Scavenging and Characterisation of Short-lived Radicals using a Novel Stable Nitroxide Radical with a Characteristic UV–visible Absorption Spectrum

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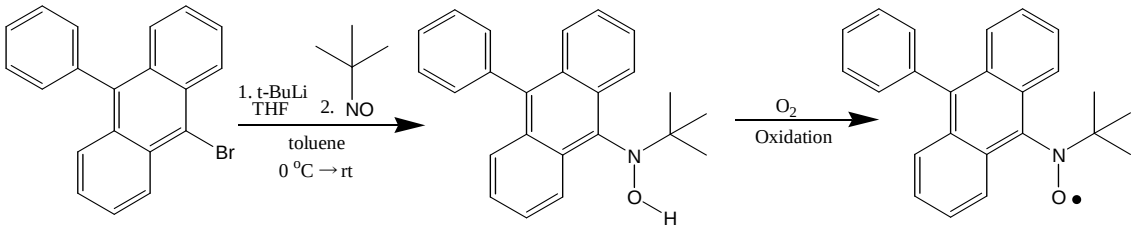
Experimental Section

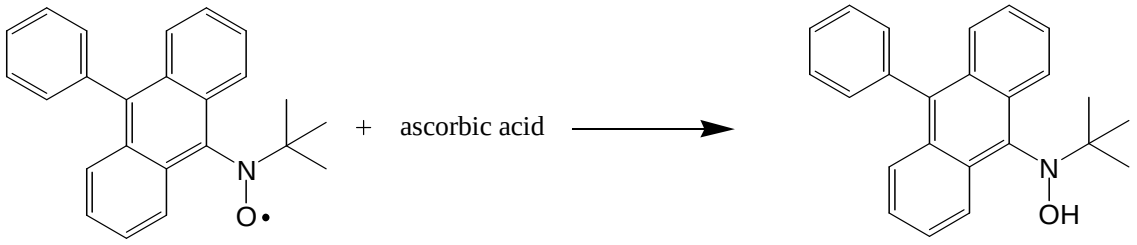
General Remarks: All reactions were carried out under Nitrogen atmosphere and monitored by thin-layer chromatography using Merck 60 F_{254} precoated silica gel plate (0.25 mm thickness). FT-IR spectra were recorded on a Nicolet iS10 FT-IR Spectrometer (KBr pellet method). ^{1}H and ^{13}C spectra were recorded on BRUKER DRX-300, JEOL ECX-400 and BRUKER DRX-500 instruments. Date for ^{1}H NMR are reported as chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration, and assignment. Date for ^{13}C NMR are reported as chemical shift. Mass spectral analysis (MS) were carried out using SHIMADZU Axima-CFR. High-resolution mass spectral analysis (HRMS) were carried out using BRUKER Autoflex speed [Standard sample : polyethylene glycol (AMW300), cationization agent : Sodium trifluoroacetate, Matrix : 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin]. Electron spin resonance (ESR) were recorded on JEOL ME-3X. Liquid chromatography–mass spectrometry (LC/MS) were recorded on Shimadzu LC-2010C HT and Shimadzu LCMS-2020, column : Wakopack Navi C18-5 ϕ 2.0 mm × 150 mm (D), t_{Ret} = retention time.

Procedure of *tert*-butyl (10-phenyl-9-anthryl)nitroxide (BPAN) (Scheme 1, compound 1)



9-Bromo-10-phenylantracene[S1] (2.0 g, 6.0 mmol) in THF (0.96 mL, 6.0 mmol) and toluene (100 mL) was added to *t*-BuLi/pentane (7.5 mL, 12.0 mmol) dropwise at 0 °C under N_2 atmosphere. The reaction mixture was stirred for 30 min at 0 °C. 2-methyl-2-nitrosopropane[S1] (0.52 g, 6.0 mmol) in toluene (50 mL) was added dropwise to the reaction mixture. The resulting mixture was gradually allowed to warm to room temperature and stirred overnight. The resulting mixture was quenched with the addition of saturated aqueous NH_4Cl (50 mL). The organic materials were extracted with ethyl acetate (30 mL) three times, dried over $MgSO_4$, and stirred overnight under air atmosphere. The organic materials were concentrated in vacuo. Flash chromatography (SiO_2, hexane : ethyl acetate = 9 : 1) afforded *tert*-Butyl(10-phenyl-9-Anthryl)nitroxide (BPAN, 1.05 g, 3.1 mmol, 52%) as a red-brown crystal. mp 193 – 193.5 °C; ESR g = 2.00404, a_N = 1.3313 [mT], Condition : FREQUENCY = 9433 [MHz], MODULATION : Fq = 100.0 kHz, Width = 0.6 mT, POWER = 4.000 mW, SWEEP TIME = 1.0 min, TIME CONSTANT = 0.03 sec, AMPLITUDE = 2.000 ; IR(KBr film) 3067, 2966, 1439, 1379, 1192, 1027, 932, 762, 701, 656 cm^{-1}; HRMS m/z 340.1698 ($C_{24}H_{22}NO^+$ required 340.1696).

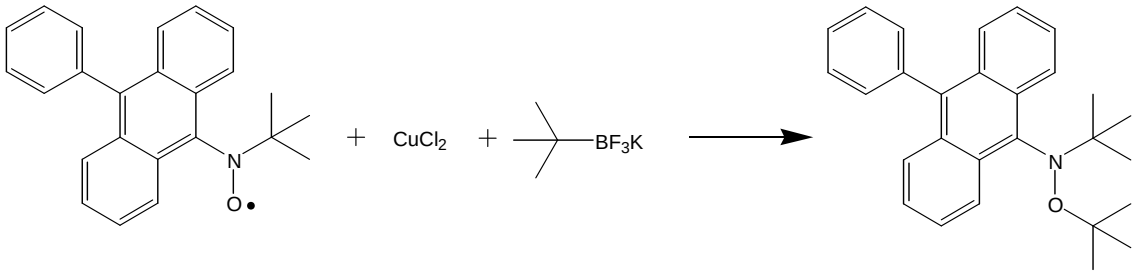
Procedure of *N-tert*-butyl *N*-(10-phenyl-9-Anthryl) hydroxylamine (BPAN-H)



A solution of BPAN (34 mg, 0.1 mmol) in MeOH (20 mL) was treated with ascorbic acid (180 mg, 1.0 mmol). After stirring the reaction mixture at room temperature for 30 min, the resulting mixture was quenched with the addition of water (15 mL). The organic materials were extracted with ethyl acetate (15 mL), washed with water three times, and dried over anhydrous $MgSO_4$, then concentrated under reduced pressure. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN-H (33 mg, 0.096 mmol,

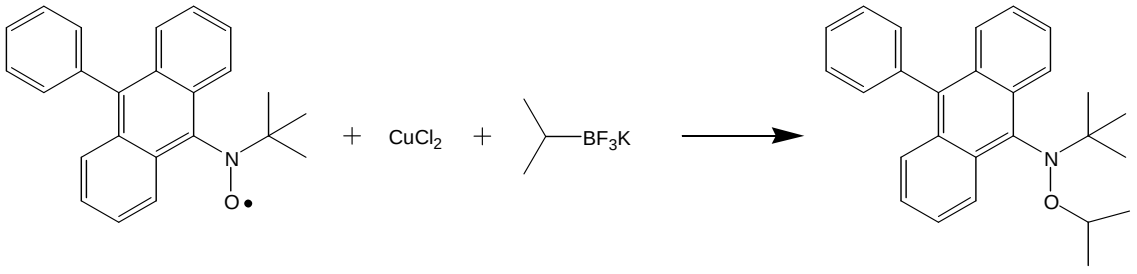
96%) as a light-yellow crystal. mp 143 – 145 °C; ^{1}H NMR(300 MHz, $CDCl_3$) δ = 8.86 (2H, d, *J* = 8.6 Hz), 7.57 – 7.22 (11H, m), 5.51 (1H, bs), 1.29 (9H, s); ^{13}C NMR(125 MHz, $CDCl_3$) δ = 140.0, 139.2, 136.4, 131.3, 131.0, 130.6, 129.4, 128.2, 127.2, 126.8, 124.6, 123.9, 62.2, 28.0; IR(KBr film) : 3528, 2975, 1675, 1374, 1358, 1202, 1030, 764, 426, 406 cm^{-1}; HRMS m/z 341.1782 ($C_{24}H_{23}NO^+$ required 341.1780).

Procedure of *N-tert*-butyl *N-tert*-butoxyl (10-phenyl-9-anthryl) amine (BPAN-*t*Bu) (Table 1 entry 4)



BPAN (8.5 mg, 0.025 mmol), $CuCl_2$ (13 mg, 0.1 mmol), and potassium *tert*-butyl trifluoroborate (16 mg, 0.1 mmol) was dissolved in Et_2O (5.0 mL). The reaction mixture was stirred at room temperature under an N_2 atmosphere for overnight. The resulting mixture was poured onto water, extracted with Et_2O, dried over $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN-*t*Bu (9.8 mg, 0.025 mmol, 98%) as a light-yellow crystal: mp 177 – 178 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.38 (1H, d, *J* = 9.0 Hz), 8.96 (1H, d, *J* = 9.5 Hz), 7.60 – 7.24 (11H, m), 1.20 (9H, s), 1.16 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 142.7, 139.6, 135.8, 131.6, 131.4, 131.3, 129.4, 128.3, 128.2, 127.2, 126.5, 124.7, 124.3, 123.8, 123.0, 79.2, 62.5, 28.8, 28.1; IR(KBr film) 2975, 1442, 1363, 1187, 1031, 929,770, 754,700, 681 cm^{-1}; HRMS m/z 397.2403 ($C_{28}H_{31}NO^+$ required 397.2400).

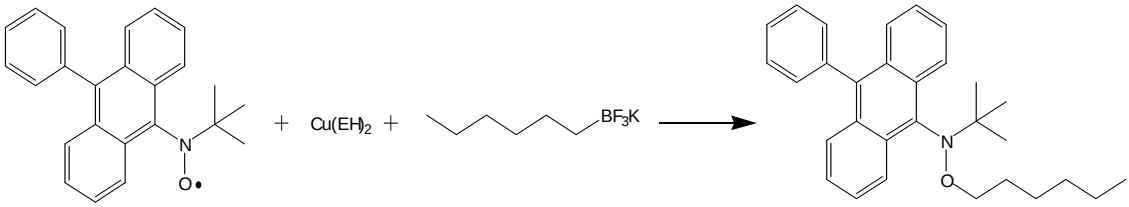
Procedure of *N-tert*-butyl *N*-isoproxyl (10-phenyl-9-anthryl) amine (BPAN-*i*Pr) (Table 1 entry 5)



BPAN (8.5 mg, 0.025 mmol), $CuCl_2$ (13 mg, 0.1 mmol), and potassium isopropyl trifluoroborate (30 mg, 0.2 mmol) was dissolved in Et_2O (5.0 mL). The reaction mixture

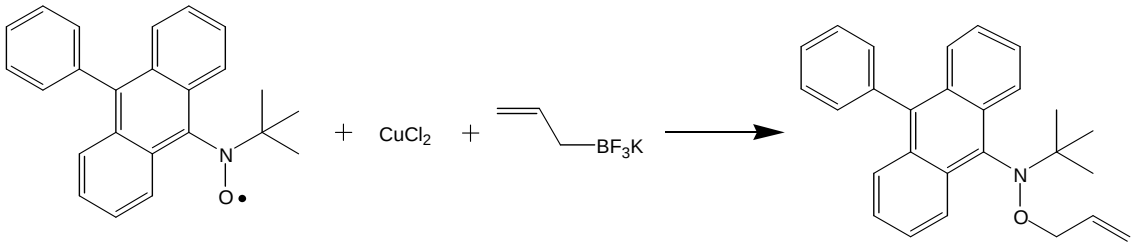
was stirred at room temperature under an N_2 atmosphere for overnight. The resulting mixture was poured onto water, extracted with Et_2O, dried over $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN-*i*Pr (8.1 mg, 0.021 mmol, 85%) as a light-yellow crystal: mp 175 – 176 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ = 9.09 (2H, bs), 7.58 – 7.25 (11H, m), 4.02 (1H, sep, *J* = 6.2 Hz), 1.24 (15H, s); ^{13}C NMR(125 MHz, $CDCl_3$) δ = 140.1, 139.5, 136.0, 131.5, 131.30, 128.3, 128.2, 127.3, 126.77, 126.75, 124.6, 123.6, 74.8, 62.3, 28.4, 21.8; IR(KBr film) 3034, 2957, 1601, 1364, 1205, 1118, 1032, 976, 930, 767, 700 cm^{-1}; HRMS m/z 383.2257 ($C_{27}H_{29}NO^+$ required 383.2249).

Procedure of *N-tert*-butyl *N*-hexyloxy (10-phenyl-9-anthryl) amine (BPAN-Hex) (Table 1 entry 6)



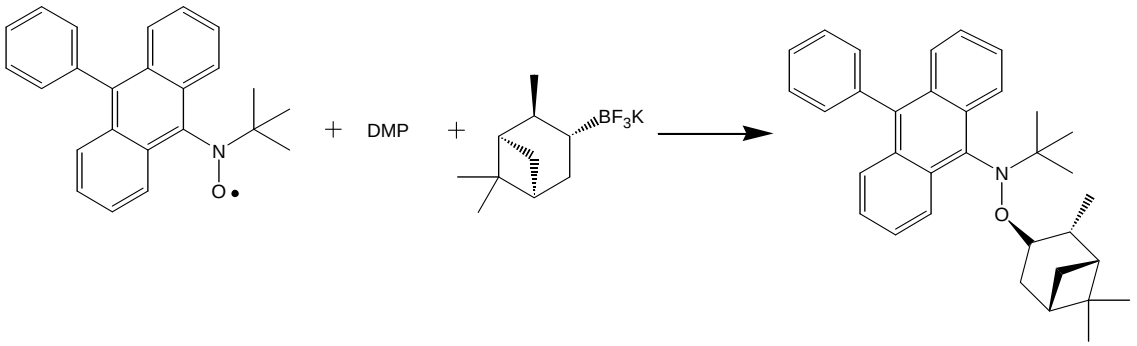
BPAN (8.5 mg, 0.025 mmol), Copper 2-Ethylhexanoate (70 mg, 0.2 mmol), and potassium hexyl trifluoroborate[S2] (38 mg, 0.2 mmol) was dissolved in Et_2O (5.0 mL). The reaction mixture was stirred at 120°C under an N_2 atmosphere for overnight. The resulting mixture was poured onto water, extracted with Et_2O, dried over $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN- Hex (8.7 mg, 0.020 mmol, 81%) as a light-yellow crystal: mp 122 – 122.5 °C; ^{1}H NMR(300 MHz, $CDCl_3$) δ = 9.01 (2H, d, *J* = 9.0 Hz), 7.60 – 7.26 (11H, m), 3.84 (2H, t, *J* = 6.6 Hz), 1.55 – 1.47 (2H, m), 1.30 – 1.11 (15H, m), 0.77 (3H, t, *J* = 6.8 Hz); ^{13}C NMR(125 MHz, $CDCl_3$) δ = 139.5, 138.9, 136.2, 131.5, 131.3, 128.33, 128.25, 127.7, 127.3, 126.7, 124.7, 123.7, 74.1, 62.2, 31.6, 28.7, 28.2, 26.0, 22.5, 13.9; IR(KBr film) 3068, 2923, 1372, 1203, 1020, 931, 769, 699, 661, 613 cm^{-1}; HRMS m/z 425.2731 ($C_{30}H_{35}NO^+$ required 425.2719).

Procedure of *N*-allyloxy *N-tert*-butyl (10-phenyl-9-anthryl) amine (BPAN-Allyl) (Table 1 entry 7)



BPAN (8.5 mg, 0.025 mmol), $CuCl_2$ (13 mg, 0.1 mmol), and potassium allyl trifluoroborate[S2] (16 mg, 0.1 mmol) was dissolved in Et_2O (5.0 mL). The reaction mixture was stirred at room temperature under an N_2 atmosphere for overnight. The resulting mixture was poured onto water, extracted with Et_2O, dried over $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN- Allyl (9.0 mg, 0.024 mmol, 94%) as a light-yellow crystal: mp 122.5 – 123 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ = 9.00 (2H, d, *J* = 9.0 Hz), 7.25 – 7.59 (11H, m), 5.89 – 5.94 (1H, m), 5.20 – 5.23 (1H, m), 5.06 – 5.08 (1H, m) 4.36 (1H, d, *J* = 6.0 Hz), 1.27 (9H, s); ^{13}C NMR(125 MHz, $CDCl_3$) δ = 139.4, 138.4, 136.5, 134.5, 131.4, 134.2, 128.35, 128.28, 127.6, 127.3, 126.7, 124.7, 123.8, 117.1, 75.1, 62.4, 28.3; IR(KBr film) 2964, 2923, 1371, 1207, 1016, 992, 930, 767, 702, 680 cm^{-1}; HRMS m/z 381.2081 ($C_{27}H_{27}NO^+$ required 381.2093).

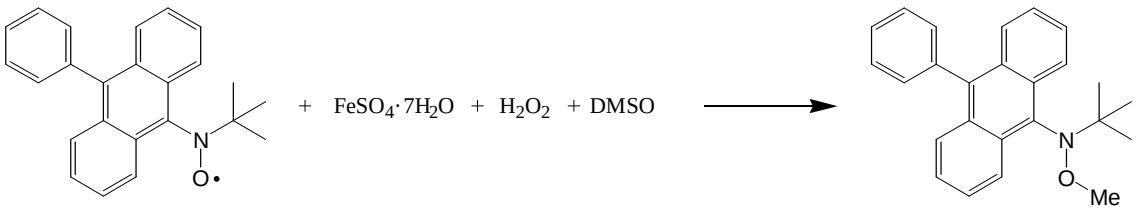
Procedure of *N*- 1-((1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yloxy) *N-tert*-butoxyl (10- phenyl-9-anthryl) amine (BPAN-Pinene) (Table 1 entry 8)



BPAN (17 mg, 0.05 mmol), $CuCl_2$ (26 mg, 0.2 mmol), and potassium isopinocampheyltrifluoroborate[S2] (49 mg, 0.2 mmol) was dissolved in Et_2O (10 mL). The reaction mixture was stirred at room temperature under an N_2 atmosphere for overnight. The resulting mixture was poured onto water, extracted with Et_2O, dried over $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN-Pinene (23 mg, 0.047 mmol, 94%) as a light-yellow crystal: mp 125 – 126.5 °C; ^{1}H NMR(500 MHz, $CDCl_3$, 323K) δ = 9.12 – 9.02

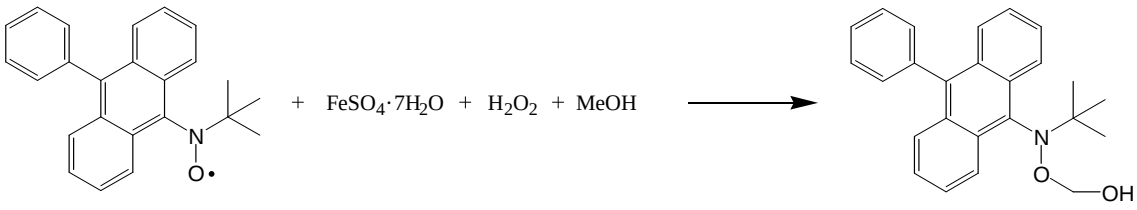
(2H, m), 7.58 – 7.24 (11H, m), 3.60 – 4.60 (1H, m), 2.35 – 2.00 (3H, m), 1.78 – 1.67 (2H, m), 1.33 – 1.18 (2H,m), 1.25 (9H, s), 1.12 – 0.88 (6H, m), 0.75 (3H, s); ^{13}C NMR(125 MHz, $CDCl_3$) δ = 139.5, 136.0, 131.5, 131.3, 130.7, 128.3, 128.2, 127.3, 126.7, 124.7, 123.6, 123.5, 77.2, 62.5, 47.4, 43.1, 41.3, 38.3, 34.7, 32.6, 28.6, 27.4, 23.7, 21.2; IR(KBr film) 2976, 2908, 1441, 1367, 1204, 1032, 987, 930, 767, 703, 679 cm^{-1}; HRMS m/z 477.3026 ($C_{34}H_{39}NO^+$ 477.3050 required).

Procedure of *N-tert*-butyl *N*-methoxyl (10-phenyl-9-anthryl) amine (BPAN-Me) (Table 1 entry 9)



A solution of BPAN (34 mg, 0.1 mmol) and $FeSO_4 \cdot 7H_2O$ (1.4 g, 5.0 mmol) in DMSO (50 mL) was added dropwise H_2O_2(0.5 mL, 5.0 mmol) by syringe to stirring solvent. After stirring the reaction mixture at room temperature for 30 min, the resulting mixture was quenched with the addition of water (30 mL). The organic materials were extracted with ethyl acetate (15 mL), washed with water three times, and dried over anhydrous $MgSO_4$, then concentrated under reduced pressure. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN-H (35 mg, 0.098 mmol, 98%) as a light-yellow crystal. mp 166 – 167 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ = 8.97 (2H, d, J = 8.8 Hz), 7.60 – 7.30 (11H, m), 3.66 (3H, s), 1.28 (9H, s); ^{13}C NMR(100 MHz, $CDCl_3$) δ = 139.3, 138.1, 136.5, 131.4, 131.2, 130.6, 128.3, 128.3, 127.5, 127.3, 126.8, 124.7, 123.9, 62.2, 61.6, 28.2; IR(KBr film) 2974, 1438, 1372, 1208, 1040, 769, 702, 677, 612, 611 cm^{-1}; HRMS m/z 355.1938 ($C_{25}H_{25}NO^+$ required 355.1936).

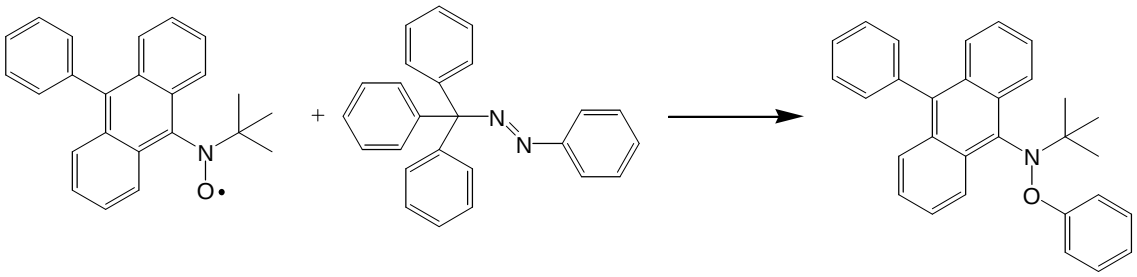
Procedure of *N-tert*-butyl *N*-hydroxymethoxy (10-phenyl-9-anthryl) amine (BPAN-MeOH) (Table 1 entry 10)



A solution of BPAN (17 mg, 0.05 mmol) and $FeSO_4 \cdot 7H_2O$ (280 g, 1.0 mmol) in MeOH

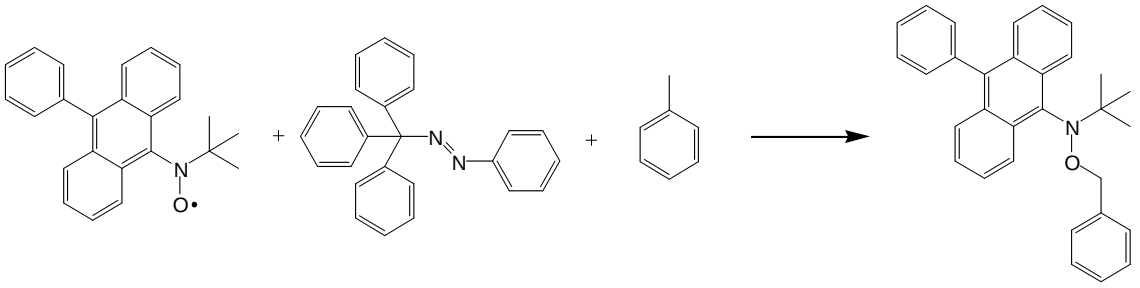
(10 mL) was added dropwise H_2O_2(1.0 mL, 10 mmol) by syringe to stirring solvent. After stirring the reaction mixture at room temperature for 30 min, the resulting mixture was quenched with the addition of water (30 mL). The organic materials were extracted with ethyl acetate (15 mL), washed with water three times, and dried over anhydrous $MgSO_4$, then concentrated under reduced pressure. Flash column chromatography (SiO_2, hexane : ethyl acetate = 9 : 1 solvent) afforded BPAN-MeOH (14 mg, 0.037 mmol, 37%) as a light-yellow crystal. mp 98 – 101 °C; ^{1}H NMR(300 MHz, $CDCl_3$) δ = 8.93 (2H, d, *J* = 9.0 Hz), 7.61 – 7.26 (11H, m), 5.10 (2H, d, *J* = 7.8 Hz), 1.30 (9H, s); ^{13}C NMR(75 MHz, $CDCl_3$) δ = 139.1, 139.0, 137.0, 131.3, 131.1, 130.6, 128.3, 127.4, 127.0, 126.9, 124.7, 124.4, 92.7, 62.4, 28.4; IR(KBr film) 3428, 2981, 1737, 1441, 1372, 1207, 1031, 1001, 768, 703 cm^{-1}; HRMS m/z 371.1883 ($C_{25}H_{25}NO_2^+$ required 371.1885).

Procedure of *N*-*tert*-butyl *N*-phenoxyl (10-phenyl-9-anthryl) amine (BPAN-Ph) (Table 1 entry 1)



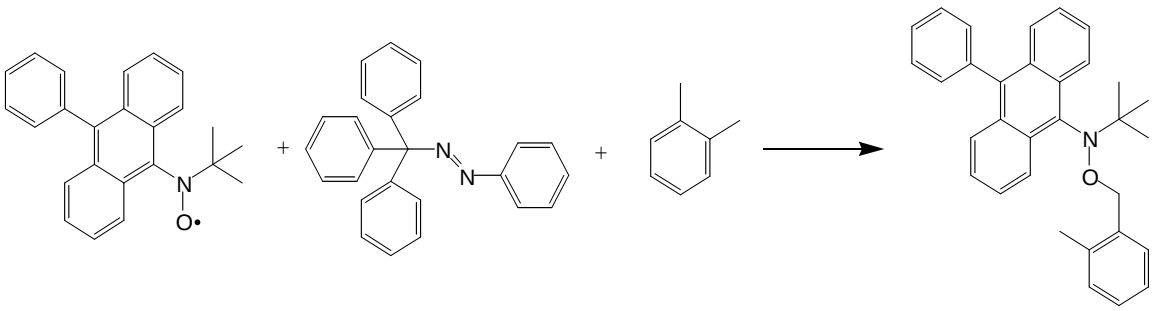
BPAN (34 mg, 0.1 mmol) and phenylazotriphenylmethane (350 mg, 1.0 mmol) was dissolved in benzene (40 mL). The reaction mixture was refluxed for 20 min, and the mixture was concentrated to dryness. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN-Ph (32 mg, 0.078 mmol, 78%) as a light-yellow crystal: mp 124 – 126 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ = 8.51 (2H, d, *J* = 9.0 Hz), 7.62 – 7.26 (16H, m), 1.31 (9H, s); ^{13}C NMR(125 MHz, $CDCl_3$) δ = 139.3, 134.2, 131.5, 130.6, 129.3, 129.0, 128.5, 128.3, 127.8, 127.4, 127.2, 127.1, 125.3, 124.8, 123.8, 118.4, 56.4, 31.5; IR(KBr film) 3027, 2923, 1598, 1488, 1389, 1261, 1085, 1031, 760, 699 cm^{-1}; HRMS m/z 417.2097 ($C_{30}H_{27}NO^+$ required 417.2093).

Procedure of *N*-benzyloxy *N*-*tert*-butyl (10-phenyl-9-anthryl) amine (BPAN-Bn) (Table 1 entry 2)



BPAN (8.5 mg, 0.025 mmol) and phenylazotriphenylmethane (87.5 mg, 0.25 mmol) was dissolved in Toluene (10 mL). The reaction mixture was stirred for 20 min at 80 °C, and the mixture was concentrated to dryness. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN-Bn (6.4 mg, 0.015 mmol, 59%) as a light-yellow crystal: mp 110 – 111 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ = 9.04 (2H, d, J = 9.0 Hz), 7.60 – 7.24 (16H, m), 4.87 (2H, s), 1.30 (9H, s); ^{13}C NMR(125 MHz, $CDCl_3$) δ = 139.4, 138.2, 137.5, 136.6, 131.4, 131.2, 130.7, 128.6, 128.4, 128.3, 128.1, 127.6, 127.3, 126.8, 124.7, 123.9, 76.2, 62.5, 28.3; IR(KBr film) 3058, 2970, 2857, 1600, 1363, 1208, 1014, 770, 701, 411 cm^{-1}; HRMS m/z 431.2251 ($C_{31}H_{29}NO^+$ required 431.2244).

Procedure of *N-tert*-butyl *N*- (2-methylphenyl)methoxy (10-phenyl-9-anthryl) amine (BPAN-OX) (Table 1 entry 3)



BPAN (8.5 mg, 0.025 mmol) and phenylazotriphenylmethane (87.5 mg, 0.25 mmol) was dissolved in *o*-xylene (10 mL). The reaction mixture was stirred for 20 min at 80 °C, and the mixture was concentrated to dryness. Flash column chromatography (SiO_2, hexane solvent) afforded BPAN-OX (9.0 mg, 0.02 mmol, 81%) as a light-yellow crystal. mp 66.5 – 67 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ = 9.05 (2H, d, J = 9.5 Hz), 7.60 – 7.10 (16H, m), 4.87 (2H, s), 2.13 (3H, s), 1.29 (9H, s); ^{13}C NMR(125 MHz, $CDCl_3$) δ = 139.4, 138.3, 137.3, 136.6, 135.4, 131.5, 131.3, 130.03, 129.98, 128.4, 128.3, 127.9, 127.7, 127.3, 126.8, 125.6, 124.8, 123.9, 74.2, 62.5, 28.3, 18.8; IR(KBr film) 2973, 1442, 1370, 1205, 1008, 930, 764, 702, 611, 408 cm^{-1}; HRMS m/z 445.2408 ($C_{32}H_{31}NO^+$ required 445.2400).

