Electronic Supplementary Information

Ullmann homocoupling of arenediazonium salts in deep eutectic solvent. Synthetic and mechanistic aspects

Giovanni Ghigo, Matteo Bonomo, Achille Antenucci, Alessandro Damin and Stefano Dughera

INDEX

Computational method.

The structures of the reactants, intermediates and transition states have been optimized by using the density functional method (DFT)[1] with the functional M06[2,3] and the basis sets def2-TZVPD. Then, the electronic energy values where refined by single-point (SP) calculations with the basis set def2-TZVPPD.[4–6] The nature of the critical points was characterized by using vibrational analysis[7] which also furnished the Zero Point Energies (ZPE) and entropies for the calculations of the Free Energies. These have been converted from the gas phase to the 1 M standard state at 1 atm and 298.15 K[8] and used to calculate the rate constant with the Eyring equation.[9] The solvent effects (glycerol, because at the present a method to mimic DES is not available) were introduced in all calculations using the Polarized Continuum Method (PCM).[10] The following parameter were used: $\varepsilon = 42.5$, $\varepsilon_{inf} = n^2 = (1.4746)^2 = 2.174$. The calculations were performed by the quantum package Gaussian 16-A.03[11] The figures were obtained using the graphical program Molden.[12]

References:

1. R.G. Parr, Density Functional Theory of Atoms and Molecules, in: Horizons Quantum Chem., Springer Netherlands, 1980: pp. 5–15. doi:10.1007/978-94-009-9027-2_2.

2. Y. Zhao and D.G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

3. Y. Zhao and D.G. Truhlar, *Acc. Chem. Res*., 2008, **41**,157.

4. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

5. F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8** , 1057.

6. B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson, and T. L. Windus, *J. Chem. Inf. Model*, 2019, **59**, 4814.

7. J. Foresman and A. Frisch, Exploring chemistry with electronic structure methods, 1996, Gaussian Inc, Pittsburgh, PA, 1996, http://gaussian.com/expchem3/(accessed June 4, 2021).

8. R.F. Ribeiro, A.V. Marenich, C.J. Cramer and D.G. Truhlar, *J. Phys. Chem. B*., 2011, **115**, 14556.

9. K.J. Laidler and M.C. King, *J. Phys. Chem.*, 1983, **87**, 2657.

10. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.

11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision A.03, (2016).

12. G. Schaftenaar and J.H. Noordik, *J. Comput. Aided Mol. Des.*, 2000, **14**, 123–134.

Table 1. Calculated absolute and relative (in kcal mol^{-1}) energies for the fluorinations of the reactants, 4-nitrobenzendiazonium tetrafluoborate **1a** and copper(I) chloride.

DiazoCation TFB Fluorination		E /au[a]	**ΔE[a]**	E^{0K} /au[a]	**ΔE^{0K} [a]**	G^{298K} /au[a]	**Δn**	**ΔG^{298K} [a]**	E(SP) /au[b]	**$\Delta E_{SP}{}^{0K}$ [c]**	**ΔG^{298K} [c]**
4-O_2N-C_6H_4-NN^+ BF_4^- (**ArN_2 BF_4**)		-969.973053		-969.856705		-969.901673	**0**		-969.975340		
F^-		-99.989585		-99.989585		-100.003744			-99.989585		
ArN_2^+ BF_4^- + F^-		-1069.962639	**0.00**	-1069.846290	**0.00**	-1069.905417	**0**	**0.00**	-1069.964925	**0.00**	**0.00**
4-O_2N-C_6H_4-NN^+ F^- (**ArN_2 F**)	**I**	-645.294983		-645.193756		-645.232857			-645.294983		
BF_4^-		-424.675305		-424.661237		-424.686468			-424.675305		
ArN_2^+ F^- + BF_4^-		-1069.970288	**-4.80**	-1069.854993	**-5.46**	-1069.919325	**0**	**-8.73**	-1069.970288	**-4.03**	**-7.29**
CuCl Re-Solvations		E /au[a]	**ΔE[a]**	E^{0K} /au[a]	**ΔE^{0K} [a]**	G^{298K} /au[a]	**Δn**	**ΔG^{298K} [a]**	E(SP) /au[b]	**$\Delta E_{SP}{}^{0K}$ [c]**	**ΔG^{298K} [c]**
Cu^ICl R=2.107		-2100.732388		-2100.731541		-2100.754908			-2100.733391		
F^-		-99.989585		-99.989585		-100.003744			-99.989585		
Cu^ICl + F^-		-2200.721974	**0.00**	-2200.721126	**0.00**	-2200.758652	**0**	**0.00**	-2200.722976	**0.00**	**0.00**
Cu^IF R=1.803		-1740.355065		-1740.353864		-1740.376183			-1740.356444		
Cl^-		-460.370444		-460.370444		-460.385467			-460.370444		
Cu^IF + Cl^-		-2200.725509	**-2.22**	-2200.724308	**-2.00**	-2200.761650	**0**	**-1.88**	-2200.726888	**-2.23**	**-2.12**

[a] M06/def2-TZVPD; [b] SP def2-TZVPPD; [c] SP enegies combined with thermal corrections calculated with def2-TZVPD.

Table 2. Calculated absolute and relative (in kcal mol^{-1}) energies for the copper/DES-catalyzed coupling of two 4-nitrobenzenediazonium to 4,4'-dinitrobiphenyl in glycerol.

1st Phase: Oxidative Addition		E /au[a]	**ΔE[a]**	E^{0K} /au[a]	**$\Delta E^{0K\,a}$**	G^{298K} /au[a]	**Δn**	**$\Delta G^{298K\,a}$**	E(SP) /au[b]	**$\Delta E_{SP}{}^{0K\,c}$**	**$\Delta G^{298K\,c}$**
4-O_2N-C_6H_4-NN^+ F^- (**ArN_2F**)	**I**	-645.294983		-645.193756		-645.232857			-645.294983		
[GL * Cu^IF]	**II**	-2085.150231		-2085.028729		-2085.066514			-2085.158668		
I + II		-2730.445214	**0.00**	-2730.222485	**0.00**	-2730.299371	**0**	**0.00**	-2730.453651	**0.00**	**0.00**
Cpl [ArN_2^+ F^- * GL * Cu^IF]	**I-1**	-2730.476320	**-19.52**	-2730.252638	**-18.92**	-2730.310709	**-1**	**-9.01**	-2730.486330	**-19.91**	**-10.00**
Cpl [ArN_2^+ F^- * GL * Cu^IF]	**I-2**	-2730.484963	**-24.94**	-2730.259713	**-23.36**	-2730.314739	**-1**	**-11.54**	-2730.495171	**-24.47**	**-12.65**
TS_{OA} to Int. Oxidat. Add.	**TS_{OA}**	-2730.435075	**6.36**	-2730.213185	**5.84**	-2730.267650	**-1**	**18.01**	-2730.446319	**4.07**	**16.25**
Int-3 Oxidat. Add. **Q=0, M=1**	**I-3**	-2730.500592	**-34.75**	-2730.277356	**-34.43**	-2730.334680	**-1**	**-24.05**	-2730.512450	**-36.58**	**-26.20**
Int-4 Oxidat. Add. (De-N_2 Int-1)	**I-4**	-2620.990367		-2620.773985		-2620.825057			-2621.002378		
DiNitrogen N_2		-109.507484		-109.501856		-109.520278			-109.507484		
Int-4 + N_2		-2730.497850	**-33.03**	-2730.275841	**-33.48**	-2730.345335	**0**	**-28.84**	-2730.509862	**-35.72**	**-31.09**

[a] M06/def2-TZVPD; [b] SP def2-TZVPPD; [c] SP enegies combined with thermal corrections calculated with def2-TZVPD.

2nd Phase: Reduction		E /au[a]	**ΔE[a]**	E^{0K} /au[a]	**ΔE^{0K} [a]**	G^{298K} /au[a]	**Δn**	**ΔG^{298K} [a]**	E(SP) /au[b]	**$\Delta E_{SP}{}^{0K}$ [c]**	**ΔG^{298K} [c]**
Int-4 Oxidat. Add. (De-N_2 Int-1)	**I-4**	-2620.990367		-2620.773985		-2620.825057			-2621.002378		
1-Glycerolate $HOCH_2CH(OH)CH_2O^-$	**III**	-344.203594		-344.099727		-344.130456			-344.225827		
Int-4 + III		-2965.193961	**0.00**	-2964.873712	**0.00**	-2964.955513	**0**	**0.00**	-2965.228205	**0.00**	**0.00**
Int-4 // ^{2}[Int-5$^-$]*		-2620.961549	***18.08***	5.54					-2620.973015		***18.43***
1-GL^- // ^{2}[1-GL*]		-344.198699	***3.07***						-344.221206		***2.90***
Λ nuclear		0.033713	*21.16*		*21.16*			*21.16*	0.033985		*21.33*
^{2}[Int-5$^-$] //+PCM Int-4*		-2621.121531	***-82.31***	-87.75					-2621.132670		***-81.76***
^{2}[1-GL] //+PCM 1-GL^-*		-343.985585	***136.80***						-344.008861		***136.15***
Λ solvent		0.086845	*54.50*		*54.50*			*54.50*	0.086675		*54.39*
Total Λ			***75.65***		***75.65***			***75.65***			***75.71***
$TS_{ET}{}^{Marcus}$	**TS_{ET}**		11.77		11.34			10.74		11.44	**10.84**
1-Glycerolyl $HOCH_2CH(OH)CH_2O$*	**IV**	-344.034330		-343.931397		-343.962984			-344.057497		
Int-5 ^{2}[Ar-Cu(GL)$(F)_2$]*$^-$	**I-5**	-2621.185081		-2620.969526		-2621.022237			-2621.195807		
Int-5 + IV		-2965.219411	**-15.97**	-2964.900923	**-17.08**	-2964.985221	**0**	**-18.64**	-2965.253304	**-16.85**	**-18.42**

[a] M06/def2-TZVPD; [b] SP def2-TZVPPD; [c] SP enegies combined with thermal corrections calculated with def2-TZVPD.

3[d] Phase: C−C Coupling		E /au[a]	**ΔE[a]**	E^{0K} /au[a]	**$\Delta E^{0K\ a}$**	G^{298K} /au[a]	**Δn**	**$\Delta G^{298K\ a}$**	E(SP) /au[b]	**$\Delta E_{SP}{}^{0K\ c}$**	**$\Delta G^{298K\ c}$**
Int-5 [2][Ar-Cu(GL)$(F)_2$]*[-]	**I-5**	-2621.160355	**I-4**	-2620.944654		-2620.996474			-2621.197067		
4-O_2N-C_6H_4-NN^+ F^- (**ArN_2 F**)	**I**	-645.273917		-645.172126		-645.210119			-645.297005		
Int-5 + I (ArN_2^+ F^-)		-3266.434271	**0.00**	-3266.116780	**0.00**	-3266.206593	**0**	**0.00**	-3266.494072	**0.00**	**0.00**
Cpl [Int-5 * I]	**I-6**	-3266.448402	**-8.87**	-3266.129003	**-7.67**	-3266.194515	**-1**	**5.68**	-3266.507467	**-7.21**	**6.15**
Cpl [Int-5-F^- * de-F-I]	**I-7**	-3266.458947	**-15.48**	-3266.140578	**-14.93**	-3266.208475	**-1**	**-3.08**	-3266.518163	**-14.57**	**-2.71**
Cpl [Ox-Int-5-F^- * Red-σ-de-F-I]	**I-8**	-3266.457839	**-14.79**	-3266.139162	**-14.04**	-3266.207563	**-1**	**-2.50**	-3266.517563	**-14.00**	**-2.45**
$TS_{N2\text{-}Detach}$	**TS_{NN}**	-3266.449372	**-9.48**	-3266.132985	**-10.17**	-3266.206205	**-1**	**-1.65**	-3266.508496	**-9.74**	**-1.23**
Cpl [Ox-Int-5-F^-*N_2* Rad.$C_6H_4NO_2$]	**I-9**	-3266.465851	**-19.82**	-3266.150409	**-21.10**	-3266.224904	**-1**	**-13.38**	-3266.525112	**-20.76**	**-13.05**
Cpl [Ox-Int-5-F^- * Rad. $C_6H_4NO_2$]	**I-10**	-3156.965055		-3156.656402		-3156.725280			-3157.020059		
Int-10 + N_2		-3266.468918	**-21.74**	-3266.154651	**-23.76**	-3266.241950	**0**	**-22.19**	-3266.527543	**-23.03**	**-21.45**
TS_{CC} [Ox-Int-5-F^- * Rad. $C_6H_4NO_2$]	**TS_{CC}**	-3156.964150	**0.57**	-3156.655986	**0.26**	-3156.722708		**1.61**	-3157.018949	**0.39**	**1.74**
TS_{CC} + N_2		-3266.468014	**-21.17**	-3266.154235	**-23.50**	-3266.239378	**0**	**-20.57**	-3266.526432	**-22.64**	**-19.71**
Cpl [2][P * (GL * $Cu^{II\,++}$* $(F^-)_3$]	**I-11**	-3157.101032		-3156.788889		-3156.855747			-3157.155660		
Int-11 + N_2		-3266.604895	**-107.07**	-3266.287138	**-106.90**	-3266.372417	**0**	**-104.06**	-3266.663143	**-105.93**	**-103.08**
4,4'-DiNitroBiphenyl (P)	**P**	-872.073641		-871.887724		-871.929640			-872.108525		
DiNitrogen N_2		-109.503863		-109.498249		-109.516670			-109.507483		
Cpl [2][(GL * $Cu^{II\,++}$* $(F^-)_3$]	**V**	-2285.020635		-2284.895827		-2284.938816			-2285.040253		
P + V + N_2		-3266.598139	**-102.83**	-3266.281800	**-103.6**	-3266.385126	**1**	**-110.14**	-3266.656262	**-102.5**	**-109.08**

[a] M06/def2-TZVPD; [b] SP def2-TZVPPD; [c] SP enegies combined with thermal corrections calculated with def2-TZVPD.

4th Step: Catalyzer Regeneration		E /au[a]	**ΔE[a]**	E^{0K} /au[a]	**ΔE^{0K} [a]**	G^{298K} /au[a]	**Δn**	**ΔG^{298K} [a]**	E(SP) /au[b]	**$\Delta E_{SP}{}^{0K}$ [c]**	**ΔG^{298K} [c]**
1-Glyceroxyl HOCH2CH(OH)CH2O*	**IV**	-344.062307		-343.959397		-343.990997			-344.076423		
IV + Gly		-344.062307	**0.00**	-343.959397	**0.00**	-343.990997	**0**	**0.00**	-344.076423	**0.00**	**0.00**
2-Glycerolyl HOCH2C*(OH)CH2OH	**VI**	-344.080103		-343.975577		-344.007981			-344.095668		
Gly + VI		-344.080103	**-11.17**	-343.975577	**-10.15**	-344.007981	**0**	**-10.66**	-344.095668	**-11.57**	**-12.08**
1-Glycerolyl HOCH2CH(OH)CH*OH	**VI'**	-344.074677		-343.971257		-344.003887			-344.090485		
Gly + VI'		-344.074677	**-7.76**	-343.971257	**-7.44**	-344.003887	**0**	**-8.09**	-344.090485	**-8.18**	**-8.82**
Cpl 2[(GL * CuII * (F)2]	**VII**	-2184.982088		-2184.857714		-2184.897721			-2185.002197		
VII + VI		-2529.062191	**0.00**	-2528.833291	**0.00**	-2528.905702	**0**	**0.00**	-2529.097865	**0.00**	**0.00**
1,3-DiHydroxyPropanone	**VIII**	-343.529531		-343.435602		-343.466783			-343.544124		
HF		-100.461682		-100.452259		-100.468666			-100.464319		
II + VIII + HF		-2529.132031	**-43.82**	-2528.907179	**-46.37**	-2528.992486	**1**	**-52.56**	-2529.167057	**-35.33**	**-41.52**
1,2-DiHydroxyPropanale	**IX**	-343.527045		-343.433112		-343.463704			-343.541421		
II + IX + HF		-2529.129545	**-42.27**	-2528.904689	**-44.80**	-2528.989407	**1**	**-50.63**	-2529.164354	**-34.00**	**-39.83**

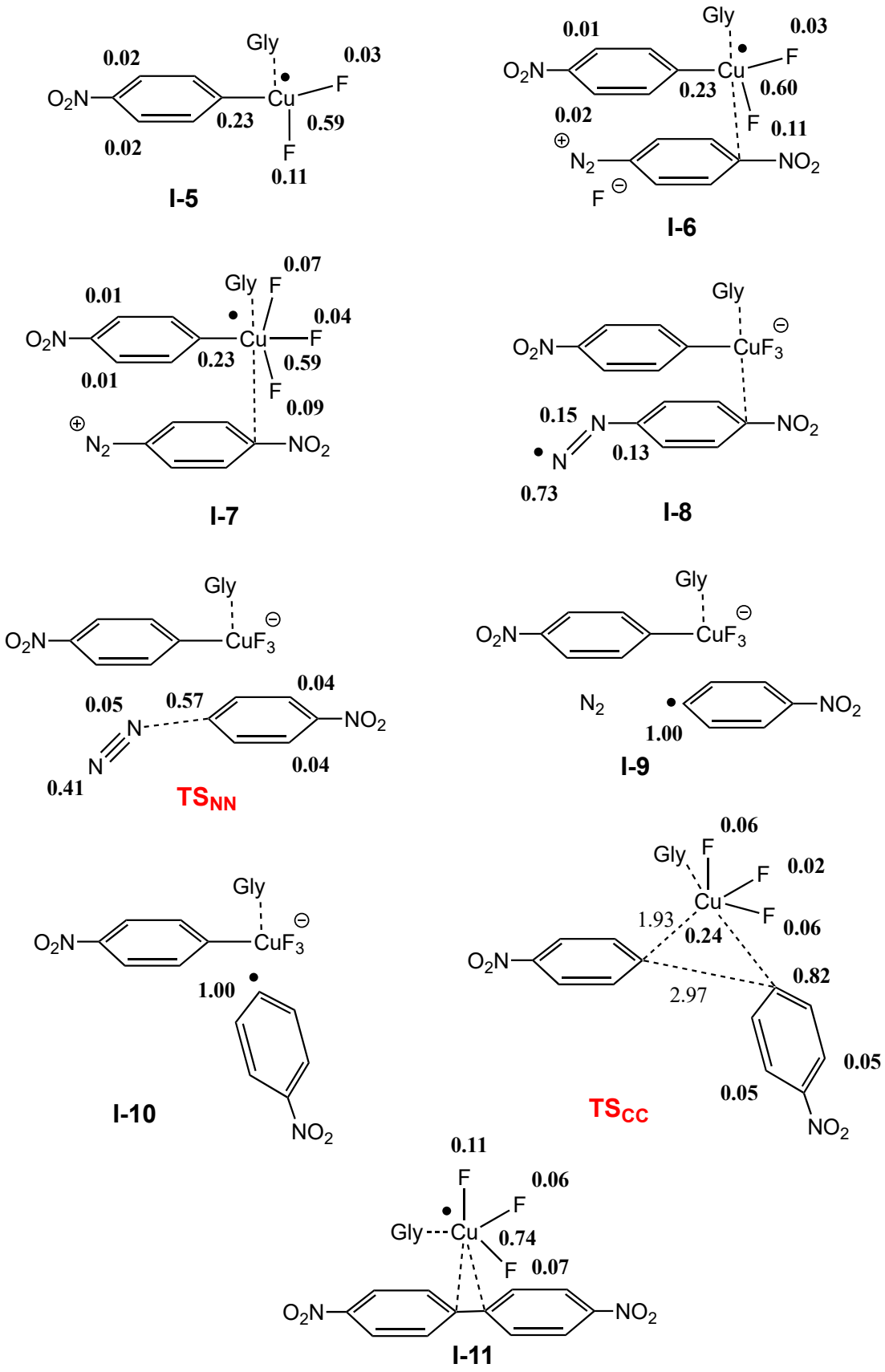
[a] M06/def2-TZVPD; [b] SP def2-TZVPPD; [c] SP enegies combined with thermal corrections calculated with def2-TZVPD.

Table 3. Calculated absolute and relative (in kcal mol^{-1}) energies for the global reaction.

Global Reaction		E /au[a]	**ΔE[a]**	E^{0K} /au[a]	**$\Delta E^{0K\ a}$**	G^{298K} /au[a]	**Δn**	**$\Delta G^{298K\ a}$**	E(SP) /au[b]	**$\Delta E_{SP}{}^{0K\ c}$**	**$\Delta G^{298K\ c}$**
4-O_2N-C_6H_4-NN^+ BF_4^- (**ArN_2BF_4**)		-969.946776		-969.830572		-969.875498			-969.975315		
Glycerol	**IV**	-344.736413		-344.618559		-344.649710			-344.752161		
2 ArN_2BF_4 + Glycerol		-2284.629964	**0.00**	-2284.279703	**0.00**	-2284.400706	**0**	**0.00**	-2284.702791	**0.00**	**0.00**
4,4'-DiNitroBiphenyl (P)	**P**	-872.073641		-871.887724		-871.929640			-872.108525		
DiNitrogen N_2		-109.503863		-109.498249		-109.516670			-109.507483		
1,3-DiHydroxyPropanone	**VIII**	-343.529531		-343.435602		-343.466783			-343.544124		
HBF_4		-425.064313		-425.040931		-425.071871			-425.071385		
P + 2 N_2 + VIII + 2 HBF_4		-2284.739524	**-68.75**	-2284.401686	**-76.55**	-2284.573505	**3**	**-108.43**	-2284.810386	**-75.31**	**-107.20**
1,2-DiHydroxyPropanale	**IX**	-343.527045		-343.433112		-343.463704			-343.541421		
P + 2 N_2 + IX + 2 HBF_4		-2284.737039	**-67.19**	-2284.399196	**-74.98**	-2284.570426	**3**	**-106.50**	-2284.807683	**-73.61**	**-105.13**

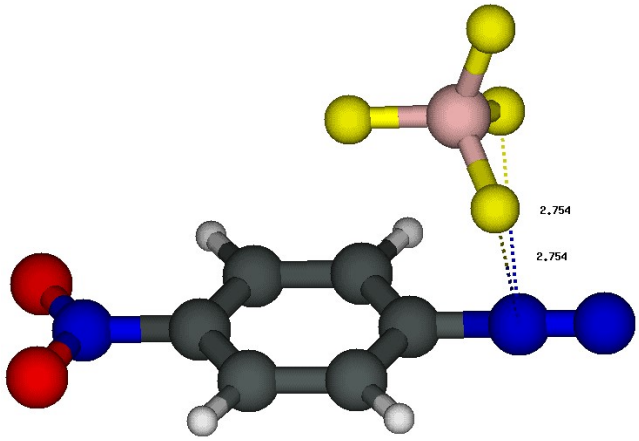
[a] M06/def2-TZVPD; [b] SP def2-TZVPPD; [c] SP enegies combined with thermal corrections calculated with def2-TZVPD.

Figure 1. Atomic spin densities in the radical intermediates



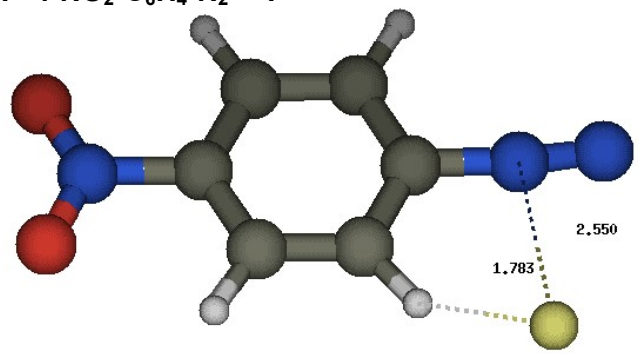
Pictures and **Cartesian coordinates** for the fluorination of reactants.

1a 4-NO_2-C_6H_4-N_2^+ * BF_4^-



1	6	0	0.002051	0.003666	0.001059
2	6	0	0.004317	0.001232	1.390034
3	6	0	1.231712	0.000721	2.013192
4	6	0	2.371070	-0.000443	1.230701
5	6	0	2.355243	0.001890	-0.151389
6	6	0	1.139234	0.002415	-0.796485
7	1	0	-0.921945	-0.013082	1.946701
8	1	0	1.310052	-0.003207	3.090643
9	7	0	3.688397	-0.006780	1.914459
10	1	0	3.281451	-0.001156	-0.707431
11	1	0	1.061382	-0.011016	-1.874355
12	7	0	-1.227886	-0.009781	-0.637350
13	7	0	-2.198425	-0.009075	-1.141108
14	8	0	4.673545	-0.008355	1.216745
15	8	0	3.684801	-0.009330	3.121648
16	9	0	-1.583544	-2.510834	0.458976
17	5	0	-0.634643	-3.182526	-0.331148
18	9	0	-0.534908	-2.509736	-1.561306
19	9	0	0.601880	-3.150514	0.310692
20	9	0	-1.037228	-4.493129	-0.540824

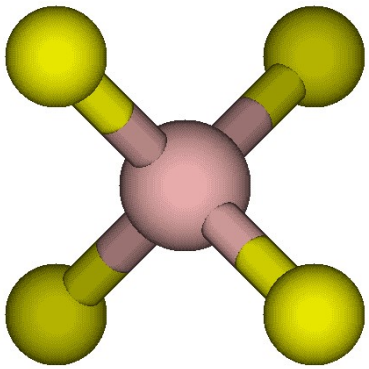
I 4-NO_2-C_6H_4-N_2^+ * F^-



1	6	0	-0.441877	-1.573911	-0.000210
2	6	0	-1.274846	-0.457680	-0.000043
3	6	0	-0.845952	0.861426	0.000121
4	6	0	0.519184	1.067581	0.000131
5	6	0	1.358800	-0.028362	-0.000018

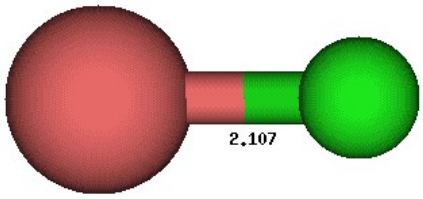
6	6	0	0.913317	-1.339289	-0.000180
7	7	0	-2.646161	-0.701896	-0.000030
8	7	0	-3.697959	-1.000268	0.000027
9	7	0	2.823485	0.208714	0.000017
10	8	0	3.200245	1.356101	-0.000489
11	8	0	3.543050	-0.761635	0.000550
12	9	0	-3.416009	1.729206	0.000081
13	1	0	-1.636424	1.623014	0.000243
14	1	0	0.932139	2.066236	0.000254
15	1	0	1.620811	-2.155593	-0.000283
16	1	0	-0.846118	-2.576678	-0.000342

BF_4^-

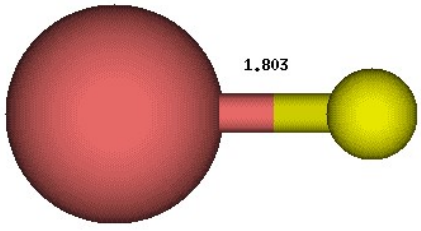


1	5	0	0.000000	0.000000	-0.000000
2	9	0	-0.000000	-0.000000	1.397730
3	9	0	1.317792	-0.000000	-0.465910
4	9	0	-0.658896	-1.141242	-0.465910
5	9	0	-0.658896	1.141242	-0.465910

CuCl

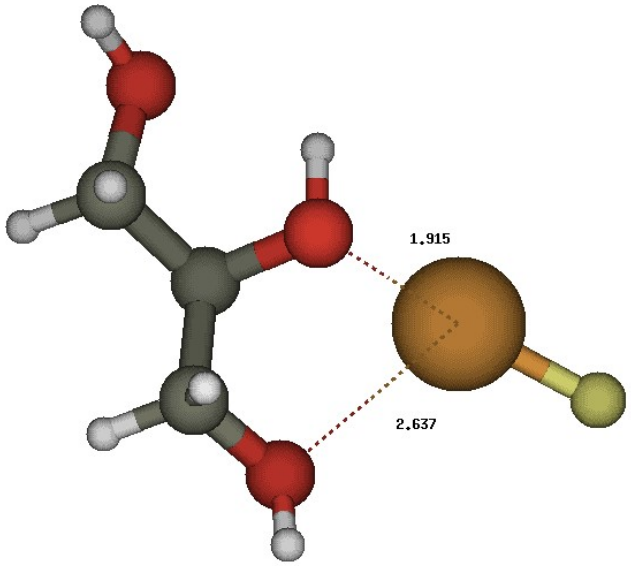


CuF



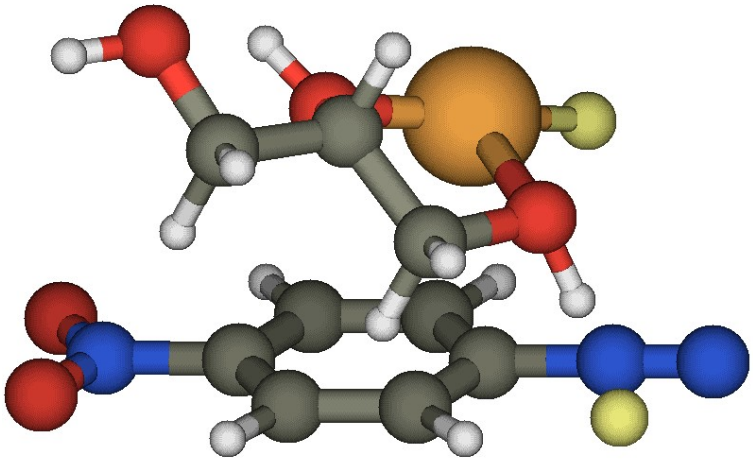
Pictures and **Cartesian coordinates** for the copper/DES-catalyzed coupling of two 4-nitrobenzene-diazonium to 4,4'-dinitrobiphenyl.

