Supporting Information

Synthesis and Photophysical Properties of Diethynylated Bibenzofuran and Benzodifuran Derivatives

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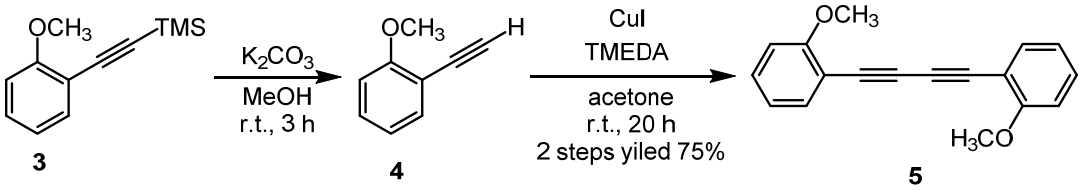
CONTENTS

1. General

FT-IR spectra were recorded on a JASCO FT/IR-4100 instrument. ^{1}H-NMR spectra were recorded at 400 MHz and ^{13}C-NMR spectra at 100 MHz on JEOL a JEOL JNM-AL400. Chemical shifts were reported in ppm relative to tetramethylsilane or residual solvent as the internal standard. MS spectral analyses were performed on a Bruker micrOTOF II spectrometer. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 m X 20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as an eluent.

2. Reaction Procedure

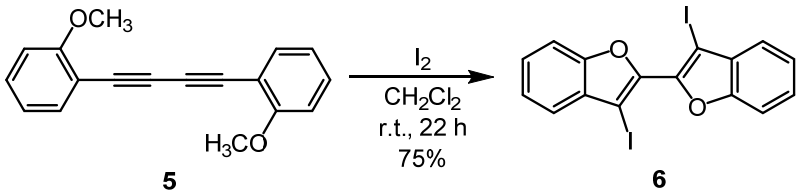
2-1. Procedure for Synthesis of Diiodo Bibenzofuran Derivative 6.



3 4 5

To a solution of **3** (3.07 g, 15.0 mmol) in MeOH (30 mL) was added K_2CO_3 (4.19 g, 30.3 mmol) at room temperature for 3 h. After filtration of the reaction mixture and the removal of solvent, the residue was diluted with AcOEt and the organic layer was washed with saturated NH_4Cl aq. and brine. The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude **4** (1.97 g) was obtained and used next step without purification.

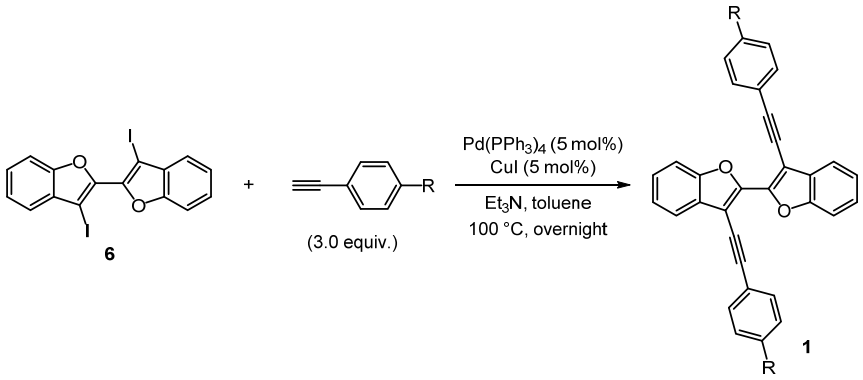
A solution of the above crude **4** was added to the solution of TMEDA (0.175 g, 1.51 mmol) and CuI (0.143 g, 0.751 mmol) in acetone (30 mL) and the reaction mixture was stirred at room temperature under air. After stirring at room temperature for 20 h, the mixture was concentrated under reduced pressure and extracted with $CHCl_3$ and water. The organic layer was washed with saturated NH_4Cl aq. and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue solid was washed with hexane to give the corresponding butadiyne **5**[1] (75% yield (2 steps from **3**), 1.48 g, 5.64 mmol).



5 6

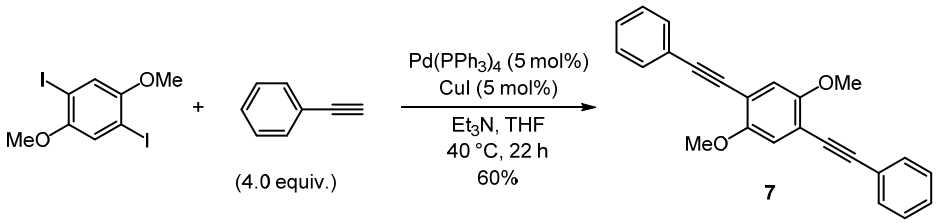
A solution of **5** (1.58 g, 6.02 mmol) in CH_2Cl_2 (40 mL) was slowly added a solution of iodine (6.10 g, 24.0 mmol) in CH_2Cl_2 (10 mL) stirred at room temperature for 22 h under a nitrogen atmosphere. The reaction mixture was diluted with saturated $Na_2S_2O_3$ aq.. The precipitation was washed with water and methanol. The solid was purified by recrystallization ($CHCl_3$) to give the corresponding diiodobenzene derivatives **6**[2] (75% yield, 2.21 g, 4.52 mmol).

2-2. General Procedure for Synthesis of 1 (GP1).

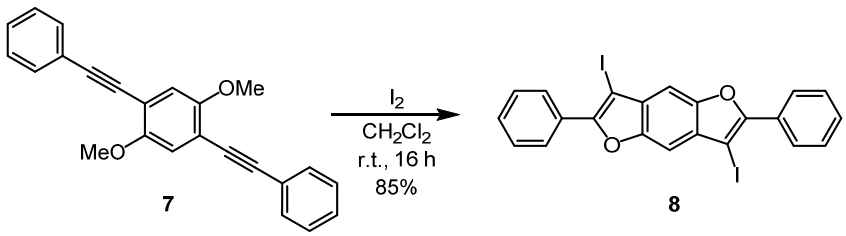


A solution of **6** (1.0 equiv.), aromatic acetylene (3.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), and CuI (5 mol%) in degassed triethylamine and degassed toluene (1:1) was stirred at 100 °C for overnight under a nitrogen atmosphere. After cooling to room temperature, hexane was added to the reaction mixture and then the precipitation was washed with hexane, methanol, and cooling $CHCl_3$. Further purification was carried out by recrystallization to give the corresponding diethynyl bibenzofuran derivatives **1**.

2-3. Procedure for Synthesis of Diiodo Benzodifuran Derivative 7.

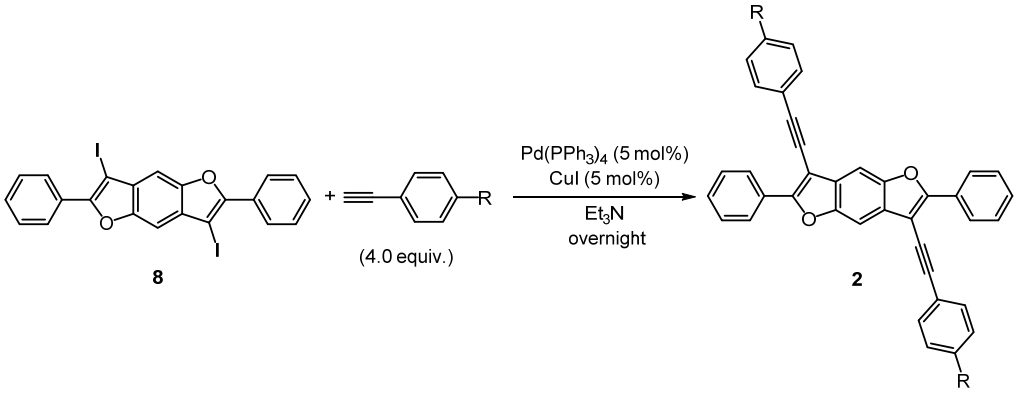


A solution of 1,4-diiodo-2,5-dimethoxybenzene (2.92 g, 7.50 mmol), phenylacetylene (2.30 g, 22.5 mmol), $Pd(PPh_3)_4$ (5 mol%; 0.435 g, 0.38 mmol), and CuI (5 mol%; 0.076 g, 0.40 mmol) in degassed triethylamine (25 mL) and degassed THF (25 mL) was stirred at 40 °C for 22 h under a nitrogen atmosphere. The reaction mixture was diluted with AcOEt and washed with saturated NH_4Cl aq. and brine. The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was washed with hexane to give the corresponding diethynylbenzene derivatives **7**[3] (60% yield, 1.52 g, 4.49 mmol).

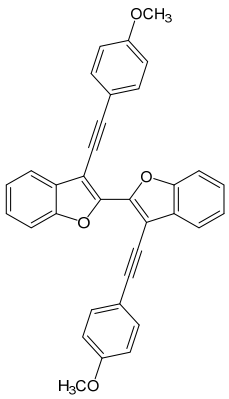


A solution of **7** (0.679 g, 2.01 mmol) in CH_2Cl_2 (24 mL) was slowly added a solution of iodine (3.06 g, 12.04 mmol) in CH_2Cl_2 (8 mL) stirred at room temperature for 16 h under a nitrogen atmosphere. The reaction mixture was diluted with AcOEt and washed with saturated $Na_2S_2O_3$ aq. and then the resulting insoluble solid was washed with water and MeOH to give the corresponding diiodobenzene derivatives **8**[3] (85% yield, 0.953 g, 1.70 mmol).

