# A Simple Route to Polysubstituted Indoles Exploiting Azide Induced Furan Ring Opening

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**Supporting Information**

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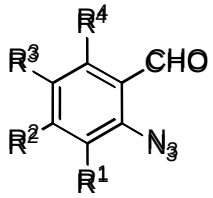
**1. General Information:**

$^{1}H$ and $^{13}C$ NMR spectra were recorded with a "Bruker AM 360" (360 MHz for $^{1}H$ and 90 MHz for $^{13}C$ NMR), a "JEOL Delta ECA 400" (400 MHz for $^{1}H$ and 100 MHz for $^{13}C$ NMR), an "Agilent 400-MR DD2" (400 MHz for $^{1}H$ and 100 MHz for $^{13}C$ NMR) and a "Bruker Avance-600" (600 MHz for $^{1}H$ and 150 MHz for $^{13}C$ NMR) spectrometers at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, $^{1}H$: δ = 7.26 ppm, $^{13}C$: δ = 77.2 ppm; [$D_6$]DMSO, $^{1}H$: δ = 2.50 ppm, $^{13}C$: δ = 39.5 ppm). Coupling constants (*J*) are given in hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets) and br (broadened). IR spectra were measured in KBr using a Prestige-21 FT-IR and Perkin Elmer FT-IR Spectrum Two spectrophotometers. Mass spectra were recorded with a Thermo Scientific TRACE1300/ISQ1300-230LT instrument and a Kratos MS-30 instrument with 70 eV electron impact ionization at 200 ºC. Elemental analyses were performed with Fisons EA-1108 CHNS elemental analyser instrument. Melting points were recorded with a Stuart SMP 30 and are uncorrected. Column chromatography was performed on silica gel KSK (50-160 μm, LTD Sorbpolymer). All the reactions were carried out using freshly distilled and dry solvents from solvent stills.

## 2. Experimental Procedures

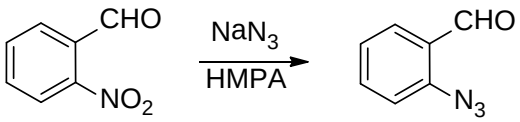
### Preparation of 2-azidobenzaldehydes




**3a-h**

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| **a** | H | H | H | H |
| **b** | H | H | $NO_2$ | H |
| **c** | H | H | Br | H |
| **d** | OMe | H | $NO_2$ | H |
| **e** | Br | H | $NO_2$ | H |
| **f** | OMe | H | Me | OMe |
| **g** | OMe | OMe | H | H |
| **h** | OMe | H | H | OMe |

**2-Azidobenzaldehyde (3a)** was synthesized by treatment of 2-nitrobenzaldehyde **S1** with sodium azide in HMPA according to the published procedure.[S1]

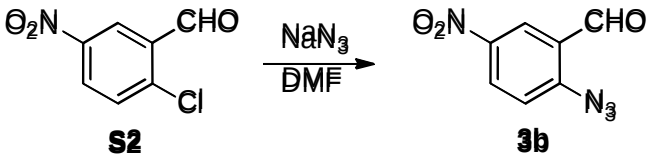



**S1** **3a**

Analytical data for **3a**: pale yellow solid; 95% yield; mp 39–40 °C (benzene/*i*-octane), lit. 33-36 °C;[S2] $R_f$ = 0.43 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.73-7.77 (m, 1H, $H_{Ar}$), 7.78–7.81 (m, 1H, $H_{Ar}$), 7.92–7.95 (m, 1H, $H_{Ar}$), 8.09–8.11 (m, 1H, $H_{Ar}$), 10.40 (s, 1H, CHO) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 124.6, 129.7, 131.4, 133.8, 134.2, 149.7, 188.2 ppm.

**2-Azido-5-nitrobenzaldehyde (3b).** Sodium azide (8 g, 123 mmol) was added at 60° C to a solution of 2-chloro-5-nitrobenzaldehyde **S2**[S3] (18.6 g, 100 mmol) in DMF (200 mL). The reaction mixture was stirred for 20 min, cooled to room temperature and poured into $H_2O$ (200 mL). The precipitate was filtered, washed with water, and air-dried. The product was found to be

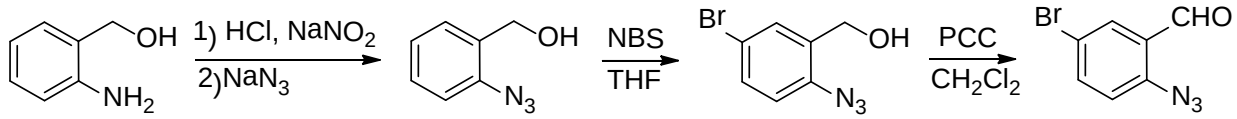
chromatographically pure and was used in further transformations without additional purification.




**S2** **3b**

Analytical data for **3b**: pale yellow needles; 75% yield; mp 95–96 °C (*iso*-octane), lit. 89–95 °C (hexane);[S4] $R_f$ = 0.44 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) 7.44 (d, $^3J$ = 8.8 Hz, 1H, $H_{Ar}$), 8.45 (dd, $^3J$ = 8.8 Hz, $^4J$ = 2.7 Hz, 1H, $H_{Ar}$), 8.69 (d, $^4J$ = 2.7 Hz, 1H, $H_{Ar}$), 10.34 (s, 1H, CHO) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) 120.2, 124.8, 126.9, 129.7, 144.6, 148.5, 186.5 ppm.

**2-Azido-5-bromobenzaldehyde (3c).** 2-Azidobenzyl alcohol **S4** was synthesized from commercially available 2-aminobenzyl alcohol **S3** according to ***Method A***.[S5] The melting point and spectra of **S4** are consistent with the published data.[S6] The bromination of **S4** with NBS [S7] afforded **S5** with spectral properties consistent with the published ones.[S8] The oxidation of **S5** with PCC[S9] afforded **3c**.




**S3** **S4** **S5** **3c**

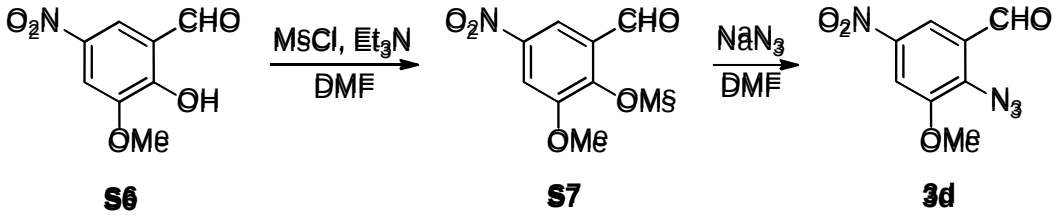
***General procedure for azide synthesis using Sandmeyer-like reaction (Method A)***

A saturated solution of $NaNO_2$ (8.2 g, 120 mmol) was added dropwise to a solution of aniline (100 mmol) in 2N HCl (145 mL) cooled to 3–5 ºC, the mixture was filtered through a paper filter if needed, and to clear solution urea (3g) was added carefully. The obtained solution was slowly (effervescence!) added to 150 mL of cold aqueous solution of $NaN_3$ (13 g, 200 mmol) and NaOAc (24 g, 293 mmol). The reaction mixture was additionally stirred for 1 h. The formed solid was filtered off, washed with water and air dried in the dark. The crude product was recrystallized from light petroleum ether – ethyl acetate (4 : 1) mixture with passing of a hot solution through a small pad of silica gel. In the case when the product was oil it was extracted with $CH_2Cl_2$ (3 × 50 mL) and dried with $Na_2SO_4$. The solvent was removed under the reduced pressure, the residue was dissolved in hot light petroleum ether – ethyl acetate (4 : 1) mixture, filtered through a small pad of silica gel, evaporated to dryness and used as such.

Analytical data for **3c**: pale yellow needles; 80% yield (from **S5**); mp 96–97 °C (petroleum ether), lit. 94–96 °C[S2]; $R_f$ = 0.64 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$)

δ = 7.15 (d, $^3J$ = 8.6 Hz, 1H, $H_{Ar}$), 7.69 (dd, $^3J$ = 8.6 Hz, $^4J$ = 2.4 Hz, 1H, $H_{Ar}$), 7.97 (d, $^4J$ = 2.4 Hz, 1H, $H_{Ar}$), 10.25 (s, 1H, CHO) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 118.4, 120.9, 128.1, 131.8, 138.1, 142.0, 187.2 ppm.

**2-Azido-3-methoxy-5-nitrobenzaldehyde (3d).** 3-Methoxy-5-nitrosalicylaldehyde **S6** was mesylated according to the described procedure (***Method B***).[S10] The treatment of the formed **S7** with $NaN_3$ in DMF (***Method C***) produced azidobenzaldehyde **3d**.




**S6** **S7** **3d**

***General procedure for mesylation of salicylaldehydes* (*Method B*)**

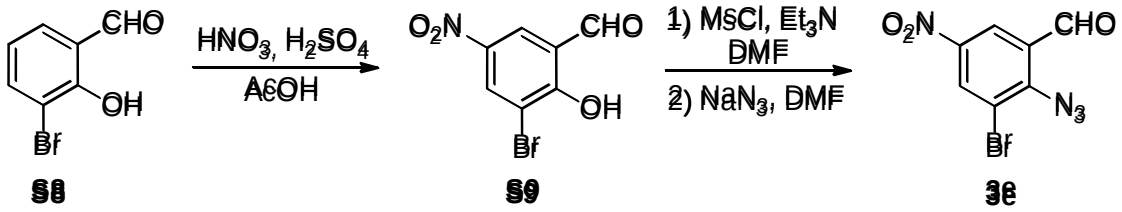
Triethylamine (4.24 g, 42 mmol) was added to a solution of salicylaldehyde (35 mmol) in DMF (25 mL). The mixture was cooled in ice bath and MsCl (4.75 g, 42 mmol) was added dropwise. The reaction mixture was stirred until discoloration of yellow salicylaldehyde anion (2–12 h), then water (150 mL) was added and the mixture was stirred for 30 min. The precipitate was filtered, washed with water and air-dried. Mesylates were used in further transformations without additional purification. Analytical samples can be obtained by recrystallization from $CCl_4$.

***General procedure for azidation of 2-mesyloxybenzaldehydes (Method C)***

Sodium azide (1 g, 15.4 mmol) was added to a solution of 2-mesyloxybenzaldehyde (10 mmol) in DMF (20 mL). The reaction mixture was stirred for 1 h at 50 °C, cooled to room temperature and water (50 mL) was added. The formed precipitate was filtered, washed with water (30 mL) and air-dried in darkness. The product was recrystallized from the appropriate solvent.

Analytical data for **3d**: yellow solid; 85% (from **S7**) yield; mp 107–108 °C (benzene); Found: C, 43.44; H, 2.92; N, 25.22%. $C_8H_6N_4O_4$ requires C, 43.25; H, 2.72; N, 25.22%; $R_f$ = 0.48 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.07 (s, 3H, $CH_3O$), 7.87 (d, $^4J$ = 2.5 Hz, 1H, $H_{Ar}$), 8.29 (d, $^4J$ = 2.5 Hz, 1H, $H_{Ar}$), 10.37 (s, 1H, CHO) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 57.1, 110.2, 115.8, 127.6, 137.7, 144.5, 154.5, 187.1 ppm; IR (KBr) $\nu_{max}$ = 2134, 1690, 1580, 1518, 1469, 1334, 1269, 1089, 952, 742 cm$^{-1}$; MS (EI, 70 eV): 222 ($M^+$, 25), 194 (64), 165 (47), 132 (21), 120 (52), 105 (66), 90 (38), 77 (76), 65 (100), 53 (58), 43 (45).

**2-Azido-3-bromo-5-nitrobenzaldehyde (3e)**. 3-Bromosalicylaldehyde **S8**[S11] was nitrated with a mixture of $HNO_3$ and conc. $H_2SO_4$ in acetic acid according to ***Method D***. The melting point and spectra of **S9** are consistent with the reported data.[S12] The compound **S9** was transformed into azide **3e** using mesylation by ***Method B*** followed by treatment of mesylate with sodium azide according to ***Method C***.



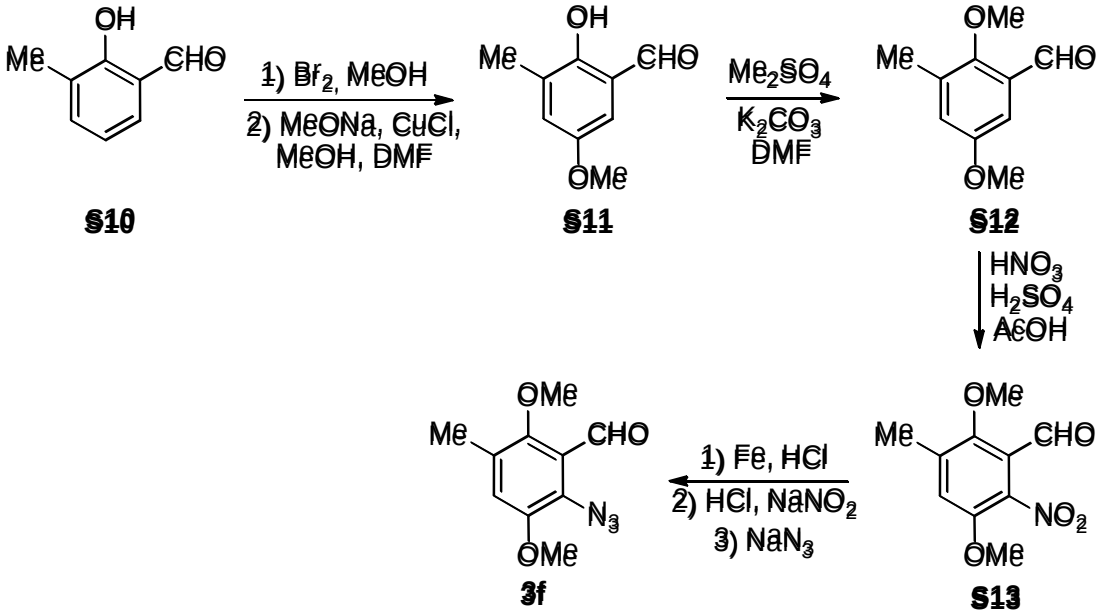

***General procedure for nitration of hydroxy- or methoxy-substituted benzaldehydes (Method D)***

To the solution of benzaldehyde (100 mmol) in acetic acid (100 mL) under cooling with water bath and intensive stirring was added $HNO_3$ (6 mL, 150 mmol, d = 1.5 g/mL) keeping the reaction temperature below 30 °C. Then conc. $H_2SO_4$ (10 mL, 200 mmol) was added dropwise for 30 min to the reaction mixture which solidified within addition. The obtained solid was kept for 30 min and water (200–300 mL) was added. The precipitate was filtered, washed carefully with water and air-dried in darkness. The product was recrystallized from appropriate solvent and used in further transformations.

Analytical data for **3e**: pale yellow needles; 77% yield (from **S9**); mp 100–101 °C (benzene); Found: C, 31.14; H, 1.14; N, 20.52%. $C_7H_3BrN_4O_3$ requires C, 31.02; H, 1.12; N, 20.67%; $R_f$ = 0.54 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.62 (d, $^4J$ = 2.6 Hz, 1H, $H_{Ar}$), 8.63 (d, $^4J$ = 2.6 Hz, 1H, $H_{Ar}$), 10.36 (s, 1H, CHO) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 119.2, 124.4, 130.1, 133.7, 144.9, 145.1, 186.8 ppm; IR (KBr) $\nu_{max}$ = 2138, 1691, 1593, 1512, 1347, 1296, 1185, 1130, 909, 740 cm$^{-1}$; MS (EI, 70 eV): 272/270 ($M^+$, 17/17), 244/242 (37/37), 198/196 (33/33), 186/184 (70/70), 170/168 (44/46), 143/141 (52/52), 117 (55), 89 (100), 74 (78), 62 (90), 53 (48), 43 (45).

**2-Azido-3,6-dimethoxy-5-methylbenzaldehyde (3f)**. 3-Methylsalicylaldehyde **S10** was methoxylated by two-step procedure described below as ***Method E***. The melting point and the spectral data of 5-methoxy-3-methylsalicylaldehyde (**S11**) are consistent with those reported in the literature.[S13] Then **S11** was methylated with dimethyl sulfate (***Method F***) affording 2,5-dimethoxy-3-methylbenzaldehyde (**S12**)[S14] which was nitrated using ***Method D***. The obtained 2-

nitrobenzaldehyde **S13**[S15] was transformed into 2-azidobenzaldehyde **3f** by treatment with Fe and HCl (***Method G***) following by azidation using the procedure described in ***Method A***.




***General procedure of salicylaldehydes methoxylation (Method E)***

Bromine (16 g, 100 mmol) was added dropwise within 40 min to a solution of salicylaldehyde (100 mmol) in methanol (50 mL) cooled to 10–15 °C. The reaction mixture was stirred for 30 min, then water (50–60 mL) was added to induce crystallization. The reaction mixture was stirred 30 min more, filtered, washed with 50% aq. methanol (50 mL) and air-dried. The bromination product was used in further transformation without purification.

To a solution of sodium (6.9 g, 300 mmol) in methanol (80–100 mL) CuCl (2.97 g, 30 mmol) was added and the mixture was heated to 60 °C for 30 min under vigorous stirring. Then a solution of bromosalicylaldehyde (100 mmol) in DMF (50 mL) was added dropwise. The reaction mixture was heated to 90 °C and stirred for 6–36 h (the reaction progress was monitored by neutralization of small aliquot with hydrochloric acid followed by TLC using benzene as an eluent). When a conversion of the substrate was completed, the reaction mixture was cooled to room temperature, poured into water (200 mL), and neutralized with HCl. The precipitate was filtered off and washed with water (30 mL). The mother liquor was extracted with $CH_2Cl_2$ (3 × 50 mL); the combined organic fractions were washed with water (50 mL), filtered solid was added to this solution which was dried over $CaCl_2$. The solvent was evaporated to dryness and the residue was distilled *in vacuo.* The obtained methoxysalicylaldehyde was utilized at the next step without additional purification.

***General procedure for methylation of salicylaldehydes (Method F)***

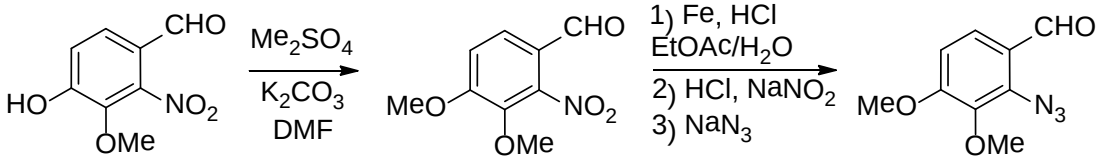
To a solution of salicylaldehyde (100 mmol) in DMF (80 mL) preheated to 80 °C, anhydrous $K_2CO_3$ (250–300 mmol) was added. Heating was stopped, the reaction mixture was stirred for 10 min and dimethyl sulfate (12 mL, 127 mmol) was added to the reaction mixture droppwise keeping the reaction temperature below 50 °C. The mixture was stirred for 20 min after addition was complete. Then, one more portion of dimethyl sulfate (7 mL, 74 mmol) was added in the same manner. When the reaction mixture discolored it was cooled and water (20 mL) was added. The precipitate was filtered off, mother liquor was extracted with $CH_2Cl_2$ (3 × 50 mL). Extracts were combined with the precipitate, dried with anhydrous $CaCl_2$ and evaporated to dryness. The residue was distilled *in vacuo* and used in further transformations without additional purification.

***General procedure for reduction of 2-nitrobenzaldehydes (Memoд G)***

To a suspension of carbonyl iron (28 g, 500 mmol) in water (100 mL) heated to 80 °C was carefully added HCl (5 mL); the mixture was stirred for 10 min. Then the warm solution of 2-nitrobenzaldehyde (150 mmol) in ethyl acetate (200 mL) was added keeping on the moderate boil of reaction mixture. When the addition was finished, the mixture was heated until full conversion of the substrate (TLC monitoring; *ca*. 30 min). The reaction mixture was cooled to room temperature, 2N NaOH solution (5 mL) was added. The mixture was stirred for 10 min and filtered through a paper filter. The precipitate was washed with EtOAc until colorless washing (*ca*. 100 mL). The organic layer was separated, the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic fractions were evaporated under reduced pressure, the residue was reextracted with $CH_2Cl_2$ (3 × 50 mL). Organic layer was passed through a small pad of silica and evaporated to dryness. The resulted oil was utilized in further transformations without additional purification.

Analytical data for **3f**: pale yellow solid; 81% (from **S13**) yield; mp 78–79 °C (ethyl acetate/petroleum ether); Found: C, 54.19; H, 4.96; N, 18.91%. $C_{10}H_{11}N_3O_3$ requires C, 54.30; H, 5.01; N, 18.99%; $R_f$ = 0.48 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.25 (s, 3H, $CH_3$), 3.72 (s, 3H, $CH_3O$), 3.86 (s, 3H, $CH_3O$), 6.89 (s, 1H, $H_{Ar}$), 10.35 (s, 1H, CHO) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 15.6, 56.6, 62.4, 119.4, 122.0, 127.9, 128.8, 150.0, 153.7, 189.4 ppm; IR (KBr) $\nu_{max}$ = 2120, 1686, 1578, 1474, 1309, 1237, 1099, 948, 776 cm$^{-1}$; MS (EI, 70 eV): 221 ($M^+$, 53), 193 (70), 178 (84), 164 (60), 151 (100), 135 (60), 106 (33), 94 (44), 81 (52), 65 (42), 53 (52), 43 (80).

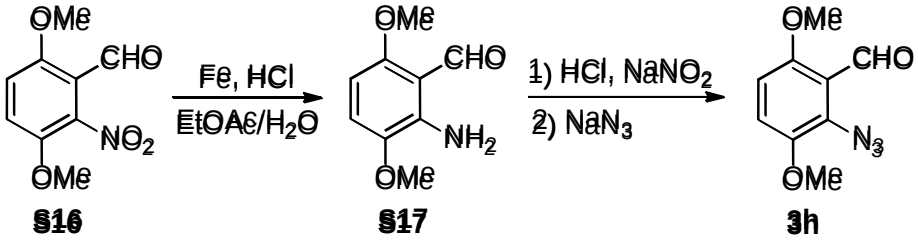
**2-Azido-3,4-dimethoxybenzaldehyde (3g)**. 2-Nitrovanillin (**S14**)[S16] was methylated (***Method F***) furnishing 3,4-dimethoxy-2-nitrobenzaldehyde (**S15**)[S17] which was transformed into azide **3g** following to the general procedures (***Method G***, ***Method A***).




**S14** **S15** **3g**

Analytical data for **3g**: pale yellow needles; 90% (from **S15**) yield; mp 96–97 °C (benzene/petroleum ether), lit. 90 °C;[S18]; Found: C, 52.24; H, 4.37; N, 20.19%. $C_9H_9N_3O_3$ requires C, 52.17; H, 4.38; N, 20.28%; $R_f$ = 0.48 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, $CDCl_3$) δ = 3.94 (s, 3H, $CH_3O$), 3.96 (s, 3H, $CH_3O$), 6.78 (d, $^3J$ = 8.8 Hz, 1H, $H_{Ar}$), 7.63 (d, $^3J$ = 8.8 Hz, 1H, $H_{Ar}$), 10.20 (s, 1H, CHO) ppm; $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 56.3, 61.8, 108.4, 121.9, 125.1, 136.6, 142.9, 158.2, 188.1 ppm; IR (KBr) $\nu_{max}$ = 2140, 1687, 1598, 1462, 1284, 1072, 943, 808 cm$^{-1}$; MS (EI, 70 eV): 207 ($M^+$, 40), 179 (68), 164 (30), 136 (60), 108 (68), 93 (100), 80 (48), 65 (92), 53 (98), 43 (42).

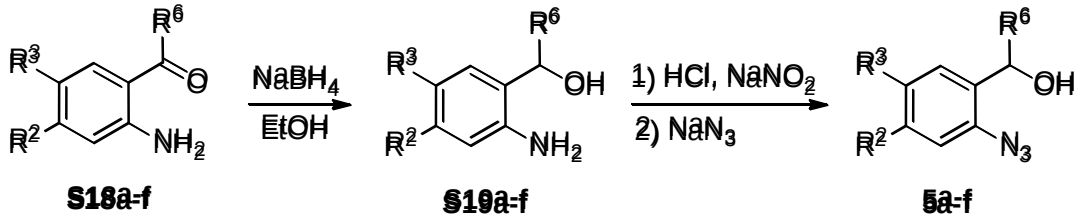
**2-Azido-3,6-dimethoxybenzaldehyde (3h)**. 2,5-Dimethoxy-6-nitrobenzaldehyde (**S16**)[S19] was reduced into the corresponding aniline **S17**[S20] (***Method G***) which was transformed into 2-azido-benzaldehyde **3h** following to the general procedure (***Method A***).




**S16** **S17** **3h**

Analytical data for **3h**: yellow solid; 84% (from **S16**) yield; mp 85–86 °C (benzene); Found: C, 52.16; H, 4.42; N, 20.26%. $C_9H_9N_3O_3$ requires C, 52.17; H, 4.38; N, 20.28%; $R_f$ = 0.34 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 3.81 (s, 3H, $CH_3O$), 3.83 (s, 3H, $CH_3O$), 6.64 (d, $^3J$ = 9.1 Hz, 1H, $H_{Ar}$), 7.00 (d, $^3J$ = 9.1 Hz, 1H, $H_{Ar}$), 10.38 (s, 1H, CHO) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 56.3, 57.0, 107.5, 117.7, 117.9, 130.5, 147.9, 155.7, 189.0 ppm; IR (KBr) $\nu_{max}$ = 2107, 1686, 1579, 1482, 1400, 1306, 1261, 1194, 1053, 952, 804 cm$^{-1}$; MS (EI, 70 eV): 207 ($M^+$, 30), 179 (100), 164 (48), 150 (50), 136 (57), 121 (35), 108 (30), 93 (40), 76 (30), 53 (30), 43 (40).

**Synthesis of 2-azidobenzyl alcohols**



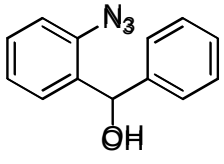

**S18a-f** **S19a-f** **5a-f**

| | $R^2$ | $R^3$ | $R^6$ |
|---|---|---|---|
| **a** | H | H | Ph |
| **b** | H | H | 4-$FC_6H_4$ |
| **c** | H | Cl | Ph |
| **d** | OMe | OMe | Me |
| **e** | OMe | OMe | Ph |
| **f** | $OCH_2CH_2O$ | | Ph |

2-Aminobenzophenones **S18a** and **S18c** are commercially available. Synthesis of ketones **S18b**,[S21] **S18d-f**[S22] was described earlier. Ketones **S18** were reduced to the corresponding alcohols **S19** following the general procedure (***Method H***) given below. The transformation of *o*-aminobenzyl alcohols **S19**[S23-S25] into *o*-azidobenzyl alcohols was carried out according to the procedure given above (***Method A***).

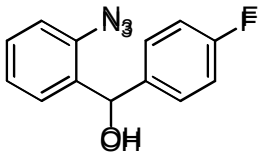
***General procedure for reduction of 2-aminophenyl ketones into 2-aminobenzyl alcohols (Method H)***

Sodium borohydride (3.6 g, 95 mmol) was added portionwise to a solution of ketone **S18** (100 mmol) in the mixture of ethanol (150 mL) and ethyl acetate (50 mL) cooled in the water bath. The reaction mixture was stirred for 0.5–2 h (TLC control) until discoloration and diluted with water (200 mL). Then NaCl (30 g) and ethyl acetate (150 mL) were added; the reaction mixture was stirred for 30 min. The organic layer was separated and dried. The solvent was removed under reduced pressure giving rise to alcohol **S19**, which was utilized in further transformations without purification.



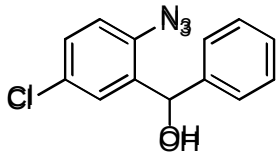

**5a**

**(2-Azidophenyl)(phenyl)methanol (5a):**[S26] pale beige solid; 88% (from **S18a**) yield; mp 68-69 °C (benzene/petroleum ether); $R_f$ = 0.45 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.60 (s, 1H, OH), 6.03 (s, 1H, C*H*OH), 7.14–7.19 (m, 2H, $H_{Ar}$), 7.28–7.41 (m, 6H, $H_{Ar}$), 7.47–7.50 (m, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 71.6, 118.3, 125.2, 126.7 (2C), 127.7, 128.1, 128.5 (2C), 128.9, 134.9, 137.1, 142.9 ppm.



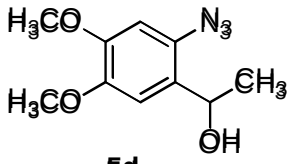
**5b**

**(2-Azidophenyl)(4-fluorophenyl)methanol (5b):** beige cubes; 83% (from **S18b**) yield; mp 96-97 °C (ethyl acetate/petroleum ether); Found: C, 64.21; H, 4.08; N, 17.20%. $C_{13}H_{10}FN_3O$ requires C, 64.19; H, 4.14; N, 17.27%; $R_f$ = 0.40 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 3.14 (s, 1H, OH), 5.95 (s, 1H, C*H*OH), 6.97–7.05 (m, 2H, $H_{Ar}$), 7.12–7.20 (m, 2H, $H_{Ar}$), 7.29–7.37 (m, 3H, $H_{Ar}$), 7.43-7.48 (m, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 70.7, 115.2 (d, $^2J_{CF}$ = 21.4 Hz, 2C), 118.2, 125.1, 127.7, 128.4 (d, $^3J_{CF}$ = 8.1 Hz, 2C), 128.9, 134.6, 136.9, 138.6 (d, $^4J_{CF}$ = 3.1 Hz), 162.1 (d, $^1J_{CF}$ = 245.7 Hz) ppm; IR (KBr) $\nu_{max}$ = 2137, 1582, 1560, 1481, 1448, 1301, 1221, 1157, 1018, 953, 779, 754 cm$^{-1}$; MS (EI, 70 eV): 243 ($M^+$, 18), 214 (100), 198 (48), 186 (62), 120 (32), 95 (48), 65 (30), 43 (16).



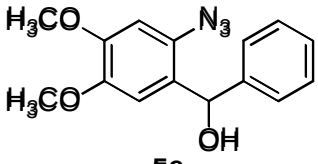
**5c**

**(2-Azido-5-chlorophenyl)(phenyl)methanol (5c):** yellow solid; 96% (from **S18c**) yield; mp 103–104 °C (ethyl acetate/petroleum ether); Found: C, 60.09; H, 3.74; N, 16.12%. $C_{13}H_{10}ClN_3O$ requires C, 60.13; H, 3.88; N, 16.18%; $R_f$ = 0.46 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.56 (br s, 1H, OH), 5.95 (s, 1H, C*H*OH), 7.04 (d, $^3J$ = 8.5 Hz, 1H, $H_{Ar}$), 7.28 (dd, $^3J$ = 8.5 Hz, $^4J$ = 2.5 Hz, 1H, $H_{Ar}$), 7.30–7.38 (m, 5H, $H_{Ph}$), 7.54 (d, $^4J$ = 2.5 Hz, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 71.2, 119.5, 126.8 (2C), 127.9, 128.0, 128.7 (2C), 128.8, 130.7, 135.5, 136.5, 142.2 ppm; IR (KBr) $\nu_{max}$ = 3350, 2125, 1479, 1293, 1184, 1021, 814, 767 cm$^{-1}$; MS (EI, 70 eV): 261/259 ($M^+$, 11/33), 233/231 (19/57), 214 (64), 202 (64), 167 (63), 105 (27), 76 (100), 63 (37), 51 (62), 43 (22).



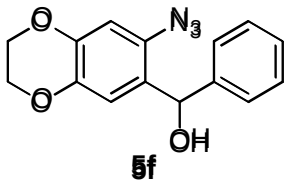
**5d**

**1-(2-Azido-4,5-dimethoxyphenyl)ethanol (5d):** beige solid; 78% (from **S18d**) yield; mp 68-69 °C (benzene/petroleum ether); Found: C, 53.79; H, 6.03; N, 18.78%. $C_{10}H_{13}N_3O_3$ requires C, 53.81; H, 5.87; N, 18.82%; $R_f$ = 0.31 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, DMSO-d6) δ = 1.26 (d, $^3J$ = 6.4 Hz, 3H, $CH_3$), 3.76 (s, 3H, $CH_3O$), 3.80 (s, 3H, $CH_3O$), 4.87 (dq, $^3J$ = 6.4, 4.3 Hz, 1H, CH), 5.08 (d, $^3J$ = 4.3 Hz, 1H, OH), 6.75 (s, 1H, $H_{Ar}$), 7.10 (s, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (150 MHz, DMSO-d6) δ = 25.0, 55.8, 55.9, 62.9, 102.6, 109.9, 126.8, 130.7, 146.5, 148.4 ppm; IR (KBr) $\nu_{max}$ = 3510, 2106, 1510, 1263, 1213, 1111, 1012, 867, 750 cm$^{-1}$; MS (EI, 70 eV): 223 ($M^+$, 92), 195 (65), 180 (95), 166 (40), 152 (100), 109 (48), 78 (32), 68 (48), 51 (50), 43 (45).



**5e**

**(2-Azido-4,5-dimethoxyphenyl)(phenyl)methanol (5e):** yellow solid; 85% (from **S18e**) yield; mp 139–140 °C (ethyl acetate/petroleum ether); Found: C, 63.32; H, 5.29; N, 14.73%. $C_{15}H_{15}N_3O_3$ requires C, 63.15; H, 5.30; N, 14.73%; $R_f$ = 0.35 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.57 (br. s, 1H, OH), 3.80 (s, 3H, $CH_3O$), 3.87 (s, 3H, $CH_3O$), 5.99 (s, 1H, C*H*OH), 6.60 (s, 1H, $H_{Ar}$), 6.96 (s, 1H, $H_{Ar}$), 7.16–7.48 (m, 5H, $H_{Ph}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 56.2, 56.3, 71.0, 101.8, 110.7, 126.4 (2C), 127.0, 127.6, 128.5 (2C), 128.9, 143.3, 146.7, 149.4 ppm; IR (KBr) $\nu_{max}$ = 3491, 2112, 1506, 1450, 1244, 1086, 829, 698 cm$^{-1}$; MS (EI, 70 eV): 285 ($M^+$, 18), 257 (40), 242 (55), 227 (20), 197 (20), 77 (100), 53 (30), 43 (20).

