2$ $[M + H]^+$ calculated: 461.1860, found: 461.1854.



***N,N′*-((1,4-phenylenebis(oxy))bis(4,1-phenylene))bis(bicyclo[4.2.0]octa-1(6),2,4-triene-3-carboxamide) (*p*-3)** (419 mg, 76%)

^{1}H NMR (400 MHz, DMSO) δ 10.19 (s, 2H), 7.80 (d, J = 9.0 Hz, 6H), 7.66 (s, 2H), 7.35 (t, J = 8.2 Hz, 1H), 7.23 (d, J = 7.7 Hz, 2H), 7.08 (d, J = 9.0 Hz, 4H), 6.69 (dd, J = 8.2, 2.4 Hz, 2H), 6.58 (t, J = 2.3 Hz, 1H), 3.21 (s, 8H).

^{13}C NMR (101 MHz, DMSO) δ 166.90, 160.49, 153.77, 149.87, 144.67, 135.58, 134.19, 128.06, 124.35, 122.37, 120.13, 111.77, 108.05, 30.39, 28.80.

HRMS (ESI) m/z for $C_{36}H_{29}O_4N_2$ $[M + H]^+$ calculated: 553.2122, found: 553.2132.

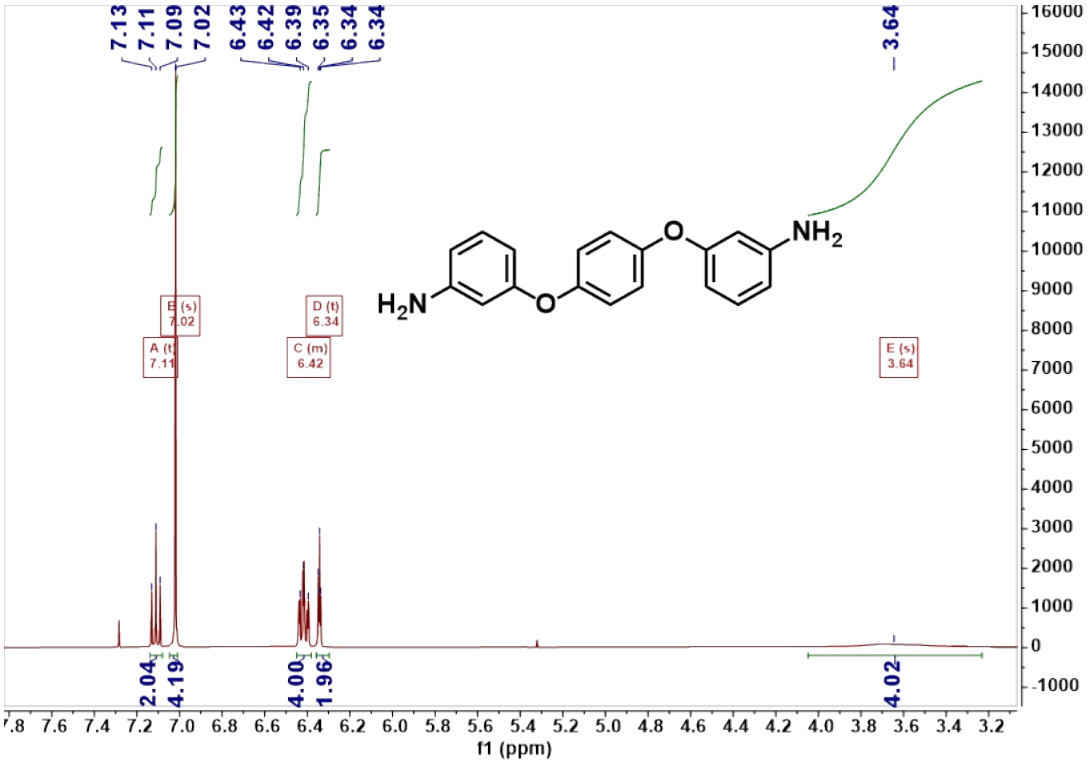


Figure S1. ^{1}H NMR spectrum of 3,3'-(1,4-phenylenebis(oxy))dianiline in $CDCl_3$.

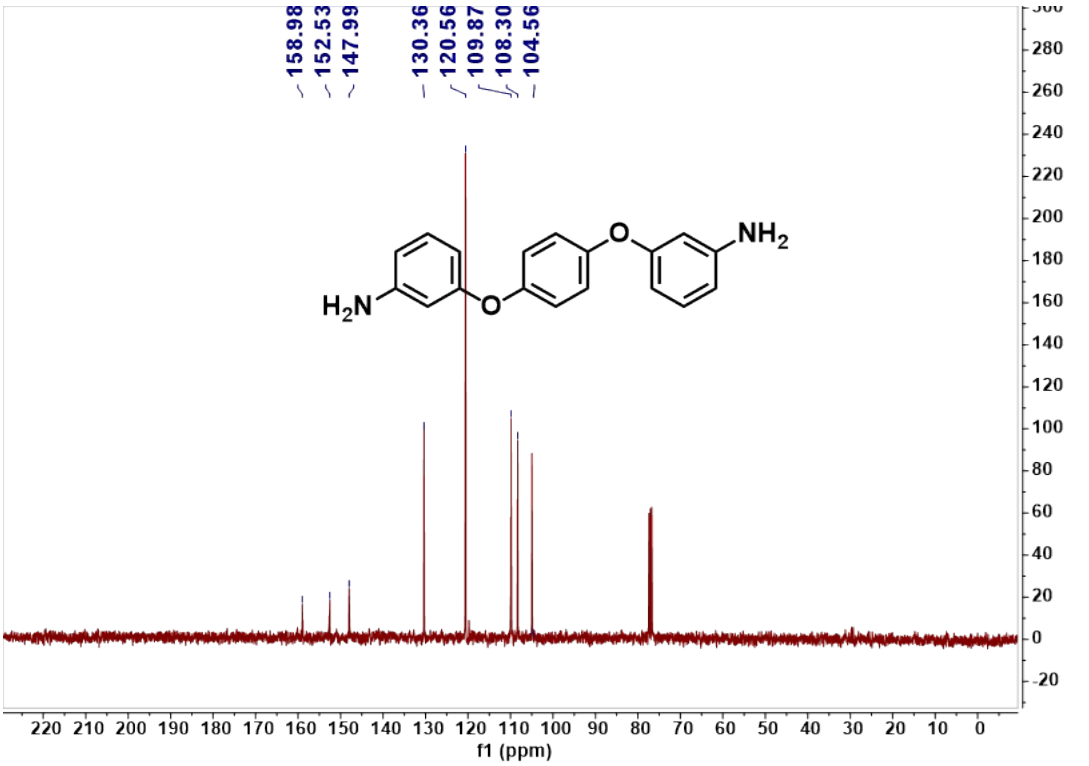


Figure S2. ^{13}C NMR spectrum of 3,3'-(1,4-phenylenebis(oxy))dianiline in $CDCl_3$.

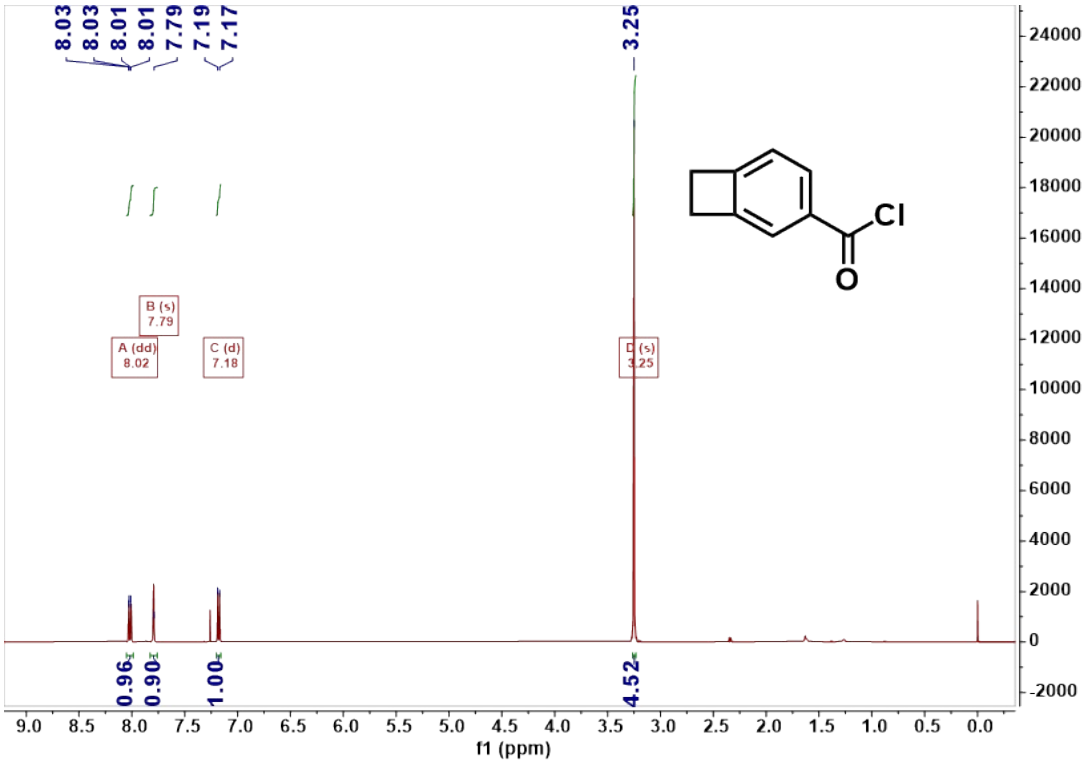


Figure S3. ^{1}H NMR spectrum of BCB-COCl in $CDCl_3$.

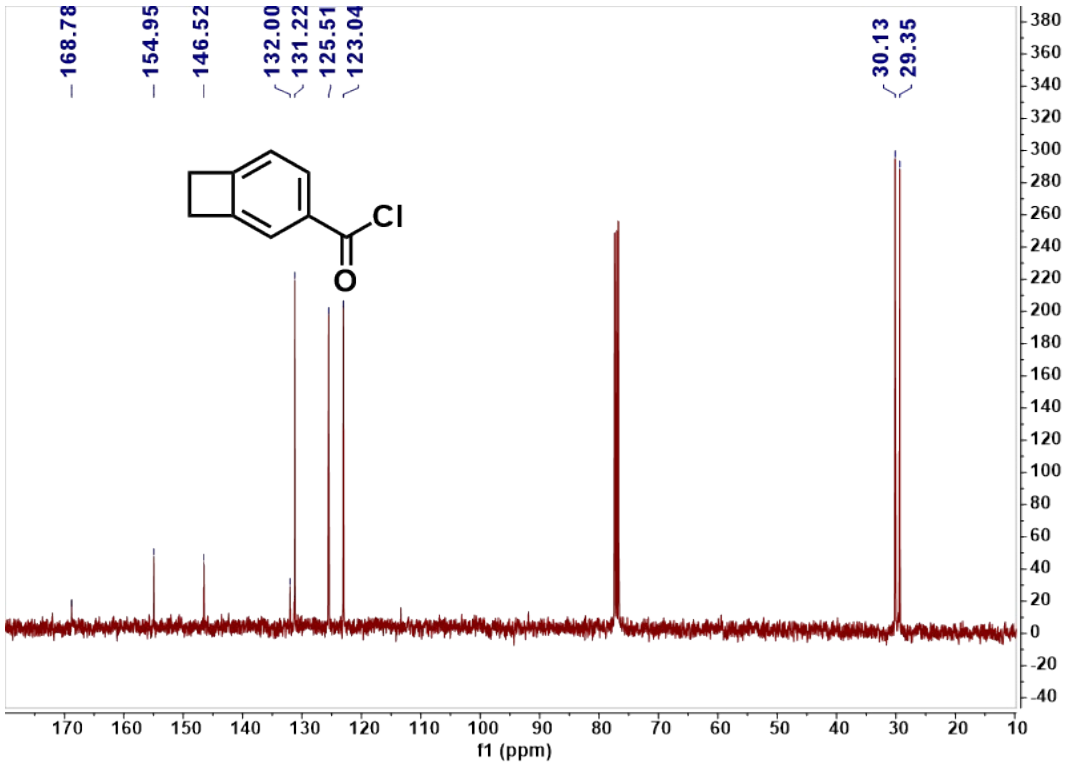


Figure S4. ^{13}C NMR spectrum of BCB-COCl in $CDCl_3$.

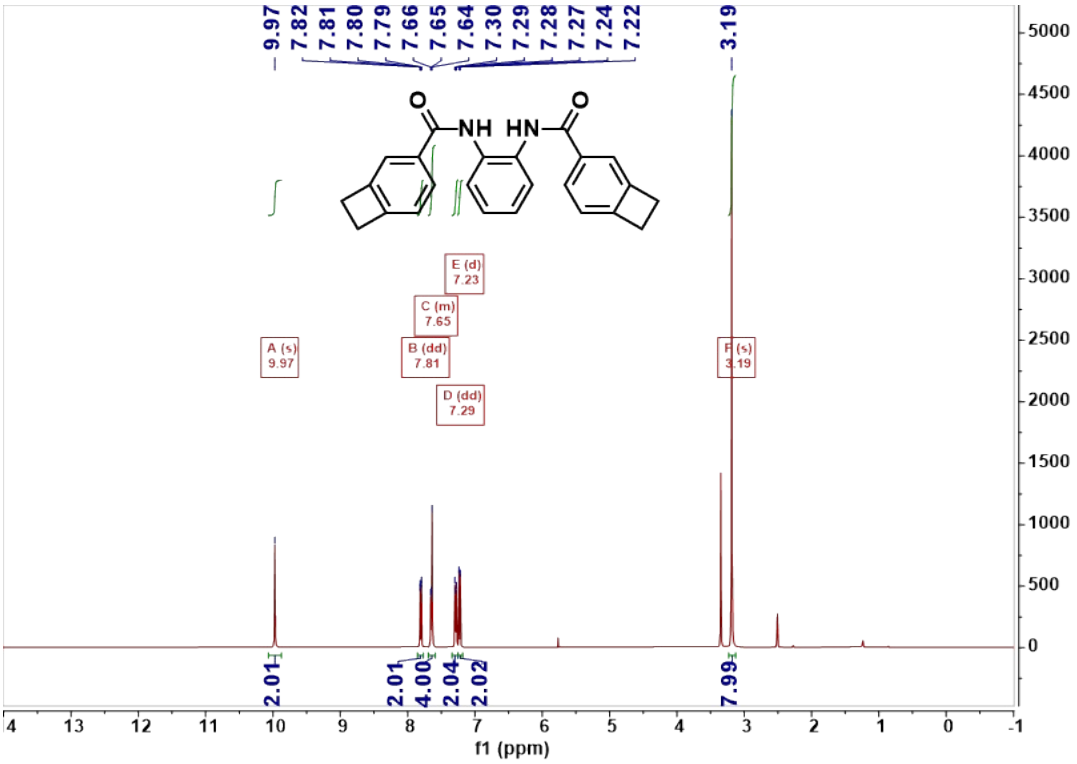


Figure S5. ^{1}H NMR spectrum of ***o*-1** in DMSO-d_6.