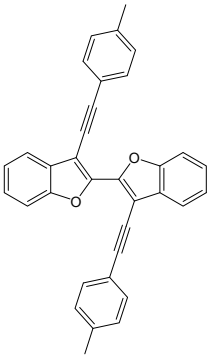
2-4. General Procedure for Synthesis of 2 (GP2).



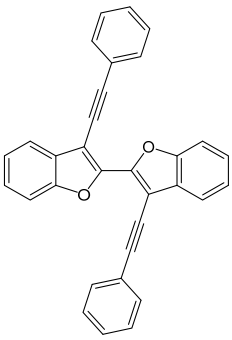
A solution of **8** (1.0 equiv.), aromatic acetylene (4.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), and CuI (5 mol%) in degassed triethylamine and degassed THF (1:1) was stirred at 60 °C (**2a**, **2b**, **2d**) or degassed triethylamine and degassed toluene (1:1) was stirred at 100 °C (**2c**) for overnight under a nitrogen atmosphere. After filtration of the reaction mixture, the resulting solid was washed with MeOH, hexane, and $CHCl_3$. The crude **2** was purified by reprecipitation (hexane and $CHCl_3$) to give the corresponding diethynyl benzodifuran derivatives **2**. Further purification was carried out by recyclable preparative HPLC, if necessary.



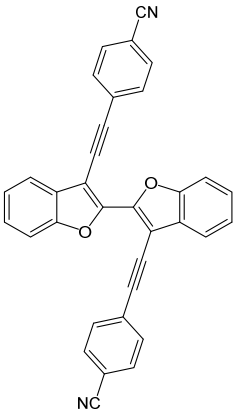
3,3'-bis((4-methoxyphenyl)ethynyl)-2,2'-bibenzofuran (**1a**): Yellow solid. mp 244-245 °C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.57-7.50 (m, 6H), 7.40 (dd, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 4H), 3.84 (s, 6H). ^{13}C-NMR data could not be obtained due to quite low solubility. IR (KBr) 3434, 2925, 2207, 1604, 1496, 1438, 1289, 1246, 1173, 1153, 1140, 1026, 831, 741, 692 cm^{-1}. MS (APCI) m/z 494 (M^+); HRMS (APCI): calcd for $C_{34}H_{22}O_4$: 494.1518 found 494.1514.



3,3'-bis(*p*-tolylethynyl)-2,2'-bibenzofuran (**1b**): Yellow solid. mp 237-238 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.59-7.53 (m, 6H), 7.42 (td, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.36 (td, *J* = 7.6 Hz, 0.8 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 4H), 2.39 (s, 6H). ^{13}C-NMR (400 MHz, $CDCl_3$) δ 148.0, 138.6, 132.3, 130.7, 129.9, 128.9, 128.4, 127.1, 124.5, 122.9, 121.8, 120.4, 110.7, 103.4, 98.2, 79.6, 21.0. IR (KBr) 2921, 2851, 2203, 1494, 1441, 1338, 1242, 1153, 1139, 875, 809, 740 cm^{-1}. MS (APCI) m/z 462 (M^+); HRMS (APCI): calcd for $C_{34}H_{22}O_2$: 462.1620 found 462.1616.

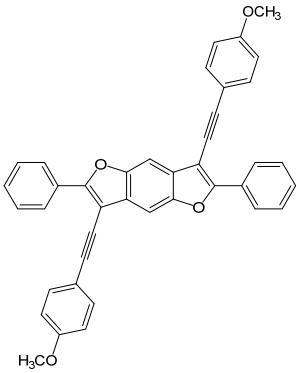


3,3'-bis(phenylethynyl)-2,2'-bibenzofuran (**1c**): Yellow solid. mp 234-235 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J*=7.2 Hz, 2H), 7.64 (dd, *J* = 7.2 Hz, 4H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.39-7.36 (m, 8H). ^{13}C-NMR (400 MHz, $CDCl_3$) δ154.5, 148.1, 131.6, 128.8, 128.5, 128.4, 126.4, 123.8, 123.4, 120.9, 111.6, 103.3, 98.0, 80.2, IR (KBr) 3443, 3057, 2207, 1483, 1473, 1442, 1337, 1240, 1153, 1140, 751, 741, 687 cm^{-1}. MS (APCI) m/z 434 (M^+); HRMS (APCI): calcd for $C_{40}H_{26}O_2$: 434.1307. found 434.1307.

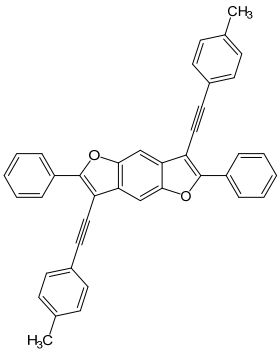


3,3'-bis((4-cyanophenyl)ethynyl)-2,2'-bibenzofuran (**1d**): Yellow solid. mp >300 ℃. ^{1}H-NMR (400 MHz, DMSO-*d*6, 150 °C) δ 7.86 (d, *J*=7.6 Hz, 2H), 7.81-7.76 (m, 8H), 7.72 (d, *J*=8.4 Hz, 7.54 (dd, *J*=7.6 Hz, 2H),

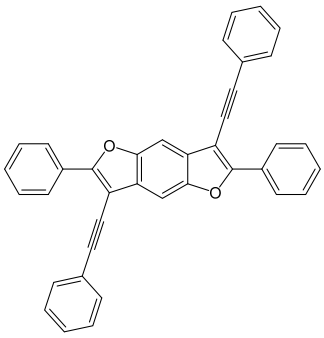
7.46 (dd, *J*=7.6 Hz, 2H). ^{13}C-NMR data could not be obtained due to quite low solubility. IR (KBr) 3441, 3057, 2210, 1636, 1602, 1489, 1442, 1339, 1242, 1156, 1144, 876, 835, 745 cm^{-1}. MS (APCI) m/z 484 (M^+); HRMS (APCI): calcd for $C_{34}H_{16}N_2O_2$: 484.1212 found 484.1201.



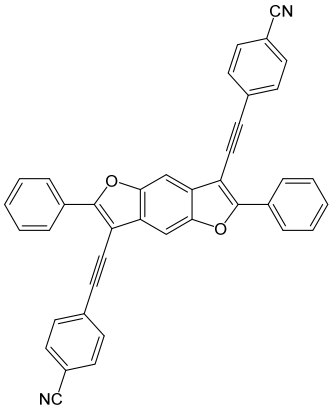
3,7-di-((4-methoxyphenyl)ethynyl)-2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]difuran (**2a**); Yellow solid; m.p. 284-285 ℃; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, *J*=8.0 Hz, 4H), 7.80 (s, 2H), 7.59 (d, *J*=8.8 Hz, 4H), 7.51 (t, *J*=8.4 Hz, 4H), 7.41 (t, *J*=7.2 Hz, 2H), 6.95 (d, *J*=8.8 Hz, 4H), 3.88 (s, 6H); ^{13}C-NMR ($CDCl_3$, 400 MHz)δ 159.8, 156.7, 150.9, 133.0, 130.3, 129.1, 128.7, 126.0, 114.2, 101.52, 101.50, 99.8, 97.2, 55.4; IR (KBr) 3058, 3002, 2964, 2938, 2911, 2838, 2533, 2206, 2045, 1945, 1869, 1609, 1513, 1491, 1464, 1447, 1426, 1391, 1290, 1253, 1174, 1115, 1027, 888, 837, 766, 683, 533 cm^{-1}; MS (APCI) m/z 570 (M^+); HRMS (APCI): calcd for $C_{40}H_{26}O_4$: 570.1831 found 570.1815.



3,7-di-(*p*-tolylethynyl)-2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]difuran(**2b**): Yellow green solid. mp >300 ℃. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.37 (d, *J*=8.4 Hz, 4H), 7.81 (s, 2H), 7.56 (d, *J*=8.4 Hz, 4H), 7.52 (t, *J*=8.0 Hz, 4H), 7.42 (tt, *J*=7.6 Hz, 1.6 Hz, 2H), 7.24 (d, *J*=8.8 Hz, 4H), 2.42 (s, 6H), ^{13}C-NMR ($CDCl_3$, 400 MHz) δ150.9, 138.7, 131.4, 129.3, 129.2, 129.1, 128.72, 128.69, 126.00, 125.98, 120.3, 101.5, 99.7, 97.4, 21.6, IR (KBr) 3053, 3027, 2919, 2861, 2209, 1888, 1685, 1600, 1562, 1513, 1492, 1427, 1395, 1360, 1251, 1152, 1113, 1095, 810, 767, 687, 505 cm^{-1}; MS (APCI) m/z 538 (M^+); HRMS (APCI): calcd for $C_{40}H_{26}O_2$: 538.1933. found 538.1914.



