Electronic Supplementary Information

Palladium-catalysed decarboxylative nitrile insertion via C-H activation or self-coupling of indole-2-carboxylic acids: A new route to indolocarbolines and triindoles

R. N. Prasad Tulichala and K. C. Kumara Swamy*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, Telangana, India.

E-mail: kckssc@uohyd.ac.in, kckssc@yahoo.com

(1) Structures showing the importance of α-carbolines/ triindoles

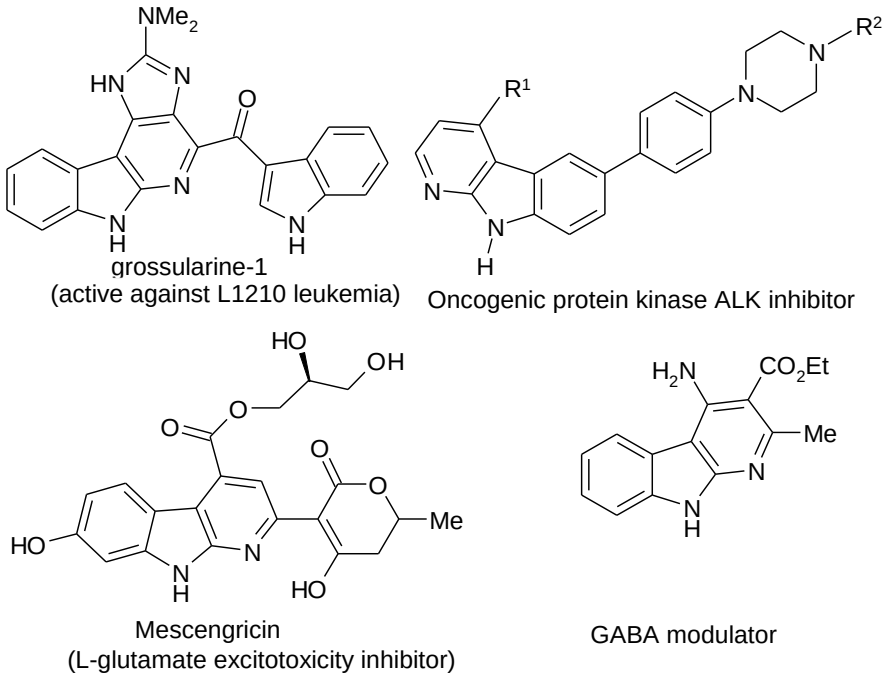


Figure S1. Selected α-carboline natural products

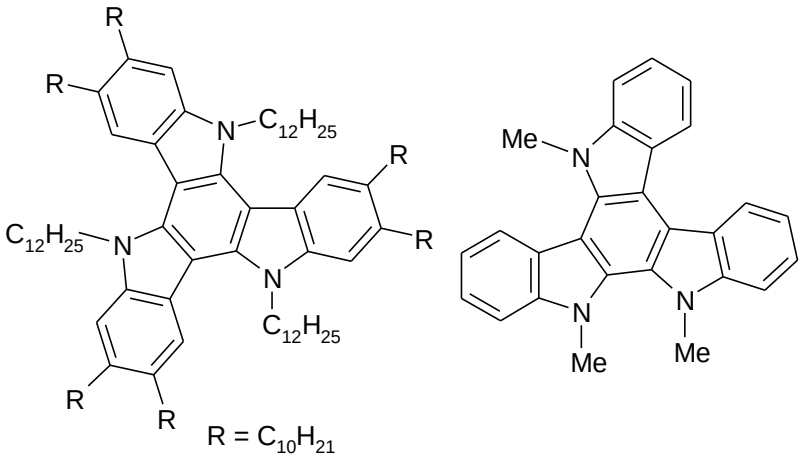
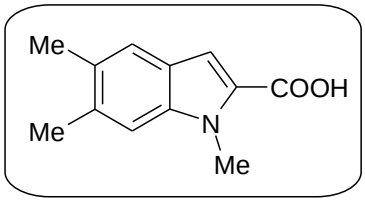


Figure S2. Selected triindole organic electronic materials

(2) Experimental section

(i) General comments and precursor synthesis. Solvents were dried according to known methods.[1] ^{1}H and ^{13}C NMR spectra (^{1}H, 400 MHz or 500 MHz; ^{13}C, 100 MHz or 125 MHz) were recorded using a 400 or 500 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were performed using a mass spectrometer with ESI-QTOF-II method. UV-Visible absorption spectra and fluorescence spectra (THF solution; typical concentration 10^{-5} M) were recorded on UV-Visible spectrometer and Fluoromax spectrofluorimeter. Single crystal X-ray diffractometric data were collected using Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved/ and refined by standard methods.[2] Indole-2-carboxylic acids **1a-l** were prepared by following literature reports.[3] Compound **1e** is new.

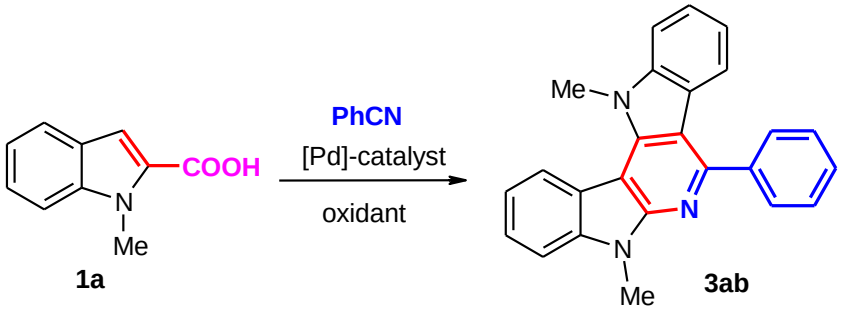


Compound 1e: Yield: 0.8 g (95%; white solid); mp 226-228 ^{0}C; IR (KBr, cm^{-1}) 2965, 2598, 1681, 1519, 1474, 1444, 1261, 1235, 1134, 1062, 997, 843; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.74 (br s, 1H, COO*H*), 7.39 (s, 1H, Ar-*H*), 7.32 (s, 1H, Ar-*H*), 7.14-7.07 (m, 1H, Ar-*H*), 3.96 (s, 3H, NCH_3), 2.35 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 163.6, 138.9, 134.4, 129.3, 128.0, 124.2, 122.2, 111.1, 109.4, 31.8, 20.9 and 20.1; LC-MS *m/z* 204 $[M+1]^{+}$; Anal. Calcd. for $C_{12}H_{13}NO_2$:C, 70.92; H, 6.45; N, 6.89. Found: C, 70.85; H, 6.51; N, 6.79.

(ii) Optimisation of the reaction conditions for the synthesis of indolocarboline 3ab

In an oven dried round-bottomed flask (25 mL), silver salt (1-3 mmol, *cf*. Table S1) was added and dried in *vacuo* (while heating if necessary) for 0.5 h. To this, [Pd]-catalyst (cf Table S1), 1-alkylindole-2-carboxylic acid (1.0 mmol) and benzonitrile (20 mmol) were added. The mixture was stirred at 80 ^{o}C (oil bath) for 12 h. After the completion of the reaction (TLC), the excess of nitrile was removed in *vacuo* and the mixture was subjected to column chromatography (ethyl acetate/hexane) to afford **3ab**. Details are summarized on Table S1.

Table S1. Optimisation of conditions for the synthesis of indolocarboline 3ab[a]



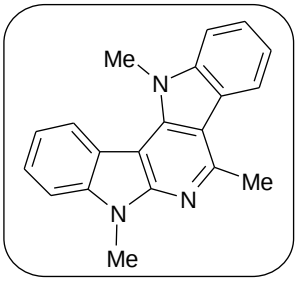
Entry	[Pd] (mol %)	Oxidant (equiv) + base/additive (equiv)	Yield (%)[b]
1	$Pd(OAc)_2$ (10)	Ag_2CO_3 (1)	51
2	$Pd(OAc)_2$ (10)	-	-
3	-	Ag_2CO_3 (1)	-
4	**$Pd(OAc)_2$ (10)**	**Ag_2CO_3 (2)**	**65**[c]
5	$Pd(OAc)_2$ (10)	Ag_2CO_3 (3)	64
6	$Pd(OAc)_2$ (10)	$Cu(OAc)_2.H_2O$ (2)	trace
7	$Pd(OAc)_2$ (10)	$CuCl_2$ (2)	trace

8	$Pd(OAc)_2$ (10)	Ag_2O (2)	43
9	$Pd(OAc)_2$ (10)	AgOAc (2)	45
10	$Pd(OAc)_2$ (10)	O_2	10
11	$Pd(OAc)_2$ (5)	Ag_2CO_3 (2)	49
12	$Pd(OAc)_2$ (2)	Ag_2CO_3 (2)	43
13	$PdCl_2$ (10)	Ag_2CO_3 (2)	47
14	$PdCl_2$ (10)	$Cu(OAc)_2.H_2O$ (2)	trace
15	$PdCl_2$ (10)	Ag_2O (2)	21
16	$PdCl_2$ (10)	AgOAc (2)	32
17	$Pd(dba)_2$ (10)	Ag_2CO_3 (2)	40
18	$Pd(TFA)_2$ (10)	Ag_2CO_3 (2)	50
19	$Pd_2(dba)_3$ (10)	Ag_2CO_3 (2)	42
20	$Pd(OAc)_2$ (10)	Ag_2CO_3 (2)/ K_2CO_3 (2)	37
21	$Pd(OAc)_2$ (10)	Ag_2CO_3 (2)/ Cs_2CO_3 (2)	40
22	$Pd(OAc)_2$ (10)	Ag_2CO_3 (2)/ $AgSbF_6$ (0.3)	48
23	$Pd(OAc)_2$ (10)	Ag_2CO_3 (2)/ AgOTf (0.3)	40

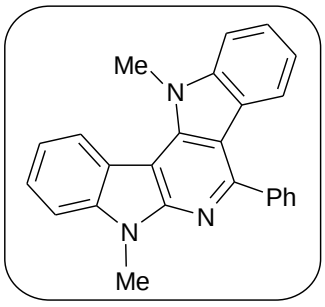
[a]Reactions were carried out using indole carboxylic acid **1a** (1.0 mmol), nitrile **2b** (20 mmol), [Pd]-catalyst (2-10 mol %), Oxidant (1-3.0 mmol) at 80 ^{0}C (oil bath) for 12 h. [b]Isolated yield.. [c]This reaction conducted at 50 ^{o}C gave lower yield (ca 20%) while at 100 ^{o}C gave the same yield (65%) as the one at 80 ^{o}C.

(iii) Optimised procedure and spectroscopic/analytical data for indole fused α-carboline derivatives (3aa-3jd)

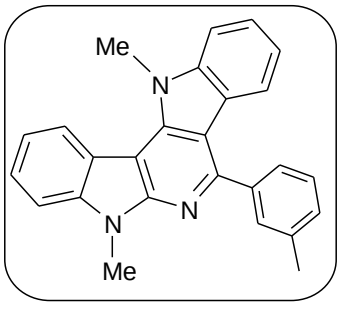
In an oven dried round-bottomed flask (25 mL), silver carbonate (2.0 mmol) was added and dried in *vacuo* while heating (ca 100 ^{o}C) using a hot air gun for 0.5 h. To this, $Pd(OAc)_2$ (10 mol %), 1-alkylindole-2-carboxylic acid (1.0 mmol) and nitrile (20 mmol) were added. The mixture was stirred at 80 ^{o}C (oil bath) for 12 h. After the completion of the reaction (TLC), the excess of nitrile was removed in *vacuo* (for liquid nitriles) and the mixture was subjected to column chromatography (ethyl acetate/hexane) to afford the desired products in 40-65 % yield. Compounds **3aa-3jd** and **A** were prepared by this procedure. For compounds **3ae** and **3ak**, only 2.5 mmol of nitrile was used.



Compound 3aa: Yield: 0.057 g (38%; brown solid); mp 204-206 ^{0}C; IR (KBr, cm^{-1}) 3054, 2939, 1618, 1593, 1481, 1325, 1257, 1024, 721, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.19 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.55-7.49 (m, 4H, Ar-*H*), 7.40-7.30 (m, 2H, Ar-*H*), 4.52 (s, 3H, NCH_3), 4.10 (s, 3H, NCH_3), 3.18 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (*C*=N), 150.3 (C=N-*C*), 142.6, 140.5, 138.7, 124.2, 123.6, 122.2, 121.3, 120.5, 119.4, 119.2, 111.9, 109.2, 108.6, 97.2 (C=N-C=*C*), 33.8, 28.1 and 24.5 (N*C*H_3); HRMS (ESI) calcd. for $C_{20}H_{18}N_3$ [M^++H] 300.1501, found 300.1506.

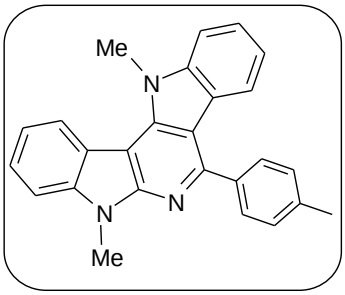


Compound 3ab: Yield: 0.117 g (65%; white solid); mp 188-190 ^{0}C; IR (KBr, cm^{-1}) 3053, 2924, 1616, 1591, 1483, 1323, 1265, 1176, 1091, 731, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.88 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.63-7.50 (m, 7H, Ar-*H*), 7.44 (t, *J* = 15.2 Hz, 1H, Ar-*H*), 7.36-7.32 (m, 1H, Ar-*H*), 7.09 (t, *J* = 15.2 Hz, 1H, Ar-*H*), 4.55 (s, 3H, NCH_3), 4.10 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (*C*=N), 150.3 (C=N-*C*), 143.2, 141.2, 140.7, 139.1, 129.4, 128.6, 128.5, 124.6, 124.5, 122.9, 122.4, 121.2, 120.0, 119.5, 119.5, 119.0, 111.4, 108.6, 97.7 (C=N-C=*C*), 33.8 and 28.2 (N*C*H_3); HRMS (ESI) calcd. for $C_{25}H_{20}N_3$ [M^++H] 362.1658, found: 362.1657.

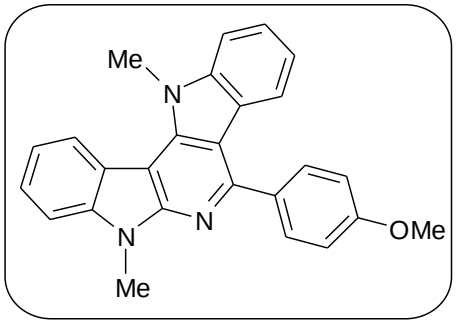


Compound 3ac: Yield: 0.114 g (61%; white solid); mp 206-208 ^{0}C; IR (KBr, cm^{-1}) 3051, 2925, 1615, 1593, 1544, 1478, 1319, 1276, 1089, 744, 722; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8 Hz, 1H, Ar-*H*), 7.69-7.34 (m, 10H, Ar-*H*), 7.10 (t, *J* = 15.2 Hz,

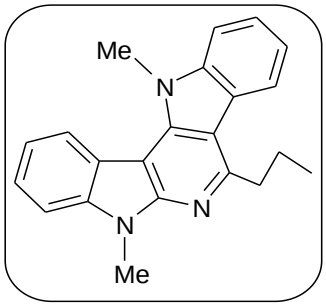
1H, Ar-*H*), 4.55 (s, 3H, NCH_3), 4.11 (s, 3H, NCH_3) and 2.51 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (*C*=N), 150.4 (C=N-*C*), 143.2, 142.3, 140.7, 139.1, 138.2, 130.1, 129.4, 128.5, 126.7, 124.7, 124.5, 123.1, 122.5, 121.4, 120.1, 119.5, 119.0, 111.4, 109.2, 108.7, 97.7 (C=N-C=*C*), 33.8 and 28.3 (N*C*H_3), 21.7 (*C*H_3); HRMS (ESI) calcd. for $C_{26}H_{22}N_3$ [M^++H] 376.1814, found: 376.1814.



Compound 3ad: Yield: 0.107 g (57%; yellow solid); mp 234-236 ^{0}C; IR (KBr, cm^{-1}) 2953, 2909, 2860, 1616, 1589, 1479, 1391, 1254, 1194, 1090, 728, 690; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8 Hz, 1H, Ar-*H*), 7.79 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.60 (d, *J* = 3.8 Hz, 1H, Ar-*H*), 7.54-7.32 (m, 7H, Ar-*H*), 7.11 (t, *J* = 14.8 Hz, 1H, Ar-H), 4.54 (s, 3H, NCH_3), 4.09 (s, 3H, NCH_3) and 2.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (*C*=N), 150.5 (C=N-*C*), 143.4, 140.9, 139.2, 138.5, 129.3, 129.2, 124.7, 124.6, 123.1, 122.5, 121.4, 120.1, 119.6, 119.2, 111.5, 109.3, 108.7, 97.7 (C=N-C=*C*), 34.0 and 28.4 (N*C*H_3), 21.6 (*C*H_3); HRMS (ESI) calcd. for $C_{26}H_{22}N_3$ [M^++H] 376.1814, found: 376.1811.

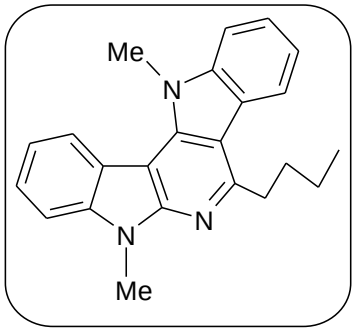


Compound 3ae: Yield: 0.115 g (59%; yellow solid); mp 240-244 ^{0}C; IR (KBr, cm^{-1}) 3046, 2926, 2832, 1621, 1589, 1506, 1468, 1326, 1265, 1243, 1178, 1024, 838, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.85-7.83 (m, 2H, Ar-*H*), 7.64 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.56-7.32 (m, 5H, Ar-*H*), 7.15-7.10 (m, 3H, Ar-*H*), 4.55 (s, 3H, OC*H*$_3$), 4.10 (s, 3H, NC*H*$_3$) and 3.96 (s, 3H, NC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (*C*-OCH_3), 152.1 (*C*=N), 150.6 (C=N-*C*), 143.5, 140.9, 139.2, 133.8, 130.8, 124.7, 124.6, 123.2, 122.5, 121.4, 120.1, 119.6, 119.2, 113.9, 111.5, 109.3, 108.7, 97.6 (C=N-C=*C*), 55.5 (O*C*H$_3$), 34.1 and 28.4 (N*C*H$_3$); HRMS (ESI) calcd. for $C_{26}H_{22}N_3O$ [M^{+}+H] 392.1764, found: 392.1761.

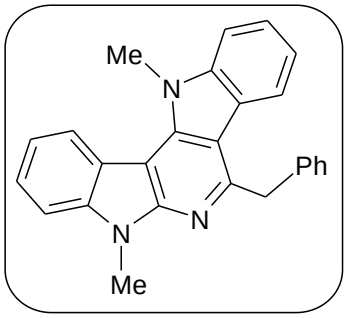


Compound 3af: Yield: 0.092 g (56%; white solid); mp 170-173 ^{0}C; IR (KBr, cm^{-1}) 3051, 2951, 1616, 1587, 1552, 1477, 1396, 1255, 1089, 746, 729; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.13 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.54-7.29 (m, 6H, Ar-

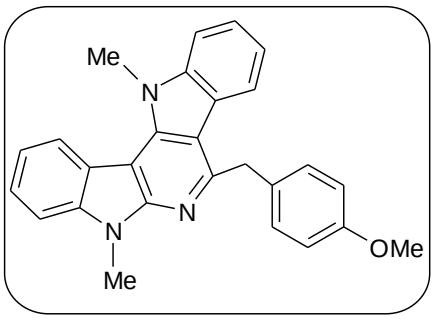
H), 4.50 (s, 3H, NC*H*$_3$), 4.09 (s, 3H, NC*H*$_3$), 3.45 (t, *J* = 15.6 Hz, 2H, C*H*$_2$-CH$_2$-CH$_3$), 2.08-2.02 (m, 2H, C*H*$_2$-CH$_3$), 1.19 (t, *J* = 15.2 Hz, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (*C*=N), 150.2 (C=N-*C*), 142.7, 140.5, 138.7, 124.0, 123.1, 122.2, 121.8, 121.3, 120.4, 119.3, 119.2, 111.2, 109.1, 108.6, 97.0 (C=N-C=*C*), 39.4 (*C*H$_2$-CH$_2$-CH$_3$), 33.6 and 28.1 (N*C*H$_3$), 21.6 (*C*H$_2$-CH$_3$), 14.6 (CH$_2$-*C*H$_3$); HRMS (ESI) calcd. for $C_{22}H_{22}N_3$ [M$^+$+H] 328.1814, found: 328.1813.



Compound 3ag: Yield: 0.090 g (53%; white solid); mp 196-198 ^{0}C; IR (KBr, cm^{-1}) 3051, 2953, 1621, 1593, 1473, 1325, 1259, 1133, 1089, 717; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8 Hz, 1H, Ar-*H*), 8.14 (d, *J* = 8 Hz, 1H, Ar-*H*), 7.55-7.27 (m, 6H, Ar-*H*), 4.52 (s, 3H, NC*H*$_3$), 4.09 (s, 3H, NC*H*$_3$), 3.48 (t, *J* = 16.8 Hz, 2H, C*H*$_2$-CH$_2$-CH$_2$-CH$_3$), 2.02-1.98 (m, 2H, C*H*$_2$-CH$_2$-CH$_3$), 1.67-1.56 (m, 2H, C*H*$_2$-CH$_3$), 1.06 (t, *J* = 14.8 Hz, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (*C*=N), 150.3 (C=N-*C*), 142.8, 140.5, 138.7, 124.1, 123.1, 122.2, 121.4, 120.4, 119.3, 119.2, 111.2, 109.1, 108.7, 97.0 (C=N-C=*C*), 37.2 (NCH$_3$), 33.8 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 30.4 (*C*H$_2$CH$_2$CH$_3$), 28.1 (NCH$_3$), 23.2 (*C*H$_2$-CH$_3$), 14.3 (CH$_2$-*C*H$_3$); HRMS (ESI) calcd. for $C_{23}H_{24}N_3$ [M$^+$+H] 342.1971, found: 342.1970.

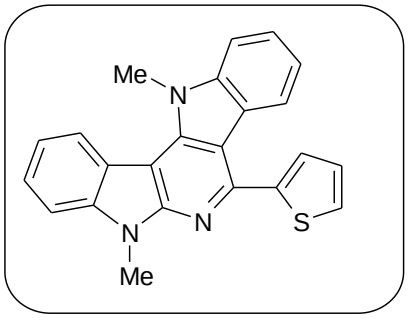


Compound 3ah: Yield: 0.113 g (60%; yellow solid); mp 208-210 ^{0}C; IR (KBr, cm^{-1}) 3068, 3024, 2915, 1616, 1589, 1473, 1326, 1254, 1106, 980, 723, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8 Hz, 1H, Ar-*H*), 8.06 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.56-7.30 (m, 7H, Ar-*H*), 7.24-7.15 (m, 4H, Ar-*H*), 4.89 (s, 2H, CH_2), 4.53 (s, 3H, NCH_3) and 4.09 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (CH_2-*C*=N), 150.4 (CH_2-C=N-*C*), 143.2, 140.7, 139.1, 139.0, 128.7, 128.4, 126.0, 124.4$_2$, 122.9, 122.4, 121.5, 120.5, 119.5, 119.2, 112.2, 109.2, 108.7, 97.5 (C=N-C=*C*), 43.0, 33.9 and 28.2 (N*C*H_3); HRMS (ESI) calcd. for $C_{26}H_{22}N_3$ [M^++H] 376.1814, found: 376.1813.

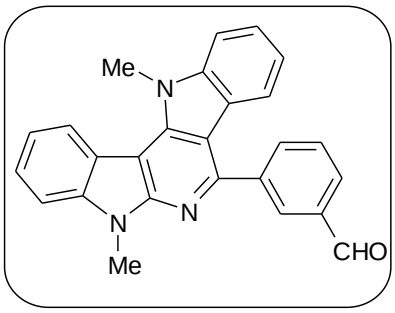


Compound 3ai: Yield: 0.112 g (55%; white solid); mp: 182-184 ^{0}C; IR (KBr, cm^{-1}) 3057, 2909, 2832, 1615, 1588, 1511, 1473, 1391, 1325, 1243, 1106, 1029, 804, 739; ^{1}H

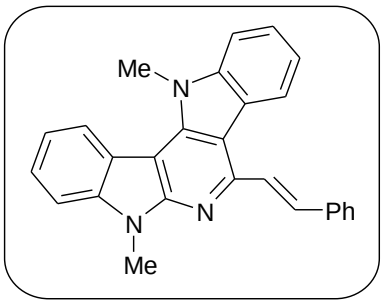
NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.08 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.53-7.24 (m, 8H, Ar-*H*), 6.79 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 4.81 (s, 2H, CH_2), 4.52 (s, 3H, CH_3), 4.08 (s, 3H, CH_3) and 3.74 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (*C*-OCH_3), 152.7 (*C*=N), 150.4, 143.3, 140.8 (C=N-*C*), 139.0, 131.2, 129.6, 126.2, 124.4, 123.0, 122.4, 121.6, 120.6, 119.6, 119.2, 113.9, 112.2, 109.3, 108.8, 97.6 (C=N-C=*C*), 55.2 (O*C*H_3), 42.1 (*C*H_2), 34.0 and 28.3 (N*C*H_3); HRMS (ESI) calcd. for $C_{27}H_{24}N_3O$ [M^++H] 406.1920, found: 406.1919.



Compound 3aj: Yield: 0.108 g (59%; yellow solid); mp 216-218 ^{0}C; IR (KBr, cm^{-1}) 3079, 2920, 2843, 1610, 1588, 1473, 1319, 1259, 1095, 733, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8 Hz, 1H, Ar-*H*), 8.03 (d, *J* = 8 Hz, 1H, Ar-*H*), 7.74-7.48 (m, 6H, Ar-*H*), 7.33-7.19 (m, 3H, Ar-*H*), 4.54 (s, 3H, N*C*H_3) and 4.10 (s, 3H, N*C*H_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0 (*C*=N), 145.1 (C=N-*C*), 143.7, 143.3, 140.7, 139.2, 127.7, 127.2, 127.0, 124.9, 124.7, 122.6, 122.5, 121.1, 120.1, 119.6, 118.9, 111.6, 109.2, 108.7, 98.0 (C=N-C=*C*), 33.9 and 28.2 (N*C*H_3); HRMS (ESI) calcd. for $C_{23}H_{18}N_3S$ [M^++H] 368.1222, found: 368.1224.

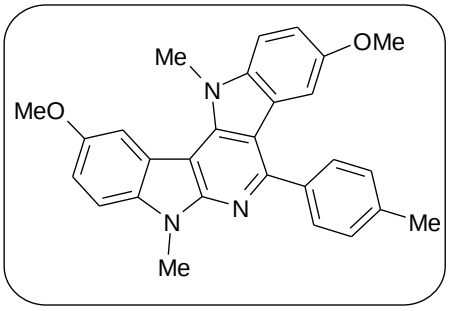


Compound 3ak: Yield: 0.117 g (60%; yellow solid); mp 232-234 ^{0}C; IR (KBr, cm^{-1}) 3046, 2920, 2848, 1714, 1582, 1473, 1374, 1325, 1276, 1155, 1089, 733; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H, C*H*O), 8.56 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.42 (s, 1H, Ar-*H*), 8.18 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 8.10 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.77 (t, *J* = 15.2 Hz, 1H, Ar-*H*), 7.57-7.34 (m, 6H, Ar-*H*), 7.10 (t, *J* = 14.8 Hz, 1H, Ar-*H*), 4.55 (s, 3H, NC*H*$_3$) and 4.09 (s, 3H, NC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3 (*C*HO), 150.5 (*C*=N), 150.4 (C=N-*C*), 143.5, 142.3, 141.0, 139.4, 136.8, 135.6, 131.6, 129.2, 125.1, 125.0, 122.7, 122.6, 120.9, 120.3, 119.8, 119.0, 111.5, 109.4, 109.0, 98.2 (C=N-C=*C*), 34.1 and 28.4 (N*C*H$_3$); HRMS (ESI) calcd. for $C_{26}H_{20}N_3O$ [M^{+}+H] 390.1607, found: 390.1606.

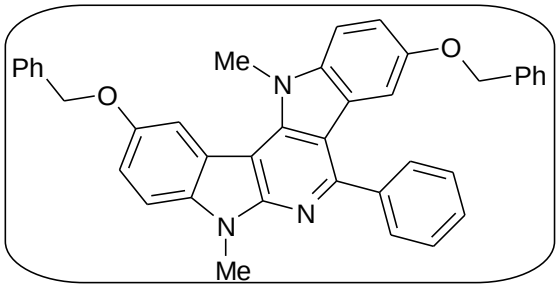


Compound 3al: Yield: 0.122 g (63%; yellow solid); mp: 228-230 ^{0}C; IR (KBr, cm^{-1}) 2920, 1632, 1583, 1467, 1319, 1254, 1095, 963, 788, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8 Hz, 1H, Ar-*H*), 8.25 (d, *J* = 8 Hz, 1H, Ar-*H*), 8.16 (d, *J* = 4.8 Hz, 2H, Ar-*H*), 7.78 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.49-7.28 (m, 9H, Ar-*H*), 4.36 (s, 3H, NC*H*$_3$) and

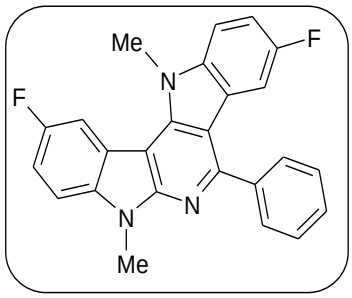
4.04 (s, 3H, NCH_3); ^{13}C NMR (400 MHz, $CDCl_3$) δ 150.3 (*C*=N), 147.2 (C=N-*C*), 143.1, 140.9, 139.5, 137.5, 133.9, 128.8, 128.2, 127.5, 125.9, 124.5, 122.9, 122.4, 121.9, 120.5, 119.4, 119.2, 112.0, 109.1, 108.8, 98.2 (C=N-C=*C*), 33.8 and 28.0 (N*C*H_3); HRMS (ESI) calcd. for $C_{27}H_{22}N_3$ [M^++H] 388.1814, found: 388.1817.



Compound 3bd: Yield: 0.127 g (58%; white solid); mp 180-182 ^{0}C; IR (KBr, cm^{-1}) 2997, 2926, 2827, 1621, 1600, 1578, 1490, 1304, 1216, 1139, 1041, 778; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H, Ar-*H*), 7.76 (d, *J* = 8 Hz, 2H, Ar-*H*), 7.44-7.34 (m, 4H, Ar-*H*), 7.18-7.03 (m, 3H, Ar-*H*), 4.48 (s, 3H, NCH_3), 4.05 (s, 3H, OCH_3) and 3.97 (s, 3H, OCH_3), 3.69 (s, 3H, NCH_3), 2.51 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 and 153.7 (*C*-OCH_3), 152.5 (*C*=N), 150.8 (C=N-*C*), 143.6, 138.4, 138.2, 135.6, 134.3, 129.3, 129.0, 123.7, 119.4, 112.7, 112.0, 110.9, 109.4, 109.0, 107.3, 105.1, 97.5 (C=N-C=*C*), 56.2 and 55.6 (O*C*H_3), 33.9 and 28.3 (2 N*C*H_3), 21.5 (*C*H_3); HRMS (ESI) calcd. for $C_{28}H_{26}N_3O_2$ [M^++H] 436.2026, found: 436.2029.

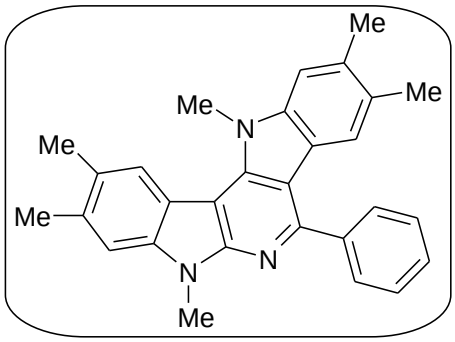


Compound 3cb: Yield: 0.183 g (64%; white solid); mp 178-180 ^{0}C; IR (KBr, cm^{-1}) 2943, 2850, 1622, 1593, 1489, 1330, 1293, 1142, 1029, 790, 715; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 7.85-7.83 (m, 2H, Ar-*H*), 7.58-7.54 (m, 5H, Ar-*H*), 7.47-7.32 (m, 10H, Ar-H), 7.25 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 7.11 (dd, *J* = 8.6 Hz, *J* = 2.2 Hz, 1H, Ar-*H*), 7.04 (d, *J* = 2.4 Hz, 1H, Ar-*H*), 5.24 (s, 2H, OCH_2), 4.90 (s, 3H, OCH_2), 4.31 (s, 3H, CH_3), 4.03 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 152.7, 152.1, 150.5, 143.3, 141.1, 137.6, 137.4, 135.5, 134.2, 129.5, 128.6, 128.5, 128.4, 127.9, 127.8, 127.6, 127.4, 123.2, 119.1, 114.1, 113.3, 110.8, 109.3, 109.2, 108.6, 105.7, 97.5 (C=N-C=*C*), 71.3, 70.3, 33.7 and 28.2; HRMS (ESI) calcd. for $C_{39}H_{32}N_3O_2$ [M^++H] 574.2494, found: 574.2494.

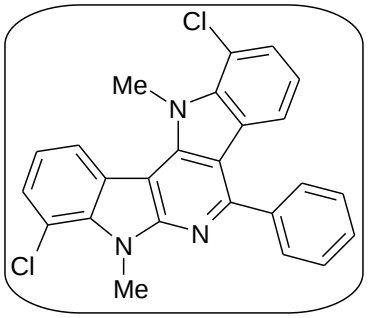


Compound 3db: Yield: 0.101 g (51%; yellow solid); mp 258-261 ^{0}C; IR (KBr, cm^{-1}) 2920, 2827, 1621, 1600, 1490, 1298, 1123, 947, 767, 706; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 8.11-7.58 (m, 5H, Ar-*H*), 7.43-7.12 (m, 5H, Ar-*H*), 4.43 (s, 3H, NCH_3) and 4.04 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 151.2,

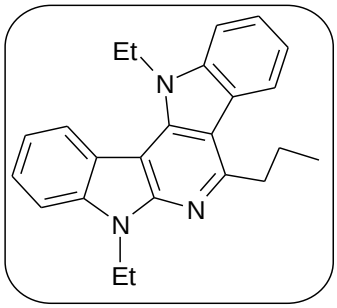
144.0, 140.6, 137.1, 135.6, 129.2, 129.0, 128.7, 112.5, 112.4, 112.3, 112.2, 109.8, 109.7, 109.3, 109.2, 108.5, 108.3, 107.5, 107.3, 34.2 and 28.5 (2 N*C*H_3); HRMS (ESI) calcd. for $C_{25}H_{18}F_2N_3$ [M^++H] 398.1470, found: 398.1468.



Compound 3eb: Yield: 0.130 g (62%; pale yellow solid); mp 256-258 ^{0}C; IR (KBr, cm^{-1}) 2917, 2851, 1610, 1594, 1448, 1393, 1295, 1050, 753, 700; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H, Ar-*H*), 7.91-7.90 (m, 2H, Ar-*H*), 7.63-7.57 (m, 3H, Ar-*H*), 7.33 (s, 1H, Ar-H), 7.29 (s, 1H, Ar-H), 7.27 (s, 1H, Ar-H), 4.51 (s, 3H, NC*H*$_3$), 4.06 (s, 3H, NC*H*$_3$), 2.53 (d, *J* = 2.0 Hz, 6H, C*H*$_3$), 2.46 (s, 3H, C*H*$_3$), 2.26 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 150.3, 143.1, 141.5, 139.8, 138.2, 133.8, 133.7, 129.5, 128.5, 128.4, 128.3, 127.8, 123.1, 121.9, 121.1, 117.2, 111.3, 109.9, 109.4, 97.7 (C=N-C=*C*), 34.1, 28.4, 20.8, 20.6 and 20.2; HRMS (ESI) calcd. for $C_{29}H_{28}N_3$ [M^++H] 418.2283, found: 418.2287.

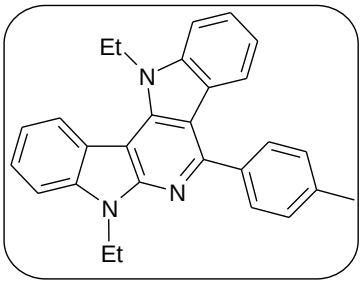


Compound 3fb: Yield: 0.122 g (56%; white solid); mp 224-226 ^{0}C; IR (KBr, cm^{-1}) 2947, 2824, 1666, 1611, 1582, 1551, 1476, 1400, 1348, 1294, 1209, 1182, 1099, 786, 727; ^{1}H NMR (500 MHz, C_6D_6) δ 8.37 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.84-7.82 (m, 2H, Ar-*H*), 7.64-7.58 (m, 3H, Ar-*H*), 7.49 (dd, *J* = 9.75 Hz, *J* = 1.25 Hz, 1H), 7.41-7.36 (m, 2H, Ar-H), 7.27-7.23 (m, 1H, Ar-H), 7.00 (t, *J* = 20.5 Hz, 1H, Ar-H), 4.67 (s, 3H, NC*H*$_3$), 4.53 (s, 3H, NC*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 153.1, 151.3, 145.6, 141.3, 138.0, 135.2, 129.5, 128.6, 128.4, 128.0, 127.9, 127.7, 127.5, 127.0, 126.6, 126.5, 122.1, 121.7, 121.5, 120.1, 120.0, 116.9, 112.1, 97.9 (C=N-C=*C*), 37.5 and 31.2; HRMS (ESI) calcd. for $C_{25}H_{18}Cl_2N_3$ [M^{+}+H] 430.0878, found: 430.0873.