II GL * Cu^{I}F



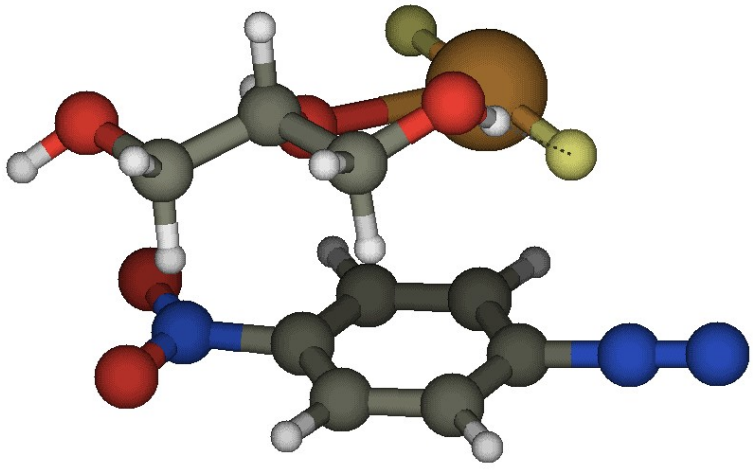
1	6	0	0.000199	0.002339	-0.001239
2	6	0	-0.002189	-0.001239	1.497606
3	6	0	1.385746	-0.001521	-0.585951
4	8	0	-0.672429	-1.187490	-0.447958
5	1	0	-0.557787	0.872795	-0.369586
6	8	0	-1.342222	0.095777	1.923132
7	1	0	0.465223	-0.927509	1.854692
8	1	0	0.598695	0.844427	1.854146
9	8	0	1.221231	-0.128399	-1.980311
10	1	0	1.898764	0.928759	-0.315254
11	1	0	1.955748	-0.843546	-0.173504
12	1	0	-0.493840	-1.282410	-1.395762
13	1	0	2.050574	-0.399849	-2.381735
14	29	0	-2.437157	-1.565611	0.192100
15	9	0	-4.101148	-2.033564	0.700042
16	1	0	-1.398155	-0.112353	2.859868

I-1



1	6	0	-0.435468	0.038380	0.253135
2	6	0	-0.181771	-0.462337	1.523599
3	6	0	1.017085	-1.026538	1.936646
4	6	0	2.029183	-1.090758	0.999990
5	6	0	1.791076	-0.600743	-0.268893
6	6	0	0.589245	-0.036625	-0.662020
7	7	0	-1.216586	-0.427309	2.451794
8	7	0	-2.014682	-0.386454	3.195680
9	7	0	2.881631	-0.686652	-1.269815
10	8	0	3.918075	-1.198548	-0.919187
11	8	0	2.661985	-0.240108	-2.370483
12	9	0	-0.061828	-2.007890	4.366398
13	1	0	1.074110	-1.414183	2.954961
14	1	0	2.988290	-1.524908	1.245303
15	1	0	0.464106	0.327981	-1.671137
16	1	0	-1.402147	0.449137	-0.000862
17	29	0	-0.892239	-3.506463	0.977863
18	9	0	-2.291100	-2.322244	0.998439
19	8	0	-0.239695	-4.160610	3.155960
20	6	0	1.056468	-4.647945	2.976856
21	6	0	1.102832	-5.461833	1.712605
22	1	0	-0.197488	-3.295995	3.694983
23	1	0	1.377539	-5.288533	3.810441
24	1	0	1.785630	-3.825626	2.898942
25	6	0	2.473108	-5.984326	1.391555
26	8	0	0.678690	-4.606296	0.638658
27	1	0	0.788962	-5.084274	-0.193752
28	1	0	0.393721	-6.296910	1.786760
29	8	0	2.365098	-6.673491	0.166056
30	1	0	3.172423	-5.141212	1.314098
31	1	0	2.813172	-6.639951	2.202644
32	1	0	3.242202	-6.838929	-0.188966

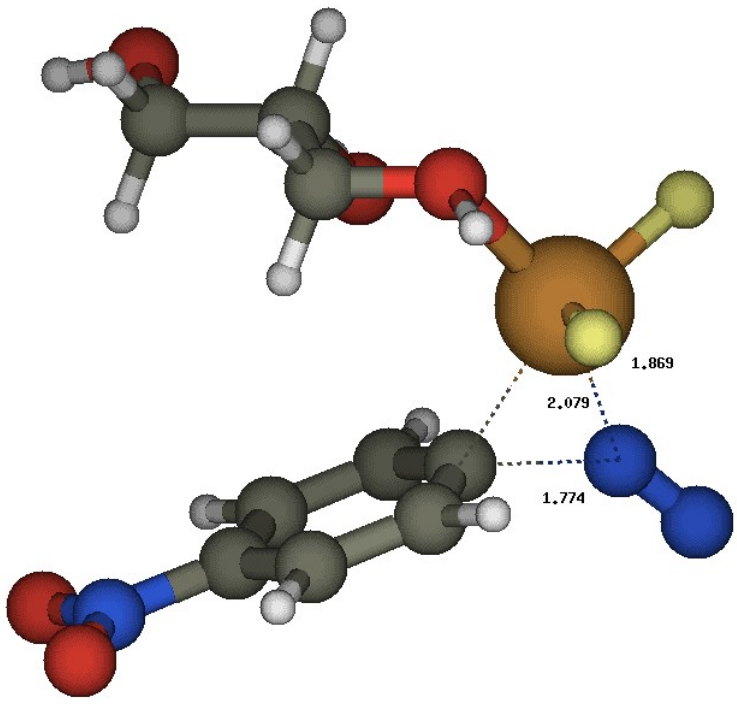
I-2



1	6	0	-0.317663	1.754585	1.286613
2	6	0	0.444104	0.793548	1.947425
3	6	0	1.596379	0.371664	1.330965
4	6	0	1.926102	0.910467	0.096783
5	6	0	1.175149	1.869987	-0.545198
6	6	0	0.006707	2.305295	0.049695

7	1	0	0.127235	0.393248	2.900406
8	1	0	2.227667	-0.379505	1.783840
9	7	0	3.124862	0.389731	-0.595296
10	1	0	1.472456	2.243939	-1.513957
11	1	0	-0.615023	3.062641	-0.407113
12	8	0	3.363197	0.821386	-1.697715
13	8	0	3.779296	-0.447726	-0.018067
14	7	0	-1.514440	2.131758	1.855795
15	7	0	-2.465918	2.436028	2.306663
16	29	0	-1.548260	0.717898	-1.576286
17	9	0	-0.797781	1.285844	-3.131992
18	8	0	-1.931732	-2.384801	-0.002976
19	6	0	-0.573085	-2.654639	0.183605
20	6	0	0.245034	-2.499589	-1.076078
21	1	0	-2.067919	-1.413093	-0.002715
22	1	0	-0.475591	-3.687051	0.536041
23	1	0	-0.137835	-2.005823	0.960147
24	6	0	1.651548	-3.010247	-0.890979
25	8	0	0.260943	-1.122134	-1.411896
26	1	0	0.691075	-1.017727	-2.269193
27	1	0	-0.239117	-3.070165	-1.882563
28	8	0	2.345171	-2.792283	-2.099688
29	1	0	2.128054	-2.468804	-0.060482
30	1	0	1.624505	-4.076281	-0.629392
31	1	0	3.286388	-2.915670	-1.952515
32	9	0	-2.338360	0.259132	0.031022

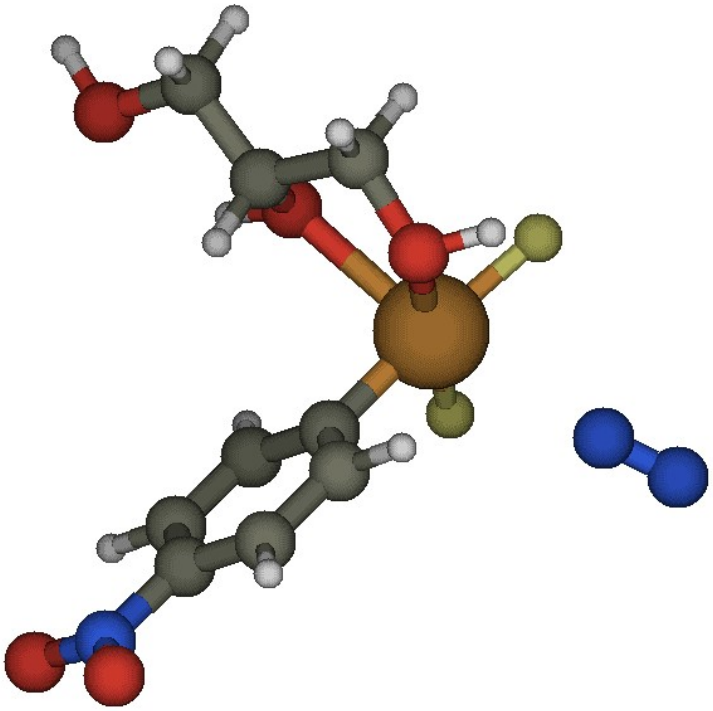
TS_{OA}



1	6	0	-0.246499	0.012310	0.148790
2	6	0	0.107870	-0.239146	1.455797
3	6	0	1.461125	-0.401314	1.686109
4	6	0	2.342215	-0.270851	0.625279
5	6	0	1.946029	0.024818	-0.664823

6	6	0	0.597247	0.201146	-0.921667
7	1	0	-0.645944	-0.361982	2.222187
8	1	0	1.830008	-0.630163	2.676062
9	7	0	3.786340	-0.449337	0.888912
10	1	0	2.677915	0.129047	-1.453241
11	1	0	0.234913	0.455868	-1.907793
12	8	0	4.539973	-0.358591	-0.051721
13	8	0	4.120505	-0.675760	2.028106
14	7	0	-1.783084	0.865080	-0.091491
15	7	0	-2.229139	1.868738	0.031039
16	29	0	-1.990815	-0.961405	-0.427828
17	9	0	-3.524319	-1.000088	-1.463239
18	8	0	-1.539356	-2.961107	-0.264707
19	6	0	-0.243264	-3.456091	-0.539248
20	6	0	-0.065360	-3.484111	-2.031319
21	1	0	-1.720847	-2.841044	0.699021
22	1	0	-0.130884	-4.465736	-0.133171
23	1	0	0.524190	-2.816132	-0.082019
24	6	0	1.305479	-3.983083	-2.409950
25	8	0	-0.268541	-2.172470	-2.513949
26	1	0	-0.022637	-2.168496	-3.447023
27	1	0	-0.819907	-4.158960	-2.463759
28	8	0	1.371450	-3.952668	-3.817425
29	1	0	2.064428	-3.325999	-1.962467
30	1	0	1.454758	-4.997227	-2.017436
31	1	0	2.282299	-4.071021	-4.098069
32	9	0	-2.421183	-1.496910	1.554250

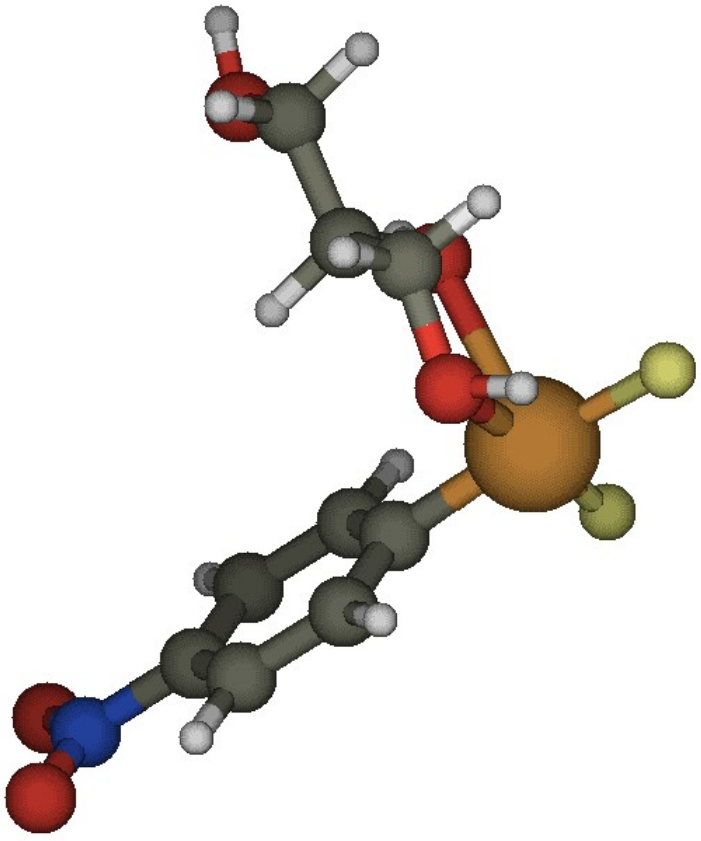
I-3



1	6	0	0.027395	-0.168245	-0.325062
2	6	0	-0.106027	-0.110203	1.166275
3	6	0	1.424932	0.179940	-0.767147
4	8	0	-0.302116	-1.491438	-0.704051

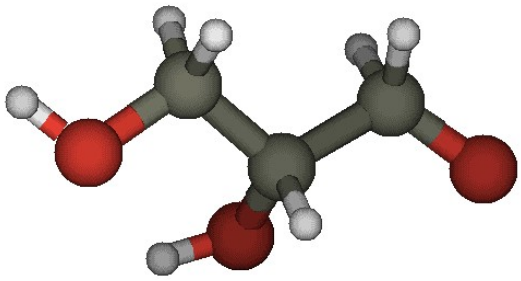
5	1	0	-0.676549	0.540914	-0.787770
6	8	0	-1.477189	-0.381306	1.533037
7	1	0	0.538844	-0.864108	1.625312
8	1	0	0.153423	0.879613	1.545405
9	8	0	1.435484	0.056484	-2.169033
10	1	0	1.671697	1.199352	-0.443923
11	1	0	2.135647	-0.512457	-0.297667
12	1	0	-0.159536	-1.574726	-1.655681
13	1	0	2.342958	0.046233	-2.483706
14	29	0	-2.318390	-1.878483	0.605999
15	9	0	-1.473594	-2.913387	1.901447
16	6	0	-3.282181	-0.720576	-0.562415
17	6	0	-3.934099	0.344420	0.015209
18	6	0	-4.609454	1.219211	-0.822934
19	6	0	-4.591286	0.986679	-2.184364
20	6	0	-3.934026	-0.093643	-2.746584
21	6	0	-3.272559	-0.979248	-1.914008
22	1	0	-3.922241	0.521059	1.082445
23	1	0	-5.136553	2.073855	-0.421828
24	7	0	-5.301384	1.919477	-3.069118
25	1	0	-3.950599	-0.244555	-3.817073
26	1	0	-2.775193	-1.848794	-2.322003
27	7	0	-4.326740	-1.780018	2.715266
28	7	0	-5.033579	-2.329963	3.334592
29	8	0	-5.267256	1.705612	-4.261509
30	8	0	-5.882961	2.852573	-2.559271
31	1	0	-1.456883	-0.803019	2.409516
32	9	0	-3.277021	-3.176864	-0.130626

I-4



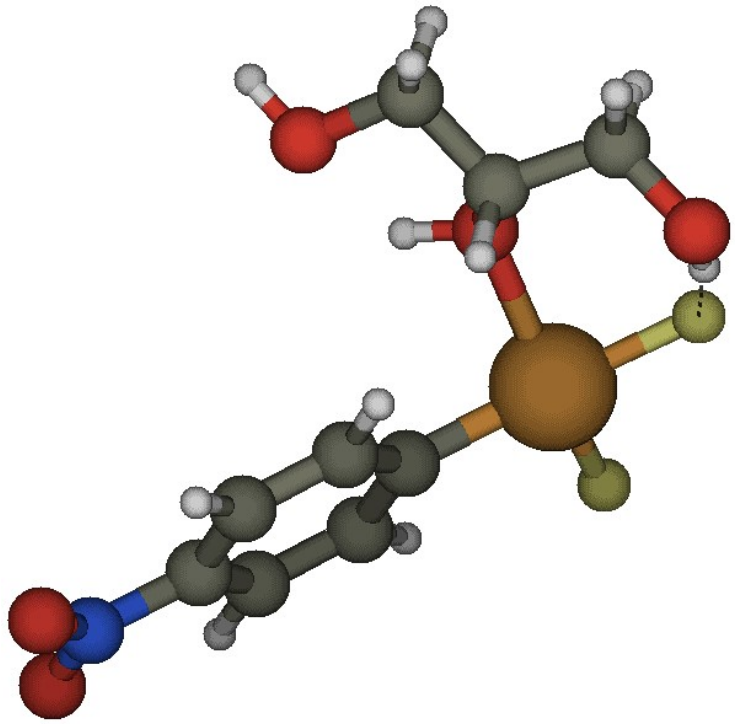
1	6	0	0.008125	-0.016107	-0.010771
2	6	0	0.005981	0.010545	1.487129
3	6	0	1.409876	-0.023319	-0.562715
4	8	0	-0.684125	-1.191132	-0.389042
5	1	0	-0.519045	0.870436	-0.396598
6	8	0	-1.356561	0.099685	1.960250
7	1	0	0.455760	-0.907501	1.874345
8	1	0	0.549432	0.877737	1.865861
9	8	0	1.278410	-0.089461	-1.962528
10	1	0	1.937943	0.884265	-0.243539
11	1	0	1.950064	-0.893801	-0.168629
12	1	0	-0.631162	-1.273579	-1.349942
13	1	0	2.123119	-0.325323	-2.354118
14	29	0	-2.630022	-1.078824	1.072942
15	9	0	-2.018365	-2.343879	2.291149
16	6	0	-3.342068	0.348194	0.032599
17	6	0	-3.689877	1.487676	0.720314
18	6	0	-4.180512	2.557843	-0.012892
19	6	0	-4.289764	2.432207	-1.384257
20	6	0	-3.942601	1.273547	-2.056559
21	6	0	-3.468533	0.196045	-1.328702
22	1	0	-3.582079	1.572441	1.793741
23	1	0	-4.466975	3.478847	0.475771
24	7	0	-4.799893	3.571367	-2.158446
25	1	0	-4.053235	1.213022	-3.130383
26	1	0	-3.219093	-0.733301	-1.822726
27	8	0	-4.889523	3.444224	-3.360296
28	8	0	-5.103013	4.577092	-1.553946
29	1	0	-1.387165	-0.351628	2.821697
30	9	0	-3.926211	-2.049747	0.353823

III $HOCH_2CH(OH)CH_2O^-$



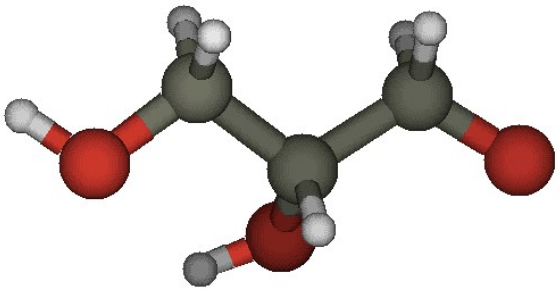
1	6	0	0.000605	-0.000523	-0.000994
2	6	0	0.002292	0.003424	1.526381
3	6	0	1.394666	-0.005394	-0.572842
4	8	0	-0.704023	-1.141591	-0.467940
5	1	0	-0.516818	0.912114	-0.346037
6	8	0	-1.195585	0.198694	2.105563
7	1	0	0.491093	-0.971428	1.801166
8	1	0	0.774973	0.772868	1.801492
9	8	0	1.288874	-0.105048	-1.984192
10	1	0	1.918967	0.913575	-0.282597
11	1	0	1.950536	-0.861554	-0.165710
12	1	0	-0.498211	-1.222435	-1.407170
13	1	0	2.143409	-0.343528	-2.351250

I-5



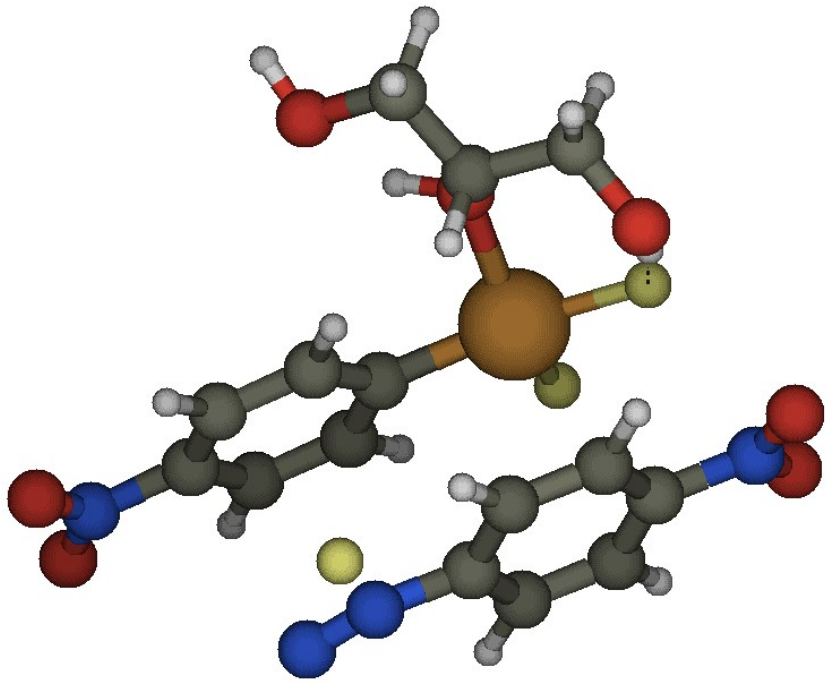
1	6	0	0.211557	0.061393	0.899346
2	6	0	0.694211	-0.804054	2.035851
3	6	0	1.341706	0.485756	-0.003434
4	8	0	-0.739199	-0.663028	0.113059
5	1	0	-0.277136	0.954648	1.317259
6	8	0	-0.254289	-0.976805	3.043577
7	1	0	1.025097	-1.766214	1.614180
8	1	0	1.575518	-0.323512	2.475237
9	8	0	0.763073	1.178171	-1.089277
10	1	0	2.038214	1.121072	0.556355
11	1	0	1.886422	-0.403608	-0.346457
12	1	0	-0.802111	-0.184088	-0.729173
13	1	0	1.389443	1.221271	-1.816159
14	29	0	-2.820331	-1.197556	0.594697
15	9	0	-2.062829	-2.400875	1.875799
16	6	0	-3.478836	0.327853	-0.440320
17	6	0	-2.916310	1.602406	-0.329412
18	6	0	-3.393516	2.680293	-1.053658
19	6	0	-4.453952	2.477102	-1.919963
20	6	0	-5.043261	1.231140	-2.064435
21	6	0	-4.554002	0.175353	-1.318921
22	1	0	-2.081512	1.776753	0.343366
23	1	0	-2.957020	3.665311	-0.956307
24	7	0	-4.963821	3.601582	-2.696565
25	1	0	-5.871685	1.104505	-2.748705
26	1	0	-5.023950	-0.797075	-1.411625
27	8	0	-5.894041	3.403652	-3.454230
28	8	0	-4.436349	4.687813	-2.552912
29	1	0	-0.971925	-1.548689	2.675766
30	9	0	-4.425880	-2.188019	0.497756

IV $HOCH_2CH(OH)CH_2O$*



1	6	0	-0.003716	-0.000622	-0.001677
2	6	0	0.001325	0.004439	1.508449
3	6	0	1.399988	-0.004905	-0.551870
4	8	0	-0.704468	-1.150522	-0.418206
5	1	0	-0.520111	0.906631	-0.353713
6	8	0	-1.202046	0.168393	2.093813
7	1	0	0.452182	-0.934405	1.893111
8	1	0	0.687619	0.780928	1.902808
9	8	0	1.288510	-0.080533	-1.955142
10	1	0	1.927789	0.904685	-0.235884
11	1	0	1.942220	-0.872233	-0.149982
12	1	0	-0.544950	-1.248503	-1.365094
13	1	0	2.142111	-0.305282	-2.333542

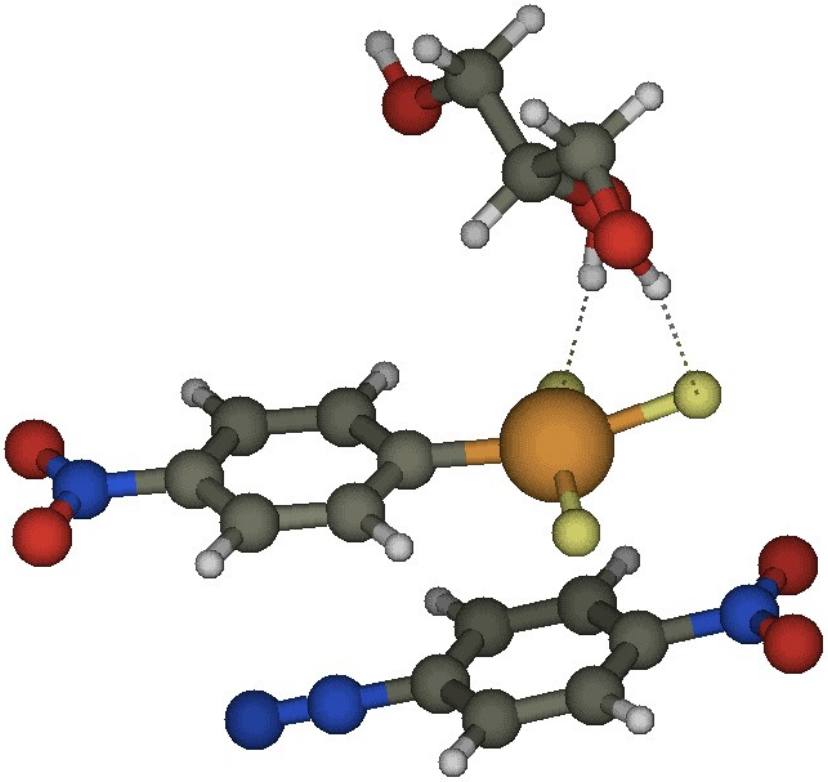
I-6



1	6	0	-0.557377	0.376121	0.099156
2	6	0	-0.673222	0.508022	1.597410
3	6	0	0.882535	0.454385	-0.345725
4	8	0	-1.083708	-0.890101	-0.322633
5	1	0	-1.138805	1.180249	-0.378019
6	8	0	-1.971773	0.763291	2.044199

7	1	0	-0.256754	-0.405710	2.049620
8	1	0	-0.038407	1.344094	1.911383
9	8	0	0.908160	0.141227	-1.724562
10	1	0	1.269905	1.461373	-0.153516
11	1	0	1.479172	-0.263775	0.231636
12	1	0	-0.668095	-1.064906	-1.183973
13	1	0	1.796700	-0.124152	-1.975386
14	29	0	-3.179702	-1.471326	-0.564104
15	9	0	-3.292386	-1.352020	1.351194
16	6	0	-3.171043	-1.079741	-2.490286
17	6	0	-2.428656	-0.037304	-3.052112
18	6	0	-2.446929	0.228268	-4.410394
19	6	0	-3.225734	-0.569796	-5.229764
20	6	0	-3.987693	-1.608237	-4.717612
21	6	0	-3.952920	-1.848681	-3.356762
22	1	0	-1.815056	0.603379	-2.425579
23	1	0	-1.871286	1.040177	-4.834918
24	7	0	-3.254765	-0.303116	-6.663807
25	1	0	-4.591681	-2.210887	-5.383196
26	1	0	-4.549974	-2.653104	-2.942315
27	8	0	-3.944208	-1.018531	-7.368084
28	8	0	-2.588870	0.622641	-7.090930
29	1	0	-2.514324	-0.039984	1.849682
30	9	0	-4.527047	-2.798139	-0.647295
31	6	0	-5.471419	1.261686	-1.865019
32	6	0	-4.654936	1.837085	-0.910056
33	6	0	-4.743628	1.348775	0.377621
34	6	0	-5.632169	0.323114	0.640312
35	6	0	-6.440071	-0.248299	-0.324364
36	6	0	-6.366566	0.227697	-1.614062
37	1	0	-4.002416	2.640038	-1.233263
38	1	0	-4.113717	1.738834	1.165615
39	7	0	-5.738121	-0.182472	2.024492
40	1	0	-7.108764	-1.056440	-0.067055
41	1	0	-6.973245	-0.190969	-2.405545
42	7	0	-5.406360	1.666359	-3.216799
43	7	0	-5.614726	1.620069	-4.294884
44	8	0	-6.359394	-1.207024	2.197960
45	8	0	-5.216890	0.472839	2.897802
46	9	0	-4.165319	3.433956	-3.006702