References

S1 9-Bromo-10-phenylantracene is commercially available. We purchased it from WAKO (http://www.wako-chem.co.jp/).

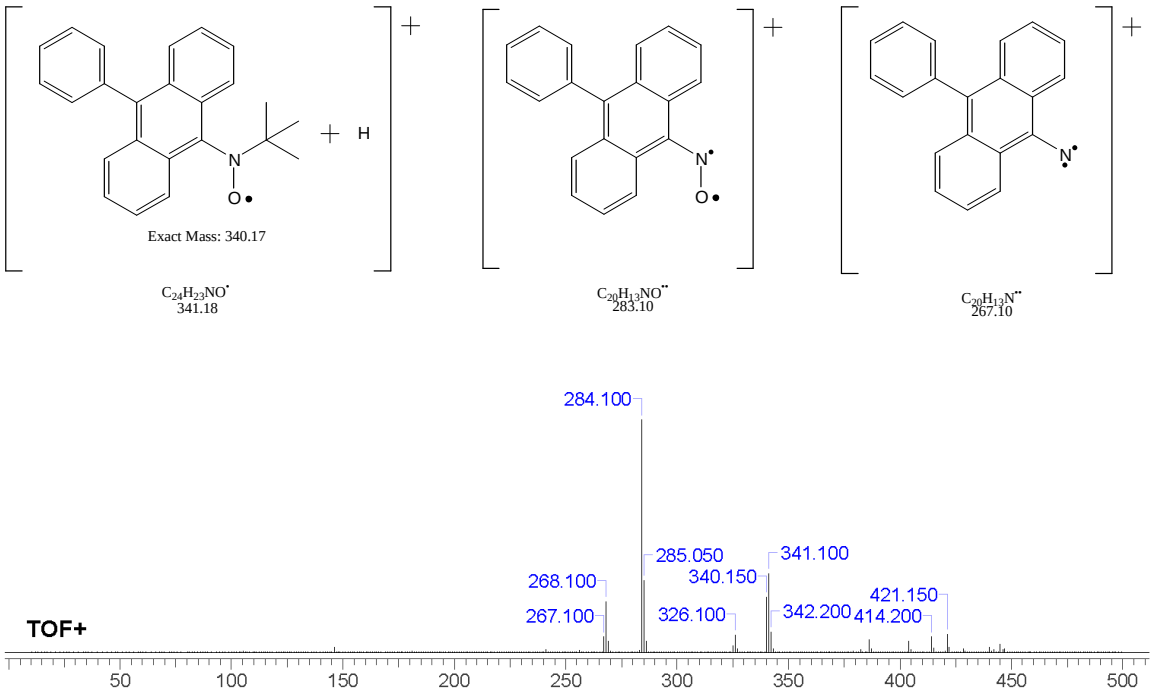
S2 Trifluoroborates were synthesized referring to the following paper. “Oxidation of Alkyl Trifluoroborates: An Opportunity for Tin-Free Radical Chemistry” Geoffroy Sorin, Rocio Martinez Mallorquin, Yohan Contie, Alexandre Baralle, Max Malacria, Jean-Philippe Goddard, and Louis Fensterbank. Angew. Chem. Int. Ed. 2010, 49, 8721 –8723

S3 We have not determined stereochemistry yet, however adduct was obtained as a single isomer. According to literature S2 , single diastereomer was also obtained in the case of the reaction between TEMPO and potassium isopinocampheyltrifluoroborate,

●Mass spectra of BPAN and BPAN adducts by LC/MS(ESI ionization).

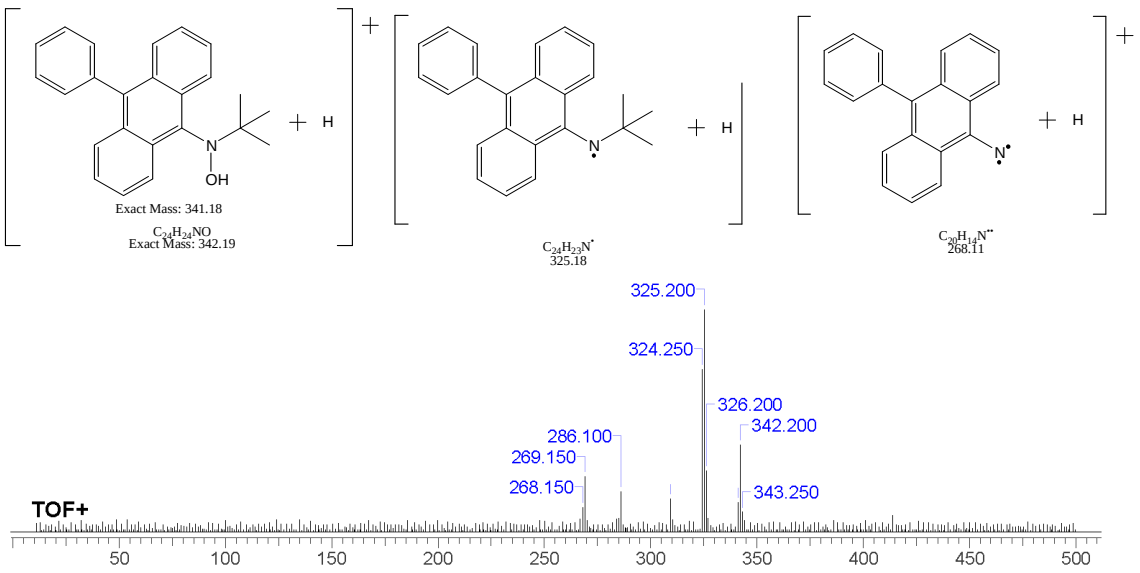
BPAN

t_{Ret} : 19.80 min



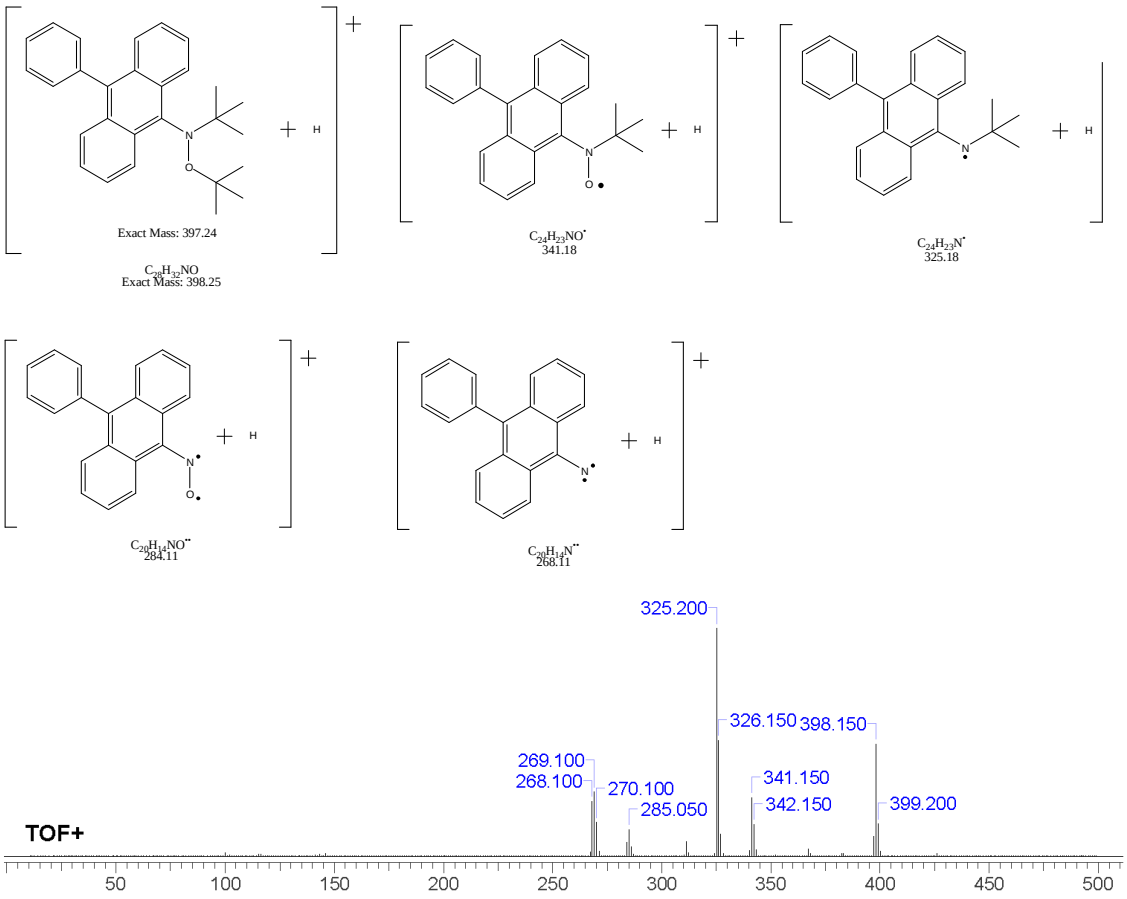
BPAN-H

t_{Ret} : 20.65 min



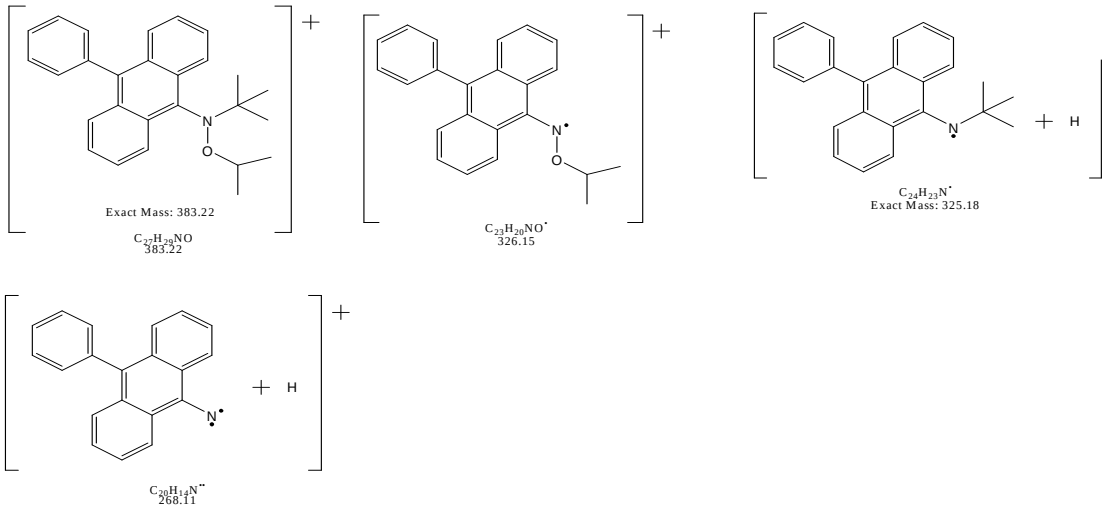
BPAN-*t*Bu

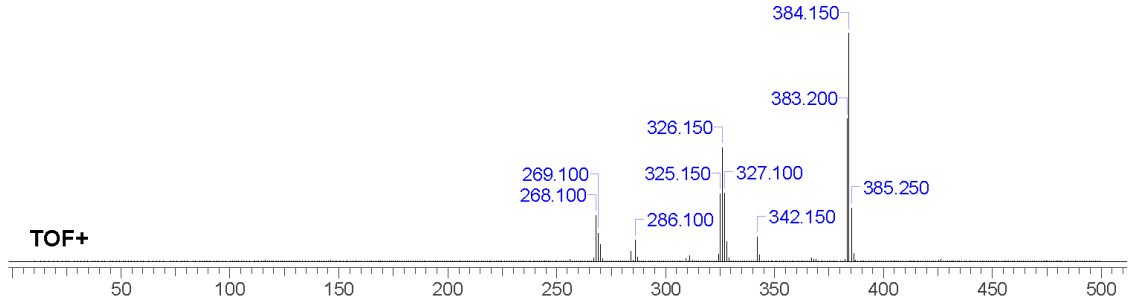
t_{Ret} : 35.80 min



BPAN-*i*Pro

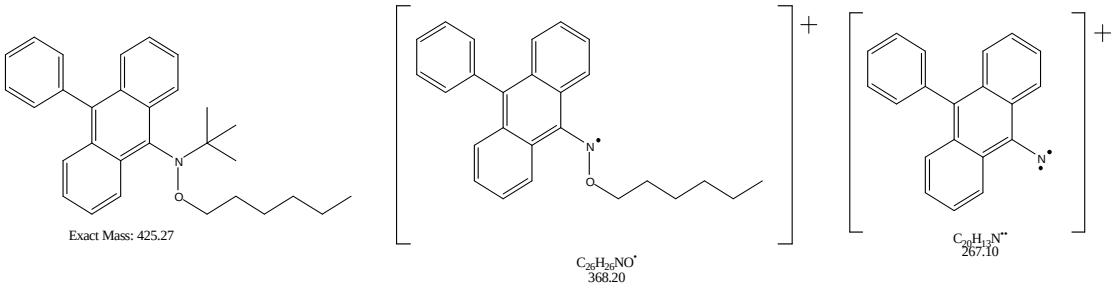
t_{Ret} : 33.56 min

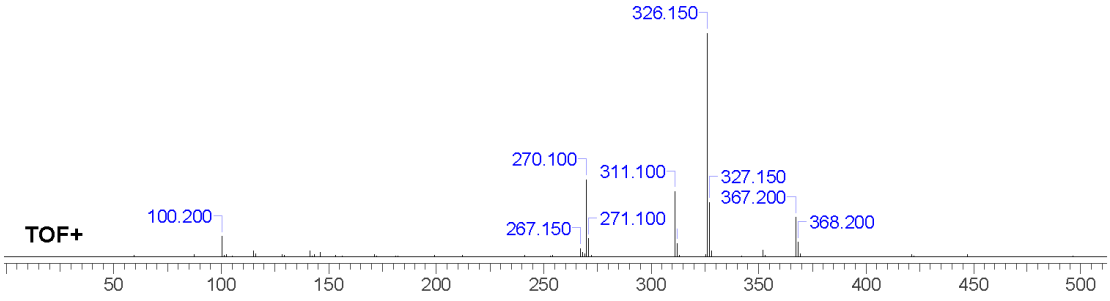




BPAN-hex

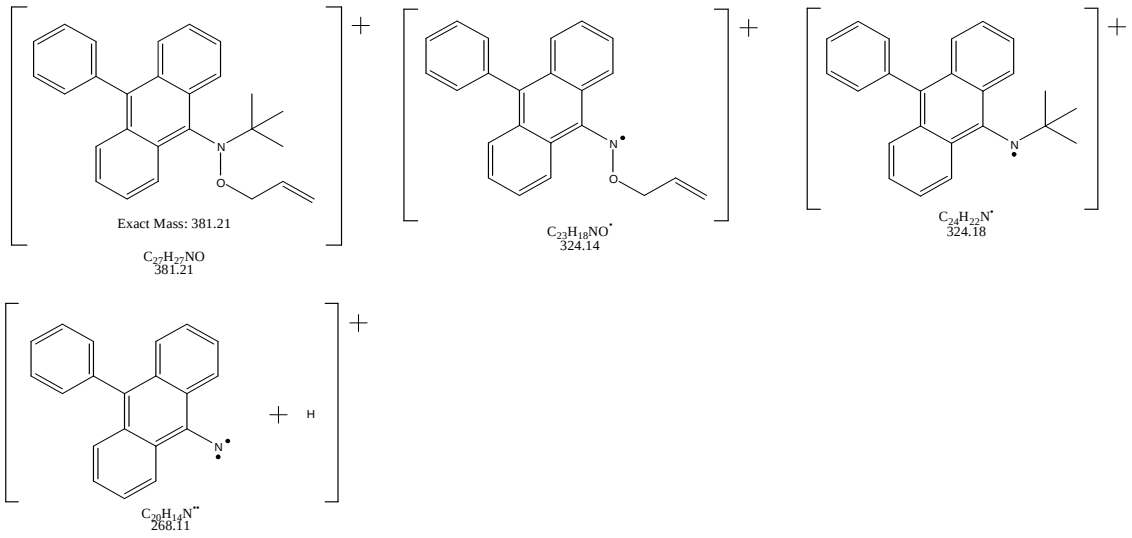
t_{Ret} : 22.92 min

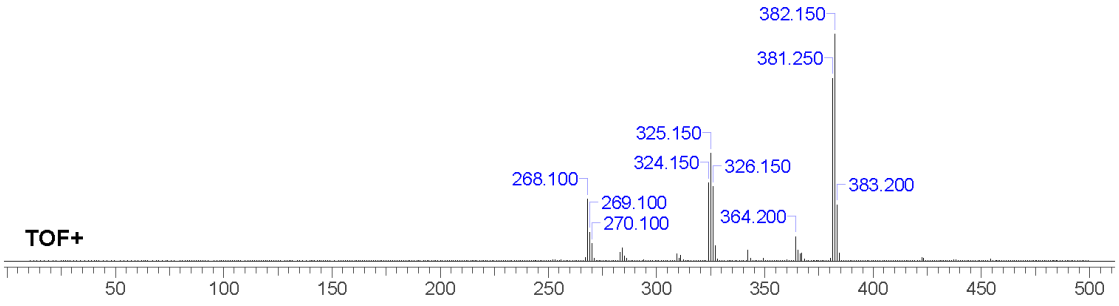




BPAN-Allyl

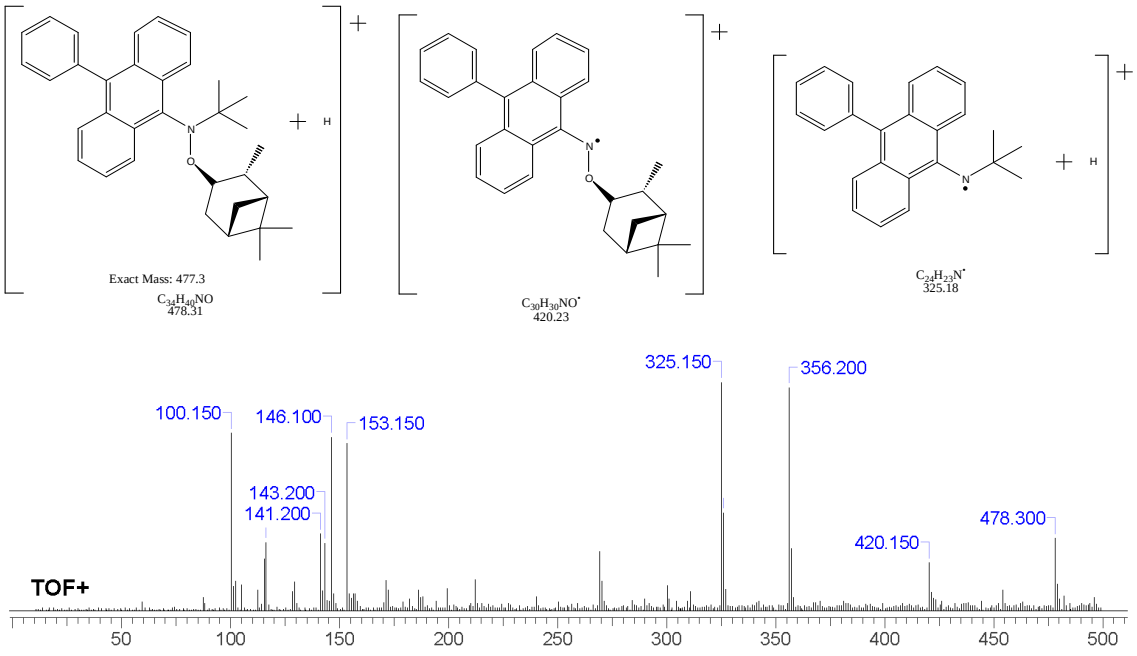
t_{Ret} : 30.02 min





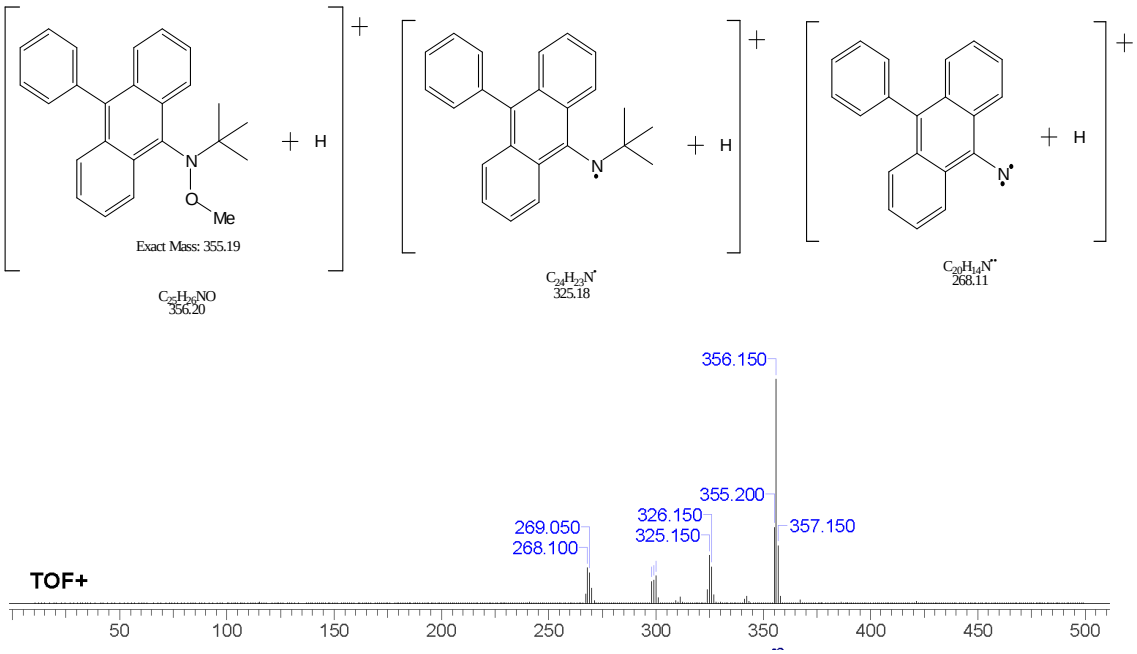
BPAN-Pinene

t_{Ret} : 28.12 min



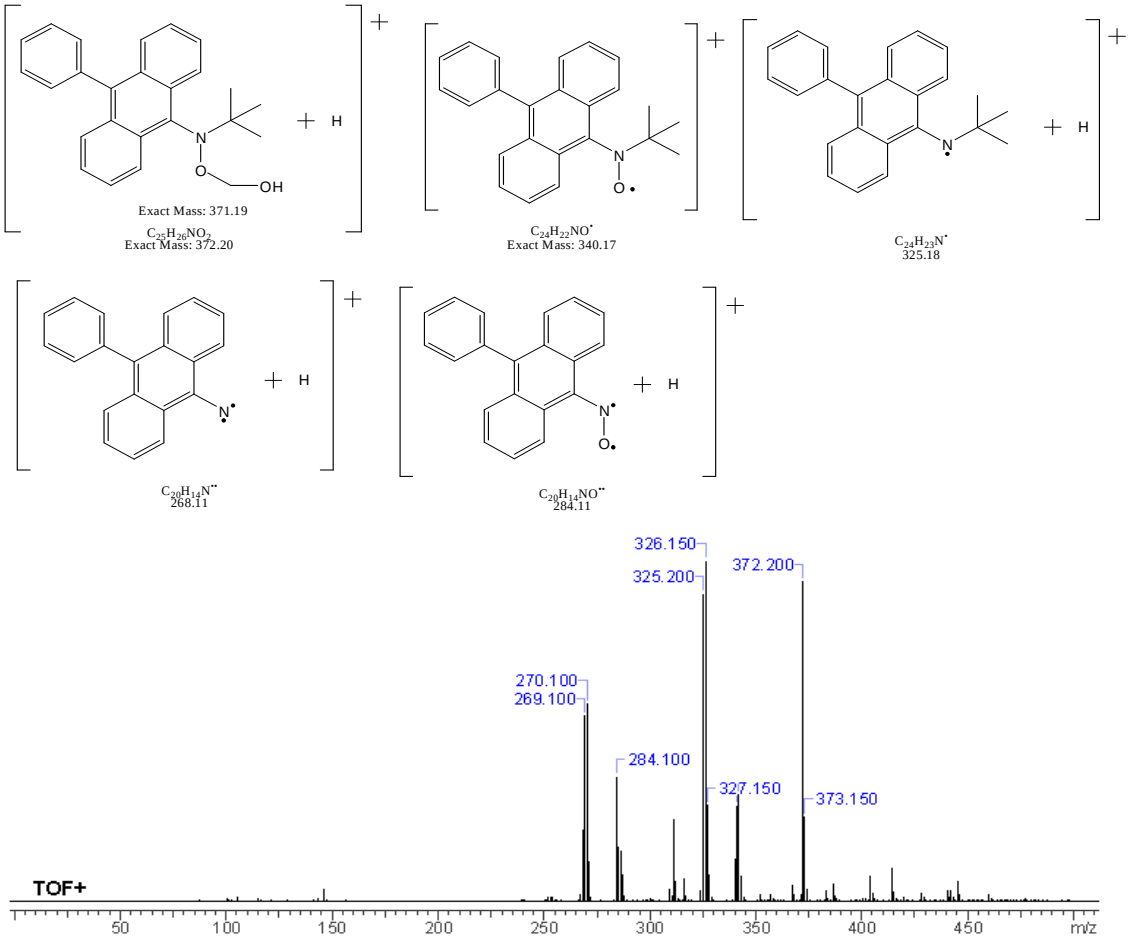
BPAN-Me

t_{Ret} : 28.28 min



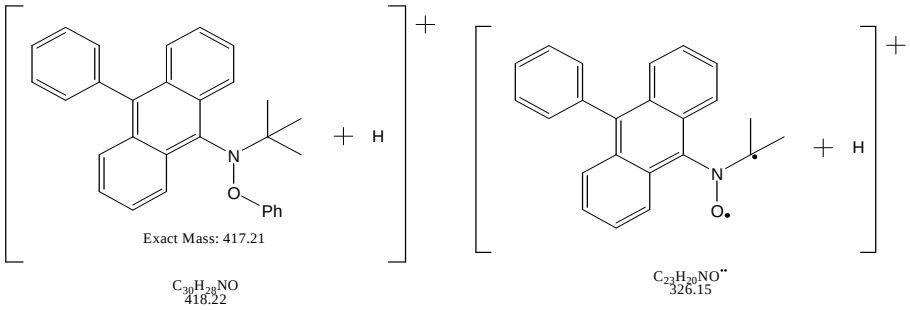
BPAN-MeOH

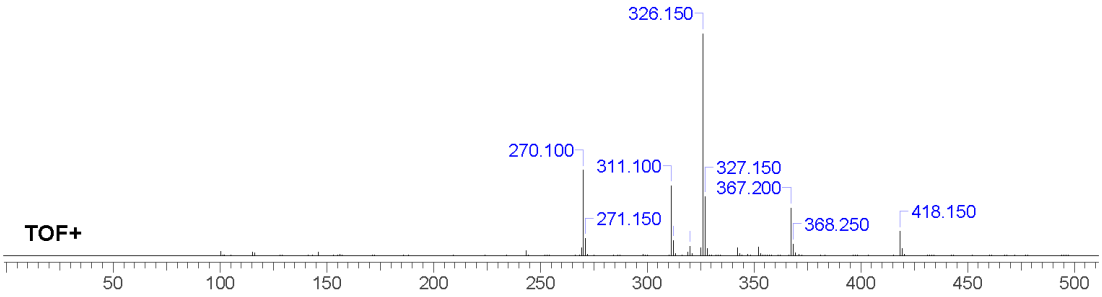
t_{Ret} : 19.30 min



BPAN-Ph

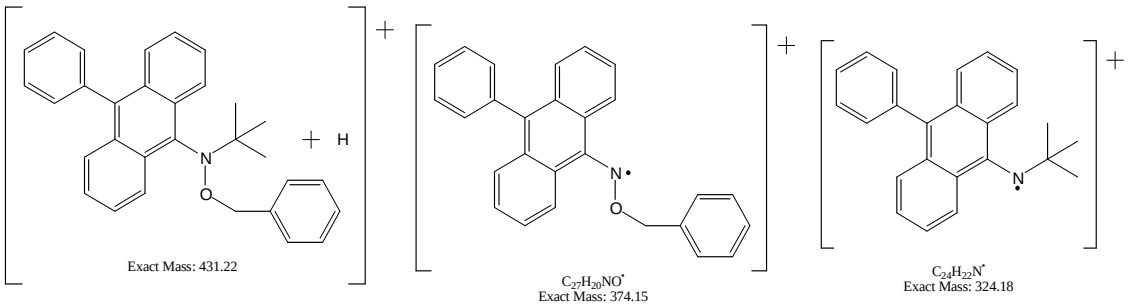
t_{Ret} : 22.98 min

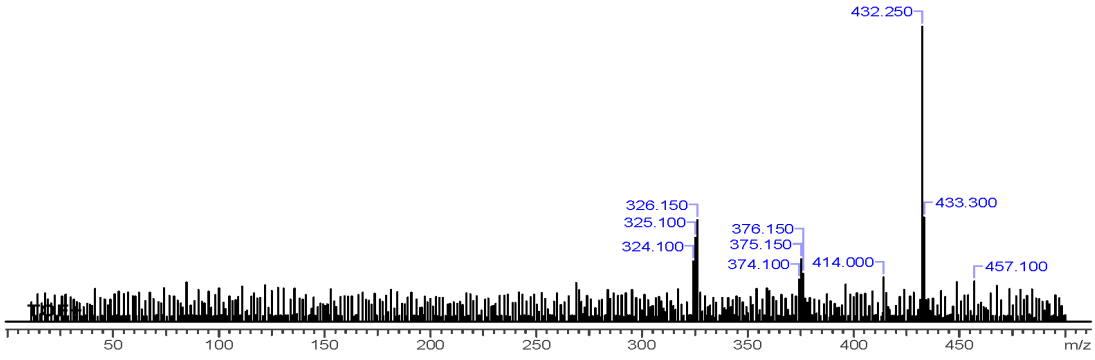




BPAN-Bn

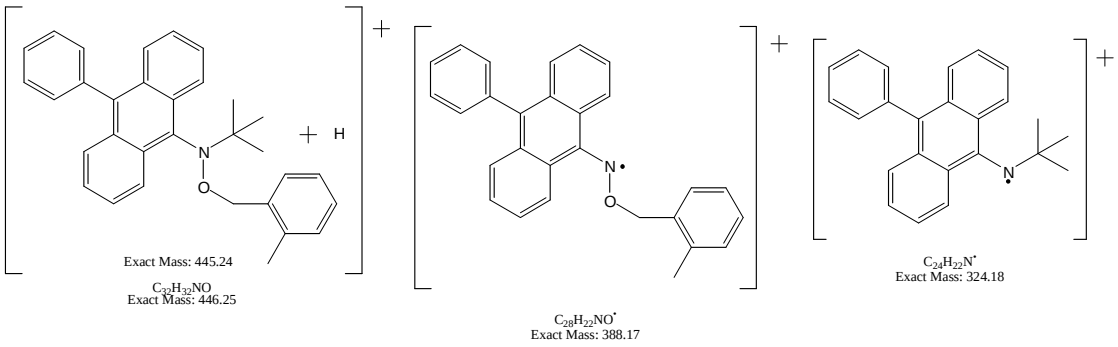
t_{Ret} : 31.72 min

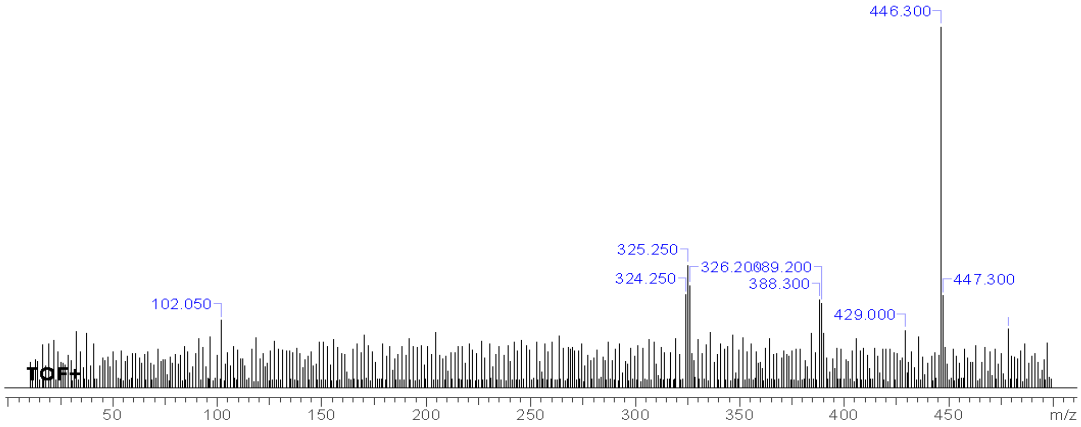




BPAN-OX

t_{Ret} : 33.88 min





●The facility to detect BPAN and BPAN adducts with their UV spectra(390nm).