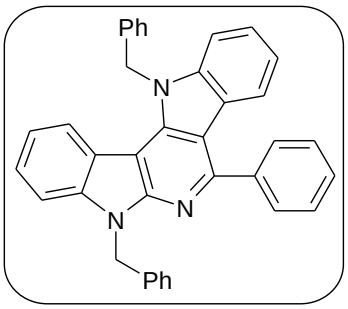


Compound 3gf Yield: 0.098 g (55%; yellow solid); mp 130-132 ^{0}C; IR (KBr, cm^{-1}) 3051, 2958, 2865, 1610, 1600, 1588, 1473, 1325, 1248,749, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.16 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.60-7.27 (m, 6H, Ar-*H*), 4.98 (qrt, 2H, NC*H*$_2$CH$_3$), 4.72 (qrt, 2H, NC*H*$_2$CH$_3$), 3.49-3.45 (m, 2H, CH_2),

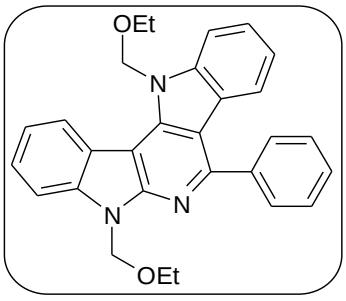
2.10-2.04 (m, 2H, C*H*$_2$-CH$_3$), 1.78 (t, *J* = 16 Hz, 3H, C*H*$_3$) 1.52 (t, *J* = 12 Hz, 3H, C*H*$_3$) and 1.20 (t, *J* = 16 Hz, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 149.5, 142.0, 139.4, 137.6, 124.0, 123.3, 122.8, 122.1, 121.4, 120.5, 119.5, 119.4, 112.7, 111.3, 109.6, 109.2, 108.6, 96.7 (C=N-C=*C*-), 40.4, 39.2, 36.6, 21.5, 16.1, 14.4, 14.0; HRMS (ESI) calcd. for $C_{24}H_{26}N_3$ [M^++H] 356.2127, found: 356.2126.



Compound 3gd: Yield: 0.111 g (55%; white solid); mp 148-150 ^{0}C; IR (KBr, cm^{-1}) 2969, 2920, 1610, 1578, 1468, 1326, 1254,794, 734; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.77 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.62-7.35 (m, 8H, Ar-*H*), 7.10 (t, *J* = 15.2 Hz, 1H, Ar-*H*), 5.05-5.00 (m, 2H, NC*H*$_2$), 4.77-4.74 (m, 2H, NC*H*$_2$), 2.54 (s, 3H, C*H*$_3$), 1.81 (t, *J* = 14.4 Hz, 3H, NCH$_2$C*H*$_3$) and 1.50 (t, *J* = 14.4 Hz, 3H, NCH$_2$C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (*C*=N), 149.8 (C=N-*C*), 142.6, 139.7, 138.4, 138.2, 129.3, 129.2, 124.7, 124.5, 123.3, 122.5, 121.5, 120.1, 119.7, 119.4, 111.5, 109.6, 109.4, 108.5, 97.4 (C=N-C=*C*), 40.6 and 36.7 (2 N*C*H$_2$CH$_3$), 21.6 (*C*H$_3$), 16.2 and 14.1 (2 NCH$_2$*C*H$_3$); HRMS (ESI) calcd. for $C_{28}H_{26}N_3$ [M^++H] 404.2127, found: 404.2124.

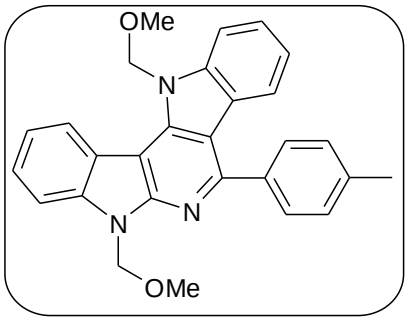


Compound 3hb: Yield: 0.146 g (57%; white solid); mp 236-238 ^{0}C; IR (KBr, cm^{-1}) 2920, 2848, 1621, 1593, 1544, 1467, 1402, 1325, 1243, 1177, 739, 711; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.94 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.62-7.22 (m, 18H, Ar-*H*), 7.10-7.07 (m, 2H, Ar-*H*), 6.16 (s, 2H, CH_2) and 5.91 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (*C*=N), 150.7 (C=N-*C*), 144.0, 141.2, 140.8, 138.6, 137.9, 137.4, 129.6, 129.2, 128.7, 128.6, 128.5, 127.8, 127.3, 127.2, 126.5, 125.0, 124.7, 123.4, 122.8, 121.4, 120.6, 120.1, 119.2, 112.0, 110.1, 109.6, 97.6 (C=N-C=*C*), 50.0, 45.5; HRMS (ESI) calcd. for $C_{37}H_{28}N_3$ [M^++H] 514.2284, found: 514.2282.



Compound 3ib: Yield: 0.113 g (50%; yellow solid); mp 158-160 ^{0}C; IR (KBr, cm^{-1}) 3057, 2969, 2893, 1616, 1589, 1473, 1380, 1326, 1260, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.88-7.40 (m, 11H, Ar-*H*), 7.12 (t, *J* = 15.2 Hz, 1H, Ar-*H*), 6.23 (s, 2H, NCH_2), 6.14 (s, 2H, NCH_2), 3.86 (qrt, 2H, CH_2CH$_3$), 3.60 (qrt, 2H, CH_2CH$_3$), 1.31 (t, *J* = 14 Hz, 3H, CH$_2$CH_3) and 1.17 (t, *J* = 14.4 Hz, 3H, CH$_2$CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (*C*=N), 150.8 (C=N-*C*), 142.8, 141.0, 138.6, 129.4, 128.7, 128.5, 125.3, 125.2, 123.4, 123.2, 121.6, 121.0, 120.9, 120.0, 112.6, 110.4, 109.1, 98.6 (C=N-C=*C*), 73.9 and 71.2 (O*C*H_2), 64.4 and 64.0 (N*C*H_2), 15.2 and 15.0 (CH_2*C*H_3); HRMS (ESI) calcd. for $C_{29}H_{28}N_3O_2$ [M^++H] 450.2182, found: 450.2182.

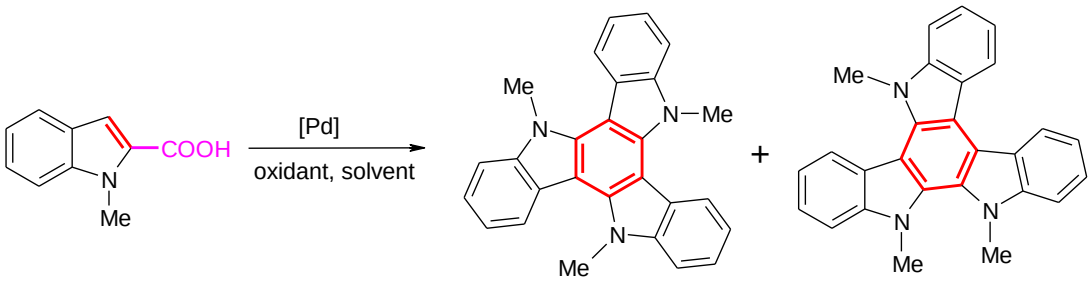


Compound 3jd: Yield: 0.105 g (48%; white solid); mp 170-172 ^{0}C; IR (KBr, cm^{-1}) 3046, 2947, 2821, 1610, 1593, 1473, 1330, 1259, 1182, 1062, 793, 728; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.78-7.52 (m, 6H, Ar-*H*), 7.47-7.41 (m, 4H, Ar-*H*), 7.12 (t, *J* = 13.2 Hz, 1H, Ar-H), 6.20 (s, 2H, NCH_2), 6.09 (s, 2H, NCH_2), 3.62 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (*C*=N), 150.9 (C=N-*C*), 142.9, 141.1, 138.6_2, 138.5_7, 138.1, 129.3, 129.2, 125.4, 125.2, 123.4, 123.2, 121.8, 121.0_3, 120.9_8, 120.0_0, 112.7, 110.3, 109.0, 98.5 (C=N-C=*C*), 75.1 and 72.7 (2 N*C*H_2OCH_3), 56.4 (O*C*H_3), 21.5 (*C*H_3); HRMS (ESI) calcd. for $C_{28}H_{26}N_3O_2$ [M^++H] 436.2026, found: 436.2024.

(iv) Optimisation of the reaction conditions for the synthesis of triindoles 4a-5a

To an oven dried round-bottomed flask (25 mL), silver salt (1-3 mmol, *cf*. Table S1) was added and dried in *vacuo* dried in *vacuo* (while heating if necessary) for 0.5 h. To this, [Pd]-catalyst (*cf* Table S2), 1-alkylindole-2-carboxylic acid (1.0 mmol) and solvent (DMF, toluene, THF or DCE; 5.0 mL) were added. The mixture was stirred at rt (25 ^{o}C) for 10 min. The RBF was flushed with N_2 and sealed with a stopper. Then the contents were heated at 80 ^{o}C (oil bath) for 10 h. After the completion of the reaction as monitored by TLC, the mixture was cooled to rt, filtered and extracted with diethyl ether (3 x 25 mL). The combined organic extracts were washed with brine solution (4 x 10 mL). The organic part was dried over anh. Na_2SO_4, and the solvent was removed using a rotary evaporator. The crude products were purified by column chromatography (230-400 mesh silica) using hexane/ EtOAc.

Table S2: **Optimisation of conditions for trimerization of indole 1a to lead to 4a-5a**[a]



1a **4a** **5a**

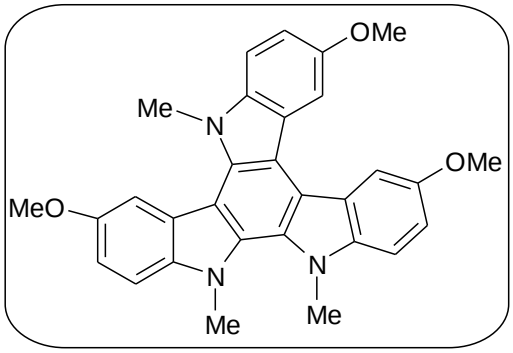
Entry	[Pd] catalyst	Oxidant	Solvent	Overall Yield (%)[b]
1	$Pd(OAc)_2$	Ag_2CO_3[a]	DMF	38
2	$Pd(OAc)_2$	-	DMF	-

3	-	Ag_2CO_3	DMF	-
4	**$Pd(OAc)_2$**	**Ag_2CO_3**	**DMF**	**48**
5	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	DMF	trace
6	$Pd(OAc)_2$	Ag_2O	DMF	36
7	$Pd(OAc)_2$	AgOAc	DMF	39
8	$Pd(OAc)_2$	Ag_2CO_3	DMA	45
9	$Pd(OAc)_2$	Ag_2CO_3	Toluene	40
10	$Pd(OAc)_2$	Ag_2CO_3	THF	28
11	$Pd(OAc)_2$	Ag_2CO_3	DME	trace
12	$PdCl_2$	Ag_2CO_3	DMF	41
13	$Pd(dba)_2$	Ag_2CO_3	DMF	35
14	$Pd(TFA)_2$	Ag_2CO_3	DMF	35
15	$Pd(OAc)_2$	Ag_2CO_3+ $AgSbF_6$ (0.3)	DMF	37
16	$Pd(OAc)_2$	Ag_2CO_3+ AgOTf (0.3)	DMF	34

[a]Reactions were carried out using **1a** (1.0 mmol), [Pd]-catalyst (10 mol %), Silver oxidant (2.0 mmol except for entry 1 where 1.0 mmol was used) and DMF (5.0 mL) for 10 h. [b]Isolated yield.

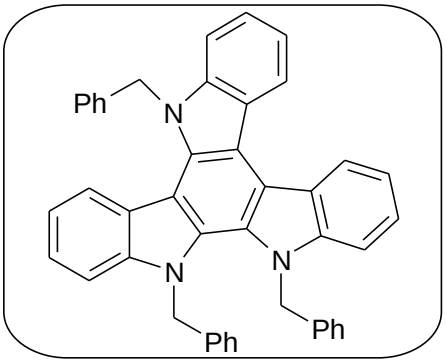
(v) Optimised procedure spectroscopic/analytical for diindolo carbazoles (4 and 5)

To an oven dried round-bottomed flask (25 mL), silver carbonate (2.0 mmol) was added and dried in *vacuo* while heating (ca 100 ^{o}C) using a hot air gun for 0.5 h. To this, $Pd(OAc)_2$ (10 mol %), 1-alkylindole-2-carboxylic acid (1.0 mmol) and DMF (5.0 mL) were added. The mixture was stirred at rt (25 ^{o}C) for 10 min. The RBF was flushed with N_2 and sealed with a stopper. Then the contents were stirred at 80 ^{0}C (oil bath) for 10 h. After the completion of the reaction as monitored by TLC, the mixture was cooled to rt, filtered and extracted with diethyl ether (3 x 25 mL). The combined organic extracts were washed with brine solution (4 x 10 mL). The organic part was dried over anhy. Na_2SO_4, and the solvent was removed using a rotary evaporator. The crude products were purified by column chromatography (230-400 mesh silica) using hexane/ EtOAc as eluent to afford the final products (**4** and **5**). Compounds **4a**, **5a** and **4l** have been reported in the literature [4-5]

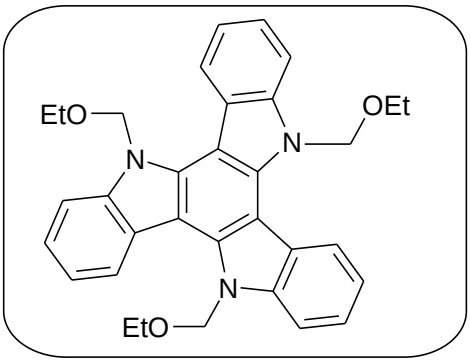


Compound 5b: Yield: 0.048 g (30%; yellow solid); mp 118-121 ^{0}C; IR (KBr, cm^{-1}) 2920 (w), 2832, 1616, 1567, 1484, 1386, 1304, 1221, 1030, 909, 783; ^{1}H NMR (400 MHz, C_6D_6) δ 8.85 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 8.80 (d, *J* = 2.8 Hz, 1H, Ar-*H*), 8.20 (d, *J* = 2.4 Hz, 1H, Ar-*H*), 7.51-7.31 (m, 6H, Ar-*H*), 4.00 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.78 (s, 3H, NCH_3), 3.51 (s, 3H, NCH_3) and 3.46 (s, 3H, NCH_3); ^{13}C

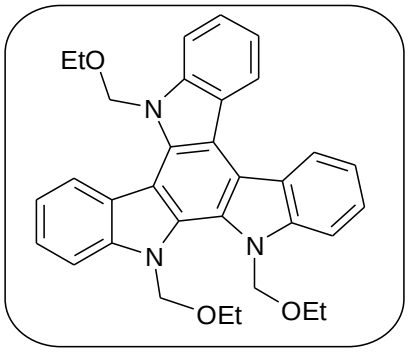
NMR (100 MHz, C_6D_6) δ 155.4, 155.3, 155.0, 141.7, 140.3, 138.4, 136.1, 133.3, 128.6, 126.8, 125.5, 125.2, 119.8, 115.1, 113.2_2, 113.1_9, 112.4_9, 112.4_5, 111.8, 111.1, 110.1, 107.5, 106.5, 105.8, 55.9, 55.8_2 and 55.7_8 (O*C*H_3), 36.9, 35.1 and 36.1 (N*C*H_3); HRMS (ESI) calcd. for $C_{30}H_{28}N_3O_3$ [M^++H] 478.2131, found: 478.2130.



Compound 5h: Yield: 0.066 g (32%; yellow solid); mp 107-109 ^{0}C; IR (KBr, cm^{-1}) 3024, 2926, 1715, 1578, 1331, 1194, 1167, 1019, 739, 690; ^{1}H NMR (400 MHz, C_6D_6) δ 9.33 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 9.27 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.33 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.48-7.23 (m, 9H, Ar-*H*), 7.11-6.92 (m, 11H, Ar-*H*), 6.80-6.76 (m, 4H, Ar-*H*), 5.82 (s, 2H, NCH_2), 5.11 (s, 2H, NCH_2) and 5.03 (s, 2H, NCH_2); ^{13}C NMR (100 MHz, C_6D_6) δ 146.1, 144.6, 143.7, 139.4, 138.0, 137.7, 136.1, 132.2, 129.6, 128.9, 128.5, 128.2, 127.8, 127.7, 127.3, 127.2, 126.8, 126.6, 126.5, 125.9, 125.8, 125.1, 124.9, 124.7, 124.0, 123.3, 123.2, 121.5, 121.3, 120.9, 120.7, 113.8, 113.1, 112.8, 112.0, 110.8, 52.9, 52.3, 52.0; HRMS (ESI) calcd. for $C_{45}H_{34}N_3$ [M^++H] 616.2753, found: 616.2752.

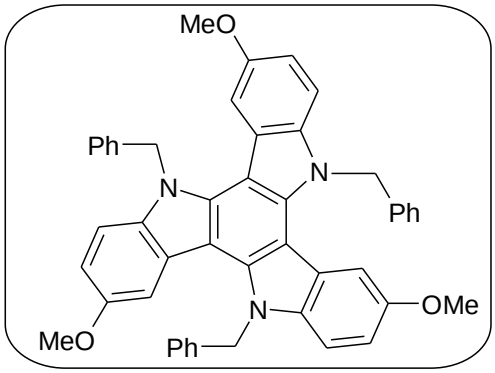


Compound 4i: Yield: 0.037 g (21%; white solid); mp 119-121 ^{0}C; IR (KBr, cm^{-1}) 2920, 2849, 1583, 1473, 1385, 1325, 1226, 1078, 1013, 755, 722; ^{1}H NMR (400 MHz, C_6D_6) δ 9.05-9.02 (m, 3H, Ar-*H*), 7.73-7.70 (m, 3H, Ar-*H*), 7.58-7.53 (m, 6H, Ar-*H*), 5.78 (s, 6H, NC*H*$_2$), 3.45 (qrt, 6H, C*H*$_2$), 1.17 (t, 9H, C*H*$_3$); ^{13}C NMR (400 MHz, C_6D_6) δ 142.7, 139.0, 124.8, 124.4, 122.4, 121.6, 111.2, 105.2, 76.1, 64.2, 15.5; HRMS (ESI) calcd. for $C_{33}H_{33}N_3O_3$ [M^{+}+Na] 542.2420, found: 542.2420.

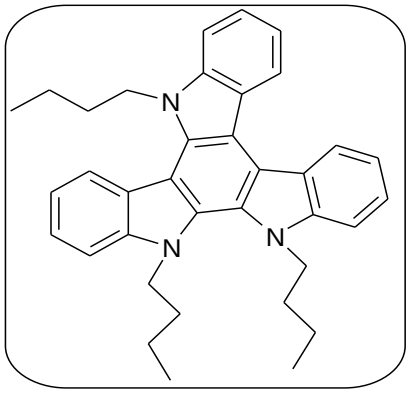


Compound 5i: Yield: 0.054 g (31%; white solid); mp 119-121 ^{0}C; IR (KBr, cm^{-1}) 2920, 2849, 1583, 1473, 1385, 1325, 1226, 1078, 1013, 755, 722; ^{1}H NMR (400 MHz, C_6D_6) δ 9.30-9.20 (m, 3H, Ar-*H*), 7.92 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.87-7.85 (m, 1H, Ar-*H*), 7.75 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.64-7.52 (m, 6H, Ar-*H*), 5.85-5.66 (m, 6H, NC*H*$_2$), 3.50-3.44 (m, 2H, OC*H*$_2$), 3.17-3.08 (m, 4H, OC*H*$_2$), 1.22-1.13 (m, 3H, OCH$_2$C*H*$_3$), 1.01-0.93 (m,

6H, OCH_2CH_3); ^{13}C NMR (100 MHz, C_6D_6) δ 145.3, 144.1, 143.2, 134.7,130.7, 128.6, 127.0, 126.6, 126.0, 125.7, 125.6, 124.8, 124.0, 123.7, 123.1, 122.2, 121.8, 121.2, 120.1, 114.0, 113.3, 112.8, 111.2, 110.9, 77.8, 77.5, 76.0, 64.2, 64.1, 64.0, 15.5, 15.3; HRMS (ESI) calcd. for $C_{33}H_{33}N_3O_3$ [M^++Na] 542.2420, found: 542.2420.



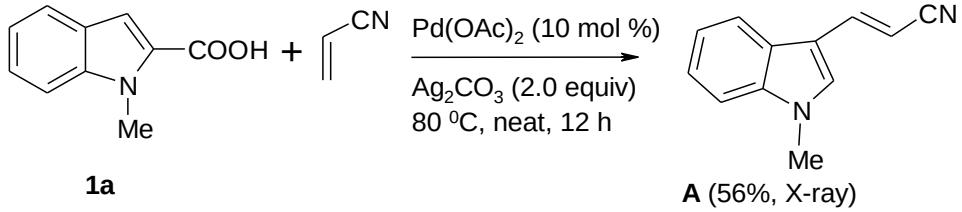
Compound 4k: Yield: 0.082 g (35%; yellow solid); mp 132-134 ^0C; IR (KBr, cm^{-1}) 2909, 2843, 1615, 1566, 1489, 1451, 1319, 1232, 1040, 914, 739; ^1H NMR (400 MHz, C_6D_6) δ 7.74 (s, 3H, Ar-*H*), 7.46 (d, *J* = 7.6 Hz, 6H, Ar-*H*), 7.18-7.07 (m, 15H, Ar-*H*), 5.80 (s, 6H, NCH_2), 3.14 (s, 9H, OCH_3); ^{13}C NMR (100 MHz, C_6D_6) δ 155.4, 140.8, 138.9, 137.1, 129.0, 127.2, 126.7, 124.3, 113.3, 111.9, 104.4, 104.2, 54.2, 51.7; HRMS (ESI) calcd. for $C_{48}H_{40}N_3O_3$ [M^++H] 706.3070, found: 706.3069.



Compound 5l: Yield: 0.052 g (30%; yellow solid); mp 131-133 ^{0}C; IR (KBr, cm^{-1}) 2920, 2860, 1572, 1456, 1402, 1336, 1128, 1024, 744, 667; ^{1}H NMR (400 MHz, C_6D_6) δ 9.37-9.31 (m, 2H, Ar-*H*), 8.58 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.67-7.47 (m, 9H, Ar-*H*), 4.77 (t, *J* = 16 Hz, 2H, NC*H*$_2$), 4.63 (t, *J* = 16 Hz, 2H, NC*H*$_2$), 4.54 (t, *J* = 16 Hz, 2H, NC*H*$_2$), 1.90-1.82 (m, 2H), 1.29-1.21 (m, 4H), 1.19-1.09 (m, 2H), 0.71-0.64 (m, 7H), 0.45-0.40 (m, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ δ 145.8, 144.4, 142.0, 135.0, 132.8, 128.6, 128.1, 127.9, 126.3, 125.4, 125.3, 124.7, 124.6, 124.0, 123.8, 123.2, 121.2, 121.1, 120.9, 120.1, 113.6, 113.4, 113.2, 110.9, 49.0, 48.4, 46.9, 32.7, 30.3, 29.9, 20.4_4, 20.3_8, 20.2, 14.1, 13.7_4, 13.7_1; HRMS (ESI) calcd. for $C_{36}H_{40}N_3$ [M^++H] 514.3223, found: 514.3223.

(vi) Reaction of 1-methyl-indole-2-carboxylic acid 1a with acrylonitrile affording the C3-alkenylated product A (cf. footnoted in Table 1)

The reaction between 1-methyl-indole-2-carboxylic acid **1a** and acrylonitrile under conditions similar to that for **3ab** afforded an unexpected decarboxylative C3-alkenylated product **A** (X-ray, FigureS7) in 56% yield. This Heck type coupled product has also been prepared by Wang and co-workers recently using *N*-methylindole.[6] However, our reaction conditions are different.



1a

A (56%, X-ray)

(3) (i) X-ray data for compounds 3aa, **3ac**, **5b**, **4k**, and **A**

Compound 3aa: $C_{20}H_{17}N_3$, M = 299.37, monoclinic, Space group $P2_1/c$, a = 17.0546(9), b = 5.5978(2), c = 16.1901(6) Å, β = 105.328(4), V = 1490.66(11) Å^3, Z = 4, μ = 0.625 mm^{-1}, data/restraints/parameters: 2844/0/212, R indices (I> 2σ(I)): R1 = 0.0583, *w*R2 (all data) = 0.1492. CCDC No. 1029448.

Compound 3ac: $C_{26}H_{21}N_3$, M = 375.46, Monoclinic, Space group $P2_1/c$, a = 13.1017(10), b = 20.7038(19), c = 7.3429(6) Å, β = 105.921(9), V = 1915.4(3) Å^3, Z = 4, μ = 0.077 mm^{-1}, data/restraints/parameters: 3032/0/265, R indices (I> 2σ(I)): R1 = 0.0507, *w*R2 (all data) = 0.1190. CCDC No. 1029449.

Compound 5b: $C_{30}H_{27}N_3O_3$, M = 477.55, Orthorhombic, Space group $Pca2_1$, a = 21.214(3), b = 8.2654(11), c = 27.017(4) Å, V = 4737.3(11) Å^3, Z = 8, μ = 0.088mm^{-1}, data/restraints/parameters: 8319/1/661, R indices (I> 2σ(I)): R1 = 0.0534, *w*R2 (all data) = 0.1193. CCDC No. 1029450.

Compound 4k: $C_{48}H_{39}N_3O_3$, M = 705.82, Monoclinic, Space group $C2/c$, a = 14.8372(17), b = 26.503(3), c = 18.224(2) Å, β = 96.420(11), V = 7121.3(17) Å^3, Z = 8, μ = 0.082 mm^{-1}, data/restraints/parameters: 6266/0/490, R indices (I> 2σ(I)): R1 = 0.0531, *w*R2 (all data) = 0.1239. CCDC No. 1029451.

Compound A: $C_{12}H_{10}N_2$, M = 182.22, Monoclinic, Space group $P2_1/c$, a = 9.0822(11), b = 14.3844(18), c = 7.6234(10) Å, β = 92.165(2), V = 995.2(2) Å^3, Z = 4, μ = 0.074 mm^{-1}, data/restraints/parameters: 1750/0/129, R indices (I> 2σ(I)): R1 = 0.0458, *w*R2 (all data) = 0.1329. CCDC No. 1029452.

(ii) Molecular structures of compounds 3aa, 3ag, 4k, 5b and A

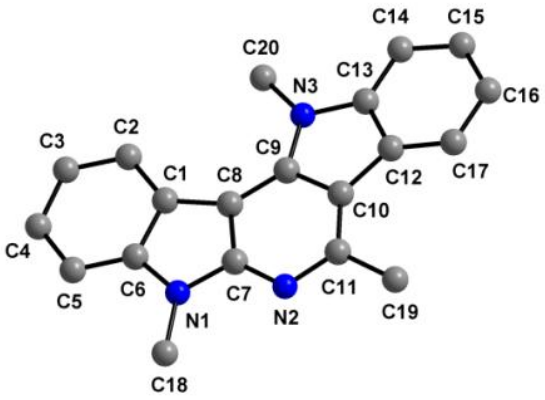


Figure S3. Molecular structure of compound **3aa**. Selected bond lengths [Å] with esd's in parentheses: N(2)-C(7) 1.339(3), N(2)-C(11) 1.341(4), C(8)-C(7) 1.413(3), C(8)-C(9) 1.402(4), C(10)-C(9) 1.418(3), C(10)-C(11) 1.400(4). Hydrogen atoms are omitted for clarity.

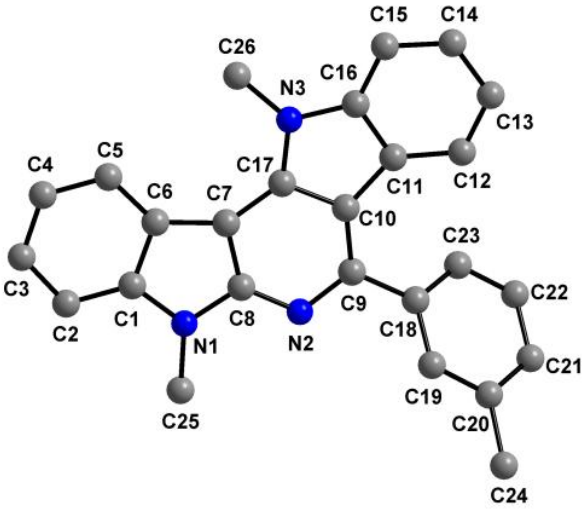


Figure S4. Molecular structure of compound **3ac**. Selected bond lengths [Å] with esd's in parentheses: N(2)-C(8) 1.331(2), N(2)-C(9) 1.335(3), C(7)-C(8) 1.414(3), C(17)-C(7) 1.399(3), C(17)-C(10) 1.420(3), C(10)-C(9) 1.401(3). Hydrogen atoms are omitted for clarity.

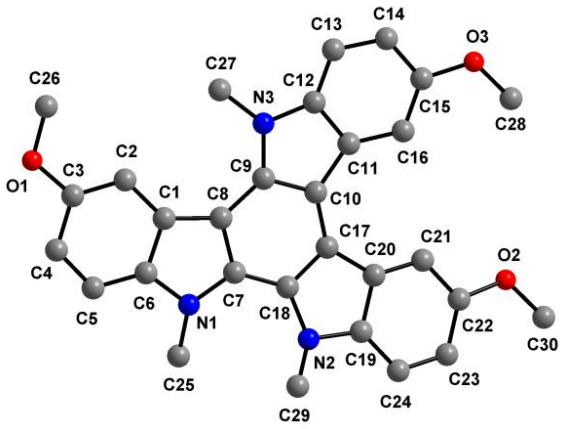


Figure S5. Molecular structure of compound **5b**. Selected bond lengths [Å] with esd's in parentheses: C(7)-N(1) 1.378(4), C(7)-C(8) 1.416(4), C(9)-C(8) 1.430(4), N(3)-C(9) 1.388(3), C(9)-C(10) 1.414(4), C(17)-C(10) 1.424(4), C(17)-C(18) 1.398(4), N(2)-C(18) 1.406(4). Hydrogen atoms are omitted for clarity.

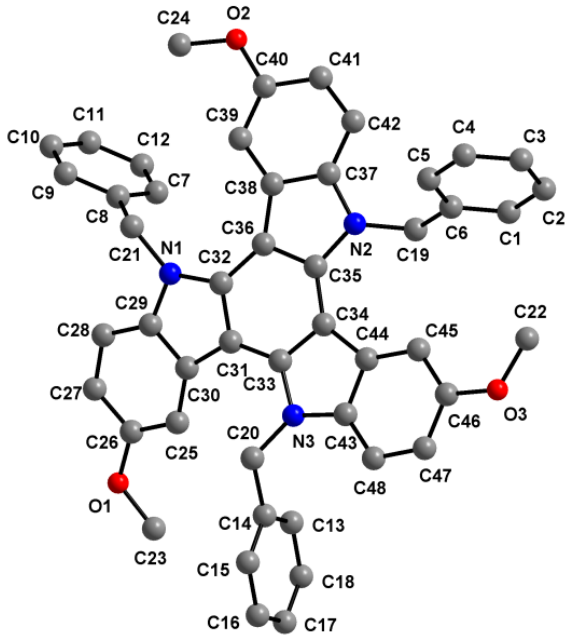


Figure S6. Molecular structure of compound **4k**. Selected bond lengths [Å] with esd's in parentheses: C(31)-C(32) 1.404(3), N(1)-C(32) 1.396(2), C(36)-C(32) 1.418(3), C(36)-C(35) 1.412(3), N(2)-C(35) 1.379(2), C(34)-C(35) 1.406(3), C(34)-C(33) 1.399(3), N(3)-C(33) 1.379(3). Hydrogen atoms are omitted for clarity.

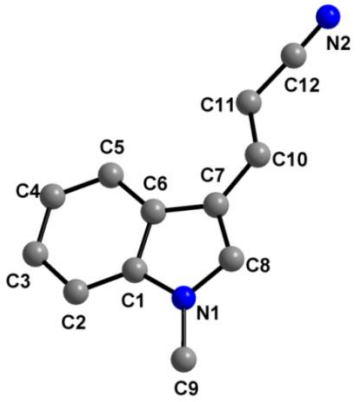


Figure S7. Molecular structure of compound **A**. Selected bond lenghs [Å] with esd's in parentheses: C(7)-C(8) 1.375(2), C(7)-C(10) 1.437(2), C(10)-C(11) 1.323(2), C(11)-C(12) 1.422(2), C(12)-N(2) 1.137(2). Hydrogen atoms are omitted for clarity.

(4) UV-Visible and fluorescence spectra of indolocarbolines (3) and triindoles (4-5)

(i) UV-Visible and Fluorescence spectra indolocarbolines 3

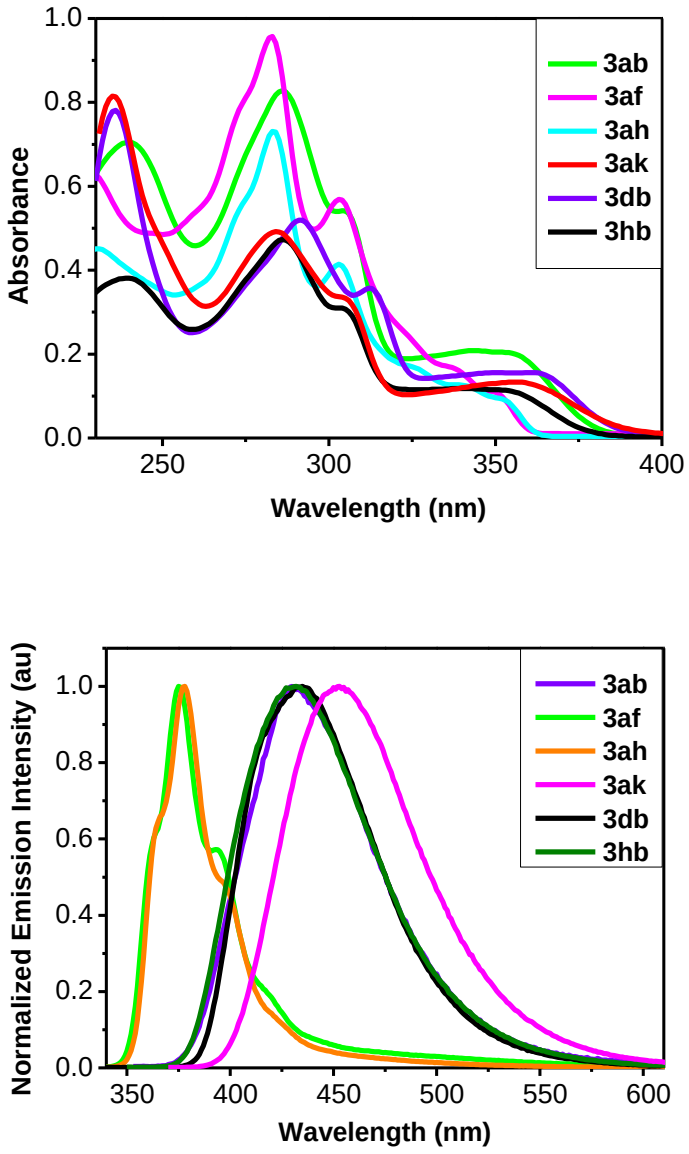


Figure S8. Top: UV-Visible spectra of **3ab**, **3af**, **3ah**, **3ak**, **3db**, and **3hb** in THF (10^{-5} M). Bottom: Fluorescence spectra of **3ab**, **3af**, **3ah**, **3ak**, **3db**, and **3hb** in THF (10^{-5} M). See Table S3 for details.

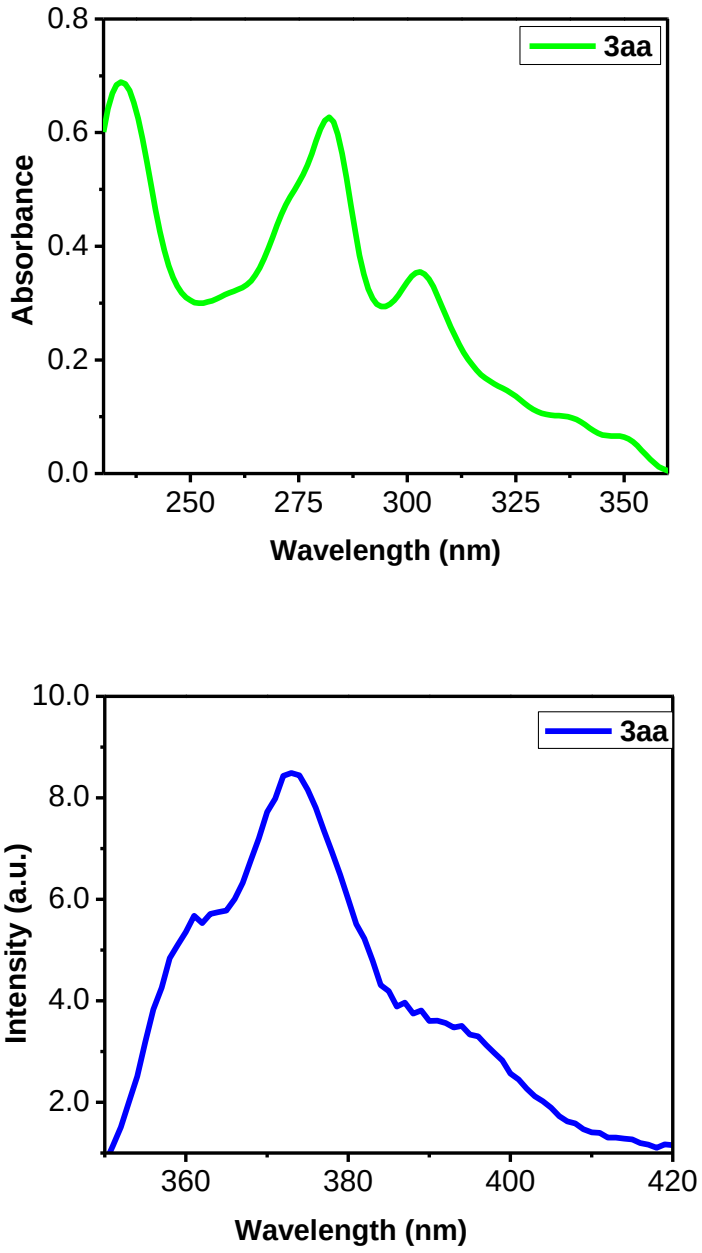
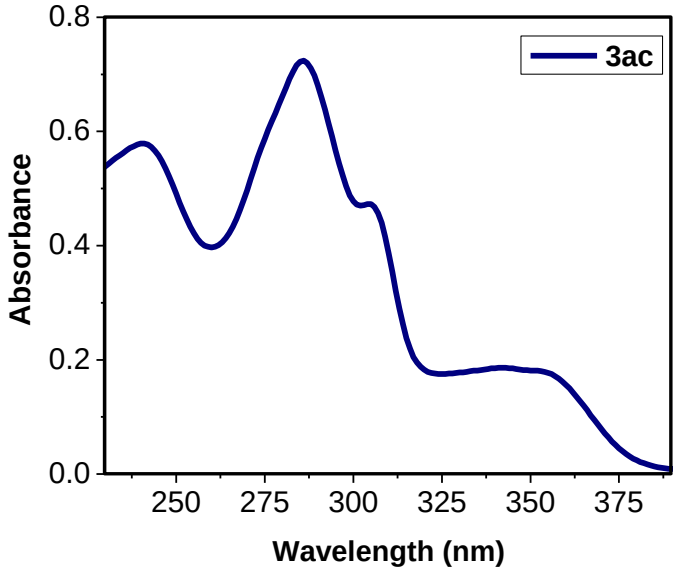


Figure S9. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3aa**.