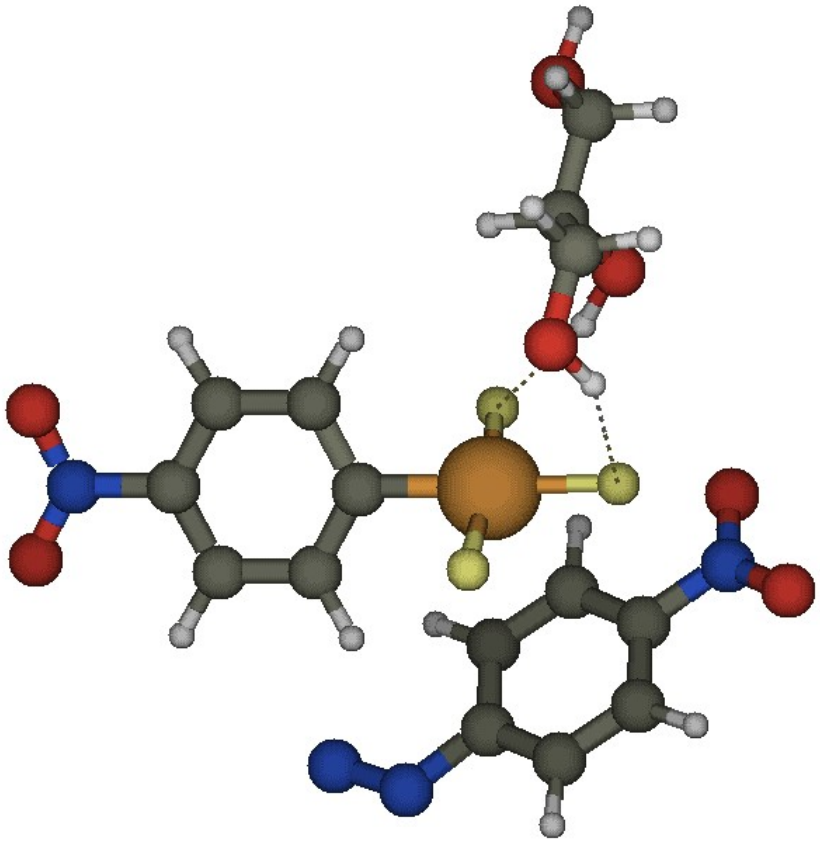
I-7



1	6	0	0.004804	-0.025787	0.116712
2	6	0	-0.041979	0.049289	1.629555
3	6	0	1.432236	-0.023779	-0.371785
4	8	0	-0.648894	-1.190259	-0.328375
5	1	0	-0.500733	0.866614	-0.289969
6	8	0	-1.317303	0.332280	2.138034
7	1	0	0.346433	-0.905357	2.023149
8	1	0	0.628049	0.841722	1.982031
9	8	0	1.434232	0.092833	-1.780754
10	1	0	1.976423	0.811310	0.089235
11	1	0	1.914909	-0.959361	-0.053065
12	1	0	-1.491716	-0.932012	-0.773437
13	29	0	-3.473303	0.882433	-0.186970
14	9	0	-3.500097	-0.651967	1.029501
15	6	0	-2.955818	2.489899	-1.233148
16	6	0	-3.407346	3.767359	-0.884883
17	6	0	-3.048628	4.895194	-1.600976
18	6	0	-2.211717	4.748706	-2.696882
19	6	0	-1.736220	3.504071	-3.081456
20	6	0	-2.115327	2.394365	-2.348400
21	1	0	-4.062384	3.870291	-0.026055
22	1	0	-3.402435	5.879881	-1.323845
23	7	0	-1.825813	5.925603	-3.460984
24	1	0	-1.083945	3.420342	-3.941110
25	1	0	-1.755893	1.415266	-2.649170
26	1	0	-2.012331	-0.205080	1.689375
27	9	0	-2.794489	-0.357880	-1.550003
28	9	0	-4.687336	1.836938	0.957636
29	1	0	2.341044	0.025854	-2.090298
30	8	0	-1.079920	5.778193	-4.414172
31	8	0	-2.265390	7.009471	-3.116333

32	6	0	-5.776593	2.036289	-3.018864
33	6	0	-6.494550	2.248679	-1.847108
34	6	0	-6.679876	1.161336	-1.025668
35	6	0	-6.156329	-0.058881	-1.413158
36	6	0	-5.447507	-0.256268	-2.584028
37	6	0	-5.244823	0.816584	-3.421098
38	1	0	-6.870015	3.229373	-1.591605
39	1	0	-7.208733	1.254246	-0.089649
40	7	0	-6.352990	-1.218731	-0.512402
41	1	0	-5.045470	-1.229389	-2.820230
42	1	0	-4.683584	0.727012	-4.340488
43	8	0	-5.890843	-2.279472	-0.864455
44	8	0	-6.969562	-1.026888	0.510658
45	7	0	-5.548114	3.134329	-3.834994
46	7	0	-5.366392	4.003461	-4.475599

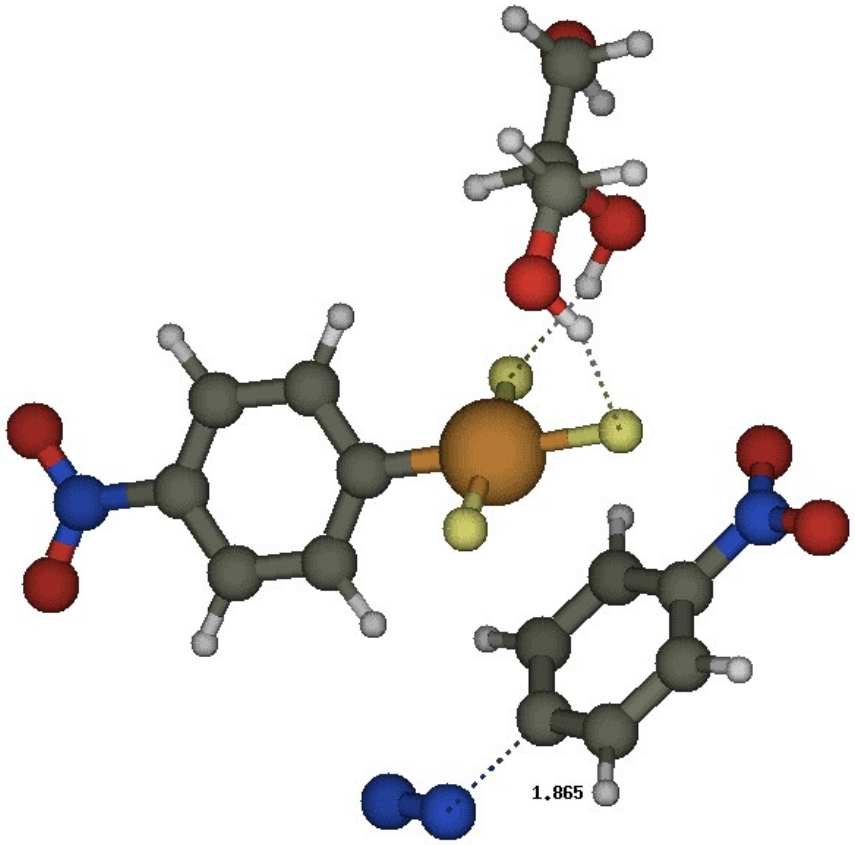
I-8



1	6	0	-0.167042	-0.128329	-0.204419
2	6	0	-0.317815	0.109120	1.285582
3	6	0	1.219543	-0.626309	-0.514255
4	8	0	-1.104582	-1.079717	-0.657710
5	1	0	-0.321376	0.827923	-0.730474
6	8	0	-1.584658	0.609107	1.633661
7	1	0	-0.107147	-0.833769	1.813676
8	1	0	0.422916	0.844615	1.615119
9	8	0	1.429469	-0.585253	-1.910098
10	1	0	1.953828	-0.001916	0.012604
11	1	0	1.312987	-1.651980	-0.129825
12	1	0	-1.936414	-0.609395	-0.854058

13	29	0	-3.985799	1.119875	0.144012
14	9	0	-3.866817	-0.573687	0.968571
15	6	0	-4.039804	2.835858	-0.659115
16	6	0	-5.251869	3.475641	-0.783203
17	6	0	-5.277756	4.712006	-1.404750
18	6	0	-4.085420	5.260622	-1.841568
19	6	0	-2.870179	4.617802	-1.687853
20	6	0	-2.846221	3.368818	-1.090737
21	1	0	-6.161256	3.040744	-0.389697
22	1	0	-6.207842	5.248014	-1.536960
23	7	0	-4.110338	6.575686	-2.488951
24	1	0	-1.960350	5.083130	-2.041416
25	1	0	-1.913426	2.829846	-0.982023
26	1	0	-2.268933	-0.071656	1.468002
27	9	0	-3.164031	0.537163	-1.343053
28	9	0	-4.830285	1.851042	1.523176
29	1	0	2.283348	-0.981729	-2.101015
30	8	0	-3.052780	7.052688	-2.849585
31	8	0	-5.187438	7.119380	-2.631040
32	6	0	-7.809017	0.832953	-1.036014
33	6	0	-8.068959	0.100394	0.106536
34	6	0	-7.288779	-1.004611	0.388064
35	6	0	-6.293542	-1.352890	-0.504237
36	6	0	-6.038714	-0.632512	-1.658390
37	6	0	-6.803331	0.483939	-1.924524
38	1	0	-8.872536	0.405008	0.765213
39	1	0	-7.449279	-1.595835	1.278433
40	7	0	-5.474085	-2.541287	-0.222432
41	1	0	-5.243272	-0.939528	-2.321703
42	1	0	-6.633587	1.080681	-2.813096
43	8	0	-4.651626	-2.870005	-1.050785
44	8	0	-5.680323	-3.135568	0.814299
45	7	0	-8.666323	1.985870	-1.284296
46	7	0	-8.413668	2.839317	-2.040473

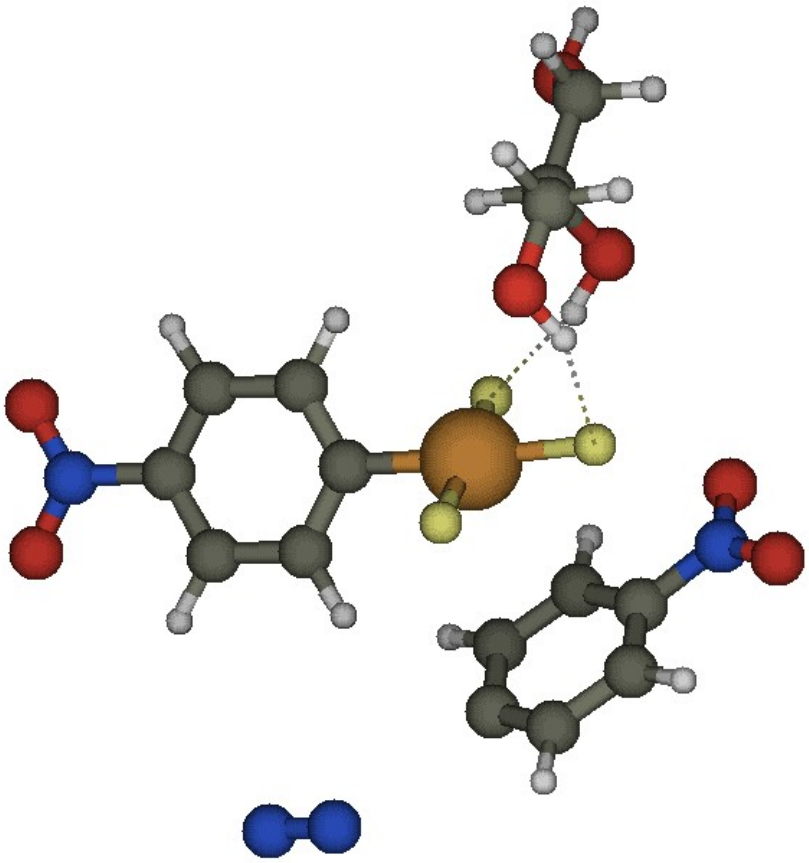
TS_{NN}



1	6	0	0.048939	0.012362	0.126926
2	6	0	0.056612	-0.105714	1.633706
3	6	0	1.452066	0.021925	-0.432680
4	8	0	-0.616414	-1.083383	-0.473631
5	1	0	-0.459326	0.948086	-0.155084
6	8	0	-1.224437	0.004942	2.201222
7	1	0	0.529152	-1.062106	1.904391
8	1	0	0.672607	0.696469	2.054899
9	8	0	1.434021	0.044639	-1.841497
10	1	0	1.993739	0.905278	-0.085609
11	1	0	1.987381	-0.867286	-0.063749
12	1	0	-1.566002	-0.863981	-0.536576
13	29	0	-3.909348	0.011432	0.858132
14	9	0	-3.158060	-1.631596	1.398250
15	6	0	-4.591452	1.705270	0.344163
16	6	0	-5.947879	1.928447	0.412117
17	6	0	-6.427500	3.161628	0.005922
18	6	0	-5.524203	4.118654	-0.420262
19	6	0	-4.160997	3.889051	-0.461180
20	6	0	-3.681252	2.647948	-0.077914
21	1	0	-6.624390	1.172272	0.788851
22	1	0	-7.485781	3.383366	0.031118
23	7	0	-6.031119	5.428401	-0.841389
24	1	0	-3.488445	4.665654	-0.798652
25	1	0	-2.621313	2.432034	-0.125845
26	1	0	-1.769139	-0.764122	1.930945
27	9	0	-3.100405	-0.065329	-0.742699
28	9	0	-4.778326	0.235286	2.387790

29	1	0	0.729221	-0.568753	-2.092321
30	8	0	-5.223821	6.262220	-1.200329
31	8	0	-7.231777	5.610622	-0.809464
32	6	0	-7.559887	-1.444344	0.167624
33	6	0	-7.386877	-2.353275	1.173549
34	6	0	-6.260460	-3.158015	1.104370
35	6	0	-5.399645	-3.001350	0.032009
36	6	0	-5.607574	-2.072242	-0.974111
37	6	0	-6.728988	-1.260902	-0.903979
38	1	0	-8.096348	-2.438445	1.988323
39	1	0	-6.046179	-3.896290	1.864869
40	7	0	-4.211410	-3.861586	-0.044040
41	1	0	-4.899160	-1.987757	-1.786382
42	1	0	-6.937222	-0.515225	-1.664995
43	8	0	-3.484225	-3.741243	-1.008024
44	8	0	-4.030268	-4.657981	0.853320
45	7	0	-9.098945	-0.396321	0.274186
46	7	0	-9.258871	0.398067	-0.498893

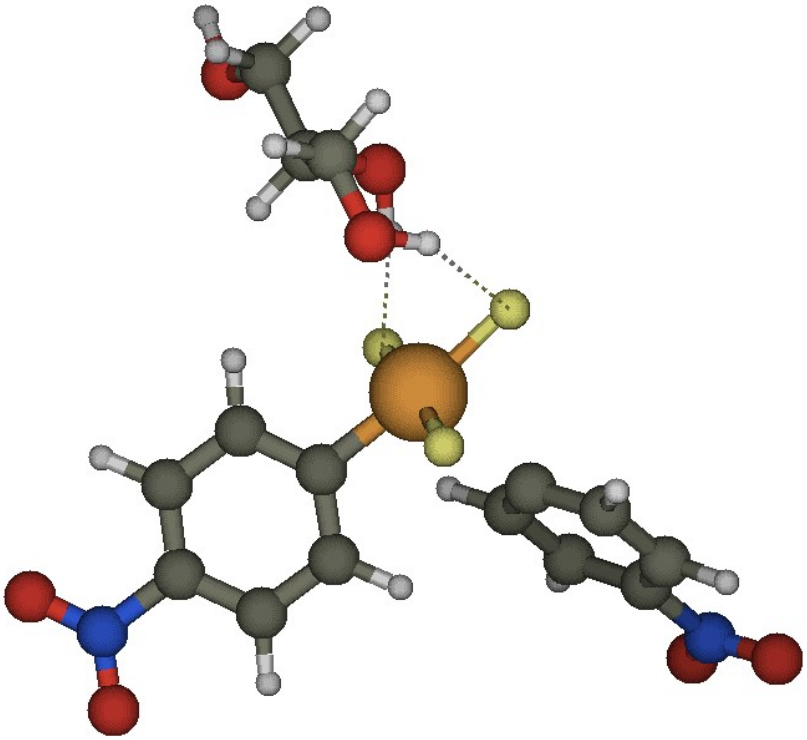
I-9



1	6	0	0.115489	-0.098532	0.051003
2	6	0	0.128036	-0.126962	1.567233
3	6	0	1.520758	-0.176259	-0.483455
4	8	0	-0.625584	-1.182481	-0.464068
5	1	0	-0.334230	0.851982	-0.279172
6	8	0	-1.156686	-0.021089	2.126433
7	1	0	0.626892	-1.052433	1.895190
8	1	0	0.716637	0.715944	1.943572

9	8	0	1.511036	0.108402	-1.866833
10	1	0	2.154391	0.537228	0.060634
11	1	0	1.909549	-1.186302	-0.290329
12	1	0	-1.565131	-0.921567	-0.482815
13	29	0	-3.864417	-0.014825	0.983637
14	9	0	-3.130366	-1.678011	1.487032
15	6	0	-4.507894	1.706636	0.518541
16	6	0	-5.858926	1.963293	0.575720
17	6	0	-6.297986	3.225361	0.214902
18	6	0	-5.363221	4.173923	-0.159450
19	6	0	-4.006192	3.908657	-0.191588
20	6	0	-3.566387	2.640527	0.148449
21	1	0	-6.564847	1.209270	0.902285
22	1	0	-7.350027	3.474984	0.234062
23	7	0	-5.828827	5.512543	-0.533504
24	1	0	-3.307977	4.679399	-0.487892
25	1	0	-2.511859	2.397342	0.110119
26	1	0	-1.683405	-0.816665	1.902683
27	9	0	-3.106075	-0.087524	-0.642208
28	9	0	-4.681355	0.219883	2.541858
29	6	0	-7.449822	-1.291440	0.192934
30	6	0	-7.322055	-2.189813	1.215668
31	6	0	-6.251462	-3.069333	1.141333
32	6	0	-5.395427	-2.982858	0.056084
33	6	0	-5.561015	-2.061089	-0.964115
34	6	0	-6.629347	-1.177495	-0.895582
35	1	0	-8.010285	-2.218648	2.052356
36	1	0	-6.070421	-3.804373	1.913803
37	7	0	-4.253548	-3.899384	-0.010341
38	1	0	-4.858263	-2.031346	-1.784883
39	1	0	-6.785781	-0.436795	-1.671233
40	1	0	2.399076	-0.020196	-2.209818
41	8	0	-4.995101	6.337082	-0.851595
42	8	0	-7.024374	5.727407	-0.506480
43	8	0	-3.496262	-3.799017	-0.954293
44	8	0	-4.128999	-4.718217	0.878007
45	7	0	-9.562093	0.524203	1.349854
46	7	0	-9.917423	1.399802	0.807498

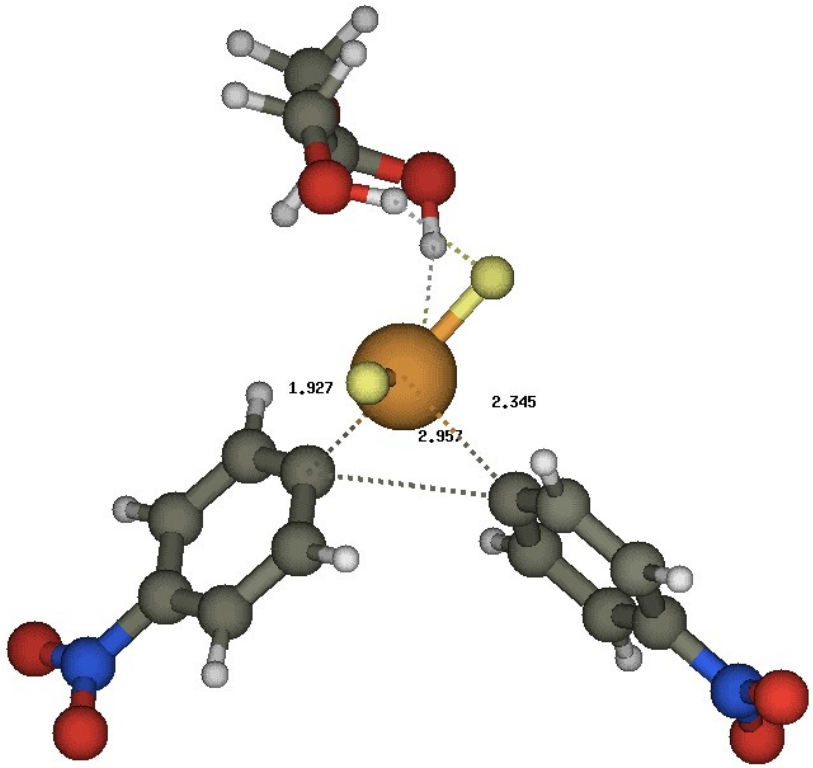
I-10



1	6	0	0.223090	0.059434	0.085994
2	6	0	0.199665	-0.192706	1.581168
3	6	0	1.638296	0.014501	-0.425243
4	8	0	-0.538568	-0.910538	-0.596797
5	1	0	-0.188361	1.063430	-0.109824
6	8	0	-1.097972	-0.151514	2.120663
7	1	0	0.678136	-1.163845	1.780758
8	1	0	0.788210	0.576590	2.091115
9	8	0	1.674077	0.508085	-1.747727
10	1	0	2.280578	0.612196	0.235852
11	1	0	1.987899	-1.026825	-0.381774
12	1	0	-1.471196	-0.622977	-0.584367
13	29	0	-3.691806	0.132124	1.059662
14	9	0	-3.128293	-1.655841	1.295203
15	6	0	-4.123487	1.968469	0.881842
16	6	0	-5.433969	2.380056	0.964379
17	6	0	-5.699011	3.731728	0.825503
18	6	0	-4.641623	4.602889	0.634056
19	6	0	-3.327609	4.175428	0.570921
20	6	0	-3.060784	2.822315	0.690889
21	1	0	-6.239513	1.679705	1.145001
22	1	0	-6.711386	4.108308	0.876660
23	7	0	-4.924046	6.034465	0.497102
24	1	0	-2.529481	4.889643	0.421853
25	1	0	-2.044121	2.454152	0.628484
26	1	0	-1.615924	-0.920912	1.806223
27	9	0	-3.001165	0.216094	-0.607533
28	9	0	-4.417609	0.244308	2.685992
29	6	0	-5.873969	-0.850397	-0.016599
30	6	0	-6.605218	-1.679193	0.788713
31	6	0	-7.759299	-2.217256	0.239338
32	6	0	-8.089993	-1.886853	-1.065162

33	6	0	-7.320459	-1.042915	-1.849899
34	6	0	-6.164959	-0.501800	-1.306845
35	1	0	-6.303625	-1.910013	1.803072
36	1	0	-8.396076	-2.882589	0.806462
37	7	0	-9.311821	-2.457432	-1.642578
38	1	0	-7.625347	-0.819415	-2.863241
39	1	0	-5.528677	0.161251	-1.880772
40	1	0	2.562921	0.390057	-2.092457
41	8	0	-3.983323	6.788311	0.345222
42	8	0	-6.084159	6.392754	0.542451
43	8	0	-9.594484	-2.159620	-2.786129
44	8	0	-9.978511	-3.198168	-0.947573

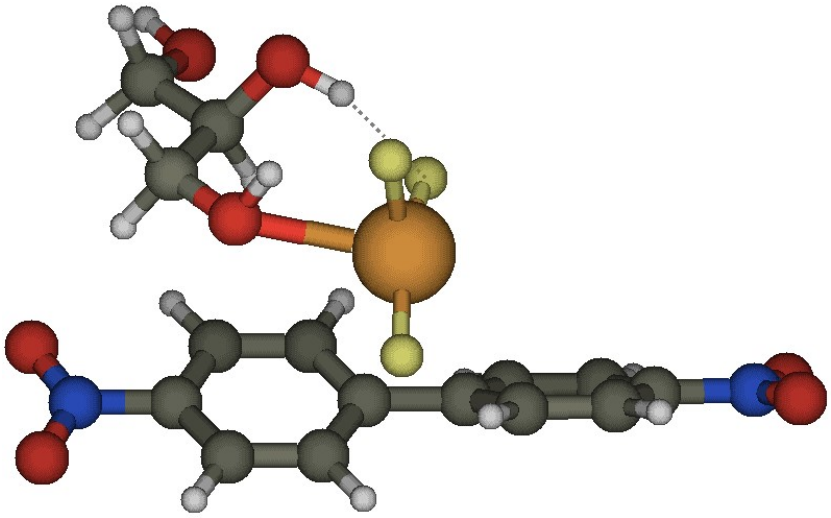
TS_{CC}



1	6	0	0.217874	-0.018315	0.091000
2	6	0	0.214419	-0.299913	1.580637
3	6	0	1.626040	-0.048352	-0.440464
4	8	0	-0.551193	-0.976763	-0.599124
5	1	0	-0.201032	0.987644	-0.076333
6	8	0	-1.074186	-0.253579	2.139955
7	1	0	0.684475	-1.280508	1.753164
8	1	0	0.819252	0.451939	2.097622
9	8	0	1.641167	0.464417	-1.756313
10	1	0	2.274497	0.543349	0.219958
11	1	0	1.981987	-1.088262	-0.417331
12	1	0	-1.483666	-0.685232	-0.571322
13	29	0	-3.731401	0.043493	1.108240
14	9	0	-3.130247	-1.733397	1.295755
15	6	0	-4.282503	1.884540	0.966746
16	6	0	-5.472293	2.309322	1.518208
17	6	0	-5.776905	3.656697	1.450332

18	6	0	-4.872465	4.517380	0.853769
19	6	0	-3.676342	4.080464	0.318298
20	6	0	-3.375024	2.728392	0.365729
21	1	0	-6.148154	1.619833	2.004639
22	1	0	-6.701122	4.038029	1.862318
23	7	0	-5.194126	5.946612	0.791123
24	1	0	-2.991829	4.784590	-0.134621
25	1	0	-2.455800	2.354590	-0.063967
26	1	0	-1.611354	-1.001753	1.807828
27	9	0	-2.983844	0.159733	-0.561795
28	9	0	-4.291995	0.132075	2.821901
29	6	0	-5.784779	-0.518801	0.125129
30	6	0	-6.554841	-1.311367	0.933480
31	6	0	-7.724370	-1.810947	0.379725
32	6	0	-8.036324	-1.478915	-0.927924
33	6	0	-7.232461	-0.668268	-1.712330
34	6	0	-6.060833	-0.165404	-1.167840
35	1	0	-6.269706	-1.544509	1.951902
36	1	0	-8.386010	-2.448968	0.949840
37	7	0	-9.275316	-2.008401	-1.508330
38	1	0	-7.522976	-0.437664	-2.728328
39	1	0	-5.400384	0.470626	-1.743547
40	1	0	2.526774	0.359294	-2.113274
41	8	0	-4.385982	6.689535	0.270801
42	8	0	-6.252142	6.312365	1.262999
43	8	0	-9.536936	-1.713313	-2.657357
44	8	0	-9.975113	-2.714023	-0.809675

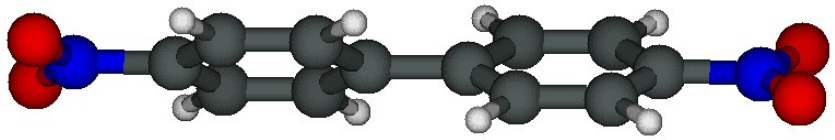
I-11



1	6	0	-0.294476	0.090964	-0.175282
2	6	0	-0.160094	0.159745	1.331321
3	6	0	1.052809	0.229623	-0.830832
4	8	0	-0.897475	-1.122481	-0.566400
5	1	0	-0.928329	0.927353	-0.501385
6	8	0	-1.404355	0.043493	1.986378
7	1	0	0.530610	-0.624027	1.672686
8	1	0	0.267282	1.125909	1.619090
9	8	0	0.870114	0.481771	-2.208266
10	1	0	1.604956	1.050239	-0.350461
11	1	0	1.620947	-0.696869	-0.667567
12	1	0	-1.855846	-0.945540	-0.630675
13	29	0	-3.777482	0.022240	1.152947
14	9	0	-3.373975	-1.729623	1.695284
15	6	0	-3.546662	3.307516	0.233390
16	6	0	-3.464385	3.558616	1.603724
17	6	0	-2.248623	3.792801	2.209712
18	6	0	-1.103212	3.762952	1.436013
19	6	0	-1.145900	3.512710	0.076516
20	6	0	-2.370112	3.289516	-0.516618
21	1	0	-4.365292	3.583224	2.202768
22	1	0	-2.181595	3.996562	3.269042
23	7	0	0.192561	3.996395	2.076485
24	1	0	-0.230988	3.481493	-0.500210
25	1	0	-2.407325	3.064320	-1.575529
26	1	0	-1.719961	-0.877341	1.929331
27	9	0	-3.401516	-0.123824	-0.622566
28	9	0	-4.489810	0.712688	2.659536
29	6	0	-4.848580	3.054209	-0.407249
30	6	0	-5.860577	2.382264	0.281617
31	6	0	-7.070652	2.118441	-0.325479
32	6	0	-7.271742	2.544497	-1.624924
33	6	0	-6.294396	3.221367	-2.330952
34	6	0	-5.085759	3.469265	-1.717395
35	1	0	-5.687449	2.029254	1.293808
36	1	0	-7.852790	1.584689	0.195871
37	7	0	-8.556275	2.272001	-2.272470
38	1	0	-6.486683	3.549286	-3.342705
39	1	0	-4.322270	4.013847	-2.259049