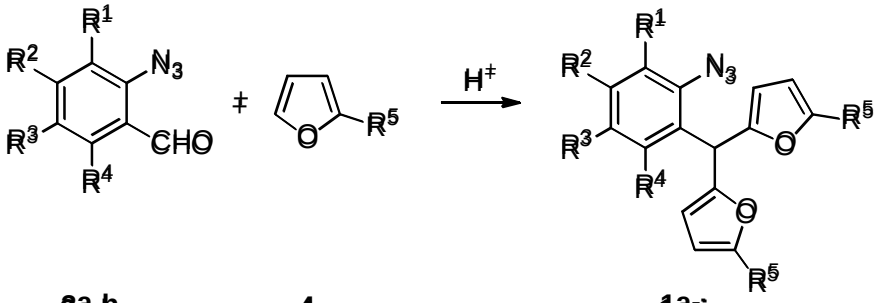


**5f**

**(7-Azido-2,3-dihydro-1,4-benzodioxin-6-yl)(phenyl)methanol (5f):** pale yellow oil; 79% (from **S18f**) yield; Found: C, 63.50; H, 4.57; N, 14.94%. $C_{15}H_{13}N_3O_3$ requires C, 63.60; H, 4.63; N, 14.83%; $R_f$ = 0.38 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.44 (br. s, 1H, OH), 4.19–4.22 (m, 2H, $CH_2$), 4.23–4.25 (m, 2H, $CH_2$), 5.93 (s, 1H, C*H*OH),

6.66 (s, 1H, $H_{Ar}$), 6.92 (s, 1H, $H_{Ar}$), 7.24–7.29 (m, 1H, $H_{Ph}$), 7.30–7.39 (m, 4H, $H_{Ph}$) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 64.4, 64.6, 71.0, 107.1, 116.9, 126.5 (2C), 127.6, 128.5 (2C), 130.1, 141.1, 143.0, 143.7 ppm; IR (KBr) $\nu_{max}$ = 3393, 2111, 1589, 1497, 1323, 1242, 1066, 698 $cm^{-1}$; MS (EI, 70 eV): 283 ($M^+$, 70), 254 (100), 226 (90), 199 (50), 170 (78), 143 (50), 94 (50), 43 (45).

**Synthesis of (2-azidoaryl)difurylmethanes**

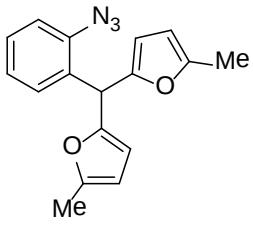



**3a-h** **4** **1a-j**

| Entry | **1** | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ |
|---|---|---|---|---|---|---|
| 1 | **a** | H | H | H | H | Me |
| 2 | **b** | H | H | H | H | Et |
| 3 | **c** | H | H | H | H | *t*-Bu |
| 4 | **d** | H | H | $NO_2$ | H | Me |
| 5 | **e** | H | H | Br | H | Me |
| 6 | **f** | OMe | H | $NO_2$ | H | Me |
| 7 | **g** | Br | H | $NO_2$ | H | Me |
| 8 | **h** | OMe | H | Me | OMe | Me |
| 9 | **i** | OMe | OMe | H | H | Me |
| 10 | **j** | OMe | H | H | OMe | Me |

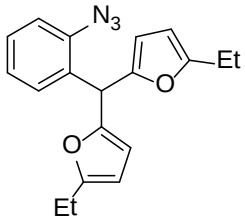
**General procedure for synthesis of compounds 1a-g *(Method I)***

Aq. $HClO_4$ (70%, 0.36 mL, 6 mmol) was added to the cooled (5–10 °C) solution of 2-azidobenzaldehyde **3** (10 mmol) and furan **4** (22 mmol) in 1,4-dioxane (10 mL). The reaction mixture was stirred at the same temperature for 8–12 h until disappearance of the starting azidobenzaldehyde (TLC control), then poured into cold water (100 mL). The product was extracted with benzene (3 × 50 mL). The combined organic fractions were washed with water, dried with $Na_2SO_4$, passed thought small pad of silica gel and evaporated to dryness under reduced pressure. The product was recrystallized from specified solvent.



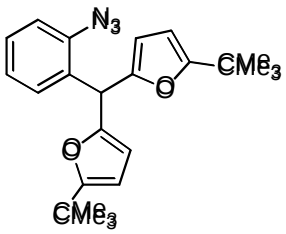

**1a**

**2,2'-[(2-Azidophenyl)methanediyl]bis(5-methylfuran) (1a):** yellow solid; 2.23 g, 76% yield; mp 59–60 °C (petroleum ether); Found: C, 69.67; H, 5.24; N, 14.24%. $C_{17}H_{15}N_3O_2$ requires C, 69.61; H, 5.15; N, 14.33%; $R_f$ = 0.55 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.26 (s, 6H, 2×$CH_3$), 5.70 (s, 1H, CH), 5.84 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 5.89 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 7.08–7.12 (m, 1H, $H_{Ar}$), 7.16–7.21 (m, 2H, $H_{Ar}$), 7.29–7.33 (m, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 13.8 (2C), 39.0, 106.2 (2C), 108.6 (2C), 118.3, 124.9, 128.5, 130.0, 131.2, 137.8, 151.7 (2C), 152.2 (2C) ppm; IR (KBr) $\nu_{max}$ = 2137, 1582, 1560, 1481, 1448, 1301, 1221, 1157, 1018, 953, 779, 754 cm$^{-1}$; MS (EI, 70 eV): 293 ($M^+$, 15), 265 (100), 250 (30), 222 (75), 208 (28), 194 (85), 180 (60), 167 (15), 141 (15), 115 (16), 77 (15), 51 (25), 43 (30).



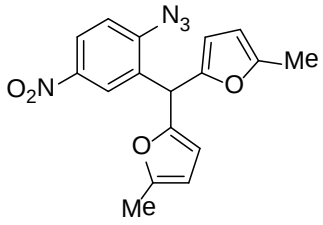

**1b**

**2,2'-[(2-Azidophenyl)methanediyl]bis(5-ethylfuran) (1b):** pale orange oil; 2.54 g, 79% yield; Found: C, 70.91; H, 6.04; N, 12.92%. $C_{19}H_{19}N_3O_2$ requires C, 71.01; H, 5.96; N, 13.07%; $R_f$ = 0.58 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 1.20 (t, $^3J$ = 7.5 Hz, 6H, 2×$CH_3$), 2.61 (q, $^3J$ = 7.5 Hz, 4H, 2×$CH_2$), 5.71 (s, 1H, CH), 5.84 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 5.90 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 7.07–7.11 (m, 1H, $H_{Ar}$), 7.16–7.18 (m, 2H, $H_{Ar}$), 7.29–7.33 (m, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 12.2 (2C), 21.5 (2C), 39.0, 104.5 (2C), 108.3 (2C), 118.3, 124.9, 128.4, 130.0, 131.3, 137.8, 152.1 (2C), 157.4 (2C) ppm; IR (KBr) $\nu_{max}$ = 2123, 1584, 1487, 1298, 1182, 1012, 777, 752 cm$^{-1}$; MS (EI, 70 eV): 321 ($M^+$, 27), 293 (100), 276 (45), 264 (80), 236 (70), 208 (67), 180 (60), 115 (28), 57 (46), 43 (31).



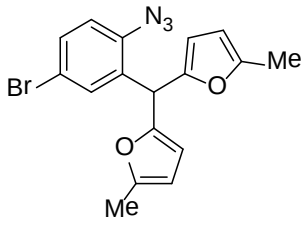
**1c**

**2,2'-[(2-Azidophenyl)methanediyl]bis(5-*tert*-butylfuran) (1c):** pale orange oil; 2.83 g, 75% yield; Found: C, 72.95; H, 7.18; N, 10.97%. $C_{23}H_{27}N_3O_2$ requires C, 73.18; H, 7.21; N, 11.13%; $R_f$ = 0.61 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 1.24 (s, 18H, $CH_3$), 5.69 (s, 1H, CH), 5.80 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 5.85 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 7.05–7.09 (m, 1H, $H_{Ar}$), 7.13–7.18 (m, 2H, $H_{Ar}$), 7.27–7.31 (m, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 29.2 (6C), 32.7 (2C), 39.2, 102.3 (2C), 107.7 (2C), 118.2, 124.8, 128.2, 130.0, 131.7, 137.7, 151.9 (2C), 163.7 (2C) ppm; IR (KBr) $\nu_{max}$ = 2965, 2124, 1584, 1554, 1487, 1362, 1296, 1196, 1126, 1015, 779, 750 cm$^{-1}$; MS (EI, 70 eV): 377 ($M^+$, 20), 349 (95), 334 (85), 292 (100), 264 (20), 236 (30), 208 (25), 180 (22), 69 (18), 57 (85), 43 (47).



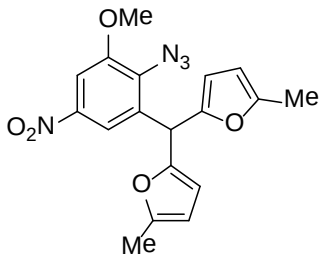
**1d**

**2,2'-[(2-Azido-5-nitrophenyl)methanediyl]bis(5-methylfuran) (1d):** pale yellow solid; 2.84 g, 84% yield; mp 118–119 °C (*i*-PrOH); Found: C, 60.28; H, 4.18; N, 16.50%. $C_{17}H_{14}N_4O_4$ requires C, 60.35; H, 4.17; N, 16.56%; $R_f$ = 0.44 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, $CDCl_3$) δ = 2.25 (s, 6H, 2×$CH_3$), 5.71 (s, 1H, CH), 5.91 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 5.93 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 7.26 (d, $^3J$ = 8.8 Hz, 1H, $H_{Ar}$), 8.09 (d, $^4J$ = 2.6 Hz, 1H, $H_{Ar}$), 8.18 (dd, $^3J$ = 8.8 Hz, $^4J$ = 2.6 Hz, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 13.7 (2C), 39.0, 106.4 (2C), 109.2 (2C), 118.6, 124.0, 125.7, 132.7, 144.5, 144.8, 150.5 (2C), 152.3 (2C) ppm; IR (KBr) $\nu_{max}$ = 2153, 1699, 1605, 1526, 1354, 1223, 1070, 1026, 920, 825, 719 cm$^{-1}$; MS (EI, 70 eV): 338 ($M^+$, 48), 310 (78), 295 (24), 267 (52), 250 (25), 221 (100), 193 (65), 179 (25), 139 (32), 53 (38), 43 (38).



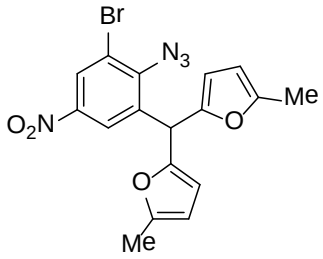

**1e**

**2,2'-[(2-Azido-5-bromophenyl)methanediyl]bis(5-methylfuran) (1e):** cream solid; 3.27 g, 88% yield; mp 116–117 °C (benzene); Found: C, 55.08; H, 3.92; N, 11.28%. $C_{17}H_{14}BrN_3O_2$ requires C, 54.86; H, 3.79; N, 11.29%; $R_f$ = 0.55 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.26 (s, 6H, 2×$CH_3$), 5.64 (s, 1H, CH), 5.86 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 5.89 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 7.03 (d, $^3J$ = 8.4 Hz, 1H, $H_{Ar}$), 7.29 (d, $^4J$ = 2.2 Hz, 1H, $H_{Ar}$), 7.41 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.2 Hz, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 13.8 (2C), 38.9, 106.3 (2C), 108.9 (2C), 118.0, 119.9, 131.5, 132.9, 133.3, 137.1, 151.3 (2C), 152.0 (2C) ppm; IR (KBr) $\nu_{max}$ = 2131, 1607, 1555, 1481, 1302, 1209, 1101, 1018, 939, 795 cm$^{-1}$; MS (EI, 70 eV): 373/371 ($M^+$, 5/5), 345/343 (49/50), 302/300 (27/27), 264 (20), 221 (100), 193 (52), 178 (30), 139 (22), 126 (23), 89 (20), 59 (35), 43 (42).




**1f**

**2,2'-[(2-Azido-3-methoxy-5-nitrophenyl)methanediyl]bis(5-methylfuran) (1f):** yellow solid; 3.39 g, 92% yield; mp 116–117 °C (ethyl acetate/petroleum ether); Found: C, 58.60; H, 4.44; N, 15.16%. $C_{18}H_{16}N_4O_5$ requires C, 58.69; H, 4.38; N, 15.21%; $R_f$ = 0.43 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.25 (s, 6H, 2×$CH_3$), 3.99 (s, 3H, $CH_3O$), 5.79 (s, 1H, CH), 5.90 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 5.92 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 7.66 (d, $^4J$ = 2.4 Hz, 1H, $H_{Ar}$), 7.72 (d, $^4J$ = 2.4 Hz, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 13.7 (2C), 39.5, 56.7, 105.4, 106.4 (2C), 109.1 (2C), 117.7, 133.0, 133.5, 144.6, 150.7 (2C), 152.1 (2C), 153.7 ppm; IR (KBr) $\nu_{max}$ = 2137, 1581, 1522, 1470, 1339, 1213, 1096, 1022, 791 cm$^{-1}$; MS (EI, 70 eV): 368 ($M^+$, 18), 340 (100), 326 (33), 297 (25), 251 (30), 237 (45), 223 (24), 208 (20), 169 (16), 127 (14), 43 (26).




**1g**

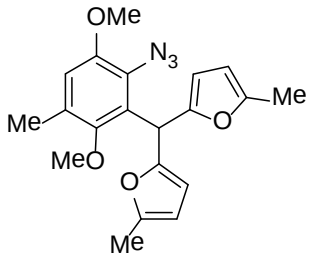
**2,2'-[(2-Azido-3-bromo-5-nitrophenyl)methanediyl]bis(5-methylfuran) (1g):** yellow solid; 3.54 g, 85% yield; mp 88–89 °C (ethyl acetate/petroleum ether); Found: C, 49.07; H, 3.28; N, 13.34%. $C_{17}H_{13}BrN_4O_4$ requires C, 48.94; H, 3.14; N, 13.43%; $R_f$ = 0.51 (acetone/petroleum ether = 1:2); $^1$H NMR (360 MHz, $CDCl_3$) δ = 2.26 (s, 6H, 2×$CH_3$), 5.87 (s, 1H, CH), 5.93 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 5.99 (d, $^3J$ = 3.2 Hz, 2H, $H_{Fur}$), 8.00 (d, $^4J$ = 2.6 Hz, 1H, $H_{Ar}$), 8.35 (d, $^4J$ = 2.6 Hz, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (90 MHz, $CDCl_3$) δ = 13.7 (2C), 40.8, 106.6 (2C), 109.5 (2C), 118.8, 124.0, 128.1, 137.5, 141.8, 145.4, 150.0 (2C), 152.5 (2C) ppm; IR (KBr) $\nu_{max}$ = 2116, 1524, 1437, 1341, 1213, 1022, 789 cm$^{-1}$; MS (EI, 70 eV): 418/416 ($M^+$, 3/3), 390/388 (100/100), 375/373 (20/21), 301/299 (39/40), 220 (20), 177 (20), 139 (15), 43 (30).

***General procedure for synthesis of compounds 1h-j (Method J)***

Polyphosphoric acid trimethylsilyl ester (5 mL; for preparation, see below) was added dropwise to the cooled (5–10 °C) solution of 2-azidobenzaldehyde **3** (10 mmol) and 2-methylfuran (**4**) (1.8 g, 22 mmol) in $CH_2Cl_2$ (10 mL). The reaction mixture was stirred for 2–3 h at the same temperature (TLC control), then poured into cold water (50 mL). Residual phosphoric acid was dissolved in acetone (3 mL) and mixed with the above aqueous solution. The product was extracted with benzene (2×50 mL). The combined organic fractions were washed with saturated aqueous $NaHCO_3$ and water, dried with $Na_2SO_4$, and passed through small pad of silica gel. The solvent was evaporated to dryness under reduced pressure. The product was recrystallized from specified solvent.

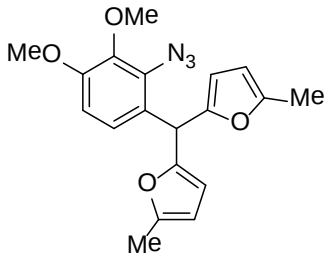
**Preparation of 2.33 M polyphosphoric acid trimethylsilyl ester solution in $CH_2Cl_2$**

Hexamethyldisiloxane (170 g, 1.05 mol) was added dropwise with stirring to a suspension of $P_2O_5$ (156 g, 1.1 mol) in dry $CH_2Cl_2$ (900 mL) maintaining moderate boiling. Then the reaction mixture was refluxed for 1 h more until reaction was complete.



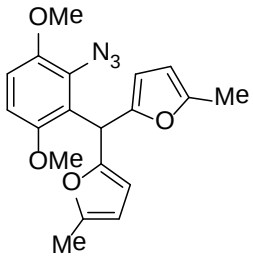

**1h**

**2,2'-[(2-Azido-3,6-dimethoxy-5-methylphenyl)methanediyl]bis(5-methylfuran) (1h):** orange solid; 3.27 g, 89% yield; mp 74–75 °C (petroleum ether); Found: C, 65.56; H, 5.96; N, 11.23%. $C_{20}H_{21}N_3O_4$ requires C, 65.38; H, 5.76; N, 11.44%; $R_f$ = 0.43 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.24 (s, 6H, 2×$CH_3$), 2.30 (s, 3H, $CH_3$), 3.55 (s, 3H, $CH_3O$), 3.85 (s, 3H, $CH_3O$), 5.90 (d, $^3J$ = 3.0 Hz, 2H, $H_{Fur}$), 5.93 (s, 1H, CH), 6.01 (d, $^3J$ = 3.0 Hz, 2H, $H_{Fur}$), 6.67 (s, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 13.7 (2C), 16.7, 37.0, 56.3, 61.2, 106.4 (2C), 107.8 (2C), 113.3, 125.5, 126.5, 128.2, 150.5, 150.6 (2C), 151.0, 152.1 (2C) ppm; IR (KBr) $\nu_{max}$ = 2111, 1557, 1477, 1338, 1231, 1104, 1018, 948, 787 cm$^{-1}$; MS (EI, 70 eV): 367 ($M^+$, 15), 339 (100), 324 (90), 283 (20), 266 (37), 254 (21), 228 (17), 95 (51), 53 (30), 43 (40).




**1i**

**2,2'-[(2-Azido-3,4-dimethoxyphenyl)methanediyl]bis(5-methylfuran) (1i):** pale yellow solid; 3.00 g, 85% yield; mp 65–66 °C (petroleum ether); Found: C, 64.53; H, 5.29; N, 11.90%. $C_{19}H_{19}N_3O_4$ requires C, 64.58; H, 5.42; N, 11.89%; $R_f$ = 0.41 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, $CDCl_3$) δ = 2.25 (s, 6H, 2×$CH_3$), 3.85 (s, 3H, $CH_3O$), 3.91 (s, 3H, $CH_3O$), 5.64 (s, 1H, CH), 5.81 (d, $^3J$ = 3.0 Hz, 2H, $H_{Fur}$), 5.87 (d, $^3J$ = 3.0 Hz, 2H, $H_{Fur}$), 6.65 (d, $^3J$ = 8.7 Hz, 1H, $H_{Ar}$), 6.81 (d, $^3J$ = 8.7 Hz, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 13.8 (2C), 39.4, 56.1, 61.7, 106.2 (2C), 108.4 (2C), 108.7, 124.2, 125.1, 131.6, 143.4, 151.5 (2C), 152.3, 152.6 (2C) ppm; IR (KBr) $\nu_{max}$ = 2148, 1683, 1564, 1479, 1398, 1273, 1033, 970, 879, 763 cm$^{-1}$; MS (EI, 70 eV): 353 ($M^+$, 5), 325 (100), 252 (48), 210 (15), 196 (16), 115 (17), 58 (17), 43 (22).




**1j**

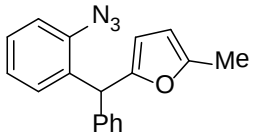
**2,2'-[(2-Azido-3,6-dimethoxyphenyl)methanediyl]bis(5-methylfuran) (1j):** pale orange solid; 2.93 g, 83% yield; mp 75–76 °C (isooctane); Found: C, 64.56; H, 5.43; N, 11.81%. $C_{19}H_{19}N_3O_4$ requires C, 64.58; H, 5.42; N, 11.89%; $R_f$ = 0.35 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.26 (s, 6H, 2×$CH_3$), 3.68 (s, 3H, $CH_3O$), 3.86 (s, 3H, $CH_3O$), 5.90 (d, $^3J$ = 3.0 Hz, 2H, $H_{Fur}$), 5.98 (d, $^3J$ = 3.0 Hz, 2H, $H_{Fur}$), 6.03 (s, 1H, CH), 6.67 (d, $^3J$ = 9.0 Hz, 1H, $H_{Ar}$), 6.79 (d, $^3J$ = 9.0 Hz, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 13.7 (2C), 36.4, 56.5, 56.8, 106.2 (2C), 107.4 (2C), 108.8, 111.0, 122.2, 128.2, 148.8, 150.4 (2C), 152.2 (2C), 152.6 ppm; IR (KBr) $\nu_{max}$ = 2114, 1598, 1479, 1260, 1074, 1020, 793 cm$^{-1}$; MS (EI, 70 eV): 353 ($M^+$, 13), 325 (100), 310 (36), 282 (19), 252 (42), 43 (15).

**Synthesis of 2-(2-azidobenzyl)furans**


| Entry | **1** | $R^2$ | $R^3$ | $R^5$ | $R^6$ |
|---|---|---|---|---|---|
| 1 | **k** | H | H | Me | Ph |
| 2 | **l** | H | H | 4-$ClC_6H_4$ | Ph |
| 3 | **m** | H | H | $CH_2$Pht | Ph |
| 4 | **n** | H | H | Me | 4-$FC_6H_4$ |
| 5 | **o** | H | Cl | Me | Ph |
| 6 | **p** | OMe | OMe | Me | Me |
| 7 | **q** | OMe | OMe | Me | Ph |
| 8 | **r** | $OCH_2CH_2O$ | | Me | Ph |

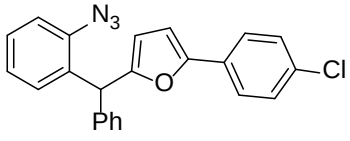
***General procedure for synthesis of compounds 1k-r (Method K)***

$BF_3 \cdot OEt_2$ (1.84 mL, 15 mmol) was added dropwise to cooled (5–10 °C) solution of 2-azidobenzyl alcohol **5** (10 mmol) and furan **4** (20 mmol) in $CH_2Cl_2$ (25 mL). The reaction mixture was stirred at the same temperature for 1–4 h until full conversion of starting 2-azidobenzyl alcohol (TLC control), then poured into cold water (50 mL) and $NaHCO_3$ was added until neutral reaction. The product was extracted with $CH_2Cl_2$ (2 × 50 mL). The combined organic fractions were dried with $CaCl_2$. The solvent was evaporated to dryness under reduced pressure. The resulting oil was dissolved in benzene and passed through small pad of silica gel. The product was recrystallized from specified solvent.




**1k**

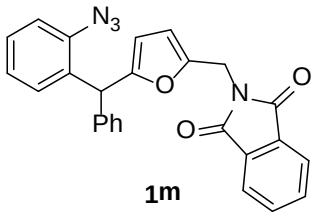
**2-[(2-Azidophenyl)(phenyl)methyl]-5-methylfuran (1k):** pale yellow solid; 2.37 g, 82% yield; mp 76–77 °C (petroleum ether); Found: C, 74.89; H, 5.15; N, 14.31%. $C_{18}H_{15}N_3O$ requires C, 74.72; H, 5.23; N, 14.52%; $R_f$ = 0.54 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.30 (s, 3H, $CH_3$), 5.75 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 5.76 (s, 1H, CH), 5.92 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 7.12–7.13 (m, 2H, $H_{Ar}$), 7.18–7.22 (m, 3H, $H_{Ar}$), 7.25–7.36 (m, 4H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 13.8, 44.9, 106.1, 109.5, 118.3, 124.8, 126.8, 128.2, 128.5 (2C), 128.9 (2C), 130.3, 133.4, 137.9, 141.3, 151.7, 154.2 ppm; IR (KBr) $\nu_{max}$ = 2126, 1581, 1487, 1301, 1218, 1167, 1023, 954, 794 cm$^{-1}$; MS (EI, 70 eV): 289 ($M^+$, 17), 261 (67), 246 (100), 218 (55), 190 (20), 165 (18), 109 (17), 77 (30), 43 (20).




**1l**

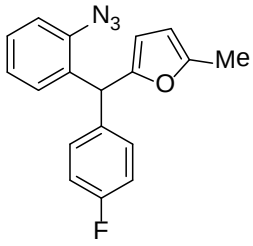
**2-[(2-Azidophenyl)(phenyl)methyl]-5-(4-chlorophenyl)furan (1l):** yellow solid; 3.04 g, 79% yield; mp 105–106 °C (petroleum ether); Found: C, 71.68; H, 4.29; N, 10.66%. $C_{23}H_{16}ClN_3O$ requires C, 71.60; H, 4.18; N, 10.89%; $R_f$ = 0.51 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 5.84 (s, 1H, CH), 5.96 (d, $^3J$ = 3.3 Hz, 1H, $H_{Fur}$), 6.58 (d, $^3J$ = 3.3 Hz, 1H, $H_{Fur}$), 7.09–7.15 (m, 2H, $H_{Ar}$), 7.19–7.23 (m, 3H, $H_{Ar}$), 7.25–7.36 (m, 6H, $H_{Ar}$), 7.52–7.55 (m, 2H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 45.1, 106.2, 111.1, 118.4, 124.9, 125.0 (2C), 127.0, 128.4, 128.6 (2C), 128.8 (2C), 128.9 (2C), 129.5, 130.3, 132.8, 133.0, 138.0, 140.9, 152.5, 156.1 ppm; IR (KBr) $\nu_{max}$ = 2134, 1579, 1482, 1449, 1302, 1092, 1029, 788 cm$^{-1}$; MS

(EI, 70 eV): 387/385 ($M^+$, 6/15), 359 (55), 328 (31), 261 (27), 217 (100), 165 (60), 139 (23), 111 (45), 51 (30), 43 (27).




**1m**

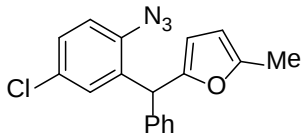
**2-({5-[(2-Azidophenyl)(phenyl)methyl]furan-2-yl}methyl)-1*H*-isoindole-1,3(2*H*)-dione (1m):** Pale orange solid; 3.21 g, 74% yield; mp 121–122 °C (benzene/petroleum ether); Found: C, 71.87; H, 4.25; N, 12.79%. $C_{26}H_{18}N_4O_3$ requires C, 71.88; H, 4.18; N, 12.90%; $R_f$ = 0.25 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.82 (s, 2H, $CH_2$), 5.68 (s, 1H, CH), 5.76 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.24 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 7.01–7.02 (m, 2H, $H_{Ar}$), 7.10–7.12 (m, 3H, $H_{Ar}$), 7.19–7.27 (m, 4H, $H_{Ar}$), 7.69–7.74 (m, 2H, $H_{Ar}$), 7.82–7.87 (m, 2H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 34.8, 44.9, 109.1, 109.8, 118.3, 123.5 (2C), 124.8, 126.8, 128.2, 128.4 (2C), 128.8 (2C), 130.2 (2C), 132.2, 133.0, 134.1 (2C), 137.9, 140.9, 148.8, 155.8, 167.6 (2C) ppm; IR (KBr) $\nu_{max}$ = 2145, 1732, 1605, 1551, 1402, 1300, 1159, 800, 732 $cm^{-1}$; MS (EI, 70 eV): 406 ($M^+$- $N_2$, 68), 404 (100), 259 (26), 246 (35), 217 (32), 176 (40), 160 (20), 122 (23), 95 (40), 43 (40).




**1n**

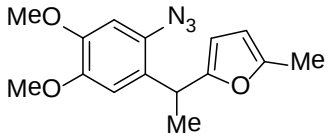
**2-[(2-Azidophenyl)(4-fluorophenyl)methyl]-5-methylfuran (1n):** pale yellow solid; 2.55 g, 83% yield; mp 90–91 °C (ethyl acetate/petroleum ether); Found: C, 70.15; H, 4.45; N, 13.59%. $C_{18}H_{14}FN_3O$ requires C, 70.35; H, 4.59; N, 13.67%; $R_f$ = 0.58 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, $CDCl_3$) δ = 2.27 (s, 3H, $CH_3$), 5.70 (s, 1H, CH), 5.72 (d, $^3J$ = 3.0 Hz, 1H, $H_{Fur}$), 5.90 (d, $^3J$ = 3.0 Hz, 1H, $H_{Fur}$), 6.97–7.02 (m, 2H, $H_{Ar}$), 7.06–7.08 (m, 1H, $H_{Ar}$), 7.09–7.15 (m, 3H, $H_{Ar}$), 7.17–7.19 (m, 1H, $H_{Ar}$), 7.30–7.33 (m, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 13.7, 44.3, 106.1, 109.6, 115.3 (d, 2C, $^2J_{CF}$ = 21.3 Hz), 118.4, 124.9, 128.3, 130.1, 130.4 (d, 2C, $^3J_{CF}$ = 7.9 Hz), 133.3, 137.1 (d, $^4J_{CF}$ = 3.2 Hz), 138.0, 151.9, 154.0, 161.8 (d, $^1J_{CF}$ = 245.1 Hz) ppm; IR (KBr) $\nu_{max}$ = 2140, 1674, 1514, 1300, 1166, 1045, 941, 796 $cm^{-1}$; MS

(EI, 70 eV): 307 ($M^+$, 8), 279 (100), 264 (63), 236 (98), 207 (18), 183 (35), 179 (40), 120 (19), 108 (23), 93 (61), 65 (38), 53 (39), 43 (71).



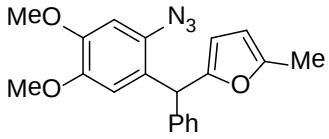

**1o**

**2-[(2-Azido-5-chlorophenyl)(phenyl)methyl]-5-methylfuran (1o):** pale cream solid; 2.85 g, 88% yield; mp 86–87 °C (ethyl acetate/petroleum ether); Found: C, 66.68; H, 4.42; N, 12.81%. $C_{18}H_{14}ClN_3O$ requires C, 66.77; H, 4.36; N, 12.98%; $R_f$ = 0.54 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, $CDCl_3$) δ = 2.28 (s, 3H, $CH_3$), 5.67 (s, 1H, CH), 5.74 (d, $^3J$ = 3.1 Hz, 1H, $H_{Fur}$), 5.90 (d, $^3J$ = 3.1 Hz, 1H, $H_{Fur}$), 7.07 (d, $^4J$ = 2.5 Hz, 1H, $H_{Ar}$), 7.08 (d, $^3J$ = 8.5 Hz, 1H, $H_{Ar}$), 7.14–7.17 (m, 2H, $H_{Ar}$), 7.24–7.28 (m, 2H, $H_{Ar}$), 7.30–7.35 (m, 2H, $H_{Ar}$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 13.8, 44.9, 106.2, 109.8, 119.5, 127.1, 128.2, 128.6 (2C), 128.9 (2C), 130.2, 130.3, 135.2, 136.7, 140.5, 152.0, 153.3 ppm; IR (KBr) $\nu_{max}$ = 2120, 1560, 1477, 1406, 1296, 1177, 1110, 1022, 898, 810, 792 $cm^{-1}$; MS (EI, 70 eV): 325/323 ($M^+$, 4/12), 297/295 (31/89), 282/280 (33/100), 267 (15), 252 (31), 217 (75), 163 (20), 101 (21), 95 (51), 51 (42), 43 (24).



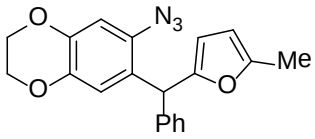

**1p**

**2-[1-(2-Azido-4,5-dimethoxyphenyl)ethyl]-5-methylfuran (1p):** yellow solid; 2.41 g, 84% yield; mp 57–58 °C (petroleum ether); Found: C, 62.96; H, 6.03; N, 14.43%. $C_{15}H_{17}N_3O_3$ requires C, 62.71; H, 5.96; N, 14.62%; $R_f$ = 0.53 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, $CDCl_3$) δ = 1.47 (d, $^3J$ = 7.2 Hz, 3H, $CH_3$), 2.24 (s, 3H, $CH_3$), 3.78 (s, 3H, $CH_3O$), 3.90 (s, 3H, $CH_3O$), 4.38 (q, $^3J$ = 7.2 Hz, 1H, CH), 5.87 (d, $^3J$ = 3.0 Hz, 1H, $H_{Fur}$), 5.93 (d, $^3J$ = 3.0 Hz, 1H, $H_{Fur}$), 6.62 (s, 1H, $H_{Ar}$), 6.66 (s, 1H, $H_{Ar}$) ppm; $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 13.7, 19.9, 32.9, 56.2, 56.3, 102.1, 105.9, 106.0, 111.6, 128.1, 129.1, 146.8, 148.6, 151.0, 156.6 ppm; IR (KBr) $\nu_{max}$ = 2107, 1608, 1516, 1323, 1245, 1090, 851, 782 $cm^{-1}$; MS (EI, 70 eV): 287 ($M^+$, 60), 259 (32), 244 (100), 216 (45), 91 (10), 43 (15).




**1q**

**2-[(2-Azido-4,5-dimethoxyphenyl)(phenyl)methyl]-5-methylfuran (1q):** pale yellow solid; 2.55 g, 73% yield; mp 96–97 °C (ethyl acetate/petroleum ether); Found: C, 68.99; H, 5.29; N, 12.05%. $C_{20}H_{19}N_3O_3$ requires C, 68.75; H, 5.48; N, 12.03%; $R_f$ = 0.51 (acetone/petroleum ether = 1:2); $^1$H NMR (360 MHz, $CDCl_3$) δ = 2.26 (s, 3H, $CH_3$), 3.73 (s, 3H, $CH_3O$), 3.91 (s, 3H, $CH_3O$), 5.67 (s, 1H, CH), 5.75 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 5.88 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.62 (s, 1H, $H_{Ar}$), 6.67 (s, 1H, $H_{Ar}$), 7.14–7.16 (m, 2H, $H_{Ph}$), 7.20–7.32 (m, 3H, $H_{Ph}$) ppm; $^{13}$C NMR (90 MHz, $CDCl_3$) δ = 13.8, 44.5, 56.3, 56.4, 102.1, 106.0, 109.3, 113.5, 125.4, 126.7, 128.4 (2C), 128.7 (2C), 129.8, 141.6, 146.5, 149.0, 151.6, 154.3 ppm; IR (KBr) $\nu_{max}$ = 2113, 1605, 1512, 1449, 1396, 1250, 1209, 1078, 1020, 785 cm$^{-1}$; MS (EI, 70 eV): 349 ($M^+$, 28), 321 (100), 306 (58), 278 (37), 262 (28), 247 (42), 232 (20), 139 (20), 77 (15), 59 (15), 43 (28).



