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Supplementary Information

Asymmetric Synthesis of Highly Functionalized Cyclohexa-1,3-dienes via Organocatalyzed One-Pot Three-Component Domino Reaction of Malononitrile with α,β-Unsaturated Imines

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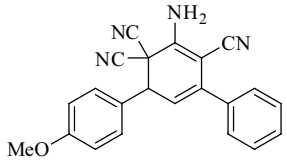
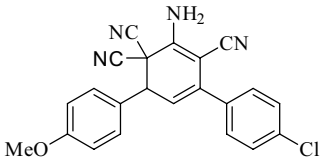
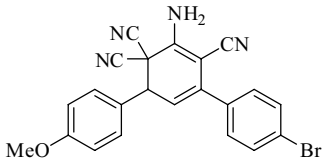


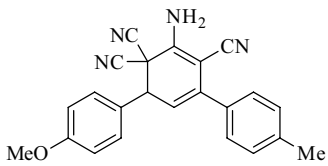
4a was obtained as a yellow solid in 42% yield after flash chromatography and the enantiomeric excess was determined to be 89% by HPLC analysis on Chiralcel OD column (20% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 10.259 min, t_{Rminor} 14.758 min; $[\alpha]_D^{20}$ –12.9 (*c* 0.233, $CHCl_3$); m.p. 191-193 °C; IR (KBr) ν_{max}/cm^{-1} 3396, 2217, 1643, 1606, 1553, 1508, 827; ^{1}H NMR (400 MHz, DMSO) δ 7.91 (s, 2H), 7.43-7.39 (m, 7H), 6.99 (d, 2H, *J* 8.7 Hz), 5.66 (d, 1H, *J* 4.1 Hz), 4.77 (d, 1H, *J* 4.0 Hz), 3.77 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.3, 149.1, 135.5, 131.3, 130.7, 130.5, 129.3, 129.2, 128.9, 127.9, 127.8, 127.0, 117.2, 116.5, 115.9, 115.1, 114.7, 114.6, 77.3, 55.8, 47.2, 44.3; HRMS (ESI) $C_{22}H_{16}N_4O$+Na $[M+Na]^+$ calcd.: 375.1216; found 375.1217.



4b was obtained as a yellow solid in 45% yield after flash chromatography and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralcel OD column (15% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 17.070 min, t_{Rminor} 13.218 min; $[\alpha]_D^{20}$ –24.0 (*c* 0.167, $CHCl_3$); m.p. 179-181 °C; IR (KBr) ν_{max}/cm^{-1} 3356, 3313, 2214, 1641, 1597, 1552, 1509, 819; ^{1}H NMR (400 MHz, DMSO) δ 7.89 (s, 2H), 7.46-7.35 (m, 4H), 7.21 (d, 2H, *J* 8.1 Hz), 6.99 (d, 2H, *J* 8.8 Hz), 5.61 (d, 1H, *J* 4.0 Hz), 4.75 (d, 1H, *J* 3.7 Hz), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.3, 149.0, 138.5, 137.2, 134.9, 132.6, 131.3, 130.7, 129.9, 129.5, 129.3, 127.7, 117.3, 115.0, 114.7, 114.6, 113.0, 112.2, 77.4, 55.6, 47.2, 44.4; HRMS (ESI) $C_{22}H_{15}ClN_4O$+H $[M+H]^+$ calcd.:387.1007; found 387.1002.



4c was obtained as a yellow solid in 40% yield after flash chromatography and the enantiomeric excess was determined to be 86% by HPLC analysis on Chiralcel OD column (10% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 21.599 min, t_{Rminor} 29.889 min; $[\alpha]_D^{20}$ –10.9 (*c* 0.367, $CHCl_3$); m.p. 234-236 °C; IR (KBr) ν_{max}/cm^{-1} 3393, 2213, 1641, 1596, 1551, 1508, 828; ^{1}H NMR (400 MHz, DMSO) δ 7.98 (s, 2H), 7.64-7.53 (m, 2H), 7.42 (d, 2H, *J* 8.7 Hz), 7.34 (d, 2H, *J* 8.4 Hz), 6.99 (d, 2H, *J* 8.7 Hz), 5.70 (d, 1H, *J* 4.1 Hz), 4.77 (d, 1H, *J* 4.0 Hz), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.4, 149.2, 136.9, 136.3, 132.5, 131.9, 131.3, 131.2, 130.9, 130.0, 127.9, 126.9, 117.1, 115.8, 115.0, 114.6, 112.9, 112.1, 76.8, 55.6, 47.2, 44.3; HRMS (ESI) $C_{22}H_{15}BrN_4O$+Na $[M+Na]^+$ calcd.: 453.0321; found 453.0312.



4d was obtained as a yellow solid in 31% yield after flash chromatography and the enantiomeric excess was determined to be 89% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV

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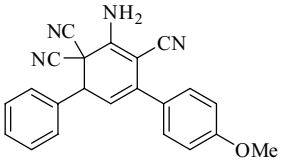
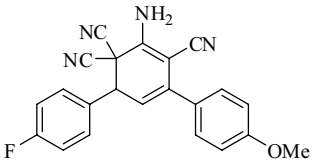
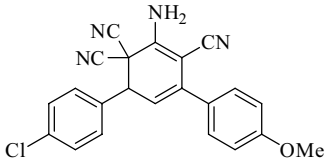
254 nm, t_{Rmajor} 10.936 min, t_{Rminor} 7.945 min; $[\alpha]_D^{20}$ +7.5 (*c* 0.133, $CHCl_3$); m.p. 208-210 °C; IR (KBr) ν_{max}/cm^{-1} 3384, 2212, 1642, 1597, 1534, 1508, 829; ^{1}H NMR (400 MHz, DMSO) δ 7.87 (s, 2H), 7.26-7.20 (m, 6H), 6.99 (d, 2H, *J* 8.8 Hz), 5.61 (d, 1H, *J* 4.1 Hz), 4.75 (d, 1H, *J* 4.0 Hz), 3.78 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.3, 149.2, 136.2, 133.7, 131.3, 131.1, 130.9, 129.7, 129.6, 129.0, 127.9, 126.9, 117.1, 116.4, 115.8, 115.0, 114.7, 114.6, 76.8, 55.6, 47.1, 44.3, 21.2; HRMS (ESI) $C_{23}H_{18}N_4O$+Na $[M+Na]^+$ calcd.: 389.1373; found 389.1365.



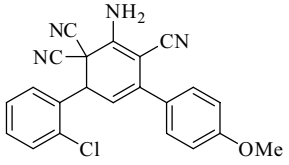
4e was obtained as a yellow solid in 31% yield after flash chromatography and the enantiomeric excess was determined to be 87% by HPLC analysis on Chiralcel IC column (15% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 14.578 min, t_{Rminor} 13.215 min; $[\alpha]_D^{20}$ –22.5 (*c* 0.133, $CHCl_3$); m.p. 183-185 °C; IR (KBr) ν_{max}/cm^{-1} 3421, 2217, 1637, 1608, 1557, 1506, 845; ^{1}H NMR (400 MHz, DMSO) δ 7.91 (s, 2H), 7.51-7.48 (m, 2H), 7.44-7.43 (m, 3H), 7.35-7.31 (m, 2H), 6.96 (d, 2H, *J* 8.7 Hz), 5.60 (d, 1H, *J* 4.0 Hz), 4.81 (d, 1H, *J* 3.9 Hz), 3.77 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.0, 149.0, 137.0, 135.6, 131.2, 130.0, 129.9, 129.7, 129.5, 129.2, 129.1, 128.8, 117.3, 114.8, 114.3, 113.7, 112.5, 112.2, 77.5, 55.7, 47.7, 44.2; HRMS (ESI) $C_{22}H_{16}N_4O$+Na $[M+Na]^+$ calcd.: 375.1216; found 375.1205.



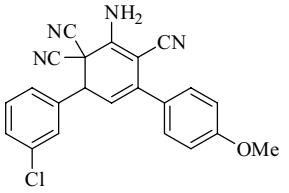
4f was obtained as a yellow solid in 50% yield after flash chromatography and the enantiomeric excess was determined to be 91% by HPLC analysis on Chiralcel OD column (30% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 7.573 min, t_{Rminor} 10.543 min; $[\alpha]_D^{20}$ –18.0 (*c* 0.167, $CHCl_3$); m.p. 211-213 °C; IR (KBr) ν_{max}/cm^{-1} 3401, 3315, 2210, 1638, 1608, 1560, 1508, 837; ^{1}H NMR (400 MHz, DMSO) δ 7.91 (s, 2H), 7.54 (dd, 2H, *J* 8.2, 5.5 Hz), 7.34-7.29 (m, 4H), 6.96 (d, 2H, *J* 8.6 Hz), 5.60 (d, 1H, *J* 3.9 Hz), 4.86 (d, 1H, *J* 3.9 Hz), 3.77 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 161.2, 160.0, 148.8, 137.1, 132.3, 132.2, 131.2, 129.9, 129.2, 117.2, 116.3, 116.1, 114.8, 114.3, 113.5, 112.8, 112.1, 77.6, 55.7, 46.9, 44.2; HRMS (ESI) $C_{22}H_{15}FN_4O$+Na $[M+Na]^+$ calcd.: 393.1122; found 393.1123.



4g was obtained as a yellow solid in 47% yield after flash chromatography and the enantiomeric excess was determined to be 86% by HPLC analysis on Chiralcel OD column (30% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 8.672 min, t_{Rminor} 10.780 min; $[\alpha]_D^{20}$ –14.0 (*c* 0.500, $CHCl_3$); m.p. 204-206 °C; IR (KBr) ν_{max}/cm^{-1} 3395, 2211, 1639, 1607, 1558, 1508, 825; ^{1}H NMR (400 MHz, DMSO) δ 7.94 (s, 2H), 7.52 (s, 4H), 7.33 (d, 2H, *J* 8.2 Hz), 6.96 (d, 2H, *J* 8.3 Hz), 5.59 (d, 1H, *J* 3.7 Hz), 4.88 (d, 1H, *J* 3.4 Hz), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.1, 148.8, 137.3, 134.5, 131.9, 131.2, 130.5, 129.9, 129.5, 129.3, 129.2, 117.2, 114.3, 113.1, 112.8, 112.0, 77.6, 55.7, 46.9, 44.0; HRMS (ESI) $C_{22}H_{15}ClN_4O$+Na $[M+Na]^+$ calcd.: 409.0827; found 409.0822.

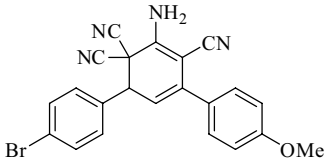


4h was obtained as a yellow solid in 41% yield after flash chromatography and the enantiomeric excess was determined to be 84% by HPLC analysis on Chiralcel IC column (20% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 9.218 min, t_{Rminor} 8.196 min; $[\alpha]_D^{20}$ –66.0 (*c* 0.167, $CHCl_3$); m.p. 223-225 °C; IR (KBr) ν_{max}/cm^{-1} 3446, 3321, 2220, 1649, 1608, 1548, 1508, 825; ^{1}H NMR (400 MHz, DMSO) δ 8.00 (s, 2H), 7.62-7.58 (m, 2H), 7.47-7.44 (m, 2H), 7.33 (d, 2H, *J* 8.7 Hz), 6.96 (d, 2H, *J* 8.7 Hz), 5.56 (d, 1H, *J* 4.1 Hz), 5.09 (d, 1H, *J* 4.1 Hz), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.1, 148.7, 137.6, 134.6, 133.1, 131.5, 130.6, 130.3, 129.7, 129.2, 128.6, 117.1, 114.3, 112.9, 112.2, 111.9, 77.8, 55.7, 44.3, 42.8; HRMS (ESI) $C_{22}H_{15}ClN_4O$+Na $[M+Na]^+$ calcd.: 409.0827; found 409.0832.

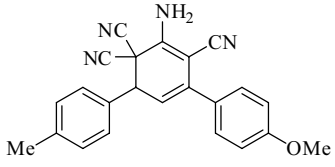


4i was obtained as a yellow solid in 40% yield after flash chromatography and the enantiomeric excess was determined to be 81% by HPLC analysis on Chiralpcel OD column (10% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 33.769 min, t_{Rminor} 38.216 min; $[\alpha]_D^{20}$ –22.5 (*c* 0.667, $CHCl_3$); m.p. 72-74 °C; IR (KBr) ν_{max}/cm^{-1} 3416, 3328, 2208, 1638, 1606, 1545, 1509, 838; ^{1}H NMR (400 MHz, DMSO) δ 7.97 (s, 2H), 7.56 (s, 1H), 7.49 (d, 3H, *J* 2.3 Hz), 7.34 (d, 2H, *J* 7.9 Hz), 6.97 (d, 2H, *J* 8.4 Hz), 5.62 (s, 1H), 4.90 (s, 1H), 3.77 (s, 3H);

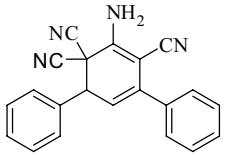
^{13}C NMR (100 MHz, DMSO) δ 160.1, 148.8, 137.9, 137.4, 133.7, 131.2, 130.0, 129.8, 129.7, 129.2, 128.6, 117.2, 114.3, 112.8, 112.7, 112.0, 77.6, 55.7, 47.1, 43.9; HRMS (ESI) $C_{22}H_{15}ClN_4O$+Na $[M+Na]^+$ calcd.: 409.0827; found 409.0826.



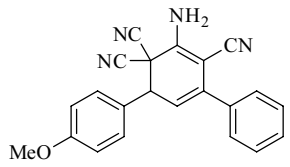
4j was obtained as a yellow solid in 43% yield after flash chromatography and the enantiomeric excess was determined to be 88% by HPLC analysis on Chiralcel OD column (20% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 17.249 min, t_{Rminor} 14.339 min; $[\alpha]_D^{20}$ –60.0 (*c* 0.133, $CHCl_3$); m.p. 198-200 °C; IR (KBr) ν_{max}/cm^{-1} 3384, 2222, 1642, 1596, 1534, 1508, 819; ^{1}H NMR (400 MHz, DMSO) δ 7.95 (s, 2H), 7.57 (s, 3H), 7.35-7.33 (m, 3H), 6.98-6.93 (m, 2H), 5.59 (d, 1H, *J* 4.0 Hz), 4.85 (d, 1H, *J* 3.9 Hz), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.1, 148.8, 137.3, 134.9, 132.4, 132.2, 132.1, 131.2, 130.6, 129.7, 129.2, 126.1, 117.2, 114.8, 114.3, 113.0, 112.8, 112.0, 77.6, 55.6, 47.1, 43.9; HRMS (ESI) $C_{22}H_{15}BrN_4O$+Na $[M+Na]^+$ calcd.: 453.0321; found 453.0310.



4k was obtained as a yellow solid in 37% yield after flash chromatography and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralcel OD column (30% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 7.008 min, t_{Rminor} 8.475 min; $[\alpha]_D^{20}$ –6.0 (*c* 0.833, $CHCl_3$); m.p. 213-215 °C; IR (KBr) ν_{max}/cm^{-1} 3431, 3319, 2207, 1647, 1608, 1560, 1511, 809; ^{1}H NMR (400 MHz, DMSO) δ 7.90 (s, 2H), 7.48 (d, 1H, *J* 7.8 Hz), 7.40-7.29 (m, 5H), 6.96 (d, 2H, *J* 8.7 Hz), 5.56 (d, 1H, *J* 3.8 Hz), 4.72 (d, 1H, *J* 3.5 Hz), 3.76 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 160.0, 149.0, 139.2, 136.9, 131.2, 130.1, 129.9, 129.8, 129.7, 129.1, 128.8, 127.3, 117.3, 114.7, 114.3, 113.9, 112.9, 112.2, 77.5, 55.6, 47.5, 44.3, 21.2; HRMS (ESI) $C_{23}H_{18}N_4O$+Na $[M+Na]^+$ calcd.: 389.1373; found 389.1358.



4l was obtained as a yellow solid in 53% yield after flash chromatography and the enantiomeric excess was determined to be 91% by HPLC analysis on Chiralcel IC column (7% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 23.269 min, t_{Rminor} 21.872 min; $[\alpha]_D^{20}$ –30.0 (*c* 1.333, $CHCl_3$); m.p. 158-160 °C; IR (KBr) ν_{max}/cm^{-1} 3426, 3317, 2204, 1644, 1622, 1564, 1495, 813; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.41 (m, 10H), 5.83 (d, 1H, *J* 3.6 Hz), 5.63 (s, 2H), 4.29 (d, 1H, *J* 3.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 137.4, 136.4, 133.8, 130.0, 129.5, 129.4, 129.3, 128.7, 127.5, 116.2, 115.7, 111.9, 110.6, 82.1, 49.1, 44.2; HRMS (ESI) $C_{21}H_{14}N_4$+Na $[M+Na]^+$ calcd.: 345.1111; found 345.1105.



4a (catalyzed by quinine) was obtained as a yellow solid in 31% yield after flash chromatography and the enantiomeric excess was determined to be 86% by HPLC analysis on Chiralcel OD column (20% 2-propanol/*n*-hexane, 1 mL min^{-1}), UV 254 nm, t_{Rmajor} 14.868 min, t_{Rminor} 10.470 min; $[\alpha]_D^{20}$ +3.3 (*c* 0.300, $CHCl_3$).