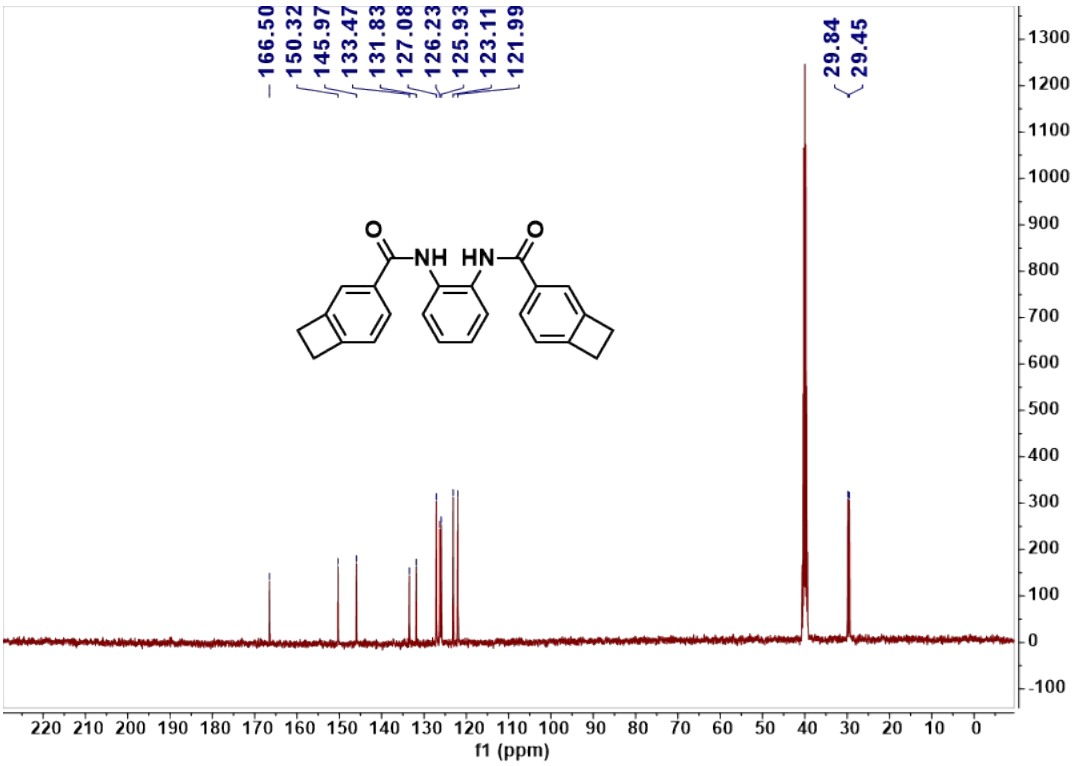


Figure S6. ^{13}C NMR spectrum of ***o*-1** in DMSO-d_6.

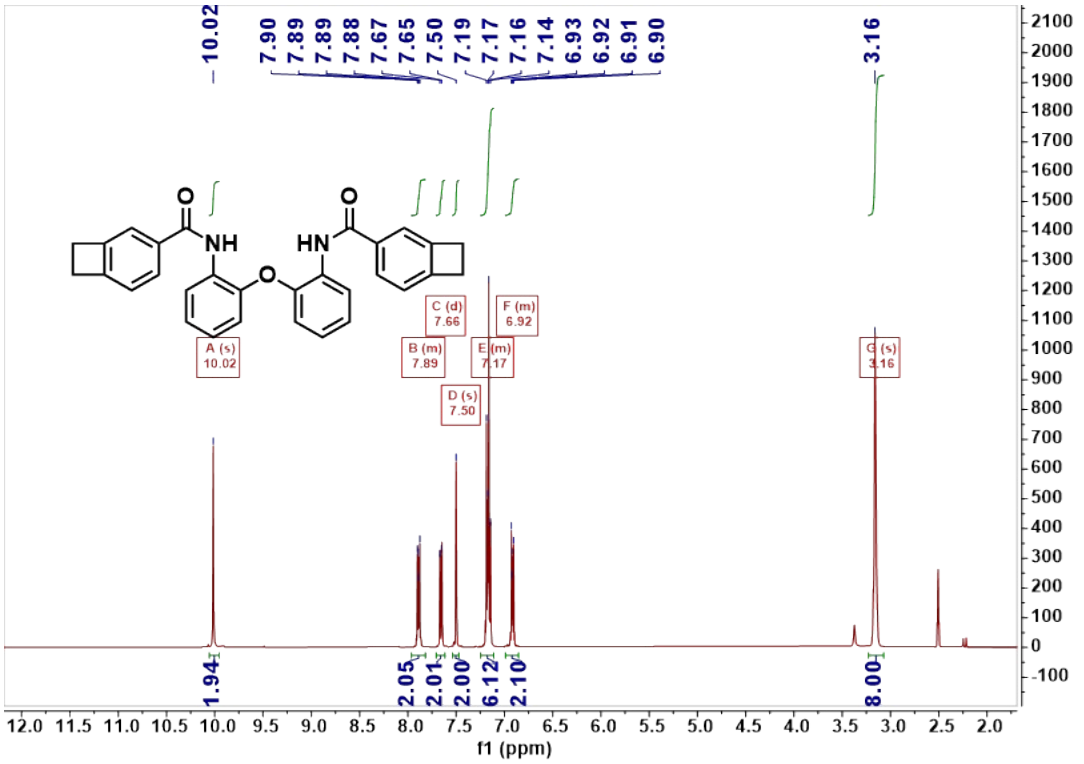


Figure S7. ^{1}H NMR spectrum of ***o*-2a** in DMSO-d_6.

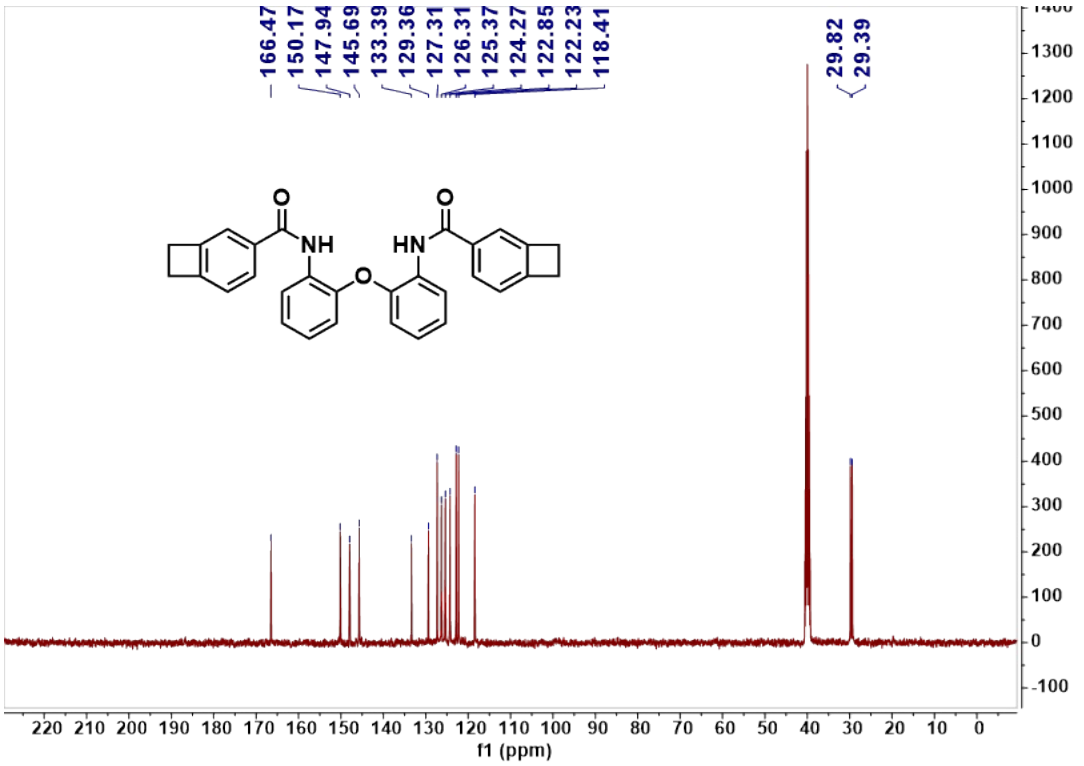


Figure S8. ^{13}C NMR spectrum of ***o*-2a** in DMSO-d_6.

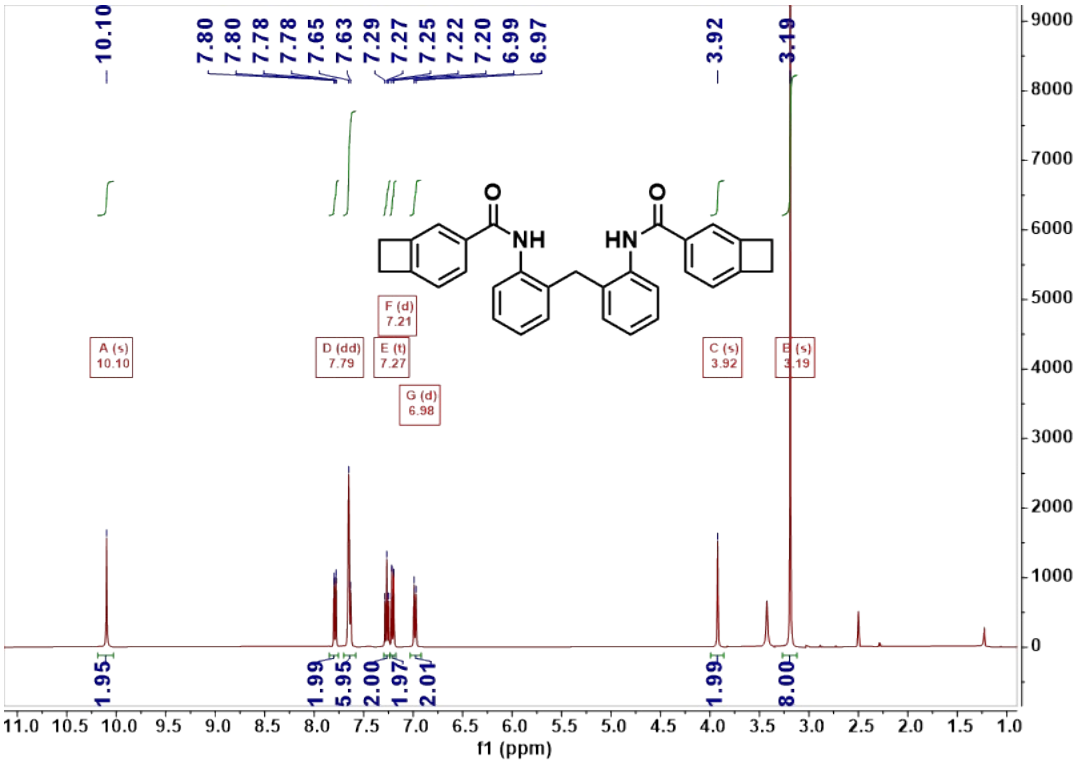


Figure S9. ^{1}H NMR spectrum of ***o*-2b** in DMSO-d_6.

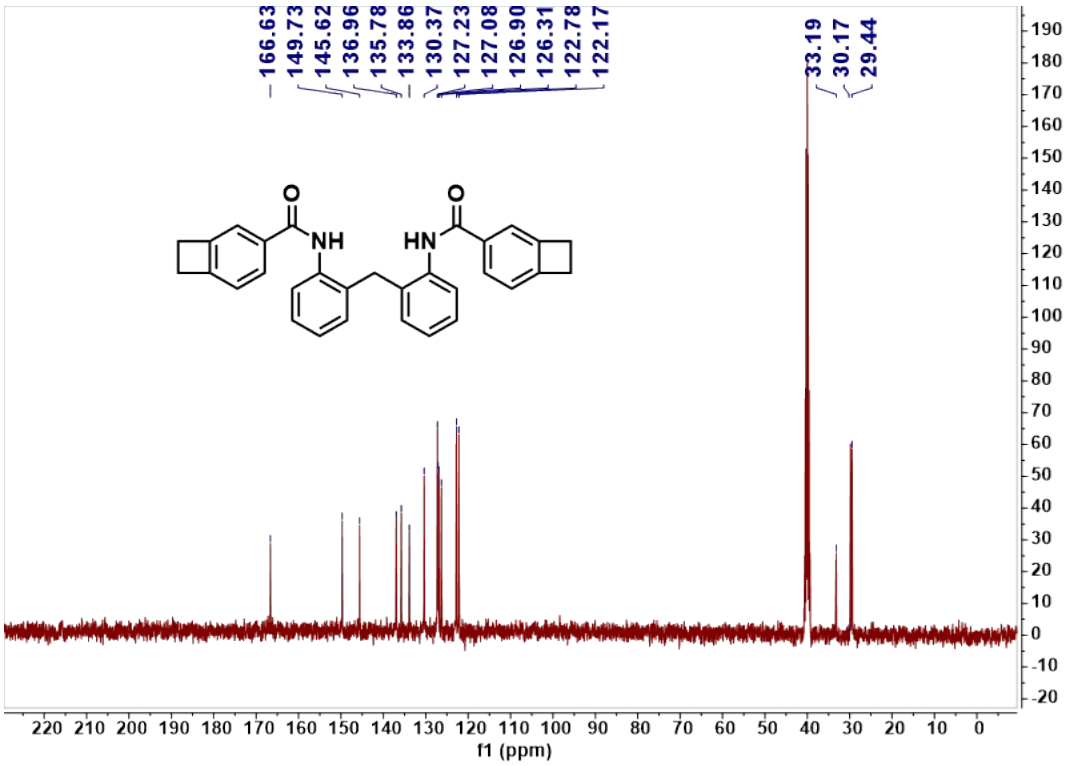


Figure S10. ^{13}C NMR spectrum of ***o*-2b** in DMSO-d_6.