Compound **2**

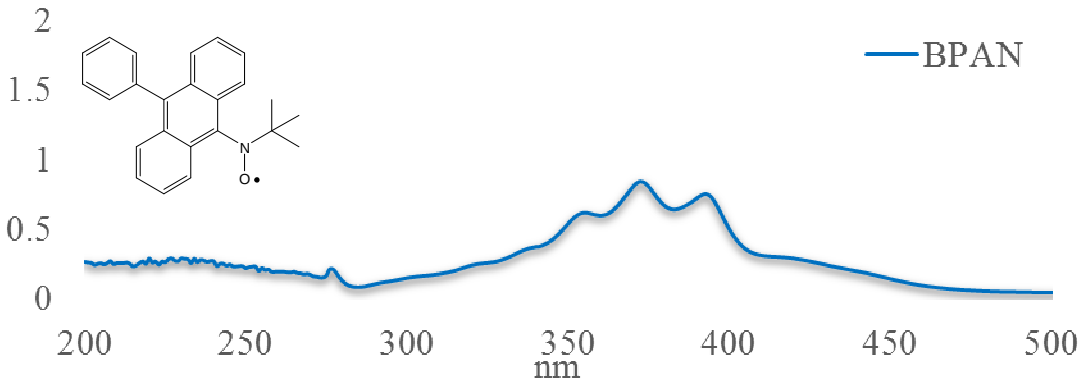


Table 1 entry 9

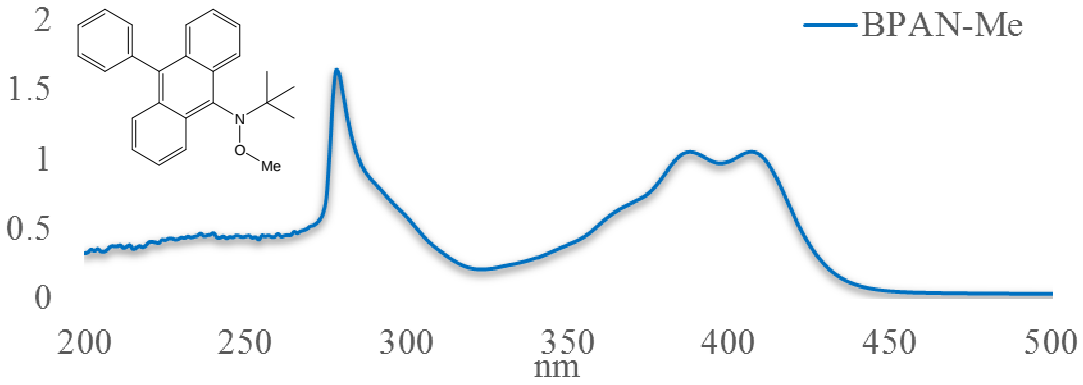


Table 1 entry 1

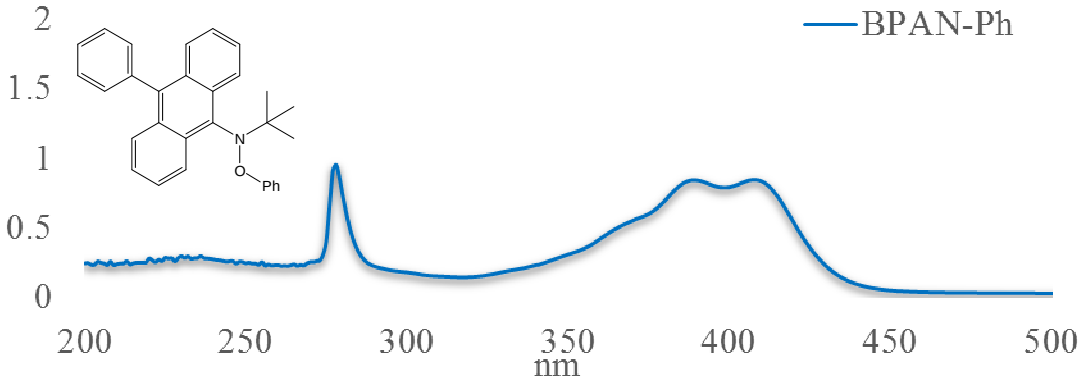


Table 1 entry 6

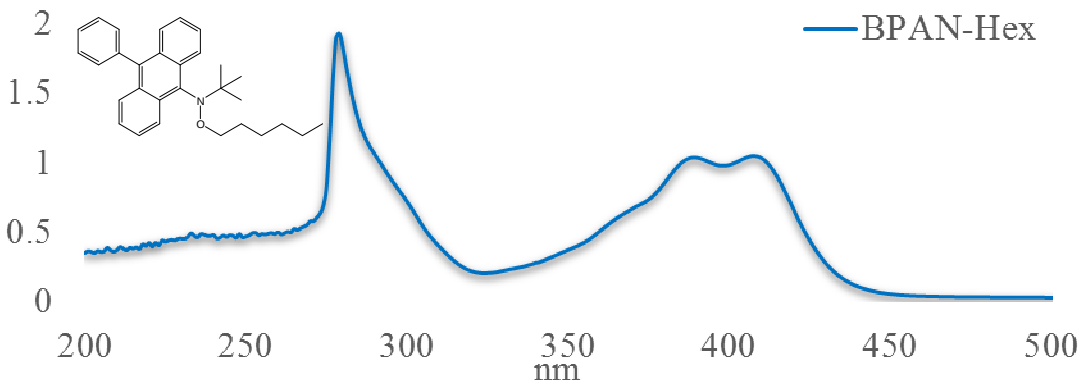
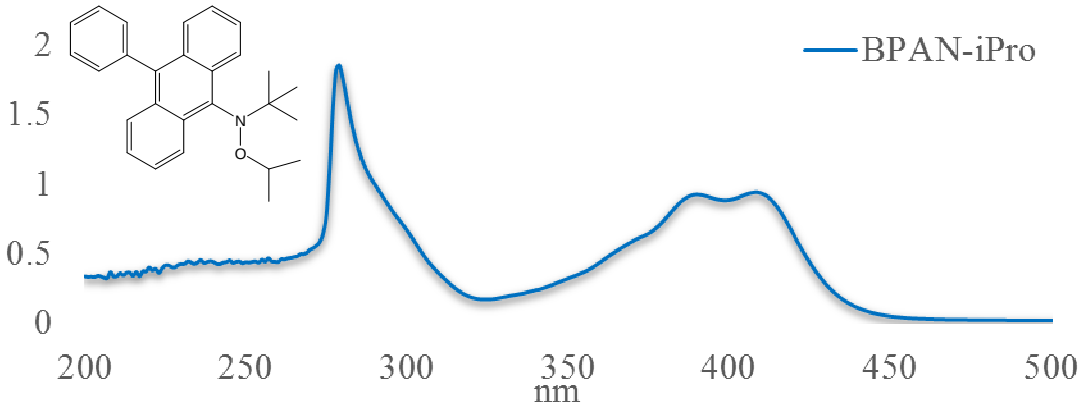
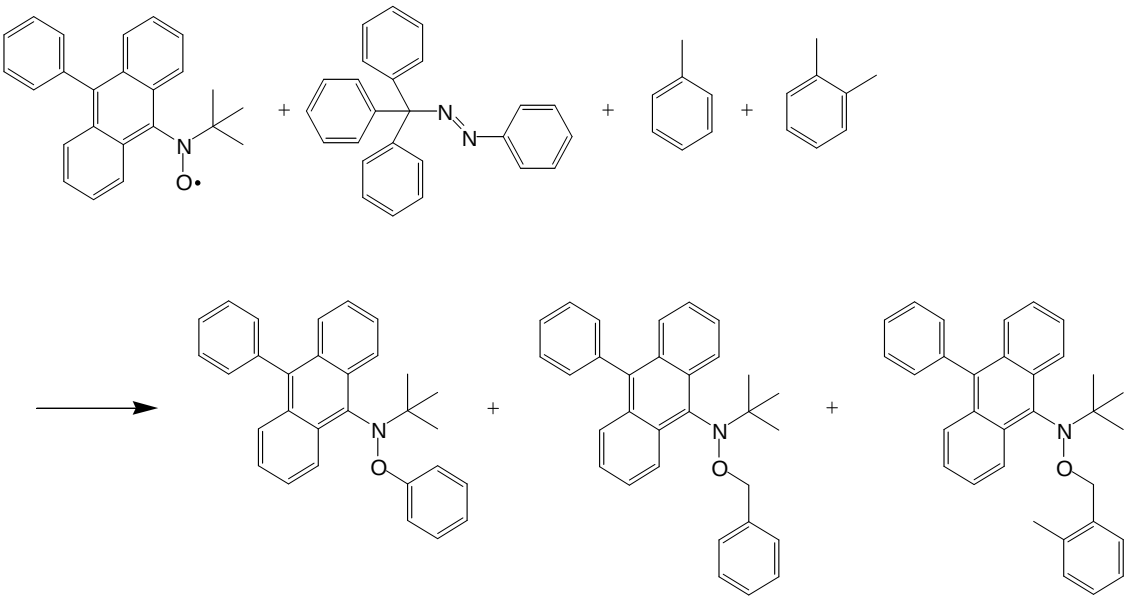


Table 1 entry 5



●Capture of reactive radicals in the presence of multiple by BPAN.



BPAN (17 mg, 0.05 mmol) and phenylazotriphenylmethane (175 mg, 0.5 mmol) was dissolved in Benzene (5 mL), Toluene (5 mL), *o*-xylene (5 mL), *n*-heptane (5 mL). The mixture was stirred for 20 min at 80 °C, and the mixture was concentrated to dryness. The residue was analyzed by LCMS. It obtained BPAN adducts (BPAN-Ph : BPAN-Bz : BPAN-OX = 11 : 32 : 57).

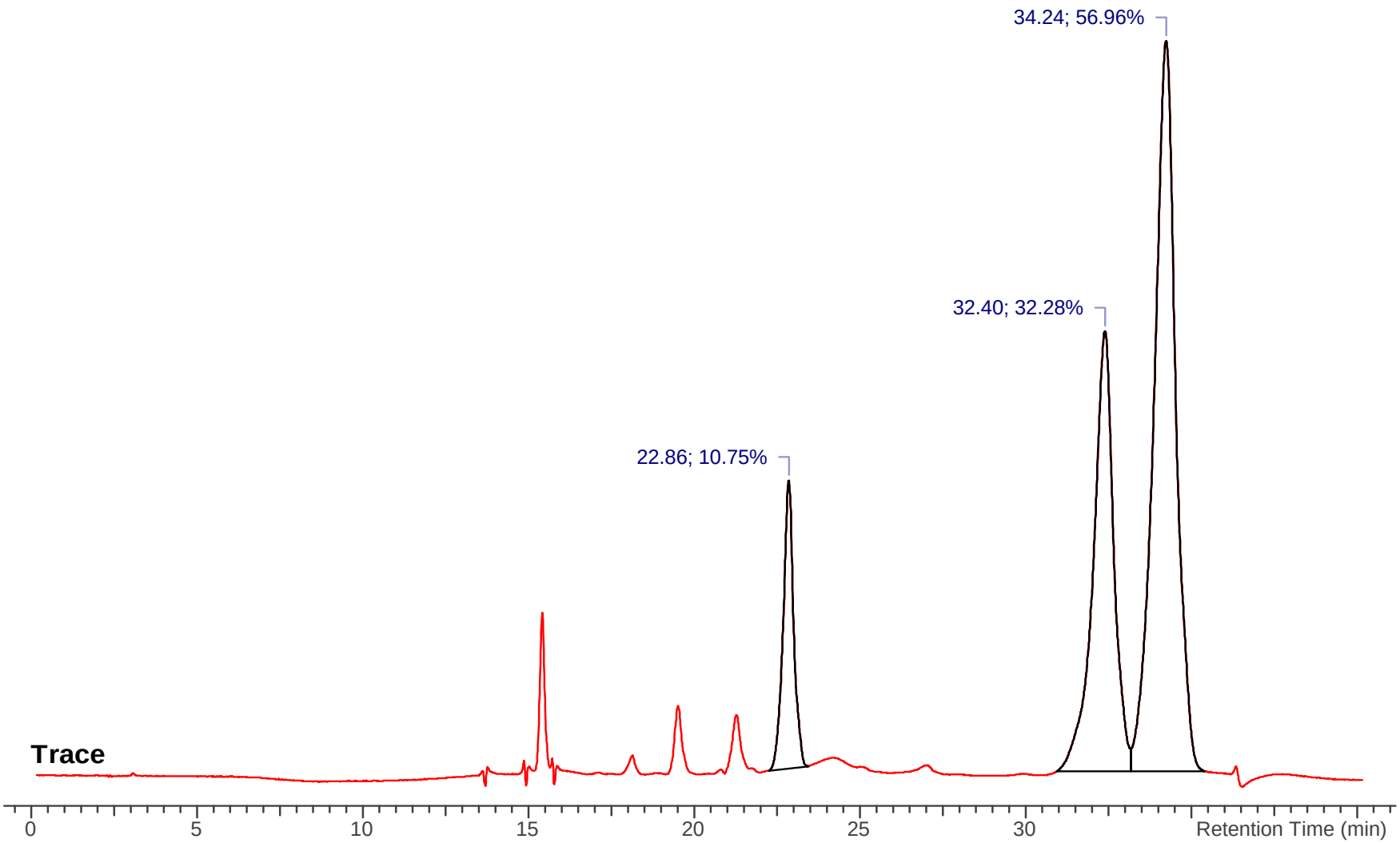
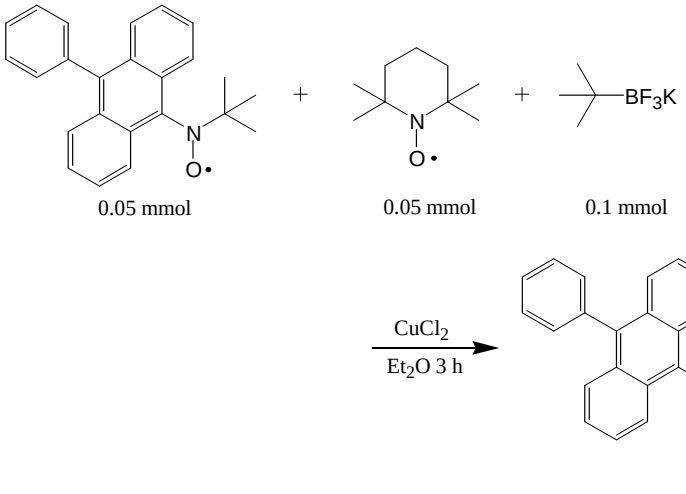


Fig.1. LCMS spectra of crude BPAN adducts(BPAN-Ph, BPAN-Bz, BPAN-OX)(UV detector :390 nm).

●Comparison of the yield of radical addition reactions of BPAN and TEMPO. (Scheme 2)



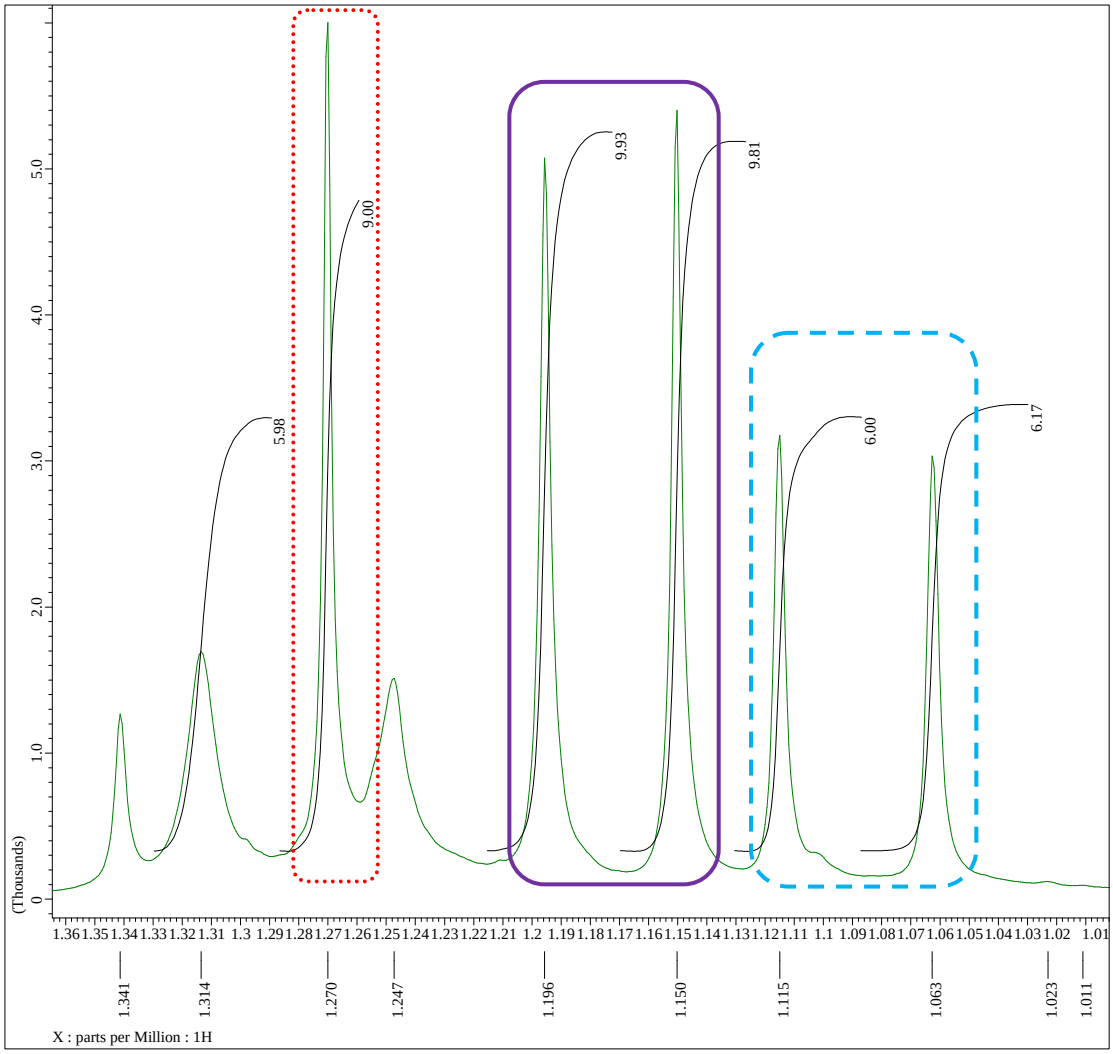
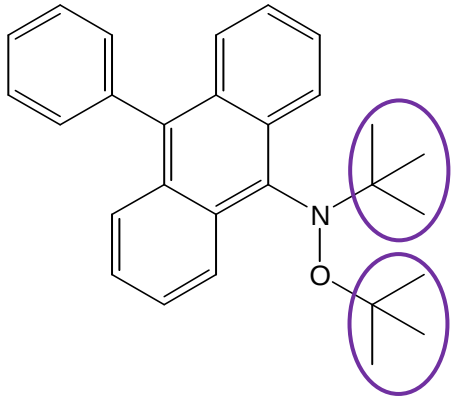


Fig. 2. NMR spectrum of BPAN-^{t}Bu and TEMPO-^{t}Bu for comparison yield of radical addition.

●Thermal stability comparison of BPAN adducts and TEMPO adducts.



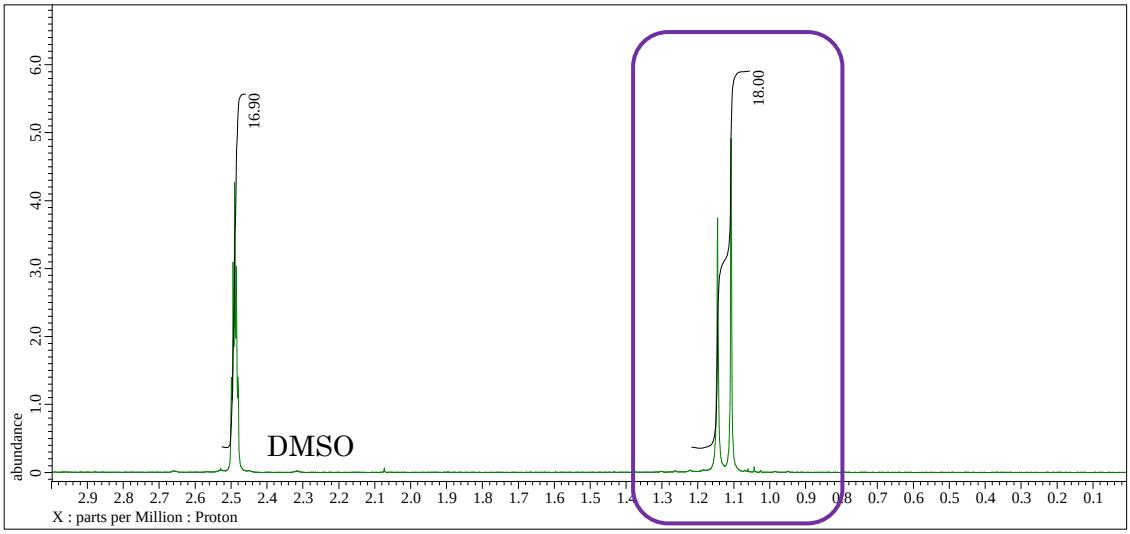


Fig. 3. NMR spectrum of BPAN-^{t}Bu at room temperature.

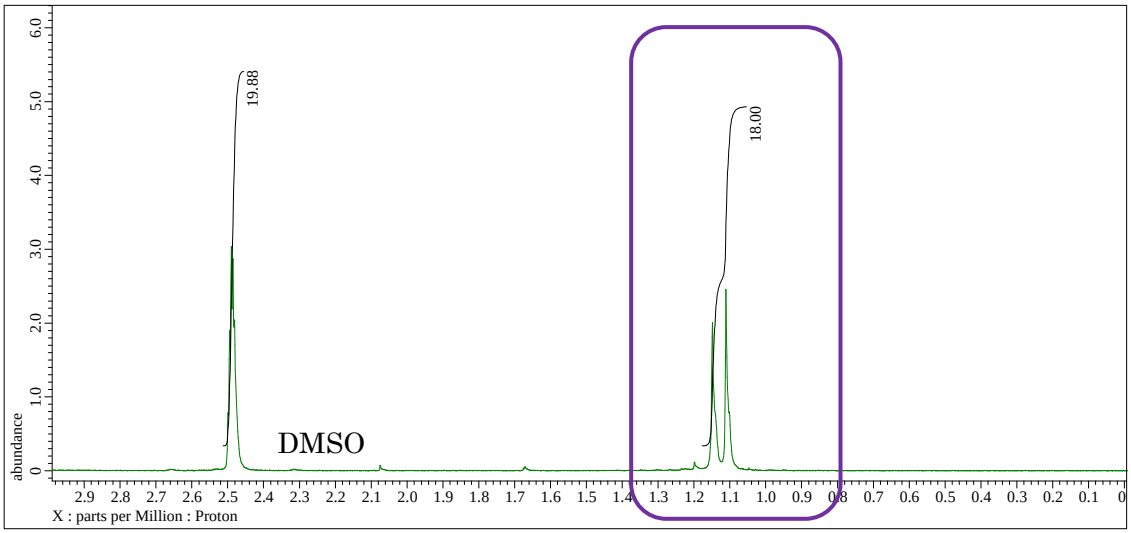
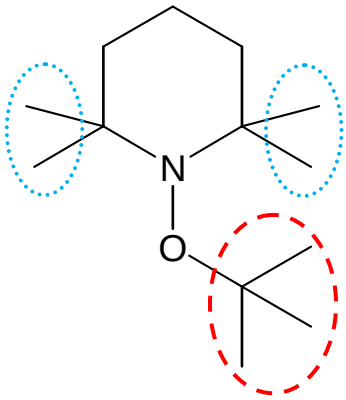


Fig. 4. NMR spectrum of BPAN-^{t}Bu at room temperature after heating one hour at 150℃.



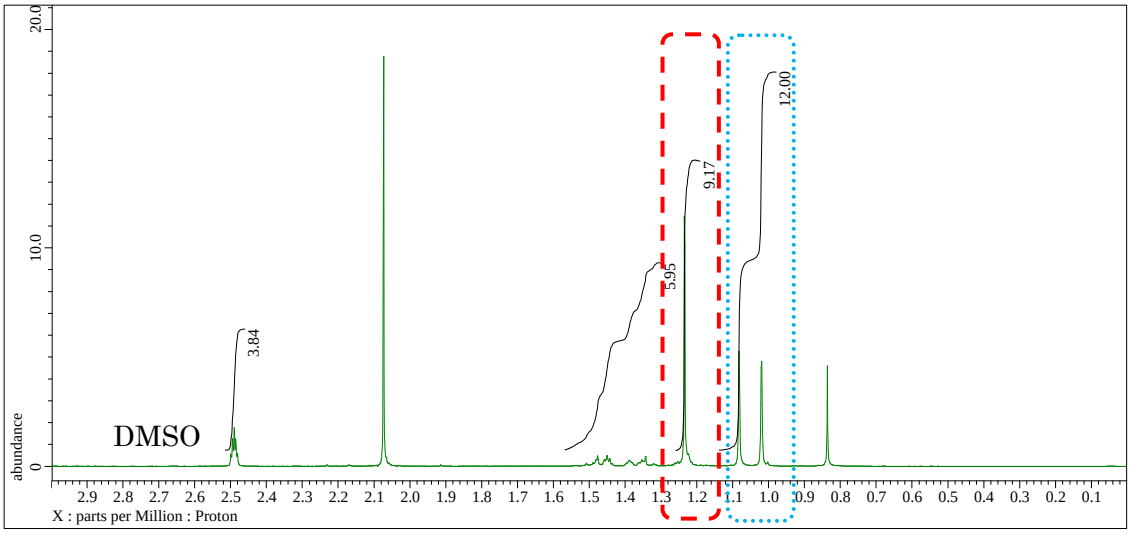


Fig. 5. NMR spectrum of TEMPO-^{t}Bu at room temperature.

