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Synthesis and optical properties of new 2-oxo-4-vinyl-2*H*-chromene-3-carbonitrile dyes

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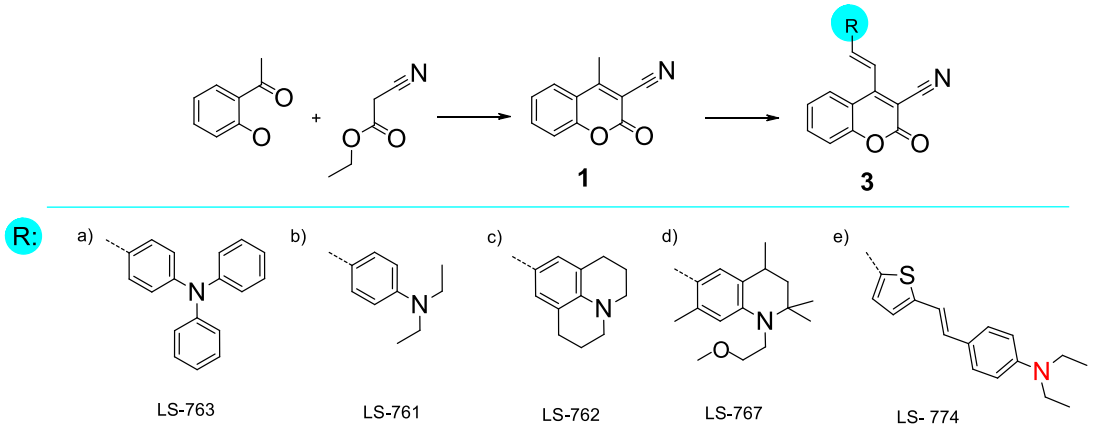


Scheme S1 Synthesis of new 2-oxo-4-vinyl-2*H*-chromene-3-carbonitrile dyes

Procedure for the preparation of compound **1**: A mixture of ethyl cyanoacetate (13.6 g) and ammonium acetate (15.4 g) was treated with *o*-hydroxyacetophenone. The reaction mixture was heated at 220°C for 15 min, left to cool and then triturated with ethanol. The solid product was collected by filtration and crystallized from ethanol. Yield 75%.

General procedure for the preparation of compounds **3a–e**: Mixture of compound **1** (1 mmol), appropriate aldehyde (1 mmol) and piperidine (two drops)/L-proline (cat. amount) were stirred in acetonitrile (5 ml) at reflux conditions for appropriate time as shown in Table 1. The precipitated solid was collected by filtration and washed with small quantity of cold acetonitrile. The products were purified by crystallization from acetonitrile or ethanol. Compound **3e** was purified by column chromatography.

Table S1 Reagents and conditions of Knoevenagel reaction, NMR and MS data of the reaction products.