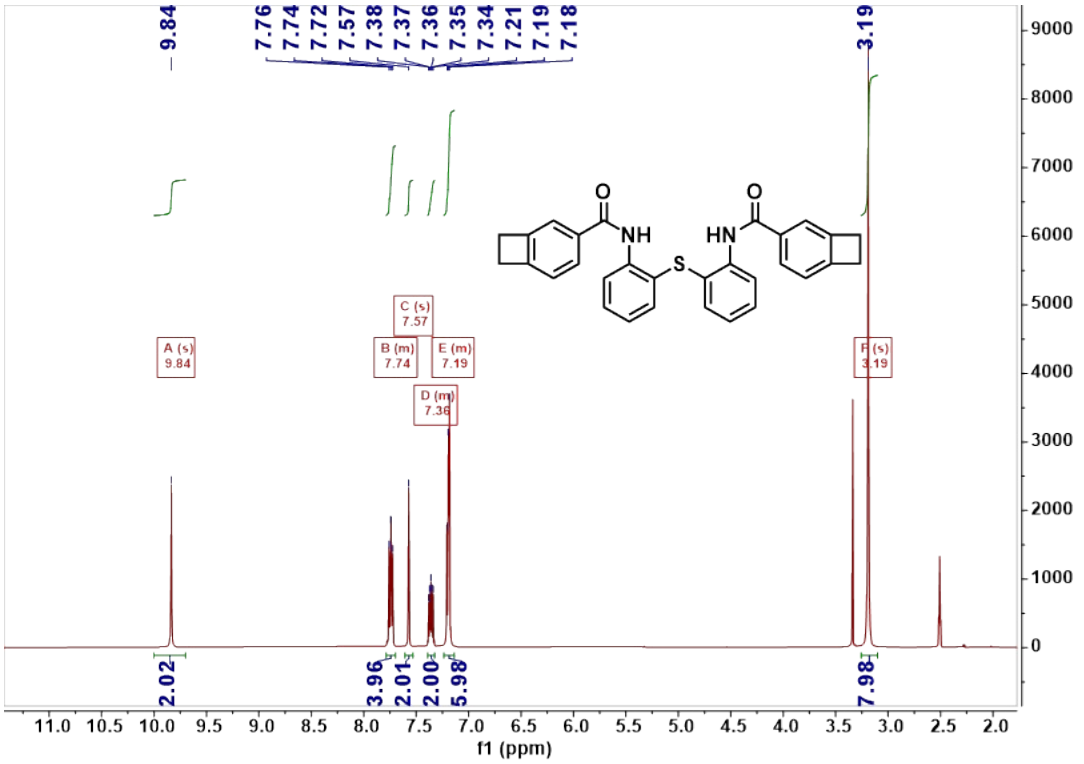


Figure S11. ^{1}H NMR spectrum of ***o*-2c** in DMSO-d_6.

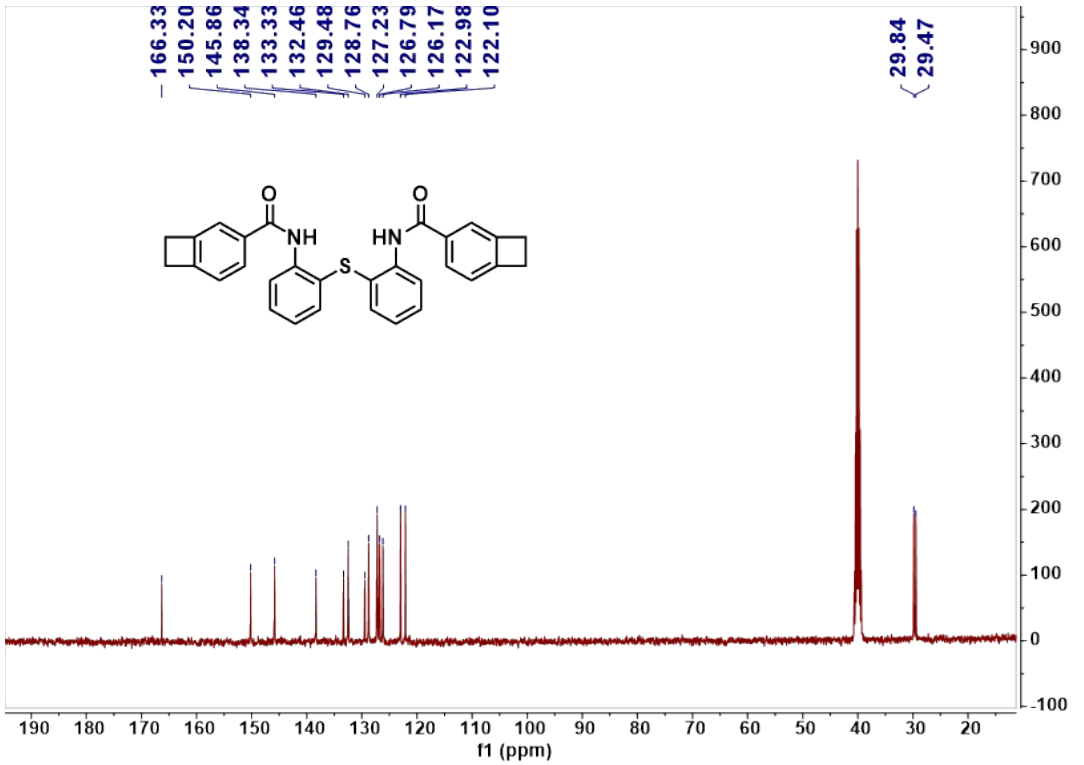


Figure S12. ^{13}C NMR spectrum of ***o*-2c** in DMSO-d_6.

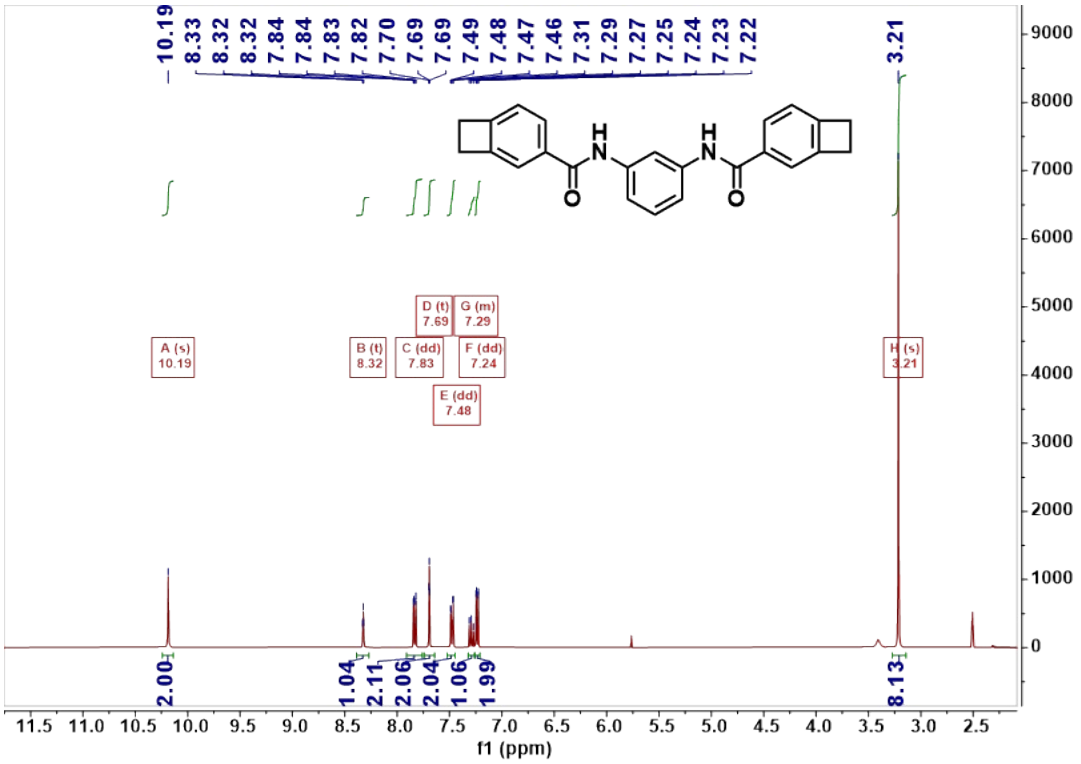


Figure S13. ^{1}H NMR spectrum of ***m*-1** in DMSO-d_6.

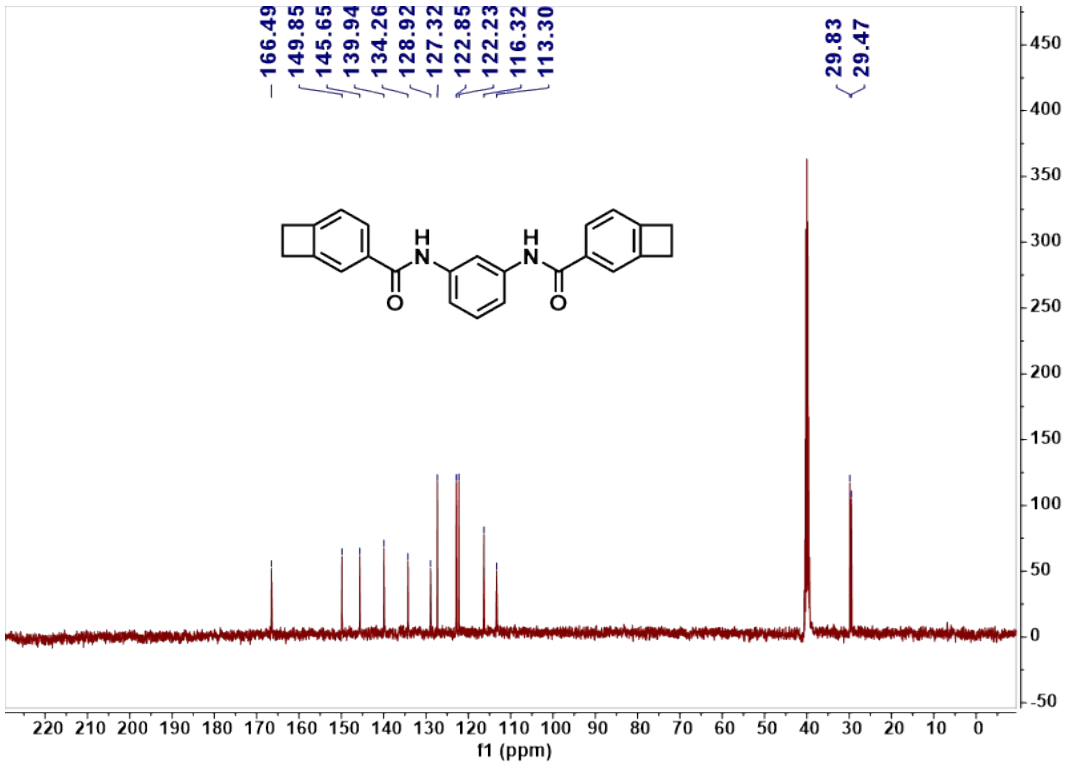


Figure S14. ^{13}C NMR spectrum of ***m*-1** in DMSO-d_6.

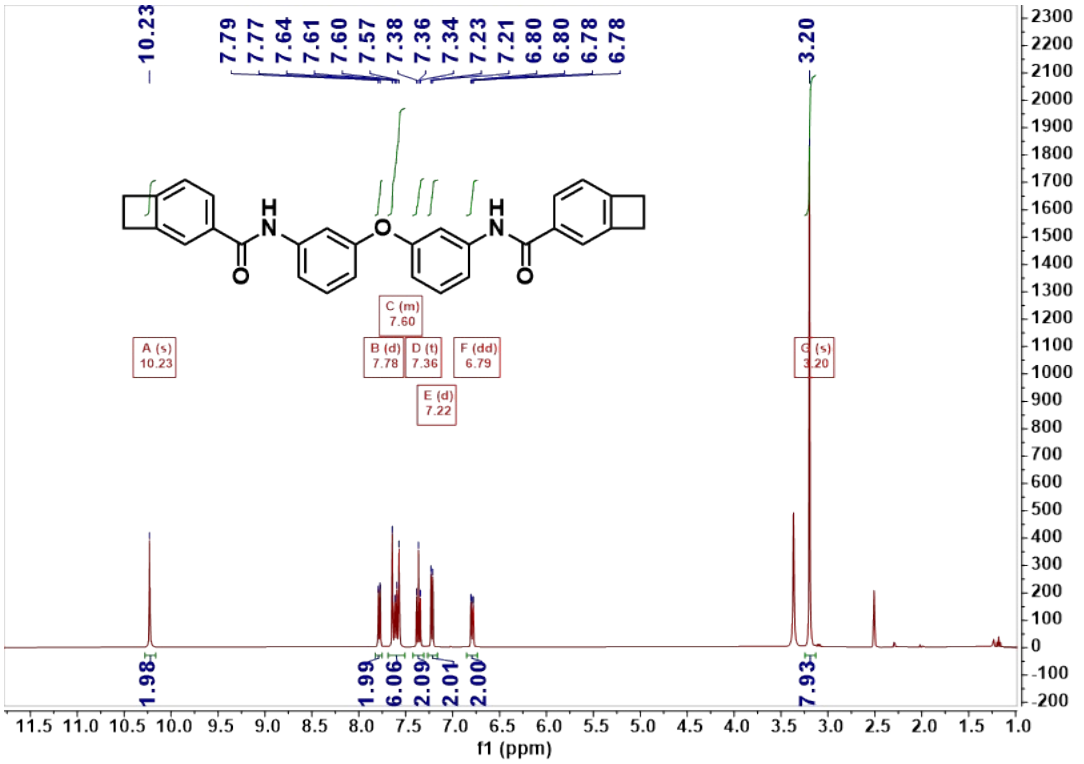


Figure S15. ^{1}H NMR spectrum of ***m*-2a** in DMSO-d_6.