3,7-di-(phenylethynyl)-2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]difuran (**2c**); Yellow green solid. mp 296-297 ℃. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, *J*=7.6 Hz, 4H), 7.80 (s, 2H), 7.66 (d, *J*=7.2 Hz, 4H), 7.52 (t, *J*=7.2 Hz, 4H), 7.43-7.42 (m, 8H); ^{13}C-NMR ($CDCl_3$, 400 MHz) δ 150.9, 131.6, 130.16, 130.15, 129.3, 128.73, 128.72, 128.5, 126.0, 123.3, 101.5, 99.6, 99.5, 97.2, 81.0. IR (KBr) 3055, 3031, 2208, 1950, 1879, 1801, 1750, 1671, 1600, 1584, 1567, 1482, 1426, 1391, 1247, 1153, 1114, 1069, 839, 764, 688 cm^{-1}. MS (APCI) m/z 510 (M^+); HRMS (APCI): calcd for $C_{38}H_{22}O_2$: 510.1620 found 510.1616.



3,7-di-((4-cyanophenyl)ethynyl)-2,6-diphenylbenzo[1,2-*b*:4,5-*b*′]difuran (**2d**); Yellow solid. mp >300 ℃. ^{1}H-NMR (DMSO-*d*6, 400 MHz, 150 ℃) δ 8.28 (d, *J*=8.0 Hz, 2H), 8.02-7.95 (m, 1H), 7.88-7.87 (m, 2H), 7.79-7.74 (m, 1H), 7.66-7.51 (m, 4H). ^{13}C-NMR data could not be obtained due to quite low solubility. IR (KBr) 3448, 2991, 2924, 2378, 2342, 2222, 2206, 1655, 1636, 1228, 1092, 957, 809 cm^{-1}; MS (APCI) m/z 560 (M^+); HRMS (APCI): calcd for $C_{40}H_{20}N_2O_2$: 560.1525 found 560.1495.

3. Computational Study of 1 and 2

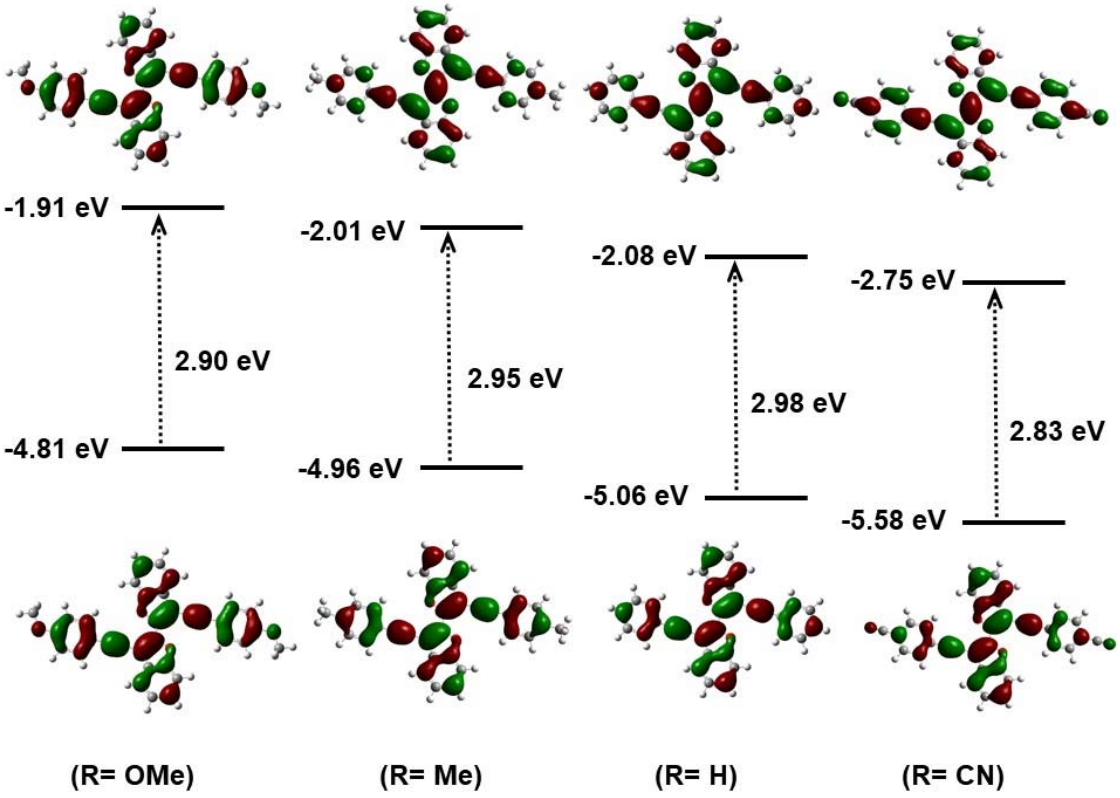


Figure S1. Plot of the Kohn-Sham HOMO and LUMO energy levels of **1** by using B3LYP/6-31G(d) level.

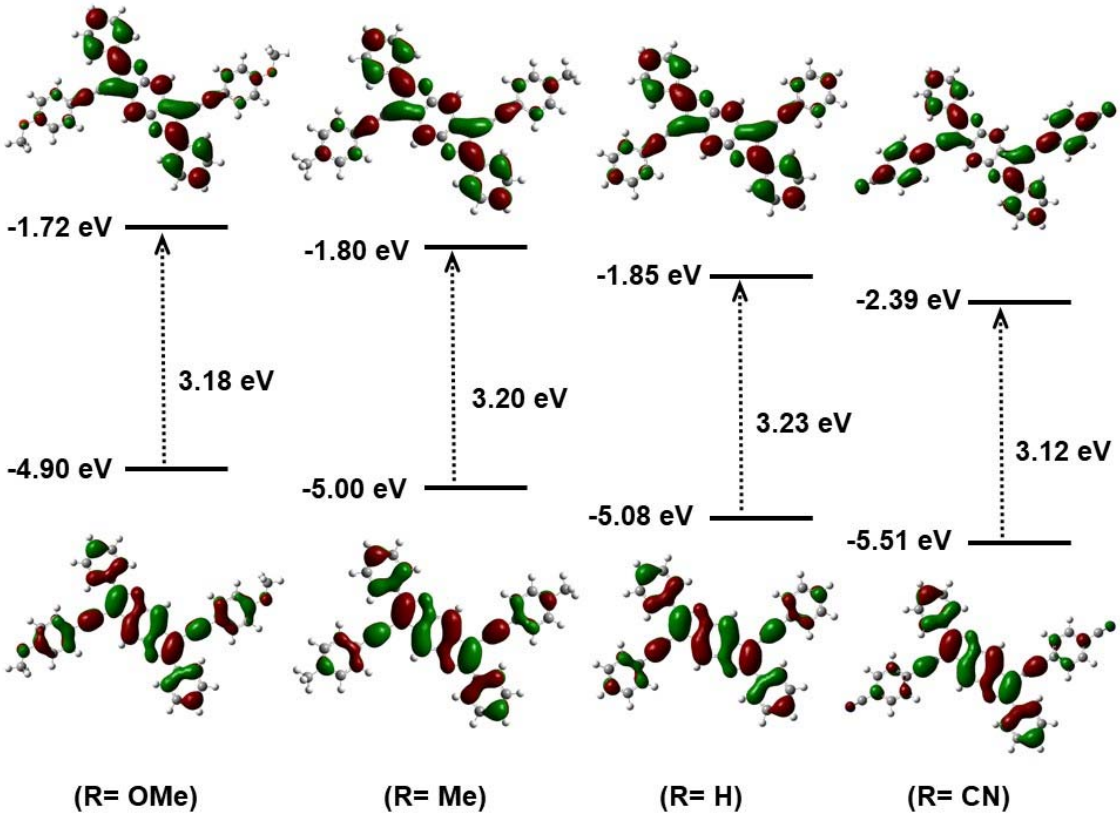


Figure S2. Plot of the Kohn-Sham HOMO and LUMO energy levels of **2** by using B3LYP/6-31G(d) level.