Compound	Catalyst	Time, h	Yield %	
3a	Piperidine/ L-proline	23/25	47/45	^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.95 (d, *J* 8.1 Hz, 1H, H-5 of coum.), 7.77–7.66 (m, 2H, H-7 of coum. and H of HC=CH), 7.52 (d, *J* 8.5 Hz, 2H, 2CH of C_6H_4), 7.46–7.11 (m, 13H, H-6 and H-8 coum., 2Ph, *H*C=CH), 7.07 (d, *J* 8.5 Hz, 2H, C_6H_4).^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.36 (s, C-4 coum.), 157.82 (s, C-2 coum.), 153.61 (s, C-10 coum.), 150.65 (s, *ipso*-C $C_6H_4NPh_2$), 146.59 (s, *p*-C $C_6H_4NPh_2$), 144.52 (s, *C*H=CH), 134.67 (s), 129.59 (s), 129.50 (s), 127.46 (s), 126.59 (s), 125.64 (s), 125.12 (s), 124.45 (s), 121.37 (s), 117.91 (s), 117.44 (s), 115.12 (s), 114.77 (s), 96.31 (s). HRMS: found, 440.1589 *m*/*z*; calculated for $[M+H]^+$ 440.1598
3b	Piperidine/ Ac_2O	24/24	50/39	^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (d, *J* 7.5 Hz, 1H, H-5 of coum.), 7.84 (d, *J* 16.0 Hz, 1H, H of HC=CH), 7.68 (t, *J* 7.8 Hz, 1H, H-7 of coum.), 7.57 (d, *J* 8.0 Hz, 2H, 2CH of C_6H_4), 7.40 (t, *J* 7.5 Hz, 2H, H-6 and H-8 coum.), 7.18 (d, *J* 15.9 Hz, 1H, H of HC=CH), 6.71 (br. s, 2H, 2CH of C_6H_4), 3.47 (q, *J* 6.9 Hz, 4H, $2CH_2$), 1.25 (t, *J* 7.1 Hz, 6H, 2Me).^{13}C NMR (126 MHz, DMSO-d_6) δ: 158.42 (s), 158.02 (s), 153.53 (s), 146.03 (s), 134.28 (s), 130.73 (s), 126.47 (s), 124.92 (s), 117.87 (s), 117.66 (s), 115.46 (s), 111.58 (s), 44.77 (s), 12.55 (s). HRMS: found, 345.1595 *m*/*z*; calculated for $[M+H]^+$ 345.1598
3c	Piperidine	24	38	1H NMR (300 MHz, $CDCl_3$) δ: 7.98 (d, *J* 8.3 Hz, 1H, H-5 coum.), 7.79 (d, *J* 15.9 Hz, 1H, H of HC=CH), 7.66 (t, *J* 7.8 Hz, 1H, H-7 of coum.), 7.43–7.33 (m, 2H, H-6 and H-8 coum.), 7.11–7.16 (s+d, 3H, 2H jul. Ar and H HC=CH), 3.33 (t, *J* 6.2 Hz, 4H, $2CH_2$ jul.), 2.81 (t, *J* 6.2 Hz, 4H, $2CH_2$ jul.), 2.05 (dt, *J* 11.8, 6.0 Hz, 4H, $2CH_2$ jul.). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.56 (s, C-4 coum.), 157.62 (C-2 coum.), 153.48 (s, C-10 coum.), 146.25 (s), 145.04 (s), 134.11 (s), 128.21 (*C*H jul.), 126.40 (s), 124.82 (s), 122.79 (s), 122.28 (s), 117.82 (s), 117.73 (s), 115.71 (s), 111.58 (s), 50.34 (*C*H_2 jul.), 27.46 (*C*H_2 jul.), 21.19 (*C*H_2 jul.). HRMS: found, 369.1595 *m*/*z*; calculated for $[M+H]^+$ 369.1598
3d	Piperidine	48	39	^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.26 (d, *J* 15.7 Hz, 1H, H of HC=CH), 7.98 (d, *J* 7.4 Hz, 1H, H-5 of coum.), 7.69 (t, *J* 7.7 Hz, 1H, H-7 of coum.), 7.63 (s, 1H, HC of Ar THQ), 7.41 (dd, *J* 7.6, 4.8 Hz, 2H, H-6 and H-8 of coum.), 7.16 (d, *J* 15.8 Hz, 1H, H of HC=CH), 6.53 (s, 1H, HC of Ar THQ), 3.73–3.45 (m, 4H, CH_2–CH_2), 3.43 (s, 3H, MeO), 3.03–2.88 (m, 1H, CH–Me), 2.48 (s, 3H, *Me*–Ar), 1.84 (dd, *J* 13.2, 4.7 Hz, 1H, H of CH_2), 1.62 (t, *J* 12.7 Hz, 1H, H of CH_2), 1.50–1.37 (m, 6H, 2Me), 1.28 (s, 3H, Me). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 158.51 (s, C-4 coum.), 158.16 (C-2 coum.), 153.55 (s, C-10 coum.), 143.37 (s), 139.21 (s), 134.23 (s), 126.28 (s), 124.89 (s), 124.51 (s), 117.92 (s), 117.84 (s), 115.73 (s), 77.28 (s), 77.02 (s), 76.77 (s), 70.62 (s, MeO), 59.10 (s, *C*H_2N), 29.54 (s), 26.88 (s), 25.21 (s), 20.18 (s), 20.13 (s). HRMS: found, 443.2335 *m*/*z*; calculated for $[M+H]^+$ 443.2329.
3e	Piperidine	21	30%	^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, *J* 15.7 Hz, 1H, H of HC=CH), 7.95 (d, *J* 7.8 Hz, 1H, H-5 of coum.), 7.71 (t, *J* 7.6 Hz, 1H, H-7 of coum.), 7.49–7.33 (m, 4H, H-6 and H-8 of coum. and 2CH of C_6H_4), 7.31–7.25 (m, 1H, CH of thioph.), 7.08 (d, *J* 15.4 Hz, 1H, H of HC=CH), 7.03–6.93 (m, 3H, CH=CH and CH of thioph.), 6.68 (d, *J* 2.7 Hz, 2H, 2CH of C_6H_4), 3.52–3.35 (m, 4H, $2CH_2$), 1.36–1.17 (m, 6H, 2Me). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.00 (s, C-4 coum.), 156.70 (C-2 coum.), 153.52 (s, C-10 coum.), 148.14 (s), 137.80 (s), 137.42 (s), 134.61 (s), 134.33 (s), 132.55 (s), 128.43 (s), 126.15 (s), 125.88 (s), 125.14 (s), 123.26 (s), 117.99 (s), 117.31 (s), 115.95 (s), 114.99 (s), 111.59 (s), 44.46 (s, *C*H_2), 12.66 (s, Me). HRMS: found, 453.1614 *m*/*z*; calculated for $[M+H]^+$ 453.1631.

