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Three-photon absorption properties of a novel symmetrical Carbazole derivative having terminal 1,10-phenanthroline rings via carbon–nitrogen (C = N) double bond

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Three-photon absorption (3PA) properties of symmetric-type carbazole derivatives show great potential for application in light-activated therapy and optical limiting. A novel symmetrical carbazole derivative (abbreviated as POCP) with end-groups of 1,10-phenanthroline rings as the donor moieties, chained via carbon-nitrogen (C=N) double bond, has been synthetized and its three photon absorption properties has been also determined by using a Q-switched Nd: YAG laser pumped with 30 ps pulses at 1064 nm in dimethylformamide. The measurement of 3PA cross-section of this compound is performed by open aperture Z-scan and σ_{3PA} is 481×10^{-78} cm⁶ · s²/photon² for the transition $S_0 \rightarrow S_1$. The influence of the molecular structure of this compound on three-photon absorption cross-sections is discussed micromechanically by Austin model 1 and Zerner's Intermediate Neglect of Differential Overlap/S method. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper.

Keywords: carbazole derivative; three-photon absorption; Zerner's Intermediate Neglect of Differential Overlap/S method; Z-scan; 1,10-phenanthroline

INTRODUCTION

Investigations of organic multiphoton absorption materials, in particular, two-photon and three-photon absorption (2PA and 3PA), have received considerable attention recently because of their potential applications in photonics and bio photonics.^[1-6] The limited irradiation penetration depth of 2PA materials has hindered their medical and biological applications because of the undesirable linear absorption and scattering caused by the simultaneous absorption of two red (or short wavelength near-infrared) photons. Compared with the one-photon absorption process in transition, the 3PA process observed in organic molecules^[7-9] and semiconductors^[10] has longer excitation wavelength. Longer excitation wavelength in the near-IR and stronger spatial confinement are better at minimizing the undesirable absorption and light scattering. Thus, greater radiation penetration depth and less damage in these materials can be achieved. Consequently, much effort has been undertaken recently to develop organic molecules with large 3PA cross-sections (σ_{3PA}) because of their promising application, such as multiphoton fluorescence imaging, $^{[1,3,11,12]}$ up-converted stimulated emission,^[13] optical limiting,^[5,13–15] and light-activated therapy.^[16]

Recently, π -conjugated carbazole derivatives of the general type D- π -D, D- π -A- π -D, and A- π -D- π -A, where D and A denote electron donating and accepting groups, have been studied in 2PA properties by many researchers.^[17–20] However, 3PA related properties of π -conjugated carbazole

derivatives have never been studied up to date, especially, nonlinear optical properties.

In previous reports, on the basis of our theoretical and experimental investigations on fluorene derivatives with differently terminal structure,^[21–24] we found that a major contribution to the σ_{3PA} values originates from the transition dipole moment from the ground state to lowest charge transfer excited state. One possible way to enhance the 3PA cross-sections is to increase the charge-transfer dimensionality by expending the π -electron conjugation length.

Carbazole, as a typical hole-transporting group (p type),^[25,26] can combined with 1,10-phenanthroline as an electronic-transporting group (n type)^[27] to form novel p–n type bipolar materials efficiently balanced electron-transporting and hole-transporting capability, which is most

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extensive application in organic light-emitting diodes. In this paper, we synthesize the novel symmetrical carbazole derivative having terminal 1,10-phenanthroline rings via carbonnitrogen (C = N) double bond, 3,6-bisphenanthrolinimidazole-*N*-n-octylcarbazole (D- π -D- π -D). Meanwhile, in an effort to make clear the three-photon absorption mechanism for D- π -D- π -D conjugated molecule, three-photon absorption cross-section of this carbazole derivative is first investigated in N,N-dimethylformamide (DMF) solution by Z-scan measurement, pumping at 1064 nm with ps laser, and combined with the quantum chemistry calculations, the different influence of intramolecular charge transfer on three-photon absorption cross-sections. Large π conjugated substituent designed the special linkage of π chain with carbon-nitrogen (C = N) double bond is discussed micromechanically. It is found that its σ_{3PA} value is much larger than that of other groups in molecules before, so this molecule has promise for irradiance limiting applications and three-photon photodynamic therapy in cancer treatment.