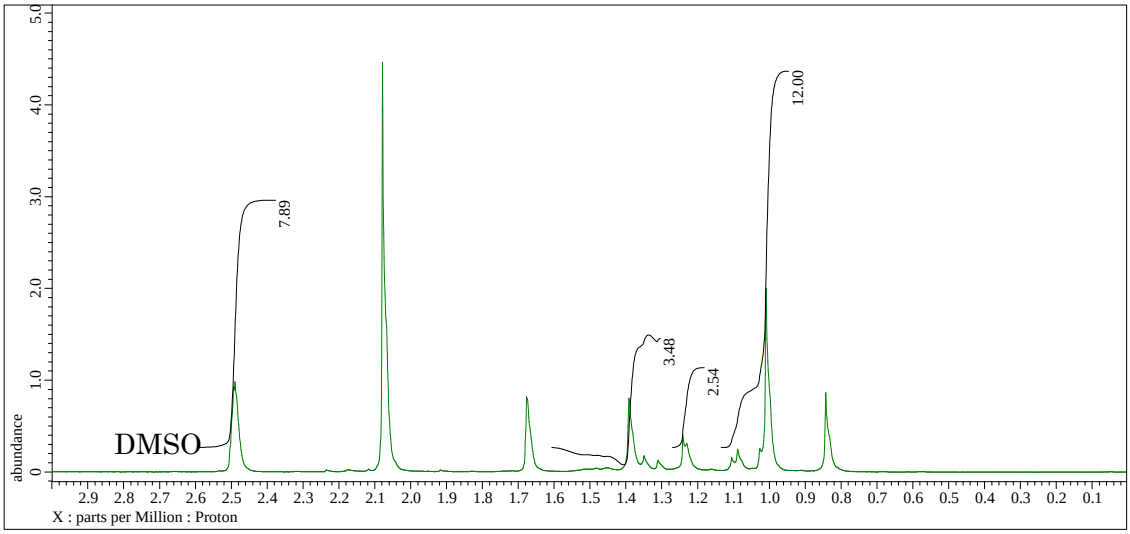


Fig. 6. NMR spectrum of TEMPO-^{t}Bu at room temperature after heating one hour at 150℃.

●Comparison of the ease of ionization by MALDI-TOFMS of BPAN-Me and TEMPO-Me with or without of matrix (5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin) .

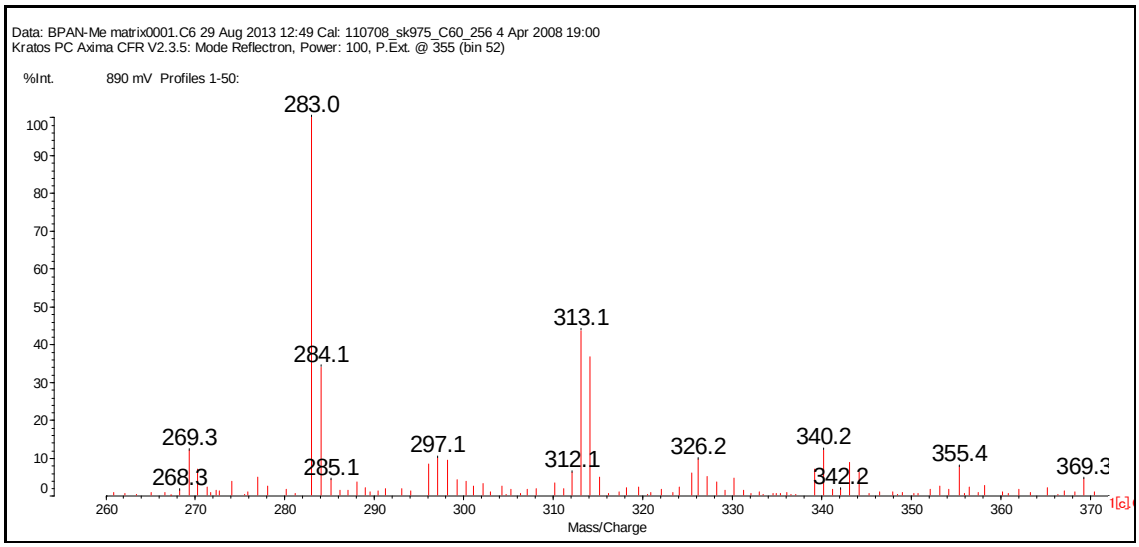


Fig. 7. Mass spectrum of BPAN-Me with matrix.

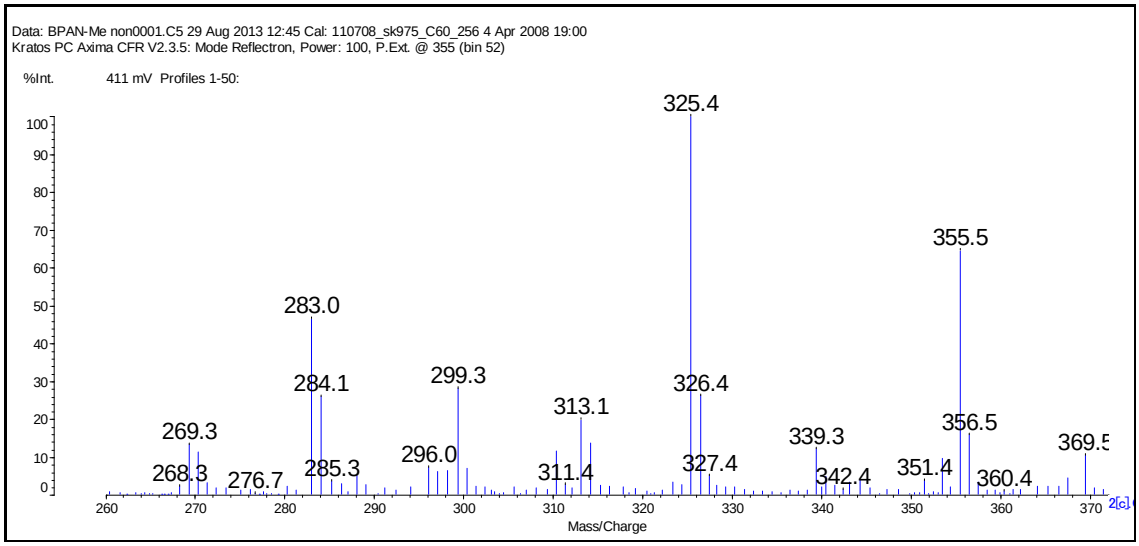


Fig. 8. Mass spectrum of BPAN-Me without matrix.

BPAN-Me : $[M]^+ = 355.5$, $[M - O\text{-}Me + H]^+ = 325.5$, $[M - tBu + H]^+ = 299.4$

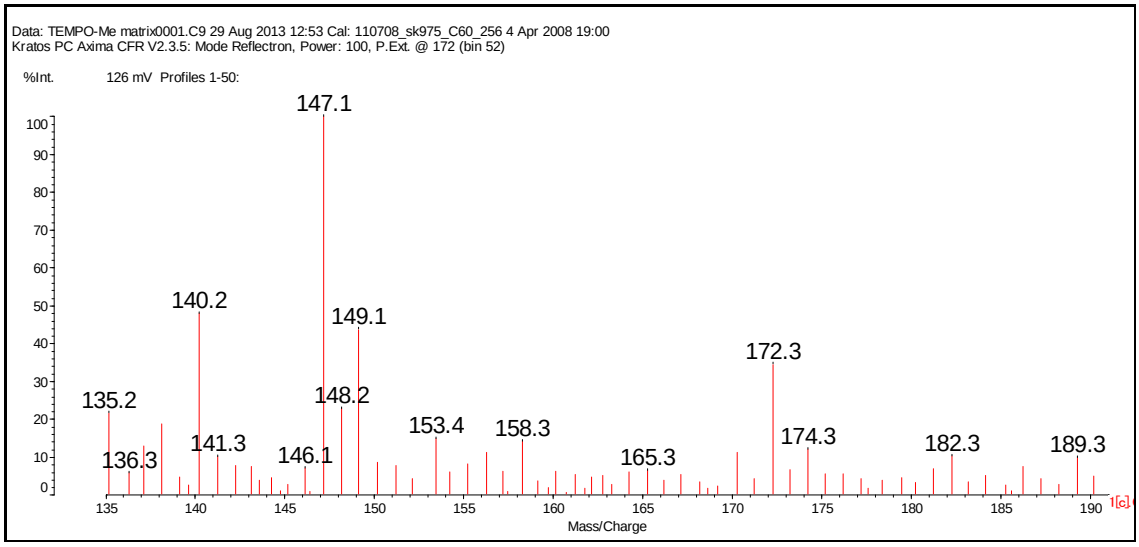


Fig. 9. Mass spectrum of TEMPO-Me with matrix.

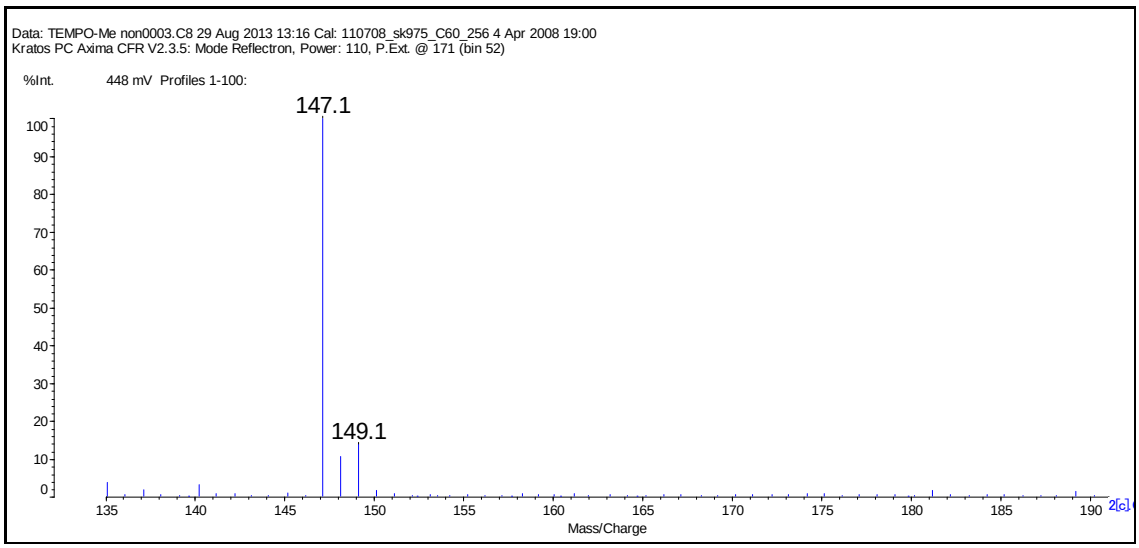
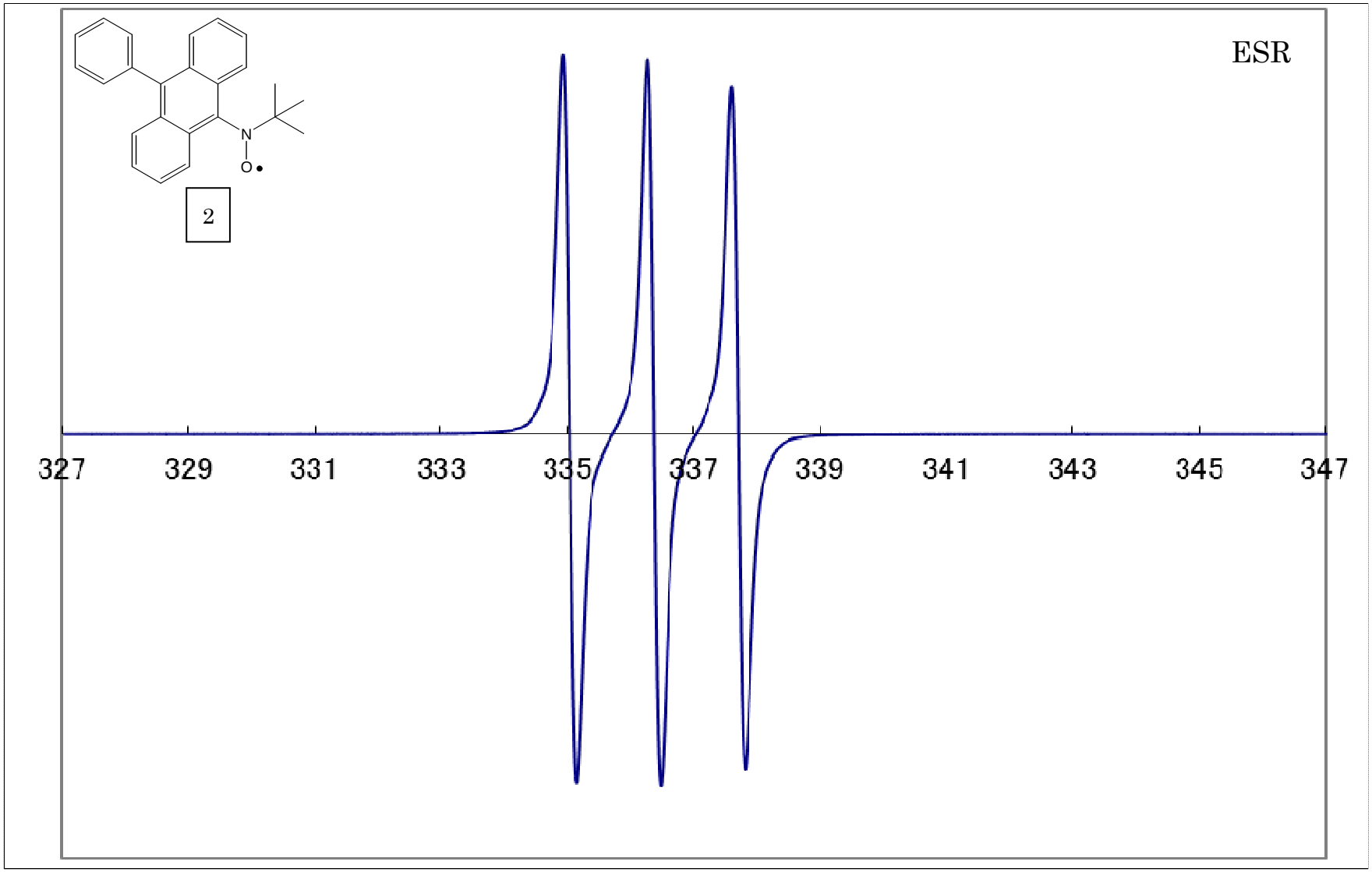


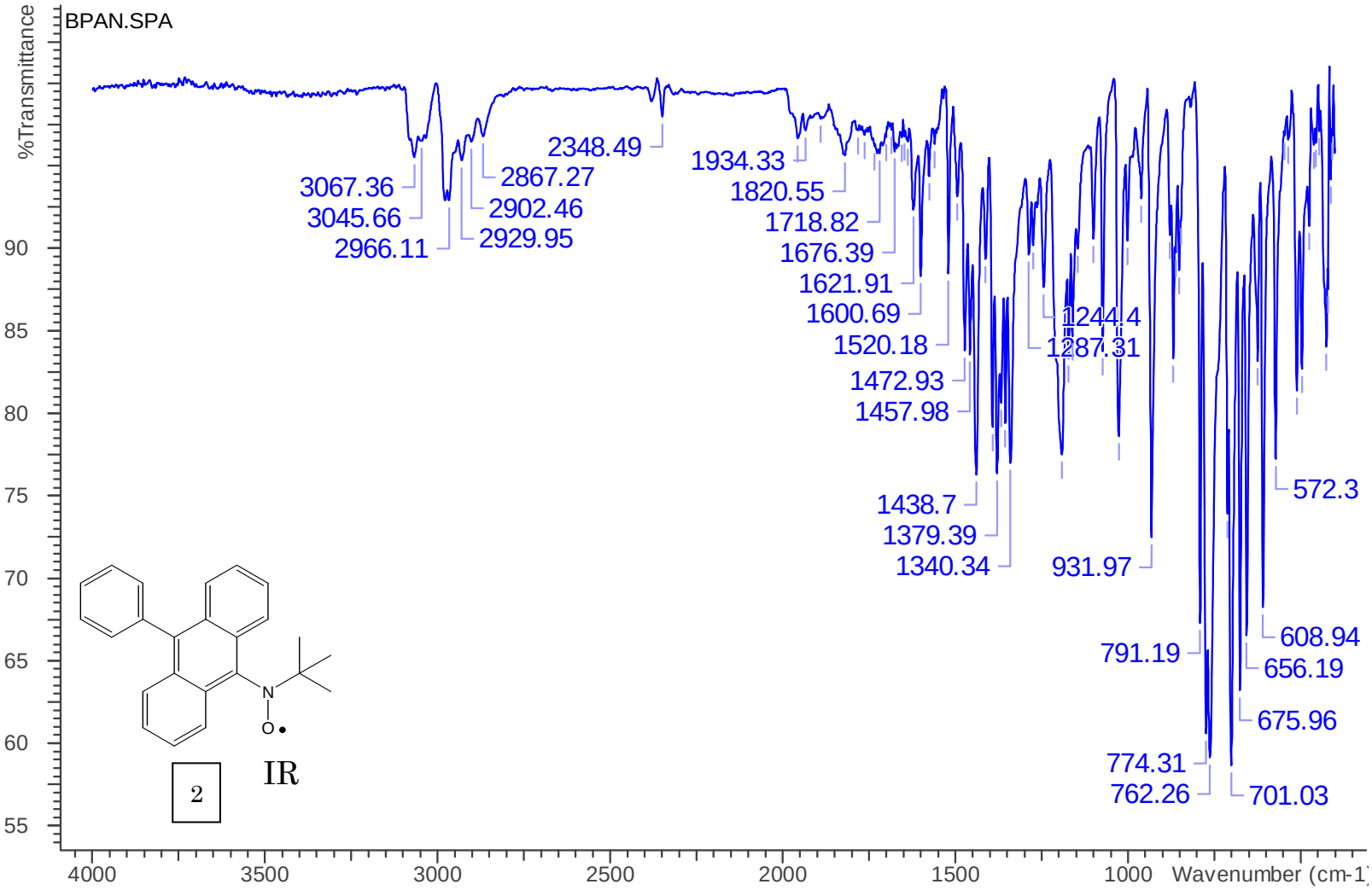
Fig. 10. Mass spectrum of TEMPO-Me without matrix.

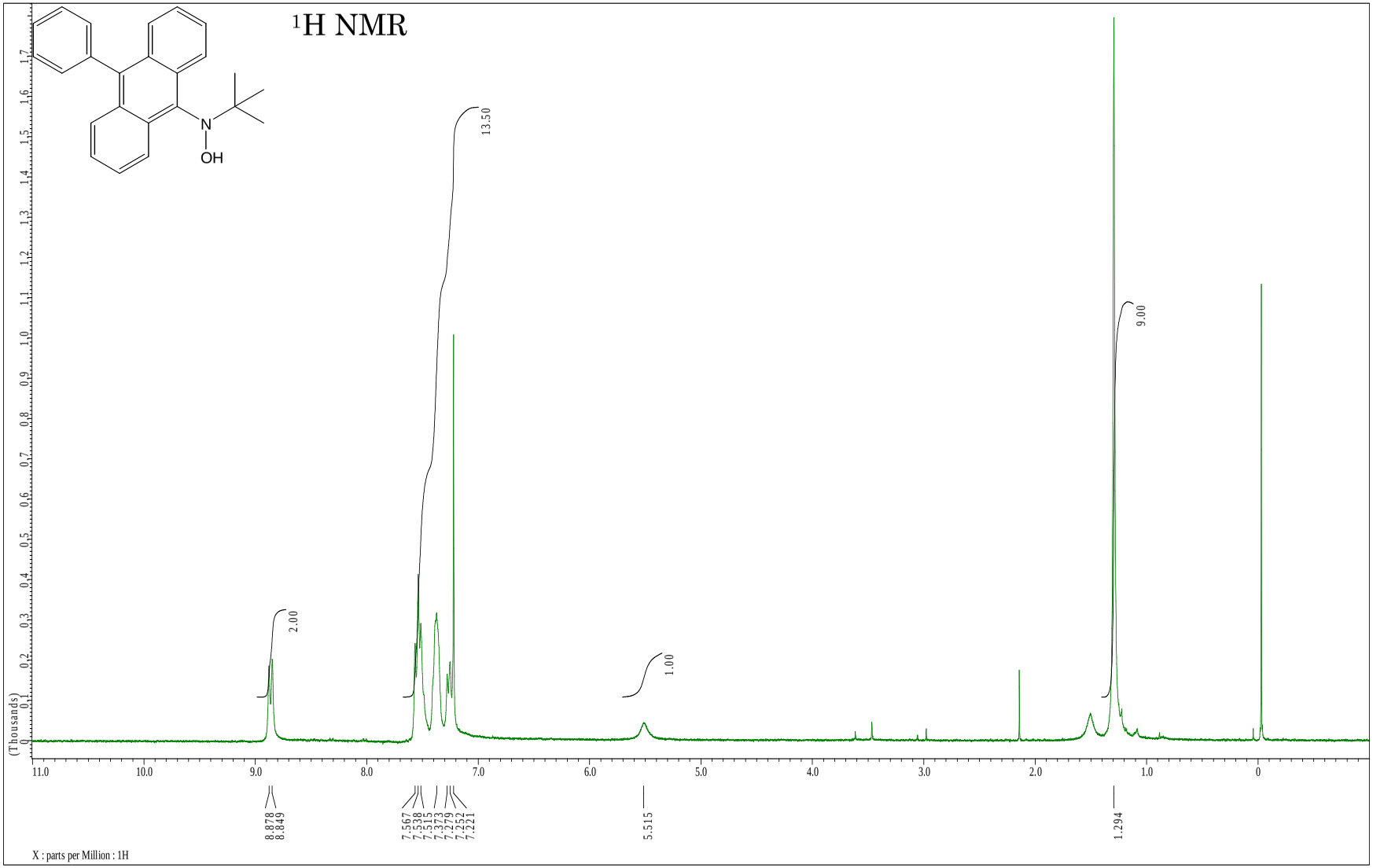
TEMPO-Me : $[M + H]^+ = 172.3$, $[M - O\text{-}Me]^+ = 140.3$

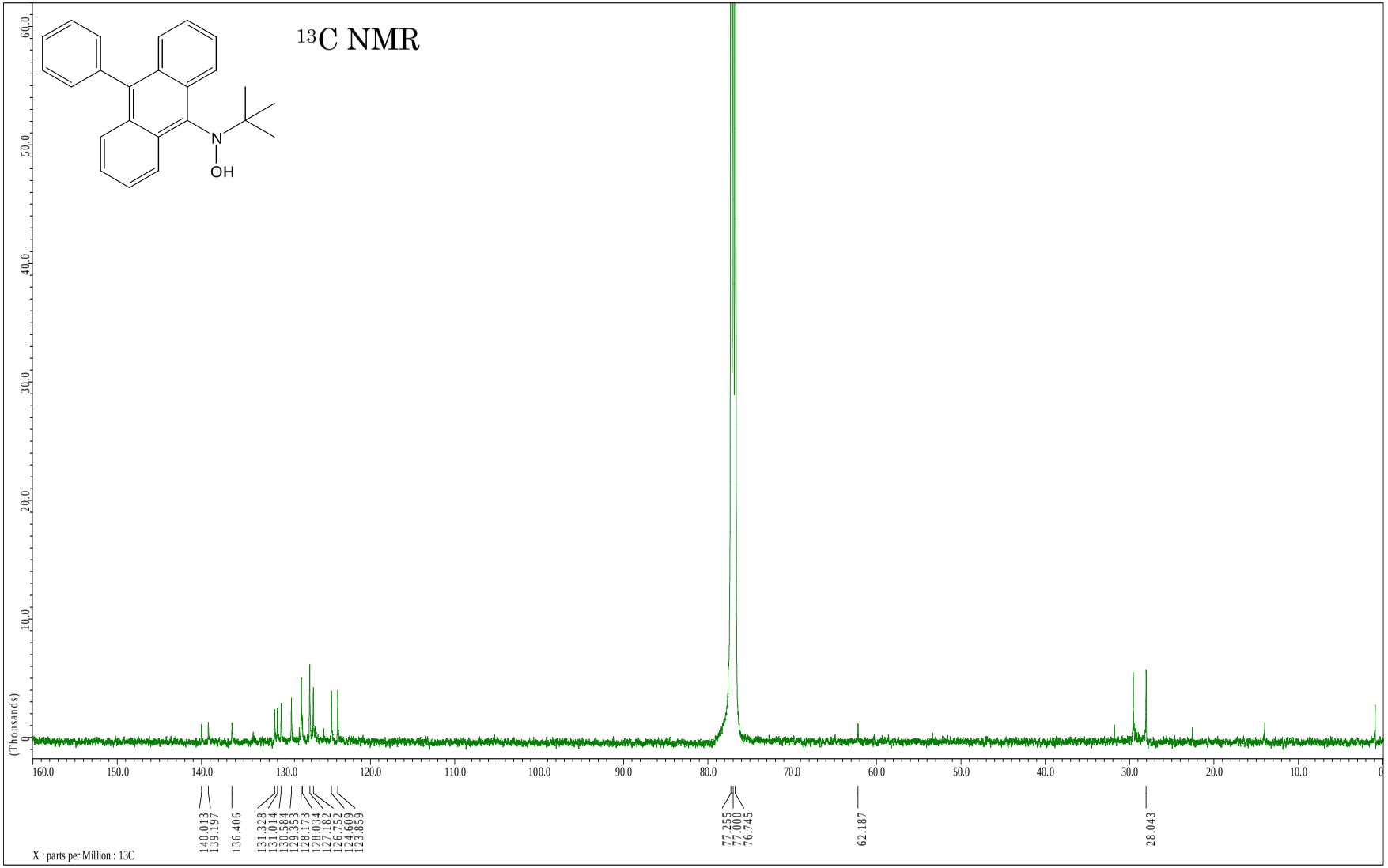
●NMR, IR, ESR Spectra for all new compounds.