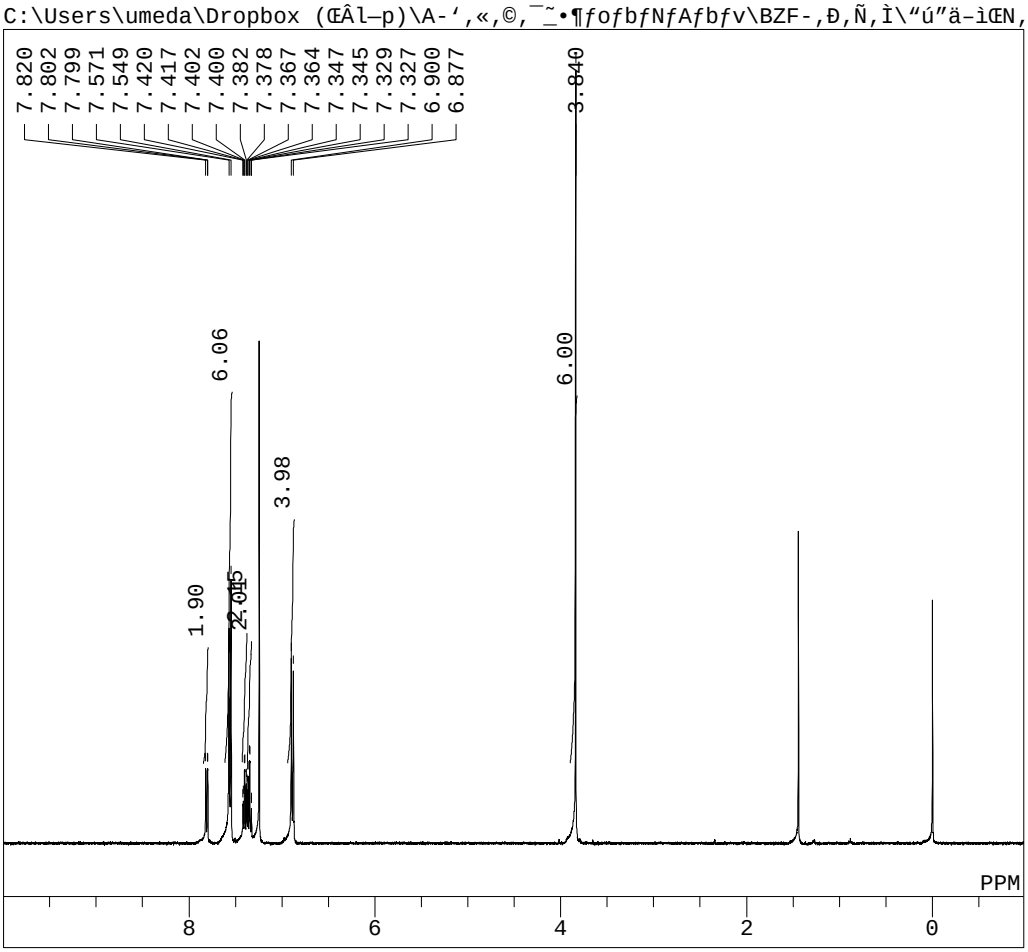
4. Referencesse

[1] Schmidt, R.; Thorwirth, R.; Szuppa, T.; Stolle, A.; Ondruschka, B.; Hopf, H. *Chem. Eur. J.* **2011**, *17*, 8129- 8138.

[2] Okitsu, T.; Nakazawa, D.; Taniguchi, R.; Wada, A. *Org, Lett.* **2008**, *21,* 4947-4970.

[3] Yue, D.; Yao, T.; Larock, R. C. *J. Org. Chem,* **2005**, *70*, 10292-10296.

5. 1H and 13C NMR Spectra of Compounds 1 and 2

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CTEMP          60.0 c
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BF             0.00 Hz
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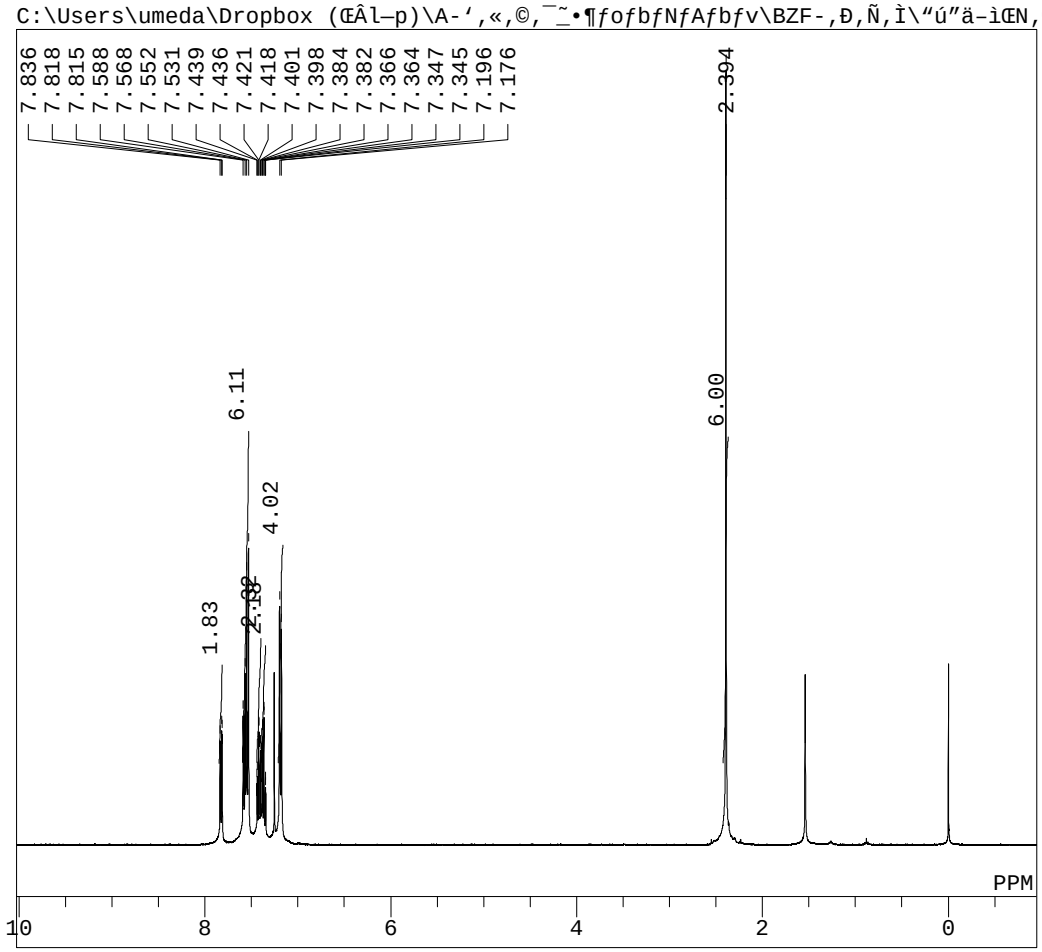
Fig. S1. 1H (400 MHz) spectrum of 1a in $CDCl_3$

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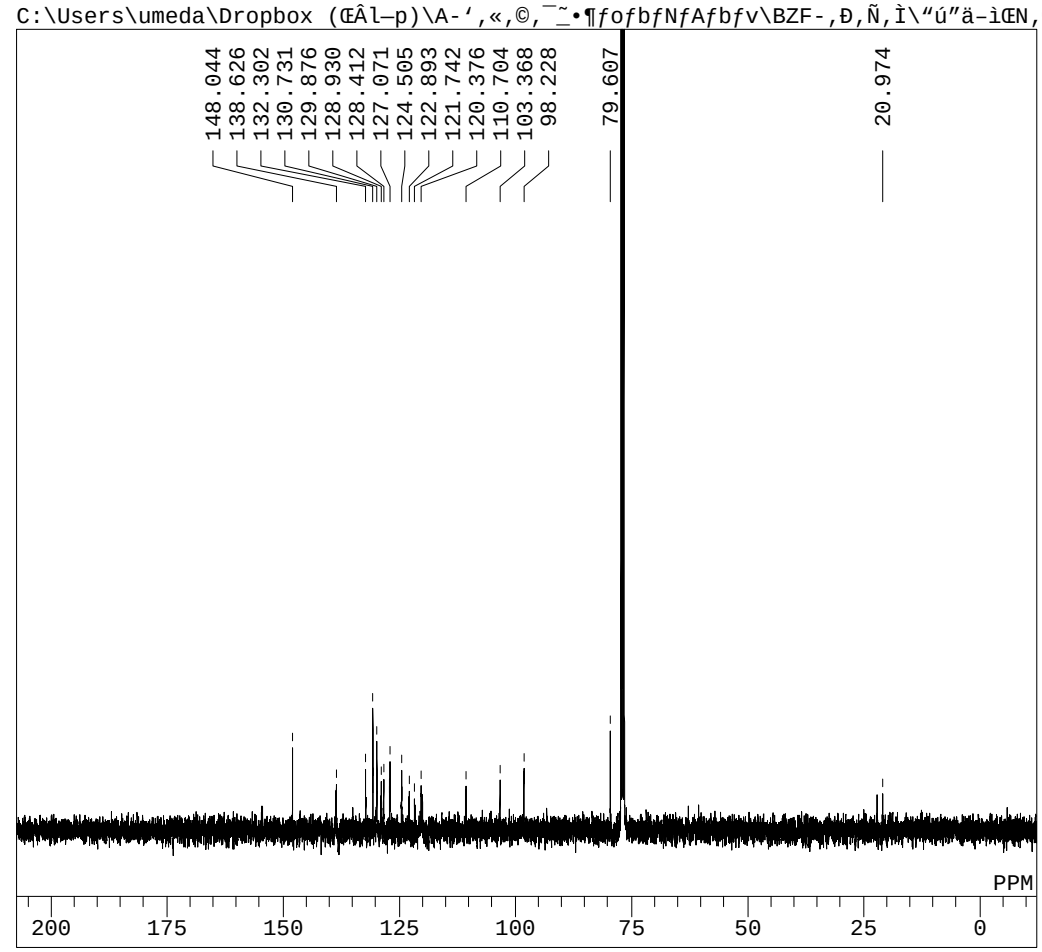