NMR spectra and HPLC chromatograms

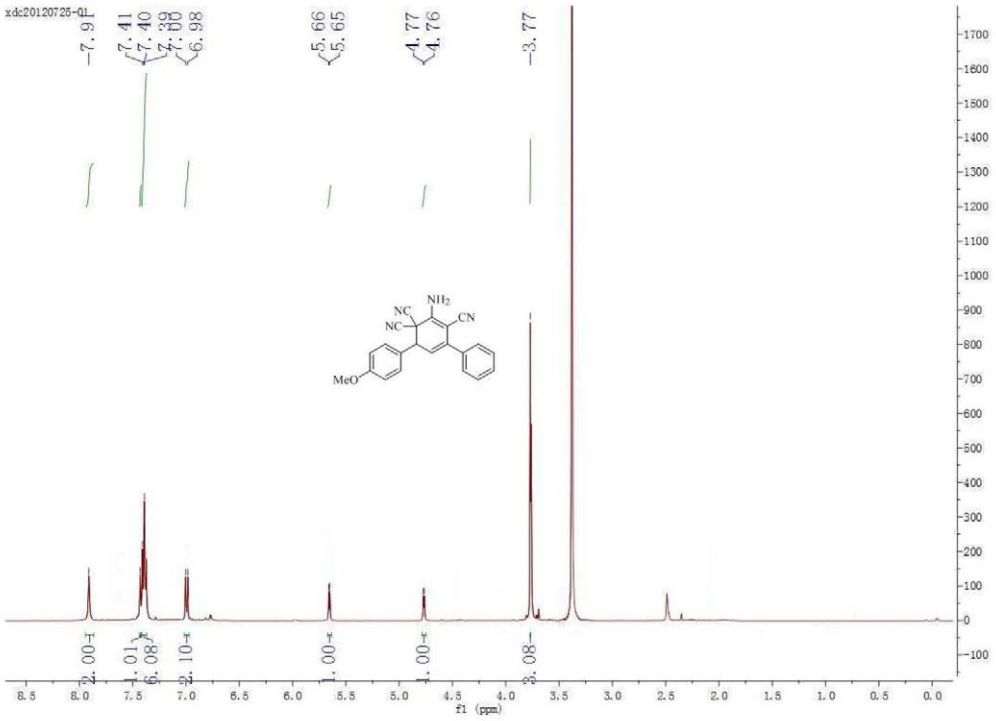


Figure S1. [1]H NMR spectrum (400 MHz, DMSO) of **4a**.

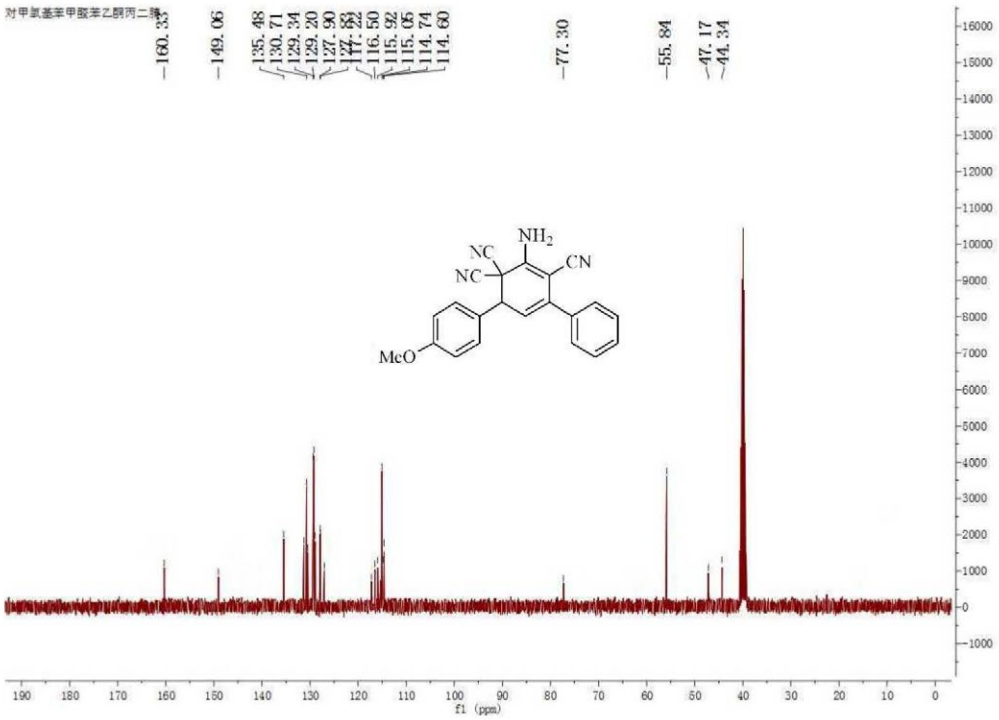


Figure S2. [13]C NMR spectrum (100 MHz, DMSO) of **4a**.

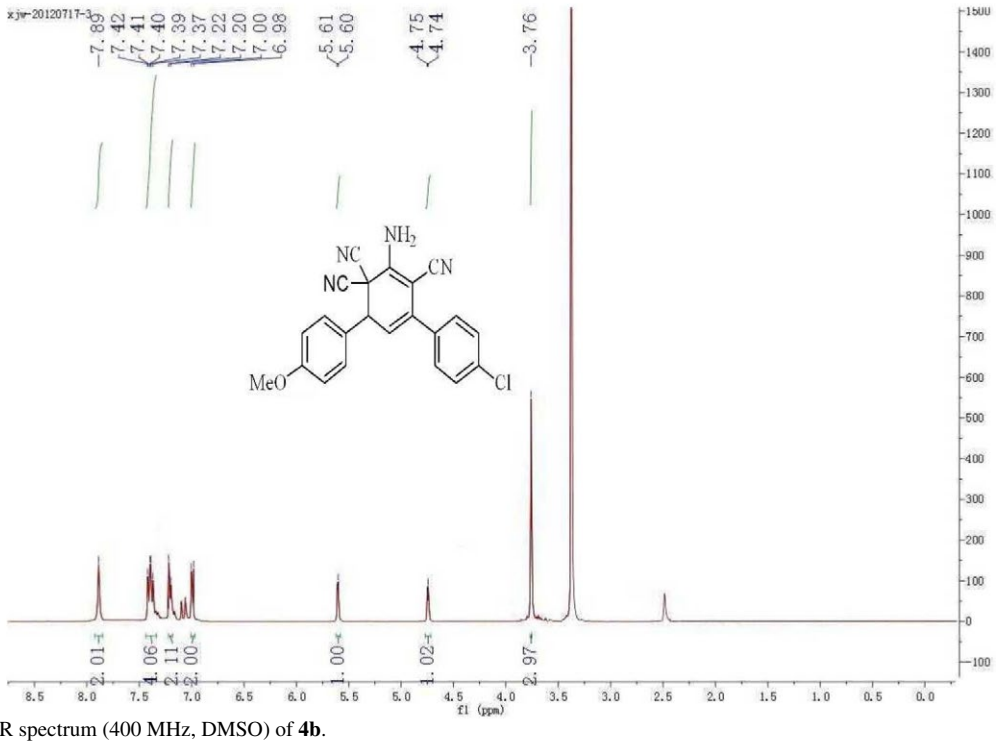


Figure S3. [1]H NMR spectrum (400 MHz, DMSO) of **4b**.

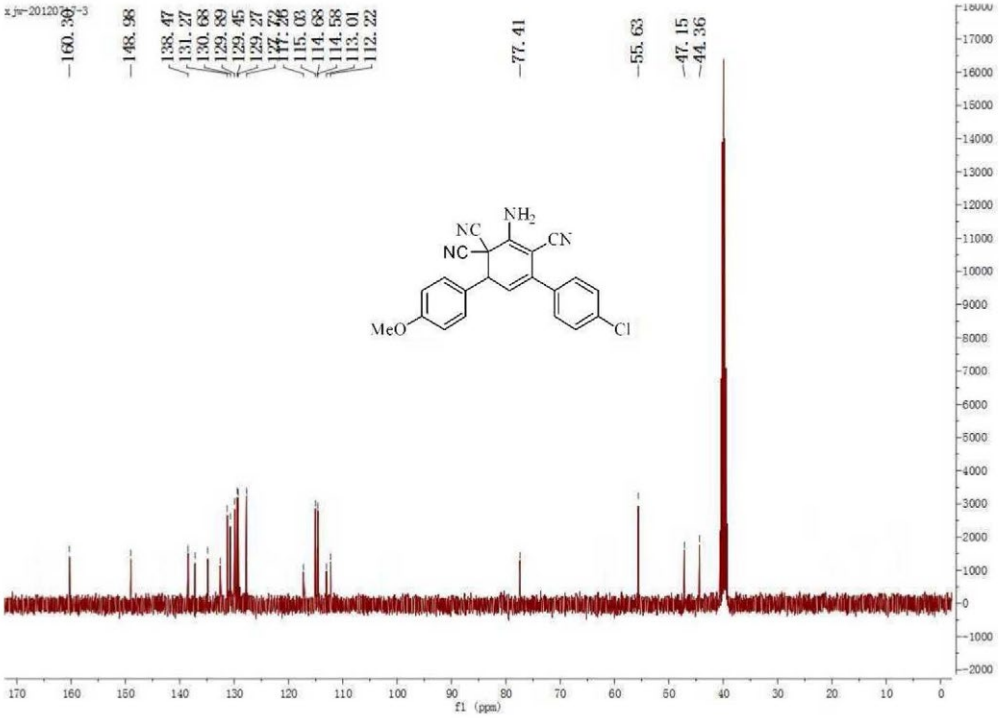


Figure S4. [13]C NMR spectrum (100 MHz, DMSO) of **4b**.

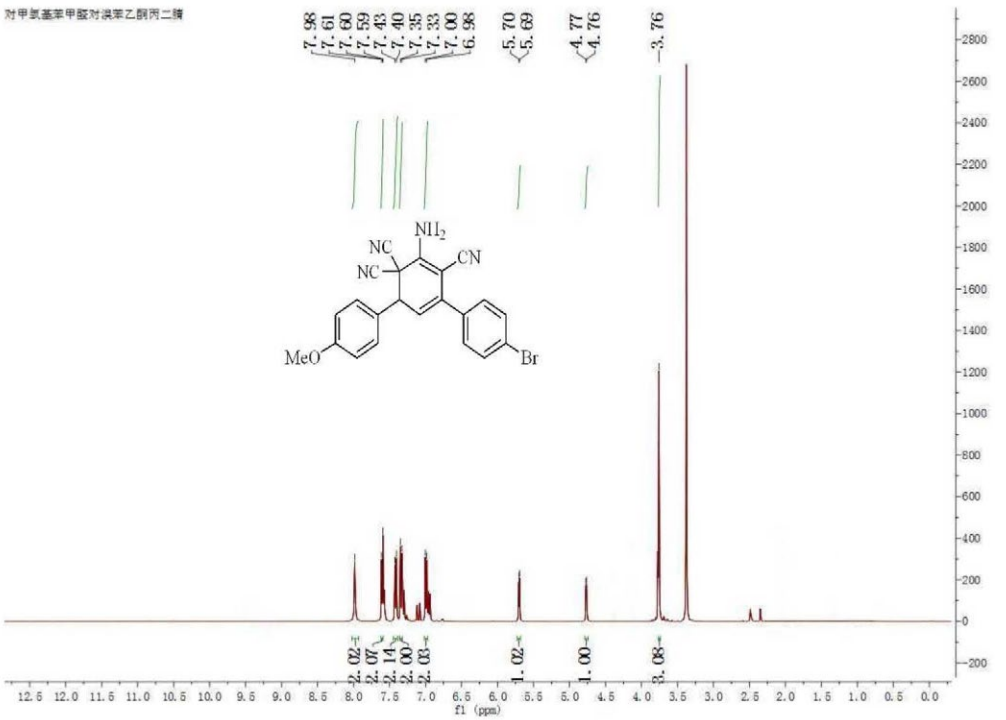


Figure S5. [1]H NMR spectrum (400 MHz, DMSO) of **4c**.

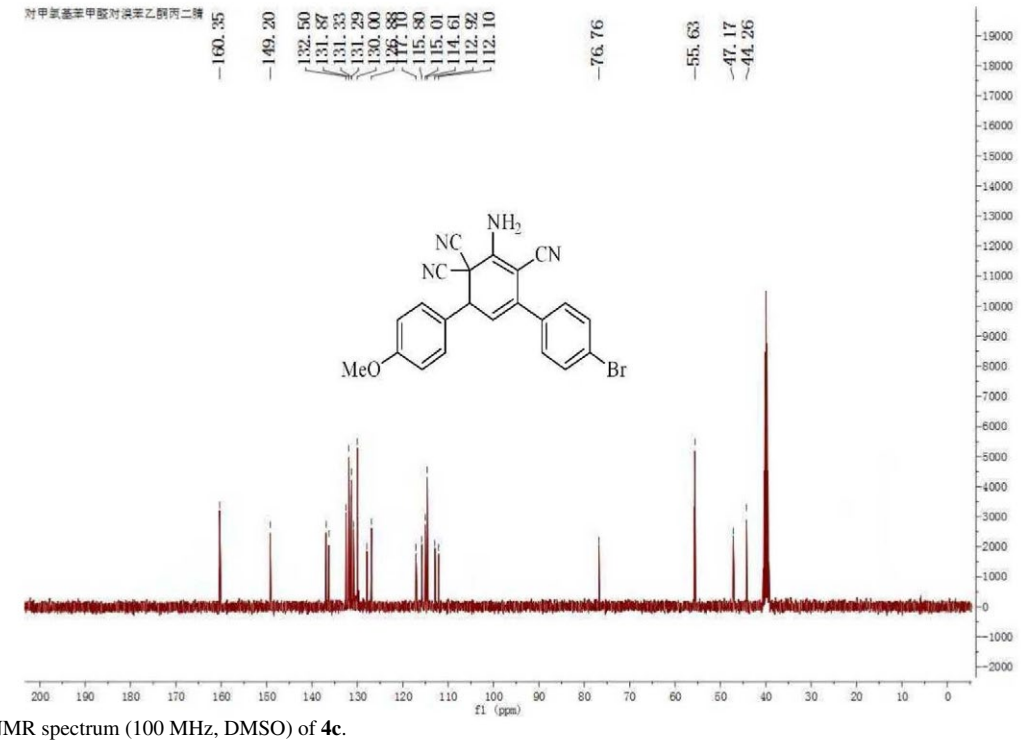


Figure S6. [13]C NMR spectrum (100 MHz, DMSO) of **4c**.

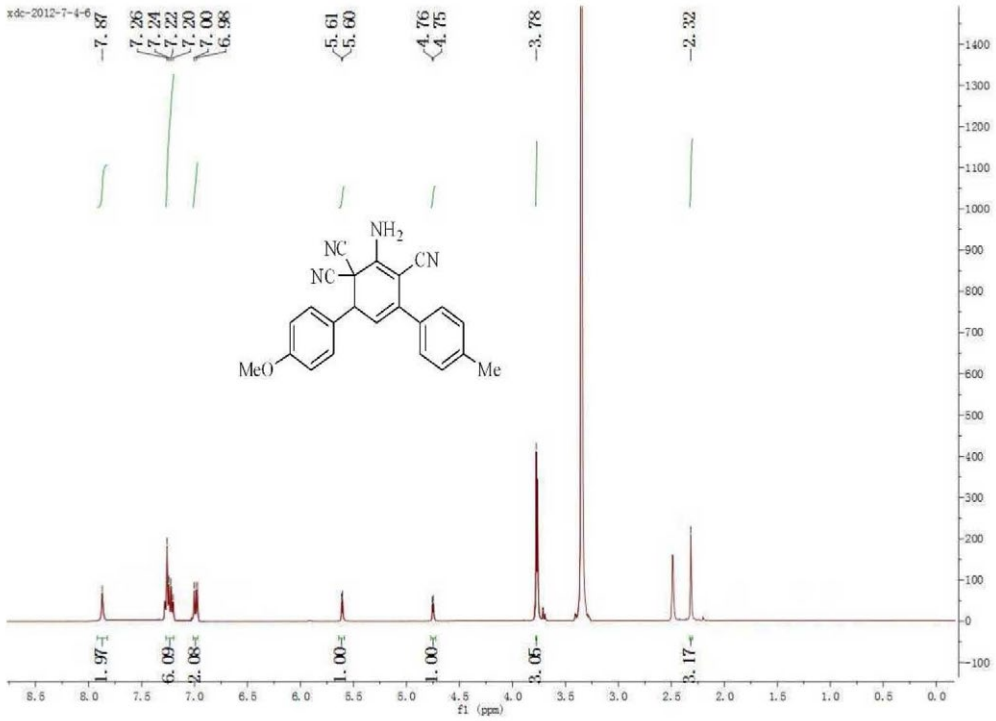


Figure S7. [1]H NMR spectrum (400 MHz, DMSO) of **4d**.