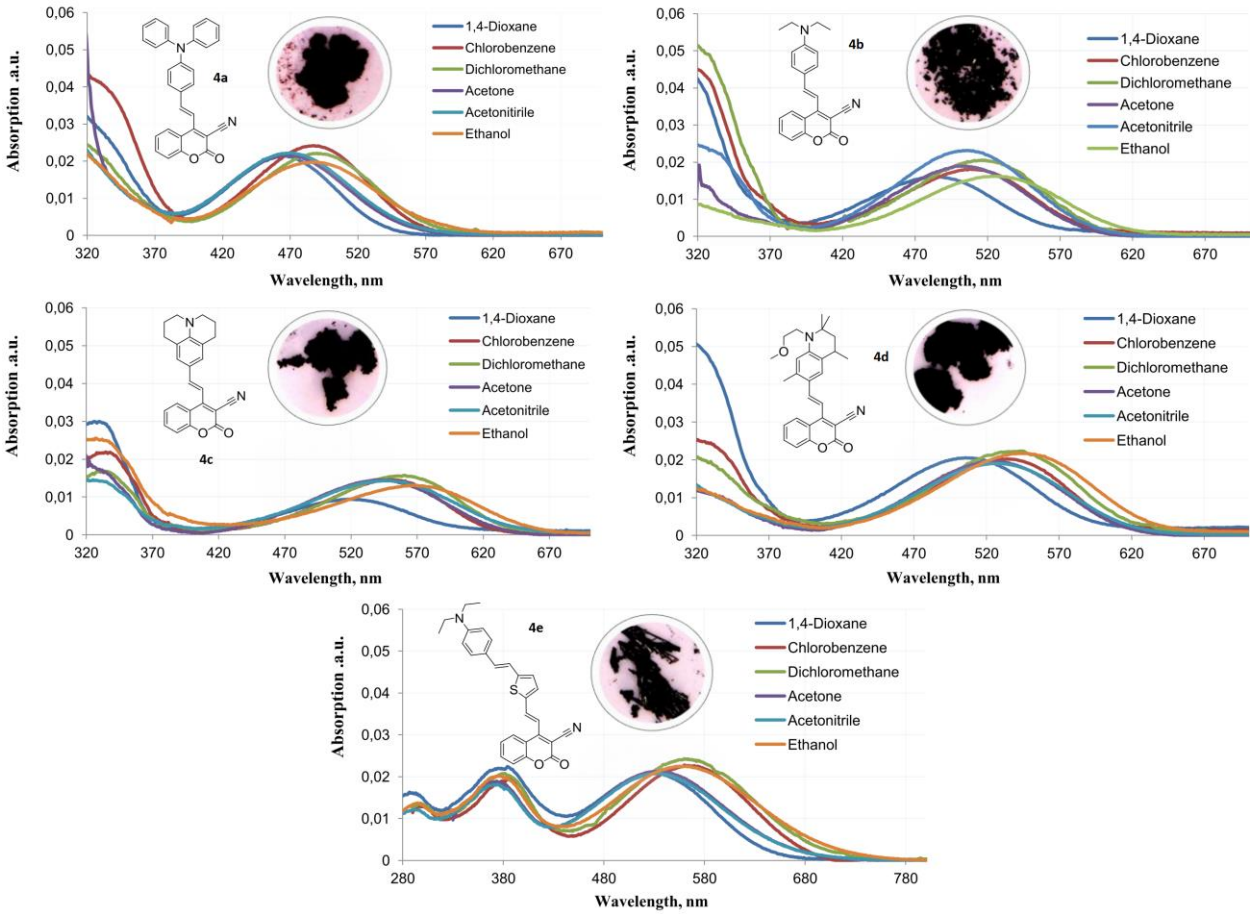


Figure S1 The absorption spectra of the synthesized products in different solvents (C = 0.003 mg ml^{-1}) and photos of the chromophore crystals.