EXPERIMENTAL

Materials

The chemical structure of the carbazole-based molecule, 3,6bisphenanthrolinimidazole-*N*-n-octylcarbazole (abbreviated as POCP), was prepared referring to literature procedures,^[28,29] shown in Scheme 1. In POCP the central carbazole is symmetrically end-capped with donor groups (1,10-phenanthroline ring) forming a D- π -D- π -D sequence. The chemical structure of this target molecule (POCP) had been identified by elemental analysis, mass spectrometry, IR, and nuclear magnetic resonance, respectively (shown in supporting information).

Synthesis of 1,10-phenanthroline-5,6-dione (1)

Concentrated sulfuric acid (50 mL) was added into a three-neck flask and the flask was cooled to below 5 °C by an ice bath. Then, 4.0 g 1,10-phenanthroline (20 mmol), 8 g potassium bromide (67 mmol),

and 25 mL concentrated nitric acid were gradually added into the flask. The reaction mixture was stirred for 2 h at 100 $^{\circ}$ C. Then it was slowly poured into 250 mL mixture with ice and water, and adjusted its pH to neutral. After vacuum filtration, the filtrate was extracted to get the crude product. Target product was obtained by recrystallization.

1,10-Phenanthroline-5,6-dione(1), yield 92.5%, m.p. 258.1–258.4 $^\circ$ C. Anal. calcd(%) for C $_{12}H_6N_2O_2$: C, 68.57; H, 2.88; N, 13.33. Found: C, 68.47; H, 2.92; N, 13.29.

Synthesis of 9-octyl-carbazole (2)

Carbazole (10 g, 0.06 mol) and NaOH (2.6 g, 0.065 mol) were added in 50 mL dimethylsulfoxide in a three-neck flask under stirring. The mixture was heated to 60 °C in a water bath for 40 min to dissolve all solids and then was gradually added with 1-bromo-*n*-octane (10.7 g, 0.065 mol). The reaction temperature was kept at 60 °C for 6 h then poured into water. The precipitation was filtered and dried under reduced pressure to yield a rude product. Compound **1** was obtained by recrystallization.

9-Octyl-carbazole (2), yield 76.8%, ¹HNMR(CDCl₃): δ (ppm) 0.8(t,3H, n-octyl, CH₃), 1.3(m,8H,n-octyl, 3-CH₂), 1.8(m,2H, n-octyl, 2-CH₂), 4.3 (t, 2H, n-octyl, 1-CH₂), 7.1–8.2 (m, 8H, carbazole); IR(KBr): 2953, 2924, 2855, 1594, 1451, 1352, 808, 749, 725 cm⁻¹; Anal. calcd (%) for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01. Found: C, 85.87; H, 9.06; N, 4.96.

Synthesis of 3,6-diformacy-9-octyl-carbazole (3)

N,*N*-Dimethylformamide (11 g, 0.15 mol) was added into a three-neck flask and the flask was cooled to 0 °C by an ice bath. Then, phosphorus oxychloride (23 g, 0.15 mol) was added into the flask and it was warmed naturally to room temperature and stirred for 1 h. Then, 4.2 g 9-octyl-carbazole (0.015 mol) dissolved in 1,2-dichloroethane (20 mL) was gradually added in the flask. The reaction solution was heated to $85 \sim 90$ °C under reflux and left at this temperature for 24 h. Then it was slowly poured into a mixture with ice and water, and extracted with chloroform three times. The product **2** was purified through column chromatography on silica gel using dichloromethane–petroleum ether (1:4) as eluent.

3,6-Diformacy-9-octyl-carbazole (**3**), yield 72.5%, ¹HNMR(CDCl₃): δ (ppm), 1.4(m, 8H,n-octyl, 3-CH₂), 1.9(m, 2H, n-octyl, 2-CH₂), 4.3



Scheme 1. The synthetic route of the target compound.

(t, 2H, n-octyl, 1-CH₂), 7.3–8.7(m, 6H, carbazole), 10.1(s, 2H, CH = O); IR (KBr): 2952, 2922, 2850, 1687, 1594, 1471, 1352, 807, 746, 729 cm⁻¹; Anal. calcd(%) for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.68; H, 7.69; N, 4.10; LC-MS: *m/z*, 335.2(335.44) [M+1].