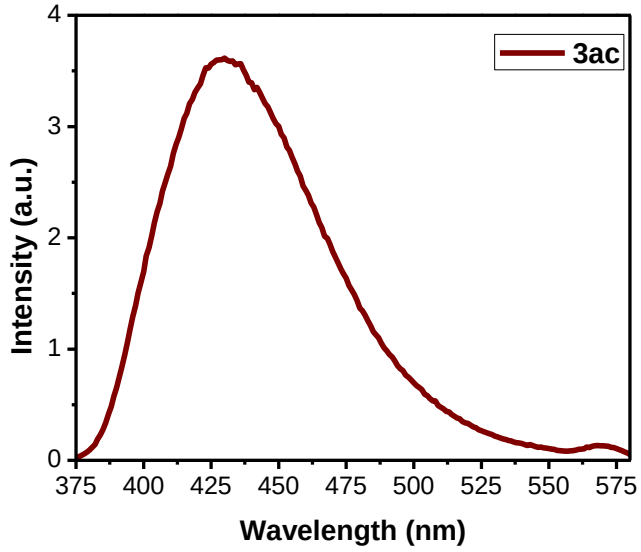


Figure S10. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3ac**.

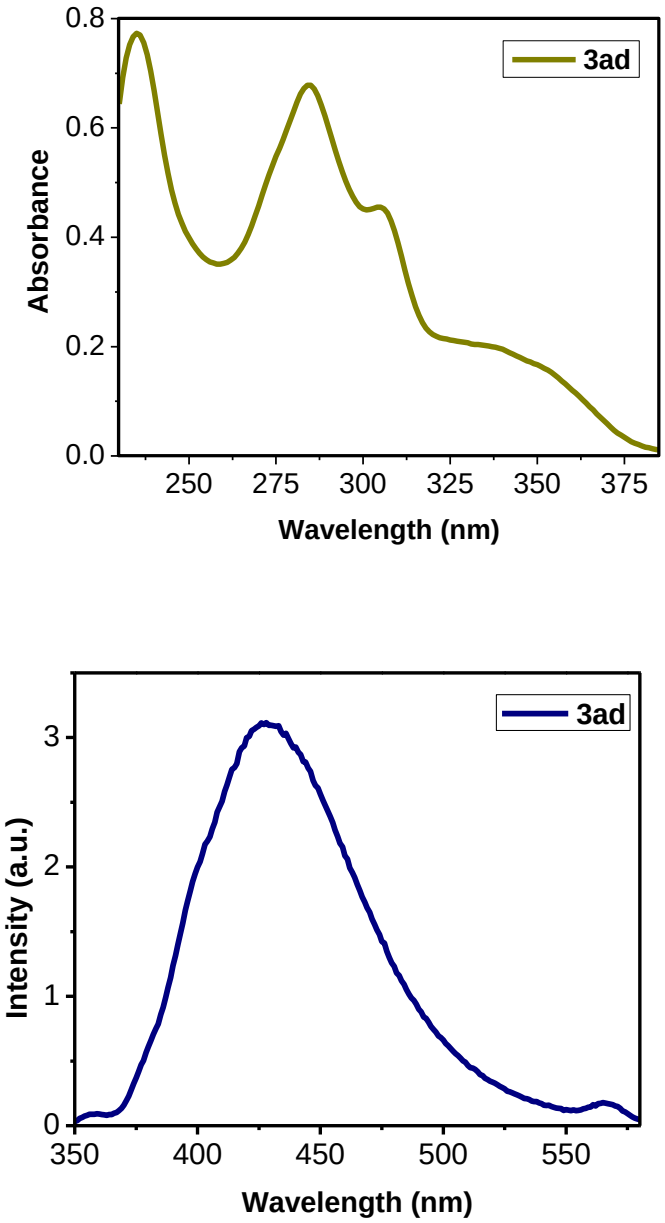


Figure S11. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3ad**.

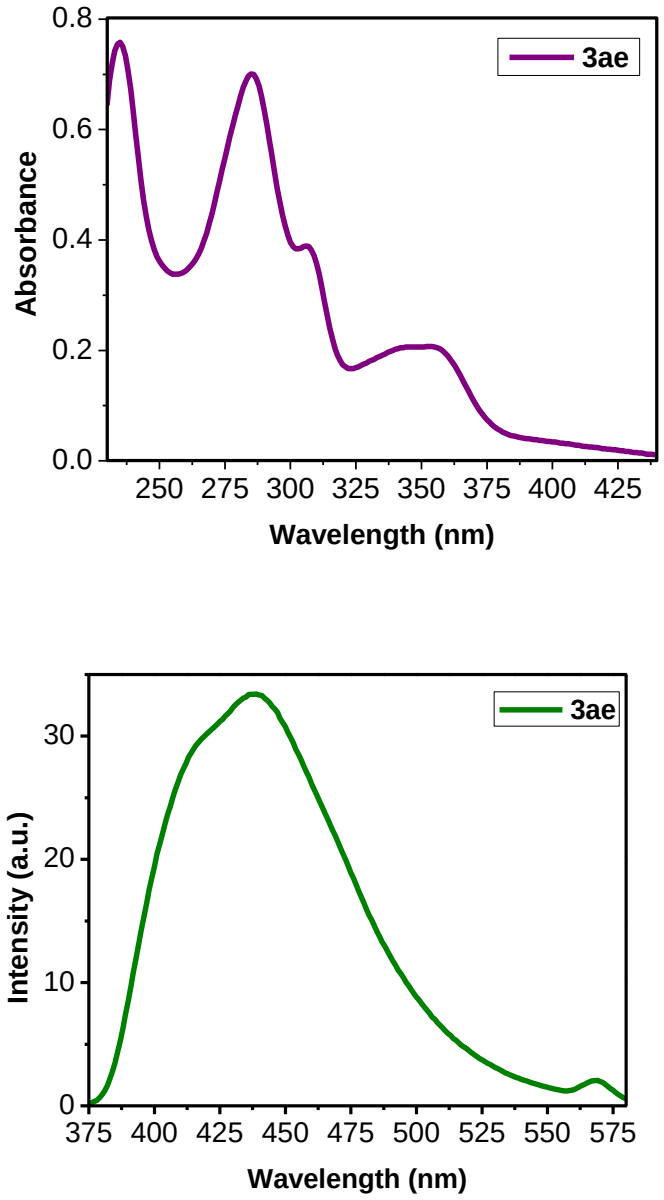


Figure S12. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3ae**.

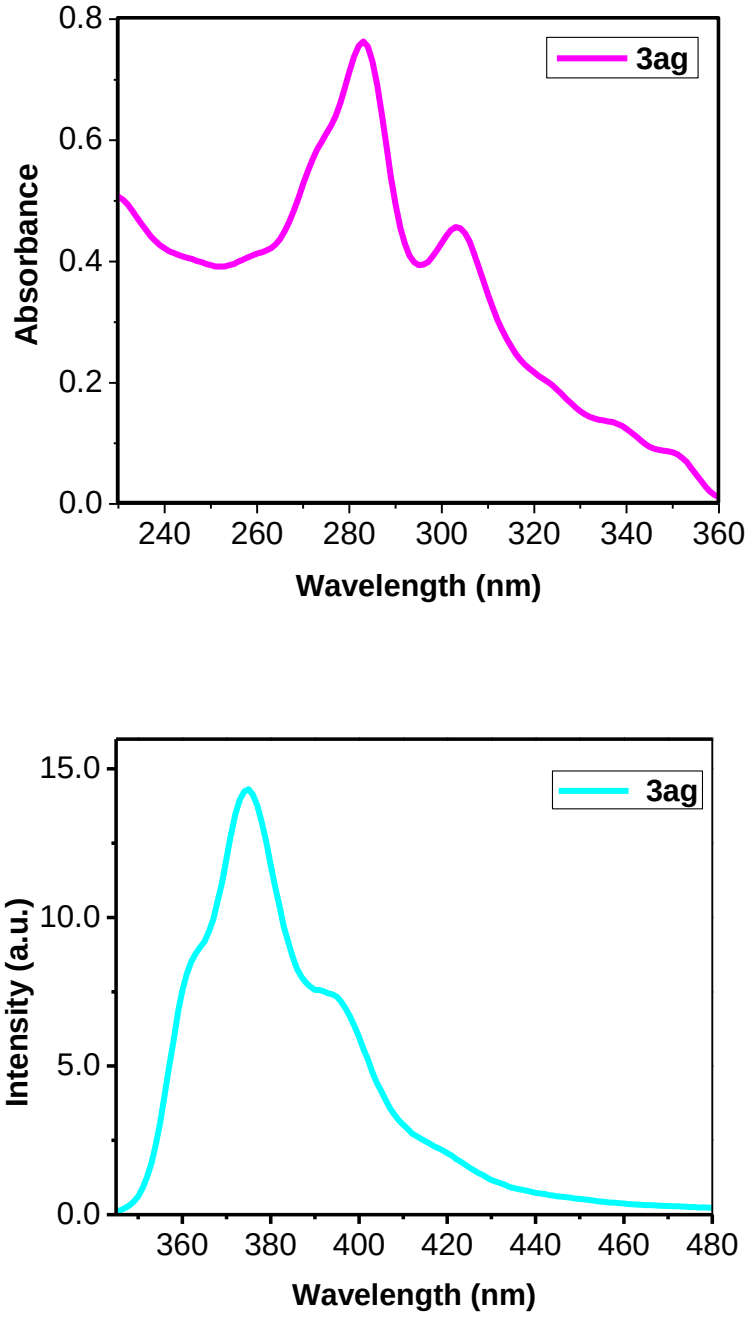


Figure S13. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3ag**.

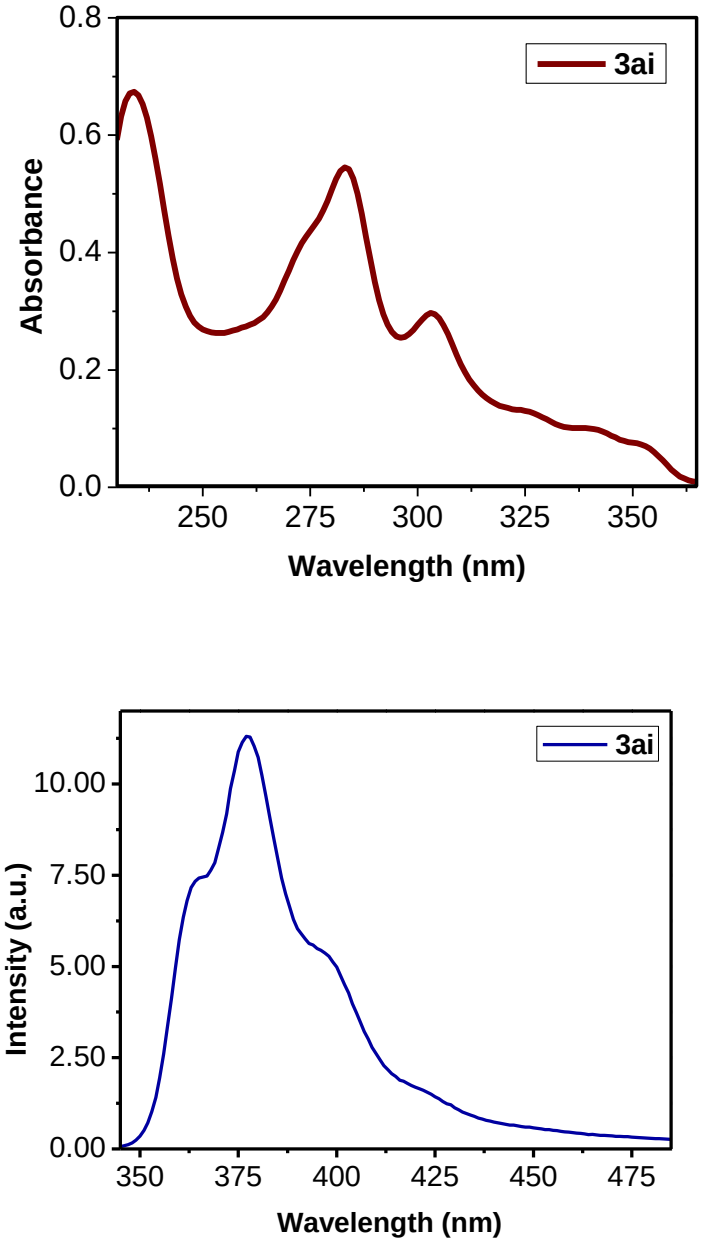


Figure S14. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3ai**

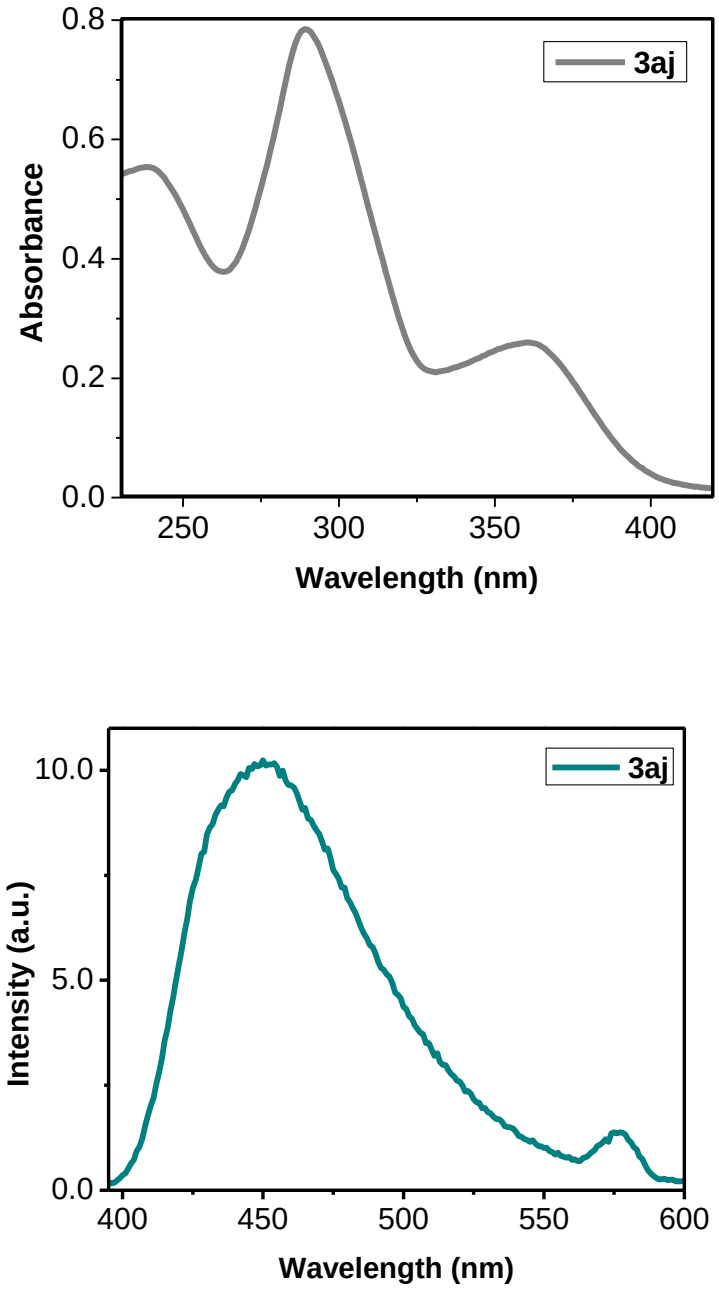


Figure S15. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3aj**

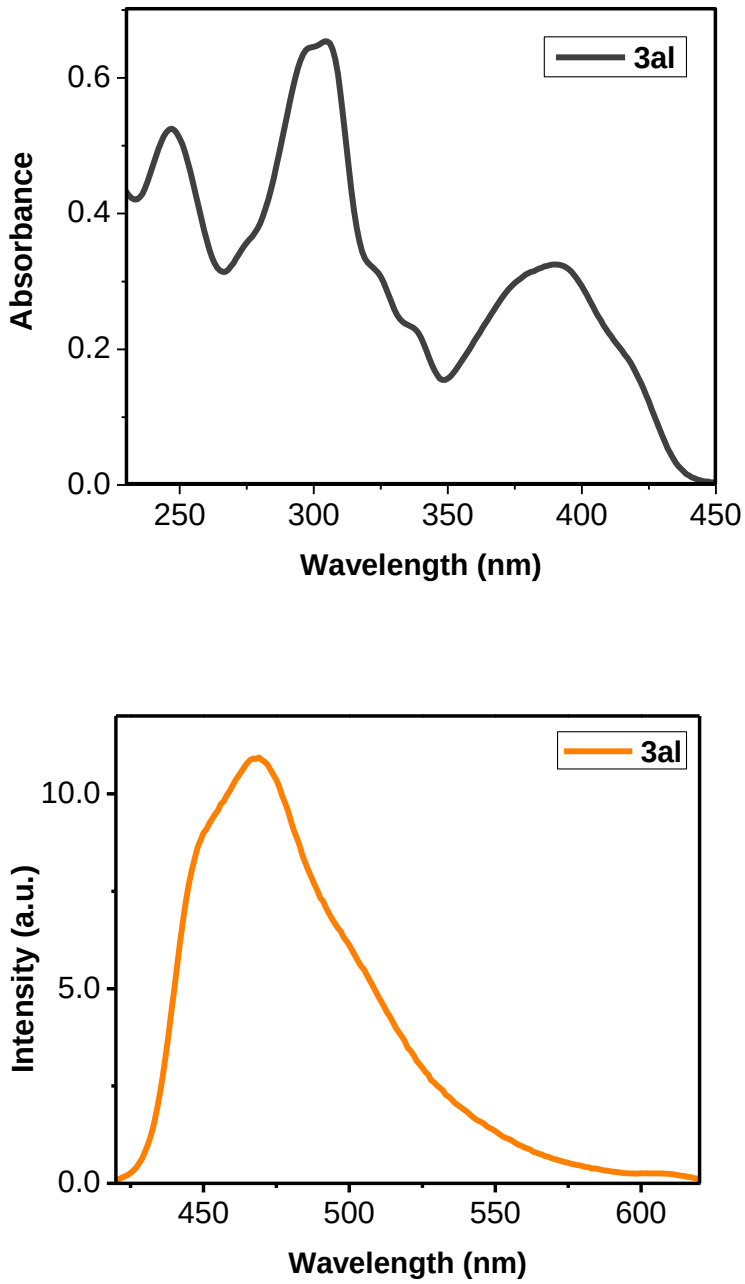


Figure S16. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3al**

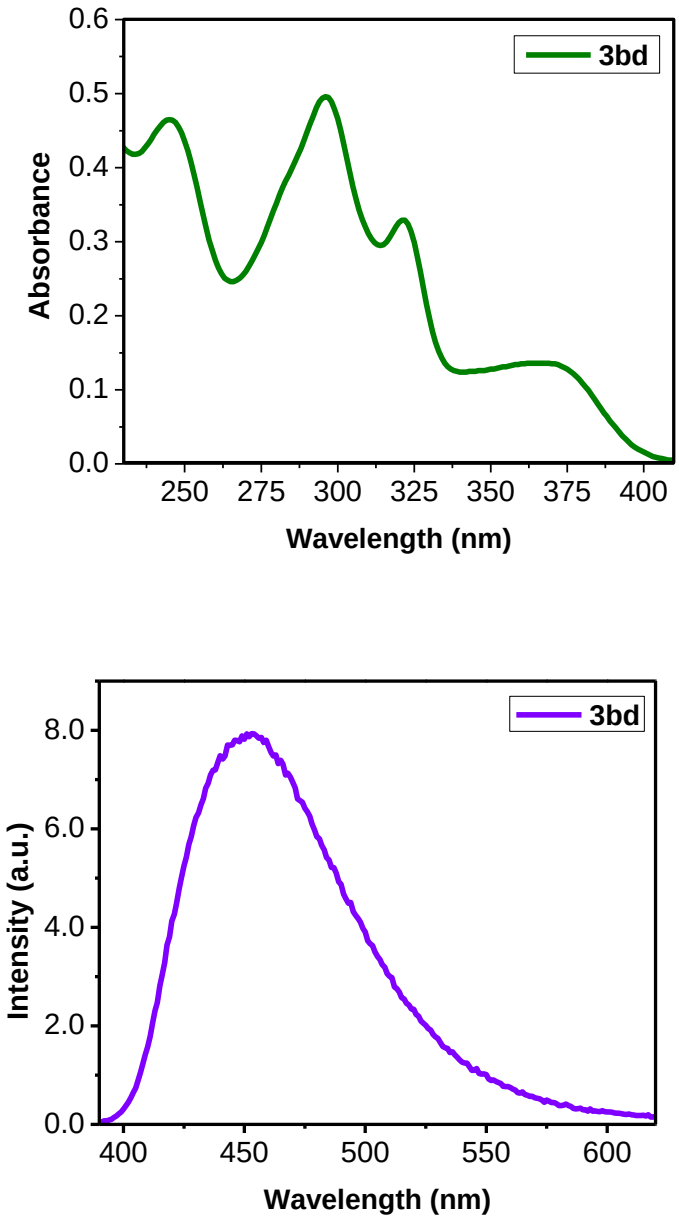


Figure S17. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3bd**

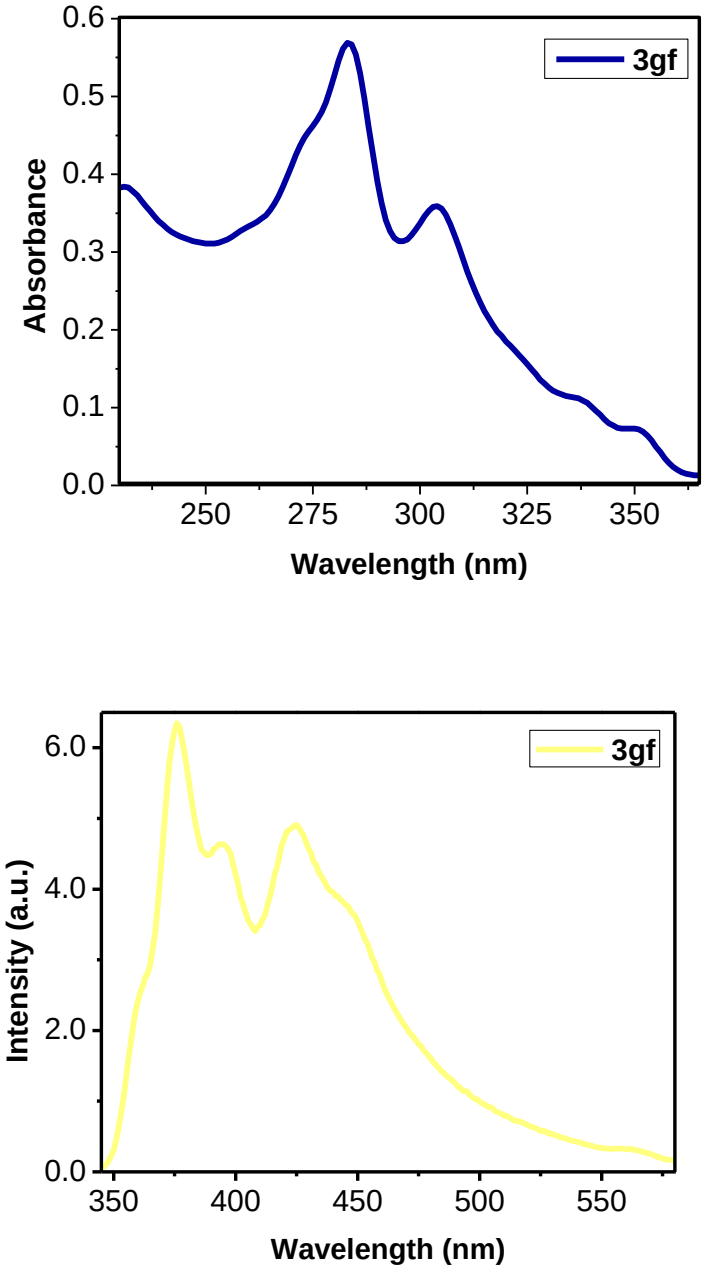
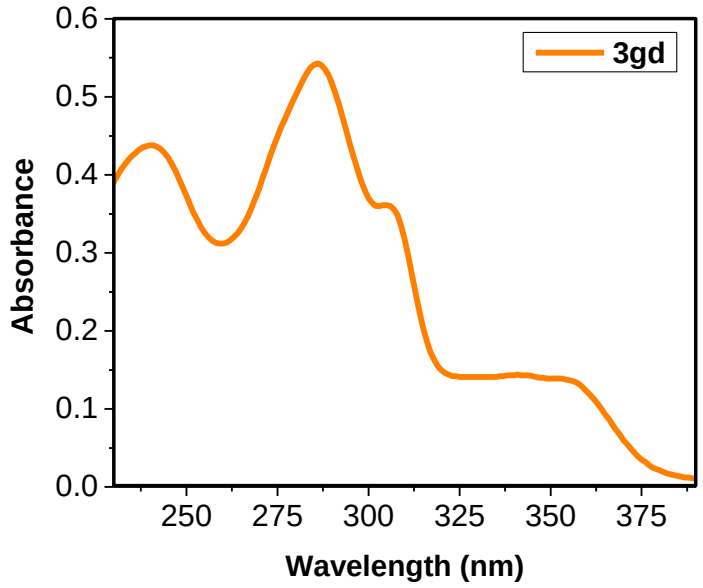


Figure S18. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3gf**



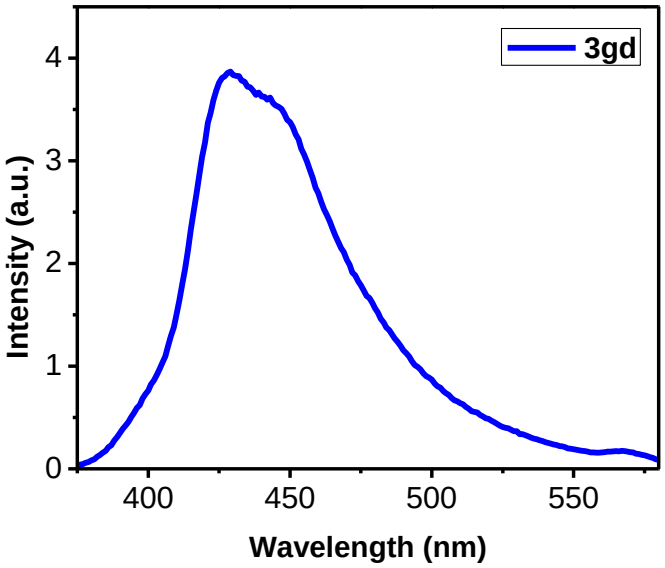


Figure S19. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3gd**

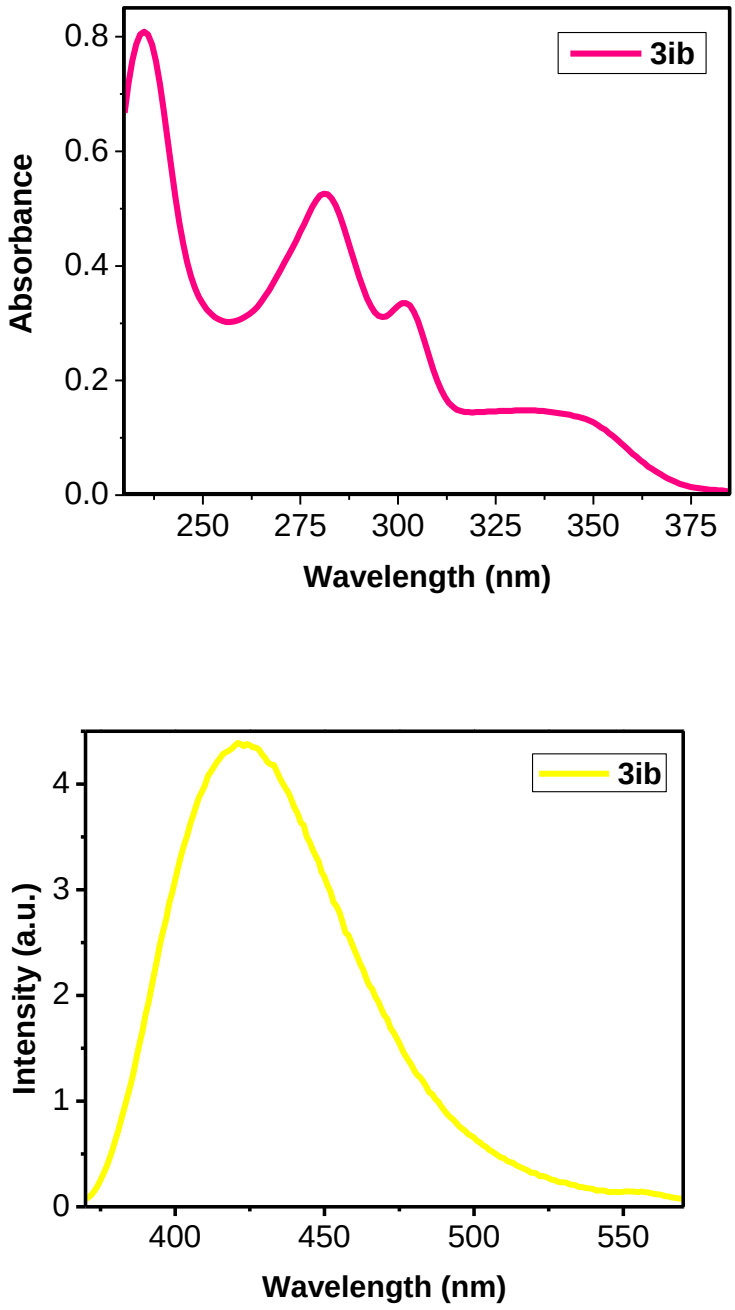


Figure S20. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3ib**

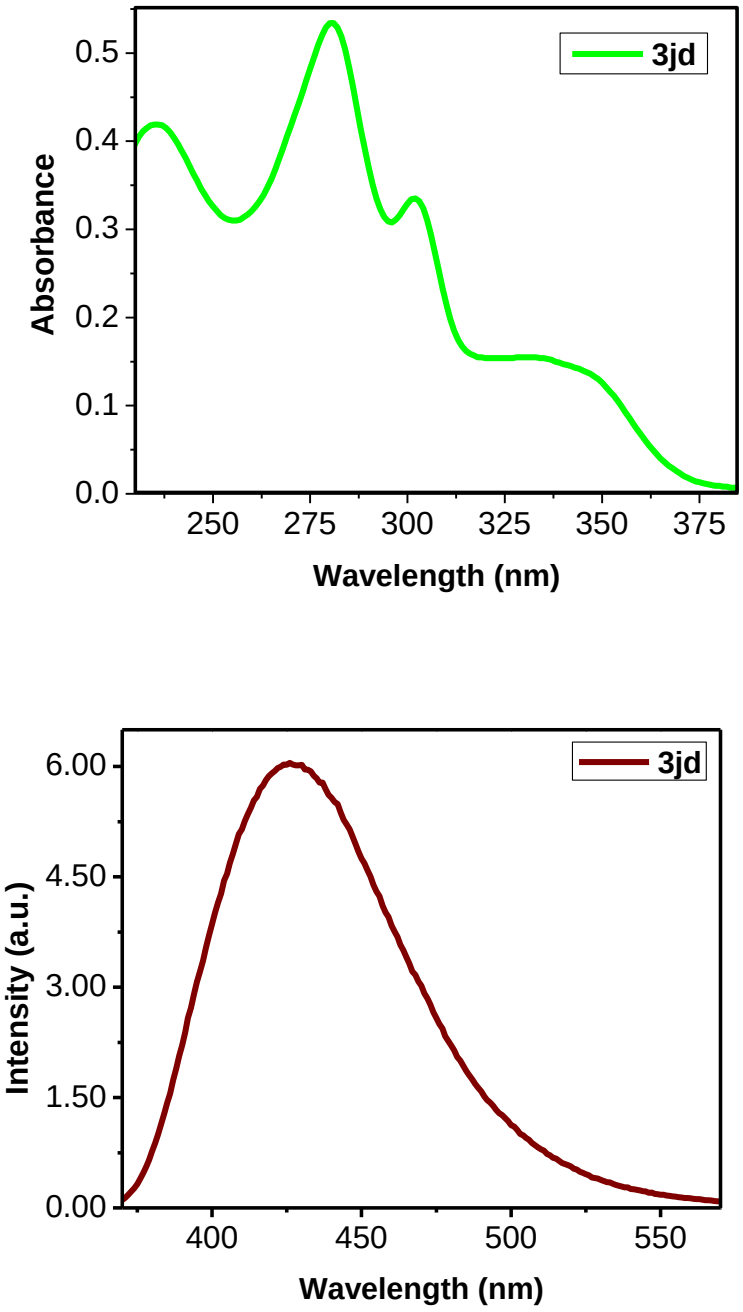


Figure S21. UV-Visible (top) and Fluorescence (bottom) spectra for compound **3jd**

Table S3. Fluorescence spectral details on indole fused α-carbolines **3aa-3jd**

Compound	λ_{abs} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{em} (nm)
3aa	282	6.2	373
3ab	286	8.2	430
3ac	286	7.2	430
3ad	285	6.7	427
3ae	285	7.0	438
3af	283	9.5	375
3ag	283	7.6	375
3ah	283	7.3	378
3ai	283	5.4	377
3aj	289	7.8	450
3ak	284	4.9	453
3al	305	6.5	468
3bd	296	4.9	453
3db	292	5.1	435
3gf	283	5.6	376, 395, 425
3gd	286	5.4	429
3hb	286	4.7	432
3ib	281	5.2	421
3jd	281	5.3	426

(ii) UV-Visible and Fluorescence spectra for triindoles

The UV-Vis and fluorescence spectra of chromophores **5b, 5h, 4i, 5i, 4k** and **5l** are shown in Figure S22 (further details in Table S4). These data are consistent with those reported for compounds **4a**, **5a** and **4l**.[4b,c,5,7]

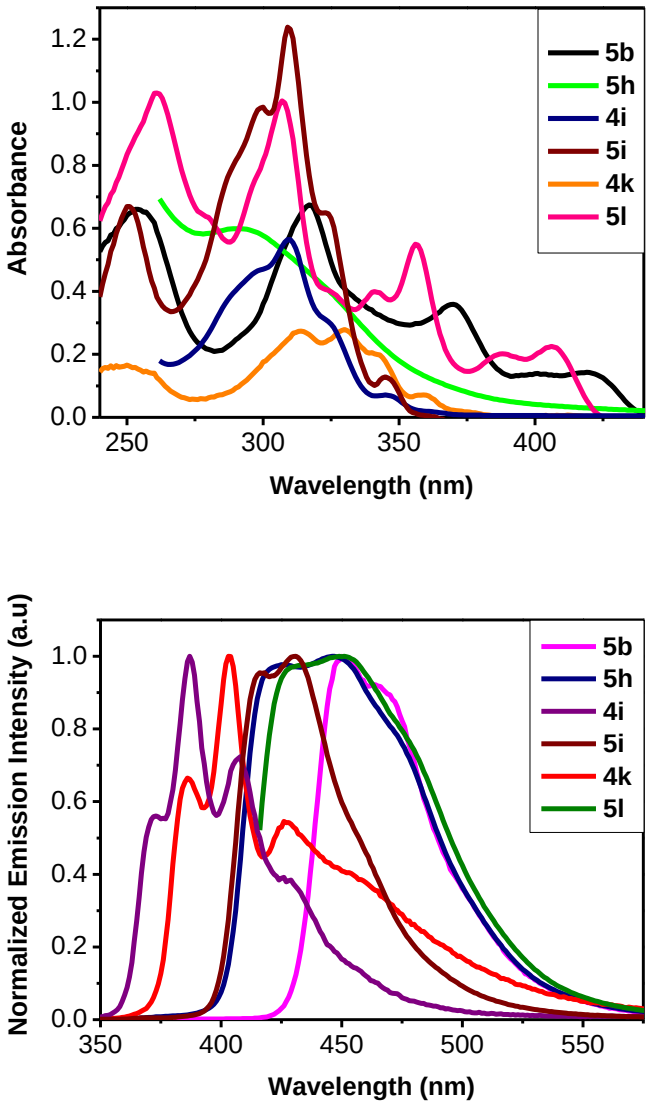


Figure S22. Top: Absorption spectra of compounds **5b**, **5h, 4i, 5i, 4k,** and **5l** in THF (10^{-5} M). Bottom: Fluorescence spectra of compounds **5b**, **5h, 4i, 5i, 4k** and **5l** in THF (10^{-5} M), excited at the λ_{abs} of their absorption spectra. See Table S4 for details.