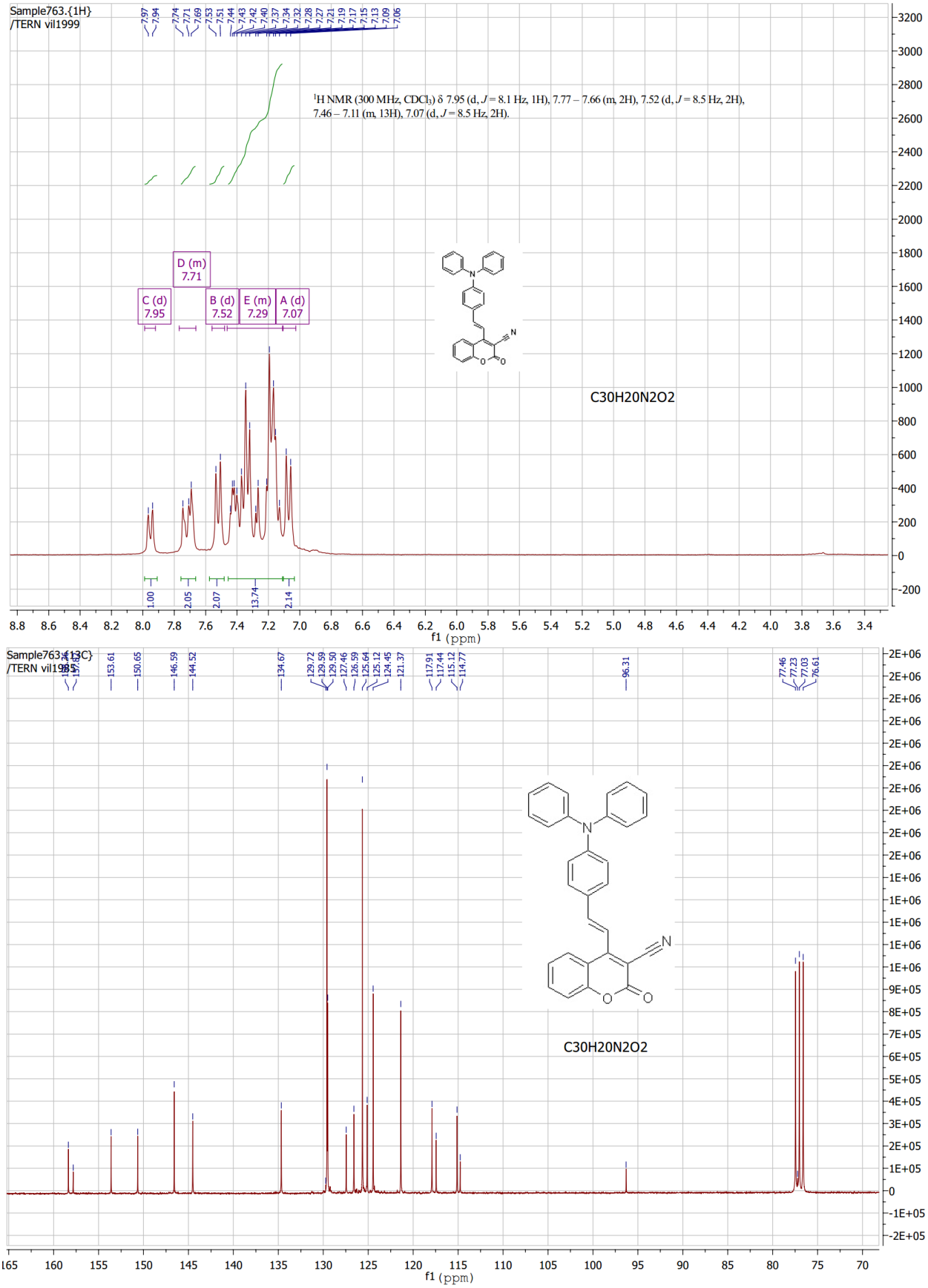


Figure S2 NMR data for compound **3a**