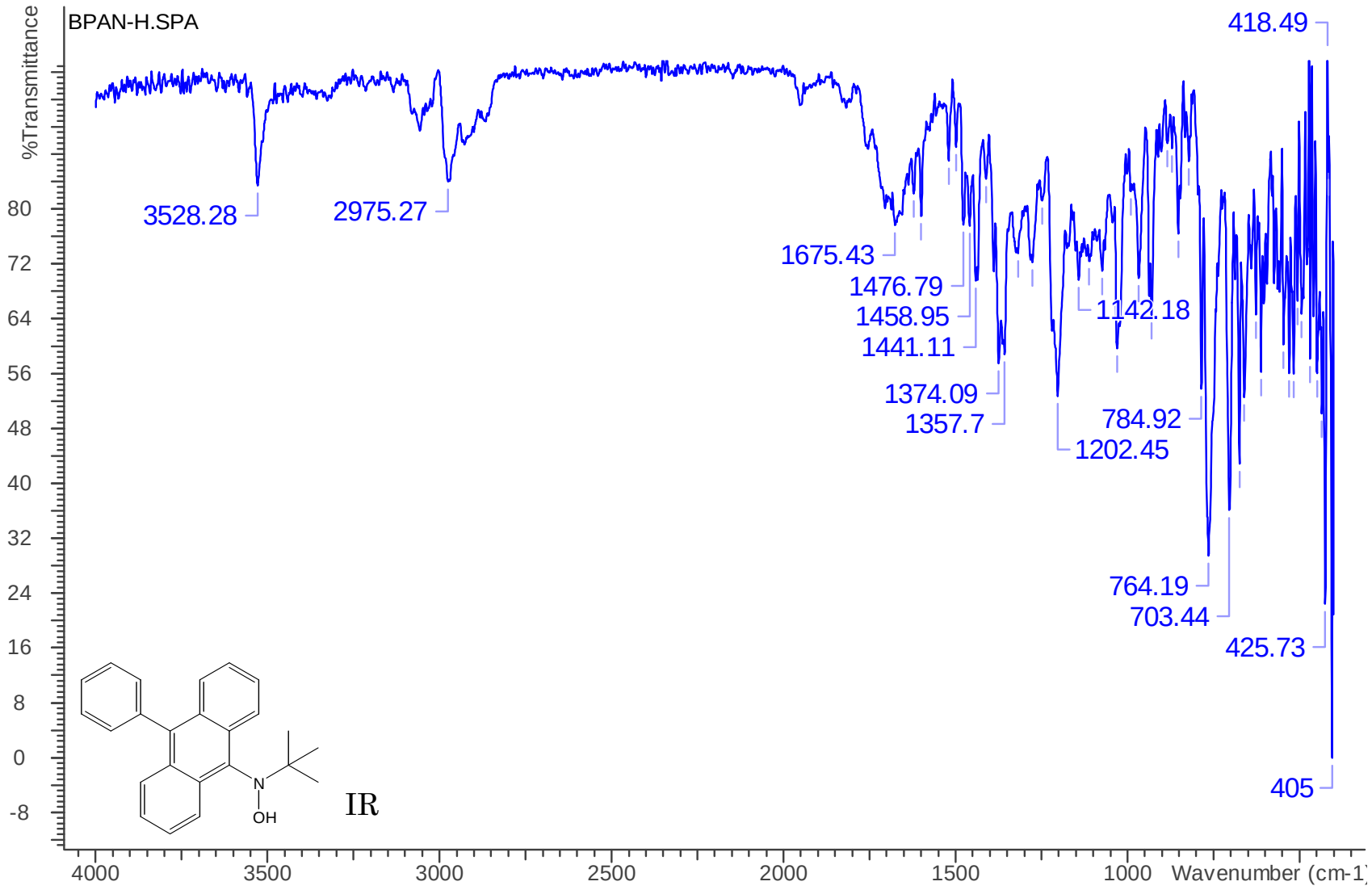

ESR
N
O•
2
327
329
331
333
335
337
339
341
343
345
347

Compound **2**

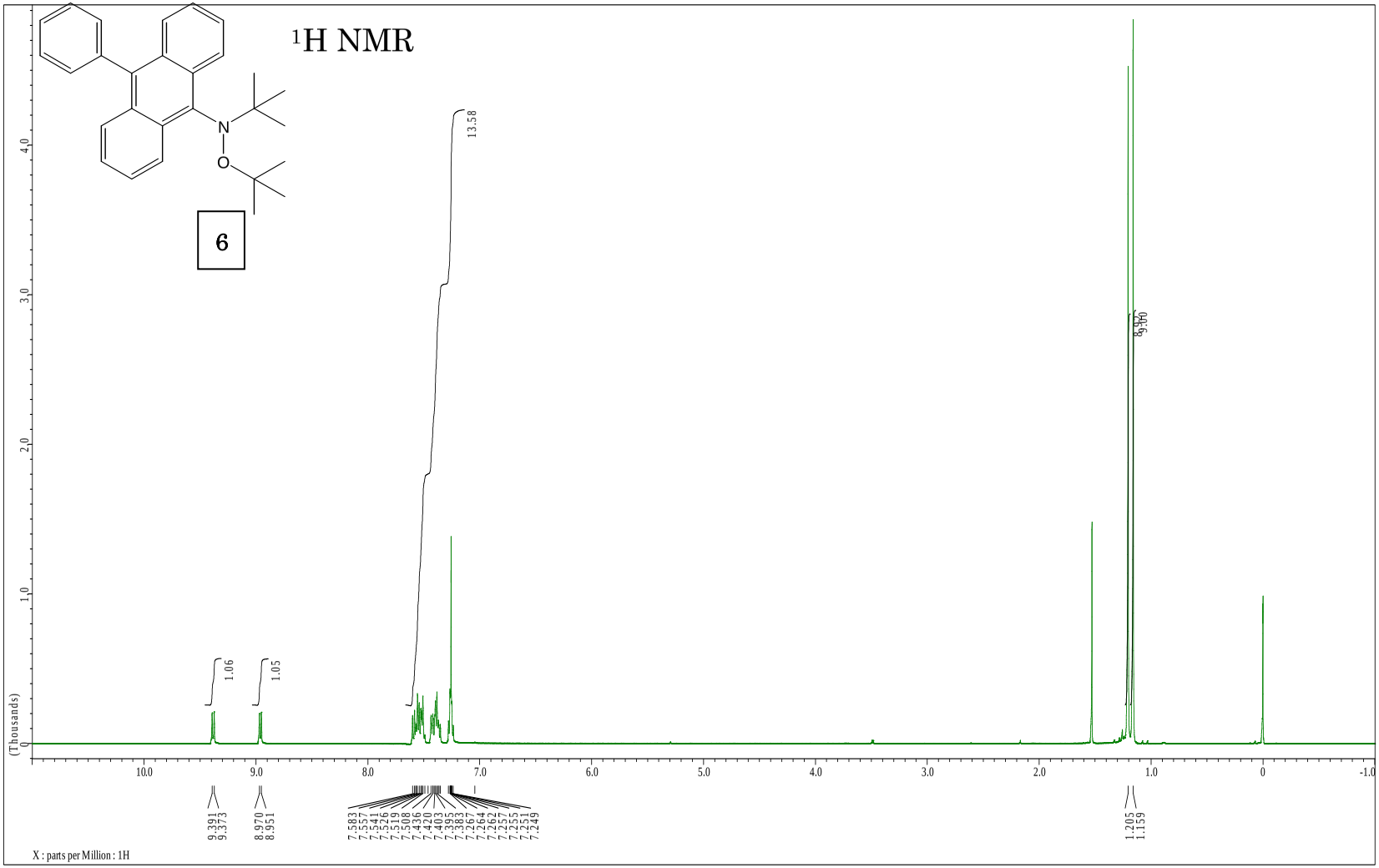

BPAN.SPA
%Transmittance
3067.36
3045.66
2966.11
2929.95
2902.46
2867.27
2348.49
1934.33
1820.55
1718.82
1676.39
1621.91
1600.69
1520.18
1472.93
1457.98
1438.7
1379.39
1340.34
1287.31
1244.4
931.97
791.19
774.31
762.26
701.03
675.96
656.19
608.94
572.3
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
N
O
2
IR


1H NMR
N
OH
13.50
9.00
2.00
1.00
(Thousands)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.878
8.849
7.567
7.538
7.511
7.373
7.279
7.252
7.221
5.515
1.294
X : parts per Million : 1H

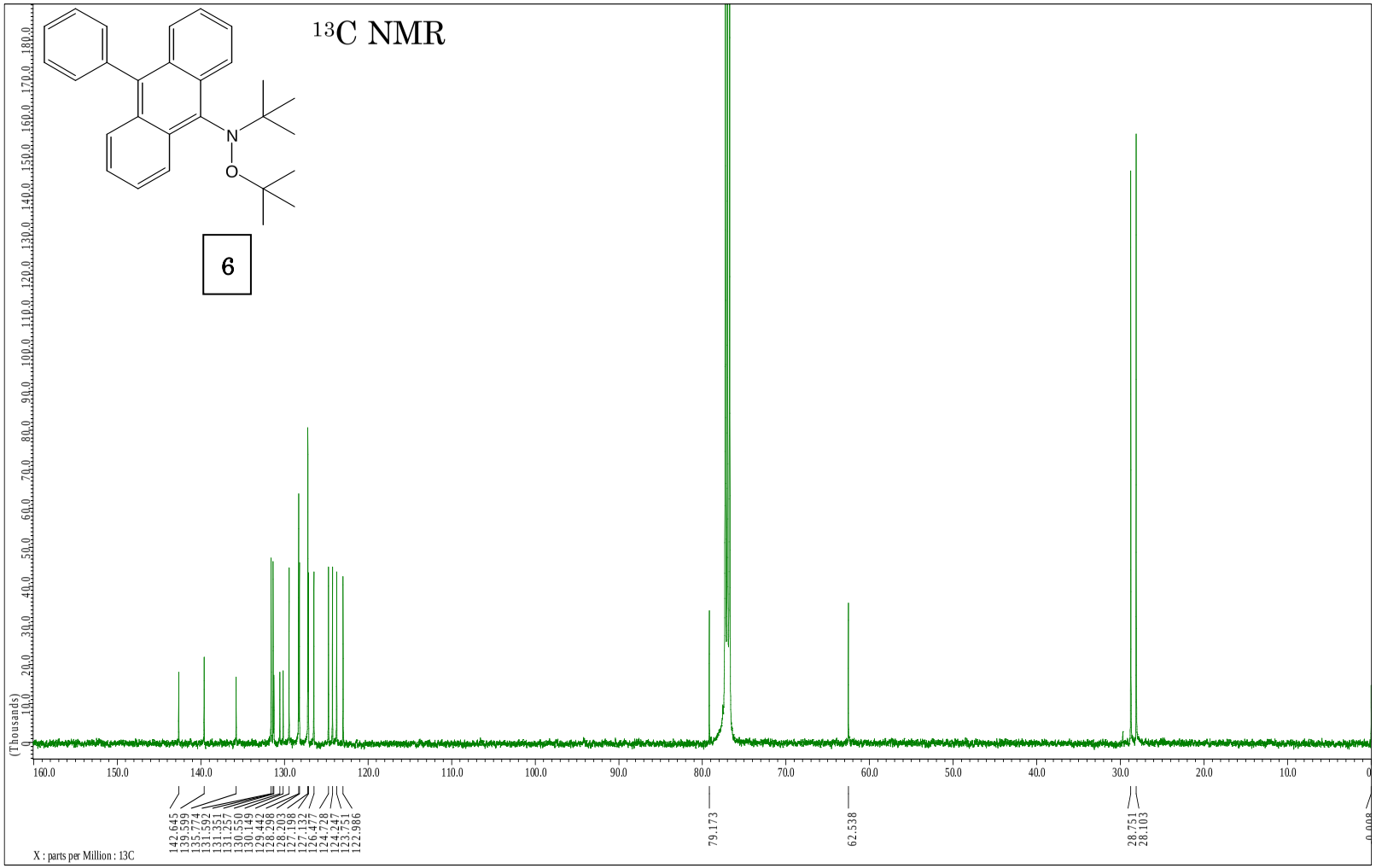

^{13}C NMR
N
OH
(Thousands)
60.0
50.0
40.0
30.0
20.0
10.0
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
140.013
139.197
136.406
131.328
131.014
130.584
129.353
128.173
128.034
127.182
126.752
124.609
123.859
77.255
77.000
76.745
62.187
28.043
X : parts per Million : 13C


BPAN-H.SPA
%Transmittance
80
72
64
56
48
40
32
24
16
8
0
-8
3528.28
2975.27
1675.43
1476.79
1458.95
1441.11
1374.09
1357.7
1202.45
1142.18
784.92
764.19
703.44
425.73
405
418.49
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
N
OH
IR

Compound **6**


^{1}H NMR
6
13.58
9.00
1.06
1.05
(Thousands)
9.391
9.373
8.970
8.951
7.583
7.557
7.541
7.519
7.508
7.436
7.420
7.403
7.395
7.383
7.267
7.264
7.262
7.257
7.255
7.251
7.249
1.205
1.159
X : parts per Million : 1H

Compound **6**


^{13}C NMR
N
O
6
(Thousands)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
142.645
139.599
135.774
131.592
131.351
131.250
130.550
130.149
129.442
128.298
128.203
127.198
127.132
126.472
124.728
124.247
123.751
122.986
79.173
62.538
28.751
28.103
X : parts per Million : 13C

Compound **6**

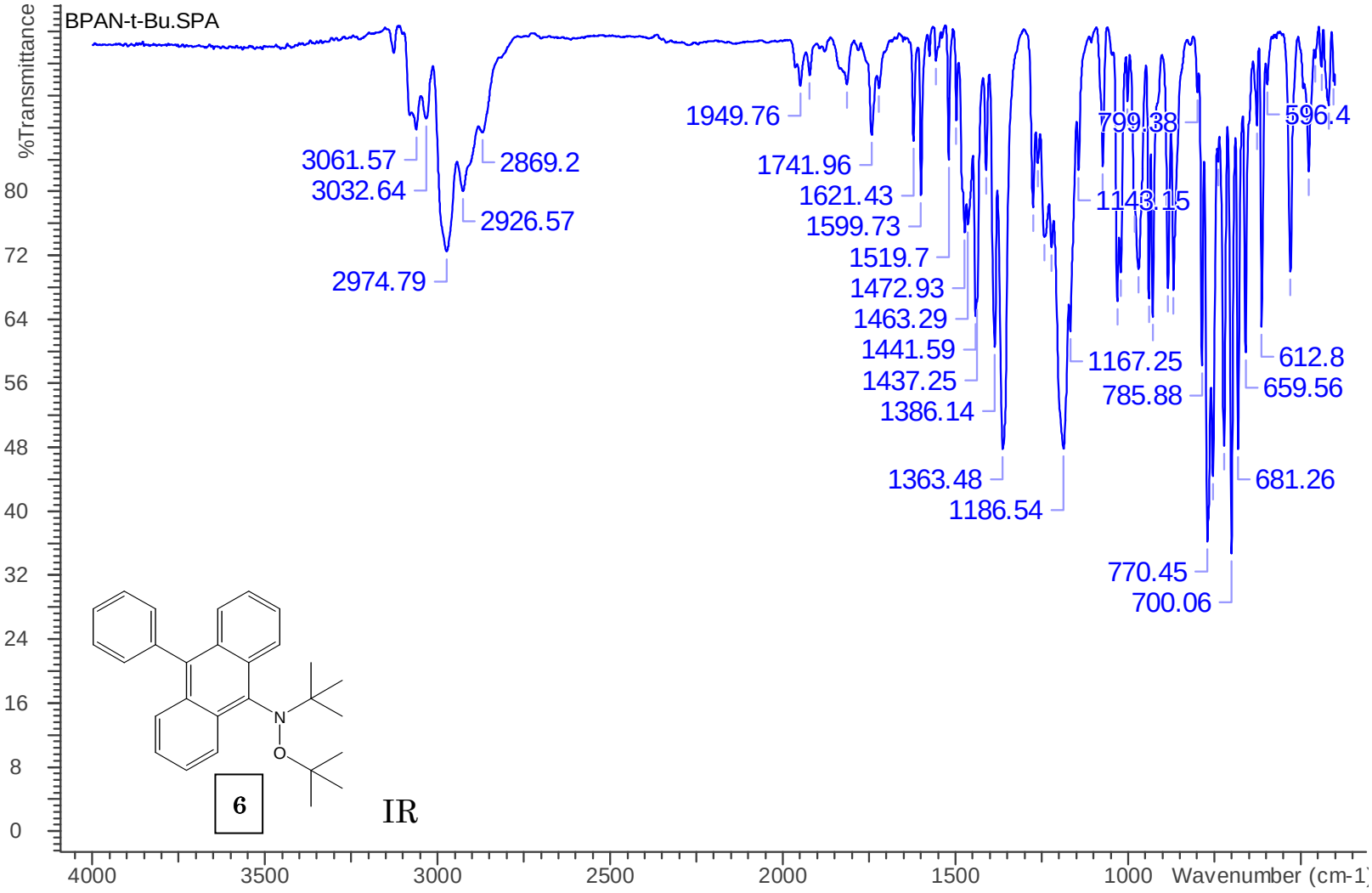

BPAN-t-Bu.SPA
%Transmittance
3061.57
3032.64
2974.79
2926.57
2869.2
1949.76
1741.96
1621.43
1599.73
1519.7
1472.93
1463.29
1441.59
1437.25
1386.14
1363.48
1186.54
1167.25
1143.15
799.38
785.88
770.45
700.06
681.26
659.56
612.8
596.4
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
N
O
6
IR

Table 1 entry 5

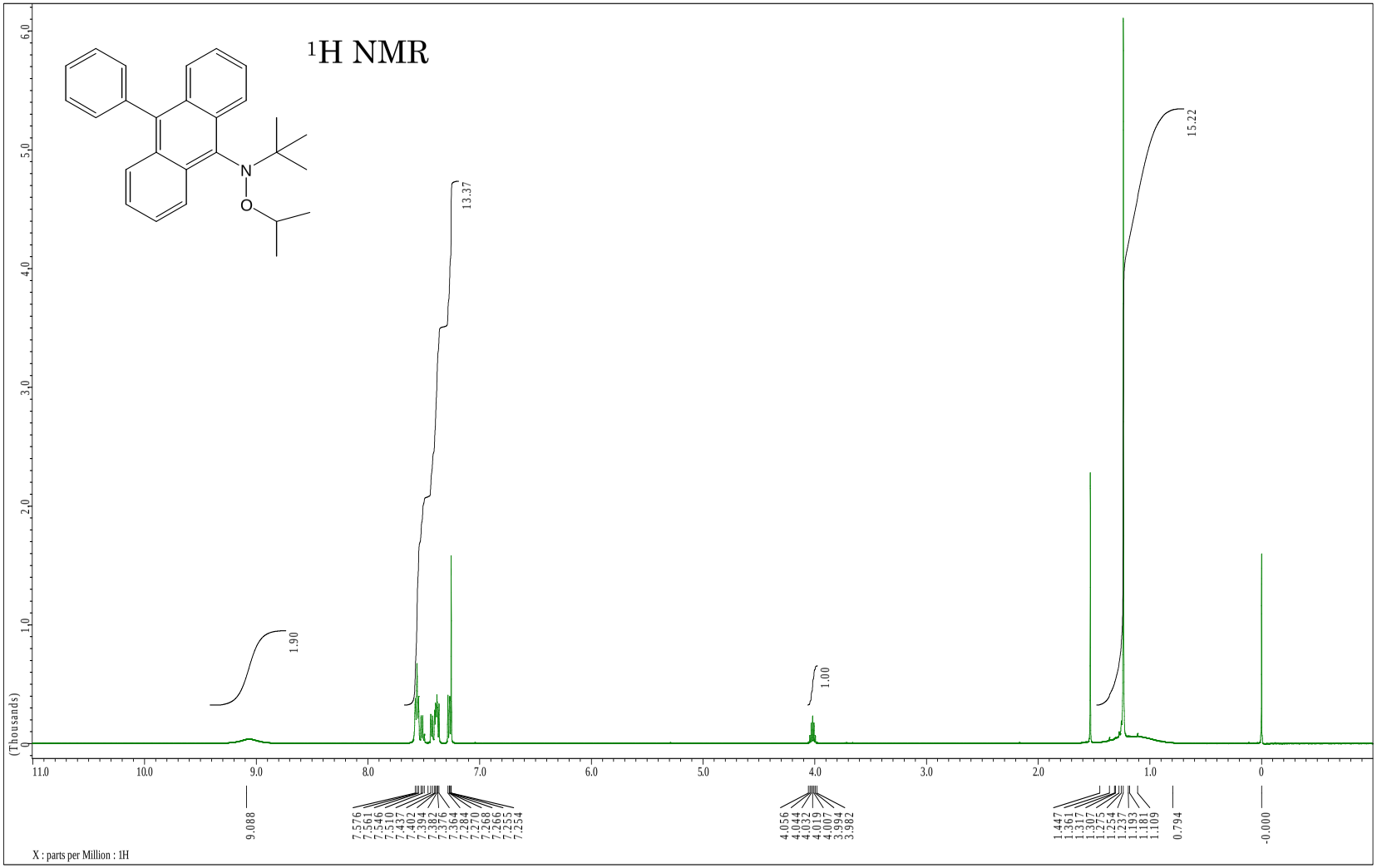


Table 1 entry 5

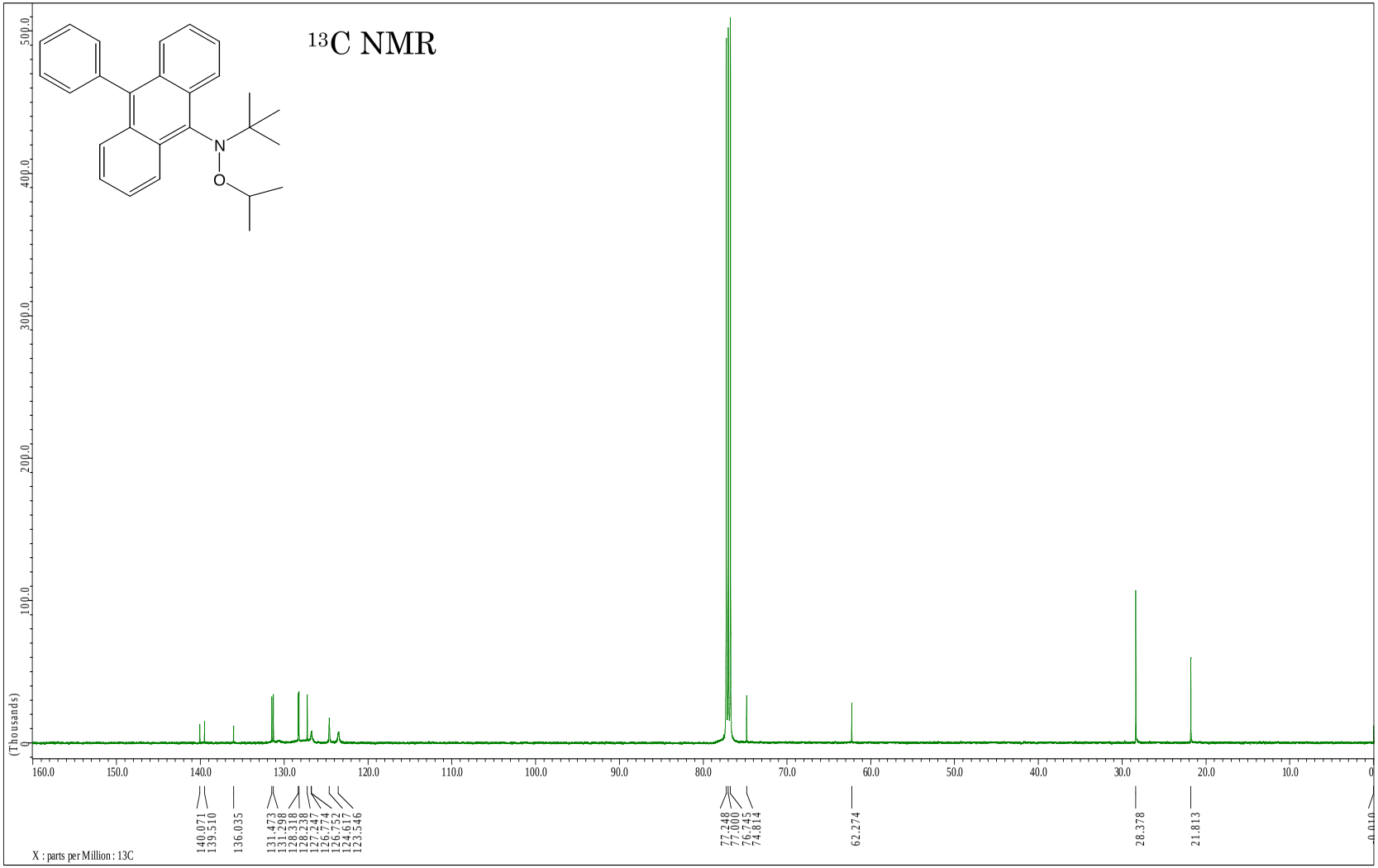


Table 1 entry 5

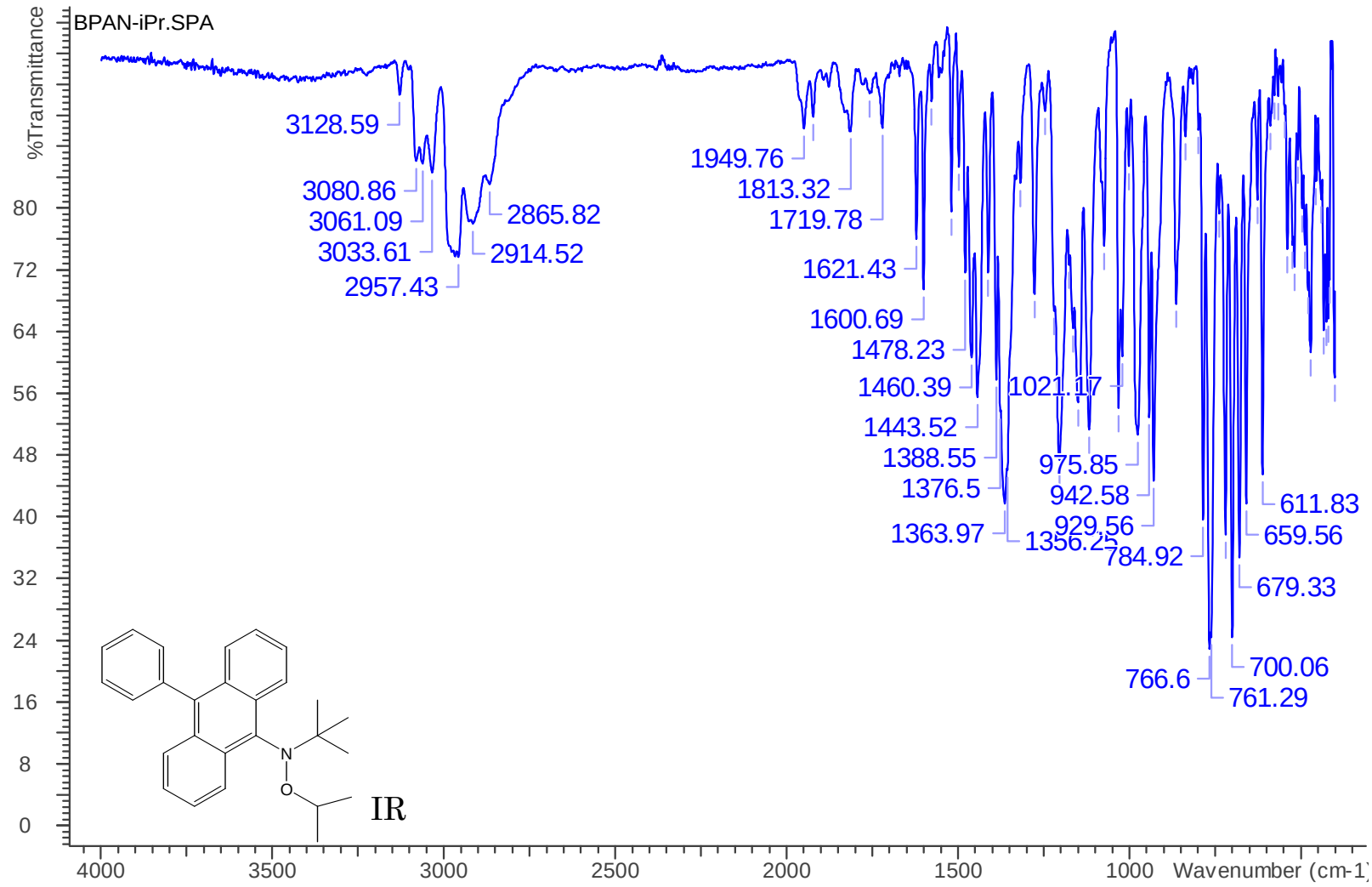


Table 1 entry 6

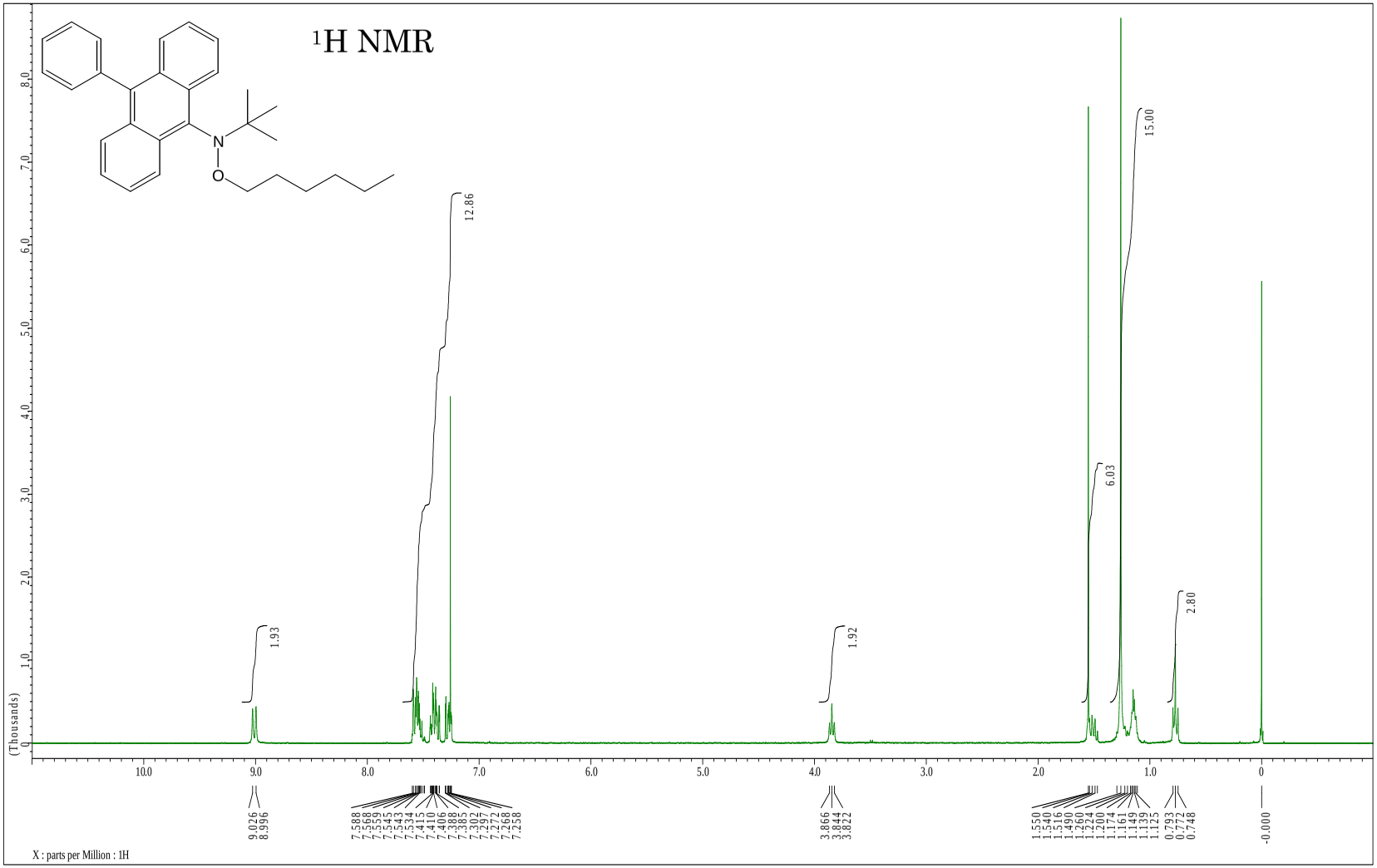
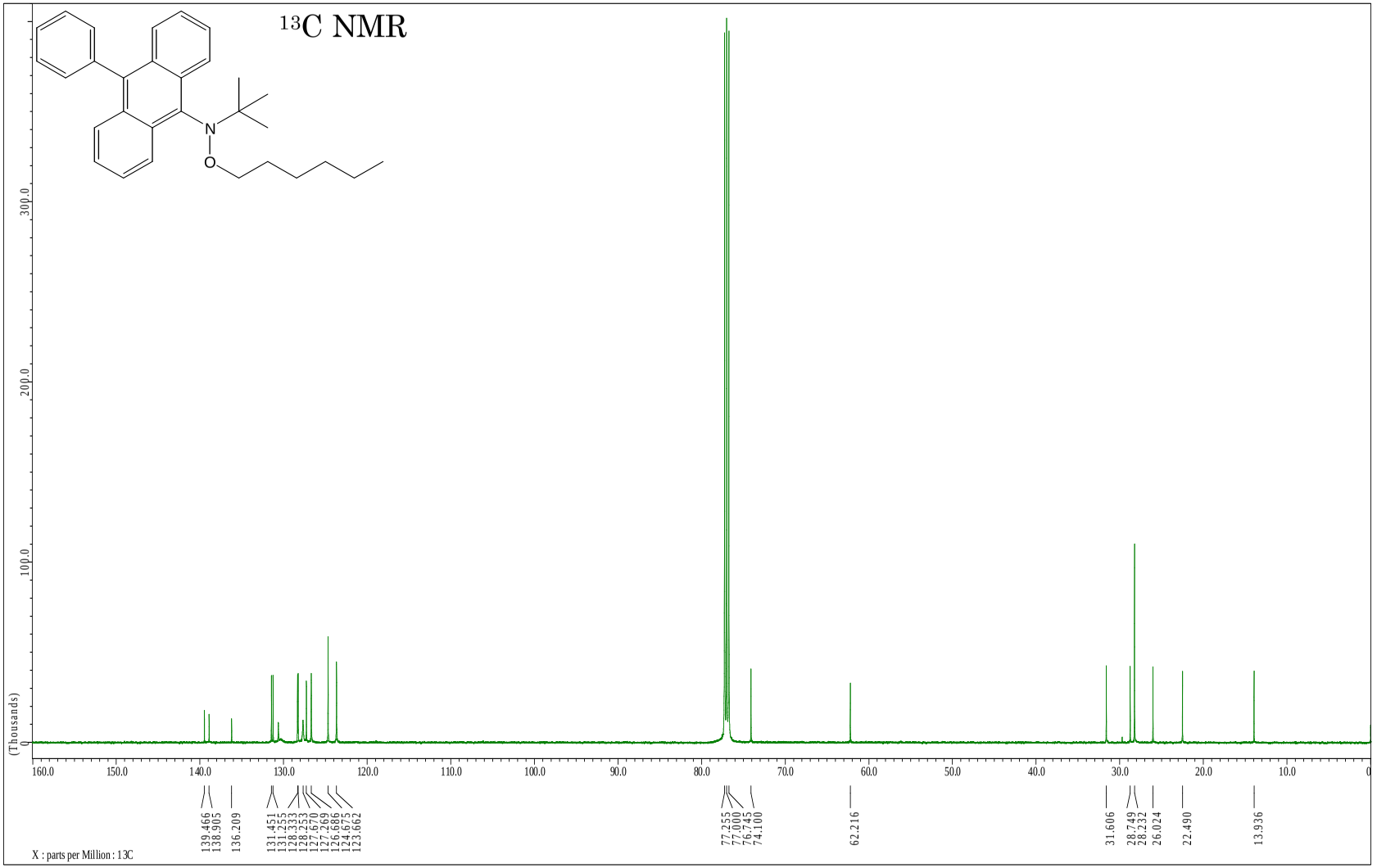