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IRNUC  1H
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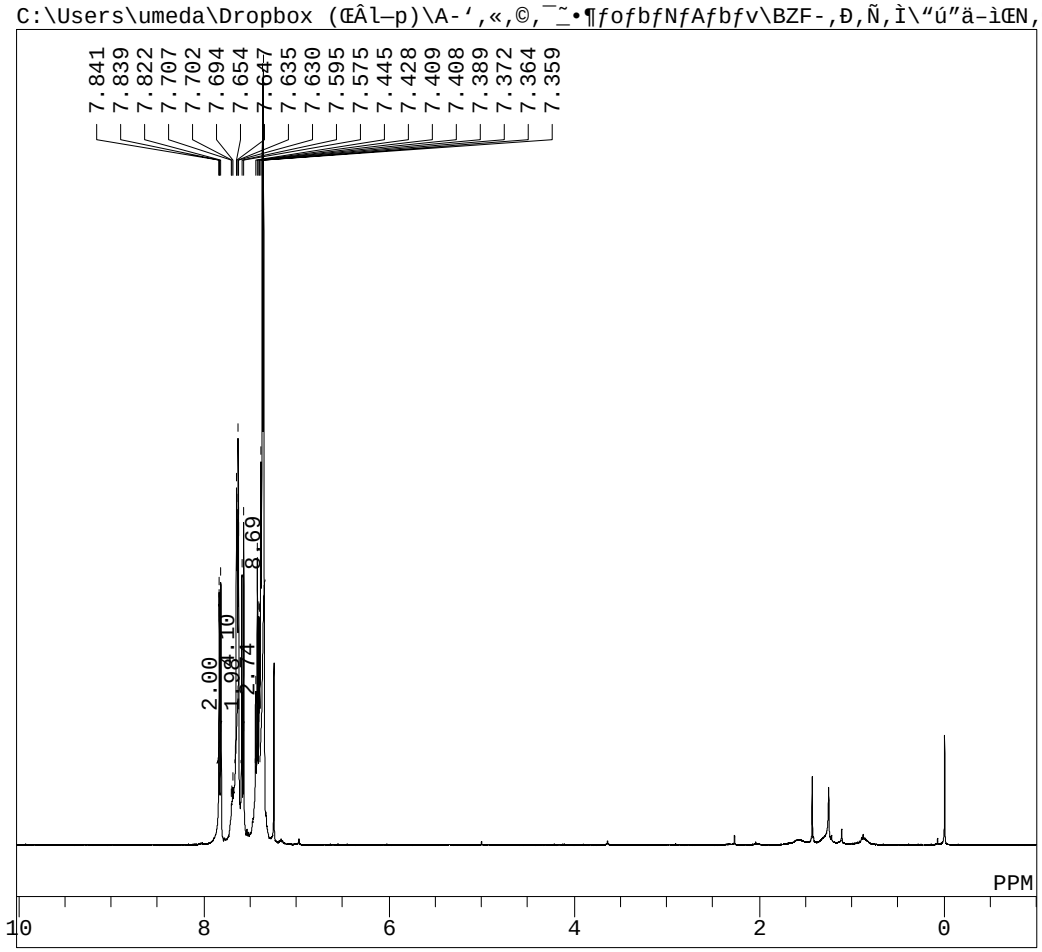
Fig. S2. 1H (400 MHz) and 13C-NMR (100 MHz) spectra of 1b in $CDCl_3$