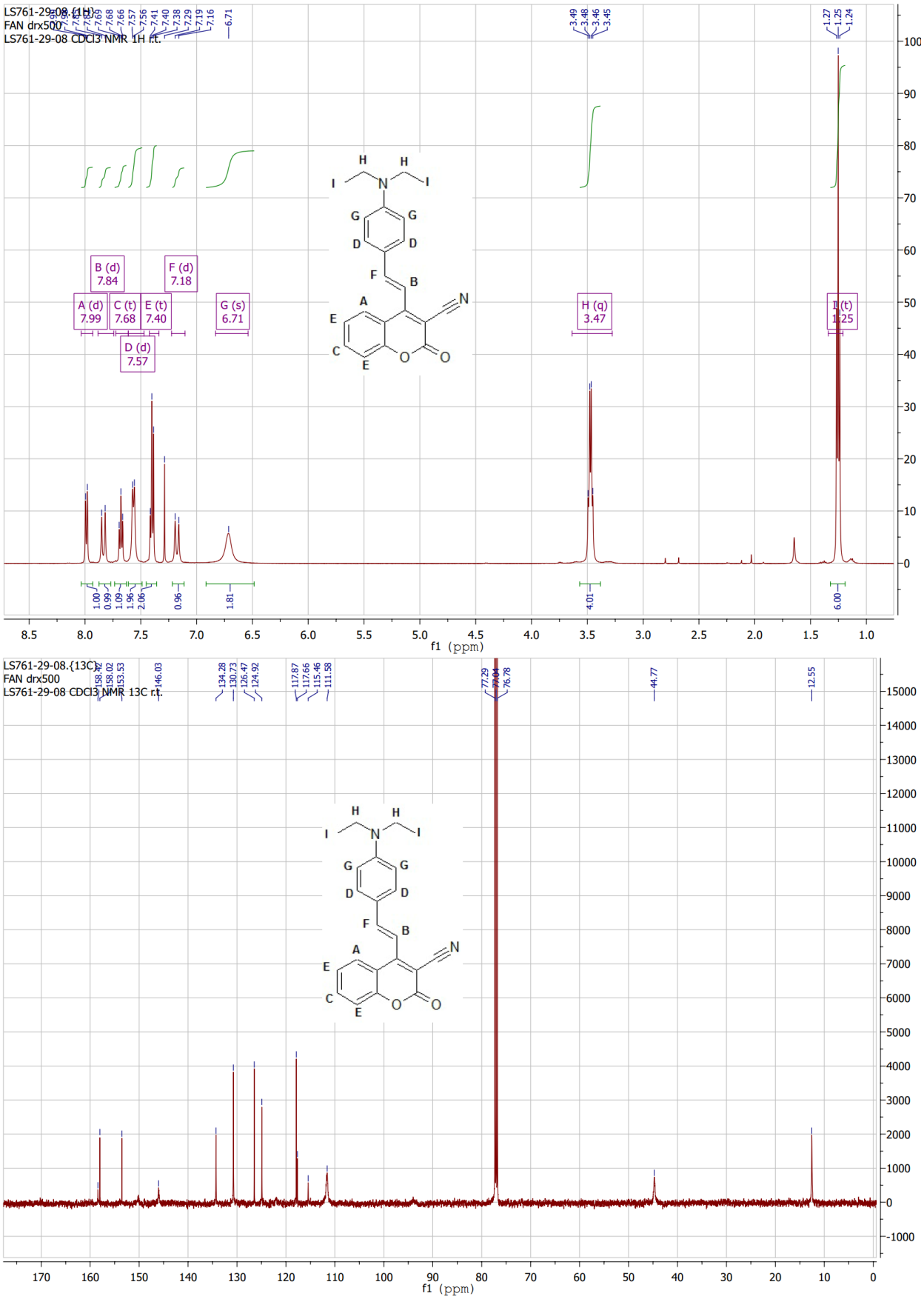
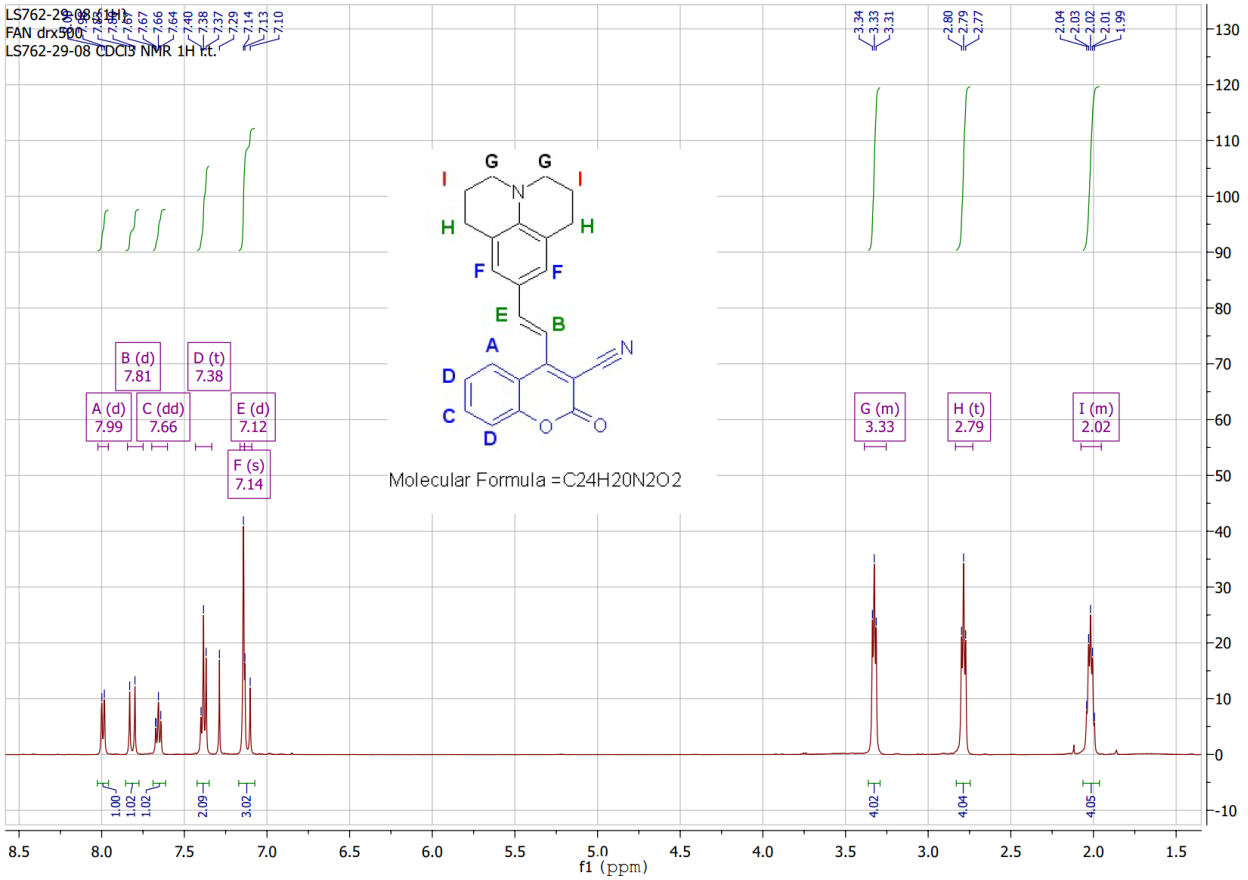