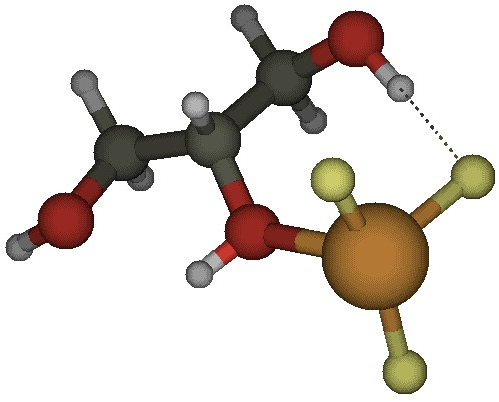
40	1	0	1.729999	0.476895	-2.636434
41	8	0	1.195381	3.825541	1.409317
42	8	0	0.198841	4.342544	3.240702
43	8	0	-8.711760	2.658244	-3.414435
44	8	0	-9.400198	1.673992	-1.634367

P 4,4'-DiNitroBiphenyl



1	6	0	0.009470	-0.000000	0.005468
2	6	0	0.039342	-0.268922	1.374181
3	6	0	1.229580	-0.272711	2.069800
4	6	0	2.399975	-0.000000	1.385626
5	6	0	2.407289	0.272711	0.029948
6	6	0	1.209747	0.268922	-0.653019
7	1	0	-0.879377	-0.502787	1.897796
8	1	0	1.259407	-0.490566	3.128076
9	7	0	3.669088	-0.000000	2.118349
10	1	0	3.338697	0.490566	-0.473359
11	1	0	1.203851	0.502787	-1.710461
12	6	0	-1.265207	0.000000	-0.730468
13	6	0	-2.433244	0.468075	-0.127821
14	6	0	-3.630402	0.473075	-0.811454
15	6	0	-3.655712	0.000000	-2.110626
16	6	0	-2.517941	-0.473075	-2.738294
17	6	0	-1.327319	-0.468075	-2.043341
18	1	0	-2.400110	0.856897	0.882441
19	1	0	-4.536047	0.844178	-0.352771
20	7	0	-4.924825	0.000000	-2.843349
21	1	0	-2.573532	-0.844178	-3.751946
22	1	0	-0.435839	-0.856897	-2.519777
23	8	0	4.684410	0.232738	1.496802
24	8	0	3.638473	-0.232738	3.308417
25	8	0	-4.922362	-0.410827	-3.984656
26	8	0	-5.911995	0.410827	-2.270563

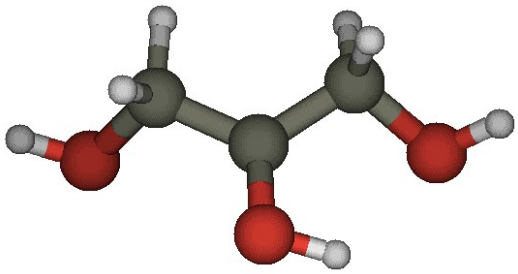
V GL * $Cu^{II}F_3^-$



1	29	0	-0.006186	-0.001864	-0.002908

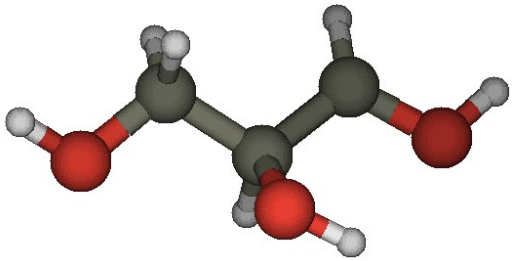
2	8	0	0.001674	-0.000483	2.219049
3	6	0	1.204446	0.002661	2.993331
4	6	0	1.913181	1.325839	2.813687
5	1	0	1.856727	-0.810843	2.647041
6	8	0	2.642434	1.440839	1.625747
7	1	0	1.160876	2.123871	2.912059
8	1	0	2.619228	1.444135	3.643491
9	1	0	2.021287	1.525158	0.866762
10	6	0	0.831770	-0.220856	4.438076
11	8	0	0.026092	-1.382983	4.482533
12	1	0	0.280662	0.653006	4.810207
13	1	0	1.741184	-0.338709	5.038720
14	9	0	0.949175	1.607696	-0.402021
15	9	0	1.307187	-1.238564	-0.213877
16	9	0	-1.726591	0.580912	-0.088513
17	1	0	-0.557390	-0.696391	2.597522
18	1	0	-0.480489	-1.387899	5.298589

VI 2-Glycerolyl $HOCH_2C^*(OH)CH_2OH$



1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.470420
3	6	0	1.242652	0.000000	-0.805120
4	8	0	-1.100472	-0.539333	-0.586770
5	8	0	-1.004441	0.887489	1.957763
6	1	0	-0.197620	-1.018289	1.849721
7	1	0	0.997723	0.296750	1.824450
8	8	0	0.885522	0.351155	-2.136407
9	1	0	1.968754	0.702884	-0.374220
10	1	0	1.716495	-1.000203	-0.809778
11	1	0	-0.963888	-0.484411	-1.545177
12	1	0	1.530076	-0.020644	-2.744530
13	1	0	-1.150969	0.694544	2.888624

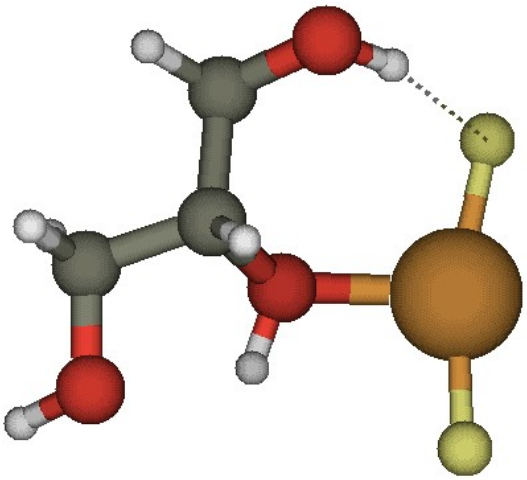
VI' 1-Glycerolyl $HOCH_2CH(OH)CH^*OH$



1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.506580

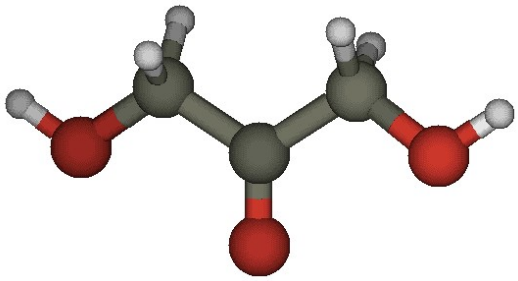
3	6	0	1.385505	0.000000	-0.524007
4	8	0	-0.727745	-1.139498	-0.447929
5	1	0	-0.534120	0.911238	-0.341559
6	8	0	-1.310975	0.258301	1.960261
7	1	0	0.361395	-0.977820	1.857672
8	1	0	0.701671	0.770250	1.859662
9	8	0	1.450516	-0.125605	-1.877136
10	1	0	2.196594	0.515497	-0.016032
11	1	0	-0.641926	-1.185559	-1.405623
12	1	0	2.361871	-0.067182	-2.180050
13	1	0	-1.330879	0.168616	2.916293

VII GL * $Cu^{II}F_2$



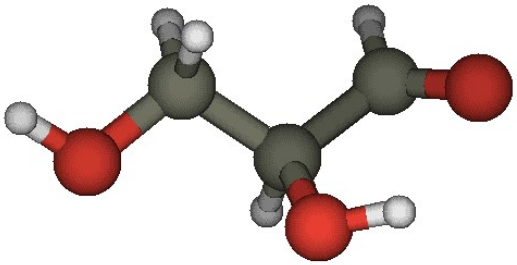
1	29	0	0.099966	-0.126627	0.156562
2	8	0	0.092315	-0.021988	2.136632
3	6	0	1.273065	0.033861	2.978504
4	6	0	1.941990	1.376459	2.835081
5	1	0	1.958170	-0.761503	2.662412
6	8	0	2.731933	1.494931	1.685375
7	1	0	1.167278	2.155277	2.885472
8	1	0	2.596805	1.513692	3.701598
9	1	0	2.137198	1.582870	0.916560
10	6	0	0.794495	-0.218505	4.385724
11	8	0	0.027792	-1.404564	4.342498
12	1	0	0.191506	0.632978	4.724923
13	1	0	1.661510	-0.317764	5.047935
14	9	0	0.868989	1.446633	-0.226606
15	9	0	-0.717394	-1.697472	0.081722
16	1	0	-0.423588	-0.782338	2.467880
17	1	0	-0.562974	-1.434400	5.099729

VIII 1,3-DiHydroxyPropanone



1	6	0	-0.001009	-0.003969	-0.000462
2	6	0	0.003558	0.020234	1.504791
3	6	0	1.376521	-0.022533	-0.607255
4	8	0	-1.009426	-0.008316	-0.655859
5	8	0	-1.274503	0.298898	1.992721
6	1	0	0.370865	-0.964428	1.832596
7	1	0	0.753035	0.753558	1.836786
8	8	0	1.304699	-0.294183	-1.974657
9	1	0	1.824299	0.961334	-0.399423
10	1	0	1.984822	-0.757983	-0.060453
11	1	0	2.193545	-0.252603	-2.337376
12	1	0	-1.244012	0.265468	2.952567

IX 1,2-DiHydroxyPropanale



1	6	0	0.002685	-0.001913	0.000580
2	6	0	-0.003082	-0.006621	1.512303
3	6	0	1.407851	-0.007362	-0.525718
4	8	0	-0.731756	-1.066980	-0.523430
5	1	0	-0.431466	0.962492	-0.320800
6	8	0	-1.319256	0.252241	1.938888
7	1	0	0.348998	-0.984957	1.864737
8	1	0	0.694167	0.761038	1.875303
9	8	0	1.777840	-0.821629	-1.329594
10	1	0	2.076550	0.787891	-0.143820
11	1	0	-0.148860	-1.512419	-1.158451
12	1	0	-1.350615	0.178739	2.896592

Physical and NMR data of biaryls 2

4,4'-Dinitrobiphenyl (2a): 179 mg (73% yield).Grey solid, mp 234–235°C (MeOH. Lit[1] 236–237°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 8.34 (d, 4H, *J* = 7.8 Hz), 7.91 (d, 4H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 148.2, 144.9, 129.1, 124.5. MS*: m/z* 244 (M^+).

4,4'-Dibromobiphenyl (2b): 222 mg (71% yield). White solid, mp 164–165°C (MeOH. Lit[2] 166°C) S. Ojha, N. Panda, Pd-Catalyzed desulfitative arylation of olefins by N-methoxysulfonamide*, Org. Biomol. Chem*., **2022**, *20*, 1292−1298*;* https://doi.org/10.1039/D1OB02360H. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.63 (d, 4H, *J* = 7.8 Hz), 7.52 (d, 4H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 140.6, 131.7, 128.6, 122.0. MS*: m/z* 312 (M^+).

4,4'-Diacetylbiphenyl (2c): 180 mg (76% yield). White solid, mp 191–192°C (MeOH. Lit[3] 193–194°C). Ligand- and Base-Free Access to Diverse Biaryls by the Reductive Coupling of Diaryliodonium Salts, *Eur. J. Org. Chem.,* **2016**, *41*, 2096–2100; https://doi.org/10.1002/ejoc.201600242. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.97 (d, 4H, *J* = 7.2 Hz), 7.65 (d, 4H, *J* = 7.2 Hz), 2.56 (s, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): 197.1, 139.3, 137.8, 128.9, 128.6, 27.8. MS*: m/z* 238 (M^+).

4,4'-Dicyanobiphenyl (2d): 150 mg (74% yield). Pale yellow solid, mp 191–192°C (MeOH. Lit[4] 193–194°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 7.80 (d, 4H, *J* = 7.8 Hz), 7.77 (d, 4H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 144.8, 133.8, 131.2, 119.1, 115.7. MS*: m/z* 204 (M^+).

Dimethyl 4,4'-biphenyldicarboxylate (2e): 191 mg (71% yield). Grey solid, mp 214–215°C (MeOH. Lit[5] 212–214°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 8.13(d, 4H, *J* = 7.8 Hz), 7.76 (d, 4H, *J* = 7.8 Hz), 3.95 (s,6H). ^{13}C NMR ($CDCl_3$, 150 MHz): 167.3, 141.3, 130.1, 129.0, 127.6, 52.1. MS*: m/z* 270 (M^+).

4,4'-Dimethoxybiphenyl (2f): 111 mg (52% yield). Pale yellow solid, mp 177–178°C (MeOH. Lit[6] 178–178.5°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 7.60 (d, 4H, *J* = 7.8 Hz), 7.05 (d, 4H, *J* = 7.8 Hz), 3.82 (s, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): 159.4, 131.2, 128.7, 114.7, 56.0. MS*: m/z* 214 (M^+).

3,3'-Dinitrobiphenyl (2g): 179 mg (73% yield). Grey solid, mp 200–201°C (MeOH. Lit[7] 201–202°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 8.06 (s, 2H) 8.26–8.24 (m, 2H), 8.03–8.02 (s, 2H), 7.71 (t, 2H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 149.8, 144.7, 137.0, 127.9, 125.2, 125.1. MS*: m/z* 244 (M^+).

3,3'-Dimethoxybiphenyl (2h): 105 mg (49% yield). Waxy solid. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.43–7.41 (m, 2H), 7.31–7.29 (m, 4H), 6.98–6.97 (m, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz): 160.8, 141.8, 128.9, 118.8, 113.7, 112.2, 56.0. MS*: m/z* 214 (M^+).

2,2'-Dichlorobiphenyl (2i): 135 mg (61% yield; Method A). Pale yellow solid mp 58–59°C (MeOH. Lit[7] 59–62 °C). ^{1}H NMR ($CDCl_3$, 600 MHz): 7.57–7.56 (m, 2H), 7.47–7.46 (m, 2H), 7.35–7.30 (m, 4H). ^{13}C NMR ($CDCl_3$, 150 MHz): 136.7, 131.2, 130.0, 128.5, 128.4, 126.7. MS*: m/z* 222 (M^+).

2,2'-Dimethoxybiphenyl (2j): 83 mg (39% yield). Grey solid mp 152–153°C (MeOH. Lit[4] 154–156 °C). ^{1}H NMR ($CDCl_3$, 600 MHz): 7.57–7.56 (m, 2H), 7.34–7.31 (m, 2H), 7.11–7.04 (m, 4H), 3.81 (s, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): 156.8, 131.0, 129.1, 127.1, 120.7, 112.7, 56.8. MS*: m/z* 214 (M^+).

2,2',4,4'-Tetranitrobiphenyl (2k): 270 mg (81% yield). White solid mp 166–167°C (MeOH. Lit[8] 168.5–169.5 °C). ^{1}H NMR ($CDCl_3$, 600 MHz): 9.27 (d, 2H, *J* = 1.8 Hz), 8.71, (dd, 2H, J^1 = 7.8 Hz,

J^2 = 1.8 Hz), 7.50 (d, 2H, J^1 = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 148.3, 147.8, 137.3, 132.3, 126.8, 119.5. MS*: m/z* 334 (M^+).

4,4'-Dimethoxy-2,2'-dinitrobiphenyl (2l): 189 mg (62% yield). Grey solid mp 132–133°C (MeOH. Lit[9] 131–132 °C). ^{1}H NMR ($CDCl_3$, 600 MHz): 7.80 (d, 2H, *J* = 7.2 Hz), 7.57–7.56 (m, 4H), 3.82 (s, 6H) . ^{13}C NMR ($CDCl_3$, 150 MHz): 161.7, 149.0, 130.1, 125.6, 118.6, 108.6, 56.2. MS*: m/z* 304 (M^+).

2,2',6,6'-Tetramethylbiphenyl (2m): 70 mg (33% yield). Pale yellow solid mp 66–67°C (MeOH. Lit[10] 67–70 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): 7.24–7.22 (m, 2H), 7.20–7.19 (m, 4H), 2.27 (s, 12H). ^{13}C NMR ($CDCl_3$, 150 MHz): 142.5, 134.8, 127.4, 125.5, 20.6. MS*: m/z* 210 (M^+).

1,1'-Binaphthyl (2n): 175 mg (69% yield). White solid mp 157–158°C (MeOH. Lit[11] 158 –159 °C). ^{1}H NMR ($CDCl_3$, 600 MHz): 7.75–7.74 (m, 4H), 7.69–7.61 (m, 2H), 7.51–7.49 (m, 2H), 7.42–7.39 (m, 4H), 7.29–7.27 (m, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz): 137.2, 133.8, 131.4, 128.3, 126.6, 126.2, 126.1, 125.7, 124.8. MS*: m/z* 254 (M^+).

3,3'-Bipyridine (2o): 106 mg (68% yield). Grey solid mp 63–64°C (MeOH. Lit[12] 64–65°C). G. Cheng, M. Luo, *Eur. J. Org. Chem.*, **2011**, *13,* 2519–2523; https://doi.org/10.1002/ejoc.201001729. ^{1}H NMR ($CDCl_3$, 600 MHz): 8.77 (s, 2H), 8.56 (d, 2H, *J* = 7.2 Hz), 7.96 (d, 2H, *J* = 7.8 Hz), 7.40 (t, 2H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): 147.4, 146.9, 137.1, 131.8, 125.6. MS*: m/z* 156 (M^+).

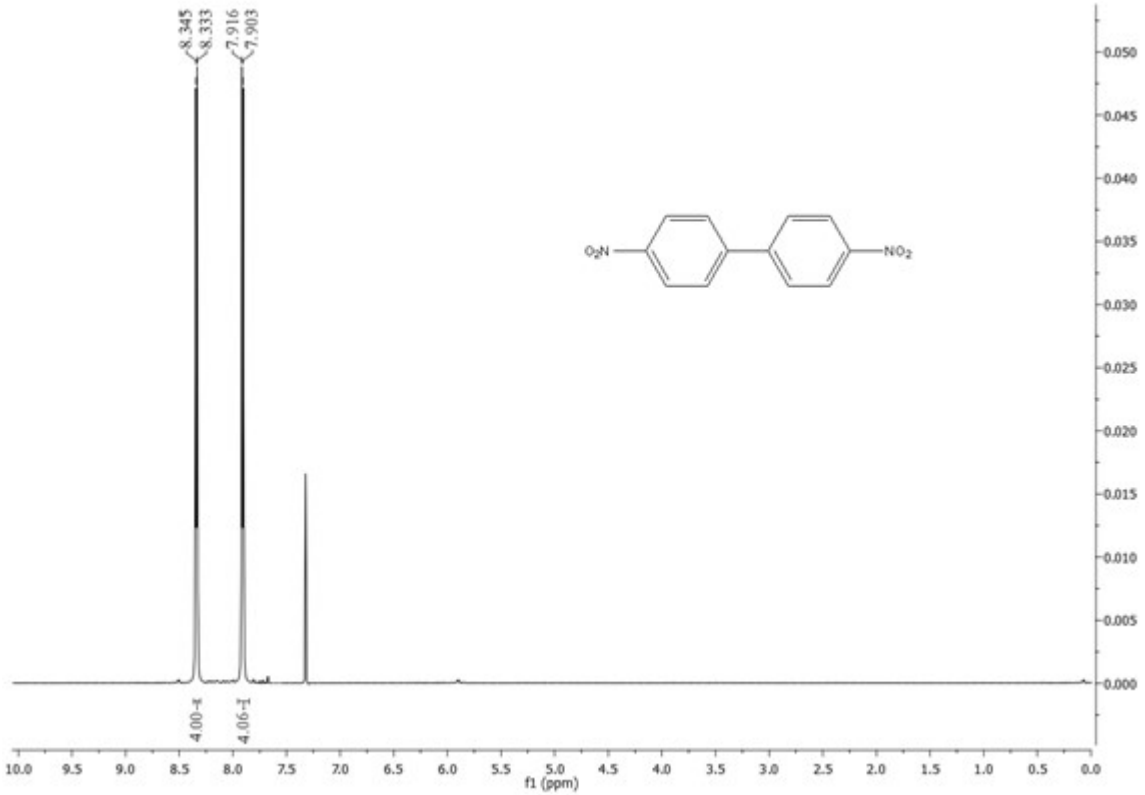
3,3'-Biquinoline (2p): 144 mg (56% yield). Pale orange solid mp 270–271°C (MeOH. Lit[13] 269–271°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 9.28 (s, 2H), 8.55 (s, 2H), 8.15–8.13 (m, 2H), 7.95–7.78 (m, 2H), 7.63–7.60 (m, 2H), 7.48–7.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz): 150.8, 146.6, 134.8, 134.7, 130.9, 129.9, 129.2, 128.7, 126.4. MS*: m/z* 256 (M^+).

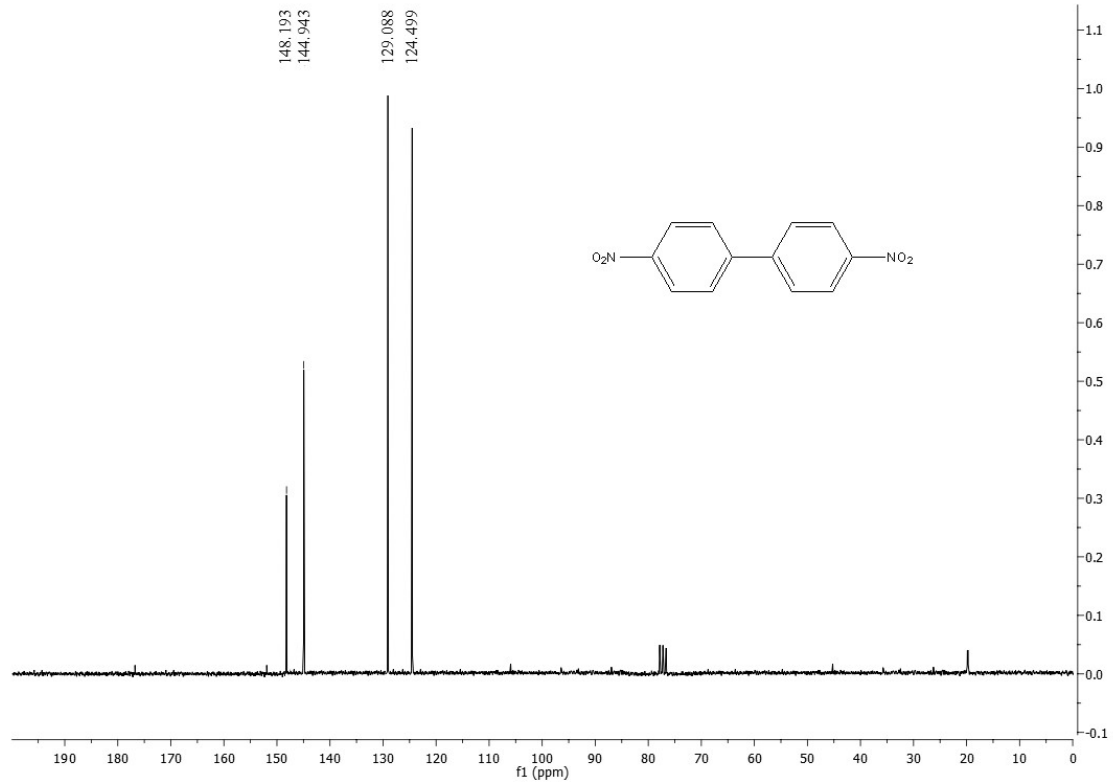
2,2'-Bibenzothiazole (2q): 90 mg (67% yield). Grey solid mp 241–242°C (MeOH. Lit[14] 239–240°C). ^{1}H NMR ($CDCl_3$, 600 MHz): 8.16–8.13 (m, 2H), 8.01–7.99 (m, 2H), 7.45–7.40 (m, 4H). ^{13}C NMR ($CDCl_3$, 150 MHz): 162.5, 153.3, 136.3, 126.9, 125.5, 123.7, 122.7. MS*: m/z* 268 (M^+).

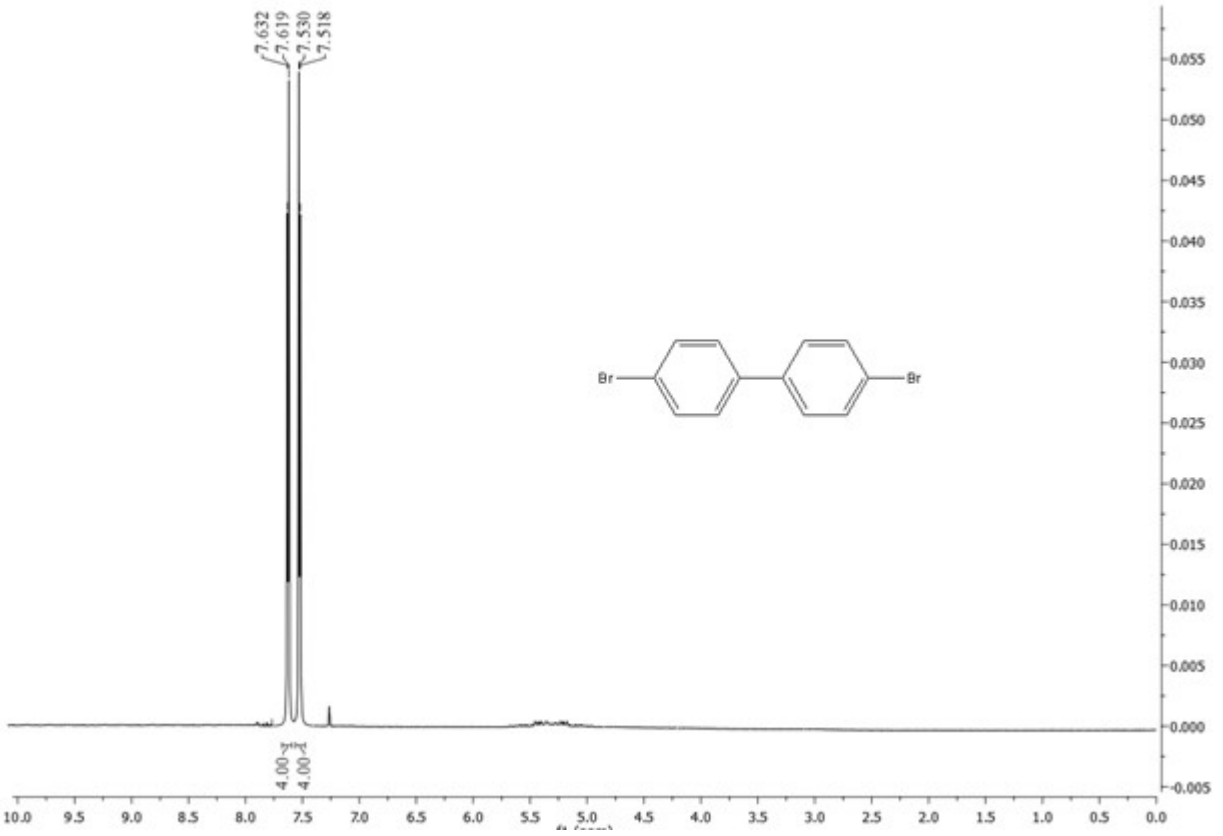
References

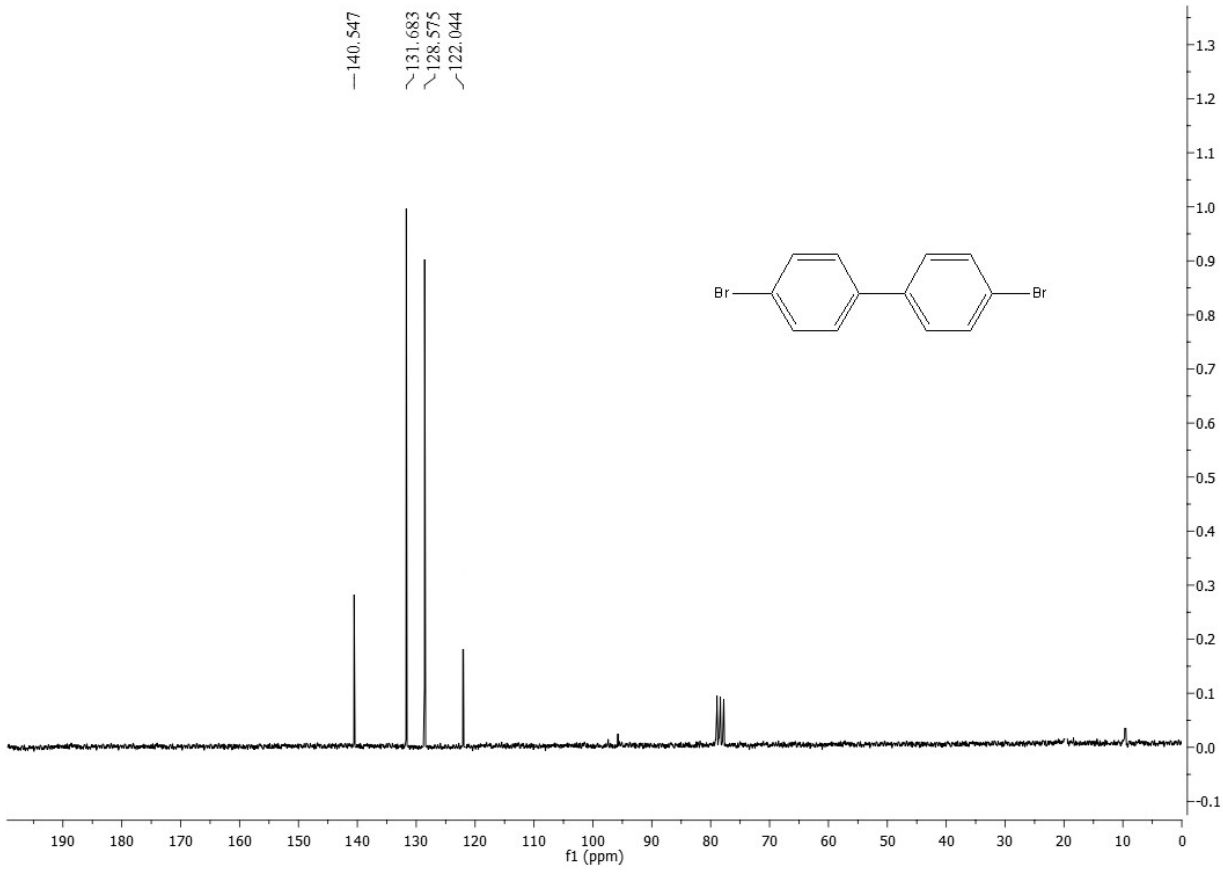
1. M.Barbero and S.Dughera, *Tetrahedron,* 2018*,* **74***,* 5758.
2. S. Ojha and N. Panda, *Org. Biomol. Chem*., 2022, **20**, 1292.
3. V. Arun, P. O. Venkataramana Reddy, M. Pilania and D. Kumar, *Eur. J. Org. Chem.,* 2016, 2096.
4. H. M. Savanur, R. G. Kalkhambkar and K. K. Laali, *Tetrahedron Lett*., 2016, **57**, 663–667.
5. J. Malineni, R. L. Jezorek, N. Zhang and V. Percec, *Synthesis*, 2016, **48**, 2795.
6. P. Wessig and S. Krebs, *Eur. J. Org. Chem.,* 2021, 6367.
7. B. Kaboudin R. Mostafalu and T. Yokomatsu, *Green Chem.,* 2013, **15**, 2266.
8. J. Cornforth,, *J. Chem. Soc., Perkin Trans. 1*, **1996**, 2889.
9. C.-L. Deng , S. C. K. Hau , X.-S. Peng and H. N. C. Wong, *Synlett,* 2016, **27**, 2095.
10. Z.-J. Wang, X. Wang, J.-J. Lv, J.-J. Feng, X. Xu, A.-J. Wang, and Z. Liang, *New. J. Chem*., 2017, **41**, 3894.
11. X. Li, D. Li, Y. Bai, C. Zhang, H. Chang, W. Gao and W. We, *Tetrahedron*, 2016, **72**, 6996.
12. G. Cheng and M. Luo, *Eur. J. Org. Chem.*, 2011, 2519.
13. A. V. Aksenov and V. I. Goncharov, *Chem. Heterocycl. Comp.* 2008*,* **44**, 1491.
14. A. A. Dar, M. Shadab, S. Khan, N. Ali and A. T. Khan, *J. Org. Chem*. 2016, **81**, 3149.