Synthesis of 3,6-bisphenanthrolinimidazole-9-octyl-carbazole (4)

3,6-Diformacy-9-octyl-carbazole (0.3 g, 1 mmol), phenanthroline-5,6dione(0.42 g, 2 mmol), and 3.2 g ammonium acetate were added in 20 mL glacial acetic acid in a 150 mL three-necked flask, then the reaction mixture was stirred for 3 h at 85 °C. Then, it was cooled to room temperature, poured into 40 mL water and its pH adjusted to neutral with concentrated ammonia. It was then filtered and dried to get the crude product. Light yellow target product was obtained by column chromatography.

3,6-Bisphenanthrolinimidazole-9-octyl-carbazole (**4**), ¹H NMR (CDCl₃): δ (ppm), 13.7(s, 2H, C = N), 7.3–9.1(m, 12H, carbazole and phenanthroline), 4.5(t, 2H, n-octyl), 1.9(m, 2H, n-octyl), 1.3(m, 8H, n-octyl), 0.8(t, 3H, n-octyl). IR (KBr): 3421, 3064, 1444, 2921, 2850, 1608, 1559, 1351, 804, 739,708. Analysis calculated (%) for C₄₆H₃₇N₉: C, 77.18; H, 5.21; N, 17.61. Found: C, 77.11; H, 5.24; N, 17.51.LC-MS: *m/z*, 716.3 (716.65) [M + 1].

One-photon optical properties measurements

The linear absorption spectrum and one-photon fluorescence spectrum were measured by using Perkin Elmer Lambda 900 UV-VIS/NIR (San Jose, California, US) recording spectrophotometer and Jasco RF-5301 (Jasco Corporation, Great Dunmow, Essex, UK), respectively. This molecule solution in DMF with a concentration of 3×10^{-5} mol/L filled in a 10 mm path quartz cuvette was used for both measurements of one-photon and three-photon, and cell effects and solvent contributions were properly subtracted.

Measurement of three-photon absorption coefficient

The open-aperture Z-scan method is used to obtain the real values,^[30] which consider a laser beam with spatial and temporal Gaussian distribution. It is used to estimate the three-photon absorption coefficient (α_3) and the values of 3PA cross-section (σ_{3PA}) because the usual nonlinear transmission method is not accurate because of the square temporal profile of the laser beam. The measurement α_3 of POCP/DMF solution at 1×10^{-2} mol/L were conducted at 1064 nm by the well-known openaperture Z-scan technique. Figure 1 exhibits the experimental setup for the open-aperture Z-scan system. The incident 1064 nm laser was provided by a Q-switched Nd:YAG laser PY61C-10 (Continuum, Santa Clara, USA) with pulse duration of 30 ps, repetition rate of 10 Hz. The laser beam was divided into two beams by the beam splitter. The weaker beam, detected by photodiodes D_1 and D_2 , was employed to monitor the incident laser energy. The stronger beam, being focused into the sample by a 21 cm focal-length lens, acted as the exciting beam. The entire transmitted intensities through the sample were totally collected to a photodiode D₃. These two photodiodes were connected with a two-channel energy meter (Molectron EPM 2000)



Figure 1. Experimental setup for open-aperture Z-scan system. The picosecond 1064 nm laser is provided by a Q-switched Nd:YAG laser. 2 mm-path quartz cell, filled with the sample solution in DMF 1×10^{-3} mol/L was used for three-photon absorption coefficient (α_3) measurements.

to record the input and output energy simultaneously. The pump energy is controlled by rotating a half-wave plate between two polarizers. The dye solution was placed in a 1 mm path cell and the beam waist at the focal plane $w_0 \cong 24 \,\mu\text{m}$. The Z-scan system was calibrated with carbon disulfide as a standard and the experimental uncertainty should be within \pm 10%. We also carried out the Z-scan measurements on a quartz glass vial of thickness $L = 1 \,\text{mm}$ and the pure DMF, shown by the inset in Fig. 3, confirming that the measured nonlinear absorption mainly originates from POCP.