Figure S3 NMR data for compound **3b**



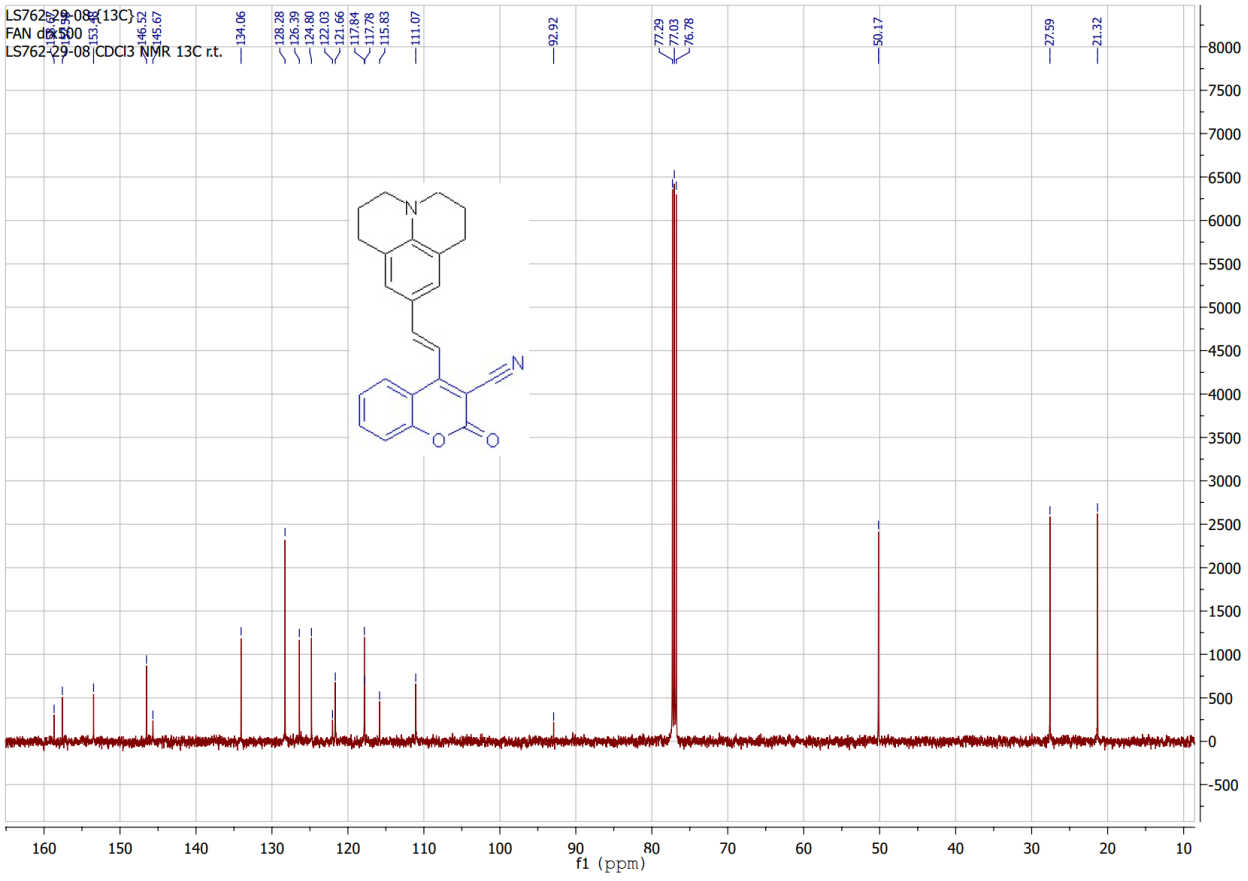


Figure S4 NMR data for compound **3c**

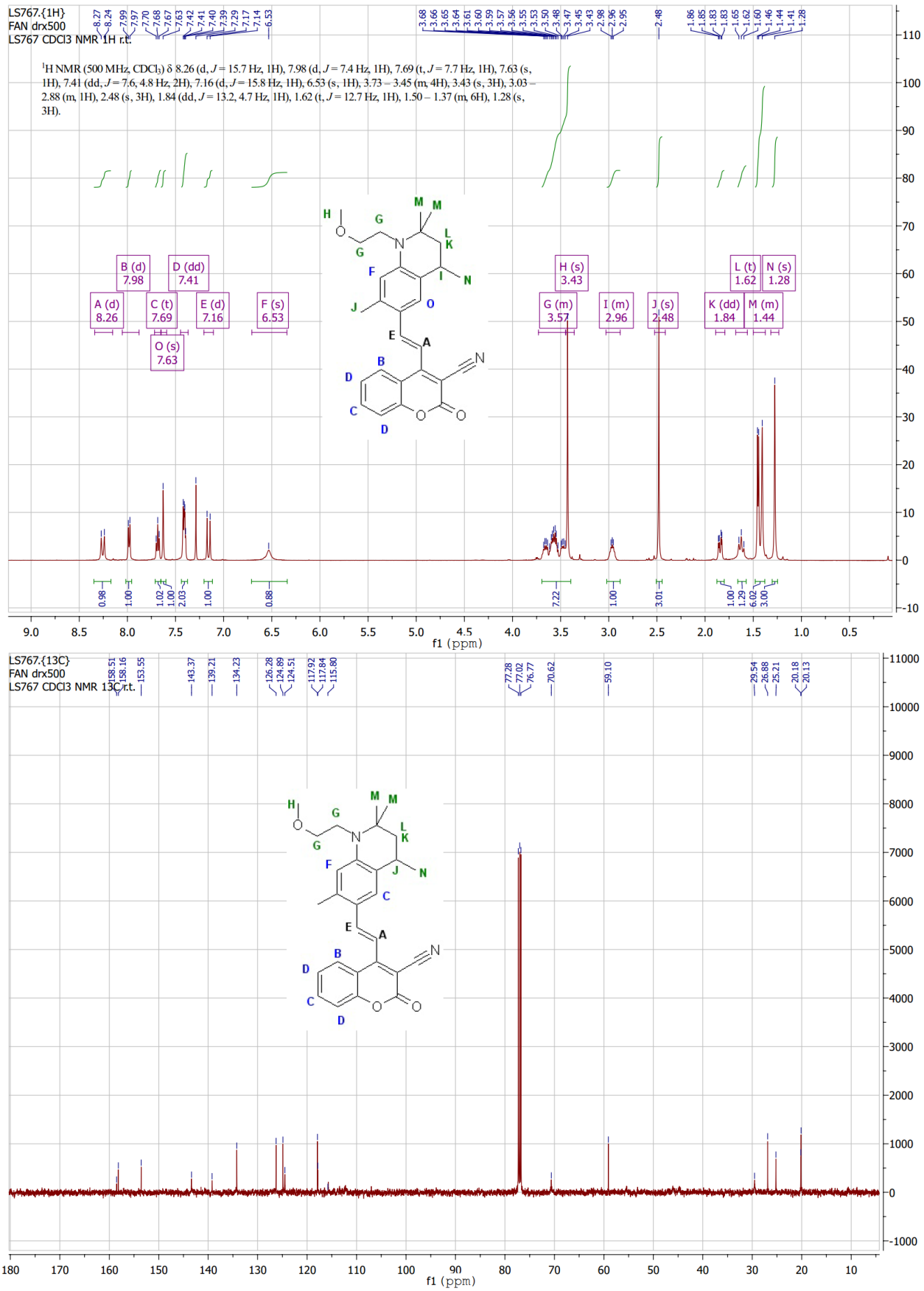