Table S4. Fluorescence spectral details on triindoles (diindolocarbazoles) **5b**, **5h, 4i, 5i 4k,** and **5l**

Compound	λ_{abs} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{em} (nm)
5b	317	6.7	450, 464
5h	291	5.9	425, 447
4i	330	2.7	386, 403, 426
5i	307	10.0	451
4k	309	5.6	373, 387, 408
5l	309	12.3	416, 431

(5) References

(1) D. D. Perrin, W. L. F. Armarego, D. Perrin, *Purification of Laboratory Chemicals*; Pergamon: Oxford UK 1986.

(2) a) G. M. Sheldrick, *SADABS, Siemens Area Detector Absorption Correction*; University of Göttingen: Germany, 1996. b) G. M. Sheldrick, *SHELX-97: A program for crystal structure solution and refinement*; University of Göttingen: Germany, 1997. c) G. M. Sheldrick, *SHELXTL NT Crystal Structure Analysis Package*, Version 5; Bruker AXS Analytical X-ray System: WI (USA), 1999, version 5.10.

(3) a) M. Sechi, M. Derudas, R. Dallocchio, A. Dessi, A. Bacchi, L. Sannia, F. Carta, M. Palomba, O. Ragab, C. Chan, R. Shoemaker, S. Sei, R. Dayam, N. Neamati, *J. Med. Chem*., 2004, **47**, 5298; (b) M. D. Ganton, M. A. Kerr, *Org. Lett*., 2005, **7**, 4777; (c) A. Putey, L. Joucla, L. Picot, T. Besson, B. Joseph, *Tetrahedron.*, 2007, **63**, 867; (d) C. Praveen, A. Ayyanar, P. T. Perumal, *Bioorg. Med. Chem. Lett*., 2011, **21**, 4170.

(4) a) J. Bergman, N. Eklund, *Tetrahedron.*, 1980, **36**, 1445; b) L. Greci, G. Tommasi, R. Petrucci, G. Marrosu, A. Trazza, P. Sgarabotto, L. Righi, A. Alberti, *J. Chem. Soc*., *Perkin Trans., 2* 2000, 2337; c) E. M. García-Frutos, E. Gutierrez-Puebla, M. A. Monge, R. Remírez, P. Andrés, A. Andrés, R. Ramírez, B.Gómez-Lor, *Org. Electron*., 2009, **10**, 643.

(5) a) E. M. García-Frutos, B. Gomez-Lor, A. Monge, E. Gutiérrez-Puebla, I. Alkorta, J. Elguero, *Chem. Eur. J*., 2008, **14**, 8555; b) M. S. Yaun, T. B. Li, W. J. Wang, Z. T. Du, J. R. Wang, Q. Fang, *Spectrochim. Acta, Part A* 2012, **96**, 1020.

(6) a) A. R. Mount, A. D. Thomson, *J. Chem. Soc., Faraday Trans*., 1998, **94**, 553; b) C. Ruiz, E. M. García-Frutos, D. A. da Silva Filho, J. T. López Navarrete, M. C. R. Delgado, B. Gómez-Lor, *J. Phys. Chem. C* 2014, **118**, 5470.