Table 1 entry 6



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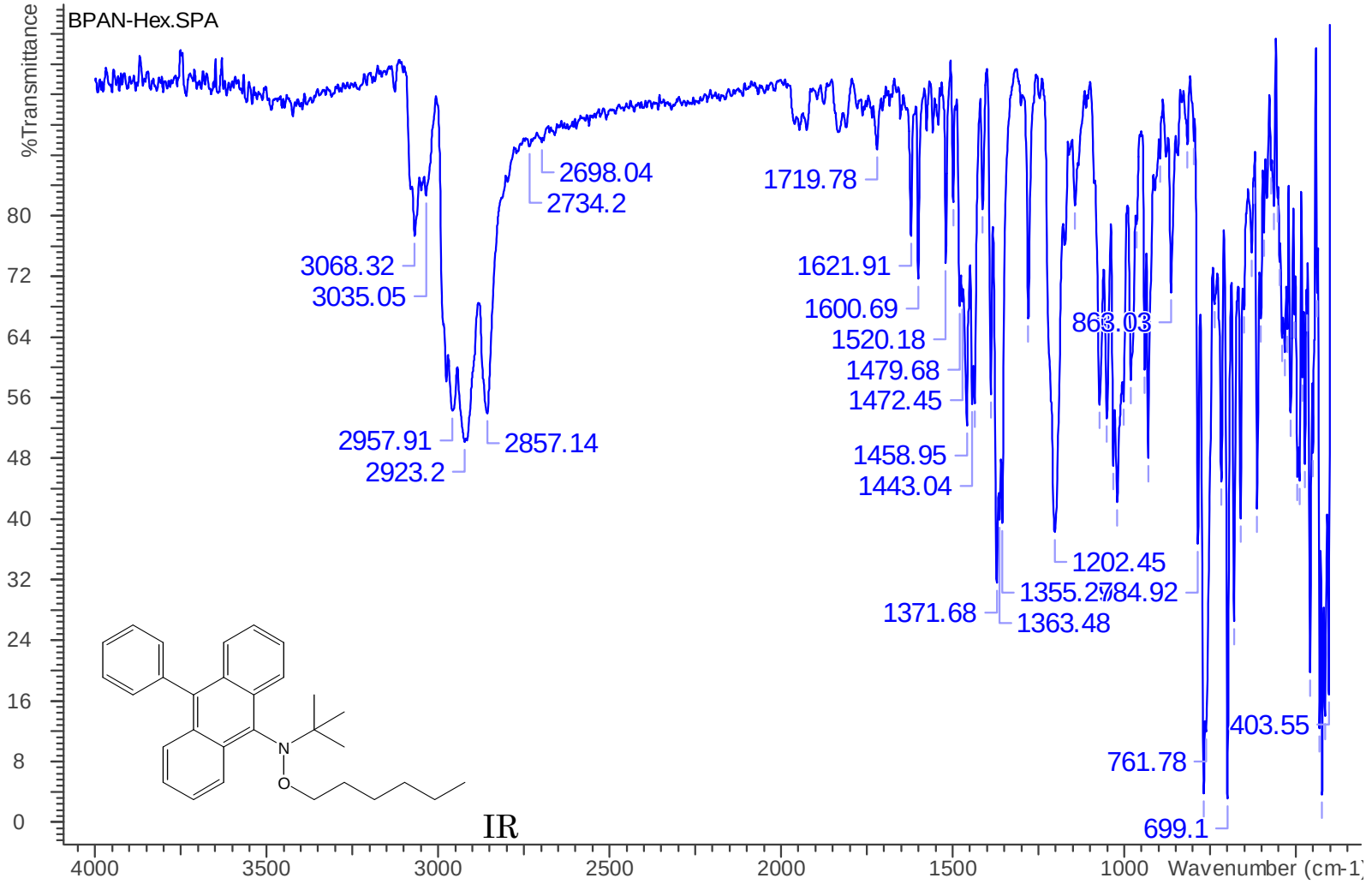

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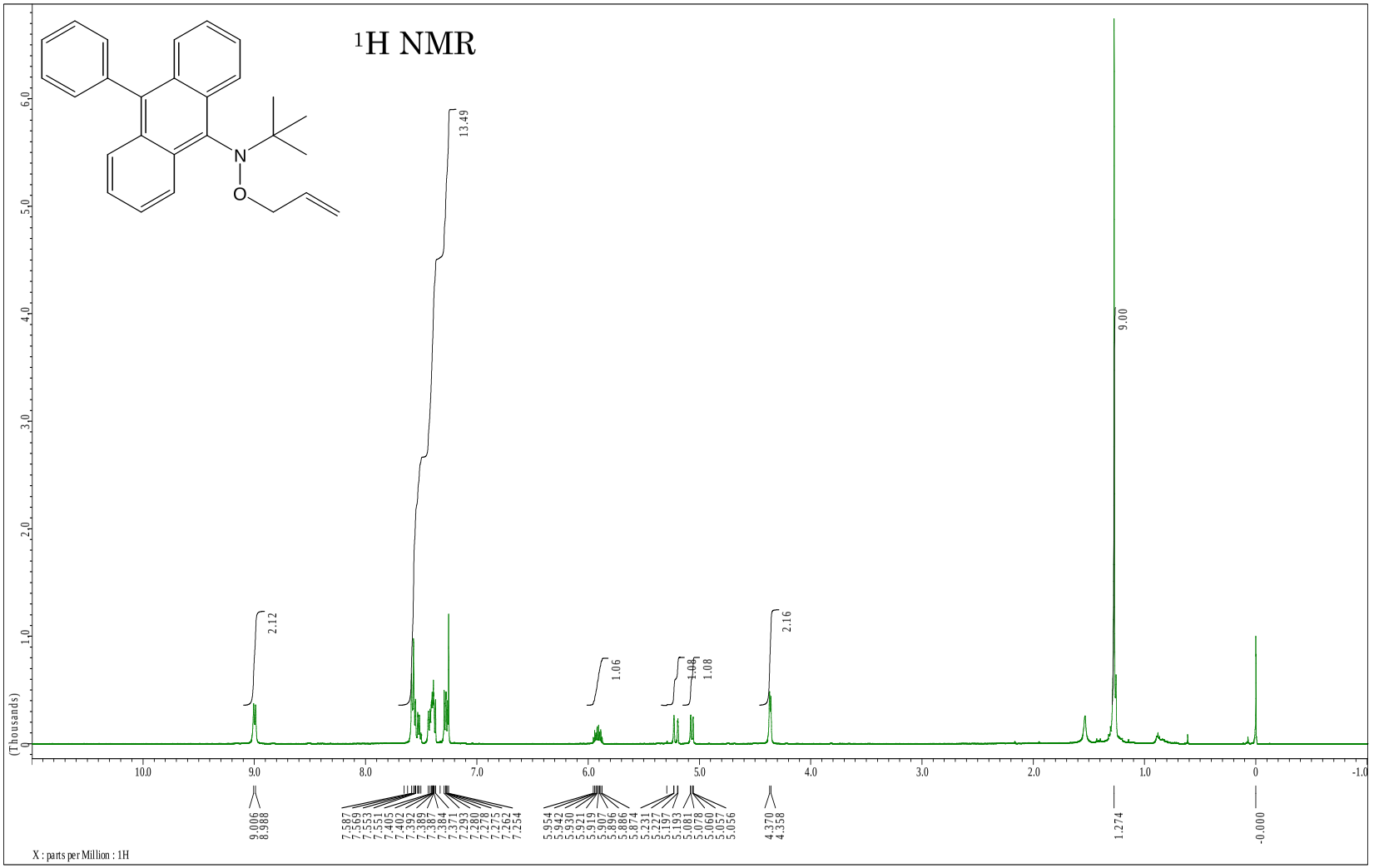

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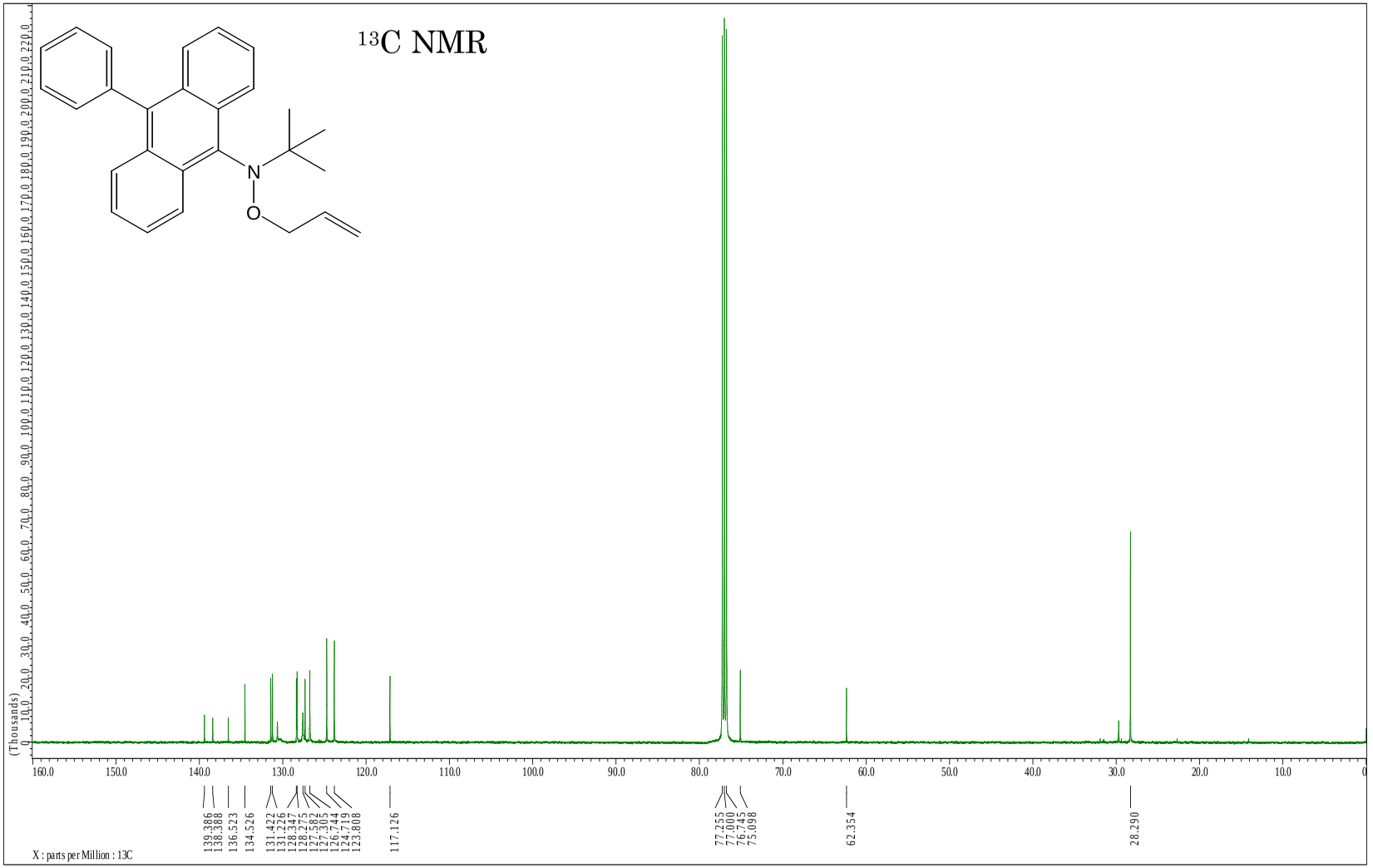

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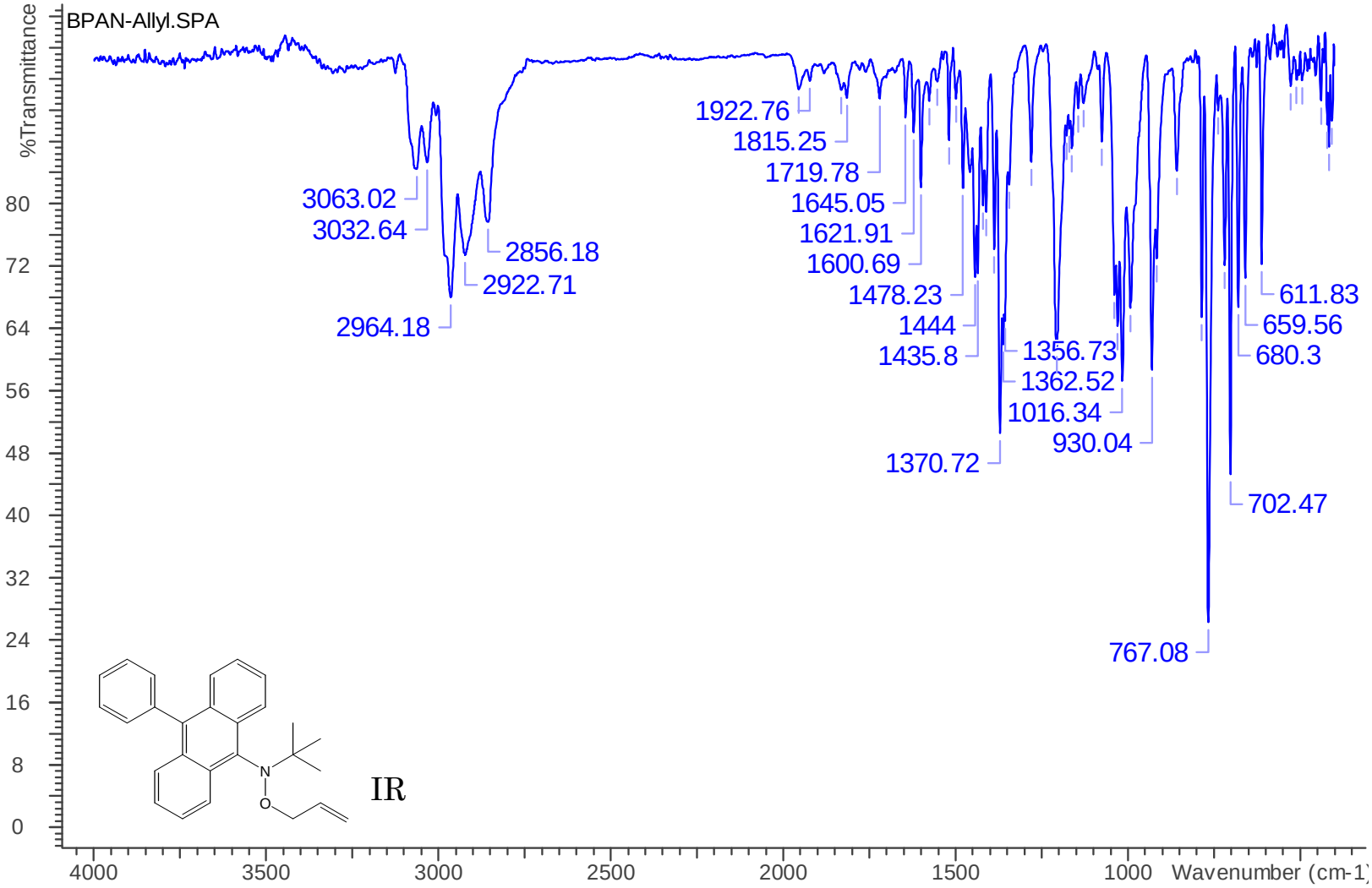

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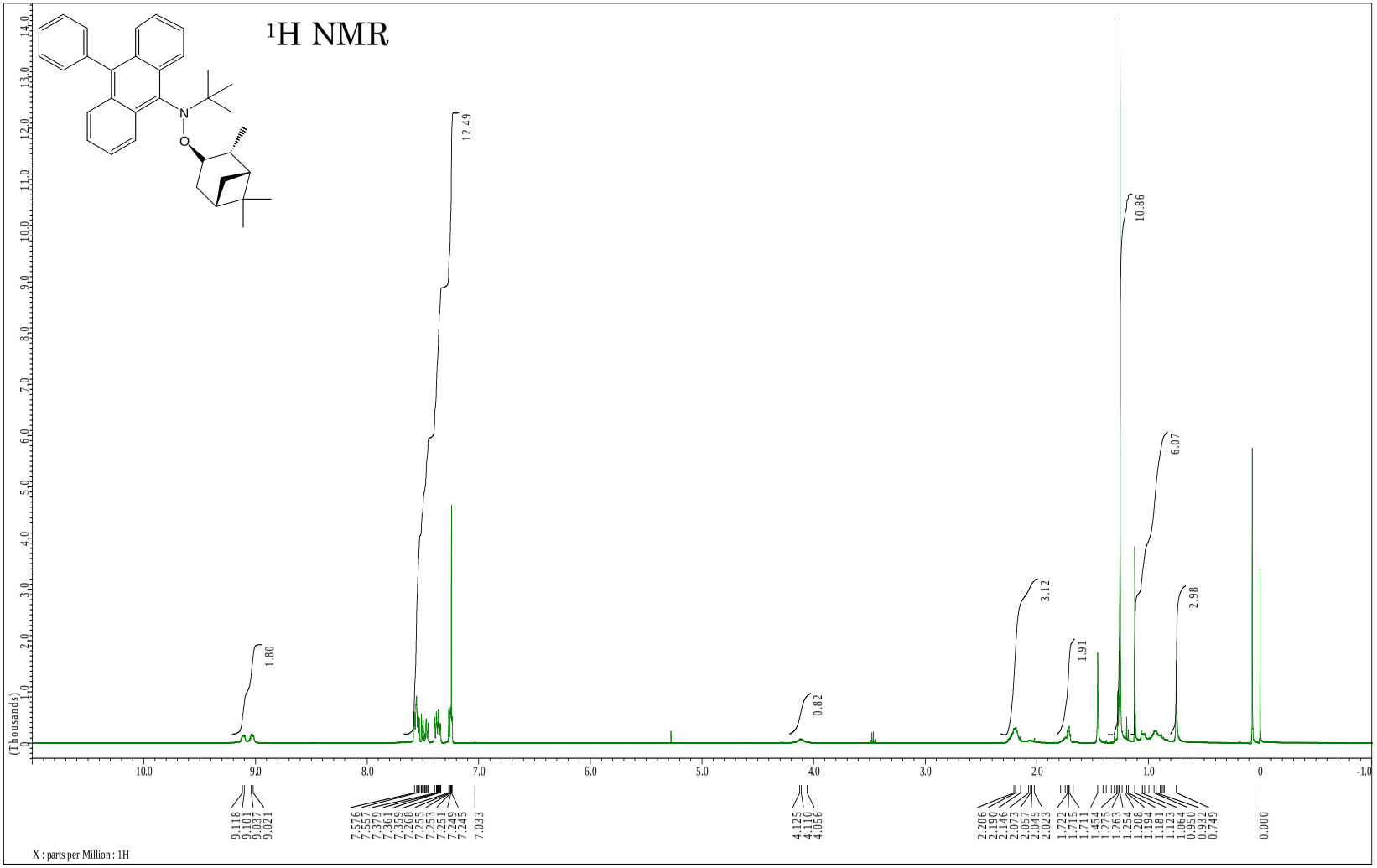

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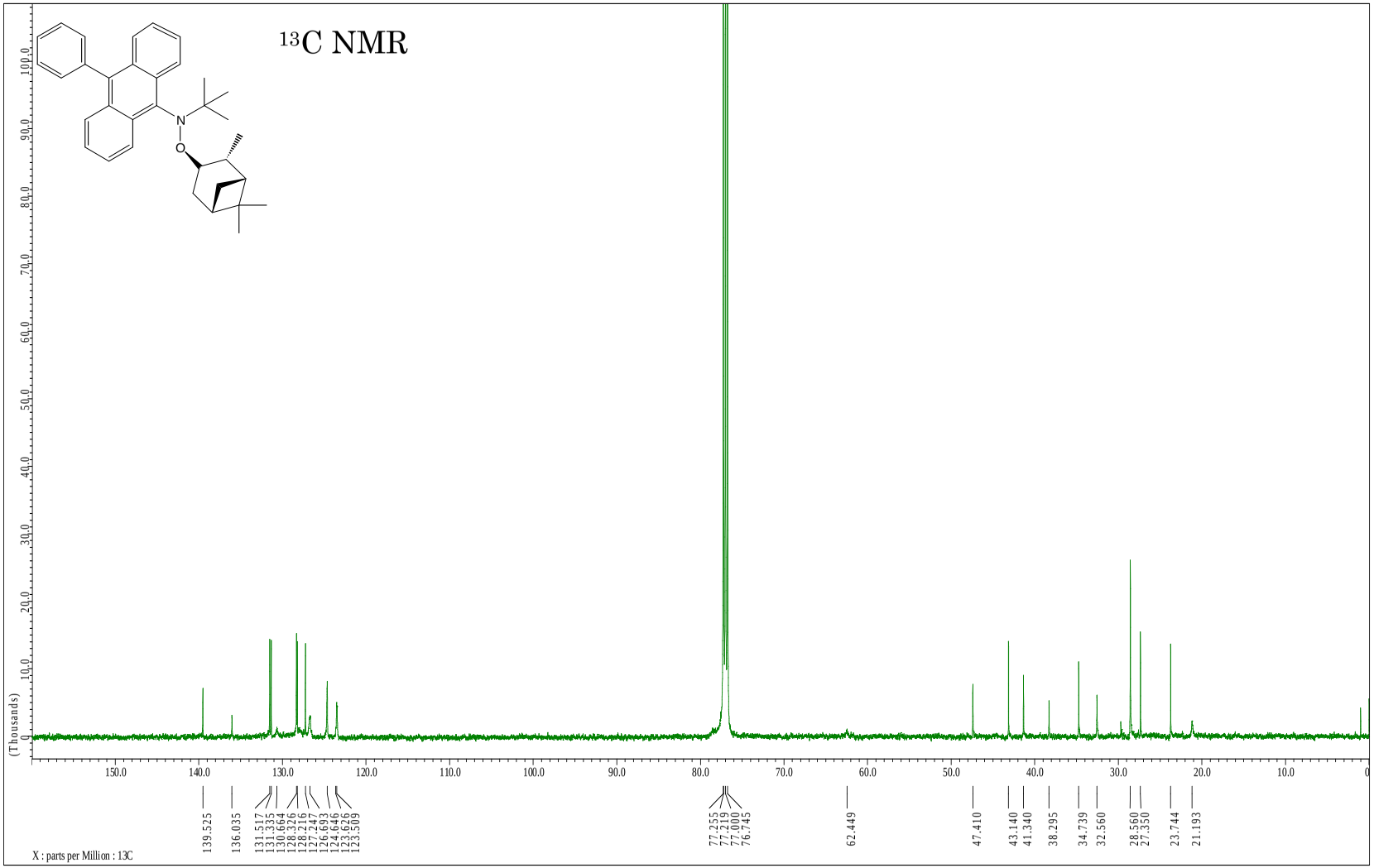

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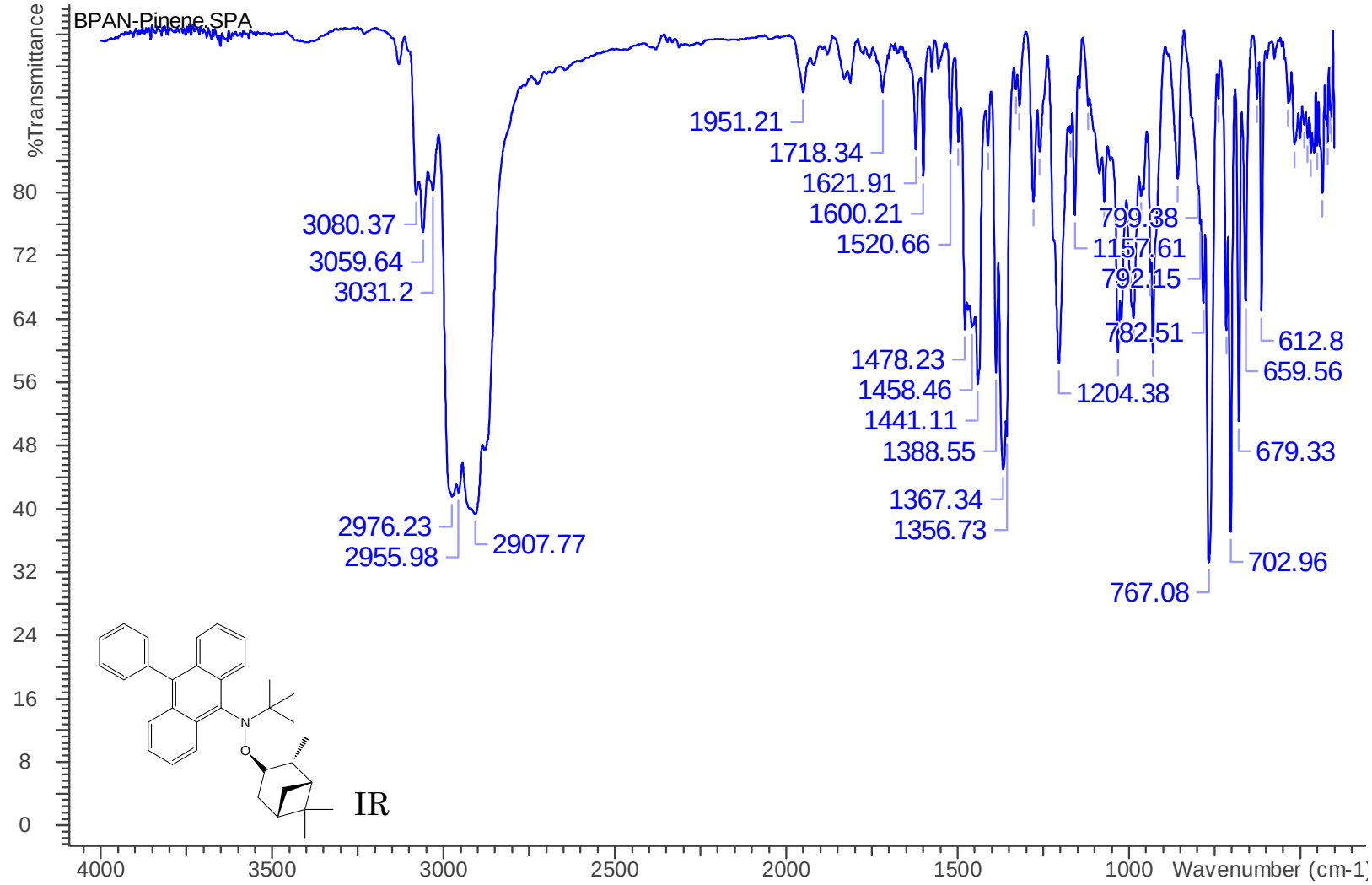