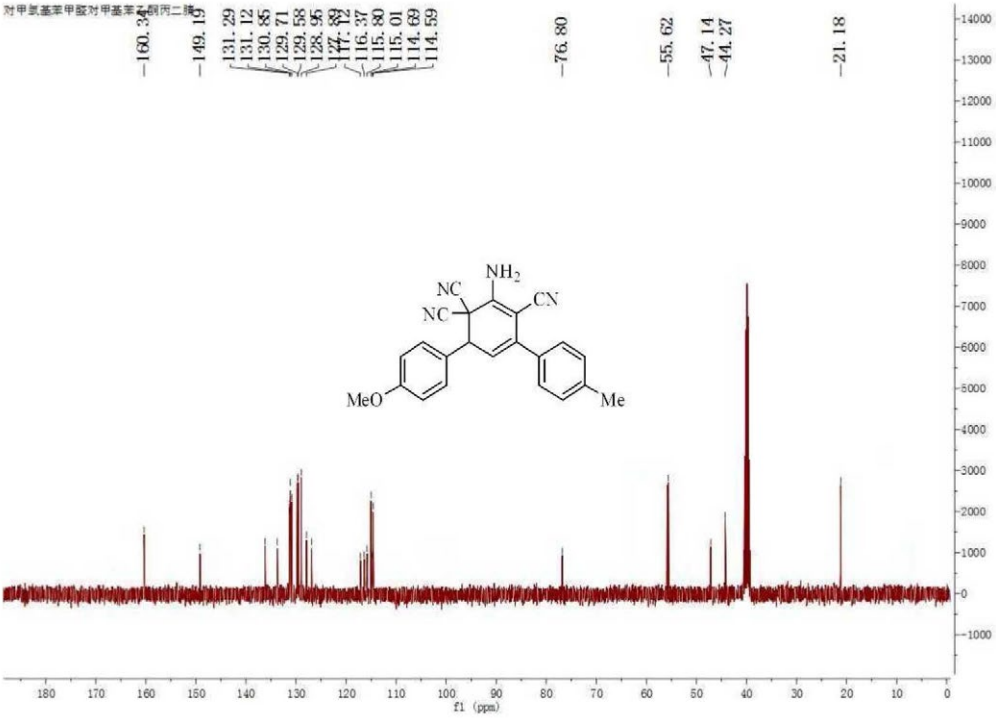


Figure S8. [13]C NMR spectrum (100 MHz, DMSO) of **4d**.

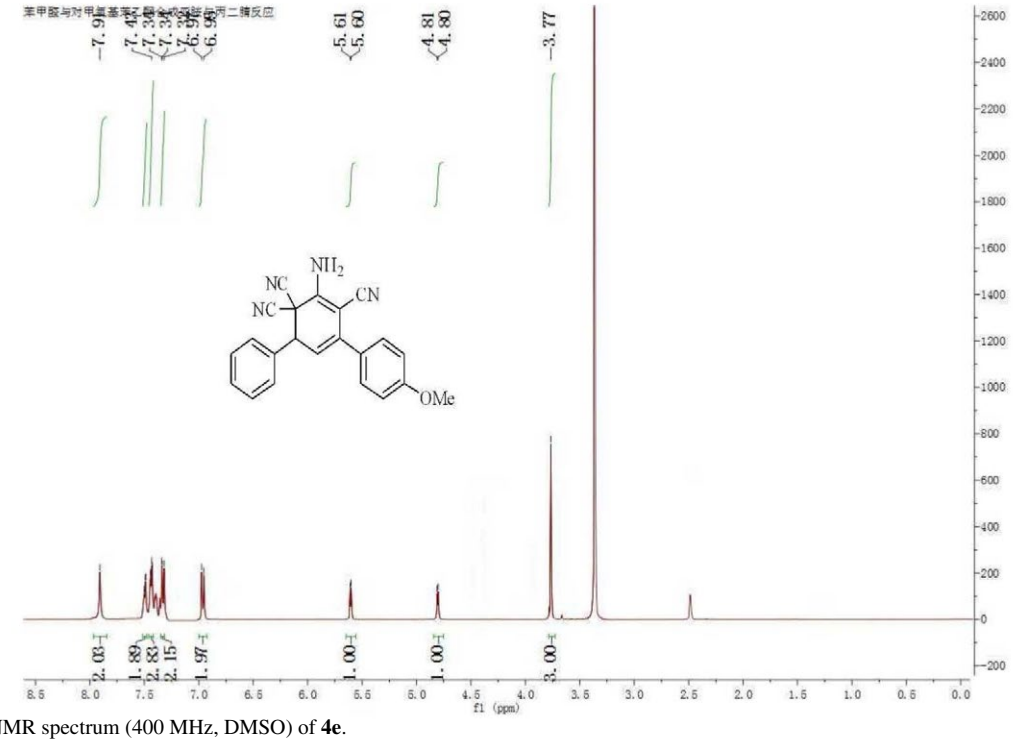


Figure S9. [1]H NMR spectrum (400 MHz, DMSO) of **4e**.

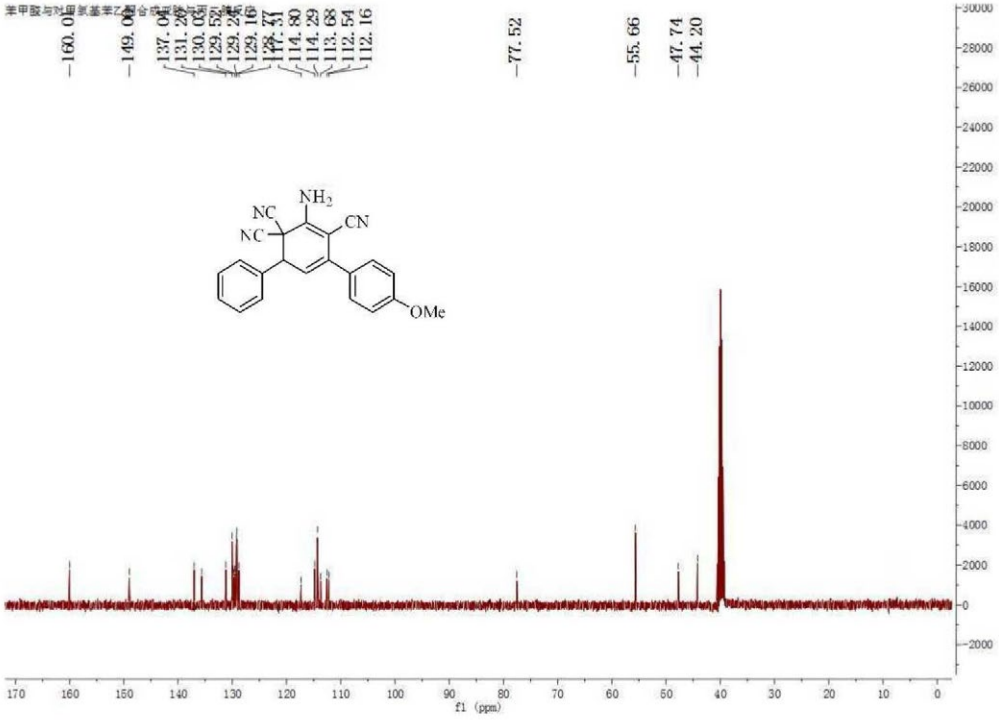


Figure S10. [13]C NMR spectrum (100 MHz, DMSO) of **4e**.

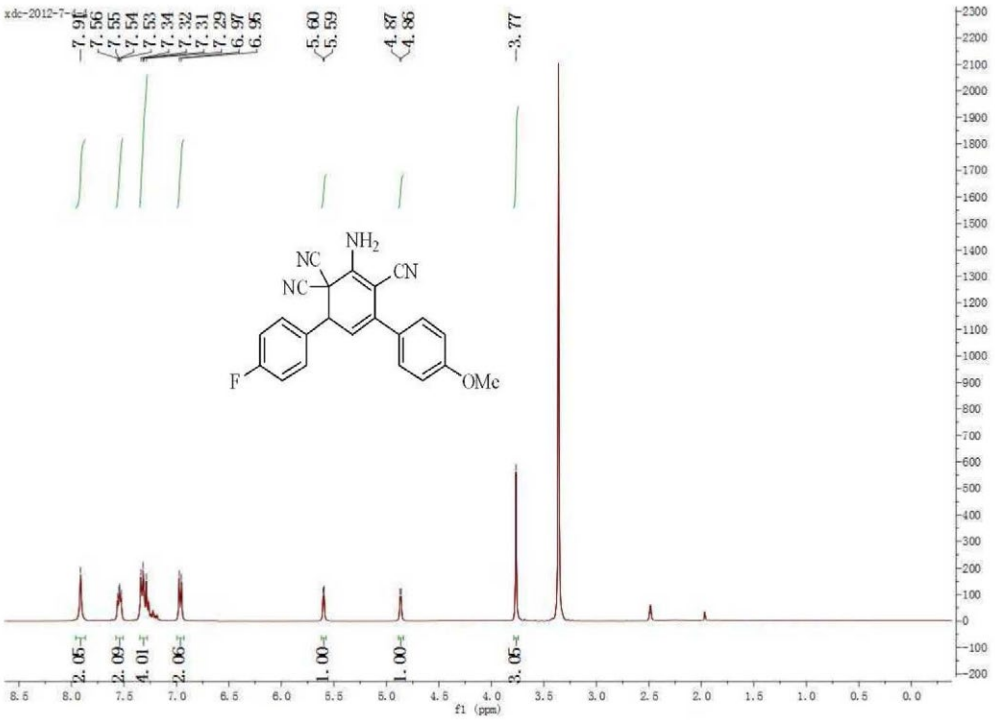


Figure S11. [1]H NMR spectrum (400 MHz, DMSO) of **4f**.

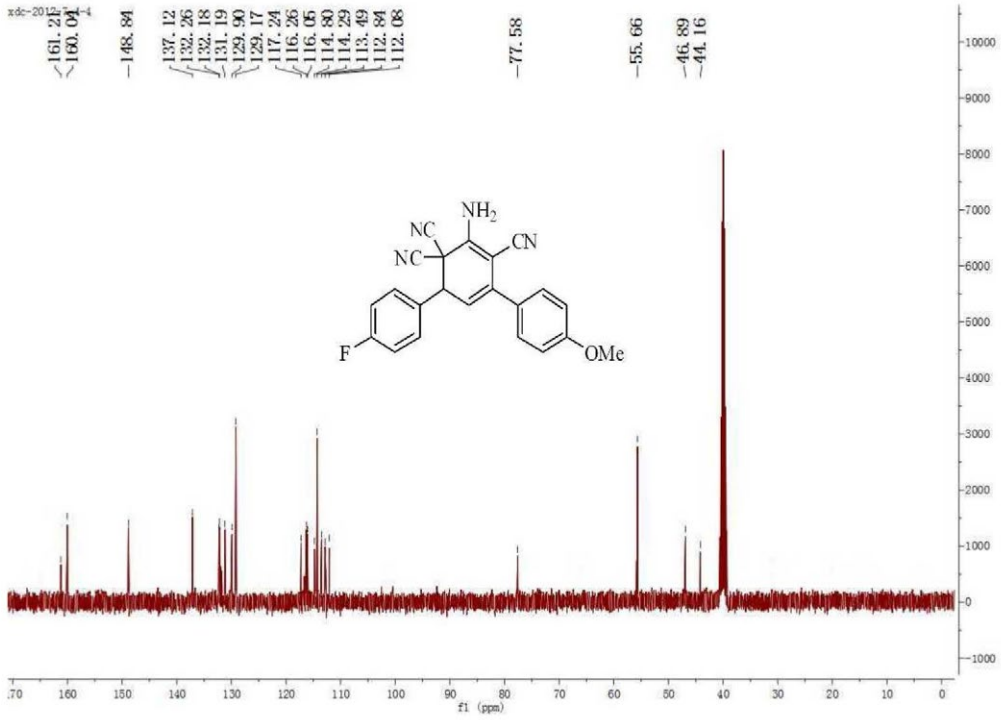


Figure S12. [13]C NMR spectrum (100 MHz, DMSO) of **4f**.

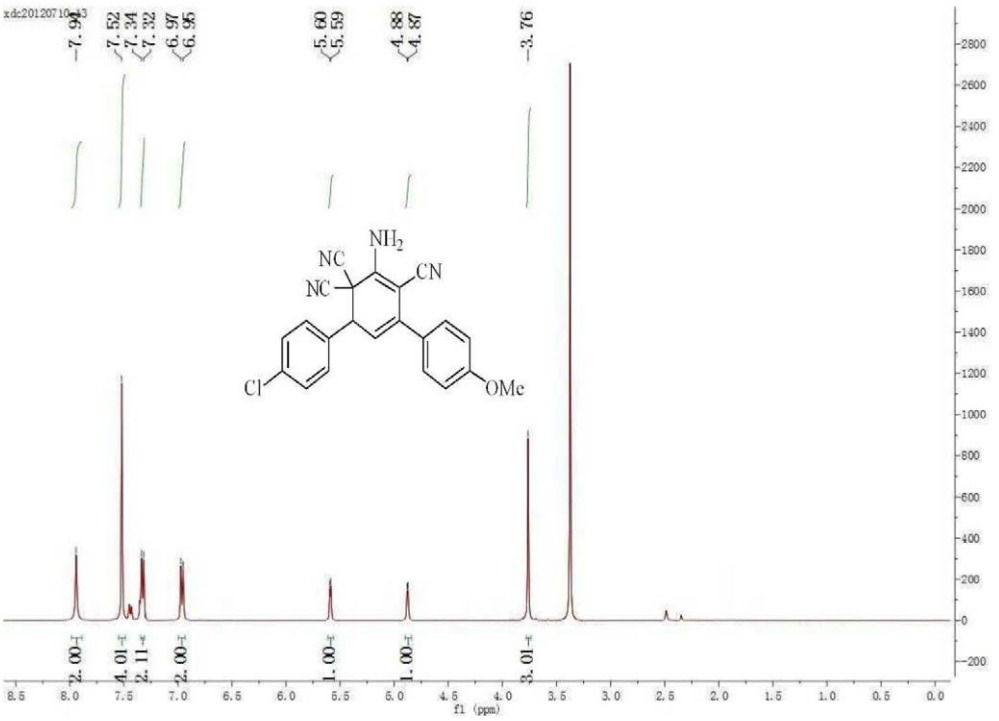


Figure S13. [1]H NMR spectrum (400 MHz, DMSO) of **4g**.

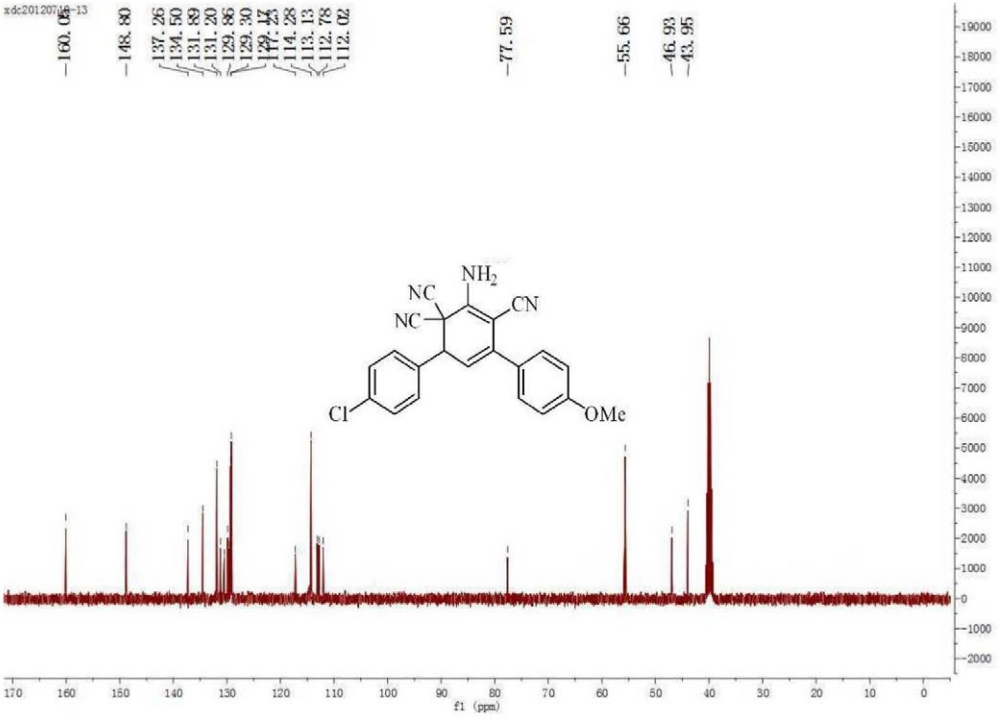


Figure S14. [13]C NMR spectrum (100 MHz, DMSO) of **4g**.

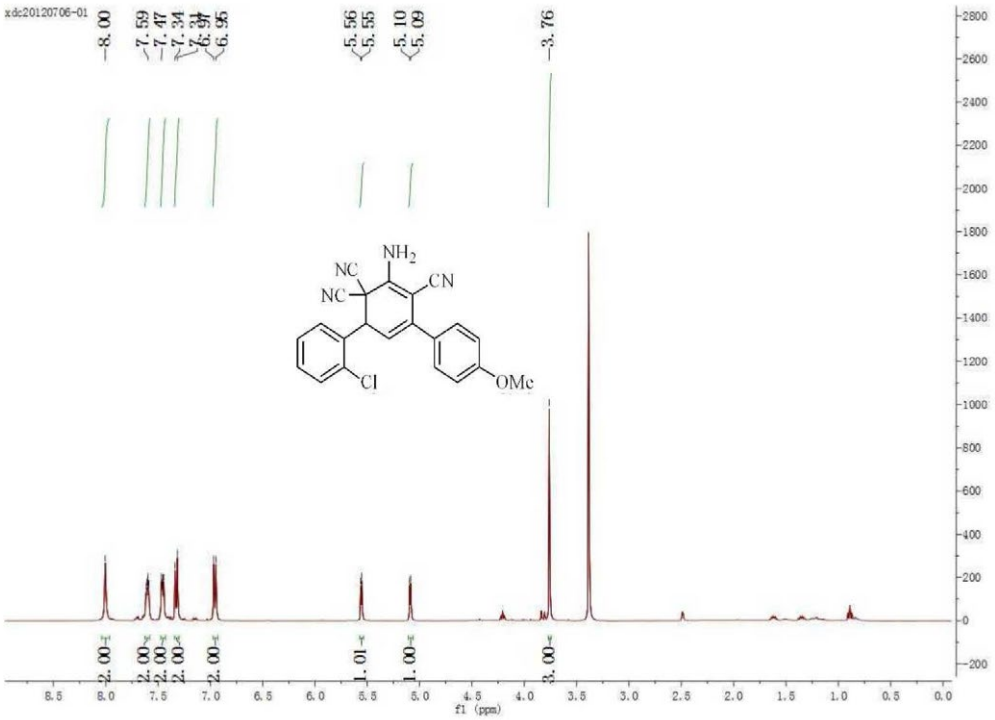


Figure S15. [1]H NMR spectrum (400 MHz, DMSO) of **4h**.