(6) Copies of ^{1}H/ ^{13}C NMR spectra

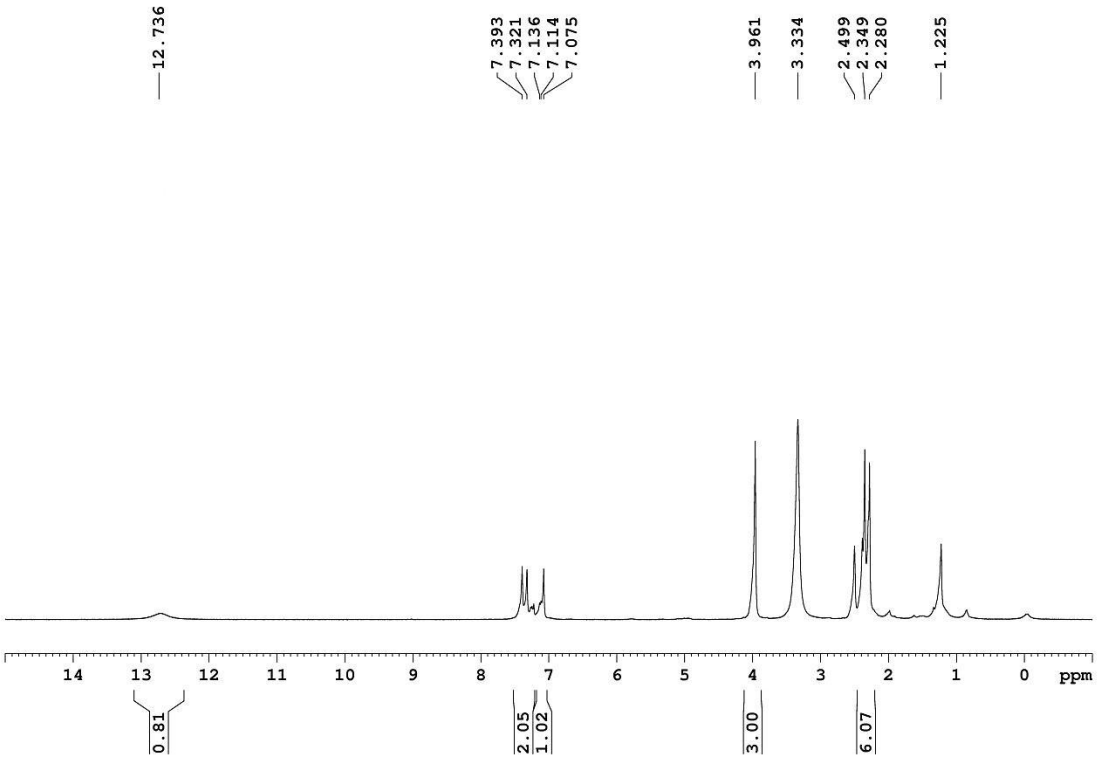


Figure S22. ^{1}H-NMR spectrum of compound **1e**

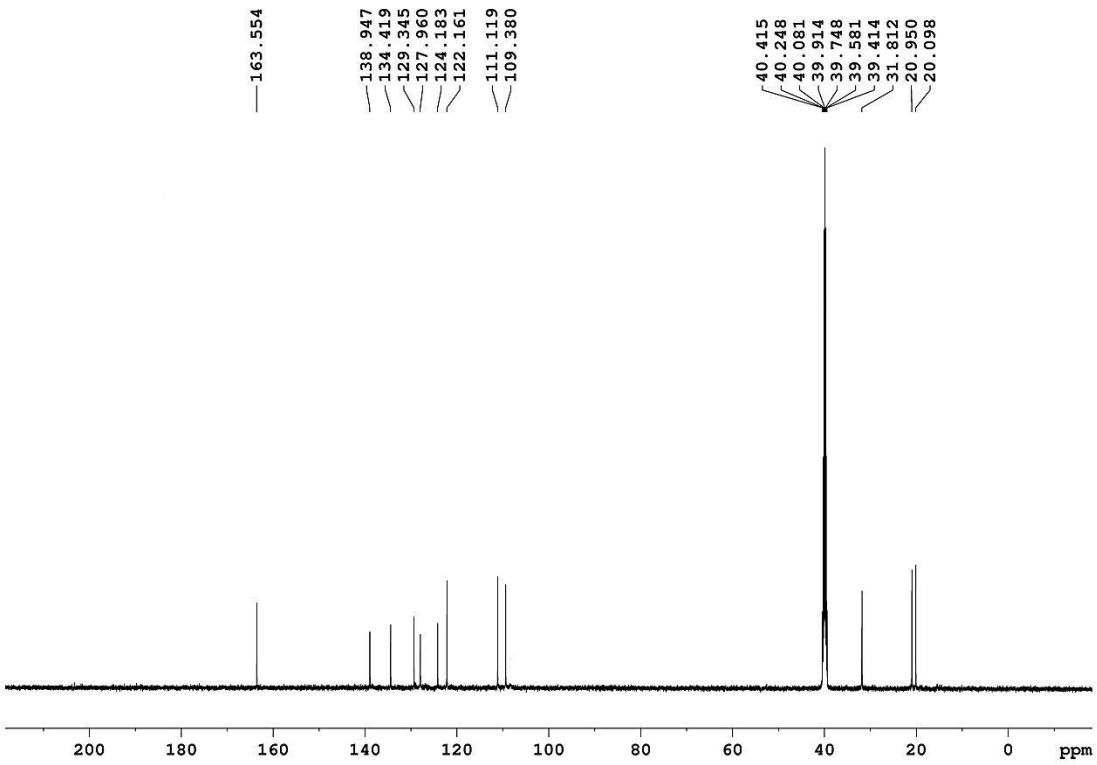


Figure S23. ^{13}C-NMR spectrum of compound **1e**

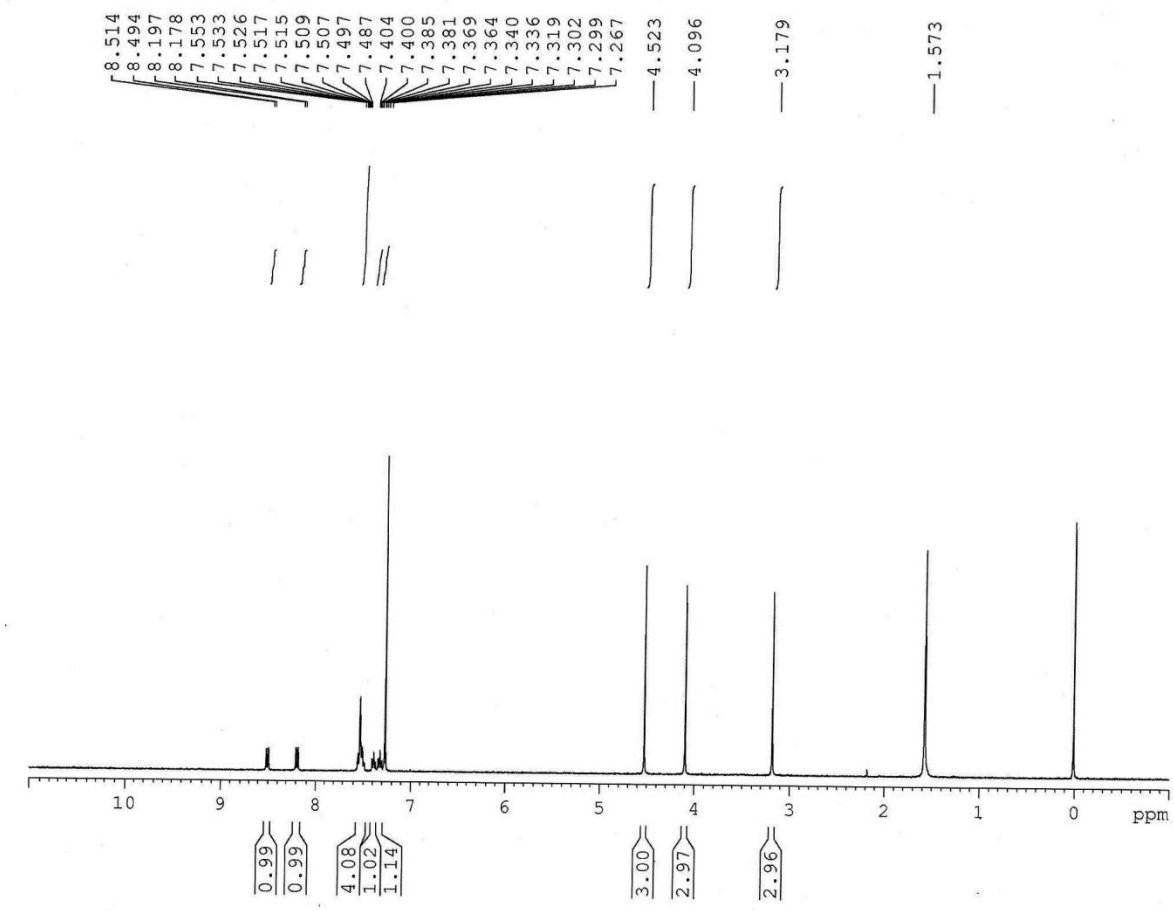


Figure S24. ^{1}H-NMR spectrum of compound **3aa**

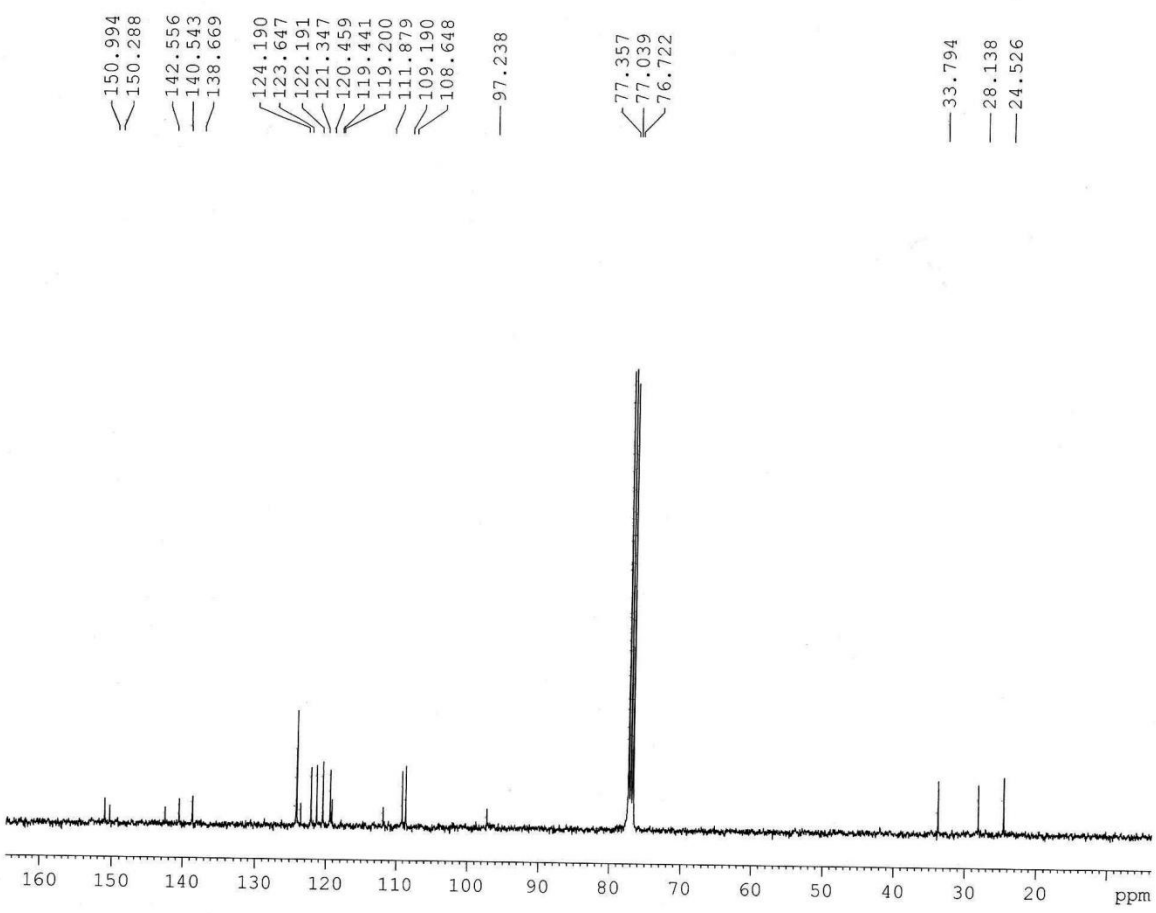


Figure S25. ^{13}C-NMR spectrum of compound **3aa**

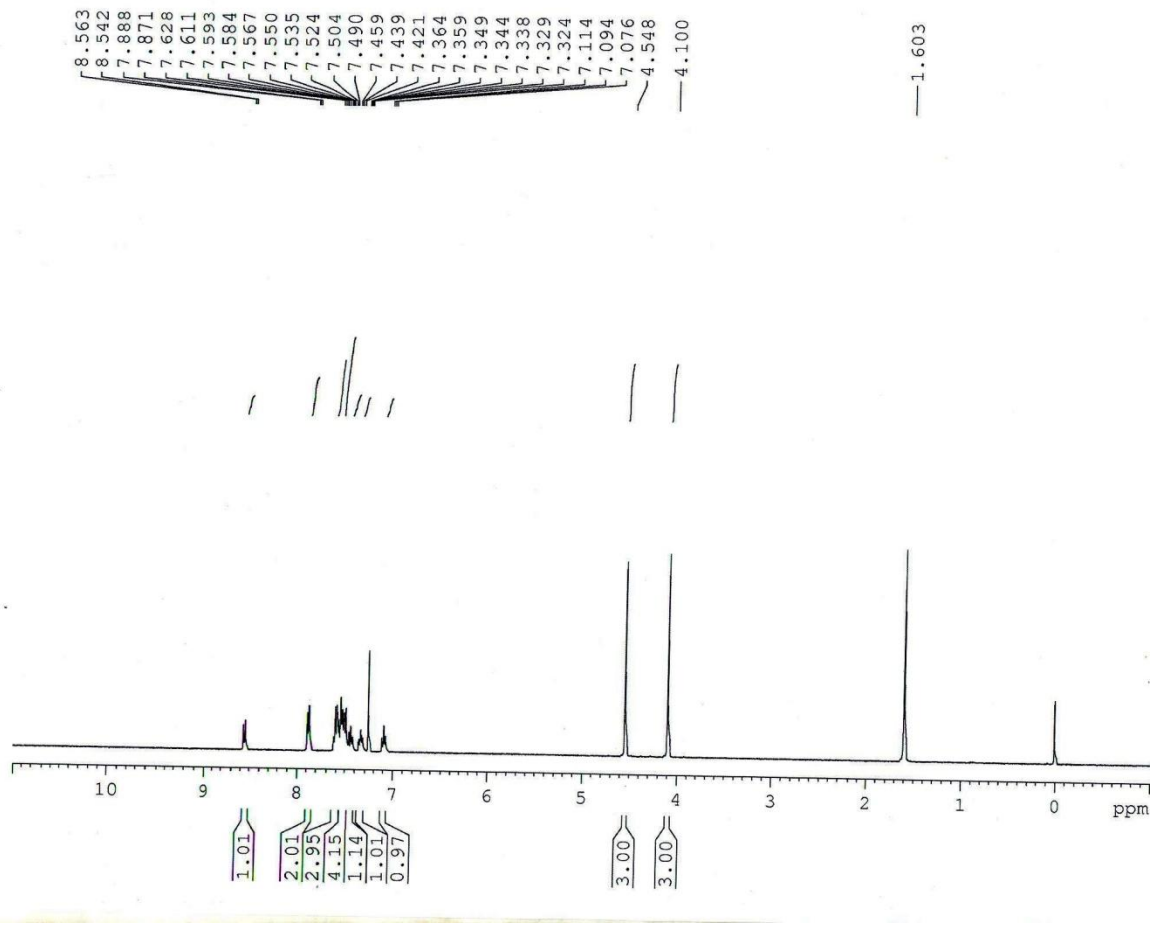


Figure S26. ^{1}H-NMR spectrum of compound **3ab**

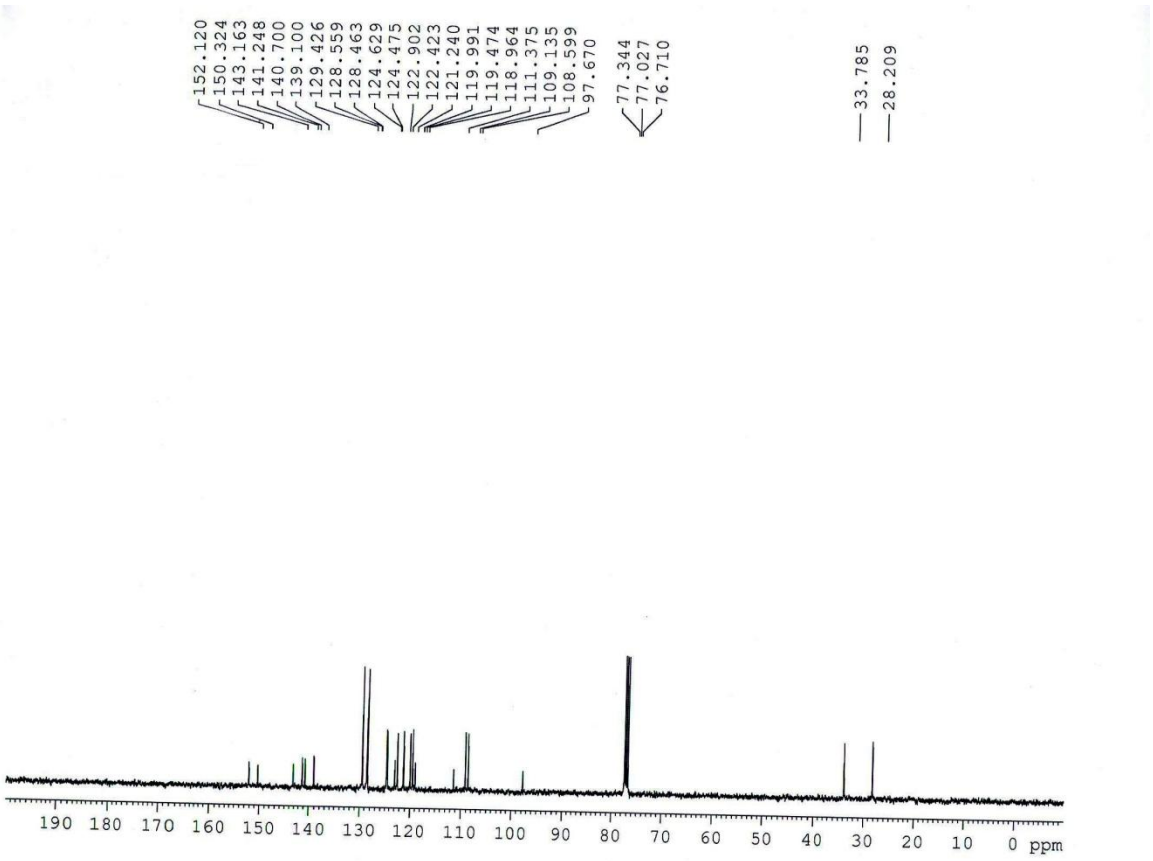


Figure S27. ^{13}C-NMR spectrum of compound **3ab**

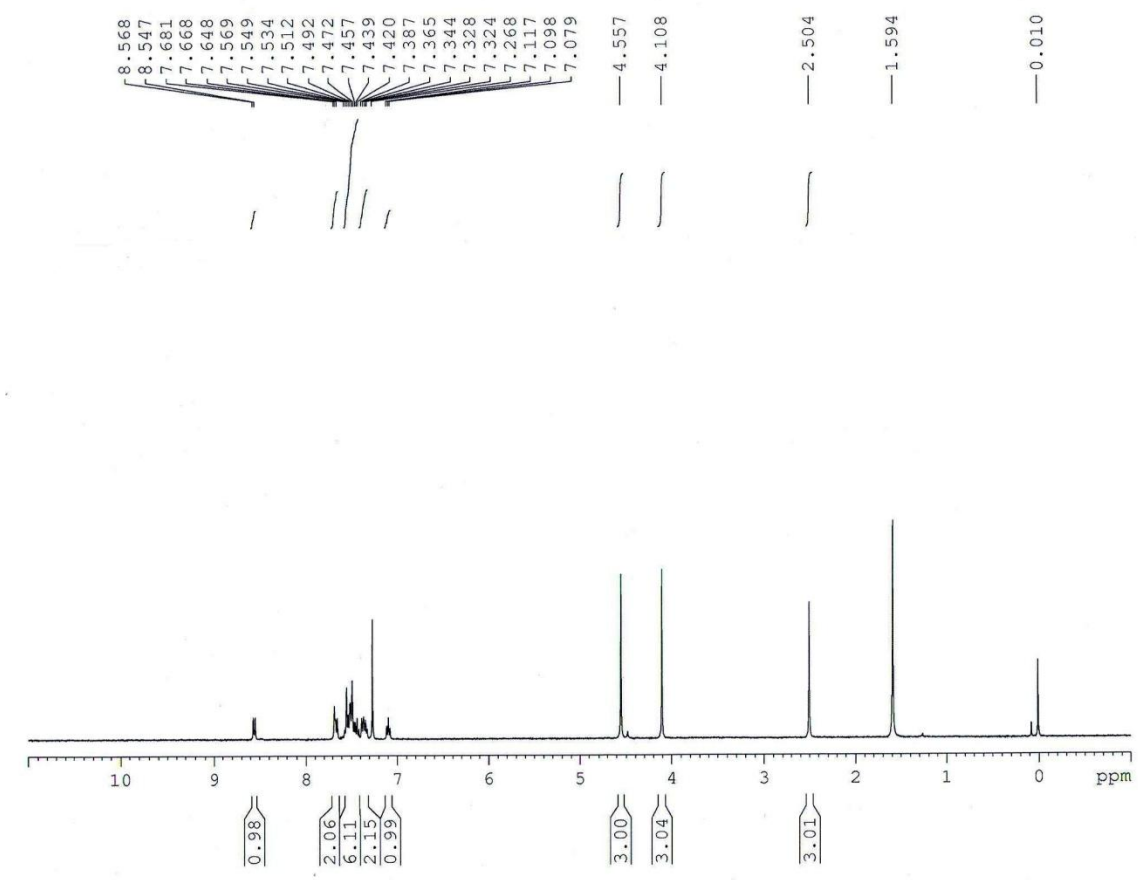


Figure S28. ^{1}H-NMR spectrum of compound **3ac**

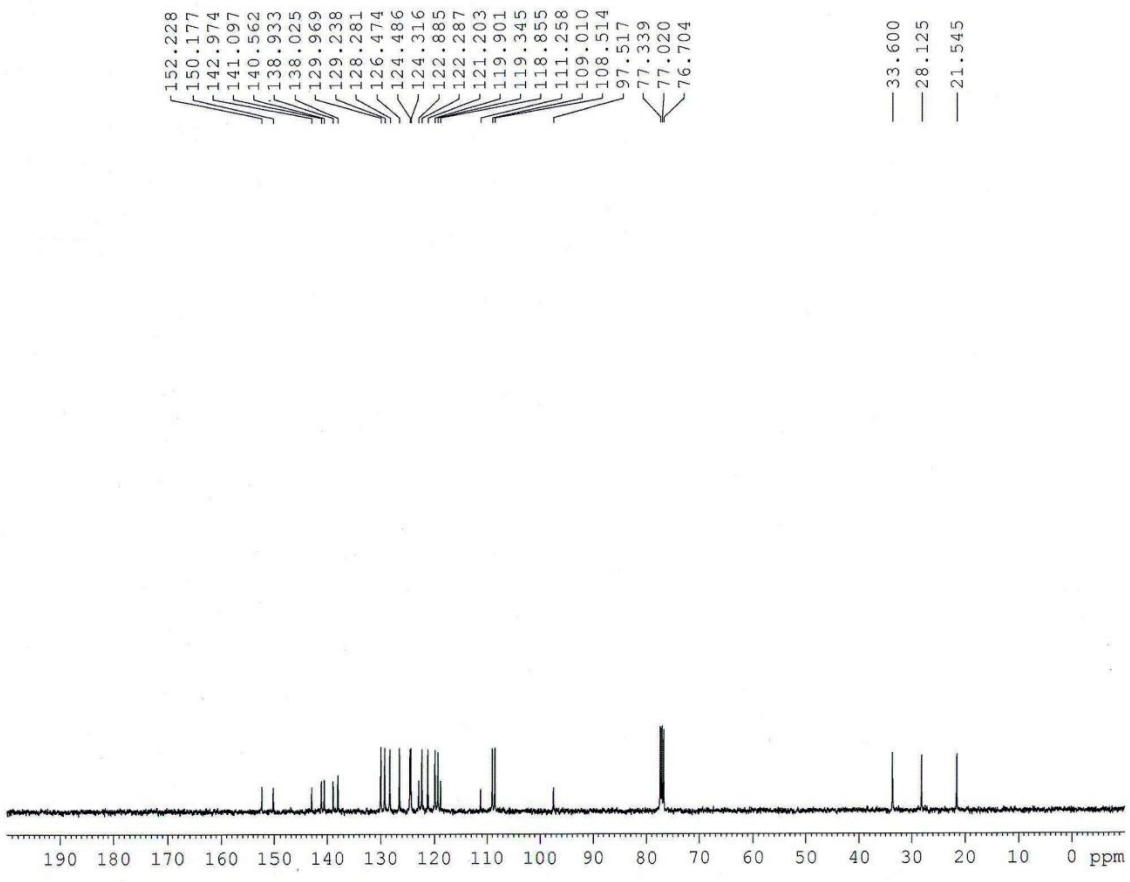


Figure S29. ^{13}C-NMR spectrum of compound **3ac**

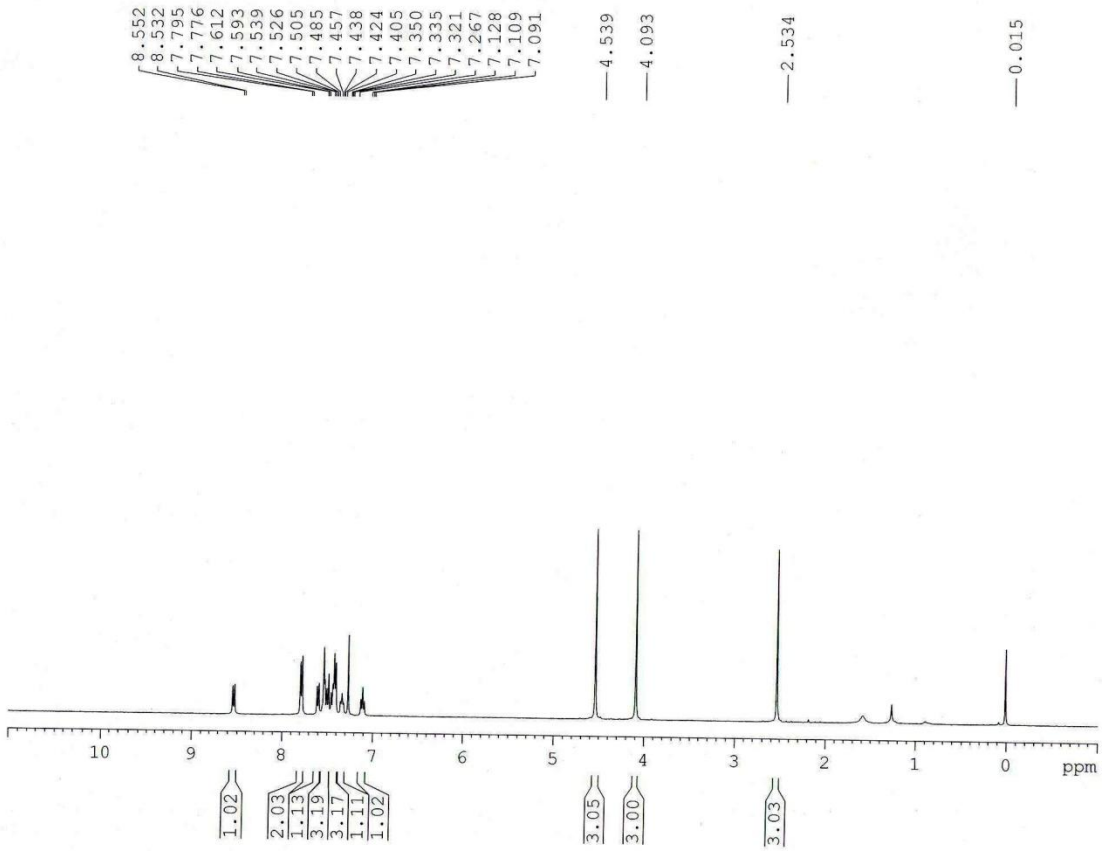


Figure S30. ^{1}H-NMR spectrum of compound **3ad**

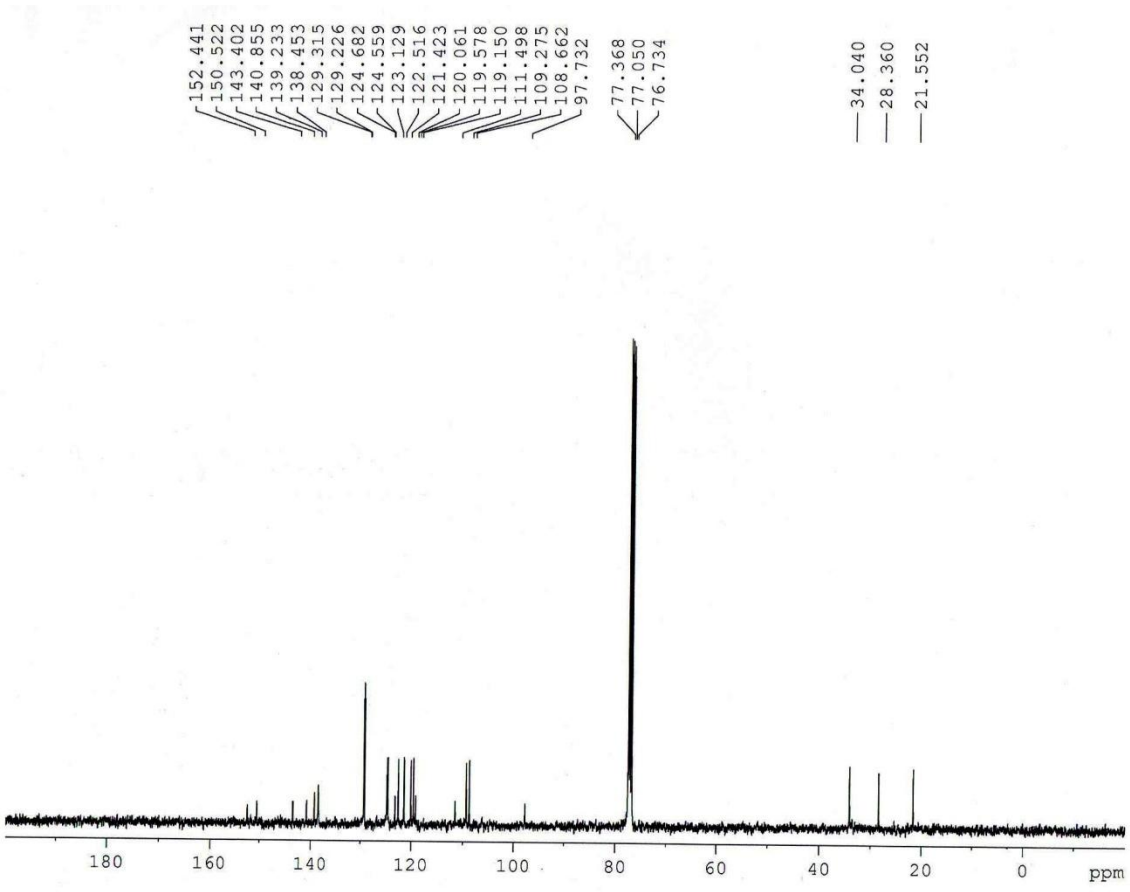


Figure S31. ^{13}C-NMR spectrum of compound **3ad**

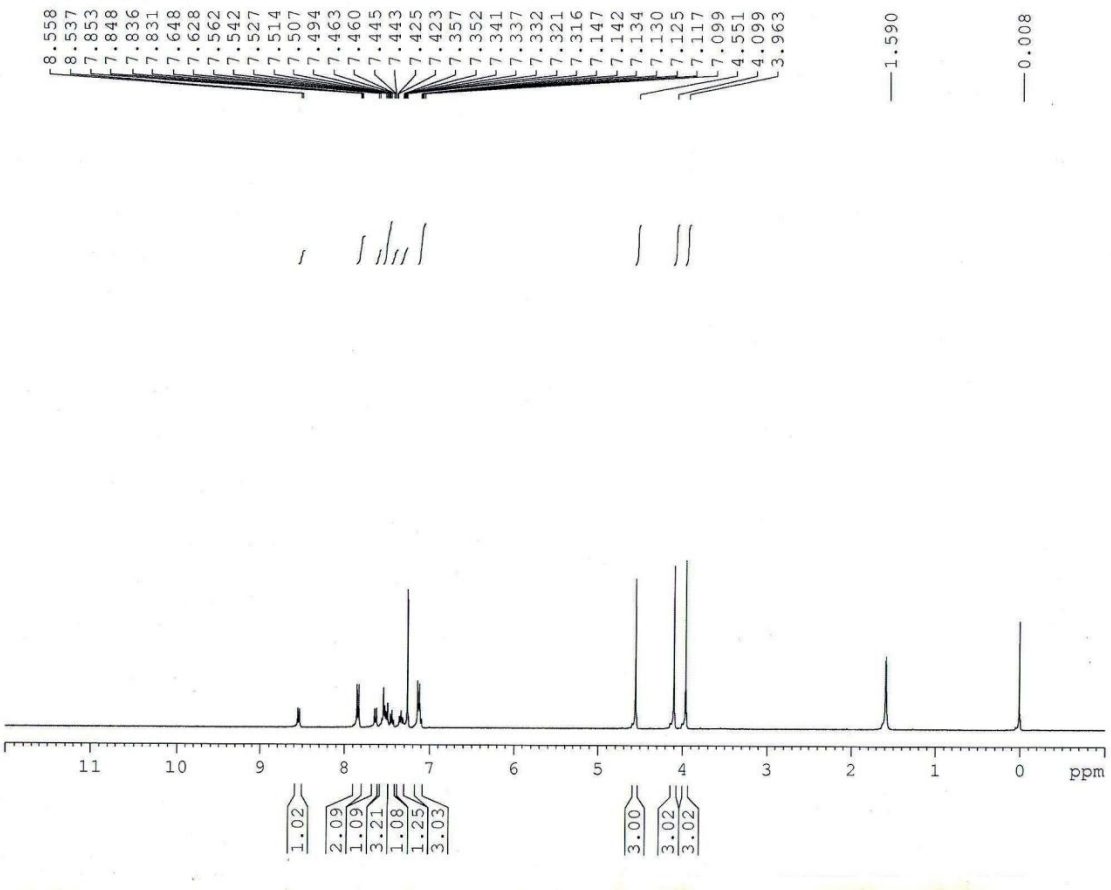


Figure S32. ^{1}H-NMR spectrum of compound **3ae**

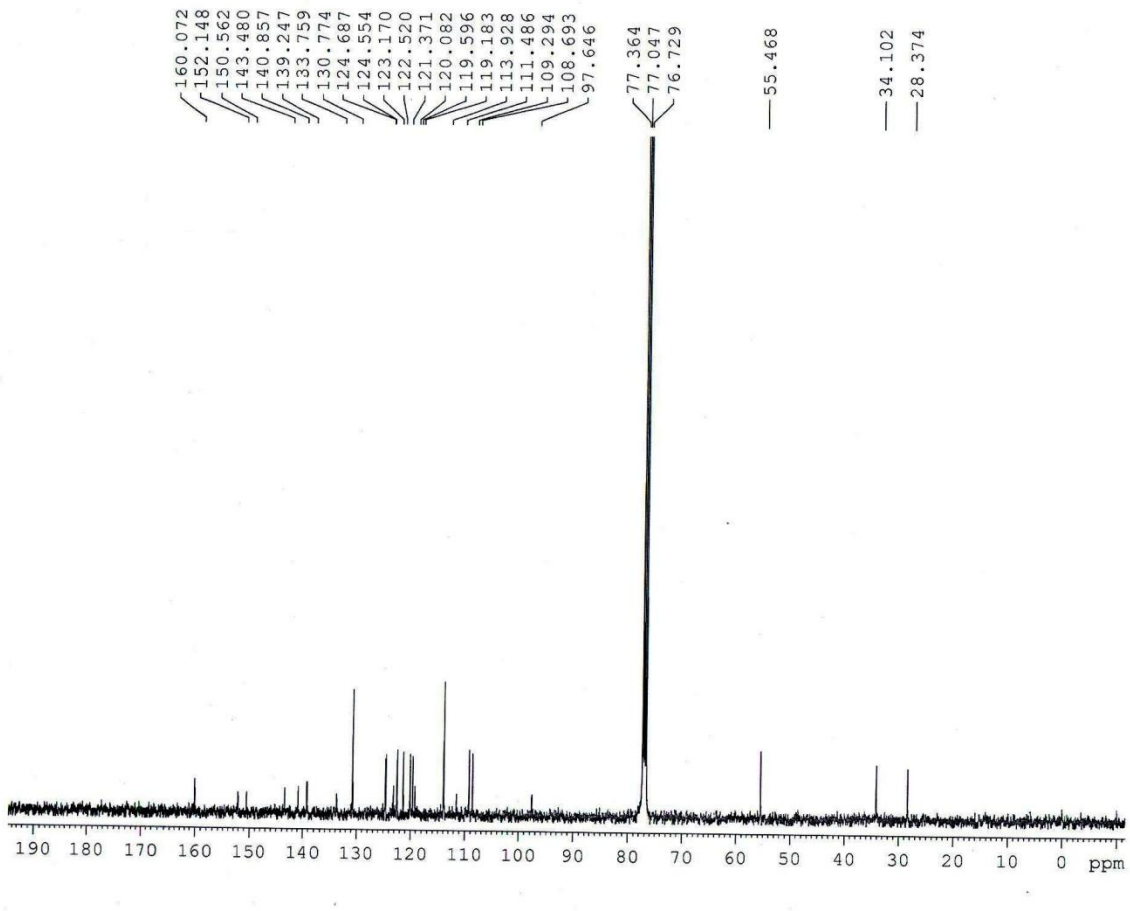


Figure S33. ^{13}C-NMR spectrum of compound **3ae**

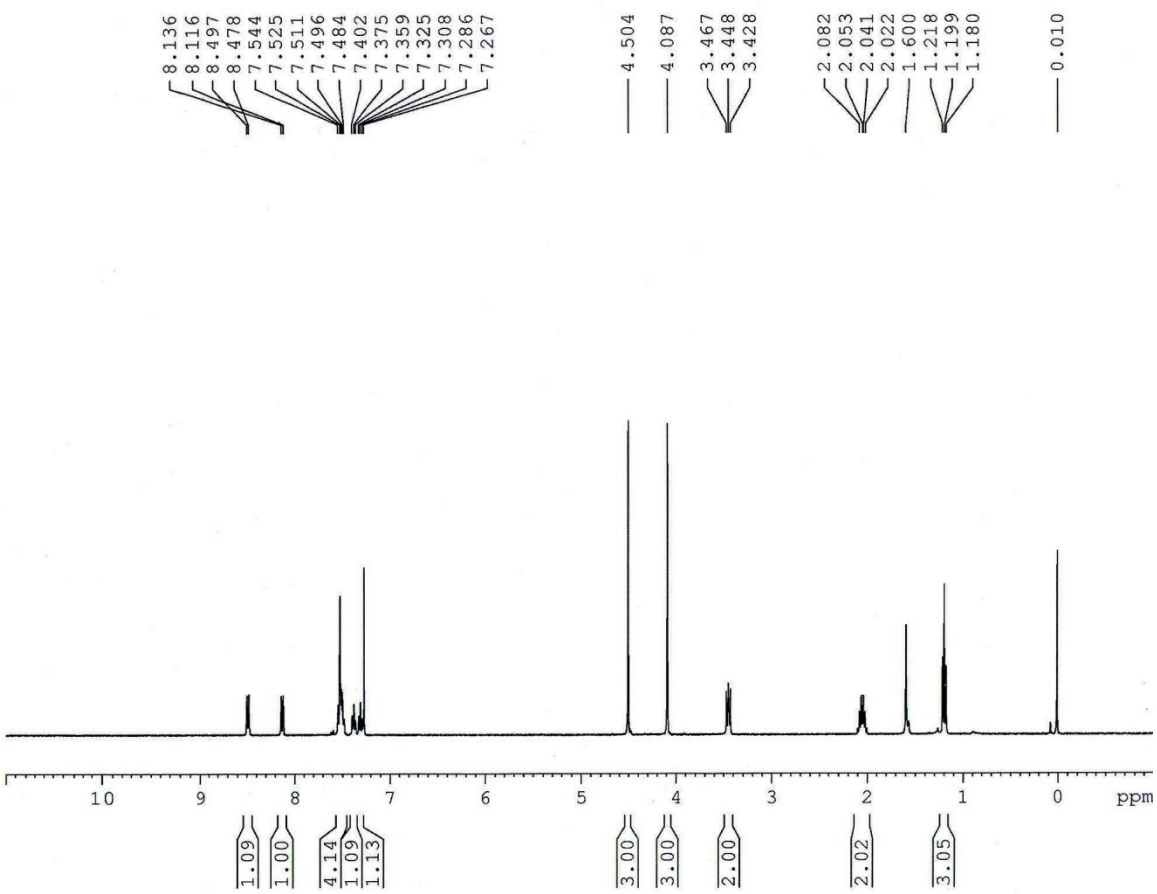


Figure S34. ^{1}H-NMR spectrum of compound **3af**

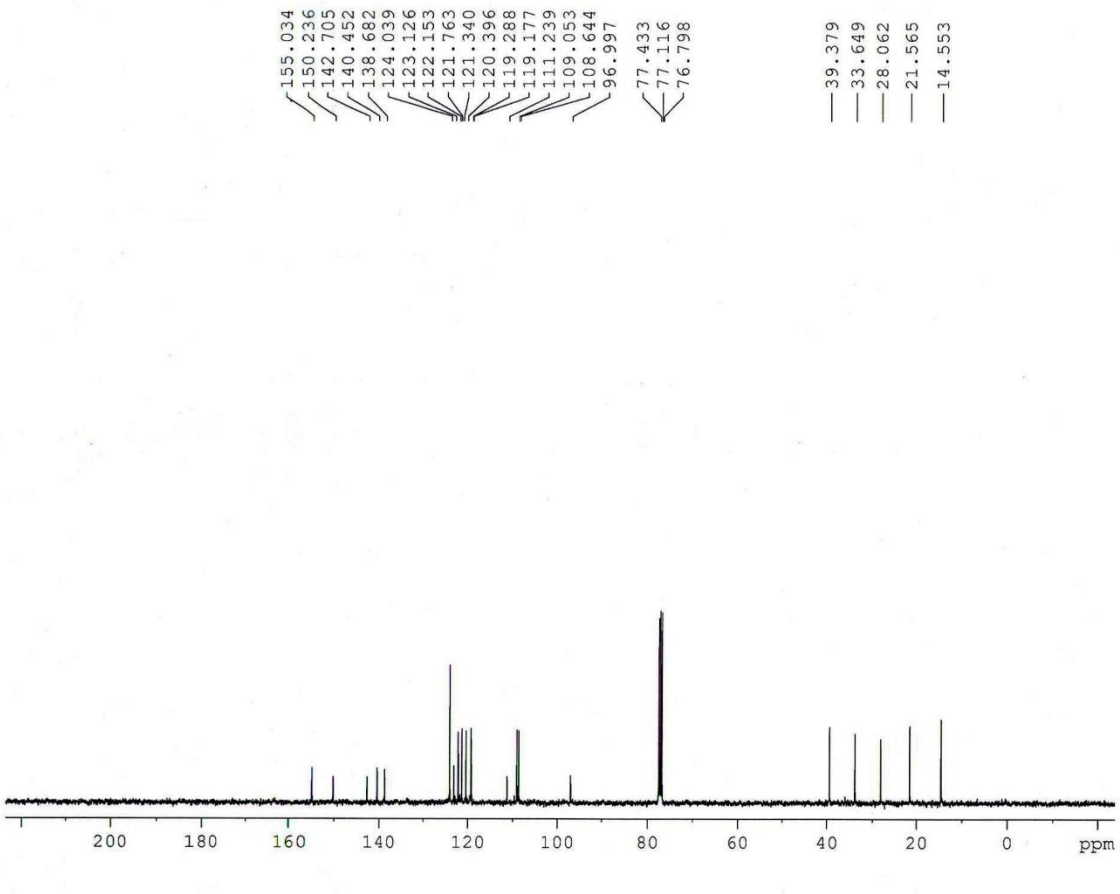


Figure S35. ^{13}C-NMR spectrum of compound **3af**