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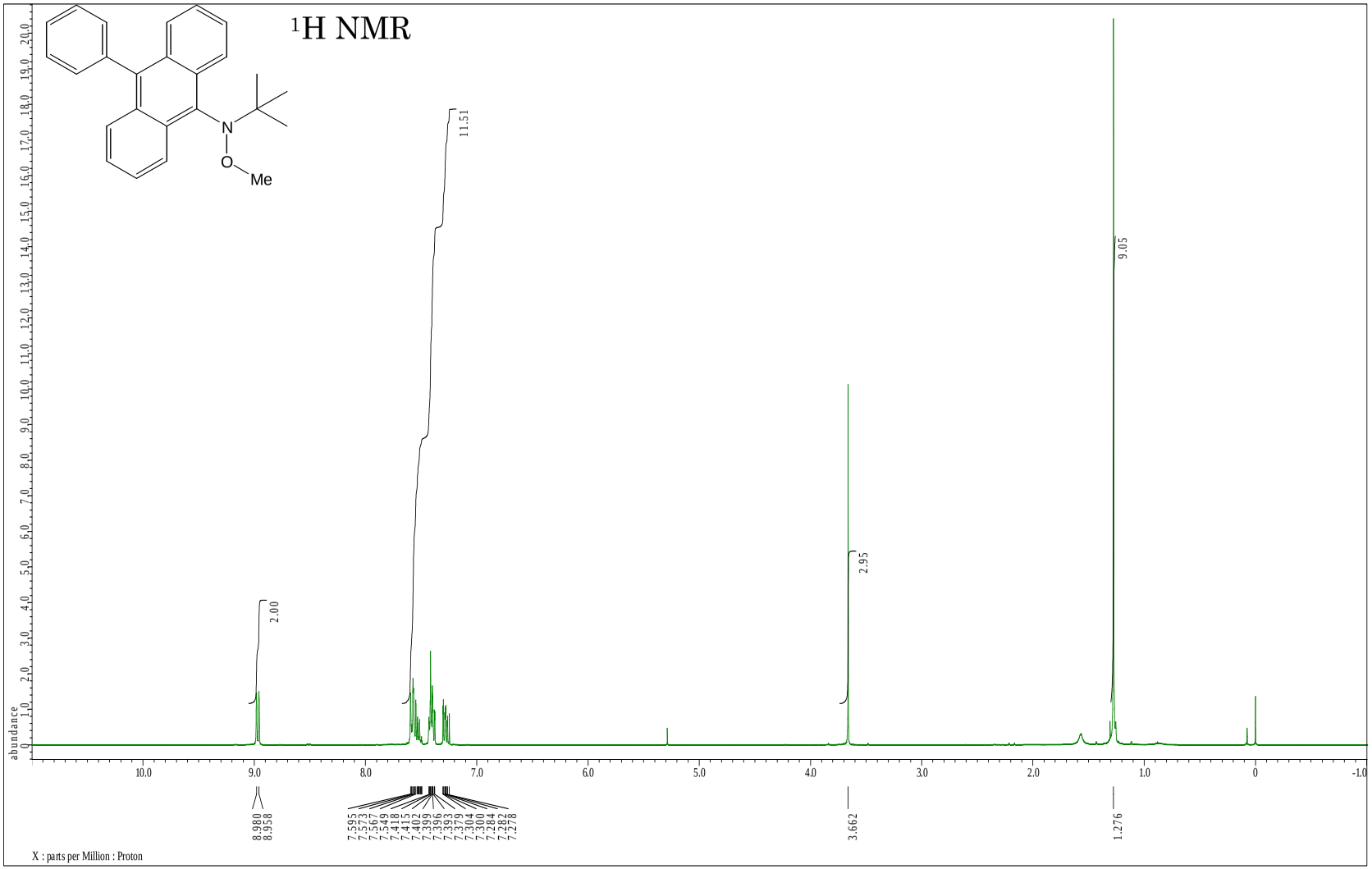

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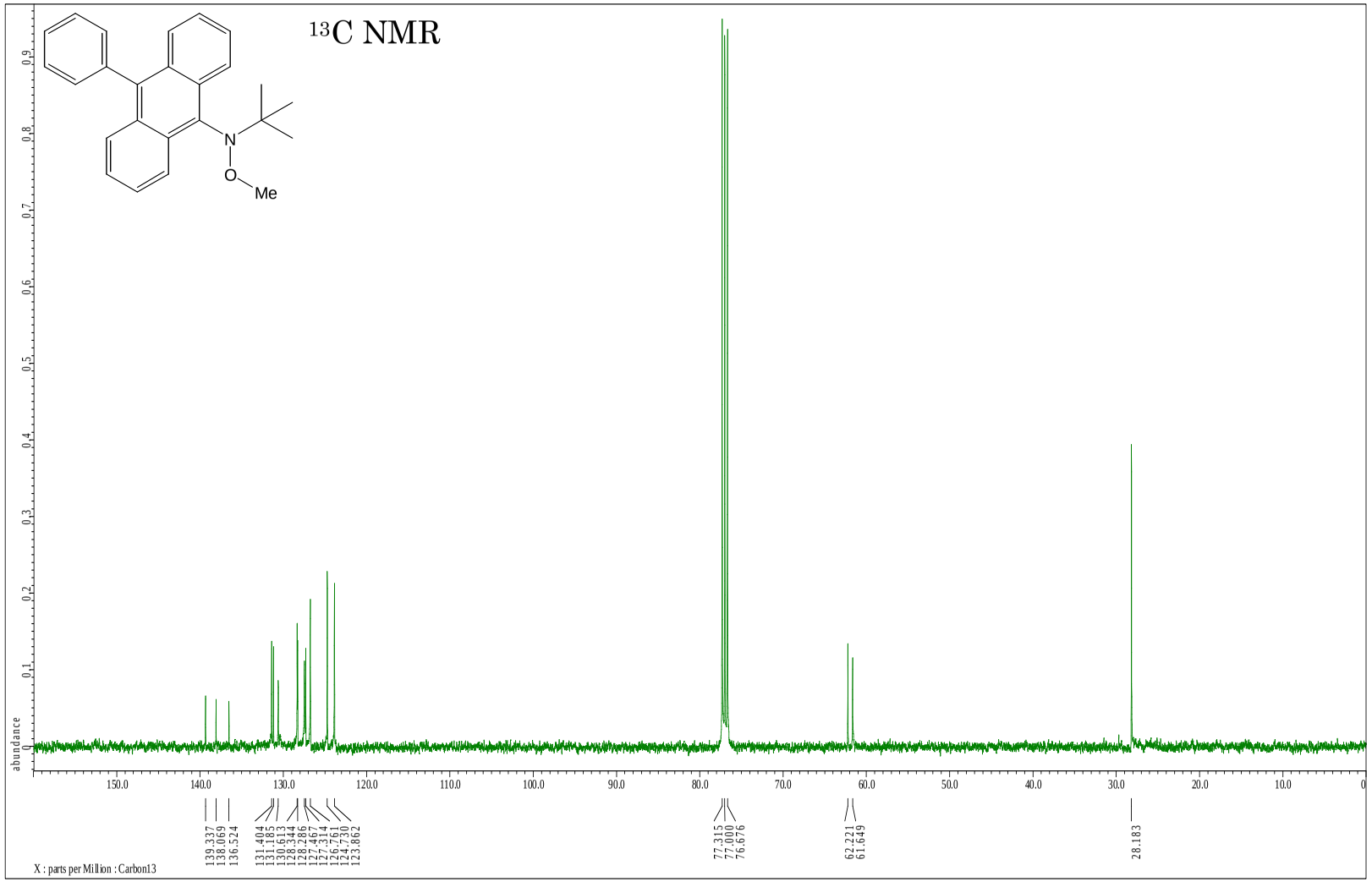

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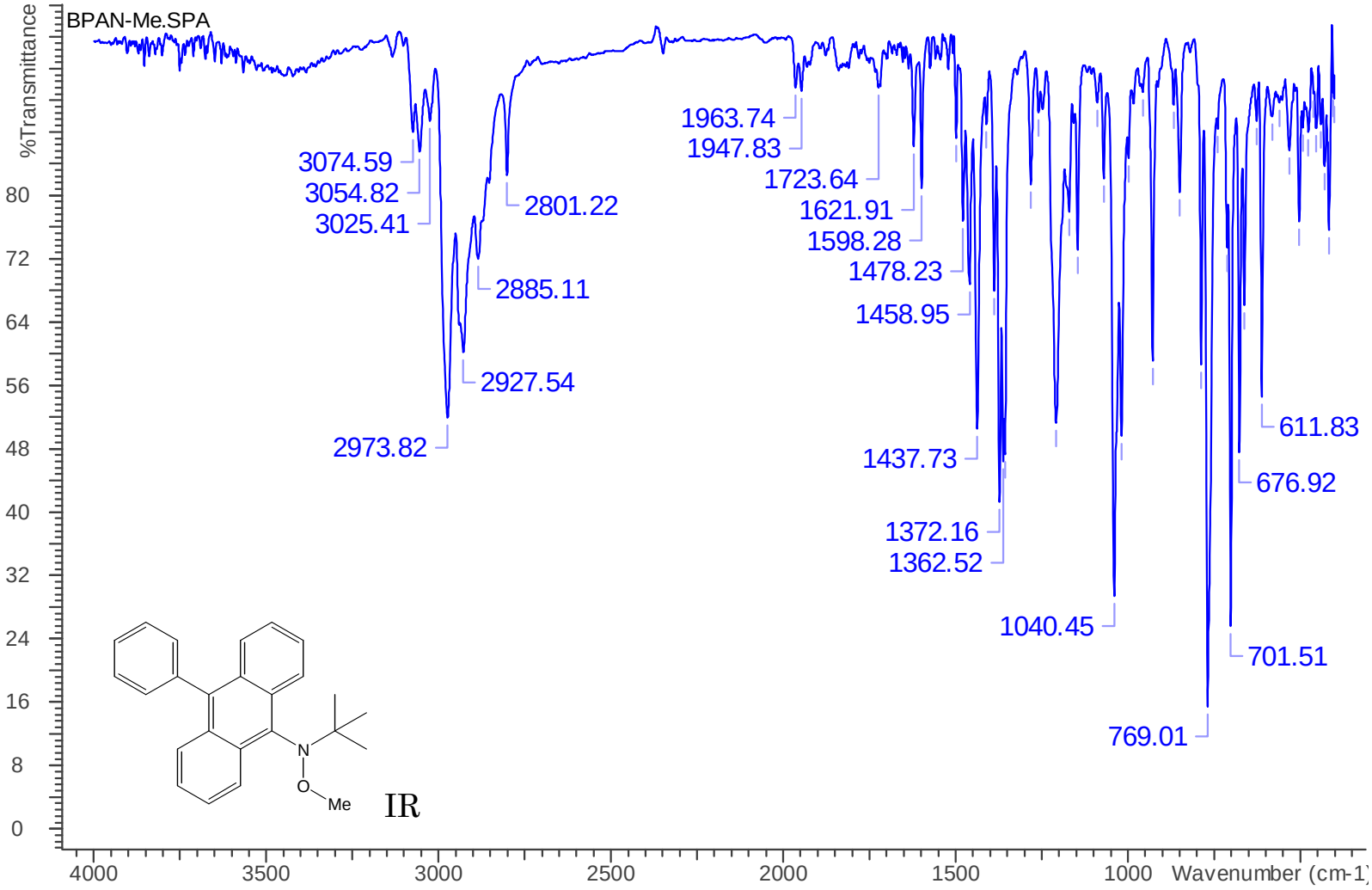

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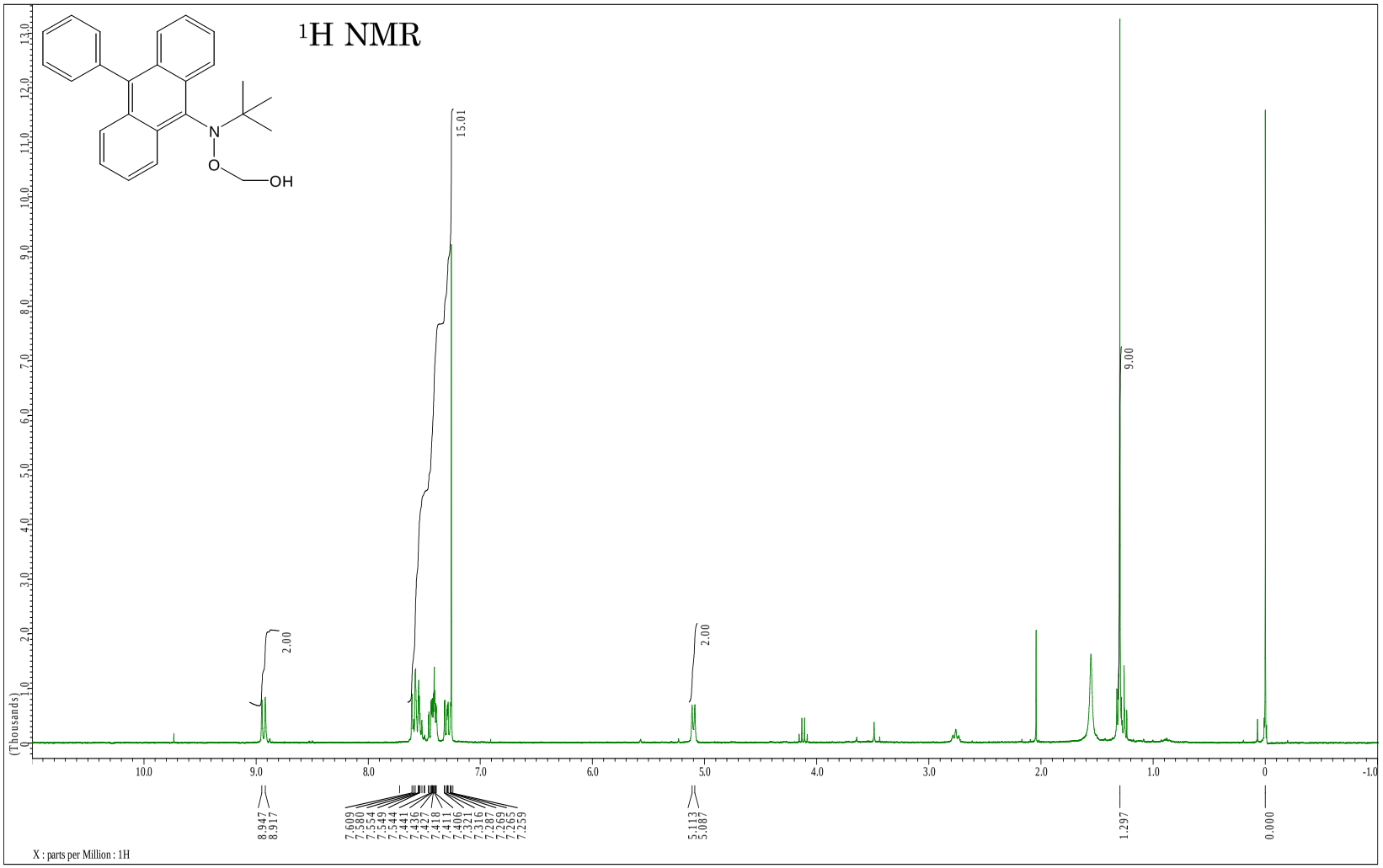

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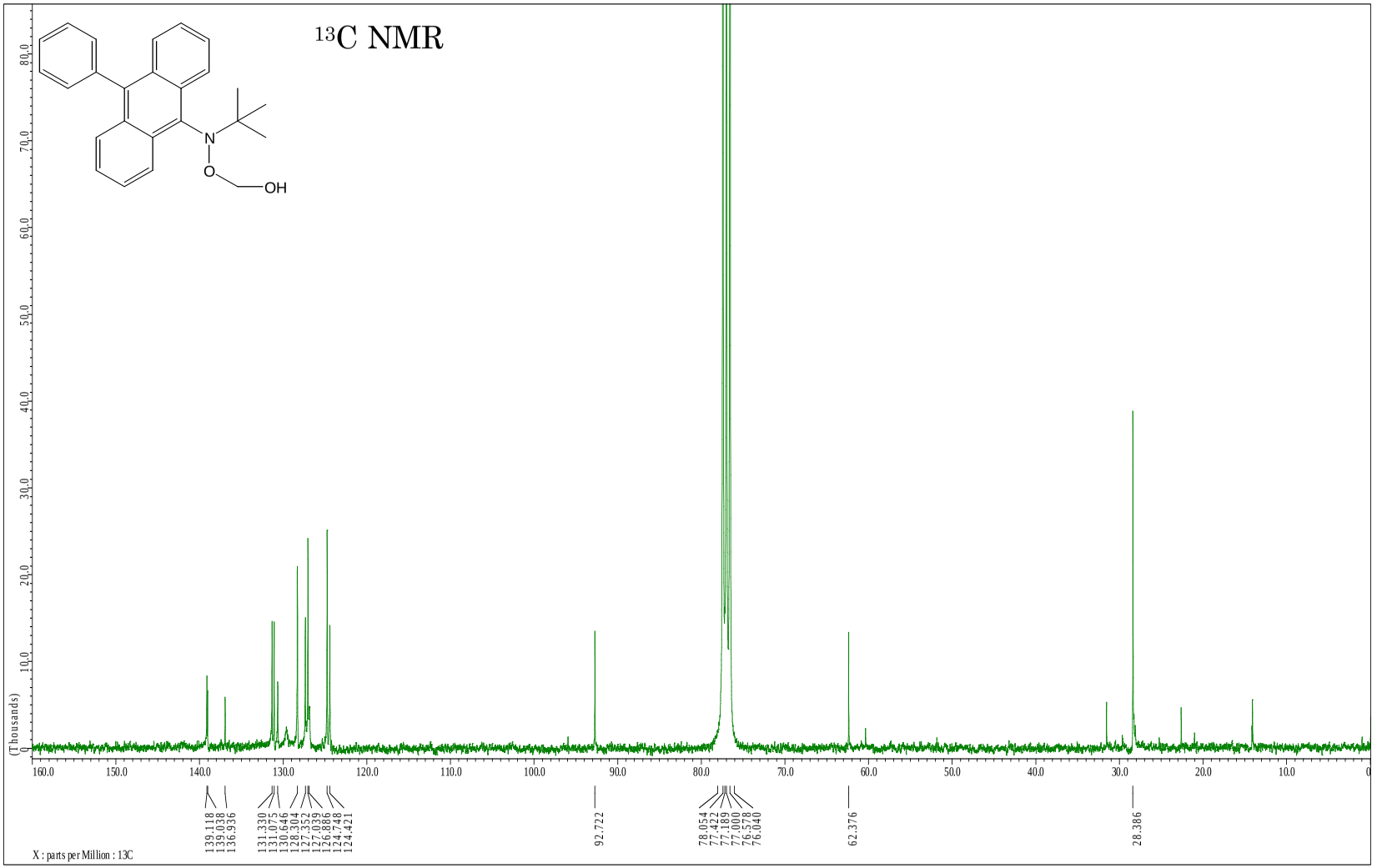

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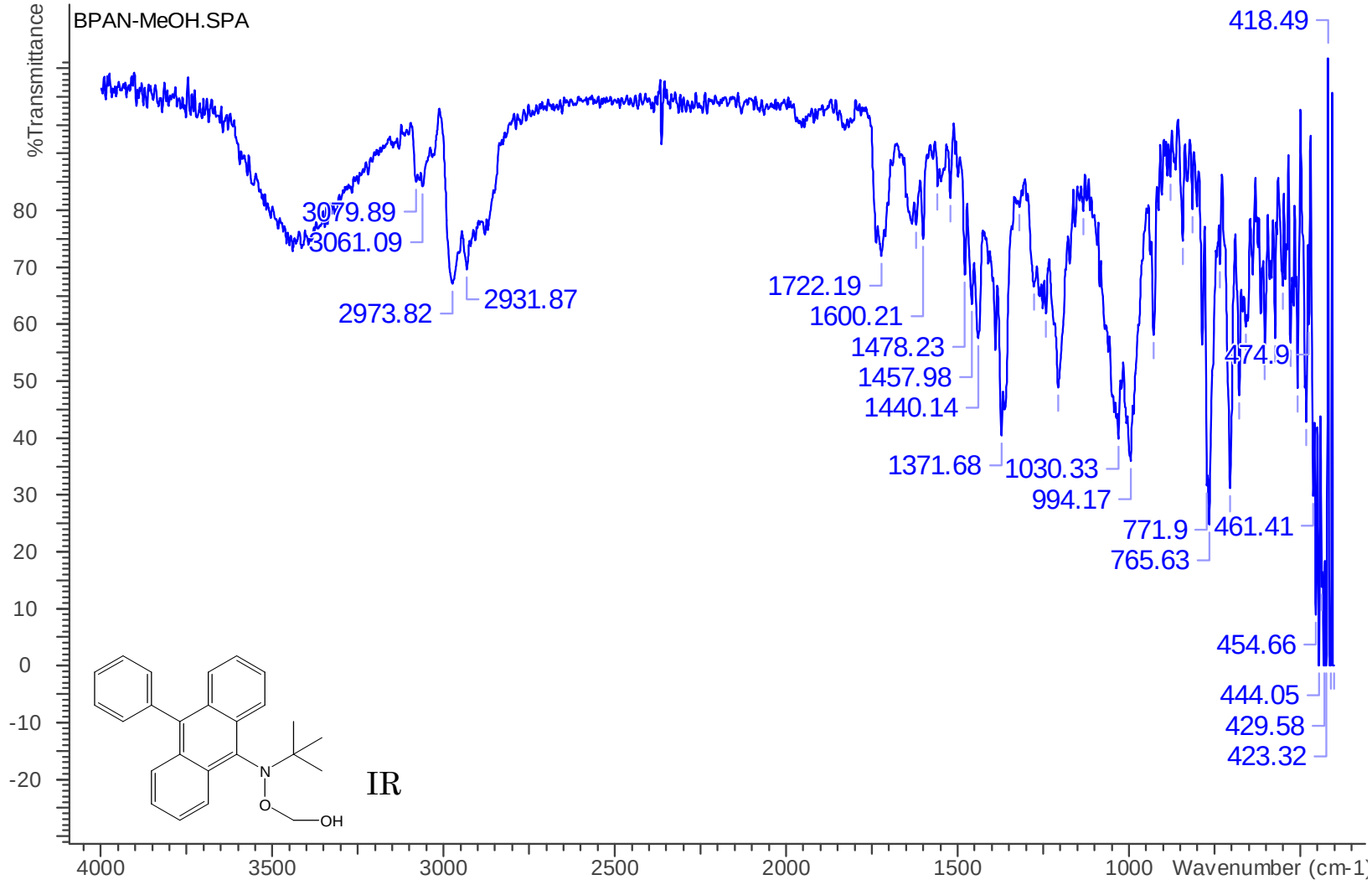

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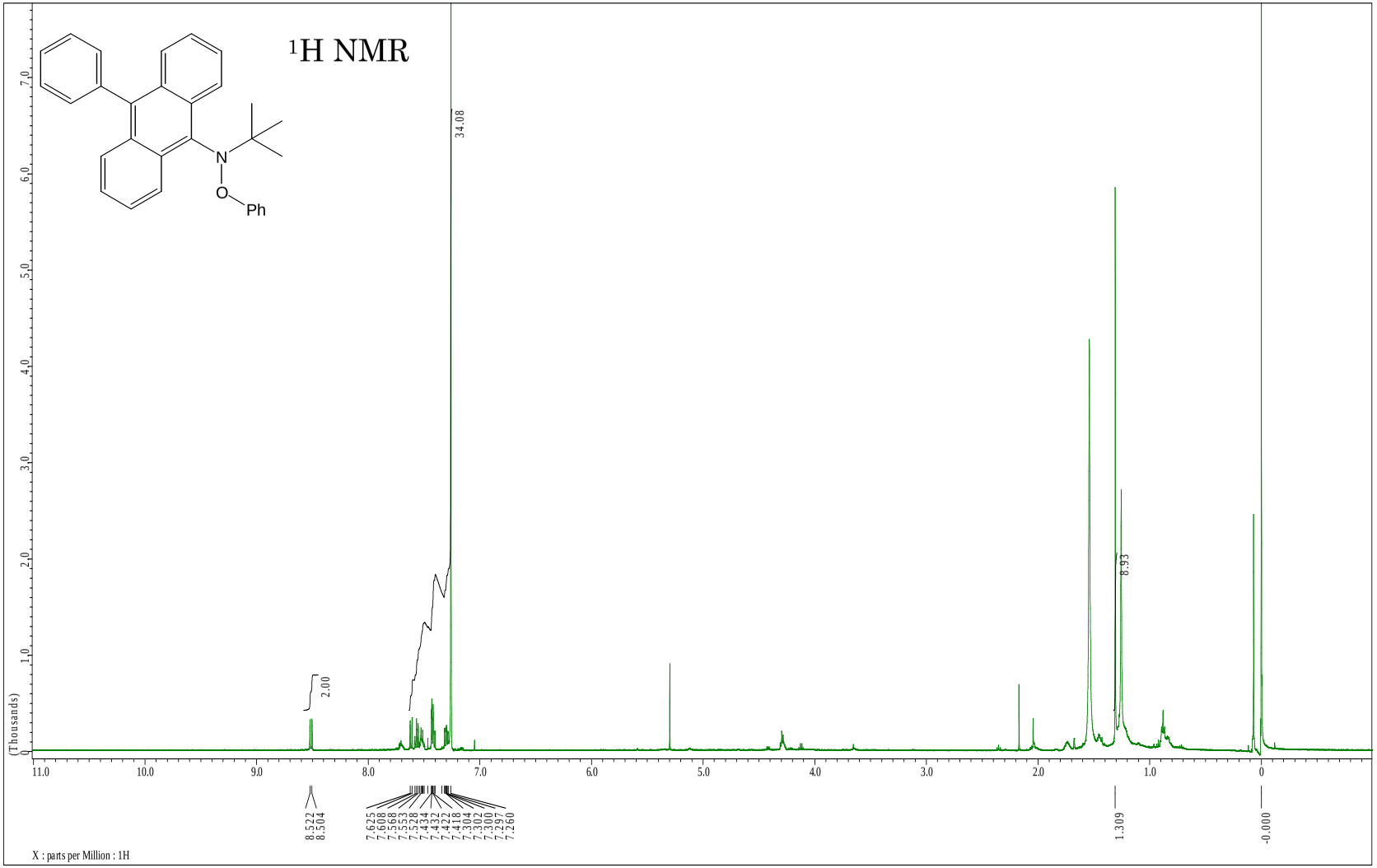

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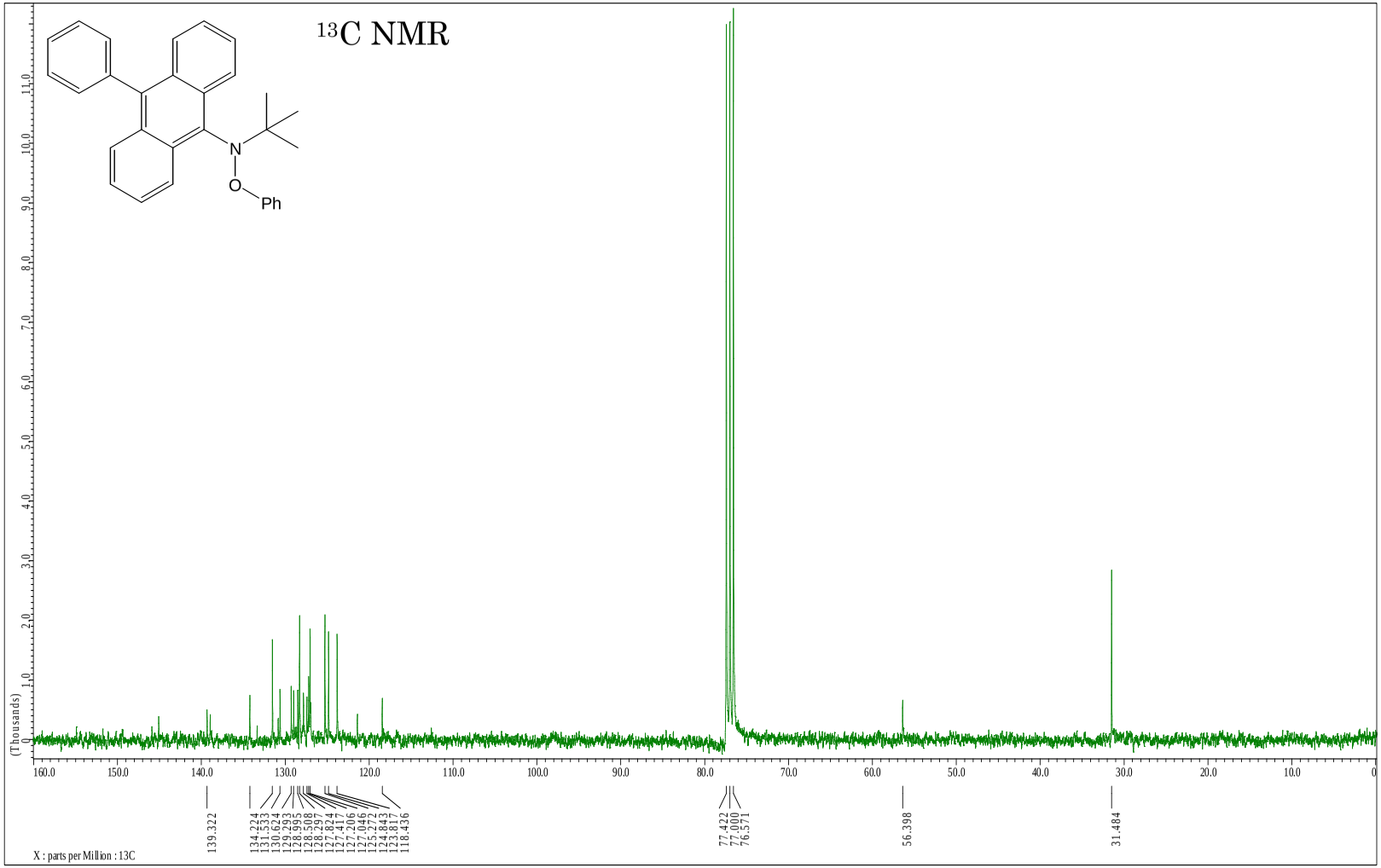