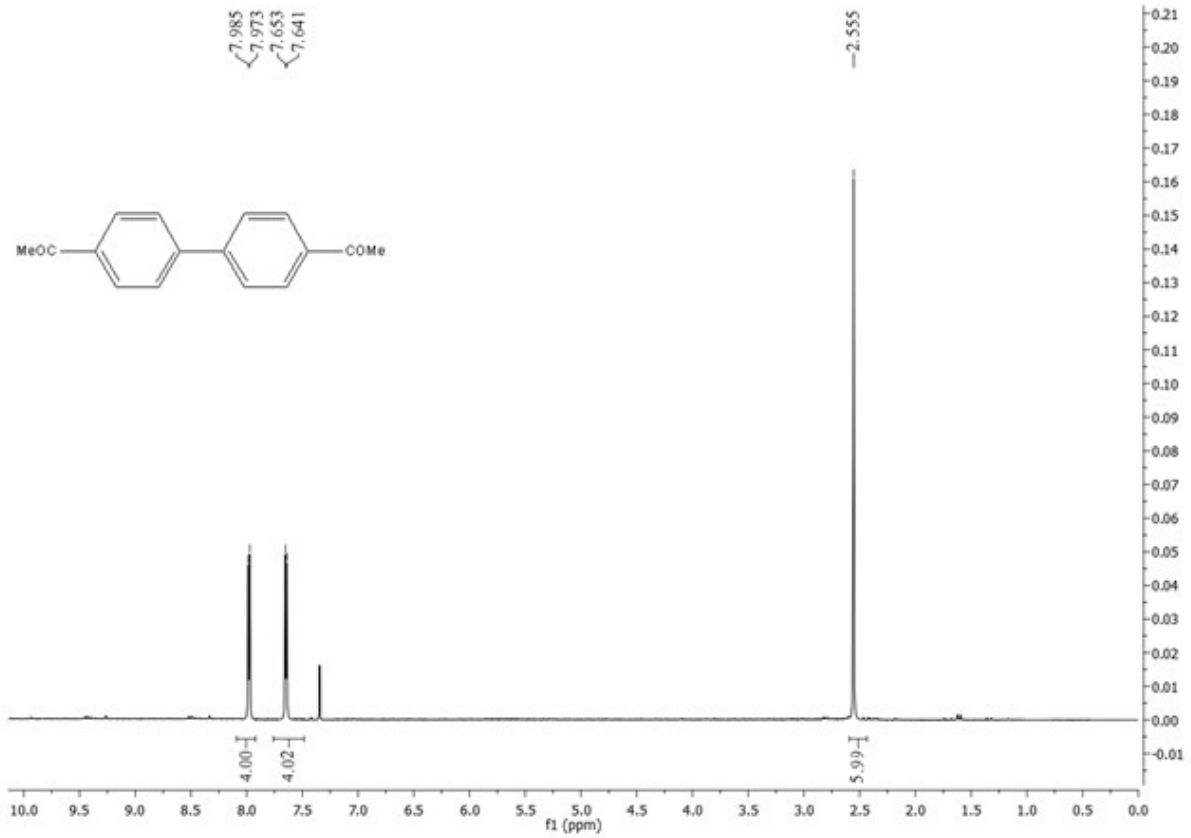
NMR spectra of biaryls 2

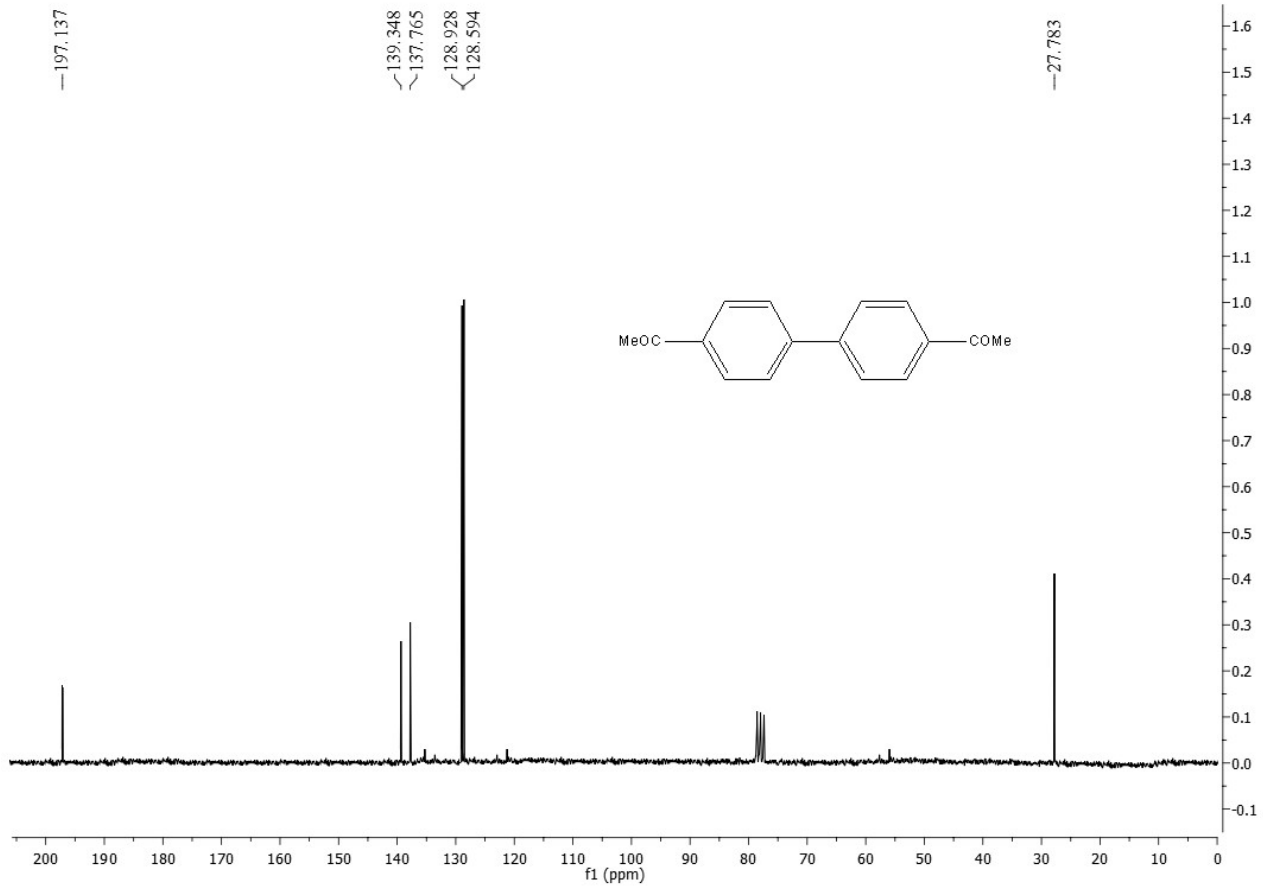


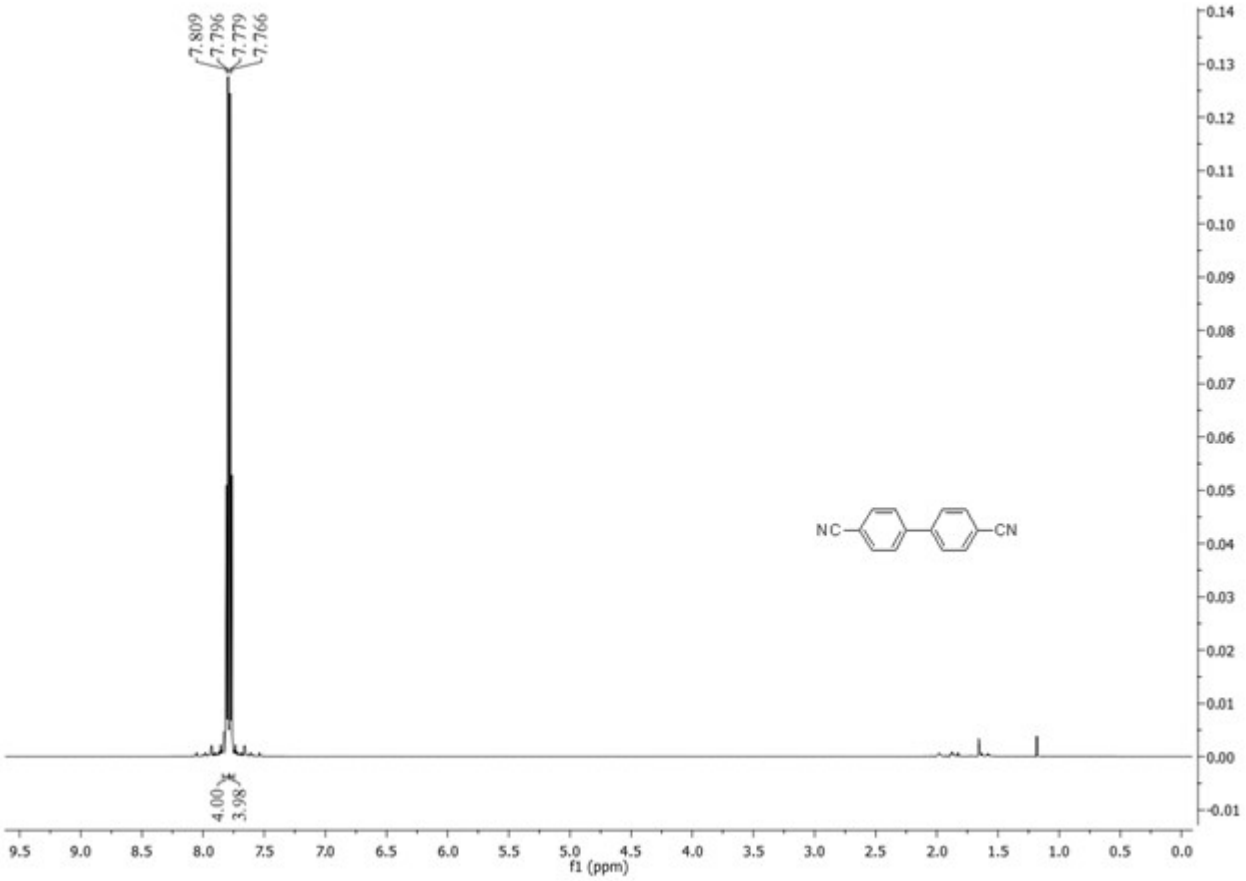


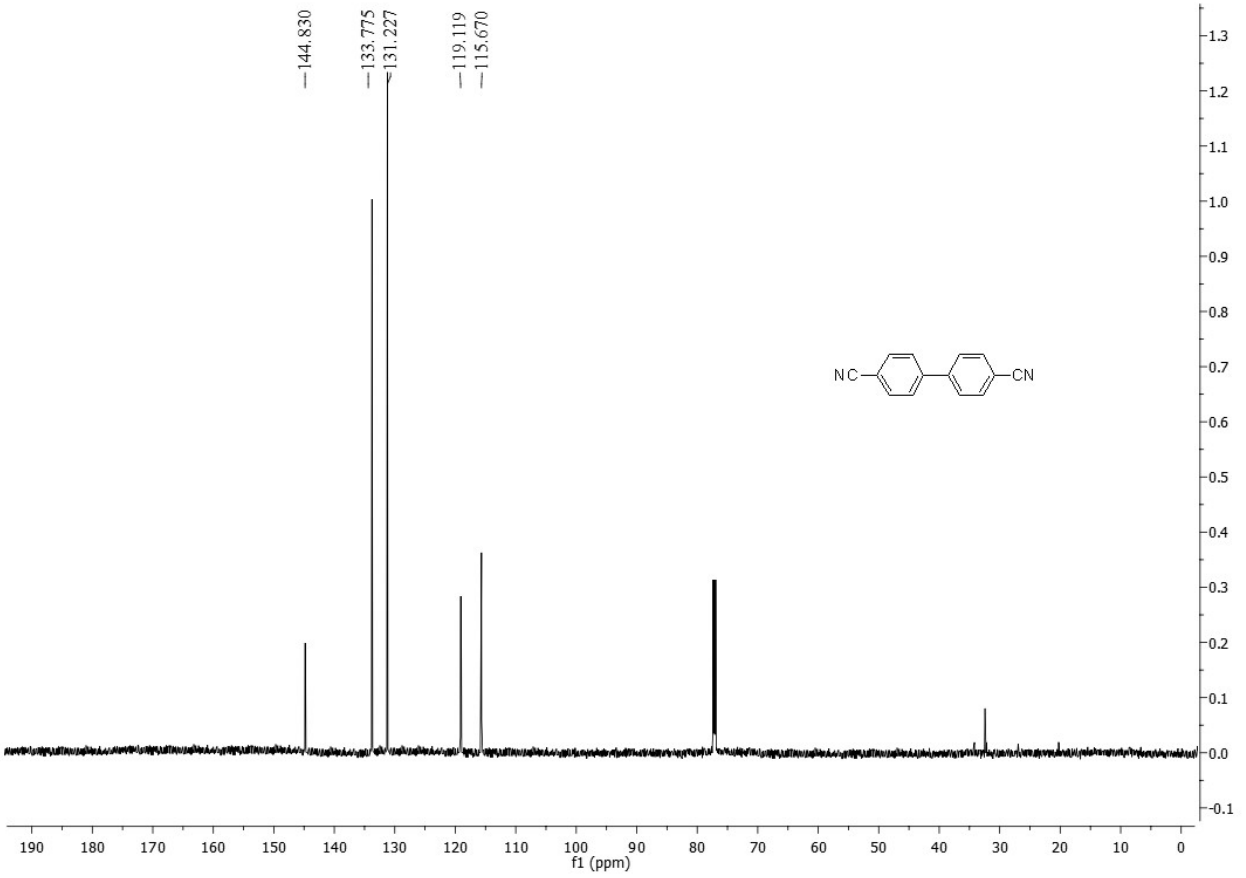

7.632
7.619
7.530
7.518
4.00
4.00
Br
Br

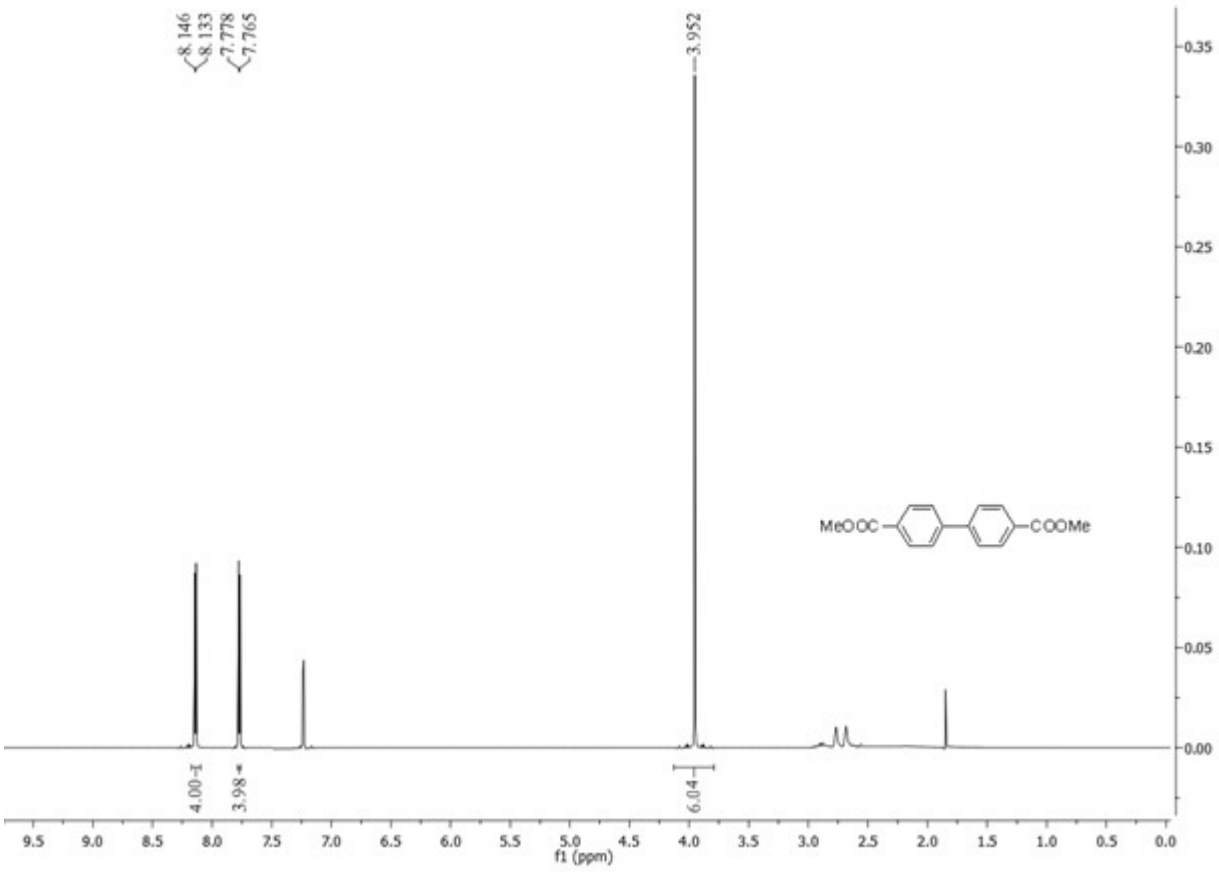

140.547
131.683
128.575
122.044
Br
Br
f1 (ppm)

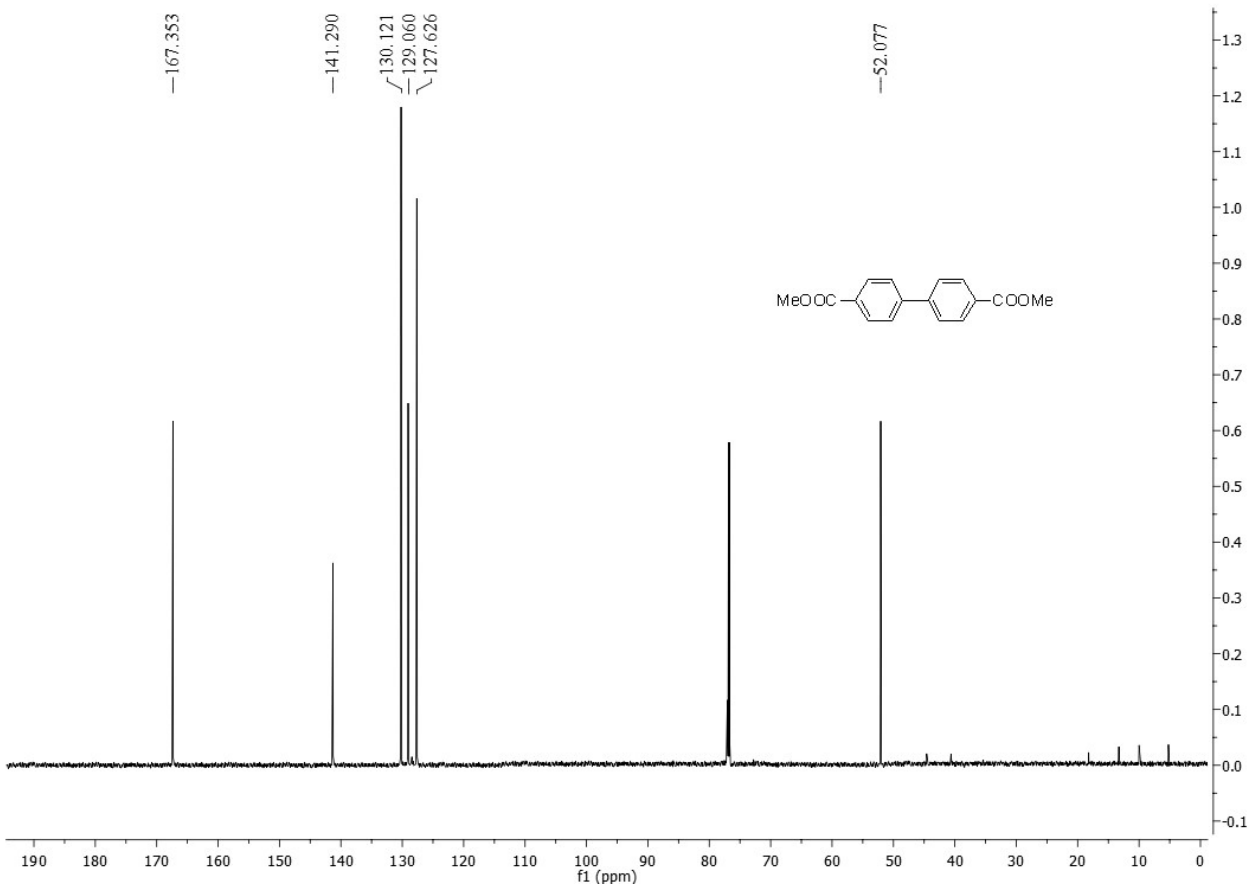

7.985
7.973
7.653
7.641
2.555
MeOC
COMe
4.00
4.02
5.99
f1 (ppm)

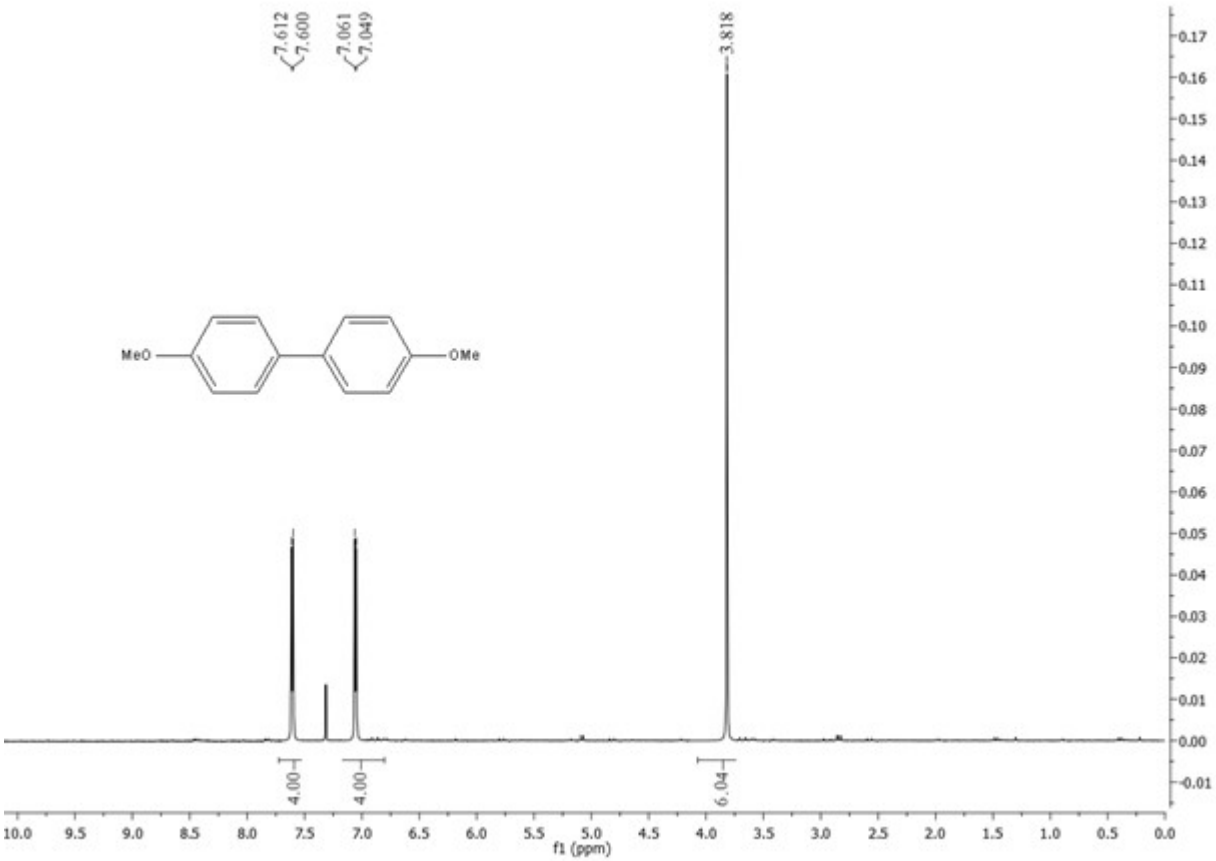

197.137
139.348
137.765
128.928
128.594
27.783
MeOC
COMe
f1 (ppm)

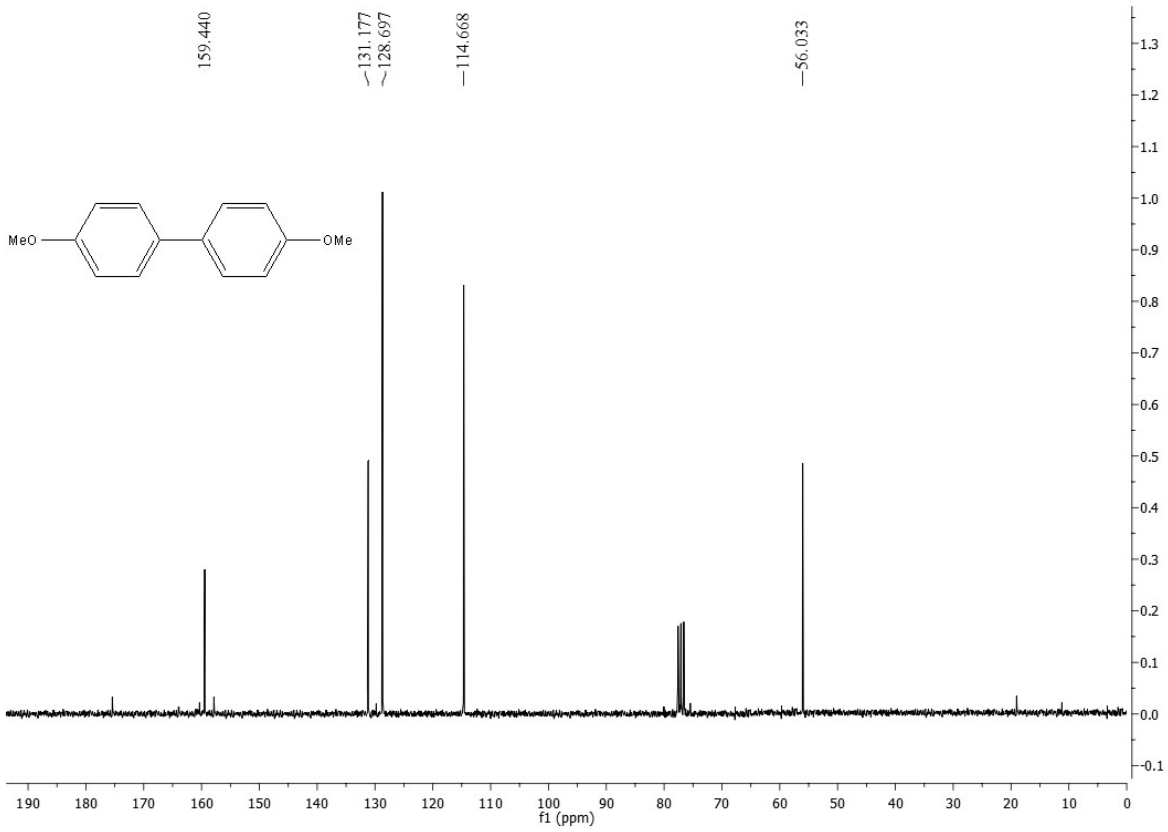

7.809
7.796
7.779
7.766
4.00
3.98
NC
CN
f1 (ppm)