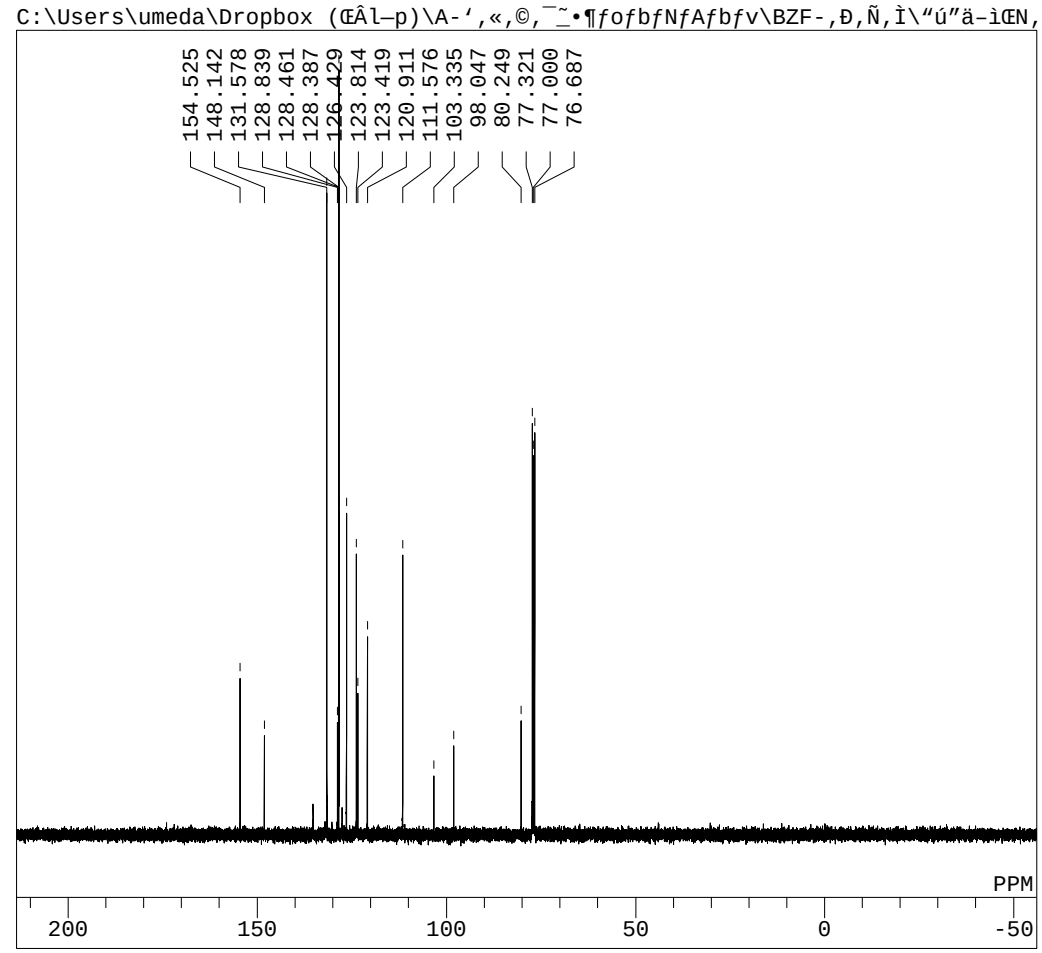


Fig. S3. 1H (400 MHz) and 13C-NMR (100 MHz) spectra of 1c in $CDCl_3$

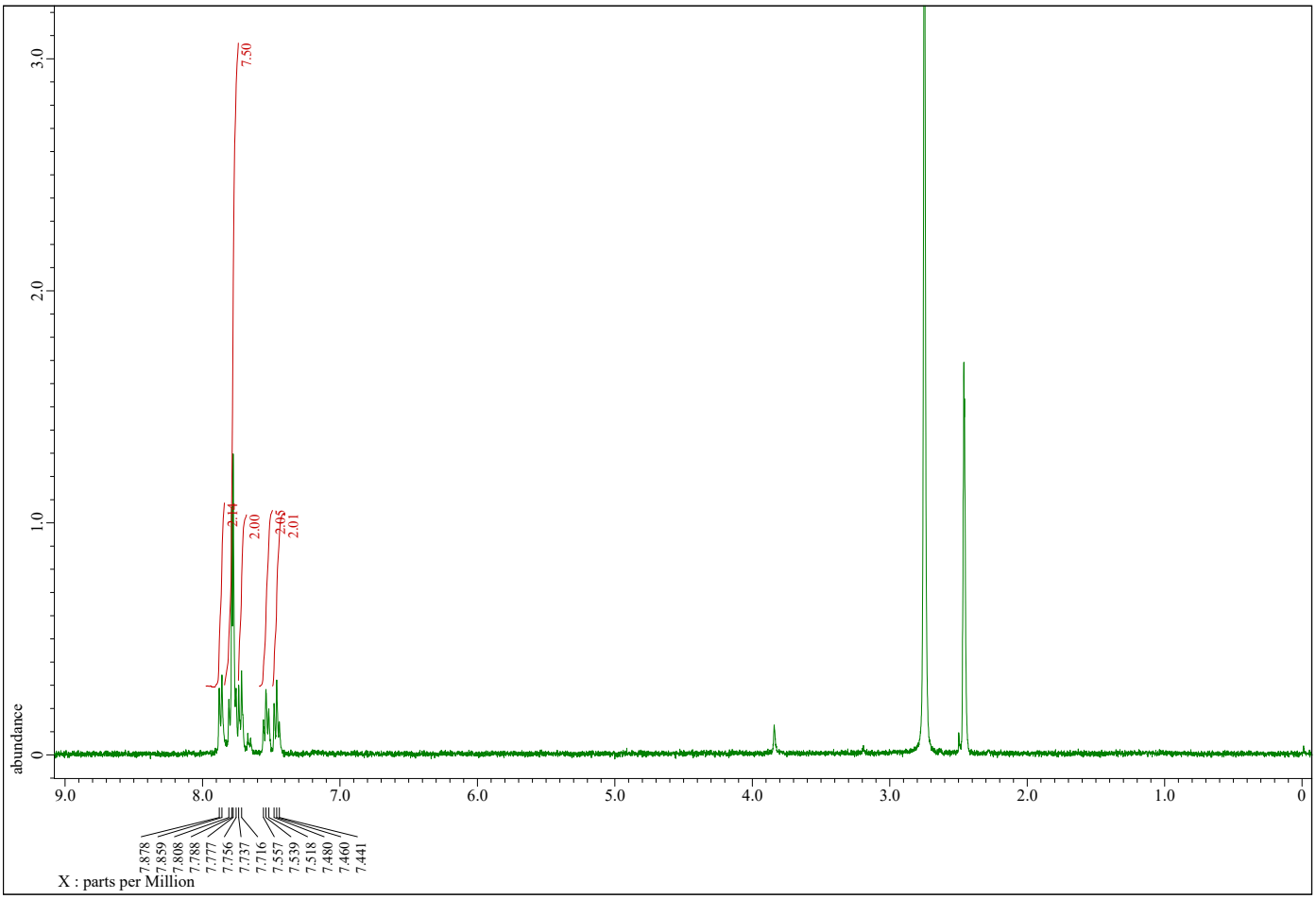
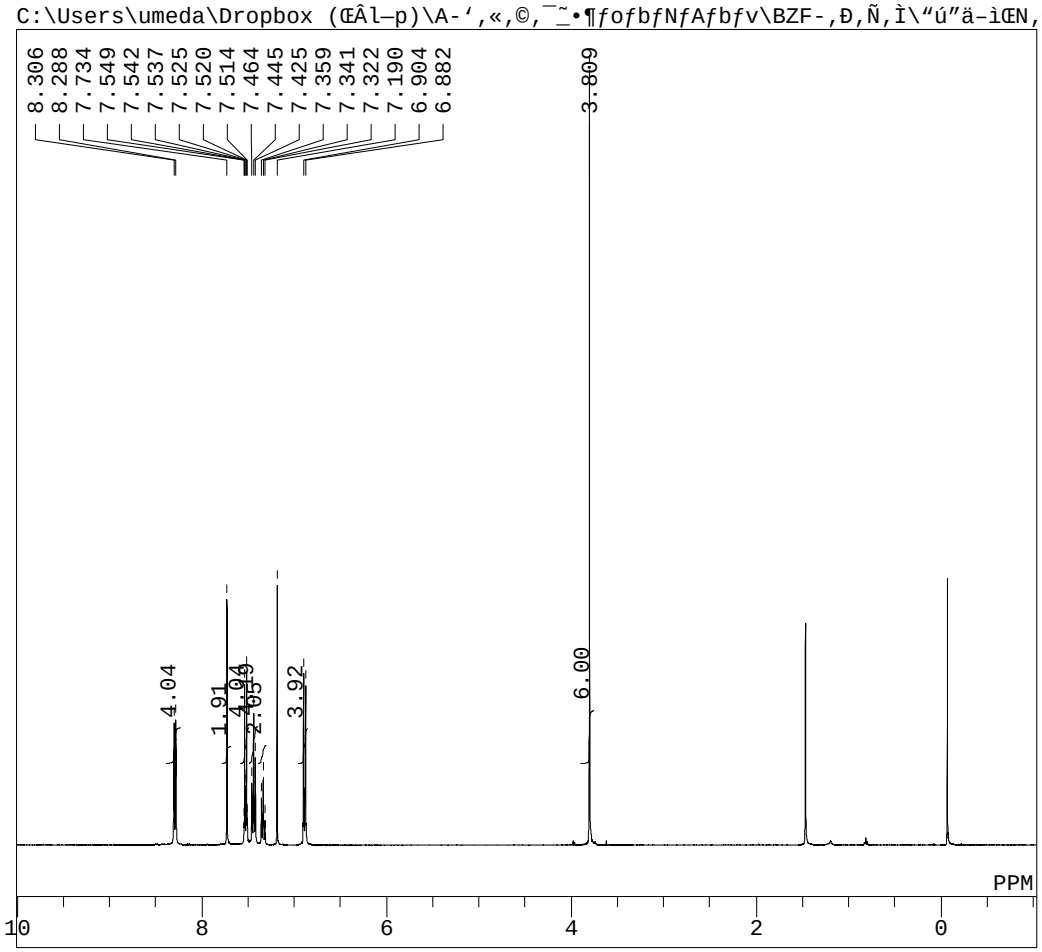