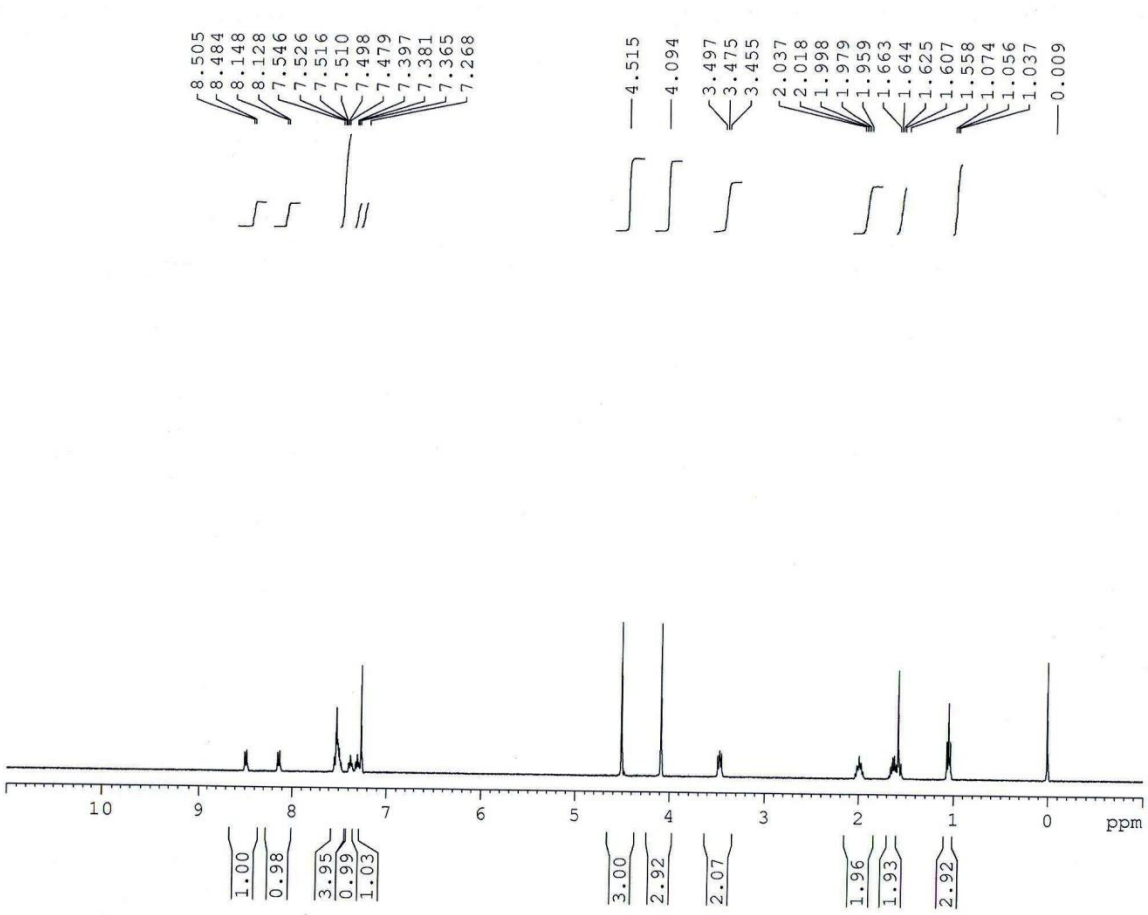


Figure S36. ^{1}H-NMR spectrum of compound **3ag**

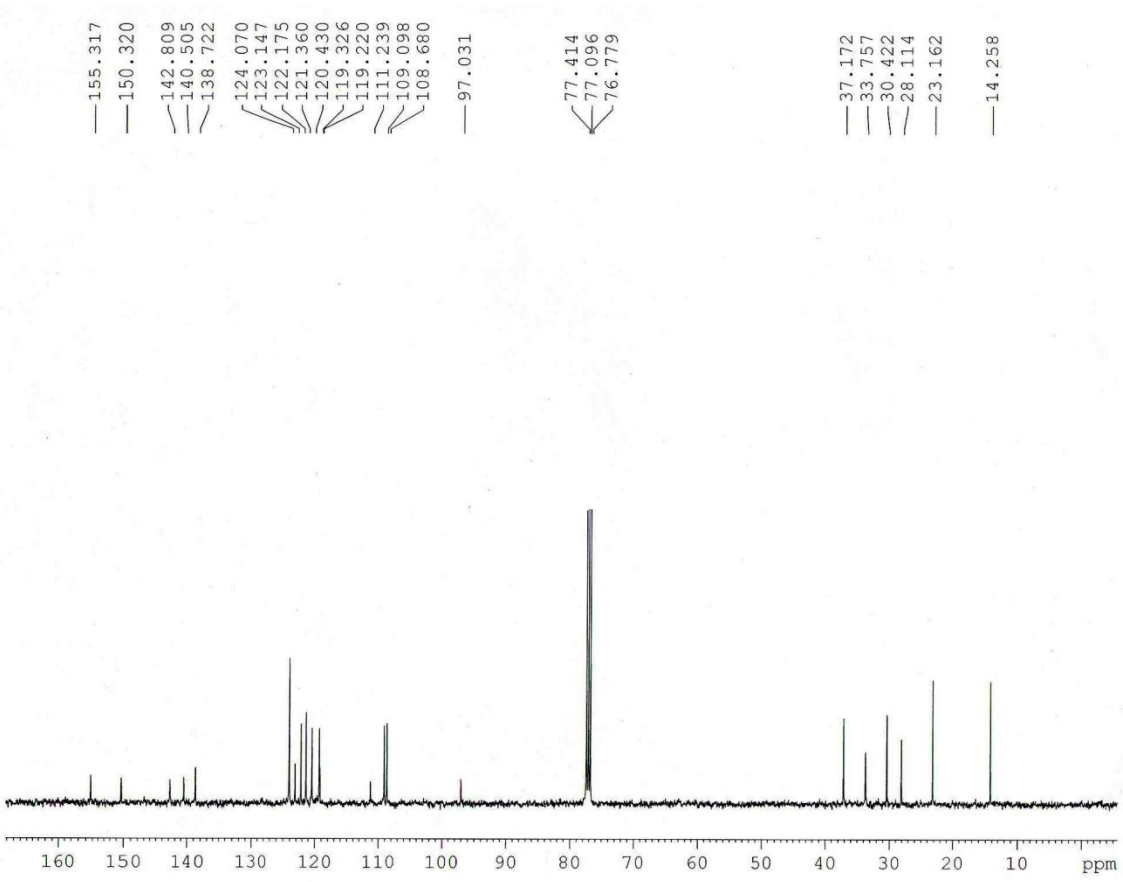


Figure S37. ^{13}C-NMR spectrum of compound **3ag**

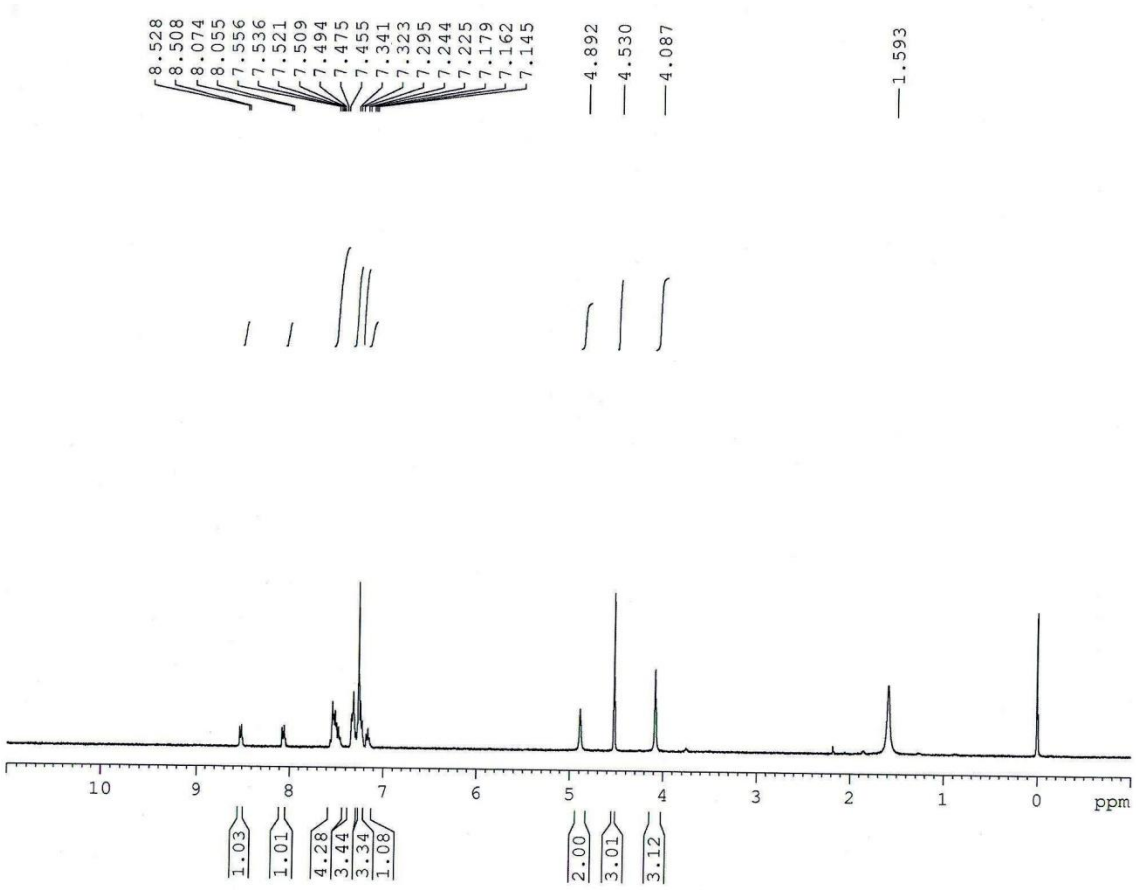


Figure S38. ^{1}H-NMR spectrum of compound **3ah**

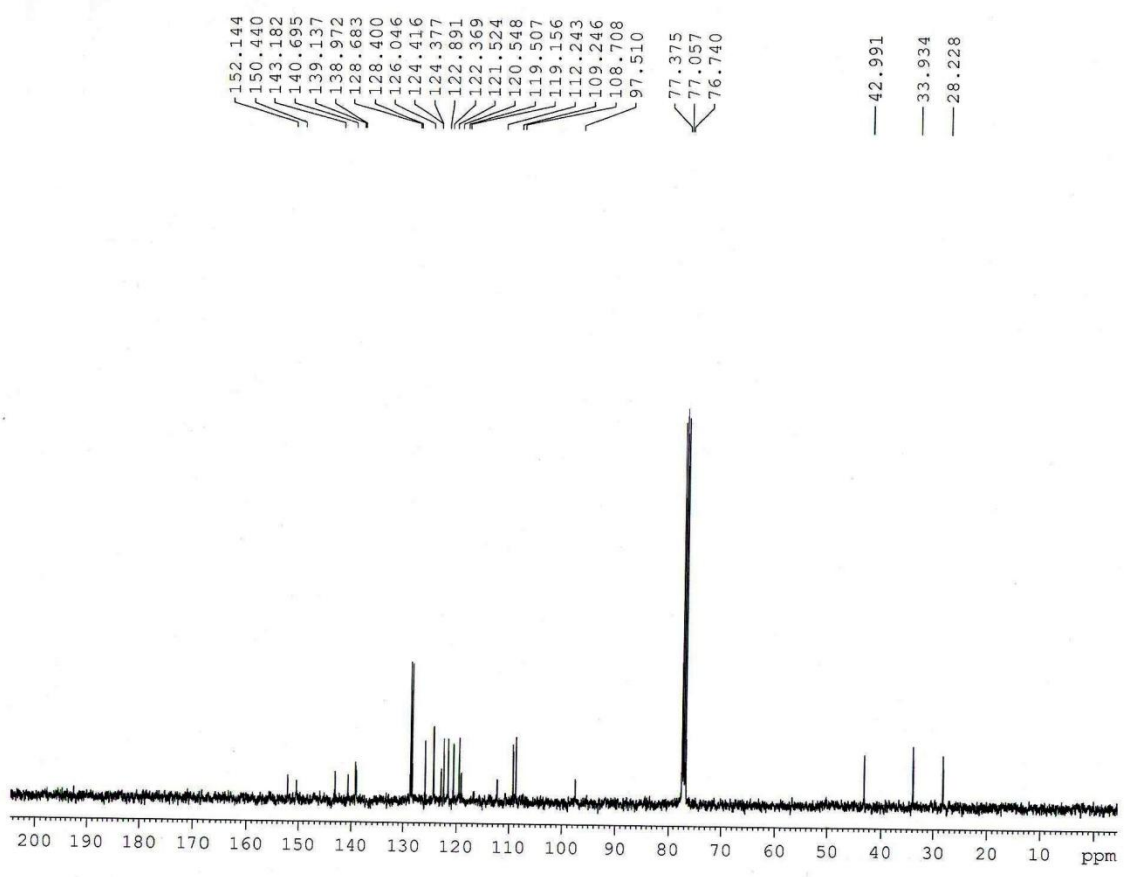


Figure S39. ^{13}C-NMR spectrum of compound **3ah**

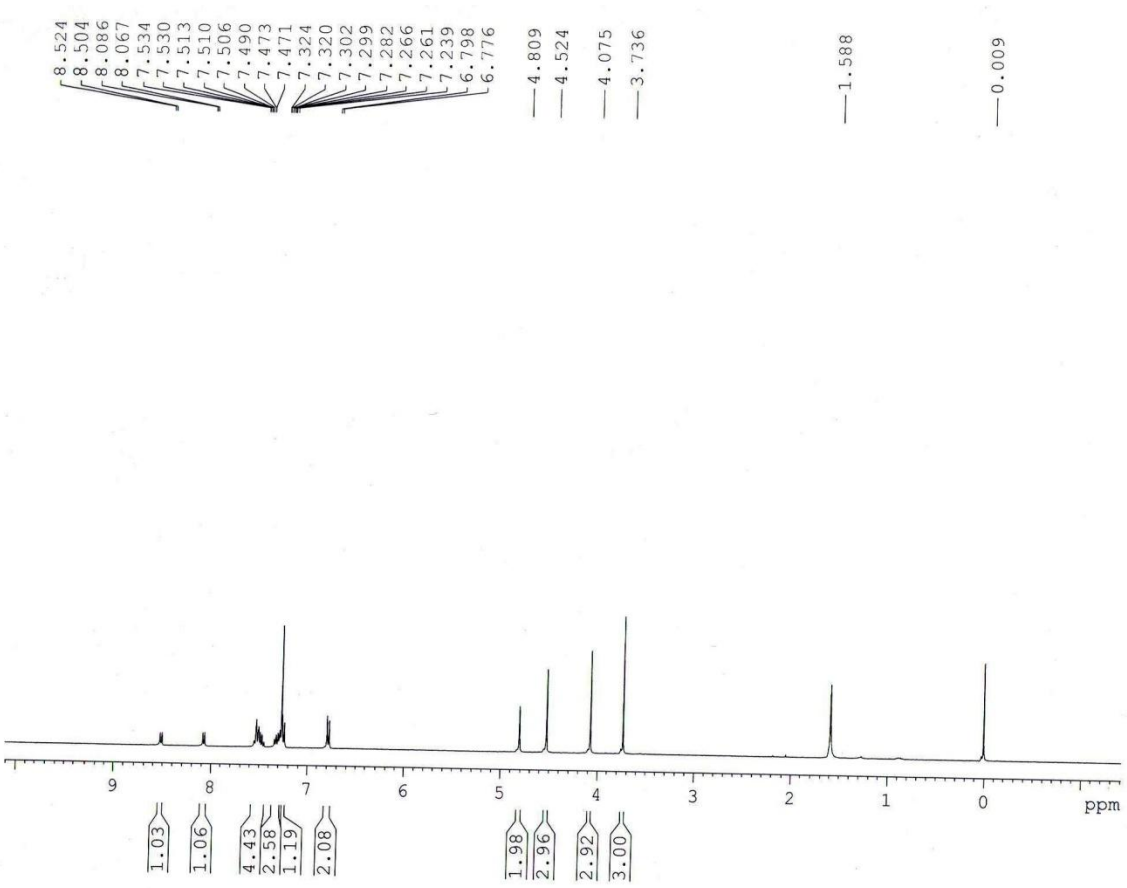


Figure S40. ^{1}H-NMR spectrum of compound **3ai**

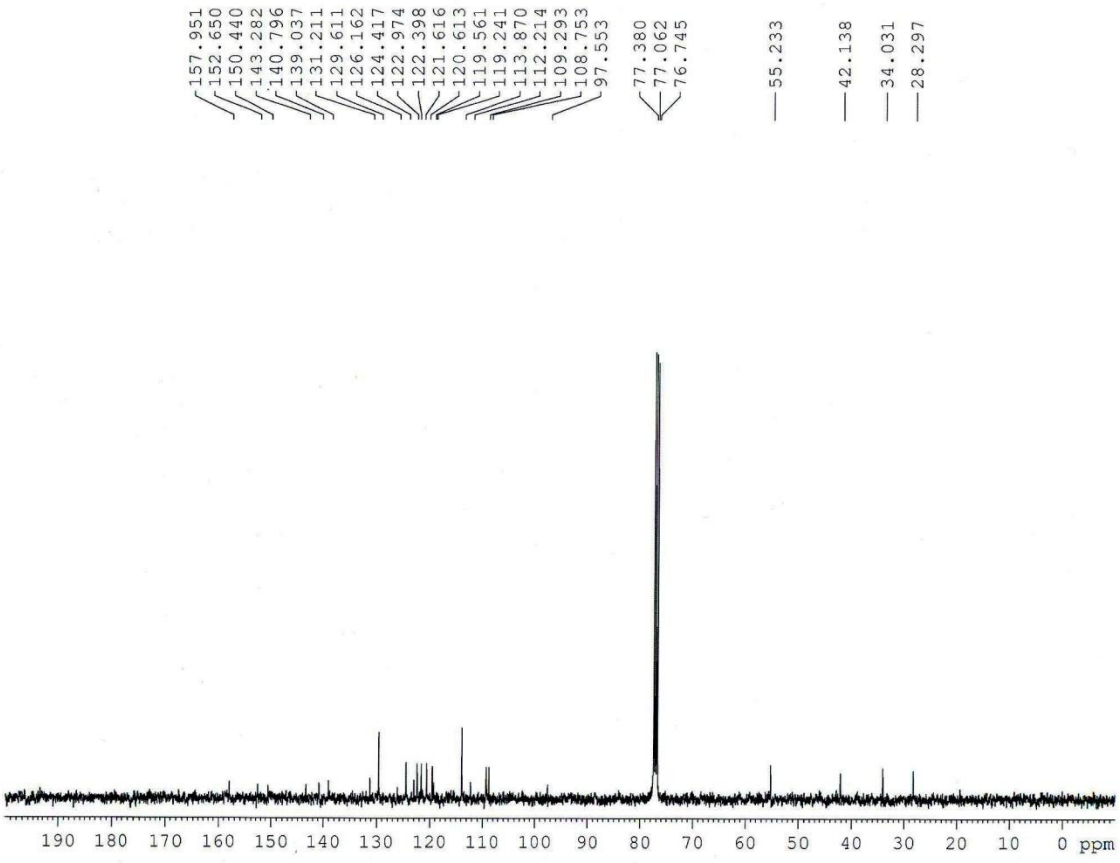


Figure S41. ^{13}C-NMR spectrum of compound **3ai**

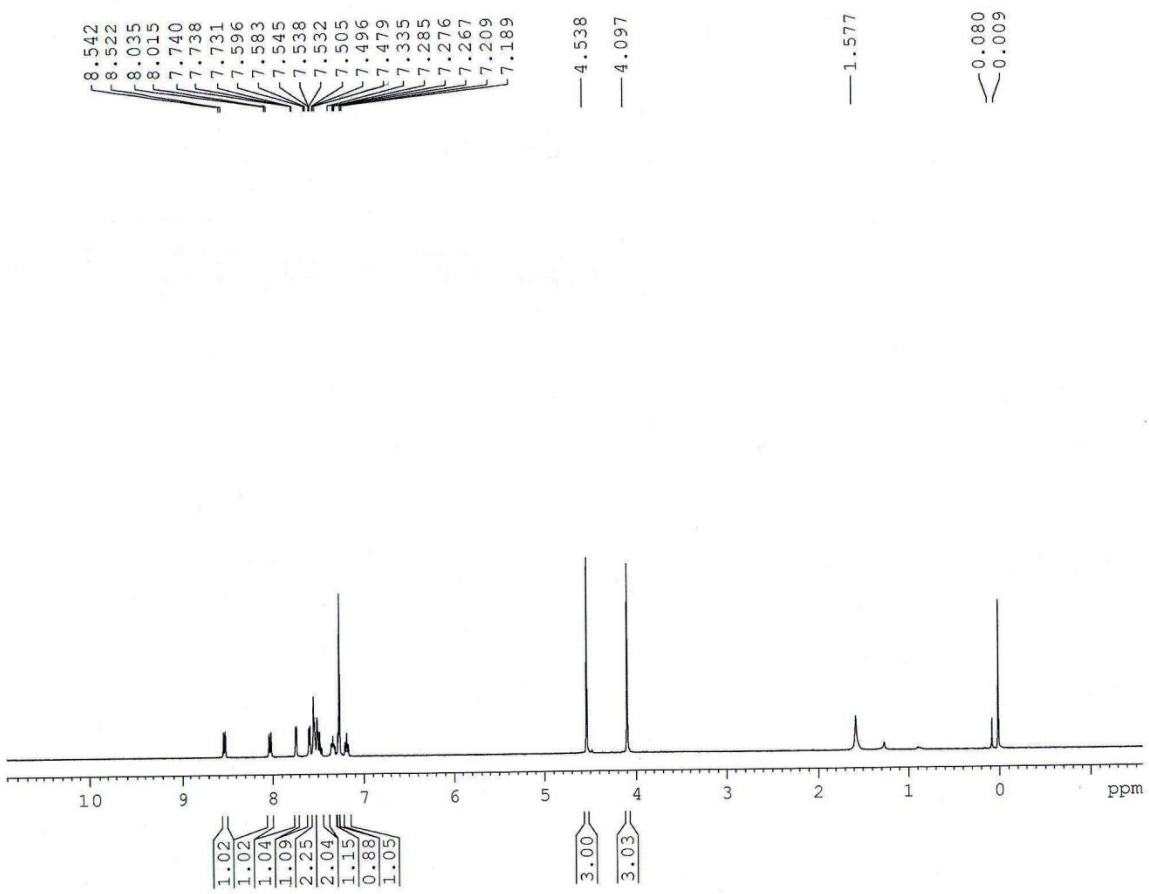


Figure S42. ^{1}H-NMR spectrum of compound 3**aj**

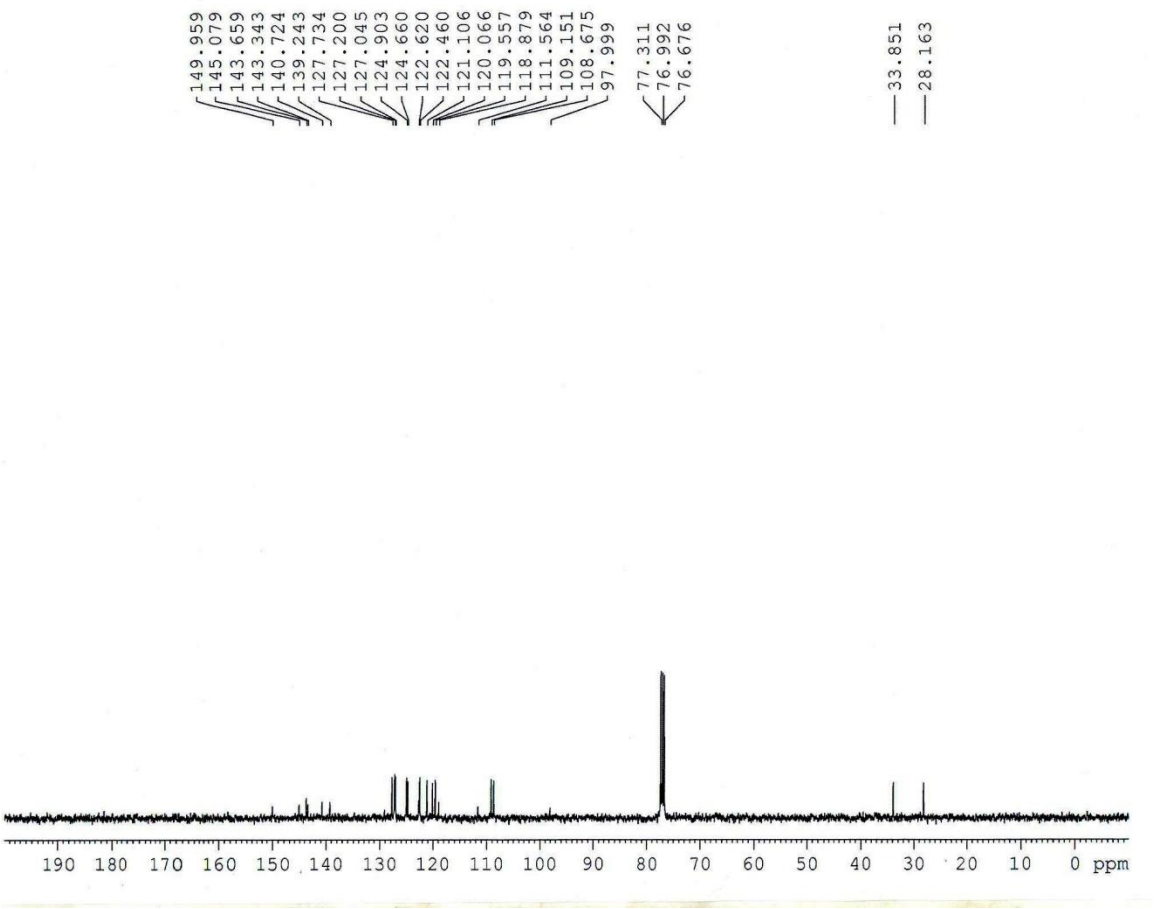


Figure S43. ^{13}C-NMR spectrum of compound **3aj**

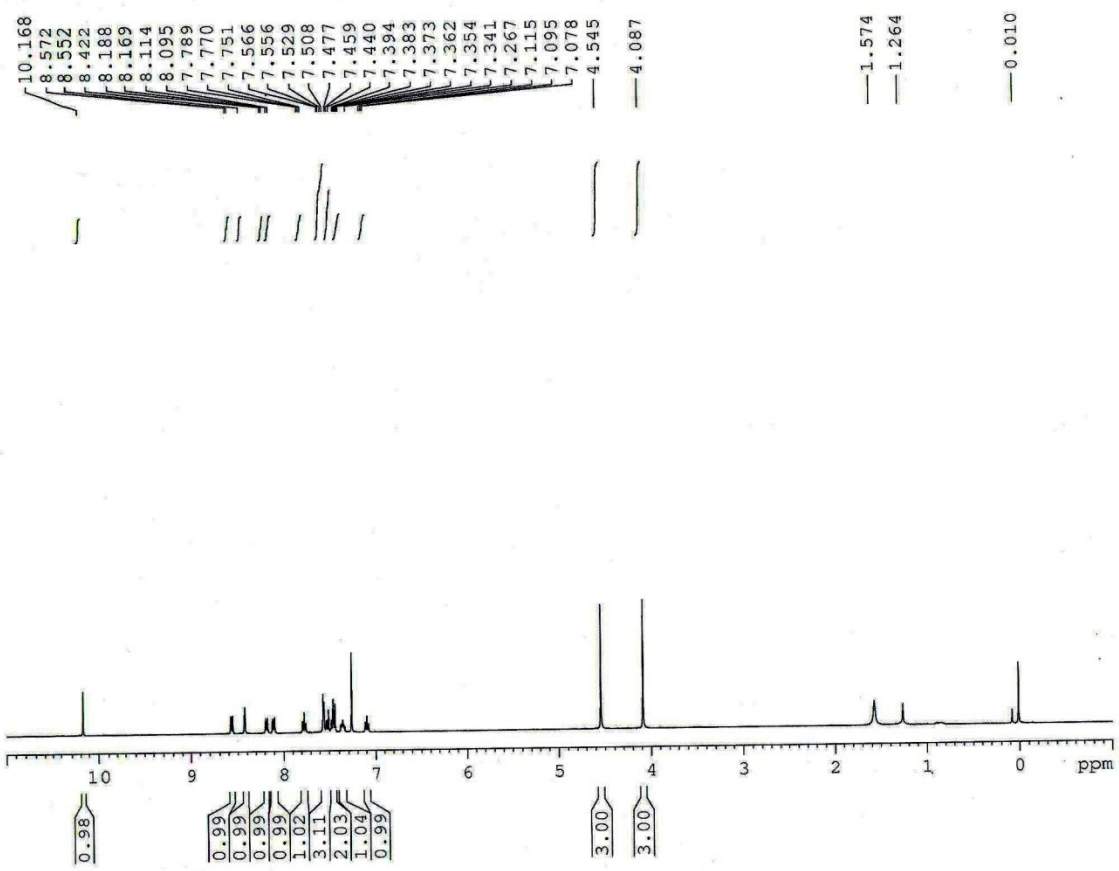


Figure S44. ^{1}H-NMR spectrum of compound **3ak**

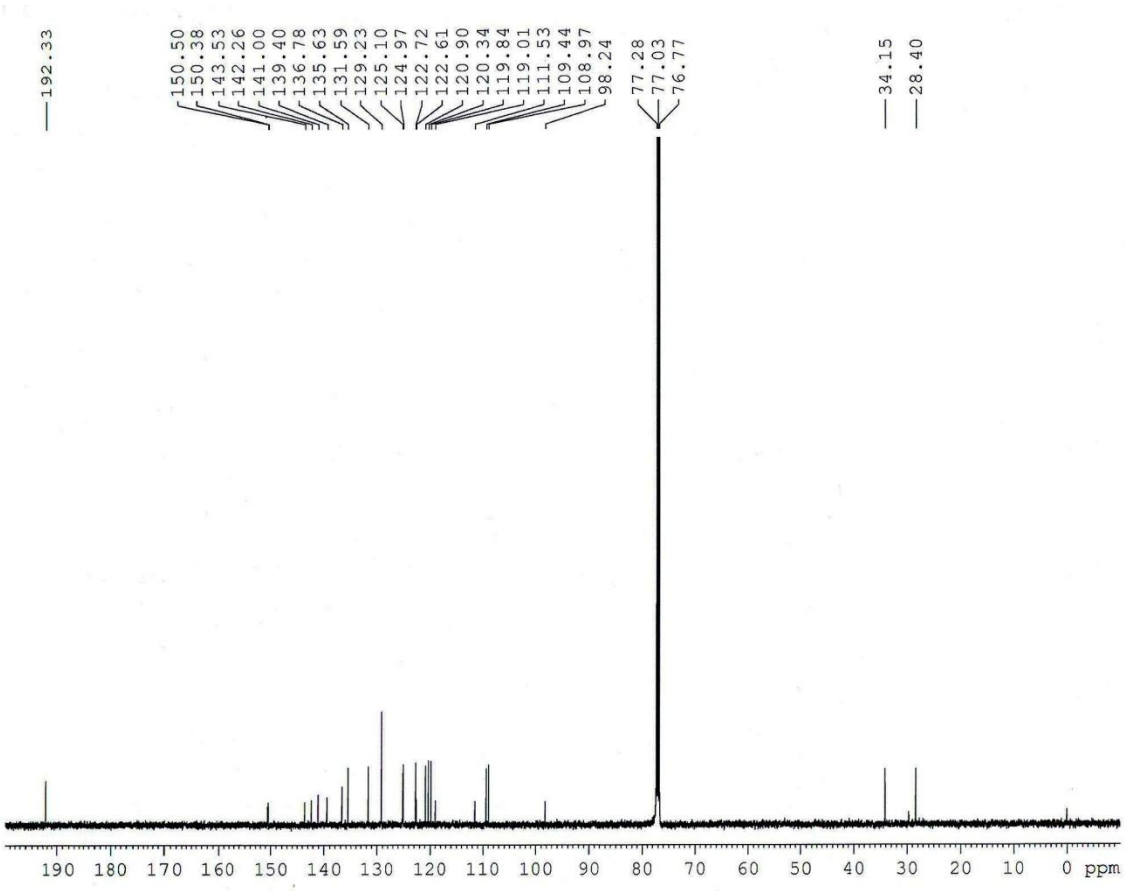


Figure S45. ^{13}C-NMR spectrum of compound **3ak**

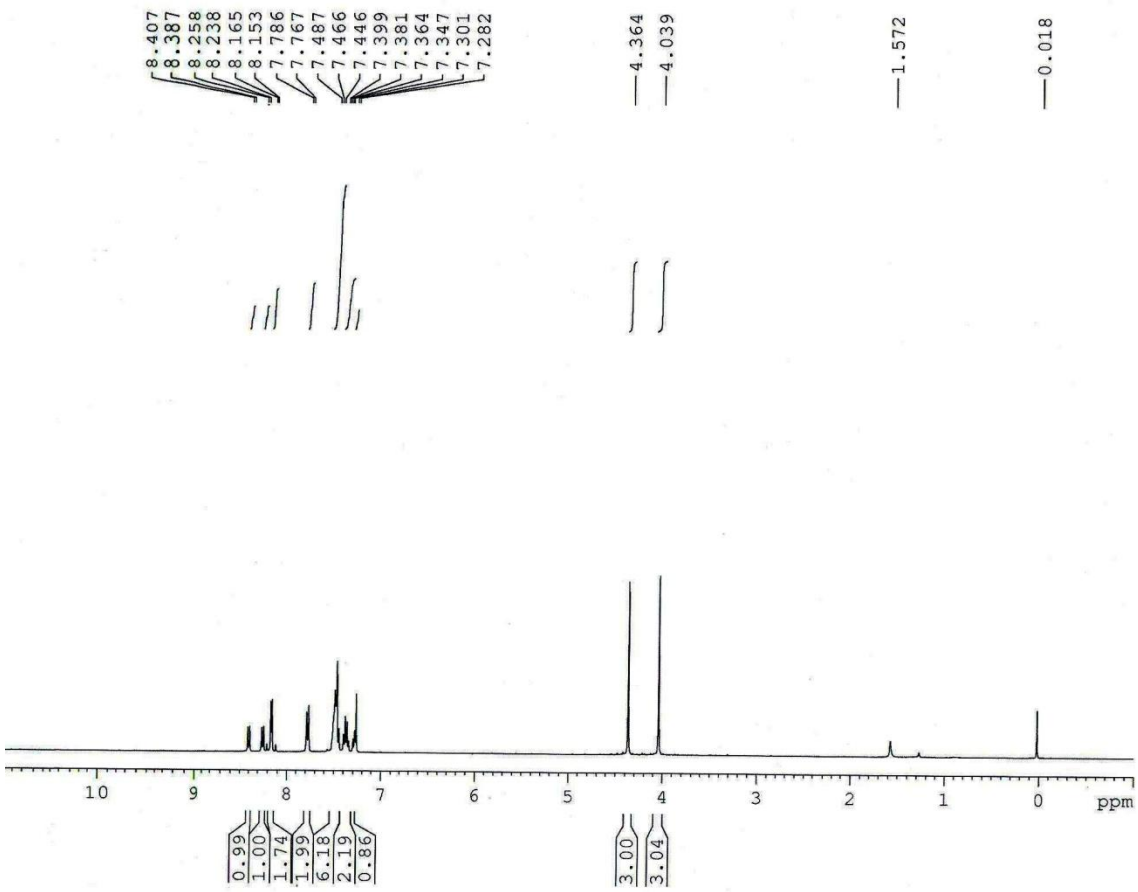


Figure S46. ^{1}H-NMR spectrum of compound **3al**

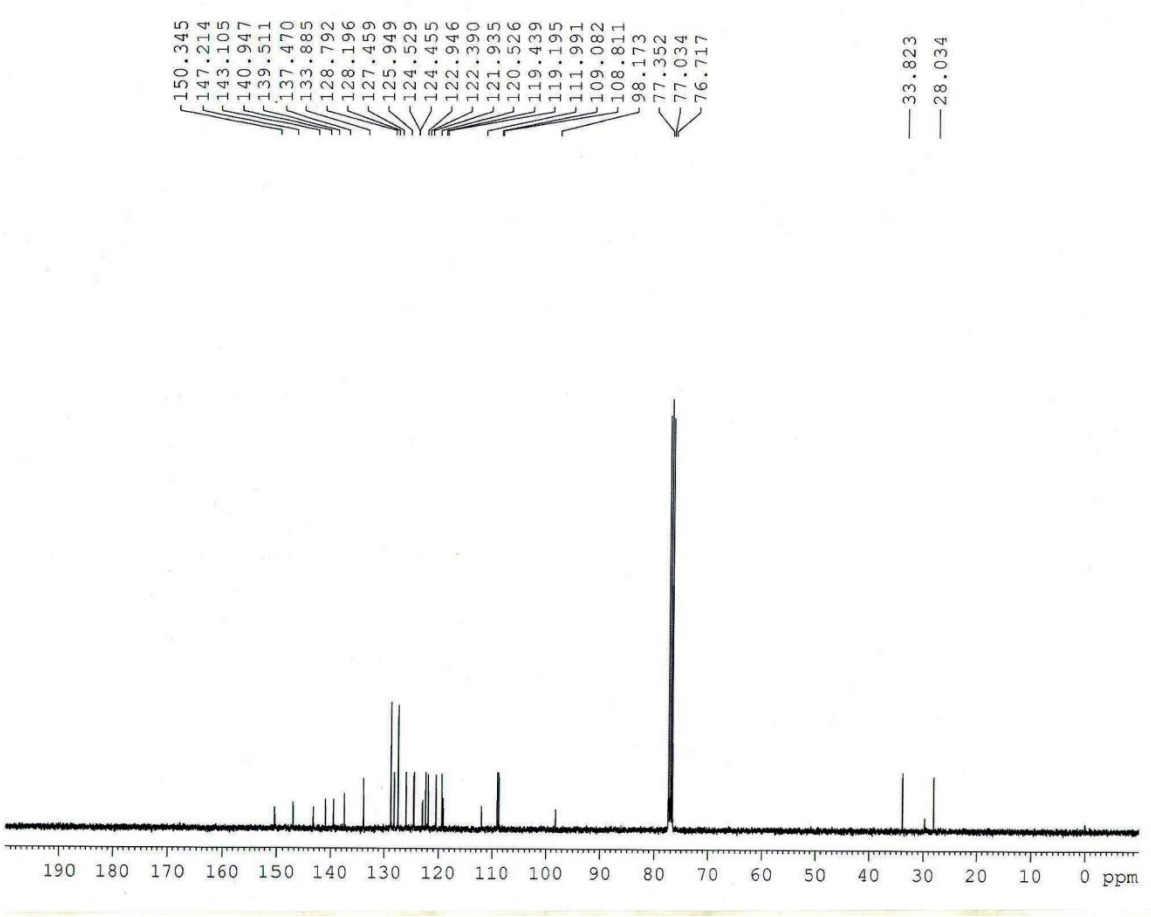


Figure S47. ^{13}C-NMR spectrum of compound **3al**

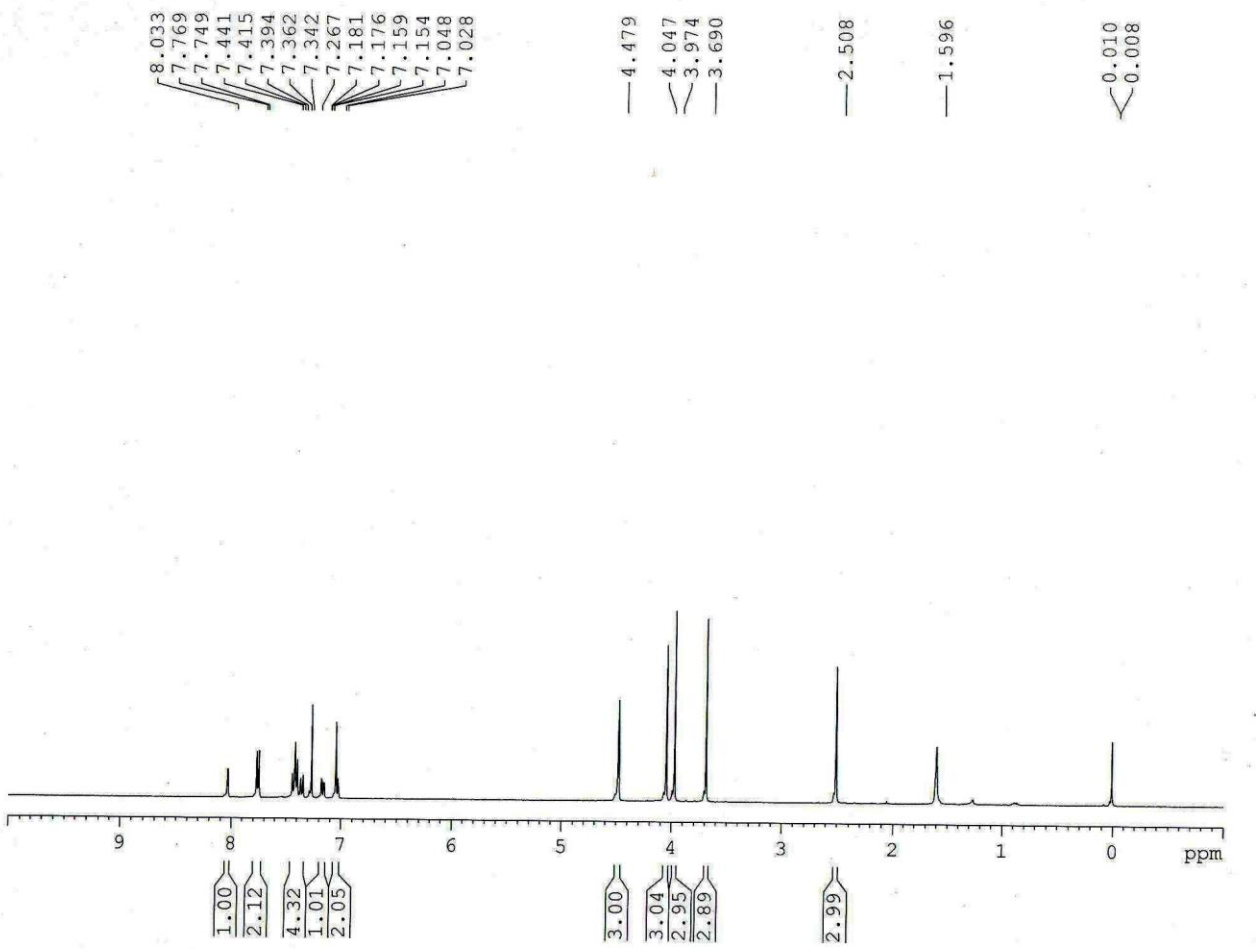


Figure S48. ^{1}H-NMR spectrum of compound **3bd**

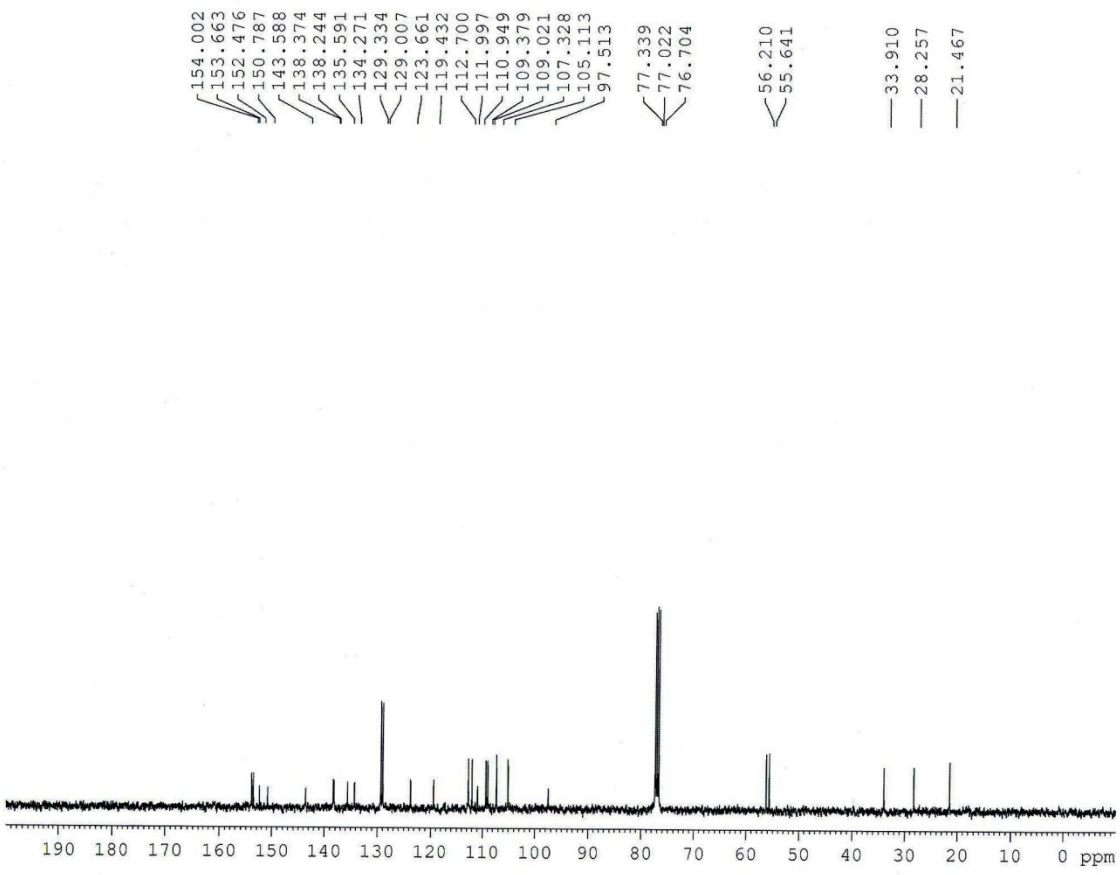


Figure S49. ^{13}C-NMR spectrum of compound **3bd**

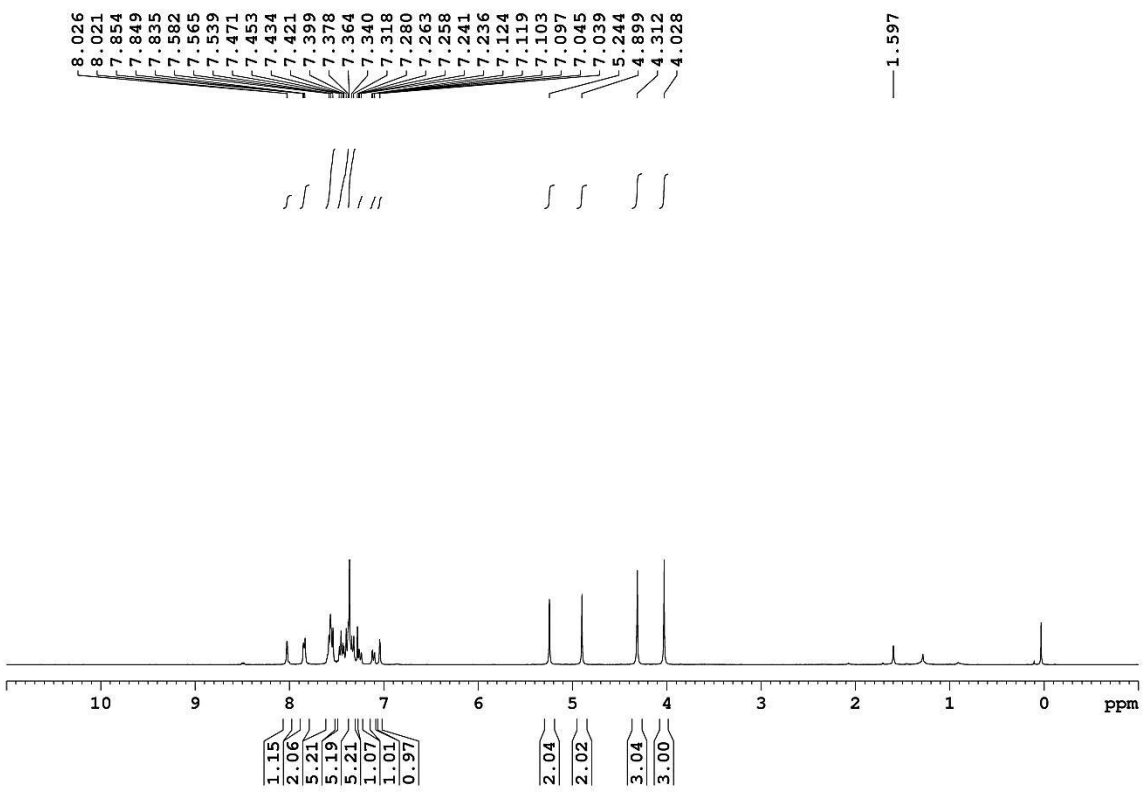


Figure S50. ^{1}H-NMR spectrum of compound **3cb**