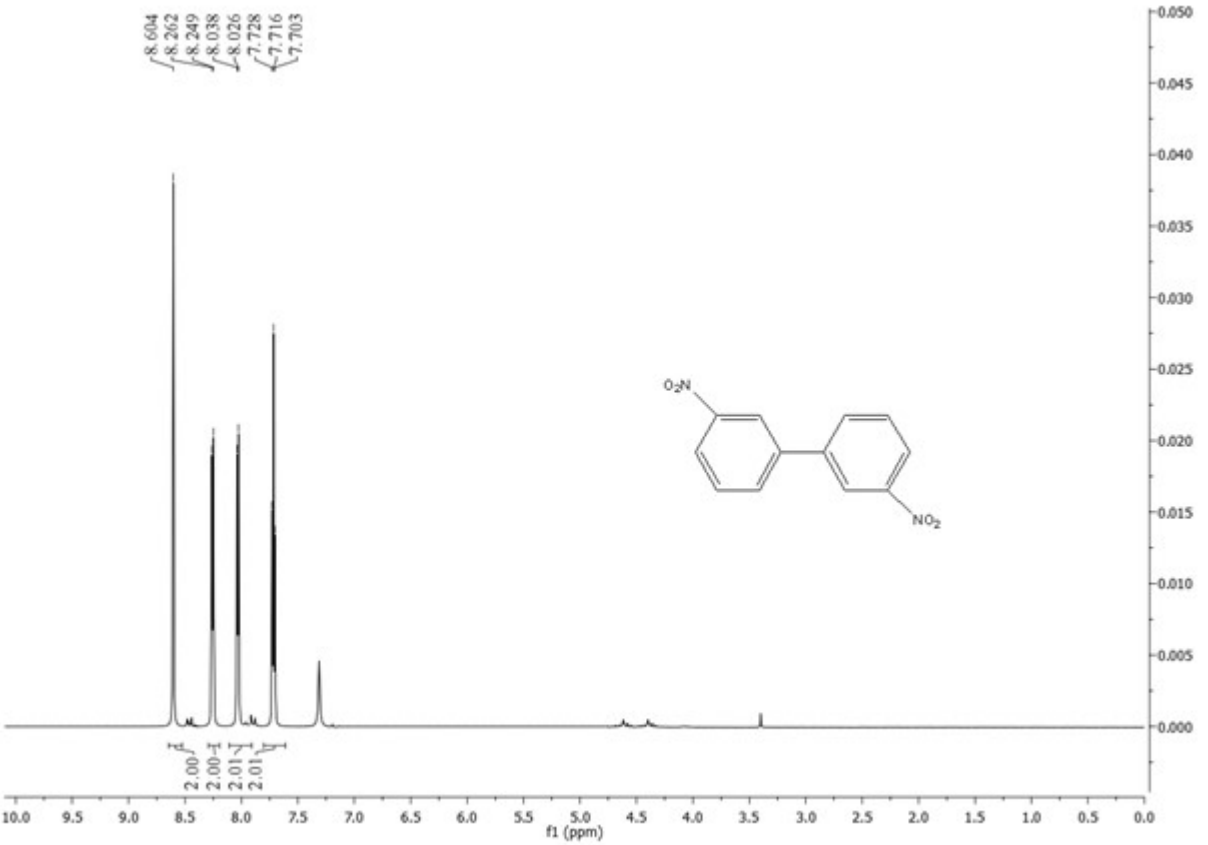

144.830
133.775
131.227
119.119
115.670
NC
CN
f1 (ppm)

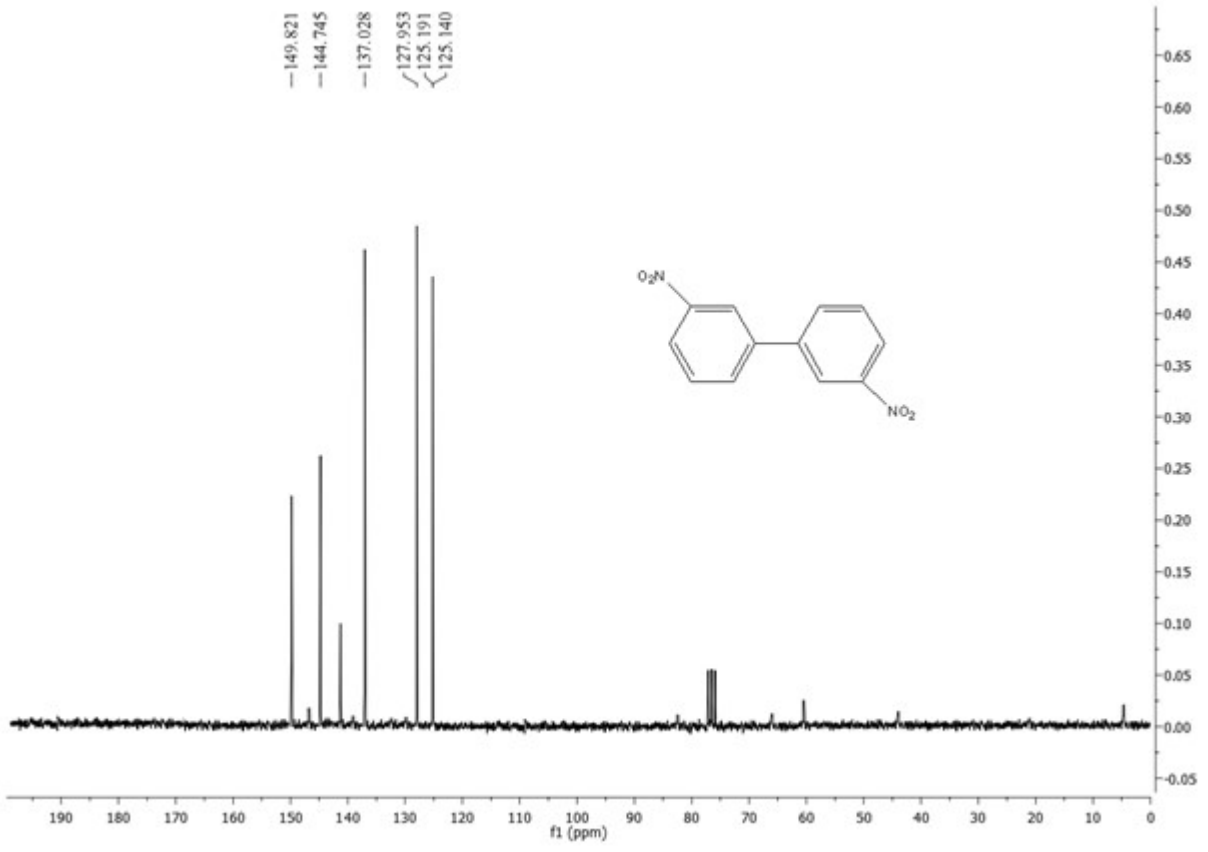

8.146
8.133
7.778
7.765
3.952
MeOOC
COOMe
4.00
3.98
6.04
f1 (ppm)

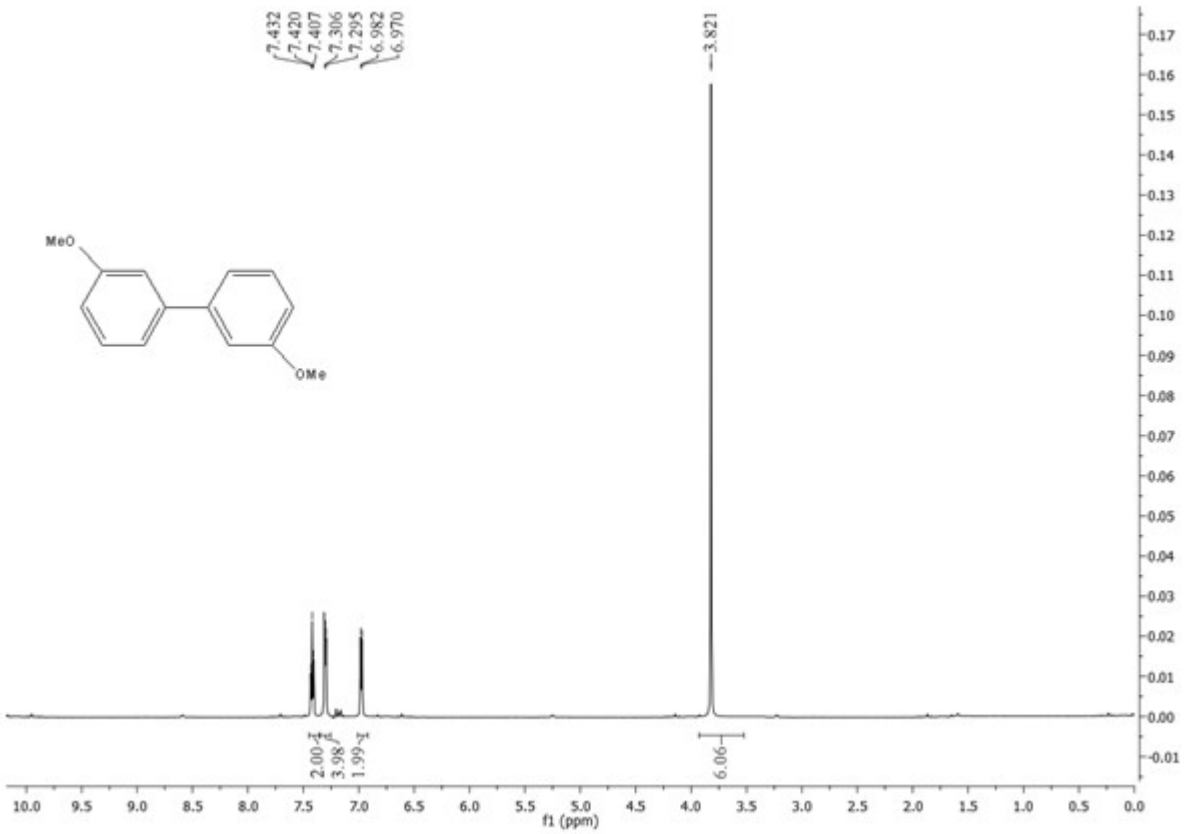

167.353
141.290
130.121
129.060
127.626
52.077
MeOOC
COOMe
f1 (ppm)

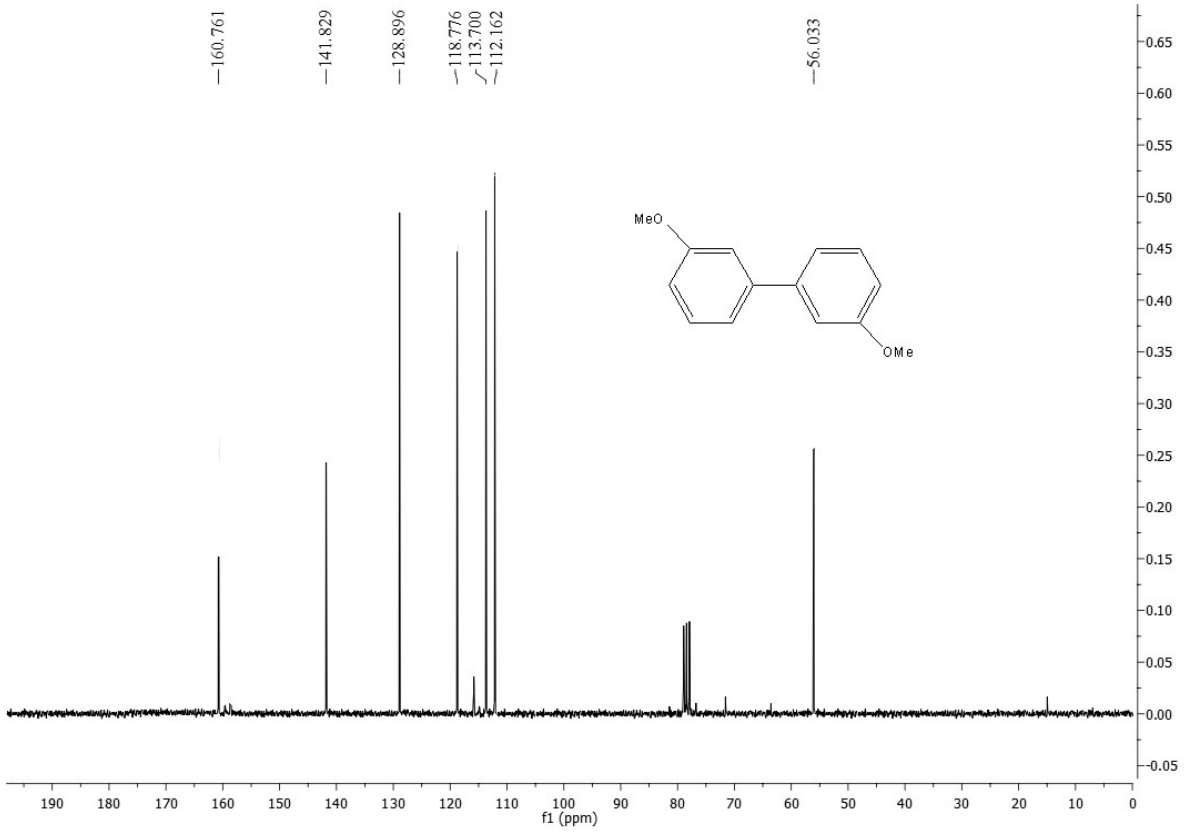

7.612
7.600
7.061
7.049
3.818
MeO
OMe
4.00
4.00
6.04
f1 (ppm)

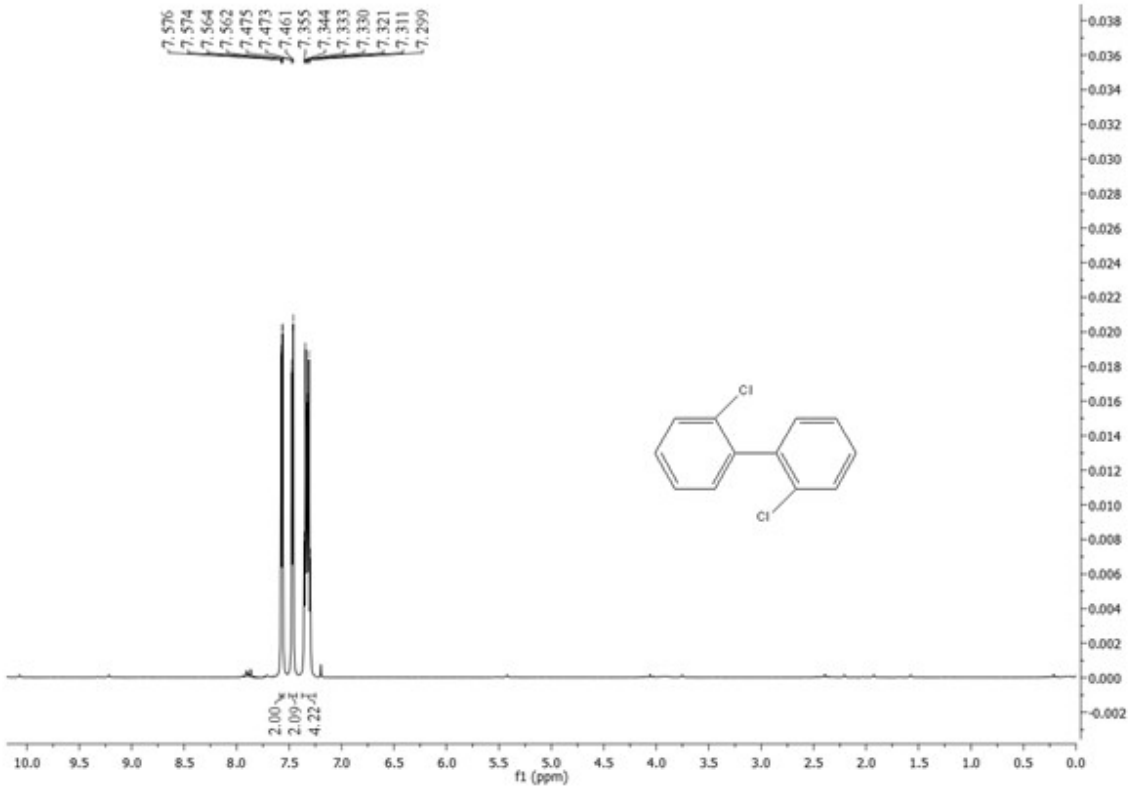

159.440
131.177
128.697
114.668
56.033
MeO
OMe
f1 (ppm)

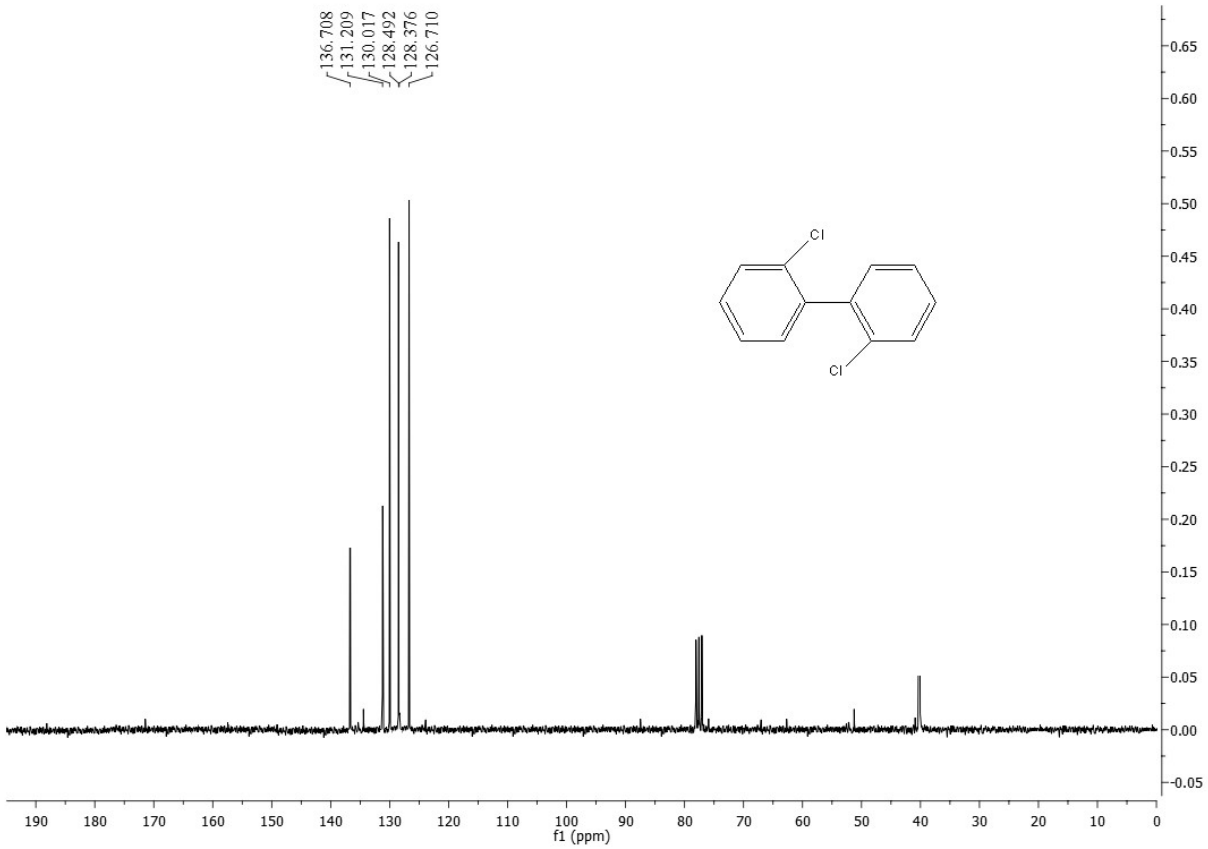

8.604
8.262
8.249
8.038
8.026
7.728
7.716
7.703
2.00
2.00
2.01
2.01
1
1
O_2N
NO_2
f1 (ppm)

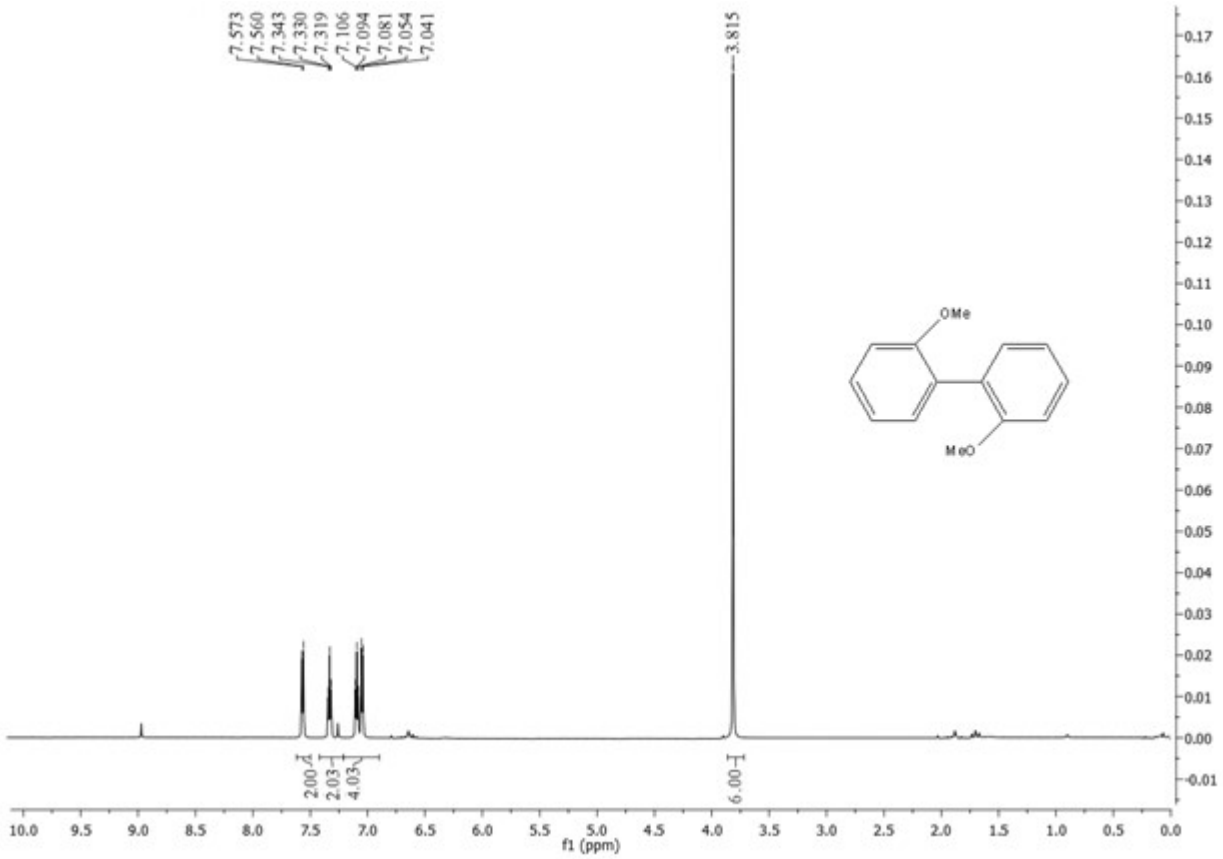

149.821
144.745
137.028
127.953
125.191
125.140
O_2N
NO_2
f1 (ppm)

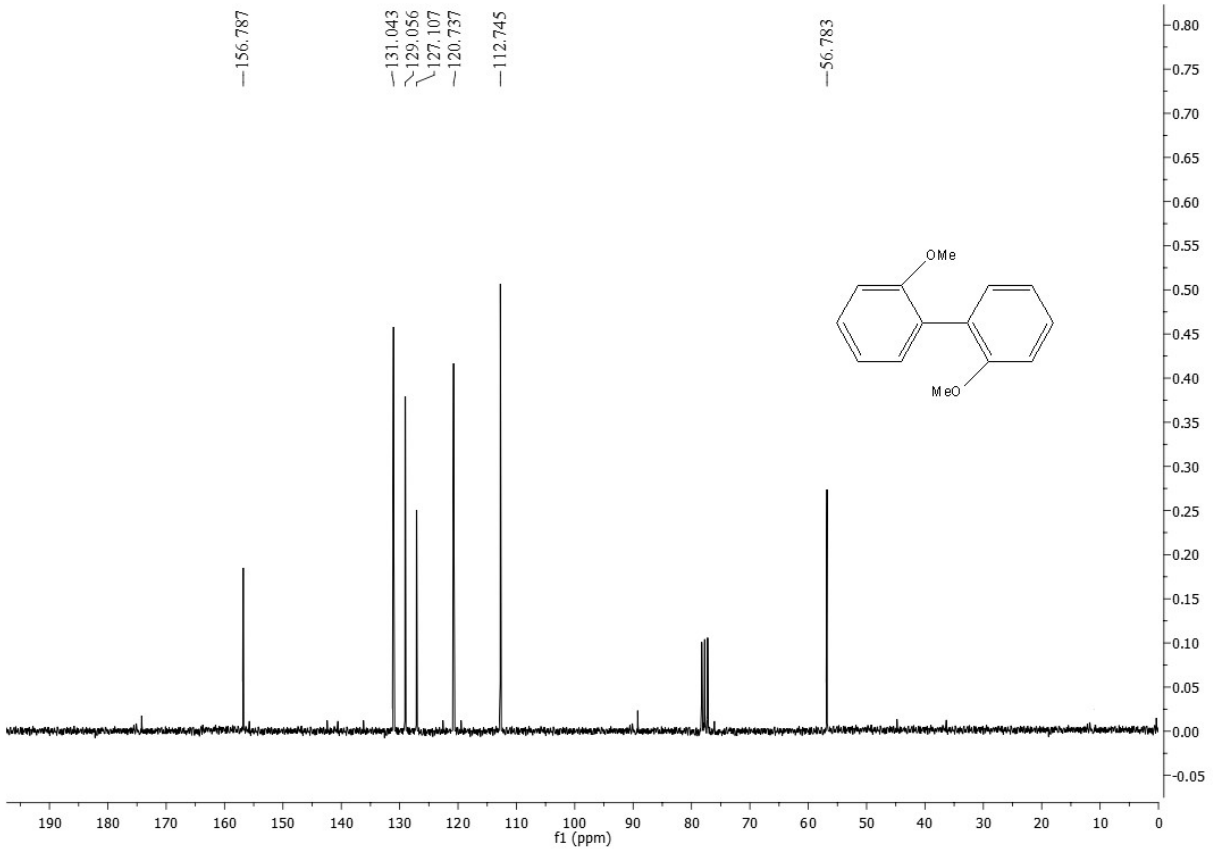

7.432
7.420
7.407
7.306
7.295
6.982
6.970
3.821
MeO
OMe
2.00
3.98
1.99
6.06
f1 (ppm)