Quantum chemistry calculations

The optimized geometry of POCP and charge density distributions in both ground-state and excited-state were calculated using Austin model 1 (AM1) semi-empirical method in the MOPAC quantum chemical package of the Gaussian 03 program package (Gaussion. Inc., Pittsburgh, Pennsylvania, US).^[21] The excited states are characterized, and the electronic transitions are computed by Zerner's Intermediate Neglect of Differential Overlap/S (ZINDO/S) method^[22,23] at the optimized geometries.

RESULTS AND DISCUSSION

Synthesis

The general synthetic route of POCP was based on a fourstep sequence. First, the 5,6 position of 1,10-phenanthroline was ketonized by concentrated sulfuric acid and nitric acid. Second, the carbazole was alkylated by n-octylbromine to produce *N*-n-octylcarbazole (compound 2). Third, 3,6-biformyl-*N*n-octylcarbazole (compound 3) was prepared via POCl₃ and 1,2-dichloroethane in DMF with *N*-n-octylcarbazole. Finally, the condensation reaction of 3,6-biformyl-*N*-n-octylcarbazole with 1,10-phenanthroline-5,6-dione (compound1) synthesized the target compound **4**.

Linear absorption and fluorescence

Figure 2 shows the linear absorption and emission spectra of POCP in DMF solution. This molecule shows strong UV absorption in the spectral range of 280–400 nm with maximum absorption peaks (λ_{absmax}) at 294 nm, which is assigned to the typical $\pi \rightarrow \pi^*$, locally excited state. In addition, the shoulder peaks can be observed at



Figure 2. One-photon absorption (solid line) and steady fluorescence emission spectra (dotted line) of D- π -D- π -D compound POCP in DMF solution at low concentration (3 × 10⁻⁵ mol/L).

348 nm originated from the electronic transition from the ground state to the intermolecular charge transfer state.[31] Compared with linear absorption spectra of carbazole derivatives with 3-styrene- substituent,^[19] it is indicated that the absorption peaks would shift to longer wavelength when the electronic π -conjugated structure are extended by C = N as π chain and the large π conjugated substituents, 1,10-phenanthroline. Meanwhile, there is no one-photon absorption for these two molecules in the entire near-IR and most (>420 nm) of the visible spectral range. The three-photon energy of 1064 nm radiation just falls into the strong UV absorption, and therefore three-photon absorption in this solution may be expected. The one-photon fluorescence spectrum of POCP is also displayed in Fig. 2 by a dotted line. One can find that the fluorescence band of this molecule is located at the blue-green region with the peak wavelength of 473 nm. Fluorescence quantum yields, ϕ , were measured for POCP $(\Phi = 0.27)$ by a standard method relative to Rhodamine B in ethanol at 25 °C (ϕ = 0.9).^[32]

Three-photon absorption cross-sections

Figure 3 shows both the experimental open-aperture Z-scan curves given by points and the theoretical fitting curves represented by solid lines, showing nonlinear three-photon absorption in POCP at $\lambda = 1064$ nm. To fit the experimental curves, we employed the equations for a three-photon absorption process considering temporal and spatial Gaussian profiles, derived by He *et al.*,^[33] which is given by

$$T(z) = \frac{1}{\pi^{1/2} p_0} \int_{-\infty}^{\infty} \ln\left\{ \left[1 + p_0^2 \exp(-2x^2) \right]^{1/2} + p_0 \exp(-x^2) \right\} dx$$
(1)

where z is located at the focusing plane of the tightly focused Gaussian beam, $x = z/z_0$ is the relative position of the sample, $p_0(z) = \left[(2\gamma l_0^2 L_{\rm eff}) / (1 + z^2/z_0^2) \right]^{1/2}$, $z_0 = \pi \omega_0^2 / \lambda$ is the Rayleigh range, ω_0 is the beam waist at the focus, and



Figure 3. Normalized open-aperture Z-scan data with a concentration of 1×10^{-2} mol/L showing three-photon absorption at =1064 nm and input irradiance l_0 =30 GW/cm². The experimental data are shown as scattered points, while the solid lines are theoretical fits. The fit (solid curve) was obtained with three-photon absorption coefficient $\gamma = (8.32 \pm 0.32) \ 10^{-20} \text{ cm}^3/\text{W}^2$. The inset is nonlinear absorption experimental data of quartz glass vial of thickness *L* = 1 mm and the pure DMF.