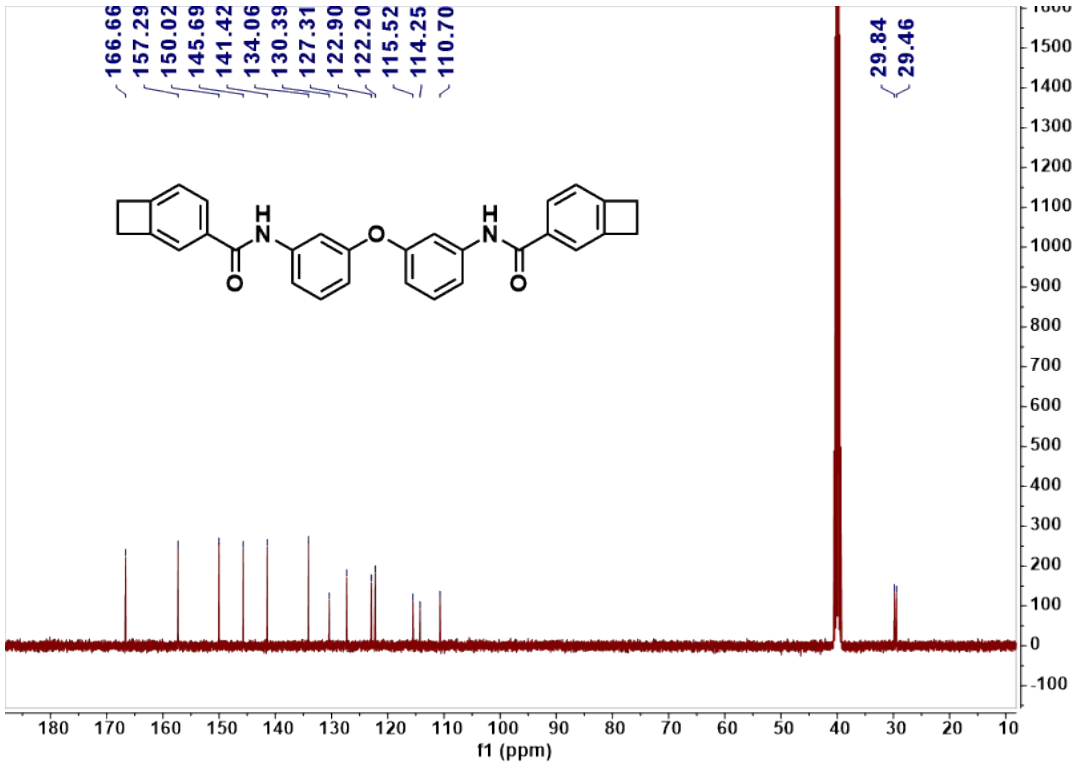


Figure S16. ^{13}C NMR spectrum of ***m*-2a** in DMSO-d_6.

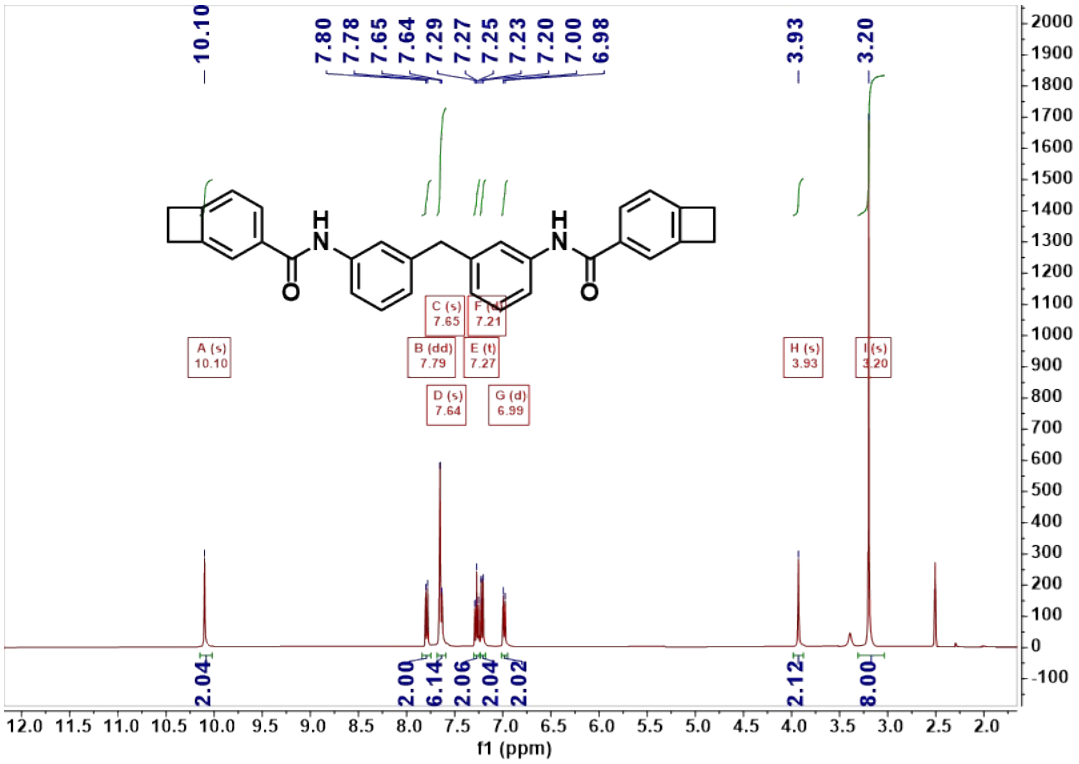


Figure S17. ^{1}H NMR spectrum of ***m*-2b** in DMSO-d_6.

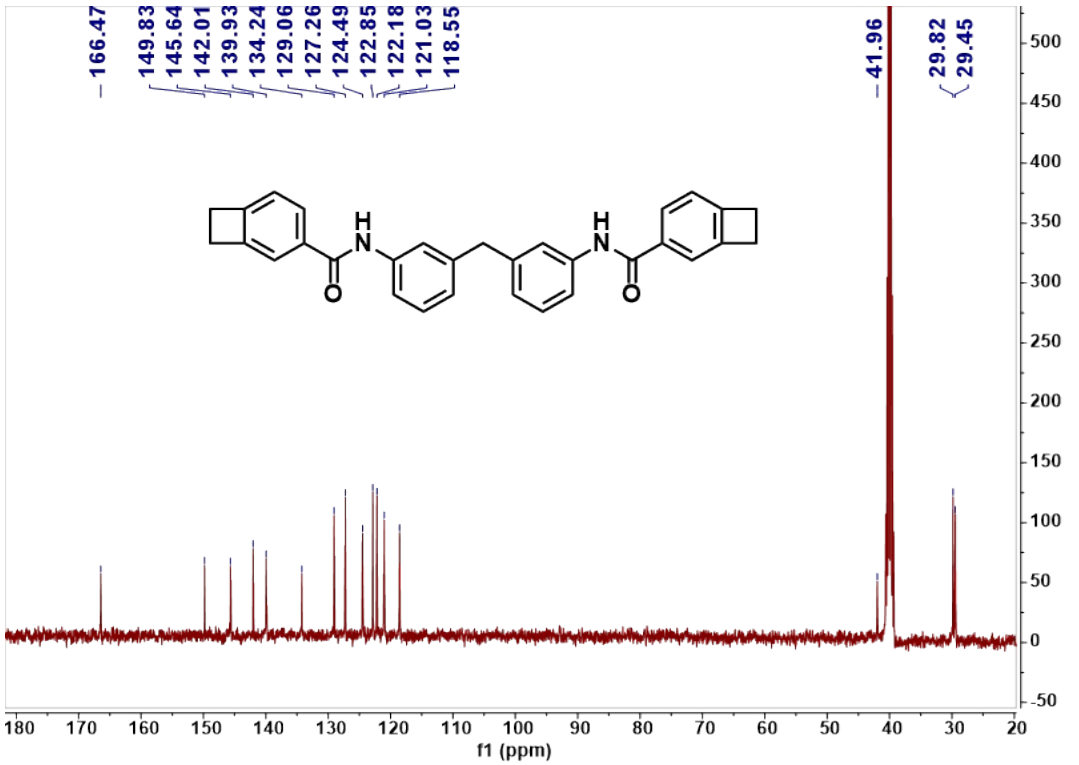


Figure S18. ^{13}C NMR spectrum of ***m*-2b** in DMSO-d_6.

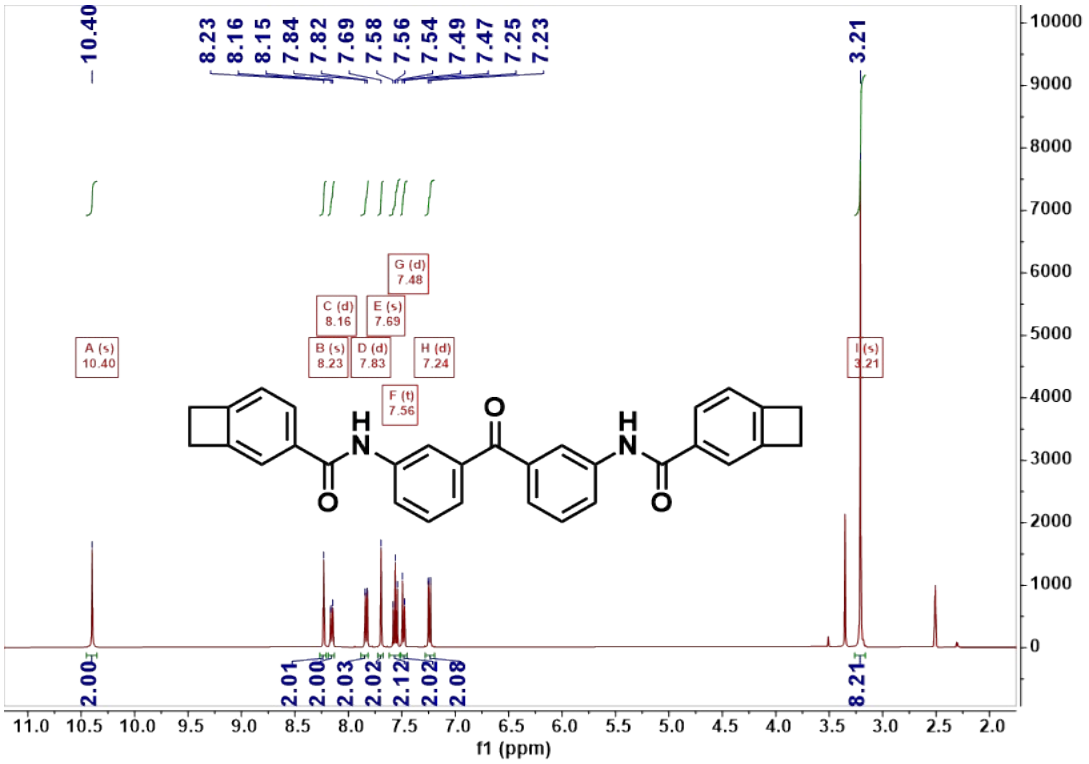


Figure S19. ^{1}H NMR spectrum of ***m*-2c** in DMSO-d_6.

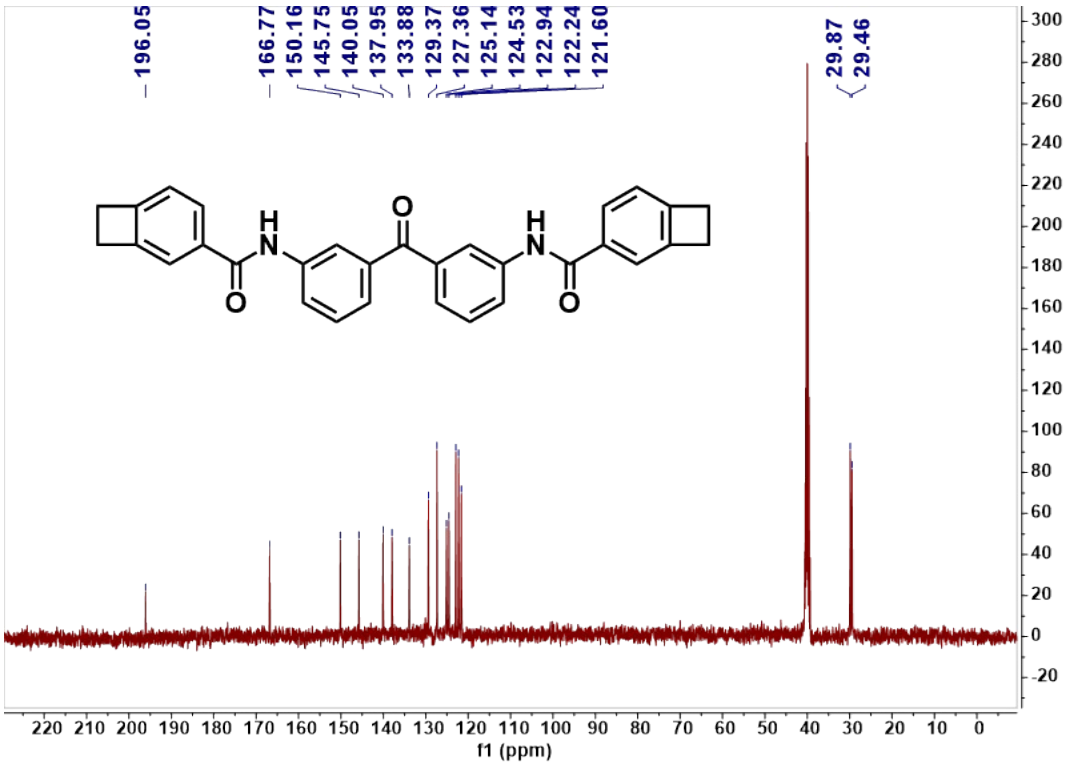


Figure S20. ^{13}C NMR spectrum of ***m*-2c** in DMSO-d_6.