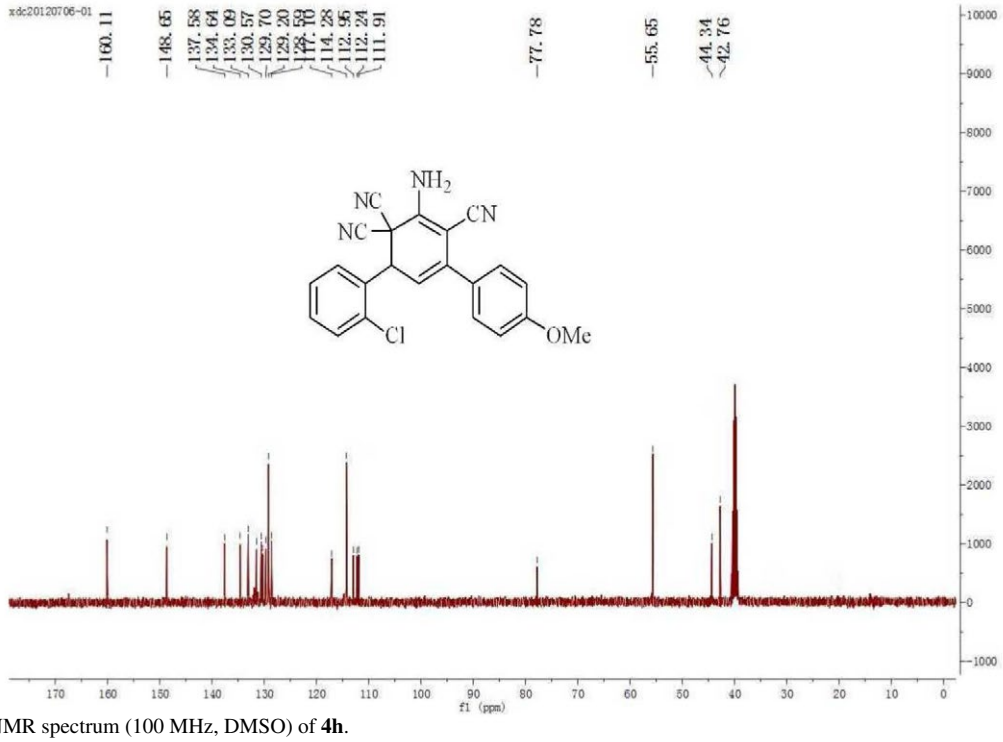


Figure S16. [13]C NMR spectrum (100 MHz, DMSO) of **4h**.

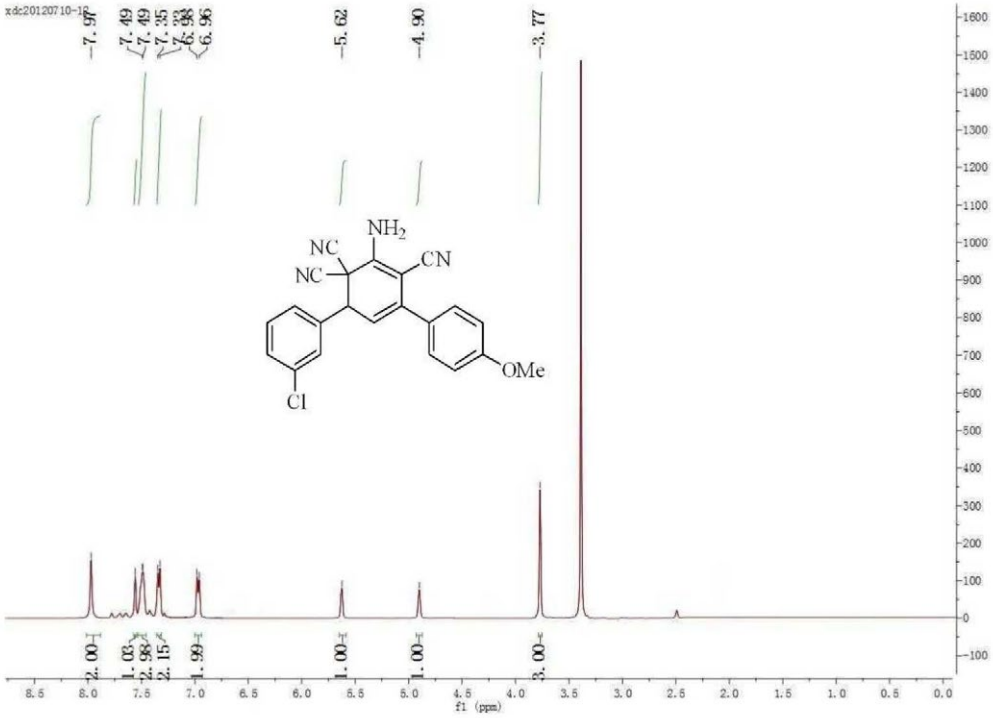


Figure S17. [1]H NMR spectrum (400 MHz, DMSO) of **4i**.

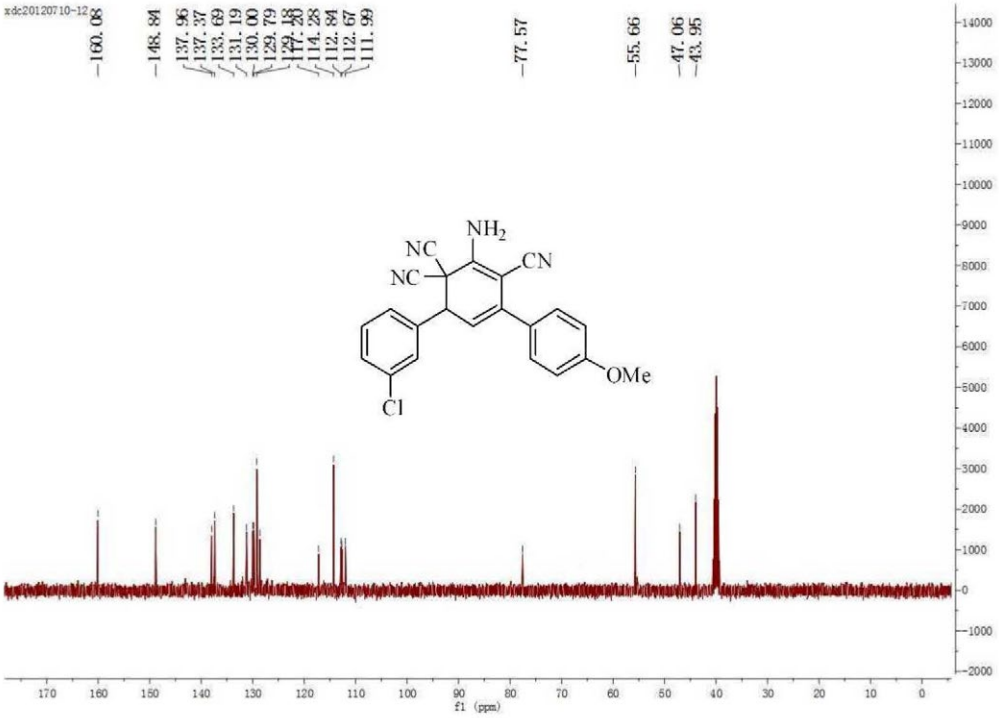


Figure S18. [13]C NMR spectrum (100 MHz, DMSO) of **4i**.

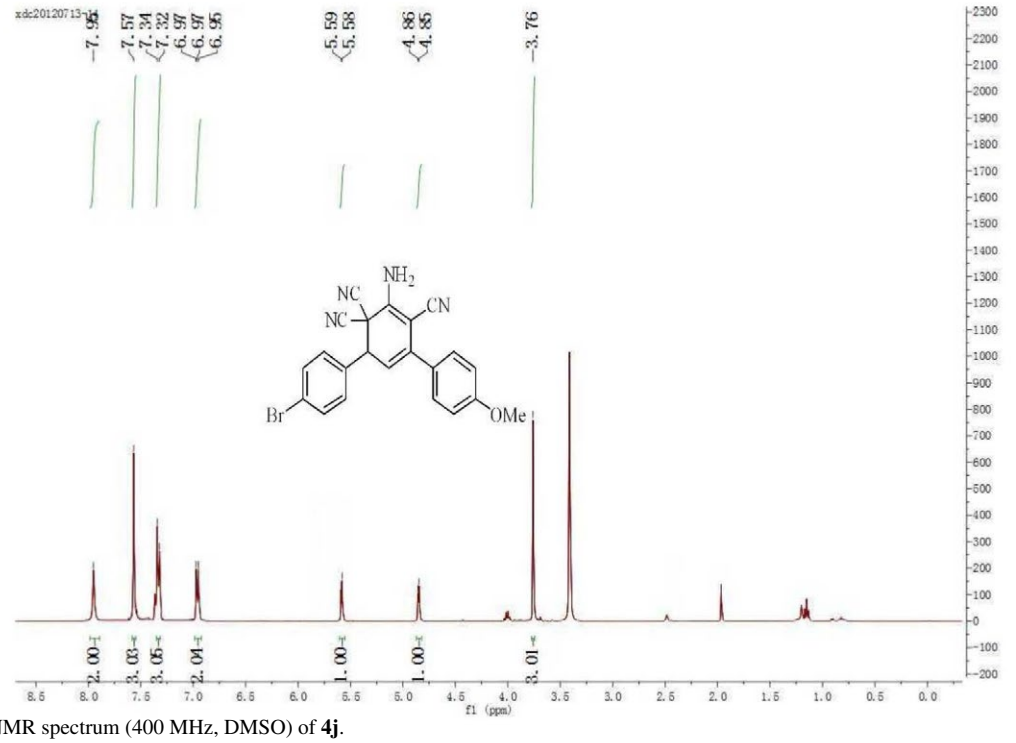


Figure S19. [1]H NMR spectrum (400 MHz, DMSO) of **4j**.

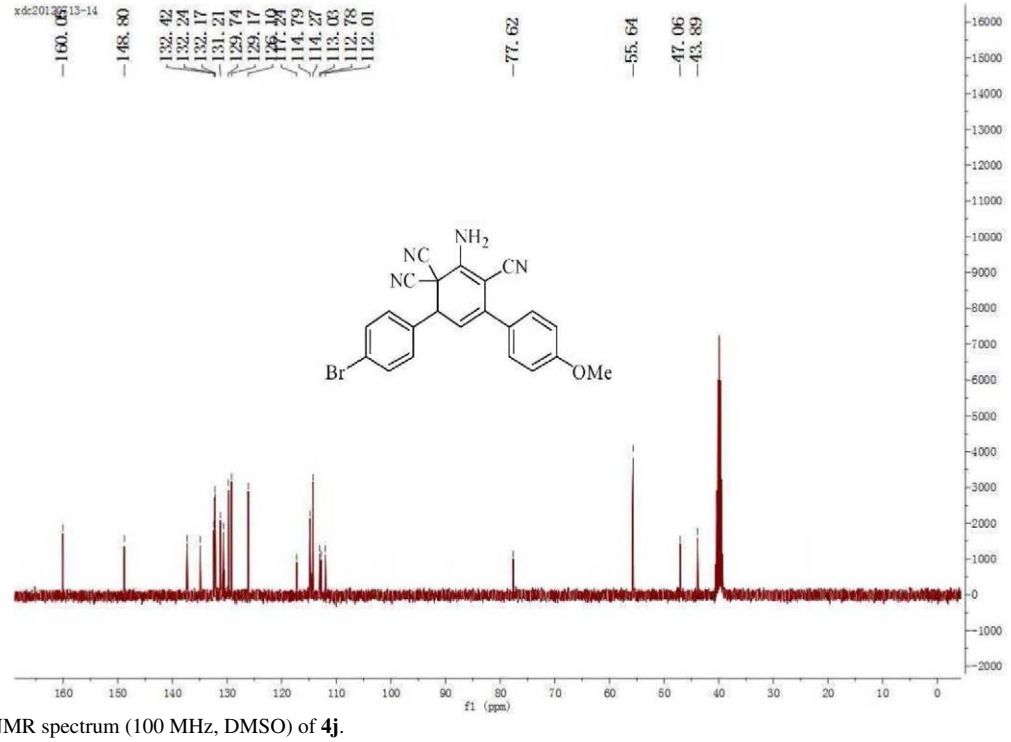


Figure S20. [13]C NMR spectrum (100 MHz, DMSO) of **4j**.

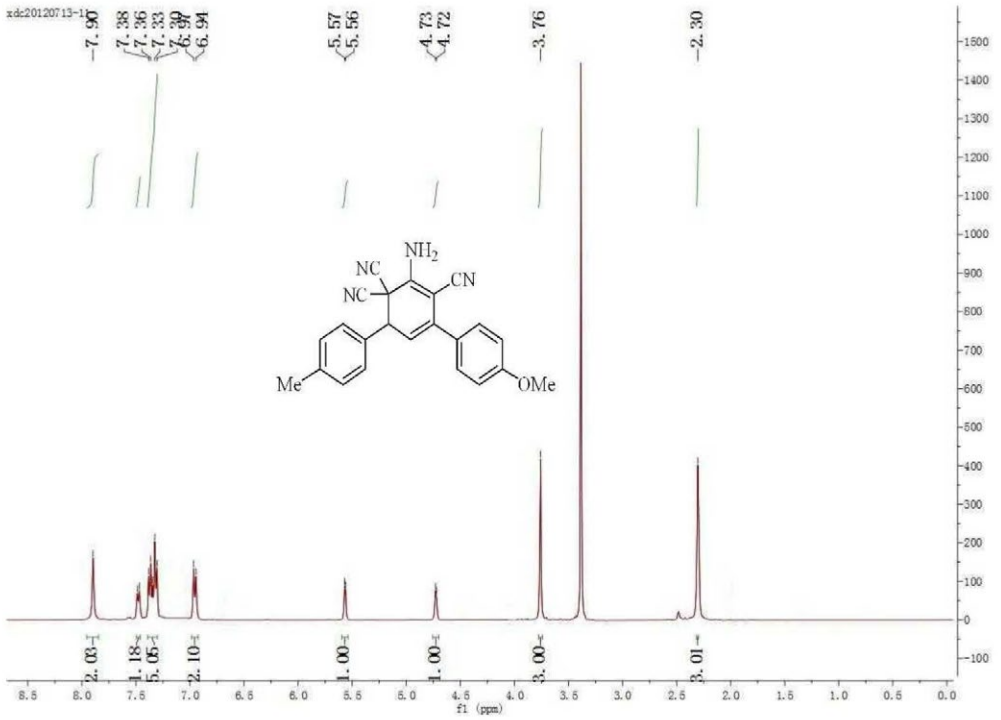


Figure S21. [1]H NMR spectrum (400 MHz, DMSO) of **4k**.

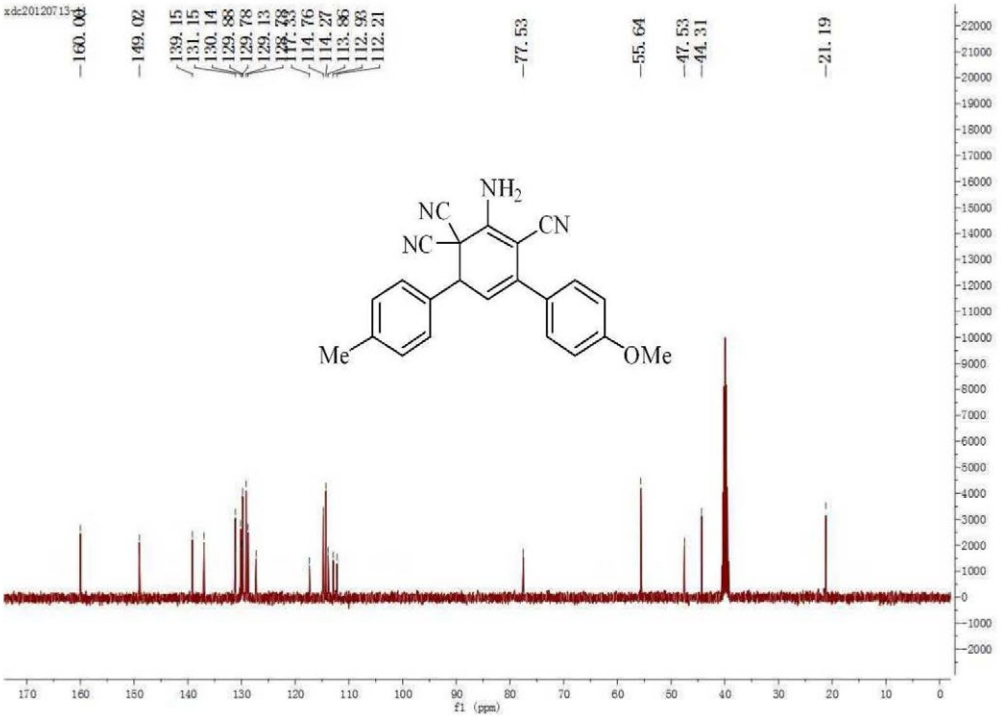


Figure S22. [13]C NMR spectrum (100 MHz, DMSO) of **4k**.