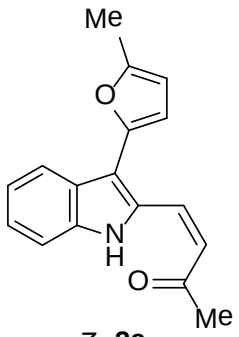

**1r**

**6-Azido-7-[(5-methylfuran-2-yl)(phenyl)methyl]-2,3-dihydro-1,4-benzodioxine (1r):** yellow solid; 2.39 g, 69% yield; mp 99–100 °C (ethyl acetate/petroleum ether); Found: C, 69.25; H, 4.81; N, 12.27%. $C_{20}H_{17}N_3O_3$ requires C, 69.15; H, 4.93; N, 12.10%; $R_f$ = 0.49 (acetone/petroleum ether = 1:2); $^1$H NMR (360 MHz, $CDCl_3$) δ = 2.26 (s, 3H, $CH_3$), 4.20–4.23 (m, 2H, $CH_2O$), 4.23–4.26 (m, 2H, $CH_2O$), 5.59 (s, 1H, CH), 5.71 (d, $^3J$ = 3.0 Hz, 1H, $H_{Fur}$), 5.86 (d, $^3J$ = 3.0 Hz, 1H, $H_{Fur}$), 6.60 (s, 1H, $H_{Ar}$), 6.68 (s, 1H, $H_{Ar}$), 7.14–7.17 (m, 2H, $H_{Ph}$), 7.20–7.31 (m, 3H, $H_{Ph}$) ppm; $^{13}$C NMR (90 MHz, $CDCl_3$) δ = 13.8, 44.5, 64.4, 64.6, 106.1, 107.2, 109.4, 118.8, 126.7, 126.8, 128.4 (2C), 128.8 (2C), 130.9, 140.8, 141.5, 143.2, 151.6, 154.3 ppm; IR (KBr) $\nu_{max}$ = 2116, 1585, 1503, 1323, 1279, 1254, 1151, 1069, 1016, 739 cm$^{-1}$; MS (EI, 70 eV): 347 ($M^+$, 25), 319 (47), 304 (20), 276 (100), 220 (40), 43 (17).

***Thermolysis 1a in xylene***

A solution of compound **1a** (1.47 g, 5 mmol) in *para*-xylene (15–20 mL) was heated under reflux for 14 h (TLC control). Then the solution was cooled; the formed precipitate of *trans*-**2a** was filtered and recrystallized from the specified solvent. Mother liquors were combined, the solvent was evaporated to dryness under reduced pressure. The residue was subjected to column

chromatography on silica gel with benzene as an eluent affording additional quantity of *trans*-**2a** as well as *cis*-**2a** (32%). The total yield of (*E*)-**2a** is 52%.



(*Z*)-**2a**

**(3*Z*)-4-[3-(5-Methylfuran-2-yl)-1*H*-indol-2-yl]but-3-en-2-one ((*Z*)-2a):** red solid; 0.42 g, 32% yield; mp 101–102 °C (petroleum ether); Found: C, 76.82; H, 5.58; N, 5.22%. $C_{17}H_{15}NO_2$ requires C, 76.96; H, 5.70; N, 5.28%; $R_f$ = 0.48 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, DMSO-d6) δ = 2.39 (s, 3H, $CH_3$), 2.40 (s, 3H, $CH_3$), 6.29 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.44 (d, $^3J$ = 12.8 Hz, 1H, CH=), 6.68 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 7.13–7.17 (m, 1H, $H_{Ind}$), 7.30–7.34 (m, 1H, $H_{Ind}$), 7.35 (d, $^3J$ = 12.8 Hz, 1H, CH=), 7.61–7.64 (m, 1H, $H_{Ind}$), 7.88–7.90 (m, 1H, $H_{Ind}$), 12.38 (s, 1H, NH) ppm; $^{13}$C NMR (100 MHz, DMSO-d6) 13.5, 31.7, 108.0, 109.6, 112.5, 113.0, 120.8, 120.9, 122.4, 124.6, 125.6, 129.7, 130.8, 135.8, 147.1, 151.7, 200.0 ppm; IR (KBr) $\nu_{max}$ = 3115, 1665, 1555, 1441, 1337, 1273, 1177, 1043, 779, 735 cm$^{-1}$; MS (EI, 70 eV): 265 ($M^+$, 100), 250 (30), 222 (50), 207 (32), 194 (70), 178 (26), 43 (42).

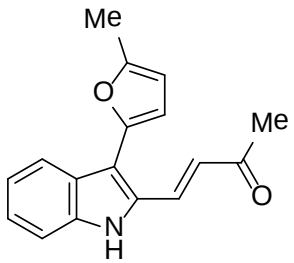
***Thermolysis 1a in dodecane***

Compound **1a** (0.88 g, 3 mmol) was added in one portion to the refluxing dodecane (10 mL). The reaction mixture was refluxed for 3 min until gas evolution was ceased. The reaction mixture was cooled. The formed suspension was transferred on a filter with a pad of silica gel (20 g). Dodecane was washed out with petroleum ether, (*Z*)-**2** was eluted with $CH_2Cl_2$, then (*E*)-**2** was eluted with acetone. Solvents were evaporated affording pure products. Yields of (*E*)-**2a** and (*Z*)-**2a** are 26% and 60%, respectively.

***General procedure for synthesis of (E)-β-(2-indolyl)-α,β-unsaturated ketones 2***

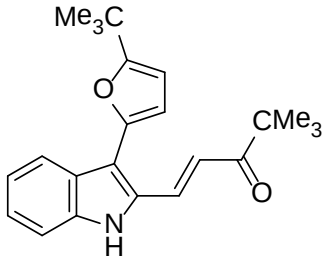
Compound **1** (3 mmol) was added in one portion to the refluxing dodecane (10-15 mL). The reaction mixture was refluxed for 2–5 min until gas evolution was ceased and then it was cooled. To the formed suspension DMF (15 mL) and DMAP (0.15 mmol) was added. The reaction mixture was heated at 160 °C for the specified time and cooled to room temperature. Solvent was

evaporated in vacuo; the residue was washed with EtOH and recrystallized from the specified solvent.



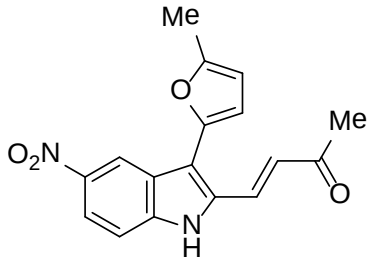

(*E*)-**2a**

**(3*E*)-4-[3-(5-Methylfuran-2-yl)-1*H*-indol-2-yl]but-3-en-2-one ((*E*)-2a)**[S27]**:** dark yellow solid; 0.67 g, 84% yield; mp 214–215 °C (1,4-dioxane); $R_f$ = 0.24 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, DMSO-d6) δ = 2.36 (s, 3H, $CH_3$), 2.41 (s, 3H, $CH_3$), 6.28 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.70 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.84 (d, $^3J$ = 16.2 Hz, 1H, CH=), 7.11–7.14 (m, 1H, $H_{Ind}$), 7.27–7.31 (m, 1H, $H_{Ind}$), 7.41–7.43 (m, 1H, $H_{Ind}$), 7.86–7.88 (m, 1H, $H_{Ind}$), 8.01 (d, $^3J$ = 16.2 Hz, 1H, CH=), 11.75 (s, 1H, NH) ppm; $^{13}$C NMR (100 MHz, DMSO-d6) δ = 13.4, 27.2, 107.9, 108.8, 111.7, 112.0, 120.4, 120.8, 124.9, 125.0, 125.7, 129.5, 131.8, 137.8, 147.4, 151.3, 197.4 ppm.



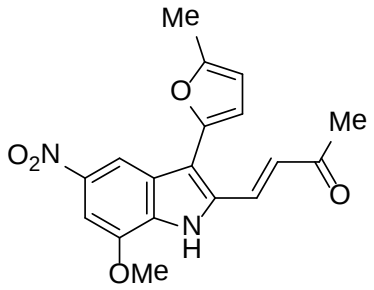

(*E*)-**2b**

**(1*E*)-1-[3-(5-*tert*-Butylfuran-2-yl)-1*H*-indol-2-yl]-4,4-dimethylpent-1-en-3-one ((*E*)-2b)**[S27]**:** orange solid; 1.00 g, 95% yield; mp 187–188 °C (benzene); $R_f$ = 0.39 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, DMSO-d6) δ = 1.20 (s, 9H, 3×$CH_3$), 1.36 (s, 9H, 3×$CH_3$), 6.23 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.65 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 7.11–7.15 (m, 1H, $H_{Ind}$), 7.28–7.32 (m, 1H, $H_{Ind}$), 7.43–7.45 (m, 1H, $H_{Ind}$), 7.44 (d, $^3J$ = 15.6 Hz, 1H, CH=), 7.83–7.87 (m, 1H, $H_{Ind}$), 8.20 (d, $^3J$ = 15.6 Hz, 1H, CH=), 11.73 (s, 1H, NH) ppm; $^{13}$C NMR (100 MHz, DMSO-d6) δ = 26.0 (3C), 28.9 (3C), 32.3, 42.7, 104.3, 108.0, 111.5, 111.9, 119.8, 120.4, 120.6, 124.7, 125.0, 130.2, 130.8, 137.6, 147.2, 162.8, 202.7 ppm.



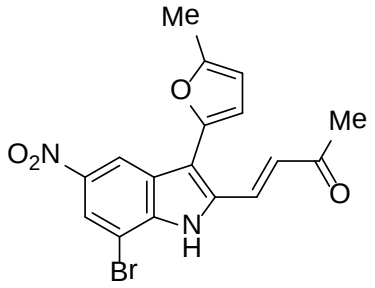

(*E*)-**2c**

**(3*E*)-4-[3-(5-Methylfuran-2-yl)-5-nitro-1*H*-indol-2-yl]but-3-en-2-one ((*E*)-2c):** orange solid; 0.89 g, 96% yield; mp 299–300 °C decomp. (1,4-dioxane); Found: C, 65.98; H, 4.60; N, 9.06%. $C_{17}H_{14}N_2O_4$ requires C, 65.80; H, 4.55; N, 9.03%; $R_f$ = 0.16 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, DMSO-d6) δ = 2.38 (s, 3H, $CH_3$), 2.42 (s, 3H, $CH_3$), 6.32 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.75 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.83 (d, $^3J$ = 16.4 Hz, 1H, CH=), 7.50 (d, $^3J$ = 8.8 Hz, 1H, $H_{Ind}$), 7.85 (d, $^3J$ = 16.4 Hz, 1H, CH=), 8.10 (dd, $^3J$ = 8.8 Hz, $^4J$ = 2.2 Hz, 1H, $H_{Ind}$), 8.64 (d, $^4J$ = 2.2 Hz, 1H, $H_{Ind}$), 12.35 (s, 1H, NH) ppm; $^{13}$C NMR (100 MHz, DMSO) δ = 13.4, 27.3, 108.2, 109.8, 112.1, 113.1, 117.5, 119.8, 123.9, 127.5, 130.4, 132.4, 140.4, 141.4, 145.9, 152.2, 197.4 ppm; IR (KBr) $\nu_{max}$ = 3271, 1641, 1603, 1477, 1335, 1273, 1252, 1080, 962, 874, 741 cm$^{-1}$; MS (EI, 70 eV): 310 ($M^+$, 100), 295 (15), 263 (17), 250 (15), 221 (19), 180 (12), 101 (30), 59 (45), 43 (57).



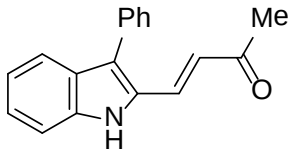

(*E*)-**2d**

**(3*E*)-4-[7-Methoxy-3-(5-methylfuran-2-yl)-5-nitro-1*H*-indol-2-yl]but-3-en-2-one ((*E*)-2d):** orange solid; 0.91 g, 89% yield; mp 277–278 decomp. °C (xylene); Found: C, 63.47; H, 4.72; N, 8.13%. $C_{18}H_{16}N_2O_5$ requires C, 63.53; H, 4.74; N, 8.23%; $R_f$ = 0.16 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, DMSO-d6) δ = 2.35 (s, 3H, $CH_3$), 2.42 (s, 3H, $CH_3$), 4.08 (s, 3H, $CH_3O$), 6.33 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.73 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 7.19 (d, $^3J$ = 16.2 Hz, 1H, CH=), 7.61 (d, $^4J$ = 1.8 Hz, 1H, $H_{Ind}$), 7.82 (d, $^3J$ = 16.2 Hz, 1H, CH=), 8.35 (d, $^4J$ = 1.8 Hz, 1H, $H_{Ind}$), 12.45 (s, 1H, NH) ppm; $^{13}$C NMR (100 MHz, DMSO) δ = 13.4, 27.5, 56.1, 99.4, 108.2, 109.9, 110.7, 113.9, 124.3, 127.9, 130.1, 131.3, 132.1, 142.2, 145.7, 145.8, 152.2, 197.6 ppm; IR (KBr) $\nu_{max}$ = 3285, 1668, 1614, 1528, 1485, 1338, 1265, 1076, 1026, 968, 810, 773 cm$^{-1}$; MS (EI, 70 eV): 340 ($M^+$, 100), 325 (30), 311 (20), 297 (23), 251 (30), 236 (16), 208 (28), 57 (13), 43 (22).



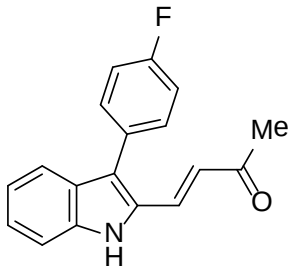

(*E*)-**2e**

**(3*E*)-4-[7-bromo-3-(5-methylfuran-2-yl)-5-nitro-1*H*-indol-2-yl]but-3-en-2-one ((*E*)-2e):** orange solid; 1.05 g, 90% yield; mp 302–303 °C (xylene); Found: C, 52.62; H, 3.54; N, 7.27%. $C_{17}H_{13}BrN_2O_4$ requires C, 52.46; H, 3.37; N, 7.20%; $R_f$ = 0.25 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, DMSO-d6) δ = 2.37 (s, 3H, $CH_3$), 2.42 (s, 3H, $CH_3$), 6.33 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 6.73 (d, $^3J$ = 3.2 Hz, 1H, $H_{Fur}$), 7.29 (d, $^3J$ = 16.2 Hz, 1H, CH=), 7.77 (d, $^3J$ = 16.2 Hz, 1H, CH=), 8.25 (d, $^4J$ = 1.8 Hz, 1H, $H_{Ind}$), 8.59 (d, $^4J$ = 1.8 Hz, 1H, $H_{Ind}$), 12.15 (s, 1H, NH) ppm; $^{13}$C NMR (150 MHz, DMSO-d6) δ = 13.3, 27.6, 104.1, 108.3, 110.5, 114.2, 116.6, 121.9, 124.8, 129.1, 129.3, 133.5, 138.8, 141.6, 145.2, 152.5, 197.6 ppm; IR (KBr) $\nu_{max}$ = 3289, 1672, 1641, 1530, 1479, 1337, 1263, 1082, 970, 770 cm$^{-1}$; MS (EI, 70 eV): 390/388 ($M^+$, 99/100), 347/345 (23/24), 300/298 (20/20), 271 (18), 257 (10), 220 (10), 191 (20), 43 (35).



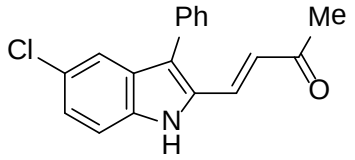

(*E*)-**2f**

**(3*E*)-4-(3-phenyl-1*H*-indol-2-yl)but-3-en-2-one ((*E*)-2f):** yellow solid; 0.66 g, 84% yield; mp 218–219 °C (1,4-dioxane); Found: C, 82.92; H, 5.77; N, 5.28%. $C_{18}H_{15}NO$ requires C, 82.73; H, 5.79; N, 5.36%; $R_f$ = 0.33 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, DMSO-d6) δ = 2.28 (s, 3H, $CH_3$), 6.89 (d, $^3J$ = 16.2 Hz, 1H, CH=), 7.06–7.11 (m, 1H, $H_{Ar}$), 7.27–7.31 (m, 1H, $H_{Ar}$), 7.40–7.60 (m, 7H, $H_{Ar}$), 7.48 (d, $^3J$ = 16.2 Hz, 1H, CH=), 11.80 (s, 1H, NH) ppm; $^{13}$C NMR (100 MHz, DMSO-d6) δ = 27.7, 111.7, 119.7, 120.3, 122.8, 124.9, 125.3, 126.7, 127.0, 128.9 (2C), 129.8 (2C), 130.1, 131.1, 133.5, 137.6, 197.1 ppm; IR (KBr) $\nu_{max}$ = 3310, 1640, 1604, 1489, 1359, 1261, 1187, 1020, 962, 773 cm$^{-1}$; MS (EI, 70 eV): 261 ($M^+$, 64), 246 (18), 217 (100), 184 (10), 43 (25).



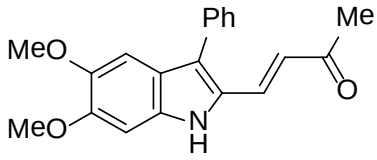

(*E*)-**2g**

**(3*E*)-4-[3-(4-fluorophenyl)-1*H*-indol-2-yl]but-3-en-2-one ((*E*)-2g):** yellow solid; 0.73 g, 87% yield; mp 209–210 °C (xylene); Found: C, 69.67; H, 5.24; N, 14.24%. $C_{18}H_{14}FNO$ requires C, 77.40; H, 5.05; N, 5.01%; $R_f$ = 0.28 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, DMSO-d6) δ = 2.28 (s, 3H, $CH_3$), 6.89 (d, $^3J$ = 16.1 Hz, 1H, CH=), 7.06–7.11 (m, 1H, $H_{Ar}$), 7.27–7.31 (m, 1H, $H_{Ar}$), 7.35–7.40 (m, 2H, $H_{Ar}$), 7.44 (d, $^3J$ = 16.1 Hz, 1H, CH=), 7.44–7.47 (m, 1H, $H_{Ar}$), 7.51–7.57 (m, 3H, $H_{Ar}$), 11.81 (s, 1H, NH) ppm; $^{13}$C NMR (150 MHz, DMSO-d6) δ = 27.6, 111.7, 115.8 (d, 2C, $^2J_{CF}$ = 21.3 Hz), 119.6, 120.4, 121.6, 124.9, 125.4, 126.7, 129.8 (d, $^4J_{CF}$ = 3.1 Hz), 130.2, 130.9, 131.7 (d, 2C, $^3J_{CF}$ = 8.1 Hz), 137.5, 161.4 (d, $^1J_{CF}$ = 244.4 Hz), 197.2 ppm; IR (KBr) $\nu_{max}$ = 3323, 1674, 1620, 1531, 1361, 1274, 1155, 1022, 840, 736 cm$^{-1}$; MS (EI, 70 eV): 279 ($M^+$, 85), 264 (40), 236 (100), 207 (14), 91 (20), 43 (35).



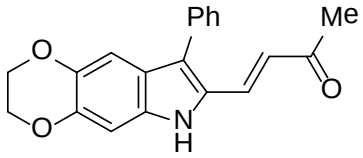

(*E*)-**2h**

**(3*E*)-4-(5-chloro-3-phenyl-1*H*-indol-2-yl)but-3-en-2-one ((*E*)-2h):** yellow solid; 0.80 g, 90% yield; mp 233–234 °C (toluene); Found: C, 73.08; H, 4.72; N, 4.81%. $C_{18}H_{14}ClNO$ requires C, 73.10; H, 4.77; N, 4.74%; $R_f$ = 0.28 (acetone/petroleum ether = 1:2); $^1$H NMR (400 MHz, DMSO-d6) δ = 2.28 (s, 3H, $CH_3$), 6.90 (d, $^3J$ = 16.2 Hz, 1H, CH=), 7.28 (dd, $^3J$ = 8.7 Hz, $^4J$ = 1.9 Hz, 1H, $H_{Ar}$), 7.45 (d, $^3J$ = 16.2 Hz, 1H, CH=), 7.40–7.50 (m, 4H, $H_{Ar}$), 7.52–7.58 (m, 3H, $H_{Ar}$), 12.02 (s, 1H, NH) ppm; $^{13}$C NMR (100 MHz, DMSO-d6) δ = 27.8, 113.4, 118.7, 122.0, 124.8, 124.9, 126.2, 127.3, 127.7, 129.1 (2C), 129.8 (2C), 130.7, 131.6, 132.8, 135.9, 197.3 ppm; IR (KBr) $\nu_{max}$ = 2924, 1641, 1607, 1468, 1379, 1275, 1038, 706 cm$^{-1}$; MS (EI, 70 eV): 297/295 ($M^+$, 16/47), 280 (25), 252 (25), 217 (100), 101 (20), 43 (7).




(*E*)-**2i**

**(3*E*)-4-(5,6-dimethoxy-3-phenyl-1*H*-indol-2-yl)but-3-en-2-one ((*E*)-2i):** dark yellow solid; 0.80 g, 83% yield; mp 214–215 °C (acetonitrile); Found: C, 74.76; H, 6.03; N, 4.36%. $C_{20}H_{19}NO_3$ requires C, 74.75; H, 5.96; N, 4.36%; $R_f$ = 0.15 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, DMSO-d6) δ = 2.24 (s, 3H, $CH_3$), 3.74 (s, 3H, $CH_3O$), 3.85 (s, 3H, $CH_3O$), 6.76 (d, $^3J$ = 16.0 Hz, 1H, CH=), 6.91 (s, 1H, $H_{Ind}$), 6.99 (s, 1H, $H_{Ind}$), 7.38–7.41 (m, 1H, $H_{Ph}$), 7.43 (d, $^3J$ = 16.0 Hz, 1H, CH=), 7.49–7.50 (m, 2H, $H_{Ph}$), 7.53–7.55 (m, 2H, $H_{Ph}$), 11.57 (s, 1H, NH) ppm; $^{13}$C NMR (150 MHz, DMSO-d6) δ = 27.5, 55.6, 55.7, 94.2, 100.8, 119.6, 123.0, 123.3, 126.9, 128.6, 129.0 (2C), 129.7 (2C), 131.4, 132.9, 133.8, 145.7, 149.7, 196.9 ppm; IR (KBr) $\nu_{max}$ = 3364, 1643, 1506, 1366, 1287, 1026, 835, 777 cm$^{-1}$; MS (EI, 70 eV): 321 ($M^+$, 100), 306 (36), 278 (30), 262 (18), 247 (28), 233 (20), 220 (18), 204 (18), 165 (15), 43 (10).




(*E*)-**2j**

**(3*E*)-4-(8-phenyl-2,3-dihydro-6*H*-[1,4]dioxino[2,3-*f*]indol-7-yl)but-3-en-2-one ((*E*)-2j):** dark red solid; 0.85 g, 89% yield; mp 282–283 °C (butyl acetate); Found: C, 75.13; H, 5.39; N, 4.34%. $C_{20}H_{17}NO_3$ requires C, 75.22; H, 5.37; N, 4.39%; $R_f$ = 0.19 (acetone/petroleum ether = 1:2); $^1$H NMR (600 MHz, DMSO-d6) δ = 2.24 (s, 3H, $CH_3$), 4.21–4.22 (m, 2H, $CH_2$), 4.27–4.28 (m, 2H, $CH_2$), 6.76 (d, $^3J$ = 16.0 Hz, 1H, CH=), 6.86 (s, 1H, $H_{Ind}$), 6.96 (s, 1H, $H_{Ind}$), 7.38–7.40 (m, 1H, $H_{Ph}$), 7.41 (d, $^3J$ = 16.0 Hz, 1H, CH=), 7.44–7.46 (m, 2H, $H_{Ph}$), 7.51–7.54 (m, 2H, $H_{Ph}$), 11.45 (s, 1H, NH) ppm; $^{13}$C NMR (150 MHz, DMSO-d6) δ = 27.6, 63.8, 64.3, 98.1, 105.3, 121.3, 122.6, 123.9, 126.9, 128.9 (2C), 129.6 (2C), 129.8, 131.1, 133.3, 133.6, 139.7, 143.5, 197.0 ppm; IR (KBr) $\nu_{max}$ = 3339, 1612, 1368, 1294, 1198, 1074, 976, 870 cm$^{-1}$; MS (EI, 70 eV): 319 ($M^+$, 100), 304 (15), 276 (42), 220 (33), 191 (10), 165 (10), 139 (15), 43 (10).

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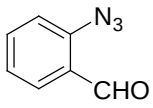
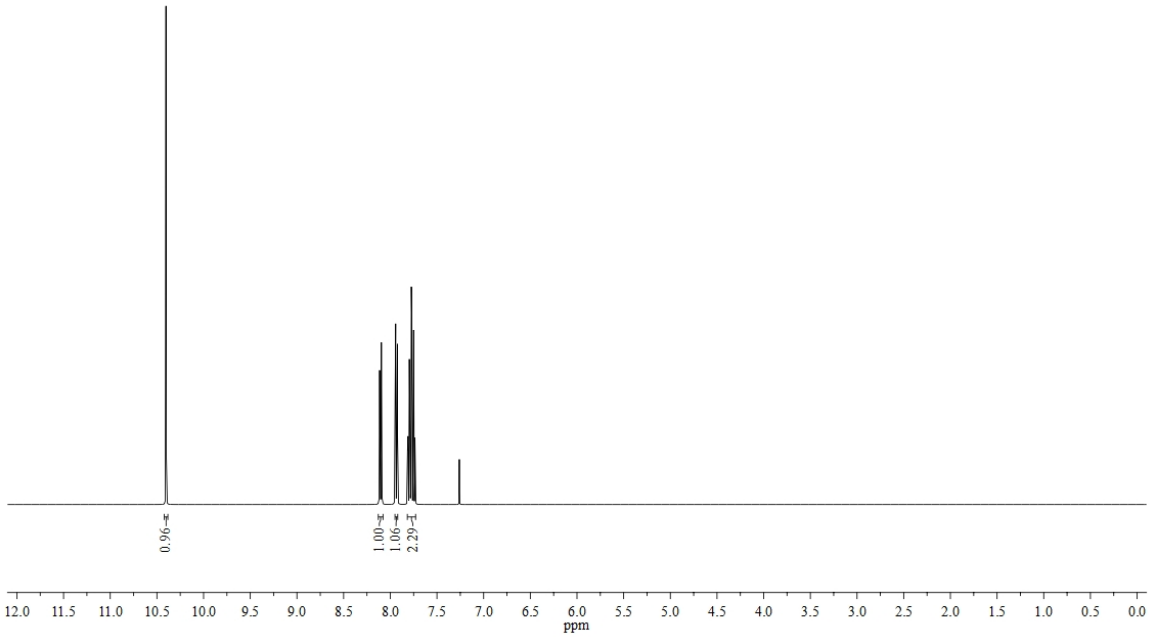

N3
CHO

**3a**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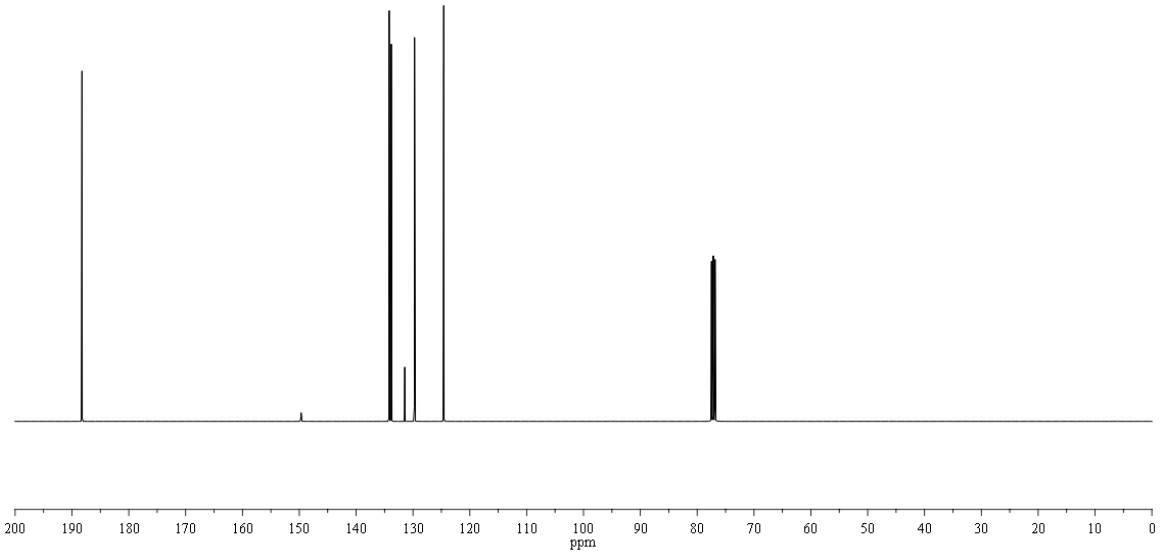
1.00
1.06
2.29
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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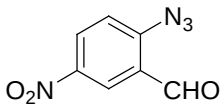
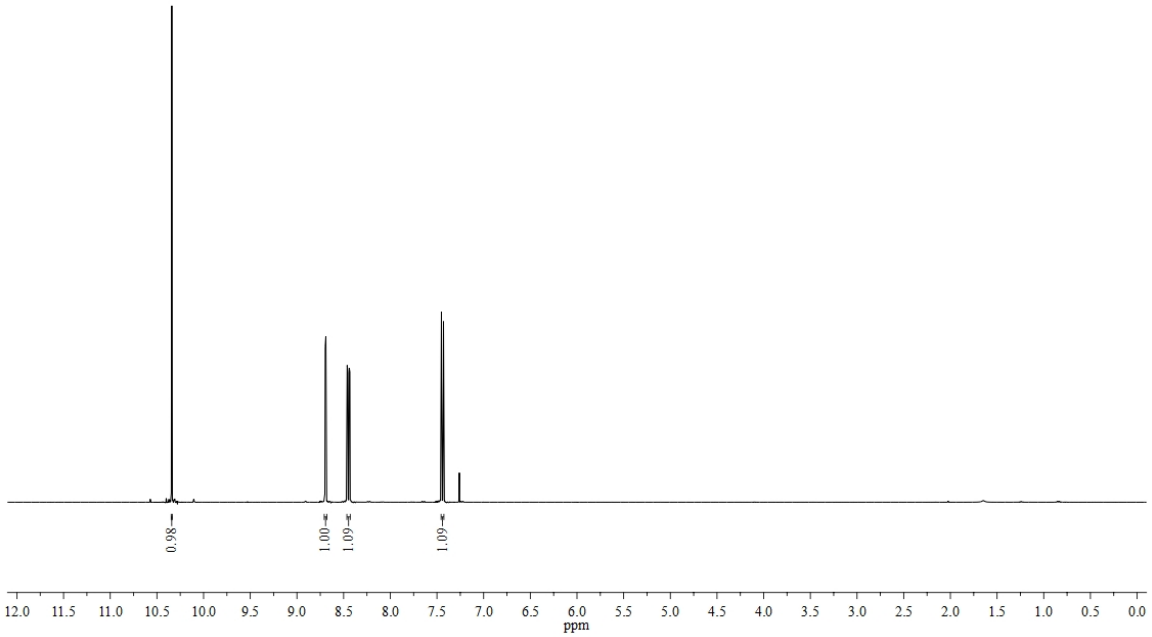
ppm


N3
O2N
CHO

**3b**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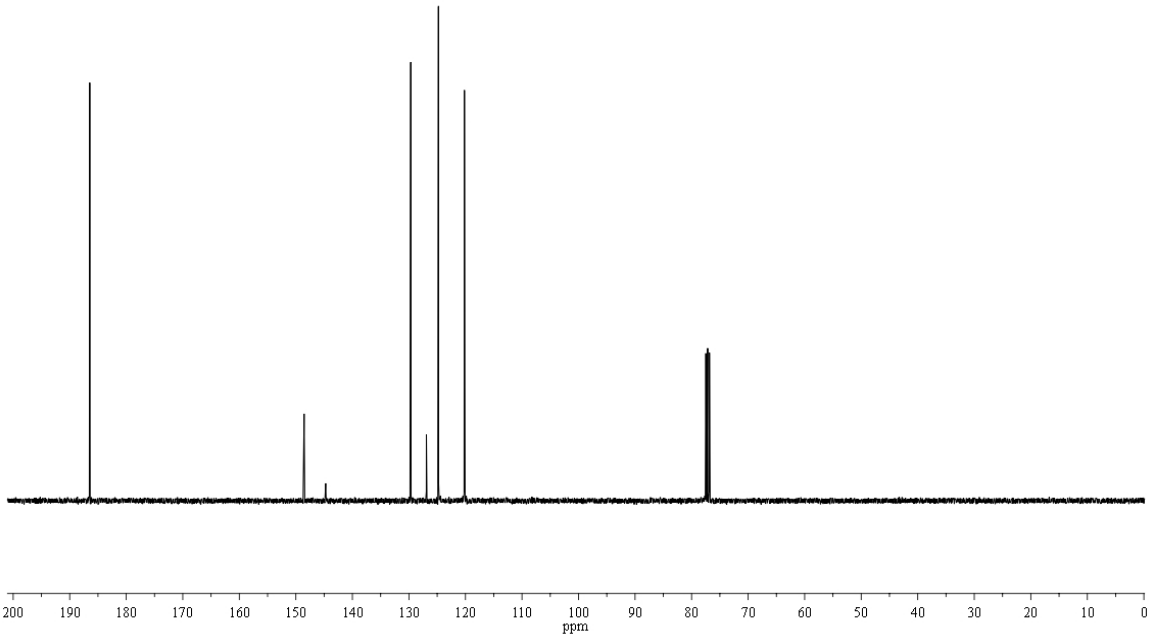
1.00
1.09
1.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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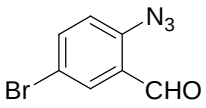
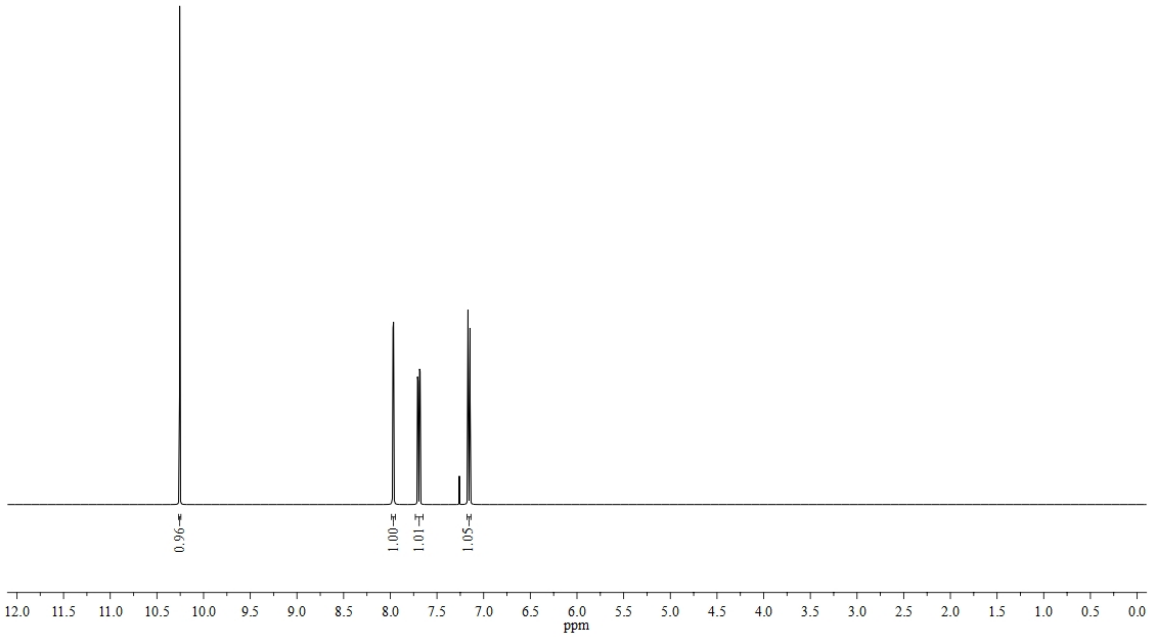
ppm