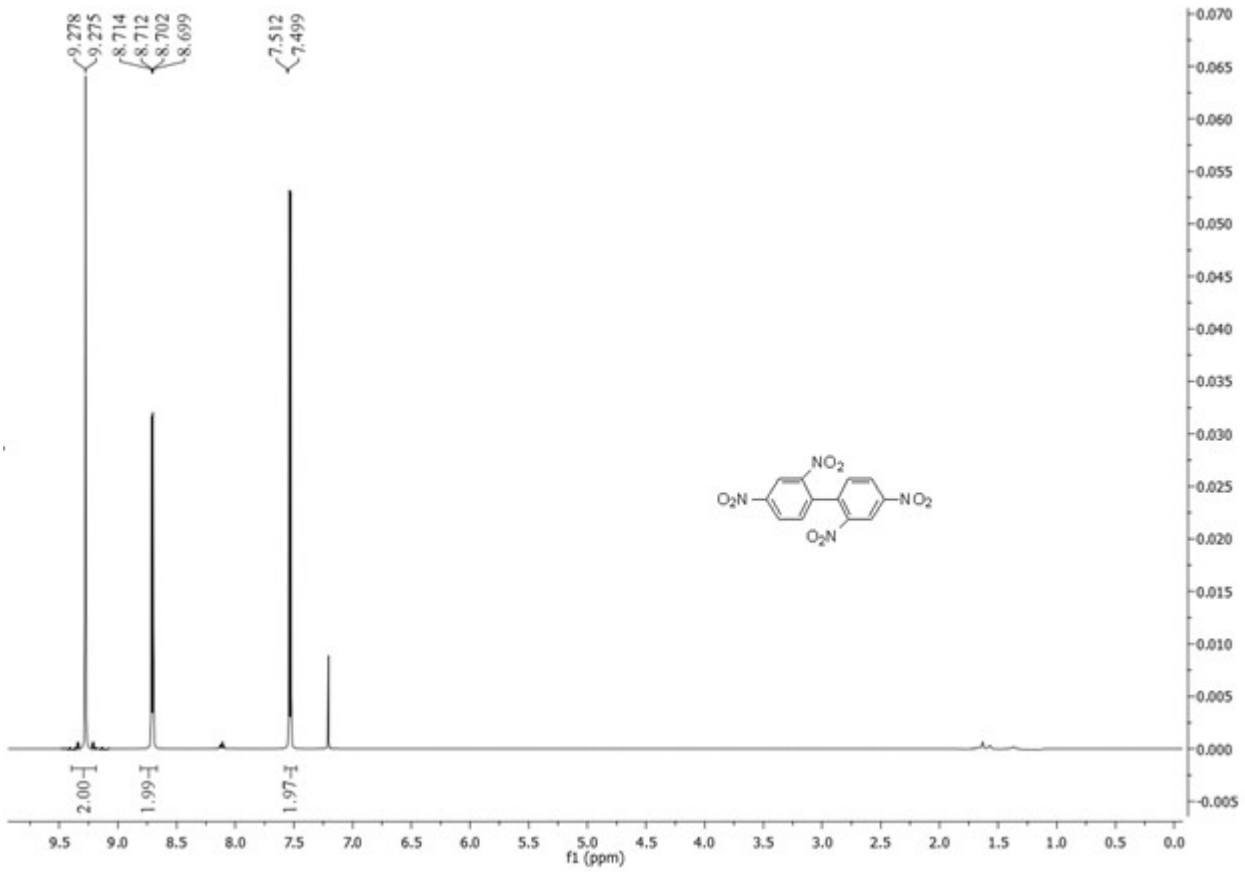

160.761
141.829
128.896
118.776
113.700
112.162
56.033
MeO
OMe
f1 (ppm)

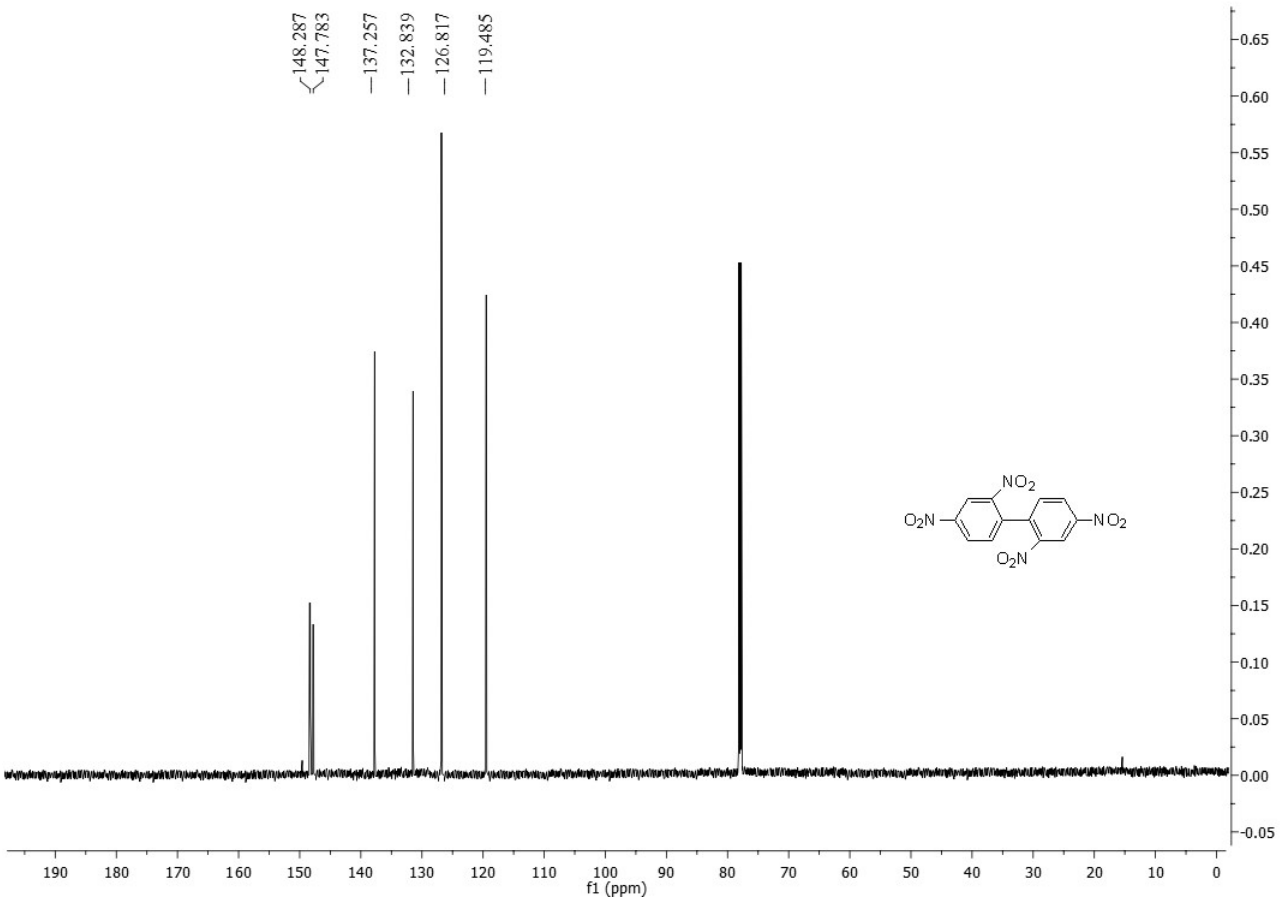

7.576
7.574
7.564
7.562
7.475
7.473
7.461
7.355
7.344
7.333
7.330
7.321
7.311
7.299
Cl
Cl
2.00
2.09
4.22
f1 (ppm)

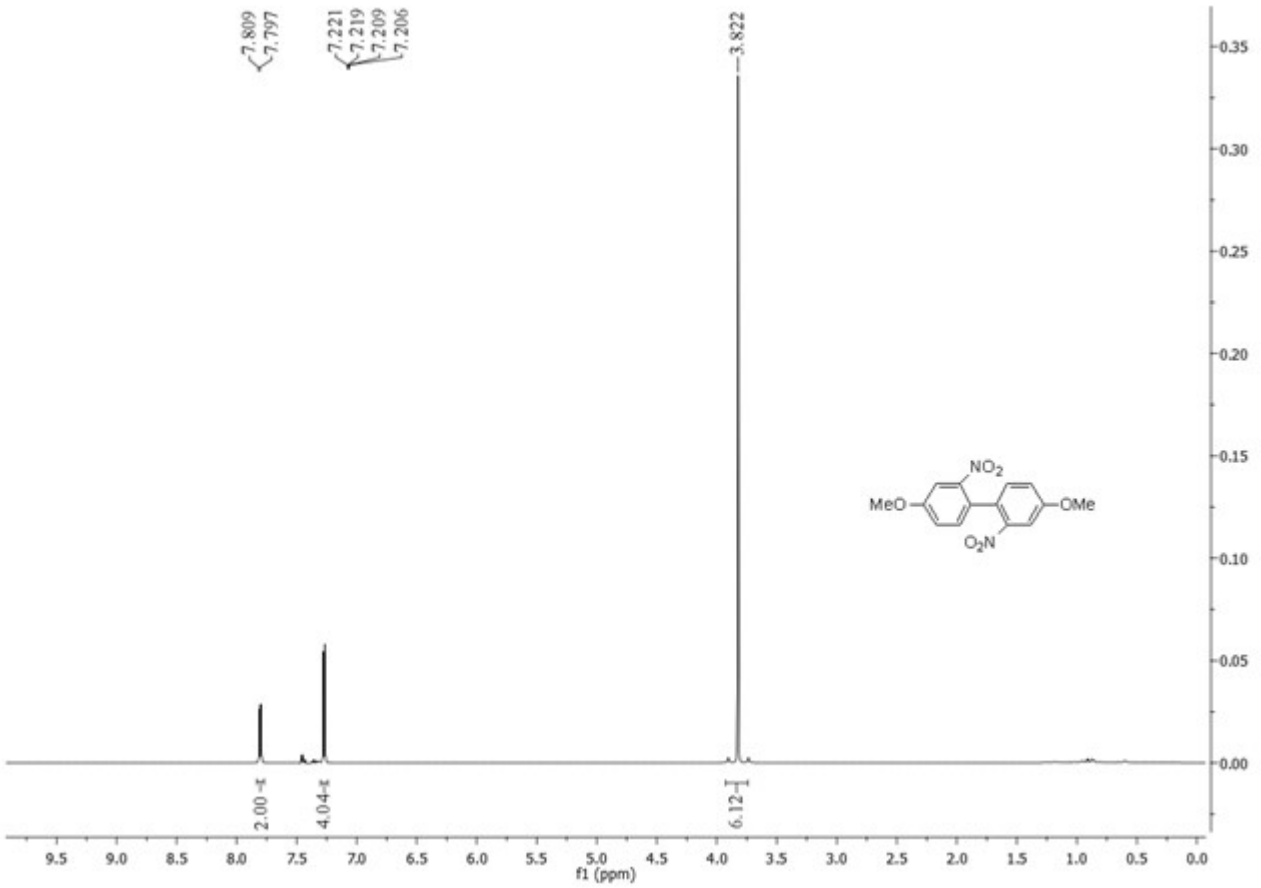

136.708
131.209
130.017
128.492
128.376
126.710
Cl
Cl
f1 (ppm)

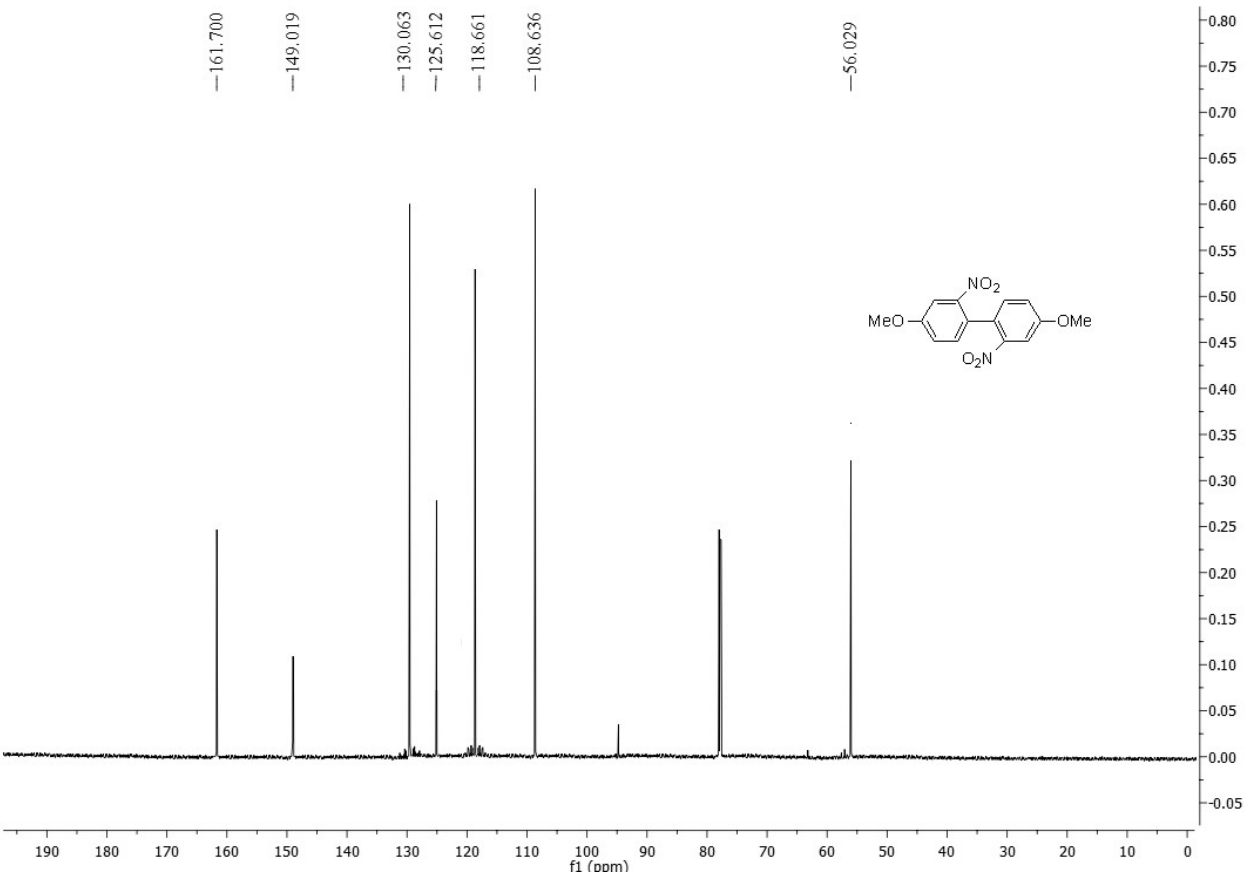

7.573
7.560
7.343
7.330
7.319
7.106
7.094
7.081
7.054
7.041
3.815
OMe
MeO
2.00
2.03
4.03
6.00
f1 (ppm)

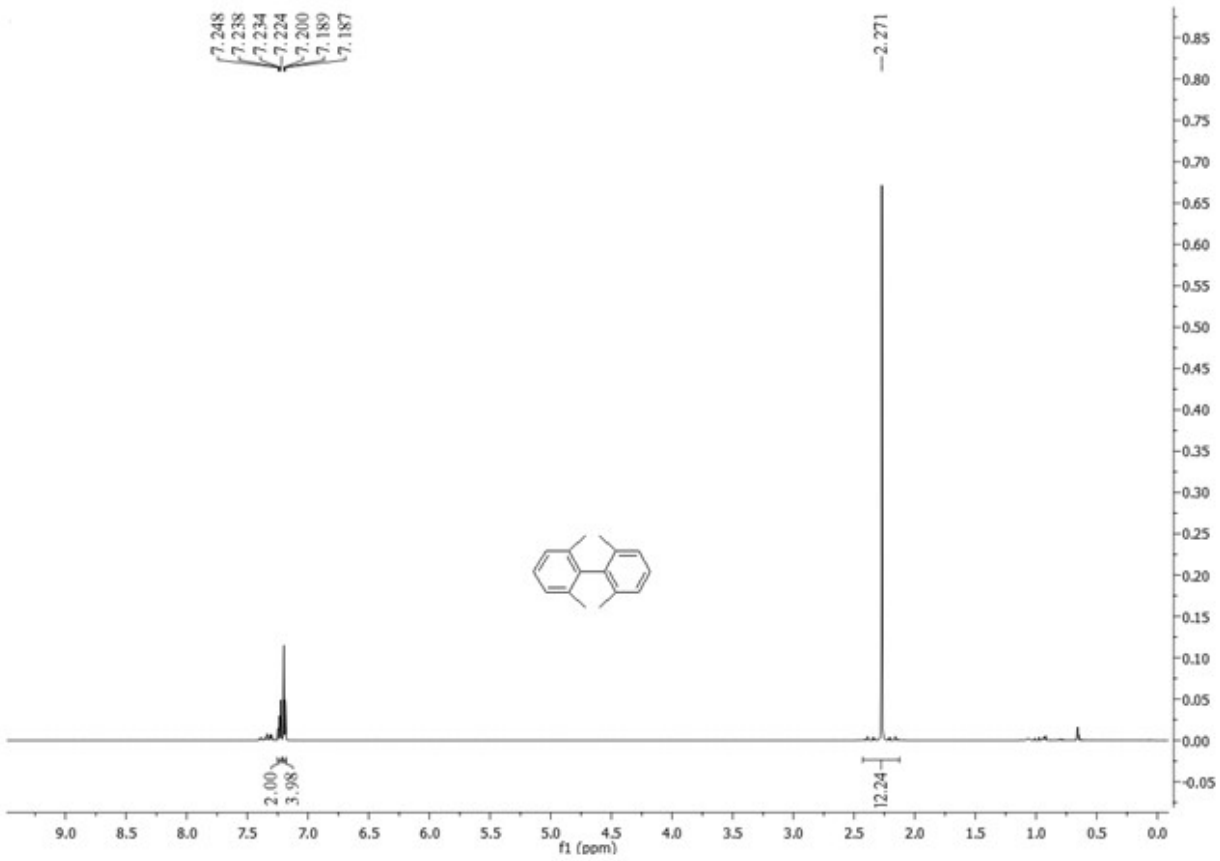

156.787
131.043
129.056
127.107
120.737
112.745
56.783
OMe
MeO
f1 (ppm)

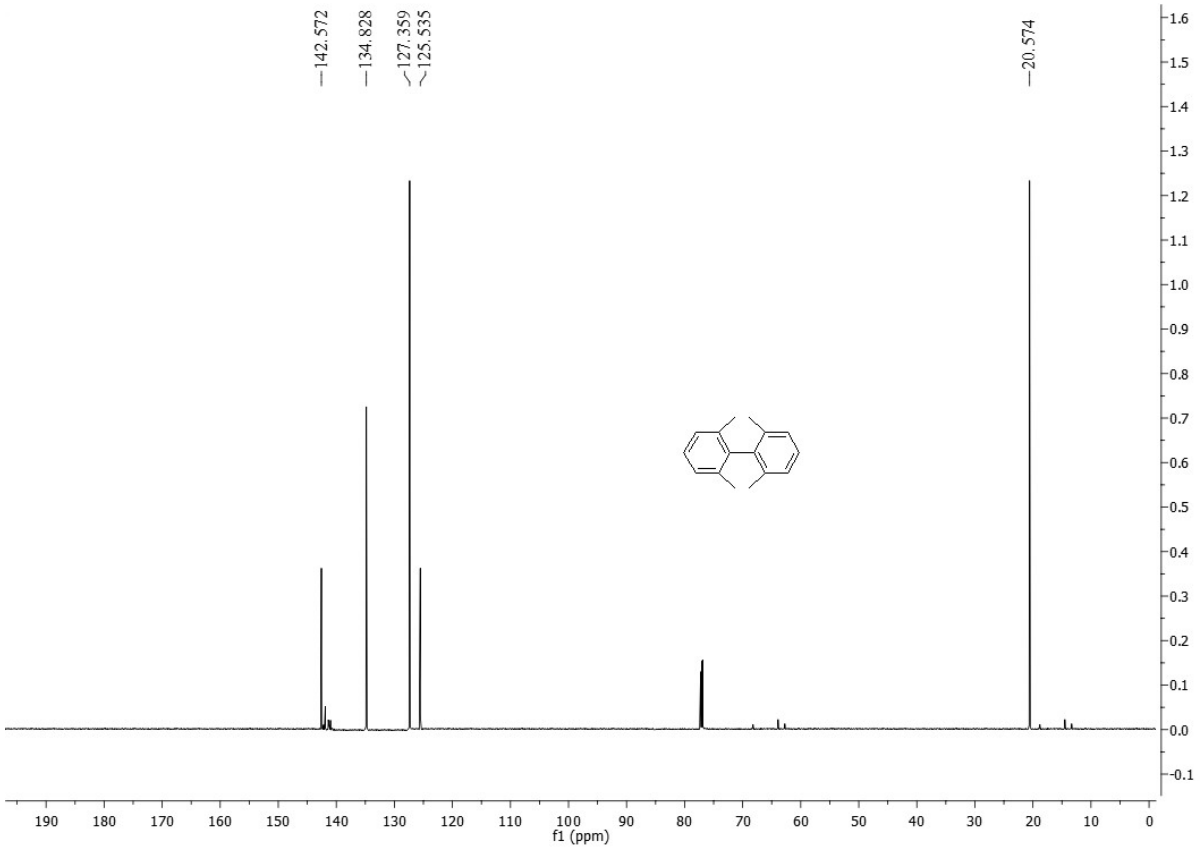

9.278
9.275
8.714
8.712
8.702
8.699
7.512
7.499
2.00
1.99
1.97
f1 (ppm)

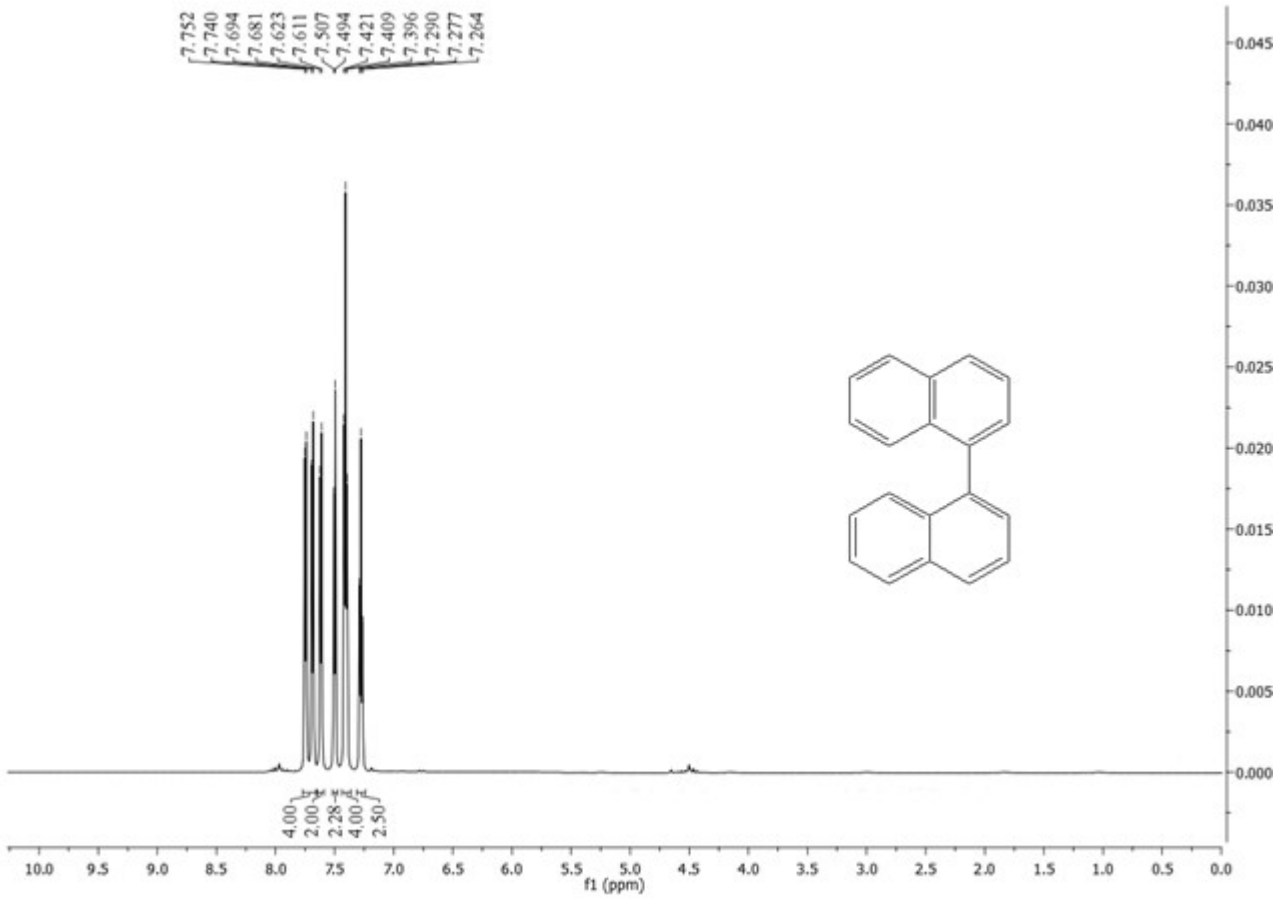

148.287
147.783
137.257
132.839
126.817
119.485
f1 (ppm)

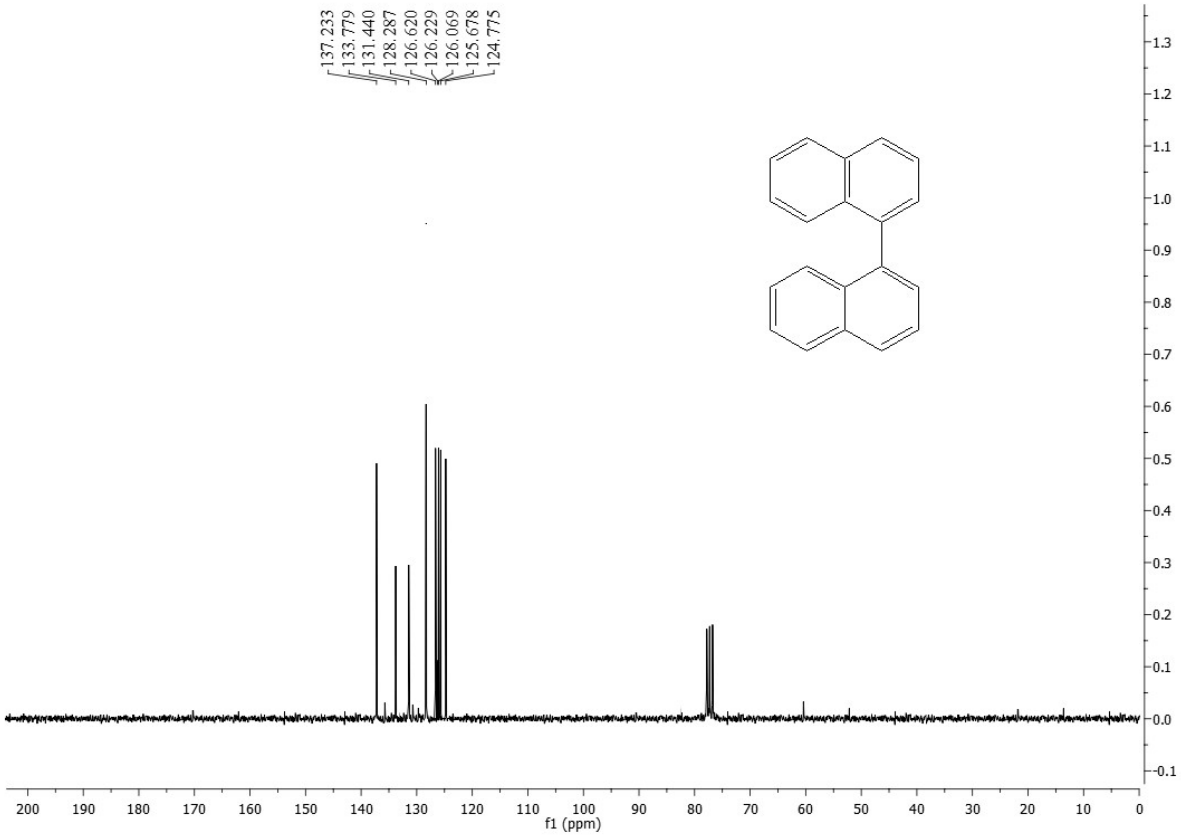

7.809
7.797
7.221
7.219
7.209
7.206
3.822
2.00
4.04
6.12
f1 (ppm)
NO2
MeO
OMe
O2N