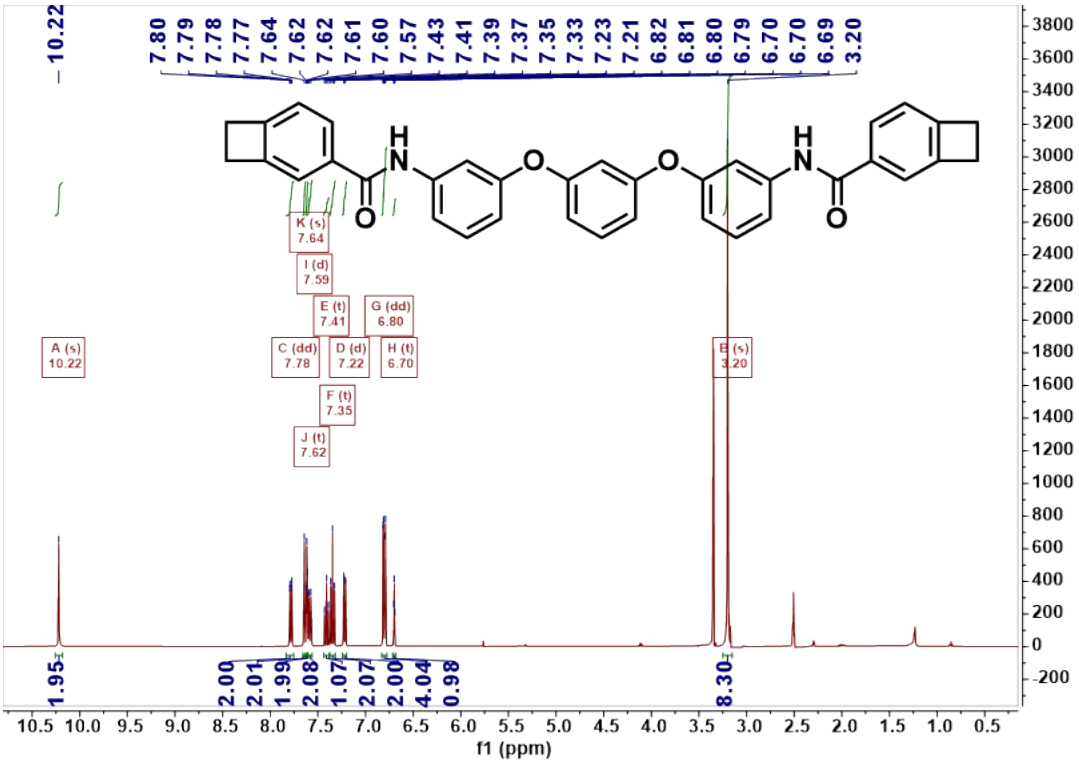


Figure S21. ^{1}H NMR spectrum of ***m*-3** in DMSO-d_6.

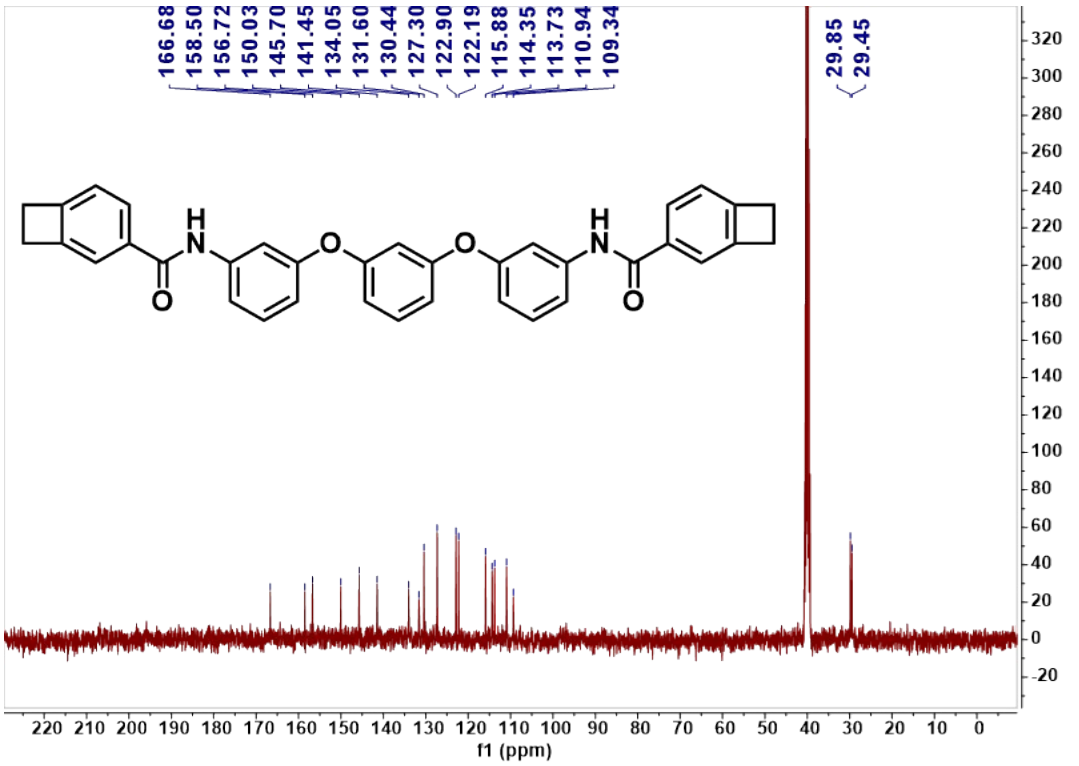


Figure S22. ^{13}C NMR spectrum of ***m*-3** in DMSO-d_6.

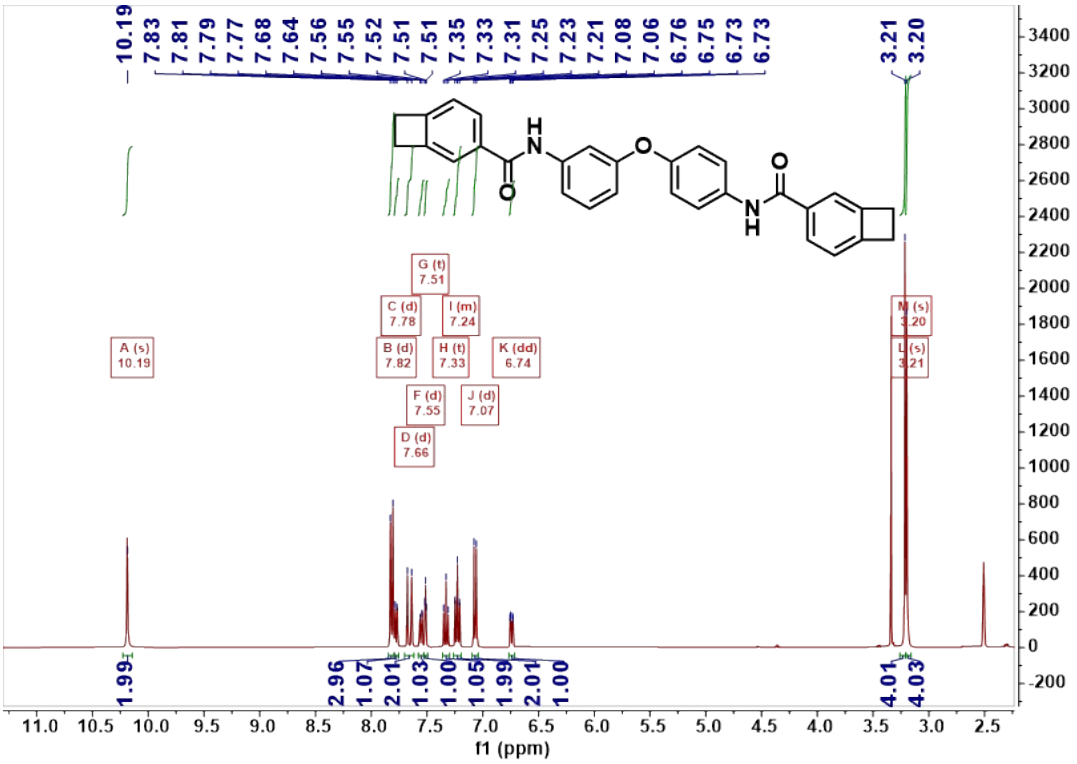


Figure S23. ^{1}H NMR spectrum of ***mp*-2** in DMSO-d_6.

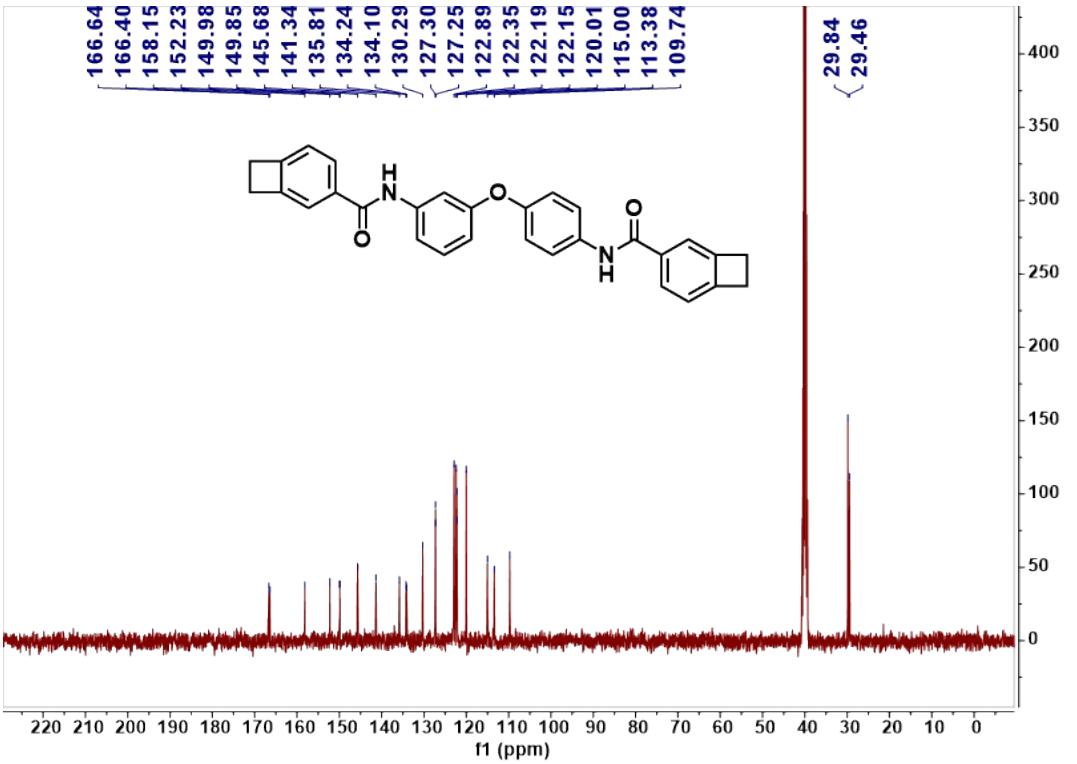


Figure S24. ^{13}C NMR spectrum of ***mp*-2** in DMSO-d_6.

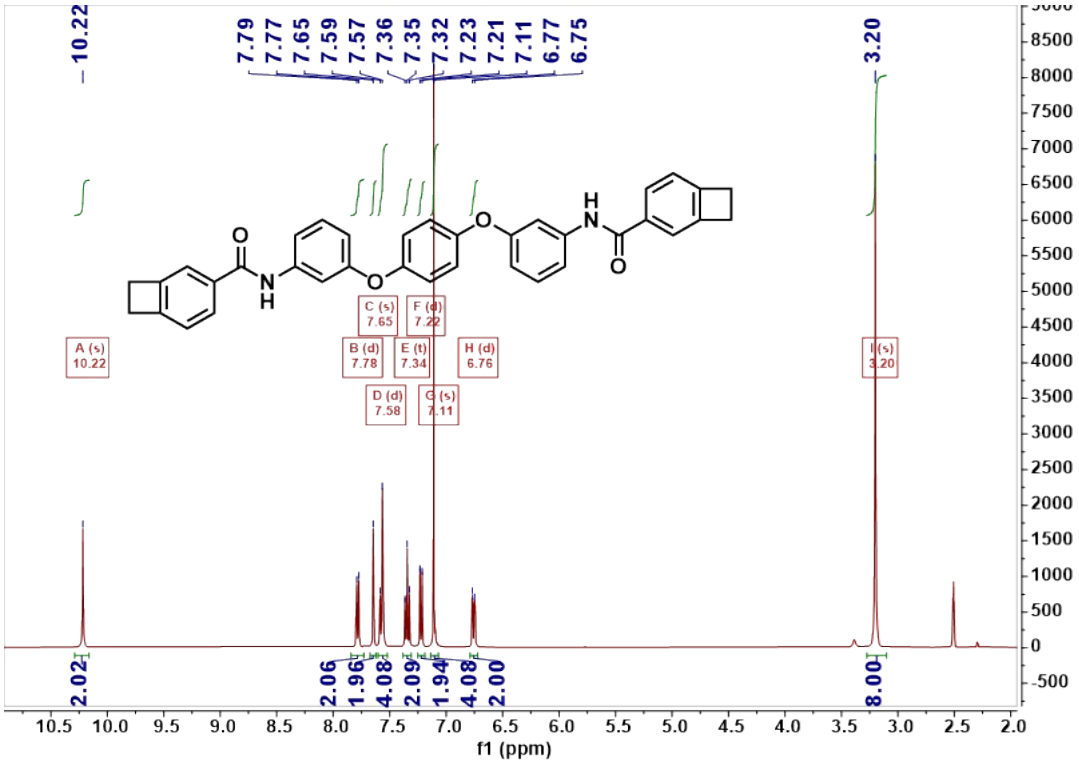


Figure S25. ^{1}H NMR spectrum of ***mp*-3a** in DMSO-d_6.

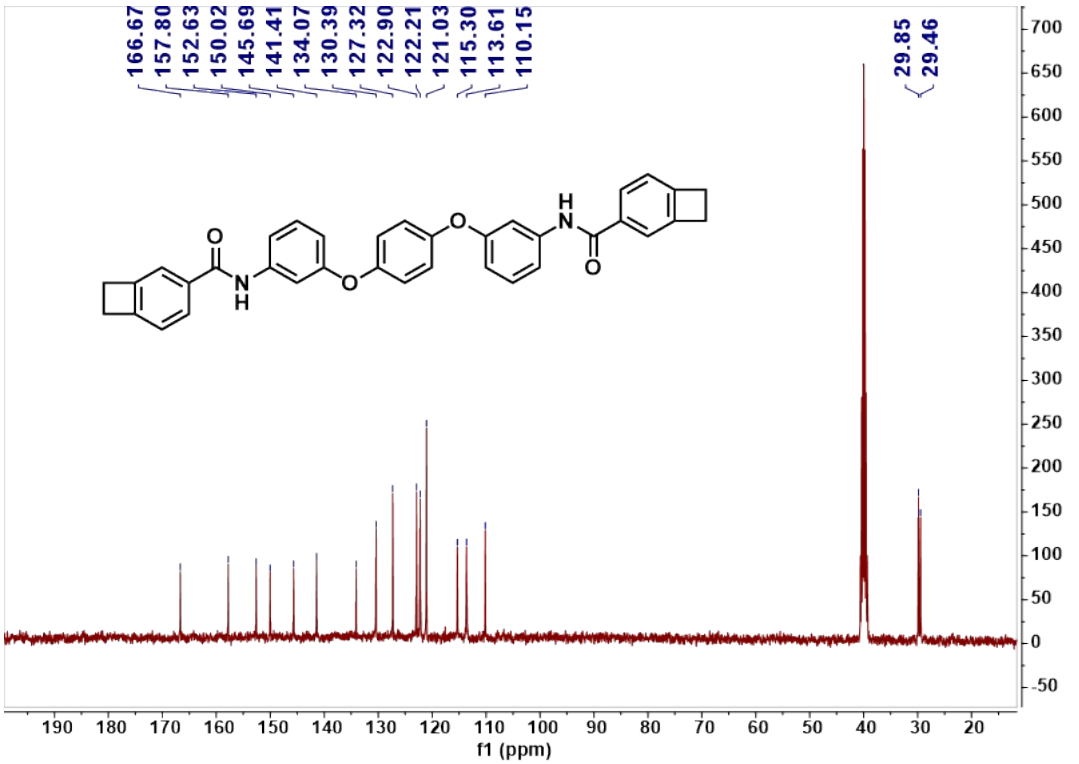


Figure S26. ^{13}C NMR spectrum of ***mp*-3a** in DMSO-d_6.