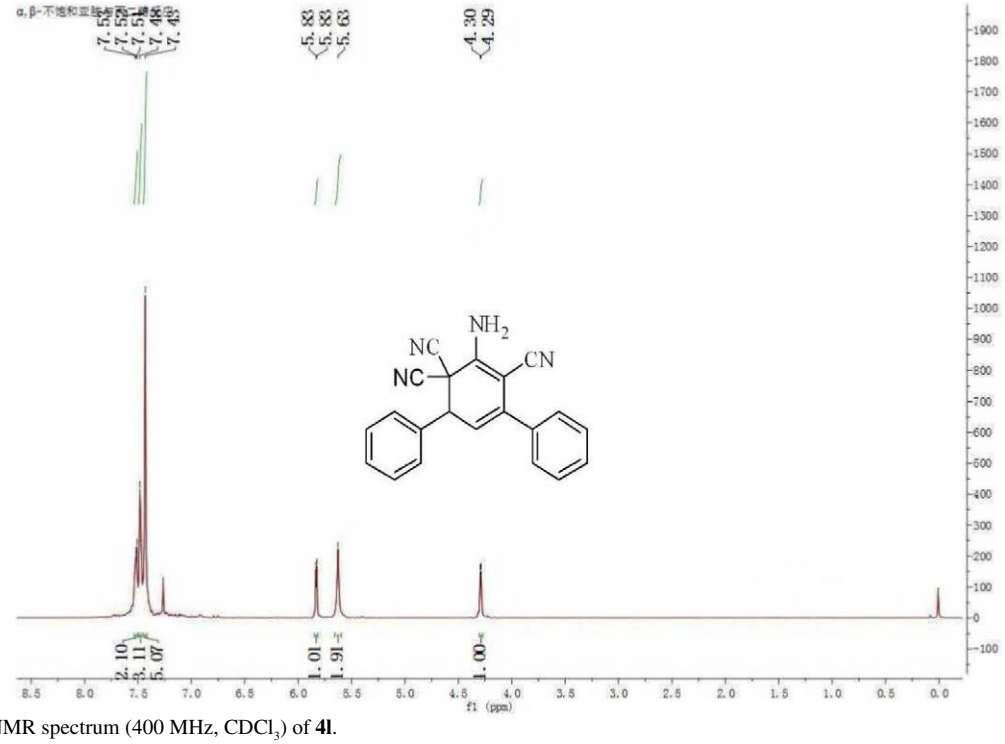


Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4l**.

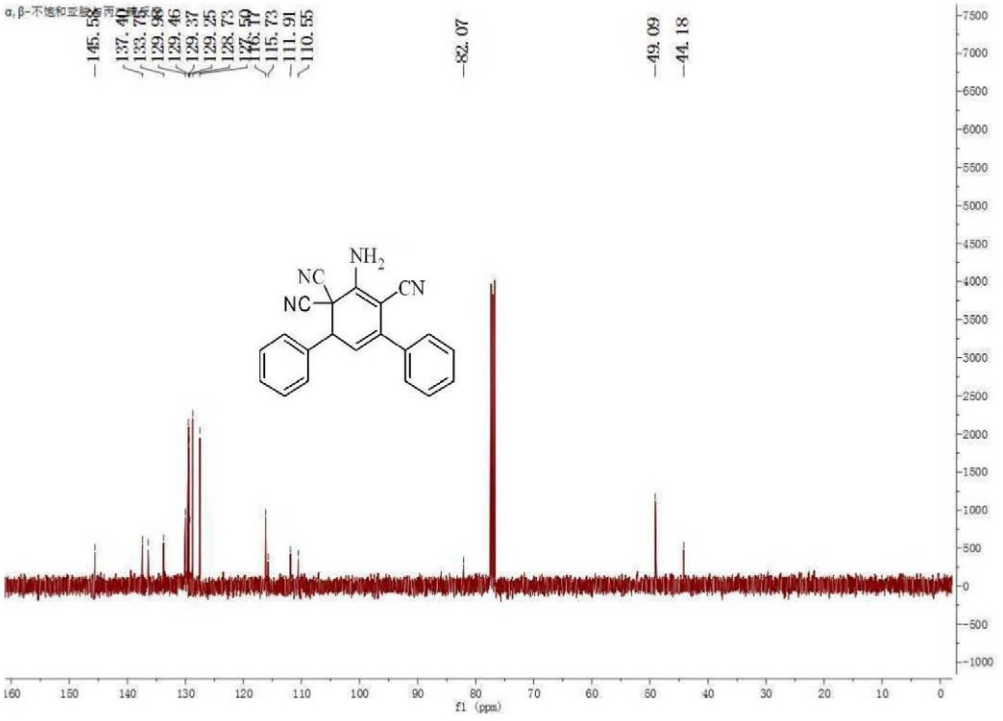
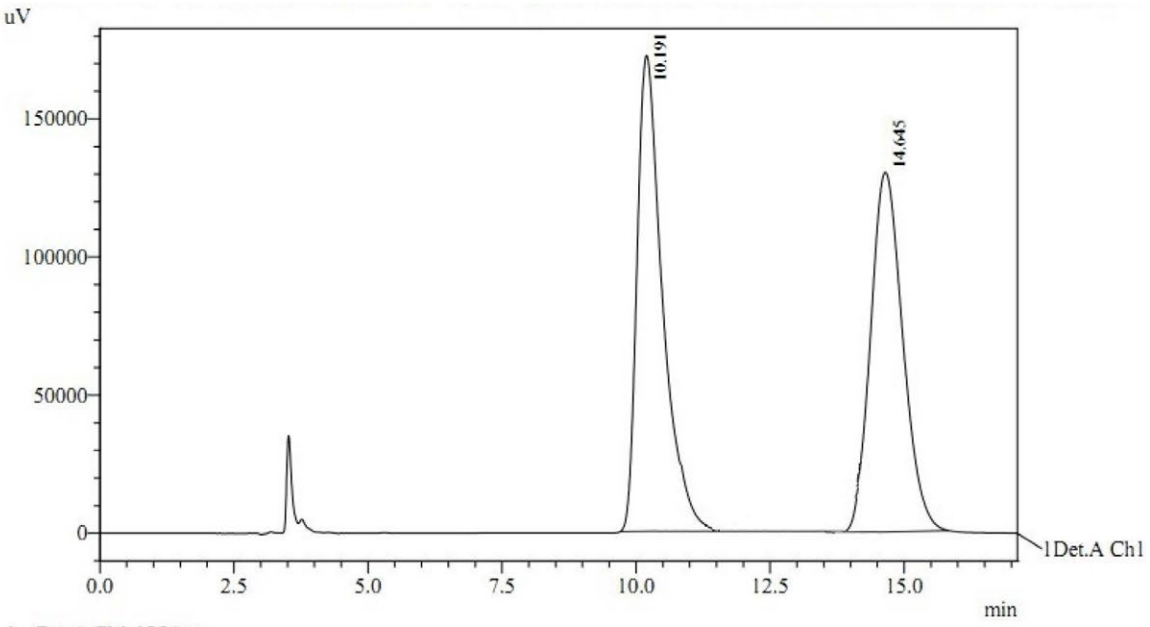


Figure S24. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4l**.

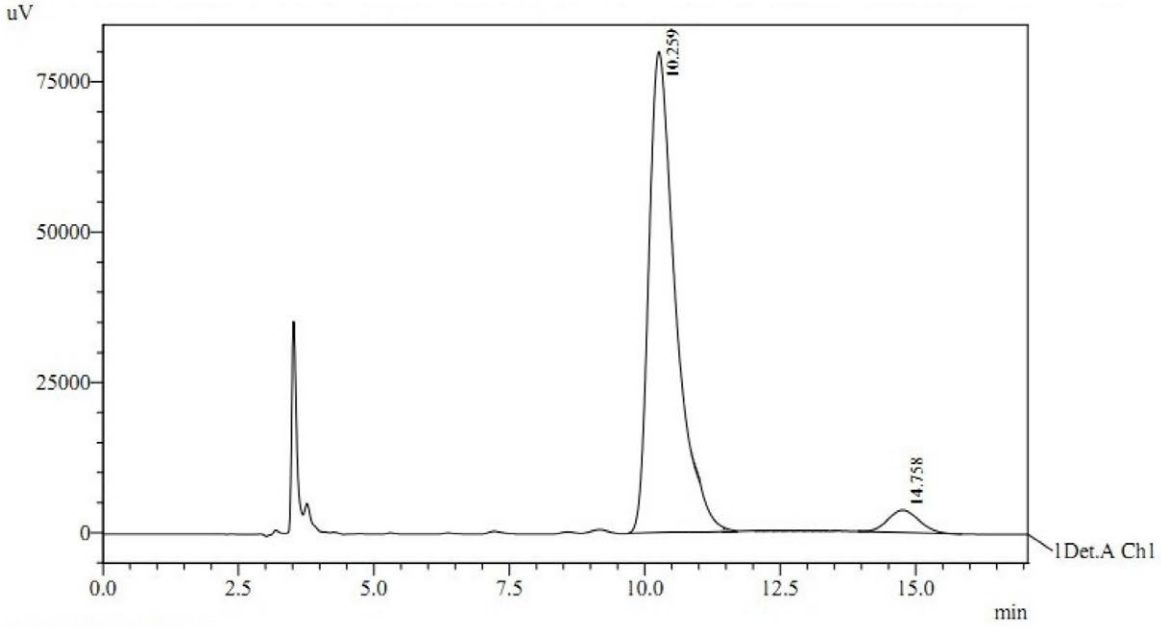


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.191	5759698	172355	50.740	56.962
2	14.645	5591781	130223	49.260	43.038
Total		11351479	302578	100.000	100.000



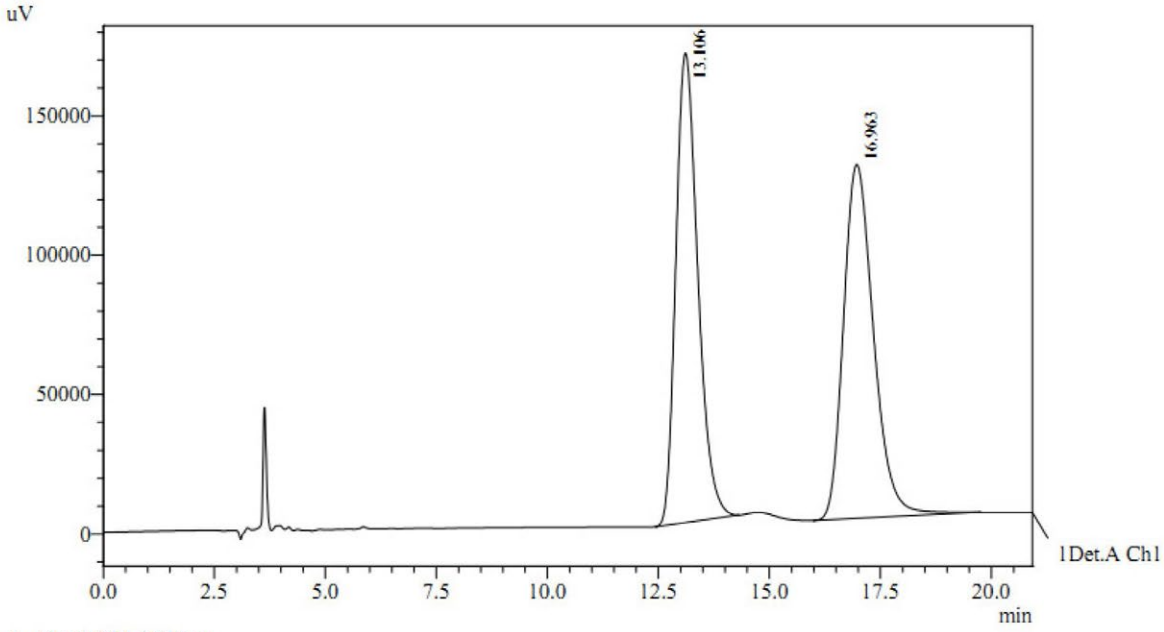
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.259	2615589	78649	94.634	95.518
2	14.758	148312	3691	5.366	4.482
Total		2763901	82339	100.000	100.000

Figure S25. HPLC chromatograms of **4a**.

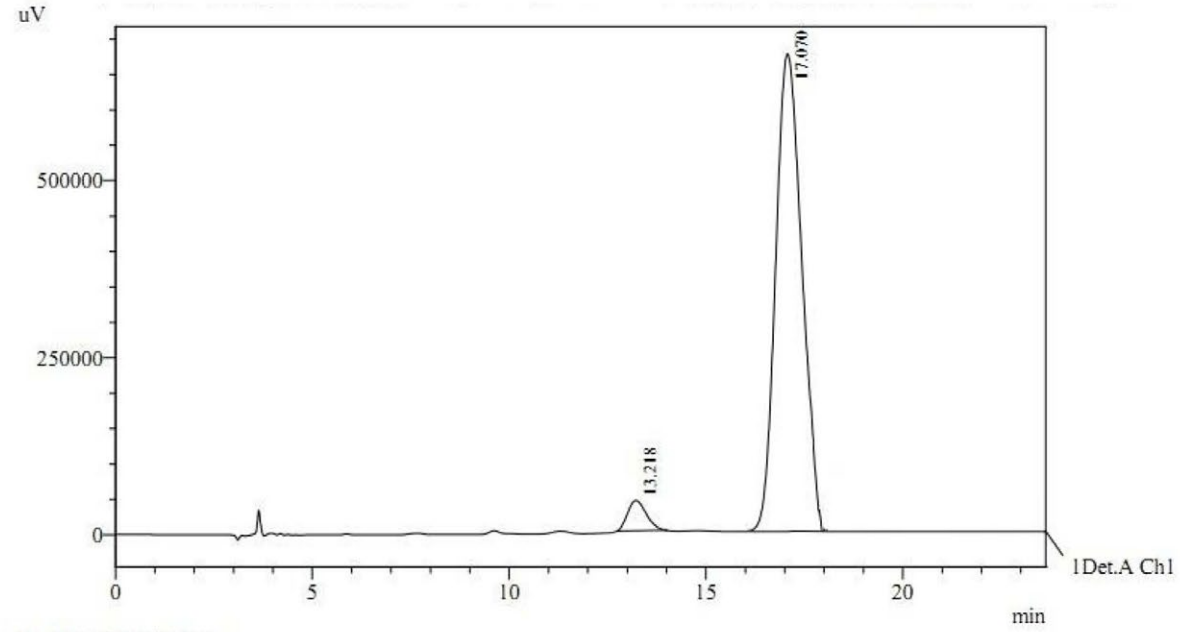


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.106	5806532	168515	49.261	57.032
2	16.963	5980748	126958	50.739	42.968
Total		11787280	295473	100.000	100.000



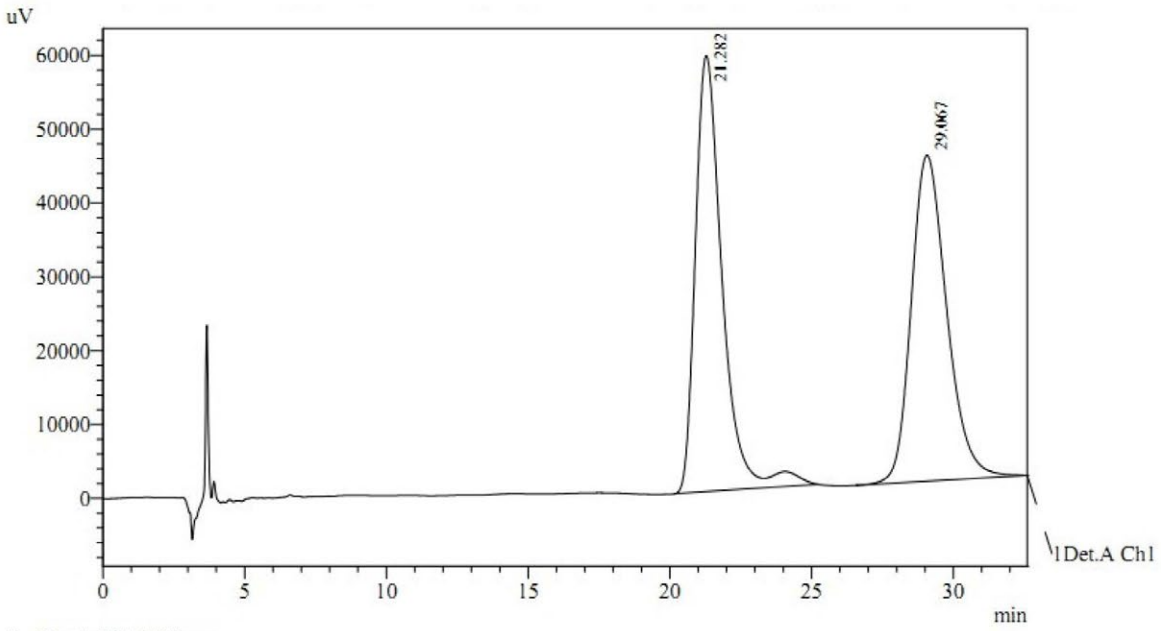
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.218	1614137	45034	5.201	6.458
2	17.070	29420066	652350	94.799	93.542
Total		31034203	697384	100.000	100.000

Figure S26. HPLC chromatograms of **4b**.