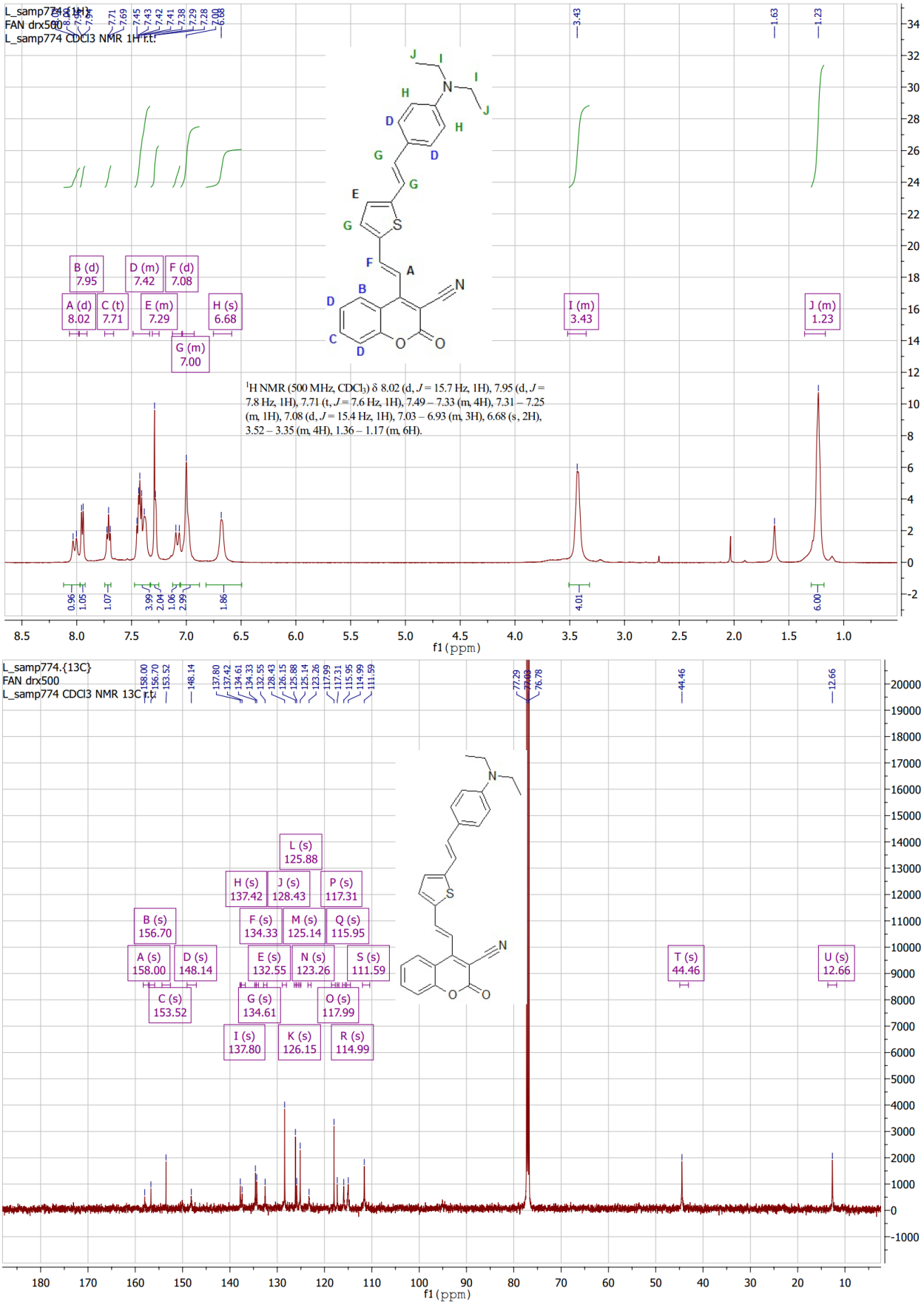


Figure S5 NMR data for compound **3d**



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 15.7 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.49 – 7.33 (m, 4H), 7.31 – 7.25 (m, 1H), 7.08 (d, J = 15.4 Hz, 1H), 7.03 – 6.93 (m, 3H), 6.68 (s, 2H), 3.52 – 3.35 (m, 4H), 1.36 – 1.17 (m, 6H).

Figure S6 NMR data for compound **3e**