Fig. S4. 1H (400 MHz) spectrum of 1d in DMSO-d_6

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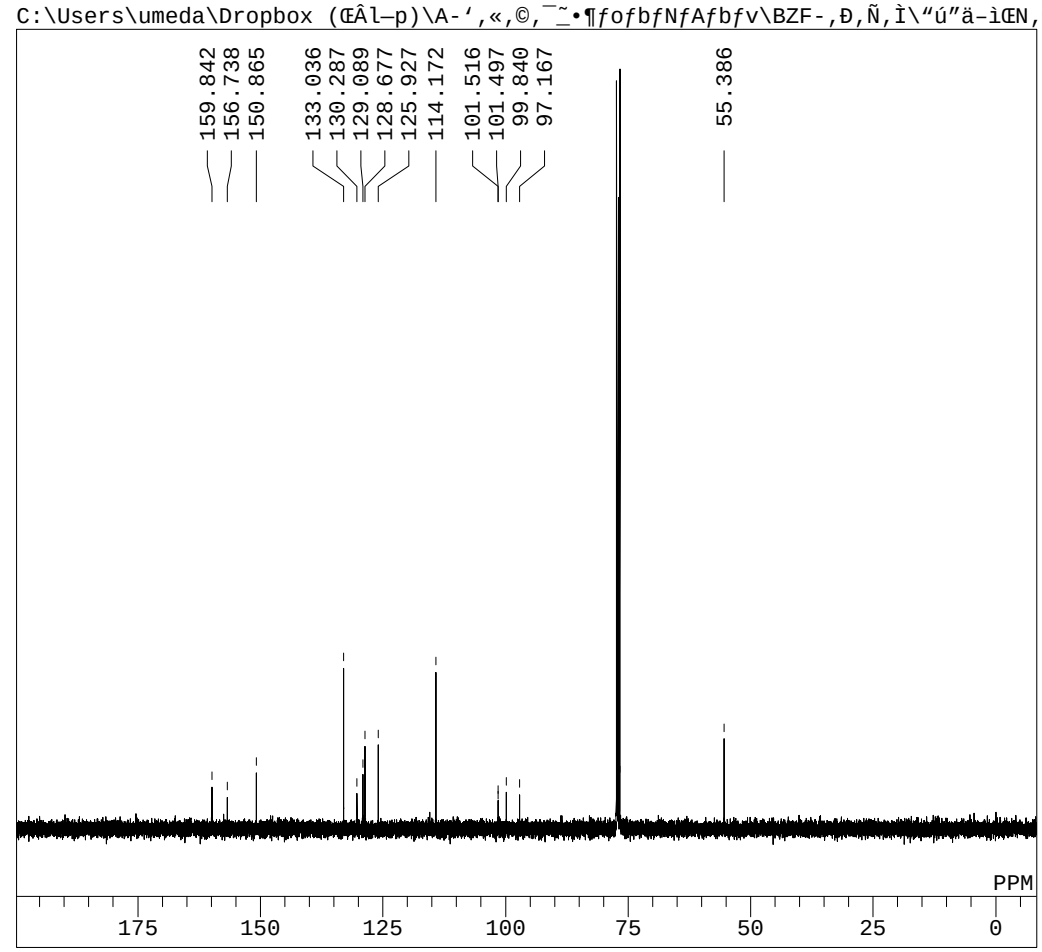
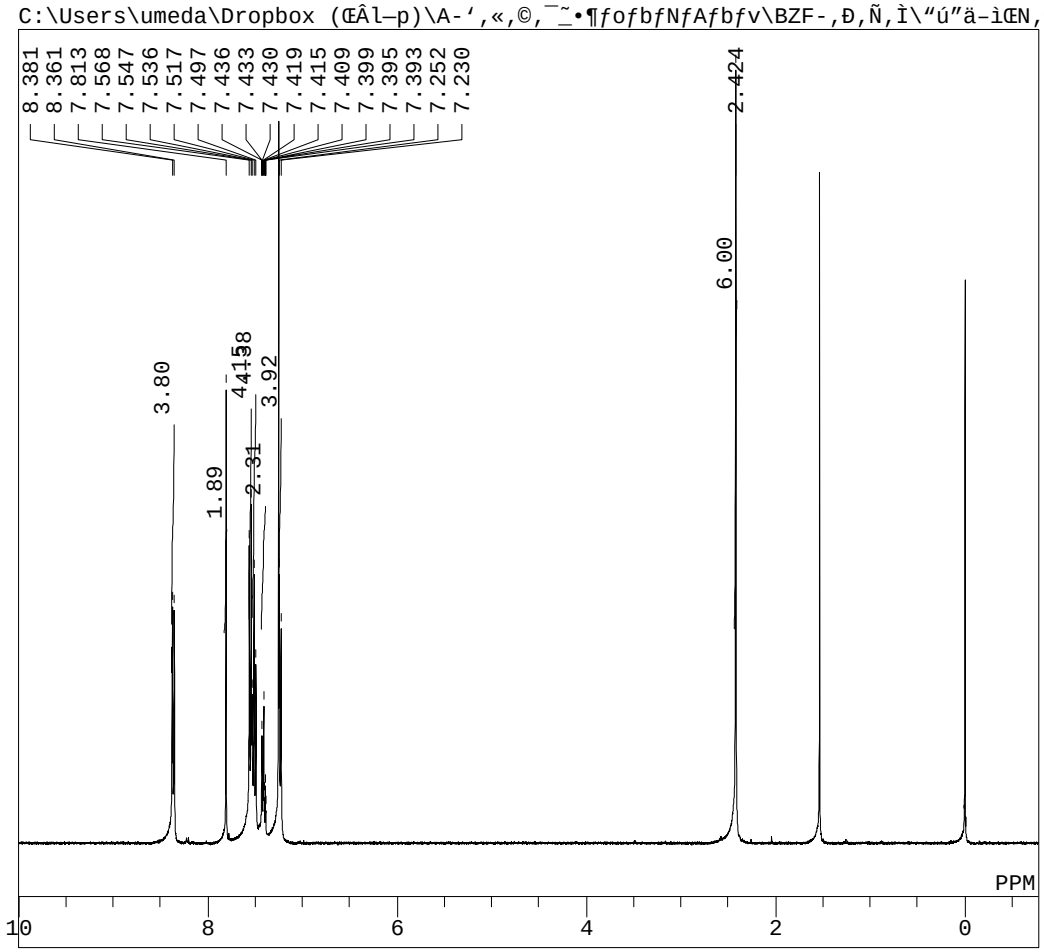
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             19
```

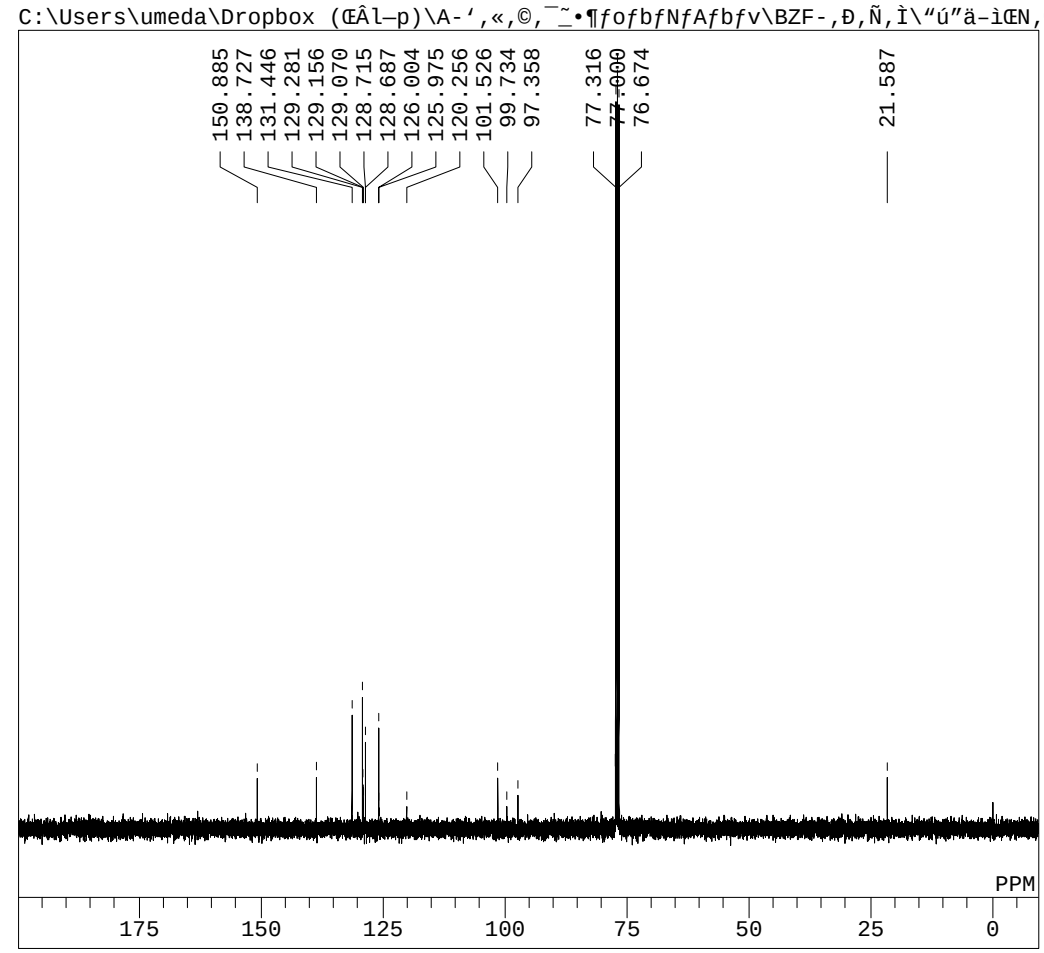



```
DFILE  2a-13C.als
COMNT  single pulse decoupled
DATIM  2021-09-27 09:49:29
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ         99.55 MHz
OBSET          5.13 KHz
OBFIN          0.98 Hz
POINT         26214
FREQU      25000.00 Hz
SCANS          1024
ACQTM         1.0486 sec
PD            2.0000 sec
PW1             3.30 usec
IRNUC  1H
CTEMP           22.6 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.00 Hz
RGAIN             60
```

Fig. S5. 1H (400 MHz) and 13C-NMR (100 MHz) spectra of 2a in $CDCl_3$

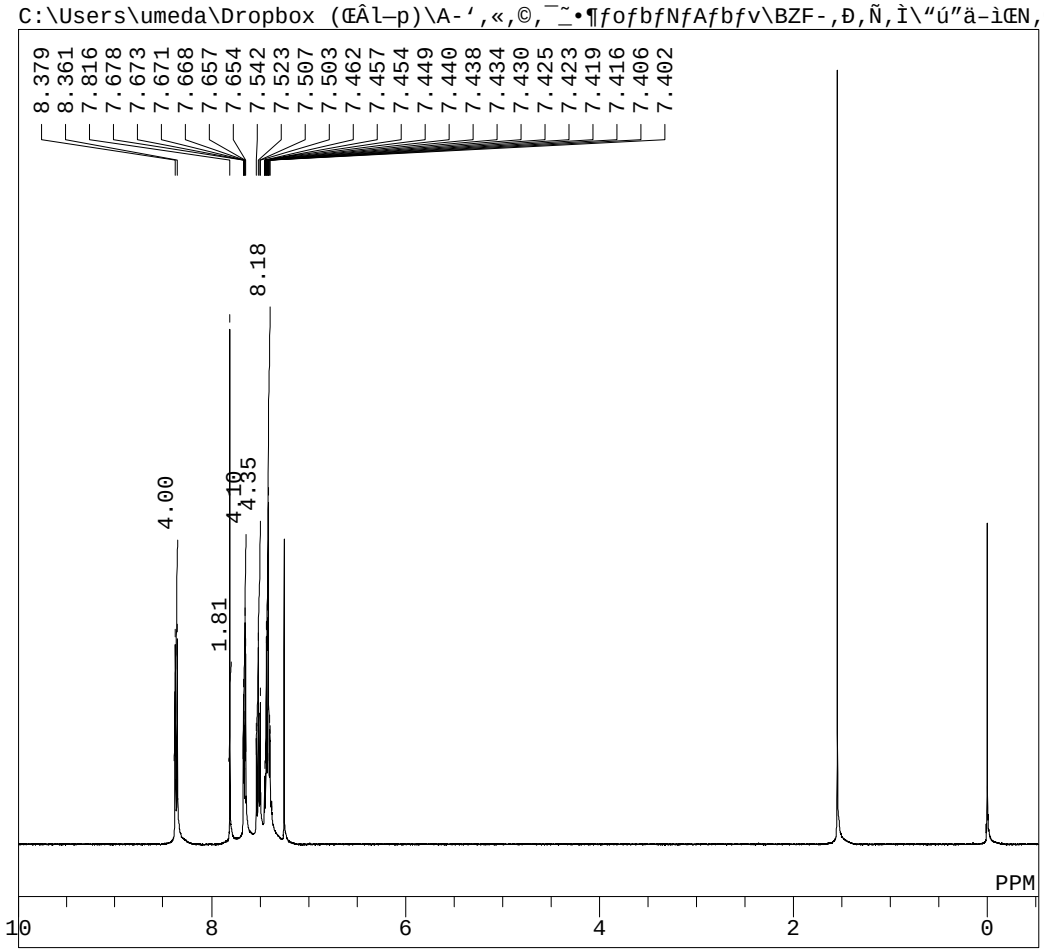