 $L_{\rm eff} = (1 - e^{-2\alpha L})/2\alpha$ is the effective sample thickness. According to our linear absorption measurement, we found that the linear absorption coefficient, α , is negligible at 1064 nm, thus $L_{\rm eff} \approx L = 1$ mm. Using the on-axis beam irradiance $l_0 = 30$ GW/cm², the three-photon absorption coefficient is given by $\gamma = (8.32 \pm 0.32) \ 10^{-20} \text{ cm}^3/\text{W}^2$. On the basis of the known γ value of the measured solution sample, the molecular absorption cross-section σ_{3PA} (in the units of cm⁶ s²) for the given sample in solution is obtained by^[34]

$$\sigma_{\rm 3PA} = \frac{\gamma}{N_A \cdot d_0 \times 10^{-3}} \left(\frac{hc}{\lambda}\right)^2 \tag{2}$$

Here, N_A is Avogadro constant, d_0 is the concentration of the sample in solution (in the units of mol/L), and $h(c/\lambda)$ is the energy of an incident photon at 1064 nm. Consequently, the intrinsic sample molecular σ_{3PA} values can be easily estimated as 481×10^{-78} cm⁶ · s²/photon² for POCP.

Compared with σ_{3PA} of the reported organic molecules in our group^[21-24] or other researcher groups,^[8] it is observed that the σ_{3PA} value of this symmetrical carbazole derivative was larger than the findings for symmetrical fluorene derivatives forming a D- π -D- π -D sequence, $\sigma_{3PA} = 20 \sim 400$ GM. Also, this result indicates that this σ_{3PA} value is strongly related to chemical structures of this molecular, which means that this symmetrical carbazole derivative designed special linkage of π chain with carbon–nitrogen (C=N) double bond is different from conventional modification methods because multiphoton absorption



Figure 4. The optimized geometry of the ground state of compound.

Table 1. Energies (ev), the gaps (ev) between the HOMO and LUMO for the studied molecule								
Molecules	HOMO(ev)	LUMO(ev)	LUMO-HOMO(ev)					
POCP BVCZF*	-6.214 -7.896	-0.682 -0.750	5.532 7.146					
*BVCZF was reported by our group. ^[24]								

Table 2. Electronic transition date obtained by the ZINOD/S semi-empirical method for POCP at the AM1-optimized geometry									
Electronic transition	Excitation	λ	Transitior	Transition electric dipole moments (au)					
	energy	[a]	X ^[b]	Y	Z				
$S_0 \rightarrow S_1$	3.3325	420	-4.6206	-0.0628	-0.0043	1.1804			
$S_0 \rightarrow S_2$	3.5487	406	0.1862	-0.3578	0.5369	0.0077			
$S_0 \rightarrow S_3$	3.5872	388	-0.9625	-0.4081	-0.0250	0.0415			
$S_0 \rightarrow S_4$	3.6611	371	-0.5201	1.2105	-0.1537	0.0672			
$S_0 \rightarrow S_5$	3.6701	360	1.5528	0.6842	0.0317	0.1440			
$S_0 \rightarrow S_6$	3.8804	356	-0.5634	1.3367	-1.2124	0.1804			
^a λ values are from ZINDO computations. ^b X is the long molecular axis. ^c Oscillator strength.									

materials via carbon–carbon (C = C) double bond and terminal π conjugated substituent, 1,10-phenanthroline, is larger than others on 3PA molecules. Consequently, the charge redistribution and the magnitude of the transition dipole moment in the different terminal substituent and C = N as π conjugated chain should result in being much more influenced on σ_{3PA} value. Using AM1 semi-empirical and ZINDO/S methods, we systematically studied the charge density distributions in both ground-state and excited-state of this molecule, and the influence of different molecular structures on 3PA cross-sections is discussed in the following section.