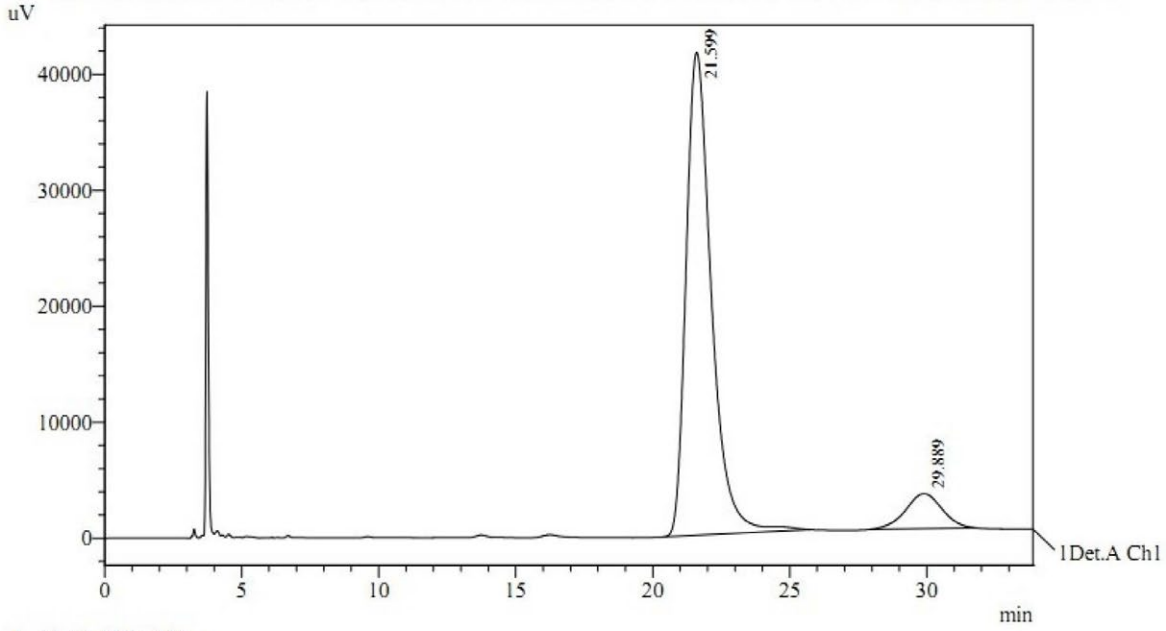


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.282	3910908	59061	50.468	57.220
2	29.067	3838442	44156	49.532	42.780
Total		7749350	103218	100.000	100.000



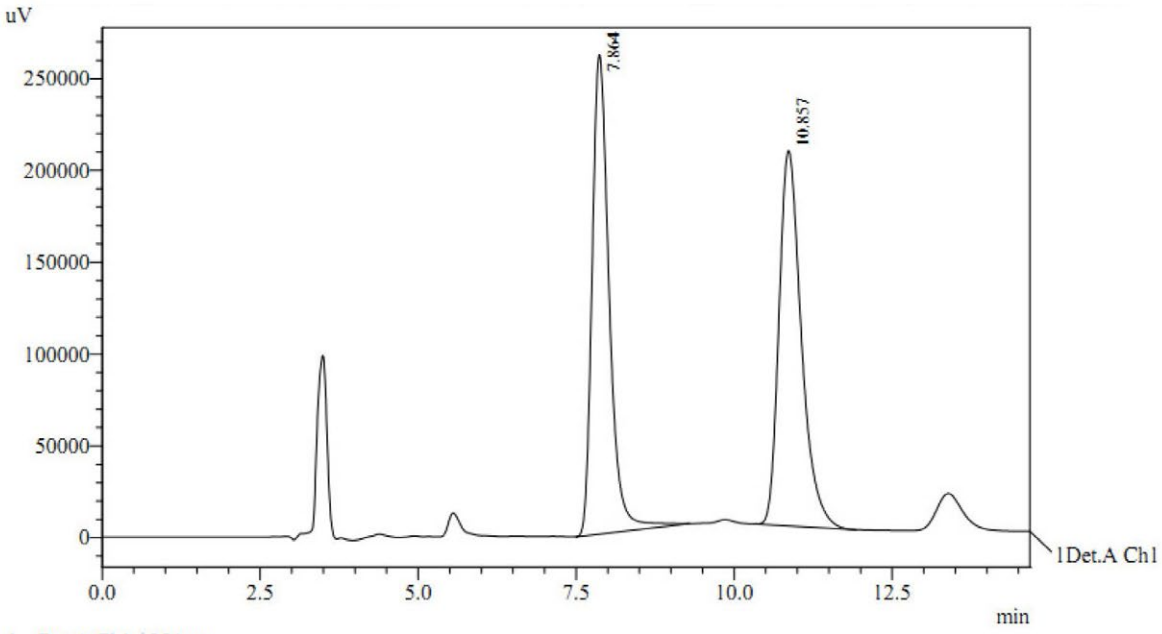
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.599	2673131	41646	92.880	94.110
2	29.889	204912	2606	7.120	5.890
Total		2878044	44252	100.000	100.000

Figure S27. HPLC chromatograms of **4c**.

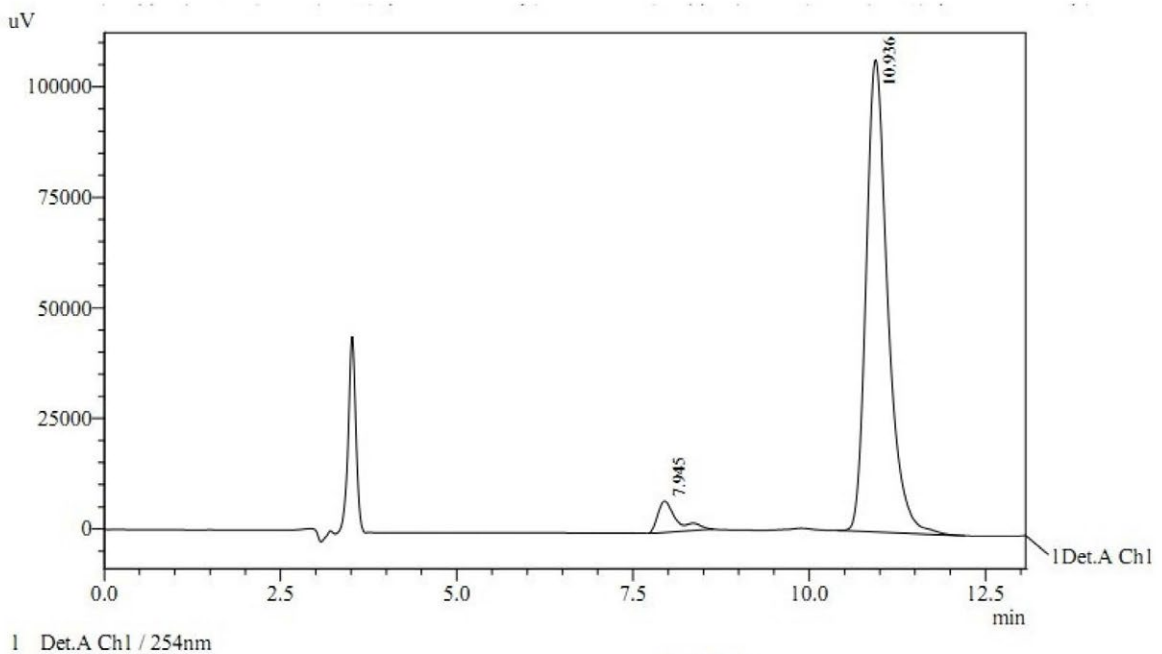


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.864	4910865	261048	49.420	56.092
2	10.857	5026168	204348	50.580	43.908
Total		9937033	465397	100.000	100.000



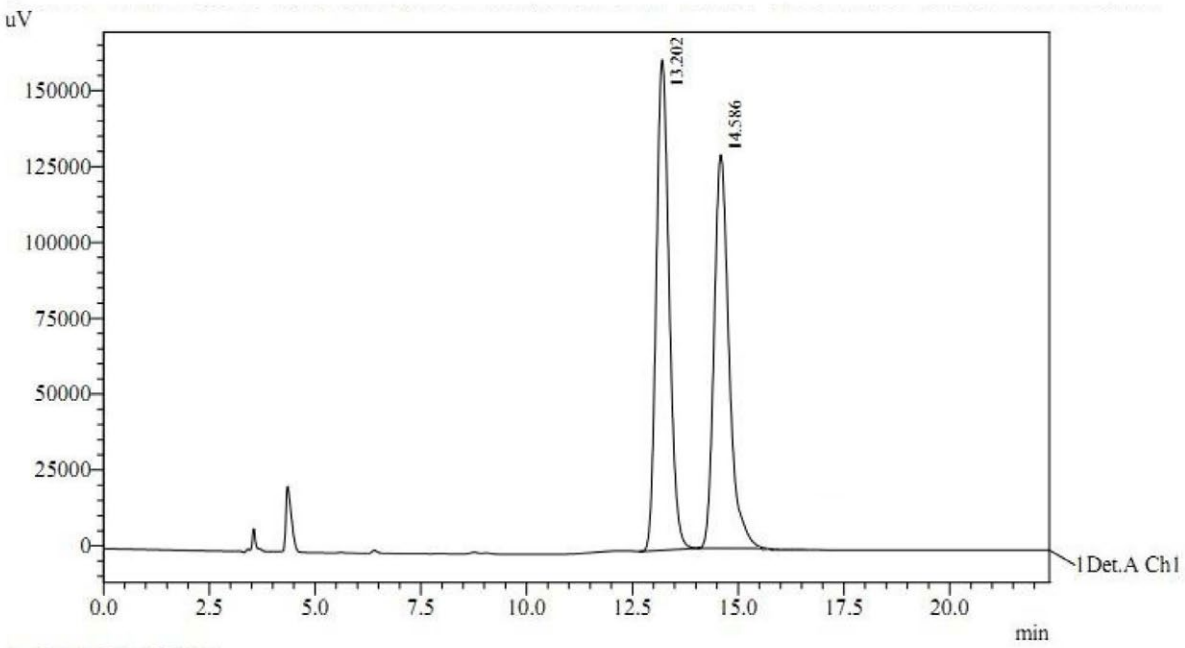
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.945	133256	7075	5.538	6.212
2	10.936	2272945	106815	94.462	93.788
Total		2406201	113890	100.000	100.000

Figure S28. HPLC chromatograms of **4d**.

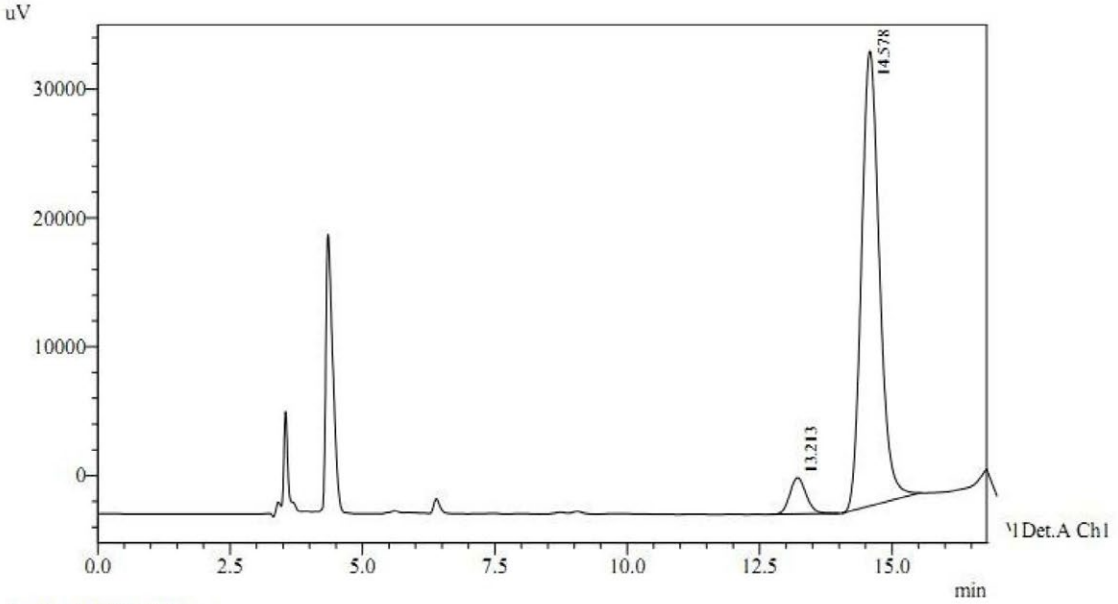


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.202	3424914	161622	50.030	55.490
2	14.586	3420838	129639	49.970	44.510
Total		6845752	291261	100.000	100.000



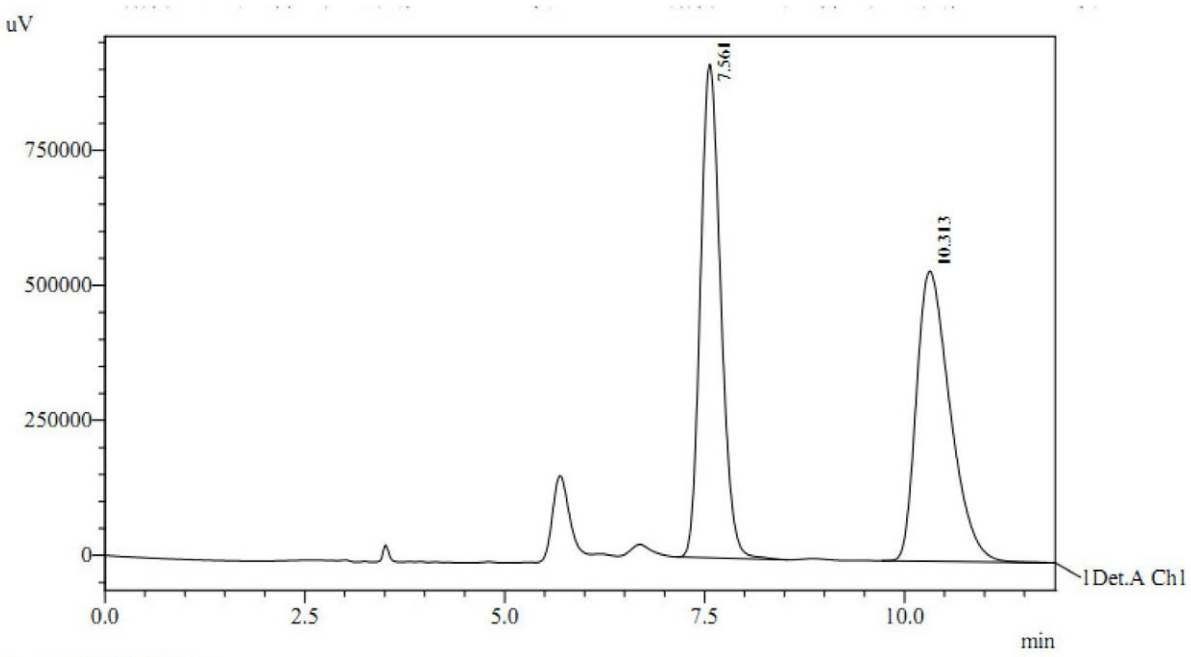
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.213	59444	2804	6.490	7.326
2	14.578	856549	35471	93.510	92.674
Total		915992	38275	100.000	100.000

Figure S29. HPLC chromatograms of **4e**.