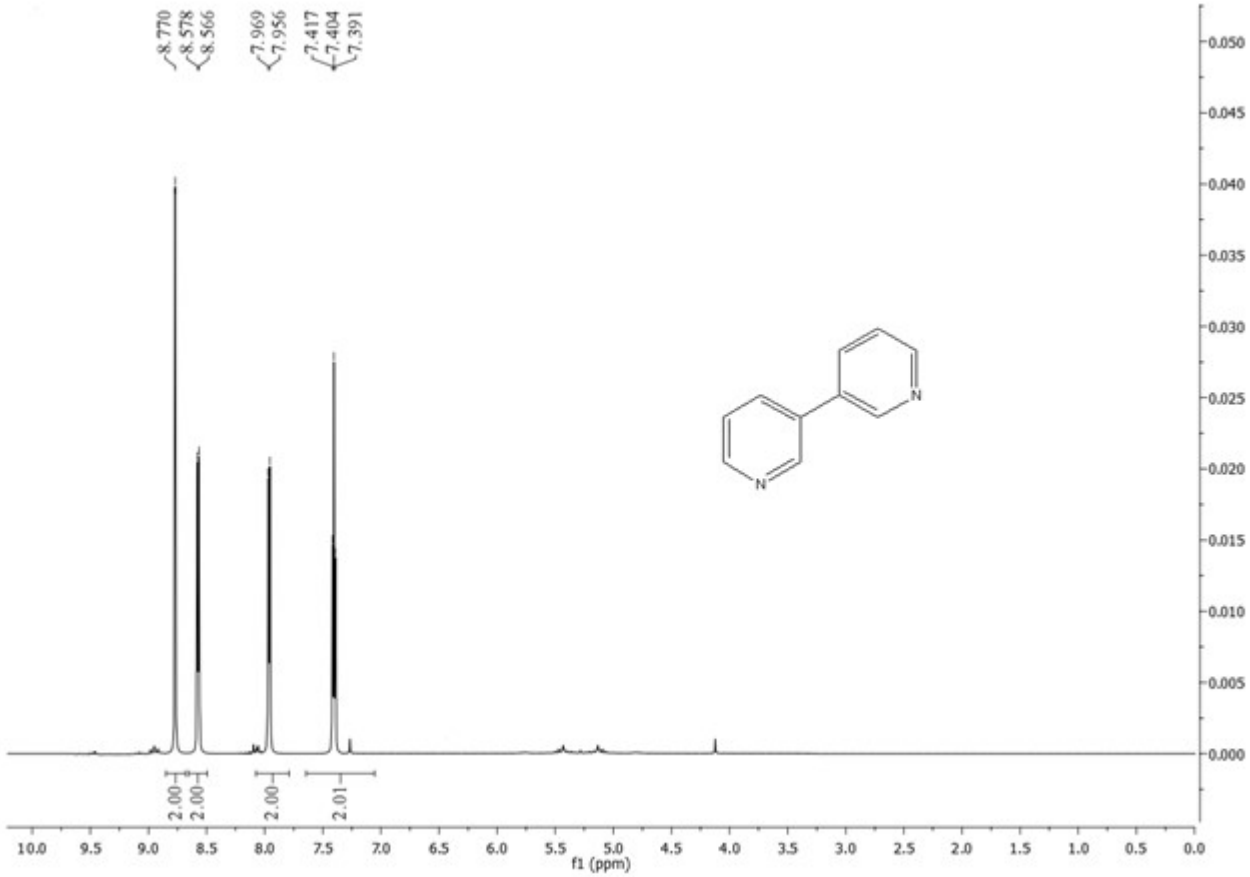

161.700
149.019
130.063
125.612
118.661
108.636
56.029
f1 (ppm)
NO2
MeO
OMe
O2N

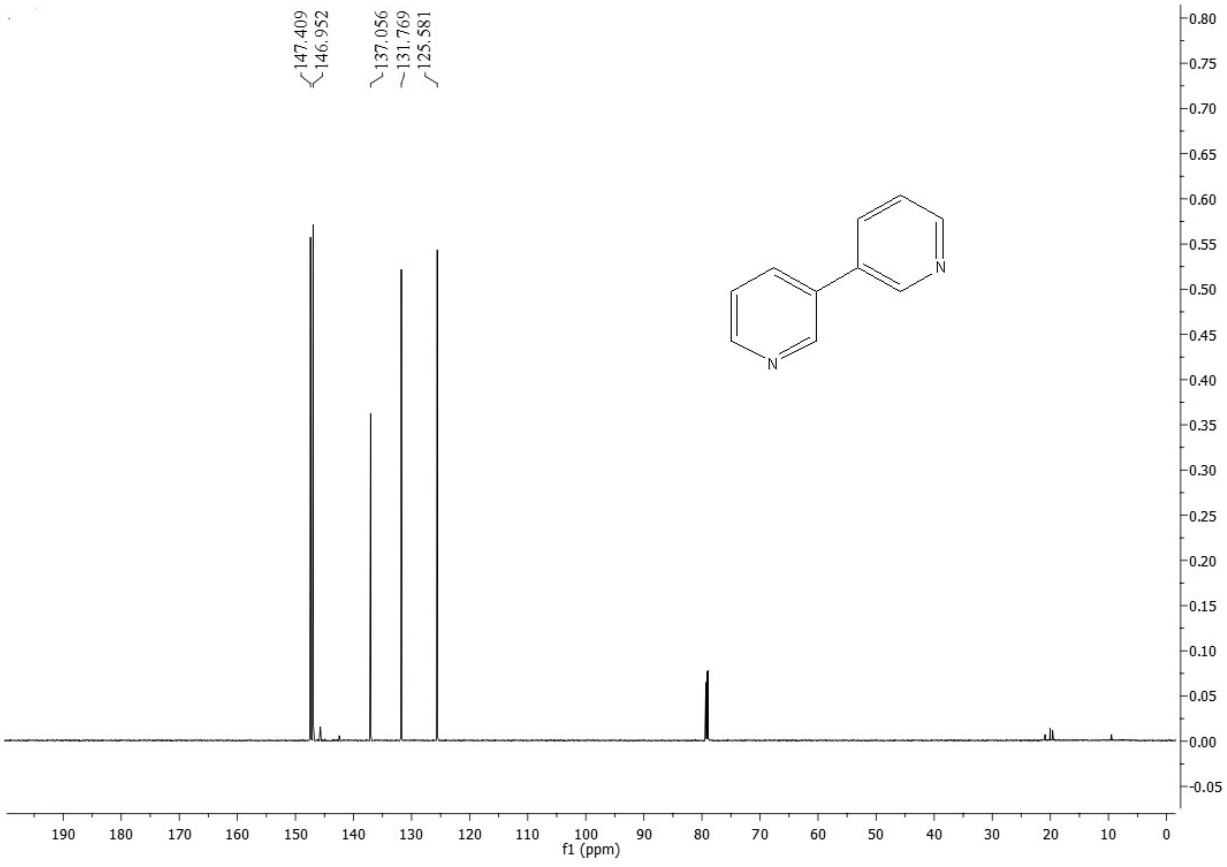

7.248
7.238
7.234
7.224
7.200
7.189
7.187
2.271
2.00
3.98
12.24
f1 (ppm)

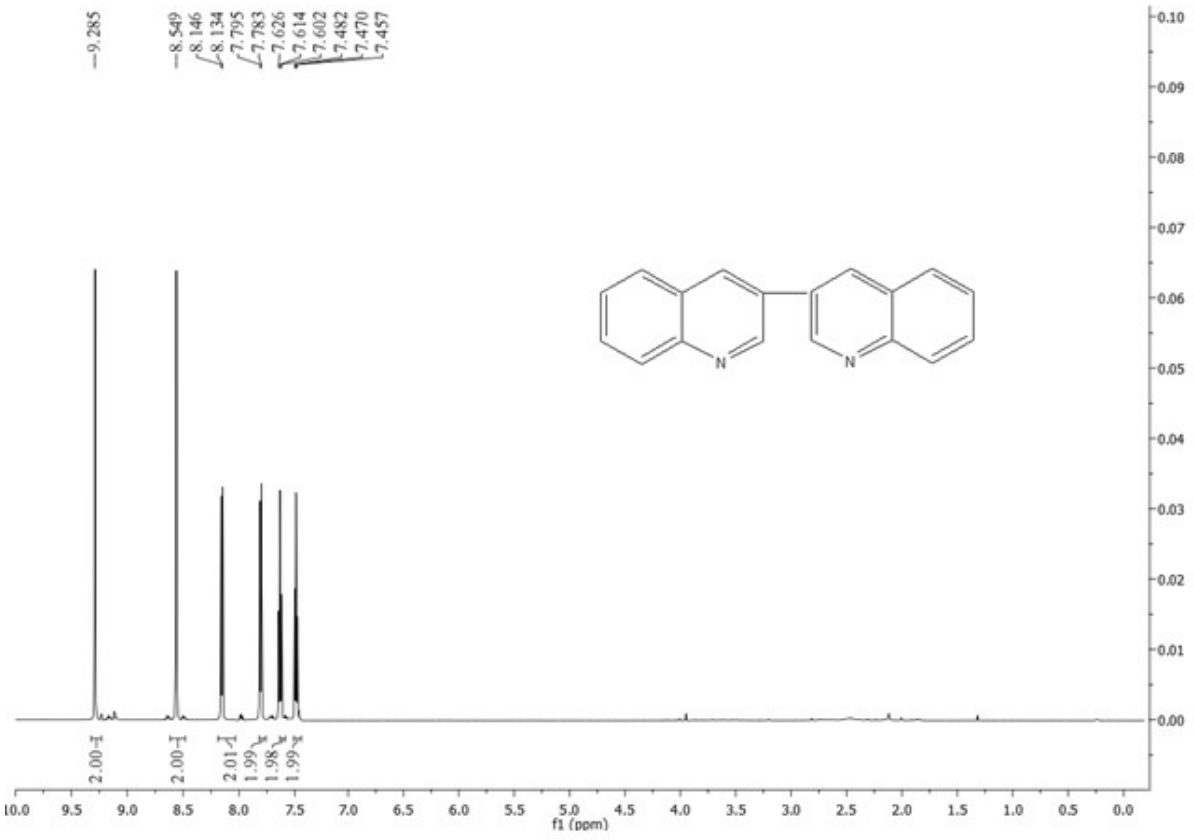

142.572
134.828
127.359
125.535
20.574
f1 (ppm)

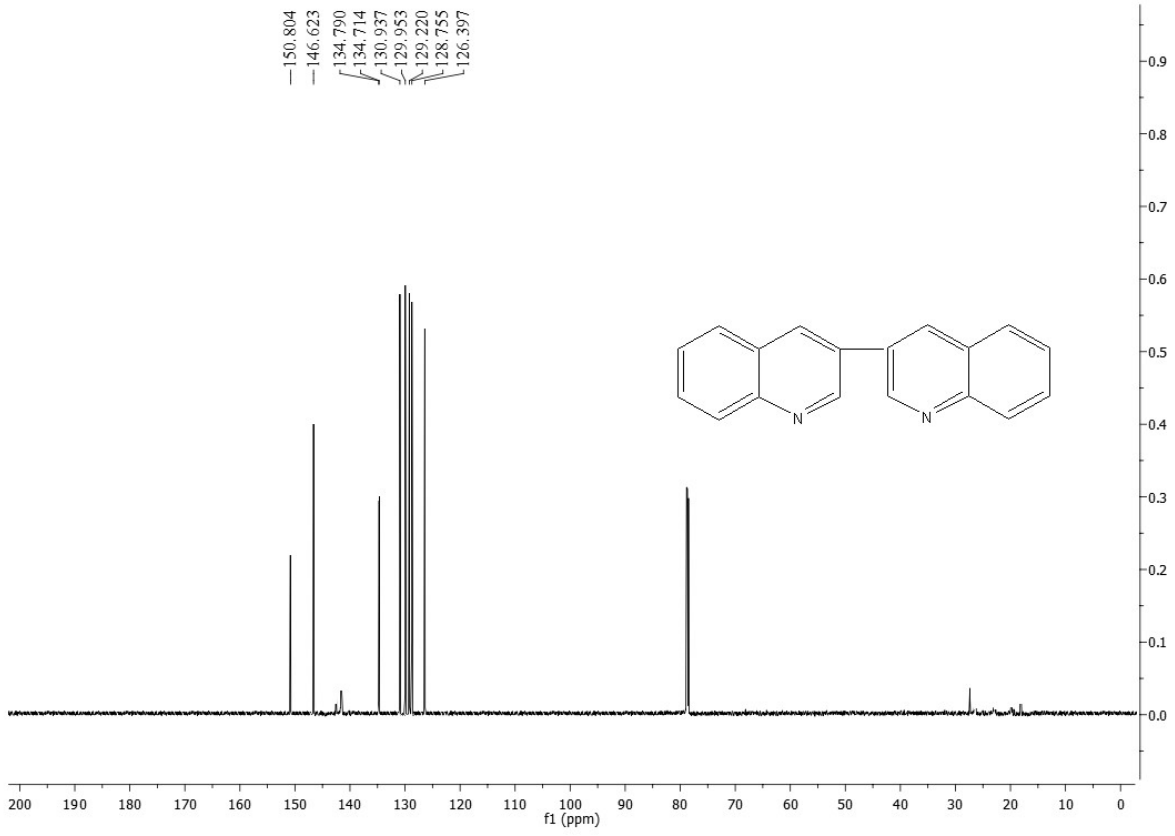

7.752
7.740
7.694
7.681
7.623
7.611
7.507
7.494
7.421
7.409
7.396
7.290
7.277
7.264
4.00
2.00
2.28
4.00
2.50
f1 (ppm)

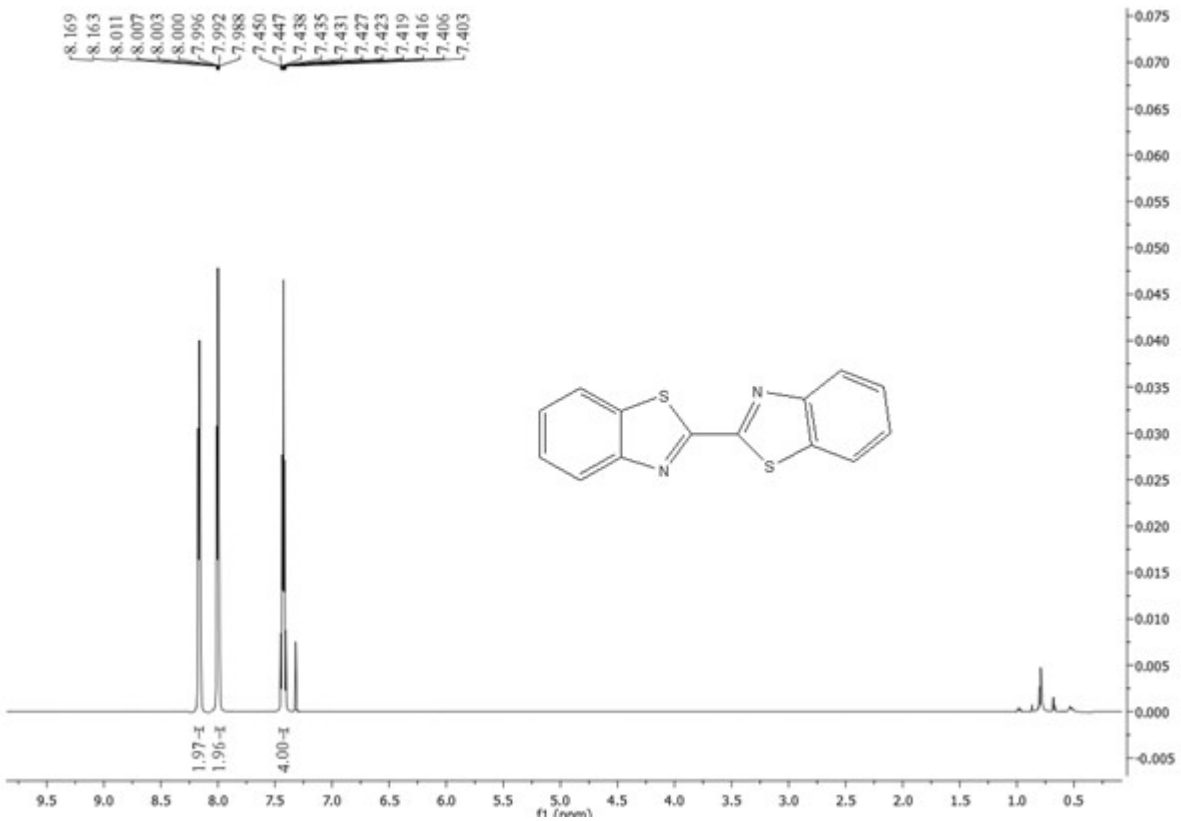

137.233
133.779
131.440
128.287
126.620
126.229
126.069
125.678
124.775
f1 (ppm)

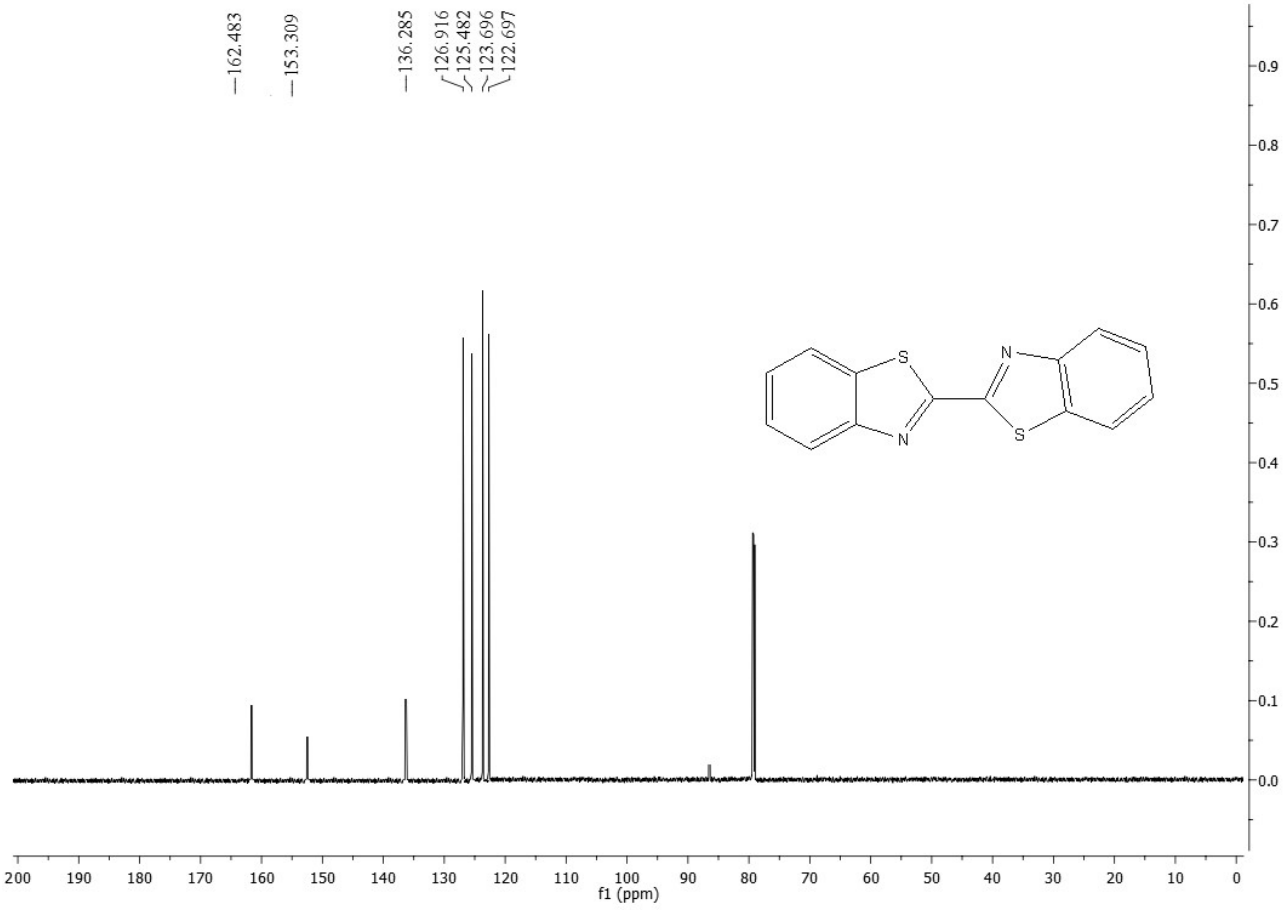

8.770
8.578
8.566
7.969
7.956
7.417
7.404
7.391
2.00
2.00
2.00
2.01
f1 (ppm)


147.409
146.952
137.056
131.769
125.581
f1 (ppm)


9.285
8.549
8.146
8.134
7.795
7.783
7.626
7.614
7.602
7.482
7.470
7.457
2.00
2.00
2.01
1.99
1.98
1.99
f1 (ppm)

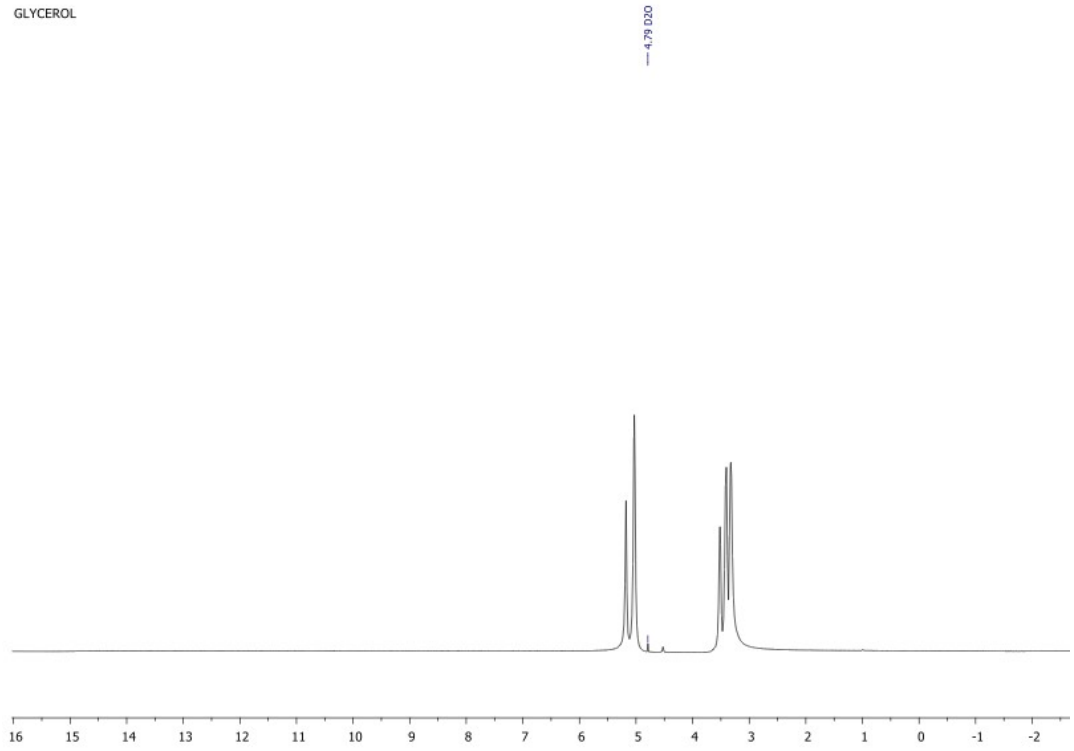

150.804
146.623
134.790
134.714
130.937
129.953
129.220
128.755
126.397
f1 (ppm)


8.169
8.163
8.011
8.007
8.003
8.000
7.996
7.992
7.988
7.450
7.447
7.438
7.435
7.431
7.427
7.423
7.419
7.416
7.406
7.403
1.97
1.96
4.00
S
N
N
S

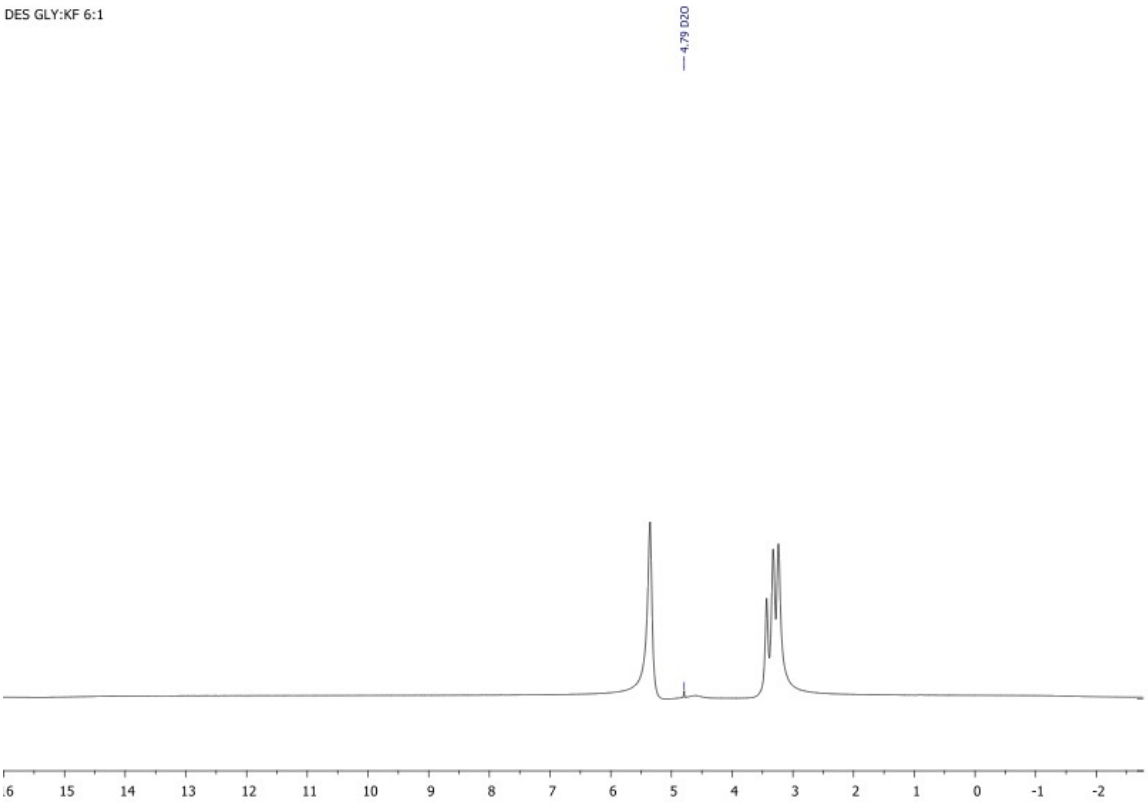

162.483
153.309
136.285
126.916
125.482
123.696
122.697
S
N
N
S
f1 (ppm)

^{1}H-NMR spectrum of DES Gly/KF 6:1 compared with that of glycerol

Glycerol

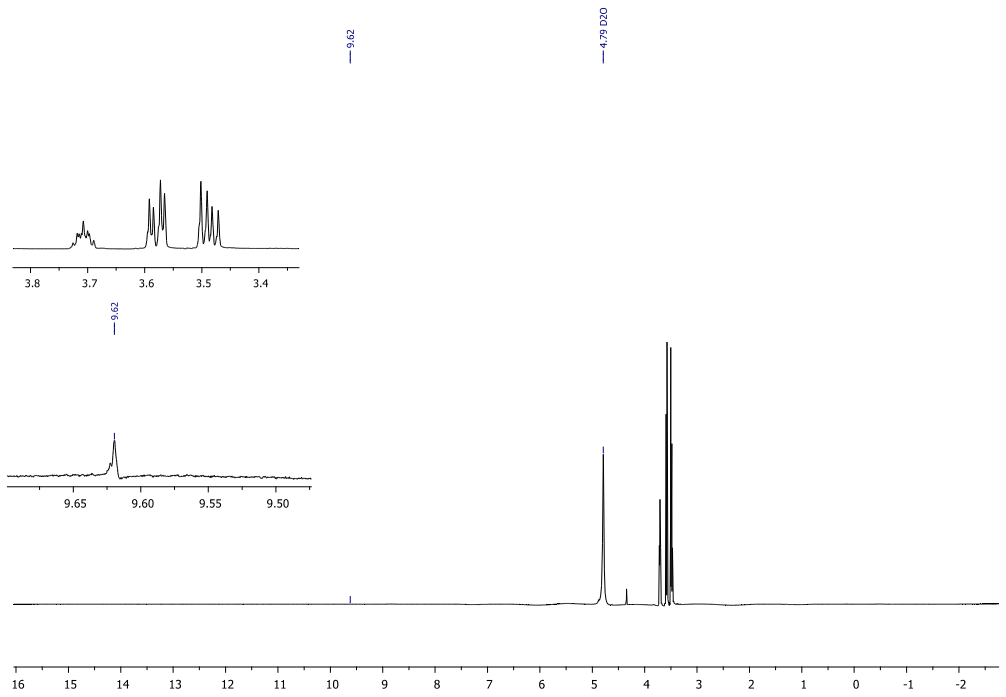


DES Gly/KF 6:1

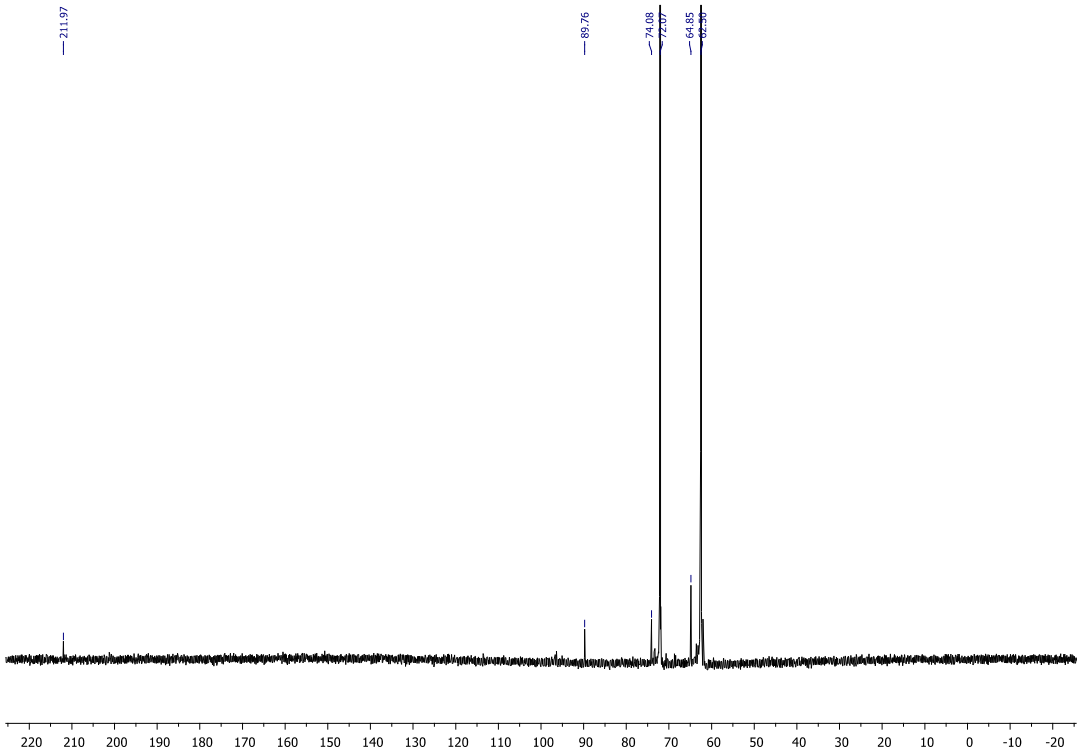


NMR Spectra of recovered DES Gly/KF

^{1}H NMR



^{13}C NMR



^{13}C NMR of DES Gly/KF