Ground-state geometries and electronic excitations

In an effort to support our experimental results, optimized ground-state geometries of POCP was obtained by the AM1 method, shown in Fig. 4. The ZINDO/S semi-empirical method was employed to obtain the energy and the transition dipole moments of the first six singlet-singlet electronic transitions. The lowest singlet excited state corresponds to the orbital energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which is called the HOMO–LUMO gap (ΔE_{H-L}). Thus, when the transition occurs from the HOMO to the LUMO by photoexcitation, the HOMO plays an important role in the photoluminescence properties of the compound. Table 1 lists the calculated HOMO and LUMO energies and energy gaps. Compared with the results of our reported compound, it was observed from Table 1 that the HOMO energies (ϵ_{HOMO}) and the LUMO energies (ϵ_{LUMO}) of POCP increased, -6.214 eV (POCP) > -7.896 eV (BVCZF, 9,9-dirthylhexyl-2,7-bis-(N,N-vinylcarbazole) filuorene) and -0.682 eV (POCP) > -0.750 eV (BVCZF) because of the influence of the D- π style character in the different terminal substituents of carbazole derivative, which meant that π conjugation of 1,10-phenanthroline is larger than that of carbazole.

Additionally, on the basis of the theoretical investigation of Cronstrand *et al.*^[35] on the possible transition paths from ground to final states, S_{f_i} involved in a three-photon absorption process, $S_0 \rightarrow S_i \rightarrow S_i \rightarrow S_f$ is present in symmetrical system and is also an important contributor. The ZINDO/S semi-empirical method was used to obtain the nature and the energy of the first six singlet-singlet electronic transitions of the compound and we find that the first excited state, S_1 , is the strongest one-photon absorption state for this carbazole derivative. In our group reported papers, the experimental and theoretical results have demonstrated

that the first excited state, S_1 , is the strongest 3PA state for this molecule and that the transition dipole moment between the ground state (S_0) and final state (S_1), $|\mu|$, is the most definitive factor for 3PA, by which the 3PA cross-section can be increased. The excitation energies, oscillator strength (f) and transition dipole moments from the ground state to the first excited state are reported in Table 2. It can be seen that the oscillator strength (f) and the transition dipole moment along the long axis of the molecule (X) of the $S_0 \rightarrow S_1$ electronic transition are the largest for this molecule, which indicates that the first excited state, S_1 , is the strongest one-photon absorption state. A strong one-photon absorption state is corresponding to a strong 3PA state as well.[35] From Table 2, it is found that the transition dipole moment, μ^{0f} , between the ground state and the first excited state along the X axis were determined for this symmetric molecule, showing 4.0206 (au), which is in proportion to the 3PA cross-sections when the electronic π -conjugated structure is extended by C=N as π chain and the large π conjugated substituents, 1,10-phenanthroline. Therefore, compared with other fluorene derivatives reported by our group, it can be seen that the transition dipole moment of the $S_0 \rightarrow S_1$ electronic transition was changed larger to enhance the 3PA cross-section of POCP via designing the special linkage of the π chain with carbon-nitrogen (C = N) double bond and large π conjugated terminal substituents, 1,10-phenanthroline. The bilateral symmetric-type carbazole derivatives are good reference molecules for 3PA properties, which are promising for determining the fundamental structure for designing 3PA materials and for research on three-photon photodynamic therapy in cancer treatment.

CONCLUSIONS

In summary, a novel symmetric-type D- π -D- π -D charge transfer carbazole-based molecule having terminal 1,10-phenanthroline via carbon–nitrogen (C=N) double bond, POCP, was synthesized. The 3PA effect of the compound was demonstrated using a picosecond pulse at 1064 nm by Z-scan because of its great potential for application in nonlinear optical materials. Also, the measured 3PA cross-section is 481×10^{-78} cm⁶ · s²/photon² for POCP. Semi-empirical calculations of the transition dipole moment between the ground state and the excited state were performed using the ZINDO/S method. The experimental and theoretical results demonstrated that the transition dipole

moment of the $S_0 \rightarrow S_1$ electronic transition of 3PA molecule was changed significantly by designing the special linkage of the π chain with carbon–nitrogen (C = N) double bond and large π -conjugated terminal substituents, 1,10-phenanthroline, to enhance the 3PA cross-section of POCP. The investigation on its applications is progressing in our laboratory, and the results will be released in the future.

SUPPORTING INFORMATION

Figure for Supporting Information the results of IR, NMR, and LCMS for the target compound.

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