N3
Br
CHO

**3c**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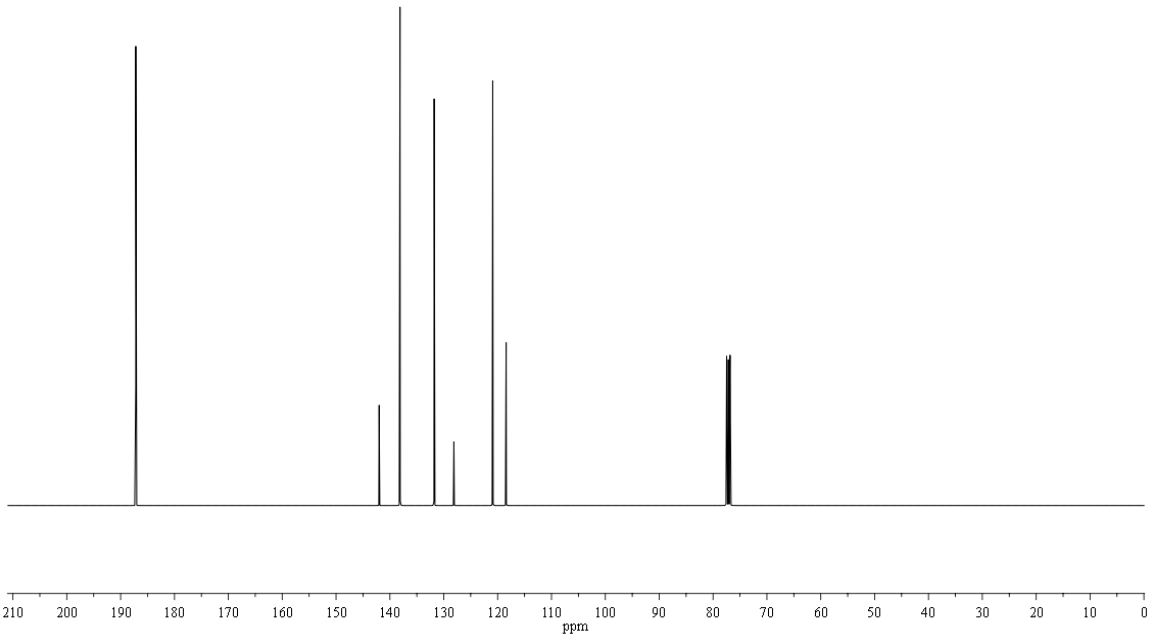
1.00
1.01
1.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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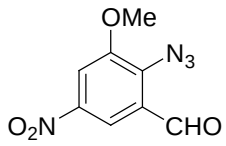
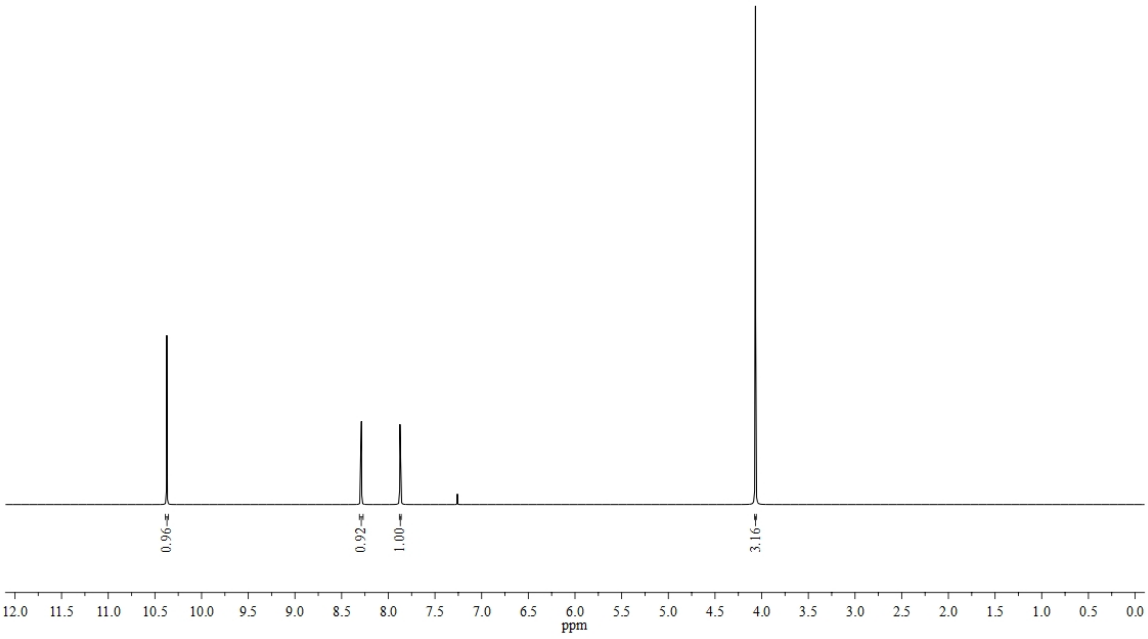
ppm


OMe
N3
O2N
CHO

**3d**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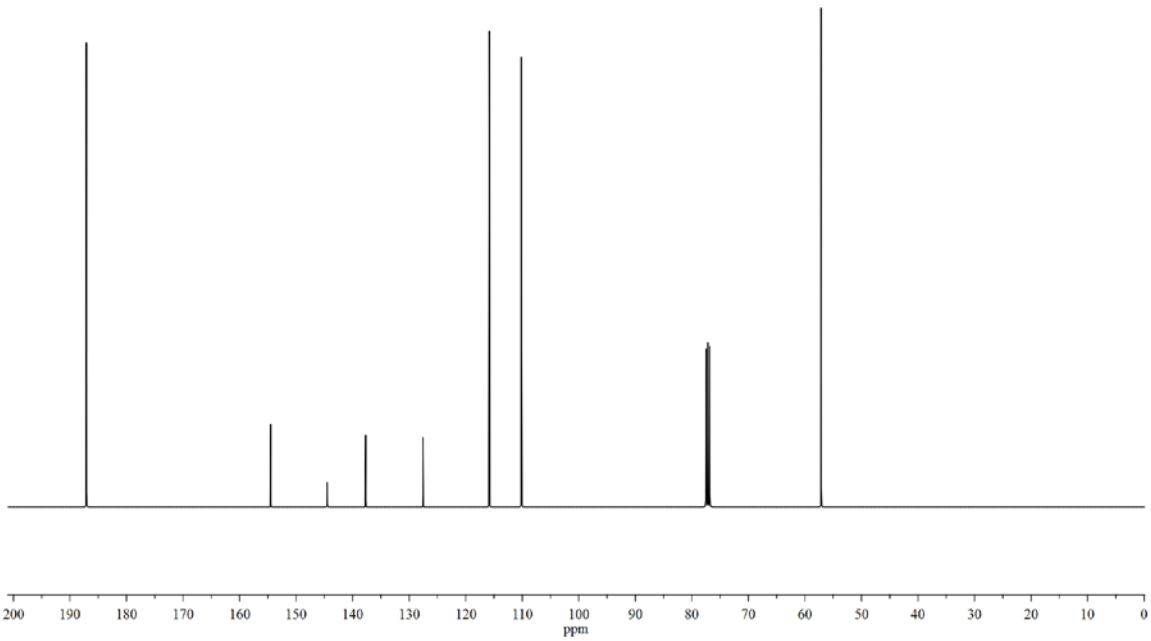
0.92
1.00
3.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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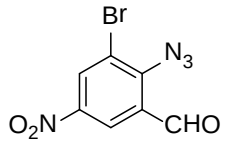
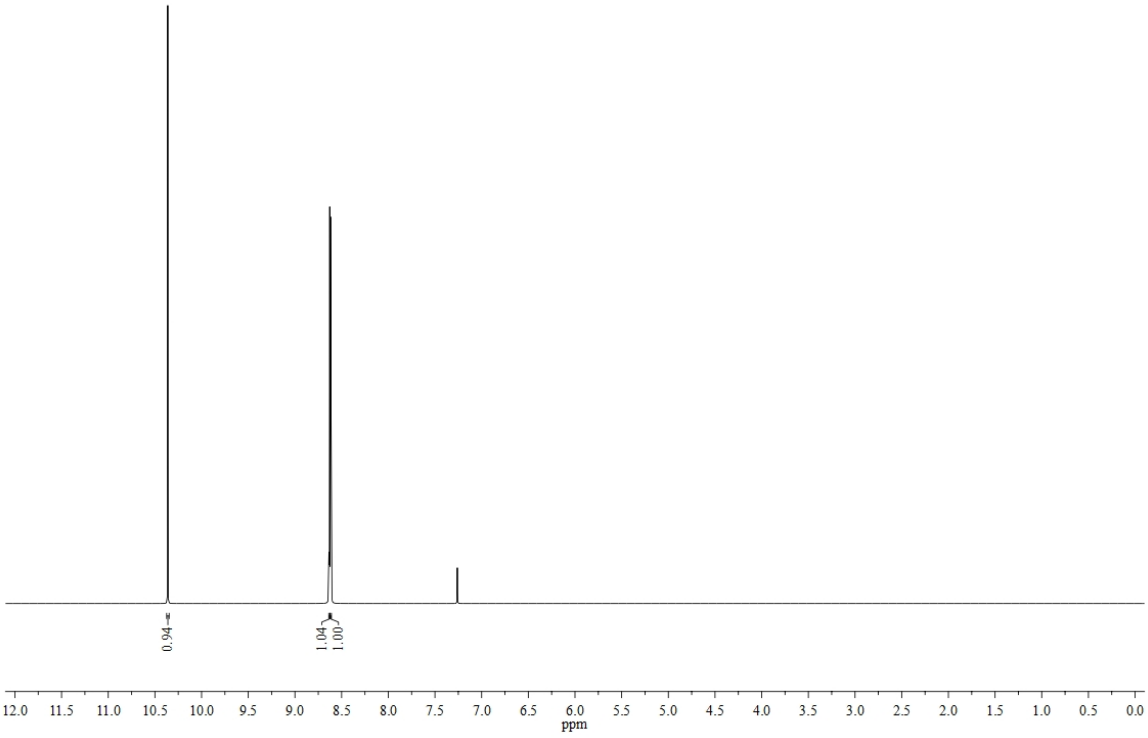
ppm


Br
N3
O2N
CHO

**3e**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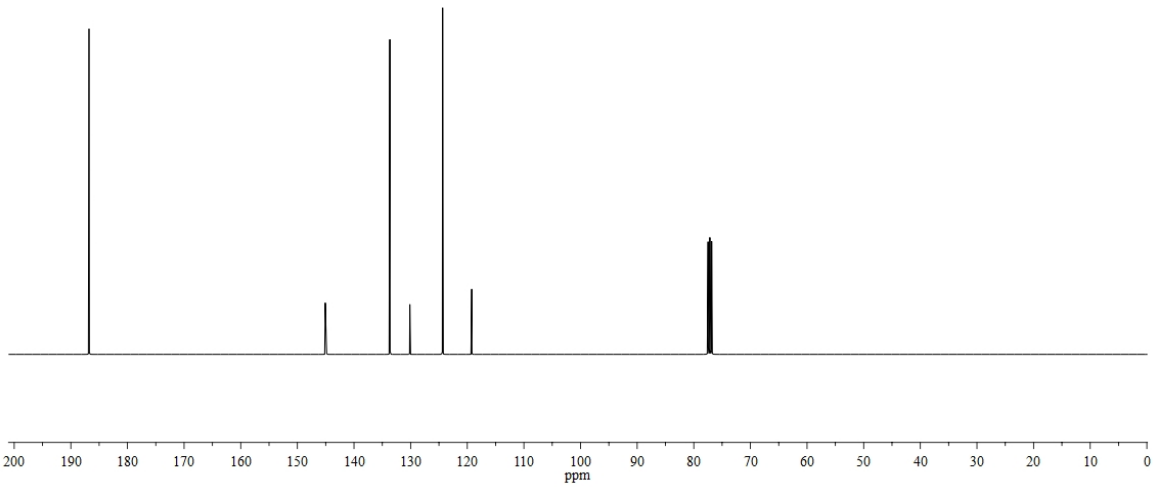
1.04
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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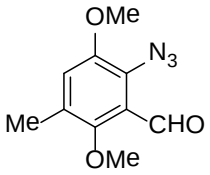
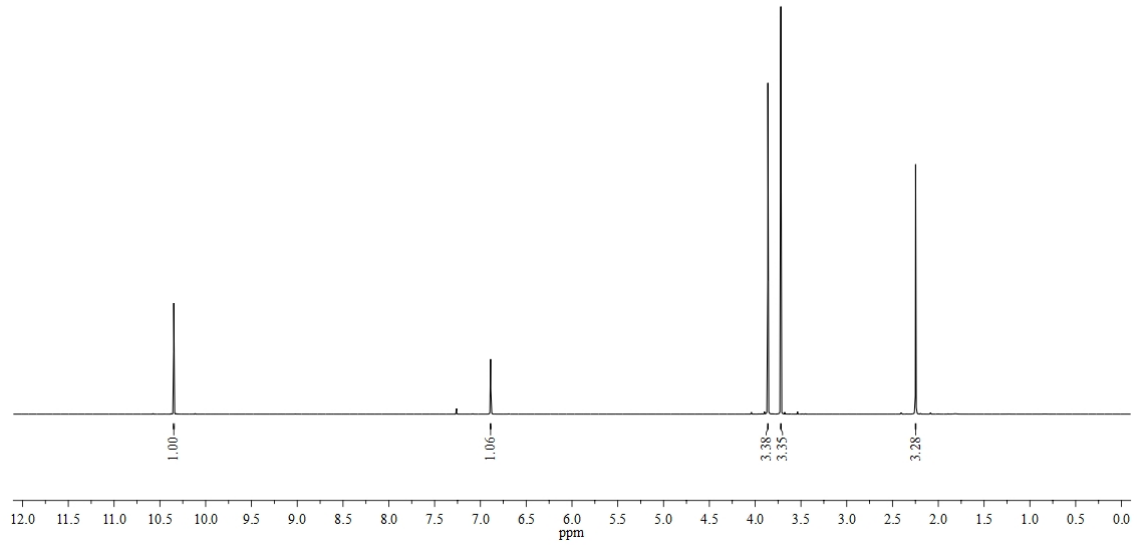
ppm


OMe
N3
Me
CHO
OMe

**3f**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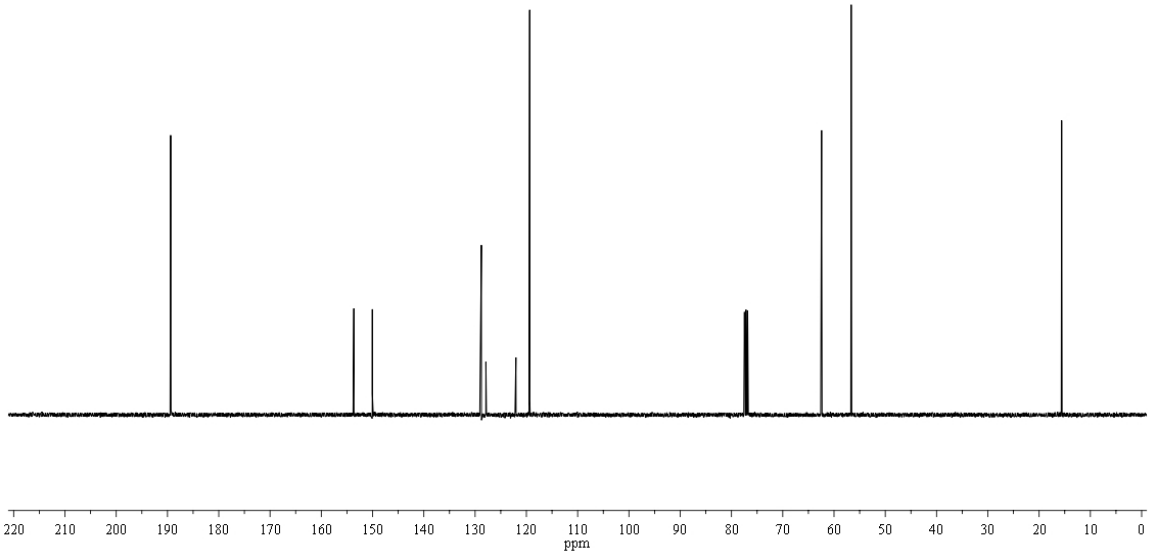
1.06
3.38
3.35
3.28
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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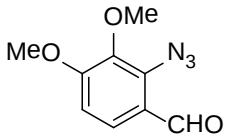
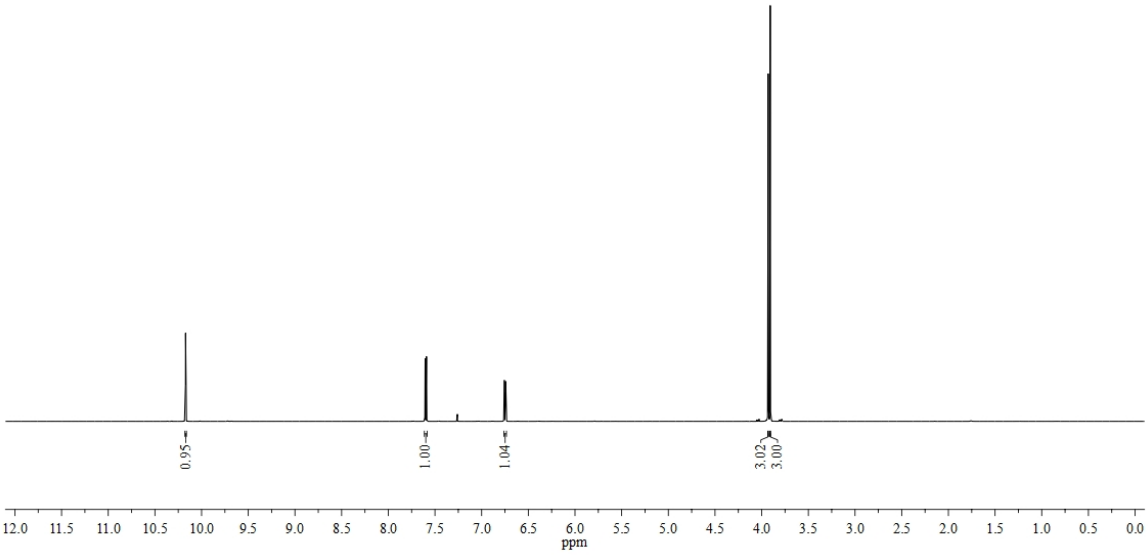
ppm


OMe
MeO
N3
CHO

**3g**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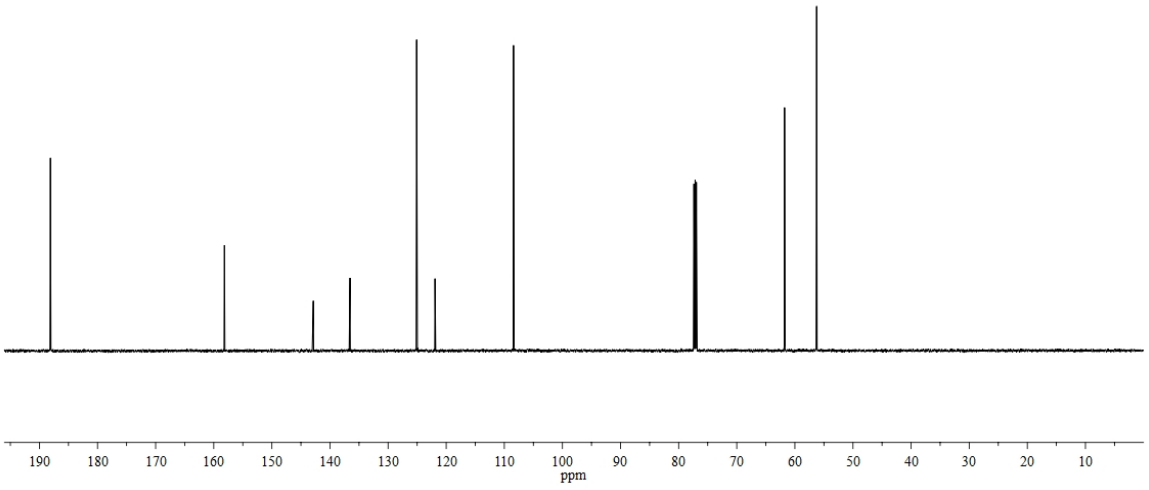
1.00
1.04
3.02
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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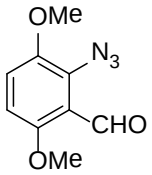
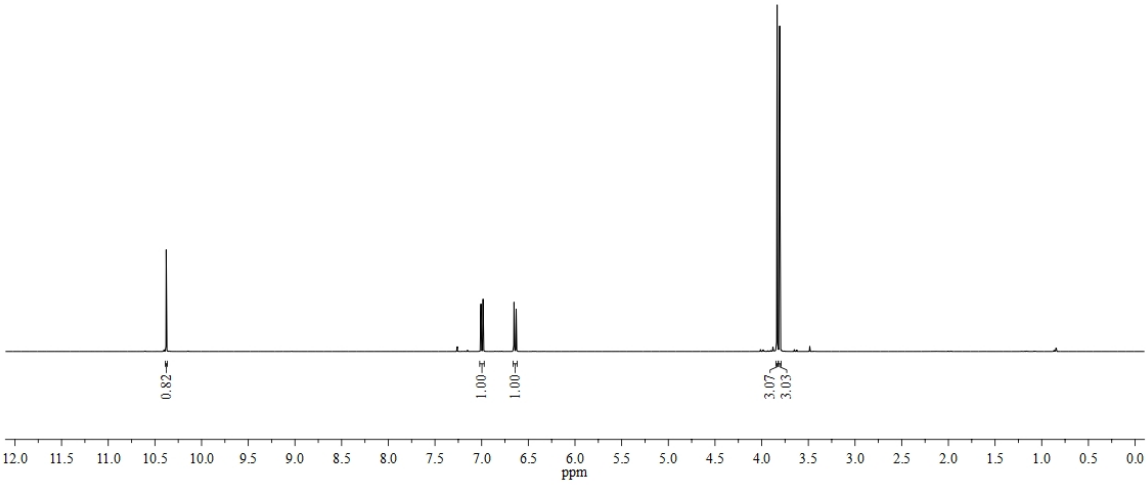
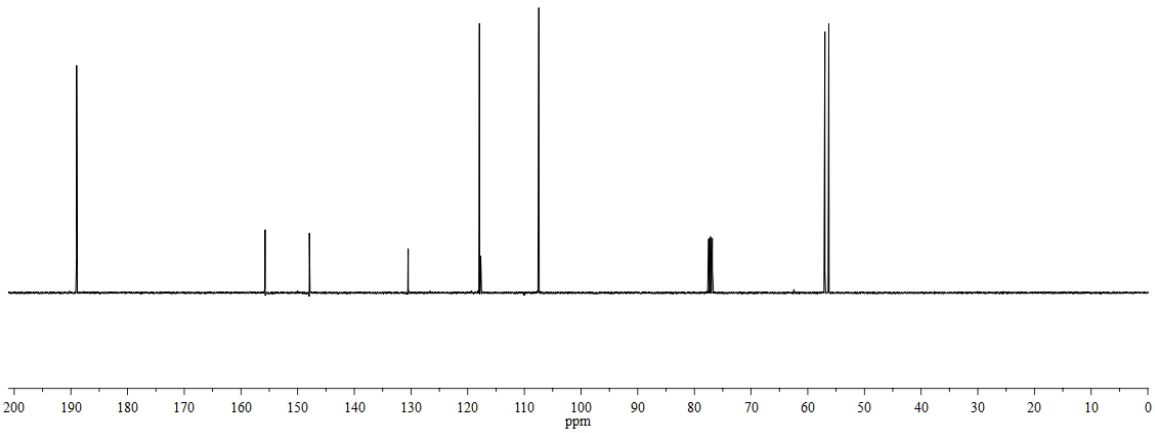
ppm


OMe
N3
CHO
OMe

**3h**


0.82
1.00
1.00
3.07
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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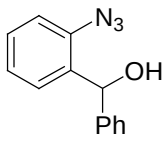
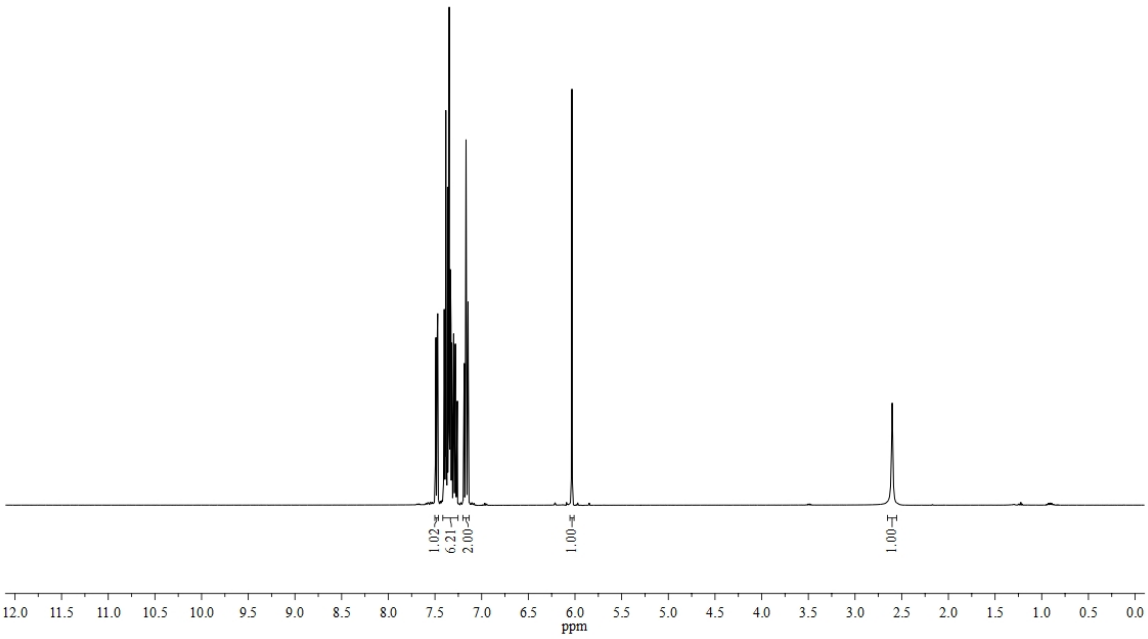
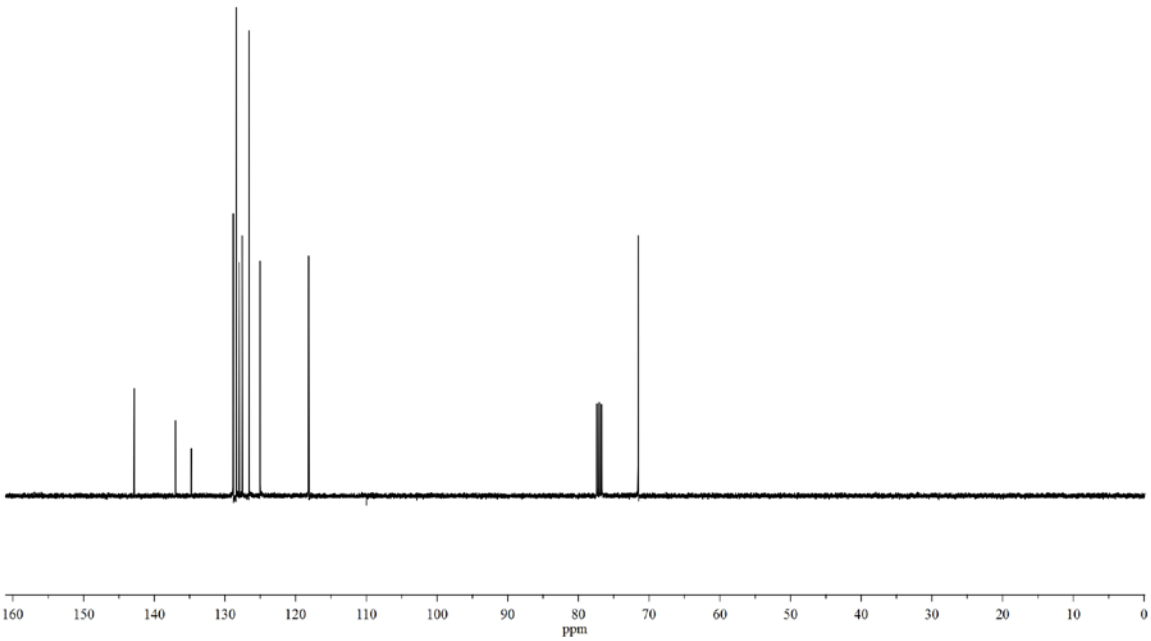
ppm


N3
OH
Ph

**5a**


1.02
6.21
2.00
1.00
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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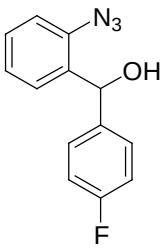
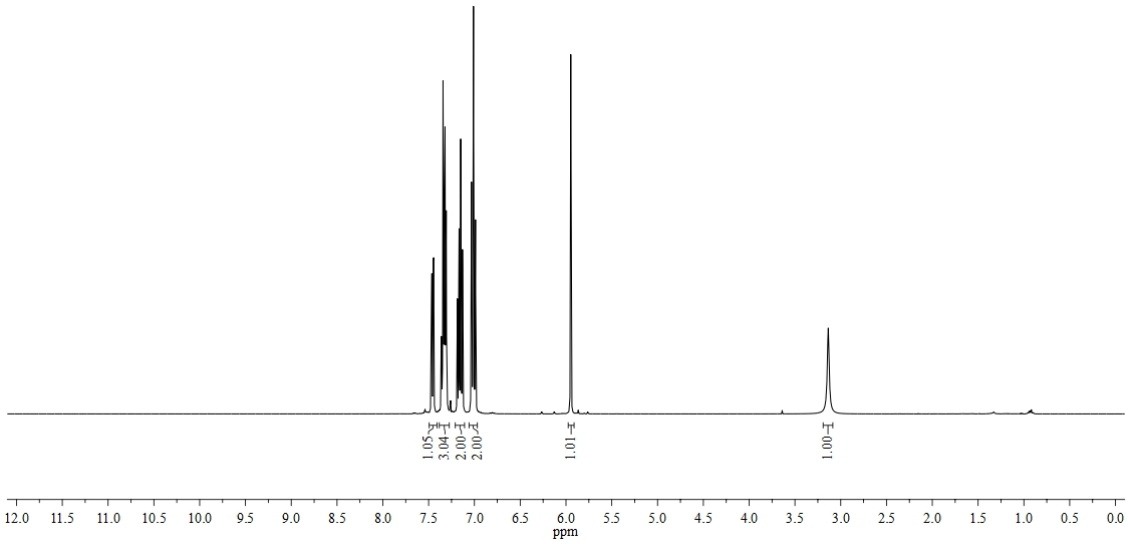
ppm


N3
OH
F

**5b**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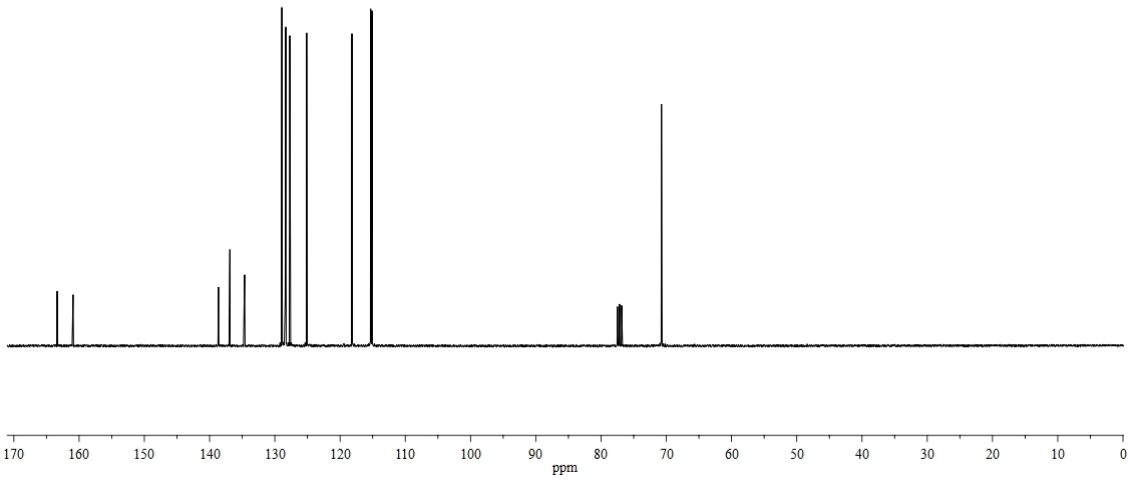
3.04
2.00
2.00
1.01
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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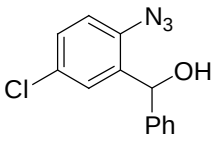
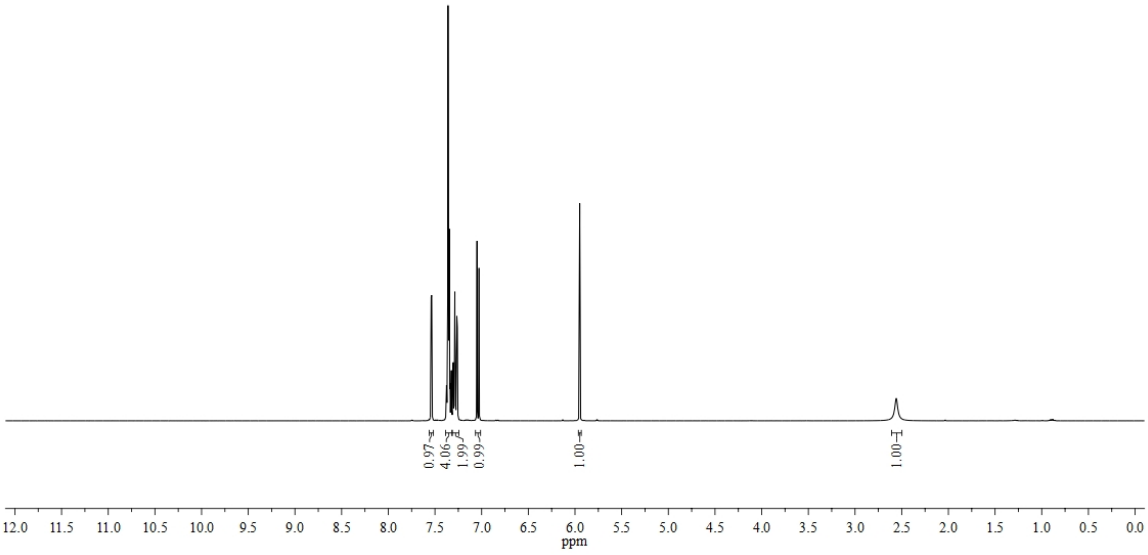
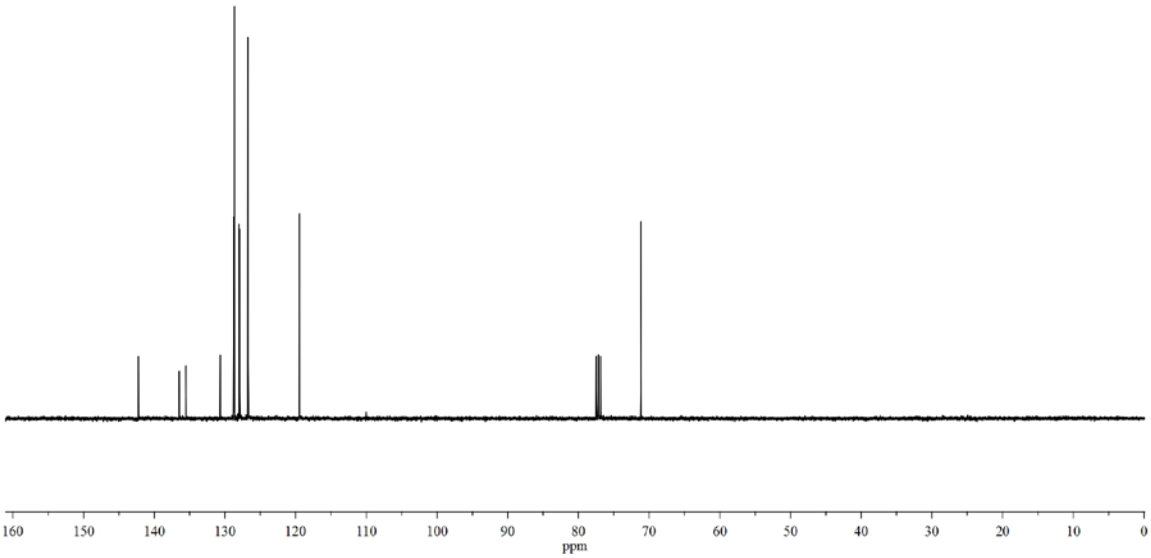