```
DFILE  2b-1H.als
COMNT  single_pulse
DATIM  2021-09-09 16:41:21
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        395.88 MHz
OBSET          6.28 KHz
OBFIN          0.87 Hz
POINT         13107
FREQU       5938.24 Hz
SCANS            16
ACQTM         2.2073 sec
PD            5.0000 sec
PW1             5.50 usec
IRNUC  1H
CTEMP          23.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.00 Hz
RGAIN            80
```

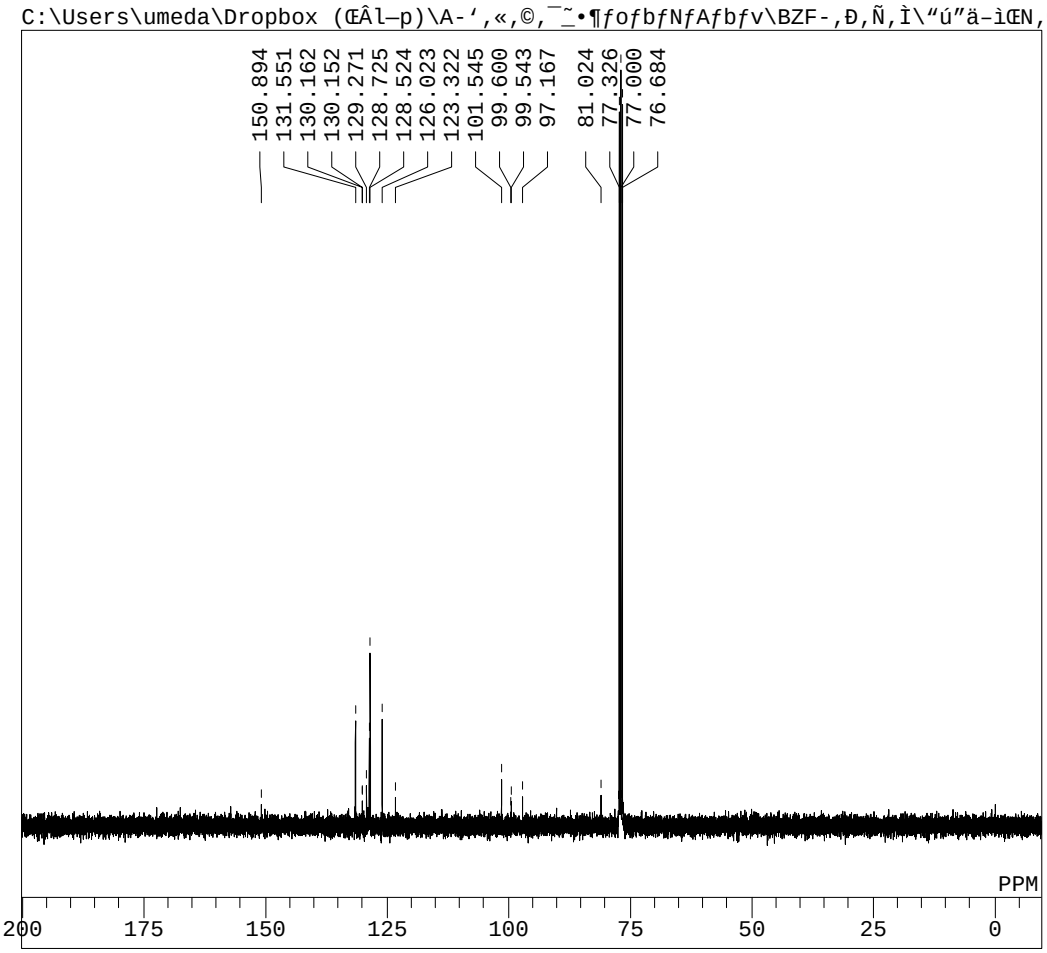



```
DFILE  2b-13C.als
COMNT  single pulse decoupled
DATIM  2021-09-13 10:10:44
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ         99.55 MHz
OBSET          5.13 KHz
OBFIN          0.98 Hz
POINT         26214
FREQU      25000.00 Hz
SCANS          1024
ACQTM         1.0486 sec
PD            2.0000 sec
PW1             3.30 usec
IRNUC  1H
CTEMP          23.1 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.00 Hz
RGAIN            60
```

Fig. S6. 1H (400 MHz) and 13C-NMR (100 MHz) spectra of 2b in $CDCl_3$

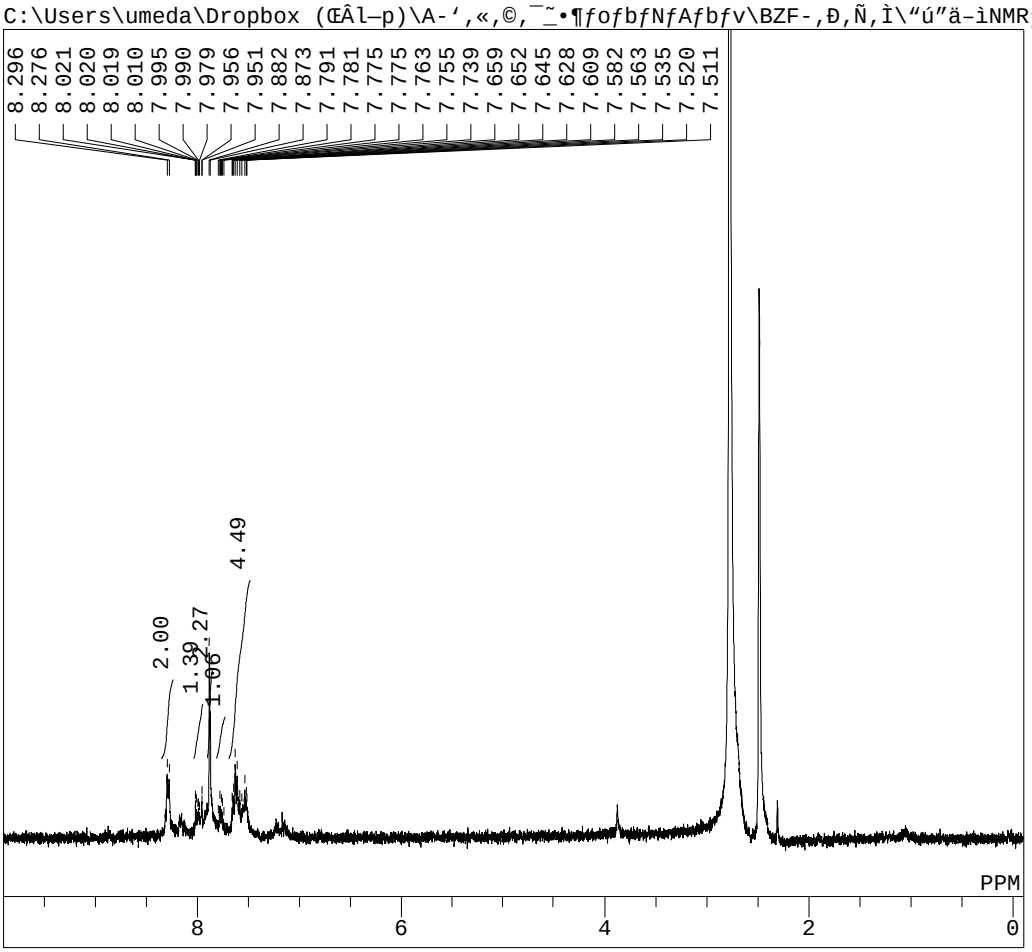



```
DFILE  2c-1H.als
COMNT  single_pulse
DATIM  2021-09-16 09:37:48
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        395.88 MHz
OBSET          6.28 KHz
OBFIN          0.87 Hz
POINT         13107
FREQU       5938.24 Hz
SCANS            16
ACQTM         2.2073 sec
PD            5.0000 sec
PW1             5.50 usec
IRNUC  1H
CTEMP           22.3 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.00 Hz
RGAIN             80
```




```
DFILE  2c-13C.als
COMNT  single pulse decoupled
DATIM  2021-09-16 08:39:15
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ         99.55 MHz
OBSET          5.13 KHz
OBFIN          0.98 Hz
POINT         26214
FREQU      25000.00 Hz
SCANS          1024
ACQTM         1.0486 sec
PD            2.0000 sec
PW1             3.30 usec
IRNUC  1H
CTEMP           22.4 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.00 Hz
RGAIN             60
```

Fig. S7. 1H (400 MHz) and 13C-NMR (100 MHz) spectra of 2c in $CDCl_3$




```
DFILE  hibino-CN-dAtype-DMSO-
COMNT  single_pulse
DATIM  2022-10-10 08:36:26
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        395.88 MHz
OBSET          6.28 KHz
OBFIN          0.87 Hz
POINT         13120
FREQU       5938.24 Hz
SCANS           256
ACQTM        2.2073 sec
PD           5.0000 sec
PW1            5.63 usec
IRNUC  1H
CTEMP         150.1 c
SLVNT  DMSO
EXREF          2.49 ppm
BF             0.00 Hz
RGAIN           102
```

Fig. S8. 1H (400 MHz) spectrum of 2d in DMSO-d_6