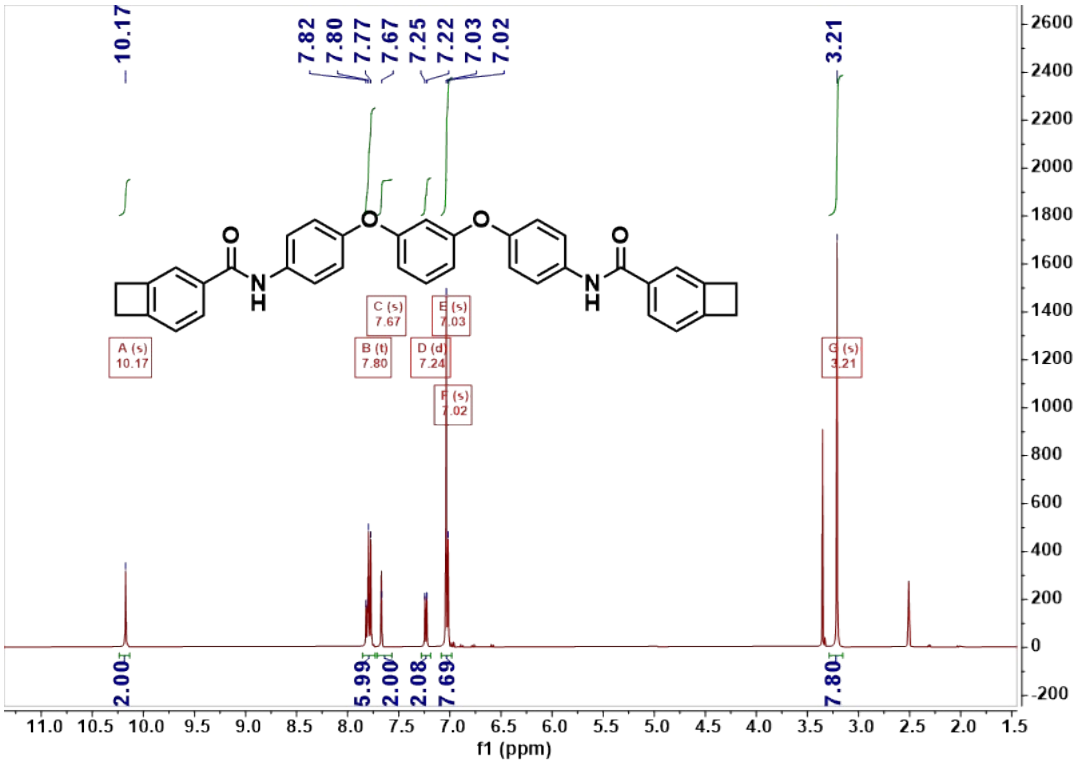


Figure S27. ^{1}H NMR spectrum of ***mp*-3b** in DMSO-d_6.

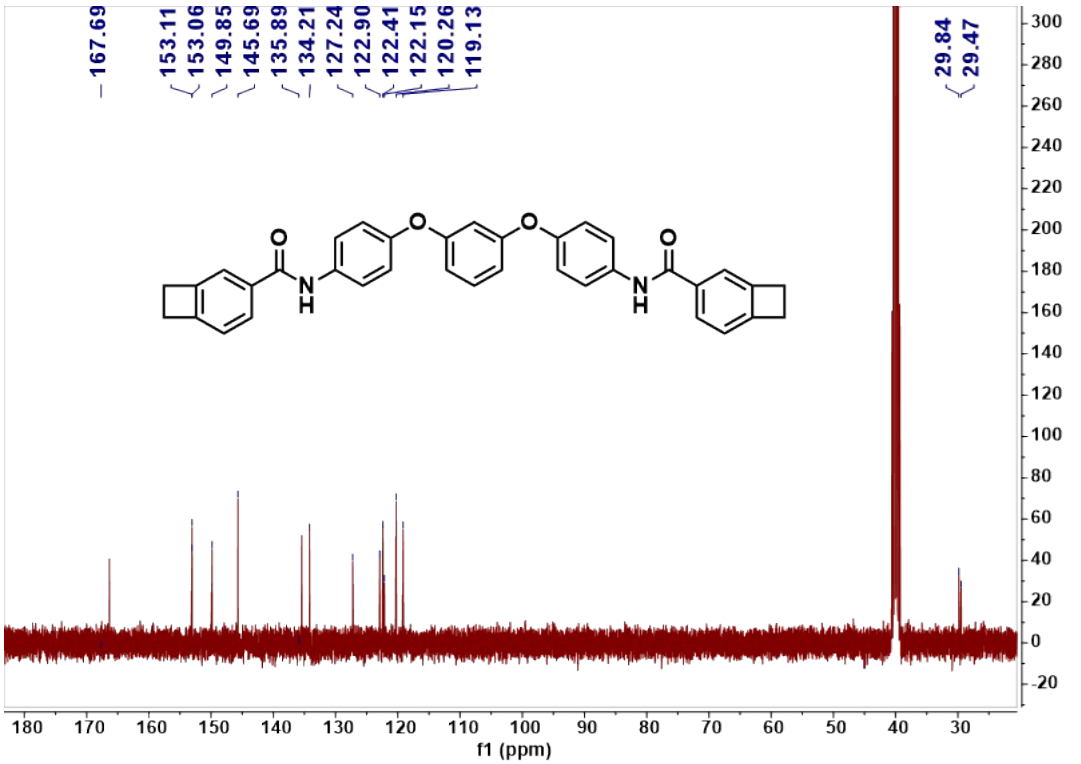


Figure S28. ^{13}C NMR spectrum of ***mp*-3b** in DMSO-d_6.

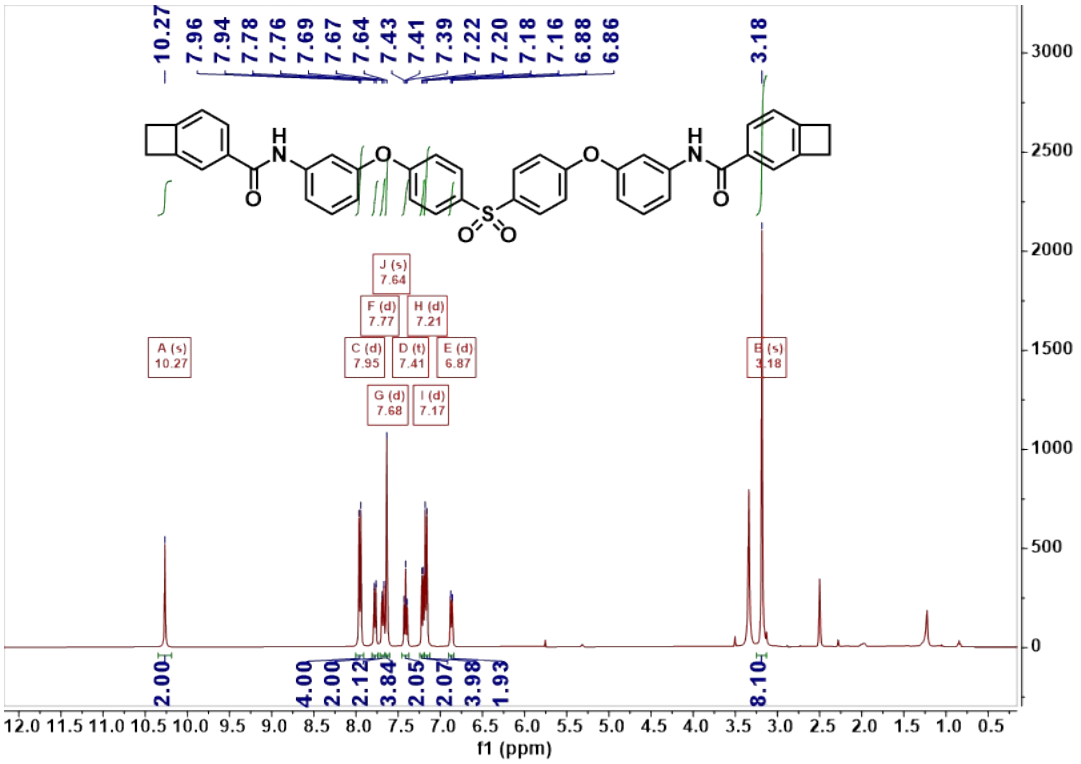


Figure S29. ^{1}H NMR spectrum of ***mp*-4** in DMSO-d_6.

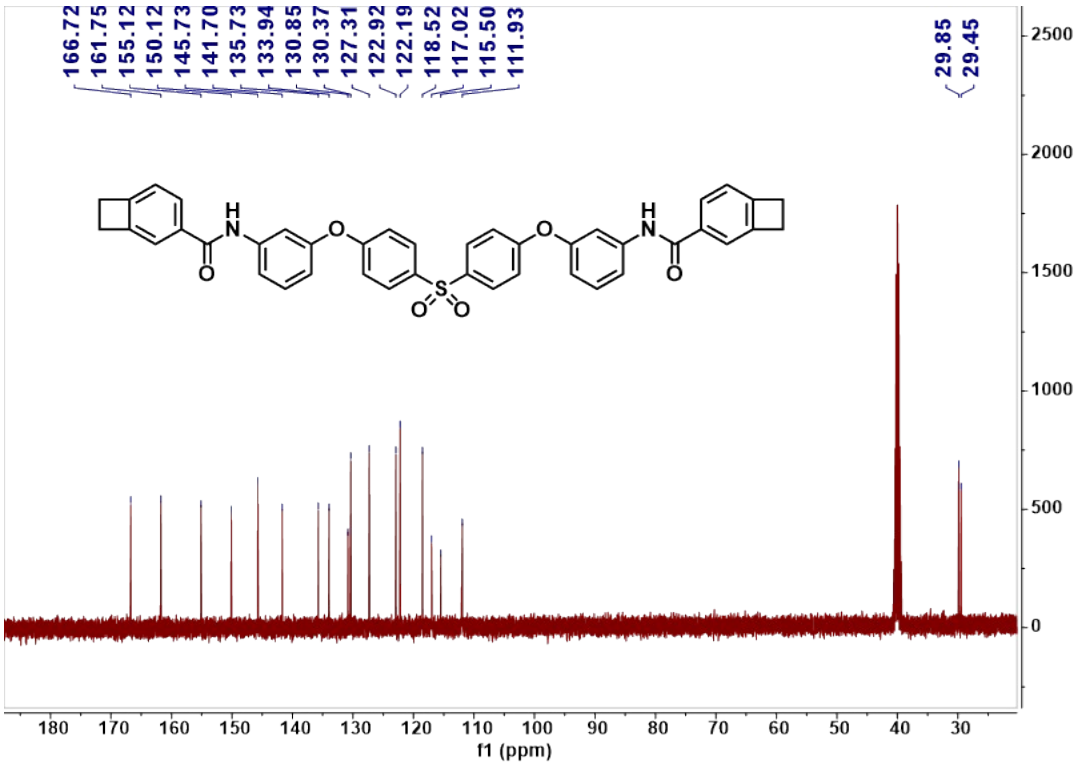


Figure S30. ^{13}C NMR spectrum of ***mp*-4** in DMSO-d_6.

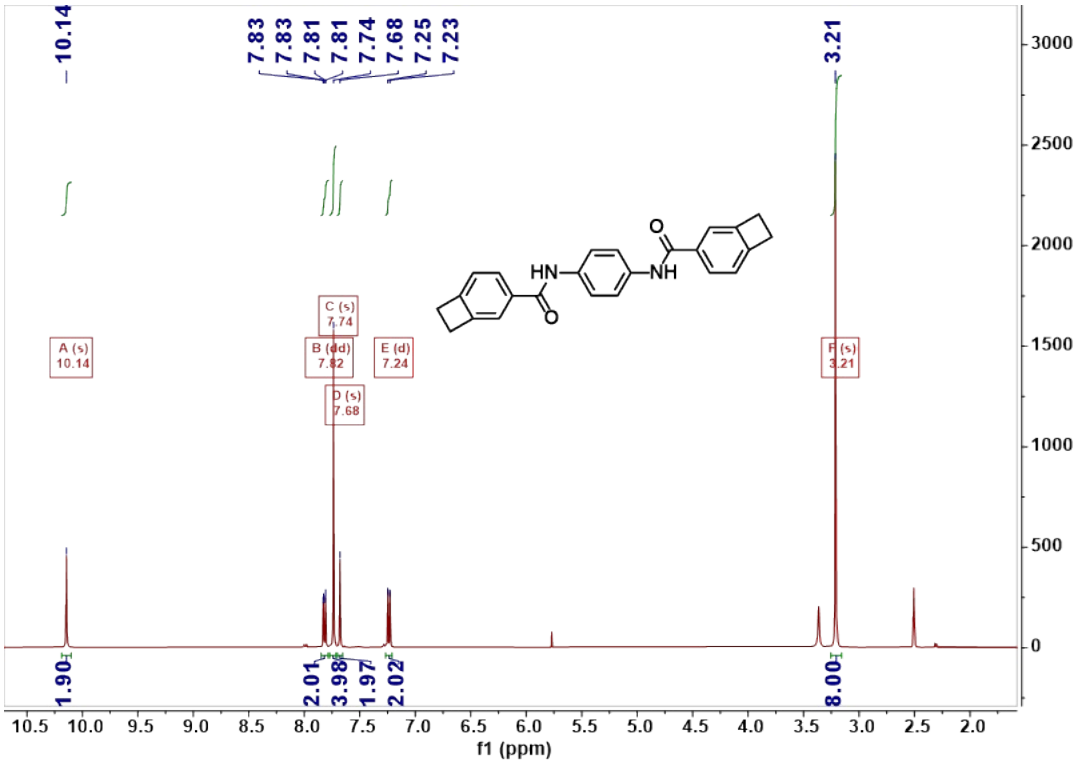


Figure S31. ^{1}H NMR spectrum of ***p*-1** in DMSO-d_6.