N3
OH
Cl
Ph

**5c**


0.97
4.06
1.99
0.99
1.00
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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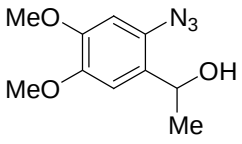
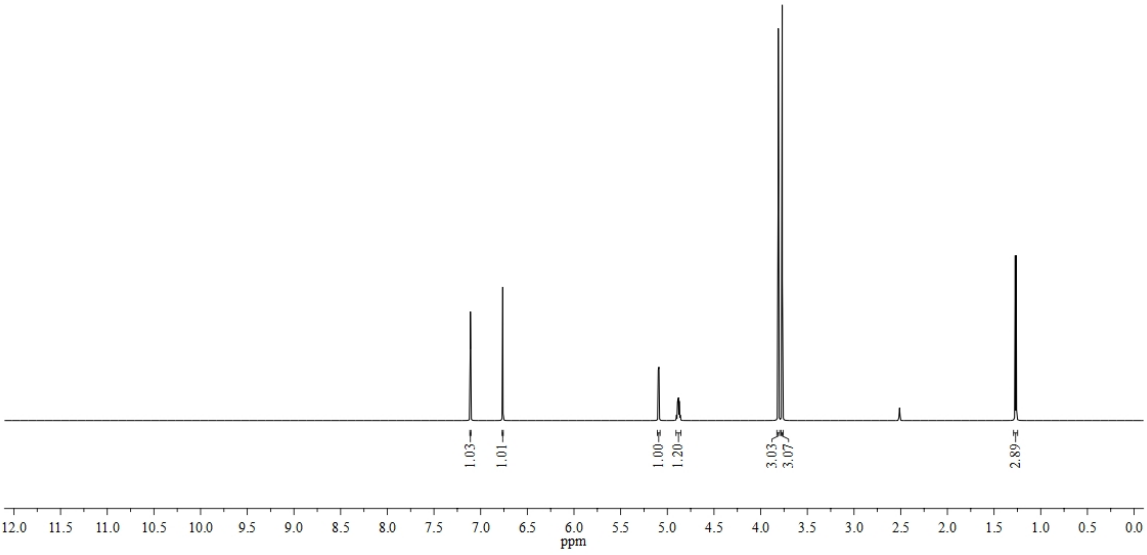
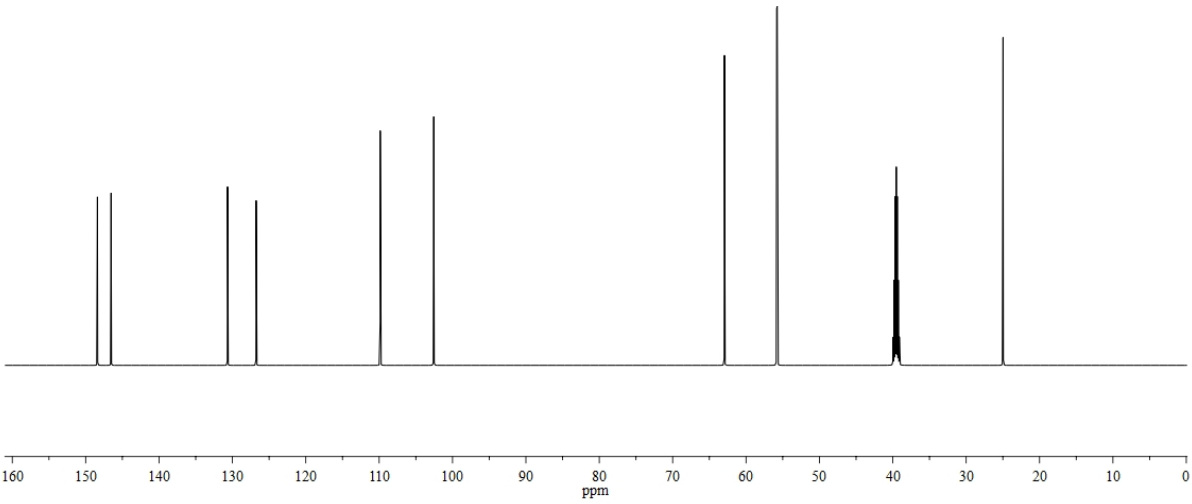
ppm


MeO
N3
OH
MeO
Me

**5d**


1.03
1.01
1.00
1.20
3.03
3.07
2.89
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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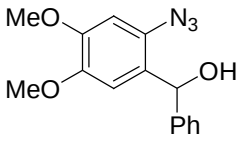
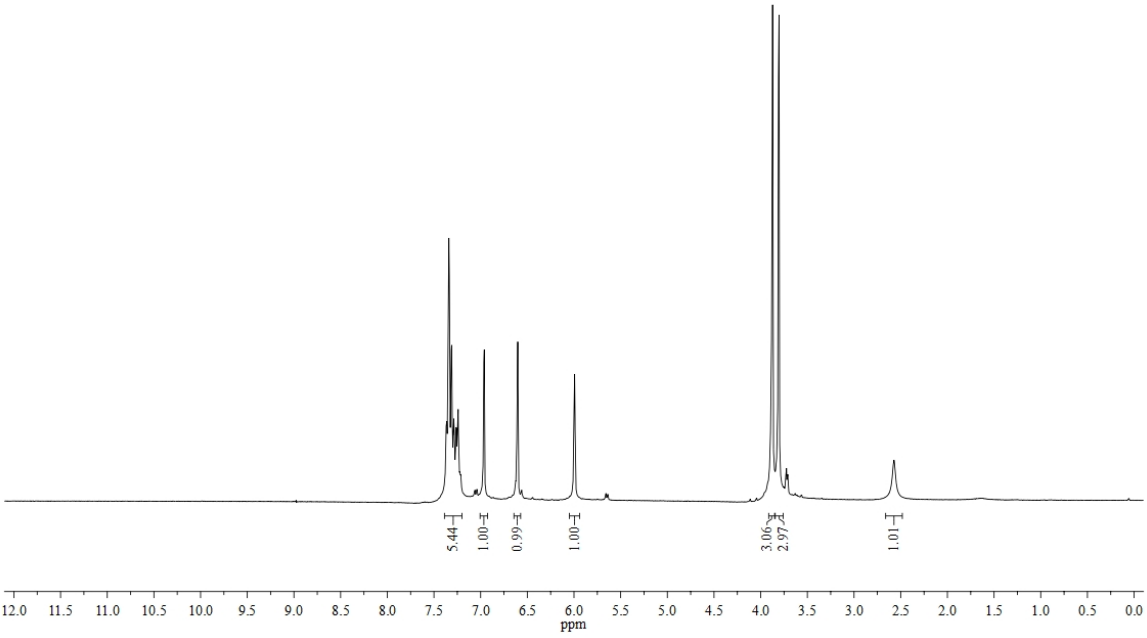
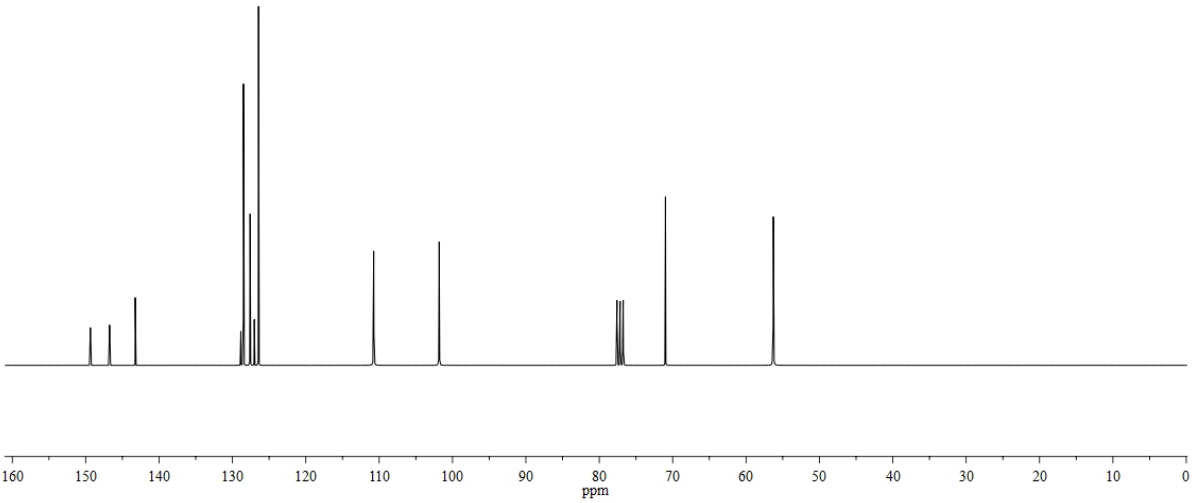
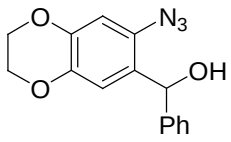
ppm


MeO
N3
OH
MeO
Ph

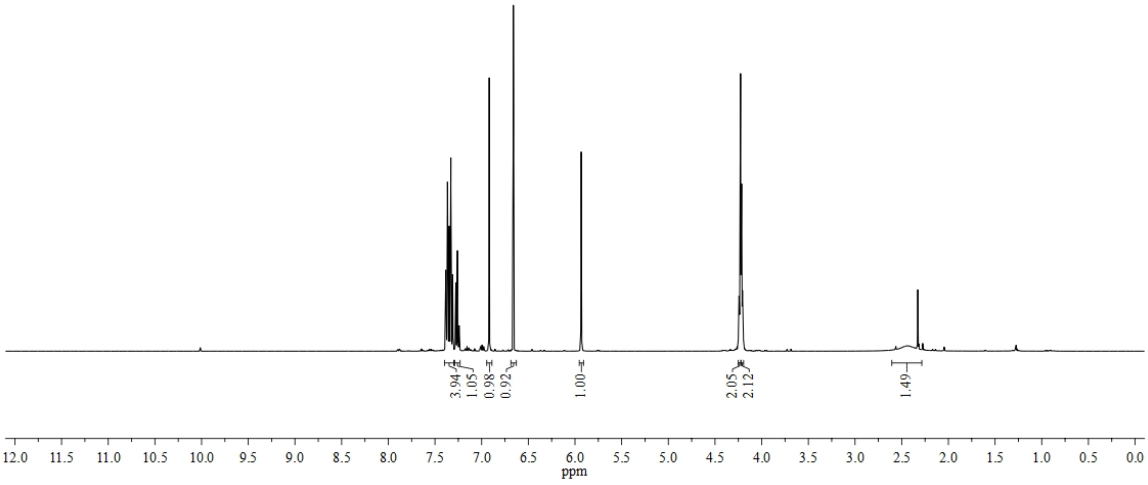
**5e**

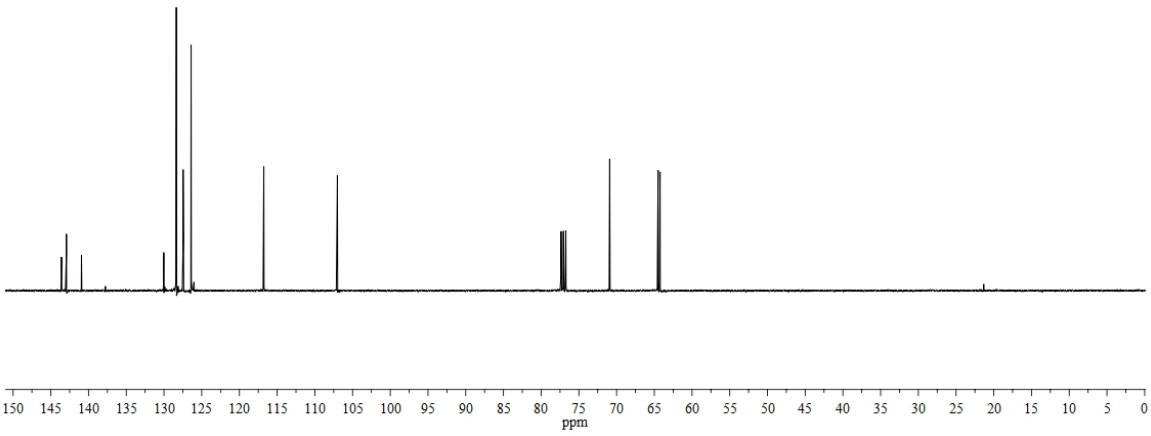

5.44
1.00
0.99
1.00
3.06
2.97
1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

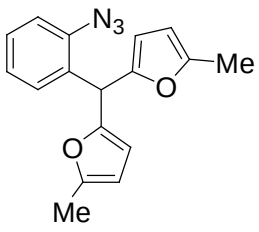

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
O
N3
OH
Ph

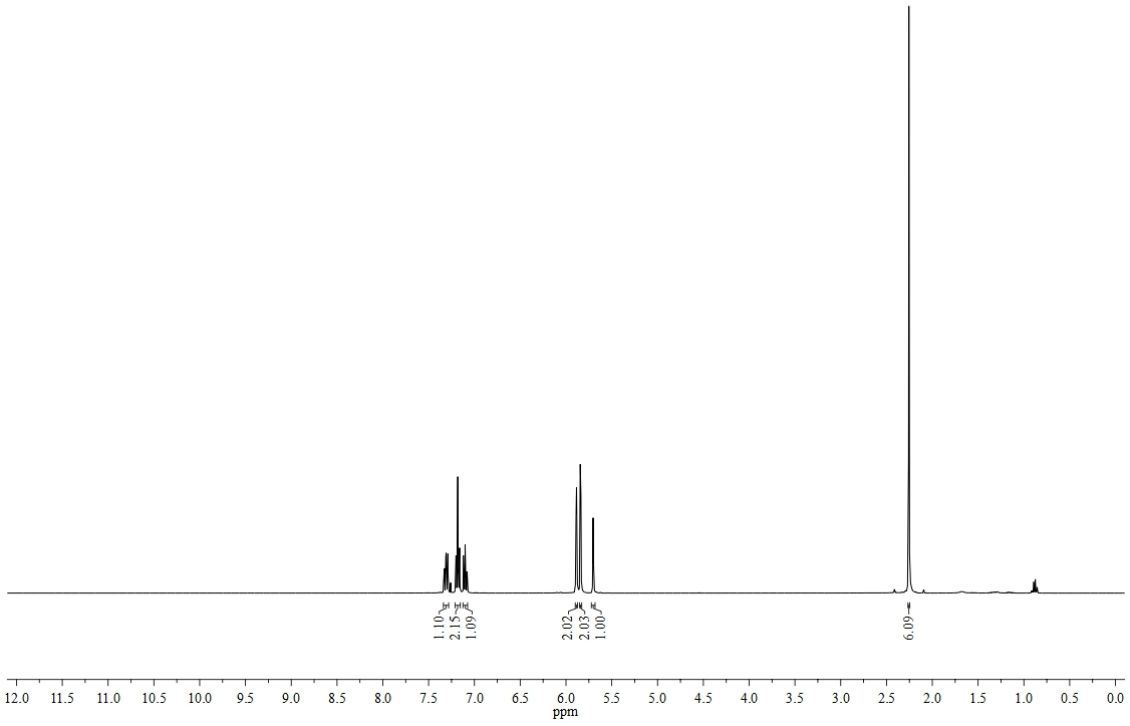
**5f**

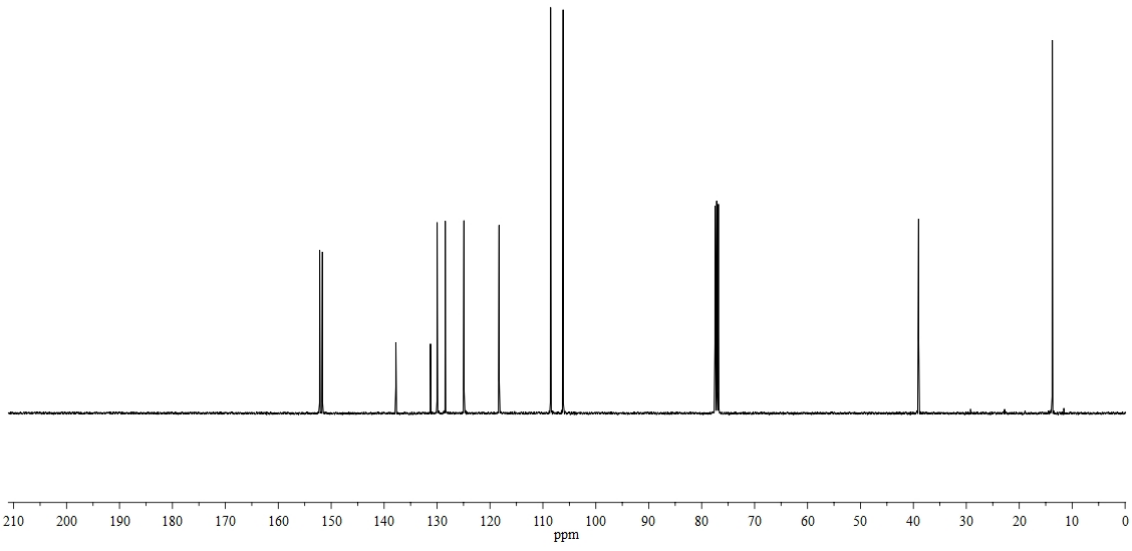

3.94
1.05
0.98
0.92
1.00
2.05
2.12
1.49
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

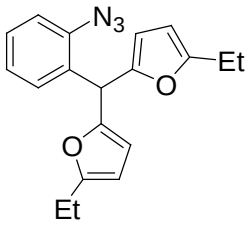

150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
ppm


N3
Me
O
O
Me

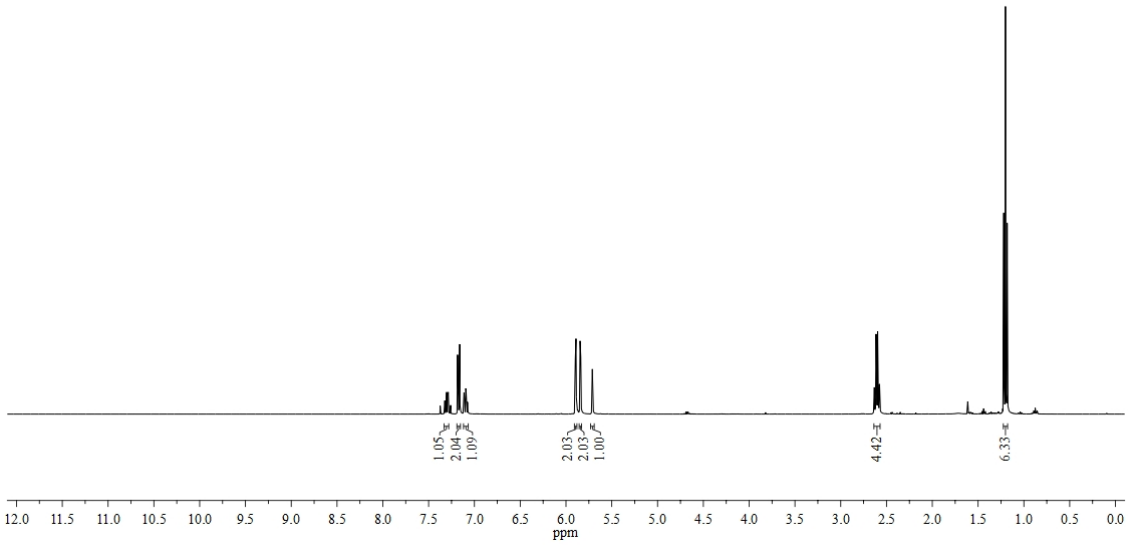
**1a**

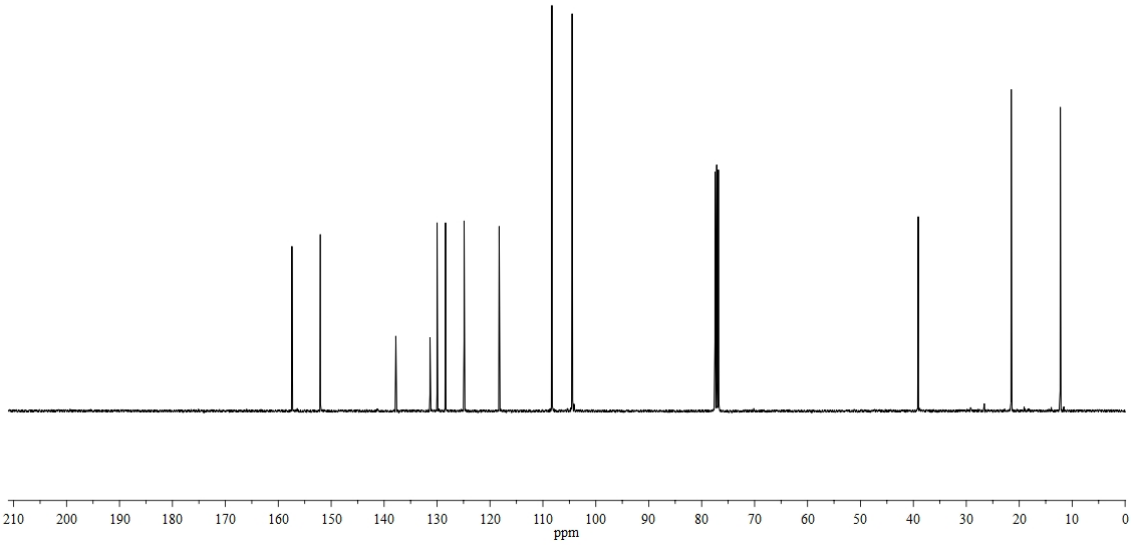

1.10
2.15
1.09
2.02
2.03
1.00
6.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

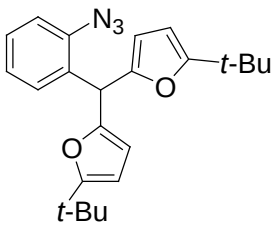

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
Et
O
O
Et

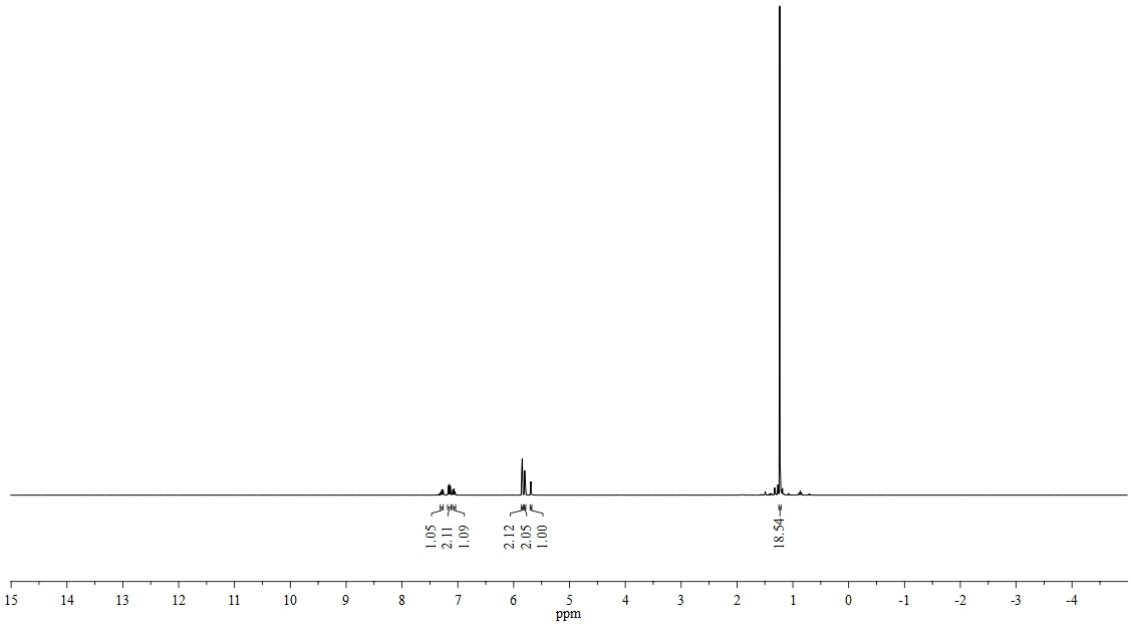
**1b**

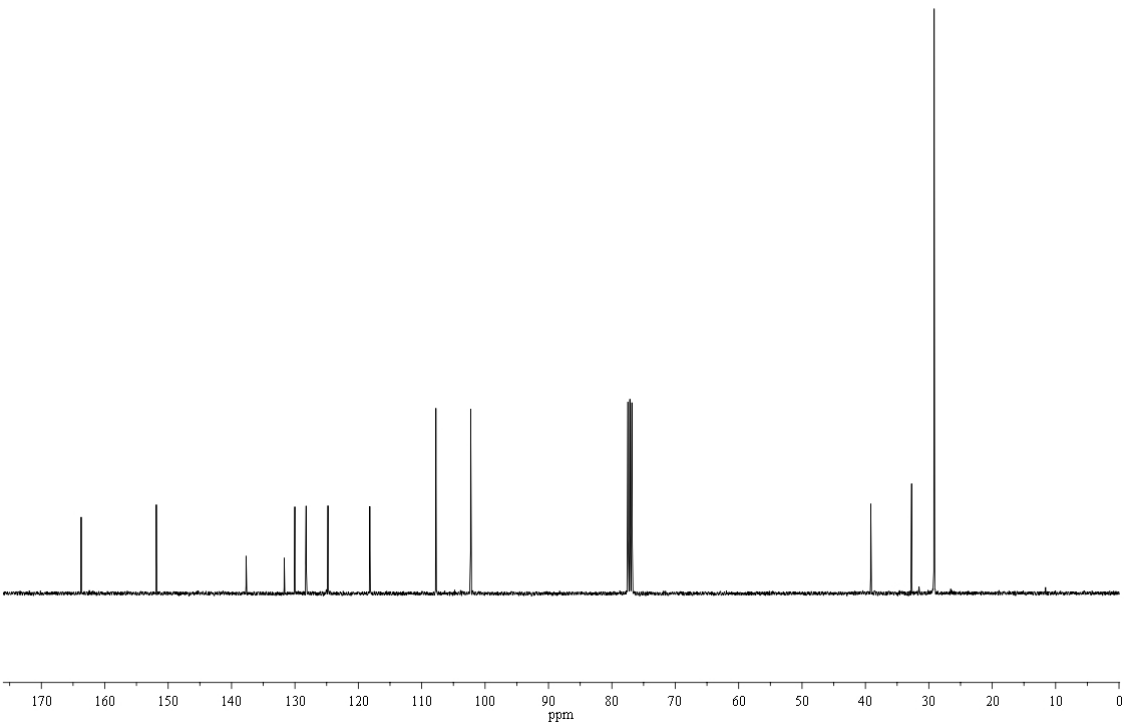

1.05
2.04
1.09
2.03
2.03
1.00
4.42
6.33
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

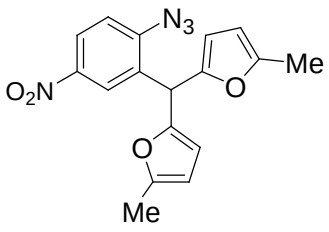

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
t-Bu
O
O
t-Bu

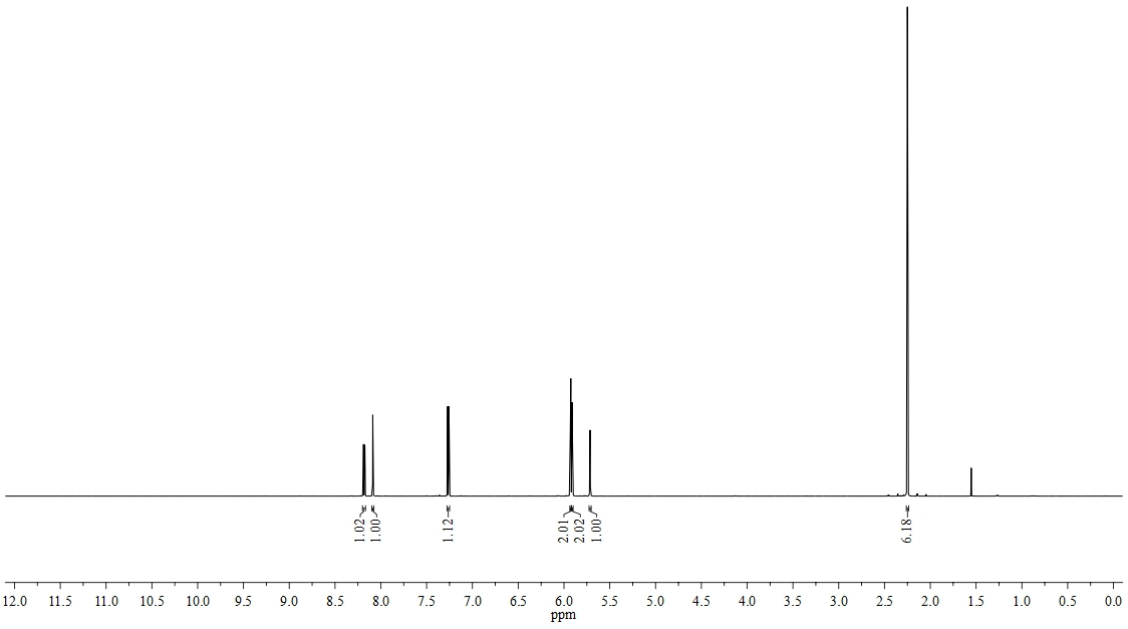
**1c**

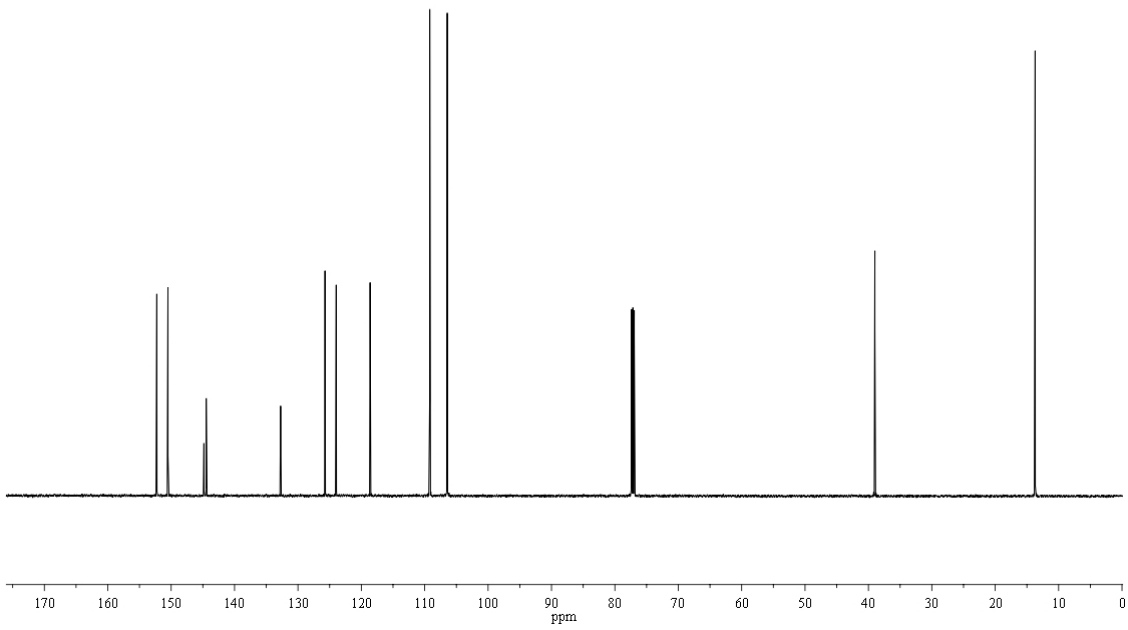

1.05
2.11
1.09
2.12
2.05
1.00
18.54
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
ppm