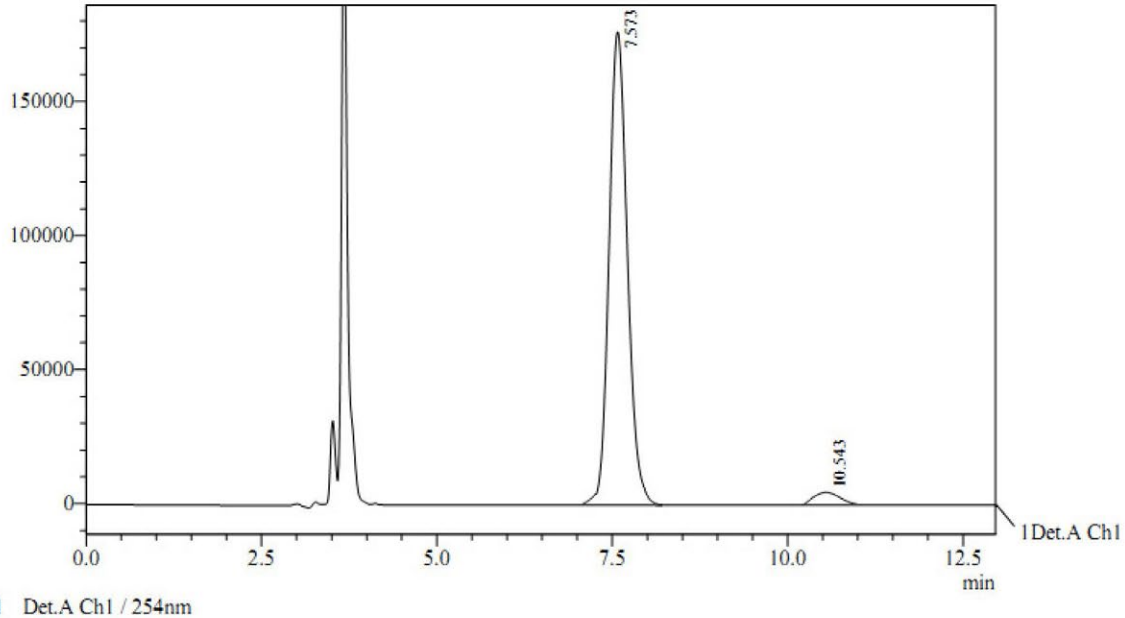


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.561	16117658	914331	50.627	62.968
2	10.313	15718673	537715	49.373	37.032
Total		31836331	1452045	100.000	100.000



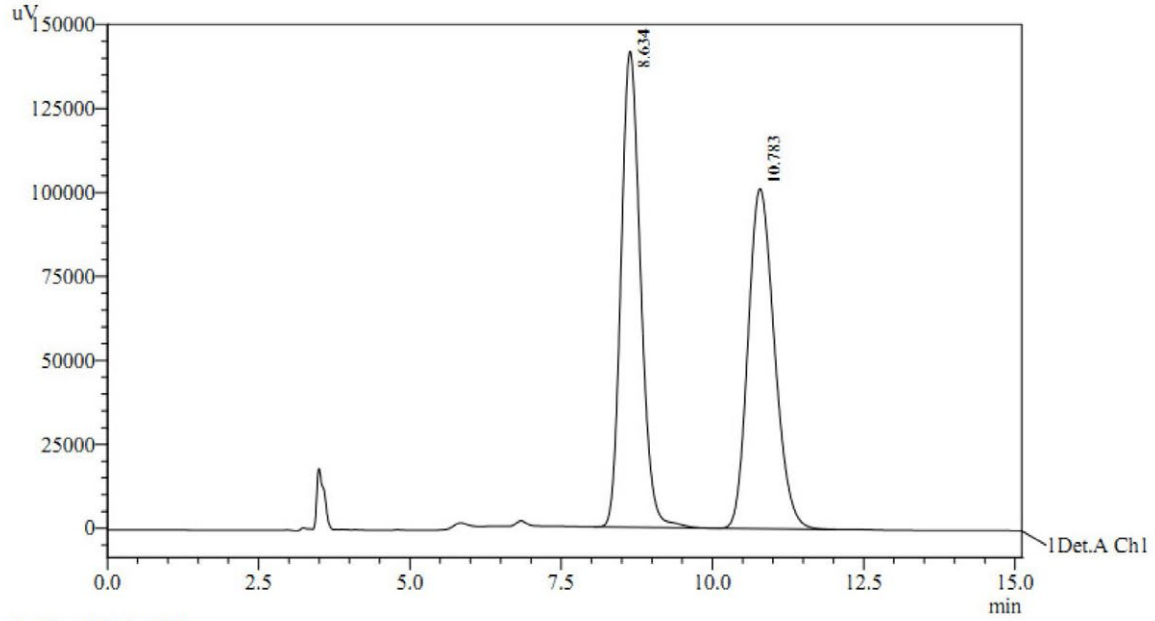
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.573	3112082	175123	95.635	97.261
2	10.543	142034	4931	4.365	2.739
Total		3254117	180054	100.000	100.000

Figure S30. HPLC chromatograms of **4f**.

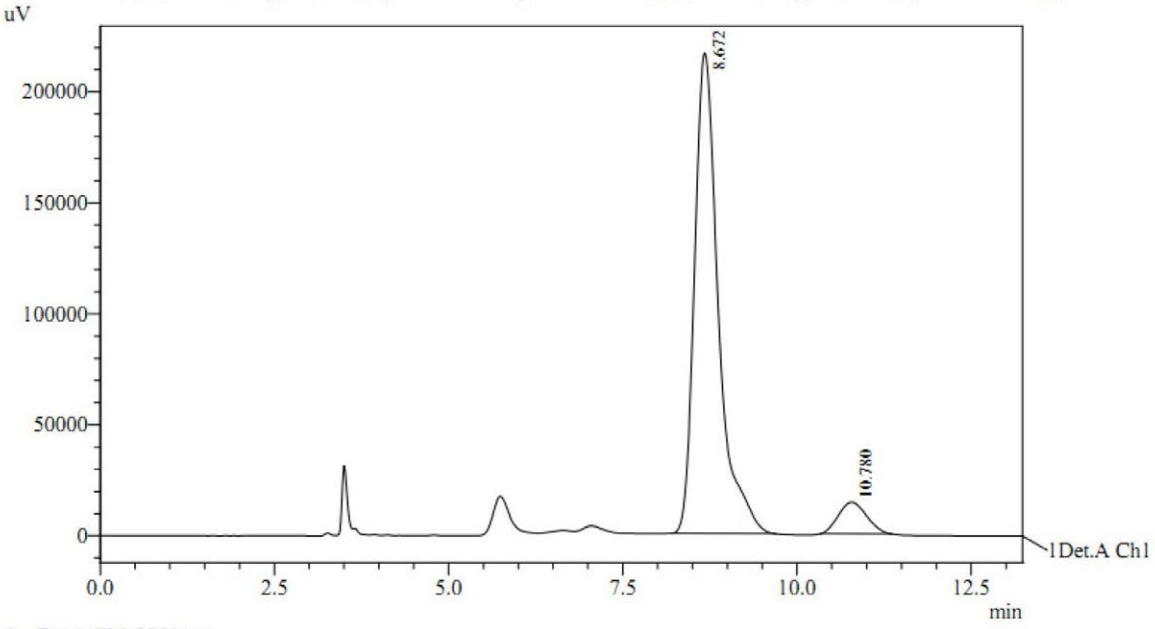


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.634	3185729	141718	50.927	58.319
2	10.783	3069813	101287	49.073	41.681
Total		6255542	243006	100.000	100.000



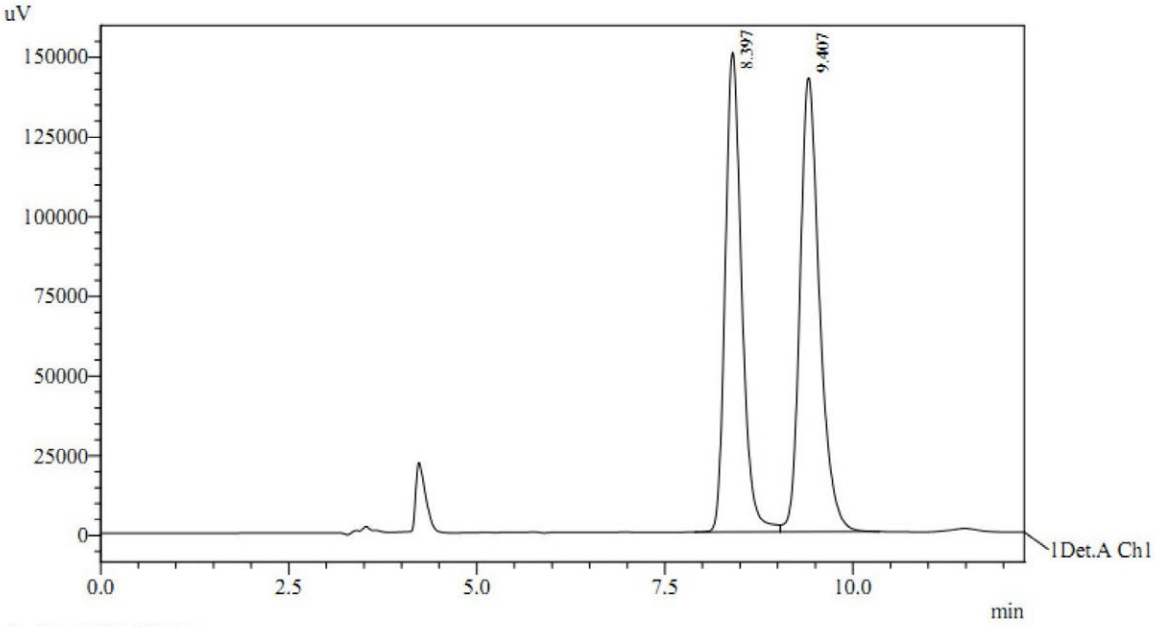
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.672	5137725	216497	92.802	93.880
2	10.780	398498	14112	7.198	6.120
Total		5536223	230610	100.000	100.000

Figure S31. HPLC chromatograms of **4g**.

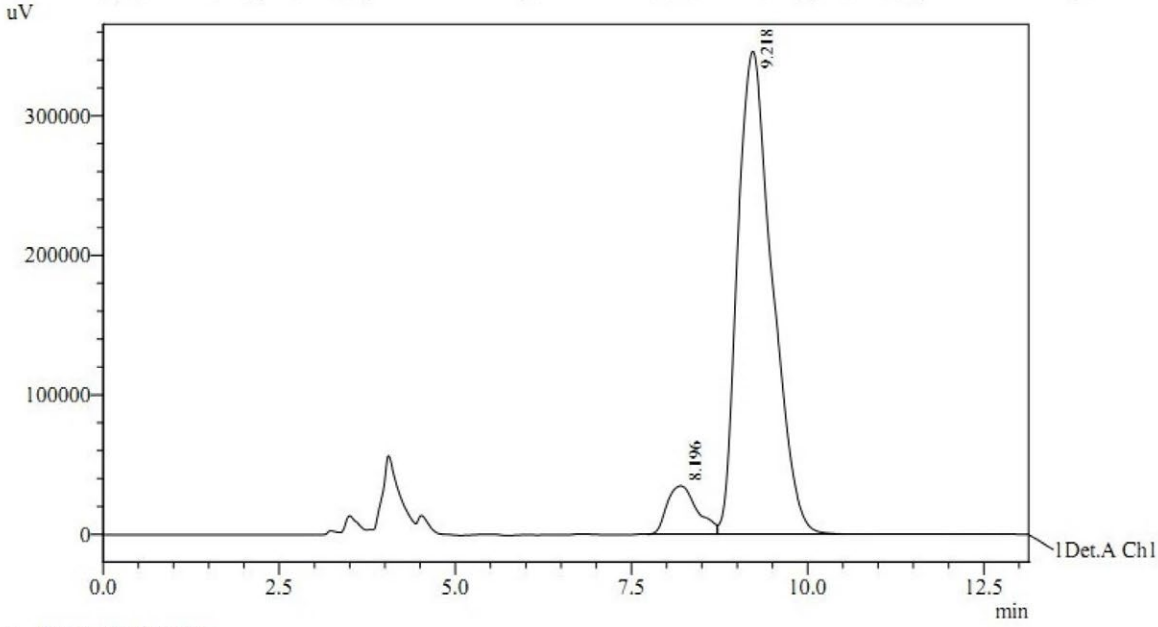


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.397	2299632	150478	47.123	51.362
2	9.407	2580408	142495	52.877	48.638
Total		4880040	292972	100.000	100.000



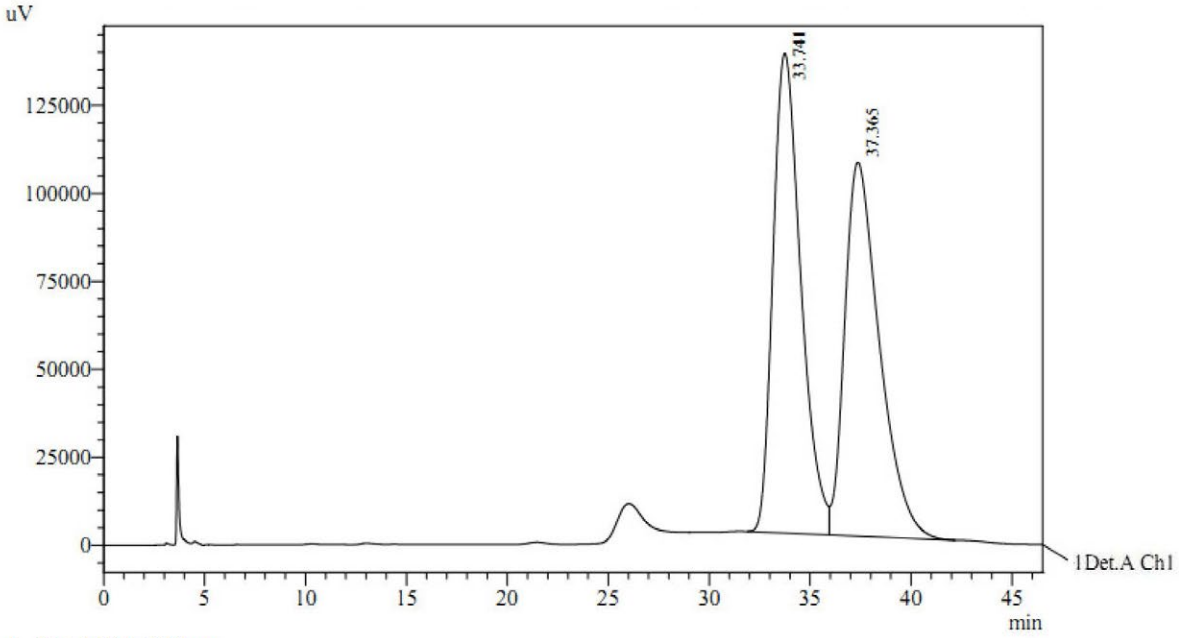
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.196	1028267	34679	8.016	9.108
2	9.218	11799010	346063	91.984	90.892
Total		12827277	380741	100.000	100.000

Figure S32. HPLC chromatograms of **4h**.

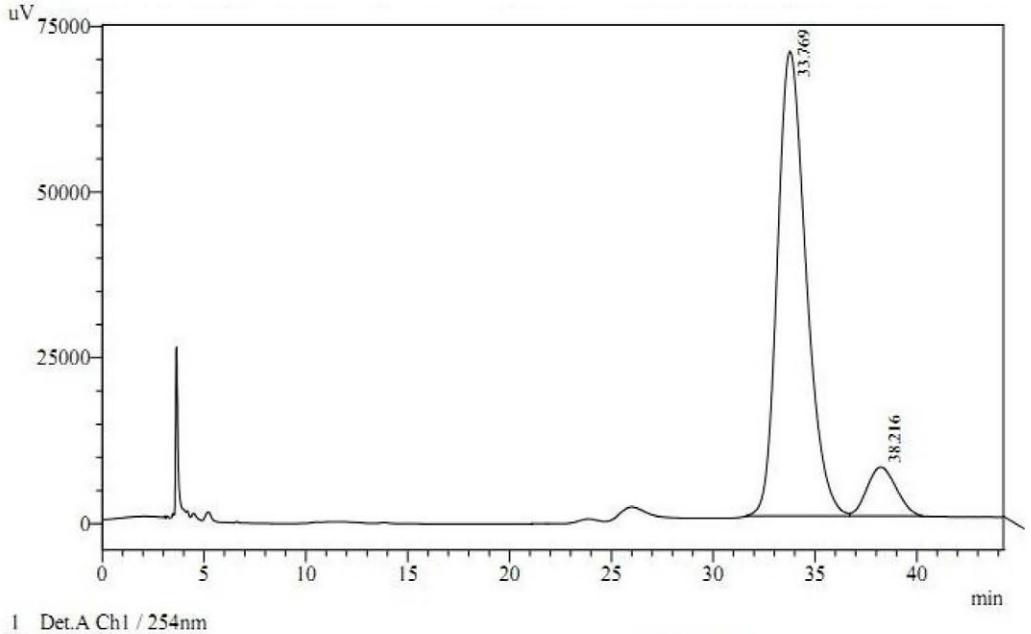


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.741	13092992	136242	50.731	56.198
2	37.365	12715619	106191	49.269	43.802
Total		25808610	242433	100.000	100.000



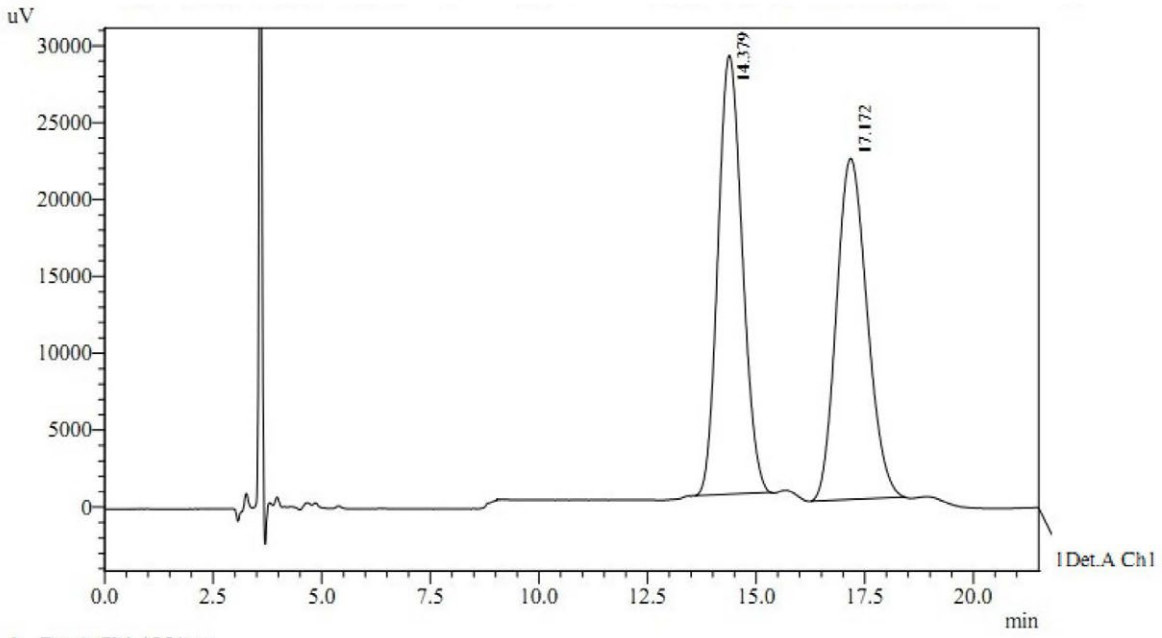
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.769	6862718	70100	90.286	90.499
2	38.216	738331	7359	9.714	9.501
Total		7601049	77459	100.000	100.000

Figure S33. HPLC chromatograms of **4i**.