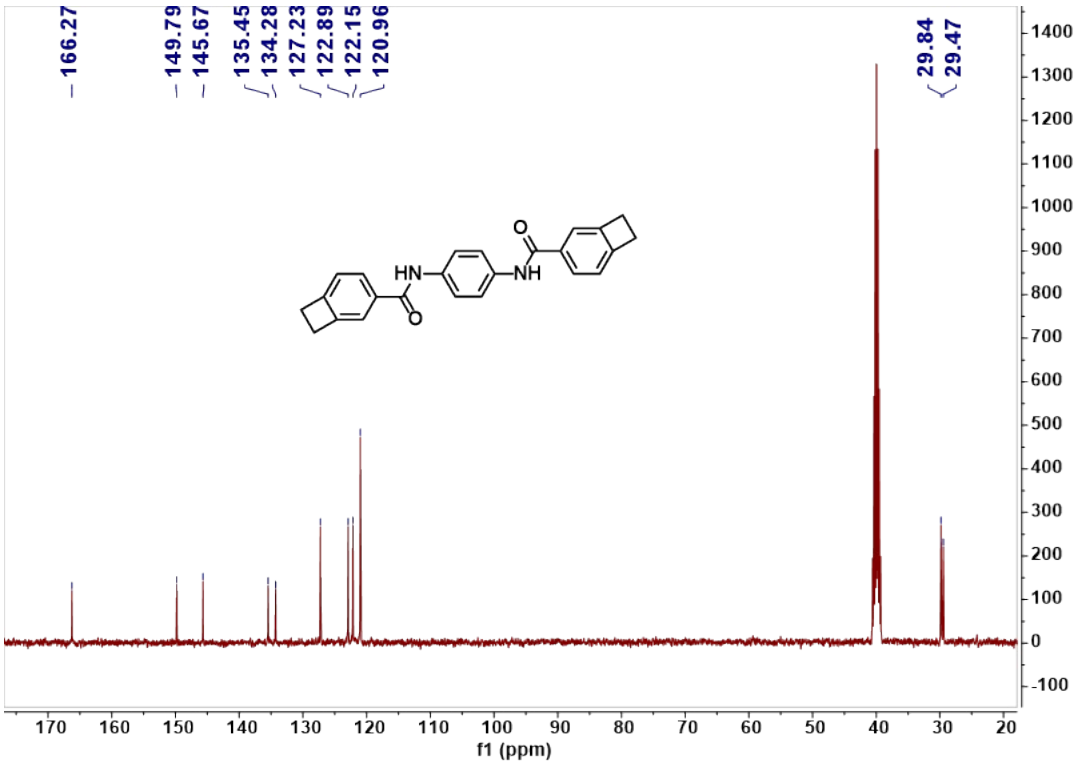


Figure S32. ^{13}C NMR spectrum of ***p*-1** in DMSO-d_6.

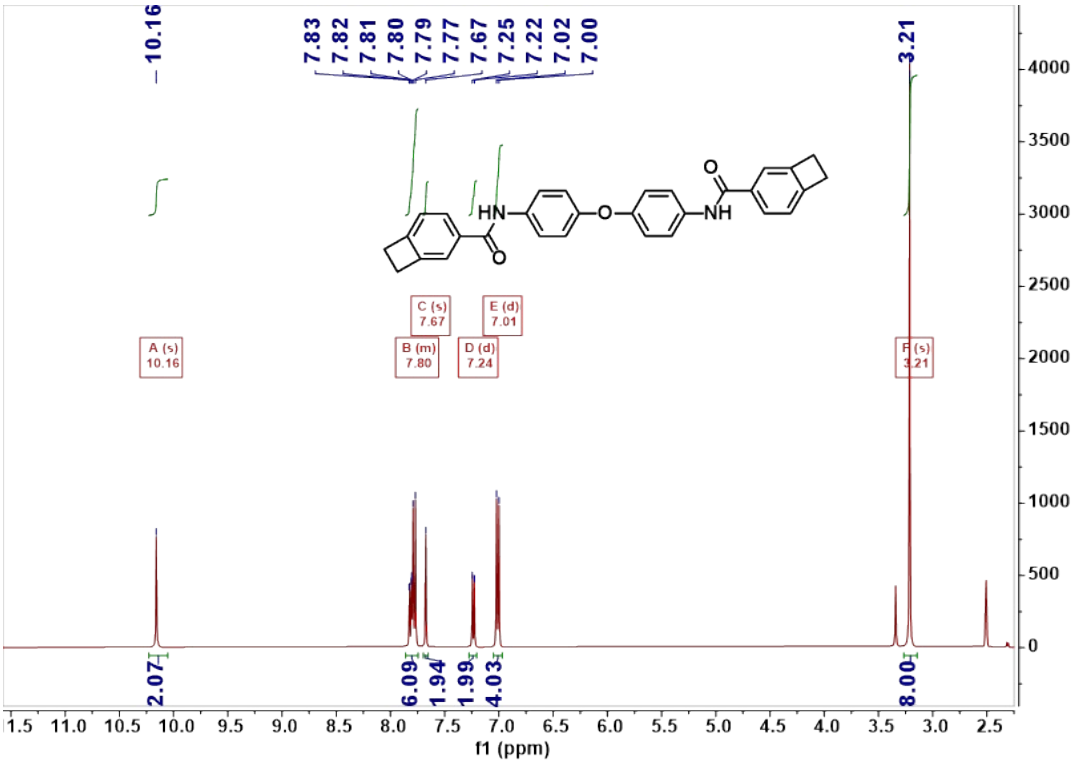


Figure S33. ^{1}H NMR spectrum of ***p*-2** in DMSO-d_6.

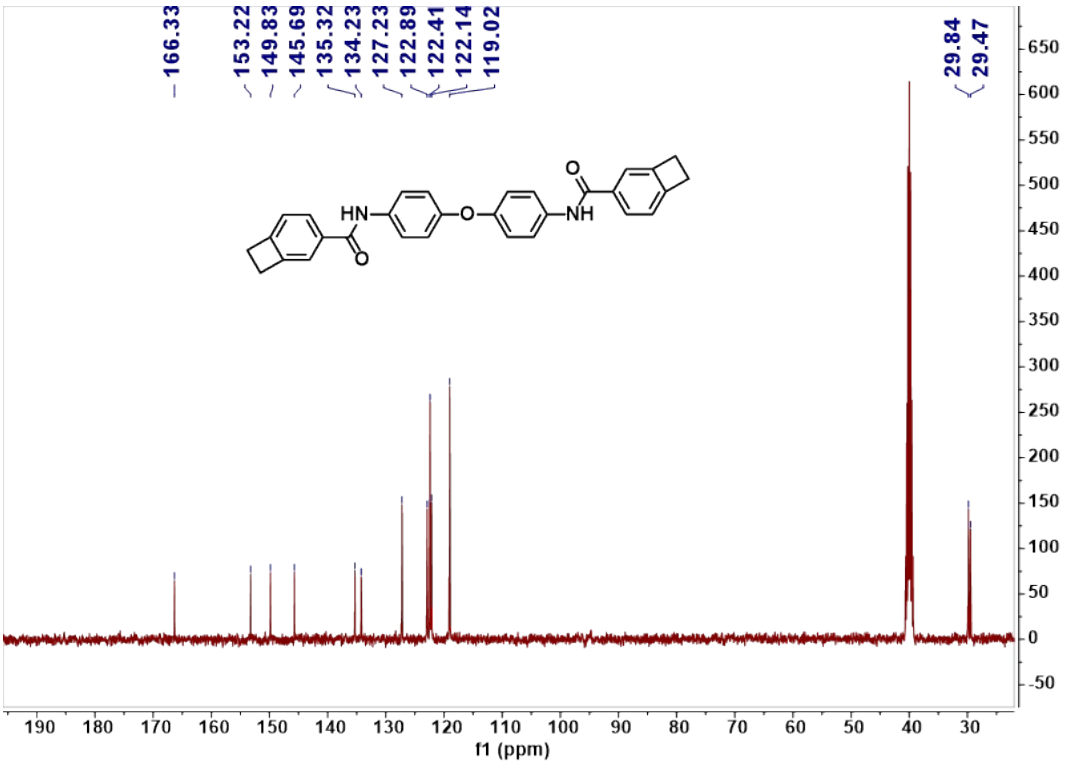


Figure S34. ^{13}C NMR spectrum of ***p*-2** in DMSO-d_6.

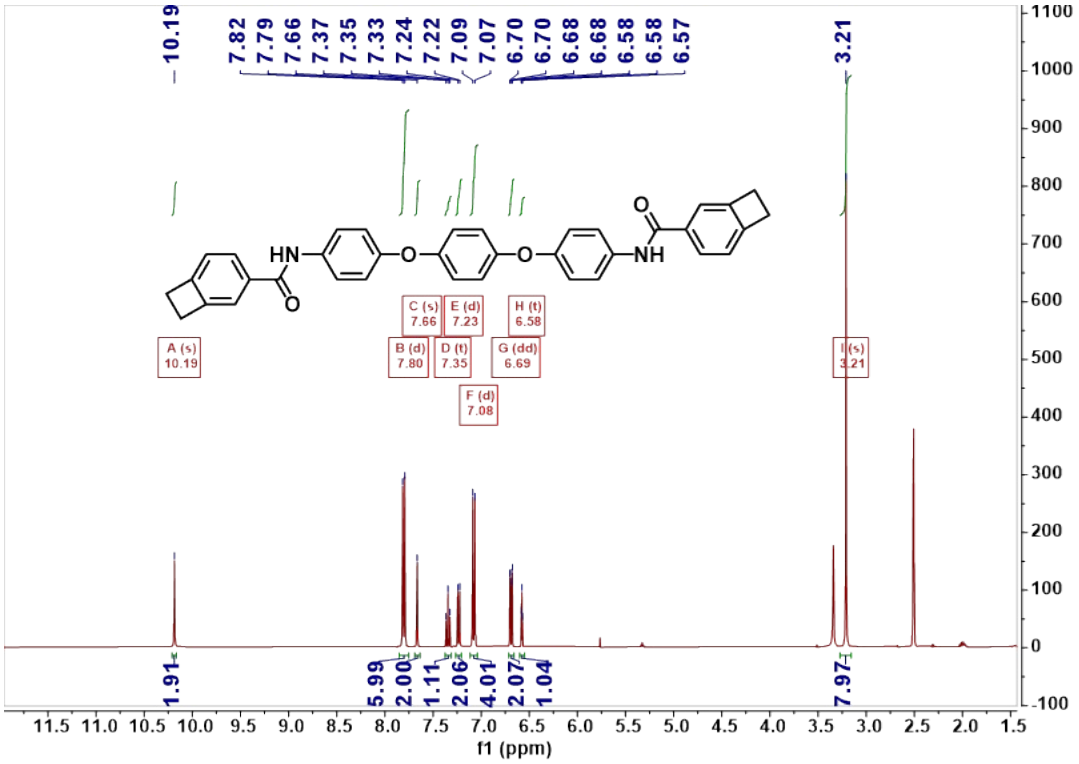


Figure S35. ^{1}H NMR spectrum of ***p*-3** in DMSO-d_6.

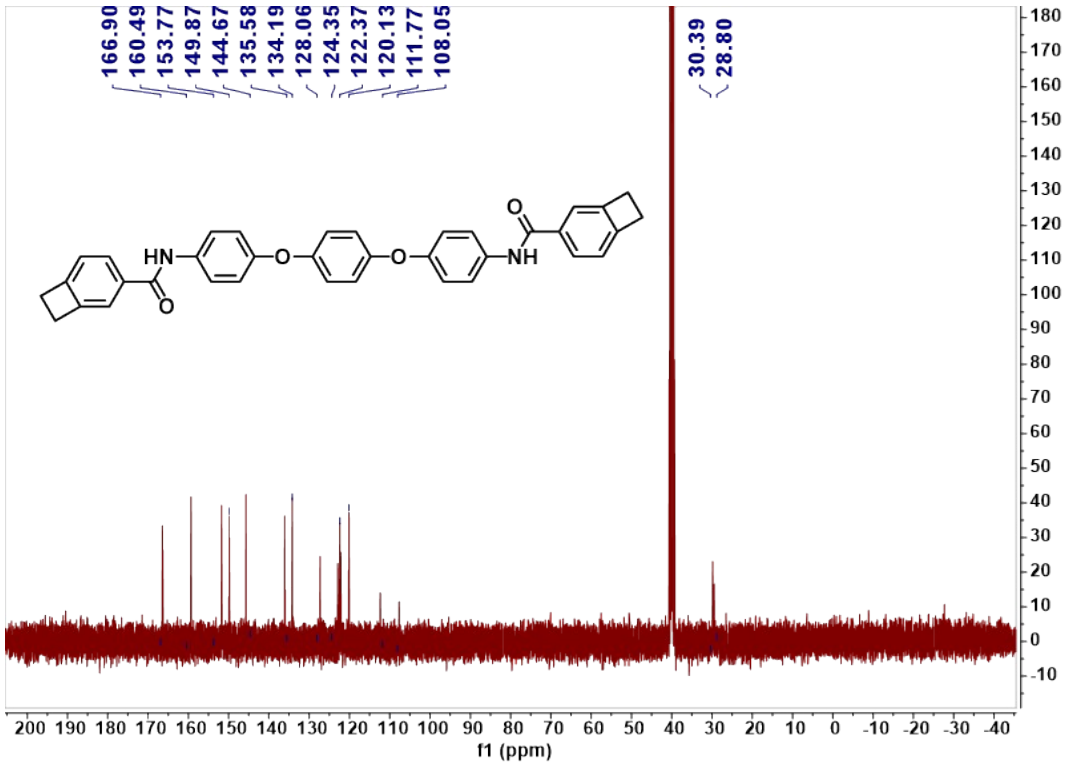


Figure S36. ^{13}C NMR spectrum of ***p*-3** in DMSO-d_6.