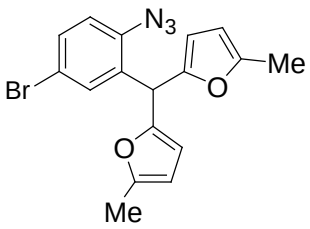

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
O2N
Me
O
O
Me

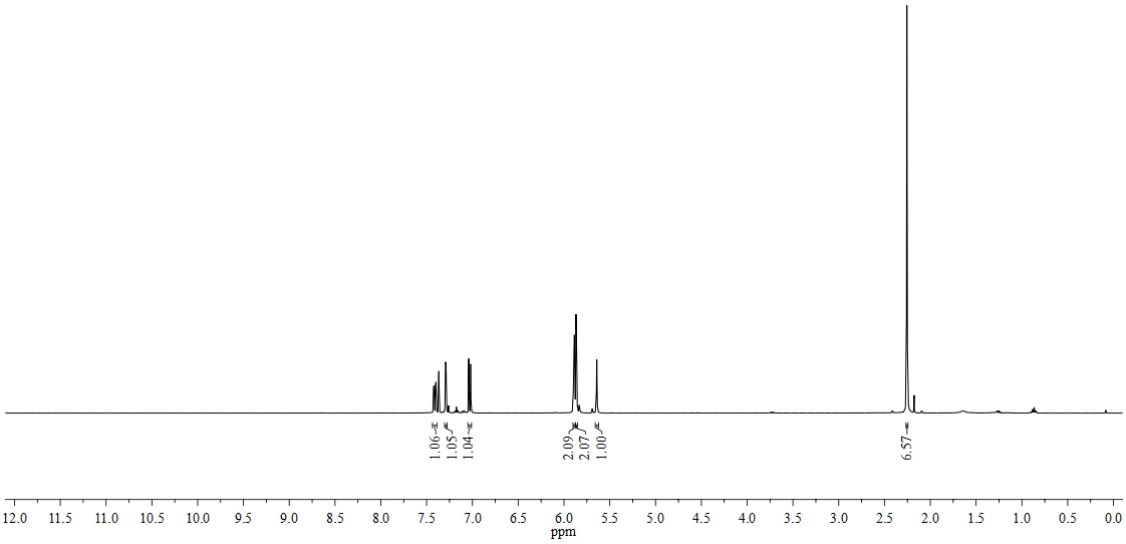
**1d**

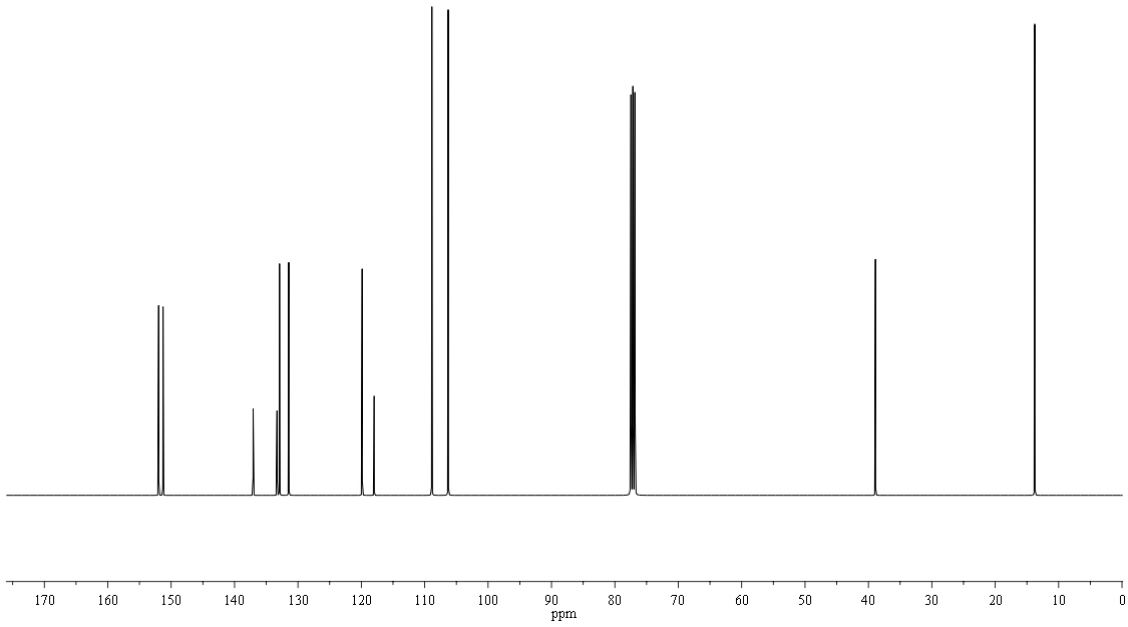

1.02
1.00
1.12
2.01
2.02
1.00
6.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

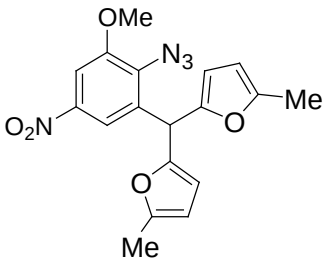

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
Br
O
Me
O
Me

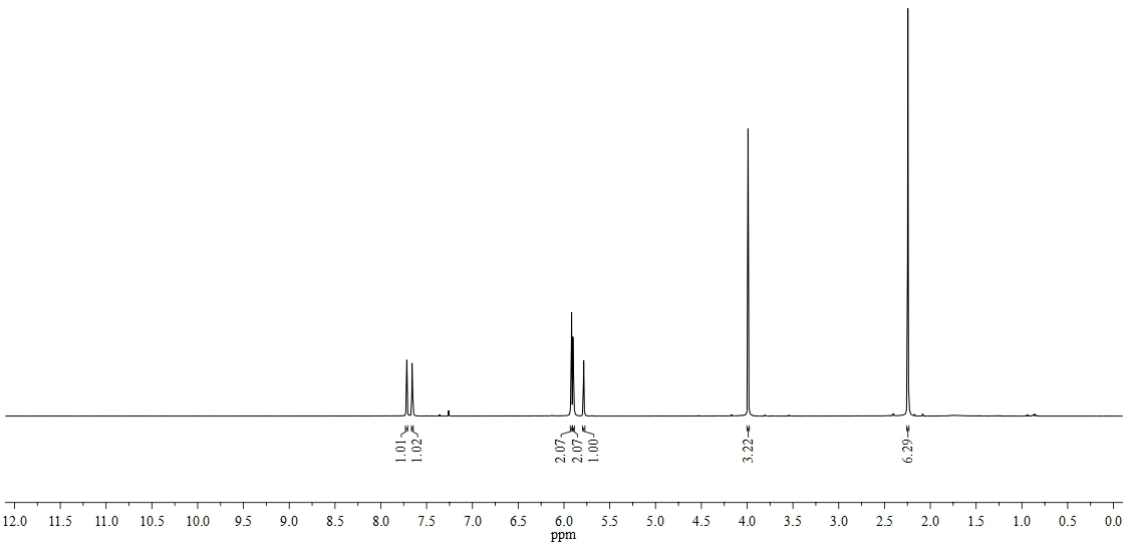
**1e**

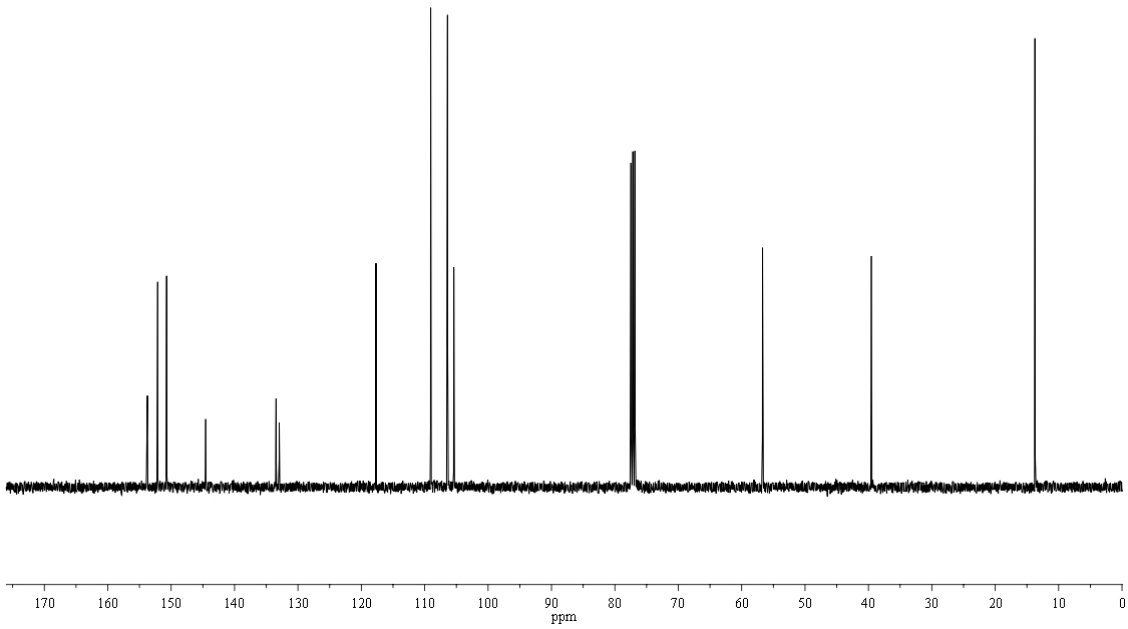

1.06
1.05
1.04
2.09
2.07
1.00
6.57
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

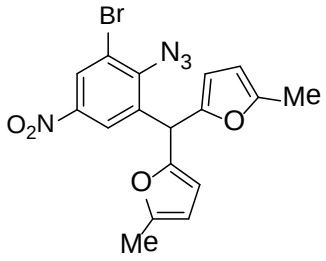

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


OMe
N3
O2N
Me
O
O
Me

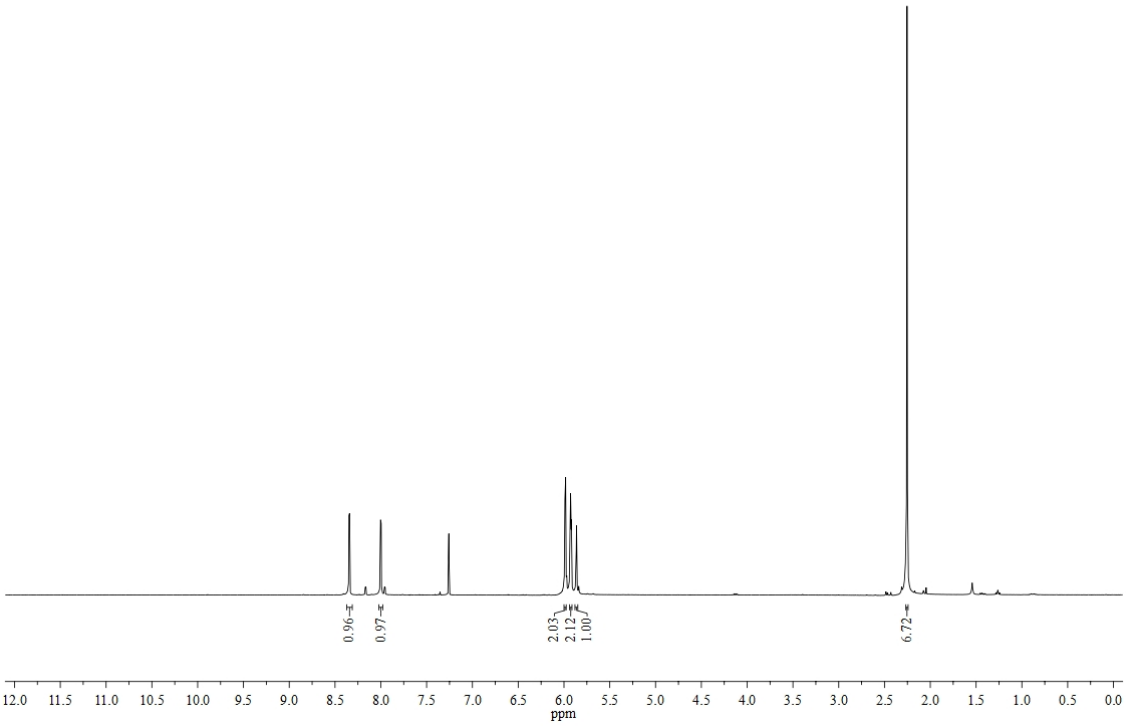
**1f**

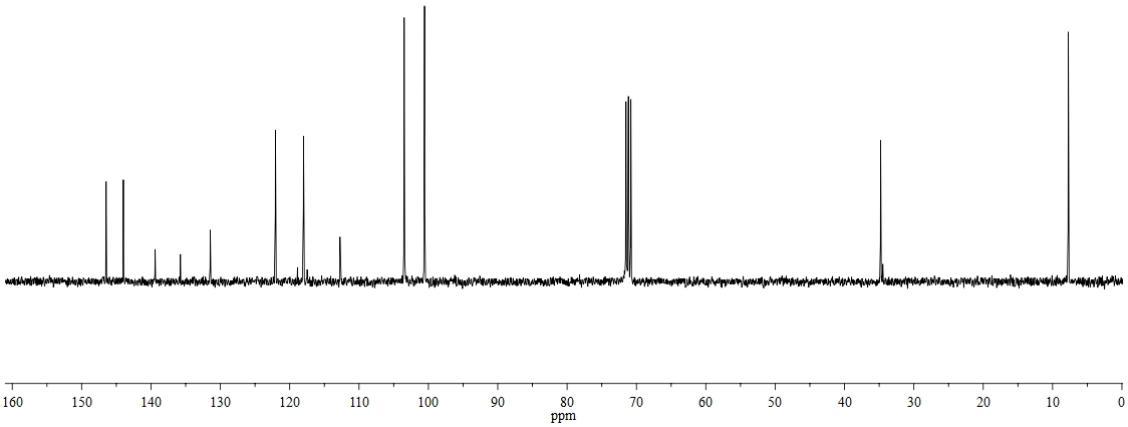

1.01
1.02
2.07
2.07
1.00
3.22
6.29
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

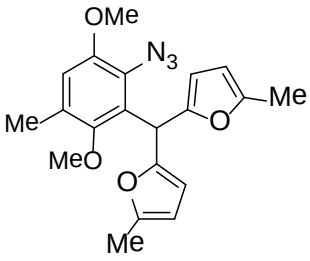

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


Br
N3
O2N
Me
O
O
Me

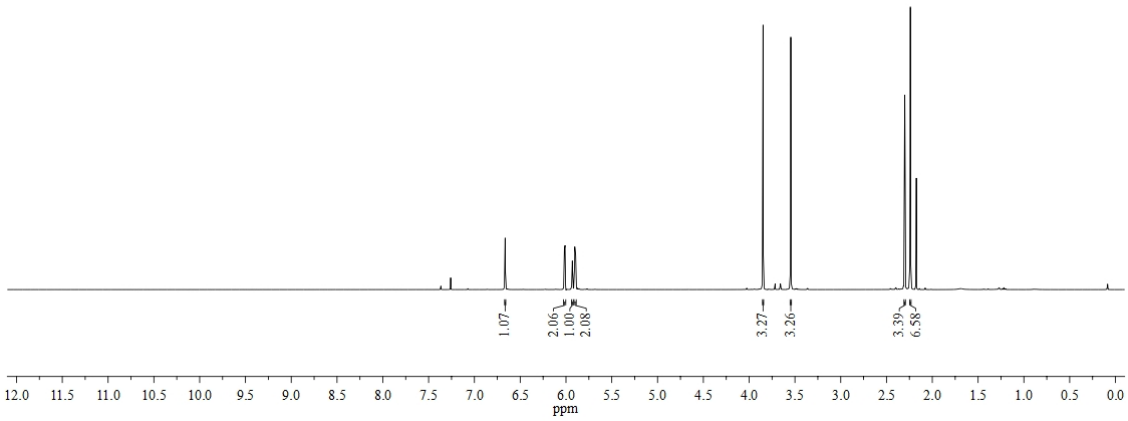
**1g**

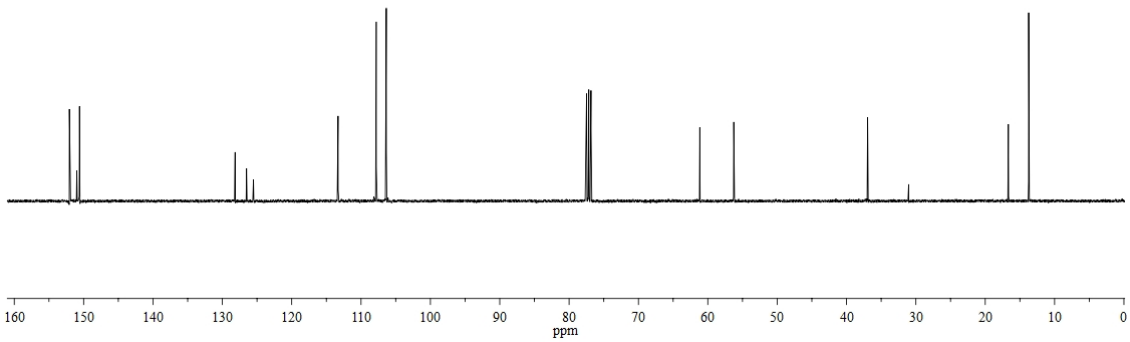

0.96
0.97
2.03
2.12
1.00
6.72
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

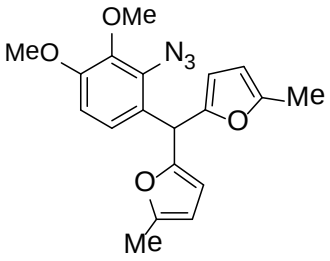

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


OMe
N3
Me
Me
O
MeO
O
Me

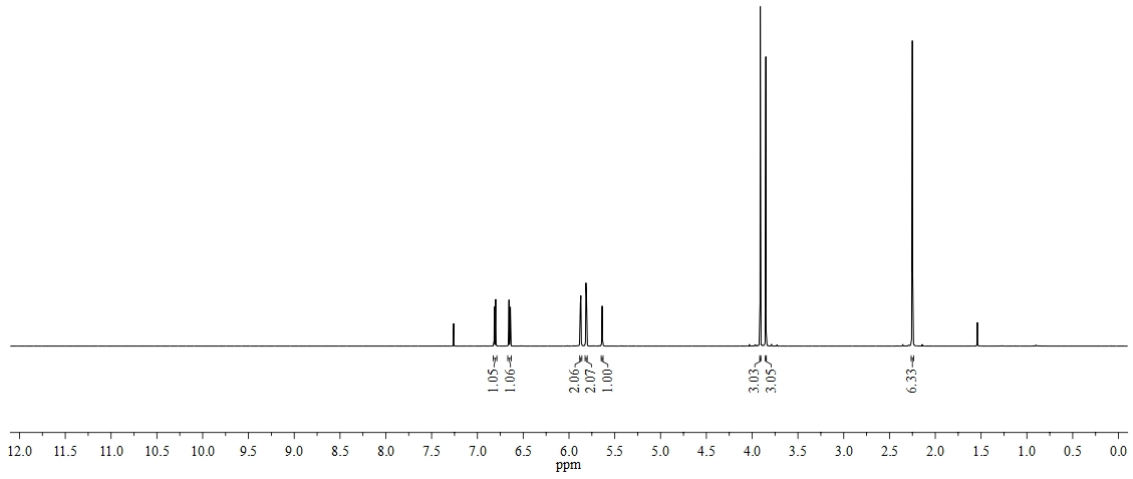
**1h**

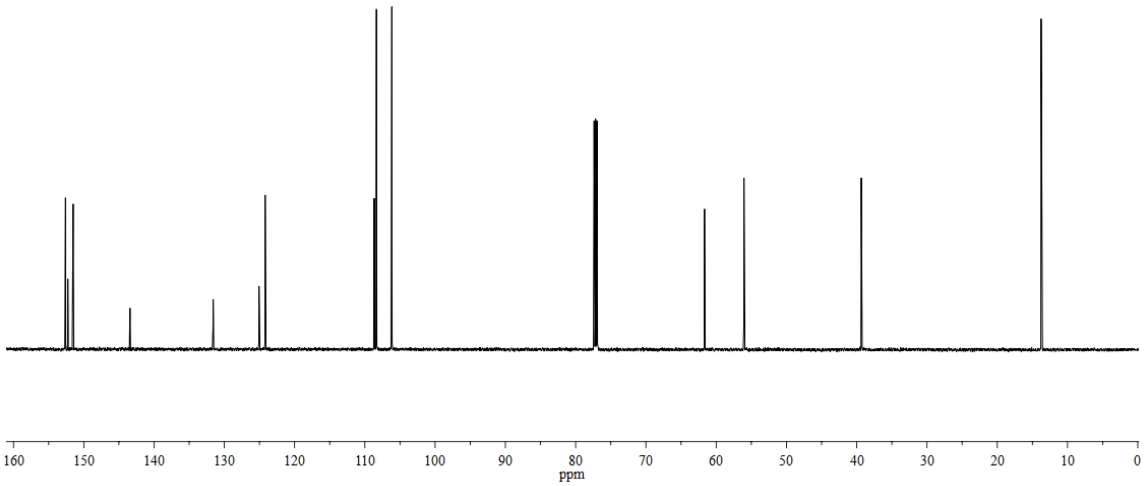

1.07
2.06
1.00
2.08
3.27
3.26
3.39
6.58
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

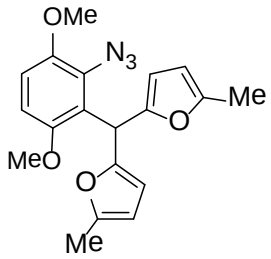

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


OMe
MeO
N3
Me
O
O
Me

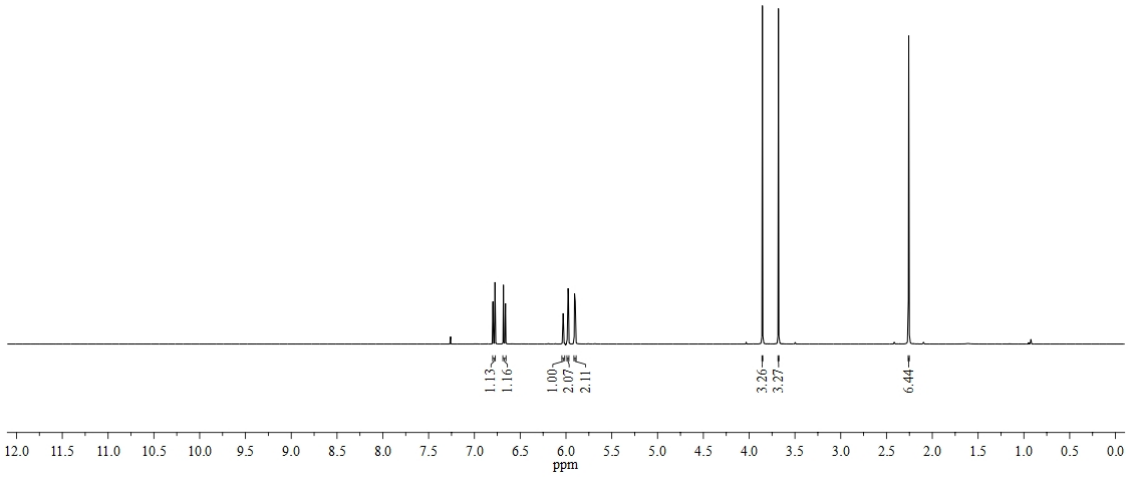
**1i**

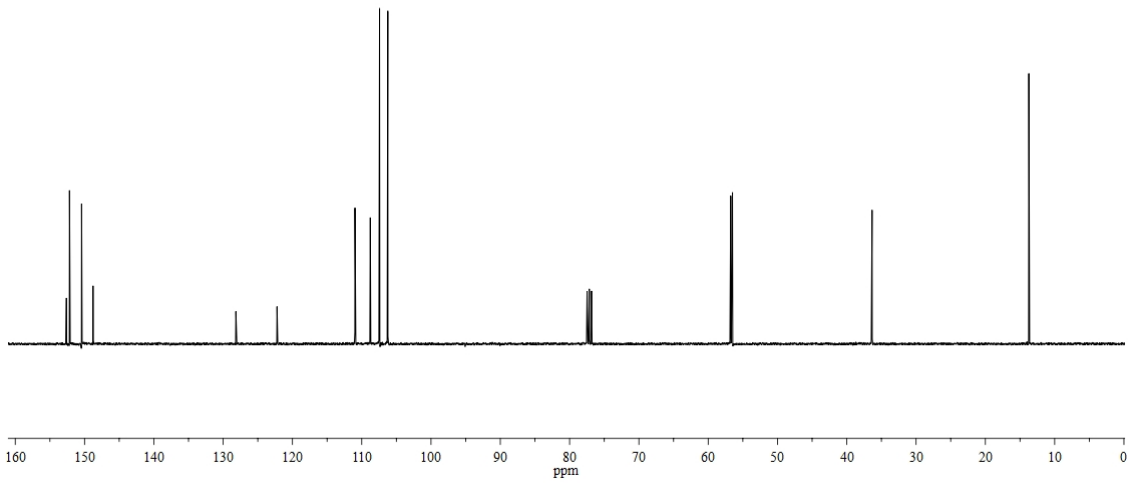

1.05
1.06
2.06
2.07
1.00
3.03
3.05
6.33
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

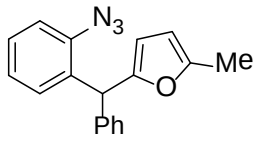

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


OMe
N3
Me
O
MeO
O
Me

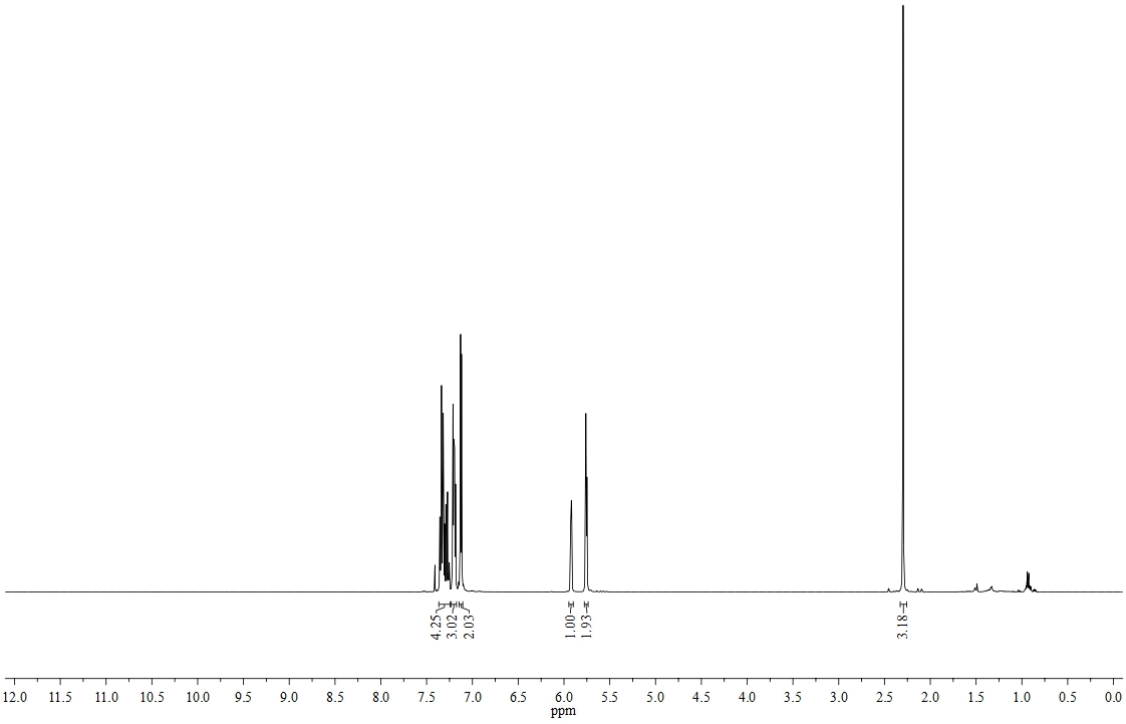
**1j**

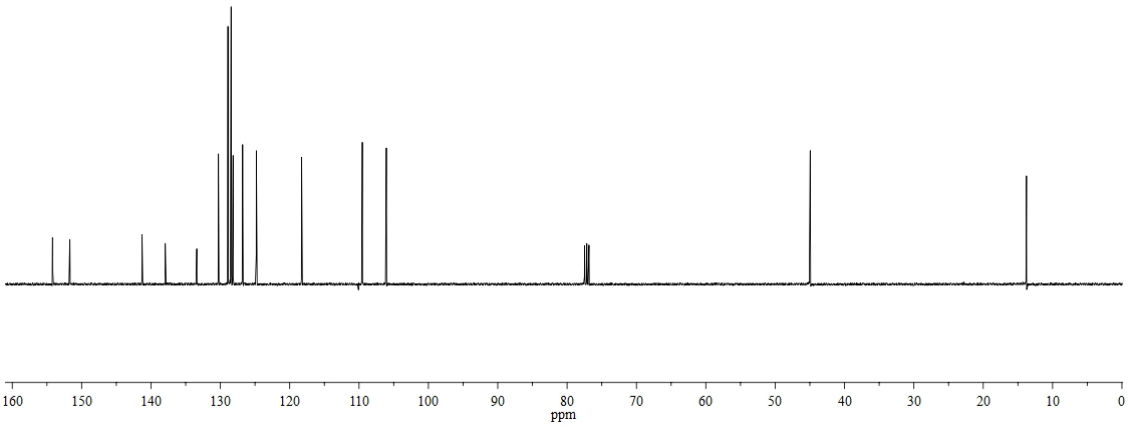

1.13
1.16
1.00
2.07
2.11
3.26
3.27
6.44
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

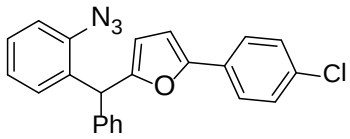

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
Me
O
Ph

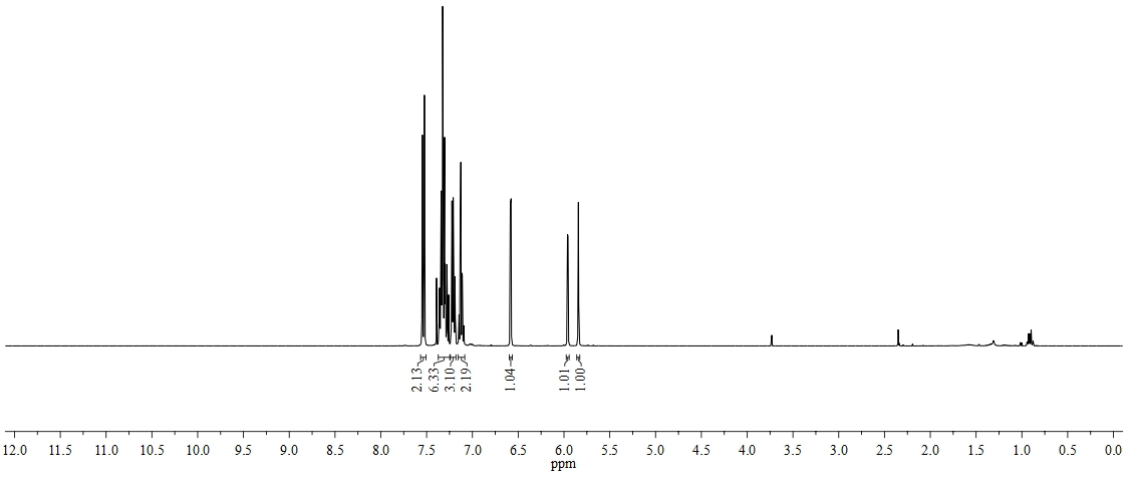
**1k**

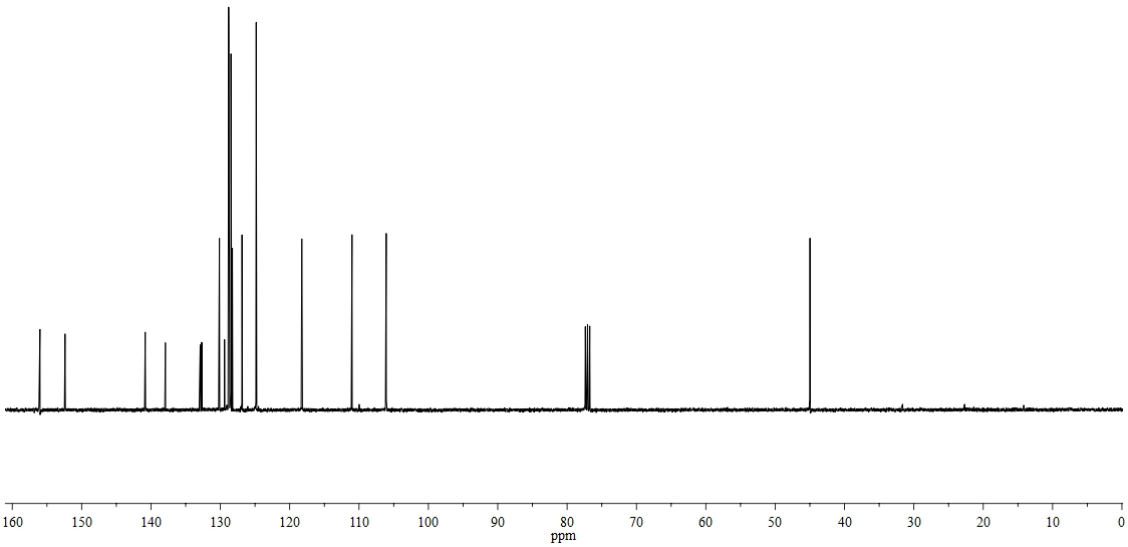

4.25
3.02
2.03
1.00
1.93
3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

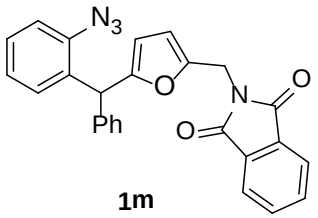

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
O
Cl
Ph

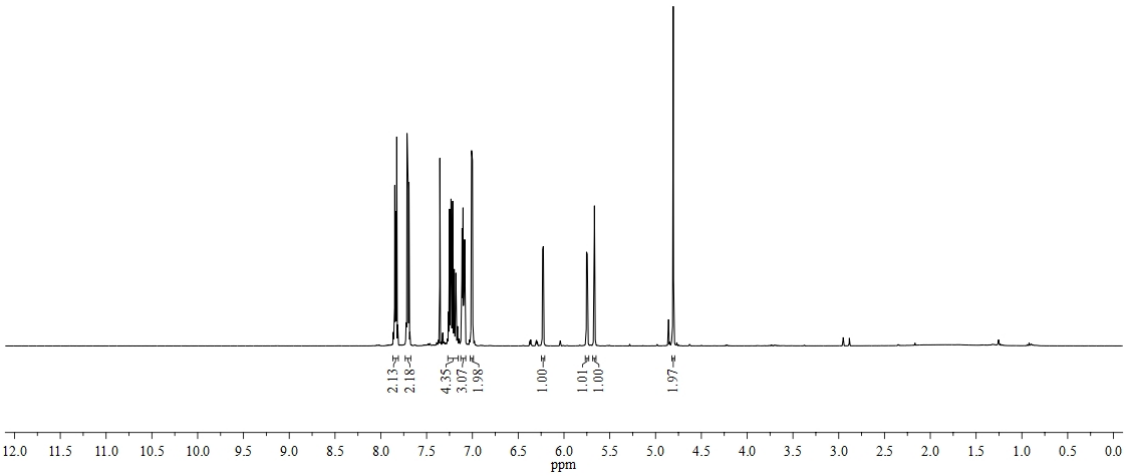
**1l**

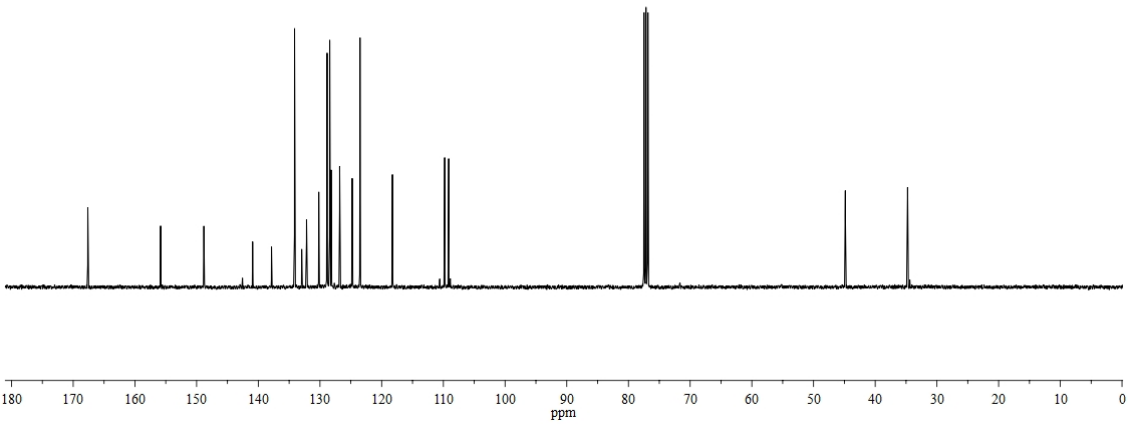

2.13
6.33
3.10
2.19
1.04
1.01
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