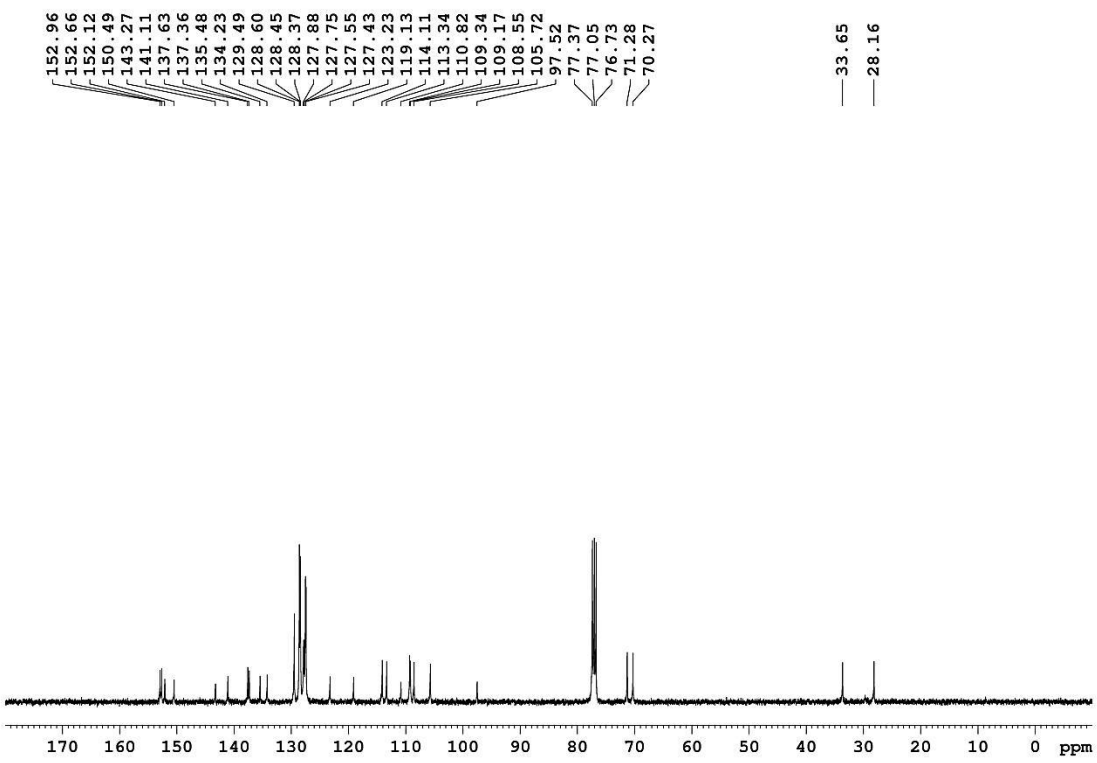


Figure S51. ^{13}C-NMR spectrum of compound **3cb**

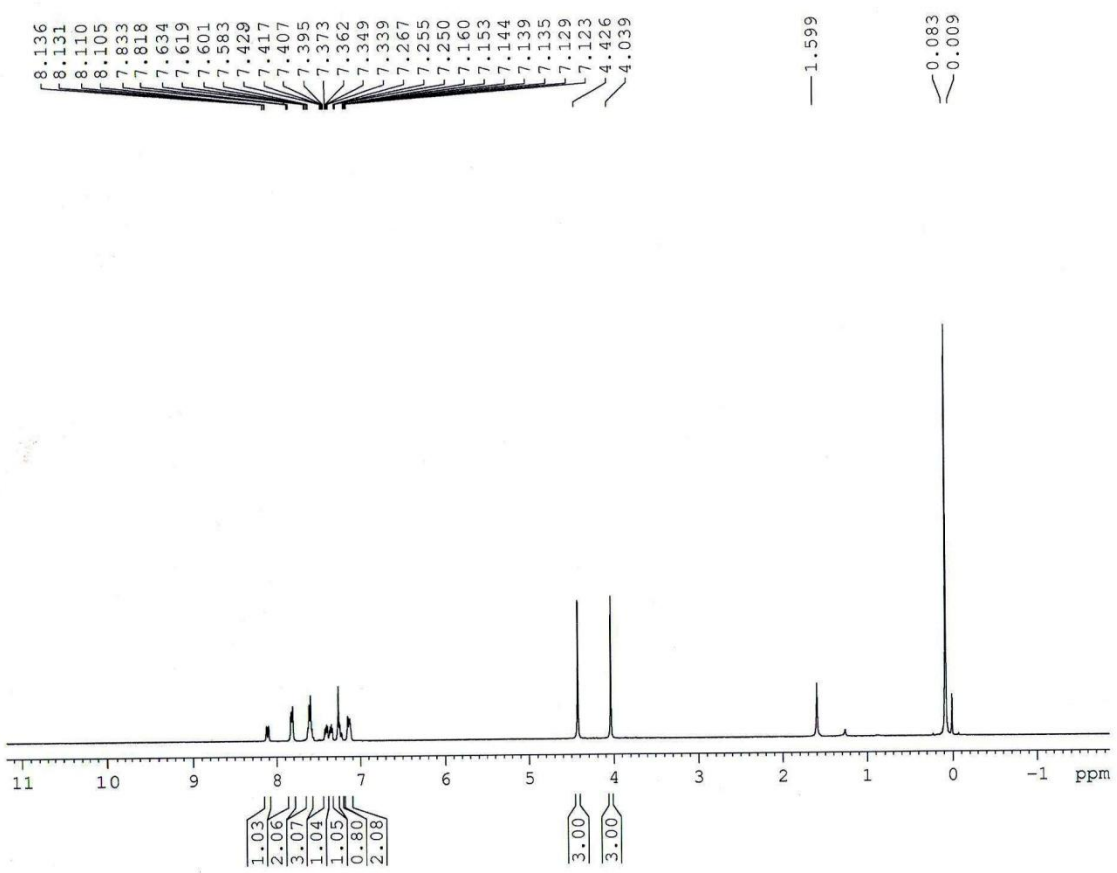


Figure S52. ^{1}H-NMR spectrum of compound **3db**

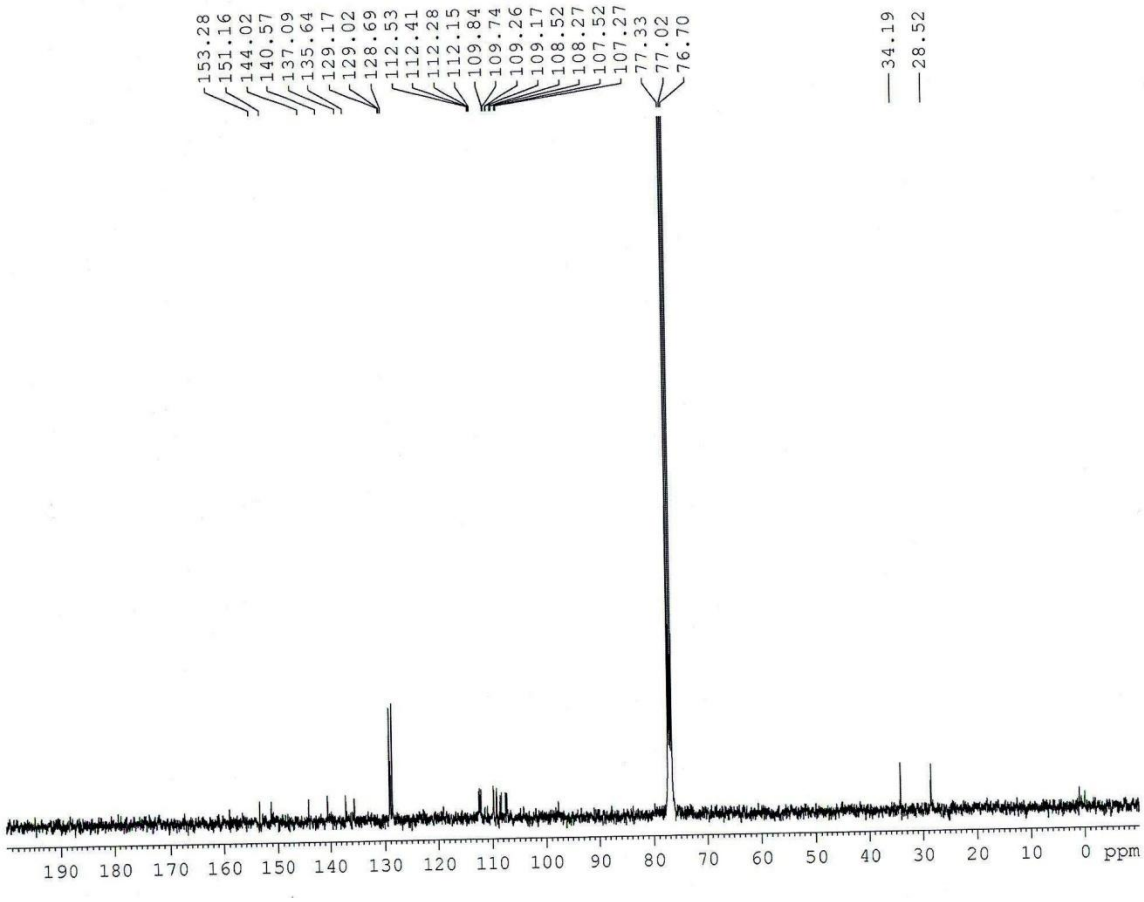


Figure S53. ^{13}C-NMR spectrum of compound **3db**

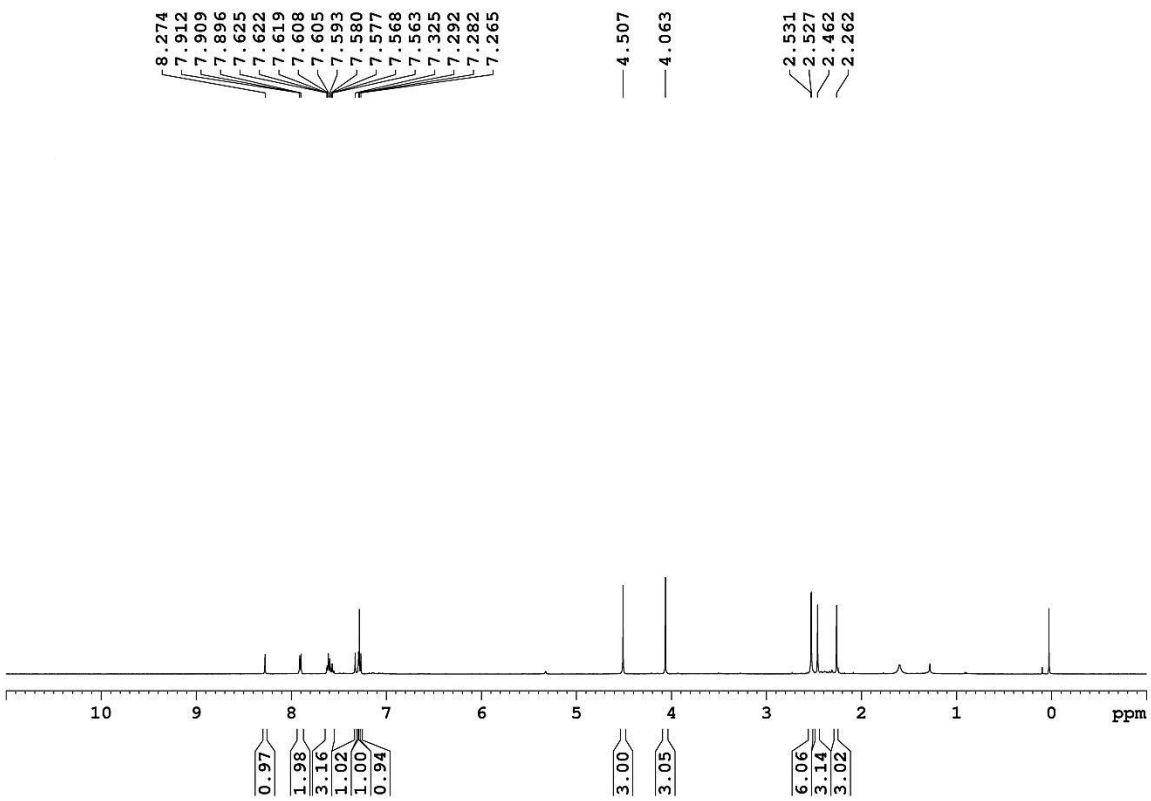


Figure S54. ^{1}H-NMR spectrum of compound **3eb**

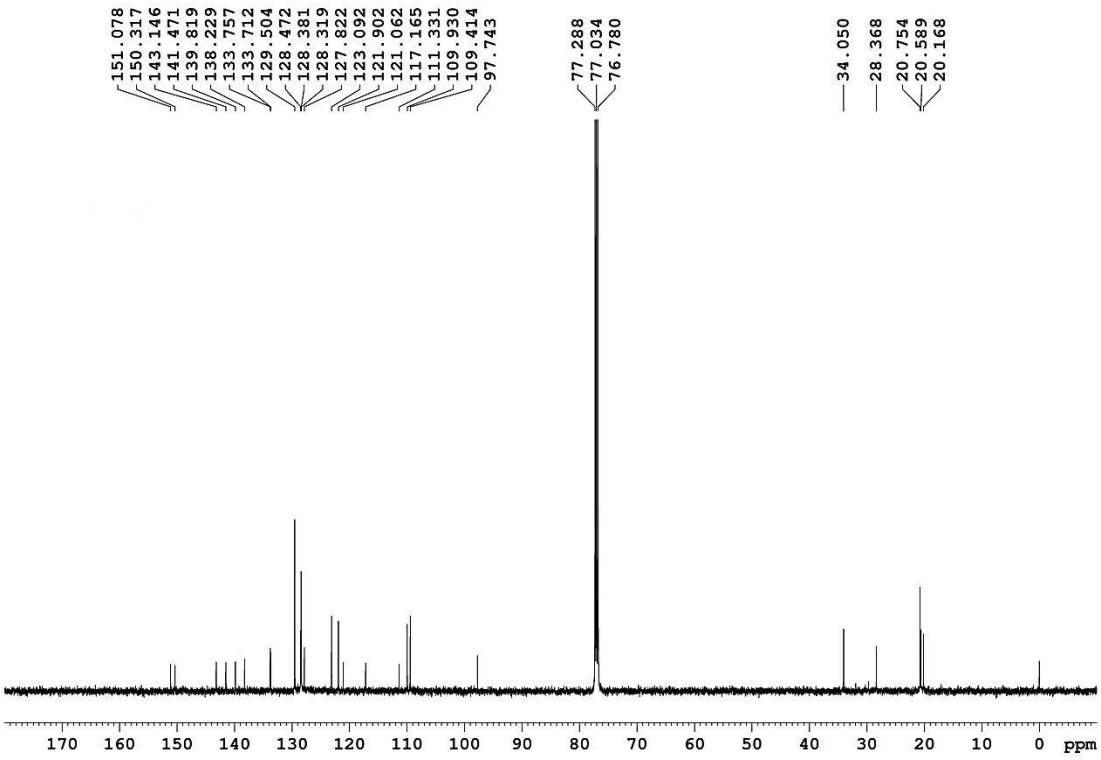


Figure S55. ^{13}C-NMR spectrum of compound **3eb**

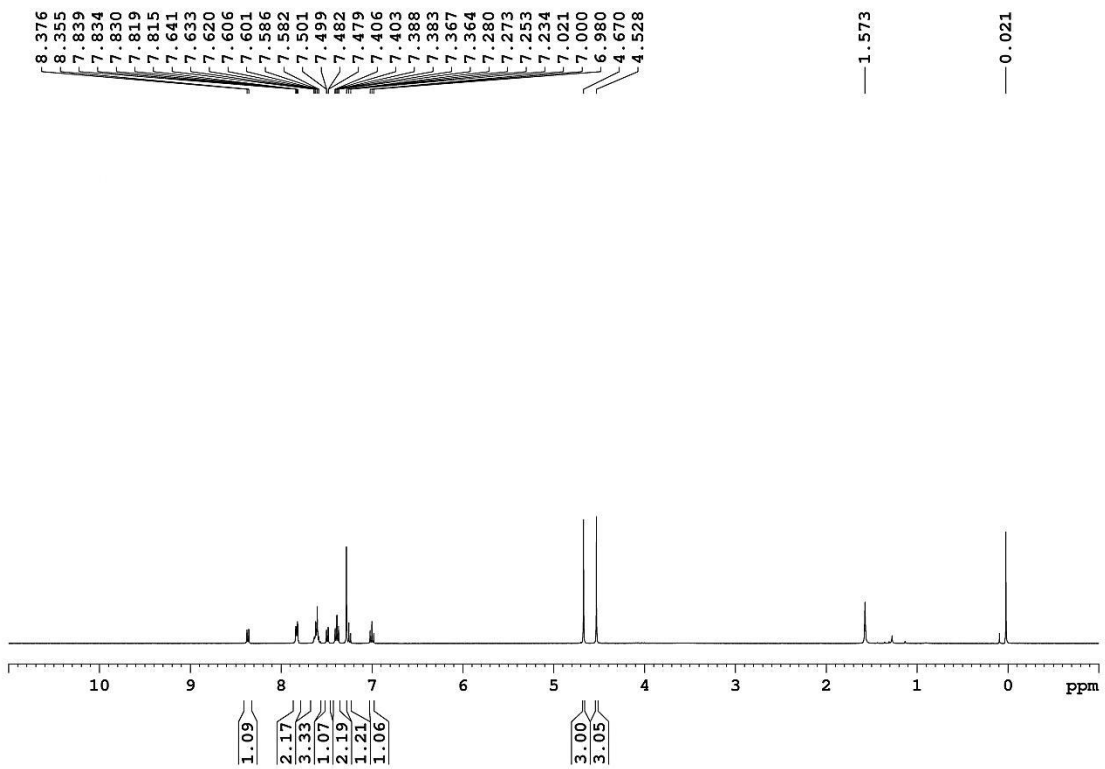


Figure S56. ^{1}H-NMR spectrum of compound **3fb**

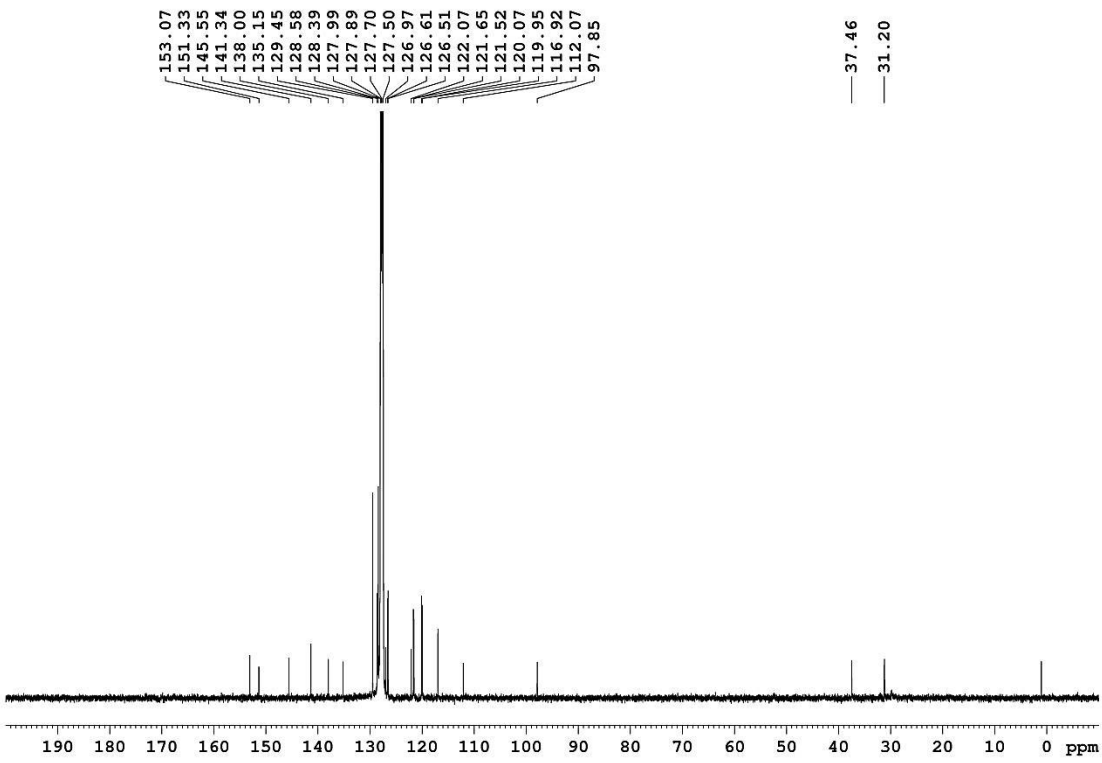


Figure S57. ^{13}C-NMR spectrum of compound **3fb**

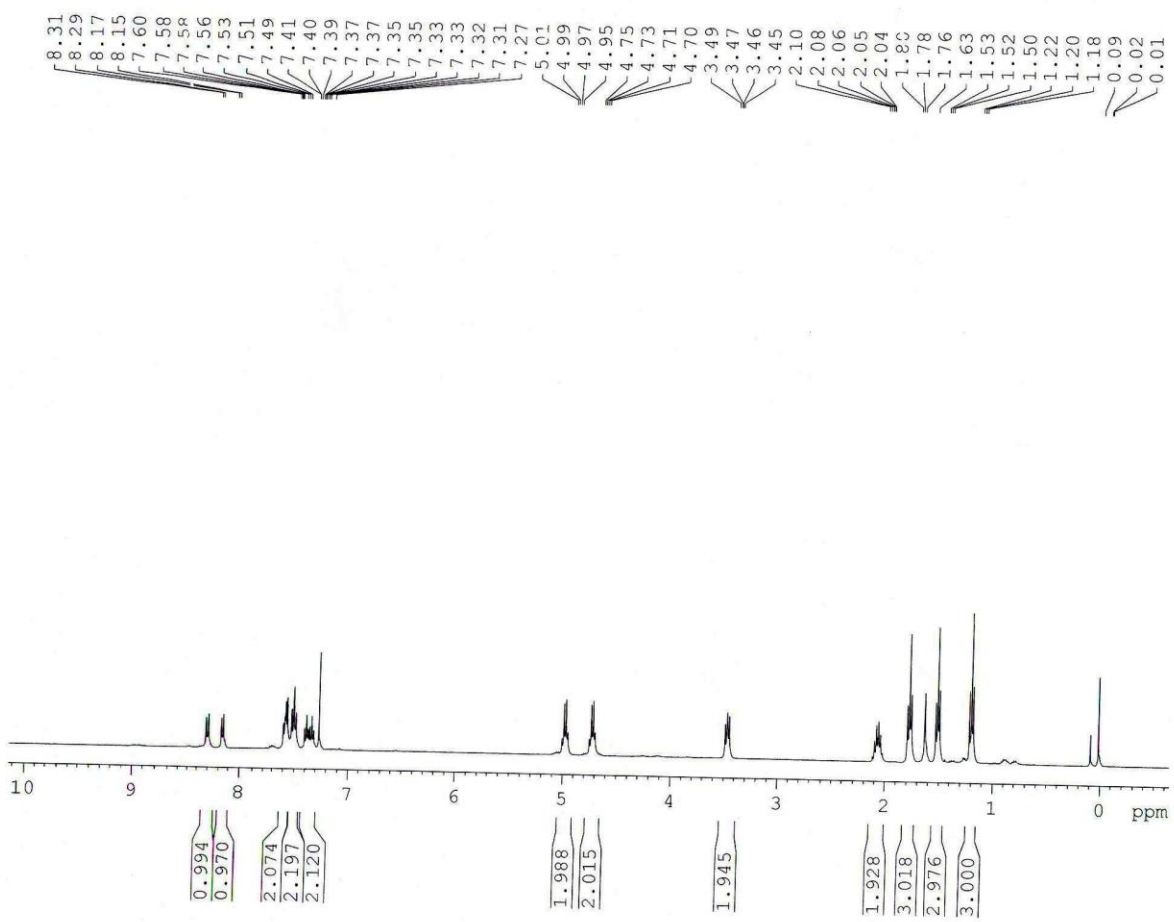


Figure S58. ^{1}H-NMR spectrum of compound **3gf**

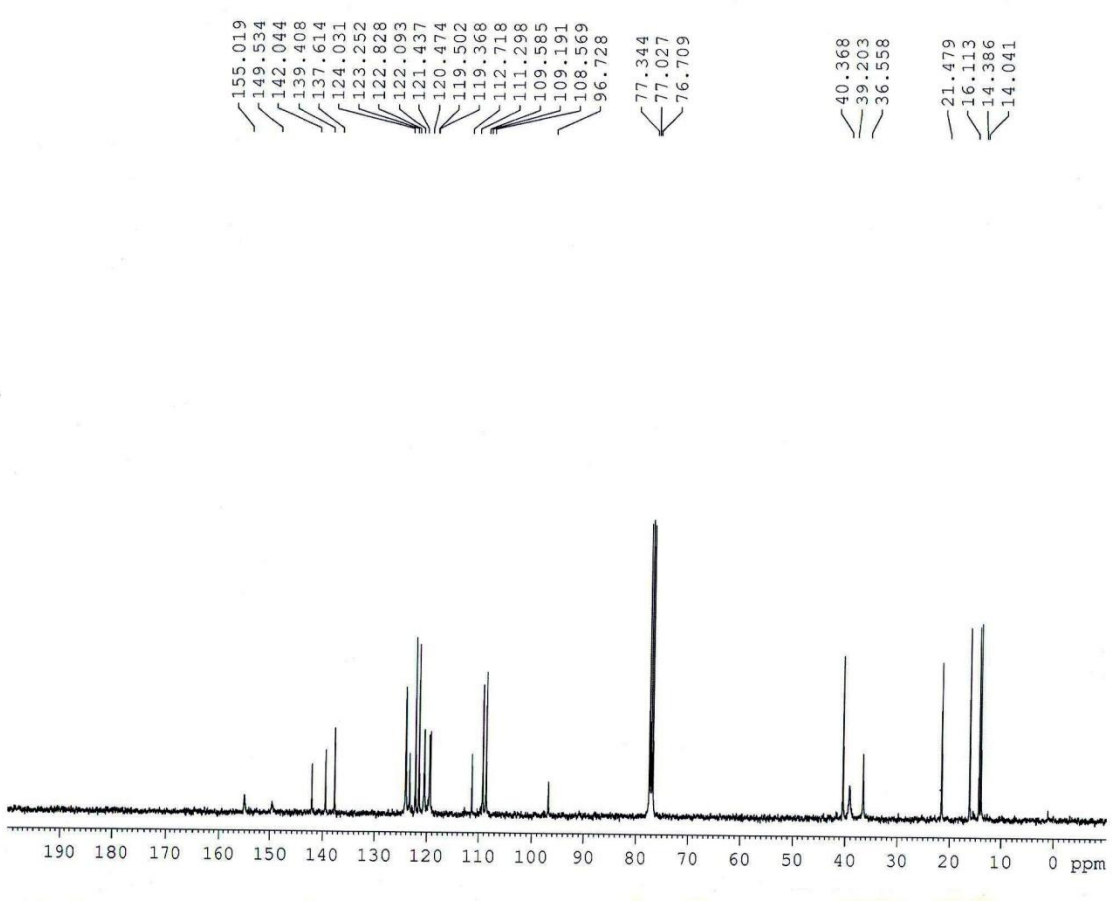


Figure S59. ^{13}C-NMR spectrum of compound **3gf**

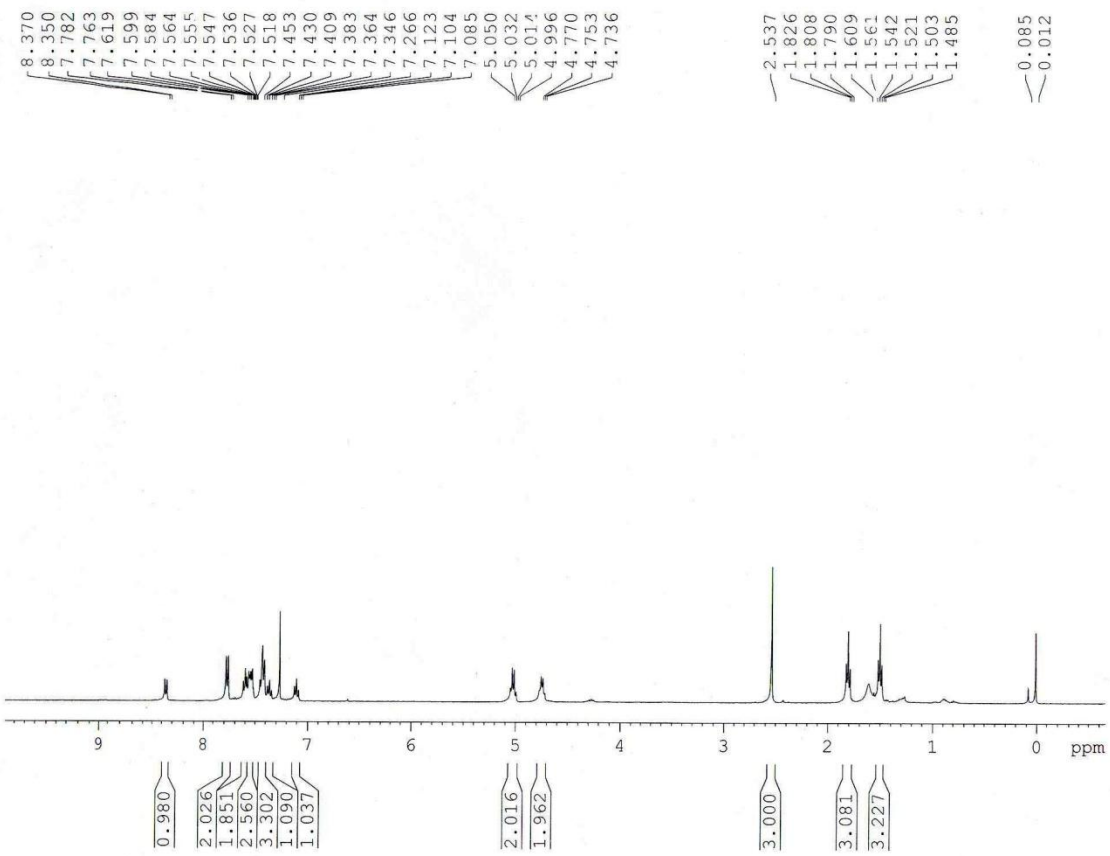


Figure S60. ^{1}H-NMR spectrum of compound **3gd**

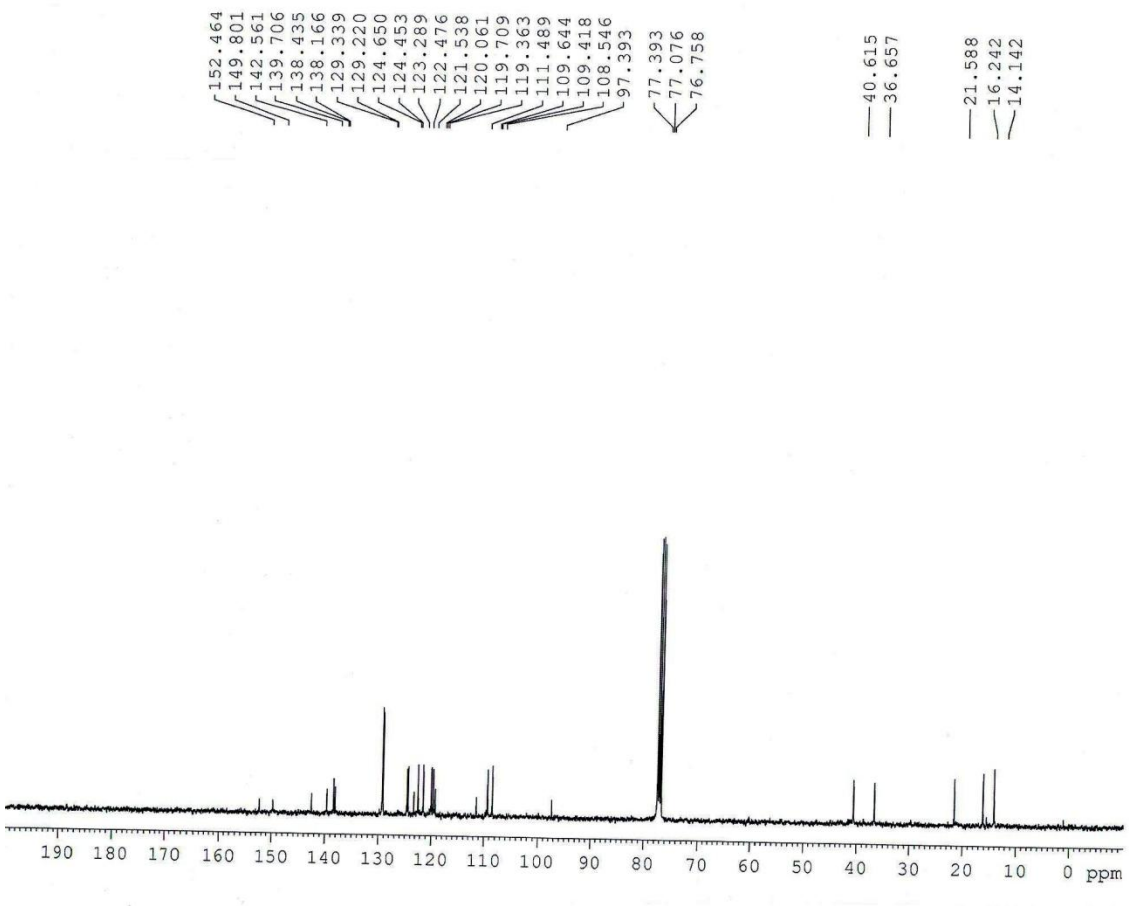


Figure S61. ^{13}C-NMR spectrum of compound **3gd**

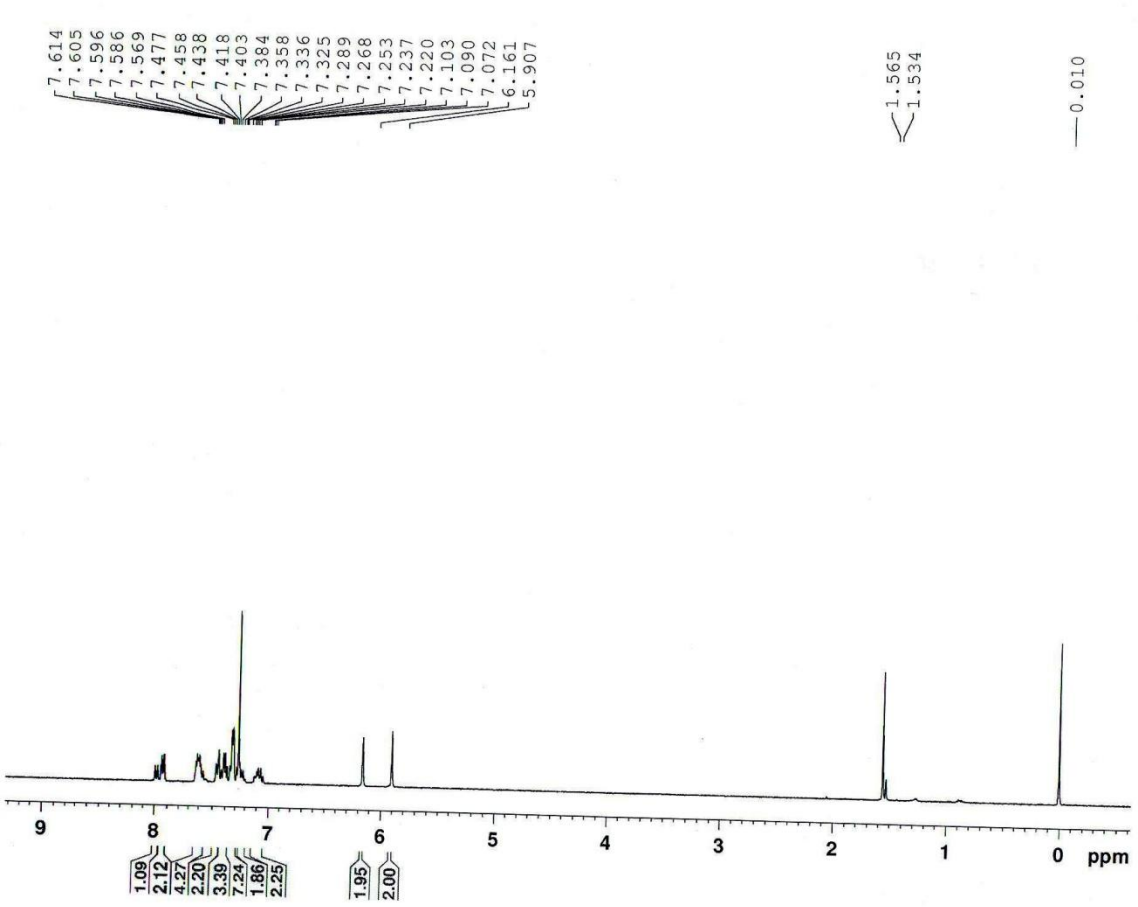


Figure S62. ^{1}H-NMR spectrum of compound **3hb**

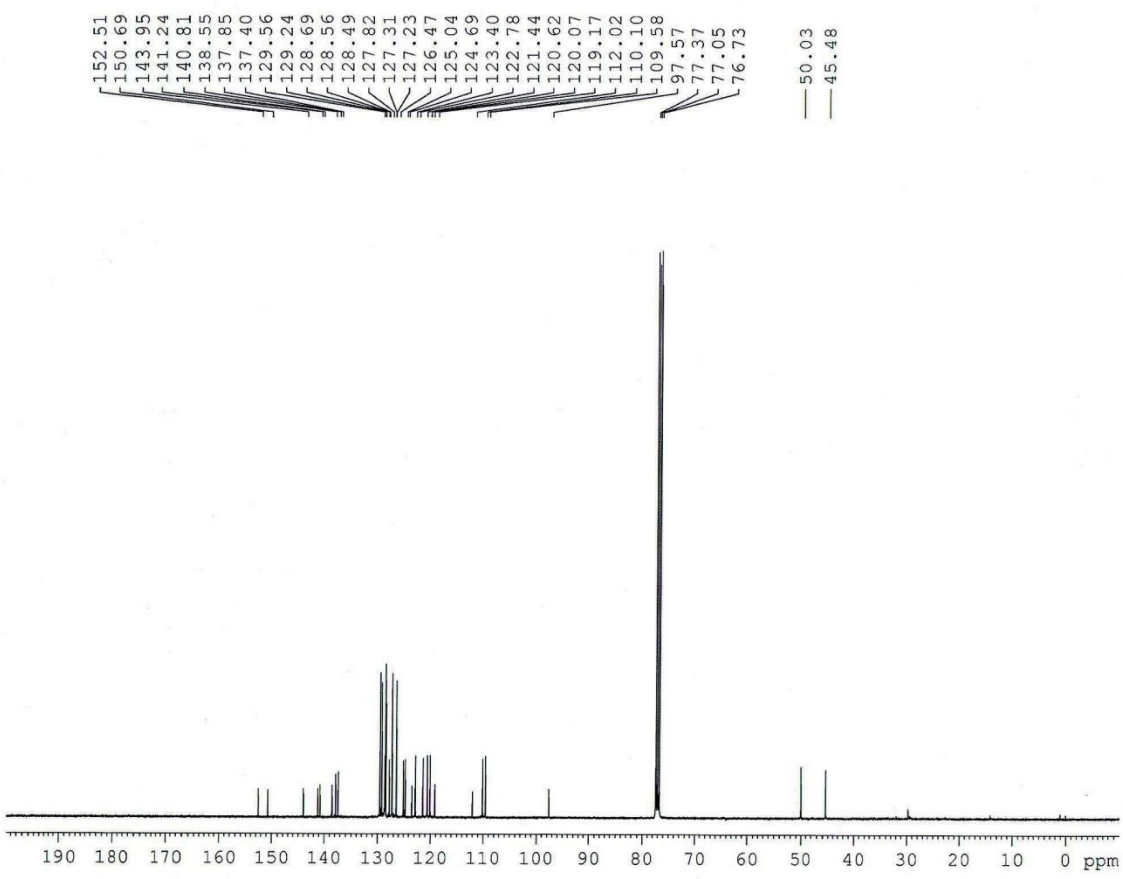


Figure S63. ^{13}C-NMR spectrum of compound **3hb**

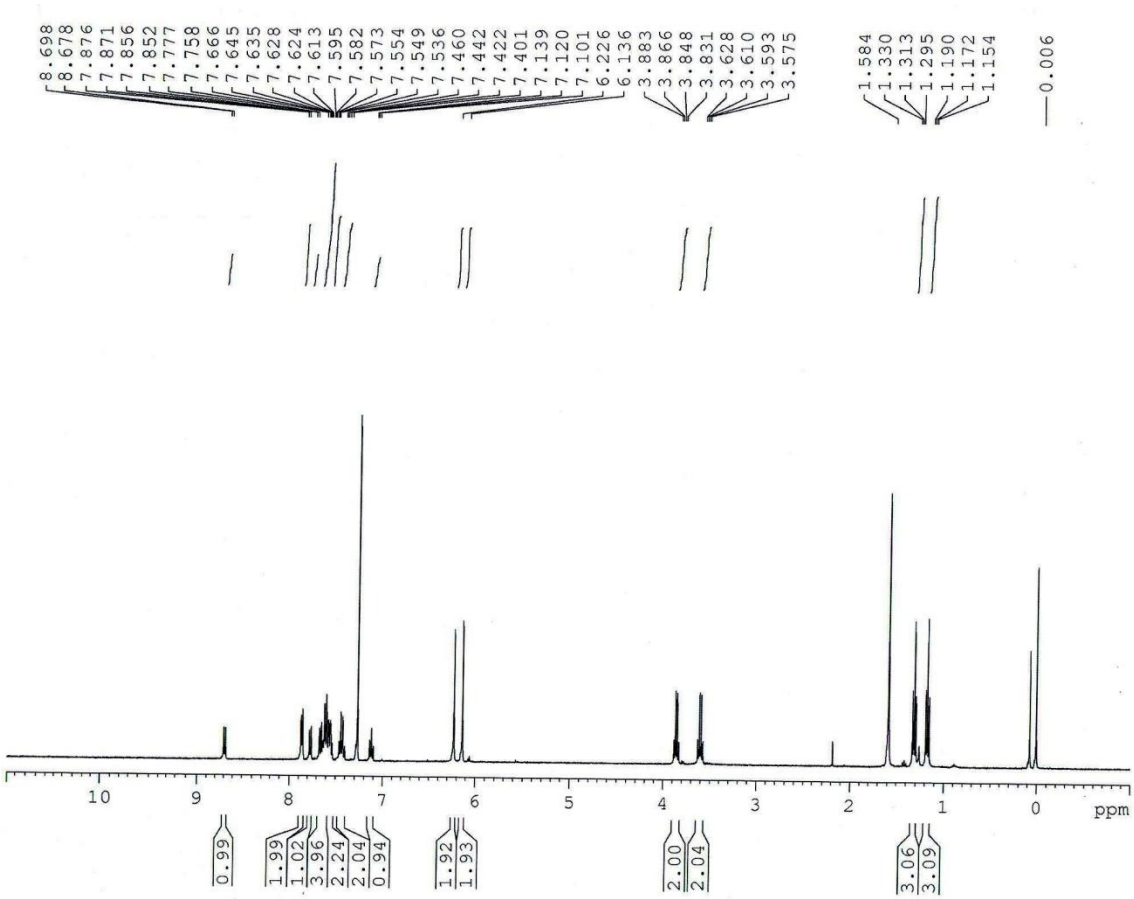


Figure S64. ^{1}H-NMR spectrum of compound **3ib**

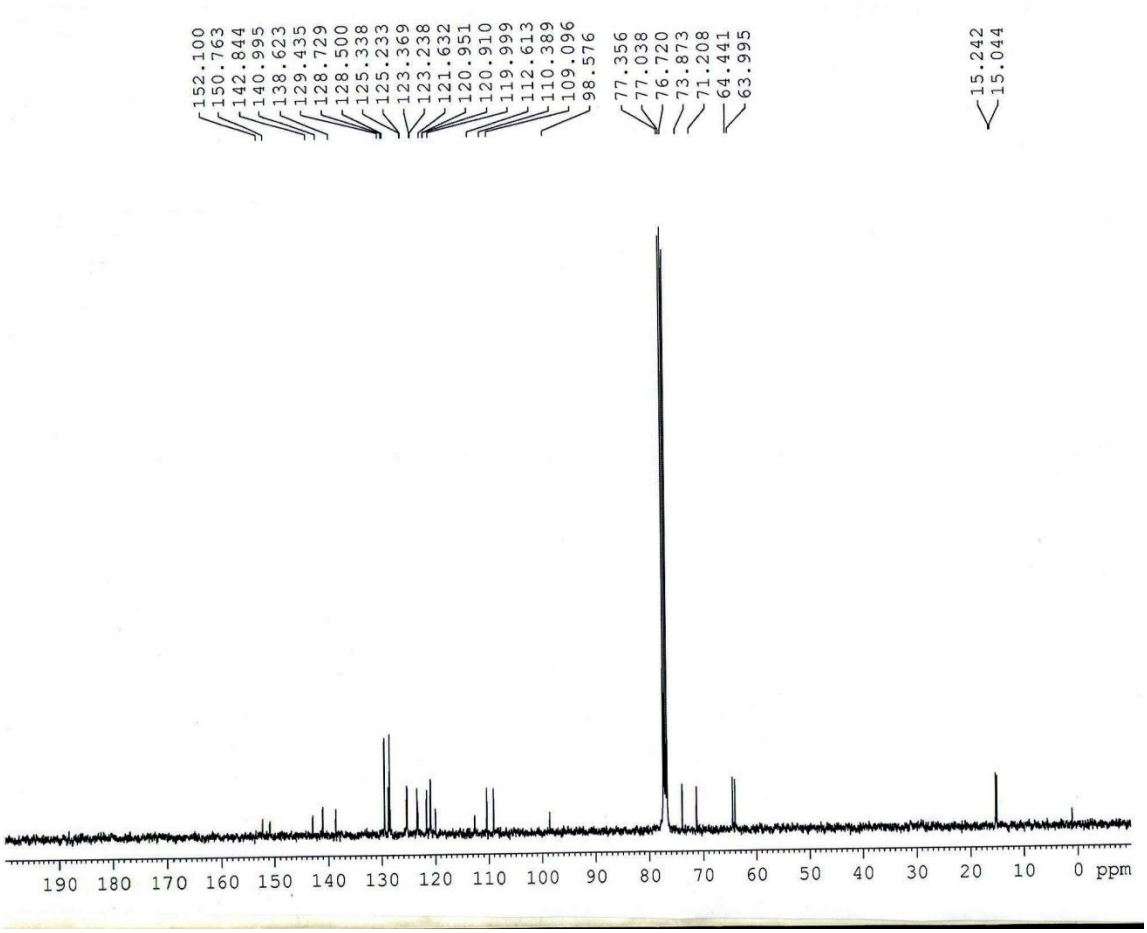