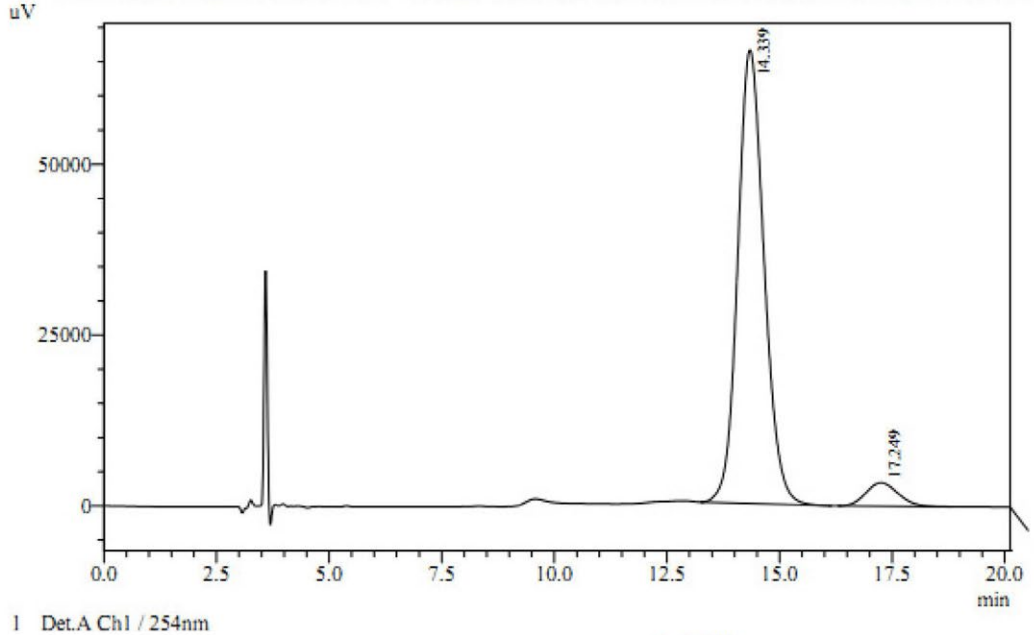


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.379	1109105	28532	50.495	56.283
2	17.172	1087359	22162	49.505	43.717
Total		2196465	50695	100.000	100.000



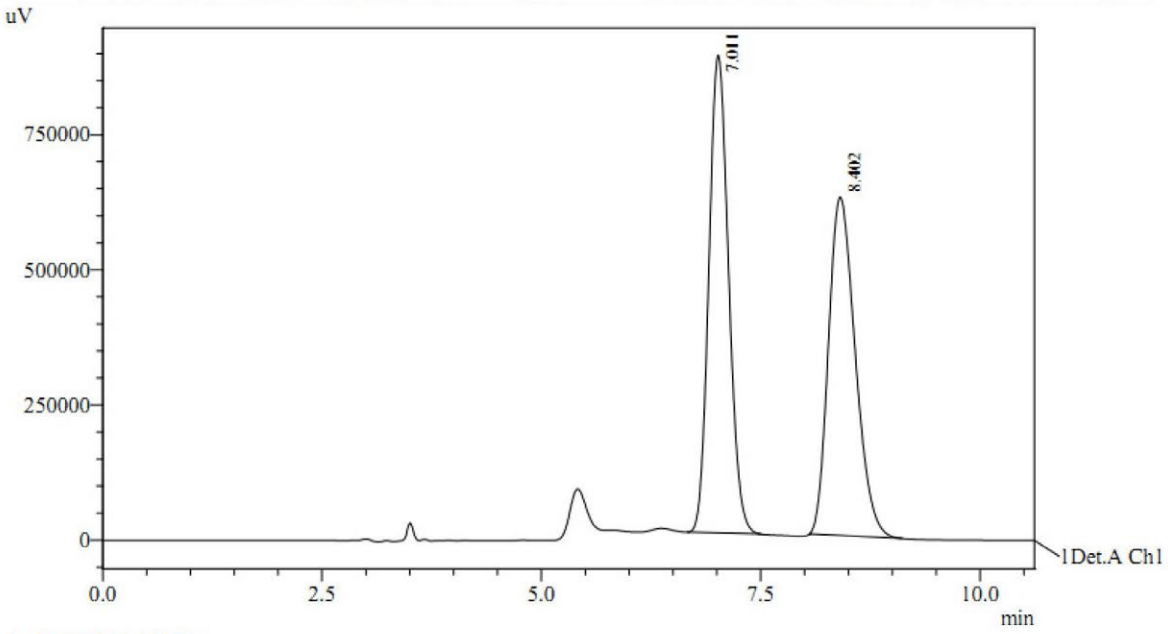
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.339	2706761	66381	94.020	95.079
2	17.249	172153	3435	5.980	4.921
Total		2878914	69817	100.000	100.000

Figure S34. HPLC chromatograms of **4j**.

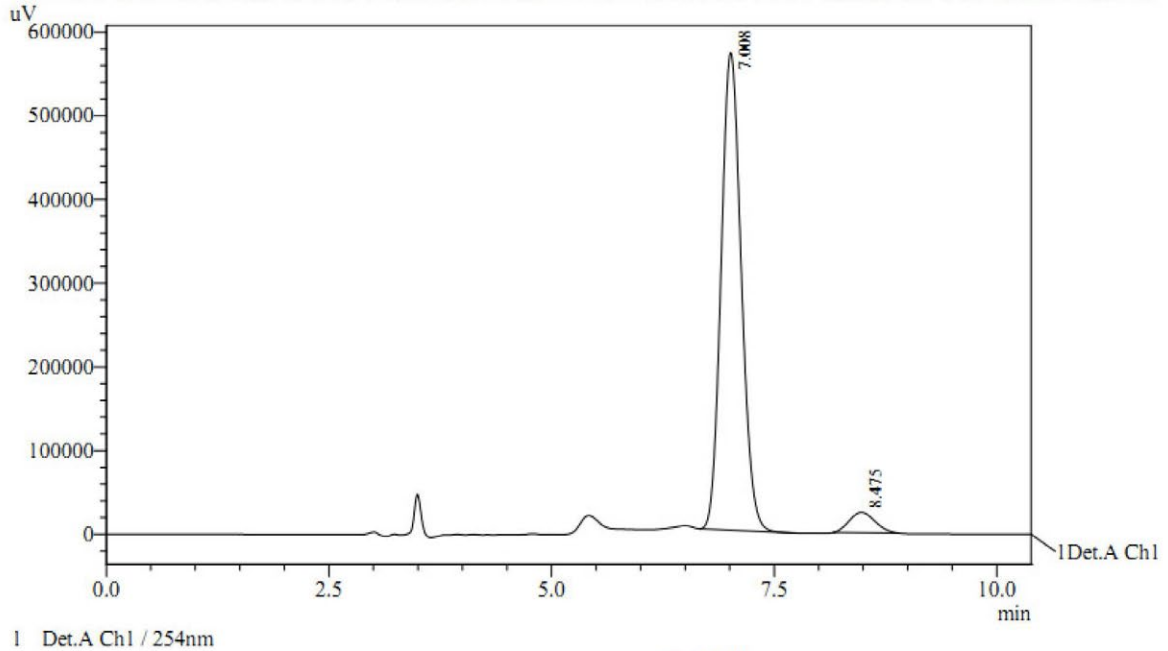


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.011	13782569	883748	50.979	58.556
2	8.402	13253284	625495	49.021	41.444
Total		27035853	1509244	100.000	100.000



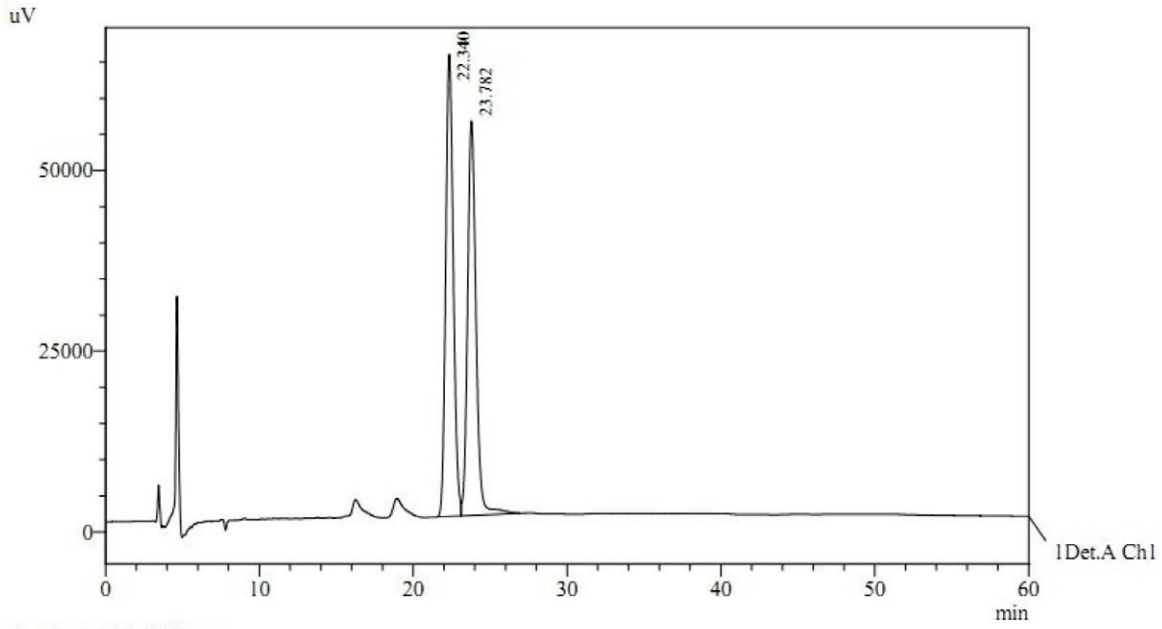
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.008	8971938	570338	94.871	95.927
2	8.475	485089	24214	5.129	4.073
Total		9457027	594551	100.000	100.000

Figure S35. HPLC chromatograms of **4k**.

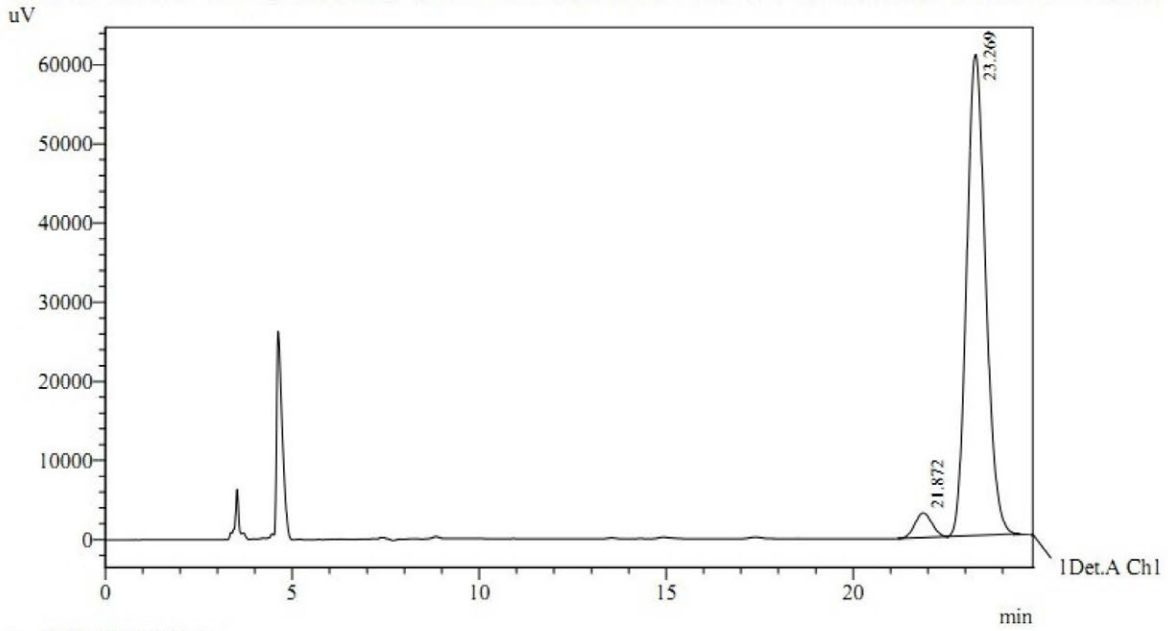


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.340	2187911	63925	51.327	53.947
2	23.782	2074740	54571	48.673	46.053
Total		4262651	118496	100.000	100.000



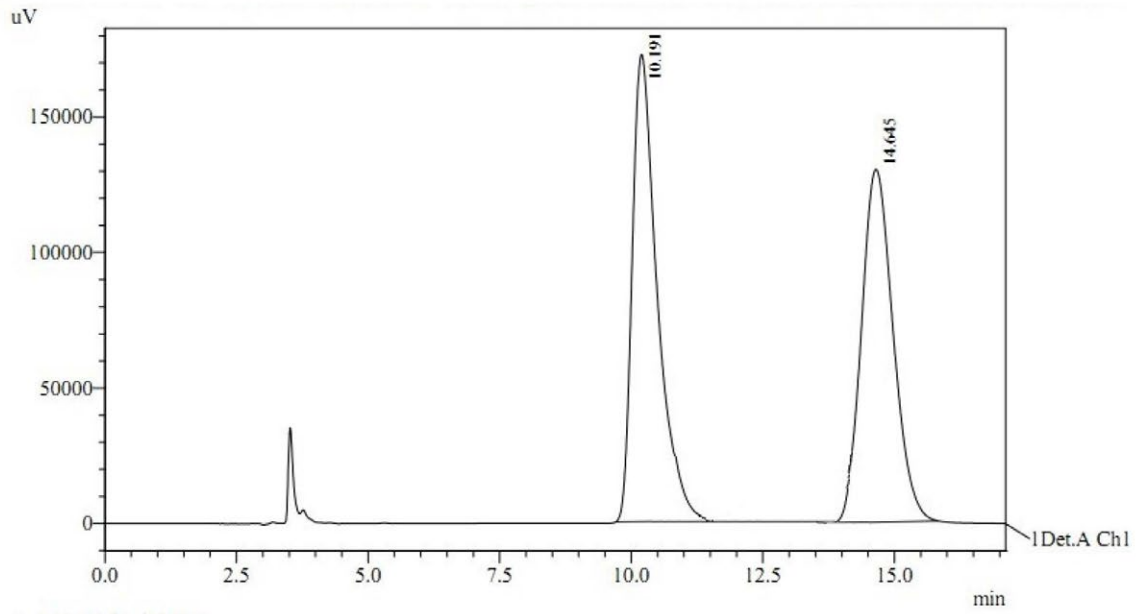
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.872	98364	3098	4.374	4.850
2	23.269	2150593	60786	95.626	95.150
Total		2248957	63884	100.000	100.000

Figure S36. HPLC chromatograms of **4l**.

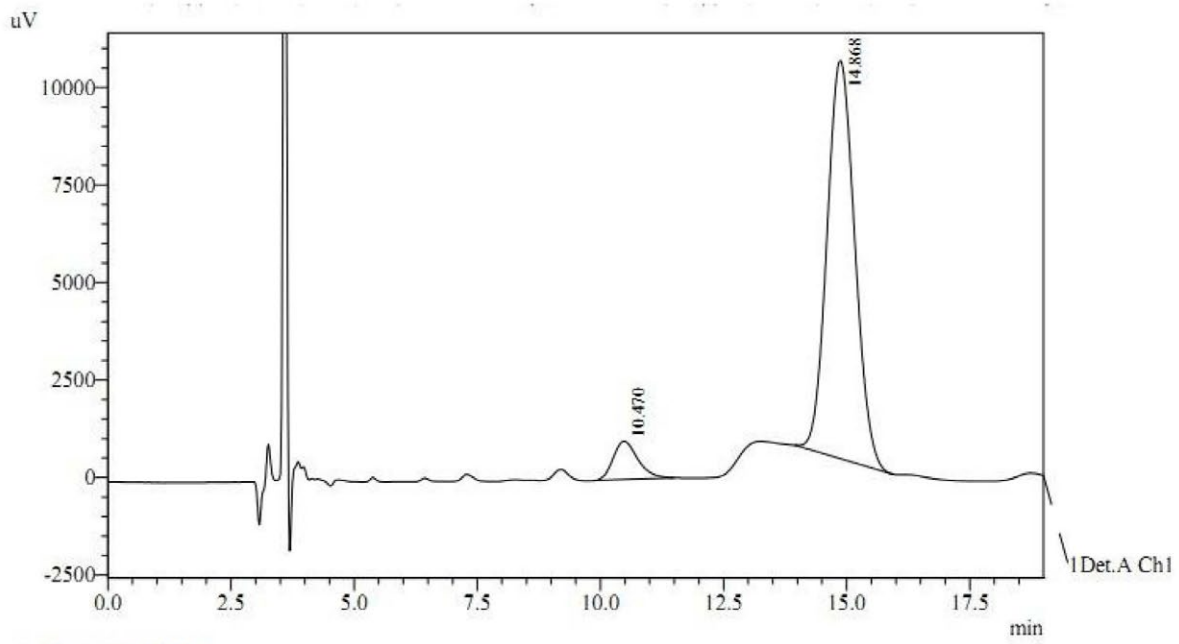


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.191	5759698	172355	50.740	56.962
2	14.645	5591781	130223	49.260	43.038
Total		11351479	302578	100.000	100.000



1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.470	34245	984	7.124	8.470
2	14.868	446431	10631	92.876	91.530
Total		480676	11615	100.000	100.000

Figure S37. HPLC chromatograms of **4a** (catalyzed by quinine).