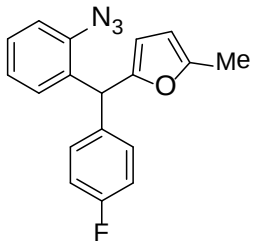

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
O
N
O
O
Ph

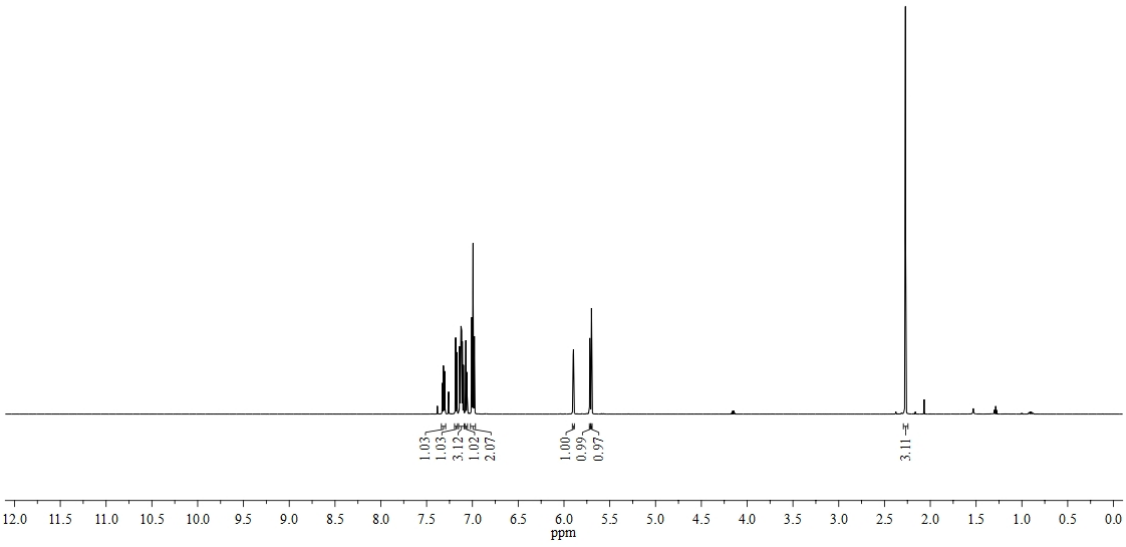
**1m**

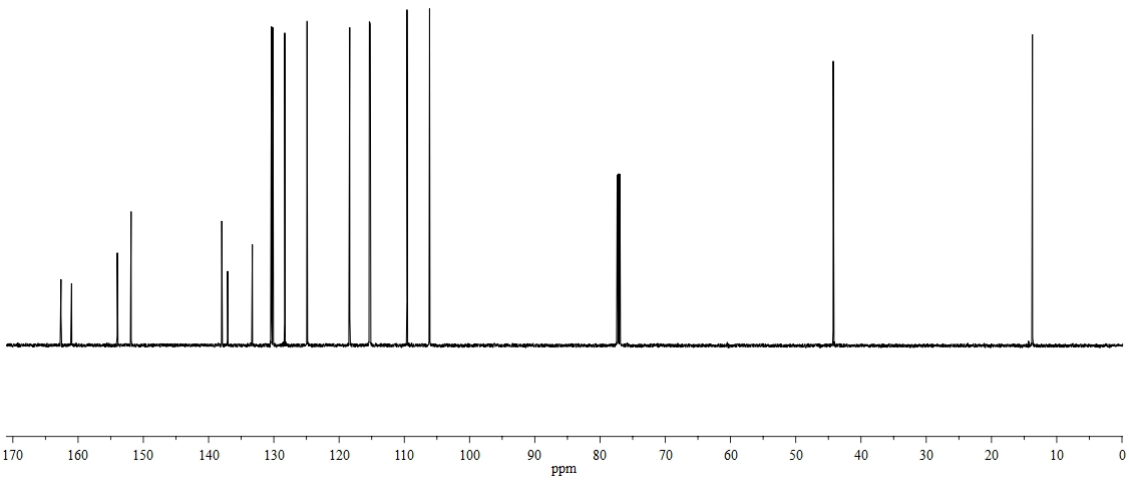

2.13
2.18
4.35
3.07
1.98
1.00
1.01
1.00
1.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

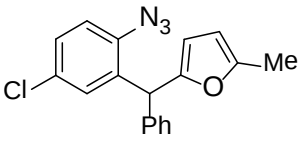

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
Me
O
F

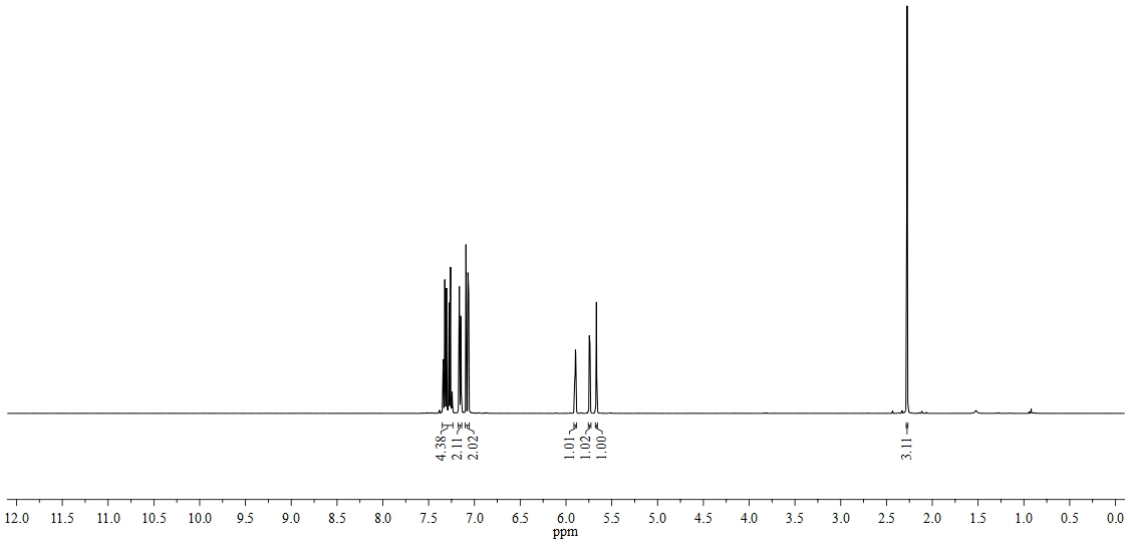
**1n**

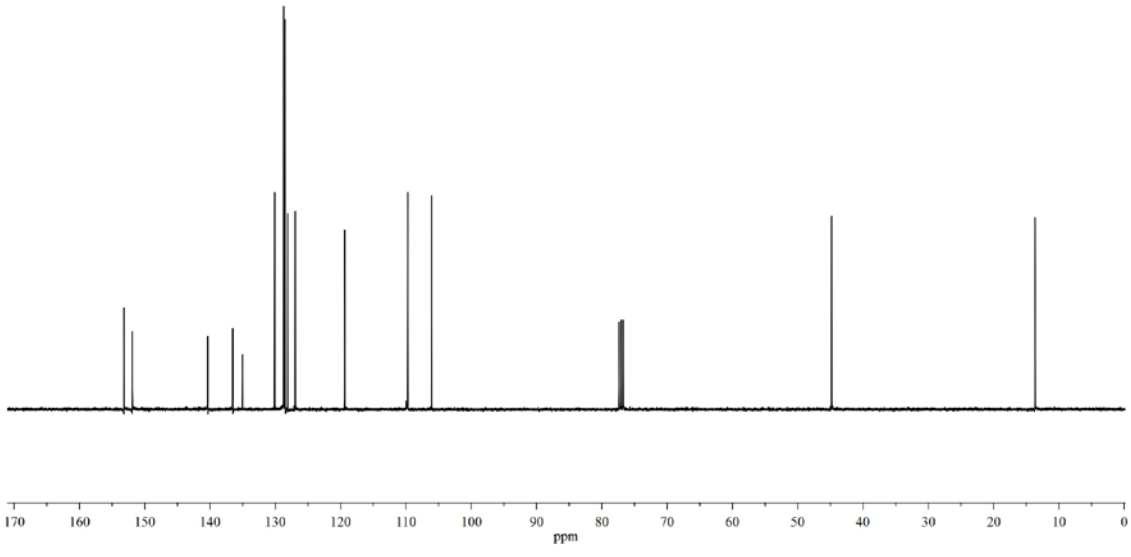

1.03
1.03
3.12
1.02
2.07
1.00
0.99
0.97
3.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

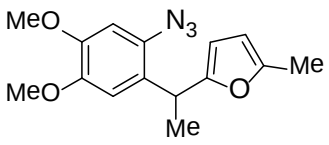

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N3
Cl
O
Me
Ph

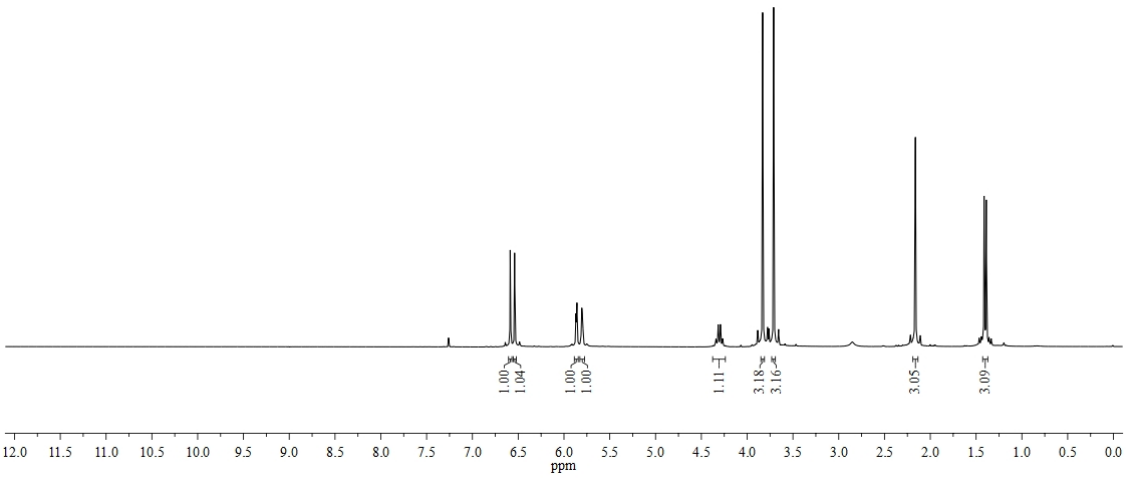
**1o**

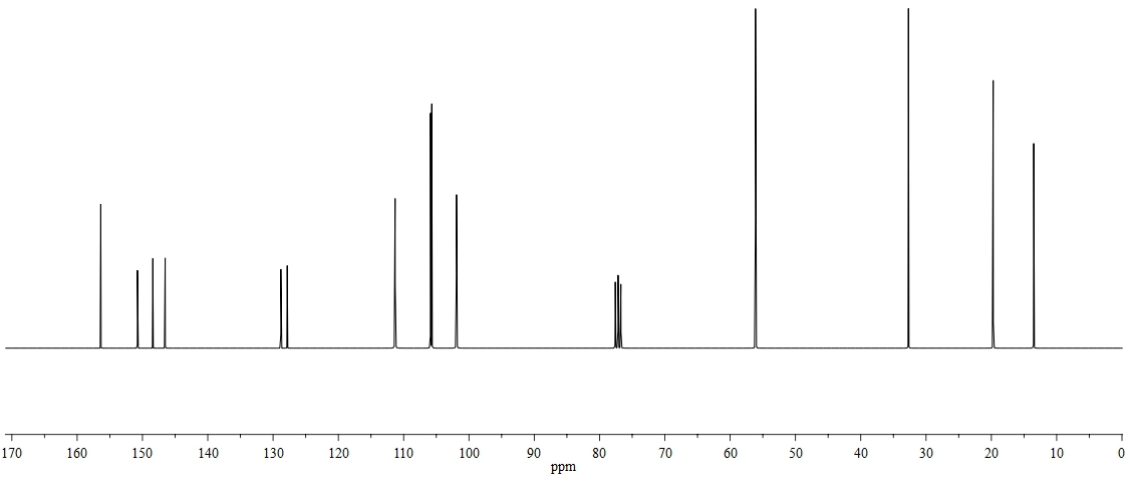

4.38
2.11
2.02
1.01
1.02
1.00
3.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

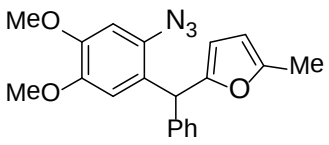

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


MeO
N3
Me
MeO
O
Me

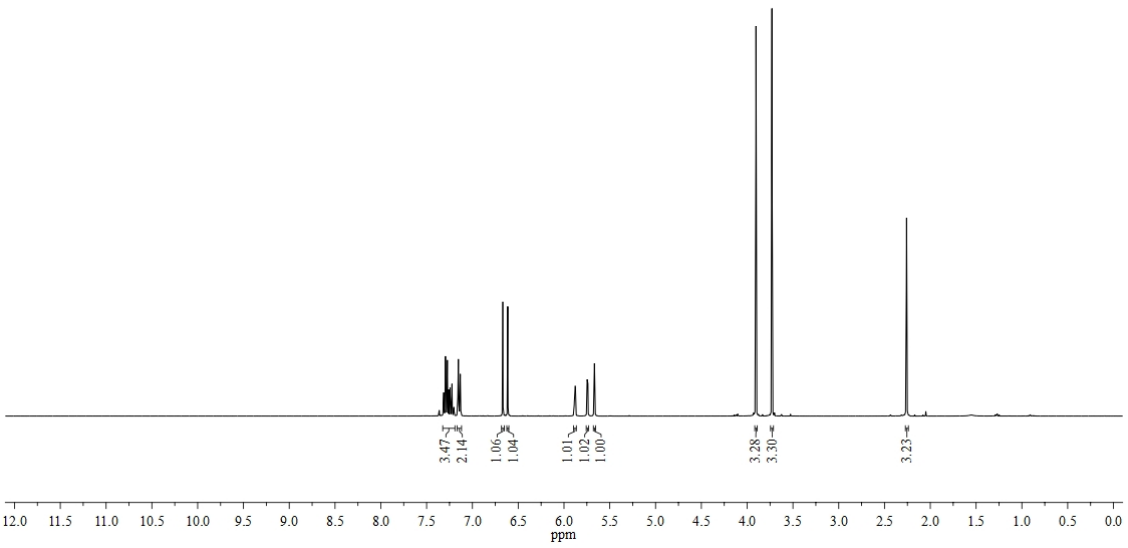
**1p**

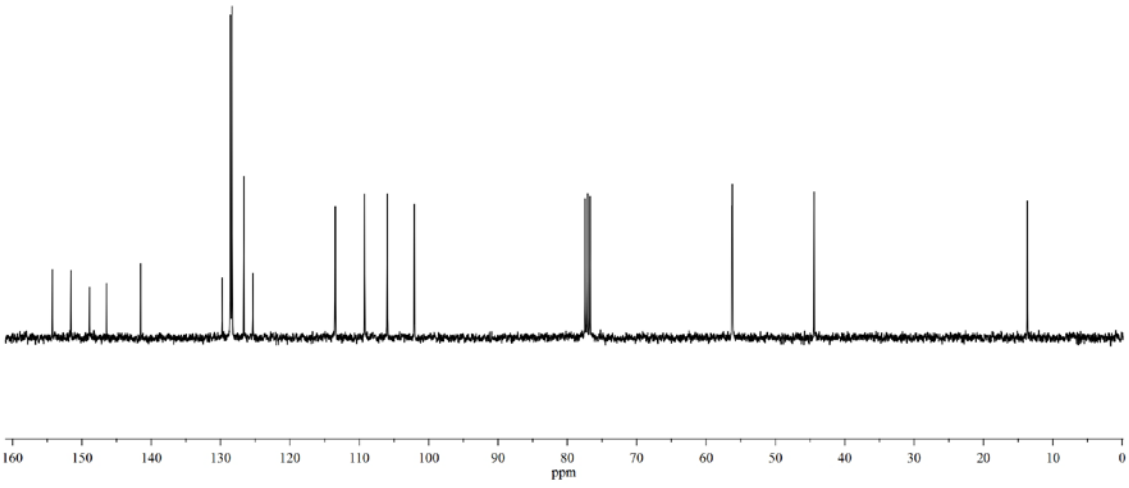

1.00
1.04
1.00
1.00
1.11
3.18
3.16
3.05
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

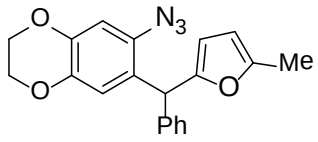

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


MeO
N3
MeO
Me
O
Ph

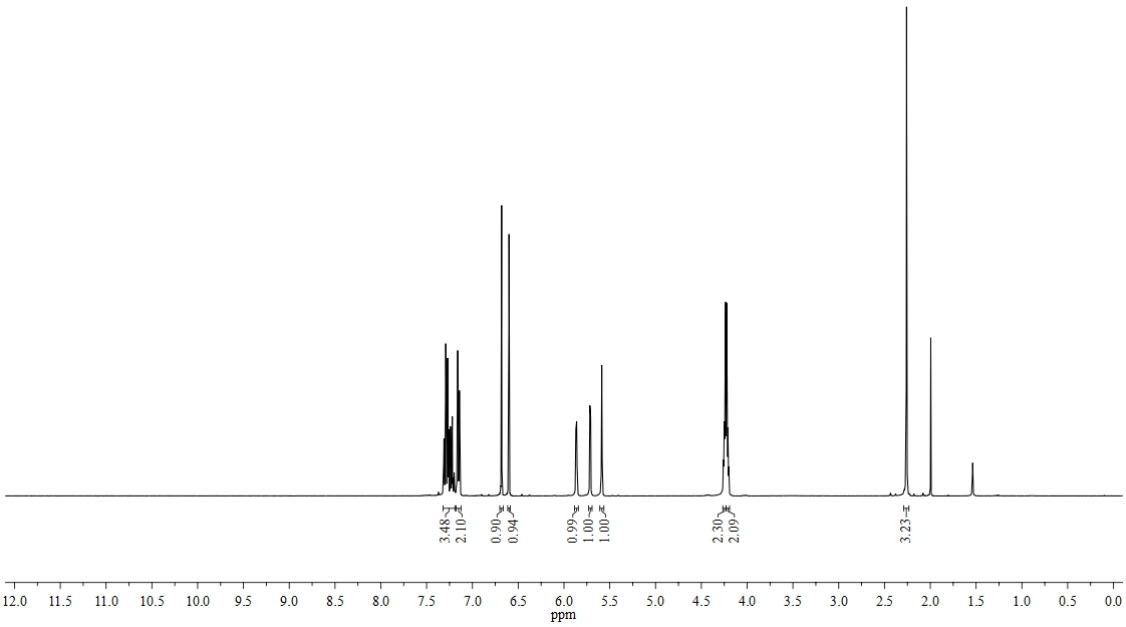
**1q**

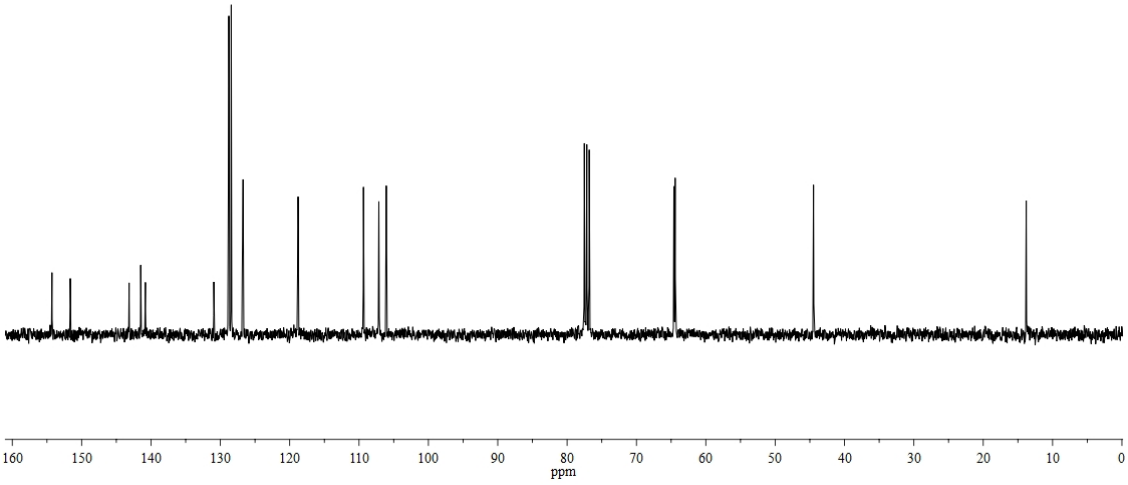

3.47
2.14
1.06
1.04
1.01
1.02
1.00
3.28
3.30
3.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

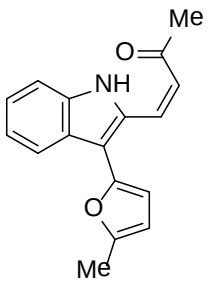

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
N3
Me
O
O
Ph

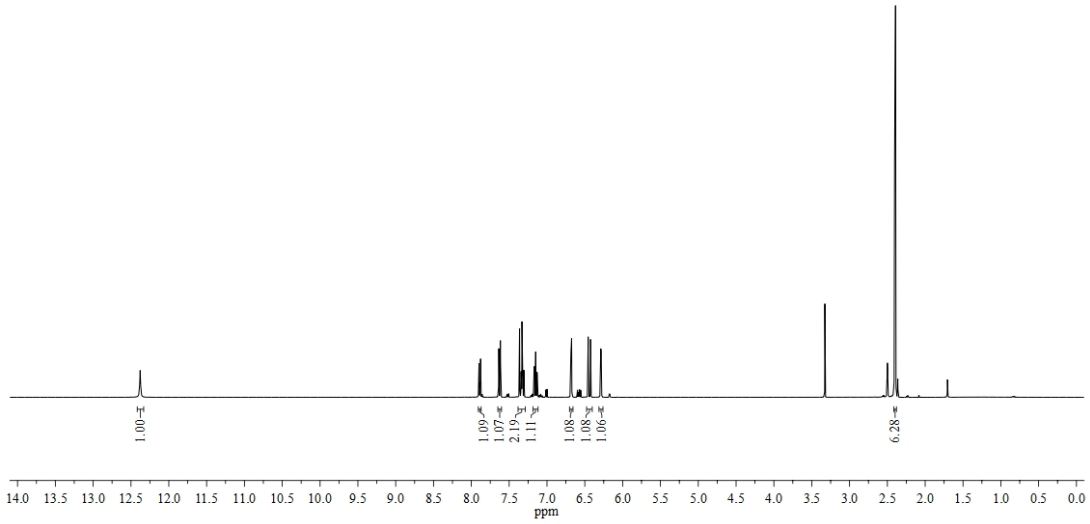
**1r**

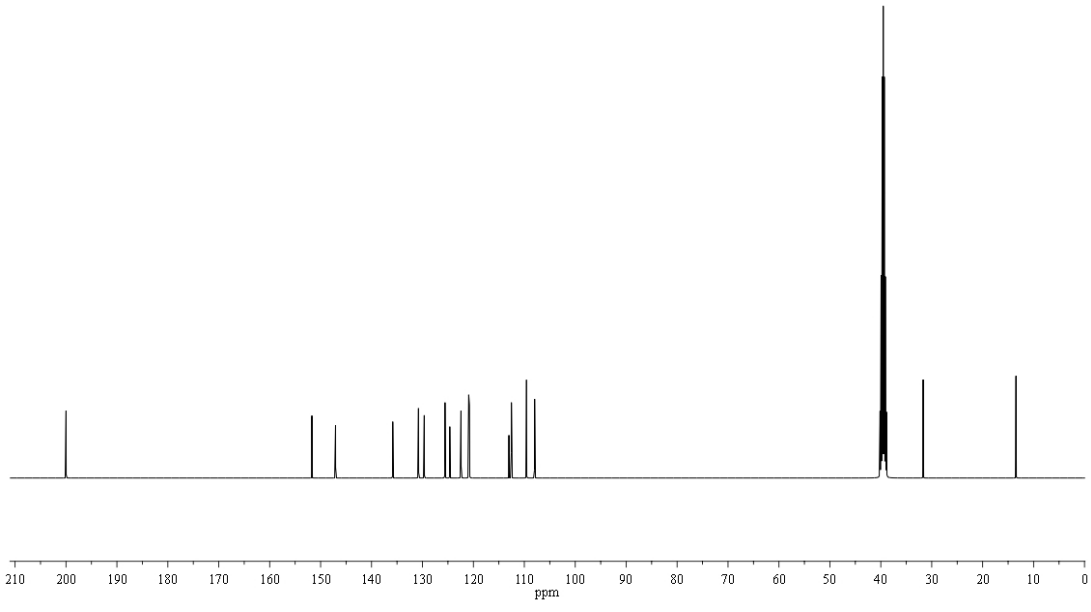

3.48
2.10
0.90
0.94
0.99
1.00
1.00
2.30
2.09
3.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

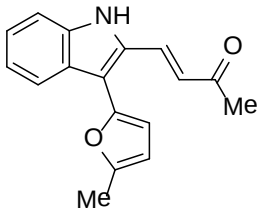

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


Me
O
NH
O
Me

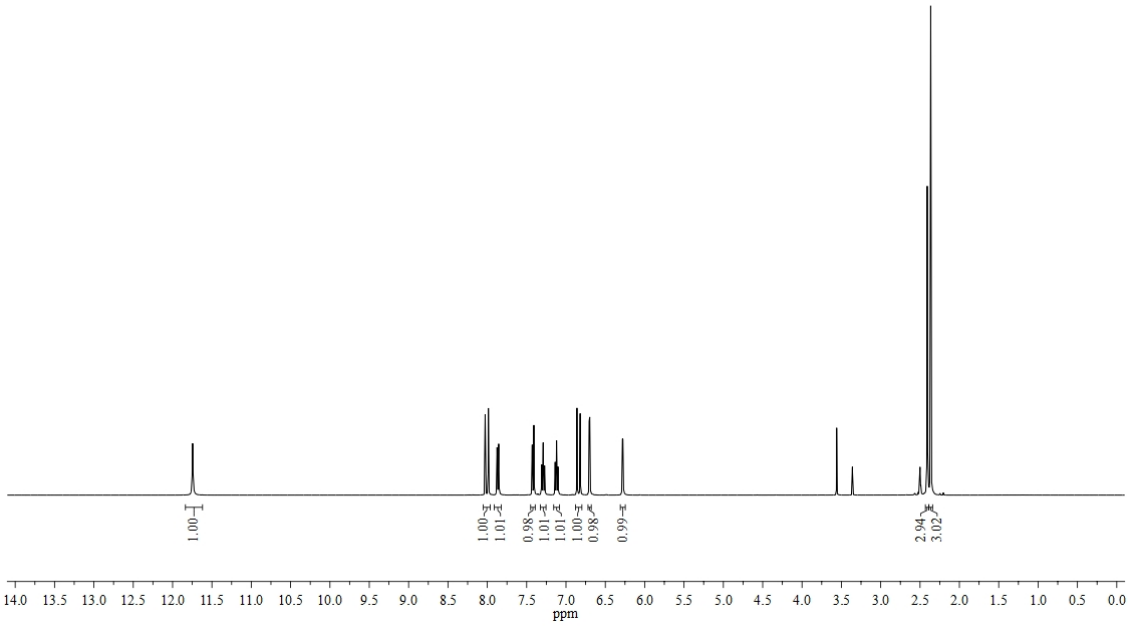
(*Z*)-**2a**

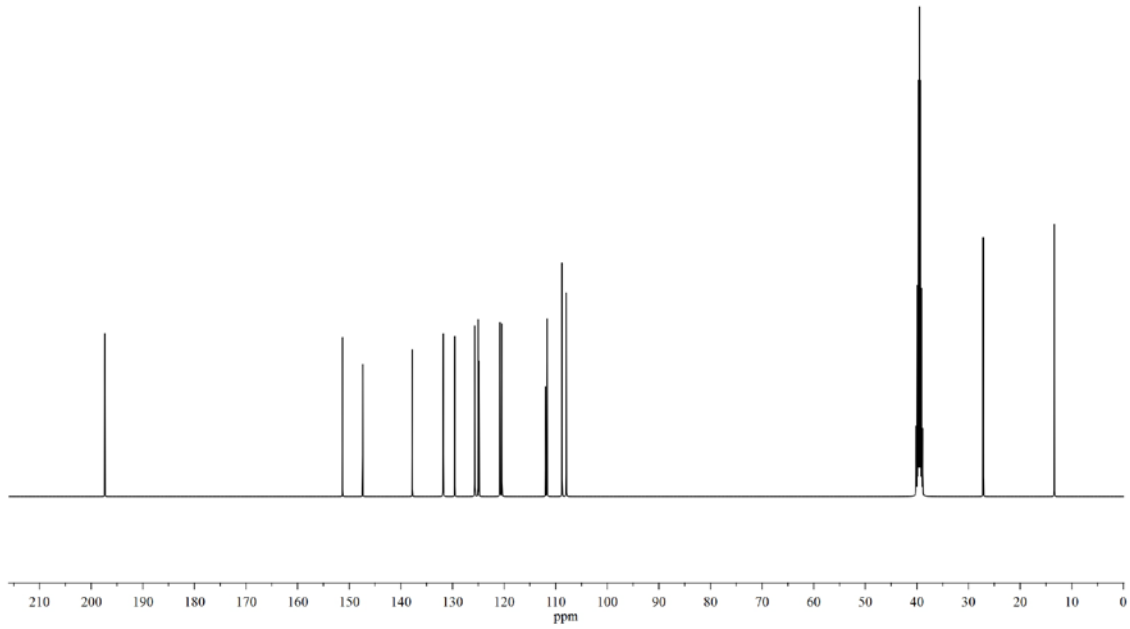

1.00
1.09
1.07
2.19
1.11
1.08
1.08
1.06
6.28
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

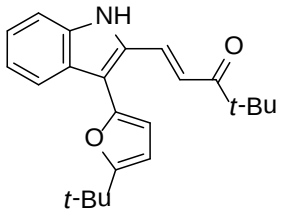

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


NH
O
Me
O
Me

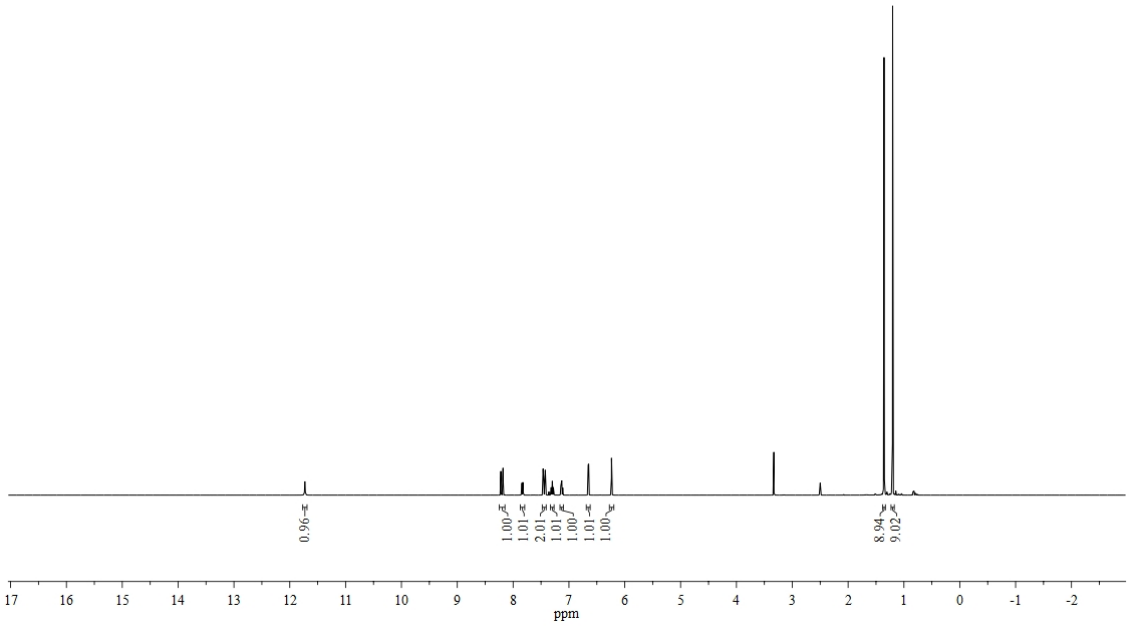
(*E*)-**2a**

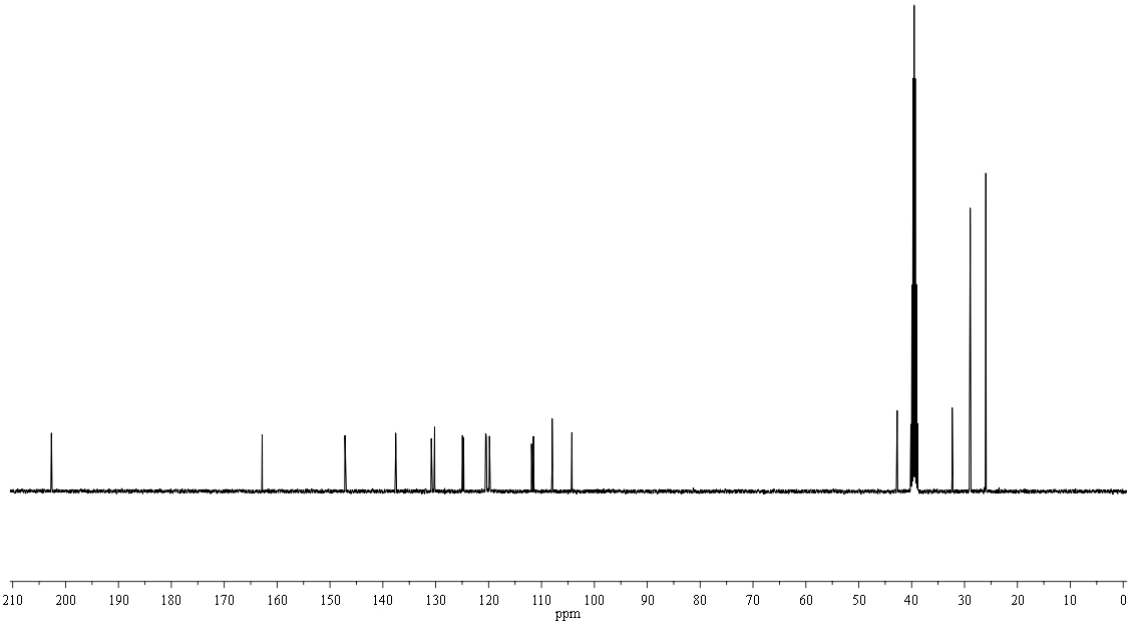

1.00
1.00
1.01
0.98
1.01
1.01
1.00
0.98
0.99
2.94
3.02
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