Figure S65. ^{13}C-NMR spectrum of compound **3ib**

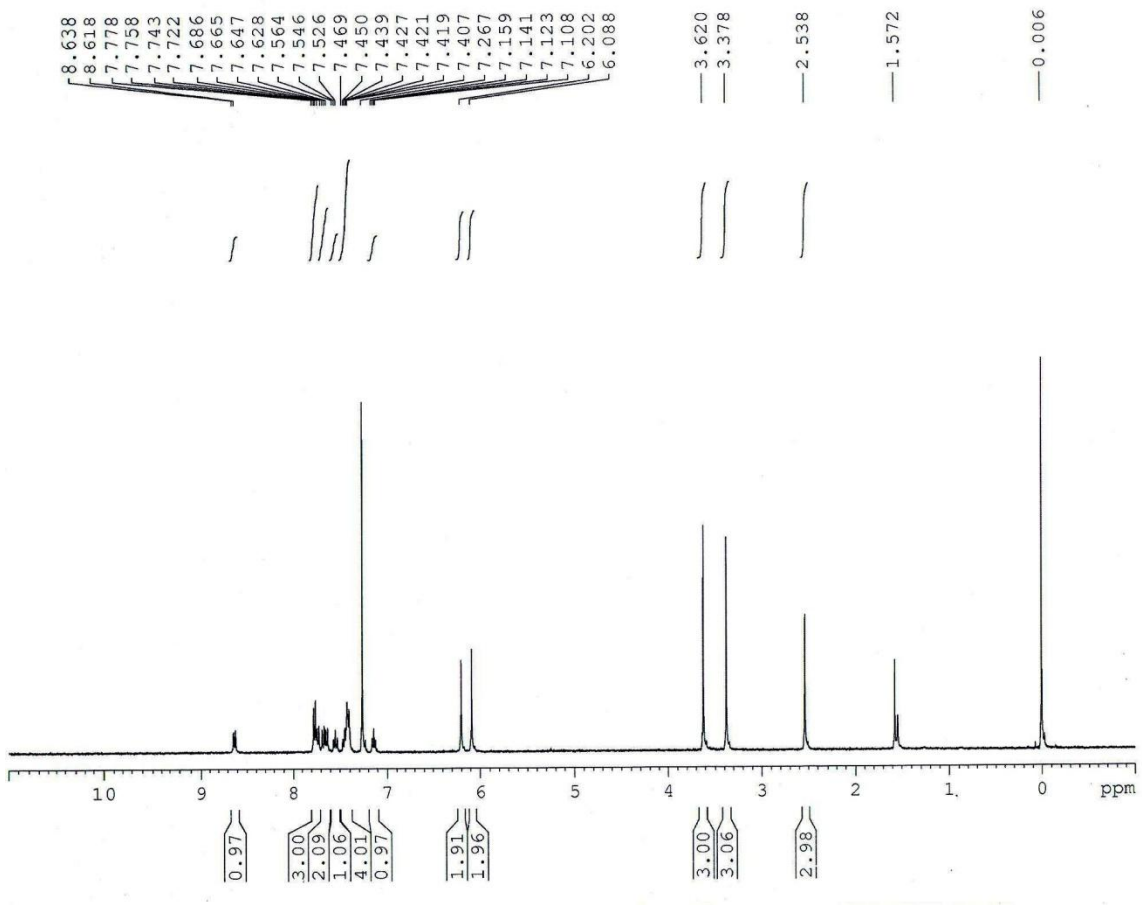


Figure S66. ^{1}H-NMR spectrum of compound **3jd**

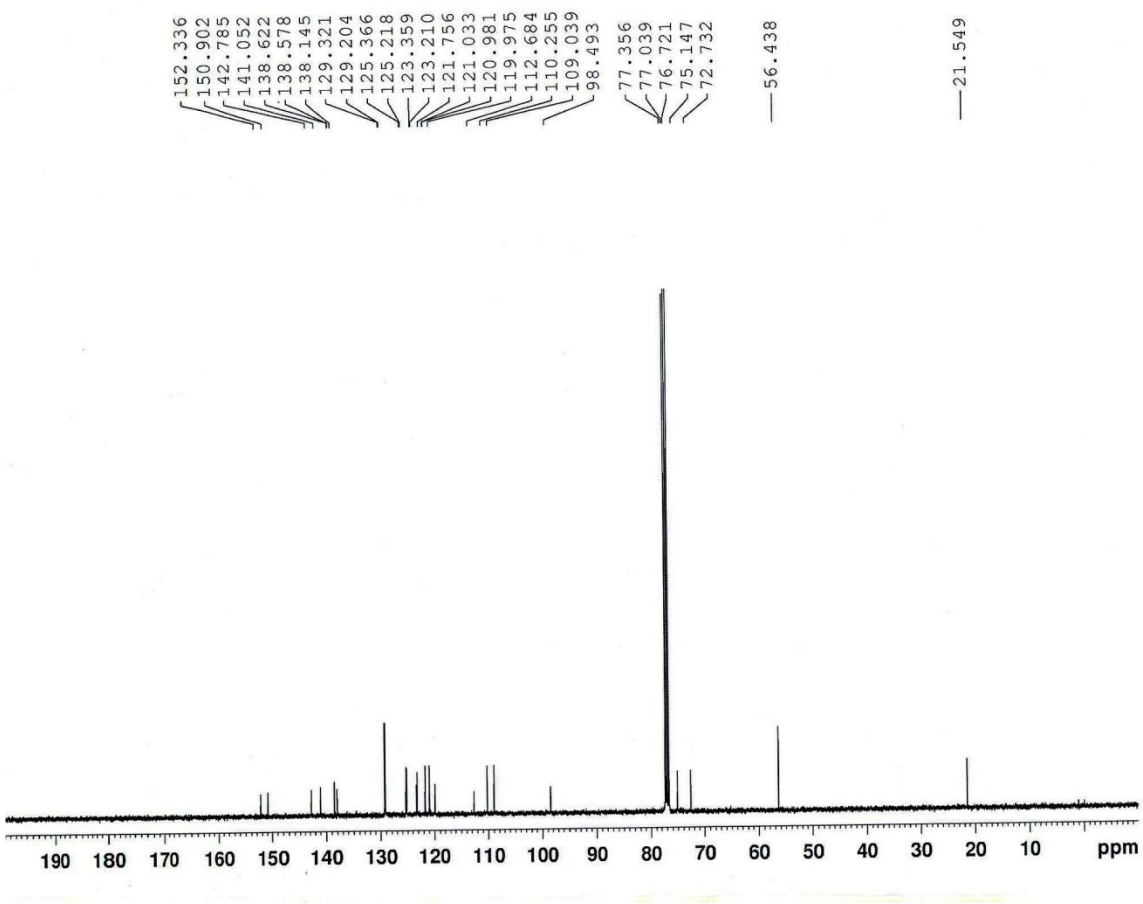


Figure S67. ^{13}C-NMR spectrum of compound **3jd**

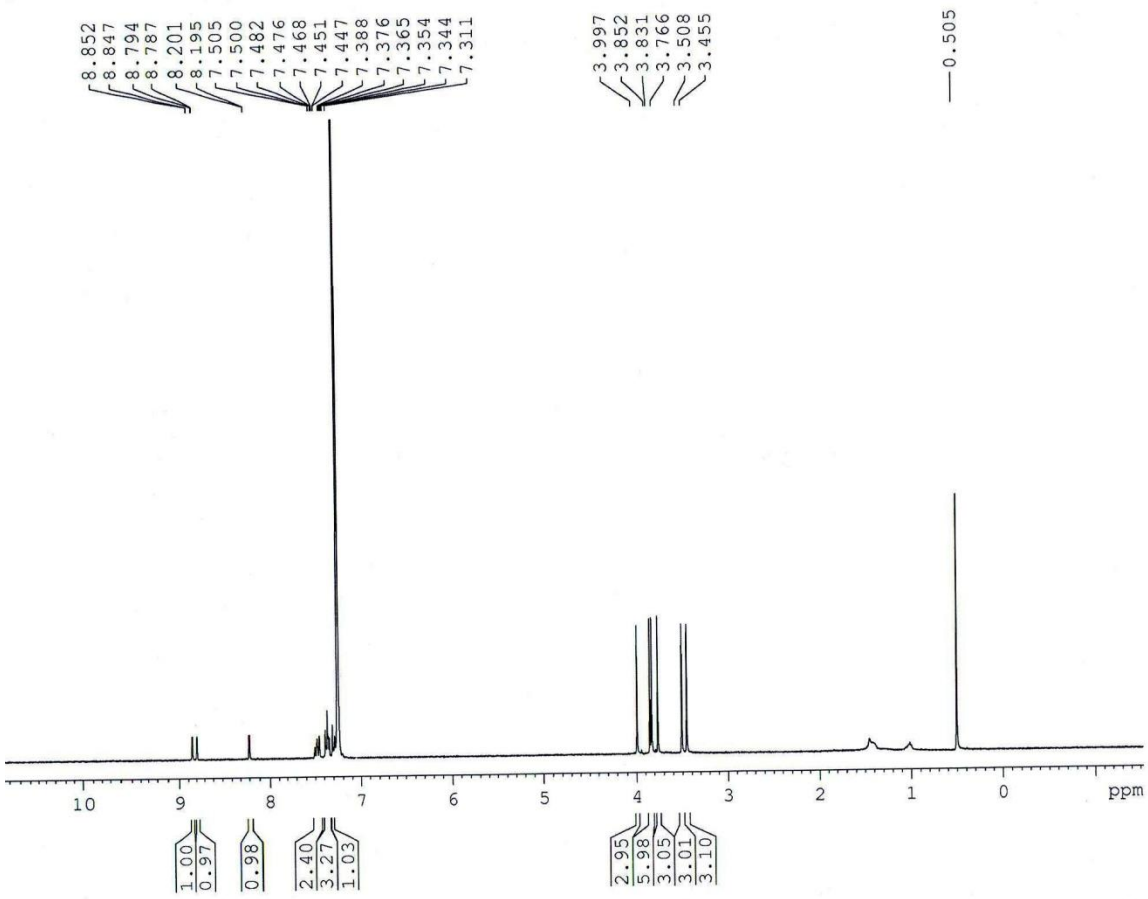


Figure S68. ^{1}H-NMR spectrum of compound **5b**

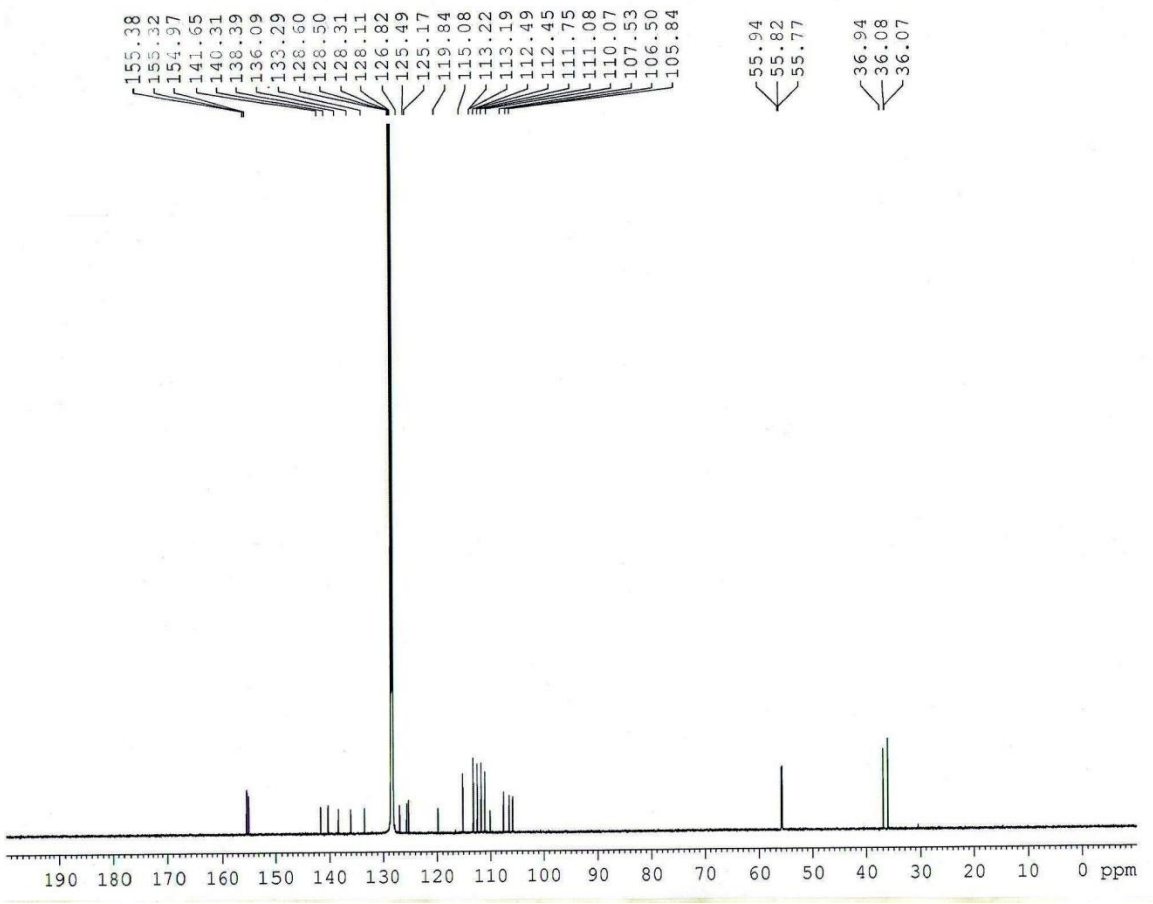


Figure S69. ^{13}C-NMR spectrum of compound **5b**

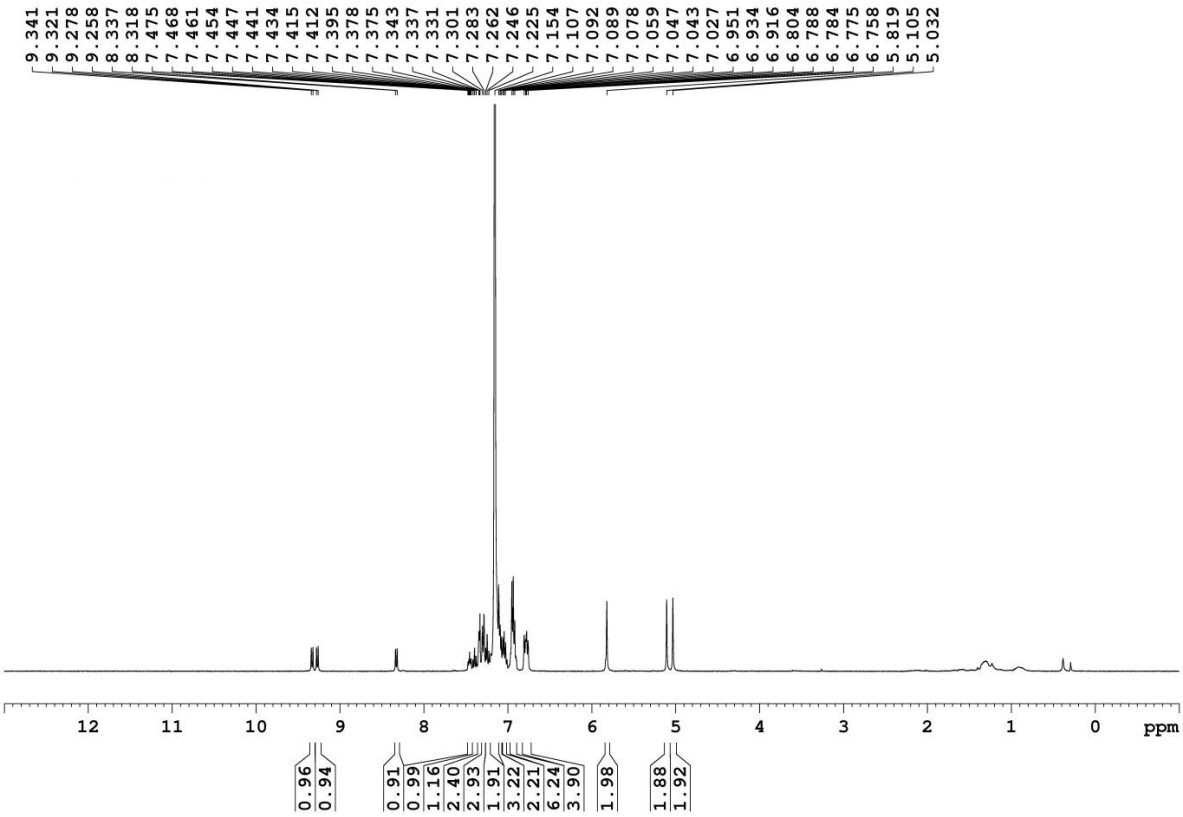


Figure S70. ^{1}H-NMR spectrum of compound **5h**

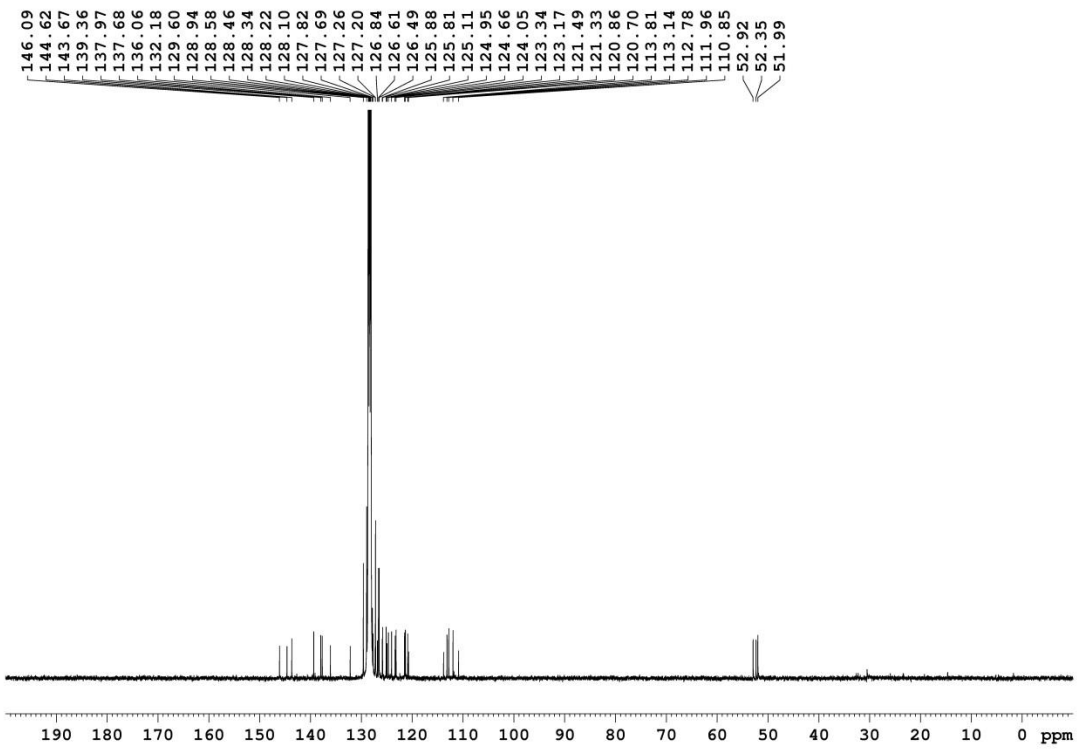


Figure S71. ^{13}C-NMR spectrum of compound **5h**

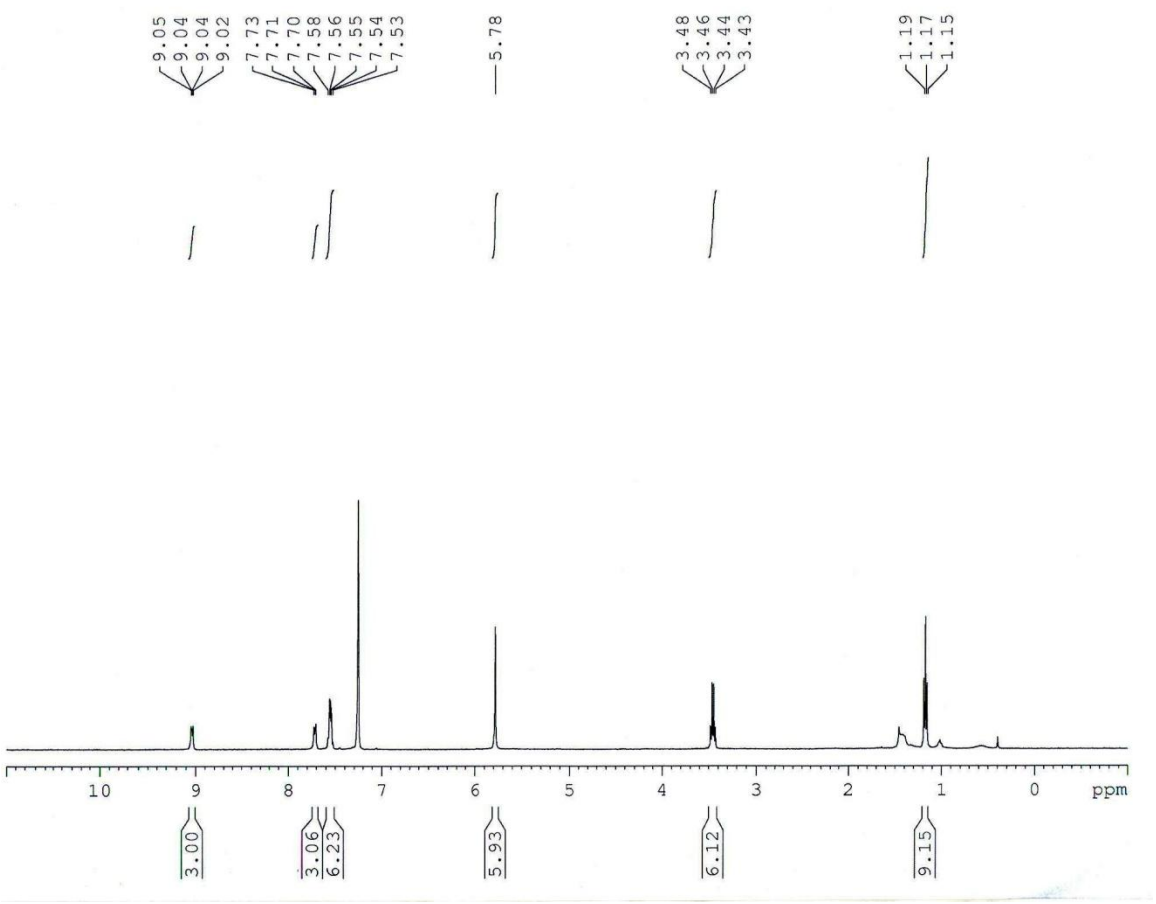


Figure **S72.** ^{1}H-NMR spectrum of compound **4i**

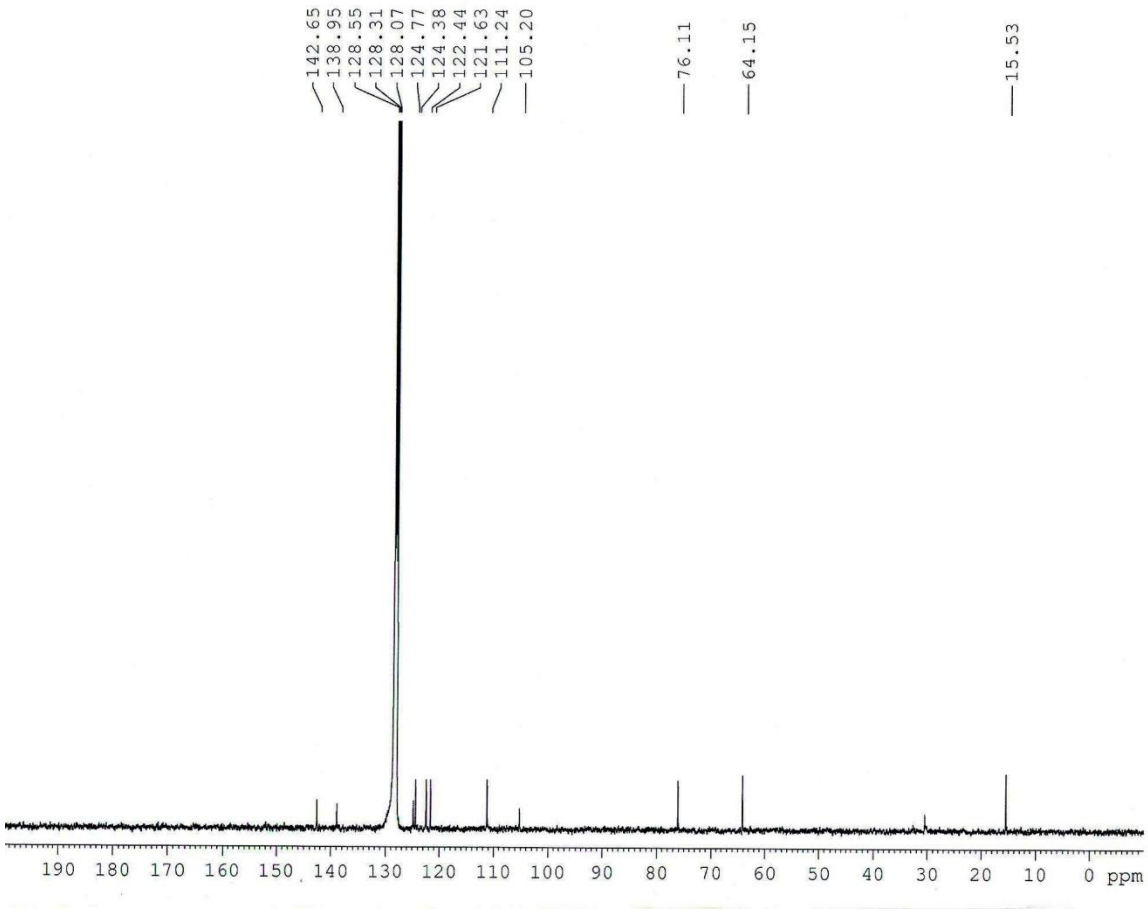


Figure **S73.** ^{13}C-NMR spectrum of compound **4i**

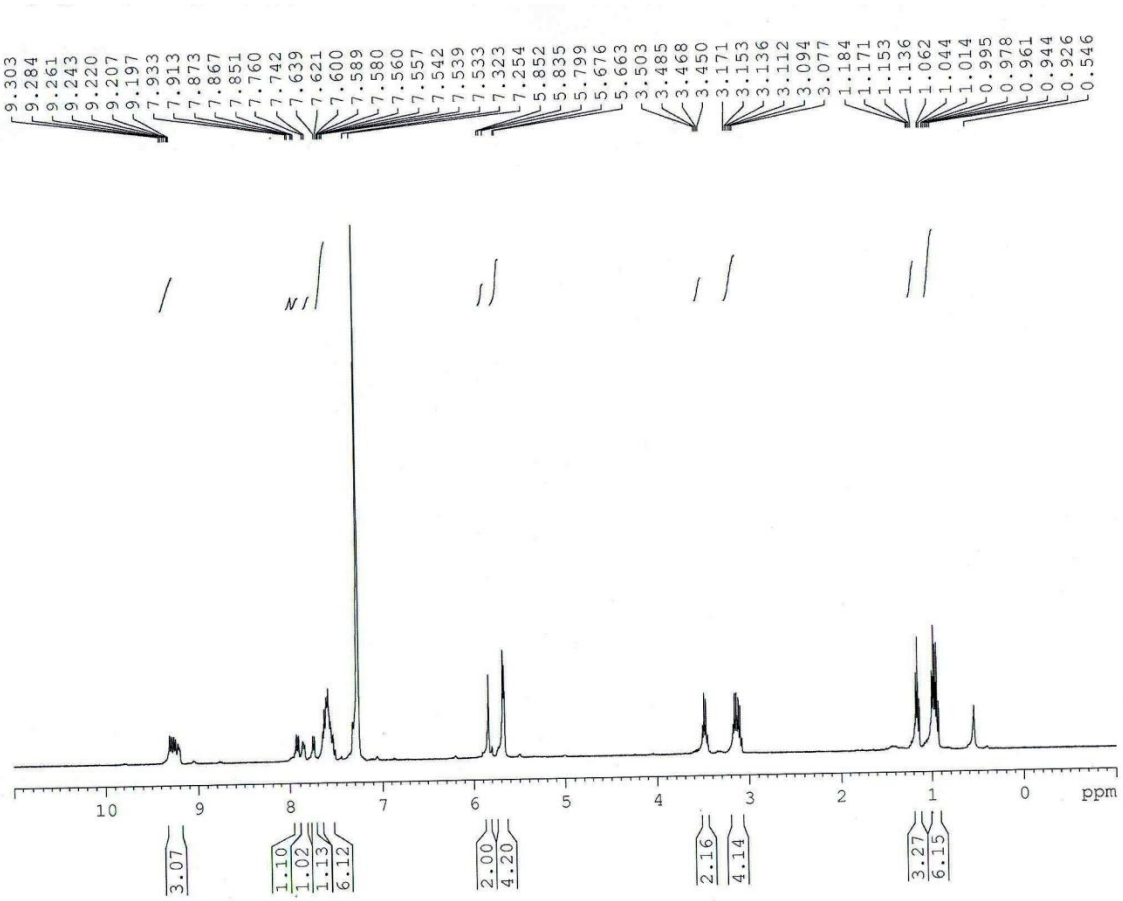


Figure **S74.** ^{1}H-NMR spectrum of compound **5i**

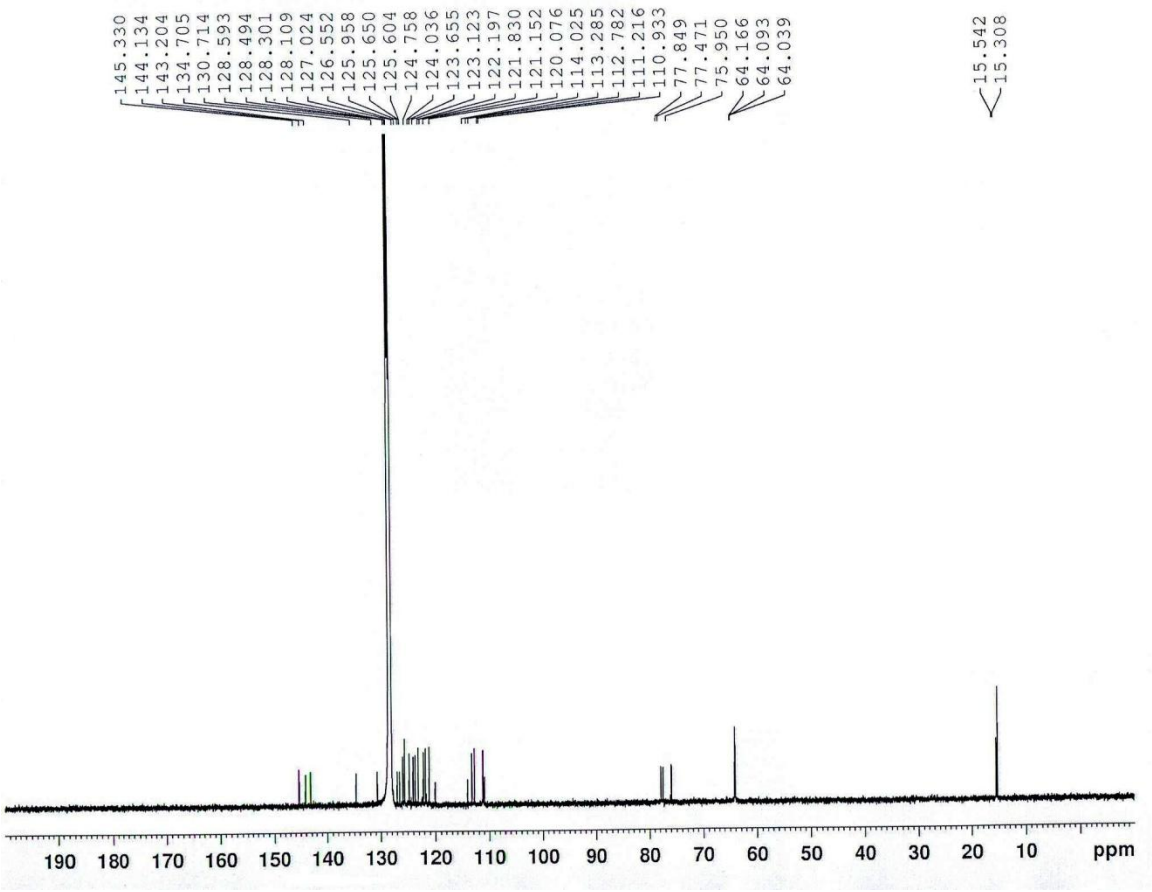


Figure **S75.** ^{13}C-NMR spectrum of compound **5i**

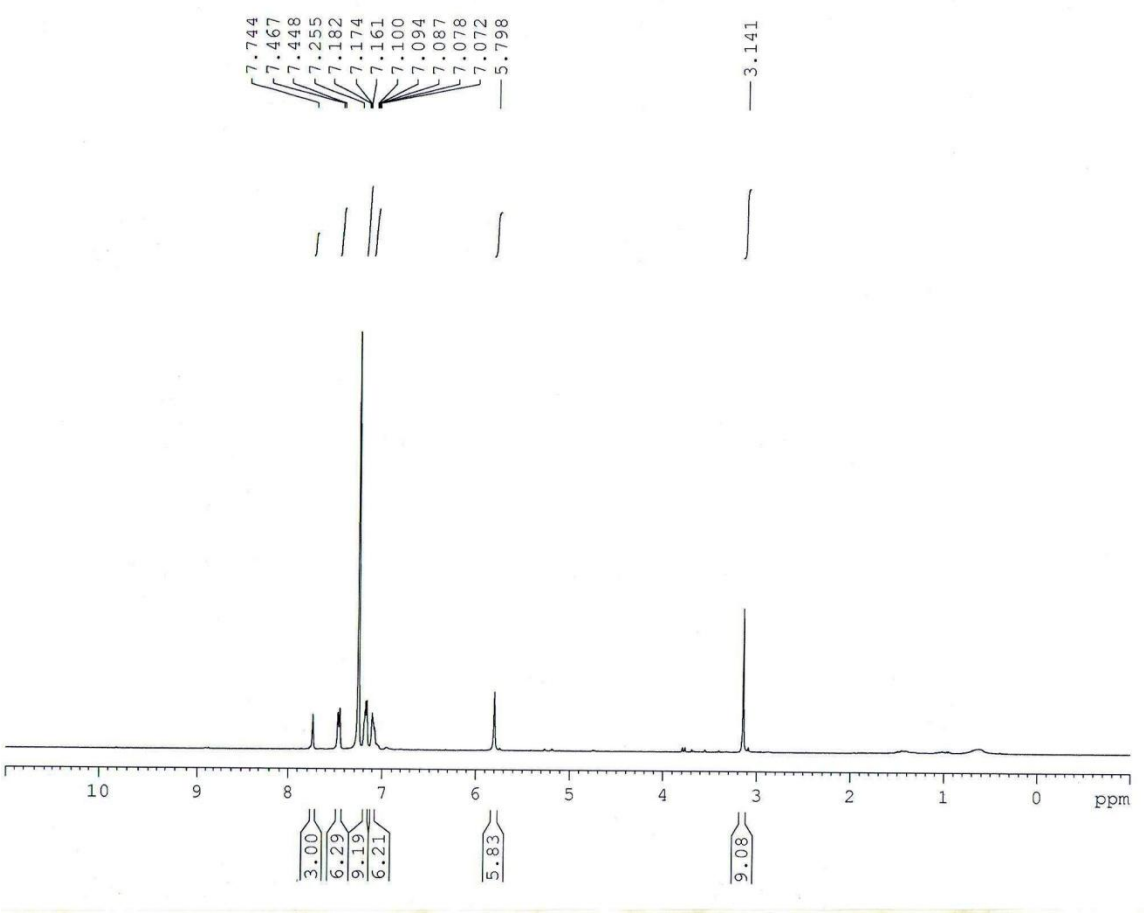


Figure S76. ^{1}H-NMR spectrum of compound **4k**

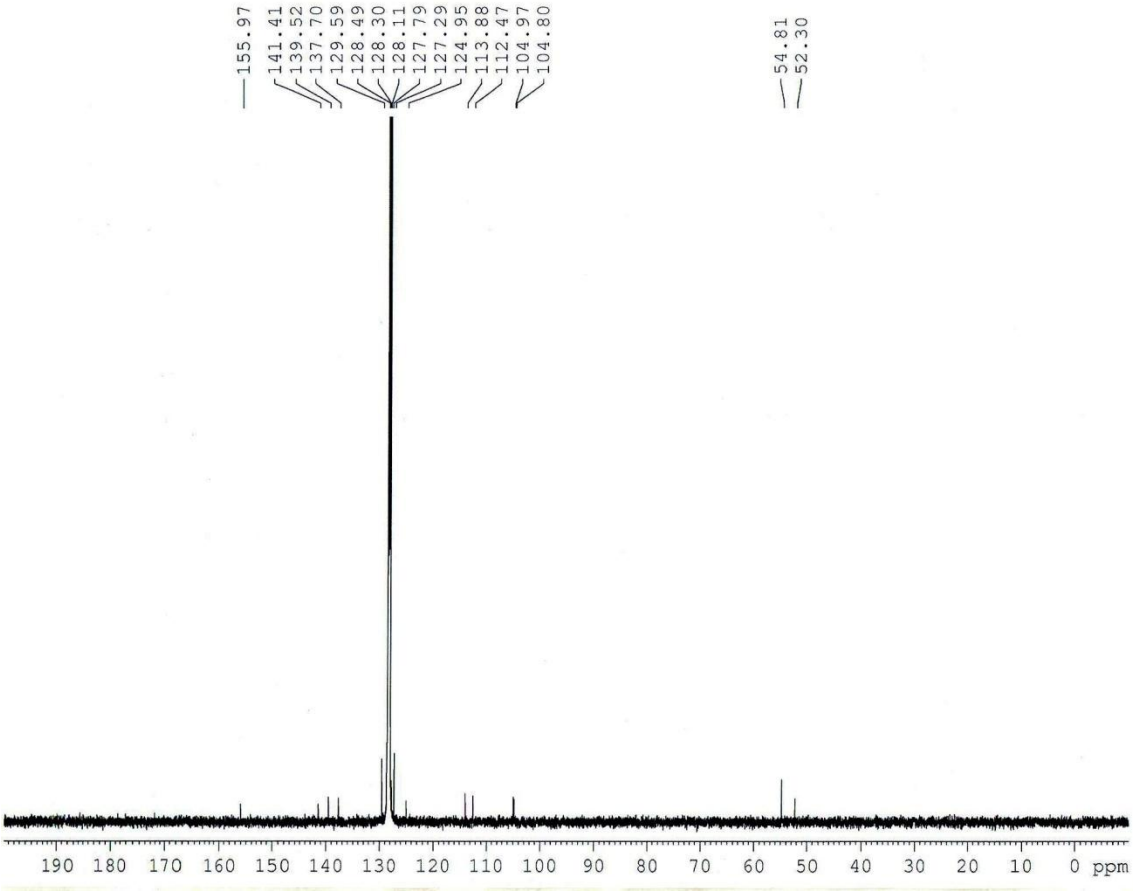


Figure S77. ^{13}C-NMR spectrum of compound **4k**

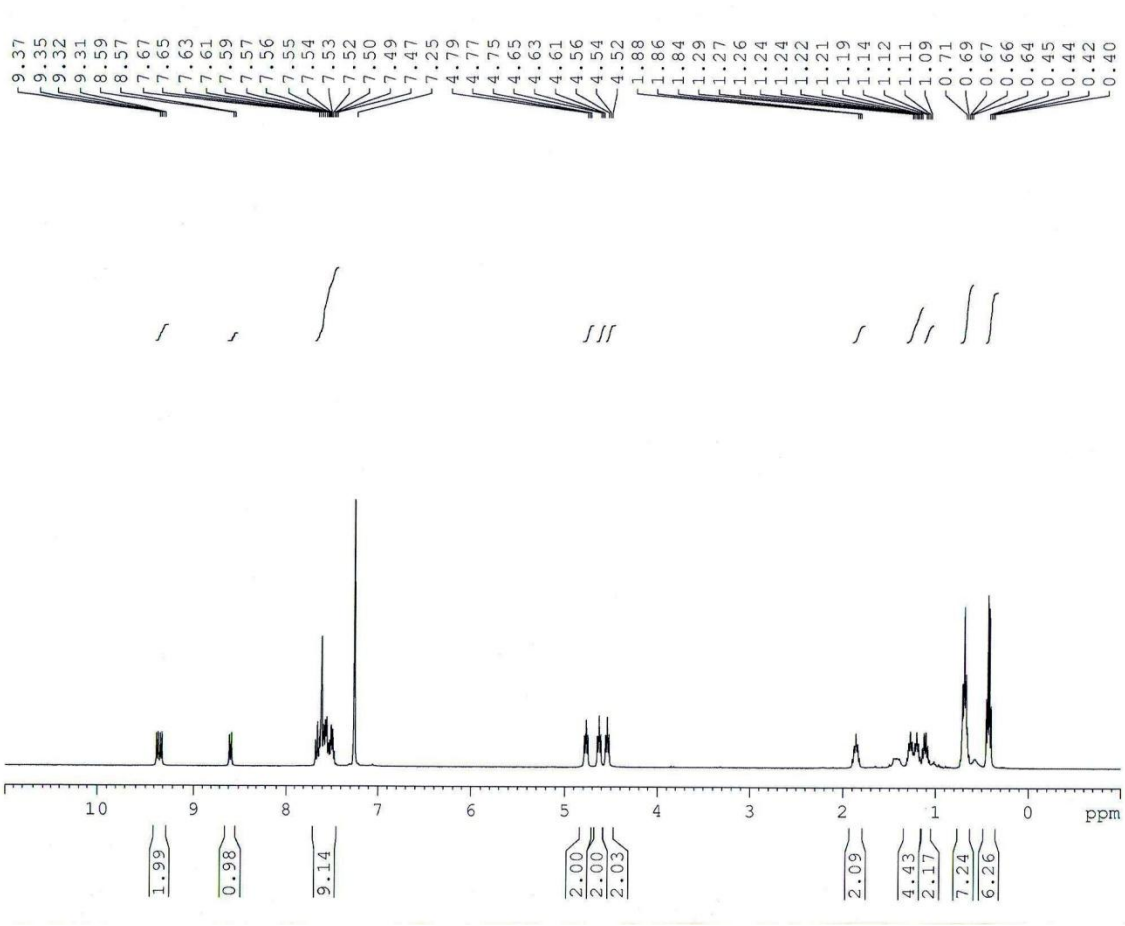


Figure S78. ^{1}H-NMR spectrum of compound **5l**

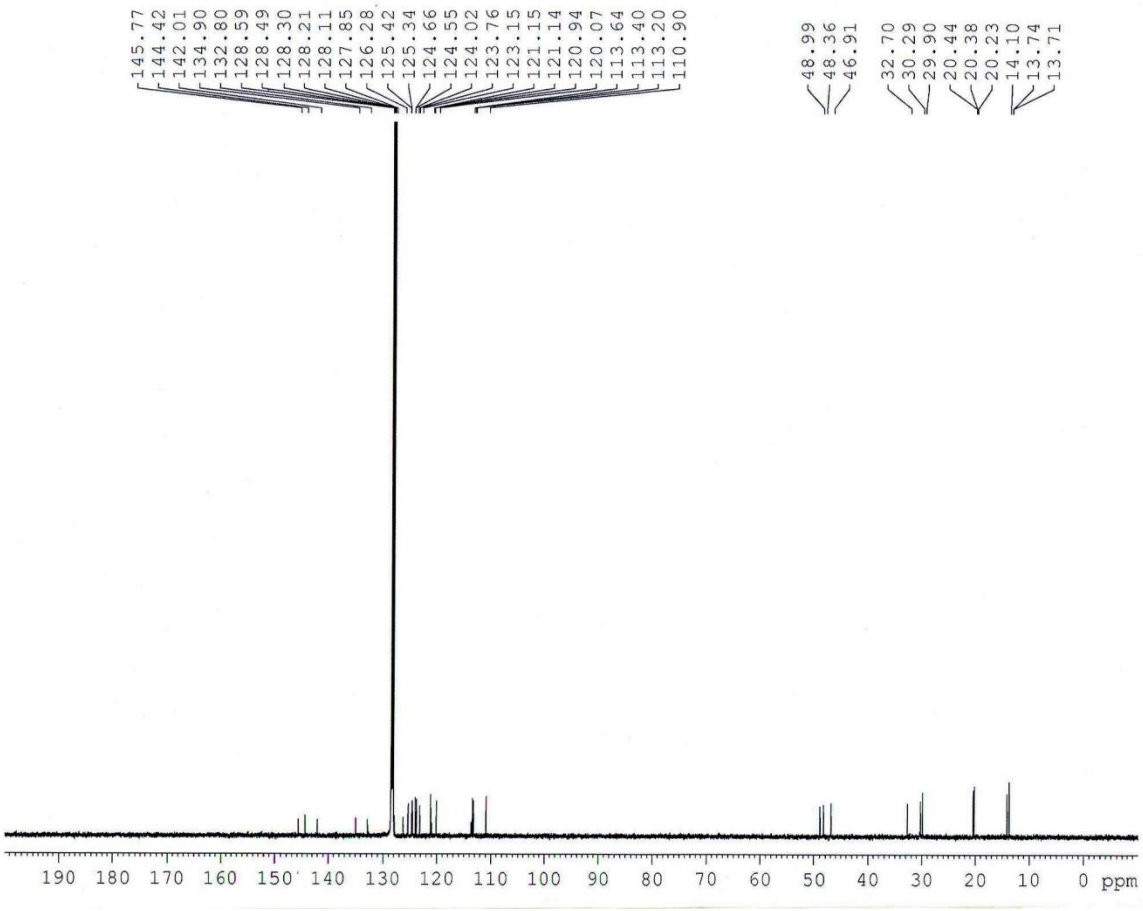


Figure S79. ^{13}C-NMR spectrum of compound **5l**