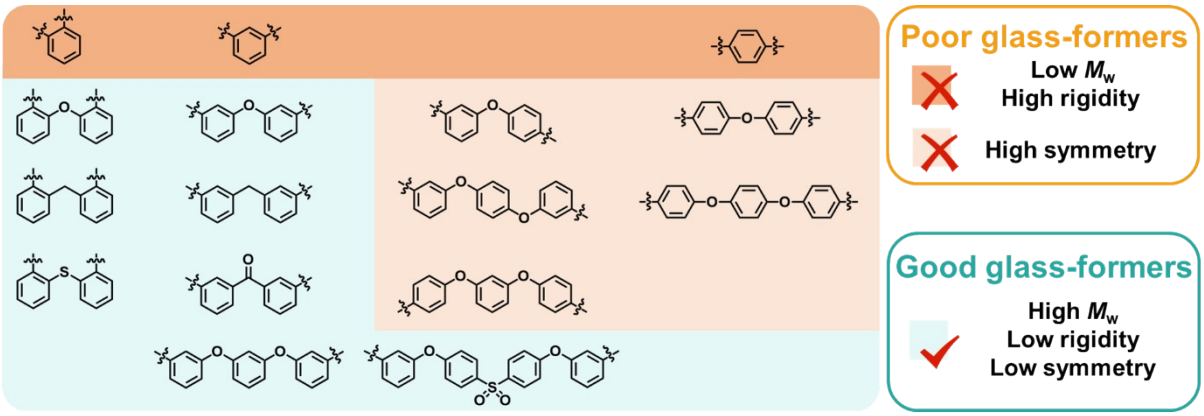


Figure S37. Molecular structures effect on the glass-forming abilities of Bis-BCB precursors.

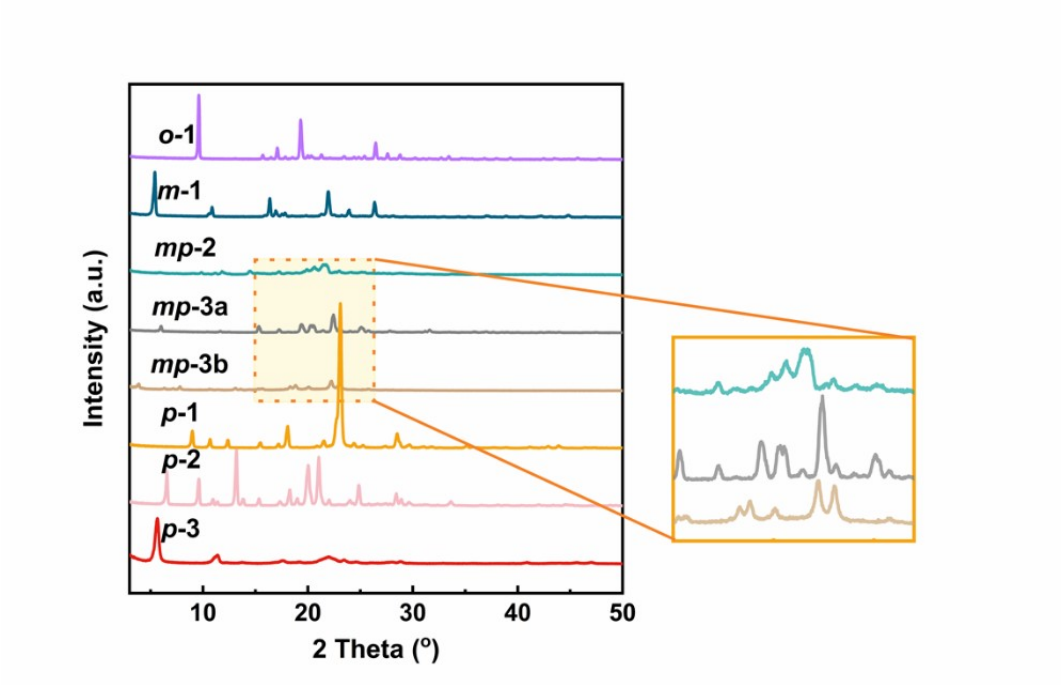


Figure S38. PXRD patterns of crystalline precursors.

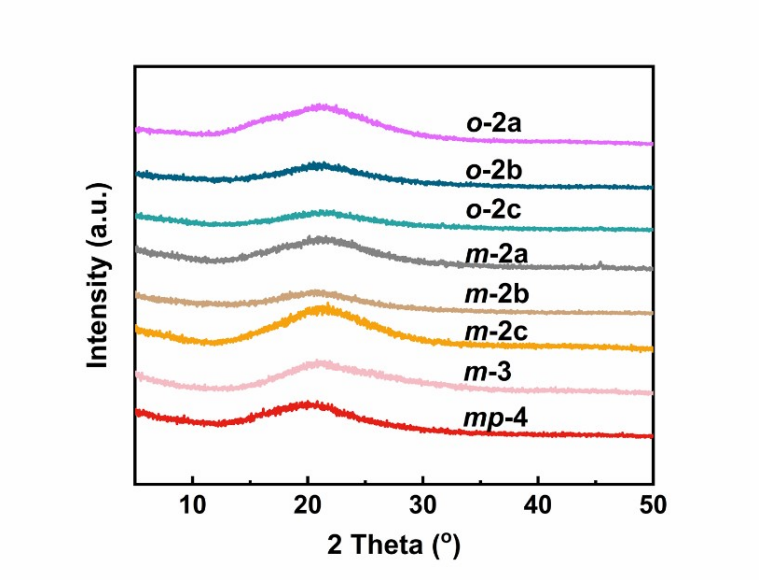


Figure S39. PXRD patterns of amorphous precursors.

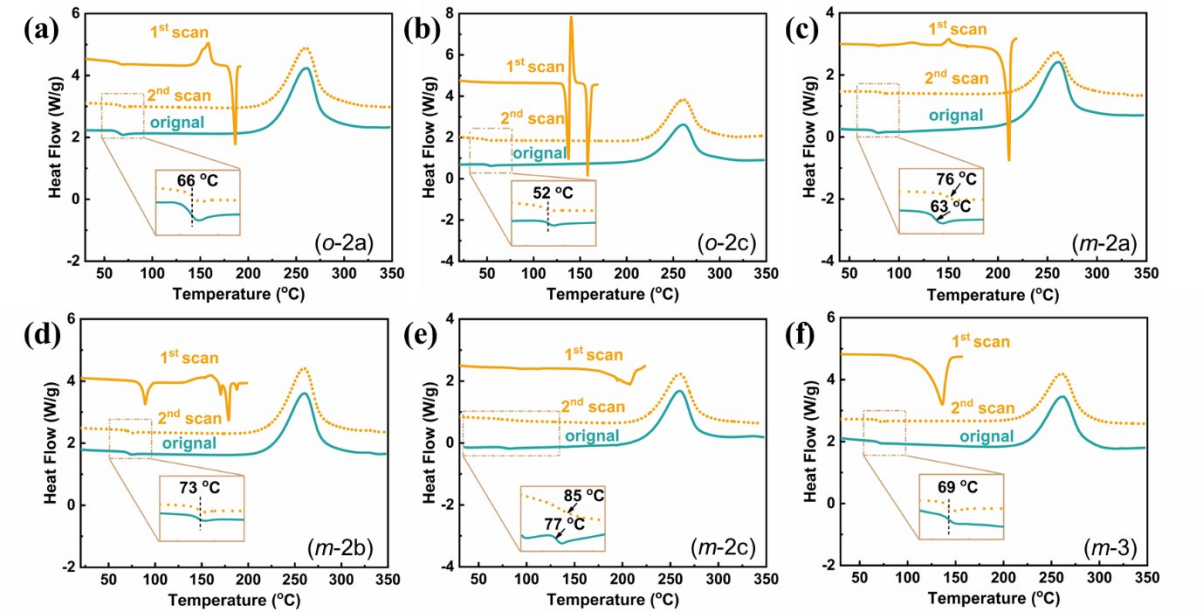


Figure S40. DSC curves of the storage stability and restorability of amorphousness. Precursors, which have aged for 30 days at room temperature, were heated to 5 to 10 °C above their T_m (if crystallized) and keeping 30 s (orange line). Then the samples were cooled to 0 °C and reheated to 350 °C (orange dotted line). Heating curves of freshly-prepared samples were added to compare the glass transition and exothermic peaks (green line). Only the heating scans are shown for clarity.

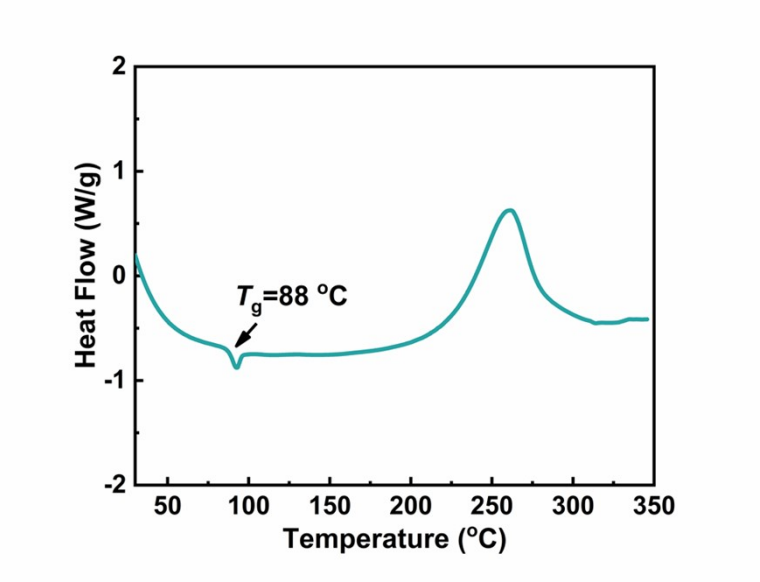


Figure S41. Evaluation of the storage stability of ***mp*-4** after six months. Aged sample was heated from 20 to 350 °C at a rate of 10 K/min in DSC.

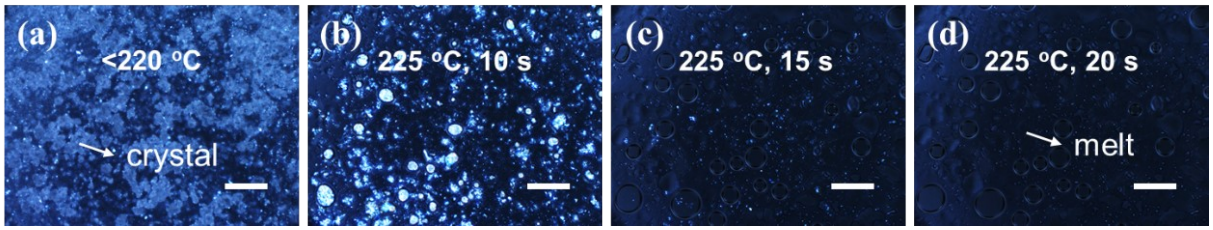


Figure S42. HSM images of ***mp*-3b** at various temperatures. All of the scale bars are 200 μm.

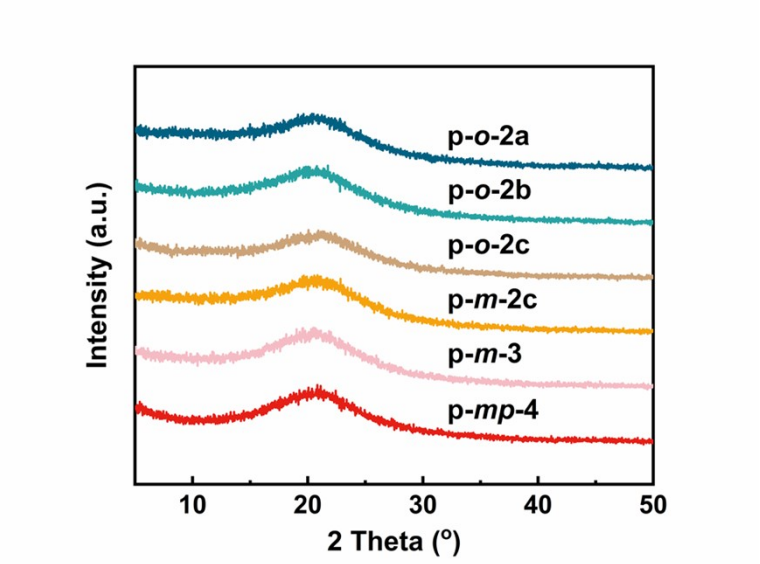


Figure S43. XRD patterns of the cured films.

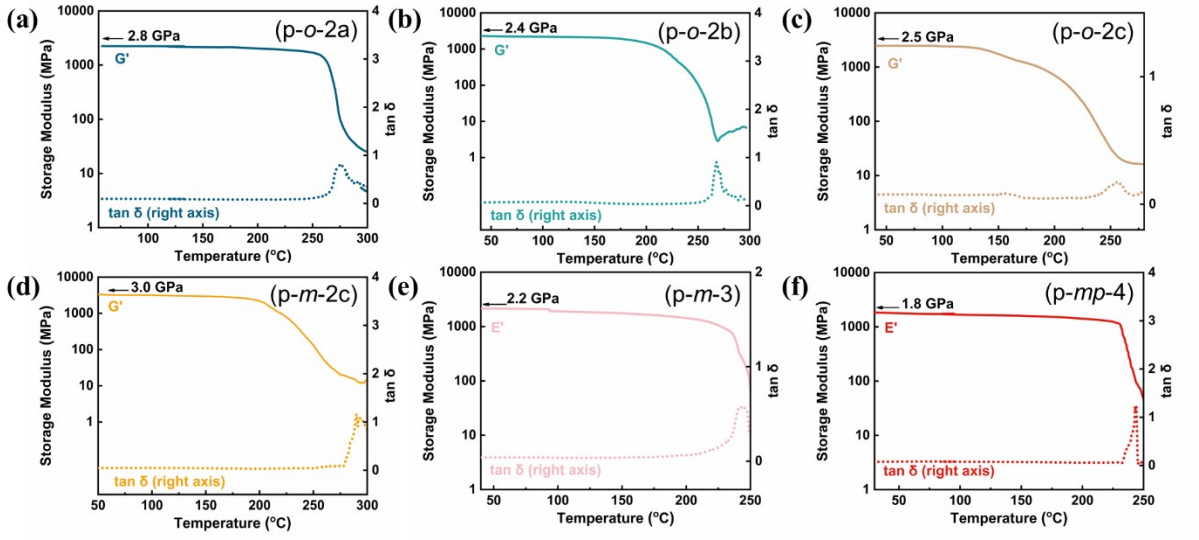


Figure S44. DMA traces of cured Bis-BCB resins at a heating rate of 10 K/min under 1 Hz in air.