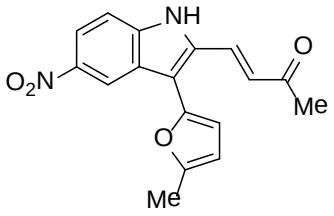

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


NH
O
t-Bu
O
t-Bu

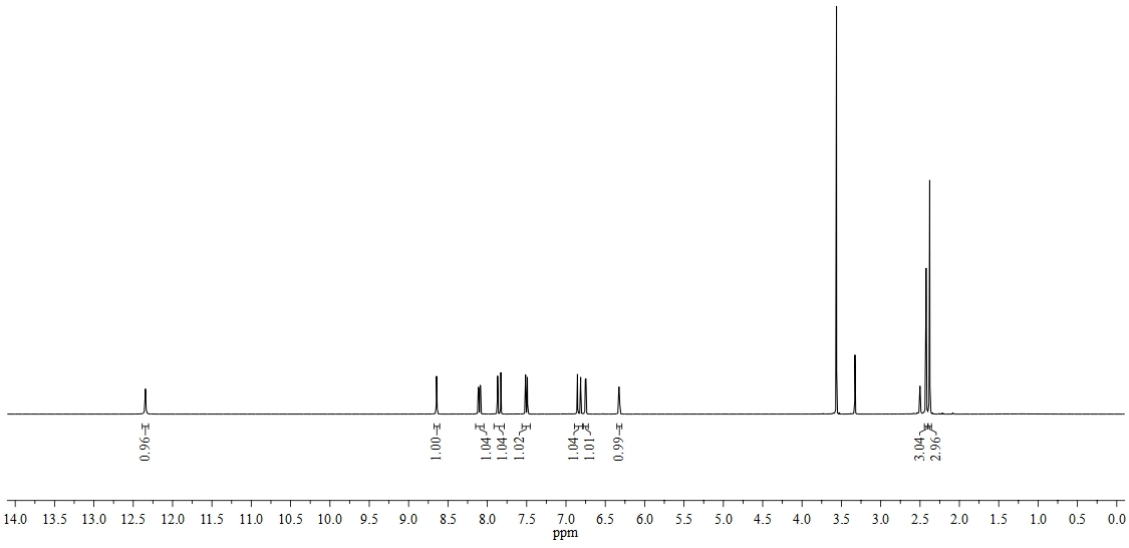
(*E*)-**2b**

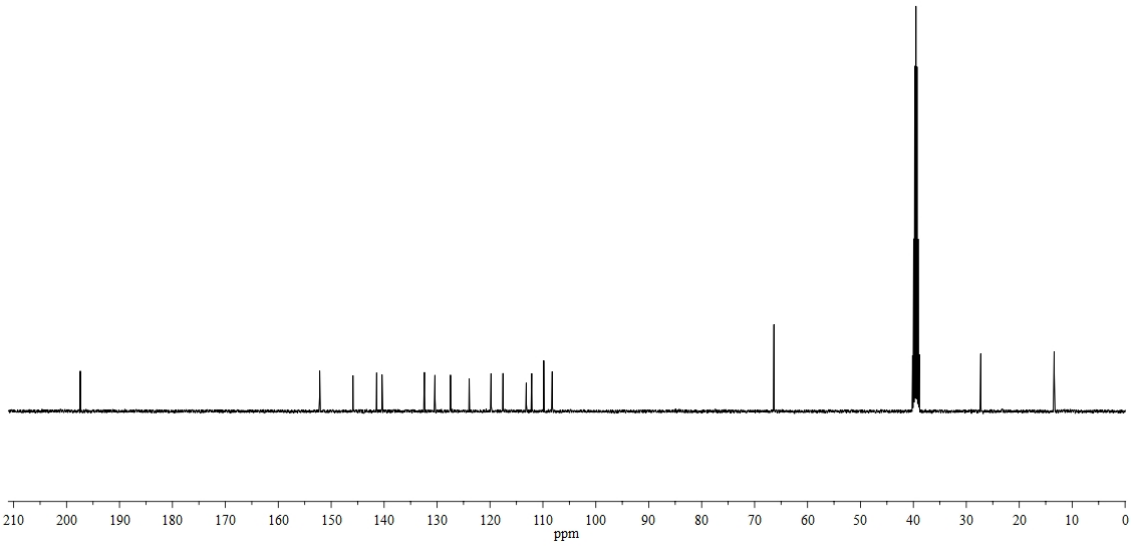

0.96
1.00
1.01
2.01
1.01
1.00
1.01
1.00
8.94
9.02
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
ppm

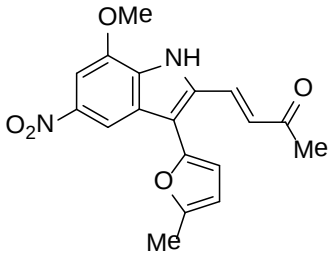

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


NH
O
$O_2N$
Me
O
Me

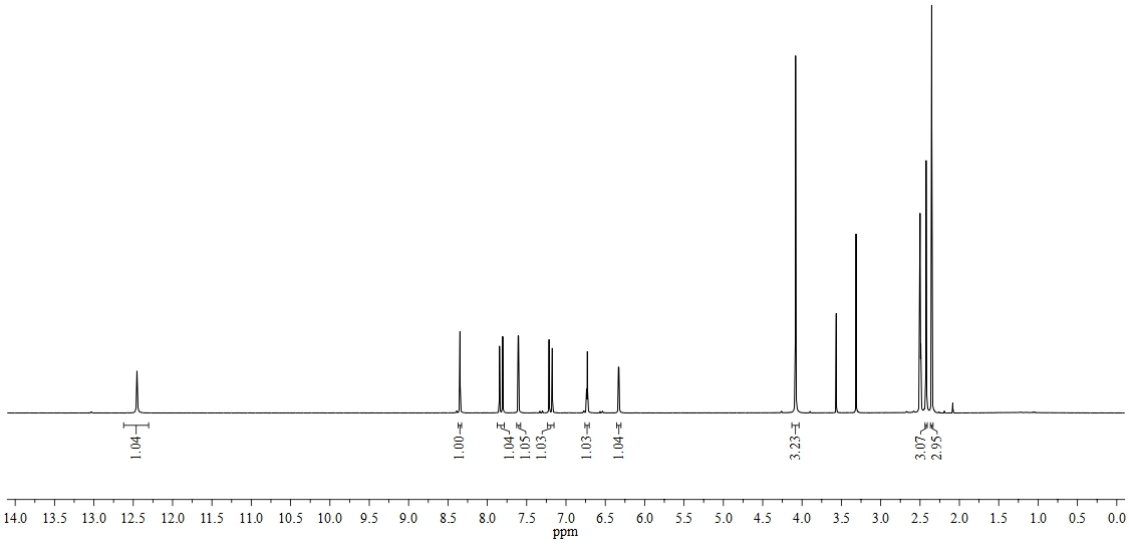
(*E*)-**2c**

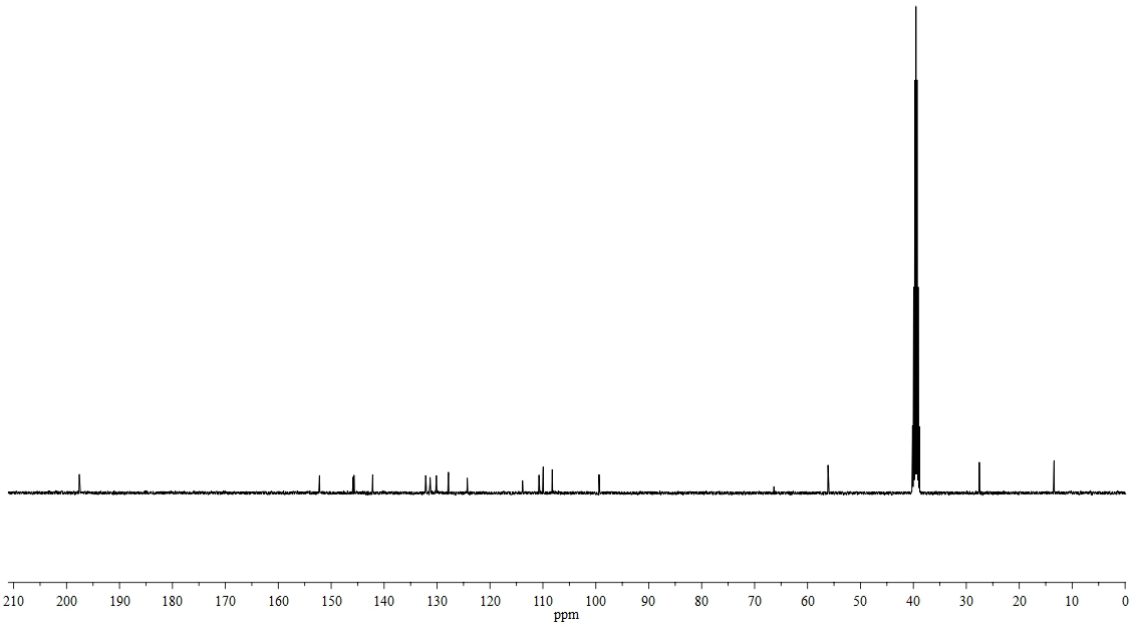

0.96
1.00
1.04
1.04
1.02
1.04
1.01
0.99
3.04
2.96
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

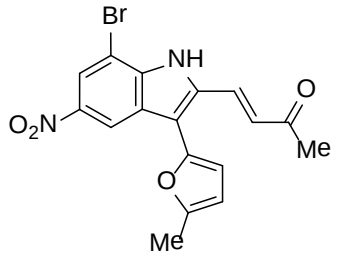

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


OMe
NH
O
$O_2N$
Me
O
Me

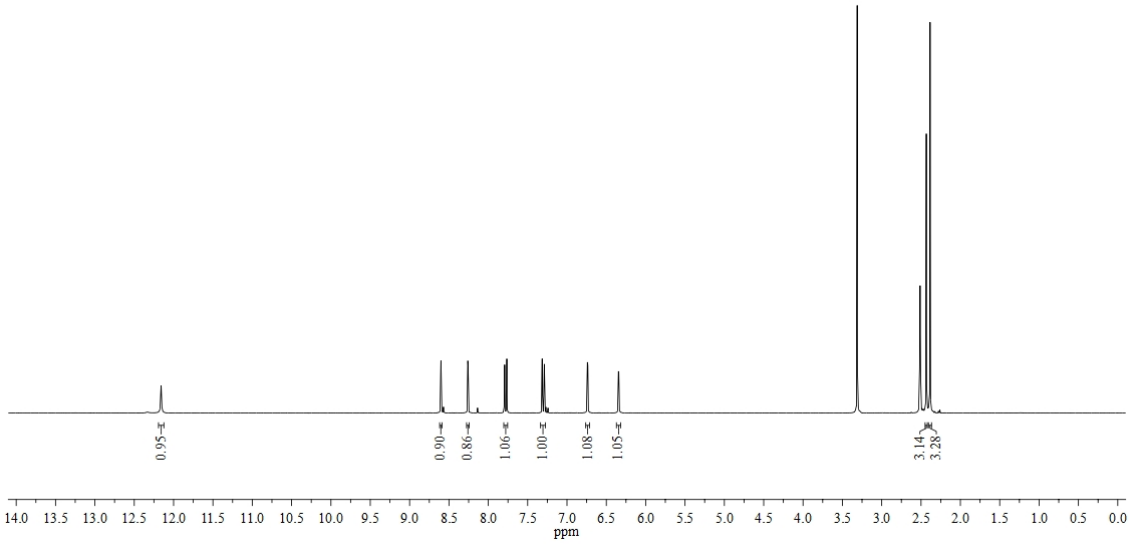
(*E*)-**2d**

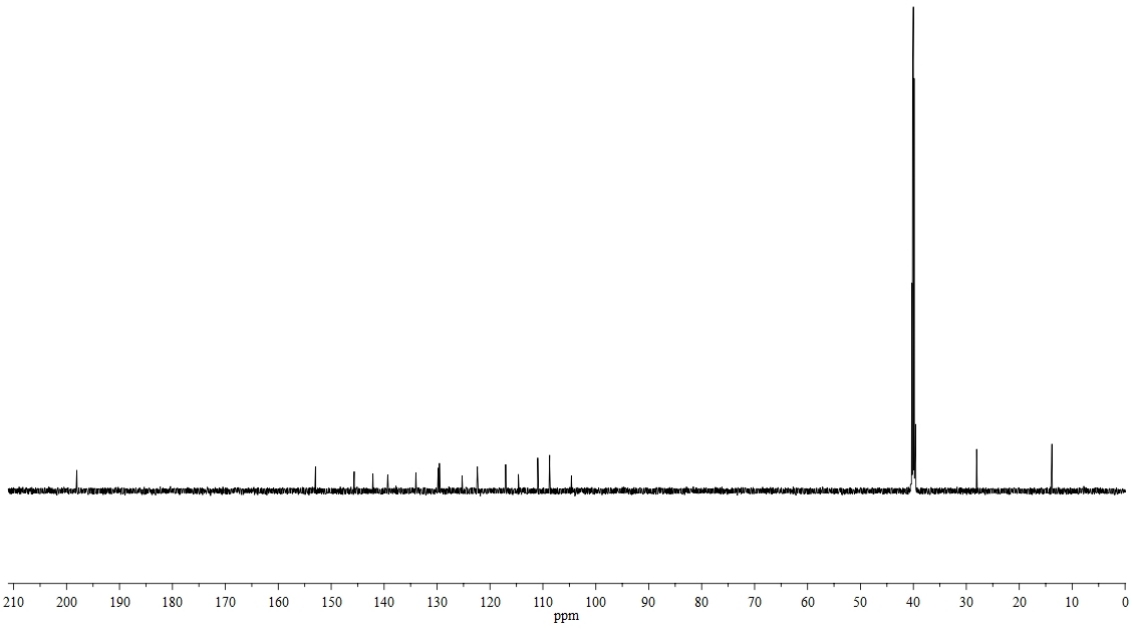

1.04
1.00
1.04
1.05
1.03
1.03
1.04
3.23
3.07
2.95
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

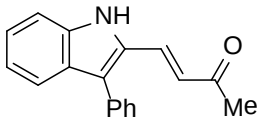

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


Br
NH
O
$O_2N$
Me
O
Me

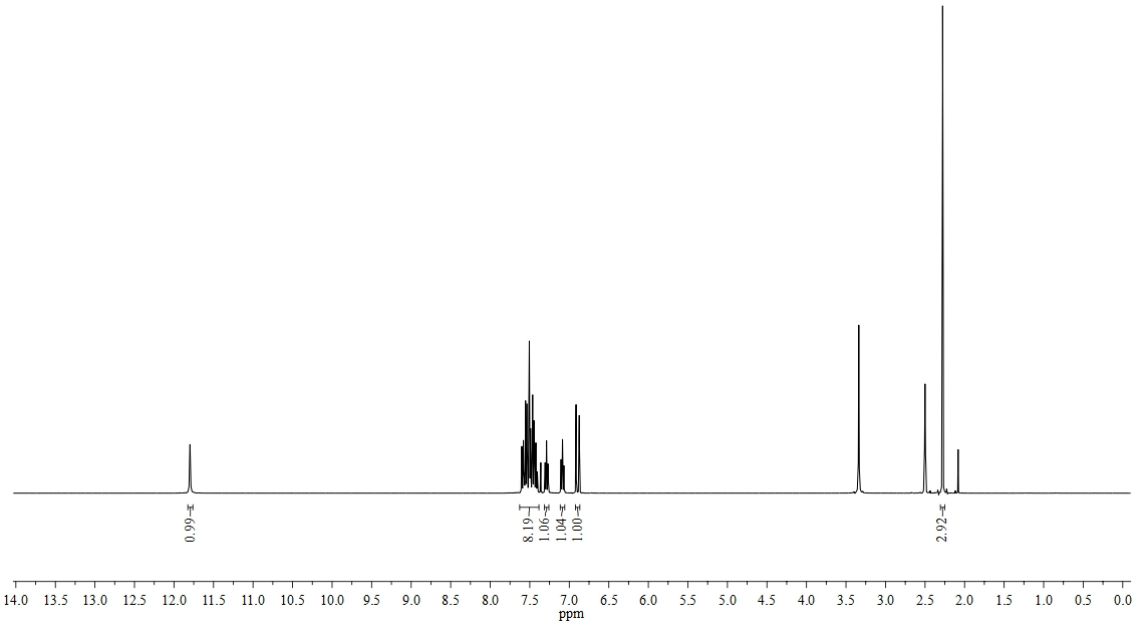
(*E*)-**2e**

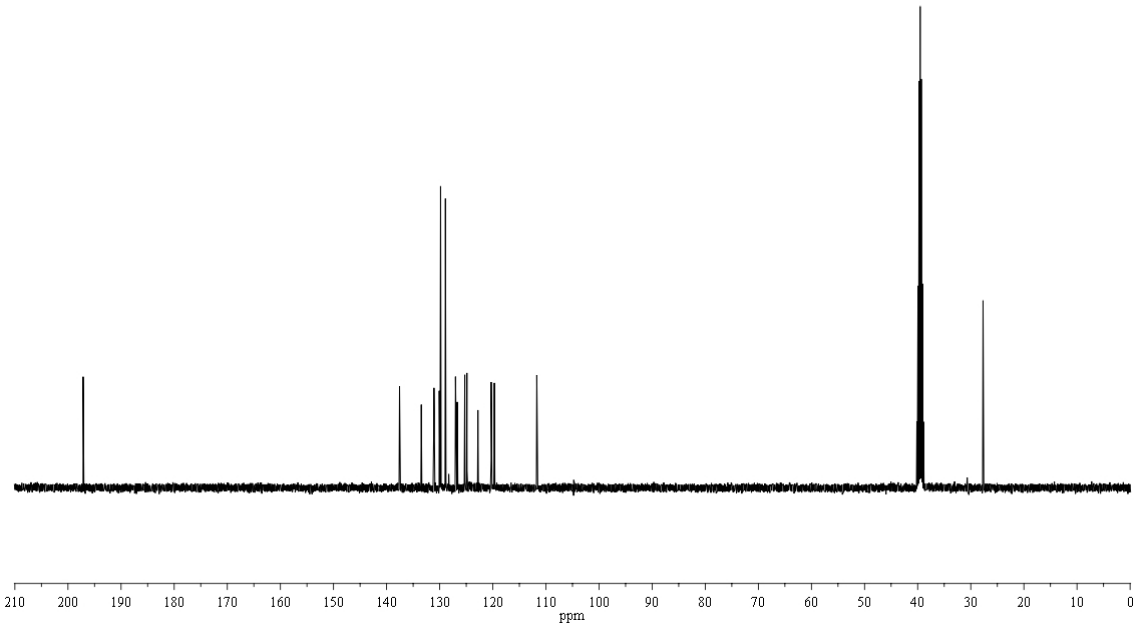

0.95
0.90
0.86
1.06
1.00
1.08
1.05
3.14
3.28
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

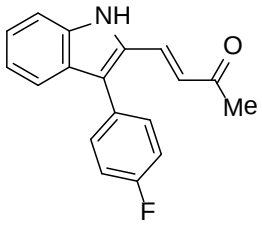

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


NH
O
Ph
Me

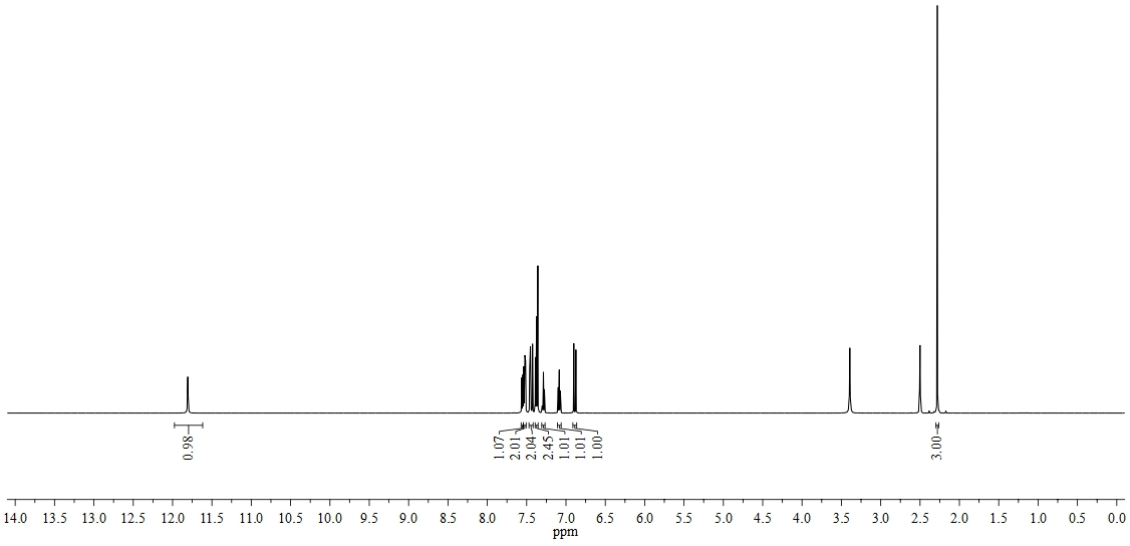
(*E*)-**2f**

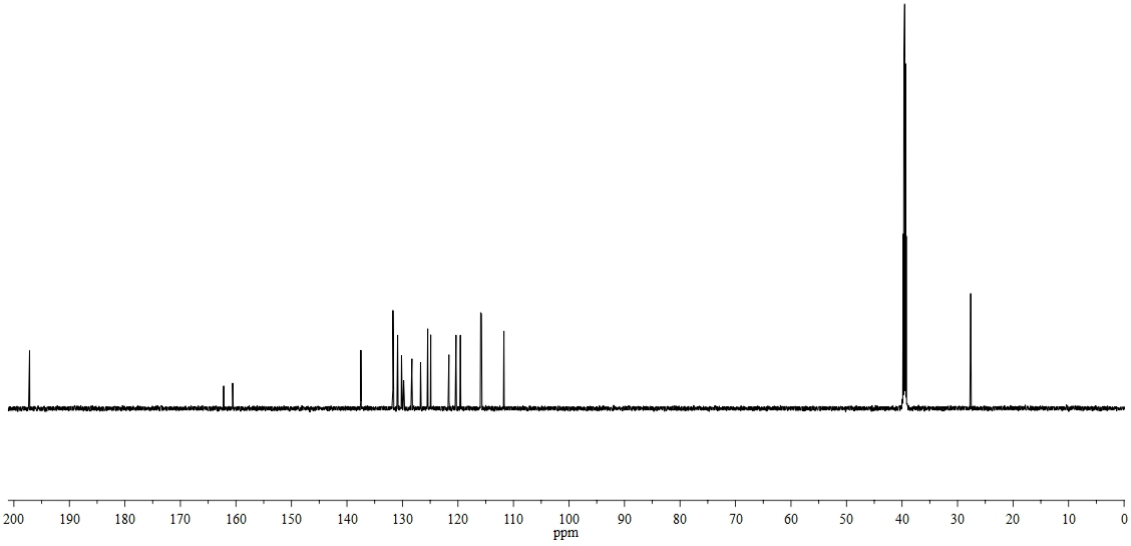

0.99
8.19
1.06
1.04
1.00
2.92
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

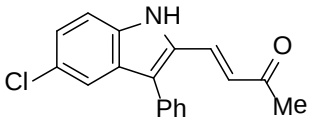

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


NH
O
Me
F

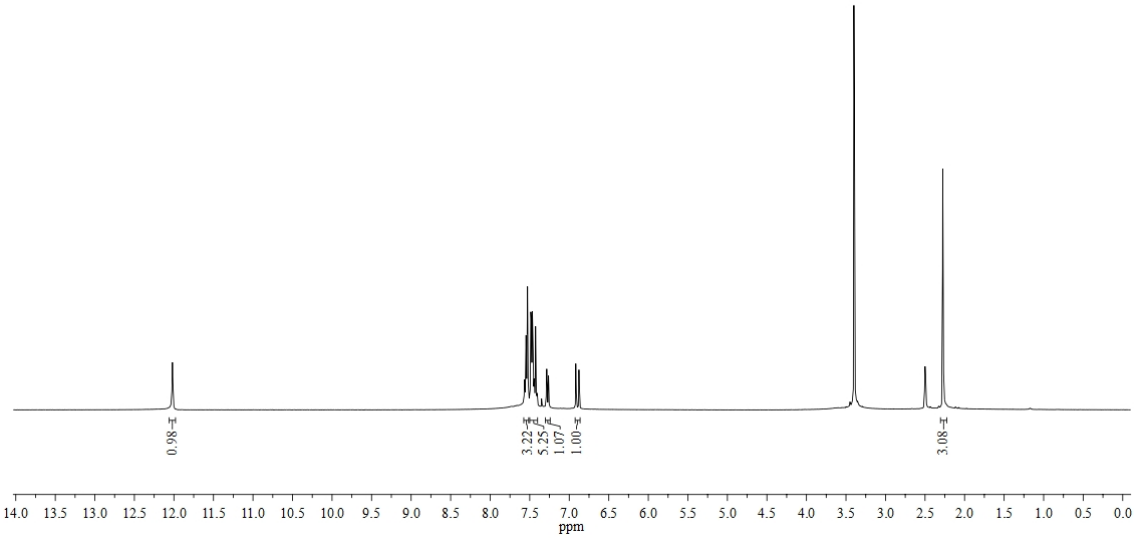
(*E*)-**2g**

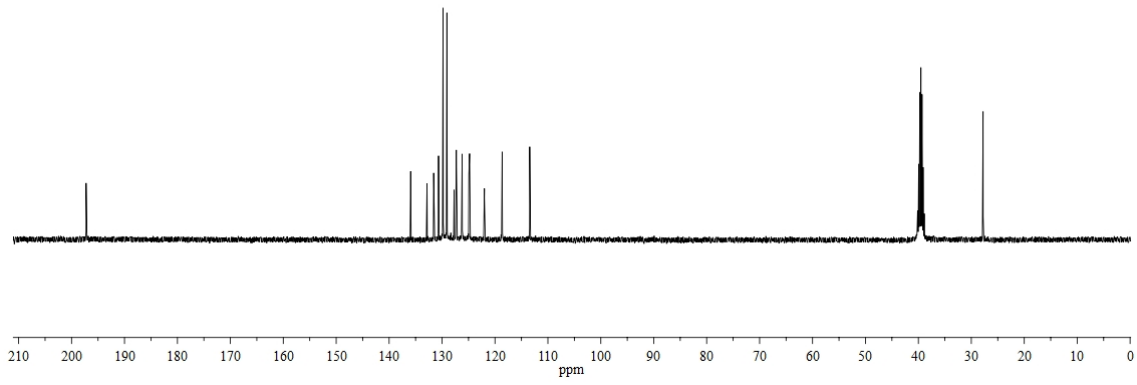

0.98
1.07
2.01
2.04
2.45
1.01
1.01
1.00
3.00
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

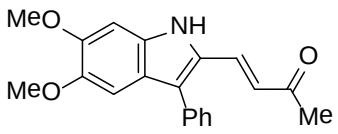

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


NH
O
Cl
Ph
Me

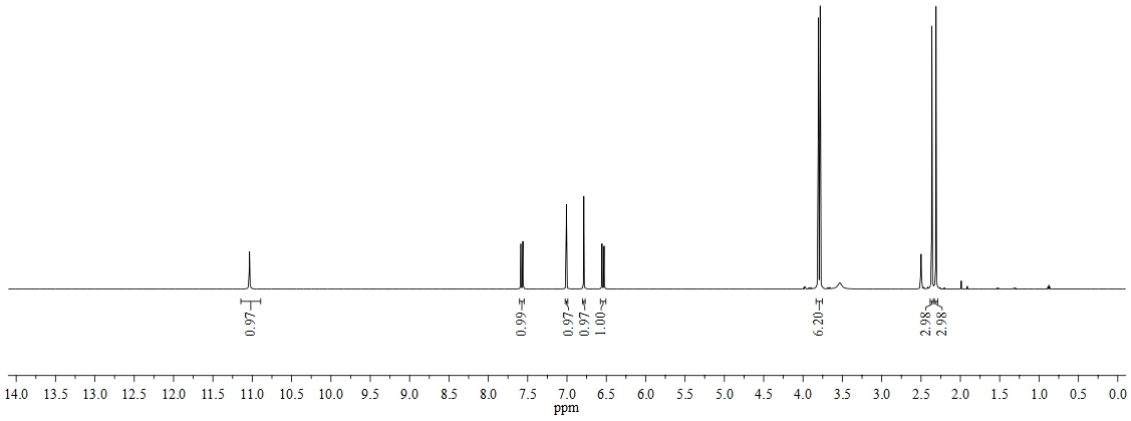
(*E*)-**2h**

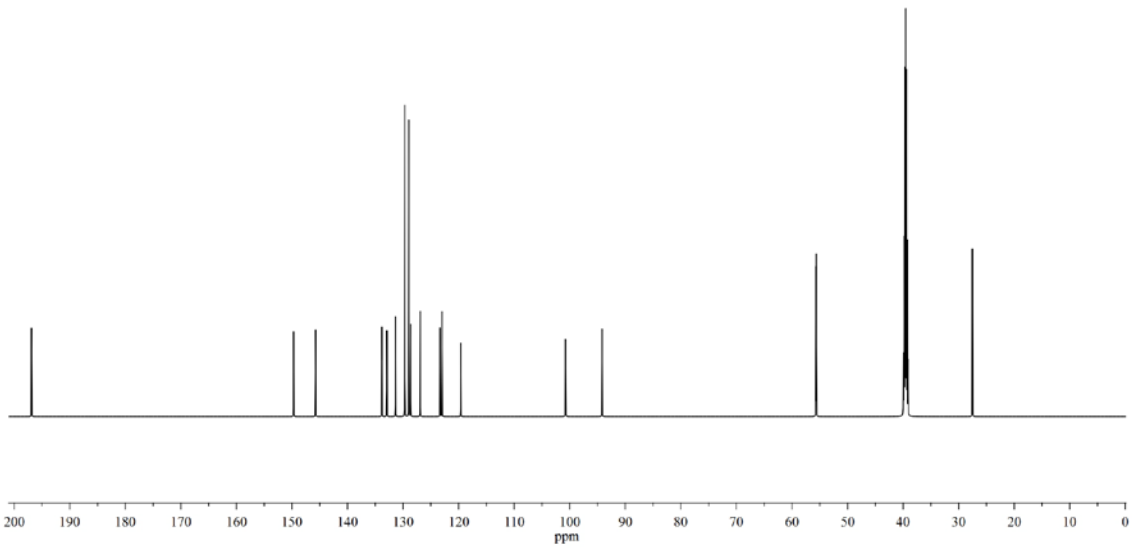

0.98
3.22
5.25
1.07
1.00
3.08
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


MeO
NH
O
MeO
Ph
Me

(*E*)-**2i**


0.97
0.99
0.97
0.97
1.00
6.20
2.98
2.98
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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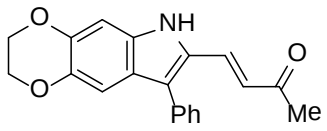
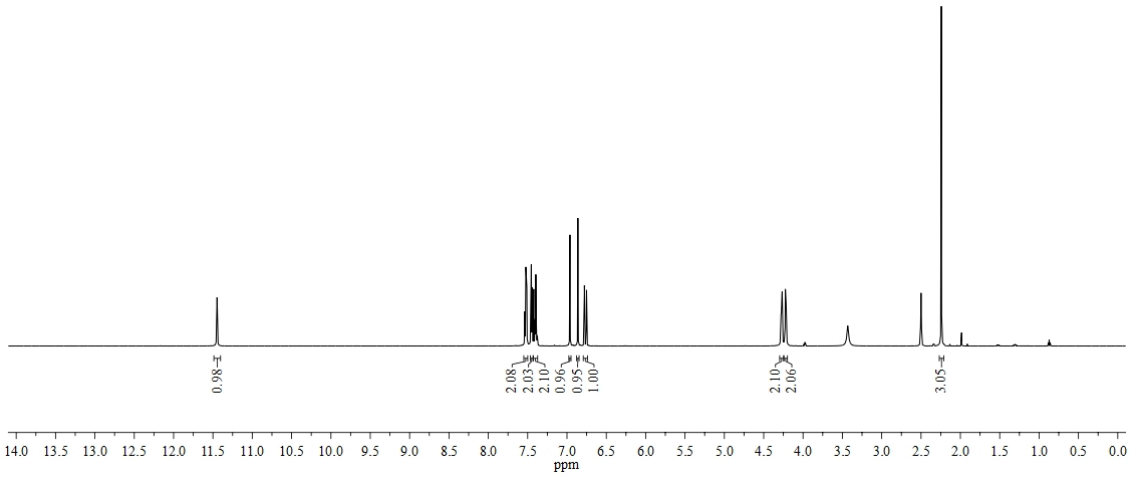
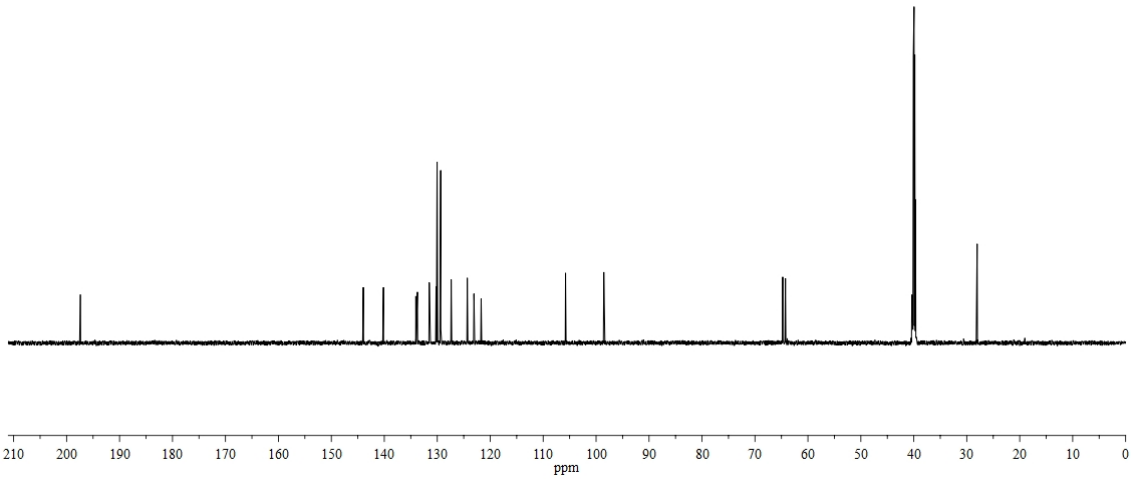
ppm


O
NH
O
O
Ph
Me

(*E*)-**2j**


0.98
2.08
2.03
2.10
0.96
0.95
1.00
2.10
2.06
3.05
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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ppm