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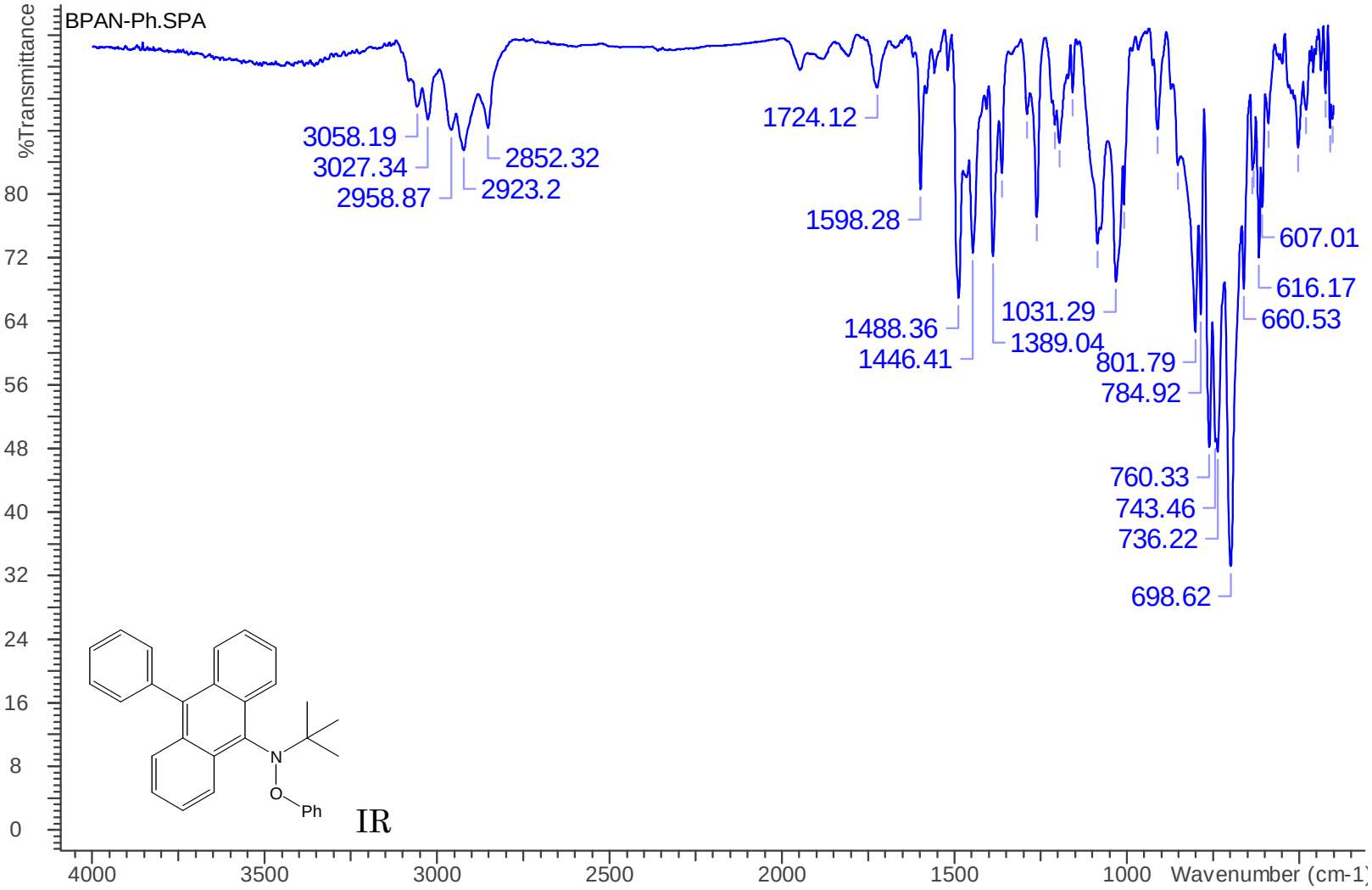

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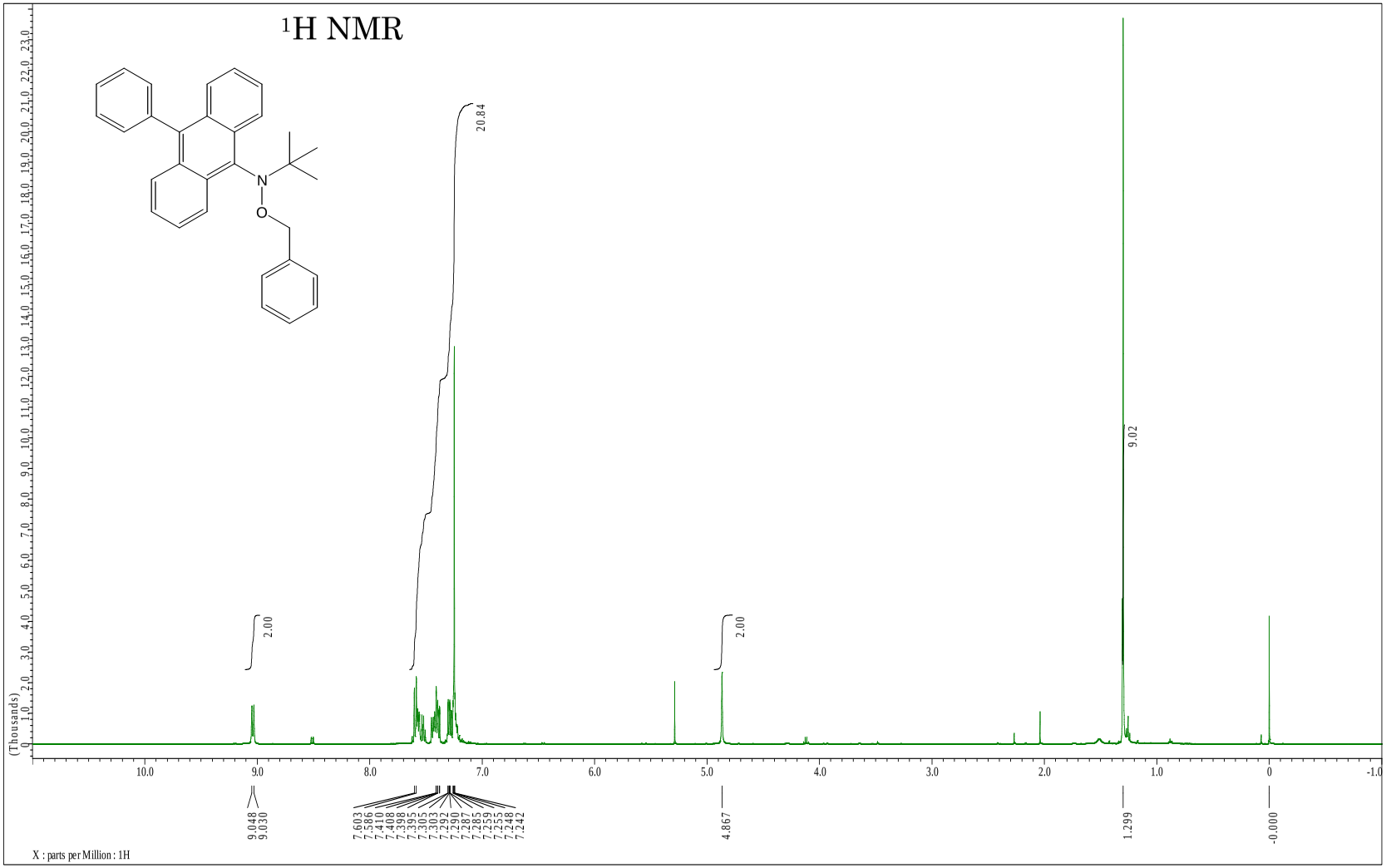

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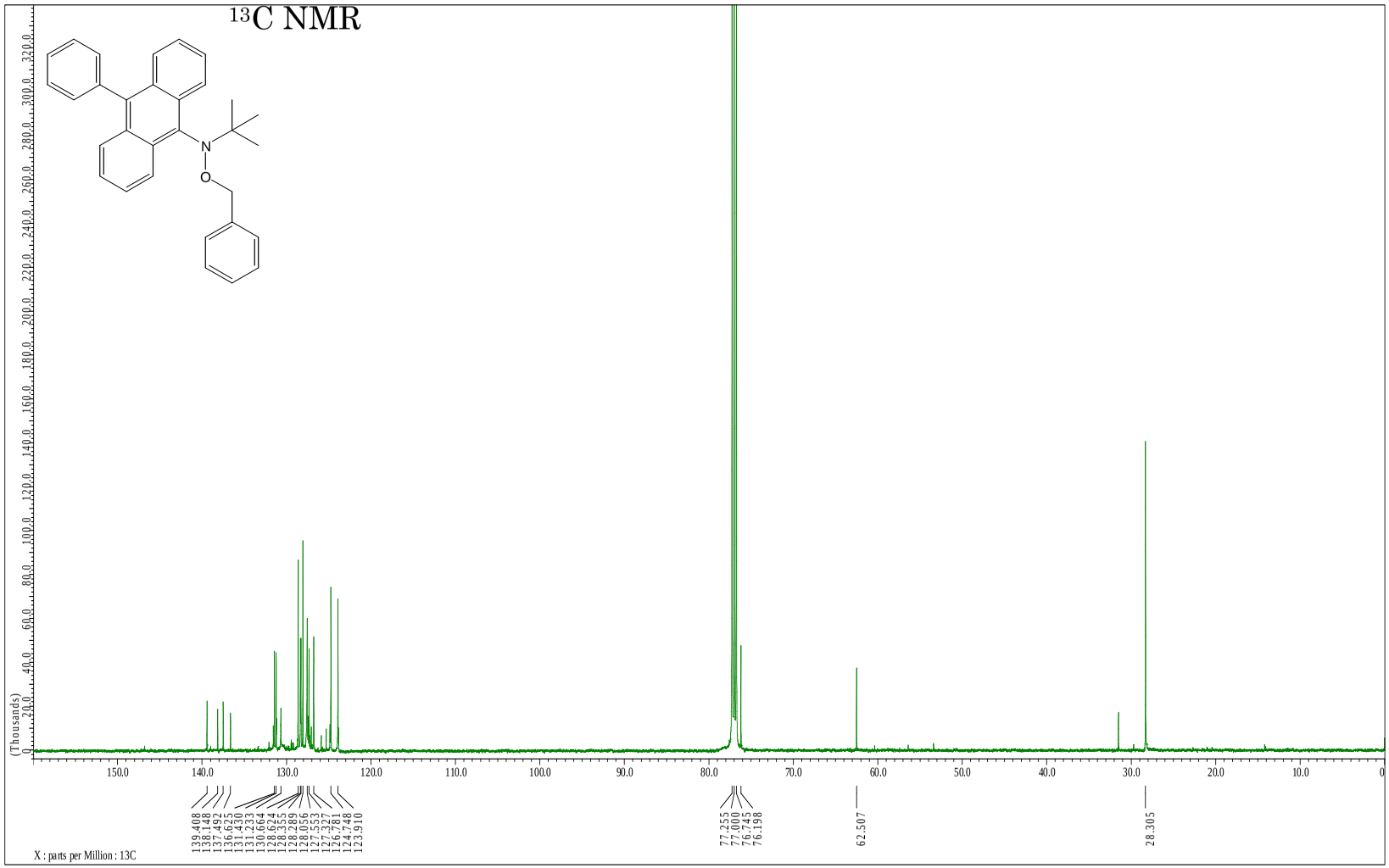

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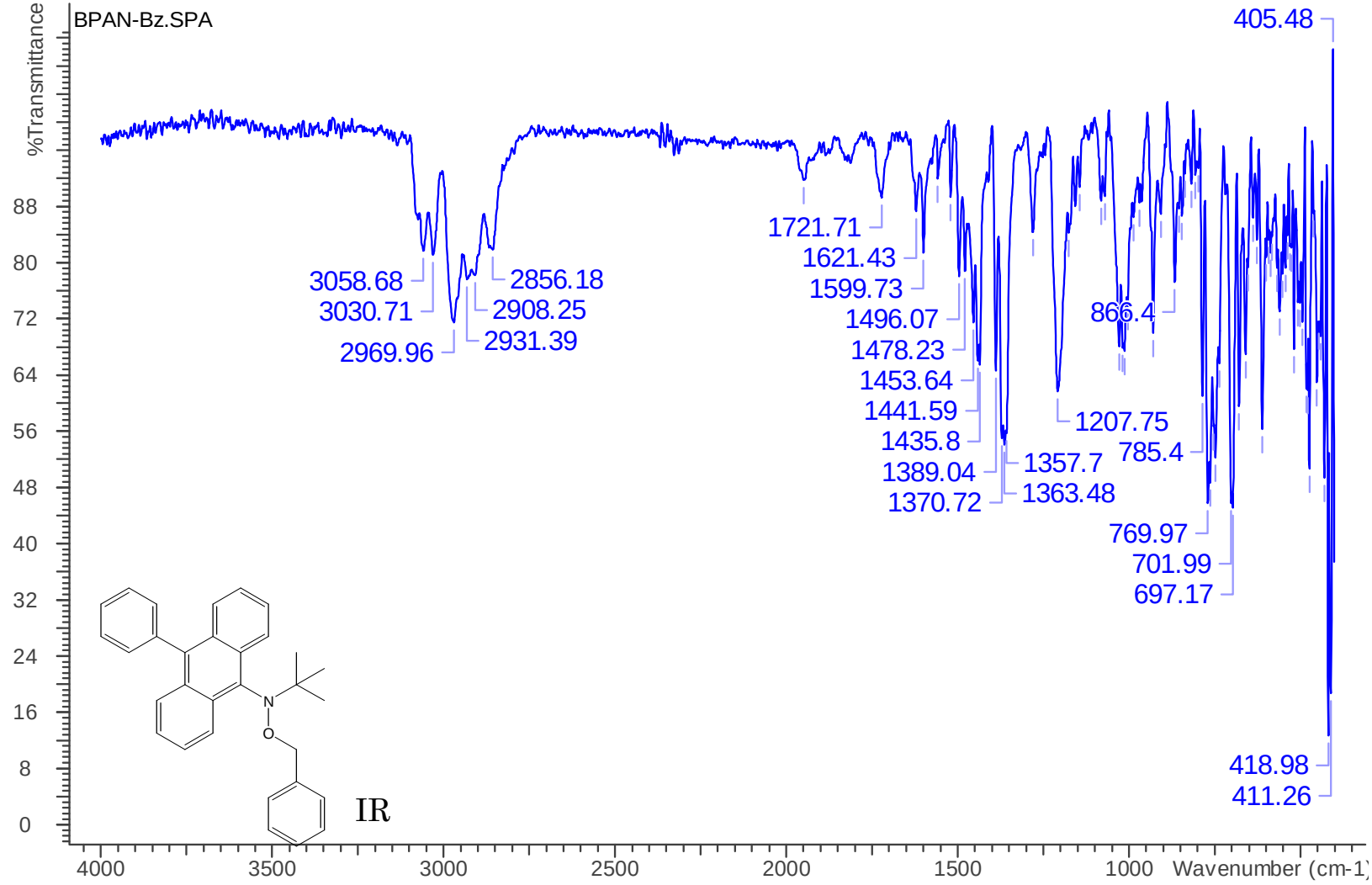

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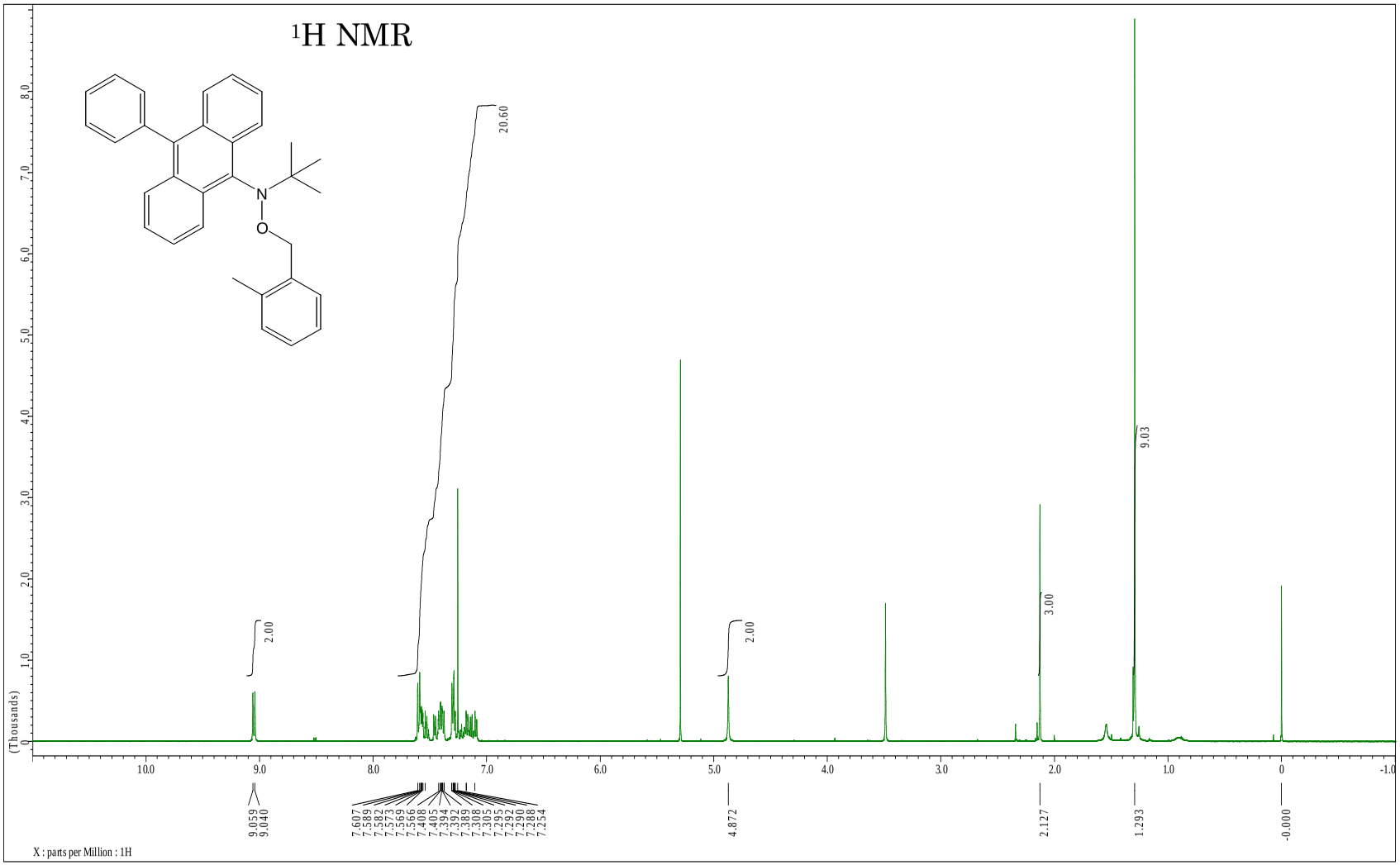

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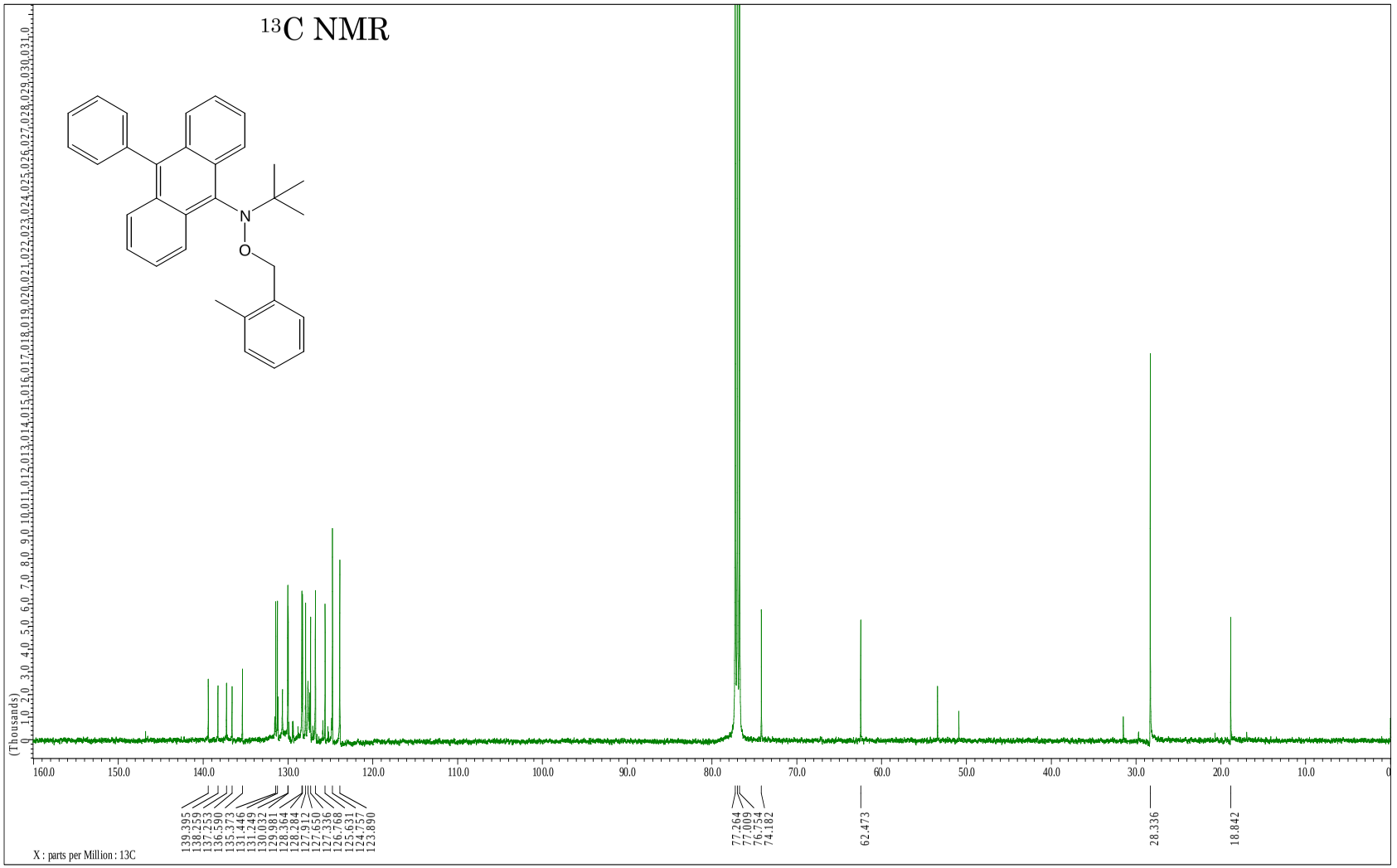

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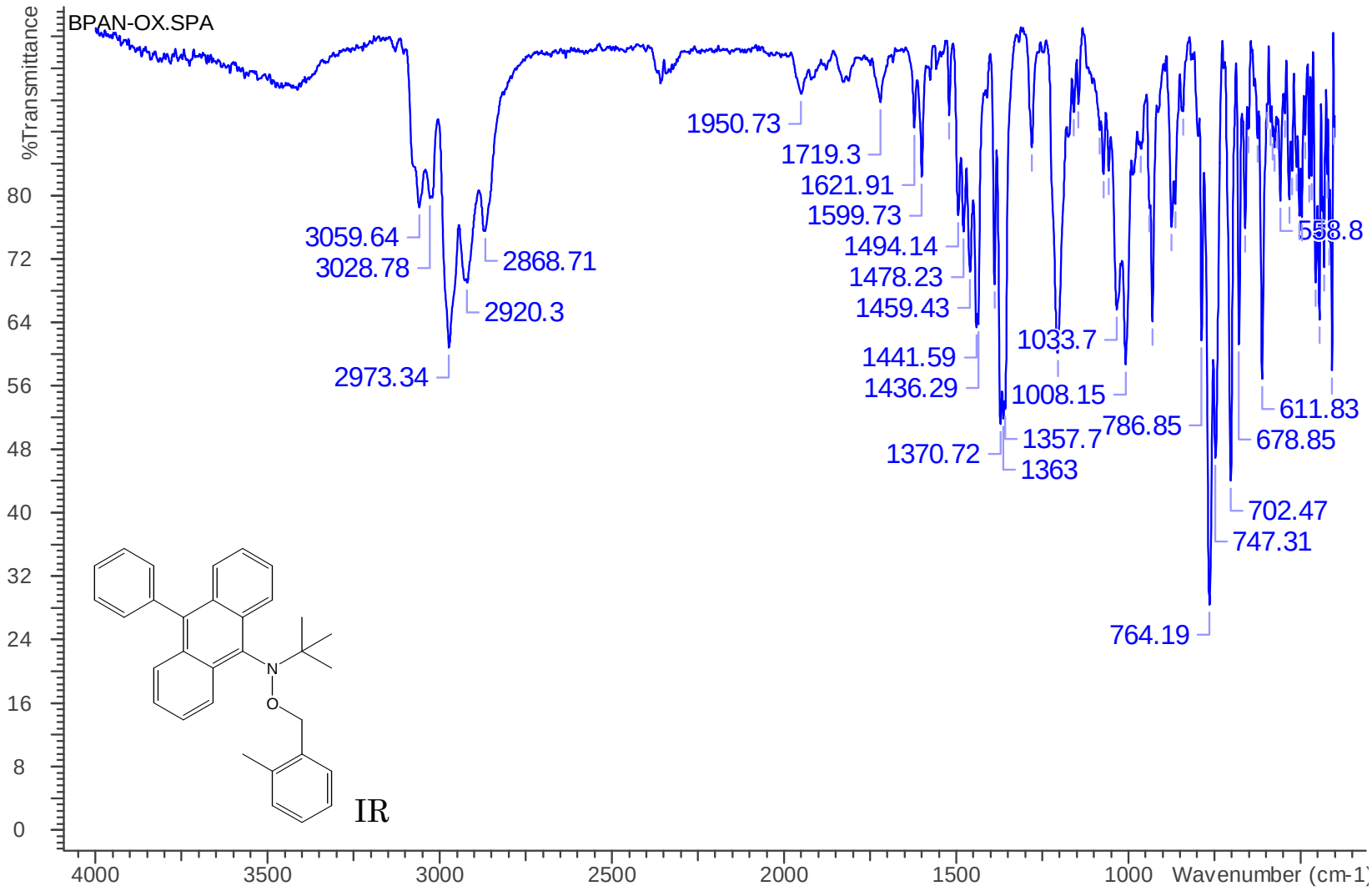
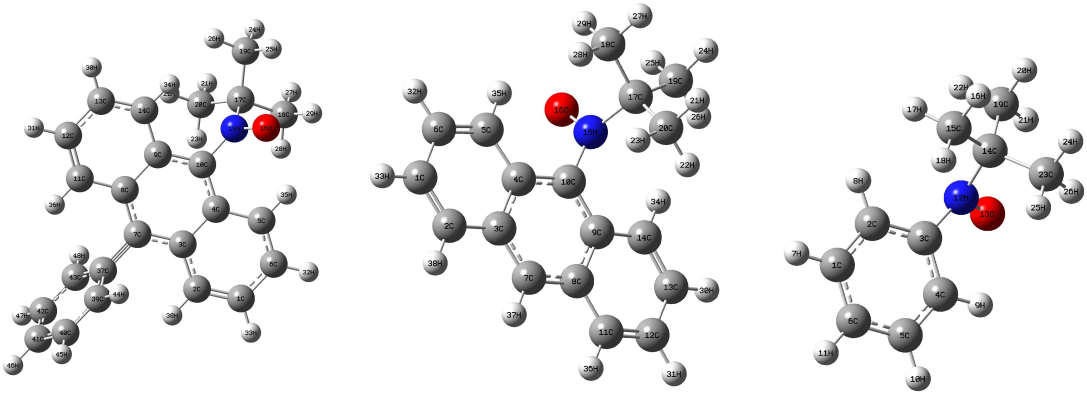


●Mulliken atomic spin densities of BPAN and ATBN and BPNO.

BPAN			ATBN			BPNO		
1	C	−0.006272	1	C	−0.002171	1	C	−0.033976
2	C	0.006419	2	C	0.002639	2	C	0.064556
3	C	−0.008834	3	C	−0.001892	3	C	−0.059355
4	C	0.031669	4	C	0.021302	4	C	0.070202
5	C	−0.008227	5	C	−0.002181	5	C	−0.034799
6	C	0.006384	6	C	0.002802	6	C	0.063204
7	C	0.025084	7	C	0.013163	7	H	0.001361
8	C	−0.009846	8	C	−0.002877	8	H	−0.002153
9	C	0.024128	9	C	0.014044	9	H	−0.003105
10	C	−0.040351	10	C	−0.004992	10	H	0.002175
11	C	0.010227	11	C	0.004480	11	H	−0.003035
12	C	−0.008015	12	C	−0.002712	12	N	0.396932
13	C	0.012173	13	C	0.006248	13	O	0.522676
14	C	−0.006881	14	C	−0.000112	14	C	−0.014896
15	N	0.431307	15	N	0.399064	15	C	0.000762
16	O	0.530472	16	O	0.520815	16	H	−0.000893
17	C	−0.021390	17	C	0.000067	17	H	0.000895
18	C	0.023627	18	C	0.018366	18	H	−0.000299
19	C	0.014135	19	C	0.010559	19	C	0.006808
20	C	0.000771	20	C	0.000398	20	H	−0.001290
21	H	−0.001078	21	H	−0.000346	21	H	−0.001077
22	H	0.000067	22	H	0.000189	22	H	0.000725
23	H	−0.000176	23	H	−0.000035	23	C	0.025783
24	H	−0.000530	24	H	0.000416	24	H	0.001165
25	H	−0.001495	25	H	−0.000411	25	H	−0.000910
26	H	−0.000199	26	H	0.000250	26	H	−0.001457
27	H	0.000757	27	H	0.001501			
28	H	−0.000425	28	H	0.000195			
29	H	−0.001661	29	H	−0.000143			
30	H	−0.000475	30	H	−0.000140			
31	H	0.000363	31	H	0.000145			
32	H	−0.000316	32	H	−0.000115			

33	H	0.000288	33	H	0.000118		
34	H	−0.000834	34	H	0.000132		
35	H	0.000038	35	H	0.001478		
36	H	−0.000345	36	H	−0.000069		
37	C	−0.002041	37	H	−0.000403		
38	H	0.000120	38	H	0.000227		
39	C	0.000652					
40	C	−0.000076					
41	C	0.000139					
42	C	−0.000060					
43	C	0.000675					
44	H	−0.000016					
45	H	0.000033					
46	H	−0.000008					
47	H	0.000039					
48	H	−0.000016					



(a) (b) (c)

Fig. 11. Labeled model of nitroxyl radical. (a) BPAN, (b) ATBM, (c) BPNO.